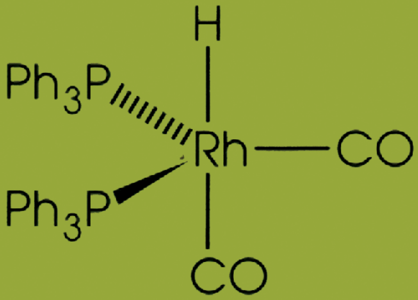

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VOLUME 26

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Organometallic Chemistry

Volume 26

A Specialist Periodical Report

Organometallic Chemistry
Volume 26

A Review of the Literature Published during 1996

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Preface

Volume 26 of this series marks a watershed in the development of the Specialist Periodical Report covering Organometallic Chemistry, in that Eddie Abel has relinquished his important role as Senior Reporter. Together with Gordon Stone he guided and influenced the way in which this exciting and important subject was reported on over a period of 25 years, and I would like to thank him for his very real contributions.

As before the aim of these Reports is to provide, on a yearly basis, a detailed survey of new work, highlighting where possible exciting new developments. This is no easy task because Organometallic Chemistry, a central and interdisciplinary science, continues to grow at a rapid pace with important implications for catalysis and synthetic organic chemistry, and I should like to thank the present contributors for their efforts. In this Volume there are new Chapters on the Organolanthanides, Organic-Organometallic Chemistry, and in addition some aspects of Phosphorus Chemistry are included in Chapter 7. A further change is the involvement of four contributors to Chapter 11 dealing with Complexes containing Transition Metal-Carbon σ-bonds.

One of the pioneers of organometallic synthesis and catalysis, Geoffrey Wilkinson died in 1996 and to mark the occasion his rhodium hydroformylation catalyst is shown on the front cover of this Volume.

Michael Green

Contents

Abbreviations

Ac	acetate
acac	acetylacetonate
acacen	NN′-ethylenebis(acetylacetone iminate)
Ad	adamantyl
AIBN	azoisobutyronitrile
Ar	Aryl
Ar*	2,4,6-tri(t-butyl)phenyl
arphos	1-(diphenylphosphinio)-2-(diphenylarsino)ethane
ATP	adenosine triphosphate
Azb	azobenzene
9-BBN	9-borabicyclo[3.3.1]nonane
BHT	2,6-dibutyl-4-methylphenyl
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
bipy	2,2′-bipyridyl
Bis	bis(trimethylsilyl)methyl
bma	2,3-bis(diphenylphosphino)-maleic anhydride
BNCT	boron neutron capture therapy
Bp	biphenyl
bpcd	4,5-bis(diphenylphosphino)-cyclopent-4-en-1,3-dione
bpk	benzophenone ketyl (diphenylketyl)
t-bupy	t-butylpyridine
Bz	benzyl
Bzac	benzoylacetonate
cbd	cyclobutadiene
1,5,9-cdt	cyclododeca-1,5,9-triene
chd	cyclohexadiene
chpt	cycloheptatriene
CIDNP	Chemically Induced Asymmetric Nuclear Polarisation
[Co]	cobalamin
(Co)	cobaloxime [Co(dmg)$_2$derivative]
cod	cyclo-octa-1,5-diene
cot	cyclo-octatriene
CP/MAS	Cross Polarization/Magnetic Angle Spinning
Cp	η^5-cyclopentadienyl
Cp*	η^5-pentamethylcyclopentadienyl
Cp′	trimethylsilylcyclopentadienyl
Cp″	tetramethylethylcyclopentadienyl
Cy	cyclohexyl
Cyclam	1,4,8,11-tetraazacyclotetradecane
Cym	*p*-cymene
Cyttp	PhP(CH$_2$CH$_2$CH$_2$PCy$_2$)$_2$

dab	1,4-diazabutadiene
dabco	1,4-diazabicyclo[2.2.2]octane
dba	dibenzylideneacetone
dbpe	1,2-bis(dibutylphosphino)ethane
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCA	9,10-dicyanoanthracene
depe	1,2-bis(diethylphosphino)ethane
depm	1,2-bis(diethylphosphino)methane
DFT	density functional theory
diars	o-phenylenebis(dimethyl)arsine
diarsop	{[(2,2-dimethyl-1,3-dioxolan-4,5-diyl)bis-(methylene)]bis[diphenylarsine]}
dien	diethylenetriamine
diop	{[(2,2-dimethyl-1,3-dioxolan-4,5-diyl)bis-(methylene)]bis-1-[diphenylphosphine]}
DIPAMP	1,2-bis(phenyl-o-anisoylphosphino)ethane
diphos	1,2-bis(diphenylphosphino)ethane
Dipp	2,6-di-isopropylphenyl
dipyam	di-(2-pyridyl)amine
DMAD	dimethyl acetylenedicarboxylate
DMAP	2-dimethylaminopyridine
DME	dimethoxyethane
DMF	NN-dimethylformamide
dmg	dimethylglyoximate
dmgH	monoanion of dimethylglyoxime
dmgH$_2$	dimethylglyoxime
DMP	dimethylpiperazine
dmpe	1,2-bis(dimethylphosphino)ethane
dmpm	bis(dimethylphosphino)methane
dmpz	1,3-dimethylpyrazolyl
DMSO	dimethyl sulfoxide
dpae	1,2-bis(diphenylarsino)ethane
dpam	bis(diphenylarsino)methane
dppa	1,2-bis(diphenylphosphino)ethyne
dppb	1,4-bis(diphenylphosphino)butane
dppbz	1,2-bis(diphenylphosphino)benzene
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1′-bis(diphenylphosphino)ferrocene
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
DSD	diamond-square-diamond
edt	ethane-1,2-dithiolate
EDTA	ethylenediaminetetraacetate
ee	enantiomeric excess
EELS	electron energy loss spectroscopy
EH MO	extended Hückel molecular orbital

ELF	electron localisation function
en	ethylene-1,2-diamine
ES MS	electrospray mass spectrometry
EXAFS	extended X-ray absorption fine structure
F_6acac	hexafluoroacetylacetonate
Fc	ferrocenyl
Fe*	$Fe(CO)_2Cp^*$
Fp	$Fe(CO)_2Cp$
Fp′	$Fe(CO)_2(^5\text{-}C_5H_4Me)$
FTIR	Fourier Transform Infra-red
FVP	flash vacuum pyrolysis
glyme	ethyleneglycol dimethyl ether
GVB	generalized valence bond
HBpz3	tris(pyrazolyl)borate
HBpz*3	tris(3,5-dimethylpyrazolyl)borate
H_4cyclen	tetraaza-1,4,7,10-cyclododecane
HEDTA	N-hydroxyethylethylenediaminetetraacetate
hfa	hexafluoroacetone
hfacac	hexafluoroacetylacetonato
hfb	hexafluorobutyne
HMPA	hexamethyl phosphoric triamide
HNCC	high nuclearity carbonyl cluster
HOMO	highest occupied molecular orbital
IGLO	individual Gauge for localized Orbitals
im	imidazole
Is*	2,4,6-tri-isopropylphenyl
ISEELS	inner shell electron energy loss spectroscopy
KTp	potassium hydrotris(1-pyrazolyl)borate
LDA	lithium diisopropylamide
LiDBB	lithium di-t-butylbiphenyl
LNCC	low nuclearity carbonyl cluster
MAO	methyl alumoxane
Me_6[14]dieneN_4	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetra-4,11-diene
Me_6[14]N_4	5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane
4,7-Me_2phen	4,7-dimethyl-1,10-phenanthroline
3,4,7,8-Me_4phen	3,4,7,8-tetramethyl-1,10-phenanthroline
Mes	mesityl
Mes*	2,4,6-tri-butylphenyl
MeTHF	Methyltetrahydrofuran
mcpba	metachloroperbenzoic acid
MLCT	Metal-Ligand Charge Transfer
nap	1-naphthyl
nb	norbornene
nbd	norbornadiene

NBS	N-bromosuccinimide
NCS	N-chlorosuccinimide
NCT	neutron capture theory
Neo	neopentyl
Np	Neophyl
np$_3$	$N(CH_2CH_2PPh_2)_3$
nta	nitrilotriacetate
OEP	octaethylporphyrin
OTf	trifluoromethanesulfonate
Pc	phthalocyanin
PES	photoelectron spectroscopy
PMDT	pentamethylenediethylenetetramine
pd	pentane-2,4-dionate
phen	1,10-phenanthroline
pmedta	pentamethyldiethylenetriamine
pp$_3$	$P(CH_2CH_2PPh_2)_3$
$[PPN]^+$	$[(Ph_3P)_2N]^+$
py	pyridine
pz	pyrazolyl
R-PROPHOS	(R)-(+)-1,2-bis(diphenylphosphino)propane
R,R-SKEWPHOS	(2R,4R)-bis(diphenylphosphino)pentane
RDF	radial distribution function
ROMP	ring opening metathesis polymerisation
sal	salicylaldehyde
salen	NN′-bis(salicylaldehydo)ethylenediamine
saloph	NN-bisalicylidene-o-phenylenediamine
SCF	self consistent field
TCNE	tetracyanoethylene
TCNQ	7,7,8,8-tetracyanoquinodimethane
terpy	2,2′,2″-terpyridyl
tetraphos	1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane
TFA	trifluoroacetic acid
tfbb	tetrafluorobenzobarrelene
tfacac	trifluoroacetylacetonato
tfo	triflate, trifluoromethylsulfonate
THF	tetrahydrofuran
thsa	thiosalicylate (2-thiobenzoate)
tht	tetrahydrothiophen
TMBD	NNN′N′-tetramethyl-2-butene-1,4-diamine
TMEDA (tmena)	tetramethylethylenediamine
tmp	2,2,6,6-tetramethylpiperidino
TMS	tetramethylsilane
tol	tolyl
TP	hydrotris(1-pyrazolyl)borate
TP*	hydrotris(3,5-dimethylpyrazolyl)borate
TPP	meso-tetraphenylporphyrin

Trip	2,4,6-triisopropylphenyl
Triph	2,4,6-(triphenyl)phenyl
triphos	1,1,1-tris(diphenylphosphinomethyl)ethane
TRIR	Time resolved infrared (spectroscopy)
Tsi	tris(trimethylsilyl)methyl $(Me_3Si)_3C$
TTF	tetrathiafulvalene
vi	vinyl
WGSR	water gas shift reaction
XPS	X-Ray Photoelectron spectroscopy
Xyl	xylyl

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Group 1: The Alkali and Coinage Metals

BY R. SNAITH

1 Alkali Metals

1.1 Introduction: Organisation and Major Advances – In line with previous years, this part of the report is organised in sections which are defined primarily by the type of organic anion (R^-) found with the alkali metal cation (M^+) in a given species. Within each section, the order of treatment is (i) synthetic uses of the alkali metal derivatives, chiefly in organic syntheses but also in the syntheses of compounds of other metals; included also are mechanistic aspects of such syntheses, probed chiefly by kinetic measurements and by molecular orbital (MO) calculations, (ii) structural studies, by X-ray crystallography in the solid state, by NMR (and other) spectroscopy in solution, and by MO optimisations.

Organo-alkali metal chemistry continued to advance rapidly in 1996, as it had done in the ten or so years previous. Lithium derivatives remain to the fore, although there are signs of increased interest in sodium and potassium species, and indeed in caesium ones: the year saw in essence a doubling of the number of known organocaesium structures. However, rubidium chemistry – in all its aspects – remains largely unexplored. The expansion in organo-Na^+, K^+, Cs^+ chemistry can be attributed firstly to improved synthetic and manipulative skills (since these species are an order of magnitude more air- and moisture-sensitive than their Li^+ analogues) and secondly to improved crystal mounting techniques and X-ray data collection/refinement (since these larger cations tend to cause aggregation to polymeric materials whose detailed structures frequently contain interactions between M^+ cations and C atoms or groups within the anion R^- as well as the formal bonds between M^+ and the actual carbanionic centres of R^-).

The above general points apart, 1996 saw notable activity and developments in the following areas of organo-alkali metal chemistry: (i) investigation of the active species present in mixed-metal/mixed-anion reagents ('superbases', e.g., of type RLi/R'OK); (ii) mechanistic and other studies on organic syntheses which employ R^-M^+ reagents, and with these an increased recognition that M^+ plays a crucial role, i.e., that the reagent is not merely a source of the carbanion/nucleophile R^-; (iii) increased application of ever more sophisticated (and quicker) *ab initio* MO calculations to probe mechanistic and structural problems; and (iv) X-ray diffraction studies on species whose structures exhibit $M^+\cdots CH_3$ or $M^+\cdots Ph$ interactions, and on π-bonded 'sandwich-type' derivatives where R^- is such as Cp^- or a heteroatom-substituted Cp^- (e.g., with B or P).

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1.2 Alkyl Derivatives – Alkyllithium species, whether commercially available ones (e.g., MeLi, BuLi) or ones generated from them (or by other means, e.g., LDA, Li metal), remain probably the most widely used organometallic reagents/intermediates in modern synthetic organic chemistry. The use of Li metal and a catalytic amount of 4,4′-di-*tert*-butylbiphenyl has been extended to produce $HOCH_2^-$ and $MeNHCH_2^-$ synthons, whose treatment with electrophiles affords functionalised carbamates, and to reductively open various N-containing heterocycles to give C,N-Li_2 intermediates whose work-up leads to functionalised amines.[1] The surprisingly stable halocarbenoid (3-pyridinylchloromethyl)lithium can be trapped with various electrophiles at low temperature to give functionalised pyridines.[2] Bis(lithiomethyl)silanes, of general type $R^1R^2Si(CH_2Li)_2$, have proved to be useful building blocks towards organosilanes and disilacyclobutanes.[3] Sulphur-containing alkyllithiums have been the subjects of three interesting studies: thiophilic addition of MeLi to sulphines RC(SMe)=S=O and then treatment with electrophiles (E^+X^-) gives specifically dithioacetal oxides RC(SMe)(E)S(Me)=O which can then be converted into aldehydes or ketones;[4] the reagent bis(lithiomethyl)sulphide, $LiCH_2SCH_2Li$, has been obtained by Li-Sn or Li-Ge exchange and then used to prepare both inorganic and organic compounds containing the -CH_2-S-CH_2- unit;[5] and the adduct $Me_3N{\cdot}SO_3$ reacts with alkyllithiums by inserting SO_3 into the Li-C bond, affording RSO_3Li and thereby sulphonic acids.[6] Another insertion reaction, this time of CO into lithiated trimethylsilyldiazomethane $Me_3SiC(Li)N_2$, forms the basis of new ketenylation reactions.[7] Two especially interesting uses of lithium reagents in inorganic chemistry have been published. Firstly, reaction of YCl_3 with Cp^*K and $[PhC(NSiMe_3)_2]Li{\cdot}OEt_2$ affords $\{Cp^*[PhC(NSiMe_3)_2]Y(\mu\text{-}Cl)\}_2$ whose treatment with MeLi/TMEDA results in $Cp^*[PhC(NSiMe_3)_2]Y(\mu\text{-}Me)_2Li{\cdot}TMEDA$, a useful precursor for other Cp^*-Y-benzamidinate derivatives.[8] Secondly, the highly unusual organolithium polymer $[(Me_2NMe_2Si)_3CLi]_\infty$, whose structure reveals a ‘free’ carbanionic centre with no C-Li attachments, has been used to transfer the bulky anion to other metals such as Sn and Hg.[9]

Regio-, diastereo- and enantio-selective lithiation/substitution syntheses continue to be of great interest, in particular regarding the mechanistic reasons for such selectivities. The area has been reviewed.[10] Organocuprate adducts $R_2CuLi{\cdot}BF_3$ and alkyllithiums RLi give *anti* and *syn* 1,2-aminoalcohols respectively when added to an α-siloxyaldimine, the stereoselectivity for RLi being explicable by a ‘chelation model’ (often referred to as the ‘complex-induced proximity effect’, CIPE) in which the reagent is first complexed by the O centre of the organic precursor.[11] Stereo-defined organofluorine compounds have been obtained by treatment of $RCH(OR')CFBr_2$ precursors with ^nBuLi to give the carbenoids RCH(OR′)CFBrLi which then add organic carbonyls diastereoselectivity, an outcome again explained in terms of chelation between Li^+ and the alkoxy O atoms.[12] Support for CIP effects has been found in the crystal structure of a tetrameric lithium carbamate complex gained by lithiation of 2,3-dimethylindole followed by CO_2 insertion into the N-Li bond; certain O atoms are near to the 2-Me groups, suggesting a reason for second lithiation occurring specifically at this position.[13] Asymmetric lithiation-substitution of an Nmethylamide by ^{s}BuLi in the presence of (−)-sparteine has been shown to proceed *via* a pathway in which asymmetry is induced in a post-deprotonation step.[14]

Lithiation mechanisms have also been probed by kinetic measurements and by MO calculations. α-Deuterium kinetic isotope effects in reactions of $(MeLi)_n$ in Et_2O may imply a pre-equilibrium between an aggregate and a reactive monomer.[15] Measurements of rates and extents of directed *ortho* metallations of anisoles using ^{n}BuLi in THF/hexane mixtures have shown, rather surprisingly, that the reactions work best in a 14% solution of THF in the hydrocarbon.[16] The different diastereoselective behaviours of dilithio compounds obtained from cinnamyl alcohol and cinnamylamines on carbolithiation have been examined by ^{1}H, ^{6}Li NMR spectroscopy and by PM3 semi-empirical calculations, the results showing that the species assume different aggregation states which in turn allow two different modes of intramolecular chelation.[17] Finally, the structures and reactivities of 'superbase' mixtures (RLi + R'OM) have been studied by *ab initio* MO calculations. For MeLi:MeOK, a 1:1 complex shows a reactivity towards MeH similar to that of MeLi alone; however a 1:3 tetramer is more promising since in its optimised structure Me^- is separated from Li^+ by three K^+ and three O^- centres.[18] Mixed aggregates of RLi and R'OM(M = Na-Cs) have also been evaluated by MP2 calculations, dimers usually being more stable than other combinations.[19]

Several interesting solid-state structures of alkyllithium compounds appeared in 1996. The lithiated phosphane imine $[Me_3SiN(PMe_2)CH_2Li]_4$ forms a Li_4C_4 cubane whose Li^+ ions are each coordinated by one N centre, while the related dimer $[Me_3SiN(P^{i}Pr_2)CMe_2Li]_2$ has a ladder-type structure.[20] The dilithiated di(trimethylsilylmethyl)-bipyridine complex $[C_5H_3NCH(SiMe_3)]_2{\cdot}[Li(TMEDA)]_2$ is monomeric, with each Li^+ being chelated by the C atom of one pyridine unit and the N atom of the other.[21] An unusual cyclic lithiate anion $[\overline{CH_2SiMe_2C(SiMe_3)_2LiC(SiMe_3)_2SiMe_2C}H_2]^-$, isolated as its $Li(TMEDA)_2^+$ salt, contains a slightly bent C-Li-C linkage.[22] Of particular interest have been solid-state structures of alkali metal species which, while not being alkyl derivatives in the formal sense, show $M^{+}{\cdots}$alkyl interactions. The mixed adduct $Me_3Al{\cdot}(PhCH_2)_2NLi{\cdot}HN(CH_2Ph)_2$ contains a central Al(Me)LiN ring whose $Li{\cdots}CH_3$ attachment stabilises the monomeric lithium amide unit.[23] In the alkoxide $[(c\text{-}CH_2CH_2CH)_2C(Me)OLi]_6$, Li^+ cations coordinate to cyclopropane ring edges and cause elongation of the C-C bonds, an electrostatic effect probed by high-level calculations for $M^+(Li^+\text{-}Cs^+)$ in general.[24] The dilithium phosphandiide $[RPLi_2(F\text{-}R)]_2$ {R = $(2,4,6\text{-}^{i}Pr_3C_6H_2)Si^{i}Pr_2$} has a $P_2Li_4F_2$ ladder framework whose Li^+ centres are stabilised electronically by $Li{\cdots}CH_3$ or by η^2-Li$\cdots$aryl interactions.[25] Perhaps expectedly, such interactions become yet more important within Na^+ and K^+ derivatives. The bis(amido)sodate salt $Na^+\{Na[N(SiMe_3)_2AlMe_3]_2\}^-$ consists of an infinite array of anions and Na^+ cations, the latter being 'complexed' by $Na^{+}{\cdots}CH_3$ interactions alone.[26] In a potassium aluminate, $K_2(Me_3AlOBu^{t})_2{\cdot}$PMDETA units are interconnected by $K{\cdots}CH_3(Al)$ interactions to give a polymer.[27]

Solution structural studies have included an NMR investigation (^{7}Li, ^{31}P) of the dynamics of solvent/complexant (HMPA, Me_2O) exchange within chiral alkyllithium reagents.[28] Finally, and regarding MO structural optimisations, the results of calculations on hyperlithiated molecules (e.g., CLi_6, Li_2CN) have been reviewed.[29] An important paper has reported the results of high-powered calculations on $(MeLi)_n$, n = 1, 2, 4, the key finding being that covalent components in polar C-Li bonds play a significant role.[30]

1.3 Alkenyl, Allyl, Vinyl, Alkynyl and Related Derivatives – Lithium species containing acyclic unsaturated anions continue to be important within organic synthetic methodologies. Chiral lithio enol ethers of type $R^*OCH{=}CHLi$ have been made and reacted with haloalkanes to give specifically new chiral *Z*-enol ethers.[31] The vinyllithium $(EtO)_2C{=}CHLi$ can be synthesised and stored in THF at −25°C, and has been used as a masked ethyl acetate synthon.[32] α, β-unsaturated carbonyl compounds have been obtained by reacting carboxylic acid derivatives with $Me_3SiC(Li){=}CH_2$.[33] Dilithiated vinyl species of type $RN(Li)CH_2CLi{=}CH_2$, with R being an aliphatic group, undergo on heating either a dimerisation or a regio- and stereo-selective cyclodimerisation, the product obtained depending upon the reaction time.[34] A solvent dependency has been observed for reactions of N,C-dilithiated 2-allylpyrrole with electrophiles, *Z*-isomers being obtained in THF but *E*-ones in Et_2O.[35] 3,4-dilithio-1,2-butadienes, $R_2C{=}C{=}C(Li)C(Li)R_2$, can be generated by treating substituted butatrienes with Li metal and then derivatised to give substituted 1,2- or 1,3-butadienes, or 2-butynes.[36] The (phosphaalkenyl)lithium carbenoid (*Z*)-$Mes^*P{=}CClLi$ can be transmetallated with $MHal_2$ (M = Mg, Zn, Hg) to give carbenoids of other metals; the Li and Mg derivatives undergo 1,2-addition with carbonyl compounds, leading to β-phosphaallyl alcohols.[37]

Several interesting solid-state structures have appeared. The cyclopropenyllithium $[Me_3Si\overline{C(CMe_2){=}C}Li{\cdot}TMEDA]_2$ has a central $(\alpha CLi)_2$ ring with tetrahedral αC centres; the cyclopropenyl ring is distorted due to rehybridisation at the lithiated carbon.[38] The structures of three novel η^3-allyl-Li and 1-azapentadienyl-Li or -K compounds have been reported; the K^+ species, for example, is a polymer in which two cations lie above and below each η^4-azapentadienyl anion.[39] In the interesting titanium 'tweezer' complex $[(C_5HMe_4)_2Ti(\eta^1\text{-}C{\equiv}CC{\equiv}CSiMe_3)_2]^-{\cdot}[Li(THF)_2]^+$, the Li^+ ion is embedded between the inner triple bonds of the diynyl ligands.[40]

Regarding structural studies in solution, a detailed NMR investigation into silyl-substituted allenyl/propargyllithium species has given insight into the thermodynamics and kinetics of allenyl-propargyl ligand interconversion, and into how these are affected by complexating solvents.[41] Ion-pair acidities ($M^+ = Li^+, Cs^+$) have been determined for some terminal acetylenes in THF over various concentrations, the results then being converted into average aggregation numbers for $(A^-M^+)_n$ ion pairs.[42] Two structural studies by computation are also noteworthy. For singlet 1,1-dilithioethene, earlier optimised structures with $H_2C{=}CLi_2$ formulations were found to be transition states; a C_s monobridged structure with a planar tetracoordinate C is now found to be the lowest lying true minimum.[43] Eight local minima have been found on the potential energy surface of C_3Li_4 calculated at high level: all show either multiple bridging lithiums or clusters of lithium atoms bound to the carbon moiety.[44]

1.4 Aryl Derivatives – Several synthetic applications of aryllithium derivatives have been reported. On warming in the presence of TMEDA, 2-(2-propenoxy) phenyllithium rearranges and undergoes an unusual cyclisation-elimination sequence to give, after methanolysis, 2-(cyclopropyl)phenol.[45] The C_6H_4 unit of the crown ether 1,3-phenylene-16-crown-5 can be lithiated selectively at the intraanular 2-position without affecting the remainder of the crown, and the resulting aryllithium can then be derivatised with various electrophiles or with metal (Sn, Hg, Mg) halides.[46] So-called *ortho* -directed lithiations of aryl groups have been used to generate selectively functionalised benzothiazoles from (haloaryl)thioamides containing the -NHC(=S)R directing group.[47] The mechanism of this type of reaction has been explored by *ab initio* MO calculations on the lithiations of *ortho*-substituted toluenes, *o*-$CH_3C_6H_4X$ (X = OH, NH_2, F); the key finding is that the regiospecificity of the reaction is not due to 'complex-induced proximity effects' in an initial complex but rather to stabilising interactions in the transition state.[48]

Regarding solid-state structures, several categories can be noted: true aryl organometallics $Aryl^-M^+$ gained by metallation/deprotonation of ArylH precursors; those of type $(ArylH^{n-})(M^+)_n$ formed by n-electron reduction of unsaturated organic molecules; and those which do not contain direct M-C(Aryl) bonds but which do exhibit $M^+\cdots$Aryl group interactions. The first category includes dimeric $[2,6\text{-}(2,6\text{-}^iPr_2C_6H_3)_2C_6H_3Li]_2$ in which each Li^+ is bound η^1 to the central phenyl ring of one $(2,6\text{-}^iPr_2C_6H_3)_2C_6H_3$ group and η^6 to an *ortho*-$2,6\text{-}^iPr_2C_6H_3$ substituent of the other aryl ligand, and monomeric $2,6\text{-}(2,4,6\text{-}^iPr_3C_6H_2)_2C_6H_3Li\cdot C_6H_6$ in which Li^+ is bound η^1 to the *ipso* C atom of the anion and (uniquely) η^6 to a benzene solvent molecule; the benzene can be replaced by an Et_2O ligand.[49] Intramolecular $N\cdots M$ and $N\cdots O$ coordination is observed in *ortho*-lithio-β-(N,N-dimethylamino)ethoxybenzene, a new kind of cubane-like tetramer structure in which two of the six edges of the Li_4 tetrahedron remain open, and in the corresponding sodium derivative, the first organosodium solid-state hexamer.[50] The mono-Et_2O and bis-THF lithium complexes of the 9-[2-(dimethylamino)ethyl]fluorenyl anion are both monomers, each with an N-Li attachment and with, respectively, η^5 and η^2 contacts to the fluorenyl central ring.[51] Lithium metal two-electron reduction of dibenzo[a,e]cyclooctatetraene in the presence of TMEDA has given a product whose structure has two $(TMEDA)Li^+$ cations located symmetrically above the central eight-membered ring and so η^8-bonded to it.[52] Similar two-electron reductions of acenaphthylene and fluoranthene have led to contrasting structures; the (15-crown-5)Na^+ complex of the former ligand is monomeric with the ten-coordinate Na^+ ions being above and below the five-membered ring of the dianion, while DME- or diglyme-solvated Li^+ and Na^+ salts of the fluoranthene dianion are polymers in which the cations interact with the six-membered rings.[53] The first structure containing a π-hydrocarbon tetraanion, that of 5,6,11,12-tetraphenyltetracene ('rubene'), has two of its four $(THF)_2Na^+$ cations above and below the central tetracene skeleton with the two others being between the peripheral bis(phenyl)pincers.[54] Several formally M-N bonded structures have revealed $M^{+}\cdots$aryl interactions. The monomeric binuclear diamino-binaphthyl derivatives $[(RN)_2C_{20}H_{12}]\cdot[Li(THF)]_2$ [R = Me_3Si or $^tBuCH_2$] each show quite short $Li^{+}\cdots$*ipso*C(N) contacts.[55] A series of alkali metal phenylhydrazides, including $[(Me_3Si)_2N\text{-}N(Ph)Li]_4$, $[PhN\text{-}N(SiMe_3)Li]_3$, $[Ph(Me_3Si)N\text{-}N(Ph)Na\cdot NH_3]_2$ and $[(Me_3Si)_2N\text{-}N(Ph)Cs\cdot nTHF]_\infty$, all show significant $M^{+}\cdots Ph$ interactions of varying hapticities.[56] The hexameric sodium phenolate complex $[2\text{-}(Me_2NCH_2)C_6H_4ONa]_6$ has a unique Na_6O_6 core of two faced-fused cubes and two of the core Na^+ ions show η^2-arene interactions.[57] It has become clear that the occurrence and structural importance of $M^{+}\cdots$aryl π-contacts increase as M^+ becomes larger/more 'ionic'. Thus, numerous such contacts are found in the structures of Cs^+ species such as the organofluorometallate $[Cs(PhCH_2)_3GaF]_2\cdot 2MeCN$ [58] and the (tetraphenylethanediyl)dicaesium complex $\{(Ph_2C\text{-}CPh_2)^{2-}\cdot[Cs^+(diglyme)]_2\}_\infty$.[59]

Finally, turning to solution structures and those suggested by MO calculation, three papers published in 1996 are noteworthy. $^6Li/^{15}N$ NMR studies on labelled *o*-$(Me_2NCH_2)C_6H_4Li$ in the presence of various complexants have identified mainly dimers with intact Me_2N-group chelation.[60] The ^6Li-[unlabelled ^{13}C]-HMQC-TOCSY NMR technique has been used to distinguish cyclic dimers from trimers or higher ring aggregates in the case of various aryllithium species.[61] *Ab initio* calculations have been done on alkali metal derivatives (M=Li-Cs) of halobenzenes (F, Cl) and the results compared with experimentally found substituent effects.[62]

1.5 Cyclopentadienyl and Related Derivatives – A method has been described for the preparation of optically pure ferrocenes with planar chirality via the enantioselective *ortho*-lithiation of substituted ferrocenes.[63] Reactions of $Ph_2PC_5H_4Li$ with YCl_3 have led to the formation of three yttrocene phosphines.[64] A series of substituted Cp ligands having functionalised groups [C(=O), C(=O)O] that may either chelate or bridge metal centres have been prepared by reacting CpNa with esters etc., and have then been reacted with metal (Mn, Co) carbonyl compounds.[65]

Several very interesting crystal structures of $Cp^-\text{-}M^+$ (M = Li, Na, K, Cs) derivatives have appeared. The benzene adduct of dimeric (pentabenzylcyclopentadienyl)lithium has a triple decker-like structure, $(\eta^5\text{-}C_5Bz_5)Li(\eta^5\text{-}C_5Bz_5)Li(\eta^2\text{-}C_6H_6)$.[66] The group which revealed the structure of the simplest metallocene sandwich, the lithocene anion Cp_2Li^-, has now reported some anionic sodocene structures. Thus, reaction of $Me_4C_2(C_5H_4Na)_2$ with Ph_4PCl in THF gives $[Ph_4P]^+\cdot[Me_4C_2Cp_2Na\cdot THF]^-$ whose *ansa*-sodacene anion has its two Cp rings bridged by a $\text{-}C(Me)_2\text{-}C(Me)_2$-chain; unbridged Cp_2Na^- was also synthesised and has a centrosymmetric (η^5, η^5) sandwich structure.[67] Polymeric $[CpK\cdot OEt_2]_\infty$ exhibits a zig-zag chain structure with $(Et_2O)K^+$ units situated either side of each η^5-Cp ring; several indenyl complexes of Na^+ and K^+ were also reported.[68] The 'tweezer' complex $[(\eta^5\text{-}C_5HMe_4)_2Ti(\eta^1\text{-}C\equiv CSiMe_3)_2]^-\ K^+$ has a structure in which K^+ is situated between the two acetylide groups (*cf.*

reference 40); however, the cation bonds simultaneously to an adjacent C_5HMe_4 ring so forming a polymeric chain.[69] The structure of the heaviest alkali metallocene, the anionic caesocene triple-decker $Cp_3Cs_2^-$, shows several interesting features: the sandwich is strongly bent and the large Cs^+ cations have intermolecular contacts with nearby Cp rings and with Ph groups of the $[Ph_4P]^+$ counter-ions.[70]

Novel π-electron systems based on C_4E rings (E = Si, Ge, P), the so-called 'heterole anions', have received some attention. The silole derivative $[K(18\text{-crown-}6)]^+_2\cdot[C_4Me_4Si^{2-}]$ is monomeric, with complexed K^+ cations either side of the five-membered ring whose similar C-C distances suggest considerable π-delocalisation, in accord with NMR and calculational studies.[71] A trisgermole dilithium complex $[Li(THF)(TMEDA)]\cdot\{Et_4\text{-}Ge,Ge\text{-}[LiEt_4C_4Ge)_2]C_4Ge\}$ has one bare Li^+ sandwiched between two C_4Ge rings which are η^5 and η^4; the latter ring forms a Ge-Li bond to the complexed Li^+ cation.[72] A kalocene-type sandwich structure has been observed for a potassium phospholide containing two $C_3PC\text{-}CPC_3$ 2,2′-biphospholide anions.[73] The first example of an anionic full-sandwich lithiacarborane structure, akin to Cp_2Li^-, has been reported, *viz.* $\{commo\text{-}1,1'\text{-}Li[2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_5]_2\}^-$; multinuclear NMR studies suggest that the structure is maintained in solution.[74] An optically active tetracyclic anion incorporating a sterically crowded Cp ring has been synthesised and the solution structures of its Li^+ salt explored by ^6Li, ^1H-HOESY and ^6Li, ^6Li-EXSY NMR spectroscopy; an *exo*-monomer is detectable at room temperature while at -110°C this species and an *exo,exo*-dimer dominate.[75]

2 Copper, Silver and Gold

2.1 Introduction: Organisation and Major Advances – In contrast to recent previous reports which have been organised on the basis of ligand bonding mode (π-complexes, then σ-bonded species), the sub-sections here deal with the three metals in turn. The reasons for this switch are firstly that many complexes contain both σ- and π-bonding ligands (or the mode is ambiguous), and secondly that most publications deal with derivatives of a particular metal rather than of two (or three) metals. Within each subsection, the ordering of treatment is largely according to organic ligand type (alkyl, aryl, alkynyl, carbido, etc).

Some general comments can be given on activity and progress in this area during 1996. Work on organosilver compounds appears to be rather thin in comparison to that within organocopper and organogold chemistries; for the last, there have been interesting studies not just on Au(I) but also on Au(II) and Au(III) species. The whole area is rather dominated by the syntheses, basic characterisation, and crystal structures of new complexes – understandably so. However, much of this effort is directed towards possible applications of well-defined complexes: notably, as luminescent materials, as candidates for metal film deposition, as anti-tumour agents, and as rigid-rod polymers having extensive delocalisation along their backbones.

2.2 Copper Compounds – Organocopper(I) reagents have found use in various organic and inorganic syntheses. A sequence of carbocupration of ethoxyethyne with PhCu followed by Pd-catalysed cross-coupling of the 2-ethoxyvinylcopper complex with ArI has afforded vinyl ethers Ph(EtO)C=CHAr.[76] A method has been devised for forming relatively thermally stable benzylic copper reagents via Grignard reagents; in the presence of TMEDA and Me_3SiCl these copper species deliver benzylic ligands in a 1,4-manner to α,β-unsaturated esters.[77] Condensation of C-copper(I) derivatives of *meta-* and *para-*carboranes with 2-bromopyridine has been used to synthesise mono- and disubstituted C-2-pyridylcarboranes.[78] Lithium cuprate reagents $R^1Cu(CN)Li$ react with lithium amides R^2R^3NLi to give, after exposure to oxygen, amines ($R^1R^2R^3N$) which are not easily accessible by normal routes; the mechanism is believed to involve oxidative intramolecular coupling of aminyl radicals with the ligands on Cu in an intermediate amidocuprate.[79]

Mixed 2:1 and 2:2 arylcopper-copper bromide aggregates have been prepared and structurally characterised, e.g., $Cu_3Br[C_6H_4(CH_2NMeCH_2CH_2NMe_2)\text{-}2]_2$ and $Cu_4Br_2[1\text{-}C_{10}H_6(CH_2NMeCH_2CH_2NMe_2)\text{-}2]_2$. Such structures, containing an R-Cu-R fragment, can be viewed as comprising a $(R_2Cu)^-$ unit stabilised by a $(Cu_2Br)^+$ or a $(Cu_3Br_2)^+$ cation and so are akin to the kinetic intermediates proposed to be present in cuprate biaryl coupling reactions.[80] In the reaction between (viph)MgBr [viph = *o*-vinylphenyl] and CuCl two unstable mixed aryl/halide intermediates were obtained, $[Mg(THF)_6]\cdot[Cu_5(viph)_2Br_4]_2$ and $[Mg(THF)_5Cl]\cdot[Cu_5(viph)_4Br_2]$, as well as $[Cu_4(viph)_4]$; the structures of the mixed-anion species show both Cu-*ipso*C (of phenyl) and Cu-η^2-vinyl interactions.[81] Alkynyl/acetylide complexes of type $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2]MR$, where R is an alkyl, vinyl, aryl, arenethiolate, halide or pseudohalide anion, have been synthesised and structurally characterised; all contain monomeric MR entities (M = Cu or Ag) in which M is trigonally coordinated by the bis(η^2-alkyne) chelate and an η^1-bonded monoionic ligand R.[82] A series of acetylidocopper(I) complexes has been synthesised and have had their photophysics (phosphorescence, photoluminescence) examined by electronic absorption spectroscopy, emission lifetime measurements, and quenching experiments. Several such species have had their solid-state structures determined, e.g., dimeric $[Cu_2(PPh_2Me)_4(\mu,\eta^1\text{-}C{\equiv}CPh)_2]$ which has a central C_2Cu_2 rhomboidal ring, the tetrameric cubane $[Cu_4(PR_3)_4(\mu_3,\eta^1\text{-}C{\equiv}CPh)_4]$ with R = *p*-MeC_6H_4, and $[Cu_4(\mu\text{-}dppm)_4(\mu_4\text{-}\eta^1,\eta^2\text{-}C{\equiv}C\text{-})](BF_4)_2$ whose four Cu atoms are arranged in a distorted rectangular array and bridged in both η^1 and η^2 modes by the -C≡C- unit in the middle of this rectangle.[83]

Several copper(I) complexes containing neutral alkyne ligands have been reported. The cyclic alkyne 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne(tmtch), $\overline{C{\equiv}C\text{-}CMe_2CH_2SCH_2CMe_2}$, is found in various mononuclear β-diketonate complexes of interest as vapour deposition precursors, e.g., [Cu(acac)tmtch], in the dinuclear μ_2-O^tBu species $[Cu(O^tBu)(tmtch)]_2$, and in the unusual μ_4-oxo derivatives $[Cu_4(O)(tmtch)_4X_2]$, X = Cl or Br.[84] A series of complexes of type (η^2-alkyne)Cu(hfac) have been prepared (hfac = hexafluoro-2,4-pentanedionato) as volatile metal precursors, e.g., mononuclear $(Me_3SiC{\equiv}CSiMe_3)Cu(hfac)$ and dinuclear $(Me_3SiC\equiv CSiMe_3)[Cu(hfac)]_2$.[85] Finally, one noteworthy theoretical study has involved *ab initio* MO calculations (structure optimisations, bond energies) on Cu and Cu^+ complexes of C_2H_2 and C_2H_4, on dimetallated ethene ($C_2H_2Cu_2$), and on tetrasubstituted ethane ($C_2H_2Cu_4$), such species being models for Cu-hydrocarbon interactions on the metal surface.[86]

2.3 Silver Compounds – Studies have concentrated on the syntheses and solid-state structures of Ag(I) complexes containing alkynyl ligands, neutral alkynes, and alkenes, with particular attention being paid to the likely materials applications of such complexes. Heteronuclear species of type $[Pt_2Ag(C\equiv CR)_4L_4]\cdot ClO_4$ have been synthesised; when R = Ph and L = PPh_3, the cation structure consists of two near-orthogonal *cis*-$[Pt(C\equiv CPh)_2(PPh_3)_2]$ units connected via an Ag^+ ion which is unsymmetrically π-bonded to all four alkynyl fragments.[87] The structure of $[Ph_3PAgC\equiv CPh]_4\cdot 3.5THF$ contains a 'flat-butterfly' Ag_4 core whose two 'hinge' Ag atoms σ-bond to two acetylides which then p-complex the apical $Ag(PPh_3)_2$ fragments; in contrast, $[Me_3PAgC\equiv C\text{-}SiMe_3]_\infty$ is polymeric while still containing $(alkynyl)_2Ag^-$ and $Ag(PR_3)_2^+$ fragments, so suggesting that the steric bulk of the (phosphine) ligands is a major influence on Ag acetylide structures.[88] An isosceles triangular metal array with two asymmetric acetylide caps is found in the structure of $[Ag_3(\mu_3\text{-}\eta^2\text{-}C\equiv CPh)_2(dppm)_3]Cl$; the complex exhibits luminescence, MO calculations indicating that the HOMO is Ag-based and that the LUMO is largely the π^* of the $PhC\equiv C^-$ ligand.[89]

Several alkyne and alkene complexes of Ag(I) have been synthesised and characterised with a view to their potential as precursors for metal film vapour deposition. Species of type $[(hfac)Ag]_n\cdot$alkyne have n = 1 or 2 depending on the identity of the alkyne ligand, e.g., mononuclear $[(hfac)Ag]\cdot PhC\equiv CPh$ and tetranuclear $\{[(hfac)Ag]_2\cdot 4\text{-octyne}\}_2$.[90] The isomerically pure (1,5-DMCOD)-$Ag(hfac)_2$, DMCOD = dimethyl-1,5-cyclooctadiene, is dinuclear in the solid with μ_2-hfac ligands and two Ag-diene bonds.[91] A series of [(β-diketonato)Ag(vinyltriethylsilane)] complexes has been prepared, that with hfac ligands being suitable as a precursor to deposit pure Ag films in the range 160–280°C.[92] Finally, an interesting study has revealed that fullerene (C_{60}) having an $NCH_2CH_2(OCH_2CH_2)_2OMe$ side chain changes its solution colour in the presence of Ag^+ ions, absorption spectra indicating that this is due to the cations interacting directly with C=C units on the C_{60} surface.[93]

2.4 Gold Compounds – Trifluoromethylgold(I) complexes of type $F_2RP\cdot AuCF_3$ have been prepared by reacting AuCl with fluorophosphine and $Cd(CF_3)_2$.[94] The first organometallic charge-transfer derivatives involving gold have been made and have had their solid-state conductivities measured; a typical species $[Au(CH_2PPh_3)_2]\cdot(TCNQ)$ has a linear C-Au-C coordination in the cation.[95] Several arylgold species, with the metal in +I, +II, or +III oxidation states or in a combination of two of these, have been structurally characterised. As an example of a series of trinuclear Au_2Ag and Au_2Cu complexes of formulation $\{[Au(\mu\text{-}mes)L]_2M\}A$, with L = PPh_3 or $AsPh_3$, M = Ag or Cu, A = $CF_3SO_3^-$, ClO_4^-, or

PF_6^-, the cation of $\{[Au(\mu\text{-mes})AsPh_3]_2Ag\}\cdot ClO_4$ has a central Ag atom linked to $Ph_3As\text{-}Au$ units by μ_2-mesitylene ligands.[96] The metal-metal bonded digold(II) complexes $Au_2X_2(\mu\text{-}C_6H_4PR_2)_2$ (R = Ph or Et, X = I or Br) isomerise in solution to give digold(I) species $Au_2X_2(\mu\text{-}R_2PC_6H_4C_6H_4PR_2)$ due to a reductive elimination in which a C-C bond is formed at the expense of two Au-C bonds.[97] The mixed-valent Au(I)-Au(III) derivatives $S(Au_2dppf)\cdot[Au(C_6F_5)_3]_2$, dppf = 1,1′-bis(diphenylphosphino)ferrocene, and $S(AuPPh_3)_2\cdot[Au(C_6F_5)_3]_2$ each contain a central μ_4-S atom with a tetrahedral coordination which is particularly distorted in the former complex due to a short Au(I)-Au(I) interaction.[98] Arylgold(III) systems have received especial attention. The Au(III)-Tl(III)-Au(III) complex $Tl(C_6F_5)_2Cl\{Au(C_6F_5)_3[Ph_2PCH_2PPh_2(O)]\}_2$ has a structure in which two $(C_6F_5)_3Au$ units are linked via their P-attached phosphine oxide O atoms to a central Tl atom.[99] Various μ-OH, -OPh, and O,O-acac-arylgold(III) compounds have been synthesised, e.g., $[Au(C_6H_4NO_2\text{-}2)_2(\mu\text{-}OH)]_2\cdot 2Et_2O$, an Au_2O_2 centrosymmetric dimer with two OH bridging groups and terminal aryl ligands.[100] New complexes of type AuX_2L have been prepared, where L is a C,N-chelate containing a phenyl group and an N-donor side-arm (oxazoline and/or Me_2NCH_2) and X is halide$^-$, NCS^-, $CH_3CO_2^-$ or $Et_2NCS_2^-$; in structures determined, the Au(III) centres have square-planar geometry.[101] The species $[AuCl_2(o\text{-}C_6H_4CH_2NMe_2)]$ has been tested *in vitro* against various microbial strains and human tumour lines, towards which it shows differential cytotoxicity similar to that of cisplatin.[102] Extended Hückel calculations have been carried out on small polynuclear complexes with Au centres bridged by aryl and other ligands, the key finding being that the strength of the Au-Au interaction depends mostly on the formal oxidation state of the metal.[103]

Several studies have concentrated on alkynyl/acetylide and isocyanide complexes of gold. The photophysics of luminescent polynuclear species such as $Au_4[1,4\text{-}(Ph_2P)_2C_6H_4](C{\equiv}CPh)_4$, which has a distorted anthracene-like structure, have been examined.[104] The first examples of monomeric bis(η^2-alkyne)Au(η^1-R) complexes have been synthesised and structurally characterised, the alkyne ligand being the chelate $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$.[105] (See also refs. 40, 69, 82). An *ab initio* and density functional theory study has probed the strength of C-H···π interactions for species such as $Cl_3CH\cdots H_3PAuC{\equiv}CAuPH_3$, a reasonably strong (*ca.* 25kJ mol^{-1}) interaction being predicted.[106] Rigid-rod polymers with Au(I) centres bridged by diisocyanides and diacetylides have been synthesised, e.g., $(PhC{\equiv}Au)_2[CNC_6H_2(^tBu)_2NC]$ whose bowed isocyanide ligand (C-N≡C, 168°) allows the molecules to pack in zig-zag chains with short intermolecular Au···Au contacts.[107] Isocyanide complexes of Au(I) containing the fluorinated tris(pyrazolyl)borate ligand $HB[3,5\text{-}(CF_3)_2Pz]_3^-$ have also been reported.[108] Large 26-membered rings with four Au(I) centres result from the strategy of using diisocyanide ligands such as $C{\equiv}N\text{-}C_6H_4\text{-}N{\equiv}C$ to link binuclear fragments of type $AuPR_2CH_2PR_2Au$.[109]

Finally, mention should be made of reported species in which Au atoms are linked to carbon centres within ligands such as carbenes and ylids, methanides, carbido-metal clusters and carboranes. Protonation or alkylation of bis(1-methylimidazolyl)aurate compounds has yielded cationic bis(carbene) complexes such as $[Au(CNRCH=CHNMe)_2]^+$, R = H or Me.[110] The first complex with a hypercoordinate ylidic C atom, $\{[Au(PPh_3)]_4CS(=O)Me_2\}\cdot(ClO_4)_2$, has a square pyramidal structure in which the unique C atom coordinates to four basal $AuPPh_3$ groups.[111] The complex $Au\{C[PPh_2(O)]_3\}(PPh_3)$ exhibits linear coordination by PPh_3 and by the carbon atom of the methanide ligand.[112] In the highly unusual cluster $[Fe_4Au_2C(CO)_{12}(dppm)]$, the carbido C bonds to three Fe atoms and one Au, which together form a distorted square, and the two Au atoms are linked by the bis(phosphine) ligand.[113] Auracarboranes based on two Ph_3PAu units and one or two $C_2B_{10}H_{10}$ cages have been synthesised and structurally characterised.[114]

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2

Group 2 (Be-Ba) and Group 12 (Zn-Hg)

BY DOMINIC S. WRIGHT

1 Introduction

This review is intended to cover a broad and representative cross-section of structural and synthetic studies of Groups 2 and 12 organometallics published in the year 1996, with the discussion concentrating on the major research directions and most important findings. While it is not intended to provide comprehensive coverage of the literature, the breadth of the material surveyed should give a sufficient basis for more in-depth exploration by the reader. A strict definition of organometallics, as compounds containing at least one direct metal–carbon bond to the Group 2 or Group 12 elements, has been used throughout.

2 Synthetic and Structural Studies

The structures of comparatively few Group 2 organometallic complexes were published in 1996. In contrast, structural studies of Group 12 (particularly Hg) organometallics have been numerous and many important findings have been reported. Perhaps one reason for the particular interest in the structures of Hg organometallics is that among the Group 2 and 12 elements the chemistry of Hg is distinctive both in terms of the oxidation states available (I or II), in its higher electronegativity and in its propensity to form metal-metal bonds. The more rigid (predominantly linear) geometry adopted by Hg is also increasingly allowing the rational assembly of large molecules, using this metal as a predictable building block.

2.1 Group 2 – σ-Bonded organometallics are most prevalent and have been most extensively characterised in the solid state for the more electronegative Group 2 (Be, Mg) and Group 12 (Zn, Cd) metals. Owing to their pre-eminence as reagents in organic synthesis, Grignard reagents (RMgX; R= alkyl, aryl, X= halide) have been the focus of most attention in the past few decades.[1] However, perhaps reflecting the well established structural patterns in these species, interest in these complexes has diminished. Among the few simple Grignards to be structurally characterised in 1996 was $[(9\text{–anthracenyl})Mg(\mu\text{-}Br).Et_2O]_2$ (**1**),[2] in which the classic dimeric, halide-bridged structure is preserved despite Lewis base solvation of Mg (as a consequence of the low steric demands of the essentially planar organic group). The less widely studied diorgano-magnesium compounds, such as the recently characterised complex [$Mg(thf)_2\{2\text{-}(CH_2{=}CH)C_6H_4\}_2$] (**2**) (a valuable transfer reagent in the synthesis of vinylphenyl Cu(I) complexes)[3] and [$Mg\{C(SiMe_3)_2(SiMe_2OMe)\}_2$] (**3**),[4] may well attract considerably more attention as reagents in organic and organometallic synthesis in future. In this context, the commercial availability of 'dibutylmagnesium' has led to the increased use of this reagent in the preparation of metallo-organic (amido and imido) magnesium derivatives in recent years.[5] The commercially supplied reagent is in fact a mixture containing approximately equal amounts of ^{s}Bu and ^{n}Bu groups as well as a small percentage of ^{n}Oct groups, to aid solubility in hydrocarbon solvents. A recent study has shown that the addition of TMEDA [= $(Me_2NCH_2)_2$] to the commercial reagent results in the selective crystallisation of the di-*sec*-butylmagnesium complex [$^{s}Bu_2Mg.TMEDA$] (**4**), a complex which is involved in a solvation-desolvation equilibrium in arene solvents.[6]

Despite the lull in the structural characterisation of simple organomagnesium complexes, these reagents continue to be a focus for synthetic and mechanistic studies.[7–12] Some fascinating insights into the mechanism of formation and propagation of Grignards have been forthcoming in a recent photomicrographic study of their formation at the surface of bulk magnesium. This illustrates that the reaction proceeds by the initiation and growth of a finite number of discrete, randomly-distributed active sites, rather than new sites developing during the reaction.[7] This observation is consistent with the active sites being crystalline defects or metal impurities. Addition of I_2 or $FeCl_3$ increases the density of active sites and the rate of reaction in these localities, whereas a Hg/Mg amalgam provides a uniformly reactive surface (but slow reaction). Two studies concerning syntheses of new organomagnesium compounds are of particular interest. The first involves the synthesis of new dialkylmagnesium compounds by living transfer oligomerisation using a lanthanocene catalyst.[8] Ethylene insertion in to the Mg-C bonds of $MgEt^{n}Bu$ is catalysed under very mild conditions (80°C) by an alkyl chain transfer through chain growth polymerisation on the lanthanocene-based catalyst [$Cp^*_2Sm(Cl)_2Li.2OEt_2$] (**5**) (Cp^*= C_5Me_5). Chain lengths of four to two hundred carbon atoms are obtained, with a narrow distribution of products. This reaction is the first example in which a polymerisation with transfer between two different metals can be considered as living, the polymer chains continuing to grow as long as the intermediate species remain in solution. The second investigation of note involves the synthesis of the first examples of permagnesiated aromatic compounds.[9] The reaction of MeMgCl with pentakis-(chloromercurio)(pentamethyl)ruthenocene, [$Cp^*Ru\{C_5(HgCl)_5\}$] (**6**) results in efficient formation of a thf-soluble pentamagnesiated pentamethylruthenocene (**7**) (85%). The observation of three (2:1:2) resonances in the ^{13}C NMR spectrum for the magnesiated cyclopentadienide ring is consistent with a dinuclear structure containing four terminal MgCl units and one cyclopentadienide-bridging Mg (Figure 1). A similar reaction of decakis(chloromercurio)ruthenocene, [$\{C_5(HgCl)_5\}_2Ru$] (**8**), results in the decamagnesiated, highly insoluble complex [$\{C_5(MgCl)_5\}_2Ru]_n$ (**9**) (*ca.* 75% on the basis of hydrolysis). Complexes **7** and **9**

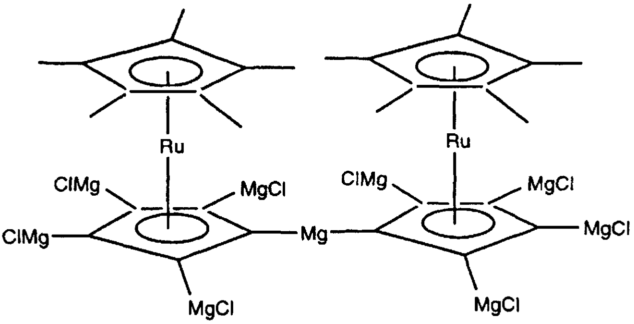


Figure 1 *Proposed structure of* **9**

react much like any other Grignard reagents and are useful in the preparation of symmetrically substituted ruthenocenes. The very efficient magnesiation of ruthenocenes can be compared to mercuration reactions of mono- and disubstituted ferrocenes with $Hg(AcO)_2$, which give mixtures of products owing to the low solubility of the higher mercurated species.[10]

Organomagnesium reagents have also proved useful in the realms of new materials. Despite the fact that H-terminated, HF-etched Si crystals are precursors for the construction of most modern electronic devices, little is known about the chemical reactivity of these surfaces under normal conditions. In a recent study it was shown that resistance to oxidation of these technologically important silicon surfaces can be achieved, without compromising desirable electronic characteristics, by a two-step process involving radical chlorination with PCl_5 followed by alkylation with alkyllithium or Grignard reagents. The resulting surfaces contain little or no Li or Mg and alkylation (particularly with longer chains) drastically impedes the rate of surface oxidation compared to the H-terminated material. This new procedure provides a route to surface functionalities which have not been available by existing methods.[11]

As a consequence of the low reactivity of the bulk metals with organic halides, the tendency for Wurtz coupling reactions of alkyl halides and the lower solubility of the organometallics, until recently very few organometallic complexes of the heavier Group 2 metals (Ca-Ba) had been prepared or characterised in the solid state.[1] The development of new synthetic strategies to active metals and the employment of sterically demanding organic groups has allowed a slow but steady increase in the number of organometallic complexes of these elements.[1] Almost all the structurally elucidated organometallics prepared so far are π complexes containing cyclopentadienide ligands (Cp= C_5H_5), with variable substitution of the Cp rings. New derivatives to be characterised have been $[(\eta^5\text{-}1,2\text{-}{}^i\text{PrCp})_2\text{Sr.thf}]$ (**10**)[13] and the heteroleptic acetylide complex $[({}^i\text{Pr}_4\text{Cp})\text{Ca}(\mu\text{-C}\equiv\text{CPh})(\text{thf})]_2$ (**11**).[14] The latter was prepared by the reaction of $[({}^i\text{Pr}_4\text{Cp})\text{CaN}(\text{SiMe}_3)_2]$ (**12**) with phenyl acetylene and has a dimeric, acetylene-bridged structure in the solid state [replacement of the second $({}^i\text{Pr}_4\text{Cp})$ ligand is not possible]. The first structurally characterised examples of indenyl (=Ind) com-

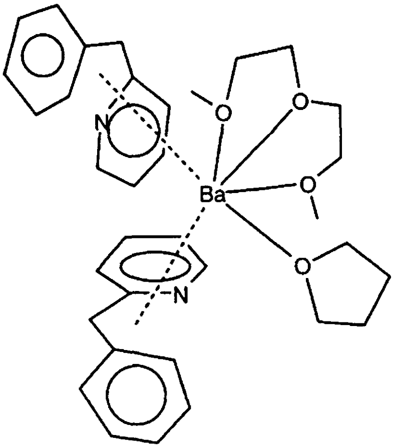


Figure 2 *Structure of* **17**

plexes of the heavier alkaline earth metals, molecular [$(Ind)_2Ca.2thf$] (**13**), [$(1,3\text{-}{}^iPr_2Ind)_2Ca.thf$] (**14**) and [$(1,3\text{-}{}^iPr_2Ind)_2Ba.2thf$] (**15**) and polymeric [$(Ind)_2Sr.thf]_\infty$ (**16**) (Ind= indenyl), were recently reported.[15] The degree of solvation in these species is dependent on the cation size and the extent of steric shielding by the organic ligands. In **16**, association of the molecular units, *via* Sr$\cdots$(π-indenyl)$\cdots$Sr interactions, accounts for the presence of only one coordinated thf ligand per metal centre.

Well characterised organometallics of the heavier alkaline earth metals containing other unsaturated anionic ligands are rare.[1] The recent synthesis of [$Ba\{\eta^5\text{-}PhCH(C_5H_4N\text{-}2\}_2\{MeO(CH_2)_2O(CH_2)_2OMe\}.thf$] (**17**) (Figure 2) introduces a new type of open metallocene, based on metallated 2–pyridylphenyl methane, and is the first complex of Ba involving a ligand other than a substituted Cp ring.[16] The preparation of the complex is achieved by the reaction of 2–pyridylphenyl methane with Ba in NH_3/thf.[17]

2.2 Group 12 – In contrast to the comparatively small number of Group 2 organometallic complexes which were structurally characterised in 1996, such studies of Zn,[18–29] Cd[30,31] and Hg[32–47] complexes have been numerous. Among the simple σ-bonded complexes characterised, some significant advances have been made in the area of Zn and Cd 'ate complexes'. The zincate complex [$Li(TMEDA)]_2[\overline{Zn(CH_2SiMe_2SiMe_2C}H_2)_2$] (**18**), in which the Zn centre of the anion is exclusively coordinated by two metalla-3,4-disilacyclopentane rings, is the first representative of this type of complex for a non-transition element.[25] The association of the two [$Li(TMEDA)_2]^+$ cations to the zincate anion in **18**, *via* bridging to the α-carbon atoms of the metallacyclic rings, can be compared to that in the acetylide complex [$Li(TMEDA)]_2[Zn(C{\equiv}CPh)_4$] (**19**) in which the [$Li(TMEDA)_2]^+$ fragments are associated with the anion by π-bonding to adjacent pairs of phenylacetylene groups.[29] The latter is the first example of a

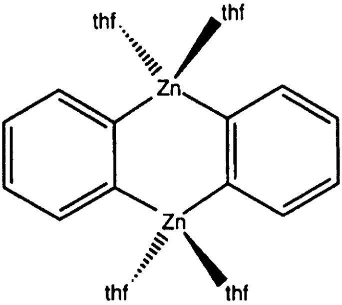
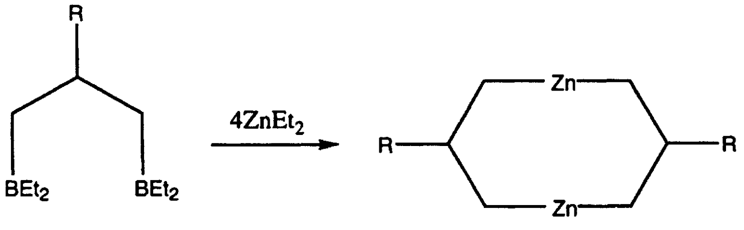


Figure 3 *Structure of* **23**

zinc acetylide to be structurally characterised. The reaction of Me_2Mg with Me_2Cd in the presence of 14-N-4 (1,4,7,11-tetramethyl-1,4,7,11-tetraazacyclotetradecane) gives the ion-separated complex [MeMg(14-N-4)][$CdMe_3$] (**20**), containing the first example of a triorganocadmium anion to be reported.[30]

The chemistry of metallated carlixarenes has been particularly popular in recent years, these ligands providing exciting opportunities for supporting elaborate metal cage arrangements.[48] The metallation of *p*-^{t}Bu-calix[4]arene (H_4L) with excess $ZnEt_2$/TMEDA in toluene gives the fully deprotonated, bis-calixarene complex [$Zn_5L_2Et_2(TMEDA)_2$] (**21**) in which the Zn-attached Et groups point *endo* to the calixarene cavity.[21] The cone-shaped arrangement of the calixarene ligands in **21** is markedly different to the double-flattened cone conformation found in [$Zn_2L'Et_2$] (**22**), resulting from the metallation of 1,3-dimethyl *p*-^{t}Bu-calix[4]arene (H_2L') with $ZnEt_2$.[21a]

Of the many σ-bonded organo Group 12 complexes structurally characterised recently, two studies stand out as particularly important. The first is the structural characterisation of the *ortho*-phenylenezinc complex [(*o*-C_6H_4)Zn.2thf$]_2$ (**23**), obtained by the reaction of the mercury analogue in thf with Zn metal. The structure is composed of a Zn_2C_4 ring core (Figure 3).[23] The strain within this arrangement is evident from the formation of trimers, [(*o*-C_6H_4)Zn.2thf$]_3$, in solution. The reason for the formation of a ring structure for the Zn complex as opposed to a more elaborate cluster structure, akin to that found for the Mg analogue,[49] has been ascribed to the lower polarity of Zn-C bonds. The second important structural finding is that of the first structure of the Simmons-Smith reagent, $IZnCH_2I$, in the solid state. The reaction of CH_2I_2 with EtZnI in the presence of 18-crown-6 gave [($IZnCH_2I$)(18-crown-6)][ZnI_2(18-crown-6)] (**24**) (the formation of ZnI_2 being a result of decomposition of 18-crown-6 at 25°C and/or during data collection).[22] The same workers had earlier been able to differentiate unambiguously the Furukawa reagent ($EtZnCH_2I$) and the Simmons-Smith reagent using NMR spectroscopy, a unique spectrum being obtained for each when complexed by a chiral ether.[50] The same study showed that $IZnCH_2I$ is not decomposed into ZnI_2 and $Zn(CH_2I)_2$ under these conditions, whereas ($EtZnCH_2I$) is involved in an equilibrium with $Zn(CH_2I)_2$ and



R= H, ^{n}Bu

Figure 4 *Boron-zinc exchange leading to 1,3-dizinc compounds*

ZnI_2. Although the structural characterisation of **24** does not prove unambiguously that $IZnCH_2I$ is the *actual* Simmons-Smith reagent present in organic reactions, it is noteworthy that the complex is an active cyclopropanating reagent.[22]

The importance of zinc organometallics in organometallic and organic synthesis has provided the motivation for the development of some new synthetic approaches to these species.[29,51–54] In addition, the use of organozinc reagents continues to be a focus of interest in organic synthesis, particularly in regard to stereo- and regio-control of products.[55] The reactions of primary alkyl halides (RX; X= Cl, Br) with diethyl zinc in the presence of $Ni(acac)_2$ furnishes the corresponding alkyl zinc halides (RZnX) *via* a halogen-zinc exchange reaction.[51] Hydrozincation of terminal alkenes ($RCH{=}CH_2$) with neat diethylzinc is catalysed by $Ni(acac)_2$ in the presence of 1,5-cyclooctadiene, giving the dialkylzinc reagents, $[Zn(CH_2CH_2R)_2]$ (**25**) in 40–95% yield.[51] The reactions of propargylic substrates $[R^1R^2C(X)C{\equiv}CH$, X= Me_2SO_2O, Cl, $R_2NCO_2]$ with a range of triorganozincates, $[(R^3)_3ZnM]$ (R^3= alkyl, alkenyl, aryl; M= Li, MgCl), provides a general method for the preparation of allenic zinc reagents, $[R^1R^2C{=}C{=}C(R^3)ZnL]$ (**26**).[52] Boron-zinc exchange also provides an important approach to cyclic 1,3-dizinc compounds (Figure 4),[53] which are difficult or hazardous to prepare by previous routes involving 1,3-dimercury compounds.[56] It has also been found that homoleptic organometallic complexes of Zn and Cd are accessible by nucleophilic substitution of $[M\{N(SiMe_3)_2\}_2]$ (M= Zn, Cd) with organolithiums, providing a halide-free route to these reagents.[29] The preparation of donor-free $Cd(CHF_2)_2$ (**27**) from the reaction of CdR_2 (R= Me, Et) gives an excellent source of the HF_2C ligand as well as a potential precursor to fluorocarbene, :CFH.[54]

The very distinctive reactivity and coordination chemistry of Hg, compared to the other Group 12 metals, has continued to provide a rich source for structural studies.[32–47] σ-Bonded organomercury compounds to be structurally characterised recently include bis(4-pyridylethynyl)mercury $[Hg^{II}(-C{\equiv}CC_5H_5N)_2]_\infty$ (**28**), having a polymeric zig-zag structure formed by intermonomer N–Hg association,[42] and the metallacyclic complex $[CH_2SiMe_2C(SiMe_3)_2Hg^{II}C(SiMe_3)_2SiMe_2CH_2]$ (**29**).[39] In addition, the tetramercurated methane complexes

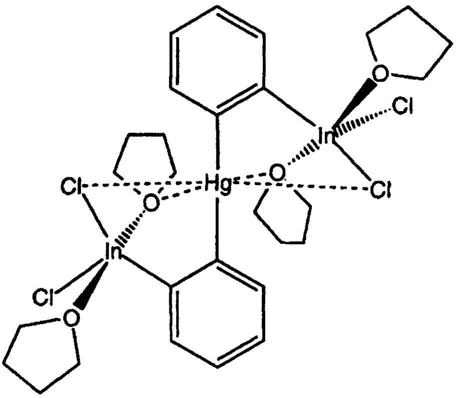


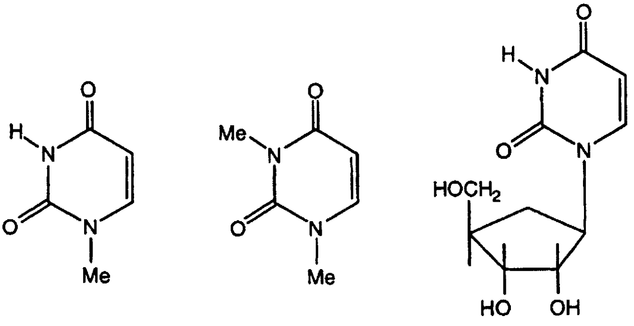
Figure 5 *Structure of* **34**

$[C(HgNO_3)_4.H_2O]$ (**30**) and $[C(HgSO_4)_2(HgOH)_2]$ (**31**), containing tetrahedral CHg_4 arrangements, are rare examples of this type of complex to be structurally elucidated.[40]

A variety of novel structural arrangements and new reactivity patterns have been observed in this area. An interesting example being the addition of $[Me_4N][SCN]$ to metallacyclic perfluoro-*o*-phenylenemercury, $[o\text{-}C_6F_4Hg]_3$ (**32**), resulting in the formation of an infinite helical stacked structure (**33**) composed of alternating $[o\text{-}C_6F_4Hg]_3$ and SCN^- anions.[43] A dramatic reaction is observed between $HgPh_2$ and In^ICl in thf. The product $[Hg\{o\text{-}C_6H_4(InCl_2.2thf)\}_2]$ (**34**) arises from *o*-metallation of the phenyl rings and can be regarded as a trifunctional Lewis acid (Figure 5).[44] The vinylation of the mercury(II) centre of $[S_2WS_2HgCl_2]^{2-}$ (**35**) by acetone, giving $[S_2WS_2Hg(CH{=}CH_2)_2]^{2-}$ (**36**) with ultimate conversion in to $[S_2WS_2Hg(C{\equiv}CH)_2]^{2-}$ (**37**), is also particularly noteworthy.[35]

A study of the binding and reaction of metals with various uracils (Figure 6) has also provided a rare insight in to the metallation behaviour of these biologically relevant ligand systems.[34] The reaction of $Hg(acac)_2$ with 1,3-dimethyluracil (1,3-DimeU) gives the C(5) metallated product [1,3-DimeU-*C5*)Hg(acac)] (**38**). The coordination of Pt(II) to the N(3) atoms of 1-methyluracil or uridine (blocking these positions), again leads to the C(5) metallated products with $Hg(acac)_2$.

A significant advance has been made in the preparation of $[Hg^{II}(CO)_2]^{2+}$ (**39**) and $[Hg_2{}^I(CO)_2]^+$ (**40**), as their $[Sb_2F_{11}]^{2-}$ salts, from the solvolysis reactions of $Hg(SO_3F)_2$ and Hg_2F_2 with HSO_3F in liquid SbF_5 at 80 or 60°C, respectively, in an atmosphere of CO (500–800mbar).[47] This synthetic method is similar to that employed in the preparation of non-classical carbonyl cations of Groups 10 and 11.[57] However, the Hg(I) and Hg(II) complexes are the first examples of carbonyl derivatives formed by a post-transition metal. For the Hg(II) cation **39**, the Raman ν_2 and ν_3 vibrations (av. 2279cm^{-1}) are the highest observed for any



1-MeUH 1,3-DiMeU Uridine

Figure 6 *Mercuration of biologically relevant ligands*

carbonyl compound. The calculated force constant for the $C\equiv O$ bond ($21.0\pm0.1 Nm^{-1}$) in the latter is close to that in $HC\equiv O$,[58] implying that there is no π backbonding involved. The small separation in the Raman-active ν_1 and IR-active ν_3 modes in both cations also indicates weak Hg–C bonding. Raman studies imply that the $[Hg_2(CO)_2]^+$ cation has a Hg–Hg bonded linear arrangement. The X-ray structure of the $[Hg(CO)_2]^{2+}$ salt shows a nearly linear geometry for the cation [C–Hg–C 177.7(7)°], with the long Hg–C bonds [2.08(1)Å] being consistent with minimum backbonding. The presence of extensive Hg···F, O···F and C···F interactions, which link the structure in to a polymeric three-dimensional arrangement, can be ascribed to the resulting $Hg^{\delta+}C^{\delta'+}O^{\delta'-}$ charge distribution. The highest ^{119}Hg–^{13}C coupling constant for any compound (5219±5Hz) is observed in the solid-state MAS-NMR spectrum of **39**.

2.3 Group 2 and Group 12 Organometallics Containing Borane and Carborane Ligands – Complexes of metals with carboranes and BH_4^- continue to be the focus of many studies throughout the periodic table.[59] There have been some exciting new developments in the chemistries of Group 2 and 12 elements using these species as ligands and molecular building blocks. Reinvestigation of the complex $[MeZn(BH_4)]$ (**41**), which is most conveniently prepared by the reaction of $[ZnMe_2]$ with B_2H_6, has shown the structure is that of a helical polymer (Figure 7) in which the BH_4^- ions doubly bridge the Zn centres;[28] a more elaborate formulation than the ionic polymer (involving essentially discrete $ZnMe^+$ and BH_4^- ions) that had been deduced from earlier spectroscopic studies.[60] The structure of **41** therefore resembles that of $Be(BH_4)_2$.

There has been a continued development of Lewis acidic multidentate host molecules containing alkyl substituted *closo*-1,2-$C_2B_{10}H_{10}$ icosahedra joined *via* their carbon vertices by electrophilic Hg(II) centres (Figure 8).[45,46] The reactions of *closo*-1,2-$Li_2[C_2B_{10}H_{10-x}R_x]$ with HgI_2 give $Li_2[C_2B_{10}H_{10-x}R_xHg)_4I_2]$ [R= Et, x= 2; R= Me, x= 2; R= Me, x= 4]. The structures of [K(18-crown-6)]$_2$[(*closo*-1,2-$C_2B_{10}H_8Me_2Hg)_4I_2$] (**42**), $[Bu_4N]_2$[(*closo*-1,2-$C_2B_{10}H_6Me_4Hg)_4I_2$] (**43**) and

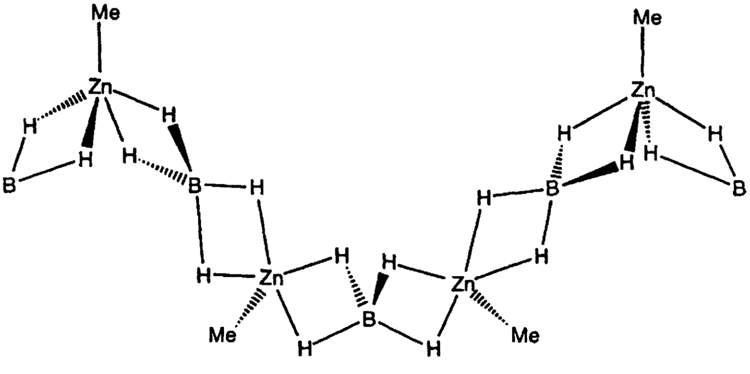


Figure 7 *Structure of* **41**

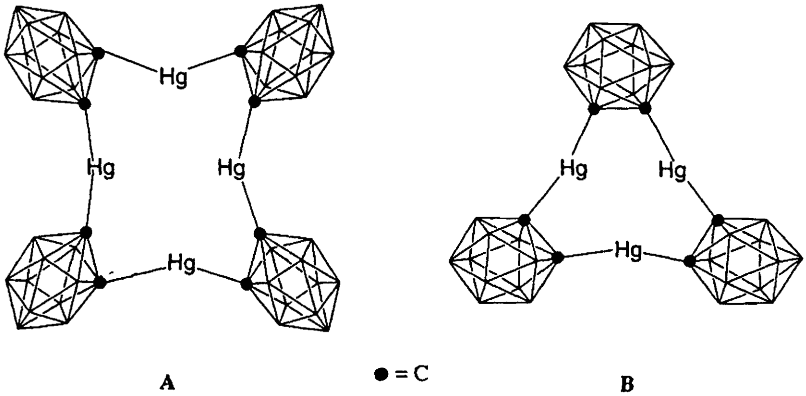


Figure 8 *Schematic representations of the structures of Lewis acidic host molecules containing four* (**A**) *and three* (**B**) *Hg centres linking CB_{10} icosadedra*

$[Bu_4N]_2[(closo\text{-}1,2\text{-}C_2B_{10}H_8Et_2Hg)_4Br_2]$ (**44**) have similar macrocyclic dianion arrangements in which the four Hg centres (**A**, Figure 8) are μ_4-bridged above and below the cavity by two I^- ions.[45] The free host molecules are obtained by reactions of the iodide complexes with stoichiometric amounts of AgOAc. ^{119}Hg NMR studies illustrate that these reactions involve sequencial removal of I^-, leading to the formation of two host-guest intermediates. Subsequent addition of one equivalent of AgAcO to $[(closo\text{-}1,2\text{-}C_2B_{10}H_8Me_2Hg)_4I_2]Li_2$ gave the complex $[(closo\text{-}1,2\text{-}C_2B_{10}H_8Me_2Hg)_4]_3I_4Li_4$ (**45**), having a remarkable stacked ('inverse-sandwich') structure in the solid state in which three macrocyclic rings are linked together by two six-coordinate I^- ions.[45]

The free host molecule $[(closo\text{-}1,2\text{-}C_2B_{10}H_8Et_2Hg)_4]$ (**46**) forms guest-host bis-adducts with $[B_{10}H_{10}]^{2-}$ and $[9,12\text{-}I_2\text{-}1,2\text{-}C_2B_{10}H_{10}]$. $[B_{10}H_{10}]^{2-}$ uses four equatorial B–H vertices to form Hg–HB four-electron three-centre bonds to each

Hg.[45] Symmetry matching of the tetrameric host (C_{4h}) and the guest appears to be a prerequisite for adduct formation, as is indicated by the failure to form a complex with $B_{12}H_{12}^{2-}$ (I_h). The complex of **46** with [9,12-I_2-1,2-$C_2B_{10}H_{10}$] involves the interaction of a guest I atom with the four Hg centres of the host (in a similar manner to that occurring in the structures of the iodide complexes **42** and **43**). 1:1 adducts are formed with $B_{10}I_{10}^{2-}$ and $B_{12}I_{12}^{2-}$.

In contrast to the tetrameric macrocyclic arrangements produced by the reactions with HgI_2, the reaction of *closo*-1,2-Li_2-9,12, Me_2-1,2-$C_2B_{10}H_8$ with $Hg(AcO)_2$ gives the trimeric macrocycle [(*closo*-1,2-$C_2B_{10}H_8Et_2Hg)_3$] (**47**) as the product (**B**, Figure 8).[46] The host-guest complex with three MeCN molecules has been structurally characterised. This difference indicates that the ring size produced depends on the anion present and the potential interaction with the Lewis acidic Hg centres of the ring.

The reaction of Mg powder with 2,4,7,9-[$(Me_3Si)_4C_4B_8H_8$] gives [$(thf)_2Mg\{(Me_3Si)_4C_4B_8H_8\}$] (**48**).[61] The structure, which can be viewed as a fused polyhedron composed of an electron-precise three coordinate B atom, a four-coordinate C atom, a $Mg(thf)_2$ unit, and an electron-deficient cluster (an *arachno*-[$(RC)_3B_6H_9$] fragment), is the first example of a carborane cluster that contains both electron-precise and electron-deficient molecular units.

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3

Scandium, Yttrium and the Lanthanides

BY ANDREA SELLA AND JOHN G. BRENNAN

1 Introduction

This review covers all organometallic complexes reported in the year 1996 and their reactions. We have included endohedral fullerenes since these represent a new all-carbon ligating framework which is receiving increasing attention.

2 Theoretical and Spectroscopic Studies

Xα calculations have been carried out to predict the geometry and electronic structure of La-CO.[1] SCF calculations of the reaction of Sc^+ with methane and $ScCH_2^+$ with H_2 have been reported. The calculations suggest significant differences (both thermodynamic and kinetic) in reactivity between Sc and the later first row transition metals.[2] *Ab initio* calculations have been carried out on the insertion steps of ethylene and propene insertions at *ansa*-bridged metallocenes including samarium.[3]

Relativistic *ab initio* calculations have been carried out on the bis(arene) lanthanide complexes of Cloke. The results correlate well with spectroscopic data and suggest that the stability arises from strong metal to ligand bonding from a metal d^3 ground state.[4] A combined relativistic *ab initio* and experimental thermochemical study of the bonding and energetics in $[M(\eta\text{-}C_6H_3Bu^t{}_3)_2]$ (M = Sc, Ti, Y, Zr, Hf, Gd, Dy, Ho, Er, Lu) has been reported. The M-arene dissociation energies measured by iodinolytic batch titration calorimetry give surprisingly large values. For the transition metals these correlate well with sublimation energies of the bulk metals and arise from strong δ-backbonding from the metal. For the rare earths good correlations with the free atom f→d promotion energies are observed.[5]

Single crystal optical and MCD studies together with SCF calculations of $Cp_3Pr(NCCH_3)_2$ (**1**) doped in the corresponding lanthanum matrix have allowed the determination of the crystal field parameters of the ion.[6] CD studies have also been carried out on $[Cp_2Sm(OR^*)]$ (R^* = various chiral groups) (**2**). Significant effects on the CD spectra of the f-f transitions was observed when the chirality is based on carbon attached to oxygen.[7] The optical spectra of [(COT)PrTp] (Tp = $HBpz_3$ and $HB(3,5\text{-}Me_2pz)$) (**3**) have allowed the crystal field parameters to be determined and the orbital energies compared with those calculated for

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[Ce(COT)$_2$] (**4**) and [Ce(COT)$_2$]$^-$ (**5**).[8] The oxidation state of cerium in cerocene and two SiMe$_3$-substituted derivatives has been probed by XANES spectroscopy and found to be +3. The experimental results support the conclusion of sophisticated *ab initio* calculations that the cerocene ground configuration should be formulated primarily as a $4f^1e^2{}_u\pi e^2{}_u{}^3$ singlet.[9] Finally, the first solid state ^{171}Yb NMR studies of cyclopentadienyl derivatives of ytterbium(II) have allowed the determination of the principal components of the chemical shift tensor by analysis of the side-bands.[10,11]

3 Gas Phase Chemistry

Fourier transform ion cyclotron resonance mass spectrometry has been used to examine the σ-bond metathesis reactions of Sc(CH$_3$)$_2^+$ with the secondary C-H bonds of cyclohexane and cyclopentane. Methane elimination, accompanied by further dehydrogenation, is the initial and dominant reaction observed.[12] The insertion of a variety of organic molecules into the Y-N bond of the Y-NH$^+$ cation has been studied by FT-ICRMS. Insertion is found to lead to a cyclic transition state which undergoes facile dehydrogenation to yield unsaturated products.[13]

The chemistry of several substituted samarocenes has been examined by FT-ICRMS and is found to be dominated by electron transfer.[14]

4 New Compounds

4.1 Cp$_3$Ln Compounds – The structures of two coordination complexes have been described: a previously unobserved phase of [Cp$_3$Nd(THF)] (**6**),[15] and the benzophenone complex [Cp$_3$Dy(OCPh$_2$)] (**7**). The latter is interesting in that the Dy-O-CPh$_2$ angle (170.6(3)°) approaches linearity.[16]

4.2 Cp$_2$LnX Compounds – A wide range of the softer metal halides were found to react with Cp$_2$Yb (**8**) to give the trivalent metallocene Cp$_2$YbCl (**9**) in 70–100% yields (reaction 1–2), with HgCl$_2$ giving the cleanest reaction. The corresponding monobromide and iodide were prepared from the mercury dihalides. Because there is a distinct tendency for this compound type to disproportionate, the structure of the iodide, as the THF solvate Cp$_2$YbI(THF) (**10**), was confirmed by single crystal X-ray diffraction. As expected, the compound has a pseudo-tetrahedral geometry, and shows an intense electronic absorption maximum at 381 nm in benzene.

$$2Cp_2Y + MCl_2 \rightarrow Cp_2YCl + 2M^0\tau(M = Hg, Pd, Cu, Zn, Sn, Pb) \qquad (1)$$

$$Cp_2Y + MCl \rightarrow Cp_2YCl\ (M = Cu, Ag, Tl) \qquad (2)$$

Complications arose in the form of potential metathesis reactions: just as Wilkinson found in early studies of Cp$_3$Ln chemistry,[17] metathesis reactions can be competitive if the more covalent metal metallocene is a particularly stable alternative product. Both $CoCl_2$ and $FeCl_2$ react with Cp_2Yb, but the yields of (**9**) were considerably lower, and ferrocene and cobaltocene formation was also observed.[18]

Rather more examples of Cp_2LnX chemistry were produced from Ln(III) starting materials. Alcohols and thiols were both used as proton transfer reagents (reaction 3) to give bimetallic compounds with bridging chalcogenolate ligands, while carboxylate derivatives were prepared by metathesis.

$$Cp_3Ln + HX \rightarrow [Cp_2LnX]_2 + C_5H_6 \, (X = OR, SR) \qquad (3)$$

There were two reports detailing the reaction of Cp_3Ln compounds with thiols. In one, Cp_3Yb was shown to react with n-propanethiol in THF at room temperature, and the product was characterized by mass spectra and single crystal X-ray diffraction, with which the thiols were shown to bridge the two metal centres.[19] The same structural observation was noted in the synthesis and characterization of a series of Cp_2LnSR compounds (Ln = Dy, Yb; R = n-Bu, n-Pr). The crystal structure of $[Cp_2Yb(SCH_2CH_2CH_2CH_3]_2$ (**11**) was determined, and the important structural features are essentially identical to the previously mentioned Pr^i derivative: the n-butylthiolate contains virtually equivalent (2.716(3) and 2.699(3) Å) Yb-S bond lengths. Bond geometries about the S atoms are, as is typical, consistent with a significant amount of pure p-hybridization. There is unfortunately no UV-visible data reported for the red Yb compounds, although the Dy compounds are described as light yellow, and so the colour presumably is due to some form of a ligand-to-Yb charge transfer absorption. Interestingly, attempts to sublime these compounds led to ligand redistribution (reaction 4), with Cp_3Dy fragments (but not Cp_3Yb fragments) observed in mass spectrometry measurements.[20]

$$3[Cp_2LnSR]_2 \rightarrow 4Cp_3Ln + 2Ln(SR)_3 \qquad (4)$$

Proton transfer reactions of Cp_3Ln with alcohols were also described. Alcohol reactions include n-pentanol and i-butanol (Dy, Yb), which produced dimeric products having pairs of alkoxides bridging the two metal centers,[21] and propargyl alcohol ($HOCH_2CCH$).[22] In contrast to the thiolate compounds, the dimeric structure of the alkoxides is maintained at least partially in the gas phase. Acetoxime ($HONCMe_2$) also reacted with Cp_3Ln (Ln = Pr, Gd, Dy, Yb) to give dimeric structures with bridging OR ligands, although the ligation is more complicated, with the NO unit acting as both a bridging and side-on donor. The structure of the Gd complex (**12**) was determined by X-ray diffraction. There are both long and short (2.27 Å, 2.37 Å) bridging Gd-O bonds, and a dative Gd-N interaction (2.42 Å) present in the structure.[23]

Metathesis reactions were also used to approach new Cp_2Ln(acetate) compounds. The reaction of sodium acetate with a series of the alkali metal halide adducts of Cp_2LnCl gave substitution products. The series of Cp, Cp*, and (C_5HMe_4) ligands were studied for Ln = Sc or Y, La, Sm, and Lu, and the structures of the (C_5HMe_4) derivatives were established by crystallography in order to understand how metal radius influences the connectivity of the dimeric products. Bidentate bridging acetates were found in the Y and Sm compounds, while with the larger La ion, tridentate bridging acetates were observed.[24]

A relatively unconventional metathetical approach to Cp_2LnX compounds gave an interesting aryl complex.[25] Cp_3La reacts with two equivalents of LiAr (Ar = 2,6-$(Me_2NCH_2)_2C_6H_3$) to form a mixture of LiAr and $Cp_2La(\eta^3$-Ar) (**13**), which was soluble in and crystallized from toluene. The structure of the LaAr complex revealed a tridentate Ar coordination to the Ln(III) ion.

4.3 $CpLnX_2$ Compounds – Because Cp ligands tend to redistribute in Ln chemistry, mono C_5H_5 complexes are rare. Early work with cyclooctatetraene dianion ($C_8H_8^{2-}$ or COT) led to the successful synthesis of (COT)LnCp compounds, and more recently, dianionic anthracenide ligand has been applied similarly, in the preparation of $CpLu(C_{14}H_{10})$ (**14**). The anthracenide ligand is considerably more reactive than COT and thus, for example, $CpLu(C_{14}H_{10})$ was found to react with $Fe(CO)_5$ in THF to give $CpLu(THF)Fe(CO)_4$ (**15**).[26]

4.4 Pentamethylcyclopentadienyl Chemistry – The pentamethylcyclopentadienyl (Cp*) ligand has continued to provide access to an extraordinary variety of new chemistry, which can be divided (roughly) into two main areas: the synthesis of compounds containing unusual bonds to the lanthanide elements and unusual Sm(II) redox chemistry, with applications in organic synthesis.

The stabilization of Ln compounds containing bond to elements from the period 3 and 4 elements was prominent. A full report describing the reaction of $(Cp^*)_2Sm$ with Ph_2EEPh_2 (E = P, As) illustrated the difficulties associated with stabilizing such complexes.[27] $(Cp^*)_2Sm$ cleaves the E-E bond in Ph_2EEPh_2 to give the trivalent $(Cp^*)_2SmEPh_2$ (**16**), and the structure of the As complex was determined. THF coordinates readily to these molecules (reaction 5), which can then be used either to form mixed-valent bridging phosphido complexes (reaction 6) by reaction with $(Cp^*)_2Sm$, or they can react further with the THF ligand (reaction 7) to produce the ring-opened product $(Cp^*)_2SmOCH_2CH_2CH_2CH_2EPh_2$ (**17**).

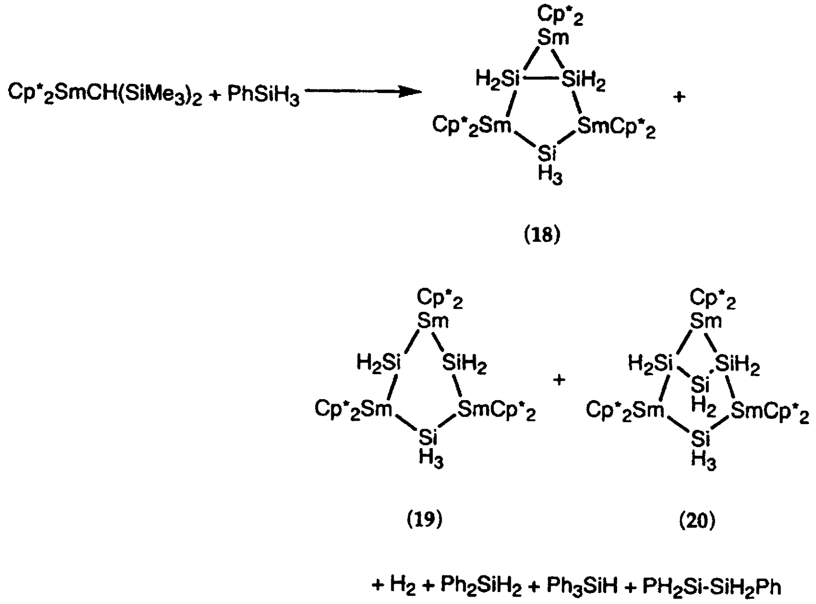
$$(Cp^*)_2Sm + \tfrac{1}{2}\,Ph_2EEPh_2 \rightarrow (Cp^*)_2Sm\text{-}EPh_2 \rightarrow (Cp^*)_2Sm\text{-}EPh_2(THF) \qquad (5)$$

$$(Cp^*)_2Sm\text{-}EPh_2(THF) + (Cp^*)_2Sm \rightarrow (Cp^*)_2Sm\text{-}E(Ph)_2\text{-}Sm(Cp^*)_2 \qquad (6)$$

$$(Cp^*)_2Sm\text{-}EPh_2(THF) \rightarrow (Cp^*)_2Sm\text{-}OCH_2CH_2CH_2CH_2EPh_2 \qquad (7)$$

Lanthanide-silicon bonds also generated considerable interest. A set of remarkable trimetallic complexes $(Cp^*_2Sm)_3(\mu\text{-}SiH_3)(\mu^3{:}\eta^1{:}\eta^2\text{-}SiH_2SiH_2)$ (**18**), $(Cp^*_2Sm)_3(\mu\text{-}SiH_3)_3$ (**19**), and $(Cp^*_2Sm)_3(\mu\text{-}SiH_3)(\mu^3{:}\eta^1{:}\eta^2\text{-}SiH_2SiH_2SiH_2)$ (**20**), were obtained in 64% from the reaction of $(Cp^*)_2SmCH(SiMe_3)_2$ with $PhSiH_3$ (Scheme 1). The reaction which is accompanied by silane redistribution and is presumed to occur by radical reactions via $(Cp^*)_2LnSiH_3$.[28] In a second report, the same starting material (Ln = Sm, Nd, Y), when reacted with an excess of $H_2Si(SiMe_3)_2$, gave a far less complicated proton transfer product (reaction 8).

Structural characterization of the Sm derivative suggests that there is an interaction between the Sm ion and Me_3Si groups on a neighboring molecule, but in pentane solution the compound is a monomer.[29]



Scheme 1

$$(Cp^*)_2Ln{-}CH(SiMe_3)_2 + H_2Si(SiMe_3)_2 \rightarrow (Cp^*)_2Ln{-}SiH(SiMe_3)_2 \qquad (8)$$

The considerable utility of Sm(II) reagents in organic synthesis has prompted a number of investigations into the coordination chemistry of organometallic Sm(II) chemistry. Because redox potentials are dependent on the identity of the anionic ligands, mixed ligand systems are potentially useful for modifying redox strength. This is particularly important in Sm(II) chemistry, where there is such a strong thermodynamic tendency to achieve a trivalent oxidation state. As an example of this redox capability, $Cp^*{}_2Sm$ was shown to react with allylic and propargylic benzylethers to reductively cleave the C-O bond and form $Cp^*{}_2Sm$-$OCH_2C_6H_5$ **(21)** and allylic- or allenic- samarium(III) bonds. Further reaction chemistry of the allylic and allenic complexes with $R_2C{=}O$ were examined to determine reaction stereoselectivity.[30,31]

The reaction of $Cp^*{}_2Sm$ with neutral cyclooctatetraene (C_8H_8, or COT) has been investigated in further detail. In contrast to the related synthesis of the uranocene half sandwich $(COT)_2UCp_2$,[32] the Sm reduction of COT is sensitive to the presence of THF and, as observed in reaction 3, only the ring-opened product $(Cp^*)_2Sm$-$OCH_2CH_2CH_2CH_2C_5Me_5$ **(22)** was isolated. The ether complex

$(Cp^*)_2Sm\text{-}OEt_2$ does react cleanly with COT to give the redistribution product $(Cp^*)_3Sm$, and this product can also be achieved by reduction of $(Cp^*)_2Pb$ with two equivalents of $(Cp^*)_2Sm$.

The latter reaction works even with the more sterically demanding C_5Et_5 ligand, and the structure of 'trigonal planar' $Sm(C_5Et_5)_3$ (**23**) has been determined.[33] Reaction of $[Cp^*{}_2La(\mu\text{-}Cl)_2K(dme)_2]$ with disodium anthracenide $[Na_2(C_{14}H_{10})]$ in toluene in the molar ratio 2:1 gave $[Cp^*{}_2La]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}(C_{14}H_{10})]$.toluene (**24**), which was characterized by X-ray crystallography.[34]

Ligand redistribution with SmI_2 appears to give excellent yields of $[SmI(OR)]_2$ (**25**), a dimer held together by weak Sm···I bonds, rather than by the sterically encumbered alkoxides. The mono-iodide reacts further with KCp* in THF/hexamethylphosphoramide (HMPA) to give $Cp^*Sm(OR)(HMPA)_2$ (**26**), which was also characterized by X-ray diffraction. This divalent product reacts readily with halogen sources such as I_2 or $ClCH_2CH_2Cl$, but only the oxidized ligand redistribution products $(RO)_2Sm\text{-}X$ (X = Cl, I) were isolated successfully.[35] In a separate report, the synthesis of (**25**) was again described, and the reactions of both one and two equivalents of KCp* were described. In the latter reaction, the organo-heterometallic coordination polymer $[(RO)Sm(\mu\text{-}Cp^*)K(\mu\text{-}Cp^*)(THF)_2]_n$ (**27**) was isolated and structurally characterized.[36]

In redox-inactive chemistry, new lanthanide benzyl (Bz) complexes were reported, including an unusual example of a mono-Cp* Ln complex. Using $LnBr_3$ (Ln = Y, Sm, Gd), KCp*, and KBz as starting materials, $[(Cp^*)_2Y(Bz)THF]$ (**28**), polymeric $[(Cp^*)_2Sm(Bz)_2K(THF)_2]_n$ (**29**), and $[(Cp^*)Gd(Bz)_2THF]$ (**30**), were selectively crystallized and characterized by X-ray diffraction.[37] An alternative synthetic approach to mono Cp* Ln complexes, using $LnCl(BH_4)_2$ starting materials (Ln = Sm, Dy, Yb), has also been reported.[38] Also, C-H bond activation was noted in the reaction of $[(Cp^*)_2SmH]_2$ with 2-phenylpyrroline, aromatic ketamines, and aldimines to give *ortho*-metallated products.[39]

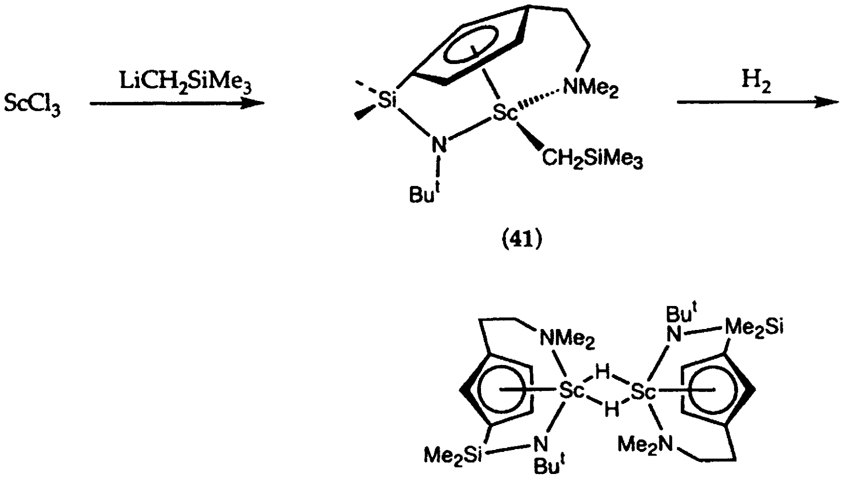
4.5 Substituted Cp ligands – Substituted Cp ligands continue to have an impact in lanthanide chemistry, and the functionalizations can be grouped into three broad categories. The first and simplest group includes complexes containing aryl or alkyl substituted Cp ligands that are designed primarily to increase complex solubility and decrease the number of available metal coordination sites. Second, there are now a number of Cp ligands containing Lewis base functional groups covalently attached to the C_5H_4 core, which can be used either to coordinate and encapsulate the Ln atom or bridge to different metals. Finally, there are now a variety of tethered Cp-X-Cp ligands, which are useful both for stopping ligand redistribution processes and/or imparting chirality. The three classes will be treated separately.

The Bu^tCp ligand has been used to inhibit ligand redistribution processes and kinetically trap a molecular lanthanide fluoride before LnF_3 could precipitate given the extraordinary insolubility of LnF_3, this is a noteworthy event. The redox reaction of divalent $(Bu^tCp)_2Sm(THF)_2$ with Me_3SnF to give the trimetallic fluoride-bridged product $[(Bu^tCp)_2SmF]_3$ (**31**) in 44% yield.[40] The same Cp ligand was also used to isolate the toluene-soluble acetylides $[(Bu^tCp)_2Ln(\mu\text{-}C{\equiv}CPh)]_2$ (Ln = Nd, Gd) (**32**),[41] which contained nearly symmetric bridging acetylides. The benzyl-substituted Cp ligand was also used to inhibit ligand redistribution in the preparation of $(Cp\text{-}CH_2Ph)_2LnCl(THF)$ (Ln = Gd, Er) (**33**).[42] Precursors to redox chemistry were evident in Yb(II) chemistry: The silylated Cp analogue Cp-$SiMe_3$ was used in the synthesis and structural characterization of $(Me_3Si\text{-}Cp)_2Yb(THF)_2$ (**34**),[43] and an unusual hexa-Yb cluster intermediate (**35**) was selectively precipitated in the attempted synthesis of $(Cp\text{-}SiMe_2Bu^t)_2Yb$.[44] The structure consists of a cube of iodides with the faces bridged by six μ_4-Yb (Me_3SiCp) units.

The Lewis acid functionalized Cp chemistry includes P, N, and O donor ligands. The phosphine chemistry is most straightforward: the diphenylphosphinocyclopentadienide ligand (Ph_2PCp) forms a variety of compounds with Y. The lithium chloride adduct $(Ph_2PCp)_2YCl_2Li(THF)_2$ (**36**) can be prepared from YCl_3, the LiCl can be removed to form the dimeric complex $[(Ph_2PCp)_2YCl]_2$ (**37**), and the bridging halide can be displaced with THF to form monomeric $(Ph_2PCp)_2YCl(THF)$ (**38**). Only the structure of the bridging chloride was determined. These molecules are potential chelating ligands toward softer metal centres, and should form a variety of heterometallic complexes containing both covalent and ionic metals. Coordination of the P donors to $Mo(CO)_x$ was examined.[45] The methoxyethylCp ligand $Cp\text{-}CH_2CH_2OMe$ was used to prepare both mono- and tris-Cp compounds. In the homoleptic series $Ln(Cp\text{-}CH_2CH_2OMe)_3$ (Ln = La, Pr, Nd, Gd, Y) (**39**), the metals all coordinate two of the three available O donors in a *trans* geometry. Coordination of two neutral donors to a Cp_3Ln fragment is well documented, although still considerably less frequent than the Cp_3Ln-L structures, and in this series aspects of both structural types are present. The Ln-Cp bond lengths and one Ln-O bond length are directly related to the metal ionic radius; smaller metals have shorter bonds. In contrast the second Ln-O bond length responds to a decrease in metal size by lengthening to decrease ligand-ligand repulsions.[46] Given the chelating interactions in these Cp_3Ln complexes, the proposed coordination of the O donor in $(Cp\text{-}CH_2CH_2O\text{-}Me)Ln(N(SiMe_3)_2)_2$ (Ln = Y, Yb) (**40**) seems reasonable. These compounds were isolated in high yields from single pot reactions of $LnCl_3/NaCp/LiN(SiMe_3)_2$, and shown to be mononuclear by mass spectrometry.[47] In a completely different approach, and one that should become increasingly useful in the synthesis of Cp ligands with readily tuned steric/stereospecific properties, the diprotic $C_5H_5\text{-}N(CH_2CH_2NMe_2)SiMe_2N(H)\text{-}{}^tC_4H_9$ was shown to react with $Sc(CH_2SiMe_3)_3$ to eliminate TMS and form the monoalkyl derivative $[Sc\{CpN(Me)SiMe_2N\text{-}(Bu^t)\}CH_2SiMe_3]$ (**41**) in a diastereoselective manner. Hydrogenolysis was found to form hydrido-bridged isomers (**42**) one of which was crystallographically characterized (Scheme 2).[48]

Finally, chelating chiral Cp derivatives were reported for Ca(II), as well as the redox active metals Sm(II) and Yb(II). The tertiary amine donor $(Cp\text{-}CH(Ph)CH_2NMe_2)$ the ether donors in $Cp\text{-}CH_2CH(R)OMe$ (R = Me, Ph) were shown to coordinate in a chelating fashion to all three divalent metals.[49]

There now exist a number of Cp ligand systems in which two Cp ligands are



(41)

(42)

Scheme 2

covalently attached through a series of covalent bonds. Early work in which CH_2 or $SiMe_2$ units bridged the two C_5H_4 ligands has now been supplemented by a wide variety of both linkages and substituted Cp ligands. Complex asymmetry can be induced by coupling different Cp groups, as in the preparation of chiral Ln derivatives (Ln = Y, Nd, Sm, Lu) of Cp-$SiMe_2$-C_5H_3(t-Bu), which were isolated as the LiCl adducts $[Cp\text{-}SiMe_2\text{-}C_5H_3(Bu^t)]Ln(\mu\text{-}Cl)_2Li(THF)(OEt_2)$ (43).[50] Other examples are discussed in the polymerization catalysis section (*vide infra*).

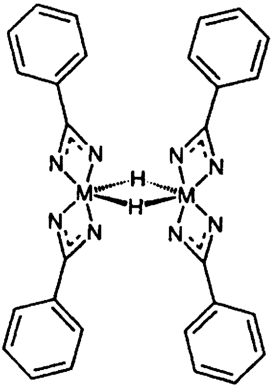
Additional donor ligands can also be incorporated into the linkage between Cp groups. Ether donors were used in both divalent and trivalent lanthanide chemistry: substituted $Cp\text{-}CH_2CH_2\text{-}O\text{-}CH_2CH_2Cp$ ligands were shown to coordinate both Cp and the oxygen donor to the monochlorides of Y, Nd, Sm, and Yb. These compounds, along with NaH, were tested as catalysts for the reductive dehalogenation of aryl halides and of 1-octene.[51] The Sm and Yb complexes could be reduced with sodium metal in THF to give divalent metallocene compounds that were isolated either as a bis-THF adduct or as the structurally characterized DME coordination complex.[52]

4.6 Metal Amides and Derivatives as Ancillary Ligands – A variety of nitrogen-based ligands have been used to stabilize organometallic complexes of these electropositive metals kinetically. Of these, the resonance stabilized benzamidinates $[Me_3Si\text{-}N{=}C(Ph)\text{-}NSiMe_3]^-$, (NCN) have led to the most detailed chemistry, particularly in Y chemistry.

Bis-NCN complexes of both Sc and Y have been described. In the Sc chemistry, the salt elimination reaction of (TMEDA)Li(NCN) with $ScCl_3$ in THF gave a mixed metal salt LiCl containing product [$(NCN)_2Sc(\mu\text{-}Cl)_2Li(TMEDA)$] (**44**), but the Li could be eliminated by using $(Et_2O)Li(NCN)$ yielding [$(NCN)_2ScCl(THF)$] (**45**). The bis-amidinate starting material (**45**) was subsequently used in the preparation of numerous mono-alkyl derivatives {$(NCN)_2ScR$, (**46**) R = CH_2SiMe_3, mesityl} and THF solvates ($(NCN)_2ScR(THF)$, (**47**) R = Me, BH_4), *via* salt elimination with the corresponding LiR reagents.

$$ScCl_3 + (Et_2O)Li(NCN) \rightarrow (NCN)_2ScCl(THF) + LiR \rightarrow (NCN)_2ScR(THF)_x \quad (9)$$

Further reactions of $(NCN)_2ScCH_2SiMe_3$ with the acidic proton on $HC{\equiv}CSiMe_3$ gave Me_4Si and the terminal acetylide $(NCN)_2ScC{\equiv}CSiMe_3$ (**48**), and the reaction with H_2 gave the dimeric bridging hydride [$(NCN)_2Sc(\mu\text{-}H)_2Sc(NCN)_2$] (**49**), which was structurally characterized. This dimeric hydride complex reacted with $PhC{\equiv}CPh$ to hydrogenate the acetylide and form $(NCN)_2ScC(Ph){=}CH(Ph)$ (**50**).[53]



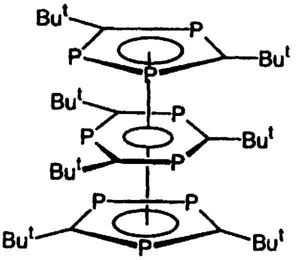
M = Sc (**49**), Y = (**52**)
N = $NSiMe_3$

Similar results were observed with yttrium. [$(NCN)_2YCl(THF)$] (**51**) was prepared from YCl_3 and the LiNCN reagent in THF, and a wider variety of derivatives ($(NCN)_2YR$, R = BH_4, $N(SiMe_3)_2$, substituted Ph, Me-LiMe, $CH_2Ph(THF)$, and CH_2SiMe_3) were prepared. As in the Sc work, the trimethylsilyl compound was hydrogenated to give the dimeric hydride [$(NCN)_2Y(\mu\text{-}H)_2Y(NCN)_2$] (**52**). Over the years, there have been numerous comparisons between NCN and the Cp* ligand which have generally concluded that the steric demands of Cp* and NCN are strikingly similar. Interestingly, in this synthetic paper semi-empirical MO calculations were undertaken in an attempt to detail the differences in electronic structure of $Cp^*{}_2YCl$ and NCN_2YCl complexes. Essentially, NCN ligands appear to be less effective than are Cp ligands in donating electron density to the metal centre, and this deduction was used to explain differences in H/D exchange with solvent or $M\text{-}CH_3$ hydrogenolysis rates. Because the metal orbitals are relatively contracted due to the increased charge on the metal, coordination of additional ligands is a less favourable process.[54] The reactivity of $(NCN)_2YR$ [R = $CH_2Ph(THF)$, H, and CH_2SiMe_3] toward a wide range of small molecules was studied in detail. A number of reaction pathways, including C-H bond activation and insertion into Y-X bonds, were observed.[55]

YCl_3 reacts with 2 equivalents of $LiCH(SiMe_3)_2$ and 1 or 2 equivalents of $LiOCMe_3$ to form the complexes $[(Me_3Si)_2CH]_2Y(\mu\text{-}OCMe_3)_2Li(THF)$ **(53)** and $(Me_3SiCH_2)_2Y(OC_6H_3Bu^t{}_2\text{-}2,6)(THF)_2$ **(54)** respectively.[56]

Reaction of $ErCl_3$ with $LiNCMe_3(SiMe_2H)$ (LiL) in Et_2O to give ErL_3 **(55)** which has been shown by X-ray diffraction to have three agostic Si-H interactions. This accounts for the low melting point and high volatility of the complex.[57]

4.7 Other organometallics – Co-condensation of scandium vapor with t-butylphosphalkyne, $[Bu^tC{\equiv}P]$, affords the triple decker sandwich complex $[(\eta^5\text{-}Bu^t{}_2C_2P_3)_2Sc_2(\mu{:}\eta^6{:}\eta^6\text{-}Bu^t{}_3C_3P_3)]$ **(56)**, which was structurally characterized by X-ray crystallography. This remarkable compound is the first example of a scandium complex in a formal oxidation state of +1 as well as the first structurally characterized example of a triphosphabenzene ligand bound in η^6 fashion to a metal atom.[58]



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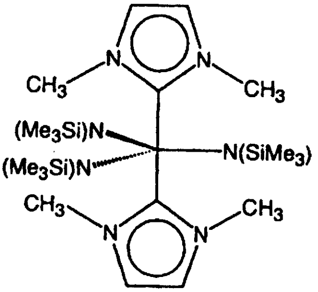

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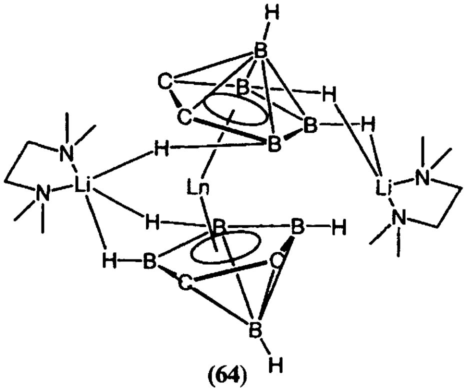
The preparation of lanthanide complexes of heterocyclic carbenes has been patented.[59] Examples are given of the preparation of ErL_3Cl_3 **(57)**, $YL(THF)_n[N(SiMe_3)_2]_3$ **(58)**, and *trans*-$YL_2[N(SiMe_3)_2]_3$ **(59)** (L = 1,3–dimethyl-imidazolin-2–ylidene).

A number of new mixed sandwich complexes of C_8H_8 have been prepared. The reaction of $[(\eta^8\text{-}C_8H_8)Ln(\mu\text{-}Cl)(THF)]_2$ (Ln = Sm, Tm, Lu) with Na(pyr*) (pyr* = $NC_4H_2Bu^t{}_2\text{-}2,5$) yields $[(\eta^8\text{-}C_8H_8)Ln(\eta^5\text{-}pyr^*)(THF)_x]$ **(60)** (Ln = Sm, x = 1; Ln = Tm, Lu, x = 0).[60] $GdCl_3$ reacted with $C_6H_5CH_2C_5H_4Na$ in THF in the ratio 1:1 at room temperature for 1 h giving $C_6H_5CH_2C_5H_4GdCl_2.nTHF$ **(61)**, which, when reacted with $K_2(C_8H_8)$/THF gave the complex $[(\eta^8\text{-}C_8H_8)Gd(\eta^5\text{-}$

$C_6H_5CH_2C_5H_4)]$ **(62)**.[61] The corresponding reaction with Nd gives $[(\eta^8\text{-}C_8H_8)Nd(\mu_2\text{-}\eta^8\text{-}C_8H_8)K(THF)(\eta^3\text{-}C_6H_5CH_2C_5H_4\text{-}\mu^2\text{-}\eta^5\text{-}C_5H_4)Nd(THF)_2(\eta^8\text{-}C_8H_8)]$ **(63)**.[62]

Sandwich compounds with carboranes as ancillaries have been prepared including $[Li(TMEDA)_2][1\text{-}Cl\text{-}1\text{-}(\mu\text{-}Cl)\text{-}2,2',3,3'\text{-}(SiMe_3)_4\text{-}5,6\text{-}[(\mu\text{-}H)_2Li(TMEDA)]\text{-}4,4',5'\text{-}[(\mu\text{-}H)_3Li(TMEDA)]\text{-}1,1'\text{-}$*commo*-$Ln(2,3\text{-}C_2B_4H_4)_2]$ (Ln = Sm,



(64)

Gd, Dy, Ho, Er) **(64)** in high yields.[63] The structural characterization of the holmium complex was reported separately. [64]

Complexes of the type $\{[LnI_2(THF)_3]_2(\mu\text{-}C_{10}H_8)\}I$ **(65)** (Ln = Ce, Pr, Nd, Gd) were obtained by the reaction of $LnI_3(THF)_3$ with Li and excess naphthalene ($C_{10}H_8$); their magnetic moments correspond to the +3 oxidation state of the metals. A Yb(II) complex, $[YbI(DME)_2]_2(\mu\text{-}C_{10}H_8)$ **(66)**, was synthesized by the reaction of $YbI_2(THF)_2$ with an equimolar amount of naphthalene lithium.[65] Finally the reaction of $CpLnCl_2(THF)_3$ (Ln = Y, Gd, Er, or Tm) with Na naphthalenide gives mononuclear complexes $CpLnC_{10}H_8(DME)$ **(67)**. Binuclear complexes $[(CpLn)_2(C_{10}H_8)(THF)_4]$ **(68)** (Ln = Sm or Yb) containing Ln(II) are formed in similar reactions of Sm and Yb complexes.[66] Reaction of $C_{10}H_8Ln(DME)$ (Ln = Eu, Yb) with $PhC{\equiv}CH$ in DME results in C-C bond formation and give complexes $Ph_2C_4H_2Ln(DME)_2$ **(69)**. Hydrolysis yielded a mixture of isomers of 1,4-diphenyl-1,3-butadiene. The reaction of **(66)** with $PhC{\equiv}CH$ leads to mixed iodo-ethynyl complexes $[ILn(\mu\text{-}C{\equiv}CPh)(DME)_2]_2$ **(70)**.[67] The reaction of $[LnI_2(DME)_3]$ with an equimolar mixture of $K(C_5H_5)$ *and* $K(C_5H_5)V(C_{10}H_8)$ in DME followed by treatment with THF gave the tetradecker polymetallic complexes $\{[(C_5H_5)V(C_{10}H_8)]_2Ln(THF)(DME)\}$ **(71)** with Ln = Eu and Sm.[68]

A dianionic lanthanide(II)-imine azametallacyclopropane complex, $[Yb(\eta^2\text{-}Ph_2CNPh)(hmpa)_3]$ **(72)** was synthesized directly by the reaction of Yb metal with N-(diphenylmethylidene)aniline in THF/HMPA. The complex acts as a basic reagent rather than a nucleophile unlike lanthanide-benzophenone and thiobenzophenone complexes in the reaction with acetone and a catalytic amount causes the selective isomerization of 1-hexyne to 2–hexyne in 95% yield.[69]

5 Catalysis

5.1 Hydrogenation, Hydrosilylation, and Cyclization – The range of catalytic applications have continued to widen. The complexes [Cp^*_2MR] {M = Sm, Yb; R = $CH(SiMe_3)_2$} have been used as catalysts for hydrogenation and hydrosilylation. Both reaction types were sterically driven and gave *cis*-diastereomers as the major products. For example, the hydrogenation of 1-methyl-3-methylenecyclohexane gave *cis*-1,3-dimethylcyclohexane. The hydrosilylation of these substrates was regiospecific, the silane being placed exclusively at the terminal position of the double bond.[70] Yttrium-catalyzed cyclization/hydrosilylation has been used in the total synthesis of lupinine.[71]

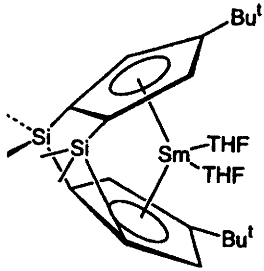
A detailed study of hydrogenation and olefin cyclization using pseudo-*meso* *ansa*-metallocene type complexes of a range of rare earth ions showed moderate stereoselectivity.[72]

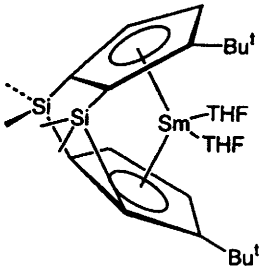
A detailed kinetic study of hydroamination/cyclization of alkynamines to give imines with metallocene catalysts suggests that the turnover-limiting step is an intramolecular alkyne insertion into the Ln-N bond followed by rapid protonolysis of the resulting Ln-C bond.[73] A related study investigated the internal hydroamination of alkynes and the results were found to parallel intramolecular examples.[74] Organolanthanide complexes $Cp^*_2LnCH(TMS)_2$ (**73**) and $Me_2SiCp'_2LnCH(TMS)_2$ ($Cp' = \eta^5\text{-}Me_4C_5$; Ln = lanthanide) (**74**) serve as precatalysts for the efficient regiospecific bicyclization of substrates of the structure $\{RC{\equiv}C(CH_2)\}_2NH$, $RC{\equiv}C(CH_2)NH(CH_2)CH{=}CH_2$, and $\{H_2C{=}CH(CH_2)\}_2NH$ to the corresponding pyrrolizidine and indolizidine skeletons.[75]

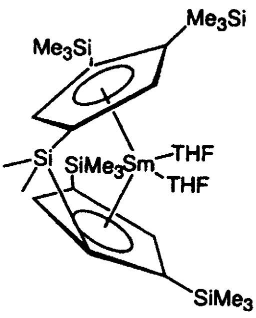
5.2 Olefin Polymerization – A short review of living polymerizations catalyzed by rare earth metallocenes has been published.[76]

Ansa-bridged metallocenes were used as polymerization initiators[77] and for the syndiotactic polymerization of methylmethacrylate.[78]

Ethylene polymerization was explored by using the racemic [$SiMe_2(2\text{-}SiMe_2\text{-}4\text{-}Bu^tC_5H_2)_2Sm(THF)_2$] complex (**75**), *meso* type [$Me_2Si(Me_2SiOSiMe_2)(3\text{-}$



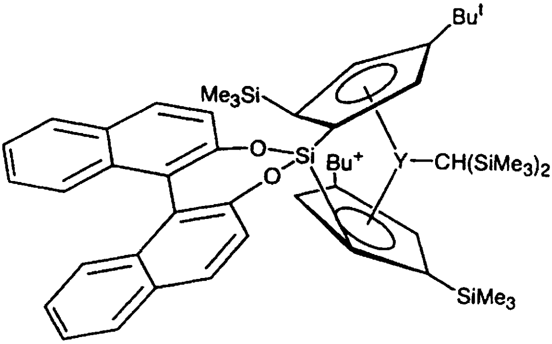




(75) **(76)** **(77)**

$Bu^tC_5H_2)_2Sm(THF)_2]$ complex **(76)**, and C_1-symmetrical $\{SiMe_2[2,4-(SiMe_3)_2C_5H_2][3,4-(SiMe_3)_2C_5H_2]Sm(THF)_2\}$ complex **(77)** in the absence of methyl-aluminoxane. The *meso* isomer exhibits highest initiating activity, but the molecular weights were relatively low. In contrast, the C_1-symmetrical complex provides the highest MW of polyethylene, $M_n > 1\,000\,000$, with relatively narrow molecular weight distribution ($M_w/M_n = 1.60$). Only **(75)** exhibits good activity for the polymerization of propylene, 1–pentene and 1–hexene.[79]

A new linked bis(cyclopentadienyl) ligand, $(C_5H_3\text{-}2\text{-}SiMe_3\text{-}4\text{-}CMe_3)_2Si(OC_{10}H_6C_{10}H_6O)$ ($BnBpH_2$), has been designed to coordinate to transition metals to afford a single enantiomeric C_2-symmetrical *ansa*-metallocene. Steric interactions between the 3- and 3′-methine positions of the 1,1′-binaphth-2,2′-diolate rings of the chiral linker with the α-trimethylsilyl substituents on the cyclopentadienyl rings force enantioselective metallation of this ligand. As anticipated, hydrogenolysis of enantiopure $(BnBp)YCH(SiMe_3)_2$ **(78)** affords directly only enantiopure homochiral dimer **(79)** which, when generated *in situ* from (R,S)-**(78)**, polymerizes 1-pentene to highly isotactic poly-1-pentene (MW_n = 119 000, PDI = 1.44, *mmmm* >95%).[80]



(78)

The stereochemistry of pentene insertion in the single component isospecific polypropylene catalysts (R,S)-(BnBp)Y-R/(S,R)-(BnBp)Y-R and racemic (±)-(BnBp)Y-R has been studied. Optically active (99% ee) (R)-1,1,3,4,4,5,5,5-octadeutero-1-pentene has been used to evaluate the stereoselectivity of Y-H and Y-n-pentyl additions for the optically pure C_2-symmetric (R,S)-(BnBp)Y-R/(S,R)-(BnBp)Y-R and racemic (±)-(BnBp)Y-R isospecific polypropylene catalysts. Deuteration and deuterodimerization of the deuterated pentene mediated by (R,S)-, (S,R)-, and (±)-(BnBp)Y-D provide alkanes whose ^1H NMR spectra indicate the sense and magnitude of olefin facial selectivity for insertions into metal-hydride and metal-n-pentyl bonds. It is shown that useful information concerning the stereochemistry of olefin insertion can be deduced from the ^2H NMR spectra of 1–pentene deuterodimers without the requirement of a stereochemically labeled pentene or a resolved catalyst.[81]

$[(C_5H_3{}^tBu_2)_2Yb.THF]$ (**80**) has been reported to polymerize hexenes.[82] Styrene polymerization using a highly active combined rare earth/magnesium catalyst has been studied.[83] A method for preparing silyl-terminated polyolefins using metallocene catalysts and silanes as chain transfer agents has been developed and patented.[84] The ring-opening co-polymerization of strained *exo*-methylenecycloalkanes with ethylene by $[Cp^*{}_2LnH]_2$ has been studied. The effectiveness of the catalyst falls as the ionic radius of the ion increases.[85]

Field desorption MS has been used to investigate how heavier olefins are incorporated into growing polyethylene chains by $[Cp^*{}_2Sm(allyl)]$ (**81**) catalysts as precursors. The reaction is shown to proceed by insertion into a Sm-H bond rather than *via* the Sm-allyl group. Metallation of the incoming olefin by the growing polymer chain competes effectively with hydrogenolysis and provides a means of controlling polymer weight.[86]

Organolanthanide complexes such as $[Sm(Cp^*)_2Me(THF)]$ (**82**) and $[Sm(Cp^*)_2H]_2$ (**82**) initiate the living polymerizations of ε-caprolactone and δ-valerolactone to give high molecular weight polyesters (Mn > 70000) with extremely narrow polydispersities, $M_w/M_n < 1.08$, while these initiators are completely inert for the polymerization of β-propiolactone.[87] The co-polymerization of THF and valerolactone using $RSmI_2$ has been demonstrated.[88] Metallocene catalysts have been used as catalysts for the preparation of acrylate block copolymers.[89]

Dienes can be polymerized by rare earth allyl complexes in solution and in the gas phase.[90] Allyl complexes such as $[La(\eta^3\text{-}C_3H_5)_3(\eta^1\text{-}C_4H_8O_2)_2(\mu\text{-}C_4H_8O_2)]$ (**84**) polymerize *trans*-1,4-butadienes. By addition of suitable Lewis acids, such as Et_2AlCl, $EtAlCl_2$, or methylaluminoxane, catalysts for *cis*-1,4-butadiene polymerization are obtainable.[91] Protonolysis of $Li[Nd(\eta^3\text{-}C_3H_5)_4]1.5$dioxane (**85**) with CpH and Cp*H gave the anionic complexes $LiNd(\eta^5\text{-}C_5R_5)(\eta^3\text{-}C_3H_5)_3]$ (**86**) as their DME solvates. Stereoselective polymerization of butadiene was observed and could be controlled by addition of appropriate Lewis acids such as BF_3, Et_2SnCl_2 and Et_2AlCl or by using donors such as THF and dipiperidylethane.[92]

6 Lanthanides in Organic Synthesis

Various aspects of organosamarium chemistry have been reviewed including the use of samarocene for the addition reactions to organic carbonyls.[93] $Cp_2Sm(THF)_2$ (**87**) has been shown to catalyse the acylation of alcohols and amines with vinyl acetates in high yield and under very mild conditions.[94] Samarocene derivatives have also been used as acylation catalysts.[95]

Samarium(II) triflate, generated from the trivalent precursor by reaction with an organolithium or a Grignard reagent, was found to be an effective reagent for the samarium Grignard reaction with ketones.[96] The effects of the TADDOL ligand on stereoselective additions of organocerium reagents have been studied.[97] Alkyl samarium complexes have been shown to react in high yield with TEMPO. Other metals react less efficiently.[98] Samarium and ytterbium benzophenone complexes have been found to react with terminal alkynes to give alkynyl complexes with diphenylmethoxo ligands. Further reaction with aldehydes or aliphatic ketones gives propargylic alcohols after hydrolysis. On the other hand aromatic ketones and alkyl halides yield coupled products.[99]

7 Endohedral Fullerenes (EF)

Two reviews of EFs have appeared discussing synthesis and characterization[100] and STM studies[101] of EFs in general. A review of $Y@C_{82}$ chemistry has appeared.[102]

A number of new EFs have been prepared together with variations and improvements on known methods: $Er@C_{60}$,[103] several members of the $Gd@C_{2n}$ series,[104] of the $Y_x@C_{2n}$ series,[105] $Ce_2@C_{80}$,[106] $Pr@C_{82}$ and $Pr_2@C_{80}$,[107] $Nd@C_{82}$.[108], $Ho@C_{82}$, $Ho_2@C_{82}$, $Ho_3@C_{82}$,[109], and $La@C_{74}$[110,111] have been prepared. $La@C_{60}$, $La@C_{82}$ and $La_2@C_{80}$ have been prepared by Nd:YAG[112] or XeCl excimer[113] laser ablation of graphite and La_2O_3. In addition, there is evidence for the existence of stable isomers of $Tm@C_{82}$.[114] Inclusion of promoters such as sulfur, bismuth or lead in the arc has been shown to improve the yield of EFs.[115]

Extraction and purification of EFs is also attracting much attention. Low temperature aniline extraction of $M@C_{60}$ is a significant improvement on earlier methods.[116] High temperature and pressure pyridine extraction of endohedral fullerenes has been reported.[117] Solid phase extraction with C_{18}-bonded silica removes 22–30% of empty fullerenes from a chlorobenzene solution of empty fullerenes and $Sc_2@C_{60}$. HPLC was used to enrich mixtures of $Ce@C_{60}$ and C_{60} dissolved in aniline.[118] An improved chromatographic method allows the preparation of milligram quantities of $M@C_{82}$.[119] Chromatographic elution on [2-(1-pyrenyl)ethyl]silyl-silica stationary phase allows estimation of the dipole moments of endohedral fullerenes to be compared with their empty counterparts.[120]

Ab initio studies to probe the motion of the endohedral metal atoms suggest scandium atoms should oscillate while lanthanum atoms will circulate within the cage.[121] *Ab initio* molecular dynamics have identified preferred adsorption sites within the cage and timescales for the motion.[122] *Ab initio* and DFT calculations have been used to explore the electronic states of $Ln_2@C_{80}$[123] and have also been used to probe the stability of hypothetical MC_x (M = Y, La) clusters.[124] The fragmentations of EFs have been studied by surface collision and show fragmentation by loss of C_2 and other even-numbered C_n units.[125]

The motion of the scandium atoms in $Sc_2@C_{84}$ has been studied by ^{45}Sc NMR spectroscopy in solution. Two environments are observed at low temperature.[126] On the other hand ^{13}C NMR spectra show the two scandium atoms to be equivalent.[127] The rotational dynamics of the $M@C_{82}$ [M = Sc, Y, La] measured by EPR in solution suggest complete decoupling from the solvent.[128]

A study of the EPR spectra of $La@C_{82}$ has been reported together with its interaction with oxygen.[129] Another study on the same species reports the nuclear quadrupole coupling constants.[130] An EPR study of the formation of $La@C_{82}$

suggests that the relative amounts of the two isomers formed depends on the evaporation rate and the helium buffer gas pressure.[131]

The electrochemistry of M@C_{82} shows one oxidation and four reductions, all reversible. The redox potentials show good correlations with ionic radius of the endohedral ion.[132] UV and XPS study of Ce@C_{82} suggests the metal ion to be trivalent.[133] Magnetic measurements on La@C_{82} show it to be paramagnetic.[134] PES studies of thin films of Gd@C_{82} and La_2@C_{80} have been reported. The spectra of the latter are significantly different from those of EFs containing a single atom.[135] EFs have also been studied with respect to their non-linear optical properties.[136]

Endohedral fullerenes are also being functionalized. Reaction of La@C_{82} yields an exohedral adduct.[137] The reaction of the isomers of La@C_{82} with 1,1,2,2-tetramethyl-1,2-disilirane have been studied by EPR.[138]

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4

Carbaboranes, Including Their Metal Complexes

BY CATHERINE E. HOUSECROFT

1 Introduction

This article covers the 1996 literature of carbaboranes and metallacarbaboranes,[1] with sections arranged according to carbaborane composition; metal complexes are included in the corresponding C_xB_y-section. Theoretical and specific NMR spectroscopic studies are considered in Section 2, rings and ring-stacking in Section 3, and studies focusing on BNCT and other medical applications appear in Section 12. The literature has been surveyed using *Current Contents*, and some literature from the end of 1995 (omitted from last year's report) falls within the remit of this review. Structures **(2)**, **(3)**, **(6)**, **(7)**, **(9)**, **(18)** and **(19)** were redrawn using coordinates taken from the Cambridge Structural Data Base, implemented through the ETH, Zürich.[2] Page restrictions for the review have meant that, in the interests of maintaining as comprehensive a survey as possible, discussion on individual papers is necessarily limited.

2 Theoretical and Spectroscopic Studies

The use of molecular mechanics has grown rapidly in recent years and a method (within the MM3 force field approach) has now been reported for applying this technique to species containing 7-vertex carbaborane or metallacarbaborane cages. Each cage is considered in terms of a 5-membered ring and two capping atoms, and cages including 2,4-$C_2B_5H_7$, 2,3-$C_2B_5H_7$, 1-Mg-2,3-$C_2B_4H_6$ and *commo*-species have been investigated.[3]

The *ab initio*/IGLO/NMR method is now well known to chemists working in the carbaborane area. A good correlation between experimental and calculated ^{13}C NMR chemical shifts for more than 40 carbaborane clusters has been found at several levels of the model, thereby adding to the established ^{11}B NMR correlations.[4] In an investigation of amine adduct formation with $C_2B_7H_9$, a comparison of the experimental ^{13}C and ^{11}B NMR spectroscopic shifts with those obtained using the *ab initio*/IGLO/NMR and *ab initio*/GIAO/NMR methods has provided evidence for an 'open-cage' structural proposal.[5] The *ab initio*/IGLO/NMR method has also been applied to confirm structural assignments of the isomers of *nido*-$C_4B_7H_{11}$.[6] The value of the technique has been further illustrated

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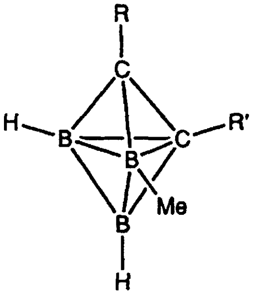
in an attempt to reproduce the literature NMR spectroscopic data for compound (**1**); this has led to the previous structural proposals being shown to be incorrect. With this result, the authors have removed this species from its place as an exception to several structural 'rules': e.g. carbon atoms occupy sites of lowest connectivity.[7] A combined synthetic (see Section 6) and theoretical investigation of the conjugate base of *arachno*-4-CB_8H_{14} has been carried out. The lowest energy structure calculated at the *ab initio* level was consistent with that confirmed by X-ray crystallography. ^{11}B NMR chemical shifts calculated for this structure using the IGLO method were not in agreement with those observed experimentally; however, when the authors allowed for a dynamic model for the anion in solution, it was possible to fit the experimental data.[8] *Ab initio* calculations at the HF/6-31G* and MP2(fc)/6-31G* levels have been carried out in combination with an electron diffraction study to investigate the structure of 7,8-dicarba-10-thia-*nido*-undecaborane(10); these data have also been complemented by ^{11}B chemical shift values determined using the IGLO method. This work also underlines the merits of combining the structural and theoretical approaches.[9] IGLO calculations have been applied for the first time to transition metal heteroboranes (see Section 8).[10]



R = Me, R' = H
or
R = H, R' = Me

(**1**)

The mechanism of carbaborane formation during the reaction of ethyne with B_4H_{10} has been revisited. The calculated activation energy for the initial loss of H_2 from B_4H_{10} was higher than is found experimentally; details of the intermediates along the pathway from C_2H_2 and B_4H_{10} to carbaboranes were discussed and compared with experimentally known species.[11]

Bonding pictures for 1,5-$C_2B_3H_5$ may be considered in both classical and non-classical manners, but a natural population analysis, complemented by additional data, clearly supports the non-classical scheme.[12] The use of Hückel theory is well recognised in two-dimensional rings, and this year has seen the extension of the theory to three-dimensional *closo*-carbaboranes. The model has been calibrated and then applied to isomerisations in $C_2B_4H_6$, $C_2B_5H_7$ and $C_2B_6H_8$. Comparisons are made between this and other methods.[13] Second moment scaled Hückel-type calculations have been used to study the potential energy surface of $[C_3B_8H_{11}]^-$ and the relative stabilities of *nido*-$[7,8,10\text{-}C_3B_8H_{11}]^-$ and *nido*-$[7,8,9\text{-}C_3B_8H_{11}]^-$; the positioning of the carbon atoms in the former isomer leads to a greater stabilisation of the two highest lying filled MOs. A pathway for the isomerisation of one *nido*-species to the other has been proposed.[14]

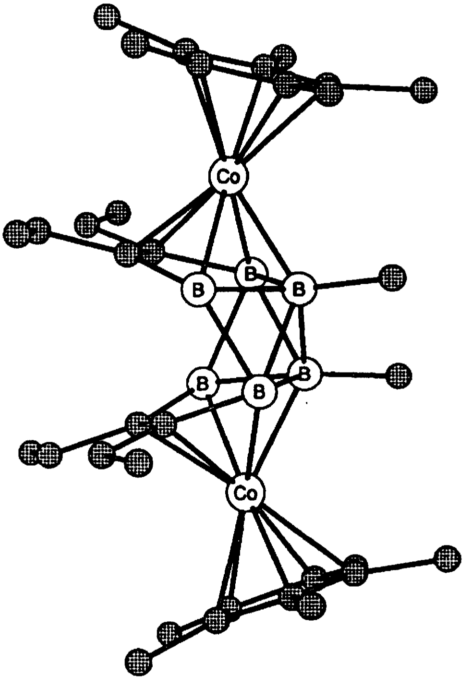
An atom-atom Lennard-Jones potential model has been derived for $C_2B_{10}H_{10}$ and has been used to study a series of simulations involving 1,2-, 1,7- and 1,12-carborane crystals under various T and P conditions. It has been possible to reproduce aspects of the structures and dynamic behaviours of the crystals, but further experimental data are required in order to improve the model.[15] The ^{11}B nuclear quadrupole couplings in $1,2\text{-}Me_2\text{-}1,2\text{-}Si_2B_{10}H_{10}$ have been measured at 77 K using a nuclear quadrupole double resonance spectrometer; the results for the silaborane have been compared with those for $1,2\text{-}C_2B_{10}H_{12}$ and differences have been explained in terms of valence bond structures.[16]

Ab initio MO calculations have been carried out on 8-vertex *closo*-heteroboranes of type $X_2B_6H_6$ including for X = CH. The results indicate that a 1,7-bisdisphenoidal isomer possesses the lowest energy, but that the energy of the cluster with a hexagonal bipyramidal geometry is relatively close.[17]

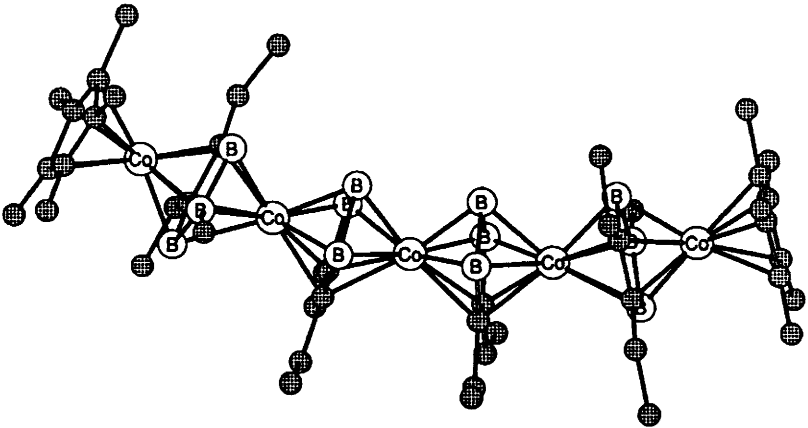
3 Rings and Ring Stacking

Previous reviews in this series have detailed the development of the area of sandwich compounds containing C_xB_y rings. In a recent survey, Grimes has given an overview that illustrates the uses of the metallacarbaborane units as building blocks in the assembly of larger species, and the properties of these systems.[18] New papers from the Grimes group constitute parts 42 to 44 of the current series. Air-stable tetradecker sandwiches of formula $[Cp^*Co(Et_2C_2B_3H_2X)]_2M$ (M = Co, CoH, Ni, Ru, Rh or Ir) have been prepared, although an attempt to use a parallel synthetic methodology with M = Fe was unsuccessful; reasons for this have been proposed, and experimental data were consistent with the Fe-centred tetradecker complexes undergoing oxidative fusion when they contact silica in air. The complex $[Cp^*Co(Et_2C_2B_3H_2X)]_2FeH$ (X = Cl, Me) could be isolated if such exposure was avoided. The oxidation in air of these complexes yields fused complexes and the crystal structure of $[(Cp^*Co)_2(Et_4C_4B_6H_4Me_2)]$ (**2**) has been determined.[19] Triple- and tetradecker sandwich compounds incorporating planar C_2B_3-rings in the stacks or terminated by pentagonal pyramidal C_2B_4 units have been prepared and characterised by mass spectrometric and NMR, ESR, and UV-VIS spectroscopic methods. Products include both paramagnetic and diamagnetic species, e.g. $[(^iPrC_6H_4Me)Ru(Et_2C_2B_3H_2Me)Co(Et_2C_2B_4H_4)]$, $[(^iPrC_6H_4Me)Ru(Et_2C_2B_3H_2Me)Co(Et_2C_2B_3H_5)]$ and $[M\{(Et_2C_2B_3H_2Me)Co(Et_2C_2B_4H_4)\}_2]$ (M = Co, NiH).[20] This type of stacked system has been extended to penta- and hexadecker compounds, and crystallographic data for compound (**3**) has provided confirmation of the assembly of one such stack.[21]

The contributions of Siebert and coworkers to this area have included a study



(2)



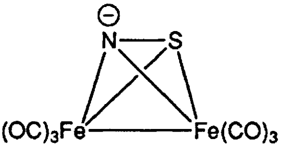
Hydrogen atoms omitted.

(3)

of the reactivity of [CpNi(1,2,3,4-Me_4-1,4-$B_2C_4H_2$)NiCp].[22] The synthesis and structural characterisation of [Cp*Fe(Me$^iPr_2C_3B_2Et_2$)] have also been reported, and in the solid state the 1,3-diborolyl ring is significantly folded; the electronic structure of the compound has been investigated. The study was extended to triple-decker, ruthenium-containing stacks and the electrochemical properties of the compounds have been described. For example, a stable anion [Cp*Fe(Me$^iPr_2C_3B_2Et_2$)]$^-$ could be generated by a reversible one-electron process at -1.26 V (*vs* SCE) and it and related species have been studied by ESR spectroscopy.[23] The reactions of [CpCo($Et_4MeC_3B_2$)]$^-$ with metal halides and dicarbaborane anions which included *nido*-[4,5-$C_2B_6H_9$]$^-$ and *arachno*-[4,5-$C_2B_7H_{12}$]$^-$ (3-component systems) have been studied. The products have been characterised by mass spectrometric and multinuclear NMR spectroscopy and the X-ray structures of [CpCo($Et_4MeC_3B_2$)Co(h^5-1,10-$C_2B_7H_9$)] and *closo*-[2-CpCo-1,6-$C_2B_7H_9$] have been elucidated. In the former, the carbon atoms reside in the capping sites of the 10-vertex cage; the Co—Co separation of 3.20 Å is consistent with the 30 VE count.[24]

4 Composition C_4B_x and C_3B_x

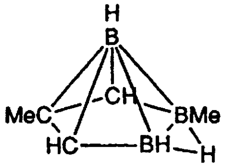
Selective bromination at the 6-position of peralkylated 2,3,4,5-$C_4B_2R_6$ (R = Me or Et) has been achieved by treatment with BBr_3; selective iodination occurs with BI_3. The reactions of the halogenated derivatives with Li[$BHEt_3$] lead to halogen-for-hydrogen exchange.[25] While transition metal cluster and carbaborane chemistries thrive as areas in their own right in the literature, few papers combine the two. A study of the reactions of anion (4) with 6-Br-1,2,3,4,5-Me_5-2,3,4,5-C_4B_2 and 1,6-Br_2-2,5-Bu_2-3,4-Et_2-2,3,4,5-C_4B_2 have resulted in substitution for Br^-, B—N bond formation and coupling of the carbaborane and transition metal cluster units; this has been confirmed by a crystal structure determination of one of the products.[26]



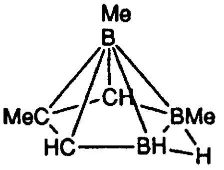
(4)

The reactions between metallic lithium or magnesium with *nido*-2,4,7,9-$(SiMe_3)_4$-2,4,7,9-$C_4B_8H_8$ in THF in the absence of aromatic solvents or naphthalene lead to the formation of [(Li(THF)$_4$][$(SiMe_3)_4C_4B_8H_9$] or [(THF)$_2$Mg($SiMe_3)_4C_4B_8H_8$] respectively. Structural characterisations of these complexes have shown that in the solid state, the former consists of discrete [Li(THF)$_4$]$^+$ and [$(SiMe_3)_4C_4B_8H_9$]$^-$ ions, while in the latter, the *s*-block metal centre is part of a metallacarbaborane cage.[27] When 2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ is treated with ^{t}BuLi in TMEDA at −78°C, the product is $[(TMEDA)Li]_2(SiMe_3)_2C_2B_4H_4$. Reaction of this compound with nickel(II) chloride yields, as one of the products, the novel carbaborane cluster $(SiMe_3)_4C_4B_8H_8$. Two isomers have been detected and the crystal structure of one with a cubeoctahedral cage has been determined. At 140–165°C, this isomer converts to the second.[28]

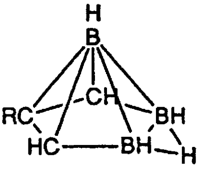
It has been reported that the reaction of B_4H_{10} with $H_2C{=}C(Me)C{\equiv}CH$ in the gas phase at 70°C yields clusters **(5a)**, **(5b)** and **(5c)** (R = Me) in addition to 3-Me-2,3,4,5-$C_4B_2H_5$. When the unsaturated organic precursors are $H_2C{=}CHC{\equiv}CH$ or $H_2C{=}CHC{\equiv}CMe$, the parent carbaborane **(5c)** (R = H) may be isolated, representing the first synthesis of *nido*-2,3,4-$C_3B_3H_7$.[29]



(5a)



(5b)



R = H, Me

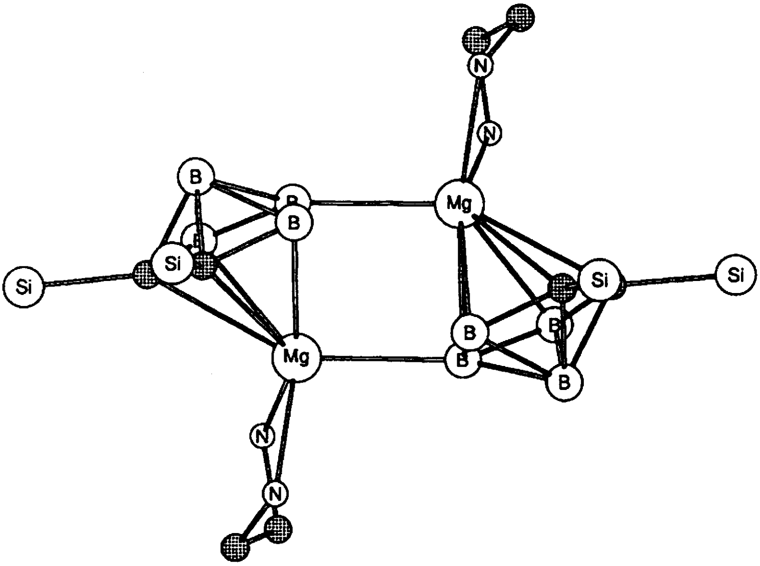
(5c)

The reactions between the anion *nido*-$[6\text{-Me-}5,6,9\text{-}C_3B_7H_9]^-$ and the dihalides MX_2 (M = Ni, Pd or Pt) have yielded a series of sandwich complexes, and an h^4-mode of interaction between carbaborane ligand and metal has been confirmed by X-ray diffraction studies. The reactivity of PMe_3 towards *commo*-$[Ni(8\text{-Ni-}9\text{-Me-}7,9,10\text{-}MeC_3B_7H_9)_2]$ has been investigated and cluster oxidation rather than adduct formation occurred.[30]

Six isomers of the 12-vertex metallatricarbaborane *closo*-$[CpFeC_3B_8H_{11}]$ have been observed as products from the reaction of $[CpFe(CO)_2I]$ with Tl[*nido*-7,8,9-$C_3B_8H_{11}$]. Only two of the isomers have so far been structurally assigned by analysis of NMR spectroscopic data.[31] The insertion of a carbon vertex (from CN or ${}^tBuCN$) into *nido*-5,6-$C_2B_8H_{12}$ or *nido*-$[5,6\text{-}C_2B_8H_{11}]^-$ has resulted in the formation of 7-NH_2-7,8,9-$C_3B_8H_{10}$ or 7-N^tBuH-7,8,9-$C_3B_8H_{10}$ respectively. Insertion of cyanide also yields *arachno*-$[9\text{-CN-}5,6\text{-}C_2B_8H_{12}]^-$. These species represent valuable starting materials for studies in C_3-carborane chemistry, and results so far reported cover methylation reactions; the X-ray structure of the *N*-NH^tBuMe derivative of the same structural type as 7-NH_2-7,8,9-$C_3B_8H_{10}$ has been determined.[32] The thermal rearrangement of 7-NMe_3-7,8,9-$C_3B_8H_{10}$ at 35 °C gives 10-NMe_3-7,8,10-$C_3B_8H_{10}$, while that of $[7,8,9\text{-}C_3B_8H_{11}]^-$ yields $[7,8,10\text{-}C_3B_8H_{11}]^-$. The 10-vertex *arachno*-5,6,9-$C_3B_7H_{13}$ was isolated as the product of the oxidative degradation of $[7,8,10\text{-}C_3B_8H_{11}]^-$.[33]

5 Composition C_2B_4

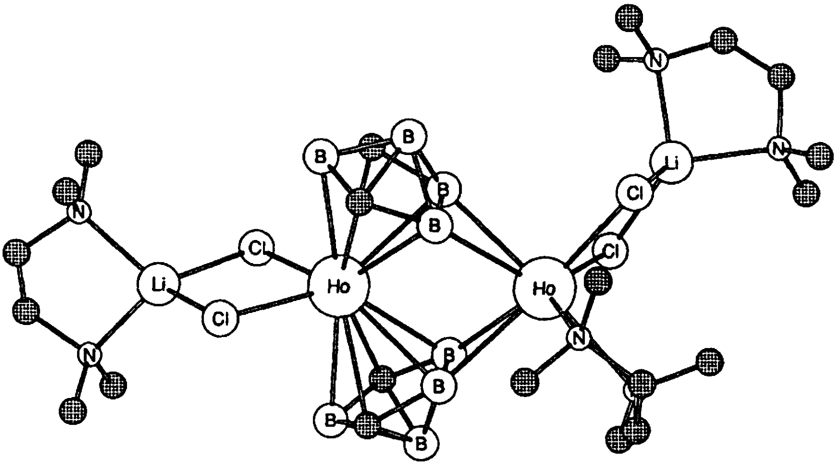
The work of Hosmane continues to dominate the chemistry of C_2B_4-metallacarbaboranes. TMEDA-solvated Na[2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$] reacts with MeMgBr or Bu_2Mg in diethyl ether to give compound (**6**) and the full sandwich complex *commo*-[1,1'-Mg{2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$}$_2$]. The crystal structures of both compounds have been determined.[34] The first example of a fully sandwiched group 1 metal in a carbaborane complex has been reported; the salt [Li(TMEDA)$_2$][Li(2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$)$_2$] was formed after the products of the reaction between 2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ and BuLi in TMEDA were heated *in vacuo* at 160–170°C for 6–7 h. An X-ray diffraction study has confirmed the sandwich-type structure and characterisation of the compound has included a ^{7}Li NMR spectroscopic study.[35]



Me groups are omitted from $SiMe_3$ and TMEDA groups

(**6**)

Lanthanoid-containing metallacarbaboranes have been further explored by Hosmane, and a crystallographic study of the bent sandwich complex [(m-Cl)$_4$-(2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$)$_2$(TMEDA)$_3$$Li_2$$Ho_2$] (**7**) has been carried out. One holmium centre is in an *exo*-polyhedral environment and the chloro ligands play an important role in stabilising the structural motif.[36] Whilst this compound is termed a 'carbons apart' complex, Hosmane has also reported the solid state structure of a related 'carbons adjacent' sandwich anion.[37] The reactions of *closo-exo*-[4,5-Li(THF)$_2$-1-Li(THF)$_2$-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$] with $LnCl_3$ (Ln = Sm, Gd, Tb, Dy, Ho) have led to the formation of a series of unusual paramagnetic complexes of the type [{1-Ln-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$}$_3${(m-1-Li-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4)_3$(m_3-OMe)}{m-Li(THF)}$_3$(m_3-O)]. These compounds have been characterised spectroscopically and by single crystal X-ray diffraction studies. In each, the Li and Ln metal atoms adopt a tricapped trigonal prismatic array with the Li atoms forming the inner prism. Some reactivity studies of these complexes have been described.[38] A paper in the same series reports the reactions of *closo-exo*-[4,5-{(m-H)$_2$Li(TMEDA)}-1-Li(TMEDA)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$] with $LnCl_3$ (Ln = Sm, Gd, Dy, Ho, Er) in a 2:1 ratio. The products are paramagnetic, bent-sandwich complexes and were characterised by IR spectroscopy, magnetic moment determinations and crystallographic studies; the latter confirmed the $MCl_2(carb)_2$-cores of each complex. Multinuclear NMR spectroscopic data were recorded for the gadolinium and dysprosium complexes.[39]



SiMe3 groups omitted for clarity.

(7)

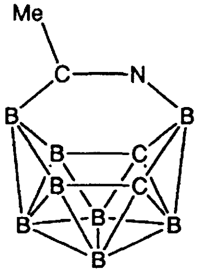
6 Composition C_2B_6 and C_2B_7

Reactions involving *nido*-[4,5-$C_2B_6H_9$]$^-$ and *arachno*-[4,5-$C_2B_7H_{12}$]$^-$, and the structural characterisations of [CpCo($Et_4MeC_3B_2$)Co(h^5-1,10-$C_2B_7H_9$)] and *closo*-[2-CpCo-1,6-$C_2B_7H_9$] were described in Section 3.[24]

7 Composition CB_8 and C_2B_8

An improved preparative route to *arachno*-4-CB_8H_{14} has been achieved.[8] It involves the reaction of *nido*-[7,9-$C_2B_{10}H_{13}$]$^-$ and Me_2S in the presence of concentrated HCl followed by treatment of the intermediate zwitterion with hexane and water. The conjugate base of *arachno*-4-CB_8H_{14} has been structurally characterised; see also Section 2.

Azacarbaborane clusters have been prepared by the nucleophilic attack of [5,6-$C_2B_8H_{11}]^-$ or $[B_{10}H_{13}]^-$ at a nitrile carbon centre, followed by hydroboration and cage-insertion. Crystal structure determinations of salts of *arachno*-[7-Me-5,7,14,12-$C_3NB_8H_{11}]^-$ (**8**) and *arachno*-[7-Me-7,12-$CNB_{10}H_{13}]^-$ have been carried out. The reaction of (**8**) with acid resulted in the extrusion of a boron vertex and loss of nitrogen, and the formation of *nido*-6-Me-5,6,9-$C_3B_7H_{10}$. In contrast, *arachno*-[7-Me-7,12-$CNB_{10}H_{13}]^-$ loses only boron when treated with acid and is converted into *hypho*-12-Me-12,13-CNB_9H_{15}, the structure of which has been elucidated; the cluster framework is in keeping with electron counting rules. The reaction of *hypho*-12-Me-12,13-CNB_9H_{15} with proton sponge led first to the formation of the conjugate base as expected, but, after rearrangement, gave *hypho*-[12-Me-12,11-$CNB_9H_{14}]^-$. Structural characterisation of the latter confirms the occurrence of cage isomerisation. The study has been extended to include several related systems.[40]

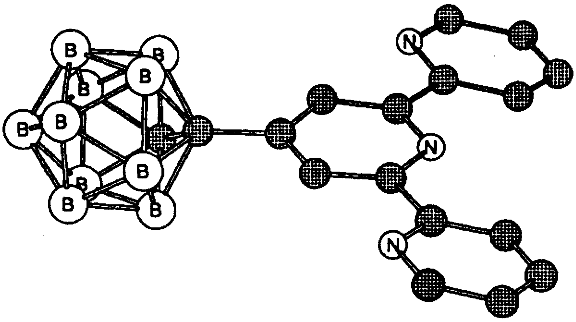


(**8**)

8 Composition CB_9 and C_2B_9

The formation of azacarbaboranes with CNB_9-cores was described in Section 7.[40]

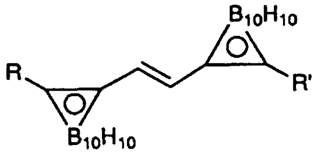
A series of functionalised 2,2′:6′,2″-terpyridine (tpy) ligands (see Section 10) has been prepared and characterised. Decapping of the *closo*-C_2B_{10} cage attached to the heterocyclic domain in compound (**9**) occurs in methanol solution, but decapping is more facile when the ligand is coordinated via the *N,N′,N″*-donor set to ruthenium(II) or iron(II) centres. When (**9**) loses a boron vertex, the product is a zwitterion, in which one proton has formally migrated from the *nido*-C_2B_9 cage to the tpy domain; the introduction of a cluster *C*-bonded Si^tBuMe_2 protecting group into (**9**) stabilises the compound with respect to boron-vertex extrusion.[41] A not unrelated zwitterion is described in Section 12.[42] The fact that decapping of phosphine substituted *closo*-C_2B_{10} cages is enhanced by metal-coordination has been noted by the Teixidor and Viñas group, and following the studies of



(9)

phosphine derivatives of carbaborane clusters that were reported in last year's survey, further details of the reactivities of the anions $[7,8\text{-}(PR_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (R = Ph, Et, ^{i}Pr and OEt) have now been reported. Comparisons between the behaviours of these species and that of $Ph_2PCH_2CH_2PPh_2$ have been made, and three differences are of particular significance: (i) the anionic nature of the ligand, (ii) the restricted conformation of the PCCP-unit, and (iii) the ability of cage H atoms to become involved in B–H–M interactions. The crystal structures of $[AuCl_2\{7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}]$ and $[RuCl_2\{7,8\text{-}(P^iPr_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$ have been determined.[43] The coordination of $[7\text{-}PPh_2\text{-}8\text{-}R\text{-}7,8\text{-}C_2B_9H_{10}]^-$ to ruthenium(II) takes place through the *P*-donor atom and two B–H–Ru interactions, but the roles of the additional ruthenium-attached ligands are crucial as is shown by comparing ^{1}H NMR spectroscopic data for the complexes in the series $[RuX(7\text{-}PPh_2\text{-}8\text{-}R\text{-}7,8\text{-}C_2B_9H_{10})LL']$ where X = Cl or H, R = Ph, H or Me, L = PPh_3, and L′ = PPh_3, CO, tht, or EtOH. Crystallographic data, which support the interpretation of the spectroscopic results, are available for the complexes $[RuCl(7\text{-}PPh_2\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ and $[RuCl(7\text{-}PPh_2\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)(EtOH)]\cdot 0.64Me_2CO$.[44] A series of new rhodium complexes containing the ligand $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ has also been prepared.[45] Gold(I) complexes of $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ may be prepared by the reaction of $[R_3PAuCl]$ (R = various) with $[1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}]$ in ethanol at reflux, the coordination of the phosphorus-donors to the gold centre being accompanied by the cage decapitation. Under similar conditions, the reactions of $[ClAu(Ph_2P(CH_2)_nPPh_2)AuCl]$ (*n* = 2 or 3) with $[1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}]$ lead to the formation of the compounds $[Au_2\{(PPh_2)_2C_2B_9H_{10}\}_2(m\text{-}Ph_2P(CH_2)_nPPh_2)]$. Related reactions have also been described. The X-ray crystal structures of $[Ph_3PAu\{(PPh_2)_2C_2B_9H_{10}\}]$ and $[Au_2\{(PPh_2)_2C_2B_9H_{10}\}_2(m\text{-}Ph_2P(CH_2)_3PPh_2)]$ have been determined, and a trigonal planar coordination geometry for the gold(I) centre in the latter complex has been confirmed.[46]

The reaction between 1,6-diphenylhexa-1,5-diyn-3-ene and decaborane(14) in the presence of MeCN leads to the formation of compound **(10)** with R = R′ = Ph. Related analogues with R and R′ as indicated in structure **(10)** have also been prepared and characterised (see Section 10). Decapitation of compound **(10)** occurs in ethanolic KOH to give the bis-*nido* species $(\mathbf{10a})^{2-}$ which has been isolated as the dithallium(I) salt. This compound reacts with [Ru(*p*-cymene)Cl_2]$_2$ to yield the bis-sandwich compound [(*p*-cymene)Ru(**10a**)Ru(*p*-cymene)], the structure of which has been crystallographically confirmed. These species are the first examples of linkage of carbaborane clusters by a simple C=C double bond.[47]



R = R' = Ph, 4-MeC_6H_4
R = Ph; R' = 4-MeC_6H_4

(10)

The synthesis of 3-Co{8,8'-(m-HC≡CCH_2S)(1,2-$C_2B_9H_{10}$)$_2$} has been reported, and the compound has been characterised by NMR, IR and UV-VIS spectroscopic and X-ray diffraction methods.[48] The stability of cobalt(III) dicarbollide complexes has been addressed by Hawthorne by the inclusion of substituents at the 8, 9 and 12 positions (i.e. those sites most susceptible to electrophilic attack). The syntheses and characterisations of Cs[*commo*-3,3'-Co(8,9,12-I_3-3,1,2-$CoC_2B_9H_8$)$_2$] and [$PMePh_3$][*commo*-3,3'-Co(8,9,12-Me_3-3,1,2-$CoC_2B_9H_8$)$_2$] have been described, with structural data for the trimethyl derivative.[49]

The first examples of mixed sandwich complexes involving a *nido*-C_2B_9-moiety and an h^5-pyrrole ring have been reported, *viz* [(h^5-C_4H_4N)Co(7-R-8-R'-7,8-$C_2B_9H_9$)] (e.g., R and R' = H or Me). The electrochemical behaviour of these complexes was found to reflect that of (h^5-Cp)Co($C_2B_9H_{11}$)].[50] The reaction between $Co_2(CO)_8$ and *nido*-7,8-$C_2B_9H_{13}$ is reported to give a mixture of products which include two isomers of [$Co_2(CO)_2$(h^5-7,8-$C_2B_9H_{11}$)$_2$]. In solution, the isomers are in equilibrium, but one isomer was successfully isolated by column chromatography and its structure determined. The dinuclear framework is supported by a Co–Co bond (250.3(2) pm) and by two B–H–Co interactions. Phosphine-for-carbonyl ligand substitution in an isomeric mixture of [$Co_2(CO)_2$(h^5-7,8-$C_2B_9H_{11}$)$_2$] has been investigated; the crystal structure of [Co_2(CO)(PMe_2Ph)(h^5-7,8-$C_2B_9H_{11}$)$_2$] has been elucidated. In addition, the compound [CoCl(PMe_2Ph)$_2$(h^5-7,8-$C_2B_9H_{11}$)] was prepared and structurally characterised. Related studies have also been reported and NMR spectroscopic data for the new complexes have been detailed.[51]

A report has appeared of the preparation and structural characterisation of the air-stable, cationic rhodadicarborane cluster, [3-MeCN-3,3-(PPh_2Me)$_2$-3,1,2-*closo*-$RhC_2B_9H_{11}$]$^+$ (isolated as the hexafluoroantimonate salt); the fact that it does not contain a charge-compensated carborane ligand makes it notable.[52]

The compounds *closo*-[3,3-(PPh_3)$_2$-3-H-3-Cl-3,1,2-$OsC_2B_9H_{11}$] and *closo*-[3,3-

$(PPh_3)_2$-3,3-H_2-1,2-Me_2-3,1,2-$OsC_2B_9H_9$] have been prepared and characterised (NMR and IR spectroscopies and X-ray diffraction studies) and are claimed to be the first *closo*-hydrido complexes of osmium with carbaborane ligands. A *nido*-analogue of the dimethyl derivative has also been prepared and spectroscopically characterised.[53]

The steric effects of substituents is not taken into account when one applies electron counting rules. In continued detailed studies of structural effects, Welch *et al* have shown that the steric crowding of the *C*-phenyl substituents in [1,2-Ph_2-3-(h^6-C_6H_6)-3,1,2-$RuC_2B_9H_9$] and [1,2-Ph_2-3-(h^6-*p*-cymene)-3,1,2-$RuC_2B_9H_9$] force the carbaborane carbon atoms apart and each cage adopts a *pseudocloso* structure. Boron-11 NMR spectroscopic data for these and two related irida- and ruthena-clusters are consistent with *pseudocloso* cages; IGLO calculations have reproduced these data and have been used to give a tentative assignment of the ^{11}B NMR spectrum of [1,2-Ph_2-3-(h^5-Cp*)-3,1,2-*pseudocloso*-$RhC_2B_9H_9$].[10] The reactions of Tl_2[7-Ph-8-R-7,8-$C_2B_9H_9$] (R = H or Ph) with [{$RhCl_2$(h-C_9Me_7)}$_2$] give the heptamethylindenyl derivatives [1-Ph-3-(h-C_9Me_7)-3,1,2-$RhC_2B_9H_{10}$] and [1,2-Ph_2-3-(h-C_9Me_7)-3,1,2-$RhC_2B_9H_9$]. Boron-11 NMR spectroscopic data for the products indicate that they possess *closo* and *pseudocloso*-structures respectively. Both the solid state structure and solution dynamic behaviour of [1-Ph-3-(h-C_9Me_7)-3,1,2-$RhC_2B_9H_{10}$] have been studied. A crystallographic study of [1,2-Ph_2-3-(h-C_9Me_7)-3,1,2-$RhC_2B_9H_9$] has also been carried out, and solution studies of the latter have exemplified for the first time the use of ^{11}B-^{11}B COSY NMR spectroscopy for a *pseudocloso*-species.[54] The compound [RuL-$(MeCN)_3$][CF_3SO_3]$_2$ (L = 1,4,7-trithiacyclononane) is formally a source of LRu^{2+} and reactions between this salt and Tl[$TlC_2B_9H_{10}$Ph] or Tl[$TlC_2B_9H_9Ph_2$] give ruthenacarbaboranes incorporating the LRu fragment. The products have been characterised by spectroscopic and crystallographic methods. Once again, the steric crowding of the two Ph substituents causes cage opening and the formation of a *pseudocloso*-species; in contrast, the derivative with one Ph group has the expected *closo*-structure.[55]

The stepwise oxidation of [(h^5-$C_2B_9H_{11}$)$Mo(CO)_3$]$^{2-}$ to [(h^1-$C_2B_9H_{11}$)-MoO_3]$^{2-}$ and [{(h^5-$C_2B_9H_{11}$)O_2Mo}(m-O){MoO_2(h^5-$C_2B_9H_{11}$)}]$^{2-}$. The products represent the first examples of oxomolybda(VI)carbaboranes, and the structures have been confirmed by X-ray diffraction methods. Solution ^{11}B and ^{13}C NMR spectroscopic studies have been used to monitor the inter-anion conversions.[56]

The Mossbauer spectrum of [Cp_2Fe][$CoC_2B_9H_{11}$] and of other ferrocenium salts have been recorded and compared. Unusually, the spectra contain bands, the broadness and asymmetry of which increase as the temperature decreases. These effects are attributed to paramagnetic relaxation effects. An analysis of the probability of the Mossbauer effect suggests that the anion-cation interaction is greater in [Cp_2Fe][$CoC_2B_9H_{11}$] than in the [$GaCl_4$]$^-$ and [MoO_4]$^{2-}$ salts which were also studied.[57]

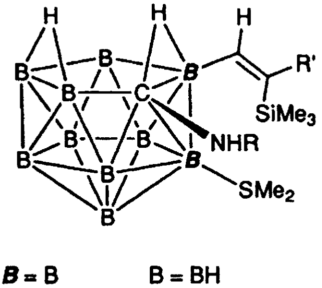
The synthesis and spectroscopic characterisation of *exo,nido*-[$Rh(PPh_3)_2$-(h^5-$C_2Me_2B_9H_{10}$) have been reported; the complex was prepared by treating [Rh(h^3-C_8H_{13})(h^5-$C_2Me_2B_9H_9$)] with PPh_3, and, in solution, it is in equilibrium with the corresponding *closo*-cluster. A mechanism by which the reaction may proceed has been proposed.[58]

Contributions from the Stone group this year have included studies on the chemistry of the $Ru(CO)_2(h^5\text{-}C_2B_9H_{11})$-unit. The complexes $[Ru(CO)_2L(h^5\text{-}C_2B_9H_{11})]$ (L = THF, NMe_3, MeCN, ^tBuCN, PPh_3) have been prepared, and reactions between $[Ru(CO)_2(THF)(h^5\text{-}C_2B_9H_{11})]$ and alkenes or alkynes have been investigated. Treatment of $[Ru(CO)_2(MeCCMe)(h^5\text{-}C_2B_9H_{11})]$ with $K[BH(CHMeEt)_3]$, followed by the addition of 18-crown-6, yields [K(18-crown-6)]$[Ru(CMeCHMe)(CO)_2(h^5\text{-}C_2B_9H_{11})]$; the ylide $[Ru(CMeCMePPh_3)(CO)_2(h^5\text{-}C_2B_9H_{11})]$ has also been isolated and characterised. A wide range of related complexes are reported in this paper, and the crystal structures of $[Ru(CO)_2(h^2{:}h^5\text{-}9\text{-}CHCH^tBu\text{-}7,8\text{-}C_2B_9H_{10})]$ and $[Ru(CO)_2(PMe_3)(h^5\text{-}9,10,11\text{-}(CHCH^tBu)_3\text{-}7,8\text{-}C_2B_9H_{11})$ have been elucidated.[59] The reaction of $[Mn(CO)_5Me]$ with $C_2B_9H_{13}$ in THF at reflux yields the zwitterionic compound $[Mn(CO)_3(h^5\text{-}7,8\text{-}C_2B_9H_{10}\text{-}10\text{-}O(CH_2)_4)]$ which has been subject to an X-ray diffraction study; the attachment of the THF ligand to the 10-position of the cage renders the carbaborane ligand neutral. In reactions of the new complex with donors, L, such as PPh_3 and NEt_3, one C–O bond of the THF molecule is ruptured and products of the type $[Mn(CO)_3(h^5\text{-}7,8\text{-}C_2B_9H_{10}\text{-}10\text{-}O(CH_2)_3CH_2L)]$ have been isolated and characterised by spectroscopic methods. The reaction of $[Mn(CO)_3(h^5\text{-}7,8\text{-}C_2B_9H_{10}\text{-}10\text{-}O(CH_2)_4)]$ with tetraethylammonium iodide leads to the formation of $[NEt_4][Mn(CO)_3(h^5\text{-}7,8\text{-}C_2B_9H_{10}\text{-}10\text{-}O(CH_2)_4I)]$, again as a result of ring-opening.[60]

9 Composition CB_{10} and CB_{11}

The anion *arachno*-$[7\text{-}Me\text{-}7,12\text{-}CNB_{10}H_{13}]^-$ was mentioned in Section 7.[40] The synthesis of $[7\text{-}OCN\text{-}7\text{-}CB_{10}H_{12}]^-$ has been achieved by treating $[7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{12}]$ with phosgene in the presence of NEt_3; the anion has been characterised by NMR and IR spectroscopies. The formation of ureas from the reactions of amines with $[7\text{-}OCN\text{-}7\text{-}CB_{10}H_{12}]^-$ has been investigated with a view towards using the products in BNCT studies.[61] The reactions between $5\text{-}SMe_2\text{-}6\text{-}\{Me_3SiC(Bu){=}CH\}B_{10}H_{11}$ or $5\text{-}SMe_2\text{-}6\text{-}\{(Me_3Si)_2C{=}CH\}B_{10}H_{11}$ and isocyanides led to monocarbon carbaboranes of type (**11**). These new compounds have been characterised on the basis of IR and multinuclear NMR spectroscopies and mass spectrometry.[62]

When $[Rh(PPh_3)_3Cl]$ is heated in MeOH solution with *nido*-$B_{10}H_{12}CNMe_3$, the products are the *closo*-clusters $[2,7\text{-}(PPh_3)_2\text{-}2\text{-}H\text{-}2\text{-}Cl\text{-}1\text{-}NMe_3\text{-}2,1\text{-}RhCB_{10}H_9]$ and $[2\text{-}PPh_3\text{-}2\text{-}Cl\text{-}1\text{-}NMe_3\text{-}2,1\text{-}RhCB_{10}H_{10}]$. The crystal structure of the former has been determined and is claimed to be the first structurally characterised hydride complex within the family of mononuclear icosahedral monocarbon metallacarbaboranes.[63] The reactions of *nido*-$7\text{-}NH_2{}^tBu\text{-}7\text{-}CB_{10}H_{12}$ with $[RhX(PPh_3)_3]$ (X = Br or Cl) in toluene gives the compounds $[RhX(PPh_3)(h^5\text{-}7\text{-}NH_2{}^tBu\text{-}7\text{-}CB_{10}H_{10}]$, and for X = Br, an X-ray diffraction study has been carried out. The reactivity of these new complexes with donor species including CN^tBu



(11)

has been investigated, and the products in this case depend on the reaction conditions. Other donor molecules used in this study were PEt_3, PMe_3, THF and 4-Mepy.[64] In an extension of this work, reactions between $[RhX(PPh_3)(h^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10}]$ (X = Cl or Br) and N_2CHCO_2Et to give $[RhX(PPh_3)(h^5\text{-}7\text{-}NH_2Bu^t\text{-}8\text{-}CH_2CO_2Et\text{-}7\text{-}CB_{10}H_9]$ have been described. For X = Br, the fact that the organic unit has inserted into a B—H bond has been confirmed by X-ray diffraction methods.[65] Related studies have been concerned with the reactions of the *nido*-clusters $7\text{-}NR_3\text{-}7\text{-}CB_{10}H_{12}$ (R_3 = Me_3, $NH_2{}^tBu$ or $NMe_2{}^tBu$) with $Ru_3(CO)_{12}$. The products are of the type $[Ru_3(CO)_8(h^5\text{-}7\text{-}NR_3\text{-}7\text{-}CB_{10}H_{10}]$ for which one representative compound have been crystallographically analysed. One ruthenium atom in the Ru_3-framework interacts with the carbaborane cage which binds in an h^5-mode. The two boron atoms in the b-sites with respect to the carbon atom in the carbaborane open (i.e. in the free ligand) face are involved in exopolyhedral B—H—Ru interactions. The reactivity of this new type of metallacarbaborane cluster has been probed and results are supported by spectroscopic and crystallographic data.[66]

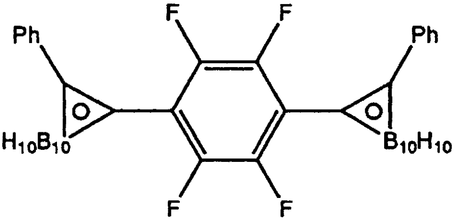
The two-step synthesis of the icosahedral cluster $[CB_{11}Me_{12}]^-$ (isolated as, for example, the Ph_4P^+ or Cs^+ salts) has been reported. The method involves the use of an excess of methyl triflate in the presence of $2,6\text{-}{}^tBu_2py$ (py = pyridine) and CaH_2. The anion has been fully characterised by multinuclear NMR and IR spectroscopies, electrochemical studies and an X-ray diffraction study.[67]

In a piece of work that might be named "in search of the R_3Si^+ cation", a comparative study of the structures of the complexes ${}^iPr_3SiX_6CB_{11}H_6$ has been made in which X = Cl, Br or I. Anions of the type $[X_6CB_{11}H_6]^-$ are weakly coordinating, and ${}^iPr_3SiCl_6CB_{11}H_6$ comes the closest of the three compounds to *approaching* the formation of an ion-pair (Si–Cl distance = 232.3(3) pm). The degree of silylium character has also been addressed by using ${}^{29}Si$ chemical shift correlations.[68]

10 Composition C_2B_{10}

Several *C*-phenyl derivatives of $C_2B_{10}H_{12}$ have been studied with an emphasis on structure. The preparation and detailed NMR spectroscopic characterisation of

1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ have been reported; the structure of the cluster has been determined in the gas phase by electron diffraction and in the solid state by X-ray diffraction. In the gas phase, the data could be fitted by several models differing in the relative orientation of the Ph group and resulted in there being no unique solution. At 199 K, the solid state structure gave a picture of the molecule which could be reproduced by theory (RHF/6-31G* level). The results of IGLO calculations (^{11}B NMR shifts) were similarly consistent with these data.[69] The X-ray crystal structure of another polymorph of 1-Ph-1,2-$C_2B_{10}H_{11}$ has also been described,[70] and the previous data for 1,7-Ph_2-1,7-$C_2B_{10}H_{10}$ have now been improved upon in a redetermination.[71] A structural determination of 1-$^iPr_2P$-2-Ph-$C_2B_{10}H_{10}$ shows an elongated cage C–C bond distance of 176.9(4) pm.[72] The crystal structure of the bis-carborane compound **(12)** has been elucidated. The twist angle of each phenyl ring is 15.6(3)° and that of the central C_6F_4 ring is 3.7(3)°. The rather long cage C–C distances of 173.0(3) pm are as expected from studies of related systems.[73]



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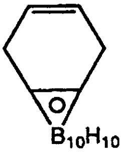

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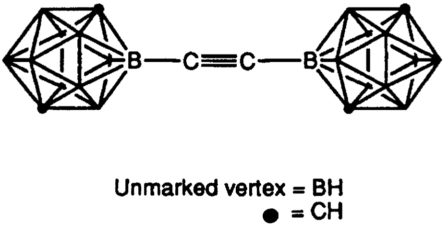
Diels-Alder adducts formed between 1,2-dehydro-1,2-carborane and benzene or naphthalene have been prepared; the 1,2-dehydro-1,2-carborane moiety may be transferred from its benzene adduct to other acceptors.[74] Crystallographic data for benzocarborane ($C_4H_4C_2B_{10}H_{10}$) and compound **(13)** have provided evidence for bond localisation, and this is further supported by bond order calculations. In the former, the cage C–C bond length is 165.4(3) pm, while in the latter its distance is 166.2(1) pm. 'Decapping' of benzocarborane can be achieved by treatment with wet Bu_4NF to give the corresponding *nido*-anion and the Diels-Alder addition maleic anhydride to this species has been reported.[75] The use of *hydrated* Bu_4NF to facilitate boron-vertex removal has been shown to be more effective than use of the anhydrous salt, and this approach has been applied to the synthesis of several hitherto elusive *nido*-carbaboranes including [7,9-R,R′-7,9-$C_2B_9H_{10}$]$^-$ (R = 4-HOC_6H_4, 4-$O_2NC_6H_4$; R′ = H; or R = R′ = 4-$PhOC_6H_4$, 4-$O_2NC_6H_4$, 2-pyridyl and 4-$H_2NC_6H_4$).[76]

Several papers have reported synthetic routes to organic derivatives of $C_2B_{10}H_{12}$. The use of 1,2-carboranyllithium reagents has been reported to be more versatile than that of normal organolithium compounds; reactions between 1,2-carboranyllithium compounds and functionalised alkyl halides such as ethyl bromoacetate have been described.[77] The reactions of lithium- and bromo-magnesium carboranes with 4-toluenesulfonyl cyanide have been shown to be successful routes to nitrile derivatives.[78] The syntheses of 1-H_2NCH_2-1,2-$C_2B_{10}H_{11}$ and 1-$H_2NCH_2CH_2$-1,2-$C_2B_{10}H_{11}$ have been described,[79] and two α-amino acids with alanine functionalities and containing 1,2- and 1,12-C_2B_{10}-cages have been prepared by the use of Oppolzer's sultam methodology.[80] The enol 1-^{i}Pr-2-{C(Ph)=C(OH)(Mes)}-1,2-$C_2B_{10}H_{10}$ (Mes = mesityl) has been prepared and it has been observed that transformation to the ketone or a keto-enol mixture does not occur even after the enol has been heated in benzene in the presence of CF_3CO_2H. The new compound is claimed to be the first stable carborane containing a simple enol substituent.[81] The synthesis of compound **(10)** with R = R′ = Ph was described in Section 8; this species has been characterised spectroscopically and by X-ray crystallography. Similar reaction strategies have been used to prepare **(10)** with R = R′ = 4-MeC_6H_4, or R = Ph and R′ = 4-MeC_6H_4.[47]

Rod-like species with alkyne backbones and incorporating C_2B_{10} units have been studied in the Hawthorne group. The reaction between 2-I-1,12-$C_2B_{10}H_{11}$ and 2-HC≡C-1,12-$C_2B_{10}H_{11}$ in the presence of $[Pd(PPh_3)_2Cl_2]$ and CuI in pyrrolidine at reflux yields compound **(14)**. Coupling also takes place between two equivalents of 2-HC≡C-1,12-$C_2B_{10}H_{11}$ in the presence of O_2 and CuI and in pyridine/toluene at reflux, and the product of this reaction has been confirmed by the results of an X-ray diffraction study. Other, related 'rigid rods' have also been prepared and characterised.[82] Carborane oligomers containing C–C and B–C linkages have been synthesised by the direct coupling of cages in the reaction of 1,2-Li_2-1,2-$C_2B_{10}H_{10}$ with copper(II) chloride. The unexpected formation of inter-cage B–C bonds has been confirmed by the spectroscopic and crystallographic characterisations of 1,3′-(1,2-$C_2B_{10}H_{11}$)$_2$ and 1,4′-(1,2-$C_2B_{10}H_{11}$)$_2$. Coupling reactions involving 1,7-$C_2B_{10}H_{12}$ have also been described.[83] Treatment of 1,3,5-$(C\equiv CH)_3C_6H_3$ with $B_{10}H_{12}(Et_2S)_2$ in toluene at 80°C yields compound **(15)**. A similar reaction has been carried out starting from HC≡C–$C_6H_4C_6H_4$–C≡CH. Both products have been characterised by EI mass spectrometry and multinuclear NMR spectroscopies, and the X-ray crystal structure of the product of the latter reaction has been determined confirming the connection of the two 1,2-C_2B_{10} cages by the rigid biphenyl spacer.[84] Hawthorne has also reported a number of novel cyclic systems such as **(16)** in a paper that reveals some stunning structural motifs; in all, eight compounds have been



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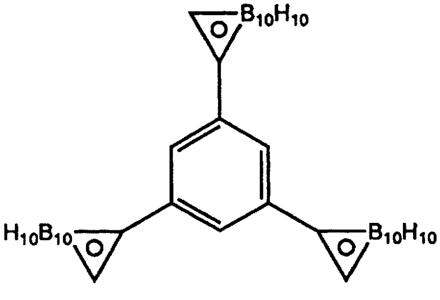

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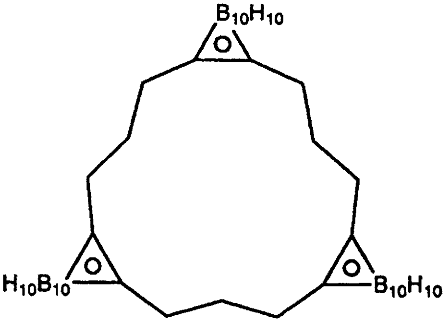
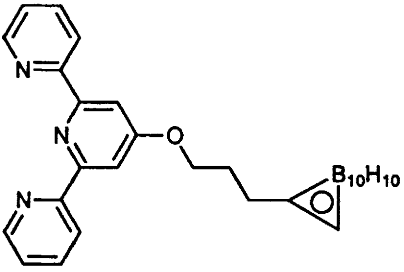


(16)

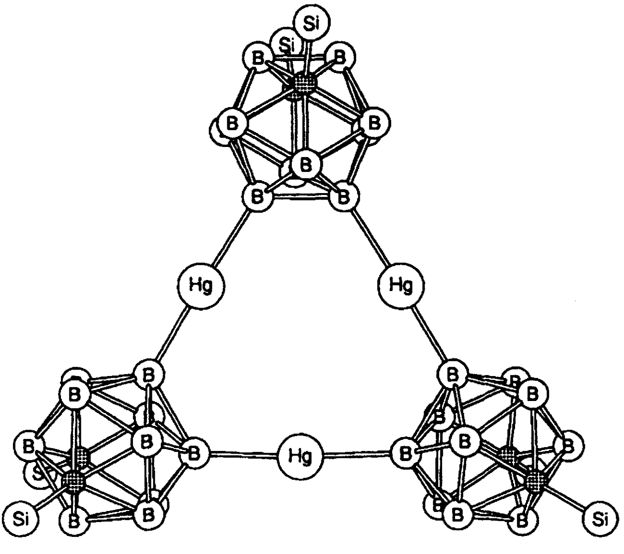
subject to X-ray diffraction studies and all the new compounds have been characterised by mass spectrometry and multinuclear NMR spectroscopies.[85] A macrocycle with pyridyl-linkages has been synthesised in the Wade group; a cyclic trimer was formed in the reaction of 2,6-Br_2py and 1,7-Cu_2-1,7$C_2B_{10}H_{10}$. In the same work, Wade and coworkers report the preparations and characterisations of the derivatives 1-R-7-R′-1,7-$C_2B_{10}H_{10}$ (or its 1,12-analogue) with R = H, R′ = 2-pyridyl, or R = R′ = 2-pyridyl. The new pyridyl derivatives are weaker bases than pyridine.[86] Studies of polymeric species involving C_2B_{10} cluster units have included that of oxidatively stable carborane-siloxane-diacetylene copolymers[87] and polyetherketones.[88]

Supramolecular chemistry is one area that is presently receiving much attention and carbaborane clusters have, in part through the work of Hawthorne (see below), entered this arena. Compound (17) is an example (crystallographically characterised) of a series of spaced (2,2′:6′,2″-terpyridine)–(1,2-C_2B_{10}) derivatives prepared by a variety of methods. Such ligands act as *N,N′,N″*-donors to iron(II) and ruthenium(II) and these complexes have been characterised by mass spectrometry, elemental analysis and NMR spectroscopy.[89] The direct linkage of the 2,2′:6′,2″-terpyridine and 1,2-C_2B_{10} domains has also been achieved, although in both the free and coordinated ligands, decapping proved to be problematical (see Section 8).[41] Use of the silyl-protecting strategy (reported in an earlier review in this series) has led to the successful isolation of the compound 1-Si^{t}BuMe$_2$-2-(2,2′:6′,2″-terpyridin-4′-yl)-1,2-$C_2B_{10}H_{10}$ which has been incorporated into a pentaerythritol-based metallodendrimer containing four carborane clusters.[90] The co-crystallisation of 1,2-, 1,7- or 1,12-$C_2B_{10}H_{12}$ with an equivalent of hexamethylphosphoramide (hmpa) leads to the assembly of supramolecular arrays in which C–H···O hydrogen bonded interactions play an architectural role. X-Ray diffraction studies reveal that 1,2-$C_2B_{10}H_{12}$·hmpa possesses dimeric motifs, while polymeric species are formed for 1,7-$C_2B_{10}H_{12}$·hmpa and 1,12-$C_2B_{10}H_{12}$·hmpa.[91]



(17)

Metallacarbaboranes incorporating C_2B_{10}-cages include a series of s-bonded species from the Hawthorne group. The reaction of the *C*-protected cluster 1,7-(^{t}BuMe$_2$Si$_2$)$_2$-1,7-$C_2B_{10}H_{10}$ with two equivalents of HgO in the presence of an excess of CF_3CO_2H leads to the formation of 1,7-(^{t}BuMe$_2$Si$_2$)$_2$-9,10-(HgO$_2$CCF$_3$)$_2$-1,7-$C_2B_{10}H_8$ in high yield. After conversion to the corresponding HgCl-compound, and treatment with $LiAlH_4$ in THF/Et$_2$O, the cyclic trimer $\{(^t\mathrm{BuMe_2Si_2})_2\mathrm{C_2B_{10}H_8Hg}\}_3$ **(18)** is formed. An X-ray diffraction study has confirmed the presence of Hg–B bonds in the cyclic array.[92] Cage-connection by carbon vertices through mercury centres features in the complexes Li$_2$[(1,2-$C_2B_{10}H_{10-x}R_x$Hg)$_4$I$_2$] (R = Et, x = 2; R = Me, x = 2, 4), the preparations and characterisations of which have been described. The anions are host-guest complexes. The methylated precursor to Li$_2$[(1,2-$C_2B_{10}H_6Me_4$Hg)$_4$I$_2$] is 8,9,10,12-Me$_4$-1,2-$C_2B_{10}H_8$ and this compound may be made in one step by treating 1,2-$C_2B_{10}H_{12}$ with MeI in CF_3SO_3H. The host macrocycles (1,2-$C_2B_{10}H_6Me_4$Hg)$_4$ can be obtained by reacting Li$_2$[(1,2-$C_2B_{10}H_6Me_4$Hg)$_4$I$_2$] with AgOAc, and a ^{199}Hg NMR spectroscopic investigation of the reaction is consistent with sequential iodide removal. These systems have been studied in detail and provide some novel structural results.[93] The reaction of 1,2-Li$_2$-9,12-Me$_2$-1,2-$C_2B_{10}H_8$ with mercury(II) acetate leads to the formation of (Me$_2$C$_2$B$_{10}$H$_8$Hg)$_3$ which has been characterised by NMR spectroscopy. The crystal structure of (Me$_2$C$_2$B$_{10}$H$_8$Hg)$_3$·3MeCN has been determined and the results confirm the presence of a C$_6$Hg$_3$-macrocycle. Halide complexes have been prepared, and



Me and ^{t}Bu substituents and cluster H atoms have been omitted for clarity

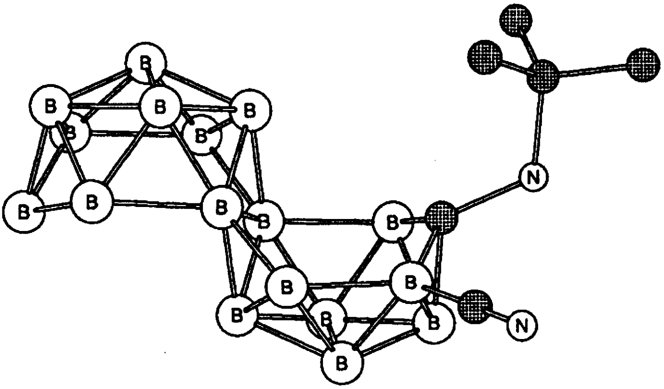
(18)

^{199}Hg NMR spectroscopy has been used to study their complex formation with Cl^-, Br^- and I^- ions.[94] Carbon-gold s-bonds are present in the compounds 1,2-$(AuPPh_3)_2$-1,2-$C_2B_{10}H_{10}$ and 1,1′-$(AuPPh_3)_2$-[2-(1′,2′-$C_2B_{10}H_{10}$)-1,2-$C_2B_{10}H_{10}$] which have been prepared and structurally characterised. In the latter compound, an Au···Au bonded interaction is present in the solid state, and a solution VT-NMR spectroscopic study shows that the energy barrier separating this and a Au·····Au non-bonded species is 46 ± 4 kJ mol^{-1}.[95]

Several phosphine derivatives of carbaborane clusters were mentioned in Section 8, and further species in this series are described here. The compounds $[CuCl(PPh_3)(1,2\text{-}\{(EtO)_2P\}_2\text{-}1,2\text{-}C_2B_{10}H_{10}]$, $[CuCl(PPh_3)(1,2\text{-}(Et_2P)_2\text{-}1,2\text{-}C_2B_{10}H_{10}]$ and $[CuCl(1,2\text{-}({}^{i}Pr_2P)_2\text{-}1,2\text{-}C_2B_{10}H_{10}]$ have been prepared and characterised, and a crystal structure determination of $[CuCl(PPh_3)(1,2\text{-}\{(EtO)_2P\}_2\text{-}1,2\text{-}C_2B_{10}H_{10}]$ confirms that the copper(I) centre is in a pseudo-tetrahedral environment.[96]

11 Macropolyhedral Species

This year's review sees the introduction of a new section representing the onset of macropolyhedral carbaborane cluster chemistry. The first such species is $({}^{t}BuNH_2)CB_{17}H_{18}(CN)$ **(19)** which is formed as one product of the reaction between *anti*-$B_{18}H_{22}$ and ^{t}BuNC.[97] The compound *neo*-$C_4B_{18}H_{22}$ has been



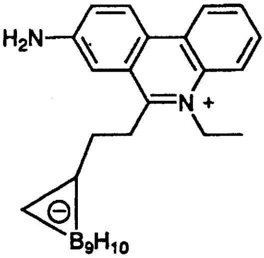
(19)

structurally characterised in the solid state by X-ray diffraction methods and studied in solution by NMR spectroscopic techniques. A compound of this formula has been reported previously, but the solid state structure presented here represents a second isomer. The structure may be described in terms of two 7,8-C_2B_9 cages which are fused by the 9,10-boron atoms.[98] This area appears as though it will generate some novel species in the years to come.

