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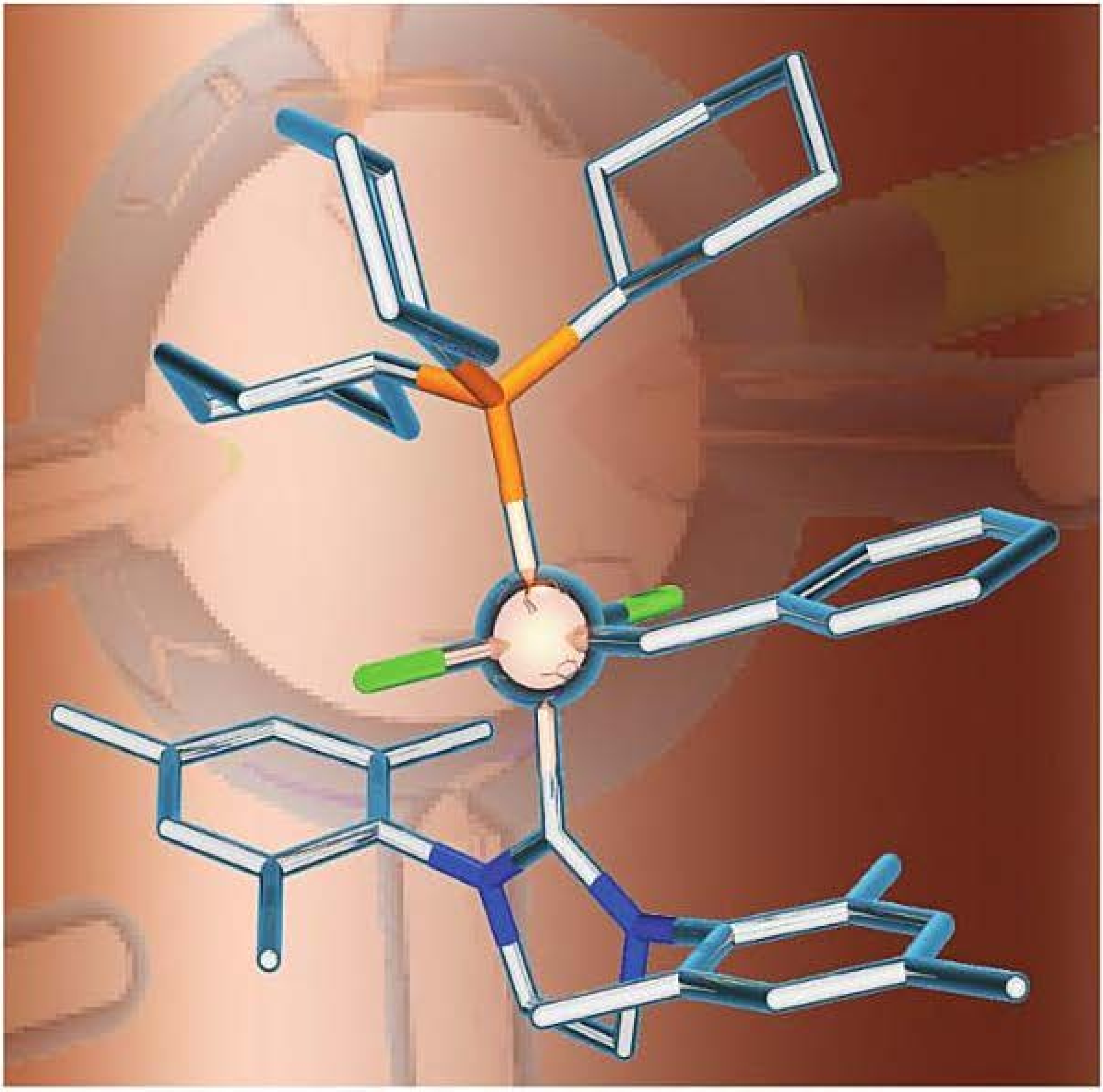
Edited by Ian Fairlamb and Jason Lynam

Organometallic Chemistry

Volume 34



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Organometallic Chemistry

Volume 34

A Specialist Periodical Report

Organometallic Chemistry
Volume 34

A Review of the Literature Published between
January 2004 and December 2005

Editors
I. Fairlamb and J. Lynam, *University of York, UK*

Authors
J.G. Brennan, *State University of New Jersey, USA*
M.P. Cifuentes, *Australian National University, Canberra, Australia*
F. García, *University of Cambridge, UK*
T.J. Geldbach, *EPFL, Lausanne, Switzerland*
M.G. Humphrey, *Australian National University, Canberra, Australia*
R.A. Layfield, *University of Manchester, UK*
T.B. Marder, *University of Durham, UK*
L.C. Miller, *University of Manchester, UK*
J.V. Morey, *University of Cambridge, UK*
D.J. Procter, *University of Manchester, UK*
I.M. Rudkin, *University of Manchester, UK*
A. Sella, *University College London, UK*
A.E.H. Wheatley, *University of Cambridge, UK*
D.S. Wright, *University of Cambridge, UK*

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Preface

Ian Fairlamb and Jason Lynam

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Volume 34 of the Specialist Periodical Reports on Organometallic Chemistry sees a change in the Scientific Editor. Professor Michael Green (University of Bristol, UK) has stepped down after many years of excellent service. Michael is thanked for all his hard work and commitment to this SPR. He is replaced by Drs Ian Fairlamb and Jason Lynam (University of York, UK).

Following on from detailed discussions with the SPR board, the new Scientific Editors, and in consultation with new and existing authors, the format of this SPR has been changed to reflect the emerging interdisciplinary interface between organic synthesis, main group applications and organometallic chemistry.

An exciting series of highlights and critical reviews have been introduced, and this is a particular feature of this volume and indeed will be in future volumes. For example, in volume 34 Professor Todd Marder reports on "*Metal boryl compounds and metal-catalysed borylation processes*", focussing specifically on important synthetic applications and providing a detailed insight into mechanistic questions that continue to emerge in this fascinating area of research. Dr Tilmann Geldbach reports on "*Organometallics in ionic liquids*", which is a topical area at the present time, particularly from a synthetic organometallic perspective. Dr David Procter reports on "*Samarium enolates and their application in organic synthesis*", specifically focussing on the role that samarium enolates play in many important synthetic transformations. We have further included the more traditional comprehensive-style reviews covering the fundamental aspects of organometallic chemistry (covering the literature between January 2004 and December 2005), which lie at the very core of this SPR series. The articles included in this volume serve to demonstrate the breadth and creativity in the field of organometallic chemistry and its application to diverse areas of chemistry.

Department of Chemistry, University of York, Heslington, York, UK YO10 5DD

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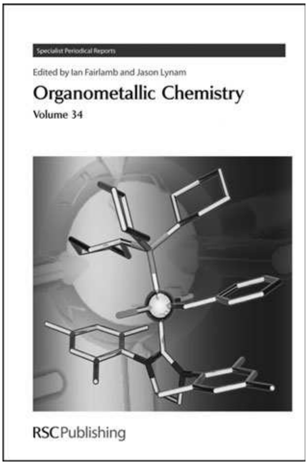

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Cover

Ball and stick representation of Grubbs generation II catalyst.

Abbreviations

Ac	acetate
acac	acetylacetonate
acacen	*N,N′*-ethylenebis(acetylacetone iminate)
Ad	adamantyl
AIBN	azoisobutyronitrile
ampy	2-amino-6-methylpyridine
Ar	aryl
Ar*	2,4,6-tri(*tert*-butyl)phenyl
Ar'_f	3,5-bis(trifluoromethyl)phenyl
arphos	1-(diphenylphosphino)-2-(diphenylarsino)ethane
ATP	adenosine triphosphate
Azb	azobenzene
9-BBN	9-borabicyclo[3.3.1]nonane
BHT	2,6-dibutyl-4-methylphenyl
Biim	biimidazole
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-ene-1,3-dione
bpk	benzophenone ketyl (diphenylketyl)
Bpz_4	tetra(1-pyrazolyl)borate
$Bu^t{}_2bpy$	4,4′-di-*tert*-butyl-2,2′-bipyridine
t-bupy	*tert*-butylpyridine
Bz	benzyl
Bzac	benzoylacetonate
cbd	cyclobutadiene
1,5,9-cdt	cyclododeca-1,5,9-triene
chd	cyclohexadiene
chpt	cycloheptatriene
CIDNP	chemically induced dynamic nuclear polarisation
[Co]	cobalamin
(Co)	cobaloxime [$Co(dmg)_2$ derivative]
cod	cycloocta-1,5-diene
coe	cyclooctene
cot	cyclooctatriene
CP/MAS	cross polarisation/magnetic angle spinning
Cp	η^5-cyclopentadienyl
Cp^R	η^5-alkylcyclopentadienyl

Cp*	η^5-pentamethylcyclopentadienyl
Cp′	trimethylsilylcyclopentadienyl
Cp″	tetramethylethylcyclopentadienyl
CV	cyclic voltammetry(ogram)
CVD	chemical vapour deposition
Cy	cyclohexyl
Cyclam	1,4,8,11-tetraazacyclotetradecane
Cym	*p*-cymene
Cyttp	$PhP(CH_2CH_2CH_2PCy_2)_2$
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-diisopropylphenyl
dipyam	di-(2-pyridyl)amine
DMAD	dimethyl acetylenedicarboxylate
DMAP	2-dimethylaminopyridine
dmbpy	dimethylbipyridine
DME	1,2-dimethoxyethane
DMF	*N,N*-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′	$Fe(CO)_2\eta^5$-(C_5H_4Me)
FTIR	Fourier transform infrared
FVP	flash vacuum pyrolysis
glyme	ethyleneglycol dimethyl ether
GVB	generalised 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 localised orbitals
im	imidazole
Is*	2,4,6-triisopropylphenyl
ISEELS	inner shell electron energy loss spectroscopy
KTp	potassium hydrotris(1-pyrazolyl)borate
LDA	lithium diisopropylamide
LiDBB	lithium di-*tert*-butylbiphenyl
LMCT	ligand to metal charge transfer
LNCC	low nuclearity carbonyl cluster

MAO	methyl alumoxane
Me_2bpy	4,4′-dimethyl-2,2′-bypyridyl
$Me_6[14]dieneN_4$	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene
$Me_6[14]N_4$	5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
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-tributylphenyl
MeTHF	methyltetrahydrofuran
mcpba	metachloroperbenzoic acid
MLCT	metal–ligand charge transfer
MTO	methylrhenium trioxide
nap	1-naphthyl
nb	norbornene
nbd	norbornadiene
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
NCT	neutron capture theory
Neo	neopentyl
Np	1-naphthyl
np_3	$N(CH_2CH_2PPh_2)_3$
nta	nitrilotriacetate
OEP	octaethylporphyrin
OTf	trifluoromethanesulfonate (triflate)
OTs	*p*-toluenesulfonate (tosylate)
Pc	phthalocyanin
PES	photoelectron spectroscopy
PMDT	pentamethylenediethylenetetramine
pd	pentane-2,4-dionate
phen	1,10-phenanthroline
pic	pyridine-2-carboxylic acid
Pin	(+)-pinanyl
Pmedta	pentamethyldiethylenetriamine
pp_3	$P(CH_2CH_2PPh_2)_3$
$[PPN]^+$	$[(Ph_3P)_2N]^+$
py	pyridine
pydz	pyridazine
pz	pyrazolyl
R-PROPHOS	(*R*)-(+)-1,2-bis(diphenylphosphino)propane
R,R-SKEWPHOS	(2*R*,4*R*)-bis(diphenylphosphino)pentane
RDF	radial distribution function
ROMP	ring opening metathesis polymerisation

sal	salicylaldehyde
salen	*N,N′*-bis(salicylaldehydo)ethylenediamine
saloph	*N,N*-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
THF	tetrahydrofuran
thsa	thiosalicylate (2-thiobenzoate)
tht	tetrahydrothiophen
TMBD	*N,N,N′,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(2,5-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

Samarium enolates and their application in organic synthesis

Iain M. Rudkin, Laura C. Miller and David J. Procter*

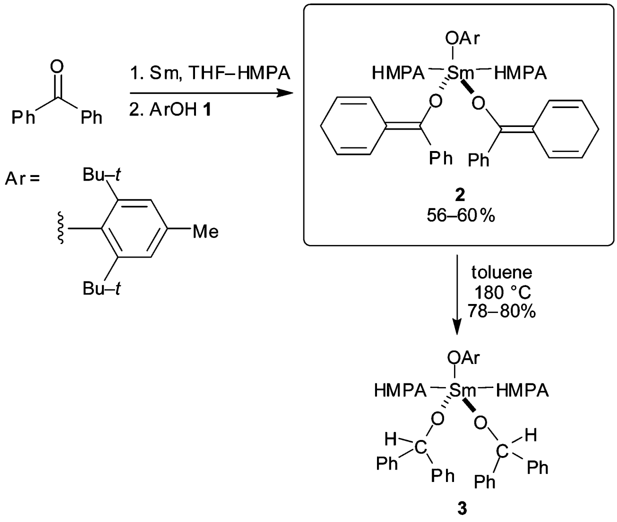
DOI: 10.1039/b606111g

1. Samarium enolates—an introduction

Metal enolates are amongst the most important organometallic species in synthetic chemistry. The generation of lithium enolates, for example, using strong lithium amide bases and reaction with carbon electrophiles represents a cornerstone of synthetic organic chemistry. Whereas the chemistry of many metal enolates is well understood and extensive structural studies have been undertaken, the chemistry of lanthanide enolates is a little studied area. Over the past 25 years, the widespread use of samarium(II) iodide (SmI_2) in organic synthesis[1–3] has brought the chemistry of samarium enolates to the fore as many processes using the popular reducing agent involve the formation and reaction of these organometallic species.

This review will discuss the role that samarium enolates play in organic synthesis drawing on illustrative examples from the recent literature. In the majority of cases, enolates are directly or indirectly formed by the reaction of substrates with SmI_2; a brief introduction to the reagent is therefore given in the following section. The remainder of the review is organised according to the method used to generate the samarium enolate with a section dedicated to the asymmetric protonation of samarium enolates. In recent years, samarium enolates have begun to find application in solution and solid-supported polymer synthesis. This area lies beyond the scope of this article and has recently been reviewed.[4]

One of the few structural studies on a samarium enolate was reported by Hou in 1994.[5] The reaction of a samarium-benzophenone dianion species with bulky phenol **1** led to protonation of the dianion species at the *para*-position of the aromatic ring to give the samarium(III) enolate complex **2** (Scheme 1). An X-ray crystallographic



Scheme 1

School of Chemistry, University Of Manchester, Oxford Road, Manchester, UK M13 9PL. E-mail: david.j.procter@manchester.ac.uk

study revealed that this complex possessed a trigonal bipyramid structure with one aryloxy substituent and two benzophenone moieties equatorial and two HMPA ligands at the apical vertices. When heated in toluene overnight, **2** isomerised to samarium complex **3** (Scheme 1).[5]

2. Samarium(II) iodide in organic synthesis

The first applications of the single electron transfer reagent SmI_2 in organic synthesis were reported by Kagan in 1977.[6] In his seminal study, Kagan carried out a thorough investigation of the organic transformations that could be performed using the reagent.[7] The reagent now enjoys a privileged status amongst reducing agents for synthetic organic chemistry.[1–3]

Due to the reagent's inclination to revert to the more stable samarium(III) oxidation state, it operates as a single electron donor. This property enables SmI_2 to mediate both radical and anionic processes or, most commonly, a combination of the two. The reagent has been used for a wide range of synthetic organic transformations such as functional group interconversions, inter- and intramolecular carbon–carbon bond-forming reactions and powerful cascade reactions that can rapidly increase molecular complexity. The popularity of SmI_2 in part arises from its ability to carry out transformations in a highly chemoselective and stereoselective manner. Added to this, the reactivity and selectivity of the reagent can be modified through the use of co-solvents or additives, thus increasing the scope of this already versatile reagent.[8]

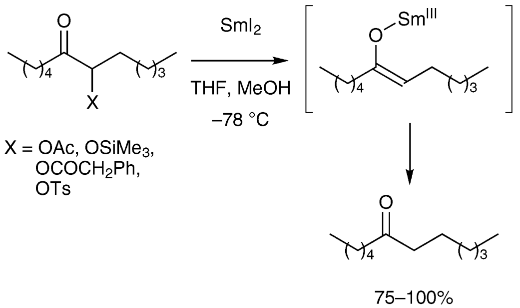
The mechanisms of many SmI_2-mediated organic reactions proceed *via* samarium enolates. Understanding and harnessing the reactivity of these organometallic intermediates is vital to the success of many known transformations and to the future development of powerful, new synthetic procedures.

3. The formation and use of samarium enolates

3.1 Reduction of α-heteroatom substituted carbonyl compounds

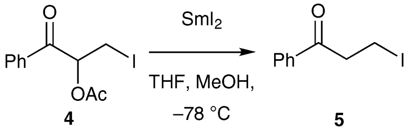
The reduction of α-heteroatom substituted carbonyl compounds is an important transformation in organic synthesis. When the reaction is carried out using SmI_2 this transformation provides a simple route to samarium enolates.

Although the reduction of α-bromoesters was reported by Kagan in 1980,[7] the first detailed study of the reduction of α-heteroatom substituted ketones with SmI_2 was carried out by Molander in 1986.[9] The reduction of a range of α-oxygenated ketones with SmI_2 was found to give the parent ketones in good yield (Scheme 2). Molander proposed the intermediacy of samarium enolates or enols that were protonated by the MeOH co-solvent.[9]



Scheme 2

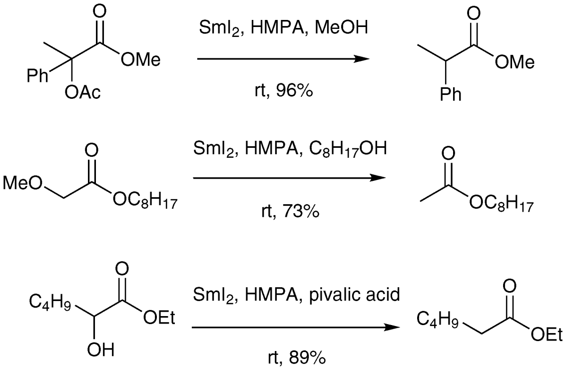
In order to explore the chemoselectivity of the reaction, α-acetoxy ketone **4** possessing a primary iodide group was treated with the reagent.[9] Chemoselective reduction of the α-acetoxy group was observed in the presence of the iodide. Surprisingly, no elimination of iodide from the presumed samarium enolate intermediate was observed and **5** was obtained in good yield. This suggests that either protonation of the enolate intermediate by the MeOH co-solvent is fast, or that an alternative mechanism is in operation for the reduction of aryl ketone **4** (Scheme 3).[9]



Scheme 3

Molander also found that α-halo, α-sulfanyl, α-sulfinyl and α-sulfonyl cyclohexanones underwent smooth reduction with SmI_2 to give cyclohexanone in good yield.[9]

In 1989 Inanaga investigated the reduction of a range of α-oxygenated esters.[10] Deoxygenation of both α-acetoxy and α-methoxy esters proceeded well at room temperature using HMPA to increase the reduction potential of SmI_2. Inanaga found that the use of a more acidic proton source was required for the reduction of α-hydroxyesters (Scheme 4).

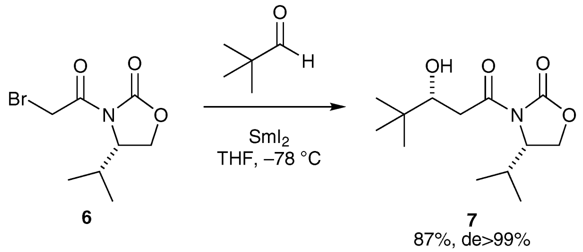


Scheme 4

In contrast, the reduction of α-heteroatom substituted amides with SmI_2 has only recently been studied by Simpkins.[11]

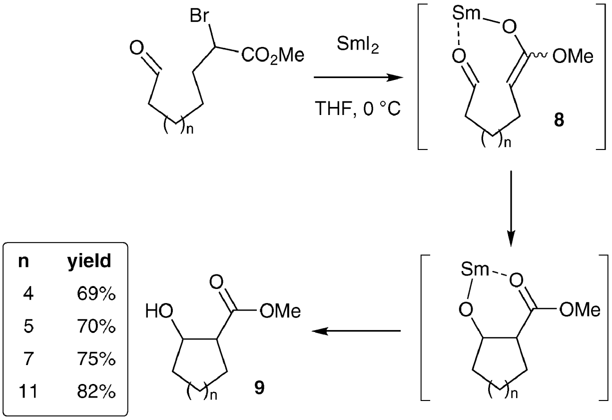
The following sections discuss the use of samarium enolates generated from a range of α-heteroatom substituted substrates.

3.1.1 Samarium enolates from the reduction of α-halo carbonyl compounds. In 1980 Kagan reported the coupling of ethyl α-bromopropionate with cyclohexanone using SmI_2. This was the first example of a samarium Reformatsky-type reaction.[7] Analogous asymmetric, samarium Reformatsky reactions of chiral 3-bromoacetyl-2-oxazolidinones have been described by Fukuzawa.[12] For example, reduction of **6** with SmI_2 generates a samarium enolate that then reacts with pivalaldehyde to give the α-unbranched β-hydroxy carboximide **7** in 87% yield and in high diastereomeric excess (Scheme 5). The reaction is synthetically noteworthy as highly diastereoselective acetate aldol processes are difficult to achieve. The samarium(III) ion is presumed to play an important role in the transition state of the reaction leading to high diastereoselectivity.[12]



Scheme 5

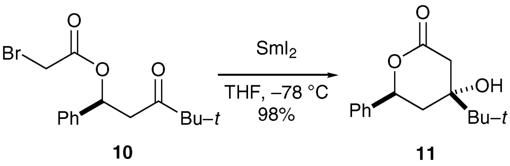
In 1986 Inanaga reported the construction of medium and large ring lactones using SmI_2-mediated *intramolecular* Reformatsky reactions.[13] In 1991 Inanaga then developed a general synthesis of medium and large carbocycles by means of the Reformatsky reaction.[14] The cyclisation of the samarium enolate intermediates **8** to give carbocycles **9** is believed to be aided by the large ionic radius, flexible co-ordination and high oxophilicity of samarium (Scheme 6).



n	yield
4	69%
5	70%
7	75%
11	82%

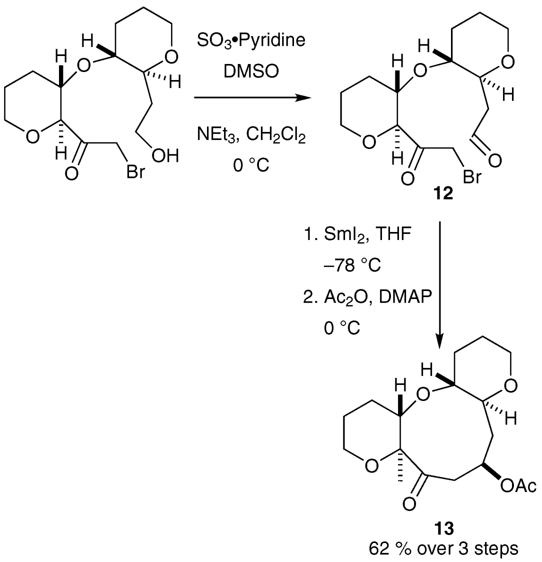
Scheme 6

In 1991 Molander investigated the diastereoselectivity of SmI_2-mediated Reformatsky-type cyclisations and found that they often proceed with high levels of selectivity.[15] For example, treatment of α-bromo ester **10** with SmI_2 gave lactone **11** in 98% yield and as a single diastereoisomer (Scheme 7).



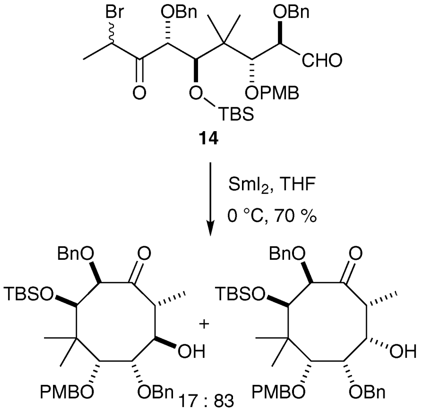
Scheme 7

The SmI_2-mediated Reformatsky reaction has since been used as a key ring forming step in the synthesis of a number of natural products and their precursors. In 1997 Tachibana reported the use of SmI_2 in the formation of the fused oxonene ring F of ciguatoxin.[16] The samarium enolate derived from α-bromoketone **12** underwent efficient cyclisation to give **13** in good yield after acetylation of the Refomatsky product (Scheme 8).



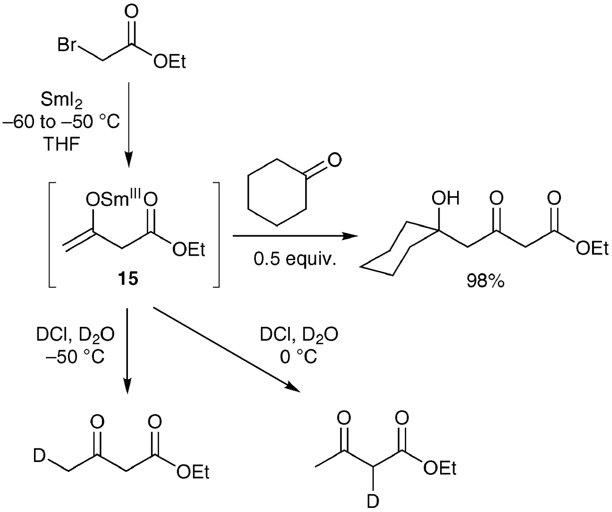
Scheme 8

Mukaiyama reported the use of SmI_2-mediated Reformatsky cyclisations in a programme that culminated in an impressive total synthesis of Taxol.[17,18] α-Bromoketone **14** underwent efficient cyclisation on treatment with SmI_2 to give the eight-membered B ring of the target in high yield and with good stereoselectivity (Scheme 9).



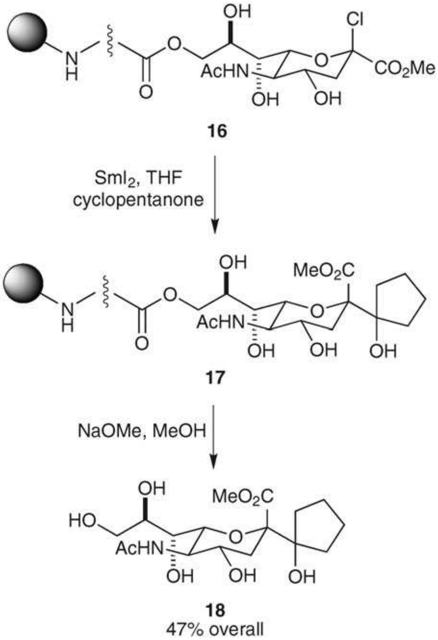
Scheme 9

Utimoto and Matsubara have generated samarium enolates, such as **15**, from α-bromoesters using SmI_2 and have found they undergo efficient aldol reactions.[19] Quenching the samarium enolates with DCl in D_2O shows the enolates are stable at −50 °C but isomerise to the more stable enolate on warming (Scheme 10). The use of two different α-haloesters allows access to more complex samarium enolates before quenching with benzaldehyde.[19]



Scheme 10

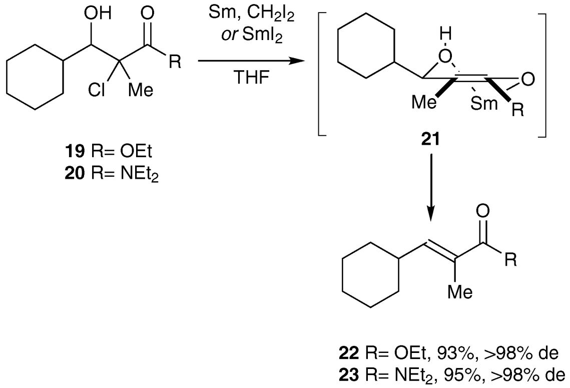
Linhardt has employed samarium enolate-aldol reactions in a solid phase synthesis of *C*-sialosides.[20] Sialyl donor **16**, immobilised on an amino-functionalised, controlled pore glass support, was treated with SmI_2 in the presence of ketone and aldehyde electrophiles, *e.g.* reaction of **16** with cyclopentanone gave adduct **17** (Scheme 11). Cleavage from the support gave *C*-glycoside **18** in good overall yield.[20]



Scheme 11

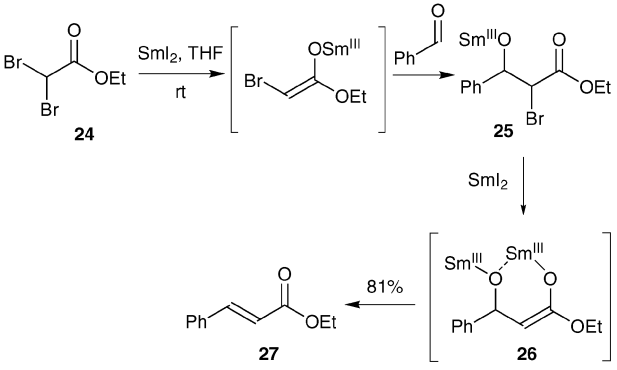
Concellón has reported a highly diastereoselective transformation of α-halo-β-hydroxy esters[21] and amides,[22] such as **19** and **20**, to *E*-α,β-unsaturated esters and amides **22** and **23** using SmI_2. Following two electron transfers, a samarium enolate

21 is formed which then undergoes elimination. The diastereoselectivity of the elimination has been explained by the intermediate samarium enolate **21** eliminating through a six-membered chelate (Scheme 12).[21,22]



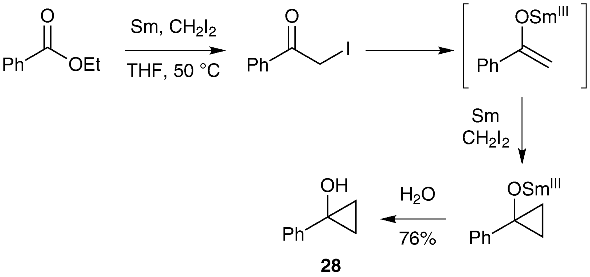
Scheme 12

A similar process involving α-dichlorosubstituted carbonyl compounds has been used to construct (*Z*)-α-chloro-α,β-unsaturated esters.[23] More recently, Concellón has reported a stereoselective method for the formation of (*E*)-α,β-unsaturated esters *via* a sequential samarium enolate-aldol reaction followed by an elimination.[24] For example, ethyl dibromoacetate **24** reacts with benzaldehyde to form samarium alkoxide **25** which is reduced to give samarium enolate **26**. Elimination then affords (*E*)-α,β-unsaturated ester **27** in good yield (Scheme 13).



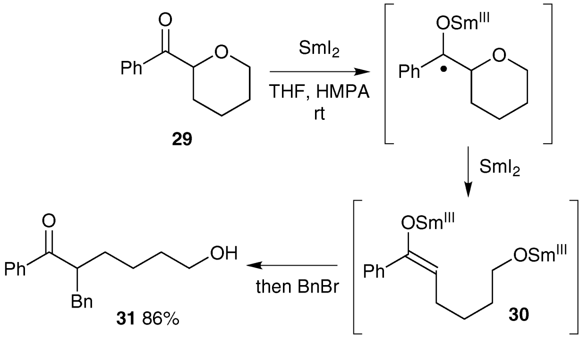
Scheme 13

Imamoto has reported the one-pot synthesis of cyclopropanols from carboxylic acid derivatives using samarium and diiodomethane.[25] The reaction proceeds *via* the preparation of an α-iodoketone, samarium enolate formation and cyclopropanation of the samarium enolate with a second equivalent of diiodomethane and samarium (Scheme 14). In the case of ethyl benzoate, cyclopropanol **28** is obtained in 76% yield. The use of other lanthanide metals led to unsatisfactory results.[25]



Scheme 14

3.1.2 Samarium enolates from the reduction of α-oxygenated carbonyl compounds. In 1995 Enholm reported the reductive cleavage of tetrahydropyrans bearing an α-ketone group.[26] Tetrahydropyran **29** was treated with SmI_2 and HMPA to produce the samarium ketyl-radical anion before a second equivalent of reagent generated the samarium enolate **30**. The enolate was then quenched with benzyl bromide to afford the alkylated product **31** in good yield (Scheme 15).[26]

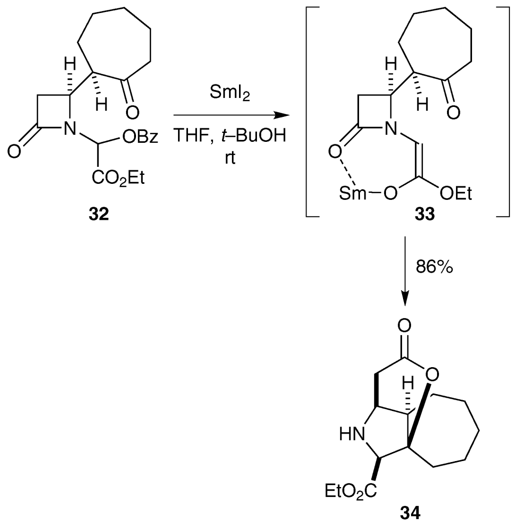


Scheme 15

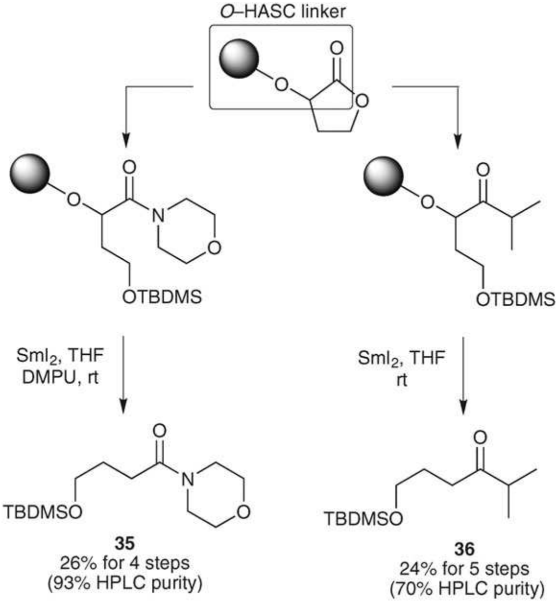
In 2002 Skrydstrup reported the diastereoselective construction of functionalised prolines by a samarium enolate-aldol cyclisation.[27] Treatment of β-lactam-derived α-benzoyloxy esters, such as **32**, with SmI_2 led to the generation of a samarium enolate **33**, aldol cyclisation and addition of the resultant samarium alkoxide to the β-lactam carbonyl. The efficient sequential reaction gave proline derivatives, such as **34**, with high diastereoselectivity and in good yield (Scheme 16).[27]

Procter has developed a linker system for use in phase tag-assisted synthesis based on the reduction of α-heteroatom substituted carbonyl compounds using SmI_2.[28] The linker has been refered to as a HASC linker (α-heteroatom substituted carbonyl linker). In 2002 an ether HASC linker was used to attach substrates to a polymer support and a solid-phase synthesis of ketones and amides, including **35** and **36**, was undertaken to assess the feasibility of the approach. α-Bromo-γ-butyrolactone was immobilised using the linker system and modified to give a range of polymer-supported amides and ketones. At the end of the sequence, traceless cleavage of the HASC linker using SmI_2 released amides and ketones from the solid support in good yields and purity (Scheme 17).[28]

Cleavage of the HASC linker with SmI_2 releases a samarium enolate into solution which is then protonated. As part of their preliminary study, Procter and co-workers carried out model studies evaluating the possibility of trapping the samarium enolate formed on cleavage with carbon electrophiles.[29] Using ketone **37** as a model for an



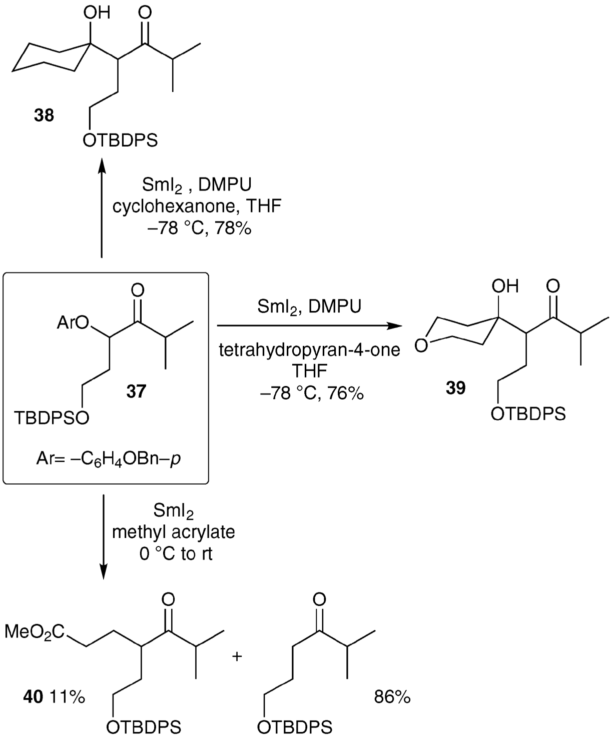
Scheme 16



Scheme 17

immobilised ketone, reduction in the presence of cyclohexanone and tetrahydropyran-4-one resulted in efficient samarium enolate-aldol reactions to give **38** and **39**, resepectively. An attempted samarium enolate-Michael process was less successful and gave the expected adduct **40** in low yield (Scheme 18).[29]

Unfortunately, attempts to trap the samarium enolate formed by the cleavage of a linkage to a polymer support was unsuccessful. It was proposed that residual proton sources contaminating the polymer support led to protonation of the samarium enolate prior to reaction with the carbon electrophile.[29]



Scheme 18

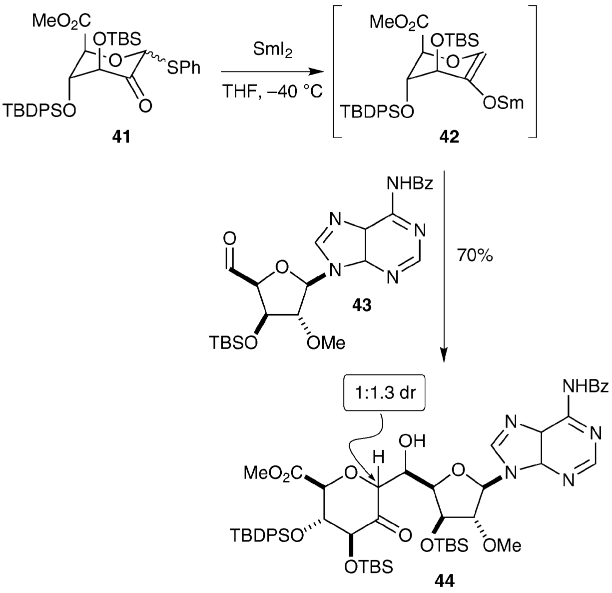
3.1.3 Samarium enolates from the reduction of α-sulfanyl and selenanyl carbonyl compounds. In 1999 Matsuda utilised an intermolecular samarium enolate-aldol reaction in the first synthesis of herbicidin B.[30] The enolate **42** was generated by the reduction of glycosylsulfide **41** with SmI_2. When TLC showed the reduction to be complete, oxygen was passed through the reaction mixture to destroy excess SmI_2 before the addition of aldehyde **43**. Aldol adduct **44** was obtained in high yield and as a mixture of diastereoisomers (Scheme 19).

In 2000 Skrydstrup utilised samarium enolates in a selective method for the introduction of carbinol side chains into glycine residues in peptides and showed the potential of this approach for peptide library synthesis.[31] The chemoselectivity of SmI_2 and the low basicity of the resultant samarium enolate species makes the lanthanide reagent ideal for this application. Treatment of α-pridylsulfide tripeptide **45** with SmI_2 at room temperature gave samarium enolate **46** that underwent aldol reaction with cyclohexanone to give modified peptide **47** in good yield (Scheme 20).

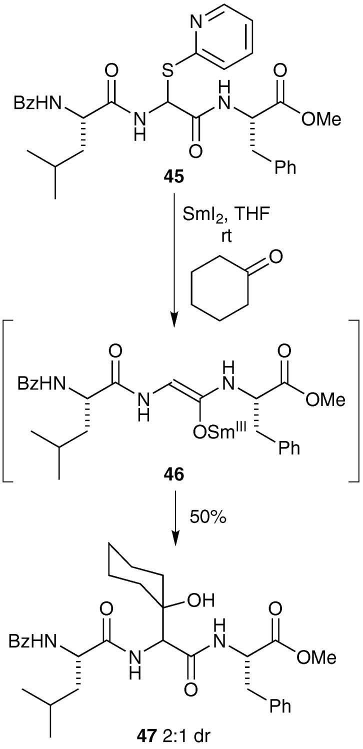
In 2002 Shuto and Matsuda utilised a samarium enolate-aldol reaction to construct 1′α-branched uridine derivatives.[32] Reaction of the samarium enolate formed by the reduction of selenide **48** with benzaldehyde proceeded with high stereoselectivity to give **49** (Scheme 21).

Samarium enolates can also react with electrophiles on oxygen. In Overman's 2001 total synthesis of Shahamin K, a samarium enolate was generated from the reduction of α-phenylsulfonyl ketone **50** and the enolate trapped to give enol acetate **51** by the addition of Ac_2O and DMAP (Scheme 22).[33]

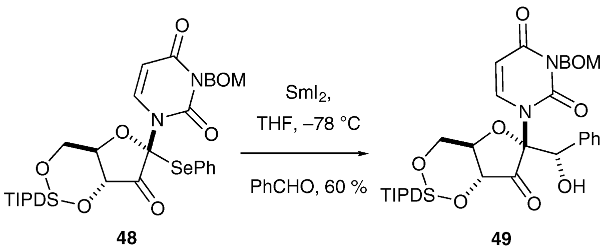
Procter and co-workers have utilised a sulfur version of their HASC linker system for the solid phase synthesis of oxindoles[34] and tetrahydroquinolones[35] using SmI_2 to cleave the linker. The samarium enolates formed by cleavage of the linker have



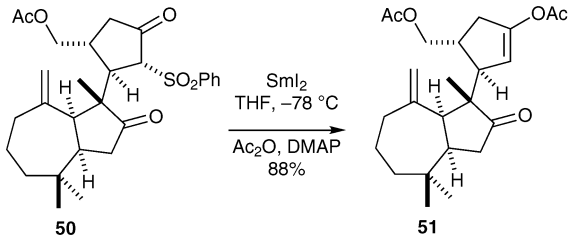
Scheme 19



Scheme 20

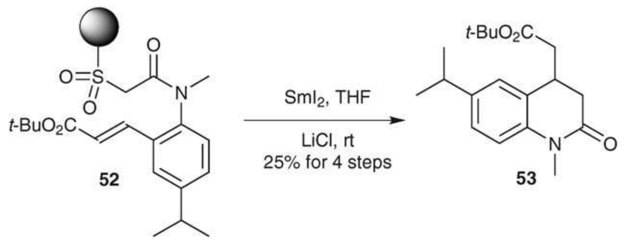


Scheme 21



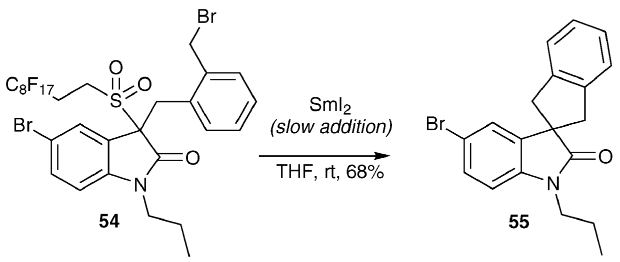
Scheme 22

been utilised, for example, cleavage of the sulfone linkage in **52** results in release of an enolate from the support and cyclisation to give tetrahydroquinolone **53** (Scheme 23).[35,36]



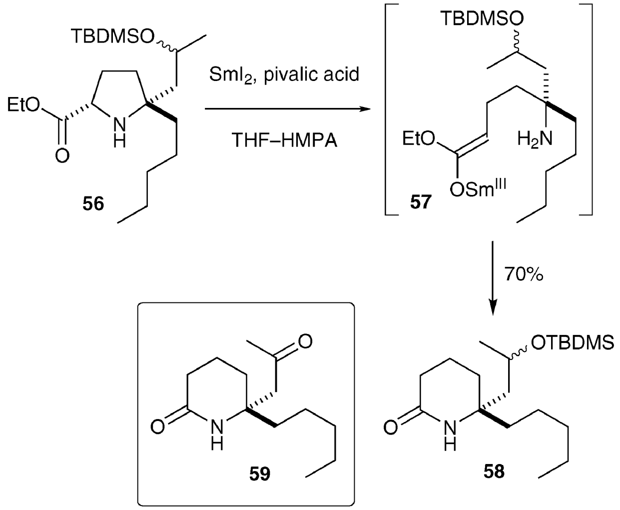
Scheme 23

An analogous sulfur HASC linker system has been utilised by Procter and co-workers for the fluorous synthesis of a range of *N*-heterocycles.[37] Again, the samarium enolate formed on cleavage of the linker can be exploited, for example, removal of the fluorous tag from oxindole **54** generates an enolate that undergoes alkylation in a cleavage-cyclisation sequence to give spirocyclic oxindole **55** (Scheme 24).[38]



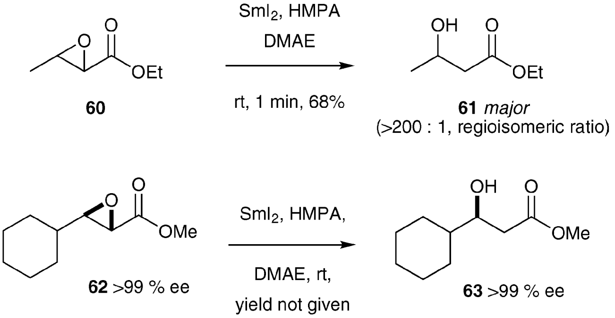
Scheme 24

3.1.4 Samarium enolates from the reduction of α-amino carbonyl compounds. In 1999 Honda reported that α-aminocarbonyl compounds can be reduced using SmI_2 in the presence of HMPA and a proton source.[39] Honda has applied this deamination process to proline derivatives and to the synthesis of a number of naturally occurring alkaloids including a concise enantioselective synthesis of (–)-adalinine **59**, a coccinellied alkaloid.[40] Treatment of **56** with SmI_2 in the presence of pivalic acid leads to generation of samarium enolate intermediate **57** (Scheme 25). Protonation and lactam formation gives **58**, an intermediate *en route* to (–)-adalinine **59**.[40]



Scheme 25

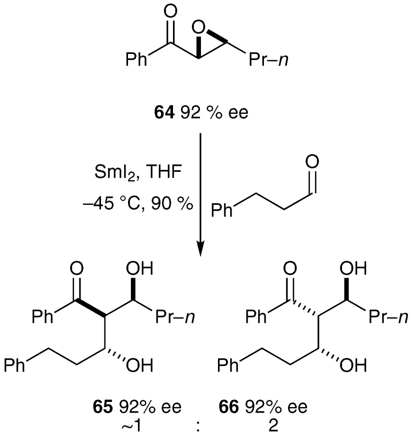
3.1.5 Samarium enolates from the reduction of epoxides and aziridines. In 1987 Inanaga investigated the opening of α,β-epoxy esters.[41] The reduction of ethyl 2,3-epoxybutyrate **60** to ethyl 3-hydroxybutyrate **61** using SmI_2 was found to be accelerated by the addition of HMPA and the yield increased greatly when a proton source was added. The presence of a strong chelating agent such as *N*,*N*-dimethylaminoethanol (DMAE) was crucial in attaining a high level of regioselectivity (Scheme 26). Inanaga surmises that the additive DMAE not only acts as a proton source, but also sequesters the Lewis acidic samarium(III) species thus preventing non-regioselective opening of the epoxide.[41] Using the optimised conditions, Inanaga converted enantiomerically pure α,β-epoxy ester **62** to β-hydroxy ester **63** with complete retention of configuration at the β-carbon (Scheme 26).



Scheme 26

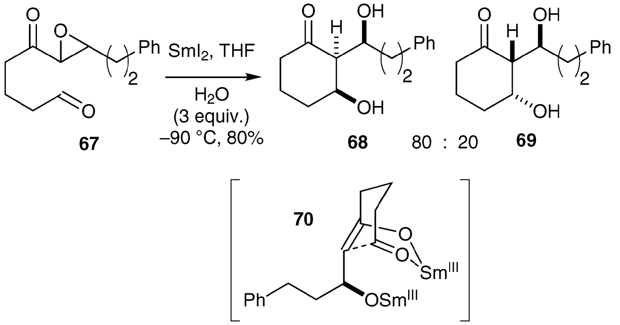
Concellón described a similar reduction of α,β-epoxy esters[42] and amides[43] that led to the formation of (*E*)-α,β-unsaturated esters and amides with high diastereoselectivity. The reaction proceeds by samarium enolate formation and elimination.[42,43]

Mukaiyama has investigated the use of samarium enolates generated from oxiranyl carbonyl compounds in aldol reactions. In 2000 the group developed a method for the synthesis of unsymmetrical *bis*-aldols using a SmI_2-mediated reaction between aldehydes and aryl or alkyl oxiranyl ketones (Scheme 27).[44] Only the *syn,syn* **65** and *anti,anti* **66** *bis*-aldols were obtained from the reaction of epoxide **64**.



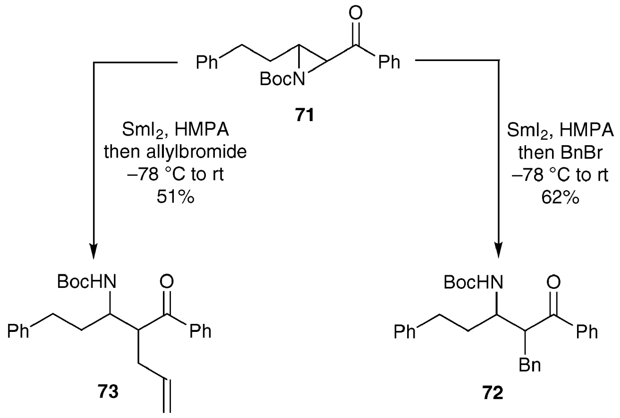
Scheme 27

Mukaiyama has also reported an intramolecular variant of this aldol process.[45] Treatment of epoxide **67** with SmI_2 leads to samarium enolate generation and aldol cyclisation to give diastereoisomeric products **68** and **69** (Scheme 28). The major product diastereoisomer is thought to be formed *via* transition structure **70**.[45]



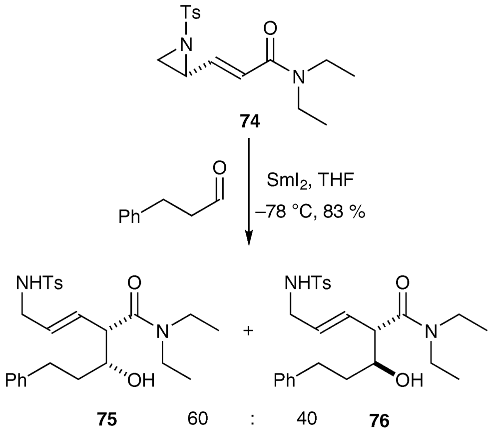
Scheme 28

In 1997 Molander described the preparation of β-amino carbonyl compounds by the reduction of 2-acylaziridines and alkylation of intermediate samarium enolates.[46] Phenyl ketone **71** was reduced using SmI_2 to give an enolate that could be alkylated using benzyl or allyl bromide affording the substituted β-amino ketones **72** and **73**, respectively, in moderate yield and as a mixture of diastereoisomers (Scheme 29).[46]



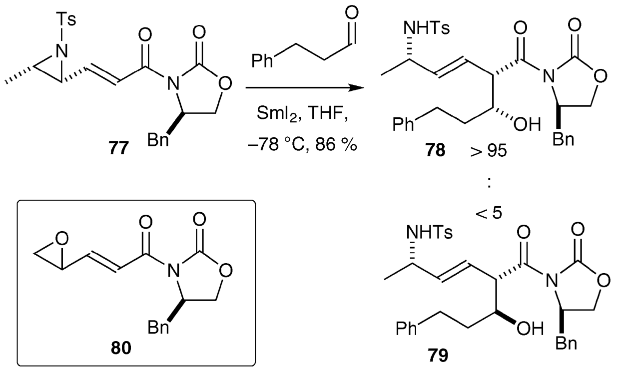
Scheme 29

In 2004 Mukaiyama investigated the synthesis of β-amino-β′-hydroxy ketones using samarium-enolate aldol reactions between aldehydes and enolates derived from aziridinyl ketones.[47] Mukaiyama also examined the construction of δ-amino-β′-hydroxy-β,γ-unsaturated carbonyl compounds, such as **75** and **76**, using the samarium enolate-aldol reaction of aldehydes and γ,δ-aziridinyl-α,β-unsaturated carbonyl compounds **74** (Scheme 30).[48] He found that the reaction was successful for both esters and amides giving good yields and high selectivity.



Scheme 30

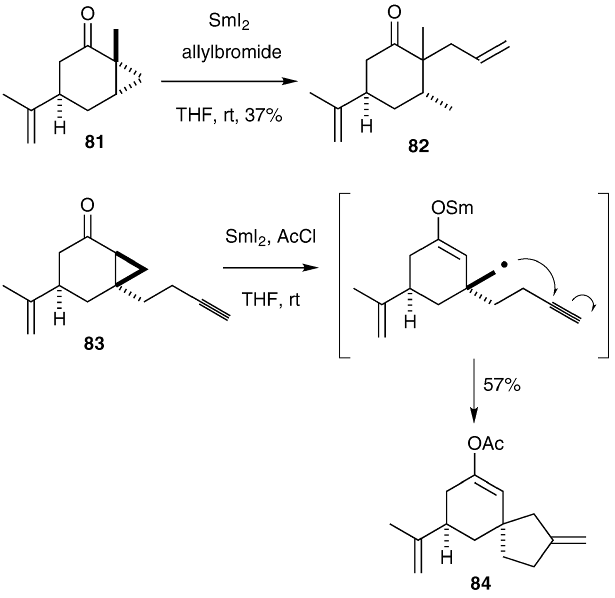
Most noteworthy was the development of an asymmetric samarium enolate-aldol process using an unsaturated aziridine bearing an Evans oxazolidinone auxiliary. For example, on treatment with SmI_2, aziridine **77** underwent smooth ring-opening, enolate formation and a highly *syn* diastereoselective aldol process to give diastereoisomers **78** and **79** in good yield (Scheme 31). Mukaiyama used epoxide **80** in an analogous asymmetric samarium enolate-aldol process to construct the C11–C17 fragment of mycinolide IV.[49]



Scheme 31

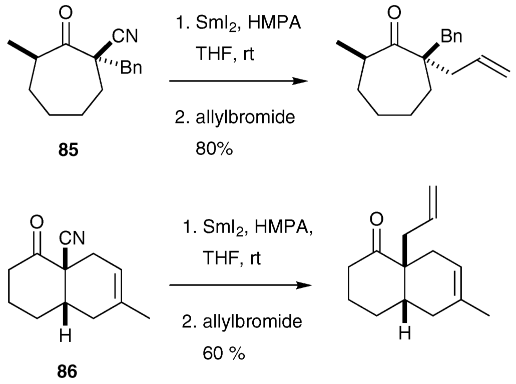
3.2 Samarium enolates from the cleavage of C–C bonds

Samarium enolates can also be formed by the SmI_2-mediated cleavage of carbon–carbon bonds. In 1991 Motherwell used the reagent to generate samarium enolates from cyclopropyl ketones.[50] The samarium enolates formed in this way could be trapped with allyl bromide—for example, the formation of **82** from **81**—acetyl chloride, and silylhalides. Of particular interest is the reaction of cyclopropyl ketone **83** with SmI_2 which triggers a radical cyclisation, concomitant enolate formation, and trapping to give enol acetate **84** (Scheme 32).[51]



Scheme 32

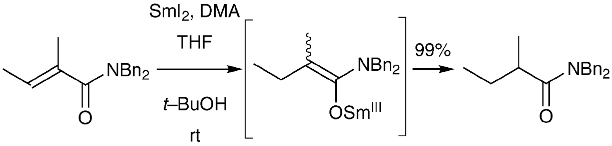
The SmI_2 reduction of α-cyano carbonyl compounds, such as **85** and **86**, has been carried out by Liu and the resultant samarium enolates trapped with allylbromide (Scheme 33).[52] In most cases, the products were obtained as single diastereoisomers in good yield. It is likely HMPA serves a dual role in these reactions, increasing the reduction potential of SmI_2 in the enolate-generating step, and increasing the reactivity of the samarium enolate in the reaction with the carbon electrophile.



Scheme 33

3.2.1 Samarium enolates from the reduction of α,β-unsaturated carbonyl compounds.

In 1991 Inanaga reported the conjugate reduction of α,β-unsaturated esters and amides using SmI_2.[53] Inanaga's reagent system, SmI_2-DMA-proton source, provided a mild method for the transformation (Scheme 34). Reduction using d_4-methanol as the proton source showed deuterium incorporation on both α and β-carbons indicating the intermediacy of samarium enolates.



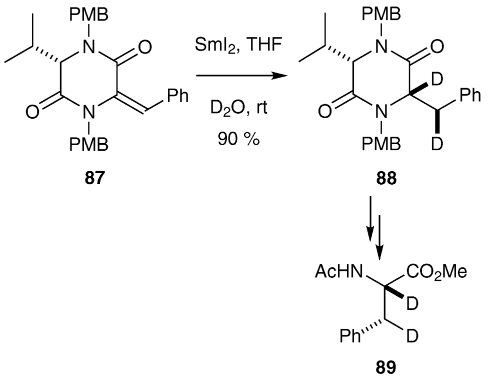
Scheme 34

In 1992 Alper extended the reduction to include α,β-unsaturated acids and anhydrides using HMPA as a promoter for the reaction.[54] Fukuzumi and Otera developed the process further still in 1997 by performing the reduction on a number of unsaturated carbonyl compounds including α,β-unsaturated cyclic ketones and lactones.[55] Interestingly, ring size plays an important role in this reaction as cyclohexenone and 5,6-dihydro-2*H*-pyran-2-one failed to undergo reduction, while larger, macrocyclic ketones and lactones underwent reduction in good yield.

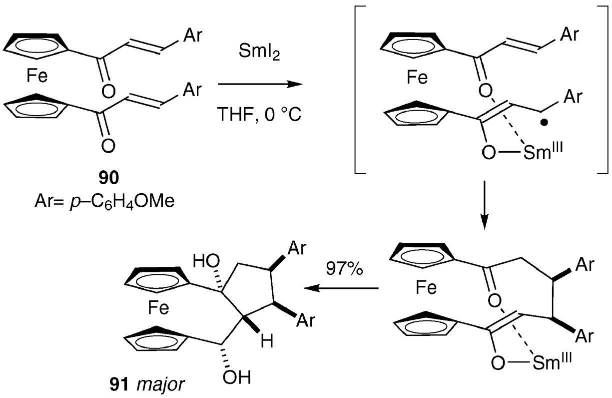
More recently, Davies has performed a diastereoselective conjugate reduction with SmI_2 and D_2O to gain access to isotopically labelled α-amino acids.[56,57] Reduction of enantiomerically pure diketopiperazine **87** generated a samarium enolate intermediate that was diastereoselectively deuterated to give **88**. Further synthetic steps yielded labelled α-amino acid **89** (Scheme 35).

While the conjugate reduction of α,β-unsaturated carbonyl compounds is a potentially useful way of accessing samarium enolates, there are few examples of the use of samarium enolates generated in this way. Fang has reported the SmI_2-mediated reductive cyclisations of 1,1′-dicinnamoylferrocenes such as **90** to give the corresponding [3]-ferrocenophane diols **91**.[58] The reactions proceed *via* a radical coupling, the aldol cyclisation of a samarium enolate intermediate and ketone reduction in a highly diastereoselective, one-pot operation (Scheme 36).

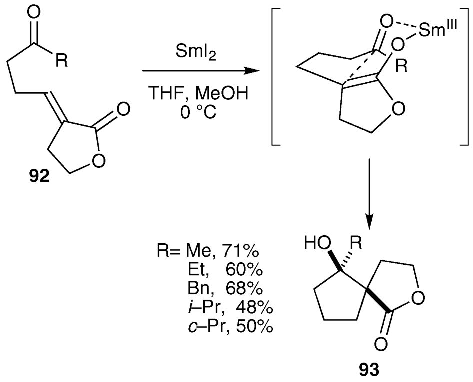
Procter has reported the diastereoselective spirocyclisation of unsaturated ketones **92** using SmI_2.[59] The cyclisation proceeds by conjugate reduction, samarium enolate generation, and a chelation-controlled aldol cyclisation to give *syn*-spirocycles **93** in good yield (Scheme 37).



Scheme 35



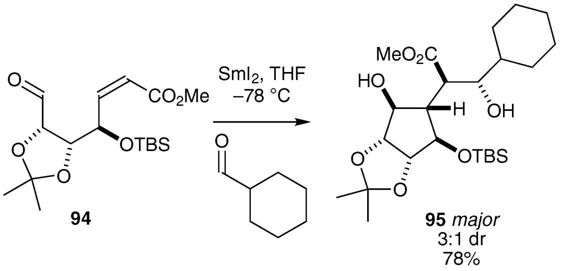
Scheme 36



Scheme 37

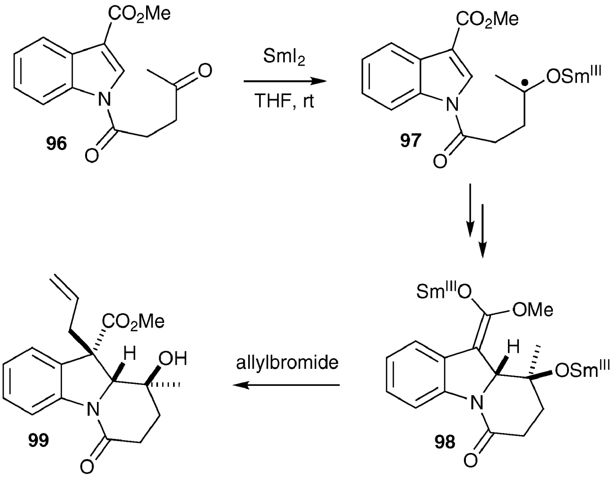
3.3 Samarium enolates from the addition of radicals to α,β-unsaturated carbonyl compounds

In 1994 Enholm described a SmI_2-mediated ketyl-olefin cyclisation/intermolecular aldol sequence.[60] A samarium ketyl-radical anion is generated by reduction of the aldehyde in carbohydrate-derived substrate **94**. Radical cyclisation and a second reduction step then generates a samarium enolate that undergoes aldol reaction with aldehydes or ketones. Products, such as **95**, are formed in high yield and as a remarkably simple diastereoisomeric mixture considering four contiguous new stereocentres are formed in the process (Scheme 38).[60]



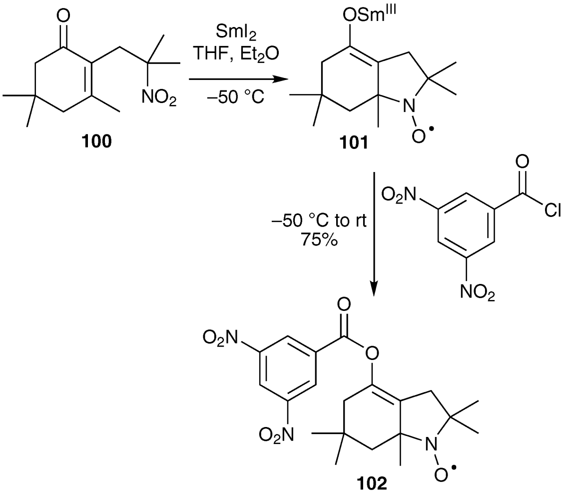
Scheme 38

In 2003 Reissig described a stereoselective synthesis of highly functionalised benzannulated pyrrolizidines and indolizidines through the SmI_2-induced cyclisations of indole derivatives.[61] After the cyclisation of samarium ketyl radical **97**, a second electron transfer gives a samarium enolate **98** that can be quenched with carbon electrophiles such as allylbromide to give products such as **99**. These cascade reactions selectively generate three contiguous stereogenic centres including a challenging quaternary centre at the 3-position of the indole moiety—a structural motif found in many indole alkaloids (Scheme 39).



Scheme 39

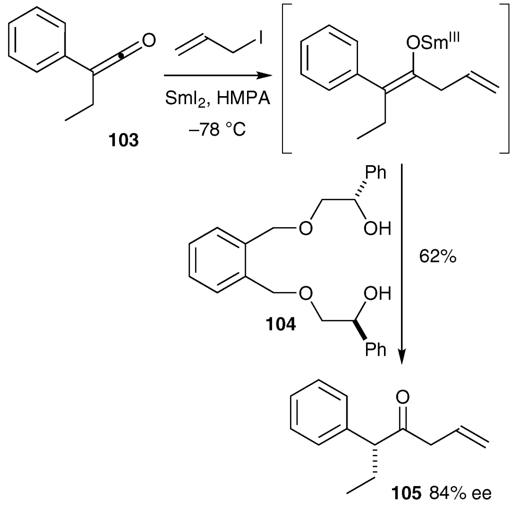
Tamura has reported the preparation of samarium enolates by the addition of nitrogen-centred radicals to α,β-unsaturated carbonyl compounds. Treatment of nitroenone **100** with SmI_2 generated the samarium enolate-radical **101** which was found to be relatively stable.[62] *O*-Acylation of the samarium enolate could be carried out using 3,5-dinitrobenzoyl chloride to give nitroxide radical **102** (Scheme 40).



Scheme 40

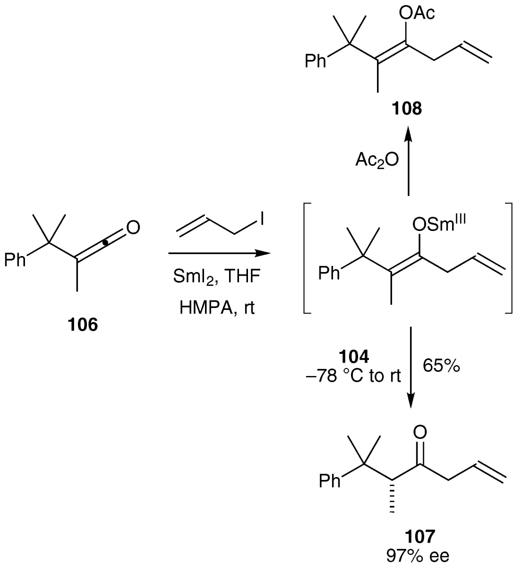
3.4 Enantioselective protonation of samarium enolates

Samarium enolates have found extensive use in asymmetric protonation studies. Takeuchi has generated samarium enolates for asymmetric protonation studies by adding an allylsamarium to ketenes, such as **103**.[63] After screening a number of chiral protonating agents in the reaction, *o*-xylene-derived diol **104** was found to give the enantiomerically enriched ketone **105** in 84% ee (Scheme 41).



Scheme 41

Takeuchi investigated the use of alkylsamariums with a range of unsymmetrical ketenes with the best result being observed for the reaction of ketene **106** giving ketone **107** in 97% ee (Scheme 42).[64] The enantioselectivities were not high in every case and Takeuchi speculated that this was due to the possibility of forming samarium enolate isomers. In order to investigate further, the samarium enolates formed from a range of ketenes were trapped as the corresponding enol acetates, such as **108** and the double bond geometry determined by NMR spectroscopy. It was



Scheme 42

apparent that the ratio of samarium enolate isomers varied with the steric difference between the groups on the ketene. In cases where single enolate isomers were produced, as in Scheme 42, high enantiomeric excesses were obtained.[64]

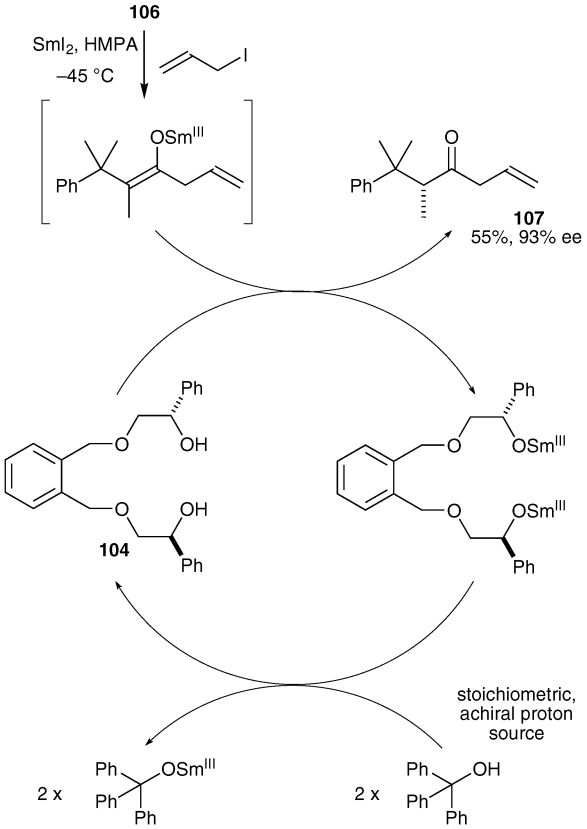
Takeuchi also studied the *catalytic* enantioselective protonation of samarium enolates,[65] where an achiral proton source is used to regenerate the chiral proton source **104**. Generation of a samarium enolate intermediate from ketene **106** was followed by protonation using a catalytic amount of **104** (15 mol%) in conjunction with trityl alcohol (Scheme 43). The trityl alcohol efficiently protonated the conjugate base of the chiral proton source but crucially did not carry out the achiral protonation of the samarium enolate.[65] This led to a highly selective *catalytic* process giving products in up to 93% ee (only slightly lower than the selectivities obtained in the analogous stoichiometric reaction).[64]

Takeuchi and Curran have also reported the use of fluorous, chiral and achiral proton sources in a biphasic, catalytic enantioselective protonation of the samarium enolate derived by allylsamarium addition to ketene **106**.[66]

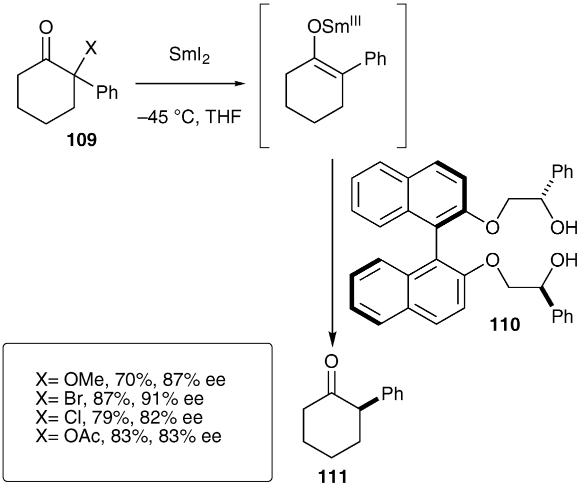
In 1997 Takeuchi turned to the SmI_2 reduction of α-heteroatom substituted carbonyl compounds as a means for forming the requisite samarium enolates needed for his asymmetric protonation studies.[67] Takeuchi examined the reduction of α-heterosubstituted cyclohexanone **109** bearing a phenyl substituent in the α-position. A number of ketone substrates were employed using the BINOL derived chiral proton source **110**. In all cases, ketone **111** was obtained in good yield and high enantiomeric excess (82% to 91% ee) (Scheme 44).