12 Studies Relating Specifically to BNCT and Other Medical Applications

Among some of the derivatives described in Section 10 were several that may have potential uses in studies relating to BNCT. In this section, work which is directly related to this topic is discussed.

Members of a series of compounds including the zwitterion **(20)** have been evaluated with respect to their DNA binding capacity using human glioma cells U-1231 in addition to calf thymus DNA. A detailed report of this evaluation is reported to be in preparation.[42]



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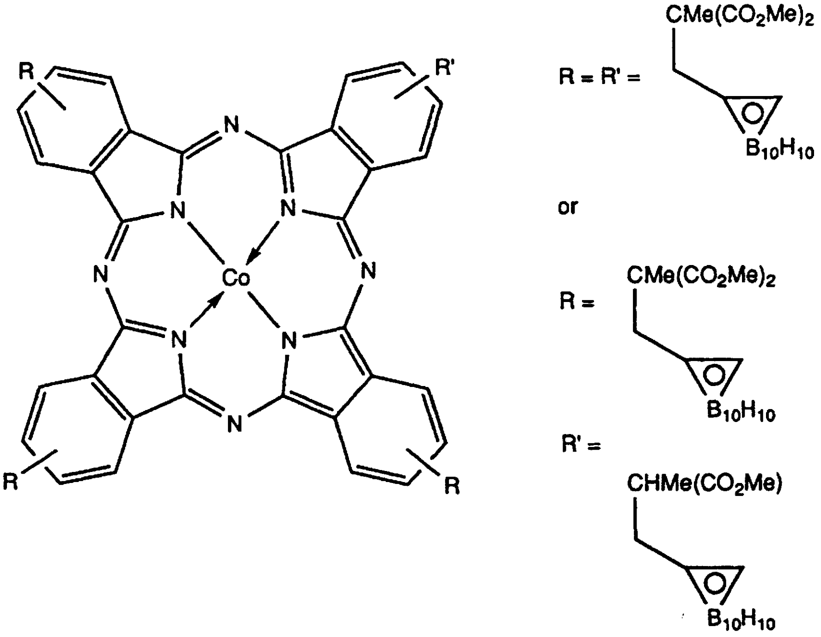
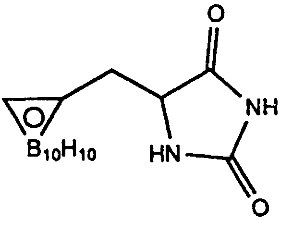
With the aim of developing new boron-containing drugs for BNCT, Radel *et al* have reported the enantioselective syntheses of L- and D-carboranylalanine in addition to a range of homologues. It is noted that these preparations may be carried out on a multigram scale.[99] The synthesis of $1\text{-CO}_2\text{H-12-NH}_2\text{-1,12-C}_2\text{B}_{10}\text{H}_{10}$ has been achieved from $1,12\text{-C}_2\text{B}_{10}\text{H}_{12}$ but only in low yield. An alternative, and more successful, route involves the initial preparation of $1\text{-CO}_2\text{H-12-NHCO}_2{}^t\text{Bu-1,12-C}_2\text{B}_{10}\text{H}_{10}$. Other related syntheses have also been reported.[100] The first fully characterised, water-soluble boronated phthalocyanine has been prepared and characterised. Assembly of the initially protected system and reaction with cobalt(II) chloride yields the complexes (**21**) which undergo ester-deprotection and cation exchange to give a water-soluble salt. The high boron content (27% by weight) suggests that the compound may be of potential use in BNCT.[101]



(21)

New boron-rich oligopeptides based upon a poly-(α,ε-L-lysine)-core have been described. Pendant arms of this core bear up to eight $1,2\text{-C}_2\text{B}_{10}\text{H}_{11}$ substituents and the core is also functionalised with a polyethyleneoxy tail to maximise water-solubility and a dansyl fluorescent probe. Antibody fragment conjugates of the new system were also prepared.[102]

The preparations of several carboranyl amino acids, hydantoins and barbiturates have been reported. Among the compounds are the hydantoin (**22**) and the barbiturate (**23**) which have been tested for their potential anti-convulsant activity; the latter showed zero activity, but (**22**) was active. Additionally,



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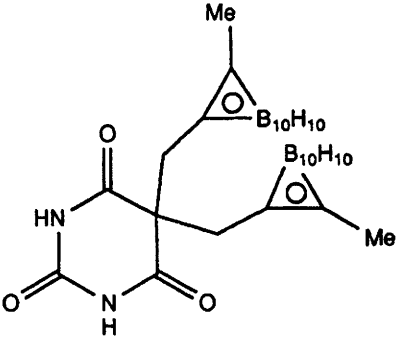
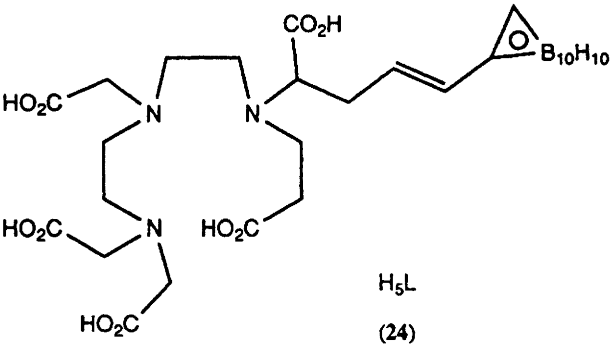


(23)

compound (22) was found to be non-toxic at doses of 300 mg kg^{-1} in mice (ip) or 50 mg kg^{-1} in rats (oral).[103]

The synthesis of the ligand H_5L (24) has been described; initially, the carbaborane cage is derivatized to give 1-{$H_2C{=}CHCH(OCO_2Et)$}-1,2-$C_2B_{10}H_{10}$ by treating 1-Li-1,2-$C_2B_{10}H_{10}$ with $CH_2{=}CHC(O)H$, followed by reaction with $ClCO_2Et$ and pyridine. The reaction between (24) and $GdCl_3$ yields the complex [GdH_2L], the biological properties of which are reported to be the subject of further investigations.[104]



H_5L

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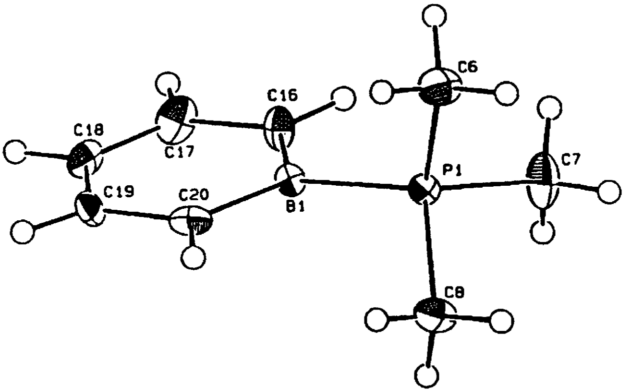
5

Group III: Boron, Aluminium, Gallium, Indium and Thallium

BY M.J. ALMOND

1 Boron

1.1 General – A range of cyclopentadienylboranes $C_5H_5BR_2$ (R = NMe_2, $\frac{1}{2}(OCMe_2)_2$, ^iPr or Me) have been synthesised from the alkali metal cyclopentadienides MCp (M = Li, Na) and $BCl(NMe_2)_2$, $ClB(OCMe_2)_2$, BCl^iPr_2 and $BBrMe_2$ respectively.[1] Some chemistry of these cyclopentadienylboranes has been investigated. For example, $C_5H_5B(NMe_2)_2$ reacts with lithium dialkylamides *e.g.* $LiNMe_2$ to give the salt $Li[C_5H_5B(NMe_2)_2]$. The chemistry of borabenzene also continues to attract attention. In a recent paper[2] an array of neutral borabenzene-ligand complexes (where the ligand is pyridine, 2,6-lutidine, NEt_3, PMe_3 or CN-^{t}Bu) have been synthesised. The structure of the PMe_3 complex is given (**1**). A range of new boron heterocycles have been made[3] including derivatives of hexaborylbenzene and tetraborylethene. The compound $[\{Li(Et_2O)_2\}\{MeO(Mes)BB(Mes)OMe\}]$ (**2**) (Mes = 2,4,6-$Me_3C_6H_2$) has been isolated and its structure determined.[4] The interest in this compound is that it allows a comparison of the B-B π-bonding between this reduced diborane derivative and the neutral precursor compound MeO(mes)BB(mes)OMe. It is found that **2** has a



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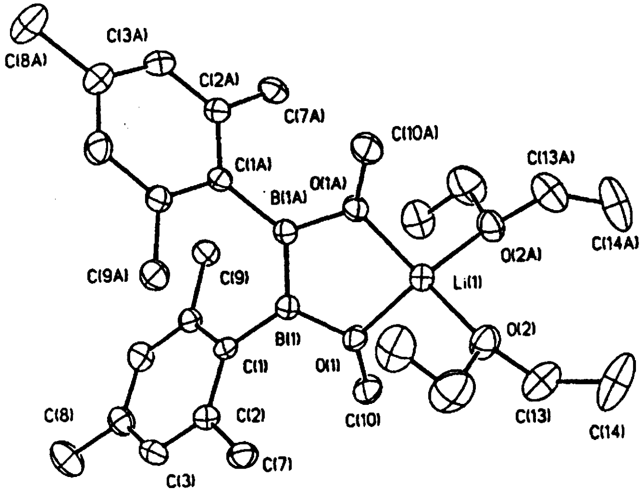

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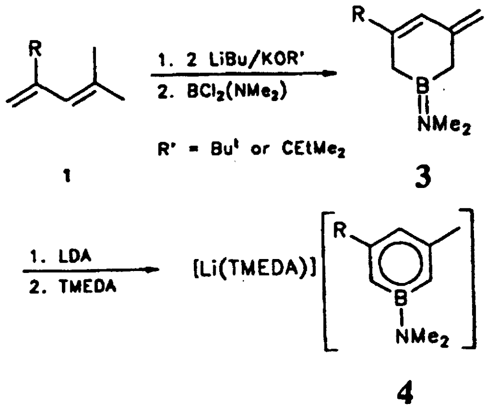
short B-B bond distance of 1.636(7) Å compared with 1.724(9) in the neutral precursor.

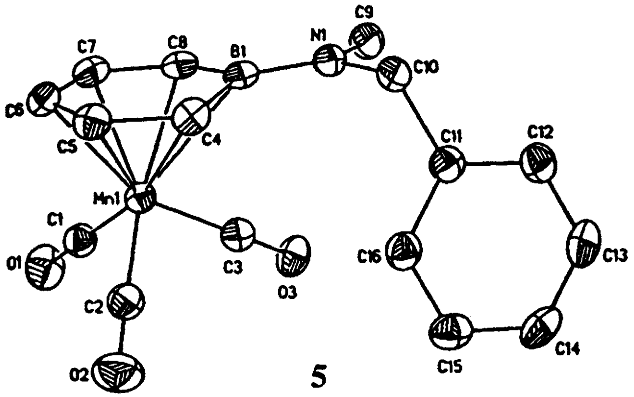
The borabenzene-trimethylphosphine complex has been synthesised and a study of its chemistry has been undertaken. In particular the mechanism for *nucleophilic substitution* of this compound has been studied.[5]

The compound $B(C_6F_5)_3$ finds a number of uses in synthetic chemistry. A recent example is its role in alkyl abstraction from $\{Me_3SiN(CH_2CH_2NSiMe_3)_2\}ZrR_2$ (R = Me or CH_2Ph) to afford cationic alkyl complexes stabilised by a diamide ligand.[6] Likewise the allyldihaloboranes are important reagents and may be used for allylboration of alkenes.[7] The use of borane reagents in the preparation of spiro-tin compounds with stannole or stannolene groups has been noted.[8]

1.2 Compounds Containing Nitrogen, Phosphorus, Oxygen or Sulfur – A number of nitrogen-containing borabenzene derivatives have been prepared.[9] The entry into this synthetic chemistry is *via* doubly kaliated pentadienes *e.g.* (*E*)-2-methyl-1,3-pentadiene reacts with $BCl_2(NMe_2)$ to form 1-(dimethylamino)-3-methylene-1,2,3,6-tetrahydroborinine (**3**). This compound readily dimerises and may be metallated to yield **4**.

An evaluation has been made of the exocyclic B-N interaction in some aminoboratabenzenes.[10] This work includes incorporation of transition metals into a number of complexes. Thus, for example lithium *N*-benzyl-*N*-methyl-1-aminoboratabenzene reacts with $Mn(CO)_3(CH_3CN)_3PF_6$ to yield **5**. The thermal degradation of tris(isopropylamino)borane *via* polyborazines to boron nitride has been investigated.[11] The starting material is found to be very thermally stable under argon, but readily reacts with ammonia to give polyborazines. On pyrolysis





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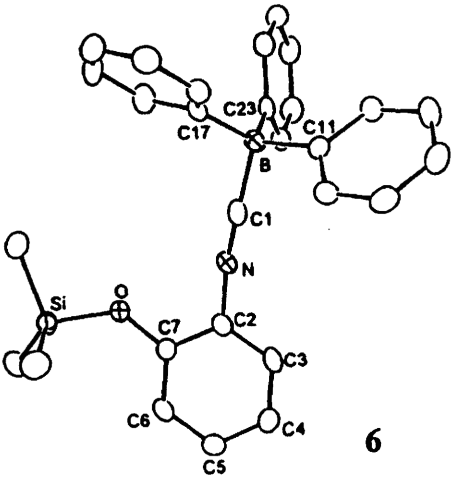
at 1000 °C the starting material gives BN containing less than 1% carbon. Some isocyanide and ylidene complexes of boron have been prepared.[12] Triphenylborane reacts at -60 °C with 2-(trimethylsiloxy)phenyl isocyanide to form the adduct **6**. **6** may be desilylated in MeOH with a catalytic amount of KF at -30 °C to give the ylidene adduct **7**. **7** has, in fact been the subject of two single crystal diffraction studies during the past year.[12,13] In the second report [13] the synthetic method used was to react triphenylborane with 2-lithiobenzoxazole followed by subsequent hydrolysis with water.

Two papers discuss the chemistry of $(CF_3)_2BNMe_2$.[14,15] In the first its reactions with Grignard and related reagents are described. After hydrolysis the dimethylamine boranes $R(CF_3)_2B.NHMe_2$ (several different R groups are reported) are produced. By contrast mesitylmagnesium bromide reacts with $(CF_3)_2BNMe_2$ to yield $(CF_3)(mes)FB\text{-}FC{=}NMe_2$ (**8**), while the phosphorus ylid $Ph_3P{=}CH_2$ reacts with $(CF_3)_2BNMe_2$ to give the adduct **9**. In a second study [15] [2+3] cycloaddition reactions of $(CF_3)_2BNMe_2$ nitrile oxides, nitrones and $Me_2C{=}SO_2$ to yield cyclic compounds *e.g.* **10** (which contains a B-N-C-N-O ring) are described. With



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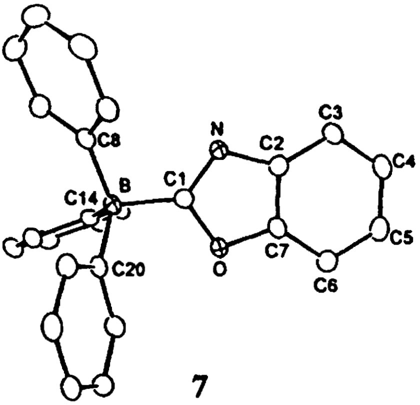

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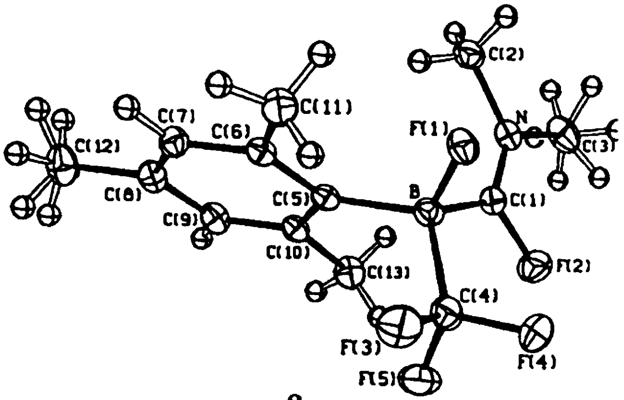
$Me_2C{=}SO_2$ a product containing a B-N-C-S-O ring is generated. The bis(borylamide) ligand $[mes_2BNCH_2CH_2NBmes_2]^{2-}$ ($[Ben]^{2-}$) has been used to prepare a number of group 4 organometallic complexes *e.g.* by reacting the ligand with $MCl_4(thf)_2$ (M = Ti or Zr) to give $(Ben)TiCl_2$ or $(Ben)ZrCl_2(THF)$. These complexes are readily alkylated by Grignard reagents in dichloromethane. The structure of (Ben)Ti(Bz)Cl (Bz = CH_2Ph) is given (**11**). This features a highly distorted "η^2" benzyl ligand with a Ti-C_α-C_{ipso} angle of only 87.0(5)°. The dimethylated $(Ben)MMe_2$ complexes cleanly decompose by metallation of the ortho methyl groups from mesityl rings on different borons. The products are dimers. Various derivatives of the novel uninegative bidentate ligand, dimethylbis(2-pyridyl)borate(1 −) ion (**12**) have been synthesised.[17] The synthesis of the ligand is as follows: $Li(py)_2BMe_2$ is formed by adding a solution of bromodimethylborane to a solution of 2-lithiopyridine; subsequent hydrolysis



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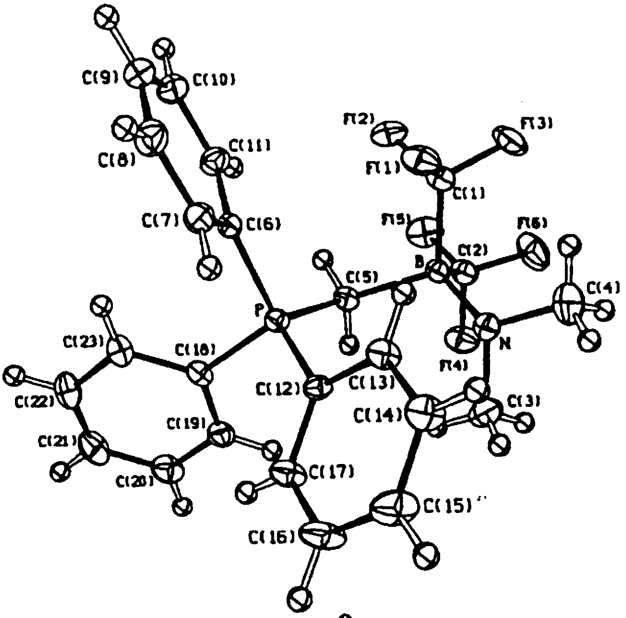

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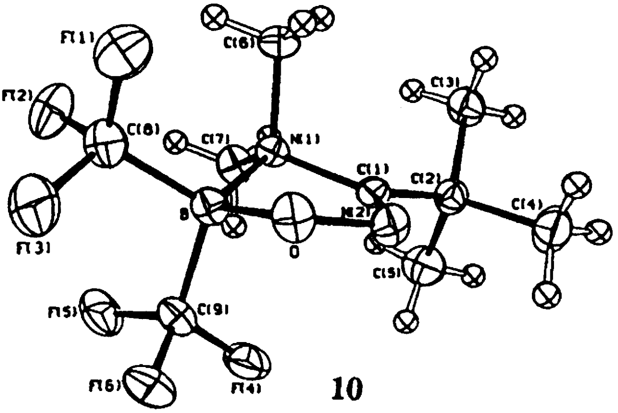
affords $H(py)_2BMe_2$. Reaction of $H(py)_2BMe_2$ with anhydrous $ZnCl_2$ or $NiCl_2$ gives either the tetrahedral complex $Zn\{(\mu\text{-}py)_2BMe_2\}_2$ or the square planar complex $Ni\{(\mu\text{-}py)_2BMe_2\}_2$.

A study has been made of the reversible adduct formation between phosphines and trialkylboron compounds. A number of such adducts have been isolated and crystal structures have been obtained; a correlation between the *length* and *strength* of the adduct bond is possible in some cases. The strong acceptor



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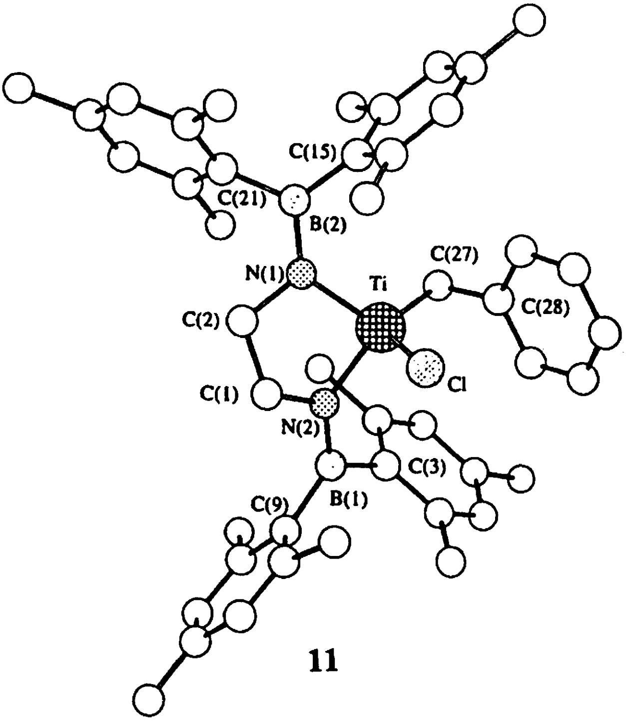

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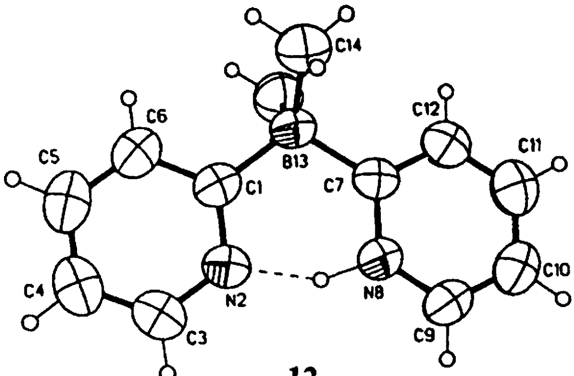
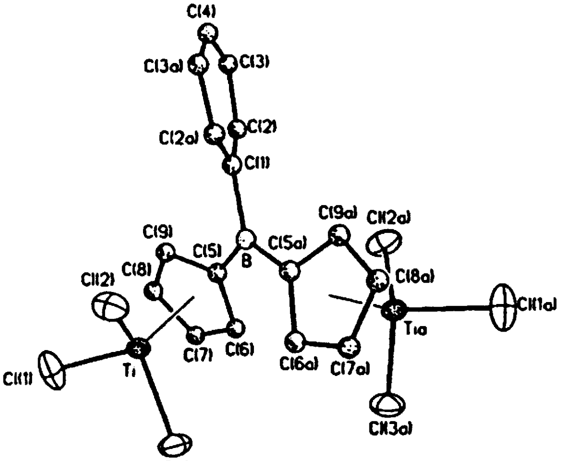
compounds have been found to form unstable adducts with water and therefore act as drying agents, ultimately producing arylboronic acids.[18] The use of boronic esters in the construction of synthetic intermediates containing two or three chiral centres *i.e.* for use in asymmetric synthesis has been explored.[19] An efficient and convenient route to *cis*-bis(boryl)alkenes is the diboration of alkenes using tetrakis(alkoxo)diborons, the reaction being catalysed by $Pt(PPh_3)_4$.[20] Sulfur-



12

containing organoboranes have been used in the synthesis of unsymmetrical sulfides.[21]

1.3 Metal-containing Compounds – A new series of half-sandwich (boracyclopentadienyl)titanium trichloride complexes have been prepared which include the boryl substituents $[1,2\text{-}(C_6H_4O_2)]B$-, Ph(Cl)B, Ph_2B and a (PbB<)-bridged bimetallic complex.[22] The structure of the phenylboron bridged bimetallic complex $PhB\{(\eta^5\text{-}C_5H_4)TiCl_3\}_2$ is given (**13**). The cyclopentadienyltitanium units of the molecule are twisted from each other, forming an angle of 41° between the ring planes. Transmetallation of $C_5H_4(SnMe_3)_2$ by $PhBCl_2$ and $ZrCl_4$ gives the first *ansa*-[1]-zirconocene dichloride with a boron-bridge atom $[(\mu\text{-}PhB)(\eta^5\text{-}C_5H_4)_2]ZrCl_2$ (**14**).[23] The organodiborate anion $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$ is a 10-membered ring structure with a transannular B-H-B bridge whose reactivity



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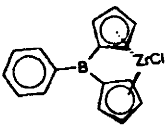
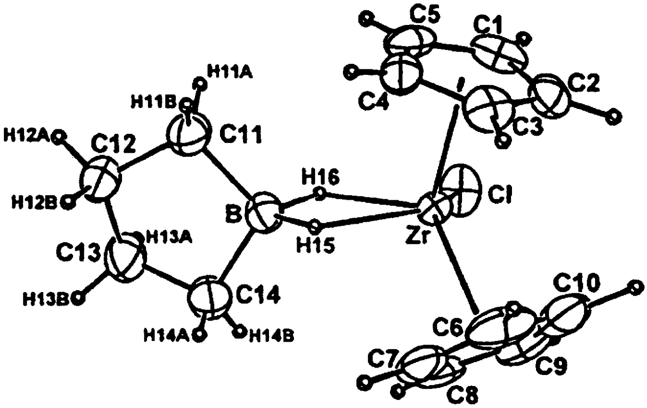


14

tends to be driven by regeneration of $B_2(\mu\text{-}H)_2(\mu\text{-}C_4H_8)_2$ – a very stable and relatively inert organoborane. However, some unexpected chemistry has been observed when this anion is reacted with $ZrCl_2$ and $HfCl_2$; here ring tranformations take place and the products are $(\eta^5\text{-}C_5H_5)_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ (**15**) and $(\eta^5\text{-}C_5H_5)_2HfCl\{(\mu\text{-}H)_2BC_4H_8\}$ respectively.[24] These are the first examples where this anion disproportionates to form a 5-membered borocyclopentane ring.

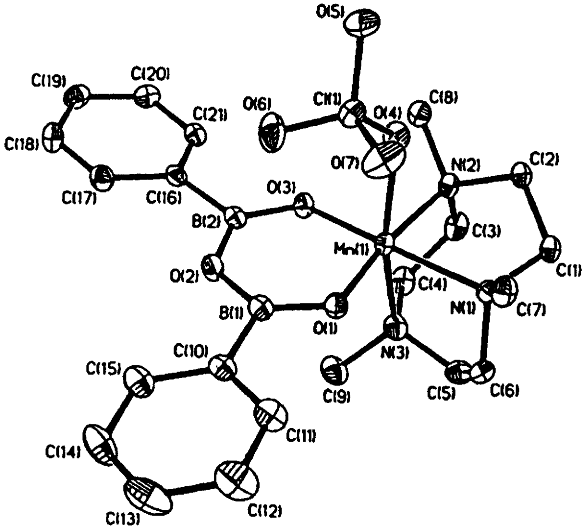


15

A zirconocene-betaine system is formed by electrophilic substitution with $B(C_6F_5)_3$ at a cyclopentadienyl ligand.[25] Some unexpected reactions of pentafluorophenylboron compounds with η-cyclopentadienyl(benzamidinato)zirconium derivatives have been reported.[26] Thus treatment of $[Zr(\eta\text{-}C_5R_5)\{\eta\text{-}CPh(NSiMe_3\}R'_2]$ (R = H, R′ = Me or CH_2Ph; R = Me, R′ = Me) with $[Ph_3C]\{B(C_6F_5)_3\}$ gives $[Zr(\eta\text{-}C_5H_5)\{\eta\text{-}CPh(NSiMe_3)_2\}_2(\eta\text{-}Cl)_2][BX(C_6F_5)_3]_2$. Further chemistry is observed when $B(C_6F_5)_3$ is used in place of $[Ph_3C]\{B(C_6F_5)_3\}$ as a starting reagent.

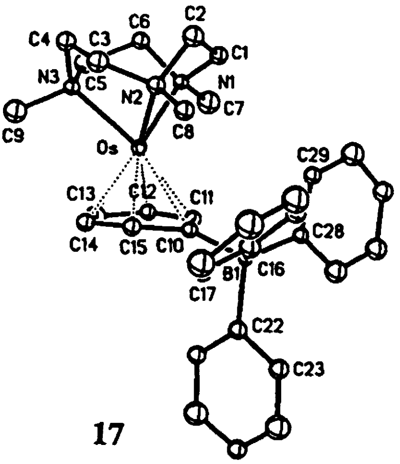
A number of η-arene derivatives of chromium and molybdenum containing Lewis-acid boron substituents have been synthesised and characterised.[27] From the corresponding $TpMo(CO)_2(\pi\text{-allyl})$ complexes, four symmetrically substituted $TpMo(CO)(NO)(\pi\text{-allyl})^+$ complexes (where the allyl group is propenyl, 2-methylpropenyl, cyclohexenyl or cyclooctenyl) were prepared and characterised.[28] The crystal structure of $[TpMo(CO)(NO)(\eta\text{-}C_3H_5)][3,5\text{-}(CF_3)_2C_6H_3)B]$ reveals a significant distortion of the allyl group suggesting η^2 rather than η^3 coordination. This supposition is supported by the results of NMR spectroscopy.

Several metalloproteins, *e.g.* the catalases in *Lactobacillus plantarum* and *Thermus thermophilus*, are found to contain the structural motif of the μ-oxo(hydroxo)-di-μ-carboxylatodimanganese unit. Model compounds containing $PhBO_2$ bridging units including **16** have recently been synthesised.[29] A variety of stereorigid *ansa*-ferrocenes some with boron-containing *o*-phenylene-type bridges have been synthesised.[30] Boron-containing ferrocenyl ligands have been synthesised and their usefulness as reagents for asymmetric catalysis has been evaluated.[31] Two triple-decker complexes with boratobenzene bridging ligands namely $[(\mu\text{-}C_5H_5BMe)(FeCp^*)_2]PF_6$ and $[(\mu\text{-}C_5H_5BMe)\{Rh(COD)\}_2]CF_3SO_3$ have been synthesised and boratobenzene transfer reactions have been studied.[32]



16

A number of osmium complexes of 1,4,7-triazacyclononane (tacn) have been prepared including the air-sensitive osmium(II) salt $[(Me_3tacn)Os(\eta^6\text{-}C_6H_5BPh_3)]BPh_4.CH_3CN$ (**17**). A number of organometallic osmium and ruthenium complexes containing boron anions have also been prepared.[34] The compound $[Ph_2Bt]_2Ni$ (**18**) has been synthesised and is proposed as a model for



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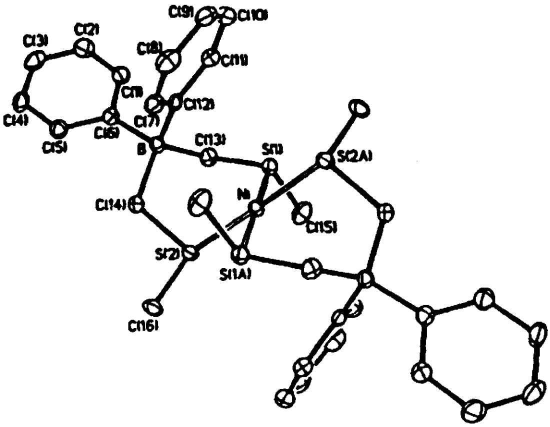

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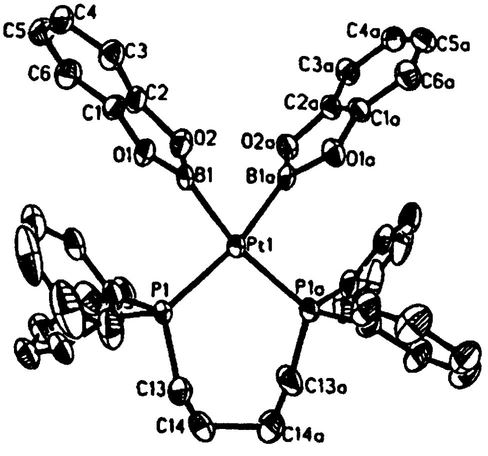
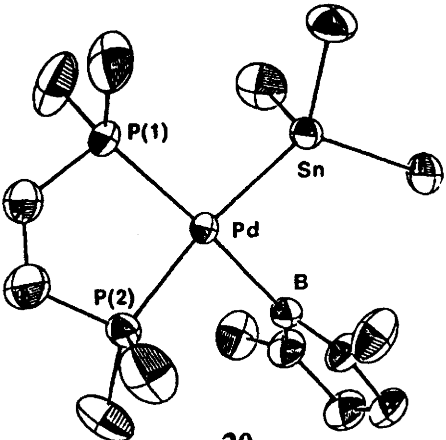
the structural unit found in certain nickel-containing enzymes *e.g.* certain hydrogenases and carbon monoxide dehydrogenases.[35] (1-ferrocenyl-η^6-borabenzene)(η^5-cyclopentadienyl)cobalt(I) has been prepared: it is a new heterobimetallic chromophore with possible applications in non-linear optic systems.

Cleavage of Pt-alkyl bonds in Pt(II) complexes by a number of strong Lewis acids including $B(C_6F_5)_3$ has been noted.[37] The reactions of the B-B bonded compounds $B_2(cat)_2$ (cat = 1,2-$O_2C_6H_4$), $B_2(4\text{-}^tBu\text{-}cat)_2$ and $B_2(OCMe_2CMe_2O)_2$ with the Pt(0)-bis(phosphine) complex $[(PPh_3)_2Pt(\eta\text{-}C_2H_4)]$ proceed *via* oxidative addition of the B-B bond to yield *cis*-bis(boryl) Pt(II) complexes *e.g.* *cis*-$[(PPh_3)_2Pt(Bcat)_2].C_6D_6$ (**19**).[38] **19** reacts smoothly with dppe ($Ph_2PCH_2CH_2PPh_2$) or dppb ($Ph_2P(CH_2)_4PPh_2$) to give *cis*-[(dppe)Pt(Bcat)$_2$] or



19

cis-[(dppb)Pt(Bcat)$_2$]. **19** and its analogues are highly active catalyst precursors for the diboration of alkynes and 1,3-diynes. A mechanistic investigation has been made of stoichiometric alkyne insertion into Pt-B bonds; such chemistry clearly relates to the catalytic diborylation of alkynes.[39] Again the diboryl complex to be investigated is [(Ph$_3$P)$_2$Pt(Bcat)$_2$]. It is proposed that the reaction proceeds by phosphine dissociation to generate a three coordinate intermediate which mediates alkyne insertion. In a related piece of chemistry the *cis* addition of the borylstannanes Me$_3$SnB[NMe(CH$_2$CH$_2$)NMe] and Me$_3$SnB(NEt$_2$)$_2$ across alkynes has been shown to be effectively catalysed by Pd(PPh$_3$)$_4$, Cl$_2$Pd(PPh$_3$)$_2$ or Me$_2$Pd[PMe$_2$(CH$_2$CH$_2$)PMe$_2$] to give (β-stannylalkenyl)boranes *e.g.* **20** in high yields.[40] The complex [Rh(COD)(DPPB)]$^+$BPh$_4^-$ (DPPB = 1,4-bis(diphenylphosphino)butane) is generated by addition of NaBPh$_4$ to [Rh(COD)(DPPB)]$^+$BF$_4^-$ in MeOH.[41] The interest in this compound is that it has the propensity to convert to the zwitterionic forms (η^6-PhBPh$_3$)$^-$Rh$^+$(COD) and (η^6-PhBPh$_3$)$^-$Rh$^+$ (DPPB) in solution, although it is quite stable as a solid. Similar chemistry for related complexes has also been observed, and these complexes are demonstrated to have value as catalysts in hydroformylation, silylformylation and hydrogenation reactions.[41] A dinuclear copper(II) complex [Cu$_2$L$_2${μ-PhB(OH)O}$_2$] [HL = 6-(2-hydroxyphenyl)-2,2-bipyridine] with phenylborate bridges has been synthesised.[42] A dinuclear holmium(III) cluster containing a carborane unit has also been prepared.[43]



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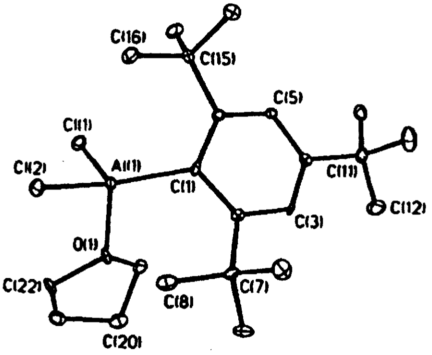
2 Aluminium

2.1 General – The reactions of AlMe$_3$, GaMe$_3$ and InMe$_3$ with CsF in acetonitrile furnish the corresponding trimethylfluorometallates Cs[Me$_3$MF].[44] In all three compounds Cs$_2$F$_2$ four-membered rings are the structure-dominating units but the solid state structures of the three compounds are quite different. When M = Al the compound consists of puckered layers of weakly associated

Cs_2F_2 rings. When M = Ga the four-membered rings form infinite ladder-type chains, whereas when M = In ring stacking leads to a heterocubane with a Cs_4F_4 core. The synthesis and structural characterisation of the compounds mes*-$AlCl_2$(thf), mes$^*AlCl_2$, mes*Al(H)Cl(thf), mes*Al(H)Cl and (mes$^*AlH_2)_2$ (mes* = 2,4,6-$^tBu_3C_6H_2$-) has been described.[45] The structure of the tetrahydrofuran adduct mes$^*AlCl_2$(thf) is given (**21**). The binding energy of $Al(C_6H_6)^+$ has been estimated as 35.2 +/-2 kcal mol^{-1} from analysis of radiative association kinetics.[46] A number of sterically encumbered derivatives of aluminium hydrides and halides are reported.[47] These compounds are: $[2,6\text{-}mes_2C_6H_3AlH_3LiOEt_2]_n$, 2,6-$mes_2C_6H_3AlH_2OEt_2$, $[2,6\text{-}mes_2C_6H_3AlH_2]_2$ (**22**) and analogues including either Cl in place of H or the Trip group (Trip = 2,4,6-$^iPr_3C_6H_2$-) group in place of the mesityl group.



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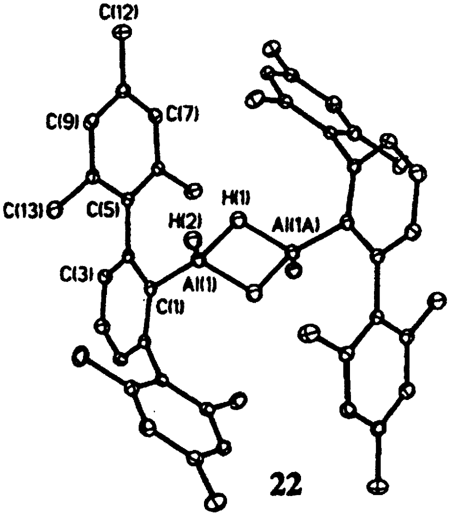
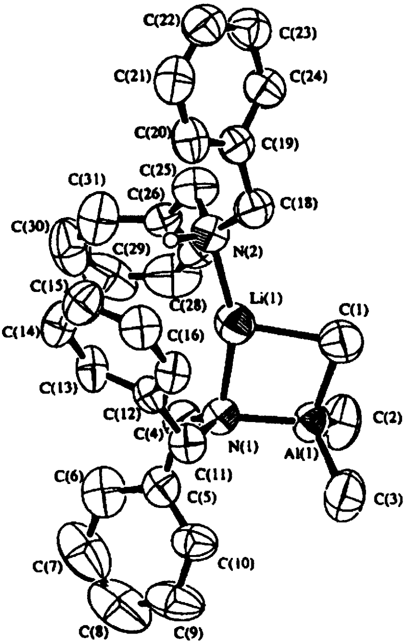


22

Tetrakis[bis(trimethylsilyl)methyl]dialane reacts with potassium in 1,2-dimethoxyethane (DME) to yield the dark blue stable radical anion $[R_2Al{\cdot}AlR_2]^-[K(DME)]^+$ ($R = CH(SiMe_3)_2$).[48] An excess of potassium or longer reaction times leads to decomposition, however, with the formation of three new compounds which have been identified as $[R_2Al(Me)(OC_2H_4OMe][K(DME)]$, $[R_2AlMe_2][K(DME)]$ and the glycolato alanate $[R_2Al(OCH_2)_2][K(DME)]$. This last compound may also be prepared by reaction of $ClAlR_2$ with $KOCH_2CH_2OK$. The novel aluminium compounds $(C_5Me_5)AlR_2$ (R = Me, Et or ^iBu) have been prepared by the reaction of $(C_5Me_5)K$ with the appropriate alkylaluminium chlorides.[49] These compounds are characterised by η^3-coordinated C_5Me_5 ligands and all of these complexes are monomeric. This situation contrasts with that when the C_5Me_5 ligand is replaced by C_5H_5 or C_5H_4Me; in these cases an equilibrium between monomeric and dimeric species exists in benzene solution. This equilibrium has been monitored by ^{27}Al NMR spectroscopy. The monomeric species show η^2-coordinated C_5H_5 or C_5H_4Me ligands, a mode of coordination which is also shown by the ligand $C_5H_4{}^tBu$ in $(^tBuCp)Al(^iBu)_2$. Selective catalytic ethylene dimerisation has been reported for Ni(II) complexes together with $AlEtCl_2$ dissolved in organoaluminate ionic liquids.[50] The solvent consists of methyl-1-butyl-3-imidazolium chloride/$AlCl_3$ molten salt. The specific nature of the products formed appears to depend principally upon the nickel compound utilised.

2.2 Compounds Containing a Group 15 Element – The reaction of $AlMe_3$ with benzo[*f*]quinoline is reported to give the adduct $[AlMe_3.(C_{13}H_9N)]$ with an Al-N bond length of 2.057(2) Å.[51] Not surprisingly this adduct is found to be much less air- and water-sensitive than is $AlMe_3$. The crystal structure of a representative mixed adduct of $AlMe_3$ with a lithium amide is reported.[52] The compound $[Me_3Al.(PhCH_2)_2NLi.HN(CH_2Ph)_2]$ (**23**) is prepared by reaction of the simple alane adduct $[Me_3Al.HN(CH_2Ph)_2]$ with the lithium amide $[(PhCH_2)_2NLi]$. **23** exhibits a four-membered mixed-metal, mixed-anion Al-C-Li-N ring core. The reaction of 2,2′-dipyridylamine with Me_3M (M = Al or Ga) gives the adducts $Me_2Ga(dpa)$ and $Me_2Al(dpa)$ (where dpa = 2,2′-dipyridylamide).[53] The gallium compound has been subjected to a single crystal structure determination which shows the Ga atom to be in a tetrahedral environment coordinated to the deprotonated chelating ligand and to the two methyl groups. The Ga-N bond distances are extremely short at 1.977(3) Å. The reaction of the unsubstituted arylamido salt $KNHC_6H_5$ with $NdCl_3$ gives an insoluble material chracterised as $[Nd(NHC_6H_5)_3(KCl)_3]$ which itself reacts with Al_2Me_6 in hexane to give the heteroleptic mixed-metal complex $\{[Me_2Al(\mu\text{-}Me_2)]_2Nd(\mu_3\text{-}NPh)(\mu\text{-}Me)AlMe\}_2$ (**24**).[54]

Addition of ^tBuLi to $[Me_2AlNH(C_6H_3{}^iPr_2\text{-}2,6]_2$ results in the formation of a surprisingly stable adduct $Me_2{}^tBuAl.NH[Li(thf)_3](C_6H_3{}^iPr_2\text{-}2,6)$.[55] The Al-N bond length is 1.976(9) Å. The molecule aminodimethylalane (Me_2AlNH_2) has been the subject of a combined matrix-isolation IR and *ab initio* theoretical study.[56] The compound is generated in a matrix by photolysis of the adduct $Me_3Al.NH_3$; IR spectra of the product are assigned to the molecule Me_2AlNH_2 on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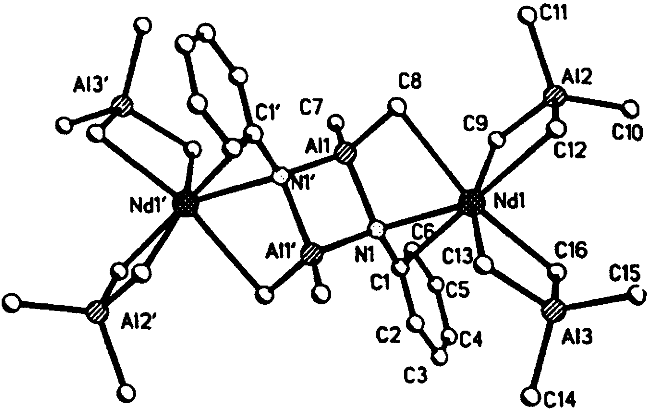
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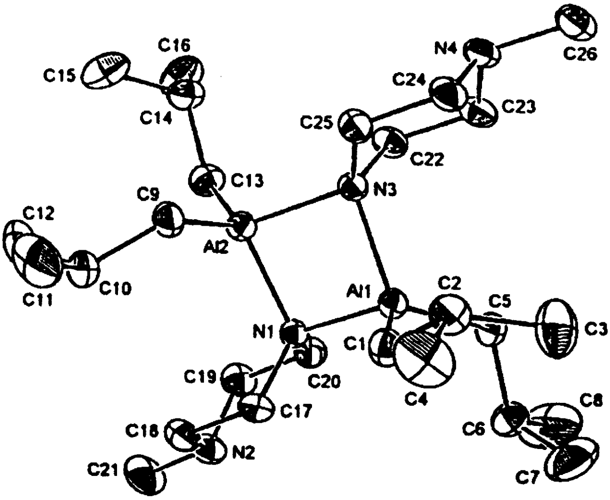
Al2'
C2
C4
Al3
C3
C14

24

the basis of isotopic substitution with ^{15}N and ^{2}H. The *ab initio* calculations suggest an Al-N bond length of 1.790 Å. The reactivity of R_2AlH (R = Me or ^{i}Bu) with selected aminoarsines and secondary amines has been investigated.[57] The aluminium compounds were reacted with a series of nine aminoarsines Me_2AsR (where R = NMe_2, N^{n}Pr$_2$, N^{i}Pr$_2$, N^{n}Bu$_2$, N^{i}Bu$_2$, NC_4H_8, NC_5H_{10}, NC_6H_{12} and $N(C_2H_4)_2NMe$) in C_6D_6 at room temperature; the reactions were monitored by ^{1}H and ^{13}C NMR spectroscopy. For most of the reactions the predominant Al-containing products were the dimeric aminoalane compounds $[Me_2AlR_2]$ or [^{i}Bu$_2$AlR$_2$] *e.g.* **25**. Although Al-N bond formation was the preferred mode of reaction Al-As bond formation was also observed when the bulky ^{i}Pr and ^{i}Bu aminoarsine derivatives were used. Other compounds of general formula $[R_2AlN\text{-}Li(thf)_nR'_2]$ (where R, R′ = Me, ^{t}Bu (n = 1); ^{i}Bu, Ph (n = 1); SiMe$_3$, Ph (n = 2)) containing the Al_2N_2 core are reported.[58] However, when the bulky R groups Mes or Dipp (Dipp = 2,6-diisopropylphenyl) are used the unusual adducts Me$_2$(^{t}Bu)Al.NHLi(thf)$_3$Dipp (**26**) and Mes$_2$(Me)Al.NLi(thf)$_2$(SiMe$_3$)$_2$ and the aluminate [^{i}Bu$_2$(^{t}Bu)AlNhDipp]$^-$[Li(thf)$_4$]$^+$ result.



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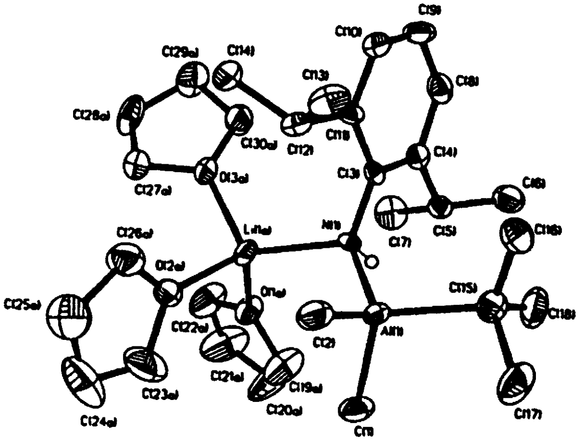
The search for precursors to thin layers of crystalline aluminium nitride drives much of the research into compounds aluminium and nitrogen. To this end structures of three aluminium adducts $(C_5H_5N)_3Al(N_3)_3$ (**27**), $[Me_2N(CH_2)_3]_2Al(N_3)$ and Me$_2$(N$_3$)Al(H$_2$N^{t}Bu) have all recently been determined by single crystal X-ray diffraction.[59] Using these compounds thin films of AlN may be grown by Organometallic Vapour Phase Epitaxy (OMVPE) at 400-850 °C. A second route to AlN film formation is the sequential reaction of Et_3Al and ammonia on an alumina surface.[60] Temperatures in excess of 500 K are required for this process.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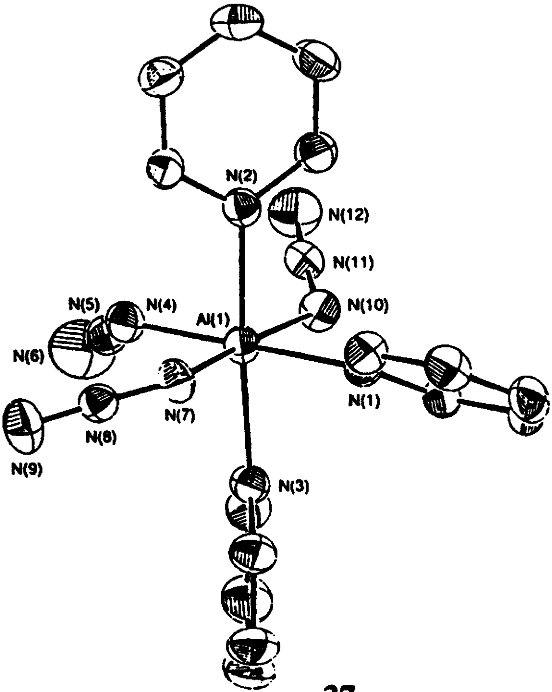
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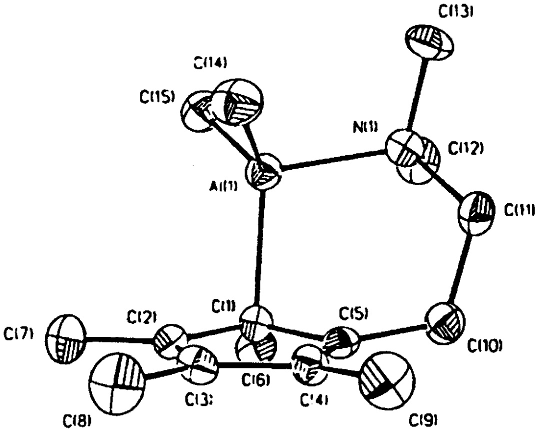
27

A series of compounds ($C_5Me_4CH_2CH_2NMe_2$)MX_2 (MX_2 = $AlMe_2$, $AlCl_2$ or $InCl_2$) has been prepared.[61] The structure of the Me_2Al derivative is given (**28**). All of these compounds are monomeric with intramolecularly-coordinated dimethylamino groups. A series of alkylaluminium complexes containing pyridyl amido ligands has also been made by the reaction of $AlMe_3$ with 2-(aminomethyl)pyridine and 4-(aminomethyl)pyridine. With 2-(aminomethyl)pyridine the product when the reagents are in a 1:1 ratio is the *cis* dinuclear compound [$Al(Me_2(NHCH_2$-2-Py)]$_2$ where the aluminium centre is five-coordinate. With 4-(aminomethyl)pyridine, when the reagents are in a 1:1 ratio, a four coordinate dinuclear complex [$AlMe_2(NHCH_2$-4-Py)]$_2$ is formed and when these same reagents are in a 2:1 ratio the product is the adduct $Me_3Al.(NH_2CH_2$-4-Py).$AlMe_3$ which gradually converts to the tetranuclear compound [Al-$Me_2(HNCH_2$-4-Py)$AlMe_3$]$_2$ in solution and in the solid state.



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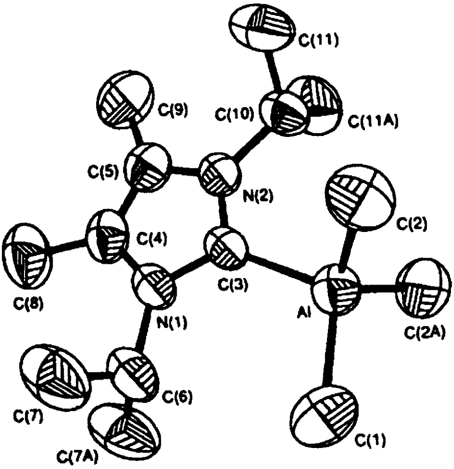
A study has been made of halide effects in the formation of four-coordinate cationic aluminium.[63] This work is part of a larger study into the factors that affect cation formation for organometallic aluminium complexes. In the work reported here the adduct $R_2AlX.NH_2{}^tBu$ (R = Me or Et; X = F, Cl or Br) and the cationic complexes [$R_2Al(NH_2{}^tBu)_2$]X (R = Me or Et; X = Br or I) were examined. The study demonstrates that the reaction of R_2AlX with excess $NH_2{}^tBu$ produces cationic complexes only when X is Br or I. A single crystal structure determination has been made on the adduct of Me_3Al with 1-methyl-4-phenylpiperazine [$Me_3Al.(C_{11}H_{16}N_2)$].[64] The Al atom is in a distorted tetrahedral environment and the Al-N bond length is 2.050(2) Å. The reaction of trimethylsilylcyanide with Me_3Al is reported.[65] Part of the interest in this work is, in fact, the synthesis of the trimethylsilylcyanide; an improved route utilising the reaction of hexamethyldisilazane with HCN is described. The product of the Me_3Al reaction is a methylaluminiumdicyanide with an oligomeric structure. It is believed to contain tetrahedral Al atoms linked by CN bridges.

The first organometallic group 13 carbenes have recently been reported.[66] These have been generated by the reaction of Me_3Al or Me_3Ga with 1,3-diisopropyl-4,5-dimethyldazol-2-ylidene. The structure of the Al product is given (**29**). A formal aluminium-nitrogen analogue of the cyclopentadienide ion is provided by the complex mes*Al(N(Ph)Al(mes*)N(Ph)NPh which contains a five-membered N-Al-N-N-Al-N ring (**30**).[67] A dimeric iminoalane [CpAl-N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$ (**31**) has been generated by the stepwise elimination of two molecules of cyclopentadiene from Cp_3Al upon its reaction with an equivalent amount of 2,6-diisopropylamine.[68] The 1:1 adduct of the two reagents was not obtained in its pure form in this reaction because it readily loses cyclopentadiene to give the dicyclopentadienylaluminium halide. The reaction of H$_2$AlMes* with



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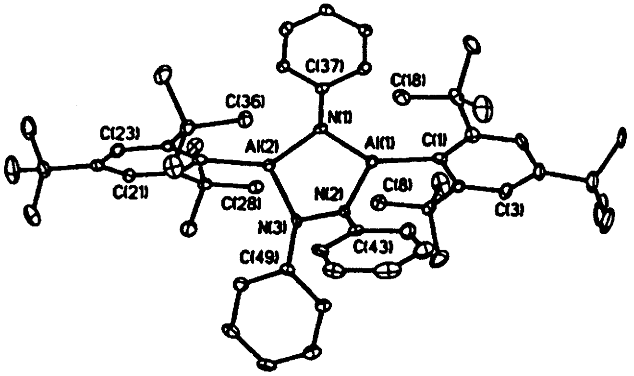

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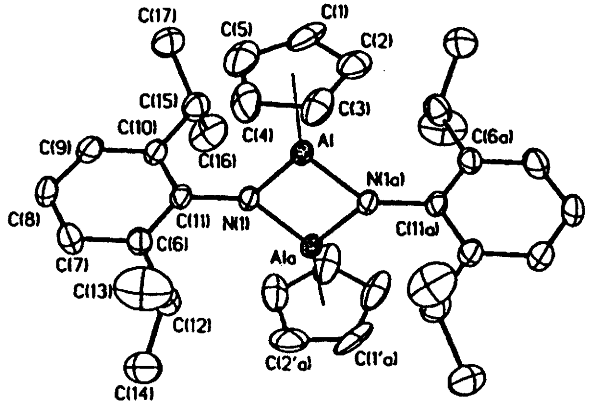

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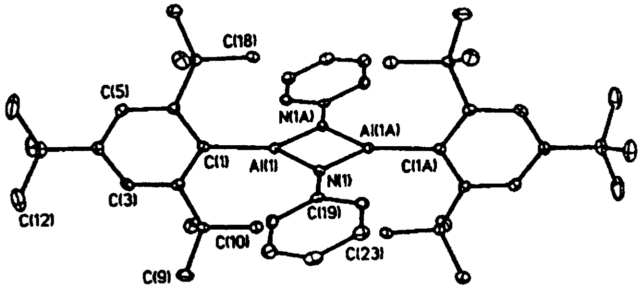
H_2EAr (E = N, P or As; Ar = aryl) gives ring compounds of general formula $(\text{Mes}^*\text{AlNPh}_2)_2$ and $(\text{Mes}_2\text{AlEPh})_3$ (E = P or As).[69] The structure of one such compound with a four-membered N-Al-N-Al ring is given (**32**). This "antiaromatic" four-membered ring may be contrasted with the five-membered ring in **30** reported elsewhere.[67] In the six-membered rings found for the heavier pnictides phosphorus and arsenic there is no evidence for significant delocalisation of the P or As lone pairs since the average Al-P and Al-As distances are consistent with single bond lengths. Another compound with a four-membered Al-N-Al-N ring is $(\text{Cp}^*\text{AlNSi}^t\text{Bu}_3)_2$ (**33**) generated by the reaction of $(\text{Cp}^*\text{Al})_4$ with organic azides.[70] This route provides an alternative to iminoalanes and gives a low degree of oligomerisation. A further example of this type of compound is provided by $[\text{Me}_2\text{AlNLi(thf)}_2\text{Ph}]_2$ (**34**).[71] This novel monolithio aluminium amide dimer is prepared by deprotonation of the corresponding neutral dimeric species $[\text{Me}_2\text{AlNHPh}]_2$ with ^{t}BuLi in thf. The Al-N distances in **31**, **32**, **33** and **34** are as follows: **31** 1.796(2) and 1.811(3) Å; **32** 1.824(2) Å (all distances identical); **33** 1.840(2) and 1.835(2) Å; **34** 1.904(5) and 1.888(5) Å.



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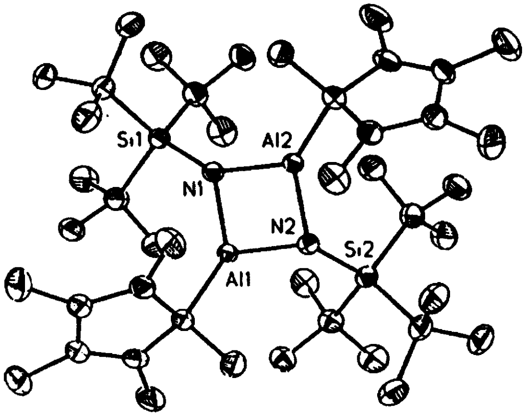
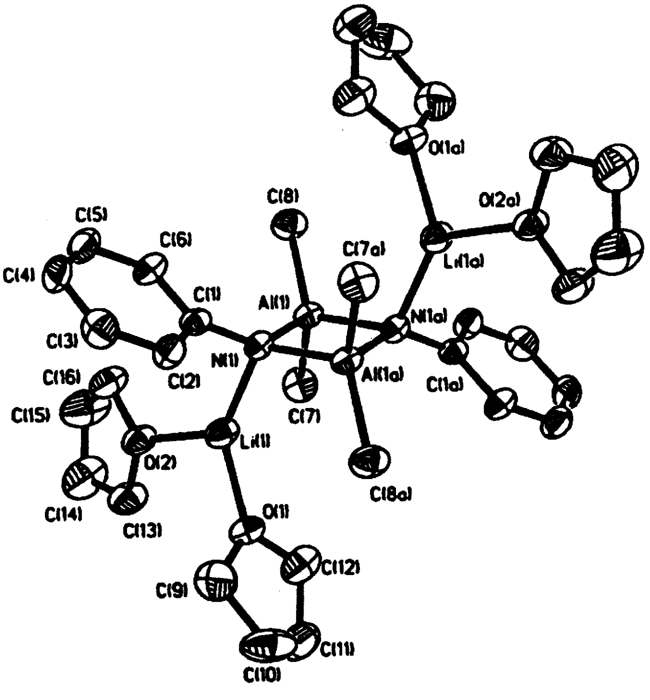
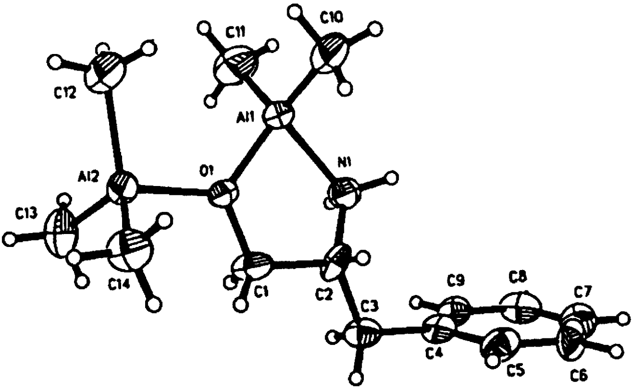

Si1
Al2
N1
N2
Si2
Al1

33


O(1a)
O(2a)
C(8)
C(5)
C(6)
C(7a)
Li(1a)
C(4)
C(1)
Al(1)
N(1a)
C(3)
N(1)
Al(1a)
C(1a)
C(16)
C(2)
C(7)
C(15)
Li(1)
O(2)
C(8a)
C(14)
C(13)
O(1)
C(12)
C(9)
C(11)
C(10)

34

The synthesis and structural characterisation of some amine alcohol complexes of aluminium have been reported. These complexes are of two general formulae: (i) [AA-AlR_2] (where AA = phenylglycinol, phenylalinol or diphenylalinol and R = Me, Et or $SiMe_3$); (ii) AA($AlMe_2$)-$AlMe_3$. All of these complexes are chiral and this work therefore increases significantly the list of known chiral group 13 complexes. The structure of one of these complexes – AA($AlMe_2$)-$AlMe_3$ (where AA is phenylalinol) is given in **35**. The Salan ligand [Salan = *N,N′*-bis(*o*-hydroxybenzyl)-1,2-diaminoethane (SaleanH_4), *N,N′*-bis(*o*-hydroxybenzyl)-1,2-diaminobenzene (SalophanH_4) or *N,N′*-bis(*o*-hydroxybenzyl)-1,2-diamino-(4,5-dimethyl)benzene (SalomphanH_4)] complexes with organoaluminium moieties have been reported.[73] Two types of such complexes are found. Type I has the general formula LHAlR(AlR_2) where L is a Salan ligand and R is Me, Et of ^{i}Bu. Type II has the general formula $[LAl(AlR_2)]_2$. It is found that the type I complexes may be converted into the trimetallic derivatives $LAlR(AlR_2)_2$ by addition of AlR_3, but that this reaction is not undergone by the type II complexes.

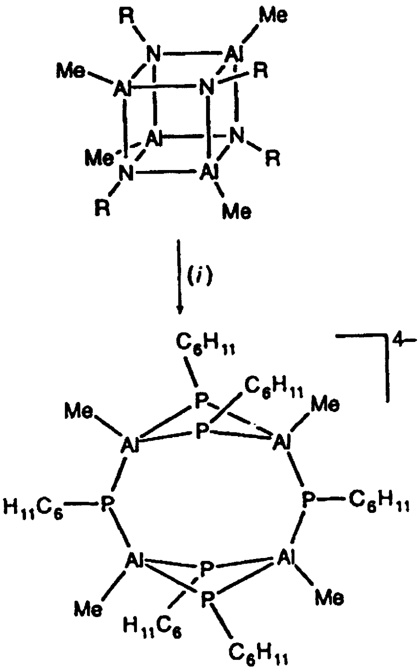


35

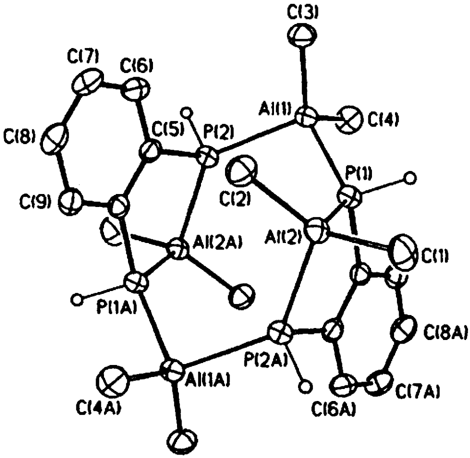
An $Al_4P_6Li_4$ cage complex containing the metallacyclic tetraanion **36** has been generated by the acid-base reaction of the Al(III) imino cubane **37** with Li[PH(C_6H_{11})].[74] **36** is the first example of an Al(III) phosphinidine anion. The counterions in **36** are $[Li(OC_4H_8)]^+$. The independent 2:1 reactions of MMe_3 (M = Al or Ga) with 1,2-$(H_2P)_2C_6H_4$ results in the formation of the novel eight-membered tetrametallic ring compounds with the general formula $\{(Me_2M)_4[(\mu\text{-}PH)_2(C_6H_4)]_2\}$ [M = Al (**38**), Ga] in a nearly quantitative yield.[75] The reaction of $AlMe_3$ and 1,2-$(H_2P_2C_6H_4)$ also yielded **38**. The reaction of $AlMe_3$ with 1,2-$(H_2N)_2C_6H_4$ in a 2:1 ratio yielded the novel asymmetric compound $[(Me_2Al)_2\text{-}Me(C_6H_4(NH)_2)_2].AlMe_3$ (**39**).[75] By contrast reaction of Me_3Ga with 1,2-$(H_2N)C_6H_4$ in a 3:2 ratio gave $\{(Me_2Ga)_3[(\mu\text{-}NH)_2(C_6H_4)(\mu\text{-}NH)(C_6H_4NH_2)]\}$ (**40**).[75]

Novel phosphido complexes of formula $(Me_2M)_4(\mu\text{-}PR)_2C_6H_4)_2$ (M = Al, R =

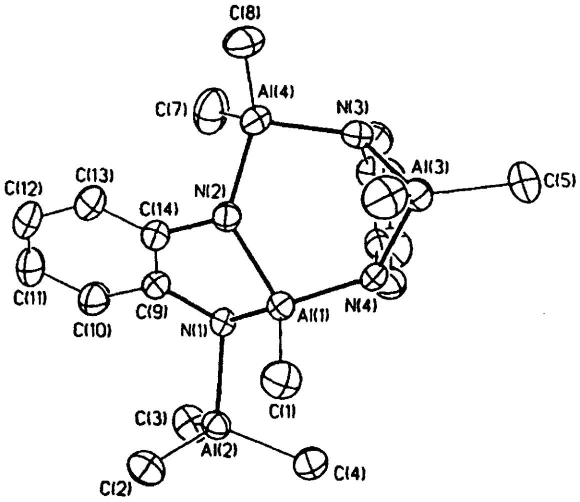
37


R
Me
N
Al
Me
R
(i)
C_6H_{11}
4–
Me
P
Al
$H_{11}C_6$

36


C(3)
C(7)
C(6)
Al(1)
C(4)
C(8)
C(5)
P(2)
P(1)
C(2)
C(9)
Al(2A)
Al(2)
C(1)
P(1A)
C(8A)
P(2A)
Al(1A)
C(4A)
C(6A)
C(7A)
C(3A)

38



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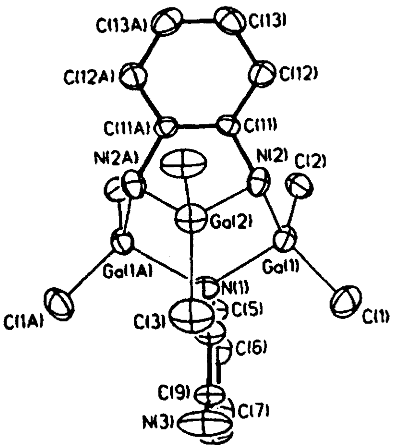
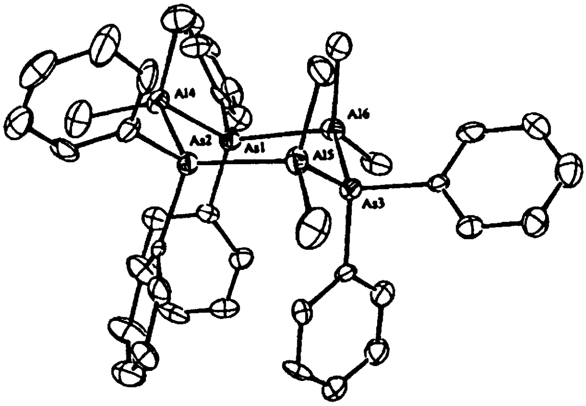


40

Me; M = Ga, R = ^{t}Bu) result when the chelating diphosphine ligand 1,2-bis(alkylphosphino)benzene is mixed with the trialkylaluminium or trialkylgallium reagent. When the potentially chelating ligand 1,2-bis(*tert*-butylphosphino)ethane is mixed with two equivalents of $AlMe_3$ under the same conditions, the secondary phosphine bis-adduct complex $Me_3Al.PH({}^{t}Bu)CH_2CH_2({}^{t}Bu)HP.AlMe_3$ is formed.[76] The independent reactions of Ph_3Al with $E(SiMe_3)_3$ (E = P or As) in 1:1 molar ratios afforded the adducts $Ph_3Al.E(SiMe_3)_3$. The attempted dehalosilylation reactions between $Ph_2(Cl)Al$ and $E(SiMe_3)_3$ in a 1:1 molar ratio yielded only the adducts $Ph_2(Cl)Al.E(SiMe_3)_3$. The adduct $Ph(Cl)_2Al.P(SiMe_3)_3$ was isolated from the reaction of equimolar amounts of $PhAlCl_2$ and $P(SiMe_3)_3$.[77] The reactions of Me_3Al with two secondary arsines, Ph_2AsH and $Ph(MeSiCH_2)AsH$ in 1:1 molar ratios have been studied.[78] The products are the trimeric compounds $[Me_2AlAsPh_2]_3.(C_7H_8)_2$ (**41**) and $[Me_2AlAs(CH_2SiMe_3)Ph]_3$ (**42**) respectively. **41** and **42** are the first Al-As six-membered rings to be structurally chracterised by single crystal X-ray diffraction. In both **41** and **42** the six-membered rings adopt the chair conformation; the Al and As centres reside in pseudotetrahedral environments and the As-Al bond lengths range from 2.512(3) to 2.542(3) Å in **41** and from 2.504(5) to 2.526(5) Å in **42**.



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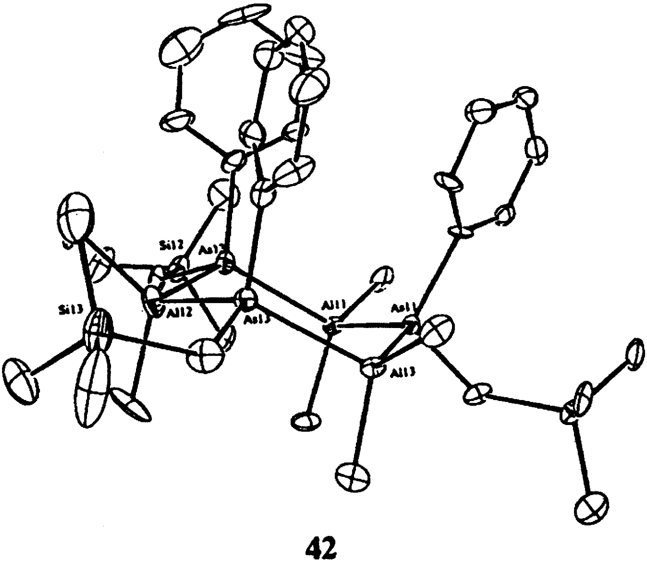
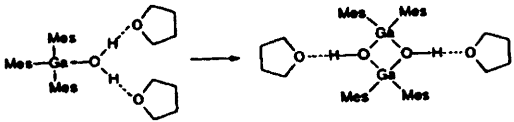


42

2.3 Compounds Containing a Group 16 Element – The hydrolysis of trimesitylaluminium and -gallium has been monitored by ^{1}H NMR spectroscopy in the temperature range -60 °C to room temperature using deuterated thf as solvent.[79] Various intermediates along the reaction pathway have been isolated and their structures determined by low-temperature single crystal X-ray diffraction methods. The first intermediate of the reaction of Mes_3Ga and water is the monomeric water adduct, $(Mes_3Ga.OH_2).2thf$ (**43**). Elimination of mesitylene leads to the dimeric hydroxide $(Mes_2GaOH)_2.thf$ (**44**).



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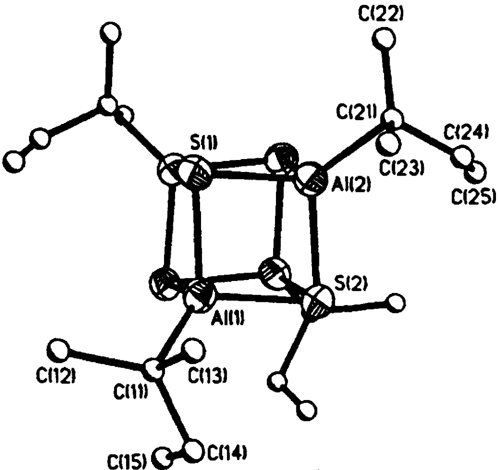
44

Excess of water gives $Mes_6Ga_6O_4(OH)_4.4thf$. The corresponding reactions of Mes_3Al give $(Mes_3AlOH_2).n$thf and $(Mes_2AlOH)_2.2thf$. The reactions of Me_3Al with aliphatic diols, derivatives of 1,4-butanediol and 1,3-propanediol, have been investigated.[80] Mixtures of linear and cyclic organoaluminium compounds were obtained; a ubiquitous product was a complex of formula $Me_5Al_3[diolate]_2$ (where diolate indicates 1,3-propanediol or 1,4-butanediol without the two hydroxyl protons). In this work multinuclear NMR, elemental analysis and molecular weight determinations were used to identify the complexes formed.

The reaction of $AlCl_3$ with 3 equivalents of the *tert*-amyl Grignard reagent $(Me_2EtC)MgCl$ yields the monomeric compounds AlR_3 (where R = *tert*-amyl). Several reactions of AlR_3 have been explored.[81] Reaction of AlR_3 with MeCN and [PPN]Cl gives the Lewis acid-base complexes $AlR_3.(MeCN)$ and $[PPN][AlClR_3]$ respectively. The hydrolysis of AlR_3 in hexane gives the trimeric hydroxide $[(R_2Al)(\mu\text{-}OH)]_3$, which is converted to the dimer $[(R_2Al)(\mu\text{-}OH)_2]_2$ on heating. The reaction of AlR_3 with H_2S at room temperature gives the cubane **45**; if this reaction is repeated at 0 °C then the hexamer **46** is isolated alongside **45**. The selenide (**47**) and telluride analogues of **45** may be produced by reaction of AlR_3 with H_2Se and Te metal respectively. The gallium cubane compounds $[RGa(\mu_3\text{-}E)]_4$ (R = *tert*-amyl; E = S, Se or Te) have been prepared by reaction of R_3Ga with the appropriate element. In this work a structural analysis is made of the M_4E_4 cubane cores and a new topological method is proposed to predict the intercage bond angles in group 13 cage compounds.

A range of intermolecularly stabilised organoaluminium and organogallium alkoxides and amides of general formula $Me_2M\text{-}O\text{-}R\text{-}OR'$ and $Me_2M\text{-}NH\text{-}R\text{-}OR'$ have been synthesised.[82] The alkoxides have been synthesised by reaction of Me_3Al or Me_3Ga with the appropriate alkoxy alcohol. Me_3Ga is found to react with $CH_3OCH_2CH_2NH_2$ and $CH_3OCH_2CH_2NH_2$ with the formation of 1:1 adducts which decompose above 110 °C to give $[Me_2Ga(\mu\text{-}NH\text{-}(CH_2)\text{-}OMe)]_2$ and $[Me_2Ga(\mu\text{-}NH\text{-}(CH_2)\text{-}OMe)]_2$ respectively. A number of sterically encumbered aluminium aryloxide complexes are also reported.[83] These include the



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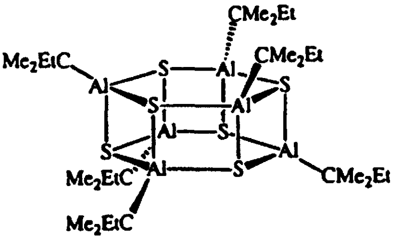

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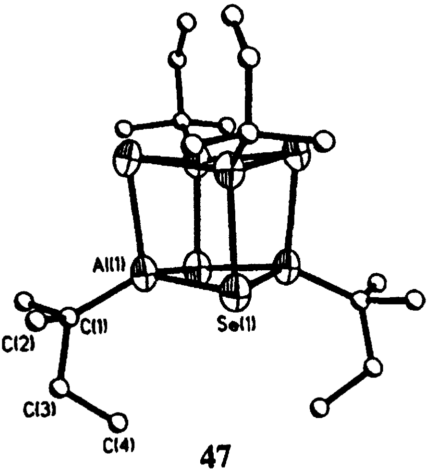
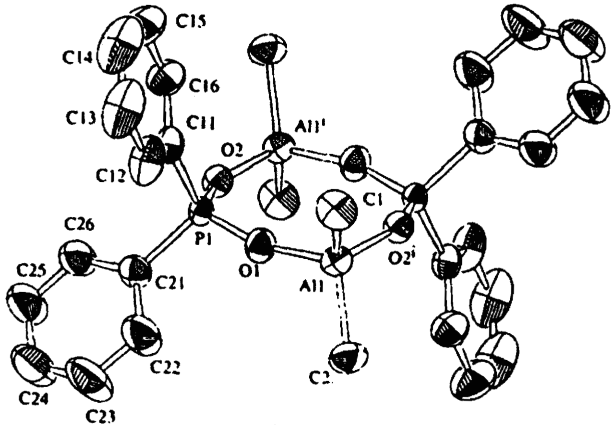


47

products of reaction of $[Me(Ph^{*}O)AlX]_2$ with excess $NH_2{}^tBu$ *i.e.* the adduct species $Me(Ph^{*}O)AlX(NH_2{}^tBu)$ (X = Cl or Br). The compound bis(μ-diphenylphosphinato-*O*:*O'*)bis(dimethylaluminium) (**48**) has been prepared and structurally characterised.[84] **48** contains a puckered eight-membered $(Al\text{-}O\text{-}P\text{-}O)_2$ ring with Al-O distances of 1.781(3) and 1.794(3) Å and P-O distances of 1.512(3) and 1.505(2) Å.

The reaction of $Cl_2AlO\text{-}{}^iPr$ with C_5H_5Na affords the isopropoxy-bridged dimer $[\eta^1\text{-}(C_5H_5)_2AlO\text{-}{}^iPr]_2$ containing a four-membered Al-O-Al-O- ring.[85] The dialane tetrakis[bis(trimethylsilyl)methyl]dialane with an Al-Al bond reacts with dimethyl sulfoxide (DMSO) and water to give a trimeric dialkyl hydroxo aluminium compound, probably $[R_2Al(\mu\text{-}OH)]_3$ (R = $SiMe_3$).[86] A similar reaction



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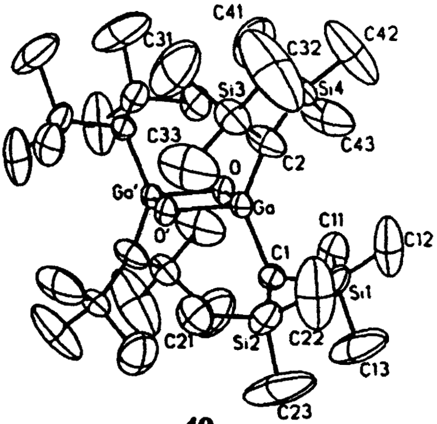
is undergone by the corresponding digallane although here the product is shown, by single crystal methods, to be an OH-bridged dimer. Treatment of the μ-hydroxo aluminium derivative with isobutyllithium does not give a deprotonation reaction, but rather yields **49** with a six-membered Al_2LiO_3 heterocycle.

There have been two recent studies of organometallic aluminium and gallium derivatives with the calixarene ligands. A pentaaluminium complex of calix[6]-arene has been prepared by the reaction of *p-tert*-butylcalix[6]arene with Me_3Al.[87] In this complex an AlMe group resides between two parallel calixarene aromatic rings. In the second study calix[4]arene or *p-tert*-butylcalix[4]arene is found to react with MMe_3 (M = Al or Ga) in toluene to give the fully deprotonated alkyl-metal rich complexes $[L(MMe_2)(MMe_3)]$ (L = calix[4]arene or *p-tert*-butylcalix[4]arene) where the calixarene adopts a double-flattened partial cone conformation.



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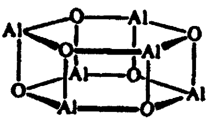
The reaction of primary and secondary amines with the hexameric *tert*-butylalumoxane $[(^t\text{Bu})\text{Al}(\mu_3\text{-O})]_6$ which contains the structural core **50** has been studied.[89] The products are $[(^t\text{Bu})_6\text{Al}_6(\mu_3\text{-O})_4(\mu\text{-O})_2(\text{NH}_2\text{R})_2]$ (R = Et, ^{n}Pr, ^{i}Pr, ^{n}Bu or ^{t}Bu). These products all contain the structural core **51** with two fused boat conformation Al_3O_3 rings derived from opening of two opposing edges of the Al_6O_6 cage (**50**). A number of organic-soluble cyclic and cage alkylaluminium-phosphates have been prepared. The structure of $[(^t\text{Bu})_2\text{Al}(\mu\text{-O})_2\text{P}(\text{OSiMe}_3)_2]_2$ is given (**52**), showing the Al-O-P-O-Al-O-P-O- eight-membered ring core. The proposed $\text{Al}_4\text{P}_4\text{O}_{12}$ core of $[(^t\text{Bu})\text{Al}(\mu_2\text{-O})_3\text{P}(\text{OSiMe}_3)]_4$ is given in **53**.



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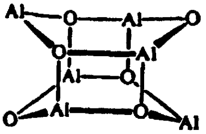
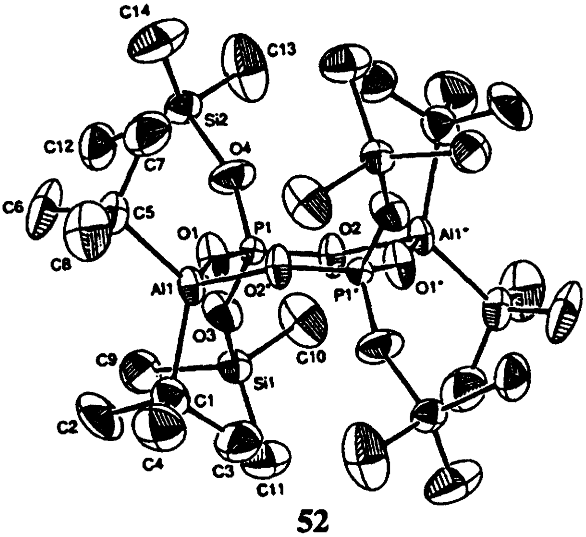
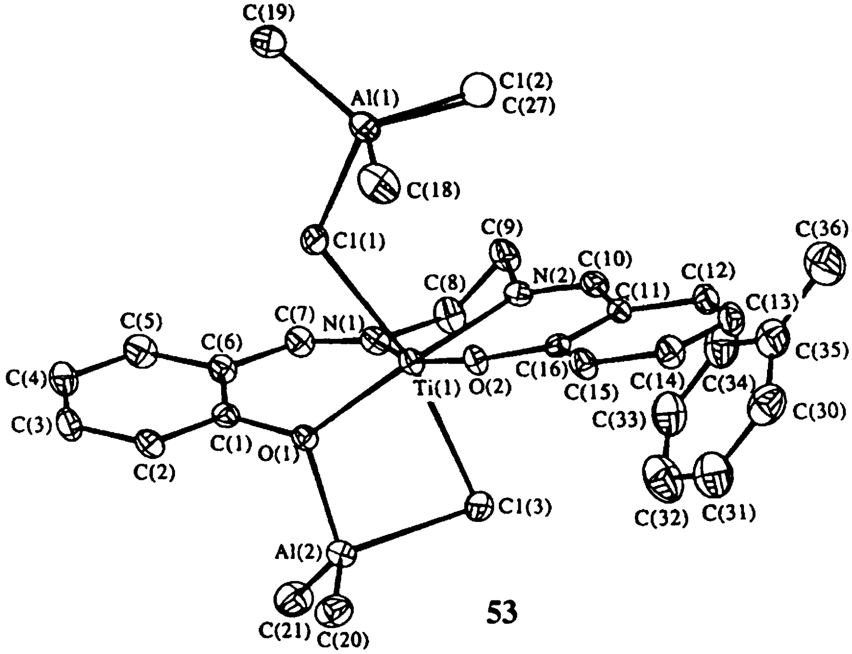


50 **51**



52

The crystal structure of $\text{Li}[(\text{Me}_3\text{Si})_3\text{CAlX}_3].\text{OC}_4\text{H}_8$ (X = ^{t}BuO or F) is reported.[91] A number of alumoxanes have been used as cocatalysts in the palladium catalysed copolymerisation of carbon monoxide and ethylene.[92] The compound (2,7-dimethyl-1,8-biphenylenedioxy)bis(dimethylaluminium) has been assessed for its reactivity and selectivity in organic synthesis.[93] A chiral organoaluminium reagent has been shown to control enantioselective radical cyclisation reactions.[94] A derivative of diphenylacetylene has been used as an organic framework to hold apart two $\text{OAl}(^i\text{Bu})_2$ Lewis acidic groups with a convergent orientation.[95] The compound contains an Al_2O_2 ring which is markedly distorted by the organic framework; the ring is puckered and its O



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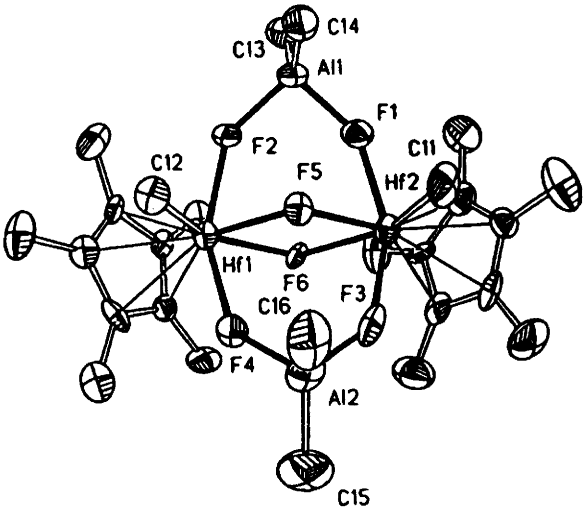
atoms are distinctly pyramidalised. The Al-O bond distances (average 1.913(2) Å) are also significantly longer than those considered normal for related dimers of alkylaluminium alkoxides and aryloxides *i.e.* 1.840 – 1.895 Å. The insertion of chalcogen atoms into Al-Al and Ga-Ga bonds to yield monomeric compounds with Al-Se-Al, Ga-S-Ga and Ga-Se-Ga groups is reported.[96] The reaction giving these products is that of tetrakis[bis(trimethylsilyl)methyl]dialane or -digallane with the chalcogen atom donors triethyl phosphonium sulfide or selenide.

2.4 Compounds Containing a Metal other than Aluminium – The reaction of [$TiCl_2$(salen)] (salen = N,N′-ethylene*bis*(salicylideneiminate)] and $AlMe_3$ in toluene solution gives the heterobimetallic [Ti{μ-Cl)($AlMe_2$)}{(μ-Cl)(Al-Me_2X)}(salen)] (X = Me or Cl) (**53**) and [TiMe{(μ-Cl)($AlCl_2$Me)}(salen)].[97] This latter product in thf forms the stable monoalkylated titanium(IV) complex [Ti(Me)Cl(salen)]. The reactions of (η^5-C_5Me_5)ZrF_3, (η^5-C_5Me_4Et)ZrF_3, (η^5-C_5Me_5)$_2ZrF_2$, (η^5-C_5Me_5)HfF_3 and (η^5-C_5Me_5)TaF_4 with $AlMe_3$ have been investigated.[98] The reaction of the hafnium derivative gives the first hafnium-aluminium-carbon clusters **54** and **55** whose structures have been obtained. **54** (stereospecifically the *cis* isomer) is the principal product and **55** is a byproduct. A range of zirconium-aluminium-carbon cluster compounds are reported.



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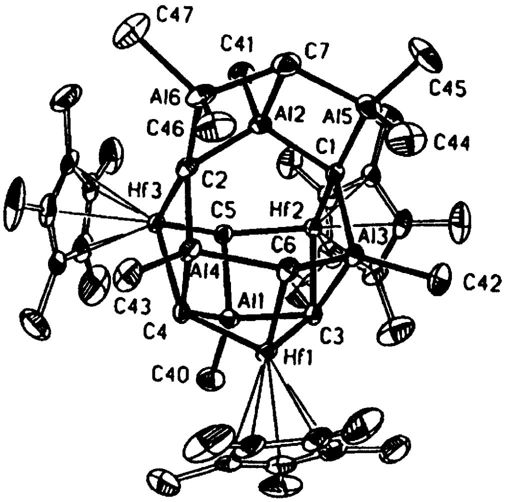

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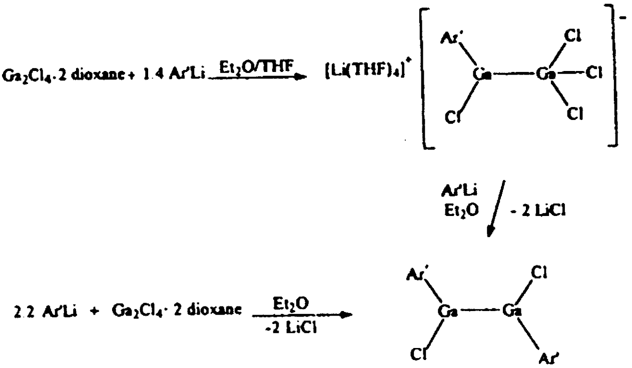
3 Gallium

3.1 General – The first examples of digallium compounds that feature both organo and halo substituents, [Li(thf)$_4$][Ar′(Cl)GaGaCl$_3$] (**56**) and Ar′(Cl)GaGa-(Cl)Ar′ (**57**) (Ar′ = 2,4,6-^{t}Bu$_3$C$_6$H$_2$-) have been prepared by the reaction of

Ga_2Cl_4.2dioxane with LiAr′. The Ga_2Cl_2 skeleton of **57** is planar with a dihedral angle of 180°.[99]



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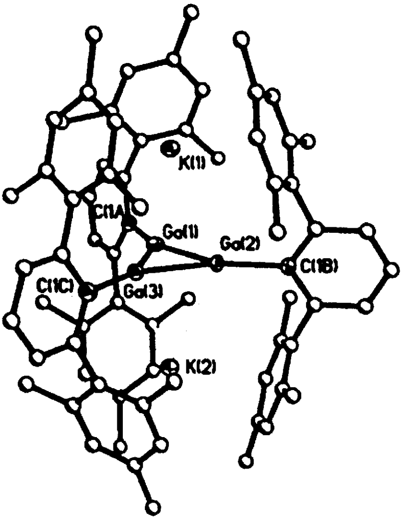
57

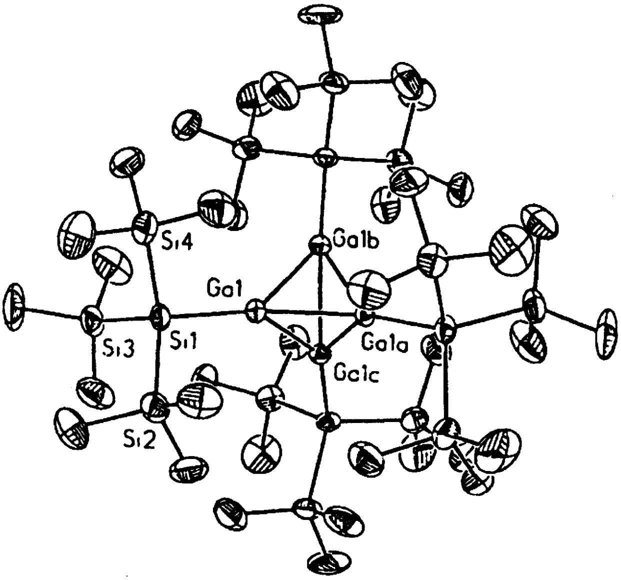
It has been found that $(PhCH_2)_2GaBr$ can be obtained by the redistribution reaction of $GaBr_3$ with $Ga(CH_2Ph)_3$ in a molar ratio 1:2.[100] Treatment of $(PhCH_2)_2GaBr$ or $(PhCH_2)_2GaCl$ with one equivalent of LiN(H)^{t}Bu gives the diorganogallium amide $[(PhCH_2)_2GaN(H)^tBu]_2$. The toluene-insoluble $PhCH_2InCl_2$ has been structurally investigated by dissolving in thf and crystallising as $[PhCH_2InCl_2(thf)_2]$; this compound is a monomer with a trigonal bipyrimidal coordination at the indium centre.[100] Association and exchange reactions of mixtures of Me_3Ga and Et_3Ga in toluene have been investigated by mass spectrometry and ^{1}H NMR spectroscopy.[101] Evidence for the presence of dimers and trimers is presented. It is found that intramolecular exchange processes are fast even at 200 K, whereas intermolecular exchange is significant only above 250 K. The gallium(I) compound $Ga_4[C(SiMe_3)_3]_4$ with a tetrahedral Ga_4 core in the solid state gives on evaporation the monomeric alkylgallium(I) compound $Ga[C(SiMe_3)_3]$ whose structure has been determined by electron diffraction.[102] The Ga-C bond length in the monomer is 206.4(17) pm; a similar value to that found in the solid tetramer and much longer than that considered normal for alkylgallium(III) compounds. The tetramer and its indium analogue may be reversibly reduced as shown by cyclic voltammetry experiments. The monomeric diiodides *s*-MesInI$_2$, *s*-MesInI$_2$, *s*-MesGaI$_2$, *s*-Mes$_2$GaI, Trip$_2$InI and (DBMP)$_2$InI (*s*-Mes = 2,4,6-tri-^{t}Bu-phenyl, Trip = 2,4,6-tri-^{i}Pr-phenyl, DBMP = 2,4-di-^{t}Bu-6-methylphenyl) have been obtained by the reaction of MI_3 (M = Ga or In) with the appropriate lithiated alkyls.[103]

The cyclogallane $K_2[Mes_2C_6H_3)Ga]_3$ (Mes = 2,4,6-trimethylphenyl) (**58**) has been prepared by either of two distinct routes,[104] first disproportionation of Ga_2Cl_4 in the presence of $(Mes_2C_6H_3)Li$ followed by potassium metal reduction in Et_2O, and secondly by alkali metal reduction of $(Mes_2C_6H_3)GaCl_2$. The cyclogallane is characterised by extremely short Ga-Ga bonds: 2.4260(5), 2.4317(5) and 2.4187(5) Å. Theoretical studies back up the experimental results that the cyclogallane dianion $[(Mes_2C_6H_3)Ga]_3^{2-}$ is a well-defined metalloaro-



58

matic system – a metallic ring system exhibiting aromatic behaviour. The tetramer $\{GaSi(SiMe_3)\}_4$ (**59**) is obtained by reaction of Ga_2Cl_4.2dioxane with $LiSi(SiMe_3)_3$.3thf. The tetramer shows a Ga_4 core with a very nearly regular tetrahedral arrangement and average Ga-Ga distances of 2.584 Å – much longer than the Ga-Ga distances in **58**.



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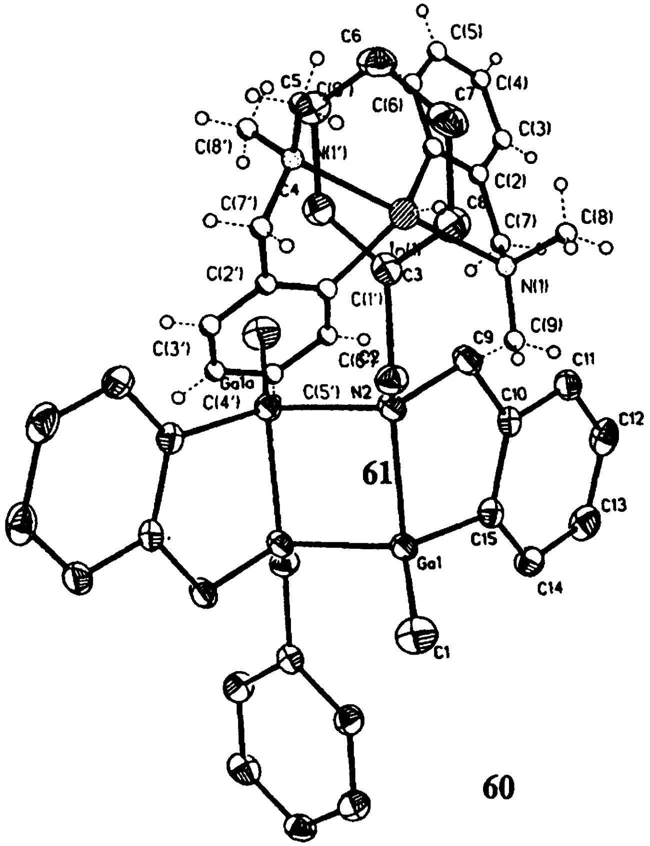
The caesium triorganofluorometallates $[Cs\{R_3MF\}]_4$ (R = Me, Et or ^iPr; M = Ga or In) have been prepared by the reaction of the appropriate R_3M compound with CsF in acetonitrile.[106] The two isopropyl derivatives show strongly distorted cubes with alternating Cs and F atoms and may be described as $(CsF)_4$ subunits of the CsF structure stabilised by $M(^iPr)_3$ groups. Some gallium siloxane cages have been synthesised as model substances for gallium-containing silicates.[107]

3.2 Compounds Containing a Group 15 Element – The adduct $[GaMe_3(C_{13}H_9N)].0.5C_{13}H_9N$ ($C_{13}H_9N$ = acridine) with a Ga-N bond length of 2.203(3) Å is formed by reaction of $GaMe_3$ with acridine in Et_2O.[108] The first benzannelated diazabutadiene complex of gallium, $C_6H_4(NSiMe_3)_2GaR$ (R = 2-(dimethylaminomethyl)phenyl) has been prepared by treatment of $C_6H_4(N(Li)SiMe_3)_2$ with $RGaCl_2$.[109]

The reaction of $MMes_3$ (Mes = 2,4,6-$Me_3C_6H_2$) with CsF in acetonitrile yields the trimesitylfluorometallates $[\{Cs(MeCN)_2\}\{Mes_3MF\}]_2.2MeCN$. $Ga(CH_2Ph)_3$ gives with CsF under the same conditions the salt $[Cs\{PhCH_2)_3GaF\}]_2.2MeCN$. These compounds all show four-membered Cs_2F_2 rings. Other related compounds are reported.[110] The alkyltrimethyltin elimination reactions of $R''R'NSnMe_3$ (R″ = ^iBu, $SnMe_3$, C_6H_{11}; R′ = ^iBu, ^iPr or C_6H_{11}) with R_3Ga (R = Me or Et) have been investigated.[111] The products are aminogallanes of the type $[R_2GaNR''_2]_2$. The compounds which have been structurally characterised by single crystal X-ray diffraction show non-planar Ga_2N_2 rings. NMR studies show that the dimeric structure persists in solution. Elimination of cyclopentadiene from $Et_2Ga(C_5H_5)$ with amines, phosphines or thiols gives wide range of diethylgallium amides, -phosphides or -thiolates.[112] Of these two crystalline compounds – $[Et_2GaP(^tBu)_2]_2$ and $[Et_2GaS(SiPh_3)]_2$ – have been characterised by X-ray structural studies.

The thermolysis reaction of Me_3Ga with $HN(CH_2Ph)_2$ in toluene appears (on the basis of multinuclear NMR spectroscopic evidence) to proceed *via* $[Me_2GaN(CH_2Ph)_2]_2$ to give the orthometallated gallium dimer **60** by a series of 1,2-eliminations of CH_4.[113] This is the first reported example of orthometallation of an aromatic ring carbon by gallium. Several new gallium compounds containing the [2-(*N,N*-dimethylamino)ethyl]cyclopentadienyl ligand (Cp^N) have been prepared. The reactions are carried out by adding GaX_3 (X = Cl, Br or I) to Cp^NK.[114] The reaction of $MeGaCl_2$ with one equivalent of $K[H_2B(3,5\text{-}Me_2pz)_2]$ (pz = pyrazoyl) gives $[H_2B(3,5\text{-}Me_2pz)_2GaMeCl$ which shows distorted tetrahedral geometry about the Ga centre.[115] Other related reactions involving Ga and In are described. The amidinato compounds $[GaMe_2L]$ (L = RNCR′NR (R, R′ = alkyl or aryl), $[GaMe(PhNCPhNPh)_2]$, $[GaEt(PhNCMeNPh)_2]$ and $[Ga(PhNCRNPh)_3]$ (R = Me or Ph) have been isolated from the reaction of the appropriate gallium trialkyl with 1, 2 and 3 mole equivalents of the amidine RNCR′N(H)R, respectively.[116] X-ray crystallographic studies on $[GaMe_2(PhNCPhNPh)]$ and $[GaMe(PhNCPhNPh)_2]$ reveal monomeric structures and the presence of chelating amidinate ligands with distorted tetrahedral and trigonal bipyramidal coordination respectively at the gallium centres. A range of organo-gallium and -indium halides with intramolecularly coordinating ligands



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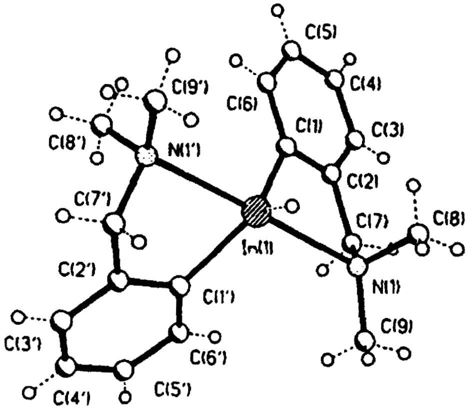
60

have been prepared.[117] Among the compounds reported in this work is the first neutral indium hydride (**61**) X_2InH where X is the ligand 2-(dimethylaminomethyl)phenyl-.

A number of primary amido gallium alkyl complexes have been reported.[118] These include: (i) the base free dimer $[^tBu_2Ga(\mu\text{-}N(H)^tBu)]_2$ which has a planar Ga_2N_2 core with the Ga and N centres in distorted tetrahedral environments (the Ga-C distances are 2.052(3) and 2.065(3) Å and the Ga-N distances are 2.060(3) and 2.069(3) Å) and (ii) the anionic complex $^nBu_2Ga[NH(2,6\text{-}Me_2\text{-}C_6H_3)]_2[Li(Et_2O)]$ which has a pseudotetrahedral gallium centre as part of a Ga-N-Li-N- distorted square core. Monomeric gallium and indium compounds $ArGaN(SiMe_3)_2Cl$, $ArIn\{N(SiMe_3)_2\}_2$, $ArGa\{P(H)Ar\}_2$, $ArIn\{P(H)Ar\}_2$ and $ArGa(SAr)_2$ [Ar = 2,4,6-$^tBu_3C_6H_2$] have been synthesised by the reaction of $ArMCl_2$ [M = Ga or In] with the corresponding lithium amide, phosphide or thiolate compound. The first three of these complexes have been studied by single crystal X-ray diffraction and it is found that the metal centre adopts a trigonal geometry with metal-group 15 atom distances of: Ga-N, 1.867(10) Å; In-N,



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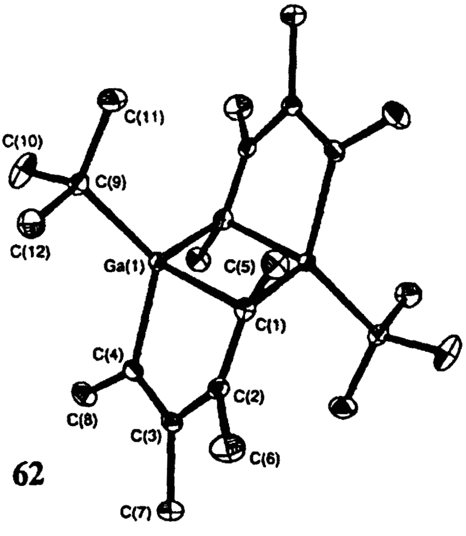
2.099(av) Å; Ga-P, 2.388(av) Å.[119] The gallole (gallacyclopentadiene) (**62**) has been found to dimerise but in a very different fashion to the corresponding borole.[120] Whereas the borole dimerises in the classical Diels-Alder manner, **62** dimerises by means of Ga-C bond formation to give **63**.[120]

[{$(Me_3Si)_2HC$}$_2$Ga-Ga{$CH(Me_3Si)_2$}$_2$] reacts with *tert*-butyl or aryl (aryl = phenyl, *o*-methylphenyl, *o*-methoxyphenyl or *p*-methoxyphenyl) by a two-fold insertion of the central carbon atoms into the Ga-Ga bond with the formation of Ga-C single bonds.[121] 1,4-Diazabutadiene derivatives are formed which, in contrast to the corresponding aluminium compounds, show only weak interac-



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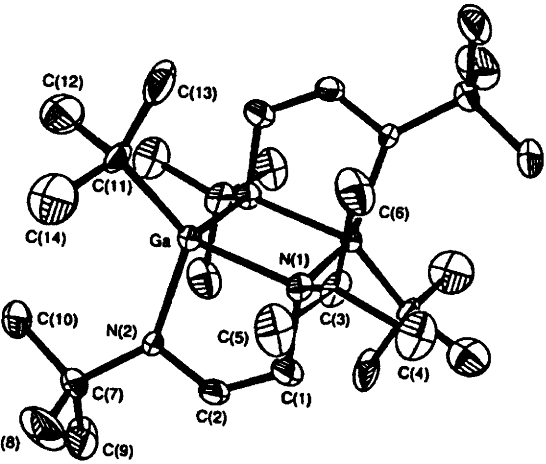
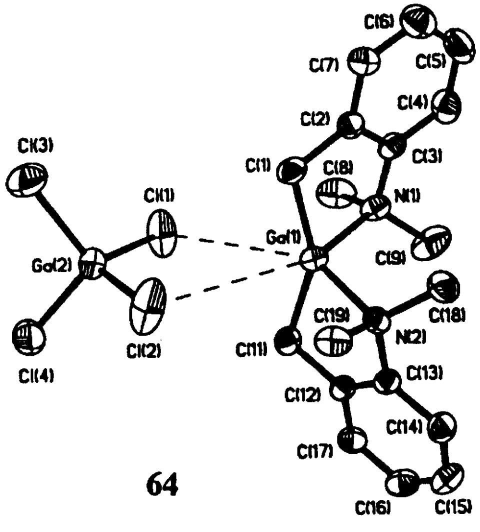


63

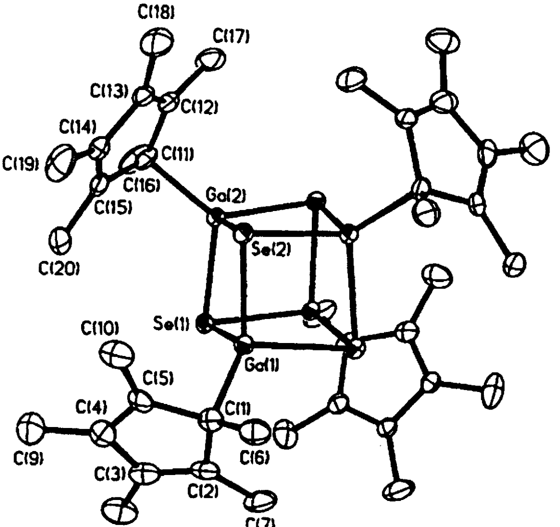
tions between the imine nitrogens and the coordinatively unsaturated gallium atoms. Some ring systems containing cationic gallium centres have been prepared.[122] These include the salt $[Bz^N{}_2Ga][GaCl_4]$ (64) (Bz^N = 2-(dimethylamino)-benzyl) formed by the Reaction of Bz^NLi with $GaCl_3$. The ionic complex $[(DAB)GaCl_2][GaCl_4]$ (DAB = 1,4-di-*tert*-butyl-1,4-diazabutadiene) has been prepared by the reaction of DAB with two equivalents of $GaCl_3$. Organogallium azides of the type $(N_3)_2Ga[(CH_2)_3NMe_2]$ have been synthesised by metathesis of the corresponding gallium chloro compound with sodium azide. The Ga-N_3 bonds readily undergo ammonolysis, so these compounds are considered as



64

possible precursors to the formation of GaN layers by MOCVD with ammonia as a reactive carrier gas.[123] An unusual phosphonate-bridged dimer $[{}^t\mathrm{Bu_2Ga}\{\mu\text{-}\mathrm{O_2P(Ph)OGa}{}^t\mathrm{Bu_2}\}]_2$ is generated by reaction of $\mathrm{Ga}{}^t\mathrm{Bu_3}$ with phenylphosphonic acid.[124] The molecular structure of this compound consists of two four- and two three-cooordinate gallium centres. The compound bis[(μ-2,6-diphenylphenoxido-*O:O*)diethylgallium] consisting of discrete dimeric molecules containing an essentially planar four-membered Ga-O-Ga-O ring has been prepared.[125]

3.3 Compounds Containing a Group 16 Element – $[\{\mathrm{(Me_3Si)_2HC}\}_2\mathrm{Ga\text{-}Ga}\{\mathrm{CH(\text{-}Me_3Si)_2}\}_2]$ reacts with two equivalents of the carboxylic acids RCOOH (R = $\mathrm{-C_6H_5}$, $\text{-}p\text{-}\mathrm{BrC_6H_4}$, $\text{-3,5-}\mathrm{Me_2C_6H_3}$, $\mathrm{CMe_3}$) to yield almost quantitatively colourless products where two bis(trimethylsilyl)methyl groups are replaced by two carboxylato ligands; the two carboxylato ligands bridge the Ga-Ga bond in a chelating manner.[126] Mixed alkylgallium and -indium compounds of general formula $\mathrm{(R_2MS_2CNMe)(CH_2)_3NMe_2}$ (R = Me, Et, Np, $\mathrm{C_5H_{11}}$; M = Ga or In) have been prepared and suggested as single source precursors for III/VI materials.[127] It is also the search for precursors to the $\mathrm{Ga_2E_3}$ (E = S or Se) compounds which has prompted recent research into gallium chalcogenide cubanes of general formula $[\mathrm{Cp^*Ga}(\mu_3\text{-E})]_4$.[128] The structure of one such compound is given (**65**). These compounds decompose to give amorphous layers of $\mathrm{Ga_2E_3}$ at 290 – 310 °C, which recrystallise to the cubic form upon thermal annealing at 500 °C. The synthesis of a range of gallium and indium compounds of sulfur donor ligands by reaction of $\mathrm{MR_3}$ (M = Ga or In; R = ^{t}Bu or Me) with 2-mercaptopyridine (HSpy) or $\mathrm{Ph_2P(S)SH}$. Compounds of the type $\mathrm{GaR_2(Spy)}$,



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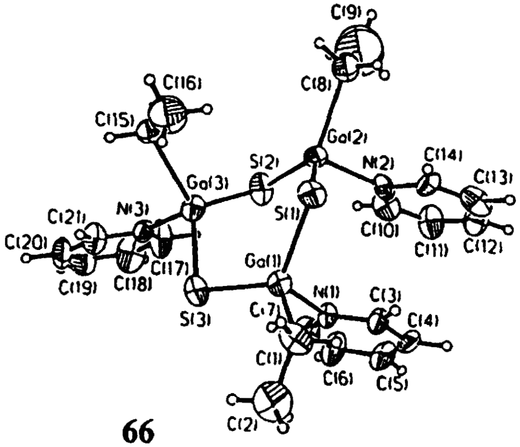
GaR(Spy)$_2$ and Ga(Spy)$_3$ are formed.[129] The reaction of Et$_3$Ga with elemental sulphur in toluene or benzene results in the insertion of sulfur into the Ga-C bonds to give the compounds Ga[(S-S)Et$_3$]$_3$ and Ga[(S-S-S)Et$_3$]$_3$.[130] Me$_3$Ga reacts similarly to give Ga[(S-S)Me$_3$]$_3$. All of these compounds react with pyridine at -30 °C to give deinsertion of the S atoms from the Ga-S-S-C bonds and formation of compounds such as **66** with six-membered Ga-S rings.



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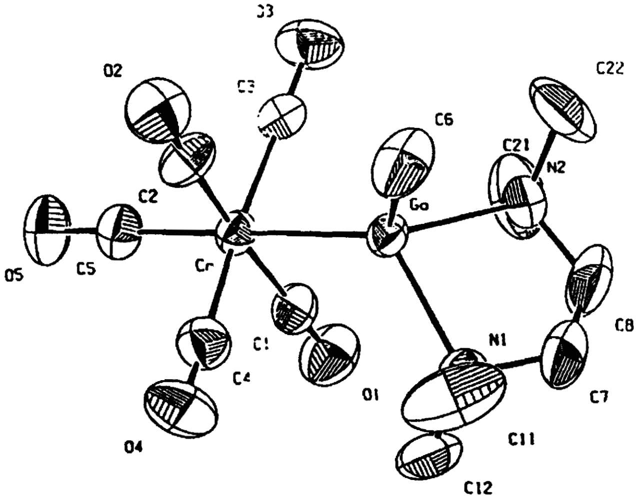
3.4 Compounds Containing a Metal Other than Gallium – The synthesis and molecular structure of Cr(CO)$_5$[PPh$_2$CH$_2$Ga(CH$_2$CMe$_3$)$_2$.NMe$_3$] is reported.[131] The synthesis of other related gallium and aluminium compounds is also noted here. The structure of the complex [(Cr(CO)$_5$Cr-Ga(CH$_3$)(tmeda)] has been determined (**67**). This compound is of interest because the Ga atom is in the



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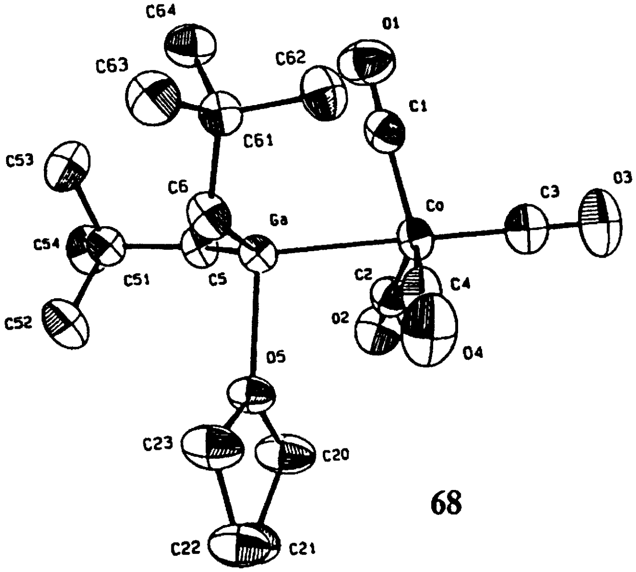
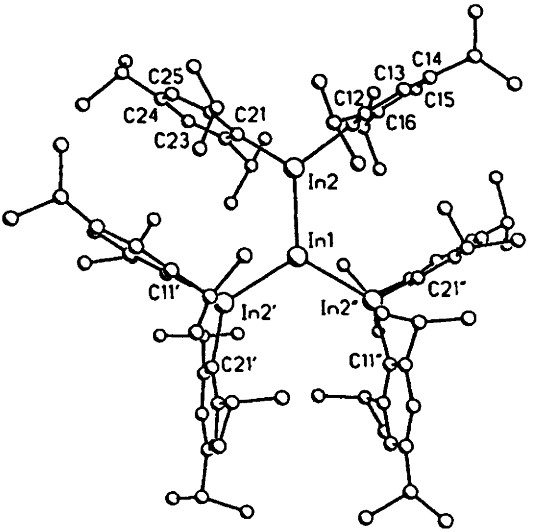
formal +I oxidation state but is stabilised by the transition metal moiety. The complex **68** contains a direct Ga-Co bond.[133] This complex and other related species have been tested for use as precursors to thin films of β-CoGa in a horizontal MOCVD reactor *in vacuo*.



68

4 Indium

A mass spectrometric and NMR spectroscopic study has shown that the compounds Me_2InEt and $MeInEt_2$ exist as single compounds.[134] The structure of the unusual adduct $[(InMe_3)diphos(Me_2InEt)][(InMe_3)diphos(InMe_3)]$ is reported.[134] The aim of this work is to find an indium source for MOCVD other than the rather involatile $InMe_3$. A study of the dihalo indium compounds of general formula X_2InCHX_2 (X = Cl, Br or I) and of their coordination chemistry has been made.[135] The synthesis of some supermesityl ($Mes^* = 2,4,6\text{-}{}^tBu_3C_6H_2$) derivatives of indium(III) is reported.[136] Crystal structures are given for $Mes^*(Br)In[CH_2C(CH_3)_2C_6H_3{}^tBu_2]$ and $Mes^*In(SePh)_2$. This last compound is made by the reaction of $In(SePh)_2I$ with Mes^*MgBr and is found to be monomeric. An interesting trigonal In_4 cluster with very short In-In bonds (2.696(2) Å) is seen in **69**.[137] The reaction between Me_3In and tetraborane(10) at room temperature gives the volatile viscous liquid dimethylindium octahydrotriborate (**70**). This is the first example of a *volatile* indium hydride. **70** depicts the crystal structure which implies a rather ionic formulation $[Me_2In]^+[B_3H_8]^-$ with the coordination at the In centre being augmented *via* secondary intermolecular interactions with terminal hydrogen atoms. Spectroscopic studies of the vapour indicate a molecular structure akin to that of $Me_2AlB_3H_8$.



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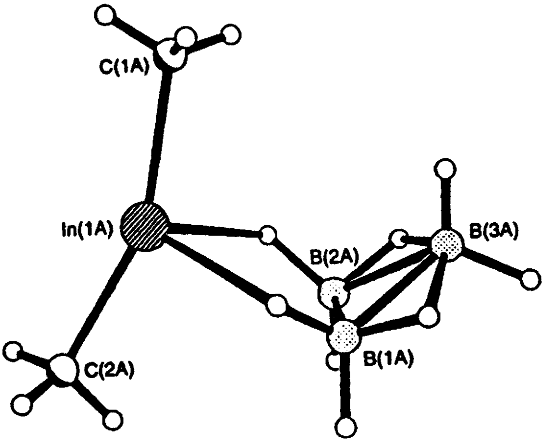

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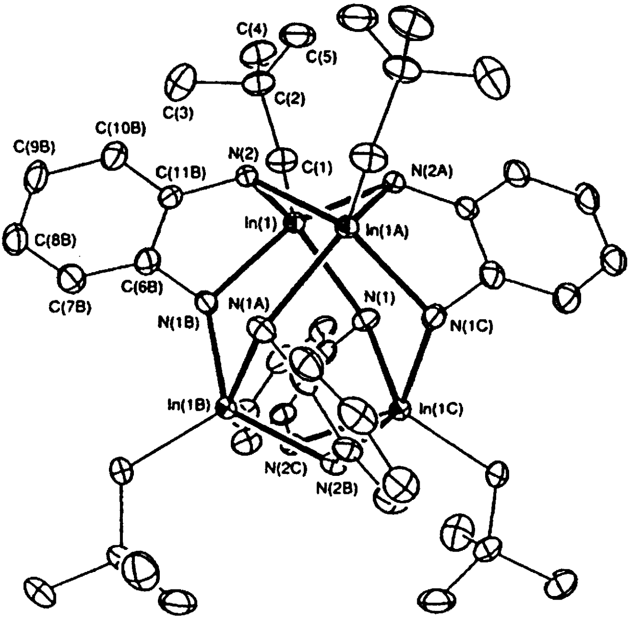
The use of allylindium reagents in reactions with aldehydes is reported.[139] A halide free route to group 12 and 13 organometallic complexes by nucleophilic subsititution of the bis(trimethylsilyl)amido groups in [In{N(SiMe$_3$)$_2$}$_3$] is discussed.[140] The reaction of $C_6H_4(NH_2)_2$-1,2 with Np$_3$In affords the tetrameric compound **71** which contains five-coordinate indium centres having square pyramidal geometry and an overall approximately tetrahedral symmetry.[141] The heterocubane [MesInPMes]$_4$ (**72**) has been prepared by treatment of MesInCl$_2$


C(4)
C(5)
C(3)
C(2)
C(10B)
C(9B)
N(2)
C(1)
N(2A)
C(11B)
In(1)
In(1A)
C(8B)
C(6B)
C(7B)
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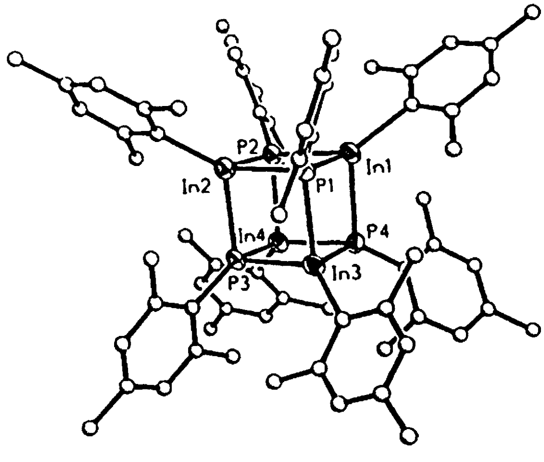
71


P2
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In3

72

with $MesPLi_2$ in Et_2O.[142] Cryoscopic molecular weight determinations suggest that **72** retains its tetrameric form in solution, in contrast to the compounds $^iPr_2InPPh_2$ and $(PhCH_2)_2InPPh_2$ which exist as a monomer-dimer equilibrium mixture.[142] An organoindium phosphide which incorporates two phosphido moieties in the same molecule, $(Me_3CCH_2)_2InP(^tBu)_2In(CH_2CMe_3)_2PPh_2$ has been synthesised from $[(Me_3CCH_2)_2InP(^tBu)_2]_2$ and $(Me_3CCH_2)_2InPPh_2$ in pentane solution. The compound exists as a single compound in the solid state but is in equilibrium with the starting materials in solution.[143] An X-ray crystal structure determination of $[InMe_3(C_{19}H_{15}OP)]$ (5-benzyldibenzo[*b,d*]phosphole-5-oxide)trimethylindium has been made. The In atom has a four-coordinate distorted tetrahedral environment with an In-O bond length of 2.261(3) Å.[144] Compounds of the type $In(C_5H_5)_{3-n}X_n$ (X = Cl or I) have been synthesised by reaction of $InCl_3$ or InI_3 with $Tl(C_5H_5)$.[145]

$[\{(Me_3Si)_2HC\}_2In\text{-}In\{CH(Me_3Si)_2\}_2]$ reacts with the chalcogen-donor molecules propylene sulfide and trimethylphosphine selenide or -telluride by insertion of chalcogen atoms into the In-In bond.[146] The products are the monomeric compounds $R_2In\text{-}E\text{-}InR_2$ (R = $(Me_3Si)_2CH$-, E = S, Se or Te). The reaction of indium(I) bromide with *ortho*-phenylenemercury and 1,2-bis(bromomercurio)-benzene leads to the isolation of the polyfunctional Lewis acid-Lewis base adducts $(o\text{-}C_6H_4(InBr(thf)_2))_2$ and $Hg(o\text{-}C_6H_4(InBr_2(thf)_2))_2$ respectively.[147]

5 Thallium

Reaction of $TlPh_2X$ with Ms_2PPh_2 gives $[TlPh_2(S_2PPh_2)]$ (X = OH, M = NH_4) and $[Et_4N][TlPh_2(S_2PPh_2)_2]$ (X = Br, M = Et_4N).[148] The synthesis of some organothallium(III) derivatives is reported.[149] These compounds have been synthesised largely as a comparison with the corresponding organomercury(II) derivatives. The compound bis(1,2,4-trimethylbenzene)thallium(I)tetrachloroaluminate(III) has been prepared from 1,2,4-trimethylbenzene, thallium(I) chloride and aluminium trichloride.[150] The synthesis and structure of $[Tl(C_6F_5)_2Cl\{Au(C_6F_5)_3(PPh_2CH_2PPh_2(O))\}_2]$ is reported.[151]

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6

Group 14: Silicon, Germanium, Tin and Lead

BY D.A. ARMITAGE

1 Introduction

A volume of Advances in Organometallic Chemistry devoted to double bonds to the p-block elements concentrates primarily on those of the Group 14 elements, with consideration of the chemistry of silenes,[1a] iminosilanes and related compounds – synthesis and reactions,[1b] silicon – phosphorus and silicon – arsenic multiple bonds,[1c] the chemistry of stable disilenes,[1d] and stable doubly bonded compounds of germanium and tin.[1e] In the field of polymerisation, reviews cover poly(silylenemethylenes) – a novel class of organosilicon polymers,[2a] silyl substitution as an aid to polymerisation reactions: oxidative coupling of silylthiophene,[2b] a route to highly conjugated polythiophene, and the ring-opening polymerisation of nitrogen-containing cyclic organosilicon monomers.[2c] Silicon substituted strained carbocyclic systems are reviewed along with silyl hydrazines, their lithium derivatives, isomerism and rings.[3] Also covered are hetero- and metallosiloxanes derived from silane diols, disilanols, silane triols, and trisilanols, and the deprotection of silyl ethers.[4] A comparison is made of phosphorus and silicon: hypervalency, stereochemistry, and reactivity,[5] while silyl triflates are assessed as valuable synthetic materials in organosilicon chemistry.[6] Silicon - hydrogen bond activation by transition metal complexes is surveyed,[7] and the substituent effects as probes of the structure and bonding in mononuclear metallocenes includes a section on Group 14 metals (silicon – lead).[8] A volume of the S. Patai series covers the chemistry of organogermanium, tin and lead compounds,[9] while organotin intermediates are used in the synthesis of radio-pharmaceuticals and chiral allylic and allenic stannanes used as reagents for asymmetric synthesis.[10] Organic Syntheses includes those of (4R)-(+)-t-butyl-dimethylsiloxy-2-cyclopenten-1-one and the (4S)-(−) isomer, stereoselective alkene synthesis via 1-chloro-1-(dimethylphenylsilyl)alkanes, and α-(dimethyl-phenylsilyl)-ketones.[11] This review includes about 1080 references.

2 The Carbon-Metalloid Bond

$t\text{-}Bu_2SiF\text{-}CLi(SiMe_3)_2$ loses LiF to generate $Me_2Si{=}C(SiMeBu\text{-}t_2)(SiMe_3)$ which as its THF adduct adds to benzophenone at -78°C to give both the colourless [2+2] and yellow [4+2]cycloadducts. The latter transforms into the former on warming, this slowly giving the [4+2]cycloadduct of t-$Bu_2Si=C(SiMe_3)_2$ (1). With Me_3SiN_3, (1) gives the unstable [3+2]cycloadduct which isomerises and then decomposes to a series of silyl substituted diazomethane derivatives.[12] $Mes_2Si=CHCH_2$Bu-t can be similarly generated, and adds to acetophenone, benzaldehyde and t-BuN=C:, while Me_3SiN_3 gives the [3+2]cycloadduct which with excess Me_3SiN_3 gives the tetrazole and t-$BuCH_2CHN_2$.[13]

Ene reactions of $Me_2Si=C(SiMe_3)_2$ with alkenes and dienes take place regio and stereoselectively, with acceleration through electron donating substituents and retardation through bulkiness.[14] $Ph_2Si=CH_2$, generated from the silacyclobutane, adds to water, alcohols, and acetic acid through a 2 step mechanism involving an initial reversible complex formation, followed by intracomplex proton transfer. Negative Arrhenius activation energies and entropies of activation are observed for MeOH and t-BuOH.[15]

The adduct formed from $(Me_3Si)_3SiMgBr$ and TipCHO loses $Me_3SiOMgBr$ to give the silene which dimerises to give the 1,2-disilacyclobutane and adds Me_3SiOLi, hydrolysis and silylation yielding $(Me_3Si)_2(Me_3SiO)SiCH_2Tip$ and $(Me_3Si)_2(Me_3SiO)SiCH(SiMe_3)Tip$.[16]

Pyrolysing 4-spiro[3,3]heptane generates 2-silaallene which readily adds alcohols to give $(RO)_2SiMe_2$, or decomposes to a polymer of SiC_2 stoichiometry,[17] while the enols RR'C=CH-CH[$Si(SiMe_3)_3$]OH (R=R'=Me; R=H,R'=Ph) result from $(Me_3Si)_3SiLi$ and 3,3-dimethylacrolein and (E)-cinnamaldehyde and generate the 1-silabutadienes RR'C=CH-CH=$Si(SiMe_3)_2$ transiently on lithiation and loss of Me_3SiOLi. They dimerise head to head to give the 1,2-disilacyclobutane and give polymer as well, while $(Me_3Si)_3SiMgBr$ and 2,5-diisopropylbenzaldehyde give the silylmethanol derivative that gives silene intermediates with PhLi or NaH.[18] Ene reactions of $Me_2Ge=C(SiMe_3)_2$ also take place both regio and stereospecifically, with acceleration for electron donating groups on the alkene or diene, and retardation for bulky substituents.[19]

Thermolysis of t-$Bu_2SiF=CLi(GeMe_3)_2.2THF$, which has distorted tetrahedral geometry at Si and C with THF donating to Li, gives the silene, which isomerises to the germene $Me_2Ge=C(GeMe_3)(SiMeBu\text{-}t_2)$ since ene adducts result for this and not the silene t-$Bu_2Si=C(GeMe_3)_2$.[20] Cp^*X_2Ge(fluorenyl) (X=Cl, F) can be lithiated with t-BuLi, subsequent silylation and loss of Me_3SiF yielding the germene $Cp^*(X)Ge=CR_2$ (CR_2 =fluorenylidene).[21] The first germaphosphaallene results from $Mes_2(F)Ge\text{-}C(Br)=PAr$, adds MeOH and MeLi to the Ge=C bond, and dimerises through head to tail Ge=C dimerisation and Ge=C/P=C dimerisation.[22]

Calculations determine the relative stability of trisilabenzene isomers, while four energetically low lying states for SiC_2 indicated the $C_{\infty v}$ and C_{2v} cyclic structures to be the most stable and the most stable isomers determined for the cation $Si_2CH_4^+$.[23]

NMR studies of an extensive range of solvated complexes of the silylium cation indicate that tetracoordinated monosolvates occur for R_3Si^+ and $R_2HSi,^+$ while pentacoordination disolvates result for $R_{3\text{-}n}H_nSi^+$ (n=1,2,3). Binding energies are in the range 170–250 kJ mol^{-1}.[24] The degree of silylium character increases with the weakly coordinating hexahalocarborane anions $X_6CB_{11}H_6^-$

(X=Cl, Br, I), i-Pr_3SiY indicating CSiC angles of 117.3°, 117°, and 115.6° for X = Cl, Br, and I respectively, with ^{29}Si downfield shifts indicating the chloro derivative least coordinating. This is therefore suggested as the most silylium-like condensed phase derivative characterised to date with some 50% silylium character.[25] However, ^{29}Si NMR studies suggest that the high electrophilicity of trivalent silicon in R_3Si^+ results in interactions with arenes, $Br_6CB_{11}H_5^-$, H_2O, and MeCN, resulting in little silicenium nature to the derivative.[26] Similar studies with tin show no free trigonal stannyl cations in solution but a greater predominance of the 5-coordinate rather than 4-coordinate solvates.[27]

Calculations support the stabilisation of silylium cations with aryl substituents carrying pendular aminoalkyl groups, the donating ability determining whether, with two such groups, the 4- or 5-coordinate cation results.[28] With methyl substituted anthryl substitutents, stabilisation results through agostic C-H interactions.[29] With $(Me_3Si)_3Si,^+$ calculations for the gas phase suggest $\delta(^{29}Si)$ for the central atom to be 920 ppm relative to TMS and results from large paramagnetic contributions. In benzene a Wheland σ-complex is produced with $\delta(^{29}Si)$ of 111 ppm, a Si-C bond of 229.3 pm and coordination energy of 56 kJ mol^{-1}.[30]

Heating $Cp_2W(SiMe_3)GeMe_2OTf$ in benzene or in the absence of solvent gives the dinuclear derivative containing what is thought to be the germyl cation with two W-Ge bond lengths of 248.7 and 258.3 pm respectively, and planarity at germanium.[31]

Tris(trimethylsilyl)cyclopropenylium cation results from the cyclopropene-3-carboxylic acid as the hexachloroantimonate. The structure shows distortion from the idealised D_{3h} symmetry due to close interionic C···Cl contacts, and has C-C bonds of 138 pm and ring Si-C bonds of 189.7 pm, a little longer than those of the Me_3Si groups.[32] Calculations suggest α-silylcarbenium ions rearrange to the silicenium ion while $Et_3Si(C_6H_6)^+B(C_6F_5)_4^-$ gives the stable β-silyl carbocation with $Ph_2C{=}CH_2$,[33] $\delta(^{29}Si)$ at 46.2 ppm, and the dihedral relationship between Me_3Si and the leaving group in 1-(Me_3Si)-bicyclo[2.2.2]octan-2-ol and its sulfonate approach orthogonality, suggesting a β-effect only from induction and is negligible.[34] A mass spectroscopic study of the addition of alkynes to Me_3Si^+ suggests β-stabilisation of the vinyl cation of some 240 kJ mol,$^{-1}$ while rates of protonation of vinylsilanes indicate marked Me_3Si acceleration, and β-Me_3Si destabilises in electrochemical silicon-directed aldol condensation.[35] Lithiation of 3,3-Me_2-1-Me silacyclopropene gives the cyclopropenyl-lithium derivative as a TMEDA coordination dimer showing considerable distortion of the ring geometry due to rehydridisation at lithiated carbon.[36]

A range of bis(chlorosilyl)methanes are used as comonomers in the pyrolytic synthesis of polysilacarbosilanes and subsequently silicon carbide, which also results as hard coatings from the plasma enhanced chemical vapour deposition using $Si(SiMe_3)_4$ as precursor, while Ru catalyses step growth copolymerisation of 3′,4′-methylene dioxyacetophenone with $(ViMe_2Si)_2X$ (X=O or C_2H_4).[37] Gas phase pyrolysis of methylsilanes, methylchlorosilanes, and polymeric $(Me_2SiCH_2)_n$ gives polycarbosilanes and ultimately β-SiC.[38] A series of carbon cross-linked poly(phenylcarbosilanes) result through Wurtz reductive coupling.[39] A new route to SiC-$MoSi_2$ ceramic compensates involves reacting Si with molybdenum carbide.[40] In the presence of either ammonia or phosphine, various SiCNH and SiCPH cations result along with SiN and SiP cations.[41]

Decamethylsilicocene $(Me_5C_5)_2Si$: adds to a range of aldehydes and ketones to give Si-O substituted heterocycles while t-Bu_2Si: with alkenes give siliranes which insert isonitriles or ring open on heating to give bis(vinylsilyl)alkenes.[42] π-Electron resonance is less extensive in the silicon and germanium analogues of imidazol-2-ylidene than in the parent carbon compound but is significant,[43] while $[(Me_3Si)_2CH]_2Ge$: adds to dichloroethenes to give vinylchlorogermanes, trans-1,2-dichloroethene giving double insertion.[44]

Calculations support the gauche conformation in the gas phase of silylmethyl-cyclo-propane due to σ-π hyperconjugation while substituted derivatives undergo mercuri-desilylation to give olefins in good yield with regioselectivity.[45] RCOCl ring expands 1-[(2-$MeOCH_2CH_2O)CH_2O$]-2-($PhSO_2$)-2-(Bu_3Sn)cyclopropane to give acylfurans. PE spectra of Me_3M substituted 3,3-dimethylcyclopropenes show changes in the lowest energy ionisations consistent with inductive and hyperconjugative interactions.[46] (Ph_3Si)ethylene oxide is ring opened by EtMgBr to give the β-hydroxysilane formed through rearrangement, while 1,2-diols result from α,β-epoxysilanes. 2-Methoxytetrahydropyrans result from ε-hydroxy-α,β-epoxysilanes,[47] optically active α,β-epoxysilanes give silylaminoalcohols, and, remarkably, 2,2-$(Me_3Si)_2$-epoxide with LDA gives the silanol $R'CH{=}C(SiMe_3)CH_2SiMe_2OH$.[48]

Silyl substituted cyclobutadiene units coupled through octatetrayne result through Hay coupling and oligomers result similarly from [1,3-diethynyl-2,4-(Me_3Si)cyclobuta-diene]Co(I)Cp and show an increase in the intensity of the UV absorptions between 312 and 348 nm, while that at 435 nm is independent of oligomer length.[49]

Bridgehead Me_3M groups enhance the rates of solvolysis of bicyclo[2.2.1]hept-1-yl triflates, while 3-Me_3Si-cyclopent-1-ene undergoes 1,3-dipolar cycloaddition to chiral spiro nitrones to provide the first enantiomerically pure synthesis of (2S,1'S)-(cyclopent-2-enyl)glycine.[50]

Electrochemical trimethylsilylation of mono and polyhalothiophenes gives a range of silylated derivatives along with silylated 1,2-butadienes and 2-butynes through ring opening.[51] Iodine readily desilylates them, providing precursors for coupling to give polyynes using $Pd/Bu_3SnC{\equiv}CSnBu_3$.[52] A stereochemical study of the protiodesilylation of 3-Me_3Si-2-thiabicyclo[2.2.1]hept-5-enes with fluoride shows the presence of a common carbanionic intermediate.[53]

Birch reduction of 2-silylfuroic acid gives α-alkoxyl silanes, while furans with allenyl ether side chains undergo Me_3Si-1,2-rearrangement to give benzofurans.[54] Stannylfuranones undergo Stille coupling with ArI, γ-butyrolactones result from ozone on 2-R_3Sn-tetrahydro-furans and 3-acetoxymethyl-2-Bu_3SnCH_2-furan gives the o-quinodimethane which adds dienophiles.[55]

Coupling 2,5-dihalo-1-silacyclopentadienes with 1-Me-2-Bu_3Sn-pyrrole provides a route to co-oligomers which show long UV-vis absorption maxima despite twisted structures, β-stannylpyrroles readily couple with aryl halides using Pd catalysts, while, remarkably, the reaction of deprotonated $TosCH_2N{=}C$: with Me_3SnCl and chalcone (E-PhCH=CHCOPh) gives the crystalline N-t-butyloxycarbonyl derivative of 3-benzoyl-4-phenyl-2-(trimethylstannyl)pyrrole and not the expected 4-benzoyl-3-phenyl derivative where only coordination to tin from the t-butoxycarbonyl group could occur. Benzoyl coordination also occurs.[56]

$Me_3SiCN_2^-$ reacts with P_4 to give the diazadiphosphole ring through [2+3]cycloaddition of $P\equiv P$, and 1-lithio-3,4-dimethylphospholene couples with Me_3MCl (M=Si, Ge, Sn), while $(Me_3Si)_2CH$ substituted 1,2,4-triphosphole complexes with the cotRu residue with a novel ring to ring proton migration.[57]

Me_3Si controls the stereochemistry of the cyclohexenone formed from o-substituted anisole tricarbonyl chromium complexes while 2-(Me_3Si)styryl $Cr(CO)_3$ complexes give cyclopropyl derivatives, and silicon directs ipso substitution of polymer bound arylsilanes in the preparation of biaryls.[58] 2-silylbenzamides can be converted into 2-fluorosilyl acetophenones, $[2\text{-}Me_3SiC_6H_4]IPh^+$ with thiobenzophenones gives isomeric 2-aryldibenzo-thiopyran derivatives through benzyne addition to the thioketone, while 4,6-disubstituted thianthrenes result from the 4,6-bis(trimethylsilyl) derivatives after bromination.[59] Acyl cations cleanly cleave aryl(styryl)silanes with styryl ketone formation preferred unless the aryl group is heavily methylated.[60]

9,10-Disilylanthracenes result from the dibromo derivative and all show intense fluorescence.[61] 9,10-Bis(diisopropyl)anthracene has a bent structure due to hydrogen repulsions and reduction with lithium gives the radical anion as blue needles from the red THF solution. Structure determinations on the anthracene and its radical anion show little change in bond lengths but they change from inversion to mirror symmetry and the twisting of the i-Pr_2SiH groups out of the anthracene plane in the radical anion destroys the Si-H$\cdots$H-C (peri-ring H) contact (205.3 pm) of the parent compound.[62]

Hydroxysilyl-2.5-cyclohexadiene can be converted to tetrahydroxycyclohexene natural products, 2,5-$(Me_3Si)_2$hydroquinone polymerises through H-bonding with or without $(MeOCH_2)_2$ solvate, Pd catalyses cross-coupling of (2-cyclohexenyl)SiF_2Ph with 4-iodo-acetophenone and cyclopropyl carbenoids insert Me_3Si activated C-H bonds in bicyclo[4.1.0]heptanes and bicyclo[3.1.0]hexanes.[63] β-Silyl and germyl substituted cyclohexyl esters show lengthened ester C-O bonds through $\sigma-\sigma^*$ hyperconjugative interaction between C-Si bonding and C-O antibonding orbitals.[64] The ligand $PhP[C_6H_3S^-\text{-}2(SiMe_3)\text{-}3]_2$ complexes with Li, Sn(IV) and Sm(II), phenyl substituted organosilicon dendrimers $Si[(CH_2)_3\text{-}SiMe_2Ph]_4$ and $Si[(CH_2)_3SiMe\{(CH_2)_3SiMe_2Ph\}_2]_4$ readily form π-complexes with $Cr(CO)_3$ residues.[65] 2-Me_3Si-4,5-Me_2phosphinine complexes iron to provide a template for [2+2+2] cycloaddition of alkynes/RCN to give substituted pyridines and arenes.[66] (Alkoxymethyl)phenylsilanes are 4 coordinating except if fluoro substituted at silicon.[67]

Palladacycles have been isolated as transmetallation intermediates in the Stille cross-coupling reaction of stannanes, 4-iodoacetophenone couple with Me_3Sn substituted benzocyclohexa-1,3-dienes, providing evidence for Pd(0) carbene intermediates.[68] Pd catalyses the coupling of stannanes with vinyl substituted ethylene oxide, allyl carbonates, and 2-bromo-Δ^2-thiazolines,[69] likewise aryl stannanes to bromoquinones to synthesise fenanthroviridone, to dichloro-1,10-phenanthroline, to bromobenzyl phosphonates, mixed triaryl phosphines, and diphenylates $PhC\equiv CPh$.[70] $ArSn(CH_2CH_2C_6F_{13})_3$ with RX gives ArR as major product, $R_fCH_2C(R)HX$ couples $R'SnBu_3$ in the presence or absence of CO to give R_fCH_2CHRR' or $R_fCH_2CHRCOR'$, [71] and aryl substituted hypervalent iodine derivatives with Bu_3SnR and CO give aryl ketones, and with $Bu_3SnC\equiv CR$ to give enediynes.[72] Mixed stannanes $ArAr'SnMe_2$ result from the cleavage of one methyl group from $ArSnMe_3$ with Li, followed by reaction with Ar'Cl, and disulfides result from the Pd catalysed reaction of sulfenyl chlorides with organostannanes.[73] The stabilisation of radical anions resulting from the electrochemical reduction of stannyl substituted adamant-1-yl and bicyclo[2.2.2]oct-1-yl bromides and iodides is compared.[74] Pharmacological discrimination is shown for Si/Ge bioisosteres, the structure of $Ph_3Sn(CH_2)_3NMe_3{}^+I^-$ determined, a range of optically active organotin compounds have been prepared for heterogeneous bimetallic catalyst and a family of 6-O-(galactopyranosyl)methyltin compounds made.[75]

Dynamic ^{13}C NMR spectroscopy shows intramolecular electron transfer and cation migration in the dianion of $(cot)_2SiMe_2$, with free energy of activation decreasing in the order $Na^+>K^+>Li,^+$ with the Na^+ and K^+ forming tight ion pairs but Li^+ existing as some loose ones.[76] Cyclo-1,2-dienes can be readily disilylated with Li/Me_3SiCl or distannylated with Me_6Sn_2 to give the 2,3-substituted cycloalk-1-ene, while cis-5-mesyloxycyclo-octyltrimethylstannane solvolyses 800 times faster than the trans isomer and forms bicyclo[3.3.0]octane exclusively, consistent with a 1,5-precaudal interaction (ε-effect) from the C-Sn σ-bond.[77]

Oxidation of 1,2-bis(1-Me_3Si-2-indenyl)ethane (2) $[(Me_3Si)_2C_{20}H_{16}]$ couples across the C-3-indenyl positions to give the tetrahydroindeno[2,1-c]fluorene $(Me_3Si)_2C_{20}H_{14}$, while the dianion of the benzo derivative gives $C_{24}H_{12}(SiMe_3)_2$ can be oxidised using TlCl to (2) or dimerised to $[C_{24}H_{13}(SiMe_3)_2]_2$.[78] Negative-ion chemical ionisation of $(Me_3Sn)_2$dihydroacepentalene gives the elusive acepentalene as the radical anion $C_{10}H_6{}^{\bullet -}$.[79]

Trimethylsilylindene exists as a pair of enantiomers which interconvert by Me_3Si migrations involving successive 1,5-shifts via the isoindene which can be trapped as a TCNE adduct.[80] The bent η^1-$(Me_3Si)3C_5H_2]_2Te$ complexes with the $W(CO)_5$ residue, and $(t\text{-}BuMe_2SiC_5H_4)_2Pb$: crystallises with rings parallel and centrosymmetric, as with the Sn(II) and Fe(II) derivatives.[81] An extensive range of silyl and stannylcyclopentadienyl, and silylmethylindenyl-$TiCl_3$ and TiX_2 (X=Cl, I) complexes have been made,[82] notably Al reducing $Me_3SiC_5H_4TiF_3$ in THF to give $[(Me_3SiC_5H_4TiF_2)_5AlF_3THF]$ with an $AlTi_5F_{13}$ core with interstitial fluoride in an $AlTi_5$ octahedron.[83]

Me_3Si substituted mono and bis dimethylsilylene bridged Cp_2MCl_2 (M=Ti, Zr, Hf) and their derivatives have been studied for olefin polymerisation.[84] Silyl substituted vanadocene dichlorides are prepared on account of the high antitumour activity of the parent compound,[85] $(Me_3SiC_5H_4)_2NbCl_2$ and its ansa derivatives are prepared, the latter adding alkynes and heterocumulenes while niobocene-ketene complexes show solution luminescence.[86] The structures of $Cp^*(Me_3SiC_5H_4)TaCl_2$ and $Cp^*[(Me_3Si)_2C_5H_3]TaH_3$ have been determined.[87]

An extensive range of Cp_2SiMe_2 and other derivatives of Mo has been made,[88] while polymers result through silylene bridged ferrocenes,[89] decaallylferrocene adds $Cp(HMe_2SiC_5H_4)Fe$ to give the dendrimer.[90] [I]-Silaferrocenophanes dimerise in the presence of Pd-PEt_3 catalysts, stanna derivatives behave similarly while $[1,3\text{-}(Me_3Si)_2C_5H_3]_2Fe_2(CO)_4$ adds sulfur.[91] Reacting $[RuCl_2(CO)_3]_2$ with $CpSiMe_3$ results in desilylation of the ring.[92]

$[(Me_3Si)_2C_5H_3]_2YbTHF$ crystallises 7-coordinate and t-$BuMe_2SiMe_4C_5^-$ (Cp^s) with YbI_2 gives the half sandwich cluster $[Cp^sYb]_6I_8^{2-}$,[93] while a range of Me_3SiCp-lanthanide complexes have been made,[94] along with a hydroxy bridged dimer of uranium.[95]

$^6Li/^{29}Si$ shift correlations are used for structural studies of α, β, and γ silyl organolithium reagents,[96] while $(EtO)_2P(O)C(X)(Li)SiMe_3$ adds to RR′CO to give α-fluorovinylphosphonates (X=F), but 1-alkynylphosphonates if X=Cl.[97] t-$BuMe_2SiC(Li)Br_2$ adds 2 moles of PhCHO to give 1,3-diol derivatives while $Me_2Si(CH_2Li)_2$ is used in the synthesis of 1,3-disilacyclobutanes and stannylmethylsilanes.[98] Esters couple with i-$PrOMe_2SiCH_2MgCl/CeCl_3$ to give 2-substituted allylic alcohols.[99]

$(ArO)_2Ta(CH_2SiMe_3)_3$ undergoes o-C-H bond activation of o-aryl substituted aryl groups through Me_4Si loss on heating, $Cp^*Ta(CH_2SiMe_3)_2CHSiMe_3$ hydrolyses with Me_3SiCH loss and complexes with aryl isonitriles to give the η^2-iminoacyl derivatives, as does Th(IV),[100] while with the alkylidene bridged 1,3-dimetallacyclobutadiene unit, isonitrile inserts the M-C bond.[101] $Cp^*(R_2O)_2CrCH_2SiMe_3^+$ loses ether to polymerise alkenes, $Cp^*Mo(NO)(CH_2SiMe_3)_2$ with $(Me_3Si)_2NLi$ gives the alkylidene bridged dimer, while $Cp^*W(NO)(CH_2SiMe_3)Cl$ with LiOMe gives a bimetallic nitride bridged complex along with $Cp^*W(O)_2(CH_2SiMe_3)$.[102] A series of silylmethyl Re(VII) and Os(VI)≡N derivatives have been made,[103] epimerisation of the α-C of $Me_3SiCH(X)Pt(X)$ derivatives is first order, while thermolysis of cis-$Pt(CH_2MMe_3)_2(PPh_3)_2$ (M=Ge, Sn) leads to β-alkyl transfer from Ge to Pt. $Pt(CH_2GeMe_3)_2(cod)$ and $Pt(CH_2SnMe_3)_2(PPh_3)_2$ pyrolyse to the 1,3-digerma-(or stanna-)cyclobutane.[104]

Trimethylsilyl-o-carborane is readily desilylated using fluoride to give the o-carborane carbanion which adds to RCHO, while $B_{10}H_{14}$ and $Me_3SiC{\equiv}CC_4H_9$ in the presence of Me_2S give the silylalkenyldecaborane/Me_2S adduct and not the closocarborane.[105] An extensive range of Me_3Si-C substituted heterocarborane complexes of lanthanides have been prepared,[106] along with lithium and magnesium derivatives.[107]

Me_3SiCN results from $(Me_3Si)_2NH$ and HCN, and substitutes both Me_3Al and $TiCl_4$.[108] $Me_3SiN(SO_2F)_2$, R_2SnCl_2, and sulfoxime/Ti(IV) are used in Me_3SiCN addition to RCHO,[109] while Me_3SiCN converts ROH to formamides, couples RCHO with amines to give aminonitriles, gives oxepanes through addition to δ-keto ethylene oxides,[110] substitutes ketals, gives α-sulfenamino nitriles from sulfenimines of (+)-camphor, converts imidazole N-oxides to 2, 4, and 5-cyano imidazoles, and chiral hydrazones to α-hydrazinonitriles.[111] Calculations suggest carbonyl complexation is not important in addition of α,β-unsaturated aldehydes to Me_3SiCN while i-Pr_3SiCN with Ni or Ti as catalyst convert enynes to bicyclic cyclopentenones.[112]

Aminomethylsilanes can be converted to α-functionalised α-aminosilanes on lithiation and are used in the total synthesis of (−)-retronecanol.[113] $CF_3C(=NAr)SiMe_3$ is used to generate the metal free anion $CF_3C{=}NAr^-$ using TBAF.[114] Alkenyl substituted α-aminomethylstannanes give 3-alkylpyrrolidines through anionic cyclisation, while N-(trialkylstannylmethyl)benzyl ammonium iodides react with RLi to give the 2-methyl benzylamine.[115] β-Lactams result in good yield with the cis isomer dominating through the addition of excess RCOCl with imines $RCH{=}NCH(SiMe_3)_2$.[116] $Me_3SiC(N_2)Li$ substitutes Rh(I), photolysis generating the transient metal substituted carbene which dimerises.[117] $R_3SiCH_2NR_2$ results from $PhSCH_2NR_2$ through C-S cleavage and silylation, $(MeS)_2Me_3SiCLi$ couples with ethylene oxides to give the cycloalkanes and $(Me_3Si)_2C{=}C{=}S$ reacts with amides, hydrolysis giving 3-oxoalkane thioamides.[118]

Calculations show vinylphosphirane pyrolyses to phosphaalkynes, thereby providing a synthetic route to $Me_3SiC{\equiv}P$, while coupling $Li[C(PPh_2)_2(SiMe_3)]$ with PCl_3 gives the first triphosphete together with $[Me_3SiC(PPh_2)_2]_2P^+$, with a PP_4 skeleton.[119] $Li[Me_3SiC(PMe_2)_2]$ reacts with MCl_4 (M=Si, Ge, Sn) and Me_2MCl_2 to give trans-$Cl_2M[C(PMe_2)_2SiMe_3]_2$ and cis-$Me_2[C(PMe_2)_2SiMe_3]_2$.[120] A range of γ-phosphinopropylstannanes $Me_2(X)Sn(CH_2)_3P(E)Ph_2$ (X=hal, E=chalcogen) have been prepared and shown to exist in solution in both open and intramolecularly coordinated forms, the latter dominating for E=oxygen.[121] $Cp^*(CO)_2Fe\text{-}P{=}C(SiMe_3)_2$ adds alkyl propiolates $HC{\equiv}CCO_2R$ to give bicyclic P-metalloylides, $Ph_2PCH_2CH_2SiMe_2^-$ (chel) chelates to Ir(III) to give $Ir(chel)_2Cl$ (distorted TBP) and two 6-coordinate derivatives, and $Ph(Me_3SiCH_2)AsH$ with Me_3Al gives trimeric $[Me_2AlAs(CH_2SiMe_3)Ph]_3$.[122]

Silylketenes give the enolate anion which with electrophiles generate silyl ynol ethers, $(R_3Si)_2C{=}C{=}O$ adds R'Li to give silylalkynes with HMPA and $Me_3SiCH{=}C{=}O$ adds RCHO to give 3-(Me_3Si)oxetan-2-ones.[123] $Me_3SiCH{=}C{=}O$ adds to acyl isocyanates to give cyclic β-lactams which decarboxylate in the presence of alkenes and alkynes to give 2-pyridones.[124]

$PhMe_2Si$ substituted mono and bisketenes result from the pyrolysis of the corresponding silyl substituted alkynyl ether, or in the case of bisketenes, also through photolysis of the cyclobutenediones.[125] The bisketenes undergo BF_3-catalysed [2+2]cycloadditions to MeCHO to give the β-lactone which decarboxylates to the vinyl ketene. [4+1]cycloaddition occurs with $RCHN_2$ (R=H, Me_3Si, Ph) to give cyclopentene-1,3-diones.[126]

The biscyclobutenedione results from the diketene $[O{=}C{=}C(SiR_3)]_2$ on warming with acid and isomerises to the tetraketene on heating under argon to 115° as yellow orange crystals which show adjacent ketenyl groups twisted at 119° to each other.[127]

SAMP/RAMP hydrazones provide for the asymmetric synthesis of α-silyl aldehydes and ketones while enamines of acylsilanes reduce to α-silyl alkylamines.[128] The optically active $(PhCH_2O)t\text{-}BuMeSiCOMe$ on reduction with *T. variabilis* to the α-hydroxysilane oxidises to (R)-(+)-1-PhCH(Me)OH and the absolute configuration of (S)-(+)-$[(PhCH_2OCH_2)t\text{-}BuMeSiCOMe]$ is determined.[129] Acylsilanes $RC(O)SiMe_3$ (R=H, Me, Ph) photolyse through decarboxylation though $MeCOSiMe_3$ gives $H_2C{=}CHOSiMe_3$ as the major product, and α-siloxy carbenium ions result from $ArCOSiMe_3$ on protonation of the photolytically generated α-siloxycarbene.[130] Acylsilanes with Bu_3SnH are generally reduced to the α-silyl alcohols, while with SmI_2, pinacol couplings occur but other products also result, depending on the acylsilane used, while ω-haloacylsilanes transform to Z-silyl enethiols and silyl thiocycloalkenes using P_4S_{10}.[131]

α-Bromo-α-silyl ketones and α-bromo-β-silyl ketones result from t-$BuMe_2SiC(Li)Br_2$ with ketones or aldehydes respectively, lithium dienolates α,β-unsaturated acylsilanes result from (1-silylallyl)lithium and CO at room temperature, and a range of aryl, alkenyl, and alkynyl acyl silanes have been prepared.[132]

Coupling $(Me_3Si)_3SiLi$ with acid chlorides gives α,β-unsaturated acylsilanes, that from $ClCOCH{=}CMe_2$ giving $(Me_3Si)_2SiHC(OSiMe_3){=}CHCMe_2Si(SiMe_3)_3$ through acylsilane rearrangement to the isomeric siladiene followed by $(Me_3Si)_3Si\cdot$ addition and H abstraction.[133] $(Me_3Si)_3SiCOR$ loses disilane with R'_3SiLi to give the lithium silenolates, which give o-silylated (R=Mes, o-tol) or Si-silylated (R=Ad, t-Bu) derivatives, depending on R, while addition of $(Me_3Si)_3SiCOPh$ to cyclopentadiene gives a 3:1 mixture of the siloxysilene Diels-Alder adducts.[134]

The structure of $Ph_3SnCH_2OCH_2$ substituted 1,3-dioxan-5-yl ethanediamide has been determined and Bu_3SnCH_2 substituted sugars can be destannylated with electrophiles.[135] Photodecomposition of $Pr_3SnC(O)Pr$-i occurs through Sn-C(O) cleavage.[136] (Z)-disubstituted olefins result from Bu_3SnCH_2O substituted alkenes while α-alkoxystannanes add enones in the presence of Cu(I).[137]

t-BuOOH oxidises $R'SiR_3$ to R'OH (R' is primary or hindered secondary), tropane derivatives result from their silylethoxytropane precursor, and trifluoromethyl thio and seleno ethers result from $CF_3SiMe_3/Bu_4NF/$ RYYR (Y=S,Se) in THF.[138]

2-$Me_3SiCHLi$-pyridine is dimeric as a TMEDA complex while complexes of this and 2-$(Me_3Si)_2C(Li)$-pyridine readily forms alkyl derivatives with first row transition metals.[139] Hindered gem-silyl derivatives of alkenes relieve steric strain through SiCSi angle widening and mixed alkali/alkaline earth derivatives of $(Me_3Si)_2CH^-$ result from $M(OSO_2Ar)_2$ (M=Ca, Sr, Ba) and $(Me_3Si)_2CHM'$ (M'=Li, Na, K) including $KM[CH(SiMe_3)_2]_3(thf)_3$.[140]

The $(Me_3Si)_2CH(R)$ group provides stabilisation for 1,2-diboretanides while the structure of μ-hydroxy derived R_2Al and R_2Ga rings are determined.[141] $[R_2M]_2$ (3) (M=Al) reacts with MeNCS through cleavage of the C=S bond to form the AlCN heterocycle, isocyanides undergo 2-fold insertion of the Ga-Ga bond of (3) (M=Ga) to give the 1,4-diazabutadiene bound to R_2Ga groups but only weakly.[142] With (3) (M=In), chalcogen atoms insert the In-In bond.[143]

$(Me_3Si)_2CHSbCl_2$ crystallises as weak chloride bridged dimers,[144] and $(Me_3Si)_2CH$- substitutes titanium, nickel, lanthanide metals and uranium.[145]

$(o\text{-}MeC_6H_4Me_2Si)_3CH$ is lithiated by MeLi only slowly, while the structure of $(Me_2NMe_2Si)_3CLi$ is polymeric with the Me_2N groups of each planar anionic unit coordinating to Li atoms.[146] $(MeOMe_2Si)(Me_3Si)_2CI$ reacts with Mg to give the chelated dialkyl $Mg\{C(SiMe_3)_2SiMe_2OMe\}_2$. The lithium derivative $MeOSiMe_2C(SiMe_3)_2Li$ results from $(Me_3Si)_2(MeOSiMe_2)CCl$ and BuLi in THF.[147]

The trihydride $Li^+[TsiAlH_3]^-.2THF$ reacts with t-BuOH or HF to give

$Li^+TsiAlX_3^-$ (X=t-BuO or F). The former crystallises as a monomer, the latter a tetramer with THF coordinated to each Li, with Al-F-Li bridges and rotation of the $CAlF_3$ units in solution.[148]

Ga_4Tsi_4 has a tetrahedral Ga_4 core in the solid state but evaporation gives the monomer in the gas phase, electron diffraction showing a Ga-C bond of 206.4 pm, similar to the tetramer and longer than those for Ga(III) compounds. In_4Tsi_4 reacts with $Co_2(CO)_8$ to give one or two TsiIn units bridging the Co-Co bond through substitution of bridging CO groups.[149] $(Me_3Si)_2(PhSMe_2Si)CCl$ on lithiation, trimethylstannylation, and reaction with iodine to replace first one Me group of Me_3Si then to displace PhS at silicon.[150] TsiZnCl and $i\text{-}Pr_3SiPHLi$ gives $i\text{-}Pr_3SiPH_2$ and $TsiZnPHSiPr\text{-}i_3$ with a short Zn-P bond while TsiHgR (R=alkyl or Ph) show higher thermal stability than R_2Hg.[151] Hydrogen atom extraction from $TsiCSiH_nR_{3-n}$ gives the radicals which in the presence of KOBu-t gives the silanone radical anions $TsiC(R){=}O{\cdot}^-$.[152]

Calculations indicate the triplet state of silacyclopropyne to lie 40 kcal mol^{-1} higher than the singlet state, the silirenyl anion is antiaromatic, while σ^*-aromaticity is confirmed by the effect of the electronegativity of substitutents on the 3-silacyclopropene.[153] Pd catalyses the coupling of dimethylsilacyclobutane with CO/RX to give 1-sila-2-oxacyclohex-3-enes, while 1,1-dimethyl-1-silacyclobutane adds fluoride in the gas phase but with OH^- or NH_2^- is deprotonated at Me. The anion so formed gives oxide and sulfide derivatives with CO_2 and CS_2.[154]

Coupling $Li[C(PMe_2)_2SiMe_2Ph].TMEDA$ (LiL) with $p\text{-}tolSiCl_3$ or 1,1-dichloro-1-silacyclobutane with gives 5 and 6-coordinate complexes $p\text{-}tolSiCl_2L$ and $L_2\overline{Si(CH_2)_3}$, 1-silacyclopentene gives aza bicyclic derivatives through free radical addition as silolanopyrroles, pyrrolidinones and quinolines, while the inefficiency of 1-silanorbornene and 2-silylnorbornene to photoalcoholyse indicated twisting of double bond is a prerequisite for protonation, the reaction being better with 1-silacyclohex-2-ene.[155]

The structure of an ester of cis-1,1-dimethylsilacyclohexane-3,4-diol shows distortion of the chair conformation, 9,10-dihydro-9-sila-10-heteroanthracenes act as new radical based reducing agents, while silastannatetrahydro-s-indacenes react with $ZrCl_4$ to give the ansa-zirconocene through Me_2SnCl_2 elimination.[156] Spirotin compounds result from 1,1-diethynyl-1-stannacyclohexane through addition of Et_3B giving the stannole fragment.[157]

9,10-Dimetallatriptycenes result from the reaction of o-phenylenemagnesium tetramer with $RMCl_3$ (M=Si, Ge, Sn), and can be tuned to give mixed metal and unsymmetrically substituted derivatives.[158] 1,1-Organoboration of $Si(C{\equiv}CR)_4$ (R=t-Bu, $SiMe_3$) gives substituted siloles.[159]

Reducing $Me_4C_4SiBr_2$ with 3 equivalents of potassium leads to the coupled dianion which with Me_3SiCl gives the tetrasilane. With 4 equivalents of potassium, however, the silole dianion results which can be stabilised with 18-crown-6 or converted, after desilylation, to the silolyl anion. The silole dianion shows considerable π-delocalisation with C-C bonds of 138–144 pm and C-Si bonds of 183–185 pm.[160] The 1-lithio derivative of 1-methyl-1-silafluorenide anion results from the cleavage of the Si-Si bond of bis(1-methyl-1-silafluorenyl) and shows little charge delocalisation, unlike that of the silole dianions where the degree of aromaticity in $(CH)_4SiLi^-$ exceeds that in $(CH)_4P$ and $(CH)_4SLi,^+$ and even approaches that of $(CH)_5Li$.[161]

Calculations on the electronic structure of 2,2′-bisilole shows the origin of the unusually long UV-vis absorption maxima of the 3,3′,4,4′-tetraphenyl derivative to be due to σ^*-π^* conjugated low-lying LUMO enhanced by structural distortions.[162]

The first pentaorganosilicate results from the reaction of o-(2-$Me_3SiC_6H_4$)-bromobenzene with MeLi, the high field ^{29}Si nmr signal (δ 116.9 ppm) supports pentavalency.[163]

Reducing 1,1-Cl_2-Et_4-1-germacyclopentdiene with Li gives the trigermole dianion which can be readily methylated. Structural data for the dianion supports a sandwich arrangement, this complexing the lithium cation and so reducing the delocalisation of the outer germole ring.[164]

The dianion of tetraphenyl germole can be similarly prepared in THF and can be crystallised from dioxan as two distinct isomers, the one as a reverse sandwich complex with two molecules of dioxan complexing to each lithium ion which are η^5 to the germole ring. The second isomer has germanium coordinating η^1 to one of the Li ions, the other η^5 to the ring. In the former isomer, the Ge-C bonds are 196 pm, in the latter, 193 pm.[165]

UV irradiation of 1,1-diazido-1-germacyclopent-3-ene gives a range of germoles resulting from germylene-germene rearrangement. The low-lying Ge-C stretching frequency supports π-conjugation in C=Ge-C=C and Ge=C-C=C units.[166]

Pd catalyses the [2+2+1]cycloaddition reaction of ethyne to $[(Me_3Si)_2CH]_2Sn$: to give the C-unsubstituted stannole through Pd=Sn intermediates, while boryl substituted stannoles react with t-BuC≡P to give boryl substituted phosphabenzenes through stannylene elimination.[167]

Lithiation of $[(Me_3Si)_2CHSiMe_2CH_2]_2$ gives the chelated lithiate which reacts with $HgBr_2$ to give the Hg derivatives. Structures indicate CLiC and CHgC angles of 171° and 165.8° respectively.[168] Condensing (2-thienyl)GeH_2 with $(HOCH_2CH_2)_2NMe$ gives the 6-aza-2-germacyclooctane with trans-annular N→Ge bond of 244.6 pm and heating $(MeO)_3Si(CH_2)_3NH(CH_2)_2NH_2$ gives MeOH and the 1,6-diaza-2-silacyclooctane.[169] Pd catalyses the coupling of 5-organo-1-aza-5-germabicyclo[3.3.3]undecane with ArBr and shows higher reactivity than organo$GeBu_3$.[170]

The gas phase structure of $Me_3SiCF=CF_2$ shows Me_3Si staggered with respect to the C=C bond, $Cl_2MeSiCH=CH_2$ occurs in the vapour phase as two stable conformers, and $RCF=CFSiMe_3$ can be stannylated using KF/Bu_3SnCl.[171]

Vinylsilanes result from N,N-diethyl cinnamyl carbonate and substituted trimethylsilyl ethanes,[172] vinyl silyl oxiranes from silylated sulfonium allylides, (Z)-1,2-$(Me_3Si)_2$-1-phenylethene reductively dimerises,[173] and vinyl silanes are used in the preparation of the iodide, and, appropriately substituted, cis-cyclopropanes, aziridines, furans,[174] isoxazolines, cyclopentenones, and functionalised vinylsilanes through addition,[175] while α-Me_3Si vinyl carbanions give α,β-unsaturated carbonyl compounds, and silylated diphosphetes can be substituted at P without ring opening.[176]

Vinylstannanes couple with aryliodonium salts, halopurines, and bromopyran-2-ones,[177] Ru-vinylidene complexes converted to the butadienyl complex with $(vinyl)_4Sn$, and as alkenylboranes give alkenyl iodides.[178] (Z)-1,2-Bis(trimethylstannyl)-1-alkenes react with a range of electrophiles while stannyldienes give stereocontrolled synthesis of part of rosaramycin.[179] Appropriately substituted, they also feature in aminoacid, iodolactone, conjugated diene and tricyclic syntheses.[180]

(E)-Allylsilanes result from intramolecular bis-silylation of chiral allyl alcohols, undergo cross-metathesis with $RCH=CH_2$,[181] trisubstituted (Z)-allylsilanes prepared stereoselectively.[182] Theoretical studies indicate fluoride assisted addition of $allylSiF_3$ to RCHO occurs through a 5-coordinate Si transition state, allylation of diketones occurs with high regio and stereoselectivity through fluorosilicate intermediates, while $Ph_3SiF_2^-$ cleaves allylsilanes to give adducts with ketones.[183] Various Ti and Sc catalysts assist in the addition of allylsilanes to RCHO.[184]

Allylsilanes can be bis substituted by $(ArE)_3CH$ (E=S,Se), add alkynes to give unconjugated dienes, give enones with RCOCl, and form vinylsilanes on lithiation followed by electrophilic addition.[185]

Appropriately substituted allylsilanes give epoxides and cyclopropanes, tetrahydropyrroles and pyrrolidines, cyclobutenones,[186] vinylcyclopentanes and chiral methylenecyclopentanes, bicyclo[3.2.0]heptenes, α-methylene cyclohexanones, and tricyclics incorporating silyl substituted THF ring.[187]

Hydrogermylation of $allyl_4Ge$ with $HGeCl_3$ leads to dendrimers and the structure of $(PhCH_2)_4Ge$ determined,[188] γ-alkoxyallylstannanes undergo transalcoholysis through acetal cleavage with Me_3SiI, alkynes give stannyl dienes and if γ-oxygenated, yield diol derivatives with aldehydes.[189] They are allylated by $allyl_4Sn$ and give $RCH(OE)CH_2CH=CH_2$ with RCHO/ECl and $allylSnBu_3$, which itself substitutes α-substituted ketones through radical pathways.[190] With $allylSnR_3$ (R=Ph, Me) with radical initiators results in the allylation of sulfonyl azides to give homolytic allylation at nitrogen.[191]

Lithiated 1-trimethylsilyl-2-butyne is in equilibrium with the allenyl isomer in solution at -150°C, $1\text{-}Me_3Si\text{-}1\text{-}Me$-allene adds to 1,4-benzoquinones to give spiro derivatives, while condensing Co atoms with (E,E)-1,4-$(Me_3Si)_2$butadiene gives $[Co\{\eta\text{-}C_4H_4(SiMe_3)_2\}_2]$.[192] Silyl/stannyl substitution allenoxy and propargyloxy substituted aldehydes cyclise to tetrahydropyrans while Pd catalysed the double nucleophilic substitution of stannyl allenes.[193]

Polyynes $X\text{-}[C{=}CC_6H_4]_nC{\equiv}CSiPr\text{-}i_3$ [X=H, $SiMe_3$] (n=1–4) result from $4\text{-}Me_3SiC_6H_4IC{\equiv}CH^+$ through Pd/Cu catalysed C-C cross-coupling and desilylation while Co and Mn catalyse the isomerisation of disilaalkylene bridged cyclic triacetylenes [prepared from $ClMe_2Si(CH_2)_nSiMe_2C{\equiv}CSiMe_2(CH_2)_nSiMe_2Cl$ and $(BrMgC{\equiv}CSiMe_2)_2(CH_2)_n$] to give arene, fulvene and dimethylenecyclobutene (n=1) and bisallene derivatives (n=2,3 only).[194] Coupling Me_2SiCl_2 with terminal bromoalkadiynes using $Mg/HgCl_2$ gives the 1-silacyclodeca-3,8-diyne while the disila derivative results similarly and $RSiCl_3$ gives the bicyclic disilatriyne along with bridged allenylmethylene derivatives.[195] A range of silylated fullerene-acetylene hybrids have been made while the radical

$(i\text{-}Pr_3SiC{\equiv}C)_5C_5\cdot$, which results from the fulvene-allene derivative on oxidation, shows surprising stability to air in both solid(weeks) and solution (days).[196]

Zn readily couples chlorosilanes to acetylenes, samarium reducing the $ZnCl_2$ so formed back to zinc,[197] while silylacetylenes functionalise halopyridines, porphyrin, tetrahydropyrans, cyclohexadienes,[198] and benziodoxoles, enynes give cyclopentanes, cyclopentenes and cyclopentadienes.[199] Propenylsilanes can be nucleophilically substituted using I^+, propargyl chlorides with $MeC(O)SiMe_3$ give α-(Me_3Si)allenyl ketones, the structures of o-$(Me_3SiC{\equiv}C)C_6H_4C(O)R$ (R=H, Ph) are determined.[200] $(Et_2N)Me_2SiC{\equiv}CR$ adds Et_3B to give the 1,2,5-azoniasilaboratole, while $Me_3Si(C{\equiv}C)_3SiMe_3$ is used to synthesis metallocumulenes with seven carbon atoms. Reacting i-$Pr_3SnCOMe$ with $RC{\equiv}CLi$ gives the propargyl stannane $RC{\equiv}CC(SnPr\text{-}i)_3(OSiMe_3)Me$, while alkynylstannanes substitute acetals to give allenyl carbinol precursors.[201]

A variety of titanocene-$Me_3SiC{\equiv}CSiMe_3$ derivatives have been prepared and their structures, catalytic properties, and thermolysis products explored,[202] along with those of analogous zirconocene precursors.[203] $CpTi[\mu\text{-}\eta^2{:}\eta^2\text{-}C_2(SiMe_3)_2]_2MgCp$ with $Me_3SiC{\equiv}CH$ gives $[\eta^5\text{-}(Me_3Si)_5C_6H_2]Ti(II)Cp$, $Me_3SiC{\equiv}CSiMe_3$ adds to $Cp^*{}_2Ti{=}C{=}CH_2$ to give the metallocyclobutane, thermolysing $Cp_2ZrMe(C_6H_4C{\equiv}CSiMe_3)$ leads to cross-conjugated polymers, and reductively coupling Cp_2ZrCl_2 with $Me_3SiC{\equiv}C(CH_2)_4C{\equiv}CSiMe_3$ gives the zirconabicyclo[4.3.0]nonadiene which catalyses olefin polymerisation.[204]

Propargylsilanes couple with chromium carbene complexes to give conjugated diene enol ethers, Mo and Pt give η^2-complexes with $Me_3SiC_2C{\equiv}CSiMe_3$, $Me_3SiC{\equiv}CLi$ with $Mo_2Cl_4(dmpm)$ gives alkyne bridged derivatives while Mo imido alkylidene complexes polymerise o-$Me_3SiC_6H_4C{\equiv}CH$.[205] $(Me_3SiC{\equiv}C)_2S$ is dimerised by CpCo derivatives to the cis- and trans-bisthiacyclobutadiene and silylalkynes substitute Rh(I) and Rh(III).[206] Silylacetylene and β-silylvinylidene Rh(I) complexes interconvert as substituted ferrocenes while boryl ferrocenes add to propynyl stannanes.[207] $Fe(C_5H_4C{\equiv}CSiMe_3)_2$ coordinates to the $Os_3(CO)_{10}$ residue through alkyne coupling about the Os_3 triangle and silyl alkynes including $Cp(CO)_2FeSiMe_2C{\equiv}CSiMe_2Fe(CO)_2Cp$ coordinate to the $Co_2(CO)_6$ residues.[208] Silylethynylferrocenes and Co carbonyl derivatives thermolyse to Fe-silicide and Co-silicide ceramics.[209]

Iodocyclobutadiene complexes couple with stannylalkynes, platina-β-diketones result through the silylalkyne intermediate while trans-$Pt(C_6F_5)_2(C{\equiv}CSiMe_3)_2{}^{2-}$ with trans-$PtHL_2(acetone)^+$ gives the trimetallo derivative through alkyne-Pt coordination.[210]

$Cp_2Ti(C{\equiv}CSiMe_3)_2$ gives tweezer complexes with Cu(I), Ag(I), and Au(I) while $Me_3PAgC{\equiv}CSiMe_3$ is polymeric.[211] Silylation of Cu(I) alkynides gives alkynylsilanes while $Me_3SiC{\equiv}CSiMe_3$ forms a η^2-complex with Cu and a μ-η^2-complex bridging two Cu atoms.[212] A similar tweezer structure results for the K derivative of the complexes $[(Me_4C_5H)_2Ti(C{\equiv}CSiMe_3)_2]^-M^+$ (M=Li, Na, K, Cs) with K^+ also interacting with adjacent Me_4C_5H rings.[213]

3 Catenation

$Mes_2Si=SiMes_2$ reacts with epoxides to give disilyl enol ethers, 3-oxa-1,2-disilacyclo-propanes and 5-membered heterocycles, while the structure of its THF adduct shows a Si=Si bond of 214.6 pm, the Mes_2Si groups planar and twisted about the Si=Si bond by 13°, and THF uncoordinated.[214] The first stable cyclic disilene, $(t\text{-}BuMe_2Si)_6$tetrasila-cyclobutene results from reductively coupling of $[t\text{-}BuMe_2SiSiBr_2]_2$ with $(t\text{-}BuMe_2Si)_2SiBr_2$ as an orange solid with Si=Si bond of 217.4 pm and a twist of 12.3°.[215] Photolysing $(t\text{-}Bu_2Si)_3$ with 3,6-$(CF_3)_2$-1,2,4,5-tetrazine gives diazasilole and diazadisilane rings while $(R_2ClSi)_2$ with biphenyl radical anions give the silylene and disilene which polymerise.[216]

Allylic trifluoroacetates can be silylated using disilanes with a Pd catalyst, which catalyses the bis-silylation of propargylic alcohols to chiral allenylsilanes and cyclises homoallyl alcohols, Ir catalyses the hydrogenation of diethynyldisilanes, while Ni catalyses the Grignard coupling of bromothienyl disilanes and a Co(III) porphyrin phosphoryl complex surprisingly results from the reaction of Me_6Si_2/MeLi in HMPA.[217]

Irradiating 1,4-$(Me_5Si_2)_2$-butadiyne gives silacyclopropene photoadducts which insert MeCHO and Me_2CO, while photolysing disilanylstilbenes establishes intramolecular-CT states which result in nucleophilic Si-Si cleavage.[218] Silenes photochemically generated from meso- and rac-$(MeEtPhSi)_2$ add carbonyl compounds to give alkoxysilyl substituted benzenes and stable 1,2-siloxetanes result from transient silenes and acetone.[219]

Cp_2MCl_2/n-BuLi (M=Ti, Zr, Hf) catalyses the dehydrogenative coupling of carbosilane monomers to give both soluble and insoluble polymers, while disilanes, both symmetric and mixed, give primarily trisilanes.[220] 8-Me_2N-1-naphthyl-1-hydrodisilane with Ni gives the silylene which gives the silole with $PhC\equiv CPh$.[221]

Rate constants for the reaction of $:SiH_2$ with di- and trisilane are consistent with lone pair interaction with the empty p-orbital leading to Si-H insertion.[222] Wurtz coupling of p-tolylSiH_2Cl gives the disilane which is readily converted to 1,2-dialkyl disilanes with CF_3SO_3H/RLi.[223] The water soluble polysilane $[Me_3N^+\text{-}CH_2C_6H_4C_2H_4(Me)Si]_n(Cl^-)_n$ shows fluorescence properties, pyrolysing Me_5Si_2H with CF_2Cl_2 gives the chlorosilane while R_3SnH hydrogenates chlorodisilanes in the presence of Lewis bases without Si-Si cleavage.[224]

Reducing 1,3-diphenyloctamethyl tetrasilacyclo-1,2-diene with Na in ether gives the solvent free allyl anion while with $CpCo(CO)_2$, pentasilacycloheptyne and hexasilacyclooctyne give the metalla substituted bicyclo[3.3.0] and [4.3.0] derivatives, while the tetrasilacyclohexyne forms the triene derivative through dimerisation.[225]

Ni catalyses the coupling of $Me_3SiC\equiv CSiMe_3$ with 1,2-disilacyclobutene to give disilacyclohexadienes and disilacyclopentenes, while Pd catalyses cyclotrimerisation of alkynes to benzene derivatives.[226] In the absence of alkynes, tetrasilacyclooctadienes (the dimer) result.[227] Cyclic disilanes add to Pd(0) or oligomerise.[228]

Li/Na alloy reduces $(ClCH_2SiMe_2)_2$ in the presence of $ZnCl_2$ to give the zinc 'ate' complex $[Li(tmeda)_2]_2Zn(CH_2SiMe_2SiMe_2CH_2)_2$,[229] disilabicyclo[2.2.2]octa-2,5-dienes result from $(ClR_2Si)_2$ and Li anthracenide,[230] while the Me_4Si_2 unit bridged the two rings of Cp_2ZrCl_2, of two $C_6H_6Cr(CO)_3$ units, and couple ferrocene.[231] Cp_2MCl_2/n-BuLi/$B(C_6F_5)_3$ catalyses dehydropolymerisation of silanes, polyphenylsilyne and branched copolysilanes result from the reductive coupling of chlorosilanes with C_8K, and can be triflate substituted then hydride substituted with $LiAlH_4$.[232] Polymer results from K^+/K^- reduction of $MePhSiCl_2$, the disproportionation of methylchlorodisilanes with base,[233] terminally substituted tungsten polysilanes result from $CpW(CO)_3Na$ and the α,ω-dichloropolysilane, polysilane Langmuir-Blodgett films show surface mediated chroism, and $Me_{26}Si_{12}$ can be vacuum-deposited and shows all trans conformations orientated perpendicular to the substrate.[234]

The ionisation energies of linear and cyclic polysilanes have been calculated with methylation of the parent silanes leading to a lowering of the first ionisation potential by 1–1.7eV, while for cyclic polysilanes, the first IP increases with the ring size but decreases for linear polysilanes.[235] A range of phenyl cyclopentasilanes have been made and converted to halo derivatives, while bond-stretch isomerism (differences in the bridgehead bond length) is predicted for derivatives of Si_4H_6.[236] The tetrahedro-tetrasilane $(t\text{-}Bu_3Si)_4Si_4$ results from $t\text{-}Bu_3SiNa$ and $(t\text{-}Bu_3SiBr_2Si)_2$ via dimerisation of the disilene $t\text{-}Bu_3SiHSi{=}SiHSiBu\text{-}t_3$.[237]

Reacting $(2\text{-}Me_2NCH_2C_6H_4)_6Si_3$ with RNCO gives cyclodi- and trisiloxanes and RNC:, the disiloxane showing N→Si coordination.[238] The octasilacubane $(t\text{-}BuSi)_8$ shows a superlattice structure while $(MeCHMeCMe_2Si)_8$ is photolytically oxidised with DMSO to the 9-oxa and 5,10-dioxa derivatives in which Si-Si bonds vary from 242.3 to 255.9pm.[239] The thermal syn-anti isomerisation of dodecaisopropyltricyclo[4.2.0.0^{2,5}]octasilane occurs at 200°C with an E_a of 42.3 kcal mol.$^{-1}$ That for the octane is much lower, indicating the bridgehead Si-Si bond to be stronger than the analogous C-C bond.[240]

σ-Complexes free of π-donor ligands result from $(Me_3MCH_2)_3M'Cl$ (M=C, Si; M'=Ti, Zr) with $LiSi(SiMe_3)_3.3THF$ (4) while $(CpCH_2CH_2NMe_2)NiI$ with (4) gives the dimethylsilylene complex with amine coordination transferred from Ni to Si.[241] With similar reaction $(Me_3P)_3RhCl$ in the presence of alkynes results in Me_3Si migration to Rh, silylene coordination to Rh and alkyne incorporation.[242]

Vibrational spectra for $[(Me_3Si)_3Si]_2M$ (M=Zn, Cd, Hg) support either D_{3h} or D_{3d} structures, with the X-ray structure of the Hg derivative supporting the latter. The Si-Hg bond length of 246.9 pm is shorter than the Si-Cd bond of the Cd analogue.[243]

With R_2GaCl, (4) gives the Ga-Si derivatives with Ga-Si bonds from 236–247 pm, depending on the electronic constraints of R. Ga_2Cl_4.2dioxan with (4) gives tetrameric $[(Me_3Si)_3SiGa]_4$ with the tetrahedral Ga_4 unit. It crystallises with $(Me_3Si)_4Si$. In addition, the tetrachloride $[(Me_3Si)_3SiGaCl]_4$ also forms with Ga-Cl-Ga bridges, together with $[(Me_3Si)_3Si]_4Ga_2$.[244]

A stable silene results from the Sila-Petersen reaction involving the coupling of $R_3SiLi.3THF$ (R=trialkylsilyl) with adamantanone and add alcohols and dienes, give cyclopropanes with acetone, while $(Me_3Si)_3SiCOR$ and $(Me_3Si)_3SiLi$ give bisacyl substituted polysilanes through oxidative coupling of the silenolate.[245]

$(Me_3Si)_3SiMgBr$ and 2,4-t-$Bu_2C_6H_3CHO$ (ArCHO) give $(Me_3Si)_3SiCH(Ar)OH$ which gives the silene on lithiation which dimerises to the 1,2-disilacyclobutane.[246] $(Me_3Si)_3SiLi$ and Cl_2CHOMe give the hindered bissilylmethane $[(Me_3Si)_3Si]_2CHOMe$ with SiCSi bond angle of 132.7°.[247] Radical addition of $(Me_3Si)_3SiH$ to α-diazo ketones $RCOCH{=}N_2$ give $RCOCH_2Si(SiMe_3)_3$ which does not isomerise to the silyl enol ether,[248] substitutes allyl phenyl sulfides, and opens bridged norbornanones to give quinanes and hydrindanes.[249]

Coupling $MeSiCl_3$ or $SiCl_4$ with $(Me_3Si)_2RSiLi$ (R=Me or Me_3Si) (5) gives the tri and tetrasilyl silanes while $MeSi(SiMe_2Cl)_3$ and $Si(SiMe_2Cl)_4$ are both fully substituted by (5) to give the silyl dendrimers which are non-fluorescent at room temperature.[250] With $GeCl_4$/Li/Me_3SiCl, $(Me_3Si)_4Ge$ results, MeLi/THF or pmdeta giving the Ge-Li derivative with Ge-Li bond of 266.6 and 265.3 pm respectively.[251] CdI_2 with $(Me_3Si)_3SiLi$ give the bridged iodide with GeCd-$(\mu$-$I)_3$CdGe skeleton, while with $GaCl_3$ in ether, $(Me_3Si)_3SiGaCl_3^-$ and $(Me_3Si)_3GeClGa(\mu$-$OEt)_2GaClGe(SiMe_3)_3$ result.[252]

Coupling t-Bu_3SiNa with $GeCl_2$ gives (t-$Bu_3Si)_4Ge_4$ with a regular Ge_4 tetrahedron with Ge-Ge bonds of 244 pm and Ge-Si bonds of 238 pm.[253] $(Me_3Si)_3SiGeCl.LiCl.3THF$ results from $(Me_3Si)_3SiLi$ and $GeCl_2$.dioxan, and adds to olefins to give the 1,2-dichloro-1,2-digermacyclobutane, 1,4-digerma-[2.2.0]hexanes resulting on reduction in the presence of Mg/$MgBr_2$ and olefin.[254] Reductively coupling 1,2-$(ClEt_2Ge)_2C_6H_4$ gives the digermacyclobutene which readily inserts oxygen, sulfur into the Ge-Ge bond, polymerises on warming and gives dibenzotrigerma heterocycles at 160°C.[255] The digermenes substituted with hindered silyl groups show temperature dependent UV-visible spectra, suggesting structural isomer equilibria in solution, as shown for the i-Pr_2MeSi in solution. No twisting of the Ge=Ge bond (226.6 and 226.8 pm) was observed.[256]

La@C_{82} adds the 2,6-diethylphenyl substituted digermirane both thermally and photolytically (empty fullerenes react only photolytically), Mes_2Ge: results photolytically from $(Me_3Si)_2GeMes_2$ and is less reactive than Ph_2Ge:, Me_2Ge: or Mes_2Si:, while $[ClMes_2Ge]_2$ results from $ClMes_2GeGeMes_2H$ (Mes_2GeCl_2 and Mes_2GeHLi) using $(BzO)_2/CCl_4$.[257] Cleavage of (t-$Bu_2Ge)_3$ with CCl_4, Br_2, or I_2 gives the 1,3-dihalotrigermane derivative with gauche-anti conformations and different Ge-Ge bond lengths.[258]

$Bu_3SnSiMe_3$ adds to allene in the presence of Pd to give a route to γ-hydroxy-α-methylene silanes and to alkynes to gem-disubstitute, while in the presence of fluoride, gives Bu_3Sn^- which eliminates bromide from gem-dibromoalkenes to give carbenes, 1,2-dibromobenzene to give benzyne, and 1,2-$(BrCH_2)_2$benzene to give o-quinodimethane.[259] Pd catalyses the reaction of $Bu_3SnGeEt_3$ with allylic halides to give 2-alkenyltriethylgermanes while Si-Ge doubly adds to Pt to give Pt(IV) complexes.[260] The mixed catenated Group 14 derivative $Me_3CSiMe_2GeMe_2SnMe_3$ photolyses with elimination of Me_2Ge: and Me_2Sn:, while BuLi cleaves the Ge-Sn bond.[261] An extensive comparison of the structures of Ar_4E and Ph_3E-$E'R_3$ shows the S_4 or C_3 symmetry of the molecule to be induced in the lattice.[262]

The trends in electronic spectra of polysilanes and Ge and Sn analogues does not support the π^* theoretical model, oligogermynes result from $RGeCl_3$ and Na in the presence of SmI_2, and give germyl radicals on photolysis, and $(Bu_2Sn)_n$ results from the Wurtz synthesis from Bu_2SnCl_2.[263] 1,2-Di and 1,2,3-tristanna ferrocenophanes result from $(C_5H_4SnMe_2H)_2Fe$, the former showing rings almost parallel while Me_6Sn_2 oxidises Pt(0) to Pt(II).[264] $Is_2Sn{=}GeMes_2$, the first characterised Ge=Sn double bond, results from its LiF adduct and adds ROH, PhCHO, and loses Mes_2Ge: on heating to give the germadistannacyclopropane.[265]

4 Hydrides

Ph_3SiH silylates prochiral alkenes using optically active thiol catalysts, permanganate oxidises hindered silanes to the silanol, including $TsiSiH_3$, using ultrasound, aryl silanes can be fluorinated using $KF/CuCl_2/CuI$, while 2,2′-$(HMe_2Si)_2$-1,1′-binaphthalene is readily hydrolysed to the cyclic disiloxane which $LiAlH_4$ reduces back to the silane.[266] Me_3SiH/BX_3 hydroborates 2-R-apopinenes, Et_3SiH reduces tosyl hydrazones, and alkyl and arylsilanes are inert to hydrogen evolution in the presence of tartaric acid unlike $(EtO)_3SiH$.[267] Cyclosilanes with Si-H side chains readily polymerise and C_{60} can be grafted onto silica using $(EtO)_2SiHMe$.[268]

Rhodium complexes catalyse the hydrosilation of mixed ketones with high e.e., the silylformylation of aldehydes, the silation of allyl alcohols to give cyclic silyl ethers, of divinylsilanes,[269] of styrene with increased selectivity as silane bulkiness increases, of bis(alkenylthiophenyl)silanes to give spirosilanes, and carbacyclisation of enediynes to exomethylene cyclopentenes,[270] carbene insertion into Si-H bonds to give silaglutarates, and the reduction of nitrobenzenes to anilines.[271]

Square planar iridium complexes add silanes and catalyse the hydrosilation of acetophenone with up to 96% e.e.[272] Platinum complexes catalyse the hydrosilation of bis(ethynyl)arenes with $bis(HMe_2Si)_2$acetylenes, the addition of $CpFe(CO)_2SiPh_2H$ to RC=CH, while dimethylfumarate adds to $[(vinylMe_2Si)_2O]_xPt$.[273]

Pd catalyses the hydroformylation of aryl triflates to give ArCHO and ArH, yields depending on the silane used, the multiple insertion of ArNC: with $PhMeSiH_2$ to give pyrrole derivatives which also result from diones and $(Me_3Si)_2NH$,[274] the reduction of alkyl and aryl halides by Et_3SiH, while 2 moles of 1,2-disilylbenzene with $Me_2Pd(dmpe)$ gives the 6 coordinate Pd(IV) derivative, implicating such derivatives as intermediates in Pd catalysed hydrosilations.[275]

Yttrium catalyses the cyclisation of 1-allyl-2-vinyl piperidine to (+)-epilupinine, titanium the hydrosilation of imines,[276] $Cr(CO)_6$ that of conjugated dienes, manganese carbonyl complexes that of ketones.[277] $PhSiH_3$ and Ph_2SiH_2 displace bridging carbonyl groups in $Fe_2(CO)_9$ but reduce bridging carbonyl groups in diruthenium complexes to give the bridging methylene derivatives.[278] Calculations predict two stable species for $OsCl(CO)(PR_3)$'H_2SiR_3', the one a η^2-H_2 derivative and the other a η^2-H-SiR_3 derivative,[279] while $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(PPr\text{-}i_3)_2$ adds Ph_2SiH_2, R_3GeH or R_3SnH to give the trihydride with olefin displacement, with $OsH(\eta^2-H_2BH_2)(CO)(PPr-i_3)_2$ adding Ph_3SiH, Ph_2SiH_2, and $PhSiH_3$, to again give the trihydride.[280]

$AdGeH_3$ adds to the surface of Rh/SiO_2 to give the surface stabilised germylene derivatives while Me_2GeH_2 replaces bridging CO groups in $Fe_2\{\mu_4-Ge[Co_2(CO)_7]\}_2(CO)_7$ to give the extended derivative $Me_2GeCo_2GeFe_2GeCo_2GeMe_2$.[281]

Thermolysing $Bu_2Sn(H)CH_2CH_2OEt$ gives $(Bu_2Sn)_x$ (x=5,6) through trivalent tin intermediates that then undergo β-elimination, while R_2SnH_2 can be converted to $R_2R'SnH$ using $i-Pr_2NLi/R'X$.[282] $Me_3SnCl/NaCNBH_3/AIBN$ converts amino acid analogues to α-methano heterocycles, while Bu_2SnHI reduces conjugated enones with regioselectivity and $(C_6F_{13}CH_2CH_2)_3SnH/AIBN$ reduces $C_{10}F_{21}I$ to $C_{10}F_{21}H$ in 72% yield and AdBr to AdH in >90% yield.[283] Lewis bases catalyse the reduction of Si-Cl using Bu_3SnH.[284]

Reducing $ZrCl_4$ with Bu_3SnH in the presence of R_3P gives cluster hydrides with 5 or 6 zirconium atoms; MCl_4(M=Zr, Hf)/Bu_3SnH reduces alkynes to vinyl stannanes.[285] $\eta^6-ArCr(CO)_3$ reacts photochemically with Ph_3SnH to give η^6-areneCr$(CO)_2H(SnPh_3)$ and η^6-areneCr$(CO)_2(SnPh_3)_2$ while trans-$[PtPhCl(Me_2S)_2]$ results from $PtCl_2(Me_2S)_2$ and Ph_3SnH.[286]

$Bu_3SnH/AIBN$ is used in the cyclisation of γ-oxygenated-α,β-unsaturated sulfones, acyl silanes, α,ω-enones, α,β-unsaturated acyl radicals and O-stannyl ketyls to the triquinane skeleton.[287] Bu_3SnH reduces N-(α-phenylacryloyl)oxazolidinone, ring opens vinylcyclopropanes in the presence of CO to give $Bu_3SnCH_2CR=CRCH_2CH_2CHO$, and Pd catalyses addition of Bu_3SnH to allylic alcohols and enediynes.[288] $Bu_3SnH/AIBN$ cyclises thio and selenoesters to the cycloalkanone, 5-hexenyl radicals in the presence of Ph_2Se_2 through a 'clock' reaction mechanism, while aryl tellurides (RTePh) give $Bu_3SnTePh$.[289]

5 Radicals, Ions and Metal Derivatives

Reducing $(t-BuO)_nPh_{3-n}SiCl$ with lithium gives the silyl-lithium reagent for n=2, but the disilyl-lithium derivative $(t-BuO)Ph_2SiSiPh_2Li$ for n=1.[290] $PhMe_2SiLi$ can be titrated using the double titration applied to organolithium reagents using CH_2Br_2 so long as excess Li is present,[291] and reacts with nitriles to give the acylsilane from pivalonitrile, 2,4,5-triphenylimidazole and benzil from PhCN, and the silane from $PhCMe_2CN$.[292] More hindered silyl-lithium reagents add once to C_{60}, but $(Me_3Si)_3SiLi$ adds twice to give the 1,29-bis-silyl derivative, and silylmethylation of C_{60} occurs preferentially as the 1,4-isomer in the C_6 ring.[293] Allylstannanes result directly from allyl alcohols using Bu_3SnLi, while $allyl_3SnLi$ randomly exchanges with methallyl-lithium.[294]

Calculations suggest homolytic substitution by CH_3 at $MeMH_3$ (M=Si, Ge, Sn) proceeds through D_{3h} intermediates, while $Ph_3Sn\cdot$ only results by cyclic voltammetry from 1 electron oxidation of Ph_3SnH or 1 electron reduction of Ph_3SnI.[295] Oxidation or reduction of Ph_3SnY (Y=Cl, OR, $SnPh_3$, SPh) gives Ph_3Sn^- or Ph_3Sn^+. $Ph_3Sn\cdot$ induces the cascade radical carbocyclisation of dodeca-1,6-dien-11-ynes to give polycyclic cyclohexenes, while $Bu_3Sn\cdot$ generates iminyl radicals from benzotriazoles imines which cyclise.[296]

The silylene-borane adduct t-Bu$\overline{\text{NCH=CH(t-Bu)NSi}}$:$\rightarrow$B$(C_6F_5)_3$ slowly rearranges at room temperature with aryl migration to Si, while 4-picoline displaces the silylene from the adduct.[297] $PhMe_2Si$-$B(NEt_2)_2$ adds across pinacol, the silyl borane so formed adding Si-B across the carbon-carbon triple bond to give 1-boryl-2-silyl alkene.[298]

The first arachno-silaborane arachno-$MeSiB_9H_{12}(NHMe_2)$ to be prepared results from arachno-$B_9H_{13}(SMe_2)$ by reacting with $MeHSi(NMe_2)_2$ and the SiB_9 cluster has Si occupying position 6 of the $B_{10}H_{14}{}^{2-}$ framework, the amino group at position 9, the prow and stern of the open boat.[299] The nido-silaborane $MeSiB_{10}H_{12}{}^{-}$ (6) which results from $B_{10}H_{12}{}^{2-}$ and $HMeSiCl_2$ has an open B_4SiMe ring readily reacts with $Et_3N.BH_3$ to eliminate hydrogen to give the first closo-monosilaborane 1-methyl-1-sila-close-dodecaborate(1-) in excellent yield. The 5-fold symmetry is supported by the ^{11}B NMR intensity ratio of 5:1:5.[300] Reacting $(Me_3Si)_2C_2B_4H_6$ with BuLi then coupling using Ni(II) gives $(Me_3SiC)_4B_8H_8$ with a distorted cuboctahedral structure.[301] Hetero silacloso-boranes result from (6) using $KH.BEt_3$ followed by closo addition of $SnCl_2$ or SbI_3 to give hetero-sila-closoboranes, while $B_{10}H_{10}{}^{2-}$ with Ph_3SnCl gives $[2\text{-}ClSnPh_2B_{10}H_9]^-$ with substitution at position 2 and suprisingly dephenylation.[302]

Reacting aluminium monochloride with t-Bu_3SiNa gives the deep violet tetra-alatetrahedrane (t-$Bu_3SiAl)_4$ which sublimes at 180°C under high vacuum. Surprisingly, indium(I) bromide and thallium(I) bromide both react with t-Bu_3SiNa to give the diindium and dithallium compounds $[(t\text{-}Bu_3Si)_2M]_2$ as deep violet and black-green crystals respectively, which are thermally unstable above 125° and 52°C respectively, and have long M-M bonds.[303]

$Cp^*{}_2SmCH(SiMe_3)_2$ induces disproportionation of Ph_2SiH_2 to Ph_3SiH and silyl-samarium clusters,[304] the silyl derivatives of Nb, Ta, W, Rh prepared,[305] while $PhC{\equiv}CH$ inserts Pt-$SiPh_3$ if cis to Me-Pt.[306] $Cp_2W(\eta^2\text{-}Me_2Si{=}CH_2)$ adds germanes to give the silyl germyl complex, and a range of distannyl and stannyl plumbyl derivatives prepared.[307] $[Zr(CO)_5(SnMe_3)_2]^{2-}$ decomposes in solution to give 8-coordinate $[Zr(CO)_4(SnMe_3)_4]^{2-}$ while cationic Pt-SnR_2X (X=Cl, Br) derivatives show stannylene character.[308]

Photolysing $CpFe(CO)_2SiMe_3$ with $(p\text{-}tol)_2GeH_2$ or p-$tolGeH_3$ gives the germylene bridged Fe_2 derivatives through desilylation, but $Cp^*Fe(CO)_2SiMe_3$ gives $Cp^*Fe(CO)_2GeH(p\text{-}tol)_2$.[309] $Fe(CO)_{5\text{-}x}[Ph_2P(CH_2)_nSnR_2R']_x$ (x=1,2) undergoes oxidative addition of Sn-R′ to Fe; $Fe_3(CO)_{12}$ reacts with diaryl stannylenes to give $Fe_2(CO)_8(\mu\text{-}SnR_2)$ but if $R{=}Me_5C_6$, then the spiro derivative $(CO)_8Fe_2SnFe_2(CO)_8$ results.[310] Orange $(Me_3Sn)_3Fe(CN)_6$ undergoes irreversible colour change to blue on UV irradiation while $(Me_3Sn)_4Fe(CN)_6$ turns deep violet under pressure or on prolonged heating.[311] Ph_3PbCl monosubstitutes $Fe_3(CO)_{11}{}^{2-}$.[312]

$Cp(Me_3P)_2RuSiH_2(\eta^1\text{-}Cp^*)$ shows Cp* static on the nmr time scale, intramolecular H site exchange occurs in the $H^*Ru\text{-}SiHR_2$ unit, and ethyne inserts the Ru-Si bond.[313] Silanes add to methylene bridged Ru_2 carbonyls with resultant C-H and Si-C activation.[314] Ph_3M (M=Ge, Sn, Pb) derivatives of Ru show long-lived $^3\sigma\pi^*$ excitation and radical anion stability,[315] and a range of germyl and stannyl clusters of Ru and Os have been prepared.[316]

β-Silyl groups stabilise organocuprates and render them more reactive, inducing conjugate addition and ketone formation, while conjugate addition of BuCu.LiI to cyclohexenone in the presence of Me_3SiI leads to direct formation of silyl enol ethers.[317] $Et_2NPh_2SiCu(CN)Li$ ring opens epoxides of cyclohexene to give the cyclohexene diol, while β-unsaturated enones are converted to the alcohols. $Me_2C{=}CHCH_2C({=}CH_2)COCH_3$ giving (±)-lavandulol.[318] $(Me_3Sn)_2$-CuLi substitutes pyran-4-ones while $(Me_3Sn)RCu(CN)Li_2$ adds ethyne to give the stannylvinyl cuprates which add to α,β-enones to give the silyl enol ethers.[319]

Tris(phosphinoalkyl)silanes complex with Ir(III) with H trans to P and Cl to Si, while $(Ph_2PCH_2CH_2SiMe_2)_2$ oxidatively adds to trans-$Ir(PPh_3)_2(CO)Cl$ to give the Ir(III) complex with CO and Cl trans.[320] $PhMe_2SiLi$ and $(Me_3P)_4IrCl$ give transient $PhMe_2SiIr(PMe_3)_3$ which undegoes o-metallation to give fac-$(Me_3P)_3Ir(o\text{-}C_6H_4SiMe_2)H$ while $(Me_3P)_2Ir(H)(Me)\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}$ with Me_3P at 60°C undergoes reductive elimination of CH_4 to give trigonal bipyramidal $(Me_3P)_3Ir[\eta^2\text{-}Me_2Si(CH_2)_2PPh_2]$ with Si axial.[321]

Complexed triflate stabilises the $Ph_2Si{=}Ir$ unit, and thermolysing $HR_2'Si$-Ir gives the silylene hydride derivative.[322] Fe will stabilise complexed silylenes while phosphenium ligand will demethylate Me_3Sn-Fe complexes to give the stannylene derivative.[323] Stannylene complexes of Pd reversibly add H_2O and MeOH, and Fe-Pd and Fe-Pt stabilise germylenes and stannylenes, while calculations support a decrease in the π-strength of the $Cr{=}EH_2$ bond (E=C,Si,Ge,Sn) from 202, 82, 72, to 51 kJ mol^{-1}.[324]

Coupling $[\eta^5\text{-}C_5H_5Mo(CO)_3]Na$ with $2,6\text{-}Mes_2C_6H_3GeCl$ in THF gives the Mo-Ge derivative with metal-metal bond length of 227.1 pm (compare 260–265pm for single bonds), suggesting multiple bond character, possibly triple, as would be expected for the 15 electron Mo fragment.[325]

6 Nitrogen Derivatives

Me_3SiNEt_2/MeI convert organic esters to the parent acid on hydrolysis, while aminosilanes/RI convert primary amines to disilazanes.[326] $[t\text{-}Bu_2MeSiNHLi]_4$ gives a range of condensed derivatives with SiF_4 and $(Me_3Si)_2C(SiF_3)_2$.[327] Lithiation of $(Me_3SiCHCH_2)_2$ in ether gives the amide which shows solution dynamics, and lithium movement occurs with dimeric $(t\text{-}BuOSiMe_2)_2NLi$ in the crystal.[328] The triple anion complex $LiBr.LiN(SiMe_3)_2.[LiOC(Bu\text{-}t){=}CH_2]_2(TMEDA)_2$ provides a new structural type with bromide bridging four Li cations, and $Li(py)(Et_2O)N(SiMe_3)(2,6\text{-}i\text{-}Pr_2C_6H_3)$ shows planarity about N and Li.[329] Competitive solvation effects in $(Me_3Si)_2NLi$ have been explored and compared with $PhCH_2(Me_3Si)NLi$,[330] $[(Me_3Si)_2N]_2Cd$ adds $(PhN)_3CLi_2$ while Ph_3CSLi displaces $(Me_3Si)_2NLi$.[331] $[(Me_3Si)_2N]_2M$ (M=Ca, Sr, Ba) deprotonate amino-pendant cyclopentadiene to give alkaline-earth metallocenes while troponiminate complexes of Sn(II) result from $[(Me_3Si)_2N]_2Sn$:.[332]

$(H_3Si)_2NOMe$ shows Si···O interactions of 292 pm in the solid state, $Mg[N(SiMe_3)_2]_2$ can be electrogenerated while $(Me_3Si)_2NLi$ converts $Cp^*{}_2PCl$ into bicyclic derivatives,[333] pendular silylaminocyclopentadiene complexes substitute Sc, and alkali metal derivatives of silylaminodienes have been prepared.[334]

Silylamides add to aldehydes, aldimines result from $RR'_2Si(Me_3Si)NLi$ and $R''CHO$, and $(Me_3Si)_2NNa$ gives cyclopropene using allyl chloride.[335] $(Me_3Si)_2NK$ converts ω-hydroxy-β-iodo vinyl sulfones to the cyclic enol ether, phosphonosulfoxides to α,β-unsaturated sulfoxides, and allylic ylides to cyclopropanes.[336]

A range of complexes result from the benzamidinate ligand $ArC(NSiMe_3)_2^-$ with Al, Sc,[337] Y,[338] Ti, and Zr,[339] while β-lactams result from addition of silyl imines to acyl chlorides.[340]

The chelating amide $(i\text{-}Pr_2PCH_2SiMe_2)_2N^-$ substitutes $AlCl_3$ to give the 5-coordinate $AlCl_2$ derivative, while $(Me_3Si)_2NH$ with $Al(X)H_2.NMe_3$ (X=H,Cl) gives $(Me_3Si)_2NAl(X)H.NMe_3$. Adding Me_3Al to $(Me_3Si)_2NNa$ in toluene gives the dimeric 'sodate' $Na^+[Na\{N(SiMe_3)_2.AlMe_3\}_2]^-$ with Na^+ interacting with five $H_3C\text{-}Al$ bonds.[341] Quinuclidine coordinates the N-silyl substituted alumin-atoimino-phosphine ring at P while the gallium analogue coordinated the $Ni(CO)_3$ residue. Monomeric $(Me_3Si)_2N$ derivatives of Ga and In result if substituted by the supermesityl group, while $[Me_3SiN(t\text{-}Bu)NSiMe_3]_2InCl$ results from $(Me_3SiN=)_2C$, t-BuLi, and $InCl_3$.[342]

A range of polysilyl hydrazines and polyhydrazino silanes have been prepared, and condense with ketones to give hydrazones.[343] Hydrazine derivatives formed from $Me_2NNMeLi$ with $SiCl_4$ and $GeCl_4$ show N_β-interactions for Si but not Ge.[344] Hydrazone coordination to Si shows exchange through $N \rightarrow Si$ cleavage.[345] Me_3SiN_3 ring opens epoxides, substitutes acid chlorides to give amines and carbamates by the Curtius rearrangement, gem-substitute glucono lactones and in the presence of PhIO substitutes silyl enol ethers.[346]

A reconsideration of the vapour phase structure of silyl isocyanate still supports a linear structure despite the non-linearity of R_3SiNCO derivatives in the solid state. The cyanate $(Me_3Si)_3CSi(CD_3)_2OCN$ isomerises in the molten state at 150°C to give the unrearranged isocyanate together with the rearranged $(Me_3Si)_2[(CD_3)_2MeSi]CSiMe_2NCO$ in the ratio 3:1 and in Ph_2O at 220° in the ratio 6:1. This supports a mechanism involving initial ionisation of the cyanate. In CCl_4 with a trace of ICl, no rearrangement accompanies isomerisation.[347]

Me_3SiNCS with alkenes gives oxazolidin-2-thiones, $Cp^*{}_2Si$: adds MeSCN and CF_3CN (1:2) to give the diazasilole but Me_3SiCN (1:1) gives the adduct $Cp^*{}_2Si(Me_3Si)CN$.[348] $(Me_3SiNSN)_2S$ gives a range of Pd complexes while Me_3SiNSO shows a planar skeleton with syn conformation in the vapour phase with Si-N bond of 175 pm and SiNS angle of 134°.[349]

$t\text{-}BuNSiMe_2N(t\text{-}Bu)Sn$: reacts with C_5H_6 to give a π-derivative (Sn-C 247–276 pm) whereas indene gives a σ-derivative (Sn-C 234.3 pm), adds Me_2NH-stabilised Fe-silylene complexes through N-H insertion, while reducing $t\text{-}BuNSiMe_2N(t\text{-}Bu)PCl$ with Li gives dimeric $[t\text{-}BuNSiMe_2N(t\text{-}Bu)P\text{-}P]_2$ with a planar P_4 rhombus structure and dimeric $[Me_2Si(NLiBu\text{-}t)_2]_2$.[350]

Silylenes derived from 1,2-diaminoarenes ($SiCl_4$/K) add MeI and EtOH, while Se and Te add to give the cyclic dimer. Calculations support π-delocalisation through Si.[351] 2,2′-Bithiophene 5,5′-substituted with bulky (2,2,5,5-Me_4-1-aza-2,5-disila-1-cyclopentyl)-methyl groups shows unique non-herringbone structure while $(2,6\text{-}i\text{-}Pr_2C_6H_3NSiMe_2)_2$ has a planar Si_2N_2 ring.[352]

Thermolysing (i-PrNSiMe$_2$)$_2$ at 850°C gives the silanimine which adds t-BuOH, but (t-BuNSiMe$_2$)$_2$ at 925°C gives [(H$_2$C=CMe)NSiMe$_2$]$_2$ through CH$_4$ elimination.[353] t-Bu$_2$Si=NSi(Bu-t)$_2$Ph adds EtOH, Me$_2$C=O and dienes while ArN$_3$ gives the tetraazasilacyclopentene, and 1-aza-2-silacyclopentanes result from P=N and EtOCH=CH$_2$ addition.[354] Endocyclic Si-N bonds (73 kcal mol^{-1}) are weaker than acyclic ones (76 kcal mol^{-1}), while t-BuSiCl$_3$ and NH$_3$ give the tetrasilabicyclo[3.3.1]nonane, a NH bridged cyclotetrasilazane with Si-N bonds of 171–173 pm.[355]

Pyrolysis of the silatrane HSi(NHCH$_2$CH$_2$)$_3$N gives the dehydrogenated cyclodisilazane dimer while calculations support a flat potential energy function for the stretch of the N→Si bond, while optically active silatranes have been made.[356] Coupling HC(Me$_2$SiNLiCHMePh)$_3$ with SnCl$_2$ gives the enantiomerically pure chiral triamidostannate.[357] 1,2-Bis(silyl)benzene and 1,8-bis(silyl)-naphthalene give ring nitrogen heterocycles while halogen substituted pentacoordinate Si heterocycles hydrolyse with ring opening.[358]

An extensive range of aminosilane, disilazane, and N-cage derivatives of Sc, Y, Er, U,[359] Ti,[360] Zr, Hf,[361] V,[362] Nb,[363] Ta,[364] Cr,[365] W,[366] Mn,[367] Fe, Co, Rh, Ir,[368] Pd,[369] Ag, and Au,[370] and a range of silyl substituted phosphanimine derivatives of Li,[371] Al, Te,[372] Cr, Pd, Cu,[373] and silylated sulfur diimide derivatives of Si, Ge, Sn and ferrocene prepared,[374] along with (C$_6$F$_5$S)$_2$NSiMe$_3$ and Ar(Me$_3$Si)NSCl fragmented by Ag$^+$ to give ArN=S.[375]

Mes$_2$FGeNHC$_6$H$_2$F$_3$-2,4,6 gives the germa-imine on lithiation which dimerises, while the silylaminogermylene gives two isomeric diazagerma heterocycles.[376] Volatile (CF$_3$)$_3$GeN$_3$ results from the iodide and AgN$_3$ and has a Ge-N bond of 187.4 pm and GeNN angle of 120.3°.[377]

Tin amines react with R$_3$Ga to give aminogallanes through RSnMe$_3$ elimination, a range of stannyl tetrazoles prepared from azide and nitriles, and (Me$_3$Sn)$_3$N and PhN(SnMe$_3$)$_2$ give stannyl imine cluster complexes of Ti, Co and Cu.[378] n-BuSn(NC$_5$H$_4$-*C,N*)$_3$LiBr results from Cp$_2$Sn:, 2-lithiopyridine, and BuBr, and complexes Cu while Me$_2$Si(t-BuN)$_2$Sn: complexes MX$_2$ (X=Cr, Fe, Co, Zn).[379]

7 Phosphorus, Arsenic, Antimony, and Bismuth Derivatives

Trichlorosilyl phosphanes result from HSiCl$_3$ while with Me$_3$SnCl and Et$_3$N, Me$_3$SnSiCl$_3$ results, Me$_3$SiPEt$_2$ gives 1,4-adducts with enones while radical reactions of Me$_3$SiPH$_2$ and (Me$_3$Si)$_2$PH with alkenes result in PH addition without significant Si-P cleavage. The reactivity decreases with increasing silylation at P.[380] (Me$_3$Si)$_3$P$_7$ and Cp*Li react with CoCl$_2$ or FeCl$_2$ to give Co$_3$(P$_2$)$_3$ and FeP$_6$ clusters.[381]

While (Ph$_3$Si)$_2$PH and BuLi gives dimeric (Ph$_3$SiPLi)$_2$, (i-Pr$_3$Si)$_2$PH gives the tetramer containing (i-Pr$_3$Si)$_2$PLi and (i-Pr$_3$Si)HPLi in the ratio 3:1.[382]

Is(i-Pr)$_2$SiPLi$_2$ is dimeric and forms a double adduct with Is(i-Pr)$_2$SiF in which F bridges a pair of Li atoms.[383]

The Si=P and Si=As double bonds result from the thermolysis of the monomeric lithium (fluorosilyl)phosphanides and arsenides $Is_2Si(F)P[LiL_n]R$ ($R=SiR'_3$) (M=P,As), and undergo an extensive series of addition reactions with electron-rich compounds.[384]

Lithium adds to the Si=P double bond of $Is_2Si=PSiPr\text{-}i_3$, the dilithio derivative then hydrolysing or reacting with Me_2SiCl_2 to give the first disilaphosphacyclopropane, or t-BuHgCl to give silyl substituted mercury-phosphorus clusters.[385]

$[(R_2P)_2P]^-$ can be silylated at the middle P atom and then desilylated with BuLi.[386] Reacting $(Me_3Si)_2PNa$ with $(t\text{-}BuCH_2O)_6M_2$ (M=Mo, W) gives $[M_4(\mu^3\text{-}PSiMe_3)(OCH_2Bu\text{-}t)_{11}]^-$ which can be readily desilylated, while $[(Me_3Si)_2N]_2Ba$ and $(i\text{-}PrMe_2Si)PH$ in THF give the barium phosphide as monomer and dimer.[387]

$(Me_3Si)_3P$ forms adducts with BX_3 (X=Cl, Br) with B-P bonds of about 200 pm, and similar to those of $[X_2BP(SiMe_3)_2]_2$, with $Ph_nAlCl_{3\text{-}n}$ (n=1–3).[388] Adducts of $(Me_3Si)_3P$ with Me_2AlH or M_3M (M=Al, Ga, In) show thermal stability to Me_4Si elimination in the order Al>Ga>In, and $(Me_3CCH_2)_2GaCl$ (7) gives a 1:1 adduct without Me_3SiCl loss, this occurring with excess (7).[389] Similar adducts result from GaX_3 (X=Cl, Br, I).[390]

$SmI_2(thf)_3$ with $(Me_3Si)_2PK$ in THF gives the unsymmetric dimer $(Me_3Si)_2PSm[\mu\text{-}P(SiMe_3)_2]_3Sm(thf)_3$.toluene with Si-P bonds of 220–221 pm, $(Me_3Si)_3P$ coordinates to V(IV), and the $(SiP)_3$ ring complexes $M(CO)_3$ residues.[391] Coupling $(C_5HMe_4)Me_2SiCl$ with R_2PCl or PCl_3 using Mg gives the mono or trisilyl phosphine, while the germyl and stannyl derivatives $Me_2(C_5HMe_4)MPPh_2$ (M=Ge, Sn) result from the silylphosphine and $Me_2(C_5HMe_4)MCl$, the Ge derivative coordinating to the $Fe(CO)_4$ residue.[392]

$(i\text{-}Pr_3SiAsH)_4AlLi$ loses H_2 on heating to give $As_7{}^{3-}$ and with $IsSiCl_3$ to gives $(IsSiAs)_4$ with Si-As bonds of 240-241 pm with angles at Si of about 100° and of 80° at As.[393]

$Me_2(i\text{-}PrMe_2C)SiAsH_2$ ($RAsH_2$) gives $(RAs)_{12}Li_{26}O$ with $BuLi/Li_2O$ in which the central Li_6O unit is surrounded by an isosahedral As_{12} unit face-bridged by 20 lithium ions. The phosphorus analogue involves a P_8 cube surrounding the Li_6O unit in $(RP)_8Li_{18}O$.[394]

Reacting $(Me_3Si)AsPh$ with AgCl or Me_3PAuCl in the presence of tertiary phosphines gives a series of Ag-As and Au-As clusters.[395] $(Me_3Si)_2E$ (E=P,As) monosubstitutes $(MeC_5H_4)_2MCl_2$ (M=Zr, Hf), the Zr-P derivative inserting $(i\text{-}PrN=)_2C$ and the Hf-As derivative inserting CS_2 and PhNC:,[396] and $Me_3SiAs=C(NMe_2)_2$ substitiutes $Cp^*Fe(CO)_2Br$, the derivative inserting dimethyl fumarate.[397]

$(Me_3Si)_3Sb$ forms adducts with R_3M (M=Ga, In) while $(Me_3CCH_2)_2MCl$ gives adducts which lose Me_3SiCl to give the associated group 13 antimonides, and Na_3Bi/K_3Bi react with Me_2SiCl_2 gives the decamethyl-1,4-dibismutha-2,3,5,6,7-pentasilabicyclo[2.2.1]heptane.[398]

The diphosphide $K_2[t\text{-}BuP\text{-}(t\text{-}BuP)_2\text{-}PBu\text{-}t]$ reacts with R_2SnCl_2 to give the stannatetraphospholanes while $K_2[t\text{-}BuP]_2$ with $SnCl_4$ results in a redox reaction yielding $(t\text{-}BuP)_{3+4}$ along with the [2.2.2]octane, $Cl(t\text{-}BuPPBu\text{-}t)_3SnCl$ with Sn-P bonds of 253 pm.[399] Di-t-butylchlorotriphosphane with $(Me_3Sn)_3P$ gives the phosphinocyclotriphosphane as a yellow solid stable below 0°C and shows a low barrier too invertion at the exocyclic P atom.[400]

8 Oxygen Derivatives

CuCl catalyses the direct synthesis of $(PhO)_3SiH$ from silicon and phenol, with a surface silylene proposed as intermediate. This is confirmed by adding C_2H_4, resulting in $Et(PhO)_2SiH$ formation.[401] $(Me_3SiO)_2CrO_2$ oxidises alcohols and cyanohydrins to RR'CO (R=organo, CN; R'=H, organo).[402] β-Siloxynitriles result from RCHO and Me_3SiCH_2CN on microwave irradiation while $(Ar_3SiCHPh)^-$ with RCHO (the Peterson reaction) gives stilbene in varying Z:E ratios depending on the steric and electronic effects of Ar.[403]

i-Pr_3SiOH allows KOH to convert primary alkyl halides to alkenes, thereby providing a potential agent for detoxifying mustard gas analogues.[404] Silanols condense with alkoxysilanes to give disiloxanes while the nmr spectra of phenoxysilanes and mass spectra of polyfunctional alkoxysilanes have been examined.[405] t-$BuMe_2Si$ ethers of hydroxyanthroquinones are hydrolytically stable while $P(MeNCH_2CH_2)_3N$ is an efficient catalyst of alcohol silylation.[406] Ni catalyses the dehydrogenative silylative coupling of $R_3SiCH{=}CH_2$ with $(EtO)_3SiH$ while reducing $ArOSiR_n(OR')_{3-n}$ with Na/Mg by sonication results in O→C silyl migration.[407]

2-$(Me_3SiO)C_6H_4NC$: forms an adduct with Ph_3B which on desilylation with KF/MeOH gives the benzoxazole derivative or dimerises on heating to give pyrazine derivatives, and $R'C{\equiv}CB(NR_2)_2$ condenses with $(Me_3SiOCH_2)_2CMe_2$ to give boronate.[408] While siloxymethyl alkynes are used in heterocycle synthesis.[409]

Siloxymethyl-Fe complexes couple with alkenes to give cyclopropanes in the presence of $CF_3SO_3SiMe_3$ which assists in siloxycyclopentadiene synthesis from cyclopentanones.[410] Siloxyindenyl zirconium complexes polymerise propylene, while $Me_3SiOOSiMe_3$ can be activated by oxo and peroxo complexes of V, Mo, and W for the sulfoxidation of thianthrene 5-oxide.[411]

Condensation of $OS(Me_2C_6H_2OH)_2$ with Me_2SiCl_2 gives the 8-membered rings with an anti-chair conformation and no OS:→Si or O→Si interactions, unlike the analogous sulfide (S→Si about 300 pm), while the sulfonyl analogues show 5-coordination.[412] Sulfur-induced pentacoordinate occurs in cyclic silanes and siliconates are intermediate in the asymmetric allylation of RCHO, diprenylbis(tropolonoato)silane is 6-coordinate, undergoes allylic migration to give the 5-coordinate derivative which readily allylates RCHO,[413] and organospirosiliconates show one long Si-O bond.[414] Six coordinate silicates derived from resorcinol and $ArSi(OMe)_3$ with spare pendant aminomethyl groups show ready protonation in methanol.[415]

t-BuOOH oxidises oxasilacyclopentanes to the dioxasilacyclohexane while iodomethyl substituted oxasilacyclopentanes result from $H_2C{=}CH(CH_2)_2SiPh_2OH$ with $I(collidine)_2PF_6$.[416] $Co_2(CO)_8$ catalyses the cyclisation of $viPh_2SiO(CH_2)_2C{\equiv}CH$ to oxasilacyclooctadiene and spirocyclic silanes with the oxasilacyclpentane ring result from the intramolecular hydrosilation of an appropriately substituted silacyclohexane.[417] Ph_2SiCl_2 in DMSO ring expands 1-oxa-2,5-disilacyclopentanes through silanone and cyclodisiloxane intermediates, while heating a C_{60} substituted siloxane above 350°C leads to siloxane loss.[418]

Condensing pyridine diols with Me_2SiCl_2 gives large ring siloxanes with a N→Si interaction for the larger ring, while $[FCH_2(Me)SiO]_4$ has SiOSi angles of 158°.[419] Pt(II) catalyses the dehydrogenation of i-$Pr_2Si(H)OH$ to give the silanone intermediate which inserts Me_3SiOMe.[420] Cleaving cyclotrisiloxanes with Li followed by reaction with RMe_2SiCl gives functionalised disiloxanes while CpTi complexes anchored to polysiloxanes show hydrogenative catalytic activity, and liquid crystal phase behaviour is exibited by supermolecules with a siloxane core.[421]

Silyl substituted nitrones cycloadd to C_{60} to give the isoxazoline derivative, $(Ph_3SiO)_3As$ has Si-O bonds of 164.6 pm, XeF_2 cleaves $ArCO_2SiMe_3$ to give fluoroformates,[422] $PhP(OSiMe_3)_2$ can be functionalised to give PhP(O)(R)OH, $Me_3SiOP(OEt)_2$ gives siloxyphosphonates with fluorinated but-2-ones[423] and silyl esters of dicarbamic acids thermolyse to the ureas.[424]

Silyl enol ethers have been used as intermediates in the synthesis of a range of linear[425] and polycyclic compounds[426] and natural products,[427] silyl substituted ketene acetals are used in aldol additions,[428] Danishefsky's diene has been used to prepare a range of phenols and nitro substituted cyclohexanones,[429] ethoxyvinylsilanes couple with R_2CO to give 1-oxa-2-silacyclopentane, 2-silylfurans result from acylsilanes and $R_3SiO(R)C{=}C{=}N_2$ gives diazaphospholes with $ArP{=}CPh_2$.[430]

An extensive range of metal substituted siloxanes have been made. These include Li and Na disiloxane diolates,[431] $Cp^*Si(OSiMe_3)_3$,[432] a range of aluminosiloxanes and aluminophosphates,[433] and siloxy substituted pnictide polytungstates,[434] and siloxy and siloxane derivatives of Yb and Nd,[435] Ti and Zr,[436] Ta, Mo and W,[437] and Rh.[438]

Condensing the silane triol $RN(SiMe_3)Si(OH)_3$ with Me_3SiCl gives the diol $RN(SiMe_3)Si(OSiMe_3)(OH)_2$ and couples with alanes to give aluminosiloxanes, while with $Ti(OR')_4$, the $Ti_4Si_4O_{12}$ cage results.[439] Me_3Ga gives the gallium silicates $(RSi)_2(MeGa)_2(Me_2Ga)_2O_6$ (from $[R(OH)SiOGaMe(solv)]_2$ and $GaMe_3$) and $(RSi)_4(Ga[solv])_4O_{12}$, and $(c\text{-}C_6H_{11})_7(Si_7O_9)(OH)_3$ $[L(OH)_3]$ reacts with BuMgEt to give $[L(OH)O_2Mg]_n$ (n=1,2); with $TiCl_4$, $[(c\text{-}C_6H_{11})_7(Si_7O_{12})MgTiCl_3]_n$ results and in the presence of Et_3Al shows high catalytic activity for ethene polymerisation. Other incompletely condensed silasesquioxanes show similar activity.[440]

Condensing $RSi(OH)_3$ (R=t-Bu or $MeCHMeCMe_2$) using $(c\text{-}C_6H_{11}N)_2C$ as dehydrating agent gives $(RSiO_{1.5})_6$ with 6 membered Si_3O_3 rings rather than the 8 membered ones, while $(HSiO_{1.5})_8$ can be derivatised using alcohols and silanols in the presence of catalytic amounts of amines.[441]

(Arylamino)silane triols condense with organotin halides to give acyclic, bicyclic, and cubic stannasiloxanes, and incompletely condensed silsesquioxanes can be deprotonated with $Ph_3P{=}CH_2$ with implication for that of the silica surface.[442] A range of functionalised silsesquioxanes have been prepared and vinyl derivatives used as a synthetic platform for epoxidation.[443] Inter and intramolecular condensation of $(EtO)_3Si(CH_2)_xSi(OEt)_3$ give cyclic disilasesquioxanes, and the spectra of metallosiloxanes derived from $RSi(OH)_3$ have been compared.[444]

Oxidation of the germylene (Mes*)$_2$Ge: with Me$_3$N$^+$-O$^-$ gives the unstable germanone which then isomerises to the germanol. The germylene slowly isomerises in Lewis acids through C-H insertion to give the germaindane.[445] The germocin 2,2′-(4,6-t-Bu$_2$C$_6$H$_2$O)$_2$GeMe$_2$ shows a boat-chair conformation for the ring both in solution and the solid states.[446] Double bond versus carbene-like isomers are compared energetically for Me$_2$XO (X=C,Si,Ge,Sn,Pb) while (ArO)$_2$M: (M=Ge,Sn,Pb) and ArO[(Me$_3$Si)$_2$N]M: are prepared.[447] Condensing CpSnCl with KM(OBu-t)$_3$ gives the novel half sandwich compounds CpSn-(OBu-t)$_3$M (M=Ge, Sn, Pb), the Ge derivative showing two bridged t-BuO groups and Cp acting η^1/η^3.[448]

The organostannates[o-C$_6$H$_4$C(CF$_3$)$_2$O]SnR$_2$(p-MeC$_6$H$_4$)$^-$ with 4 Sn-C bonds are unique in forming complexes but are inert to typical electrophiles,[449] while the 1,5,9-trioxa-4,8-disila-2,6-distannanonane shows a bicyclo[3.3.1]nonane structure.[450]

Stannoxanes catalyse the condensation of lactic acid and reductively couple aryl bromides using Mg/BrCH$_2$CH$_2$Br,[451] while (Bu$_2$SnO)$_n$ is used in oligosaccharide synthesis,[452] and stannylene acetals used in the generation of polyethylene glycols.[453] 1,5-Ph$_3$Ge and 1,6-Bu$_3$Sn groups transfer from enoxy oxygen to alkoxy oxygen occurs through radical mechanisms in keto epoxides and oxetanes,[454] while Sn(IV) enolates result from allylic O-stannyl ketyls and give unsymmetrical ketones.[455] A range of organosubstituted tungstosilicates result from the tin halide and Keggin tungstosilicate heteropolyanions.[456]

ArPb(OAc)$_3$ arylates methyl substituted phenols and N-arylates amides,[457] while vinyl-M (M=Hg, B, Sn) substitutes Pb(OAc)$_4$ to give vinylPb(OAc)$_3$ and (vinyl)$_2$Pb(OAc)$_2$ (M=B).[458]

9 Sulfur, Selenium and Tellurium Derivatives

The asymmetric allylation of RCHO using Ti(IV) is accelerated by Me$_3$SiSPr-i, while coupling alkynyl silyl sulfides with ynamines leads to unstable unsymmetric cyclobutadienes via cyclo-2-enethiones.[459] Pyrolysing HC$\equiv$C-CH$_2$SSiMe$_2$H gives allene and Me$_2$Si=S which dimerises or adds ketene to generate thioketone and (Me$_2$SiO)$_3$.[460] Fluorescence spectra of (Et$_3$Si)$_2$S show the HOMO to be strongly bonding but antibonding for [Et$_3$Si(CH$_2$)$_n$]$_2$S (n=1,2,3), while (Me$_3$Si)$_2$S converts bicyclo[2.2.1]hept-5-enes to bicyclo[3.3.0]octa-3,7-dienes and o-azido aldehydes of furan and thiophene to o-amino thioaldehydes, and WF$_6$ to WSF$_4$.[461]

Cp*$_2$Si: reacts with COS and CS$_2$ to give dithiadisiletanes while RNCS yields Cp*$_2$SiS$_2$C=NR.[462] The disilene R(Mes)Si=Si(Mes)R with CS$_2$ gives the 1,2,4-thiadisiletane-3-thione through silylene addition to CS$_2$ followed by rearrangement of the 3,3′-spirobi(1,2-thiasilirane) intermediate.[463] (Me$_3$Si)$_3$CSiH$_3$ (TsiSiH$_3$) reacts with sulfur to give the Tsi substituted polythia-1,3-disilabicyclo[3.2.1]octane and [2.2.1]heptane.[464]

Rh catalyses the addition of Ar$_2$SiH$_2$ with arene dithiols to give polymers and with ArSH, while 6-coordinate (EtS)$_3$Si substitutes M-H (M=Rh, Ir) eliminates

$(EtS)_3SiH$.[465] $[Me_3Ru(N)Br]^-$ can be thiolated with Me_3SiSNa, hydrolysis giving the Ru(VI) thiol.[466]

$Me_3SiSePh$ gives cluster derivatives with Cd(II) and Hg(II), while $(Me_3Si)_2E$ (E=S,Se) give clusters with Cp^*GaCl_2 and Cu(I) acetate,[467] $[(Me_3Si)_2N]_2VE'SiR_3$ (E'=Se, Te; R=Ph, $SiMe_3$) and $M[E'Si(SiMe_3)_3]_4$ (M=Ti, Zr) from $R_3SiE'Li$[468] while $(Me_3Si)_2Te$ and CuCl give phosphine stabilised copper telluride clusters with up to 28 copper ions depending on the solvent and phosphine chosen.[469]

$Me_2Ge(SLi)_2$ gives the tetrathiagermolane or dithiadigermetane with S_2Cl_2 or Ph_2GeCl_2, which with a 1,4-dithia-2,3-disila-5-titanacyclopentane displace Cp_2TiCl_2 to give the corresponding tetrathiacyclohexane or germa substituted cyclopentane.[470] Oxidising germaketene dithioacetals gives the 1,3,2-dithiagermetan-4-one and the germanone which hydrolyses to the germane diol.[471]

The octamethyldibenzotetraaza[14]annulene dianion $[\eta^4\text{-}Me_8taa^{2-}]$ gives Ge and Sn chalcogenides derivatives $\eta^4\text{-}Me_8taaM{=}X$ (X=S,Se) which add RI and ring open ethylene sulfide (M=Sn).[472]

Tetrathiastannolanes can be desulfurised with Me_3P, the stannylene so formed adding 1,4- to dienes and giving the stannane thione with styrene episulfide.[473] $TbtBSSnPh_2S$ loses $(Ph_2SnS)_3$ on heating while $(R_2SnS)_3$ (R=Me, Ph) add to square planar Pt(II) to give the PtSSnSSn ring.[474]

A series of organotin thioesters have been prepared,[475] while Me_3Al promotes the reaction of organotin thiolates and selenolates with esters.[476] Pyrolysing $Me_3SnTeC_2F_5$ gives $CF_3(F)C{=}Te$ while Ti catalyses the dehyrogenative coupling of Bu_3SnH with $Bu_3P{=}Te$ to give $(Bu_3Sn)_2Te$.[477]

10 Halogen Derivatives

$(C_6F_5)_nSiF_{4-n}$ result from ethoxysilanes using $SOCl_2/SbF_3$, while fluorination of bulky chlorosilanes using hexafluorosilicate salts is accelerated by ultrasound and water.[478] $F_3(X)SiCH_2NMe_2R$ (X=F,Me; R=H,Me) show dynamic behaviour as does $[(F_2SiCH_2)_3F]^-$.[479] Vibrational analysis shows $EtSiHF_2$ to occur as both trans and gauche conformations in the liquid and gas phases, while the conformations of a range of bis(halomethyl)silanes are determined.[480] Me_3SiX (X=Cl, Br) halo substitute a range of transition metal complexes,[481] $X_2Si(I)(tolyl)$ result from SiX_2 (X=F, Cl, Br, I) and I_2 in toluene, the structure of $BrSiH_2CH_2CH_2SiH_2Br$ has been determined, with *gauche* configuration and Si-Br bond of 223.6 pm, while Me_3SiI gives cyclic sulfonium salts through intramolecular RO displacement.[482]

Pd catalyses the cross-coupling of ArCl with chlorosilanes while $R_3SiCl/B(OTf)_3$ provides a supersilylating agent.[483] Ammonium salts induce the redistribution of $RMeSiCl_2$ with $RMeSiH_2$, and CH_2Cl_2/HCl give bis(chlorosilyl)-methanes directly from Si/Cu.[484] Me_3SiCl converts hindered alanes to the chloride, assists in the Clemmensen reduction of metallocenyl ketones, and the Ireland-Claisen rearangement of acrylates, while Me_nMX_{4-n} (M=Si, Ge, Sn; X=Cl, Br, I) add trans to square planar Pt(II).[485]

Tricyclohexyltin fluoride has a polymeric structure,[486] while Me_3SnF fluorinates Cp^*WCl_4 in air to give Cp^*WF_5, cyclopentadienyl substituted imidotitanium chlorides, and various cyclopentadienyl substituted Ti and Zr chlorides.[487] ω-(Trichlorostannyl)alkyl acetates show O-coordination and the structure of $(m\text{-}MeOC_6H_4)_3SnCl$, $(p\text{-}MeSO_2C_6H_4)_3SnCl$, Ph_2SnI_2, and $vi_2SnCl_4^{2-}$are determined, while $(C_6F_5)_2SnBr_2$ catalyses aldol condensations.[488]

11 Organotin-Oxygen Compounds and Complexes

The structures of a range of organotin esters[489] and distannoxanes have been determined,[490] along with studies of P-O derivatives,[491] pyrazoles,[492] N-complexes,[493] S-heterocycles,[494] porphyrin and phenanthroline,[495] and other ligand derivatives.[496]

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The abbreviations below are used for the journal titles, and all refer to 1996 unless otherwise stated, though some are included for clarity. The journal reference alone is quoted for the last section.

ACIE	Angew. Chem., Int. Ed. Engl. **35**,
ACRC	Acta Crystallogr., **C52**,
ACS	Acta Chem. Scand., **50**,
ADOC	Adv. Organomet. Chem.,
AJC	Aust. J. Chem., **49**,
AOC	Appl. Organomet. Chem., **10**,
BCSJ	Bull. Chem. Soc. Jap., **69**,
BSCB	Bull. Soc. Chim. Belges., **105**,
BSCF	Bull. Soc. Chim., Fr.,
CB	Chem. Ber., **128**,
CE	Chem. Express, **11**,
CJC	Can. J. Chem., **74**,
CL	Chem. Lett.,
CPL	Chem. Phys. Lett.,
CR	Chem. Rev., **96**,
CZ	Chem. Ztg., **120**,
EJC	Chem. Eur. J., **2**
GCI	Gazz. Chim. Ital., **126**,
HCA	Helv. Chim. Acta, **79**,
HET	Heterocycles,
IC	Inorg. Chem., **35**,
ICA	Inorg. Chim. Acta,
JACS	J. Amer. Chem. Soc., **118**,
JCC	J. Chem. Soc., Chem. Commun.,
JCRS	J. Chem. Res., (S),
JD	J. Chem. Soc., Dalton Trans.,
JF	J. Chem. Soc., Faraday Trans., **92**,
JFC	J. Fluorine Chem.,
JMS	J. Mol. Struct.,
JOC	J. Org. Chem., **61**,
JOMC	J. Organomet. Chem.,
JP1	J. Chem. Soc., Perkin Trans. 1,
JP2	J. Chem. Soc., Perkin Trans. 2,
JPC	J. Phys. Chem., **100**,
LA	Liebigs Annalen,
MGMC	Main Group Metal Chem., **19**,
MONC	Monatsh. Chem., **127**,
NJC	New J. Chem., **20**,
OMS	Org. Mass Spectrom., **30**,
OPPI	Org. Prep. Prop. Int., **28**,
OR	Organometallics, **15**,
PAC	Pure Appl. Chem., **68**,
PO	Polyhedron, **15**,
PSSi	Phosphorus, Sulfur, and Silicon,
RTC	Rec. Trav. Chim. Pays-Bas., **115**,
SAA	Spectrochim. Acta, Part A, **52**,
SC	Synth. Comm., **26**,
SL	Synlett.,
SRIM	Synth.React.Inorg.Met-org.Chem.,**26**,
SY	Synthesis,
TA	Tetrahedron Asymmetry, **7**,
TET	Tetrahedron, **52**,
TL	Tetrahedron Lett., **37**,
ZAAC	Z. Anorg. Allg. Chem., **622**,
ZC	Z. Chem., **36**,
ZN	Z. Naturforsch., Teil B, **51**,

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130. M.Trommer and W.Sander, *OR* 189; W.Kirmse, M.Guth, and S.Steenken, *JACS* 10838.
131. T.-H.Chuang, J.-M.Fang, W.-T.Jiaang, and Y.-M.Tsai, *JOC* 1794; B.F.Bonini, M.Comes-Franchini, M.Fochi, G.Mazzanti, and A.Ricci, *TET* 4803.
132. H.Shinokubo, K.Oshima, and K.Utimoto, *TET* 14533; I.Ryu, H.Yamamoto, N.Sonoda, and S.Murai, *OR* 5459; A.R.Katritzky, Z.Wang, and H.Lang, *OR* 486.
133. A.G.Brook, A.Ionkin, and A.J.Lough, *OR* 1275.
134. J.Ohshita, S.Masaoka, Y.Masaoka, H.Hasabe, M.Ishikawa, A.Tachibana, T.Yano, and T.Yamabe, *OR* 3136; A.S.Batsanov, I.M.Clarkson, J.A.K.Howard, and P.G.Steel, *TL* 2491.
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136. A.I.Kruppa, M.B.Taraban, S.A.Svarovsky, and T.V.Leshina, *JP2* 2151.
137. K.Fujii, O.Hara, Y.Fujita, and Y.Sakagami, *TL* 389; R.K.Bhatt, J.Ye, and J.R.Falck, *TL* 3811.
138. J.H.Smitrovich and K.A.Woerpel, *JOC* 6044; J.S.Koh and J.A.Ellman, *JOC* 4494; T.Billard and B.R.Langlois, *TL* 6865.
139. W.-P.Leung, K.S.M.Poon, T.C.W.Mak, and Z.-Y.Zhang, *OR* 3262; M.B.Hursthouse, K.J.Izod, M.Motevalli, and P.Thornton, *PO* 135; W.-P.Leung, H.K.Lee, L.-H. Weng, B.-S.Luo, Z.-Y.Zhou, and T.C.W.Mak, *OR* 1785.
140. M.Laguerre and M.Grignon-Dubois, *JMS* 1994, **319**, 167; A.D.Frankland and M.F.Lappert, *JD* 4151.
141. D.Steiner, H.-J.Winkler, C.Balzereit, T.Happel, M.Hofmann, G.Subramanian, P. von R. Schleyer, W.Massa, and A.Berndt, *ACIE* 1990; W.Uhl, I.Hahn, M.Koch, and M.Layh, *ICA* **249**, 33.
142. W.Uhl, U.Schutz, S.Pohl, and W.Saak, *ZAAC* 373; W.Uhl, I.Hahn, U.Schutz, S.Pohl, W.Saak, J.Martens, and J.Manikowski, *BC* 897.
143. W.Uhl, R.Graupner, and H.Reuter, *JOMC* **523**, 227.
144. M.A.Mohammed, K.H.Ebert, and H.J.Breunig, *ZN* 149.
145. A.R.Johnson, W.M.Davis, and C.C.Cummins, *OR* 3825; T.R.Belderrain, M.Paneque, V.Sernau, E.Carmona, E.Gutierrez, and A.Monge, *PO* 3501; N.S.Radu, T.D.Tilley, and A.L.Rheingold, *JOMC* **516**, 41; S. Di Bella, G.Lanza, I.L.Fragala, and T.J.Marks, *OR* 205.
146. A.I.Almansour, *JOMC* **510**, 117; F.Adam, C.Eaborn, P.B.Hitchcock, and J.D.Smith, *JCC* 741.
147. C.Eaborn, P.B.Hitchcock, A.Kowalewska, Z.-R.Lu, J.D.Smith, and W.A.Stanczyk, *JOMC* **521**, 113.
148. A.G.Avent, W.-Y.Chen, C.Eaborn, I.B.Gorrell, P.B.Hitchcock, and J.D.Smith, *OR* 4343.
149. A.Haaland, K.-G.Martinsen, H.V.Volden, W.Kaim, E.Waldhor, W.Uhl, and U.Schutz, *OR* 1146; W.Uhl, S.U.Keimling, W.Hiller, and M.Neumayer, *CB* 143.
150. D.A.Antonov, C.Eaborn, J.D.Smith, P.B.Hitchcock, E.Molla, V.I.Rozenberg, W.A.Stanncyk, and A.Kowaleska, *JOMC* **521**, 109.
151. M.Westerhausen, M.Wieneke, K.Doderer, and W.Schwarz, *ZN* 1439; S.S.Al-Juaid, C.Eaborn, P.D.Lickiss, J.D.Smith, K.Tavakkoli, and A.D.Webb, *JOMC* **510**, 143.
152. A.G.Davies, C.Eaborn, P.D.Lickiss, and A.G.Neville, *JP2* 163.

153. C.D.Sherrill, C.G.Brandow, W.D.Allen, and H.F.Schaefer III, *JACS* 7158; E.J.P.Maler, *TET* 4697; A.Goller, H.Heydt, and T.Clark, *JOC* 5840.
154. B.P.S.Chauhan, Y.Tanaka, H.Yamashita, and M.Tanaka, *JCC* 1207; R.Damrauer and J.A.Hankin, *JOMC* **521**, 93.
155. H.H.Karsh, R.Richter, and E.Witt, *JOMC* **521**, 185; D.Damour, M.Barreau, F.Dhaleine, G.Doerflinger, M.Vuilhorgne, and S.Mignani, *SL* 890; M.G.Steinmetz, Q.Chen, and Y.Zheng, *JOMC* **516**, 25.
156. J.M.White, W.-Y.Tham, and A.J.Green, *ACRC* 1493; M.Oba, Y.Kawahara, R.Yamada, H.Mizuta, and K.Nishiyama, *JP2* 1843; M.Huttenhofer, M.-H.Prosene, U.Rief, F.Schaper, and H.-H.Brintzinger, *OR* 4816.
157. B.Wrackmeyer, U.Klaus, W.Milius, E.Klaus, and T.Schaller, *JOMC* **517**, 235.
158. M.A.Dam, O.S.Akkerman, F.J.J. de Kanter, F.Bickelhaupt, N.Vedman, and A.L.Spek, *EJC* 1139.
159. B.Wrackmeyer, H.E.Maisel, J.Suss, and W.Milius, *ZN* 1320.
160. W.P.Freeman, T.D.Tilley, G.P.A.Yap, and A.L.Rheingold, *ACIE* 882.
161. J.-H.Hong, P.Boudjouk, and I.Stoenescu, *OR* 2179; B.Goldfuss, P. von R. Schleyer, and F.Hampel, *OR* 1755.
162. S.Yamaguchi and K.Tamao, *BCSJ* 2327.
163. A.H.J.F. de Keijzer, F.J.J. de Kanter, M.Schakel, R.F.Schmitz, and G.W.Klumpp, *ACIE* 1127.
164. J.-H.Hong, Y.Pan, and P.Boudjouk, *ACIE* 186.
165. R.West, H.Sohn, D.R.Powell, T.Muller, and Y.Apeloig, *ACIE* 1002.
166. V.N.Khabashesku, S.E.Boganov, D.Antic, O.M.Nefedov, and J.Michl, *OR* 4714.
167. J.Krause, K.-J.Haack, K.-R.Porschke, B.Gabor, R.Goddard, C.Pluta, and K. Seevogel, *JACS* 804; B.Wrackmeyer and U.Klaus, *JOMC* **520**, 211.
168. C.Eaborn, Z.-R.Lu, P.B.Hitchcock, and J.D.Smith, *OR* 1651.
169. E.Lukevics, S.Belyakov, and O.Pudova, *JOMC* **523**, 41; W.Ziche, B.Zeimer, P.John, J.Weis, and N.Auner, *JOMC* **521**, 29.
170. M.Kosugi, T.Tanji, Y.Tanaka, A.Yoshida, K.Fugami, M.Kameyama, and T.Migita, *JOMC* **508**, 255.
171. S.K.Ritter, R.L.Kirchmeier, J.M.Shreeve, and H.Oberhammer, *IC* 4067; V.A.Naumov, M.B.Zuev, D.W.H.Rankin, and H.E.Robertson, *JMS* 1994, **318**, 151; L.Xue, L.S.Pedersen, Q.Liu, R.Narske, and D.J.Burton, *TL* 1921.
172. P.H.Mason and N.D.Emslie, *SC* 1473; S.Menichetti and C.J.M.Stirling, *JP1* 1511.
173. Y.-G.Zhou, A.-H.Li, X.-L.Hou, and L.-X.Dai, *JCC* 1353; B.Bohler, D.Huis, and H.Gartier, *TL* 8719.
174. D.P.Stamos, A.G.Taylor, and Y.Kishi, *TL* 8647; S.Yamazaki, M.Tanaka, and S.Yamabe, *JOC* 4046; R.S.Atkinson, M.P.Coogan, and I.S.T.Lochrie, *TL* 5179; M.M.Kabat, *TL* 7437.
175. E.Lukevics, V.Dirnens, A.Kemme, and J.Popelis, *JOMC* **521**, 235; V.Fiandanese, G.Marchese, A.Punzi, and G.Ruggieri, *TL* 8455; D.Mesnard, N.Hanai, and L.Miginiac, *JOMC* **509**, 125.
176. A.R.Bassindale, I.Katampe, P.A.Kyle, and P.G.Taylor, *JP1* 327; M.Sanchez, R.Reau, F.Dahan, M.Regitz, and G.Bertrand, *ACIE* 2228.
177. S.-K.Kang, H.-W.Lee, S.-B.Jang, T.-H.Kim, and J.-S.Kim, *SC* 4311; S.-K.Kang, T.Yamaguchi, T.-H.Kim, and P.-S.Ho, *JOC* 9082; G.Langli, L.-L.Gundersen, and F.Rise, *TET* 5625; Z.Liu and J.Meinwald, *JOC* 6693.
178. T.Braun, P.Meuer, and H.Werner, *OR* 4075; M.-F.Zou and M.-Z.Deng, *JOC* 1857.
179. M.Niestroj, W.P.Neumann, and T.N.Mitchell, *JOMC* **519**, 45; V.Fargeas, P. Le Menez, I.Berque, J.Ardisson, and A.Pancrazi, *TET* 6613.

180. F.D'Aniello, A.Mann, and M.Taddei, *JOC* 4870; J.Thibonnet, M.Abarbri, J.-L. Parrain, and A.Duchene, *TL* 7507; E.Piers, E.J.McEachern, and M.Romero, *TL* 1173; E.Piers amd E.J.McEachern, *SL* 1087.
181. M.Suginome, A.Matsumoto, and Y.Ito, *JACS* 3961; W.E.Crowe, D.R.Goldberg, and Z.J.Zhang, *TL* 2117.
182. P.V.Fish, *SC* 433.
183. K.Omoto, Y.Sawada, and H.Fujimoto, *JACS* 1750; R.Gewald, M.Kira, and H.Sakurai, *SY* 111; A.S.Pilcher and P.DeShong, *JOC* 6901.
184. D.R.Gautier, jr., and E.M.Carriera, *ACIE* 2363; Y.Horiuchi, K.Oshima, and K.Utimoto, *JOC* 4483; V.K.Aggarwal and G.P.Vennali, TL *3745*.
185. C.C.Silveira, G.L.Fiorin, and A.L.Braga, *TL* 6085; N.Asao, E.Yoshikawa, Y.Yamamoto, *JOC* 4874; C. Le Roux and J.Dubac, *OR* 4646; F.J.Blanco, P.Cuadrado, A.M.Gonzalez, and F.J.Pulido, *SY* 42.
186. Y.Landais and L.Parra-Rapado, *TL* 1205; M.-R.Schneider, A.Mann, and M.Taddei, *TL* 8493; T.Kercher and T.Livinghouse, *JACS* 4200; Y.Yamamoto, M.Ohno, and S.Eguchi, *BCSJ* 1353.
187. H.Pellissier, S.Wilmouth, and M.Santelli, *TL* 5107; C.W.Holzapfel and T.L. van der Merwe, *TL* 2303 and 2307; H.Monti, G.Audran, M.Feraud, J.-P. Monti, and G.Leandri, *TET* 6685; C.Kuroda, N.Mitsumata, and C.Y.Tang, *BCSJ* 1409; D.Schinzer and G.Panke, *JOC* 4496.
188. V.Huc, P.Boussaguet, and P.Mazerolles, *JOMC* **521**, 253; G.Ferguson and C.Glidewell, *ACRC* 1889.
189. I.Kadota, T.Sakahaira, and Y.Yamamoto, *TL* 3195; K.Miura, D.Itoh, T.Hondo, H.Saito, H.Ito, and A.Hosomi, *TL* 8539; J.A.Marshall and A.W.Garofalo, *JOC* 8732; Y.Nishigaichi, M.Yoshikawa, Y.Takigawa, and A.Takuwa, *CL* 961.
190. T.M.Cokley, R.L.Marshall, A.McCluskey, and D.J.Young, *TL* 1905; J.K.Whitesell and R.Apodaca, *TL* 3955; S.Kobayashi and S.Nagayama, *JOC* 2256; X.Li, J.J.Chen, and D.D.Tanner, *JOC* 4314.
191. H.-S.Dang and B.P.Roberts, *JP1* 1493.
192. H.J.Reich and J.E.Holladay, *ACIE* 2365; T.A.Engler, K.Agrios, J.P.Reddy, and R.Iyengar, *TL* 327; F.G.N.Cloke, M.G.Gardiner, C.L.Raston, and S.J.Simpson, *JOMC* **507**, 245.
193. S.Kadota, D.Hatakeyama, K.Seki, and Y.Yamamoto, *TL* 3059; Y.Yamamoto, M. Al-Masum, and N.Fujiwara, *JCC* 381.
194. O.Lavastre, L.Ollivier, P.H.Dixneuf, and S.Sibandhit, *TET* 5495; K.Ebata, T.Matsuo, T.Inoue, Y.Otsuka, C.Kabuto, A.Sekiguchi, and H.Sakurai, *CL* 1053.
195. R.Gleiter and H.Stahr, *TL* 1179.
196. P.Timmerman, H.L.Anderson, R.Faust, J.-F.Nierengarten, *TET* 4925; N.Jux, K.Holczer, and Y.Rubin, *ACIE* 1986.
197. H.Sugita, Y.Hatanaka, and T.Hiyama, *SL* 637.
198. R.Ziessel, J.Suffert, and M.-T.Youinou, *JOC* 6535; S.Wilson and H.L.Anderson, *SL* 1039; E.Alvarez, R.Perez, M.Rico, R.M.Rodriguez, M.C.Suarez, and J.D.Martin, *SL* 1082; M.R.Attwood, T.M.Raynham, D.G.Smyth, and G.R.Stephenson, *TL* 2731.
199. V.V.Zhdankin, C.J.Kuehl, A.P.Krasutsky, J.T.Bolz, and A.J.Simonsen, *JOC* 6547; E.Lorthiois, I.Marek, and J.-F.Normant, *TL* 6693; D.Llerana, C.Aubert, and M.Malacria, *TL* 7353; I.Sato, Y.Akshori, K.-i.Iida,and M.Hirama, *TL* 5135.
200. M.Kida, T.Sueda, S.Goto, T.Okuyama, and M.Ochiai, *JCC* 1933; R.F.Cunico and S.K.Nair, *SC* 803; J.G.Garcia, B.Ramos, A.Rodriguez, and F.R.Fronczek, *ACRC* 259.

201. B.Wrackmeyer, J.Suss, and W.Milius, *CB* 147; G.Roth and H.Fischer, *OR* 5766; R.F.Cunico, *TL* 437; R.J.Linderman and S.Chen, *TL* 3819
202. P.T.Witte, R.Klein, H.Kooijman, A.L.Spek, M.Polasek, V.Varga, and K.Mach, *JOMC* **519**, 195; V.Varga, L.Petrusova, J.Cejka, V.Hanus, and K.Mach, *JOMC* **509**, 235; V.Varga, K.Mach, M.Polasek, P.Sedmera, J.Hiller, U.Thewalt, S.I.Troyanov, *JOMC* **506**, 241.
203. P.Arndt, C.Lefeber, R.Kempe, A.Tillack, and U.Rosenthal, *CB* 1281; J.Hiller, U.Thewalt, M.Polasek, L.Pertrusova, V.Varga, P.Sedmera, and K.Mach, *OR* 3752; N.Peulecke, A.Ohff, A.Tillack, W.Baumann, R.Kempe, V.V.Burlakov, and U.Rosenthal, *OR* 1340; N.Peulecke, C.Lefeber, A.Ohff, W.Baumann, A.Tilack, R.Kempe, V.V.Burlakov, and U.Rosenthal, *CB* 959; C.Lefeber, W.Baumann, A.Tillack, R.Kempe, H.Gorls, and U.Rosenthal, *OR* 3486; P.Arndt, C.Lefeber, R.Kempe, and U.Rosenthal, *CB* 1281.
204. V.Varga, M.Polasek, J.Hiller, U.Thewalt, P.Sedmera, and K.Mach, *OR* 1268; R.Beckhaus, T.Wagner, and B.Ganter, *OR* 1176; S.S.H.Mao and T.D.Tilley, *JOMC* **521**, 425; K.Oouchi, M.Mitani, M.Hayakawa, T.Yamada, and T.Mukaiyama, *JOMC* **516**, 111.
205. J.W.Herndon and P.P.Patel, *JOC* 4500; M.I.Bruce, P.J.Low, A.Werth, B.W.Skelton, and A.H.White, *JD* 1551; K.D.John, S.J.Geib, and M.D.Hopkins, *OR* 4357; R.R.Schrock, S.Luo, J.C.Lee, Jr., N.C.Zanetti, and W.M.Davis, *JACS* 3883.
206. H.Wadepohl, A.Wolf, and H.Pritzkow, *JOMC* **506**, 287; O.Gevert, J.Wolf, and H.Werner, *OR* 2806; M.A.Esteruelas, F.J.Lahoz, E.Onate, L.A.Oro, L.Rodriguez, P.Steinert, and H.Werner, *OR* 3436.
207. H.Katayama, K.Onitsuka, and F.Ozawa, *OR* 4642; B.Wrackmeyer, U.Dorfler, W.Milius, and M.Herberhold, *ZN* 851.
208. L.P.Clarke, J.E.Davies, P.R.Raithby, and G.P.Shields, *JD* 4147; H.Lang, M.Weinmann, and L.Zsolnai, *JOMC* **522**, 277; E.Ramirez-Oliva, J.Cervantes, F.Cervantes-Lee, R.N.Kapoor, and K.H.Pannell, *JOMC* **510**, 57.
209. R.J.P.Corriu, N.Devylder, C.Guerin, B.Henner, and A.Jean, *JOMC* **509**, 249.
210. U.H.F.Bunz and J.E.C.Wiegelmann-Kreiter, *CB* 785; D.Steinborn, M.Gerisch, K.Merzweiler, K.Schenzel, K.Pelz, and H.Bogel, *OR* 2454; I.Ara, J.R.Berenguer, J.Fornies, E.Lalinde, and M.T.Moreno, *OR* 1820.
211. M.D.Janssen, M.Herres, L.Zsolnai, A.L.Spek, D.M.Grove, H.Lang, and G. van Koten, *IC* 2476; H.Lang, W.Frosch, I.Y.Wu, S.Blau, and B.Nuber, *IC* 6266; C.Brasse, P.R.Raithby, M.-A.Rennie, C.A.Russell, A.Steiner, D.S.Wright, *OR* 639; H.Lang, K.Kohler, and L.Zsolnai, *JCC* 2043.
212. H.Sugita, Y.Hatanaka, and T.Hiyama, *CL* 379; P.Doppelt and T.H.Baum, *JOMC* **517**, 53.
213. V.Varga, J.Hiller, M.Polasek, U.Thewalt, and K.Mach, *JOMC* **514**, 219, and **515**, 57.
214. J.E.Mangette, D.R.Powell, T.K.Firman, and R.West, *JOMC* **521**, 363; M.Wind, D.R.Powell, and R.West, *OR* 5772.
215. M.Kira, T.Iwamoto, and C.Kabuto, *JACS* 10303.
216. M.Weidenbruch, P.Will, K.Peters, H.G.von Schnering, and H.Marsmann, *JOMC* **521**, 355; H.Sakurai, M.Yoshida, and K.Sakamoto, *JOMC* **521**, 287.
217. Y.Rsuji, M.Funato, M.Ozawa, H.Ogiyama, S.Kajita, and T.Kawamura, *JOC* 5779; M.Siginome, A.Matsumoto, and Y.Ito, *JOC* 4884; M.Suginome, S.-i.Matsunaga, T.Iwanami, A.Matsumoto, and Y.Ito, *TL* 8887; J.Ohshita, H.Niwa, M.Ishikawa, T.Yamabe, T.Yoshii, and K.Nakamura, *JACS* 6853; A.Kunai, T.Ueda, K.Horata, E.Toyoda, I.Nagamoto, J.Ohshita, M.Ishikawa, and K.Tanaka, *OR* 2000; A.K.-S.Tse, R.-J.Wang, T.C.W.Mak, and K.S.Chan, *CC* 173.

218. S.T.Lee, E.K.Baek, and S.C.Shim, *OR* 2182; G.Liu, L.Heisler, L.Li, and M.G.Steinmetz, *JACS* 11412.
219. J.Ohshita, H.Niwa, and M.Ishikawa, *OR* 4632; N.P.Toltl and W.J.Leigh, *OR* 2554.
220. R.M.Shaltout and J.Y.Corey, *OR* 2866; J.Y.Corey and S.M.Rooney, *JOMC* **521**, 75.
221. K.Tamao, M.Asahara, and A.Kawachi, *JOMC* **521**, 325.
222. R.Becerra, H.M.Frey, B.P.Mason, and R.Walsh, *JOMC* **521**, 343.
223. M.Soldner, A.Schier, and H.Schmidbaur, *JOMC* **521**, 295.
224. T.Seki, A.Tohnai, T.Tamaki, and A.Kaito, *CL* 361; M.P.Clarke, M.Conqueror, G.H.Morgan, and I.M.T.Davidson, *JOMC* **521**, 395; U.Herzog, E.Brendler, and G.Roewer, *JOMC* **511**, 85.
225. F.Hojo, T.Terashima, and W.Ando, *OR* 3480; F.Hojo, K.Fujiki, and W.Ando, *OR* 3606.
226. A.Naka, M.Hayashi, S.Okazaki, A.Kunai, and M.Ishikawa, *OR* 1101; A.Naka, T.Okada, and M.Ishikawa, *JOMC* **521**, 163.
227. Y.Uchimaru and M.Tanaka, *JOMC* **521**, 335.
228. M.Suginome, H.Oike, S.-S.Park, and Y.Ito, *BCSJ* 289; M.Suginome, H.Oike, P.H.Shuff, and Y.Ito, *OR* 2170.
229. R.Wyrwa, H.-O.Frohlich, and H.Gorls, *OR* 2833.
230. S.Kyushin, M.Ikarugi, K.Takatsuna, M.Goto, and H.Matsumoto, *JOMC* **510**, 121.
231. K.-H.Thiele, C.Schliessburg, K.Baumeister, and K.Hassler, *ZAAC* 1806; P.J.Dyson, A.G.Hulkes, and P.Suman, *CC* 2223; N.P.Reddy, T.Hayashi, and M.Tanaka, *CC* 1865.
232. V.K.Dioumaev and J.F.Harrod, *JOMC* **521**, 133; W.Uhlig, *JOMC* **516**, 147.
233. B.Lacave-Goffin, L.Hevesi, and J.Devaux, *CC* 765; U.Herzog, R.Richter, E.Brendler, and G.Roewer, *JOMC* **507**, 221.
234. A.Zechmann and E.Hengge, *JOMC* **508**, 227; M.Yoshida, T.Seki, F.Nakanishi, K.Sakamoto, and H.Sakurai, *CC* 1381; T.Yatabe, M.Shimomura, and A.Kaito, *CL* 551.
235. Y.Apeloig and D.Danovich, *OR* 350.
236. U.Poschl, H.Siegl, and K.Hassler, *JOMC* **506**, 93; U.Poschl and K.Hassler, *OR* 3238; J.A.Boatz and M.S.Gordon, *OR* 2118.
237. N.Wiberg, C.M.M.Finger, H.Auer, and K.Polborn, *JOMC* **521**, 377.
238. J.Belzner, H.Ihmels, B.O.Kneisel, and R.Herbst-Irmer, *CB* 125.
239. K.Furukawa, M.Fijino, and N.Matsumoto, *JOMC* **515**, 37; M.Unno, T.Yokota, and H.Matsumoto, *JOMC* **521**, 409.
240. S.Kyushin, Y.Yagihashi, and H.Matsumoto, *JOMC* **521**, 413.
241. L.H.McAlexander, M.Hung, L.Li, J.B.Diminnie, Z.Xue, G.P.A.Yap, and A.L.Rheingold, *OR* 5231; S.Nlate, E.Herdtweck, and R.A.Fischer, *ACIE* 1861.
242. G.P.Mitchell and T.D.Tilley, *OR* 3477.
243. K.W.Klinkhammer, and J.Weidlein, *ZAAC* 1209.
244. G.Linti, R.Frey, W.Kostler, and H.Urban, *CB* 561; G.Linti, *JOMC* **520**, 107; G.Linti and W.Kostler, *ACIE* 550.
245. Y.Apeloig, M.Bendikov, M.Yuzefovich, M.Nakash, and D.Bravo-Zhivotovskii, *JACS* 12228; M.Ishikawa, S.Matsui, A.Naka, and J.Ohshita, *OR* 3836; J.Ohshita, S.Masaoka, and M.Ishikawa, *OR* 2198.
246. F.Luderer, H.Reinke, and H.Oehme, *CB* 15.
247. E.Jeschke, T.Gross, H.Reinke, and H.Oehme, *CB* 841.
248. H.-S.Dang and B.P.Roberts, *JPI* 769.

249. C.Chatgilialoglu, M.Ballestri, D.Vecchi, and D.P.Curran, *TL* 6383; C.Chatgilialoglu, C.Ferreri, M.Ballestri, and D.P.Curran, *TL* 6387; C.Dufour, S.Iwasa, A.Fabre, and V.H.Rawal, *TL* 7867.
250. J.B.Lambert, J.L.Pflug, and J.M.Denari, *OR* 615.
251. S.Freitag, R.Herbst-Irmer, L.Lameyer, and D.Stalke, *OR* 2839.
252. S.P.Mallela, F.Schwan, and R.A.Geanangel, *IC* 745 and *JD* 4183.
253. N.Wiberg, W.Hochmuth, H.Noth, A.Appel, and M.Schmidt-Amelunxen, *ACIE* 1333.
254. T.Ohtaki and W.Ando, *OR* 3103.
255. H.Komoriya, M.Kako, Y.Nakadaira, and K.Mochida, *OR* 2014.
256. M.Kira, T.Iwamoto, T.Maruyama, C.Kabuto, and H.Sakurai, *OR* 3767.
257. T.Akasaka, T.Kato, S.Nagase, K.Kobayashi, K.Yamamoto, H.Funasaka, and T.Takahashi, *TET* 5015; N.P.Toltl, W.J.Leigh, G.M.Kollegger, W.G.Stibbs, and K.M.Baines, *OR* 3732; J.A.Cooke, C.E.Dixon, M.R.Netherton, G.M.Kollegger, and K.M.Baines, *SRIM* 1205.
258. M.Weidenbruch, A.Hagedorn, K.Peters, and H.G. von Schnering, *CB* 401.
259. A.G.M.Barrett and P.W.H.Wan, *JOC* 8667; N.Isono and M.Mori, *JOC* 7867; H.Sato, N.Isono, I.Miyoshi, and M.Mori, *TET* 8143.
260. T.Nakano, K.Ono, and T.Migita, *CL* 697; M.Suginome, H.Oike, P.H.Shuff, and Y.Ito, *JOMC* **521**, 405.
261. H.K.Sharma, F.Cervantes-Lee, L.Parkanyi, and K.H.Pannell, *OR* 429.
262. L.Parkanyi, A.Kalman, K.H.Pannell, F.Cervantes-Lee, and R.N.Kapoor, *IC* 6622.
263. A.Modelli, D.Jones, L.Favaretto, and G.Distefano, *OR* 380; K.Mochida, T.Ohkawa, H.Kawata, A.Watanabe, O.Ito, and M.Matsuda, *BCSJ* 2993; N.Devylder, M.Hill, K.C.Molloy, and G.J.Price, *CC* 711.
264. M.Herberhold, U.Steffl, W.Milius, and B.Wrackmeyer, *ACIE* 1803; Y.Obora, Y.Tsuji, K.Nishiyama, M.Ebihara, and T.Kawamura, *JACS* 10922.
265. M.-A.Chaubon, J.Escudie, H.Ranaivonjatovo, and J.Satge, *CC* 2621.
266. M.B.Haque and B.P.Roberts, TL 9123; P.D.Lickiss and R.Lucas, *JOMC* **521**, 229; A.Kunai, T.Sakurai, E.Toyoda, and M.Ishikawa, *OR* 2478; F.Fabris and O. De Lucchi, *JOMC* **509**, 15.
267. U.P.Dhokte and H.C.Brown, *OR* 3504; P.-L.Wu, S.-Y.Peng, and J.Magrath, *SY* 249; M.J.Roth, M.A.Brook, and H.B.Penny, *JOMC* **521**, 65.
268. E.Hengge, P.Gspaltl, and E.Pinter, *JOMC* **521**, 145; J.-M.Planeix, B.Coq, L.-C. de Menorva, and P.Medina, *CC* 2087.
269. T.Langer, J.Janssen, and G.Helmchen, *TA* 1599; Y.Nishibayashi, K.Segawa, J.D.Singh, S.-i.Fukuzawa, K.Ohe, and S.Uemura, *OR* 370; M.E.Wright and B.B.Cochran, *OR* 317; X.Wang, W.W.Ellis, and B.Bosnich, *CC* 2561; Y.Kawanami and K.Yamamoto, *BCSJ* 1117.
270. R.Takeuchi and H.Yasue, *OR* 2098; K.Tamao, K.Nakamura, H.Ishii, S.Yamaguchi, and M.Shiro, *JACS* 12469; I.Ojima, J.V.McCullagh, and W.R.Shay, *JOMC* **521**, 421; I.Ojima, D.F.Kass, and J.Zhu, *OR* 5191.
271. J.-P.Barnier and L.Blanco, *JOMC* **514**, 67; R.T.Buck, M.P.Doyle, M.J.Drysdale, L.Ferris, D.C.Forbes, D.Haigh, C.J.Moody, N.D.Pearson, and Q.-L.Zhou, *TL* 7631; H.R.Brinkman, W.H.Miles, M.D.Hilborn, and M.C.Smith, *SC* 973.
272. Y.Nishibayashi, K.Segawa, H.Takada, K.Ohe, and S.Uemura, *CC* 847; M.A. Esteruelas, M.Olivan, and L.A.Oro, *OR* 814; M.A.Esteruelas, F.J.Lahoz, E.Onate, L.A.Oro, and L.Rodriguez, *OR* 823.
273. D.Y.Son, D.Bucca, and T.M.Keller, *TL* 1579; M.Rivera-Claudio, J.Rozell,

E.Ramirez-Oliva, J.Cervantes, and K.H.Pannell, *JOMC* **521**, 267; L.N.Lewis, J.Stein, R.E.Colborn, Y.Gao, and J.Dong, *JOMC* **521**, 221.

274. H.Kotsuki, P.K.Datta, and H.Suenaga, *SY* 470; T.Tanase, T.Ohizumi, K.Kobayashi, and Y.Yamamoto, *OR* 3404; B.Rousseau, F.Nydegger, A.Gossauer, B.Bennau-Skalmowski, and H.Vorbruggen, *SY* 1336.
275. R.Boukherroub, C.Chatgilialoglu, and G.Manuel, *OR* 1508; S.Shimada, M.Tanaka, and M.Shiro, *ACIE* 1856.
276. G.A.Molander and P.J.Nichols, *JOC* 6040; X.Verdaguer, U.E.W.Lange, M.T.Reding, and S.L.Buchwald, *JACS* 6784.
277. W.Abdelqader, D.Chmielewski, F.-W.Grevels, S.Ozkar, and N.B.Peynircioglu, *OR* 604; M.D.Cavanaugh, B.T.Gregg, and A.R.Cutler, *OR* 2764.
278. R.S.Simons and C.A.Tessier, *OR* 2604; M.Akita, R.Hua, T.Oku, and Y.Moro-oka, *OR* 2548.
279. F.Maseras and A.Lledos, *OR* 1218.
280. M.L..Buil, P.Espinet, M.A.Esteruelas, F.J.Lahoz, A.Lledos, J.M.Martinez-Ilarduya, F.Maseras, J.Modrego, E.Onate, L.A.Oro, E.Sola, and C.Valero, *IC* 1250.
281. M.Taoufik, C.C.Santini, J.-P.Candy, A. de Mallmann, and J.M.Basset, *JACS* 4167; S.G.Anema, K.M.Mackay, and B.K.Nicholson, *JD* 3853.
282. R.Xi, J.R.Babcock, and L.R.Sita, *OR* 2849; M.-F.Connil, B.Jousseaume, and M.Pereyre, *OR* 4469.
283. S.Hanessian, U.Reinhold, and S.Ninkovic, *TL* 8967; T,Kawakami, M.Miyatake, I.Shibata, and A.Baba, *JOC* 376; D.P.Curran and S.Hadida, *JACS* 2531.
284. U.Patzold, G.Roewer, and U.Herzog, *JOMC* 508, 147.
285. L.Chen, F.A.Cotton, and W.A.Wojtczak, *IC* 2988; N.Asao, J.-X.Liu, T.Sudoh, and Y.Yamamoto, *JOC* 4568.
286. A.Khaleel and K.J.Klabunde, *IC* 3223; P.Kapoor, V.Yu. Kukushkin, K.Lovqvist, and A.Oskarsson, *JOMC* **517**, 71.
287. J.Adrio, J.C.Carretero, and R.Gomez Arrayas, *SL* 640; Y.-M.Tsai, K.-H.Tang, and W.-T.Jiaang, *TL* 7767; D.S.Hays and G.C.Fu, *JOC* 4; C.J.Hayes and G.Pattenden, *TL* 271; E.J.Enholm and Z.J.Jia, *TL* 1177.
288. M.-J.Wu, C.-L.Fu, T.-H.Duh, and J.-Y.Yeh, *SY* 462; S.Tsunoi, I.Ryu, M.Tanaka, M.Komatsu, and N.Sonada, *TL* 6729; M.Lautens, S.Kumanovic, and C,Meyer, *ACIE* 1329; F.Ferri and M.Alami, *TL* 7971.
289. S.Kim and S.Y.Jon, *CC* 1335; D.Crich, X.-Y.Jiao, Q.Yao, and J.S.Harwood, *JOC* 2368; C.H.Schiesser and M.A.Skidmore, *CC* 1419.
290. A.Kawachi and K.Tamao, *OR* 4653.
291. I.Fleming, R.S.Roberts, and S.C.Smith, *TL* 9395.
292. I.Fleming, M.Solay, and F.Stolwijk, *JOMC* **521**, 121.
293. T.Kusukawa and W.Ando, *ACIE* 1315; E.Nagashima, M.Saito, Y.Kato, H.Goto, E.Osawa, M.Hage, and K.Itoh, *TET* 5053.
294. S.Weigand and R.Bruckner, *SY* 475; Y.Horikawa and T.Takeda, *JOMC* **523**, 99.
295. C.H.Schiesser, M.L.Styles, and L.M.Wild, *JP2* 2257; H.Tanaka, H.Ogawa, H.Suga, S.Torii, A.Jutand, S.Aziz, A.G.Suarez, and C.Amatore, *JOC* 9402.
296. J.Marco-Contelles, *CC* 2629.
297. N.Metzler and M.Denk, *CC* 2657.
298. M.Suginome, H.Nakamura, and Y.Ito, *CC* 2777.
299. L.Wesemann and B.Ganter, *OR* 2569.
300. L.Wesemann and U.Englert, *ACIE* 527; J.A.Dopke, A.N.Bridges, M.R.Schmidt, and D.F.Gaines, *IC* 7186.

301. N.S.Hosmane, H.Zhang, J.A.Maguire, Y.Wang, C.J.Thomas, and T.G.Gray, *ACIE* 1000.
302. L.Wesemann, Y.Ramjoie, B.Ganter, and H.Maisch, *CB* 837; C.Nachtigal and W.Preetz, *ZN* 1061.
303. N.Wiberg, K.Amelunxen, H.Noth, M.Schmidt, and H.Schwenk, *ACIE* 65.
304. N.S.Radu, F.J.Hollander, T.D.Tilley, and A.L.Rheingold, *CC* 2459.
305. L.Li, J.B.Diminnie, X.Liu, J.L.Pollitte, and Z.Xue, *OR* 3520; M.L.H.Green and A.K.Hughes, *JOMC* **506**, 221; U.Schubert and H.Gilges, *OR* 2373; M.D.Fryzuk, L.Rosenberg, and S.J.Rettig, *OR* 2871.
306. F.Ozawa and T.Hikida, *OR* 4501.
307. L.K.Figge, P.J.Carroll, and D.H.Berry, *OR* 209; S.Seebald, G.Kickelbick, F.Moller, and U.Schubert, *CB* 113.
308. J.E.Ellis, P.Yuen, and M.Jang, *JOMC* **507**, 283; C.J.Levy, J.J.Vittal, and R.J.Puddephatt, *OR* 35.
309. A.El-Maradny, H.Tobita, and H.Ogino, *CL* 83 and *OR* 4954.
310. U.Schubert and S.Grubert, *OR* 4707; C.J.Cardin, D.J.Cardin, M.A.Convery, M.M.Devereux, B.Twamley, and J.Silver, *JD* 1145.
311. S.E.H.Etaiw and A.M.A.Ibrahim, *JOMC* **522**, 77.
312. R.Reina, O.Rossell, M.Seco, M.A.Pellinghelli, A.Tiripicchio, and D. de Montauzon, *OR* 5347.
313. F.R.Lemke, R.S.Simons, and W.J.Youngs, *OR* 216; D.G.Gusev, T.T.Nadasdi, and K.G.Caulton, *IC* 6772; S.M.Maddock, C.E.F.Rickard, W.R.Roper, and L.J.Wright, *OR* 1793.
314. M.Akita, R.Hua, T.Oku, M.Tanaka, and Y.Moro-oka, *OR* 4162; R.Hua, M.Akita, and Y.Moro-oka, *CC* 541.
315. M.P.Aarnts, D.J.Stufkens, M.P.Wilms, E.J.Baerends, A.Vlcek, Jr., I.P.Clark, M.W.George, and J.J.Turner, *EJC* 1556; M.P.Aarnts, M.P.Wilms, K.Peelen, J.Fraanje, K.Goubitz, F.Hartl, D.J.Stufkens, E.J.Baerends, and A.Vlcek, Jr., *IC* 5468.
316. C.J.Cardin, D.J.Cardin, M.A.Convery, Z.Dauter, D.Fenske, M.M.Devereux, and M.B.Power, *JD* 1133; W.K.Leong, F.W.B.Einstein, and R.K.Pomeroy, *OR* 1589 and 1582.
317. S.H.Bertz, M.Eriksson, G.Miao, and J.P.Snyder, *JACS* 10906; M.Eriksson, A. Johansson, M.Nilsson, and T.Olsson, *JACS* 10904.
318. K.Tamao, A.Kawachi, Y.Tanaka, H.Ohtani, and Y.Ito, *TET* 5765; I.Fleming and D.Lee, *TL* 6929.
319. A.Kirschning and J.Harders, *SL* 772; O.Z.Pereira and T.-H.Chan, *JOC* 5406.
320. R.A.Gossage, G.D.McLennan, and S.R.Stobart, *IC* 1729; M.Murakami, T.Yoshida, and Y.Ito, *CL* 13.
321. M.Aizenberg and D.Milstein, *OR* 3317; M.Okazaki, H.Tobita, and H.Ogino, *OR* 2790.
322. W.Chen, A.J.Andrews, M.A.Esteruelas, F.J.Lahoz, M.Olivan, and L.A.Oro, *OR* 2185; M.Okazaki, H.Tobita, and H.Ogino, *CL* 477.
323. H.Sun, X.Zhou, X.Yao, and H.Wang, *PO* 4489; P.Braunstein, C.Stern, C. Strohmann, and N.Tong, *CC* 2237; K.Ueno, K.Nakano, and H.Ogino, *CL* 459; H.Lang, M.Weinmann, M.Buchner, and B.Schiemenz, *CC* 1299; H.Nakazawa, Y.Yamaguchi, and K.Miyoshi, *OR* 1337; P.Braunstein, C.Charles, A.Tiripicchio, and F.Ugozzoli, *JD* 4365.
324. F.Schager, K.Seevogel, K.-R.Porschke, M.Kessler, and C.Kruger, *JACS* 13075; M.Knoor, E.Hallauer, V.Huch, M.Veith, and P.Braunstein, *OR* 3868; H.Jacobsen and T.Ziegler, *IC* 775.

325. R.S.Simons and P.P.Power, *JACS* 11966.
326. Y.Yamamoto, H.Shimizu, and Y.Hamada, *JOMC* **509**, 119 and **510**, 1.
327. L.Ruwisch, U.Klingebiel, S.Rudolph, R.Herbst-Irmer, and M.Noltemeyer, *CB* 823.
328. M.G.Gardiner and C.L.Raston, *IC* 4162; M.Veith, M.Zimmer, K.Fries, J.Bohnlein-Maus, and V.Huch, *ACIE* 1529.
329. K.W.Henderson, A.E.Dorigo, P.G.Williard, and P.R.Bernstein, *ACIE* 1322; A.J.Blake, P.Mountford, and G.I.Nikonov, *ACRC* 1911.
330. B.L.Lucht and D.B.Collum, *JACS* 2217 and 3529; D.R.Armstrong, M.G.Davidson, R.P.Davies, H.J.Mitchell, R.M.Oakley, P.R.Raithby, R.Snaith, and S.Warren, *ACIE* 1942; D.R.Armstrong, D.R.Baker, F.J.Craig, R.E.Mulvey, W.Clegg, and L.Horsburgh, *PO* 3533.
331. P.J.Bailey, L.A.Mitchell, P.R.Raithby, M.-A.Rennie, K.Verhorevoort, and D.S.Wright, *CC* 1351; A.J.Edwards, A.Fallaize, P.R.Raithby, M.-A.Rennie, A.Steiner, K.L.Verhorevoort, and D.S.Wright, *JD* 133.
332. M.L.Hays, T.P.Hanusa, and T.A.Nile, *JOMC* **514**, 73; H.V.R.Dias and W.Jin, *IC* 6546.
333. N.W.Mitzel, E.Breunig, A.J.Blake, H.E.Robertson, B.A.Smart, and D.W.H.Rankin, *JACS* 2664; D.Bonafoux, M.Bordeau, C.Biran, P.Cazeau, and J.Dunogues, *JOC* 5532; A.Dombrowski, M.Nieger, and E.Niecke, *CC* 1705.
334. Y.Mu, W.E.Piers, D.C.MacQuarrie, M.J.Zaworotko, and V.G.Young, Jr., *OR* 2720; P.B.Hitchcock, M.F.Lappert, and Z.-X.Wang, *CC* 1647.
335. A.P.Johnson, R.W.A.Luke, R.W.Steele, and A.N.Boa, *JP1* 883; A.P.Johnson, R.W.A.Luke, G.Singh, and A.N.Boa, *JP1* 907; G.Cainelli, D.Giacomini, P.Galletti, and A.Gaiba, *SL* 657; P.Binger, P.Wedemann, R.Goddard, and U.H.Brinker, *JOC* 6462.
336. G.L.Edwards, C.A.Muldoon, and D.J.Sinclair, *TET* 7779; K.Kokin, S.Tsuboi, J.Motoyoshiya, and S.Hayashi, *SL* 637; Y.Tang, Y.-Z.Huang, L.-X.Dai, Z.-F.Chi, and L.-P.Shi, *JOC* 5762.
337. R.Duchateau, A.Meetsma, and J.H.Teuben, *CC* 223; A.Hagadorn and J.Arnold, *OR* 984; R.Duchateau, C.T.van Wee, A.Meetsma, P.Th.van Duijnen, and J.H.Teuben, *OR* 2279.
338. R.Duchateau, C.T.van Wee, andd J.H.Teuben, *OR* 2291; R.Duchateau, A.Meetsma, and J.H.Teuben, *OR* 1656.
339. K.-H.Theile, H.Windisch, H.Windisch, F.T.Edelmann, U.Kilimann, and M.Noltemeyer, *ZAAC* 713; D.Walther, R.Fischer, M.Friedrich, P.Gebhardt, and H.Gorls, *CB* 1389.
340. E.Bandini, G.Martelli, G.Spunte, A.Bongini, and M.Panunzio, *TL* 4409.
341. M.D.Fryzuk, G.R.Giesbrecht, G.Olovsson, and S.J.Rettig, *OR* 4832; M.G.Gardiner, G.A.Koutsantonis, S.M.Lawrence, F.-C.Lee, and C.L.Raston, *CB* 545; M.Niemeyer and P.P.Power, *OR* 4107.
342. N.Burford, P.Losier, P.K.Bakshi, and T.S.Cameron, *CC* 307; W.-P.Leung, C.M.Y.Chan, B.-M.Wu, and T.C.W.Mak, *OR* 5179; Y.Zhou and D.S.Richeson, *IC* 2448.
343. K.Bode, U.Klingebiel, H.Witte-Abel, M.Gluth, M.Noltemeyer, R.Herbst-Irmer, and M.Schafer, *PSSi* 108, 121; K.Knipping, C.Drost, U.Klingbiel, and M.Noltemeyer, *ZAAC* 1215.
344. N.W.Mitzel, B.A.Smart, A.J.Blake, S.Parsons, and D.W.H.Rankin, *JD* 2095,
345. I.Kalikhman, S.Krivonos, A.Ellern, and D.Kost, *OR* 5973.
346. J.L.Leighton and E.N.Jacobsen, *JOC* 389; S.E.Schaus and E.N.Jacobsen, *TL* 7937; M.Khoukhi, M.Vaultier, A.Benalil, and B.Carboni, *SY* 483; J-P.Praly, F.Pequery,

C.Di Stefano, and G.Descotes, *SY* 577; P.Magnus, J.Lacour, P.A.Andrews, M.B.Roe, and C.Hulme, *JACS* 3406.

347. T.Veszpremi, T.Pasinszki, and M.Feher, *JOMC* **507**, 279; A.I.Almansour, G.A.Ayoko, and C.Eaborn, *JOMC* **514**, 277.

348. S.Rajesh, M.M.Reddy, and J.Iqbal, *TL* 7315; P.Jutzi, D.Eikenberg, B.Neumann, and H.-G.Stammler, *OR* 3659; M.Weidenbruch, P.Will, and K.Peters, *ZAAC* 1811.

349. P.F.Kelly, A.M.Z.Slawin, and A.Soriano-Rama, *JD* 53; K.I.Gobbato, C.O.D.Vedova, and H.Oberhammer, *JMS* 1995, **350**, 227.

350. M.Veith, M.Olbrich, W.Shihua, and V.Huch, *JD* 161; P.Braunstein, V.Huch, C.Stern, and M.Veith, *CC* 2041; W.Frank, V.Petry, E.Gerwalin, and G.J.Reiss, *ACIE* 1512.

351. B.Gehrhus, P.B.Hitchcock, M.F.Lappert, J.Heinicke, R.Boese, and D.Blaser, *JOMC* **521**, 211; P.Blakeman, B.Gehrhus, J.C.Green, J.Heinicke, M.F.Lappert, M.Kindermann, and T.Veszpremi, *JD* 1475.

352. H.Muguruma, S.Hotta, and I.Karube, *CL* 501; S.A.A.Shah, H.W.Roesky, P.Lubini, and H.-G.Schmidt, *ACRC* 2810.

353. A.Systermans and J.-L.Ripoll, *TL* 3317.

354. J.Niesmann, U.Klingebiel, and M.Noltemeyer, *JOMC* **521**, 191; J.Niesmann, U.Klingebiel, S.Rudolph, R.Herbst-Irmer, and M.Noltemeyer, *JOMC* **515**, 43.

355. M.G.Voronkov, V.A.Klyuchnikov, and L.I.Marenkova, *JOMC* **510**, 263; H.-J.Rakebrandt, U.Klingebiel, M.Noltemeyer, and Z.Zak, *ZN* 498.

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367. M.Niemeyer and P.P.Power, *CC* 1573.
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369. J.Louie, F.Paul, and J.F.Hartwig, *OR* 2794.
370. P.B.Hitchcock, M.F.Lappert, and L.J.-M.Pierssens, *CC* 1189; M.Contel, K.W. Hellmann, L.H.Gade, I.J.Scowen, M.McPartlin, and M.Laguna, *IC* 3713.
371. M.D.Fryzuk, J.B.Love, and S.J.Rettig, *CC* 2783; A.Muller, B.Neumuller, and K.Dehnicke, *CB* 253.
372. P.Braunstein, R.Hasselbring, and D.Stalke, *NJC* 337; T.Chivers, X.Gao, and M.Parvez, *IC* 9.
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374. M.Herberhold, S.Gerstmann, W.Milius, B.Wrackmeyer, and H.Borrmann, *PSSi* **112**, 261; M.Herberhold, S.Gerstmann, and B.Wrackmeyer, *PSSi* **113**, 89; M. Herberhold, B.Distler, H.Maisel, W.Milius, B.Wrackmeyer, and P.Zanello, *ZAAC* 1515.
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382. M.Driess and H.Pritzkow, *ZAAC* 1524.
383. M.Driess, S.Rell, H.Pritzkow, and R.Janoschek, *CC* 305.
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387. T.A.Budzichowski, M.H.Chisholm, K.Folting, W.E.Streib, and M.Scheer, *IC* 3659; M.Westerhausen, G.Lang, and W.Schwarz, *CB* 1035.
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389. L.K.Krannich, C.L.Watkins, S.J.Schauer, and C.H.Lake, *OR* 3980; R.L.Wells, R.A.Baldwin, P.S.White, W.T.Pennington, A.L.Rheingold, and G.P.A.Yap, *OR* 91.
390. J.F.Janik, R.A.Baldwin, R.L.Wells, W.T.Pennington, G.L.Schlmek, A.L.Rheingold, and L.M.Liable-Sands, *OR* 5385.
391. G.W.Rabe, J.Riede, and A.Schier, *OR* 439; W.Plass and W.Schwarz, *ZAAC* 1756; M.Driess, H.Pritzkow, and M.Reisgys, *CB* 247.
392. H.Schumann, M.Schafers, H.Hemling, and R.Weimann, *ZAAC* 1487.
393. M.Dreiss, K.Merz, H.Pritzkow, and R.Janoschek, *ACIE* 2507.
394. M.Dreiss, H.Pritzkow, S.Martin, S.Rell, D.Fenske, and G.Baum, *ACIE* 986.
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396. F.Lindenberg, J.Sieler, and E.Hey-Hawkins, *PO* 1459; F.Lindenberg, U.Muller, A.Pilz, J.Sieler, and E.Hey-Hawkins, *ZAAC* 683.
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399. D.Bongert, H.-D.Hausen, W.Schwarz, G.Heckmann, and H.Binder, *ZAAC* 1167 and 1793.
400. M.Baudler and L. de Riese-Meyer, *ZN* 101.
401. M.Okamoto, N.Watanabe, E.Suzuki, and Y.Ono, *JOMC* **515**, 51.
402. J.G.Lee, J.A.Lee, and S.Y.Sohn, *SC* 543.
403. S.Jolivet, S.Abdallah-El Ayoubi, D.Mathe, F.Texier-Boullet, and J.Hamelin, *JCR* 300; A.R.Bassindale. R.J.Ellis, and P.G.Taylor, *JCR* 34.
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408. C.Blanchard, E.Framery, and M.Vaultier, *SY* 45; M.Tamm, T.Lugger, and F.E.Hahn, *OR* 1251.
409. T.Konno and T.Kitazume, *CC* 2227; C.-Y.Chen, D.R.Lieberman, L.J.Street, A.R.Gubin, R.D.Larsen, and T.R.Verhoeven, *SC* 1977; D.J.L.Clive and W.Yang, *CC* 1605.
410. H.Du, F.Yang, and M.M.Hossain, *SC* 1371; H.Plenio and C.Aberle, *CC* 2123; H.Plenio and A.Warnecke, *OR* 5066.
411. R.Leino, H.Luttikhedde, C.-E.Wilen, R.Sillanpaa, and J.H.Nasman, *OR* 2450; W.Adam, D.Golsch, J.Sundermeyer, and G.Wahl, *CB* 1177.
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413. N.V.Timosheva, T.K.Prakasha, A.Chandrasekaran, R.O.Day, and R.R.Holmes, *IC*

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417. H.Kagoshima, M.Hayashi, Y.Hashimoto, and K.Saigo, *OR* 5439; D.G.J.Young, M.R.Hale, and A.H.Hoveyda, *TL* 827.
418. P.Lu, J.K.Paulasaari, and W.P.Weber, *OR* 4649; H.Nagashima, Y.Kato, H.Satoh, N.Kamegashima, K.Itoh, K.Oi, and Y.Saito, *CL* 519.
419. T.K.Prakasha, A.Chandrasekaran, R.O.Day, and R.R.Holmes, *IC* 4342; H.Beckers, D.J.Brauer, H.Burger, R.Gielen, and P.Moritz, *JOMC* **511**, 293.
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421. A.Mori, H.Sato, K.Mizuno, T.Hiyama, K.Shintani, and Y.Kawakami, *CL* 517; J.Cermak, M.Kvicalova, V.Blechta, M.Capka, and Z.Bastl, *JOMC* **509**, 77; G.H.Mehl and J.W.Goodby, *CB* 521.
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423. E.A.Boyd, M.E.K.Boyd, and V.M.Loh, Jr., *TL* 1647; U.Dieckbreder and G.-V. Roschenthaler, *PSSi* **116**, 101.
424. R.Szalay, Zs.Bocskei, D.Knausz, Cs.Lovasz, K.Ujszaszy, L.Szakacs, and P.Sohar, *JOMC* **510**, 93.
425. S.Kobayashi, M.Moriwaki, R.Akiyama, S.Suzuki, and I.Hachiya, *TL* 7783; L.Peidro, C.Le Roux, A.Laporterie, and J.Dubac, *JOMC* **521**, 397; T.Okazaki, H.Isobe, T.Kitagawa, and K.Takeuchi, *BCSJ* 2053; K.Ishihara, S.Nakamura, M.Kaneeda, and H.Yamamoto, *JACS* 12854; Y.Tanaka, H.Yamashita, and M.Tanaka, *OR* 1524.
426. C.Z.Liu and P.W.Rabideau, *TL* 3437; H.Sano, H.Mashio, T.Nakayama, and M.Kosugi, *TL* 8891.
427. G.Kennedy, T.Rossi, and B.Tamburini, *TL* 7441; K.Krohn and G.Schafer, *LA* 265; M.Igarashi and M.Tada, *SY* 465; H.Angert, R.Czerwonka, and H.-U.Reissig, *LA* 259.
428. M.Fujita, S.Fukuzumi, G.Matsubayashi, and J.Otera, *BCSJ* 1107; D.A.Evans, J.A.Murry, and M.C.Kozlowski, *JACS* 5814; D.Enders, U.Frank, P.Fey, B.Jandeleit, B.B.Lohray, *JOMC* **519**, 147.
429. Y.Yamamoto, K.Nunokawa, M.Ohno, and S.Eguchi, *SY* 949; M.Node, K.Nishide, H.Imazato, R.Kurosaki, T.Inoue, and T.Ikariya, *CC* 2559.
430. S.Kashimura, M.Ishifune, Y.Murai, and T.Shono, *CL* 309; C.S.Siedem and G.A.Molander, JOC 1140; B.Manz and G.Maas, *TET* 10053.
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432. P.Jutzi, G.Strassburger, M.Schneider, H.-G.Stammler, and B.Neumann, *OR* 2842.
433. V.Chandrasekhar, R.Murugavel, A.Voigt, H.W.Roesky, H.-G.Schmidt, and M. Noltemeyer, *OR* 918; M.R.Mason, R.M.Matthews, M.S.Mashuta, and J.F.Richardson, *IC* 5756.
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438. S.S.D.Brown, S.N.Heaton, M.H.Moore, R.N.Perutz, and G.Wilson, *OR* 1392.
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445. P.Jutzi, H.Schmidt, B.Neumann, and H.-G. Stammler, *OR* 741.
446. S.D.Pastor, A.R.Smith, and G.Rihs, *PSSi* **115**, 169.
447. J.Kapp, M.Remko, and P. von Rague Schleyer, *JACS* 5745; J.Barrau, G.Rima, and T.El Amraoui, *ICA* **241**, 9.
448. M.Veith, C.Mathur, and V.Huch, *OR* 2858.
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450. K.Jurkschat, F.Rosche, and M.Schurmann, *PSSi* **115**, 161.
451. J.Otera, K.Kawada, and T.Yano, *CL* 225; A.S.-Y.Lee and W.-C.Dai, *TL* 495.
452. T.B.Grindley and H.Namazi, *TL* 991.
453. G.Godjoian, V.R.Wang, A.Ayala, R.V.Martinez, R.Martinez-Bernhardt, and C.G.Gutierrez, *TL* 433; S.Roelens, *JOC* 5257.
454. S.Kim, J.Y.Do, and K.M.Lim, *CL* 669.
455. E.J.Enholm and P.E.Whitley, *TL* 559.
456. F.Xin, M.T.Pope, G.J.Long, and U.Russo, *IC* 1207; F.Xin and M.T.Pope, *IC* 5693.
457. J.Morgan, T.W.Hambley, and J.T.Pinhey, *JP1* 2173; P.Lopez-Alvarado and J.C.Menendez, *JOC* 5865.
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459. C.-M.Yu, H.-S.Choi, W.-H.Jung, and S.-S.Lee, *TL* 7095; M.Muller, W.-R.Forster, A.Holst, A.J.Kingma, A.Schaumann, and G.Adiwidjaja, *EJC* 949.
460. V.Lefevre and J.-L.Ripoll, *TL* 7017
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462. P.Jutzi, D.Eikenberg, A.Mohrke, B.Neumann, and H.-G.Stammler, *OR* 753.
463. N.Tokitoh, H.Suzuki, and R.Okazaki, *CC* 125.

464. N.Choi, K.Asano, N.Sato, and W.Ando, *JOMC* **516**, 155.

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7

Organometallic Chemistry of Group 15 Elements

BY CAMERON JONES

1 Phosphorus

Due to space restrictions a comprehensive review of organophosphorus chemistry cannot be included here. Instead, emphasis has been placed on developments in low coordination phosphorus chemistry and heterocyclic systems containing phosphorus. In these areas reviews have appeared on the synthesis and coordination chemistry of 2,2′-biphosphinines[1] and metallophosphaalkenes.[2] In addition, the chemistry of λ^5-phosphorus substituted cyclobutadiene rings has been highlighted.[3]

Various reports dealing with phosphaalkynes have appeared which include a computational investigation of the mechanism of vinylphosphirane pyrolysis which yields $P{\equiv}CMe$.[4] Hydrometallation of $P{\equiv}CBu^t$ with $[RuHCl(CO)(PPh_3)_3]$ afforded the coordinatively unsaturated complex $[RuCl(P{=}CHBu^t)(CO)(PPh_3)_2]$ **(1)** regioselectively. Two electron donors readily add to **(1)** to give complexes such as [**(1)**(CNR)] **(2)**, R = $C_6H_3Me_2$-2,6.[5] Protonation of **(2)**, providing $[RuCl(PH{=}CHBu^t)(CO)(CNR)(PPh_3)_2]BF_4$, followed by HF addition yielded a fluorophosphine complex $[RuCl(PHFCH_2Bu^t)(CO)(CNR)(PPh_3)_2]BF_4$ (X-ray).[6] Treatment of $B_{10}H_{12}(CH_3CN)_2$ with $P{\equiv}CR$, R = adamantyl (Ad), Bu^t, produces *nido*-$RC(H)PB_{10}H_{13}$ which NMR studies show to be structurally similar to *nido*-$[B_{11}H_{11}]^-$.[7,8] A 1,2-addition reaction of $P{\equiv}CAd$ with $[HPPh_3][CF_3SO_3]$ to give $[AdC(H){=}PPh_3][CF_3SO_3]$ has also been described.[9] The phosphametallacycle $[(ArN)(RO)\overline{Mo{=}C(Bu^t)P(OR)C}HBu^t]$ (X-ray) results from a [2+2] cycloaddition of $P{\equiv}CBu^t$ with $[(ArN)(RO)_2Mo{=}CHBu^t]$, Ar = $C_6H_3Pr^i{}_2$-2,6, R = $CMe(CF_3)_2$, with an accompanying metal to ligand alkoxide shift.[10] The spirocyclotrimerisation of a range of phosphaalkynes with group 13 halides has been reported.[11] Scandium vapour reacts with $P{\equiv}CBu^t$ to give the remarkable triple decker scandium(I) complex $[\{(\eta^5\text{-}P_3C_2Bu^t{}_2)Sc\}_2(\mu\text{-}\eta^6,\eta^6\text{-}P_3C_3Bu^t{}_3)]$ (X-ray) which has a formal 22 electron count.[12] The P-C triple bond of $P{\equiv}CBu^t$ has been cleaved in reaction with [Cp′CoCl] and Na/Hg, Cp′ = $C_5H_5(CH_2)_2PBu^t{}_2$, producing the μ_3-phosphido, μ_3-carbyne bridged cluster $[(Cp'Co)_3(\mu_3\text{-}P)(\mu_3\text{-}CBu^t)]$ (X-ray) **3**; all P-centres in **3** are readily oxidised.[13] Gas phase FTICR studies on the phosphaalkyne tetramer, tetraphosphacubane ($P_4C_4Bu^t{}_4$) reveal it to be an unusually strong P-base relative to its solution behaviour.[14]

A range of sterically unprotected phosphaalkenes, RP=CHR′ **(4)**, have been

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synthesised by the dehydrochlorination of α-chlorophosphines, $\mathrm{RHP\text{-}CHClR'}$. The synthetic potential of (**4**) was addressed.[15] Treatment of fluorenyl lithium with Mes*NPCl, Mes* = $\mathrm{C_6H_2Bu^t_3}$-2,4,6, yielded the new phosphaalkene Mes*N(H)P=fluorenylidene (X-ray).[16] The phosphaalkenyl lithium species, Mes*P=CClLi, has been used in transmetallation reactions with $\mathrm{MCl_2}$ affording $\mathrm{[(Mes^*P{=}CCl)_nMX_{2\text{-}n}]}$, n = 1 or 2, M = Mg, Zn, Hg, X = Cl, Br.[17] The reactivity of the metallophosphaalkenes $\mathrm{[Cp^*(CO)_2FeP{=}CR_2]}$ Cp* = $\mathrm{C_5Me_5}$, R = $\mathrm{SiMe_3}$, $\mathrm{NMe_2}$, toward $\mathrm{HC{\equiv}CCO_2R'}$, R′ = Me, Et, has been examined; a range of products were obtained.[18] Debromofluorination of MesGe(F)C(Br)=PMes*, Mes = mesityl, leads to the first metastable germaphosphaallene, $\mathrm{Mes_2Ge{=}C{=}PMes^*}$, the reactivity of which was explored.[19] A bidentate diphosphaalkene, 1,2-$\mathrm{(Mes^*P{=}CH)_2C_6H_4}$, L, (X-ray) has been synthesised and shown to act as a P-donor in the chelate complex, $\mathrm{[PdLCl_2]}$ (X-ray).[20] The first *para*-diphosphaquinone, 1,4-$\mathrm{(Mes^*P{=})_2C_6H_4}$, has been prepared as a mixture of its Z- and E-isomers, both of which form P-donor complexes with the $\mathrm{[Cr(CO)_5]}$ fragment.[21] Treatment of $\mathrm{[Li(thf)_n\{P(SiMe_3)_2\}]}$ with an excess of $\mathrm{ClP{=}C(SiMe_3)_2}$ provides the 6π electron, delocalised triphosphapentadienide, $\mathrm{[Li(DME)_3]\ [(SiMe_3)_2CPPPC(SiMe_3)_2]}$ (X-ray) DME = 1,2-dimethoxyethane , the anion of which adopts the W-form in solution and the solid state.[22]

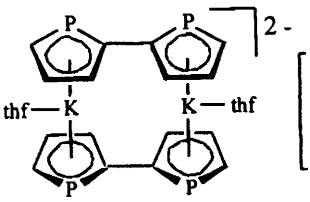
A novel P-C coupling occurs in the reaction of $\mathrm{[RhCl({=}C{=}C{=}CPh_2)(PPr^i_3)_2]}$ with $\mathrm{PhC{\equiv}CH}$ to give the π-coordinated ylide complex $\mathrm{[RhCl\{\eta^3\text{-}\mathit{anti}\text{-}CH(PPr^i_3)C(Ph){=}C{=}C{=}CPh_2\}(PPr^i_3)]}$ **5** (X-ray). The free ylide, $\mathrm{Pr^i_3P{=}C(H)C(Ph){=}C{=}C{=}CPh_2}$, can be generated by treating **5** with CO.[23] The preparation of charge delocalised C-phosphonio phosphorus vinyl ylides, e.g. $\mathrm{[(Pr^i_2N)_2PCP(H)(NPr^i_2)_2][CF_3SO_3]}$, and their use as synthons has been reported.[24] A series of $\mathrm{d^1\ Ti^{III}}$ and $\mathrm{d^2\ V^{III}}$ complexes react with the ylide, $\mathrm{CH_2PPh_3}$, to give a range of paramagnetic complexes, e.g. $\mathrm{[(Cy_2N)_2V(Cl)CH_2PPh_3]}$ (X-ray), Cy = cyclohexyl.[25]

Two diphosphiranes, $\mathrm{Mes^*\overline{PC(Cl)_2P}R}$, R = Mes* or $\mathrm{C(SiMe_3)_3}$ (X-ray), were shown to contain very short P-P bonds. Several diphosphirane P-P cleavage reactions were also reported.[26] The 1-phenylphosphiranes and -phosphetanes, $\mathrm{PhP(CH_2)_n}$, n = 2 (**6**), 3 (**7**), were prepared from $\mathrm{PhPLi_2}$ and $\mathrm{Cl(CH_2)_nCl}$ and used in the synthesis of P-donor complexes $\mathrm{[Mo(CO)_3(\mathbf{6}\ or\ \mathbf{7})_3]}$ (X-ray) and $\mathrm{[CpFe(\mathbf{7})_3]PF_6}$ (X-ray).[27] The azaphosphete, $\mathrm{R_2\overline{P{=}N\text{-}C(R'){=}C}(R')}$, L, R = $\mathrm{NPr^i_2}$, R′ = $\mathrm{CO_2Me}$, was used in the formation of N-donor complexes, e.g. $\mathrm{[L_2PdCl_2]}$.[28] Phosphaalkynes have been reacted with $\mathrm{(PCF_3)_4}$ to produce a range of 1,2,3-triphosphetenes, e.g. $\mathrm{Pr^i_2\overline{NC{=}PP(CF_3)P}(CF_3)}$, the structure of which suggests involvement of the N-lone pair in bonding.[29] A range of reactions have been described for the diphosphetene, $\mathrm{(Me_3Si)\overline{C{=}C(Bu^t)\text{-}P{=}P}(NPr^i_2)_2}$.[30] Chelating diphosphinomethanide ligands, $\mathrm{[R_2PCR'PR_2]^-}$, have been used in the preparation of a variety of four membered P-heterocycles which include $\mathrm{[\mathit{p}\text{-}tolylSiCl_2\{\eta^2\text{-}(PMe_2)_2C(SiMe_2Ph)\}]}$ (X-ray) and $\mathrm{[\overline{CH_2(CH_2)_2Si}\{\eta^2\text{-}(PMe_2)_2C(SiMe_2Ph)\}_2]}$ (X-ray) which possess five and six coordinate silicon centres respectively,[31] hexacoordinate $\mathrm{[Me_2E\{\eta^2\text{-}(PMe_2)_2C(SiMe_3)\}_2]}$, E = Si, Ge, Sn (X-ray),[32] $\mathrm{[E\{\eta^2\text{-}(PPh_2)_2C(SiMe_3)\}]}$ E = P, As (X-ray) and $\mathrm{[P\{\eta^2\text{-}(PPh_2)_2C(SiMe_3)\}_2]BPh_4}$ (X-ray).[33]

Treatment of P_4 with $[\text{Me}_3\text{SiCN}_2]\text{Li}$ yielded the 1,2,3,4-diazadiphospholyl anion $[\overline{\text{NNPPC}}(\text{SiMe}_3)]^-$ which is readily protonated in the 2-position to give $\overline{\text{NN(H)PPC}}(\text{SiMe}_3)$ (X-ray).[34] A kalocene type structure has been found for the potassium 2,2′-biphospholyl complex dianion (**8**).[35] Several new di- and tri-phosphaferrocenes have been prepared and used as P-donor ligands in the preparation of heterobimetallic complexes, e.g. $[\text{Fe}(\eta^5\text{-Cp}^*)(\eta^5\text{-1,2,4-P}_3\text{C}_2\text{Bu}^t_2)\{\text{Mo(CO)}_5\}]$ (X-ray).[36] Similar complexes have been formed between tri- and pentaphosphaferrocenes, and iridium carbonyl clusters, e.g. $[\text{Fe}(\eta^5\text{-Cp})(\eta^5\text{-1,2,4-P}_3\text{C}_2\text{Bu}^t_2)\{\text{Ir}_4(\text{CO})_{11}\}]$ (**9**) (X-ray); further reactivity of (**9**) was also observed.[37] The first ruthenium(0) triphosphole complex $[\text{Ru}(\eta^4\text{-C}_8\text{H}_{12})\{\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2[\text{CH}(\text{SiMe}_3)_2]\}]$ (X-ray) has been reported to undergo hydrogen migration reactions from the C_8H_{12} ligand to the heterocycle.[38] A number of 3,5-diphosphino-1,2-diphospholide cations, e.g. (**10**) (X-ray), have been synthesised and their chemistry examined.[39] Compound (**10**) can be methylated at the 1-position whilst retaining six π-electrons within the heterocycle.[40]

A number of papers have dealt with the synthesis of 2-halophosphinines and their use as precursors to 2-ethyl,[41] 2-phosphino[42] or 2-metallo (Mg, Zn, Sn)[43] substituted phosphinines. Their use as P-donor ligands has been addressed.[43] Similarly, a series of 2-metallo (As, Sn, Cu, Ag, Hg) substituted phosphinines have been prepared *via* transmetallation reactions with a range of 2-organozinc phosphinines.[44] The reaction of 4,4′,5,5′-tetramethyl-2,2′-biphosphinine (tmbp) with $[\text{RuCp}^*(\eta^4\text{-C}_6\text{H}_{10})\text{Cl}]$ affords the chelate complex [RuCp*(tmbp)Cl] (**11**) (X-ray) which undergoes a series of chloride substitution reactions. The electrochemistry of (**11**) was investigated.[45]

Radical catalysed coupling of the vinyl functions in the complex $[\text{Cr}(\text{PH}_2\text{CH}_2\text{CH=CH}_2)_3(\text{CO})_3]$ afforded the triphosphacyclododecane complex [Cr(**12a**)(CO)$_3$] (X-ray).[46] Trialkylation of [Mo(**12a**)(CO)$_3$] yields the complexes [Mo(**12b-d**)(CO)$_3$] which can be oxidised to [Mo(**12b-d**)(CO)$_2$Br$_2$] (**13**). The free macrocycles (**12b-d**) can be generated as syn,syn-isomers by digestion of (**13**) in



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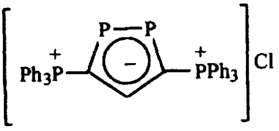

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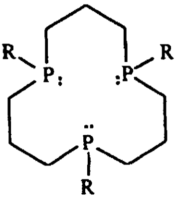


12a R = H
b R = Pr^i
c R = Et
d R = Bu^i

NaOH/EtOH.[47] The crystal structure of **(12b)** has been reported.[48] Bicyclic diphosphonium systems, e.g. $[PhCH_2P\{(CH_2)_3\}_3PCH_2Ph][triflate]_2$ **(14)** (X-ray), have been prepared. Debenzylation of **(14)** yields the bicyclic diphosphine $[P\{(CH_2)_3\}_3P]$.[49] Multiple step syntheses produced a variety of *cis*-dialkyldiphosphacycloalkanes, e.g. $[MeP\{(CH_2)_n\}_2PMe]$, n = 3 or 4 (X-ray).[50]

Treatment of $[Cp^*{}_2UMeCl]$ with $[KPHMes^*]$ in the presence of $OPMe_3$ yielded the first terminal phosphinidene-actinide complex $[Cp^*{}_2U(PMes^*)(OPMe_3)]$ (X-ray) which has a U-P-C angle of 143.7(3)° in the solid state.[51] Reaction of $[(SnNBu^t)_4]$ with CyP(H)Li affords a phosphinidene bridged tin(II) complex $[\{Sn_2(\mu\text{-}PCy)_3\}_2Li_4.4thf]$ (X-ray) which contains a fourteen membered $[Sn_4P_6Li_4]$ cage core.[52] The complexes $[MRu_3\{\mu_4\text{-}PC(CO)Bu^t\}_2(\mu\text{-}CO)(CO)_{10}]$, M = Ru or Fe (X-ray), display two μ_4-phosphinidine ligands that cap an MRu_3 square planar array.[53] The first phosphametallacyclobutenes, $[Cp_2ZrP(Mes^*)C(R){=}C(Ph)]$ **(15)** R = Ph or Me, are prepared by reversible [2+2] cycloaddition reactions between *in-situ* generated $[Cp_2Zr{=}PMes^*]$ and $RC{\equiv}CPh$;[54] further chemistry of **15** and related compounds has been examined.[54,55] The Zr=P bond of $[Cp_2Zr({=}PMes^*)(PMe_3)]$ has been shown to readily insert into E-H bonds, E = O,S,N,P, to give phosphide complexes such as $[Cp_2Zr\{P(H)Mes^*\}(NHPh)]$.[56]

Numerous reports have dealt with the synthesis and reactivity of metal phosphide complexes, a few examples follow. The reactivity of $[CpZrMe\{P(H)Mes^*\}]$ toward ketones and aldehydes has been closely examined.[57] Treatment of $[M(OSO_2CF_3)]$, M = La, Yb, Sm, with $[LiPBu^t{}_2]$ yielded either $[M\{(\mu\text{-}PBu^t{}_2)_2Li(thf)\}_2]$, M = Yb, Sm (X-ray) or $[(Bu^t{}_2P)_2La\text{-}\{\mu\text{-}PBu^t{}_2)_2Li(thf)\}]$ (X-ray), the former being strongly photoluminescent.[58,59] The reaction of $[NiCp_2]$ with PH_2Mes yields dimeric $[\{NiCp(\mu\text{-}PHMes)\}_2]$ (X-ray) which has a syn-/anti- equilibrium in solution.[60] Many phosphido bridged cluster complexes have been reported, e.g. $[NBu_4][Pt_3(\mu\text{-}PPh_2)_2(C_6F_5)_5]$ (X-ray).[61]

The di- and triphosphene radical anions, $[Bu^tP{=}PBu^t]^{\cdot -}$ and $[Bu^tP\text{-}P(Bu^t)\text{-}PBu^t]^{\cdot -}$, have been generated and studied by EPR spectroscopy. Theoretical studies on $[P_3H_3]^{\cdot -}$ were also reported.[62] A triplet ground state phosphinyl diradical, $[Mes^*P(1,3\text{-}C_6H_4)PMes^*]^{\cdot\cdot}$, was prepared by treating $Mes^*P(Cl)(1,3\text{-}C_6H_4)P(Cl)Mes^*$ with an electron rich olefin at 100K in a toluene glass matrix.[63]

There have been many reports examining the chemistry of water soluble phosphines, examples include the synthesis of the triphosphine $PhP[CH_2CH_2P(CH_2OH)_2]_2$ (tp) and its water soluble tripodally coordinated complexes [RhCl(tp)] and [PtCl(tp)]Cl.[64] Bidentate water soluble phosphines, e.g. $[HO(CH_2)_3]_2PCH_2CH_2P[(CH_2)_3OH]_2$ (dp) (X-ray) have also been prepared and used in the synthesis of water soluble chelate complexes, $[Ni(dp)_2Cl]Cl$ (X-ray) and $[Rh(dp)_2]Cl$ (X-ray).[65] Multi-step syntheses have yielded monodentate water soluble phosphines, e.g. $Cy_2P(CH_2)_2NMe_3{}^+Cl^-$ (mp), which have been used in the synthesis of effective water soluble ROMP catalysts, e.g. $[Ru\{{=}C(H)Ph\}(Cl)_2(mp)_2]$.[66] A variety of related hemilabile ether phosphine ligands, e.g. trifunctional $PhCH_2P[(CH_2)_2OCH_2CH_3]_2$ **(16)** and tetrafunctional $PPh[(CH_2)_2CHMe_2][(CH_2CH_2O)_3Me]$ **(17)**, have been reported and employed as ligands in the synthesis of $[TiCl_4(\eta^2\text{-}\mathbf{16})]$ (X-ray), $[Mo(CO)_3(\eta^1\text{-}\mathbf{16})(\eta^2\text{-}\mathbf{16})]$ (X-ray)[67] and [$RuCl_2(PPh_3)(\eta^3$-17)] (X-ray)[68] which possess uncoordinated ether functionalities.

2 Arsenic, Antimony and Bismuth

Reviews have appeared on the chemistry of arsaalkenes ($RAs{=}CR'_2$) and arsaalkynes ($As{\equiv}CR$);[69] and the synthesis, properties and applications of bismuthonium salts, $[BiR_4]^+X^-$, and ylides, $Ar_3Bi{=}CR_2$.[70] Diarsa-, distiba-, and dibismaferrocenes have also been reviewed.[71]

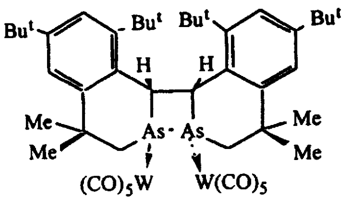
A number of reports have appeared describing low coordination organoarsenic and -antimony compounds. Thermally stable C-halogenated arsaalkenes, $Mes^*As{=}CX_2$, X = Cl, Br, I, were prepared by treating Mes^*AsF_2 with $LiCHX_2$.[72] The arsaalkene, $(SiMe_3)As{=}C(NMe_2)_2$, was synthesised and reacted with [$Cp^*Fe(CO)_2Br$] to form the metalloarsaalkene [$Cp^*(CO)_2FeAs{=}C(NMe_2)_2$] (**18**) (X-ray). Treating (**18**) with dimethylfumarate yields the 1,2-dihydroarsete [$Cp^*(CO)_2Fe$-As-$C(NMe_2)_2$-$CH(CO_2Me)$] (X-ray).[73] Coupling of the arsaalkyne, $As{\equiv}CMes^*$, was achieved in its reaction with [$W(CO)_5(THF)$] which yields the first examples of 1,3-diarsacyclobutadiene and 1,2-diarsetane complexes, *viz* [$\{W(CO)_5\}_2(1,3\text{-}\eta^1As_2C_2Mes^*_2)$] (X-ray) and [$\{W(CO)_5\}_2\{1,2\text{-}\eta^1\text{-}As_2C_2(C_6H_2Bu^t_2CMe_2CH_2)_2\}$] (**19**) (X-ray) respectively. The former displays localised As-C double bonds.[74] A stable iminoarsane, $Ar'As{=}NAr'$ (X-ray) Ar' = 2,4,6-$C_6H_2(CF_3)_3$, has been prepared as a mixture with $Ar'As(NHAr')_2$ in the reaction of $Ar'AsCl_2$ with $Ar'NHK$.[75] Several silylidenearsanes and -phosphanes, $R_2Si{=}E(SiR_3)$, E = As, P, have been reported and their chemistry extensively investigated.[76] A series of 2-arsa- and 2-stiba-1,3-dionato lithium complexes, [$Li\{OC(R)EC(R)O\}(solvent)$], E = As, Sb, were synthesised and found to be dimeric in the solid state though NMR studies suggested monomer-dimer fluxionality in solution.[77] The first diphosphastibolyl ring anion, $[C_2Bu^t_2P_2Sb]^-$, reacts with $[Cp^*Ru(CH_3CN)_3]PF_6$ to give the sandwich complex [$Cp^*Ru(\eta^5$-$C_2Bu^t_2P_2Sb)$], the X-ray structure of which shows a fully delocalised heterocycle and intermolecular $P\cdots P$ contacts.[78] Although not organometallic it is worth mentioning the independent syntheses of [$(N_3N)M{\equiv}As$], M = W, Mo[79,80] (X-ray), $N_3N = N(CH_2CH_2NSiMe_3)_3$, both of which have been examined by FT-Raman spectroscopy and the force constants of their $M{\equiv}As$ bonds calculated.[79]

Insertion into the Zr-E bond of [$(C_5H_4R)_2ZrCl\{E(SiMe_3)_2\}$] with $Pr^iN{=}C{=}NPr^i$ yields [$(C_5H_4R)_2Zr\{N(Pr^i)C(ESiMe_3)N(Pr^i)\}Cl$], R = Me, E = As (X-ray); R = H, E = P; the structure of the former shows the arsaguanidino ligand to be bidentate.[81] A range of phosphido and arsenido bridged complexes, e.g. [$Cp_2Zr\{\mu\text{-}As(SiMe_3)_2\}Cr(CO)_4$] (X-ray) react rapidly with methylaluminoxane (MAO) to yield high turnover ethylene polymerisation catalysts.[82] The complexes [$Cp^*_2Sm(thf)_n$] n = 0, 2, have been shown to cleave the E-E and E-C bonds of Ph_2EEPh_2 and EPh_3, E = P, As, Sb, Bi, to give a range of compounds which include [$Cp^*_2Sm(AsPh_2)(thf)_n$] n = 0, 1 (X-ray).[83]

Treatment of [$(Mes^*AlH_2)_2$] with $PhEH_2$, E = P, As, affords the cyclic, trimeric species [$(Mes^*AlEPh)_3$] *via* H_2 elimination. X-ray crystallography shows each to adopt a boat configuration with no apparent E lone pair delocalization.[84] Two other cyclic aluminium arsenides, $[(Me_2AlAsRR')_3]$, R = Ph, R′ = Ph or CH_2SiMe_3 (X-ray), were prepared and found to adopt a chair conformation in the solid state.[85] A planar four membered ring was found for $[\{(Me_3SiCH_2)_2InSb(SiMe_3)_2\}_2]$ (X-ray). The adducts, $[Et_3Ga.Sb(SiMe_3)_3]$ and $[(Me_3SiCH_2)_3In.Sb(SiMe_3)_3]$ (X-ray) were also described.[86] Reaction of $RSbCl_2$, R = $(SiMe_3)_2CH$-, with Na_2E, E = S, Se, Te, yields the compounds $[(RSbE)_n]$ as a mixture of dimers, trimers and tetramers in solution and the gas phase.[87] A new polymorph of $[(Cp^*Sb)_4]$ has a transannular Sb···Sb interaction (3.518 Å) which stabilises a distorted four membered ring.[88] Several metallo-phosphaarsiranes, e.g. $[Cp^*(CO)_2Fe\text{-}\overline{AsC(SiMe_3)_2P}\text{-}Fe(CO)_2Cp^*]$ (X-ray) were reported.[89] The tetraarsatetrasilacubane $[\{AsSi(2,4,6\text{-}C_6H_2Pr^i_3)\}_4]$ (X-ray) has been described.[90]

Pentaaryl antimony compounds were used as chemoselective arylating agents towards acid halides. Arylation of ketones was promoted by the addition of Lewis acids.[91] The ^{121}Sb Mössbauer spectra of $PhSbX_2$ (X = Cl, Br, I) have been determined.[92] A series of mono- and dicationic aryl bismuth compounds, $[BiAr_2L_2]^+X^-$ and $[BiArL_4]^{2+}X^-_2$ (X-ray), L = neutral Lewis base, were prepared and shown to have disphenoid and square pyramidal geometries respectively.[93] The reaction of $BiCl_3$with $[Li_2(biph).tmeda]$, biph = 2,2′-biphenylene, affords $[Bi_2(biph)_3]$ **(20)** (X-ray) which possesses intermolecular Bi···Bi contacts.[94] The first water stable, seven coordinate aryl bismuth(V) complexes, e.g. $[Bi^V(p\text{-tolyl})_3\{\eta^2\text{-}1,2\text{-}O,O(C_7H_5)\}_2]$ (X-ray), have been prepared.[95] X-ray crystallography has shown the intramolecularly base stabilised arylpnictide compounds $[\overline{E\{C_6H_4(2\text{-}CH_2N}Me_2)\}_3]$ to be monomeric, six coordinate with N···E interaction strength increasing in the order E = As<Sb<Bi.[96] Intramolecular base stabilisation has also been employed to induce chirality in the synthesis of the diastereomerically pure bismuth substituted ferrocene **(21)**.[97] A variety of arylbismuth(III) and (V) complexes containing pyridyl or amino functional groups have been reported, e.g. $[Bi\{p\text{-}C_6H_4CH_2(NPr^i_2)\}_3]$.[98] Aryl bismuthonium ylides, $[Ph_3Bi{=}CHC(O)R]$ R = Bu^t, Ph, have been generated *in-situ* and used to transform organic dicarbonyl complexes into a variety of species.[99]

The gas phase structures of $MeAsF_2$ and Me_2AsF have been determined by a combination of electron diffraction and *ab initio* calculations.[100] The compounds $[Cp^*AsX_2]$ X = F, Cl, Br, I, have been synthesised and structurally characterised.[101] The first potentially tridentate stibine ligand, $MeC(CH_2SbPh_2)_3$ (tts), has been prepared and used in the formation of a number of complexes, e.g. $[(tts)Mo(CO)_3]$ (X-ray).[102] Homoleptic silver(I) tertiary stibine complexes have been studied by ^{109}Ag NMR and X-ray crystallography which show a tetrahedral silver geometry in $[Ab(SbPh_3)_4]BF_4$.[103] Treating nickel or cobalt powder with $MeAsI_2$ yielded the arsine complexes $[MI_3(AsMe_3)]$ M = Co, Ni (X-ray).[104] Similarly, reacting gallium powder with $(p\text{-}MeOC_6H_4)_3AsI_2$ or Et_3AsI_2 afforded monomeric $[GaI_3\{As(p\text{-}MeOC_6H_4)_3\}]$ (X-ray) and the gallium-gallium bonded species $[Ga_2I_4(AsEt_3)_2]$ (X-ray) respectively.[105] Addition of Me_2SbBr to $Me_2SbSbMe_2$ did not give the expected neutral adduct but $[Me_2SbSb(Me_2)SbMe_2][Me_2SbBr_2]$ (X-ray) *via* a proposed



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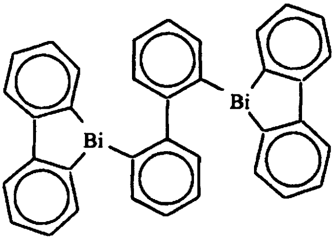

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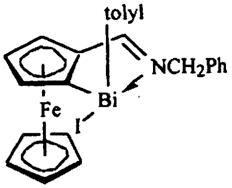

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oxidative addition route. The cation exists as a non-linear chain with equal Sb-Sb bond lengths (2.820(1)Å).[106]

The reaction of $SbPh_3$ with I_2 in CH_3CN/H_2O yields an adduct of the oxo-bridged species $(Ph_3SbI)_2O$ with I_2. X-ray crystallography revealed linear $(I\text{-}I\cdots ISb(Ph)_3OSb(Ph)_3I\cdots)_n$ chains in which the I-I bond lengths are longer than in I_2 itself.[107] A range of di- and tetrameric oxo-diphenylantimony phosphonate cages have been reported which include $[\{Ph_2Sb(\mu\text{-},\mu\text{-}O_2PCy_2)\mu\text{-}O\}_2]$ (X-ray).[108]

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8

Organic Aspects of Organometallic Chemistry

BY LOUISE TONKS AND JONATHAN M.J. WILLIAMS

1 Introduction

Most complex multi/step organic syntheses rely heavily on organometallic methods. This Chapter describes some of the interesting advances in organometallic chemistry as judged from an 'organic chemistry perspective'. Several current and emerging themes have been given particular attention, including; catalysed carbon-heteroatom bond formation, alkene metathesis, the increasing use of scandium triflate as a Lewis acid, combinatorial synthesis and catalysis.

2 Coupling Reactions

This section describes some of the huge number of synthetic applications of metal catalysed coupling reactions. Very typically, such reactions involve the formation of a single C-C bond or a carbonylation. However, some of the current research includes the formation of multiple bonds in cascade processes, and examples of such reactions are also included.

As well as C-C bond formation, the application of these catalytic coupling reactions to C-X bond formation is now synthetically viable, and is described in the next section.

2.1 Catalysed Carbon-Heteroatom Bond Formation – Whilst allylic substrates and carbonylation reactions have an extensive pedigree in the catalytic formation of C-X bonds, the use of aryl and vinyl substrates in catalytic cross coupling reactions has been, until recently, less viable.

The direct palladium catalysed amination of aryl halides has been independently investigated over the last few years by the research teams of Hartwig and Buchwald, although others have also published in this area.[1]

The conversion of aryl iodides into anilines is efficiently performed in dioxane using a palladium catalyst and sodium t-butoxide. Representative examples include the conversion of **1** and **2** into the products **3** and **4**.[2]

The use of bidentate ligands has proven to be important for these reactions. Using bis(diphenylphosphino)propane (dppp) as the ligand, 2,6-dibromopyridine **5** was converted into the product **6**.[3] bis(Diphenylphosphino)ferrocene (dppf)

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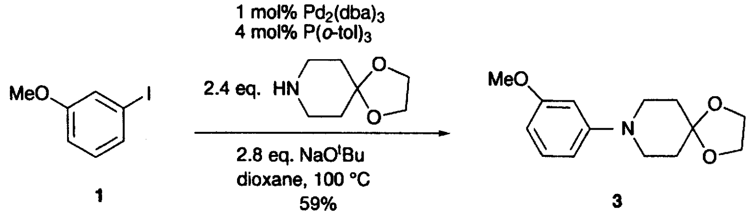

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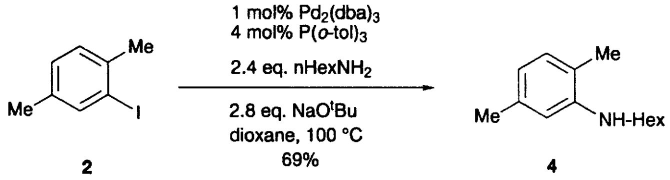
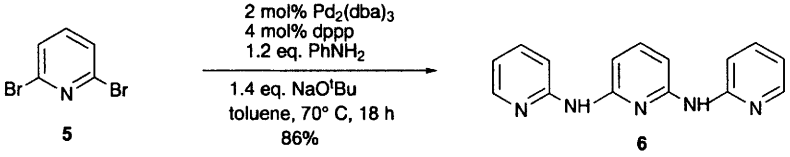


2 4

also provides a particularly competent catalytic system. Thus, the aryl bromide **7** was transformed into the aniline **8** in outstanding yield.[4]



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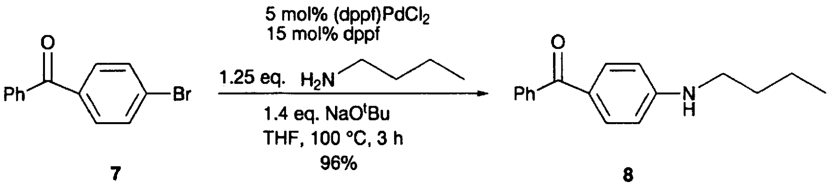
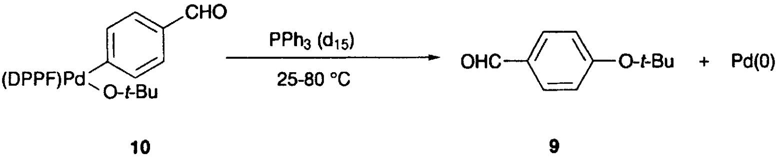


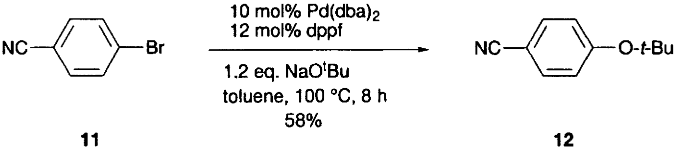
7 8

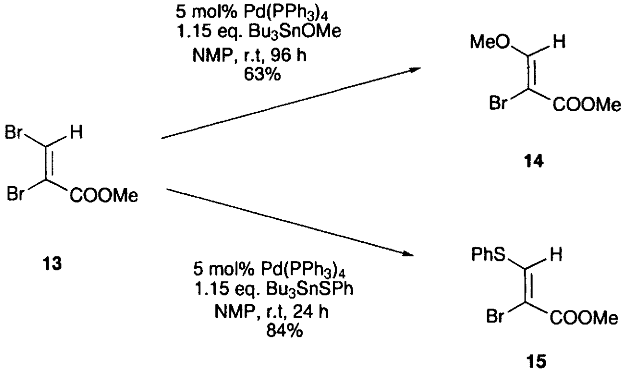
Mann and Hartwig have observed the reductive elimination of ether **9** from the palladium complex **10**.[5] They extended this work to demonstrate a palladium catalysed etherification of electron-deficient aryl halides. For example p-bromobenzonitrile **11** is converted into ether **12** in reasonable yield.

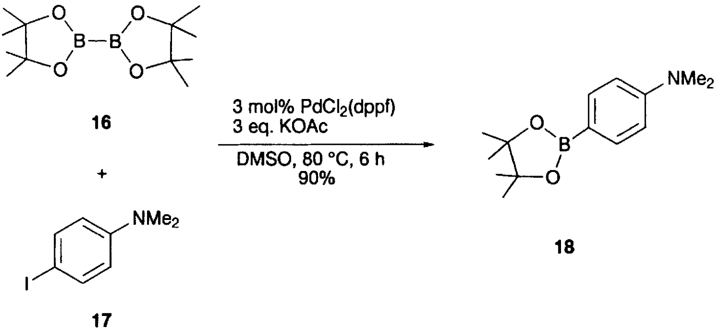
The conversion of vinyl bromides into vinyl ethers and vinyl sulfides has also been reported.[6] The dibromoalkene **13** was reacted with a palladium catalyst and either methoxytributylstannane or phenylthiotributylstannane to give the corresponding products **14** and **15**. The vinyl ether **14** is synthetically useful for the incorporation of the β-methoxyproperoate unit into fungicidal aromatic compounds.

The reaction of aryl halides with the diboronate ester **16** provides a route to





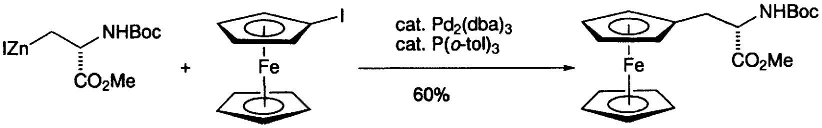




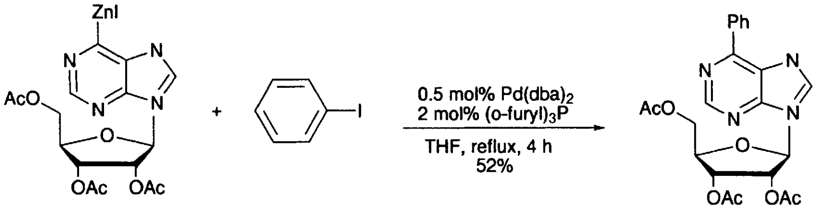
arylboronate esters.[7] For example, the reaction of the iodide **17** with diboronate ester **16** affords the coupled product **18** in good yield.

2.2 Cross-coupling Reactions – Each year there are now hundreds of papers published describing palladium-catalysed cross-coupling reactions. This is surely testament to the synthetic power of these reactions.

Organozinc reagents are often employed as the 'nucleophilic' components of coupling reactions, and this is partly due to their tolerance of other functional groups. For example, Jackson and co-workers have coupled the organozinc reagent **19** (derived from serine) with iodoferrocene **20** to provide the ferrocenylalanine derivative **21**.[8] The preparation of the organozinc nucleoside reagent **22** and its subsequent cross-coupling reaction with iodobenzene **23** have been reported by Knochel and co-workers.[9]

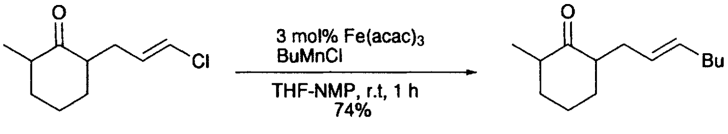


19 **20** **21**



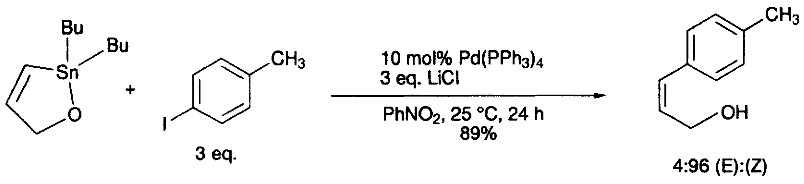
22 **23** **24**

Organomanganese reagents have also been employed in cross-coupling reactions, using an iron catalyst.[10] Using this procedure the ketone-containing vinyl chloride **25** was coupled with butylmanganese chloride in good yield without compromising the ketone functionality.



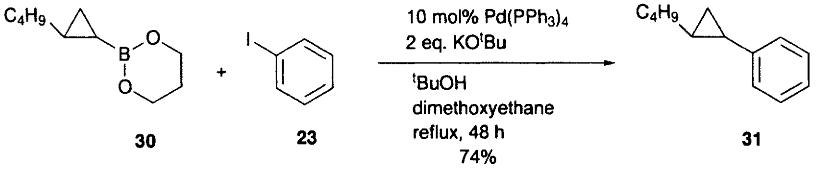
25 **26**

The use of organostannanes as the nucleophilic coupling partner is known as the Stille coupling. Kraus and Watson have reported a useful procedure involving the cyclic stannoxane **27**.[11] Coupling of this stannoxane with iodotoluene **28** provides the Z-alkene product **29** with good yield and selectivity. The Z-selectivity is a consequence of the cyclic nature of the stannoxane reagent.

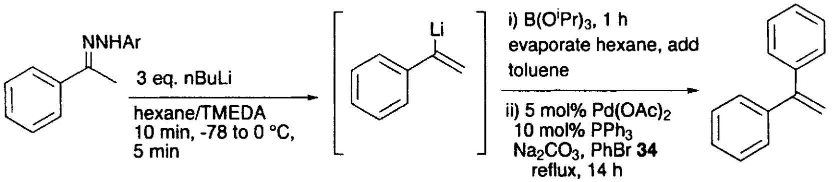


27 **28** **29**

Boronic acids have been used in cross-coupling reactions, and such reactions are known as Suzuki couplings. Generally, aryl and vinyl boronic acids are used as the substrates, although it has now been shown that cyclopropyl boronate esters can also be partners in the coupling reaction.[12] Thus, the cyclopropylboronate **30** undergoes coupling reaction with iodobenzene **23** to give the product **31** in good yield. The generation of vinyl boronates from a Shapiro reaction and addition of tri-isopropylborate forms the basis of a one pot Shapiro-Suzuki sequence.[13] Treatment of the hydrazone **32** with butyllithium affords a vinyllithium intermediate **33** via the Shapiro reaction, and addition of tri-isopropylborate generates the corresponding vinylborate. The so-formed vinylborate is then subjected to a Suzuki coupling with bromobenzene **34** to give the coupled product **35**.

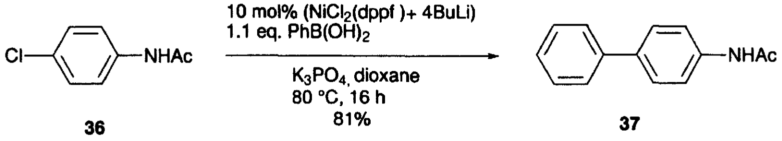


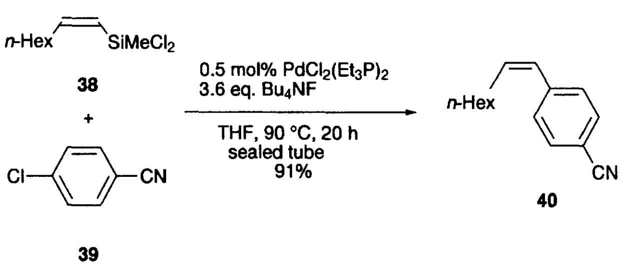
30 **23** **31**



32 **33** **35**

Whilst the use of iodo- and bromo- arenes is conventional for the 'electrophilic' coupling partner, reports of arenediazonium salts[14] and aryliodonium salts[15] have also appeared, as well as the use of aryl chlorides.[16] In this latter case, the normally less reactive aryl chlorides are found to undergo Suzuki-coupling using a nickel catalyst. For example, the aryl chloride **36** is converted into the biaryl **37** in good yield. Normally organosilanes are insufficiently reactive to undergo coupling reactions, although organochlorosilanes show considerably enhanced reactivity.[17] Vinylsilane **38** undergoes coupling reactions, even with relatively unreactive aryl chlorides, such as substrate **39** to give the product **40** with preservation of the Z-geometry of the alkene.

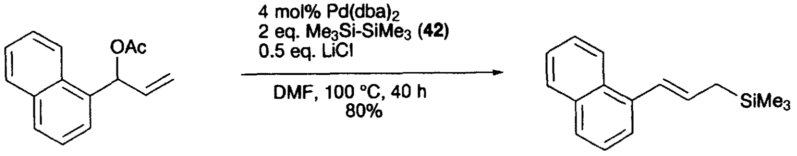




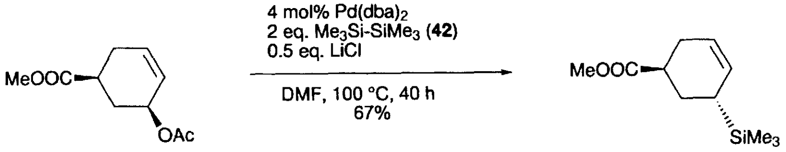
2.3 Allylic Substitution Reactions – suitable allylic substrates undergo nucleophilic substitution reactions either catalysed or promoted by transition metals. For most transition metals, the mechanism involves an intermediate π-allylmetal complex. Generally, the nucleophiles employed are carbon-based, and perhaps these are synthetically the most useful. Nevertheless recent reports have described the preparation of allylsilanes and allylboronates, which are themselves useful reagents. Treatment of the allylacetate **41** with hexamethyldisilane **42** and a combination of a palladium bis(dibenzylideneacetone) catalyst and lithium chloride afforded the allylsilane **43**.[18] The substrate **44** was converted into the trans-disposed allylsilane **45**, indicating that the reaction proceeds with overall inversion of stereochemistry. Use of the diboronate ester **46** as the nucleophile allows access to allylboronates.[19] Thus, allyl acetate **47** was converted into the corresponding allylboronate **48** in good yield.

Vinyl cyclopropanes may be prepared using the substrate **49**,[20] with two replaceable leaving groups and the nucleophile **50**, with two hydrogens available for deprotonation. The reaction is assumed to proceed via intramolecular attack on the π-allylpalladium complex **51**. The reaction proceeds with complete diastereoselectivity, and the product **52** can be further manipulated to provide coronamic acid **53**.

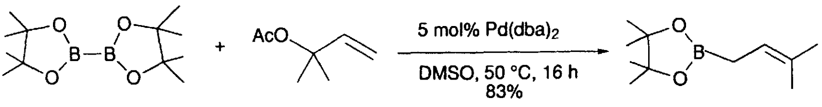
Eschavarren and co-workers have reported that the palladium catalysed



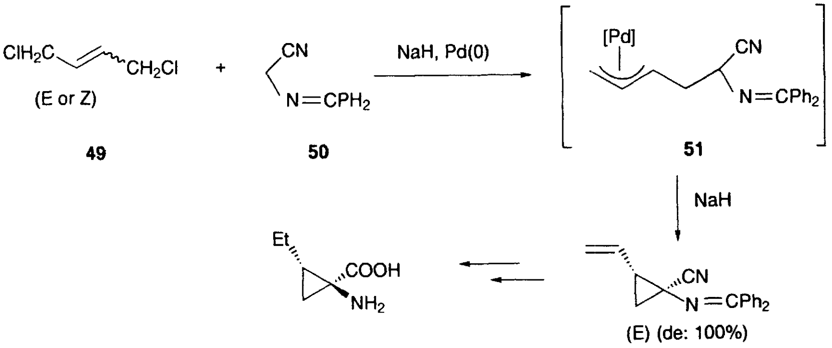
41 **43**



44 **45**



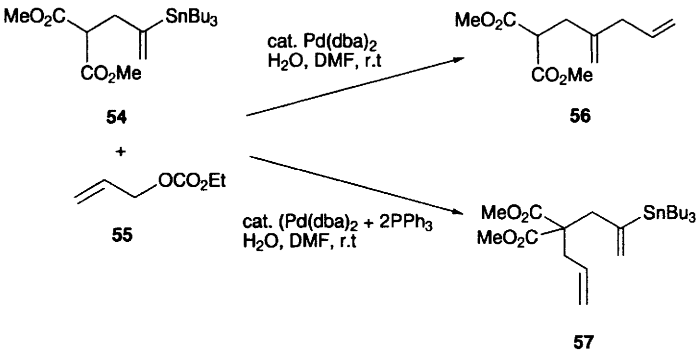
46 **47** **48**

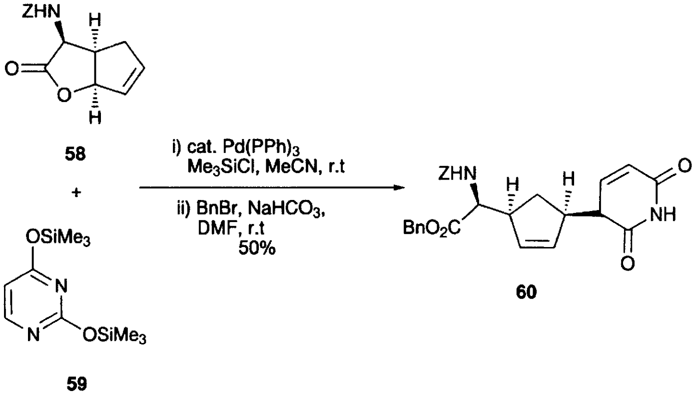


53 **52**

reaction between the vinylstannane **54** and **55** involves either a Stille coupling or an allylic substitution reaction, depending on the exact catalyst used.[21] The presence of a phosphine ligand favours the allylic substitution pathway to give product **57**. Palladium catalysed allylic substitution reactions have been employed as a key step in many complex syntheses. A recent example involves the reaction between the allyl lactone **58** and O,O-bis(trimethylsilyl)uracil **59**, which provides the ester **60** after *in situ* benzylation.[22]

There have also been many enantiomerically pure ligands employed in the





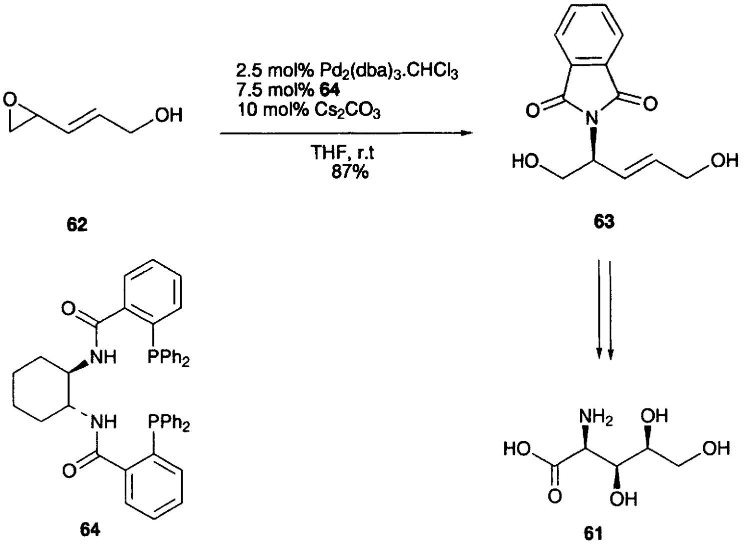
palladium catalysed allylic substitution reaction, and recent advances have been reviewed by Trost and Van Vranken.[23]

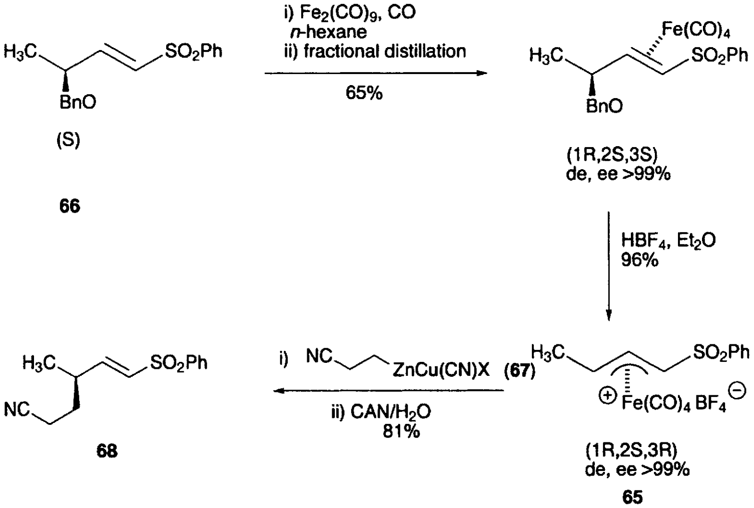
An asymmetric example which is incorporated into the synthesis of polyoxamic acid **61** has been reported by Trost and co-workers.[24] The vinyl epoxide **62** and potassium phthalimide undergo an enantioselective substitution reaction to give compound **63** in the presence of a palladium catalyst and ligand **64**, and further transformations provide polyoxamic acid **61**.

The η^3-allyliron complex **65** can be obtained from the enantiomerically pure allyl benzyl ether **66**.[25] Functionalised zinc-copper reagents, including compound **67** can be added with complete chirality transfer and regiocontrol to form the product **68**.

2.4 Heck Cyclisations and Related Reactions – The Heck reaction is one of the more useful C-C bond forming reactions, and is a widely used synthetic transformation.

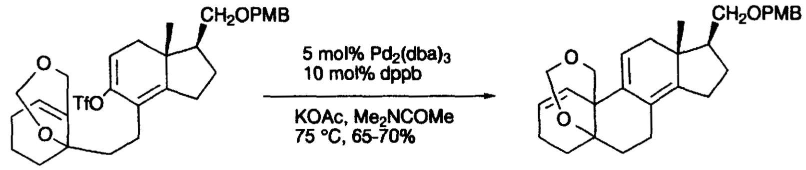
An elegant example of a cyclisation via a Heck reaction has been described by Overman and co-workers.[26] The dienyltriflate **69** cyclised to provide the steroid-type skeleton **70** which has synthetic possibilities to structurally complex cardeno-



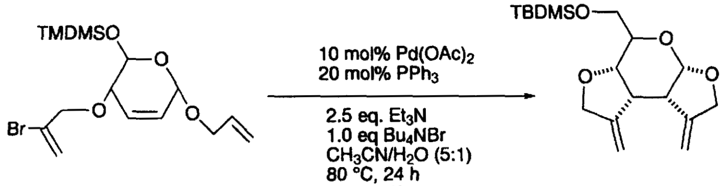


lides. Tandem and cascade reactions provide opportunities for the formation of complex products from simpler precursors. Sinou and co-workers have reported an interesting tandem Heck reaction of the substrate **71**.[27] The initial Heck-type cyclisation is unable to eliminate Pd-H and undergoes a second Heck cyclisation step to give the product **72**.

Reaction cascades which are initiated in a similar way to the previous example can be terminated in different ways. The aryl iodide **73** undergoes an initial Heck

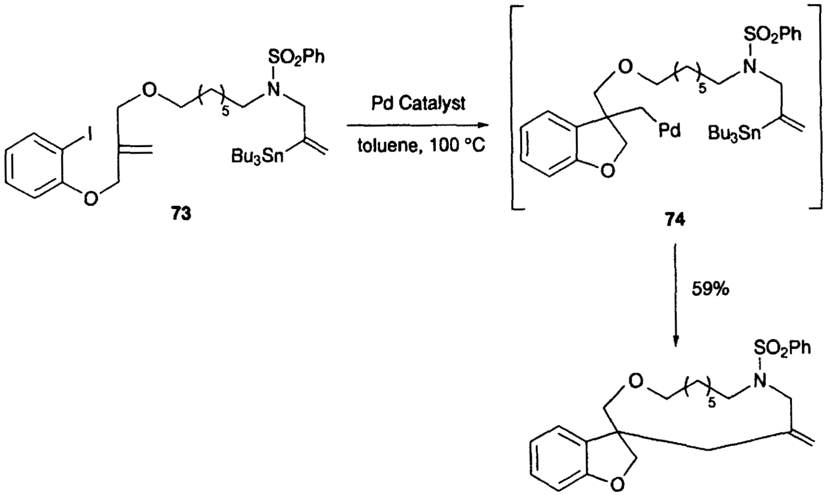


69 **70**



71 **72**

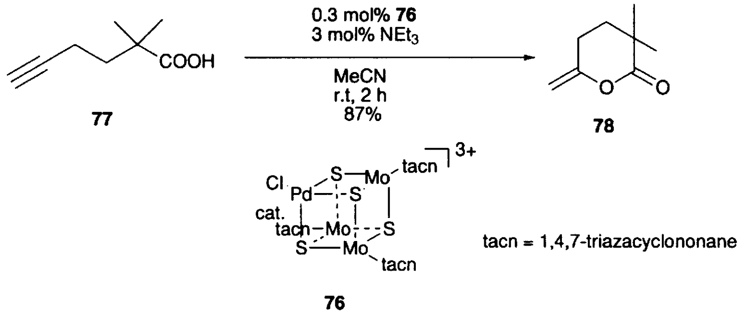
cyclisation to give the intermediate **74**, which has no available hydrogen for elimination, and hence a Stille macrocyclisation takes place to give product **75**.[28]



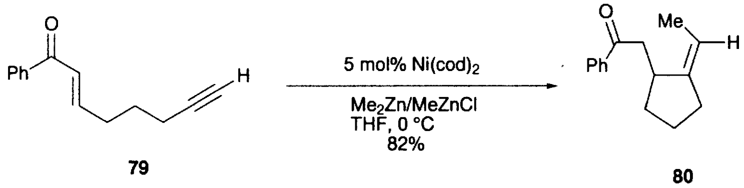
73 **74** **75**

2.5 Cyclisation Reactions Involving Alkynes – The alkyne functional group is usually straightforward to incorporate into an organic substrate, and furthermore alkynes readily undergo transition metal promoted reactions. It is therefore not surprising that there is a rich chemistry of catalysed alkyne transformations known. Several cyclisation reactions involving alkynes have been reported during 1996, and selected examples are described here.

The sulfide cluster **76** has been used to catalyse the cyclisation of compound **77** into the enol lactone product **78**.[29] The cluster was found to be more active than a conventional palladium catalyst ($PdCl_2(PhCN)_2$).

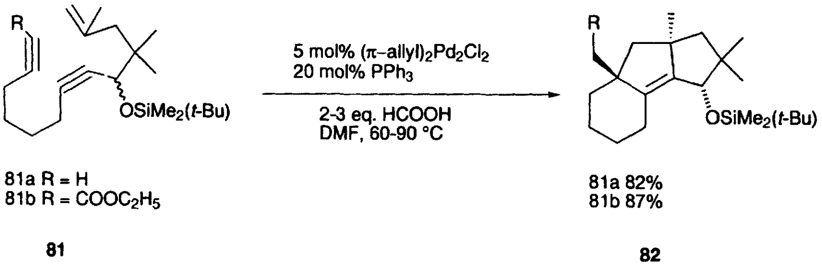


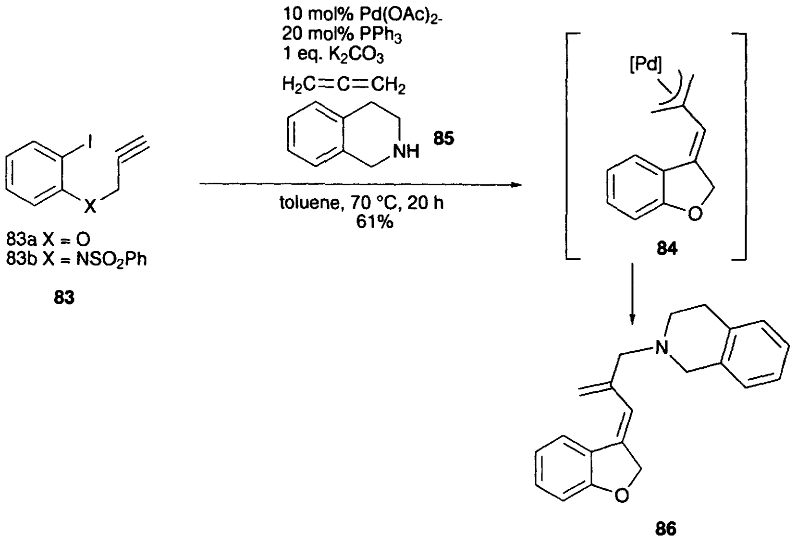
The reductive cyclisation of enynes is a synthetically useful process.[30] A development of this reaction by Montgomery and Savchenko involves an alkylative cyclisation.[31] The enyne **79** undergoes cyclisation catalysed by nickel(0) and organozinc reagents to give the cyclised product **80**. Two points are noteworthy: firstly the alkene geometry of the product is defined and secondly, no direct conjugate addition to the α,β-unsaturated ketone takes place.



Enediynes also undergo cyclisation reactions, and under reductive conditions, the conversion of enediyne **81** into the tricyclic product **82** has been achieved in good yield. This provides a very rapid access to functionalised polycyclic structures. The research group led by Grigg at Leeds has investigated many cascade cyclisation reactions. The following cascade involves cyclisation onto the alkyne **83** and allene addition to give the allylpalladium intermediate **84** which reacts with an amine **85** to give the product **86** in good isolated yield.[33]

A spectacular one-pot reaction sequence has been achieved by a French group led by Malacria.[34] The triyne **87** initially undergoes cobalt catalysed cyclisation to the monocyclic compound **88**, which could be isolated at this stage. However, addition of bis(trimethylsilyl)ethyne **89** affords the benzocyclobutene adduct **90**, which on heating undergoes electrocyclic ring opening to an ortho-quinodimethane and an intramolecular Diels Alder to give the product **91** in 42% yield. An extraordinary increase in the complexity of the compound occurs during this



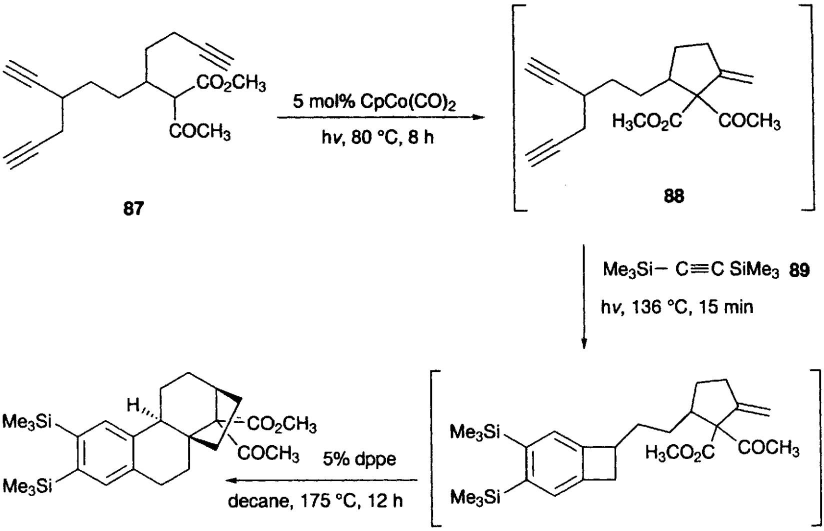


one-pot sequence. Cyclisation reactions of appropriate alkynes can also lead to benzannulation, as described in the next section.

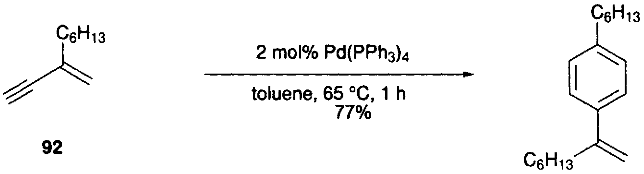
2.6 Benzannulation Reactions – Organic synthesis involving the synthesis of compounds containing a benzene unit generally involves modification of the functional groups around the aromatic core. Whilst there is considerable precedent for transition metal catalysed formation of aromatic compounds, the following examples are worthy of note.

Y. Yamamoto and co-workers have shown that conjugated enynes undergo benzannulation to give the corresponding styrenes.[35] The reaction is illustrated by the dimerisation of enyne **92** to give styrene **93**, and by the remarkable synthesis of paracyclophane **95** from the acyclic precursor **94**.

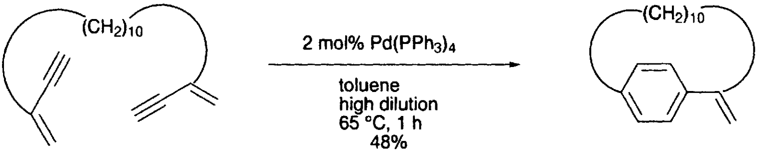
Merlic and Pauly screened various ruthenium catalysts for the cyclisation of the alkyne **96** into the benzofuran **97**.[36] The authors presented evidence that the reaction pathway proceeded via a vinylidene complex.