Subsequent work resulted in a library of tetradentate chiral alcohols that were effective for the protonation of samarium enolates formed from a range of cyclic, α-heterosubstituted ketones and lactones.[67,68] Scheme 45 shows the SmI_2 reduction-asymmetric protonation of bromo-lactone **112** using tetradentate chiral alcohol **113** (Scheme 45).

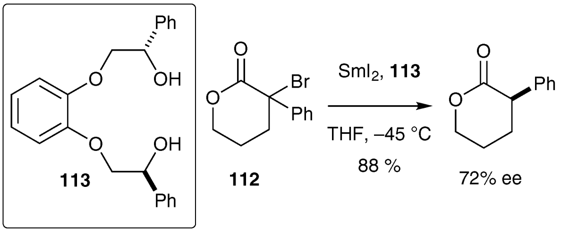
Takeuchi has proposed a transition state model to explain the enantioselectivity observed in the reaction (Fig. 1). In transition state T_1—**114**, the aryl substituent on the enolate has no unfavourable interactions with the phenyl ring of the proton source. As a result, protonation by the chiral alcohol takes place from the *si* face giving the product with (*R*)-configuration. Conversely in transition model T_2—**115**, steric interactions between the aryl substituent on the enolate and the phenyl ring of



Scheme 43



Scheme 44



Scheme 45

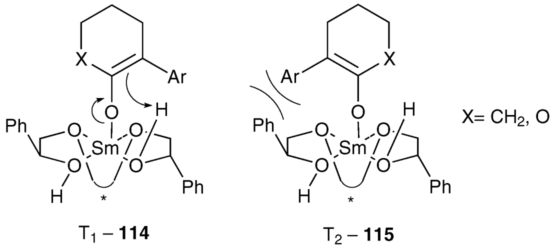
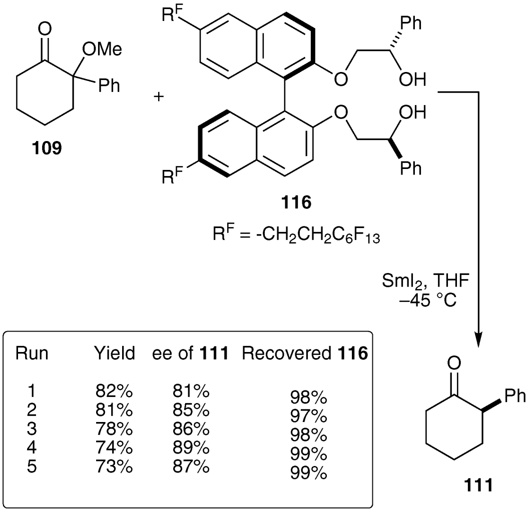


Fig. 1

the proton source gives rise to a higher energy conformation disfavouring protonation by this path.[67,68]

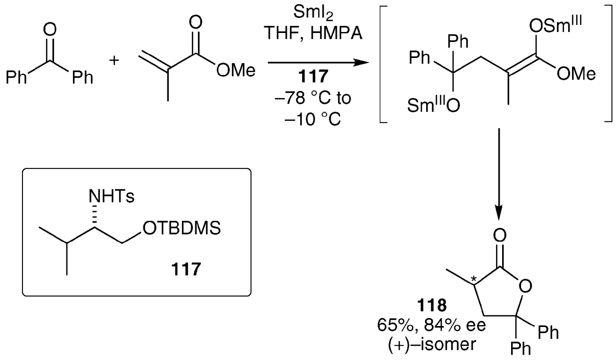
In 2000 Takeuchi reported the synthesis of the fluorous BINOL derivative **116** and used it in the stoichiometric asymmetric protonation of the samarium enolate derived from **109** (X = OMe) (Scheme 46).[69] The chiral proton source **116** could be easily recovered from the product mixture using fluorous solid phase extraction (FSPE). Recycling **116** gave little loss in the yield and enantioselectivity of the process.



Run	Yield	ee of **111**	Recovered **116**
1	82%	81%	98%
2	81%	85%	97%
3	78%	86%	98%
4	74%	89%	99%
5	73%	87%	99%

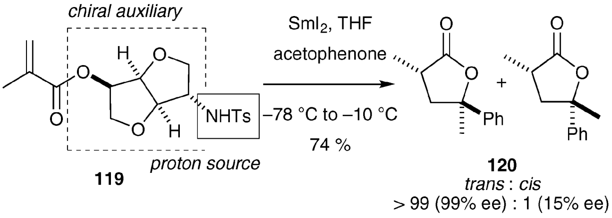
Scheme 46

Aside from the work of Takeuchi there are few examples of the enantioselective protonation of samarium enolates. One notable exception is the recent work of Lin on the reductive coupling of ketones with methyl methacrylate. Lin's process also involves the interception of a samarium enolate with a chiral proton source (Scheme 47).[70] Prior to Lin's studies, Fukuzawa examined the role of the proton donor in this reaction and used deuterium labelling to show that a samarium enolate is protonated during the course of the reaction.[71,72] Lin looked at a range of chiral alcohols, amides, and amino alcohols for the enantioselective protonation of the presumed, acyclic samarium enolate intermediate. Chiral sulfonamides were the most promising chiral proton sources. For example, in the coupling of benzophenone with methyl methacrylate, the product γ-butyrolactone **118** was obtained in good yield and enantiomeric excess using the sulfonamide chiral proton source **117** (Scheme 47).[70]



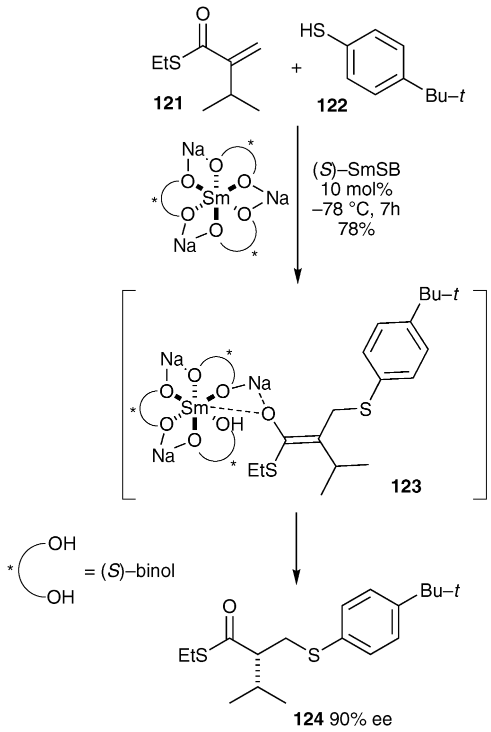
Scheme 47

Lin followed up these studies by examining the reactions of enoate substrates bearing carbohydrate-derived auxiliaries that also functioned as chiral proton sources.[73] Lin found that the diastereoselectivity of the coupling of substrate **119** with acetophenone varied greatly (50:50 to 99:1 in favour of the *trans* isomer) as did the enantiomeric excess of each diastereoisomer of the product **120** (Scheme 48).[73]



Scheme 48

Finally, Shibasaki has reported the use of a samarium-sodium-binol, heterobimetallic complex ([$Na_3(Sm(binol)_3$], SmSB) in the asymmetric conjugate addition of thiols to α,β-unsaturated carbonyl compounds.[74] For example, treatment of thioester Michael acceptor **121** with thiophenol **122** generates a samarium/sodium enolate intermediate **123** that undergoes catalytic asymmetric protonation from the samarium complex to generate product **124** in high enantiomeric excess (Scheme 49).[74]



Scheme 49

4. Conclusions

This review has examined the many methods reported for the generation of samarium enolates. The resultant samarium enolates have been shown to react with a range of electrophiles although it is clear that they have a very different reactivity profile compared to more conventional metal enolates. There are several examples of sophisticated, intermolecular samarium enolate-aldol reactions, including asymmetric variants employing substrates bearing chiral auxiliaries. Samarium enolate-aldol processes are presumably facile due to the Lewis acidic properties of the samarium(III) ion resulting in activation of the aldehyde and ketone electrophiles. The reaction of samarium enolates with alkylhalides is more limited and appears to require reactive electrophiles such as allyl- and benzylbromide. Samarium enolates have also played a major role in the development of asymmetric protonation as a synthetic methodology.

Although relatively little is still known about the structure and reactivity of samarium enolates, they are clearly versatile intermediates for synthesis. The literature reports discussed in this review show that it is often necessary to generate the samarium enolate in the presence of the carbon electrophile in order to obtain good yields of adducts. This suggests that samarium enolates are less stable than other common metal enolates. Despite this limitation, processes involving samarium enolates are beginning to find application in a number of areas including target synthesis and the development of high-throughput methods using solid-phase and fluorous technologies. Further study, including detailed kinetic investigations and a fundamental understanding of the coordination chemistry of these intriguing organometallic species, is needed to fully assess their synthetic potential.

Abbreviations

BINOL	1,1′-Binaphthalene-2,2′-diol
Boc	*tert*-butoxy carbonyl
BOM	Benzyloxymethyl
Bz	Benzoyl
DMA	*N*,*N*-dimethylacetamide
DMAE	*N*,*N*-dimethylaminoethanol
DMAP	4-Dimethylaminopyridine
DMPU	1,3-Dimethyl-3,4,5-tetrahydro-2(1*H*)-pyrimidinone
DMSO	Dimethyl sulfoxide
dr	Diastereomeric ratio
ee	Enantiomeric excess
equiv.	Equivalents
FSPE	Fluorous solid phase extraction
h	Hour
HASC	Heteroatom substituted carbonyl
HMPA	Hexamethylphosphoramide
HPLC	High performance liquid chromatography
Mol	Moles
NMR	Nuclear magnetic resonance
PMB	*para*-methoxybenzyl
rt	Room temperature
TBDMS	*tert*-butyldimethylsilyl
TBDPS	*tert*-butyldiphenylsilyl
TBS	see TBDMS
THF	Tetrahydrofuran
TIPDS	Tetraisopropyldisiloxane-1,3-diyl
TLC	Thin layer chromatography
Ts	*para*-toluenesulfonyl

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Metal boryl compounds and metal-catalysed borylation processes: synthetic applications and mechanistic considerations

Todd B. Marder

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1. Introduction

In this review, I take the liberty of highlighting several recent aspects of boron chemistry pertaining especially to metal boryl (M-BR_2) complexes[1] and both stoichiometric and catalytic borylation reactions[2] which struck my fancy. Thus, the paper is in no way intended to be comprehensive even within the above topics as it merely reflects some of my own interests, so I offer my apologies in advance to all whose work is not represented. My intention is to inform the reader of a few interesting advances which I expect will have an impact on organic synthesis, and to stimulate discussion about the reactivity of the boryl complexes, the mechanisms of the stoichiometric and catalytic processes, and where this chemistry might lead.

We have seen some really exciting breakthroughs in the last few years in terms of new metals employed in this chemistry, new reactivity patterns, and new catalytic processes which would not have been anticipated a decade or so ago. In addition, with the continued expansion of the applications of the Suzuki-Miyaura cross-coupling technology,[3] and the resulting birth of new companies[4] around the world specialising in the production of diboron esters (*e.g.*, B_2pin_2,[5] B_2neop_2,[6] and B_2cat_2;[7] pin = pinacolato = $OCMe_2CMe_2O$, neop = neopentane glycolato = $OCH_2CMe_2CH_2O$, cat = catecholato = 1,2-$O_2C_6H_4$), aryl- and vinylboronates and boronic acids, the chemistry of metal boryl complexes and related catalytic methods for preparing organoboronates have really come of age. I note that some of the diboron esters are now being produced commercially on 100 kg scale, and that the prices of these reagents have dropped accordingly, making the chemistry more accessible and more economical, and attracting new research groups into the field.

2. Synthesis and reactivity of a novel lithium boryl compound

One of the key recent developments is that of Segawa *et al.*,[8] who reported the isolation of the first structurally characterised lithium boryl compound, LiB(RNCH═CHNR) (**3**) where R is the bulky 2,6-$^iPr_2C_6H_4$ group (Fig. 1). This was prepared by reduction of the BrB(RNCH═CHNR) precursor **2** using a combination of lithium powder and naphthalene at −45 °C. A single crystal structure of the adduct, **3 DME**, shows it to be dimeric in the solid-state, with the two Li cations bridged by DMEs. The Li–B separation is 2.291(2) Å, 8.5% longer than the sum of the covalent radii of Li and B. The ^{11}B NMR spectrum of **3** (δ 45.4, peak width at half-height = 535 Hz) was interpreted in terms of the boron centre having anionic character and a highly polarised B–Li bond in solution. Compound **3** reacts with H_2O and D_2O to give the corresponding boranes $(R_2N)_2BH$ and $(R_2N)_2BD$, respectively. In order to appreciate the importance of this finding, we must first consider that when R is small (*e.g.* Me,[9] or NR_2 = pyrrolidine[10]), $XB(NR_2)_2$ compounds undergo reductive dimerisation to $(R_2N)_2B$-$B(NR_2)_2$ when treated with alkali metals such as Na or K (eqn (1)). Note that $(Me_2N)_2B$-$B(NMe_2)_2$ is the immediate and key synthetic precursor to all of the diboron esters mentioned above. We will return to these later.

Department of Chemistry, Durham University, South Road, Durham, UK DH1 3LE.
E mail: todd.marder@durham.ac.uk; Fax: 0191-384-4737; Tel: 0191-334-2037

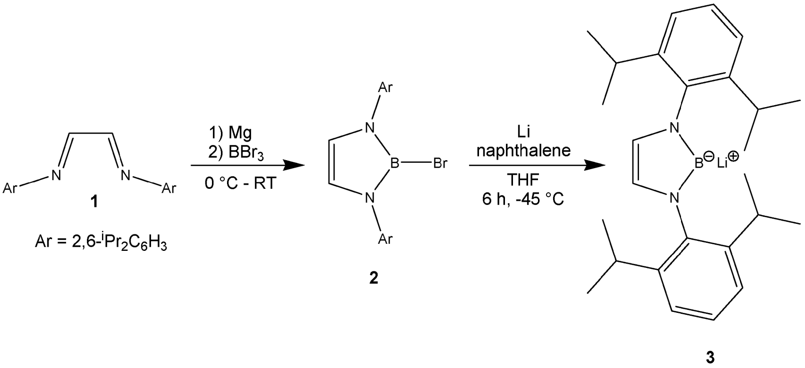


Fig. 1 Synthesis of the first structurally characterised lithium boryl compound.

$$(\mathrm{Me_2N})_2\mathrm{B}-\mathrm{X}(\mathrm{X}=\mathrm{Cl},\ \mathrm{Br}) \xrightarrow{\text{Na or K}} (\mathrm{Me_2N})_2\mathrm{B}-\mathrm{B}(\mathrm{NMe_2})_2 \tag{1}$$

Thus, the use of the bulky 2,6-$^{i}Pr_2C_6H_4$ groups prevents close approach of the two borons during reduction, inhibiting formation of the diboron compound. Compound **3** is thus isoelectronic with the "Arduengo" N-heterocyclic carbenes (NHCs).[11] Secondly, **3** clearly reacts as a boron nucleophile as indicated in Fig. 2. Thus, it is methylated by MeOTf to give **4**, reacts with 1-chlorobutane to give the butylborane **5** and, more interestingly, reacts with benzaldehyde *via* nucleophilic attack at the carbonyl carbon atom to give, after workup, the α-boryl benzylalcohol **6**.

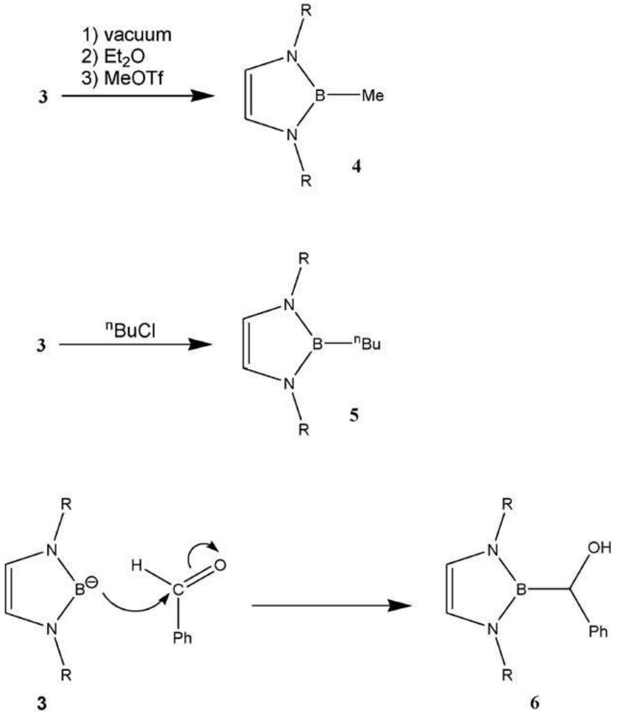


Fig. 2 Nucleophilic reactivity of **3**.

While a few examples of alkali metal salts of $[BR_2]^-$ have been reported to react with electrophiles,[12] clear indications of nucleophilicity of boryl units are rare, especially in well-characterised systems (*vide infra*), none of the previous alkali metal boryl salts having been characterised spectroscopically or structurally. Having an isolable lithium salt opens up a new avenue for synthesis, *via* reactions with other organic electrophiles, as well as with transition metal and main-group halides. Thus, we can expect a rich chemistry to develop based on this finding.

3. Copper boryl complexes and Cu-catalysed borylation reactions

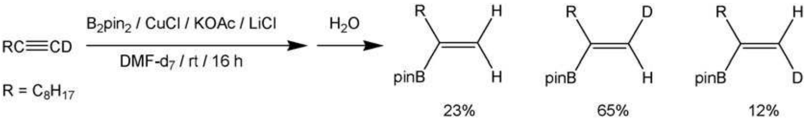
There is a similarity worth developing between the above lithium boryl and transition metal or post-transition metal boryl complexes. In 1995, we reported[13] the first gold-catalysed borylation process, namely the diboration of alkenes using B_2cat_2. Indeed, it was the first catalytic borylation reaction using any of the 'coinage', *i.e.* group 11, metals. Our reasoning was that the major problem we encountered with group 8 and related metal catalysed alkene diborations was competitive β-hydride elimination from the β-borylalkyl complex which results from insertion of an alkene into a metal-boryl bond in a metal-bis(boryl) complex. Whereas a B–C reductive elimination process would give the desired alkene diboration product, β-hydride elimination generates a metal hydridoboryl complex and a vinylboronate, and numerous byproducts result. While it is interesting to use this β-hydride elimination to prepare vinylboronates selectively,[14a] stopping the β-hydride elimination was not easy. We noted one Rh-system which worked reasonably effectively[14b] and which has now been adapted to an efficient asymmetric version by Morken *et al.*,[15] but our thinking which led to the choice of a gold catalyst was as follows: (1) if the metal d-orbitals are low enough in energy (*cf.* a post transition metal) we would destabilise the metal olefin π-complex in favour of the alkyl; and (2) if we choose a metal which does not readily form mononuclear hydrides (*e.g.* Au), we would also destabilise the hydride in favour of the alkyl. In other words, we would disfavour β-hydride elimination. Indeed, this logic worked insofar as we obtained only the diborated product, but the catalyst was neither very active nor very stable.

Subsequently, two groups in Japan reported[16–18] the use of copper for either stoichiometric or catalytic borylation (diboration?) of α,β-unsaturated carbonyl compounds and related species. I use the term 'diboration' with a question mark, as the products isolated were those resulting from hydrolytic workup and thus constitute overall 1,4-hydroboration products. Whether or not the actual 1,4-diboration product (a β-boron substituted boron enolate) is formed in these reactions[16–19] is not known as the hydrolytic work-up would rapidly hydrolyse any O-bound boron enolates. In the case of platinum-catalysed reactions of B_2pin_2 with α,β-unsaturated carbonyl compounds, the β-boron substituted (C- or O-bound) boron enolates have been observed directly, and their hydrolysis has been monitored.[19a,b] Miyaura *et al.* proposed the formation of a nucleophilic copper boryl complex (eqn (2)) as a key intermediate in what they describe as a copper–promoted Michael addition to the α,β-unstaturated carbonyl compounds.[16,18]

$$B_2pin_2 + CuCl/KOAc \rightarrow pinB - Cu \cdot KCl \qquad (2)$$

While indirect evidence was obtained for a Cu–Bpin complex *via* trapping with allyl chloride to produce $CH_2{=}CH{-}CH_2Bpin$, the only direct spectroscopic evidence for the boryl complex was the appearance of an extra singlet resonance for a Bpin group in the ^1H NMR spectrum when a mixture of CuCl and KOac was treated with B_2pin_2 in DMF-d_7. A similar signal was observed when CuOAc was treated with B_2pin_2 in DMF-d_7. However, no ^{11}B NMR spectroscopic data was reported and the species was not isolated. Almost simultaneously, Hosomi *et al.*[17] reported the boration of α,β-unsaturated enones with B_2pin_2 in the presence of *ca.* 5 mol% $[(CuOTf)_2 \cdot C_6H_6]$/10 mol% Bu_3P, followed by hydrolysis. No mechanism was postulated, but the reaction is presumably related to that of Miyaura *et al.*[16,18] B_2cat_2 was also effective in the Hosomi reactions.

Reaction of $C_8H_{17}C{\equiv}CD$ with B_2pin_2 in the presence of CuCl/KOAc/LiCl, followed by treatment with H_2O gave a mixture of "hydroboration" products, all containing boron at the internal carbon (eqn (3)).[18]



(3)

Vinyl copper species arising from insertion of alkyne into putative Cu–Bpin systems were proposed, but the overall mechanism of the reactions with alkynes is anything but clear. Of interest is their report[16] that "addition of BuLi to B_2pin_2 in toluene at −78 °C also afforded a nucleophilic boron species, presumably a B–Li complex" which reacted with cinnamyl bromide. Such a "B–Li" complex might be related to Segawa's lithium boryl species described above,[8] but the nature of this reactive material is unknown. Particularly relevant is the nucleophilicity of the supposed copper boryl complex. Although there is no information on the direction of insertion of the α,β-unstaturated carbonyl compounds into the presumed Cu–B bonds, the ideas of "nucleophilicity" and "Michael addition" suggest that it is the boryl unit which migrates to the β-carbon giving a C- or O- bound β-boryl substituted Cu-enolate intermediate, and these have been proposed recently by Yun et al.[20] who have developed a phosphine/Cu-promoted "β-boration" of α,β-unstaturated carbonyl compounds which is also accelerated by addition of alcohols (*e.g.* MeOH). In addition, these authors demonstrated the asymmetric β-borylation of cinnamonitrile using (*R*)-(*S*)-Josiphos as the chiral ligand and, after oxidation, the product, containing a Bpin group at the position β to the CN moiety was obtained in 84% yield with 82% ee (Figs. 3 and 4).

We will return to this chemistry shortly. It is first instructive to consider the one related metal boryl complex for which an insertion product of an α,β-unstaturated carbonyl compound has been characterised spectroscopically by Onozawa and Tanaka (Fig. 5).[21]

Note that the direction of insertion found here is *opposite* to that apparently implied by the previous studies, in that in the documented Pd case, the boron migrated to the carbonyl oxygen and it is the Pd which has apparently taken on the role of nucleophile. One might anticipate this being the thermodynamic product of insertion, given the oxophilicity of boron and the fact that late transition metal oxygen bonds in alkoxy complexes are very reactive due to the presence of the lone pairs on oxygen leading to antibonding π-interactions with filed metal d-orbitals.[22] At this juncture, it is important to highlight two critical issues. Whilst it is indeed very useful to carry out stoichiometric reactions which model possible catalytic processes, and to characterise fully the products, as done by Onozawa and Tanaka,[21] it must be appreciated that the isolation or characterisation of a species does NOT imply that it is catalytically relevant. Second, catalytic mechanisms are based on the most favourable kinetic processes, and not on the thermodynamic stability of the

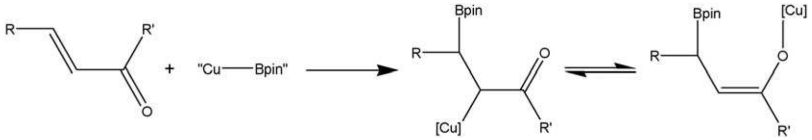


Fig. 3 Insertion of an α,β-unsaturated carbonyl compound into a Cu–B bond.

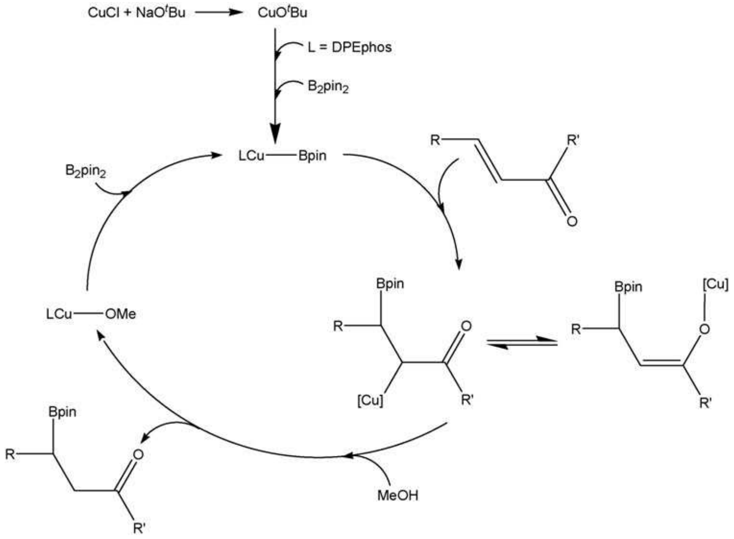


Fig. 4 Proposed mechanism for the methanol-promoted, copper-catalysed borylation of α,β-unsaturated carbonyl compounds.

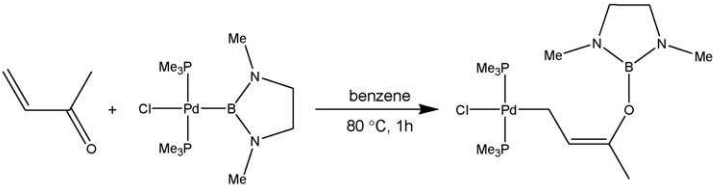


Fig. 5 Onozawa and Tanaka's methylvinylketone insertion into a Pd–B bond.

intermediate species. Indeed, if the intermediates are too stable, then the kinetic barriers to the overall process will be very large and the reaction is unlikely to be catalytic! Thus, one must be especially careful when interpreting the results of stoichiometric model studies in the absence of information on reaction energetics. Could it therefore be that both insertion processes are possible, with the boryl migration to the β-carbon being the kinetically favoured process and the boryl migration to the carbonyl oxygen being thermodynamically preferred? We will examine such a case shortly. An alternative, of course, is that Cu is different than Pd, or that with the specific combination of the particular Pd boryl complex and methylvinyl ketone, the kinetically preferred direction of insertion is reversed from that with purported Cu–Bpin species. This remains to be investigated, and such studies are in progress *via* DFT calculations.[23] However, given our recent theoretical studies of Pt$^{(II)}$-boryl complexes,[24] which showed conclusively that the boryl ligands are amongst the strongest σ-donor ligands known, and that they therefore also have amongst the strongest *trans*-influence of any ligands, we might anticipate nucleophilic behaviour from other metal boryl systems. Let us now examine two especially relevant examples for which the kinetics and thermodynamics of the insertion process are in opposition.

4. Copper catalysed reduction of CO_2 to CO

We were intrigued by a recent report of Sadighi *et al.*[25] on the catalytic reduction of CO_2 to CO using NHC-ligated copper boryl catalysts (NHC=N-heterocyclic carbene) and B_2pin_2, wherein the oxygen is trapped by formation of pinB–O–Bpin,

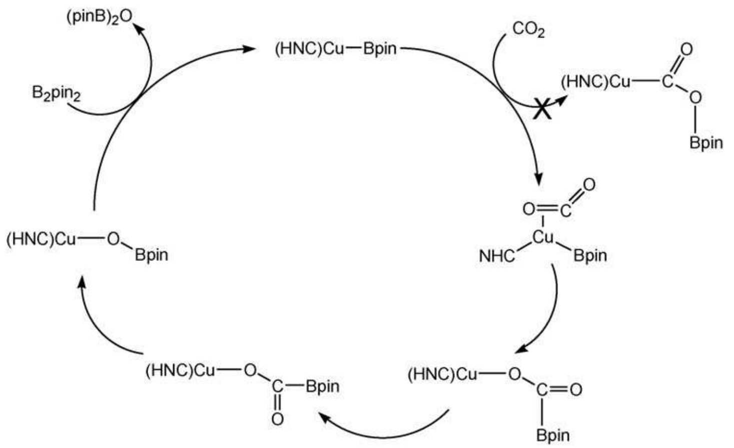


Fig. 6 Proposed cycle for the Cu-catalysed reduction of CO_2 to CO.

providing the thermodynamic driving force for the reaction. Initially, the (NHC)-Cu–Bpin compound is formed by reaction of the corresponding Cu–O–^{t}Bu complex with B_2pin_2, an important reaction, very likely related to the finding of Yun *et al.* on MeOH promotion of the Cu-catalysed borylation of α,β-unsaturated carbonyls, *vide supra*.[20] Thus, metathesis of diboron reagents with Cu–OR systems is apparently very efficient, and serves as the catalyst initiation step. In fact, this reaction led to the first structurally characterised copper-boryl complex.[25] Reaction of this complex with CO_2, *via* insertion into the Cu–B bond, led to CO and the (NHC)Cu–O–Bpin species, which was also characterised by single-crystal X-ray diffraction. The latter complex can react efficiently with more B_2pin_2 giving pinB–O–Bpin and regenerating the (NHC)Cu–Bpin complex, completing the catalytic cycle. What was not at all clear was the direction of insertion of CO_2 into the Cu–B bond. Does this give the Cu–C(=O)–O–Bpin species or the isomeric Cu–O–C(=O)–Bpin complex? In collaboration with Prof. Zhenyang Lin, we decided to examine the energetics of these insertions and the potential surface for the catalytic reaction by means of DFT calculations.[26] The results of this study showed conclusively that the kinetic barrier to insertion giving the Cu–O–C(=O)–Bpin complex was significantly lower than that giving the Cu–C(=O)–O–Bpin species, and we were able to delineate the rest of the catalytic pathway. The key point to be made is that the boryl moiety (or, more accurately, the Cu–B bond) is very *nucleophilic*, in line with many of the ideas noted above, and thus, boron attacks the *carbon* of CO_2. It is this nucleophilicity which is the determining factor in the catalytic pathway, rather than the oxophilicity of boron; thus, even though the Cu–C(=O)–O–Bpin species is *thermodynamically* more stable than isomeric Cu–O–C(=O)–Bpin, the former is kinetically inaccessible!

5. Copper catalysed diboration of aldehydes

We now turn our attention to a related reaction, namely the copper-catalysed diboration of aldehydes, also described very recently by Sadighi *et al.*[27] This process begins with a copper–boryl complex, (NHC)Cu–Bpin, as described above. Insertion of the aldehyde into the Cu–B bond is followed by reaction with additional B_2pin_2 giving the diborated product and regenerating the (NHC)Cu–Bpin complex. So again, we have the question of which way the aldehyde C=O bond inserts into the Cu–B bond. Does it give the Cu–C–O–Bpin species, or the isomeric Cu–O–C–Bpin species. Interestingly, Sadighi's group carried out the stoichiometric experiment, reacting their (NHC)Cu–Bpin complex with mesitylaldeyhde *in the absence of excess B_2pin_2*, and obtained the Cu–C(H)Ar–O–Bpin complex, which was characterised both by NMR spectroscopy and by single-crystal X-ray diffraction. Thus, it might seem that this is the direction of insertion relevant to the catalysis. One interesting point is that this insertion product is capable of initiating catalysis, but the process is rather slow starting with this species. However, following discussions with Prof. Z. Lin and myself, and based on our preliminary theoretical studies,[28] they carried out another experiment, namely an attempt to prepare the isomeric (NHC)Cu–O–C(H)Ar(Bpin) species, by reaction of (NHC)Cu–Me with ArC(H)(Bpin)OH in the absence of added B_2pin_2. Elimination of methane was fast, but the (NHC)Cu–O–C(H)Ar(Bpin) complex *was not observed!* Instead, within the time of mixing, this complex rearranged to the thermodynamically more stable (NHC)Cu–C(H)Ar–O–Bpin complex, *i.e.*, the one which they observe directly from reaction of (NHC)Cu–Bpin with the aldehyde when no excess of B_2pin_2 is present. While the mechanism of this rearrangement is under investigation *via* DFT calculations, what emerges at this point is that again, the boryl ligand is nucleophilic and thus (NHC)Cu–O–C(H)Ar(Bpin) is the kinetic product of insertion whereas (NHC)Cu–C(H)Ar–O–Bpin is the thermodynamic product. Under catalytic conditions, the latter would not be expected to be observed due to rapid conversion of the former to (NHC)Cu–Bpin *via* metathesis with excess B_2pin_2. Thus, we believe strongly that the isolation and structural characterisation of (NHC)Cu–C(H)Ar–O–Bpin *does not* demonstrate its kinetic competence to be an intermediate on the catalytic reaction pathway, providing further support for the warning provided above. Details of our theoretical study of the reaction surface will be submitted shortly, and additional experimental studies are clearly warranted to confirm our mechanistic proposals. What also appears to be important is the much higher reactivity of Cu–OR *vs.* Cu–R species with B_2pin_2 to regenerate the Cu–Bpin species.

6. Nucleophilicity of copper boryl complexes—a return

With the above information in hand, it is now appropriate to speculate further on the mechanism of the copper-catalysed borylation of α,β-unsaturated carbonyl compounds, and indeed, the basic features seem likely to be those intimated by Miyaura *et al.*[18] and proposed in a scheme by Yun *et al.*,[20] as depicted in Fig. 4. Thus, it is reasonable to assume that a Michael-type addition occurs with the boryl ligand being the nucleophile, attacking the β-carbon of the α,β-unsaturated carbonyl compound, generating either the Cu–O or Cu–C β-boron-substituted enolate. While the Cu–O enolate might react quickly with B_2pin_2, the Cu–C enolate would be expected to react much more slowly. Thus, addition of MeOH would lead to enhanced activity, as found experimentally by Yun *et al.*,[20] if it reacted quickly with the Cu–C enolate to form the Cu–OMe complex. Again, calculations are in progress and further experiments will also be carried out to address this issue.

Further confirmation of the nucleophilicity of the Cu–Bpin species comes from both experimental[29a] and theoretical[29b] studies of the regiochemistry of insertion of alkenes into the Cu–B bonds in Sadighi's (HNC)Cu–Bpin complexes. In addition, β-hydride elimination can lead to vinylboronate esters, which can reinsert into the Cu–H bond, giving unusual α-boryl-substituted Cu-alkyl complexes. These observations will not be discussed in detail here, but are, of course, relevant to the catalytic diboration of alkenes using Cu, Ag, and Au-based metal catalysts, *vide infra*. Another example of the apparent nucleophilicity of Cu-boryl species appears[30] in the Cu-catalysed substitutions of allylic carbonates with B_2pin_2.

7. Diboration of unsaturated carbon–carbon bonds employing Cu, Ag, and Au–NHC systems

Following our initial results using Au-based catalysts for alkene diboration,[13] Fernández and Peris *et al.* have recently developed both Ag[31,32] and Au[32] alkene diboration catalyst systems containing NHC ligands, and Fernández and Peréz have reported[33] Cu(NHC)-based catalyst systems for alkene and alkyne diboration. In their first paper,[31] they reported that a new catalyst system based on a silver–NHC dimer, containing a chiral NHC derived from menthol, namely $[(\text{mentimid})_2\text{Ag}]^+[\text{AgCl}_2]^-$, catalysed the diboration of alkenes using B_2cat_2 with conversions of 10–76% for styrenes and 90% for vinylcyclohexane at room temperature. The conversions were determined by ^1H NMR spectroscopy prior to oxidative workup which gave the respective diols. Acceptor-substituted styrenes were diborated less efficiently than styrene itself. However, in spite of the use of a chiral substituent on the NHC, no asymmetric induction was observed, and it was suggested that the chiral centre lies too far from the silver. The key finding was the lack of products derived from β-hydride elimination. In a further study, using both Ag- and Au-based catalysts incorporating chiral NHC ligands, ee's of 4 and 9% were obtained for styrene diboration with the silver system, again using B_2cat_2, although conversions were still low. Clearly, more active systems are required as are more efficient chiral NHC (or other) ligands. In a third study, the authors employed inexpensive neutral and cationic copper systems containing achiral NHC ligands for the diboration and hydroboration of styrene as well as the diboration of phenylacetylene and diphenylacetylene. A mechanism was proposed based on DFT calculations, and the oxidative addition of the diboron reagent to Cu(I) was excluded, which is not a surprising result.

What is clear is that these coinage metal-based catalysts are active for a wide variety of borylation reactions, but the mechanistic details of many of the reactions remain to be elucidated. Detailed experimental studies including isolation of a wider array of group 11 metal boryl complexes containing a variety of donor ligands (including phosphines and NHC's) is required, as are additional DFT calculations. I also note that some reactions were carried out using B_2pin_2 whilst others employed B_2cat_2. Clearly, these two reagents, whilst quite similar in many regards, offer differences in reactivity which remain to be fully elucidated and exploited.

8. β-boryl elimination processes

Another process which is especially relevant to catalysed reactions of alkenes involving metal boryl complexes is the possibility of β-boryl elimination reactions in addition to β-hydride eliminations, *vide supra*. Thus, Marciniec *et al.* recently described[34] a novel catalytic synthesis of vinylboronate esters *via* "*trans*-borylation", namely, the transfer of a boronate moiety from one alkene (*e.g.*, vinyldioxaborolane) to another (*e.g.*, styrene). The ability to distinguish this pathway from a cross-metathesis alternative,[35] and additional mechanistic insight, were obtained from an elegant deuterium labeling study[34] using perdeuterostyrene (Fig. 7). This study demonstrated the reversibility of the alkene insertion into a Ru–B bond, which

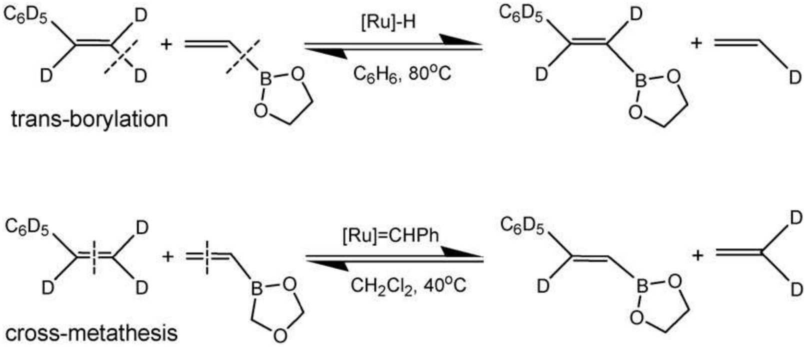
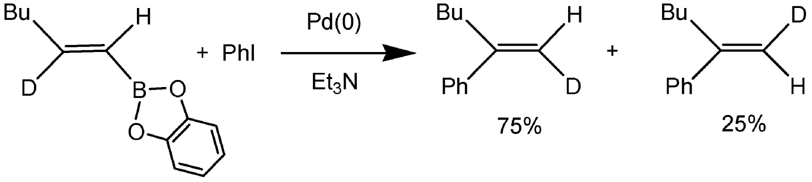


Fig. 7 *Trans*-borylation *vs.* cross-metathesis of styrene-d_8 with vinyldioxaborolane.

provided clear evidence for the β-boryl elimination reaction. Insertion of a vinylboronate ester into a Pd–aryl bond followed by β-boryl elimination was proposed[36] in 1981 by Miyaura and Suzuki to account for the results of the labeling study shown in eqn (4). Again, in collaboration with Lin *et al.*, we have carried out DFT calculations[37] on boryl ligand migration to coordinated alkenes and the reverse process, *i.e.*, the β-boryl elimination reaction. While it is beyond the scope of this review to present the details of our finding, the results of these theoretical studies have shown that the 'empty' p-orbital on boron is not important in either process, and that β-boryl elimination (and β-silyl elimination) as well as β-hydride elimination processes can proceed with low energy barriers, so that these must all be considered when mechanisms of relevant catalytic processes are being examined.



(4)

9. Catalysed borylation of C–H bonds

Finally, it is not appropriate to discuss recent advances in the field of metal boryl chemistry without mentioning one of the most interesting areas of current investigation, namely the catalytic borylation of C–H bonds. Thus, following from our discovery[38] of the borylation of the solvent, toluene, at room temperature during the reaction of [(η^5-indenyl)Ir(COD)] with an excess of catecholborane, several groups, notably those of Smith, Hartwig, and Ishiyama and Miyaura, as well as our own, have advanced this field rapidly, with examples of the catalytic borylation of aryl, heteroaryl, benzyl, and alkyl C–H bonds.[39,40] In fact, using a combination of [Ir(COD)(μ-OMe)]$_2$ and 4,4′-^{t}Bu$_2$-2,2′-biyridine (dtbpy), with B$_2$pin$_2$ or HBpin as the boron source, arenes can be converted to useful arylboronate esters even at room temperature, with excellent catalytic efficiency. Studies are in progress to delineate further the mechanism of the C–H activation step, to understand electronic contributions to selectivities in the reactions, and to design new catalysts for the process. In addition, applications of the borylation to organic synthesis have been and are continuing to be developed including one-pot procedures for C–H borylation followed by Suzuki-Miyaura or other cross-coupling reactions, and for derivatisation of the boronate esters. This represents one of the 'Holy Grails' of homogeneous catalysis, namely the direct functionalisation of hydrocarbons, and promises to be a most useful set of catalytic reactions given the wide utility of boronic acids and boronate esters.[41]

10. Conclusions

The field of metal boryl chemistry has come of age, with the development of new and unusual metal boryl compounds such as the Li–boryl and Cu–boryl species discussed above, as well a many applications in important catalytic processes. Our understanding of the bonding and reactivity of metal boryl complexes has improved considerably in recent years *via* a combination of synthetic, structural and reactivity as well as theoretical studies. New catalytic processes are still being discovered to incorporate boronate ester groups into organic compounds, catalysed by a variety of transition and post-transition metals. The chemistry of the group 11 (coinage metal) boryl complexes is still young and will no doubt yield new and exciting discoveries in the coming years, while metal boryl compounds containing yet other metal centres remain to be synthesized and studied. The room temperature borylation of C–H bonds provides an exceptional example in homogeneous catalysis, and an outstanding methodology for the preparation of especially useful organoboronate esters, and is a direct result of the strong σ-donor property of boryl ligands in metal boryl complexes. The differences in reactivity of B_2pin_2, B_2cat_2, B_2neop_2 and other diboron reagents remain largely unexplored, and the study of such effects represents a promising direction for new experiments and theoretical investigations.

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Organometallics in ionic liquids—catalysis and coordination chemistry

Tilmann J. Geldbach

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1. A brief introduction to ionic liquids

The field of ionic liquid related chemistry has seen a tremendous growth in the past years and a key-word search gives some 2200 hits for the year 2005 alone. Accordingly this chapter is by no means comprehensive, but highlights some of the developments of organometallic chemistry in ionic liquids, mainly focusing on (a) ionic liquids comprised of organometallic salts, (b) reactions between ionic liquids and transition metal complexes and (c) novel catalysts designed for the task of biphasic ionic liquid catalysis together with mechanistic considerations. Most of the examples on the following pages stem from the literature of 2004–2006, but as this topic has not been part of previous books of this series, some older publications are also taken into account.

Interest in ionic liquids has increased considerably over the last few years, fuelled by the development of new synthetic routes to ionic liquids, the preparation of new ionic liquids, together with an ever increasing range of potential applications. Initially developed for electrochemical purposes and subsequently regarded predominantly as alternative, environmentally benign reaction media, ionic liquids have in recent years found many other potential applications which now span from, for example, storage media for toxic gases,[1] lubricants,[2] performance additives in pigments[3] through to propellants in satellites.[4]

The physical properties that render ionic liquids a special class of solvents have been repeatedly named in numerous review articles[5–9] and there is no need to give a detailed account here. However, it might be worth mentioning that it is incorrect to make generalisations about the physical properties of ionic liquids as commonly stated in earlier publications. For example, ionic liquids were originally perceived to be highly polar, but it is now known that most of the commonly used ionic liquids have polarities similar to alcohols, but very low polarity ionic liquids, *e.g.* with perfluorinated chains, can also be made. In addition, some ionic liquids can indeed be distilled, despite the general opinion being that this class of solvents does not possess a significant vapour pressure.[10]

Although the possibilities to design new and task specific ionic liquids are almost without limits, a very low number of commonly used ionic liquids account for the overwhelming part of published works. Much research is still based on ionic liquids composed of the 1-butyl-3-methylimidazolium cation, also known as bmim and hereafter abbreviated as $[C_4C_1im]^+$, with mainly $[BF_4]^-$ or $[PF_6]^-$ as anions. Related imidazolium cations, which differ with respect to the alkyl substitution pattern are also common. Other, less frequently used cations include, for example, pyridinium, piccolinium, pyrrolidinium and tetraalkylammonium, to name a few and this restriction is reflected in the organometallic chemistry observed in ionic liquids.

Several books and review articles have appeared in the last few years, dealing in part or entirely with the aspect of organometallic chemistry in ionic liquids and a selection of references is provided: A general overview on ionic liquids in synthesis appeared some years ago[11] and several symposia dealt with a wide range of aspects concerning ionic liquids.[12] An issue of the *Journal of Organometallic Chemistry* has been dedicated to the topic of transition-metal chemistry in ionic liquids[13] and

Institute des Sciences et Ingenierie Chimiques, EPFL, LCOM BCH, CH-1015, Lausanne, Switzerland

numerous reviews on this topic have appeared.[14–20] In the area of catalysis, a comprehensive textbook on metal-catalysed reactions in ionic liquids is available.[21] Further, articles focusing on supported ionic liquid phase catalysis[22,23] and on chemical and biochemical transformations have been published,[24–26] as have reports on the application of chiral ionic liquids[27] and the synthesis and use of functionalised ionic liquids.[28]

2. Metal-containing ionic liquids and related salts

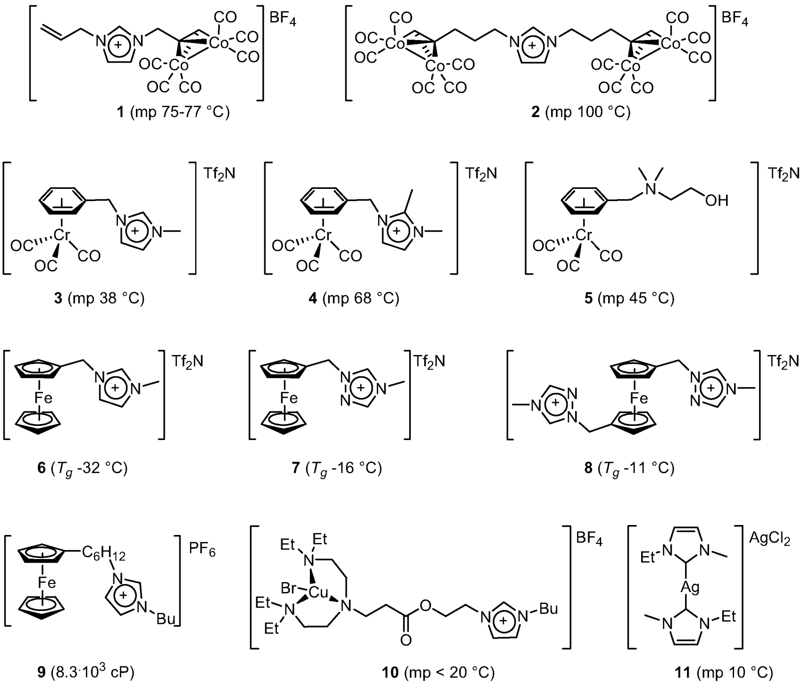
The field of metal-containing ionic liquids has been summarised recently[29] and a review article on ionic liquid crystals is also available.[30] Ionic liquids containing metals are widespread and the first "modern" ionic liquid which was perceived as such was comprised of chloroaluminate anions.[31] Many other simple metal halide anions such as $[FeCl_4]^-$,[32] $[CuX_3]^-$,[33] $[SnX_3]^-$,[34] $[AuCl_4]^-$,[35] $[CoCl_4]^{2-}$ and $[NiCl_4]^{2-}$,[36] $[PdCl_4]^{2-}$ and $[CuCl_4]^{2-}$ [37]—to name just a few—have been employed in combination with, for example, imidazolium, phosphonium or ammonium cations to yield an ionic liquid. Further, room temperature liquid salts of chromium and molybdenum, $[C_4C_1im][Cr(O)_3Cl]$ and $[C_4C_1im]_2[Mo(O)_2(NCS)_4]$ have been prepared and used as self-supported catalysts for oxidation reactions.[38] Also, a phosphotungstate imidazolium complex, $[C_4C_1im]_3[PO_4(W(O)(O_2)_2)_4]$ has been prepared and used as catalyst for the oxidation of alcohols in $[C_4C_1im][BF_4]$.[39] The first liquid rare-earth complexes have been reported by Nockemann *et al.* and were made by reaction of $[C_4C_1im][SCN]$ with a lanthanide perchlorate to afford *e.g.* liquids of the composition $[C_4C_1im]_3[Ln(NCS)_6(H_2O)_2]$ (Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er and Yb).[40]

Truly organometallic ionic liquids are, however, scarce. Of the few compounds that are known to date, and which are briefly described below, very little physical data is available and particularly information on their viscosity is lacking. Thus, whether the definition that an ionic liquid should be "free-flowing" is entirely fulfilled is not clear and in some cases the reported liquid might rather be described as a sticky oil.

Probably the first example of an organometallic room temperature ionic liquid was reported by Dyson and co-workers, who described the synthesis of a low-melting cobalt carbonylate salt obtained from the reaction of $[C_4C_1im]Cl$ with $Na[Co(CO)_4]$ in acetone to afford $[C_4C_1im][Co(CO)_4]$.[41] It can be expected that such highly symmetrical carbonylates, in which the charge is diffused over a rather large volume, would afford a range of other organometallic liquids. A liquid variant of the Monsanto catalyst, $[C_4C_1im][RhI_2(CO)_2]$, obtained from the reaction of $Rh_2I_2(CO)_4$ with $[C_4C_1im]I$ to afford the product as a deep red-brown, air-sensitive liquid, has also been described.[42] Reaction of $Co_2(CO)_8$ with alkyne functionalised imidazolium salts afforded the low-melting salts **1**[43] (mp. 75–77 °C) and **2**[44] (mp. 100 °C), shown in Fig. 1, the latter just qualifying as ionic liquid.

Several chromium carbonylates, **3–5**, bearing an imidazolium or ammonium fragment tethered to a η^6-coordinated arene have been reported.[45] Quaternisation of $Cr(CO)_3(\eta^6\text{-}C_6H_5\text{-}CH_2Br)$ with 1-methylimidazolium and subsequent anion exchange with $Li[Tf_2N]$ afforded the low-melting salt **3** with a reported melting point of 38 °C. The related salts **4** (mp. 68 °C) and **5** (mp. 45 °C) are accessible *via* quaternisation with 1,3-dimethylimidazolium and *N,N*-dimethylethanol, respectively.

Shreeve and co-workers reported a number of room temperature liquid ferrocenium salts with glass transition points (T_g) well below 0 °C.[46] Starting from mono- or bis-trimethylammonium ferrocenium iodide, reaction with imidazole and triazole, respectively, and subsequent quaternisation/anion exchange with $MeI/LiTf_2N$ afforded compounds **6–8**. These liquids have been proposed to be of interest as potential catalysts or anti-tumor drugs.



1 (mp 75-77 °C) **2** (mp 100 °C)

3 (mp 38 °C) **4** (mp 68 °C) **5** (mp 45 °C)

6 (T_g -32 °C) **7** (T_g -16 °C) **8** (T_g -11 °C)

9 ($8.3 \cdot 10^3$ cP) **10** (mp < 20 °C) **11** (mp 10 °C)

Fig. 1

Other liquid ferrocenated imidazolium salts such as **9** were prepared by Marray and co-workers who employed these compounds for electrochemical studies.[47] Viscosities were usually high, ranging from 8.3×10^3 *cP* to 1.4×10^7 *cP*, depending on the nature of the linker between the ferrocene and imidazolium moiety and the length of the alkyl substituent.

Shen and co-workers prepared a liquid copper complex, **10**, which was employed for the biphasic atom transfer radical polymerisation (ATRP) of methyl methacrylate.[48] The copper halide is complexed by the tetraethylenediethylenetriamine unit, forming a green ionic liquid. No melting point is reported, but the complex is a liquid at room temperature. Reuse of the liquid catalyst was possible, however only after reactivation with copper(0) which is presumed to be required to reduce $\mathrm{Cu}^{(\mathrm{II})}$ formed during the polymerisation.

To conclude this section, a liquid bis(imidazole-2-ylidene)silver salt, **11**, was reported by Sentman *et al.* which was employed as a catalyst for the ring-opening polymerization of lactide as well as for the transesterification of methyl benzoates.[49] The thermal stability of **11** is somewhat limited and decomposition occurs around 90 °C through liberation of the free carbene ligand.

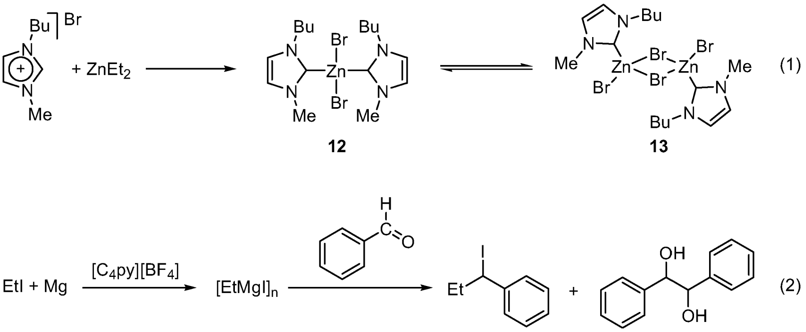
3. Preparative organometallic chemistry in ionic liquids

Despite the current popularity of ionic liquids, still very little is known with respect to employing these solvents for preparative organometallic reactions. This certainly has to do with the difficulty involved in removing organometallic substances from the ionic liquid phase. Here, the properties that render ionic liquids so attractive for many other applications, namely lack of a significant vapour pressure at moderate temperatures, pose a severe obstacle. Thus, the most practical way to isolate a desired complex is by either extraction of the organometallic species or washing away the ionic liquid. Both techniques are essentially applicable to neutral organometallic molecules exclusively, or if task-specific solvents such as lipophilic perfluorated ionic liquids are employed. Due to this limitation, ionic liquids may mainly be of interest as solvents for the preparation of products that are otherwise only accessible with difficulty in conventional solvents or if intermediates can be stabilised, *e.g.* for the elucidation of a reaction mechanism. Another factor which needs to be considered is purification and recyclability of the ionic liquid used. If the main motivation to use this class of solvents is with the purpose of making a given reaction more environmentally benign, a suitable procedure to eliminate all residues prior to the recycling of the solvent has to be devised, which might prove difficult.

3.1 Organometallic reagents in ionic liquids

Few stoichiometric organometallic reactions have been reported in ionic liquids in the past years, such as the allylation of tetraalkylstannane in $[C_4C_1im][BF_4]$ and $[C_4C_1im][PF_6]$[50] or the utilization of *in situ* generated zinc reagents for the Reformatzky reaction in a variety of ionic liquids.[51]

Many organometallic reagents such as Grignard or organolithium compounds are likely to react with quaternary salts commonly present in ionic liquids and alternative reagents must be sought. Dialkyl zinc reagents react with $[C_4C_1im]Br$ to afford carbene complexes **12** and **13**, as shown in reaction 1 in Scheme 1. By using ionic liquids with weakly coordinating anions such as *e.g.* $[BF_4]^-$, this reaction could be suppressed sufficiently to employ dialkyl zinc reagents in such solvents for the alkylation of aldehydes.[52] In contrast to common volatile organic solvents, in which the alkylation reaction proceeds only sluggishly, high yields and smooth conversions were obtained with *N*-butylpyridinium tetrafluoroborate, $[C_4py][BF_4]$, as the solvent.



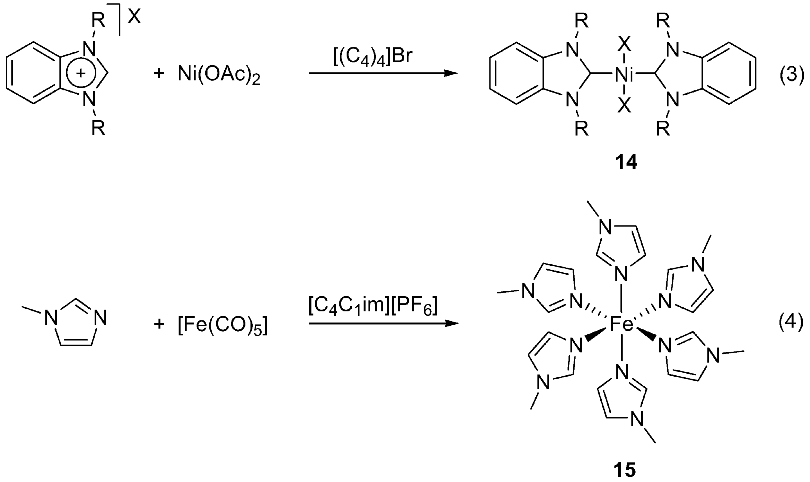
Scheme 1

Alkylzinc reagents can be formed directly in *N*-butylpyridinium tetrafluoropborate from zinc metal and alkyl iodide if an additional halide source is present in the ionic liquid.[53] The latter is proposed to assist in the solvation of the zinc metal. The ensuing reagents have been used for the alkylation of aldehydes. The ionic liquid was also successfully recycled. In addition, Grignard reagents have been prepared directly in $[C_4py][BF_4]$ from magnesia and ethyliodide.[54] In contrast to conventional solvents the reactivity pattern of the Grignard reagent in the ionic liquid turned out to be different. Instead of the expected alcoholate the reaction of ethylmagnesium iodide with benzaldehyde afforded a mixture of 1-phenyl-1-iodopropane and 1,2-diphenyl-1,2-ethanediol when $[C_4py][BF_4]$ was employed as solvent, as shown in reaction 2.

A base-stable ionic liquid derived from the 1-butyl-2-isopropyl-3-methyl imidazolium cation has been prepared and successfully applied to the addition of Grignard reagents to carbonyl compounds, affording the alcohol products in good to excellent yield.[55]

3.2 Synthesis of organometallics in ionic liquids

A rhenium cluster has been prepared in $[C_2C_1im][AlBr_4]$ at 70 °C and the product precipitated with diethyl ether.[56] Several bis(benzimidazolin-2-ylidene) complexes of nickel(II), **14**, have been prepared in molten $[(C_4)_4N]X$ (X = Br, I, BF_4) from $Ni(OAc)_2$ at 120 °C under vacuum, as exemplified in Scheme 2. The products were isolated from the ionic liquid by washing away the solvent with water.[57] This result is noteworthy as by carrying out the reaction in an ionic liquid medium, a product could be obtained that otherwise was only accessible in very poor yield when using more traditional conditions.



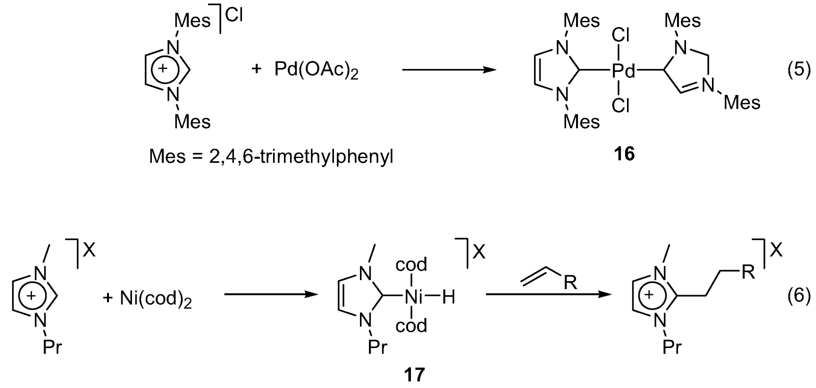
Scheme 2

The sonochemical reaction of $Fe(CO)_5$ with 1-methylimidazole in $[C_4C_1im][PF_6]$ afforded a homoleptic hexaimidazole complex, $[Fe(C_1im)_6][PF_6]$, **15**, within 30 minutes at a temperature of 40–50 °C.[58] At the end of the reaction, ethanol was added to the mixture, leading to precipitation of the product as a grey powder. In an extension to this work, other nickel and iron carbonyl complexes were reacted with 1-methylimidazole in $[C_4C_1im][PF_6]$ and $[C_4C_1im][BF_4]$, respectively, to afford the expected metal-imidazole complexes.[59]

3.3 Complexes derived from ionic liquid cations

During the advent of modern ionic liquid chemistry, liquids comprised of imidazolium cations with weakly coordinating anions such as $[BF_4]^-$ or $[PF_6]^-$ were perceived as innocent solvents. Yet, to date, there are plenty of examples that show that ionic liquids can react with organometallic complexes, leading to new and sometimes unexpected species.[60–63] Imidazolium-based ionic liquids are particularly reactive due to the presence of the weakly acidic proton at the 2-position of the ring, ($pK_a = 21–23$) and Dupont and Spencer summarized some of the reactions that can occur between an organometallic compound and 1,3-dialkylimidazolium based ionic liquids.[64] Indeed, the formation of *N*,*N*-heterocyclic carbene complexes from imidazolium based ionic liquids is relatively facile and depending on the specific circumstances, this can be either detrimental or advantageous. Various transition metal carbene complexes have been deliberately prepared in imidazolium-based ionic liquids and these compounds are often found to be active catalysts.[65–67]

The presence of a base is not necessarily mandatory for the formation of carbene complexes, as has been demonstrated by Nolan and co-workers in the reaction between $Pd(OAc)_2$ with $[Mes_2im]Cl$, which led to the formation of **16**, shown in Scheme 3. However, instead of the expected symmetric carbene complex a



Scheme 3

zwitterionic species was isolated which turned out to be a significantly more active catalyst than the bis-carbene species.[24]

A number of examples of the reactivity of imidazolium salts with late transition metals such as platinum, palladium and nickel have been published by Cavell and co-workers.[68] Oxidative addition of imidazolium salts to low-valent transition metal complexes can take place under mild conditions, affording the corresponding carbene hydride complex, **17**, through C2 activation.[69,70] The resulting complexes can catalyze the addition of an imidazolium moiety to an alkene, see reaction 6. More recent work from the same group showed that protection of the acidic C2-position is not necessarily sufficient to block unwanted carbene formation. Oxidative addition of 1,2,3-trialkyl imidazolium salts to $Pt^{(0)}$ complexes was observed at C4 and C5, giving rise to compounds **18a** and **18b**, respectively, shown in Scheme 4.[71] In the presence of an alkene, reductive elimination of the imidazolium salt can be observed, affording the neutral $Pt^{(0)}$ complex **19**.

The formation of a palladium bis-imidazole complex, **20**, has further been reported to take place from a low-melting (mp. = 58 °C) palladium ionic liquid in the presence of the radical initiator 2,2′-azabisisobutyronitrile, see reaction 8.[72]

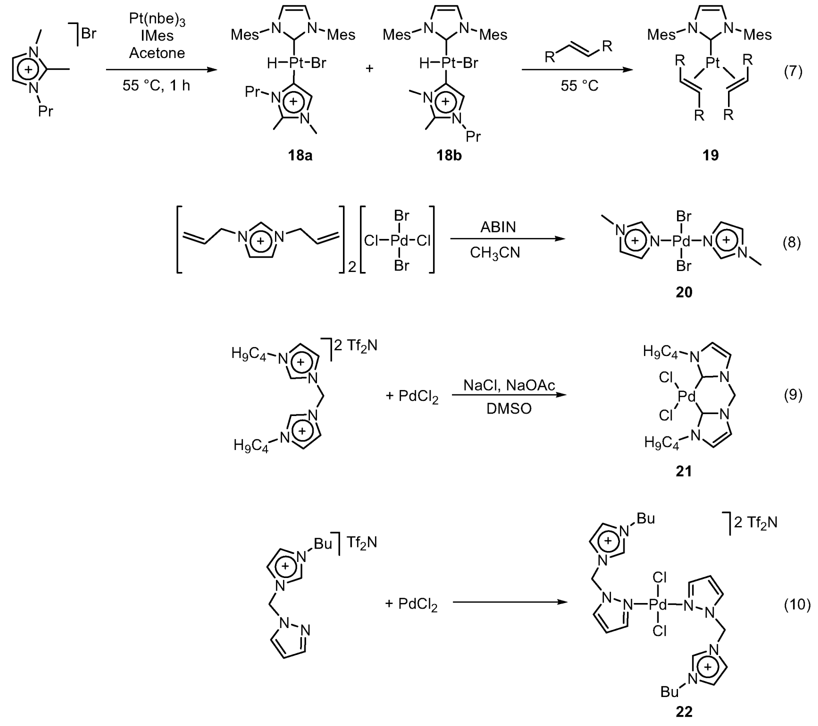
A palladium complex with a chelating bis-carbene was prepared by Shreeve and co-workers from the reaction of liquid 1,1′-methylenebis(imidazolium) and 1,1′-methylenebis(triazolium) salts with $PdCl_2$, affording *e.g.* complex **21**.[73] The presence of a weak base such as NaOAc was required for the synthesis of these pincer palladium carbene complexes. In an extension to this work, pyrazolyl-functionalised ionic liquids have been reported which act as both ligands and solvents in palladium-catalysed Heck and Suzuki reactions to give rise to the bis-cationic palladium species **22**.[74] The pendant imidazolium moiety ensures good immobilization in the ionic liquid and allows for repeated recycling of the catalyst phase.

The beneficial effect of ionic liquids functionalised with weakly coordinating moieties has been demonstrated previously by Dyson and co-workers, who employed nitrile functionalised imidazolium and pyridinium ionic liquids in Heck- and Suzuki coupling reactions.[75] Recently, they reported on pronounced anion and cation effects with these ionic liquids in the Stille reaction and markedly improved recycling upon utilisation of such liquids.[76]

Carbene complexes have also been identified from the reaction of iridium nanoclusters with imidazolium-based ionic liquids by Finke and co-workers, affording carbenes ligating a nanoclusters surface.[77]

3.4 Complex formation involving ionic liquid anions

While metal-halide based anions are often relatively nucleophilic and can easily interact with a metal complex, anions such as $[BF_4]^-$ and $[PF_6]^-$ are often perceived



Scheme 4

to be inert, meaning that decomposition under normal reaction conditions does not take place and that they do not coordinate to the metal. However, it has been known for some time that the presence of water results in hydrolysis of $[BF_4]^-$ and $[PF_6]^-$, which ultimately can lead to the deactivation of a catalyst or decomposition of a complex, though the products are seldom isolated or characterized. Anion hydrolysis is not an issue with $[Tf_2N]^-$ and this anion was long considered as non-coordinating in ionic liquid chemistry. However, it was recently found that this anion can indeed bind to the metal centre, even under mild conditions.

Oldham and co-workers published a series of complexes containing the $[Tf_2N]^-$ anion as ligand in a range of different coordination modes, as shown in Fig. 2.[78] Reaction of $(C_5H_5)Fe(CO)_2Me$ with HTf_2N in $[C_2C_1im][Tf_2N]$ afforded complex **23**; analogous methods led to the bis-Tf_2N complexes **24** and **25**.