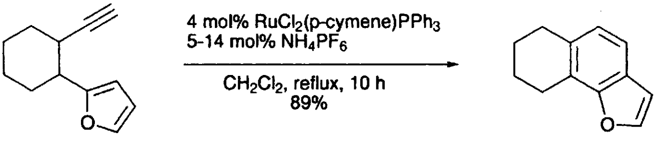
87 **88** **91** **90**



92 **93**



94 **95**

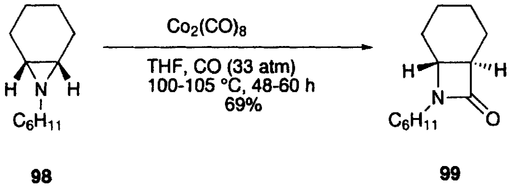


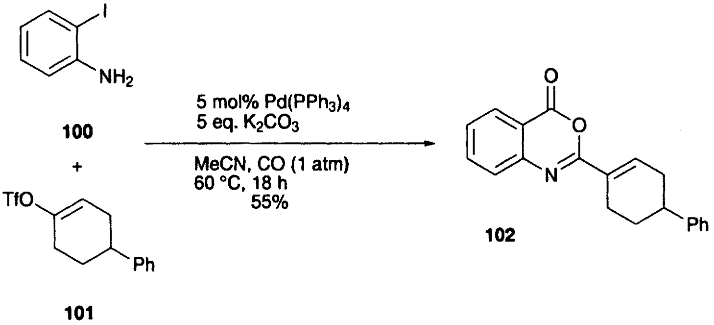
96 **97**

3 Carbonylation Reactions

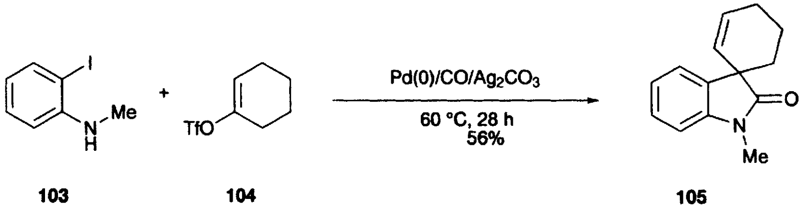
Many transition metal catalysed reactions performed in the presence of carbon monoxide incorporate a carbonyl moiety into the product.

Piotti and Alper have demonstrated that the dicobaltoctacarbonyl catalysed carbonylation of aziridines occurs with inversion of stereochemistry to give β-lactams.[37] Using the bicyclic aziridine **98** afforded the strained bicyclic lactam **99**. An unusual 'double-carbonylation' of o-iodoaniline **100** occurs with a range of vinyl triflates and aryl iodides including triflate **101**.[38] The mechanism is likely to proceed via carbonylation to give an amide followed by a second carbonylation process into the aryl iodide and trapping by the amide.

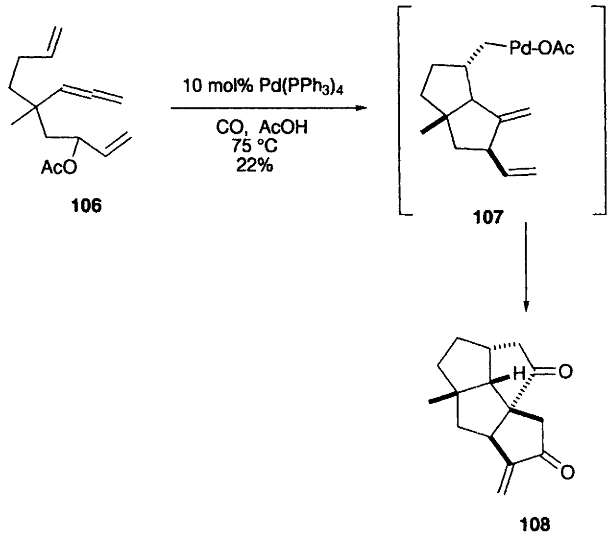




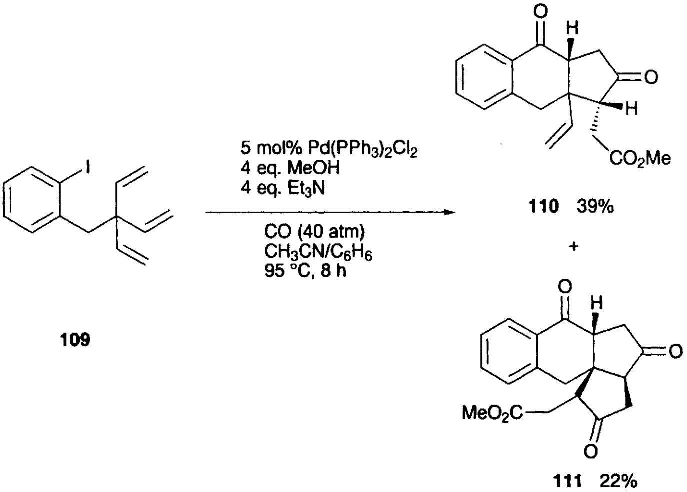
However, a related reaction between the secondary amine **103** and vinyl triflate **104** gives a carbonylation to provide a tertiary amide followed by a Heck cyclisation to give the oxindole **105**.[39]



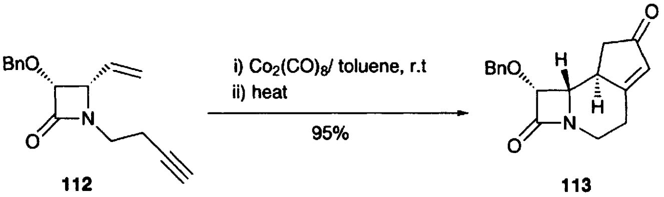
Some spectacular examples of multiple carbonylative cyclisations have been reported. The allyl acetate **106** forms an allylpalladium complex, which is attacked by the allene and then by the isolated alkene to afford the intermediate **107**. Two carbonylation/cyclisation events followed by elimination affords the tetracyclic product **108**, albeit in modest yield.[40]



Negishi and co-workers have reported a series of carbonylative cyclisations,[41] including examples of angular tricyclisation.[42] The triene **109** affords the products **110** and **111** of bicyclisation and tricyclisation.



3.1 Pauson-Khand Cyclisation – The Pauson-Khand cyclisation is a very attractive synthetic reaction, providing rapid access to the cyclopentenone moiety, often as part of a bicyclisation reaction. A recent example involving the functionalisation of the precursor **112** into the functionalised β-lactam product **113** elegantly demonstrates the power of the reaction.[43]



For large scale reactions, the general requirement for stoichiometric amounts of dicobaltoctacarbonyl may be discouraging, and although catalytic variants have been reported, none are really performed under mild conditions. A recent catalytic example uses a combination of Co(acac)$_2$ and sodium borohydride which proved to be effective at 100°C under a pressure (30–40 atm) of carbon monoxide.[44]

The research group of Buchwald at MIT has developed a variant of the Pauson-Khand reaction which uses trialkylsilyl cyanides and a titanium catalyst.[45] Titanocene dichloride is used as the catalyst precursor, which is activated by treatment with two equivalent of butyllithium followed by an enyne, e.g. enyne **114**, which provides a catalytic amount of the titanacycle **115**. Addition of triethylsilyl cyanide affords the silyl imine **116**, which can be converted into the cyclopentenone **117** (as for a Pauson-Khand reaction) or reduced and acylated to provide the allyl amide **118**. The one-pot reaction sequences were applied to the preparation of other more complex cyclopentenones and allylamides.

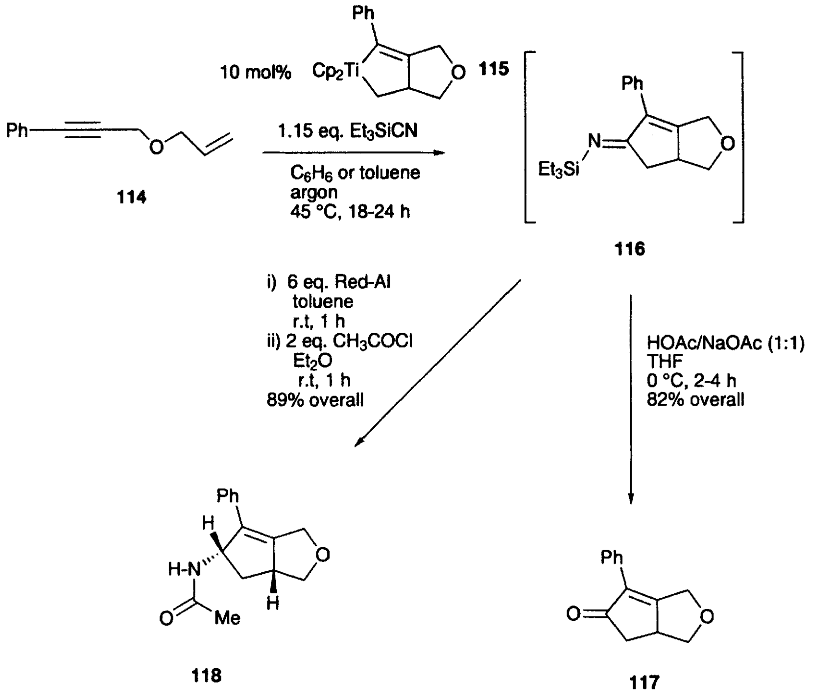
A related nickel catalysed reaction has considerable synthetic potential.[46] The enyne **119** is converted into the cyclopentenone **120** in good yield using a nickel(0) catalysed reaction with triisopropylsilyl cyanide and subsequent hydrolysis of the silylimine.

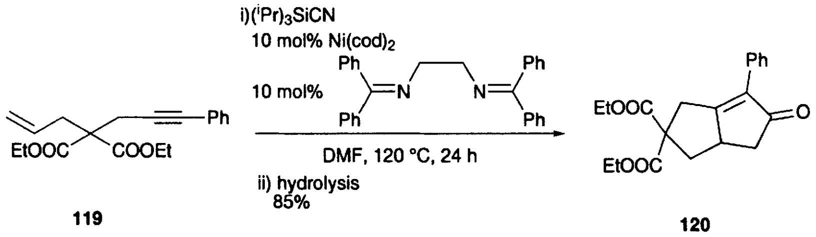
The Buchwald team has also reported a hetero-Pauson-Khand transformation.[47] Thus acetophenone **121** is converted into the lactone **122** using a titanium catalyst in the presence of carbon monoxide.

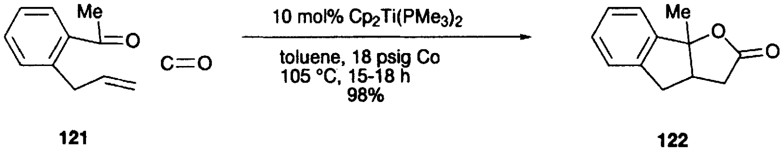
The exciting developments in catalytic reactions related to the Pauson-Khand cyclisation are certain to lead to renewed interest in this type of process.

4 Organometallic Methods of C-C Bond Formation

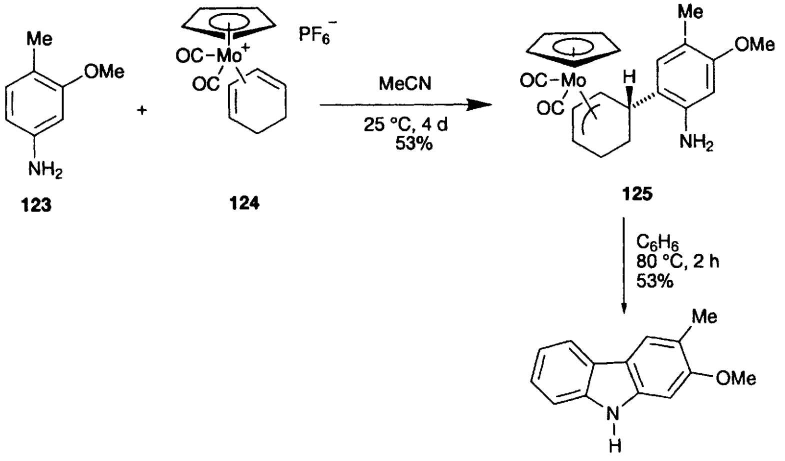
As well as standard cross-coupling and carbonylation reactions, there are other synthetically valuable approaches to C-C bond formation using organometallic methods.







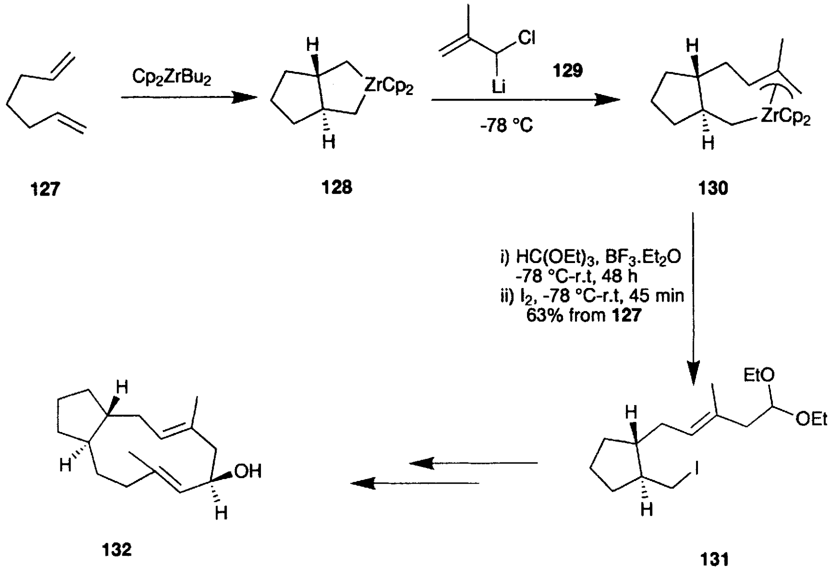
4.1 Transition Metal Templates – The idea of using a transition metal complex of an organic molecule to control the chemical reactivity is a well established concept. Several synthetically interesting examples have been reported in 1996. Semmelhack[48] and Pearson[49] have independently reported the use of chiral auxiliaries to control additions of nucleophiles to arene-tricarbonyl-chromium(0) complexes. Carbazoles have been prepared using a molybdenum-medium synthesis.[50,51] Thus, electrophilic aromatic substitution of aniline **123** with the (η^4-diene) molybdenum complex **124** affords the allyl molybdenum compound **125**. Subsequent oxidative cyclisation affords the fully aromatised carbazole **126**. A series of natural products was obtained using this methodology.



123 **124** **125** **126**

Luker and Whitby have employed organozirconium chemistry in the construction of the dolabellane skeleton.[52] Treatment of diene **127** with dibutylzirconocene provided the known zirconacycle **128**. This zirconacycle undergoes an insertion reaction with reagent **129** to give the allylzirconium complex **130**. The allylzirconium complex **130** was elaborated by treatment with triethylorthoformate and borontrifluoride etherate and then iodine, which gives the iodo-compound **131**. Further functionalisation including cyclisation via the chromium(II)-mediated Nozaki-Hiyama reaction afforded the dolabellane skeleton **132**.

4.2 Alkene Metathesis – Catalytic ring closing metathesis reactions are becoming an increasingly popular route to cyclic alkenes.[53,54] For example, König and Horn have reported the application of ring closing metathesis to the construction of the crown ether **133** from the acyclic podand **134** using the ruthenium catalyst **135**.[55] Using the molybdenum catalyst **136**, Hölder and Blechert[56] have used ring closing metathesis in the conversion of the diene **137** into the cyclic alkene **138**. Simple hydrolysis of the ketal, isomerisation of the alkene with base and hydrolysis of the ester affords coronafacic acid **139**. Barrett, Gibson and co-workers have shown that alkene metathesis is an efficient strategy in the preparation of a range of novel β-lactams.[57] For example substrate **140** was



converted into the new alkenes **141** upon treatment with the molybdenum catalyst **136**.

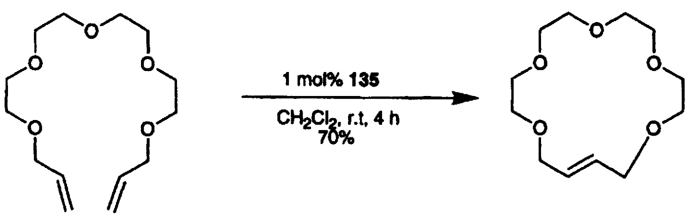
The Grubbs team at Caltech, who generated the current interest in ring closing metathesis reactions, have developed the reaction to include systems which lead to the formation of fused bicyclic rings.[58] The dienyne **142** undergoes bicyclisation in the presence of catalyst **143** to give the product **144**.

4.3 [4+2]-Cycloaddition – Traditionally, a Diels-Alder reaction between a diene and dienophile can be catalysed by conventional (oxophilic) Lewis acids. Wender and Smith have reported several examples of the nickel catalysed intramolecular [4+2]-cycloaddition reaction of enynes.[59] These reactions are not, mechanistically, Diels-Alder reactions. Enyne **145** is converted into the cyclised product **146** which was exploited in the synthesis of yohimbine-analogues.

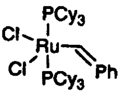
5 Emerging Areas of Organometallic-dependent Organic Synthesis

Sections 5.1–5.7 detail recent novel approaches to organic synthesis which rely on organometallic reagents or catalysts. The wide scope of chemistry discussed in these sections is an indicator of the utility of organometallic chemistry in organic synthesis.

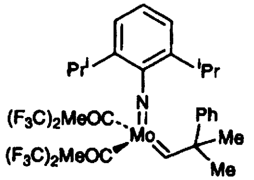
5.1 Catalytic Asymmetric Aminohydroxylation – The Sharpless group has reported another remarkable asymmetric catalytic process. An extension of the catalytic AD process allows catalytic asymmetric aminohydroxylation (AA) reactions to



134 **133**



135



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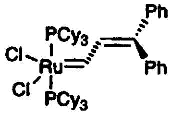
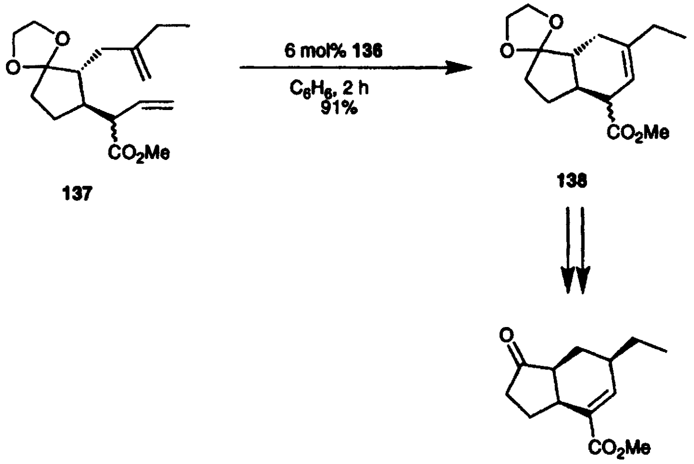


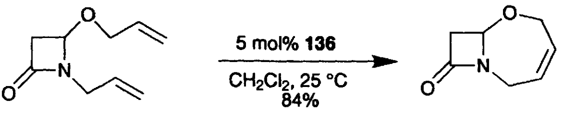
143



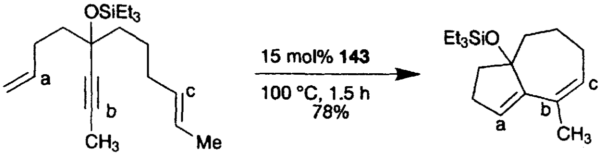
137 **138** **139**

be performed on suitable alkenes. There are many natural products and drugs which contain an enantiomerically pure amino alcohol motif, and so there is considerable excitement about the scope of the reaction.

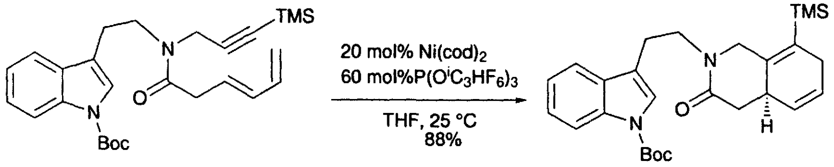
In the first communication,[60] the Sharpless group employed chloramine T trihydrate (TsNClNa.3H_2O) as the source of the nitrogen function in the products, as illustrated by the conversion of a general alkene **147** into the N-tosyl protected β-amino alcohol **148**. Representative examples of this procedure include the conversion of alkenes **149** and **150** into the corresponding products **151** and **152** with good yields and enantioselectivities.



140 141



142 144



145 146

In subsequent communcations,[61,62] the use of other N-chlorosulforamide salts and especially N-chlorocarbamate salts was shown to provide a more efficient catalytic asymmetric aminohydroxylation process.

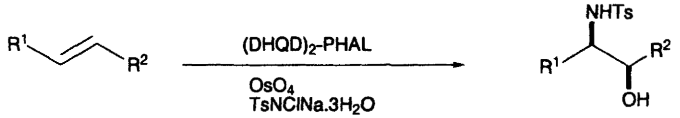
Using propanol/water (50:50) as solvent, very impressive levels of enantioselectivity were obtained in the aminohydroxylation of 2-vinylnaphthalene **153**. Choice of ligand dictated the formation of either **(R)-154** or **(S)-154** as the major enantiomer. The selectivity was also improved using these conditions for the conversion of other alkenes.

Styrene can now also be successfully converted into product efficiently, whereas the earlier conditions were unsuccessful here. Furthermore substrates which are inappropriate for the AD reaction (since they would give meso products) have been employed in the AA reaction. Thus, cyclohexene **155** is converted into product **156**. The use of EtOCONClNa led to a particularly efficient aminohydroxylation of substrate **149**.

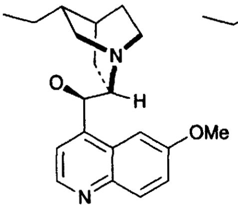
Since carbamates are generally easier to deprotect than sulfonamides, the use of carbamates has additional synthetic advantages.

5.2 Asymmetric Reduction of Ketones – The asymmetric reduction of ketones has been achieved using various reducing reagents. The use of hydrogen transfer reagents under catalytic conditions avoids the use of H_2 gas.

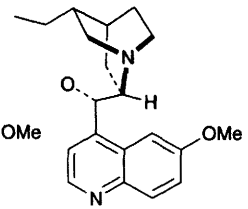
Recent developments include very enantioselective transfer hydrogenations.



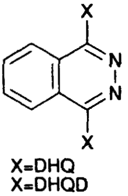
147 **148**

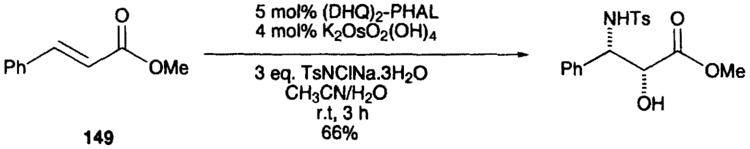


DHQ



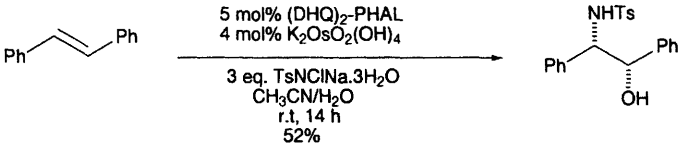
DHQD





149

151 81%ee

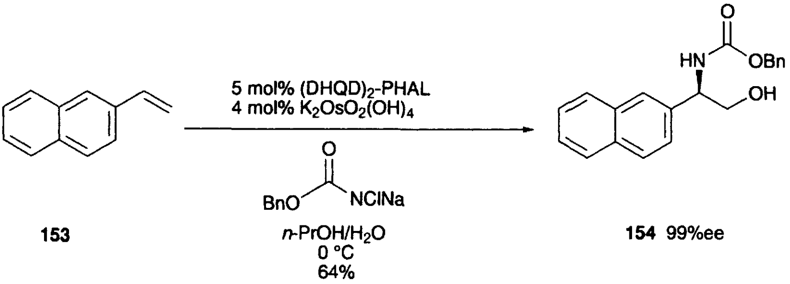


150 **152** 62%ee

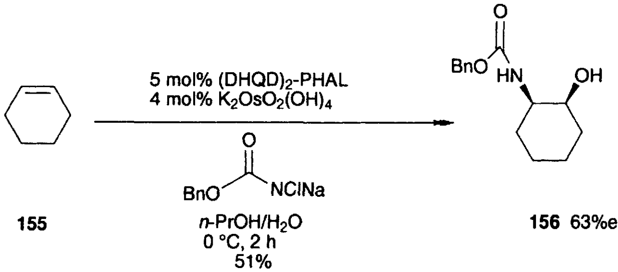
Knochel and co-workers have reduced acetophenone **158** to phenethyl alcohol **159** using formic acid and a ruthenium catalyst with ligand **160**.[63] Noyori's team has used the ruthenium catalyst **161** to effect a similar conversion.[64]

The same reduction process may also be effected by hydrosilylation. The ligand **162** provides an asymmetric environment for rhodium and iridium catalysed reactions (the first formed silyl ethers are hydrolysed to the alcohols).[65] Surprisingly, the products from the rhodium and iridium catalysed reactions are formed with the opposite enantiomer predominating.

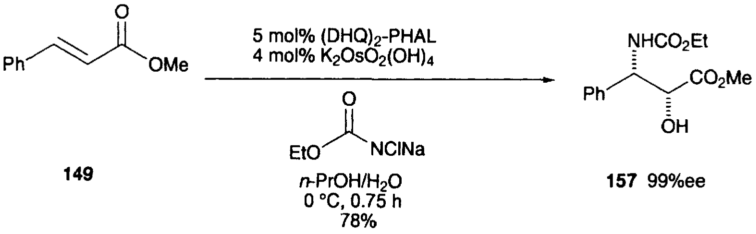
5.3 Reactions Catalysed by Scandium Triflate – Scandium triflate has found many applications as a convenient Lewis acid catalyst. The use of this catalyst was developed by Kobayashi, and his group reviewed progress in 1994.[66] Although organometallic intermediates are not involved in the catalytic cycles, the reactions



153 **154** 99%ee



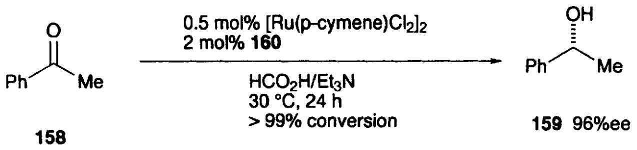
155 **156** 63%ee

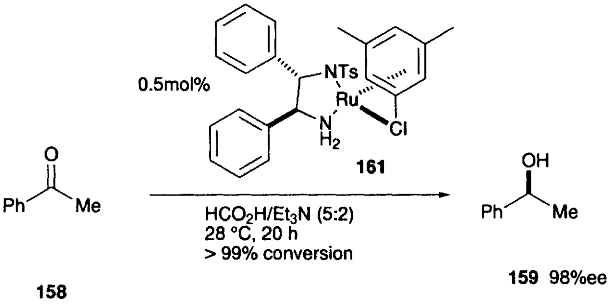


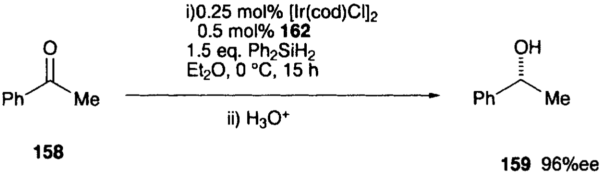
149 **157** 99%ee

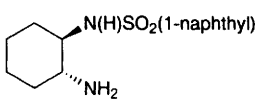
of scandium triflate do fit well in this chapter. Applications reported in 1996 include the work of Aggarwal and Vennall, who have shown that scandium triflate catalyses the addition of allyltrimethylsilane **163** to aldehydes.[67] Using 2 mol% of the catalyst, benzaldehyde **164** was converted into the homoallylic alcohol **165** in good yield. H. Yamamoto and co-workers have employed scandium as a catalyst for the acetalisation of ketones.[68] For example, ketone **166** and diethyltartrate **167** were converted into the corresponding cyclic acetal **168** in excellent yield using just 1 mol% scandium triflate.

Scandium triflate has also been found to be an efficient catalyst for the addition of lithium enolates to epoxides. Crotti and co-workers examined several oxophilic catalysts for the reaction between enolate **169** and propene oxide **170**.[69] These researchers found that the highest yield of product **171** was obtained using scandium triflate as a catalyst, although none of the catalysts provided good control of the syn:anti ratio for this reaction.

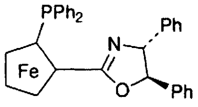








160



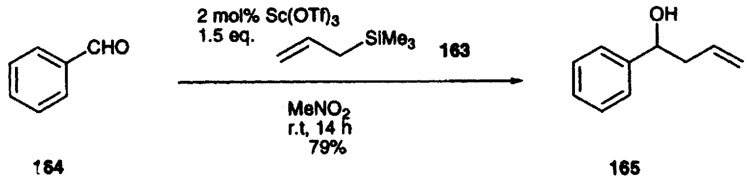
162

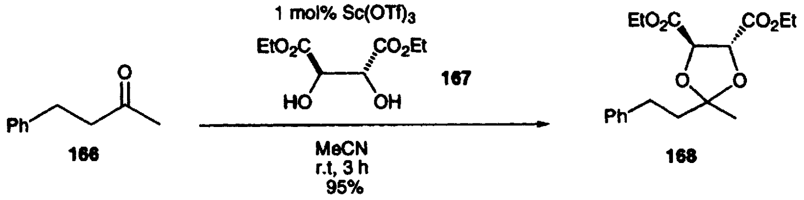
Friedel-Crafts alkylation reactions have been catalysed by scandium triflate.[70] The benzylation of mesitylene **172** with benzyl alcohol **173** affords the product **174** (in quantitative yield based on benzyl alcohol).[71]

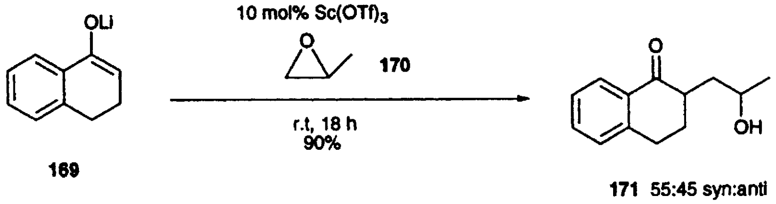
The use of either scandium triflate or scandium triflimide catalyst has been shown to be effective for acylation of alcohols.[72,73] For example, treatment of menthol **175** with acetic anhydride and 1mol% scandium triflimide affords the ester **176**.

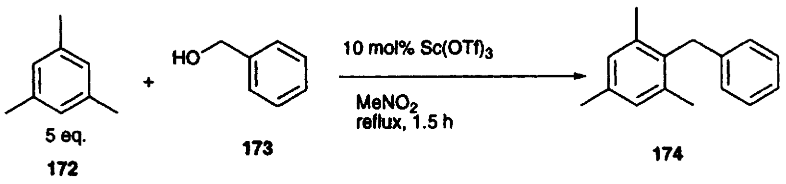
Hafnium triflate has also been shown to act as a Lewis acid catalyst in the reaction of phenol **177** with acetyl chloride to give the 2-acetylated adduct **178**.[74] The reaction is believed to proceed via both direct C-acylation and also by O-acylation and subsequent Fries rearrangement to the C-acylated product **178**.

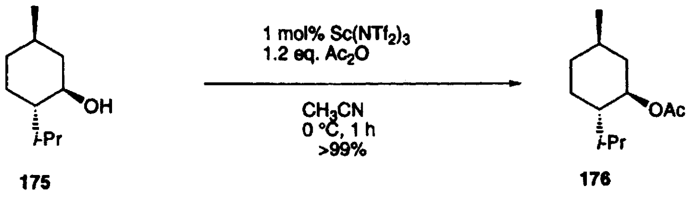
5.4 Organometallic Nucleophilic Catalysts – The acylation of alcohols may be catalysed by nucleophiles. Typically, 4-(dimethylamino)-pyridine (DMAP) **179** is employed for such reactions, as indicated in the conversion of alcohol **180** into ester **181**.

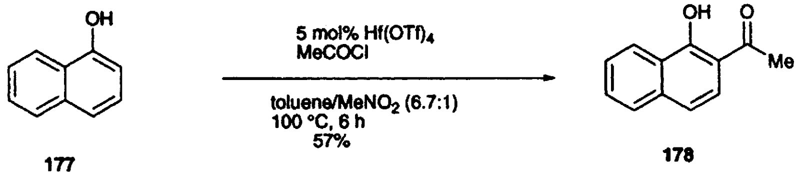

CHO
2 mol% Sc(OTf)₃
1.5 eq.
SiMe₃
163
MeNO₂
r.t, 14 h
79%
OH
164
165

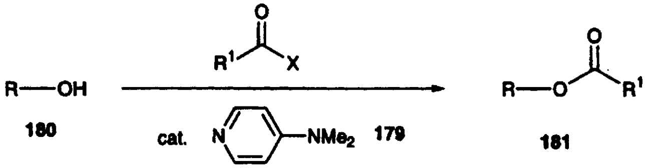

1 mol% Sc(OTf)₃
EtO₂C
CO₂Et
HO
OH
167
O
Ph
166
MeCN
r.t, 3 h
95%
EtO₂C
CO₂Et
O
O
Ph
168

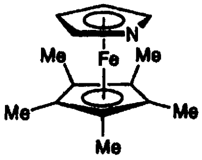

OLi
10 mol% Sc(OTf)₃
O
170
r.t, 18 h
90%
O
OH
169
171 55:45 syn:anti


+
HO
10 mol% Sc(OTf)₃
MeNO₂
reflux, 1.5 h
5 eq.
172
173
174

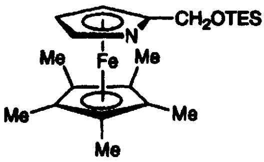

OH
i-Pr
1 mol% Sc(NTf₂)₃
1.2 eq. Ac₂O
CH₃CN
0 °C, 1 h
>99%
OAc
i-Pr
175
176


OH
5 mol% Hf(OTf)₄
MeCOCl
toluene/MeNO₂ (6.7:1)
100 °C, 6 h
57%
OH
O
Me
177
178

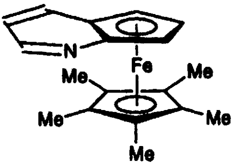




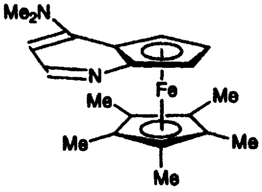
182



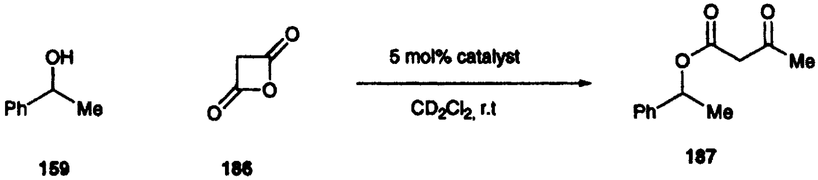
183



184



185



<u>complex</u>	<u>$t_{1/2}$</u> (min)
182	16
183	810
184	~50,000
185	<3

Ruble and Fu have produced four interesting heterocyclic π-complexes (**182**)–(**185**) as catalysts for such reactions.[75] The half-lives for the arylation of phenethyl alcohol **159** with diketene **186** to give the β-ketoester **187** are indicated for each of these catalysts. Using an enantiomerically pure version of catalyst **185**, the reaction of alcohol **159** with diketene **186** provides a kinetic resolution. At 67% conversion the remaining alcohol **159** was recovered in 87% e.e. All four complexes also functioned as catalysts for the cyanosilylation of aldehydes and the addition of alcohols to ketenes. In each case catalyst **185** proved to give the fastest reaction.

5.5 Dynamic Resolution Reactions – There has been a significant interest in Dynamic Kinetic Resolution (DKR) reactions in recent years. A large proportion of the reported work has employed enzymes to distinguish between the enantiomers of starting material. Under suitable conditions, the starting material can racemise, enabling the unreactive enantiomer to convert into the reactive one. Therefore, both enantiomers of starting material can be converted into one enantiomer of product.

There have been three reports of the use of transition metals to effect the racemisation of starting material in the presence of the enzyme.

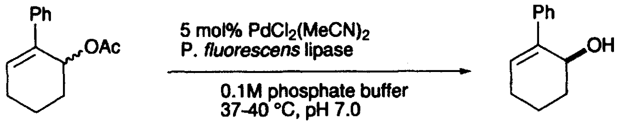
In the first example, Allen and Williams have used a Pd(II) catalyst to effect the racemisation of substrate **188**.[76] A hydrolytic enzyme selectively hydrolyses one enantiomer of acetate **188** to give the product **189**. Under the dynamic resolution conditions, high conversion and yield were obtained.

Related examples have been independently reported for the acylation of alcohols and amines under dynamic resolution conditions. The use of a rhodium catalyst in combination with an enzyme provides for the conversion of alcohol **159** into acetate **190**.[77] The racemic amine **191** is converted into the amide **192** with excellent selectivity.[78]

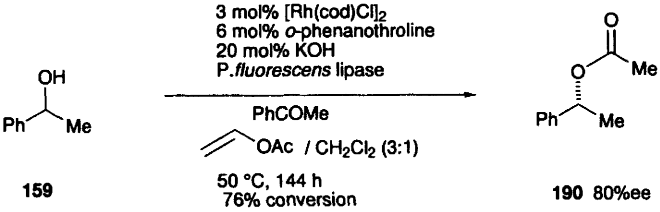
Schaus and Jacobsen have reported an interesting catalytic dynamic resolution which is not dependent on enzymes.[79] Racemic epichlorohydrin **193** undergoes enantioselective azidosilylation to give the product **194** in high enantioselectivity and in greater than 50% yield using chromium catalyst **195**. The reaction pathway may involve a meso dichloro intermediate, allowing the dynamic resolution to occur.

5.6 Combinatorial Synthesis – The generation of large numbers of compounds organised into libraries as well as rapid biological screening techniques has rapidly become of tremendous importance in looking for new drug candidates.[80] Combinatorial synthesis has found applications in both polymer-supported and solution-phase chemistry. The power and versatility of transition metal catalysed reactions is again demonstrated in applications of combinatorial synthesis.

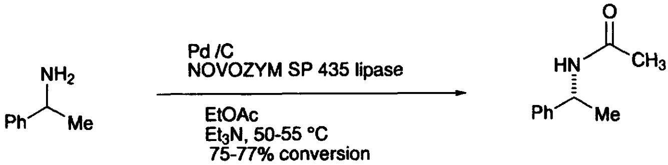
Polymer-bound substrate **196** was converted into a range of allylamides **197** by acylation and allylation. These polymer-bound amides could be converted into the corresponding indoles using a palladium catalysed Heck reaction. Subsequent release of the indole with trifluoroacetic acid affords the indole product **198**,



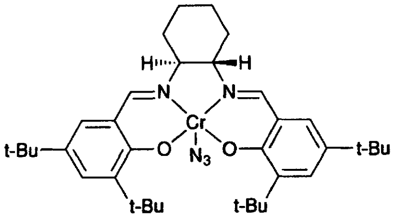
188 **189**



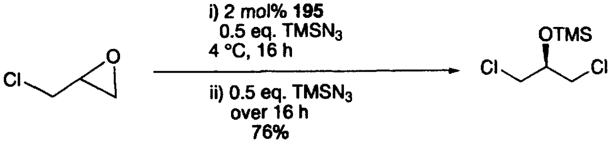
159 **190** 80%ee



191 **192** 99%ee



195

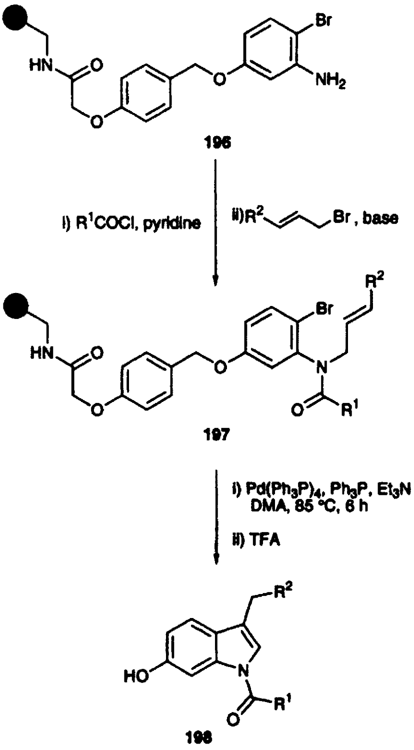


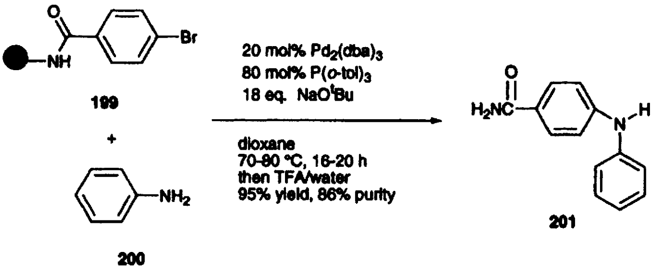
193 **194** 97%ee

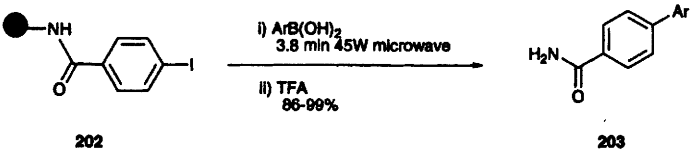
demonstrating the principle that a library of such compounds can be generated by variation in the acid chloride and allyl bromide employed.

There have been independent reports of the solid-phase synthesis of arylamines.[82,83] For example, the aryl bromide **199** and aniline **200** can be converted into the product **201** after liberation from the support.

Various arylboronic acids were coupled via the Suzuki reaction to the resin-

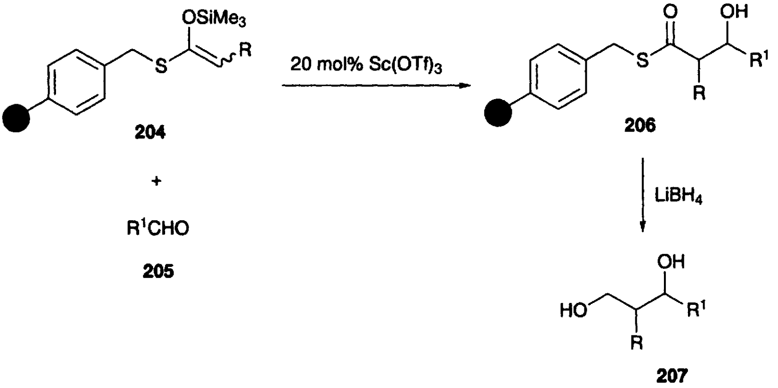

Br
HN
O
O
NH2
196
i) R1COCl, pyridine
ii) R2 Br, base
R2
Br
HN
O
O
N
O
R1
197
i) Pd(Ph3P)4, Ph3P, Et3N
DMA, 85 °C, 6 h
ii) TFA
R2
HO
N
O
R1
198


O
NH
Br
199
+
NH2
200
20 mol% Pd2(dba)3
80 mol% P(o-tol)3
18 eq. NaOtBu
dioxane
70-80 °C, 16-20 h
then TFA/water
95% yield, 86% purity
O
H2NC
N
H
201


NH
O
I
202
i) ArB(OH)2
3.8 min 45W microwave
ii) TFA
86-99%
Ar
H2N
O
203

bound substrate **202**.[84] In this case microwave irradiation was found to be beneficial. The products **203** were obtained after removal from the resin with trifluoroacetic acid. Kobayashi and his team have been investigating the catalysed aldol reaction and related reactions on solid supports.[85] In this way they demonstrate the preparation of aldol, diol and amino alcohol libraries. Resin-bound silyl enol ethers **204** underwent a scandium triflate catalysed Mukaiyama aldol reaction with a range of aldehydes **205**. Treatment of the aldol adducts **206** with lithium borohydride afforded diols **207**. Alternatively, β-hydroxyaldehydes were obtained by reduction with DIBAL-H, and β-hydroxycarboxylic acids were obtained by basic hydrolysis.

The use of imines or aldehyde/amine mixtures provided the opportunity to convert the silyl enol ethers **204** into 48 amino alcohol library.[86,87]



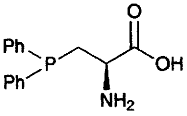
5.7 Combinatorial Catalysis – In an interesting 'twist' on combinatorial chemistry the possibility that the performance of a catalyst or ligand can be enhanced by using combinatorial techniques has been described.

Gilbertson and Wang have reported a combinatorial synthesis of enantiomerically pure phosphine ligands. The peptide **208** was one of 63 prepared in the library. The positions of the phosphine containing amino acid residues (Pps and Cps), as well as other amino acids in the central portion of the peptides were varied. Whilst still attached to the solid support the library of phosphine-containing peptides was screened in the rhodium-catalysed hydrogenation of alkene **209** into the chiral amido ester **210**. Whilst asymmetric induction was modest, there are clearly future possibilities for this approach to ligand design.

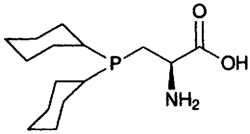
Snapper, Hoveyda and co-workers at Boston College have reported the discovery of ligand **211** for titanium catalysed opening of meso-epoxide **212** with TMSCN.[89] The ligand was obtained by the high throughput screening of ligand candidates which were systematically optimized. In the basic structure **214**, firstly a series of 10 systems was tried with variation in AA1. Having established which group to use here, AA2 was varied, and then the aldehyde moiety. Using this

Ac-Ala-Aib-Ala-Cps-Ala-Ala-Val-Pps-Ala-Aib-Ala-NH_2

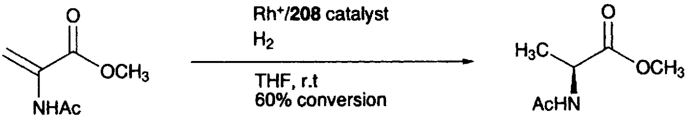
208



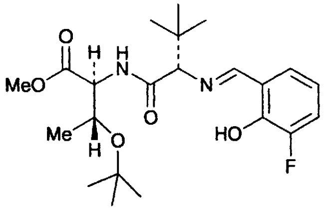
Pps



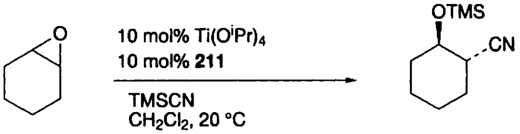
Cps



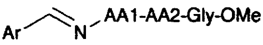
209 **210** 12.7%ee



211



212 **213**



214

iterative process, the ligand **211** was identified for use in the titanium-catalysed reaction.

Catalyst screening has also been investigated. Burgess and co-workers examined an array of 96 potential catalysts for examination of C-H insertion reactions.[90] Using one catalyst per well in the solution phase provided rapid screening of the reactivity and selectivity of the catalysts.

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9

Metal Carbonyls

BY JOHN A. TIMNEY

1 Introduction

This report deals with those publications describing advances in the chemistry of the metal carbonyls and metal carbonyl hydrides, halides and pseudohalides for 1996. In the year when *Chemical Abstracts* is 90 years old, activity in this area continues to run at a relatively high level, with the number of papers exceeding preceding years. Readers of *Chemical Abstracts* will have noticed that the format has now changed so that all groups are covered in every volume, unlike previous years. So, organometallic compounds and inorganic reactions are now surveyed in every issue.

The general structure of this report is similar to that of previous years. Like the previous four years this chapter contains information about the general chemistry of metal carbonyls which have Group 15 and/or Group 16 donor ligands. So, for example, whilst the chemistry of $Ni(CO)_2(PF_3)_2$ would be included in this chapter, $Ni(PF_3)_4$ would not appear unless it led to the formation of some carbonyl-containing product. Interest in these groups is concentrated on phosphorus in Group 15, but more evenly spread between sulfur, selenium and tellurium in Group 16. Hydrocarbon-containing complexes are dealt with elsewhere, but where they specifically involve reactions of CO ligands (with hydrocarbons merely being spectators to the chemistry) they will generally receive a mention in this chapter. Unlike previous years, the section dealing with the catalytic activity of metal carbonyl complexes has been omitted. Any work dealing with catalytic processes are now included in the section devoted to that particular metal.

The information superhighway as it applies to metal carbonyl chemistry in the form of the Internet has not been dealt with in this chapter, although several dozen sites contain information of interest to workers in this field. This reporter is compiling a list of relevant websites and, hopefully, there will be a section devoted to this type of information in next year's chapter. In the meantime, such information is available *via* e-mail.[1]

We have maintained our practice of recent years whereby a handful of relevant papers which were missed in the 1995 review (usually because they are published in obscure journals or have been awaiting a translation) are included here.

Organometallic Chemistry, Volume 26

2 Reviews

Before moving to those publications which deal directly with metal carbonyl chemistry a general review entitled *Organometallic Chemistry: Challenges and Opportunities* has been released[2] which is accessible and worth adding to the reading list of undergraduates and, perhaps, younger, aspiring organometallic chemists.

The title: *New Surprises in Metal Carbonyl Chemistry* is bound to attract a ready readership in this field, although the surprises were limited due to the shortness of the review.[3] Of much more weight was a survey on technetium cluster compounds[4] and a significant review of redox reagents for organometallic compounds.[5] The compounds of post-transition elements of Groups 12–14 containing $Fe(CO)_4$ and related iron carbonyl ligands are also reviewed comprehensively.[6]

Organometallic chemists have three new books to add to their shelves in the form of *Metals and Ligand Reactivity: An Introduction to the Organic Chemistry of Metal Complexes* edited by E.C. Constable,[7] *Synthetic Methods of Organometallic and Inorganic Chemistry* edited by W.A. Herrmann[8] and *Advances in Metal-Organic Chemistry* edited by L.S. Liebeskind.[9] Although none is specifically devoted to metal carbonyl chemistry, all contain sections of interest to those who are looking to synthesise new carbonyl compounds.

There have been a number of general reviews to attract the interest of workers in this field. For those working with phosphites, Masson[10] has described the reactions of phosphites with thiocarbonyl compounds. The versatile group of ligands, the metallophosphaalkenes, have been reviewed and their development traced from what were once considered exotic compounds to what are now generally commonplace building blocks.[11] Budzelaar and Van Lenthe[12] have provided a general review on quantum chemistry associated with organometallic compounds. An interesting review of carbonyl migratory insertions appeared in the same volume.[13] The organometallic complexes of pyrazoles has also been reviewed.[14] Although not technically reviews, the detailed study of tripodal phosphines by Stoesel *et al*[15] and the latest in a long series on oligophosphines[16] contain much to interest a carbonyl chemist as does a paper on P_4 and P_8 ligands.[17]

Chemists dealing with metal clusters (whether they contain CO groups or not) may well find interest in a survey of their development and possible research trends in the area.[18] Also, a survey of organometallic cluster compounds mentioned in the literature of 1994 has been published[19] (although the time lapse between this extensive report and its publication may render some of its content obsolescent).

Later on in this chapter the work of Aubke and co workers receives attention as they – yet again – have produced unusual carbonyl containing species in high oxidation states. The whole issue of solvolysis reactions in liquid antimony pentafluoride is reviewed by Aubke[20] in a fascinating review of what has become a relatively convenient and versatile synthetic method.

Although not quite within the scope of this chapter we would mention here –

on isoelectronic grounds – the review of nitrosyl (N-O) bond cleavage during reactions of organometallic nitrosyl complexes of Group 6 elements.[21]

3 Theoretical, Spectroscopic and General Studies

3.1 Theoretical Studies – The optical spectra of $Ni(CO)_4$ and $Cr(CO)_6$ have been studied in detail using multiconfigurational perturbation theory (the CASSCF/CASPT2 approach). In both cases, the new assignment of the spectra differs from previous studies which may throw new light on the role played by ligand field states in the photochemistry of these and other carbonyl compounds.[22] This paper is extremely interesting in that, by implication, it casts doubt on the findings of many studies in the past.

As part of the *Femtochemistry* conference at Lausanne (1995), Heitz[23] has released a study of the (theoretical) excited-state dynamics of the two relatively simple metal carbonyl hydrides $HCo(CO)_4$ and $H_2Fe(CO)_4$. On the same time scale, if not the same subject matter exactly, Grun and co-workers[24] have shown (by mutiphoton ionization mass spectrometry combined with a femtosecond burst from a laser to set the process going) that there is sequential loss of CO from the well-known carbonyls of iron, chromium, molybdenum and tungsten.

As part of a long-running series,[25] there has been a theoretical study of donor-acceptor properties in $M(CO)_5L$ (M=Cr, Mo, W) and $M(CO)_3L$ complexes (M=Ni, Pd, Pt) complexes (L = phosphine, phosphite etc.). The authors conclude (from an *ab initio* quantum mechanical standpoint) that the standard classification of ligands (viz. 'good' or 'poor' π-acceptor) is justified.

In a sizeable and detailed paper, Jacobson and Ziegler[26] have carried out theoretical calculations (*viz.* density functional analyses) on the transition metal Fischer-type complexes $(OC)_5Cr{=}EH_2$ (where E= C, Si, Ge and Sn) and $(CO)_5M{=}CH_2$ (where M=Mo, W and Mn^+).

The activation of the C-H bond in methane has been something of Holy Grail in recent years and, although the experimental work is far from over, some insight into the problem is forthcoming in a detailed theoretical consideration of the problem by Siegbahn.[27] The main thrust of the study is directed towards methane activation by CpM(CO) complexes (M = Co, Rh and Ir). Looking at the possibility of SN_2 transition states in the reaction of iodomethane with metal carbonyl halide anions, Griffin *et al*[28] contend that such species are part of the substitution mechanism in oxidative addition.

In a paper close to this reporter's heart, Li and Ziegler have reported some interesting trends in Periodic Table position and ligand effects in the known transition metal η^2-H_2 complexes.

Finally, a comparison of aromaticity in benzene and in (benzene)$Cr(CO)_3$ has been carried out.[29]

3.2 Spectroscopic Studies – The ever-maturing technique of time-resolved infrared (TRIR) spectroscopy has produced an interesting study[30] of the UV photochemistry of $[CpFe(CO)_2]_2$ at the *picosecond* level. The loss of CO is very fast (probably at the femtosecond level) and the primary photoproduct, CpFe(μ-CO)$_3$FeCp is formed within 10ps. It might have been expected that the primary photoproduct (which must, one assumes, be CpFe(CO)$_2$Fe(CO)Cp) might have lived long enough to be observed as the rearrangement in the molecule to form the three bridging CO groups is considerable. However, it seems churlish to wish for faster TRIR. It was not many years ago that TRIR was at the millisecond level and we are a factor of 10^9 better than that now. The progress has been remarkable.

Like TRIR, the use of supercritical fluids in metal carbonyl chemistry is a relatively new innovation. Poliakoff and co-workers[31] have approached the problem of CH_4 activation (and general C-H activation, by extending their work to C_2H_4 and C_2H_6) by reaction of the alkane with Cp*Ir(CO)$_2$ in supercritical CO_2, Xe and CHF_3. Then, taking the next logical step, they have moved into a 'solvent free' mode of operation by using the alkanes/alkenes themselves as supercritical fluids so that they are, in effect, their own solvents.

The same group has combined TRIR and supercritical fluids in a successful attempt to detect organometallic noble gas compounds in solution at room temperature.[32] Just to flesh out the story somewhat, Perutz and Turner (in the mid-1970s) discovered that the visible absorption of matrix isolated M(CO)$_5$ (M = Cr, Mo, W) varied markedly on the matrix material. In a mixed matrix (say Ne/Xe) the photofragment could be converted from having one noble gas in the vacant site to having the other. Now, with the rapidly developing technology of TRIR and the increasing accessibility of supercritical fluids, M(CO)$_5$L (where L is supercritical Ar, Kr, Xe or CO_2) has been detected as a short-lived photoproduct. It should not be long, one suspects, before Fe(CO)$_5$ (which forms the complex Fe(CO)$_4$.CH_4 in a methane matrix at 20K) is put under the same microscope.

The photoelectron spectroscopy of CpCo(CO)$_2$, CpRh(CO)$_2$ and CpIr(CO)$_2$ has been carried out[33] in a successful attempt to place the energies of the molecular orbitals into a coherent order. Variable energy photoelectron spectroscopy of Os(CO)$_5$ and Os(CO)$_4$PMe$_3$ has been carried out by Hu *et al.*[34] They found that the orbital layout of Os(CO)$_5$ was very similar to that for Fe(CO)$_5$.

The ^{13}C and ^{17}O chemical shift tensors (ie. in the NMR) of the carbonyl groups in two relatively small and symmetrical molecules, Fe$_2$(CO)$_9$ and Rh$_6$(CO)$_{16}$ have been measured by Kaupp.[35]

Using a combination of FTIR and matrix isolation the reactions of single atoms and small clusters of iron (Fe, Fe$_2$, Fe$_3$) with gaseous CO have been observed.[36] The one major surprise in what was otherwise a predictable outcome was that Fe$_2$ did not react to form Fe$_2$(CO)$_9$ but formed the unsaturated Fe$_2$(CO)$_8$ (first observed many years ago by Poliakoff in matrices containing Fe$_2$(CO)$_9$ after UV irradiation). Where this study differed from earlier metal vapour + CO studies was that the clusters were mass selected so that the matrix did not contain a large number of different clusters. One of the problems attached to studies such as these in the mid-1970s was that the matrix contained metal clusters of many sizes, so it was sometimes impossible to identify the new molecules. Also making use of FTIR (in the same way as Hamnett observed the electrochemical processes of Re(I) carbonyl complexes three years ago), Lin *et al*[37] have observed the electrochemical redox processes of the cluster carbonyl $Os_6(CO)_{18}$ and a number of other related species. Finally, the breakdown of $RhCo_3(CO)_{12}$ clusters on silica has been studied[38] using IR (reflectance).

The synthesis of metal films of closely controlled thickness and purity has immense industrial application and – like they have so many times – metal carbonyls have been found to be useful in such a scenario. Using laser stimulated decomposition of molybdenum, chromium and iron carbonyls, Alexandreson has published[39] the details of such metal-film deposition.

3.3 General – Buckminsterfullerene chemistry has yet to really get into its stride when it comes to bonding this potentially interesting ligand to transition metal species. Reports have emerged in the last few years, but not in any particular sequence and certainly not in the deluge-like numbers that the $ReX(CO)_3(N\text{-}N)$ compounds managed over the period 1993–96. However, we do now have[40] buckminsterfullerene (in the soccer ball form) bonding in an interesting way to the remnants of a ruthenium dodecacarbonyl molecule as $Ru_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$. This reporter remains convinced that this story has a long way to run.

Metal carbonyl-hydride complexes have long been a feature of this chapter and this trend continues. For example the kinetic isotope effects on metal to nitrogen proton transfers in the $[CpW(CO)_3H]$ to phenylamine (in an ethanonitrile solution) have been examined.[41] The partial transfer of protons (*viz.* hydrogen bonding) is mentioned elsewhere in this chapter, but of a general nature there has been a study of N-H···Co hydrogen bonding which has noted that the strength of the bond increases as the basicity of the H-acceptor increases.[42] The two compounds used to highlight this point are $(DABCO)H^+[Co(CO)_4]^-$ and $(DABCO)H^+[Co(CO)_3PPh_3]^-$ (where DABCO is 1,4-diazabicyclooctane).

A gas-phase study of the formation and dissociation of $H_2Fe(CO)_4$ has been published. The authors[43] were particularly keen to discover the kinetics of the process and from this, estimate the Fe-H bond energy. The figure that they eventually arrived at (260kJ mol^{-1}) is not too far different to other measurements of the same bond.

Ligands with fluorine attached in some way are far more apparent than in previous years. For example, Hughes and Trujillo have shown selective solubility of a number of metal carbonyl complexes in saturated fluorocarbons.[44] They made use of the $C_5H_4[(CH_2)_n(CF_2)_mF]$ ligand (the side chain being described as a 'ponytail') and varied both n (either 0 or 2) and m (6, 8, 10 and 12). The solubility dependence on the ponytail length and number of fluorine atoms was quite striking. Another use of fluoro-compounds was in a study by Li *et al*[45] who looked at a whole range of new multifunctional fluoro-aromatic bis(phosphinimines) and their reactions with $[Rh(CO)_2Cl]_2$.

The inclusion of Group 15 (N, P, As, Sb and Bi) ligands in this chapter some years ago coincided with an enormous upturn in the use of amine (aromatic and aliphatic) ligands attached to metal carbonyl complexes. At a fairly simple level, in terms of the complexity of the ligand, the reactions of the vinylphosphines

$Ph_2PCH{=}CH_2$ and *cis*-$Ph_2PCH{=}CHPPh_2$ have been used[46] in reactions with cobalt carbonyls. In the same area of endeavour, Hursthouse *et al*[47] have released a study of the reactions of CO with pyridine-functionalised metal alkyls. The problem of cyanogen activation is considered by Ruiz *et al*[48] who make use of the CN unit bonded to bis(diphenylphosphino)methanide, $[(PPh_2)_2C\text{-}CN]^-$, and make use of this as a building block in constructing metal carbonyl complexes. It goes without saying that functionalised tripodal phosphines may be difficult to work with because of their ligating properties and/or their Lewis basicity. Stoessel *et al*[49] have devised a relatively simple procedure whereby an $Mo(CO)_3$ unit is attached to the phosphine group in advance of further reaction as an organometallic protection group.

A mixture of Group 15 and Group 16 atoms gives such interesting molecules as As_4S_4 and As_4S_3 which, quite clearly, have potential as σ-donor/π-acceptor ligands with low valency metal complexes. This potential has been explored[50] by reacting these molecules with $(C_5Me_4Et)Fe_2(CO)_4$. However, where simple CO replacement may heve been expected, it was found that molecules such as $(C_5H_4Et)_2Fe_3(CO)_6As_3S_3$ and $(C_5H_4Et)Fe_3(CO)_6As_3S_2$ were formed (amongst others). The combination of phosphorus and sulfur to make phosphinothiol ligands (eg. $PPh(C_6H_4SH)_2$) has been well explored by Dilworth *et al*[51] who have reacted this ligand with Mo, W, Re, Fe, Ru, Os, Rh, Ir and Ni organometallics.

The 'heterocyclohexanes' are a class of compounds which mimic cyclohexane in structure but contain atoms such as phosphorus or silicon in the ring. One such compound is $[SiRH\text{-}PR]_3$ (where R = cyclohexyl). With this molecule in the chair configuration the three phosphorus atoms are positioned such that they can bond to a transition metal in a fairly conventional manner and this property has been exploited to prepare[52] (by direct reaction of $Cr(CO)_3(NCMe)_3$ with the heterocyclohexane ligand) the complex $Cr(CO)_3[SiRH\text{-}PR]_3$. A not dissimilar type of compound containing the heterocyclohexane-type molecule $(CH_2PH)_3$ has been prepared[53] by reaction with a $Cr(CO)_3$ group to give $(CH_2PH)_3Cr(CO)_3$.

Wang and co-workers[54] have been examining possible hydride and methide transfers between complexes such as $[Fe(CO)_4R]^-$ where R is methyl or hydrogen, $[W(CO)_5R]^-$ where R is methyl, hydrogen or a halogen atom and the cationic complexes $[Mn(CO)_6]^+$ and $[Re(CO)_6]^+$. They report that several products are formed and make the logical conclusion that several mechanisms must be in play to give this array of products.

The growth in the knowledge-base of high-nuclearity clusters has been spectacular in the past decade and molecules are now being designed before construction, as opposed to earlier studies where new complexes were rescued out of the debris of a pyrolysis experiment, for example. A good example of this newer approach is a study outlining the synthesis of high nuclearity clusters by assembling $\text{-}CCo_3(CO)_9$ units into aromatic spacer molecules[55] and the linking of metal clusters with bis(diphenylphosphino)ethyne.[56]

Some years ago, a number of studies appeared which used metal carbonyl groups as markers on proteins and (using infrared spectroscopy and the very high extinction coefficients of ν(CO) absorptions in a relatively sparse region of the spectrum) detection levels at the nanomole level were reported. Studies last year in this interesting area included the use of a multi-functionalised tungsten tricarbonyl complex,[57] $[RW(CO)_3\{C_5H_4COON(CO)_2CH_2CHR\}]$ to label proteins in specific places. A related study[58] has gone rather further and used an Os_3 carbonyl grouping to label certain protein sites.

4 Chemistry of the Metal Carbonyls

This section deals with the general chemistry of the metal carbonyls in triads. As is usual, the Titanium and Vanadium groups are poorly represented, with activity picking up in the Chromium, Manganese, Iron and Cobalt triads. Unlike the previous three years, there have been a number of studies involving the metals of the Nickel triad.

4.1 Titanium, Zirconium and Hafnium – Very little carbonyl chemistry involves this group and nothing has come to light for this report, although mixed metal carbonyls announced in 1996 have contained a metal from this group.

4.2 Vanadium, Niobium and Tantalum – Studies dealing with the metal carbonyl chemistry of elements within this group have always been in short supply, with only two studies coming to this reporter's notice. A tris(pyrazole)-borato niobium(I) complex (see Fig. 1) has been prepared[59] which is included here by virtue of the single CO group that the complex contains. Secondly, the complex $(MeC_5H_4)Nb(CO)CH_2Ph$ has been formed after a CO_2 insertion reaction.[60]

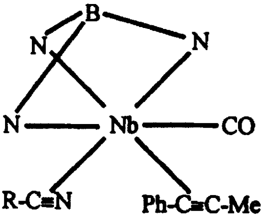

Figure 1 *Tris(pyrazole)borato niobium(I) complexes (Ref. 59)*

4.3 Chromium, Molybdenum and Tungsten – In a reaction which sees the production of a four-membered ring containing three different types of atoms from a six-membered ring, Bieger *et al*[61] have linked a $W(CO)_4$ unit to a cyclobutadiene analogue containing phosphorus and nitrogen. In the reaction (Fig. 2) the original six-membered ring is treated with $W(CO)_5(THF)$ prepared photochemically from $W(CO)_6$ in THF. The six-membered ring initially replaces the THF and then, by losing N_2 from the ring (the very high $N\equiv N$ bond energy must always favour such an elimination reaction) and CO from the pentacarbonyl residue the product is finally formed. Similar photochemical procedures are present at the first stage of the production of $W(CO)_4(Ph_2PCH_2CH_2SiHMe_2)_2$ by Schubert and Gilges[62] and two $Mo(CO)_4$ units have been coupled[63] by using the 1,4-bis(diphenylphosphino)-2,5-difluorobenzene ligand (dpfb) to make $[\{Mo(CO)_4(\mu\text{-dpfb})\}_2]$. Substitution reactions of the radical complex $(C_5Ph_5)Cr(CO)_3$ to yield $(C_5Ph_5)Cr(CO)_2L$ (where L is either a phoshine or a phosphite) have been studied by Hammack *et al.*[64]

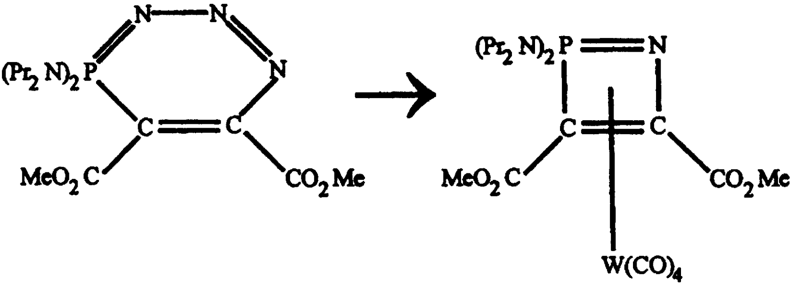

Figure 2 *Formation of a heterocyclic cyclobutane-type complex of tungsten (Ref. 61)*

Organic chemistry, rather than strictly organometallic, is the theme in a study[65] of the catalytic ring-opening cyclo-oligomerization of thietane by $M(CO)_5L$ complexes (M = Cr, Mo, W; L = thietane, CO). The catalytic macrocyclization of 3-methylthietane by tungsten and rhenium complexes has also been studied.[66] The rhenium complex is the better catalyst for this reaction. In the same rich vein of quasi-organic chemistry, $MoI_2(CO)_3(CH_3CN)_2$ reactions with hydrotris(3,5-dimethylpyrazol-1-yl)borate have also been studied;[67] hexacarbonyltungsten(O) in a THF solution has been used to initiate and induce the cyclization of alkynyl alcohols;[68] a mechanism[69] for the single-step hydride transfer from $CpMo(CO)_2PPh_3H$ to protonated ketones has been worked through.

In recent years the use of N-N′ type ligands (more often than not of the bipyridyl variety)has been concentrated in the Mn-Re group rather than Group 6. Alyea and Jain[70] have righted this somewhat with the publication of an in-depth study of $Mo(CO)_4$(N-N′) and $W(CO)_4$(N-N′) studies (where N-N′ are bipyridyl-like ligands, but are, in this detailed and interesting paper, many and varied).

The use of the $[Cr(CO)_5]^{2-}$ ion (as the $K_2Cr(CO)_5$ salt) with compounds of the general formula Cl_2ER (E = Al, Ga; R = Me, Et or Cl) has been the subject of a study by Shulte *et al.*[71] Having formed their initial intermediate compound, they proceeded to react this with TMEDA to form five-membered rings containing aluminium or gallium.

The complex *fac*-$[Mo(CO)_3\{MeC(CH_2SbPh_2)_3\}]$ has been prepared[72] by direct substitution of CO by the Sb-containing ligand. In addition to the preparative techniques, IR, crystallographic, ^1H and ^{13}C NMR data are also provided. $Mo(CO)_6$ was also used[73] as a starting material in the reaction with hydrotris(3,5-dimethyl-1,2,4-triazol-1-yl) borate which produces the complex

[NEt$_4$][{HB(Me$_2$tz)$_3$}Mo(CO)$_3$]. Multi-dentate ligands in the shape of 1,3,5-diheterophosphorinanes have been employed[74] to prepare new molybdenum and tungsten carbonyls. Along the same lines, 3,5-di-tert-butylcatecholate (DTBCatH$_2$) has been used to prepare new Group 6 complexes[75] and 4-bromo-2-cyclopentenone has been used[76] to replace the acetonitrile ligands in M(CO)$_3$(MeCN)$_3$ (M= Cr, Mo, W) to give M(η^3-C$_5$H$_5$O)(CO)$_2$(MeCN)$_2$Br.

Zintyl-type ligands made an appearance in this chapter some years ago and their development continues[77] with new Mo and W complexes [η^2-P$_7$M(CO)$_4$]$^{3-}$, [η^2-HP$_7$M(CO)$_4$]$^{2-}$ and [η^2-RP$_7$M(CO)$_4$]$^{2-}$ (R = alkyl).

High oxidation-state carbonyl complexes of iridium are mentioned later in this article. Matching them in oxidation state, at least, is the stable 17e compound Cp*MoCl(CO)(PMe$_3$)$_2$ prepared by Fettinger *et al.*[78] The protonation of metal carbonyl hydrides by triflic acid (HOT$_f$) receives some attention from Bullock and co-workers. They have succeeded[79] in protonating CpW(CO)$_2$(PMe$_3$)H to give [CpW(CO)$_2$(PMe$_3$)(H)$_2$]$^+$[OT$_f$]$^-$.

Cyclic vinylphosphirane complexes of tungsten have been prepared by Wang and co-workers[80] (Fig. 3) and cyclic and non-cyclic selenium-containing complexes (Fig. 4) have been synthesised by Fischer *et al.*[81] The electrochemical reduction (and subsequent chemistry) of the metal hexacarbonyls of this group in the absence and presence of organic halides has been published.[82]

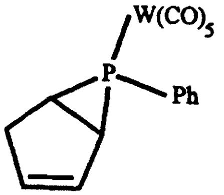

Figure 3 *Cyclic vinyl phosphorane complex of tungsten (Ref. 80)*

As always, complexes containing more than one Group 6 atom are in short supply as the chemistry of the metals Cr, Mo and W is dominated by mononuclear complexes. Where polynuclear complexes are prepared they are often bridged by Group 15 or 16 atom ligands and this is the case for [(Cp)W(CO)$_3$]$_2$Se$_3$, for which the structure and synthesis has been reported.[83]

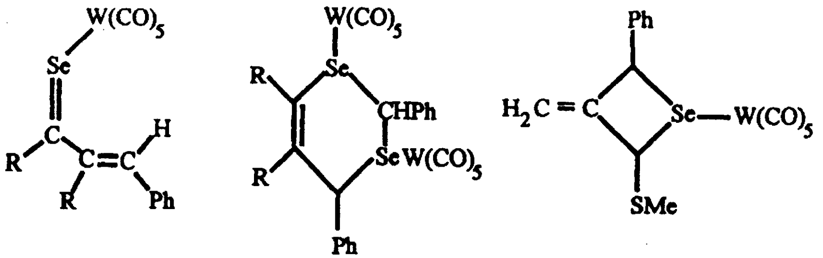

Figure 4 *Selenium-containing tungsten pentacarbonyl complexes (Ref. 81)*

4.4 Manganese, Technetium and Rhenium – Over the past few years there has been a deluge of papers concerning molecules with the general formula [Re(CO)$_3$XL$_2$] where X is typically a halogen and L is typically an amine. The number of such papers dropped dramatically in 1996, but there are examples still to be found. Garcia *et al*[84] have released details of the fluxionality of [Re(CO)$_3$XL$_2$] where L$_2$ is 2,6-bis(4-methylpyrazol-1-yl). Apparently the molecule is fluxional in the sense that the nitrogen oscillates between two equivalent bonding modes. They have calculated the activation energy which is around 60 kJmol^{-1}. Quite clearly then, this is an internal rearrangement rather than a dissociative process. The mechanism of the alkyl-dependent photochemical homolysis of the Re-alkyl bond in Re(R)(CO)$_3$(α-diimine) complexes via a reactive $\sigma\pi$* excited state is published by Stufkens *et al*,[85] a group which contributed a great deal to the study of these fascinating complexes.

In an elegant study of the complex CpRe(CO)L(N$\equiv$N) (where L = CO, trimethylphosphine or trimethylphosphite), Cusanelli and Sutton[86] have discovered end-to-end rotation of the rhenium-bound nitrogen. They succeeded in finding this by very careful use of ^{14}N$\equiv$^{15}N isotopically labelled species.

As every carbonyl chemist knows, [Mn(CO)$_5$]$^-$ is a trigonal-bipyramid like its isoelectronic twin Fe(CO)$_5$. Not so, it appears. Seidel and co-workers[87] have very good evidence that [Ph$_4$P]$^+$[Mn(CO)$_5$]$^-$ leaves the [Mn(CO)$_5$]$^-$ in a square-base pyramid, presumably due to cation-anion interaction.

Mononuclear complexes of both Mn and Re have been prepared using 3,5-di-tert-butyl-1,2-benzosemiquinone (DBSQ). M(CO)$_{4-n}$(L)$_n$(DBSQ) complexes (M = Mn, Re and n = 0, 1, 2) have been made.[88] An interesting study of what the authors term 'network hydrogen bonding' is described[89] in the case of two new co-crystals sustained by [Mn(CO)$_3$(μ-OH)]$_4$, which acts as a tetrahedral hydrogen-bond donor. Manganese compounds have also been used as models for the homogeneous hydrodesulfurisation of benzothiophene.[90]

The redox behaviour of [Mn(CO)$_4$(S$_2$CPCy$_3$)]$^+$[ClO$_4$]$^-$ has been followed using cyclic voltammetry. New metal nitro- and nitrito-complexes of manganese have been prepared by Sieker and co-workers.[91] A solution of Mn(CO)$_5$Cl, [(PPh$_3$)$_2$][NO$_2$] and Me$_3$NO in dichloromethane gave, first of all, *cis*-[Mn(CO)$_4$(NO$_2$)$_2$]$^-$ which went on to react further and produced the tri-manganese complex [Mn$_3$(CO)$_6$(μ-NO$_2$)$_4$(μ-ONO)$_2$]$^{2-}$. Ionic rhenium compounds are also noted. Ruf and co-workers[92] have reacted *trans*-[Re(CO)$_4$-(MeCN)(NS)]$^{2+}$ with chloride ions. The cationic manganese complex [Mn(CO)(Ph$_2$PC$_2$H$_4$PPh$_2$)$_2$]$^+$ has been found to react[93] with both hydrogen (acting as η^2-H$_2$) and nitrogen.

Diastereoselective substitution of CO by PR'$_3$ ligands (R = various alkyl groups) has been observed[94] in the carbohydrato and menthyloxycarbene complexes of manganese. In short, Cp(CO)$_2$Mn=C(OR)Ph complexes (where R = mannofuranosyl or menthyloxy) have been converted to Cp(CO)(PR'$_3$)-Mn=C(OR)Ph.

The molecule (η^5-C$_5$H$_4$Me)Re(CO)$_2$Br$_2$ exists as two isomers – lateral and diagonal (or *cis* and *trans* if you prefer). Cheng and Coville[95] have revealed that the mixture of the isomers is a phase dependent property and is reversible. They also found that refluxing the complex in methylbenzene converted all the diagonal isomers to lateral isomers.

Complexes containing two or more metal atoms are always at a premium in this section but they are represented[96] by the molecule $[(CO)_4Mn\{(PPh_2)C\text{-}S_6\text{-}C(PPh_2)\}Mn(CO)_4]$ which splits a tetraphosphinobis(methanide) ligand in half and inserts a hexasulfur bridge. Another di-manganese complex to be used last year was $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ which was reacted with a variety of organic acids and the reactivity quantified.[97]

Rhenium complexes containing two metal atoms have been produced[98] from dirhenium decacarbonyl by oxidative decarbonylation in Me_3NO using bridging phosphine ligands. The final products of such reactions are $Re_2(\mu\text{-}OMe)_2\text{-}[\mu\text{-}Ph_2P(CH_2)_nPPh_2](CO)_6$ (where n = 1–4). The compound $Cp^*(CO)_2Re{=}Re(CO)_2Cp$ has been observed to react with dimethylacetylenedicarboxylate.[99] The decacarbonyl was also the starting material in an interesting sequence of reactions performed by Haupte and co-workers.[100] Firstly, $Re_2(CO)_{10}$ was irradiated with UV light in a solution containing MeCN to give *eq*-$Re_2(CO)_9(MeCN)$. This was then reacted with $(Me_3Si)_3P$ to give *ax*-$Re_2(CO)_9(PH_3)$, a most unexpected result as the mode of bonding of the MeCN and the phosphine are, ostensibly, similar. UV photolysis of this compound gave, perhaps not surprisingly, larger clusters containing phosphine and CO in a variety of bonding modes. A further di-rhenium complex (although the Re atoms are well-separated by a sulfur-nitrogen heterocycle) has been prepared by Adams and Huang[101] and some of the extensive chemistry of $Re_2(\mu\text{-}H)(\mu\text{-}C_2Ph)(CO)_8$ has been explored.[102]

Technetium has been mentioned earlier (as part of a review) but actual carbonyl chemistry of this element is always limited due partly to its radioactive nature (which always confines the interest in an element somewhat). However, starting from $^{99}TcO_4^-$, Alberto *et al*[103] have, in a single relatively simple step, produced $[^{99}TcH_3(CO)_{12}]$ which may prove to be a useful starting material for a number of technetium carbonyl syntheses.

Containing three rhenium atoms, the cluster anion $[Re(CO)_9(\mu_2\text{-}OH)_3(\mu_3\text{-}OH)]^-$ has been prepared by Herrmann *et al*[104] and a simple synthesis of $Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)$ has been proposed.[105] By passing hydrogen gas through $Re_2(CO)_8(NCMe)_2$ in toluene solution at 80°C the tri-rhenium complex is produced in 90% yield. Also containing three rhenium atoms, but with one of the Re atoms linked with a bridging hydrogen atom, the cluster $[Re_2(CO)_9\text{-}\{(\mu\text{-}H)ReH(CO)_4\}]$ has been thoroughly investigated[106] and its reactivity scrutinized. The complex forms when $[Re(CO)_5]^-$ reacts with the dinuclear species $[Re_2(\mu\text{-}H)_2(CO)_8]$, so the internal re-organization of the atoms is considerable.

4.5 Iron, Ruthenium and Osmium

– The first metal carbonyl in this group, $Fe(CO)_5$, appeared in a paper published[107] late in 1995 devoted to studying the β-H transfer from C_3H_6 to the carbonyl in real-time under vacuum-UV radiation:

$$Fe(CO)_5 + C_3H_6 \rightarrow HFe(CO)_3(\eta^3\text{-}C_3H_5) + 2CO$$

Also at a fairly basic level, the thermal decomposition of $Fe(CO)_5$ in halogen-rich solvents (bromotrichloromethane and tetrachloromethane) has been investigated. Tararov and co-workers[108] found that the presence of the bromine atom greatly increases the rate of decomposition. The same group has discovered the mechanism[109] of the Kharasch Reaction catalysed by $Fe(CO)_5$.

Containing a single iron atom, the first alkyloxalyl compound, $K^+[Fe(CO_2{}^tBu)_3(CO)_3]^-$ has been prepared.[110] Although marginally outside the reach of this chapter, Franck-Neumann and co-workers have succeeded in synthesising a tricarbonyl iron complex with a butadiene ligand containing a free diazo group[111] (Fig. 5). Like the previous two groups of the Periodic Table, there is a growing interest in the organic side of carbonyl-based organometallic chemistry and the reaction of iron dicarbonyl phosphines of 2-(phenylazo)pyridine with dimethylethynedicarboxylates is a typical example.[112] We look forward to some interesting chemistry with this molecule. In a similar vein, the reactivity of metallophosphaalkenes (such as $[Cp^*(CO)_2FeP{=}CR_2]$ where $R{=}SiMe_3$ or NMe_2) to methyl and ethyl priopolate has been examined.[113] Iron pentacarbonyl has been used to catalyse a [4+1] cyclization of 5-methyl-3,4-hexadien-2-one in a low temperature matrix (or glass, technically) of 2-methyltetrahydrofuran.[114]

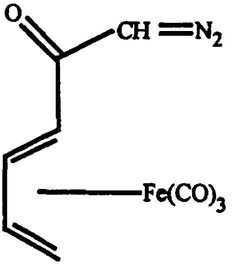

Figure 5 *Butadiene-tricarbonyl iron complex with a free diazo-group (Ref. 111)*

Iron carbonyl complexes (such as $Fe(\eta^3\text{-}S_2CPR_3)(CO)_3)$ containing the novel sulfur-phosphorus-containing ligand ($\eta^3\text{-}S_2CPR_3$) have been prepared.[115] Similarly, starting from relatively humble feedstock (in this case C_5Bz_5H and $Fe(CO)_5$ [Bz = benzene], the dinuclear iron complex $[(\eta^5\text{-}C_5Bz_5)Fe(CO)_2]_2$ has been prepared.[116]

An astonishing pair of molecules have been synthesised by Wiegelman-Kreiter and Bunz[117] (Fig. 6). Their dumbell-shaped peralkyated cyclobutadiene complexes are quite spectacular – much more beautiful than can be suggested by a diagram on paper. Equally impressive (Fig. 7) are the six-membered rings containing two iron atoms, two chalcogens (S, Se or Te) and an alkene bond prepared by Mathur *et al.*[118,119]

Single ruthenium or osmium atom carbonyl complexes have been rather scarce in recent years, so it is pleasing to report that the reactions of $Ru(\eta^5\text{-}C_5Me_4Et)(CO)_2Cl$, $Ru(\eta^5\text{-}C_5Me_4Et)(CO)_2Br$ and $Ru(\eta^5\text{-}C_5Me_4Et)(CO)_2I$ with a variety of phosphorus and arsenic ligands have been published.[120]

The di-ruthenium complex $[Ru_2(\mu\text{-}CO)(CO)_2\{\mu\text{-}({}^iPrO)_2PNEtP(O^iPr)_2\}_2]$ has been the subject of an electrochemical study designed to investigate its oxidation

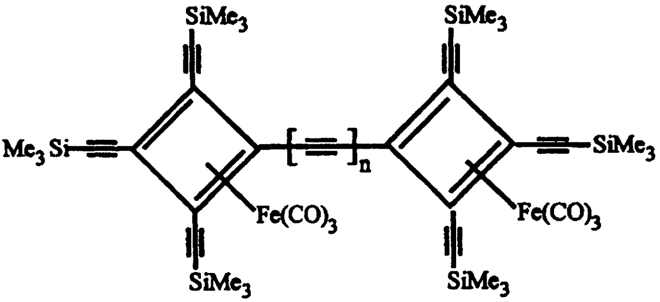

Figure 6 *Dumbell-shaped bis(iron tricarbonyl) complexes (Ref. 117)*

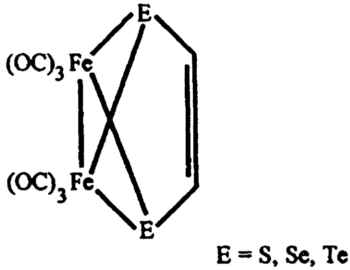

Figure 7 *Six-membered rings containing two iron atoms, two chalcogens and an alkene bond (Refs. 118 and 119)*

behaviour.[121] Di-osmium complexes include $Os_2(CO)_8(PbMe_2)_2$ and $Os_2(CO)_7(SnMe_2)_2L$ complexes (where L is a phosphorus ligand)[122] (compounds of iron with a similar structure such as $Fe_2(CO)_6(\eta^1\text{-dppm})(SnBu_2)_2$ have also been reported[123] only one page further on in the same journal). A molecule containing two iron atoms held together by selenium alkyls, $[(OC)_3Fe(\mu\text{-}CH_2)Se]_2$, is reported.[124]

Like every other year for many years, there has been considerable activity in the trinuclear carbonyl complexes of this group. At the simplest level, the decarbonylation of $[Ru_3(CO)_{12}]$ on ZrO_2 and Al_2O_3 surfaces has been studied using IR and TPDE-GC.[125] The rather bulky ligand 7,7,8,8-tetracyanoquinodimethane (TCNQ) has been used in the preparation of some relatively low-nuclearity ruthenium clusters.[126] Similar, surface-mediated organometallic synthesis of osmium complexes on silica in the presence of sodium or potassium carbonate has also been reported.[127] The addition of the bromonium ion, Br^+, to $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ has been reported.[128] Both compounds end up as $[M_3(CO)_{12}Br]^+$ (M = Ru, Os). What is most surprising is that the structures are very different. The ruthenium complex has a bent chain of ruthenium atoms bridged across two of them by the bromine atom. Interestingly, the ruthenium that is left unbonded with the Br has five CO groups. The osmium compound more closely resembles the original carbonyl. The tri-dentate phosphine

$HC(PPh_2)_3$ has been reacted,[129] with some success, to both $H_3Ru_3(CO)_{12}$ and $HRuCo_3(CO)_{12}$. The parent carbonyl, $Ru_3(CO)_{12}$ has been used[130] in a reaction with diazoindene (in THF). Nitrogen is lost in the reaction along with two CO molecules, leaving $Ru_3(CO)_{10}(\eta^5{:}\eta^1\text{-}C_9H_6)$. The parent dodecacarbonyl has also been transformed[131] into $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}PhCH_2CH_2C{=}NPh)]$. At the more complex tri-ruthenium level, the electron deficient molecule $[(\mu_2\text{-}H)\text{-}Ru_3(CO)_9\{\mu_3\text{-}NS(O)MePh\}]$ has been prepared[132] and found to contain a chiral sulfoximido cap and (echoing the use of fluorine-containing ligands in earlier sections) the complex $[Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}C_6F_5NNNC_6F_5)]$ has been prepared.[133] The pyrolysis of the tri-ruthenium cluster $Ru_3(\mu\text{-dppm})(CO)_9PPh_3$ has been investigated and, perhaps predictably, many products are produced in the reaction.[134]

Iron clusters are never abundant (compared to ruthenium and osmium, at least) but always present. The tri-iron cluster anion $[Fe_3(CO)_9(\mu\text{-}CO)_2\{PbPh_3\}]^-$ has been prepared by Roser *et al*;[135] the penta-iron cluster $[Fe_5S_4(CO)_{12}]^{2-}$ and the hexa-iron cluster $[Fe_6S_6(CO)_{12}]^{2-}$ have both been prepared and fully characterised by Barber *et al*[136]. Iron clusters with sulfur ligands have been reported. The synthesis and electrochemical behaviour of the compounds $[N(PPh_3]_2[Fe_5S_2(CO)_{14}]$ and $[N(PPh_3]_2[Fe_6S_6(CO)_{12}]$ has been described in some detail.[137]

A tetra-ruthenium carbonyl complex, $Ru_4(CO)_9(\mu_3\text{-}C_{15}H_{20})$, has been synthesised[138] from $Ru_3(CO)_{12}$ and tri-isopropylbenzene ($C_{15}H_{18}$). Penta-ruthenium units have been constructed by Adams and co-workers. Two new complexes have been described[139]: $Ru_5(\mu^5\text{-}C_2)(\mu\text{-}PPh_2)(\mu\text{-}Cl)_2(CO)_{11}$ and $Ru_5(\mu\text{-}H)\text{-}(\mu^5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}Cl)(CO)_{12}$. A follow-up communication[140] described two further pentanuclear ruthenium complexes: $[Ru_5(\mu^5\text{-}CCCPhCH)(\mu\text{-}SMe)_2\text{-}(\mu\text{-}PPh_2)_2(CO)_{10}]$ and $[Ru_5(\mu^5\text{-}CCCPhCPh)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$. Hexanuclear ruthenium compounds have been prepared directly from $Ru_3(CO)_{12}$ and hexamethylbenzene reacting in octane.[141] The unusual ligand $\eta^2\text{-}\mu^4\text{-}CO$ is present in the product, $Ru_6(\eta^2\text{-}\mu^4\text{-}CO)(CO)_{13}(\eta^6\text{-}C_6Me_6)$ and six ruthenium atoms are again gathered together[142] in a second isomer of $[(PPh_3)_2N][Ru_6C(CO)_{15}(C_3H_5)]$.

Like cobalt complexes, the carbonyl compounds of ruthenium are becoming more widely used as catalysts/intermediates for organic reactions. The homogeneous hydrogenation of diphenylethyne has been studied and found to be promoted by tri-ruthenium clusters.[143] Indeed, the authors claim that there is direct kinetic evidence for the clusters acting as catalysts.

The activation of C-H bonds is now a long-running saga in organometallic chemistry and isolated examples keep appearing without any general underlying trend emerging. The activation via Ru-Ru bond fission is studied by Blake *et al*[144] who have found that heating $Ru_3(CO)_8(C_9H_{10})$ produces $Ru_3(CO)_8(C_9H_8)$. Furthering the scope of knowledge in this area, we now have good evidence[145] for the reaction of $Ru_3(\mu\text{-dppm})(CO)_{10}$ with unsaturated hydrocarbons. Reversible oxidative addition of hydrogen across a Ru-Ru bond in the complex $(\mu\text{-}H)_2Ru_3(CO)_8(\mu\text{-}P(^tBu)_2)_2$ has been observed by Safarowic *et al.*[146]

Tri-osmium compounds are still in evidence although, like iron and ruthenium, there is a drift towards functionalising the molecules with organic ligands. A good example of this[147] is the reduction of $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-CCO})$ with $BH_3.THF$ to give the slightly different $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CMe})$. Along the same lines, the dodecacarbonyl is used in a reaction[148] with tetramethylthiourea to give $[Os_3(CO)_{11}\{\eta^1\text{-SC(NMe)}_2\}]$ and indoline tetrahydroquinoline has been combined[149] with $Os_3(CO)_{10}(MeCN)_2$. Continuing on this theme,[150] a ferrocene residue with what is essentially an ester linkage has been grafted on to $Os_3(CO)_{10}(MeCN)_2$ to give $HOs_3(CO)_{10}(O_2CC_5H_4FeC_5H_5)$. Over a number of years, $Os_3(CO)_{10}(MeCN)_2$ has been found to be a useful starting material and it is used as such to good effect in a reaction[151] with 2,2′-dithiosalicylic acid to give $[\{Os_3(CO)_{10}(\mu\text{-H})\}_2(O_2CC_6H_4S)_2]$ and also in the reaction with 4-methylthiazole.[152] The pendant vinyl group is suspended interestingly on $Os_3(CO)_{11}(Ph_2PCH{=}CH_2)$ and looks likely to have an attractive future[153] if the reactions described in this study are developed further. The cycloalkane analogues using sulfur or phosphorus atoms in rings have been mentioned earlier. The cyclophosphane $(EtP)_5$ has been shown to react[154] with $Os_3(CO)_{10}(MeCN)_2$ and $Os_3(CO)_{10}(\mu\text{-H})_2$ by replacement of various ligands. Two-dimensional ^{31}P NMR was used to elucidate the structure. The reaction of $Os_3(CO)_9(\mu\text{-H})_2PPh_3$ with ethene and ethyne has also been reported.[155] Some NMR work has also been carried out[156] with tri-osmium and tri-ruthenium clusters bonded to the related cyclophosphane $(PPh)_5$.

Away from the organic tendencies of tri-osmium compounds, there has been a detailed study of the hydrogen/deuterium exchange in $Os_3(CO)_{10}(H)_2$. Starting with $Os_3(CO)_{10}(MeCN)_2$, Aime *et al* have prepared $Os_3(CO)_{10}(H)_2$, $Os_3(CO)_{10}(D)_2$ and $Os_3(CO)_{10}(H)(D)$ by reaction with HD or a mixture of H_2/D_2. In both cases, the three possible isomers of the tri-osmium compound are formed and, quite clearly, there is an isotopic exchange mechanism operating. The authors calculate that the activation energy for the reaction is 43.7 kJ mol^{-1} which is in line with other similar measurements of this type of process.[157]

Moving up one metal atom to tetra-osmium complexes, the reaction of $Os_4(\mu\text{-H})(CO)_{10}(MeCN)_2$ with cyclohexa-1,3-diene has been shown to make a variety of Os_4 complexes.[158] Hexa-osmium complexes are represented[159,160] in the 1996 literature by $[Os_6(\mu\text{-H})(CO)_{22}(\mu\text{-PH}_2)]$ and $[HOs_6(CO)_{22}(\mu\text{-}\eta^2\text{-NC}_5H_4CH{=}CH)]$ respectively. Joining two Os_3 units by a dppp ligand, Choi *et al*[161] have produced the hexa-osmium complex $[\{Os_3(\mu\text{-H})_2(CO)_9(\mu_3\text{-C})\}_2(\mu\text{-dppp})]$.

Before leaving this group, it is worth noting that the number of water soluble carbonyl complexes has been increased somewhat by the discovery[162] of at least two chloro-hydroxy carbonyls of Ru(II) and Os(II). The complexes $[Ru(CO)_2Cl(OH)]_n$ and $[Os(CO)_2Cl(OH)]_n$ (where n is variable) can now be added to the list.

4.6 Cobalt, Rhodium and Iridium – Over the past few years, there has been no shortage of papers dealing with the carbonyl chemistry of the metals in this group and last year was no exception. Perhaps the highlights of 1996 were two papers by Aubke and co-workers dealing with Ir(III) carbonyls. In one[163] they describe the formation of $[Ir(CO)_3(SO_3F)_3]$ from a solution of $Ir(SO_3F)_3$ in HSO_3F under a pressure of CO gas. The complex crystallises out as the *mer*-isomer (with ν(CO) at 2249, 2208 and 2198cm^{-1}), but there is spectroscopic evidence (ν(CO) bands at 2233 and 2157cm^{-1}) for the *fac*-isomer in solution. These complexes are the first thermally stable, structurally characterised σ-bonded carbonyls of a metal in the +3 oxidation state. This study was followed up by equally important piece of work[164] dealing with two complexes $[Ir(CO)_6]^{3+}$ and $[Ir(CO)_5Cl]^{2+}$. The former is isoelectronic with $W(CO)_6$, the latter with $Re(CO)_5Cl$. The hexacarbonyl complex is strictly octahedral with ν(CO) absorptions at 2295 (a_{1g}), 2276 (e_g) and 2254cm^{-1} (t_{1u}). We now know of a long series of isoelectronic hexacarbonyls ranging from $[Hf(CO)_6]^{2-}$ all the way, without gaps, to $[Ir(CO)_6]^{3+}$, a total of six molecules.

Starting with the proto-organometallic complex, Vaska's compound, Al-Jibori[165] has produced (in high yield) $[Ir(OH)(CO)(PPh_3)_2]$ by treating it with 50% $NaOH_{(aq)}$ and benzyl(triethyl)ammonium hydroxide.

An interesting paper (remembering the terms of reference of this chapter which include reactions of the sulfur group with metal carbonyls) was to be found under the names of Cartwright and Hill.[166] They reacted $[IrCl(CO)(PPh_3)_2]$ with seleninyl chloride ($SeOCl_2$). Although an intermediate was formed, the final product, after SeO was 'extruded' was $[IrCl_3(CO)(PPh_3)_2]$ and so – in a rather round-about way – oxidative addition had taken place. Superficially similar compounds to the starting material above have been prepared by Holloway *et al.*[167] They mixed $IrCl_3$ or $IrBr_3$ with $P(C_6F_5)_3$ under a pressure of CO to produce two new compounds containing the perfluoroaryl phoshines: $[IrCl(CO)\{P(C_6F_5)_3\}]$ and $[IrBr(CO)\{P(C_6F_5)_3\}]$.

There is a recurrent theme through many of the papers mentioned here: the linking of metal carbonyl sub-units by multifunctional ligands. One such study[168] uses the TPTA ligand (TPTA = 1,4,8,11-tetrakis-(diphenylphosphinomethyl)-1,4,8,11-tetraazacyclo-tetradecane) to link both $Cr(CO)_4$ units (to make $[Cr(CO)_4]_2(TPTA)$) and $Cr(CO)_5$ units (to make $[Cr(CO)_5]_4(TPTA)$).

Cobalt carbonyl species have long been used in organic syntheses and this repertoire was extended in 1996 with the publication[169] of a study dealing with the synthesis of cyclopentenones and alkenylsilanes (two very different classes of compound) using alkyne-dicobalt hexacarbonyls.

The chemistry of polynuclear carbonyl complexes continues to play a large part in this section. At a fairly simple level, the A-frame complex $Rh_2(\mu\text{-}CO)(Ph)_2(dmpm)_2$ has been prepared.[170] Moving up in complexity, and starting from $Ir_4(CO)_{12}$, a series of complexes of the general format $[Ir_4(\mu\text{-}CO)_3(CO)_5(\mu\text{-}PR_3)(PR_3)_2]$ have been prepared.[171] Similarly, starting from $Co_2(CO)_8$ and $Co_4(CO)_{12}$, Angelici *et al*[172] have prepared a number of new complexes by reaction with an iridathiabenzene complex.

4.7 Nickel, Palladium and Platinum – The interest in the carbonyl chemistry of this group has been very limited in recent years but in 1996 there were considerably more than the usual very few examples to include here. There was, many years ago, a spate of papers where tetracarbonylnickel was reacted with a relatively simple ligand. There are echoes of this type of work in the preparation of $Ni(CO)_3$(1-azabicyclo[2.2.2]-octane), but the authors[173] go on to react this with 2-(diisopropylamino)phosphaethyne. A group of trinuclear nickel clusters make these pages in the form of $[Ni_3(\mu_3\text{-}CO)(\mu_3\text{-}X)(\mu_2\text{-}dppm)_3]^+$ cations where X is either iodine or bromine.[174]

Dicationic carbonyl complexes of nickel are something of a rarity, although they are becoming more commonplace in other groups. However, $[Ni(PP_3E)(CO)]^{2+}$ has been prepared[175] as its BF_4^- salt. The PP_3E ligand – itself rather scarce – is tris(2-(diethylphosphino)ethyl)phosphine.

Zintyl ligands have been mentioned earlier and their use[176] has spread to the Ni-Pd-Pt triad in the form of three new complexes, $[\eta^4\text{-}P_7Ni(CO)]^{3-}$, $[\eta^4\text{-}P_7HNi\text{-}(CO)]^{2-}$ and $[\eta^2\text{-}P_7PtH(PPh_3)]^{2-}$.

Nickel carbonyl complexes immobilised on silica have been a regular feature in this section over the years and in 1996 Behringer and Bluemel carried out a solid-state NMR study of $Ni(CO)_4$ and bifunctional phosphines on silica.[177]

The largest cluster of the year[178] (and it usually crops up in this group or involves the metals of this group) was the complex $[Ni_{32}C_6(CO)_{36}]^{6-}$.

Platinum clusters have appeared regularly in this chapter for several years now and the literature of 1996 contained a study of hexa-platinum clusters containing CO and a variety of phosphine ligands which have been prepared by Hao and co-workers.[179]

4.8 Copper, Silver and Gold – Although this group is never bursting with metal carbonyl activity there has been a steady trickle of papers over the past five years. Last year the synthesis and characterisation of cationic [tris(pyrazole)methane]-copper(I) carbonyl complexes was reported[180] and the cation $[(NH_3)_3(CO)Cu]^+$ was characterised.[181]

4.9 Mixed Metal Carbonyls – In keeping with previous years, a number of papers outlining the preparation of carbonyl complexes containing more than one transition metal atom have been noted.

Vanadium rarely figures in this section, so it is pleasing to note that two complexes (one a cobalt-vanadium pairing, the other containing platinum and vanadium) have been prepared:[182] $(PPh_3))Co(\mu\text{-}CO)_2V(CO)_2Cp$ and $(PPh_3)HPt\text{-}(\mu\text{-}CO)(\mu\text{-}PPh_2)V(CO)_2Cp$.

It is quite unusual for the first period transition elements to figure in polynuclear clusters without the presence of at least one second- or third-period metal. However, such a combination has been discovered by Harakas and Whittlesey[183] who have linked manganese/THF groups to an iron carbonyl unit in $\{\mu\text{-}Mn(THF)_2\}_2Fe_2(CO)_8$.

Electrophilic addition of mono, di- and tri-gold units to the isoelectronic species $[Mn_3(CO)_{11}(\mu\text{-}H)]^{2-}$ and $[Fe(CO)_{11}]^{2-}$ has been carried out by Rossell *et al.*[184] Gold also figures in the preparation of $[Fe_4Au_2C(CO)_{12}(\mu\text{-}dppm)][C_7H_8]$ which was used to highlight the effect of diphosphine ligands on the metal framework to hetero-bimetallic clusters[185] and in the preparation[186] of $Mo\text{-}(CO)_9(AuPPh_3)_3(\mu\text{-}OEt)_2$ and $W(CO)_9(AuPPh_3)_3(\mu\text{-}OEt)_2$.

A Co_2Mo unit bridged by a μ_3-CPh unit has been prepared by Wu *et al*[187]

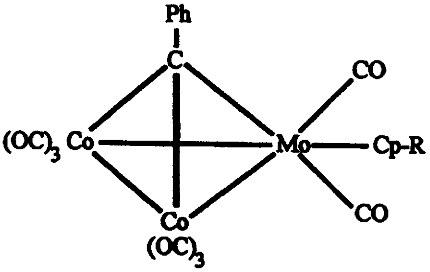

Figure 8 *Dicobalt-molybdenum grouping bridged by a μ-CPh ligand (Ref. 187)*

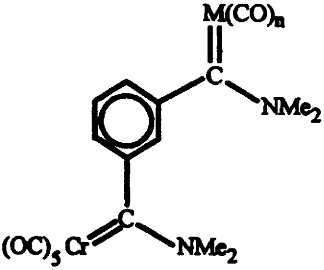

Figure 9 *(μ-Bis(aminocarbene)) dimetal complexes of chromium and iron (Ref. 188)*

(Fig. 8) and a μ-bis(aminocarbene) complex has been prepared by Havranek *et al*[188] which couples together iron and chromium carbonyl units (Fig. 9). Cobalt and molybdenum also figure in a number of Co-Mo 'butterfly clusters'[189] and cobalt is used again (starting as dicobalt octacarbonyl) in a reaction[190] with the indium organometallic compound $In_4[C(SiMe_3)]_4$ to make two new complexes, one of which has the cobalt atoms bridged by CO and indium and the second which is doubly bridged by indium atoms. Cobalt and lead are paired[191] in the complex $[Pb\{Co_3(CO)_9(\mu_3\text{-}CCO_2)\}_2]$, whilst platinum and tin are combined in $[Pt_6(\mu_3\text{-}SnBr_3)_2(\mu\text{-}CO)_6(\mu\text{-}PhPCH_2PPh_2)_3]$ and related complexes.[192] Some of the reactions that they describe can be classified as bi-cluster oxidative additions which are a new reaction type. In a paper of considerable length and detail, the reaction of alkynes with the mixed-metal complex $[RhIr(Me)\text{-}CO)_3(Ph_2PCH_2PPh_2][CF_3SO_3]$ have also been reported.[193] Cobalt also appears[194] in the complex $Co_2Ru_3(\mu_4\text{-}C_2Ph)(\mu\text{-}dppm)(\mu\text{-}CO)_2(CO)_9$. The same pairing of cobalt and ruthenium surface again[195] in the complex $HRuCo_3(CO)_9[HC(PPh_2)_3]$ and its reaction with PMe_2Ph. Mixed clusters (of relatively low nuclearity) of iron are always fairly scarce, but some interesting examples emerge in the literature from time to time. More for the interesting μ_4-S ligand than anything else, the tri-iron cluster $[CpFe_3Co(CO)_{11}(\mu_4\text{-}S)]$ has been prepared.[196] The combination of cobalt and iron has been used in the preparation of the cluster $FeCo_2(CO)_9\text{-}(\mu_3\text{-}NH)$ where the μ_3-NH ligand sits atop the three metal atoms like a tripod.

The main thrust of the paper is, however, the use of this complex as a precursor for azatrimetallate complexes.[197]

Tungsten and osmium appear together in the multi-faceted complex $CpWOs_3(CO)_{10}(\mu_3\text{-CTol})$ prepared by Chung *et al.*[198] Another Group 6 metal, chromium in the form of $Cr(CO)_3(\mu^6\text{-PhC}_2Ph)$, has been welded into mixed clusters[199] with $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$.

Ruthenium-rhodium clusters have been made in great abundance in previous years and last year was no exception. The whole issue of $Ru\text{-}Rh_4$ geometrical variations is the subject of a study by Hattersley *et al.*[200] Beginning with relatively humble starting materials ($Ru_3(CO)_{12}$ and $[Rh(CO)_4]^-$), Fumagalli *et al*[201] have prepared $[Ru_2Rh_2(CO)_7(\mu\text{-CO})_5]^{2-}$, $[Ru_2Rh_2(CO)_9(\mu\text{-CO})_3(\mu\text{-H}]^-$ and $[Ru_2Rh_2(CO)_7(\mu\text{-CO})_5(\mu_3\text{-AuPPh}_3]^{2-}$. The iron-tungsten cluster $[(\mu\text{-H})Fe_2W(CO)_8(\mu_3\text{-Se})\text{-}Cp]$ has been prepared by Konchenko and co-workers[202] and the iridium-tungsten cluster $Cp_3W_3Ir_4(CO)_{12}(\mu\text{-H})$ has also been reported.[203]

Ruthenium is also present[204] in a number of ruthenium-tin clusters which contain bulky phosphine ligands in addition to the much smaller CO groups found elsewhere and also in a series of ruthenium-iron clusters.[205]

Six osmium atoms and one palladium atom (a metal not often featured in mixed metal clusters) have been used to build $Os_6Pd(CO)_{18}(bipy)$ and other similar complexes.[206]

Rhenium-platinum anionic clusters have been made by Bergamo and co-workers.[207] In a detailed study they report the formation of $[Re_2Pt(CO)_9(\mu\text{-H})_2\{Re(CO)_5\}]^-$ and the somewhat larger cluster $[Re_2Pt(CO)_9(\mu\text{-H})_2\{Re_2(CO)_9\}]$. Using bridging CO groups between phosphorus atoms (Fig. 10) Weber *et al*[208] have linked two $Fe(CO)_2Cp^*$ units and a $Cr(CO)_5$ residue.

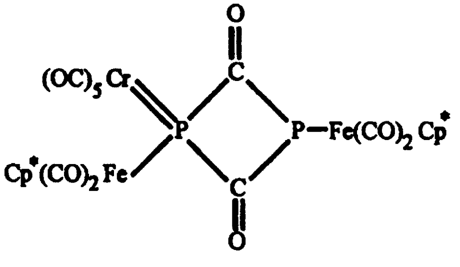

Figure 10 *Phosphine and CO bridged mixed metal carbonyl containing iron and chromium (Ref. 208)*

The platinum-ruthenium cluster $Pt_3Ru_6(CO)_{21}(\mu^3\text{-H})(\mu\text{-H})_3$ is used to prepare a number of new complexes.[209]

Combining three metals (platinum, rhenium and mercury), Hao *et al*[210] have described an extensive cluster chemistry. Mercury is also present in the Hg-Os clusters prepared by Au and Wong.[211] If tellurium is counted as a metal, then three-metal clusters have also been prepared by Mathur *et al*,[212] using iron, molybdenum and tellurium. The series has been extended further by some of the same group[213] with the two-metal plus two-chalcogen complex $[Fe_2(CO)_6(\mu_3\text{-}$

Se)(μ_3-Te)]$_2$Mo(CO)$_2$. Tellurium appears again[214] in the Fe-Te cluster [Fe$_2$(CO)$_6$(μ-Cl)(μ-TeCl)$_2$]$_2$[η^2,μ_2,μ_2-Te$_2$Cl$_{10}$]. With germanium in a cluster as a third metal (if that is not pushing the definition of metal too far) the reactions of [Ge$_2$Co$_4$Fe(CO)$_{21}$] with methyl germanes has been published.[215] The multi-functional organometallic CpIr(2,5-dimethylthiophene) has been coupled to a number of relatively simple metal carbonyls (namely Ru$_3$(CO)$_{12}$, Mn$_2$(CO)$_{10}$ and Re$_2$(CO)$_{10}$) to produce a number of new clusters.[216]

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10

Organo-Transition Metal Cluster Compounds

BY MICHAEL I. BRUCE

1 Introduction

This chapter covers the chemistry of metal carbonyl and organometallic clusters containing three or more metal atoms. The treatment is in Periodic Group order, homometallic compounds being followed by heterometallic clusters. The majority of numbered compounds are illustrated, those which are not being indicated by an asterisk; in most cases, terminal CO groups are not shown. Coverage is essentially restricted to papers published during 1996, but some late appearing papers have also been included to preserve continuity with last year's report. An annual survey of organometallic clusters for 1994 is available.[1]

2 General Reviews

A notable Dalton discussion was held in Southampton during January and the contributed papers were published in *Dalton Transactions* soon after. Evans has provided a personal overview which conveys some of the flavour of the meeting.[2] Most of the contributions are mentioned in the appropriate sections below: some were concerned with non-organometallic species. An interesting study of metallohedrene and related metal-containing carbon clusters is included,[3] while Schmid reviewed recent results on ligand-stabilised metal clusters and colloids.[4]

Other reviews survey the newly recognised 'xenophilic' clusters combining hard- and soft-donor ligands on two metals which are involved in donor-acceptor metal-metal bonding,[5] the synthesis, structure and bonding of planar M_4 clusters containing two capping ligands, with applications to catalysis and as precursors to new materials,[6] coordination of amino acids to osmium, ruthenium and cobalt clusters,[7] the formation of magnetically active sulfur-bridged heterometallic clusters,[8] and hetero-polynuclear alkynyl complexes containing Pt and Group 11 metals.[9]

3 Spectroscopic Studies

3.1 Nuclear Magnetic Resonance – ^1H and ^2D NMR studies of clusters containing hydrides show strong similarities in H/D chemical shifts in solid state

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and solution, except for $[Co_6H(CO)_{15}]^-$. Shifts to high field have been correlated with displacement of the H atom from the centre of the M_6 octahedron. Differences in fluxional behaviour include oscillation of H about M-M edges (solid state) rather than migration between edges (solution) for $Rh_2Ru_2(\mu\text{-}H)_2(CO)_{12}$, and no migration of H in solid $[Rh_{13}H_n(CO)_{24}]^{(5-n)-}$ (n = 2, 3).[10] Calculation of ^{13}C and ^{17}O NMR chemical-shift tensors by density functional theory (DFT) has given excellent agreement with available data for interstitial carbides in Fe, Os and Rh clusters; an ELF (electron localisation function) view of bonding in $Rh_6(CO)_{16}$ has also been given.[11]

3.2 Mass Spectrometry – Electrospray mass spectrometry (ES MS) has been applied extensively to metal cluster complexes, despite an initial report claiming that the technique was not generally useful.[12] Subsequent investigations have defined the operating conditions necessary for success. Derivatisation of metal carbonyl clusters in situ by addition of NaOMe/MeOH (or corresponding Et or Pr^i systems) is a widely applicable method for generating useful negative ion ES MS, and is generally to be preferred over the Ag^+ ionisation reported last year. Examples of cluster complexes which have given satisfactory spectra include $Os_3(CO)_{12}$, $Ir_4(CO)_{12}$ and $Ru_6C(CO)_{14}(\eta\text{-}PhMe)$, which contain ions in which one CO group is converted to CO_2R.[13] ES MS was also applied to heterometallic anionic clusters, including $[Fe_3\{\mu\text{-}Hg[M]\}(CO)_{11}]^-$ [M = Mo/W(CO)$_3$Cp, Fe(CO)$_2$Cp; Mn(CO)$_5$, Co(CO)$_4$] and $[AuFe_6C(CO)_{16}(PPh_3)]^-$.[14] Comparison of ES with FAB MS shows that much more control over fragmentation can be achieved with the former method. As communicated last year, UV-laser desorption of $Ru_6C(CO)_{17}$ and its η^6-arene derivatives gives fragment ions by loss of CO groups, together with aggregate ions extending to *m/z* > 35000.[15]

4 Structural Studies

Patterns of solid-state structures of organometallic clusters (among others) are variously determined by van der Waals, hydrogen bonding and anion-cation interactions between molecules and ions to give the observed supramolecular aggregation.[16] The study of H-bonding in organometallic crystals has been continued, examples involving M-H...O interactions with coordinated CO groups being considered: a CCDC search gave 17 examples with M-H...O < 2.8 Å.[17] The overall conclusion is that the M-H...O bond is a soft intermolecular interaction which is similar in strength to C-H...O bonds.

Agostic C-H...M interactions are also considered in a wider context,[18] including $Fe_4(\mu\text{-}H)(\mu_4\text{-}CH_2)(CO)_{12}$, in which one C-H is shown (by neutron diffraction) to be involved in an interaction with a CO group of an adjacent molecule. Other supramolecular arrangements include stacks of mutually attractive $[PPh_4]^+$ cations resulting from edge-to-face interactions of the Ph groups (quadruple or sextuple phenyl embraces: energetically comparable with hydrogen bonds): several examples are found in salts of metal carbonyl cluster anions.[19]

X-ray structural studies of the following complexes have been reported: $Ti_6(\mu_3\text{-}Te)_6(\mu_3\text{-}O)_2Cp_6$,[20] $Fe_3(CO)_9\{P(OR)_3\}_3$ (R = Me, Pr^i),[21] $Fe_3(\mu_3\text{-}PBu^t)(\mu_3\text{-}PPh)(CO)_9$,[22] $Fe_2M(\mu_3\text{-}Se)_2(CO)_{10}$ (M = Mo, W),[23] $Ru_3(\mu\text{-}H)(\mu\text{-}C_5H_4N\text{-}2)(CO)_{10}$,[24] a comparative study of $M_3(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)(\mu\text{-}CO)\ (CO)_9$ (M = Ru, Os),[25] a second form (triclinic) of [ppn] $[Ru_6C(CO)_{15}(\eta\text{-}C_3H_5)]$,[26] a second crystal form of $Os_5(\mu\text{-}H)_2(CO)_{16}$,[27] $Co_4(\mu_4\text{-}PPr^i)_2(CO)_{10}$,[22] $Co_4(\mu_4\text{-}PPh_2)(CO)_8(PMe_2Ph)_2$,[28] $Ir_4\{\mu\text{-}PPh_2(C_5H_4N\text{-}2)\}(CO)_8\{PPh_2(C_5H_4N\text{-}2)\}_2$,[29] and $Pd_3(\mu\text{-}O_2CMe)_4(C_6H_3Me_2\text{-}2,5)_2(SBu^i{}_2)_2$ (*al* isomer).[30]

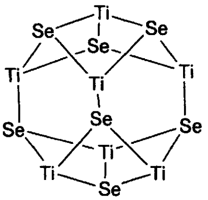
Some otherwise unpublished cluster structures have been deposited with the Cambridge Crystallographic Data Bank. Of relevance to the present survey are the following, which are recorded as 'private communication' or 'to be published': $[NEt_4]_3[Re_6C(\mu\text{-}H)(CO)_{18}]$,[31a] $Fe_3(\mu_3\text{-}PBu^t)(\mu\text{-}CO)(CO)_8\{C\text{-}(OEt)_2\}$,[31b] $Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}CO)(CO)_8(PMe_3)$,[31c] $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$,[31d] $Os_3(CO)_{11}\{PO(CF_3)_2\}$,[31e] $Os_3\{\mu\text{-}P(C_6F_5)_2C_2H_4P(C_6F_5)_2\}(CO)_{10}$,[31f] $Os_3(\mu\text{-}H)(\mu\text{-}O{=}C\text{-}C_4H_3NH)\ (CO)_9(NMe_3)$,[31g] $Os_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}NHC_6H_5Ph)(CO)_9$,[31h] $Os_3\{\mu_3\text{-}MeC_2(\mu\text{-}C_2[Co_2(CO)_6])\}\ (CO)_{10}$,[31i] $Ru_2W(\mu_3\text{-}NPh)(\mu\text{-}\eta^1{:}\eta^2\text{-}C(CF_3){=}CH(CF_3))\}(\mu\text{-}CO)(CO)_6Cp^*$,[31j] $[ppn]_2[Re_2Rh_2(\mu_6\text{-}C)\ (CO)_{24}]$,[31k] and $Co_3Ru(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_7(SMe_2)$.[31l]

5 Theoretical Studies

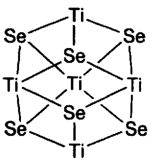
The bonding of η^n-coordinated π-bonding ligands (Cp, arene, etc.) to clusters has been examined using a modified VE SCF method using a 'dummy atom' approach.[32] This publication considers particularly the stereochemistry and dynamics of $M_3(CO)_3L_3$ (L = Cp, Cp*, ind) and $Co_3(\mu_3\text{-}arene)Cp_3$, but the method is general and is considered to be a further contribution to building up a general force field for metal carbonyl clusters.

6 Group 4

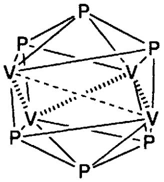
Reduction of $\{TiCp\}_4(\mu_3\text{-}Se)_3(\mu\text{-}Se)_3$ with $SnHBu^n{}_3$ gave $\{Ti(\mu_3\text{-}Se)Cp\}_7$ (**1**) and paramagnetic (one unpaired electron) $\{TiCp\}_5(\mu_3\text{-}Se)_6$ (**2**), the latter also being formed by oxidation of $TiCl_2Cp_2$ with H_2Se/NEt_3.[33]



1 Ti = TiCp



2 Ti = TiCp



3 V = VCp*

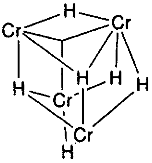
7 Group 5

The cubane cluster $\{V(\mu_3\text{-}N)Cp^*\}_4$ was prepared by Na/Hg reduction of $\{V(\mu\text{-}N)ClCp^*\}_2$; it has short V-V and V-N bonds and can be reduced to the mono-anion.[34] Thermolysis of $V(CO)_4(Cp^R)$ (Cp^R = Cp, Cp^{Me}, Cp^{Bu^t}) with P_4 in xylene gave $V_4(\mu\text{-}P_3)_2(Cp^R)_4$ (**3**).[35]

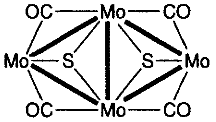
8 Group 6

The hydride $Cr_4(\mu_3\text{-}H)_2(\mu\text{-}H)_5Cp''_4$ (**4**; Cp'' = C_5Me_4Et) has been obtained from $Cr_4(\mu_3\text{-}H)_4Cp''_4$ and H_2 (60 atm., 25°C, 5 d) and fully characterised by a neutron diffraction study. The Cr-Cr distances are between 2.70 and 2.80 Å. Strong magnetic behaviour results from seven unpaired electrons having an intramolecular antiferrimagnetic alignment.[36]

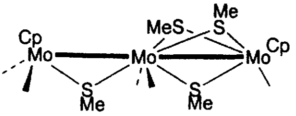
Trace amounts of $Mo_3(\mu_3\text{-}Spy)_2(\mu\text{-}Spy)_2(CO)_6$ were obtained from $Mo(CO)_3(NCMe)_3$ and $PySH/PPh_3$.[37] The reaction between $Fe_2(\mu\text{-}SEt)_2(CO)_6$ and $\{Mo(CO)_3(Cp^{CO_2Et})\}_2$ gave $Mo_4(\mu_3\text{-}S)_2(\mu\text{-}CO)_4(Cp^{CO_2Et})_4$ (**5**), together with a small amount of $FeMo_2(\mu_3\text{-}S)(CO)_7(Cp^{CO_2Et})_2$.[38] One of the products obtained (15-25% yield) from $MoH(CO)_3Cp$, allyl chloride and dimethyl disulfide is the open cluster $Mo_3(\mu\text{-}SMe)_4(CO)_5Cp_2$ (**6**), containing one normal (2.800 Å) and one long (3.115 Å) Mo-Mo bond.[39] A new synthesis of $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cp^*_3$, by Na/Hg reduction of $Mo(SBu^t)_3Cp^*$, is reported.[40] EH MO calculations and comparisons with the mono-cation show that the $[Mo_3S_4]^{4+}$ core expands when the extra electron is added.



4 Cr = CrCp''



5 Mo = Mo(η-$C_5H_4CO_2Me$)



6

Unusual site selectivity is found for $W_6H(\mu\text{-}H)_4(\mu\text{-}CPr^i)(\mu\text{-}OPr^i)_7(OPr^i)_5$ which undergoes H/D exchange in D_2 and reversible reactions with C_2H_4. Reduction of C_2H_4/H_2 proceeds exclusively via reaction of the terminal W-H group, while only one terminal OPr^i group reacts with $Pr^iOH\text{-}d_8$.[41]

9 Group 7

Two further examples of crystalline adducts formed by the tetrahedral H-bond donor $\{Mn(\mu\text{-}OH)(CO)_3\}_4$ ($\geq \{Mn_4\}$), with compositions $\{Mn_4\}$.2,3,5,6-Me_4-pyrazine.$2H_2O$.2MeCN and $\{Mn_4\}$.4,4'-bpy.2MeCN, have been described.[42]

Cubanes $\{Mn(\mu_3\text{-}SR)(CO)_3\}_4$ (R = Ph, CHMePh, furfuryl) were obtained from $Mn(CO)_3(\eta^5\text{-}C_5H_7)$ and the corresponding thiol.[43] Unexpectedly, treatment of $Mn_2(CO)_{10}$ with Na_2Te afforded both $[Mn(CO)_5]^-$ and paramagnetic (one unpaired electron) $[Mn_3(\mu_3\text{-}Se)_2(CO)_9]^{2-}$.[44] An asymmetric CO group bridges one Mn-Mn bond and serves to redistribute electron density among the metal atoms.

Reduction of $[^{99}TcO_4]^-$ with $BH_3(thf)$ under CO (1 atm.) gave $^{99}Tc_3(\mu\text{-}H)_3(CO)_{12}$ as the major product (X-ray structure); NaOH/MeOH converts it to $[\{^{99}Tc(CO)_3\}_2(\mu\text{-}OH)_3]^-$, which with HCl gave $[^{99}TcCl_3(CO)_3]^{2-}$. A second product from the reduction was tentatively identified as $[^{99}Tc_3(\mu_3\text{-}H)(\mu\text{-}H)_3(CO)_9]^-$. Similar chemistry was found with a sample of $[^{188}ReO_4]^-$.[45]

Trinuclear anions $[MRe_2(\mu\text{-}H)H(CO)_{13}]^-$ (M = Mn, Re) were obtained from $Re_2(\mu\text{-}H)(CO)_8$ and $[M(CO)_5]^-$; the Re_3 anion is also formed from $[ReH_2(CO)_4]^-$ and $Re_2(CO)_9(thf)$ or, in lower yield, $Re_3(\mu\text{-}H)(CO)_{14}$, or from $[Re_2H(CO)_9]^-$ and $ReH(CO)_5$.[46] Dynamic processes occurring in this anion include exchange of two H and the CO groups *trans* to them via a windshield-wiper motion of the $ReH_2(CO)_4$ fragment, and migration of H between the two Re-Re bonds. On heating, loss of CO gives $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$. Protonation results in fragmentation to $ReH(CO)_5$ and $Re_2(\mu\text{-}H)_2(CO)_8$.

The ^{31}P longitudinal relaxation times in several phosphine-containing Re_3 clusters have been measured: T_1 values for ax-PR_3 are much longer than those for eq-PR_3 ligands.[47] Values of T_1 depend on ^1J(Re-P) and absolute values are affected by several factors, but comparisons of T_1 in similar compounds can be used to establish relative coordination geometries.

Hydrogen reacts with $Re_2(\mu\text{-}PAr_2)(CO)_8$ (Ar = Ph, C_6H_4F-4) to give several complexes, including $Re_3(\mu\text{-}H)_2(\mu\text{-}PAr_2)_3(CO)_6$, $Re_4(\mu\text{-}H)_2(\mu_4\text{-}PAr)(\mu\text{-}PAr_2)_4(CO)_8$ and $Re_4(\mu\text{-}H)(\mu_4\text{-}PAr)_2(\mu\text{-}PAr_2)_3(CO)_8$, all of which are homogeneous catalyst precursors for hydrogenation and isomerisation of hex-1-ene.[48] Reactions of $Re_3(\mu\text{-}H)_3(CO)_{12}$ with $SC(NEt_2)\{NH(tol)\}$ afford $Re_3(\mu\text{-}H)_3\{\mu\text{-}S{=}C(NEt_2)[NH(tol)]\}(CO)_{10}$, containing the first μ-*S*-bonded thiourea.[49]

Addition of Cl^- in non-donor solvents to tetrahedral 56-e $Re_4(\mu_3\text{-}H)_4(CO)_{12}$ affords $[Re_4H_4Cl(CO)_{12}]^-$; the reaction is reversed by addition of $TlPF_6$.[50] Fragmentation to unsaturated Re_3 cluster anions occurs with weak donors. In dmf/$CHCl_3$ mixtures, $Re_4(\mu\text{-}H)_4(CO)_{12}$ gives $[Re(CO)_3(dmf)_3][Re_3(\mu\text{-}H)_4(CO)_9]$ containing the 44-e anionic cluster. Donor-acceptor interactions between the H atoms bridging the Re=Re double bond and the vacant site on the third Re atom of a second cluster result in antiprismatic stacking in the solid state. In solution, ^1H and ^{13}C NMR spectra are consistent with a delocalised Re_3 structure with one μ_3-H and three μ-H ligands. Rapid reactions with a variety of ligands give $[Re_3H_4(CO)_9(L)]^-$.[51]

The anion $[Re_3(\mu_3\text{-}OH)(\mu\text{-}OH)_3(CO)_9]^-$ has been employed as a novel tripodal ligand in complexes of Mn^{2+} and Cu^{2+}, when neutral $MRe_6(\mu_3\text{-}OH)_8(CO)_{18}$ are obtained as air- and water-stable compounds. These compounds have the double-cubane structure (with no Re-Re bonds) with a hydrophobic carbonyl shell. Intermolecular arrangements lead to layers by formation of H-bonds, the detailed structure of which depends on M.[52]

10 Group 8

10.1 The $M_3(CO)_{12}$ Problem – The molecular structures and dynamic processes found in the various $M_3(CO)_{12}$ species continue to be centres of attention. Thus, for $Fe_3(CO)_{12}$, molecular mechanics calculations on a flexible $Fe_3(CO)_{12}$ molecule in a rigid crystal lattice have been used to rationalise completely the solid state dynamics of the Fe_3 core within the ligand polyhedron.[53] The computed energies are consistent with in-plane 60° jumps which are fast enough to average both the intra- and inter-molecular surroundings of the CO groups. Further analysis of Mössbauer data has also provided support for this dynamic process.[54]

Variable temperature X-ray structure determinations have also contributed to our understanding of the changes observed in the molecules. For $Ru_3(CO)_{12}$, data in the range 100-150 K show that there is no dynamic disorder, the whole molecule being essentially isotropic, its translational and librational motion being that of a rigid body. Each $Ru(CO)_4$ group is rigid, while showing some bending of the Ru-CO bond; each librates to a different degree about an axis through the Ru atom and the mid-point of the opposite Ru-Ru vector. This can be related to the overall solid-state structure, in which adjacent molecules are found interlocking between $(CO)_4$ units formed by two CO pairs at right-angles to the Ru-Ru vector. This motif is common in cluster complexes.[55]

Several mixed systems $MM'_2(CO)_{12}$ have been studied. The Fe_2Ru complex has the $Fe_3(CO)_{12}$ structure and at 223 K is perfectly ordered; above this temperature, partial 'Star of David' disorder appears and at 313 K a phase change occurs with a 1:1 disorder of the metal atoms. The $FeRu_2$ compound is the first to be described with a D_3 structure, which is ordered at 173 K. As the temperature is raised, increasing disorder of the M_3 triangle appears. At 223 K, two coplanar disordered triangles (ratio 86/9) together with a third (5%) which is out of the plane of the other two. Above the phase transition (228 K), two major and four minor component triangles are observed. It is suggested that these indicate the pathway for the M_3 rotation: it is interesting that this involves substantial out-of-plane movements for the Ru atom.[56]

In the $FeOs_2$ complex, these studies (120-323 K) were coupled with ^{13}C MAS NMR spectroscopy to show that two independent CO exchange processes occur. One is an in-plane rotation of the Fe_2Os triangle in 60° steps within the rigid $(CO)_{12}$ polyhedron, while the other is localised *ax-eq* CO exchange on the $Os(CO)_4$ group. There is no disorder at the lowest temperatures and the 12:1 disorder found at r.t. decreases to 1.4:1 at 323 K.[57]

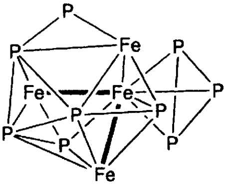
10.2 Iron – Co-deposition of Fe_3^+ (size-selected cluster ions from a metal cluster beam) with CO on a CsI window at 25 K produced enough $Fe_3(CO)_{12}$ for an IR n(CO) spectrum: a band at 1820 cm^{-1} confirms the compound has the usual di-CO-bridged structure.[58] Under phase-transfer-catalysis conditions, $Fe_3(CO)_{12}$ and hydroxide form the radical anion $[Fe_3(CO)_{11}]^{\cdot -}$. This is the reactive species in the reduction of nitrobenzene to aniline by iron carbonyls, $[Fe_3H(CO)_{11}]^-$ being inactive.[59]

Reactions of $Fe_3(CO)_{12}$ with a variety of $Sn(aryl)_2$ gave only Fe_2 derivatives;

with $E\{CH(PPh_2)_2\}_2$, $Fe_2(\mu\text{-dppm})(\mu\text{-CO})(CO)_6$ was formed in high yield.[60] With $SnRR'$ (R = mes*, $R' = CH_2CMe_2C_6H_3Bu^t{}_2\text{-}3,5$), $Fe(SnRR')(CO)_4$ was formed.[61] The anion $[Fe_3(PbPh_3)(\mu\text{-CO})_2(CO)_9]^-$, with a Pb-spiked Fe_3 triangle, was obtained from $[Fe_3(CO)_{11}]^{2-}$ and $PbClPh_3$/ $TlBF_4$.[62]

The cluster anion $[Fe_6N(CO)_{15}]^{3-}$ (from $[Fe_4N(CO)_{12}]^-$ and $[Fe_2(CO)_8]^{2-}$) can be mono-protonated to the dianion, and oxidatively decapped to $[Fe_5N(CO)_{14}]^-$; a short-lived (15 ms) intermediate radical is $[Fe_6N(CO)_{15}]^{2\cdot}$. Thermal substitution of CO by $PPhFc_2$ afforded $[Fe_4N(CO)_{11}(PPhFc_2)]^-$, which contains an Fe_4 butterfly with an exposed μ_4-N bridging the wing-tips and the P coordinated to a wing-tip Fe atom.[63] Electrochemical studies showed that electron transfer between the Fc nuclei is improved by coordination.

Reactions of $Fe_3(CO)_{12}$ with bidentate phosphines, induced by Me_3NO, have given $Fe_3(\mu\text{-P-P})(\mu\text{-CO})_2(CO)_8$, $Fe_3(\mu\text{-CO})_2(CO)_9\{\mu\text{-P-P}[Fe(CO)_4]\}$ and $\{Fe_3(\mu\text{-CO})_2(CO)_9\}_2(\mu\text{-P-P})$ (P-P = dppe, dppb, dppbz, dppf); electrochemical studies are also reported.[64] Addition of $C_2(PPh_2)_2$ (dppa) to one or two eq. of $[Fe_3(\mu\text{-H})(\mu_3\text{-C=CH}_2)(CO)_9]^-$ gave $[\{Fe_3(\mu_3\text{-CMe})(CO)_9\}_n(dppa)]^{n-}$ (n = 1,2). The former reacts with $\{Fe(CO)_2Cp\}_2$ in the presence of $[FcH]^+$ to give zwitterionic $\{Fe_3(\mu_3\text{-CMe})(CO)_9\}(\mu\text{-dppa})\{Fe(CO)_2Cp\}$, also prepared (in much lower yield) from the vinylidene anion and $[Fe(CO)_2(dppa\text{-}P)Cp]^+$. Crystallographic and spectroscopic evidence support the zwitterionic formulation.[65] Zintyl clusters have been expanded with transition metals in the reactions of $P_7(SiMe_3)_3$: with LiCp* and $FeCl_2$, $\{FeCp^*\}_3\{(\eta^3\text{-}P_3)Fe\}P_5$ (7) was obtained.[66]



7 Fe = FeCp*

Clusters $Fe_4(\mu_3\text{-}S_2)_2(\mu_3\text{-}S)_2(Cp^{Si})_4$ [$Cp^{Si} = C_5H_4SiMe_3$, $C_5H_3(SiMe_3)_2\text{-}1,3$] are formed from $\{Fe(CO)_2(Cp^{Si})\}_2$ and S_8 in toluene via intermediates $Fe_2(\mu\text{-}S_2)_2(Cp^{Si})_2$, which was the major product with the $C_5H_3(SiMe_3)_2$ complex.[67] Organometallic derivatives of the Fe_4S_4 cluster were prepared from $[Fe_4S_4Cl_4]^{2-}$ and the cyanides [M]CN [M = $[W(CO)_5]^-$, $[Mn(CO)_2Cp]^-$, Fe(dppe)Cp, $Ru(PPh_3)_2Cp$] in order to study the effects of coupling the redox properties of the Fe_4S_4 cluster and M-CN-M′ systems.[68] The complexes are essentially diamagnetic by strong antiferromagnetic coupling; their electronic spectra differ from those of $[Fe_4S_4R_4]^{2-}$ (R = Cl, SR′).

A new, high quality, structural investigation of $Fe_3(\mu_3\text{-Se})_2(CO)_9$ was prompted by the related study of the Mn_3Se_2 dianion (see above).[44] In this case, both outer Fe atoms have identical ligand environments, leading to the proposal that in $[M_3E_2(CO)_9]^z$ (E = S, Se, Te; z = -2 to +1), electronic inequivalence in the basal

M atoms leads to a semi-bridging CO group. Application to the adduct $Fe_3(\mu_3\text{-}S)_2(CO)_9.Fe_2(\mu\text{-}S)_2(CO)_9$ (new X-ray determination at −120°C) reveals an extended charge-transfer chain formed by S...S contacts (3.157 Å), resulting in an electron deficient Fe_3S_2 cluster. A further result leads to identification of $[Fe_2Mn(\mu_3\text{-}Se)_2(CO)_9]^-$ (ref. 69) as having Fe and Mn as basal M atoms, with a CO semi-bridging the Fe-Mn bond.

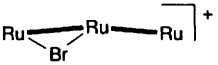
Several clusters, including $Fe_3(\mu_3\text{-}Se)_2(CO)_{9-n}(PPh_3)_n$ (n = 0-2) and $Fe_3(\mu_3\text{-}Se)(\mu\text{-}CO)(CO)_7(PPh_3)_2$, have been obtained from $Fe_3(CO)_{12}$ and $SePPh_3$.[70] Various cationic iron-sulfur and -selenium cluster anions were synthesised from iron carbonyls and $[E_8][X]_2$ (X = SbF_6, Sb_2F_{11}); X-ray structural studies of $[Fe_3(Se_2)_2(CO)_{10}]^{2+}$ and $[Fe_4(Se_2)_3(CO)_{12}]^{2+}$ showed $Fe_x(Se_2)_y$ clusters containing only Fe-Se and Se-Se bonds.[71] Reactions of $Fe_2(\mu\text{-}Se_2)(CO)_6$ with $LiBu^n$, followed by $Br(CH_2)_3Br$, gave $\{Fe_2(\mu\text{-}SeBu)(CO)_6\}_2(\mu_4\text{-}Se)$.[72] The cluster anion $[Fe_3(\mu\text{-}H)(\mu_3\text{-}Te)(CO)_9]^-$ is obtained from $Fe_3(CO)_{12}$ and either $Na_2Te_2/[PPh_4]Br$ or Cs_2Te_3 in MeOH.[73] Microwave heating of $Fe_3(CO)_{12}$ and thiophene or benzothiophene in the presence of Fe_3O_4 results in faster reactions; no desulfurisation of benzothiophene was found. In contrast, detelluration of tellurophene, dibenzotellurophene and 2-telluraindane occurs to give $Fe_3(\mu_3\text{-}Te)_2(CO)_9$ or FeTe (according to conditions), together with mono- or di-nuclear organo-iron complexes.[74]

Kinetic studies of associative reactions of $Fe_5C(CO)_{15}$ with tertiary phosphines and phosphites (L) suggest that reactions proceed via opening of the cluster to the bridged-butterfly $Fe_5C(CO)_{15}(L)$. The rate constants depend on electronic and steric properties of L as found for the Ru analogue, although rates of adduct formation are *ca* 10^3 times smaller for Fe.[75]

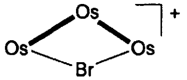
10.3 Ruthenium – *Ru_3 and Ru_4 Clusters.* The Br^+ transfer reagent [adadBr][BR_4] [adad = adamantylideneadamantyl; R = $C_6H_3(CF_3)_2$-3,5] reacts with both $M_3(CO)_{12}$ (M = Ru, Os) in CH_2Cl_2 to give $[M_3Br(CO)_{12}]^+$, which have markedly different structures. For M = Ru (**8**), an $Ru(CO)_5$ ligand is coordinated to an $Ru_2(\mu\text{-}Br)(CO)_7$ unit *trans* to the Ru-Ru bond, with a Ru-Ru donor bond length of 2.89 Å. In contrast, for M = Os (**9**), the Br atom bridges the ends of a bent Os_3 chain.[76] These results are related to the initial products of bromination of the neutral carbonyls, which for M = Ru at −50°C, is *cis,cis*-$Ru_3Br_2(CO)_{12}$, and for M = Os at −20°C, is *cis,trans*-$Os_3Br_2(CO)_{12}$, which then isomerises to the *cis, cis* isomer (3 h, r.t.).

Carborane ligands. In contrast with the parent carbaborane, which gives mononuclear complexes, *nido*-7,8-Me_2-7,8-$C_2B_9H_{11}$ and $Ru_3(CO)_{12}$ give a 1:2 mixture of $Ru(CO)_3(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)$ and $Ru_3(CO)_8(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)$ (**10**). Treatment of (**10**) with various tertiary phosphines resulted in substitution of one or two CO groups on the Ru atoms bonded via Ru-B and Ru-H-B interactions.[77] Cluster fragmentation to give binuclear complexes occurs in reactions with $CH_2(NMe_2)_2$ or pyridine. The clusters $Ru_3(CO)_8(\eta^5\text{-}7\text{-}NR_3\text{-}7\text{-}CB_{10}H_{10})$ are obtained from $Ru_3(CO)_{12}$ and *nido*-7-NR_3-7-$CB_{10}H_{12}$ (R_3 = Me_3, H_2Bu^t, Me_2Bu^t).[78] Although the carborane ligand is η^5-bonded to one Ru, 3c-2e B-H-Ru bonds are formed with the other two metal atoms.

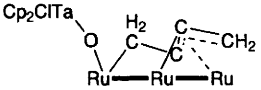
Hydrocarbon ligands. Kinetic studies of the transformations of $Ru_3(\mu\text{-}H)_3\{\mu_3\text{-}C(CO_2Me)\}(CO)_9$ to $Ru_3(\mu\text{-}H)_2\{\mu_3\text{-}CH(CO_2Me)\}(CO)_9$ and of $Ru_3(\mu\text{-}H)_3\{\mu_3\text{-}C(SEt)\}(CO)_9$ to $Ru_3(\mu\text{-}H)(\mu_3\text{-}CH_2SEt)(CO)_9$, together with earlier results, have shown changes in mechanism from CO-associative through CO-independent to CO-dissociative as a result of the further coordinating ability of the methylidyne substituents.[79] The reaction of $Ru_3(CO)_{12}$ with $Ta(CH_2)MeCp_2$ gives **(11)** in a reaction that proceeds via deoxygenation of a CO ligand to give $TaOMeCp_2$, coupling of the C with CH_2 and other CO-derived carbons, perhaps via a bis-vinylidene, to give a rather distorted, cluster-bonded $CH_2{=}C{=}C{=}CH_2$ fragment.[80]



8 Ru = $Ru(CO)_4$



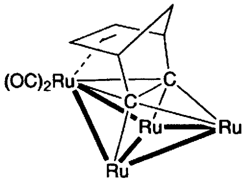
9 Os = $Os(CO)_4$



11 Ru = $Ru(CO)_3$

The chemistry of Ru and Os clusters containing cyclic unsaturated organic ligands has been reviewed.[81] Reactions of norbornene and norbornadiene with $Ru_3(CO)_{12}$ afford $Ru_3(\mu\text{-}H)_2$ $(\mu_3\text{-}C_7H_8)(CO)_9$ and $Ru_4(\mu_4\text{-}C_7H_6)(CO)_{11}$ **(12)**, respectively.[82] The former contains a complexed norbornyne ligand, while in the latter, the hydrocarbon (norbornenyne) is attached via both olefinic and alkyne linkages. The formal electron deficiency of these clusters is relieved by agostic C-H...Ru interactions. The cyclic olefins *cis*-cyclooctene and *cis*/*trans*-cyclododecenes react with $Ru_3(CO)_{12}$ to give $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}C_8H_{12})(CO)_9$, containing cyclooctyne, and $Ru_3(\mu\text{-}H)(\mu_3\text{-}2\eta^1,\eta^3\text{-}C_{12}H_{19})(CO)_9$, containing a cyclic allyl ligand, respectively. The former is converted to $Ru_3(\mu\text{-}H)(\mu\text{-}C_8H_{11})(CO)_9$ on further heating, in which the C_8 ligand is thought to be derived from *trans*-cyclooctene.[83] Reactions of $Ru_3(CO)_{12}$ and cod afford several complexes, including two isomers of $Ru_4(\mu_4\text{-}L)(CO)_{12}$ [L = $\eta^2\text{-}C_8H_{10}$ **(13)**, $\eta^2{:}\eta^2\text{-}C_8H_{10}$ **(14)**], which are 60- and 62-e butterfly clusters, respectively. EH MO calculations are used to rationalise the two structures.[84] Diazoindene reacts with $Ru_3(CO)_{12}$ to give $Ru_3(\mu\text{-}\eta^5,\eta^5\text{-}C_9H_6C_9H_6)(CO)_8$, containing 1,1′-bis(indenylidene), and $Ru_3(\mu\text{-}\eta^1{:}\eta^5\text{-}C_9H_6)(CO)_{10}$, together with two cyclic non-cluster trimers $\{Ru(\mu\text{-}\eta^1{:}\eta^5\text{-}C_9H_6)(CO)_2\}_3$.[85] The initial reaction occurs by formal insertion of the C_9H_6 fragment into an Ru-Ru bond.

Reactions between $Ru_3(CO)_{10}(L)_2$ (L = CO or NCMe) and $PhC{\equiv}CC{\equiv}CPh$



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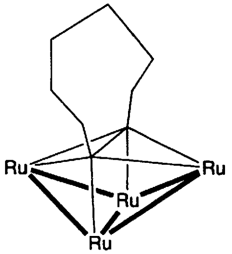

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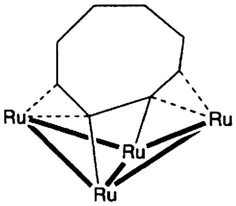
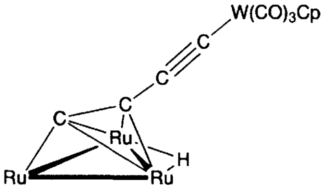


14

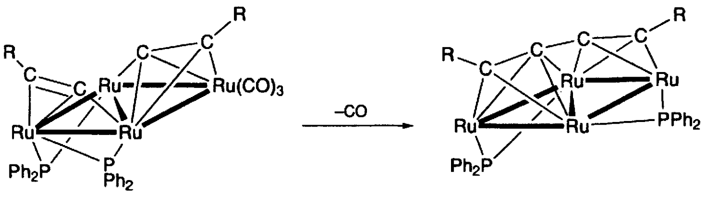
Unless otherwise indicated, Ru = Ru(CO)$_3$

have given $Ru\{C(C{\equiv}CPh){=}CPhC(C{\equiv}CPh){=}CPh\}(CO)_3(NMe_3)$, $Ru_2\{\mu\text{-}C(C{\equiv}CPh){=}CPhC(C{\equiv}CPh){=}CPh\}(CO)_6$, $Ru_2\{\mu\text{-}[C(C{\equiv}CPh){=}CPh]_2CO\}(CO)_6$, $Ru_3(\mu_3\text{-}PhC_2C{\equiv}CPh)(\mu\text{-}CO)(CO)_9$ and $Ru_4(\mu_4\text{-}PhC_2C{\equiv}CPh)(CO)_{12}$ (where C_2 and $C{\equiv}C$ distinguish metal-bonded and -non-bonded $C{\equiv}C$ triple bonds).[86] Reaction of $Ru_3(CO)_{12}$ with $Co_2(\mu\text{-}SiMe_3C_2C{\equiv}CH)(\mu\text{-}dppm)(CO)_4$ gives the hydrido-alkynyl derivative, while addition of $HC{\equiv}CC{\equiv}CSiMe_3$ to $Ru_3(\mu\text{-}dppm)(CO)_8$ affords the μ_3-alkyne complex.[87] On heating, the μ_3-alkyne complex **15** [from $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ and $Ru_3(CO)_{10}(NCMe)_2$] forms $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2C{\equiv}C[W(CO)_3Cp]\}(CO)_9$ (**16**), containing the C_4 ligand in a novel bonding mode.[88]



16 Ru = Ru(CO)$_3$

The 62-e butterfly cluster $Ru_4(\mu\text{-}PPh_2)_2(\mu\text{-}C_2Bu^t)_2(CO)_9$ (**17**), obtained by heating $Ru_2(\mu\text{-}PPh_2)(\mu\text{-}C_2Bu^t)(CO)_6$ in toluene, is converted to (**18**) (also 62-e) by C-C coupling between the two acetylides. Treatment of the latter with CO gave $Ru_3(\mu_3\text{-}Bu^tC_2C{\equiv}CBu^t)(\mu\text{-}PPh_2)_2(CO)_7$.[89]

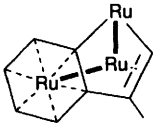


17 R = Bu^t; Ru = Ru(CO)$_2$ **18**

The chemistry of a range of cluster carbonyls (mainly Ru) containing arenes has been reviewed.[90] Topics covered include photo-isomerisation to benzyne complexes, production of cluster polymers from arenes such as [2.2]paracyclophane and $Ph(CH=CH)_3Ph$, graphitic arene-arene interactions producing extended structures (chains, ribbons), and relevance to surface adsorption of benzene.

The first complex containing $\eta^6\text{-}C_{60}$ was isolated from its reaction with $Ru_3(CO)_{12}$: in $Ru_3(\mu_3\text{-}\eta^6\text{-}C_{60})(CO)_9$, a six-membered ring of the fullerene caps the Ru_3 triangle.[91] In $Ru_4(\mu_4\text{-}C_6H_8)(CO)_9(\eta\text{-}C_6H_6)$, obtained from $Ru_4(\mu_4\text{-}C_6H_8)(CO)_{12}$ and cyclohexa-1,3-diene, the C_6H_6 is coordinated to a wing-tip Ru atom.[92] Other minor products were an isomer in which the C_6H_6 is attached to a hinge atom, $Ru_4(\mu_4\text{-}C_6H_8)(CO)_8(\eta^4\text{-}C_6H_8)_2$, in which both cyclohexadienes are attached to the wing-tip atoms, and $Ru_3(\mu_3\text{-}C_6H_8)(CO)_8(\eta^4\text{-}C_6H_8)$. In all cases, the $\mu\text{-}C_6H_8$ ligands are cyclohexyne.

Continuing studies of the reactions of isopropenylbenzenes with ruthenium carbonyl clusters have shown the formation of $Ru_3(\mu_3\text{-}2\eta^1:\eta^2:\eta^6\text{-}CH=CMeC_6H_4)(CO)_8$ (**19**) by pyrolysis (refluxing heptane) of $Ru_3(\mu_3\text{-}\eta^2:\eta^2:2\eta^2\text{-}PhCMe=CH_2)(CO)_8$.[93] Two other complexes contain the hydrocarbon attached to Ru_3 and Ru_5 clusters by only the side chain, namely $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^1:\eta^1:\eta^3\text{-}CHCPhCH)(CO)_9$ (**20**) and $Ru_5(\mu_3\text{-}H)(\mu_4\text{-}\eta^1:\eta^1;\eta^3:\eta^3\text{-}CHCPhCH)(CO)_{14}$ (**21**).[94] The further reaction of (**20**) with $Ru_3(CO)_{12}$ gives only $Ru_6C(\mu_3\text{-}HC_2Ph)(CO)_{15}$. In reactions of $Ru_3(CO)_{12}$ with $1,4\text{-}(CH_2=CMe)_2C_6H_4$, the hydrocarbon acts as a template for cluster build-up, leading to the formation of nine Ru_n (n = 2-7) complexes. In the Ru_6 products, the arene acts as an 11-e donor; the cores have the novel geometry shown in (**22**).[95] With 1,3,5-triisopropenylbenzene and $Ru_3(CO)_{12}$, isomeric clusters $Ru_4(CO)_9(C_{15}H_{20})$ (**23a**, **23b**) result from transfer of 2H to different side-chains.[96] A third complex is $Ru_4(\mu_3\text{-}C_{15}H_{14})(CO)_{11}$ (**24**), formed by breaking four C-H bonds to form a bicyclic metallacycle.[97]



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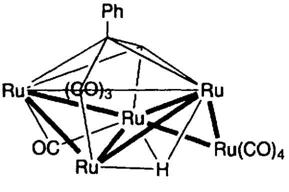
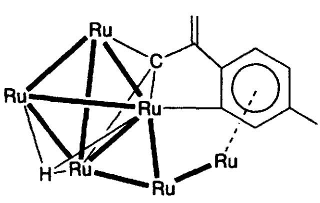


21 Ru = Ru(CO)$_2$

Further examples of Ru_4 clusters have been obtained from $Ru_3(CO)_{12}$ and allylbenzene and 4-phenyl-1-butene. In (**25**), two conformations (**a** and **b**) of the μ_3-ligand by a rotation of the hydrocarbon relative to the Ru_3 face are found; the bonding modes correspond to $\eta^2:\eta^2:\eta^4$ and $\eta^2:\eta^3:\eta^3$.[98]

Other Group 14 ligands. Reactions of $Ru_3(CO)_{12}$ with either SnR_2 or $\{SnR_2\}_3$ (R = tripp) have given $Ru_3(\mu\text{-}SnR_2)_n(CO)_{12-n}$ (n = 2, 3); combination of the same or different SnL_2 [L = $CH(SiMe_3)_2$] with the former gave mixed systems $Ru_3(\mu\text{-}SnR_2)_2(\mu\text{-}SnL_2)(CO)_9$. For R = $CH(SiMe_3)_2$, L = tripp, the solid-state structure



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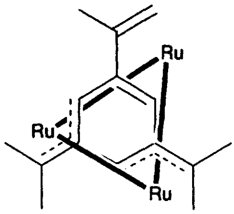
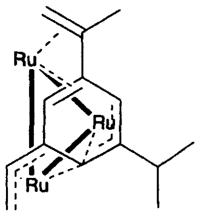
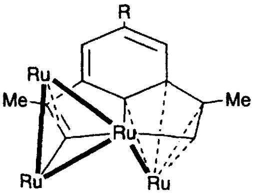


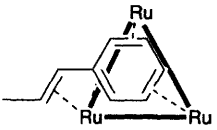
23a



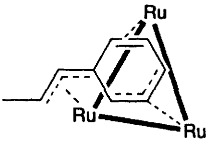
23b



24 R = $CMe{=}CH_2$



25a $\eta^2{:}\eta^2{:}\eta^4$

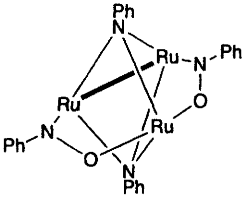


25b $\eta^2{:}\eta^3{:}\eta^3$

reveals aryltin twisting in only two groups, leading to chirality and the formation of spiral packing. Similar reactions with $Ru_3(\mu\text{-dppm})(CO)_{10}$ were also described.[99] Curiously, a quantitative yield of the latter complex is obtained from $Ru_3(CO)_{12}$ and $E\{CH(PPh_2)_2\}_2$ (E = Sn, Pb).

Nitrogen ligands. The useful MeCN derivatives of $Ru_3(CO)_{12}$ have been reinvestigated, along with related compounds derived from $1,4\text{-}(CN)_2C_4H_8$ and $C_6H_4(CH_2CN)_2$.[100] Up to three MeCN ligands can be introduced, while the dinitriles remain η^1-coordinated; in all cases, the nitriles are in axial positions. Spectroscopic studies indicate the structures $Ru_3(\mu\text{-CO})_3(CO)_{9-n}(NCMe)_n$ for n = 2, 3; the latter can be obtained in high yield. The CO groups are fluxional via in-plane terminal-bridging CO exchange.

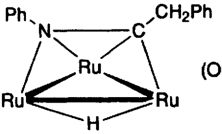
Methylation of $[Ru_3(CO)_{10}(NO)]^-$ gives $Ru_3(\mu_3\text{-NOMe})(\mu_3\text{-CO})(CO)_9$ (**26**) as the major product, which on hydrogenation gave $Ru_3(\mu\text{-H})_2(\mu_3\text{-NR})(CO)_9$ (R = H, OMe). Heating (**26**) in toluene (90°C) gave $Ru_4(\mu_4\text{-N})(\mu\text{-OMe})(CO)_{12}$ (**27**).[101] Compound (**28**) was obtained from $Ru_3(\mu_3\text{-NPh})(CO)_{10}$ and PhNO (thf, r.t.); the Ru_3 cluster has fragmented to leave only one Ru-Ru bond.[102] The sulfoximine (*R*)-MePhS(O)NH reacts with $Ru_3(CO)_{12}$ to give 46-e $Ru_3(\mu\text{-H})\{\mu_3\text{-}(R)\text{-}$



28 Ru = $Ru(CO)_2$

$N[S(O)MePh]\}(CO)_9$ which reversibly takes up CO, probably containing a μ-NS(O)MePh ligand.[103]

Complexes containing μ-azavinylidene ligands were obtained from $Ru_3(CO)_{12}$ and $LiN{=}CPh_2$, followed by protonation.[104] The resulting complex, $Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}$ (**29**), reacts with dppm to give $Ru_3(\mu\text{-}H)(\mu\text{-}dppm)(\mu\text{-}N{=}CPh_2)(CO)_7(L)$ [L = CO, dppm-*P*] in which the three bridging ligands are located about the same Ru-Ru bond. Thermolysis of the octacarbonyl gave the $\mu_3\text{-}N{=}CPh_2$ complex. With PPh_3, (**29**) forms mono- and di-substituted complexes, the latter undergoing orthometallation to give $Ru_3(\mu\text{-}H)_2(\mu\text{-}N{=}CPh(C_6H_4)\}(CO)_7(PPh_3)_2$, a reaction which is reversed by CO (1 atm, 18°C). Reactions of PhCH=CHCH=NPh with $Ru_3(CO)_{12}$ have given $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}PhCH_2CH_2C{=}NPh)(CO)_9$ (**30**; major product), $Ru_3(PhC{=}CHCH{=}NPh)_2(CO)_6$ (**31**) and $Ru_4(PhC{=}CHCH{=}NPh)_2(CO)_{10}$ (**32**).[105] The first reaction contrasts with the normal azadiene chemistry in that coordination of the C=N double bond activates the C=C double bond towards reduction by H transfer via the cluster.



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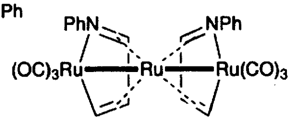

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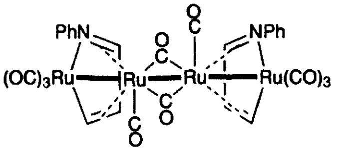

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Comparisons were made of two routes to Ru_3 complexes of diamino-, aminohydroxy- and aminomercapto-benzenes from (a) thermal reactions with $Ru_3(CO)_{12}$ or (b) carbonylated $RuCl_3$ solution in 2-methoxyethanol, followed by addition of ligand and reduction with zinc.[106] The products were not always the same: whereas $Ru_3(\mu\text{-}H)(\mu\text{-}NHC_6H_2Me_2NH_2)(CO)_9$ and $Ru_3(\mu\text{-}\eta^2\text{-}OC_6H_4H_2)_2(CO)_8$ are obtained by both routes, the complexes $Ru_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}EC_6H_4NH_2)(CO)_9$ [E = O, S (X-ray structure)] can only be prepared from the preformed cluster.

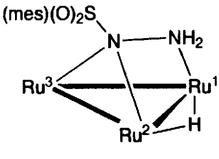
The parent compound and $Pt(\eta^2\text{-}nb)(PPr^i_3)_2$ (nb = norbornene) give only $Ru_3(\mu\text{-}H)(\mu\text{-}C_5H_4N\text{-}2)(CO)_9(PPr^i_3)$ in which the H and C_5H_4N ligands bridge different Ru-Ru vectors, while the phosphine is attached to a non-C_5H_4N-bridged Ru atom.[24] In $Ru_3(\mu\text{-}H)_2(\mu\text{-}C_5H_4N)_2(CO)_8$ the H atoms bridge the same Ru-Ru bonds as the metallated pyridyl ligands.[107] The dephenylated dppm derivative $Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(\mu\text{-}C_5H_4N)(CO)_8$ is among several products obtained with dppm. Electrochemistry of $M_3(\mu\text{-}H)\{\mu\text{-}NC_5H_3(C_6H_4Fc\text{-}4)\}(CO)_{10}$ (M = Ru, Os) showed reversible 1-e oxidation at iron and irreversible oxidation of the cluster.[108]

Ready reaction of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ampy)(\mu\text{-}CPh{=}CHPh)(CO)_8]^+$ with PPh_3 occurs to give mono- (two isomers), di- and tri-substituted (two isomers) complexes. Reductive elimination of *cis*-stilbene occurs in the reaction with dppm, which affords $[Ru_3(\mu_3\text{-}ampy)(\mu\text{-}dppm)(CO)_7(dppm\text{-}P)]^+$. The cation is deprotonated with NaOMe, but loses *cis*-stilbene on treatment with NaOH to give $Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_9$.[109]

Protonation of $[Ru_3(\mu\text{-dmpz})(\mu\text{-}CO)_3(CO)_7]^-$ (from Hdmpz and $[Ru_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$) affords the corresponding hydrido cluster, which reacts with $PHPh_2$ or PPh_3 to give $Ru_3(\mu\text{-}H)(\mu\text{-dmpz})(CO)_9(PR_3)$, in which the phosphine is *cis* to H and dmpz ligands.[110] Thermolysis of the $PHPh_2$ derivative gave $Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)_2(\mu\text{-dmpz})(CO)_7$ and $Ru_2(\mu\text{-}PPh_2)(\mu\text{-dmpz})(CO)_6$. Both the hydrido cluster and the derived anion react with dppm to give derivatives in which the dmpz and dppm ligands bridge different edges; slow symmetrisation of the hydrido cluster gives an isomer in which the same Ru-Ru edge is bridged by H, dmpz and dppm.

Sulfonylhydrazines react with $Ru_3(CO)_{12}$ to give $Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^2\text{-}NH_2NS(O)_2R\}(CO)_9$ (**33**; R = tol, mes); protonation of the cluster gives the dihydrido cation. Further chemistry involves substitution of CO at Ru(1) by PPh_3 or $PPh_2(C{\equiv}CPh)$, the latter affording the usual $Co_2(\mu\text{-alkyne})(CO)_6$ derivative with $Co_2(CO)_8$. Atoms Ru(2) and Ru(3) are bridged by dppm, while dppp and dppf bridge the Ru(1)-Ru(3) vector in the respective derivatives.[111] 1,3-Diaryltriazenido clusters $Ru_3(\mu\text{-}H)(\mu\text{-RNNNR})(CO)_{10}$ ($R = C_6H_4X\text{-}4$; X = H, F, Br, I) were obtained directly from $Ru_3(CO)_{12}$ and the triazenide in toluene; the C_6F_5 complex shows H-atom fluxionality.[112]

Phosphorus ligands. Electron transfer-catalysed substitution of $Ru_3(CO)_{12}$ by PR_3 (R = Me, Bu, Ph, OMe) or Bu^tNC has been achieved electrochemically by using dibenzoylethene as a mediator, with high concentrations of carbonyl and ligand.[113] The Na[bpk]-catalysed reaction of $Ru_3(CO)_{12}$ with $PPh_2(CH{=}CH_2)$ (L) gave $Ru_3(CO)_{12\text{-}n}(L)_n$ (n = 1, 2), which by mild thermolysis or photolysis are converted into $Ru_3(\mu\text{-}H)\{\mu_3\text{-}PPh_2(CH{=}CH)\}(CO)_9$ and $Ru_3(\mu\text{-}H)\{\mu_3\text{-}PPh_2(CH{=}CH)\}(CO)_8(L)$, respectively.[114] The reaction of $Ru_3(CO)_{12}$ with PPh_2(anthracyl) afforded several products, including $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}C_{14}H_7PPh_2)(CO)_8$, $Ru_4(\mu_4\text{-}C_{14}H_7PPh_2)(CO)_9$ and $Ru_5(\mu_5\text{-}C_{14}H_8PPh)(CO)_{13}$ (**34**).[115] The first two contain anthracyne ligands formed by metallation of an unsubstituted ring. The latter contains a bow-tie cluster attached to the anthryl group by two η^3-allyl units and the isolated η^2 double bond, together with the bridging phosphido group. Thermolysis of $Ru_3(CO)_{11}\{PPr^i_2[(\eta\text{-}Ph)Cr(CO)_3]\}$ gave (**35**), containing cluster-bound benzyne-$Cr(CO)_3$, but similar reactions of $Ru_3(CO)_{11}\{PPh_2[(\eta\text{-}Ph)Cr(CO)_3]\}$ gave only two isomers (probably *cis* and *trans* Ph) of $Ru_3(\mu_3\text{-}C_6H_4)\{\mu\text{-}PPh[(\eta\text{-}Ph)Cr(CO)_3]\}_2(CO)_7$.[116]



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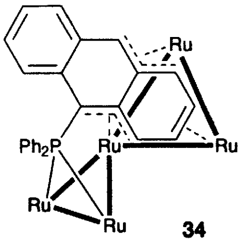

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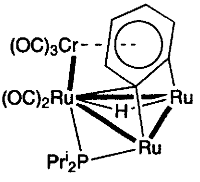
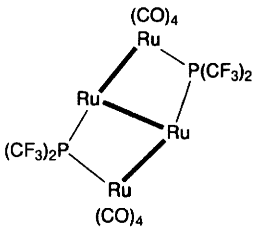


35

A mechanistic study of the reversible addition of H_2 to $Ru_3(\mu\text{-}H)_2(\mu\text{-}PBu^t{}_2)_2(CO)_8$ to give $Ru_3H_2(\mu\text{-}H)_2(\mu\text{-}PBu^t{}_2)_2(CO)_8$, which occurs with cleavage of an Ru-Ru bond,[117] indicates that although the reaction is promoted by the presence of the large $PBu^t{}_2$ groups, both addition and loss of H_2 involve prior loss of CO.[118] The energy of the Ru-Ru bond that is broken is estimated at 47-59 kJ mol^{-1}.

Four tetranuclear complexes were obtained from $Ru_3(CO)_{12}$ and $P_2(CF_3)_4$, characterised by X-ray studies as $Ru_4(\mu\text{-}H)_3\{\mu\text{-}P(CF_3)_2\}(CO)_{12}$ **(36)**, $Ru_4\{\mu\text{-}P(CF_3)_2\}_2(CO)_n$ [n = 13 **(37)**, 14 **(38)**] and $Ru_4\{\mu\text{-}P(CF_3)_2\}_4(CO)_{11}$ **(39)**; the first three were also obtained from $Ru_3(CO)_{12}$ and $PH(CF_3)_2$.[119] In **(36)**, the butterfly core is bridged by $P(CF_3)_2$ across the wing-tips. Complex **(37)** is electron-rich, as shown by long Ru-Ru separations in the planar Ru_4 rhomboid; in **(38)**, there is a zig-zag Ru_4 chain.

Complex **(39)** has a novel 66-e structure, described as a fan with three long Ru-Ru bonds. Complexes $\{Ru[\mu_3\text{-}P(CF_3)](CO)_3\}_4$ and $Ru_5\{\mu_4\text{-}P(CF_3)\}(CO)_{15}$ were obtained from $Ru_3(CO)_{12}$ and $\{P(CF_3)\}_n$ (n = 4, 5) in 1:1 and 1:2 molar ratios, respectively; at 80°C, the product is $Ru_4\{\mu_4\text{-}P(CF_3)\}(CO)_{14}$ **(40)**. With $Ru_4(\mu\text{-}H)_4(CO)_{12}$, both cyclophosphines gave the non-cluster complex $\{Ru_2(\mu\text{-}H)(CO)_6\}\{\mu,\mu\text{-}P(CF_3)\}_2\{Ru_2(\mu\text{-}H)[\mu\text{-}P(CF_3)](CO)_6\}$.[120] Reactions of $[Ru_4(CO)_{13}]^{2-}$ with $PCl_2(NPr^i{}_2)$ afford $Ru_4\{\mu_4\text{-}P(NPr^i{}_2)\}(CO)_{13}$, thermal decarbonylation of which gave $Ru_4\{\mu_4\text{-}P(NPr^i{}_2)\}(CO)_{12}$. Chromatography results in cleavage of the P-N bond and formation of the anionic μ_3-P=O complex, $[Ru_4(\mu_3\text{-}PO)(CO)_{12}]^-$ **(41)**.[121] The osmium analogues were also prepared. The related phosphinidene complex $Ru_3\{\mu_3\text{-}PC(CO)Bu^t\}_2(CO)_9$, prepared from $Ru_3(CO)_{12}$ and $P{\equiv}CBu^t$, adds $Fe(CO)_2$ or $Ru(CO)_2$ fragments to give $MRu_3\{\mu_4\text{-}PC(CO)Bu^t\}_2(\mu\text{-}CO)(CO)_{10}$ **(42)**.[122]



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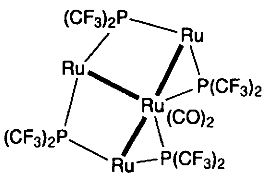

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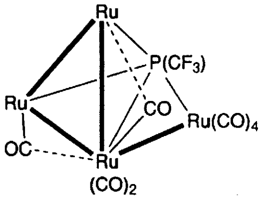

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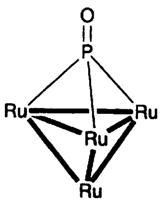

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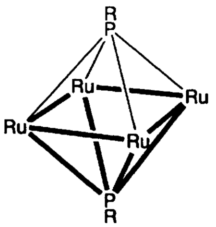
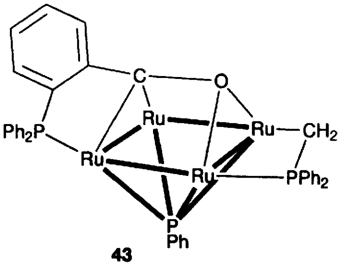


42 R = C(CO)Bu^t



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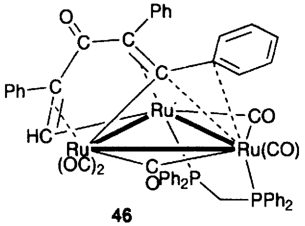
Thermolysis of $Ru_3(\mu\text{-dppm})(CO)_9(PPh_3)$ gave $Ru_4(\mu_4\text{-PPh})(\mu_4\text{-PPh}_2C_6H_4CO)(\mu\text{-PPh}_2CH_2)(CO)_8$ (**43**) and $Ru_3\{\mu_3\text{-PPh}(C_6H_4)\}(\mu\text{-PPh}_2CH_2)(\mu\text{-PPh}_2)(\mu\text{-CO})(CO)_6$ as major products, together with $Ru_3\{\mu_3\text{-PPhCH}_2PPh(C_6H_4)\}(CO)_9$ and $Ru_2(\mu\text{-PPhC}_6H_4PPhCH_2)(CO)_{6-n}(PPh_3)_n$ (n = 0, 1).[123] No products containing ligands formed by coupling of fragments obviously derived from dppm with those from PPh_3 were found. Secondary phosphines PHR_2 (R = Bu^t, ad) react with $Ru_3(\mu\text{-dppm})(CO)_{10}$ to form $Ru_3(\mu\text{-dppm})(CO)_9(PHR_2)$, which thermolyse to electron-deficient $Ru_3(\mu_3\text{-H})(\mu\text{-H})(\mu\text{-dppm})(\mu\text{-PR}_2)_2(\mu\text{-CO})(CO)_4$; these do not react with H_2 or CO.[124] In contrast, less sterically demanding $PHCy_2$ afforded $Ru_3(\mu\text{-H})(\mu\text{-dppm})(\mu\text{-PCy}_2)_2(CO)_6$.

The 46-e cluster $Ru_3(\mu\text{-dppm})(\mu\text{-PhC}_2Ph)(CO)_7$ (**44**) and the 48-e octacarbonyl complex (**45**) are formed from $[Ru_3(\mu\text{-Cl})(\mu\text{-PhC}_2Ph)(CO)_9]^-$ and dppm.[125] Complex (**44**) is highly reactive, reacting with H_2, CO and dppm to give $Ru_3(\mu\text{-H})_2(\mu\text{-PhC}_2Ph)(CO)_7(dppm)$ (two isomers), (**45**) and $Ru_3(\mu\text{-PhC}_2Ph)(CO)_6(dppm)_2$, respectively. Phenylethyne reacts with (**44**) to give $Ru_3\{\mu\text{-HCCPhC(O)CPhCPh}\}(\mu\text{-dppm})(CO)_6$ (**46**) and the dimetallacyclopentadiene $Ru_2(\mu\text{-dppm})(\mu\text{-HCCPhCPhCPh})(CO)_4$. The formal unsaturation of (**46**) is countered by a weak bond between a C-Ph bond and one Ru centre. Thermal isomerisation of **46** gives $Ru_3(\mu\text{-H})\{\mu\text{-CCPhC(O)CPhCPh}\}(dppm)(CO)_6$ (**47**).[125] Reactions of $Ru_3(\mu\text{-dppm})(CO)_{10}$ with cycloocta-1,3,5,7-tetraene have given a series of Ru_3 clusters resulting from CO substitution, C-H and P-C bond cleavage of the dppm (including a rare σ-Ph complex **48**) and H transfer to the C_8 ring (in **49**).[126]



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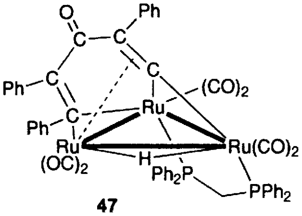

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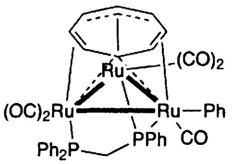

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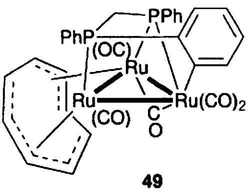

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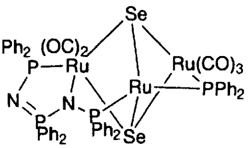

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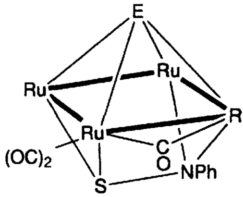
The novel $PPh_2NPPh_2NPPh_2$ ligand (L) is *N, 2P*-coordinated in $Ru_3(\mu_3\text{-Se})_2(\mu\text{-L})(\mu\text{-PPh}_2)(CO)_6$ (**50**), obtained from $Ru_3(CO)_{12}$ and $P(Se)Ph_2NPPh_2NP(Se)Ph_2$; the Ru...Ru distances are between 3.08 and 3.67 Å, indicating some cluster fragmentation during the reaction.[127]

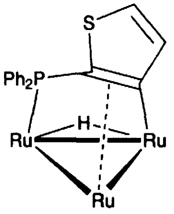
Chalcogen ligands. The $[Ru_3(\mu_3\text{-O})(CO)_9]^{2-}$ anion was prepared in situ by passing air through solutions of $[Ru_3(CO)_{11}]^{2-}$, but could not be isolated. It was characterised by formation of mixed-metal clusters containing Mn or Re (*q.v.*).[128] The μ_3-O ligand is highly nucleophilic (more so than in the analogous iron complex) which leads to further reactions, preventing its isolation.

Pyrazine-bridged oligomers have been obtained by photolytic displacement of the CO group in $Ru_3(\mu_3\text{-}O)(\mu\text{-}O_2CMe)_6(CO)(py)(OH_2)$.[129] The electrochemical properties of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}O_2CMe)_6(mbpy)_2(CO)]^{3+}$ (mbpy = *N*-methy-4,4′-bipyridinium) have been explored: seven reversible 1-e redox steps are found between +0.90 and -2.32 V (vs FcH/FcH^+), with an irreversible step at -2.99 V.[130]

Whereas reactions of PhN=S=O with $Ru_3(CO)_{10}(NCMe)_2$ give only $Ru_3(\mu_3\text{-}S)(\mu_3\text{-}NPh)(CO)_9$ **(51)** and CO_2, thermal reactions with $Ru_3(CO)_{12}$ afford a variety of clusters, including **(51)**, $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ and $Ru_4(\mu_4\text{-}E)(\mu_4\text{-}SNPh)(\mu\text{-}CO)(CO)_{10}$ (**52**; E = NPh, S).[131] The 4,5-$(PPh_2)_2$-4-cyclopentene-1,3-dione (bpcd) ligand in $Ru_3(\mu_3\text{-}S)_2(CO)_7(bpcd)$ chelates in axial and equatorial positions. Electrochemical studies showed reversible 1-e reduction centred on the bpcd ligand and irreversible oxidation of the cluster. EH MO calculations were reported for $Ru_3(\mu_3\text{-}S)_2(CO)_7(bpcd\text{-}H_4)$, where H replaces Ph in the ligand.[132]



52 E = NPh, S



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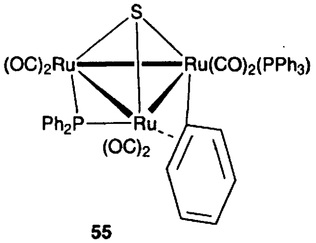

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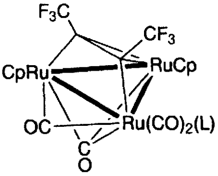
Both isomers of $Ir(2,5\text{-}Me_2T)Cp^*$ (2,5-Me_2T = 2,5-dimethylthiophene) react with $Ru_3(CO)_{12}$ to give $Ru_3(CO)_{11}\{(\mu\text{-}S,\eta^4\text{-}2,5\text{-}Me_2T)IrCp^*\}$.[133] Cyclometallation of the thiophene ring occurs on reaction of $Ru_3(CO)_{12}$ with $PPh_2(C_4H_3S\text{-}2)$, to give $Ru_3(\mu\text{-}H)\{\mu\text{-}PPh_2(C_4H_2S\text{-}2)\}(CO)_9$ **(53)** and $Ru_3(\mu\text{-}H)\{\mu_3\text{-}PPh_2(C_4H_2S\text{-}2)\}(CO)_8\{PPh_2(C_4H_3S)\}$.[134] The thienyl group is η^1:η^2 bonded to two Ru atoms, interchanging on the NMR time scale. Further reaction of **(53)** with $Ru_3(CO)_{12}$ gave $Ru_4(\mu_4\text{-}PPh)(\mu_4\text{-}L)(CO)_{11}$ (L = C_4H_2S, C_6H_4) by elimination of benzene or thiophene, respectively. In these two complexes, thiophyne is coordinated diagonally across and perpendicular to the Ru_4 plane (as a 4-e donor), while benzyne is tilted (as a 6-e donor). Polysubstitution of $Ru_3(\mu\text{-}H)\{\mu_3\text{-}SC(NHPh)NPh\}(CO)_9$ occurs with PPh_3 to give $Ru_3(\mu\text{-}H)\{\mu_3\text{-}SC(NHPh)NPh\}(CO)_{9\text{-}n}(PPh_3)_n$ [n = 1, 2 **(54)**]; dppe coordinates to bridge an Ru-Ru bond.[135] Thermolysis of **(54)** gave $Ru_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}Ph)(CO)_7(PPh_3)$ **(55)**, containing a rare example of a bridging phenyl group. Reactions of $Ru_3(CO)_{12}$ with one or two equivalents of 4-methylthiazole in the presence of Na[bpk] gave $Ru_3(\mu\text{-}H)_n(\mu\text{-}2,3\text{-}\eta^2\text{-}C{=}NCMe{=}CHS)_n(CO)_{12\text{-}2n}$ (n = 1, 2, respectively).[136]

Cleavage of 1,2,5,6-tetrathiacyclooctane occurs in its reaction with $Ru_3(CO)_{12}$

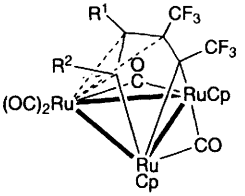
which affords *anti*- and *syn*-$Ru_3(\mu\text{-}SC_2H_4S)_2(CO)_7$. On heating, the *anti* isomer is converted to the *syn* complex and $Ru_2(\mu\text{-}SC_2H_4S)(CO)_6$.[137]

A source of selenium-containing clusters is the reaction between $Ru_3(CO)_{12}$ and $SePPh_3$: isolated products include $Ru_3(\mu_3\text{-}Se)_2(CO)_{9-n}(PPh_3)_n$ (n = 1-3) and $Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)_2(CO)_{9-n}(PPh_3)_n$ (n = 1, 2).[70]

Chemistry of Ru_3Cp_3 clusters. Both coupling and fragmentation of alkynes on Cp-containing Ru_3 clusters has been observed. Reactions of the alkyne complex **56** [from $Ru_3\{\mu_3\text{-}C_2(CF_3)_2\}(\mu_3\text{-}CO)(\mu\text{-}CO)Cp_2$ (**57**) and $Me_3NO/MeCN$] with other alkynes $R^1C{\equiv}CR^2$ ($R^1 = R^2$ = Me, Ph; R^1 = Me, $R^2 = CO_2Me$) results in coupling of the two alkynes to give the $C_4R^1R^2(CF_3)_2$ ligand in (**58**). In contrast, $C_2(CO_2Me)_2$ gave (**59**) ($R^1 = R^2 = CO_2Me$) via a structurally uncharacterised pentacarbonyl, while $C_2(CF_3)_2$ gave (**60**) (R = CF_3).[138] Complexes (**59**) ($R^1 = R^2$ = Me, Ph, CO_2Me; R^1= Me, $R^2 = CO_2Me$) can be obtained directly from (**57**) and the alkyne, together with isomers containing $C(CF_3)CR^1R^2C(CF_3)$ ligands (for $R^1 = R^2$ = Me, Ph). Complexes (**58**) are intermediates in the formation of (**59**) and related species (**60**; R = CF_3, Me) in which the alkyne has cleaved and which are obtained directly from (**57**) and C_2R_2.



56 L = MeCN
57 L = CO



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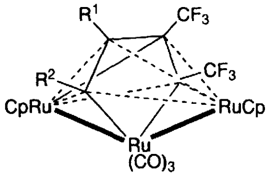

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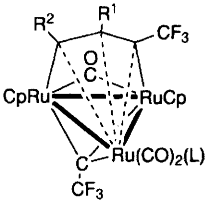

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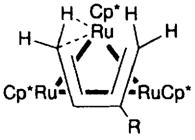

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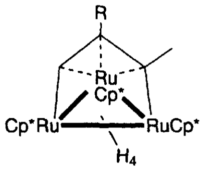

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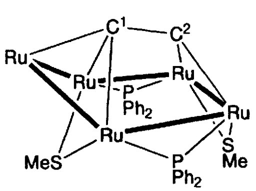
Reactions of $Ru_3(\mu_3\text{-}H)_2(\mu\text{-}H)_3Cp^*_3$ with dienes proceed via an intermediate fluxional μ_3-diene complexes (**61**), which contains an agostic C-H...Ru interaction, to give $Ru_3(\mu\text{-}H)_4(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}CHCRCMe)Cp^*_3$ (**62**; R = H, Me).[139] The transformation is consistent with a concerted reaction in which the diene coordinates to two metal centres while the third activates the C-H bond.

Conversion of $\{Ru(\mu_3\text{-}Cl)Cp^*\}_4$ to $\{Ru(\mu\text{-}SH)_2ClCp^*\}_2$ occurred on reaction with excess H_2S; on heating in refluxing toluene, further condensation to the cubane $[\{Ru(\mu_3\text{-}S)Cp^*\}_4]Cl_2$ occurred.[140]

10.3.2 Complexes of Higher Nuclearity – The PBu^n_2 analogue of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$ (**63**), an Ru_5 cluster containing an exposed C_2 ligand, was prepared similarly in 41% overall yield from $Ru_3(CO)_{12}$ and $C_2(PBu^n_2)_2$.[141] The chloro analogue of (**63**) was obtained from $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ and methallyl chloride photodimer; also formed was (**64**), which retains the C_2PPh_2 ligand found in the precursor.[142]

An interesting transformation of (**63**) occurs on treatment with $CNBu^t$: the resulting adduct (**65**), orginally reported as having a planar tetracoordinate carbon atom, is probably more correctly described as another example of an electron-rich cluster with long Ru-Ru bonds (2.96 Å). The C_2 ligand is converted to a 4-e donor. Ready loss of CO from **65** affords a $CNBu^t$-substituted derivative of (**63**).[143]



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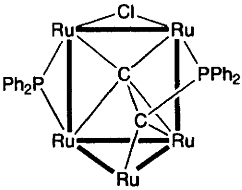

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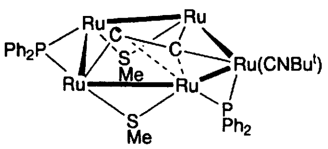

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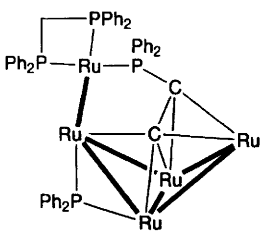
A variety of Ru_5 cluster geometries are present in products obtained from (**63**) and functional phosphines.[144] Addition of dppm results in opening to a spiked butterfly in (**66**), while the open envelope configuration is found in (**67**), obtained from $PPh_2(C_6H_4NH_2\text{-}2)$. A complex reaction ensues with $PPh_2(C_6H_4CH{=}CH_2\text{-}2)$ (sp): two products are (**68**), in which one Ru atom is cleaved from the cluster, but not lost from the complex, and (**69**) in which a bow-tie cluster supports a



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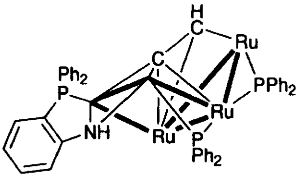

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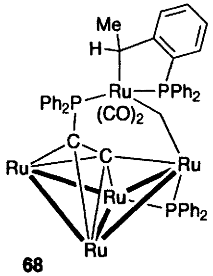

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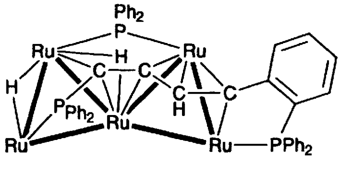
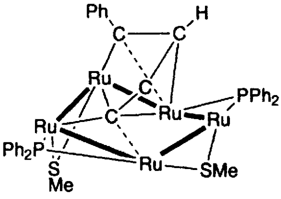


69

diphosphine ligand formed by coupling of the C_2PPh_2 and sp ligands with H migration to the cluster.

Complex (**63**) also reacts with terminal alkynes to give (**70**), in which coupling of the C_2 ligand with the alkyne has occurred; the resulting ligand is attached to the cluster by all four carbon atoms. In contrast, the product (**71**) from C_2Ph_2 also contains a coupled ligand, but only two carbons are bonded, the Ru_5 core adopting a folded envelope conformation.[145] A different cluster was obtained from $C_2(SiMe_3)_2$, in which loss of an $SiMe_3$ group has occurred. In addition, coupling of the C_2 ligand in (**63**) with the vinylidene $C{=}CH(SiMe_3)$ occurs; removal of the second $SiMe_3$ group gave the first cluster-bound butatrienylidene ligand in (**72**). Treatment of (**72**) with CO afforded **73**, in which the $CCCCH_2$ ligand interacts with all five Ru atoms.[146]



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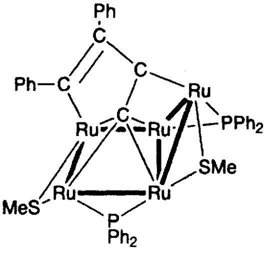

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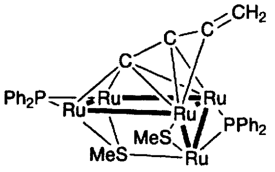

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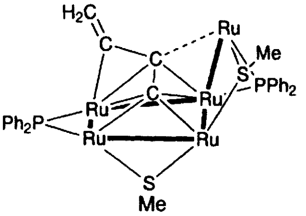

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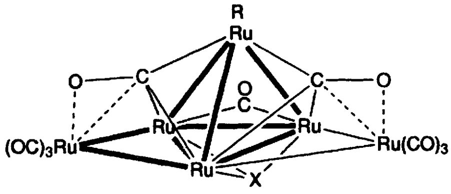
With HC_5Me_5 in heptane, $Ru_6C(CO)_{17}$ affords $Ru_6C(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_5)(\mu\text{-}CO)(CO)_{13}$, while if $NiCp_2$ is used as a source of Cp, $Ru_6C(CO)_{12}Cp_2$ is formed.[147] Another account of these reactions reports the formation of $Ru_6(\mu_3\text{-}H)(\mu_4\text{-}\eta^2\text{-}CO)_2(\mu\text{-}CO)(CO)_{12}(\eta\text{-}C_5R_5)$ (**74**; R = H, Me) in octane.[148] The related complex (**75**) is formed by heating $Ru_3(CO)_{12}$ with C_6Me_6 in octane (reflux, 4 h). In both (**74**) and (**75**), the two μ_4-CO ligands are held within Ru_4 butterflies formed by the two edge-bridging Ru atoms and the corresponding Ru_3 faces.[149] In contrast with the similar mesitylene complex, no rearrangement of (**75**) to an Ru_6C cluster occurs.

The η^6- and $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$-isomers of $Ru_6C(CO)_{14}(\eta^6\text{-arene})$ [arene = $C_6H_4(CO_2Me)_2$-1,4] were obtained from $Ru_6C(CO)_{17}$ and cyclohexa-1,3-diene 1,4-$(CO_2Me)_2$ in $Bu^n{}_2O$; the extended solid-state structures were also discussed.[150] Reactions of $Ru_6C(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})(CO)_{14}$ ($C_{16}H_{16}$ = [2.2]paracyclophane) with PR_3/Me_3NO (R = Ph, Cy) gave the mono-substituted complexes,



Ru = $Ru(CO)_2$

74 R = Cp*, X = H
75 R = C_6Me_6, X = absent

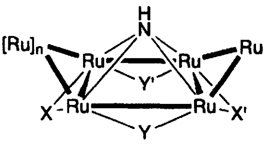
in which the PR_3 ligand is attached to an Ru atom in the Ru_3 face opposite that to which the hydrocarbon is bonded.[151] ^1H NMR studies of several cyclophane cluster complexes showed that chemical shift differences could be related to through-space interactions between the μ_3-ring and the cluster, and between both rings.

Conversion of $[Ru_6C(CO)_{16}]^{2-}$ to $[Ru_6C(CO)_{15}(NO)]^-$ occurs on reaction with NO; further reaction results in decapping to give $Ru_5C(CO)_{14}(NO)(NO_2)$. Similar reactions with $[Ru_6C(CO)_{14}(C_3H_5)]^-$ gave neutral $Ru_6C(CO)_{14}(NO)(C_3H_5)$ and $Ru_5C(CO)_{11}(NO)_2(NO_2)(C_3H_5)$, while further addition of NO to the former gave $Ru_5C(CO)_{13}(NO_2)(C_3H_5)$.[152]

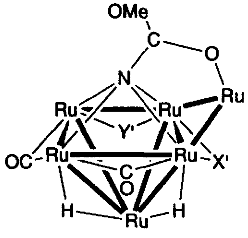
A series of μ_4-nitrene ruthenium clusters has been obtained by thermolysis of methylated trinuclear nitrosyl clusters.[101] Heating $Ru_3(\mu_3\text{-}NOMe)(\mu_3\text{-}CO)(CO)_9$ (**26***) in toluene (90°C) gave $Ru_6(\mu_4\text{-}NH)(\mu\text{-}OMe)_2(\mu\text{-}CO)_2(CO)_{16}$ (**76**). Other hexanuclear clusters described were $Ru_6(\mu\text{-}H)(\mu_4\text{-}NH)\{\mu_3\text{-}C(O)OMe\}(\mu\text{-}CO)(CO)_{16}$ (**77**), also obtained as a by-product from methylation of $[Ru_3(CO)_{10}(NO)]^-$, $Ru_6(\mu_4\text{-}NH)\{\mu_3\text{-}NHC(O)OMe\}(\mu\text{-}OMe)(\mu\text{-}CO)_2(CO)_{15}$ (**78**), $Ru_6(\mu\text{-}H)_2\{\mu_5\text{-}NC(O)OMe\}(\mu\text{-}CO)_2(CO)_{14}$ (**79**) and $Ru_6(\mu_4\text{-}NH)(\mu\text{-}OMe)(\mu\text{-}NCO)(\mu\text{-}CO)_2(CO)_{16}$ (**80**) [from pyrolysis of $Ru_3(\mu\text{-}H)_2(\mu\text{-}NOMe)(CO)_{10}$ at 140°C]. Hydrogenation of (**26**) in the presence of $Ru_3(CO)_{12}$ gave $Ru_5(\mu\text{-}H)_3(\mu_4\text{-}NH)(\mu_3\text{-}OMe)(CO)_{13}$ (**81**) and $Ru_6(\mu\text{-}H)(\mu_4\text{-}NH)_4(\mu\text{-}OMe)(\mu\text{-}CO)_2(CO)_{16}$ (**82**). In refluxing octane, (**26**) affords $Ru_6(\mu_5\text{-}N)(\mu_3\text{-}NH)(\mu_3\text{-}OMe)\{\mu\text{-}C(O)OMe\}(\mu\text{-}CO)(CO)_{13}$ (**83**), together with (**27**).[153] A common structural feature of most of the Ru_6 clusters is a central square-pyramidal $Ru_4(\mu_4\text{-}NH)(CO)_8$ fragment in which opposite basal edges are bridged by $Ru(CO)_n$ groups.

The reaction between $Ru_3(CO)_{12}$ and 2-methyl-5-phenyloxazolin-2-ylmethanol (HL) gave $Ru_6(\mu_3\text{-}H)_2(\mu_4\text{-}L)_2(CO)_{14}$ (**84**), containing a novel cluster architecture.[154] Simple substitution of CO by PPh_3 at the apical, *S*-bonded Ru atom occurs with $Ru_6(\mu\text{-}H)(\mu_5\text{-}S)\{\mu_3\text{-}\eta^2\text{-}SC(NHPh)NPh\}(CO)_{16}$ (**85**) as shown by an X-ray structure; other 2-e donor ligands [PBu^n_3, $P(OMe)_3$, $P(OPh)_3$, SMe_2, $CNBu^t$] substitute a different CO group, as shown by the structure of the $CNBu^t$ complex (**86**), where the entering ligand is found on the opposite Ru atom.[155]

The anion $[Ru_{10}H_2(CO)_{25}]^{2-}$ has been obtained by thermolysis of $Ru_3(CO)_{12}$ in refluxing EtOH (18 h), while in aqueous MeOH or better, MeCN containing traces of water (after several days), $[Ru_{11}H(CO)_{27}]^{3-}$ is formed.[156] This paper



	n	X	X'	Y	Y'
76	1	OMe	OMe	CO	CO
77	1	*	H	*	CO
78	1	NC(OMe)O	OMe	CO	CO
80	1	NCO	OMe	CO	CO
81	0	H	OMe*	H	H
82	1	H	OMe	CO	CO



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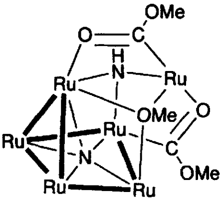

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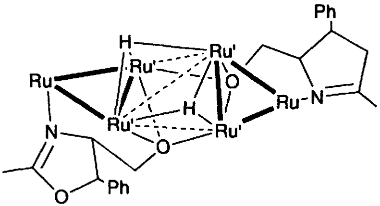

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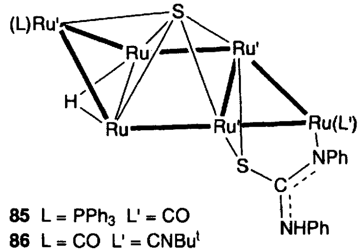


85 L = PPh_3 L' = CO
86 L = CO L' = $CNBu^t$

contains a discussion of possible cluster build-up reactions which result in higher nuclearity clusters.

The salt $[Ru_2(\mu\text{-}H)(\mu\text{-}NC_5H_4\text{-}2)_2(CO)_4(py)_2][Ru_{10}(\mu_6\text{-}C)(\mu\text{-}H)(CO)_{24}]$ (**87**) is obtained in 80% yield by thermolysis of $Ru_3(\mu\text{-}H)(\mu\text{-}C_5H_4H)(CO)_{10}$ in PhCl;[107,157] similarly, heating a mixture of $Ru_3(\mu\text{-}H)(\mu\text{-}C_5H_4N)(CO)_{10}$ and $[PPh_4]Cl$ gives the $[PPh_4]^+$ salt, although attempted metathesis of (**87**) gave only $[PPh_4]_2[Ru_{10}C(CO)_{24}]$.[157] Substitution reactions with PPh_3 proceed at apical Ru atoms to give $[Ru_{10}C(\mu\text{-}H)(CO)_{24\text{-}n}(PPh_3)_n]^-$ (n = 1, at r.t.; n = 2-4 at higher temperatures). Polysubstitution also occurs on reaction with $P(OMe)_3$: up to four CO groups (on each of the apical Ru atoms) can be replaced, but forcing conditions are required to isolate the pure tetrasubstituted anion as its $[Ru_2(\mu\text{-}H)(\mu\text{-}C_5H_4N)_2(CO)_4\{P(OMe)_3\}_2]^+$ salt. A large excess of $P(OMe)_3$ gives $Ru_6C(CO)_{13}\{P(OMe)_3\}_4$ by decapping reactions.[159] The μ-dppa-linked bis-cluster dianion $[\{Ru_{10}C(\mu\text{-}H)(CO)_{23}\}_2(\mu\text{-}dppa)]^{2-}$ is also described.

10.3.3 Synthesis of Lower Nuclearity Species – $Ru_3(CO)_{12}$ has been used as a precursor for the synthesis of $\{Ru(CO)_2(Cp^R)\}_2$ (Cp^R = $C_5H_{5\text{-}n}Bu^t{}_n$; n = 1, 2;[160] $C_5H_3(SiMe_3)_2\text{-}1,3$[161]) and for binuclear cyclopentadienone complexes used as catalyst precursors for reduction of aldehydes and ketones to alcohols by formic acid.[162] Reactions of $Ru_3(CO)_{12}$ with spiro[2.4]hepta-4,6-diene give $Ru_2(\mu\text{-}C_5H_4CHMe)(CO)_6$.[163] In the reaction with $Ni\{\eta^1,\eta^2\text{-}C_5H_5C_2(CO_2Me)_2\}Cp$, transfer of Cp and $C(CO_2Me){=}CH(CO_2Me)$ from Ni to Ru occurs to give

$Ru_2\{\mu-\eta^1:\eta^2-C(CO_2Me)=CH(C(O)OMe\}$ $(CO)_4Cp$.[164] Reactions of $Ru_3(CO)_{12}$ with 2,6-bis(chloromethyl) pyridine give a structurally unidentified intermediate which reacts with MeOH or PPh_3 to give trinuclear but non-cluster derivatives containing the m-η^1(*C*):η^2(*C,N*)-$CH_2C_5H_3NCH_2C(O)$ ligand.[165]

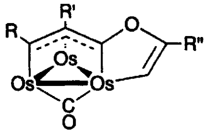
10.4 Osmium – High-yield syntheses of Os_3 (up to 90%), Os_4 (up to 90%), Os_5C (74%) and $Os_{10}C$ (81%) clusters involve reductive carbonylation or hydrogenation of $OsCl_3$ or $\{OsCl_2(CO)_3\}_2$ on silica in the presence of M_2CO_3 (M = Na, K).[166] The preparation of derivatives of $[Os_4(CO)_{13}]^{2-}$ (analogous to the ruthenium complexes) from mixtures of $[Os(CO)_4]^{2-}$ and $Os_3(CO)_{12}$ suggests that this reaction may be a synthetically useful source of this dianion.[121] Relative stabilities of $Os_x(CO)_y$ (x = 3-7) and Os-Os bond enthalpy terms formation enthalpies have been estimated from a previously derived Os-Os bond enthalpy/Os-Os bond length relationship. As the x/y ratio increases so does the use of electrons in Os-Os bonding. Relationships between Os-C and C-O distances and the Os-CO bond enthalpy were also suggested.[167]

Protonation of $Os_3(CO)_{12}$ occurs in liquid HF: the cation was isolated as $[Os_3(\mu-H)(CO)_{12}]$ $[W_2O_2F_9]$ by adding WF_6.[168] Kinetic studies of reactions of HD or H_2/D_2 mixtures with $Os_3(CO)_{12-n}(NCMe)_n$ (n = 1, 2), which give mixtures of $Os_3(\mu-X)_2(CO)_{10}$ (X = H, D), suggest that reversible oxidative addition/reductive elimination of H_2 occurs on $Os_3(\mu-H)_2(CO)_{10}$ via a fluxional $(H/D)_4$ derivative.[169] Oxidation of $[Os_3(\mu-H)(\mu-CO)(CO)_{10}]^-$ with Cu(II) salts gave $\{Os_3(\mu-H)(CO)_{10}\}_2\{\mu-\eta^2(C,O):\mu-\eta^2(2O)-CO_2\}$ as the only new product.[170]

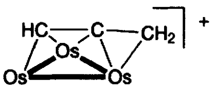
Many osmium cluster complexes are obtained from $Os_3(CO)_{12-n}(NCMe)$ [n = 1 (**A**), 2 (**B**)] or $Os_3(\mu-H)_2(CO)_{10}$ (**C**), which will be so abbreviated in the following account.

Hydrocarbon ligands. Reactions of $Os_3(\mu-H)_2(CO)_9(PPh_3)$ with ethyne or ethene (500 psig) give $Os_3(\mu-H)(\mu-\eta^1:\eta^2-CH=CH_2)(CO)_9(PPh_3)$ as two slowly equilibrating isomers, in which the μ-H ligand and μ-vinyl group bridge different edges. The latter reaction proceeds via $Os_3(\mu-H)_2(\mu-CHMe)(CO)_9(PPh_3)$.[171]

Reactions of **C** with functional alkynes gave a variety of products.[172] A mixture of $Os_3\{\mu_3-HC_2CH_2(OH)\}(\mu-CO)(CO)_9$ (**88**) and $Os_3(\mu-H)\{\mu-\eta^1:\eta^2-CH=CH(OH)\}(CO)_{10}$ was obtained from $HC\equiv CCH_2OH$, while $HC\equiv CCMe=CH_2$ afforded $Os_3(\mu-H)(\mu-\eta^1:\eta^2-CH=CHCMe=CH_2)(CO)_{10}$ and $Os_3(CO)_{10}(\eta^4-CH=CMeCH=CH_2)$. The alkyne cluster $Os_3(\mu_3-HC_2CMe=CH_2)(\mu-CO)(CO)_9$ (**89**) was obtained from **B**. Thermolysis of (**88**) and (**89**) afforded the hydrido-alkynyl complexes $Os_3(\mu-H)(\mu_3-C_2R)(CO)_9$ (R = CH_2OH, $CMe=CH_2$), together with, in the case of (**89**), $Os_3\{\mu_3-\eta^1:2\eta^1:\eta^3-CHC(CMe=CH_2)COC(CMe=CH_2)=CH\}(\mu-CO)(CO)_8$ (**90**). Protonation of $Os_3\{\mu_3-HC_2CR_2OH\}(\mu-CO)(CO)_9$ (R = H, Me) resulted in loss of OH and formation of the propargyl clusters $[Os_3(\mu_3-\eta^1:\eta^2:\eta^2-HCCCR_2)(\mu-CO)(CO)_9]^+$ (**91**).[172] Similarly, the hydrido-alkynyl clusters $Os_3(\mu-H)(\mu_3-C_2R')(CO)_9$ [R′ = CR_2OH (R = H, Me) or $CMe=CH_2$] gave $[Os_3(\mu-H)(\mu_3-CCCR_2)(CO)_9]^+$ (**92**). The cationic complexes contain carbocations stabilised by interaction with the Os_3 cluster. For (**92**) (R = Me), exchange of the CMe_2 group between two equivalent Os atoms has $DG^\#$ =



	R	R'	R''
90	H	CMe=CH$_2$	CMe=CH$_2$
93	Fc	H	Fc



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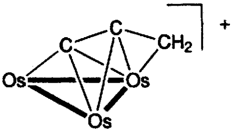

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Unless otherwise indicated, Os = Os(CO)$_3$

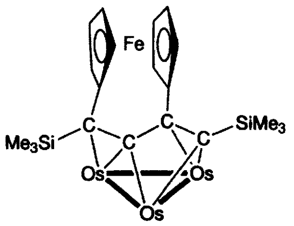
13.3 kcal mol^{-1}. Addition of PPh$_3$ to the coordinated carbocations afforded alkynyl- (from **91**) or allenyl-phosphonium (from **92**) clusters.

Products from the reactions between **B** and HC$\equiv$CFc include Os$_3$(μ_3-HC$_2$Fc)(μ-CO)(CO)$_9$ and complex (**93**), containing a substituted vinyl allyl ether ligand, analogous to that found in (**90**) above.[173] The unusual coupling results in two inequivalent Fc groups, which show two 1-e redox processes. Irreversible 2-e oxidations of the cluster residues are also observed. The related reaction using 1,1′-(SiMe$_3$C$\equiv$C)$_2$-ferrocene gave the μ_3-alkyne complex Os$_3${μ_3-SiMe$_3$C$_2$-η-C$_5$H$_4$Fe(η-C$_5$H$_4$C$\equiv$CSiMe$_3$)}(μ-CO)(CO)$_9$, in which only one C$\equiv$C triple bond is coordinated, together with complex (**94**), in which an unusual coupling and SiMe$_3$ group-migration has occurred to give a 6-e dienediyl ligand.[174] Reversible 1-e oxidation is found together with the usual irreversible 2-e reduction of the cluster nucleus.

Two isomers of Os$_3$(μ_3-HC$_2$C$_2$SiMe$_3$)(CO)$_{10}$ were obtained from the diyne and **B**, probably by coordination of the Os$_3$ cluster to each C$\equiv$C triple bond; the mixture reacted with Co$_2$(CO)$_8$ to give only a single isomer, in which the Co$_2$(CO)$_6$ group bridges the C$_2$SiMe$_3$ portion of the ligand.[87] Reaction of Fe$_2$(μ-CH(Se)=C(Se)C$\equiv$CMe}(CO)$_6$ with **B** resulted in coordination of the free C$\equiv$C triple bond to give Os$_3${μ_3-MeC$_2$C(Se)=CH(Se)[Fe$_2$(CO)$_6$]}(CO)$_{10}$.[175]

A potentially useful modification of organometallic labelling procedures for proteins has been demonstrated by addition of an Os$_3$(CO)$_{10}$ fragment to the succinimido pentynoate reagent previously used to add radioactive iodine nuclei. Complexing the Os$_3$ cluster to give the anticipated μ_3-alkyne complex (**95**) was followed by linking to benzylamine, several amino acids and bovine serine albumin; the labelled protein contained about 20 clusters per protein molecule.[176]

The μ_3-carbene complex Os$_3$(μ_3-η^1:η^2:η^2-C$_6$H$_5$Ph)(CO)$_9$ readily adds O or



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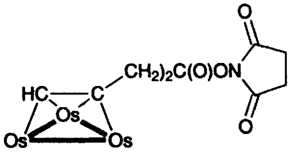

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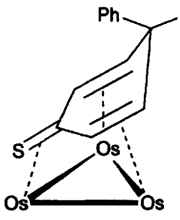

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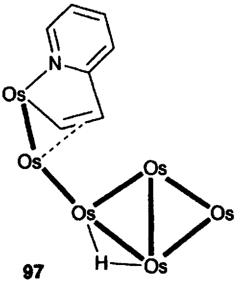
CH_2 to give cyclohexadienylidene derivatives. Similar reactions with S_8/NEt_3 or with cyclohexene sulfide gave the thioketone cluster (**96**), while reactions with H_2S/dbu afforded an anionic thiol cluster. These complexes are interconvertible by hydride addition/abstraction, demonstrating ambivalent behaviour for the thiol group.[177]

Reduction of $Os_3(\mu\text{-}H)_2(\mu_3\text{-}CCO)(CO)_9$ to $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CMe)(CO)_9$ by BH_3(thf) is described; the related $\mu_3\text{-}C{=}CH_2$ complex is unaffected by this reagent.[178] Replacement of Cl in $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CCl)(CO)_9$ (**D**) with donor molecules by reactions in the presence of dbu continue to excite interest. The complex from $NC_5H_4(CH{=}NC_6H_4OC_{16}H_{33}\text{-}4)\text{-}4$ and the related cyclometallated cluster, obtained from the Schiff base and **B**, were both rod-like molecules.[179] Similar reactions with **D** and 4-[2-(9-anthryl)-vinyl- and -ethyl]pyridines were reported; in the former there is significant metal-anthracene interaction via the conjugated system.[180] The 2-vinylpyridine derivative $Os_3(\mu\text{-}H)_2\{\mu_3\text{-}C(NC_5H_4CH{=}CH_2)\}(CO)_9$ reacts with **B** to give the 94-e planar cluster (**97**) in a reaction involving loss of a CH_2 fragment.[181] Reactions of **D** with bidentate phosphines resulted in formation of one C-P bond for dppm and dppe, and of the linked bis-cluster $\{Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}C)\}_2(\mu\text{-}dppp)$.[182] Further reactions of these complexes result in the diphosphine bridging a C-Os bond.

A variety of Os_4 clusters has been prepared from $Os_4(\mu\text{-}H)_4(CO)_{10}(NCMe)_2$ and cyclohexa-1,3-diene, including the novel complexes (**98**), $Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}PhC_6H_9)$ and $Os_5(\mu\text{-}H)_2(CO)_{13}(\eta^4\text{-}C_6H_8)$.[183] Loss of H_2 from $Os_4(\mu\text{-}H)_3(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_6H_9)(CO)_{11}$ affords $Os_4(\mu\text{-}H)_2(\mu_3\text{-}C_6H_8)(CO)_{11}$.



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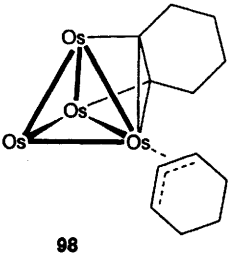

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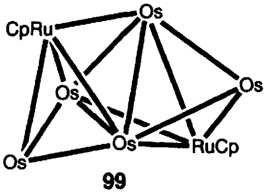
Build-up of osmium clusters by reaction of $[Os_5(CO)_{15}]^{2-}$ with $[Ru(NCMe)_3Cp]^+$ gave $Os_5Ru_2(CO)_{15}Cp_2$ (**99**), in which the Ru atoms occupy apical sites in a bicapped trigonal pyramidal core.[184] Similar reactions of $[Os_5C(CO)_{14}]^{2-}$ with $[M(NCMe)_3(\eta\text{-}C_6H_6)]^{2+}$ (M = Ru, Os) have given $MOs_5C(CO)_{14}(\eta\text{-}C_6H_6)$; the Ru complex adds CO to give unstable $Os_5RuC(CO)_{15}(\eta\text{-}C_6H_6)$ which eliminates an $Os(CO)_3$ fragment to give (**100**).[185]

Other Group 14 ligands. A range of new Os-Ge clusters have been prepared from $[Os(CO)_4]^{2-}$ and $GeCl_2Me_2$, followed by photolysis or thermolysis.[186] Complex (**101**) has an Os_3Ge_2 bow-tie skeleton, while (**102**) contains an Os_3Ge_3 raft. The latter is related to the major product obtained by thermolysis of $\{Os(\mu\text{-}SnMe_2)(CO)_4\}_2$ (**103**), while irradiation of (**103**) gave the planar Os_4Sn_4 cluster



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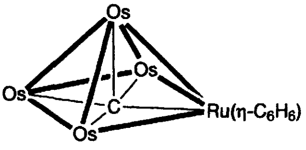

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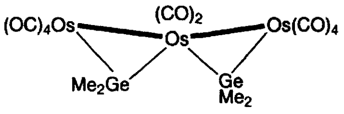

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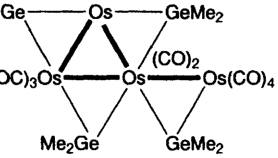

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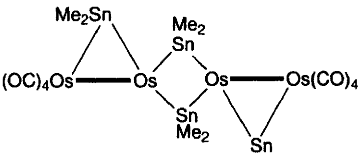

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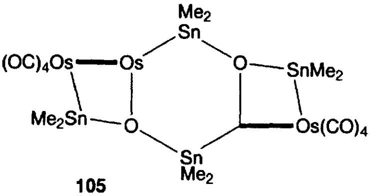

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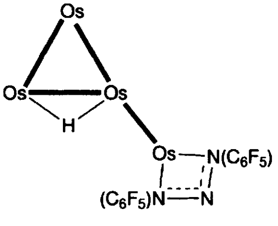
(**104**). Treatment with Me_3NO resulted in formation of the μ_3-oxo cluster (**105**).[187] An unidentified purple cluster, obtained by heating $Os_3(\mu\text{-}H)_3(SnHMe_2)(CO)_{10}$, reacts with PEt_2Ph to give $Os_3(\mu\text{-}H)_3\{\mu_3\text{-}Sn[Os_3(\mu\text{-}H)(CO)_{10}(PEt_2Ph)]\}(CO)_9$.[188]

Nitrogen ligands. Direct synthesis of $[Os_3(\mu\text{-}\eta^2\text{-}ONO)(CO)_{10}]^-$ from **B** and [ppn][NO_2] has been reported, together with its protonation to $Os_3(\mu\text{-}H)(\mu\text{-}ONO)(CO)_{10}$; these contain rare examples of cluster-coordinated nitrite ligands.[189] 2-Substituted anilines react with **B** to give $Os_3(\mu\text{-}H)(\mu_3\text{-}XC_6H_2R_2NH_2)(CO)_9$ (X = NH, R_2 = 4,5-Me_2; X = O, $R_2 = H_2$) and $Os_3(\mu\text{-}H)(\mu\text{-}SC_6H_4NH_2)(CO)_{10}$.[190]

Linear Os_3 chains are present in $Os_3X(CO)_{11}(C_6F_5NNNC_6F_5)$ (X = H, Cl), obtained from **A** and the triazenide; the X atom is attached to a terminal Os, while the triazenido ligand chelates the other terminal Os atom.[112] Alternatively, reaction in hexane at 60°C under vacuum gave the spiked-triangular $Os_4(\mu\text{-}H)(CO)_{14}(\eta^2\text{-}C_6F_5NNNC_6F_5)$ (**106**).[191] The reaction of the triazene with **B** gave the unusual Os_6 cluster (**107**; L = CO), which contains an Os_4 tetrahedron attached to an Os_2 chain. NMR studies revealed the intermediacy of $Os_6(\mu\text{-}H)(\mu\text{-}CO)(CO)_{19}(NCMe)_2(\eta^2\text{-}C_6F_5NNNC_6F_5)$ (**107**, L = MeCN; obtained as two isomers).[192] The mono-MeCN cluster is converted into $Os_5(CO)_{16}$ and $Os_5(\mu\text{-}H)(CO)_{17}(\eta^2\text{-}C_6F_5NNNC_6F_5)$ (**108**) on heating.[191]

Ambiguities in locations of μ-H ligands in $Os_3(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}C{=}NC_3H_6)Br(CO)_9$ (**109**) have been resolved by the X-ray structure of the $\mu\text{-}\eta^2\text{-}NC_4H_5Me\text{-}2$ complex; the solution dynamics are also described.[193] An excess of HBr reacts with (**109**) with cluster breakdown to give $Os_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CHNHC_3H_6)Br_2(CO)_6$. Reaction of (**109**) with $HgPh_2$ gives a $\mu\text{-}\eta^1$-Ph complex which on heating gives $Os_3(\mu\text{-}\eta^1{:}\eta^6\text{-}Ph)(\mu\text{-}\eta^2\text{-}C{=}NC_3H_6)(CO)_8$ (**110**).[193]



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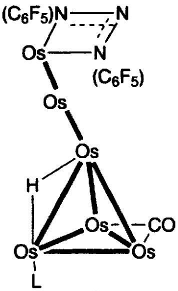

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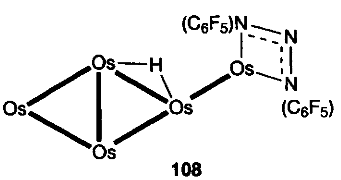

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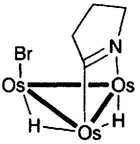
The usual N-H bond cleavage and decarbonylation reactions occurred on treatment of **B** with indoline and tetrahydroquinoline, and subsequent thermolysis.[194] Dehydrogenation of both tautomers (**111a**) and (**111b**) (from indoline) gave (**112**). Tetrahydroquinoline afforded the analogous tautomers, together with $Os_3(\mu\text{-}H)(\mu\text{-}C_9H_{10}NMeCN)(CO)_{10}$ (**113**), apparently formed by reaction with coordinated MeCN; the latter loses CO on heating to give (**114**). Changes in the structures are related to the nature of the heterocyclic precursor. Reversible protonation of (**111a**) occurs at the N atom. In contrast to these results, isotetrahydroquinoline gave the μ- and μ_3-imidoyl clusters $Os_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}C_9H_8N)(CO)_n$ (n = 10, 9).

Phosphorus ligands. Reactions of $Os_3(CO)_{11}(PH_3)$ with **A** in toluene gave



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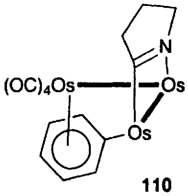

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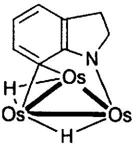

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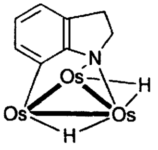

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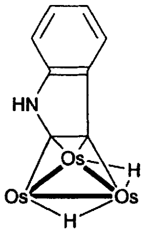

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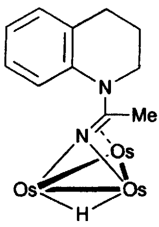

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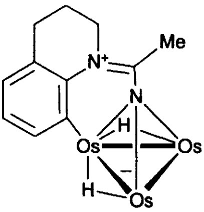

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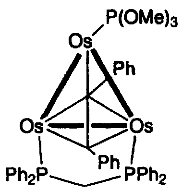
$Os_3(CO)_{11}\{(\mu\text{-}PH_2)\ Os_3(\mu\text{-}H)(CO)_{10}\}$ and $Os_3(\mu\text{-}H)(CO)_{11}\{(\mu_3\text{-}PH)Os_3(\mu\text{-}H)(CO)_{10}\}$; similarly, **B** gave $Os_6(\mu\text{-}H)(\mu\text{-}PH_2)(CO)_{21}(NCMe)$; further heating gave known $Os_6(\mu_6\text{-}P)$ clusters.[195] A series of Os_6 clusters containing $\mu\text{-}PH_2$ or $\mu\text{-}PH$ groups has been obtained from $Os_3(CO)_{11\text{-}n}(L)_n(NCMe)$ [$n = 1$, $L = CNBu^t$, PMe_3; $n = 2$, $L = P(OMe)_3$] and $Os_3(CO)_{11}(PH_3)$ or $Os_3(\mu\text{-}H)(\mu\text{-}PH_2)(CO)_{10}$. In the cases of $Os_6(\mu\text{-}H)(\mu\text{-}PH_2)(CO)_{20}\{P(OMe)_3\}$ and $Os_6(\mu\text{-}H)_2(\mu_3\text{-}PH)(CO)_{19}\{P(OMe)_3\}$, the phosphite ligands cause a change in relative orientation of the Os_3 triangles from those observed for the CO-precursors.[196]

Reactions of $PPh_2(CH{=}CH_2)$ (L) with **A** and **B** gave $Os_3(CO)_{12\text{-}n}(L)_n$ [$n = 1$ (**115**), 2, respectively], while addition to **C** gave $Os_3(\mu\text{-}H)H(CO)_{10}(L)$. β-Elimination of H to the cluster and coordination of the olefin occurred on heating (**115** to give $Os_3(\mu\text{-}H)\{\mu_3\text{-}PPh_2(CH{=}CH)\}(CO)_9$.[114] The metallated $PPr^i\{(\eta\text{-}C_6H_4)Cr(CO)_3\}$ ligand (L) is found in $Os_3(\mu\text{-}H)_2(\mu_3\text{-}L)(CO)_8\{PPr^i_2[(\eta\text{-}Ph)Cr(CO)_3]\}_n$ ($n = 1, 2$), obtained by pyrolysis of $Os_3(CO)_{11}\{PPr^i_2[(\eta\text{-}Ph)Cr(CO)_3]\}$. Thermal decomposition of $Os_3(CO)_{11}\{PPh_2[(\eta\text{-}Ph)Cr(CO)_3]\}$ gave $Os_3\{\mu_3\text{-}P[(\eta\text{-}Ph)Cr(CO)_3]\}(\mu_3\text{-}C_6H_4)\{(CO)_9$ and the 46-e complex $Os_3\{\mu_3\text{-}PPh(C_6H_4)\}(CO)_8\{PPh_2[(\eta\text{-}Ph)Cr(CO)_3]\}$.[116]

A series of complexes containing monodentate ligands has been derived from **C** and dppm or $PPh_2(C_5H_4N\text{-}2)$.[197] The dppm-*P* complex (**116**) only slowly converts to the μ-dppm derivative, and in principle can be used to prepare complexes containing a second mono- or poly-nuclear metal fragment. Reaction of two equivalents of **C** with dppm gave $\{Os_3(\mu\text{-}H)(CO)_{10}\}_2(\mu\text{-}dppm)$, which exists as isomers with *syn* and *anti* arrangements of the two terminal H ligands. Addition of (**116**) to $RuCl_2(dppm)(\eta\text{-}C_6H_6)$ gave $Os_3H(\mu\text{-}H)(CO)_{10}\{(\mu\text{-}dppm)RuCl_2(\eta\text{-}C_6H_6)\}$.

In refluxing diglyme, the 46-e cluster $Os_3(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}dppm)(\mu\text{-}PBu^t_2)_2(CO)_5$ is formed from $Os_3(\mu\text{-}dppm)(CO)_{10}$ and $PHBu^t_2$. In contrast with the Ru complex, no μ-CO ligand is present, nor does it react with CO, so that stabilisation appears to result from the bulk of the PR_2 ligands.[198] Addition of phosphines and phosphites to the 46-e cluster $Os_3(\mu_3\text{-}C_2Ph_2)(\mu\text{-}dppm)(CO)_7$ gave $Os_3(\mu_3\text{-}C_2Ph_2)(\mu\text{-}dppm)(CO)_7(L)$, which can exist in three forms in solution, depending on solvent polarity. These result from coordination of the entering ligand to two different metal atoms.[199] The $P(OMe)_3$ adduct can be decarbonylated to a further example of a 46-e cluster, $Os_3(\mu_3\text{-}C_2Ph_2)(\mu\text{-}dppm)(CO)_6\{P(OMe)_3\}$ (**117**).

Cyclopolyphosphines are a rich source of cluster complexes. Thus, the thermal reaction (209°C) of $Os_3(CO)_{12}$ with *cyclo*-$\{P(CF_3)\}_4$ gave (**118**). Reactions of *cyclo*-$\{P(CF_3)\}_n$ ($n = 4, 5$) with **A** gave the phosphido-bridged bis-cluster $\{Os_3(CO)_{11}\}\{\mu\text{-}PH(CF_3)\}\{Os_3(\mu\text{-}H)(CO)_{11}\}$ and with **C**, $Os_3(\mu\text{-}H)\{\mu\text{-}PH(CF_3)\}(CO)_{10}$ and $Os_3(\mu\text{-}H)_2(CO)_9\{P(CF_3)P(CF_3)Os_3(\mu\text{-}H)_2(CO)_9\}$.[120] Complexes $Os_3(\mu\text{-}H)(\mu\text{-}P_5Et_5H)(CO)_8$ (**119**) and $Os_3(\mu\text{-}1,3\text{-}\eta^2\text{-}P_5Et_5)(CO)_{10}$ were obtained from *cyclo*-$(PEt)_5$ and **C** (80°C); at r.t., the 1,2-η^2 isomer was formed. The Ph analogue of (**119**) was obtained from *cyclo*-$(PPh)_5$ at r.t.; in both compounds the P_5 ring has opened. Extensive use of two-dimensional ^{31}P NMR spectroscopy enabled structural assignments to be made.[200] Reactions between *cyclo*-$(PPh)_5$ and **A** gave $\{Os_3(CO)_{11}\}_n\{(PPh)_5\}$ ($n = 1, 2$) while **B** gave $Os_3\{\mu\text{-}\eta^2\text{-}(PPh)_5\}(CO)_{10}$ (obtained as two inversion isomers). The mixed bis-cluster was



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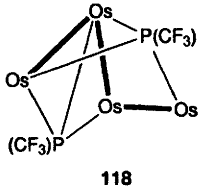

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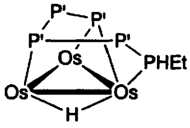


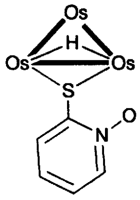
119 P' = PEt

obtained from n = 1 and $Ru_3(CO)_{11}(NCMe)$. The *cyclo*-$(PPh)_5$ ligand chelates via P(1) and P(3).[201]

Oxygen and sulfur ligands. A variety of complexes have been obtained by oxidative addition of O-H or S-H bonds across an Os-Os bond in Os_3 carbonyls (usually **A** or **B**). Examples reported during the year include $Os_3(\mu\text{-}H)(\mu\text{-}O_2CFc)(CO)_{10}$ and $\{Os_3(\mu\text{-}H)(CO)_{10}\}_2\{(\mu\text{-}O_2C\text{-}\eta\text{-}C_5H_4)_2Fe\}$ from the corresponding ferrocenecarboxylic acids, for which reversible 1-e redox processes occur at the Fe centres,[202] $\{Os_3(\mu\text{-}H)(CO)_{10}\}_2(\mu\text{-}O_2CC_6H_4CO_2)$ and $\{Os_3(\mu\text{-}H)(CO)_{10}\}\{\mu\text{-}O_2CC_6H_4C(O)O\}\{Os_3(\mu\text{-}H)(CO)_{11}\}$, related by CO dissociation, from phthalic acid,[203] $\{Os_3(\mu\text{-}H)(CO)_{10}\}_2\{\mu\text{-}2,6\text{-}(O_2C)_2C_5H_3N\}$[204] and $\{Os_3(\mu\text{-}H)(CO)_{10}\}_2(\mu,\mu\text{-}SC_6H_4S)$ from $1,2\text{-}(HS)_2C_6H_4$.[203] Complexes derived from 2-mercaptobenzoic and 3-mercatopropionic acids contain two Os_3 clusters linked via μ-S and $\mu\text{-}O_2C$ groups;[204] similarly, 2,2′-dithiosalicylic acid gave $\{Os_3(\mu\text{-}H)(CO)_{10}\}_2(\mu\text{-}O_2CC_6H_4S)_2$, which with H_2 formed $Os_3(\mu\text{-}H)(\mu\text{-}O_2CPh)(CO)_{10}$.[205] Thiosalicylic acid gave $\{Os_3(\mu\text{-}H)(CO)_{10}\}_2(\mu\text{-}SC_6H_4CO_2)$ and $\{Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}SC_6H_4C(O)O\}\{Os_3(\mu\text{-}H)(CO)_{11}\}$, which are related by CO loss. Fragmentation of the latter gives $Os_3(\mu\text{-}H)(\mu\text{-}SC_6H_4CO_2H)(CO)_{10}$.[203] With one equivalent of 2,2′-dithiosalicylaldehyde, both $Os_3(\mu\text{-}H)$ $(\mu\text{-}SC_6H_4CHO)(CO)_{10}$ and $Os_3(\mu\text{-}SC_6H_4CHO)_2(CO)_{10}$ are formed.

The *N*-oxide group in complexes derived from $2\text{-}S{=}C_5H_4N(OH)$ can adopt a variety of bonding modes. The thione reacts with **A** to give $Os_3(\mu\text{-}H)\{\mu\text{-}\eta^n\text{-}SC_5H_4N(O)\}(CO)_{10}$ [n = 1 (**120**), 2 (**121**)] and (**122**); the latter predominates after long reaction times.[206] With $Os_3(CO)_{10}(CNR)(NCMe)$ (R = CH_2Ph, Pr) complexes $Os_3(\mu\text{-}H)(CO)_9(CNR)\{\eta^2\text{-}SC_5H_4N(O)\}$, $Os_3(\mu\text{-}H)$ $\{\eta^1\text{-}SC_5H_4N(O)\}\text{-}(CO)_9(CNR)$, and $Os_3(\mu\text{-}H)\{\eta^1\text{-}SC_5H_4N(O)\}(\mu\text{-}C{=}NHCH_2Ph)(CO)_{10}$ are obtained. Thermolysis of **120** at 80°C gives $Os_3(\mu\text{-}X)(\mu_3\text{-}SC_5H_4N)$ $(CO)_9$ (X = H, OH).

Thiourea reacts with $Os_3(CO)_{12}/Me_3NO$ in MeOH to give $Os_3(\mu\text{-}H)\{\mu\text{-}S\text{-}NHC(S)NH_2\}(CO)_{10}$ and $Os_3(\mu\text{-}H)\{\mu_3\text{-}N,S\text{-}NHC(S)NH_2\}(CO)_9$; the former can also be obtained directly from **B** and thiourea.[207] In contrast, tetramethylthiourea in MeOH gave $Os_3(CO)_{11}\{S{=}C(NMe_2)_2\}$ and $Os_3(\mu\text{-}OH)(\mu\text{-}OCOMe)\text{-}(CO)_9\{S{=}C(NMe_2)_2\}$. The $SC(NMe_2)_2$ can be displaced by PPh_3 or MeCN at room temperature, while pyridine gives $Os_3(\mu\text{-}H)(\mu\text{-}C_5H_4N\text{-}2)(CO)_{10}$ at 80°C. Photochemical reaction of Os_3 complexes containing 2-mercaptopyridine-derived ligands resulted in CO being displaced by N to give $Os_3(\mu\text{-}H)\{\mu\text{-}SC_5H_3(R)N\}(CO)_9$ (R = H, OH) and $\{Os_3(\mu\text{-}H)(CO)_9\}\{\mu\text{-}SC_5H_3(CO_2)\text{-}N\}\{Os_3(\mu\text{-}H)(CO)_{10}\}$.[208]



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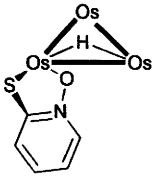

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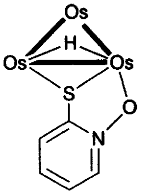

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4-Methylthiazole undergoes the expected addition to **B** to give $Os_3(\mu\text{-}H)(\mu\text{-}2,3\text{-}\eta^2\text{-}C{=}NCMe{=}CHS)(CO)_{10}$; subsequent reaction with PPh_3 gave mono- (three isomers) and di-substitution products (four isomers).[136] Further reaction with 4-methylthiazole gave clusters containing two thiazolide ligands attached in different modes.

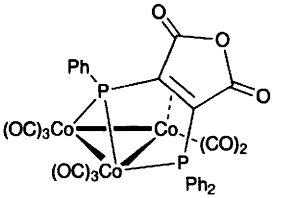
11 Group 9

An interesting theoretical study has considered the possibility of incorporation of tetrahedral M_4 (M = Co, Rh, Ir) clusters into the tetrahedral holes in solid f.c.c. C_{60}.[209] Eight of the C_6 rings in C_{60} face the eight holes. In the unchanged C_{60} lattice, Co_4 and Rh_4 tetrahedra fit with M-C distances of 1.92 (Co), 1.85 Å (Rh); although these are shorter than the 2.1-2.3 Å found in η^6-arene complexes, it is suggested that expansion of the lattice might accommodate the clusters. The resulting $C_{60}(Co_4)_2$ is predicted to be metallic, with overall donation of about 2 e to each Co_4. With Rh, the situation is reversed, the metal atoms donating 1.4 electrons to C_{60}, although it is also expected to be metallic. It is likely that molecular $M_4(\eta^6\text{-arene})_4$ clusters are relatively unstable.

11.1 Cobalt – Trinuclear clusters are obtained from $Co_4(CO)_9(\eta\text{-}C_6H_3Me_3)$ and 2,3-$(PPh_2)_2$-maleic anhydride (bma), which give $Co_3\{\mu\text{-}\eta^1,\eta^2\text{-}PPhC{=}C(PPh_2)C(O)CC{=}O\}(CO)_7$ (**123**) and the mono-PPh_3 derivative, in addition to two binuclear complexes.[210] The PPh_3 is formed by C-Ph cleavage in the bma ligand and transfer of the Ph group to a transient PPh_2 ligand. EH MO calculations and redox behaviour of these and related clusters are reported; there is some stabilising Co_3-π^* interaction between the ligand and the cluster.

Exchange of mesitylene with the iridathiabenzene isomer of $Ir(2,5\text{-}Me_2T)Cp^*$ under mild conditions gave $Co_4(CO)_9\{(\mu\text{-}\eta^6{:}S,C\text{-}2,5\text{-}Me_2T)IrCp^*\}$; at higher temperatures, the *S*-bonded complex $Co_4(CO)_{11}\{S\text{-}(2,5\text{-}Me_2T)IrCp^*\}$ is formed, which can be desulfurised to the linear cluster $\{CoIr(\mu\text{-}CO)_2(2\eta^1\text{-}CMe{=}CHCH{=}CMe)\}_2$, also prepared directly from $Co_2(CO)_8$ and $Ir(CMe{=}CHCH{=}CMe)(CO)Cp^*$.[211]

The reaction between $Co_2(CO)_8$ and $S(C_6F_5)_2$ affords $Co_3(\mu_3\text{-}S)(C_6F_5)(CO)_8$, in which the C_6F_5 group occupies an equatorial position.[212] Comparison with the 49-e $Co_3(\mu_3\text{-}S)(CO)_9$ shows that the latter has longer Co-Co distances. It is likely



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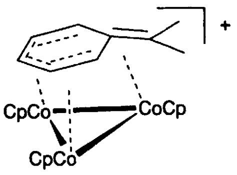

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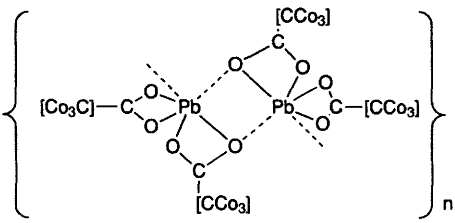
that the compound previously reported[213] as $Co_2\{S_2(C_6Cl_5)_2\}(CO)_6$ is the analogous cluster $Co_3(\mu_3\text{-}S)(C_6Cl_5)(CO)_8$.

Paramagnetic (46-e) $Co_3(\mu\text{-}H)(\mu_3\text{-}CH)Cp^*_3$ was obtained from Co(acac)Cp* and LiMe; it reacts with H_2 to give diamagnetic $Co_3(\mu\text{-}H)_3(\mu_3\text{-}CH)Cp^*_3$.[214] Protonation of $Co_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-arene})Cp_3$ gives $[Co_3(\mu_3\text{-}H)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-arene})Cp_3]^+$ for arenes with saturated side chains (Pr^i, 1,4-Et_2, -C_2H_4-) and cluster-stabilised η^7-benzyl cations (**124**) with several styrenes. Isomerisation of (**124**) (R = Me) to paramagnetic $[Co_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-arene})Cp_3]^+$ occurs on attempted crystallisation.[215] EH MO and DFT methods were used to rationalise the different protonation sites as well as the geometry of (**124**, R = Me). The non-planar η^7-benzyl ligand has the slipped eclipsed arrangement, this being energetically more favoured than a staggered substituted benzene. Nucleophilic substitution of F by H or Ph occurs on treatment of $Co_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}4\text{-}FC_6H_4CMe{=}CH_2)Cp^*_3$ [from $CoCp^*(\eta\text{-}C_6Me_6)$ and $4\text{-}FC_6H_4CMe{=}CH_2$] with $Li[BHEt_3]$ or LiPh.[216]

Thermal or photochemical reactions between $Co(\eta\text{-}C_2H_4)_2Cp^*$ and $\{Fe(\mu\text{-}NO)Cp^*\}_2$ result in NO transfer from Fe to Co, giving $Co_3(\mu_3\text{-}NO)(\mu_3\text{-}X)Cp^*_3$ (X = NO and CMe), together with $Co_3(\mu_3\text{-}O)(\mu_3\text{-}CO)Cp^*_3$ (of obscure origin).[217] Cleavage of the $C{\equiv}P$ triple bond in $P{\equiv}CBu^t$ occurs on reaction with three equivalents of $CoCl(PBu^t{}_2C_2H_4\text{-}\eta\text{-}C_5H_4)$ in the presence of sodium amalgam, when $Co_3(\mu_3\text{-}P)(\mu_3\text{-}CBu^t)(Cp^P)_3$ (**125**; $Cp^P = \eta\text{-}C_5H_4C_2H_4PBu^t{}_2$) is obtained; smaller amounts of analogous complexes were obtained from $\{CoClCp^*\}_2$, but the reaction appears to require the presence of the pendant phosphine to proceed in high yield.[218] Further reactions of (**125**) with chalcogens gave $Co_3(\mu_3\text{-}PE')(\mu_3\text{-}CBu^t)(Cp^{PE})_3$ [E′ = E = O, S; E′ = O, E = S; $Cp^{PE} = \eta\text{-}C_5H_4C_2H_4P(E)Bu^t{}_2$]. Reactions of As_2S_3 and As_4S_n (n = 3, 4) with $Co(CO)_2Cp^*$ (Cp* = C_5Me_5, C_5Me_4Et) afford mixtures from which $Co_xAs_yS_z$ clusters (x/y/z = 1/4/3, 4; 2/2/2,3; 3/2/4; 3/4/2) have been identified.[219]

Complexes derived from $Co_3\{\mu_3\text{-}C(CO_2H)\}(CO)_9$ often exhibit novel architectures. Recent examples include extended oxometallic systems obtained from $Ti(OR)_4$ (R = Et, Pr^i, Ph) or $Ti(OPr^i)_2(O_2C_6H_4)$ and $Co_3\{\mu_3\text{-}C(CO_2H)\}(CO)_9$.[220] A chain-like structure involving bridging CO_2 groups is found in $\{[Co_3(CO)_9(\mu_3\text{-}CCO_2)]_2Pb\}_n$ (**126**). Thermal decomposition results in loss of CO, then CO and/or CO_2, to give materials which are heterogeneous hydrogenation catalysts for buta-1,3-diene.[221] Reactions of $Co_3\{\mu_3\text{-}C(CO_2H)\}(CO)_9$ with $W_2(O_2CCF_3)_4$ gave the expected product, $W_2\{O_2CCCo_3(CO)_9\}(O_2CCF_3)(thf)_2$. However, in the presence of CF_3CO_2Na, $\{Na[W_2\{[\mu_3\text{-}(O_2C)C]Co_3(CO)_9\}(O_2CCF_3)_4(thf)_2\}_2$

(127), containing a dimer of W_2 complexes with bridging cluster carboxylates, is formed.[222] Dimerisation occurs via interaction of free ends of $CF_3CO_2^-$ ligands with Na^+ cations; each W_2 unit is in the mixed W^{II}-W^{III} valence state.



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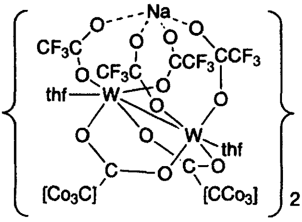

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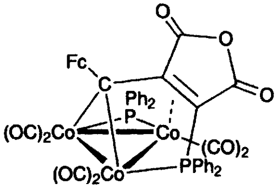
Methylidyne-bridged cobalt clusters continue to be the sources of unusual complexes, some of which have been shown to be active catalyst precursors for hydroformylation of 1-hexene with high conversions and chemoselectivities. In some cases, however, this may occur because of conversion to $Co_2(CO)_8$. In the solid-state, eight units of $Co_3\{\mu_3\text{-}C[Si(OH)_3]\}(CO)_9$ form a supramolecular assembly via H-bonding. The silanetriol fragments are protected by the hydrophobic cobalt carbonyl groups. Derivatisation of the triol can be readily achieved by alcoholysis of the precursor cluster $Co_3\{\mu_3\text{-}C(SiCl_3)\}(CO)_9$. Compounds with μ_3-$CSi(OR)_3$ groups [R = $CH(CH_2OEt)_2$, $(C_2H_4O)_2Me$, $C_2H_4(OC_2H_4)_2OMe$ and $C_2H_4(OC_2H_4)_9OH$] were prepared: a solution of the latter in PE 400 is miscible with water.[223]

Reactions between the silanetriol and MMe_3 (M = Al, Ga, In) have given heterosiloxanes $\{Co_3(CO)_9[\mu_3\text{-}C\{SiO_3M(thf)\}]\}_4$, which contain cubic $M_4O_{12}Si_4$ cores, with pendant Co_3 clusters attached to each Si.[224] The Co_3 clusters are of three types, with all terminal, three μ-CO, or two μ-CO and one semi-bridging CO around the basal Co_3 unit.

Reactions of $Co_3(\mu_3\text{-}CR)(CO)_9$ (R = Me, CO_2Me) with $PPh_2(CH{=}CH_2)$ (L) gave $Co_3(\mu_3\text{-}CR)(CO)_{9-n}(L)_n$ (R = Me, n = 1, 2; R = CO_2Me, n = 1-3); on heating reversible loss of CO from complexes with n = 1 gives $Co_3(\mu_3\text{-}CR)(\mu\text{-}P{:}\eta^2\text{-}PPh_2CH{=}CH_2)(CO)_7$. Two isomers containing *ax*- (major) or *eq*-olefin coordination are formed.[225] Similar chemistry with *cis*-$PPh_2CH{=}CHPPh_2$ (dppee) gave $Co_3(\mu_3\text{-}CR)(\mu\text{-dppee})(CO)_7$. Three reversible redox couples ($0/1^+$, $0/1^-$, $1^+/2^+$) are found in $Co_3(\mu\text{-}PPh_2)\{\mu\text{-}CFcC{=}C(PPh_2)C(O)OC{=}O\}(CO)_6$ **(128)**, formed by rapid conversion of $Co_3(\mu_3\text{-}CFc)(CO)_7(bma)$. EH MO calculations enable the electrochemistry to be related to nature of the frontier orbitals.[226] Several complexes $Co_3(\mu_3\text{-}CR)(\mu_3\text{-}SCHR^1SCHR^2SCHR^3)(CO)_6$ (R = Cl, Me, Ph; R^1, R^2, R^3 = H, Me, CH_2Ph) have been prepared and contain the trithiane coordinated to the Co_3 face in axial sites. In contrast, $Co_3(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_5\{\eta^3\text{-}(SC_2H_4)_3\}$ contains the crown thioether chelating one Co atom.[227]



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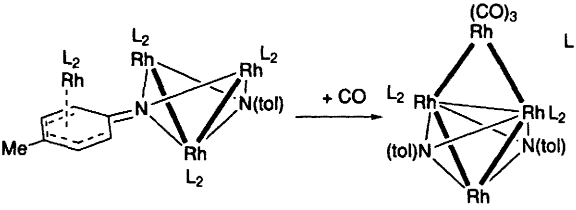
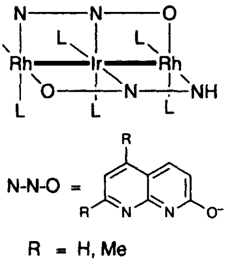
11.2 Rhodium – Reactions of $Rh_3\{\mu_3\text{-}N[(\eta^5\text{-}C_6H_4Me\text{-}4)Rh(L\text{-}L)]\}\{\mu_3\text{-}N(tol)\}(L\text{-}L)_3$ (**129**; L-L = cod, tfbb) with CO result in displacement of three L-L ligands to give (**130**), containing a 62-e Rh_4 raft cluster. Further CO results in displacement of the fourth L-L ligand in a reversible reaction. Slow loss of CO from (**130**) gives the CO analogue of (**129**). These reactions appear to be controlled by preferential coordination of 12-e $[Rh(L\text{-}L)]^+$ to an arene ring, whereas the 14-e $[Rh(CO)(L\text{-}L)]^+$ fragment is coordinated by two Rh atoms in the Rh_3 core.[228]



129 **130**



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Naphthyridine-2-ones (5,7-R_2-napyOH, R = H, Me) have several coordination sites and have been used in the stepwise synthesis of homo- and heterotrinuclear complexes $[M_3(\mu_3\text{-}Me_2\text{-}napyO)_2(CO)_2(diene)_2]^+$ (**131**; M = Rh, Ir; diene = cod, nbd, tfbb).[229] Thus, reaction between $IrCl(CO)_2\{NH_2(tol)\}$ and $\{Rh(\mu\text{-}R_2\text{-}napyO)(diene)\}_n$ proceeds via $(diene)Rh(\mu\text{-}R_2\text{-}napyO)_2\,Ir(CO)_2$ to give the $IrRh_2$ compounds. Chemical oxidation (Ag^+) afforded $[Ir_{3\text{-}n}Rh_n(\mu_3\text{-}Me_2\text{-}napyO)_2(CO)_2(cod)_2]^{2+}$ (n = 0-2), in which the unpaired electron is delocalised on the M_3 core.

Reaction of $\{Rh(\mu\text{-}Cl)(CO)_2\}_2$ with 2,2′-bis[(1,1′-biphenyl-2,2′-diyl)phosphite]-1,1′-binaphthyl (bpnap) under CO gave $Rh_4(\mu\text{-}bpnap)(CO)_{10}$ (**132***) which partially converted to a structural isomer on recrystallisation (CH_2Cl_2/thf). Alternative syntheses of a mixture of (**132**), its isomer, and hydrido compounds from $Rh(acac)(CO)_2$ under CO/H_2 were described. Cluster (**132**) is a catalyst precursor for isomerisation and hydroformylation of 1-octene.[230]

11.3 Iridium – A synthesis of $[Ir_6(CO)_{15}]^{2-}$ by reaction of CO (100°C, 1 atm.) with $Ir(acac)(CO)_2$ supported on γ-Al_2O_3 has been described, together with its conversion to supported Ir_6 clusters by heating (300 °C in He). Extraction of the cluster anion with [ppn]Cl gave $[ppn]_2[Ir_6(CO)_{15}]$.[231]

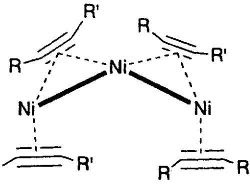
Several phenanthroline and bipyridyl ligands (N-N) chelate a basal iridium atom in $Ir_4(CO)_{10}$(N-N), obtained from $[Ir_4X(CO)_{11}]^-$ and N-N in the presence of Ag^+, via unstable η^1-N-N complexes.[232] Similarly, $[Ir_4Br(CO)_{11}]^-$ gives $Ir_4(\mu$-$CO)_3(CO)_7\{PPh_2(C_5H_4N$-$2)\}_2$ with $PPh_2(C_5H_4N$-2), which undergoes *ax-eq* scrambling of the phosphine at r.t.[233] Alternatively, 2-pyridylphosphines $PPh_{3-n}(py)_n$ (L; py = 2-C_5H_4N, n = 1-3) react with $Ir_4(CO)_{12}$ to give $Ir_4(\mu$-L)(μ-$CO)_3(CO)_5(L)_2$, in which one L bridges an Ir-Ir bond by *N,P*-coordination. Under CO in solution, the complexes are in equilibrium with $Ir_4(\mu$-$CO)_3(CO)_6(L)_3$.[234]

Polyphosphaferrocenes Fe{η-$P_3(CBu^t)_2$-1,3}{η-1,3-$P_2(CBu^t)_3$} (L^1) and FeCp{η-$P_3(CBu^t)_2$-1,3} (L^2) can act as ligands to clusters: reactions with $[Ir_4Br(CO)_{11}]^-$ in the presence of Ag^+ afforded $Ir_4(CO)_{12-n}(L)_n$ [L = L^1, L^2; n = 1 (**133***), 2]. In solution, both C_{3v} and T_d isomers are present, although the crystals contain only the latter. Loss of CO from (**133**, L = L^1) gave $Ir_4(\mu$-$L^1)(CO)_{10}$, while (**133**, L = L^2) reacted with further $[Ir_4Br(CO)_{11}]^-/Ag^+$ to give $\{Ir_4(CO)_{11}\}_2(\mu$-$L^2)$, which in turn readily converted to $Ir_4(\mu$-H)$(CO)_{10}$\{μ-FeCp[η^5-$P_3CBu^tC(CMe_2CH_2)$]\}$Ir_4(CO)_{11}$.[235]

12 Group 10

The chemistry of Group 10 *triangulo* clusters (mainly of Pt) has been reviewed.[236]

12.1 Nickel – Homoleptic $Ni_3(\mu$-η^2-alkyne$)_4$ [**134**; alkyne = $Me_3SiC_2CMe_2(OH)$] is stabilised in the solid-state by a hydrogen-bonding network, but is unstable in solution.[237] In contrast with the carbon analogue it does not form spontaneously from Ni(η^2-alkyne$)_2$. Reactions of (**134**) with $Bu^tC{\equiv}CCMe_2(OH)$ and some alkynediols gave Ni(η^2-alkyne$)_2$, while cycloocta-1,3,5,7-tetraene gave $\{Ni(C_8H_8)\}_2$.



134 R = $SiMe_3$; R' = $CMe_2(OH)$

A series of 48-e Ni_3 clusters containing μ_3-CO and μ_3-CNR (R = Me, Pr^i, Bu^t, Cy, CH_2Ph and ten aryl groups) ligands has been prepared by displacement of iodide from $Ni_3(\mu_3$-$I)_2(\mu$-dppm$)_3$ by the ligand; some bromo analogues were also made. All have similar spectroscopic and electrochemical properties, a feature explained by a lack of interaction between the cluster LUMO and the capping ligand MOs. The isocyanide clusters showed two ν(CN) bands as a result of Fermi resonance effects.[238] MO calculations rationalised differences between complexes containing π-acceptor (halide) and π-donor (isocyanide) capping ligands.

Reaction between LiMe and Ni(acac)Cp* gave paramagnetic (49-e) $Ni_3(\mu\text{-}H)(\mu_3\text{-}CH)Cp^*_3$.[214] Cubane $Ni_4\{\mu_3\text{-}P[Cr(CO)_5]\}(\mu_3\text{-}P)_3Cp^*_4$ was formed by heating the major product obtained from a reaction between P_4, $Cr(CO)_5(thf)$ and $\{Ni(\mu\text{-}CO)Cp^*\}_2$.[239]

Degradation of $[Ni_{38}C_6(CO)_{42}]^{6-}$ (CO, 1 atm) or thermolysis of $[Ni_{10}C_2(CO)_{16}]^{2-}$ (diglyme, 110°C) gave $[Ni_{32}C_6(\mu\text{-}CO)_{36}]^{6-}$, which contains an outer Ni_{24} truncated octahedron enclosing an Ni_8 cube capped on each face by C. All CO groups are edge-bridging, stabilising the $[Ni_{32}C_6]^{6-}$ unit, which is isoelectronic with the $Cr_{32}C_6$ unit in $Cr_{23}C_6$.[240]

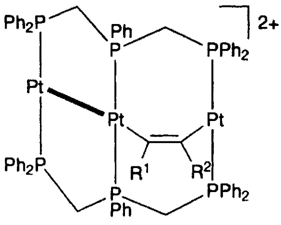
12.2 Palladium – The DFT-calculated ground state geometry of $[Pd(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ is in excellent agreement with the experimental structure. In the $^3A_2$ excited state, a predicted lengthening of *ca* 0.19 Å in the Pd-Pd separations has been confirmed by analysis of its emission band.[241] The cluster contains a large cavity formed by the Ph groups and the binding capacity for halide (I > Br > Cl) was determined.[242] Replacement of P by As results in enlargement of the Ph_6-cavity in $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}dpam)_3]^{2+}$ with resulting increase in bonding constants for a variety of neutral and anionic substrates.[243] An X-ray structure of the hexafluorophosphate shows the counter-anion inside the cavity. A further effect of replacing dppm by dpam is the facile oxidation of $[Pd_3(\mu_3\text{-}I)(\mu_3\text{-}CO)(\mu\text{-}dpam)_3]^{2+}$ to $Pd_2(\mu\text{-}dpam)_2I_4$.

With $PPh_n\{C_6H_3(OMe)_2\text{-}2,6\}_{3-n}$ ($n = 1,2$) and $[Pd_3(CNxy)_8]^{2+}$, substituted clusters $[Pd_3(CNxy)_8(PR_3)_2]^{2+}$ were obtained, but with n = 0, cluster fragmentation resulted to give $[Pd_2(CNxy)_4(PR_3)_2]^{2+}$.[244]

Formation of $Pd_4(\mu_3\text{-}CR)(\mu\text{-}Cl)_3(PBu^t_3)_4$ (R = H, F) occurs on reaction of $Pd_2(dba)_3$, PBu^t_3 and $CRCl_3$. Substitution by Br^- or PR_3 occurs and the clusters are catalyst precursors for ethene polymerisation.[245] The isomerism of $\{Pd(\mu\text{-}O_2CR)(\mu\text{-}CO)\}_4$, whereby the metal framework may change from square (R = Ph) through rectangular (R = Bu^t) to rhomboidal (R = CF_3) as R changes, was investigated by quantum chemical methods.[246] The chemistry of these complexes, and of the related $\mu\text{-}CPh_2$ cluster, has been summarised.[247] Addition of a Pd-C_6F_5 unit to the vinyl group of $PhSCH{=}CH_2$ gives a three-membered palladacycle which isomerises to a tetrameric complex: crystals of the *meso* form were obtained stereospecifically.[248]

12.3 Platinum – Reactions of $[Pt_3(CNxy)_8]^{2+}$ with PR_3 ($R_3 = Ph_{3-n}[C_6H_3\text{-}(OMe)_2\text{-}2,6]$, n = 1-3) gave $[Pt_3(CNxy)_8(PR_3)_2]^{2+}$.[244] A variety of complexes have been obtained from $[Pt_3(\mu\text{-}dpmp)_2(CNxy)_2]^{2+}$ [dpmp = $PPh(CH_2PPh_2)_2$] and small ions or molecules, such as H^+ or CNR.[249] Electron-deficient alkynes gave $[Pt_3(\mu\text{-}dpmp)(\mu\text{-}R^1C_2R^2)(CNxy)_2]^{2+}$ (**135**; R^1, R^2 = H, CO_2Me) with A-frame structures. Combination of $MCl_2(cod)$ (M = Pd, Pt) with $[Pt_2(\mu\text{-}dpmp)_2(CNxy)_2]^{2+}$ gave the related cations $[MPt_2(\mu\text{-}dpmp)_2Cl_2(CNxy)_2]^{2+}$.

The 44-e cluster $Pt_3H(\mu\text{-}P^tBu_2)_3(CO)_2$ is obtained from $Pt_2H_2(\mu\text{-}P^tBu_2)_2(BH^tBu_2)_2$ and CO (1 atm.); formally it contains an open $Pt^{I}_2Pt^{II}$ cluster. It forms by equilibration of $Pt(CO)_2(PH^tBu_2)_2$ and $Pt_3(\mu\text{-}CO)_3(PH^tBu_2)_3$, which are produced under high pressure, while in the presence of free PR_3, $Pt(CO)(PR_3)_3$ (R = Et, Ph) are formed.[250] An unusual $\mu_3\text{-}PPh_2$ group is present in the open Pt_3 cluster anion $[Pt_3(\mu\text{-}PPh_2)_2(C_6F_5)_5]^-$ (**136**), obtained from *cis*-$Pt(C_6F_5)_2(thf)_2$ and $[Pt_2(\mu\text{-}PPh_2)_2(C_6F_5)_4]^{2-}$. One of the Ph groups is involved in an η^2 interaction with an outer Pt atom, while one of the C_6F_5 ligands semi-bridges a Pt-Pt vector.[251]



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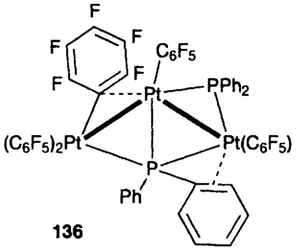

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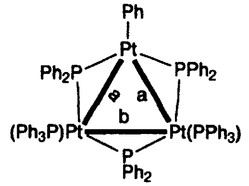
An extensive synthetic and theoretical study of $Pt_3(\mu\text{-}PPh_2)_3(Ph)(PPh_3)_2$, of which at least four isomeric forms are known (**137**), has been reported.[252] The compounds are made by thermolysis of $Pt(\eta\text{-}C_2H_4)(PPh_3)_2$, followed by recrystallisation from various solvents. Structural comparisons are made for 34 Pt_3L_n [n = 6 (42-e), 7 (44-e)] complexes. The isomerism results from reversible Pt-Pt bond-breaking and -making reactions, while changes from 42-e to 44-e systems result in lengthening of the Pt-Pt separations. EH MO calculations suggest relative stabilities in aggreement with observation. Replacement of a PR_3 ligand by a better σ-donor (Ph) seems to be the reason for the existence of two structural isomers although the isomerism is a result of the flexibility of the $\mu\text{-}PR_2$ ligands. Oxidation of (**137**) with I_2 leads to recombination of PPh_2 and Ph ligands to give $[Pt_3(\mu\text{-}I)(\mu\text{-}PPh_2)(PPh_3)_3]I$.[253]

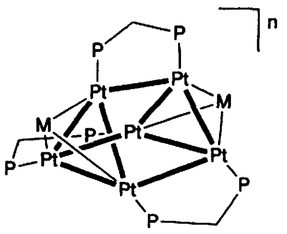
Complexes containing two Pt_3 clusters linked by bidentate phosphines $PPh_2(CH_2)_nPPh_2$ (P-P), are formed from $PtCl_2(SMe_2)_2$, P-P and $NaBH_4$ under CO. With n = 2 and 3, the closed $Pt_6(\mu\text{-}dppe)_3(\mu\text{-}CO)_6$ and open $\{Pt_3(\mu\text{-}CO)_3(dppp)\}_2(\mu\text{-}dppp)_2$ clusters, respectively, were obtained.[254,255]

A new type of reaction, bi-cluster oxidative addition, has been used to make 86-e Pt_6 clusters. The reaction has analogies in oxidative addition to mono- and bi-nuclear complexes, where new bonds to the metal (including new M-M bonds in the latter) are formed. Suitable precursors are $\{Pt_3(\mu\text{-}CO)_3\}_2(\mu\text{-}dppm)_3$ (84-e) and $[Pt_6(\mu\text{-}dppm)_3(CO)_6]^{2+}$ (82-e). Either of these reacts with $[SnX_3]^-$ (X = F, Cl, Br) or HgX_2 (X = Cl, Br, I) to give (**138**), containing capped trigonal prismatic cores.[256]



Isomer	a	b
1	2.785	3.630
2	2.758	3.586
3	2.956	3.074

137



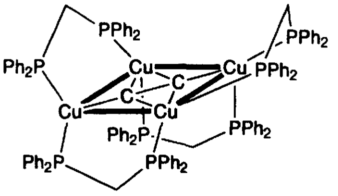
138 M = SnX_3, n = −1
M = Hg, n = 0

13 Group 11

Tetrameric copper(I) aryls, Cu_4Ar_4, are formed from the lithio derivatives and $\{Cu(SC_6H_4NMe_2\text{-}2)\}_3$; in the presence of CuBr, complexes Cu_3BrAr_2 or $Cu_4Br_2Ar_2$ are formed [Ar = $C_6H_4CH_2NMe_2$-2, $C_6H_4\{CH_2NMe(CH_2)_2NMe_2\}$-2, 1-$C_{10}H_6\{CH_2NMe(CH_2)_2NMe_2$-2]. The structures of the aggregates are described as $[CuAr_2]^-$ units stabilised by $[Cu_2Br]^+$ or $[Cu_3Br_2]^+$ cations.[257]

Long-lived photoluminescent behaviour is exhibited by $[Cu_3(\mu_3\text{-}C_2R)_n(\mu\text{-}dppm)_3]^{3-n}$ (n = 1, 2; R = Bu^t, Ph); the new complex (n = 1, R = Bu^t) was obtained from the reaction between $[Cu_2(NCMe)_2(\mu\text{-}dppm)_2]^{2+}$ and $LiC{\equiv}CBu^t$.[258] The related complex $Cu_4(\mu_3\text{-}C{\equiv}CC_6H_4OMe\text{-}4)_3(PPh_3)_4]^+$, which also shows luminescence, was prepared from $[Cu(NCMe)_4]^+/PPh_3$ and $\{Au(C{\equiv}CC_6H_4OMe\text{-}4)\}_n$. It contains an open-cube structure, with Cu...Cu distances of between 2.45 and 2.47 Å.[259] Several related complexes $Cu_4(\mu_3\text{-}C{\equiv}CPh)_4(PR_3)_4$ (R = Ph, tol, C_6H_4F-4, C_6H_4OMe-4) show a rich photoluminescent behaviour; in these complexes, the acetylide ligand is attached by the terminal C atom and the Cu...Cu distances are between 2.56-2.61 Å.[260] Addition of $LiC{\equiv}CSiMe_3$ to $[Cu_2(\mu\text{-}dppm)_2(NCMe)_2]^{2+}$ give the unusual cluster (**139**), which contains a C_2 ligand sitting almost in the plane of a distorted Cu_4 rectangle, in which the Cu...Cu separations are between 3.245 and 3.264 Å.[261] Intense green and yellow-green emissions occur on excitation with λ > 350 nm radiation.

Solid-state structures of $Ag(C_2R)(PR_3)$ often result from aggregation of



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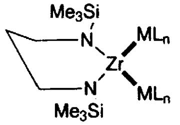
$[Ag(PR_3)_2]^+$ and $[Ag(C_2R)_2]^-$ units. For R = Ph, the Ag_4 core is a flattened butterfly, with the hinge atoms attached to the C_2Ph groups, whereas polymeric chains are found for R = $SiMe_3$.[262] However, it is the bulk of the phosphine ligands which determines the final structure. Ag...Ag separations of 2.866, 2.983 Å are present in $[Ag_3(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_2(\mu\text{-dppm})_3]Cl$, obtained from $\{Ag(CPh)\}_n$ and dppm in CH_2Cl_2. EH MO calculations show that the HOMO contains contributions from Ag and C_2Ph, while the LUMO is the π^* orbitals of the C_2Ph ligands. Solid-state emission occurs at 555 nm (lifetime 0.4 ms).[263]

Aurophilicity (the tendency to form Au-Au bonding interactions in gold complexes) has been reviewed in many different contexts,[264] including clusters, infinite and catenane compounds[265] and the chemistry of trinuclear Au(I) complexes.[266] EH MO calculations on a variety of Au_n clusters show that Au-Au interactions are influenced mostly by the formal oxidation state, the ligand donor atoms and the nature of the bridging ligands. Weak Au-Au interactions occur in Au(I) complexes by virtue of mixing of *s* and *p* with *d* orbitals. In $Au_5(\mu\text{-mes})_5$, stronger interactions are present. The calculations allow formal oxidation states to be assigned to the mixed-valence clusters $[Au_4(C_6F_5)_2\{CH(PPh_2)_2\}(PPh_3)_2]^{2+}$, $[(C_6F_5)_2Au\{Au_2[\mu\text{-}(CH_2)_2PPh_2]_2\}_2]^+$ and $[Ar\{Au_2[\mu\text{-}(CH_2)_2PPh_2]_2\}_3Ar]^{2+}$ (Ar = $C_6H_2F_3$-2,4,6), where the outer Au atoms are more highly oxidised.[267]

The [2]catenane $\{Au(C{\equiv}CBu^t\}_n$ contains interlocked hexameric rings; the Au-Au interactions are weak, but are probably a cause of the assembly of this unusual complex.[268] In $[\{Au(PPh_3)\}_4\{CS(O)Me_2\}]^{2+}$, obtained from $[Me_3S{=}O]^+$ and $Au(acac)(PPh_3)$, followed by reaction with $AuCl(PPh_3)/AgClO_4$, the four Au atoms form the base of a CAu_4 square pyramid. Hypermetallation of the Me group of the precursor is aided by aurophilicity.[269] Reaction of $AuCl(PMe_2Ph)$ and $GeCl_2$(dioxane) led to self-assembly of $\{[Au(PMe_2Ph)_2]^+[Au(GeCl_3)_2]^-\}_2$, containing an Au_4 chain.[270]

14 Heterometallic Clusters

Zr-Fe, Ru, Co – The complex $ZrCl_2(thf)_2\{[N(SiMe_3)CH_2]_2CH_2\}_2$ has been used to prepare polar metal sequences ZrM_2 (**140**; ML_n = Fe, Ru, Co) by reactions with $[Fe(CO)_2Cp]^-$, $[Ru(CO)_2Cp]^-$, or $[Co(CO)_3(PPh_3)]^-$.[271] Rapid rotation of the Fe/Ru fragments about the M-Zr bond shows little steric interaction with the amide substituents. Redistribution between the chloride and the $Zr(Fe/Ru)_2$ compounds gives the Cl-Zr-M complexes, while CNMe (but not CO) inserts into one Zr-Fe/Ru bond to give μ-η^1:η^2-CNMe complexes.



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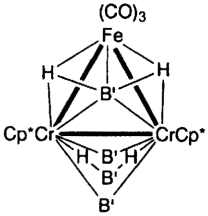
Ti-Rh – Reaction of $Ti(SH)_2Cp_2$ with $\{Rh(\mu\text{-}OMe)(tfbb)\}_2$ affords the incomplete cubane $CpTi\{(\mu\text{-}S)Rh(tfbb)\}_3$, from which the tfbb can be displaced by CO or CO/PPh_3.[272]

Mo, W-Re – The tetrahedral cluster anion $[Mo_3Re(\mu_3\text{-}H)(CO)_{12}]^{3-}$ was obtained from $[ReH_9]^{2-}$ and $Mo(CO)_3$(diglyme); some of the CO groups, but none of the H ligands, are fluxional.[273] Fragmentation of $Re_2W(\mu_3\text{-}C_2Ph)(O)(CO)_8Cp^*$ occurs during the reaction with PhSH to give $ReW(\mu\text{-}H)(\mu\text{-}CCPh)(O)(CO)_4Cp^*$.[274]

Cr, Mo, W-Fe – The electron-deficient chromaborane $\{CrCp^*\}_2B_4H_8$ reacts with $Fe_2(CO)_9$ to coordinate an $Fe(CO)_3$ fragment in (**141**). The complex undergoes a fluxional process whereby the $Fe(CO)_3$ unit swings between two pairs of B-H groups.[275]

Reactions of $Fe_2(\mu\text{-}EE')(CO)_6$ (E, E′ = S, Se, Te) with $M(CO)_5$(thf) (M = Mo, W) afford $Fe_2M(\mu_3\text{-}E)(\mu_3\text{-}E')(CO)_{10}$, containing square pyramidal M/Fe_2EE' cores.[23,276,277] In contrast, a bent FeMoFe sequence is present in $Fe_4Mo(\mu_3\text{-}Se)_2(\mu_3\text{-}Te)_2(CO)_{14}$ (**142**), obtained from $Fe_2(\mu\text{-}SeTe)(CO)_6$. Several Mo-Fe clusters were obtained by heating a mixture of $\{Mo(CO)_3Cp\}_2$ and $Fe_3(\mu_3\text{-}S)(\mu_3\text{-}Te)(CO)_9$, including $Fe_2Mo_2(\mu_3\text{-}S)(\mu_3\text{-}Te)(CO)_7Cp_2$ (**143**; major product), $Fe_2Mo_2(\mu_4\text{-}Te)(\mu_3\text{-}E)(\mu_3\text{-}E')(CO)_6Cp_2$ (**144**; E = E′ = S, Te; E = S, E′ = Te), $Fe_2Mo_2(\mu_3\text{-}S)(\mu_3\text{-}Te)(CO)_7Cp_2$ and $FeMo_2(\mu_3\text{-}E)(CO)_7Cp_2$ (E = S, Te).[278] Complex (**143**) reacts with Se to give a cluster containing all three chalcogens, $Fe_2Mo_2(\mu_4\text{-}Te)(\mu_3\text{-}S)(\mu_3\text{-}Se)(CO)_7Cp_2$. The two major products of the reaction between $\{W(CO)_3Cp\}_2$ and $Fe_3(\mu\text{-}H)_2(\mu_3\text{-}Se)(CO)_9$ are $Fe_2W(\mu\text{-}H)(\mu_3\text{-}Se)(CO)_8Cp$ and $FeW_2(\mu_3\text{-}Se)(CO)_7Cp_2$.[279]



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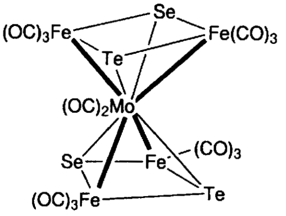

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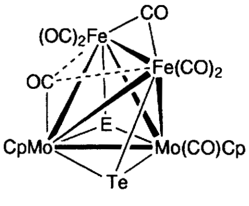

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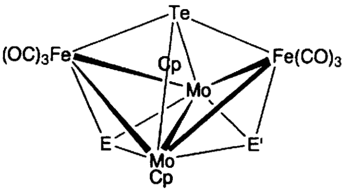

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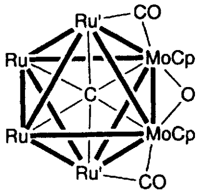
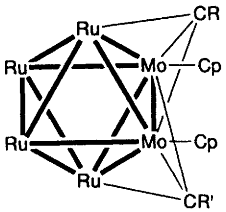
Mo-Ru – The oxo-carbido cluster (**145**) has been obtained from $Ru_3(CO)_{12}$ and $\{Mo(CO)_2Cp\}_2$ in refluxing toluene; the crystal contains two isomers, one (shown) with two μ-CO ligands on Mo-Ru edges, the other with two weakly semi-bridging CO groups on Ru-Ru edges.[280]

The orange vinylidene complexes $Mo_2Ru(\mu\text{-}C{=}CHR)(CO)_7Cp_2$ (R = H Me, Ph, CO_2Me) have been obtained from $Mo_2(\mu\text{-}HC_2R)(CO)_4Cp_2$ and $Ru_3(CO)_{12}$; the organic ligand is π-bonded to the Ru atom.[281] In addition, blue 84-e clusters $Mo_2Ru_4(\mu_3\text{-}CH)(\mu_3\text{-}CR)(CO)_{12}Cp_2$ (**146**) are formed in smaller amounts; a similar complex is obtained from C_2Me_2.



145 Ru = $Ru(CO)_3$
Ru' = $Ru(CO)_2$



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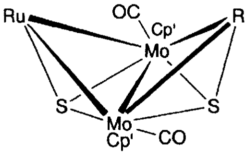
Reactions of $\{Mo(\mu\text{-}SPh)(CO)(Cp^R)\}_2$ (R = H, CO_2Me) with $Ru_3(CO)_{12}$ (refluxing xylene) gave $Mo_2Ru_2(\mu_3\text{-}S)_2(CO)_6(Cp^R)_2$ (**147**).[282] Similarly, the carbonyl-free compounds $\{Mo(\mu\text{-}S)(\mu\text{-}SR)Cp\}_2$ (R = Et, Pr^i) give $Mo_2Ru_2(\mu_3\text{-}S)_2(\mu\text{-}SR)_2(CO)_4Cp_2$ (**148**), containing a tetrahedral core.[283] Complexes $MRu_2(\mu_3\text{-}S)(\mu\text{-}S_2)(\mu\text{-}S)_2(S)Cp^*_2$ (**149**; M = Mo, W) are formed from $[MS_4]^{2-}$ and $\{Ru(\mu\text{-}Cl)ClCp^*\}_2$; with PEt_3, conversion to $W\{(\mu\text{-}S)_2Ru(PEt_3)Cp^*\}_2$ occurs.[284]



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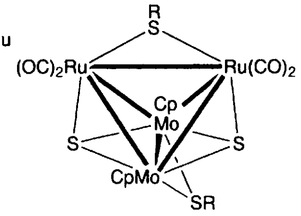

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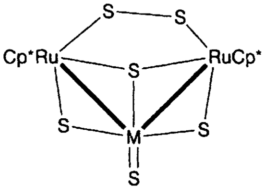

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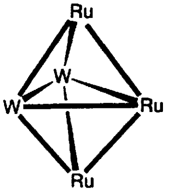
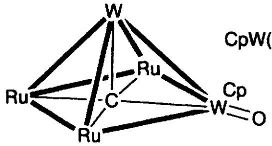
W-Ru – Pentanuclear $Ru_3W_2(CO)_{13}Cp_2$ (**150**) was prepared from $Ru_3W(\mu\text{-}H)(CO)_{12}Cp$ and $WH(CO)_3Cp$[285] and was shown to be the complex obtained earlier from a photochemical reaction between $Ru_3(CO)_9(BH_5)$ and $\{W(CO)_3Cp\}_2$.[286] On heating, slow loss of CO afforded the 76-e oxo-carbido cluster $Ru_3W_2(\mu_5\text{-}C)(O)(CO)_{11}Cp_2$ (**151**). The short W≡O bond (1.70 Å) is consistent with the O acting as a 4-e donor. Related clusters were obtained by thermal condensation of $Ru_3W(\mu\text{-}H)(CO)_{12}(L)$ and $WH(CO)_3(L')$ (L, L′ = Cp, Cp*). Labelling studies showed the C and O atoms come from cleavage of CO, perhaps by μ_4-η^2-interaction in an unobserved intermediate.

Reaction of $Ru_3\{\mu_3\text{-}HC_2C{\equiv}C[W(CO)_3Cp]\}(\mu\text{-}CO)(CO)_9$ with excess $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ results in an unusual addition with incorporation of two CO ligands to form the dimeric ligand found in **152**.[88] The presence of the carbenic interaction with W suggests that electronic rearrangement of the diynyl ligand to a dicarbene may occur during the course of the reaction.



150 Ru = $Ru(CO)_3$
W = $W(CO)_2Cp$



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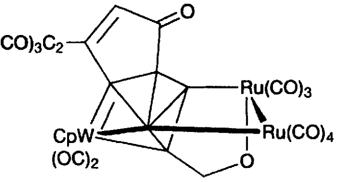

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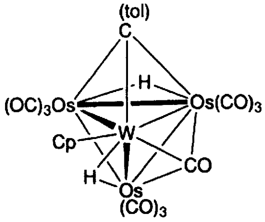
W-Os – Reaction of $Os_3W\{\mu_3\text{-}C(tol)\}(CO)_{11}Cp$ with H_2 gives $Os_3W(\mu\text{-}H)_2\{\mu_3\text{-}C(tol)\}(CO)_{10}Cp$ (**153**; 60-e butterfly), while reaction with water affords $Os_3W\{\mu_3\text{-}C(tol)\}(O)(CO)_{10}Cp$ (**154**).[287] Reductive elimination of H_2 from (**153**) occurs with CO, but PPh_3 adds to give $Os_3W(\mu\text{-}H)_2\{\mu_3\text{-}C(tol)\}(CO)_{10}(PPh_3)Cp$ (**155**; 62-e butterfly). In the presence of water, thermolysis of (**153**) gives *syn*-$Os_3(\mu\text{-}H)(\mu\text{-}O)\{\mu\text{-}CH(tol)\}(CO)_9Cp$ (**156**), while thermolysis of (**154**) gives $Os_3W\{\mu_3\text{-}C(tol)\}(\mu\text{-}O)(CO)_9Cp$ (tetrahedral), which reacts with H_2 to give two isomers of *anti*-$Os_3W(\mu\text{-}H)$ $(\mu\text{-}O)\{\mu\text{-}CH(tol)\}(CO)_9Cp$ (**157**), which are converted to (**156**) in refluxing toluene.[287] Coupling of CO and $HC{\equiv}CPh$ occurs to give $Os_3W(\mu\text{-}H)\{\mu_3\text{-}CHCPhC(OH)\}(CO)_{12}$ in the reaction of the alkyne with $[Os_3W(\mu\text{-}H)(CO)_{14}]^-$.[288] This paper also describes several reactions of the Os_3W anion with Ag^I, Au^I and pyridine to give Os_3 clusters.

Cr-Rh. The Cr-spiked Rh_4 butterfly cluster (**158**) is formed from $Rh_4(CO)_{12}$ and $Cr(CO)_3(\eta^6\text{-}PhC{\equiv}CPh)$, the Cr acting as a 2-e donor to the Rh atom. Other



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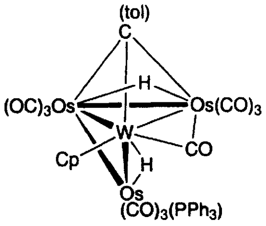

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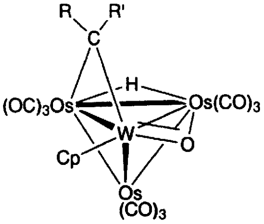
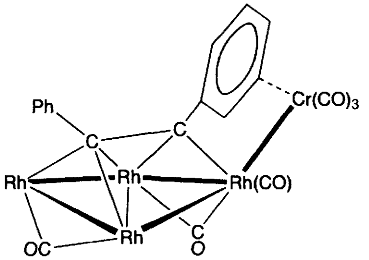
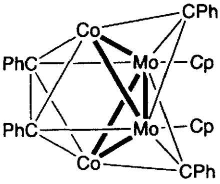


156 *syn* R = H, R' = tol
157 *anti* R = tol, R' = H

unusual interactions of the Rh atoms, with two Cr-bonded CO groups and with the C≡C triple bond, are also present.[289] The product contrasts with that obtained from $Co_4(CO)_{12}$, which is the conventional $Co_2\{\mu\text{-}\eta^2\text{-}PhC_2(\eta^6\text{-}Ph[Cr(CO)_3])\}(CO)_6$ complex.



158 Rh = Rh(CO)2



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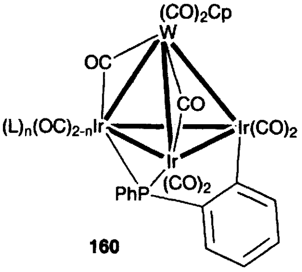
Mo-Co – EH MO calculations were used to study barriers to rotation in $Co_2Mo(\mu_3\text{-}CH)(CO)_8Cp$; the process involves rotation of the $Mo(CO)_2Cp$ fragment about an axis joining the Mo to the centre of the CCo_2Mo tetrahedron.[290]

Two routes to $Co_2Mo_2(\mu_4\text{-}C_2Ph_2)(\mu_3\text{-}CPh)_2(CO)_4Cp_2$ (**159**) involve heating of mixtures of $Co_2(\mu\text{-}C_2Ph_2)(CO)_6$ with $Mo_2(\mu\text{-}C_2Ph_2)(CO)_4Cp_2$, or of $Mo_2(\mu\text{-}C_4Ph_4)(CO)Cp_2$ with $Co_2(CO)_8$: the facility of the latter reaction, which results in the formation of one C_2Ph_2 and two CPh fragments from C_4Ph_4, suggests the intermediacy of the latter in the first reaction.[291] Clusters containing $C_2Co_2Mo_2$ cores were also obtained from $Co_2(CO)_8$ and $Mo_2(\mu\text{-}C_2R_2)(CO)_4Cp_2$ (R = H, Me, Ph, CO_2Me); the Co atoms occupy the hinge positions of the M_4 butterfly.[292] Reactions of organosulfur compounds with $Co_2Mo_2S_3(CO)_4Cp_2$ and $Co_2Mo_2S_4(CO)_2Cp_2$ which result in C-S bond cleavage have been reviewed in the context of hydrodesulfurisation reactions over CoMoS catalysts.[293]

W-Ir – Site-selective substitution of CO-*Ir* by tertiary phosphines in $Ir_3W(CO)_{11}Cp$ has been reported.[294] The products contain three μ-CO ligands, either around an Ir_2W face (PPh_3) or around the Ir_3 face (PMe_3). Fluxionality can be frozen out at 230 K, and the crystallographic results are applied to the general assignment of coordination geometry for related complexes. Thermolysis of the mono- and di-PPh_3 complexes gave $Ir_3W\{\mu_3\text{-}\eta^2\text{-}PPh(C_6H_4)\}(\mu\text{-}CO)_2(CO)_{7\text{-}n}(PPh_3)_nCp$ (**160**; n = 1 or 2, respectively); the tris-PPh_3 derivative gave a mixture.[158] Also formed from the mono-PPh_3 complex was $Ir_3W(CO)_{11}Cp$ (32%). Heating $Ir_2W_2(CO)_{10}Cp_2$ in the presence of NPh_3 gave the bicapped t.b.p. cluster $Ir_4W_3(\mu\text{-}H)(CO)_{12}Cp_3$ (**161**).[295]



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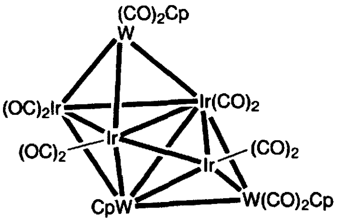

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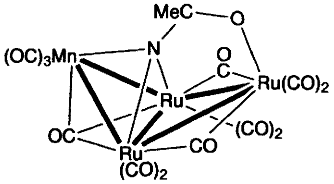
Mo, W-Ni – Mixed $Mo_nW_{3-n}Ni$ (n = 0-3) clusters $[M_3Ni(\mu_3\text{-}S)_4(OH_2)_{10}]^{4+}$ take up C_2H_4 in aqueous or polar organic solutions to give the corresponding π-complex, the W-containing clusters being the more reactive; the C_2H_4 coordinates to the Ni site, which has a formal oxidation state of +2.[296]

Mn, Re-Fe – So-called 'xenophilic' clusters contain metal carbonyl or related fragments containing π-acid ligands attached to metals bonded to ligands that have no π-acid properties. A new example is paramagnetic (4 unpaired electrons) $Fe_2Mn_2(CO)_8(thf)_4$, obtained from $Mn\{Mn_7(thf)_6(CO)_{12}\}_2$ and $Fe(CO)_5$. The Fe-Mn separations are nearly 0.2 Å shorter than those found in $FeMn_2(CO)_{14}$ and the electron distribution is consistent with a covalent model with substantial polar character for the Fe and Mn components.[297]

The products of reaction of $[Re(CO)_5]^-$ and $[Fe_3\{\mu_3\text{-}C_2OC(O)Me\}(CO)_9]^-$ are the metallated acetylide $[Fe_3\{\mu_3\text{-}C_2[Re(CO)_5]\}(CO)_9]^-$ and homometallic $[Fe_3(\mu_3\text{-}CCO)(CO)_9]^-$.[298]

Mn, Re-Ru – The unstable $[Ru_3(\mu_3\text{-}O)(CO)_9]^{2-}$ was used to prepare Mn- and Re-containing clusters by reaction with $[M(CO)_3(NCMe)_3]^+$, but the products (**162**) contain μ_3-NC(O)Me ligands, formed by attack of the highly nucleophilic μ_3-O ligand on coordinated MeCN.[128]



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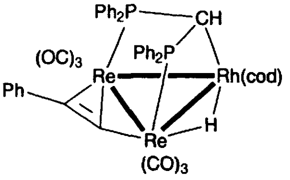

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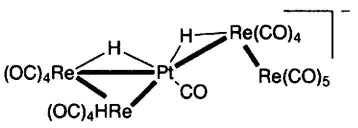
Re-Rh. Metallation of $Re_2(\mu\text{-}H)(\mu\text{-}dppm)(\mu\text{-}C_2Ph)(CO)_6$ with LiMe, followed by addition of $\{Rh(\mu\text{-}Cl)(cod)\}_2$, gave $Re_2Rh\{\mu_3\text{-}CH(PPh_2)_2\}(\mu\text{-}C_2Ph)(CO)_6(cod)$ (**163**).[299]

Substitution of $[Re_7RhC(CO)_{23}]^{2-}$ by a range of PR_3 occurs exclusively at Rh and is first order both in cluster and in phosphine. Comparison of reaction rates with those of $Rh(CO)_2(Cp^X)$ showed that the Rh centre in the cluster is less electron-rich than in the mononuclear complex, leading to faster substitution rates in the cluster.[300]

Re-Pt – Anionic Re- and Re_2-spiked $PtRe_2$ clusters have been obtained from $PtRe_3H(\mu\text{-}H)_2(CO)_{14}$ **(164)** by deprotonation: OH^-/MeOH gives $[PtRe_3H(\mu\text{-}H)(CO)_{14}]^-$ **(165)**, via an intermediate CO_2Me complex, together with $[PtRe_4H(\mu\text{-}H)_2(CO)_{18}]^-$ **(166)**.[301] A minor product is the bow-tie custer $[PtRe_4(\mu\text{-}H)_5(CO)_{16}]^-$. Alternative routes to **(165)** and **(166)** involve treatment of $PtRe_2(\mu\text{-}H)_2(CO)_8$(cod)/CO with $[Re(CO)_5]^-$ or $[HRe_2(CO)_9]^-$ (from $HRe(CO)_5$ and $[Re(CO)_5]^-$), respectively, while **(164)** is also converted to **(165)** by reaction with $[Re(CO)_5]^-$.



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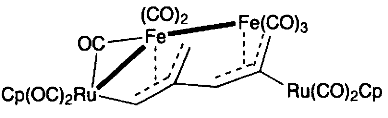


167

Fe-Ru – Among the products of reactions of $Fe_2(CO)_9$ with $Ru(CH{=}C{=}CH_2)(CO)_2Cp$ are Fe_2Ru clusters containing $\mu_3\text{-}C(CH{=}CH_2)$ and $\mu_3\text{-}CHC(CH_2)CHC\{Ru(CO)_2Cp\}CH_2$ ligands.[302] The former may be $\mu\eta^1$ or $\mu_3\text{-}\eta^1{:}\eta^3$ (the latter formed by displacement of CO by the C=C double bond); in solution, the two forms are in equilibrium. The latter bridges a bent $RuFe_2$ chain in the $\eta^1{:}\eta^3{:}\eta^3$ mode. Related C(CH=CHPh) complexes were described in 1994.[303] Reaction of the $\mu_3\text{-}\eta^1$ compound with PPh_3 leads to substitution at Fe and coordination of the C=C double bond. Also formed is $Fe_2Ru_2(\mu_4\text{-}C_6H_6)(\mu\text{-}CO)(CO)_8Cp_2$ **(167)**, in which the $CHC(CH_2)CHCCH_2$ ligand, formed by β-γ coupling of two allenyl ligands, is η^3-bonded to each Fe atom and η^1-bonded to each Ru.[304]

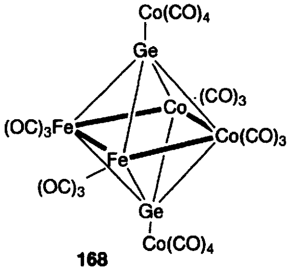
Fe-Co – Several mixed Fe-Co clusters containing borane ligands have been obtained from reactions between $Co_2(CO)_8$ and ferraboranes. Replacement of HFe by Co in the cluster results in a decrease in mobility of H atoms and their avoidance of the more electronegative Co atoms. Clusters containing $CoFe_2(BH_2)$ and $Co_2Fe(BH)$ cores were isolated, together with two isomeric systems with $HFe_3Co(BH)$ and $Fe_3Co(BH_2)$ units.[305]

Reactions of $Co_3\{\mu_3\text{-}C(CO_2R)\}(CO)_9$ (R = Me, Et) with $Na_2Fe(CO)_4$ gave the expected $Co_2Fe(\mu\text{-}H)\{\mu_3\text{-}C(CO_2R)\}(CO)_9$ together with the coupled products $Co_2Fe\{\mu_3\text{-}C_2(CO_2R)_2\}(CO)_9$ and homo-metallic $Co_4\{\mu_4\text{-}C_2(CO_2R)_2\}(CO)_{10}$.[306]

Among the pyrolysis products of $Fe_2\{\mu_4\text{-}Ge[Co_2(CO)_7]\}_2(\mu\text{-}CO)(CO)_6$ were **(168)** and $Fe_3\{\mu_3\text{-}Ge[Co(CO)_4]\}_2(CO)_9$.[307] Only very low yields of $Co_2Fe(\mu_3\text{-}$

NO)(μ_3-NH)Cp$^*_3$ were obtained from Co(η-C_2H_4)$_2$Cp* and {Fe(μ-NO)Cp*}$_2$.[217]

Reactions of $Co_2Fe(\mu_3\text{-}S)(CO)_9$ with PPh_2CH_2SR (R = Me, Ph) give green $Co_2Fe(\mu_3\text{-}S)(\mu\text{-}PPh_2CH_2SR)(CO)_7$ in which the Co-Co bond is bridged; in solution, CO displaces the SR group, but these brown $(CO)_8$ complexes could not be isolated.[308] Reactions of $Fe_2(\mu\text{-}STe)(CO)_6$ with $Co(CO)_2Cp$ gave $CoFe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)(CO)_6Cp$; the X-ray structure of the (μ_3-Se)(μ_3-Te) analogue is reported.[309] Direct reaction of $FeCl(CO)_2Cp$ with $CoFe_2(\mu\text{-}H)(\mu_3\text{-}S)(CO)_9$ (thf, r.t.) gave $CoFe_2\{\mu_4\text{-}S[Fe(CO)_2Cp]\}(CO)_9$.[310] EH MO studies of rotation of the $Fe(CO)_3$ fragment in $Co_2Fe(\mu_3\text{-}S)(CO)_9$ confirm a weakening of the Co-Fe bonds.[290]



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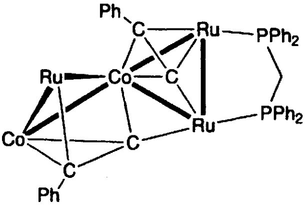

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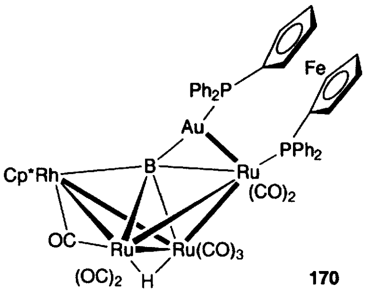
Ru-Co – The product (**169**) from $Co_2(CO)_8$ and $Ru_3(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)(\mu\text{-}dppm)(CO)_8$ contains a twisted bow-tie core. The original diyne has cleaved at the central C-C bond to give μ_3- and μ_4-C_2Ph ligands.[311]

Reactions of $CoRu_3(\mu\text{-}H)_3(CO)_{12}$ and $Co_3Ru(\mu\text{-}H)(CO)_{12}$ with $HC(PPh_2)_3$ gave derivatives in which the triphosphine caps $CoRu_2$ and Co_3 faces, respectively.[312] The product from reaction of the $CoRu_3$-triphosphine complex with PMe_2Ph contains the triphosphine as an η^2-chelate to one Ru and the PMe_2Ph attached to a second Ru atom. With $Co_3Ru(\mu\text{-}H)\{\mu_3\text{-}(PPh_2)_3CH\text{-}\mathit{Co}\}(CO)_9$, substitution of a CO group on the Ru atom occurs, the triphosphine remaining capping the Co_3 face.[313]

Ru-Rh, Ir. Reaction of $Ru_3(CO)_{12}$ with $[Rh(CO)_4]^-$ gives tetrahedral $[Rh_2Ru_2(\mu\text{-}CO)_4(CO)_8]^{2-}$, which with acids gives $[Rh_2Ru_2(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_9]^-$. Difficulties in Rh/Ru distinction in the X-ray studies were partially overcome by considerations of local stereochemistry and geometries of semi-bridging CO groups. Fluxional CO exchange is not frozen at 178 K.[314] The butterfly cluster $IrRu_3(\mu\text{-}H)_2(\mu\text{-}Cl)(CO)_{12}$ is obtained from $\{IrCl(CO)_3\}_n$ and $[Ru_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$; the Cl bridges the wing-tip Ru atoms, while the H atoms bridge Ru-Ru edges.[315]

The 78-e cluster $RhRu_4B(H)_2(\mu\text{-}Cl)(CO)_{12}Cp^*$ is formed from $[Ru_4(\mu\text{-}BH)(\mu\text{-}H)(CO)_{12}]^-$ and $\{RhCl_2Cp^*\}_2$; the $RhRu_4$ core forms an edge-bridged square (envelope).[316] Addition of bidentate phosphines dppf and dppa to $RhRu_3(\mu\text{-}H)(\mu\text{-}BH_2)(CO)_9Cp^*$ gave the mono-substituted complexes, in which one H atom has migrated from B to the cluster. The dppf derivative reacts with [ppn]Cl/ $(AuCl)_2(\mu\text{-dppf})$ to give **(170)**, although some $RhRu_3B(\mu\text{-H})_3(\mu\text{-dppf})(CO)_7Cp^*$ is also formed.[317]



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The reaction between $\{Ru(\mu\text{-SH})ClCp^*\}_2$ and $RhCl(PPh_3)_3$ afforded $RhRu_2(\mu\text{-}H)(\mu_3\text{-}S)_2Cl_2(PPh_3)Cp^*{}_2$.[79]

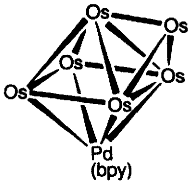
Fe-Pt – The clusters $Fe_2Pt(CO)_8(dppp)$ and $Fe_3Pt(\mu_4\text{-}C{=}CHPh)(CO)_9(dppp)$ are among the products formed in stepwise reactions from $Fe_2(CO)_9$ and $MnPt(\mu\text{-}C{=}CHPh)(CO)_2(dppp)Cp$.[318]

Os-Pd, Pt – $Os_6Pd(CO)_{18}(bpy)$ **(171)** is formed from **B** and $Pd(CO_2Me)_2(bpy)$; with excess of I_2 and $[NBu_4]I$, cluster breakdown to $Os_6(CO)_{18}$ and $[Pd_2I_6]^{2-}$ occurs. In contast, **C** reacts with the Pd reagent to give $Os_3Pd_2(CO)_{12}(bpy)_2$ **(172)**, molecules of which are stacked in the solid state. Addition of Cl^- to **(172)** affords $[Pd(bpy)\}_2(\mu\text{-H})(\mu\text{-CO})][Os_4(\mu\text{-H})_3(CO)_{12}]$.[319]

Mixed-metal carbide clusters were obtained from $Os_5C(CO)_{15}$, which reacts with $Pd(PPh_3)_4$ to give $Os_5PdC(\mu\text{-CO})_2(CO)_{12}(PPh_3)_2$ **(173)** and with $PdCl_2(PPh_3)_2$ to give $Os_5PdC(\mu\text{-Cl})_2(CO)_{15}(PPh_3)$ **(174)**.[320] Only in the latter is there a Pd-C bond.

In the reaction between $Os_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C_2H_4)(CO)_8$ and $Pt(\eta\text{-}C_2H_4)(PPh_3)_2$, three isomers of $Os_2Pt(CO)_8(PPh_3)_2$ **(175a-c)** were formed by redistribution of the PPh_3 and CO ligands. The three isomers interconvert on the NMR time scale via two pathways involving olefin-like rotation of the Os_2 fragment about the Pt atom, and a trigonal twist at Os.[321]

Co-Pd – EH MO calculations of $[CoPd_2(\mu\text{-dppm})_2(CO)_4]^+$ show the lowest energy electronic absorptions are charge transfer from Co to Pd_2.[242] Functionalised bridging diphosphines were introduced into heteronuclear complexes either from $[Co(CO)_4]^-$ with $Pd_2[(\mu\text{-}PPh_2)_2NR]Cl_2$ [R = $(CH_2)_3Si(OMe)_3$], which gave $Co_2Pd_2(\mu_3\text{-CO})_2\{\mu\text{-}(PPh_2)_2NR\}_2(CO)_5$, or by reaction of $[CoPd_2\{\mu\text{-}(PPh_2)_2NH\}_3(CO)_2]^+$ with $KH/I(CH_2)_3Si(OMe)_3$ to give $[CoPd_2\{\mu\text{-}(PPh_2)_2NR\}(CO)_2]^+$.[322]



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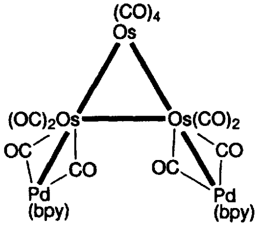

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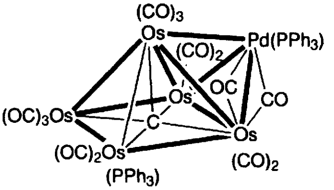

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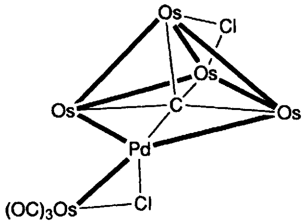

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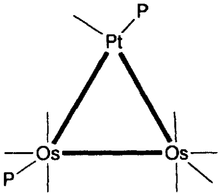

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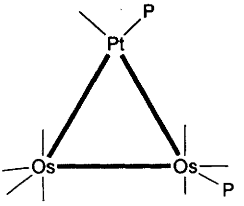

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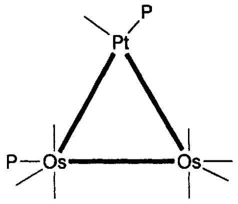


175c

Rh, Ir-Pt. Complexes [MPt$_2$(μ-dpmp)$_2$(Cl)(CNxy)$_2$]$^{2+}$ (M = Rh, Ir), from [Pt$_2$(μ-dpmp)$_2$(CNxy)$_2$]$^{2+}$ and {M(μ-Cl)(cod)}$_2$, contain linear Pt-Pt-M chains; asymmetric double A-frame clusters MPt$_2$(μ-Cl)(μ-dpmp)$_2$(CNxy)$_2$]$^{2+}$ were also formed.[323] In the former, the M-Pt bond is considered to be a d^8-d^9 dative bond.

Ni-Pd – The hexagonal close-packed cluster core of [Ni$_9$Pd$_{33}$(CO)$_{41}$(PPh$_3$)$_6$]$^{4-}$, obtained from the reaction between PdCl$_2$(PPh$_3$)$_2$ and [Ni$_6$(CO)$_{12}$]$^{2-}$, contains five triangular layers stacked in a 10/6/10/6/10 array, with the Ni atoms at the corners of each 10-atom layer. The c.v.e. count of 518 agrees with both the PSEP theory of Mingos and the shell model and inclusion principle developed for close-packed clusters by Teo and Zhang.[324]

15 Heterometallic Clusters Containing Group 11 Metals

Trinuclear complexes $[M\{Au(\mu\text{-mes})(L)\}_2]^+$ (M = Ag, Cu), obtained from Au(μes)(L) and Ag(OTf), $AgClO_4$ or $[Cu(NCMe)_4]^+$, form chain polymers with Au-M bonds and long Au...Au contacts (3.13 Å for M = Ag).[325] The $AgAu_2$ complexes react further with ligands (L′) to give binuclear cations $[AgAu(\mu\text{-mes})(L)(L')]^+$.

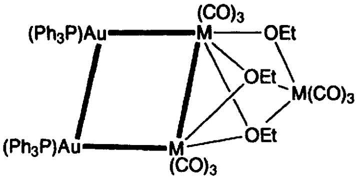
The product obtained from equimolar amounts of $\{Ag(C{\equiv}CPh)\}_n$, $\{Au(C{\equiv}CPh)\}_n$ and $[Au_3Cu_2(C_2Ph)_6]^-$ has been shown to contain both anions of $[ppn][Au_3M_2(C_2Ph)_6]$ (M = Ag, Cu) cocrystallising in the asymmetric unit, rather than the trimetallic $[Au_3AgCu(C_2Ph)_6]^-$ anion previously reported.[326] The Ag or Cu atoms occupy apical positions of the t.b.p. core.

Nb, Ta – The adducts $[\{NbH(Cp^{RR'})_2(\mu\text{-}H)_2\}_2M]^+$ (M = Ag, Au, Cu); R, R′ = H, $SiMe_3$) were obtained from $NbH_3(Cp^{RR'})_2$ and Ag^+, $[Au(tht)]^+$ and $[Cu(NCMe)_4]^+$. These compounds are fluxional, variations in the ^1H NMR spectra being explained by formation of two isomeric cations, one containing two μ-H and one terminal H, the other containing one μ-H and one $\eta^2\text{-}H_2$ ligand. Activation energies for exchange are 42-45 (Cu), 37 (Ag) and 40 kJ mol^{-1} (Au).[327] Reaction of $[Ta(CO)_5]^{3-}$ with $AuCl(PPh_3)$ affords $Au_3Ta(CO)_5(PPh_3)_3$.[328]

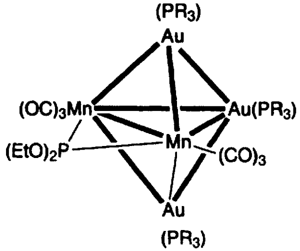
Mo, W – Fluxional complexes $Au_3M_3(\mu_3\text{-}OEt)_2(\mu\text{-}OEt)(CO)_9(PPh_3)_3$ (**176**; M = Mo, W) were prepared from $[M_3(\mu_3\text{-}OEt)_2(\mu\text{-}OEt)(CO)_9]^{3-}$ and $AuCl(PPh_3)$/$TlPF_6$; the related derivative $[Au_3W_3(\mu_3\text{-}OEt)_2(\mu\text{-}OEt)(\mu\text{-dppm})(CO)_9]^-$ is also described. The dynamic process probably involves Au-Au bond making/breaking.[329]

Mn, Re – Reactions of anionic metal carbonyls with copper(I)-amine compounds have given several novel metal-metal bonded complexes, including the tetranuclear cluster $\{CuMn(CO)_5(NH_3)\}_2$, which contains a planar Cu_2Mn_2 raft.[330]

The bidentate diphosphine bridges two $AuMn_2$ clusters in $\{AuMn_2(\mu\text{-}PPh_2)(CO)_8\}_2(\mu\text{-P-P})$ [P-P = dppf (**177***), dppe], obtained from $(AuCl)_2(\mu\text{-P-P})$ and $[Mn_2(\mu\text{-}PPh_2)(CO)_8]^-$; the former is formed via $AuCl(\mu\text{-dppf})\{AuMn_2(\mu\text{-}PPh_2)(CO)_8\}$.[331] The dppf can be displaced from (**177**) by PPh_3 or $P(OEt)_3$ (L) to give $AuMn_2(\mu\text{-}PPh_2)(CO)_8(L)$. Reaction of $[Mn_2(\mu\text{-}PPh_2)(CO)_8]^-$ with AuCl(tht) gave $[Au\{Mn_2(\mu\text{-}PPh_2)(CO)_8\}_2]^-$, containing a twisted bow-tie cluster. EH MO calculations on Mn_2, $AuMn_2$ and $AuMn_4$ clusters rationalise the longer Mn-Mn distances in the latter two. Quasi-reversible redox processes are shown by $[\{AuMn_3(\mu_3\text{-}H)(CO)_{12}\}_2(\mu\text{-dppe})]^{2-}$ and $[\{AuMn_3(\mu_3\text{-}H)(CO)_{12}\}_n\{triphos\text{-}(AuCl)_{3-n}\}]^{n-}$ (n = 1-3).[332] Anionic clusters $[MMn_2\{\mu\text{-}P(OEt)_2\}\{\mu\text{-}OP(OEt)_2\}(CO)_6(PR_3)]^-$ (M = Ag, Au, Cu; R = Et, Ph) have been obtained from $[Mn_2\{\mu\text{-}P(OEt)_2\}\{\mu\text{-}OP(OEt)_2\}(CO)_6]^{2-}$ and $MCl(PR_3)$; the neutral M_2Mn_2 (M = Ag, Au only) complexes are thermally unstable. However, decomposition in the presence of $AuCl(PR_3)$ afforded unsaturated $Au_3Mn_2\{\mu\text{-}P(OEt)_2\}(CO)_6(PR_3)_3$ (**178**) in low yield.[333]



176 M = Mo, W



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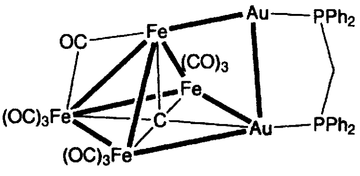
A minor product obtained from the reaction of $Re_2(\mu\text{-}H)(\mu\text{-}C_2Ph)(CO)_7(NCMe)$ with $Na[Co(CO)_4]/AuCl(PPh_3)$ was $AuRe_2(\mu\text{-}C_2Ph)(CO)_8(PPh_3)$. Reaction of $Re_2(\mu\text{-}H)(\mu\text{-}dppm)(\mu\text{-}C_2Ph)(CO)_6$ with $AuMe(PPh_3)$ gave $AuRe_2(\mu\text{-}dppm)(\mu\text{-}C_2Ph)(CO)_6(PPh_3)$.[299]

Fe, Ru, Os – DFT calculations show that comparatively weaker Ag-Ag and Ag-Fe bonds are found in $[M_4\{Fe(CO)_4\}_4]^{4-}$ compared with the Au and Cu analogues, as a result of larger *d-sp* mixing in the latter; charge transfer from M to $Fe(CO)_4$ occurs to give essentially M^1 as suggested by the observed square-planar geometry. The clusters are electron-deficient and are stabilised by addition of electrons.[334] Similar calculations on $[Ag_{13}\{Fe(CO)_4\}_8]^{n-}$ (n = 0-5) show the highly stabilising effect of the central Ag atom. The single unpaired electron in the tetra-anion is localised mainly on the Fe atoms and to a modest extent on the central Ag but only to a small extent on the Ag_{12} periphery.

Products from $(AuCl)_2(\mu\text{-}P\text{-}P)$ and $[Fe_6C(CO)_{16}]^{2-}$ depend on the nature of the diphosphine P-P. With dppm, $Au_2Fe_4C(\mu\text{-}dppm)(CO)_{12}$ (**179**) [a skeletal isomer of $Au_2Fe_4C(CO)_{12}(PEt_3)_2$] is obtained, whereas for dppe, $\{AuFe_6C(CO)_{16}\}_2(\mu\text{-}dppe)$ is formed.[335] A useful method of incorporating the $Au_2(PR_3)_2$ fragment (R = Ph, OMe) into metal clusters is by using $[O\{Au(PR_3)\}_3]^+$ in the presence of a nucleophile, such as acetate or $[Co(CO)_4]^-$, which serves to remove one $Au(PR_3)$ group from the trigold-oxonium reagent.[336] The aurophilicity principle results in an Au-Au bond being present in most derivatives obtained, except for $Ru_6C(\mu\text{-}CO)_2(CO)_{14}\{Au(PPh_3)\}_2$. Formally, the $Au_2(PR_3)_2$ group replaces a CO group in these reactions, unless hydride is present, when preferential replacement of H by $Au(PR_3)$ occurs.



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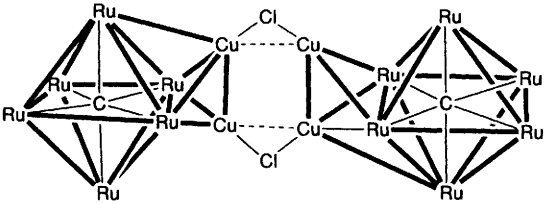
Differences in M-M distances of up to 0.13 Å found in the two $CuRu_4$ clusters in $\{CuRu_4(\mu_3\text{-}H)(CO)_{12}\}_2(\mu\text{-dppe})$ are ascribed to crystal packing forces and are consistent with the generally held view of the softness of metal frameworks.[337] Dynamic behaviour of the dppf ligand in $M_2Ru_4(\mu_3\text{-}H)_2(\mu\text{-dppf})(CO)_{12}$ (M = Cu, Ag, Au) involves inversion at P accompanied by twisting of the C_5 rings. Site exchange between the M atoms also occurs. The metal core of the $AuCuRu_4$ cluster is a trigonal bipyramid (*ap*-Au, *eq*-Cu) whereas that of the Au_2Ru_4 analogue is a capped square pyramid with one of the H ligands bridging an Ru-Ru edge.[338]

The reaction between CuCl and $[Ru_6C(CO)_{16}]^{2-}$ affords $[\{Cu_2Ru_6C(CO)_{16}\}_2(\mu\text{-}Cl)_2]^{2-}$ (**180**) in quantitative yield.[339] The Cl atoms hold the two cluster halves of the anion together: the Cu...Cu separation (3.01 Å) and Cu-Cl-Cu angle (86.9°) suggest some Cu...Cu interaction. Related Cu_6Ru_{12} and Cu_7Ru_8 anions are mentioned. Copper is extracted from $Cu_2Ru_6(\mu_6\text{-}C)$ $(CO)_{16}(NCMe)_2$ by 1,5,9-trithiacyclododecane (12S3), which forms $[Cu(\eta^1\text{-}12S3)(\eta^3\text{-}12S3)]$ $[Ru_6C(CO)_{16}]$ in 56% yield.[340]



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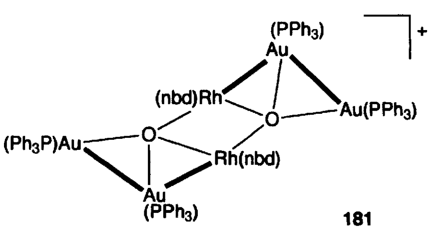
The cluster anion $[Ru_{11}H(CO)_{27}]^{3-}$ affords $[AuRu_{11}H(CO)_{27}(PPh_3)]^{2-}$ on treatment with $AuCl(PPh_3)/TlPF_6$.[156] Reduction of $[Os_{10}(CO)_{26}]^{2-}$ with K[bpk], followed by addition of $[Au(PPh_2R)_2]^+$ (R = Me, Ph), gave $Au_4Os_{10}(CO)_{24}(PPh_2R)_4$ in which the metal core appears to contain fused octahedra of Os atoms. Further examination reveals that not all Os...Os vectors are bonding, so that the overall structure of the core assumes a tubular form.[341] Evidently reduction of the Os_{10} cluster dianion results in transfer of electron density to Os-Os anti-bonding orbitals; the c.v.e. count is 132, inconsistent with current cluster electron book-keeping methods.

Co, Rh, Ir – Formation of $Au_2Co_2(\mu\text{-dppm})_2(CO)_6$ from $\{Co(CO)_4Au\}_2(\mu\text{-dppm})$ and dppm proceeds through $[Au_2(\mu\text{-dppm})_2][Co(CO)_4]_2$, which could be isolated from toluene solution. Similar results were obtained with $CMe_2(PPh_2)_2$.[342]

T.b.p. coordination of O by Au and Rh atoms, which are within bonding distances of each other, is found in complexes (**181**) obtained from reactions of $\{Rh(\mu\text{-}Cl)(diene)\}_2$ (diene = cod, nbd) and $[O\{Au(PPh_3)\}_3]^+$.[343]

Reactions of $Ir_4(\mu\text{-}CO)_3(CO)_7\{PPh_2(C_5H_4N\text{-}2)\}$, in which the pyridine N atoms are not coordinated, with $[Cu(NCMe)_4]^+$, Ag^+ or AuCl(tht), gave $MIr_4(CO)_{10}\{PPh_2(C_5H_4N\text{-}2)\}_2$ (**182**; Au compound not fully characterised) containing a t.b.p. MIr_4 core in which the M atom is also coordinated to the pyridyl group.[233]



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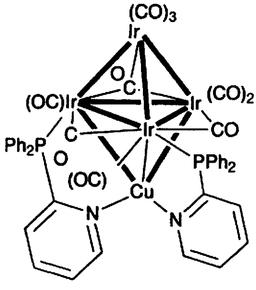

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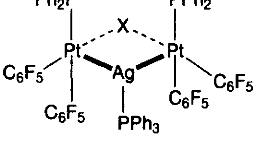
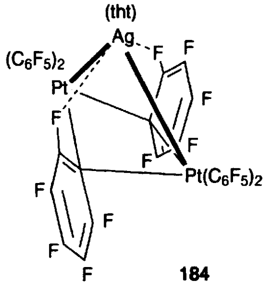
Pt – Addition of $AgClO_4$ to $[Pt(C_6F_5)_2(acac)]^-$ gave{$AgPt(\mu$-acac)-$(C_6F_5)_2(ClCH_2Cl)\}_2$ in which the Ag is bonded via O of the acac ligands; also unusual is the presence of an Ag-coordinated CH_2Cl_2. Facile cleavage of the Ag-O bond occurs on addition of PPh_3 or tht, with formation of binuclear products.[344] Similarly, $[\{Pt(C_6F_5)_2\}_2(\mu\text{-}X)(\mu\text{-dppm})]^-$ (X = Cl, Br) has given $AgPt_2(\mu\text{-}X)(\mu\text{-dppm})(C_6F_5)_4(OH_2)$ (with wet $AgClO_4$) and $Ag(\mu\text{-}X)(\mu\text{-dppm})(C_6F_5)_4(PPh_3)$ [**183**; X = Cl] [with $Ag(OClO_3)(PPh_3)$], which contain bent Pt-Ag-Pt chains.[345] The Ag activates the μ-X towards substitution, as shown by the reaction of (**183** with water to give (**183**; X = OH), also obtained from $[\{Pt(C_6F_5)_2\}_2(\mu\text{-OH})(\mu\text{-dppm})]^-$ with $Ag(OClO_3)(PPh_3)$. Intramolecular Ag...F interactions are present in $[AgPt_2(\mu\text{-}C_6F_5)(C_6F_5)_4(tht)]^-$ (**184**), obtained from $Ag(OClO_3)(tht)$ and $[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]^{2-}$. The *ortho*-F atoms of the C_6F_5 groups bridging the two Pt atoms are between 2.64 and 2.72 Å from the Ag atom.[346]



183 X = Cl, Br



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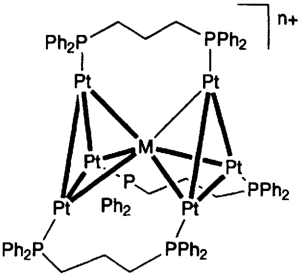


185 M = Hg, n = 0
M = Tl, n = +1

The cationic complexes $[Ag\{(\mu\text{-}RC_2)_2PtL_2\}_2]^+$, obtained from *cis*-$Pt(C\equiv CR)_2L_2$ (R = Ph, Bu^t; L = PEt_3, PPh_3; L_2 = dppe) and $AgClO_4$, have non-bonded Ag...Pt separations of 3.38-3.51 Å; the related $[Ag_2\{Pt(C_2R)_2L_2\}_2]^{2+}$ cations are believed to have similar structures.[347]

Treatment of the electron-rich cluster $Pt_3(\mu\text{-}PPh_2)_3(Ph)(PPh_3)_2$ with

AgO_2CCF_3 gives $AgPt_3(\mu\text{-}PPh_2)_3(O_2CCF_3)(Ph)(PPh_3)_2$.[253] The reaction of $[Au(PPh_3)]^+$ with $Pt_6(\mu\text{-dppe})_3(\mu\text{-CO})_6$ affords $Au_2Pt_6(\mu\text{-dppe})_3(\mu\text{-CO})_6(PPh_3)_2$ (**185**).[254]

16 Clusters Containing Group 12 Metals

Trimetallic complexes $Hg\{Nb(L)Cp^{Si})_2\}_2$ (L = CO, $CNBu^t$, PMe_3) are formed by reversible attack of radicals $[Nb(L)(Cp^{Si})_2]\cdot$ on Hg in the amalgam used to reduce the corresponding chloro complexes.[348]

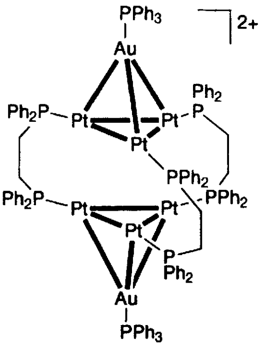
Reactions of HgClPh with dianions containing bis(cyclopentadienyl) ligands bridging two $M(CO)_3$ units (M = Cr, Mo, W) have given M-Hg-M sequences bridged by the organic ligands, which have the form $\eta\text{-}C_5H_4\text{-}Z\text{-}\eta\text{-}C_5H_4$ [Z = $C(O)C_2H_4C(O)$ or $C_2H_4OC_2H_4$].[349]

The reaction between $ZnCl_2(bpy)$ and $[Mn_2\{\mu\text{-}P(OEt)_2\}\{\mu\text{-}OP(OEt)_2\}(CO)_6]^{2-}$ gave $Mn_2Zn\{\mu\text{-}P(OEt)_2\}\{\mu\text{-}OP(OEt)_2\}(CO)_6(bpy)$.[333] Electrochemical properties of $[Hg\{Mn_3(\mu_3\text{-}H)(CO)_{12}\}_2]^{2-}$ have been described.[332]

Reduction of $[Os_{18}Hg_n(C)_2(CO)_{42}]^{2-}$ (n = 2, 3) with Na[bpk] gave a hexa-anionic cluster; after chromatography, this afforded $[Os_{18}Hg(C)_2(CO)_{42}]^{4-}$, containing two Os_9C units linked via a μ_6-Hg atom.[350] This can be converted into $[Os_{18}Hg_2(C)_2(CO)_{42}]^{2-}$ with $Hg(OTf)_2$, while the related mono-hydrido trianion $[Os_{18}Hg_2H(C)_2(CO)_{42}]^{3-}$ was also obtained.

A series of supposed Pt_3 clusters $[Pt\{Pt(P\text{-}P)(CNR)\}_2]^{2+}$ (ref. 351) have been shown to contain mercury and have the similar formulations $[Hg\{Pt(P\text{-}P)(CNR)\}_2]^{2+}$ (P-P = dppee, dppp, dtbpe; R = xy, mes).[352]

The bis-Pt_3 cluster $\{Pt_3(\mu\text{-}CO)_3(dppp)\}_2(\mu\text{-dppp})_2$ reacts with Hg^0 or Tl^+ to form $[Pt_6(\mu_6\text{-}M)(\mu\text{-dppp})_3(\mu\text{-}CO)_6]^{n+}$ (**186**; M = Hg, n = 0; M = Tl, n = 1) in which the Hg or Tl atom is encapsulated in a manner reminiscent of cryptand ligands. In these, redistribution of the dppp ligands to bridge the two Pt_3 cores has occurred.[254,255] If the reduction is carried out in the presence of Hg, analogues of **186** (Hg) with n = 3-6 can be obtained directly, together with $Pt_6(\mu_6\text{-}Hg)\{\mu\text{-}PPh_2(CH_2)_nPPh_2\}_2(\mu\text{-}CO)_6(CO)_2$ (for n = 5, 6).[254]



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17 Compounds Containing Three Different Metal Atoms

The metal atoms in $Ti\{(\mu\text{-}SPh)_2Pt(C_6F_5)_2\}\{\mu\text{-}(\eta\text{-}C_5H_4PPh_2)_2[Mo(CO)_4]\}$ are probably too far apart for there to be significant metal-metal bonding.[353] Full details of the W-Rh-Cu clusters built up from the components $[WO_nS_{4-n}]^{2-}$ (n = 0, 1), CuCl and $Rh\{P(OEt)_3\}Cp^*$ (to prevent polymerisation and confer solubility) are now available.[354] With water, $\{Cp^*Rh[P(OEt)_3](\mu\text{-}WS_4)(CuCl)Cu\}_2(\mu\text{-}Cl)_2$ undergoes a change in core geometry giving the linked incomplete cubane $\{Cp^*Rh[P(OEt)_3](\mu\text{-}WOS_3)(CuCl)Cu\}_2(\mu\text{-}Cl)_2$, in which a μ-S atom has been converted into terminal O. With H_2S, the monomer and Cu_2S are formed. The trinuclear $Cp^*Rh\{P(OEt)_3\}(\mu\text{-}WOS_3)CuCl$ has also been characterised.

Electrochemical studies of $[Mn_3\{\mu\text{-}Hg[M]\}(\mu\text{-}H)(CO)_{12}]^-$ {M = Mo/W$(CO)_3Cp$, $Mn(CO)_5$, $Fe(CO)_2Cp$, $Co(CO)_4$] show quasi-reversible redox processes, together with irreversible reduction.[332]

The anticipated metal exchange reaction of $Co_2M\{\mu_3\text{-}C(CO_2Et)\}(CO)_8(Cp^{Me})$ (M = Mo, W) with $[Fe(CO)_4]^{2-}$ gave $CoFeM(\mu\text{-}H)\{\mu_3\text{-}C(CO_2Et)\}(CO)_8(Cp^{Me})$ together with the ketenylidene clusters $CoFeM(\mu_3\text{-}CCO)(CO)_8(Cp^{Me})$.[306] Thermal metal exchange reactions of $Co_2Fe(\mu_3\text{-}S)(CO)_9$ with $[M(CO)_3(Cp^R)]^-$ gave chiral $CoFeM(CO)_8(Cp^R)$ (M = Mo, W; R = CHO, MeCO, EtOCO).[355] Substitution of CO by dppe gave $CoFeMo(\mu_3\text{-}S)(\mu\text{-}dppe)(CO)_6(Cp^{Me})$, in which the dppe ligand bridges the Co-Fe bond.[356] Analogous Mo-Cp^R (R = CHO, MeCO) compounds were reduced ($NaBH_4$) to the corresponding $Cp^{R'}$ [R′ = $CH_2(OH)$, CHMe(OH)] derivatives.[357]

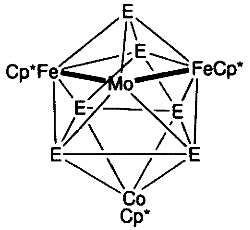
Reactions of $Mo(CO)_5(thf)$ with $\{CoCp^*\}\{FeCp^*\}_2(\mu_3\text{-}P_2)_2(\mu\text{-}P_2)$ and $\{CoCp^*\}\{FeCp^*\}_2(\mu_3\text{-}As_3)_2$ have given trimetallic cluster complexes containing P or As as skeletal atoms (E) in Co_2FeMoE_6 polyhedra (**187**).[358]

Addition of $AuCl(PPh_3)$ to mixtures of $Os_3(CO)_{11}(NCMe)$ and $[W(CO)_3(Cp^R)]^-$ (R = H, Me) afforded $AuOs_3W(CO)_{12}(PPh_3)(Cp^R)$. Hydrogenation of both clusters gave $AuOs_3W(\mu\text{-}H)_2(CO)_{11}(PPh_3)(Cp^R)$. All complexes were fluxional.[359]

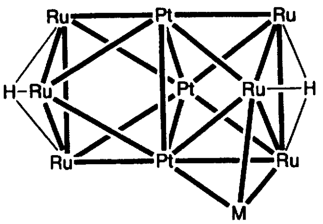
Addition of $\{PdCl(\eta\text{-}C_3H_5)\}_2$ to $[CoFe_3C(CO)_{12}]^-$ gave chiral $CoFe_3PdC(CO)_{12}(\eta\text{-}C_3H_5)$, with Pd bridging the Fe wing-tips, and all five metal atoms attached to the central C atom.[360] The optically-active β-pinenyl analogue shows strong Cotton effects in the CD spectrum induced by electronic interactions of the cluster with the chiral allylic ligand.

Addition of $AuCl(PPh_3)$ to $[Rh_2Ru_2(CO)_{12}]^{2-}$ gave $[AuRh_2Ru_2(\mu\text{-}CO)_4(CO)_8(PPh_3)]^-$ containing an Au/Rh_2Ru/Ru t.b.p. core; fluxional CO behaviour is frozen out at 250 K.[314] Reactions of $[Ru_4(\mu\text{-}BH)(\mu\text{-}H)(CO)_{12}]^-$ with mixtures of $\{Rh(\mu\text{-}Cl)(nbd)\}_2$ and $AuCl(PR_3)$ (R = Ph, $2\text{-}MeC_6H_4$, Cy) gave $AuRh_2Ru_4B(CO)_{16}(PR_3)$ containing octahedral Rh_2Ru_4B cores. Also formed are $AuRhRu_4B(\mu\text{-}H)(CO)_{12}(PR_3)(nbd)$, with square pyramidal $RhRu_4$ cores, which show fluxional behaviour of the nbd ligand and the $Au(PR_3)$ group. With CO, nbd is displaced to give $AuRhRu_4B(\mu\text{-}H)(CO)_{14}(PR_3)$.[316]

The Ph groups in $[CoPdPt(\mu\text{-}dppm)_2(CO)_3(CNBu^t)]^+$ form only a small cavity and the binding constants for halide ions are much lower than those found for the corresponding Pd_3 cluster.[242]



187 E = P, As
Mo = $Mo(CO)_3$



188 M = $IrCp^*$, HgI^-;
Pt = Pt(CO);
Ru = $Ru(CO)_3$

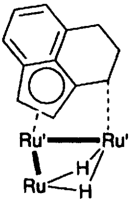
Layer-segregated clusters (**188**) have been prepared from $[Pt_3Ru_6(\mu\text{-}H)_2(CO)_{21}]^{2-}$ and $[Ir(NCMe)_3Cp^*]^+$ or HgI_2, respectively. In both cases, the third metal atom caps a $PtRu_2$ face, with the hydrides moving to cap Ru_3 faces.[361]

18 Metal Cluster Complexes in Catalysis

In addition to catalytic applications of complexes mentioned above, the following specific studies of metal clusters in catalysis appeared. Spectroscopic studies of $Ru_3(CO)_{12}$/bpy adsorbed on silica suggest that mononuclear Ru-CO-bpy complexes are the active catalyst precursors.[362] Physisorbed $Ru_3(CO)_{12}$ can be chemisorbed on to Vycor glass by UV irradiation to give $Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OSi)$, which forms an adduct with 1-pentene which can be isomerised on further irradiation.[363] Nanoclusters containing Ru or CoC clusters can be obtained by thermolysis (under H_2 at 500-700°C) of silica xerogels in which $Ru_3(\mu\text{-}H)\{\mu\text{-}S(CH_2)_3Si(OMe)_3\}(CO)_{10}$ or $Co_3\{\mu_3\text{-}C[Si(OH)_3]\}(CO)_9$ have been covalently incorporated.[364]

In CF_3CO_2H, ruthenium carbonyls catalyse the water gas shift reaction. The mechanism involves attack by water on an electron deficient carbonyl, loss of CO_2 to give hydride and reductive elimination of H_2. Intermediate complexes include $Ru_3(CO)_{12}$, $\{Ru(\mu\text{-}O_2CCF_3)(CO)_3\}_2$ and *fac*-$[Ru(O_2CCF_3)_3(CO)_3]^-$.[365] The cluster carbonyl is a catalyst precursor for oligomerisation of propene or C_2H_4/C_3H_6 mixtures in hydrogen-donor solvents.[366]

Selective hydrogenation of acenaphthylene and aceanthrylene in the presence of $Ru_3(CO)_{12}$ and CO has given the 4,5-dihydro hydrocarbons for the first time. It is considered that intermediate formation of cluster-bound hydrocarbon complexes, such as (**189**), is a key step in this process.[367] Hydrogenation of C_2Ph_2 is catalysed by $Ru_3(\mu_3\text{-}C_2Ph_2)(\mu_3\text{-}CO)(\mu\text{-}CO)(CO)_3Cp_2$; while this study seems to support catalysis by a cluster, other binuclear products have been isolated. Possible precursor complexes may contain μ_3-||-alkyne ligands.[368] Kinetic studies of the same reaction catalysed by $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ampy)(\mu\text{-}\eta^1{:}\eta^2\text{-}CH{=}CHPh)(CO)_8]^+$ (333 K, <1 atm. H_2) suggest that reaction intermediates are also cationic.[369] The formation of allylic amines from cyclohexene and aromatic nitro compounds is catalysed by $Ru_3(CO)_{12}$ in the presence of DIAN-R (**190**); high selectivities are found, by-products being the corresponding anilines.[370] Similarly, 4-acylation of imidazoles with CO/olefin mixtures occur with high yield and efficiency in the presence of $Ru_3(CO)_{12}$.[371]



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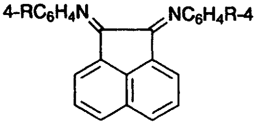

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Mixed Co-Rh complexes, including $Co_2Rh_2(CO)_{12}$, catalyse silylcarbobicyclisation of 4,4-disubstituted 1,6-heptadiynes with $SiHMe_2Bu^t$ under CO (50 atm.) to give 7,7-disubstituted 2-silylbicyclo[3.3.0]octa-1,5-dien-3-ones.[372] Bimetallic Co-Rh catalysts are also used to hydroformylate pinenes with 95% stereoselectivity; catalyst precursors include $Co_2Rh_2(CO)_{12}$ or stoichiometric mixtures of $Co_2(CO)_8$ with either $Rh_4(CO)_{12}$ or $Rh_6(CO)_{16}$.[373]

Selective hydrogenation (H_2/CO) of α,β-unsaturated aldehydes to allylic alcohols is catalysed by $Rh_6(CO)_{16}$ on aminated polystyrene.[374] Catalysis of hydrogenation of CO_2 to EtOH has been achieved with $[Rh_{10}Se(CO)_{22}]^{2-}$ on TiO_2 (83% selectivity; 6×10^{-2} mol h^{-1} g^{-1}); other Rh clusters on TiO_2, or $Rh_{10}Se$ on other inorganic oxides, are less efficient.[375]

Catalytic reduction of redox active co-factors and proteins has been achieved with $[Pt_{15}(CO)_{30}]^{2-}$ on QAE-Sephadex anion exchanger; the mechanism may involve intermediate formation of a Pt_{12} cluster.[376] Impregnation of FSM-16 (a folded-sheet mesoporous material with channels of 20-100 Å diameter) with H_2PtCl_6, followed by carbonylation (CO, then CO/H_2O) gave olive-green material containing $[Pt_{15}(CO)_{30}]^{2-}$, which could be extracted with [ppn]Cl. Evacuation resulted in formation of higher nuclearity Pt_n clusters (n = 35-55; Pt clusters of diameter 15 Å were seen by electron micrography). In the presence of $[NR_4]^+$, more stable clusters were formed, which were active catalysts for the water-gas shift reaction.[377]

The structural isomers of $[IrRe_7C(CO)_{23}]^{2-}$ have been used to deposit a series of bimetallic catalysts on Al_2O_3. After activation by H_2, the materials hydrogenolyse ethane; the more active materials were characterised as having Ir at the centre of an h.c.p. particle, while lesser activity was found for layer structures.[378]

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11

Complexes Containing Metal-Carbon σ-Bonds of the Groups Titanium to Manganese, Including Carbenes and Carbynes

BY NICHOLAS CARR, PATRICK C. MCGOWAN, ELIZABETH M. PAGE AND SHERYLIN A. WASS

Part I: Group 4 *by Patrick C. McGowan*

This article will highlight the formation of σ-carbon bonds of Group 4 compounds. Cationic alkyl complexes of Group 4 metallocenes of the type $[MCp_2R]^+$ (M = Ti, Zr or Hf, Cp = C_5H_5) have been recognised as the catalytically active species in metallocene-based olefin polymerisation catalysts. The preparation of new types of cyclopentadienyl compounds is of great importance due to the catalytic activity of some of these molecules.[1] There are many new compounds of this type being produced and this article will not attempt to cover all the catalytic chemistry of these.

The first chiral-at-titanium alkyl complexes containing a simple alkyl ligand are reported.[2] New methyl and benzyl complexes have been prepared by reaction of $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)Cl_2]$ and the appropriate Grignard reagent. While the indenyl ligand in the racemic, chiral-at-metal complex $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)(CH_2SiMe_3)Cl]$ is bound in an η^5 fashion, X-ray structural data clearly indicate that there is some 'η^3 ring-slip' character to the bonding. Mono- and disubstituted titanium(IV) alkyl and benzenethiolate complexes of the form $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)(CH_2SiMe_3)Cl]$ and $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-ring})R_2]$ (ring = C_9H_7 or $C_5H_4Bu^t$; R = Me, CH_2Ph, CH_2SiMe_3 or SPh) are synthesised.

The use of sterically demanding ligands for the stabilisation of low co-ordinate transition metal complexes allows the synthesis of a number of titanium complexes. A range of complexes are synthesised including $Ti(NRAr_F)_2(NMe_2)_2$ ($R{=}C(CD_3)_2CH_3$, $Ar_F{=}2{,}5\text{-}C_6H_3FMe$), $Ti(NRAr_F)_2(NMe_2)I$, $Ti(NRAr_F)_2(NMe_2)(CH_2SiMe_3)$, $Ti(NRAr_F)I(NMe_2)(CH_2SiMe_3)$. The complexes $Ti(NR'Ar)(NMe_2)_3$ ($R'{=}C(CD_3)_2Ph$), $Ti(NR'Ar)(NMe_2)_2(OAr'')$, ($Ar''{=}\ C_6H_3{}^tBu_2$), and $Ti(NR'Ar)(NMe_2)(OAr'')I$, are also prepared in high yield. The latter yields the cyclometallated compound $Ti(NR'Ar)(O\text{-}2,\ 6\text{-}C_6H_3[{}^tBu][CMe_2CH_2])I$ **1** on treatment of $Ti(NR'Ar)(NMe_2)_2(OAr'')$ with (i) neopentyl-lithium, (ii) thermolysis at 65°C, and (iii) excess methyl iodide at 70°C.[3]

The synthesis of a variety of titanium complexes that contain $(Et_3SiNCH_2CH_2)_3N$, $(C_6F_5NCH_2CH_2)_3N$, or $(Me_3SiNCH_2CH_2CH_2)_3N$ ligands is reported. Complexes in the first category include $[(Et_3SiNCH_2CH_2)_3N]TiCl$, $[(Et_3SiNCH_2CH_2)_3N]Ti(OTf)$, and $[(Et_3SiNCH_2CH_2)_3N]Ti\text{-}({}^tBu)$. Complexes in

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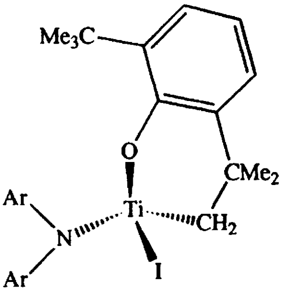
the second category include $[(C_6F_5NCH_2CH_2)_3N]TiX$ (X = Cl, Br, I, OTf) and $[(C_6F_5NCH_2CH_2)_3N]TiR$ (R = Me, Et). Complexes in the third category include $[(Me_3SiNCH_2CH_2CH_2)_3N]TiCl$ and $[(Me_3SiNCH_2CH_2CH_2)_3N]TiCH_3$ **2**.[4]



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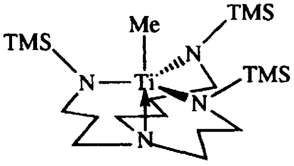

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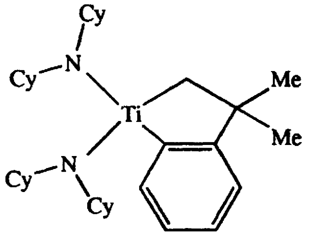
The synthesis, characterisation and thermal stability of some mono- and dinuclear Ti(III) and Ti(IV) alkyls and factors affecting their stability are examined.[5] The alkyls are synthesised by reactions of both trivalent $[(Cy_2N)_2Ti(\mu\text{-}Cl)_2Li(TMEDA)]$ and tetravalent $[(Cy_2N)_2TiCl_2]$ with R'Li in THF or diethyl ether gives Ti(IV) complexes $[(Cy_2N)_2TiR'_2]$ (R' = CH_2CMe_3, CH_2CMe_2Ph, CH_2SiMe_3). Conversely, the reactions of the paramagnetic complexes $[(Cy_2N)_2Ti(\mu\text{-}Cl)_2Li(TMEDA)]$, $[\{(i\text{-}Pr)_2N\}_2TiCl_2][Li(TMEDA)_2]$, $[\{(Me_3Si)_2N\}_2TiCl_2][Li(TMEDA)_2]$ with R'Li [R' = Me, Ph, CH_2Ph] gives the corresponding trivalent $[(Cy_2N)_2Ti(\mu\text{-}Bz)_2Li(TMEDA)]$, $[(Cy_2N)_2Ti(\mu\text{-}Me)_2Li(TMEDA)]$, $[\{(i\text{-}Pr)_2N\}_2TiPh_2][Li(TMEDA)_2]$, $[\{(Me_3Si)_2N\}_2Ti(CH_2Ph)_2][Li(TMEDA)_2]$ via simple ligand metathesis reactions. Oxidation of the latter molecule with diphenylfulvene gives $[\{(Me_3Si)_2N\}_2Ti(CH_2Ph)_2]$. All of these compounds are thermally labile and yielded intractable materials upon thermolysis. Only in the case of the neophyl derivative $(Cy_2N)_2Ti(CH_2CMe_2C_6H_5)_2$ is a cyclometallated compound $(Cy_2N)_2Ti(CH_2CMe_2C_6H_5)$ **3** isolated and crystallised from the thermolyzed solution. The reaction of $[(Cy_2N)_2Ti(\mu\text{-}Cl)_2Li(TMEDA)]$ with styrene oxide provided the Ti-oxo complex $[(Cy_2N)_2TiCl]_2O$ which gives, upon alkylation with MeLi, the corresponding dinuclear alkyl derivatives $[(Cy_2N)_2TiMe]_2O$.

Treatment of $Cp^*{}_2Ti(C_2H_4)$ with one equivalent of Me_3SiCHN_2 yields $Cp^*{}_2TiN_2CHSiMe_3$. The crystal structure of this complex shows the Me_3SiCHN_2 fragment bound to the titanium in a side-on fashion through the two nitrogen atoms. This thermally unstable complex decomposes to the fulvene complex $Cp^*FvTiCH_2SiMe_3$ **4**.[6]

Thermolysis of bis(tetramethylcyclopentadienyl)-stabilised titanium(III) compounds $[(\eta^5\text{-}C_5HMe_4)_2TiR]$ (R = Me, Ph) yields, in marked contrast with the bis(pentamethylcyclopentadienyl) analogue, the dimeric product $[(\eta^5\text{-}C_5HMe_4)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5Me_4Ti]_2$ with a bridging metallated tetramethylcyclopentadienyl ligand. The hydride$[(\eta^5\text{-}C_5HMe_4)_2TiH]$, synthesised by hydrogenolysis of the alkyl substituted product, reacts with N_2 to form the dinuclear Ti(II) di-nitrogen



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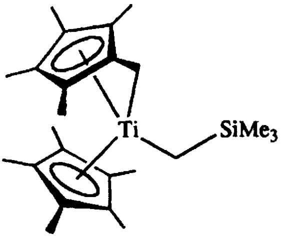

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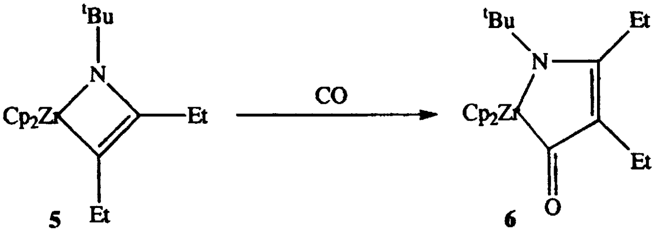
compound $[(\eta^5\text{-}C_5HMe_4)_2Ti]N_2$. Under a dynamic vacuum, the di-nitrogen complex loses the N_2 ligand to give the titanocene $[(\eta^5\text{-}C_5HMe_4)_2Ti]$.[7]

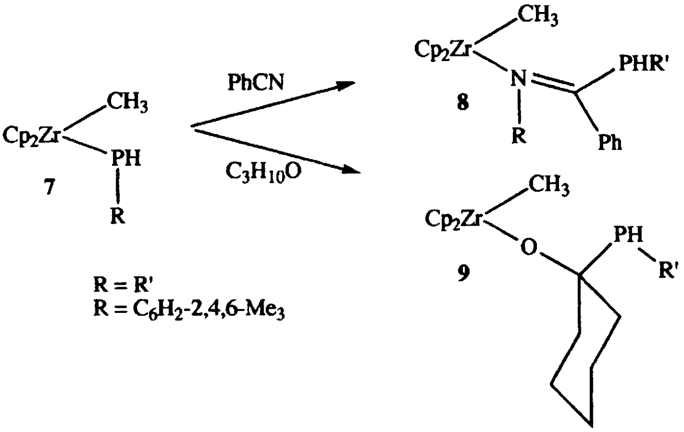
Interest has been shown in utilising some zirconocene molecules in 'NR' transfer to organic systems. Azametallacyclobutene $Cp_2ZrN^tBuCEt{=}CEt$ **5** undergoes an insertion reaction with CO to form the acyl complex $Cp_2Zr(N^tBuCEt\text{-}CEtCO)$ **6**. The addition of acetone to azametallacyclobutene $Cp_2Zr(NArCMeCPh)$, Ar=2,6-dimethylphenyl) yielded the N-bonded enamine and O-bonded enolate complex of zirconocene $Cp_2Zr(NArCMeCPhH)(OCMeCH_2)$. The addition of aldehydes RCOH to metallacycle $Cp_2Zr(NArCMeCPh)$ resulted in the insertion of the aldehyde into the Zr-C bond to form complexes $Cp_2Zr(NArCMeCPhCRHO)$ and $Cp_2Zr(NArCMeCPhC(^iPr)HO)$.[8]



5 **6**

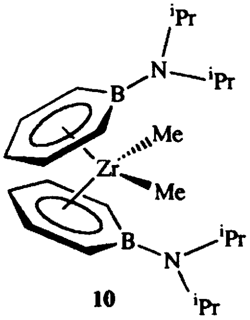
Insertion reactions occur in Zr-P bonds in preference to methane elimination. The reaction of $Cp_2ZrMe(PHR)$ **7** with benzophenone, cyclohexanone, acetone, benzaldehyde, and benzophenone results in the insertion of the organic substrate into the Zr-P bond. In this way, the complexes $Cp_2ZrMe(OCPh_2PH(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3))$, $Cp_2ZrMe(OC_6H_{10}PH(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3))$ **8**, $Cp_2ZrMe\ (OCMe_2PHR)$ ($R = (C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)$, $R = (C_6H_2\text{-}2,4,6\text{-}t\text{-}Me_3)$, and $Cp_2ZrMe(NC(Ph)PH\text{-}(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3))$ **9** are prepared.[9]

The preparation, characterisation and carbonylation products of the ring-functionalised alkyl zirconocenes, $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4P(C_6H_5)_2Zr(CH_2Ph)_2$ and $[(\eta^5\text{-}C_5H_4P(C_6H_5)_2]_2Zr(CH_2Ph)_2$ are described. These compounds insert one molecule of CO to give products which interconvert between an acyl form and a phosphonium-alkoxide form at ambient temperatures via a nucleophilic attack of the phosphine at the carbenium-like η^2-acyl carbon as shown through variable-temperature ^1H and ^{31}P NMR studies.[10]



Reaction of 1-(N,N-diisopropylamino)boracyclohexa-2,5-diene with 1 equivalent of LDA produces the corresponding boratabenzene lithium. One equivalent of this ligand is reacted with $Cp^{*}ZrCl_3$ to produce $[C_5H_5BN(i\text{-}Pr_2)_2]ZrCp^{*}Cl_2$; two equivalents react with $ZrCl_4$ to produce $[C_5H_5BN(i\text{-}Pr_2)_2]_2ZrCl_2$. From this the dimethyl analogue $[C_5H_5BN(i\text{-}Pr_2)_2]_2ZrMe_2$ **10** is synthesised using 2 equivalents of methyllithium. Reaction with $HNMe_3Cl$ or CD_2Cl_2 gives the monomethyl compound $[C_5H_5BN(i\text{-}Pr_2)_2]_2ZrMeCl$.[11]

The dialkyl derivative $(ATI)_2Zr(CH_2SiMe_3)_2$ **11** is prepared by treating $Zr(CH_2SiMe_3)_4$with 2 equiv. of the free ligand (ATI)H (ATI=N-isopropyl-2-(isopropylamino)troponimine). The Group IV metallocene dichlorides of the same ligand are also prepared.[12]



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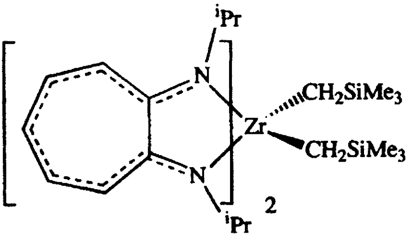

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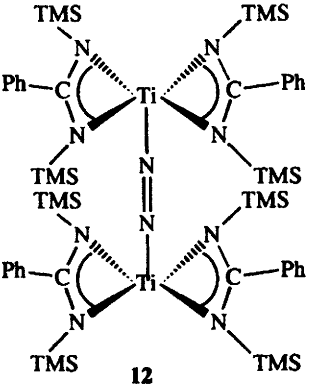
Organometallic benzaminidato compounds have received considerable attention in 1996. A rare example of a Ti(III) product is prepared by Na/Hg reduction of $[PhC(NSiMe_3)]_2TiMeCl$ to produce the paramagnetic product $[PhC(NSiMe_3)]_2TiMe$. The isolation of a diamagnetic dinitrogen complex is also observed when $[PhC(NSiMe_3)]_2TiCl_2$ is reduced with Na/Hg to produce $\{[PhC(NSiMe_3)]_2Ti\}_2(\mu\text{-}N_2)$ **12**. The X-ray structure of this molecule reveals a five-coordinate titanium with an end-on bonding mode of the bridging N_2.[13] It is shown that $[PhC(NSiMe_3)]_2TiCl_2$ reacts with TMEDA to produce two products, $[PhC(NSiMe_3)]_2TiNSiMe_3$ and $[PhC(NSiMe_3)]_2Ti[\eta^2\text{-}Me_3SiNC(H)Ph)[\eta^3\text{-}CH_2N(Me)CH_2CH_2N(Me)_2]$.

Tetramethyltitanium reacts with excess N,N′-bis(trimethylsilyl)-benzamidine to give bis[N,N′-bis(trimethylsilyl)benzamidinato]dimethyl-titanium via protolysis. This compound is isolated and characterised by X-ray crystal structure analysis showing octahedral co-ordination with the methyl groups in cis-positions. The monomethyl complexes $[PhC(NSiMe_3)_2]_2M(Me)Cl$ (M = Ti, Zr) have been prepared by treatment of the dichloro precursors with one equivalent of methyllithium.[14]



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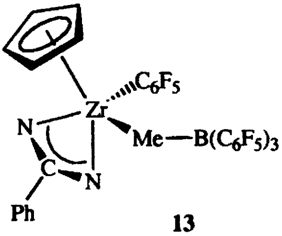

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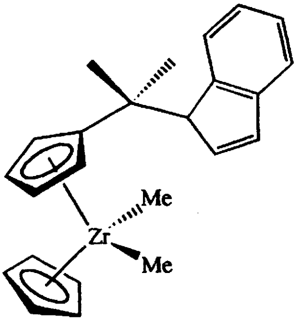
The compounds $[Zr(\eta^5\text{-}C_5R_5)\{\eta^3\text{-}CPh(NSiMe_3)_2\}R'_2]$ (R = H, R′ = Me or CH_2Ph; R = Me, R′ = Me) react with $[Ph_3C][B(C_6F_5)_4]$ giving $\{[Zr(\eta^5\text{-}C_5R_5)\{\eta^3\text{-}CPh(NSiMe_3)_2]\}_2(\mu\text{-}Cl)_2\ [BX(C_6F_5)_3]$ (R = H, X = Me or CH_2Ph; R = Me, X = C_6F_5). Treatment of $[Zr(\eta^5\text{-}C_5H_5)\{\eta^3\text{-}CPh(NSiMe_3)_2Me_2]$ with $B(C_6F_5)_3$ gives $[(C_6F_5)\{\eta^3\text{-}CPh(NSiMe_3)_2PhC\}(\eta^5\text{-}C_5H_5)Zr(\mu\text{-}Me)B(C_6F_5)_3]$ **13**, the crystal structure of which is reported. The compound $[Zr(\eta^5\text{-}C_5R_5)\{\eta^3\text{-}CPh(NSiMe_3)_2\}(CH_2Ph)_2]$ with $B(C_6F_5)_3$ in benzene or dichloromethane gives $[Zr(\eta^5\text{-}C_5H_5)\{\eta^3\text{-}CPh(NSiMe_3)_2\}L][B(CH_2Ph)(C_6F_5)_3]$ (L = C_6H_6 or CH_2Cl_2).[15]

A series of mononuclear and binuclear Zr and Hf methyl and chloro complexes have been prepared and characterised. These ansa-metallocenes include $[M\{Me_2C(\eta^5\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta^5\text{-}C_5H_5)Cl]$ (M = Zr, Hf), $[M\{(CH_2)_5C(\eta^5\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta^5\text{-}C_5H_5)Cl].0.5C_6H_5Me$ (M = Zr, Hf), $[Zr\{Me_2C(\eta^5\text{-}C_5H_4)(\eta^3\text{-}C_{13}H_8)\}(\eta^5\text{-}C_5H_5)Cl]$, $[M\{Me_2C(\eta^5\text{-}C_5H_4)_2\}(\eta^5\text{-}C_5H_5)Cl]$ (M = Zr, Hf), $[X_2(\eta^5\text{-}C_5H_5)M\{\eta^5\text{-}C_5H_4)(CMe_2)\ C_9H_6)\}M^*(\eta^5\text{-}C_5H_5)X_2\}]$ (X = Cl, M, M* = Zr, Zr, Hf, Hf; Zr, Hf; or Hf, Zr, X = Me, M, M* = Zr, Zr; Zr, Hf; Hf, Zr; or Hf, Hf), $[Cl_2(\eta^5\text{-}C_5H_5)Zr\{\eta^5\text{-}C_5H_4)(CMe_2)\ C_9H_6)\}Zr(\eta^5\text{-}C_5H_5)\ Cl_2]$, $[M\{\eta^5\text{-}C_5H_4)(CMe_2)C_9H_7)\}(\eta^5\text{-}C_5H_5)Cl_2]$ (M = Zr or Hf) and $[Zr\{(\eta^5\text{-}C_5H_4)(CMe_2)\text{-}C_9H_7)\}(\eta^5\text{-}C_5H_5)Me_2]$ **14**.[16] The activity of the metallocenes as co-catalysts for the polymerisation of ethene and propene have been evaluated but will not be discussed here.

Authors have shown that dicarbonyltitanocene is an efficient and highly selective catalyst for alkyne hydroborations by catecholborane leading to exclusive anti-Markovnikov regiochemistry and to exclusive single additions of catecholborane across alkynes. It is also shown that dimethyltitanocene is an efficient and highly selective catalyst for alkene hydroborations.[17] Two titanium(III) complexes, $Cp_2Ti(H_2Bcat)$ and $Cp_2Ti(Bcat_2)$, are isolated from the reaction mixtures.



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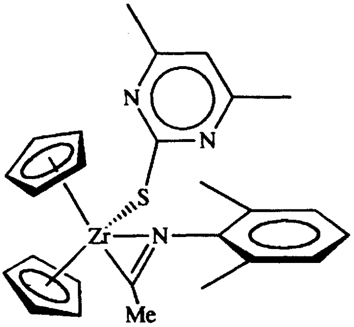

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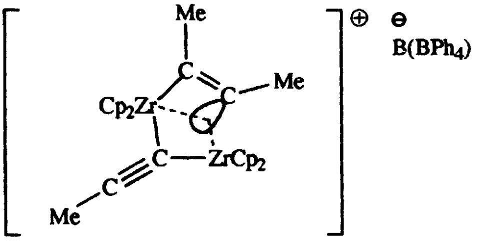
The first examples of a dimethylpyrimidine-thiolate containing zirconocene complex are reported where the thiolate-alkylzirconocene complex $Cp_2ZrMe(SR)$ (SR = 4,6-dimethylpyrimidine-2-thiolate) can be prepared by reacting the corresponding dialkylmetallocene complex Cp_2ZrMe_2 with 1 equivalent of 4,6-dimethyl-2-mercaptopyrimidine.[18] X-ray structure analysis revealed that the thiolate group is bonded in an η^2 fashion through the sulfur and one of the nitrogen atoms. Reaction with different acidic reagents gives formation of methane and different zirconium complexes. Reaction with HSR renders $Cp_2Zr(SR)_2$ and with $(NHEt_3)(BPh_4)$ the cationic complex $[Cp_2Zr(SR)][BPh_4]$. A hydride thiolate complex, $Cp^*_2ZrH(SR)$ can also be prepared by reaction of 'Cp^*_2Zr' with HSR by an oxidative addition reaction. Addition of 2,6-dimethylphenylisocyanide leads to $Cp_2Zr(\eta^5\text{-MeCNXylyl})(SR)$ **15**.

Addition of $[Cp_2ZrCH_3THF]^+$ $[BPh_4]^-$ to $[Cp_2Zr(C{\equiv}CMe)_2]$ produces the dimeric complex $[(Cp_2Zr)_2(\mu\text{-}MeC_2Me)(\mu\text{-}C{\equiv}CMe)]^+$ $[BPh_4]^-$ **16**. This reacts readily with alkyl isocyanides $RN{\equiv}C$ by displacement of the bridging 2-butyne ligand to give the cationic $[(\mu\text{-acetylide})(\mu\text{-isonitrile})(Cp_2Zr)_2]$ complexes in high yield.[19] A mixed hafnium-zirconium product is obtained by a similar reaction to give the product $[(Cp_2Zr)(Cp_2Hf)(\mu\text{-}MeC_2Me)(\mu\text{-}C{\equiv}CMe)]^+[BPh_4]^-$.[20] Reaction of $[Cp_2ZrCH_3THF]^+$ $[BPh_4]^-$ with $(R'C{\equiv}C)_2SiR_2$ gives $[(Cp_2Zr)(Si(CH_3)_2)(\mu\text{-}C{=}CMe_2)(\mu\text{-}C{\equiv}CMe)]^+$ $[BPh_4]^-$.[21] A planar-tetracoordinate carbon atom is observed in $[(Cp_2Zr)_2(\mu\text{-}Cl)(\mu\text{-}\eta^1{:}\eta^2\text{-}RCCCH_3]^+$ $[BPh_4]^-$ (R=-CH_2Ph,-$CH_2CH_2CH_3$,-CH_3) which is synthesised by addition of $[Cp_2ZrCH_3THF]^+$ $[BPh_4]^-$ to $Cp_2Zr(Cl)(C{\equiv}CR)$.[22] $B(C_6F_5)_3$ reacts with the (η^2-acetaldehyde)zirconocene dimer by hydride transfer from the methyl group of a CH_3CHO ligand to boron.[23] Dimethylzirconocene reacts with the imidazole $B(C_6F_5)_3$ adduct to give



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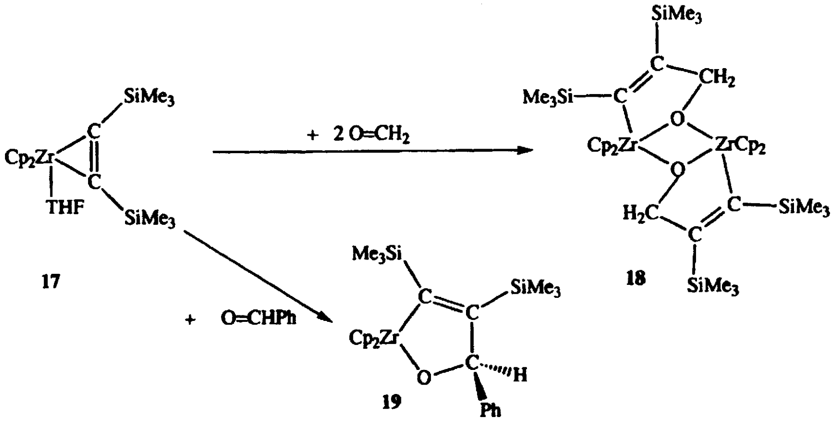
methane and the methylzirconocene/imidazole/ tris(pentafluorophenyl)borane-betaine complex.[24]

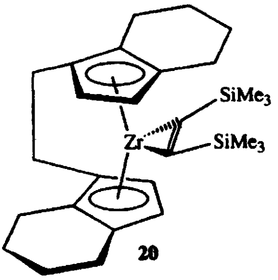
The titanocene alkyne complex, without any additional ligands, $Cp_2Ti(SiMe_3C{\equiv}CSiMe_3)$ and the zirconocene alkyne complexes free from stabilising phosphine ligands $Cp_2ZrL(SiMe_3C{\equiv}CSiMe_3)$ (L = THF, pyridine) as well as the metallacyclic complex $Cp_2Zr\text{-}O\text{-}CMe_2\text{-}C(SiMe_3){=}C(SiMe_3)$ react with some substrates in an unusual manner depending on metals M, ligands L and the substituents R of the substrates.[25] Formaldehyde reacts with $Cp_2Zr[\eta^2\text{-}C_2(SiMe_3)_2](THF)$ **17** by an insertion of the carbonyl unit into a Zr-C bond to yield the dimeric structure $[Cp_2ZrOCH_2(CSiMe_3){\equiv}CSiMe_3)]_2$ **18**.[26] Reactions with larger aldehydes and ketones, produce a monomeric species, e.g., reaction with PhCH=O yields $[Cp_2ZrOCHPh(CSiMe_3){\equiv}CSiMe_3)]$ **19**. The reaction of $Cp_2Zr[\eta^2\text{-}C_2(SiMe_3)_2](L)$ (L = THF, py) with equimolar amounts of $H_2C{=}CMe\text{-}CHO$ at room temperature depends on the ligands L and the solvents that are used as to what product is obtained. With L = THF, in THF solution the insertion product $[Cp_2Zr\text{-}O\text{-}CH{=}CMe(SiMe_3C{\equiv}CSiMe_3)$ is isolated, whereas by conducting the reaction in n-hexane solution an alkyne substitution with 1,4-coordination of the methacrolein takes place and the binuclear complex $[Cp_2Zr\text{-}O\text{-}CH{=}CMe\text{-}CH_2]_2$ is obtained. In contrast, with L = py (a stronger ligand) only a 1:1 ratio of the above products is observed in both THF and in n-hexane.[27]



Reaction of the zirconocene alkyne complexes $Cp_2Zr[\eta^2\text{-}C_2(SiMe_3)_2](L)$ (L = Py, THF; R = $SiMe_3$, ^{t}Bu) with benzoxazole and other thiazoles yields ring-adducts $Cp_2Zr(CSiMe_3){=}C(R)\text{-}CH{=}N\text{-}o\text{-}C_6H_4\text{-}X$ (X = O, S) and $Cp_2Zr(CSiMe_3){\equiv}CSiMe_3)\text{-}CH{=}N\text{-}C(R'){=}C(R')\text{-}X$ (R′ = Me, H) by formal C-X bond cleavage and coupling with the co-ordinated alkyne.[28] The reaction of $Cp_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$ with terminal disubstituted α,ω-diynes $RC{\equiv}C\text{-}(CH_2)_n\text{-}C{\equiv}CR$ affords, after substitution of bis(trimethylsilyl)acetylene, bicyclic titanacyclopentadienes via intramolecular cyclisation.[29]

Reduction of the complex $[(\eta^5\text{-}C_5H_4)\text{-ansa-}(\eta^5\text{-}C_5H_4)Ti]Cl_2$ (ansa = $Me_2Si\text{-}O\text{-}SiMe_2$), with magnesium in the presence of bis(trimethylsilyl)acetylene in THF at room temperature gives the ansa-titanocene alkyne complex $[(\eta^5\text{-}C_5H_4)\text{-ansa-}(\eta^5\text{-}C_5H_4)Ti(\eta^2\text{-}C_2(SiMe_3)_2]$. The pyridine stabilised zirconium analogues are obtained by analogous reactions and addition of pyridine: $[(\eta^5\text{-}C_5H_4)\text{-ansa-}(\eta^5\text{-}C_5H_4)Zr(L)(\eta^2\text{-}C_2(SiMe_3)_2]$ (L = pyridine).[30] The first zirconocene-alkyne complexes with no additional ligands is prepared in the same manner as above by the reduction of rac-(EBTHI)$ZrCl_2$ [EBTHI = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)] to form rac-(EBTHI)$Zr(\eta^2\text{-}C_2(SiMe_3)_2$ **20**.[31] The cationic d^1-titanocene complexes $[Cp_2Ti(L)CH_3THF]^+$ $[BPh_4]^-$ (L=THF and pyridine) are prepared by the reaction of $[(Cp)_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$ and trimethylammonium-tetraphenylborate via a $1e^-$-oxidation of the $14e^-$-Cp_2Ti-unit to the paramagnetic titanium(III) complex under evolution of molecular hydrogen and the alkyne. The authors claim that is the first example of such a cationic-only neutral-ligand containing complexes without anionic ligands that has been characterised by an X-ray structure analysis.[32]

The titanocene-bis(trimethylsilyl)acetylene complexes $Cp'_2Ti[\eta^2\text{-}C{\equiv}CSiMe_3)_2]$ (Cp′ = C_5H_5, C_5Me_4H, and C_5Me_5) react with 2,2′-bipyridine (bipy) to give the corresponding Cp'_2Ti(bipy) complexes. EPR evidence of the electronic triplet state in these compounds implies the transfer of one of the Ti d^2 electrons to the bipy ligand. An analogous electron transfer to 4,5-diazafluorene (dafH) affords (4,5-diazafluorenyl)titanocene (Ti-III) complexes Cp'_2Ti(daf) (Cp′ = C_5H_5, C_5Me_4H, and C_5Me_5) with a release of one hydrogen atom from the sp^3 carbon atom of the ligand.[33]



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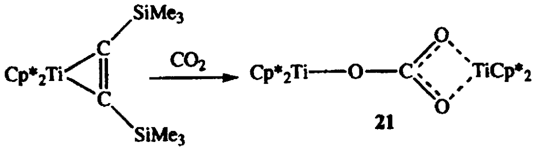

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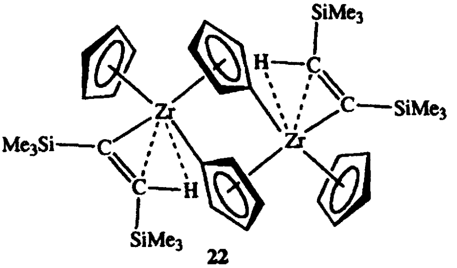
Reaction of carbon dioxide with the bis(trimethylsilyl)acetylene complex of permethyltitanocene $Cp^*{}_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$, leads to displacement of bis(trimethylsilyl)acetylene from the titanium co-ordination sphere and carbon dioxide undergoes disproportionation to form $Cp_2{}^*Ti(CO)_2$ and the binuclear carbonate complex of permethyltitanocene $(Cp_2{}^*Ti)_2CO_3$ **21**.[34]

Some reactions of the bis(trimethylsilyl)acetylene bis-cyclopentadienyl derivatives of Ti and Zr with lactams are also reported.[35] Ligand exchange reactions with N-methyl-ε-caprolactam give compounds of the type $(C_5H_{5-n}Me_n)_2Zr[\eta^2\text{-}C_2(SiMe_3)_2][O{=}C\text{-}N(Me)\text{-}(CH_2)_5]$.

The $(C_5H_{5-n}Me_n)_2Ti[\eta^2\text{-}C_2(SiMe_3)_2]$ (n = 0-5) complexes are prepared by the reduction of the corresponding titanocene dichlorides with magnesium in THF in the presence of bis(trimethylsilyl)acetylene (BTMSA).[36] The complexes decompose at temperatures in the range 100–200°C. The C_5Me_5 complex yields quantitatively (η^3:η^4-1,2,3-trimethyl-4,5 dimethylenecyclopentenyl)(pentamethylcyclopentadienyl)titanium and BTMSA is hydrogenated to a mixture of cis- and trans-bis(trimethylsilyl)ethene.[36] The other complexes yield mixtures of products on heating. The zirconium analogues $(C_5H_{5-n}Me_n)_2Zr[\eta^2\text{-}C_2(SiMe_3)_2]$ (n = 2-5; 1,3-dimethyl, 1,2,3-trimethyl) complexes are prepared in a similar fashion.[37] The nonisolated complex $(C_5H_4Me)_2Zr[\eta^2\text{-}C_2(SiMe_3)_2]$ (THF) rearranges after the loss of THF to give the dimer $[(\eta^5\text{-}C_5H_4Me)(\eta^1\text{-}C\text{-}(SiMe_3){=}CH(SiMe_3))Zr(\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_5H_3Me)]_2$ **22**.

The titanium-magnesium complex $[(\eta^5\text{-}C_5H_5)Ti][\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_2(SiMe_3)_2]_2\text{-}[(\eta^5\text{-}C_5H_5)Mg]$ containing perpendicularly bridging bis(trimethylsilyl)acetylene ligands reacts with excess (trimethylsilyl)ethyne to give mainly (η^5-1,2,4,5,6-pentakis(trimethylsilyl)(cyclohexadienyl)-(η^5-cyclopentadienyl)titanium(II) **23**.[38] Thus, the formation of the cyclohexadienyl ligand of this half-open 14 electron species is achieved from acetylenic precursors at the (η^5-cyclopentadienyl)-titanium(II) moiety. The X-ray crystal structure shows that the $SiMe_3$ group at C(6) is in exo-position and the Cp ring and of the dienyl part of the cyclohexadienyl ring are nearly parallel.