A number of homoleptic bis{(trifluoromethyl)sulfonyl}amide complexes have been prepared by Earle *et al.* by reacting metal carbonates, hydroxides or oxides with HTf_2N and the crystal structure of $Zn(Tf_2N)_2$ determined, which is shown in Fig. 3.[79]

More recently, Mudring *et al.* reported the first discrete, homoleptic $[Tf_2N]^-$ complex, namely $[C_3C_1pyr]_2[Yb(Tf_2N)_4]$, which was isolated from the reaction of

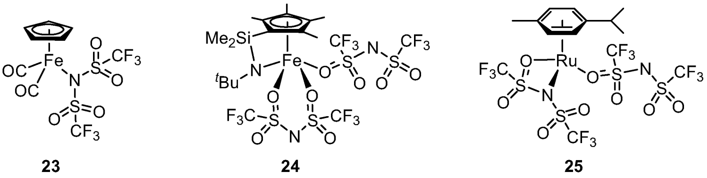


Fig. 2

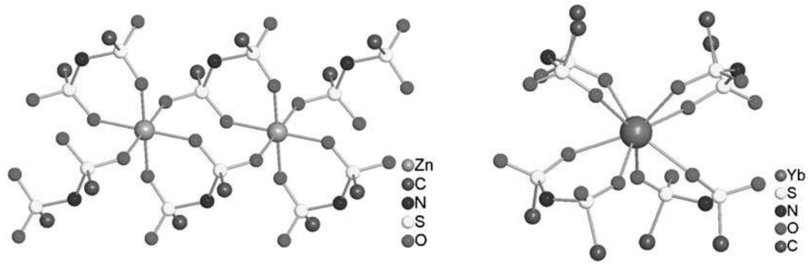


Fig. 3 left: Ball-and-stick representation of the X-ray structure of $Zn(Tf_2N)_2$; right: Ball-and-stick representation of the anionic component of the X-ray structure of $[C_3C_1pyr]_2[Yb(Tf_2N)_4]$. Fluorine atoms have been omitted for clarity in both structures.

YbI_2 with the pyrrolidinium ionic liquid $[C_3C_1pyr][Tf_2N]$.[80] Ytterbium–oxygen distances in this structure range from 2.421(3) to 2.517(3) Å, the latter being probably the longest Yb–O bond so far observed. It is important to note that even the weakly coordinating $[Tf_2N]^-$ anion complexes to the metal if stronger ligands are absent. The observation of $[C_3C_1pyr]_2[Yb(Tf_2N)_4]$ helps explain how inorganic salts might be dissolved in an ionic liquid. Further support for the observation that the $[Tf_2N]^-$ anion must not be regarded as non-nucleophilic comes from the heterolytic dediazoniation reaction, where $[Tf_2N]^-$ was found to be more reactive than Br^-.[81]

4. Catalysis with metal complexes in ionic liquids

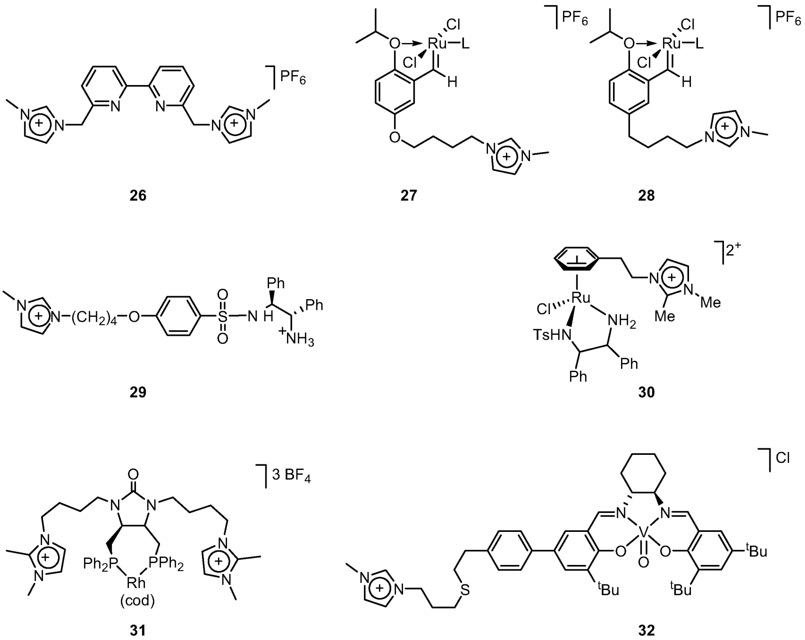
Chiral ionic liquids can be easily obtained using anions available from the chiral pool. Their utilisation to induce asymmetry has so far been met mostly with rather limited success. However, good chiral induction was reported by Afonso and co-workers, who used guanidinium-based ionic liquids with chiral anionic components such as for example lactate or mandelate. Enantiomeric excess up to 85% was achieved in the osmium-catalyzed Sharpless asymmetric dihydroxylation, notably in the absence of any intentially added chiral ligand, which is otherwise required for this reaction.[82]

A review on the effect of different classes of ionic liquids on palladium-benzothiazol-2-ylidene complexes on their performance as catalysts is available.[83] Quatenary ammonium salts were found to be superior relative to imidazolium- and pyridinium-based ionic liquids, although direct comparisons were seldom possible.

The biggest effort in the field of organometallic chemistry in conjunction with ionic liquids has been dedicated so far to the modification of catalysts, mostly with the aim of increasing their affinity to the ionic media and thereby decreasing loss of the catalyst from the ionic liquid phase, increasing their recyclability. A comprehensive overview on the various ligands that have been synthesized has been reported,[21] and only a few representative recent catalytic transformations are listed here, which are shown in Fig. 4 and Fig. 5. In most cases ligand modification implies the attachment of a charged moiety and as such imidazolium groups are particularly common.

An imidazolium-grafted 2,2′-bipyridine, **26**, has been prepared and successfully used as ligand in copper-catalysed oxidation reactions.[84] Primary and secondary alcohols were thus converted to the corresponding aldehydes and ketones under mild conditions in $[C_4C_1im][PF_6]$ and repeated reuse of the catalyst phase was possible with no marked depletion in catalyst activity.

Task-specific ruthenium catalysts for olefin metathesis have been prepared independently by two different groups by attaching imidazolium tags to second generation Hoveyda-Grubbs complexes, affording complexes **27**[85,86] and **28**[87–89] with either triphenylphosphine or a *N*-heterocyclic carbene as neutral ligand. In both

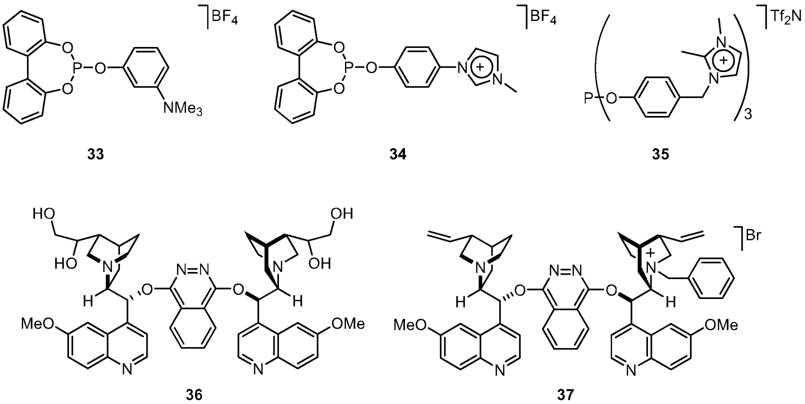


26 **27** **28**

29 **30**

31 **32**

Fig. 4



33 **34** **35**

36 **37**

Fig. 5

cases the recyclability of the ligand was markedly increased when immobilised in $[C_4C_1im]X$ with yields higher then 90% after 10 catalytic runs.

Complexes of the type $[Ru(\eta^6\text{-arene})(L)Cl]^+$ (L = diamine or aminoalcohol) are widely used catalysts for enantioselective transfer-hydrogenation reactions and two different ways for improved immobilisation of such catalysts in ionic liquids have been demonstrated. In one example, modification of a chiral diamino ligand to afford **29** was undertaken[90] while in the other case a charged imidazolium moiety was attached to the η^6-bound arene, yielding the dicationic complex **30**.[91] In both cases, improved catalyst immobilisation was observed relative to the neutral catalyst system.

Modification of a phosphine ligand with imidazolium substituents affords the highly charged rhodium catalyst **31**, which was successfully used for the enantioselective reduction of *N*-acetylphenylethenamine in $[C_4C_1im][SbF_6]$/2-propanol.[92] Use of this charged phosphine ligand reduced catalyst leaching to below ICP-OES detection limits, relative to 2% catalyst loss with the non-derivatised ligand, and this is mirrored in the improved catalytic activity during recycling.

An imidazolium-tagged vanadium catalyst, **32**, which has been tested for the preparation of cyanohydrins, has been prepared by addition of a thiol-functionalised imidazolium salt to an olefin.[93]

While ionic phosphine ligands are plentiful, ionic phosphites and phosphinites are rare, which to some extent stems from their incompatibility with aqueous reaction media. Almost a dozen novel charged phosphites were synthesized by Vallée *et al.* and some are shown in Fig. 5, **33–35**,[94] The ligands were tested in the Nickel-catalyzed hydrocyanation of olefins in imidazolium-based ionic liquids, and after careful optimization of the reaction conditions, results similar to those obtained in molecular solvents were obtained. Yet, no information on the recyclability of the catalyst was provided which might be a possible motivation for performing catalysis in ionic liquids.

An elegant solution to increase retention of chiral osmium catalysts for enantioselective dihydroxylation lies in the use of 1,4-bis(9-*O*-quininyl)phtalazid as a ligand: Under reaction conditions present in asymmetric dihydroxylation this ligand is converted to the more polar, dihydroxylated derivative **36**, which leads to significantly better catalyst retention in the ionic liquid. While up to 80% of an analogous ligand devoid of hydroxy groups were detected in the organic phase of a diethyl ether/ $[C_4C_1im][PF_6]$ mixture, less then 1% ligand leaching was detected with **36** as ligand.[95] Catalyst retention can be further optimised if a charged derivative of the $(QN)_2$PHAL-ligand is used. Quaternisation of one of the nitrogen atoms with benzyl bromide affords the cationic ligand **37**, and indeed recyclability was improved in the presence of this ligand, however at the cost of lower *ee*.[96]

5. Mechanistic investigations

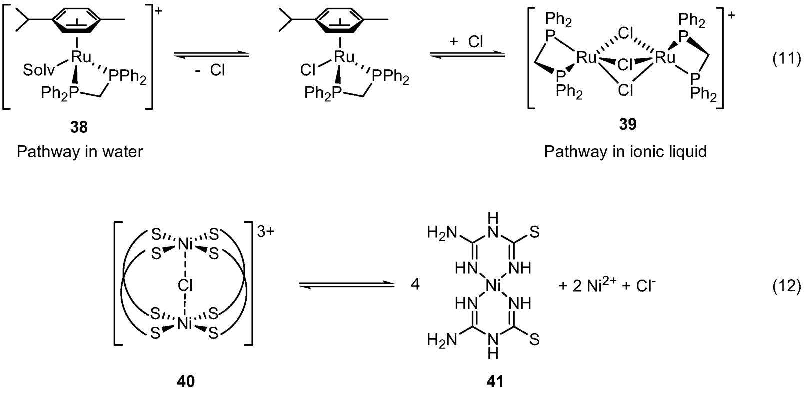
Surprisingly little is known so far with respect to reaction mechanisms in ionic liquids and no coherent picture has yet emerged. Ionic liquids can have a pronounced influence on the outcome of a reaction as first demonstrated by Earle *et al.* in the nitration of toluene.[97] Many catalytic cycles require the displacement of a nucleophilic ligand, often resulting in a charged species as the key intermediate. Such charged species are likely to be stabilized in a highly ionic environment, which might have an impact on the rate and selectivity of a given reaction.

The stabilization of a rhodium(I) species in a chloroaluminate ionic liquid has been reported some years ago[98] and in one example from a catalysed hydrogenation it was noted that immobilisation of the catalyst in an ionic liquid did not appear to affect the reaction mechanism relative to a homogeneous system.[99] It has been hypothesized that the frequently observed acceleration of transition-metal catalysed reactions in ionic liquid media are the result of promoted displacement of an anionic ligand and subsequent stabilisation of the ensuing charged intermediate.

From S_N2 substitution reactions it has been found that halides are less nucleophilic in imidazolium-based ionic liquids relative to aprotic molecular solvents.[100] However, in case of a cationic ruthenium complex, $[RuCl(\eta^2\text{-}PPh_2CH_2PPh_2)(\eta^6\text{-}p\text{-cymene})]^+$, it was observed that chloride dissociation was inhibited in the ionic liquid $[C_4C_1im][OTf]$ while dissociation readily took place in water.[101] Catalytic activity in the hydrogenation of styrene was therefore only observed when the ionic liquid was mixed with water or when a chloride-free analogue, *viz.* $[Ru(CH_3CN)(\eta^2\text{-}PPh_2CH_2PPh_2)(\eta^6\text{-}p\text{-cymene})]^{2+}$ was used. This finding was refined in a second publication; it was found that a different reaction mechanism operates in the ionic liquid relative to that postulated in water.[102] Whereas in water the dissociation of chloride is believed to take place to generate complex **38**, as evidenced by mass-spectrometric measurements, loss of *p*-cymene was observed and the dimeric species **39** postulated, depending on the ionic liquid tested. The presence of residual chloride was found to be of importance in affording an active catalyst. On the basis of kinetic measurements it was determined that higher catalytic activities were measured in those ionic liquids that provide lower chloride solvation and thereby favor formation of the new chloro-containing species.

It has been suggested that the aforementioned inhibition of chloride-dissociation from the ruthenium centre might be due to the selected ionic liquid anion (triflate) in the study; it was found that chloride dissociation from a platinum complex, $PtCl_2(PPh_3)_2$ proceeded faster in a chlorostannate ionic liquid.[103] Chloride dissociation was also measured in the same system with $[C_4C_1im][Tf_2N]$ as the solvent, however only in the presence of $[C_4C_1im][SnCl_3]$ as a co-solvent.

The strong colour change upon chloride-templated formation of the nickel-(II)-metallacage **40** from the nickel-(II)-aminidothiourea complex **41** was employed as a chloride solvation probe in a number of $[Tf_2N]^-$-anion based ionic liquids.[104] Better solvation of the chloride anion should shift the equilibrium shown in Scheme 5 to the right. From the measured reaction enthalpies the chloride solvation capability is lowest in the tetraalkylammonium-based ionic liquid and follows the trend $[C_5(C_3)_3N] < [C_4C_1pyr] < [C_4C_1im] < [C_4C_1C_1im] < [C_4py]$. These results underline the importance in carefully selecting the appropriate solvent for a given reaction where dissociation of chloride might be of key importance.

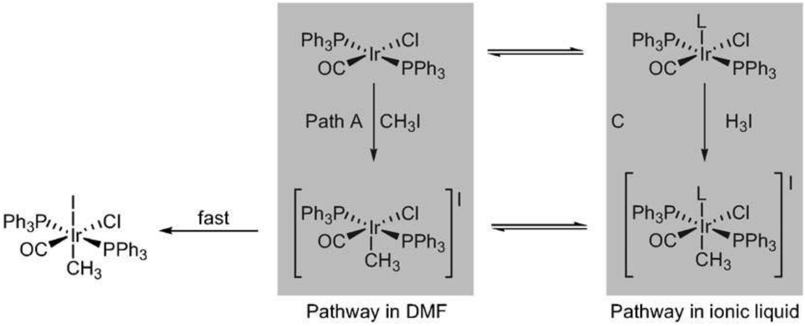


Scheme 5

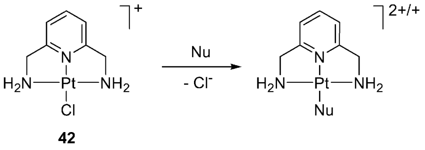
Another example, where dissociation of an anionic ligand proceeds easily has been provided by Shaughnessy and co-workers, who reported that ionic liquids promoted the substitution of nitrate in a d^8 rhodium complex, $Rh(NO_3)(CO)(PPh_3)_2$ in the presence of an amine base and that the ionic liquid stabilises the charge-separated rhodium complex more efficiently than dichloromethane.[105] From the same group also comes a kinetic study on the oxidative addition of methyl iodide to $IrCl(CO)(PPh_3)_2$.[106] On the basis of the measured rate-constants, a different reaction pathway relative to that occurring in DMF was proposed, shown in Scheme 6, which involves a ligand-accelerated sequence with the nature of the ligand yet unknown.

The first systematic study on the pressure dependence of a reaction in an ionic liquid was published on the ligand substitution reaction on a square planar platinum(II) complex, **42**.[107] The exchange of chloride on a cationic bisaminopyridine platinum complex for either thiourea or iodide was determined in $[C_4C_1im][Tf_2N]$ at different pressures. The dissociation rate was comparable to that in methanol and indicates an entirely ''normal'' behaviour of the ionic liquid in this particular substitution reaction. It was further possible to directly correlate the observed activation volume with volume changes established from bond lengths and angles on going to the transition state.

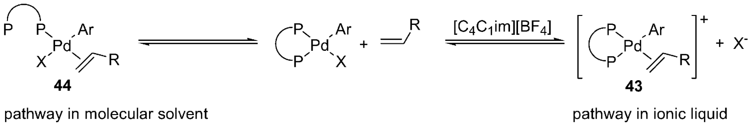
It can be expected that, where a reaction can proceed either by a neutral or a charged pathway, the latter should be favoured in an ionic liquid. Indeed it was



Scheme 6



(13)



(14)

Scheme 7

found that at least for electron-rich olefins the Heck reaction proceeds predominantly *via* a cationic intermediate when the reaction was performed in $[C_4C_1im][BF_4]$, which is mirrored in markedly increased regioselectivity in the reaction between a range of olefins and aryl bromides or iodides.[108] It was proposed that by performing the reaction in the ionic liquid, halide abstraction from the catalyst precursor is facilitated and the reaction proceeds *via* cationic intermediate **43** rather than the neutral species **44**, hence favouring the branched coupling product. The presence of halide impurities in the solvent shifts the equilibrium, ultimately resulting in poorer selectivity. While the authors don't comment on asymmetric catalysis, significant differences in *ee* are likely upon switching from a molecular solvent to an ionic liquid due to the different binding modes of the bis-phosphine ligand.

Finally, the bimolecular rate of solvent displacement from a neutral chromium complex, *viz*. $Cr(C_6H_6)(CO)_2$(solvent) was measured in the ionic liquid $[C_4C_1im][PF_6]$ and compared to that in molecular solvents.[109] From these measurements, the strength of solvent interaction was established as $C_6H_{12} < [C_4C_1im][PF_6] < C_2H_4Cl_2$, whereas the kinetics for displacement by acetonitrile follow the reverse order. The displacement of the ionic liquid is two orders of magnitude faster than that of $C_2H_4Cl_2$. However, it was pointed out that due to the hygroscopic nature of many ionic liquids, the water content might cause a problem in that it efficiently coordinates to the metal.

6. Spectroscopic investigations

A recent review on analysis/analytical methods using ionic liquids has been reported.[110] While neat ionic liquids have been studied intensively with respect to their spectroscopic properties, little work has so far been devoted to the spectroscopy of organometallic compounds in these liquids.

The suitability of non-deuterated ionic liquids for ^{1}H and ^{13}C-NMR measurements has been established.[111] By employing well-established methods such as solvent-suppression and standard 2-D sequences such as ^{1}H^{1}H-COSY and ^{1}H-^{13}CHMQC, the detection of small quantities of an organic substance in the ionic liquids was possible. To what extent these techniques work for organometallic species in low concentration has yet to be tested.

Electrospray mass spectrometry has been demonstrated to be a useful and sensitive tool for the detection of charged organometallic fragments present in an ionic liquid.[42,112] While analysis from neat ionic liquids is feasible, the presence of a molecular co-solvent is required for the detection of organometallic compounds at picamolar levels.

Paramagnetic molybdenum and tungsten species have been studied by ESR-spectroscopy in imidazolium and pyridinium-based ionic liquids under conditions present in catalytic olefin metathesis.[113] This allowed the determination of the kinetics of *e.g.* W^{6+} reduction by an olefin and it could be further shown that the reaction can be considered as heterogeneous due to the low solubility of the olefin in the ionic liquid.

The groups of Mudring and Giernoth used $[C_{12}C_1im][Tf_2N]$ as solvent for luminescence studies of anhydrous lanthanide(III) iodides.[114] Provided that the ionic liquid was essentially water-free, intense near-infrared luminescence of the lanthanide complexes was observed with, as in the case of *e.g.* neodymium(III) high quantum yields and long luminescence time. Most studied lanthanide cations show transitions in this ionic liquid, that are quenched in molecular solvents.[115] The authors attribute this observation to the absence of C–H, N–H or O–H bonds in the immediate neighbourhood of the rare earth cation.

7. Concluding remarks

Despite the great advances that have been achieved in ionic liquid chemistry over the past two decades, many fundamental aspects of organometallic chemistry in these solvents have yet to be explored. While many catalytic processes have already been optimised to a remarkable degree, mechanistic considerations are still only in their infancy. Preparative organometallic chemistry might only be attractive in selected cases while on the other hand the stabilisation of charged species for spectroscopic analysis could become an attractive area of study.

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Groups 1 and 11: the alkali and coinage metals

J. V. Morey and A. E. H. Wheatley

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1. Alkali metals

1.1 Introduction

Part 1 of this review is concerned with the alkali metals (M^+). It is sub-categorized primarily according to the organic anion component (R^-) of organometallics of the type $R^{n-}(M^+)_n$. Except in cases of extreme interest, discussion will be limited to compounds that contain at least one carbon–alkali metal interaction. An overview of synthetic and mechanistic investigations of alkali metallated organics is to be found at the start of each section. Structural studies are then arranged by analytical method used; solid-state investigations are followed by solution and gas phase studies in that order.

1.2 Alkyl derivatives

The contribution made by Snaith to organolithium chemistry has been remembered recently in a review of ring stacking and laddering in the solid state.[1] Meanwhile, organolithium substrates have featured heavily in a review of routes to allenes, with discussion focussing on their use both as precursors to lithiocuprates (see below) and as nucleophiles in transition metal-catalyzed processes. Mention was also made of examples whereby (organolithium) nucleophiles are employed directly in addition or substitution reactions and the limitations of these procedures were considered.[2] The use of organolithium substrates and also (see below) alkalide reagents in ether-bond cleavage has been the subject of a recent review.[3]

Methyllithium has recently been employed in the synthesis of a monomeric organolithium compound that features a free pyramidal carbanion. Accordingly, the inhibition of π-delocalization has been shown to be crucial in generating the monomeric (pseudo)tetrahedral carbanion $[(3,5\text{-Me}_2\text{pz})_3\text{C}]^-$ from tris(3,5-dimethylpyrazolyl)methane.[4] *n*-Butyllithium has been employed in conjunction with 2-phenylaminopyridine in order to yield the corresponding lithium salt, with the subsequent introduction of higher Group 1 metal alkoxides in the presence of crown ethers giving a series of 2-phenylamidopyridines.[5] The same organolithium substrate has also been used in conjunction with $\text{Ph}_2\text{P(O)N(Bz)Me}$ in the presence of 2,6-di-*tert*-butyl-4-methylphenol to give a mixed dimer, $[\{\text{Ph}_2\text{P(O)N(Bz)Me}\}\cdot(\text{4-Me-2,6-Bu}^t\text{-C}_6\text{H}_2\text{OLi})\cdot\text{PhMe}]_2$, that has been interpreted as a model for the pre-complexation step preceding phosphinamide metallation.[6] The use of Bu^nLi in the presence of either (−)-sparteine or (4*S*)-2,2′-(1-ethylpropylidene)bis-4-(1-methylethyl)-4,5-dihydro-oxazole has allowed the double ring-opening of dihydropyrrole epoxides and 7-azanorbornene-type epoxides[7] and the alkylative desymmetrization of epoxides.[8,9] Alkyllithium reagents have been employed in the development of an efficient route to *N*-methyl-*O*-*tert*-butylhydroxylamine, in a piece of work that provides a new route to modified Weinreb amides.[10] Moreover, the enantioselective addition of alkyl- (and also aryl-) lithium reagents to quinoline has yielded 2-alkyl- (and 2-aryl-) 1,2-dihydroquinolines.[11] A variety of alkyl/aryllithium substrates have been used in conjunction with *o*-isocyano-β-methoxystyrenes to give 2,4-disubstituted quinolines.[12] The addition of Bu^nLi to *N*-(tri-*n*-butylstannylmethyl)phthalimides has afforded *N*-(tri-*n*-butylstannylmethyl) cyclic carbinol amides that act as precursors to azomethine ylides, themselves important intermediates *en route* to highly

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University Chemical Laboratory, Department of Chemistry, Lensfield Road, Cambridge, UK CB2 1EW. E-mail: aehw2@cam.ac.uk

functionalized pyrrolizidines (1,2,3,9b-tetrahydropyrrolo[2,1-*a*]isoindol-5-ones).[13] Excess Bu^nLi has been employed lately, in conjunction with *N*-Boc-1-ferrocenylmethylamine or -ethylamine, to give selectively *N*,1′-dimetallated precursors to electrophilically trapped 1,1′-disubstituted ferrocenes.[14] Both *n*- and *t*-butyllithium have been employed in the cascade synthesis of functionalized indole ring systems from *o*-aminostyrene. The process involves nucleophilic addition to the styrene double bond followed by electrophilic trapping of the newly formed organolithium, ring closure and dehydration. Importantly, functionalization is now rendered possible at all positions on the indole superstructure.[15] Bu^tLi has been used in the synthesis of the main group interstitial hydride complex $[(Bu^t{}_2AlMe_2)_2Li]^-[\{Ph(2\text{-}C_5H_4N)N\}_6HLi_8]^+$, with single crystal neutron diffraction having been employed to successfully establish the identity and exact location of the encapsulated hydride ion.[16] The metallation of diarylmethane derivatives has recently afforded benzylic lithium salts. The enhancement of this process by methoxyethoxy substituents has been the subject of recent study.[17] For example, 2-methoxyethoxyphenyl phenyl methane has been lithiated in high yield and ee using Bu^sLi/(–)-sparteine.[17] Benzyllithium intermediates have also been noted in the course of the lithium metal/4,4′-di-*tert*-butylbiphenyl-induced reductive opening of 1*H*,3*H*-benzo[*de*]isochromene. This work has facilitated the development of new 1,8-difunctionalized naphthalenes.[18] Highly functionalized organolithium substrates derived from L-serine have been prepared. Their reactions with various electrophiles have yielded enantiomerically pure adducts capable of being converted into homochiral alcohols and nonproteinogenic α-amino acids.[19]

Leading on from its inclusion in a review of ether-bond cleavage reactions,[3] treatment of the alkalide $[K]^-[K \cdot 2(15\text{-c-}5)]^+$ with various alcohols has affected the formation of methylpotassium, which then opens the crown ether ring to give potassium tetraethylene glycoxide vinyl ether and methane.[20] In a similar vein, butylpotassium has been employed in the cleavage of 15-c-5 as a means of producing organopotassium ethers and hence ethylene.[21] The initiation of alkalide-induced vinyloxirane and 3-butenyloxirane polymerisation has also been studied in detail.[22]

The straightforward structure of thf-adduct $Me_2HSi(Me_2PhC)_2CLi \cdot 2thf$ has been published,[23] while that of the internally coordinated dimer of $\{\mu_2$-1,5-bis(*N*,*N*-dimethylamino)pent-3-yl$\}$lithium has been reported privately.[24]

The solid-state structure of a newly prepared dimeric adduct of methyllithium with (+)-sparteine has been described.[25] The simple benzyllithium complex $MeSi(NMe_2)_2CH(Li \cdot tmeda)Ph$ has recently been reported.[26] Reaction of 2-ethyl-*N*,*N*′-diisopropylbenzamide with Bu^tLi in the presence of pmdeta has yielded the monomeric complex $\{2\text{-}(MeCH)C_6H_4C(O)NPr^i{}_2\}Li \cdot pmdeta$ which, in spite of deprotonation having occurred at the α-position of the ethyl unit, lacks C–Li interactions in the solid state.[27] Directed metallation has also been probed in the context of the treatment of ethyl phenyl sulfide with Bu^nLi/tmeda. Crystallography has revealed that the product of reaction in the presence of OEt_2 is the ortholithiate $(2\text{-}EtSC_6H_4Li \cdot tmeda)_2$.[28] A recent study into the formation of mixed aggregates between alkyllithium reagents and coordinating chiral auxiliaries has yielded the structures of both the hexameric lithium alkoxide based on 1-methyl-(*S*)-2-(hydroxymethyl)pyrrolidine and the novel hexanuclear 6:1 adduct between the same alkoxide and benzyllithium.[29]

Treatment of the carborane $1,2\text{-}(MeOCH_2CH_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ with excess sodium metal in thf has yielded $([\eta^6\text{-}\{(MeOCH_2CH_2)_2C_2B_{10}H_{10}\}Na]Na \cdot thf)_\infty$.[30]

The solid-state structures of both the 18-c-6 complex of methoxy(trimethylsilyl)silyl potassium and its condensation product, $MeO(Me_3Si)_2SiK$, have been shown to exhibit polymeric motifs by virtue of the ability of Si-bonded methyl groups to stabilize metal centres.[31]

Addition of MeLi to a homoleptic complex of the type $(1\text{-aza-}1,3\text{-diene})_2Ti$ has resulted in methane evolution and has yielded the metallocyclic titanium alkylidene complex {PhC(H)C(Me)C(H)N(dipp)}Ti{PhC(Li · OEt_2)C(Me)C(H)N(dipp)}, wherein both C(H)–Ti and C(Li)=Ti units are observable crystallographically.[32]

The behaviour of MeLi in etherate solvents has been probed using ^{1}H, ^{6}Li and ^{13}C NMR spectroscopies, with the emphasis placed on structural effects that arise from the introduction of lithium bromide or iodide. Data suggest the essential retention of tetrameric aggregates with different halogen contents in each case.[33] So-called No-D ^{1}H NMR spectroscopy involves recording the ^{1}H NMR spectra of compounds dissolved in ordinary, non-deuterated laboratory solvents. It provides a potentially useful route to monitoring the concentration of many commonplace reagents and has lately been employed as a means of titering the isomers of butyllithium in samples treated with a precisely known amount of 1,5-cyclooctadiene as an internal integration standard.[34] Both ^{1}H and ^{13}C NMR spectroscopies suggest that the pyramidal $[(3,5\text{-}Me_2pz)_3C]^-$ ion noted in the solid-state structure of $[(3,5\text{-}Me_2pz)_3C]^-[Li\cdot thf]^+$ is retained in solution.[4] Moreover, ^{7}Li and ^{1}H NMR diffusion measurements have suggested equivalent hydrodynamic radii for cations and anions, suggesting either a tight ion pair without direct C–Li bonding or a zwitterionic structure (*cf.* the solid state). High resolution ^{15}N, ^{1}H correlation spectroscopy points to the latter motif being retained in solution.[4] The existence of both sp^3-hybridized C(H)–Ti and sp^2-hybridized C(Li)=Ti units in {PhC(H)C(Me)C(H)N(dipp)}Ti{PhC(Li · OEt_2)C(Me)C(H)N(dipp)} has been confirmed by ^{13}C NMR spectroscopy with the C(H)Ti resonance at δ 79.96 and the C(Li)Ti signal at δ 236.10.[32]

A detailed computational study of organolithium compounds and their corresponding hydrocarbon conjugate acids has been undertaken at the MP2/6-311 + G(2df,2pd) level with single point energy calculations being done also at the CCSD(T) and B3LYP levels with the same triple split-valence basis set. Major conclusions drawn were that α-lithio anions exist as ground-state triplets, that lithium is an acid enhancing substituent and that lithium also significantly weakens α- and β–C–H bonds.[35]

1.3 Alkenyl, allyl, vinyl, alkynyl and related derivatives.

The synthetic utility of both 1-lithio- and 1,4-dilithio-1,3-dienes has been the subject of recent review.[36] Moreover, the reactivities of 1,4-dilithio-butadiene derivatives with isothiocyanates and isocyanates have been studied. In this context, isothiocyanates have been used to generate iminocyclopentadienes while isocyanates have given a diverse mixture of products due to their high reactivity with respect to 1,4-dilithiobutadienes.[37] The reactions of 1,4-dilthiobutadienes with aldehydes and ketones have also been studied.[38]

As well as butylpotassium, vinylpotassium has been used to cleave 15-c-5 and to generate organopotassium ethers capable of going on to form ethylene as well as potassium alkoxide by-products.[21]

The lithium γ-phosphino-β-diketiminate (dipp)NC(Me)C(PPh_2)C(Me)N(dipp)Li · PhMe has recently been fully characterized.[39] The polymeric nature of allyllithium compound $[\{PhMe_2Si(CH)_3SiMe_2Ph\}Li]_\infty$ has also been discussed. It was isolated and characterized as part of a study into the formation of new 1,2-dichloro-1,2-diborolanes and aromatic tetraboranes.[40]

A variety of allyllithium compounds have recently been synthesized and found to exhibit mono-, di- and polymeric aggregation motifs in the solid state with the metal invariably residing closest to one of the terminal allyl carbon centres.[41]

Sodium and potassium complexes of 2,3-pyrazyl-linked bis(1-azaallyl) systems have recently been shown to incorporate extensive NCCCN-metal support.[42]

In a heterometallic context, reaction of $(\eta^5\text{-}C_5HMe_4)_2(\eta^3\text{-}Me_3SiCH{=}CSiMe_3)(\eta^1\text{-}RC{\equiv}C)Zr$ (R = Bu^t, Me_3Si, Ph, Fc) with $Me_3SiC{\equiv}CLi$ in toluene has yielded the diamagnetic species $\{(\eta^5\text{-}C_5HMe_4)_2(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)(\eta^1\text{-}Me_3SiC{\equiv}C)Zr\}Li$, a full characterization of which reveals that the Li$^+$ ion resides in close proximity to the alkynyl triple bond and to C$_\beta$ of the η^2-$Me_3SiC{\equiv}CSiMe_3$ unit.[43] A series of alkali metal tetraethynylzincates have recently been prepared, with the polymer of compound $(C_2H)_4ZnCs_2$ having been fully characterized and the caesium ions found to be η^2-coordinated by six ethynyl ligands.[44]

Recently elucidated allyllithium compounds exhibit mono-, di- and polymeric aggregation motifs in the solid state, have also been extensively studied by NMR spectroscopy and have been found to exist as mono- and dimers in solution. Lineshape analysis of the metal-bonded carbon resonance has yielded insights into the process of inversion at the lithiated atom. The dynamics of lithium 1,3-sigmatropic rearrangements have been found to vary widely according to steric effects.[41] The 1,2-addition of $PhC{\equiv}CLi$ to quinazolinones has been studied using ^{6}Li, ^{13}C and ^{19}F NMR spectroscopies with data suggesting that a mixture of lithium quinazolinide/lithium phenylacetylide dinuclear and mixed tetranuclear aggregates along with lithium phenylacetylide dimers are formed. ^{19}F NMR spectroscopy pointed to a first-order dependence on mixed dinuclear species, a zero-order dependence on thf solvent and a half-order dependence on lithium phenylacetylide concentration. These data are consistent with the addition of disolvated lithium phenylacetylide monomers to the mixed dinuclear aggregates.[45]

1.4 Aryl derivatives

The preparation of various new azulenyllithium reagents has been facilitated through the use of halogen–metal exchange reactions involving iodoazulene starting materials.[46] Aryllithium substrates have been utilized recently to provide the aromatic components of new penta- and hexaorganotellurium compounds of the types Ar_5Te and $Ar_{6-n}Me_nTe$, respectively.[47] A simple synthetic pathway to biologically important arene-fused piperidines involves the conjugate addition of 2-hydroxymethylaryllithiums to nitroalkenes followed by reduction of the nitro group (to an amine) and cyclization. Recently, advances have been made in this field by the achievement of *chiral* arene-fused piperidines through the enantioselective addition of 2-trityloxymethylaryllithiums to cyclic and acyclic nitroalkenes.[48] Both 4-bromo-6-fluoro-2-(trifluoromethyl)- and 4-bromo-7-fluoro-2-(trifluoromethyl)-quinoline have been regioselectively functionalized *via* directed lithiation in the presence of trimethylsilyl and iodo auxiliary ligands. Importantly, neither organolithium generation nor protecting group removal jeopardized the 4-bromo centre.[49] The aryllithium substrates 8-methoxy-1-naphthyllithium and 2,6-bis(alkoxymethyl)-phenyllithium have been used to generate 1-(8-methoxy-1-naphthyl)-1,2,2-tris-(trimethylsilyl)silene and various 1-{2,6-bis(alkoxymethyl)phenyl}-1,2,2-tris-(trimethylsilyl)silenes, respectively, from (dichloromethyl)tris(trimethylsilyl)silane. The first of these (inherently unstable) products was trapped using excess naphthyllithium reagent to give 1,1-bis(8-methoxy-1-naphthyl)-1-{bis(trimethylsilyl)methyl}-2,2,2-trimethyldisilane.[50] Lithium di-*tert*-butylbiphenylide has been employed to affect the reductive lithiation of α-aminonitriles to give α-aminoorganolithium reagents. Transmetallation and 1,4-addition across enones has then enabled the preparation of quaternary carbon centres adjacent to nitrogen atoms.[51] Reaction of two equivalents of lithium naphthalenide with 2,7-dihydrodinaphthoheteroepines has given dianionic intermediates *en route* to unsymmetrically 2,2′-disubstituted binaphthyls.[52] Contrastingly, symmetrically 2,2′-disubstituted binaphthyls are found to result if the initial lithiation is achieved using excess lithium along with catalytic 4,4′-di-*tert*-butylbiphenyl.[52] Lithium naphthalenide has also been used, in conjunction with tin chloride or elemental tin, in order to achieve lithium stannides. These have been shown to reductively cleave carbon–halogen bonds and to affect pinacol coupling with aldehydes.[53] The directed lithiation of *N*-pyridylbenzamides has been studied, with data suggesting that, unlike for anilides (where metallation proceeds smoothly at the *ortho*-position), deprotonation is favoured on the pyridine ring.[54] Ethyl-2-(4-chloro-2-pyridyl)benzoic acid, 2-(4-chloro-2-pyridyl)benzoate and

N,*N*-diisopropyl-2-(4-chloro-2-pyridyl)benzamide have been treated with lithium 2,2,6,6-tetramethylpiperidide at low temperature to give the corresponding regiospecific C5′-lithio derivative. Only at elevated temperature does the benzamide react at the C3′ position. This latter intermediate cyclizes to give 1-chloro-4-azafluorenone—precursor to the potentially useful alkaloid, onychine.[55] Optically enriched amines have been prepared recently through the addition of aryllithium substrates to aromatic imines in the presence of the mediating chiral ligand *N*,*N*′-tetramethylcyclohexane-1,2-diamine.[56]

Whereas the recently determined solid-state structure of the adduct of methyllithium with (+)-sparteine reveals a straightforward 2:2 dimer, adduct formation between PhLi and (+)-sparteine instead yields an unusual 4:2 $(CLi)_4$ ladder wherein each terminal metal ion is *N*,*N*′-chelated.[25] In contrast to its reactivity in the presence of strongly donating pmdeta, 2-ethyl-*N*,*N*′-diisopropylbenzamide reacts with Bu^tLi in thf solution to afford dimers of 2-ethyl-6-lithio-*N*,*N*′-diisopropylbenzamide.[27] Similarly, significant solvent effects have been reported in the directed metallation of ethyl phenyl sulfide by Bu^nLi/tmeda. Whereas the presence of OEt_2 is known to induce ortholithiation, dissolution of the product in thf leads to isomerization and isolation of the tmeda-bridged species $\{PhSCH(Me)Li\}_2 \cdot tmeda$.[28] Dimeric $[1,3\text{-}(Bu^tBpz_2)\{Bu^tB(OH)pz\}C_6H_4Li\text{-}2]_2$ reveals two different coordination environments for the metal centers—a $[Bu^tBpz_2]^-$ and a $[Bu^tB(OH)pz]^-$ group.[57] Enantiopure and racemic aggregates of the type Ar_4Li_4 [Ar = 2-$\{Me_2NC(H)Me\}C_6H_4$] have recently been reported on. Whereas *rac*-{1-(dimethylamino)ethyl}benzene reacts with Bu^tLi to give a tetramer incorporating (*R*)- and (*S*)-enantiomer-based dimers, use of the (*R*)-enantiomeric substrate with Bu^nLi yields only a 1:1:1 complex of Bu^nLi, [(*R*)-2-$\{Me_2NC(H)Me\}C_6H_4]_4Li_4$, and (*R*)-{1-(dimethylamino)ethyl}benzene.[58]

Reaction of a 1,3-diphosphetane-2,4-diyl with elemental lithium has successfully achieved an aniomesolytic cleavage in order to give a dilithium complex. Specifically, $(Me_3SiCP)_2(Li \cdot dme)_2$ reveals a core planar, C_i-symmetric $(CP)_2$ ring with metal centres residing 2.066(2) Å above and below the ring centroid.[59] Meanwhile, the lithium amide dimer of $(Mes)N{=}P(Ph)_2(C_6H_4\text{-}1,2)N(dipp)Li$ reveals η^2-metal stabilization by aryl systems[60] and η^6-sandwiching of metal centres is responsible for aggregation in the unusual tetramer of $(3\text{-}Ph_2PC_6H_4)(Bu^t_2CH)NLi$.[61] In a similar vein, tmeda-solvated alkali metal ions have been observed linked to a dianionic 9,11-diboratacarbazole unit.[62]

A series of alkali metal silanides, Bu^t_2PhSiM (M = Na, K) have been prepared and fully characterized, with X-ray crystallography revealing solid-state dimers that link to give polymers due to η^6-aryl stabilization of the metals.[63] Similarly, arene support of sodium and potassium has been noted in a group of recently prepared tetraorganylcyclopentaphosphanides and tetraorganyltetraphosphane-1,4-diides.[64] Unlike in the solid-state structure of ion-separated radical anion-containing $[\{C_6H_4(NEt)_2\text{-}1,2\}Si]_4^{\cdot -}[K \cdot 6thf]^+$, η^2-support of each of the two alkali metal ions is noted in $[\{C_6H_4(NEt)_2\text{-}1,2\}Si]_4^{2-}([K \cdot 3dme]^+)_2$.[65] Arene–potassium η^2-interaction is responsible for polymerisation in the solid-state structure of the supramolecular stack between (*trans*-1,2,2,3,4,4-hexa-*tert*-butyl-1,3-cyclotetrasilanediyl)-dipotassium and benzene.[66] Both η^2 and η^6 arene interactions with potassium ions are observed in the polymeric structure of the sterically congested amidopyridine salt potassium (2,6-diisopropylphenyl){6-(2,6-dimethylphenyl)pyridin-2-yl}amide.[67] The sterically hindered organofluorosilane $2,6\text{-}Mes_2C_6H_3SiF_3$ reacts with excess potassium hydroxide in thf solution to give a singly deprotonated terphenyl-substituted disiloxane-1,3-tetrol wherein the metal ions are stabilized by interaction both with hydroxide and aryl units.[68] Just as arene-potassium supporting interactions are seen in $3\text{-}HOC_6H_4OK$,[69] so they are also observed in the rubidium analogue of this system, the metals interacting with up to eight phenylene rings.[69] A series of rubidium alkoxides and rubidium-titanium alkoxides have also been prepared lately, with extensive π-support offered to the alkali metal through Odipp and Odmp ligands.[70]

A homologous series of reduced digermanes have been reported, with synthesis achieved using Li, Na or K (= M) in etherate solution to yield the conversion from $\{(\mathrm{dipp})(\mathrm{H})\mathrm{Ge}\}_2$ to $\{(\mathrm{dipp})(\mathrm{H})\mathrm{Ge}\}_2\mathrm{M}_2$. In each case, reduction is accompanied by extension of the Ge–Ge distance and the alkali metal ions bridge this interaction whilst each being flanked by two dipp units.[71] Reduction of the tris(di-*tert*-butylmethylsilyl)stannyl radical using lithium in benzene has given the monomeric η^6-complex $(\mathrm{Bu}^t{}_2\mathrm{MeSi})_3\mathrm{SnLi}\cdot\mathrm{C_6H_6}$.[72] A paramagnetic dimer, $[\{\mathrm{Et_2C}(2\text{-}\mathrm{C_4H_3N})_2\}_2\mathrm{MoLi}]_2(\mathrm{Li}\cdot\mathrm{thf})_4$, has been yielded by the interaction of $\mathrm{Me_8Mo_2}(\mathrm{Li}\cdot\mathrm{thf})_4$ with $\mathrm{Et_2C}(2\text{-}\mathrm{C_4H_3NH})_2$. The location of the alkali metal centres is thought to be indirectly responsible for the paramagnetic behaviour by virtue of the resultant 45° rotation of the two Mo(dipyrrolide) moieties.[73] The same study has also reported reaction of the dipotassium salts of $\mathrm{Ph_2C}(2\text{-}\mathrm{C_4H_3NH})_2$ and 2-{1,1-bis(1*H*-pyrrol-2-yl)ethyl}pyridine with $(\mathrm{MeCO_2})_4\mathrm{Mo_2}$ to afford the diamagnetic species' $[\{\mathrm{Ph_2C}(2\text{-}\mathrm{C_4H_3N})_2\}\mathrm{MoOAc}]_2(\mathrm{K}\cdot 3\mathrm{thf})\mathrm{K}\cdot\mathrm{thf}$ and $[\{(2\text{-}\mathrm{C_4H_3N})(\mathrm{Me})\mathrm{C}(2\text{-}\mathrm{C_4H_3N})_2\}\mathrm{MoOAc}(\mathrm{K}\cdot\mathrm{thf})]_2$.[73] As part of an investigation into potentially useful compounds containing multiple bonds between phosphorus atoms the synthesis of an anionic terminal phosphide of niobium has been reported. Its precursor—the dimer of $\{\mathrm{Bu}^t(3,5\text{-}\mathrm{Me_2C_6H_4})\mathrm{N}\}_3\mathrm{Nb}{\equiv}\mathrm{PNa}\cdot\mathrm{OEt}$—reveals aromatic support of the sodium ions in the solid state.[74] Phenylthiolate has been revealed to act as a σ- and π-donor in the 3-dimensional coordination polymer $\{(\mathrm{PhS})_4\mathrm{FeK_2}\}_\infty$.[75] Arene–potassium interactions have been found to be responsible for polymerisation in the solid-state structure of the bis(diamide) complex $[\{(\mathrm{dipp})\mathrm{N}(\mathrm{CH_2})_3\mathrm{N}(\mathrm{dipp})\}_2\mathrm{Y}(\mathrm{K}\cdot\mathrm{PhMe})]_\infty$.[76] Unlike in the sodium and potassium analogues, rubidium and caesium 1-phenyl-1*H*-1,2,3,4-tetrazole-5-thiolate salts have revealed support of the metal centres through not only nitrogen and sulfur centres, but also through the phenyl ring.[77] The straightforward structure of (η^6-tetraphenylborato)caesium · 12-c-6 has been communicated privately.[78]

An extensive multinuclear magnetic resonance investigation (^{1}H, ^{2}H, ^{7}Li, ^{13}C, ^{31}P) has allowed elucidation of the mechanism by which *N*-benzyl-*N*-methyldiphenylphosphinamide undergoes dearomatizing anionic cyclization upon metallation using an alkyllithium substrate. Consistent with the operation of a CIPE mechanism, initial *ortho*-deprotonation is followed by translocation of the metal to the benzylic position in the presence of hmpa.[79] The observation of ^{119}Sn–^{7}Li coupling points to the intermetallic bond noted in the solid-state structure of $(\mathrm{Bu}^t{}_2\mathrm{MeSi})_3\mathrm{SnLi}\cdot\mathrm{C_6H_6}$ being retained in solution even at room temperature.[72] NMR spectroscopic studies suggest that the observed dichotomy whereby 2-ethyl-*N*,*N*′-diisopropylbenzamide reacts with $\mathrm{Bu}^t\mathrm{Li}$ in thf solution to afford $[\{2\text{-}\mathrm{EtC_6H_3C(O)NPr}^i{}_2\}\mathrm{Li}\cdot\mathrm{thf}]_2$ and in pmdeta to give $\{2\text{-}(\mathrm{MeCH})\mathrm{C_6H_4C(O)NPr}^i{}_2\}\mathrm{Li}\cdot\mathrm{pmdeta}$ can be explained in terms of the products being kinetic and thermodynamic, respectively.[27] Extensive NMR spectroscopic investigation of $(\mathrm{Me_3SiCP})_2(\mathrm{Li}\cdot\mathrm{dme})_2$ has revealed deshielded phosphorus centres, consistent with a phospha-aromatic system, and shielded lithium ions, suggestive of a diatropic ring current.[59]

1.5 Cyclopentadienyl and related derivatives

As part of a study into the synthesis of new copper(II) alkoxy-*N*-heterocyclic carbene complexes, the lithiated tetranuclear pseudo-cubane $[\{1\text{-}\mathrm{C(NCHCHNMe)}\}\mathrm{CH_2CH(Bu}^t)\mathrm{OLi}]_2(\mathrm{ILi}\cdot\mathrm{OEt_2})_2$ has been isolated and fully characterized.[80] A new route to hybrid scorpionate/cyclopentadienyl ligands has lately been reported, with the lithium derivative of the tridentate anionic ligand $[\{\mathrm{Me_2C_3N_2}\}_2\mathrm{C(H)C(Ph_2)C_5H_4}]^-$ having been structurally characterized.[81] A $\mathrm{C_5Me_4}$ unit is noted to augment support of one of the otherwise methylpyrazolyl and thf bonded alkali metal centres in the complex $\mathrm{B}\{(3\text{-}\mathrm{Mepz})_2\mathrm{Li}\cdot 2\mathrm{thf}\}(3\text{-}\mathrm{Mepz})(\mathrm{C_5Me_4})\mathrm{Li}\cdot\mathrm{thf}$.[82]

It has been shown that η^5-stabilisation of the metal centres by Cp units accounts for polymerisation in the compound (8-quinolyl)cyclopentadienylsodium.[83] The simple complexes $[Cp(Na\cdot 15\text{-}c\text{-}5)_2]^-$,[84] {$\eta^2$-9-(trimethylsilyl)fluorenyl}-potassium · 18-c-6,[85] and η^3-fluorenylpotassium · 18-c-6[86] have been noted. Meanwhile, the ESR characterization of a spin-localized cyclopentadienyl radical annelated with homoadamantene frameworks has required reaction of the corresponding potassium cyclopentadienyl salt with ClAg or F_6SbAg. The structure of the said potassium substrate has revealed η^5-support of the metal.[87] Just as a C_5Me_4 unit stabilises an alkali metal centre in $B\{(3\text{-}Mepz)_2Li\cdot 2thf\}(3\text{-}Mepz)(C_5Me_4)Li\cdot thf$, so comparable interaction is reported in the structure of polymeric $\{B(3\text{-}Mepz)_3(C_5Me_4)(K)_2\cdot 2thf\}_\infty$.[82]

In a heterobimetallic context, a study into complexes incorporating linked carboranyl-indenyl ligands with tethered oxygen and nitrogen has included a report of the solid-state structure of $[\{(\mu\text{-}\eta^5\text{:}\eta^2)\text{:}\eta^1\text{:}\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2X)(C_2B_{10}H_{10})\}_2Yb](Li\cdot 2thf)_2$ (X = OMe,[88] NMe_2[89]). These complexes have revealed both oxygen/nitrogen and η^2 indenyl stabilization of the alkali metal centres. Surprising mixed π-ferrocene π-toluene stabilization of potassium has lately been noted in ion-separated $[(hmds)_3Mg]^-[(\eta^3\text{-}PhMe)_2(\eta^5\text{-}Fc)_2K]^+$.[90]

A series of regioselectively tetradeprotonated Group 8 metallocenes has been prepared *via* a mixed Na/Mg tris(diisopropylamide) synergic base. Accordingly, $\{(C_5H_3)_2M\}(Pr^i{}_2N)_8Mg_4Na_4$ (M = Fe, Ru, Os) have been prepared.[91] Trinuclear imido-nitrido $(\mu_3\text{-}N)\{Ti(\eta^5\text{-}Cp^*)(\mu\text{-}NH)\}_3$ has been reacted with CpNa to yield the heterocubane-type adduct $[(\mu_3\text{-}N)\{Ti(\eta^5\text{-}Cp^*)(\mu\text{-}NH)\}_3]\cdot NaCp$.[92] The systematic study of 2,3,4,5-tetraethylarsolides and -stibolides of sodium, potassium, rubidium and caesium has yielded two series' of complexes that each reveal η^5-C_4H_4E (E = As, Sb) support of the alkali metal. Notwithstanding dimeric $\{(Et_4C_4As)Na\cdot tmeda\}_2$, these systems all form polymeric chains in the solid state.[93] A series of alkali metal (Na, K) tetrakis(3,5-di-*tert*-butylpyrazolato)lanthanoidate(III) complexes have recently been reported.[94]

2. Copper, silver and gold

2.1 Introduction

Part 2 of this review is divided into three categories, in each of which the organometallic chemistry of a different coinage metal is considered. As with Section 1, compounds that contain at least one carbon–metal interaction are discussed. For each of the coinage metals, synthetic and mechanistic studies are reported first and these are then followed by solid-state, solution and gas phase investigations in that order.

2.2 Copper compounds

Lithium diorganocuprates have been known for some time to enable S_N2' substitution processes at propargylic acetates and to thus enable allene synthesis. This frequently applied phenomenon has recently featured significantly in a review article on allene preparation.[2] The Gilman reagent $Me_2CuLi\cdot ILi$ has recently been treated with bis(enones) to afford the products of both Michael cyclization and [2 + 2] cycloaddition. Data suggest that selectivity for one or the other pathway may be achieved by manipulating the loading of the Gilman reagent, its rate of addition, and the concentration of the reaction mixture.[95] A variety of lithium α-(alkoxy)alkyl- and α-(*N*-carbamoyl)alkylcuprates prepared from organostannanes have been employed, in conjunction with vinyl iodides, propargyl mesylates, and α,β-unsaturated ketones, to give enantioselectively coupled products.[96] α-(*N*-Carbamoyl)alkylcuprates have been reacted with allylic phosphates to give homoallylic amines, with regioselectivity being controlled by steric constraints associated with both the cuprate and the phosphate substrates. Rational design has allowed systems to be tailored toward S_N2 or S_N2' substitution, while enantioselectivity is achieved using either a scalemic α-di{(*N*-carbamoyl)alkyl}cuprate and an achiral phosphate or else with an achiral cuprate and a scalemic allylic phosphate.[97] Also, carbamoyl chlorides have been treated with cyano-Gilman cuprates in order to achieve the synthesis of tertiary amides.[98] Homo- and mixed lithium di-α-(heteroatom)alkylcuprates have recently been shown to readily dimerize upon treatment with halogens or *N*-halosuccinimides to give coupled products in high yields. Moreover, limited enantioselectivity has been achieved for the oxidative coupling of lithium *n*-butyl(2-pyrrolidinyl)cuprate.[99]

The catalysis of allylic substitution reactions by copper *N*-heterocyclic carbenes has been discussed recently. Interest has focussed on the application of these systems to enantioselective synthesis. Hence, reaction of allyls with alkyl Grignard substrates in the presence of catalytic copper species proceeded, *via* predominantly S_N2' reaction, to give γ-substituted products, with asymmetric reaction enabled by the employment of optically active carbene ligands.[100] Bidentate *N*-heterocyclic carbenes are known to promote various organic transformations, and it is in this context that that Cu-catalyzed enantioselective allylic alkylation has recently been reported.[101]

Bridging copper carbenes have been studied in terms of Cu-catalyzed cyclopropanation. Treatment of the known styrene cyclopropanation catalyst $[HC\{C(Me)N(dmp)\}_2]Cu(\eta^2\text{-ethylene})$ with N_2CPh_2 has yielded the crystalline dicopper bridging carbene $[HC\{C(Me)N(dmp)\}_2]_2Cu_2(\mu\text{-}CPh_2)$.[102] The same study has also reported synthesis and characterization of the terminal carbene $[HC\{C(Me)N(Mes)\}_2]Cu(\mu\text{-}CPh_2)$.

The solid-state structure of $\{\mu_2\text{-}\eta^2,\eta^2\text{-bicyclo}(2.2.1)\text{hepta-2,5-diene}\}$-bis(hexafluoroacetylacetonato-*O*,*O*′)-dicopper has been privately communicated.[103] Stable, dimeric Cu(I) complexes incorporating 2-, 3- and 4-pyridylacrylic acid ligands have been reported, with hydrogen bonding resulting in the formation of 3-dimensional networks, and the olefinic component of the acid ligand acting as an η^2-donor with respect to the metal ions.[104] Similarly, vinyltrimethylsilane has been shown to stabilize the metal ion in (1,1,1,3,5,5,5-heptafluoropentane-2,4-dionato)copper(I).[105] A combination of the pyridyl *N*-centre and η^2-action of the olefin moiety allows bridging of two metal ions by vpy as seen in the solid-state structure of $[bdptz(\mu\text{-vpy})Cu_2]^+$.[106] Divinyl molecules have also been noted to act as bridging ligands in the binuclear copper(I) hfac complexes $\{(hfac)Cu\}_2X$ (X = 1,5-hexadiene, 1,3-divinyltetramethyldisiloxane), with each olefin function η^2-supporting a different metal.[107] Three supramolecular isomers that incorporate η^2-interactions between pbq and copper have recently been presented. The treatment of dimetallic Cu(II) acetate with hbq in ethanol has resulted in formation of a solution containing the molecular building block $(\mu_2\text{-AcO})_2(\mu_2\text{-pbq})Cu_2$. If this is stored at ambient temperature then the isomers $\{(\mu_2\text{-AcO})_2(\mu_4\text{-pbq})Cu_2\}_\infty$ and $\{(\mu_2\text{-AcO})(\mu_3\text{-AcO})(\mu_3\text{-pbq})Cu_2\}_\infty$ deposit. However, at elevated temperatures, $\{(\mu_3\text{-AcO})_2(\mu_2\text{-pbq})Cu_2\}_\infty$ is generated instead.[108]

A series of trinuclear copper(I) and silver(I) complexes containing divynyl ligands have been prepared recently. As part of this study the solid-state structures of $[(\eta^1\text{-}\mu_3\text{-}RC{\equiv}CC{\equiv}C)_2(\mu\text{-dppm})_3Cu_3]^+$ (R = H, Ph) have been reported.[109]

The self-assembly and structure of the octanuclear Cu(II) cluster $\{(PhSiO_2)_6Cu_6\}\{NCCu(Me_6tren)\}_2$ has been reported.[110] The straightforward structures of 2-[111] and 3-dimensional[112] NCCu coordination polymers—the latter including thermally stable (up to 270 °C) $\{(in)_2(NC)Cu_3\}_\infty$[113]—and of cyano(2,2′-bipyridine-*N*,*N*′)(triphenylphosphane)copper(I),[114] have been reported. Cross-linking of $(NCCu)_6$ rings in a variety of polymeric cyanocuprates(I) has been analysed for $\{[(NC)_3Cu]^{2-}\}_\infty$.[115] Polymeric arrays based on anionic sheets of connected $(NCCu)_6$ rings have revealed structures in which α,ω-alkanediammonium spacers are incorporated between the layers.[116] A re-determination of the solid-state structure of the mixed-valence copper cyanide coordination polymer $\{(NC)_2Cu_5 \cdot 4dmf\}_\infty$ has been reported.[117] Carbon–carbon bond cleavage has been affected by an unusual dinuclear Cu(II) cryptate, as evidenced by the observation of a CuNCCu motif in the structure of the cation $[LCu_2(CN)]^{3+}$ [$L = N\{(CH_2)_2NHCH_2(C_6H_4\text{-}4)\text{-}CH_2NH(CH_2)_2\}_3N$].[118] A study into the formation of oligomers based on 1,8-diisocyano-*p*-menthane ligands has yielded the simple complex $(dppp)Cu(CNBu^t)_2$.[119] The cyano-bridged mixed valence Cu(II)/Cu(I) species $[(oxpn)Cu_2\{Cu(CN)_2\}_2]_\infty$ has been fully characterized, with the structure consisting of threefold interpenetrating 3-dimensional frameworks.[120] The investigation of SPS-based pincer ligands derived from 1-*R*-1-*P*-phosphahexadienyl anions has led to the synthesis and characterization of $CNBu^t$ and CNdmp stabilized monomeric complexes of copper.[121]

An extensive study into mixed-ligand coordination in oligomers and polymers of Cu(I) and Ag(I) employing diphosphine and mono- and diisocyanide ligands has included report of the solid-state structure of $[(dppm)_2(Bu^tNC)_3Cu_2]^{2+}$, wherein two of the isocyanate ligands are terminal while one bridges the two metal centres.[122]

The simple tetrameric structure of $(2\text{-}Me_2NCH_2C_6H_4Cu)_4$ has been communicated privately.[123] Creation of the thermally stable tris(pyridyl) Al(III) reagent $MeAl(2\text{-}C_5H_4N)_3Li \cdot thf$ has facilitated new pyridyl-transfer processes, one such involving the introduction of copper chloride and giving rise to the Cu(I) organometallic $[\{(2\text{-}C_5H_4N)Cu\}_3]_\infty$. In this case, polymerisation results from the formation of short metal–metal contacts between 3- and 4-coordinate copper(I) centres.[124] Meanwhile, interactions of η^2-type have been noted between the metal and the phenyl ring of the ligand sidearm in an array of compounds incorporating tridentate ligands based on the *N*,*N*-bis{2-(2-pyridyl)ethyl}-2-phenylethylamine motif. The nature of this interaction has been found to vary extensively according to the placement of substituents at the *p*-position of the phenyl ring. The reactivities of these systems towards oxygen has been tested, with data suggesting the formation of (μ-η^2:η^2-peroxo)dicopper(II) complexes.[125]

The structure of tetra-μ-chloro-chloro(tmeda)(1,1,3-trimethyl-2-imidazolium)-dicopper(I)-copper(II) has been reported.[126] The molecular structure of the simple, monomeric *N*-heterocyclic carbene complex {1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene}copper chloride has also been noted.[127,128,] Moreover, the analogous acetate, methyl,[128] *tert*-butoxide and 3-hex-3-enyl[129] species have also been presented. Concerning the methyl species, the complex has been shown to insert CO at ambient temperature and pressure, to yield the acetate system.[128] Meanwhile, the vinyl complex is yielded by the hydrocupration of 3-hexyne by the Cu–Cu bonded dimer of {1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene}copper.[129] The structural characteristics of the octahedral hexanuclear copper ferrocenylacetylide $[(FcC{\equiv}C\text{-}\eta^1\text{-}\mu_3)(\mu\text{-}dppm)_2Cu_6]^+$ have been reported.[130] The nature of the metal-carbon bond in Group 11 complexes of *N*-heterocyclic carbene ligands has been studied, with the solid-state structure of the D_3-symmetrical copper(I) complex $[(time^{Me})_2Cu_3]^+$ having been reported.[131] As already mentioned, bidentate *N*-heterocyclic carbene chiral ligands have been utilized for Cu-catalyzed enantioselective allylic alkylations. In this context a chiral, dimeric Cu-complex has been characterized that sheds light on the identity of the active catalyst.[95]

The Cu(I)–Na/K complexes $bpym_2Cu_2Na(CN)_3$ and $bpymCuK(CN)_2$ have been shown to assemble into 2- and 3-dimensional networks, respectively, with the cyano groups acting as *N*-donors towards the alkali metal centres and as *C*-donors to Cu(I) ions.[132]

The sequential reaction of the copper aryl dmpCu with the stannanediyl $\{1,2\text{-}(Bu^tCH_2N)_2C_6H_4\}Sn$ and Bu^tOLi has yielded a tin(II)-oxo cluster, $\{SnO(dmpCu)\text{-}Li(\cdot OEt_2)OBu^t\}_2$, which is based on a pseudo-cubic $(Bu^tO)_2O_2Sn_2Li_2$ core.[133]

Reaction of {(*S*)-(–)-bi-2-naphthol}P(O)Na {*S*-binolP(O)Na} with $CpCo(CO)I_2$ has afforded a chiral C_3-symmetric, tripodal, oxygen-donor ligand which, upon treatment with Cu(I) in the presence of $PhC{\equiv}CH$ and $Me_3SiC{\equiv}CSiMe_3$ has yielded CpCo{*S*-binolP(O)}$_3$Cu(η^2-alkyne).[134] In order to probe their luminescent properties, a series of hexa-, octa-, and hexadecanuclear clusters of Ag(I)/Cu(I) have been synthesised *via* the reaction of polymeric $(4\text{-}R_6H_4C{\equiv}CM)_\infty$ (R = H, Me, MeO, O_2N, MeOC; M = Cu, Ag) with $[(\mu\text{-}Ph_2PXPPh_2)_2(MeCN)_2M'_2]^{2+}$ (X = CH_2, NH; M′ = Cu, Ag). The resulting luminescent complexes reveal phosphorescent emission that appears to derive from a ^{3}LMCT transition, mixed with a metal cluster-based (d → s) excited state.[135] A study of sulfur-bridging activity in *cis*-planar $N_2S_2Ni(II)$ systems has led to the creation and characterization of a variety of heterometallic complexes, amongst them $Ni(L_R\text{-}S_2N_2)Cu(CN)PPh_3$ {L_R = *trans-rac-N*,*N*′-bis(2-mercapto-2-methylprop-1-yl)-1,2-cyclohexanediamine(2–)}.[136] The ability of cyano copper(I) units to form networks has already been discussed and has been utilized in order to bind (1,10-dithia-18-crown-6)-complexed $(NC)_2Hg$ units in the solid state.[137] As part of an investigation into the optical limiting properties of tungsten–copper–sulfur clusters, the treatment of $[(\eta^5\text{-}Cp^*)WS_3]^+$ with excess NCCu in MeCN has yielded the butterfly complex $[(\eta^5\text{-}Cp^*)WS_3(CuCN)_2]^+$. Reaction of this species with excess PPh_3 or pyridine yielded the hexanuclear clusters $\{(\eta^5\text{-}Cp^*)WS_3Cu_2(PPh_3)(\mu\text{-}CN)\}_2$ and $[\{(\eta^5\text{-}Cp^*)WS_3Cu_2py\}_2(\mu\text{-}CN)]^+$, respectively, wherein analogous butterfly units are cyano-linked.[138] As part of an investigation into the solution structures and fluxional behaviours of copper(I) and tungsten(0)-copper(I) triphospholyl triphenylphosphane complexes, the crystal structure of monomeric $(OC)_5W$-complexed (3,5-di-*tert*-butyl-1,2,4-triphospholyl)-$Cu(PPh_3)$ has been reported. It reveals η^5-triphospholyl stabilization of the copper centre.[139] As part of a study into the formation of metal–metal bonded polymers, the structures of $\{tacn(NC)_6Ag_4Cu\}_\infty$ and $\{tacn(NC)_4Au_2Cu\}_\infty$ have been reported. These exhibit very different structural motifs, largely by virtue of the Ag(I) centre being three-coordinate and the Au(I) ion adopting a linear geometry.[140] Treatment of $(Ph_3P)_2Pt(C{\equiv}CPh)_2$ with excess copper(I) bromide has afforded [*trans*-$(Ph_3P)_2Pt\{(\eta^2\text{-}C{\equiv}CPh)CuBr\}_2]_\infty$. Reaction of this with silver(I) nitrate has afforded trimetallic *trans*-$(Ph_3P)_2Pt\{(C{\equiv}CPh)CuNO_3\}_2$. Both of these mixed Pt–Cu systems have been fully characterized and both reveal acetylenic units that σ-bond to the Pt whilst acting as η^2 π-donors to Cu.[141]

In order to probe the potential of $\{(in)_2(NC)Cu_3\}_\infty$ as a second-order NLO candidate, second harmonic generation measurements have been carried out. Data suggest the powder intensity of this species to approximate to that of potassium dihydrogen phosphate, this also being the first example of second-order NLO behaviour by Cu(I).[113]

$MeCuPCy_3$ exhibits reversible ligand redistribution at depressed temperatures to yield a tight ion pair $[Me_2Cu]^-[(Cy_3P)_2Cu]^+$ whose structure can be extrapolated from ^{13}C NMR spectroscopy. Moreover, $MeCuPCy_3$ has been shown to initiate the polymerisation of acrylonitrile.[142] Copper complexes incorporating *N*,*N*-bis{2-(2-pyridyl)ethyl}-2-phenylethylamine-type ligands, known to exhibit η^2 metal–phenyl interactions in the solid state, appear to retain these bonds in non-polar solution according to the observation of an intense MLCT band around 290 nm, and measurement of ^{1}H and ^{13}C NMR spectra and the redox potentials $E_{1/2}$ of the metal ion.[125]