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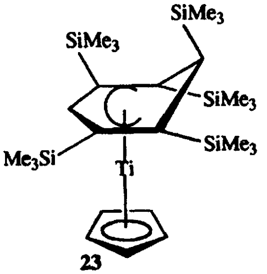

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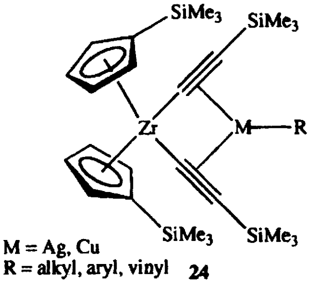
The complex $[(\eta^5\text{-}C_5HMe_4)_2Ti(\eta^1\text{-}C{\equiv}CC{\equiv}CSiMe_3)_2]^-[Li(THF)_2]^+$ is obtained by the reaction of $[(\eta^5\text{-}C_5HMe_4)_2TiCl_2$ with 2 equivalents of $LiC{\equiv}CC{\equiv}C\text{-}SiMe_3$ in THF. An X-ray crystal structure determination revealed that the lithium ion is embedded between the inner triple bonds of the 4-trimethylsilyl-1,3-butadiyn-1-yl tweezer arms.[39] Analogous complexes complex $[(\eta^5\text{-}C_5HMe_4)_2Ti\text{-}(\eta^1\text{-}C{\equiv}CSiMe_3)_2]^-[M]^+$ (M = Li, Na, K, and Cs) are prepared by the redox reaction of $(\eta^5\text{-}C_5HMe_4)_2Ti(\eta^1\text{-}C{\equiv}CSiMe_3)_2$ with the alkali metals in toluene.[40]

The synthesis and characterisation of the complexes $[(\eta^5\text{-}C_5H_4SiMe_3)_2\text{-}Ti(C{\equiv}CSiMe_3)_2]MX$ (M = Cu, X = OTf, SC_6H_5, $SC_6H_4NMe_2$-2, SC_6H_4-CH_2NMe_2-2, S-1-$C_{10}H_6NMe_2$-8 , Cl, $(N{\equiv}CMe)PF_6$; M = Ag, X = OTf) are described.[41] These complexes contain monomeric MX entities, which are η^2-bonded by both alkyne functionalities of the organometallic bis(alkyne) ligand $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2]$. Reactions of $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2]CuOTf$ with the Lewis bases $N{\equiv}CPh$ and $N{\equiv}CC(H){=}C(H)C{\equiv}N$ afford the cationic complexes $\{[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2]Cu(N{\equiv}CPh)\}OTf$ and $\{[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2]Cu\}_2(N{\equiv}CC(H){=}C(H)C{\equiv}N)(OTf)_2$, respectively. The copper arenethiolate complexes are fluxional in solution.[42]

The mono (σ-alkynyl) titanocene chlorides $[(\eta^5\text{-}C_5H_2SiMe_3)_2Ti(Cl)(C{\equiv}CR)]$ (R = Ph, $SiMe_3$) are prepared by reaction of one equivalent of $LiC{\equiv}CR$.[43] Treatment of the mono-chlorides with $ClMgCH_2SiMe_3$ or $LiC{\equiv}CR'$ yields $[(\eta^5\text{-}C_5H_4SiMe_3)_2TiCH_2SiMe_3(C{\equiv}CSiMe_3)]$ or $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CR)\text{-}(C{\equiv}CR')]$ (R = Ph, R′ = $SiMe_3$; R = R′ = Ph; R = R′ = $SiMe_3$), respectively. Heterobimetallic titanium-copper complexes are produced in a similar way to above, with the heterobimetallic compounds AgX (X = Cl; X = Br) also being synthesised.[44] The copper(I) and silver(I) alkyl, vinyl and aryl analogues are described in a separate paper **24**.[44] The organogold(I) compounds possess a trigonal-planar environment, formed by two η^2-coordinated alkyne units and a η^1-bonded organic group.[45]



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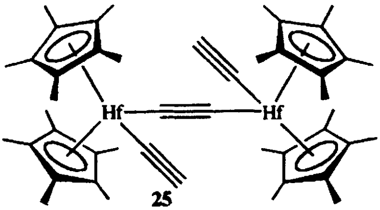

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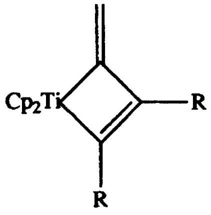
Reaction of $Cp^*{}_2HfCl_2$, with excess sodium acetylide at room temperature results in the synthesis of $Cp^*{}_2Hf(CCH)_2$. The identical reaction in refluxing THF results in the dimeric product $[(\mu_2\text{-}C_2)(Cp^*{}_2HfCCH)_2]$ **25**. Subsequent reaction of the monomer with lithium diisopropylamide (LDA) in the presence of trimethyltin chloride resulted in the trimetallic $Cp^*{}_2Hf(CCSnMe_3)_2$.[46]

The titanocene vinylidene intermediate $[Cp^*{}_2Ti{=}C{=}CH_2]$, formed by ethylene or methane elimination from $Cp^*{}_2TiCH_2CH_2C{=}CH_2$ and $Cp^*{}_2Ti\text{-}(CH{=}CH_2)(CH_3)$ respectively, reacts with symmetrical alkynes such as acetylene, 2-butyne, 1,2-diphenylacetylene, 1,2-bis(trimethylsilyl)acetylene, and 1,2-bis(tri-n-butyl-stannyl)acetylene by a [2 + 2] cycloaddition to give metallacyclobutenes $Cp^*{}_2TiCR{=}CRC{=}CH_2$ **26**. When unsymmetrical alkynes are used, different regioisomers can be isolated.[47] Reaction of the vinylidene intermediate with 1,3-diynes $RC{=}C\text{-}C{=}CR$ (R = Me, Ph, $SiMe_3$, CMe_3) by a [2 + 2]- cycloaddition, giving metallacyclobutenes Cp*$_2$TiC(C≡CR)=CRC=CH$_2$ **27**. Using the unsymmetrical 1,3-diyne RC≡CC≡CR^1 (R = CMe$_3$, R^1 = SiMe$_3$), a 9:1 mixture of the metallacyclobutenes Cp*$_2$TiC(C≡CR)=CR^{1}C=CH$_2$ and Cp*$_2$TiC-(C≡CR) =CR^{1}C=CH$_2$ is formed. In all cases, exclusive formation of one regioisomer exhibiting the C=CR substituent in the alpha-position of the metallacycle is observed.[48] The unusual coupling of Cp*$_2$Ti(CH=CH$_2$)(CH$_3$) and the Fischer carbene complex (CO)$_5$Cr=C(OCH$_3$)CH$_3$ is observed to give **28** and **29** which is the first example of an intramolecular coupling of inversely polarised carbene ligands.[49]



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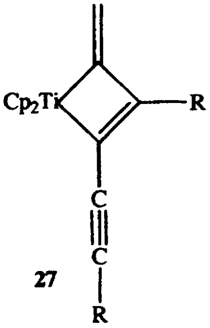

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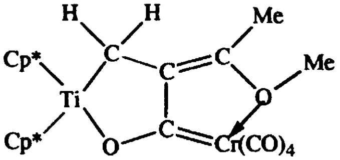

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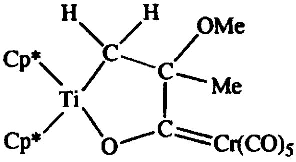
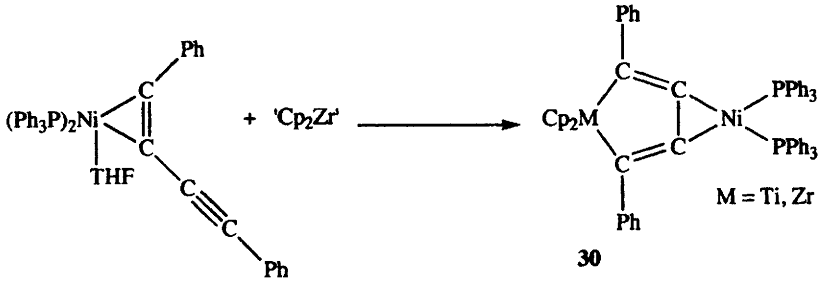


29

An unexpected activation of the central C-C single bond of PhC=C-C=CSiMe$_3$ and of one P-C bond in Ph$_3$P and coupling of the fragments to PhC=CSiMe$_3$ is observed in the reaction of [Ni(PPh$_3$)$_2$(η^2-PhC=C-C=SiMe$_3$)] with‘(C$_5$H$_5$)$_2$Ti’ providing, via the tweezer-like titanocene nickel(0) triphenylphosphine bisacetylide complex [(C$_5$H$_5$)$_2$Ti(μ-σ,η^2-C=CSiMe$_3$)(C=CPh)Ni(PPh$_3$)], the phosphido-bridged σ-π-acetylide complex [(C$_5$H$_5$)$_2$Ti(μ-σ,η^2-C=CPh)(μ-PPh$_2$)-Ni(PPh$_3$)].[50] Similar products are obtained where the bridging fragment is formed from an alkene-alkyne fragment **30**.[51]

Cyclopentadienyl-zirconium(IV) and -titanium(IV) halides and alkyls react with hydroquinones to give bridged dinuclear complexes **31**. Such compounds are also formed upon treatment of titanium(III) precursors with benzoquinone. It is also shown that the formation of the monobridged products is independent of the steric requirements of the substituents of the quinonide ring.[52]

Trimethylsilylcyclopentadiene-siloxy ethers Me$_3$SiC$_5$H$_4$(CH$_2$)$_n$OSiMe$_3$ (n = 2, 3) react with TiCl$_4$ to give (2-(cyclopentadienyl)-eth-1-oxy)titanium dichloride,



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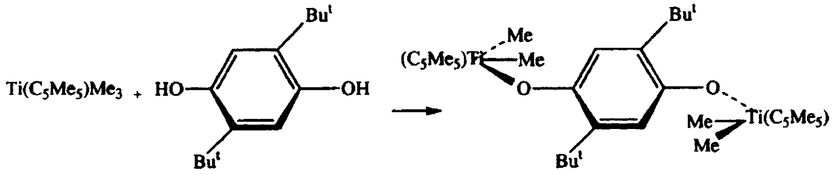
$[(\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2O]_2TiCl_2$ and (3-(cyclopentadienyl)-prop-1-oxy)titanium dichloride $[(\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_3O]_2TiCl_2$, by release of two equivalents of Me_3SiCl. Molecular structure determination shows that $[(\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2O]_2\text{-}TiCl_2$ is dimeric in the solid state with the alkoxide function bridging two centres, whereas $[(\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_3O]_2TiCl_2$ is a monomer with a bidentate cyclopentadienyl-alkoxide ligand.[53]



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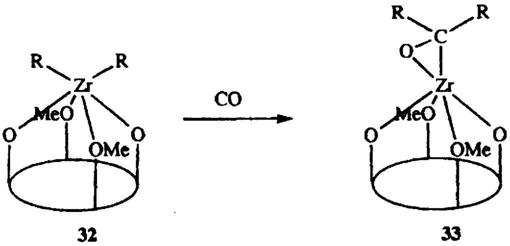


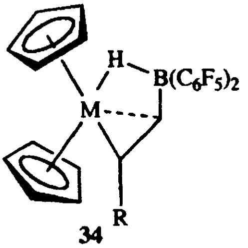
32 **33**

The homologation of meso-octaethylporphyrinogen to meso-octaethyltris(pyrrole)monopyridine and to meso-octaethylbis(pyrrole)bispyridine are carried out by reacting carbon monoxide with Zr-C and Zr-H functionalities respectively, supported by the auxiliary ligand meso-octaethylporphyrinogen, $[Et_8N_4H_8]$. A novel mode of electrophilic activation of aliphatic C-H bonds, assisted by zirconium(IV) in conjunction with an excess of MH [M = Li, Na, K], allows the metallation and then functionalisation of the meso-octaethylporphyrinogen periphery.[54] The dimethoxy-*p*-*tert*-butylcalix[4]ene dianion is reacted with $ZrCl_4$ to give the $ZrCl_2$ calixarene compound. The dimethyl **32** and dibenzyl analogues are synthesised by reaction with MeLi or benzyl Grignard reagent. CO insertion occurs when the dimethyl and dibenzyl compounds are reacted with carbon monoxide to give **33**.[55]

Reaction of $Si(C_5H_3\text{-}1,3\text{-}^tBu_2)Me_3$ with $HfCl_4$ in toluene or hexane at room temperature affords the new trichloro monocyclopentadienyl derivatives $[Hf(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}^tBu_2)_2Cl_3]$. Treatment of which with the appropriate alkylating reagent in hexane gives the mono[1,3-di(tert-butyl)cyclopentadienyl] trialkyl hafnium complexes $[Hf(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}^tBu_2)_2R_3]$, (R = CH_3, $CH_2C_6H_5$, $CH_2Si(CH_3)_3$]. When $[Hf(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}^tBu_2)_2Cl_3]$ reacts with 1 equivalent of TlCp in toluene at room temperature the mixed dicyclopentadienyl complex $[Hf(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}^tBu_2)_2\text{-}(\eta^5\text{-}C_5H_5)Cl_2]$. Reaction of the latter with LiMe led to the dimethyl complex $[Hf(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}^tBu_2)_2(\eta^5\text{-}C_5H_5)(CH_3)_2]$.[56]

β-Me elimination from cationic neopentyl complexes, $[Cp'_2Zr(CH_2CMe_3)]^+$, has been demonstrated. The more crowded complex (Cp′ = C_5Me_5) eliminates isobutene instantaneously at −75°C, whereas the less crowded analogue (Cp′ = C_5H_5) is stable in solution at 0°C but reversible β-Me elimination at 25°C; strong anion or Lewis base co-ordination suppresses β-Me elimination, consistent with involvement of a 14-electron species.[57]

Zirconocene olefin complexes $Cp_2Zr(PPh_2Me)(\eta^2\text{-}RCH{=}CH_2)$ (R = H, Et, Ph) react rapidly with 2 equivalents of $[HB(C_6F_5)_2]_n$ to give the zwitterionic products $Cp_2Zr\{\eta^3\text{-}[CH(R)CH_2BH(C_6F_5)_2\}$ (R = H, Et, Ph) **34** and the borane-phosphine adduct $Ph_2MeP.HB(C_6F_5)_2$. Spectroscopic and structural evidence confirms an interaction between zirconium and the beta-carbon attached to boron, resulting in pentacoordinated carbon.[58]



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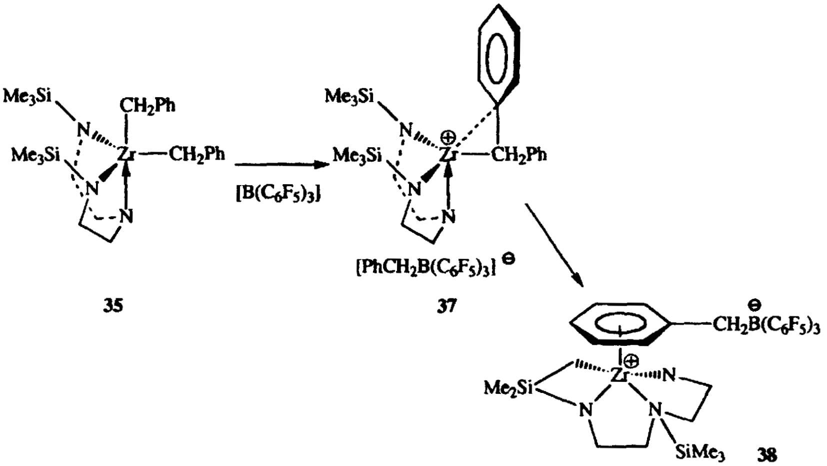
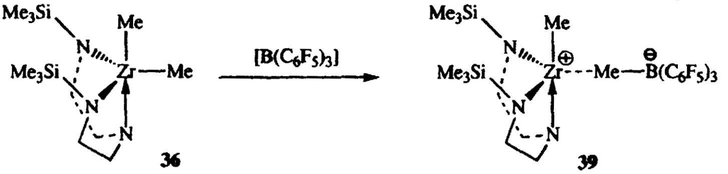
Alkyl abstraction from $\{Me_3SiN(CH_2CH_2NSiMe_3)_2\}ZrR_2$ (N_3ZrR_2; R = CH_2Ph **35**, Me **36**) using $B(C_6F_5)_3$ affords cationic alkyl complexes stabilised by a diamide ligand. The ionic η^2-benzyl adduct decomposes slowly to give a cationic cyclometalation product **37**, which co-ordinates the $[PhCH_2B(C_6F_5)_3]^-$ anion **38**; **36** reacts with $B(C_6F_5)_3$ to give methyl cation which co-ordinates the anion $[MeB(C_6F_5)_3]^-$ via a Zr...Me-B interaction **39**. Fluxional exchange of the environments of the axial and equatorial benzyls is observed and attributed to the dissociation of an amino nitrogen followed by inversion and reco-ordination.[59]

Functionalisation of a cyclopentadienyl ligand of the metallocyclic compound 1,1-bis(cyclopentadienyl)-2,3,4,5,-tetramethylzirconacyclocyclopentadiene, $[(\eta^5\text{-}C_5H_5)_2Zr(C(Me)C(Me)C(Me)C(Me)]$, occurs with the reaction of with $B(C_6F_5)_3$ to give **40**.[60] The complex formally exhibits a betaine structure with positive partial charge on zirconium and negative partial charge on boron.

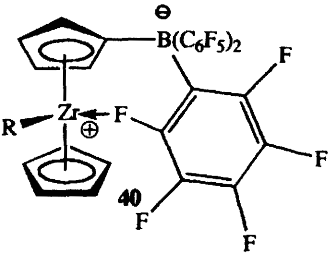
Treatment of the neutral trimethyl compounds Cp^*MMe_3 (M = Ti, Zr, Hf) with the highly electrophilic borane $B(C_6F_5)_3$ in methylene chloride in the



35 **37** **38**



36 **39**



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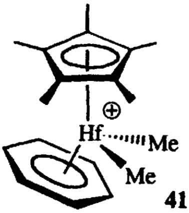
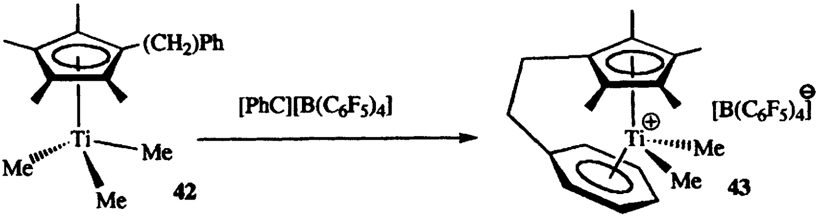


41 $\overset{\ominus}{MeB}(C_6F_5)_3$

presence of various arenes results in methyl carbanion abstraction and coordination of the arene to form complexes of the type [Cp*Me$_2$(η^6-arene)][MeB(C$_6$F$_5$)$_3$] **41** (M = Ti, Zr, Hf; arene = benzene, toluene, m- and p-xylene, anisole, styrene, mesitylene).[61]

A series of monocyclopentadienyltitanium complexes containing the 1-(2-phenylethyl)-2,3,4,5-tetramethylcyclopentadienyl ligand ($C_5Me_4CH_2CH_2Ph$) have been synthesised and characterised. The reaction of $C_5Me_4(SiMe_3)(CH_2CH_2Ph)$ with $TiCl_4$ is used to synthesise the trichloro $(C_5Me_4CH_2CH_2Ph)TiCl_3$, which is converted to $(C_5Me_4CH_2CH_2Ph)TiMe_3$ **42**. Reaction of the latter with 1 equivalent of $[Ph_3C][B(C_6F_5)_4]$ is almost quantitative to give the 'cationic' compound $[(C_5Me_4CH_2CH_2Ph)TiMe_2]^+$ $[B(C_6F_5)_4]^-$ **43**. This is thermally unstable in solution and very moisture sensitive.[62]

The authors have reported the first C$_2$-symmetric quadridentate Schiff-base complex and zirconium analogues thereof. The Schiff-base ligand was synthesised by addition of 2,2′-diamino-6,6-dimethylbiphenyl and 3,5-di-*tert*-butylsalicylaldehyde and after conversion to the disodium salt, it was reacted with $ZrCl_4(THF)_2$ to give *cis*-(±)-$[ZrLCl_2]$ **43**.[63]



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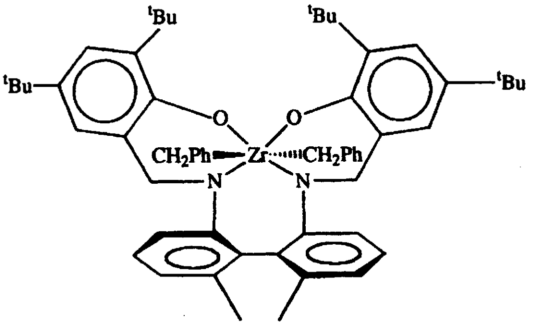
The novel alkene polymerisation co-catalysts $[Zr(CH_2Ph)_2(ArDABP)]$ containing the biphenyl-bridged ligands 2,2′-di-(N-benzyl)amino-6,6′-dimethylbiphenyl (ArDABP, Ar = $CH_2C_6H_4{}^tBu$-4 or $CH_2C_6H_4$-Ph) display averaged C-2-symmetry in solution and an η^5-benzyl co-ordination mode in the solid state **45**.[64]



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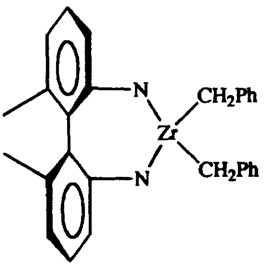
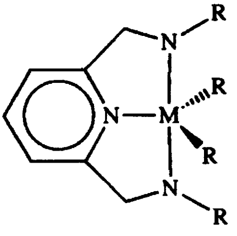


45

Titanium complexes bearing a pyridinediamide ligand $[2,6\text{-}(RNCH_2)_2NC_5H_3]^{2-}$ (R = 2,6-diisopropylphenyl (BDPP); R = 2,6-dimethylphenyl (BDMP)) have been synthesised. The dichloride complexes $[2,6\text{-}(RNCH_2)_2NC_5H_3]TiCl_2$ are prepared in high yield from $\{2,6\text{-}[(Me_3Si)RNCH_2]_2NC_5H_3\}$ and $TiCl_4$ via the elimination of 2 equivalents of $SiMe_3Cl$. Mono(alkyl) and bis(alkyl) **46** complexes are prepared from $[2,6\text{-}(RNCH_2)_2NC_5H_3]TiCl_2$ and various Grignard reagents. A single-crystal X-ray diffraction study of $(BDMP)TiBr(CH_2CMe_2Ph).C_6H_6$ revealed a distorted square pyramid structure with the neophenyl group occupying the axial position.[65] The zirconium derivatives have been reported elsewhere.[66]

Zirconium complexes of the multidentate ligand CpH(NMe)SiN(H)R (SiNR = $\text{-}SiMe_2N\text{-}t\text{-}butyl$; NMe = $\text{-}CH_2CH_2NMe_2$) are prepared and characterised via amine and alkane elimination procedures. Reaction of the multidentate ligand with $Zr(NMe_4)$ gives a mixture of bis-amido complexes in which the ligand is 1,2 and 1,3 substituted. This mixture is converted to the analogous dichlorides using



M = Ti, Zr

46

$Me_2NH.HCl$ and 1,3-3 product is purified at this stage; alternatively, 1,3-3 is obtained in one pot from 1 and $Zr(NMe_2)_4$ in approximately 70% yield. Conversion of 1,3-3 to dimethyl compound $(Cp(NMe)SiNR)Zr(CH_3)_2$ is accomplished via reaction of the dichloride with methyllithium; methide abstraction with the Lewis acids $B(C_6F_5)_3$ $[Ph_3C]^+[B(C_6F_5)_4]^-$ generated the cationic alkyls $[(Cp(NMe)SiNR)Zr(CH_3)]^+[R'B(C_6F_5)_3]^-$ ($R' = CH_3$, C_6F_5), which are characterised by NMR spectroscopy.[67]

Zirconacyclopentadiene complexes containing gem-dimetallated carbon atoms by zirconium and tin is prepared by the oxidative coupling reaction of 'Cp_2Zr' with distannyldiyne compounds.[68]

It has been asserted that the first examples of anionic π free ligands and a new class of metal silyl complexes are synthesised. The alkyl-silyl complexes $(Me_3ECH_2)_3MSi(SiMe_3)_3$ (E =C, Si; M = Zr, Ti), which are free of anionic π ligands such as cyclopentadienyl, are synthesised by the metathetic reactions of chlorotrialkyl complexes $(Me_3ECH_2)_3MCl$ with silyllithium reagent $LiSi(SiMe_3)_3(THF)$. The structures of $(Me_3ECH_2)_3MSi(SiMe_3)_3$ (E = C, Si] are determined by X-ray diffraction show that the three alkyl groups on the metal centres are staggered with respect to the trimethylsilyl groups on the central silicon atoms.[69]

Insertion of methyl isocyanate is observed into a host of newly generated metal-metal bonds (this reaction is analogous to α-additions to isocyanides). These heterobimetallic complexes are produced by the co-ordination of a novel type of tripodal amido ligand providing the key to the synthesis of stable M-M′ (M = Ti, Zr, Hf; M′ = Fe, Ru) $[MeSi(SiMe_2N(C_6H_4Me\text{-}4)\}_3M\text{-}M'(\eta^5\text{-}C_5H_5)(CO)_2]$, with unsupported metal-metal bonds.[70] The crystal structures of the Ti- and Zr-Fe complexes are reported, the latter being the first X-ray structure of a compound containing a Zr-Fe bond.[71] Insertion products are also observed with the X=C=Y heteroallenes and the Zr-Fe or Zr-Ru heterobimetallics to yield the insertion products $HC(SiMe_2NC_6H_4F\text{-}2)_3Zr(XYC)M(CO)_2(\eta^5\text{-}C_5H_5)$, (X = O, S; Y = O, S, NR); single-crystal X-ray structure analyses establish the mode of co-ordination of the substrates to the two metal centres.[72]

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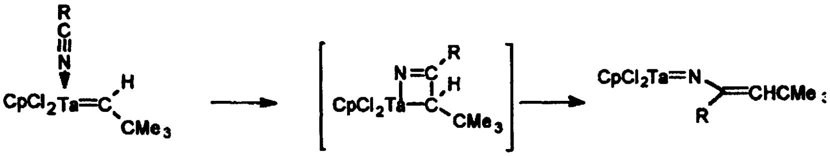
Part II: Group 5 *by Elizabeth M. Page*

1 Reviews

A review which discusses the reactions of organonitriles with transition metal complexes contains some material of relevance to Group 5 elements. The reactions of nitriles with nucleophilic alkylidene complexes to form alkenyl imido complexes are summarised in equation i.[1]



equation i

The use of transition metals in organic synthesis has been highlighted in an annual review which surveys the literature for 1994.[2] A short review which describes different routes to V(II) complexes starting from the metal and from higher oxidation states has been published.[3]

2 Alkyl Complexes

The gas phase structure of Me_3TaCl_2 determined by electron diffraction was found to have trigonal bipyramidal geometry (Ta-C = 2.158(5)Å, Ta-Cl = 2.317(3) Å).[4]

The V(III)-Me complex $[(Me_3Si)_2N]_2VMe(THF)$ has been prepared by methylation of the V-Cl derivative with Me_2Mg and its reactions with RNC (R = Bu^t, Xylyl), styrene and its thermal behaviour have been investigated.[5]

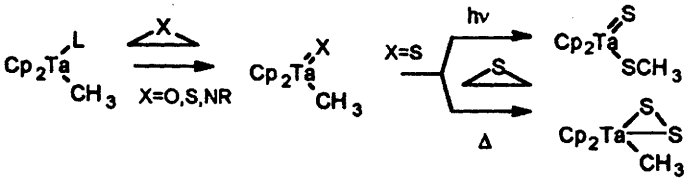
The tantalum(V) imido pentamethylcyclopentadienyl dimethyl and chloro methyl complexes undergo insertion of CO into the Ta-Me bonds to give dinuclear diolate and oxoiminoacyl derivatives respectively. Insertion of RNC leads to the iminoacyl complexes.[6]

A series of CO_2 complexes of the type $Cp'_2Nb(\eta^2\text{-}CO_2)R$ ($Cp' = MeC_5H_4$, R = CH_2SiMe_3, CH_2CMe_3, CH_2Ph, CH_3) has been prepared and their behaviour upon thermolysis investigated.[7]

The complex $Cp^*[C_4H_4BMe]TaMe_2$ has been prepared by reaction of excess $AlMe_3$ with $Cp^*[C_4H_4BMe]TaMeCl$ and its structure compared with those of $Cp^*[C_4H_4BN(CHMe_2)_2]TaMe_2$ and $[Cp^*[C_4H_4BNH(CHMe_2)_2]TaMe_2][B(C_6F_5)_4]$. The rates of hydrogenation of the complexes were investigated.[8]

The complex $[Cp\{(C_7H_6)_3C\}TaMe_2]$, analogous to Group 4 bent metallocenes, has been obtained by substitution of a Cp group by the dianionic ligand $[C(CHC_6H_5)_3]^{2-}$ and its structure determined.[9]

Irradiation of $Cp_2Ta(C_2H_4)(CH_3)$ or thermolysis of $Cp_2Ta(PMe_3)(CH_3)$ promotes the formation of an intermediate which behaves as $Cp_2Ta(CH_3)$ abstracting heteroatoms and groups from oxiranes, thiiranes and aziridines according to equation (ii). The sulfido product $Cp_2Ta(=S)(CH_3)$ is capable of abstracting a further S atom from thiirane to give $Cp_2Ta(\eta^2\text{-}S_2)(CH_3)$.[10] $Cp_2Ta(PMe_3)(CH_3)$ undergoes reaction with aryl azides ArN_3 (Ar = C_6H_5, p-$CF_3C_6H_4$, p-$NMe_2C_6H_4$) to give uncommon terminal phenylazido complexes $Cp_2Ta(CH_3)(N_3Ar)$ and free phosphine. Heat or UV irradiation affords N_2 and the imido species $Cp_2Ta(CH_3)(=NAr)$.[11]



equation ii

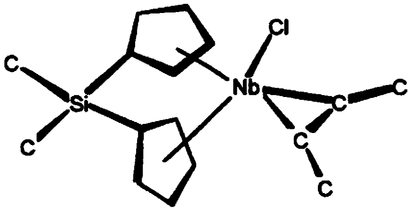
The reaction of $Nb(\eta^6\text{-mes})$ with I_2 in THF yields $Nb_2(\eta^6\text{-mes})_2(\mu\text{-}I)_4$. In the solid state the mes ligands were found to exist in non-planar boat configurations showing 1,4-diene type π-electron delocalisation.[12]

3 Alkyne Complexes

Treatment of $NbCl_3(DME)$ with first an alkyne ($PhC{\equiv}CCH_3$, $PhC{\equiv}CCH_2CH_3$, $PhC{\equiv}CCH_2CH_2CH_3$, $CH_3C{\equiv}CCH_3$, $PhC{\equiv}CPh$) and then KTp* provides a high yield one-pot synthesis of $Tp^*NbCl_2(alkyne)$. The dimethyl derivatives, $Tp^*NbCl_2(alkyne)$, were obtained for several of the alkynes from the appropriate dichloro complex. In all cases the alkyne group was shown to occupy the molecular mirror plane.[13]

A further article has appeared on the synthesis of $TpNbCl_2(RC'CR')$ (R = Ph, R′ = Me; R = R′ = Me, Et, $SiMe_3$, Ph) from the reaction between $NbCl_3(DME)(RC{\equiv}CR')$ and KTp. Again spectroscopic measurements showed the alkyne to be in the molecular mirror plane. However in $TpCpNb(Cl)PhC{\equiv}CCH_3$ the alkyne was observed parallel to the Cp plane in both solution and in the crystal structure. M.O. calculations suggest that orbital interactions dictate the geometry in this latter complex.[14]

The *ansa*-niobocene(IV) complex, $[Me_2Si(\eta^5\text{-}C_5H_4)_2]NbCl_2$, has been prepared by reaction of $NbCl_4(THF)_2$ and $[Me_2Si(C_5H_4)_2]Tl_2$ in THF. Reduction of $[Me_2Si(\eta^5\text{-}C_5H_4)_2]NbCl_2$ in the presence of an alkyne (2-butyne or diphenylacetylene) yields the *ansa*-niobocene(III)monochloride alkyne complexes $[Me_2Si(\eta^5\text{-}C_5H_4)_2]NbCl(RC{\equiv}CR)$ (R = Me (**1**), Ph).[15]



(1)

The first examples of mixed alkyne-nitrile complexes $[Tp^*Nb(CO)(PhC{\equiv}CMe)(RCN)]$, (R = Me, Et, Ph), where the η^2-bound ligands formally contribute three electrons each to the metal centre have been reported and structurally characterized ((**2**) R=Ph). The complexes were synthesised from $[Tp^*Nb(CO)_2(PhCCMe)]$ and the nitrile in refluxing THF.[16]

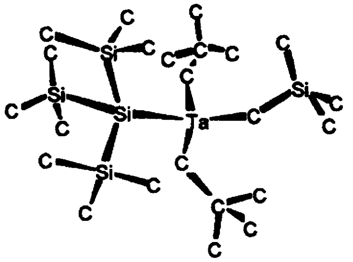
Insertion of activated alkynes $R'C{\equiv}CR'$ into the Nb-H bond of hydride isocyanide complexes leads to the corresponding alkenyl isocyanide complexes. Reaction of a trihydride niobocene complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)_3$ with alkyne yields $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)[\eta^2\text{-}RO_2C(H){=}C(H)CO_2R]$ (R = Me, or Bu^t).[17]

Close intraatomic C...C distances in the Nb(III) isonitrile complex $[NbI_2(CNBu^t)_6]I$ result in C-C coupling with the formation of $[NbI_2(CNBu^t)_4(Bu^tNHC{\equiv}CNHBu^t)]I$ which contains a 4-electron donating acetylene. Similar couplings are also possible in the Nb(I) complex $[NbI(CO)_2(CNCy)_2dppe]$.[18]

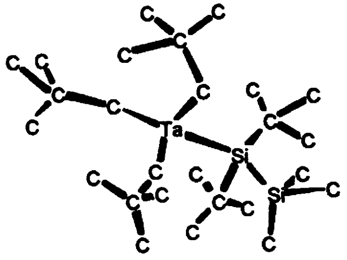
Photoreaction between $[NbI(CO)_2(PMe_2Ph)_2(Ph_2PC{\equiv}CPPh_2)]$, having side-on coordinated alkyne acting as a 4-electron donor, and $Mo(CO)_6$ yields the C-C coupling product $[\{Mo(CO)_4\}_2\{\mu\text{-}(Ph_2P)_2C{=}CHCH{=}C(PPh_2)_2\}]$.[19]

4 Alkylidene Complexes

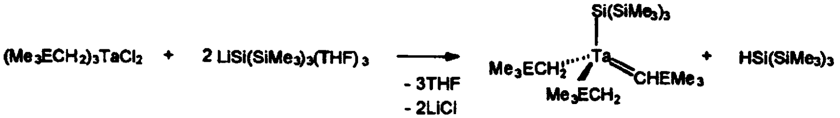
In a reaction which involves the elimination of silane, complexes of the type $(Me_3ECH_2)_2Ta({=}CHEMe_3)Si(SiMe_3)_3$ (E = C (**3**), Si (**4**)) have been obtained according to equation (iii) with the formation of alkylidene bonds.



(3)



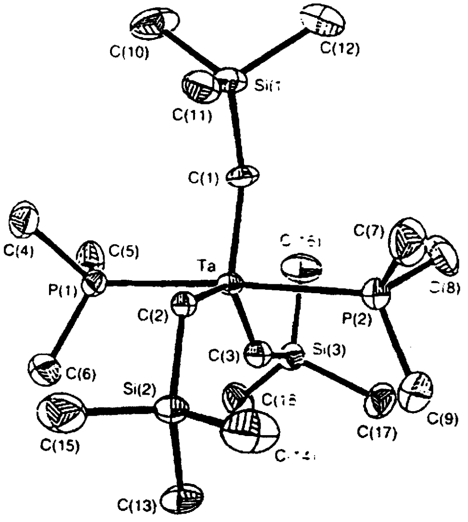
(4)



E = C, Si

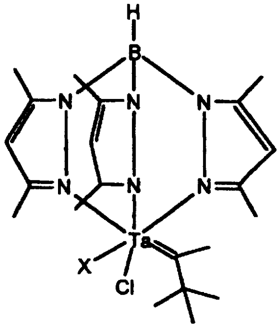
equation iii

Kinetic and mechanistic studies were carried out on the formation of **4** and are discussed.[20] **3** and **4** react with PMe_3 to form bis(alkylidene) complexes $(Me_3ECH_2)Ta(PMe_3)_2(=CHEMe_3)_2$ via preferential silane elimination. The structure of the Si analogue was determined (**5**).[21]



(5)

The electronically unsaturated six-coordinate Ta alkylidene complexes, Tp*Ta(=CHBu^t)(X)(Y) (**6**) (X = Halide, Y = Halide, NR_2, OR) have been synthesised. NMR studies indicated a strong agostic interaction between the alkylidene C-H bond and the metal centre reflected in the value of $J_{C\text{-}H\alpha}$ and modulated by changes in the π donor properties of the ancillary ligands.[22]

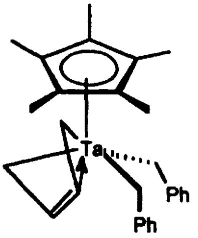


X = OMe, OPr ^{i}, NMe $_2$, Cl

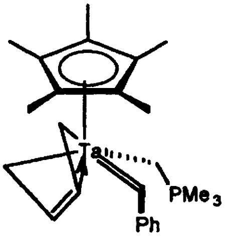
(6)

Thermolysis of Cp*(η^4-C_4H_6)Ta(CH_2Ph)$_2$ (**7**) generates a benzylidene species which is trapped by PMe_3 to give Cp*(η^4-C_4H_6)Ta(=CHPh)(PMe_3) (**8**). Protonolysis of (**8**) with MeOH and 3,3-dimethyl-1-butyne produces Cp*(η^4-C_4H_6)Ta(CH_2Ph)(OMe) and the alkyne Cp*(η^4-C_4H_6)Ta(CH_2Ph)(C≡CMe_3) respectively.[23]

Alkylation of TaCp*Cl_4 with Li(2-CH_2NMe_2)C_6H_4 has resulted in the synthesis of trichloroalkyl and dichlorocyclometalated Ta(V) complexes. Treatment of these compounds with different Li-amides results in α-H elimination and the formation of Ta alylidene complexes.[24]



(7)



(8)

Reaction of CS_2 with Cp'$_2$Nb(H)(η^2-CH_2=CH_2) or Cp'$_2$Nb(H)(η^2-CH_2=CHPh) results in the alkylniobocene complexes Cp'$_2$Nb(Et)(η^2-CS_2-*C,S*) and Cp'$_2$Nb(CH_2CH_2Ph)(η^2-CS_2-*C,S*) respectively. The interactions of η^2-CS_2 containing complexes Cp'$_2$NbCl(η^2-CS_2-*C,S*) with alkynes bearing electron withdrawing groups to give 1,3-dithiol-2-ylidene nibocene, $Cp'_2NbX(=\overline{CS(R)C=C(R)S})$ species ($X = Cl, Et, CH_2CH_2Ph$,; $R = CF_3, COOMe, COOBu^t$) was investigated.[25]

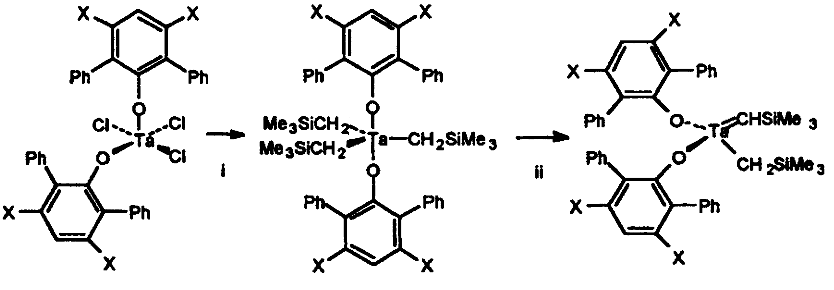
$$Cp'_2Nb(X)(\eta^2\text{-}CS_2\text{-}C,S) + RC{\equiv}CR \rightarrow Cp'_2NbX(=\overline{CS(R)C=C(R)S})$$

equation iv

5 Aryl Oxides and Other Oxygen Containing Complexes

Reaction of the Ta monohydride complex, $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2(H)(PMe_2Ph)_2]$ with organic isocyanides, RNC, yields the η^2-iminoformyl complexes $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2\{HC(PMe_2Ph)NR\}]$ ($R = 2,6$-diisopropylphenyl, 2,6-dimethylphenyl, Bu^t). The diisopropyl complex undergoes reaction with PMe_3 to produce $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2\{HC(PMe_3)NC_6H_3Pr^i_2\text{-}2,6\}]$. The dimethylphenyl derivative reacts with 2,6-dimethylphenyl isocyanide to produce the ylide complex $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_3Cl_2\{RN{=}CHC({=}PMe_2Ph)NR\}]$ ($R = C_6H_3Me_2\text{-}2,6$).[26]

An attempt has been made to quantify the resistance to cyclometalation of *ortho*-phenyl rings in 3,5-disubstituted-2,6-diphenylphenoxides coordinated toTa by variation of the *meta*-substituent. Alkylation of tantalum trichlorides, $TaCl_3(OC_6HX_2\text{-}3,5\text{-}Ph_2\text{-}2,6)_2$, ($X = H, Ph, Me$) by $LiCH_2SiMe_3$ yields $[Ta(OC_6HX_2\text{-}3,5\text{-}Ph_2\text{-}2,6)_2(CH_2SiMe_3)_3]$, **(9)**. Solutions of **(9)** in C_6D_6 undergo high yield conversion to the alkyl, alkylidene compounds, $[Ta({=}CHSiMe_3)(OC_6HX_2\text{-}3,5\text{-}Ph_2\text{-}2,6)_2(CH_2SiMe_3)]$ **(10)** upon photolysis (scheme i). NMR measurements indicate only minimal C-H agostic interaction between the metal and the α-CH bond of the alkylidene ligand. The stability of **(10)** towards cyclometalation and the formation of **(11)** was found to be strongly dependent upon the nature of the *meta*-substituent on the aryloxide ligand.[27]



(9) (10) (11)

i = 3 equiv. $LiCH_2SiMe_3$, C_6H_6 ii = hv / $SiMe_4$

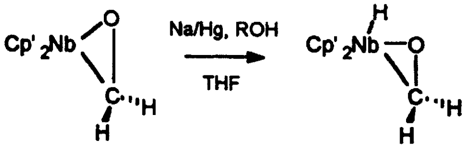
X = H, Ph, Me

scheme i

Facile dehydrogenation of the *ortho*-substituent of a 2,6-diisopropylphenoxide ligand in $[Nb(OC_6H_3Pr^i_2\text{-}2,6)_3Cl_2]$ upon Na reduction in THF solvent produces

$[Nb(OC_6H_3Pr^i\text{-}\eta^2\text{-}CMe{=}CH_2)(OC_6H_3Pr^i_2\text{-}2,6)_2(THF)]$. Dehydrogenation is thought to proceed via C-H bond activation within a d^2-Nb(III) aryloxide followed by β-hydrogen abstraction of H_2. Further reactions of $[Nb(OC_6H_3Pr^i\text{-}\eta^2\text{-}CMe{=}CH_2)(OC_6H_3Pr^i_2\text{-}2,6)_2(THF)]$ with py, $Ph_2C{=}O$, $PhC{\equiv}CPh$ and ring expansion were investigated.[28]

Reduction of $Cp'_2Nb(Cl)(\eta^2\text{-}OCH_2)$ yields initially the paramagnetic formaldehyde precursor **(12)** and ultimately the hydride **(13)** (equation (v)) in the presence of ROH which is assumed to promote H-bond activation of **(13)**.[29]



equation v

(12) **(13)**

Alkylation of the complex $[(calix[4]OMe)TaCl_2]$ leads to $[(calix[4]OMe)TaR_2]$ ($R = Me, PhCH_2, p\text{-}MeC_6H_4$). These dialkyl derivatives undergo photochemical or thermal dealkylation at the methoxy group to give [calix[4]TaR]. Reactions of $[(calix[4]OMe)TaR_2]$ with CO and Bu^tNC lead to the corresponding η^2-ketones $[(calix[4]OMe)Ta(\eta^2\text{-}COR_2)]$ and η^2-imenes, $[(calix[4]OMe)Ta\{\eta^2\text{-}N(Bu^t)CR_2\}]$ respectively.[30]

6 Nitrogen Containing Complexes

$[NbCl_2\{N(SiMe_3)_2\}_2]$ has been employed to obtain the Nb(IV) amido complexes $[NbCl\{N(SiMe_3)_2\}_2Ph]$ and $[(Cp)_2\overline{NbN(SiMe_3)SiMe_2CH_2}]$ by reaction with $ZnPh_2$ and $Zn(Cp)_2$ respectively.[31]

The reactions of $[\{(Me_3Si)_2N\}_2VCl(THF)]$ and $[\{(C_6H_{11})_2N\}_2V(\mu\text{-}Cl)_2\text{-}Li(THF)_2]$ with CH_2PPh_3 proceed to form the corresponding zwitterionic complexes $[(R_2N)_2VCl(CH_2PPh_3)]$ whose structures were determined.[32]

The highly reactive V(III) organometallics $[Et_8(m\text{-}MeC_5H_2N)(C_5H_3N)\text{-}(C_4H_2N)_2VCl]$ and $[Et_8(m\text{-}MeC_5H_2N)(C_5H_3N)(C_4H_2N)_2VMe)]$ have been obtained by reaction of $VCl_3(THF)_3$ with the lithium derivative of meso-octaethylporphyrin. Carbonylation of the methyl derivative leads to $[Et_6(m\text{-}MeC_5H_2N)(C_5H_3N)(C_4H_2N)_2V\text{-}O\text{-}C\text{-}(CEt_2)(Me)]$ via an intermediate η^2-acyl derivative.[33] In a similar reaction the methyl and η^2-iminoacyl complexes of $[(\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-}Et_8N_4)Nb\text{-}Cl]$ have been obtained. In addition reaction of $[(\eta^5{:}\eta^1{:}\eta^1{:}\eta^1\text{-}Et_8(C_4H_2N)_3(p\text{-}MeC_5H_2N)Nb{=}O]$ with LiMe resulted in α-metalation of one of the *meso*-ethyl groups of the porphyrin.[34]

7 Other Complexes

The first early transition metal complexes to contain the σ-bonded fluoromes ligand have been reported. Treatment of $VCl_3(THF)_3$ with $Li[C_6H_2(CF_3)_3\text{-}2,4,6]$ yielded $[V\{C_6H_2(CF_3)_3\text{-}2,4,6\}_2Cl(THF)]$ (1:3 molar ratio) and $[V\{C_6H_2(CF_3)_3\text{-}2,4,6\}_3OLi(THF)_3]$ (1:*ca* 3.5 molar ratio), both of which complexes exhibit multiple intramolecular V...F interactions.[35]

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Part III: Group 6 *by Nicholas Carr*

Numerous aspects of the organometallic chemistry of chromium, molybdenum and tungsten have been covered in review articles. Topics include the organometallic chemistry of monometallic species,[1] the literature on metal-carbon triple bonds covering the period from early 1990 to mid 1994,[2] the organometallic chemistry of halocarbonyl complexes of Mo(II) and W(II) including a section on alkylidene and alkylidyne complexes,[3] the organometallic[4] and coordination[5] chemistry of carbon monoxide, the reactivity of transition metal alkylidene complexes with alkenes and alkynes with examples of carbene-alkyne-alkene three-component coupling reactions,[6] transition metal alkane complexes including those of the type [$M(CO)_5$(alkane)] (M = Cr, Mo, W),[7] the effect of the spin-state on the stability, structure and reactivity of 'open-shell' organometallic compounds,[8] recent developments in the chemistry of dinuclear complexes having four-electron donor unsaturated hydrocarbon bridging ligands,[9] and new developments in organometallic chemistry during 1994 with sections on organometallic compounds in new materials and in organic synthesis.[10] Some work of relevance to this review can be found in reviews of the coordination chemistry of chromium,[11] molybdenum[12] and tungsten.[13]

Two articles have covered the ever increasing use of transition metal complexes, including Group VI alkylidene complexes, in organic synthesis.[14,15] More specifically, the use of molybdenum alkylidene complexes as catalysts for carbocyclisations[16] and the role of β-amino substituted α,β-unsaturated Fischer carbene complexes in organic transformations[17] have been discussed.

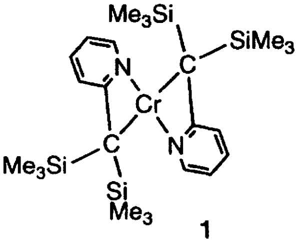
Several density functional and/or ab initio calculations have been reported:

optimised geometries and M-L bond dissociation energies for the complexes $[ML(CO)_5]$ (L = CO, SiO, CS, N_2, NO^+, CN^-, NC^-, HCCH, CCH_2, CH_2, CF_2, H_2) have been calculated and agree well with experimental observations.[18] The intrinsic π-bond strength $D_{\pi,\mathrm{int.}}$(M=C) for the carbene complexes $[M(=CH_2)(CO)_5]$ (M = Cr, Mo, W) and $[Cr(=EH_2)(CO)_5]$ (E = Si, Ge, Sn) has been shown to be significantly greater for E = C (*ca.* 202 *cf.* < 100 kJmol^{-1}) but relatively insensitive to the metal (*ca.* 200 kJmol^{-1} for M = Cr, Mo and W). Molecular orbital arguments are provided to explain these trends.[19] The equilibrium structure of $[W(CH_3)_6]$ was predicted to be a distorted trigonal prism with a C_{3v} WX_6 backbone, slight twisting of the methyl groups giving rise to C_3 overall symmetry.[20] Almost at the same time the actual molecular structure of $[W(CH_3)_6]$ was determined by a single crystal X-ray diffraction study at −163°C and confirmed the conclusions from the theoretical study.[21] Calculations on the model complexes $[\{(OH_2)_n(OH)_{3-n}M\}_2(\mu\text{-}C_2)]$ (M = Ti, V, Cr, Mn; n = 0, 1, 2) have led to a simple MO model allowing the prediction of the interaction mode of the bridging 'C_2' unit in dinuclear complexes.[22] Which of the three possible limiting structures (M-C≡C-M, M=C=C=M, M≡C-C≡M) is adopted depends on the d-configuration, the oxidation state of the metal and the nature of the ancillary ligands. Extended Hückel calculations predict that the lowest excited state of the tungsten and molybdenum arylcarbyne complexes $[M(\equiv CAr)(CO)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ (Ar = Phenyl, *o*-tolyl, α-naphthyl) is based on a $d(M)\rightarrow\pi^*(M\equiv C\text{-}Ar)$ configuration.[23] Absorption, emission and transient absorption spectroscopic studies would appear to confirm this.

Two nuclear magnetic resonance (NMR) studies of note have been published: the dynamics of the methyl groups in $[W(CH_3)_4(\eta\text{-}C_5Me_5)][PF_6]$ have been investigated by solid-state ^2H and ^{13}C spectroscopy,[24] and a method to assign the conformation of Fischer carbene complexes of the type $[M\{=C(Ar)OCH_2Ar'\}(CO)_5]$ (M = Cr, W; Ar, Ar′ = aryl) through the diastereotopicity of the methylene protons of the benzyl groups has been described.[25]

Treatment of $CrCl_2$ with $Li_2[(btsmp)_2]$ and $[Li(tsmp)(OEt_2)]_2$ [btsmp = 2-pyridino(bistrimethylsilyl)methyl, tsmp = 2-pyridino(trimethylsilyl)methyl] affords the chromium(II) pyridine functionalised alkyls $[Cr(btsmp)_2]$ **1** and $[Cr(tsmp)_2]$, respectively, the former of which has been characterised by an X-ray diffraction study.[26] The η^1-enolate complex $[W\{CH_2C(O)O\overline{NC(O)CH_2CH_2C}O\}(CO)_3(\eta\text{-}C_5H_5)]$ has been synthesised from $Na[W(CO)_3(\eta\text{-}C_5H_5)]$ and *N*-succinimidyl chloroacetate.[27] Similarly, reaction of 1-chlroro-4-methyl-4-penten-2-yn-1-yl with $Na[W(CO)_3(\eta\text{-}C_5H_5)]$ gives $[W\{CH_2C\equiv CC(Me)=CH_2\}(CO)_3(\eta\text{-}C_5H_5)]$, which in turn affords *anti*-$[W\{\eta^3\text{-}CH_2C(CO_2Me)C(H)C(Me)=CH_2\}(CO)_2(\eta\text{-}C_5H_5)]$ when heated with CF_3SO_3H and MeOH.[28]

The complex $[W(Me)(CO)_3(\eta\text{-}C_5H_5)]$ reacts with the acid $[H(OEt_2)_2][B\{C_6H_3(CF_3)_2\}_4]$ to afford $[W(OEt_2)(CO)_3(\eta\text{-}C_5H_5)][B\{C_6H_3(CF_3)_2\}_4]$ through activation of the α-CH bond of normally unreactive acyclic Et_2O.[29] In a similar reaction, $[H(OPr^i{}_2)_2][B\{C_6H_3(CF_3)_2\}_4]$, $[Cr(CH_2SiMe_3)_2(\eta\text{-}C_5Me_5)]$ and Et_2O give $[Cr(OEt_2)_2(CH_2SiMe_3)(\eta\text{-}C_5Me_5)][B\{C_6H_3(CF_3)_2\}_4]$, which was shown to be a homogeneous catalyst for the polymerisation of ethene and α-olefins such as propene and 1-hexene.[30]



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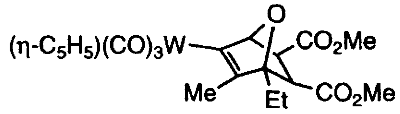


2

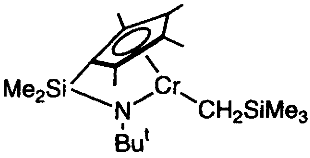
In the presence of $BF_3{\cdot}Et_2O$, the η^1-propargyl complexes $[W(CH_2C{\equiv}R)(CO)_3(\eta\text{-}C_5H_5)]$ (R = Me, Ph) react with aldehydes [R'C(H)O] to give the η^1-2,5-dihydro-3-furyl complexes $[W\{C{=}C(R)CH(R')OCH_2\}(CO)_3(\eta\text{-}C_5H_5)]$, which in turn afford the η^1-3-furylidene complexes $[W\{{=}CC(R){=}C(R')OCH_2\}(CO)_3(\eta\text{-}C_5H_5)][BF_4]$ upon treatment with $[Ph_3C][BF_4]$. At temperatures >5°C these 3-furylidene species rearrange to the 2-furylidene isomer, $[W\{{=}CC(H){=}C(R)CH(R')O\}(CO)_3(\eta\text{-}C_5H_5)][BF_4]$, whereas treatment with triethylamine at −60°C gives the η^1-3-furyl complexes $[W\{C{=}C(H)OC(R'){=}C(R)\}(CO)_3(\eta\text{-}C_5H_5)]$ which in turn are isomerised to the 2-furyl isomer upon treatment with acid.[31] A series of η^1-oxabicyclic complexes of tungsten (*e.g.* 2) have been stereoselectively formed by reaction of $[W\{C{=}CHOC(Et){=}CMe\}(CO)_3(\eta\text{-}C_5H_5)]$ with dimethyl fumarate, *N*-phenylmaleimide, ethyl propiolate or dimethyl acetylene dicarboxylate. Protonation of these compounds leads to atypical carbon-carbon bond scission and deoxygenation involving an intermediate η^1-2-hydrofurylium cation.[32] Treatment of $[Mo(CO)_3(\eta^6\text{-}C_6H_6)]$ or $[W(NCEt)_3(CO)_3]$ with methyl or ethyl methacrylate affords the oxadiene complexes $[M\{H_2C{=}C(Me)C(O)OR\}_2(CO)_2]$ (M = Mo, W; R = Me, Et). The bonding mode of the unsaturated ester ligand in these species appears from an X-ray diffraction study (M = W, R = Me) to be intermediate between η^1 and η^2-π at the carbonyl oxygen atom. The ester ligands are labile towards substitution, thereby allowing other complexes of 1-oxa-1,3-dienes to be prepared. This methodology has been successfully applied to the synthesis of tungsten complexes of temperature sensitive α,β-unsaturated ketones.[33]

Alkyl complexes of the type $[M(R)(SnPh_3)(\eta\text{-}C_5H_5)]$ (M = Mo, W) have been prepared through the reaction of the salts $Li[M(SnPh_3)(\eta\text{-}C_5H_5)]$ with the alkyl halides CH_3I, BuBr, $PhCH_2Br$, PhC(O)Cl and $Br(CH_2)_nBr$ (n = 4,5).[34] Reaction of $[WCl(CO)_2(Tp^*)]$ [Tp* = 1,3-dimethyltris(pyrazolyl)borate] with the Grignard reagents RMgBr [R = $CH_2CH_2CH{=}CMe_2$, $CH_2CH_2CH{=}CH_2$, $CH_2C(Me){=}CH_2$, $CH_2CH{=}CH_2$ and $CH{=}CMe_2$] and subsequent oxidation of the paramagnetic intermediates by molecular oxygen gives vinyl, allyl and homoallyl complexes $[W(R)(O)_2(Tp^*)]$ in 40–70% yield. The oxyfunctionalisation of the alkenyl tungsten complexes by singlet oxygen and dioxirane has been studied and some stereoselectivity is observed in the resultant epoxide and allylic hydroperoxide reaction products. This appears to be controlled by electronic and steric factors of the '$W(CO)_2(Tp^*)$' fragment.[35] The molecular structure of $[W(CH_2SiMe_3)(O)_2(\eta\text{-}C_5Me_5)]$ has been determined from an X-ray diffraction study and exhibits the three-legged piano stool geometry typical of complexes of this type.[36]

A series of fulvalene (Fv) dichromium alkyl and acyl complexes of types $[Cr_2(CO)_{6-n}(L)_n(R)(R')(\eta^5,\eta^5\text{-}Fv)]$ and $[Et_4N][Cr_2(CO)_{6\text{-}n}(L)_n(R)(\eta^5,\eta^5\text{-}Fv)]$ (R, R′ = Me, CH_2CN, COMe; L = CO, PMe_2Ph; n = 0, 1, 2) have been prepared from $[Et_4N]_2[Cr_2(CO)_6(\eta^5,\eta^5\text{-}Fv)]$.[37] The halomethyl complexes $[Mo(CH_2X)(NO)_2(\eta\text{-}C_5H_5)]$ (X = Cl, Br) were isolated in 80-90% yield by treatment of $[MoX(NO)_2(\eta\text{-}C_5H_5)]$ with diazomethane in the presence of copper powder.[38] Single crystal X-ray diffraction studies indicate that the donor properties of the halomethyl ligands are intermediate between halide and alkyl ligands. Reactions of these compounds with dioxygen are also reported.

Treatment of the silylalkyl complex $[WCl(CH_2SiMe_3)(NO)(\eta\text{-}C_5Me_5)]$ with $K[OBu^t]$ or K[OMe] gives the expected metathesis product $[W(CH_2SiMe_3)(NO)(OR)(\eta\text{-}C_5Me_5)]$ when the reaction is carried out in Et_2O or thf (tetrahydrofuran), whereas the bimetallic compounds $[W(CH_2SiMe_3)(NO)(\eta\text{-}C_5Me_5)\{\mu_2\text{-}\eta^1\text{:}\eta^2\text{-}NC(H)SiMe_3\}WCl(O)(\eta\text{-}C_5Me_5)]$ and $[WCl(CH_2SiMe_3)(NO)(\eta\text{-}C_5Me_5)(\mu\text{-}N)W\{\eta^2\text{-}N(O)(H)CH_2SiMe_3\}(Cl)]$, respectively, are obtained if the reactions are carried out under heterogeneous conditions in pentane.[39]

The chromium(III) alkyl complexes $[Cr(R)(\eta^5\text{-}C_5Me_4SiMe_2NBu^t)]$ (R = CH_2SiMe_3, Ph, Me) are obtained from the reactions of $[CrCl(thf)(\eta^5\text{-}C_5Me_4SiMe_2NBu^t)]$ with LiR and structurally characterised by an X-ray diffraction study of $[Cr(CH_2SiMe_3)(\eta^5\text{-}C_5Me_4SiMe_2NBu^t)]$ **3**.[40] These compounds catalyse the polymerisation of ethene and the dimerisation and polymerisation of α-olefins. A rare example of a σ-alkyl complex of chromium(VI), $[Cr(\equiv N)(CH_2SiMe_2Ph)(NPr^i_2)_2]$, has been obtained from the reaction of $[Cr(\equiv N)(I)(NPr^i_2)_2]$ with 0.5 equivalents of $Mg(CH_2SiMe_2Ph)_2$.[41]



3

Treatment of the dinuclear compounds $[Cr_2Cl_4(L\text{-}L)(\eta\text{-}C_5H_5)_2]$ (L-L = dmpm, dmpe, dppe) with 2 equivalents of methyllithium gives the dinuclear 15-electron complexes $[Cr_2Me_4(\mu\text{-}L\text{-}L)(\eta\text{-}C_5H_5)_2]$. Thermally unstable mononuclear compounds $[CrMe_2(L\text{-}L)(\eta\text{-}C_5H_5)]$ are obtained from $[CrCl_2(thf)(\eta\text{-}C_5H_5)]$ by treatment with methyllithium in the presence of an excess of diphosphine. These mononuclear adducts have a 15-electron configuration with a dangling phosphine ligand rather than a 17-electron configuration with a chelating phosphine. This is explained in terms of the energy required to pair the electron into the required spin doublet state exceeding the energetic gain of forming the new bond.[42]

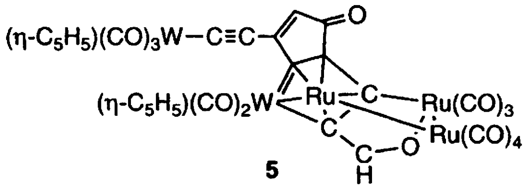
The bonding of *p*-anisaldehyde in $[M\{O(H)CC_6H_4OMe\text{-}4\}(\eta\text{-}MeC\equiv CMe)(CO)(Tp)]$ [M = Mo, W; Tp = hydridotris(pyrazolyl)borate] has been assessed by spectroscopic and X-ray diffraction techniques. The data suggests that the aldehyde is σ-bound in the molybdenum complex but π-bound to tungsten.[43]

Reaction of the acyl complexes $[Mo\{C(O)R\}(CO)(PMe_3)_2(L)]$ [L = $H_2B(pz)_2$,

$H_2B(dmpz)_2$; pz = pyrazolyl, dmpz = 3,5-dimethyl pyrazolyl; R = Me, CH_2SiMe_3, CH_2CMe_3] with CO gives the dicarbonyl derivatives $[Mo\{C(O)R\}(CO)_2(PMe_3)(L)]$. Similar reactions with isocyanides, CNR′, afford either acyl-isocyanide complexes $[Mo\{C(O)R\}(CO)(CNR')(PMe_3)(L)]$ or aminoacyls $[Mo\{C(NR')R\}(CO)_2(PMe_3)(L)]$ (R′ = $C_6H_3Me_2$-2,6, C_6H_4OMe-4, CH_2Ph, C_6H_{11}), depending on the nature of L and R.[44]

The alkyne $HC\equiv CCO_2Me$ reacts with $[Mo(CO)(DMF)(dppe)_2]$ to give the alkynylhydrido complex $[Mo(C\equiv CCO_2Me)(H)(CO)(dppe)_2]$, whereas aryl alkynes in hot benzene afford vinylidene complexes $[Mo(=C=CHR)(CO)(dppe)_2]$ (R = Ph, C_6H_4Me-4). Similar reactions with $[W(CO)(DMF)(dppe)_2]$ gave only alkynylhydrido complexes with either $HC\equiv CCO_2Me$ or $HC\equiv CR$. Protonation $[HBF_{4(aq)}]$ of the molybdenum vinylidene complex gave the cationic alkylidyne complex $[Mo(\equiv CCH_2Ph)(CO)(dppe)_2][BF_4]$ and the reactions of the molybdenum and tungsten alkenylhydrido species with $HBF_4{\cdot}OEt_2$ also result in formation of alkylidyne complexes $[M(\equiv CCH_2CO_2Me)(CO)(dppe)_2][BF_4]$. The latter (M = Mo) in turn reacts with Na[OMe] to give the vinylidene complex $[Mo(=C=CHCO_2Me)(CO)(dppe)_2]$.[45]

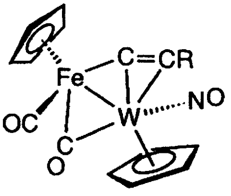
In the presence of NEt_3 and CuI catalyst, reactions of $[MCl(CO)_3(\eta\text{-}C_5H_5)]$ (M = Mo, W) with a five-fold excess of buta-1,3-diyne afford complexes $[M(C\equiv CC\equiv CH)(CO)_3(\eta\text{-}C_5H_5)]$ **4**, the acetylenic hydrogen atom of which can be readily replaced by either metal or non-metal groups. For example, treatment of **4** (M = W) with $[WCl(CO)_3(\eta\text{-}C_5H_5)]$ gives the bis-metallated diynediyl complex $[\{(\eta\text{-}C_5H_5)(CO)_3W\}_2(\mu\text{-}C\equiv CC\equiv C)]$ in 80% yield, whereas deprotonation with lithium diisopropylamide (LDA) and capture of the resultant anion with $SiClMe_3$, $PClPh_2$ or $[MnBr(CO)_5]$ gives $[W(C\equiv CC\equiv CSiMe_3)(CO)_3(\eta\text{-}C_5H_5)]$, for example. Homo-coupling of the diynyl ligand of **4** (M = W) ($CuCl_2$-tmeda, O_2 purge) gives the dimetallated tetrayne $[(\eta\text{-}C_5H_5)(CO)_3W\text{-}C\equiv CC\equiv CC\equiv CC\equiv C\text{-}W(CO)_3(\eta\text{-}C_5H_5)]$.[46] The reaction between **4** and $[Ru_3\{\mu_3\text{-}HC_2C\equiv C[W(CO)_3(\eta\text{-}C_5H_5)]\}(\mu\text{-}CO)(CO)_9]$ affords the WRu_3 cluster **5** in which dimerisation of the diynyl ligand with incorporation of two molecules of CO has occurred, as revealed by an X-ray diffraction study.[47]

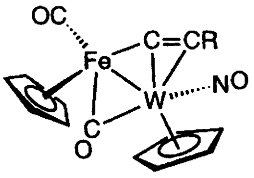


5

The complexes $[MoI(CO)_3(\eta\text{-}C_5H_5)]$ and $[FeI(CO)_2(\eta^5\text{-}C_9H_7)]$ have been linked in a σ-fashion to the ethynyl edges of 2,5-diethynylthiophene (thiop) using $[PdCl_2(NCMe)_2]$ to give the heterobimetallic complex $[(\eta\text{-}C_5H_5)(CO)_3Mo\text{-}C\equiv C(thiop)C\equiv CFe(CO)_2(\eta^5\text{-}C_9H_7)]$ *via* the mononuclear metal complex $[(\eta\text{-}C_5H_5)(CO)_3Mo\text{-}C\equiv C(thiop)C\equiv CSiMe_3]$.[49] Reaction of the metallate anions $[W(C\equiv CR)(CO)(NO)(\eta\text{-}C_5H_5)]^-$ (R = C_6H_4Me-4, CMe_3, $SiMe_3$) with $[Fe(CO)_2(thf)(\eta\text{-}C_5H_5)][BF_4]$ affords the bimetallic η^2-alkyne complexes $[(\eta\text{-}C_5H_5)$-

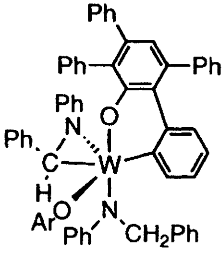
(NO)(CO)W{η^2-RC≡CFe(CO)$_2$(η-C$_5$H$_5$)], which are converted to diastereomeric mixtures of σ, π-acetylides (*e.g.* **6a** and **6b**) upon photodecarbonylation. An X-ray diffraction study of one of each type of complex is presented.[50]





6a R = C_6H_4Me-4, CMe_3, $SiMe_3$ **6b**

Reaction of the bis(cyclometallated) compounds [W(OC$_6$H$_3$Ph-C$_6$H$_4$)$_2$(L)$_2$] (L = PMe$_2$Ph, PMePh$_2$) with C$_2$H$_4$ and α-olefins (RCH=CH$_2$, R = Ph, SiMe$_3$, CF$_3$) affords the η^2-alkene complexes [W(OC$_6$H$_3$Ph-C$_6$H$_4$)$_2$(η^2-alkene)(L)]. An X-ray structural analysis of the ethene compound revealed W-C(alkene) bond distances consistent with minimal back-bonding from the metal to the alkene.[51] The 16-electron complex [W(OC$_6$HPh$_3$-η^6-Ph)(OC$_6$H$_4$Ph$_4$)(η^1-dppm)] reacts with PhCH=NPh to give the η^2-imine complex **7**, which was characterised by X-ray crystallography. A variety of products have been obtained through reactions of the same compound with aldehydes and ketones, *e.g.* the reaction with cyclopentanone gives rise to complex **8**.[52]



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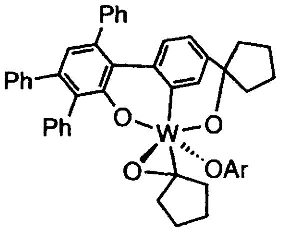
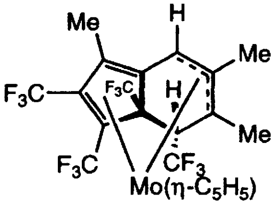


8

The reaction between [Mo(σ,η^2-CH$_2$C$_2$R)(η^2-MeC$_2$R)(η-C$_5$H$_5$)] **9** (R = Me) and hexafluoro-but-2-yne gives the X-ray crystallographically characterised complex **10**, *via* cocyclisation of two molecules of CF$_3$C$_2$CF$_3$, a but-2-yne molecule and a prop-2-ynyl fragment. Reactions of **9** (R = Me, Ph) with CO afford the complexes [Mo{η^2,η^3-C(R)C(O)C(Me)C(R)CCH$_2$}(CO)(η-C$_5$H$_5$)], while protonation (HBF$_4$·OEt$_2$) (R = Me) gives the salt [Mo{η^2,η^3-C(Me)C(OH)C(Me)C(Me)CCH$_2$}(CO)(η-C$_5$H$_5$)][BF$_4$] through protonation of the keto-group rather than the η^3-allylic CH$_2$ group.[53] The alkyne trimerisation products **11** and **12** having different oligomeristion sequences depending on whether MeO$_2$CC≡CCO$_2$Me occupies a terminal or central position in the alkyne chain, $C(CF_3)C(CF_3)C(CF_3)C(CF_3)C(CO_2Me)C(CO_2Me)$ or $C(CF_3)$-$C(CF_3)C(CO_2Me)C(CO_2Me)C(CF_3)C(CF_3)$, result from reaction of the η^2-*C,C* vinyl complexes $[M\{\eta^3\text{-}C(CF_3)C(CF_3)SR\}(F_3CC{\equiv}CCF_3)(\eta\text{-}C_5H_5)]$ (M = Mo, W; R = Me, Et, Pr^i) with $MeO_2CC{\equiv}CCO_2Me$. NMR studies established reaction sequences involving butadienyl intermediates $[M\{\eta^2\text{-}C(CF_3)C(CF_3)C(CO_2Me)C(CO_2Me)SPr^i\}(F_3CC{\equiv}CCF_3)(\eta\text{-}C_5H_5)]$ to give trienyl derivatives, *e.g.* $[M\{\eta^5\text{-}C(CF_3)C(CF_3)C(CF_3)C(CF_3)C(CO_2Me)C(CO_2Me)SPr^i\}(\eta\text{-}C_5H_5)]$.[54]



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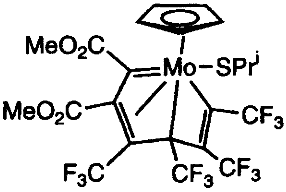

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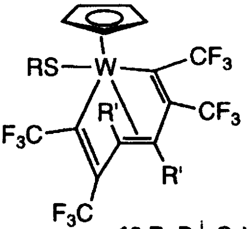
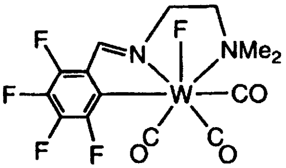


12 R=Pr^i, C_6H_4Me-4
R'=CO_2Me

Photolysis of a toluene solution of the tetrafluoroaryl metallacycle **13** in the presence of the electron deficient alkynes $CF_3C{\equiv}CCF_3$ or $PhC{\equiv}CPh$ affords the η^2-vinyl complex **14**, which is smoothly converted to the thermodynamic isomer by heating in toluene.[55] With electron rich alkynes, $MeC{\equiv}CMe$ and $MeCH_2C{\equiv}CH_2Me$, a competitive reaction involving formation of 4-electron donor alkyne complexes is favoured.[56] Detailed mechanistic studies for these reactions are reported.



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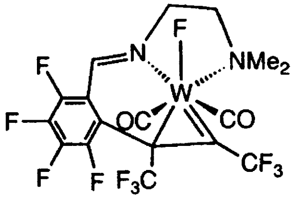

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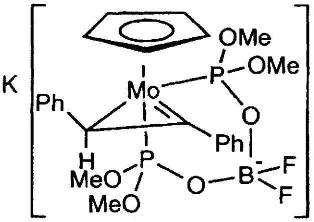
The zwitterionic acetylene complexes $[Mo(\eta^2\text{-}RC_2Ph)\{\eta^2\text{-}P(OMe)_2OBF_2OP\text{-}(OMe)_2\}(\eta\text{-}C_5H_5)]$ (R = Ph, Me) are converted to anionic η^2(3e)-vinyl complexes

$K[Mo\{=C(R)CH(Ph)\}\{\eta^2\text{-}P(OMe)_2OBF_2OP(OMe)_2\}(\eta\text{-}C_5H_5)]$ **15** upon reaction with $K[HBBu^s_3]$. Protonation ($HBF_4{\cdot}OEt_2$) of the η^2-vinyl complexes followed by addition of CO, $P(OMe)_3$ or $PhC{\equiv}CPh$ affords *trans*-stilbene and the compounds $[Mo(L)_2\{\eta^2\text{-}P(OMe)_2OBF_2OP(OMe)_2\}(\eta\text{-}C_5H_5)]$ $\{L = CO, P(OMe)_3; (L)_2 = PhC{\equiv}CPh\}$. Addition of the Grignard reagent $CH_2{=}CHCH_2MgBr$ to $[Mo(\eta^2\text{-}PhC_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ and subsequent addition of $P(OMe)_3$ gives $[Mo\{\eta^3\text{-}C(Ph){=}C(Ph)CH_2CH{=}CH_2\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$, the identity of which was confirmed by an X-ray diffraction study.[57]



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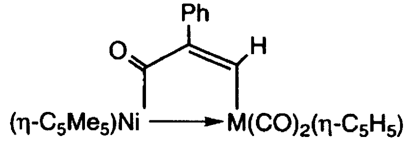
Treatment of the carbyne complexes $[W({\equiv}CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = alkyl, aryl) with R'_2PCl (R′ = alkyl, aryl) in the presence of $Tl[PF_6]$ yields the η^2-phosphinocarbene complexes $[W\{=C(R)PR'_2\}(CO)_2(\eta\text{-}C_5H_5)][PF_6]$, the structures of which were confirmed by an X-ray structure determination of $[W\{=C(C_6H_4Me\text{-}4)PMe_2\}(CO)_2(\eta\text{-}C_5H_5)][PF_6]$.[58] The related complex $[W\{=C(C_6H_4Me\text{-}4)PPh_2\}(CO)_2(\eta\text{-}C_5H_5)][BPh_4]$ reacts with Li[SPh] *via* carbonyl substitution to afford the neutral species $[W\{=C(C_6H_4Me\text{-}4)PPh_2\}(CO)(SPh)(\eta\text{-}C_5H_5)]$, whereas $[W\{=C(C_6H_4Me\text{-}4)PPh_2\}(CO)(PMe_3)(\eta\text{-}C_5H_5)][BF_4]$ adds the cyclopentadienyl anion at the carbene carbon atom. Deprotonation of $[W\{=C(Me)PPh_2\}(CO)_2(\eta\text{-}C_5H_5)][BPh_4]$ with $Li[NEt_2]$ affords the η^2-phosphinovinyl complex $[W\{C(=CH_2)PPh_2\}(CO)_2(\eta\text{-}C_5H_5)]$.[59]

The previously unseen coordinated CSP_2S ring system has been structurally characterised in the dinuclear metal complex $[Mo_2\{\mu\text{-}\eta^3\text{-}Ph_2PC(H)SP_2S\}(CO)_3(\eta\text{-}C_5H_5)_2]$, the product of the reaction between $[Mo_2(\mu\text{-}\eta^2\text{-}P_2)(CO)_3(PPh_2H)(\eta\text{-}C_5H_5)_2]$ and $Li[Bu^n]$ and subsequent reaction with excess CS_2.[60] The reaction of the unsaturated heterobimetallic complexes $[(\eta\text{-}C_5Me_5)NiM(CO)_3(Cp')]$ (M = Mo, W; Cp′ = $\eta\text{-}C_5H_5$, $\eta\text{-}C_5H_4Me$) with $PhC{\equiv}CH$ gives the metallacyclic species $[(\eta\text{-}C_5Me_5)Ni\{\mu\text{-}\eta^3,\eta^1\text{-}C(H)C(Ph)C(O)\}M(CO)_3(Cp')]$ **16** as the major product. Subsequent alkylation with $[Me_3O][BF_4]$ results in methylation of the metallacyclic carbonyl ligand and a structural rearrangement affords the cationic four-membered metallacycles $[(\eta\text{-}C_5Me_5)Ni\{\mu\text{-}\eta^3,\eta^2\text{-}1,3\text{-}C(H)C(Ph)C(OMe)\}M(CO)_2(Cp')][BF_4]$, which upon treatment with $[Bu^nN]I$ and Me_3NO gives the neutral species **17**, which was characterised by an X-ray diffraction study.[61]

Reactions of 3,3-diphenylcyclopropene with the complexes $[WCl_2(O)(PX_3)_3]$ $[X_3 = (OMe)_3, MePh_2]$ afford the η^2-cyclopropene complexes $[W\{\eta^2\text{-}C(H){=}C(H)CPh_2\}(Cl)_2(O)(PX_3)_2]$, which upon treatment with 2 equivalents of



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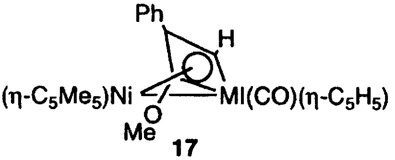

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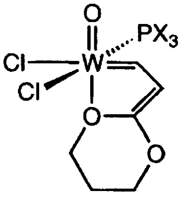


18 X_3 = $(OMe)_3$, $MePh_2$, Me_2Ph

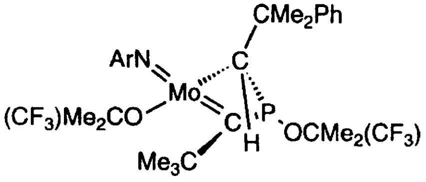
$Li[OC\text{-}(Me)(CF_3)_2]$ give the vinyl alkylidene complexes $[W\{=C(H)C(H)=CPh_2\}(O)\{OC(Me)(CF_3)_2\}_2(PX_3)]$.[62] The same reagents give the oxo-ketal alkylidene **18** when treated with 4,8-dioxaspiro[2,5]oct-1-ene (ketalcyclopropene).[63] If an excess of ketalcyclopropene is employed vinyl alkylidene complexes that adopt different coordination modes are formed. The chloride ligands of these species are exchanged by reaction with lithium alkoxides.

Diaminoallenylidene complexes$[M\{=C=C=C(NMe_2)_2\}(CO)_5]$ (M = Cr, W) have been synthesised by reaction of $[M(thf)(CO)_5]$ with $Li[C{\equiv}CC(NMe_2)_3]$ and $BF_3{\cdot}OEt_2$. Employing $Li[C{\equiv}CC{\equiv}CC(NMe_2)_3]$ and $BF_3{\cdot}OEt_2$ gives the pentatetraenylidene complexes $[M\{=C=C=C=C=C(NMe_2)_2\}(CO)_5]$ **19**, for which an X-ray diffraction study (M = W) revealed a strong alternation of the CC bond lengths within the MC_5 chain. Reaction of **19** with $HNMe_2$ affords $[M\{=C=C=C(NMe_2)C(H)=C(NMe_2)_2\}(CO)_5]$ having the *s-cis* conformation.[64] The substituted pentatetraenylidene complex $[W\{=C=C=C=C=C(NMe_2)C(H)=C(NMe_2)_2\}(CO)_5]$ is obtained in the same manner from $HNMe_2$ and $[W\{=C=C=C=C=C=C=C(NMe_2)_2\}(CO)_5]$, the latter being generated *in situ* by sequential treatment of $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CC(NMe_2)_3$ with $Li[Bu^n]$, $[W(thf)(CO)_5]$ and $BF_3{\cdot}OEt_2$. The alkenyl(butatrienyl) carbene complex $[W\{=C(C{\equiv}CSiMe_3)C(Bu^n)=C=C=C(NMe_2)_2\}(CO)_5]$ is also formed and was subjected to an X-ray diffraction analysis.[65] Hydroxylamines [RN(H)OH] and $[M\{=C=C=C(C_6H_4NMe_2\text{-}4)_2\}(CO)_5]$ (M = Cr, W) give the previously unknown isoxazolidinylidene complexes $[M\{=CN(R)OC(C_6H_4NMe_2\text{-}4)_2CH_2\}(CO)_5]$ (R = Me, $C_6H_4CH_2$, Pr^i, cyclo-C_6H_{11}). In contrast, the sterically hindered hydroxylamine $Bu^tN(H)OH$ and the weak nucleophile $C_6H_4N(H)OH\text{-}4$ afford alkenyl-(amino)carbene complexes $[W\{=C[N(H)R]C(H)=C(C_6H_4NMe_2\text{-}4)_2\}(CO)_5]$ (R = Bu^t, *p*-tolyl), rather than heterocyclic complexes, by addition of amine which arises through dismutation of the hydroxylamine.[66] The allenylvinylidene complexes $[W\{=C=C(H)C=C(H)(CH_2)_nCH_2CH_2\}(CO)_3(dppe)]$ (n = 1, 3, 4) have been prepared by reaction of $[W(OMe_2C)(CO)_3(dppe)]$ with the appropriate 1-ethynylcycloalcohol. Treatment with $HBF_4{\cdot}OEt_2$ gives the isomeric alkenyl carbyne complexes $[W\{\equiv CC(H)=CCH_2(CH_2)_nCH_2CH_2\}(CO)_3(dppe)][BF_4]$ and $[W\{\equiv CCH_2C=CH(CH_2)_nCH_2CH_2\}(CO)_3(dppe)][BF_4]$, which undergo carbonyl substitution with neutral (PMe_3, $NCCH_3$) or anionic (halide) substrates.[67]

The high oxidation state alkylidene compounds $[Mo\{=C(H)Bu^t\}(=NC_6H_3Pr^i_2\text{-}2,6)\{OCMe(CF_3)_2\}_2]$ and $[Mo\{=C(H)CMe_2Ph\}(=NC_6H_3Pr^i_2\text{-}2,6)(OCMe_2CF_3)_2]$ react with $P\equiv CBu^t$ to give the complexes $[Mo\{=C(Bu^t)P\{OCMe(CF_3)_2\}C(H)Bu^t\}(=NC_6H_3Pr^i_2\text{-}2,6)\{OCMe(CF_3)_2\}]$[68] and $[Mo(\equiv CBu^t)\{(NC_6H_3Pr^i_2\text{-}2,6)P=C(H)(CMe_2Ph\}(OCMe_2CF_3)_2]$,[69] respectively. The phosphametallacycle present in the former of these compounds formally results from head-to-tail cycloaddition of the phosphaalkyne to the Mo=C double bond.[68] The (phosphaalkenyl)amido ligand of the alkylidyne complex results from cleavage of the $P\equiv CBu^t$ triple bond. This compound cleanly rearranges to the phosphamolybdacyclobutene complex **20**, which was characterised by X-ray crystallography.[69] The related alkylidene species $[Mo\{=C(H)CMe_2Ph\}(=NC_6H_3Pr^i_2\text{-}2,6)\{OCMe(CF_3)_2\}_2]$ has been used as a catalyst for the elaboration of monocyclic and bicyclic β-lactam ring systems *via* alkene metathesis reactions.[70] Thermolysis of the dialkyl chromium complex $[Cr(CH_2Bu^t)_2(=NC_6H_3Pr^i_2\text{-}2,6)_2]$ affords the Cr(VI) alkylidene complex $[Cr\{=C(H)Bu^t\}(=NC_6H_3Pr^i_2\text{-}2,6)_2(thf)]$ through elimination of CMe_4.[71]

The heterocyclic carbene complexes $[M\{=CN(R)(CH_2)_nNH\}(CO)_5]$ (M = Cr, Mo, W; R = H, Et, Ph; n = 1, 2, 3) were prepared by reaction of the metal hexacarbonyl with $RNH(CH_2)_nN=PPh_3$, *via* intramolecular cyclisation of the initially formed isocyanide complexes.[72] Subsequent deprotonation and reaction with alkyl iodides gives the corresponding *N*-alkylated compounds. A general synthesis of 6-membered ring oxacarbene complexes $[W(=CCH_2CH_2CH_2CH_2O)(CO)_5]$ through reaction of $[W(thf)(CO)_5]$ with 1-alkyn-5-ols *via* an intramolecular cyclisation process, has been developed.[73] The complexes $[Mo(=CCH_2CH_2CH_2O)(Br)(CO)_2(\eta\text{-}C_5H_4R)]$ (R = H, Me, $SiMe_3$), containing a 5-membered cyclic oxacarbene, are obtained from the reactions of $Br(CH_2)_3Br$ with the anions $[Mo(CO)_3(\eta\text{-}C_5H_4R)]^-$ in diglyme, while dinuclear carbene complexes are obtained from the anions $[Mo_2(CO)_6(\eta\text{-}C_5H_4R)_2]^-$.[74] Similarly, the reaction between hydroxy-alk-1-ynes and either $[Mo(OCMe_2)(L)_2(\eta\text{-}C_7H_7)][PF_6]$ or $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$ and $[NH_4][PF_6]$ gives the cyclic oxacarbene complexes $[Mo\{=CCH_2(CH_2)_nCH_2O\}(L)_2(\eta\text{-}C_7H_7)][PF_6]$ [n = 1, $(L)_2$ = dppm, dppe or $(CO)_2$; n = 2, $(L)_2$ = dppm, $(CO)_2$], *via* isolable hydroxyvinylidene complexes of the type $[Mo\{=C=C(H)CH_2CH_2CH_2(OH)\}(dppe)(\eta\text{-}C_7H_7)][PF_6]$.[75] The *N*-heterocyclic carbene complexes $[Mo\{=CN(Me)C(H)=C(H)N(Me)\}_3(Cl)(O)_2]$ and $[W\{=CN(Me)C(H)=C(H)N(Me)\}_2(Cl)(O)_2]$ **21** were obtained by addition of 1,3-dimethylimidazoline-2-ylidene to thf solutions of $[MCl_2(O)_2]$ (M = Mo, W).[76]

The vinylidene complex $[Cr\{=C=CCH_2CH_2CH_2CH_2CH_2\}(CO)_5]$ has been prepared by reaction of $K_2[Cr(CO)_5]$ with cyclohexylcarbonylchloride followed by treatment with trifluoroacetic anhydride and DBU.[77] With alkenyl complexes of the type $[Fe(C\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = Me, Bu^n, Ph, CO_2Me, $C_6H_4NO_2\text{-}4$) this vinylidene complex affords heteronuclear complexes $[(OC)_5CrCC(R)C\text{-}$



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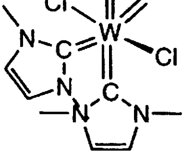
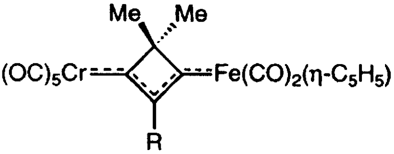
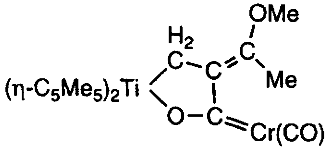


21

$\{(CH_2)_5\}Fe(CO)_2(\eta\text{-}C_5H_5)]$ with a spirocyclic bridging ligand. Analogous reactions with $[Cr(=C=CMe_2)(CO)_5]$ give the complexes **22** with unusual cyclic 'C_4R_3' bridging ligands, resulting from cycloaddition of the C≡C triple bond to the C=C double bond. X-ray diffraction studies on these complexes revealed that the two $C(sp^2)$-$C(sp^2)$ distances are essentially the same.[78] Similar compounds having exocyclic C=C bonds and delocalised π-systems are obtained from the reactions of the allenylidene complexes $[M(=C=C=CR_2)(CO)_5]$ (M = Cr, W; R = C_6H_4Me-4, C_6H_4OMe) with $[Fe(C\equiv CR')(CO)_2(\eta\text{-}C_5H_5)]$ (R' = Bu^n, Ph).[79] Other heteronuclear alkylidene complexes have been obtained from the reaction between $[Cr\{=C(OMe)Me\}(CO)_5]$ and the titanaallene species $[Ti(=C=CH_2)(\eta\text{-}C_5Me_5)_2]$ (*e.g.* **23**),[80] and reactions of the diethoxycyclopropenylide complexes $[M\{C_3(OCH_2CH_3)_2\}(CO)_5]$ (M = Cr, Mo, W) with $K[Fe(CO)_2(\eta\text{-}C_5H_5)]$ to afford the cyclopropenylidene species $[(OC)_5M\{\mu_2\text{-}C_3(OCH_2CH_3)\}Fe(CO)_2(\eta\text{-}C_5H_5)]$. The structural parameters of the latter complex indicate that the C_3 ring has a good deal of cyclopropenium character.[81]



22 R = Bu^n, Me, Ph, $C_6H_4NO_2$-4, CO_2Me



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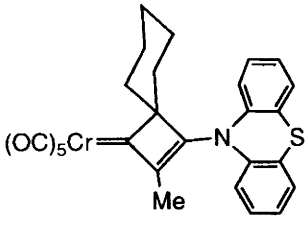
The reaction between $[Cr(=C=CPh_2)(CO)_5]$ and MeC≡CSMe gives the cyclobutenylidene complex $[Cr\{=CC(Me)=C(SMe)CPh_2\}(CO)_5]$, which was characterised by X-ray crystallography. Similarly, reaction of $[Cr(=C=CCH_2CH_2CH_2CH_2CH_2\}(CO)_5]$ with *N*-(1-propynyl)phenothiazine affords the *N*-(2-methyl)-4,5,6,7,-tetrahydroindenyl)phenothiazine complex **24**, stable below 0°C.[77] The thermally unstable alkylidene complexes $[Cr\{=C(H)N(CHMe)_2\}(X)(CO)_2(\eta\text{-}C_5Me_5)]$ have been prepared through the reaction of the alkylidyne complex $[Cr\{\equiv CN(CHMe)_2\}(CO)_2(\eta\text{-}C_5Me_5)]$ with anhydrous hydrogen halides, HX, at −50°C. Abstraction of the halide ligand with $Tl[PF_6]$ in the presence of phosphines, phosphites or isocyanides (L) gives the thermally stable aminocarbene complexes $[Cr\{=C(H)N(CHMe)_2\}(CO)_2(L)(\eta\text{-}C_5Me_5)][PF_6]$. The solid-state structure of the complex with L = EtNC was established.[82] Reaction of the (dialkyl)nitrosyl complex [Mo(CH_2-

$SiMe_3)_2(NO)(\eta\text{-}C_5Me_5)]$ with $Li[N(SiMe_3)_2]$ gives the anionic alkylidene complex $[Li_2(thf)_3][Mo(=CHSiMe_3)(CH_2SiMe_3)(NO)(\eta\text{-}C_5Me_5)]_2$ through deprotonation at the α-C atom of one of the alkyl groups. The molecular structure is as expected with the lithium atoms coordinated to the nitrosyl oxygen atoms.[83] The (nitrosyl)alkylidene complex $[Cr\{=C(OR)Ph\}(CO)(NO)(\eta^5\text{-}C_6H_7)]$ (R = Me, Et) is formed by reaction of phenyllithium with the cyclohexadienyl complex $[Cr(CO)_2(NO)(\eta^5\text{-}C_6H_7)]$.[84] The oxo-alkylidene complex *syn*-$[W\{=C(H)Bu^t\}(O)\text{-}(OC_6H_3Ph_2\text{-}2,6)_2(PMe_3)]$, prepared by heating $[W\{=C(H)Bu^t\}(O)(PMe_3)_2(Cl)_2]$ with 2 equivalents of $K[OC_6H_3Ph_2\text{-}2,6]$, has been shown to be an active catalyst for the polymerisation of substituted norbornadienes, giving polymers that are >95% *cis* and >95% isotactic.[85] The α, β-unsaturated mononuclear bisylidene complex **25** was isolated from the reaction of $[W\{=C(cyclopentyl)\}(\overline{NCH_2CH_2OCH_2CH_2})(CO)_4]$ with $K[OBu^t]$ and subsequent *N*-alkylation.[86]



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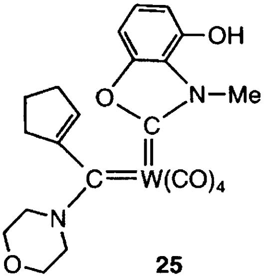

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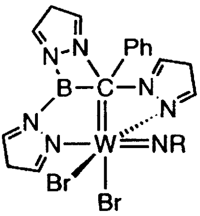
Formal insertion of an alkylidyne group into a W-N bond leading to a tris(pyrazolyl)borate (Tp) ring expansion occurs when the complex $[W(\equiv CPh)(Br)_2(Tp)]$ is treated with primary amines to afford the imido complexes $[W(=CPh)(=NR)(Br)(Tp)]$ (R = CMe_3, adamantyl, $C_6H_3Me_2\text{-}2,6$), which are subsequently treated with bromine to give the compounds **26**.[87] Oxaboralane derivatives are produced by heating the acylates $[M\{=C(OLi)CR\}(CO)_5]$ with dialkylchloroboranes, $\{R^1(R^2)C(H)C(H)R^3\}_2BCl$, to generate thermally unstable dialkylboroxycarbene complexes which release the oxaboralane on warming to room temperature. This transformation involves insertion of the carbene into the borane C_β-H bond.[88]

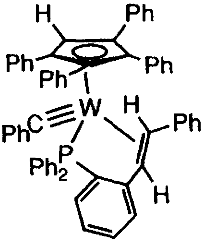
The migration of an alkyl group to a coordinated carbene has been reported



26 R = CMe_3, adamantyl, $C_6H_3Me_2\text{-}2,6$

for the complex [W{=C(H)Ph}(Me)(CO)$_2$(η-C$_5$H$_5$)] to give the η^3-benzyl complex [W{η^3-C(H)(Me)Ph}(Me)(CO)$_2$(η-C$_5$H$_5$)].[89] Molybdenum and tungsten alkylidene complexes of the new chelating chiral diol ligands (1*S*,2*S*)- and (1*R*,2*R*)-1,2-bis(2-hydroxy-2, 2-bis(trifluoromethyl)ethyl)cyclopentane have been prepared.[90]

Reactions of the alkyne complex [W(η^2-PhC$_2$CPh)$_3$(NCMe)] with *o*-diphenylphosphino-styrene and -allylbenzene in refluxing toluene proceed *via* cleavage of C-C double and triple bonds or insertion of PhC≡CPh into C-H bonds to give the alkylidyne and alkylidene compounds **27** and **28**, respectively.[91] The alkylidyne complex *cis*-[W(≡CC$_6$H$_4$Me-4)(Br)(CO)$_2$(PPh$_3$)$_2$] reacts with K[HB(pz)$_3$] to give [W(≡CC$_6$H$_4$Me-4)(CO)$_2${HB(pz)$_3$}], whereas the thermally unstable *trans*-isomer, generated by photolysis of the *cis*-isomer, initially gives the ketenyl complex [W(η^2-OCCC$_6$H$_4$Me-4)(CO)(PPh$_3$){HB(pz)$_3$}] which exudes CO to afford [W(≡CC$_6$H$_4$Me-4)(CO)(PPh$_3$){HB(pz)$_3$}] and reacts with Cl$_2$PPh$_3$ to afford the chloro-alkyne complex [W(η^2-ClC≡CC$_6$H$_4$Me-4)(Cl)(CO){HB(pz)$_3$}]. Photolysis of [M(≡CC$_6$H$_4$Me-4)(CO)$_2${HB(pz)$_3$}] (M = Mo, W) in the presence of P(OMe)$_3$ or PPh$_3$ (L) gives [M(η^2-OCCC$_6$H$_4$Me-4)(CO)(L){HB(pz)$_3$}], which in turn react with (S$_2$PC$_6$H$_4$OMe-4)$_2$ to give the η^2-thioketenyl complexes [M(η^2-SCCC$_6$H$_4$Me-4)(CO)(L){HB(pz)$_3$}].[93]



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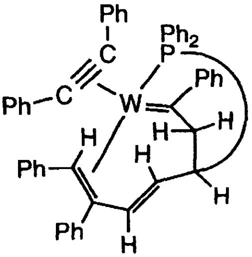

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Derivative carbyne complexes, *e.g.* [(Tp*)(CO)$_2$Mo≡CCH$_2$C≡Mo(CO)$_2$-(Tp*)] are prepared by deprotonation of [M(≡CMe)(CO)$_2$(Tp*)] and reaction of the resultant anion with [Mo(≡CCl)(CO)$_2$(Tp*)]. Mixed metal species are similarly obtained from the anion [W(=C=CH$_2$)(CO)$_2$(Tp*)]$^-$ and [Mo(≡CCl)-(CO)$_2$(Tp*)]. Both protons of the bridging carbon of these species can be removed sequentially to give [(Tp*)(CO)$_2$W≡CCHC≡Mo(CO)$_2$(Tp*)]$^-$ and [(Tp*)(CO)$_2$Mo=C=C=C=Mo(CO)$_2$(Tp*)]$^{2-}$, while oxidation yields the ketone-bridged species [(Tp*)(CO)$_2$Mo≡CC(O)C≡Mo(CO)$_2$(Tp*)].[94]

The alkylidyne complexes [W(≡CPh)(X)(CO)(PMe$_3$)$_3$] (X = pyrrolide, indolide, phenoxide, alkylsulfide) are obtained from the reaction of Na[X] with the complex [W(≡CPh)(Cl)(CO)(PMe$_3$)$_3$]. X-ray diffraction studies show that the strong π-donor ligand X occupies the coordination site *trans* to the alkylidyne group. Anionic complexes, [NEt$_4$][W(≡CPh)(X)$_2$(CO)(PMe$_3$)$_2$] are obtained when 2 equivalents of Na[NC$_4$H$_4$] or Na[NC$_8$H$_6$] are employed.[95] The thermally stable unsaturated hydroxy carbyne complex [W$_2$(μ-COH)(μ-dppm)(CO)$_2$-

(η-C_5H_5)$_2$]-[BF_4] has been obtained through protonation ($HBF_4{\cdot}OEt_2$) of [W_2(μ-dppm)-$(CO)_4$(η-C_5H_5)$_2$]. The analogous methoxy carbyne complex is similarly obtained and an X-ray structural analysis indicates the presence of a W=W double bond. Treatment of this species with $BF_3{\cdot}THF$ gives the rare methylidyne-borane complex [W_2(μ-$CHBH_3$)(μ-dppm)$(CO)_2$(η-C_5H_5)$_2$][BF_4], containing the 6-electron donor [$CHBH_3$]$^-$.[96]

The reaction chemistry of the radical cations generated by photo-oxidation of the metal carbyne complexes [M($\equiv$CR)(L^1)(L^2)(η-C_5H_5)] [M = Mo, W; R = alkyl, aryl; L^1, L^2 = CO, $P(OMe)_3$] has been summarised. The radical cations undergo both characteristic metal radical reactions and organic reactions at the carbyne ligand, and a variety of organic products can be obtained, *e.g.* alkenes, cyclopentanones.[97]

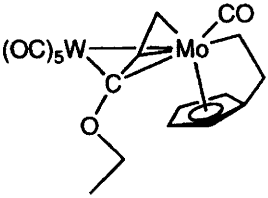
The homobinuclear complex [Mo_2(μ-OCH_2Bu^t)(μ-S)(=CAr_2)$(OCH_2Bu^t)_5$] is formed through reaction of [$Mo(OCH_2Bu^t)_6$] with diarylthiophenes *via* cleavage of the C=S double bond. The Lewis base adduct [Mo_2(μ-OCH_2Bu^t)(μ-S)-(=CPh_2)$(OCH_2Bu^t)_5$(PMe_3)] was structurally characterised and has both 5- and 6-coordinate Mo atoms.[98] The reactivity of tungsten hexalkoxides towards a variety of organic substrates (alkenes, alkynes, ketones, aldehydes) has also been discussed.[99]

Oxidation of [Mo_2(μ-C_8Me_8)(η-C_5H_5)$_2$] with[Fe(η-C_5H_5)$_2$][PF_6] gives the radical cation [Mo_2(μ-C_8Me_8)(η-C_5H_5)$_2$]$^+$, isolated and structurally characterised as its [PF_6]$^-$ salt, in which the C_8 chain acts as a double μ-allylidene ligand while bonding to one Mo centre as an η^2-alkene. Reactions with a source of the trityl radical or with ferrocenium give [Mo_2(μ-$C_8Me_7CH_2$)(η-C_5H_5)$_2$][PF_6] through activation of one C-H bond.[100] Reaction between Li_2[cyclo-C_8H_8] and [$W_2Cl_2(NMe_2)_4$] affords [W_2(μ-η^5:η^5-C_8H_8)$(NMe_2)_4$], which is described as being derived from a non-planar $C_8H_8{}^{4-}$ anion coordinated to a $W_2{}^{8+}$ template. This is supported by molecular orbital calculations.[101]

In hot toluene, $MeOCH_2C{\equiv}CCH_2OMe$ and [$Mo_2(CO)_6$(Fv)] (Fv = fulvalene) gives the propargyl ether complex [Mo_2(μ-η^2:η^3-$MeOCH_2C{\equiv}CCH_2OMe$)-$(CO)_4$(Fv)], which upon protonation affords the dicarbenium complex [Mo_2-(μ-η^3:η^3-$CH_2C{\equiv}CCH_2$)$(CO)_4$(Fv)][BF_4]$_2$. This in turn reacts with mild nucleophiles (*e.g.* MeOH) to give monocarbenium complexes of the type [Mo_2(μ-η^2:η^3-$MeOCH_2C{\equiv}CCH_2$)$(CO)_4$(Fv)][BF_4]. Stronger nucleophiles (*e.g.* PPh_3) result in double nucleophilic attack to give complexes of the type [Mo_2(μ-η^2:η^2-Ph_3-$PCH_2C{\equiv}CCH_2PPh_3$)$(CO)_4$(Fv)][BF_4]$_2$.[102] The carbenium ion salts [Mo_2-{μ-η^2:η^3-HC$\equiv$CC(H)(Fc)}$(CO)_4$(η-C_5H_5)$_2$][BF_4] and [{Mo_2(μ-η^2:η^3-HC$\equiv$CCH)$(CO)_4$(η-C_5H_5)$_2$}$_2$Fc][BF_4]$_2$ (Fc = ferrocenyl) are obtained by protonation ($HBF_4{\cdot}OEt_2$) of the parent μ-alkyne complexes. Addition of Li[C$\equiv$CC(Me)=CH_2] to the monocationic complex yields the μ-σ:η^2(4e) mono allenylidene complex [Mo_2{μ-σ:η^2-C=C=C(Fc)(H)}$(CO)_4$(η-C_5H_5)$_2$)], while an excess of Li[C$\equiv$CC(Me)=CH_2] and the dicationic complex gives the diallenylidene compound [{Mo_2(μ-σ:η^2-C=C=CH)$(CO)_4$(η-C_5H_5)$_2$}$_2$Fc].[103] The reactivity of the allenylidene complexes [Mo_2(μ-σ:η^2-C=C=CR^1R^2)$(CO)_4$(η-C_5H_5)$_2$)] towards nucleophiles and electrophiles has been investigated. Nucleophiles attack at the C_γ carbon atom whereas electrophiles affect the C_α atom. Hückel MO calculations suggest that electrophilic attack is charge controlled and nucleophilic attack is under orbital control.[104]

Photolysis of the compounds $[Mo_2(\mu\text{-}H)(\mu\text{-}SR)(CO)_4(\eta\text{-}C_5H_5)_2]$ (R = Me, Ph) in the presence of but-2-yne gives the μ-vinyl complexes $[Mo_2\{\mu\text{-}\sigma{:}\eta^2\text{-}C(Me)=CH(Me)\}(\mu\text{-}SR)(CO)_2(\eta\text{-}C_5H_5)_2]$, which were characterised by X-ray crystallography.[105] Treatment of the quadruply M-M bonded dimer $[Mo_2Cl_4(dmpm)_2]$ with $Li[CCSiMe_3]$ and $HCCSiMe_3$ in dimethoxyethane (dme) affords the complex $[Mo_2(C{\equiv}CSiMe_3)(\mu\text{-}\eta^2{:}\eta^2\text{-}HC{\equiv}CSiMe_3)\{\mu\text{-}\eta^1\text{-}C{=}C(SiMe_3)\text{-}\eta^2\text{-}C{\equiv}CSiMe_3(\mu\text{-}dmpm)_2][Li(dme)]$, containing an alkenylvinylidene ligand derived from head-to-tail coupling of two alkenyl ligands.[106]

Reaction between the cycloheptatrienyl cations $[M(CO)_3(\eta\text{-}C_7H_7)]^+$ and the cyclopentadienyl anions $[M'(CO)_2(\eta\text{-}C_5R_5)]^-$ (M = Cr, Mo, W; M′ = Ru, Fe: R = H, Me) affords the cycloheptatrienyl-bridged bimetallic complexes $[M(CO)_3(\mu\text{-}\eta^6{:}\eta^1\text{-}C_7H_7)M'(CO)_2(\eta\text{-}C_5R_5)]$,[107] while the anions $[M'(CO)_3(\eta\text{-}C_5H_4R)]^-$ react with α, α′-*m*- and *o*-dichloroxylenes to give dinuclear *m*- and *o*-xylene bridged complexes. One of these, $[(\eta\text{-}C_5H_4Me)Mo(CO)_3]_2\{\mu\text{-}C_6H_4\text{-}(CH_2)_2\text{-}1,2\}$ has been characterised by an X-ray diffraction study.[108] The molecular structure of the bimetallic ethoxy-propenylidene bridged complex **29** has been determined by X-ray crystallography and shows that the propenylidene unit has essentially equal C-C bond lengths and is η^3-coordinated to Mo and η^1-coordinated to W.[109]



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Two species both of which contain a crosswise bridging acetonitrile ligand, $[Mo_2(\mu\text{-}\eta^2\text{-}CH_3CN)(\mu\text{-}dppa)\{\mu\text{-}NC(CH_3)PPh_2NPPh_2\}(CH_3CN)_5][BF_4]_3$ and $[Mo_2(\mu\text{-}\eta^2\text{-}CH_3CN)(\mu\text{-}O)(\mu\text{-}dppa)_2(CH_3CN)_4][BF_4]_2$, have been isolated from the reaction of $[Mo_2(CH_3CN)_8][BF_4]_4$ with bis(diphenylphosphino)amine (dppa) in acetonitrile.[110] The trinuclear oxo-acetylide cluster $[(\eta\text{-}C_5Me_5)W(O)Re_2(CO)_8\text{-}(\mu\text{-}CCPh)]$ reacts with PhSH in hot toluene to give the dinuclear metal complex $[(\eta\text{-}C_5Me_5)W(O)Re(CO)_4(\mu\text{-}CCPh)]$, which upon treatment with Me_3NO produces the head-to-tail dimer $[(\eta\text{-}C_5Me_5)WRe(CO)_3(\mu\text{-}O)(\mu\text{-}H)(\mu\text{-}CCPh)]_2$ through the formation of two W≡O-Re bridges.[111]

Numerous articles on the use of Group VI carbene complexes of general type $[M(=CR^1R^2)(CO)_5]$ in organic synthesis have appeared. A brief summary of this work follows: Photolysis of the chromium carbene complexes $[M(=CR^1R^2)(CO)_5]$ [R = H, Me, $(CH_2)_3O$; X = OMe, $OC_6H_4CH_2$, NMe_2, $(CH_2)_3O$] in the presence of tertiary allylic amines and a Lewis acid catalyst gives rise to unsaturated lactams *via* a zwitterionic aza Cope rearrangement.[112] A [4+3] cycloaddtion of alkenyl carbene complexes affording both σ-complexed, $[Cr^{-}\{C=C(R^3)C(H)R^1C(H)=C(H)N^+(R^2)=C(OMe)\}(CO)_5]$, and metal-free azepines was achieved by reaction of azadienes, $R^1C(H)=C(H)C(H)=NR^2$, with complexes of the type $[M\{=C(OMe)C\equiv CR^3\}(CO)_5]$. The driving force for the cyclisation is thought to involve a novel [1, 2] shift of the $Cr(CO)_5$ moiety.[113] Excellent yields of cyclopropylpyrrolidines are obtained by treating allyl-propargyl amides with $[Mo\{=C(OMe)Bu\}(CO)_5]$ and HCl,[114] while reactions of the conjugated diynes $R^1C\equiv C\text{-}C\equiv CR^2$ with complexes $[Cr\{=C(OR^3)R^4\}(CO)_5]$ give good yields of acetylenic arenes with high selectivity for the regioisomers in which the substituent R^2 is incorporated adjacent to the phenol function. Bis(phenols) are generated by reaction of these alkynylarenes with the carbene complexes.[115] The dioxenyl complex $[Mo\{=C(OMe)C=C(H)OCH_2CH_2O\}(CO)_5]$ readily reacts with enzymes to form tetracyclic products *via* intramolecular [4+2] cycloaddition of an initially formed trialkoxycyclopentadiene derivative.[116] A series of conjugated diene enol ethers have been synthesised through reaction of propargylsilanes with complexes of the type $[Cr\{=C(OR^1)R^2\}(CO)_5]$. The key step of the reaction is migration of a $SiMe_3$ group to an electrophilic centre and occurs in preference to other established reaction pathways for vinylcarbene complex intermediates.[117] Intramolecular [2+2] cycloaddition reactions of γ, δ-unsaturated chromium complexes, *e.g.* $[Cr\{=C(OC_6H_4CH_2)CH_2CH_2CH=CH_2\}(CO)_5]$ are induced photolytically to afford cyclobutanones, whereas cyclopropyl carbene complexes undergo a vinylcyclopropyl rearrangement with formation of α-alkoxy cyclopentanone.[118] Good yields of 2-acylvinyl ethers are produced by irradiation of equimolar mixtures of sulfur ylides, $Me_2S^+C^-(H)C(O)R$, and alkoxychromium carbene complexes.[119]

Reactions of 2,6-disubstituted aryl carbene complexes having a phenol function with alkynes yields hydrindenone products, the alcohol function preventing aromatisation to an indene product by a tautomerisation of a metal complexed vinyl alcohol intermediate.[120] In the presence of acetic anhydride and triethylamine, thermal reaction of the complexes $[Cr\{=C(OR^1)R^2\}(CO)_5]$ with propargylic alcohols provides a new and efficient route to functionalised β-lactones.[121] Nucleophilic addition at the aromatic ring carbon of carbene complexes, rather than at the carbene carbon, has been achieved by introducing a bulky alkoxy group. Thus, treatment of $[Cr\{=C(OMen)Ph\}(CO)_5]$ (Men = (±)-menthyl) with alkyllithium reagents affords the aromatic products of *para* substitution, $[Cr\{=C(OMen)C_6H_4R\text{-}4\}(CO)_5]$ ($R = Bu^s, Bu^t, Ph$).[122]

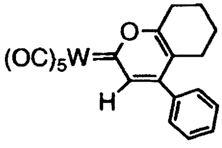
Aminolysis of the pyranylidene $[W\{=CC(H)=C(Ph)C\{CO(Me)\}=C(Me)O\}(CO)_5]$ gives amino-tungsta-1,3,5-hexatrienes, *via* ring opening, with different structural types depending on the reaction temperature and the type of amine used.[123] A stereoselective route to aminoalkenyl carbene complexes of chromium has been described.[124] Thus, reaction of lithioalkynes with complexes $[Cr(CNR)(CO)_5]$ gives *N*-lithio iminoacylates $[Cr\{=C(NRLi)C\equiv CR'\}(CO)_5]$ which are protonated or alkylated to give the complexes $[Cr\{=C(NRX)C\equiv CR'\}(CO)_5]$ (X = H, Me, Et, *etc.*) in predominantly the *E*-conformation. The stereochemical course of the reaction is strongly influenced by the substituents at nitrogen, as well as by the type of electrophile used. A widely applicable 'easy' method for preparing stereodefined disubstituted alkenylaminocarbene complexes of Cr and W, $[M\{=C(NR^1R^2)C\equiv CR^3\}(CO)_5]$, involves initial aminolysis of an alkoxy carbene complex with a primary amine, followed by base deprotonation and subsequent reaction with an electrophile to introduce the second substituent.[125] A convenient method for the 'one-pot' *N, N*-dialkylation of aminocarbene complexes under phase-transfer conditions has been reported[126] and involves treatment of $[M\{=C(Me)NH_2\}(CO)_5]$ (M = Cr, W) with MeI, $[Bu_4N]Br$ and NaOH to obtain a separable mixture of the mono- and dimethylated products. The method can be applied to azetidine derivatives using α,ω-dihaloalkanes.

Michael-type addition of enolisable 1,3-diones to the 1-alkynyl carbene complexes $[M\{=C(OEt)C\equiv CPh\}(CO)_5]$ (M = Cr, W) affords 2-(alkynyloxy)ethenyl complexes $[M\{=C(OEt)C(H)=C(O\text{-alkynyl})Ph\}(CO)_5]$ along with pyran-2-ylidene complexes *via* C-addition of the enolate unit of the dione. Reactions of phenol and 2-naphthol are highly regio- and stereo-selective affording *E*-$[M\{=C(OEt)C(H)=C(OAr)Ph\}(CO)_5]$. Dihydroxyaryl compounds afford binuclear carbene complexes,[127] while tertiary 1-aminocycloalkenes, $CH=C(NR_2)_2CH_2$, give cyclopentadiene annulation products in an overall [3+2] cycloaddition process. The reaction is highly regioselective and involves metalla-heptatrienes $[M\{=C(OEt)C(H)=C(Ph)CHC(NR_2)=CH\}(CO)_5]$ and hexatrienes $[M\{=C(OEt)C(H)=C(Ph)C=C(NR_2)CH_2\}(CO)_5]$ as key intermediates. Hydrolysis of the metalla-heptatriene complexes affords pyran-2-ylidene complexes, which were characterised by an X-ray diffraction study of **30**.[128] Cyclic enamines react with these pyran-2-ylidene complexes to generate 5-amino-1,3-cyclohexadiene by elimination of $[M(CO)_6]$.[129]

2-Alkynylanilincarbene complexes of chromium bearing a rigid arene C_2 spacer between the aminocarbene and alkyne units, *e.g.* **31**, have been prepared from complexes of the type $[M\{=C(OAr)R\}(CO)_5]$, acetyl bromide and 2-alkynylanilines. These compounds undergo intramolecular cyclisation to give, depending on the substitution pattern at the alkyne terminus, 3-indolylketenes, benzocarbazoles or indeno[1,2]indoles.[130]

A series of air-stable pyridinium ylide complexes, *e.g.* $[M\{C(H)(Me)(py)\}(CO)_5]$, have been prepared from reactions of alkoxycarbene complexes of Cr and W with 1,2- and 1,4-dihydroxypyridines, *via* a hydride transfer, alcohol elimination and pyridine fixation on the carbene carbon.[131]

The tricyclic carbene complexes **32** were prepared by reaction of $[Cr(\eta^2\text{-octene})(CO)_5]$ with 9-diaza-9*H*-fluorene-2,9-diaza-9*H*-xanthene and 5-diaza-5*H*-



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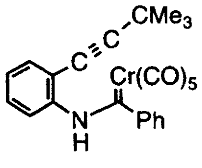

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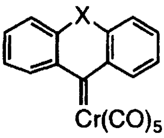

32 X =

dibenzo[*a,d*]cycloheptene,[132] and the methoxy(enynyl)carbene complexes [W{=C(XR)(C[[NU]]=C(H)C≡CR′)}(CO)$_5$] by direct activation of terminal and silylated 1,4-diyn-3-ols through photolysis.[133] Oxidation of thioether carbene complexes to their respective phenylsulfinyl complexes has been achieved with [ReMe(O)$_3$] and hydrogen peroxide.[134]

The mechanism and stereochemistry of the thermally induced rearrangement of the complexes [W{=C(Ar)(OCHRAr′}(CO)$_5$] (M = Cr, W; R = H, Me) to ketones ArC(O)CHRAr′Cr(CO)$_3$ or ArC(O)CHRAr′ (M = W) has been investigated.[135] Decomplexation of the complex [W{=C(OEt)C(H)=C(Ph)(NEt$_2$)}-(CO)$_5$] using dimethyldioxirane has been studied,[136] as has the subject of benzannulations and cyclohexadienone annulations of carbene complexes in the synthesis of decala-2,4-dien-1-ones and tetralin chromium tricarbonyl complexes.[137]

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Part IV: Group 7 *by Sherilyn A. Wass*

Some useful information may be found in a review on the structural and crystallographic data of over seven hundred manganese coordination compounds.[1] Structural and spectroscopic data are reported in a review on the design of reparameterised empirical Herschbach-Laurie relationships between homonuclear binuclear complexes applicable to Cr, Mo, W, Re and Ir. Data are given for isocyanate derivatives of $Re_2(CO)_{10}$.[2]

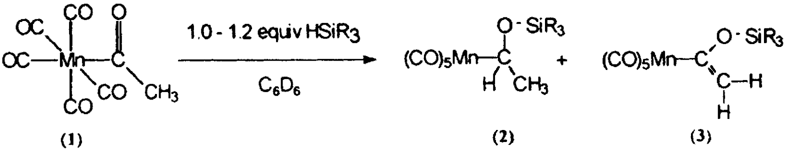
The synthesis, electrochemistry, photophysics and photochemistry of a series of photoluminescent nitrido complexes with long-lived excited states, $[ReNL_2X]^{n+}$ (L = dppe, X = F, Cl, Br, NCS, NCO, N_3 (n = 1) or MeCN (n = 2); L = dppbz, X = Cl (n = 1) or MeCN (n = 2)), have been investigated. Their properties are compared with those of $[ReNR_2(PPh_3)_2]$ (R = $C(CBu^t$, C_6H_4Me-*p*).[3] Similar investigations have been carried out on some Re(V)-benzylidene complexes $[Re(CR)(pdpp)_2Cl]^+$ (R = $C_6H_2Me_3$-2,4,6), $[Re(CR)L_2(CO)(H_2O)Cl]^+$ (L = PPh_3, $P(C_6H_4OMe$-*p*$)_3$, PMe_2Ph) and *trans*-$[Re(CR)(dppe)(CO)_2Cl]^+$.[4]

The octahedral complex $[Mn(CN$-C_6H_4-CN-4$)_6][SO_3CF_3]$ has been prepared by the reaction of $[Mn(CO)_5Br]$ and CN-C_6H_4-CN-4 in THF. It combines with compounds such as $[Rh_2(O_2CCF_3)_4]$ to form three-dimensional molecular solids.[5] $[ReCl_3(PPh_3)L]$ and $[ReL_3]BPh_4$ (L = $(CN(CH_2)_3$-O-CH_2-$)_2$) have been prepared and characterised by spectroscopic, analytical and conductimetric studies.[6]

The substitution kinetics of the aqua ligand in $[Re(NO)(H_2O)(CN)_4]^{2-}$ by SCN^-, N_3^- and thiourea have been investigated. $(AsPh_4)_2[Re(NO)(SC(NH_2)_2)(CN)_4]$ has been isolated, and has a *cis* arrangement of thiourea relative to the nitrosyl group.[7] Redox properties of *trans*-$[Re(CNEt)_2(dppe)_2][PF_6]$, formed by treatment of $[NBu_4]$*trans*-$[Re(CN)_2(dppe)_2]$ (*1*) with $[Et_3O][PF_6]$ in CH_2Cl_2, and *trans*-$[Re(CNH)(CNSiMe_3)(dppe)_2]CF_3SO_3$, formed by treatment of *1* with $Me_3SiO_3SCF_3$, have been studied.[8] *Trans*-$[Re(CN)L(dppe)_2]$ (L = N_2, CO) have been prepared by the reaction of *trans*-$[ReCl(CNH_2)(dppe)_2][BF_4]$ (*2*) with NBu_4OH under N_2 or CO. With organonitriles *2* gives complexes such as *trans*-[Re(CN)(NCMe)(dppe)$_2$].[9]

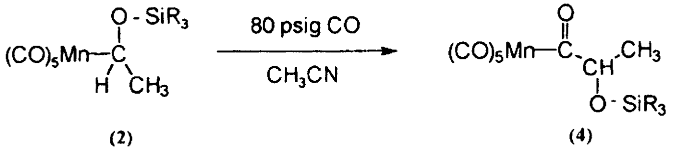
[ReCl(NC_6H_4Me-4)(OMe)(Bu^tNC)$_2$(PPh_3)][BPh_4], which has a distorted octahedral structure with a *cis* arrangement of isocyanide ligands and a *trans* arrangement of chloride and phosphine ligands, has been prepared by the reaction of [$ReCl_3$(NC_6H_4Me-4)(PPh_3)$_2$] with excess $CNBu^t$ in methanol.[10] Re($CNBu^t$)$_3$(PCy_3)$_2$H, obtained by the reaction of Re(PCy_3)$_2H_7$ with $CNBu^t$ in toluene, reacts with CH_2Cl_2 to give first Re($CNBu^t$)$_3$(PCy)$_2$Cl (*3*),and then [Re($CNBu^t$)$_3$(PCy_3)$_2$Cl]Cl.3CH_2Cl_2. *3* undergoes an unaided substitution reaction with H_2 yielding [Re($CNBu^t$)$_3$(PCy_3)$_2$(H_2)]Cl (*4*). Salts of *4* with non-coordinating anions reversibly lose H_2 in the solid state.[11] Displacement of the η^2-H_2 ligand from [(triphos)Re(CO)$_2$(η^2-H_2)]BF_4 produces [(triphos)Re(CO)$_2$]$^+$, which gives primary Re(I) vinylidene complexes on treatment with HC≡CR (R = H, Ph, *p*-Tolyl, COOEt, *n*-C_6H_{13}, $SiMe_3$). The reactivity of these complexes towards nucleophiles has been investigated.[12]

$(CO)_5MnC(O)CH_3$ (**1**) reacts rapidly at room temperature with monohydrosilanes according to eq. 1. (**2**) were the main products in all the reactions except that with $HSiEt_3$ where (**3**) was the main product. Some compounds of type (**2**) react with CO to give (**4**) according to eq. 2. Mechanistic studies have been carried out on the formation of (**2**) and (**3**).[13] Nucleophilic addition of lithium aldimine Bu^tN=C(Bu^t)Li to $Mn_2(CO)_{10}$ affords the corresponding α-iminoacyl carbonylmetalate which undergoes methylation of the acyl oxygen atom on treatment with Me_3OBF_4.[14]



(1)

SiR_3 = $SiMe_2Ph$, $SiMePh_2$, $SiMe_2Ph$, $SiMe_2OSiMe_3$, $SiMe_2Et$, $SiMeEt_2$, SiMe($OSiMe_3$)$_2$, SiMe(OMe)$_2$, $SiMe_2Cl$, $SiEt_3$

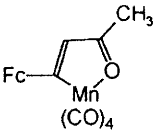


(2)

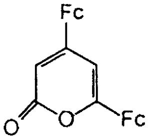
SiR_3 = $SiMe_2Ph$, $SiMePh_2$, $SiMe_2OEt$, $SiMe_2OSiMe_3$, $SiMe_2Et$

Laser flash photolysis has been used to investigate the kinetics of (μ-H)(μ-alkenyl)$Re_2(CO)_8$ formation by UV irradiations of $Re_2(CO)_{10}$ in the presence of olefins. The results show that the hydride alkenyl complexes are formed as a result of the reaction between olefin and *eq*-$Re_2(CO)_9$.[15] LCAO density functional calculations have been carried out on [{(H_2O)$_n$(OH)$_{3-n}$M}$_2$(μ-C_2)] (M = Ti, V, Cr, Mn; n = 0,1,2) as models for μ-acetylide-bridged complexes of early to mid transition metals in high oxidation states, with π-donor ligands in a pseudotetrahedral coordination.[16] The reaction of Re$_2$(μ-H)(μ-C$_2$Ph)(CO)$_7$(NCMe) (*5*) with PMe$_3$ and dppm yields Re$_2$(μ-H)(μ-C$_2$Ph)(CO)$_6$(PMe$_3$)$_2$ and Re$_2$(μ-H)(μ-dppm)(μ-C$_2$Ph)(CO)$_6$ (*6*), respectively. Sequential treatment of *5* with Na[Co(CO)$_4$] and AuCl(PPh$_3$) affords AuRe$_2$ (μ-C$_2$Ph)(CO)$_8$(PPh$_3$). Reaction of *6* with AuMe(PPh$_3$) gives AuRe$_2$(μ-dppm)(μ-C$_2$Ph)(CO)$_6$(PPh$_3$).[17] (η^5-C$_5$Me$_5$)W(O)Re(CO)$_4$(μ-H)(μ-CCPh), prepared from (η^5-C$_5$Me$_5$)W(O)Re$_2$(CO)$_8$(μ-CCPh) and thiophenol in refluxing toluene, gives first (η^5-C$_5$Me$_5$)W(O)Re(CO)$_3$(NCMe)(μ-H)(μ-CCPh) and then [(η^5-C$_5$Me$_5$)WRe(CO)$_3$(μ-O)(μ-H)(μ-CCPh)]$_2$ on decarbonylation.[18] The photophysical and electrochemical properties of [Re(Bu$^t_2$bpy)(CO)$_3$(C≡CC≡C)ReBu$^t_2$bpy)(CO)$_3$] and [Re(Bu$^t_2$bpy)(CO)$_3$(C≡CC$_6$H$_{13}$)] have been studied.[19] Rhenium-capped oligomers of up to 20 sp carbon atoms have been prepared by addition of alkyne or diyne building blocks to [(η^5-C$_5$Me$_5$)Re(NO)(PPh$_3$)C≡C-C≡C-H].[20]

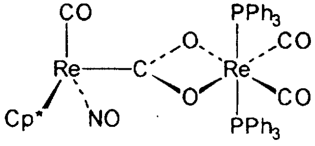
The reaction of FcC≡CMn(CO)$_5$ and MnBr(CO)$_5$ with excess MeLi in THF affords FcC≡CMn(CO)$_5$, (**8**) and (**9**).[21] [2,4-diphenyl-pyranyl-η^5]Mn(CO)$_3$ derivatives have been prepared by refluxing derivatives of [[1-phenyl-2-phenylcarbonyl-κ*O*]ethenyl-κ*C*^{1}]tetracarbonylmanganese with alkynes in carbon tetrachloride.[22] (**11**) are obtained by insertion of SO$_2$ into the Mn-C bond of orthometallated derivatives of substituted acetophenones, benzophenone or 2-acetylthiophene. Some compounds of type (**11**) are readily converted to (**12**). Treatment of (**11**) with H$_2$O$_2$ results in oxidative demetallation to give the corresponding aryl-sulfinates or -sulfonates.[23] Reaction of PhN=S=O with (**13**) yields (**14**) by replacement of the ketone oxygen with a Ph-N group. No insertion into the Mn-C bond was observed.[24] Orthomanganated *N,N*-dimethylbenzamide reacts with SO$_2$ to give Mn$_4$(thsa)$_2$(CO)$_{16}$, having four Mn(CO)$_4$ units linked by two triply bridging (S,O,O) thsa ligands.[25]



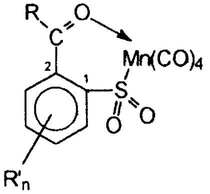
(**8**)



(**9**)

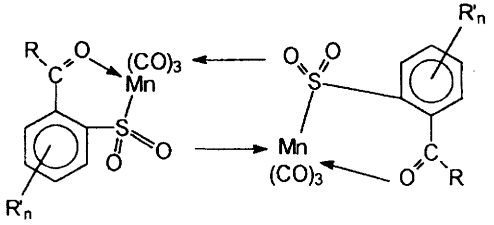


(**10**)



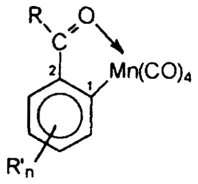
R = Me R'$_n$ = 5-OMe
R = Me R'$_n$ = H
R = Me R'$_n$ = 5-Cl
R = Me R'$_n$ = 3,4,5-(OMe)$_3$
R = Ph R'$_n$ = H

(**11**)



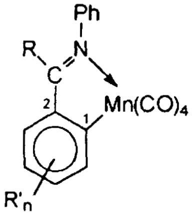
R = Me R'$_n$ = 3,4,5-(OMe)$_3$
R = Ph R'$_n$ = H

(**12**)



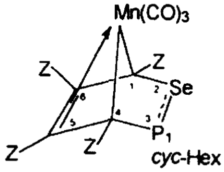
R = Me R'$_n$ = H
R = Me R'$_n$ = 3,4,5-(OMe)$_3$
R = Me R'$_n$ = 3-Cl
R = Me R'$_n$ = 5-OMe

(13)



(14)

$(OC)_4Mn(\eta^2$-Se-P*cyc*-Hex$_2$), formed by the reaction of $BrMn(CO)_5$ and *cyc*-Hex$_2$HPSe, undergoes cyclotrimerisation of the P-Se function with ZC≡CZ (R = CO_2R; R = Me, Et, Pr^i, *cyc*-Hex) to yield **(15)**.[26] The reaction of ZC≡CZ (Z = CO_2R; R = Me, Et, Pr^n, Pr^i, Bu^n, Pent^n, *neo*-Pent, *cyc*-Hex) with **(16)** in *n*-hexane yields **(17)**, **(18)** and **(19)**, whereas in THF only **(18)** are formed.[27]



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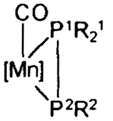
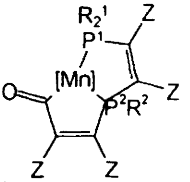


R^1 = Ph R^2 = Bu^t
R^1 = Ph R^2 = Cy
R^1 = R^2 = Cy
[Mn] = Mn(CO)$_3$

(16)



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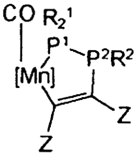

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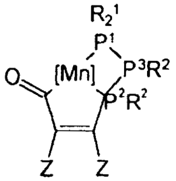


(19)

$Re(CO)_4[C(CH_2CO_2Me)=C(H)CO_2Me]$ (*7*), prepared by the reaction of $Re_2(CO)_9(NCMe)$ (*8*) and $MeO_2C(H)C=C=C(H)CO_2Me$ (*9*) in refluxing hexane, yields *fac*-$Re(CO)_3(PMe_2Ph)[C(CH_2CO_2Me)=C(H)CO_2Me]$ on treatment with PMe_2Ph. The reaction of $Re_2(CO)_8(PMe_2Ph)(NCMe)$ (*10*) with *9* affords *fac*- and *mer*-$Re_2(CO)_6(PMe_2Ph)[\mu$-η^3-η^1-$MeO_2C(H)CCC(H)CO_2Me]$ (*11*), and small amounts of *fac*- and *mer*-$Re(CO)_3(PMe_2Ph)[MeO_2CCH_2CC(H)CO_2Me]$ and (*7*).[28] $Re(CO)_4[$*s-trans*-μ-*C,S*-$EtO_2CN=CS]Re(CO)_5$, $Re(CO)_4[\mu$-*C,S,N*-$EtO_2CN=CS]Re(CO)_4$ (*12*), $Re(CO)_4[\mu$-*C,N,S*$_2$-$(EtO_2C)_2NC=NCS_2]Re(CO)_4$ (*13*), $Re(CO)_4[\mu$-*C,N,S*$_2$-$(EtO_2C)_2NC=NCS_2]Re(CO)_3(NCMe)$ (*14*) and a small amount of $Re(CO)_4[\mu$-*C,N,S*$_2$-$(EtO_2C)(H)NC=NCS_2]Re(CO)_4$ have been obtained from the reaction of *8* with $EtO_2CN=C=S$ in refluxing hexane.[29,30] $Mn_2(CO)_7(PMe_2Ph)[\mu\text{-}\eta^2\text{-}\eta^2\text{-}MeO_2C(H)CCC(H)CO_2Me]$ and $Mn_2(CO)_6(PMe_2Ph)[\mu\text{-}\eta^3\text{-}\eta^1MeO_2CC(H)CC(H)CO_2Me]$ are formed by the reaction of $Mn_2(CO)_8(PMe_2Ph)(MeCN)$ with *9*.[31]

$[(XylNC)(MeCN)ClRe(\mu\text{-}dppm)_2ReCl_2(CO)]O_3SCF_3$ is formed with retention of stereochemistry at the Re_2 unit by the reaction of the open bioctahedral form of $(XylNC)Cl_2Re(\mu\text{-}dppm)_2ReCl_2(CO)$ (*15*) with TlO_3SCF_3 in MeCN. Reaction of *15* with TlO_3SCF_3 in a non-coordinating solvent affords $[(XylNC)(CO)ClRe(\mu\text{-}dppm)_2ReCl_2]O_3SCF_3$.[32] Thermolysis of $[(XylNC)_2ClRe(\mu\text{-}dppm)_2ReCl_2(CO)]^+$, having a Re-Re bond order of 3, results in quantitative conversion to $[(XylNC)(OC)Re(\mu\text{-}Cl)_2(\mu\text{-}dppm)_2ReCl(CNXyl)]^+$, having a Re-Re bond order of 0.[33] The reaction of XylNC with $[Re_2Br_3(\mu\text{-}dppm)_2(CO)(CNXyl)]Y$ ($Y = O_3SCF_3, PF_6$) gives two forms of $[(CO)BrRe(\mu\text{-}Br)_2(\mu\text{-}dppm)_2Re(CNXyl)_2]^+$ with similar bis(μ-halo)-bridged edge-sharing bioctahedral structures, and $[(XylNC)_2BrRe(\mu\text{-}dppm)_2ReBr_2(CO)]^+$, which has an open bioctahedral structure.[34]

The spectroscopic and photochemical properties of $Mn(R)(CO)_3(R'\text{-}DAB)$ ($R = Me, Bz$; $R' = Pr^i$, *p*-Tol) have been studied. The Me complexes lose CO from the lowest MLCT state on irradiation into their MLCT bands whereas the visible excitation of the Bz complexes results in homolysis of the Mn-Bz bond from the lowest $\sigma\pi^*$ state.[35] A comparative spectroelectrochemical study has been carried out at variable temperatures on the one-electron reduction of $[ReBr(CO)_3(R'\text{-}DAB)]$ ($R' =$ *p*-An, *p*-Tol, Pr^i) (*16*) , and $[Re(R)(CO)_3(Pr^i\text{-}DAB)]$ ($R = Me, Et, Bz$) (*17*). *16* forms the corresponding radical anions in equilibrium with the solvento radicals $[Re(Pr^nCN)(CO)_3\ (R\text{-}DAB)]$. *17* gives stable radical anions of the type $\{[Re(CO)_3(Pr^i\text{-}DAB)]^-...R\}$.[36]

$(NEt_4)_2[MCl_3(CO)_3]$ ($M = Tc, Re$), used in the preparation of complexes containing the *fac*-$(CO)_3$ unit, are readily prepared from $[MO_4]^-$ and CO at 1 atm pressure. Stepwise substitution of Cl by $CNBu^t$ in $(NEt_4)_2[ReCl_3(CO)_3]$ gives $[Re(CNBu^t)_3(CO)_3]^+$. Substitution of $CNBu^t$ by $HSCH_2CH_2OH$ in $[Tc(CNBu^t)_3(CO)_3](NO_3)$ affords $(NEt_4)[Tc_2(\mu\text{-}SCH_2CH_2OH)_3(CO)_6]$. Reaction intermediates have been studied using IR and ^{99}Tc NMR spectroscopy.[37] *Fac*-$[Mn(CNBu^t)(CO)_3\{(PPh_2)_2CCN\}]$, prepared by the reaction of *fac*-$[Mn(CNBu^t)(CO)_3\{(PPh_2)_2CH\}]$ with cyanogen, affords complexes such as *fac*-$[Mn(CNBu^t)(CO)_3\{(Ph_2P)_2CCNAuPPh_3\}]PF_6$ and *fac*-$[\{Mn(CNBu^t)(CO)_3\{(Ph_2P)_2CCN\}\}_2Cu]BF_4$ by coordination of metallic fragments through the free nitrogen atom of the cyano group.[38]

$[M\{(\mu\text{-}NC)MnL_x\}_2]^+$ ($M = Cu, Ag, Au$; $L_x =$ *cis*- or *trans*-$(CO)_2[P(OR)_3](dppm)$ ($R = Ph, Et$), *cis*-$(CO)_2(PEt_3)(dppe)$ or $(CO)(dppm)_2$) contain two Mn(CN) ligands linearly bound as donors to Cu(I), Ag(I) and Au(I). Spectroscopic and voltammetric studies suggest that intramolecular electron transfer depends on the arrangement of the ancillary ligands at Mn, and on the identity of M.[39] The effects of altering the ancillary ligands in the redox-active Fe and Mn centres on intermetallic interaction and delocalisation of unpaired electron density in the paramagnetic complexes $[FeI\{(\mu\text{-}NC)MnL_x\}(NO)_2]$, $[Fe(PPh_3)\{(\mu\text{-}NC)MnL_x\}(NO)_2][PF_6]$ and $[Fe\{(\mu\text{-}NC)MnL_x\}_2(NO)_2][PF_6]$ (L_x = mixed CO and phosphorus ligands) have been investigated.[40]

$Tc(CO)_3(C(O)H)(PPh_3)_2$, formed by the reaction of *trans*-$[Tc(CO)_4(PPh_3)_2]BF_4$ (*18*) with $LiEt_3BH$, gives $[Tc(CO)_3(=C(OMe)H)(PPh_3)_2]SO_3CF_3$ on treatment with 1 equivalent of $CH_3SO_3CF_3$ in toluene. Treatment of *18* with the OH^- or ROH (R = Me, Et), yields $Tc(CO)_3(C(O)OR)(PPh_3)_2$ (R = H, Me, Et).[41]

η^2(4e)-donor alkyne complexes $[ReBr_2(\eta^2\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)]$ and $[ReBr_2(\eta^2\text{-}MeC_2Ph)(\eta\text{-}C_5H_5)]$ have been prepared by the reaction of *cis-/trans*-$[ReBr_2(CO)_2(\eta\text{-}C_5H_5)]$ and the corresponding alkyne. On treatment with $AgBF_4$ or $TlPF_6$ in the presence of PPh_3, $PMePh_2$ or $P(OMe)_3$, they form $[ReBr\{\eta^2(4e)\text{-alkyne}\}L(\eta\text{-}C_5H_5)]^+$complexes such as $[ReBr(\eta^2\text{-}PhC_2Ph)(PMePh_2)(\eta\text{-}C_5H_5)][PF_6]$. The neutral η^2(3e)-vinyl complexes $[Re\{=C(ph)CHPh\}Br(L)(\eta\text{-}C_5H_5)]$ (L = PPh_3, $PMePh_2$) have been obtained by the reaction of the $[BF_4]^-$ and $[PF_6]^-$ salts of $[ReBr(\eta^2\text{-}PhC_2Ph)(L)(\eta\text{-}C_5H_5)]^+$ with $K[BHBu^s{}_3]$.[42]

Cis/trans-$CpRe(CO)_2(\eta^1\text{-}PhCO)Br$, obtained by the reaction of $Li[CpRe(CO)_2(\eta^1\text{-}PhCO)]$ or $Cp(CO)_2Re{=}C(OEt)Ph$ with Br_2, form *cis/trans*-$CpRe(CO)_2Br_2$ on treatment with Br_2 in CH_2Cl_2. The reaction of *cis/trans*-$CpRe\text{-}(CO)_2Cl_2$ with Na/Hg and RNC affords $CpRe(CO)_2(CNR)$ (R = Et, Pr^i, Bu^t).[43]

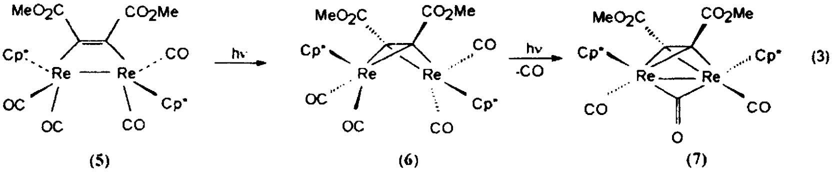
The low temperature reaction of $[Mn(\equiv CPh)(\eta\text{-}C_5H_5)(CO)_2]BBr_4$ with $[NEt_4]_2[Fe_2(CO)_8]$ in THF yields $[MnFe\{\eta\text{-}C(COEt)Ph\}(\eta\text{-}C_5H_5)(CO)_5]$, $[\{(OC)_2(\eta\text{-}C_5H_5)Mn(=CPh)\}_2Fe(CO)_8]$ and $[Mn(\eta\text{-}C_5H_5)(CO)_3]$.[44] Studies have been made of the diastereoselective substitution of CO by PR_3 in $[(\eta^5\text{-}C_5H_5)(CO)_2Mn = C(OR^*)Ph]$. The diastereoselectively pure complex $[(S_{Mn})\text{-}Cp(CO)(p\text{-}Tol_3)Mn{=}C(Ph)OR^*]$ (OR^*= β-mannofuranosyl) has been isolated, which gives $[(S_{Mn})\text{-}Cp(CO)(p\text{-}Tol_3)COMn\equiv C(Ph)]BF_4$ on treatment with BF_3.[45] $(\eta^5\text{-}C_5H_5)(CO)_2Re(C{=}O)[(\eta^5\text{-}C_5H_4)Re(CO)_3]^-Li^+$ (*19*) is formed by reaction of $(\eta^5\text{-}C_5H_4Li)Re(CO)_3$ with $(\eta^5\text{-}C_5H_5)Re(CO)_3$. Protonation and methylation of *19* yields $(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C(OH)[(\eta^5\text{-}C_5H_4)Re(CO)_3]$ and $(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C(OCH_3)[(\eta^5\text{-}C_5H_4)Re(CO)_3]$ (*20*), respectively. Treatment of *20* with Bu^nLi affords $(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C(CH_2CH_2CH_2CH_3)[(\eta^5\text{-}C_5H_4)Re(CO)_3]$.[46]

Alkylation of *cis*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Cl_2$ using RCu (R = Me, Et) yields *cis*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Me_2$ (*21*) and *trans*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Et_2$. *21* is converted to the *trans* isomer on photolysis in frozen toluene-d_8.[47]

Low temperature studies of $Cp^*ReXY(p\text{-}N_2C_6H_4OMe)$ by variable temperature ^1H NMR (X = H, Y = CO; X = CH_3, Y = CO) and ^{31}P NMR (X = Cl, Y = PR_3, R = Me, OMe) spectroscopy, show two isomers having the aryl group oriented *syn* to either X or Y, that interconvert on the NMR timescale. Variable temperature ^{31}P NMR spectra of $Cp^*ReC(PPh_3)(p\text{-}N_2C_6H_4OMe)$ show only one isomer having *syn* orientation of the aryl group to Cl.[48] $Cp'(CO)_2Mn{=}C{=}CH(R)$ (R = H, Me) undergo net [2 + 2] cycloaddition reactions with 1,4-diphenyl-1 azabutadiene (*22*) yielding $Cp'(CO)_2Mn{=}CN(Ph))CH(CH{=}CH(ph))CH(R)$, which is also formed by treatment of $[Cp'(CO)_2Mn\equiv CCH_2R]^+$ with *22*, followed by triethylamine. $[Cp'(CO)_2Mn{=}C(OEt)CHR]^-$ undergo net [2 + 4] cycloaddition reactions, giving $Cp'(CO)_2Mn{=}CN(Ph)C(H){=}C(H)CH(Ph)CH(R)$ and $Cp'(CO)_2Mn{=}CN(Ph)C(H){=}C(H)C(Ph){=}CH$.[49]

Single crystal X-ray diffraction shows that $[Re_2(CO_2)(NO)(C_{10}H_{15})(C_{18}H_{15}P)_2(CO)_3]$ **(10)** has a carbon dioxide ligand bridged between two octahedral rhenium centers.[50]

Reaction of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ (*23*) with $HC{\equiv}CH$ gives $Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^3\text{-}CH{=}CHCO)Re(CO)Cp^*$. With $CH_3C{\equiv}CCH_3$ at −60°C *23* gives $Cp^*(CO)_2Re(\mu\text{-}CO)Re(CO)(\eta^2\text{-}CH_3C{\equiv}CCH_3)Cp^*$ (*24*), which slowly converts at −40°C to a mixture of dimetallacyclopentenone $Cp^*(CO)_2Re[\mu\text{-}\eta^1,\eta^3\text{-}(CH_3)C{=}C(CH_3)CO]Re(CO)Cp^*$ (*25*) by a fluxional process involving an intermediate, $Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^1\text{-}CH_3CC{=}CCH_3)Re(CO)_2Cp^*$. Two fragmentation products, $Cp^*Re(CO)_3$ and $Cp^*Re(CO)(CH_3C{\equiv}CCH_3)$ (*26*), are also formed. At room temperature, *25* converts to additional $Cp^*Re(CO)_3$ and *26*.[51] Photochemical and thermal rearrangement of $Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^1\text{-}CH_3O_2CC{=}CCO_2CH_3)Re(CO)_2Cp^*$ (5), obtained by the reaction of *23* with DMAD, yields $Cp^*(CO)_2Re(\mu\text{-}\eta^2,\eta^2\text{-}CH_3O_2CC{\equiv}CCO_2CH_3)Re(CO)_2Cp^*$ (6). On photolytic decarbonylation (6) forms $Cp^*(CO)_2Re(\mu\text{-}\eta^2,\eta^2\text{-}CH_3O_2CC{\equiv}CCO_2CH_3)(\mu\text{-}CO)Re(CO)Cp^*$ (7) (eq. 3).[52] Time-resolved infrared spectral studies of the photochemical transformation of (5) to (6) indicate the formation of a short-lived bis(metallocarbene) intermediate.[53]

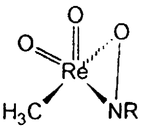


Exo-$PCpRe(CO)_3$ undergoes a sequence of ligand substitutions to give the 'chiral-at-rhenium' derivatives $[PCpReNO(CO)PPh_3]BF_4$ and $PCpReNO(CH_3)PPh_3$ as a 1:1 inseparable mixture of diastereomers.[54]

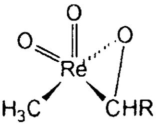
$[C_5H_5\text{-}\{(\eta^5\text{-}C_6H_6)(CO)_2Mn{=}C(OC_2H_5)Ar\}]$ (Ar = C_6H_5, *o*-$CH_3C_6H_4$) have been prepared by the reaction of tricarbonyl(*exo*-cyclopentadienyl-η^5-cyclohexadienyl)manganese with ArLi in ether at low temperature, followed by alkylation with Et_3OBF_4 in aqueous solution at 0°C.[55] UV irradiation of $[(\eta^5\text{-}C_6H_7)Mn(CO)_3]$ and 1 or 2 equivalents of $PhC{\equiv}CR$ (R = H, Me, Ph) in toluene results in metal-mediated cycloaddition yielding [5 + 2] adducts $[\{\eta^{2:3}\text{-}C_8H_7\text{-}Ph(R)\}Mn(CO)_3]$ and tricyclic [5 + 2], *homo*[5 + 2] double adducts $[(\eta^{1:2:2}\text{-}C_{10}H_7Ph_2R_2)Mn(CO)_3]$.[56]

Photolysis of $CH_3ReO(O_2)_2.H_2O$ in CH_2Cl_2 yields molecular oxygen in the triplet spin state. The quantum yield of photolysis depends on wavelength, and is the result of one single excited state. Detection of both a fluorescence and phosphorescence emission for this complex has enabled determination of both the S_1 and the T_1 energy levels.[57]

CH_3ReO_2 (MDO) is formed by the reaction of CH_3ReO_3 (MTO) and $H_2P(O)OH$ in acidic aqueous solution. The kinetics and thermodynamics for oxygen transfer reactions of MDO and MTO have been studied.[58] Investigations have been carried out on the kinetics of the initial oxidation step for the oxidation of cyclic β-diketones by H_2O_2 in the presence of MTO catalyst in CH_3CN/H_2O (1:1 v/v) at 25°C.[59] Rate studies for the stepwise oxidation of thiophene and its derivatives by H_2O_2 catalysed by MTO have been reported.[60] The MTO-catalysed epoxidation of several olefins has been carried out and shows that the hydrolytic ring-opening of the epoxide to give the corresponding diol with H_2O_2 can be avoided by using the urea/hydrogen peroxide adduct as primary oxidant.[61] MTO catalyses several classes of reactions of ethyl diazoacetate and organic azides which do not involve hydrogen peroxide. These, and their possible nitrenoid (**20**) and carbenoid (**21**) intermediates, have been investigated.[62]



(**20**)



(**21**)

The charge transfer reaction between CH_3ReO_3 and aqueous $[Fe(CN)_6]^{4-}$ probably produces the labile binuclear complex $[(Me)O_3Re(\mu\text{-}NC)Fe(CN)_5]^{4-}$, which is characterised by a metal-to-metal charge transfer absorption at λ_{max} = 437 nm. Fe(II) to Re(VII) charge transfer excitation results in a redox photolysis producing the oxidation product $[Fe(CN)_6]^{3-}$ with $\phi = 0.033$ at $\lambda_{irr} = 436$ nm.[63]

The hydrolytic decomposition of MTO in dilute aqueous solution produces methane gas and perrhenate. The kinetics have been studied as a function of temperature and pressure using UV-visible spectrophotometry. At higher MTO concentrations a faster reversible polymerisation-precipitation reaction occurs yielding a polymeric solid, $(C_{0.92}H_{3.3}ReO_{3.0})_n$. Rate studies, investigated as a function of temperature in D_2O by ^1H NMR, show first-order reversible kinetics.[64] *Ab initio* Hartree-Fock (SCF) calculations have been carried out on MTO and its dimers, trimer and tetramer. Results for the tetramer show that it is a model for the interpretation of the IR and Raman spectra of the polymeric form of MTO, and that the negatively charged bridging oxygen atoms in polymeric MTO are probable binding sites for the excess protons that are present.[65]

Low-temperature alkylation of $ReO_2(CH_2CMe_3)Br(py)$ with $ZnPh_2$ affords $ReO_2(CH_2CMe_3)_2Ph$ (*27*). Photolysis of $ReO_2(CH_2CMe_3)_3$ in pyridine gives neopentane and $ReO_2(CHCMe_3)(CH_2CMe_3)$. Neopentylbenzene and $ReO_2(CH_2CMe_3)(py)_3$ are obtained on thermolysis of *27* in pyridine.[66] (*t*-bupy)CH_3ReOCl_2, obtained by reductive halogenation of MTO in the presence of *t*-bupy, undergoes substitution of the chloride or pyridine ligands with chelating N- and P-bases or Schiff base ligands giving methylrhenium(V) complexes having asymmetric coordination of the ligands.[67]

$(HBpz_3)ReO(R)OTf$ (*28*) (R = Me, Et, Bu^n) undergo room temperature oxidation by pyridine *N*-oxide and DMSO forming $(HBpz_3)ReO_3$ and the corresponding aldehyde. Addition of 2,6-lutidine to a low-temperature oxidation of $(HBpz_3)ReO(Et)OTf$ by DMSO gives *cis*-2-butene rather than acetaldehyde. Studies suggest that oxygen atom transfer to *28* forms $[(HBpz_3)ReO_2R]^+$.[68] The reaction of (R = Ph) with DMSO affords $[(HBpz_3)ReO(Ph)(OSMe_2)]OTf$. This undergoes phenyl-to-oxo migration at 25 °C forming Me_2S and [$(HBpz_3)$ReO-

(OPh)(OSMe$_2$)]OTf, which loses Me$_2$S reversibly and slowly oxidises Me$_2$SO to Me$_2$SO$_2$. [(HBpz$_3$)ReO$_2$(Ph)]OTf is an intermediate in these reactions.[69] [ReO(CH$_2$SiMe$_3$)$_3$(CN)]$^-$, [ReO(CH$_2$SiMe$_3$)$_3$(bipy)] and [ReO(CH$_2$PMe$_3$)(CH$_2$SiMe$_3$)$_3$] are prepared by the reaction of [ReO(CH$_2$SiMe$_3$)$_3$(PMe$_3$)] (*29*) with CN$^-$, bipy and trimethylmethylenephosphorane, respectively. Treatment of *29* with diazomethane yields [ReO(CH$_2$PMe$_3$)(CH$_2$SiMe$_3$)$_3$] by a formal insertion of methylene into the Re-P bond.[70] [ReO(C(O)CH$_2$SiMe$_3$)(CH$_2$SiMe$_3$)$_2$(PMe$_3$)] (*30*) has been characterised by X-ray crystallography. With KCN and excess water *30* forms K[ReO(CN)(C(O)CH$_3$)(CH$_2$SiMe$_3$)$_2$] as a result of substitution by PMe$_3$ and cleavage of the C-Si bond.[71]

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12

Complexes Containing Metal-Carbon σ-Bonds of the Groups Iron, Cobalt, and Nickel, including Carbenes and Carbynes

BY STEPHEN J. SIMPSON

1 Introduction, Reviews, and Articles of General Interest

The general format of this chapter is very similar to that used in previous years. The review is restricted to detectable complexes of the iron, cobalt, and nickel triads which contain a metal-carbon σ-bond, including carbenes and carbynes. Species postulated in catalytic cycles have normally been excluded and coverage of metal cluster complexes has been kept to a minimum.

A review of the organometallic chemistry of carbon dioxide has appeared which includes examples of metal acyl and metal carbene intermediates and compounds.[1] The chemistry of transition metal alkane complexes, particularly of rhodium, has been reviewed.[2] Activation of C-H and Si-H bonds at transition metal centres has been briefly reviewed with reference to isolable alkane complexes.[3] The protonation of unsaturated hydrocarbon ligands has been summarised, in particular the topics of product specificity, and regio- and stereoselectivity have been addressed.[4] The use of ruthenium complexes in organic transformations of alkynes often involving alkyl and carbene intermediates has been reviewed by Trost.[5] Carbonylation of methanol using rhodium and iridium catalysts has been briefly reviewed[6] and the hydrogenation and hydrogenolysis of thiophenes by soluble catalysts of these metals has been surveyed.[7] Two reviews on the preparation and properties of homo- and hetero- polynuclear complexes containing acetylide[8] and polyacetylide[9] ligands have been published.

2 Metal-Carbon σ-Bonds Involving Group 8, 9 or 10 Metals

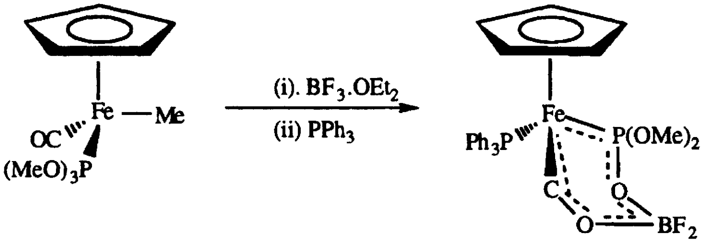
2.1 The Iron Triad – A theoretical investigation of C-C and C-H bond activation in propane by Fe^+ concludes that for C-H activation a [1,2]-H_2 elimination is favoured over [1,3]-H_2 elimination.[10] Infrared multiphoton dissociation of the ions $[MC_nH_{2n}]^+$, where M is Fe, Co, Ni, reveals that most ions produce a single photodissociation product; twenty six of the forty ions studied were photoactive at 944 cm^{-1}, the wavelength of the CO_2 laser used.[11] The same group later extended the technique to the $[MC_4H_6]^+$ ions where the hydrocarbon fragments were butadiene or acetylene plus ethylene.[12] The gas phase reaction of $[Fe(CO)]^+$ and $[Fe(H_2O)]^+$ with methane and ethane revealed that the latter is more efficient at σ-bond activation, preferring to activate C-H bonds, whereas the carbonyl ion activates C-C and C-H bonds comparably.[13]

The preparation of the brown three co-ordinate $[Fe(mesityl)_2(2,4,6\text{-trimethylpyridine})]$ and red-brown four co-ordinate $[Fe(2,4,6\text{-tri\{isopropyl\}benzene})_2(pyridine)_2]$ and their temperature dependent ^1H nmr spectra have been reported; X-ray crystallography reveals their geometries to be trigonal planar and tetrahedral respectively.[14] Reaction of 2-{lithiobis(trimethylsilyl)methyl}pyridine with ferrous chloride produces the yellow bicyclic $[Fe(NC_5H_5\text{-}2\text{-}C\{SiMe_3\}_2\text{-}\kappa\text{-}C,N)_2]$ which sublimes at 116°C and 10^{-2} mm Hg. Related quinoline based complexes and the monocycle $[Fe(NC_5H_5\text{-}2\text{-}C\{SiMe_3\}_2\text{-}\kappa\text{-}C,N)(tmeda)]$ are reported to be stable up to their melting points in the range 110°–159°C. Crystallography reveals distorted tetrahedral geometries supporting a high spin d^6 formulation with $\mu_{eff} = 4.24 - 4.96$ BM.[15]

A thorough ^{57}Fe nmr study of ligand effects in cyclopentadienyliron alkyls looked at four classes of compound; for the series $[Fe(\eta^5\text{-}C_5H_5)(CO)_2R]$ there is a linear correlation between $\delta(^{57}Fe)$ and the rate of migratory insertion driven by triphenylphosphine, a strong electronic effect operates in the series $[Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)R]$ where more electronegative alkyl groups produce decreased shielding with a spread of over 2000 ppm. A linear correlation of $\delta(^{57}Fe)$ and Tolman cone angle was found for the acyl compounds $[Fe(\eta^5\text{-}C_5H_5)(CO)(L)\text{-}COMe]$ and a similar relationship involving the Taft parameter σ_I of the Y groups (*inter alia* Me, $SiMe_3$, I, Ph, CO_2Me) applied in the series $[Fe(\eta^5\text{-}C_5H_4Y)(CO)(PPh_3)Me]$.[16]

Both infrared and UV-visible spectroscopy were used to monitor the kinetics of migratory insertion in the compounds $[Fe(\eta^5\text{-}C_5H_5)(CO)_2R]$ and $[Fe(\eta^5\text{-}C_9H_7)(CO)_2R]$ where (R = Me, $CHMe_2$), induced by the phosphines PMe_2Ph, $PMePh_2$, and PPh_3 in both toluene and tetrahydrofuran. It was concluded that the reaction is associative, alkyl migration is rate determining, and that there is a rapid pre-equilibrium between the phosphine and the metal starting material probably ruling out η^3- ring slipped intermediates. The lack of a solvent effect on the rate was noted together with the fact that the cyclopentadienyl compounds bind less efficiently to the phosphine in the loose adduct than the indenyl compounds; the relative reaction rates differed by a factor of ten in favour of the latter.[17] Reaction of $[Fe(\eta^5\text{-}C_5H_5)(CO)(P\{OMe\}_3)Me]$ with boron trifluoride etherate and triphenylphosphine provides the first example of the precedence of carbonyl migratory insertion over an alkoxy group abstraction from an ancillary phosphite ligand induced by this reagent. The structurally characterised product $[Fe(\eta^5\text{-}C_5H_5)(PPh_3)(P\{OMe\}_2O\{BF_2\}OC\text{-}\kappa\text{-}P,C)]$ is described as a carbene phosphite metallacycle; the six membered ring system is boat shaped (*Scheme 1*).[18]

The decomposition of an isomeric pair of ferra-γ-ketoesters has been reported; dichloromethane solutions of *cis*-$[Fe(CO)_4(COMe)(COCO_2Me)]$ convert at -3°C to *cis*-$[Fe(CO)_4(COMe)(CO_2Me)]$ whereas *cis*-$[Fe(CO)_4(CO_2Me)(COCOMe)]$ transforms to the structurally characterised metallacyclic *cis*-$[Fe(CO)_4\text{-}(C\{O\}OC\{Me\}\{OMe\}C\{O\}\kappa\text{-}C,C))]$. The latter reaction is an intramolecular



Scheme 1

process accelerated by replacing the solvent by methanol. The iron centre seems to increase the nucleophilic character and mobility of the methoxy fragment in the methoxycarbonyl ligand.[19]

Photochemical insertion of carbon disulfide into the metal-alkynyl bond in [Fe(η^5-C_5H_5)(dppe)-(C≡CR)], where R is phenyl or *tert*-butyl, produces a green dithiocarbamate [Fe(η^5-C_5H_5)(dppe-κ^1-*P*)(S_2CC≡CR-κ-*S,S*)], which shows evidence in solution of a fluxional process involving η^2-S,S′ and η^3-S,C,S′ forms. The related complexes derived from [Fe(η^5-C_5H_5)(CO)(PPh_3)(C≡CR)] are blue.[20] Protonation of the hydrido(acetylides) [FeH(C≡CR)(PPh{OEt}$_2$)$_4$] (R = phenyl, p-tolyl, *tert*-butyl), leads to a mixture of [FeH(η^2-H_2)(PPh{OEt}$_2$)$_4$]$^+$ and [Fe(C≡CR)(C=CHR)(PPh{OEt}$_2$)$_4$]$^+$ salts consistent with reaction at both anionic ligands. Some ruthenium analogues were also prepared.[21] Molecular wires with chains up to length 13Å have been prepared from oxidative coupling of [Fe(η^5-C_5Me_5)(dppe)(C≡C-C≡CH)] using copper acetate and a free radical source in pyridine. The resulting burnt orange μ-octatetrayne compound can be oxidised to a green 35 electron Fe(II) / Fe(III) cation with ferrocenium hexafluorophosphate. Cyclic voltammetry reveals two reversible one electron processes involving [Fe(II)]$_2$ / [Fe(II)Fe(III)] and [Fe(II)Fe(III)] / [Fe(III)]$_2$ couples. The neutral and cationic bridged compounds both display two infrared active acetylenic stretches at 2109, 1949 and 1879, 1784 cm^{-1} respectively compared to 2099, 1960 cm^{-1} for the mononuclear precursor.[22]

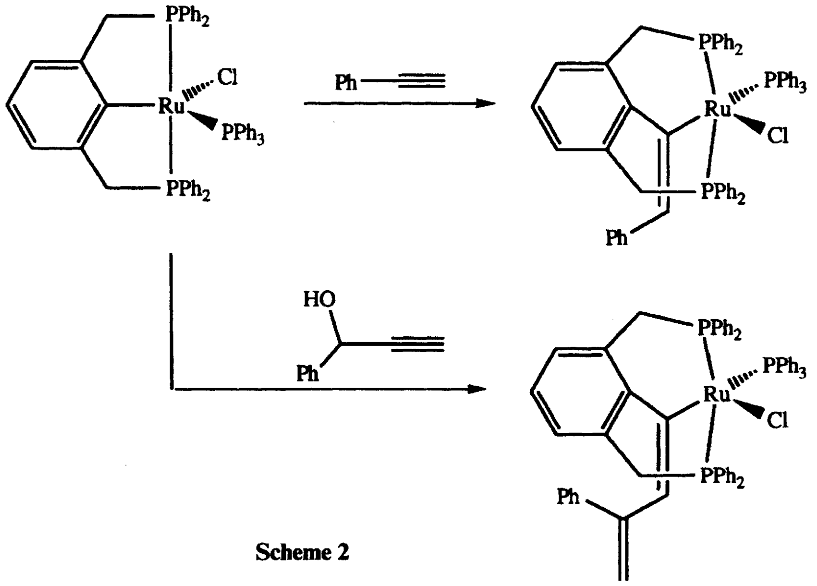
The first structurally characterised organometallic nitrosyl porphyrin complex [Ru(ttp)(NO)R], has been obtained from reacting the *meso*-tetratolylporphyrinato compound [Ru(ttp)(NO)Cl] with *para*-fluorophenylmagnesium chloride. The metal – carbon bond length was 2.095(6)Å and the nitrosyl ligand was bent (152° at nitrogen). The methyl analogue was also reported, the methyl group resonates at δ-6.74 in the ^1H nmr spectrum.[23]

Tetrafluoroethylene and sodium hydride react with [Ru(Cl)$_2$(PPh_3)$_4$] in acetonitrile to produce the metalla-octafluorocyclopentane [Ru{(CF_2)$_4$}(PPh_3)$_4$] which is unreactive towards hydrogen up to 20 bar pressure even in the presence of 2% palladium on alumina.[24] Addition of hexafluorobenzene to a tetrahydrofuran solution of *cis*-[Ru(H)$_2$(dmpe)$_2$] leads to an instant reaction at -78°C. The product, *trans*-[Ru(H)(C_6F_5)(dmpe)$_2$] was structurally characterised. Extension of this C-F bond activation chemistry using, *inter alia* pentafluorobenzene, 1,2,3-trifluorobenzene, and 1,2-difluorobenzene gave in each case the product with the aromatic hydrogens remote from the metal centre. The speed of the reaction and product pattern strongly indicates an electron transfer involving a caged radical pair, rather than a nucleophilic substitution or concerted oxidative addition pathway.[25]

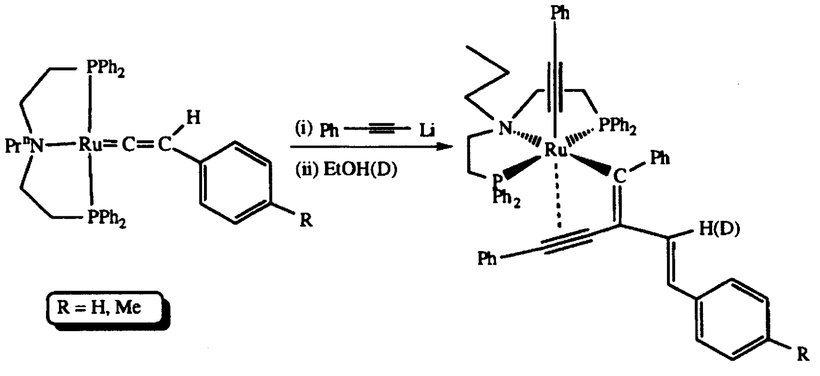
One pot reactions of the acetylenes HC≡CH, PhC≡CPh, HC≡C-*p*-tolyl, and PhC≡C-C≡CH with 1,4,7-trithiacyclononane and $[RuH(Cl)(CO)(PPh_3)_3]$ produces the facial isomer of the tris(thioether) chelate complexes $[Ru\{SCH_2CH_2\}_3(vin)(CO)(PPh_3)]$. The simple vinyl compound where (vin) is $CH{=}CH_2$ was structurally characterised. Two dimensional nmr spectroscopy allowed assignment of all twelve diastereotopic proton environments in $[Ru\{SCH_2CH_2\}_3(CH{=}CH\{p\text{-tolyl}\})(CO)(PPh_3)]$.[26] Acetylene inserts into the metal-silicon bond of the compounds $[Ru(Cl)(CO)\text{-}(PPh_3)_2(SiR_3)]$, ($R_3$ = Me_3, Et_3, Ph_3, Me_2Cl, Me_2OEt), producing the vinyls $[Ru(Cl)(CO)(PPh_3)_2(CH{=}CHSiR_3)]$. These five co-ordinate compounds readily add carbon monoxide *trans* to the vinyl group; the structure of $[Ru(Cl)(CO)(PPh_3)_2(CH{=}CHSi\{Me_2OEt\}_3)]$ was determined. The dimethylhydroxysilyl starting material forms a six co-ordinate vinyl compound where the hydroxyl oxygen atom co-ordinates at the metal centre. Further reaction of this product with silver ion in the presence of neutral ligands gave the cations $[Ru(L)(CO)(PPh_3)_2(CH{=}CHSi\{Me_2\}O\{H\}\text{-}\kappa\text{-}C,O)]^+$, (L = CO, MeCN, CN-*p*-tolyl) which can be reversibly deprotonated to the neutral chelated vinyl ether form. The *p*-tolylisonitrile cation was structurally characterised.[27]

Organoruthenium dendrimers containing up to forty eight $[Ru(\eta^5\text{-}C_5H_5)(CO)_2]$ units exclusively at the periphery have been prepared from poly(benzyl phenyl ether) dendrimer precursors; these appear to be the first excursion of organoruthenium chemists into the dendrimer world.[28]

Coupling of terminal acetylenes with a cyclometallated Ru-C bond has been reported and the phenylacetylene product was structurally characterised (*Scheme 2*).[29] The starting material has also been prepared by another group.[30]



Scheme 2

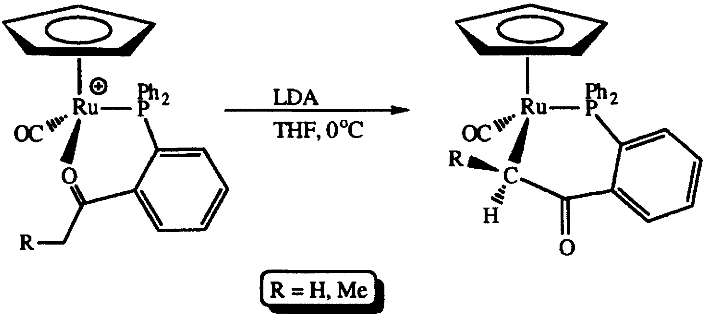


Scheme 3

Dienynyl ligands resulted from the coupling of neutral ruthenium vinylidenes with acetylides. The *p*-tolyl derivative in *Scheme 3* was structurally characterised. Possible mechanisms were discussed.[31]

The same group have illustrated the hydration of phenylacetylene with an extension of some of the chemistry illustrated in *Scheme 3* in that reaction of *mer-,trans*-$[Ru(Cl)_2(PNP)(PPh_3)]$ with the acetylene in wet tetrahydrofuran produces toluene and *fac-,cis*-$[Ru(Cl)_2(PNP)(CO)]$; reaction at lower temperatures leads to a mixture of this product and *mer*-$[Ru(Cl)(CH_2Ph)(PNP)(PPh_3)]$. A mechanistic study suggests that the key steps are an (η^2-alk-1-yne) to vinylidene tautomerism, intramolecular attack by water on the vinylidene, deprotonation of the hydroxycarbene producing an acyl, deinsertion of CO, and elimination of the hydrocarbon by protonation of the benzylruthenium species.[32]

Selectivity in the deprotonation rection shown in *Scheme 4* is kinetic, ranging from 3:1 to 9:1 between preparations when R is methyl. X-ray crystallography reveals that the major diastereomer is $S_{Ru}R_C(R_{Ru}S_C)$ with the methyl group *syn* to the cyclopentadienyl ligand as shown in the scheme. This is also the least soluble diastereomer.[33]



Scheme 4

A number of groups have looked at non-linear optical materials based on ruthenium acetylides this year. The vinylidene cations *trans*-$[RuCl(dppm)_2(=C=C\{H\}C_6H_4\text{-}p\text{-}X)]^+$ were prepared from *cis*-$[Ru(Cl)_2(dppm)_2]$ and the appropriate acetylene, ($X = NO_2$, $C_6H_4C_6H_4\text{-}p\text{-}NO_2$, $CH{=}C\{H\}C_6H_4\text{-}p\text{-}NO_2$). Deprotonation by triethylamine gave neutral acetylides *trans*-$[RuCl(dppm)_2(C{\equiv}C_6H_4\text{-}p\text{-}X)]$ which exhibited good non-linear optical properties; the vinyl linkage compound where the phenyl rings are maintained co-planar was particularly promising.[34] The related rigid-rod bis(acetylides) *trans*-$[Ru(dppm)_2(C{\equiv}C_6H_4\text{-}p\text{-}X)_2]$ have been structurally characterised[35] and their cubic molecular optical non-linearities were measured by the Z-scan technique.[36]

Reaction of *trans*-$[Ru(Cl)_2(depe)_2]$ with acetylide anions provides a high yield route to the *trans*-bis(acetylides) *trans*-$[Ru(C{\equiv}C_6H_4\text{-}p\text{-}X)_2(depe)_2]$, {depe = 1,2-bis(diethylphosphino)ethane; X = H, OMe, $C{\equiv}CH$, ${}^tBu$}. Use of two acetylenes allowed mixed acetylides to be prepared.[37]

Large second order non-linear optical properties were observed for the arylenynyl compounds in *Figure 1*; in particular very large quadratic hyperpolarisabilities were measured, in excess of those normally found for metallocene based systems.[38,39]

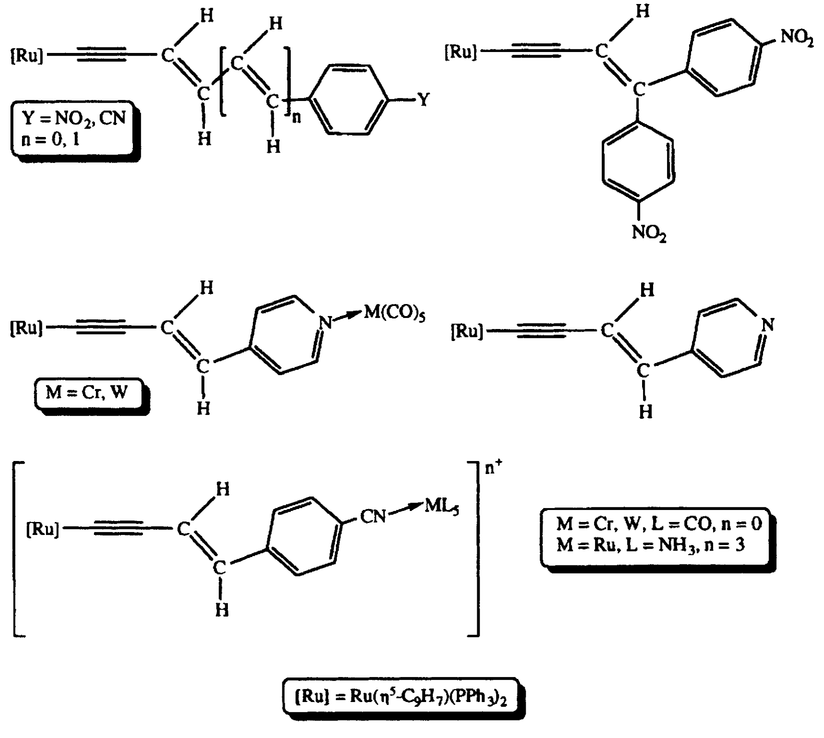


Figure 1

The five co-ordinate phenylruthenium and -osmium compounds [M(Cl)Ph(PPh_3)$_2$(CNR)], where R is *p*-tolyl or *p*-chlorophenyl, oxidatively add dioxygen with concurrent migration of the phenyl group to the isonitrile ligand. Both the product [Os(Cl)(η^2-O_2)(PPh_3)$_2$(C{Ph}NR-κ-*C,N*)] and its product of sulfur dioxide insertion [Os(Cl)(η^2-SO_4)(PPh_3)$_2$(C{Ph}NR-κ-*C,N*)] were structurally characterised for the case of R is *p*-chlorophenyl.[40]

Addition of phenyllithium to the vinyl compound [OsCl(CO)-(P^iPr_3)$_2$(CH=CHPh)] causes an unusual C-H bond activation of the vinyl derived phenyl group. The product is in equilibrium in solution between agostic and non-agostic forms. X-ray crystallography shows it to be five co-ordinate [OsH(CO)-(P^iPr_3)$_2$(C_6H_4-*o*-CH=CHPh)] in the solid state. Use of $LiCD_3$ in place of LiPh gives [OsH(CO)(P^iPr_3)$_2$(C_6H_4-*o*-CH=$CHCD_3$)] which isomerises over twenty minutes in solution to the osmium allyl [OsD(CO)(P^iPr_3)$_2$(η^3-CD_2CHCHPh)].[41]

Treatment of osmium tetroxide with a tetrahydrofuran solution of *o*-tolylmagnesium halide produces the tetraalkyl [Os(C_6H_4-*o*-Me)$_4$] which reacts with one equivalent of PMe_3 by aryl coupling, forming [Os(C_6H_4-*o*-Me)$_2$(PMe_3)(η^6-{2-Me}$C_6H_4C_6H_4${2′-Me})]. An excess of the phosphine displaces the biaryl and yields [Os(C_6H_4-*o*-Me)$_2$(PMe_3)$_4$]. A kinetic study was undertaken.[42]

2.2 The Cobalt Triad – A theoretical study comparing methane C-H bond activation by the species [M(η^5-C_5H_5)(CO)], (M = Co,Rh, Ir), confirms the experimental result that the cobalt species is unreactive; the origin of this lies in its triplet ground state. Calculations for the rhodium case also agree well with experiment; the C-H bond activation barrier is 5.9 kcal mol^{-1} and C-D activation is estimated to be 0.7 – 1.0 Kcal mol^{-1} less favourable.[43] The rate determining step in C-C bond cleavage of ethane by $[Co]^+$ is calculated to be a [1,3]-hydrogen shift leading to a $[Co(CH_2)(CH_4)]^+$ transition state. The complex $[Co(C_2H_4)(H_2)]$ is important in the C-H bond activation branch.[44] An experimental study has investigated the potential energy surface of $[Co(C_2H_6)]^+$ by a guided ion beam method.[45]

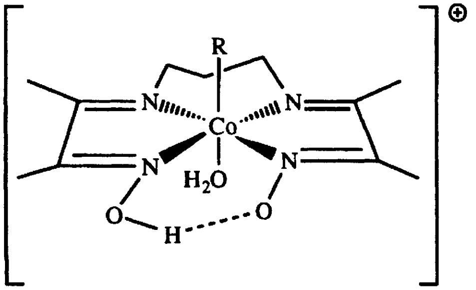
A rare example of a stable Co(II) alkyl compound has been reported. Cobaltous chloride reacts with (2,6-dimesityl)phenylmagnesium iodide to yield a dark blue crystalline dimer [Co(THF)(2,6-$mes_2C_6H_3$)(μ-Br)]$_2$ which was structurally characterised. The cobalt – cobalt separation is 3.5Å indicating the absence of a bond and the geometry found was trigonal bipyramidal with one axial site empty rather than distorted tetrahedral. The source of the bromide ligands was the Riecke magnesium procedure used to prepare the bulky Grignard reagent. The compound has μ_{eff} = 4.7 BM at room temperature.[46] Perfluorobenzyl iodide reacts with [M(η^5-C_5R_5)(CO)$_2$], (R = H, Me, M = Co; R = Me, M = Rh), in benzene producing the expected products [M(η^5-C_5R_5)($CF_2C_6F_5$)(I)(CO)] which react with PMe_3 in benzene by simple substitution of the carbonyl ligand. The cyclopentadienylcobalt product was structurally characterised. Remarkably if the reaction of the pentamethylcyclopenta-dienylcobalt compound is carried out using tetrahydrofuran in place of benzene a double ring activation takes place with loss of HF forming [Co(I)(η^5-$C_5Me_4CH_2C_6F_4$-*o*-C{F}$_2$)-κ^1-*C*)(PMe_3)]. The structure of this unusual product was confirmed by X-ray crystallography.[47]

The carbonylation and decarbonylation reactions of carbomethoxymethylcobalt complexes has been studied and extensive, ^{1}H, ^{13}C, ^{31}P, and ^{17}O nmr and infrared data reported for the prepared compounds [Co(CO)$_3$(L)(CH{R}-CO$_2$Me)], (R = H, CH$_2$CO$_2$Me; L = CO, PPh$_3$). The secondary complexes undergo reversible carbonylation – decarbonylation whereas the primary alkyls do not. [Co(CO)$_3$(PPh$_3$)(CH$_2$CO$_2$Me)] exhibits an acyl stretch at 1657 cm^{-1} in the infrared spectrum suggesting a cobalt – oxygen interaction, the other compounds absorbing at 1720 -1748 cm^{-1}, and readily decomposes *via* homolytic bond cleavage to [Co(CO)$_3$(PPh$_3$)]$_2$. The first direct evidence for alkyl migration in carbonycobalt chemistry is claimed from nmr spectroscopic evidence for the intermediacy of *cis*-[Co(CO)$_3$(PPh$_3$)(CH$_2$CO$_2$Me)] in the decarbonylation of *trans*-[Co(CO)$_3$(PPh$_3$)-(C{O}CH$_2$CO$_2$Me)].[48]

A crystallographic study of the trigonal bipyramidal complexes [Co-(CO)$_3$(PPh$_3$)(CH$_2$CO$_2$R)], where R is Me, Et, ^{n}Pr, ^{i}Pr, (*RS*)-^{s}Bu, ^{t}Bu, ^{c}Hex, CH$_2$Ph, (*S*)-lactate, *D*-menthyl, and *L*-menthyl, and the compound [Co-(CO)$_3$(PPh$_2${menthyl})(CH$_2$CO$_2$^{i}Pr)] has revealed that the conformations of the carboalkoxymethyl group and the phosphine develop concertedly. The ester fragment is always quasi-parallel (± 30°) to the equatorial [Co(CO)$_3$] plane, only a single helical enantiomeric conformer of the PPh$_3$ ligand accompanies a single conformer of the carboalkoxymethyl group. Some calculations suggest that the propeller chirality of the PPh$_3$ ligand is the dominating factor.[49]

The first X-ray crystal structure of a B$_{12}$ protein has been determined. Methylcobalamin is not bound in the 'base on' form in the B$_{12}$ binding domain of the methionine synthase of E. coli. A histidine residue co-ordinates at the cobalt centre of the protein co-factor in place of the nucleotide functionality.[50] X-ray absorption spectroscopy of six 'Costa type' organocobalt B$_{12}$ model compounds (*Figure 2*) has revealed that the cobalt – carbon bondlengths correlate with the pK$_a$ and Taft σ^* of the alkyl groups, the length decreases with increase of the first and increases as σ^* increases.[51]

Cobalt Schiff base complexes [Co(salen)(γ-picoline)(R)] with the base and alkyl groups co-axial have been reported. The isobutyl and propyl complexes were structurally characterised as was the five co-ordinate [Co(Me$_4$-salen)(Et)] con-



R = Me, ^{i}Pr, ^{i}Bu, CH$_2$Ph, OAc, CH$_2$CF$_3$

Figure 2

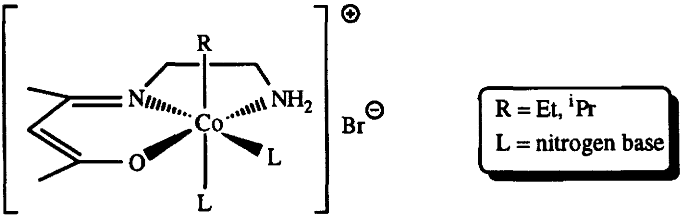


Figure 3

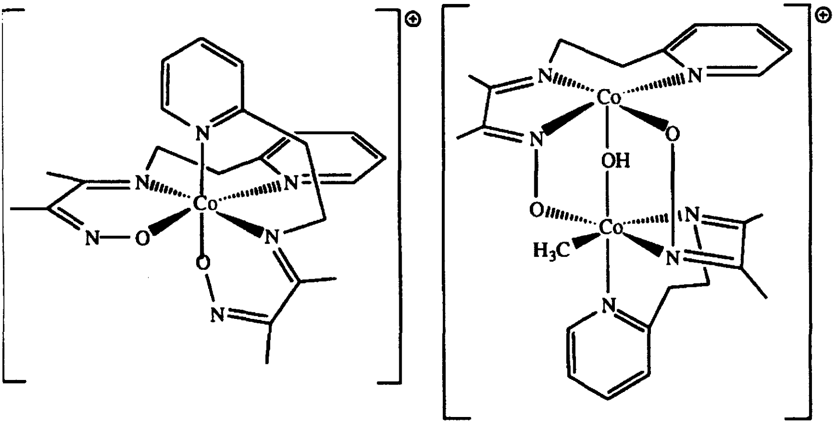
taining the bulky 1,1,2,2-tetramethyl-N,N′-ethylenebis-(salicylideneamine) ligand. The cobalt – carbon bond was weakest in the five co-ordinate compound.[52]

Long chain functionalised alkyl groups have been bound to cobalt in a search for novel liquid crystal properties. $[Co(Hdmg)_2\{(CH_2)_nI\}(NC_5H_5)]$ where n is 5,6,8,9,10 and $[Co(Hdmg)_2\text{-}\{(CH_2)_3OC(O)C_6H_4R\}(NC_5H_5)]$ where R is H, *o*-, *m*-, *p*-OMe, *p*-OC_7H_{15}, or *p*-OC_9H_{19} were prepared but no useful properties were observed. A useful model for future B_{12} model studies was discovered in that $[Co(Hdmg)_2\{(CH_2)_3OH\}]$ is water soluble.[53]

Cobalt compounds of the basic type exemplified in *Figure 3* have been tested *in vitro* against carcinomas, with promising results. In particular the ethylenediamine cationic compounds provide a pH dependent source of free radicals.[54]

Another rare example of a tridentate ligand stabilising a cobalt – carbon bond comes from reduction of $[Co(L)_2]ClO_4$ (**A**) with $NaBH_4$ to an anionic Co(I) intermediate which on treatment with iodomethane gave red crystals of a dinuclear cation (**B**) (*Figure 4*).[55]

A near infrared and FT-Raman spectroscopic study of methyl-B_{12}, cobalamins, and imidazole and imidazolate methylcobinamide derivatives in aqueous solution



(A) **(B)**

Figure 4

reveals that even though there is virtually no frequency change of $\nu_{Co\text{-}C}$ from *ca.* 505 cm^{-1} on co-ordination of imidazoles, the intensity changes can be useful to characterise axial substituents.[56] A second group using resonance Raman spectroscopy on alkylcobalamins has confirmed that *trans*-ligands such as benzimidazole do not affect this stretching mode.[57] Correlation of structure and nmr parameters (^1H, ^{13}C, and ^{31}P) has been investigated for 'base-on' cobalamins; ^{13}C nmr parameters were sensitive to conformational changes.[58]

The isomerisation of α- and β-alkylcobinamides is promoted by organic free radicals generated by a Fenton reaction from $R(Me)_2COOH$. Evidence was found for multiple *trans*-alkylations and for corrin ring side-chains controlling relative steric assessibility of the faces of the cobalt corrinoids.[59]

Solvent cage effects were observed in the thermal homolysis of α- and β-cyanomethylcobinamides; the β-isomer is thermodynamically favoured by entropy while enthalpy favours the α-isomer, indicating that in the ground state the α-isomer has a shorter cobalt – carbon bond.[60] The kinetics of cobalt – alkyl homolysis has been studied for a number of analogues of neopentyl-cobalamin which were modified in their side-chain structure, including a C(13) epimer where the e-propionamide side-chain has an 'upwardly' axial conformation and some c-side-chain modified analogues. Binding to the B_{12} binding protein, chicken haptocorrin, stabilises the neopentylcobalamins towards thermolysis by *ca.* 380 fold (*ca.* 3.5 kcal mol^{-1}).[61] The effect of axial *p*-substituted pyridine bases on the thermolysis of the cobalt – carbon bond in adocobinamide, the 'base off' analogue of coenzyme B_{12}, reveals that the rate of bond cleavage increases with increasing electron donor power of the pyridines. The homolysis rate constant is relatively constant with the heterolysis rate constant increasing dramatically; this has biological relevance for evolutionary pressures of base selection since only homolysis is biologically relevant.[62]

High valent σ-phenyl bonded cobalt corroles have been synthesised and their spectroscopy, electrochemistry, and structure has been explored. [Co(OEC)(Ph)] (OEC = 2,3,7,8,12,13,17,18-octaethylcorrole trianion) exhibits strong Co(IV) character and the Co-C bondlength in the Co(V) cation [Co(OEC)(Ph)]ClO_4 at 1.970(7)Å is surprisingly longer than the value of 1.937(3)Å found for the neutral compound.[63]

A ^{103}Rh nmr study of alkylrhodoximes $[Rh(Hdmg)_2R(L)]$ has been carried out using (^1H, ^{103}Rh) or (^{31}P, ^{103}Rh)-{^1H} inverse correlation methods. For the three series where L is H_2O, pyridine, or PPh_3, the range of ^{103}Rh chemical shifts covers δ 2033 – 2818 and is affected by distortions of co-ordination geometry due to steric bulk of the alkyl group; shielding decreases in the order Et > Me > ^nBu > ^iPr > ^sBu > $^{neo}Pent$ > ^tBu. Values of $^1J_{Rh\text{-}P}$ indicate a *trans* effect in the phosphine series.[64]

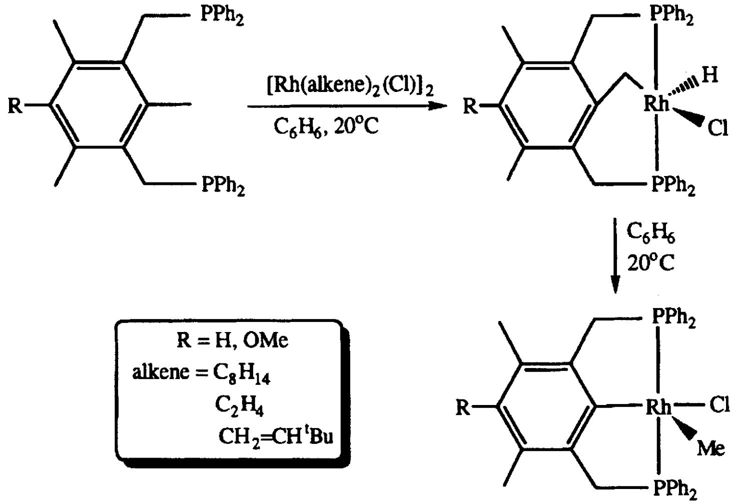
X-ray crystal structures of *fac*-$[Rh(Me)_3(NNN)]$, where the hard σ-ligand set was 1,4,7-trimethyl-1,4,7-triazacyclononane or the 1,4,7-tris(neohexyl) analogue, have been reported. The compounds react stepwise with HOTf, HCl, or HBF_4 at -80°C to produce the *fac*-$[Rh(Me)_2(X)\text{-}(NNN)]$ and *fac*-$[Rh(Me)(X)_2(NNN)]$ compounds.[65] Later work measured the X-ray photoelectron spectra (Rh{$3d_{5/2}$} and {$3d_{3/2}$}) of these compounds and their tripod phosphine analogues *fac*-

$[Rh(Me)_3(\{Me_2PCH_2\}_3CMe)]$. The binding energy increases as methyl groups are replaced and is greater for the nitrogen than for the phosphorus series; the difference is not so pronounced for the trimethyl compounds.[66]

The phenyl and vinyl compounds $[Rh(R)(CO)(P^iPr_3)_2]$ and the vinyl compound $[Rh(CH=CH_2)\text{-}(CS)(P^iPr_3)_2]$ were prepared from Grignard reagents; in the $^{13}C\{^1H\}$ nmr spectrum of the carbonyl vinyl compound, C_α resonates at $\delta 173.7$ ($J_{Rh\text{-}C} = 27.1$ Hz, $J_{P\text{-}C} = 16.6$ Hz) whereas the corresponding values for the carbonylsulfide compound were $\delta 172.9$ ($J = 23.3$, 17.2 Hz). There is no reaction of either $[Rh(R)(CO)(P^iPr_3)_2]$ compound with CO at ambient conditions.[67]

The vinylallene $Me_2C=C=CHC(Ph)=CH_2$ reacts with $[RhCl(PPh_3)_3]$ by a π- to σ-conversion of the 1,3-diene system; orange crystals of $[RhCl(CH_2C\{Ph\}=CHC\{=CMe_2\})(PPh_3)_2]$ were structurally characterised. Reactions with hydrogen, triethylsilane, and carbon monoxide retain the transoid 1,3-diene geometry.[68]

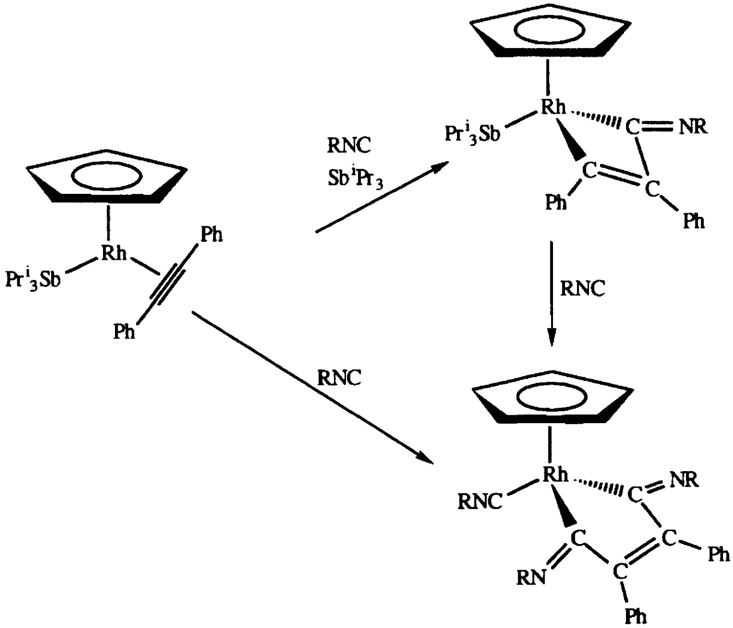
Direct metal insertion into a non-strained carbon – carbon bond is thermodynamically and kinetically favoured over carbon – hydrogen activation (*Scheme 5*) and involves a three centre mechanism similar to those commonly proposed for C-H activation. The product was examined by X-ray crystallography. The iridium system demonstrates the same selectivity.[69]



Scheme 5

Treatment of $[Rh(acac)(PCy_3)(\eta^2\text{-}C_8H_{14})]$ with monoacetylenes in the presence of PCy_3 yields the hydrido acetylides $[RhH(C{\equiv}CR)(acac)(PCy_3)_2)]$, (R = Ph, Cy, $SiMe_3$), which protonate with tetrafluoroboric acid to produce vinyl complexes. $[Rh(CH=CHCy)(acac)(PCy_3)_2)]BF_4$ was crystallographically characterised. Three possible routes are discussed.[70] The diacetylenes $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ and $Me_3SiC{\equiv}CC{\equiv}CSnPh_3$ react with $[Rh(OH)(CO)(P^iPr_3)_2]$ to produce the structurally characterised $\{[Rh(CO)(P^iPr_3)_2]_2(\mu\text{-}C{\equiv}CC{\equiv}C)\}$ and $[Rh(CO)(P^iPr_3)_2(C{\equiv}CC{\equiv}CSiMe_3)]$ respectively.[71]

Reaction of $\{[Rh(Cl)(CO)]_2(\mu\text{-dppm})_2\}$ with phenylmagnesium chloride in tetrahydrofuran at -80°C produced orange-red crystals of the A-frame complex $\{[Rh(Ph)]_2(\mu\text{-CO})(\mu\text{-dppm})_2\}$. The eight membered $Rh_2P_4C_2$ ring has a chair conformation.[72] Stable red crystals of $[Rh(C\{N_2\}SiMe_3)(PEt_3)_3]$ were prepared from $[RhCl(PEt_3)_3]$ and $LiC(N_2)SiMe_3$. The corresponding five co-ordinate $[Rh(C\{N_2\}SiMe_3)(PMe_3)_4]$ compound immediately decomposes in the solid state but is solution stable over several days. The triethylphosphine compound can be photolysed at -30°C to produce an oily green solid spectroscopically characterised as $\{[Rh(PEt_3)_2]_2(\mu\text{-}C\{SiMe_3\}PEt_3)\}$ which decomposes at room temperature. Treatment of $[Rh(C\{N_2\}SiMe_3)(PEt_3)_3]$ with ^tBuNC produces a 1*H*,-1,2,3-triazolato complex $[Rh(CN\{^tBu\}N_2C\{SiMe_3\})(PEt_3)(^tBuNC)_2]$ which was structurally characterised. The metal bound carbon atom of $[Rh(C\{N_2\}SiMe_3)(PEt_3)_2(CO)]$ resonates at δ11.2 ($J_{Rh\text{-}C}$ = 28 Hz, $J_{P\text{-}C}$ = 14 Hz) in the $^{13}C\{^1H\}$ spectrum.[73]



Scheme 6

Single and double insertions of methylisonitrile or *tert*-butylisonitrile into a rhodium alkyne compound yields metallocyclobutenes and metallocyclopentenes; both methylisonitrile products have been structurally characterised.[74]

Treatment of partially dehydroxylated silica with tris(π-allyl)rhodium produces surface attached bis(π-allyl)rhodium groups which undergo an η^3- to η^1- shift on reaction with PMe_3 and co-ordination of three phosphine molecules accompanied by loss of propene. Carbon monoxide causes migratory insertion to leave an oxobutenylrhodium dicarbonyl surface attached species.[75]

Photochemical reaction of $[Rh(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_2H_4)(PMe_3)]$ with pentafluoroanisole proceeds with intermolecular C-H and C-F activation. The product, $[Rh(\eta^5\text{-}C_5H_5)(CH_2O\text{-}m\text{-}C_6F_4)(PMe_3)]$ reacts with trityl cation forming a cyclic carbene cation by hydride abstraction at 220 K; the product which decomposes at room temperature was characterised by signals at δ308.6 and δ13.09 associated with the carbene group in the $^{13}\{^1H\}$ and ^1H nmr spectra respectively.[76]

Thiophene reacts with $[Rh(HB\{3,5\text{-dimethylpyrazolato})_3\})(\eta^2\text{-}C_2H_4)(PMe_3)]$ giving both C-H and C-S activation products, with C-H activation in the 2-position being thermodynamically favoured. This contrasts with the pentamethylcyclopentadienyl analogue where C-S activation was preferred.[77] The formation of six membered metallocyclic products on reaction of substituted dibenzothiophenes by C-S bond cleavage is controlled mainly by steric factors in the sulfur bound intermediate with electronic factors being minor. Strongly π- donating groups in the 2-position favour cleavage of the bond away from the substituted ring. A number of X-ray crystal structures were presented.[78] A low temperature nmr spectroscopic study of C-H bond activation of thiophene by $[Rh(PMe_3)_2(CO)Cl]$ under ultra-violet irradiation reveals only C-H insertion at the 2- and 3-positions. Insertion only at the 3-position was found for 2,3-dimethylthiophene.[79]

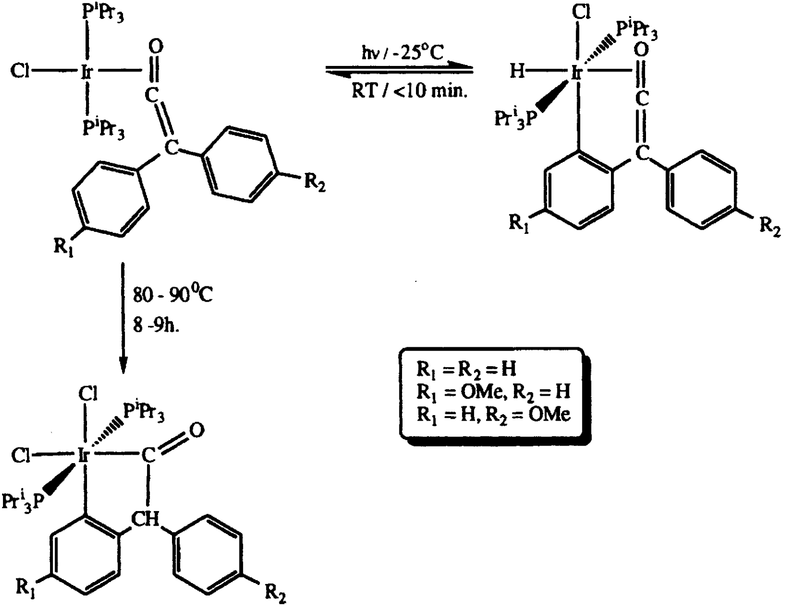
A theoretical study of intra- versus intermolecular C-H bond activation has concentrated on three transformations; $[M(\eta^5\text{-}C_5H_5)(PH_3)]$, (M = Rh, Ir) with CH_4, $[M(\eta^5\text{-}C_5H_4\{CH_2\}_nH)(PH_3)]$ with intra-Cp activation, and $[M(\eta^5\text{-}C_5H_5)(PH_2\{CH_2\}_nH)]$ by intra-P activation. The exothermicity decreases in the order inter > intra-P > intra-Cp with smaller differences as the ring size (n = 1,2) increases.[80]

Theoretical and experimental evidence was analysed for the existence of S_N2 transition states in the oxidative addition of iodomethane to $cis\text{-}[M(CO)_2I_2]^-$. Optimisation of transition state geometry and comparision of computed kinetic isotope effects with experimental data supports inversion at carbon in the transition state.[81]

The origin of the low quantum yields for C-H bond activation by $[M(\eta^5\text{-}C_5Me_5)(CO)_2]$, (M = Rh, Ir) has been investigated by picosecond transient absorption spectroscopy. Excited state molecules relax by non-dissociative excited states without CO loss in a process lasting 30 – 40 picoseconds.[82] Similarly $[Rh(HB\{pyrazolato)_3\})(CO)_2]$ activates cyclohexane and pentane at room temperature over the time period 1 – 500 nanoseconds.[83] Photochemical C-H activation of pentane, hexane, heptane, and *iso*-octane at room temperature by $[Rh(HB\{3,5\text{-dimethylpyrazolato})_3\})(CO)_2]$ was monitored with UV-visible and FT-infrared spectroscopic methods. At 458 nm a clean η^3- to η^2- conversion of the pyrazolylborate ligand occurs, while rapid CO dissociation occurs at 313 and 366 nm leading to efficient C-H bond activation.[84]

Photolysis of benzene solutions of $[Ir(H)_2(HB\{3,5\text{-dimethylpyrazolato})_3\})(\eta^2\text{-}$

$C_8H_{14})]$ in the presence of $P(OMe)_3$ liberates hydrogen and cyclooctene in producing $[Ir(H)Ph(HB\{3,5\text{-dimethyl-pyrazolyl})_3\})]$. The primary photoproduct is formed by alkene loss; use of $P(OCD_3)_3$ indicates that this is also activated for C-D bond breaking.[85] Intramolecular C-H activation occurs in the form of an η^2-ethene to vinyl hydride transformation; $[Ir(OC\{O\}Me)(P^iPr_3)_2(\eta^2\text{-}C_2H_4)]$ is photolysed to $[Ir(O_2CMe)H(CH{=}CH_2)(P^iPr_3)_2]$. Simple addition of phenylacetylene to the ethene complex yields the corresponding acetylide hydride.[86] A reversible photochemical *ortho*-metallation of a ketene compound and a thermal reaction which is formally a [1,3]-hydride shift and metallation are shown in *Scheme 7*. Detailed spectroscopic and kinetic evidence suports an enol intermediate in this transformation.[87]



Scheme 7

Supercritical fluid solutions of methane, ethane, and ethylene in CO_2(sc), Xe(sc), or CHF_3(sc) were photochemically reacted with $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$. Products were isolated from milligram scale reactions by rapid depressurisation of the solvent. The hydrocarbons were also used as supercritical solvents and in some cases the presence of traces of hydrogen improved the production of the alkyl hydride products.[88]

Sterically hindered isonitrile ligands such as 2,6-(dimethyl)phenylisonitrile react with the imido compounds $[Ir(\eta^5\text{-}C_5Me_5)(=N^tBu)]$ and $[Ir(\eta^5\text{-}C_5Me_5)(=N\{2,6\text{-diisopropylphenyl}\})]$ with a combined double coupling and metallation reaction. The product is shown in *Figure 5*, a mechanism was discussed.[89]

Treatment of $[IrCl(\eta^4\text{-}C_8H_{12})(P\{OPh\}_3)]$ with methyl lithium followed by

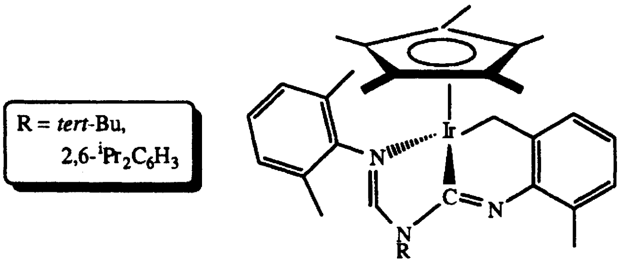


Figure 5

methanol produces a product derived from double *ortho*-metallation, [IrH(η^4-C_8H_{12})(P{OPh}{*m*-OC_6H_4}$_2$)]. The analogues derived from tri(2,4-di[*tert*-butyl]-phenyl)phosphite and tri(2-[*tert*-butyl]phenyl)phosphite were prepared from {[Ir(η^4-C_8H_{12})(μ-OMe)]$_2$} and both were structurally characterised.[90]

The tripod compound [Ir(H)$_2$(Et)({Ph_2PCH_2}$_3CH_3$)] breaks only the C-S bond of dinaphtho[2,1-*b*:1′,2′-*d*]thiophene even at 70°C.[91] The relative basicity and nucleophilicity of [Ir(η^5-C_5R_5)(PR_3)-(CO)], (R = H, Me), towards trifluoromethanesulfonic acid and iodomethane has been investigated by calorimetric studies coupled to rate studies using nmr measurements. In the nucleophilic reaction the rate for the pentamethylcyclopentadienyl compound is forty times greater than that of the cyclopentadienyl analogue. The rates of protonation were less different than expected probably due to the steric effect of the methyl groups.[92]

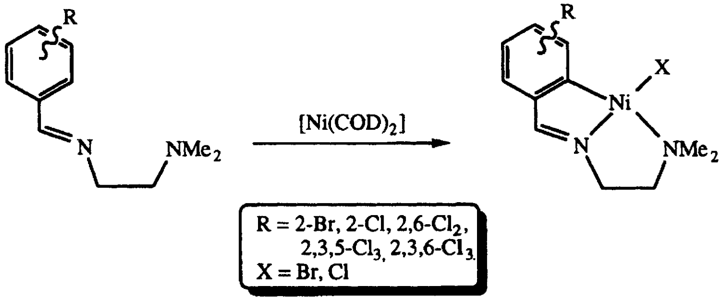
2.3 The Nickel Triad – Nickelocene reacts with 1-norbornyl lithium at -50°C producing an unstable 16e norbornyl, co-addition of a variety of alkynes yields stable alkyls [Ni(1-norbornyl)(η^5-C_5H_5)(RC≡CR)], (R = Me, $SiMe_3$, Ph, CH_2OMe, CH_2NMe_2, and CH_2OSiMe_3). Binuclear complexes {[Ni(1-norbornyl)-(η^5-C_5H_5)]$_2$(μ-η^2:η^2-RC≡CR)} and {[Ni(η^5-C_5H_5)-*Ni*-*Ni*]$_2$(μ-η^2:η^2-RC≡CR)} were also isolated.[93] Similarly {[Ni(η^3-C_3H_5)]$_2$(μ-Cl)$_2$} reacts to produce the unstable [Ni(1-norbornyl)(η^3-C_3H_5)] which can deposit metallic nickel. Use of [Ni(Cl)(η^3-C_3H_5)(PR_3)] yields stable [Ni(1-norbornyl)-(η^3-C_3H_5)(PR_3)], (R = Ph, Cy); nmr spectroscopy indicates that the allyl group is static in these compounds and their palladium analogues.[94] The nickelaperfluorocyclopentanes [Ni({CF_2}$_4$)(L)$_2$], (L = PPh_3, dppe, dppp, and bipy), were obtained as pale yellow solids from [$NiBr_2$(L)$_2$], sodium hydride, and tetrafluoroethylene in acetonitrile. They are very resistant to hydrogenation.[24]

Reaction of [Ni(L)$_2$(η^2-C_2H_4)] with 1,2-dibromocyclohexene yields the vinyl compounds [NiBr(2-bromocyclohexen-1-yl)(L)$_2$], (L_2 = (PPh_3)$_2$, (PEt_3)$_2$, dcpe), which can be converted to cyclohexyne compounds. Addition of iodomethane to the bis(dicyclohexylphosphino)ethane complex proceeds by a [1,4]-addition yielding [NiI(2-methylcyclohexen-1-yl)(dcpe)].[95]

A dark green air sensitive seven-membered ring nickelacycle [Ni(CH_2{2,2′-biphenyl}CH_2)-(bipy)] is formed by intramolecular C-C coupling when 1,2-

dihydro-1-magnesacyclobutabenzene reacts with [Ni(Cl)$_2$(bipy)].[96] A bulky alkyl {[Ni(CH{SiMe}$_2$)(PMe$_3$)(μ-Cl)]$_2$} prepared by a Grignard reaction was used as a synthon for a range of mononuclear alkyl compounds; one of them, [Ni(CH{SiMe}$_2$)(PMe$_3$)$_2$] was structurally characterised.[97]

Preferential oxidative addition of C-X bonds over ortho- C-H bonds leads to five membered ring nickelacycles (*Scheme 8*), the product with a *meta*-chloro substituent and metal bound chloride was structurally characterised.[98]



R = 2-Br, 2-Cl, 2,6-Cl$_2$, 2,3,5-Cl$_3$, 2,3,6-Cl$_3$
X = Br, Cl

Scheme 8

Stable nickel(II) aryl complexes have been prepared containing a N,O-chelating picolinate ligand. A range of simple aryl and phosphine auxiliary ligands were used and one example, [Ni(mesityl)-(PPh$_3$)(OC{O}-2-C$_5$H$_5$N-κ-*N,O*)] was examined by X-ray crystallography.[99]

Measurement of the electronic absorption spectra of [Ni(η^5-C$_9$H$_7$)(X)(PPh$_3$)], (X = Cl, Br, Me), and their 1-methylindenyl analogues together with EHMO calculations allowed orbital and relative energy assignments to be made.[100]

Detailed theoretical studies of Ni(II) and Pd(II) catalysed alternating polymerisation of ethylene and carbon monoxide examine the insertion steps in particular. Palladium catalysts have better selectivity but lower reactivity than those of nickel for which the rate determining step is migratory insertion.[101] The aptitude of cationic ethyl- and methylpalladium moieties to associate ethylene and undergo migratory insertion has been investigated. Ethylene co-ordinates strongly to naked [PdR]$^+$, nitrogen donors (NH$_3$) reduce the property and β-agostic structures become important in the ethyl species. The migratory insertion is endothermic for 12 electron [Pd(C$_2$H$_4$)R]$^+$ moieties and exothermic for 16 electron species with two nitrogen donor ligands. Computed barriers to insertion compare well with experimental values.[102] The kinetics of carbonyl insertion were measured for a wide range of terdentate nitrogen donor containing methylpalladium cations [Pd(Me)(NNN)]$^+$. Norbornadiene inserts into the acyls [Pd(COMe)(NNN)]$^+$ by [1,2]- addition giving [Pd(norbornyl-2-COMe)(NNN)]$^+$.[103] These authors also investigated the migratory insertion reaction of CO with methylpalladium(II) compounds containing bidentate α-diimine ligands; four X-ray crystal structures of reactants and acyl products were determined.[104] Ab initio calculations for the carbonylation of Pd(II) alkyls of mixed bidentate anionic ligands provide evidence for five co-ordinate intermediates and transition states and suggest that nitrogen donors are weakly bound in the transition state.[105]

Tetrabenzyltin and tetraethyltin were used to prepare $[Pd(Cl)(R)(\eta^4\text{-}C_8H_{12})]$. The X-ray structure of the benzyl compound suggests the ligand exerts a strong *trans-* effect. Carbonylation of that compound leads to decomposition; the methyl derivatives reacted cleanly. The ethyl compound was unstable decomposing to ethene and a transient hydridopalladium species. The final product of this decomposition was $\{[Pd(\eta^1{:}\eta^2\text{-}C_8H_{13})]_2(\mu\text{-}Cl)]_2\}$ plus metallic palladium, cyclooctadiene and $[Pd(Cl)_2(\eta^4\text{-}C_8H_{12})]$.[106]

Phenols and $(CF_3)_2CHOH$ react with $[Pd(Me)_2(Ph_2PCH_2CH_2NMe_2)]$ yielding phenoxy methylpalladium compounds where the phenoxy group is *trans* to the phosphine functionality.

Some of the pale orange solid products $[Pd(Me)(OAr)(Ph_2PCH_2CH_2NMe_2)]$ were structurally characterised. Monoacetylenes react the hexafluoroisopropoxy product by alcohol elimination producing an acetylide compound, no evidence for insertion into the Pd-O bond was found.[107]

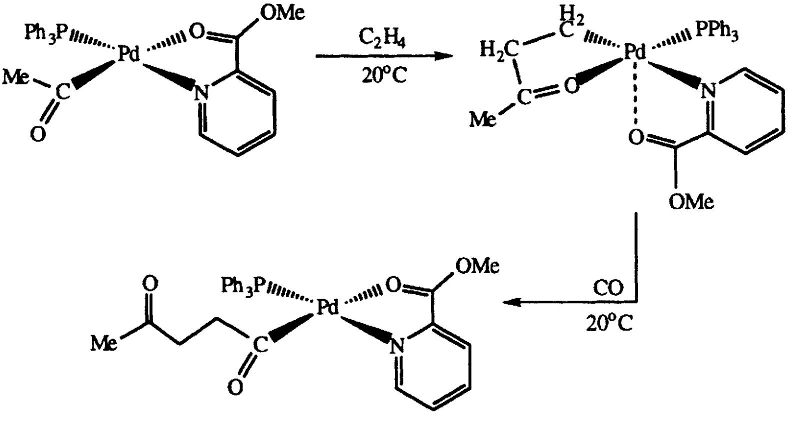
The four co-ordinate Pd(II) anion $[Pd(\{CH_2\}_4)(HB\{pyrazolyl)_3\text{-}\kappa\text{-}N,N')]^-$ reacts with water or halogens with oxidation to yield octahedral Pd(IV) compounds $[PdX(\{CH_2\}_4)(HB\{pyrazolyl)_3)]$, (X = OH, Cl, Br, and I). Evidence is also provided for methyl group transfer from Pd(IV) to Pd(II) in reactions of $[Pd(Me)_2(HB\{pyrazolyl)_3\text{-}\kappa\text{-}N,N')]^-$ with water.[108] The first mononuclear hydroxy-phenylpalladium complexes have been reported. Solid $[Pd(Ph)(OH)(L)_2]$ samples containing a bulky phosphine are stable but dimerise in solution to $\{[Pd(Ph)(L)]_2(\mu\text{-}OH)_2]\}$. The equilibrium set up was investigated by $^{31}P\{^1H\}$ nmr spectroscopy; addition of hexane precipitates the monomers which are colourless air stable solids. The hydroxy moiety resonates around δ 3.2 in the ^1H nmr spectrum of fresh monomer samples.[109]

Alkenyl sulfides $^nBuSCH_2CH_2CH{=}CH_2$ and $PhSCH_2CH_2CH{=}CH_2$ insert into the Pd – aryl bond of $[Pd(C_6F_5)Br(NCMe)_2]$ producing the bromo-bridged dimers $\{[Pd(RSCH_2CH_2CH\text{-}\{CH_2C_6F_5\}\text{-}\kappa\text{-}S,C)]_2(\mu\text{-}Br)_2\}$. Heating the product liberates methallylpentafluorobenzene and a polymeric palladium product.[110]

The product of ethylene insertion into a palladium – acyl bond has been isolated and structurally characterised. There is a weak axial interaction with the ester group of the auxiliary ligand with a metal to oxygen separation of 2.78Å and a value of 1733 cm^{-1} for ν_{CO} in its infrared spectrum (*Scheme 9*).[111] Carbonylation of $[Pd(Me)(OR)(NN)]$, (R = Ph, $CH\{CF_3\}_2$; NN = tmeda, bipy) produces acetic esters and metallic palladium. The yields were superior to those found for phosphorus ligated systems. Addition of dialkylamines yields amides and α-keto-amides. In contrast carbonylation of $[Pd(Me)(OMe)(NN)]$ allows stable $[Pd(CO_2Me)(Me)(NN)]$ and $[Pd(CO_2Me)_2(NN)]$ to be isolated.[112]

The bulky aryl complexes *trans*-$[Pd(mes^f)(Cl)(L)_2]$ and *trans*-$[Pd(mes^f)_2(L)_2]$ have been reported where L is PPh_3 or tetrahydrothiophene (tht) for the former and (tht) for the latter. Use of cyclo-octadiene or bipyridyl as auxiliary ligands permitted *cis-* products of each type to be isolated. The single crystal X-ray structures of *trans*-$[Pd(mes^f)_2(tht)_2]$ and *cis*-$[Pd(mes^f)_2(bipy)_2]$ were determined.

The barrier to rotation (Δ_G) about the Pd-P bond in *trans*-[Pd(mes^f)(Cl)(PPh$_3$)$_2$] was measured as 12.8 kcal mol^{-1}, due to steric butressing by the 2,4,6-tris(trifluoromethyl)phenyl group (mes^f).[113]



Scheme 9

Reaction of [Pd(phen)(Me)(OET$_2$)]$^+$ with *para-* substituted styrenes at low temperature gives the expected alkene cation which rearranges by β-methyl migration from metal to carbon yielding a *para*-1-methylbenzyl cationic product. The free energy of activation for the process correlates with the binding affinities of the styrenes.[114]

Key intermediates in the Heck reaction (arylation of methyl acrylate) have been observed by nmr spectroscopy using $^{13}CH_2{=}CHCO_2Me$, in particular [Pd(PR$_3$)$_2$(^{13}CH$_2$CH$_2$C{OMe}O-κ-*C,O*)]$^+$ was spectroscopically characterised.[115]

Thermolised [Pd]$^+$ produced by laser desorption of metallic palladium activates iodomethane by selective C-H bond cleavage. The Pd-C bond strength was reported to be stronger than 103 kcal mol^{-1} for [Pd(CH$_2$I)]$^+$, surprising as the values for [Pd(CH$_3$)]$^+$ and [Pd(CH$_2$)]$^+$ are 59±5 and 71±2 kcal mol^{-1} respectively. Optimised calculations suggest the ion has Pd-C and Pd-I bondlengths of 2.021Å and 2.581Å respectively and a Pd-C-I angle of 78.2°.[116] A subsequent paper corrects this report; the ion [Pd(CH$_2$I)]$^+$ is produced stepwise *via* [Pd(CH$_3$)]$^+$, and recalculation of the Pd-C bond energy gives 83 kcal mol^{-1}, which is still quite large.[117]

Cyclopalladation has proved as popular this year as previously; palladium acetate has been reacted with 2-phenylaniline and (R)-α-methylbenzylamine,[118] unsubstituted 2-phenylimidazoles required protection of the heterocyclic N-H group by acetylation prior to cyclometallation. Hydrochloric acid removes the protecting group accompanied by a small amount of Pd-C bond cleavage.[119] Monomeric and dimeric 2-phenylimidazoline complexes were reported by a second group,[120] cyclopalladated complexes with bidentate Schiff bases,[121] and α-amino acid complexes of cyclometallated 2-benzylpyridine and 2-

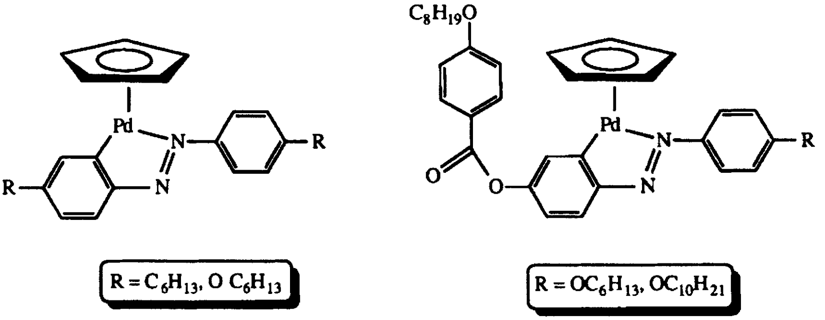


Figure 6

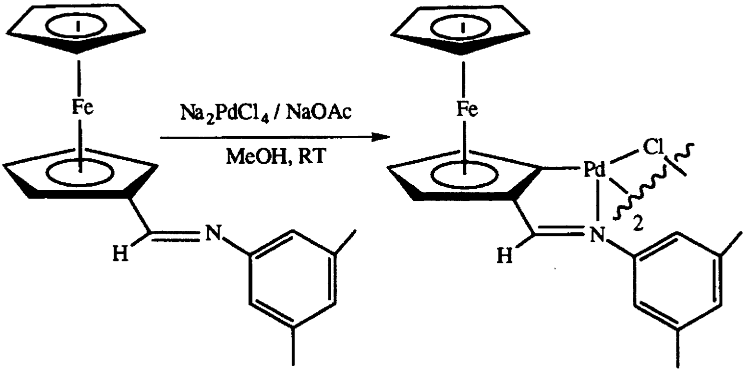
phenylpyridine have been described.[122] The X-ray crystal structure of [Pd(acac)(4-formyl-2-$CH_2N\{C_6H_{11}\}$-κ-*C,N*)] contains four independent molecules per asymmetric unit differing only by the conformation of the formyl group, only one species was present in solution.[123] Orthopalladated complexes of substituted benzo -imidazole, -oxazole, and -thiazole ligands were synthesised and subjected to one- and two- dimensional NMR spectroscopic analysis.[124] Palladium acetate forms five membered *endo* metallacycles with the N-benzylideneamines, 3,4-$(MeO)_2C_6H_3CH{=}N(CH_2)_nC_6H_4R$, (R = 2-OMe, n = 0; R = 4-OMe, n = 1,2), and a six membered metallacyle containing a Pd-O bond by reaction of the *ortho*-OMe bond when 2,4,6-$(MeO)_3C_6H_2.CH{=}NPh$ was used.[125]

Monomeric and dimeric orthometallated Pd(II) imine systems have been investigated as liquid crystals with bridging chiral carboxylate groups used in the dimers. Short alkyl chains in the carboxylate ligand such as acetates do not show liquid crystal properties but others gave nematic, smectic A, and smectic C phases.[126] Mesogenic complexes were examined by a second group (*Figure 6*); the esters exhibited nematic behaviour with high clearing temperatures up to 70°C and glassy states on cooling. The other compounds were isotropic fluids with no liquid crystal phases.[127]

Activation of a C-H bond of an imine functionalised ferrocene proceeds smoothly at room temperature by tetrachloropalladate dianion. The use of a 2,2′-di-*p*-tolyl spacer allowed dinuclear and dangling mononuclear analogues to be prepared (*Scheme 10*).[128]

Bimetallocycles containing both a C,N-metallated (dimethylamino)benzyl and a (dimethylamino)-methylnaphthyl ligand have been prepared and reacted with *tert*-butylhydroperoxide. Oxygen insertion preferentially occurs into the naphthyl derived Pd-C bond. Ring methyl substituents deactivate the insertion but do not reverse the preference. An oxidatively induced nucleophilic pathway is suggested.[129]

The cyclopalladation of 8-ethylquinoline by tetrachloropalladate dianion has been reinvestigated using a 1-d_1-ethyl group. The system is a model for general electrophilic activation of alkanes by Pd(II) and Pt(II) in protic media; the main



Scheme 10

conclusions were that there is net retention at C_α and a lack of isotopic scrambling. The kinetic isotope effect was greater than 11.[130] Chloropalladation of propargyl thioethers has been reported, producing a series of five membered thiapalladacycles $\{[Pd(RSCH\{R'\}C\{Cl\}=C\{Ph\}\text{-}\kappa\text{-}S,C)(\mu\text{-}Cl)]_2\}$, (R,R′ = Ph, Me, ^{i}Pr).[131]

Insertion of monoalkynes into the Pd-C(sp^3) bond of [Pd(norbornyl-2-phenyl)(methylisonicotinate-N)$_2$] liberates 1-acetylido-2-phenylnorbornanes *via* an η^2-alkyne intermediate. Reaction with disubstituted alkynes produces tricyclic products by insertion of the alkyne between the metal bound C(sp^3) and C(sp^2) centres.[132]

Linear unidimensional polymers $[\text{-}C{\equiv}CC_6H_4C{\equiv}C\{Ru(dppe)_2C{\equiv}CC_6H_4C{\equiv}C\{Pd\{P^nBu_3\}_2\text{-}]_n$ and zig-zag rigid-rods of $[\text{-}C{\equiv}CC_6H_4C{\equiv}C\{[C_5H_4]_2Fe\}C{\equiv}CC_6H_4C{\equiv}C\{M\{P^nBu_3\}_2\text{-}]_n$, (M = Ni, Pd), where the ferrocenyl ring rotations provide the zig-zag have been synthesised.[133]

Platinum groups bond at two types of 6-6 ring junctions in $\{[Pt(PPh_3)_2]_4C_{70}\}$.[134] Reaction of *cis*-[Pt(Cl)$_2$(DMSO)$_2$] with tetramethyltin produces *trans*-[PtCl(Me)(DMSO)$_2$]. While X-ray quality crystals could not be obtained, the crude reaction mixture deposited crystals after redissolution in dichloromethane. These were structurally characterised as a co-crystallite of the *trans*-product and [ClMe$_2$SnOSnMe$_2$Cl] in the form of an infinite chain polymer with Pt-Cl····Sn interactions.[135]

Some very rare examples of trigonal bipyramidal Pt(II) complexes with two axial alkyl groups have been prepared; the compounds [PtR(CHR′R″)(NN)(η^2-dimethylfumarate)], (R = Me, Bz; R′,R″ = H, NO$_2$, CO$_2$Me; NN = 2,9-dimethyl-1,10-phenanthroline), had their geometry assigned by nmr spectroscopic considerations.[136] The *cis*- dialkyls [Pt(CH$_2$GeMe$_3$)(L)$_2$], (L = PPh$_3$, PPh$_2$Me; L$_2$ = dppe, COD), and [Pt(CH$_2$SnMe$_3$)(L)$_2$] were reported. Thermolysis of [Pt(CH$_2$GeMe$_3$)(PPh$_3$)$_2$] in toluene caused β-alkyl migration subsequent to phosphine dissociation yielding [PtMe(CH$_2$Ge-{Me}$_2$CH$_2$GeMe$_3$)(PPh$_3$)$_2$]. The migration was more facile than for the silicon analogue. In line with the mechanism and kinetic analysis the bis(diphenylphosphino)ethane compound was inert under identical conditions.[137]

Phenylation of $[PtCl(SMe_2)_3]^+$ by BPh_4^- to yield *trans*-$[Pt(Ph)(Cl)(SMe_2)_2]^+$ occurs in the solid state (95°C) or in nitromethane solution (100°C). The solid state reaction produces monoclinic crystals which contain two crystallographically distinct complexes whereas the material obtained from hot benzene solutions of $[Pt(Cl)_2(SMe_2)_2]$ and Ph_3SnH is triclinic.[138] Carbonylation of $[Pt(Me)_2$-$(5,5'$-$^tBu_2$-2,2'-bipyridyl)] in the presence of $B(C_6F_5)_3$ produces [Pt(Me)(5,5'-$^tBu_2$-2,2'-bipyridyl)-(CO)][$BMe(C_6F_5)_3$], a useful reactive Pt(II) cation, by methyl abstraction.[139]

Reaction of $[Pt(CH_2Cl)_2(dppm)]$ with PPh_3 or PPh_2H in pyridine drives a methylene insertion reaction forming a metallaylide $[Pt(Ph_2PCH_2PCH_2)(CH_2Cl)(PR_3)]PF_6$ after anion exchange. When dichloromethane is used with PPh_2H a slow reaction occurs which yields a dicationic salt, $[Pt(Ph_2P\text{-}CH_2PCH_2)_2](PF_6)_2$, formally requiring a triple methylene insertion.[140]

Some new square planar Pt(II) cations containing a methyl group and an η^2-alkene in mutually *cis* positions were prepared by reaction of trimethyloxonium tetrafluoroborate on [Pt(phen)(η^2-dimethylfumarate)]. The alkene ligand in the product [PtMe(phen)(η^2-dimethylfumarate)]BF_4 reversibly dissociates in solution and can be replaced by ethylene, styrene, or propene. Only the latter compound shows coupling to ^{195}Pt in the ^1H nmr spectrum.[141]

The first examples of η^1-ketenyls with an ylide group $[MCl(\eta^3\text{-}CH_2C\{R\}CH_2)(C\{PPh_3\}{=}C{=}O)]$ and $[M(\eta^3\text{-}CH_2C\{R\}CH_2)(C\{PPh_3\}{=}C{=}O)(PPh_3)]BF_4$, (M = Pd, Pt), have been prepared and the cationic platinum compound was structurally characterised.[142] Treatment of $H[Pt(Cl)_3(\eta^2\text{-}C_4H_8)]$ formed *in situ* with $Me_3SiC{\equiv}CH$ or $Me_3SiC{\equiv}CSiMe_3$ in hot butanol yields the dinuclear platina-β-diketone $\{[Pt(C\{Me\}CO)_2H]_2(\mu\text{-}Cl)_2\}$. The X-ray structure reveals that the compound is all planar; the carbonyl groups resonate at δ228.1 in the $^{13}C\{^1H\}$ nmr spectrum, comparable with known acyl and carbene platinum compounds. The value of $^1J_{Pt\text{-}C}$ at 1457 Hz is larger than that usually found for acyls and carbenes by 300-500 Hz. The ethyl analogue was prepared from $Me_3C{\equiv}CSiMe_3$.[143]

The chemical shift anisotropy of sixteen platinum alkyls has been examined by solid state nmr spectroscopy. There is a strong dependence on the nature of the other ligands, chelating dienes cause very large anisotropies.[144]

Pressurisation of aqueous tetrachloroplatinic acid with ethylene at 800 psi over five days precipitates $\{[Pt(Et)(\eta^2\text{-}C_2H_4)]_2(\mu\text{-}Cl)_2\}$ which was structurally characterised. This compound is a useful synthon for, *inter alia* [Pt(Et)(Cl) (phen)], $[Pt(Cl)_2(Et)(\eta^2\text{-}C_2H_4)]^-$, $\{[Pt(Et)(CO)]_2(\mu\text{-}Cl)_2\}$, and $\{[Pt(COEt)(CO)]_2(\mu\text{-}Cl)_2\}$.[145] The kinetics of the insertion of phenylacetylene into the isomers of $[Pt(Me)(SiPh_3)(PMe_2Ph)_2]$ has been investigated. The *cis*-isomer converts over a period of hours to *cis*-$[Pt(Me)(C\{Ph\}{=}CHSiPh_3)(PMe_2Ph)_2]$ whereas the *trans*-isomer yields only *trans*-$[Pt(SiPh_3)\text{-}(C{\equiv}CPh)(PMe_2Ph)_2]$ after five days. The rate determining step is phosphine loss implying that the triphenylsilyl group exerts a stronger *trans*- effect than a methyl group or a phosphine.[146] A letter[147] and reply[148] disagree on the *trans*-labilising effect of a metallocycle C(sp^3) atom versus a non-metallocycle centre; Elding states there is no difference whereas van Eldik suggests that the metallocycle centre is four to five orders of magnitude better!

Reaction of 2,6-bis(diisopropylphosphino)mesitylene with $[Pt(Cl)_2(COD)]$ proceeds with C-H bond activation of the 1-methyl group. Further treatment with hydrogen chloride eliminates chloromethane producing the *ortho*-metallated product $[PtCl(2,6\text{-}{}^{i}Pr_2CH_2\text{-}3,5\text{-}Me_2\text{-}C_6H)]$, formally the C-C bond activation product of the initial reaction. The C-H bond activation is kinetically preferred but C-C bond breaking is the thermodynamic preference in this system.[149]

High pressures facilitate oxidative addition of iodomethane and iodoethane to $[Pt(Me)_2(bipy)]$; the kinetic data over 0-200 MPa supports an S_N2 attack on C_α, and an overall rate increase of 1000 fold is found at 200 MPa.[150]

Copper iodide catalysed coupling of $[PtI(PR_3)_2(C_6H_4\text{-}p\text{-}X)]$ and $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4\text{-}C{\equiv}CH)]$, (X = OMe, Me, H,Cl, CO_2Et), produced dinuclear products whose redox potentials were not influenced by the nature of X.[151] The heterodinuclear compounds $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4C\text{-}\{O\}PtX(PEt_3)_2]$, (X = Cl, Br, NCS) and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4C\{NR\}PtX(PEt_3)_2]$, (R = *p*-tolyl, *p*-anisolyl, *p*-nitrophenyl) have been prepared by insertion of CO and CNR into the appropriate metallated cyclopentadienyl complex.[152] The tetranuclear tetracations *sym*-$\{[Pt(dppe)(C{\equiv}C\text{-}p\text{-}C_5H_5N)M(dppe)]_2\}[OTf]_4$, (M = Pd, Pt), have been studied by FAB-MS; the parent ion for the all platinum salt is $\{[M][OTf]_2\}^{2+}$, whereas the mixed metal salt only shows $[PdH(dppp)(OTf)_2]^+$.[153]

The epimerisation of $[Pt(CHX\{SiMe_3\})(X)(R,R\text{-chiraphos})]$ has been followed; the major product is (*R*)- at C_α on preparation for all three halides, and the iodide compound epimerises rapidly, the bromide at room temperature over hours while the chloride requires refluxing chloroform. The proposed mechanism involves a carbene intermediate $[Pt(X)_2({=}CHSiMe_3)(R,R\text{-chiraphos})]$.[154]

The first examples of conjugated rigid-rod oligomers or polymers containing Pt-Pt bonds in the backbone are the insoluble yellow products $\{Cl[Pt_2(\mu\text{-}dppm)]C{\equiv}C\{Ar\}C{\equiv}C\}_n$, (n = 5, Ar = C_6H_4; n = 12, Ar = $C_6H_2Me_2$; n = 3, Ar = $C_6H_4C_6H_4$), prepared by reaction of the appropriate diacetylene with $[Pt_2Cl_2(\mu\text{-}dppm)_2]$.[155] Polymerisation *via* the backbone vinyl group has been realised for the vinyl bipyridyl $[Pt(Me)_2(5\text{-vinyl-}5'\text{-methyl-}2,2'\text{-bipyridyl})]$ which can also undergo oxidative addition with haloalkanes.[156] High dilution techniques were required to prepare the platinum polyacetylides $[Pt\{(Ph_2PC_5H_4)_2Fe\}(C{\equiv}C\text{-}o\text{-}C_6H_4C{\equiv}CC_6H_4\text{-}o\text{-}C{\equiv}C)]$ and $[Pt(PEt_3)_2]_2(\mu\text{-}\ 2,2',\text{-}6,6'\text{-tetra}\{\text{acetylenyl}\}C_6H_4C{\equiv}CC_6H_4)]$. Both compounds were structurally characterised and all the alkyne functions were essentially co-planar.[157] Infrared and Raman spectra of the rigid-rod polymers of the type $[Pt(P^nBu_3)_2(C{\equiv}C\{Ar\}C{\equiv}C)]_n$ and $[Pt(P^nBu_3)_2(C{\equiv}CC{\equiv}C)]_n$ show them to be centro-symmetric, with alternating unsaturation despite other evidence of conjugation, and with vibrations strongly coupled to electronic transitions of a delocalised backbone.[158] Organoplatinum dendrimers containing up to 28 platinum atoms have been prepared by extending the strategy of oxidatively adding 4,4′-bis(bromomethyl)-2,2′-bipyridine to $[Pt(Me)_2(4,4'\text{-bis}(\textit{tert}\text{-butyl})\text{-}2,2'\text{-bipyridyl})]$; subsequent reaction with $\{[Pt(Me)_2(\mu\text{-}SMe_2)]_2\}$ generates the next pair of metal centres.[159] Later work describes dendrimers with Pt(II) in inner generation layers and Pt(IV) in outer layers.[160] Reaction of $CH_2{=}C(CO_2Me)CH_2Cl$, $CH_2{=}CHC_6H_4$-3-CH_2Cl, or $CH_2{=}CHC(O)Cl$ with [Pt(Me)$_2$(4,4′-bis(*tert*-butyl)-2,2′-bipyridyl)] and its bipyridyl analogue proceeds by *trans*-oxidative addition, the [Pt(Me)$_2$(Cl)(vinyl′)(4,4′-bis(*tert*-butyl)-2,2′-bipyridyl)] product can be polymerised *via* the vinyl function using a free radical initiator such as AIBN.[161]

Cationic Pt(IV) complexes with alkyltin ligands such as [Pt(Me)$_2$(Sn{Me}$_2$X)(4,4′-bis(*tert*-butyl)-2,2′-bipyridyl)]BF_4 undergo rapid halide exchange at platinum but not at tin, for example Me_3SnCl or [PtCl(Me)$_2$(Sn{Me}$_2$Cl)(4,4′-bis(*tert*-butyl)-2,2′-bipyridyl)] can be used to exchange a bromo- or iodo-cation.[162]

[Pt(Me)$_3$(OTf)(4,4′-bis(*tert*-butyl)-2,2′-bipyridyl)] reacts with $NaBH_4$ producing the Pt(IV) hydridomethyl complex [Pt(Me)$_3$(H)(4,4′-bis(*tert*-butyl)-2,2′-bipyridyl)] which reacts further with acid to give {[Pt(Me)$_3$(4,4′-bis(*tert*-butyl)-2,2′-bipyridyl)]$_2$(μ-H)}OTf. Both preparations can be reversed by use of acid or base respectively.[163]

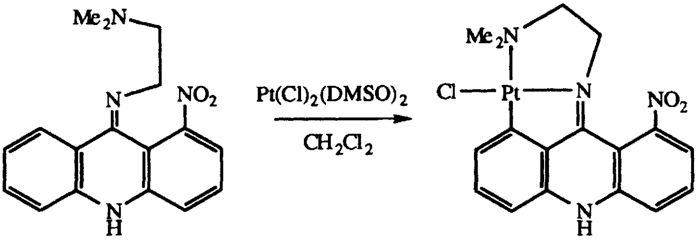
Some aqueous C-H activation chemistry by Pt(II) systems provides evidence for alkylhydrido-platinum(IV) species and for σ-alkane adducts. Protonolysis of [PtCl(Me)(tmeda)], [PtCl(CH$_2$Ph)-(tmeda)], [Pt(Me)$_2$(tmeda)], and [Pt(Me)(Cl)(PEt$_3$)$_2$] provides no spectroscopic evidence for a σ-alkane adduct; detailed kinetics and isotope effect studies were used to support the hypothesis.[164] Related aqueous chemistry of Pt(II) in acid solution is presented elsewhere.[165]

A fluxional process involving a switch of nitrogen donor ligand from pyridyl to pyrazolyl has been studied in *fac*-[Pt(Me)$_3$(3-pyrazolyl-2,2′-bipyridyl-κ-*N,N*)].[166]

The solid state structure of [PtH(Me)$_2$(HB{3,5-dimethylpyrazolyl}$_3$)] has been determined and a variety of Pt(IV) compounds were isolated from reaction of HCl, I_2, or MeI on K[Pt(R)$_2$(HB{3,5-dimethylpyrazolyl}$_3$)], (R = Me, Ph). The hydridomethyl compound does not eliminate methane in solution or in the solid state.[167] The tris(pyridin-2-yl)methanol ligand switches from bidentate in [Pt(R)$_2$(HOC{2-C_5H_4N}$_3$)], (R = Me,Ph), to tridentate on dissolution in wet acetone. The hydroxy cation product [Pt(R)$_2$(OH)(HOC{2-C_5H_4N}$_3$)]$^+$ (R = Ph) reacts further with dilute nitric acid to produce the structurally characterised [Pt(Ph)$_2$(OH$_2$)(HOC{2-C_5H_4N}$_3$)][NO$_3$]$_2$.[168]

Chlorinated N-benzylidenebenzylamines have been used to prepare cyclometallated Pt(II) and Pt(IV) by C-Cl and C-H bond activation.[169] Related compounds formed from N-(4-chlorophenyl)-α-benzoylbenzylideneamine have in vitro cytostatic activity. Screening against breast carcinoma and leukemic tumour cells revealed good activity; the presence of an acetate group on platinum allows binding and DNA modification.[170] The reaction of [Pt$_2$(Me)$_4$(μ-SMe$_2$)$_2$] with imines produces cyclometallated products with chelation of the least hindered *ortho*- C-H bond of 3,4-(dimethoxy)-N-benzylbenzylideneamine or 3-methyl-N-benzylbenzylideneamine. More bulky imines do not ortho-metallate.[171]

Co-ordination and *peri*- metallation of 1-nitro-9-[(2-aminoethyl)amino]acridines (*Scheme 11*) occurs with the ligand in the imino form. The anti-tumour activity of the free ligands may explain the reactivity with platinum; the toxicity



Scheme 11

of the metal compound and cationic derivatives is comparable to that of the free acridines.[172]

Some α-(bromo)amino acids have been platinated at the α- position by $[Pt(Me)_2(bipy)]$ in a trans-oxidative addition. The structure of $[Pt(Me)_2Br(CH\{CO_2Me\}NHC\{O\}Ph)(bipy)]$ was determined by X-ray crystallography.[173]

Bright yellow compounds which luminesce at *ca.* 650 nm when irradiated at 410 or 431 nm are obtained when [Pt(Me)$_2$(4,4′-bis(*tert*-butyl)-2,2′-bipyridyl)] is reacted with $(Ph_2SnS)_3$ or $(Me_2SnS)_3$. The products *cis*-[Pt(Me)$_2$(SSn{R}$_2$SSn{R}$_2$-κ-*Sn,S*)(4,4′-bis(*tert*-butyl)-2,2′-bipyridyl)] contain six membered rings and a mixed phenyl – methyl product was also prepared.[174]

3 Carbene and Carbyne Compounds of Groups 8, 9, and 10

The alkynoyl compounds $[Fe(\eta^5-C_5H_5)(C\{O\}C{\equiv}CR)(CO)_2]$, (R = Me, Ph, $SiMe_3$) were prepared by a mixed acid anhydride procedure using the acetylenic acid and N-methylmorpholine isobutylchloroformate with $[Fe(\eta^5-C_5H_5)(CO)_2]^-$, since the simple acetylenic acid chlorides did not provide the required products. Further reaction with $[(MeO)_2CH]^+$ gave $[Fe(\eta^5-C_5H_5)(CO)_2(=C\{OMe\}C{\equiv}CR)]^+$ which reacted with primary amines to yield the aminocarbenes $[Fe(\eta^5-C_5H_5)(CO)_2(=C\{NHR'\}C{\equiv}CR)]^+$ as syn/anti mixtures.[175] These cations were used as dienophiles in Diels-Alder reactions with cyclopentadiene.[176]

The carbene cations $[Fe(\eta^5-C_5Me_5)(CO)(PMe_3)(=C\{OMe\}Me)]^+$, $[Fe(\eta^5-C_5Me_5)(dppe)-(=CHMe)]^+$, and $[Fe(\eta^5-C_5Me_5)(dppe)(=C\{OMe\}Me)]^+$ were prepared; the ethylidene compound was structurally characterised. Each cation can be deprotonated with KO^{t}Bu at -78°C forming a seventeen electron radical cation $[Fe(\eta^5-C_5Me_5)(L)_2(C\{X\}=CH_2)]^{+\bullet}$ (X = H, OMe). Chemical preparation of these species occurs with use of ferrocenium hexafluorophosphate, and is followed by a stereoselective coupling reaction to yield dicationic $[Fe(\eta^5-C_5Me_5)(L)_2(=C\{X\}CH_2CH_2C\{X\}=)Fe-(\eta^5-C_5Me_5)(L)_2]^{2+}$. The stereoselectivity depends on the auxiliary ligands but the diastereomers were easily separable.[177] Reaction of *trans*-$[FeH(Cl)(dppe)_2]$ with methylpropargylate in the presence of $TlBF_4$ leads to a cyclic vinyl complex [Fe(dppe)$_2$(=CHCH=C{OMe}O-κ-*C,O*)]$^+$; the ring is planar and the carbene carbon is located at δ239.8 ($J_{P\text{-}C}$ = 24.4 Hz).[178] Deprotonation of the vinyl alcohol cation $[Fe(\eta^5-C_5H_5)(CO)_2(\eta^2-$

$CH_2=CHCH_2OH)]^+$ by triethylamine proceeds with carbonyl insertion producing $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(\eta^2{:}\eta^1\text{-}CH_2=CHCH_2OC\{O\})]$ which can be methylated by $[Me_3O]BF_4$ to the alkene(carbene) product $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(=C\{OMe\}OCH_2\text{-}\eta^2\text{-}CH=CH_2)]BF_4$.[179] The crystallographic determination of the structure of the latter can be down-loaded as 3D structure on the Internet (pdb format).[180] The reactions of the cation with nucleophiles are described in detail elsewhere[181] and in a microreview.[182]

Bimetallic carbene intermediates may be generated when $[W(\eta^5\text{-}C_5H_5)(C\equiv CR)(NO)(CO)]^-$ reacts with $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(thf)]^+$ with transfer of the σ-acetylide (R = Ph, *p*-tolyl, ^tBu, $SiMe_3$) from tungsten to iron yielding $\{[Fe(\eta^5\text{-}C_5H_5)(CO)_2](\mu\text{-}\eta^1{:}\eta^2\text{-}C\equiv CR)[W(\eta^5\text{-}C_5H_5)(NO)(CO)]\}$. The phenylacetylide product was structurally characterised.[183]

Preparation of a number of unusual ruthenacyclobutenes is illustrated in *Scheme 12*. An X-ray single crystal structure of the thiocarbonyl compound was determined.[184]

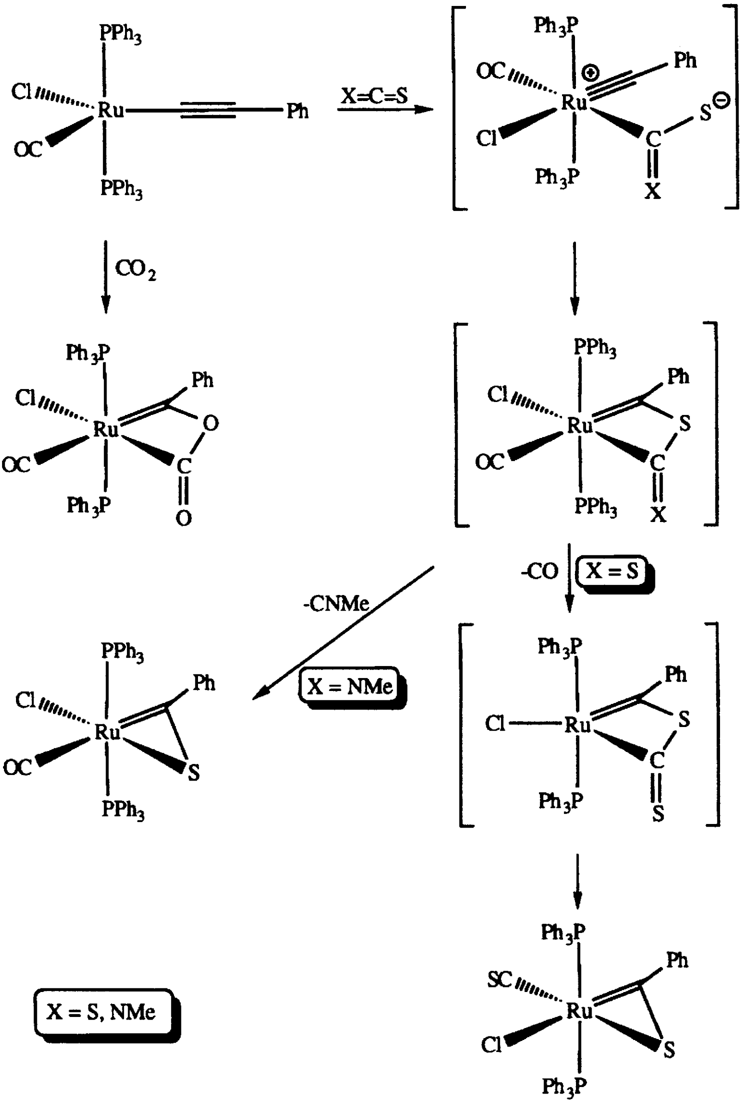
The X-ray single crystal structures of an oxacyclopentylidene and an oxacyclohexylidene compound have been determined; in $[Ru(\eta^5\text{-}C_5H_5)(dppe)(=C\{CH_2\}_nO)]BF_4$, (n = 3, 4), the carbene ligand is vertical with the oxygen atom located downwards away from the cyclopentadienyl ligand.[185]

Diazoalkanes $RCH=N_2$ react with $[Ru(Cl)_2(PPh_3)_3]$ at -78°C to yield neutral carbenes $[Ru(Cl)_2(PPh_3)_2(=CHR)]$, (R = Me, Et, $p\text{-}C_6H_4X$); the compounds were tested for alkene metathesis properties. Tricyclohexylphosphine analogues prepared by simple exchange were particularly efficient ROMP catalysts. The effect of various electron withdrawing groups (X) on the rate was found to be small.[186] Both $[Ru(Cl)_2(PCy_3)_2(=CHPh)]$ and $[Ru(Cl)_2(PCy_3)_2(=CHCH=CPh_2)]$ induce living polymerisation of functionalised norbornenes and 7-oxanorbornenes under phase transfer conditions in dichloromethane – water.[187] $[RuCl(PPh_3)(=C=CHPh)(HB\{pyrazolyl\}_3)]$ is a catalytic precursor for the dimerisation of mono-substituted acetylenes to 1,4- and 1,2- disubstituted butenynes.[188]

The structurally determined *cis*-$[Ru(Cl)(Pr^i_2PCH_2CH_2OMe\text{-}\kappa^2\text{-}P,O)_2(=C=CHPh)]OTf$ deprotonates on basic alumina to give a mixture of the *cis*- and *trans*-acetylides, these can react with carbon monoxide with release of both ether ligands from the co-ordination sphere producing a *cis*- and *trans*-mixture of $Ru(Cl)(CO)_2(Pr^i_2PCH_2CH_2OMe\text{-}\kappa^1\text{-}P)_2(C\equiv CPh)]$. An allenylidene cation *cis*-$[Ru(Cl)(Pr^i_2PCH_2CH_2OMe\text{-}\kappa^2\text{-}P,O)_2(=C=C=CHPh)]OTf$ was also crystallographically characterised.[189]

Treatment of $[RuCl(\eta^5\text{-}C_5Me_5)(PPh_3)_2]$ with phenylacetylene under the standard conditions in methanol produces the expected vinylidene cation $[Ru(\eta^5\text{-}C_5Me_5)(PPh_3)_2(=C=CHR)]^+$ but also the neutral $[RuCl(\eta^5\text{-}C_5Me_5)(PPh_3)(=C=CHR)]$. The latter is the unique product when benzene is used as the solvent and it undergoes another novel reaction; treatment with sodium methoxide in the presence of acetonitrile, carbon monoxide, tertiary phosphines or phosphites causes [1,3]-elimination of hydrogen chloride. The sole products are $[Ru(C\equiv CPh)(\eta^5\text{-}C_5Me_5)(PPh_3)(L)]$.[190]

The single crystal X-ray structure of $[M(\eta^5\text{-}C_9H_7)(PPh_3)_2(=C=C=CPh_2)]PF_6$,



Scheme 12

prepared from $HC\equiv CCPh_2OH$ and the appropriate metal chloride, has been determined for both the ruthenium and osmium indenyl compounds. The use of $HC\equiv CCPh(Me)OH$ produces a mixture of the allenylidene $[M(\eta^5\text{-}C_9H_7)(PPh_3)_2(=C=C=CPh\{Me\})]PF_6$ and a vinylidene $[M(\eta^5\text{-}C_9H_7)(PPh_3)_2(=C=CHC\{Ph\}=CH_2)]PF_6$, which on treatment with base produces the single acetylide $[M(\eta^5\text{-}C_9H_7)(PPh_3)_2(C\equiv CC\{Ph\}=CH_2)]$.[191]

Cyclopentadiene and $[RuH(Cl)(CO)(P^iPr_3)_2]$ react in methanol producing $[RuH(\eta^5\text{-}C_5H_5)\text{-}(P^iPr_3)(CO)]$ which can be protonated with tetrafluoroboric acid in acetone. The orange solid product $[Ru(\eta^5\text{-}C_5H_5)(P^iPr_3)(CO)(Me_2CO)]BF_4$ is a useful synthon which can be reacted with alkynols to produce allenylidene cations. $[Ru(\eta^5\text{-}C_5H_5)(P^iPr_3)(CO)(=C=C=CPh_2)]BF_4$ reacts with water producing an isolable hydroxycarbene which yields the acylvinyl product $[Ru(\eta^5\text{-}C_5H_5)(P^iPr_3)(CO)(C\{O\}CH=CPh_2)]$. Protonation of this material regenerates the cationic hydroxycarbene. The alkynol $HC\equiv CCH_2OH$ reacts to produce $[Ru(\eta^5\text{-}C_5H_5)(P^iPr_3)(CO)(=C\{OH\}CH=CH_2)]BF_4$ directly which can also be reversibly converted into a neutral acylvinyl complex.[192] Purple $[Ru(\eta^5\text{-}C_5Me_5)(dppe)(=C=C=CHCH=C=)Ru(\eta^5\text{-}C_5Me_5)(dppe)][BF_4]_2$ can be converted to tautomeric deep blue $[Ru(\eta^5\text{-}C_5Me_5)(dppe)(=C=C=CHC\equiv C)Ru(\eta^5\text{-}C_5Me_5)\text{-}(dppe)][BF_4]$.[193]

Treatment of $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(thf)]^+$ with diacetylene in the presence of diphenylamine or N-methylpyrrole produces $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(=C=C=C\{Me\}NPh_2)]^+$ and $[Ru(\eta^5\text{-}C_5H_5)\text{-}(PPh_3)_2(=C=C=C\{Me\}\text{-2-pyrrole})]^+$ respectively, the former was structurally characterised. The reaction consists of trapping an intermediate butatrienylidene cation formed by a [1,4]- shift rather than the [1,2]- shift found for alkynes which would lead to ethynylvinylidene products in this case.[194]

An unusual C-O bond cleavage and alcohol elimination from a dangling acetal functionality allowed the thermal conversion of $[Ru(\eta^5\text{-}C_5H_5)(NCMe)_2(PPh_2\text{-2-}\{(RO)_2CH\}C_6H_4)]^+$ to the cyclic carbene $[Ru(\eta^5\text{-}C_5H_5)(NCMe)(=C\{OR\}PPh_2C_6H_4\text{-2-}PPh_2\text{-}\kappa\text{-}P,C)]^+$, (R = Me, Et).[195]

Reaction of $[Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-1-methallyl})(PPh_3)]$ with methylpropargylate followed by hydrochloric acid produces $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)(=C=CHCO_2Me)]$ which can be converted to the (2-4-η)-butadienyl complex $[Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}CH_2CHC=CHCO_2Me)(PPh_3)]$ using copper iodide and tetra(allyl)tin. A (3-5-η)-pentatrienyl complex was prepared by a related reaction.[196]

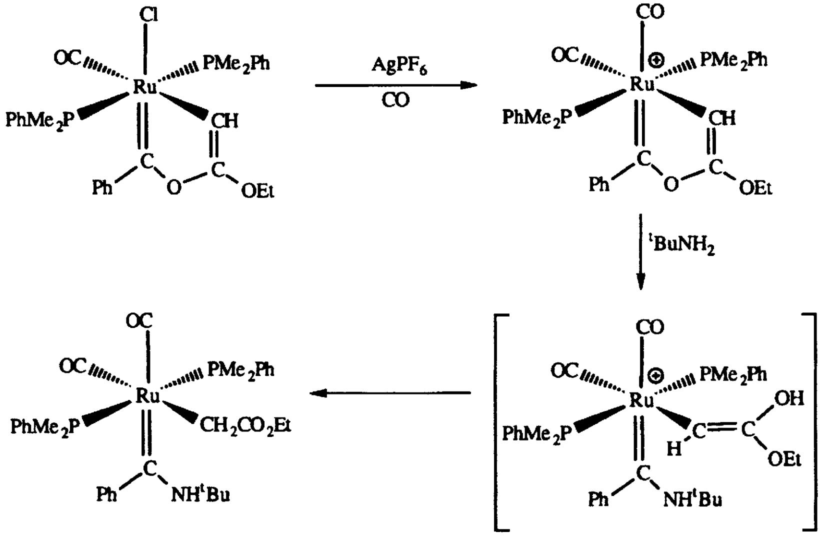
The dinuclear bis(allenylidene) cations $\{[Ru(PPh_3)_2(=C=C=C\{Ar\}_2)]_2(\mu\text{-}Cl)_3\}PF_6$, (Ar = Ph, $p\text{-}ClC_6H_4$, $p\text{-}FC_6H_4$), can be converted to mononuclear $[RuCl(PPh_3)_2(=C=C=C\{Ar\}_2)]PF_6$ with phosphine exchange if required. While a number of these cations can be made directly from the appropriate $[Ru(Cl)_2(L)_4]$ precursor this provides another entry in cases when this precursor is unknown.[197]

Long chain conjugated bis(allenylidene) dimers of the type $[RuCl(dppe)\text{-}(=C=C=CH\{X\}C=C=C=RuCl(dppe)][PF_6]_2$ where the spacer is a benzene or thiophene ring have been examined by cyclic voltammetry. The metal centres interact with the thiophene conjugated compound being the most efficient.[198]

Five co-ordinate 16 electron Ru(II) carbene and vinylidene complexes are obtained in the reaction of $[Ru(H)_2(Cl)_2(P^iPr_3)_2]$ with phenylacetylene in dichloromethane. $[Ru(Cl)_2(P^iPr_3)_2(=C=CHPh)]$ is the major product and the minor product $[Ru(Cl)_2(P^iPr_3)_2(=CHCH_2Ph)]$ was structurally characterised.[199]

Molecular hydrogen compounds $[RuH(H_2)(PCy_3)_2(X\text{-2-pyridyl-}\kappa\text{-}X,N)]$ and the 8-X-quinoline analogue (X = O, NH), reacted with (trimethylsilyl)ethylene to produce isolable (hydrido)vinylidenes in the pyridyl series but a stable product was only obtained in the quinoline series for the oxygen chelate.[200]

The neutral ruthenafurans in *Scheme 13* are not nucleophilic, however their cationic derivatives are reactive towards primary amines. The product was crystallographically characterised.[201]



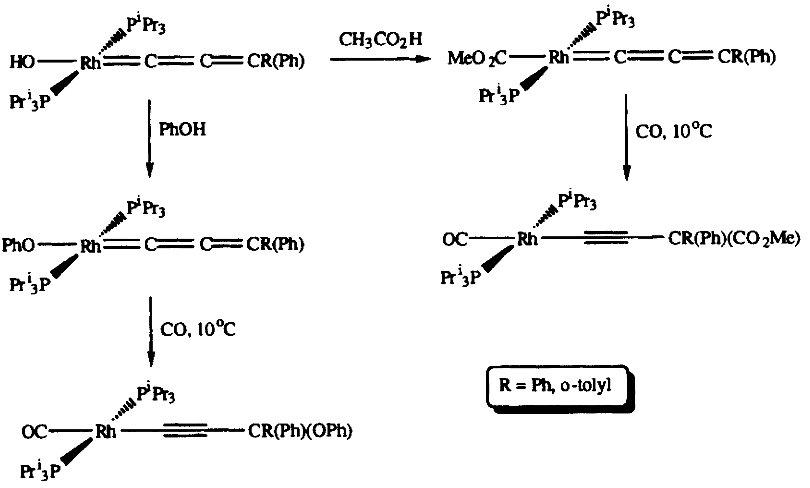
Scheme 13

The electron-rich alkene bis[1,2-bis(methylamino)phenyl]ethylene reacts as a carbene source towards $[Ru(\eta^6\text{-arene})(Cl)_2]_2$, (arene = cymene, mesitylene, hexamethylbenzene), yielding $[Ru(\eta^6\text{-arene})(Cl)_2(=CN\{Me\}C_6H_4N\{Me\})]$. $[Ru(Cl)_2(=CN\{Me\}C_6H_4N\{Me\})_3]$ was also prepared but was unable to catalyse the transformation of (Z)-3-methylpent-2-en-4-yn-1-ol to 2,3-dimethylfuran whereas the arene compounds were all excellent catalysts for this transformation.[202]

The first indenylosmium half-sandwich compounds have been described including a number of alkynyl, vinylidene, and cyclic carbene compounds. ^1H and $^{13}C\{^1H\}$ nmr data were supplied.[203]

There are few reported examples of vinylidenecobalt compounds, the η^2-alkyne form usually being the stable tautomer. Reaction of $[Co(\eta^5\text{-}C_5H_4\,CH_2CH_2P^tBu_2\text{-}\kappa^{5,1}\text{-}C,P)(\eta^2\text{-}C_2H_4)]$, which contains a chelating phosphine chain attached to the cyclopentadienyl group with acetylene produces $[Co(\eta^5\text{-}C_5H_4CH_2CH_2P^tBu_2\text{-}\kappa^{5,1}\text{-}C,P)(=C=CH_2)]$. The α-carbon appears as a sharp resonance at δ303.7 in the $^{13}C\{^1H\}$ nmr spectrum. In contrast the corresponding resonance for $[Co(\eta^5\text{-}C_5H_4CH_2CH_2P^tBu_2\text{-}\kappa^{5,1}\text{-}C,P)(=C=CH^tBu)]$ has a half-height width of 100 Hz at δ302.7. This compound was prepared from *tert*-butylacetylene by sodium amalgam reduction of $[CoCl(\eta^5\text{-}C_5H_4CH_2CH_2P^tBu_2\text{-}\kappa^{5,1}\text{-}C,P)]$.[204]

Generation of γ-functionalised alkynyl ligands by migratory insertion of allenylidene ligands into a rhodium-aryloxide bond has been demonstrated (*Scheme 14*).[205]



Scheme 14

Carbon-carbon and carbon-phosphorus coupling has been demonstrated from reactions of $[RhCl(P^iPr_3)_2(=C=C=CPh_2)]$; addition of vinylmagnesium bromide yields the [3-5-η]-pentatrienyl compound $[Rh(P^iPr_3)_2(\eta^3\text{-}CH_2CHC=C=CPh_2)]$ which reacted further with carbon monoxide to produce an η^1-pentatrienyl $[Rh(P^iPr_3)_2(CO)(C\{CH=CH_2\}=C=CPh_2)]$ which was structurally characterised. The allenylidene reacted with phenylacetylene to yield the structurally characterised unsaturated ylide $[RhCl(P^iPr_3)(\eta^3\text{-}CH\{P^iPr_3\}C\{Ph\}C=C=CPh_2)]$, which liberates the free butatrienylylide on treatment with carbon monoxide.[206]

Chiral carbenes generated from deprotonation of chiral imidazolium salts were complexed to a rhodium centre in $[RhCl(\eta^4\text{-}C_8H_{12})(=CN\{(R)\text{-}CHMe(R)\}CH=CHN\{(R)\text{-}CHMe(R)\})$, (R = phenyl, naphthyl). The compound acts as a chiral catalyst for the hydrosilylation of benzophenone with Ph_2SiH_2; ninety turnovers gave a product of 32% e.e. while at nine hundered turnovers the enantiomeric excess was 26%.[207] A full report and X-ray crystal structure of the catalyst (R = cyclohexyl) and $[Ru(\eta^6\text{-}cymene)(Cl)_2(=CN\{(R)CHMe(R)\}\text{-}CH=CHN\{(R)\text{-}CHMe(R)\})]$ has appeared.[208]

Evidence of reversible α-H migration has been found in the C-H activation of methyl and cyclic ethers. The neutral carbene complexes $[IrH(\eta^5\text{-}C_5Me_5)(PMe_3)(=CH\{OR\})]$, (R = Me, ^{t}Bu), and $[IrH(\eta^5\text{-}C_5Me_5)(PMe_3)(=C\{CH_2\}_3O)]$ were isolated from reaction of $ROCH_3$ and tetrahydrofuran respectively with $[IrMe(OTf)(\eta^5\text{-}C_5Me_5)(PMe_3)]$.[209]

It is this reviewer's sad last entry to record the passing of the father of transition metal alkyl chemistry; Professor Sir Geoffrey Wilkinson was an inspiring man and chemist – his philosophy that chemistry was best done rather than talked about, inspired all of his co-workers and continues to be valid advice for any young chemist who values peer respect.

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13

Hydrocarbon Transition Metal π-Complexes other than η-C_5H_5 and η-Arene Complexes

BY K.R. FLOWER

1 Introduction

This survey of the 1996 literature relating to metal π-hydrocarbon complexes of the transition elements other than η-C_5H_5 and η-arene complexes is similar in nature to previous reports.[1] This chapter is divided into the following sub sections dealing with: reviews; complexes derived from allyls and monoalkenes; unconjugated alkenes; conjugated alkenes; acyclic alkenes; alkynes; and polymetallic complexes.

2 Reviews

The following specialist reviews have appeared on the use of π-hydrocarbon complexes in organic synthesis: in particular, dealing with the reactivity of π-allyl;[2,3] diene iron tricarbonyl complexes;[4] transition metal catalysed carbocyclisation reactions;[5] transition metal catalysed cycloadditions;[6] the reactivity of carbene complexes with alkenes and alkynes[7] as well as unsaturated metallacyclic carbene complexes;[8] ruthenium catalysed isomerisation and reactivity of alkynes[9] and the reactivity of titanocene and zirconocene alkyne complexes.[10] The use of palladium compounds for the formation of carbon-carbon bonds[11] and the hydrogenolysis of allylic and propargylic compounds have also been reviewed.[12] The reactivity and fluxionality of dimeric complexes bridged by four electron donor hydrocarbons has been described.[13] Reviews on the recent advances in the chemistry of π-organochromium complexes;[14] transition metal complexes of the fullerenes;[15] the use of bis (alkynyl)titanocenes as chelating ligands for Cu(I)[16] and the chemistry of cyclobutyne and cyclobutenyl ligands in metal cluster complexes have appeared.[17] A report discussing highly stereoselective and regioselective reactions of alkyne-$Co_2(CO)_6$ complexes has appeared.[18] Reviews dealing with: halocarbonyl complexes of molybdenum(II) and tungsten(II);[19] open shell organometallics as a bridge between Werner-type and low valent organometallic complexes[20] and the organometallic chemistry of CO_2[21] have appeared and all contain material of interest.

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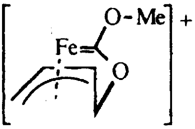
3 Allyl Complexes and Complexes Derived from Monoalkenes

3.1 Cr, Mo and W – Reaction of [Mo(2,6-lutidine)$_2$] with allyl chloride afforded [Mo(2,6-lutidine)(η^3-C_3H_5)Cl]$_2$ which has been structurally characterised and its reactivity investigated.[22] A series of substituted Mo allyl compounds containing hydrotris(1-pyrazolyl)borate were prepared by t-butyldimethylsilylchloride promoted oxidative addition of unsaturated aldehydes, cyclic and acyclic ketones to [Mo(CO)$_3$(dmf)$_3$] followed by ligand metathesis with potassium hydrotris(pyrazolyl)borate.[23] Conversion of [TpMo(CO)$_2$(η^3-C_3H_5)] to [TpMo(CO)(NO)(η^3-C_3H_5)][BF$_4$] proceeds smoothly with [NO][BF$_4$]; structural characterisation of [TpMo(CO)(NO)(η^3-C_3H_5)][B{C_6H_3-3,5-(CF_3)$_2$}] showed noticeable η^3 to η^2 distortion of the allyl ligand.[24] The stereochemistry of some Mo(II) tris(pyrazolyl)borate allyl complexes has been investigated.[25] Treatment of the compound [MoCl(CO)$_2${η^3-$CH_2C(COCl)C{=}CH_2$}(phen)] with RSH (R = Et, ^{n}Pr, ^{i}Pr, ^{n}Bu or ^{i}Bu) yielded [MoCl(CO)$_2${η^3-$CH_2C(COSR)C{=}CH_2$}(phen)].[26] The molecular structure of [Mo(O_2CCF_3)(η^3-C_3H_5)(1,10-phen)(CO)$_2$] has been reported.[27] A series of Mo allyl complexes of the type [Mo(CO)$_2$(η^3-C_6H_8R)Cp] were prepared by nucleophilic attack of zinc reagents on the cyclohexadiene ligand in the cationic molybdenum complexes [Mo(CO)$_2$(η^4-C_6H_8)Cp]$^+$; the R group was then subject to further modification.[28] A collection of η^3-γ-lactonyl complexes of molybdenum were prepared and subjected to ligand-based modification reactions.[29] Treatment of the complex [Mo(σ:η^2-CH_2C_2Me)(η^2-MeC_2Me)Cp] with $CF_3C_2CF_3$ led to the preparation of an η^3:η^4-ligated bicyclo[4.3.0]nonyl ring, formed by the cocyclisation of two $CF_3C_2CF_3$, MeC_2Me and the prop-2-ynyl fragment.[30] The cationic complexes [M(CO)$_2$(η^4-C_5H_4O){HB(Pz)$_3$}][PF$_6$] and [MBr(CO)$_2$(bipy)(η^4-C_5H_4O)][PF$_6$] (M = Mo or W) have been reacted with carbon, nitrogen, phosphorus and sulfur based nucleophiles and shown to yield η^3-cyclopentenoyl complexes.[31] Theoretical calculations on the d^2-W(NR$_2$) fragment and its complexation properties to alkenes has been investigated.[32] The *bis*(alkene) complexes [W(CO)$_4$(η^2-alkene)] (alkene = 1-pentene, 1, 2 or 3-hexene, 1-heptene, 1-octene, 1-decene, cyclopentene, cyclohexene, cycloheptene or cyclooctene) have been synthesised, spectroscopically characterised and the barriers of alkene rotation determined by VT ^{1}H NMR spectroscopy.[33] Reaction of [WH(CO)$_3$Cp] with $CH_2{=}CHCH(OEt)_2$ and HOTf affords [WH(η^2-$CH_3CH{=}CHOEt$)(CO)$_3$Cp][OTf] which has been structurally characterised.[34] Treatment of [WCl$_2$(O)(PX$_3$)] {PX$_3$ = P(OMe)$_3$ or PMePh$_2$} with 3,3-diphenylcyclopropene afforded the η^2-alkene adducts [WCl$_2$(O)(PX$_3$)(η^2-diphenylcyclopropene)]:[35] the molecular structure of the analogous complex [WCl$_2$(O)(PPh$_2$Me)(η^2-diphenylcyclopropene)] was reported elsewhere.[36] The complexes [W(OC_6H_3Ph-C_6H_4)$_2$L(η^2-C_2H_4)] (OC_6H_3Ph-C_6H_4 = cyclometallated 2,6-diphenylphenoxide; L = PMe$_2$Ph, PMePh$_2$) were prepared by bubbling ethene through a solution of the *bis*(phosphine) precursor [W(OC_6H_3Ph-C_6H_4)$_2$L$_2$]. The *bis*(ethene) complex also reacts with the α-alkenes $RCH{=}CH_2$ (R = Ph, SiMe$_3$, CF$_3$) to form equilibrium mixtures of [W(OC_6H_3Ph-C_6H_4)$_2$L(η^2-C_2H_4)] and [W(OC_6H_3Ph-C_6H_4)$_2$L(η^2-$RCH{=}CH_2$)] which have been studied by NMR spectroscopy.[37] Treatment of Na[W(CO)$_3$Cp] with 2-methylene-4-phenyl-3-butyn-1-yl tosylate and Me$_3$NO afforded the π-allyl complex [W(CO)$_2${η^3-2-(phenylethynl)allyl}Cp] and subsequent protonation afforded a trimethylenemethane complex.[38] Ring slippage of the indenyl moiety in [(η^5-ind)M(CO)$_2$L$_2$][BF$_4$] (M = Mo or W; L = NCMe or dmf) on treatment with excess L afforded [(η^3-ind)M(CO)$_2$L$_3$][BF$_4$].[39]

3.2 Fe, Ru and Os – The gas-phase chemistry of simple [Fe(alkene)]$^+$ complexes with CH$_3$X (X = OH, F, Cl, Br, I) has been investigated by Fourier-transform cyclotron mass spectrometry.[40] The molecular structure of [Fe(CO)$_4$-(C$_{14}$H$_{17}$NO$_4$S)] {C$_{14}$H$_{17}$NO$_4$S = (*R*)-5-isopropoxy-1-(toluene-4-sulfonyl)-1,5-dihydropyrrol-2-one} has been determined by a single crystal X-ray diffraction study.[41] The [Fe(CO)$_4$(η^3-allyl)]$^+$ fragment has been reacted with a variety of nucleophilic reagents yielding: γ-substituted alkenylsulfones;[42] 6-oxoenolates;[43] and enantiomerically enriched 1,6-dicarbonyl compounds that have retained the *E* configuration about their double bond.[44] The exocyclic allylcarbene complex (1) react with a series of nucleophiles to afford for example diene complexes of the type [Fe(CO)$_4$(η^4-diene)].[45] In a mechanistic study on the thermally [Fe(CO)$_5$] mediated insertion of CO into vinylcyclopropanes the formation of hydridoallyl iron complexes were observed.[46] A series of unsaturated ether chelate complexes of the type [Ru{η^5:η^2-C$_5$Me$_4$ CH$_2$O(CH$_2$)$_n$CH=CHR^{1}R^2}(CO)$_2$] (R^1 = R^2 = H, n = 1 or 2; R^1 = H, R^2 = Me, n = 1; R^1 = Me, R^2 = H, n = 1) were prepared by heating [Ru{η^5-C$_5$Me$_4$CH$_2$O(CH$_2$)$_n$CH=CHR^{1}R^2} (CO)$_2$Cl] in an appropriate alcohol with subsequent halide extraction by Ag[BF$_4$].[47] Selective O alkylation of the carbon bound enolate complexes [Ru (CO){η^2-PPh$_2$C$_6$H$_4$-*o*-C(O)CHR}Cp] (R = H or Me) with MeOSO$_2$CF$_3$ afforded the methylenol ether complexes [Ru(CO){η^1:η^2-PPh$_2$C$_6$H$_4$-*o*-C(OMe)CHR}Cp][SO$_3$CF$_3$] which are ligated to the metal through the phosphorus and the carbon–carbon double bond.[48] A series of alkene complexes of the type [Ru(CO)$_2$(η^2-alkene)(η^5-7,8-C$_2$B$_9$H$_{11}$)] (alkene = C$_2$H$_4$, MeCH=CH$_2$, Me$_3$SiCH=CH$_2$, norbornene) have been prepared; a series of analogous alkyne complexes have also been synthesised; and their reactivity investigated.[49] Treatment of the compound [RuH$_2$(H$_2$)$_2$(PCy$_3$)$_2$] with ethene affords the complex [RuH{η^3-(C$_6$H$_8$)PCy$_2$}(η^2-C$_2$H$_2$)(PCy$_3$)] where one cyclohexyl ring of the tricyclohexylphosphine ligand is η^3-bound. Addition of varying amounts of the α-substituted alkenes CH$_2$=CH(SiEt$_3$) or CH$_2$=CH^{t}Bu lead to the formation of the trihydride [RuH$_3${(η^3-C$_6$H$_8$)PCy$_2$}(PCy$_3$)]: C-H activation of two rings to give [RuH{(η^3-C$_6$H$_8$)PCy$_2$}{(η^2-C$_6$H$_9$)(PCy$_2$}] was achieved on treatment with 5 equivalents of alkene.[50] Treatment of the allyl complex [Ru(NCMe)$_2$(cod)(η^3-C$_3$H$_5$)][BF$_4$] (cod = cycloocta-1,5-diene) with (*R*)-binap yields by elimination of the allyl fragment and modification of the cod bonding



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mode $[Ru(NCMe)(binap)(\eta^3{:}\eta^2\text{-}C_8H_{11})][BF_4]$ {binap = (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl the reactivity of this complex was further investigated.[51] Reaction of $[Ru(H)_2(H_2)(Sb^iPr_3)_3]$ with propene affords $[Ru(\eta^3\text{-}C_3H_5)_2(Sb^iPr_3)_2]$ which has been structurally characterised.[52] The complex $[Ru(\eta^3\text{-}PhC_3CHPh)(PMe_2Ph)_4][PF_6]$, was prepared by dimerisation of PhC_2H by $[RuHL_5]^+$ and has been structurally characterised.[53] Treatment of $[RhCl(CCCPh_2)(P^iPr_3)_2]$ with $(CHCH_2)MgBr$ affords the complex $[Rh(\eta^3\text{-}CH_2CHCCPh_2)(P^iPr_3)_2]$.[54] A similar treatment of $[CpRuCl(CCCO_2Me)(PPh_3)]$ with $Sn(CHCH_2)_4/CuCl$ afforded the allyl complex $[CpRuCl(\eta^3\text{-}CH_2CHCCHCO_2Me)(PPh_3)]$.[55] The *bis*(allyl) complexes (**2**), (**3**) have been shown to be efficient ROMP catalysts.[56] The complexes $[Ru(hedta)\ (\eta^2\text{-alkene})]^-$ (hedta = N-hydroxyethylethylenediaminetetraacetate; alkene = 1-cyclohexene-1-methanol, 2-cyclohexene-1-one, pyrithyldione, 1,3-dimethyluracil, 3-deazuracil, 3-methylcytosine) have been examined by ^1H, ^{13}C NMR and electrochemical studies.[57] Three different methods have been used to prepare the vinyl ether complexes of osmium $[Os(NH_3)_5(\eta^2\text{-vinyl ether})]$ namely: direct coordination of a vinyl ether; alcohol addition to a coordinated alkyne or nucleophilic substitution of η^2-vinyl ether species.[58] Furthermore a series of η^2-substituted aniline complexes of the type $[Os(NH_3)_5(\eta^2\text{-substituted aniline})]$ have been prepared and shown to undergo ligand-based reactivity with a variety of electrophiles.[59]

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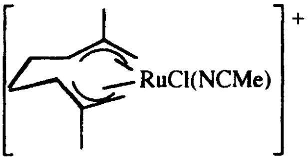

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3.3 Co, Rh and Ir – The reactivity of cationic cobalt cobaloximes π-alkene complexes have been shown to react with nucleophiles and they are sufficiently electrophilic to add to the electron rich sp^2 centres in allyltrimethylsilane and pyrrole.[60] The unique rhodium complex $[RhH(O_2)\{\eta^2{:}\eta^2\text{-}CH_2{=}C(CH_2CH_2P^tBu_2)_2\}]$ which contains a hydride, alkene and dioxygen ligands *cis* to each other has been characterised spectroscopically and crystallographically.[61] Treatment of $[RhH(GeEt_3)(acac)(PCy_3)]$ with HC_2R (R = CO_2Me or Ph) afforded the complexes $[Rh\{\eta^2\text{-}CH(GeEt_3){=}CHR\}(acac)(PCy_3)]$ where the alkyne has inserted into the rhodium germanium bond.[62] The η^3-cyclooctenyl complex $[Rh(\eta^3\text{-}C_8H_{13})(dppb)]$ {dppb = bis(diphenylphosphino)butane} has been prepared by hydride migration from Rh to a coordinated cod ligand under hydrogenation conditions.[63] Grafting of the $[Rh(\eta^3\text{-}C_3H_5)_2]$ fragment onto silica has been achieved and its reactivity investigated.[64,65] A series of Rh(III) allyl complexes containing heterocyclic nitrogen ligands have also been prepared.[66] The complex $[IrH_2(CH_2CHCO_2{}^tBu)(Tp\text{-}3,5\text{-}Me_2)]$ has been synthesised.[67] The synthesis and molecular structure of $[IrCl(\eta^2\text{-}C_2H_4)(Sb^iPr_3)_2]$ has been reported.[68] Similarly the synthesis of $[IrCl(\eta^2\text{-}C_2H_4)_n(PEt_3)_2]$ (n = 1 or 2) has been reported and the interconversion of the two complexes in solution has been probed by VT ^{1}H NMR and the formation of [IrCl(η^2-C_2H_4)(PEt_3)$_2$] has been shown to be thermodynamically favourable.[69] Treatment of [Ir(tripod)(cod)] {tripod = $MeC(CH_2PPh_2)_2$} with alkoxide nucleophiles has been investigated and shown to yield mainly the *exo* isomer of [Ir(tripod)(alkoxycycloocta-5-en-1-yl)]; similar nucleophilic attacks were observed in the analogous rhodium norbornadiene complexes.[70] A series of cationic tripodal phosphine iridium complexes of the type [Ir(tripod)(CO)(η^2-C_2H_4)][BPh_4] (tripod = *cis,cis*-1,3,5-$X_3C_6H_6$; X = H, CO_2Me or CN) have been prepared and shown to be fluxional by VT ^{1}H NMR spectroscopy.[71] Reaction of [Ir(cod)Cl]$_2$ with the cyclam 1,4,8,11-tetraazacyclotetradecane results in oxidation to the Ir(III) species [Ir(cyclam)(coei)]$^+$ (coei = 4-cycloocten-1-ide) and the molecular structure of the dominant diastereoisomer was determined as the triflate salt.[72] Treatment of [MH(CO)(PPh_3)$_3$] (M = Rh or Ir) or [MH(η^4-C_8H_{12})(PPh_3)] (M = Rh or Ir) with C_{60} or C_{70} afford the simple PPh_3 substituted adducts.[73] The synthesis and structural characterisation of [IrCl(CO)(PPh_3)$_2$(η^2-$C_{70}O$)]0.5C_6H_6 has been reported, there was a lot of disorder in the structure.[74] In a similar reaction treatment of $C_{60}O$ with [IrCl(CO)($AsPh_3$)$_2$] afforded the crystallographically characterised adduct [IrCl(CO)($AsPh_3$)(η^2-$C_{60}O$)]; however, treatment of $C_{60}O$ with [IrCl(CO)(PPh_3)$_2$] lead to partial deoxygenation of the fullerene.[75] The synthesis, reactivity and molecular structure of [Ir(H)(OTf)(dfepe)(η^3-C_3H_5)] {dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$, OTf = O_2SOCF_3} has been reported.[76]

3.4 Ni, Pd and Pt – A theoretical study on the polymerisation of ethene by [NiH(acac)] using density functional theory has been carried out.[77] A similar study has been carried out concerning the polymerisation of buta-1,4-diene according to the π-allyl insertion mechanism on nickel centres.[78] The X-ray crystal structure of [Ni(N,N,N′,N′Me_4en)(2,5-dihydrofuran-2,5-dione)] has been determined.[79] The compounds [MCl(PPh_3)(η^3-allyl)] (M = Ni or Pt) react with lithium bicyclo[2.2.1] heptan-1-yl to afford the chloride substituted products.[80] The Ni compounds [Ni(η^3-2-methylallyl) L_2]$^+$ (L = phosphine) have been investigated to study the effect of phosphine ligands on the polymerisation of styrene.[81] The complex [Pt(CH_3)(phen){η^2-(*E*)-$Me_2CCH{=}CHCO_2Me$}][BF_4] which contains a *cis*-alkene and methyl group has been prepared and the dimethylfumarate can easily be displaced by electron rich alkenes.[82] The trigonal bipyramidal Pt(II) complexes [Pt{CHR(R′)}(R″)(dmphen)(η^2-alkene)] or [Pt(CH_2NO_2)(R″)(dmphen)(η^2-alkene)] (dmphen = 2,9-dimethyl-1,10-phenanthroline; R, R′ = CO_2Me, COMe, CN; R″ = Me or CH_2Ph) have been prepared by reacting the compounds [Pt(R″)L(dmphen)(η^2-alkene)]$^+$ (L = NCMe, H_2O) with KCH_2NO_2 or KR(R′)CH.[83] A series of fifteen platinum alkene complexes of the form [Pt(PPh_3)$_2$(η^2-alkene)] have been prepared with two of the complexes characterised crystallographically.[84] The synthesis and crystal structures of the complexes [Pt(Me)$_2$(η^1:η^2-L)] {L = $Ph_2P(CH_2)_2CH{=}CH_2$, $Me_2As(CH_2)_2CH{=}CH_2$} have been reported.[85] Zeise's salt has been treated with a variety of phosphorus and arsenic keto-stabilised ylides to afford complexes of the type [$PtCl_2$(η^2-C_2H_2)(ylide)].[86] The synthesis, characterisation, chemical vapour deposition and mechanistic decomposition (in aromatic solvents) of *cis-bis*(η^2:η^1-pent-4-en-1-yl)platinum has been described.[87] A series of addition elimination equilibria involving the platinum(0) compounds [Pt(N,N′)((η^2-alkene)], the organometallic species R_mMX_n (M = Hg or Sn; X = Cl, Br, I; R = hydrocarbyl group) and the five coordinate Pt(II) complexes [PtX(R_mMX_{n-1})(N,N′)(η^2-alkene)] have been investigated.[88] The photo-reactivity of [Pt{P(OPh)$_3$}(η^2-C_{60})] has been studied by UV-Vis; irradiation at 770 nm causes dissociation of the Pt fragment which was trapped by either $CHCl_3$ or O_2.[89] The optically active complex [Pt(diop)(η^2-C_{60})] {diop = 2,3-O,O′-i-propylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane} has been prepared by a variety of different routes and its crystal structure determined.[90] Theoretical papers considering the interconversion of η^3-η^1-bonding modes and reductive elimination reactions in Pd(II) and Pt(II) allyl hydride complexes;[91] the effect of ancillary ligands on palladium carbon bonding and its implication for nucleophilic attack at the allylic carbons;[92,93] the regioselectivity of nucleophilic attack on Pd allyl complexes containing imine and phosphine ligands[94] and cycloaddition of methylene cyclopropane with alkenes[95] have been reported. The preparation of π-allyl complexes from η^3-propargyl/allenyl compounds of Pt and Pd, has been reported.[96,97] A series of Pt and Pd allyl complexes were prepared by treatment of oxodimethylenemethane complexes with electrophiles.[98] Pt and Pd complexes containing the ketenylenetriphenylphosphine ligand have been prepared and the molecular structure of [Pt(η^3-C_3H_5){η^3-C(PPh_3)(CO)}(PPh_3)][BF_4] was described.[99] A collection of π-allyl complexes of the di-terpene carvone were prepared and their chemistry investigated.[100] The complexes [Pd(η^3-$CH_2(CH)_2CH_3$)(C_6H_3-2,5-Cl)(PR_3)] were prepared and the effect of the phosphine ligand on the reductive elimination of the crotyl and aryl ligands was investigated.[101] The synthesis, reactivity and molecular structure of [Pt(η^3-1,3-PhC_3H_3){(*S*-)binap}] has been reported and the observed dissimilarity of the phenyl groups was proposed as an origin of selective nucleophilic attack.[102] A series of Pd π-allyl complexes containing the ligand {bis-(*p*-anisylimino)acenaphthene} were prepared by the insertion of allenes into alkyl or acyl carbon bonds with displacement of a ligated nitrogen of the bidentate ligand.[103] The synthesis of [Pd{η^3-CH(CH_2CH_3)}(C_6H_4-*p*-X)(phen)]$^+$ have been prepared by β-methyl migratory insertion into a styrene ligand.[104] A selection of compounds of the type [Pd(η^3-2-MeC_3H_4)(pzpy)][Tf] {pzpy = 2-(1-hydropyrazol-1-yl)pyridine; Tf = CF_3SO_3} have been prepared and shown to be fluxional: the source of fluxionality was dechelation of the nitrogen ligand.[105] A collection of Pd allyl complexes containing a tripodal oxygen ligand were prepared and their reactivity investigated.[106, 107] The mechanism of allyl transfer to Pd(0) from allylic ammonium cations has been investigated.[108] A number of Pd (η^3-allyl) tetrafluoroborates have been prepared using N-allyl-2,4,6-triphenylpyridinium tetrafluoroborates as transfer reagents.[109] A series of Pd allyl complexes with novel P-N,[110–115] P-O,[116,117] P-S,[118] PNS and NN′S[119] and PP[120] ligand sets have been prepared by various groups. Treatment of [PdBr(C_6F_5)($NCMe)_2$] with a variety of penta-1,4-dienes afforded a selection of π-allyl compounds.[121] The symmetry of cationic π-allyl Pd intermediates was discussed in relation to allylic alkylations.[122] The use of Pd allyl complexes in synthetic organic transformations continues to receive attention; examples include.[123–127] The use of hemilabile ligands has been investigated in the codimerisation of styrene with ethene.[128] The use of Pd η-allyl complexes for catalytic alkene dimerisation has been investigated[129] and cationic η^3- allyl Pd compounds have been shown to be active for the polymerisation of norbornene containing a variety of functional groups.[130] The molecular structure of [PdBr(η^3-C_3H_5)(cytidine)] has been reported.[131] [Pd(η^3-C_3H_5)Cp] has been selectively introduced into the cages of zeolite NaY *via* chemical vapour deposition and subsequently thermally converted to Pd clusters.[132]

3.5 Other Metals – The synthesis and reactivity of [Ti(O^iPr)$_2$(η^2-propene)] has been reported.[133] Hydrotitanation of 1,3-dienes afforded η^3-π-allyl complexes which undergo regioselective addition of methylchloroformate to yield β-γ unsaturated esters.[134] A series of Zr allyl complexes containing N-N′ *bis*(trimethylsilyl)benzaminidinato ligands were reported and evidence was obtained for intermediate η^1-η^3 allyl bonding, thus serving as a model for the often observed allyl interconversion.[135] Treatment of [Zr(η^4-C_4H_6)Cp_2] with $B(C_6F_5)_3$ afforded a π-allyl complex which reacted with an *ortho*-fluoro atom of one C_6F_5 ring.[136] The preparation of planar chiral Mn (η^2-alkene) complexes and their use for diastereoselective C-C bond formation was reported.[137] A collection of half sandwich complexes of the type [Cp^*Re(η^3-allyl)L_2)]$^+$ were synthesised from [Cp^*Re(η^3-allyl)(NCMe)$_2$]$^+$; simple substitution was not always observed, rather nucleophilic attack often occurred either at the allyl or ligated NCMe moieties.[138] The non-polar polymer poly(methylphenylsiloxane) dissolves Ag(CF_3CO_2) which then forms adducts with cyclohexene or benzene. Ligand exchange constants have been calculated[139] and the use of this material in gas-liquid chromatography for separation of cyclohexene and cyclohexane has been evaluated.[140]

4 Complexes Derived from Unconjugated Alkenes

A collection of seven coordinate halocarbonyl-terpy complexes of Mo were prepared and the molecular structure of [MoBr(CO)(η^4-nbd)(terpy)] (nbd = norbornadiene) reported.[141] The preparation and molecular structure of the phosphine complex [Fe(η^4-cod){η^4-2-(trimethylsilyl)-4,5-dimethylphosphinine}] has been reported.[142] The synthesis and X-ray structures of the ruthenium complex [Ru(η^4-C_8H_{12}){η^5-$P_3C_2{}^tBu_2$[CH($SiMe_3$)]}] which contains a 6e donor 1,2,4-triphosphole, and [Ru(η^5-C_8H_{11}){η-$P_3C_2{}^tBu_2H$[CH($SiMe_3$)]}] where a hydrogen migration from the coordinated cod to the phosphole has occurred has been described.[143] The complex [RuHCl(bpzm)(cod)] {bzpm = *bis*(pyrazol-1-yl)methane} has been used to prepare a variety of cationic hydrido complexes after halide extraction with Ag[CF_3SO_3] and their catalytic properties investigated.[144] The enthalpies of reaction and relative binding energies of tertiary phosphine ligands in ruthenium complexes has been measured by anaerobic calorimetry.[145,146] A series of divalent ruthenium cod complexes containing the

1,4,7-trithiacyclononane have been prepared and their reactivity investigated.[147] The complex [RhCl(cod)(CQ)] (CQ = free base of chloroquinine) has been prepared and its medicinal properties tested.[148] The synthesis and catalytic activity of a collection of tripodal phosphine rhodium cod complexes has been reported.[149,150] The complex [Ru{$C_6H_3(CH_2NMe_2)$-2,6}Cl(nbd)] has been prepared from the reaction of [$RuCl_2$(nbd)]$_n$ and [Li{$C_6H_3(CH_2NMe_2)$-2,6}]$_2$ and this air stable complex has been characterised by X-ray crystallography.[151] The rhodium compounds [Rh(nbd)(N-N)][X] (N-N = bipy, 1,10-phen, X = ClO_4, BPh_4) react with TCNQ (7,7,8,8-tetracyanoquinodimethanido) to afford partial to total anion exchange leaving the coordination sphere unaltered, whereas if monodentate nitrogen ligands are present substitution occurs.[152] A collection of complexes containing cod and late transition metals with multidentate heterofunctional phosphine ligands have been reported.[153] The complexes [RhCl(L)(cod)] (L = hydrophilic phosphine) have been prepared where the phosphines contain a variety of water solubilising functional groups such as, carboxylic acids, sulfonates, trimethylammonium, and hydroxyl.[154] The interconversion of the effective carbonylation catalyst [Rh(η^6-$C_6H_5BPh_3$)(cod)] between a zwitterionic and cationic form has been demonstrated by dynamic NMR studies.[155] The carbene complexes [MCl(=CNMeCHCHNMe)(cod)] and [M(=CNMeCHCHNMe)$_2$(cod)]$^+$ have been prepared by a variety of synthetic routes and characterised by X-ray crystallography.[156] A series of optically active rhodium catalysts containing: cod; optically active chelating phosphines; optically active 1,3-diketones or 1,3-diketimines based on camphor have been investigated as homogeneous hydrogenation catalysts.[157] Asymmetric hydrogenation of prochiral alkenes was carried out with chiral complexes of the type [Rh(L)(PP*)]$^+$ (L = cod, nbd, PP* = chiral phosphines that afford 7-membered chelate rings): the reactions have been studied by ^{31}P NMR spectroscopy and UV-Vis.[158] The rhodium fragment [Rh(cod)(PP*)] {PP* = (*S*)-binap or (*S*)-(*R*)-bppfa} have been supported in layer clays and the asymmetric hydrogenation of α,β-unsaturated carboxylic acids investigated.[159] A collection of cationic Rh(I) and Ir(I) complexes of the form [M(L_2)(L'_2)][BF_4] (M = Rh, L_2 = 2,2′-diamino-1,1′-binaphthyl, L'_2 = cod, nbd, hexa-1,5-diene; M = Ir, L_2 = 2,2′-diamino-1,1′-binaphthyl, L'_2 = cod; M = Rh or Ir; L_2 = N,N′-dimethyl-2,2′-diamino-1,1′-binaphthyl, L'_2 = cod) and their use as asymmetric hydrogenation catalysts investigated.[160] Treatment of a polymeric ligand TentaGel (a polyethene oxide grafted styrene matrix) with [Rh(cod)$_2$][BF_4] lead to the preparation of an active hydrogenation catalyst.[161] Reaction of the rhodium compounds [Rh(μ-Cl)(diene)]$_2$ (diene = cod, nbd) with the amidine bases dbu or dbn under differing conditions afforded the complexes [Rh(diene)L_2][PF_6] (diene = cod, nbd, L = dbu, dbn) or [RhCl(nbd)L] (L = dbu, dbn) and these complexes have been shown to be active polymerisation catalysts for phenylacetylene.[162] The fragments [RhCl(cod)] or $PtCl_2$ have been incorporated into thin films of poly-[Fe(vb-py)$_2$(CN)$_2$] by coordination to the cyano or uncomplexed vinyl-bipyridyl groups. These compounds were shown to be good electrocatalysts for the reduction of CO_2.[163] The [ML(diene)]$^+$ (M = Rh, Ir, L = 2,2′-bipy, 1,10-phen, diene = cod, nbd) have been prepared and studied by electrochemical techniques.[164] The molecular structure of $[Rh\{PPh_2(CH_2)_3PMe_2\}_2(nbd)][BF_4]_3$ has been determined.[165] The synthesis and molecular structure of [IrHCl(chel)(cod)] (chel = $Ph_2P(CH_2)_2SiMe_2$) has been reported.[166] Two new Ir(I) complexes with ligated diphosphine and diphosphinite calix[4]arene ligands have been prepared and characterised spectroscopically: extended Hückel molecular orbital calculations have also been carried out on these molecules.[167] The Ir(I) complexes $[Ir(C_6H_4CH_2NRR')(cod)]$ (R = R′ = Et; R = Me, R′ = ^{t}Bu) have been prepared and an X-ray diffraction study of $[Ir(C_6H_4CH_2NEt_2$-2-*C,N*)(cod)] shows a weak agostic interaction between a methyl-H atom on one of the ethyl groups. Treatment with MeI affords the complex $[IrI(C_6H_4CH_2NEtCHMe$-*C,N,C′*)(cod)] which results from intranuclear C-H activation.[168] The synthesis and asymmetric hydrogenation activity of some new Rh(I) and Ir(I) cod and nbd complexes containing C_2 symmetric PNP ligands has been reported.[169] A series of di-orthometalated iridium complexes of the type $[IrH(cod)\{P(OC_6H_4)_2(OC_6H_5)\}]$ have been prepared and their use as imine hydrogenation catalysts investigated.[170] The molecular structure of $[Ir(cod)(ONC_5H_4\text{-}2\text{-}S)]$ has been reported.[171] The reactivity of the tetrafluorobarrelene complex $[Ir(C_2Ph)(tfb)(PCy_3)]$ (tfb = tetrafluorobarrelene) towards trialkyl silanes has been investigated.[172] The crystal structure of $[Ni(cod)(PEtPh_2)_2]$ has been reported.[173] The complex $[PdCl_2(C_9H_{12})]$ (C_9H_{12} = bicyclo[3.3.1]nona-2,6-diene) has been studied by 2D NMR and its molecular structure determined by a single crystal X-ray diffraction study.[174] The synthesis and molecular structure of the triazatrimethylenemethane complex $[Pt(cod)\{C(NPh)_3\}]$ has been reported.[175] The Pt complex [Pt{NMeC(=NCN)S}(cod)] has been prepared, structurally characterised and its electrospray mass spectrum recorded.[176] A series of Pt(II) ureylene complexes have been prepared by treatment of $[Pt(Cl)_2(cod)]$ or $[Pt(Cl)_2(PPh_3)_2]$ with mono- or disubstituted ureas in the presence of an excess of Ag_2O. The crystal and molecular structure of [Pt{PhNC(O)NAd}(cod)] (Ad = adamantyl) has been reported.[177] The Pt compounds $[Pt(cod)(CH_2EMe_3)]$ (E = Ge, Sn) have been prepared and their thermal decomposition products investigated.[178] The complex $[Pt\ (1,2\text{-}O\text{-}C_6H_4)(cod)]$ has been synthesised and characterised by electrochemical techniques and its molecular structure determined by a single crystal X-ray diffraction study.[179]

5 Complexes Derived from Cyclic Conjugated Alkenes

5.1 Cr, Mo and W – A density functional theory study on intermediates and transition structures of the benzannulation of heteroatom-stabilised chromium carbene complexes with ethyne has been carried out and contains some interesting data.[180] The complex $[Cr(CO)_3(\eta^4{:}\eta^2$-8,9-dimethylbicyclo[4.4.1]undeca-2,4,8-triene)] was prepared by the treatment of $[Cr(CO)_2(thf)(\eta^6\text{-}1,3,5\text{-}C_7H_8)]$ with 2,3-dimethylbutadiene followed by CO.[181] The $[Cr(CO)_3(\eta^6\text{-}1,3,5\text{-}C_7H_8)]$ fragment has been treated with alkynes[182] and alkylisocyanates[183] to build up polycyclic molecules. A series of functionalised (at the 1, 2 or 3 positions) cycloheptatriene chromium complexes of the type [Cr(CO)$_3$(cht)] (cht = cycloheptatriene) have been resolved enzymatically and subsequent [$6\pi + 4\pi$] cycloaddition reactions afforded chiral, non-racemic bicyclo[4.4.1]undecadiene adducts.[184] The kinetics and mechanisms of ligand substitution reactions in [Cr(CO)$_3$(η^6-1,3,5-C$_7$H$_8$)] have been studied.[185] Refluxing the complex [Cr(CO)$_3$(η^7-C$_7$H$_6$C$_6$H$_4$-Me)][PF$_6$] in toluene afforded the mixed arene cycloheptatrienyl complex [Cr(η^7-C$_6$H$_5$Me)(η^7-C$_7$H$_6$C$_6$H$_4$-Me)][PF$_6$] which was shown to undergo a reversible one electron oxidation to the radical dication.[186] The cycloheptadienyl complexes [Cr(CO)$_3$(SnPh$_3$)(η^5-C$_7$H$_8$R)] and the cyclohexadienyl complexes [Cr(CO)$_3$(NO)(η^5-C$_6$H$_6$R)] react with alkynes to give multicyclic products *via* sequential [5 + 2] and *homo* [5 + 2] cycloadditions to the dienyl manifold.[187] The synthesis of a wide range of cyclohexadienyl and cycloheptatrienyl complexes ligated to the [M(CO)$_3$] or [M(CO)$_2$(NO)] (M = Cr, Mo or W) fragments and their reactivity towards a range of nucleophiles was investigated; some Mn complexes were also reported.[188] The preparation of [Mo(CO)$_2$(η^4-C$_6$H$_8$)Cp][PF$_6$] by hydride abstraction from the allyl precursor [Mo(CO)$_2$(η^3-C$_6$H$_9$)Cp] was reported and its application to total synthesis of natural products reported.[189, 190] The complex [Mo(CO)$_2$(η^4-C$_6$H$_7$-2-SPh)Cp][PF$_6$] has been synthesised and shown to react with carbon and sulfur nucleophiles to give predominantly C-4 addition products.[191] The molecular structure of [Mo(CO)(η^4-C$_6$H$_8$){η^5-(κN)-CpCH$_2$CH$_2$NHMe}][PF$_6$] has been reported.[192] The cycloheptatrienyl complexes [Mo{CCH$_2$(CH$_2$)$_n$CH$_2$O}L$_2$(η^7-C$_7$H$_7$)][PF$_6$] (n = 1 or 2, L = CO, L$_2$ = Ph$_2$PCH$_2$PPh$_2$ or Ph$_2$PCH$_2$CH$_2$PPh$_2$) which contain a cyclic oxycarbene have been prepared from [Mo(η^6-C$_6$H$_5$Me)(η^7-C$_7$H$_7$)][PF$_6$].[193] In a detailed study on hapticity interconversion (η^7- to η^3-) in the complexes [MX(CO)$_2$(η^7-C$_7$H$_7$)]$^{n+}$ (M = Mo or W, X = variety of monoanionic ligands) it was found that the interconversion depends upon the X group and the incoming ligand.[194] Treatment of [W(CO)Cp$_2$] with an excess of CCl$_4$ affords the cyclopentadiene complex [WCl(CO)(η^4-C$_5$H$_5$-exo-CCl$_3$)Cp].[195] The cationic cyclopentadienone complexes [M(CO)$_2$(η^4-C$_5$H$_4$O)(HBpz$_3$)][PF$_6$] (M = Mo or W), [MBr(CO)$_2$(bipy)(η^4-C$_5$H$_4$O)][PF$_6$] (M = Mo or W) [WBr(CO)$_2$(Ph$_2$PCH$_2$PPh$_2$)-(η^4-C$_5$H$_4$O)][PF$_6$] have been prepared by hydride abstraction, using [Ph$_3$C][PF$_6$], from the analogous π-allyl complexes.[196]

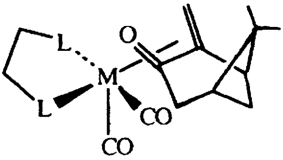
5.2 Fe, Ru and Os – Consecutive butylations of the cyclopentadienyl ring in [Fe(CO)$_2$(PPh$_3$)Cp]$^+$ to afford the complexes [Fe(CO)$_2$(PPh$_3$)(η^4-C$_5$H$_{5-n}$Bu$_n$)] (n = 1 - 5) has been reported.[197] The synthesis and remarkable stability of the complex [Fe(CO)$_3$(η^4-C$_5$HBz$_4$)] has been reported, as has its molecular structure.[198] The cycloheptadiene complexes [Fe(CO)$_3$(η^4-C$_7$H$_9$-5-R)] {R = (CH$_2$)$_2$CO$_2$Et, (CH$_2$)$_2$CN or CH$_2$N(CH$_3$)CH$_2$CO$_2$Et} were prepared by nucleophilic attack of the highly functionalised Zn-Cu reagents on the cationic cycloheptadienyl precursor [Fe(CO)$_3$(η^4-C$_7$H$_9$)]$^+$ and the reactivity of these complexes was further investigated.[199] Treatment of the complex [Fe(CO)$_3$(η^4-C$_6$H$_7$)]$^+$ with 4-aminobenzofuran allowed substitution to occur at the 5-position, exclusively *ortho* to the amino group, and afford the diene complex [Fe(CO)$_3${η^4-C$_6$H$_7$-5-(4-aminobenzofuran)}] which was subsequently oxidised to afford the alkaloid furostifoline.[200] A series of new chiral cyclohexa-1,3-diene complexes were prepared from 1,3-cyclohexanedione and 5,5-dimethyl-1,3-cyclohexanedione after they had been converted to their 1,3-diacetoxy derivatives with subsequent carbonyl substitution by chiral phosphines afforded complexes $[Fe(CO)_2(L)(\eta^4$-C_6H_6-1,3-OCOMe)] (L = a series of chiral phosphines).[201] A study into the selective oxyfunctionalisation of (tricarbonylcyclohexadiene) iron-substituted furans with singlet oxygen, dimethyldioxirane and *m*-chloroperoxybenzoic acid has been carried out and a variety of products obtained.[202] The use of $[Fe(CO)_3(\eta^4$-C_6H_6-5-R)] as mediator for cyclisation reactions in the synthesis of carbazoles has been carried out and the regio- and stereospecificity was determined by deuterium labelling studies.[203,204] Reaction of substituted cyclohexadienyl complexes of the type $[Fe(CO)_3(\eta^4$-C_6H_5-2,3,5-R)] with modified Sorenson-type nucleophiles allowed coupling to occur in the 5-position and ultimately allowed the preparation of complexed N-deprotected amino acids.[205] The complex $[Fe(CO)_3(\eta^4$-C_6H_5-2-OMe-5-CH_2)], which contains an exocyclic double bond, reacts regio-, stereo-, and chemoselectively with reactive 1,3-dipoles (eg, nitrile oxides, ozone, diazoacetate, the oxoallyl cation) allowing the rapid synthesis of spiro[4.5]decane systems.[206] A series of mono-, di-, tri-, and tetraalkynylated tricarbonyl cyclobutadieneiron complexes have been prepared and subsequently oligomerised into rings and chains.[207] A novel methodology for the enantioselective synthesis of planar chiral tricarbonyl(diene) complexes of iron was described.[208] The synthesis and crystal structure $[Fe(CO)_3(\eta^4$-3,5-C_6H_4-1,2-C_{60})] has been reported and its molecular structure shows there is significant steric compression between the C_{60} and $Fe(CO)_3$ moieties.[209] A series of planar chiral $[Fe(CO)_3(\eta^4$-cyclohexadiene)] complexes were separated into enantiomers by HPLC using commercially available β-cyclodextrin columns.[210] The preparation of an α-diazocarbonyl-tethered iron tricarbonyl (η^4-cyclohexadiene) complex was reported and its decomposition by [Rh(acac)$_2$] to give a complexed bicyclic product has been reported.[211] The regio- and stereoselective oxyfunctionalisation of triene species by singlet oxygen and dimethyldioxirane has been investigated in complexes of the type $[Fe(CO)_3(\eta^4$-cyclohexadiene-5-R)] where R is an exocyclic alkene moiety.[212] The complex $[Fe(CO)_3(\eta^4$-C_6H_7-1-OTf)] was shown to undergo Stille Pd coupling with $Bu_3SnCH{=}CH_2$ and also to couple with HC_2SiMe_3 in the presence of CuI to afford the triflate substituted products $[Fe(CO)_3(\eta^4$-C_6H_7-1-R)] (R = $CHCH_2$, C_2SiMe_3).[213] The synthesis of the complex $[Fe(CO)_3(\eta^4$-C_6H_7-1-SO_2Ph)] has been reported and on treatment with $[Ph_3C][PF_6]$ gave a cationic cyclohexadienyl complex which was then reacted with a variety of nucleophiles to either regenerate a η^4- complex in the case of soft nucleophiles or with harder nucleophiles σ-η^4- complexes were obtained.[214, 215] The complexes $[Fe(CO)_2(PPh_3)(\eta^4$-C_6H_7-1-R-4-OMe)] {R = OMe, $(CH_2)_2OH$, $(CH_2)_2NH_2$, $(CH_2)_2OCH_3$, $(CH_2)_2NPh_2$} have been prepared and converted into the cyclohexadienyl complexes by reaction with $[Ph_3C][PF_6]$.[216] The electrochemical behaviour and reactivity of complexes of the type $[Fe(CO)_3(\eta^5$-cyclohexadienyl-R-R')]$[PF_6]$ (R = H, Me, ^{n}Bu, MeO, Ph, $MeOC_6H_4$, $CF_3C_6H_4$), $[Fe(CO)_3(\eta^5$-cyclohexadienyl-1-OEt)]$[PF_6]$, $[Fe(CO)_3(\eta^5$-cyclohexadienyl-2-R)] $[PF_6]$ (R = R′ = MeO or Me; R = Me, R′ = MeO) or $[Fe(CO)_2(PPh_3)$

(η^5-cyclohexadienyl-R)][PF_6] has been reported.[217] Electrospray mass spectra of a variety of π-hydrocarbon complexes have been recorded.[218] The dynamic behaviour of the complexes [$Fe(CO)_3(\eta^5$-$C_7H_9)$][BF_4] and [$Fe(CO)_3(\eta^5$-$C_6H_7)$][BF_4] in the solid state has been investigated by VT NMR spectroscopy and phase transitions have been observed.[219] A series of functionalised [$Fe(CO)_3$(η-tropone)] complexes have been prepared and regioisomerisation observed. The interconversion has been investigated by ^1H NMR spectroscopy and activation parameters calculated.[220] A method for the synthesis of vinyl substituted [$Fe(CO)_3$(η^5-cyclohexadienyl)] complexes was reported and the reaction displayed a switch from direct to conjugate addition when stabilised enolates with different metal counterions were used, the use of organocuprates allowed regio- and stereocontrol.[221] A series of bicyclooctenones were prepared by carbonylation of cycloheptadienyl iron carbonyl complexes.[222] A series of cationic cycloheptadienyl complexes with new substitution patterns have been prepared starting from [$Fe(CO)_2(L)$(η^4-eurocarvone)] (L = phosphines and phosphites), by conversion to the cycloheptadienyl complexes by hydride abstraction and subsequent reaction with nucleophiles.[223] A [1,7] boron sigmatropic shift has been observed in the complex [$Fe(CO)_3(\eta^7$-C_7H_7-$BPr_2)$] by NMR spectroscopy, however, in total there were three different fluxional processes observed in this molecule.[224] A series of cyclohexadienyl hydridotrispyrazolylborate ruthenium(II) species have been prepared *via* nucleophilic attack on ligated arenes, the molecular structure of [$Ru(\eta^5$-$C_6H_6CN)(HBpz_3)$] was also described.[225] The closely related cyclohexadienyl complexes [$Ru(\eta^5$-C_6H_6-$X)(L)$][PF_6] {X = CN, H, OH, L = (2-pyridylethyl)(2-pyridylmethyl)methylamine} have been prepared *via* nucleophilic attack on the coordinated arene in [$Ru(\eta^6$-$C_6H_6)(L)]^{2+}$ and the molecular structure of the cyano- containing complex was reported.[226] The ruthenium complex [$Ru(\eta^6$-$C_8H_{10})$(1-3:5-6-η-C_8H_{11}]$^+$ was prepared by the reaction of solvated Ru^{2+} ions with a large excess of buta-1,3-diene.[227]

5.3 Other Metals - A 'serendipitous' synthesis of the Ti complex [$Ti(\eta^5$-C_6H-1,2,4,5,6-$SiMe_3)Cp$] from reaction of [{$Ti(\mu$-η^2:η^2-$Me_3SiC_2SiMe_3)_2Cp$}($MgCp$)] with an excess of *bis*(trimethylsilyl)ethyne has been described and the analogous 4-alkyl complexes [$Ti(\eta^5$-C_6H-1,2,5,6-$SiMe_3$-4-R)Cp] (R = ^{t}Bu, ^{n}Bu, Ph, Cy) were prepared in a similar way using an excess of the relevant substituted alkyne.[228] The UV and visible spectra of the compounds [$V(\eta^7$-$C_7H_7)Cp$] and [$Ta(\eta^7$-$C_7H_7)CpMe$] were shown to change dramatically on going from solution to vapour phase due to the appearance of intense Rydberg lines which were subsequently assigned on the basis of their term values.[229] The complexes [$M(OAr)_3(\eta^4$-$C_6H_8)$] and [$MCl(OAr)_2(\eta^4$-$C_6H_8)$] (M = Nb or Ta, Ar = 2,6-diisopropylphenoxide) were prepared by amalgam reduction of the aryloxide compounds [$MCl_3(OAr)_2]_2$ in the presence of cyclohexa-1,3- or 1,4-diene.[230] The η^5-thiophene complexes [$Mn(CO)_3(\eta^5$-$SC_4H_4)$] have been treated with nucleophiles and found to react preferentially at the sulfur atom to afford the neutral η^4-diene complexes [$Mn(CO)_3(\eta^4$-$C_4H_4SR)$].[231] The compounds [$Mn(CO)_3(\eta^5$-C_6H_7-R)] (R = alkoxy, halogeno, dimethylamino, and thio) react with hydride then proton sources to yield complexes resulting from cleavage of the R group; the intermediate η^5-complexes underwent an elimination of an agostic hydrogen followed by the R group.[232] Irradiation of $[Mn(CO)_3(\eta^5\text{-}C_6H_5\text{-}2,4\text{-}Me)]$ in thf affords $[Mn(CO)_2(thf)(\eta^5\text{-}C_6H_5\text{-}2,4\text{-}Me)]$ which on treatment with PhC_2Ph affords a variety of cycloaddition compounds which were successfully separated by HPLC.[233] Furthermore UV irradiation of $[Mn(CO)_3(\eta^5\text{-}C_6H_7)]$ in toluene in the presence of PhC_2R (R = H, Me, Ph) affords the [5 + 2] adducts $[Mn(CO)_3(\eta^2{:}\eta^3\text{-}C_8H_7\text{-}PhR)]$ and the tricyclic [5 + 2], *homo*, [5 + 2] double adducts $[Mn(CO)_3(\eta^2{:}\eta^2{:}\eta^2\text{-}C_{10}H_7\text{-}Ph_2R_2)]$: several of the products have been characterised crystallographically.[234] Reaction of the compound $[Mn(CO)_3(\eta^5\text{-}C_6H_6\text{-}exo\text{-}C_5H_5)]$ with aryl lithium reagents afforded *via* nucleophilic attack on a carbonyl ligand a variety of alkoxy carbene complexes several of which were structurally characterised.[235] The complexes $[Co(\eta^4\text{-dialkene})(\eta^6\text{-}C_6Me_6)]$ (dialkene = cyclohexa-1,3-diene, cyclohepta-1,3-diene, nbd and cod) have been shown to form 19 electron radical species on electrochemical reduction in non-aqueous solutions. The radicals have been further studied by ESR spectroscopy.[236] The synthesis and polymerisation under Hay conditions in boiling butanone of the cyclobutadiene complex $[Co(\eta^4\text{-}C_4\text{-}1,3\text{-}C_2H\text{-}2,4\text{-}SiMe_3)Cp]$ has been reported.[237] The synthesis of ten cyclobutadiene complexes of the type $[Co(\eta^4\text{-}C_4Ph_4)(\eta^5\text{-}C_5H_4\text{-}R)]$ has been described.[238] The compounds $[Rh(\eta^4\text{-}C_4H\text{-}1,3\text{-}R\text{-}2\text{-}C_2R)(\eta^5\text{-}C_5Me_5)]$ (R = Ph or *p*-tolyl) have been prepared by a trimerisation of the alkynes HC_2R (R = Ph or *p*-tolyl) by the rhodium complex $[RhCl\{NH_2CH(Me)C(O)O\}(\eta^5\text{-}C_5Me_5)]$ in the presence of base.[239] Reaction of the complex $[Co(\eta^5\text{-}C_4H_2S\text{-}2,5\text{-}Me_2)(\eta^5\text{-}C_5Me_5)]^{2+}$ with the reducing agent $[CoCp_2]$ affords the complex $[Co(\eta^4\text{-}C_4H_2S\text{-}2,5\text{-}Me_2)(\eta^5\text{-}C_5Me_5)]$ as well as small amounts of other products.[240] Nickel-1,3-diene complexes have been demonstrated to have remarkable regio-control in nickel catalysed cyclisation reactions.[241] The crystal and molecular structure of $[PtCl_2(SbPh_3)(\eta^4\text{-}C_4Me_4)]$ has been determined.[242]

6 Complexes Containing Acyclic Alkenes

Reaction of $[TaCl_2(\eta^4\text{-}C_4H_6)Cp^*]$ with BnMgBr (Bn = benzyl) affords the *bis*(benzyl) complex $[Ta(Bn)_2(\eta^4\text{-}C_4H_6)Cp^*]$ which on thermolysis yields a benzylidene complex which was trapped by the addition of PMe_3. Both of these complexes have been structurally characterised and their use for the polymerisation of norbornenes investigated.[243] Photocatalytic hydrosilylation of conjugated dienes in the presence of $[Cr(CO)_6]$ has been reported.[244] A series of molybdenum pentadienyl complexes have been prepared from $[K(diglyme)][Mo(CO)_3(\eta^5\text{-}C_5H_3\text{-}2,4\text{-}Me)]$ which was synthesised by treatment of $[Mo(CO)_3(diglyme)]$ with $K(C_5H_3\text{-}2,4\text{-}Me)$.[245] A collection of neutral η^4-oxadiene complexes of molybdenum and tungsten have been prepared **(4)** and their reactivity investigated. For example, complexation of the carbonyl group of the oxadiene moiety resulted in reduced reactivity of the carbonyl to O-alkylation and anions generated on treatment with MeLi reacted more selectively with electrophiles.[246] Two general



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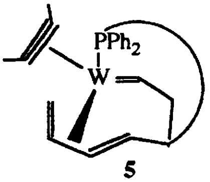
routes for the resolution of chiral [Fe(CO)$_3$(η^4-trimethylenemethane)] complexes have been described.[247] Reaction of [Fe(CO)$_3$(η^5-C$_5$H$_5$)]$^+$ with 2-cyano-zinc-copper cyclopentadiene afforded the complex [Fe(CO)$_3$(η^5-C$_5$H$_5$-5-C$_5$H$_8$-2-CN)] which was further modified to a tri-functionalised bicyclic.[248] A series of complexes of the type [Fe(CO)$_3$(η^4-polyene)] have been converted to [Fe(CO)$_3$(η^4-1,6-dienal)] complexes by a two step osmylation periodate oxidation, whereas, ozonolysis destroyed the polyene complexes.[249] The compound [Fe(CO)$_3${η^4-C$_4$H$_2$-1-C(O)H-4-Ph}] has been reacted with the primary amine NH$_2$(CH$_2$)$_2$CO(CH$_2$CH$_2$)OCH$_2$CH$_3$ to give the condensation product [Fe(CO)$_3${η^4-C$_4$H$_2$-1-CHN(CH$_2$)$_2$CO(CH$_2$CH$_2$)OCH$_2$CH$_3$-4-Ph}] which has been further modified to afford the natural product (±)-dienomycin along with its C-4 epimer.[250] The enantioselective synthesis of the C11 - C24 segment of macrolactin A {an anti-viral agent against Herpes, Simplex (I) and (II) and HIV} has been prepared by utilising the reactivity of a series of [Fe(CO)$_3$(η^4-diene)] fragments.[251] The reactions of the complex [Fe(CO)$_3$(η^4-*meso*-2,4-hexadiene-1,6-dial)] with a selection of alkyl zinc reagents has been investigated in the presence (*S*)-(+)-diphenyl(1-methylpyrrolidine-2-yl) methanol. The reactions have been shown to proceed with high enantiotropic group and face selectivity yielding mono-alchoholic functionality with d e > 90% and e e > 98%.[252] A collection of optically active [Fe(CO)$_3$(η^4-amino-dialkene)] complexes have been prepared by nucleophilic attack of primary and secondary amines on complexes of the type [Fe(CO)$_3${η^4-1(*R*)-CH$_3$-nopadienyl}]$^+$.[253] The iron(iminobutadiene) complex [Fe(CO)$_3$(η^4-C$_4$H$_4$-1-CHNBu)] has been shown to react with organometallic nucleophiles in a stereospecific manner.[254] A series of (*Z*)-dienol complexes were prepared by nucleophilic attack of alkyl lithium reagents on complexes of the type [Fe(CO)$_3${η^4-(*Z*)-dieneone}], however, the use of Grignard or alkyl aluminium reagents allowed reaction with isomerisation to the *E*- isomers.[255] Asymmetric induction in the Diels Alder reaction of 1,3-dienes with α,β unsaturated ketones adjacent to planar chiral [Fe(CO)$_3$(η^4-diene)] fragments was observed when the reactions were carried out in the presence of a variety of Lewis acids.[256] Secondary phosphines have been shown to add to the cationic [Fe(CO)$_3$(η^4-1(*R*)-CH$_3$-nopadienyl)]$^+$ complex to yield optically active phosphines.[257] The absolute configuration of some methyl substituted [Fe(CO)$_3$(η^4-butadiene-Me)] complexes has been determined and their chiro-optical properties probed by circular dichroism.[258] A series of butadiene complexes have been prepared by nucleophilic attack on iron(ω-alkenyl)carbene complexes.[259] The fluxionality of azabutadiene complexes of the type [Fe(CO)$_3$(η^4-1-aza-buta-1,3-diene)] has been investigated by ^{13}C{^{1}H} NMR spectroscopy and the molecular structure of [Fe(CO)$_3$(η^4-1-*p*-anisyl-4-phenyl-butadiene)] reported.[260] The synthesis and reactions of the chiral transfer reagent [Fe(CO)$_2$(PPh$_3$)(η^4-4-R-1-R$'$-1,3-azabutadiene)] has been reported along with single crystal X-ray diffraction study of the complex [Fe(CO)$_2$(PPh$_3$)(η^4-4-PhCHCHNCHMePh)].[261] A report concerning bond shift isomerisation of heterodienes ligated to the [Fe(CO)$_3$] fragment has appeared.[262] Treatment of methyl oleate with [Fe(CO)$_5$] under photolytic conditions affords [Fe(CO)$_2$(PPh$_3$)(η^4-α,β-ester)] where the methyl oleate has isomerised on complexation to yield an η^4-oxadiene complex. The isomerised product can be obtained by oxidative decomplexation in >70% yield which is much higher than for previously observed isomerisation processes.[263] The molecular structure of [Fe(CO)$_3$(η^5-C$_5$H$_3$-2,4-Me)][BF$_4$] has been described.[264] A series of cyclic and acyclic pentadienyl complexes of the general form [Fe(CO)$_2$(L)(η^4-1-alkoxy-pentadienyl)]$^+$ (L = CO, PPh$_3$) have been prepared and NMR studies suggest that where L = CO the acyclic complexes have reduced stability, which was proposed to be a result of solvolysis reactions; furthermore, the reactivity of the complexes with a variety of nucleophiles was investigated and several of the products characterised crystallographically.[265] Density functional theory has been used to investigate the bonding of buta-1,3-diene and *o*-xylylene to ruthenium(0) centres.[266] A series of ruthenium diene complexes of the type [Ru(acac)$_2$(η^4-diene)] (diene = 2,5-dimethyl-hexa-2,4-diene, isoprene, 1,2,3,5-tetramethyl-cyclohexa-1,4-diene) have been synthesised by reaction of [Ru(acac)$_3$] with excess diene in the presence of Zn as a reducing agent. The acyclic products show a preference for transoid coordination as revealed by X-ray crystallography.[267] A range of Ru(IV) (η^4-diene) and (η^3-allyl) complexes have been prepared *via* Br$_2$ oxidation of complexes with the general formula [RuBr(η^4-diene)(η^5-C$_5$Me$_5$)]. Two of the complexes have been structurally characterised and the η^4-diene coordination mode strongly approaching the σ^2-η- metallocyclopentene structure.[268] C-C bond formation between vinylidene and alkynyl ligands in the coordination sphere of Ru(II) complexes has lead to the preparation of a diverse range of enyl, dienyl and alkyne complexes, which in some instances have been characterised crystallographically.[269] Linear dienes have been shown to interact with the complex [Ru(NH$_3$)$_4$(OCMe$_2$)$_2$][PF$_6$]$_2$.[270] Cocondensation of 1,4-*bis*(trimethylsilyl)-buta-1,3-diene with cobalt atoms afforded the homoleptic cobalt complex [Co{η^4-C$_4$H$_4$-1,4-(SiMe$_3$)$_2$}$_2$].[271] The complex [Co(η^5-1-propylpentadienyl)(η^5-C$_5$Me$_5$)] was synthesised by treatment of [Co(η^4-cod)(η^5-C$_5$Me$_5$)] with HBF$_4$.OMe$_2$ and the reaction was proposed to proceed *via* an η^3-cyclooctenyl complex containing an agostic hydrogen interaction.[272] Methyl iodide was used as a source of CH$_2$ for the generation of 1,1-disubstituted butatriene complexes of rhodium.[273] The coordination and coupling of OH functionalised C$_2$ units at rhodium centres has been investigated and found to afford a variety of alkene, alkyne, and eneyne products which have been characterised spectroscopically and in some instances by single crystal X-ray diffraction studies.[274] The synthesis and photo-isomerisation of divinyltetramethyldisiloxane and the analogous disilazane complexes has been investigated and the molecular structure of [Rh{η^4-(CH$_2$CH)SiMe$_2$OSiMe$_2$(CHCH$_2$)}(η^5-C$_5$Me$_5$)] determined.[275] Chirality transfer from the asymmetric ligands (L) to the diene in [Rh(η^4-*cis*-1,2-divinylcyclohexane)L] complexes has been observed causing one of the two enantiomeric chair conformations of the cyclohexane ring to be preferred. The use of this conformation preference has been utilised in Pd catalysed oxidative cyclisation reactions using chiral carboxylate nucleophiles.[276]

7 Alkyne Complexes

Quantum mechanical calculations have been carried out on the metal carbonyl species $[M(CO)_5L]$ (M = Cr, Mo or W, L = HC_2H) and $[M(CO)_3L]$ (M = Ni, Pd or Pt, L = HC_2H) and the results obtained agreed well with experimental data.[277] A quantum chemical study has been carried out on the addition of acetylene to Ti-H and Ti-CH_3 bonds.[278] A series of methylated titanocene *bis*(trimethylsilyl)-acetylene complexes have been prepared and their thermal degradation products identified.[279] The permethyltitanocene *bis*(trimethylsilyl)acetylene complex has been shown to be an efficient catalyst for the head to tail dimerisation of alk-1-ynes.[280] *In situ* generated titanium alkyne complexes have been shown to react with a variety of aldehydes.[281,282] The ability of titanocene and zirconocene alkyne complexes to isomerise alkenes has been investigated.[283] The complexes $[Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)(\eta^5\text{-}C_5H_{5-n}Me_n)_2]$ have been prepared.[284] *Ansa*-titanocene and zirconocene *bis*(trimethylsilyl)acetylene complexes have been prepared by the reduction of the corresponding chlorides with Mg in the presence of the free alkyne.[285,286] The compound $[Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ (py = pyridine) reacts with ε-caprolactam to form the O-ligated adduct $[Cp_2Zr(\varepsilon\text{-caprolactam})(\eta^2\text{-}Me_3SiC_2SiMe_3)]$.[287] The synthesis and molecular structure of the vanadium aryne complex $[V(PMe_3)_2(\eta^2\text{-}C_6H_4)(\eta^5\text{-}C_5H_5)]$ has been reported.[288] The preparation and molecular structure of the *ansa*-niobocene alkyne complex $[\{Me_2Si\}(\eta^5\text{-}C_5H_5)_2NbCl(\eta^2\text{-}MeC_2Me)]$ has been reported.[289] The niobium centred coupling of ligated isonitriles in $[NbI_2(CN^tBu)_6][I]$ to yield $[NbI_2(CN^tBu)_4(\eta^2\text{-}{}^tBuNHC_2NH^tBu][I]$ has been discussed.[290] A series of Nb alkyne complexes containing pyrazolylborate ancillary ligands have been prepared;[291–293] additionally the molecular geometries of some of the complexes have been studied theoretically using EHMO calculations.[294] The structure and bonding in redox active d^4, d^5 and d^6 Cr, Mo and W alkyne complexes has been discussed in terms of the metal alkyne moieties acting as electron sinks.[295] Treatment of the complex $[MoCl(CO)_3\{\sigma\text{-}C_6H_4\text{-}2\text{-}CHN(CH_2)_2NMe_2\}]$ with alkynes principally afforded η^{2-}vinyl complexes by alkyne insertion into the metal aryl σ bond, however, 4e donor alkyne complexes were observed spectroscopically;[296] subsequent use of a perfluoroaryl analogue in the analogous tungsten system allowed the structural characterisation of the alkyne containing complex $[WF(CO)\{\sigma\text{-}C_6F_4\text{-}2\text{-}CHN(CH_2)_2NMe_2\}(\eta^2\text{-}EtC_2Et)]$.[297] Treatment of $[Mo(CO)_2(S_2CNMe_2)_2]$ with 1,4,7-trithiacycloundeca-9-yne afforded the dicarbonyl substituted product $[Mo(\eta^2\text{-}RC_2R)(S_2CNMe_2)_2]$.[298] The synthesis and molecular structure of $[MoCl_4(\eta^2\text{-}PhC_2SeC_4H_9)(SEt_2)]$ has been reported.[299] The two Mo(III) alkyne complexes [MoCl(thf)L] (L = PhC_2Me or PhC_2Et) have been prepared and structurally characterised.[300] A series of Mo halo alkyne complexes of the type $[MoX(\eta^2\text{-}RC_2R)_2L]$ (X = Cl, Br, I, L = Cp or Ind) were reported and their conversion by protonation into η^4(5e)-butadienyl complexes discussed.[301] Reaction of the complexes $[Mo(\eta^2-RC_2R')\{P(OMe)_3\}_2Cp][BF_4]$ with R″MgX (R′ = R′ = Me, Ph; R = Ph, R′ = Me; R″ = Me, Et or $PhCH_2$) afforded good yields of compounds $[Mo(\eta^2-RC_2R')R''\{P(OMe)_3\}Cp]$ whereas, treatment with the di-Grignard $CH_2(MgI)_2$ afforded the zwitterionic complexes $[Mo(\eta^2-RC_2R')\{\eta^2-P(OMe)_2OBF_4OP(OMe)_2\}Cp]$: the PhC_2Ph analogue was characterised crystallographically. In the case of the corresponding reaction with $CH_2{=}CHMgBr$ η^3-cyclopropenyl are formed.[302] In a study on the trimerisation of alkynes at Mo centres a series of fluoro-alkyne complexes were prepared.[303] A theoretical study on the bonding of alkynes in high and low valent W complexes has been carried out.[304] *Bis*(alkyne) complexes of the types $[WCl_2(CO)_2(\eta^2\text{-alkyne})_2]$ and $[WCl(SnCl_3)(CO)_2(\eta^2\text{-alkyne})_2]$ (alkyne = PhC_2H, ${}^tBuC_2H$, EtC_2Et and PhC_2Ph) have been prepared by the reaction of the dimeric complex $[(CO)_4W(\mu-Cl)_3WCl(SnCl_3)(CO)_3]$ with alkynes.[305] The synthesis and molecular structure of $[WI_2(CO)(NCPh)(\eta^2-MeC_2Me)_2]$ has been reported.[306] Treatment of the *bis*(alkyne) complexes $[WI_2(CO)(NCMe)(\eta^2-RC_2R)_2]$ with either tridentate sulfur or tridentate phosphorus ligands afforded complexes of the type $[WI_2(CO)(L_2L')(\eta^2-RC_2R)]$ where the non-coordinated sulfur or phosphorus atom has been ligated to a variety of other metal centres allowing the preparation of a variety of multimetallic species.[307,308] Chiral W(II) alkyne complexes containing imine ligands have been synthesised by oxidation of the corresponding amido compounds.[309] Reaction of $[W(NCMe)(\eta^2-PhC_2Ph)_3]$ with *o*-allylphenyldiphenylphosphine in refluxing toluene afforded the tungsten carbene complex (5) which contains an η^4-1,3-diene, a chelated diphenylphosphine ligand and a



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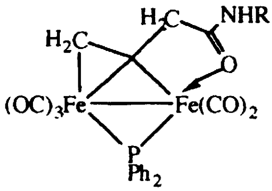
ligated 4e-PhC_2Ph.[310] In contrast, the corresponding reaction with o-styryldiphenylphosphine leads to apparent alkyne and alkene metathesis.[310] The labile complex $[Re(NO)(PPh_3)(CH_2Cl_2)Cp][BF_4]$ reacts with a series of propargylic alcohols to afford the CH_2Cl_2 substituted products $[Re(NO)(PPh_3)(\eta^2\text{-alkyne})Cp][BF_4]$ in good yield.[311] A range of oxoalkylrhenium(VII) alkyne complexes have been prepared.[312, 313] Propargyl complexes have been prepared by hydride abstraction from a variety of Re alkyne complexes and the molecular structure of $[Re(CO)_2(\eta^2-HC_2CH_2OH)Cp^*]$ reported.[314] A range of 4e-alkyne complexes of the type $[ReBr_2(\eta^2\text{-alkyne})Cp]$ (alkyne = PhC_2Ph, PhC_2Me) were prepared by refluxing the dicarbonyl complex $[ReBr_2(CO)_2Cp]$ in toluene in the presence of the alkyne; the reactivity of these complexes was investigated and a series of η^2-vinyl complexes were synthesised.[315] The molecular structure of the ruthenium complex *anti-mer*-[*bis*(2-diphenylphosphinoethyl)(*n*-propyl)amine-*N,P,P′*](phenylethynyl)[(Z)-1-*p*-tolyl-4-phenyl-η^3-but-1-en-3-ynyl]ruthenium(II).$CHCl_3$ has been reported.[316] A series of ω-(phosphinyl)alkylcyclopentadienyl cobalt(I) alkyne complexes have been synthesised by displacement of a ligated alkene from analogous alkene precursors: the molecular structure of the PhC_2Ph derivative has been reported.[317] Treatment of $[RhCl(Sb^iPr_3)(\eta^2\text{-}RC_2R)]$ with NaCp afforded the complexes $[RhCp(Sb^iPr_3)(\eta^2\text{-}RC_2R)]$. The reactivity of these complexes was investigated and the stilbene ligand was found to be readily displaced by CO or CNR affording the simple substitution products $[RhCp(L)(\eta^2\text{-}RC_2R)]$: the addition of an excess of the isonitrile caused alkyne isonitrile coupling to occur.[318] The mechanism of isomerisation of *trans*-$[RhCl(FcC_2SiMe_3)]$ to *trans*-$[RhCl\{CCFc(SiMe_3)\}]$ (Fc = ferrocenyl) has been investigated and the results were consistent with the isomerisation process occurring *via* a 1,2 sigmatropic $SiMe_3$ migration.[319] Reaction of the complexes $[M(acac)(PCy_3)(\eta^2\text{-cyclooctene})]$ (M = Rh or Ir) with alkynes has been investigated and the simple alkyne substituted products $[M(acac)(PCy_3)(\eta^2\text{-alkyne})]$ have been obtained.[320,321] Treatment of nickelocene with 1-norbornyllithium and alkynes affords complexes of the type $[Ni(\eta^2\text{-}RC_2R)(1\text{-nor})Cp]$ (R = Me, $SiMe_3$, Ph, CH_2OMe, CH_2NMe_2, CH_2OSiMe_3, CH_2OH).[322] The molecular structure of $[Ni(\eta^2\text{-}Me_3SiC_2SiMe_3)\{^tBu_2P(CH_2)_2P^tBu_2\}]$ has been reported.[323] The synthesis and molecular structure of the cyclohexyne complex $[Ni(\eta^2\text{-}C_6H_8)\{PCy_2(CH_2)_2PCy_2\}]$ has been reported.[324] A series of homoleptic tetrasubstituted alkynediol complexes of the type $[M(\eta^2\text{-}HOR^1R^2C_2R^1R^2OH)_2]$ (M = Ni, Pt, $R^1 = R^2 =$ Et; $R^1 =$ Me, $R^2 =$ Et, Pr, $\text{-}(CH_2)_5\text{-}$, ^iBu): the molecular structure's of several of these complexes show extended hydrogen bonding interactions.[325] The alkyne complex $[Pt(\eta^2\text{-}C_7H_6)(PPh_3)_2]^*$ (* two possible isomers) were converted into the tropyne complex $[Pt(\eta^2\text{-}C_7H_5)(PPh_3)_2]$ on reaction with $[Ph_3C][BF_4]$.[326] The mechanism of alkyne insertion into Pt-B bonds has been investigated.[327] A series of complexes of the type $[Cu(hfac)(\eta^2\text{-alkyne})]$ (hfac = 1,1,1,5,5,5-hexafluoropentadionate; alkyne = $Me_3SiC_2SiMe_3$ or 3,3,6,6-tetramethyl-1-thia-cycloheptyne) have been synthesised.[328,329] Silver complexes $[Ag(hfac)]_n(\eta^2\text{-alkyne})$ (hfac = 1,1,1,5,5,5-hexafluoropentadionate; n = 1 alkyne = PhC_2Ph, $Me_3SiC_2SiMe_3$; n = 2; alkyne = MeC_2Me, 2-hexyne, 4-octyne) have been prepared and the complex $[Ag(hfac)(\eta^2\text{-}PhC_2Ph)]$ has been structurally characterised.[330]

8 Polymetallic Complexes

8.1 Bimetallic Complexes – The compound $[ZrCp_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2Me)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}MeC_2Me)][BPh_4]$ reacts with alkyl isonitriles to yield complexes of the type $[ZrCp_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2Me)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CNR)][BPh_4]$ by displacement of the bridging but-2-yne ligand.[331] Treatment of the complex $[Mo_2(\mu\text{-}C_8Me_8)Cp_2]$ with one equivalent of $[FeCp_2][PF_6]$ in CH_2Cl_2 affords $[Mo_2(\mu\text{-}C_8Me_8)Cp_2][PF_6]$ which reacts further with either $[FeCp_2]$ or trityl radical $[Ph_3C]^\cdot$ to give $[Mo_2(\mu\text{-}C_8Me_7CH_2)Cp_2]^+$. The mechanism of C-H activation in this complex has been probed electrochemically and discussed in terms of either an EC or EEC mechanism depending upon the oxidant used.[332] Alkyne bridged Mo-Mo dimers containing a selection of functionalised cyclopentadienyl co-ligands of the type $[\{Mo(CO)_2(\eta^5\text{-}C_5H_4\text{-}R)(\eta^5\text{-}C_5H_4\text{-}R')\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}HC_2H)]$ (R = R′ = CO_2Me, C(O)Me; R = CO_2Me, R′ = C(O)Me; R = C(O)Me, R′ = H; R = CO_2Me, R′ = H) have been synthesised. The functional groups on the cyclopentadienyl moiety were shown to be able to undergo modification without affecting the remainder of the complex, for example the acetyl group was converted to a secondary alcohol by $Na[BH_4]$.[333] The synthesis and reactivity of a series of bridging alkylidene complexes of the form $[\{Mo(CO)_2Cp\}_2(\mu\text{-}\eta^2\text{-}CCCRR')]$ have been described. The complexes have been shown to be attacked by nucleophiles at Cγ and electrophiles at Cα; EHMO calculations carried out suggested nucleophilic attack occurs under orbital control, whereas, electrophilic attack is under charge control.[334] Treatment of the fulvalene complex$[FvMo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^2\text{-}MeOCH_2C_2CH_2OMe)]$ with HBF_4 gives the dicarbenium complex $[FvMo_2(CO)_4(\mu\text{-}\eta^3{:}\eta^3\text{-}CH_2C_2CH_2)][BF_4]_2$. This complex has been shown to react with weak nucleophiles like H_2O, anisole and MeOH to quench one of the carbenium centres affording $[FvMo_2(CO)_4(\mu\text{-}\eta^3{:}\eta^2\text{-}CH_2C_2CH_2Nu)][BF_4]$; however, on treatment with stronger nucleophiles like PPh_3 and pyridine both carbenium centres are quenched affording complexes of the type $[FvMo_2(CO)_4(\mu\text{-}\eta^3{:}\eta^2\text{-}NuCH_2C_2CH_2Nu)][BF_4]_2$.[335] The molecular structure of the complex $[Mo(CO)(\eta^4\text{-}C_4H_4)(\mu\text{-}\sigma^1\text{-}\eta^5\text{-}ind)(\mu\text{-}H)Mo(CO)_2(\eta^5\text{-}ind)]$ has been determined.[336] Treatment, in hydrocarbon solvents, of the alkoxide complexes $[M_2(O^tBu)_6]$ (M = Mo or W) with ethyne in the presence of pyridine yields either polyacetylene or the ethyne bridged dimers $[M(O^tBu)_3(\mu\text{-}O^tBu)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2H_4)M(O^tBu)_2(py)]$ by competing pathways.[337] A series of alkyne bridged Mo-W heterobimetallic complexes containing functionalised cyclopentadienyl ligands have been synthesised and their reactivity investigated.[338] Reaction of the tungsten complex $[W_2Cl_2(NCMe)_4]$ with $Li_2C_8H_8$ afforded the W=W bridged complex $[W_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_8H_8)(NCMe)_4]$ and NMR spectroscopy has shown that there are two isomers present in solution; one isomer has been characterised crystallographically and the C_8H_8 ring shown to have a tub like configuration. Fenske-Hall calculations have been carried out on the complex and the results obtained were found to be in good agreement with the experimental results.[339] Treatment of the manganese complex $[Mn_2(CO)_8(NCMe)(PMe_2Ph)]$ with the allene ($MeO_2CHC{=}C{=}CHCO_2Me$) yielded two bridging complexes: $[Mn_2(CO)_7(PMe_2Ph)(\mu\text{-}\eta^2{:}\eta^2\text{-}MeO_2CHCCCHCO_2Me)]$ were slowly transformed into the second $[Mn_2(CO)_6(PMe_2Ph)(\mu\text{-}\eta^3{:}\eta^1\text{-}MeO_2CHCCCHCO_2Me)]$, in which one of the ester carbonyl groups coordinates to one manganese centre.[340] The reactivity of the complex $[Re_2(\mu\text{-}H)(\mu\text{-}C_2Ph)(CO)_8]$ towards a variety of potentially mono- and bidentate ligands has been investigated yielding a selection of carbonyl and hydride substituted products; the molecular structures of the following products were described: $[Re_2(\mu\text{-}H)(\mu\text{-}C_2Ph)(CO)_6(PMe_3)_2]$; $[Re_2\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}C_2Ph)(CO)_8]$; $[Re_2(\mu\text{-}X)(\mu\text{-}dppm)(\mu\text{-}C_2Ph)(CO)_6]$ {X = H, Br, $AuPPh_3$)}; $[Re_2(\mu\text{-}Br)_2(\mu\text{-}dppm)(CO)_6]$.[341] Reaction of the complex $[Re(CO)_2(\eta^5\text{-}C_5Me_5)]_2$ with dimethyl acetylenedicarboxylate affords the dimetallacyclobutene complex $[\{Re(CO)_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}MeCO_2C_2CO_2Me)\}]$ which under photolytic conditions rearranges to $[\{Re(CO)_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}MeCO_2C_2CO_2Me)\}]$:

both complexes have been structurally characterised.[342] The rearrangement of the alkyne ligand in these complexes has been further studied by time resolved IR spectroscopy.[343] The dimer $[Re(CO)_2(\eta^5\text{-}C_5Me_5)]_2$ has been shown to react with NCMe, PMe_3, and C_2H_4 at low temperature to form the complexes $[\{Re(CO)_2(\eta^5\text{-}C_5Me_5)\}(\mu\text{-}CO)Re(CO)(L)(\eta^5\text{-}C_5Me_5)]$ which fragment on warming. If fragmentation occurs in the presence of alkynes, insertion into the bridging CO ligand is observed by the formation of a dimetallacyclopentenone complex.[344] The mechanism for the preparation of the alkenyl complexes $[\{Re(CO)_4\}_2(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^2\text{-alkenyl})]$ by irradiation of the dimer $[Re_2(CO)_{10}]$ in the presence of the alkenes styrene, *trans*-stilbene, 4-methyl-1-cyclohexene, and ethene has been investigated by laser flash photolysis at 350nm.[345] Competitive nucleophilic attack of primary amines on the allenyl complex $[Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CH{=}C{=}CH_2)]$ has been observed this affording complexes **6** and **7**.[346] Treatment of the selenide bridged dimers $[Fe_2(CO)_6(\mu\text{-}Se)_2]$ with the diynes HC_2C_2R (R = Me or Bu) affords both $[Fe_2(CO)_6(Se)_2(\mu\text{-}HC_2C_2R)]$ and $[\{Fe_2(CO)_6(Se)_2\}_2(\mu\text{-}HC_2C_2R)]$, the former complex reacts with $[Os_3(CO)_{10}(NCMe)_2]$ to afford a pentanuclear cluster.[347] Reaction of the complex $[Fe_2(CO)_6(\eta^2\text{-}EtC_2Et)_2]$ with phosphorus donors in the presence of Me_3NO resulted in CO coupling with the ligated alkynes to form a flyover bridged complex. Similar insertion reactions were observed when the incoming ligand was an alkyne and thermal displacement of the coupled organic fragments lead to the isolation of tropones amongst other organic products. The molecular structure of the complex $[Fe_2(CO)_5\{\eta^2\text{-}(CEt_2)C(O)(CEt)_2CHCPh\}]$ was also described.[348] Thermal rearrangement of the dimetallacyclopentenone complex $[Fe_2(CO)_5\{\mu\text{-}\sigma\text{:}\eta^3\text{-}C(O)CHCH\}(\mu\text{-dppm})]$ to the bridging vinyl complex $[Fe_2(CO)_6\{\mu\text{-}C(CH_2)PPh_2CH_2PPh_2\}]$ *via* intramolecular attack of the phosphorus on the carbon metallacycle has been observed; more substantial heating lead to a variety of other rearrangements.[349] Reaction of the complex $[Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CH{=}C{=}CH_2)]$ with dppm yields initially the complex $[Fe_2(CO)_6(\mu\text{-}PPh_2)(\eta^1\text{:}\eta^2\text{-}PPh_2CH_2PPh_2CH{=}C{=}CH_2)]$ *via* nucleophilic attack of dppm at Cα leading to the breaking of the Fe-Fe bond and internuclear migration of one CO ligand; leaving the complex to stand leads to decarbonylation. The reactivity of these complexes was investigated further, and several of the compounds prepared were structurally characterised.[350] Several functionalised butatriene diiron complexes have been prepared from but-2-yne-1,4-diols.[351] Reaction of $[Fe_2(CO)_9]$ with 1,6-dimethylheptalene afforded two complexes that contained two $[Fe(CO)_3]$ moieties



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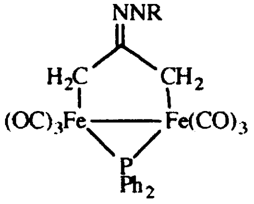

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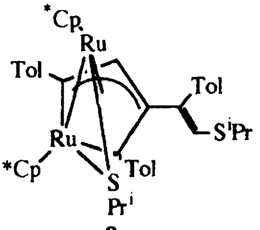
ligated to 1,6-dimethylheptalene, either in a *cis* or *trans* configuration, both of which have been structurally characterised. Complexation of only one $[Fe(CO)_3]$ fragment was also observed.[352] A series of mono-, di- and tri-metallic complexes of the ligand 9,10-dihydro-9,10-dimethyl-9,10-diboraanthracene which contain ancillary π-coligands such as allyl and alkene have been prepared.[353] Reduction of the bridging vinylidene complex $[Ru_2(\mu\text{-}CCH_2)(CO)(\mu\text{-}CO)(NCMe)Cp_2]$ with hydrosilanes has been investigated and yielded complexes of the type $[Ru_2(\mu\text{-}\sigma\text{-}\eta^2\text{-}CCH_2)(CO)_2(SiR_3)Cp_2]$.[354] Reaction of the complexes $[Ru_2(CO)_6\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(Ph)CCH_2\}(\mu\text{-}PPh_2)]$ or $[Ru_2(CO)_6(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CCPh)(\mu\text{-}PPh_2)]$ with an excess of diphenylacetylene affords the analogous compounds where the alkynyl or allenyl ligands oligomerise with the incoming alkyne.[355] Reaction of the nickel complex $[Ni\{\mu\text{-}\eta^1\text{:}\eta^2\text{-bicyclo[2.2.1]hepta-2,5-dien-7-yl-1,2-}CO_2Me\}Cp]$ with $[Ru_3(CO)_{12}]$ affords the ruthenium complex $[Ru_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(CO_2Me){=}CHC(O)OMe\}\text{-}(CO)_4Cp]$ where the bicyclodienyl ligand has been transferred from Ni to Ru.[356] Reaction of the dinuclear complex $[\{Ru(\eta^5\text{-}C_5Me_5)_2\}(\mu\text{-}S^iPr)_2]$ with terminal alkynes afforded the dinuclear ruthenacyclopentenyl complexes (**8**) and it was shown that these compounds react with ^{t}BuNC to afford ring opened μ-alkynyl complexes.[357] Treatment of $[\{Ru(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}H)_4]$ with MeCN or EtCN in the presence of toluene or naphthalene yielded complexes of the type $[\{Ru(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}L)(\mu\text{-}H)(\mu\text{-}NCHR)]$ (L = arene, R = Me or Et) which then react further with ethene to give $[\{Ru(\eta^2\text{-}C_2H_4)(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}H)(\mu\text{-}NCHR)]$. These complexes then undergo dehydrogenative coupling to afford the bridging butadiene complexes $[\{Ru(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}CH_2CHCHCH_2)(\mu\text{-}H)(\mu\text{-}NCHR]$, for R = Et the complex has been structurally characterised.[358] Reaction of the carbene precursors R'_2CN_2 with complexes of the type $[Ru_2(CO)_6(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CCCCR)(\mu\text{-}PPh_2)]$ elongated the carbon chain mainly by attack at the Cα carbon of the butadienyl chain yielding the 1-ynyl-allenyl complexes $[Ru_2(CO)_6\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(CCR)CCRR'\}(\mu\text{-}PPh_2)]$; when R′ = Ph attack was also observed at Cβ yielding an indenyl containing complex **9**.[359] Activation of the methylene protons in the complexes $[Co(\eta^4\text{-}C_5H_6)(\eta^5\text{-}C_5R_5)]$ was observed on treatment with ethene affording the products $[(\eta^5\text{-}C_5R_5)Co(\mu\text{-}C_5H_4)Co(\eta^2\text{-}C_2H_4)(\eta^5\text{-}C_5R_5)]$ which contained cobalt centres linked by a μ-cyclopentadienylidene bridge; the ethene ligand was shown to be labile and easily substituted by CO, ^{t}BuNC, PMe_3 and $P(OMe)_3$.[360] Intermediates in the $Co_2(CO)_8$ initiated living polymerisation of 3-methyl-buta-1,2-diene have been isolated and structurally characterised. The



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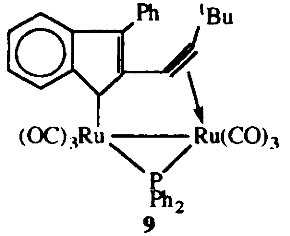

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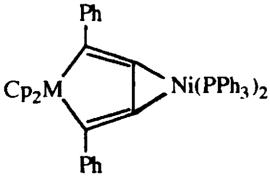
compounds show the presence of η^3-3,3-dimethylallyl moieties bound to the cobalt centres.[361] Room temperature synthesis of alkyne (pentacarbonyl)dicobalt complexes containing the chiral ligand (*R*)-(+)-glyphos has been described. The procedure requires removal of a CO ligand using Me_3NO in the presence of the phosphine with separation of the optically active isomers obtained by preparative HPLC.[362] Another approach for the mild synthesis of alkyne (pentacarbonyl)dicobalt complexes containing phosphine ligands has been described. It was reported that linearly polarised UV light produces results that are comparable with conventional thermal synthetic techniques, however the method was found to be superior when the alkyne contained reactive functional groups.[363] The different complexation abilities of the tetraalkynyl group 14 compounds $M(CCSiMe_3)_4$ (M = Si, Ge, Sn) to $Co_2(CO)_8$ were accounted for on the basis of steric interactions. For example, for Si and Ge only two $Co_2(CO)_6$ fragments could be complexed to the triple bonds, whereas for Sn all of the triple bonds could be utilised.[364] The complexes $[Co_2(CO)_6(\mu\text{-}RC_2R')]$ (R = H, R′ = Ph, ᵗBu; R = Me, R′ = Ph) react with the phosphine 2,3- *bis*(diphenylphosphino)malaic anhydride (bma) either thermally or in the presence of Me_3NO to afford the CO substituted complexes $[Co_2(CO)_4(bma)(\mu\text{-}RC_2R')]$ where the phosphine behaves as a chelating ligand. However, isomerisation occurs to complexes containing a bridging bma ligand on warming. Furthermore heating in excess of 60 °C causes the bma ligand to nucleophilically attack the sterically less hindered acetylenic carbon of the ligated alkyne to give the zwitterionic hydrocarbyl complexes $[Co_2(CO)_4\{\mu\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{:}\eta^1\text{-}RCC(R')PPh_2CCPPh_2C(O)OC(O)\}]$.[365] The preparation of the complex $[Co_2(\mu\text{-}CO)_6(CO)_4(\mu\text{-}PPh_2NHPPh_2)]$ has been reported and its reactivity towards alkynes discussed.[366] The use of dicobalt hexacarbonyl alkyne complexes has continued to receive attention in the area of organic synthesis.[361–371] Replacement of ethene in the complexes $[\{Rh(\mu\text{-}RPz)(\eta^2\text{-}C_2H_4)_2\}_2]$ (R = H, 3-Me, 3,5-Me₂) occurs readily on treatment with ᵗBuNC yielding $[\{Rh(\mu\text{-}RPz)(CN^tBu)_2\}_2]$; where R = H the compound has also been prepared from $[\{Rh(\mu\text{-}RPz)(\eta^4\text{-cod})\}_2]$; it was found that an equilibrium exists between the products and the starting materials in the latter example, and the intermediate formed was identified as $[(cod)Rh(\mu\text{-}RPz)Rh(CN^tBu)_2]$.[372] The reactivity of the co-ordinated hexafluorobut-2-yne containing complexes $[Rh(CO)_2(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)]$ and $[Rh(CO)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)]$ towards a variety of mono- and bidentate phosphines has been investigated.[373] A series of multifunctional imino-phosphino-cyano-fluoro-aromatics have been synthesised and shown to form a diverse range of complexes with Rh(I) either by ligation through the imine or nitrile moieties.[374] The synthesis, molecular structure and bridge cleavage reactions of the complex $[\{Rh(\eta^4\text{-nbd})\}_2(\mu\text{-}OSiMe_3)_2]$ have been described.[375] The molecular structure of the cod analogue has also been reported.[376] Single crystal X-ray diffraction studies on the complexes $[\{Rh(\eta^4\text{-cod})\}_2(\mu\text{-}OEt)_2]$[377] and $[\{Rh(\eta^4\text{-nbd})\}_2(\mu\text{-}Cl)_2]$[378] have been carried out and their molecular structures reported. Treatment of $[\{Rh(\eta^4\text{-cod})\}_2(\mu\text{-}Cl)_2]$ with deprotonated *N*-[(*R*)-1-phenylethyl] thiobenzamide affords the chloro substituted product $[\{Rh(\eta^4\text{-cod})\}_2\{\mu\text{-}SC(Ph)NR_2\}_2]$ which has been structurally characterised.[379] Hetero- and homobimetallic complexes with the general formula $[\{Rh(\eta^4\text{-dialkene})\}_2(\mu\text{-}Cl)(\mu\text{-}SPPh_2)]$ (dialkene = cod, nbd, tetrafluorobenzobarrelene) and $[Rh(\eta^4\text{-dialkene})(\mu\text{-}Cl)(\mu\text{-}SPPh_2)Pd(\eta^3\text{-}C_3H_5)]$ (dialkene = cod, nbd) have been prepared by redistribution reactions of the homobridged analogues.[380] The molecular structure of the complex $[\{Rh(\eta^4\text{-cod})\}_2(\mu\text{-}O_2CH)_2]$ has been reported along with its reactivity towards CO and phosphines.[381] The synthesis of similar series of *bis*(ethene) Rh and Ir carboxylato complexes have been reported and their reactivity towards phosphines and alkynes investigated.[372] The reactivity of the compounds $[Ir_2(H)(CO)_3(\mu\text{-}CH_2)(\mu\text{-dppm})_2][CF_3SO_3]$ and $[RhIr(CH_3)(CO)_3(\mu\text{-dppm})_2][CF_3SO_3]$ towards alkynes has been investigated; for the homometallic Ir complex alkyne and vinylidyne bridged complexes have been isolated, whereas the heterobimetallic species was found to be more reactive, initially forming analogous complexes which under went further ligand-based reactions.[383] A series of Rh_2, Ir_2, RhIr, complexes with dimethylphosphonate and pyrazolate bridging ligands have been prepared in which the cyclic dienes cod and nbd are to be found within the coordination sphere.[384] Treatment of [Ni(cdt)] (cdt = cyclododeca-1,5,9-triene) with functionalised alkynes followed by ethylenediamines gave complexes of the type $[Ni(\text{diamine})(\mu\text{-alkyne})(\eta^2\text{-alkyne})]$. Of particular interest were complexes prepared from alkyne diols as they showed supramolecular structures held together by hydrogen bonds.[385] The complex $[Ni(\eta^2\text{-}C_6H_6)(^tBu_2PC_2H_4P^tBu_2)]$ has been prepared, and found to exist in equilibrium with the dimer $[\{(^tBu_2PC_2H_4P^tBu_2)Ni\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_6)]$, either by thermolysis of $[Ni(Me)_2(^tBu_2PC_2H_4P^tBu_2)]$ or the reduction of $[NiCl_2\text{-}(^tBu_2PC_2H_4P^tBu_2)]$ by Mg in a mixture of thf/C_6H_6. The $(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_6)$ ligand is formally considered to be a cyclohexatriene to which two nickel moieties are ligated in an antarafacial arrangement: this has been confirmed by a single crystal X-ray diffraction study. Furthermore the coordinated benzene in the monomeric complex can be readily displaced by C_6F_6 to yield $[Ni(\eta^2\text{-}C_6F_6)(Bu_2PC_2H_4P^tBu_2)]$ which has also been structurally characterised.[386] Neutral, anionic and cationic Pd(I) dimers have been prepared where the two Pd centres are bridged by conjugated diene ligands.[387] A wide range of Pd-Pd μ-allyl complexes have been synthesised by treatment of $[\{Pd(\eta^3\text{-allyl})\}_2(\mu\text{-}Cl)_2\}]$ with $[Pd(\eta^2\text{-}C_2H_4)\}(PPh_3)_2]$. The allyl groups employed contained electron withdrawing or donating substituents in both the terminal and central carbon positions.[388] The σ-alkynyl complexes *cis*-$[Pt(C_5F_5)_2(C_2R)_2]^{2-}$ and $[Pt(C_2R)_4]^{2-}$ have been shown to react with $[\{Pd(\eta^3\text{-allyl})\}_2(\mu\text{-}Cl)_2\}]$ to give a series of bimetallic complexes by halide displacement reactions at Pd. The alkynyl ligands remain η^1-coordinated to the

Pt precursor and ligate in an η^2- fashion to the Pd centres. This bonding mode has been confirmed by a single crystal X-ray diffraction study.[389] The complex $[\{Pt(Et)(\eta^2\text{-}C_2H_4)\}_2(\mu\text{-}Cl)_2\}]$ has been isolated from the reaction of $K_2[PtCl_4]$ and C_2H_4 in water and its reactivity investigated.[390] Separation of the isomeric mixture of 1,5-dimethyl-cycloocta-1,5-diene and 1,6-dimethyl-cycloocta-1,5-diene has been facilitated by treatment with AgO and Hhfac (Hhfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione). The isomeric silver alkene complexes that are prepared can be successfully separated by fractional crystallisation and the molecular structure of $[\{Ag(\eta^4\text{-}1,5\text{-dimethyl-}1,5\text{-cyclooctadiene})(\mu\text{-hfac})\}_2]$ has been determined.[391] Treatment of $[MCp_2]$ (M = Ti, Zr) with the 1,4-disubstituted Ni diyne complexes $[Ni\{\eta^2\text{-}C(Ph)CCCPh\}(PPh_3)]$ afforded Ni(0) complexes of the five membered titana and zicona cumulenes **(10)**.[392] The synthesis of the mono-alkynyl Ti complexes $[TiCl(CCR)(\eta^5\text{-}C_5H_4SiMe_3)]$ (R = Ph, $SiMe_3$) has been reported. They have subsequently been shown to form complexes with Cu(I)X salts (X = halide or pseudo halide), whereas on treatment with AgX analogues no reaction was observed. However, the *bis*(alkynyl) complexes $[Ti(CCPh)(CCSiMe_3)(\eta^5\text{-}C_5H_4SiMe_3)]$ did form heterobimetallic species with AgX as well as CuX salts.[393] The compound $[Ti(CCSiMe_3)_2(\eta^5\text{-}C_5H_4SiMe_3)]$ has been shown to behave as a diyne ligand towards a series of Cu(I) and Ag(I) σ-alkynyl, vinyl and aryl species and a molecular orbital description of the alkyne bonding in these species was discussed.[394] Additionally a complementary report on the reactivity of these titanium alkynyl complexes towards Cu(I) and Ag(I) halides, pseudohalides and arene thiolates has appeared.[395] The complex $[Ti(CCSiMe_3)_2(\eta^5\text{-}C_5H_4SiMe_3)]$ has also been shown to form trigonal planar complexes with Au(I) alkyl species and the molecular structure of the complex $[Au\{\eta^1\text{-}C_6H_2\text{-}2,4,6\text{-}(CF_3)_3\}\{\eta^2{:}\eta^2\text{-}(Me_3SiCC)_2Ti(\eta^5\text{-}C_5H_4SiMe_3)\}]$ has been reported.[396] The synthesis and reactivity of a series of cycloheptatrienyl bridged bimetallic species of the type $[M(CO)_3(\mu\text{-}\eta^5{:}\eta^1{:}C_7H_7)M'(CO)_2(\eta^5\text{-}C_5R_5)]$ (M = Cr, Mo or W; M′ = Fe or Ru; R = H or Me) have been reported.[397] A series of sesquifulvalene complexes of the type $[CpFe\text{-}Z\text{-}(\eta^7\text{-}C_7H_6)Cr(CO)_3]$ (Z = C_2, *trans*-CHCH-) have been prepared and shown to exhibit an unusually large hyperpolarizability β^{**}.[398] The compounds $[M(CO)(\mu\text{-}H)(\mu\text{-}C_7H_7)Co(\eta^5\text{-}C_5Me_5)]$ (M = Cr, Mo or W) have been prepared by reacting $[Co(\eta^2\text{-}C_2H_4)_2(\eta^5\text{-}C_5Me_5)]$ with $[M(CO)_3(\eta^6\text{-}C_7H_7)]$ and a single crystal X-ray diffraction study reveals that the C_7H_7 ligand adopts a boat conformation ligating η^4 to M and η^3 to Co with the M-Co vector bridged by a 3c2e hydrido ligand.[399] Hydride reduction of the complex $[Pt(PPh_3)_2(\mu\text{-}\eta^2{:}\eta^7\text{-}C_7H_5)Mo(CO)_3]$



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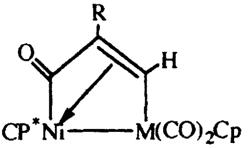
afforded three isomeric products and the major product contained a ligated cyclohepta-1,2,3,5-tetraene ring which was confirmed by a single crystal X-ray diffraction study.[400] The preparation and fluxionality of a bimetallic Pt-Mo complex containing the cyclohepta-1,2,4,6-tetraene ligand has been discussed.[401] The bimetallic complexes [W(CO)(NO)Cp(η^2-RCC)Fe(CO)$_2$Cp] were prepared by reaction of the metallate anion [W(CCR)(CO)(NO)Cp]$^-$ (R = Ph, C$_6$H$_4$-4-Me, ^{t}Bu or SiMe$_3$) with [Fe(CO)$_2$(thf)Cp].[402] Reaction of PhC$_2$H with [Ni(η^5-C$_5$Me$_5$)M(CO)$_3$(η^5-Cp′)] (M = Mo or W, Cp′ = C$_5$H$_5$ or C$_5$H$_4$Me) gave the metallacyclic species (**11**). Alkylation was observed on treatment with [Me$_3$O][BF$_4$] to give the four membered molybdena or tungsta heterocycles (**12**).[403] The dinuclear complex [W(O)(η^5-C$_5$Me$_5$)(μ-H)(μ-CCPh)Re(CO)$_4$] has been prepared by reaction of [Re$_2$(CO)$_8$(μ-CCPh)W(O)(η^5-C$_5$Me$_5$)] with PhSH in refluxing toluene. This complex reacts further with Me$_3$NO in NCMe to give [Re(CO)$_3$(NCMe)(μ-H)(μ-CCPh)W(O)(η^5-C$_5$Me$_5$)] which then dimerises through the oxo ligand by displacement of the ligated NCMe.[404] The Os compound [OsH$_3$(Hbiim)(P^{i}Pr$_3$)] (Hbiim = 2,2′-biimidazole) reacts with the dimers [{M(η^4-cod)}$_2$(μ-OMe)$_2$] (M = Rh or Ir) to form the heterobimetallic species [OsH$_3$(H-biim)(P^{i}Pr$_3$)(μ-biim)M(η^4-cod)].[405] A series of homo- and heterobridged dinuclear complexes that contain the [Rh(C$_6$F$_5$)$_3$] fragment have been prepared starting from the mononuclear complex [RhCl(C$_6$F$_5$)(Hpz)]$^-$ (Hpz = pyrazole).[406]



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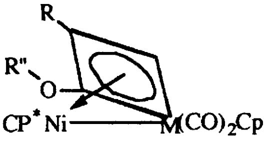

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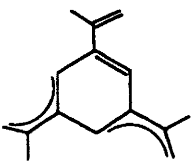
8.2 Multimetallic Complexes

– Reaction of *cis*-[Mo(CO)$_4$(piperidene)] with 1,4-*bis*(diphenylphosphino)but-2-yne afforded two complexes: [{Mo(CO)$_4$}$_2$(μ-dppbu)$_2$] where the phosphine bridges two metal centres and [Mo(CO){η^2-C$_2$(CH$_2$PPh$_2$)CH$_2$PPh$_2$)Mo(CO)$_4$}$_3$] where the phosphine chelates and three of these moieties coordinate to the [Mo(CO)] fragment through the alkyne triple bond.[407] The reaction between [Ru$_3$(CO)$_{12}$] and [Ru$_3$(CO)$_{10}$(NCMe)$_2$] and 1,4-diphenylbuta-1,3-diyne in the presence of Me$_3$NO has been investigated. Two major products were obtained from the reaction with [Ru$_3$(CO)$_{12}$], namely [Ru$_2$(CO)$_6$(PhC$_2$C$_2$Ph)] and [Ru$_2$(CO)$_7$(PhC$_2$C$_2$Ph)], whereas the more reactive acetonitrile containing compound yielded a more complex mixture which included the following [Ru(CO)$_3$(NMe$_3$)(PhC$_2$C$_2$Ph)$_2$], [Ru$_3$(μ_3-PhC$_2$C$_2$Ph)(μ-CO)(CO)$_9$] and [Ru$_4$(CO)$_{12}$(NCMe)$_2$(μ_3-PhC$_2$C$_2$Ph)]. Three of the complexes were characterised by X-ray crystallography.[408] Furthermore the structure of [Ru$_3$(μ_3-PhC$_2$C$_2$Ph)(μ-CO)(CO)$_9$] was reported elsewhere.[409] The reaction between [Ru$_3$(CO)$_3$(μ-CO)(μ_3-CO)(μ_3-CF$_3$C$_2$CF$_3$)Cp] and the acetonitrile derivative $[Ru_3(NCMe)(CO)_2(\mu\text{-}CO)(\mu_3\text{-}CO)(\mu_3\text{-}CF_3C_2CF_3)Cp]$ with alkynes has been investigated and gives rise to a diverse range of products based upon fragmentation and oligomerisation of the ligated $CF_3C_2CF_3$ and the incoming alkyne. Several of the compounds formed have been structurally characterised.[410] A series of papers have appeared concerning the reaction of $[Ru_3(CO)_{12}]$ with the arenes iso-propenylbenzene, 1,4-di-*iso*-propenylbenzene and 1,3,5-tri-*iso*-propenylbenzene. Thermolysis of $[Ru_3(CO)_{12}]$ with *iso*-propenylbenzene afforded amongst other products two in which the cluster only interacted with the arene's side arm, namely $[Ru_3(\mu_3\text{-}H)(CO)_9(\mu_3\text{:}\eta^1\text{:}\eta^1\text{:}\eta^3\text{-}C_3H_2Ph)]$ and $[Ru_5(\mu_3\text{-}H)(CO)_{14}(\mu_4\text{:}\eta^1\text{:}\eta^1\text{:}\eta^3\text{-}C_3H_2Ph)]$ both of which were structurally characterised. Further heating of the trinuclear species afforded $[Ru_6C(CO)_{15}(\mu_3\text{:}\eta^1\text{:}\eta^1\text{:}\eta^3\text{-}C_3H_2Ph)]$.[411] Heating 1,4-di-*iso*-propenylbenzene with $[Ru_3(CO)_{12}]$ afforded a series of clusters with nuclearities ranging from 2–7 in yields < 4% each and four of the complexes have been structurally characterised. Two hexanuclear clusters with the formula $[Ru_6(H)(CO)_{15}(C_{12}H_{15})]$ were structurally characterised in the same crystal and shown to differ only in the non-coordinated side chain which had been hydrogenated in one.[412] Thermolysis of $[Ru_3(CO)_{12}]$ with 1,3,5-tri-*iso*-propenylbenzene lead to the isolation and structural characterisation of two $[Ru_4(CO)_9(C_{15}H_{20})]$ clusters the difference being in the $C_{15}H_{20}$ ligand fragments **(13)**, **(14)**.[413] Thermolysis of $[Ru_3(CO)_{12}]$ with allylbenzene or 4-phenylbut-1-ene afforded the face bound tetranuclear clusters $[Ru_4(CO)_{10}(C_9H_{10})]$ and $[Ru_4(CO)_{10}(C_9H_{12})]$, where in both cases the alkenes have been isomerised to β-alkylstyrenes. The complex formed on reaction with allylbenzene displayed two different arene coordination modes in the solid state namely: $\eta^2\text{:}\eta^2\text{:}\eta^4$- and $\eta^3\text{:}\eta^3\text{:}\eta^3$-. Force field calculations showed the energy differences between the two structures to be minimal.[414] The reaction between norbornene and norbornadiene afforded the tri- and tetranuclear clusters $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{:}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}C_7H_8)]$ and $[Ru_4(CO)_{11}(\mu_4\text{:}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}C_7H_6)]$. Both of these complexes were characterised by single crystal X-ray diffraction studies and the molecular structures discussed in relation to the interactions of nbe (norbornene) and nbd on a Pt(III) surface.[415] The cluster compounds $[M_3(CO)_7(Ph_2PCH_2PPh_2)(\eta^2\text{-}PhC_2Ph)]$ (M = Ru or Os) have been studied electrochemically and it was found that oxidation led the alkyne to orientate perpendicular to the metallic triangle, whereas in the reduced form the alkyne was orientated parallel to the metallic triangle.[416] The synthesis of $[Ru_3(\mu\text{-}PhC_2Ph)(CO)_7(dppm)]$ and $[Ru_3(\mu\text{-}PhC_2Ph)(CO)_8(dppm)]$ occur in >90% yield on reaction of $[PPN][Ru_3(\mu\text{-}Cl)(\mu\text{-}PhC_2Ph)(CO)_9]$ in the presence of dppm $(Ph_2PCH_2PPh_2)$. $[Ru_3(\mu\text{-}PhC_2Ph)(CO)_7(dppm)]$ was subse-



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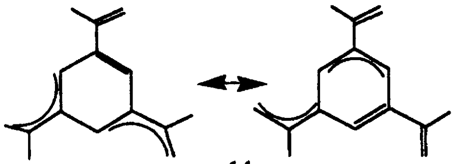

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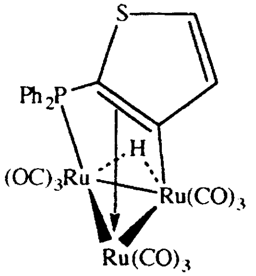
quently reacted with a variety of donor ligands, for example treatment with terminal alkynes led to the formation of some coupled products including the flyover complex $[Ru_3(\mu\text{-}HCC(Ph)C(O)(PH)CCPh)(CO)_6(dppm)]$ and a complex containing a diruthenacyclopentadiene moiety.[417] The cationic cluster $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(\mu\text{:}\eta^1\text{:}\eta^2\text{-}PhC_2HPh)(CO)_8][BF_4]$ (Hampy = 2-amino-6-methylpyridine) has been shown to be an active homogeneous catalyst for the conversion of diphenylacetylene into cis and trans stilbene.[418] Treatment of $[Ru_3(CO)_{12}]$ with diphenylthiophenylphosphine in refluxing toluene yields two compounds **(15)**, **(16)** both of which have been structurally characterised, further treatment with $[Ru_3(CO)_{12}]$ yielded two tetranuclear clusters with elimination of thiophene.[419]



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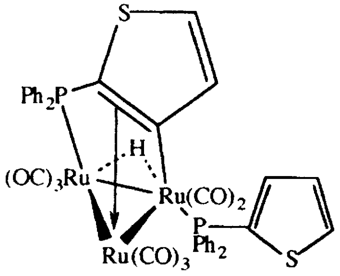