Dynamic ^{31}P NMR spectroscopy has been employed to monitor the fluxional processes exhibited by copper(I) triphospholyl triphenylphosphanes in solution.[139] Data suggest that (3,5-di-*tert*-butyl-1,2,4-triphospholyl)$Cu(PPh_3)$ exists as a fluxional monomer in solution, favouring η^5 π-coordination of the Group 11 metal at room temperature but with two interconvertible and spectroscopically distinguishable σ-complexes forming at depressed temperatures. Whilst one of these σ-complexes is thought to operate *via* the action of an sp^3 hybrid orbital on P, the other is considered to utilize a lone pair in an sp^2 P orbital.[139] NMR analysis of phosphine stabilized Group 11 1-azaallyl compounds has suggested that the bonding mode of the 1-azaallyl component is strongly dependent on the choice of metal centre. Hence, $Me_3SiN{=}C(Bu^t)CH(SiMe_3)CuPBu^i_3$ is an enamide complex whilst the silver and gold analogues (see below) are best described as iminoalkyl systems.[143]

The simple, solvent-free monomer of methylcopper has been prepared and observed using millimeter-wave rotational spectroscopy. Synthesis in the gas phase was achieved by the reaction of copper vapour with either methane, tetramethyltin or tetramethylsilane, and the alkyl carbon–copper(I) bond, the shortest such known, has been measured at 1.8809 Å.[144]

A recent B3LYP density functional study on carbon–carbon bond formation through reductive elimination from a π-allylcopper(III) compound suggests that reaction proceeds *via* an enyl[σ + π]-type transition state.[145] Calculations on bridging and terminal copper carbenes have recently pointed to stronger C–Cu π-back-bonding involving the two metal centres of bridging carbene systems.[102] DFT studies have suggested that copper–arene interactions in complexes containing tridentate ligands based on *N*,*N*-bis{2-(2-pyridyl)ethyl}-2-phenylethylamine are substantially based on the interaction of Cu(I) d_{z^2} and an aryl π-orbital.[125] At the same level of computational sophistication, analysis has suggested that *N*-heterocyclic carbene ligands, rather than acting purely as σ-donors, are capable of participating in both σ- and π-interactions with Group 11 metal ions.[131]

2.3 Silver compounds

The first examples of fully characterized silver tetrahydropyrimid-2-ylidene complexes have been reported lately.[146] A series of silver–phosphine complexes of highly methylated carborane anions have been prepared. X-ray crystallography reveals that the Ag(I) salt of [*closo*-1-$HCB_{11}Me_{11}]^-$ incorporates short Me···Ag distances. The introduction of monodentate phosphines has, in turn, yielded [*closo*-1-$HCB_{11}Me_{11}]AgPR_3$ (R = Ph, cyclohexyl, dmp), in each of which short Me···Ag distances are retained.[147] A survey of routes by which to obtain perfluoroorganosilver(I) compounds has been published. It discussed the convenient reaction of silver fluoride with trimethyl(perfluoroorgano)silanes to this end and also presented the crystal structure of $[ClAgCF_3]^-[(Ph_3P)_2{=}N]^+$.[148]

The same study into the synthesis of oligomers incorporating 1,8-diisocyano-*p*-menthane ligands that has yielded (dppp)Cu$(CNBu^t)_2$ has also reported the corresponding Ag(I) complex.[119] The straightforward structure of {(phen)CuCN}phen has been reported, with a threefold interpenetrating 3-dimensional network arising from the self-assembly of C–H···N hydrogen bonds and π–π stacking interactions.[149] Metal–metal bonding is responsible for the formation of anionic chains in the structure of $\{[(NC)_2Ag]^-[emi]^+\}_\infty$.[150]

A systematic study of double, triple and quadruple salts of silver acetylide has recently led to the preparation and characterization of $nH_2O \cdot 6NO_3Ag \cdot C_4Ag_2$ (n = 2, 3). In either case, each terminal carbon of the C_4^{2-} ion is capped by a butterfly-shaped Ag_4 basket.[151] The structure of trinuclear $(pn)_2Cu(NCAgCN)_2$ has been reported.[152] Meanwhile, work on mixed-ligand coordination employing diphosphine and isocyanide ligands has yielded the solid-state structure not only of $[(dppe)_2(Bu^tNC)_3Cu_2]^{2+}$, but also of a variety of oligo- and polymeric Ag(I) systems. Accordingly, the structure of $[(dppe)_2(Bu^tNC)_2Ag_2(OClO_3)]^+$ and also those of polymers based on $[(dpppen)(Bu^tNC)Ag]^+$, $[(dpppen)(Bu^tNC)_2Ag]^+$, and $[(dppb)_3(Bu^tNC)_2Ag_2]^+$ motifs have been reported.[122] The structure of the simple complex $\{Ph_3P(MeNC)AgBr\}_2$ has also been published.[153]

Triangulated layers based on $(\eta^2\text{-arene})_3Ag$ motifs have been noted in the solid-state structure of $[1\text{-}MeCB_{11}F_{11}]^-[(CHPh_3)Ag]^+$.[154] Treatment of pcp with silver(I) trifluoroacetate and sliver(I) pentafluoropropionate has afforded three new polymers based on $(F_3CCO_2)_4Ag(pcp)$ units. These have been isolated and found to contain either intercalated pcp, mesitylene, or benzene. In each case, the structure has been based on a 2-dimensional layered framework involving metal–π interactions and with pcp acting as a μ-tetra-η^2 donor.[155] Reaction of the cyclotriphosphazene $(BzNH)_6P_3N_3$ with various inorganic silver salts has yielded supramolecular coordination compounds that feature aryl stabilization of the Ag(I) centre.[156]

Side-on η^2-coordination of silver is noted in the network formed through the self-assembly of bis(pyrrol-2-ylmethylene)hydrazine silver(I).[157] The solid-state structure of an *N*-heterocyclic carbene complex of Ag(I), known to allow Cu-catalyzed enantioselective allylic alkylation, has been reported.[101] Moreover, work on the preparation of *N*-heterocyclic carbene complexes of Ag(I) and Rh(I) from caffeine has seen synthesis of the imidazolium cation 1,3,7,9-tetramethylxanthinium methyl sulfate (obtained by reacting caffeine with dimethyl sulfate) and its reaction with silver oxide to give a linear *N*-heterocyclic carbene silver(I) species.[158] An extensive study into the role of pyridine substituted *N*-heterocyclic carbene ligands in the support of silver(I)–gold(I) interactions has recently been published and, as part of this, the structure of bis{1,3-bis(pyrid-2-yl)imidazol-2-ylidene}silver(I) tetrafluoroborate has been reported.[159]

Concerning heterometallic systems, the 3-dimensional coordination polymer $\{(dien)Cu(NC)AgCN\}_\infty$ has been noted.[160] The silver analogue of the copper ferrocenylacetylide $[(FcC{\equiv}C\text{-}\eta^1\text{-}\mu_3)(\mu\text{-dppm})_2Cu_6]^+$ has been reported.[130] The solid-state structure of $\{(\eta^5\text{-}Me_3SiC_5H_4)_2Ti(C{\equiv}CSiMe_3)_2Ag\}_2$(1,4-pyrazine) has been recorded. This species consists of two Ti–Ag tweezer fragments with the Ag(I) centres being coordinated by two π-bonding alkynes and the datively-bonded pyrazine bridge.[161] In a similar vein, the structure of $[\{(\eta^5\text{-}Me_3SiC_5H_4)_2Ti(C{\equiv}CSiMe_3)_2\}_2Ag]^+$ has also been published, with the Group 11 ion receiving π-electron density from four η^2-bonding acetylide units.[162] A series of tetraalkynylplatinate(II) complexes have been prepared and found to exhibit intense luminescence by virtue of MLCT transitions. As part of this work, the solid-state structure of the Pt–Ag aggregate $(4\text{-}MeC_6H_4C{\equiv}CC{\equiv}C)_4Pt(Ag\cdot thf)$ has been shown to incorporate bis(η^2-alkynyl) coordination of each silver centre.[163] Treatment of *trans*-$(Ph_3P)_2Pt(C{\equiv}CPh)_2$ with excess silver triflate has yielded a polymeric species, [*trans*-$(Ph_3P)_2Pt\{(\mu\text{-}\sigma,\eta^2\text{-}C{\equiv}CPh)AgOTf\}_2]_\infty$, in which 8-membered $(OSOAg)_2$ metallocycles span $(Ph_3P)_2Pt(C{\equiv}CPh)_2$ fragments.[164] The cyclotrimerization of arylacetylide units has facilitated the development of new luminescent $Au(I)_5Ag(I)_8$ complexes containing the new $[1,2,3\text{-}C_6(C_6H_4R\text{-}4)_3]^{3-}$ (R = H, Me, Bu^t) ion. In this context, reaction of $PhC{\equiv}CAg$ with $[(MeCN)_2(\mu\text{-dppm})_2Au_2]^{2+}$ has allowed the synthesis, isolation and full characterization of $(1,2,3\text{-}C_6Ph_3)_3(\mu\text{-dppm})_4Au_5Ag_8$.[165]

2.4 Gold compounds

Two ketonylgold(III) complexes have been reported as part of an investigation into C–H bond activation in ketones by Au(III) systems. Whereas (C^1, *N*-ppy){MeC(O)-CH_2}AuCl was obtained serendipitously, (ppy){MeC(O)CH_2}$AuNO_3$ was achieved by reacting (C^1,*N*-ppy)$Au(NO_3)_2$ with acetone.[166] Variations in the coordinative behaviour of the polyfunctional ylide $EtOC(O)CH_2C(O)CH{=}PPh_3$ with respect to Pd(II), Pt(II) and Au(I) have been studied. Treatment of this species with ClAu · tht has yielded monomeric $EtOC(O)CH_2C(O)CH(PPh_3)AuCl$, the solid-state structure of which has been reported.[167]

A linear chain based on the formulation $[\{Me_3NB(H)_2NC\}_2Au]I_2Au$ and comprising gold–gold interactions has been found to result from treatment of the (isocyanoborane)gold(I) chloride adduct $\{Me_3NB(H)_2NC\}AuCl$ with KI.[168] The reaction of Au(III) oxocomplexes with alkenes has afforded new systems of the type [(alkene)(*N*,*N*)Au]$^+$. By way of an example, the straightforward structure of $[(\eta^2\text{-}CH_2{=}CHPh)(bipy^{ip})Au]^+$ has been reported.[169] Attempts to synthesize phosphine stabilized Group 11 1-azaallyl compounds have resulted in the characterization of $Me_3SiN{=}C(Bu^t)CH(SiMe_3)MPBu^t_3$ (M = Cu, Ag, Au), with the crystal structure of the gold complex being reported recently.[143] An investigation into the metal-binding properties of ethynylcrown ethers incorporating polynuclear gold(I) complexes has led to the structural characterization of both (4,5-benzo-15-crown-5)-$(C{\equiv}CAuPPh_3)_2$ and (4,4′,5,5′-dibenzo-15-crown-5)$(C{\equiv}CAuPPh_3)_4$.[170]

A group of gold(III) phenylphosphides and -phosphodiides derived from the primary phosphine $PhPH_2$ have recently been prepared using $(C_6F_5)_nAu\cdot tht$ (n = 1–3).[171] Moreover, treatment of $\{(C_6F_5)_2Au(\mu\text{-}Cl)\}_2$ with $PhPH_2$ has yielded the cyclic trinuclear complex $\{(C_6F_5)_2Au(\mu\text{-}PPhH)\}_3$.[171] Reactions of Cl_2(damp-C^1,*N*)Au with 2-pyridineformamide thiosemicarbazones have yielded new thiosemicarbazonato complexes of Au(III). Accordingly, two species have been reported, both of which reveal that the thiosemicarbazones deprotonate and act as mononegative, tridentate *N*,*N*,*S*-ligands while [damp-C^1,*N*]$^-$ is *N*-protonated.[172]

The same study into Group 11 complexes of *N*-heterocyclic carbene ligands that yielded the solid-state structure of the D_3-symmetrical copper(I) complex $[(time^{Me})_2Cu_3]^+$ has also produced that of the gold(I) analogue.[131] A systematic probe of dinuclear gold(I) complexes of bridging imidazolium-based dicarbenoid ligands has afforded a series of structures.[173] The study into pyridine substituted *N*-heterocyclic carbene ligands that gave the structure of bis{1,3-bis(pyrid-2-yl)imidazol-2-ylidene}silver(I) tetrafluoroborate has also afforded structural insights into various gold-containing and heterometallic species.[159] Carbene transfer from the silver species above has allowed the characterization of $[\{(2\text{-}C_5H_4N)_2im\}_2Au]^+$, while the structure of the pyridylmethyl species $[\{(2\text{-}C_5H_4NCH_2)_2im\}_2Au]^+$ has also been noted. This last system reveals a discrete trimetallic gold carbene product, $[\{(2\text{-}C_5H_4NCH_2)_2imAg\cdot NCMe\}_2Au]^+$, upon treatment with silver(I). Contrastingly, reaction of $[\{(2\text{-}C_5H_4N)_2im\}_2Au]^+$ with an excess of silver tetrafluorborate gives the polymeric chain $([\{(2\text{-}C_5H_4N)_2im\}_2Ag(\cdot NCMe)Au]^+)_\infty$, the helical structure of which is revealed by X-ray crystallography.[159]

A series of straightforward diynyl complexes—$CpRu(\cdot 2PPh_3)C{\equiv}CC{\equiv}CAuPPh_3$, $Cp^*Ru(\cdot dppe)C{\equiv}CC{\equiv}CAuPPh_3$, and $Cp^*Ru(\cdot dppe)C{\equiv}CC{\equiv}CAuP(C_6H_4Me\text{-}4)_3$—have been reported.[174] An interdigitating complex incorporating dicyanoaurate(I) anions has been seen to derive from the formation of gold–gold and hydrogen bonding interactions. Accordingly, the structure of $(H_2O)_2(nitppy)_2Co(NCAuCN)_2$ reveals a 2-dimensional network in which the Co centres are coodinated to two organic radicals and two dicyanoaurate(I) anions in the equatorial plane.[175]

The vapochromic behaviour of $\{(C_6Cl_5)_2TlAu\}_\infty$ has been studied.[176] Solid-state and solution reactions between this polymer and various volatile organic substrates have yielded selective and reversible colour changes suggesting sensor applications. The products of these transformations have been crystallized and characterized and reveal extended linear chains of alternating gold and thallium centres, with pendant C_6Cl_5 groups still associated with the former and the organic substrate of choice interacting with the Tl centres.[176] Thallium(I) acetylacetonate units have been employed lately as building blocks in luminescent supramolecular systems, the heteropolynuclear complexes $(R_2TlAu)_\infty$ (R = C_6F_5, C_6Cl_5) having been treated with (acac)Tl. The products $[(C_6F_5)_2Au]^-[(acac)_2Tl_3]^+$ and $\{[(C_6Cl_5)_2Au]^-\}_2[(acac)_2Tl_4]^{2+}$ have both been the subject of X-ray diffraction studies.[177] Gold–thallium arrays have also been achieved recently by employing 4,4′-bipyridine linkers. In this way the reaction of $\{(C_6Cl_5)_2TlAu\}_\infty$ with 4,4′-bipy under a variety of conditions has yielded a series of 2- and 3-dimensional luminescent networks.[178]

Abbreviations

acac	Acetylacetonato
bdptz	1,4-Bis(2,2′-dipyridylmethyl)phthalazine
S-binol	(*S*)-(–)-bi-2-naphthol
$bipy^{ip}$	6-Isopropyl-2,2′-bipyridine

Boc	*Tert*-butyloxycarbonyl
bpym	Bipyrimidine
Bz	Benzyl
CIPE	Complex-induced proximity effect
Cy	Cyclohexyl
damp	2-(*N*,*N*-dimethylaminomethyl)phenyl
dien	1,2-Diaminoethane
dipp	2,6-Diisopropylphenyl
dme	Dimethoxyethane
dmf	Dimethylformamide
dmp	2,6-Dimethylphenyl
dppb	Bis(diphenylphosphino)butane
dppm	Bis(diphenylphosphino)methane
dppp	Bis(diphenylphosphino)propane
dpppen	Bis(diphenylphosphino)pentane
ee	Enantiomeric excess
emi	1-Ethyl-3-methylimidazolium
Fc	Ferrocenyl
hfac	Hexafluoroacetylacetonate
hmds	Hexamethyldisilamide
hmpa	Hexamethylphosphoramide
im	Imidazolium
in	Isonicotinate
LCMT	Ligand–metal charge transfer
Me_6tren	Tris(2-(dimethylamino)ethyl)amine
Mes	Mesityl
nitppy	2-(4′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide
No-D	No deuterium
oxpnH_2	*N*,*N*′-bis(3-aminopropyl)oxamide
OTf	Triflate
pbq	*p*-Benzoquinone
pcp	[2.2]Paracyclophane
phen	1,10-Phenanthroline
pmdeta	*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine
pn	1,2-Diaminopropane
ppy	2-Phenylpyridine
py	Pyridine
pz	Pyrazolyl
tacn	1,4,7-Triazacyclononane
tht	Tetrahydrothiophene
time^{Me}	1,1,1-Tris(3-methylimidazol-2-ylidene)methylethane
tmeda	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine
vpy	Vinylpyridine

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Group 2 (Be–Ba) and Group 12 (Zn–Hg)

Felipe García and Dominic S. Wright

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Scope and organisation of the reviews for 2004 and 2005

This review presents a perspective of the important structural and synthetic studies reported in 2004 and 2005, which are separated into two yearly reports. The strict definition of an organometallic compound as one containing at least one C-metal bond or contact has been used throughout the literature survey. The review is not intended to be comprehensive, although it is based on a comprehensive search. Individual topics are highlighted in bold in the text in order to facilitate rapid access to a particular area of the literature. Generally, although structural studies of group 2 and 12 organometallics continue to be active areas of research, there were fewer such studies published in 2004 and 2005 compared to previous years. Synthetic applications of group 2 and 12 organometallics continue to be highly active areas of research and several new innovations have been introduced recently concerning the discovery of new group 2 and 12 reactions and reagents in organic and organometallic synthesis.

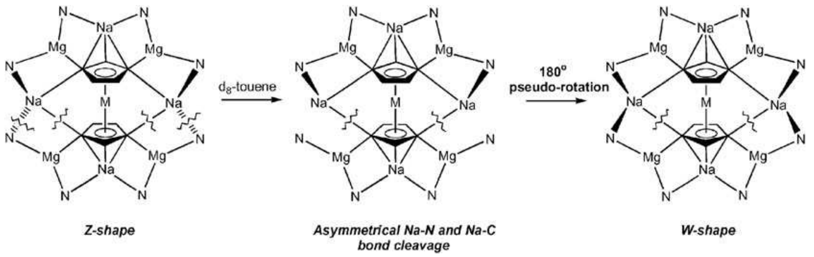
Review of 2004

1 Group 2

Structural studies involving σ-bonded organometallics of Mg have continued to be a major area of interest in the year 2004.[1–6] Of particular note have been reports of the activation of organic and organometallic species using superbases and the resulting formation of Lewis acidic, (so-called) 'inverse crown' arrangements involving alkali or alkaline earth elements. After the initial report of the quadruple deprotonation of ferrocene (Cp_2Fe) by $[NaMg(N^iPr_2)_3]$ (**1**) in 2001,[1b] the analogous reactions with ruthenocene and osmocene have been explored.[1a] X-ray studies reveal that all of the resulting complexes $[\{M(C_5H_3)_2\}Ma_4Mg_4(N^iPr_2)_8]$ [M = Fe (**2**), Ru (**3**), Os (**4**)] have the same structure in which 1,3-deprotonation of each of the Cp-rings of Cp_2M has occurred, with the $[M(C_5H_3)_2]^{4-}$ tetraanions being stabilised within a sixteen-membered $[(NaNMgN)_4]^{4+}$ macrocyclic host. Variable-temperature NMR spectroscopic studies of **2–4** show that these complexes exist as two distinct interconverting (*Z*- and *W*-shaped) conformers in arene solution (Scheme 1). In contrast to the behaviour of $[NaMg(N^iPr_2)_3]$ (**1**) with ferrocene, addition of ferrocene to a toluene solution of the related potassium magnesiate $[KMg(HDMS)_3]$ (**5**) gives $[(FeCp_2)\{(toluene)_2K\}]^+[Mg(HMDS)_3]^-$ (**6**), in which no deprotonation of Cp_2Fe has occurred.[2] The K^+ cation of **6** is coordinated by two η^3-toluene molecules and by two η^5-Cp groups of the *intact* Cp_2Fe molecules. When prepared *in situ*, **6** polymerises methyl methacrylate to give syndio-rich polymethylmethacrylate. The first homometallic inverse crown arrangement is found in $[\{^nBuMg_2[\mu\text{-}N(H)Dipp]_2(\mu_3\text{-}O^nBu)\}_2]$ (**7**) (Dipp = 2,6-$^iPr_2C_6H_3$) (Fig. 1), obtained initially fortuitously from the reaction of ^nBuMgCl with NaN(H)Dipp.[3] The presence of ^nBuO groups was traced to the initial Grignard reagent, but **7** can be prepared in improved yield from the reaction of Bu_2Mg with $[Mg\{N(H)Dipp\}_2]$ and ^nBuOH (1:1:1 equiv.).

Significant advances have been made also in the elucidation of new superbases themselves. The addition of the Lewis base TMEDA (= $Me_2NCH_2CH_2NMe_2$) to a mixture of BuNa, Bu_2Mg and TMP(H) [TMP = 2,2,6,6-tetramethylpiperidine, $(Me)_2CCH_2CH_2CH_2C(Me)_2N^-$] in hexane gives $[(TMEDA)Na(\mu\text{-}Bu)(\mu\text{-}TMP)$

Department of Chemistry, Cambridge University, Lensfield Road, Cambridge, UK CB2 1EW



Scheme 1

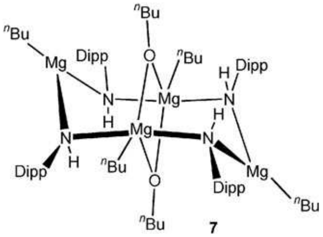
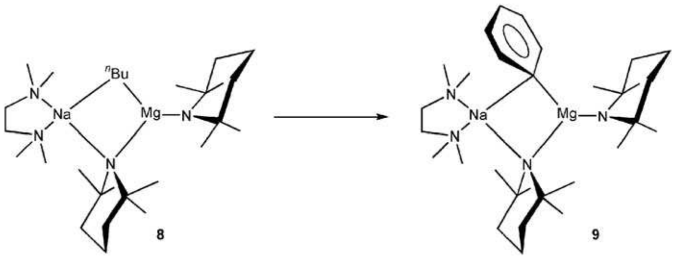


Fig. 1

Mg(TMP)] (**8**) as one of the major products.[3] This species is an important intermediate in the formation of Mg/Na inverse crown arrangements and an interesting new superbase in its own right. Addition of benzene to **8** results in deprotonation and in the formation of [(TMEDA)Na(μ-Ph)(μ-TMP)Mg(TMP)] (**9**) (Scheme 2). The orientation of the bridging Ph-group in **9** suggests predominant σ-bonding to Mg, but with a greater π-bonding component to the Na$^+$ cation within the central ring unit.

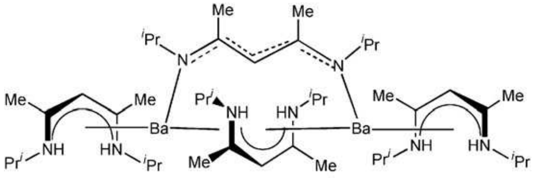


Scheme 2

Very few structural reports of **σ-bonded organometallics of the heavier alkaline earth elements** appeared in the year 2004.[7–13] Hydrocarbon elimination and desilylation have been used as new synthetic approaches to these still comparatively rarely studied compounds.[11] The ion-paired complex [Ba(CHPh$_2$)$_2$(18-crown-6)] (**10**) is obtained from the deprotonation reaction of Ph$_2$CH$_3$ with dibenzyl barium, [Ba(CH$_2$Ph)$_2$] (**11**), in thf as the solvent. **10** is also produced in good yield by the reaction of [Ba(O^{t}Bu)$_2$] (**12**) with (Me$_3$Si)CHPh$_2$ (**13**) in the presence of ^{n}BuLi (a reaction which may well involve highly reactive *n*-butyl barium intermediates). However, if this reaction solution is concentrated significantly to initialise crystallisation then the ion-separated complex [(18-crown-6)Ba(μ-OCH=CH$_2$)·thf}]$_2{}^{2+}$-2[Ph$_2$CH]$^-$ (**14**) is isolated. In contrast to the synthesis of **10**, the reaction of [Sr(CH$_2$Ph)$_2$] (**15**) with Ph$_2$CH$_3$ also results in cleavage of thf and in the formation of the ion-separated complex [(18-crown-6)Sr(μ-OCH=CH$_2$)}]$_2{}^{2+}$ 2[Ph$_2$CH]$^-$ (**16**).

The formation of the benzyl calcium complexes *trans*-$[(4\text{-}^t\mathrm{Bu{-}C_6H_4})_2\mathrm{Ca}\cdot 4\mathrm{thf}]$ (**17**) and *cis*-$[(\mathrm{PhCH_2})_2\mathrm{Ca}\cdot 4\mathrm{thf}]$ (**18**) in the reactions of the corresponding benzyl potassium precursors with CaI_2 is of particular interest.[12] In contrast to previous reports, this most recent study shows that the presence of stabilising Me_3Si- or Me_2N-substituents (at the benzylic C-atom or the aromatic ring) is not after all required for stabilisation or solubility. A future direction in this area is applications of the heavier group 2 elements as reagents in organic chemistry. A recent study has investigated the use of mono- and heterometallic alkali and alkaline earth amide bases in the deprotonation of ketones.[13] As part of this study, the interesting new Ca/K heterometallics $[\mathrm{K_2Ca_2(O\overset{\cdots}{-}C(Mes){=}CH_2)_4\cdot 2thf}]$ (**19**) and $[\mathrm{K_2Ca(O\overset{\cdots}{-}C(Mes){=}CH_2)_4\cdot 6thf}]$ (**20**) were structurally characterised.[13]

***π*-Bonded complexes of group 2 metals** continue to be a highly active and varied area of study.[14–18] A recent study has used solid-state ^{9}Be and ^{13}C NMR spectroscopy, in tandem with variable-temperature X-ray crystallographic studies and DFT calculations to examine the inversion of the Cp rings in $[\mathrm{Cp_2Be}]$ (**21**) between η^1- and η^5-bonding modes. The activation energy for inversion in **21** has been determined to be 36.9 kJ mol^{-1} from chemical exchange analysis of the ^{13}C variable-temperature CP/MAS NMR spectra, whereas $[\mathrm{Cp^*{}_2Be}]$ (**22**) and $[(\mathrm{C_5Me_4H})_2\mathrm{Be}]$ (**23**) exhibit few changes in molecular geometry with changing temperature in the solid state.[14] Other studies of π-complexes of group 2 metals have explored 'non-classical' π-ligands. Studies of the structures of Mg complexes with β-diketiminato ligands reveal that the majority of these complexes have η^2-(N,N)-coordinated in which no π-bonding is observed.[15] However, the presence or otherwise of π-bonding appears to be highly dependent on the steric bulk of the substituents attached to the N-centre of the β-diketiminato ligand as well as the coordination number of the Mg ion. This last feature is illustrated in the structure of $[\mathrm{CpMg\{N(^tBu)\overset{\cdots}{-}C(Me)\overset{\cdots}{-}\}_2CH}]$ (**24**) which exhibits π-bonding with the β-diketiminato ligand as a result of the coordinatively unsaturated nature of the Mg centre. However, coordination of the 4-*tert*-butylpyridine (4-^{t}Bu-py) to the Mg centre of **24** gives $[\mathrm{CpMg\{N(^tBu)\overset{\cdots}{-}C(Me)\overset{\cdots}{-}\}_2CH\cdot(4\text{-}^tBu\text{-}py)}]$ (**25**) in which no π-bonding of the β-diketiminato ligand is observed. Complexes $[\mathrm{Mg\{N(R)\overset{\cdots}{-}C(Me)\overset{\cdots}{-}\}_2CH\}_2}]$ [R = ^{i}Pr (**26**), ^{t}Bu (**27**)], in which the Mg atoms are four coordinate, show no such π-bonding of the β-diketiminato ligands. In contrast, related complexes of the heavier group 2 metals all exhibit π-bonding. Thus the majority of the heavier analogues of the Mg complexes **26** and **27** $[\mathrm{M\{N(R)\overset{\cdots}{-}C(Me)\overset{\cdots}{-}\}_2CH\}_2}]$ [M = Ca (**28**), R = ^{i}Pr, ^{t}Bu; Sr (**29**), R = ^{i}Pr, ^{t}Bu; Ba (**30**), R = ^{t}Bu] have bent sandwich structures in which the β-diketiminato ligands are found in η^5-coordination modes.[16] Of particular interest is the structure of the Ba complex $[\mathrm{Ba_3\{N(R)\overset{\cdots}{-}C(Me)\overset{\cdots}{-}\}_2CH\}_4}]$ (**31**) in which the β-diketiminato ligands exhibit three different coordination modes (terminal η^5-, bridging η^5,η^5-, and bridging η^1,η^1-) (Fig. 2). A dramatic example of π-bonding to heavier group 2 metals is found in Ba@C_{74} (**32**), obtained in crystalline form as a co-complex with Co(II) octaethylporphyrin and benzene.[18] The structural characterisation of **32** by single-crystal synchrotron diffraction represents a significant first, the first time that any mono-metallofullerene has been characterised by such a single-crystal X-ray diffraction study. The Ba^{2+} cation within the $C_{74}{}^{2-}$ anion is located off-centre by

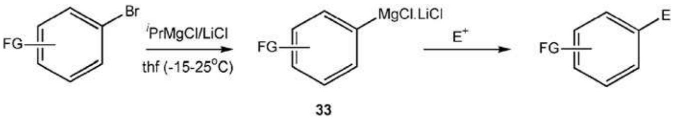


31

Fig. 2

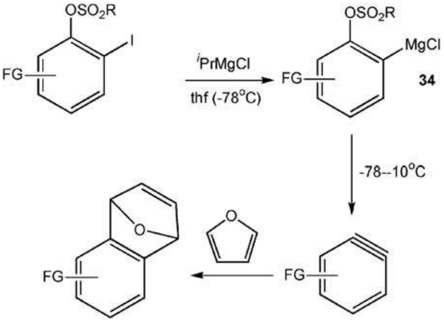
ca. 1.27 Å as a result of the interaction of the valance electrons of the C_{74}^{2-} anion with the Co(II) octaethylporphyrin unit. The shortest C···Ba interactions with the C_6 and C_5 units on the inner surface of the cavity of the C_{74}^{2-} anion are *ca.* 2.65 Å.

Applications of group 2 organometallics in organic,[19–34] **inorganic and materials chemistry**[35–39] remain dominated by organomagnesium compounds. Studies of organic systems have broadly involved fundamental investigation of new organo-Mg reagents[19–25] and the development of new synthetic methodologies (particularly involving transition metal mediation).[26–34] The addition of LiCl to ^{i}PrMgCl results in a reagent with enhanced reactivity, probably as a consequence of increased 'ate-character (*e.g.*, the formation of species such as $^i\text{PrMgCl}_2^-\text{Li}^+$).[19–21] This reagent is capable of effecting Mg/Br exchange reactions of functionalised aromatic substrates, giving functionalised aryl and heteroaryl-Mg compounds **33** (Scheme 3).[19] Normally only the corresponding iodides are reactive enough under these conditions with ^{i}PrMgCl. The addition of electrophiles (E^+) to the intermediate organo-Mg species allows the further elaboration of the original precursors. This procedure can even be extended to the Mg/I exchange reactions of aromatic and heteroaromatic rings bearing hydroxyl groups[20] and to Mg/I exchange reactions of acyclic functionalised alkenyl iodides.[21]

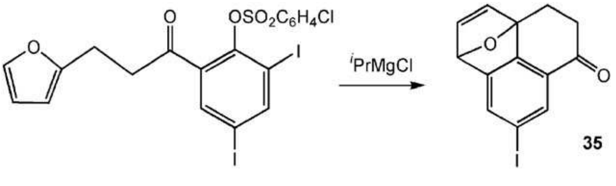


Scheme 3

Interestingly, the organo-Mg reagents **34**, generated from magnesiation of diaryl sulfonates with ^{i}PrMgCl, undergo spontaneous elimination of $MgCl(SO_3R)$ on warming, giving functionalised benzynes which can be reacted *in situ* with furan (Scheme 4).[22] This simple method can be used to access elaborate frameworks if the furan function is already present within the aryl iodide precursor, as illustrated by the formation of the polycyclic iodoketone **35** in one dramatic step (Scheme 5).

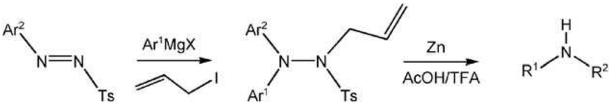


Scheme 4



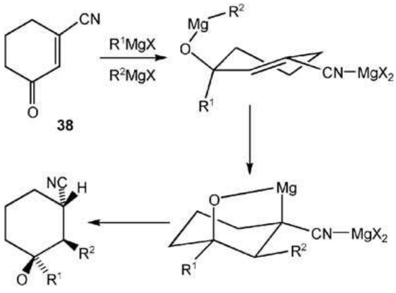
Scheme 5

A recent study showed that addition of functionalised aryl Grignard reagents Ar^1MgX occurs readily to the N=N bond in arylazo tosylates Ar^2–N=N–Ts (**36**).[26] Reduction of the N–N single bond gives high yields of polyfunctional aryl amines (**37**) (63–84%) (Scheme 6). The preparation of polyfunctional diarylamines is important since these are common building blocks in pharmaceuticals. The multi-component addition–alkylation reactions of Grignard reagents to cyclic oxonitriles (**38**) can be used to access a diverse range of cyclic nitriles (**39**) with control over the three stereogenic centres present.[27] This control is believed to occur due to the chelation of the Mg centre within the mechanism (Scheme 7).



36 **37**

Scheme 6



38 **39**

Scheme 7

Interesting applications of organo-Mg reagents to the synthesis of inorganic compounds and materials include the synthesis of boron-centred, spiro-organo-cycloborates (like **40**, Fig. 3) *via* spontaneous ring closure of bromine-substituted tris-alkylboranes.[35] This new approach provides access to a rarely-studied class of borate anions. Also worthy of note is the use of Grignard reagents in surface modification of mesoporous silicates, the approach providing high-loadings of complex organic groups within the pores.[36] Applications of organometallics of the heavier group 2 elements in organic and inorganic synthesis continued to be rare in 2004.[40]

2 Group 12

Structural reports of σ-bonded Zn and Cd organometallics have been dominated by those of Zn and have involved a very broad range of species in 2004, including 'ate complexes,[41–43] and complexes containing carbene,[44] phosphate and siloxide,[45,46] sulfide,[47] and a variety of N-based ligands.[41,48–53] A particular theme in many studies

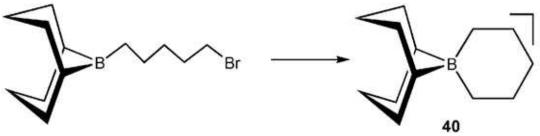


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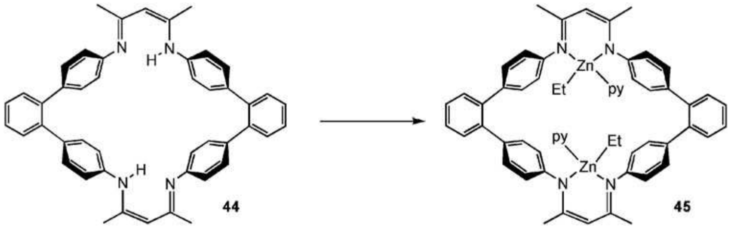
Fig. 3

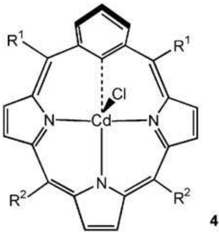
has been the use of ligands to encourage the formation of polynulcear cage arrangements. The ability for multidentate N-based ligands to encourage aggregation of heterometallic Zn/alkali metal cages is one of the themes of a recent review article focused on the structural and synthetic aspects of zincate complexes.[41] Recently reported examples of highly-nuclearity Zn(II) complexes are the hexanuclear complex $[\{(ZnEt)_3(Zn\cdot thf)_3\{^tBuPO_3\}\{\mu_3\text{-}OEt\}]$ (**41**),[45] the heptanuclear cage $[Zn_7Me_2(thf)_5(O_3SiR)_4]$ (**42**) and the octanuclear complex $[Zn_8Me_7(dioxane)_2(O_3SiR)]$ (**43**).[46] Also worthy of note has been the synthesis of the macrocylic β-diketimine ligand **44** and the formation of the metallated complex **45** by reaction with Et_2Zn (Scheme 8).[48] The latter potentially paves the way for the exploration of dinuclear catalysts for the polymerisation of a range of organic substrates.[49]



Scheme 8

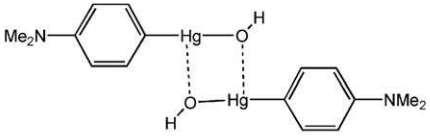
Studies of π-complexes of Zn and Cd have been rare in 2004. However, one of the highlights of the year was the chance discovery that the reaction of $[Cp^*_2Zn]$ with $[Et_2Zn]$ at −10 °C gives the remarkable dizinc compound [Cp*Zn–ZnCp*] (**46**), the first molecular species containing a (very short) Zn–Zn single bond [2.305(3) Å].[54] **46** is also generated by the similar reaction of $[Cp^*_2Zn]$ with $[Ph_2Zn]$ (along with [Cp*ZnPh]). Weak arene···Cd bonding has been observed in macrocylic Cd complexes such as **47** (2.71–2.76 Å) (Fig. 4).[55] Remarkably, the close proximity of the Cd centre to the tilted arene ring within the macrocyclic units in these species is directly detected by the presence of ^1H- (4.4–9.5 Hz) and ^{13}C–$^{111,113}Cd$ (6.5–13.6 Hz) scalar coupling.

The unique characteristics of Hg in group 12 are again seen in the **structural reports of Hg organometallics** in 2004.[52,56–60] Several reports are worthy of particular mention. The first 'true' simple Hg(II) hydroxide $4\text{-}Me_2N\text{–}C_6H_4\text{–}Hg\text{–}OH$ (**48**) (Fig. 5), obtained by the reaction of $4\text{-}Me_2N\text{–}C_6H_4\text{–}Hg\text{–}AcO$ (**49**) with $NaOH_{(aq)}$, has been structurally characterised.[56] Monomer units of **48** exhibit a characteristic linear geometry at the Hg(II) centre, aggregating into loosely associated dimers *via* longer-range Hg···O interactions. The Hg(II)bis(tricarbido) complex $[Hg\{C{\equiv}C\text{–}C{\equiv}W(CO)_2Tp\}_2\cdot 4DMSO]$ (**50**) (Tp = hydrotrispyrazolylborate) (Fig. 6) is the first structurally characterised six-coordinate diorganomercury complex (of the



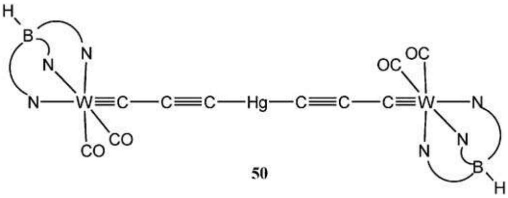
47

Fig. 4



48

Fig. 5



50

Fig. 6

type ‘HgR_2L_4’) with monodentate ligands (L).[57] The bond lengths and angles within the W≡C–C≡C– units of **50** as well as IR spectroscopy suggest little or no delocalisation.

The applications of $[(1,2\text{-}C_6F_4)Hg]_3$ (**51**) as a Lewis acidic (‘inverse’) ligand continue to be of interest. The formation of the 2:1 host–guest compounds $(\mathbf{51})_2\cdot[Cp_2M]$ (M = Fe, Ni) (Fig. 7a)[58] and $(\mathbf{51})_2\cdot[Fe(CN)_5Y]^{x-}x[(Ph_3P)_2N^+]$ [Y = CN ($x = 3$); NO ($x = 2$)] (the anions being shown in Fig. 7b)[59] are particular landmarks in this area. These are the first complexes of this type in which neutral or charged transition metal fragments have been coordinated. Similar association of the molecules and anions of $(\mathbf{51})_2\cdot[Cp_2M]$ and $(\mathbf{51})_2\cdot[Fe(CN)_5Y]^{x-}x[(Ph_3P)_2N^+]$ is found in their lattices, in which the neutral or anionic sandwich units form infinite stacks as a result of closed-shell Hg· · ·Hg interactions. Perhaps the most remarkable feature of the structures of $(\mathbf{51})_2\cdot[Fe(CN)_5Y]^{x-}x[(Ph_3P)_2N^+]$ is the apparent involvement of both the C and N atoms of the CN^- ligands with Hg(II). Interestingly, the 20e Cp_2Ni unit in $(\mathbf{51})_2\cdot[Cp_2Ni]$ is stabilised to such an extent by coordination that it is air stable (*cf.* Cp_2Ni itself which is readily oxidised in air). Another interesting feature of the complex is its deep red colour which can be compared to the green colour of uncoordinated Cp_2Ni. This difference apparently results from a heavy-atom effect. The consequence of increased spin–orbit coupling gives rise to an increase in the intensity of the formally spin-forbidden $^3A_{2g} \rightarrow {}^1E_{1g}$ transition at 516 nm. Spectroscopic studies indicate that the π-interactions found in $(\mathbf{51})_2\cdot[Cp_2M]$ are weak so that the stabilisation of Cp_2Ni must be structural

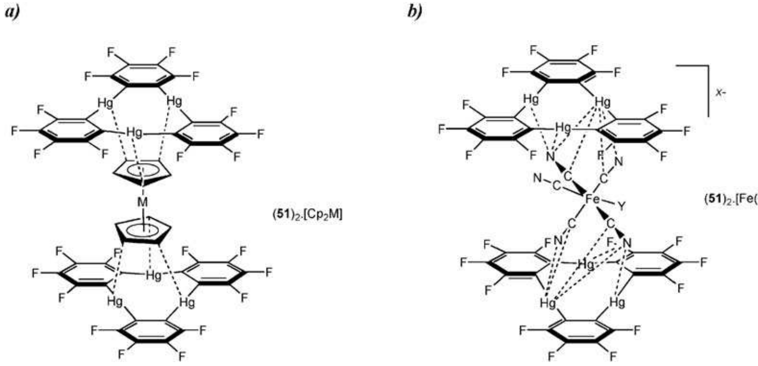
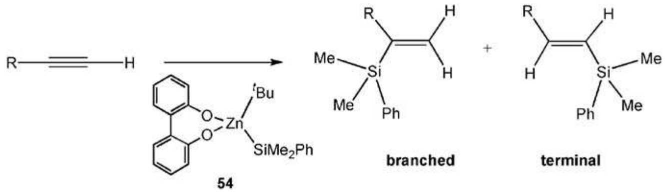


Fig. 7

(*e.g.* steric) rather than electronic. For example, the ^{119}Hg NMR spectrum of $(\mathbf{51})_2\cdot[Cp_2Fe]$ is essentially the same as that of uncomplexed **51**. As expected, the coordination of the transition metal anions in $(\mathbf{51})_2\cdot[Fe(CN)_5Y]^{x-}x[(Ph_3P)_2N^+]$ is considerably stronger, resulting in detectable changes in the ^{119}Hg chemical shifts and CO and NO stretching frequencies in the IR spectra (reducing by *ca.* 14–24 cm^{-1} compared to the uncoordinated $[Fe(CN)_5L]^{x-}$ anions).

Various new **applications of Zn organometallics in organic synthesis** were introduced in 2004.[43,61–66] In comparison, applications of other group 12 organometallics were far less widespread.[67] Applications of Zn organometallics include the use of the aryl-Zn complex $[(C_6F_5)_2Zn]$ (**52**) as a new initiator for the production of isobutene copolymers with high isoprene content (up to 14.7 mol%).[43] The mode of activation involves ionisation of a suitable alkyl halide (RX) to give $R^+[Zn(X(C_6F_5)_2]^-$. The formation of non-nucleophilic zincate anions in this type of reaction is demonstrated by the reaction of Ph_3CCl with **52**, which gives $[Ph_3C]^+[Zn(C_6F_5)_3]^-$ (**53**). The zincate anion of **53** is the first example with sufficiently low nucleophilicity that it can stabilise carbocations. Silyl-zincates have also been shown to be highly effective reagents for the functionalisation of terminal alkynes. The reagent (SiBNOL-Zn-ate) (**54**) is particularly effective in the formation of vinylsilanes, forming mainly the branched isomers on direct reaction with terminal alkynes in the absence of transition-metal mediation (Scheme 9). This is the first example of an efficient branch-selective silylmetallation reaction which has broad substrate generality. Also worthy of mention is a fundamental study of the nature of the active species involved in the Soai asymmetric autocatalyst reaction. Extensive NMR spectroscopic studies and DFT calculations strongly support the formation of a dimeric Zn_2O_2 dimer **55** which strongly binds $^iPr_2Zn$ in the active species **56** (*e.g.*, like that shown in Fig. 8). No evidence for the previously proposed aldehyde–Zn^iPr_2 active species could be found in this study.



Scheme 9

Review of 2005

1 Group 2

Structural studies of σ-bonded organometallics of Mg in 2005 were motivated by a number of interests.[68–76] A particularly important area was the applications of

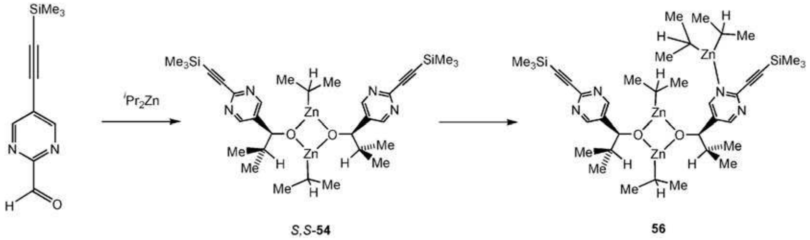
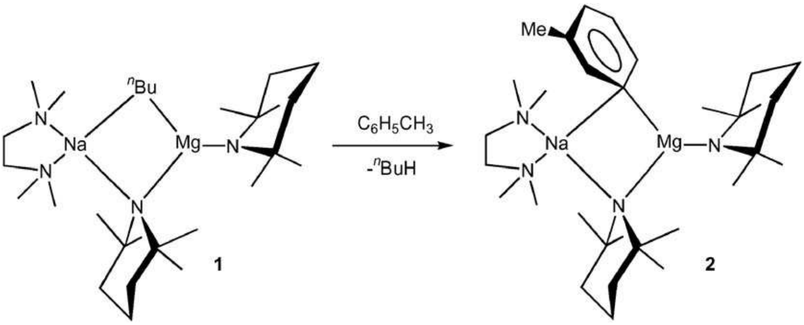


Fig. 8

highly active mixed-metal Mg complexes in the selective deprotonation of organic and organometallic substrates.[68,69] The superbase [(TMEDA)Na(μ-Bu)(μ-TMP)Mg(TMP)] (**1**) [TMP = 2,2,6,6-tetramethylpiperidine, $(Me)_2CCH_2CH_2CH_2C(Me)_2N^-$] (compound **8** in the review for 2004) has been shown to deprotonate toluene at the *meta* position in the product **2** (Scheme 10).[68] Theoretical calculations show unexpectedly that deprotonation at this position is the most stable alternative in the absence of TMEDA solvation. The preference for reaction at this position over more obvious deprotonation at the Me group can be explained by the contribution of π-arene···Na interactions in the *meta* complex, which are absent in the CH_3-metallated species (owing to the unfavourable orientation of the C_6H_6 ring). Although TMEDA solvation has some effect on the relative stabilities of the alternative (*meta*-, *para*-, *ortho*- or CH_3-) metallated products, significantly the *meta*-product is nonetheless one of the most stable species calculated. Interestingly, although toluene is metallated at the Me-group by DABCO-activated $Na_2Mg(Bu)_4$ (**3**) [DABCO = $N(CH_2CH_2)_3N$] (containing the tetraorganomagnesiate anion $[Mg(Bu)_4]^{2-}$), no reaction occurs with $NaMg(Bu)_3$ (**4**) (containing the *tris*-organomagnesiate anion $[Mg(Bu)_3]^-$).[70] This result shows how sensitive the activity of this type of mixed-metal reagent is to changes in stoichiometry.



Scheme 10

The reaction of an equimolar mixture of $[KN(SiMe_3)_2]$ and $[Mg\{N(SiMe_3)_2\}_2]$ with dibenzene chromium $[(C_6H_6)_2Cr]$ gives $[K\{(C_6H_6)_2Cr\}_2]^+[Mg\{N(SiMe_3)_2\}_3]^-$ (**5**), in which no metallation of either C_6H_6 ring has occurred.[70] However, a mixture of $PhCH_2M$ (M = Na, K), Bu_2Mg, TMP(H) and TMEDA (similar to that from which **1** is obtained) successfully deprotonates $[(C_6H_6)_2Cr]$ selectively at one of the C_6H_6 rings in yields of up to 67%.[70] The new complexes [(TMEDA)M-$\{(\mu-C_6H_5)Cr(C_6H_6)\}$($\mu$-TMP)Mg(TMP)] [M = Na (**6a**), K (**6b**) (Fig. 9)] have been structurally characterised.

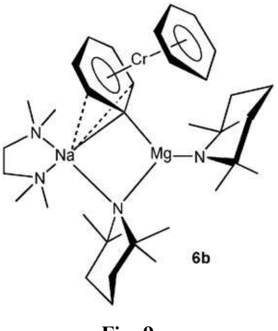


Fig. 9

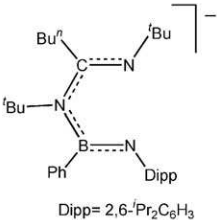
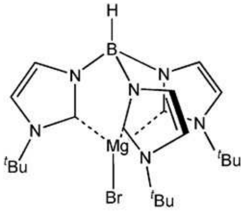


Fig. 10

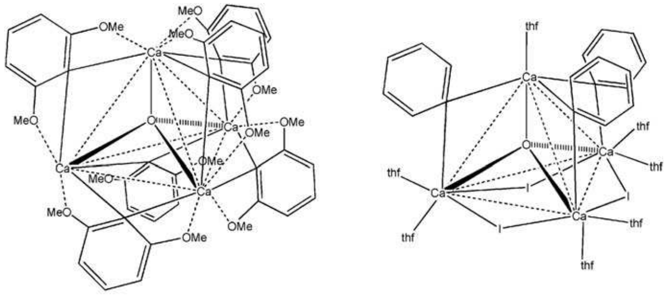


7

Fig. 11

Other noteworthy advances in the chemistry of σ-bonded oganomagnesium compounds have concerned the development or incorporation of new ligand frameworks. Notable examples have included the synthesis of magnesium complexes of boraamidinate/amidinate ligands (Fig. 10), which are relevant to the polymerisation of lactides,[72] and a new route to bulky *tris*(imidazol-2-ylidene)borate ligands (Fig. 11), allowing the steric and electronic character of these little-studied ligands to be tuned readily.[73] Notably, the magnesium complex [HB(^{t}BuIm)$_3$MgBr] (**7**) has proved to be a convenient reagent for the transfer of the *tris*(imidazol-2-ylidene)-borate anion [HB(^{t}BuIm)$_3$]$^-$ to other metals.

Studies of **σ-bonded organometallics of the heavier alkaline earth metals** have been sparse in 2005.[77–79] Although considerable progress has been made in this area in recent years, surprisingly little information has been available concerning aryl derivatives. This situation has been remedied recently by the synthesis and structural characterisation of [{2,6-(MeO)$_2$C$_6$H$_3$}$_2$Ca}$_3$(CaO)] (**8**)[77] and [{thf$\cdot$CaPhI}$_3${thf$\cdot$CaO}] (**9**).[78] Both of these complexes have similar structures in the solid state, composed of a Ca$_4$(μ_4-O) tetrahedral arrangement with the six edges of the tetrahedron being bridged by aryl-C and I$^-$ anions (Fig. 12). **8** is obtained from



8 **9**

Fig. 12

the reaction of $[\{2,6\text{-}(MeO)_2C_6H_3\}K]$ with CaI_2 in thf,[77] while **9** is formed in the reaction of Ca metal with PhI.[11] The reasons for the presence of μ_4-O atoms in both compounds are unclear (whether resulting from thf cleavage, aerial oxidation or hydrolysis). The formation of dimeric, acetylene-bridged Ca complexes $[\{HC(MeC\overset{\cdots}{-}NDipp)_2\}Ca\{\mu\text{-}C{\equiv}CR\}]_2$ (**10**) in the reactions of the heteroleptic β-ketiminato complex $[Ca\{(NDipp\overset{\cdots}{-}CMe)_2\overset{\cdots}{-}CH\}\{N(SiMe_3)_2\}\cdot thf]$ (**11**) with terminal alcetylenes $RC{\equiv}CH$ provides a new route to little-studied acetylene complexes of heavier alkaline earth metals. Theoretical calculations reveal that the asymmetry of the μ-$C{\equiv}CR$ bridges in **10** is dependent on the degree of π-bonding of the $C{\equiv}C$ bond to either Ca centre.

Some significant breakthroughs have been made in recent studies of **π-bonded complexes of group 2**.[80a,81–83] Following on from an earlier communication of the synthesis and structure of the heteroleptic cyclopentadienyl/cyclooctatetraenyl Ba complex $[\{(^iPr_4C_5H)Ba\}_2(C_{10}H_{10})]$ (**12**),[80b] the analogous Ca complex $[\{(^iPr_4C_5H)\text{-}Ba\}_2(C_{10}H_{10})]$ (**13**) has been prepared,[80a] both complexes containing almost linear geometries at the metal centres. The cyclononatetraenyl complex $[Ba(C_9H_9)_2]$ (**14**) has been prepared, although no structural data is currently available.[80a] The reactions of [(allyl)MgI] with $LnI_3(thf)_n$ unexpectedly give the heterometallic Ln/Mg complexes $[Ln(\eta^3\text{-allyl})_3(\mu\text{-1,4-dioxan})\cdot Mg(\eta^1\text{-ally})_2(\mu\text{-1,4-dioxan})_{1.5}]_\infty$ (**15**) which, although relatively rare examples of group 2 allyl complexes, do not in fact contain π-allyl ligands bonded to Mg.[81] Isolelectronic with the allyl ligand $[CH_2\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2]^-$ are triazenide ligands of the type $[RN\overset{\cdots}{-}N\overset{\cdots}{-}NR]^-$. A recent report has described the first complexes of the latter with any group 2 metals.[82] The reactions of the parent ligand $[ArN\overset{\cdots}{-}N\overset{\cdots}{-}NHAr']$ with $[Hg(C_6H_5)_2]$ and the alkaline earth metals give the new complexes $[(C_6F_5)M(ArN\overset{\cdots}{-}N\overset{\cdots}{-}NAr')]$ (M = Sr or Ba) (**16**) or $[(C_6F_5)Ca(thf)(ArN\overset{\cdots}{-}N\overset{\cdots}{-}NAr')]$ (**17**) in good yields. X-ray studies show that both **16** and **17** are stabilised by π-arene$\cdots$metal interactions (*e.g.*, **16** shown in Fig. 13). Similar 'auxiliary' π-arene interactions have been observed in the solid-state structure of the Mg complex $[\{(^tBuPh_2Si)(Me_3Si)N\}_2Mg]$ (**18**), which compensate for the low (two-coordinate) geometry of the Mg centre.[83]

Applications of Grignard and related reagents in organic synthesis continue to be a major area of research, which would be too numerous to describe comprehensively in this short review. Nonetheless, some of these studies stand out as of particularly important.[84–87] Quantum mechanical calculations have shown recently that the activity of the reagent $[^iPrMgCl\cdot LiCl]$ (**19**) in Br/Mg exchange reactions suggest a more complicated picture than previously proposed.[84] It appears that low temperatures and the use of strong donor solvents (L) in the reactions of **19** with aryl bromides favour a two-step pathway involving 'ate complexes containing $[ArBr^iPr]^-$ anions and $[MgCl_2L]$, whereas higher temperatures and weaker donors favour the formation of 'ate transition states in a one-step mechanism. On this basis, the new reagent $[^iPr_2Mg\cdot LiCl]$ (**20**) was developed, with a marked increase in the rate of Br/

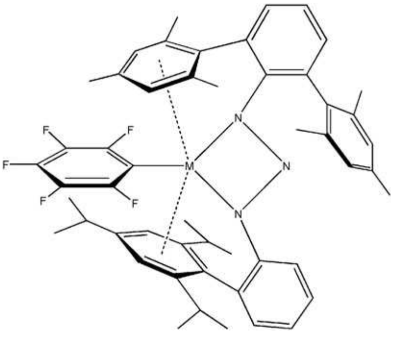
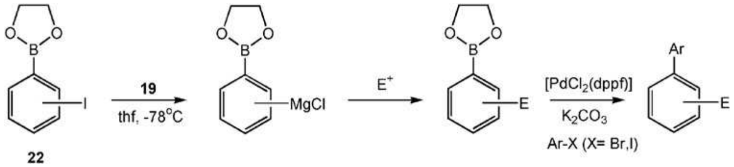


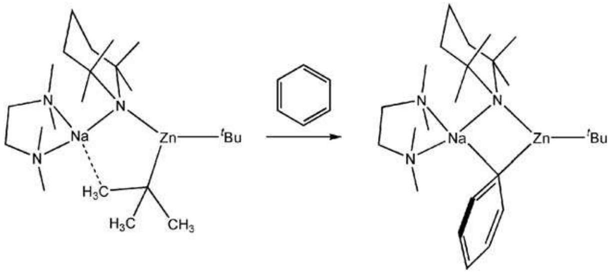
Fig. 13

Mg exchange over the previous reagent **19** arising from increased 'ate character. The related reagent [^{s}Bu$_2$Mg · LiCl] (**21**) also exhibits much higher activity than **19**.[84] Interestingly, reagent **19** has also been applied in the activation of aromatic and heteroaromatic boronic esters **22** (Scheme 11). Importantly, both the Mg and boron functionalities are reactive (*i.e.*, with electrophiles and *via* Suzuki cross-soupling reactions), allowing step-wise multiple functionalisation of the aromatic skeleton. It is noteworthy that the use of ^{i}PrMgCl alone only results in reaction at the boronic ester functionality.



Scheme 11

Structural studies involving σ-bonded Zn organometallics have been numerous in 2005.[88–98] Studies of the applications of heterometallic Zn/alkali metal complexes as reagents for the selective deprotonation of organic molecules have paralleled related complexes of Mg (mentioned earlier, like **1**). The reagent [(TMEDA)Na(μ-^{t}Bu)(μ-TMP)Zn^{t}Bu] (**23**) has been shown to function as an alkyl rather than amide base in the deprotonation of organic substrates.[88] This is indicated in a model study of the reaction of **23** with benzene, producing [(TMEDA)Na(μ-Ph)(μ-TMP)Zn^{t}Bu] (**24**) (rather than, for example, [(TMEDA)Na(μ-^{t}Bu)(μ-Ph)Zn^{t}Bu]) (Scheme 12). Importantly, deprotonation of benzene does not occur with [Zn^{t}Bu$_2$] or Na(TMP) alone, so that the deprotonation of benzene by **23** can be described as *synergic*.[88] Interestingly, **23** also functions as a source of ^{t}Bu$^-$ in its reaction with benzophenone Ph$_2$C=O, adding the ^{t}Bu group in an unusual 1,6-manner (*i.e.*, at the *para*-position of one of the Ph groups) rather than the more obvious 1,2-addition (at the *ortho*-position).[22] Again, there is a synergic effect operating since [^{t}Bu$_2$Zn] alone will not react with Ph$_2$C=O and ^{t}BuLi is known to be far more aggressive in its reaction with this substrate. The heterometallic base [(TMEDA)Li(μ-^{n}Bu)(μ-TMP)Zn^{n}Bu] (**25**) (having a similar structure to **23**) has also been used in the deprotonation of ferrocene [Cp$_2$Fe], giving efficient mono-deprotonation of one of the Cp rings as shown be the structural characterisation of the new complexes [{CpFe(C$_5$H$_4$)}$_2$-Zn · TMEDA] (**26**) and [Li(thf)$_4$]$^+$[{CpFe(C$_5$H$_4$)}$_3$Zn]$^-$ (**27**).[90]

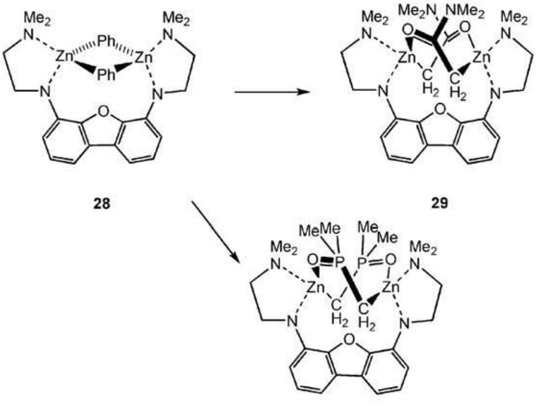


23

24

Scheme 12

Other structural studies of σ-organozinc complexes relevant to organic synthesis have also appeared.[91–93] Particularly interesting was the structural characterisation of the first α-zincated (Reformatsky) amides and phosphine oxides.[92] The novel dizinc complex **28** reacts with $Me(Me_2N)C{=}O$ or $Me_3P{=}O$ according to Scheme 13, giving the structurally-characterised α-zincated amide and phosphine oxide complexes **29** and **30**. The intramolecular stabilisation of the bis(alkylzinc)imide **31** (Fig. 14) is also worthy of note. **31** is formed *via* C–C coupled intermediates from the reaction of *bis*(2-pyridylmethyl)amine with Et_2Zn.[93]



Scheme 13

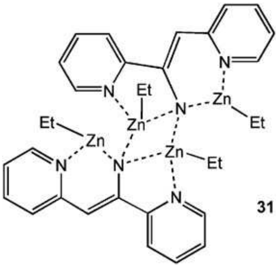
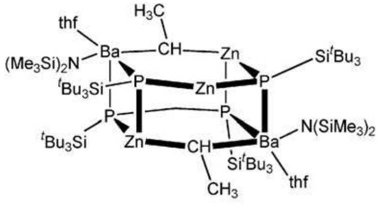


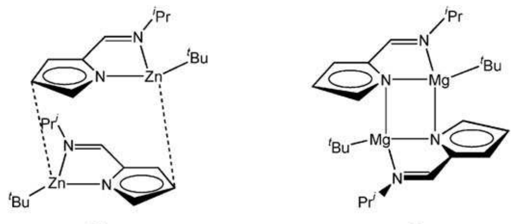
Fig. 14

Also of interest in regard to studies of σ-bonded organozinc compounds is a report of the activation of a Zn-bonded Et group in the reaction of the phosphide dimer $[EtZn(\mu\text{-}PHSi^tBu_3)]_2$ (**32**) with the Ba base $[(thf)Ba\{N(SiMe_3)_2\}_2]$.[94] The product of this reaction is the heterometallic cage $[\{(Me_3Si)_2N\}Ba(thf)Zn_2(\mu\text{-}Et)(\mu_3\text{-}PSi^tBu_3)_2]_2$ (**33**) (Fig. 15).



33

Fig. 15

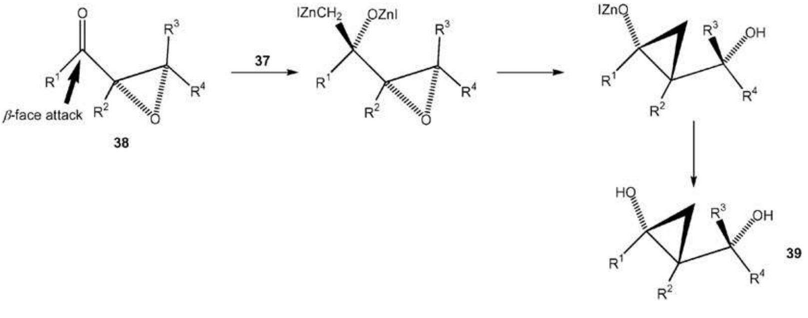


35 **36**

Fig. 16

Structural studies of Group 12 π-bonded complexes have (as usual) been few and far between in 2005.[99–101] Following on from the dramatic report of the synthesis of the first molecular species containing a Zn–Zn bond [Cp*ZnZnCp*] (**34**) [compound **46** (ref. 54) in the report for 2004], a more efficient method of synthesis has been reported involving the reaction of $[Cp^*_2Zn]$ with KH in thf at room temperature.[99a] Significantly, the new procedure involves a one-pot reaction of a mixture of [Cp*K], $ZnCl_2$ and KH (2:1:1 equivalents, respectively), giving **34** in 60–80% yield. DFT calculations show that the Zn–Zn bond is comparatively strong (*ca.* 60 kcal mol^{-1}) and composed mainly of Zn 4*s* character with very little involvement of the 4*p* orbitals. π-Arene interactions are responsible for the interesting loose dimerisation of the Zn complex **35** (Fig. 16), containing a bifunctional pyrrolylaldiminato ligand. Both **35** and its Mg analogue **36** are monomeric in benzene solution, however, in the case of the Mg complex dimerisation occurs *via* M–N bonds as opposed to π-arene···Mg interactions.[100]

Like Grignard and related Mg reagents, **organozinc compounds** are key reagents that are frequently encountered in **organic synthesis**.[102–104] One of the interesting developments recently introduced has been the use of *bis*(iodozincio)methane $[CH_2(ZnI)_2]$ (**37**) in the stereospecific and selective preparation of 2-(1-hydroxy-alkyl)-1-alkylcyclopropanols (**39**) from α,β-epoxy ketones (**38**) (Scheme 14).[101] A fundamental study using neutron and anomalous X-ray scattering shows that **37** is essentially a monomer in thf solution.[103]



Scheme 14

Studies of Hg organometallics have been numerous in 2006, concentrating mainly on the supramolecular and coordination chemistry of species of the type [RHgX] and $[R_2Hg]$[105–114] as well as (on occasions) the physical properties of organomercury(II) compounds.[115] The monomeric diorganomercury compound $[(C_6F_5)_2Hg]$ (**40**) has been shown to coordinate halide ions within $[\{(C_6F_5)_2Hg\}_3(\mu_3\text{-}X)]^-$ (**41**) (X = Cl, Br, I) or $[\{(C_6F_5)_2Hg\}_2(\mu_2\text{-}X)]^-$ (**42**) (X = Br) anions.[105] Similarly to the behaviour of **40** in the latter, the trinuclear Hg(II) macrocycle $[(o\text{-}C_6F_4)Hg]_3$ (**43**) can coordinate organic radicals such as TEMO (= 1,1,5,5-tetramethylpentamethylene nitroxide, Fig. 17) and NIT-Ph [2-(phenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-

oxide, Fig. 17].[106] The new paramagnetic adducts [**43** · TMPO], [(**43**)$_2$ · NIT-Ph] and [(**43**) · NIT-Ph]$_\infty$ have been structurally characterised. [**43** · TMPO] and [(**43**)$_2$ · NIT-Ph] are molecular whereas [(**43**) · NIT-Ph]$_\infty$ has a polymeric helical structure, all three complexes involving the coordination of the O-atoms of the organic radicals by the three Hg centres of **43**. In [(**43**)$_2$ · NIT-Ph], π-arene···Hg bonding is also involved.

Other macrocyclic Hg(II) species have also been introduced, an interesting example being the donor/acceptor species **44** (Fig. 18).[107] **44** coordinates the Cu$^+$ ions within the cavity using the four N-atoms. The complex [(**44**)Cu]$^+$[ClO$_4$]$^-$ has a polymeric structure in the solid state which contains d^{10}–d^{10} (closed-shell) intermolecular Hg···Hg [3.20 Å] and intramolecular Hg···Cu [2.92 Å] interactions. Although not strictly speaking an organomercury compound, the tetrameric Hg(II)–Si bonded macrcyclic species [{(Me$_2$Si)$_2$Si}Hg]$_4$ (**45**) is also of interest as a potential host for anion coordination.[108] A further example of an organomercury(II) macrocyle is found in [(CF$_3$)$_2$Hg(Pur)]$_4$ (Pur = purine) (**46**) (Fig. 19), formed by the coordination of [(CF$_3$)$_2$Hg] (**47**) by Pur.[108]

Finally, entry into a new class of metallocene-fused imidazole-2-ylidenes has been proved by the synthesis of the structurally-characterised heterometallic Ru/Hg compound **47** (Fig. 20).[110] The methodology potentially allows the incorporation

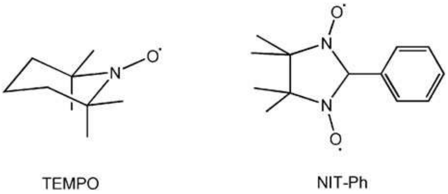
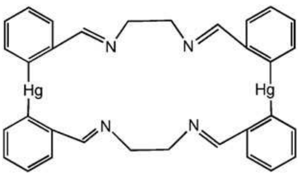
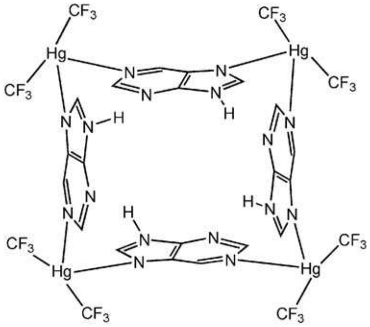


Fig. 17



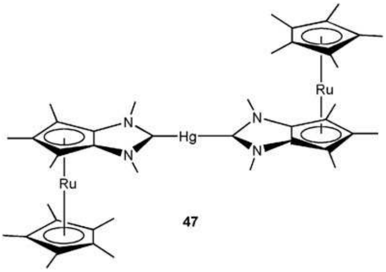
44

Fig. 18



46

Fig. 19



47

Fig. 20

of two or more metals *via* a combination of σ- and π-bonding to the imidazole fragment of the ligand.

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Scandium, yttrium and the lanthanides

John G. Brennan[a] and Andrea Sella[b]

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1. Introduction

This review covers the synthesis, characterization, and reaction chemistry of organometallic complexes of Sc, Y and the lanthanides reported in the years 2004 and 2005. For the first time we have included reports of genuine fullerene compounds. Non-molecular carbides and related species are still excluded. As in previous years reports are classified largely by ancillary group, a process that necessarily requires cross-referencing wherever possible. Notable discoveries include a wealth of multimetallic clusters connected by bridging H, X, BH_4, and NO_3 ligands, an interesting series of liquid ammonia preparations in which Ln reduces a range of nitrogen heterocycles, and an extensive series of Cp^*_3Ln reactivity studies. Compounds with organoboron ligands were plentiful, while studies of the catalytic addition of H–X (X = N, P, Si) to C=C continue to attract significant attention.

2. Hydrocarbyls of various kinds

Alkyl complexes without sterically demanding ancillary ligand systems continued to develop, both because of the exceptional reactivity of these more accessible cationic sites, as well as for more fundamental motivations. Investigations into the catalytic behavior of $Ln(OR)_3/MgR_2$ combinations led to the preparation of the trinuclear complex $[Nd_3(\mu_3\text{-}O^tBu)_2(\mu_2\text{-}O^tBu)_3(\mu\text{-}O^tBu)_4(THF)_2]$, monomeric $[Nd(OC_6H_2\text{–}{}^tBu_2\text{-}2,6\text{-}Me\text{-}4)_3(THF)]$, and $[Mg(R')_2(Et_2O)]$. Reaction of these compounds gave $[(THF)Nd(\mu_3\text{-}O^tBu)_2(\mu_2\text{-}O\text{–}{}^tBu)_2(O^tBu)Mg_2(R')_2]$ and the alkyllanthanide complex $[Nd(OC_6H_2\text{–}{}^tBu_2\text{-}2,6\text{-}Me\text{-}4)_2(R')(THF)_2]$. The pentacoordinate complexes $[(4\text{-}Me\text{-}2,6\text{-}{}^tBu_2C_6H_2O)_2Nd(R')(THF)_2]$ and $[(4\text{-}Me\text{-}2,6\text{-}{}^tBu_2C_6H_4O)Mg(R')]_2$ were also isolated.[1]

Reaction of $o\text{-}Me_2NC_6H_4CH_2K$ with $LnCl_3$ (Y, La) in THF yielded the extremely stable light yellow $[Ln(o\text{–}Me_2NC_6H_4CH_2)_3]$ with prismatic coordination spheres. The complexes deprotonate $9\text{-}{}^tBuN(H)SiMe_2$ fluorene to give the monomeric constrained geometry $(\eta^3\text{-}9\text{-}{}^tBuNSiMe_2\text{fluorenyl})(o\text{-}Me_2N\text{benzyl})Ln(THF)$ with allylic coordination of the fluorenyl ring and bidentate coordination of the benzyl ligand. This complex was hydrogenated to yield the dimer $[(9\text{-}{}^tBuNSiMe_2\text{fluoren-}9\text{-yl})YH(THF)_2]_2$, which has an η^1-fluorenyl ligand. Attempted synthesis of $(o\text{-}Me_3SiC_6H_4CH_2)_3La$ from $o\text{-}Me_3SiC_6H_4CH_2K$ and $LaCl_3$ unexpectedly gave $[Li(THF)_4]^+[(o\text{-}Me_3SiC_6H_4CH_2)_4La]^-$, the source of the Li^+ ion being impure $o\text{-}Me_3SiC_6H_4CH_2K$. In this structure the La has a distorted tetrahedral coordination sphere.[2] The same ligand was used to generate isostructural pairs of Yb(II) and Ca(II) benzyl complexes. While the physical properties of each pair were nearly identical, only the homoleptic bisbenzylytterbium(II) complex produces polystyrene of high syndiotacticity.[3]

Fluxional processes were in evidence. A reaction of 2,6-diisopropylaniline with $La[N(SiMe_3)_2]_3$ produced homoleptic amido dimers $La_2(NHAr)_6$ (**1**) with the metals bridged by the increasingly well known intermolecular η^6-arene interactions of a unique arylamide ligand attached to an adjacent metal centre. THF cleaved these dimers to give fac-octahedral $La(NHAr)_3(THF)_3$ while pyridine yielded monomeric

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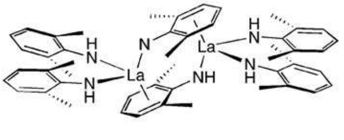
[a] *Department of Chemistry and Chemical Biology, Rutgers, the State University of New Jersey, 610 Taylor Road, Piscataway NJ 08854-8087, USA. E-mail: bren@ccbmail.rutgers.edu*

[b] *Christopher Ingold Laboratories, University College London, 20 Gordon Street, London, UK, WC1H 0AJ . E-mail: a.sella@ucl.ac.uk; Tel: 020 7679 4687*

trigonal biypyramidal La$(NHAr)_3(py)_2$. The π-arene-bridged dimer is maintained in solution, but a monomer-dimer equilibrium exists at elevated temperature. In contrast, variable-temperature ^{1}H NMR spectroscopic investigations of the aryloxide analog $La_2(OAr)_6$ showed that the bridging and terminal aryloxide groups exchange by a mechanism in which the dimeric nature of the compound is retained. DFT calculations indicate that the formation of η^6-arene interactions is energetically favored over monomeric LaX_3 (X = OPh or NHPh) with the aryloxide π-arene interaction being stronger than the arylamide π-arene interaction.[4] Metathesis between LaI_3 and $\{R(C_6H_4\text{-}2\text{-}CH_2NMe_2)P\}K$ gave the heteroleptic complex $\{R(C_6H_4\text{-}2\text{-}CH_2NMe_2)P\}_2LaI$, which reacted *in situ* with KOR to give the corresponding mixed phosphide/alkoxide complexes $\{R''(C_6H_4\text{-}2\text{-}CH_2NMe_2)P\}_2La(OR)$ (R = ^{t}Bu, ^{i}Pr). A similar *in situ* reaction with KR [R = Bz, R′, R″] yielded the cyclometallated product $\{(R'')(C_6H_4\text{-}2\text{-}CH_2NMe_2)P\}La(THF)[P(C_6H_4\text{-}2\text{-}CH_2NMe_2)[CH\{SiMe_3\}\{SiMe_2CH_2\}]]$ (**2**) and RH. Reaction of LaR''_3 with the secondary phosphine $R(C_6H_4\text{-}2\text{-}CH_2NMe_2)PH$ yielded the same metallated product, suggesting that the cyclometallation reaction is intramolecular in nature. The cyclometallation product displays a surprisingly rapid and reversible inversion at phosphorus, which equilibrates the stereoisomers.[5] Protonation of the heteroleptic, cyclometallated phosphide $[R''(C_6H_4\text{-}2\text{-}CH_2NMe_2)P]La(THF)[P(C_6H_4\text{-}2\text{-}CH_2NMe_2)\text{-}\{CH(SiMe_3)(SiMe_2CH_2)\}]$ with $[Et_3NH][BPh_4]$ yields cationic $[(THF)_4La[P(C_6H_4\text{-}2\text{-}CH_2NMe_2)\{CH(SiMe_3)(SiMe_2CH_2)\}]][BPh_4]$.[6]

Other cations were also investigated. Tetraphenylborate salts of solvated Ln(II) cations $[Eu(C_6F_5)(THF)_6]^+$ and $[Yb(C_6F_5)(THF)_5]^+$ (**3**) were readily synthesized in high yield by reactions of Ln with $HgPh(C_6F_5)$ and Me_3NHBPh_4 in THF. The Yb cationic fragment was also observed in the mixed-valent complex $[Yb(C_6F_5)\text{-}(THF)_5][Yb(C_6F_5)_2\{N(SiMe_3)_2\}_2]$, fortuitously isolated in low yield from a reaction of Yb metal, $HgPh(C_6F_5)$, and $HN(SiMe_3)_2$ in THF. ^{171}Yb–^{19}F coupling was observed in the low-temperature ^{171}Yb NMR spectra.[7]



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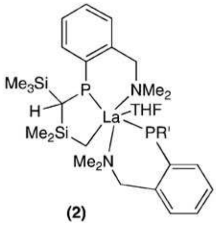

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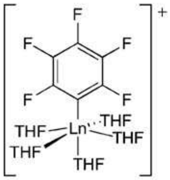


(3)

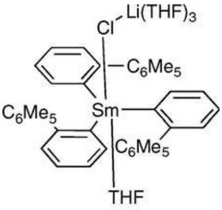
The tris-alkyls $[LnR''_3]$ [Ln = Y, Ce] reacted with nitriles to form crystalline adducts rather than β-diketiminato-metal insertion products. The β-diketiminato-Ce complex $[Ce\{(N(SiMe_3)C(C_6H_4Bu\text{-}4))_2CH\}\{N(SiMe_3)_2\}_2]$ was obtained from $[Ce\{N\text{-}(SiMe_3)_2\}_3]$ and the β-diketimine $H[\{N(SiMe_3)C(C_6H_4Bu\text{-}4)\}_2CH]$. The Ce alkyl and $[Ln\{CH(SiMe_3)(SiMe_2OMe)\}_3]$ [Ln = Y, Ce] were obtained by metathesis. Heating the Y derivative with benzonitrile afforded 2,2-dimethyl-4,6-diphenyl-5-trimethylsilyl-1,3-diaza-2-silacyclohexa-3,6-diene, a member of a new class of heterocycles.[8]

The alkyl complex $[LuR'_3(THF)_2]$ reacted with Cp*H, giving $[Cp^*LuR'_2(THF)]$ that reacted with DME to give $[Cp^*LuR'_2(DME)]$, and with 2,2′-bipyridine (bipy) to give $[Cp^*LuR'_2(bipy)]$. The bipy complex reacted with 2,6-diisopropylaniline to give the mixed alkyl-anilide $[Cp^*Lu(NHAr)R'(bipy)]$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) and the bis(anilide) $[Cp^*Lu(NHAr)_2(bipy)]$. The latter was independently synthesized in high yield by treatment of the DME compound with 2,6-diisopropylaniline or the bipy alkyl with 2,6-diisopropylaniline. The DME compound also reacted with $PhC{\equiv}CH$ to afford dimeric $[\{Cp^*Lu(C{\equiv}CPh)(bipy)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}PhC_4Ph)]$, which reacted further with THF and pyridine, giving terminal (bis)acetylide complexes $[Cp^*Lu(C{\equiv}CPh)_2(bipy)(THF)]$ and $[Cp^*Lu(C{\equiv}CPh)_2(bipy)(py)]$, respectively.[9]

In other fundamental studies, charge neutral [(THF)Li(μ-A)(μ-Cl)(μ_3-OMe)Zn]$_2$, [Li(μ-A)$_2$Tl]$_2$, [Li_4(μ-A)$_3$(μ_3-OMe)], [(μ-A)Li_2(μ-A)$_2$(μ_3-OMe)Ce(A)] and [Ce(A)-(μ_2-OMe){μ_2-OS(O)(CF_3)O}]$_2$ [A = CH($SiMe_3$){SiMe($OMe)_2$}] were isolated and fully characterized. The principal novel features include a diversity of ligand-to-metal bonding modes, including C,O–, C,O,O′-bridging and O,O′-chelating, C,O,O′-bridging, and C,O-chelating. Further, the ligand readily fragments by Si–OMe cleavage to give bridging methoxy ligands.[10] A new Sm complex described as a carbene was synthesized from bis(diphenylthiophosphinoyl)methane dianion and SmI_3(THF)$_{3.5}$. The carbene label was based upon reactivity, rather than structural studies (more conventional carbene complexes are discussed in Section 7.2).[11]

Homoleptic [Ln($AlMe_4$)$_3$] (Ln = Y, Lu) complexes were described as effectively masked [$LnMe_3$]$_n$ species, which are produced reversibly upon equimolar addition of a Lewis base to the former. [$LnMe_3$]$_n$ are thermally stable and readily form peralkylated heterobimetallic complexes with Lewis acids such as alkyl-aluminum, -gallium, and -magnesium reagents.[12] The last work in this section reported that Lu(R′)$_3$(THF)$_2$ decomposes slowly at room temperature with formation of Me_4Si, in what is thought to be an γ-H elimination process. The related compounds Lu(R′)$_3$([d_8]-THF)$_2$, Lu(R′)$_3$(THF)(DME), and Lu(R′)$_3$(THF)(diglyme) were used to probe this decomposition.[13]

Ionic compounds were equally diverse. A series of mono- and dicationic trimethylsilylmethyl complexes supported by THF and 12-crown-4 ligands with [BPh_4]$^-$, [BPh_3R']$^-$, [B(C_6F_5)$_4$]$^-$, [B(C_6F_5)$_3$R′]$^-$, and [AlR'_4]$^-$ anions were prepared from corresponding neutral precursors [Ln(R′)$_3$L] (Ln = Sc, Y, Lu; L = THF, n = 2 or 3; L = 12-crown-4, n = 1) as solvent-separated ion pairs. The syntheses of the monocationic derivatives [Ln(R′)$_2$(12-crown-4)$_n$(THF)$_m$]$^+$[A]$^-$ proceed rapidly in THF solution at room temperature. When BPh_3 was used to generate the ion, the presence of 12-crown-4 was required for complete conversion. Addition of a second equivalent of 12-crown-4 and a third equivalent of [NMe_2PhH]$^+$[B(C_6F_5)$_4$]$^-$ Abstracts a third alkyl group from [Ln(R′)(12-crown-4)$_2$(THF)$_x$]$^{2+}$[B(C_6F_5)$_4$]$^-_2$ (Ln = Y, Lu). The X-ray structure of [Sc(R′)$_3$(12-crown-4)] exhibits incomplete 12-crown-4 coordination, and VT NMR spectroscopy revealed fluxional 12-crown-4 coordination on the NMR timescale.[14]



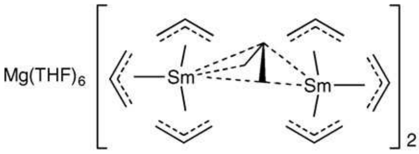
(4)

Finally, the samarate [(THF)$_3$Li][ClSm(2′,3′,4′,5′,6′-pentamethylbiphenyl)$_3$(THF)] (**4**) has a trigonal bipyramidal Sm with the propeller-like biphenyls in the equatorial positions that display strong agostic interactions with the metal centre.[15]

2.1 Allyls

The past couple of years have a seen growing attention given to allyic complexes. The tris(η^3-allyl) complexes [La(η^3-C_3H_5)$_3$(κ^1-dioxane)]$_2$(μ-dioxane) and [Ln-(η^3-C_3H_5)$_3$(μ-dioxane)]$_\infty$ (Ln = Y, Sm, Nd) were prepared. Subsequent reaction of [La(η^3-C_3H_5)$_3$(κ^1-dioxane)]$_2$(μ-dioxane) and [Ln(η^3-C_3H_5)$_3$(μ-dioxane)]$_\infty$ with the diketimine ligand 2-(2,6-diisopropylphenyl)amino-4-(2,6-diisopropylphenyl)imino-2-pentene generated the β-diketiminato complexes Ln(η^3-C_3H_5)$_2${κ^2-HC-(MeCNAr)$_2$} (Ar = 2,6-$C_6H_3{}^iPr_2$; Ln = La, Y, Sm, Nd) with propene elimination. All complexes were highly effective single-component catalysts for the ring-opening polymerization of ε-CL and *rac*-lactide. Polymer end group analysis showed, as expected, that the polymerization process is initiated by allyl transfer to monomer.[16]

Ionic mixed-metal complexes $[Ln(\eta^3\text{-}C_3H_5)_3(\mu\text{-}C_4H_8O_2)Mg(\eta^1\text{-}C_3H_5)_2(\mu\text{-}C_4H_8O_2)_{1.5}]_\infty$ (Ln = La, Y) were prepared by reaction $Mg(C_3H_5)$ with LnI_3. By contrast, when Ln was Sm, $[Mg(THF)_6][Sm_2(\eta^3\text{-}C_3H_5)_6(\mu\text{-}\eta^3{:}\eta^3\text{-}C_3H_5)]_2$ (**5**) was obtained, which contains the unprecedented $\mu\text{-}\eta^3{:}\eta^3\text{-}C_3H_5$ motif. For Ln = Nd, $[Mg(THF)_6][Nd(\eta^3\text{-}C_3H_5)_4]_2$ was isolated. On reaction with a mild protic acid such as the diketimine 2-(2,6-diisopropylphenyl)amino-4-(2,6-diisopropylphenyl)imino-2-pentene, the Sm product is converted into $[Mg(THF)_6][Sm(\eta^3\text{-}C_3H_5)_4]_2$, alongside $Sm(\eta^3\text{-}C_3H_5)_2\{\kappa^3\text{-}HC(MeCNC_6H_3{}^iPr_2\text{-}2,6)_2\}$ (**6**).[17]



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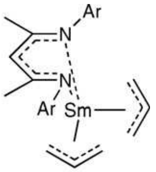


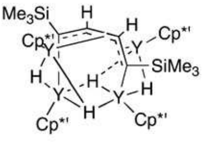
(6)

Using a more sterically congested ligand, reaction of $K(1,3\text{-}Me_3Si\text{-}allyl)$ with SmI_2 and the triflate salts of Ce, Eu, Tb, and Yb gave the corresponding allyl lanthanide complexes $Ln(allyl)''_2(THF)_2$ (Ln = Eu, Sm, Yb) and $Ln(allyl)''_3(THF)$ (Ln = Ce, Tb), respectively. These complexes, which have been crystallographically characterized, initiate the polymerization of Me methacrylate (MMA), but with poor turnover frequencies when compared with the corresponding salt complexes of the type $K[Ln(allyl)''_3]$. One striking point made in this study was the report that Yb(II) triflate can be made by reacting the trivalent compound with EtMgBr.[18] Finally, the product of $Sc(R')_3(THF)_2$ and 1,4,7-trithiacyclononane is a precursor to ethylene, styrene, and 1-hexene polymerization catalysts upon activation with $B(C_6F_5)_3$ or $[CPh_3][B(C_6F_5)_4]$.[19]

3. Cyclopentadienyl-based ancillaries

3.1 Cp* and other fully substituted cyclpentadienyl ligand chemistry

A multitude of multimetallic materials were prepared with connecting ligands that ranged from hydrides and halides to BH_4^- and NO_3^-. Hou's tetrameric hydrides, reported in 2003, are proving to be a very fertile area for reactivity studies. The reaction of CO_2 with the tetrameric complex $[Cp^{*\prime}Y(\mu\text{-}H)]_4(L)$ (L = $Me_3\text{-}SiC{=}C(H)C(H){=}CSiMe_3$) (**7**) rapidly afforded the corresponding bis(methylene diolate) complex $[(Cp^{*\prime}Y)_4(\mu\text{-}O_2CH_2)_2(L)]$ (**8**) and over a longer timescalegives the carbonate $[(Cp^{*\prime}Y)_4(\mu\text{-}O_3C)_2(L)]$ (**9**), while the reactions of naphthyl isocyanate led to selective formation of the μ_3-oxo complexes $[(Cp^{*\prime}Y)_4(\mu\text{-}O)(\mu\text{-}H)_2(L)]$ or $[(Cp^{*\prime}Y)_4(\mu\text{-}O)_2(L)]$, depending on the Yb:substrate ratio. Both the methylene diolate and the oxo complexes underwent CO_2 insertion reactions to give the corresponding carbonate complexes. These reactions shed new light on the mechanistic aspects of the heterogeneous hydrogenation of CO_2.[20] In related work from the same group, the tetranuclear polyhydrido complexes $[(C_5Me_4SiMe_3)Ln(\mu\text{-}H)_2]_4(THF)$ (Ln = Lu, Y) react with unsaturated compounds such as benzonitrile, γ-butyrolactone, styrene, and 1,4-bis(trimethylsilyl)-1,3-butadiyne to afford structurally characterizable polynuclear complexes that possess novel structures. Most of these reactions are unprecedented and can be attributed to the unique cooperative effects of multiple active sites in the polyhydrido rare earth metal complexes.[21]



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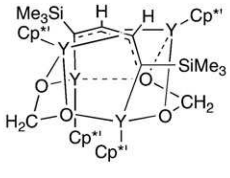

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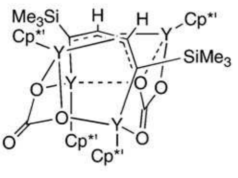
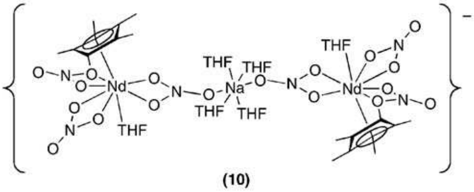


(9)

In what may prove to be a useful route to anhydrous starting materials, hydrated neodymium nitrates were readily transformed to anhydrous ether solvates that are useful organometallic precursors, *i.e.* $Nd(NO_3)_3(H_2O)_6$ in THF generates $Nd(NO_3)_3(THF)_3$. The DME analog $Nd(NO_3)_3(DME)_2$ was prepared similarly. Addition of NaCp* to the THF compound generates $\{[Cp^*Nd(NO_3)_2(THF)(\mu\text{-}NO_3)]_2Na(THF)_4\}[Na(THF)_6]$ (**10**), or $[Cp^*Nd(THF)(\mu\text{-}NO_3)_3Na(THF)_2]_n$, depending on the conditions. Addition of KCp* and 18-crown-6 generates another extended complex $[Cp^*Nd(THF)(NO_3)(\mu\text{-}NO_3)_2K(18\text{-crown-}6)]_n$.[22]

Beautiful hexanuclear clusters held together with BH_4 anions were isolated and characterized. The reaction of $Ln(BH_4)_3(THF)_3$ or $LnCl_3(THF)_3$ (Ln = Sm, Nd) with KCp^{*Pr} ($Cp^{*Pr}{=}C_5Me_4n\text{–}Pr$) afforded $Cp^{*Pr}LnX_2(THF)_n$ and $[Cp^{*Pr}LnX_2]_m$. Crystals of $[Cp^{*Pr}{}_6Ln_6(BH_4)_{(12-x)}Cl_x(THF)_n]$ (**11**) exhibit a hexameric structure in the solid state containing the $[Cp^{*Pr}{}_3Ln_3X_5(THF)]$ building block. The clustering of THF adducts can be reversed upon addition of THF.[23] Preliminary isoprene polymerization experiments with $[Cp^{*Pr}Nd\{((p\text{-tol})\text{-}NC(Me)CHC(Me)N(p\text{-tol})\}(BH_4)]$ in the presence of an alkylmagnesium coactivator showed that the resulting Nd/Mg system was an efficient and highly stereospecific catalyst with the synthesis of *trans*-1,4-polyisoprene with $>98\%$ regularity.[24]



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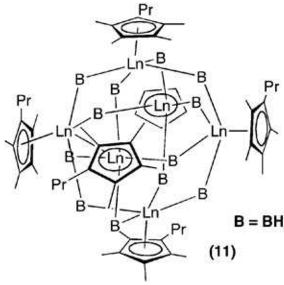


(11)

Numerous Cp compounds were examined for polymerization activity. Oligomeric $[Cp^*ScCl_2]_n$ reacted with $Bu_3P{=}O$ in THF to give monomeric $[Cp^*({}^tBu_3P{=}O)ScCl_2]$. Alkylation with MeLi gave $[Cp^*({}^tBu_3P{=}O)ScMe_2]$, a compound with a three-legged piano stool geometry about the scandium centre. The free and coordinated R_3PO exchange *via* an associative mechanism. Activation of the methyl compound with $B(C_6F_5)_3$ gave the contact ion pair $[Cp^*({}^tBu_3P{=}O)ScMe]^+[MeB(C_6F_5)_3]^-$ which is an active ethylene polymerization catalyst.[25]

Evans has continued to develop the chemistry of the ultra-crowded tris-Cp* systems. The displacements of the Me substituents away from the metal and out of the cyclopentadienyl ring plane were compared in sterically crowded $Cp^*{}_3Ln$ complexes *vs.* sterically normal f-element compounds. In general, the Me displacement values of sterically crowded complexes overlap with those in the other complexes, which demonstrates that the basis of the observed structural distortions is complex. However, the most extreme out-of-plane displacement in each of the sterically crowded complexes appears to be a basis for predicting cyclopentadienyl reactivity.[26] $Cp^*{}_3Sm$ and $Cp^*{}_2Sm(EPh)$ (E = S, Se, Te) complexes were synthesized and treated with substrates reduced by $Cp^*{}_3Sm$: cyclooctatetraene, azobenzene, phenazine. Reactions of PhEEPh with $Cp^*{}_2Sm(THF)_2$ and $Cp^*{}_2Sm$ produced THF-solvated monometallic complexes, $Cp^*{}_2Sm(EPh)(THF)$, and their unsolvated dimeric analogs, $[Cp^*_2Sm(\mu\text{-}EPh)]_2$, respectively. Only the $(TePh)^-$ complexes show reduction reactivity and only upon heating to 65°.[27] In closely related work, the previously inaccessible smallest member of the $(C_5Me_4H)_3Ln$ series, $(C_5Me_4H)_3Lu$, was synthesized from $[(C_5Me_4H)_2Lu][(\mu\text{-}Ph)_2BPh_2]$ and KC_5Me_4H and reduced with K under dinitrogen to form $[(C_5Me_4H)_2(THF)Lu]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$.[28]

The new complexes Cp^*_3Ce and Cp^*_3Pr display longer Ln–C distances than any previously described Ce or Pr complexes containing the Cp* ligand. The η^1-Cp* alkyl-like reactivity of these complexes was investigated with CO, ethylene, THF, and H_2. Reaction of Cp^*_3Pr and Cp^*_3Ce with CO afforded $Cp^*_2Ln(C_7Me_5O_2\text{–}O,O)$, where $C_7Me_5O_2$ is the non-classical 1,4,5,6,7-pentamethylbicyclo[2.2.1]heptadiene-2,3-diolato-7-onium monoanion. Reaction with ethylene produces polyethylene; dihydrogen gives di-μ-hydride $Cp^*_2Ln(\mu\text{-}H)_2LnCp^*_2$. THF undergoes ring opening, giving $Cp^*_2(THF)LnO(CH_2)_4(5\text{-}Cp^*)$. With $SePPh_3$, $AgBPh_4$, cyclooctatetraene and phenazine; the reactions afford the di-μ-selenides, $Cp^*_2Ln(\mu\text{-}Ph)_2BPh_2$, $Cp^*Ln(\eta^8\text{-}C_8H_8)$ and $Cp^*_2Ln(\mu\text{-phenazine})LnCp^*_2$ along with dimerization product 5,5′-Cp^*_2. All of these data indicate that Cp^*_3Ln reactivity increases with decreasing size of the metal and hence increased steric crowding. The reactivity of Cp^*_3Ln with CO_2 and with Et_3NHBPh_4 was also examined since each substrate could react by either η^1-Cp* alkyl or SIR pathways. In both cases, alkyl-like reactivity is observed: CO_2 forms the insertion product $Cp^*_2Ln(O_2CCp^*)$, containing a carboxylate with a pentamethylcyclopentadiene substituent, and Et_3NHBPh_4 forms $[Cp^*_2Ln]\text{-}[(\mu\text{-}Ph)_2BPh_2]$ and Cp*H. The reactions of Cp^*_3Sm with aryl halides and primary alkyl halide radical clocks (RX) yield Cp*R, Cp*X, Cp^*_2, R–R, and $[Cp^*_xSmX_y]_z$ as products, which indicate that SIR is not the only reaction pathway with these substrates.[29]

In a polymerization study, $[Cp^*_2Sm(\mu\text{-}O_2CPh)]_2$ reacts with $^iBu_3Al$ activator to form $[Cp^*_2Sm(\mu\text{-}O_2CPh)(\mu\text{-}^iBu)Al(^iBu)_2]$, that displays two different carboxylate orientations toward the metals in a single crystal. The stability of the mixed metal carboxylate complex shows balanced Lewis acidity, which is of importance in olefin polymerization and isomer selectivity.[30] The samarocene carboxylate also reacts with $AlEt_3$ to form a mixture of metallocene-stabilized ethylaluminum compounds, including an ethylaluminum oxide complex, $[Cp^*_2Sm]_2[(\mu\text{-}Et)_4Al_4Et_6O_2]$, that displays $\mu\text{-}\eta^1{:}\eta^2$-Et coordination similar to that found in $[Cp^*_2Sm(\mu\text{-}Et)(\mu\text{-}Cl)\text{-}AlEt_2]_2$.[31]

The aluminum reagents R_2AlCl (R = Me, Et, ^{i}Bu) replace a carboxylate ligand with chloride in reactions with $[Cp^*_2Sm(O_2CC_6H_5)]_2$, but instead of forming a simple chloride complex like $[Cp^*_2SmCl]_3$, bimetallic lanthanide Al dichloro complexes $Cp^*_2Sm(\mu\text{-}Cl)_2AlR_2$ were isolated. An analogous reaction between $Cp^*_2Sm(THF)_2$ and Et_3Al gives $Cp^*_2Sm(THF)(\mu\text{-}\eta^2\text{-}Et)AlEt_3$, which contains the first Ln(III)-(η^2-Et) linkage. An attempt to prepare $Cp^*_2Ln(\mu\text{-}Cl)(\mu\text{-}R)AlR_2$ complexes instead gave $[Cp^*_2Y(\mu\text{-}Cl)(\mu\text{-}R)AlR_2]_x$; the Me complex is a dimer and the others are monomers.[32]

The ionic metallocene complex $[Cp^*_2Sc][BPh_4]$ was synthesized and structurally characterized. The anion interacts weakly with the metal centre through one of the Ph groups, and reacts with fluorobenzene and 1,2-difluorobenzene to yield $[Cp^*_2Sc(\kappa F\text{–}FC_6H_5)][BPh_4]$ and $[Cp^*_2Sc(\kappa^2F\text{-}1,2\text{-}F_2C_6H_4)][BPh_4]$. With the perfluorinated anion $[B(C_6F_5)_4]^-$, $[Cp^*_2Sc(\kappa^2F\text{–}C_6F_5)B(C_6F_5)_3]$ contact ion pairs are noted. The nature of the metal-fluoroarene interaction was studied by DFT calculations and by comparison with the corresponding THF adducts and is predominantly electrostatic.[33]

The $[BPh_4]^-$ ion in $[Cp^*_2Ln(\mu\text{-}Ph)_2BPh_2]$ can be readily displaced by alkyllithium or potassium to give oligomeric Me derivatives $[Cp^*_2LnMe]_n$ (Ln = La, Sm, Lu), while reaction of $[Cp^*_2Sm(\mu\text{-}Ph)_2BPh_2]$ with MeLi in toluene afforded the transmetalation product, $[Cp^*_2Sm(\eta^3\text{-}CH_2Ph)]$ and double-metalated $[[Cp^*_2Sm]_2(C_7H_6)]$, which was carboxylated by CO_2 to give $[Cp^*_2Sm(O_2CC_6H_4Me\text{-}3)]$. The same reaction with MeLi in benzene afforded $[Cp^*_2SmPh]_2$ and the dimetalation product, $[Cp^*_2Sm(\mu\text{-}1,4\text{-}C_6H_4)SmCp^*]$.[34]

The homoleptic complexes $Ln(AlMe_4)_3$ (Ln = Y, La, Nd, Lu) were reacted with Cp*H to yield the corresponding half-sandwich complexes $Cp^*Ln(AlMe_4)_2$ in high yield and purity. NMR spectroscopic studies revealed a highly dynamic nature of the bridging and terminal alkyl groups, even at −85°. In the solid state, the tetramethylaluminato ligands coordinate differently to the metal centre: one of the aluminate ligands adopts an unusual distorted μ:η^3 coordination mode, while the other bonds in a routine μ:η^2 fashion. An alcoholysis reaction of $Cp^*Y(AlMe_4)_2$ with $HOCH^tBu_2$ gave the heteroleptic complex $Cp^*Y(OCH^tBu_2)(AlMe_4)$. $Cp^*Nd(AlMe_4)_2$ was reacted with dehydrated periodic mesoporous SiO_2 MCM-41, affording surface-grafted $Cp^*Nd(AlMe_4)_2$@MCM-41. The half-metallocene bis(aluminate) complexes were converted into donor-free $[Cp^*LnMe_2]_3$ (Ln = Y, Lu) *via* stoichiometric THF-induced cleavage and reversibly regenerated by addition of trimethylaluminum.[35]

3.1.1 Ln with nitrogen-donor radicals.

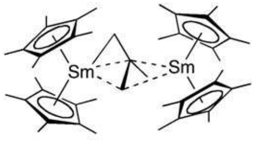
In an important study Booth and Andersen have provided evidence from XANES and magnetic studies that a species reported on in previous years, $[YbCp^*_2(bipy)]$, is in fact a molecular Kondo state with significant coupling between the metal centre and the ligand.[36] Related work is reported in Section 4 in the context of magnetic studies of cerocene.

Addition of 4′-cyano-2,2′:6′,2″-terpyridine (^{t}pyCN) to $[Cp^*_2Yb(OEt_2)]$ in toluene gave dark blue $[Cp^*_2Yb(^tpyCN)]$. The ^{t}pyCN ligand stabilizes the CT state by 60 mV more than that with the unsubstituted ^{t}py ligand complex and by 110 mV more than that in the unsubstituted bpy ligand complex. Magnetic susceptibility measurements corroborate the enhanced stabilization of the $4f^{13}\pi^{*1}$ configuration by the substituted terpyridyl ligand complex. Differing coordination modes for the ^{t}pyCN ligand to the ytterbocene centre also were confirmed by isolation and X-ray crystallographic characterization of complexes binding through either the cyano N of ^{t}pyCN or the three terpyridyl N atoms of ^{t}pyCN.[37]

An analysis of $[MCp^*_2(bipy)]$ (M = Ce, U) structures revealed that the extent of donation of electron density into the LUMO of bipy is more important in the actinide than in the lanthanide compound. Related adducts $[MCp^*_2(terpy)]I$, neutral complexes $[MCp^*_2(terpy)]$ and the salts $[MCp^*_2(terpy)][MCp^*_2I_2]$ were also prepared. Electron transfer rates were probed with electronic spectroscopy. Similar analyses of $[MCp^*_2(terpy)]$ shows that the U–N distances are much shorter, by 0.2 Å, than those expected from a purely ionic bonding model. This difference is believed to reflect the differing extents of electron transfer between the metal and the terpy ligand in the actinide compounds. The suggestion is also supported by small but systematic structural variations within the terdentate ligands, which strongly suggest that the LUMO of terpy is more filled in the actinide than in the lanthanide complexes and that significant contributions to the structures are made by the canonical forms $[U^{+4}Cp^*_2(terpy^{\bullet -})]I$ and $[U^{+4}Cp^*_2(terpy^{2-})]$.[38]

The synthesis and characterization of Sc(III) and Sc(II) complexes containing a $Cp^*Sc(R_2bpy)$ (R_2bpy = 4,4′-R_2-2,2′-bipyridine, R = H, Me) motif $[Cp^*_2Sc_2(\mu\text{-}I)_2(bpy)_2]$ and $[Cp^*_2Sc_2(\mu\text{-}Cl)_2(bpy)_2]$ were prepared. Analysis of the bond distances of the bipyridine ligands, together with IR and UV/vis spectroscopic data, suggest that the bipyridine ligands in these molecules exist as radical anions that display π–π interactions.[39]

The reaction of Me_3CCH_2Li, with $[Cp^*_2Sm][(\mu\text{-}Ph)_2BPh_2]$ gave the first f element trimethylenemethane dianion complex, $[Cp^*_2Sm]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}C(CH_2)_3]$, (**12**). Formation of the $[C_4H_6]^{2-}$ trimethylenemethane ligand from the $[C_5H_{11}]^{1-}$ neopentyl precursor can be explained by a combination of a β-Me elimination reaction to form isobutene and $[Cp^*_2SmMe]_3$, with subsequent C–H activation reactions. This sequence was modeled in several ways.[40]



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A series of Sc dihydrosilyl complexes $Cp^*_2ScSiH_2R$ was synthesized by addition of the appropriate hydrosilane to Cp^*_2ScMe. Studies of these complexes in the context of hydrocarbon activation led to discovery of catalytic processes for the dehydrogenative silation of hydrocarbons (including methane, isobutene and cyclopropane) with Ph_2SiH_2 *via* σ-bond metathesis.[41]

In structure determination work, variable-temperature 1D and 2D COSY ^1H NMR spectra of paramagnetic sandwich organolanthanides [Cp′LnL] (Ln = Sm(III), Sm(II), Nd(III); Cp′ = η^5-$C_5H^iPr_4$; L = Cp′, COT, BH_4) revealed that the solution structures appear to differ from structures previously determined in the solid state.[42]

The reaction of $[Cp^*_2LaH]_x$ with BEt_3 gives $Cp^*_2La[(\mu\text{-}H)(\mu\text{-}Et)_2BEt]$, and its THF adduct $Cp^*_2La(THF)[(\mu\text{-}H)(\mu\text{-}Et)BEt_2]$, and both were compared with that of the hydride-bridged tuckover complex $Cp^*_2La(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)$-$LaCp^*$.[43]

$C_5Me_4HPMe_2$ reacts with 1-adamantyl azide to form (adamantan-1-yl)-$NHPMe_2^+(C_5Me_4^-)$, which is metalated with $Lu(CH_2SiMe_3)_3(THF)_2$ to give the cyclopentadienyl-phosphazene CGC [({adamantan-1-yl}$NPMe_2${C_5Me_4})-$Lu(CH_2TMS)_2$].[44]

3.2 Other Cp ligands

In an interesting assessment of the factors that influence coordination of L to Ln(III) and An(III), reactions of azine molecules with the trivalent metallocenes $[M(C_5H_4R)_3]$ (M = Ce, U; R = Bu^t, $SiMe_3$) were studied. Lewis base adducts $[M(C_5H_4R)_3(L)]$ (L = pyridine, 3-picoline, 3,5-lutidine, 3-chloropyridine, pyridazine, pyrimidine, pyrazine, 3,5-dimethylpyrazine and s-triazine) were isolated, except where U(III) oxidized the ligand, *i.e.* 3-chloropyridine, pyridazine, pyrazine and s-triazine. In the pairs of analogous compounds of Ce(III) and U(III), *i.e.*, $[M(C_5H_4Bu^t)_3(L)]$ (L = pyridine, picoline) and $[M(C_5H_4SiMe_3)_3(L)]$ (L = pyridine, lutidine, pyrimidine and dimethylpyrazine), the M–N and av. M–C distances are longer for M = Ce than for M = U; however, within azine adducts of the same metallocene, no significant variation in M–L distance is noted. The equilibrium between $[M(C_5H_4R)_3]$, L and $[M(C_5H_4R)_3(L)]$ were studied by ^1H NMR spectroscopy, where the U ion clearly forms stronger bonds to L. Thermodynamic parameters indicate that the enthalpy–entropy compensation effect holds for these complexation reactions. Competition reactions of $[Ce(C_5H_4R)_3]$ and $[U(C_5H_4R)_3]$ with L show that the selectivity of L in favor of U(III) increases with the π donor character of the metallocene and is proportional to the π accepting ability of the azine molecule, consistent with greater covalency of the uranium complex.[45,46]

In a second study contrasting 4f and 5f complexes, $[UCp^*_2(dddt)]$ (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) was isolated and reduced with Na/Hg in the presence of 18-crown-6 to give the first uranium(III) dithiolene compound, $[Na(18\text{-}crown\text{-}6)(THF)_2][UCp^*_2(dddt)]$. The corresponding lanthanide complexes $[\{LnCp^*_2(dddt)K(THF)_2\}_2]$ (Ln = Ce, Nd) were also prepared and transformed into the cation–anion pairs $[K(15\text{-}crown\text{-}5)_2][LnCp^*_2(dddt)]$ (Ln = Ce, Nd). In these structures, the U–S and U–CCp* distances are shorter than those expected from a purely ionic bonding model; the relatively small folding of the dddt ligand suggests that the interaction between the C=C double bond and the metal centre is weak.

Relativistic DFT calculations reproduce experimental trends. A detailed orbital analysis shows that the shorter M–S bond length for U is related to significant uranium 5f orbital–ligand mixing. Comparison of the two $[UCp^*_2(dddt)]^{-,0}$ species reveals a higher ligand-to-metal donation in the case of the U(IV) complex.[47]

In structure reports, reaction of $[(Bu^tCp)_2Er(\mu\text{-}Cl)]_2$ with Bu^tLi afforded the trimetallic erbium tetrahydride complex $[Li(THF)_4][\{(Bu^tCp)_2Er(\mu\text{-}H)\}_3(\mu_3\text{-}H)]$ by β-hydrogen elimination.[48] In a short structural paper, the reaction of NaCp* and $SmCl_3$ is said to yield $[Cp^*_2Sm(\mu_2\text{-}Cl)_2Li(OEt_2)_2]$. The source of the lithium can only be guessed at.[49] The benzyl Cp complex $(C_6H_5CH_2C_5H_4)NdCl_2$ was used with $AlEt_3$ to polymerize butadiene.[50] The reaction of YCl_3 with two equivalents of $^tBuMe_2SiC_5H_4K$ in THF gave $[(^tBuMe_2SiC_5H_4)_2YCl]_2$.[51] $[Cp'_2LuCl]_2$ also shows the expected structure.[52] $[Cp_2(MeCp)Sm(THF)]$ was prepared.[53] Reaction of the fluorinated alcohol $(CF_3)_3$-$C_6H_2CH_2OH$ with $LnCp_3$ in a 1:1 molar ratio afforded the mono-alkoxide derivatives $Cp_2Ln(OCH_2RF)$ (Ln = Nd, Sm, Yb). With l a 3:1 ratio the homoleptic aryloxide is obtained.[54] Finally, $(EtSCH_2CH_2Cp)_2LnCl$ [Ln = Gd, Dy] and $Cp_2(EtSCH_2CH_2Cp)_2$-Ln (Ln = Yb, Sm, Dy, Y) were prepared from $LnCl_3$ or Cp_2LnCl in THF. In the chloride derivative, the pendant thioether coordinates to the metal centre.[55]

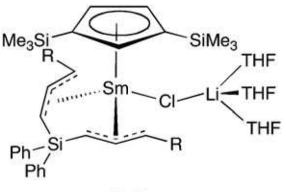
In proton transfer chemistry, treatment of Cp_3Yb in THF with 2,6-di(^{t}Bu)phenol, *N*,*N*-dimethyl-2-aminoethanol or *N*,*N*-diethyl-2-aminoethanol gave $[Cp_2Yb(O\text{–}C_6H_3{}^tBu\text{-}2,6)(THF)]$, $[Cp_2Yb(\mu\text{-}OCH_2CH_2NMe_2)]_2$ and $[Cp_2Yb(\mu\text{-}OCH_2CH_2\text{-}NEt_2)]_2$, respectively. In solution the tethered NMe_2 ligands dissociate reversibly.[56]

The reaction of KCp″ with NdI_3 affords two products, $Cp''NdI_2(THF)_{1.25}$ and $Cp''_2NdI(THF)_2$. The reaction of YCl_3 with the ansa-bis(allyl) ligand K_2-$[_3\text{-}(C_3H_3SiMe_3\text{-}1)_2SiPh_2]$ in THF/OEt_2 gave$[Y\{3\text{-}(\eta^3\text{-}C_3H_3SiMe_3\text{-}1)_2SiPh_2\}_2\{\mu\text{-}K\}\text{-}(THF)_{0.5}(Et_2O)_{1.5}]_\infty$ as a bright orange solid. Reaction of $Cp''_2LnCl_2Li(THF)_2$ (Ln = Y or Sm) with $[K_2\{3\text{-}(\eta^3\text{-}C_3H_3SiMe_3\text{-}1)_2SiMe_2\}]$ in THF led to the ligand redistribution product $[Li(OEt_2)(THF)_3][Ln\{3\text{-}(\eta^3\text{-}C_3H_3SiMe_3\text{-}1)_2SiMe_2\}_2]$ (Ln = Y, Sm) (**10**). Reaction of $Cp''_2YCl_2Li(THF)_2$ with $[K_2\{3\text{-}(\eta^3\text{-}C_3H_3SiMe_3\text{-}1)_2SiPh_2\}]$ afforded the Y/K polymer, while $Cp''_2SmCl_2Li(THF)_2$ and $[K_2\{3\text{-}(\eta^3\text{-}C_3H_3SiMe_3\text{-}1)_2SiPh_2\}]$ gave a red crystalline solid, $\{[Cp''Sm\{3\text{-}(\eta^3\text{-}C_3H_3SiMe_3\text{-}1)_2SiPh_2\}\text{-}(\mu\text{-}Cl)Li(THF)_3]\}$ (**13**). Above 50° the NdI compound as well as $Cp''_2LnCl(THF)$ and Cp''_2YCl initiate the rapid polymerization of ε-CL. The anionic complexes and $[Y\{3\text{-}(\eta^3\text{-}C_3H_3SiMe_3\text{-}1)SiMe_2\}_2\{\mu\text{-}K(THF)\}\cdot(THF)_n]_\infty$ are very active for both ε-CL and MMA polymerization at room temperature. The stereoselectivity is dependent on the solvent and the countercation, with lithium salts producing syndio-rich PMMA.[57] New pendant phenyl-substituted Cp compounds were reported. Both monomeric, unsolvated $(PhCMe_2C_5H_4)_2LnCl$ (Ln = Er, Sm, Gd, Y, Nd); and dimeric, unsolvated $[(PhCH_2CMe_2C_5H_4)_2LnCl]_2$ (Ln = Gd, Y, Sm, Er) were prepared. The complexes are efficient catalysts for the polymerization of MMA in conjunction with $AlEt_3$ or NaH.[58]

3.3 Ansa complexes

In addition to the complexes described here, there is an extensive series of ansa compounds to be found in the Organic Synthesis section, as they are applied to hydroamination processes. Reactions of ionic $[(Cp\text{–}CMe_2\text{–}Flu)YCl_2][Li(ether)_4]$ ($Cp{=}C_5H_4$, Flu = 9-$C_{13}H_8$) with equimolar amounts of RLi give alkyl mono-THF complexes $[(Cp\text{–}CMe_2\text{–}Flu)]Y(R)(THF)$ (R = R′, R″) in high yields. The solid-state structure of the disilyl derivative shows ring slippage of the fluorenyl moiety. Hydrogenolysis of these alkyls with H_2 or $PhSiH_3$ gives the hydride $\{[(\mu\text{:}\eta^5,\eta^5\text{-}Cp\text{–}CMe_2\text{–}Flu)]Y(\mu\text{-}H)(THF)\}_2$, a dimeric structure with both bridging Cp–CMe$_2$–Flu and hydride ligands. Reaction of the chloride with BzMgBr gives, instead of a benzyl derivative, the neutral base-free bromo complex $[(\eta^5,\eta^5\text{-}Cp\text{–}CMe_2\text{–}Flu)Y(\mu\text{-}Br)]_2$. Introduction of a bulky ^{t}Bu substituent on the Cp ring enabled the preparation of the neutral chloro complex $[((3\text{-}^tBuCp)\text{–}CMe_2\text{–}Flu)YCl(THF)]$.

Further reaction with LiR″ gave the THF-free alkyl complex [(3-^{t}BuCp)–CMe$_2$–Flu)YR″].[59]



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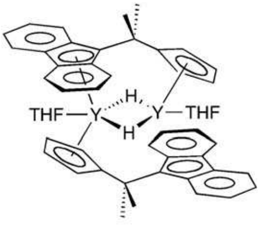
With indenyl components, mesomeric divalent 1,1′-(3-oxapentamethylene)-bridged bis(indenyl)metallocenes, *meso*-[O(CH$_2$CH$_2$C$_9$H$_6$)$_2$]Ln(DME) (Ln = Sm, Yb), were synthesized from *rac*/*meso*-[O(CH$_2$CH$_2$C$_9$H$_6$)$_2$]LnCl (Ln = Sm, Yb) or LnI$_2$ (Ln = Sm, Yb) starting materials. Unbridged (CH$_3$OCH$_2$CH$_2$C$_9$H$_6$)$_2$Ln (Ln = Sm, Yb) were also synthesized from LnI$_2$, and stereoselective polymerization of MMA was investigated.[60]

Ansa ligands with fluorenyl components were both interesting and useful. A reaction of pyridine with the constrained geometry fluorenyl(hydrido)yttrium complex {[(3,6-^{t}Bu$_2$Flu)SiMe$_2$N^{t}Bu]Y(H)(THF)}$_2$ (**14**) selectively gave the 1,4-addition product [η^5:η^1-(3,6-^{t}Bu$_2$Flu)SiMe$_2$N^{t}Bu]Y(η^1-NC$_5$H$_6$)(py)$_2$.[61]



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In the patent literature, (FluR″Cp)M(η^3-C$_3$R′$_5$)(ether)$_n$ were manufactured for use as catalysts for controlled polymerization of polar and nonpolar monomers.[62] Metallocene complexes of Group IIIB metals having a fluorenyl ligand bonded to a hydrocarbyl-substituted Si which is, in turn, bonded to a (substituted) N so as to constrain the geometry of the fluorenyl ligand, were also applied to the controlled polymerization of polar or nonpolar monomers.[63]

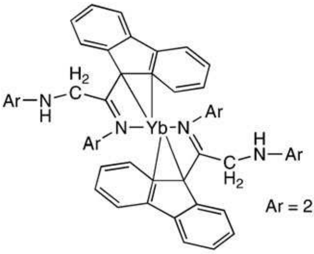
A Yb compound with the ansa-bridged PhEtSiIndCp ligand was also reported.[64]

Reaction of the divalent ansa-bridged complex [*rac*-(CH$_2$-1-C$_9$H$_6$)$_2$Yb(THF)$_2$] and its unlinked indenyl analog with ^{t}BuN=CHCH=N^{t}Bu (DAD) in toluene gave the paramagnetic complexes [(C$_9$H$_7$)$_2$Yb(DAD)] and [*rac*-(CH$_2$-1-C$_9$H$_6$)$_2$Yb-(DAD)]. Magnetic and spectroscopic data suggest that in the solid state and non-coordinating media both complexes are Yb(III) derivatives containing the DAD radical-anion, whereas in THF solution, the ^{1}H NMR and UV/visible spectra are consistent with divalent Yb.[65]

3.4 Indenyl, fluorenyl, and other aromatic π-complexes

In a reaction similar to that described in the previous section, (C$_9$H$_7$)$_2$Yb(THF)$_2$ reacts with 2,2′-bipyridine afforded the diamagnetic (C$_9$H$_7$)$_2$Yb(bipy) compound, whose structure was established by X-ray diffraction. Under similar conditions, the reaction with 1,4-bis(2,6-diisopropylphenyl)-1,4-diazabuta-1,3-diene (DiAD) led to oxidation of Yb giving rise to the paramagnetic (C$_9$H$_7$)$_2$Yb(DiAD) complex. The behaviour of these species in the solid state and solution is analogous to those for the simple DAD complexes.[66] Surprisingly, the reactions of divalent [Flu$_2$Yb(THF)$_2$]

with diazadienes (2,6-^{i}Pr$_2$C$_6$H$_3$)N=CRCR=N(2,6-^{i}Pr$_2$C$_6$H$_3$) (R = H, Me) result in unexpected Yb(II) complexes, which arise either from the coupling of the fluorene and the diazadiene ligands (when R = H, **15**) or from C–H bond activation of the diazadiene ligand (when R = Me, **16**).[67]



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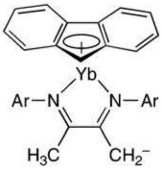

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Donor functionalized indenyl ligand systems were developed with enthusiasm. Both Yb(II) and Eu(II) complexes were obtained by tandem silylamine elimination/homolysis of Ln–N (Ln = Yb, Eu) bonds. The interaction of $C_9H_7CH_2CH_2CH_2NMe_2$ with $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu) in refluxing toluene produced divalent $[(\eta^5{:}\eta^1\text{-}C_9H_6CH_2CH_2CH_2NMe_2)_2Ln]$ [Ln = Yb, Eu]. Treatment of $Me_2Si(Me_2NCH_2CH_2C_9H_6)(NH^tBu)$ with $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ in toluene afforded divalent $[\eta^5{:}\eta^1\text{-}Me_2Si(Me_2NCH_2CH_2C_9H_5)(NH^tBu)]_2Eu$. The interaction of $Me_2NCH_2CH_2C_9H_6SiMe_3$ with $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ produced divalent $[\eta^5{:}\eta^1\text{-}(Me_2NCH_2CH_2C_9H_5SiMe_3)]_2Eu$. Treatment of $Me_2NCH_2CH_2C_9H_7$ with $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ in toluene gave divalent $(\eta^5{:}\eta^1\text{-}Me_2NCH_2CH_2C_9H_6)_2Eu$. Catalytic activities were examined; all of the complexes can function as single-component MMA polymerization catalysts.[68] Reaction of 3-(2-pyridylmethyl)indenyl lithium with $LnI_2(THF)_2$ (Ln = Sm, Yb) in THF produced the divalent organolanthanides $(C_5H_4NCH_2C_9H_6)_2Ln(THF)$ (Ln = Sm, Yb), and with $LnCl_3$ (Ln = Nd, Sm, Yb) to give bis(3-(2-pyridylmethyl)indenyl)lanthanide chlorides $(C_5H_4NCH_2C_9H_6)_2LnCl$ (Ln = Nd, Sm); the Yb compound spontaneously reduced to Yb(II). The divalent compounds show moderate polymerization activities for ε-CL.[69] Similarly, reactions of two tetrahydrofurfuryl indenyl lithium with anhydrous $LnCl_3$ in THF afforded bis(tetrahydrofurfurylindenyl) lanthanide chlorides $(C_4H_7OCH_2C_9H_6)_2LnCl$, Ln = La, Pr, Lu. Structures of the La and Lu compounds were determined.[70] The reaction of methoxyethyl functionalized indene compounds [C_9H_6-1-*R*-3-CH_2CH_2OMe, R = ^{t}BuNHSiMe$_2$, Me$_3$Si, H] with $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ [Ln = Yb, Eu] produced new Yb(II) and Eu(II) complexes *via* tandem silylamine elimination/homolysis of the Ln–N (Ln = Yb, Eu) bond. Treatment of the Ln(III) amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ [Ln = Yb, Eu] with two equivalents of these ligands, produced, after workup, the Yb(II) complexes $[\eta^5{:}\eta^1\text{-}Me_2Si(MeOCH_2CH_2C_9H_5)(NH^tBu)]_2Yb$, $(\eta^5{:}\eta^1\text{-}MeOCH_2CH_2C_9H_5SiMe_3)_2Yb$, $(\eta^5{:}\eta^1\text{-}MeOCH_2CH_2C_9H_6)_2Yb$ and the corresponding Eu(II) complexes $[\eta^5{:}\eta^1\text{-}Me_2Si(MeOCH_2CH_2C_9H_5)(NH^tBu)]_2Eu$, $(\eta^5{:}\eta^1\text{-}MeOCH_2CH_2C_9H_5SiMe_3)_2Eu$ and $(\eta^5{:}\eta^1\text{-}MeOCH_2CH_2C_9H_6)_2Eu$. All of the new products were single-component MMA polymerization catalysts.[71]

The syntheses and reactivities of Y alkyl and hydride complexes containing a sterically demanding heptamethylindenyl (Ind*) ligand were reported. Complex reaction mixtures were obtained when Ind*$_2$YCl(THF) was treated with $KSi(SiMe_3)_3$ or $(THF)_3LiSi(SiMe_3)_3$, although it reacted readily with MeLi to yield the Me complex Ind*$_2$YMe(THF). Treatment of the methyl compound with H_2 or $PhSiH_3$ gave the base-stabilized hydride complex Ind*$_2$YH(THF). The base-free chloride complex Ind*$_2$YCl was also synthesized by metathesis in toluene. Treatment of this chloride with LiR″ yielded the base-free alkyl complex Ind*$_2$YR″, a compound that reacts with H_2 or $PhSiH_3$ but not CH_4.[72]

In structure reports, $[Na(THF)_6][(\eta^5\text{-Ind})_3Yb(\mu\text{-Cl})Yb(\eta^5\text{-Ind})_3]$ was described. The product reacted further with Na to form the reduced species $Ind_2Yb(THF)_2$.[73] Reaction of $LnCl_3$ with 2-phenylindenyl (2-PhInd) lithium in THF resulted in $(2\text{-PhInd})LnCl_2$ (Ln = La, Pr, Nd, Sm, Gd, Dy, Yb, Y).[74]

Substituted indenyl ligands with a variety of tethered pyridine donors were used to form stable Ln(II) compounds.[75] Furfuryl- and tetrahydrofurfuryl-functionalized indenyl ligands were also obtained. Treatments of trivalent $(N'')_3Ln(\mu\text{-Cl})Li(THF)_3$ (Ln = Yb, Eu) with $C_4H_7OCH_2C_9H_7$, $C_4H_3OCH_2C_9H_7$, $C_4H_7OCH_2C_9H_6SiMe_3$ or $C_4H_3OCH_2C_9H_6SiMe_3$ afforded the corresponding divalent complexes. Studies on the catalytic activities of these complexes showed that having silyl group functionalized indenyl ligands imparts high catalytic activities on ε-CL polymerization.[76] Structural descriptions of divalent Sm, Eu, and Yb compounds with O-heterocycle-substituted indenyl were also published.[77]

In slightly more applied work, a 1,2-bis(indenyl)ethane-derived ytterbium amide $[(CH_2)_2(C_9H_6)_2YbN'']$ was synthesized by the reaction of 1,2-bis(indenyl)ethane with $(N'')_3Yb(\mu\text{-Cl})Li(THF)_3$ in toluene.[78]

Finally, in this section, while in the past we have not included fullerene compounds, there are reports describing the synthesis and characterization of discrete, 'pure', Ln-fullerene materials that seem appropriate to include here. The 'molecular' complex $Cp_2La(\eta^2\text{-}C_{60})$ was prepared by the reaction of C_{60} with $LaCp_3$ though no structural information was obtained.[79] In a different direction, three isomers of Y_2C_2 endohedral metallofullerenes, *i.e.*, $(Y_2C_2)@C_{82}$ were synthesized and isolated for the first time. The structures were characterized by ^{13}C NMR measurements, identifying C_s, C_{2v}, and C_{3v} molecular symmetries. A pure diyttrium metallofullerene, $Y_2@C_{82}$ was also was synthesized and structurally characterized.[80]

A structural analysis of the Sc_3C_{82} molecule by ^{13}C NMR spectroscopy and X-ray single-crystal structure analysis revealed that the correct formulation is $Sc_3C_2@C_{80}$. Crystal structures were determined for the adamantyl derivatives, $Sc_3C_2@C_{80}(Ad)$ and $(Bu_4N)[Sc_3C_2@C_{80}(Ad)]$.[81]

4. COT chemistry

Cerocene, that controversial molecule which supposedly contains the strong Ce(IV) oxidant next to the strong COT^{2-} reductant, is once again in the spotlight. In this continuing saga, an efficient synthesis of $Ce(COT)_2$ is found in the reaction of $K[Ce(COT)_2]$ with allyl bromide. The product reacts only slowly with UCl_4 to give uranocene. In solution studies, $K[Ce(COT)_2]$ and cerocene were found to undergo electron exchange on the NMR timescale that was shown by electrochemistry to be reversible with a relatively low reduction potential (−0.6 V *vs.* normal H electrode). The corresponding praseodymium salt, $K[Pr(COT)_2]$, does not undergo comparable reversible oxidation, and the overall conclusion is that the chemical properties of cerocene resemble those of di-π-([8]annuleneactinide(IV) compounds.[82] $Ce(COT'')_2$ was examined with absorption, MCD and luminescence spectra at room temperature as well as at low temperatures, from which the authors suspect they are dealing with a Ce(III) compound[83] confirming earlier XANES work. In addition XANES and magnetic studies on $Ce(COT)_2$ lend further support to the idea that this molecule is an example of a molecular Kondo state with a trivalent Ce centre.[36]

New COT compounds were more plentiful. Neutral triple-decker complexes of the heavy alkaline earth metals and ytterbium with tetraisopropylcyclopentadienide anions as terminal ligands and a cyclooctatetraene dianion as a middle deck have been synthesized from tetraisopropylcyclopentadienyl metal halide precursors and disodium cyclooctatetraenide. The neutral triple-decker metallocene $[\{(C_5{}^iPr_5)Yb\}_2(C_8H_8)]$ was prepared from Yb metal, cyclooctatetraene, and the free $^\bullet C_5{}^iPr_5$ radical. This complex, along with Ca and Ba derivatives, has an almost linear arrangement of ring centres and metal that are modeled quite accurately with DFT calculations.[84] A series of COT bis(phosphinimino)methanide complexes of Y and the lanthanides, [{CH(PPh$_2$NSiMe$_3$)$_2$}Ln(η^8-C$_8$H$_8$)] (Ln = Y, Sm, Er, Yb, Lu), were synthesized by various metathesis routes. The solid-state structures of these complexes show that both ligands completely shield the metal centre, resulting in inequivalent M–L bonds. A moderate hydroamination/cyclization catalytic activity at elevated temperature was observed.[85] Similarly, the complexes [{CH(PPh$_2$NSiMe$_3$)$_2$}Ln(η^8-COT″)] (Ln = Y, Er) were characterized by single crystal X-ray diffraction.[86]

In structural work, characterization of the monomeric complexes (η^8-COT)(μ-terphenyl)Ln-μ-Cl-[Li(THF)$_3$] (Ln = Y,[87] Lu[88]) revealed σ-bonded terphenyl ligands. Similarly, the bis(phosphinimino)methanide complex [{CH(PPh$_2$NSiMe$_3$)$_2$}Sm(η^8-COT)] was isolated, structurally characterized, and found to exhibit moderate activity as a catalyst for the hydroamination/cyclization reaction of aminoolefins and aminoalkynes.[89] Mixed diphosphinylamido/COT complexes are discussed in the amido section.[90]

5. Carborane-based supporting ligands

Although exotic at first sight, substituted carboranes with pendant donor ligands are proving their worth as ancillary ligands, capable of stabilizing the metal centre while permitting catalytic reactivity. In this grouping are compounds with O, N, and P donor ligands. Reactions of 1,2-(MeOCH$_2$CH$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ with LnCl$_3$ in the presence of excess Li or Na metal gave the half-sandwich 13-vertex closo-metallacarboranes [{η^7-[(CH$_3$OCH$_2$CH$_2$)$_2$C$_2$B$_{10}$H$_{10}$]Er}{Na(MeCN)$_2$}]$_2$ and [{η^7-[(CH$_3$OCH$_2$CH$_2$)$_2$C$_2$B$_{10}$H$_{10}$]Y}{Li(THF)$_3$}]$_2$. [[{[η^7-(CH$_3$OCH$_2$CH$_2$)C$_2$B$_{10}$H$_{11}$]Er(THF)}{Na(MeCN)(THF)}]$_2$]$_n$ and [{[η^7-(CH$_3$OCH$_2$CH$_2$)C$_2$B$_{10}$H$_{11}$]Y(THF)}{Na(THF)$_3$}]$_2$ were prepared in a similar manner from the monosubstituted o-carborane 1-(CH$_3$OCH$_2$CH$_2$)-1,2-C$_2$B$_{10}$H$_{11}$, LnCl$_3$, and excess Na in THF. The Lewis base-functionalized sidearms have intramolecular effects on the coordination environments of the central metal atom between the donor atoms of the sidearms and Lewis acidic metal ions, but do not change the gross structures of the 13-vertex lanthanacarboranes.[91] Similar reactions gave the complex salts [{[η^5:σ-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)]Ln(THF)(μ-Cl)$_3$Ln[η^5:η^1:σ- Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)]}$_2${Li(THF)}][Li(THF)$_4$] (Ln = Y, Yb). Upon heating, the Yb compound was converted into [η^5:η^1:σ-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)]Yb(THF)(μ-Cl)$_2$Yb[η^5:η^1:σ-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)] by eliminating LiCl. Treatment of the complex salts with metal amides gave [η^5:η^1:σ-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)]Y(NHC$_6$H$_3$-2,5-^{t}Bu$_2$)(μ-Cl)Li(THF)$_3$ or [η^5:η^1:σ-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)]Yb(NHC$_6$H$_3$-2,6-^{i}Pr$_2$)(μ-Cl)Li(THF)$_3$. An equimolar reaction of SmI$_2$ with the di-lithium salt in THF gave, after addition of LiCl, [{[η^5:σ-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)]$_2$Sm}{Li(THF)}]$_n$ and [{η^5:η^1:η^6-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)Sm}$_2$(μ-Cl)][Li(THF)$_4$]. In sharp contrast, a less reactive YbI$_2$ produced only the salt metathesis product [η^5:η^1:σ-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)]Yb(DME)(THF), that reacts further to give ionic {[(μ-η^5:η^2):η^1:σ-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)]$_2$Yb}{Li(THF)$_2$}$_2$.[92]

Tethered amido ligands were also described, such as [[Me$_2$Si(η^5-C$_9$H$_5$CH$_2$CH$_2$NMe$_2$-κN)(C$_2$B$_{10}$H$_{10}$-κC$_2$)]YbCl$_2$][Li(THF)$_4$], which was converted stepwise on heating to [[Me$_2$Si(η^5-C$_9$H$_5$CH$_2$CH$_2$NMe$_2$-κN)(C$_2$B$_{10}$H$_{10}$-κC$_2$)]$_2$Yb$_2$(μ-Cl)$_3$][Li(THF)$_4$] and finally to [[Me$_2$Si(η^5-C$_9$H$_5$CH$_2$CH$_2$NMe$_2$-κN)(C$_2$B$_{10}$H$_{10}$-κC$_2$)]$_2$Yb$_2$(μ-Cl)$_2$] *via* the elimination of LiCl. Treatment of the Yb$_2$Li product or its Sm analog with sodium amide gave [[Me$_2$Si(η^5-C$_9$H$_5$CH$_2$CH$_2$NMe$_2$-κN)(C$_2$B$_{10}$H$_{10}$-κC$_2$)]YbNHAr] (**17**) or [[Me$_2$Si(η^5-C$_9$H$_5$CH$_2$CH$_2$NMe$_2$-κN)(C$_2$B$_{10}$H$_{10}$-κC$_2$)]Sm(μ-Cl)(μ-NHAr)Li(THF)] (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$), while an equimolar reaction with SmI$_2$ generated, after addition of LiCl, [[Me$_2$Si(η^5-C$_9$H$_5$CH$_2$CH$_2$NMe$_2$-κN)][μ-η^6:η^6-(C$_2$B$_{10}$H$_{10}$)$_2$]Sm$_2$(μ-Cl)][Li(THF)$_4$]. In sharp contrast, a less reactive YbI_2 reacted in THF, producing only the metathesis product $[[Me_2Si(\eta^5\text{-}C_9H_5CH_2CH_2NMe_2\text{-}\kappa N)(C_2B_{10}H_{10}\kappa\text{-}C_2)]Yb(DME)]$, a complex that reacts further to give the ionic complex $[[(\mu\text{-}\eta^5{:}\eta^2){:}\eta^1{:}\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2NMe_2)(C_2B_{10}H_{10})]_2Yb[Li(THF)_2]_2]$.[93]

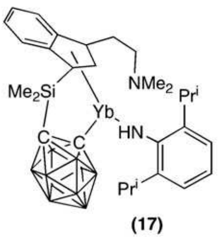
Phosphorus-bridged ligands were also prepared, including the divalent complex $[\eta^5{:}\sigma\text{-}{}^iPr_2NP(C_9H_6)(C_2B_{10}H_{10})]Yb(DME)_2$, which reacts further with the monolithium ligand to give trivalent $[\{\eta^5{:}\sigma\text{-}{}^iPr_2NP(C_9H_6)(C_2B_{10}H_{10})\}_2Yb][Li(THF)_3(Et_2O)]$. In comparison, treatment of SmI_2 with $[{}^iPr_2NP(C_9H_6)(C_2B_{10}H_{10})]Li_2(OEt_2)_{1.5}$ generated trivalent $[\{\eta^5{:}\sigma\text{-}{}^iPr_2NP(C_9H_6)(C_2B_{10}H_{10})\}_2Sm][Li(DME)_3]$. Reaction of $LnCl_3$ with two equivalents of $[{}^iPr_2NP(C_9H_6)(C_2B_{10}H_{10})]Li_2(OEt_2)_{1.5}$ gave ionic $[\{\eta^5{:}\sigma\text{-}{}^iPr_2NP(C_9H_6)(C_2B_{10}H_{10})\}_2Ln][Li(DME)_n]$ (Ln = Sm, Nd, Er; Y). Reaction between equimolar amounts of $LnCl_3$ and $[{}^iPr_2NP(C_9H_6)(C_2B_{10}H_{10})]Li_2(OEt_2)_{1.5}$ resulted in the isolation of the lanthanocene chlorides $[\{[\eta^5{:}\sigma\text{-}{}^iPr_2NP(C_9H_6)(C_2B_{10}H_{10})]LnCl\}_2(\mu\text{-}Cl)_3Li(DME)][Li(DME)_3]_2$ (Ln = Er, Y). The chloro groups in these complexes can be replaced by other moieties such as borohydride. However, reaction of the Y compound with KBz afforded the unexpected compound $\{[\eta^5{:}\sigma\text{-}{}^iPr_2NP(C_9H_6)(C_2B_{10}H_{10})]_2Y\}\{(\eta^6\text{-}C_6H_5CH_3)_2K\}$.[94] Heteroleptic dimers of the type $[(\eta^5\text{-}2,4\text{-}(Me)_2Cp)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Ln]_2$ (Ln = Tb, Er) were prepared as orange and yellow solids, respectively.[95]