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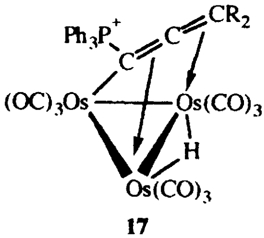
The trinuclear pentahydride complex $[\{Ru(\eta^5\text{-}C_5H_5)\}_3(\mu\text{-}H)_4(\mu_3\text{-}H)_2]$ reacts with buta-1,3-diene or isoprene to give the 1,3-dimetallaallyl complexes $[\{Ru(\eta^5\text{-}C_5H_5)\}_3(H)_4\{\mu_3\text{:}\eta^3\text{-}C(Me)CHC(R)\}_2]$ (R = H or Me), the isoprene derivative has been structurally characterised.[420] The reactivity of the cationic hydridoalkenyl cluster $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(\mu\text{:}\eta^1\text{:}\eta^2\text{-}PhC_2HPh)(CO)_8][BF_4]$ towards neutral and anionic nucleophiles has been investigated. Reaction with PPh_3 or $P(Ph\text{-}4\text{-}Me)_3$ yields the CO substituted products $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(\mu\text{:}\eta^1\text{:}\eta^2\text{-}PhC_2HPh)(L)_n(CO)_{8-n}][BF_4]$ (n = 1 - 3), whereas, reaction with two equivalents of dppm causes elimination of *cis*-stilbene with the formation of $[Ru_3(\mu_3\text{-ampy})(\mu\text{-dppm})(dppm)(CO)_7][BF_4]$.[421] The reaction between the cluster $[Ru_3(\mu\text{-dppm})(CO)_{10}]$ and cycloocta-1,3,5,7-tetraene in refluxing thf affords four products, all of which have been structurally characterised. The compound $[Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(\mu_3\text{-}C_8H_8)(Ph)(CO)_5]$ is noteworthy as being the first example of a cot ligand capping the Ru_3 face in such a cluster.[422] The reaction of $[Ru_3(CO)_{12}]$ with the cyclic alkenes: *cis*-cyclooctene and *trans*-cyclododecane have been investigated and found to yield $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}C_8H_{12})(CO)_9]$ and $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}C_{12}H_{19})(CO)_9]$ where the cycloctene ring coordinates *via* two σ bonds and a π interaction to the Ru_3 triangle, and the cyclododecene ring coordinates by two σ bonds from the allyl moiety to two Ru atoms bridged by an hydrido ligand and η^3- to the third Ru atom.[423] Heating the compound $[Ru_2(\mu\text{-}PPh_2)(\sigma\text{-}C_2{}^tBu)(CO)_6]$ in toluene afforded the tetranuclear butterfly $[Ru_4(\mu\text{-}PPh_2)_2(\sigma\text{-}C_2{}^tBu)(CO)_9]$ cluster and further heating of this compound caused stereospecific head to tail coupling of the alkynyl groups producing an 8e donor butadiyne fragment bound to the Ru_4 cluster.[424] The synthesis and molecular structure of the metallabicyclic cluster 2a-ruthenacyclopent[c,d]indenyl-triruthenium undecacarbonyl from thermolysis of 1,3,5-triisopropylbenzene and $[Ru_3(CO)_{12}]$ has been reported.[425] The ruthenium clusters $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4\text{-}2,4\text{-}CO_2Me)_2(\sigma\text{-}C_2{}^tBu)(CO)_9]$ and $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_4\text{-}2,4\text{-}CO_2Me)_2(\sigma\text{-}C_2{}^tBu)(CO)_9]$ have been prepared and shown by single crystal X-ray diffraction studies to show coordination isomerisation.[426] The anionic allyl containing cluster $[PPN][Ru_6C(CO)_{15}(\eta^3\text{-}C_3H_5)]$ $\{PPN = (Ph_3P)_2N\}$ reacts with $NO_{(g)}$ to give the neutral clusters $[Ru_6C(CO)_{15}(\eta^3\text{-}C_3H_5)]$ and $[Ru_5C(CO)_{11}(NO)_2(NO_2)(\eta^3\text{-}C_3H_5)]$ which have been structurally characterised.[427] A new solid state isomer of $[PPN][Ru_6C(CO)_{15}(\eta^3\text{-}C_3H_5)]$ has been reported, the difference to the previously described structures is the position of the CO and allyl ligands and was attributed to crystal packing forces.[428]. The complex $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}]$ has been reacted with a series of functionalised phosphines including $Ph_2PCH_2PPh_2$, $Ph_2PC_6H_4\text{-}2\text{-}NH_2$, $Ph_2PC_6H_4\text{-}2\text{-}CHCH_2$, leading to the preparation of a variety of substitution products several of which were structurally characterised.[429]. The butatrienylidene fragment ($CCCCH_2$) has been successfully prepared and structurally characterised within a Ru_5 cluster by reaction of $[Ru_5(\mu_4\text{-}C_2)(\mu\text{-}PPh_2)(\mu\text{-}SMe)(CO)_{11}]$ with $Me_3SiC_2SiMe_3$ followed by alkaline hydrolysis yielding $[Ru_5(\mu_4\text{-}CCCCH_2)(\mu\text{-}PPh_2)(\mu\text{-}SMe)(CO)_{10}]$ which was structurally characterised.[430] Other reports from these workers on the reactions of diynes and terminal alkynes with Ru clusters have appeared.[431,432] The compounds $[M_3(CO)_{12-n}\{PPh_2(CHCH_2)\}_n]$ (M = Ru or Os, n = 1 or 2) have been synthesised and thermolysis of $[M_3(CO)_{11}\{PPh_2(CHCH_2)\}]$ causes β-elimination from the vinyl fragment to occur yielding $[M_3(CO)_9(\mu\text{-}H)\{PPh_2(CHCH)\}]$. The report also contained many other examples of β-eliminations associated with the vinyl moiety.[433] Protonation of the clusters $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HC_2R)]$ and $[Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}C_2R)]$ $\{R = CH_2OH, C(Me)_2OH, C(Me)CH_2OH\}$ has been found to afford the complexes $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HCCR'_2)]^+$ and $[Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}CCCR'_2)]^+$ that contain either 5e or 6e donor propargyl ligands. These clusters were shown to react with PPh_3 yielding the phosphonium derivatives $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HCCR'_2PPh_3)]^+$ and $[Os_3(CO)_9(\mu\text{-}H)\{\mu_3\text{-}C(PPh_3)CCR'_2\}]^+$ the latter containing an unusual phosphonium allenyl ligand (**17**).[434] The molecular structures of the two



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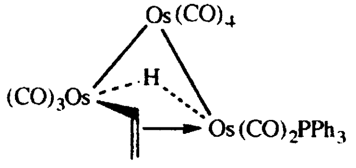
complexes (**18**), (**19**) prepared from the reaction of $[Os_3(\mu\text{-}H)(CO)_9(PPh_3)]$ and ethyne have been determined; VT ^{13}C NMR studies show the isomers



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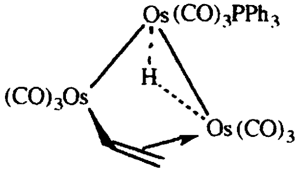

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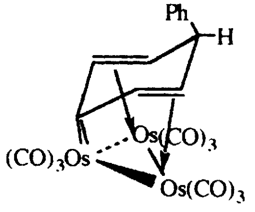
interconvert in solution.[435] The thioketone containing complex **(20)** has been prepared by reacting the side-bound carbene containing complex **(21)** with either S_8 or cyclohexene sulfide.[436] The cluster $[Os_6(H)(CO)_{20}\{\mu\text{-}\eta^2\text{-}NC_5H_4\text{-}2\text{-}(CHCH_2)\}]$ has been prepared from the coupling of the two clusters $[Os_3(H)_2(CO)_9\{\mu_3\text{-}NC_5H_4\text{-}2\text{-}(CHCH_2)\}]$ and $[Os_3(CO)_{10}(NCMe)_2]$.[437] The bridging alkylidene containing complexes $[Co_3(\mu_3\text{-}CR)(CO)_9]$ (R = Me or CO_2Me) react with $PPh_2(CHCH_2)$ to give the CO substituted complexes $[Co_3(\mu_3\text{-}CR)(CO)_{9-n}\{PPh_2(CH{=}CH_2)\}_n]$ (R = Me, n = 1 or 2: R = CO_2Me, n = 1, 2 or 3). Thermolysis of these compounds results in CO dissociation and coordination of the vinyl moiety. Reaction with the bidentate phosphine $Ph_2PCH{=}CHPPh_2$ leads only to the dicarbonyl substituted product $[Co_3(\mu_3\text{-}CR)(\mu\text{-}Ph_2PCH{=}CHPPh_2)(CO)_7]$.[438] Treatment of the diyne complex $[Co_3(\mu_3{:}\eta^2{:}\eta^2\text{-}PhC_2C_2Ph)(CO)_6]$ with 2,3-*bis*(diphenylphosphino)malaic anhydride (bma) under reflux gave three new complexes **(22)**, **(23)**, **(24)** in low yields, however the use of milder conditions, Me_3NO, CH_2Cl_2 gave the thermally sensitive tetranuclear complex **(25)**. EHMO calculations have been carried out on several of the compounds prepared.[439] The cyclobutadiene complex $[Co\{\eta^4$-trans-



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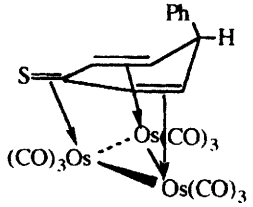

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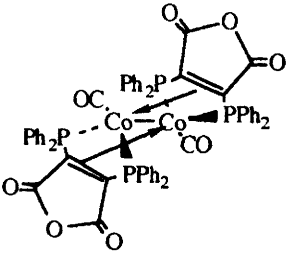

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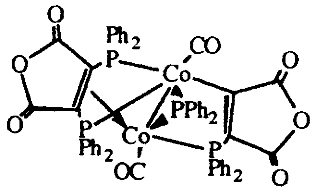

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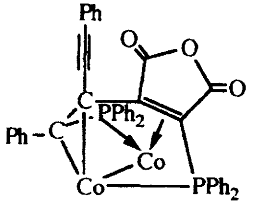

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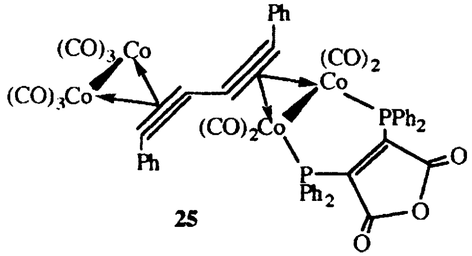

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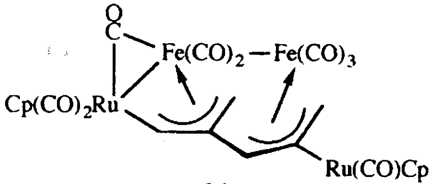
$C_4(SC_2SiMe_3)_2(SiMe_3)_2\}Cp]$ was prepared by a [2 + 2] cycloaddition reaction of $(Me_3SiCC)_2S$ mediated by either $[Co\{\eta^2\text{-}C_2H_4)_2Cp]$ or $[CpCo(\mu\text{-}C_5H_4)Co\{\eta^2\text{-}C_2H_4)Cp]$. The compound then reacted further with $Co_2(CO)_8$ leading to complexation of $[Co_2(CO)_6]$ fragments to the pendant alkyne moieties of the cyclobutadiene ring.[440] The synthesis of hexakis(but-3-ynl)benzene has been reported along with its coordination *via* the alkyne groups to six $[Co_2(CO)_6]$ fragments.[441] The synthesis and molecular structures of the 60e clusters $[Rh_4(\mu\text{-}p\text{-}MeC_6H_4N(diene)_4]$ (diene = cod or tetrafluorobenzobarrelene) have been described and the organoimido moiety was shown to bridge a trimetallic Rh core with the final Rh η^5- bound to an arene ring.[442] Treatment of these compounds with CO caused migration of the isolated Rh atom into the main cluster core leading to a butterfly arrangement of Rh atoms.[443] Stepwise construction of a collection of homo- and heteronuclear Rh and Ir clusters has been reported to be aided by the ligand benzimidazole-2-thiol (H_2bzimt) thus reaction of $[\{M(acac)(cod)\}_2]$ with affords the dinuclear compound $[M(\mu\text{-}Hbzimt)_2(cod)_3]^+$ which reacts further with $[M(cod)(OCMe_2)]^+$ to give $[M_3(\mu\text{-}Hbzimt)(cod)_2]$.[444] The synthesis of the tetranuclear complexes $[M_4(\mu_4\text{-}PyS_2)_2(dialkene)_4]$ (M = Rh, dialkene = cod, nbd, tetrafluorobenzobarrelene; M = Ir, dialkene = cod; PyS_2 = 2,6-pyridinedithiolate) has been reported to occur on reaction of $[\{M(\mu\text{-}Cl)(dialkene)\}_2]$ with $Li_2(S_2Py)$, which was generated *in situ*, in high yield. This synthetic method was extended to the preparation of $[M_4(\mu_4\text{-}PyS_2)_2(allyl)_4]$ and the reactions of these complexes with CO and PPh_3 was also described.[445] A series of trinuclear Rh and Ir cod clusters containing 1,8-naphthyridin-2-one have been prepared and shown to be fluxional on the NMR time scale.[446] Reaction of [Ni(cdt)] (cdt = cyclododeca-1,5,9-triene) with 2-methyl-4-trimethylsilyl-3-butyn-2-ol gives the homoleptic compounds $[Ni_3(alkyne)_4]$ which have been structurally characterised. The structure shows a bent chain of Ni atoms connected by two bridging alkyne units.[447] The synthesis and structure of the tetranuclear C_{70} derivative $[C_{70}\{Pt(PPh_3)_2\}_4]$ has been reported.[448] Reaction of $[NBu_4]_2$ *trans*-$[Pt(C_2R)_2(C_6F_5)_2]$ (R = Ph, $SiMe_3$, ^tBu) with two equivalents of *trans*-$[PdH(L)_2(OCMe_2)]^+$ (L = PPh_3 or PEt_3) afforded the trinuclear complexes *trans-trans-trans*-$[\{Pt(C_6F_5)_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2R)_2\}\{PdH(L)_2\}_2]$.[449] The alkyne 3,3,6,6-tetramethyl-1-thia-cyclohept-4-yne has been used in the preparation of a series of polynuclear Cu(I) alkyne complexes.[450,451] The synthesis and optical properties of the compound $[Cu_4(\mu\text{-}dppm)_4(\mu_4\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}C_2)][BF_4]_4$ has been reported.[452] The silver cluster $[Ag_3(\mu_3\text{-}$

$C_2Ph)_2(dppm)_3]$ which contains an isosceles triangular arrangement of Ag atoms and two asymmetric phenylacetylide capping ligands was prepared from the reaction between $[AgC_2Ph]$ and dppm in CH_2Cl_2.[453] Treatment of of $[Cr(CO)_3(\eta^6\text{-}PhC_2Ph]$ with $[M_4(CO)_{12}]$ (M = Co or Rh) causes cluster fragmentation and complexation to the free CC triple bond. For Co, complexation occurs as the $[Co_2(CO)_6]$ moiety, whereas, for Rh, three CO ligands dissociate affording on complexation $[Rh_4(CO)_9(\mu_5\text{-}\eta^2\text{:}\eta^6\text{-}PhC_2Ph)Cr(CO)_3]$, which was characterised by a single crystal X-ray diffraction study.[454] The diyne $Me_3SiC_2C_2SiMe_3$ reacts with $[\{Mo(CO)_2Cp\}_2]$, $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ and $[Ru_3(CO)_{10}(NCMe)_2]$ to afford $[Mo_2(\mu\text{-}\eta^2\text{-}\ Me_3SiC_2C_2SiMe_3)(CO)_4Cp_2]$, $[Pt(\eta^2\text{-}Me_3SiC_2C_2SiMe_3)(PPh_3)_2]$ and $[Ru_3(\mu_3\text{-}\eta^2\text{-}Me_3SiC_2C_2SiMe_3)(\mu\text{-}CO)(CO)_9]$ respectively. The non-complexed alkyne moieties readily form adducts with other fragments such as $[Co_2(CO)_8]$. The silyl groups were easily removed on reaction with $[NBu_4]F$ in wet thf yielding complexes containing the $(\eta^2\text{-}RC_2CCH)$ fragment. The alkyne carbon C-H bond was found to oxidatively add to a variety of species leading to higher nuclearity clusters.[455] The heteronuclear butterfly complex $[Co_2Mo_2(\mu_3\text{-}CPh)_2(\mu_4\text{-}PhC_2Ph)(CO)_4Cp_2]$ has been prepared from the reaction of $[Mo_2(\mu\text{-}PhC_2Ph)(CO)_4Cp_2]$ with $[Co_2(\mu\text{-}PhC_2Ph)(CO)_6]$ or treatment of $[Mo_2(\mu\text{-}PhC_2C_2Ph)(CO)_4Cp_2]$ with $[Co_2(CO)_8]$.[456] Furthermore the analogous Mo_2 clusters containing the following alkynes HC_2H, MeC_2Me, $MeO_2CC_2CO_2Me$, PhC_2H, MeC_2H or $MeCO_2C_2H$ have been shown to react to give similar heteronuclear compounds.[457] Treatment of $[PPN][Fe_3(CO)_9(\mu\text{-}C_2OC(O)Me)]$ with the carbonylate anion $[Re(CO)_5]^-$ led to the preparation of the mixed metal compound $[PPN][Fe_3(CO)_9(\mu\text{-}C_2)Re(CO)_5]$ which has been structurally characterised.[458] The crystal and molecular structure of the compound $[Cp_2Ru_2Fe_2(CO)_8(\mu\text{-}CO)(\mu_4\text{-}\eta^6\text{-}C_6H_6)]$ (**26**) has been described.[459] This compound had previously been observed as a minor component in the reaction mixture obtained on reaction of $[Ru(CO)_2(CHCCH_2)Cp]$ with $[Fe_2(CO)_9]$.[460] Reaction of the cationic compounds $[Fe(CO)_2\ \{PPh_2(C_2R)\}Cp][BF_4]$ (R = H, Me, Ph or *p*-tolyl) with $[Co_2(CO)_8]$ yield the heteronuclear compounds $[CpFe(CO)_2\{\mu\text{-}\sigma\text{-}\eta^2\text{-}PPh_2(C_2R)\}Co_2(CO)_6][BF_4]$, where R = Ph the compound has been structurally characterised.[461] The iron containing silylacetylene $[Cp(CO)_2FeSi(Me)_2C_2Si(Me)_2Fe(CO)_2Cp]$ has been shown to react with $[Co_2(CO)_8]$ where the $[Co_2(CO)_6]$ moiety is found to coordinate to the alkyne triple bond.[462] A series of dicobalt complexes of the type $[Co_2(\mu\text{-}RC_2R)(CO)_6]$ have been reacted with Ph_2PCH_2SR (R = Me or Ph) and found to afford the CO substituted products $[Co_2(\mu\text{-}RC_2R)(CO)_5(L)]$. Heating causes chelation of the sulfur with further displacement of a CO ligand. However, treatment of the



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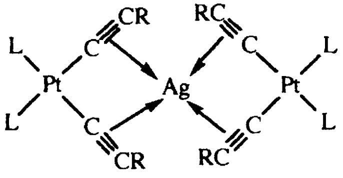
cluster $[Co_2Fe(\mu_3\text{-}S)(CO)_9]$ with Ph_2PCH_2SR only yielded the bridged compounds $[Co_2Fe(\mu_3\text{-}S)(Ph_2PCH_2SR)(CO)_7]$.[463] Reaction of the vinylidene containing compound $[Cp(CO)_2MnPt(\mu\text{-}CCHPh)\{Ph_2P(CH_2)_3PPh_2\}]$ with $[Fe_2(CO)_9]$ proceeded stepwise by *trans*-metallation of the vinylidene ligand to give $[(dppp)PtFe(\mu\text{-}CCHPh)(CO)_4]$ and $[(dppp)PtFe_3(\mu_4\text{-}CCHPh)(CO)_9]$.[464] The reaction of the complex with $[Ir(\eta^4\text{-}C_4H_2S\text{-}2,5\text{-}Me)Cp^*]$, $[Co_2(CO)_8]$, $[Co_4(CO)_{12}]$, $[Co_4(CO)_9(\eta^6\text{-}C_6H_3Me_3)]$, $[Ru_3(CO)_{12}]$, $[Re_2(CO)_{10}]$, $[Mn_2(CO)_{10}]$ or $[\{RuCl_2(\eta^6\text{-}C_6H_6)\}_2]$ has been investigated and shown to yield a variety of multimetallic clusters.[465,466] Reaction of the anion $[Ru_4H(CO)_{12}BH]^-$ with $[\{Rh(nbd)\}_2(\mu\text{-}Cl)_2]$ and $[Au(PR_3)Cl]$ (R = Ph, C_6H_{11}, C_6H_4-2-Me) led to the preparation of the cluster compound $[RhRu_4H(nbd)(CO)_{12}BAu(PR_3)]$ which for R = Ph was structurally characterised. It was also found that the nbd ligand could be readily displaced by donor ligands.[467] Reaction of the alkynyl compounds *cis*-$[Pt(C_2R_2)L]$ (R = Ph, L = 2 PPh_3, 2 PEt_3, dppe; R = ^tBu, L = 2 PPh_3 or dppe) with 0.5 equivalents of $AgClO_4$ afford compounds of the type $[Pt_2Ag(C_2R_2)_4L_4][ClO_4]$. The compound where R = Ph and L = PPh_3 has been structurally characterised and showed that the Ag atom was π-bound to all four alkyne fragments **(27)**. Reaction with one equivalent of $AgClO_4$ lead to a series of complexes believed to have the empirical formula $[Pt_2Ag_2(C_2R_2)_4L_4]][ClO_4]$ **(28)**.[468]



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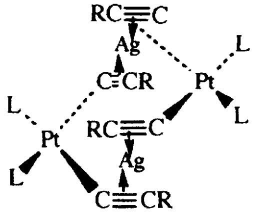

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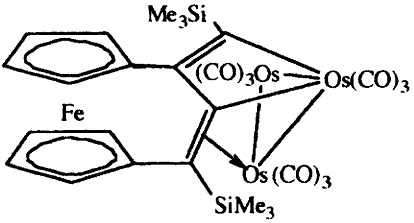
8.3 Ferrocenyl Containing Complexes - The synthesis of the ferrocenyl substituted cyclopentadienide $Li[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4\text{-}C_5Me_4)]$ and its reactivity towards the allyl containing complexes $[MoBr(CO)_2(NCMe)(\eta^3\text{-}C_3H_5)]$ and $[WCl(CO)_2(NCMe)(\eta^3\text{-}C_3H_5)]$ has been reported and the products of the reactions were the bimetallic complexes $[FeCp(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{-}C_5Me_4)M(CO)_2(\eta^3\text{-}C_3H_5)]$. Treatment of the analogous molybdenum complex $[FeCp(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{-}C_5H_2Me_2)Mo(CO)_2(\eta^3\text{-}C_3H_4\text{-}Ph)]$ with $[Cr(CO)_6]$ in Bu_2O/thf afforded the trimetallic complex $[FeCp(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4\text{-}C_5H_2Me_2)Mo(CO)_2(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4\text{-}Ph)Cr(CO)_3]$.[469] Deprotonation of the propargyl site in racemic or enantiomerically pure $[TpWI(CO)(\eta^2\text{-}MeC_2Ph)]$ yields an η^2-allenyl anion which was then quenched with a variety of aldehydes and ketones including formyl ferrocene, the latter yielded $[TpWI(CO)(\eta^2{:}\eta^5\text{-}PhC_2CHC(Me)C_5H_4FeCp)]$ which has been structurally characterised.[470] The synthesis of the tetranuclear cluster complexes $[RuM_3(\mu\text{-}H)(CO)_{12}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2{:}C_2Fc)]$ (M = Ru or Os, Fc = ferrocenyl) has been reported.[471] The reaction of 1,4-diphenylferrocenyl-buta-1,3-diyne with $[Ru_3(CO)_{12}]$ has been investigated and shown to yielded a variety of products based upon alkyne coupling reactions.[472] Treatment of the complex $[Os(\mu\text{-}CO)(CO)_9(\eta^3\text{-}Me_3SiC_2Me)]$ with $[FeCp(\eta^5\text{-}C_5H_4C_2H)]$ affords $[Os(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2\text{-}C(SiMe_3)C(Me)CHCFc)]$ the molecular structure of this compound has been confirmed by an X-ray diffraction study.[473] Addition of $[Fe(\eta^5\text{-}C_5H_4C_2SiMe_3)_2]$ to $[Os_3(CO)_{10}(NCMe)_2]$ afforded two products $[Os_3(CO)_{10}\{\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}Me_3SiC_2C_5H_4Fe(\eta^5\text{-}C_5H_4C_2SiMe_3)\}]$ and $[Os_3(CO)_9\{\mu_3\text{-}\eta^4\text{-}Fe(\eta^5\text{-}C_5H_4C_2SiMe_3)_2\}]$ the latter having been characterised crystallographically. The structure revealed that the Os_3 triangle is capped by a dienediyl fragment derived from the two alkyne functionalities; furthermore, one of the $SiMe_3$ groups has undergone a 1,2-shift during the rearrangement (**29**).[474] Treatment of the diyne complexes $[RC_2Co(CO)_6C_2Co(CO)_6R']$ $\{R = Ph,\ R' = Fe(\eta^5\text{-}C_5H_4)Cp\}$ with $P(OMe)_3$ affords complexes of the type $[RCCC_2Co(CO)_{6\text{-}n}\{P(OMe)_3\}_nR']$ (n = 1 - 3) and the reaction with dppm was found to give two compounds $[RC_2C_2Co(CO)_4(dppm)R']$ and $[RC_2C_2Co(CO)_4(\mu\text{-}dppm)C_2Co(CO)_4R']$. The complexes have been studied electrochemically and the results suggest there is communication between the Fc and Co_2C_2 units.[475] Reaction of the cationic complex $[Ir(py)_2(\eta^4\text{-}cod)]^+$ with the chelating bidentate phosphines 1,1′-*bis*(diphenylphosphino)ferrocene, 1-(diisopropylphosphino)-1′-(diphienylphosphino)ferrocene and 1,1′-*bis*(diisopropylphosphino) ferrocene afford the pyridine substituted complexes $[Ir(L\text{-}L)(\eta^4\text{-}cod)][PF_6]$. These complexes distort towards a tetrahedral geometry, to reduce steric interactions, and so chirality is induced. The interchange between the stereoisomers has been investigated by VT ^1H NMR spectroscopy.[476] Treatment of the ferrocenyl complex (**30**) with $Li_2[PdCl_4]$ in the presence of NaOAc afforded a chloro bridged Pd allyl compound (**31**). The halo bridge was cleaved by PPh_3 and the product was characterised by a single crystal



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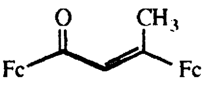

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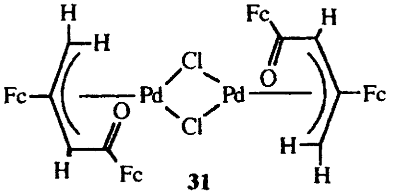

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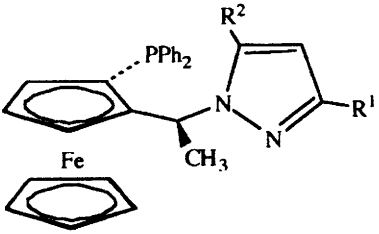
X-ray diffraction study.[477] A series of PN ligands based upon the ferrocenyl backbone (**32**) has been prepared and used as ligands in Pd complexes used for asymmetric allylic amination reactions. The molecular structures of the complexes [Pd(η^3-C_3H_3-1,3-Ph_2)(L-L)][PF_6] (L-L = (**32**), R^1 = Ph, R^2 = Me; R^1 = H, R^2 = 9-triptycyl) were reported.[478] Further crystallographic studies on Pd allyl complexes containing these PN ferrocenyl ligand types have been reported.[479] A chiral PS auxiliary ligand derived from thioglucose has been prepared (**33**) and the molecular structure of the complex [Pd(η^3-C_3H_3-1,3-Ph_2)(**33**)][CF_3SO_3] has been described.[480] A chiral planar PSO ligand containing a ferrocenyl backbone has been prepared (**34**) and its complexation to Pd(II) allyl species investigated. The molecular structures of the compounds [Pd(η^3-C_3H_5)(**34**)] and [Pd(η^3-C_3H_3-1,3-Ph_2)(**34**)] have been reported.[481] A collection of Pd(0), Pd(II), Pt(0) and Pt(II) complexes containing the ligand [Cp{η^5-4-endo-N'N'-dimethylamino-3-(diphenylphosphino)-4,5,6,7-tetrahydro-1-indenyl}]iron have been prepared and



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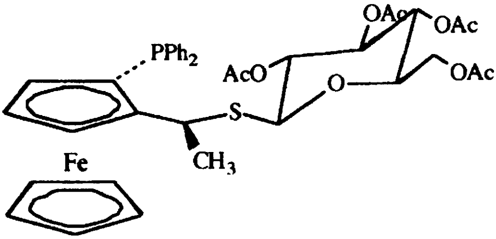

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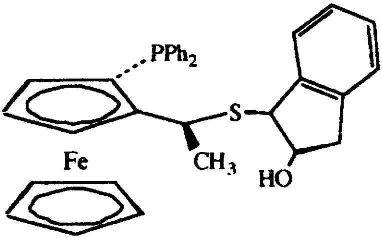

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studied as Grignard cross-coupling catalysts: three of the complexes prepared were structurally characterised.[482]

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14

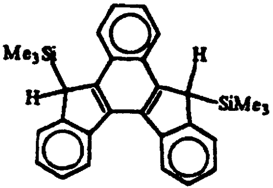
η^5-C_5H_5 and η-Arene Substituted Transition Metal Complexes

BY I.R. BUTLER

1 Introduction[1]

The format of this review[1] has changed to some extent this year because of space limitations which has meant that the total number of references covered is reduced. Thus priority has been placed on those references dealing with the chemistry of cyclopentadienyl and arene ligands rather than merely covering all compounds which contain these ligands. Other references for cyclopentadiene containing ligands may be found in earlier chapters of this book.

1.1 General and Main Group – The reaction of compound (**1**) with *n*-BuLi followed by treatment with a number of metal-halides results in the formation of novel complexes exemplified by the crystallographically characterised (**2**).[2] The mechanism of solid state *cis-trans* isomerism in *pseudo*-five-coordinate complexes of the general type $CpML_4$ has been shown to probably occur via a combined Berry *pseudo* rotation/turnstile mechanism.[3] The reactions of lithium cyclopentadienide with a range of isocyanates yields mono-carbamoyl-substituted cyclopentadienes of the type $[(C_5H_4CONHR)^-]$ which can be used in the direct preparation of carbamoyl-substituted metallocenes.[4] A fibre optic probe has been used to obtain *in situ* infrared spectra of electrolysed solutions of organometallic species such as acetylferrocene.[5]



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[1] Throughout this review the abbreviations Cp, Cp′, Cp*, Cp#, Bz, hmb and Fp explicitly denote (η^5-C_5H_5), (η^5-C_5H_4Me), (η^5-C_5Me_5), (unspecified range of substituted cyclopentadienyls), (η^6-C_6H_6), (η^6-C_6Me_6) and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ respectively. Other abbreviations are as listed in the Abbreviations list.

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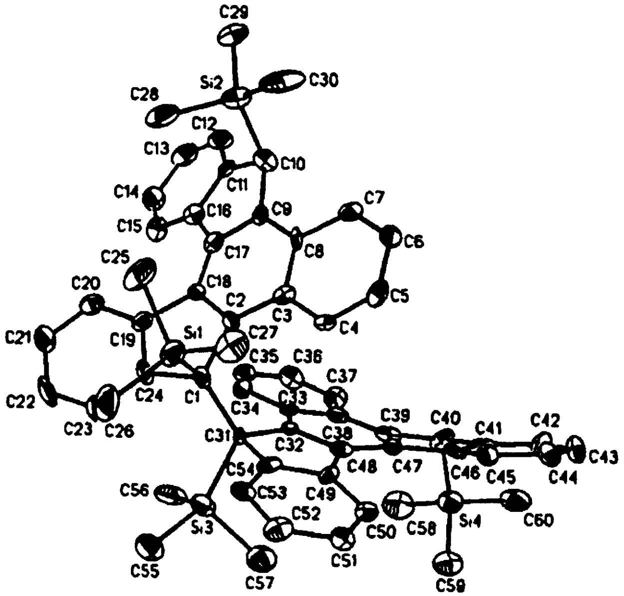

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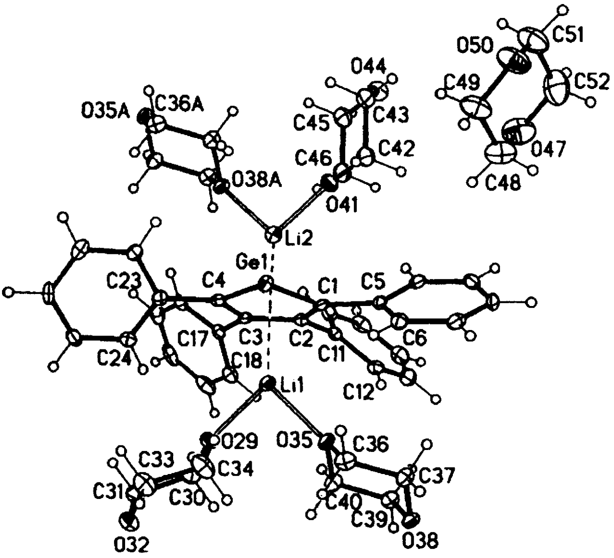
The plumbocene, bis{(*tert*-butyldimethylsilyl)-tetramethylcyclopentadienyl}-lead, has been synthesised and structurally characterised – the cyclopentadienyl ligands are planar and staggered in the solid state.[6] The nitrogen donor adducts of plumbocene [Cp_2Pb.tmeda] and [Cp_2Pb(4,4-Mebipy)] have been obtained in the direct reaction of plumbocene with the N-donor ligands.[7] The general valence force field of the free cyclopentadienyl anion has been developed with internal coordinates and this has been applied to the TlCp and KCp systems.[8]

A range of alkaline earth metallocenes with pendant substituents have been structurally characterised – these were obtained in the reactions of the appropriate cyclopentadienyl anions with $M[N(SiMe_3)_2]_2$, M = Ca, Sr, Ba in toluene,[9] while the successful synthesis of sodocene sandwich complexes $[Cp_2Na]^-$ $[PPh_4]^+$ and $[Me_2C_2Cp_2Na^-.thf][PPh_4]^+$ has been achieved.[10] The compound [CpSn(μ_2-$OBu^t)_2Ge(OBu^t)$], which shows an average between η^1 and η^3-binding modes for the Sn-Cp bond, has been structurally characterised in a paper dealing with salt elimination reactions of [CpSnCl] with potassium alkoxometallates.[11] The metallation of cyclopentadienylboranes [$C_5H_5BR_2$] (R = NMe_2, $0.5(OCMe_2)_2$, Pr^i, Me) gave the corresponding borylcyclopentadienes, $M[C_5H_5B_2]$, M = Li, Na.[12] The reaction chemistry of lithium cyclopentadienide with dimethyldichlorosilane has once again been used in the preparation and isolation of a range of dimethylsilyl linked dimetallocenes,[13] and the reaction chemistry of decamethylsilicocene [$Cp^*{}_2Si$] with a range of small molecules, e.g. CO_2, COS, CS_2 and PhNCS has been explored. In the case of CS_2 a multistep rearrangement occurs with the formation of a highly unusual dithiadisiletane complex.[14] The ligand [2-(*N*,*N*-

dimethylamino)ethyl]cyclopentadienide as its anion has been reacted with gallium chlorides to yield σ-bonded gallium-Cp complexes.[15] Related work on a range of novel gallium chalcogen cubanes $[Cp^{\#}Ga(\mu_3\text{-}E)]_4$, E = S, Se, $Cp^{\#}$ = Cp, Cp^* were obtained in the dehalosilylation reactions of $E(SiMe_3)_3$ with $Cp^{\#}GaCl_2$.[16] Charge density topological studies of the Group 2 metallocenes $M(Cp)_2$, M = Mg, Ca have been carried out and it has been demonstrated that the geometries of these species can be understood in terms of the repulsive interactions between the ligands and between the ligands and the metal atom core.[17]

The cyclopentadienylaluminium complex $[\eta^1\text{-}(C_5H_5)_2AlO^iPr]_2$ has been prepared and fully characterised by NMR and X-Ray structural analysis,[18] while the$[Al(C_5H_5)_2]^+$ cation has been used as an initiator in the cationic polymerisation of isobutene.[19] The rubene salt species $[\{Na^+(thf)\}_4(rubene^{4-})]$ has been crystallographically characterised.[20] The synthesis of chiral *O*-functionalized isobornyloxy, menthgloxyl and fenchyloxy cyclopentadienyl ligands has been achieved in a relatively simple synthetic methodology (four steps).[21] A general synthesis of a 'molecular pinwheel', [3.3.3.3.3.3](1,2,3,4,5,6)-cyclophane may captivate the imagination of bis-arene chemists for future synthetic studies synthesis.[22] The synthesis of tetraalkylcyclopentadiene using ostensibly a one pot procedure has been documented – the methodology utilises phase transfer coupling reactions.[23] A new route to optically pure 3-oxodicyclopentadiene has been described using racemic 4-*tert*-butoxycyclopent-2-en-1-one as a precursor in lipase-mediated synthetic approach.[24] Further work has been carried out on tetraphenylgermole dianions which have been shown to be aromatic. An intriguing X-ray characterisation of a dilithium salt (3) appears in this publication.[25] Again a kalocene-type



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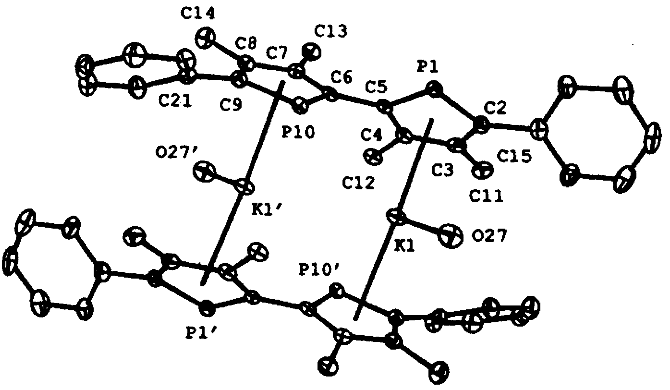

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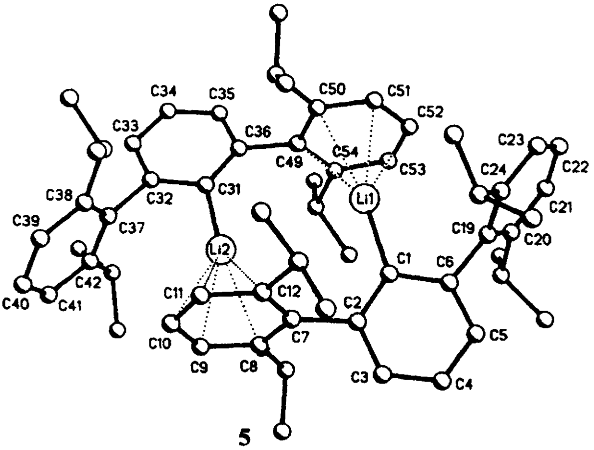
phosphole has been obtained in the cleavage reaction of a phosphole tetramer with potassium in DME – this compound is shown as (**4**).[26]

Multinuclear NMR studies have been carried out on tris(indenyl)methylsilane[27] while in a study of a vast range of compounds dealing with the rationalisation of metal-A-metal (A=*p*-block element) cyclopentadienyl complexes are included in the broad range of ancillary ligand classes.[28] The pentaethynylcyclopentadienyl radical has been described as unusually stable in a synthetic paper which utilizes the coupling reactions of tetra-bromocyclopentadienes with alkynes.[29] The X-ray structure of the lithium cyclopentadienide $[Ph_2PMe_2][(\eta^5\text{-}C_5H_4Bu^t)_2Li]$ has been determined in a procedure developed for ytterbium cyclopentadienyl complex synthesis.[30] The interesting synthesis of a σ- and π-arene bound lithium complex of a tetra-isopropyl-substituted diaryl has been reported – the structurally characterised complex is shown as (**5**).[31]



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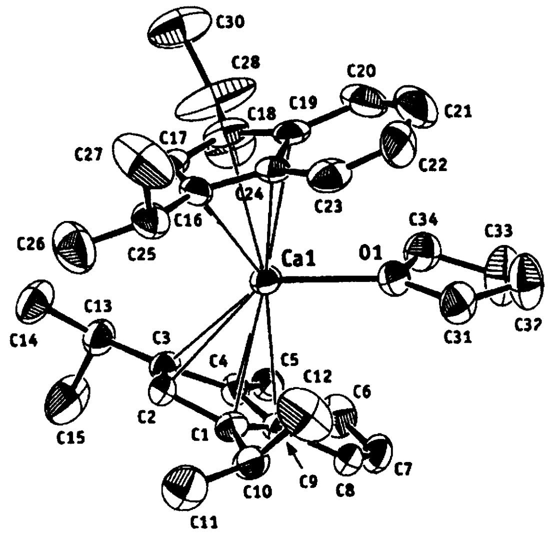
A general paper on the stereochemistry of group 5 organometallic complexes utilizes the chemistry of the t-butyl(dimethyl)cyclopentadienyl ligand,[32] while the chemistry of the bis(2,4-di-*tert*-butyl-1,3-cyclopentadien-1-yl)disulfane ligand has been described in a purely synthetic paper.[33] Again, the 8-quinolylcyclopentadienyl ligand has been obtained in the direct reaction of 8-lithioquinoline with tetramethylcyclopentenone.[34]

The reaction of zinc diiodide with the potassium salts of 1,2,4-tri- and 1,2,3,4-tetra(isopropyl)cyclopentadiene results in the facile formation of zinc metallocenes with slipped sandwich structures.[35] The novel organoaluminium reagents Cp^*AlR_2, R = Me, Et, ^iBu were obtained in the reaction of Cp^*K with dialkylaluminium chlorides. These derivatives have been fully characterised by ^1H, ^{13}C and ^{27}Al NMR spectroscopy.[36] 1,4-Dimethyl-2,3-diphenylfulvene has been used as a precursor to heteroatom-substituted-1-methyl-2,5-dimethyl-3,4-diphenylcyclopentadienyl transition metal complexes.[37] The reaction of $[Cp_2Sn(CH_3)_2]$ with $[Zr(NMe_2)_4]$ or $[Sn(C_5H_4)]$ respectively afford the tin-bridged zirconocene catalyst complexes $[(CH_3)_2Sn(C_5H_4)_2]Zr[N(CH_3)_2]_2$ and $[Sn\{(C_5H_4)Zr[N(CH_3)_2]_2\}_2]$, which are capable of high yielding ethylene polymerisation.[38]

A number of cyclopentadienyl complexes are included in reviews of luminescent and redox complexes[39] chiral redox reagents[40] and metallophosphaalkene synthesis.[41] In a paper on sesquifulvalene complexes interesting ligand properties are described which may be of general interest to the cyclopentadienyl chemist[42] and finally some aesthetically pleasing complexes of calcium, strontium and barium have been structurally characterised, [see for example (**6**)].[43]



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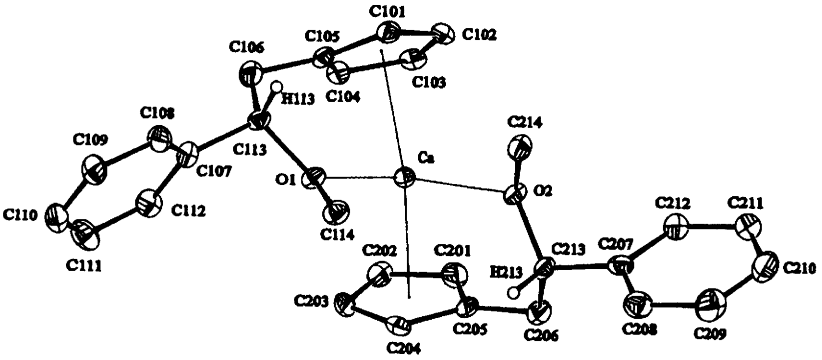
2 Monocyclopentadienyls

2.1 Lanthanides and Actinides – A total of 12 optically active metallocene complexes of Ca, Sm(II) and Yb(II) which contain cyclopentadienyl ligands with pendant chiral donors has been prepared – a typical representative example is shown as 7.[44] In part B in a series on organolanthanide chemistry, the preparation and characterisation of 3-oxa-pentamethylene-bridged *ansa*-metallocenes has been considered.[45] The reaction of Cp_3Pr with diethylmalonate affords



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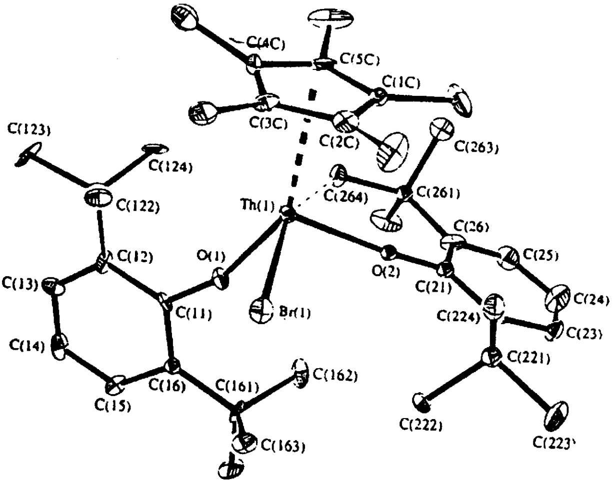
$[CpPr\{CH(CO_2C_2H_5)_2\}\{\mu\text{-}CH(CO_2C_2H_5)_2\}]_2$ which has been structurally characterised[46] while the reaction of $[Tl(C_5H_4PPh_2)]$ with metallic Eu or Yt in the presence of mercury in thf followed by recrystallisation from dimethoxyethane yields $[(\eta^5\text{-}C_5H_4PPh_2)_2M(DIME)]$, M = Eu, Yb complexes.[47] Again the reaction chemistry of $[Cp^*ThBr_3(thf)_3]$, which was obtained from $[ThBr_4(thf)_4]$ with $[Cp^*MgBr(thf)]$, with KOAr, Ar = 2,6-t-$Bu_2C_6H_4$ and related reagents has been investigated, with the crystallographic characterisation of $[Cp^*ThBr(o\text{-}2,6\text{-}tBuC_6H_3)_2]$, shown as (**8**).[48] The multidentate ligand $CpH^{NMe}SiN(H)R$ (SiNR= $SiMe_2N$-*tert*-butyl; NMe = $3\text{-}CH_2\text{-}CH_2NMe_2$) which was obtained in good yield from CpH^{NMe}, Me_2SiCl_2 and t-butylamine has been used in the synthesis of scandium cyclopentadienyl complexes.[49] An improved method of preparation of $Li[Nd(\eta^3\text{-}C_3H_5)_4]$.1.5dioxane has been used towards the preparation of the salts $Li[NdCp^\#(\eta^3\text{-}C_3H_5)_3]$ solvent Cp = Cp, Cp^*.[50] A useful synthetic paper has described a methodology towards $[C_5R_4PPh_2U(BH_4O)_3]$, R = H, CH_3 and their borane adducts.[51] *N,N'*-Bis(trimethylsilyl)-benzamidenate ligands have been used to stabilise mono-(pentamethylcyclopentadienyl)yttrium compounds.[52] Menthyl-containing cyclopentadienyl ligands are used in a study which deals with the reaction of asymmetric catalysis (hydrogenation) of olefins using organoyttrium and organolutetium complexes.[53] Finally a synthetic and structural investigation has been carried out on the complex $[CpPr\{CH(CO_2C_2H_5)_2\}\{\mu CH(CO_2C_2H_5)_2\}]_2$.[54]



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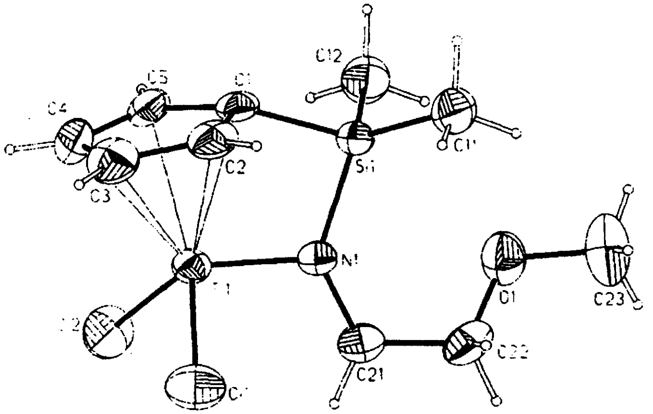
2.2 Titanium, Zirconium, and Hafnium – The complexes [$(Cp^{\#})(Ind)MCl_2$], $Cp^{\#}$ = Cp, Cp^*, Ind = η^5-indenyl, M = Ti, Zr which were prepared in the simple reactions of $Cp^{\#}MCl_3$ with indenyllithium are active catalysts for homogeneous ethylene polymerisation[55] as are the bent sandwich complexes containing the [2-(diisopropylamino)ethyl]-cyclopentadienyl ligand.[56] The μ-imido complexes [$CpTi(Cl)(\mu\text{-}NPh)_2TiCp_2$] and [$CpTi(Cl)(\mu\text{-}NPh)]_2$ have been obtained in good yields in the reaction of Cp_2TiCl_2 or $CpTiCl_3$ with [$((thf).MgNPh)_6$].[57] The syndiospecific polymerisation of styrene has been achieved using [$Cp^*Ti(CH_3)_3$] as a precatalyst in the presence of $B(C_6H_5)_3$,[58] while the polymerisation of ethylene, styrene and α-methylstyrene have been achieved using the related [$Cp^*TiK_2]^+$ cations, R = alkyl.[59]

The reaction of allyl or crotyl Grignard reagents with the reagent [$\{Ti(Cp^*)(\mu\text{-}O)Cl\}_3$] using a range of controlled stoichiometries has allowed the characterisation of six new complexes which are the products of chloride metathesis. As an example, a typical complex obtained is [$Cp^*Ti(\mu\text{-}O)_3(Ti\text{-}C_3H_5)_3$].[60] In similar chemistry the metathesis reactions of a number of alkyl-substituted lithium fluorenyl salts have been reacted with Cp^*MCl_3, M = Zr, Hf to give eleven new complexes,[61] some of which have been used in ethylene polymerisation.[62] A range of *ansa*-cyclopentadienylfluorenyl complexes which contain a dimethyl- or diphenylsilyl bridge are also useful polymerisation catalysts.[63]

A bimetallic compound [$CpTi(\mu_3\text{-}S)_3\{Rh(tfbb)\}_3$] has been discussed as a possible model for use in the deactivation of metal sulfide catalysts.[64] The dilithium salt of the complex ligand 2-(tertiarybutyl-3-cyclopentadienyl)-2-(fluorenyl)propane when treated with $ZrCl_4$ in pentane has yielded the crystallographically characterised [$(\eta^5\text{-}C_5H_3C_3H_9\text{-}CMe_2\text{-}\eta^5\text{-}C_{13}H_8)ZrCl_2$] product.[65]

Meanwhile the redox behaviour of a number of cyclopentadienyl(oxo)titanium derivatives e.g. $[Ti_4\{\eta^5\text{-}C_5H_4(SiMe_3)\}_4(\mu\text{-}O)_6]$ have been investigated in non-aqueous media.[66] The multidentate ligand $[CpH^{NMe}SiN(H)R]$, SNR = $\text{-}SiMe_2N\text{-}$C-butyl, NMe = $\text{-}CH_2CHNMe_2$, has been used in the reaction of $Zr(NMe_2)_4$ to give an array of amidoproduct complexes,[67] similar work with related ligands has been carried out by others[68,69] the latter reporting the interesting structure $[Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2NCH_2CH_2OMe)Cl_2]$, shown as **(9)**. Continuing the overall trend towards Ziegler-Natta catalysts a synthetic paper has highlighted the preparation of a number of alkylsubstituted indenyl complexes which are effective catalysts,[70] while an optically active variant of the ligand **(10)** has been obtained using two independent synthetic methodologies.[71] The molecular structure of $[\{[Cp^*Zr(\eta\text{-}CPh(NSiMe_3)_2]\}(\mu\text{-}Cl)_2][B(C_6F_5)]_4$ has been obtained in a study of the reactions of $[Cp^*Zr(L)_2R'_2]$, (L) = $(\eta\text{-}CPh(NSiMe_3)_2)$, R′ = Me, Bz with $[Ph_3C][B(C_6F_5)_4]$.[72]

New examples of half sandwich complexes such as $[PhB\{(\eta^5\text{-}C_5H_4)TiCl_3\}_2]$, which has been structurally characterised, have been prepared however an



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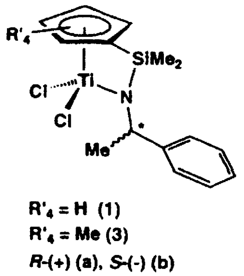

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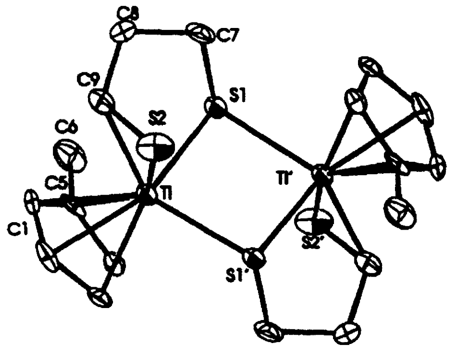

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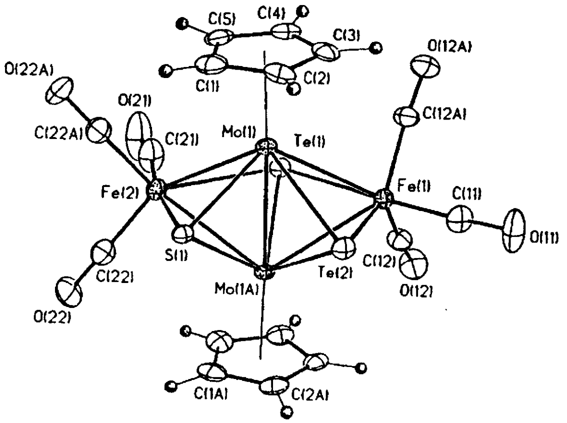
attempted correlation between ^1H and ^{13}C chiral shifts with the Lewis acidity of the attached boryl group was inconclusive.[73] Continuing the excellent work on thiatitanocenes the complexes $[Cp^{\#}Ti(SCHCH_2CH_2S)]_2$ $Cp^{\#}$ = Cp, Cp′ have been fully characterised, an example is shown as **11**.[74] It has been observed that cyclopentadienyl-zirconium(IV) and titanium(IV) halides and alkyls react with hydroquinone with the formation of μ-dioxoaryl bridged products such as $[(Cp^*M_2Cl)_2(\mu\text{-}OC_6H_4O)]$.[75] The reaction of $[Cp^*MCl_3]$, M = Zr, Hf with lithium 2,6-diisopropylphenyl)(trimethylsilyl)amide gives $[Cp^*M\{2,6\text{-}Pr^i{}_2C_6H_3N(Si\text{-}Me_3O)\}Cl_2]$ in which the chloride ligands can be further displaced to give the difluorides, using Me_3SnF.[76]

2.3 Vanadium, Niobium, and Tantalum – The U.V. visible spectra of $[(\eta^7\text{-}C_7H_7)CpV]$ and $[(\eta^7\text{-}C_7H_5)Cp'Ta]$ have been examined and interpreted, in particular the large changes in the spectra in going from the vapour to the solution phase has been accounted for.[77] The molecular structure of cyclopentadienylvanadium carbonyl has been determined by gas phase electron diffraction,[78] and a synthetic paper documents the synthesis of $[CpNbCl_2(NOBu^t)]$.[79] The first amido-functionalized niobium and tantalum complexes of the *ansa*-structural type $[(\eta^5\text{-}C_5H_4)\text{-}Si(CH_3)_2\text{-}NR]M[N(CH_3)_2]_3$, M = Nb, Ta, have been obtained in a simple synthesis from $M[N(CH_3)_2]_5$ with the functionalised ligand $C_5H_5\text{-}Si(CH_3)_2\text{-}NHR$ using a double imine elimination strategy.[80] The synthesis of tantalocycloalkyls resulting from the reaction of $[Cp^*TaCl_4]$ with $Li[2\text{-}(CH_2NMe_2)C_6H_4]$ has been achieved. Typically cyclometallated products are obtained initially which then undergo further cyclometallation and α-elimination reactions.[81] On treatment of $[Cp^*TaCl_4]$ with MOR, M = Li, Na reagents in different stoichiometries the family of complexes of generic formula $[Cp^*TaCl_n(R)_{4\text{-}n}]$; n = 1,2,3, R = alkyl, aryl, triphenylsilyl, etc, were produced.[82] Two mixed ligand complexes $[Cp^*Ta\{o\text{-}C_6H_4(NSiPr^i{}_3)_2\}Y_2]$, Y = Cl, CH_3 have been reported and in the case of Y = Cl the diamide ligand assumes an η^4-coordination mode utilising electron density from the phenylene ring.[83] Norbornene polymerisation has been carried out using the catalyst precursor $[Cp^*(\eta^4\text{-}$

$C_4H_6)Ta(CH_2Ph)_2]$ which generates a benzylidene complex on thermolysis.[84] A range of paramagnetic complexes of the type $[CpVCl_{2-n}(C{\equiv}CPh)_n(PMe_3)_2]$, n = 1,2 have been obtained in the metathesis reactions of $[CpVCl_2(PMe_3)_2]$.[85] The complex $[TpCpNb(Cl)(PhC{\equiv}CMe)]$, formed from $[TpNbCl_2(PhC{\equiv}CMe)]$ in a simple synthesis, has been structurally characterised[86] and finally the interesting multi-metallic species $[CpV(C_{10}H_8)]_2Eu(thf)(DME)$ have been prepared and structurally characterised.[87]

2.4 Chromium, Molybdenum, and Tungsten – A large number of synthetic papers have appeared which can be summarised as follows: the preparation of ring-coupled cyclopentadienyl and indenyl bimetallic complexes of Cr, Mo and W of the type $[M_2(CO)_4(\eta^5,\eta^5\text{-}C_5H_4\text{-}C(CH_3)_2\text{-}C_5H_4)]$.[88] The reactions of $SmI_2(thf)_x$ with $[Cp^{\#}Mo(CO)_3]_2Hg$; $Cp^{\#}$ = Cp, Cp^* have been explored and the molecular structure of a product $[(thf)_4I_2Sm(\mu\text{-}OC)Mo(CO)_2Cp]$ has been published.[89] A compilation of synthetic/structured papers have appeared with the X-ray work in each case being carried out by the Rheingold group; for example C-H bond activation in diethyl ether solvent has been achieved in the reaction of the carbene complex $[Cp^*W(CO)_3(OEt_2)]^+\ BAr_4^-$ with tertiary phosphines, the products of which are neutral tricarbonyl hydrides and $[CH_3C(H)(OEt)PR_3]^+\ BAr_4^-$.[90] Other structurally characterised complexes are for example $[Mo(\eta^5\text{-}1,2\text{-}C_5H_3{}^tBu_2)(CO)_3]_2$, $[Mo(\eta^5\text{-}1,2\text{-}C_5H_3{}^tBu_2)(CO)_3Br]$;[91] $[Cp_2Mo_2Fe_2(\mu_4\text{-}Te)(\mu_3\text{-}S)(\mu_3\text{-}Se)(CO)_6]$, shown as **(12)**, $[Cp_2Mo_2Fe_2(\mu_4Te)(\mu_3\text{-}S_2)(CO)_6]$ and $[Cp_2Mo_2Fe_2(\mu_4\text{-}Te)(\mu_3\text{-}S)(CO)_6]$.[92]



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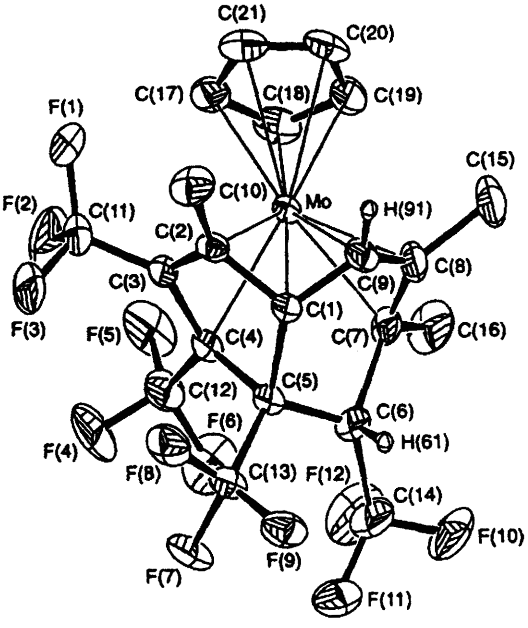
In work with the main theme on η^4-butadienyl substituted molybdenum complexes the reactions of $[Cp(\text{or } \eta^5\text{-}C_9H_7)Mo(NCMe)(\eta^2\text{-alkyne})_2]$ with lithium halides result in the formation of the $[CpMo(X)(\eta^2\text{-alkyne})]$, X = Cl, Br, I complexes some of which have been further reacted with $HBF_4.E_2O$ to furnish aqua complexes such as $[CpMo\{=C(R)\text{-}\eta^3\text{-}[C(R)C(R)CHR]\}X(OH_2)][BF_4]$; R = Me, Et,[93] while in related research the reactions of $[CpMo\{\eta^2\text{-(4e)}PhC_2Ph\}\{P(OMe)_3\}_2][BF_4]$ with Grignard reagents, RMgX lead to the formation of $[CpMo\{\eta^2\text{-(4e)-}PhC_2Ph\}R\{P(OMe)_3\}]$ complex products.[94] The cocyclization reactions of prop-2-ynl, alkyne and CO ligands in a Cp-capped Mo complex intermediate have resulted in the formation of the complex $[CpMo\{\eta^2,\eta^3\text{-}C(R)C(O)C(Me)C(R)CCH_2\}(CO)]$ shown as **13**,[95] while a synthetic paper by the same group has focussed on the preparation of related compounds such as $[CpMo\{\eta^2\text{-}OC(O)CHCHCHCO\}(NCMe)(CO)]$.[96]



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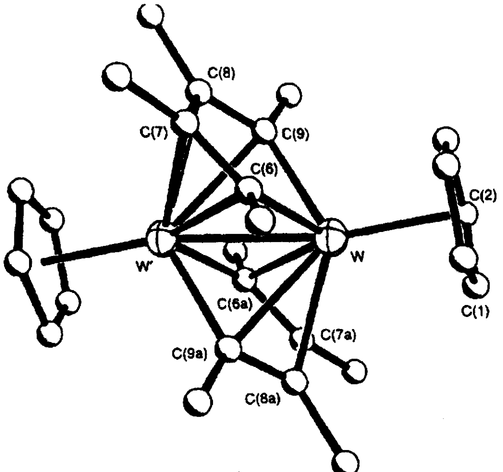
A series of molybdenum and tungsten thiolate complexes have been reported in a useful synthetic paper – the initial reactions investigated involved the reaction of, for example, $[CpWCl_3(CO)]$ with $[TlSC_6H_5Me\text{-}4]$ and $[CpWBr_3(CO)_2]$ with TlSR, R = Ph or $[C_6H_4Me\text{-}4]$.[97] The mechanism of alkyne trimerisation on molybdenum and tungsten centres containing a cyclopentadienyl ligand has been explored[98] and a reinvestigation of the reactions between $[CpMo(CO)_3H]$, allyl chloride and dimethylsulfide has produced the structurally characterised product $[CpMo(CO)(\mu\text{-}SMe)Mo(CO)_2Cp]$.[99] A related paper by the same group reports the structural characterisation of $[Mo_2Cp_2(\mu\text{-}SPh)\{\mu\text{-}\sigma{:}\eta^2\text{-}C(CH_3){=}CHCH_3\}(CO)_2]$ in work detailing the chemistry of $[Cp_2Mo_2(\mu\text{-}H)(\mu\text{-}SR)(CO)_4]$ (R = Me, Ph), complexes.[100] The lithium salt of the alkylidene complex $[Cp^*Mo(NO)(CH_2SiMe_3)(=CHSiMe_3)]_2\,[Li_2(thf)_3]$ has been obtained by the simple reaction of $[Cp^*Mo(NO)(CH_2SiMe_3)_2]$ with either $LiN(SiMe_3)_2$, LDA or $LiPPh_3$.[101] Chloride metathesis or nitrosyl bond cleavage reactions in $[Cp^*W(NO)(CH_2SiMe_3)Cl]$ on reaction with alkali-metal alkoxides has been explored with the formation of several novel complexes such as $[Cp^*W(NO)(CH_2S.Me_3)](\mu_2\text{-}\eta^1{:}\eta^2\text{-}NC\{H\}SiMe_3)[Cp^*W(Cl)(O)]$ in the case of alkoxide = $KOCMe_3$.[102] The transformation of dicarbonylcyclopentadienyl carbyne complexes $[Cp(CO)_2M{\equiv}CR]$, R = alkyl, aryl, to metalla-phosphacyclopropene complexes $[Cp(CO)M{=}C(R)\text{-}PR'_2][PF_6]$ has been achieved by the use of chlorodialkyl or diarylphosphanes in the presence of $TlPF_6$,[103] and the same research group has reported the reactivity of η^2-phosphinocarbene complexes such as $[Cp(CO)_2W{=}C(WI)PPh_2][BPh_4]$ towards anionic nucleophiles.[104]

The synthesis and structure of the first cyclopentadienyl(halo)metal(VI) complex $[Cp^*WFs]$ has appeared[105] together with further work on the reactivity of $[Cp^*MCl_4]$, M = Mo, W complexes.[106] The first MO_4S_2 cluster containing a functionally substituted cyclopentadienyl ligand, $[(\eta^5\text{-}MeO_2CC_5H_4)_4Mo_4(\mu_3\text{-}S)(\mu\text{-}CO)_4]$[107] has appeared together with a range of related papers from the same group.[108,109,110] The preparation and crystal structure of the trimetallic $[Cp'MoFeCo(CO)_6(\mu\text{-}\eta^4\text{-}Ph_2P(CH_2)_2PPh_2)(\mu_3\text{-}S)]$ has appeared[111] and a report of the metathesis reactions of $Na[CpMo(CO)_3]$ with $[CoCl(PPh_3)]$ and $[CoCl(P(OMe)_3)_5]$, has been published.[112] The X-ray structure of $[(Cp'_2Mo(CO)_3)(\alpha,\alpha'\text{-}\mu\text{-}o\text{-}C_6H_4(CH_3)_2)]$, obtained in the reaction of $[Cp'Mo(CO)_3]$ with *o*-dichloroxylene has also been described.[113] In the tenth paper in the series of substituted cyclopentadienyl ligands, the intramolecular steric interaction in $[(\eta^3\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_2(L)I]$, L=phosphine, phosphates have been examined.[114] In a paper intriguingly entitled 'oxidatively induced carbon chain growth at a ditungsten centre', the ferrocinium oxidation of $[W_2(\mu\text{-}C_4Me_4)_2Cp_2]$ to $[W_2(\mu\text{-}C_4Me_4)_2Cp_2]^{2+}$, z=1, 2 has been reported with the production of the product $[W_2(\mu\text{-}C_8Me_7CH_2)Cp_2]^+$ which then adds hydride to give $[W_2(\mu\text{-}C_8Me_8)(Cp)_2]$ shown as (**14**).[115] Some similar reaction chemistry with molybdenum has been



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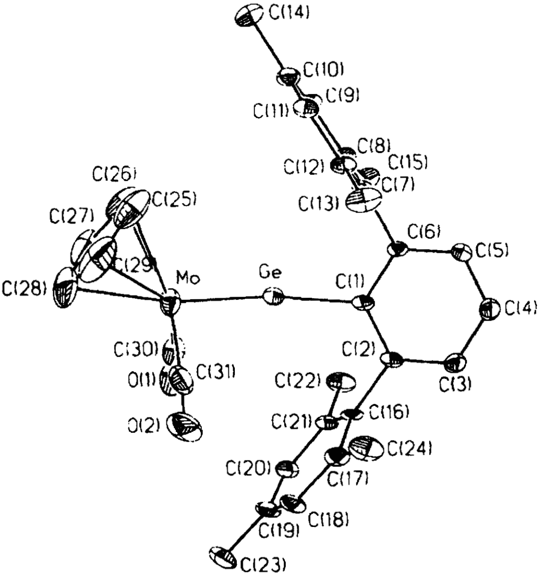

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followed up.[116] The synthesis of the cluster $[Co_2Mo_2(\mu_4\text{-}C_2Me_2)(\mu\text{-}CO)(CO)_4Cp_2]$, obtained on reaction of $Co_2(CO)_8$ with a dimolybdenum alkyne complex, has appeared[117] and the interesting germylyne complex $[Cp(CO)_2Mo\text{-}Ge(C_6H_3\text{-}2,6\text{-}MeS)_2]$, shown as (**15**) has been reported.[118] The structure of the complex $[(MoO)_2(\mu\text{-}N^tBu)_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2\}]$ is discussed in a paper with the general theme of dimetallic complexes of molybdenum and tungsten with bis-Cp ligands,[119] and the related study examines the molybdenum cyclopentadienyl triphos complexes.[120] The reactivity of $[CpWOs(CO)_{11}(\mu_3\text{-}C\text{-}tol)]$, tol = paratolyl, towards dihydrogen and water has been explored with the production of a number of structurally characterised products in each case.[121] The complexes $[M(CO)_3(CH_3CN)_3]$, M = Mo, W react with 4-bromo-2-cyclopentenone to yield $[M(\eta^3\text{-}C_5H_5O)(CO)_2(CH_3CN)Br]$, which was further reacted with other ligand types to give neutral complexes of the type $[M(\eta^3\text{-}C_5H_5O)(CO)_2(L\text{^}L)Br]$, which again on treatment with $Ph_3C^+\ BF_6^-$ in CH_2Cl_2 gave η^4-cyclopentadienone complexes by hydride abstraction.[122] The complex $[\eta^4\text{-}\{C_6H_7(SPh)\}CpMo^{\#}(CO)_2]^+\ PF_6^-$ was obtained from 3-bromo-2-(phenylthio)-cyclohexene in a two-step reaction using $[Mo(CO)_3(CH_3CN)_3]$ and LiCp as key reagents[123] and finally the reaction of water, methanol and anisole with the dicarbenium fulvalene complex $[FvMo_2(CO)_4(\mu\text{-}\eta^3\text{:}\eta^3\text{-}CH_2C{\equiv}CCH_2)][BF_4]$ yielded a monocarbenium species.[124] A number of other papers worthy of mention in this section are summarised as follows as themes: cycloaddition reactions of $[Cp^{\#}W(CO){=}PH(^tBu)]$, $Cp^{\#}$ = Cp, Cp′ complexes with S, Se and Te;[125] the synthesis and electrochemistry of heterobimetallic Mo/Pt complexes;[126]

the structure and reactivity of (dibenzo(b,e)fulvalene)$Mo_2(CO)_6$;[127] the formation of 1:1 and 1:2 phosphine adducts of $[CpCrX_2]$, X = Cl, CH_3;[128] the reaction of sodium amalgam with the complexes $[Cp_2Mo_2(CO)_4\{\mu\text{-}\eta^2\text{:}\eta^3\text{-}HC{\equiv}C\text{-}C(H)(Fc)\}][BF_4]$;[129] the synthesis of $[(\eta\text{-}C_5R_5)M(\mu\text{-}CO)_3RuCp^*]$, M = Cr, M, W, R = Me, Et, complexes;[130] the molecular structure of $[CpMoCl(MeCN)_4][SbCl_6]_2.MeCN$;[131] the preparation of the cluster $[CpWIr_3\{\mu_3\text{-}\eta^2\text{-}PPh(C_6H_4)\}(\mu\text{-}CO)_2(CO)_7]$ and related compounds;[132] an EHMO study of vertex rotations in $[CpMoCo_2(CO)_8CR]$ and $[Cp_2Mo(CO)_4(RC{\equiv}CR)]$ species;[133] an examination of the methyl to alkylidene migration in the complex *trans*-$[WMe(=CHPh)(CO)_2Cp]$;[134] the use of $[Cp^{\#}Cr(OR_3)_nCH_2SiMe_3]^+[BR_4]^-$ complexes in ethylene polymerisation;[135] the preparation of Cr-carbenes of divalent chromium;[136] the structure and reaction properties of fulvalene dichromium hexacarbonyl;[137] the reactions of [MSeW(CO)Cp], M = Li, Na, with organodi- and tetrahalides;[138] the oxidation reactions of cyclopentadienyltungsten selenolates;[139] $[Cp_2Mo(CO)_6]$ substituted polyamides;[140] the synthesis and characterisation of highly fluorinated tungsten(II) metallacyclopropenes;[141] the crystal structure of $[Cp_3W_3Ir(\mu\text{-}H)(CO)_{12}]$;[142] the coordination of CS_2 to $[Cp^*{}_2Cr_2B_4H_8]$;[143] the structure and reactivity of $[Cp^*Mo(NO)_2(E)]$; E = halide, halomethyl or alkyl complexes;[144] the synthesis of $[CpMoCl(PMe_2Ph)_3]$ from $[CpMoCl_2]_n$;[145] and finally the preparation of $[CpMo(CO)_2(PPh_3)H]$ in the presence of acetone and CF_3SO_3H in acetonitrile to give *trans*-$[CpMo(CO)_2(PPh_3)(i\text{-}PrOH)]^+$ during ionic hydrogenation.[146]

2.5 Manganese, Rhenium, and Technecium – Dirhenium carbene complexes have been obtained in the reaction of $[(\eta^5\text{-}C_5H_4Li)Re(CO)_3]$ with $[CpRe(CO)_3]$ following the usual trimethyloxonium ion trapping reaction,[147] while the same group have explored the ligand addition reaction of $[Cp^*Re(CO)_2]_2$ and their consequent fragmentation product reactions,[148] together with the synthesis of an η^3-propargyl rhenium complex $[Cp^*(CO)_2Re(\eta^3\text{-}CHR\text{-}C{\equiv}CR'')^+][PF_6{}^-]$ by hydride abstraction from the alkyne complex $[Cp^*(CO)_2Re(R'C{\equiv}CR)]$.[149] The kinetic parameters pertaining to the equilibration of the chiral complex $[CpRe(NO)(PPh_3)(N(H)CH(CH_3)Ph)]$ in d_8-thf have been measured which shows a slow rate determining PPh_3 dissociation step.[150] The same group have examined the electronic effects on binding in $[CpRe(NO)(PPh_3)(N(H)=C(CF_3)X)]^+$ TfO^- complexes.[151]

The geometrical isomers of $[Cp^*Re(CO)(N=NAr)X]$ complexes have been examined using low temperature ^1H NMR spectroscopy,[152] while the complexes $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(L)][BF_4]$, L = CO, CH_3CN have been characterised again by the same group[153] who have also been involved in mechanistic work; the ^{15}N labelled N_2-complexes $[Cp^{\#}Re(CO)(L)(^{15}N^{14}N)]$, $Cp^{\#}$ = Cp, Cp^*; L = CO, PMe_3, $P(OMe)_3$ have been prepared from $[Cp^{\#}Re(CO)(L)(^{15}N^{14}NC_6H_4OMe)]^+$ $[BF_4]^-$ on reaction with Ph_3C^+, Cp_2Co, Na(Hg) or $NaBH_4$ and the N-labelled scrambling has subsequently been monitored; a mechanism for end to end rotation is proposed via a side bonded N_2 intermediate and it is also concluded that linkage isomerism of the N_2-ligand is intramolecular and dissociative.[154] The X-ray structure of *trans*-$[Cp^*Re(CO)_2Et_2]$ has appeared[155] and the cycloaddition reactions of the manganese vinylidene complexes [Cp'(CO)$_2$Mn=C=C(H)R] and their related carbyne and anionic carbene complexes, with 1,4-diphenyl-1-azabutadiene have been reported.[156]

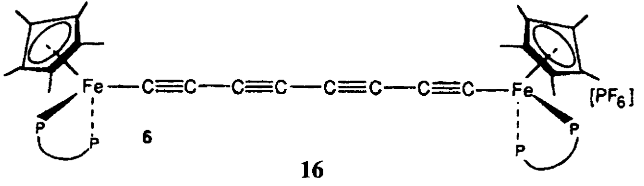
The NQR spectral parameters of ^{55}Mn and ^{187}Re in a range of cyclopentadienylmetal carbonyl complexes at 77 K have been reported and the results discussed in terms of electron-nuclear motions.[157] Meanwhile the preparation of a number of half-sandwich compounds has been carried out, namely aminorhenium-nitrosyls where the cyclopentadienyl ligand contains an N,N-dimethylaminoethyl-substituent,[158] together with the synthesis of a range of complexes of the type [η^1-CpRe(CO)$_3$L$_2$].[159] Further synthetic work has also been carried out on substituted cyclopentadienylmanganese dicarbonyl complexes, for example, chelates of [(η-C$_5$H$_4$C(O)CH$_2$OCH$_3$)Mn(CO)$_3$] and related derivatives have been prepared.[160] Furthermore the reactions of vinylchlorosilanes with [CpMn(CO)$_3$] have been exploited.[161] A variety of transformational chemistry has been carried out on acyl-rhenium complexes including the conversion of the complex *trans*-[CpRe(CO)$_2$Cl$_2$] to the nitrile complex [CpRe(CO)$_2$(CNR)] by reduction in alkylnitriles.[162]

An interesting report on the step growth approach to metal capped one dimensional carbon allotropes has appeared – the rhenium acetylide [Cp*Re(NO)(PPh$_3$)C$\equiv$C-C$\equiv$CH] has been used as a precursor to bicapped linear chains which contain up to 10-triple bonds between the metal centres.[163] Cymantrene containing organometallic polymers have been obtained using a simple Suzuki coupling methodology.[164] The mechanism of the photoreactions of *cis*-[CpRe(CO)$_2$I$_2$] with P(OMe)$_3$ has been investigated by FTIR and the reaction has been shown to occur by initial I$^-$ loss to generate a solvent-caged ion pair which then reacts with the phosphite.[165] In a highly interesting ligand synthesis paper penta(cyclopentadienylidene)cyclopentane has been targetted as the ultimate 'fulvaleneradialene' – in this connection iodo-substituted cyclopentadienyl-ligand complexes such as [(η-C$_5$H$_4$I)Mn(CO)$_3$] have been used as reaction precursors and tetra-substituted products of the type [{(C$_5$H$_2$)(ML)$_4$}], ML = CpMn(CO)$_3$ have been obtained already.[166] The diastereoselective substitution of PR$_3$ for CO in manganese and menthyloxy complexes have been investigated[167] and the synthesis of a number of ring-substituted cyclopentadienyl derivatives in the complexes [(C$_5$H$_8$R)Mn(CO)$_3$], where R = potential chelating group have been reported.[168] Sesquifulvalenes have also been obtained in the reaction of [(η^5-C$_5$H$_4$Li)Mn(CO)$_2$] with tropylium fluoroborates.[169] The two-dimensional polytrypism of 'crystalline' [Cp*ReO$_3$] has been discussed[170] and finally in the second paper of a series on optically active complexes the *endo* and *exo* isomers of [PCpRe(CO)$_3$], PCp = pinene fused Cp have been structurally characterised.[171]

2.6 Iron, Ruthenium and Osmium – An extraordinary number of synthetic papers have been reported during the year covered by this review, thus the numbers being outside the possible scope of this review therefore a representative selection of references have been chosen. The references have been broken down into four sections.

General – The enthalpies of reaction of [Cp′Ru(COD)Cl] with a series of *N*-pyrrolyl-substituted monodentate tertiary phosphines have been quantified and the steric and electronic effects in the reaction have been distinguished.[172] The aqueous organometallic chemistry of the electrophilic fragment $[Cp^*Ru(NO)]^{2+}$ has been quantified.[173] A theoretical study has been carried out on the tricarbido cation $[\{Fe(CO)_2Cp\}_3(\mu_3\text{-}C_3)]^+$ in an effort to examine the relative stabilities of the orientations of $Fe(CO)_2Cp$-fragments.[174] The effects of the ancillary groups on the oxidative addition of Si-H bonds in cyclopentadienylruthenium complexes has been investigated,[175] while a reinvestigation on the reaction of $[RuCl_2(CO)_3]_2$ with $[C_5H_5(SiMe_3)]$ has been carried out and the crystal structure of $[CpRu(CO)_3][\textit{fac}\text{-}RuCl_3(CO)_3]$ determined.[176] A range of organopolysilane polymers have been prepared and the molecular structure of the silylmethyl derivative $[\eta^5\text{-}MeSiMe_2SiC_5H_4(CO)Fe(CO)_2Fe(CO)\text{-}\eta^5\text{-}C_5H_4SiMe_2Me_3]$ has also been determined.[177] A group of ten novel $[Cp^*Ru(\eta^6\text{-monosubstituted naphthalene})]^+$ $O_3SCF_3^-$ complexes have been prepared in a study dealing with the arene-ring coordination site preferences in substituted naphthalene complexes.[178] A general ^{57}Fe NMR investigation has been carried out on the ligand effects in cyclopentadienyliron complexes[179] while a study on the linking of alkynes at a triruthenium centre has detailed the complexation chemistry in cyclopentadienylruthenium clusters.[180] A number of dinuclear complexes of the type $[(Cp^*Ru)_2(\mu\text{-}L)(\mu\text{-}H)(\mu\text{-}N{=}CHR)]$, R = Me, Et, L = MeCN, arene, have been investigated as precursors of active species for bimetallic activation with the dehydrogenative coupling of ethylene in a dinuclear ruthenium complex as an example.[181] The comparative chemistry of $\mu\text{-}\eta^1{:}\eta^2$-allenyl and $\mu\text{-}\eta^1{:}\eta^2$-acetylide complexes has been investigated and the coupling of such ligands leads to the formation of cyclopentadienyl ligands on a metal centre, thus this is a useful method of synthesis of highly substituted cyclopentadienyl ligands.[182] Further details on the cationic aqua complex $[(\eta\text{-}C_5Me_4Et)Fe(CO)_2(OH_2)][BF_4]$ and its thf analogue as useful synthons have been explored.[183]

Synthesis – The molecular wire complex (**16**) which contains four alkyne units between the iron centres has been prepared and characterised – it exhibits very strong electronic coupling between the metal centres (V_{ab} = 0.32 eV).[184] The family of stable 16-, 17- and 18-electron compounds with the $[Cp^*Fe(dppe)]$ general backbone have been obtained in one electron transfer reactions,[185] while the direct reaction of cyclopentadiene with $[\textit{trans}\text{-}Os(H)Cl(PPr^i_3)(CO)]$ affords $[CpOsH(CO)(PPr^i_3)]$ which in itself is a useful synthon.[186] A range of bimetallic complexes $[Fp(\mu_2\text{-}C_3(OCH_2CH_3))M(CO)_5]$, Fp = $Fe(CO)_2Cp$, M = Cr, Mo, W,



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have been obtained in the reaction of KFp with $[M(CO)_5\{C_3(OCH_2CH_3)_2\}]$ by simple ethoxide displacement.[187] The stepwise treatment of $[CpRu(PPh_3)(\eta^3$-$C_3H_4Me)]$ with $HC\equiv CCO_2Me$ and HCl leads to the formation of a vinylidene-ruthenium complex, which on reaction with tetravinyltin gives $[CpRu(PPh_3)(\eta$-$CH_2CHC{=}CHCO_2Me)]$, a 2,4-η-butadienyl compound.[188] Following on from previous years' work the synthesis of $[CpCoFe_2(CO)_2(\mu_3\text{-}S)(\mu_3\text{-}Te)]$ has been achieved[189] and a number of neutral vinylidene complexes of the type $[Cp^*RuCl(C{=}CHR)(PPh_3)]$, R = Ph, ^{t}Bu, $SiMe_3$, CO_2Me have been obtained in the reaction of $[Cp^*Ru(PPh_3)_2Cl]$ with alkynes.[190] The preparation of a range of μ-methylthiolate complexes obtained in the reaction of $[CpM(CO)_2]_2$, M = Fe, Ru, with $[Me_2SMe]BF_4$ has been reported and their alternative synthesis discussed,[191] while the preparation of the thiolate and disulfide complexes of the type $[Cp^*Ru(\mu\text{-}S_2)(\mu\text{-}SR)_2RuCp^*]$ has utilised $[Cp^*RuCl(\mu\text{-}SR)_2RuCp^*Cl]$ as a precursor in the reaction with Li_2S_2.[192] The unsymmetrical coupling of two allenyl groups has led to the production of the complex $[Cp^*Ru_2Fe_2(CO)(\mu$-$CO)(\mu_4\text{-}\eta^6\text{-}C_6H_6)]$ in an unusual templated reaction.[193] The synthesis and structural chemistry of palladium and platinum complexes of (η^5-cyclopentadienyl)-(η^5-*4-endo*-N,N-dimethylamino-3-diphenylphosphino-4,5,6,7-tetrahydro-1-*H*-indenyl)iron have been described,[194] while the structural chemistry of the complex $[CpFe(CO)_2SiMe_2Cl_2]$ and its related cobalt hexacarbonyl adduct has been detailed.[195] The synthesis of $[CpFe(CO)(PPh_3)COCH_2SCH_3]$ by methyl thiolation with dimethylsulfide of the acetyl anion of the appropriate acycliron complex has been detailed[196] while the complexes $[CpRu(CO)(CH_2)_5Ru(CO)_2Cp]$ and $[Cp(CO)_2RuCH_2CH_3]$ have been used as models for Fischer-Tropsch surface intermediates.[197] A simple synthetic procedure has been developed for the production of $[Cp^*Fe(CO)_2(SiH_3)]$ by reduction of the dichlorosilane precursor[198] while a related methodology has been used in the preparation of $[Cp^*Ru(CO)_2$-$SiR_2H]$, R = Me, *o*-tol in the work of the same research group.[199] Again the synthesis of a number of aminocarbene complexes of the type $[Cp(CO)_2$-$Fe(C(NHR')C\equiv CR)]^+\ [PF_6]^-$ obtained in the reaction of primary amines with the methoxy carbene $[Fp(C(OMe)C\equiv CR)]^+[PF_6]^-$ has appeared.[200] Pentafluorophenyl-substituted cyclopentadienes have been used as ligands towards iron and ruthenium.[201] The osmium complexes $[Cp^*OsL_2Br]$, $[Cp^*OsL_2H]$ and $[Cp^*Os($-$NO)Br_2]$ have been obtained from the general precursor $[Cp_2^*Os_2Br_2]$.[202] Meanwhile further 2,3-dihydro-1,3-diborolyl derivatives of cyclopentadienyliron and ruthenium have been obtained; for example $[Cp^*Fe\{(\eta^5\text{-}(CiPr)_2(BEt)_2CMe_2)\}]$ where *C* = carbolyl, has been produced in the reaction of $[\{Cp^*FeCl\}_x]$ with the 2,3-dihydro-1,3-diborole, $[(CiPr_2)_2(BEt)_2CHMe]$.[203] The synthesis of bis(methoxycarbene) and alkylidene ligands bridging two iron centres in the $[Cp^*Fe(L1)(L2)]$ series has been achieved.[204] The triflate salts of a series of transition-metal complexes of the general type $[ML_5(\eta^2\text{-}CpH)]$; $ML_5 = [Os^{II}(NH_3)_5]^{2+}$ and related species have been prepared and combined with electrophiles such as TfOH and $CH_2(OMe)_2$ to give η^3-allyl products.[205] The chemistry of pentabenzylcyclopentadienyliron derivatives has been expounded[206] and the characterisation of a new μ_4-S cluster compound $[CpFe_3Co(CO)_{11}(\mu_4\text{-}S)]$, which was prepared in a simple metathesis, has been carried out.[207] Finally in this section it would be remiss not to give an exhaustive coverage of the synthetic literature. Therefore a list of other synthetic papers follows with only short descriptions or a title to allow a summary: the synthesis of $[CpRu(\eta^2\text{-dmpm})(\eta^1\text{-dmpm})]Cl$,[208] $[CpFe(CO)_2AsC(NMe_2){=}C(CO_2Me)\text{-}CH(CO_2Me)]$,[209] iron-tungsten metallophosphenium cluster complexes,[210] complexes with tetrahydropentalenyl ligands,[211] $[Cp_2Fe_2(L)(CN)(\mu\text{-}CO)\{\mu\text{-}CN(R')R\}]$, $L = CN^-$, CNMe etc, $R,R' = Me$,[212] $[CpFe(CO)_2(P(O)R_2)]$ and $[CpFe(CO)_2(PR_2)]$, $R = {}^tBu$ complexes,[213] $[Cp^*RuCl(L)(\text{-}O)]$, L = CO, $P(OEt)_3$, P-O = η^1-(P) coordinated ether-phosphine ligand,[214] $[Cp_2^*Os(NO)_2(\mu\text{-}L)_2]$, L = S, Se, Te,[215] the cyclo adducts derived from $[CpFe(CO)\{C(NHR)C{\equiv}CSiMe_3\}][PF_6]$, R = Ph, *p*-tol,[216] the first metal substituted diboranes $[Cl(Me_2N)B\text{-}B(NMe_2)Fe(Cp)(CO)_2]$,[217] the intriguing stable radical $[(\eta\text{-}C_5(CHMe_2)_5)Fe(CO)_2]$,[218] the products of the reaction of $[Cp_2^{\#}Fe_2(CO)_4]$, $Cp^{\#}$ = trimethylsilyl substituted Cp's with elemental sulfur,[219] $[Cp^*Ru(NO)(\eta^2\text{-naphthalene})]$ and related complexes,[220] the complex $[Cp^*RuCl(dippe)]$, dippe = 1,2-bis(diisopropylphosphino)ethane,[221] the complex $[\{Cp_2Fe(CO)_2\}_2Bi\{OP(NMe_2)_3\}_2]$,[222] Cp^*Ru alkoxide complexes with σ-bridging phenoxide groups, e.g. $[Cp^*Ru(\mu\text{-}OMe)(\mu\text{-}OC_6H_3\text{-}2,4\text{-}({}^tBu)_2)]$,[223] octacarbonyltriruthenium monocarbollide complexes,[224] clusters of the type $[Ru_3(CO)_{10}(\eta^5{:}\eta^1\text{-}C_9H_6)]$,[225] Cp^*Ru adducts of functionalised arenes such as $[Cp^*Ru(\eta^6\text{-N-succinimidyl-3(4-methoxyphenyl)propionate})][CF_3SO_3]$,[226] an improved method of synthesis of pentabenzylcyclopentadiene and its iron complexes,[227] vinylidine osmium indenyl complexes and related compounds,[228] unsaturated ether chelate complexes for example $[Ru\{\eta^5C_5H_4CH_2O(CH_2)_nCH{=}CR^1R^2\}(CO)_2Cl]$, R = H, Me,[229] cyclopentadienyliron-μ-thiocarbene complexes,[230] iron-rhodium complexes of the type $[CpFe(\mu\text{-}CO)_2(\mu dppm)RhI_2]$,[231] trinuclear heterometallic clusters with bridging disulfide and sulfide ligands,[232] the synthesis of $[(CH_3)_2C(C_5H_4)_2][Fe(\mu\text{-}CO)_2(CO)_2]$,[233] polyaromatic azine derivatives of Fp- and $[(\eta^5\text{-}C_9H_7)Fe(CO)_2\text{-}]$,[234] and the synthesis of $[CpFe(CO)(PPh_3)COCH_2SCH_3]$.[235]

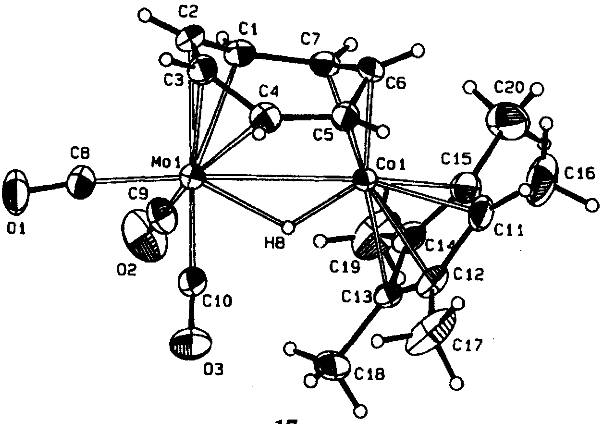
Reactions – The oxygen-promoted C-H activation in the complex $[Cp^*RuCl_2]$ to give the tetramethylfulvalene derivatives $[\{(\eta^6\text{-}C_5H_4CH_2)RuCl_2\}_2]$ and its solvates (py, Me_2SO) has been described,[236] while the addition reaction of bromine with $[Cp^{\#}Ru(\eta\text{-diene})]$ complexes has yielded η^3-allyl products except for 2,3-disubstituted-1,3-butadiene species which afford novel Ru(IV) dibromo complexes.[237] The complexes $[(C_5Ph_5)Fe(CO)_2]_2$ and $[(C_5Ph_5)Fe(p\text{-tolyl})]_2$ have been shown to undergo spontaneous thermal homolysis to their 17e-monomers.[238] The reaction chemistry of the dihydrides $[Cp^{\#}RuH_2(dippe)]^+$ BPh_4^-, $Cp^{\#}$ = Cp, Cp^*, with emphasis on their deprotonation chemistry has been explored; the analogous dinitrogen complex when reacted with dioxygen leads to dinitrogen displacement by the dioxygen.[239] The complex $[CpFe(CO)(CH_3)\{P(OMe)_3\}]$ reacts with $BF_3.OEt_2$ followed by PPh_3 to yield a metallocyclic product $[CpFe(PPh_3)\{C(Me)OBF_2OP(OMe)_2\}]$ in an unusual migration reaction.[240] Further coupling reactions of a range of cyclopentadienylcarbonyl metal iodides with trimethylstannyl-substituted alkynes have been carried out to yield thienyl spaced half sandwich dimers, e.g. $[CpMo(CO)_3(\mu\text{-}2,5\text{-}(C{\equiv}C)\text{-thienyl})\text{-}$

Fe(CO)(η-indenyl)].[241] The hydrosilane reduction of the μ-CH_2 complex [$Cp_2Ru_2(\mu$-$CH_2)(\mu$-$CO)(CO)_2$] results in the formation of methane in addition to a range of other byproducts.[242] The addition of amino acids and imidazoles to the ethylenic bond in [CpFe$(CO)_2(\eta^1$-*N*-maleimidoto)] in water has been examined[243] while the structure of [$Ru_4(\mu$-H)(μ_3-$PPhCH_2PPh_2)(\mu$-η^1:η^5-$CH_2C_5Me_4)(CO)_8$], which was obtained in the reaction of $Ru_3(\mu$-dppm$)(CO)_{10}$ with pentamethylcyclopentadiene, has been examined.[244] The Arbuzov rearrangement products [(η^5-C_5Ph_5)(p-tolyl)Fe$(CO)_2$R] and related compounds have been obtained on the reactions of [{(η^5-C_5Ph_4)p-tolyl}Fe$(CO)_2$] with tertiary phosphines.[245]

The oxidative addition of disulfides to the fragment [CpFe(dppe)]$^+$ to give [CpFe(dppe)-SR]PF_6, R = alkyl, phenyl, have been reported in terms of steric and chelative reaction control,[246] together with the reaction of [Cp_2Fe(CO)(CNMe)(μ-CO)(μ-$CNMe_2$)]$^+$ with trifluoromethanesulfonic acid to protonate the nitrile ligand.[247] A detailed paper has examined the [3+2] cycloaddition reactions of [CpFe$(CO)_2(\eta^1$-indenyl)] with maleic anhydride.[248] An interesting contrast in reactivity has been observed between [$Cp^{\#}$Fe(μ-NO)$_2$], $Cp^{\#}$, Cp′ or Cp^*; derivatives with the complexes containing the Cp^* ligand reacting far more slowly both thermally and photochemically in NO transfer reactions.[249] The reactivity of the imido group in [CpOs$(NCH_3)(CH_2SiMe_3)_2$][SO_3CF_3] with nucleophiles has been examined,[250] while the protonation reactions of [$Cp^*Os(CO)_2H$] by triflic acid results in the formation of the dihydride product.[251] Deoxygenative reduction of the diruthenium carbonyl complexes [(η^5-$C_5H_4R)_2Ru_2(\mu$-$CO)_2$(CO)] with hydrosilanes leads to methylene bridged species,[252] and the displacement of acetone by thioethers in [$Cp^{\#}$Fe(CO)(acetone)(COMe)]$^+$ has been studied using square-wave voltammetry; the rate constants obtained have been rationalized.[253] The reactivity of cyclopentadienyliron alkyls with respect to the migrating insertion of carbon monoxide has been compared to that observed in similar indenyl complexes.[254] The electrochemical activation of nucleophilic substitution in aryl- and vinyl-halides with Fp^- in redox catalysis has been explored.[255] Several other key reactions which have appeared in the literature worthy of mention are as follows: the Fp_2 catalysed reaction of FpX complexes with phosphines,[256] the photochemical reactions of alkynyliron(II) complexes with CS_2,[257] the investigation of the non-linear optical properties of the consecutive butylations on the cyclopentadienyl ring in [CpFe$(CO)_2(PPh_3)$]$^+$,[258] the synthesis of a complex which includes the first structural characterisation of a μ_3-P=S species,[259] the reaction of the trinuclear pentahydride [$(Cp^*Ru)_3(\mu$-$H)_3(\mu_3$-$H)_2$] with 1,3-butadiene,[260] and the photoinduced rearrangements of ring-coupled bis(cyclopentadienylrutheniumdicarbonyl) compounds.[261]

General, Chirality Catalysis – The diastereoselectivity of chloride substitution in cyclometallated chiral phenylethylamine complexes has been studied[262] and the diastereoselectivity in the enolate coordination in the complexes [Cp(CO)Ru{η^2(*P,C*)-$Ph_2PC_6H_4$-*o*-C(O)CHR)}] has been investigated.[263] Meanwhile the optical resolution of planar-chiral cyclopentadienyliron complexes using liquid chromatography with aqueous β-cyclodextran has been achieved.[264] The molecular structure of the *ortho*-aluminated complex $[CpFe(CO)_2]ArRAr$, Ar = 2-(dimethylamino)methylbenzene has been determined.[265] The electron transfer salts derived from *N,N'*-dicyano-*p*-benzoquinone diamines and $[Fe_2(Cp^*)_2(\mu\text{-}SEt)_2(CO)_2]$ results in the formation of isolatable salts.[266] In the third paper on 'Organometallic complexes for non-linear optical applications' the series of complexes $[CpRu((E)\text{-}4,4'\text{-}C{\equiv}CC_6H_4X{=}CC_6H_4NO_2)(PR_3)_2]$, X = CH, R = Ph etc have been prepared and their molecular quadratic optical non-linearities have been experimentally determined,[267] while large second order non-linear properties have been observed for related species.[268] Neutron diffraction studies have been carried out at 20 K on the two complexes $[Cp(PMe_3)_2RuH]$ and $[Cp(PMe_3)_2\text{-}RuH_2][BF_4]$.[269] Lastly the following references may be summarized as follows: the synthesis of polymers containing Fe-Fe bonds,[270] the examination of the steric effects of trimethylsilyl groups in cyclopentadienylruthenium complexes[271] the measurement of the enthalpies of reaction of $[Cp^*Ru(OCH_2CF_3)]_2$ with $P(Cy)_3$ and $P(iPr)_3$ using solution calorimetry,[272] and the use of $[RuHCl(CO)(\text{-}PiPr_3)]$ to a range of cyclopentadienyl complexes.[273]

2.7 Cobalt, Rhodium and Iridium – In the continuing series of articles on the chemistry of iridathiabenzene the reaction chemistry of $[Cp^*Ir(2,5\text{-dimethylthiophene})]$ complexes has been explored further by formulating reactions with cobalt carbonyl complexes. A number of unusual products were obtained such as $[Cp^*Ir(C(Me){=}C\text{-}CHCH{=}C(Me))(\mu\text{-}CO)_2Co]_2$ and $[Cp^*Ir\{(C(Me){=}CHCH{=}C\text{-}(Me)\}(CO)]$ both of which were structurally characterised.[274] Further reactions of the same complex with $Ru_3(CO)_{12}$, $Re_2(CO)_{10}$, $Mn(CO)_{10}$ and $[(\eta^6\text{-}C_6H_4)RuCl_2]_2$,[275] $[(\mu\text{-}S)_2Fe_2(CO)_6]^{2-}$ and $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ [276] and a range of nucleophiles (e.g. Ph^-, Me^- and OH^-)[277] were subsequently explored while the effects of cyclopentadienyl and phosphine ligands on the basicities of $[Cp'Ir(CO)(PR_3)]$ complexes were reported by the same group.[278] The reaction chemistry of $[(\eta^5$-benzoylcyclopentadienyl)- and $(\eta^5$-carbomethoxycyclo-pentadienyl)$(\eta^4$-tetraphenylcyclobutadiene)cobalt] has been explored with emphasis on its reactions with diphenylacetylene,[279] while the reaction chemistry of the complex $[(CpCo\{P(OR)_2O\}_3)Pd(propenyl)]$ with sodium malonate has been developed.[280,281] The electron transfer reactions and chloride ligand dissociation in the family of complexes $[Cp^*M(Cl)_x(bpy)]^{y+}$, x = 1, y = 1; x = 0, y = 0-2; M = Co, Rh, Ir, have been contrasted. In these complexes the electron transfer differs between Co (two 1e step) and Rh,Ir (rapid 2e step).[282] The reaction of $[Cp^*RhCl_2]_2$ with diphenylvinylphosphine results in the isolation of the monophosphine complex while in the presence of $NaPF_6$ the cationic bisphosphine complex was obtained. On heating the cationic complex in the presence of KO^tBu intramolecular of the alkene with a methyl group on the cyclopentadienyl ligand to afford isomers of the complex $[\{\eta\text{-}C_5Me_3(CH_2CH_2CH_2PPh_2)_2\}RhCl]^+$ PF_6^-.[283] The synthesis of divinyltetramethylsilazene complexes of $[Cp^\#R]$ $Cp^\#$ = Cp, Cp^*, together with slow photoisomerisation, which follows first order kinetics, has been reported. The obtained products are structurally fascinating.[284] The reaction of $[Cp^*Co(C_2H_4)_2]$ with $[(CO)_3Mo(\eta^6\text{-}C_7H_8)]$ affords the complex



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17, which contains a boat-shaped cycloheptatrienyl ligand and a metal bridging hydride.[285] The same research group have also reported the synthesis of the dinuclear complexes of the type $[Cp^{\#}Co(\mu\text{-}C_5H_4)(Cp^{\#'})]$ which were obtained from $[Cp^{\#}Co(\eta^4{=}C_4H_6)]$ and $[Cp^{\#'}Co(C_2H_4)_2]$.[286] The crystal structure of $[Cp^*Ir\{PO(OMe)_2\}_2\{\eta^2\text{-}(SPPh_2)_2CH_2SCH_2\text{-}S,S'\}]BF_4.0.5Me_2CO$ has been reported in a general paper dealing with the coordination properties of cyclopentadienyliridium phosphorus chalcogenide complexes [287] and the structure of $[(\eta^5\text{-}C_5H_4COONS)Co(CO)_2]$, NS = N-succinimidyl was reported to use as an activated ester for protein labelling.[288]

A range of stilbine containing complexes $[CpRh(RC{\equiv}CR')(SbiPr_3)]$ have been obtained on treatment of the $[ClRh(RC{\equiv}CR')(SbiPr_3)_2]$ with sodium cyclopentadienide,[289] and a number of cationic iridium cyclopentadienyl complexes have been prepared for further C-H activation studies.[290] Metal complexes of the type $[Cp^*M(bpy)(H_2O)]^{2+}$, M = Co^{III}, Rh^{III} have been the subject of a theoretical reinvestigation,[291] while further triple decker cyclopentadienyl cobalt sandwich complexes have been obtained[292] and the dimerisation of $[(Me_3SiC_2)_2S]$ which is moderated by CpCo- has been examined by the same group (see also refs. 286, 287).[293] The formation of a μ-non-sulfido link was the result of the reaction of $[Cp^*K(\mu\text{-}SiPr)_2IrCp^*]$ with elemental sulfur,[294] while an improved route to the preparation of cyclopentadienylcobalt complexes with pendant phosphines has been reported.[295]

The interesting photochemical insertion reaction of $[CpRh(PMe_3)(C_2H_4)]$ in pentafluoroanisole following proton abstraction ultimately yields $[Cp(PMe_3)Rh{=}C(H)OC_6F_5]PF_6$.[296] In a synthetic study the reactions of the complexes $[Rh^{II}(solv)(\mu\text{-}CpPPh_2)_2]_2^{2+}$ with nitriles, amines and pyridine have been examined,[297] while the photochemical activation of CH_4, C_2H_4 and C_2H_6 by $[Cp^*Ir(CO)_2]$ in a supercritical fluid has produced interesting synthetic results.[298] In the continuing work on aqueous organometallic chemistry the diastereoselective reactions of $[Cp^*Rh(H_2O)_3]^{2+}$ with nitrogen ligands over a pH range of 4–6 have been reported,[299] and theoretical studies on the C-H activation process in rhodium and iridium cyclopentadienyl complexes have been carried out,[300] and an experimental study using [$Cp^*IrCl(\mu\text{-}Cl)$] with phosphines results in the addition of the ligand to the cyclopentadienyl ring.[301]

Other significant work in this area is highlighted as follows: the reactions of imido complexes of Ir, Rh and Cu;[302] trinuclear cyclopentadienylcobalt clusters,[303] the synthesis of [$CpIr\{OC(Ph){=}NNCOPh\}$][304] and [$(R)(\eta^1\text{-}C_5Me_5)P{=}Co(CO)_3$];[305] further reactions of [Cp^*RhCl_2]$_2$ with silver carboxylates;[306] cyclopentadienylcobalt clusters;[307,308] the room temperature CpCo-mediated cyclisation of α,σ,ω-enediynes,[309] and imido-rhodiumcyclopentadienyl complex synthesis.[310]

2.8 Nickel, Palladium and Platinum – The oxidative cleavage of the dimer [$\{(\eta\text{-}C_5H_4(CH_2CH_2NMe_2))Ni\}_2(\mu\text{-}CO)_2$] with iodine results in the formation of the compound [$(\eta\text{-}C_5H_4CH_2NMe_2)NiI$] which has been further treated with triphenylphosphine and $Li\{Si[Si(CH_3)_3]\}$ to obtain a number of new monomeric species.[311] The pentamethylcyclopentadienyl complex [$Pd(\eta^4\text{-}C_5MeH)Cl_2$] when reacted with $AgBF_4$ in the presence of pentamethylcyclopentadiene results in the formation of [$Pd(\eta^4\text{-}C_5Me_5H)(C_5Me_5)$]$^+$ BF_4^- which can be further oxidised to the metallocene dication [Cp_2Pd]$^{2-}$ $2[BF_4]^-$.[312] The reaction chemistry of [$CpNi(1\text{-}norbornyl)$], prepared from nickelocene on the reaction with the 1-lithium norboryl salt, with alkynes has been explored and used to obtain several novel complexes.[313] A study of the electronic structure of [$CpNi(NO)$] using variable-photon-energy photoelectron spectroscopy has been carried out and the theoretical observations have been compared with experimental results.[314,315] The reactions of the complexes [$CpNi(PR_3)Br$], R = CH_3, Ph, with elemental indium and indium bromides have been carried out and the single crystal structure of [$CpNi(PPh_3)\text{-}InBr(OPPh_3).thf$] has been determined.[316] In a preliminary communication the preparation of the phospholyl nickel complex [$\{Ni(\eta^5\text{-}C_5Me_4P)(\mu\text{-}\eta^1\text{-}C_4Me_4P)\}_2$] from $NiCl_2$ with two equivalents of KC_4Me_4P has been reported and some tetranuclear mixed nickel/uranium complexes have been obtained in further reaction chemistry.[317] The synthesis and structure of the bridging phosphido complex [$CpNi(\mu\text{-}PHMes)$]$_2$, Mes = 2,4,6-$Me_3C_6H_2$, which was obtained on treatment of nickelocene with (PH_2Mes), has been published – the paper includes NMR characterisation of the syn- and anti isomers of the aforementioned and two related complexes.[318] Two Lewis-base adducts of the types [$(\eta^5{:}\eta^1\text{-}C_5H_4[(CH_2)_2NMe_2])NiI$] and [$(\eta^5\text{-}\mu\text{-}C_5H_4[(CH_2)_2NMe_2])(Me_3P)Ni\text{-}InI_2$] have been obtained, cf. ref. 311[319] and finally the reaction of [$Cp^*MeM(CO)_3Cp^\#$], M = Mo, W; $Cp^\#$ = Cp, Cp′, with PhC_2H results in the formation of the four-membered metallacyclic products [$Cp^*Ni\{\mu\text{-}\eta^3\text{-}(\mathit{Ni}),\eta^1\text{-}(1\text{-}\mathit{M})C(H)CPhC(O)\}M(CO)_2Cp$].[320]

3 Bis-Cyclopentadienyls

3.1 Main Group, Lanthanides and Actinides – A concise review article which has examined general lanthanoid complexes with neutral π-donor ligands details many examples of biscyclopentadienyllanthanide species.[321] Lanthanide metallocenes have also been used as catalysts in the intermolecular addition of primary amines to alkenes and alkynes,[322] while organoactinide metallocenes are effective catalysts for the intermolecular hydroamination of terminal alkynes.[323] The complex $[Cp_2La(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, prepared in the direct reaction of $[Cp_3La(thf)]$ with $[Li(C_6H_3\{CH_2NMe_2\}_2)\text{-}2,6]$ has been structurally characterised[324] while, in an interesting synthesis, $[Cp^*_2La(\mu\text{-}Cl)K(dme)_2]$ serves as a useful starting material for the preparation of $[Cp^*_2La]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}(C_{14}H_{10})].2\text{-tol}$ – (the other reagent was disodium anthracenide).[325] Again the reaction of $[Cp^*_2LnCH(SiMe_3)_2]$, Ln = Sm, Nd, Y, with neat $H_2Si(SiMe_3)_2$ at 85°C results in the formation of the new complexes $[Cp^*_2LnSiH(SiMe_3)_2]$.[326] Two new alkynide bridged complexes were obtained in the reaction of $[(^tBuC_5H_4)_2LnCH_3]_2$, Ln = Nd, Gd with $PhC{\equiv}CH$.[327] The room temperature reduction of $[O(CH_2CH_2C_5H_4)_2LnCl]$ with sodium results in the formation of $[O(CH_2CH_2C_5H_4)_2Ln(thf)]$, Ln = Sm, Yb. The thf is readily displaced; for example on recrystallisation with DME, the thf is exchanged for DME.[328] The interesting reaction of Eu or Yb powder with [(diphenylphosphino)cyclopentadienyl]thallium in the presence of mercury followed by a recrystallisation in DME leads to the isolation of the complexes $[(\eta^5\text{-}C_5H_4PPh_2)_2M(DME)]$, M = Eu, Yb.[329] A study of the circular dichroism of a range of samarium metallocenoids which contain the isomenthoxide ligand has highlighted significant intensity trends which have been related to the conformations of the chiral ligand.[330] *Ortho*-metallation with $[(Cp^*_2SmH)_2]$ occurs with 2-phenylpyrroline.[331] The crystallographically characterised complex $[(\eta\text{-}C_5Me_4Et)_3Sm]$ has been obtained using a new synthetic route which can be considered as general to the preparation of sterically enriched complexes.[332]

The gas phase reaction chemistry of $[Cp^*_2Sm]^+$, generated from either $[Cp^*_2Sm]$ or from C_5Me_5H and Sm^+, has been investigated using Fourier transform ion cyclotron resonance mass spectrometry.[333] The single-crystal structure of $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)_2Yb(thf)]$ shows a formally 7-coordinate Yb atom.[334] Lanthanide metallocenes of general formula Cp_3Ln, Ln = Dy, Yb react with thiols RSH to give dimeric products of the type $[Cp_2Ln(\mu\text{-}SR)]_2$.[335] The reactions of $[UMe_2(Cp^*)_2]$ with primary aromatic or aliphatic amines lead to the rapid formation of monomeric complexes formulated as $[Cp^*_2U(NHR)_2]$ which can be reacted with terminal alkynes to give the appropriate bis-acetylide species.[336] U.V. photoelectron spectroscopy, together with *ab initio* ROHF/CI calculations have been used to probe the electronic structure of $[Cp^*_2UCH\text{-}[Si(CH_3)_3]_2]$.[337] A group of 12 new optically active complexes of Cu, Sm(II) and Yb(II) which contain cyclopentadienyl ligands with chiral pendant chains have been prepared and fully characterised.[338] The oxidation of $[YbCp_2]$ with metal and organic halides has led to the formation of the complexes $[YbCp_2Cl(thf)_{0.5}]$, $[YbCp_2X(thf)]$, X = Br, I and $[(YbCp_2X)_2]$, X = Cl, Br, I which will serve as useful synthetic precursors in the future.[339] The structure of 1,1′,2,2′-tetra-*tert*-butyluranocene dichloride has been determined in a paper which has examined the general reactions of the 1,2-di-*tert*-butylcyclopentadienyl anion.[340] Finally the reactions of $[Cp_3UCl]$ with thiolate anions and the oxidation of $[Cp^{\#}_3U(thf)]$

with disulfides or dimethyldiselenide has led to the production of a range of complexes of the type [$Cp^{\#}_3UER$], E = Se, R = Me, E = S, R = Me, Et, ^{i}Pr, ^{t}Bu, Ph,[341] and a related structural determination of [$Cp_2Yb(\mu\text{-}SCH_2CH_2CH_3)]_2$ has been carried out.[342]

3.2 Titanium, Zirconium and Hafnium – Once again there has been a significant increase in the number of papers published in this section, many of which target the obvious application of olefin polymerisation catalysts. The review will focus on two principal areas – synthesis and applications chemistry.

General Synthesis – Novel zirconocene complexes which contain bridging silylium ligands have been isolated from the [Cp'_2ZrCl_2]/BuLi/$B(C_6F_5)_3$ catalysed silane dehydropolymerisation reactions.[343] The reaction of bis-(pentafluorophenyl)-borane with phosphine-olefin complexes of zirconocene yield interesting zirconocycles,[344] while the same group have published the crystal structure of [$Cp^*(\pi\text{-}\eta^5\text{:}\sigma\text{-}\eta^1$-tetramethylfulvene)titanium(II)].[345] The addition of PhOH, PhSH, $PhNH_2$, $PhPH_2$ etc to [$Cp_2Zr(PR^*)(PMe_3)$] results in the formation of the complexes [$Cp_2Zr(PHR^*)(ER)$], ER = OPh, SPh, NHPh etc, R^* = 2,4,6-*t*-BuC_6H_2, in a facile manner.[346] The reaction of [$Cp_2Zr(Me)(PHR)$], R = C_6H_2-2,4,6-Me_3, with benzophenone results in the insertion of the organic fragment into the Zr-P bond e.g. in the case of benzophenone [$Cp_2Zr(CH_3)(OC(Ph)\text{-}MeP(H)R)$] was obtained.[347] The titanocene vinylidene [$Cp^*Ti{=}C{=}CH_2$] reacts with 1,3-diynes to yield methylene metallacyclobutenes of the type [$Cp^*_2TiC(C{\equiv}CR){=}CRC{=}CH_2$],[348] while the complex [$Cp_2Zr(CH_3)_2$] on treatment with one equivalent of 4,6-dimethyl-2-mercaptopyrimidine liberates methane to give *S* and *N*-bonded thiolate products.[349] The bis-formato complex [$CpTi(\mu\text{-}\eta^1\text{-}(O)CHO)_2(C_{10}H_8)$] was obtained in the reaction of [$CpTi(\mu\text{-}H)_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)$] with CO_2.[350] The acetylide bridged dimeric complex [$\{Cp^*_2Hf(CCH)\}_2\mu\text{-}C_2$] was obtained on refluxing the monomeric complex [$Cp^*_2Hf(C{\equiv}CH)_2$] in thf.[351] The [2+2] cycloaddition reaction of allene with [$Cp^*_2TiO(pyr)$] results in the formation of the metallacyclobutane [$Cp^*_2Ti(OC(CH_2)CH_2$] which slowly converts to [$Cp^*(C_5Me_4CH_2)Ti\{OC(CH_2)Me\}$] in solution.[352] The reaction of [$Cp^*_2TiCl_2$] with 1 equivalent of 2-mercaptoethanol in the presence of a weak base results in the monomeric chelate [$Cp^*_2Ti(OCH_2CH_2S)$] while in the identical reaction of [$Cp^*_2ZrCl_2$] the oxygen bonded monomeric product (with one chloride retained) was formed.[353]

An interesting intramolecular cyclisation reaction occurs in the reaction of [$Cp_2Ti(Me_3SiC_2Me_3)$] with α, ω-diynes of the general type $RC{\equiv}C\text{-}(CH_2)_n\text{-}C{\equiv}CR$ to yield bicyclic titanacyclopentadienes.[354] The solvated complexes [$\{Cp_2Ti(S)_2{}^+\}\{BPh_4{}^-\}$], S = pyr, thf were obtained in the reaction of [$Cp_2Ti(Me_3SiC{\equiv}CSiMe_3)$] with trimethylammonium tetraphenylborate following $1e^-$ oxidation, with the evolution of H_2 and the alkyne.[355] A series of ring-functionalised alkyl zirconocenes such as [$Cp(\eta^5\text{-}C_5H_4\text{-}PPh_2)Zr(CH_2Ph)_2$] have been prepared and carbonylated to η^2-acyl products.[356] Continuing the work over the past two years the reactivity of [$Cp_2(thf)Zr{=}N\text{-}^tBu$] has been further examined: in the reaction with metal carbonyl complexes three different oxozirconocenes are obtained namely the generalised $[\mathrm{Cp_2Zr{=}O}]_n$; $[(\mathrm{Cp_2Zr})_2(\mu\text{-O})(\mu\text{-N-}t\mathrm{Bu})]$ and $[(\mathrm{Cp_2Zr})_2\mathrm{O_3CCPh_2}]$.[357] In related chemistry to ref. 356, the synthesis of $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_4PPh_2})_2(\mathrm{SC})_2]$, R = Et, Ph complexes and some of their metal carbonyl adducts have been reported.[358] The molecular structure of $[\mathrm{CpTi}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{CH_2SiMe_3})\mathrm{Cl}]$ has been reported in a paper dealing with the overall synthesis of [Cp(η^5-ring)titanium alkyl], η^5-ring = η^5-$\mathrm{C_5H_4{}^tBu}$ or η^5-indenyl, complexes.[359] The displacement of an η^5-Cp ligand in $[\mathrm{Cp_2ZrCl_2}]$ with three equivalents of n-BuLi to afford $[\mathrm{CpZr(n\text{-}Bu)_3}]$ and LiCp has been used in a useful synthetic strategy.[360] The preparations of $[\mathrm{Cp_2Ti(B_6H_9)}]_2$ and $[\mathrm{Cp_2ZrCl}\{(\mu\text{-H})_2\mathrm{BC_4H_8}\}]$ have been documented in the continuing work on borane derivatives of the group 4 metallocenes.[361,362] The first example of an ionic titanium fulvalene complex $[\{\mathrm{CpTi(H_2O)}\}_2(\mathrm{C_{10}H_8O})]^{2+}(\mathrm{SO_3CF_3}^-)_2.0.5\mathrm{thf}$, which was obtained from dinuclear titanocene trifluorosulfonic acid in the presence of trace water, has been reported.[363] A number of complexes of the type $[(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\text{-}\mathrm{Ti(C{\equiv}CSiMe_3)_2}]\mathrm{MX}$, M = Cu, X = OTf, SPh, etc, have been prepared and their reactions with Lewis bases PhCN and NCC(H)=C(H)CN further pursued. A broad range of products were obtained all of which are structurally interesting.[364] The synthesis and structure of titanium(III) tweezer complexes of the type $[(\eta^5\text{-}\mathrm{C_5HMe_4})_2\mathrm{Ti}(\eta^1\text{-}\mathrm{C{\equiv}SiMe_3})_2]^-\ \mathrm{M}^+$, M = Li, Na, K, Cs have been reported – these species were obtained in the reaction of $[(\eta^5\text{-}\mathrm{C_5HMe_4})_2\mathrm{Ti}(\eta^1\text{-}\mathrm{C{\equiv}CSiMe_3})_2]$ with alkali metals in toluene,[365] while the same group have prepared η^2-alkyne complexes on treatment of titanocene dichloride in the presence of the alkyne and Mg.[366] Similar work has been carried out on diynes.[367] A range of propylthio-substituted zirconocenes have been obtained directly from the appropriately substituted cyclopentadienyl salt.[368] The formation of stable planar tetracoordinate carbon compounds which contain the cationic fragment $[(\mathrm{Cp_2Zr})_2(\mu\text{-Cl})](\mu\text{-}\mathrm{R^1CCR^2})$ is the theme of a paper which documents the reaction of $[\mathrm{Cp_2Zr(Cl)(C{\equiv}CR)}]$ with $[\mathrm{Cp_2Zr(Me)(thf)}]^+\ \mathrm{BPh_4}^-$,[369] while the same research group have communicated the formation of a zirconocene-betaine system, formed in the electrophilic substitution reaction of a cyclopentadienyl ligand of 1,1-biscyclopentadienyl-2,3,4,5-tetramethylzirconacyclopentadiene, with $\mathrm{B(C_6F_5)_3}$.[370] A number of zirconocenophane complexes which contain two disiloxene-bridged indenyl ligands have been prepared using an alternative strategy to the previous literature method.[371] A new class of zirconocenes which contain an N-atom directly linked to an η^5-Cp or η^5-Ind ligand have been reported – these reactions make use of indanone or 3,4-diphenylcyclopent-2-enone precursors,[372] while pendant alkoxy-functionalised cyclopentadienyl ligands have been obtained in a simple synthetic strategy.[373] Three further communications from the Erker group include the reaction of alkylzirconocene cations with $(\mathrm{R\text{-}C{\equiv}C\text{-}})_2\mathrm{SiR_2}$ reagents,[374] the hydride abstraction from (η^2-acetaldehyde) zirconocene dimers using $\mathrm{B(C_6F_5)_3}$[375] and the stabilisation of a tetracoordinate planar carbon centre by zirconocene and halfrocene (cf. ref. 369).[376] Further references worthy of inclusion in this section are listed as follows: the first example of a titanium enolate radical cation in solution;[377] intramolecular carbene coupling on a titanocene centre;[378] the addition of 1,3-dipoles in bimetallic zirconocene-iridium cyclopentadienyls;[379] the synthesis of

$[Cp^*_2ZrOSiPh_2OLiOH]_2$;[380] the reactions of $Cp_2MCl_2/^nBuLi$ in the presence of unsymmetrical disilanes;[381] the preparation of a complex with the bulky amidofluorenyl ligand;[382] the synthesis of a range of methoxy-bridged titanocenes;[383] the synthesis of $[Cp_2Ti(\eta^2\text{-}COR)B(Ph)_3CN)]$;[384] the preparation of titanocene and zirconocene triflates,[385] *tert*-butylcyclopentadienyl derivatives of hafnium;[386] an amido titanium and zirconium complexes,[387] the interaction of carbon dioxide with $[Cp^*_2Ti(C{\equiv}CSiMe_3)_2]$;[388] the crystal structures of $[Cp_2Ti(CN)(OMe)]$ and $[Cp_2Ti(CN)]_2O$[389] and $[\{(\eta^5\text{-}C_5H_4SiMe_3)TiF_2\}_5AlF_3\text{-}(thf)]$,[390] the regiospecific reaction of phosphaimines with a zirconocene-benzyne[391] and the similar reaction with 1,1-diphosphines.[392]

Ansa and Chiral Metallocenes – A range of 2-dimethylamino substituted bisindenylzirconocenes with and without a dimethylsilyl bridge is the subject of a paper dealing with the general propene polymerisation[393] while the reduction of $[(\eta^5\text{-}C_5H_4)$-*ansa*-$(\eta^5\text{-}C_5H_4)]TiCl_2$ with magnesium in the presence of $Me_3SiC_2\text{-}SiMe_3$ results in the expected *ansa* alkyne derivatives, *ansa* = $Me_2Si\text{-}O\text{-}SiMe_2$.[394] The dinuclear hydrides $[M(CpSi_2Cp)H(\mu\text{-}H)]_2$, M = Zr, Hf, $CpSi_2Cp$ = $[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]$, have been prepared by reduction of the dichloride precursors.[395] The *ansa*-2,2′-bis[(4,7-dimethylinden-1-yl)methyl]-1,1′-binaphthyl and *ansa*-2,2′-bis[(4,5,6,7-tetrahydroinden-1-yl)methyl]-1,1′-binaphthyl titanium and zirconium dichlorides have been obtained in the direct reactions of the appropriate lithium salts with the metal tetrachlorides.[396] Spirosilane bridged zirconocenes have been prepared[397] together with further dimethylsilyl-bridged zirconocenes, the latter obtained from silastannatatetrahydro-5-indacenes, which were in turn prepared from silanediyl-bridged dicyclopentadienes.[398] Again polysiloxane-bridged titanocenes have been prepared[399] in addition to *ansa*-titanocenes containing homotopic ligands,[400] *ansa*-zirconocenes with ethyl-linked indenyl ligands,[401] dimethylsilyl-linked indenyls[402] and dimethylsilyl-linked substituted cyclopentadienes.[403] Finally in a preliminary communication a series of unsymmetrical *ansa*-metallocenes of zirconium and hafnium[404] and doubly bridged *ansa*-zirconocenes based on the norbornadiene skeleton have been examined in a quantum mechanical study.[405]

Optically pure C_2-symmetric CpTi-complexes have been obtained from dibornacyclopentadiene, which was in turn obtained from (1R)-(+)-verbenone.[406] (*s,s*)-Ethylenebis(η^5-tetrahydroindenyl)titanium difluoride has been used in highly enantioselective imine hydrogenation,[407] and an efficient synthesis of chiral *ansa*-metallocenes by amine elimination has appeared.[408] An improved method of resolution for (rac)-ethylenebis(tetrahydroindenyl)titanium derivatives makes the previous reactions more accessible.[409]

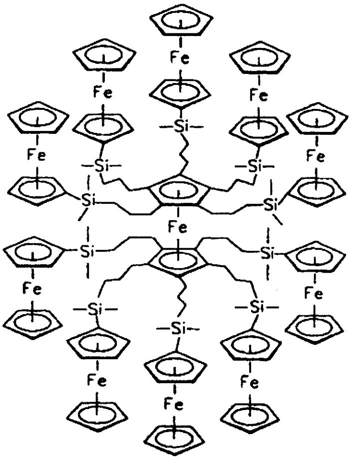
Polymerisation – A general review article examines the enantioselective C-C and C-H bond formation mediated by chiral titanocenes and zirconocenes,[410] while a further review article examines the Group 4 metallocenes in polymerisation generally.[411] A significant number of individual papers on the use of metallocenes in polymerisation reactions have appeared: dimethylsilylene bridged species for propene polymerisation,[412] the formation of isotactic polypropylene using a

$[(\eta^5\text{-}C_5H_3C_4H_9\text{-}(Me_2\text{-}\eta^5\text{-}C_{13}H_8))ZrCl_2]$ as a catalyst precursor;[413] the synthesis of 17 new catalyst precursors of which contain fluorenylidene ligands;[414] the synthesis of eight C_5-symmetric complexes of the general formula $[(C_{13}H_{8\text{-}n}R_nCR'R''C_5H_4)MCl_2]$[415] and new use in propylene polymerisation; the synthesis of three of the four Cs-symmetric bis(fluorenyl)zirconocene complexes;[416] the use of substituted fluorenylidene ligands and their influence on the syndiospecific polymerisation reactions;[417] a one pot synthesis of CH_2- and CHR-bridged fluorenylidene ligand systems;[418] the related preparation of zirconocene systems bearing Cp, fluorenyl, α-olefin or PMe_3 ligands;[419] the synthesis and structures of $[M\{Me_2C(\eta\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(Cp)Cl]$, M = Zr, Hf and their evaluation as cocatalysts;[420] the synthesis of new *ansa*-bridged complexes of the type $[ZrX(\eta\text{-}C_5H_4)_2](Cp)Cl]$ where X = $SiMe_2$, CMe_2CMe_2 etc and related hafnocene derivatives and their use in ethene and propene polymerisation;[421] the use of ferrocene containing zirconocene complexes for olefin polymerisation;[422] the synthesis of a range of doubly bridged zirconocenes for syndiotactic propene polymerisation;[423] an examination of the conformational analysis of non-bridged bent metallocene Ziegler catalyst precursors;[424] a review dealing with the α-agostic interactions and the olefin insertion process in metallocene polymerisation;[425] the use of non-*ansa* alkyl-substituted cyclopentadiyls for ethene polymerisation;[426] the use of mixed bent sandwich titanocenes which contain the (2-diisopropylamino)ethylcyclopentadienyl ligand for ethene polymerisation;[427] a density function theoretical paper on the influence of rotation between agostic structures on ethene interaction with a zirconocene polymerisation site;[428] the polymerisation of hex-1-ene in compressed solution;[429] the use of permethyltitanocene-bis(trimethylsilyl)acetylene as a catalyst precursor in the head to tail dimerisation of 1-alkynes;[430] the use of tin bridged *ansa*-metallocenes in olefin polymerisation;[431] the use of phosphido- and arsenido-bridged complexes as catalyst precursors;[432] the use of annulated 12-membered ring Cp-ligand containing compounds;[433] the preparation of cross-conjugated polymers using the condensation of a zirconocene benzyne complex;[434] a systematic analysis of the structure-reactivity trends in silane dehydropolymerisation;[435] the 'error' formation in *ansa*-zirconocene catalysed isotactic propene polymerisation[436] and finally the hydroformylation of olefins catalysed by $[Cp_2ZrH(CH_2PPh_2)]$ and related catalyst precursors.[437]

3.3 Vanadium, Niobium and Tantalum – The reaction of arylazides with $[Cp_2Ta(CH_3)(PMe_3)]$, affords arylazido complexes by phosphine liberation,[438] while the thermolysis of the same tantalum precursor complex in the presence of oxiranes, thiaranes and aziridines yield $[Cp_2Ta(=X)CH_3]$, X = O, S, NR, species[439] (in the case of X = S a further reaction occurs to yield $[CpTa(\eta^2\text{-}S_2)CH_3]$. The crystal structures of $[Cp^{\#}{}_2TaS_2H\{Cr(CO)_5\}_n]$ adducts, n = 1,2, have been determined on these species are the products of the addition of -$Cr(CO)_5$ to the $Ta(\eta^2\text{-}S_2)$ moiety in $Cp^{\#}Ta(S_2)H$, $Cp^{\#}$ = $^tBuC_5H_4$, C_5Me_4Et,[440] while the same research group have looked at similar reactions with $Fe(CO)_5$.[441] The electron density distribution of vanadocene has been accurately mapped following an accurate molecular structure determination.[442] The transmetallation of the PMe_2H ligand in a range of niobocene complexes has been studied, e.g. to dinuclear monomeric complexes $[Cp_2Nb(PMe_2H)(\mu\text{-}PPh_2)M(CO)_5]$ give $[Cp_2Nb(\mu\text{-}PPh_2)(\mu\text{-}CO)M(CO)_3(PMe_2H)]$ on U.V. irradiation.[443] An interesting investigation has been carried out on the insertion of activated alkynes into the Nb-H bond in niobocene hydride complexes,[444] while a range of mixed cyclopentadienyl complexes of the types $[Cp^*Ta(\eta^5H_4SiMe_3)Cl_2]$ and $[Cp^*Ta\{(\eta^5\text{-}C_5H_3(SiMe_3)_2)\}H_3]$, which were obtained directly from Cp^*TaCl_4 with the lithium salt of the second cyclopentadienide, have been structurally characterised.[445] In the study of the thermolysis of $[Cp'_2Nb(\eta^2\text{-}CO_2)R]$, R = CH_3, CH_2Ph the extent of decarbonylation versus insertion has been quantified – the reactions are concentration dependent.[446] The direct thermal reactions of $[Cp_2NbH_3]$ with $SiMe_3H$ give $[Cp_2NbH_2(SiMe_3)]$ which then undergo $SiMe_3H$ loss to the niobocene monohydride fragment which can be intercepted by addition of trimethylphosphine.[447] The synthesis, structure and redox reactivity of the niobocene formaldehyde complex $[Cp'_2Nb(Cl)(\eta^2\text{-}CH_3O)]$ has been explored,[448] and the same research group have also looked at the generation of organoniobium(II) radicals in the amalgam reduction of the compounds $[Cp'_2Nb(Cl)(L)]$, L = CO, PMe_3, CN^tBu.[449] A chiral tantalum atom centre is observed in the formation of the bimetallic complexes (both diastereoisomers) of $[Cp^{\#}CpTa^*(CO)(\mu\text{-}PMe_2)W(CO)_4L^*]$, $Cp^{\#}$ = $1\text{-}^tBu\text{-}3,4\text{-}Me_2C_5H_2$, L = PAMP, ((R)-(+)-phenyl-*o*-anisylmethylphosphine).[450] The reaction of $[Cp'_2Nb(H)(\eta^2\text{-}CH_2{=}CH_2)]$ with CS_2 results in the formation of $[Cp'Nb(Et)(\eta^2\text{-}CS_2\text{-}C,S)]$ which has been used as a further synthetic precursor,[451] while further work by the same group has detailed the electrochemical synthesis of carbonato-niobocene complexes.[452] Finally further work has been carried out in the formation of amido complexes, e.g. $[Cp_2NbN(SiMe_3)SiMe_2CH_2]$ has been obtained from $[NbCl\{N(SiMe_3)_2\}_2Ph]$ on treatment with $ZnCp_2$.[453]

3.4 Chromium, Molybdenum and Tungsten – The crystal structure of chromocene has been determined at low temperature and exhibits an average Cr-C bond length of 1.151 Å.[454] The reactivity of tungstenocene with respect to B-B and B-H bonds has been studied.[455] A solid state NMR study has been reported on the Union Carbide catalyst $[Cp_2Cr(SiO_2)]$ has shown the presence of one mononuclear and two dinuclear surface-attached complexes.[456] The electrophilic addition of CCl_4 to a cyclopentadienyl ligand in tungstenocene carbonyl results in the formation of $[CpW(\eta^4\text{-}C_5H_5\text{-}exo\text{-}CCl_3)(CO)Cl]$.[457] Meanwhile the synthesis of a range of molybdenocene derivatives coordinated to chiral carboxylato ligands has been achieved using three distinct approaches which use the molybdenocene dihydride as precursor.[458] The complexes of the type $[\{Cp(\eta^5\text{-}C_5H_4PPh_2)M(CO)_5\}W(H)Cl]$ have been obtained in the simple metathesis of $[PPh_2M(CO)_5]Li$ salts with tungstenocene dichloride.[459] The reduction of chromium(III) chloride with sodium indenyl leads ultimately to the dimeric $[(indenyl)_4Cr_2]$.[460] The structure and reaction chemistry of a range of tungstenocene boryl complexes of the type $[Cp_2W(H)(Bcat)]$ (cat = $O_2C_6H_4$) and $[Cp_2W(BL)_2]$, (L = $O_2C_6H_3\text{-}^tBu$ or $(O_2C_6H_2\text{-}^tBu_2)]$ has been clarified.[461] The reaction of $Li[Cp_2MSnPh_3]$, M = Mo, W with alkyl halides has been examined with the resultant formation of the anticipated metathesis products.[462] The synthesis of a germylidyne bridged complex has been achieved in the thermolytic reaction of [$Cp_2W(SiMe_3)(GeMe_2OTf)$].[463] Finally the direct conversion of α-substituted ketones to metallo-1,2-enedithiolates has been achieved on a molybdenocene template.[464]

3.5 Iron, Ruthenium and Osmium – The synthesis of ferrocene-based redox-active polymers have been achieved using palladium catalysed coupling reactions – essentially ferrocenes disubstituted with halobenzenes, with and without spacers have been used as monomers in copolymerisation with chlorozinc substituted arenes.[465] Following on from last year's communication further 1,2-heterodisubstituted ferrocenes have been obtained from 1-lithio-1′-bromoferrocene; these include 1′-substituted methylferrocenes and biferrocenes.[466] A series of interesting deca-allylferrocene-derivatives have been obtained from penta-allylcyclopentadiene. The crystallographically characterised deca-allylferrocene has been used in the catalytic preparation of dendritic silylferrocenes for examples as shown in (**18**).[467] Further dendrimers based on flexible poly(propylenimine) cores have been obtained with 4, 8, 16, 32 and 64 peripheral ferrocenes as indicated in (**19**).[468] In these molecules all ferrocene centres are electrochemically independent. Ferrocenylthiaaliphatic acids [$Fc\text{-}C(R)_9CHSXCO_2H$], X = CH_2, CH_2CH_2, $CH_2CH(CH_3)$; R = CH_3, Ph, *p*-tol prepared from 1-ferrocenyl ethanol or related alcohols have been used in the synthesis of ferrocene-containing oligomers in an attempted cyclisation with trifluoroacetic anhydride.[469] A further report has appeared on the enantioselective lithiation of ferrocenes in the presence of chiral amines; for example sulfonylferrocenes have been lithiated in the presence of chiral tetramethyldiamines and aminomethylferrocene has been lithiated in the presence of the same chiral amines to give up to 80% e.e.[470] Meanwhile an



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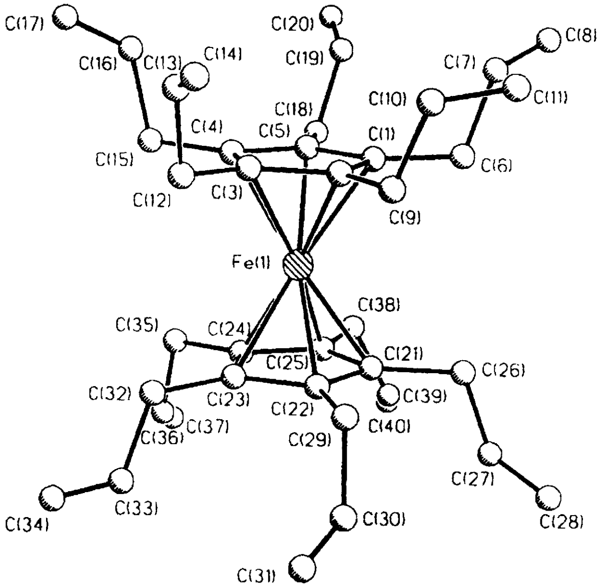

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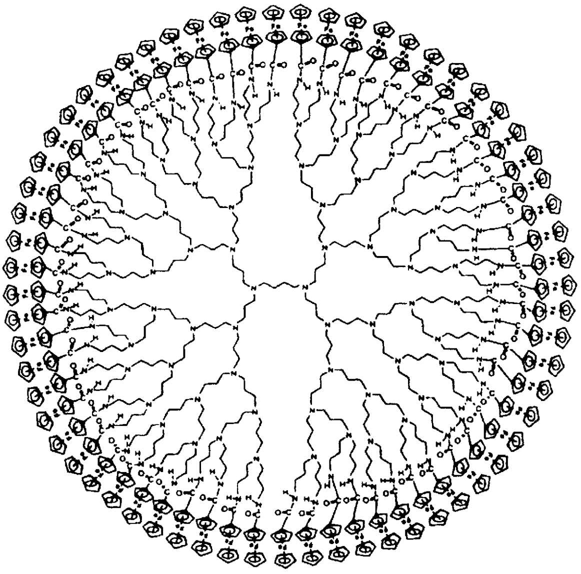

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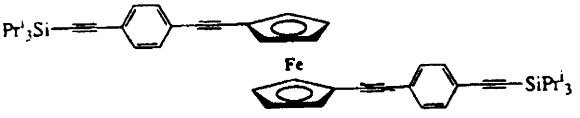
extremely mild method of reduction of acylferrocenes has been reported which involves the mild Lewis acid/reductant combination of $BF_3.OEt_2$ and sodium cyanoborohydride.[471] The synthesis of some ferrocene derivatives containing anthracenes linked by spacer units has been reported in a methodology which involves the coupling of phenol-substituted anthracenes with chloroacetylferrocene in the presence of base.[472]

Further work has been published on the assessment of the degree of permercuration of substituted ferrocenes with an emphasis on dimethylferrocene substitution.[473] Again following last year's reports on ethynylferrocene synthesis a similar synthesis using chloromethylenetriphenylphosphonium ylid and ferrocenecarboxaldehyde has appeared[474] – this adds to the recent preparation in 'Organic Synthesis'.[475] A further study on the lithiation of ferrocene has appeared as an addendum to a previously published paper on ferrocene aldehyde synthesis,[476] complementing the work published by Kagan and Guillaneus in the previous year. 1,2-Distanna[2]- and 1,2,3-tristanna[3]-ferrocenophenes have been obtained in a synthetic methodology beginning with 1,1′-(chlorodimethylstannyl)-ferrocene, which was reduced in the presence of $LiAlH_4$ and coupled indirectly ($[Sn(NEt_2)_4]$ as reagent) or directly coupled ($[Hg(SiMe_3)_2]$ as reagent).[477]

A series of side-chain perfluoroalkylferrocenes have been investigated[478] while similar work has been focussed on the synthesis of fluoroalkylferrocenes and ferricinium salts.[479] Pyrazole-bridged *ansa*-ferrocenes have been prepared from 1,1′-bromoalkylboraferrocenes in the presence of pyrazole and the factors affecting bridge stability have been discussed.[480] Ridged rod complexes have been obtained from the ferrocene tetrayne (**20**) using Ni or Pd catalysed coupling reaction. The product properties are compared with ruthenium phosphine tetraynes of the type (**21**).[481] Two new amino acid ferrocene derivatives have been prepared in the reaction of ferrocenecarbonyl chlorides with the methyl ester hydrochloride of valine – the ordered conformations in these compounds have been examined.[482] This work may be of interest to those using chiral ferrocenyl]-oxazolines (see later section). The asymmetric alcohol condensation of acetylferrocene with aromatic aldehydes using β-cyclodextrin inclusion methods has been



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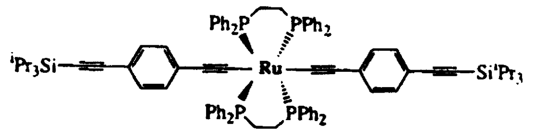

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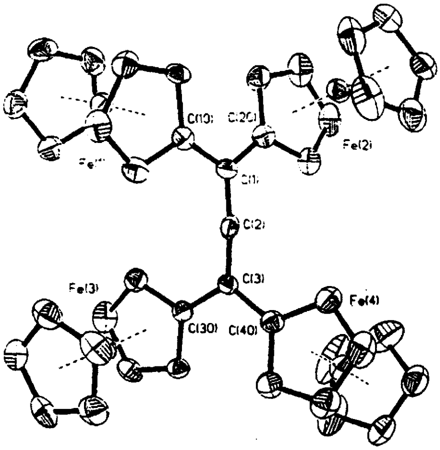
examined; however the optical yields are only between 6 and 30%.[483] A number of interesting di- and tri-nuclear ferrocene substituted N-alkylpyrazolyl pyridine complexes have been obtained by treatment of diacetylferrocene with base in the presence of ethylpicolinate.Et_2O followed, after acidic work up, by the reaction of hydrazine and reduction. Molybdenum complexes of these unusual ligands have been thus obtained.[484]

A further range of mono- and bis-allenes with ferrocenyl substituents have been prepared in reactions which involve the treatment of triferrocenylallenylium tetrafluoroborate with 1-cuprioferrocene using nucleophilic addition. The structure of tetraferrocenylallene is shown as **(22)**.[485] Meanwhile a range of new $[1^4]$-metallocenophanes containing alternating unmethylated and methylated cyclopentadienyl rings, e.g. **(23)**, have been prepared from termetallocenes substituted with pendant difulvenes.[486] The structure and reactions of 2,4-diferrocenyl-1,3-dithiadiphosphetane 2,4-disulfide, prepared by the direct reaction of ferrocene with P_4S_{10}, have been reported.[487] The first diphosphastibolyl complexes, $[Ru(\eta^5\text{-}C_5R_5)(\eta^5\text{-}C_2Bu^t_2P_2Sb)]$, R = H, Me, have been obtained in the reaction of $[Cp^{\neq}Ru(MeCN)_3]PF_6$ with $[C_2Bu^t_2P_2Sb]$, $Cp^{\neq}$ = Cp, Cp′.[488] The reaction of ethynylferrocene with $[Os_3(CO)_{10}(MeCN)_2]$ yielded the previously known cluster $[Os_3(CO)_{10}\{CpFe(C_5H_4CCH)\}]$ and the bis-ferrocenyl containing compound $[Os_3(CO)_9(CpFeC_5H_4CCH)_2CO]$ which was structurally characterised.[489]

The oxidation of [1.1]-ferrocenylruthenocenophane with bromo- or chlororuthenocenium salts has been carried out to yield the interesting diamagnetic salt where the deprotonation of a bridging methylene group has occurred. In the case where the iodoruthenium salt is used as the oxidising agent the ruthenocene is oxidised to give the iodoruthenocenium compound.[490] In a



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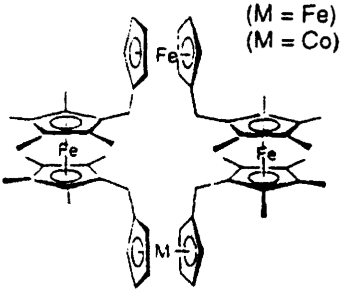

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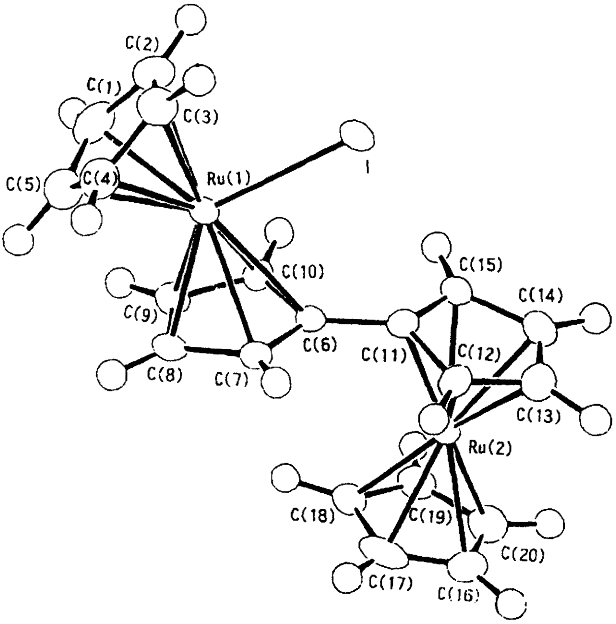
previous paper iodobiruthenocenium salts have been structurally characterised, e.g. as shown in (**24**).[491] Further studies on these compounds including Mössbauer and further oxidation reactions have also been reported in a related article,[492] and in structural papers.[493,494] The reactions of lithioferrocene or dilithioferrocene with camphor and fenchone activated with cerium(III) chloride have been carried out resulting in the formation of the interesting ferrocenyl alcohols, a representative example of which is shown as (**25**).[495] The 1,1′-ferrocenediylbis(N-methylene-N-n-butyl-N′-benzoylthiourea) has been obtained in the reaction of 1,1′-bis(n-butylaminomethylene)-ferrocene with two



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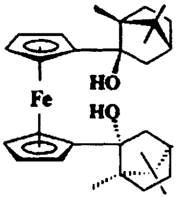

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equivalents of benzoylisothiocyanate, while the identical reaction of 1,1'-bis(ethylaminomethylene)ferrocene yields 2-N-ethylammonium-[3]-1,1'-ferroceneophane thiocyanate.[496]

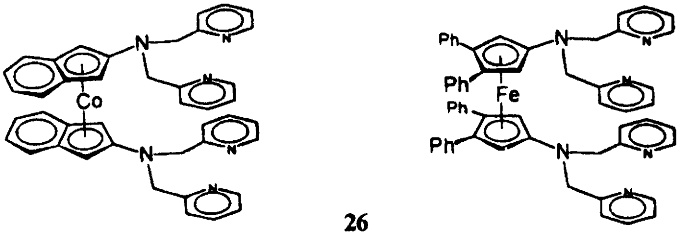
The structural chemistry of organotinferrocenecarboxylic esters, i.e. the reaction of ferrocene carboxylic acids with organotin reagents to give the tin adducts, has been reported together with ^{119}Sn NMR results.[497] The first synthetic preparation of 1,2-(1,1'-ferrocenediyl)ethene has been reported – it was a six step synthesis which involves the key step of alkylation of the known ferrocenylsulfide $[\{(\eta\text{-}C_5H_4\text{-}CH_2\text{-})_2S\}Fe]$.[498] The trimethylchlorosilane-modified Clemmenson reduction of ferrocenylketones has been re-examined and some 'trapped' products have been crystallographically characterised.[499] The photoreduction of zinc and aluminium-2,3-naphthalocyanine in the presence of azaferrocene under red light has been examined and thus the electron transfer between the photoexcited macrocycle and the azaferricene has been scrutinised.[500] The Mössbauer spectra of ferrocene enclathrated in deoxycholic acid have been studied in an effort to gauge the molecular motion of ferrocene thus encapsulated.[501] The linear and non-linear properties of further conjugated ferrocenes have been examined; for example 1-ferrocenyl-4-*E*,*E*-(4-nitrophenyl)butadiene in polymethylmethacrylate.[502] Again a further diazamacrocyclic complex 1,1'-(2,6-diazahepta-1,6-diene)-ferrocene has been obtained in some standard Schiff base reactions of ferrocenebiscarboxaldehyde.[503] The direct synthesis of ferrocenyl amino acids has utilized the palladium catalysed coupling reactions of diiodoferrocene with zinc salts of protected amino acids.[504] Ferrocene nucleobase conjugates have been obtained in the reactions of *N*,*N*-dimethylaminomethylferrocene with 1-(3-bromopropyl)thymine.[505]

A few further metallocene papers are as follows with key words only shown: the synthesis and reactions of 2-ferrocenylmethylamino-5-methylbenzoic acid and 2-bis-(ferrocenylmethyl)ammonium-5-methylbenzoic acid perchlorate;[506] the structure of 1,1'-bis(N-phenylhydroxyaminocarbonyl)ferrocene[507]; further ferrocene Schiff base chemistry;[508] the preparation of a ferrocenylozaolidinone;[509] the synthesis of the complexes ferrocene substituted arenes trapped with chromium tricarbonyl as potential redox switches,[510] and a structural and electrochemical comparison of diarylferrocenylmethylium ions with its isolobal cobalt analogues.[511]

Electrochemistry/Redox Processes – The oxidation of [Fc-C≡C-Fe(P^P)Cp′], (Cp′ = Cp, Cp*, P^P = dppe, dppm, dmpe), which was prepared from the corresponding dicarbonyl complex, using DDQ affords the stable oxidized complexes [Fc-C≡C-Fe(P^P)Cp′]$^+$ A$^-$; A = DDQ.[512] Continuing their work on ferrocene-based liquid crystals the Deschenaux group have examined the chemical oxidation of non-mesophoric persubstituted ferrocenes to yield the corresponding ferrocenium species.[513] The reaction of titanocene dichloride with [FcC≡CC≡CLi] yields [Cp_2Ti(C≡CC≡CFe)$_2$] which yields [FcC≡C-C≡C-C≡C-C≡CFc] on electrochemical oxidation.[514] The structural and electrochemical features of pyrazole bridged ferrocene[515] has followed the initial synthetic report (see ref. 480). The redox behaviour of the di(1-azulenylferrocenemethyl)$^-$ cations which were obtained in the direct reactions of ferrocenecarboxaldehyde with azulenes has been examined and it has been found that the ferrocene redox properties are not affected greatly by attachment to the azulenyl cations.[516]

A series of 16 ferrocenes have been prepared in which the pendant surfactants containing vinyl ethers have been used as models for redox switched bilayer studies.[517] Similarly the behaviour of (11-ferrocenylundecyl)(trimethylammonium bromide) has been examined in great detail in an extremely interesting paper which concludes that the velocity of fluid motion at a solution surface can be controlled by the electrode potential in these systems.[518] The single crystal structure of 2,5,19,22-tetraaza[6.6](1,1′-)ferrocenophane-1,5-diene has been determined in a study which examines the use of the hydrogenated version of this compound as a potential pH responsive red or receptor.[519] A range of diferrocenylpolyenes with one to six vinylic spacers between the ferrocene termini have been prepared and the intervalence transitions in the mixed valence state have been studied. The results show that the decay of metal-metal coupling with distance is exponential.[520]

A range of 'pincer' aminocobaltocenes and ferrocenes, e.g. (**26**) have been obtained from substituted cyclopentenones in a few simple steps.[521] The redox properties of diferrocenylmethane and diferrocenylmethanol have been studied and the electrochemistry has been related to their crystallographically determined structures.[522] The structures and electrochemistry of some ferrocenylazines for example [4_2][1,1′-bis(1,4-dimethyl-2,3-diazabuta-1,3-diene)ferrocenophane] have been reported and their structural features have been related to solution stability



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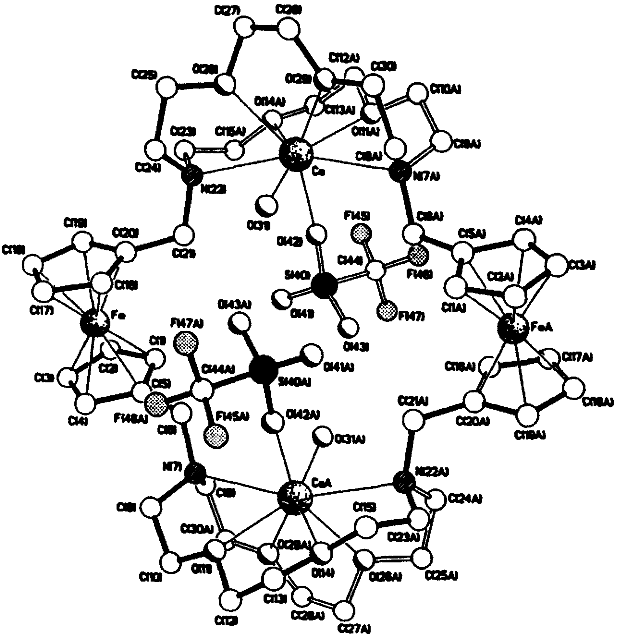
of the derived ferrocenium ions – the study concludes that the ferrocenium ions of acetylferrocene and the azines are stable in solution while those of ferrocenylhydrazones are not.[523] A series of oligo- and poly-1,1′-dihexylferrocenylenes have been obtained in the reaction of the dihexylfulvalene dianion with $[FeCl_2(thf)_2]$ and the electrochemical properties of the pentamers and hexamers of these molecules have also been reported. In addition it was found that the charge transfer complexes of poly(dihexylferrocenylene); M = 5000, dispersity 1.2, with tetracyanoethylene and TCNQ show interesting photoconductive properties.[524] A range of new open chain ferrocenes have been obtained in the reactions of ferrocene-1,1′-dicarbaldehyde with N,N-dimethyl- or N-methylethane-1,2-diamine following reduction. These interesting new ligands have thus been used as hosts to coordinate a range of divalent metal ions and the electrochemical behaviour of the metal complexes have been probed.[525]

A range of cryptates from 1,12:1′,1-bis(1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-dimethylene)bisferrocene have been reported – for example the calcium $(CF_3SO_3^-)_4$ cryptate shown as **(27)** has been structurally characterised.[526] In related work the same research group have obtained a cryptand of ferrocene containing the phenanthroline unit.[527] In the same vein a series of ferrocenes containing a hydrophobic aromatic channel or 'pocket' have been prepared in the reactions of ferrocenylethanol or 1,1′-ferrocenedicarbonylchloride with halo- or thio-aromatic reagents.[528] The encapsulation of trimethylamino-



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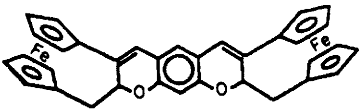
(Reproduced by permission from *J. Organomet. Chem.*, 1996, **523**, 13) methylferrocene salts into a β-cyclodextrin host and the self-exchange kinetics have been tabulated.[529,530] The acid catalysed condensation reaction of 1,3-dihydroxybenzene with ferrocene aldehydes has yielded a range of highly novel ferrocenyl bisphenols and related compounds,[531] for example (**28**). The same group has reported the luminescent binding of dihydrogenphosphate anions to a bipyridyl-bisferrocene receptor.[532] The condensation of acetylferrocene and aromatic aldehydes has been studied using the formation of the β-cyclodextrin inclusion complexes as reaction templates.[533] A ferrocenylhydroxytamoxifen compound has been prepared as a prototype reagent for oestradiol receptor site studies.[534]



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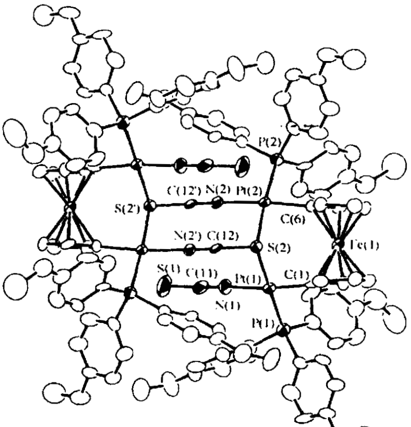
Complexes – The palladation reactions of this bis(ferrocenylimine)[CpFe{(η^5-C_5H_4)-CH=N-(C_6H_3-2-CH_3)$_2$-}]$_2$ have been carried out and depending on the metal to ligand ratio one of two products [Pd_2{CpFe[(η^5-C_5H_3)-CH=N-(C_6H_3)-2-CH_3-]}$_2$(μ-Cl)]$_2$ or [Pd{CpFe(η^5-C_5H_4)}(μ-Cl)]$_2$ results.[535] Five new cyclopalladates ferrocenylketimines of the general formula [PdCl(η^5-C_5H_5)Fe(η^5-$C_5H_3CMe{=}NC_6H_4R$)(PPh_3)], R = 2-OMe, 2-OEt, 2-Me, 2-Br or 2,4,6-trimethyl, have been obtained in similar reaction chemistry.[536] The optically active ruthenocenes (+) and (−) RcCH(OH)Ph, and (+) 1-hydroxymethyl-2-methylruthenocene have been reacted with iodine to give the corresponding iodoruthenocenium salts and in the same paper the asymmetric palladation of $RcCH_2NMe_2$ has been described.[537] The preparation and properties of Mn(I) metallocenylacetylides have been described – the reaction of lithium ferrocenyl or ruthenocenylacetylide with $MnBr(CO)_5$ gives the expected metathesis product but when ferrocenylacetylene is treated with methyl lithium in the presence of the same manganese complex two additional products are obtained both of which have been crystallographically characterised: the first is a manganocenocyclic product and the second is a 4,6-diferrocenyl-N-pyrone.[538] The reaction of 1,3-diferrocenylbut-2-en-1-one with Li_2PdCl_4 in the presence of NaOAc results in the formation of an η^3-allylpalladium complex with bridging chloride ligands which can be further reacted with triphenylphosphine to yield a monomeric species.[539] The reaction of *trans*-FcPt(PEt_3)$_2$X, X = Cl, Br, NCS with carbon monoxide at pressures of 30 kg cm^{-2} at ambient temperature results in the formation of the CO insertion product *trans*-FcC(O)Pt(PEt_3)$_2$X in good yields (*ca.* >70%) while the reaction of the initial complex, X = Cl with arylisocyanides gives the related isocyanide insertion products.[540]

In a departure from their work on chiral catalysts the Togni group have followed up their work with synthesis of 1,1′-disubstituted ferrocenes with interesting conductivity properties. They have examined the reactions of ferrocene-based electron donors such as 1,1′-bis[((2-4-methylthio)phenyl)(*E*)-ethenyl]-ferrocenes with ferrocenium bis(maleonitriledithiolato)-nickelate(1-) to yield the 1:1 paramagnetic salts.[541] The structure of the complex (**29**) obtained in the reaction of 1,1′-ferrocenediyldiplatinum complex $[\{C_5H_4Pt(COD)NCS\}_2Fe]$ with $P(C_6H_4OCH_3\text{-}p)_3$ is illustrated.[542] The reaction of $[(Bz)RuCl_2]_2$ with substituted thallium cyclopentadiamide salts has been used as a method for the preparation of chiral mixed arene/Cp salts.[543] In work relating to ref. 535 the bis(cyclopalladated)tetranuclear complex $[\{Pd(CpFe)(\eta^5\text{-}C_5H_3)(Me{=}N)Cl(PPh_3)\}_2]$ has been obtained and the *meso* form of this compound has been structurally characterised.[544] A very interesting complex of dppf shown as **30** has been obtained in the reaction of $[(PhCN)_2PtCl_2]$ with dppf and 2,2′-diethynyltolan.[545] The compounds 2-(4-pyridyl)ethylferrocenecarboxamide and 2-(2-pyridyl)ethylferrocenecarboximide have been used as ligands in the reaction of $[PdCl_2(MeCN)_2]$ in



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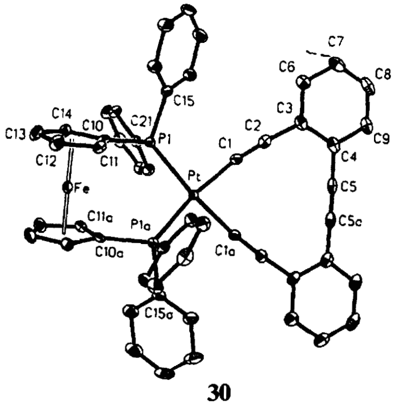

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which the pyridyl nitrogen binds to the palladium in bis ligand complexes.[546] Two conformers of the complex bis[1,1'-bis(dimethylarsino)-ferrocene]dibromonickel(II) have been observed in a crystal structural analysis.[547] The reaction of further ferrocenecarboxamide ligands (see ref. 546) with palladium have been reported in which the ligands, e.g. *N,N'*-bis{2-(2-pyridyl)ethyl}-1,1'-ferrocenedicarboxamide act as bidentate donors.[548]

Chiral – The chiral ferrocenophane[1-(diphenylphosphino)-2,1'-{(1-*N,N*-dimethylamino)-1,3-propanediyl}-ferrocene] has been obtained by lithiation of the chiral precursor ferrocenylamine. The $PdCl_2$ complex of this ligand has been structurally characterised and thus the absolute stereochemistry has been defined.[549] The reaction chemistry of (S,R)-1,1'-bis(diphenylphosphino)-2-(1-acetoxyether)ferrocene with a range of amines has been used as the basis for the preparation of a series of boron-containing ferrocenylphosphine ligands.[550] In the total synthesis of vinblastine, a chiral ferrocenylamine has been used as an auxiliary in secodine-type reactions.[551] A range of chiral 1,2,1'-trisubstituted ferrocenyl ligand have been obtained in the reactions of chiral ferrocenecarboxaldehydes with the hetero ring-directing lithiating reagent system of N-methylpiperazide recently described by the same authors.[552] A series of ruthenium complexes derived from chiral chelating ferrocenyldiphosphines has been made and used as precatalysts in asymmetric hydrogenation.[553] A short review has highlighted the synthetic methods available for the preparation of chiral planar ferrocenes – this serves as a useful update to the reviews which were published in this area in the early 1980s.[554] Some mercaptoethylferrocenes specifically the sodium salt of (R)-1-[(S)-(diphenylphosphino)ferrocenyl]ethyl mercaptan has been further derivatized by reaction of an indanyl expoxide.[555] A follow-up paper on the earlier reviews has been carried out on the subtle influence of ligand structural changes on the outcome of asymmetric transformations carried out by metal complexes of planar chiral ferrocenyl diphosphines and aminophosphines.[556]

Chiral ferrocenyl-α-ethylamines have been used in the ruthenium-catalysed transfer hydrogenation of acetophenone with up to 90% e.e. being achieved.[557]

In the continuing work using chiral oxazolylferrocenes the iridium(I) asymmetric hydrosilation of ketones has been carried out with a diphenylphosphinoferrocenyloxazoline,[558] while a further amendment to the synthesis of chiral ferrocenyloxazolines themselves have been reported.[559] The author of the first ferrocenyloxazoline work has followed up the initial research with a paper on the mechanism of *ortho* direction in the lithiation of the ferrocenyloxazolines.[560] A useful paper has appeared on the use of ferrocenylsulfoxides as *ortho*-lithiation directors – a range of new 1,2-disubstituted chiral compounds have hence been obtained.[561] The ethylation of 2-(*N,N*-dimethylaminomethyl)ferrocenecarboxaldehyde without the need for a catalyst occurs stereospecifically in high yields and diastereoselectivity in an intramolecular asymmetric autocatalytic process.[562] A new ferrocene-based *P,S*-chiral auxiliary has been obtained from thioglucose in a simple reaction of the well known PPFA ligand.[563] The 1:1 complex of (*R,R*)-BMPD(1,3-bis(2-methylferrocenyl)propane-1,3-dione) and yttrium isopropoxide, which was prepared *in situ*, has been used as an efficient catalyst for asymmetric silylcyanation.[564] Meanwhile the 2-(diphenylphosphine)ferrocene carboxaldehyde has been reacted with ethane diamine to yield the anticipated bisiminebisphosphine complex which has been used as a ligand towards ruthenium(II) and copper(I) centres.[565] This follows the chiral synthesis of this precursor reported last year by the same group. A further paper on the theme of isomeric diphosphines of heteroannularly bridged ferrocene has dealt with the synthesis separation and structural elucidation of these ligands,[566] cf. ref 549.

Biferrocenes – Electron Transfer – In their continuing work on mixed valence biferrocenes the Dong research group have examined the electron transfer in valence tripped 2,1′:3,2′:2″,1:3″,2-tetrakis(propane-1,3-diyl)-1,1″-biferrocenium triiodide.[567] This has been followed up with a further synthetic paper on ethyl-substituted biferrocenium triiodide salts which examines the effects of zero-point energy difference on the intramolecular electron transfer.[568] Again phase transitions on similar alkylbiferrocenium salts has been the subject of a related paper.[569]

Ligands – In this section the commonly used ligand bisdiphenylphosphinoferrocene is abbreviated *dppf*. Three rhenium complexes [{hydrido-tris(1-pyrazoyl)borate)}Re(O)Cl_2], [Cp^*Re(O)Cl_2] and [Cp^*Re(N^+Bu)Cl_2] have been reacted with the dilithium salts of 1,1′-ferrocene dithiol and 1,1′-ferrocenedithiol to give six new complexes which have all been spectroscopically characterised.[570] The redox behaviour of ferrocenediols with general formula [{η^5-C_5H_4CCR′(OH)}$_2$Fe] and their mono-substituted counterparts has been studied by cyclic voltammetry and controlled-potential coulometry and these compounds have been shown to undergo quantitative one electron oxidations at potentials which reflect the inductive effects of the cyclopentadienyl ring substituents.[571] A range of 1,1′-bis(diphenylphosphino)-ferrocenes with side chain substituents have been similarly examined.[572] The ferrocenylphosphine [$FcCH_2P(CH_2OH)_2$] prepared from the salt [$FcCH_2NMe_3{}^+I^-$] on treatment with $P(CH_2OH)_3$ in refluxing methanol has been structurally characterised.[573] Meanwhile ferrocenylhydroxyquinolines have been obtained in the one step reactions of lithioferrocenes with the lithium salts of 8-hydroxyquinoline.[574] The crystal structure of the complex [RuH(CO)(CH_3CN)(PPh_3)(*dppf*)][BF_4] has been determined in a paper concerned with the catalytic hydrogenation of ruthenium phosphine complexes.[575] A number of new ferrocene-based mono- and bifunctional tris-1-pyrazolylborate ligands have been described – they are obtained in the direct reaction of (dibromoboryl)ferrocene with pyrazol in triethylamine.[576] Further ligation studies of *dppf* have been carried out in reactions of [$Cp^*Ru(PPh_3)_2Cl$]; the product complex [Cp^*Ru(*dppf*)Cl] on treatment with $AgBF_4$ in acetonitrile yielded [Cp^*Ru(*dppf*)(CH_3CN)]BF_4.[577] Ruthenocenylacetylene has been used as a ligand precursor in its reaction with *trans*-[PtI(C_6H_4X-*p*)(PPh_3)$_2$], X = H, Me, OMe, Cl, CO_2Me which result in the halide exchanged acetylide complexes.[578]

The reaction of the potassium salt of 3(5)-(ferrocen-1-yl)pyrazole with 2-bromopyridine in diglyme at 130 °C followed by an aqueous quench resulted in the formation of 3-(ferrocen-1-yl)-1-(pyridin-2-yl)pyrazole which was subsequently used as a ligand in reactions with Pd- and Pt-allyl complexes.[579] The single crystal structure of the complex $[Au_2(dppf)(C_{16}H_9)_2]$, $C_{16}H_9$ = pyren-1-yl, has been determined in a paper which considers the synthesis and characterisation of complexes of the general type $[Au_2(dppf)R_2]$, R = alkyl, aryl, alkynyl.[580] The ferrocenylpyridyl ligand with a phenyl spacer $[CpFe(\eta^5\text{-}C_5H_4C_6H_4C_5H_4N)]$, obtained on coupling the halophenylarametapyridine with ferrocene zinc chloride, has been used as a ligand in its reactions with $[Os_3(CO)_{10}(CH_3CN)_2]$.[581] Further *dppf* complexes including $[RhR_3H_2(Cp^*)(CO)_8(\mu\text{-}dppf,P,P')AuB]$ have been characterised in the direct reactions of *dppf* with suitable precursor complexes.[582] In a paper appropriately titled 'substituted metal carbonyls 27...' *dppf* has again been used as a suitable ligand in metal cluster complexes.[583] A number of phosphaferrocenes have been used as ligands in iridium carbonyl cluster complexes[584] and tungsten carbonyl complexes[585] while the palladium complexes of 1,1′-bis(2-pyridyl)ferrocene have been further explored.[586] The synthesis and structure of the gold mixed valence compound $[S(Au_2dppf)\{Au(C_6F_5)_3\}_2]$ has also been reported.[587] Some interesting $[(\pi\text{-heterocyclic})FeCp^*]$ complexes e.g. $[(\eta^5\text{-}C_4H_4N)FeCp^*]$ have been used in the preparation of a number of chiral metal complexes.[588] These ligands were prepared many years ago but now they are only beginning to find applications. The well established ligand *N,N*-dimethylaminoethylferrocene has been used in *ortho*-metallations to give titanium and vanadium complexes.[589] The compound $[(\eta^5\text{-}C_5H_4CH(OH)C{\equiv}CH)_2Fe]$ has been used as a precursor ligand in reactions with $Cp_2Mo_2(CO)_4$.[590] Finally the complexes $[\{RuCp^*Cl(\mu\text{-}ER)\}_2]$, E = S, Se, Te, R = ferrocenyl have been obtained in the direct reactions of $[Cp^*Ru(\mu_3\text{-}Cl)\}_4]$ with diferrocenyldichalcogenide ligands,[591] while a number of tripodal ferrocenylphosphines have been prepared in a simple synthetic methodology.[592]

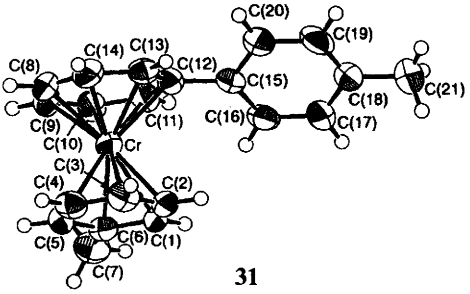
Ring Opening – There continue to be a very large number of papers based on the ring openings of strained ferrocenophanes – only a small selection are included here which can be used to reference all others. A general report has highlighted the full area of ring opening polymerisation reactions of silicon-bridged ferrocenophanes,[593] while tin-bridged ferrocenophanes have been prepared for the first time.[594] The reaction of [1]-silaferrocenophane with palladium and platinum results in metal insertion to form metallasilaferrocenophanes.[595,596] Ferrocenophanes with chlorosubstituents on the silicon bridge have been polymerised by both thermal and transition-metal catalysed processes.[597] The molecular mechanics of the oligomerisation (ring opening) process have also been examined,[598] and finally the ring opening reaction of 1,1′-(phenylphosphino)ferrocenophane with phenyllithium followed by a CO_2/H^+ quench has been re-examined.[599]

3.6 Cobalt, Rhodium, and Iridium – The redox-catalytic reduction of dioxygen at a carbon paste electrode takes place when trace amounts of cobaltocenium salts, which are substituted with electron-withdrawing groups, are present.[600] Variable temperature X-ray diffraction on $[Cp_2Co]PF_6$ has shown the crystal to undergo two fully reversible phase changes with a change in the relative orientation of the cations.[601] In a paper ostensibly dealing with the synthesis of trisubstituted cyclopentadienyl(cymene)ruthenium(II) complexes cobaltocenium models are discussed.[602] A variable temperature NMR study and the reductively-induced isomerisation and decomposition of $[CpCr(CO)_2(SPh)]_2$ has been carried out and the X-ray structure of $[Cp_2Co\{CpCr(SPh)_3\}]$, obtained in the cobaltocene reduction reaction, has been reported.[603] The reaction of cobaltocene with *p*-tolSbCl has been used to obtain $(p\text{-tolSb})_n$, the structure of $[(Cp_2Co)(p\text{-tolSbCl}_3)]$ was also reported.[604] The complexes $[(C_5Me_4R)_2Co_2(CO)_2]$, R = Me, Et react with As_4Sn, n = 3,4 or As_2S_3 to give a series of interesting mixed metal/metaloid complexes, e.g. $Cp^{\#}{}_2Co_2As_2S_3$, $Cp^{\#}Co_3As_2S_4$ etc.[605] An anion receptor has been designed based on a poly-substituted cobalticinium complexes which contain a hydrophobic cavity.[606] The mixed cyclopentadienyl-dithiolene metal complex $[Cp_2Co][Ni(C_3S_5)_2]_3.2MeCN$ has been obtained in the reaction of the cobaltocenium cation with $[Ni(C_3S_5)_2]^-$.[607] Finally a chloride and dihydrogenphosphate-selective anion recognition has been achieved using acyclic mono-, bis- and tris-cobaltocenium receptors.[608]

3.7 Nickel, Palladium and Platinum – The synthesis of the decaphenylnickelocene has been achieved by treating $[Ni(CO)_2(PPh_3)_2]$ with 5-bromo-1,2,3,4,5-pentaphenylcyclopenta-1,3-diene with Zn dust,[609] while decamethylnickelocenium hydrogen-7,7,8,8,-tetracyanoperfluoro-*p*-quinodimethandiide has been prepared and structurally characterised.[610] The reaction of nickelocene with $[Ru_3(CS)_{11}]$ has been used as a source of Cp-transfer to yield cyclopentadienylruthenium clusters.[611]

4 Bis-Arenes

4.1 Chromium – The synthesis of a 2′-methylspiro[cyclohexane-1,3′-3*H*-indole]-chromium tricarbonyl together with its $LiAlH_4$ reduction chemistry to give a mixture of *exo*- and *endo*-complexes has appeared,[612] and the first report of a new class of cycloheptatrienylchromium complexes of the type **(31)** $[(\eta^6\text{-}C_6H_5Me)Cr(\eta\text{-}C_7H_4C_6H_4\text{-Me-4})][PF_6]$ has dealt with the redox chemistry of the new species.[613] FTIR spectra of tricarbonylchromium π-arene complexes, arene = benzoic acid, amidine and phenol have been recorded over a range of pH's in an



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(Reproduced by permission from *J. Chem. Soc. Dalton Trans.*, 1996, 4035) effort to correlate the carbonyl stretching frequencies with pH for applications in sensor technology.[614] The nucleophilic substitution reactions of [(η^6-*o*-fluoroanisole)Cr(O)$_3$] and [(η^6-fluorotoluene)Cr(CO)$_3$] with a range of organolithium reagents, RLi, R = phenylacetylido, fluorenyl, indolinyl, carbazolinyl have been used to obtain the appropriately substituted reagents.[615]

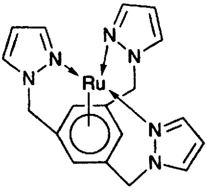
Further synthetic work has been carried out to obtain α,α-diphenylhexatriene complexes – these were obtained by treatment of [(4-substituted benzaldehyde)Cr(CO)$_3$] complexes with bisphosphoranes.[616] The tricarbonylchromium complex of 1,2-dioxobenzocyclobutene has been obtained by hydrolysis of a diacetal precursor. The product has been found to undergo double nucleophilic substitution at the two keto groups.[617] Palladium catalysed coupling reactions have been carried out using 2,6-disubstituted-1-bromoborene chromium tricarbonyl complexes in the presence of arylboronic acids to give the corresponding biphenyl complexes.[618] ^{17}O NMR has been used to elucidate the mechanism of the regiocontrolled functionalisation of [(η^6-1-*tert*-butoxycarbonyl-2,3-dimethylbenzene)chromium tricarbonyl],[619] while the chiral base mediated benzylic functionalisation of [(alkylbenzylether)tricarbonylchromium complexes has been achieved in high e.e. (>97%) and high yields (86–96%).[620] The asymmetric synthesis of benzaldehyde and *o*-anisaldehydemethylisopropylacetals has been achieved in a four step process utilising chiral [(2-methoxybenzaldehyde)Cr(CO)$_3$] as a precursor.[621] Further work on the displacement of fluoride in η^6-fluorobenzene chromium complexes with phenylacetylide salts has resulted in the crystallographic characterisation of [(η^6-(3-phenylethynyl)anisole)chromium(CO)$_3$], cf ref 615.[622] The photochemical synthesis of [(η^6-arene)chromium hydrostannyl] and [(η^6-arene)chromium-bis-(stannyl)] complexes has been achieved in a simple manner – the method utilises the direct photolysis of the arene tricarbonyl complex in the presence of triphenyltinhydride.[623]

A theoretical investigation has been carried out into the factors which control the regio- and stereochemical reactions of nucleophiles with metal carbonyl complexes,[624] while the kinetics and mechanism of the exchange reactions of *trans*[Cr(CO)$_3$-indenylRh(CO)$_2$] with olefins have been probed and it has been shown that the presence of -Cr(CO)$_3$ greatly enhances the rate of 'Rh-(CO)' substitution.[625] The first [(η^6-arene)tricarbonylchromium] complexes which are thermotropic liquid crystals have been prepared and their mesomorphic properties have been studied.[626] A series of cyclic oxacarbene complexes [(η-C$_7$H$_7$)MoL$_2$], L = CO, P-donor ligand has made use of [(η^6-tol)Mo(η-C$_7$H$_7$)]$^+$ as a precursor.[627] A mechanistic study has also been carried out on the mechanism of ligand substitution in [Cr(π-ligand)(CO)$_2$] complexes, where the π-ligand is naphthalene, pyrene, thiophene or 2,6-dimethylpyridine.[628] The asymmetric addition of organolithiums to prochiral arenetricarbonyl complexes particularly arene imines and oxazolines has been investigated.[629] Finally further work has been carried out on the functionalisation of arenes using a lithiation coupling sequence in oxalozinylarene chromium tricarbonyls[630] and a key paper has been published which sheds new light on the formation of the primary product in the Fischer-Hafner synthesis of bisbenzene chromium – the crystal structure of [(BzO)$_2$Cr]-[Al$_3$OCl$_8$] has been reported.[631]

4.2 Manganese – The cyclomanaganation reactions of [(η^6-acylaryl)Cr(CO)$_3$] complexes has been explored with the formation of three new bimetallic complexes one of which has been crystallographically characterised.[632] The interesting hydroquinone complexes of manganese tricarbonyl have been obtained and the structure of [(η^6-hydroquinone)Mn(CO)$_3$]$_2$SiF$_6$ has been crystallographically determined.[633] The same research group have prepared a number of manganese tricarbonyl cations of benzothiophenes to serve as models in the homogeneous hydrosulfurization process.[634] Lastly the molecular structures of [(η^6-toluene)Mn(CO)$_2$L$_{3-x}$]PF$_6$ complexes L = phosphine, phosphite have been explored and the substitution reactions which lead to the formation of (η^5-cyclohexadienyl) complexes.[635]

4.3 Iron – The reaction of 1,8-dichloroanthracene with ferrocene in the presence of AlCl$_3$ yields both [η^6-(1,8-dichloro-9,10-dihydroanthracene)-FeCp][PF$_6$] and [η^6:η^6-(1,9-dichloro-9,10-dihydroanthracene)(FcCp)$_2$]OF$_6$ which have both been characterised using NMR spectrometry.[636] The reactions of [(η^6-*p*-chlorotoluene)(η^5-cyclopentadienyl)iron(II) hexafluorophosphate with the phenolic hydroxyl group of estrane steroids has been used to obtain estrane, estradiol and 17-α-ethynylestradiol labelled with iron.[637] The X-ray structures of [(Bz)RuCl(dippe)][BPh$_4$] and [(Bz)RuH(dippe)(dippe)][BPh$_4$] has been reported in a synthetic paper which utilised the reactions of [FeCl$_2$(dippe)] with cyclohexadienyllithium,[638] while the structures of the cluster compounds [Os$_6$C-(CO)$_{14}$(Bz)],[RuOs$_5$C(CO)$_{14}$(Bz)] and [RuOs$_4$C(CO)$_{12}$Bz] have been determined as products obtained in the reactions of [M(Bz)(MeCN)$_3$]$^{2+}$, M = Ru, Os with carbonyl cluster complexes.[639] Meanwhile the selective chloride displacement from cyclopentadienyl(1,4-dichlorobenzene)iron(1+) with cyclic secondary amines has been described,[640] and the double nucleophilic aromatic substitution reactions between [(η^6-1,2-dichlorobenzene)RuCp]$^+$ and substituted 1,2-benzendiols have been carried out under mild conditions.[641] The reaction of [RuCl$_2$(η^6-arene)]$_2$ with the ammonium salt of dialkyldithiophosphoric acid in 1:1 or 1:2 stoichiometries has been used to obtain a range of areneruthenium(I)dialkyldithiophosphate complexes.[642] The derivatives [Ru(η^5-C$_6$H$_6$X)(Pz$_3$BH)], Pz = pyrazolyl, have been obtained in the addition reactions of nucleophiles with the complex cation [(Bz)Ru(Pz$_3$BH)]$^+$.[643] An electrochemical investigation into a number of polyene-iron complexes which contain ether, sulfide and sulfone bridges have been reported.[644] The migration of a phenyl group from a phosphorus centre to a ruthenium in [(η^6-arene){η^2-Ph$_2$PC(RO=C(R)O)}RuCl] has been observed in refluxing methanol.[645] An interesting flywheel ligand which contains three methylene linked pyrazole units attached to an aromatic ring has been used to bind metals to the arene. A ruthenium complex is shown as **(32)**.[646] Clean benzylation of polymethylaromatic complexes has been achieved using a simple deprotonation/quench strategy.[647]

In part 108 in the series on optically active transition metal complexes the synthesis of an (η^6-benzene)-ruthenium(II) complex with chiral salicylaldiminato ligands has been reported.[648,649] Some other papers worthy of inclusion are listed as follows: the synthesis of a range of [Cp*Ru(η^6-arene)]$^+$ complexes of phenalene



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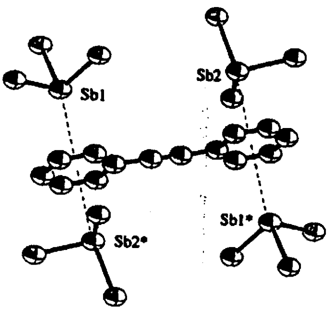
derivatives;[650] the importance of steric effects on the synthesis of *C,N*-cyclometallated amines;[651] the reactions of $[(\eta^6\text{-arene})RuCl_2]_2$ with aromatic phosphines containing methoxy groups;[652] the coordination of aquo and amine ligands to organoruthenium cations of the type $[(Bz)Ru(bpop)]^{2+}$, where bpop = 2,2-bis[4(*R*)-phenyl-1,3-oxazolon-2-yl]propane;[653] the use of $[CpFe(arene)]^-$ complexes as selective electrocatalysts;[654] the activation of 2-propyn-1-ol derivatives by indenylruthenium(II) complexes;[655] the use of $[RuCl_2(carbene)(arene)]$ complexes in the catalaytic synthesis of furans;[656] the synthesis and reactions of areneruthenium pyranone and pyridinone complexes;[657] general arene cluster compound synthesis, isolation and characterisation[658] and finally the use of sodium oximates as starting materials for the synthesis of arene(oximato)osmium half sandwich complexes.[659]

4.4 General Arenes – The reaction of $[CpCo(\eta\text{-}C_6Me_6)]$ with *p*-fluoro-α-methylstyrene leads to the formation of a new cluster complex $[(CpCo)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}p\text{-fluoro-}\alpha\text{-methylstyrene})]$ in which the fluorine can be displaced as fluoride by H^- or Ph^-.[660] The ligand class $[ArX(CH_2)PPh_2]$, Ar = C_6H_5, X = O, CH_2; C_6H_5, X = CH_2, have been used as mixed phosphine/arene donors to rhodium in a study which details the free arene exchange reaction monitors by 2-D NMR.[661] A series of metal-bridged hydrido cluster complexes of the type $[(\mu_3\text{-}H)(CpCo)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-arene})]^+$ have been obtained in simple protonation reactions and their theory of the site protonation of the precursor complexes expounded.[662] The orange complex $[Rh(COD)(DPPB)]^+$ BPh_4^- has been isolated in high yield and it has been observed that this complex reacts with H_2 under ambient conditions to give $[\{(\eta^6\text{-}PhBPh_3)^-\}Rh(DPPB)]$ in quantitative yield.[663] A palladium propyne complex has been isolated in the deprotonation reaction of $[(PPh_3)_2Pd(\eta^2\text{-}C_7H_6)]$,[664] while the crystal structure of $[SbCl_3]_4[PhCH_2CH_2Ph]$ shown as (**33**) shows extensive π-donor arene coordination ability.[665]

A theoretical *ab initio* study has been carried out on zero valent yttrium and gadolinium bis-arene sandwich complexes.[666] The titanium arene complex $[(\eta^6\text{-}Me_6C_6)TiCl_3]^+$ $AlCl_4^-$ has been structurally characterised and further derivatives in the series, M = Zr, Hf (with different counter ions) have been obtained using a simple synthetic methodology.[667] Meanwhile the complex bis(1,2,4-trimethylbenzene)thallium(I) tetrachloroaluminate has been obtained in the direct reaction of 1,2,4-trimethylbenzene thallium(I) chloride in the presence of $AlCl_3$.[668] A novel



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intermediate-valent dinuclear niobium complex [Nb$_2$(η^6-mesitylene)$_2$(μ-I)]I has been obtained in the reaction of [(η^6-mes)$_2$Nb] with iodine – it has been fully characterised using a range of spectroscopic techniques and X-ray diffraction.[669] Finally the crystal structure of [Nb(η-C$_6$H$_5$Me)$_2$] a zero valent complex has been determined.[670]

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