Deliberate, stoicheiometric hydrolysis of closo-exo-5,6-$Na(THF)_2$-1-$Na(THF)_2$-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4/LnCl_3$ (Ln = La, Nd, Gd, Tb, Ho, Lu) with H_2O yielded the new oxo clusters $[[\eta^5\text{-}1\text{-}Ln(THF)_n\text{-}2,4\text{-}(SiMe_3)_2\text{-}2,4\text{-}C_2B_4H_4]_4(\mu\text{-}Cl)_2(\mu_4\text{-}O)]_y THF$ (Ln = La, Nd, Gd, Tb, Ho, Lu) (**18**). The X-ray structure shows Ln–H–B bridges.[96]

Finally, metathesis reactions produced the dimeric half-sandwich "carboranes adjacent" [closo-1-(X)-1,1-$(THF)_2$-2,3-$(SiMe_3)_2$-1-$Ln(\eta^5\text{-}C_2B_4H_4)]_2$ along with one equivalent of the neutral nido-carborane precursor, 2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$.[97]

Reactions of $[nido\text{-}(Me_2NCH_2CH_2)RC_2B_{10}H_{10}]Na_2$ (R = H, $MeOCH_2CH_2$, $Me_2NCH_2CH_2$) with $SmI_2(THF)_x$ gave metallacarboranes with η^7-arachno-carboranyl ligands, in which the heteroatom-containing pendant sidearms are both electronically and entropically necessary for the formation of complexes with the central metal ions in the highest oxidation state. The reaction mechanism for the electron transfer step was clarified by DFT/B3LYP calculations.[98]

A related series of 13-vertex closo-lanthanacarboranes with pendant tertiary amine functional groups were also reported,[99,100] as was a series of Cp compounds with dioxoboryl substituents.[101]



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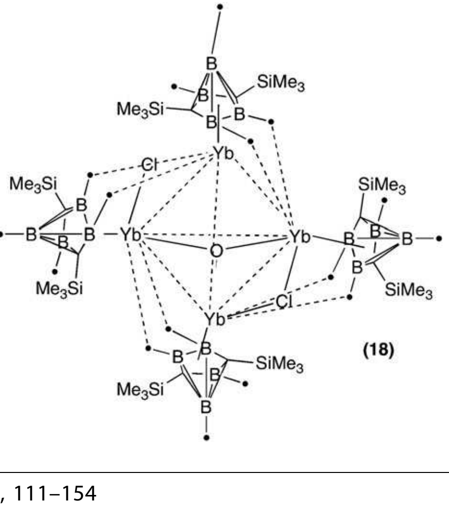

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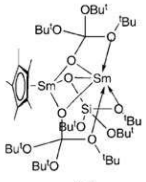
6. Redox chemistry

Dimeric [Cp(THF)Sm(μ-η^2:η^2-N_2Ph_2)]$_2$ was isolated from a disproportionation redox reaction of divalent $Cp_2Sm(THF)$ with azobenzene. In the structure each samarium atom is involved in two single bonds (one to each N_2Ph_2 unit) and two donor bonds (one to each N_2Ph_2 unit).[102] Similarly, $MeCp_2Sm(THF)$ reacted with carbodiimides (RN=C=NR) (R = ^{i}Pr or Cy) in the presence of HMPA to give, *via* a reductive coupling, the corresponding bimetallic oxalamidino complex [μ-$C_2(NR)_4$][$MeCp_2Sm(HMPA)$]$_2$.[103] Also, N_2 was reduced with diamagnetic Ln(III) complexes using a combination of a trivalent metallocene and potassium graphite. Both [$(C_5Me_4H)_3La$] and [$Cp^*{}_2La$][BPh_4] reduced dinitrogen in the presence of KC_8 to give structures containing the $[N{=}N]^{2-}$ anion.[104]

The reaction of $Cp^*{}_2Sm(THF)_2$ with $({}^{t}BuO)_3SiOH$ in toluene gave the unsymmetric binuclear Sm(II) complex [Cp*Sm{μ-OSi$(O^tBu)_3$}$_3$Sm] (**19**). Addition of excess HMPA to a toluene solution of this product gave Cp*Sm{OSi$(O^tBu)_3$}-$(HMPA)_2$ as the only isolable product, while azobenzene in toluene gave the corresponding binuclear Sm(III) azobenzene-dianion complex [Cp*Sm{μ-OSi-$(O^tBu)_3$}$_2$(μ,η^1:η^2-N_2Ph_2)SmOSi$(O^tBu)_3$]. When (**19**) was treated with ArOH (Ar = $C_6H_2{}^{t}Bu_2$-2,6-Me-4) or phenylacetylene in toluene, a novel trinuclear Sm(II)/Sm(III) mixed valence inverse sandwich complex, [{$({}^{t}BuO)_3SiO$}$_3$Sm(μ,η^5:η^5-Cp*)-Sm{μ-OSi$(O^tBu)_3$}$_3$Sm] (**20**), was isolated which could alternatively be obtained in higher yields by reaction of (**14**) with one equivalent of either Sm{OSi$(O^tBu)_3$}$_3$-$(THF)_2$ or [Sm{μ-OSi$(O^tBu)_3$}{OSi$(O^tBu)_3$}$_2$]$_2$. Similarly, the reactions of (**19**) with Gd{OSi$(O^tBu)_3$}$_3(THF)_2$ and $Sm(OSiPh_3)_3(THF)_3\cdot(THF)$ yielded the corresponding Sm(II)/Gd(III) heterometallic complex [{$({}^{t}BuO)_3SiO$}$_3$Gd(μ,η^5:η^5-Cp*)Sm-{μ-OSi$(O^tBu)_3$}$_3$Sm] and the Sm(II)/Sm(III) mixed valence complex [{Ph_3SiO}$_3$Sm (μ,η^5:η^5-Cp*)Sm{μ-OSi$(O^tBu)_3$}$_3$Sm], respectively. The reaction of (**19**) with the Sm(II) silylamido complex Sm{$N(SiMe_3)_2$}$_2(THF)_2$ in toluene yielded a linear pentanuclear Sm(II) ion-pair complex, [Sm{μ-OSi$(O^tBu)_3$}$_3$Sm(μ,η^5:η^5-Cp*)Sm-{μ-OSi$(O^tBu)_3$}$_3$Sm][Sm{$N(SiMe_3)_2$}$_3$] (**21**).[105]

Finally, Sm(II) has once again been used to cleave C–Se bonds, this time resulting in the formation of the heterometallic ionic cluster [$(THF)_8Ln_4Se(SePh)_8$]-[$Zn_8Se(SePh)_{16}$].[106]



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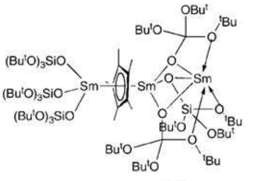

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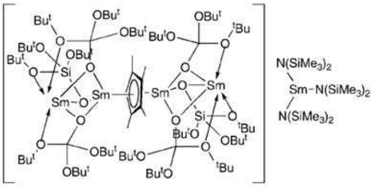

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7. Nitrogen-based ancillary ligand systems

7.1 Amido ligands

Amido compounds continue to attract significant attention because of the facility with which amido substituents can be tailored, the ease of selecting denticity, and their resultant applications in organic transformations, including cyclization reactions and polymerizations. New diamidoamine yttrium complexes [Y(Mes_2N_2NMe)-{$N(SiHMe_2)_2$}(THF)] ($Mes_2N_2NMe_2{}^{-}$ = (2,4,6-$Me_3C_6H_2NCH_2CH_2)_2NMe^{2-}$)), [Y($Ar_2N_2NMe$){$N(SiMe_3)_2$}], and [Y($Ar_2N_2NMe$)(o-$C_6H_4CH_2NMe_2$)] ($Ar_2N_2$-$NMe^{2-}$ = $(ArNCH_2CH_2)_2NMe^{2-}$ with Ar = 2,4,6-$Me_3C_6H_2$, 2,6-$Et_2C_6H_3$, 2,6-$Cl_2C_6H_3$) were prepared by transamination or arene elimination reactions. The structures of [Y(Mes_2N_2NMe){$N(SiHMe_2)_2$}(THF)] and [Y{(2,6-$Et_2C_6H_3)_2N_2N$-Me}(*o*-$C_6H_4CH_2NMe_2$)] are trigonal bipyramidal, where the amine donor and coordinated THF in $[Y(Mes_2N_2NMe)\{N(SiHMe_2)_2\}(THF)]$, and both amine donors in $[Y\{(2,6\text{-}Et_2C_6H_3)_2N_2NMe\}(o\text{-}C_6H_4CH_2NMe_2)]$, occupy axial positions. All complexes catalyze intramolecular hydroamination of aminoalkynes and aminoalkenes. Those having bis(trimethylsilyl)amido or $(o\text{-}C_6H_4CH_2NMe_2)$ ligands show significantly higher activity than the complex containing the bis(dimethylsilyl)amido ligand, whose activity is impeded by sluggish initiation rather than by THF coordination. $[Y(Mes_2N_2NMe)(o\text{-}C_6H_4CH_2NMe_2)]$ decomposes by a first-order rate law. The corresponding 2,6-diethylphenyl- and 2,6-dichlorophenyl-substituted complexes are significantly more stable. The electron-withdrawing effect of the dichlorophenyl substituents increases the stability of the catalyst toward protonolysis, as exemplified by a superior activity in the cyclization of pent-4-enylamine and 5-phenylpent-4-ynylamine. Ring-closing of 1-methylpent-4-enylamine proceeds with high *trans* selectivity and good activity, and cyclization of 2-allyl-2-methylpent-4-enylamine gave a mixture of endo,exo- and exo,exo-2,4,6-dimethyl-1-aza-bicyclo[2.2.1]heptane.[107]

Use of the bulky cyclopentadienyl ligand Cp''' allows for the isolation of $(Cp''')LaI_2(py)_3$ and $(Cp''')_2LaI(py)$. Addition of KNHAr (Ar = $2,6\text{-}{}^iPr_2C_6H_3$) to the dihalide in THF generates the mono-anilido compound $(Cp''')LaI(NHAr)(THF)_2$, which may be converted to the more stable pyridine adduct $(Cp''')LaI(NHAr)(py)_2$ by the addition of pyridine. Addition of KNHAr to $(Cp''')LaI_2(bipy)(py)$, yields the mono-anilido complex $(Cp''')LaI(NHAr)(bipy)(py)$; this compound may also be prepared by displacing the py in $(Cp''')LaI(NHAr)(py)_2$.[108]

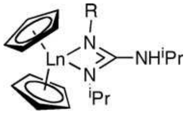
The reaction of anhydrous $LuCl_3$ with a twofold molar excess of lithium guanidinate $[Li\{(Me_3Si)_2NC(N^iPr)_2\}]$ yields the "ate" complex $[Lu\{(Me_3Si)_2NC(N^iPr)_2\}_2(\mu\text{-}Cl)_2Li(THF)_2]$. The alkyllutetium derivative $[Lu\{(Me_3Si)_2NC(N^iPr)_2\}_2(R')]$ was synthesized by a metathesis reaction with LiR′. Subsequent reaction with $PhSiH_3$ gave the first known dimeric lanthanide hydride in a bis(guanidinate) coordination environment, $[Lu\{(Me_3Si)_2NC(N^iPr)_2\}_2(\mu\text{-}H)]_2$. This hydrido complex was found to catalyze polymerization of ethylene, propylene and styrene.[109]

In polymerization chemistry, recrystallization of $\{[2,6\text{-}\{[2,6\text{-}({}^iPr)_2C_6H_3]NC({=}CH_2)\}_2C_5H_3N]Nd(THF)\}(\mu\text{-}Cl)_2[Li(THF)_2]$ from DME gave the corresponding ionic $\{[2,6\text{-}\{[2,6\text{-}({}^iPr)_2C_6H_3]NC({=}CH_2)\}_2C_5H_3N]NdCl_2(DME)\}\{Li(DME)_3\}$. With the exception of (allyl)MgBr, which proceeded readily with the dichloride to form the allyl derivative $\{[2,6\text{-}\{[2,6\text{-}({}^iPr)_2C_6H_3]NC({=}CH_2)\}_2C_5H_3N]Nd(\eta^3\text{-}C_3H_5)Br\}\{Li(DME)_3$, these halides are not suitable starting substrates for further alkylation reactions. A viable synthetic strategy for the preparation of alkyl derivatives consisted instead of the pretreatment of $NdCl_3(THF)_3$ with RLi [R = Me_3SiCH_2, CH_3] at low temperature followed by treatment with either the diimine ligand or the dianion. With this relatively clever approach, $[2,6\text{-}\{[2,6\text{-}({}^iPr)_2C_6H_3]NC({=}CH_2)\}_2C_5H_3N]Nd[R'](THF)$, $\{[2,6\text{-}\{[2,6\text{-}({}^iPr)_2C_6H_3]NC({=}CH_2)\}_2C_5H_3N]Nd\}(\mu\text{-}CH_3)_2[Li(THF)_2]$, and $\{[2,6\text{-}\{[2,6\text{-}({}^iPr)_2C_6H_3]NC({=}CH_2)\}_2C_5H_3N]Nd\}(\mu\text{-}Cl)_{1.5}(\mu\text{-}CH_3)_{0.5}[Li(THF)_2]$ were isolated. The methyl compounds are reported as "potent" catalysts for the *cis*-polymerization of butadiene.[110]

Using a sterically demanding amidinate ancillary ligand and an *in situ* alkylation procedure, neutral mono(amidinate) dialkyl and cationic mono(amidinate) monoalkyl complexes $\{[PhC(NAr)_2]M(R')_2(THF)$ and$\{[PhC(NAr)_2]M(R')_2(THF)_2\}$ (M = La, Gd, Nd) were prepared for metals spanning the full size range of the Group 3 and lanthanide metals. The activity of the cationic monoalkyls in catalytic ethene polymerization varied by over two orders of magnitude depending on the metal ionic radius, the intermediate metal sizes being found to be the most effective.[111]

Reaction of $CpYCl_2(THF)_3$ with LiN^iPr_2 followed by two ${}^iPrN{=}C{=}N^iPr$ in THF gave the organoyttrium guanidinates $Y[{}^iPrNC(N^iPr_2)N^iPr]_3$ and $Cp_2Y[{}^iPrNC(NiPr_2)N^iPr]$ which result from ligand redistribution of the putative initial diinsertion product $CpY[{}^iPrNC(N^iPr_2)N^iPr]_2$. Treatment of ${}^iPrN{=}C{=}N^iPr$

with $[Cp_2LnNH\ {}^{t}Bu]_2$ (Ln = Yb, Er, Dy, Y) gave the unexpected products $Cp_2Ln[{}^{t}BuNC(NH^{i}Pr)N^{i}Pr]$ (**22**) indicating that a 1,3-hydrogen shift takes place along with the insertion into the Ln–N σ-bond. As such, this represents an efficient synthesis of complexes with asymmetric guanidinate ligands.[112]



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Novel Y chelating diamide complexes $[(Y\{ArN(CH_2)_xNAr\}(Z)(THF)_n)_y]$ (Z = I, R″, CH_2Ph, H, $N(SiMe_3)_2$, OC_6H_3-2,6-${}^{t}Bu_2$-4-Me) were made *via* salt metathesis and further reaction with H_2. The R″ derivatives underwent unprecedented exchange of Y for Si on reaction with phenylsilane to yield $(Si\{ArN(CH_2)_xNAr\}PhH)$ and $(SiR''PhH_2)$.[113]

Two new monoanionic tetradentate triamino-amide ligands, $[(Me_2NCH_2CH_2)_2$-N–EH_2–$N({}^{t}Bu)]^-$ (E = C, Si) react with $YR'_3(THF)_2$, yielding $[(Me_2NCH_2CH_2)_2$-N–CH_2–$N({}^{t}Bu)]YR'_2$, which decomposes at ambient temperature *via* metalation of one of the NMe_2 Me groups. The R′ derivative resulted in very rapid ligand metalation. Both Y compounds react with $[PhNMe_2H][B(C_6F_5)_4]$ to generate the corresponding cation by elimination of alkane. The metalated complex reacts with ethene and with pyridine by stoichiometric insertion into the Y–CH_2N bond, and the latter product was structurally characterized. In (ligand)Y(X)(R′) complexes, the Y-amine distance *trans* to X is very sensitive to the nature of X, suggesting the presence of a *trans* influence.[114]

In monosubstituted diphosphinylamide complexes $[LnCl_2\{(Ph_2P)_2N\}(thf)_3]$ (Ln = Y, Sm, Er, Yb) the diphosphanylamide ligand is always η^2-coordinated through the nitrogen atom and one phosphorus. Further reaction of $[SmCl_2\{(Ph_2P)_2N\}(thf)_3]$ with K_2COT or reaction of $[LnI(\eta^8\text{-}COT)(thf)_3]$ with $[K(thf)_n][N(PPh_2)_2]$ in THF gives the corresponding COT complexes $[Ln\{(Ph_2P)_2N\}(\eta^8\text{-}COT)(thf)_2]$ (Ln = La, Sm). Surprisingly, the compound resolves spontaneously. The more soluble complex $[Y\{(Ph_2P)_2N\}(COT'')(thf)_2]$ was obtained by transmetalation of Li_2COT'' with YCl_3 in THF followed by the addition of one equivalent of $[K(thf)_n][N(PPh_2)_2]$.[90] Bis(diphosphinylamide) complexes of the lanthanides were synthesized. Reaction of $YbCl_3$ with a slight excess of $[K(THF)_n][N(PPh_2)_2]$ gave $[\{(Ph_2P)_2N\}_2$-$YbCl(THF)_2]$, which was further reacted with KCp* to give $[\{(Ph_2P)_2N\}_2YbCp^*]$. Reversing the order of addition, NaCp was treated with $SmCl_3$ to generate $[CpSmCl_2(THF)_3]$ *in situ*, and further reaction with $[K(THF)_n][N(PPh_2)_2]$ gave the desired complex $[\{(Ph_2P)_2N\}_2SmCp(THF)]$.[115]

Structural investigations include the reactions of the diol $(CF_3)_2C(OH)CH_2N$-$Me(CH_2)_nNMeCH_2C(OH)(CF_3)_2$ (n = 2, 3) with $Y[N(SiHMe_2)_2]_3(THF)_2$ and $Y(R')_3(THF)_2(diol)Y(R)(THF)$ (R = $N(SiHMe_2)$). The X-ray structure of the alkyl derivative reveals Y···F coordination to one of the four CF_3 substituents which is not observed in solution.[116] The potassium salt $[K(Ph_2PCHPPh_2NSiMe_3)]_n$ was used in a metathesis reaction to give the samarium complex $[(\eta^5\text{-}Cp^*)_2Sm(Ph_2$-$PCHPPh_2NSiMe_3)]$, in which the $(Ph_2PCHPPh_2NSiMe_3)^-$ ligand coordinates in η^3-heteroallylic fashion *via* the N atom and the methine group to the metal.[115]

A number of papers involving nitrogen macrocycles have been reported this year. Reaction of $SmCl_3$ with KL (L = [DippNC(Me)CHC(Me)NDipp]; Dipp = 2,6-${}^{i}Pr_2C_6H_3$) in THF afforded the dimeric samarium dichloride $LSmCl_2(THF)Cl_2SmL$ in high yield. Reactions of this product with $NaN(SiMe_3)_2$, KNHAr (Ar = 2,4,6-${}^{t}Bu_3C_6H_2$), $KBHEt_3$, and KCp* yielded various new complexes: $LSmClN(SiMe_3)_2$, $LSm[N(SiMe_3)_2]_2$, $LSmNHAr(HBEt_3)$, $LSm(NHAr)_2$, and LSmCp*Cl, whereas reaction with $NaN(SiMe_3)_2$ followed by treatment with excess $AlMe_3$ afforded a unique heterometallic samarium tetramer $Cl_3L_2Sm_2(AlMe_4)_2Sm_2L_2Cl_3$. Reaction of the Sm–NHAr product with LiMe or $LiCH_2SiMe_3$ afforded LSmCp*Me and LSmCp*R′ in excellent yield, and reaction of the former with $B(C_6F_5)_3$ in toluene yielded the cationic borate species $(LSmCp^*)[MeB(C_6F_5)_3]$.[117]

Divalent bis(phosphinimino)methanide lanthanide complexes of composition $[\{(Me_3SiNPPh_2)_2CH\}EuI(THF)]_2$ and $[\{(Me_3SiNPPh_2)_2CH\}YbI(THF)_2]$ have been prepared by salt metathesis reactions of $K\{CH(PPh_2NSiMe_3)_2\}$ and LnI_2. Further reactions of these complexes with $[K(THF)_nN(PPh_2)_2]$ led selectively to the heteroleptic amido complexes $[\{(Me_3SiNPPh_2)_2CH\}Ln\{(Ph_2P)_2N\}(THF)]$ (Ln = Eu, Yb). The ytterbium complex can also be obtained by reduction of $[\{CH(PPh_2NSiMe_3)_2\}Ybv(Ph_2P)_2N\}Cl]$ with elemental K. Single crystals of $[\{(Me_3SiNPPh_2)_2CH\}Ln\{(Ph_2P)_2N\}(THF)]$ contain enantiomerically pure complexes. Related alkaline earth complexes were also prepared. In the solid-state the $\{CH(PPh_2NSiMe_3)_2\}^-$ ligand acts as tridentate donor forming a long methanide carbon metal bond. Thus, all complexes presented can be considered as organometallic compounds. $[\{(Me_3SiNPPh_2)_2CH\}YbI(THF)_2]$ was also used as a precatalyst for the intramolecular hydroamination/cyclization reaction of different aminoalkynes and aminoolefins. Good yields but moderate activities were observed.[85]

Reaction of divalent $(Ph_2N)_2Sm(THF)_4$ with azobenzene produced the complex $[(Ph_2N)(DME)Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2Ph_2)_2$ in good yield. The N–N bond length suggests the N_2Ph_2 ligands are dianions. The complex also shows an unusually close Ln-η^2-arene interaction, and catalyzes the polymerization of MMA and acrylonitrile.[118]

A new family of ionic Ln complexes derived from chiral, substituted (*R*)-binaphthylamine ligands, $[Li(THF)_4][Ln\{(R)\text{-}C_{20}H_{12}(NR)_2\}_2]$ (Ln = $YbCl_3$, Sm, Nd, or Lu), was synthesized and characterized. All complexes were tested as new catalysts for the hydroamination/cyclization of 1-(aminomethyl)-1-allylcyclohexane. The Yb complexes proved to be both the most active and the most enantioselective, and the use of $[Li(THF)_4][Yb\{(R)\text{-}C_{20}H_{12}(NPr)_2\}_2]$, gave the corresponding spiropyrrolidine in high yield with up to 70% ee.[119]

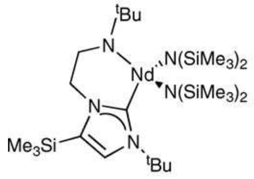
Y and lanthanide complexes with different P/N donor ligands were synthesized. First, the chloride complexes $[\{CH(PPh_2NSiMe_3)_2\}Ln\{(Ph_2P)_2N\}Cl]$ [Ln = Y, La, Nd, Yb] having the bulky $[CH(PPh_2NSiMe_3)_2]^-$ and the flexible $[(Ph_2P)_2N]^-$ ligands in the same molecule were prepared by three different synthetic pathways. Single-crystal X-ray structures show that the conformation of the six-membered metallacycle (N–P–C–P–N–Ln), which is formed by chelation of the $[CH(PPh_2NSiMe_3)_2]^-$ ligand to the lanthanide atom, is influenced by the ionic radius of the central metal atom. As observed in earlier work, there is tridentate coordination of this ligand (both N atoms and the central methine C atom). In solution, dynamic behavior of the $[(Ph_2P)_2N]^-$ ligand rapidly exchanges the two different P atoms. Further reaction of the La compound with $KNPh_2$ resulted in $[\{(Me_3SiNPPh_2)_2CH\}La\{N(PPh_2)_2\}(NPh_2)]$. All four products are active in the ring-opening polymerization of ε-CL and the polymerization of MMA. In some cases high molecular weight polymers with good conversions and narrow polydispersities were obtained. In both polymerizations the catalytic activity depends on the ionic radius of the metal.[120]

7.2 Nitrogen heterocycles

The capacity of N-heterocyclic carbene molecules to discriminate between trivalent lanthanide and actinide ions was revealed by competition reactions of analogous U(III) and Ce(III) compounds with $C_3Me_4N_2$ and a comparison of the crystal structures of the corresponding carbene adducts. The uranium compounds are more covalent in nature.[121] In work which begins to extend the use of chelating carbenes to the lanthanides, the reaction of tethered N-heterocyclic carbene complex $Ln(L)N''_2$ (Ln = Nd, Ce; L = $^tBuNCH_2CH_2[C\{NCHCHN^tBu\}]$) with Me_3SiI unexpectedly functionalized the carbene backbone at the C4-carbene ring position to afford the silylated complex Ln(L′)N″I (L′ = ^{t}BuNCH$_2$CH$_2$[C{NC(SiMe$_3$)CHN^{t}Bu}]). (**23**) Ln(L′)N″$_2$ was isolated after attempted reduction using KC$_8$. The isolation of these complexes has allowed interesting structural comparisons to be made.[122] Such chemistry is not easy. The low temperature reaction of the amine-functionalized N-heterocyclic carbene ^{t}BuNHCH$_2$CH$_2$[C{^{t}BuN(CHCH)N}] (HL1), KMe, and 0.5 equivalents of [CeI$_3$(THF)$_4$] in DME/diethyl ether solutions does not afford the expected cerium amido carbene [(L1)$_2$CeI]. However, transamination of [(HL1)LiBr] with CeN″$_3$ successfully affords the compounds [{(L1)Ce(N[SiMe$_3$]$_2$)(μ-Br)}$_2$] and [(L1)Ce{N(SiMe$_3$)$_2$}$_2$]. The complex [{(L1)Ce(N[SiMe$_3$]$_2$)(μ-I)}$_2$] was obtained by bromide exchange.[123]

In a real deviation from conventional synthetic approaches, intensely colored crystals of [Eu$_2$(Indolyl)$_4$(NH$_3$)$_6$] (**24**) were obtained by low-temperature oxidation of Eu metal with indole (C$_8$H$_6$NH) in liquid NH$_3$ at −50° and subsequent melting of the reaction mixture in excess indole at 120°. [Eu$_2$(Indolyl)$_4$(NH$_3$)$_6$] has a dimeric structure and contains divalent Eu. The coordination sphere around the Eu atoms consists of 5 N atoms of 2 cisoid indolate anions and 3 NH$_3$ molecules as well as an η^5-coordinating π-system of another indolate ligand, bridging to the next Eu atom with an sp^2-orbital.[124] In similar reactions using pyrrole, the compounds [Yb$_2$(C$_4$H$_4$N)$_2$(NH$_3$)$_8$], [Yb(C$_4$H$_4$N)$_5$(NH$_3$)], [Yb(C$_4$H$_4$N)$_3$(C$_4$H$_5$N)$_2$(NH$_3$)$_2$] and [[Yb$_5$(C$_4$H$_4$N)$_{12}$(NH$_3$)$_4$(NH$_2$)] · 2 C$_4$H$_5$N]$_n$ (Pyr = pyrrolate anion, C$_4$H$_4$N$^-$; PyrH = pyrrole, C$_4$H$_4$NH) were obtained by oxidation of ytterbium with pyrrole in liquid ammonia. Single crystals of all three phases are formed next to each other, their yield depending on the temperature gradient of a subsequent thermal process in sealed glass ampoules. These are the first unsubstituted pyrrolates of a lanthanide element and illustrate the decisive role of ammonia and the reaction conditions.[125]

In a higher temperature approach, bright yellow crystals of [Eu(pyrazolide)$_2$(pyrazole)$_2$]$_n$ (**25**) were obtained by the reaction of Eu metal in a pyrazole melt. The compound exhibits a 1-dimensional chain structure including both unsubstituted pyrazolate anions as well as unsubstituted neutral pyrazole molecules as ligands. The latter are isoelectronic with the cyclopentadienyl anion and link two adjacent Eu(II) centres in an η^1-σ-bridging as well as Cp analogous η^5-π-binding mode, while the pyrazolate anions are N-η^1-coordinating terminal ligands.[125]



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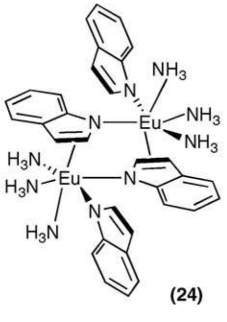

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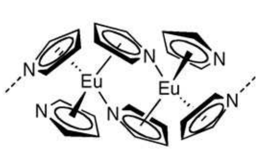

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In a similar vein, the direct reaction of lanthanoid metals with 3,5-diphenylpyrazole (Ph$_2$pzH) in the presence of Hg gave crystalline [Ln$_3$(Ph$_2$pz)$_9$] (Ln = La or Nd) or [Ln$_2$(Ph$_2$pz)$_6$] (Ln = Er or Lu). Similar reactions provided heteroleptic [Ln(Ph$_2$pz)$_3$(Ph$_2$pzH)$_2$] (Ln = La, Nd, Gd, Tb, Er and Y). The last was obtained only from impure Ph$_2$pzH, but was subsequently prepared by treatment of [Yb(Ph$_2$pz)$_3$(THF)$_2$] with Ph$_2$pzH. Reactions of Yb with Ph$_2$pzH gave a poorly soluble divalent species that reacted with 1,2-DME to give [Yb(Ph$_2$pz)$_2$(dme)$_2$]. X-ray structures established a bowed trinuclear pyrazolate-bridged structure for [Ln$_3$(Ph$_2$pz)$_9$] (Ln = La or Nd). There are two η^2-Ph$_2$pz ligands on the terminal Ln atoms and one on the central metal with adjacent Ln atoms linked by one μ-η^2:η^2 and one μ-η^5 (to terminal Ln):η^2 pyrazolate group. By contrast, [Ln$_2$(Ph$_2$pz)$_6$]

(Ln = Er or Lu) complexes are dimeric with two terminal (η^2) and two bridging (μ-η^2:η^2) pyrazolates and eight-coordinate lanthanoids. All six heteroleptic complexes $[Ln(Ph_2pz)_3(Ph_2pzH)_2]$ (Ln = La, Nd, Gd, Tb, Er or Yb) are isomorphous with three equatorial η^2-Ph_2pz groups, transoid η^1-pyrazole ligands, and eight-coordinate Ln throughout.[126]

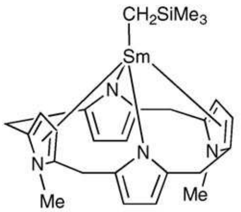
In subsequent studies, the oxidation of Eu and Yb with pyrrole and carbazole gave the pyrrolate $[Eu_2(Pyr)_4(PyrH)_2(NH_3)] \cdot PyrH$ (Pyr = C_4H_4N) and the carbazolate $[Yb_2(Cbz)_4(NH_2)_2(NH_3)_4] \cdot 3CbzH$ (Cbz-=$C_{12}H_8N$), respectively. The highly thermally stable Eu complex is a 1-dimensional polymer of η^5-pyrrolate, η^5-pyrrole groups and one equivalent of ammonia coordinating and bridging divalent europium centres. In contrast, the dimeric Yb complex is trivalent and no π-interactions are observed.[127]

Single crystals of $[Yb_2(Cbz)_4(Phpip)_4] \cdot 2Phpip$, $[Sm(Cbz)_3(Phpip)_2] \cdot 8/3Phpip$, and $[Yb(Cbz)_2(Phpip)_3][Yb(Cbz)_3(Phpip)_2]$ were obtained by competitive reactions of $[Yb_2(Cbz)_4]_\infty$ and $\{[Sm_2(Cbz)_5](CbzH)\}_\infty$ (Cbz = carbazolate anion, $C_{12}H_8N^-$) with N-phenylpiperazine (Phpip = $(C_6H_5)C_4H_8NNH$) and carbazole ($C_{12}H_8NH$). π-interactions linking building units in the adducts are completely substituted by N-phenylpiperazine resulting in the chain structures being cut down to monomeric units with complete nitrogen coordination of the Ln ions.[128]

With porphyrins, Sm (II) and (III) complexes with the promising *trans-N*,*N*-dimethylated porphyrinogen ligand gives products that are amenable to highly controllable reaction chemistry. Thus Sm(II) bis(THF) adduct, Sm(III) chloride and bis(trimethylsilyl)amide complexes (**26**) were synthesized.[129] The reaction of $LnN''_3 \cdot [LiCl(THF)_3]_x$ (Ln = Yb and Er) with N-confused tetraphenylporphyrin (H_2NCTPP) followed by treatment with Kläui's ligand, Na(LOMe) (LOMe = $(C_5H_5)Co[P(O)(OMe)_2]$), gives (NCTPP)Ln(LOMe) (**27**), whose X-ray structures exhibit η^2 agostic interactions between the metal centre and the inner C–H bond of the NCTPP ligand.[130] A potassium salt of *trans*-dioxaporphyrinogen $K_2[cyclo\text{-}(C_4H_2N)_2(C_4H_2O)_2(CEt_2)_4]$ reacted with SmI_2 to give, after I_2 oxidation and reaction with NaN″, the samarium(III) half-sandwich silazanide. In the presence of excess NaN″, one methyl group undergoes γ-deprotonation affording a cyclometalated complex (**28**) in a reaction thought to be driven by macrocyclic stabilization of the sodium cation in the cavity afforded by the porphyrinogen.[131] Alkylsamarium(III) complexes of a dimetallated, modified porphyrinogen $[cyclo\text{-}(C_4H_2NMe)_2(C_4H_2N)_2\text{-}(CEt_2)_4]$ were synthesized. The monomeric complexes unfortunately appear not to be very reactive.[131] A binuclear porphyrinogen samarium(III) complex featuring the μ-η^1:η^1-bound dianion of 1,4-di-*t*-butyl-1,4-diazabuta-1,3-diene (**29**) has been prepared which exhibits reversible redox behavior, reverting to the samarium(II) precursor when dissolved in THF, releasing the butadiene ligand.[132]

The one-pot transmetalation/deprotonation reaction of the bulky triazene $Dmp(Tph)N_3H$ with bis(pentafluorophenyl)mercury and europium or ytterbium affords the structurally characterized unsolvated metal(II) pentafluorophenyl triazenides $[Dmp(Tph)N_3MC_6F_5]$ (M = Eu, Yb; Dmp = 2,6-$Mes_2C_6H_3$ with Mes = 2,4,6-$Me_3C_6H_2$; Tph = 2-TripC_6H_4 with Trip = 2,4,6-$^iPr_3C_6H_2$) (**30**) or, depending on the molar ratio, the solvated complex $[Dmp(Tph)N_3YbC_6F_5(THF)]$.[133]

The first examples of organometallic compounds containing the tris(3,5-dimethylpyrazolyl)methane ($HC(Me_2pz)_3$) and 1,3,5-trimethyltriazacyclohexane ($Me_3[6]aneN_3$) ligands were reported. Reaction of $MR'_3(THF)_2$ (M = Sc, Y) with $Me_3[9]aneN_3$ (1,4,7-trimethyltriazacyclononane), $HC(Me_2pz)_3$, or $Me_3[6]aneN_3$ gave the corresponding $M(Me_3[9]aneN_3)R'_3$ (M = Sc, Y), $M\{HC(Me_2pz)_3\}R'_3$ (M = Sc, Y), and $M(Me_3[6]aneN_3)(R')_3$ (M = Sc, Y). $Sc\{HC(Me_2pz)_3\}(OAr)_3$ was obtained by protonolysis. Attempts to prepare tris-R′ complexes with the more sterically demanding tris(3-R-pyrazolyl)methanes (R = ^iPr, Ph, ^tBu) or the related tris(pyrazolyl)methylsilane ligand were unsuccessful. However, the trichlorides $M\{HC(Me_2pz)_3\}Cl_3$, $M\{HC(^iPrpz)_3\}Cl_3$ and $M\{MeSi(Me_2pz)_3\}Cl_3$ (M = Sc, Y) could be made. Competitive ligand exchange reactions for the tris(alkyl) compounds $M(L)(R')_3$ established the binding preference L = $Me_3[9]aneN_3 > Me_3[6]aneN_3 >$



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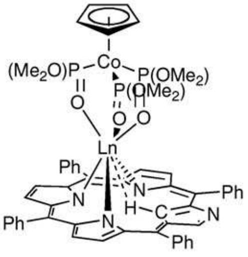

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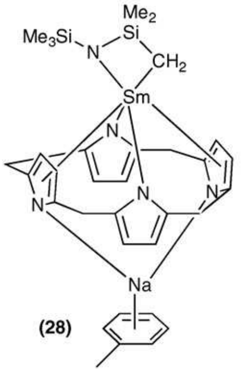

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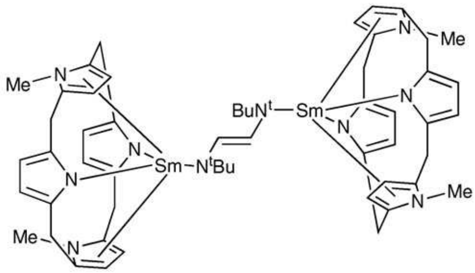

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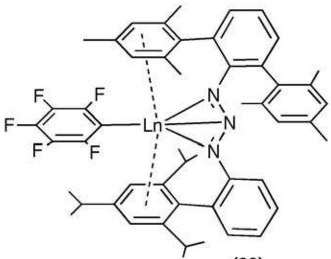
$HC(Me_2pz)_3$ for M = Sc and L = $Me_3[9]aneN_3 > HC(Me_2pz)_3 > Me_3[6]aneN_3$ for M = Y. Reaction of $ScPh_3(THF)_2$ with the functionalized ligands, 1-(3,5-di-*t*-butyl-2-hydroxybenzyl)-4,7-dimethyltriazacyclononane (HL1) or 1-(3,5-di-*t*-butyl-2-hydroxybenzyl)-4,7-diisopropyltriazacyclononane (HL2) gave organoscandium derivatives of mono(phenoxy)-substituted triazacyclononane ligands, $Sc(L1)Ph_2$ and $Sc(L2)Ph_2$ from which $Sc(L1)(OTol)_2$ could be prepared by protonolysis.[19]



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7.3 Ketiminates

Diketiminato support systems were pursued less heavily this year. Reduction of $[Yb(N(SiMe_3)C(R)CHC(R')N(SiMe_3))_2Cl]$ gave $[Yb\{(\mu\text{-}LR,R')Li(THF)\}_2]$ (R = Ph, C_6H_4Ph-4). Use of a Yb-naphthalene complex instead of Li in the reaction with $[Yb(N(SiMe_3)C(R)CHC(R')N(SiMe_3))_2]$ led to the isolation of Yb_3 and Yb_5 clusters.[134]

Treatment of the scandium dichlorides $\{[ArNC(R)CHC(R)NAr]ScCl_2\}_n$ (Ar = 2,6-$^iPr_2C_6H_3$; R = CH_3; ^{t}Bu) with lithium amides gave scandium amido derivatives such as $[2,6\text{-}^iPr_2C^6H_3rNC(CH_3)CHC(CH_3)N2,6\text{-}^iPr_2C_6H_3]Sc(NH^tBu)_2$ regardless of the amount of amide reagent employed, suggesting that facile ligand redistribution occurs when the ligand is the less bulky methyl-substituted example. Mono-amido chlorides (*i.e.* [ArNC(^{t}Bu)CHC(^{t}Bu)NAr]ScCl(NHR′) (R′ = ^{t}Bu; R′ = 2,6-^{i}Pr$_2$C$_6$H$_3$) are obtained in good yields, and these compounds can be alkylated with MeLi to provide mono-amido Me compounds. The amido ligand occupies the *exo* coordination site exclusively, and there is no evidence in solution for a diastereomer with an *endo*-amido group. DFT calculations suggest that there is a strong steric preference and a slight electronic bias for the amido ligand to assume the *exo* position. Thermolysis of the amido Me complex leads to loss of CH_4 and production of a scandacyclic product, formed *via* metalation of an N-aryl ^{i}Pr Me groups. Deuterium labeling experiments suggest that the scandacycle is produced *via* direct metalation rather than *via* a scandium imido intermediate.[135] In the patent literature, Sc compounds prepared from Sc(R′)$_3$ and 2,6-bis[[N-(2,6-diisopropylphenyl)amino]methyl]pyridine gave the corresponding (ketiminate)Sc(R′) that polymerizes MMA to give PMMA with an average molecular weight of 129 000.[136]

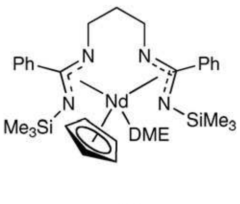
The β-diketiminate lanthanide dichloride [*p*-ClC$_6$H$_4$NC(Me)CH(Me)N(C$_6$H$_3$-2,6-^{i}Pr$_2$)]YbCl$_2$(THF)$_2$ and the mixed-ligand β-diketiminate ytterbium chloride (^{t}BuCp)Yb[*p*-ClC$_6$H$_4$NC(Me)CH(Me)N(C$_6$H$_3$-2,6-^{i}Pr$_2$)](μ-Cl)$_2$Li(THF)$_2$ were prepared by metathesis and characterized "exhaustively".[137]

Similarly, the linked bis(amidinate) [Me$_3$SiNC(Ph)N(CH$_2$)$_3$NC(Ph)NSiMe$_3$]-Yb(μ-Cl)$_2$YbL(THF) was prepared, and recrystallization from hexane in the presence of THF formed a monomeric ytterbium chloride that reacts with NaCp to give the Cp derivative.[138]

A rare family of base-free organoscandium alkyl cations stabilized by β-diketiminato ligands was prepared by reaction of [(ArN=C^{t}BuCHC^{t}Bu=NAr)ScR$_1$R$_2$] [Ar = 2,6-^{i}Pr–C$_6$H$_3$; R$_1$ = R$_2$ = Me, R′, CH$_2$^{t}Bu; or Ar = 2,6-^{i}Pr–C$_6$H$_3$; R$_1$ = R′, R$_2$=CH$_2$^{t}Bu] with B(C$_6$F$_5$)$_3$ and perfluoro-9-(pentafluorophenyl)-9-borafluorene; cationic ion-pairs such as [(ArN=C^{t}BuCHC^{t}Bu=NAr)ScR$_3$]$^+$[Me(C$_6$F$_5$)$_3$]$^-$ were isolated. Complexes with methyl-substituted ancillary β-diketiminato ligand, [(ArN=CMeCHCMe=NAr)ScR$_1$R$_2$] undergo pentafluorophenyl group migration from boron to scandium, giving ion pairs [(ArN=CMeCHCMe=NAr)Sc(C$_6$F$_5$)]$^+$ [BMe$_2$(C$_6$F$_5$)$_2$]$^-$. Detailed NMR studies (low-temperature EXSY) allowed for observation of both inter- and intramolecular ion pair reorganization processes, whose mechanism is discussed in terms of the involvement of "solvent separated ion pairs". This is the first such study involving non-metallocenium Group 3 metal based ion pairs.[139]

Attempted synthesis of sterically demanding bis- or tris-β-diketiminato complexes resulted in ligand deprotonation and the formation of products containing both a normal and a deprotonated ligand. On protonation one of these gave the first cationic β-diketiminato-Ln complex.[140]

Novel types of hexa-1,5-diene-1,6-diamide neodymium complexes were prepared. The molecular structures of the new complexes revealed that the chelating hexa-1,5-diene-1,6-diamide can be bound either as an enamide or as an azaallyl-type ligand (**31**). The prepared complexes were tested as catalysts for 1,3-butadiene polymerization.[141]



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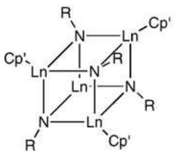
Organometallic and coordination compounds of Group IIIB and IVB elements supported by tetradentate diamino-bis(phenolate) ligands L1 and L2 [H$_2$L1, H$_2$L2

= 2-$C_5H_4NCH_2N(CH_2C_6H_2$-2-OH-3,5-$R_2)_2$, where R = ^{t}Bu, Me] were prepared and characterized. Monomeric and dimeric scandium bis-phenolates [ScCl(L1-*N*,*N*′,O,O′)] and [Sc_2Cl_2(μ-O–L2-*N*,*N*′,O,O′$)_2$] were prepared by metathesis. Protonolysis of MR'_3 by free ligand gave the corresponding organometallic derivative [Ln(R′)(THF)(L1-*N*,*N*′,O,O′)] (Ln = Sc, Y). Reaction of Na_2L1 and YCl_3 in neat pyridine gave the chloride-bridged, seven-coordinate dimer [Y_2(L1-*N*,*N*′,O,O′$)_2$(μ-Cl$)_2$(py$)_2$]. The one-pot reaction of $ScCl_3$ with Na_2L_n and Li[PhC(NSiMe$_3)_2$] gave the fluxional benzamidi nate derivatives [Sc(Ln-*N*,*N*′,O,O′)[PhC(NSiMe$_3)_2$]].[142]

Metal imido compounds

Imido compounds are at last beginning to appear in lanthanide chemistry on a regular basis. In the continuing cluster story from the Hou group, nucleophilic addition of cubane-like imido complexes [(Cp′Ln$)_4$(μ_3-RCH$_2$N$)_4$] (Ln = Y, Lu; R = Ph, Me) (**32**) with benzonitrile gave [(Cp′Lu$)_2$[μ-PhC=N(NCH$_2$Ph)-*N*,*N*′]], (**33**) benzonitrile trimer complexes [Cp′Ln(PhCN)(μ-N=CPhN=CPhNCHPhN=CHPh-*N*,*N*″,*N*‴,*N*‴)(μ-PhCH$_2$NCPh=N)] (Ln = Lu, Y) (**34**), and crown-shaped [(Cp′Y$)_4$(μ-PhCH=N$)_4$(μ-MeCH$_2$N$)_2$] (**35**). The strikingly highly reactive bridging imido ligands are the characteristic feature of these complexes, in comparison with their rather unreactive d-block counterparts. Catalytic cyclotrimerization of benzonitrile affording 2,4,6-triphenyl-1,3,5-triazine accompanies these reaction and occurs by a unique combination of C–N bond-formation, hydrogen-transfer, and C–N bond-cleavage reactions.[143]



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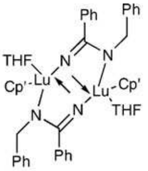

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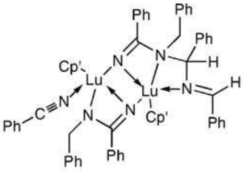

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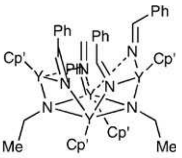

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8. Organometallics in materials synthesis

Superb high-dielectric properties of Ln oxides continue to motivate significant efforts towards the preparation of organolanthanide compounds with both volatility and suitable hydrolytic instability. With volatile compounds, Y_2O_3 thin films were grown on Si by atomic layer deposition using Cp_3Y, and $(MeCp)_3Y$, with H_2O as the O source. The films deposited at 300 °C had carbon impurity levels of 0.5 and 0.2 atom%, respectively.[144] Lu_2O_3 was grown by ALD using the dimeric $\{Cp'_2LuCl\}_2$ complex, which was synthesized for this purpose. Annealing the films in nitrogen at 950 °C leads to crystallization in the cubic bixbyite structure. The dielectric constant of the as-grown Lu_2O_3 layers was 12 ± 1.[145] Films of Y_2O_3 on SiO_2 were grown with $(BuCp)_3Y$.[146] The patent literature described the synthesis of oxide layers with SiOH functionalized surfaces from Ln methyl compounds [147] and the MOCVD deposition of Ln_2O_3 thin films with Cp_3Ln compounds on Si substrates held at 150–400 °C.[148]

(C_5H_4-^{s}Bu$)_3$Ln (Y, La, Pr, Er) were also used as CVD sources for the preparation of Ln_2O_3 thin films,[149] and $(C_5H_4Me)_3Er$ was used in the atomic layer deposition of Er_2O_3 thin films.[150] A number of La_2O_3 materials were also investigated. [151,152] The synthesis and structure of the novel octametallic cluster [{Yb_4(μ_4-O)(μ_2-OPr^i$)_2$(μ_2-Me$)_4$}{(μ_2-Me)(μ_2-O^{i}Pr)AlMe$_2$}] and its use to form $Yb_3Al_5O_{12}$ under ambient conditions was reported. The compound was formed by combining $AlMe_3$ with

$Yb(O^iPr)_3$. In the structure each $AlMe_2$ unit is joined to a Yb atom by bridging Me and O^iPr groups.[153] Gd oxide thin films were deposited on Si(100) by ALD using either a β-diketonate-type chelate, $Gd(thd)_3$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedione) and ozone or a true organometallic $(CpCH_3)_3Gd$ together with H_2O. The resultant Gd_2O_3 films obtained by the Cp-based process were crystalline with cubic C-type structure when deposited even at 150 °C.[154]

In non-oxide materials, local structures of Er doped ErP grown with $EtCp_3Er$ were studied by extended X-ray absorption fine structure (EXAFS) measurement. The EXAFS analysis revealed that NaCl-type ErP and Er–O(–C) compounds coexisted. These impurity Er–O(–C) compounds were observed in significant concentrations, and attributed to residual O and/or C in $Er(EtCp)_3$.[155] Lanthanide doped semiconductor powders were also prepared with vapor phase introduction of the Ln as well as with wet chemical methods. Photonic devices employing the materials were described. Multiple dopants were employed to produce multiple colors of luminescence.[156,157] The preparation of injection-type 1.5 μm LEDs with Er,O-codoped GaAs (GaAs:Er,O) fabricated by OMVPE was also noted. [158]

9. Polymerization chemistry

As in previous years a number of synthetic papers have described polymerization reactions so some of the material is of necessity split between sections that outline reactions with olefins and those that focus on the polymerization chemistry of polar monomers. Each section is further grouped according to the specific type of monomer. Although we have provided some cross-references, this is not comprehensive for reasons of space.

9.1 Olefin polymerization

Heterometallic $[CpMCl_2][(C_5H_4)SiMe_2(C_5H_4)]$ [CpSmCl] (M = Ti, Zr) activated by MAO were used for the polymerization of ethylene. [Catalyst], [Al]/[Cat], temperature and time were studied as variables. The dinuclear catalysts were less active than monometallic systems, and the molecular weight, melt point and crystallinity of polyethylene produced are somewhat lower.[159] In one study, $Cp^*{}_2NdCl_2Li(OEt_2)_2$-mediated ethylene polymerization was performed in conjunction with butyloctylmagnesium and the polymer was functionalized with TEMPO and terminated with alkoxyamine.[160]

With more complicated enes, heterobimetallic $[Ln\{(\mu\text{-}R)_2(AlR_2)\}_3]$ (R = Me, Et) were used to study metal-size effects in mixed Ziegler catalysts. Binary precatalyst $[Nd(AlMe_3)_4]/Et_2AlCl$ and heterogenized single-component variants, such as the hybrid material obtained after the immobilization of $[Nd\{(\mu\text{-}Me)_2(AlMe_2)\}_3]$ and Et_2AlCl on MCM-48, efficiently transformed isoprene to a high-*cis* polymer.[161] Poly-4-vinylpyridine was prepared in the presence of a wide variety of lanthanide compounds, including polyamido compounds, Cp, indenyl, and aryloxy derivatives, in toluene, benzene, THF, or 1,2-dimethoxyethane.[162]

In co-polymer systems, 1-hexene and ethylene were polymerized in the presence of Al^iBu_3, dimethylsilylene(η^5-C_5Me_4H)(3-*t*-butyl-5-methyl-2-phenoxy)titanium dimethoxide, and a treatment product manufactured from Sylopol 948 (SiO_2), $Sc(Cp)_3$, and C_6F_5OH to give a polymer showing Mw/Mn 28.9![163] On treatment with $[Ph_3C][B(C_6F_5)_4]$, the scandium complex $[Cp^{*\prime}Sc(R')_2(THF)]$ polymerized styrene at room temperature in toluene. This catalyst system also effected the syndiospecific copolymerization of styrene with ethylene to yield copolymers with syndiotactic styrene–styrene sequences and styrene contents higher than 80%.[164] Homogeneous C_2H_4/2-phenyl-1-methylenecyclopropane random copolymers were prepared with $Cp^*{}_2ZrMe^+B(C_6F_5)_4{}^-$, $[Cp^*{}_2LuH]_2$, $[Cp^*{}_2SmH]_2$, and $[Cp^*{}_2YH]_2$ with cyclopropane enchained in a ring-opened fashion. Random copolymers of ring-opened 7-methylenebicyclo[4.1.0]heptane and C_2H_4 were produced with the catalysts

$Me_2Si(Me_4C_5)(^tBuN)ZrMe_2$, $Me_2Si(Me_4C_5)(^tBuN)TiMe_2$ (activated by either $(C_6H_5)_3C^+\ B(C_6F_5)_4^-$ or $B(C_6F_5)_3$), and $[Cp^*{}_2LuH]_2$.[165]

In a surprising piece of work, a simple scandium complex $[ScCp''R'(THF)]^+$, prepared from the bis hydrocarbyl by normal activation, proves to be an excellent catalyst for the alternating copolymerization of ethylene and norbornene. The reaction yields exclusively the alternating copolymer in the presence of both monomers and affords poly(ethylene-alt-norbornene)-b-polyethylene block copolymers when a relatively small quantity of norbornene is used under a constant flow of ethylene. The selectivity is attributed to the steric demand of the norbornene which prevents a second molecule binding.[166] Yttrocenes with pendant Ph substituents were also patented in the stereospecific polymerization of olefins.[167]

C_3-chiral ancillary ligands such as tris(oxazolinyl)ethane (L) have been shown to allow stereocontrol in olefin polymerization. An alkyl Sc catalyst $[ScLR'_2]^+$ polymerizes 1-hexene with activities ranging from 2000 to 36 000 kg mol^{-1} h^{-1} and good tacticity control at low temperatures.[168]

Ethylene polymerization using a mixed catalyst system containing Cp_2MCl_2 (M = Ti, Zr) and (Me or $^tBuCp)_2SmCl$, activated with MAO was also studied. The resulting polymers were of high polydispersity.[169]

Primary and secondary phosphines were investigated as chain-transfer agents for organolanthanide-mediated olefin polymerization. Ethylene polymerizations were carried out with $[Cp^*{}_2LnH]_2$ and $Cp^*{}_2LnR''$ (Ln = La, Sm, Y, Lu) precatalysts in the presence of dicyclohexyl-, diisobutyl-, diethyl-, diphenyl-, cyclohexyl-, and phenylphosphine. In the presence of secondary phosphines, high activities and narrow product polymer polydispersities were obtained. For lanthanocene-mediated ethylene polymerizations, the phosphine chain-transfer efficiency correlated with the rate of Ln-R″ protonolysis by the same phosphines and followed the trend $H_2PPh \gg H_2PCy > HPPh_2 > HPEt_2 \approx HP^iBu_2 > HPCy_2$. Polymerizations conducted in the presence of primary phosphines produced only low-molecular-weight products.[170]

Catalyst systems for the homo- or co-polymerization of styrene were prepared with metallocenes of the general formula $(Flu–R''\text{-}Cp)M(\eta^3\text{-}C_3R'_5)(ether)_n$, wherein Cp is a cyclopentadienyl, substituted or unsubstituted, Flu is a fluorenyl, substituted or unsubstituted, M is a Group III metal, and R″ is a structural bridge imparting stereorigidity to the component, each R′ is the same or different and is hydrogen or an hydrocarbyl. Styrene–ethylene copolymers having a high styrene content were prepared with this catalyst.[171] Allylic complexes of lanthanides bearing a fluorenyl-based ligand were active single-component catalysts for the polymerization of styrene, giving highly syndiotactic polymers and narrow polydispersities.[172] A patent describing the use of a divalent bis 2-(dimethylaminophenyl)(trimethylsilyl)methyl complex of ytterbium as an initiator for the syndiotactic anionic polymerization of styrene and other substituted olefins was also filed.[173]

9.2 Dienes

Two new divalent samarocenes, $Cp^{*\prime}{}_2Sm(THF)$ and $(CpPh_3)_2Sm(THF)$ ($Cp^{*\prime}$ = $C_5Me_4{}^nPr$, $CpPh_3$ = $H_2C_5Ph_3$-1,2,4), were synthesized and characterized by ^1H NMR and elemental analysis. The activity of both as butadiene polymerization catalysts were studied in the presence of MAO and MMAO, and compared to $Cp^*{}_2Sm(THF)_2$ and $(Cp4i)_2Sm$ (III) (Cp* = Cp*, Cp4i = $C_5H^iPr_4$), in the same conditions. The $Cp^{*\prime}{}_2Sm(THF)$/MAO system presents the highest activity. The MMAO cocatalyst is sensitive to the steric hindrance of the samarocenes: the activity decreases from MAO to MMAO. The divalent compounds react with $AlMe_3$ to give bimetallic compounds.[174] Lanthanide metallocenes, aluminoxane, and Al alkyls or alkylhydrides polymerize 1,3-butadiene to give polymer with a high content of *cis*-1,4 structure and a narrow molecular weight distribution.[175] Conjugated dienes such as 1,3-butadiene were polymerized in the presence of $Al(^iBu)_3$, $(^iBu)_2AlH$, $Cp^*{}_2Sm(THF)_2$, and $[Ph_3C][B(C_6F_5)_4]$.[176] Compositions of natural and synthetic rubbers were prepared with the synthetic portion prepared with $Cp^*{}_2Sm(THF)_2$ and MMAO to give materials with a *cis*-1,4-linkage concentration of 99%.[177]

Lanthanide complexes containing amido or phosphido groups polymerize conjugated polyunsaturated compounds to give high molecular weight products.[178] Similar descriptions of Y, Ln, and An compounds combined with one or more activator compounds gave polymers having a high percentage of the fraction of residual olefinic double bonds that are *Z* or *cis* units and low 1,2-polybutadiene content.[179] Ethylene and butadiene were copolymerized with a silylene-bridged bis(fluorenyl) complex $\{[Me_2Si(C_{13}H_8)_2]NdCl\}$ in combination with various alkylating agents ($BuLi/AlH(^iBu)_2$, (Bu)MgCl, Mg(Bu)(Oct)). These copolymers had a unique microstructure since they contain 1,2-cyclohexane rings and unsaturations along the polymer chain.[180] Isoprene rubber with perfect 1,4-*cis* regularity was obtained with a Gd metallocene catalyst. Butadiene–isoprene rubber having low glass temperatures was prepared similarly.[181] Ansa fluorenyl-Cp compounds catalyze the co-polymerization of butadiene and units that incorporate 1,2-cyclohexane. The catalytic system includes a co-catalyst belonging to the group comprising a magnesium alkyl, a lithium alkyl, an aluminum alkyl, a Grignard reagent or a mixture of these.[182]

Cationic yttrium alkyl complexes $[YMe_{2-n}(solv)_x]^{n+1}$ ($n = 0, 1$) were used as functional models for the industrially applied catalysts for the polymerization of 1,3-dienes. Yttrium complex cations are particularly amenable to being isolated with the tetraphenylborate counterion, and because of yttrium's diamagnetism and nuclear spin of $I = 1/2$, can be characterized in solution by NMR spectroscopy. With the perfluorinated tetraphenylborate ion they catalyze the polymerization of 1,3-butadiene and isoprene. These results support the hypothesis that the 1,4-*cis*-selective polymerization of 1,3-butadiene proceeds with allyl rare-earth metal dications $[Ln(allyl)]^{2+}$.[183]

An ansa ligand system with coupled Cp and fluorenyl components was used with Nd and LiR/MgR_2 co-catalysts in the preparation of diene polymers having molecular weight $> 30\,000$.[184]

A rubber compound for use in a part of tires comprises a polybutadiene having a *cis*-1,4 bonding content of $\geq 99.0\%$ and a vinyl bonding content of $\leq 0.3\%$, as measured by FTIR spectroscopy. The polybutadiene, having appropriate Mn and Mw/Mn was prepared by using a Gd metallocene catalyst.[185]

A new route to poly(ethylene/butadiene) preparation uses a homogeneous neodymocene/butyloctylmagnesium catalyst which exhibits high activity and allows the polymerization to be easily controlled, both in terms of molecular weight and microstructure of the product. The polymerization mechanism involving the catalyst was discussed. The s-*trans*-η^4-butadiene complex described in the document is thought to be an essential intermediate of the initiation reaction.[186] Similar ethylene/dicyclopentadiene and styrene materials were prepared using a cationic half-sandwich scandium catalyst.[187]

In a development that will have sports fans quivering with anticipation, the polymerisation of butadiene in the presence of $(^iBu)_3Al$, $(^iBu)_2AlH$, $[SmCp^*{}_2(THF)_2]$, and $CPh_3[B(C_6F_5)_4]$ gave a polymer used to prepare golf balls.[188] Mixtures of $^iBu_3Al$, R-functionalized $Y(R')_3(THF)_2$, and $[NMe_2HPh][B(C_6F_5)_4]$ also gave 1,4-*cis*-polybutadiene.[189] Homopolymers containing 10–100 mol% $CH_2CH{=}C{=}CH(SiR_3)$ and 0–90 mol% $CH{=}CHC{=}CSiR_3$ (R=C1-5 alkyl), and copolymers with conjugated diene (*e.g.*, butadiene) were prepared from $Me_2Al(\mu\text{-}Me_2)GdCp^*{}_2$, $Al(^iBu)_3$, and $Ph_3C^+B(C_6F_5)_4$.[190] A patent has been also been filed for the polymerization of 1,3-butadiene in the presence of TIBA, DIBAH, $[SmCp^*{}_2(THF)_2]$, and $Ph_3CB(C_6F_5)_4$ and graft-polymerized with styrene to give an impact-resistant polymer.[191]

Highly stereospecific polymerization of isoprene was achieved using borohydridoneodymium complexes. In combination with stoichiometric amounts of MgR_2, $Nd(BH_4)_3(THF)_3$ and $Cp^{*\prime}Nd(BH_4)_2(THF)_2$ ($Cp^{*\prime} = C_5Me_4{}^nPr$) afford very efficient catalysts. The activity reaches 37 300 (g of polyisoprene/mol of Nd)/h. The metallocene gave rise to polyisoprene, 98.5% *trans*-regular, the highest content yet described for a homogeneous organometallic catalyst. NMR experiments argue for the formation of bimetallic Nd(μ-BH_4)Mg active species.[192] Isoprene was also polymerized with $[Me_2Si(C_5Me_4)(PCy)YCH_2SiMe_3]_2$ and $[Ph_3C][B(C_6F_5)_4]$,[193] and polyisoprene rubbers were prepared in the presence of $Me_2Al(Me)_2GdCp^*_2$, $Ph_3C^+B(C_6F_5)_4^-$, and $Al(^iBu)_3]$.[185]

The isospecific 3,4-polymerization of isoprene was also achieved using a combination of a binuclear rare earth metal dialkyl complex, such as $[Me_2Si(C_5Me_4)(\mu\text{-}PCy)YCH_2SiMe_3]_2$ (Cy = cyclohexyl), and an equimolar amount of $[Ph_3C][B(C_6F_5)_4]$ as a catalyst system. A DFT calculation suggested that a binuclear monocationic monoalkyl species, such as $[Me_2Si(C_5Me_4)(\mu\text{-}PCy)Y(\mu\text{-}R')Y(\mu\text{-}PCy)(C_5Me_4)SiMe_2]^+$, in which the alkyl group bridges the two metal centres, could be the true catalyst species.[194] Trivalent borohydrides of Nd polymerized isoprene effectively, as discussed in the Cp* section.[24]

9.3 Acetylenes

Polymerized diyne compounds, *i.e.* $HC{\equiv}CArR_2C{\equiv}CH$ [R = H, alkyl, alkoxy, (un)substituted aryl; Ar = arylene, heteroarylene] were prepared in the presence of *cis*-selective bis metallocene polymerization catalysts such as $Me_2Si(C_5Me_4)N(C_6H_2Me_3\text{-}2,4,6)LuR'(THF)$ to give polymers with up to 100% *cis* content.[195]

9.4 Caprolactone and lactide

The monoborohydride lanthanide complex $[SmCp^*_2(BH_4)(thf)]$ was successfully used for the controlled ring-opening polymerization of ε-caprolactone (ε-CL). The Sm initiator $[SmCp^*_2(BH_4)(thf)]$ produced α,ω-dihydroxytelechelic poly(ε-CL) displaying relatively narrow polydispersity indexes (<1.3). The polymers were characterized by ^1H and ^{13}C NMR, SEC, and MALDI-TOF MS analyses. Use of the single-site initiator allowed for identification of the intermediate compound $[SmCp^*_2(BH_4)(\varepsilon\text{-}CL)]$. One molecule of ε-CL initially displaced the coordinated THF in the initiator and then ε-CL opening (through cleavage of the cyclic ester oxygen–acyl bond) and insertion into the Sm-HBH_3 bond, followed by reduction of the carbonyl function by the BH_3 end-group ligand, led to the samarium alkoxy–borane derivative $[SmCp^*_2\{O(CH_2)_6O(BH_2)\}]$. This compound subsequently initiates the polymerization of ε-CL through a coordination–insertion mechanism. Finally, upon hydrolysis, α,ω-dihydroxy-poly(ε-CL), $HO(CH_2)_5C(O)\{O(CH_2)_5C(O)\}_nO(CH_2)_6OH$, was recovered.[196]

Polymerization of racemic lactide initiated by alkyl– and amido–yttrium complexes of a non-chiral tetradentate alkoxy-amino-bis(phenolate) ligand proceeded rapidly to give heterotactic-rich polylactic acid. The crystal structure of the lanthanum compound was determined.[197]

Random and block copolymerization of L- or D-lactide with ε-CL using a novel anionic initiator, $Cp^*_2SmMe(THF)$, resulted in partial epimerization, generating D,L- or *meso*-lactide polymers with enhanced biodegradability. These materials were blended with a variety of polymers to deliver higher melting temperature, lower elongation at break, and a remarkably higher tensile modulus, or higher degradability materials.[198] The comparison of organolanthanide complexes, $Cp^*_2SmMe(THF)$ and $[Cp^*_2Sm]_2(PhC{=}C{=}C{=}CPh)$, with tin compounds, $Bu_2Sn(OMe)_2$ and $Bu_2Sn(OCH_2CH_2CH_2O)$, in the preparation of random and diblock copolymers composed of L-lactide (L-LA) or D,L-LA and ε-CL, and the preparation of triblock copolymers composed of L-LA/CL/L-LA was studied and the biodegradabilities of the resulting copolymers with proteinase K and a compost were determined. The Sm-THF catalyzed product had better degradability than the materials prepared with Sn.[199]

The ring-opening polymerization (ROP) of ε-CL using lanthanide thiolate complexes $[(CH_3C_5H_4)_2Sm(\mu\text{-}SPh)(THF)]_2$ and $Sm(SPh)_3(HMPA)_3$ as initiators has been investigated for the first time. Both were found to be highly efficient initiators for the ROP of ε-CL. The poly(ε-CL) had molecular weight M_n up to 2×10^5 and relatively narrow molecular weight. According to the polymer yield, the tris-thiolate showed much higher activity. However, the number-average molecular weight of PCL obtained with the metallocene was greater. The possible polymerization mechanism of the ε-CL polymerization has been proposed based on the results of the end group analysis of the ε-CL oligomer.[200] Samarium thiolate derivatives were also found to be efficient initiators for homo- and copolymerization of 2,2-dimethyltrimethylene carbonate and ε-CL.[201]

As mentioned in Section 2.1 allylic complexes such as $[La(\eta^3\text{-}C_3H_5)_3(\kappa^1\text{-dioxane})]_2(\mu\text{-dioxane})$ have been found to be effective catalysts for lactide and ε-CL polymerization.[17]

A series of new alkoxy-amino-bis(phenols) were synthesized and the coordination properties of these di-anionic ligands towards Y, La, and Nd have been studied. The resulting complexes have been used as initiators for the ring-opening polymerization of *rac*-lactide to provide poly lactic acids (PLA). The polymerizations are living, as evidenced by the narrow polydispersity of the isolated polymers, together with the linear natures of number average molecular weight *vs.* conversion plots and monomer-to-catalyst ratios. Complex $[Y(L_6)\text{-}\{N(SiHMe_2)_2\}(THF)]$ polymerized *rac*-lactide to heterotactic PLA and *meso*-lactide to syndiotactic PLA. The *in situ* formation of $[Y(L_6)(O^iPr)\text{-}(THF)]$ resulted in narrower molecular weight distributions (polydispersity index = 1.06). The natures of the ligand substituents were shown to have a significant influence on the degree of control of the polymerizations, and in particular on the tacticity of the polymer.[202]

9.5 Acrylates

After activating with $AlEt_3$, Ln complexes with mixed ligands of substituted Cp, indene, and COT catalyzed the conversion of MMA into partially syndiotactic PMMA with narrow mass distribution. The COT complex $[(\eta^5\text{-}MeOCH_2CH_2C_5H_4)Nd(\eta^8\text{-}COT)(THF)]$ had the highest activity. Activity was inversely proportional to the steric saturation of the complex and to the size of the central ionic radius. Reactivity increased with the decrease of catalyst concentration. The effect of the co-catalyst concentration on monomer conversion was not obvious, while the molecular mass of PMMA decreased with the increase of [catalyst]. The syndiospecificity of the catalyst was negligibly affected by polymerization conditions.[203] Benzyl-substituted Cp ligands form monomeric, unsolvated Ln complexes. In conjunction with $AlEt_3$, these complexes were efficient catalysts for the syndiotactic polymerization of MMA; *i.e.* $(PhCH_2C_5H_4)_2YCl$ gave syndiotactic (rr = 66%) PMMA of high molecular weight (Mn = 105 000).[204] Similarly, $AlEt_3$/Ln complexes with substituted Cp and Schiff Base ligands polymerized MMA into high molecular weight PMMA with narrow molecular weight distribution. Lower steric hindrance led to higher activity.[205]

Vinyl methacrylate was polymerized with $Cp^*_2SmMe(THF)$ to give high molecular weight 92 (rr) poly(vinyl methacrylate).[206]

MMA polymerization catalysis was affected by $Cp^*_2SmMe(THF)$ adsorbed on a series of $AlMe_3$-treated mesoporous silicates of various pore sizes. With silicates of large pore sizes (> 29 Å) highly syndiotactic poly(MMA)s were obtained with higher weights compared with those obtained from $Cp^*_2SmMe(THF)$ alone. Similar catalyst systems with smaller pore sizes were much less active.[207]

A variety of acrylates including vinyl methacrylate were polymerized in the presence of $SmCp^*_2$ to give poly(vinyl methacrylate) with Mn 77 000, polydispersity 1.49, syndiotacticity 92%, and vinyl group survival rate 100%.[208] The ansa-lanthanocenes $[LLnCl]_2$ [$L = Me_2Si(\eta^5\text{-}C_5H_3CMe_2Ph)_2$; Ln = Er, Gd, Sm, Dy], in conjunction with $AlEt_3$ or nanosized NaH, were efficient catalysts for MMA homopolymerization. The activity was found to be comparable to that of single component organolanthanide hydride catalysts.[209]

9.6 Miscellaneous monomers

Condensation of germane $(C_6F_3)_3GeH$ treated with the naphthalene complex of ytterbium (II) $C_{10}H_8Yb(THF)_3$, gave poly(phenylenegermanes).[210]

The reaction of Et_2Zn with $NaOCH_2CH_2OH$ yielded a bimetallic zinc complex. Reactions of $NaOCH_2CH_2OZnEt$ with Ph_3SnCl, Cp_2TiCl_2, and $Cp_2LuCl(THF)$ afforded the corresponding complexes $Ph_3SnOCH_2CH_2OZnEt$, $Cp_2Ti(OCH_2CH_2OZnEt)_2$, and $Cp_2LuOCH_2CH_2OZnEt$. $Cp_2Ti(OCH_2CH_2OZnEt)_2$ catalyzes copolymerization of CO_2 with cyclohexene oxide at room temperature to give polycarbonate. The Sn/Zn compound is catalytically inert under these conditions, and with $Cp_2LuOCH_2CH_2OZnEt$ only the polyether was formed.[211]

A comparative study of the effectiveness of organolanthanide complexes, $Cp^*{}_2SmMe(THF)$ and $[Cp^*{}_2Sm]_2(PhC{=}C{=}C{=}CPh)$, with tin compounds, $Bu_2Sn(OMe)_2$ and $Bu_2Sn(OCH_2CH_2CH_2O)$ for the preparation of random, diblock, and triblock copolymers composed of L-lactide (L-LA), D,L-LA and cyclic carbonates, trimethylene carbonate (TMC) or 2,2-dimethyltrimethylene carbonate was reported. The biodegradabilities of the resulting copolymers were examined.[212]

9.7 Block copolymers

Block copolymns. of 1-pentene or 1-hexene with MMA or ε-CL were explored using $[Me_2Si(2\text{-}SiMe3\text{-}4\text{-}{}^tBuMe_2SiC_5H_2)_2YH]_2$ or $[Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}{}^tBuC_5H_2)_2SmH]_2$ as an initiators in toluene or in neat mixtures by the successive addition of monomers in this order. Random copolymerizations of 1-pentene with 1-hexene, and random copolymerization of ethylene with 1-hexene were also performed using the Y initiator.[213] Similar experiments produced butadiene/MMA or butadiene/*p*-acrylonitrile block copolymers.[214] Block co-polymers such as 2,7-diethynyl-9,9-dioctylfluorene/CL were prepared with a $Cp^*{}_2La(CH_2SiMe_3)_2{}^-$ catalyst.[215] Finally, giant rod-coil amphiphilic block copolymers were prepared by metallocene-catalyzed polymerizations.[216]

10. Spectroscopy

Electronic spectroscopy continues to be a useful source for probing how neutral and anionic ligands influence Ln crystal fields, though only a single research group is involved in this work. The absorption spectra of trigonal planar $Nd(\eta^5\text{-}C_5H_4{}^tBu)_3$, $NdCp'_3$ and trigonal pyramidal $[Nd(\eta^5\text{-}C_5H_4{}^tBu)_3(THF)]$ have been studied. Truncated crystal field (CF) splitting patterns of these compounds could be derived, and simulated by fitting the parameters of a phenomenological Hamiltonian.[217] Lanthanide complexes $[LnCp_3(OP(OR)_3)]$ ($Ln = La$, $R = Et$; $Ln = Pr$, $R = Me$; $Ln = Pr$, $R = Et$) and $[Pr(Ind)_3(OP(OEt)_3)]$ were prepared, and oriented single crystal absorption spectra, solution magnetic CD spectra, and luminescence spectra of powdered materials allowed a nearly complete CF splitting pattern to be derived for the Pr(III) ion; the pattern was simulated by fitting the free parameters of another phenomenological Hamiltonian. Interestingly, the optical spectra of the indenyl compound suggest that two different species exist at low temperatures, thus preventing a successful CF analysis.[218] Polarized single crystal studies of Nd-doped Cp_3La(methylacetate, or MA) were carried out, based on the structure of $Cp_3Pr\cdot(MA)$. Some differences were seen with the sequences of crystal field states that agree with those calculated for $Cp_3Nd\cdot CNC_6H_{11}$ and $Cp_3Nd\cdot MeTHF$.[219] The absorption and luminescence spectra of trigonal planar $[Sm(\eta^5\text{-}C_5H_4{}^tBu)_3]$, low symmetry [SmCp($\eta^3$-TpMe$_2$)($\eta^2$-TpMe$_2$)] (TpMe$_2$ = hydrotris(3,5-dimethylpyrazolyl)borato) as well as ψ trigonal pyramidal [Sm(η^5-$C_5H_4{}^tBu)_3$(THF)], [Sm(η^5-Cp)$_3$(THF)] and [Sm(η^5-Cp)$_3$(CNC_6H_{11})] were measured at room and low temperatures. The ligands have been placed into a truncated nephelauxetic and relativistic nephelauxetic series.[220] Finally, Amberger used comparisons of nephelauxetic ratios β of a number of molecular Pr(III) compounds, and the Slater parameters F2 (or Racah parameters E1) of molecular Nd(III) and selected Sm(III) compounds to identify more covalent types of Eu(III). The $^7F_0 \rightarrow {}^5D_0$ absorption transitions for dissolved and crystalline [Eu{N(SiMe$_3$)$_2$}$_3$], "[Eu{OC(^{t}Bu)$_3$}$_3$]" and [Eu(η^5-C_5H_5)$_3$(CNC_6H_{11})] were larger in energy than those of $[Eu(H_2O)_9]^{3+}$ or even gaseous Eu^{3+}, indicating quasi "anti-nephelauxetic" effects. Crystal field calculations, however, reveal that lower Slater parameters F2 (or Racah parameters E1) have to be used than those of $[Eu(H_2O)_9]^{3+}$ in order to reproduce the experimentalenergy differences between $^7F_0$ and $^5D_0$, thus indicating the expected nephelauxetic effects of more covalent Eu(III) compounds.[83]

In a very different focus, evidence for Kondo coupling in $Ce(C_8H_8)_2$ and Cp*$_2$Yb(bipy) was deduced from magnetic susceptibility and L_{III}-edge X-ray absorption spectroscopy. These well-defined systems provide a new way to study the Kondo effect on the nanoscale indicate the importance of this often-ignored contribution to bonding in organometallics.[36]

11. Gas phase studies

Gas phase studies focused significantly on the interaction of Ln with polyunsaturated hydrocarbons, with C_8H_8 receiving the majority of the attention. Multidecker sandwich clusters of $Eu_n(COT)_n^-$ (n = 1–4; COT = 1,3,5,7-cyclooctatetraene), were synthesized in the gas phase, and studied with PES. A theoretical bonding scheme, charge distributions, valence orbital energies, and photodetachment energies were calculated. The ground electronic state X^- and the 1st excited electronic state A^- both have strong ionic bonding and a characteristic charge distribution. Also, the valence orbital energies of Eu (6s) and COT (Lδ) depend strongly on cluster size and their positions in the clusters. The experimental PE spectra was assigned and from this analysis the authors suggest spectral assignments.[221] A molecular beam of $Eu_n(COT)_m$ sandwich nanowires was also produced by laser vaporization, and the formation mechanism was quantitatively revealed by PE and photoionization spectroscopies of the Eu-COT species, together with supporting theoretical calculations. Growth processes extending the length of Eu-COT nanowires are thought to involve elementary reactions in which efficient charge transfer occurs at the terminal reaction sites. In every elementary step, the reaction proceeds between one reactant having low ionization energy and the other reactant having high electron affinity.[222] Lastly, the magnetic properties of gas-phase $Tb_n(C_8H_8)^{n+1}$ were measured using a Stern-Gerlach type magnetic deflection approach. Beams of $Tb_n(C_8H_8)^{n+1}$ complexes displayed 1-sided deflection toward high field indicating that fast spin relaxation occurs within the complexes as they pass through the magnetic field. The magnetic moment for $Tb_n(C_8H_8)^{n+1}$ (n = 1–5) was evaluated using the Langevin model. Evolution of magnetic moment with the complex size was discussed with electronic structures for oxidation states of $Tb^{3+/2+}$ ions, implying the possibility of antiferromagnetic interaction of two adjacent Tb^{2+} ions.[223]

With arenes, cocondensation of Eu and Sm with 4′-pentyl-1,1′-biphenyl-4-carbonitrile (ArH) at low temperature gave evidence for formation of mono- and bimetallic sandwich arene complexes $(ArH)_2M$ and $(ArH)_2M_2$ with anti-parallel arrangement of the ligands and bis-π-arene bonding off the metal centre. Structures of the europium complexes $(ArH)_2Eu$ and $(ArH)_2Eu_2$ were optimized at DFT level with hybrid B3LYP potential, revealing an antiparallel disposition of ligand molecules. The spectral shifts for ligand CN group stretching vibrations and the relative thermal stability of the complexes were discussed.[224] Similarly, $Sc(C_6H_6)_{1,2}$ were produced by interactions between the laser-vaporized Sc and benzene vapor in pulsed molecular beams, and identified by photoionization time-of-flight mass spectrometry and photoionization efficiency spectroscopy. The electron-spin multiplicities and geometries of these complexes and their ions were determined by combining pulsed field-ionization zero electron kinetic-energy spectroscopy and DFT calculations. For $Sc(C_6H_6)$, a short-range quartet ground state is determined for the neutral complex, and a low-energy triplet state is probed for the ion. For the bis-arene complex, the neutral ground state is a doublet, and two low-energy ion states are singlet and triplet. Ionization energies and metal-ring stretching wavenumbers were measured for both complexes.[225]

In small molecule reactions, $Sc_2[\eta^2(\mu_2\text{-C,O})]$, the first homoleptic dinuclear metal carbonyl with an unprecedented bridging and side-on-bonded CO, was obtained in the laser-ablation of Sc atoms with CO in a solid argon matrix. The compound exhibits an unusually low C–O stretching frequency at 1193 cm^{-1}, characteristic of an anomalously weakened C–O bond. This CO-activated molecule undergoes UV-visible photoinduced rearrangement to the CO-dissociated molecule, c-Sc_2-(μ-C)(μ-O). The activation energy for the isomerization of $Sc_2[\eta^2(\mu_2\text{-C, O})]$ to c-Sc_2(μ-C)(μ-O) is calculated to be 15 kcal/mol. Experimental and theoretical results schematically depict an activation process to CO dissociation[226]

Y- and La-carbide cluster cations YC_n^+ and LaC_n^+ (n = 2, 4, and 6) were generated by laser ablation of carbonaceous material containing Y_2O_3 or La_2O_3 and reacted with benzene and cyclohexane. The FTICR mass spectrometry study shows that the reactions of YC_2^+ and LaC_2^+ with benzene produce $M(C_6H_4)(C_6H_6)^{n+}$, $M(C_8H_4)(C_6H_6)^{n+}$, and $M(C_8H_6)(C_6H_6)^{m+}$. For YC_4^+, LaC_4^+, and LaC_6^+, benzene addition gives products such as $MC_n(C_6H_6)^{m+}$. In the reaction with cyclohexane, all the metal-carbide cluster ions form metal–benzene complexes. Collision-induced-dissociation experiments were performed on the major reaction product ions, and the different levels of energy required for the fragmentation suggest that both covalent bonding and weak electrostatic interaction exist in these organometallic complexes.[227] Similarly, reactions of Ln^+, with 1,2,3,4,5-pentamethylcyclopentadiene, HCp* gave $[MCp^*]^+$ (+ H), as well as additional products.[228]

12. Theoretical studies

The 2004/5 theory papers can be divided into works that focused on the prediction of fantasy molecules, those that attempt to rationalize the properties of real molecules, and works that attempt to elucidate molecular reactivity. In addition, a review discussed some relations between the electronic structure and the reactivity of lanthanide complexes.[229]

On the subject of unreal molecules, electronic and geometric structure of the 3d-transition metal monocarbonyls MCO (M = Sc, Ti, V, Cr) was investigated through coupled cluster (CC) and multireference variational methods (MRCI) combined with large basis sets. The Sc–CO dissociation energies was calculated to be 36 kcal/mol with respect to Sc(4F). The bonding is rather complicated and could be attributed mainly to π-conjugation effects between the M and CO π-electrons, along with weak σ-charge transfer from CO to M atoms.[230]

Ab initio and DFT calculations were performed on $ScCH_n$, n = 1–3. Although multiple bonding was expected from the Lewis bonding scheme, the results indicate an almost pure ionic bond for all of the systems studied. The net charge transfer from the metal to the C atom ranges from 0.5 to 1 e^-, and the electronic structure of the CH_n^- moiety is unaltered after the interaction with the metal cation, showing little or no effect on the shape of the electron pairing. The bond paths corresponding to a possible α-agostic bond for these systems were not present.[231]

The low lying electronic states of 3d transition-metal–benzene complexes ScBz were studied by performing complete active space SCF and multireference CI calculations. Geometries, energetics, and electronic structure were presented and discussed. The results concerning both the geometry and the spin multiplicity of the ground-state contrast with those obtained from previous DFT calculations. The disagreements between single-reference-based approaches and multireference methods in the characterization of neutral 3d-metal complexes were discussed.[232] A long-range model adding a repulsive term from SCF calculations and an attractive term from dispersion evaluated in an oblate spheroidal formalismwas also proposed for the interaction energy between Sc and benzene.[223]

The nature of the chemical bonding in the 1:1 complexes formed by Sc with 14 electrons (N_2, CN^-, C_2H_2) and 10 electrons (NH_3, H_2O, F^-) ligands revealed that the bonding is ruled by the nature of the ligand. The 10 electron and anionic ligands are very poor electron acceptors and therefore the interaction with the metal is mostly electrostatic. The electron acceptor ligands which have at least a lone pair form linear or bent complexes involving a dative bond with the metal.[234]

Ab initio, many-body methods were used to determine structures, relative energies, and vertical electron-detachment energies of $ScC_6H_6{}^-$. The two lowest anionic structures are singlets that display boat and inverse-boat conformations of the C_6H_6 ligand and have energies that are within 0.1 eV of each other. The principal peaks in a recently reported anion photoelectron spectrum are assigned to Dyson orbitals that are dominated by Sc 4s or $3d_{x2-y2}$ contributions in the boat form or by Sc 4s or $3d_{xy}$ contributions in the inverse-boat form.[235]

With real molecules, DFT calculations revealed that in $[(C_5Me_4SiMe_3)_4Ln_4H_8]$ (Ln = Lu, Y) the optimized Ln_4H_8 core prefers a pseudo-C_{3v}-symmetric structure with one body-centreed μ_4-H, one face-capped μ_3-H, and six edge-bridged μ_2-H atoms. Metal-metal orbital interactions *via* the hydride bridges were also observed in these complexes.[236]

A comparison of electronic structure and bonding in a homologous series of bent metallocene complexes Cp_2CeF^+, Cp_2CeO, $Cp_2Ce(NH)$, $Cp_2Ce(CH_2)$, and $Cp_2Ce(CH)^-$ and the Lewis base adduct $Cp_2Ce(CH_2)(NH_3)$ was presented. In Cp_2CeZ systems, the Ce–Cp interactions are best described as largely ionic in nature, whereas the Ce–Z interactions have a stronger covalent component. The optimized Ce–Z bonds are short, and the bonding analysis indicates the formation of metal–ligand σ and π bonds. The theoretical studies suggest that a unique hybridization of Ce 4f, 5d, and 6p valence orbitals gave very covalent metal–ligand σ bonds when compared to the transition element analogue. In contrast, the hybridization of Ce 4f and 5d valence orbitals in π bonds results in weaker metal–ligand π bonding than in the transition element analog. The main result of the present computational study is the recognition that species with terminal multiple bonds between lanthanide ions (such as tetravalent Ce) and main group elements appear to be legitimate synthetic targets.[237]

A DFT study of the divalent lanthanide complexes $[C_5Me_4SiMe_2({}^iPr_2\text{-tacn})]LnI$ (Ln = Sm, Yb; tacn = 1,4-diisopropyl-1,4,7-triazacyclononane) accurately predicted the geometry of the complexes as distorted trigonal bipyramids, with the essential structural features correctly reproduced. Model studies show that the computations can be simplified by replacing the Me groups (which do not interact with the lanthanide centre directly) with hydrogen atoms to still provide reasonable predictions for the structure of the complex.[238]

DFT calculations were also carried out to compare several models of the Cp ligand for the insertion of ethylene into the Ln–C bond of Cp_2Ln–Et and β-H transfer to the incoming monomer. Calculations were carried out for Cp* where all atoms are explicitly treated at the DFT level, for Cp* where the Me groups are taken into account by a molecular force field, Cp and Cl. Comparisons of these systems provide information about the stereoelectronic effects of the ligands on the elementary steps of the reaction. Cp* has the steric properties of Cp* but the electronic properties of Cp, the geometry and energy barriers are very close for Cp* and Cp suggesting that steric effects outweigh the electronic effects of the Me groups of the Cp ligand.[239]

Finally, in the area of mechanistic theory, a DFT study of the complete catalytic reaction course for the organolanthanide-mediated intramolecular hydroamination/cyclization (IHC) of (4E,6)-heptadiene-1-amine by a prototypical achiral $Cp^*_2LaCH(TMS)_2$ precatalyst was found to involve rapid substrate association/dissociation equilibrium and facile intramolecular diene insertion, linked to turnover-limiting protonolysis of the η^3-butenyl-Ln functionality, with the amine-amidodiene-Ln adduct complex representing the catalyst's resting state. The thermodynamic and kinetic factors that determine the high regio- and stereoselectivity of the mechanistically diverse IHC of aminodienes were elucidated.[240,241] Similarly, a DFT investigation into the hydroamination reaction suggested that the reaction proceeds in two discrete steps: namely, cyclization *via* C=C insertion into the Cp_2La–P(phosphido) linkage to form La–C and C–P bonds and subsequent La–C protonolysis. The cyclized phosphinoalkane is released in the latter process and the active catalyst regenerated. The picture that emerges is one of approximately thermoneutral insertion of the alkene fragment into the Cp_2La–P(phosphido) bond *via* a highly organized, seven-membered chairlike cyclic transition state. The resulting cyclopentylmethyl complex then undergoes turnover-limiting but exothermic protonolysis to yield a phosphine–phosphido complex, the likely resting state of the catalyst. Interestingly, this energetic ordering of barriers is exactly reversed from that in the formally analogous hydroamination/cyclization process, where C=C insertion is turnover-limiting and protonolysis is rapid. The calculations provide evidence that, in the hydrophosphination/cyclization process, there is competition at the lanthanide centre between cyclized product and incoming unconverted substrate and, therefore, some inhibition of the protonolysis step, in accord with experiment.[242]

Optimized geometries and a potential energy surface were calculated for the hydroamination-cyclization of 4-pentene-1-amine, with $CpLaR''$ reacting with $H_2N(CH_2)_3CH{=}CH_2$ to afford the pentenylamido complex, with subsequent intramolecular hydroamination/cyclization giving the 2-pyrrolidinylmethyl complex Cp_2LaCH_2-cyclo-2-$CH(CH_2)_3NH$, which is then protonated by $MeNH_2$, regenerating the active catalyst *via* the amine–amido complex. The reaction is found to occur in two steps, namely, cyclization to form La–C and C–N bonds, and subsequent La–C protonolysis. Calculations were carried out for (i) insertion of the olefinic moiety into the La–N bond *via* a four-centre transition state and (ii) protonolysis by a second substrate molecule. The cyclized amine then dissociates, thus restoring the active catalyst. A DFT energy profile was determined for the turnover-limiting insertion of the 1-amidopent-4-ene C=C double bond into the La–NH bond. The concerted insertion of the alkene fragment into the La–N(amido) bond *via* a highly organized, seven-membered chairlike cyclic transition state is the rate-limiting, slightly endothermic reaction step. The resulting 2-pyrrolidinylmethyl complex then undergoes exothermic protonolysis to yield an amine-amido complex, the resting state of the catalyst. These steps agree with experimental data.[243]

The Y/acetylene cyclotrimerization reaction was studied theoretically, employing DFT in its B3LYP formulation. The complete reaction mechanism was analyzed, identifying intermediates and transition states. Both the ground spin state and at least one low-lying excited state were considered to establish whether possible spin crossings between surfaces of different multiplicity can occur. Results show that the overall reaction is highly favorable from a thermodynamic point of view and ground state transition states lie always below the energy limit represented by ground state reactants. After the activation of two acetylene molecules and formation of a bis-ligated complex, the reaction gives a metallacycle intermediate.[244]

A study of alternative mechanisms for chain initiation of the organolanthanide-promoted ring-opening polymerization of 2-phenyl-1-methylenecyclopropane (PhMCP) with an archetypical [Cp_2SmH] model catalyst was presented. Overall, chain initiation of the samarocene-mediated ring-opening polymerization of PhMCP is predicted to be a smooth, kinetically facile process.[245]

Sm(III) carbenoid I_2SmCH_2I-promoted cyclopropanation reactions with ethylene have been investigated and are predicted to be highly reactive, similarly to the divalent samarium carbenoid $ISmCH_2I$. The methylene transfer and carbometalation pathways were explored and compared with and without coordination of THF solvent molecules to the carbenoid. The methylene transfer was found to be favored, on the addition of one THF molecule.[246]

12. Organolanthanides in organic synthesis

The oxophilic tendencies of Ln ions continue to find applications in the stoicheiometric and catalytic transformation of small organic molecules. As evidenced by the theory section, hydroamination and related reactions continue to be a major focus. Intramolecular 5-endo-dig hydroaminations of homopropargylamine derivatives were efficiently catalyzed by [$Cp^*{}_2YbR''$] to give endocyclic enamine products. For example, the hydroamination of N-(3-butynyl)-2-(ethenyl)benzeneethanamine gave 1-[2-[2-(ethenyl)phenyl]ethyl]-2,3-dihydro-1H-pyrrole. In this reaction a 5-endo-dig hydroamination is taking place in the presence of a second olefinic group positioned for 6-exo-cyclization.[247]

The constrained geometry complex [$Me_2Si(\eta^5\text{-}Me_4C_5)(^t BuN)$]$LnE(TMS)_2$ (E = CH, N) mediates intramolecular hydroamination/cyclization of sterically demanding amino-olefins to afford disubstituted pyrrolidines in high diastereoselectivity (*trans*/*cis* = 16/1) and good to excellent yield. In addition, chiral C_1-symmetry organolanthanide catalysts of the type [$Me_2Si(OHF)(CpR^*)$]$LnN(TMS)_2$ (OHF = η^5-octahydrofluorenyl; Cp = $\eta^5\text{-}C_5H_3$; R* = (–)-menthyl; Ln = Sm, Y), and [$Me_2Si(\eta^5\text{-}Me_4C_5)(CpR^*)$]$SmN(TMS)_2$ (Cp = $\eta^5\text{-}H_3C_5$; R* = (–)-menthyl) mediate asymmetric intramolecular hydroamination/cyclization of amines bearing internal olefins and afford chiral 2-substituted piperidine and pyrrolidine with significant enantioselectivity.[248]

The related constrained geometry complex (CGC)LuN(TMS)(THF) (CGC′ = [Me_2Si(3-pyrrolidinyl-1-η^5-indenyl)(^{t}BuN)]$^{2-}$) was also found to be an active precatalyst for the intramolecular hydroamination/cyclization of representative aminoalkenes.[249] The amino alkene-yne $NH_2CH_2CMe_2CH_2CH{=}CH(CH_2)_2CH{=}CH_2$ was regiospecifically bicyclized by [$Me_2Si(\eta^5\text{-}Me_4C_5)(^t BuN)$]$LnE(TMS)_2$ to the corresponding indolizidine skeleton in good yield and high diastereoselectivity. Interestingly, thermolysis of Cp^*LaR'' was found to release $CH_2(SiMe_3)_2$ (with the possible formation of a fulvene). The thermolysis product readily reverts to active catalyst upon protonolysis by substrate and exhibits the same catalytic activity in the cyclization of *cis*-2,2-dimethylhept-5-enylamine as the unthermolyzed material. $Cp^*{}_2La(NHR)(NH_2R)_n$ and [$Me_2Si(\eta^5\text{-}Me_4C_5)(^t BuN)$]$Sm(NHR)(NH_2R)_n$ were also shown to be catalytically active and thermally robust.[248]

Alkylscandium catalysts $PhMe_2SiCH_2Sc(L1)_2$ (L1 = 3-^{t}Bu–N–Ar-salicylaldiminate-κN,κO; Ar = 2,6-$^i PrC_6H_3$ or mesityl) and β-diketiminato complexes MeR1Sc(ArN=C^{t}BuCH=C^{t}BuN–Ar-κN,κN′) (Ar = 2,6-$^i Pr_2C_6H_3$, R1 = Me, $MeB(C_6F_5)_3^-$) were used for heterocyclization of $PhC{\equiv}CCH_2CH_2CH_2NH_2$ and $CH_2{=}CHCH_2CR_3R_4CH_2NH_2$, affording 5-benzyl-3,4-dihydro-2H-pyrrole and 2-methyl-4,4-R3$_2$-pyrrolidines. Similar reactions of $CH_2{=}CHCH_2CHMeCH_2NH_2$, $CH_2{=}CHCH_2CH_2Cph_2CH_2NH_2$ and $CH_2{=}CHCH_2CH_2CHMeNH_2$ gave 2,4-dimethylpyrrolidine, 2-methyl-5,5-diphenylpiperidine and 2,5-dimethylpyrrolidine, respectively. Complex structure/catalyst activity investigations resulted in the identification of a highly catalytically active cationic, β-diketiminato scandium complex.[250]

Chiral binaphtholate yttrium aryl complexes were highly active and enantioselective catalysts for the asymmetric hydroamination of aminoalkenes, as well as the kinetic resolution of α-substituted 1-aminopent-4-enes to give trans-2,5-disubstituted pyrrolidines with good enantiomeric excess.[251] The biphenolate alkyl complex [La{*R*-biphen}R″(THF)$_3$] shows high catalytic activity for hydroamination/cyclization of aminoalkenes, but only low enantio-selectivity, with higher catalytic activity than the THF-free homochiral dimer in the cyclization of 2,2-dimethylpent-4-enylamine, suggesting that the dimeric structure of the catalyst system prevails under catalytic conditions in the absence of THF. Addition of HN(SiHMe$_2$)$_2$ to [La{*R*-Biphen}R″(THF)$_3$] results in the formation of [La{*R*-Biphen}{N(SiHMe$_2$)$_2$}(THF)$_3$] which is in equilibrium with its homochiral dimer [La{*R*-Biphen}{N(SiHMe$_2$)$_2$}(THF)]$_2$ at elevated temperatures. The biphenolate alkyl complexes also catalytically hydrosilylated styrene, 1-hexene and norbornene with high diastereoselectivity.[252] In structural work, the homochiral dimer [La{(*R*-Biphen)R″]$_2$ was prepared by alkane elimination starting from [LaR″$_3$] and enantiopure (*R*)-3,3′-di-*t*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diol [H$_2${(R)-Biphen}]. An intramolecular process scrambles the phenolates rapidly in solution.

A solvent-free H-atom-substitution (Si-bonded H-atom) of polysiloxanes for alcohol functional groups involves reactions of $R_2(R')SiO(SiR_2O)_x(SiHRO)_ySiR_2R''$ with alcohols catalyzed by Sc Y, La and lanthanide organometallics.[253]

For Y, the dimeric hydrido complex [Y(L)(THF)(μ-H)]$_2$ (L = $C_5Me_4CH_2Si$-Me_2NCMe_3) catalyzed the hydrosilylation of 1,5-hexadiene, 1,7-octadiene and vinylcyclohexene by PhSiH$_3$. For 1,7-octadiene, the product distribution of the hydrosilylation strongly depends on the molar ratio of the reagents. In the absence of PhSiH$_3$, the stoichiometric reaction of the dimer with 1,5-hexadiene gave [Y(L){CH$_2$CH(CH$_2$)$_4$*trans*-stilbene and alkynes such as ^{t}BuC≡CH were not hydrosilylated. *Trans*-stilbene inserted into the Y–H bond to give the 1,2-diphenylethyl complex [Y(L){CH(CH$_2$Ph)Ph^{t}BuC≡CH gave the dimeric acetylide [Y(L)(CsCCMe$_3$)]$_2$. In an attempt to detect a mo}nomeric hydrido species the hydride dimer was reacted with DME to form the sparingly soluble, dimeric 2-methoxyethoxy complex [Y(L)(μ-OCH$_2$CH$_2$OMe-κO)]$_2$.[254]

Organolanthanide-mediated hydrophosphination and ethylene polymerization were coupled in a catalytic cycle to produce diphenylphosphine-terminated polyethylenes. High activities and narrow polydispersities were observed in the polymerization/chain transfer process. Polyethylene molecular weights were found to be inversely proportional to diphenylphosphine concentration, supporting a chain transfer mechanism. This is apparently the first example of an electron-rich phosphine functioning efficiently as a chain transfer agent in a single-site f^n/d^0-mediated olefin polymerization process.[255]

Monocyclopentadienyl alkyllutetium 2,2′-bipyridine reacts with carbon monoxide by a carbonylation-insertion pathway, yielding the bipyridine C–H-bond activation product. Carbonylation of [Cp*LuR(bpy)(R′)] (R=NH(2,6-${}^iPr_2C_6H_3$), R′) resulted in insertion of carbonylated alkyl group into the 2,2′-bipyridine C–H-bond.[256]

Treatment of [Cp$_2$Ln(μ-SEt)]$_2$ with PhRC=C=O gave dimeric [Cp$_2$Ln(μ-η^1:η^2-OC(SEt)=CPhR)]$_2$ [R = Ph, Ln = Yb, Er, Sm, Y; R = Et, Ln = Er], the first examples of ketene insertion into a metal-sulfur bond. This reactivity is an efficient method for the synthesis of organolanthanides with a β-thiolate-substituted enolate ligand and only a single insertion was observed.[257] The dimeric organosamarium hydride [(Ind)$_2$SmH]$_2$ reacts with unsaturated carbonyl compounds to give the corresponding reduction products with a high selectivity. The carbonyl groups were reduced while the C=C bonds were not affected.[258]

In other areas, metalation of 1,3-diphenyl-2-benzylpropene with YbPh$_2$, followed by electrophilic quenching with Ph$_3$SnCl afforded (PhCHSnPh$_3$)$_2$C=CHPh.[259] Neutral triazacyclononane-amide lanthanum dialkyl and dialkynyl complexes were synthesized and structurally characterized. A cationic triazacyclononane-amide lanthanum monoalkyl species was generated and shown to be highly active in the rare cis-selective catalytic linear dimerization of phenylacetylene.[260]

The chiral multidentate ligand, (R,R,R,R)-*N*,*N*,*N*′,*N*′-tetra(2-hydroxy-2-phenylethyl)-1,3-xylylene diamine encapsulates two Ln(III) ions and efficiently effects the asymmetric transfer hydrogenation of aryl ketones in high enantioselectivity (up to $>99\%$ ee).[261]

A new method for preparing α-branched enones from carboxylic acid derivatives was reported. Reactions of N,O-dimethylamides with a masked acyl anion equivalent, followed by the addition of $Me_3SiCH_2CeCl_2$ gave intermediates that undergo Lewis acid mediated olefination to produce enol ethers that can be hydrolyzed to afford simple α-branched enones in high overall yields.[262]

Several complexes (M=Ce, Er, Sm, Y, Yb, La) were evaluated for catalysis of crossed silyl-benzoin addition and the La complex was identified as the best. The catalyst effects the selective coupling of aryl and alkyl acylsilanes with aryl, heteroaryl, α,β-unsaturated, and aliphatic aldehydes to give α-hydroxy or α-silyloxy ketones.[263] Finally, in what appears to be a rather perverse process, enantiomerically enriched α-aminonitriles were racemized by contact with lanthanide alkoxides and lanthanocenes.[264]

The catalytic addition of terminal alkynes to carbodiimides has been achieved with $\{Me_2Si(C_5Me_4)(NPh)\}Y(R')(THF)_2$, which offered a straightforward, atom-economic route to the *N*,*N*′-disubstituted propiolamidines, that contain a conjugated C–C triple bond. A rare earth metal amidinate species was confirmed to be a true catalytic species in this process, thus demonstrating that an amidinate unit can participate in a catalytic reaction under appropriate conditions. Silylene-bridged fluorenyl compounds were found to efficiently transform ketones into cyano trimethylsilyl ethers.[265] Aromatic aldehydes undergo cyanosilylation to afford α-trimethylsiloxybenzeneacetonitriles in quantiattive yields. A new series of silylene-bridged rare-earth bis-9-fluorenyl complexes was prepared by silylation of 9-lithiofluorene and subsequent reaction of MePhSi(9-fluorenyl)$_2$ with BuLi and $LnCl_3$. The prepared lanthanocenes, $[LnCl[(\eta^5\text{-}C_{13}H_8)_2SiMePh]]$ (Ln = Yb, Dy, Pr, Sm, Nd) were very efficient Lewis acidic catalysts, giving areneacetonitriles $XC_6H_4CH(OSiMe_3)CN$ and α-trimethylsiloxy-1-naphthaleneacetonitrile.[266] Catalytic isomerization of 1,5-hexadiene by Cp_2Ln Schiff base/NaH systems was studied in detail. The isomerization resulted in a mixture of 1,4-hexadiene, 2,4-hexadiene, 1,3-hexadiene, methylenecyclopentane, and methylcyclopentene. 1,4-Hexadiene and methylenecyclopentane were the intermediate products, while 2,4-hexadiene and methylcyclopentene were the end-products.[267] Organolanthanide catalyzed cyclization-silylation of nitrogen-containing polyunsaturated systems allows access to core structures commonly found in naturally occurring alkaloids. The reaction was particularly effective for substrates with terminal alkenes. Interestingly, sterically hindered sulfonamides, which were previously believed to render the catalyst inactive, were actually compatible with the catalyst, thus affording the cyclized products after prolonged reaction times. Variations using fused ring systems were also investigated.[268] And finally, $Ln(CN)_3$ were found to be superior catalysts for cross silyl benzoin addition reactions between acylsilanes and aldehydes. Unsymmetric aryl-, heteroaryl-, and alkyl-substituted benzoin adducts were approached. The mechanism of was investigated, and formation of the carbon–carbon bond is believed to be the last irreversible step.[269]

Two new routes to access camphor-derived chiral diol were developed. One route employs camphorquinone as the starting material in only two steps the desired diol in 55% overall yield. The second route, from camphor, leads to the desired diol in an efficient four-step synthesis with an overall yield of 55%,[270] and a method for preparing enantiomerically rich esters from a mixture of enantiomers was awarded a patent.[271] Finally the utility of Sm(II) as a reducing agent was reviewed.[272]

Abbreviations

Ln	Lanthanide
R′	CH_2SiMe_3
R″	$CH(SiMe_3)_2$
Cp	C_5H_5
MeCp	C_5H_4Me
Cp*	C_5Me_5
Cp′	$C_5H_4(SiMe_3)$
Cp″	$–C_5H_3(SiMe_3)_2$
Cp‴	$–2,4\text{-}C_5H_2(SiMe_3)_3$
Cp*′	$C_5Me_4SiMe_3$
Cp^{Bu}	$C_5H_4Bu^t$
Cp^{Bu2}	$1\text{-}C_5H_3Bu_2{}^t$
Cp^{Bu_3}	$1,2,4\text{-}Bu_3{}^tC_5H_2$
Ind	$\eta\text{-}C_9H_7$, indenyl
Flu	$\eta\text{-}C_{13}H_8$, fluorenyl
tmp	$\eta\text{-}C_4Me_4P$
COT	C_8H_8
COT″	$1,4\text{-}C_8H_6(SiMe_3)_2$
TMEDA	tetramethylethylenediamine (1,2-bis(dimethylamino)ethane)
TMS	$SiMe_3$
HMPA	$OP(NMe_2)_3$
DME	$CH_3OCH_2CH_2OCH_3$
MMA	methylmethacrylate
MAO	methylaluminoxane
DFT	density functional theory
SIR	sterically induced reaction

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Group 14: silicon, germanium, tin and lead

Richard A. Layfield

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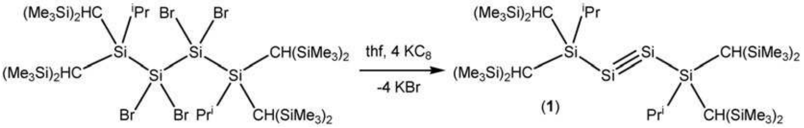
1. Introduction

Rather than providing an exhaustive survey of Group 14 organometallic chemistry published in 2004–2005, this chapter takes the form of a 'highlight' review and will focus primarily on low-coordinate, multiply bonded organo-derivatives of silicon, germanium, tin and lead. Transition metal complexes in which Group 14 elements are present as ligands in a formally subvalent form will be described but ligands of the tetryl type (*e.g.* R_3Si, silyl) are omitted. Naked cluster species, in which supporting organic ligands are absent, are also not covered by this review.

2. A silicon-silicon triple bond

In recent editions of Specialist Periodical Reports, this chapter has begun with summaries of unsuccessful attempts to synthesize and structurally authenticate the silicon-silicon triple bond. It seems fitting, therefore, that the current review should open on a more positive note since in 2004 the elusive disilyne was finally reported by Sekiguchi and co-workers.[1] Thus, a stable compound containing two 2-coordinate silicon centres can be prepared and isolated according to Scheme 1



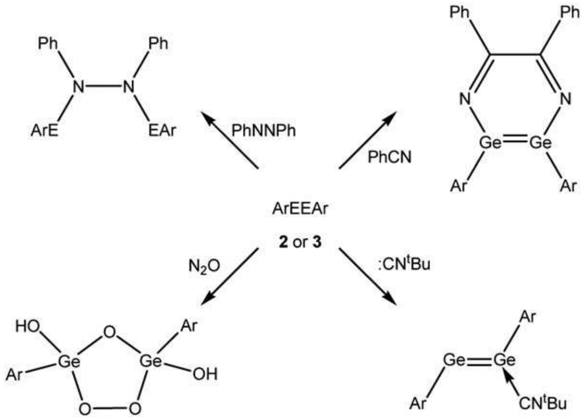
Scheme 1

Green crystals of compound **1** are stable up to 100 °C and the silicon-silicon distance is 2.0622(9) Å. An interesting structural feature that contrasts with the analogous carbon compounds is the significant degree of bending at the disilyne silicons, resulting in a bond angle of 137.44(4)°. The ^{29}Si NMR spectrum of **1** reveals that the *sp*-hybridized silicons have a chemical shift of 89.9 ppm and hence are shielded relative to the chemical shift values typical of disilenes, $R_2Si{=}SiR_2$. Additional support for the claim of a genuine triple bond in **1** was provided by a density functional theory (DFT) study, which determined an Si-Si bond order of 2.618.

The importance of ^{29}Si NMR spectroscopy in the characterization of $Si{\equiv}Si$ triple bonds was underlined in detailed *ab initio* and DFT investigations into a series of compounds of general formula $RSi{\equiv}SiR$. The main conclusions of this work were that small changes in the $Si{\equiv}Si$ bond distance and the bond angles in and around the $RSi{\equiv}SiR$ unit strongly affect the ^{29}Si chemical shift.[2] Notable, however, was that the accuracy of the theoretical predictions is dependent on the density functional employed to determine $\delta(^{29}Si)$. A related, quantum chemical study of disilynes corroborated the finding that substituents do exert a considerable influence on ^{29}Si chemical shifts.[3]

Although reported previously,[4] the heavier alkyne analogues ArEEAr where Ar = C_6H_3-2,6-(C_6H_3-2,6-$^iPr_2)_2$ and E = Ge (**2**) and Sn (**3**) had not been subjected to detailed investigations into their chemistry. In an extensive study, the 'digermyne' **2** was found to react readily with a range of unsaturated substrates yet the 'distannyne' **3** was much less reactive (Scheme 2).[5]

School of Chemistry, University of Manchester, Oxford Road, Manchester, UK M13 9PL

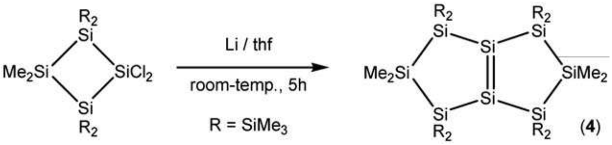


Scheme 2

Despite the predictions of reactivity made on the basis of bond enthalpies and kinetic factors, the noticeably higher reactivity of **2** can be attributed to ArGeGeAr possessing considerable singlet diradical character. Compound **2** also reacts with molecular hydrogen under ambient conditions to produce an interesting mixture of the digermene Ar(H)Ge=Ge(H)Ar, the digermane $ArH_2Ge–GeH_2Ar$ and the primary germane $ArGeH_3$. The direct addition of dihydrogen to an unsaturated, closed-shell Main Group compound in this way is thought to be without precedent.[6]

3. Other multiply bonded Group 14 compounds

A considerable number of Si=Si double bonds are now known and many of these have been structurally authenticated in the solution-phase and solid-state. The fused bicyclic disilene **4** (Scheme 3) contains a particularly interesting silicon-silicon double bond due to the similarities between its structure and that of the active site of the Si(001) surface, which is thought to contain a network of fused 5- and 6-membered rings containing Si=Si units.

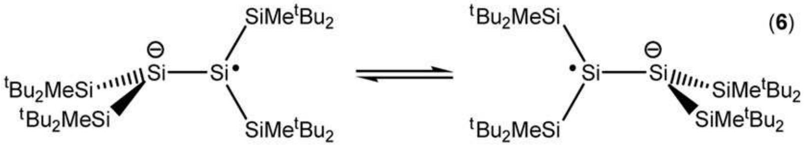


(4)

Scheme 3

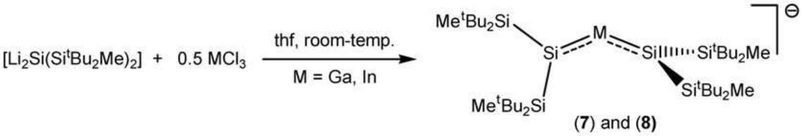
Although the similarities between the Si=Si double bond in **4** and the Si(001) surface were pointed out as being somewhat limited, compound **4** has afforded insight into the reactivity of silicon surfaces towards a range of small molecule substrates. Hence by acting as an extruded segment of bulk silicon, compound **4** promises to yield further valuable information on the chemistry of silicon surfaces.[7]

The first crystallographically characterized example of a molecule containing both an anionic and a radical centre was obtained upon reduction of $(^tBu_2MeSi)_2$-Si=Si$(SiMe^tBu_2)_2$ (**5**) with KC_8. The resulting silyl-radical species **6** displays a structure which is essentially orthogonal about the central Si–Si bond (Scheme 4). Particularly interesting are the hyperfine couplings in the EPR spectrum of **6**, which revealed a rapid spin exchange between the central Si atoms on the EPR timescale.[8]

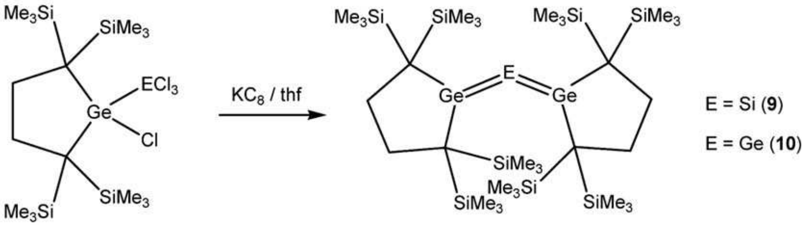


Scheme 4

The first examples of cumulated multiple bonds between silicon and the Group 13 elements gallium and indium were prepared in near quantitative yield according to Scheme 5. The [Si···E···Si] units within the allenic anions **7** and **8** (E = Ga, In, respectively) are bent and display pyramidal geometries at the allenic silicons. The Si···E bond distances in **7** and **8** are similar at 2.2828(9) and 2.2775(9) Å for **7** and 2.4849(9) and 2.4792(9) Å for **8**, respectively, and are considerably shorter than the distances measured for typical Si–E bonds.[9] The related 1,3-disilagermaallene **9** and trigermallene **10** were synthesized using a different methodology (Scheme 6).



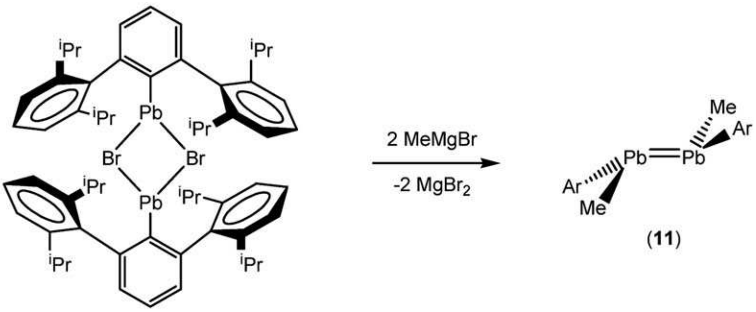
Scheme 5



Scheme 6

The yields of compounds **9** and **10** were quite low, being 15 and 24%, respectively, and the molecular structures are considerably bent along the allenic connectivity.[10]

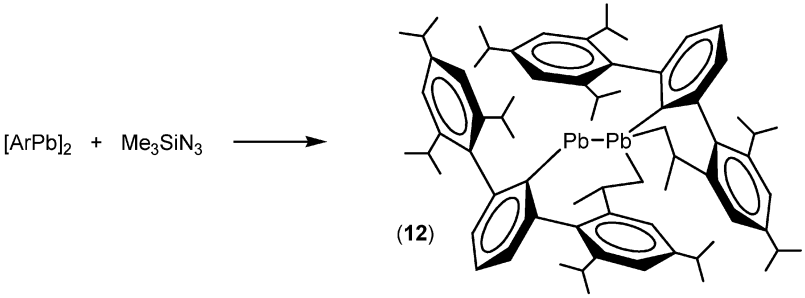
The establishment of 'heavy alkenes' as a class of experimentally accessible, isolable organometallic compound was highlighted in a recent review of the area.[11] One of the main challenges in the area of $E^1{=}E^2$ chemistry, where E^1 and E^2 are heavy Group 14 elements, remains the synthesis of a series of heteronuclear, lead containing derivatives (*i.e.* silaplumbenes, germaplumbenes and stannaplumbenes), which were still unknown at the time of writing. However, several examples of low-coordinate lead–lead bonded organometallics are known, although it has been noted that problems with stability stem from the fundamental weakness of lead–lead bonds and the tendency of diplumbenes to dissociate into monomers, which can be traced to the reluctance of Pb(II) to involve the $6s^2$ pair of electrons in chemical bonding. Inroads into the stabilization of low-coordinate lead–lead bonded species have been made through the use of extremely bulky terphenyl substituents. It was recently shown that removal of a *para* substituent from the aryl groups bonded to the 2- and 6- positions of the lead-bonded aryl group enables a weakly associated dimeric diplumbene **11** to be isolated (Scheme 7).[12]



Scheme 7

The Pb–Pb distance in **11** was measured as 3.1601(6) Å and its dimeric structure contrasts to a related monomeric compound that bears additional substituents in the *para* positions of the flanking aryl rings. However, the weakness of the lead–lead interaction in **11** was revealed by ^{209}Pb NMR spectroscopy, which displayed a resonance at 8738 ppm and was indicative of a monomeric plumbylene species, PbR_2.

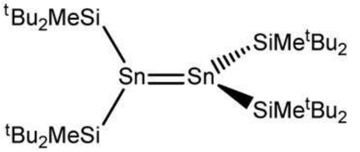
The outcome of the reaction between the lead–lead bonded dimer of bis-2,6-(2,4,6-triisopropylphenyl)phenyllead and trimethylsilyl azide afforded the first stable lead analogue of 'methylenemethyl' (**12**) (Scheme 8).



Scheme 8

Compound **12** features a bond between Pb(II) and Pb(IV), *i.e.* between plumbylene and plumbyl centres, and is therefore a valence isomer of a diplumbene. This unusual reaction proceeds in low-yield (3%) and **12** appears to be stabilized through the incorporation of the Pb_2 unit into an 8-membered ring. Interestingly, the valence isomer **12** is predicted to much more unstable with respect to formation of the symmetrical isomer than the germanium and tin analogues.[13]

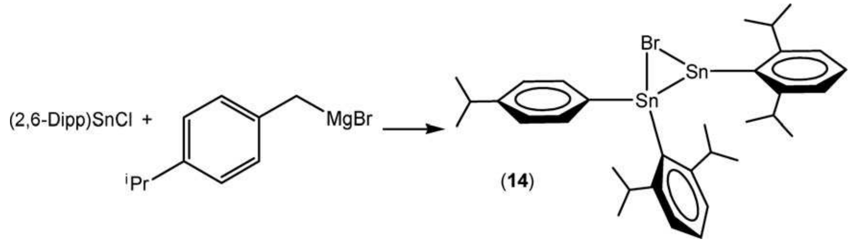
The acyclic distannene **13** was the first example of an Sn=Sn double bond to display stability with respect to dissociation into monomers in solution and is also notable for possessing the shortest known tin-tin distance of 2.6683(10) Å. The planar geometry around the tin atoms contrasts sharply to previous examples of distannenes which all show significant bending at tin.



(**13**)

The steric bulk of the substituents means that the structure of **13** is twisted about the double bond, which necessitated a reappraisal of the Sn═Sn bonding scheme since such an arrangement cannot be accounted for using the standard distannene or alkene bonding models. The planar but twisted structure of **13** is thought to arise as a consequence of interactions between two triplet stannylene units in an out-of-plane manner.[14]

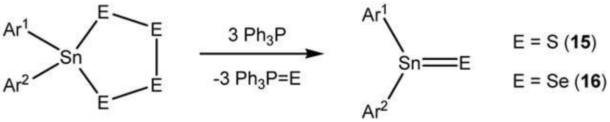
Despite the tendency of distannenes to dissociate into monomers, it has also been predicted by theory that other isomeric, bimetallic forms may exist. Of the predicted structure types, pyramidal unbridged dimers, trans, doubly-bridged dimers and unbridged E(II)–E(IV) valence isomers have previously been observed by experiment. A fourth structural type was also reported (Scheme 9).



Scheme 9

The singly bridged structure of **14** is unique for a tin(II) organometallic and its existence means that only the cis, doubly bridged isomer remains to be isolated.[15]

A diarylstannathione (**15**) and a diarylstannaselenone (**16**) were obtained by use of extremely sterically bulky aryl substituents (Ar^1 = 2,4,6-tris(bis(trimethylsilyl)-methyl)phenyl; Ar^2 = 2,6-bis(2-isopropyl)phenyl)phenyl), which stabilized the Sn═S and Sn═Se double bonds with respect to dimerization *via* ring formation (Scheme 10).

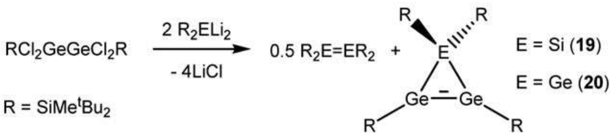


Scheme 10

The presence of low-coordinate tin in solution was confirmed by ^{119}Sn NMR spectroscopy, which revealed indicative low-field chemical shifts of 531 and 440 ppm for **15** and **16**, respectively. X-ray crystallographic analysis of **16** also revealed a planar Sn centre and a very short Sn═Se distance of 2.373(3) Å, suggesting close similarities between **16** and conventional ketones. Extensive studies into the chemistry of both **15** and **16** revealed a strong tendency for them to react with a range of unsaturated substrates to afford a series of interesting heterocycles.[16]

Alkali metal reduction of the digermene Ar(H)Ge═Ge(H)Ar (**17**) resulted in the formation of previously unauthenticated dianions $[M_2\{Ge(H)Ar\}_2]$ (M = Li, **18a**; Na, **18b**; K, **18c**). Each of **18a–c** features a Ge–Ge bond that is lengthened relative to that in **17**, yet their precise structures differ considerably and the alkali metal is thought to play a significant role in determining the precise geometry about the central Ge_2 unit.[17]

Heavy analogues of cyclopropene continue to provide a source of intrigue. The first examples of a 1*H*-siladigermirene (**19**) and 1*H*-trigermirene (**20**) were reported (Scheme 11).

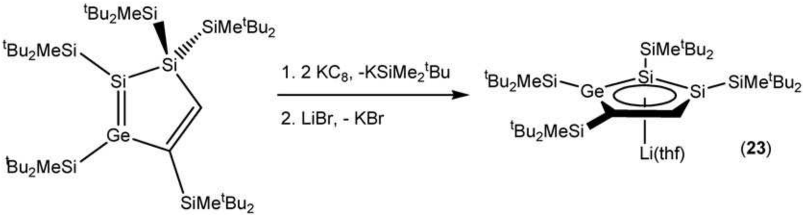


Scheme 11

The concomitant formation of disilene and digermene by-products from this reaction was taken as evidence for a mechanism that features an intermediate 2,3-dichlorosiladigermirane. The ring-expansion reaction that occurs when CH_2Cl_2 is added to **19** and **20** was revealed by DFT to due to the relief of ring strain.[18]

4. Aromatic compounds

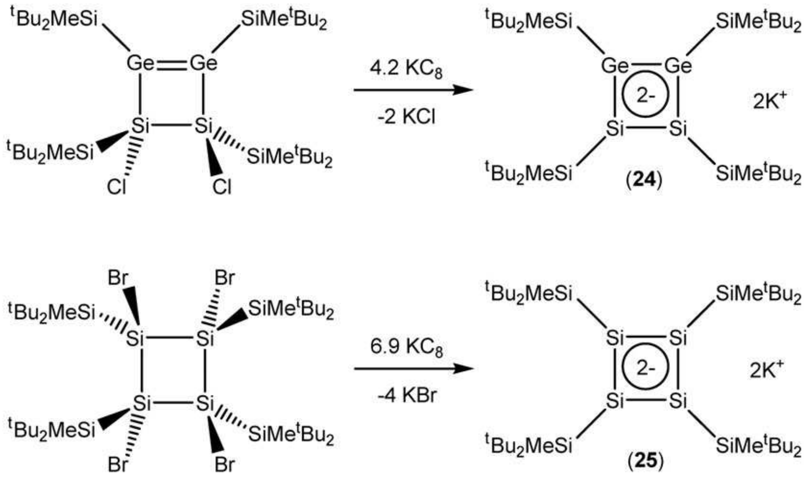
Reduction of the disilagermacyclopentadiene **21** resulted in formation of the remarkable heavy cyclopentadienide analogue **22**, which could be converted into the corresponding lithium salt **23** by treatment with dry LiBr (Scheme 12).



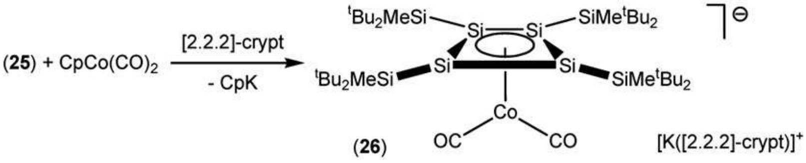
Scheme 12

The 5-membered ring of **23** is near-planar and the lithium cation is directly bonded to each ring atom to result in a classical η^5-coordination mode. Furthermore, relative to the double bonds in the precursor **21**, those in **23** are elongated, whereas the single bonds in **21** are shortened upon reduction to form **23**, which strongly suggests a degree of aromaticity in the ring of **23**. In addition to the solid-state structural parameters, further evidence for the aromatic character of **23** in non-coordinating solvents was provided by multinuclear NMR spectroscopy in toluene-*d*$_8$: the ^{29}Si NMR spectrum confirmed the presence of two silicon environments with the two chemical shifts of 54.4 and 69.1 ppm suggesting bonding character somewhere between the extremes of sp^3- and sp^2-type hybridization; the ^{7}Li NMR spectrum displayed a very high-field shift of −5.4 ppm as is commonly found in lithium cyclopentadienides. In thf solvent, however, a change in hapticity to η^1- became apparent as the ^{7}Li environment registered at a chemical shift more normally associated with the localized Ge–Li bond found in germyllithiums.[19]

The first heavy cyclobutadienide dianions, the 1,2-disila-3,4-digermacyclobutadiendiide **24** and the tetrasilacyclobutadiendiide **25**, were synthesized according to Scheme 13. The structures of both **24** and **25** are based on 4-membered butterfly-like rings that acts as μ:η^2-ligands to two $[K(thf)_2]^+$ cations positioned above and below the rings. The Si–Si bond lengths in **25** are not equal, which is thought to be due to the orientation of the $^tBu_2MeSi$ groups, and the ring Si atoms display pyramidal geometries. Furthermore, the nucleus-independent chemical shifts calculated for **25** are not suggestive of aromatic character within the 4-membered ring although a degree of delocalization was proposed. In the ring of **24**, ^{29}Si NMR spectroscopy suggests that the negative charge is localized on the germanium centres and further evidence for this was provided by the reaction of **24** with Me_2SO_4, which selectively methylates the germaniums.[20]

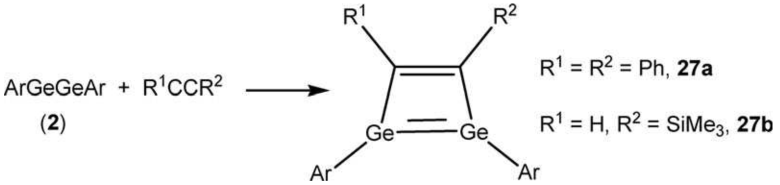

Scheme 13

The ability of compound **25** to act as a ligand towards transition metal centres was strikingly illustrated upon reaction with $CpCo(CO)_2$, which replaced the cyclopentadienide ligand to afford the 18-electron complex **26** (Scheme 14).


Scheme 14

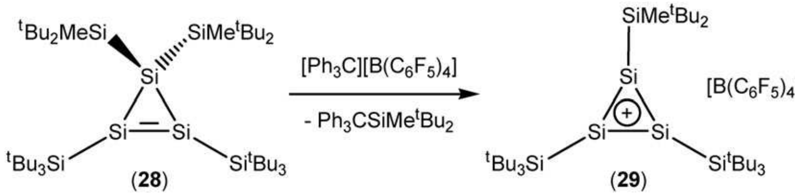
The ^{29}Si NMR spectrum of **26** revealed a resonance at the very high-field chemical shift of -43.2 ppm, which was taken as an indication of back-bonding from the cobalt 3d orbitals into the π^* molecular orbitals of the ligand. The Si_4 unit of the ligand is much nearer to planarity than in **25** and the silyl substituents are similarly much nearer to adopting a planar arrangement relative to each other, as is normally found in cyclobutadiene complexes of transition metals.[21]

The digermyne **2** reacts with alkynes to afford stable the digermacyclobutadienes **27a** and **27b** in yields of up to 80% (Scheme 15).


Scheme 15

Crystallographic characterization of **27a** shows that the Ge_2C_2 ring is trapezoidal and almost planar, with the sum of the internal angles being essentially 360°. Both **27a** and **27b** are very reactive towards alkynes and result in the formation of unusual 1,4-digermabicyclo[2.2.2]octa-2,5-dienes.[22]

Reaction of the sterically crowded cyclotrisilene **28** with $[CPh_3][B(C_6F_5)_4]$ afforded the long-awaited, first example of a cyclotrisilenylium cation (**29**) in quantitative yield (Scheme 16).

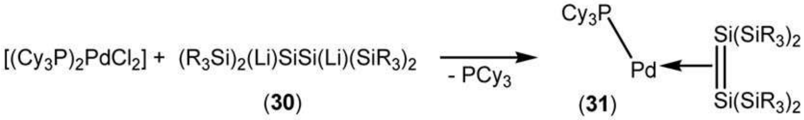


Scheme 16

The ^{29}Si NMR spectrum of **29** revealed low-field chemical shifts for the Si_3 ring silicons at 284.6 and 288.1 ppm in a 2:1 ratio, indicating the presence of a silylium cation. X-ray crystallography revealed that Si–Si distances within the ring Si_3 ring were very similar at 2.221(3), 2.218(3) and 2.211(3) Å and that the three silyl substituents have coplanar silicon atoms, all of which point to the formation of a persilaaromatic compound.[23]

5. Transition metal complexes of heavy Group 14 ligands

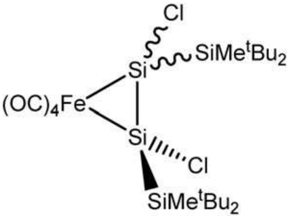
The disilene palladium(0) complex **31** was prepared by the action of the 1,2-dilithiodisilane **30** on $[(Cy_3P)_2PdCl_2]$ in thf solvent according to Scheme 17.



Scheme 17

With a formal valence electron count of 14, the palladium atom in **31** is 3-coordinate and resides in a trigonal planar environment by virtue of a PCy_3 ligand and an η^2-disilene ligand, with Pd–Si distances of 2.3610(9) and 2.4168(8) Å. Although several disilene complexes of palladium and platinum are known, their structural parameters suggest that the metal-disilene connectivity posseses little π-character. In **31**, however, the disilene silicons display near-planar geometries, meaning that the palladium-disilene bond does possess significant π-character and which is thought to arise as a result of the electron deficiency of the palladium centre.[24]

The iron(ɪɪ)-disilene complex **32** has a valence electron count of 18 and the silicon donor atoms possess considerable pyramidal character, observations that suggest it is best considered a disilametallacyclopropane rather than a π-complex of a disilene.[25]

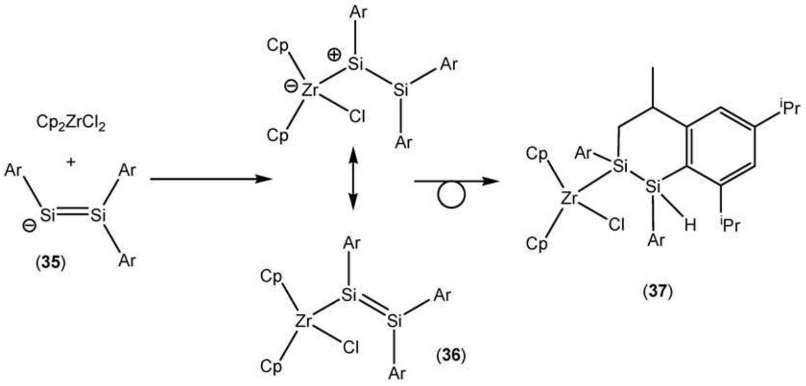


(32)

E:Z = 3:1

Reaction of the dipotassiodisilane $(Me_3Si)_2(K)Si–Si(K)(SiMe_3)_2$ (**33**) with hafnocene dichloride, Cp_2HfCl_2, furnished $[Cp_2Hf\{\eta^2\text{-}Si_2(SiMe_3)_4\}]$ (**34**) which displayed a ^{29}Si chemical shift of 132.8 ppm, a value that is similar to what is normally observed in a 'free' disilene and was taken as evidence of π-coordination by the disilene ligand. However, a DFT study of the zirconium analogue of **34** produced a long Si–Si distance of 2.56 Å and pyramidalization of the silicon donor atoms, which suggested partial disilylene character to the ligand in **34**.[26]

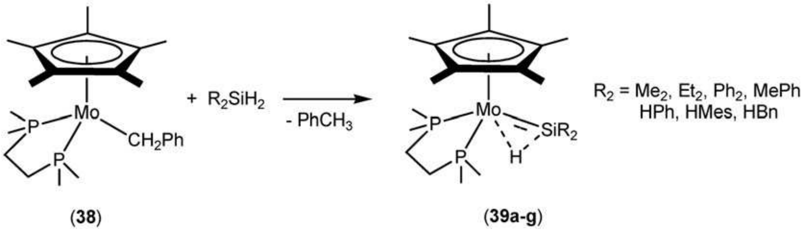
The reaction of the disilenide anion $[Ar_2Si{=}SiAr]^-$ (Ar = 2,4,6-tri-isopropylphenyl) (**35**) with Cp_2ZrCl_2 affords the corresponding σ-bonded zirconium disilenide complex **36** in almost quantitative yield. The chemical shifts of the silicon donor atom and the other disilene silicon occur at relatively low-field, being 152.5 and 116.8 ppm, respectively, and indicate a degree of silylene character, as illustrated in Scheme 18.



Scheme 18

Complex **36** undergoes a rearrangement at room temperature to the zirconocene silyl complex **37**, a reaction that is unprecedented within disilene chemistry.[27]

Transition metal silylene complexes continue to attract much attention due to their intrinsic interest and the possible insight that they offer into a variety of metal-catalyzed, silicon-based reactions such as alkene hydrosilylation. The coordinatively unsaturated molybdenum(II) complex **38** was found to react with a range of dihydrosilanes to give the series of silylene hydrides **39a–g** that feature weak Si···H interactions (Scheme 19).

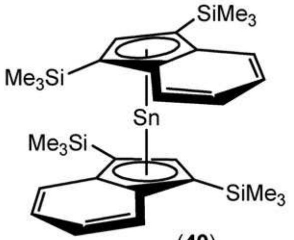


Scheme 19

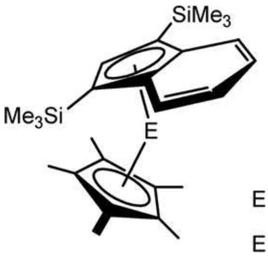
The formulation of the silicon ligands in **39a–g** as genuine silylenes was made on the basis of the planar arrangement of the $[MoSiR_2]$ unit and their low-field chemical shifts, although the appreciable H–Si coupling constants of 30–48 Hz did suggest a structure that is more accurately represented by the μ-H-containing structure **39**.[28]

6. Cyclopentadienyl derivatives

The first η^n-indenyl complexes of tin(II) were prepared by the straightforward transmetallation reaction of the lithium salt of 1,3-bis(trimethylsilyl)indene with $SnCl_2$ and Cp*SnCl (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl) to afford **40** and **41**, respectively.



(**40**)



E = Sn, **41**

E = Pb, **42**

The ligands in **40** are arranged in a gauche fashion so as to minimize steric repulsion between the substituents and the hapticity of the ligands fall between what would be expected for η^2- and η^3-coordination, and the [centroid–Sn–centroid] angle is 175.9°, suggesting that the tin lone pair resides in an atomic 5s orbital. Compounds **41** and **42** have similar structures and both reveal the η^5-Cp* ligand to be more closely bound to the metal than the indenyl ligand. The [centroid–E–centroid] angles were measured to be 151.6° and 147.3° for **41** and **42**, respectively.[29]

The triple decker cations $[(Cp^*E)_2(\mu{:}\eta^5{:}\eta^5\text{-}Cp^*E)]^+$ (E = Sn, **43**; Pb, **44**) were prepared by the action of $[Cp^*E][B(C_6F_5)_4]$ on the corresponding Cp_2^*E compounds. Both cations display a cisoid arrangement of the three Cp* ligands with the [centroid–E–centroid] angles being 154.7° and 152.6° in **43** and **44**, respectively, which contrasts to the transoid arrangement found in the structures of related triple decker anions.[30]

In a rare, interesting application of a Group 14 metallocene in materials chemistry, germanocene, Cp_2Ge (**45**), which was discovered in 1986, was used to prepare germanium nanowires in high yield by a chemical vapour deposition (CVD) method. The significance of this method stems from the fact that germanium nanowires can be grown without pre-application of metal particles as is necessary for the vapour–liquid–solid (VLS) growth method.[31]

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Organo-transition metal cluster complexes

Mark G. Humphrey* and Marie P. Cifuentes*

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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. Ligands are not shown for high-nuclearity clusters, emphasis being placed on core geometry.

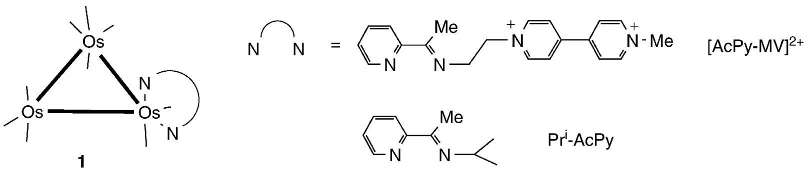
2 Spectroscopic studies

The first gas-phase infrared spectra of a range of anionic iron clusters ($[Fe_3(CO)_{10}]^-$ to $[Fe_5(CO)_{14}]^-$) have been reported. Spectral data of this type were combined with DFT calculations for smaller complexes ($[Fe(CO)_4]^-$, $[Fe_2(CO)_7]^-$, $[Fe_2(CO)_8]^-$) to obtain structural information for the cluster anions.[1] Spectroelectrochemical and computational studies on the reversible two-electron reduction of bis(alkynyl) clusters $Ru_4(\mu_4\text{-}\eta^2\text{-}RC_2R)_2(\mu\text{-}CO)(CO)_{10}$ show the first-formed product, which contains a square-planar metal core with the alkyne ligands coordinated to opposite faces, quickly isomerizes to a thermodynamically more stable product where the alkyne ligands lie parallel to each other across the metal framework.[2] Quantitative IR analysis of $Rh_4(\mu\text{-}CO)_3(CO)_9$, combined with deconvolution techniques, has been used to obtain a spectrum of the all-terminal CO complex $Rh_4(CO)_{12}$, even though it constitutes only *ca.* 1% of the sample.[3]

Laser desorption time-of-flight mass spectrometry affords the best results for anionic clusters when they are examined in the absence of matrix, the parent ion being observed in the majority of cases. In contrast, the spectra of neutral clusters show high-mass cluster aggregation and decarbonylation, with the CO:M ratio dropping with increasing cluster size, suggesting a metal-core rearrangement.[4]

A picosecond time-resolved UV/Vis and IR spectroscopic study of the photolysis of $Os_3(CO)_{10}$(*s-cis*-cyclohexa-1,3-diene), combined with DFT calculations on the geometry-optimized $Os_3(CO)_{10}$(buta-1,3-diene), indicates products result from stepwise formation of two bridging carbonyl ligands, with each intermediate containing a cleaved Os–Os bond bridged by the 1,3-diene ligand.[5] Similar comparisons of the photochemical reactivity of the diimine clusters $Os_3(CO)_{10}(\eta\text{-}L)$ ($L = [AcPy\text{–}MV]^{2+}$, Pr^i–AcPy, **1**) show that irradiation of the methyl viologen cluster results in transfer of a cluster-core electron to the lowest π^* orbital of the MV^{2+} unit, resulting in formation of a charge-separated state that is stable in acetonitrile, but either decays to regenerate the starting cluster (88%) or forms stable open-core biradicals (12%) in acetone. Electrochemical reduction of the viologen cluster decreases the electron-accepting characteristics of the ligand such that irradiation results in formation of zwitterions analogous to those observed from the irradiation of related non-substituted $Os_3(CO)_{10}(\alpha\text{-diimine})$ clusters.[6] The related mixed-metal cluster $RuOs_2(CO)_{10}(Pr^i\text{–}AcPy)$ contains the diimine ligand coordinated to the ruthenium atom and also produces biradical products on irradiation in weakly coordinating solvents, and zwitterions in acetonitrile, whereas the triosmium analogue $Os_3(CO)_{10}(Pr^i\text{–}AcPy)$ primarily forms biradical products.[7]

Department of Chemistry, Australian National University, Canberra ACT 0200, Australia.
E-mail: Mark.Humphrey@anu.edu.au, Marie.Cifuentes@anu.edu.au; Fax: +61 2 6125 0760;
Tel: +61 2 6125 2927, +61 2 6125 4293



3 Theory

The number of c.v.e. donated by μ_3-alkenyl and μ_4-alkyne ligands has been examined using fragment molecular orbital (FMO) calculations on two representative clusters, $Ru_3(\mu_3\text{-}H_2NNH)(\mu_3\text{-}CHCH_2)(\mu\text{-}CO)(CO)_7$ and $Ru_4(\mu_4\text{-}HC_2H)(CO)_{12}$. Results suggest donation of three and four electrons, respectively, the observed stability of these unsaturated clusters attributed to the large HOMO–LUMO gaps.[8] DFT calculations on the series of triosmium–fullerene complexes $Os_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})(CO)_8L$ (L = CO, PMe_3) and their anions (-1 to -4) show that all three metal atoms are π-coordinated to the C_6 unit of the fullerene in the neutral, mono- and dianionic complexes, but consist of mixed σ–π-coordination in the tri- and tetra-anionic cases, affording $[Os_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^1\text{-}C_{60})(CO)_8L]^{3-}$ and $[Os_3(\mu_3\text{-}\eta^2{:}\eta^1{:}\eta^1\text{-}C_{60})\text{-}(CO)_8L]^{4-}$.[9] Interstitial nickel and palladium atoms in icosahedral and pentagonal antiprismatic clusters with five-fold symmetry have been shown to be analogous to endohedral noble gas atoms in fullerenes.[10] The electronic structure and bonding of the omnicapped truncated tetrahedral Au_{20} cluster has been examined, its large band gap (1.77 eV) rationalized, and its structure related to those of other M_{20} complexes.[11]

4 Structural studies

A single-crystal neutron diffraction study of $Co_4(\mu_3\text{-}H)_4(\eta^5\text{-}C_5Me_4Et)_4$ has revealed the presence of four face-capping hydride ligands.[12]

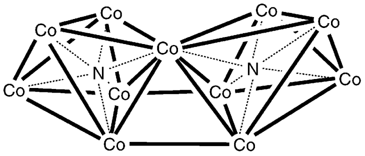
5 High-nuclearity clusters

5.1 Homonuclear high-nuclearity clusters

The dinitrido cluster tetraanion $[Co_{10}(\mu_6\text{-}N)_2(CO)_{19}]^{4-}$ can be chemically or electrochemically oxidized to give $[Co_{11}(\mu_6\text{-}N)_2(CO)_{21}]^{3-}$ (**2**) *via* three spectroscopically-identified intermediates. The 154 c.v.e. cluster contains a bent bioctahedral metal cage with 10 of the carbonyl ligands bridging Co–Co bonds and has four excess electrons; cyclic voltammetry indicates reversible loss of two electrons.[13] Reaction of $Pd_{10}(CO)_{12}(PEt_3)_6$ with $Pd_2(dba)_3$ (dba = dibenzylideneacetone) or $[Pd(NCMe)_4]^{2+}$ affords $Pd_{52}(CO)_{36}(PEt_3)_{14}$ (*ca.* 5%) or $Pd_{66}(CO)_{45}(PEt_3)_{16}$ (13%), respectively. The clusters can be considered to be derived from a common Pd_{38} core *via* condensation of Pd_7 caps and form mixed ccp/hcp layered structures.[14] $[Pt_{38}(CO)_{44}]^{2-}$ has been prepared in high yield by carbonylation (800 mmHg) of $[PtCl_6]^{2-}$ salts in water; a similar carbonylation at 900 mmHg affords quantitative yields of $[Pt_{3n}(CO)_{6n}]^{2-}$ ($n > 6$).[15]

The double salt $Ag_{12}(C_2)_2(O_2CCF_3)_8(2\text{-pyzCONH}_2)_3$ (**3**) is prepared from a mixture of Ag_2C_2, RCO_2Ag (R = CF_3) and $AgBF_4$ and contains a $\mu_8\text{-}\eta^2\text{-}C_2$ unit embedded in an Ag_8 cage and a second μ_6-bound C_2 unit contained in an open arrangement of six silver atoms, one of which forms the common vertex of the infinite column structure. The triple salt $Ag_{20}(C_2)_4(O_2CC_2F_5)_8(2\text{-pyzCOO})_4$-

$(2\text{-pyzCONH}_2)(\text{OH}_2)_2$ is formed from a similar mixture using RCO_2Ag ($\text{R} = \text{C}_2\text{F}_5$) and contains mixed ligands derived from hydrolysis of the pyrazine-2-carboxylate.[16]



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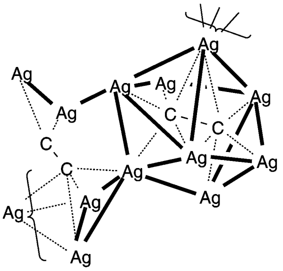

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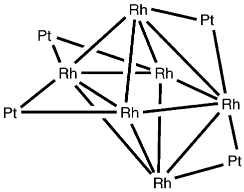
5.2 Heteronuclear high-nuclearity clusters

Reaction of $\text{Rh}_4(\text{CO})_{12}$ with $\text{Pt}(\text{PBu}^{t}_{3})_2$ at 68 °C affords decanuclear $\text{Rh}_6\text{Pt}_4(\mu_3\text{-CO})_4(\mu\text{-CO})_8(\text{CO})_4(\text{PBu}^{t}_{3})_4$ (**4**). NMR studies suggest that the four $\text{Pt}(\text{PBu}^{t}_{3})$ groups are able to migrate around the surface of the Rh_6 octahedron.[17] $\text{Ir}_4(\text{CO})_{12}$ reacts with an excess of $\text{Pt}(\text{PBu}^{t}_{3})_2$ at 110 °C to give $\text{Ir}_8\text{Pt}_4(\text{CO})_{12}(\text{PBu}^{t}_{3})_4$ (**5**) and $\text{Ir}_6\text{Pt}_4(\text{CO})_{10}(\text{PBu}^{t}_{3})_4$ (**6**), whereas the same reaction at room temperature yields a number of lower nuclearity products (see below). Complex **6** is hydrogenated to give a tetrahydrido cluster, maintaining the metal connectivity.[18]



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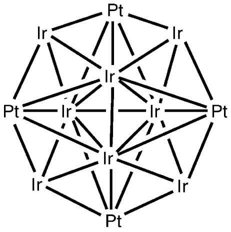

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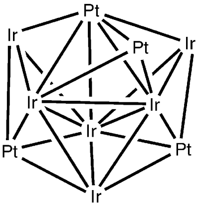

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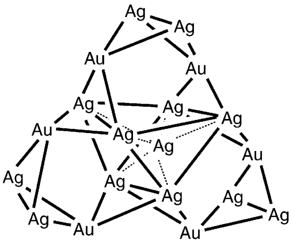


7

Crystal structures of several high-nuclearity Ni–Pt clusters have been reported. Both $[\text{HNi}_{24}\text{Pt}_{17}(\text{CO})_{46}]^{5-}$ and $[\text{Ni}_{32}\text{Pt}_{24}(\text{CO})_{56}]^{6-}$ are prepared from the condensation of preformed Ni–Pt complexes with Pt carbonyl clusters. The hydride ligand in the former was not located crystallographically or detected by NMR, but its presence is demonstrated by the reversible deprotonation to $[\text{Ni}_{24}\text{Pt}_{17}(\text{CO})_{46}]^{6-}$. Both structures are based on fragments of a ccp latice, with the hexaanion showing substitutional Ni/Pt disorder.[19] Reaction between $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ and $\text{PtCl}_2(\text{SEt}_2)_2$ affords $[\text{HNi}_{35}\text{Pt}_9(\text{CO})_{48}]^{5-}$, which can also be deprotonated to give the structurally disordered $[\text{Ni}_{35}\text{Pt}_9(\text{CO})_{48}]^{6-}$. A similar reaction using $\text{PdCl}_2(\text{SEt}_2)_2$ affords the hexaanion $[\text{Ni}_{36}\text{Pd}_8(\text{CO})_{48}]^{6-}$ amongst a mixture of products, stepwise protonation giving tetraanionic $[\text{H}_2\text{Ni}_{36}\text{Pd}_8(\text{CO})_{48}]^{4-}$.[20]

High-nuclearity Pd–Au clusters $Pd_{21}Au_2(CO)_{20}(PR_3)_{10}$ (R = Me, Et) and $[Pd_{22}Au(CO)_{20}(PMe_3)_6(PPh_3)_4]^-$ have been shown to be structurally closely related to the known homometallic cluster $Pd_{23}(CO)_{20}(PEt_3)_{10}$. Cyclic voltammetric analysis of $Pd_{21}Au_2(CO)_{20}(PR_3)_{10}$ (292 c.v.e.) shows four reversible one-electron redox processes, the range corresponding to $Pd_{23}(CO)_{20}(PEt_3)_{10}$ (290 c.v.e.) and $Pd_{23}(CO)_{22}(PEt_3)_{10}$ (294 c.v.e.).[21] $Pd_{41}Au_2(CO)_{27}(PEt_3)_{15}$ is obtained in good yield from thermolysis of $Pd_{21}Au_2(CO)_{20}(PEt_3)_{10}$, and contains two novel 13-coordinated Au-centred $AuPd_{13}$ polyhedra.[22] The Pt–Au cluster $Pt_{13}Au_4(CO)_{10}(PPh_3)_8$ contains a centred Pt_{13} icosahedron and is similar to the previously reported $Pt_{17}(\mu\text{-}CO)_4(CO)_8(PEt_3)_8$, suggesting a steric and electronic similarity between the corresponding capping groups $(Ph_3P)Au_2(PPh_3)$ and $(PEt_3)_2Pt_2(\mu\text{-}CO)$.[23]

Reaction of $[Au_2(\mu\text{-dppm})_2(NCMe)_2]^{2+}$ with three equivalents of $\{Ag(C{\equiv}CC_6H_4R\text{-}4)\}_n$ (R = H, Me, Bu^t) with exclusion of light affords metastable, light-sensitive green alkynyl complexes $[Ag_{13}Au_6(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4R\text{-}4)_{14}(\mu\text{-dppm})_3]^{5+}$ (**7**) which readily photolyze to red $[Ag_8Au_5\{\mu_5\text{-}1,2,3\text{-}C_6(C_6H_4R\text{-}4)_3\}(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4R\text{-}4)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CC_6H_4R\text{-}4)_3(\mu\text{-dppm})_4]^{3+}$ by cyclotrimerization of the arylacetylide unit. The $Ag_{13}Au_6$ complex has a novel cage structure and is intensely luminescent, in contrast to the Ag_8Au_5 complex which exhibits a weaker luminescence with lower energy.[24,25]

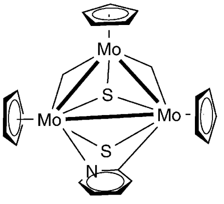
6 Group 6

The triangular dianionic cluster $[Cr_3(\mu_3\text{-}Te)_2(CO)_{10}]^{2-}$ is formed *via* M–M bond formation and loss of a chromium fragment from the binuclear ring-complex of $[Cr_2\{\mu\text{-}TeCr(CO)_5\}_2(CO)_8]^{2-}$. Analogous mixed-metal complexes are formed from $M_2\{\mu\text{-}TeCr(CO)_5\}_2(CO)_8]^{2-}$ (M = Mo, W).[26] Reaction between $Mn_2(\mu\text{-}\eta\text{-}NC_5H_4S)(CO)_6$ and $\{Mo(CO)_2Cp\}_2$ affords the 46 c.v.e. triangular cluster **8** (10%) amongst a mixture of products. Although the cluster is two-electrons deficient, it is unreactive towards CO or PPh_3.[27]

7 Group 8

7.1 Iron

Reaction of $[Fe_3(\mu_3\text{-}Te)(CO)_9]^{2-}$ and excess propargyl bromide in MeCN affords binuclear or linked metal complexes, whereas reaction in dichloromethane also affords the triiron propynyl cluster **9**.[28] $Fe_3(CO)_{12}$ has been coordinated to the periphery of the organic dendrimer core DAB-dendr-$\{N(CH_2PPh_2)_2\}_8$ to give an Fe_{24} complex. Atomic force microscopy of the complex on Si substrate shows the formation of different types of aggregates depending on deposition conditions, with nanorings, cluster islands and continuous films observed.[29]



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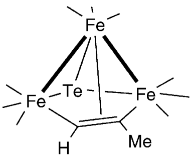
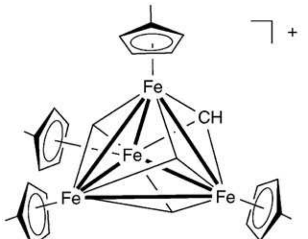


9

Stepwise reduction of the four face-capping CO ligands on $Fe_4(\mu_3\text{-}CO)_4Cp'_4$ with $LiAlH_4$ gives the series of products **10–13**, the first direct conversion of a μ_3-CO to μ_3-methylidyne. Formation of the acetylene ligand in **12** *via* coupling of two methylidyne units is accompanied by a change in metal core structure from tetrahedral to butterfly geometry and finally to a distorted square on formation of the second acetylene ligand in **13**. Reaction of the dicationic complex **11** with $CoCp_2$

affords neutral $Fe_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}HC_2H)(\mu_3\text{-}CO)_2Cp'_4$ containing a butterfly metal core; the reaction is reversible on addition of NH_4PF_6 in air and is the first example of a reversible C–C bond cleavage/formation between acetylene and two methylidyne units *via* two-electron oxidation/reduction.[30,31] Stepwise bromination of the acetylene ligands in **13** using *N*-bromosuccinimide affords the spectroscopically characterized series $[Fe_4(C_4H_{4-n}Br_n)Cp'_4]^+$ (n = 1–4), a crystal structure of $[Fe_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}BrC_2Br)_2Cp'_4]^+$ confirming the same distorted square metal geometry as **13**. The reactivity of the bromoacetylene cluster $[Fe_4(\mu_4\text{-}\eta^2\text{-}HC_2H)(\mu_4\text{-}\eta^2\text{-}HC_2Br)Cp'_4]^+$ has been investigated. Reaction with water affords **12** *via* C–C bond cleavage, with the oxygen atom of the CO ligand derived from the H_2O, together with a small amount of **13**; subsequent treatment of this mixture with $CoCp_2$ results in the one-electron reduction of cluster **13** but leaves cationic **12** intact. Substitution reactions of $[Fe_4(\mu_4\text{-}\eta^2\text{-}HC_2H)(\mu_4\text{-}\eta^2\text{-}HC_2Br)Cp'_4]^+$ with pyridine or $ZnMe_2$ at room temperature affords **13**, R = NC_5H_5 or Me, respectively.[32]



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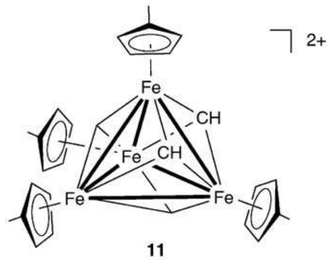

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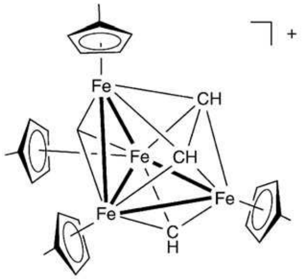

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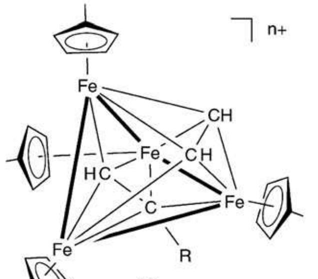
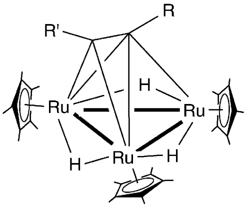


13

R = H, Me, n = 1
R = NC_5H_5, n = 2

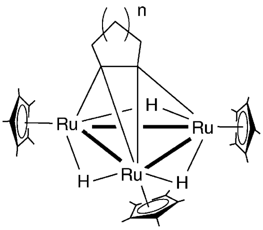
7.2 Ruthenium

Reaction of $Ru_3(\mu_3\text{-}H)_2(\mu\text{-}H)_3Cp^*_3$ with substituted alkynes $RC{\equiv}CR'$ (R = Ph, R′ = H, Me; R = Bu^t, R′ = H) leads to the formation of a single product containing a μ_3-alkyne unit coordinated perpendicular to one of the Ru–Ru bonds (**14**), the first example of direct formation of a μ_3-($\perp$)-1-alkyne complex without prior formation of a μ_3-alkynyl intermediate. The ^{13}C NMR signals for the five-coordinate "inner" carbon are significantly upfield (δ 60.4–73.7) of those for the "outer", μ-carbenic carbon (δ 161.1–181.1).[33] Similarly, reaction of $Ru_3(\mu_3\text{-}H)_2(\mu\text{-}H)_3Cp^*_3$ with cyclopentene or cyclohexene affords **15** as the sole product, containing perpendicular coordination of the cycloalkyne ligand resulting from vinylic C–H bond cleavage. The cluster is coordinatively unsaturated (46 c.v.e.); reaction with CO results in transformation to parallel coordination, affording **16** quantitatively. Fluxionality studies indicate migration of the inner acetylenic carbon atom to the outside of the triruthenium core, in contrast to the phenylethynyl complex **14** (R = Ph, R′ = H) where only one isomer has been observed.[34]



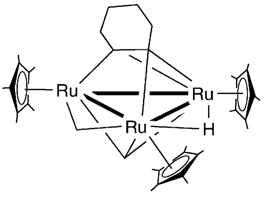
14

R = Ph, R' = H, Me
R = Bu^t, R' = H



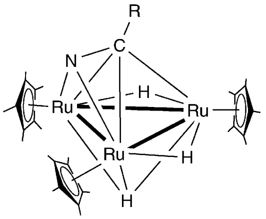
15

n = 1, 2



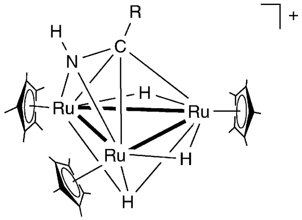
16

Triruthenium trihydrido clusters containing perpendicular coordination of nitrile and iminoacyl ligands have also been prepared. Reaction of $Ru_3(\mu_3\text{-}H)_2(\mu\text{-}H)_3Cp^*_3$ with RCN (R = Ph, Bu^t) gives a single product, **17**, containing μ_3-η^2:η^2-($\perp$)-nitrile; the cluster is structurally similar to the alkyne clusters **14** and **15**, the nitrile ligand acting as a four-electron donor. Subsequent protonation affords the μ_3-η^2:η^2-($\perp$)-iminoacyl cluster **18**, a reaction that is reversed on addition of base.[35]



17

R = Ph, Bu^t



18

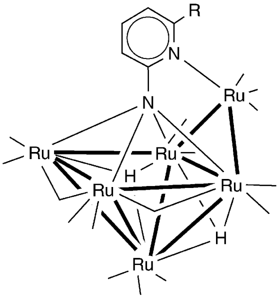
R = Ph, Bu^t

The cationic hexahydrido cluster $[Ru_3(\mu\text{-}H)_6Cp^*_3]^+$ has been used in the reductive cleavage of hydrazine without the need of a proton source or reducing agent, the reaction proceeding at room temperature to afford the intermediate $Ru_3(\mu\text{-}H)_3(\mu_3\text{-}NH)Cp^*_3$ which converts readily to the bis(imido) complex $Ru_3(\mu\text{-}H)(\mu_3\text{-}NH)_2Cp^*_3$. The proposed pathway involves nucleophilic attack of hydrazine on the ruthenium cluster to form the mono-imido complex together with ammonia, hydrogen and a proton which then catalyzes the formation of the bis(imido) cluster; the hexahydrido complex is thus acting as both electrophile and acid.[36]

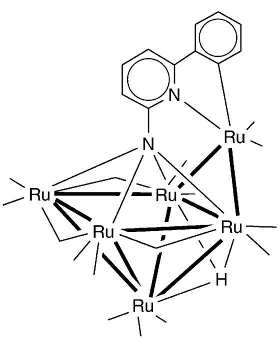
A systematic study into the nature of the true catalyst involved in benzene hydrogenation by $[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}O)(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2]^+$ has been carried out using a variety of techniques including kinetic studies, NMR spectroscopy, transmission electron microscopy, and Hg(0) and other poisoning techniques; results show that catalysis is a heterogeneous process involving trace Ru(0) nanoparticles derived from the ruthenium cluster. The findings were verified using a chiral analogue of the triruthenium oxo cluster; no transfer of chirality was observed in the hydrogenation products of the prochiral substrate methyl 2-acetamidoacrylate, suggesting that the catalytically active species is not the intact cluster.[37]

The hydrazido-capped triruthenium cluster $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}HNNMe_2)(CO)_9$ has been shown to react with a variety of alkynes, affording either edge-bridged closed triangular or M–M-opened face-capped products. A study of the reactivity of $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}MeNNHMe)(CO)_9$ with RC$\equiv$CR′ (R = R′ = H, Ph; R = H, R′ = Ph), including kinetic and structural analysis and DFT calculations, has shown that the position of the methyl substituent on the hydrazido ligand determines which of the M–M bonds will be spanned by the alkyne ligand, and also influences the relative orientation of the hydrazido and alkenyl ligands in the face-capped products; the kinetic aspects of the migratory insertion process have little influence on the selectivity of the reaction.[38]

$Ru_3(CO)_{12}$ reacts with 2-amino-6-phenylpyridine (H_2apyPh) to give a mixture of $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-HapyPh-}N,N)(CO)_9$, $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^3\text{-HapyC}_6H_4\text{-}N,N,C)_2(CO)_6$, and hexaruthenium products **19** (R = Ph) and **20**. Complex **20** is related to **19** through the cyclometallation of the aminopyridyl ligand and was also obtained from thermolysis of **19** with $Ru_3(CO)_{12}$. In contrast, $Os_3(CO)_{10}(NCMe)_2$ requires irradiation of either of the first-formed products $Os_3(\mu\text{-}H)(\mu\text{-}\eta^1\text{-HapyPh-}N)(CO)_{10}$ and $Os_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-HapyPh-}N,N)(CO)_{10}$ to form the analogous $Os_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-HapyPh-}N,N)(CO)_9$.[39] The reactivity of the related cluster **19** (R = Me, obtained in higher yield from 2-amino-6-methylpyridine, H_2ampy) towards phosphines and diphenylacetylene has been investigated, including the formation of a heptanuclear derivative, $Ru_7(\mu_5\text{-}\eta^2\text{-ampy})(\mu_5\text{-}\eta^4\text{-PhC}_2\text{Ph})(CO)_{17}$.[40,41]



19
R = H, Me, Ph

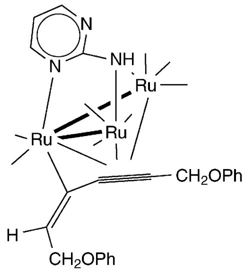


20

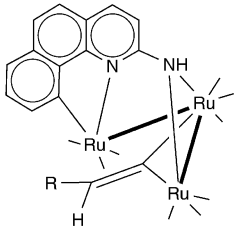
$Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-apyr})(CO)_9$ (Hapyr = 2-aminopyrimidine) reacts with 1,6-diphenoxy-2,4-hexadiyne to give the edge-bridged derivative $Ru_3(\mu_3\text{-}\eta^2\text{-apyr})(\mu\text{-}\eta^3\text{-PhOCH}_2\text{CH}{=}\text{CC}{\equiv}\text{CCH}_2\text{OPh})(\mu\text{-CO})_2(CO)_6$, which converts to the face-capped, open-triangular complex **21** on thermolysis. DFT calculations show the two isomers have very similar stabilities.[42] The reactivity of the related non-hydrido complex $Ru_3\{\mu_3\text{-}\eta^3\text{-}(C,N,N)\text{-Habq}\}(CO)_9$ (H_2abqH = 2-amino-7,8-benzoquinoline) towards a number of substrates has been examined. Reaction with terminal alkynes gives the vinylidene complexes **22**, in which the amido NH fragment spans a closed Ru–Ru bond, whereas propargyl alcohol affords **23**, resulting from coupling of the allyl unit to the benzoquinolinyl ligand. Internal alkynes 3-hexyne and diphenylacetylene both gave a complex mixture of products, with **24**, which contains no alkyl fragment, isolated in both cases. The stannylene derivatives **25** are obtained *via* facile conversion of the first-formed terminal hydridostannyl complexes.[43]

The unsaturated dicationic arene cluster $[Ru_4(\mu_3\text{-}H)_4(\eta^6\text{-}C_6H_6)_4]^{2+}$ reacts with two equivalents of thiophene, benzothiophene or dibenzothiophene under biphasic conditions to give $[Ru_4(\mu_3\text{-}H)_2(\mu_3\text{-}S)_2(\eta^6\text{-}C_6H_6)_4]^{2+}$ along with the corresponding desulfurized organic product. The cluster product is the first example of an organometallic complex extracting two sulfur equivalents.[44]

The μ_5-phosphido cluster **26** has been isolated from reaction of $Ru_5(\mu_4\text{-PNPr}^i{}_2)(\mu\text{-dppm})(CO)_{13}$ and HCl.[45] The heterodentate ligand 2,2′-bis(diphenylphosphino)-4,4′-bipyridine has been used to prepare a series of linked-cluster assemblies, including **27**, where $[Ir_4Br(CO)_{11}]^-$ was used as the core unit.[46] $Ru_6(\mu_6\text{-}C)(\mu\text{-CO})(CO)_{16}$ reacts with $GaCp^*$ to give air-sensitive $Ru_6(\mu_6\text{-}C)(\mu_3\text{-GaCp}^*)_2(\mu\text{-GaCp}^*)(\mu\text{-CO})(CO)_{13}$, and the structure of $Rh_6(\mu_3\text{-GaCp}^*)_4(CO)_{12}$ has been reported.[47]



21



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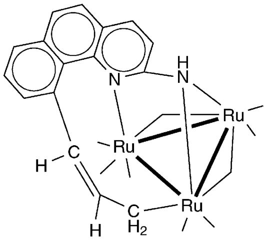
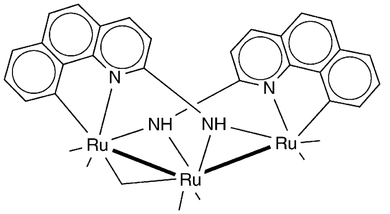
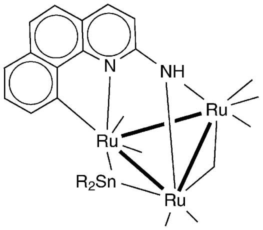


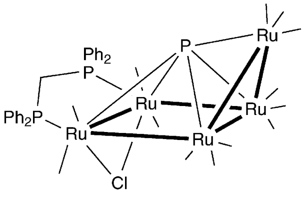
23



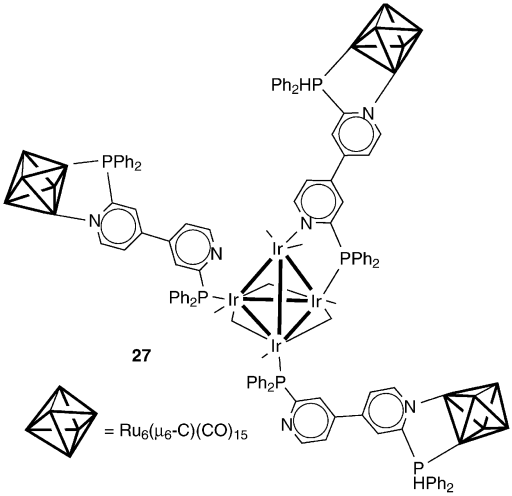
24



25 R = Ph, Bu



26



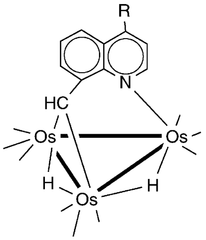
27

7.3 Osmium

A self-assembled monolayer consisting of a porphyrin dyad unit anchored to an ITO electrode *via* a 3-(triethoxysilyl)propyl isocyanide-substituted triosmium–fullerene complex has been shown to produce unusually high photocurrent efficiency.[48]

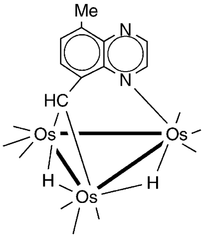
The unsaturated clusters $Os_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C_9H_6RN)(CO)_9$ (R = H, 4-Me) react with diazomethane by insertion of a methylene group into the M–C σ-bond to give **28**. In contrast, the related diaza-cluster $Os_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C_8H_4RN_2)(CO)_9$ affords the double insertion product **29**, in addition to the mono-insertion product **30**.[49]

Reaction of $Os_3(\mu\text{-}H)_2(CO)_{10}$ with $CNNPPh_3$ affords the phosphinazine cluster **31** which readily loses N_2 to give the alkylidyne complex **32**. Thermolysis of **32** in toluene results in CO insertion to form **33**, the second oxygen atom of the face-capping $CC(O)OCH_2Ph$ ligand presumably derived from trace amounts of water or O_2.[50]



28

R = H, Me



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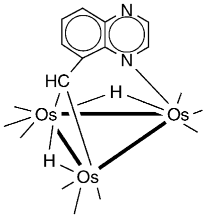

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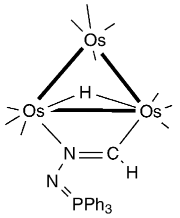

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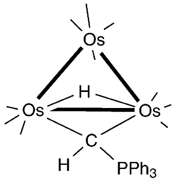

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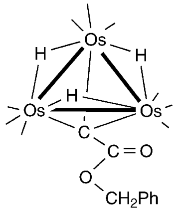


33

Kinetic and thermodynamic studies on the reversible isomerization of the bridged phosphine cluster $Os_3\{\mu\text{-}(Z)\text{-}Ph_2PCH{=}CHPPh_2\}(CO)_{10}$ to the chelated form $Os_3(CO)_{10}\{\eta^2\text{-}(Z)\text{-}Ph_2PCH{=}CHPPh_2\}$ suggests a nondissociative phosphine migration.[51]

8 Group 9

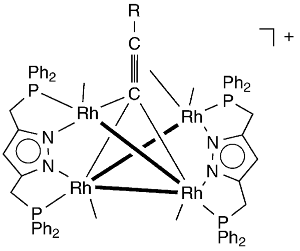
8.1 Cobalt

The carbon chain-linked cluster complex $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_7C\}$ has been formed *via* the deauration and coupling of $Co_3\{\mu_3\text{-}C(C{\equiv}C)_2Au(PR_3)\}$-$(\mu\text{-dppm})(CO)_7$ (R = Ph, Tol) with $I(C{\equiv}C)_3I$, a reaction sequence that has been used in the preparation of a number of carbon-linked metal complexes.[52]

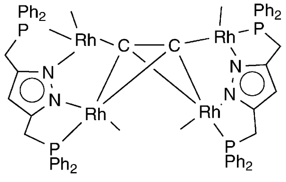
8.2 Rhodium

Reaction of $Rh_2(\mu\text{-}OH)_2(\eta^2{:}\eta^2\text{-COD})_2$ (COD = 1,5-cyclooctadiene) with $Et_3N\cdot 3HF$ or 50% aqueous HF affords the cationic triangular cluster $[Rh_3(\mu_3\text{-}OH)_2(\eta^2{:}\eta^2\text{-COD})_3]HF_2$ in almost quantitative yield. The cluster reacts with excess PPh_3 to give a mixture of $RhF(PPh_3)_3$ and $Rh_2(\mu\text{-}OH)_2(PPh_3)_4$ (4:1), whereas the same reaction with PPr^i_3 gives $RhF(PPr^i_3)(COD)$, suggesting that Rh(I) has a greater affinity for fluoride when phosphine-coordinated rather than COD-ligated, as evidenced by the reaction of $Rh_2(\mu\text{-}OH)_2(PR_3)_4$ (R = Ph, Pr^i) with $Et_3N\cdot 3HF$ to give $Rh_2(\mu\text{-}F)_2(PR_3)_4$.[53] Reaction of $Rh_2(\mu\text{-}OH)_2(\eta^2{:}\eta^2\text{-COD})_2$ with 73% HF has also been shown to produce the same trinuclear dihydroxy cluster, rather than the fluoride complex $\{RhF(COD)\}_n$ as previously reported, although rhodium fluoride complexes $Rh_2(\mu\text{-}F)_2(COE)_4$ can be prepared from $Rh_2(\mu\text{-}OH)_2(\eta^2\text{-COE})_2$ and $Et_3N\cdot 3HF$.[54]

$[Rh_2(\mu\text{-PNNP})(CO)_4]^+$ [PNNP = 3,5-bis{(diphenylphosphino)methyl}pyrazolato] reacts with terminal alkynes $RC{\equiv}CH$ (R = *p*-Tol, Bu) or with the dinuclear alkynyl complex $Rh_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CR)(\mu\text{-PNNP})(CO)_2$ (R = H, $SiMe_3$) to give the tetranuclear cluster **34**, containing a bent chain of rhodium atoms with the α-carbon of the alkynyl unit bound to all four metal atoms, and the $C{\equiv}C$ unit π- bound to one of the "wing-tip" rhodiums. Complex **34** exhibits fluxionality involving alkynyl flipping between the "wing-tip" metal atoms and between the intra-PNNP-unit hinge metal atoms. Reversible deprotonation of **34** (R = H) affords the neutral complex **35**, with a μ_4-dicarbide unit and an open metal framework resulting from Rh–Rh bond cleavage.[55]

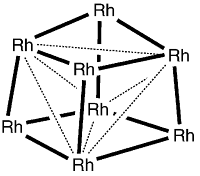


34
R = H, Tol, Bu, SiMe3

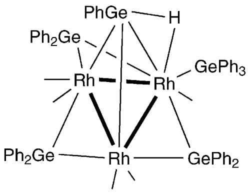


35

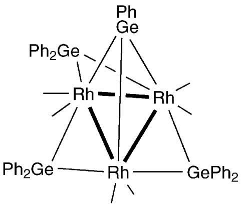
Treatment of $[Rh(nbd)(PPr^i_3)_2]^+$ (nbd = norbornadiene) under 4 atm of hydrogen affords $[Rh_6(\mu\text{-}H)_{12}(PPr^i_3)_6]^{2+}$, an octahedral cluster containing hydride ligands bridging each Rh–Rh bond. The 76 c.v.e. cluster is 10 electrons deficient for a Rh_6 octahedral cluster, and thus is structurally related to early transition metal clusters such as $[Nb_6(\mu\text{-}Cl)_{12}Cl_6]^{4-}$.[56] Remarkably, the cluster and its tricyclohexylphosphine analogue[57] react reversibly with two equivalents of hydrogen to give quantitative yields of $[H_{16}Rh_6(PR_3)_6]^{2+}$ (R = Pr^i, Cy). ^1H NMR spectroscopy and DFT calculations suggest the presence of 15 surface and one interstitial hydride, although this could not be confirmed by the crystallographic results. The facile and reversible uptake of hydrogen is unusual in a cluster with such a high hydride:metal atom ratio, suggesting applications in the study of hydrogenation catalysis.[58] The octanuclear complex $Rh_8(\mu_4\text{-GePh})_6(CO)_{12}$ (**36**) is formed together with trinuclear **37** from the reaction between $Rh_4(CO)_{12}$ and $GeHPh_3$, the same reaction under hydrogen affording **36** as the sole product in better yield. Complex **36** consists of a distorted cube metal core with μ_4-bound GePh on each of the six faces and 12 terminal carbonyl ligands with weak Rh–Rh interactions evident between the four rhodium atoms bearing a single carbonyl ligand; the cluster is deficient by four electrons. Reaction of **36** with PMe_2Ph affords the tetraphosphine derivative obtained by substitution of a carbonyl ligand on each of the $Rh(CO)_2$ units, and carbonylation of **37** results in loss of the terminal $GePh_3$ and bridging hydride groups to give **38**.[59]



36 metal core

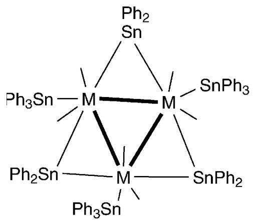


37

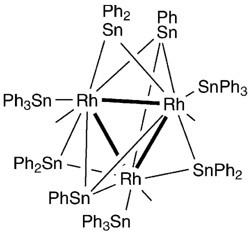


38

$M_4(CO)_{12}$ (M = Rh, Ir) reacts with $SnHPh_3$ to give **39**; the rhodium example can be reacted on to form **40**, containing $SnPh_3$, $SnPh_2$ and SnPh groups in terminal, bridging and face-capping modes.[60]



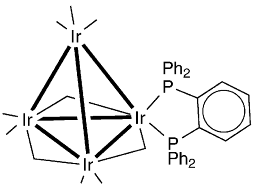
39 M = Rh, Ir



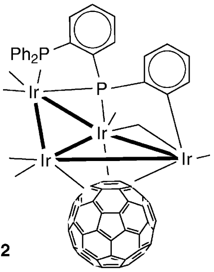
40

8.3 Iridium

Thermolysis of $Ir_4(\mu\text{-}CO)_3(CO)_7(PPh_3)_2$ in chlorobenzene affords the *ortho*-phosphorylated tetrahedral cluster **41**; this reacts with C_{60} to give the butterfly complex **42**, where the *ortho*metallated phosphine spans three of the metal centres.[61]

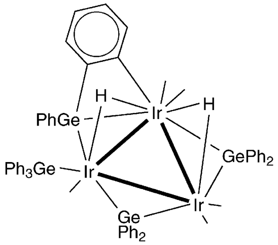


41



42

A study into the reactivity of $Ir_4(CO)_4$ with $GeHPh_3$ has afforded the series of clusters **43–47** containing $GePh_3$, $GePh_2$ and GePh in a variety of coordination modes, including *ortho*-metallated and μ_4-face-capping.[62]



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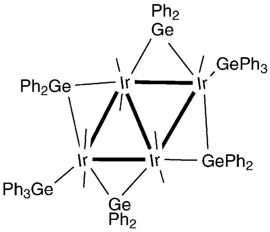

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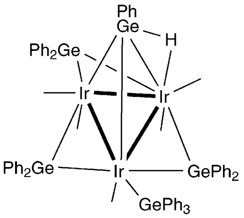

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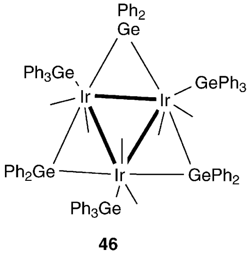

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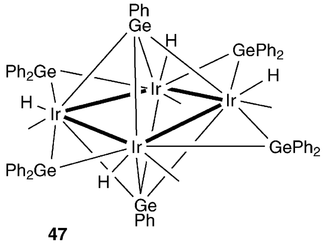


47

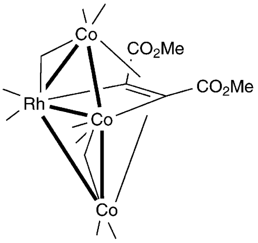
8.4 Clusters containing mixed group 9 metal atoms

Reaction of the tetrahedral complex $Co_2Rh_2(CO)_{12}$ with two equivalents of dimethyl acetylenedicarboxylate (dmad) results in cluster fragmentation and metal redistribution to give **48** and **49**; the expected simple substitution product $Co_2Rh_2(\mu_4\text{-dmad})(CO)_{10}$ is not observed.[63]

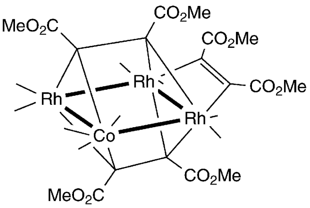
9 Group 10

9.1 Palladium

$Pd_9\{\mu_3\text{-}TlCo(CO)_3(PEt_3)\}(\mu_3\text{-}CO)_3(\mu\text{-}CO)_6(PEt_3)_6$ (**50**) is formed from reaction of $Pd_4(CO)_5(PEt_3)_4$ and/or $Pd_{10}(CO)_{12}(PEt_3)_6$ with $TlCo(CO)_4$. The complex consists of a distorted octahedron of Pd atoms, with one triangular face bridged by $Pd(\mu\text{-}CO)_2(PEt_3)$ units and containing a face-capping $TlCo(CO)_3(PEt_3)$ ligand, affording a pseudo-C_{3v} geometry. This is the first example of a cluster containing the trigonal-bipyramidal $TlCo(CO)_3(PEt_3)$ unit, presumably stabilized by the tripalladium coordination. NMR spectroscopy suggests that the complex undergoes reversible dissociation of the $TlCo(CO)_3(PEt_3)$ unit from the cluster.[64]



48



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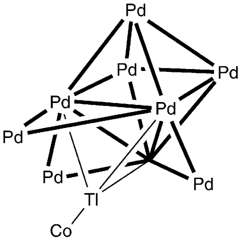
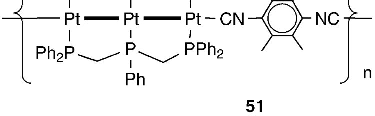


50
metal framework

9.2 Platinum

$[Pt_3(\mu\text{-dpmp})_2(CNXyl)_2]^{2+}$ [dpmp = bis(diphenylphosphinomethyl)phenylphosphine] has been used to prepare a series of rigid-rod organometallic polymers (**51**, **52**) connected by π-conjugated bis(isocyanide) ligands. Similar reaction with less bulky bis(isocyanides) affords the linked cluster complexes **53**, containing elongated Pt–Pt bonds, suggesting a decreased σ-donating character of the terminal CN group, which results in a decreased tendency for polymerization at these groups. The cluster polymer **51** adds H^+ across a Pt–Pt bond, and reacts with NO^+, tetracyanoethylene and electron-deficient alkynes to give substituted cluster polymers derived from insertion of the small molecule and concomitant Pt–Pt bond scission.[65] Treatment of $[Pt_2M(\mu\text{-dpmp})_2(CNXyl)_2]^{2+}$ (M = Pt, Pd) with $NaBH_4$ or NaOMe results in cluster coupling to give the linear hexanuclear cluster $[Pt_4M_2(\mu\text{-}H)(\mu\text{-dpmp})_4(CNXyl)_2]^{3+}$ with the hydride ligand bridging the central M–M bond. Chemical oxidation results in deprotonation to give $[Pt_4M_2(\mu\text{-dpmp})_4(CNXyl)_2]^{4+}$.[66]



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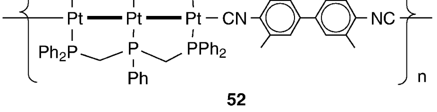

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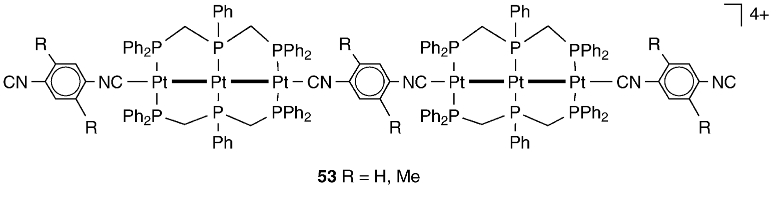
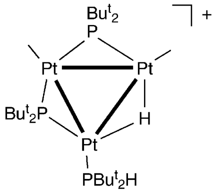


53 R = H, Me

Protonation of the triplatinum hydride cluster $Pt_3(H)(\mu\text{-}PBu^t_2)_3(CO)_2$ with equimolar triflic acid under a CO atmosphere proceeds *via* the previously reported tertiary phosphine complex **54** to give **55**, whereas stirring $Pt_3(H)(\mu\text{-}PBu^t_2)_3(CO)_2$ with excess acid for 30 min followed by carbonylation gives the coupled product **56**. The hexanuclear cluster undergoes three reduction steps: two reversible one-electron processes and a quasi-reversible two-electron process, ultimately affording the unstable dianion $[Pt_6(\mu\text{-}PBu^t_2)_4(CO)_6]^{2-}$. DFT calculations on the reduction products suggest the primary cluster geometry remains unchanged, but that there is a progressive and concerted out-of-plane rotation of the phosphido bridges resulting in a change from D_{2d} to D_2 symmetry.[67] Electrochemical and spectroelectrochemical studies on the bis(ferrocenylethynyl) hexaplatinum cluster **57** show photochemically-induced electron transfer from the cluster to the peripheral ferrocenyl units, stepwise two-electron oxidation resulting in the growth of a NIR band.[68]



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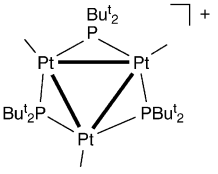

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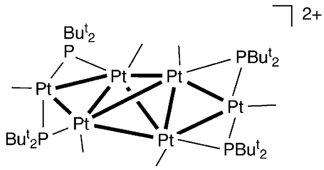

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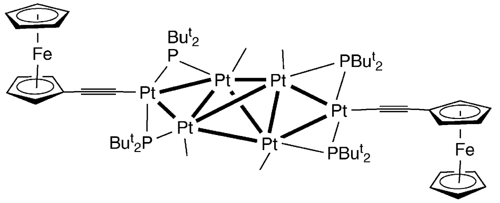
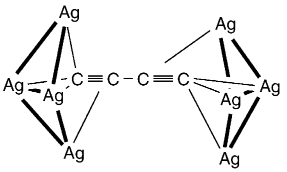


57

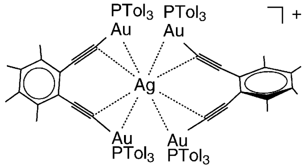
10 Group 11

The double salts $Ag_2C_4 \cdot 6AgNO_3 \cdot 2H_2O$ and $Ag_2C_4 \cdot 6AgNO_3 \cdot 3H_2O$ are formed by varying the crystallization conditions of the Ag_2C_2 product formed from reaction between $AgNO_3$ and $LiC{\equiv}CC{\equiv}CLi$ (2:1). The complexes consist of Ag_4 butterfly units linked by $(\mu_4\text{-}\eta^2\text{-}C_2)_2$ chains (**58**) and represent the highest ligation number for linear carbon chains linking metal complexes.[69]

Luminescent heteronuclear Cu–Ag alkynyl complexes formed from $\{Ag(C{\equiv}C\text{-}4\text{-}C_6H_4R)\}_n$ and $[Cu_2(\mu\text{-}Ph_2PXPPh_2)(NCMe)_2]^{2+}$ include hexanuclear $[Cu_2Ag_4(\mu_4\text{-}\eta^1\text{-}C{\equiv}C\text{-}4\text{-}C_6H_4R)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C\text{-}4\text{-}C_6H_4R)(\mu\text{-}Ph_2PXPPh_2)_4]^{2+}$ (R = H, Me) when X = NH and either octanuclear $[Cu_2Ag_6(\mu_4\text{-}\eta^1\text{-}C{\equiv}C\text{-}4\text{-}C_6H_4R)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C\text{-}4\text{-}C_6H_4R)_2(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C{\equiv}C\text{-}4\text{-}C_6H_4R)(\mu\text{-}Ph_2PXPPh_2)_3(NCMe)]^{2+}$ (R = H, Me, OMe, NO_2) or linked octanuclear arrays $[\{Cu_2Ag_6(\mu_4\text{-}\eta^1\text{-}C{\equiv}C\text{-}4\text{-}C_6H_4R)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C\text{-}4\text{-}C_6H_4R)(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C{\equiv}C\text{-}4\text{-}C_6H_4R)(\mu\text{-}Ph_2PXPPh_2)_3\}_2(\mu_4\text{-}\eta^1(C){:}\eta^1(O)\text{-}C{\equiv}C\text{-}4\text{-}C_6H_4R)_2]^{4+}$ [R = C(O)Me] for X = CH_2.[70] The *ortho*-arenediethynyl heteronuclear cluster **59** has been prepared from reaction of $1,2\text{-}C_6Me_4\{C{\equiv}CAu(PTol_3)\}_2$ and $AgClO_4$. Using the isolobal analogy between $AuPR_3$ and H, complex **59** can be considered as containing four C–($AuPR_3$)···Ag or "metalagostic" interactions.[71]



58
showing metal and carbon framework

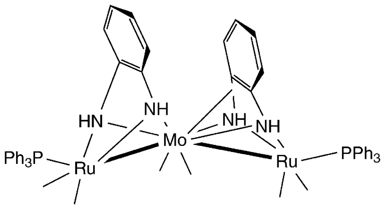


59

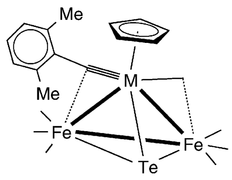
11 Mixed-metal clusters

11.1 Group 6

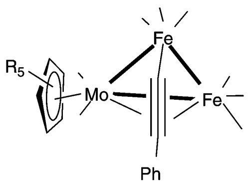
Chemical oxidation of $MoRu_2\{\mu\text{-}C_6H_4(NH)_2\text{-}o\}_2(CO)_6(PPh_3)_2$ results in selective oxidation of one of the *ortho*-phenylenediamido ligands to give **60**, containing a η^2-*o*-phenylenediamido and η^4- *o*-diiminobenzene ligands; the reaction is reversible on reduction wth sodium amalgam. DFT calculations show that the two bonding modes are similar in energy, and NMR spectra suggest fast exchange at room temperature.[72] $MFe(\mu\text{-}CXyl)(CO)_5Cp$ (M = Mo, W; Xyl = $2,6\text{-}C_6H_3Me_2$) reacts with elemental tellurium using ultrasonic activation to give **61**, probably *via* a binuclear $MFe(\mu\text{-}TeCXyl)(CO)_5Cp$ intermediate.[73] Photolysis of $Fe(CO)_5$ with $Mo(C{\equiv}CPh)(CO)_3R$ gives a mixture of **62** (R = Cp, Cp^*) and **63** (R = Cp), whereas the same reaction in the presence of phenylacetylene affords **64** (R = Cp^*); no further reaction was observed between phenylacetylene and **62** or **63** using thermal or photolytic methods.[74]



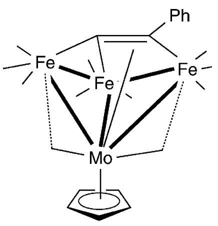
60



61 M = Mo, W



62 R = H, Me



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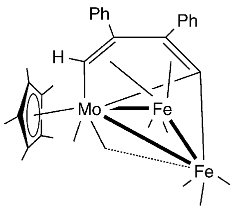
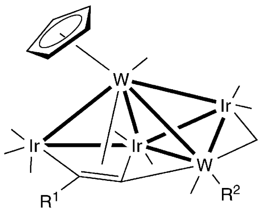


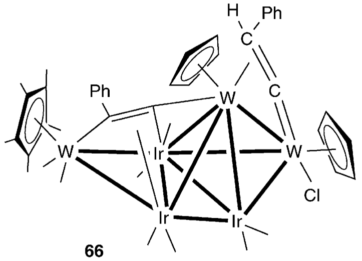
64

The tetrahedral complexes $WIr_3(\mu\text{-}CO)_3(CO)_8Cp^*$ and $WIr_3(CO)_{11}Cp$ have been used in a series of cluster metal core expansion reactions using metal-alkynyl $[W(C{\equiv}CPh)(CO)_3Cp]$, –ethyndiyl $[\{Ru(CO)_2Cp\}_2(\mu\text{-}C{\equiv}C)]$ and –butadiyndiyl $[\{W(CO)_3Cp\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)]$ reagents to afford *inter alia* products **65** and **66** containing five and six metal atoms. A similar reaction between $W_2Ir_2(CO)_{10}Cp_2$ and $\{Ru(CO)_2Cp\}_2(\mu\text{-}C{\equiv}C)$ affords the heterotrimetallic cluster **111** where one of the ruthenium atoms is bound to the cluster core.[75]



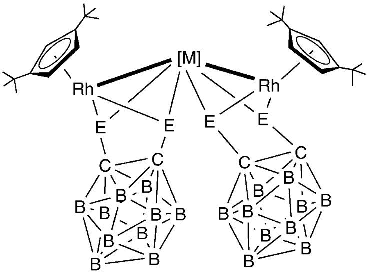
65

R^1 = Ph, $C{\equiv}CW(CO)_3Cp$
R^2 = Cp, Cp$'$,Cp*

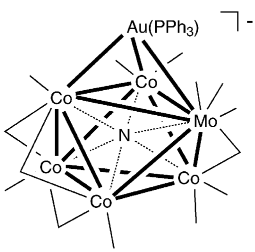


66

Reaction of $Rh(\eta^2\text{-}E_2C_2B_{10}H_{10})(\eta^5\text{-}C_5H_3Bu^t{}_2\text{-}1,3)$ (E = S, Se) with low-valent transition metal complexes $Mo(CO)_3(NC_5H_5)_3$ and $Ni(COD)_2$ affords the linked complexes **67**, containing a carborane 1,2-dichalcogenate bridging a mixed-metal bond.[76] $[MoCo_5(\mu_6\text{-}N)(CO)_{14}]^{2-}$ consists of an octahedral metal cage with an interstitial N atom; addition of $AuCl(PPh_3)$ affords the heptanuclear anionic cluster **68**, which shows three reversible reduction processes.[77]



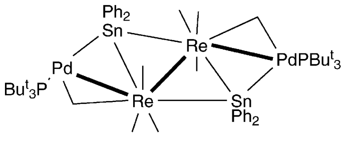
67
[M] = $Mo(CO)_2$, Ni
E = S, Se
carborane H's omitted for clarity

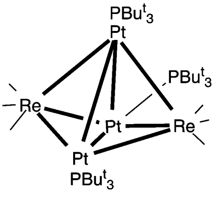


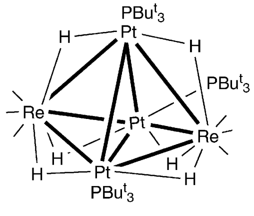
68

11.2 Group 7

$M(PBu^t{}_3)_2$ (M = Pd, Pt) has been shown to form electron-deficient bonds across transition metal M–M bonds, and transition metal–main group metal M–M bonds. The metal–metal bonding in the dirhenium complex $Re_2(\mu\text{-}SnPh_2)_2(CO)_8$ is dominated by the Re–Sn interactions; addition of two molecules of $Pd(PBu^t{}_3)_2$ gives **69**, the palladium increasing the Re–Sn overlap in the Pd-bridged Re–Sn bonds compared to the unbridged bonds.[78] The Re–Pt cluster **70** is ten electrons deficient, and adds three equivalents of hydrogen at room temperature to give the hexahydrido cluster **71**, with the metal-core connectivity remaining intact.[79]



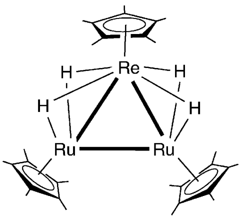




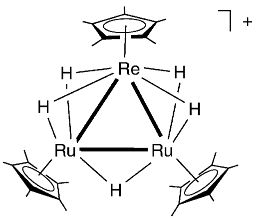
69 **70** **71**

Clusters **72** and **73** are prepared from reacting ReH_6Cp^* with $\{Ru(\mu\text{-}H)_2Cp^*\}_2$ and protonation of $ReRu(\mu\text{-}H)_3(H)_2Cp^*$, respectively, and are the first polyhydride

Re–Ru complexes to have Cp* (rather than CO) as co-ligands; treatment of **73** with base affords a more facile route to **72**.[80]

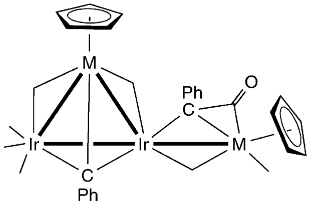


72

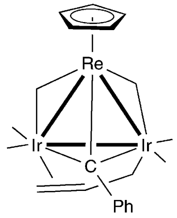


73

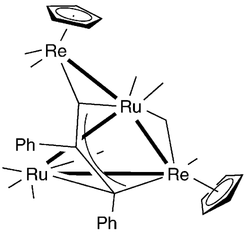
The group 7 carbyne complexes $[M(\equiv CPh)(CO)_2Cp]^+$ (M = Mn, Re) react with $[Ir(CO)_4]^-$ to give the tetranuclear cluster **74**, containing a bridging carbene and a face-capping carbyne ligand. In the manganese reaction $Mn_2Ir_2(\mu_3\text{-}CPh)(\mu\text{-}CPh)(\mu\text{-}CO)_3(CO)_3Cp_2$, a related complex containing bridging and face-capping carbyne ligands, is also obtained whereas the rhenium reaction affords the tetrahedral allylic cluster **75** as the coproduct. Similar reactions with $[Ru(CO)_4]^{2-}$ afford a trinuclear hydrido cluster $MRu_2(\mu\text{-}H)(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6Cp$ (M = Mn, Re) and, in the case of the rhenium reaction, the carbene cluster **76**.[81]



74
M = Mn, Re



75

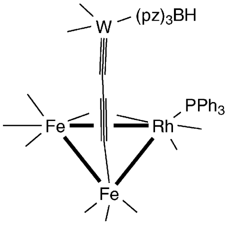


76

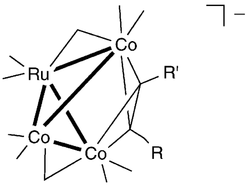
11.3 Group 8

Cluster **77** has been prepared from reaction of the coordinatively unsaturated binuclear tricarbido complex $WRh(\mu\text{-}\eta^1{:}\eta^1\text{-}CC{\equiv}C)(CO)_3(PPh_3)_2\{HB(pz)_3\}$ and $Fe_2(CO)_9$.[82] A series of alkyne-ligated butterfly cluster anions $[RuCo_3(\mu_4\text{-}\eta^2\text{-}RC_2R')(\mu\text{-}CO)_2(CO)_8]^-$ [R = H, R′ = MeC=CH$_2$, CH$_2$OCH$_2$C≡CH (**78**), CH$_2$N(H)C(O)C≡CPh; R = R′ = C(O)OMe] has been prepared from $[RuCo_3(CO)_{12}]^-$, with isomers differing in the orientation of the alkyne with respect to the Ru–Co hinge bond being obtained. Subsequent reaction with $[Cu(NCMe)_4]^+$ results in formal loss of a $[Co(CO)]^-$ unit to give $RuCo_2(\mu_3\text{-}\eta^2\text{-}RC_2R')(CO)_9$ [R = H, R′ = MeC = CH$_2$; R = R′ = C(O)OMe]. Functionalized [PhC≡CC(O)-NH(CH$_2$)$_3$Si(OEt)$_3$ and 1,4-bis(trimethylsilyl)butadiyne] alkyne clusters were also prepared, reaction of the latter with $[Cu(NCMe)_4]BF_4$ resulting in proto-desilylation of the core-bound SiMe$_3$ group, and with AuCl(PPh$_3$) or PPh$_3$ giving selective substitution of a ruthenium-bound carbonyl group with PPh$_3$. Sonogashira coupling of $[RuCo_3(\mu_4\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CH)(\mu\text{-}CO)_2(CO)_8]^-$ affords the dianion $[\{RuCo_3(\mu\text{-}CO)_2(CO)_8\}_2(\mu_8\text{-}\eta^4\text{-}Me_3SiC_2C{\equiv}C\text{-}4\text{-}C_6H_4C{\equiv}CC_2SiMe_3)]^{2-}$.[83]

The bis(phosphine) complexes $M(PBu^t_3)_2$ (M = Pd, Pt) have been used to add $M(PBu^t_3)$ units across metal–metal bonds affording a large range of new group 8-group 10 clusters. Reaction of $M(PBu^t_3)_2$ with $Ru(CO)_5$ affords **79**, the intermediate triangular cluster **80** also being isolated in the reaction with the platinum reagent. The tetranuclear complex **79** reacts with hydrogen to give a dihydrido tetrahedral product **81**. These reaction products represent addition of the group 10 fragment to $Ru_2(CO)_9$, a relatively unstable reagent; similar reaction with $Fe_2(CO)_9$ affords the iron analogue of **80**.[84]

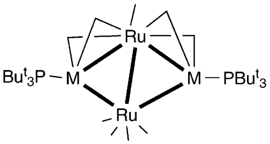


77

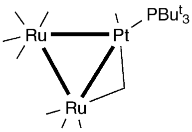


78

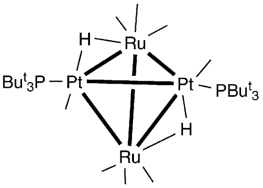
R = H, R' = MeC=CH$_2$, CH$_2$OCH$_2$C≡CH
R = MeC=CH$_2$, CH$_2$OCH$_2$C≡CH, R' = H



79 M = Pd, Pt

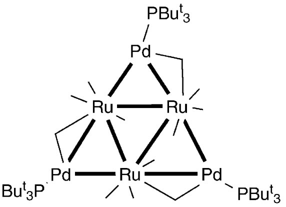


80



81

A series of hepta- and octa-nuclear Ru–Pd and Ru–Pt clusters, including **82** and **83**, has been prepared from $Ru_3(CO)_{12}$, $Ru_6(\mu_6\text{-}C)(CO)_{17}$ or $Ru_6(\mu_6\text{-}C)(CO)_{14}(\eta^6\text{-}C_6H_6)$ and $M(PBu^t_3)_2$. Cluster **83** exists as two isomers with one of the $Pd(PBu^t_3)$ groups coordinated in either bridging or face-capping modes.[85] Similar reactions with $Ru_5(\mu_5\text{-}C)(CO)_{12}(\eta^6\text{-}C_6H_6)$ afford products with an open octahedral metal core containing one (**84**) and two (**85**) (phosphine)platinum adducts. NMR studies suggest that **84** exists as two isomers in solution, a bridged square-pyramidal structure due to Pt–C bond scission the most likely metal framework. The two $Pt(PBu^t_3)$ groups in complex **85** are also fluxional, with exchange probably occuring through an intermediate consisting of a square-pyramidal ruthenium core with two apical-bridging platinum units. Both clusters add hydrogen to give a dihydrido octahedral species **86**.[86]



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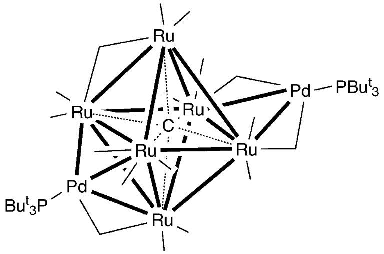

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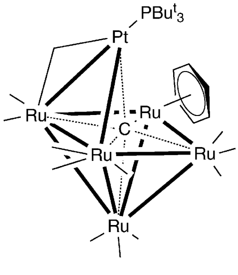

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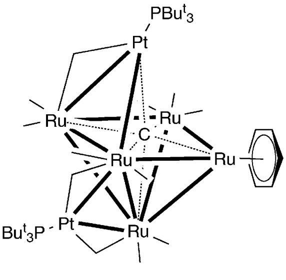

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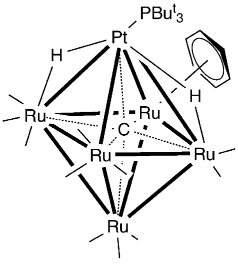
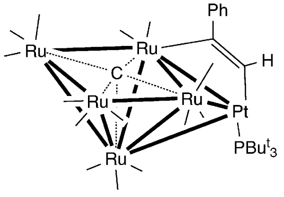
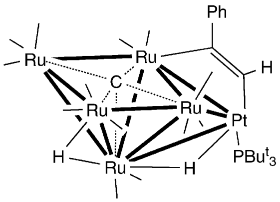


86

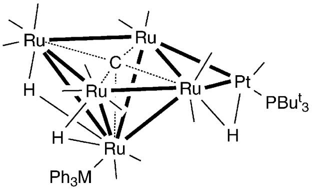
The platinum atom in $Ru_5Pt(\mu_6\text{-}C)(CO)_{15}(PBu^t_3)$ has been shown to be directly involved in the activation of both hydrogen and phenylacetylene, reaction with hydrogen giving a dihydride complex $Ru_5Pt(\mu\text{-}H)_2(\mu_6\text{-}C)(CO)_{14}(PBu^t_3)$ related to **86**, and phenylacetylene affording **87**. In addition, treatment with hydrogen in the presence of a large excess of phenylacetylene affords styrene catalytically, with complex **88** being isolated from the reaction mixture. Complex **87** reacts further with one or two equivalents of $Pt(PBu^t_3)_2$ by addition across the basal Ru–Ru bonds.[87,88] Reaction of $Ru_5Pt(\mu_6\text{-}C)(CO)_{15}(PBu^t_3)$ with $MHPh_3$ (M = Ge, Sn) results in carbonyl ligand substitution and Pt–Ru bond scission to give the bridged square-pyramidal cluster **89**, which loses benzene on thermolysis, reforming the octahedral metal core to give **90**.[89]



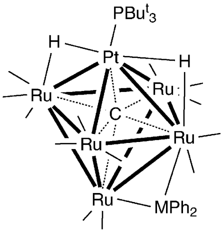
87



88



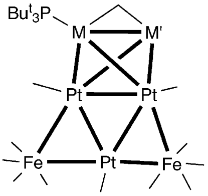
89 M = Ge, Sn



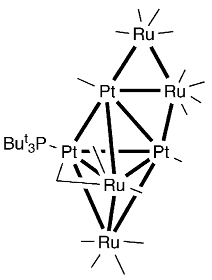
90 M = Ge, Sn

The mixed-metal raft cluster $Fe_3Pt_3(CO)_{15}$ reacts with $M(PBu^t_3)_2$ (M = Pd, Pt) to give the mono-addition product **91** [M′ = $Fe(CO)_3$], and the vertex replacement product **74** (M′ = $MPBu^t_3$), a four-electron deficient cluster resulting from replacement of an $Fe(CO)_3$ unit by the group 10 metal phosphine unit. Reaction of $Ru_4Pt_2(CO)_{18}$ with $Pt(PBu^t_3)_2$ gives the addition product **92**.[90]

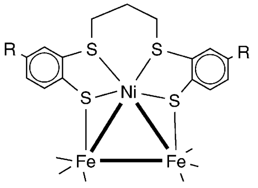
The redox-active clusters **93** have been prepared as models for the active site of [NiFe] hydrogenase; structural studies show the clusters contain a similar nonplanar NiS_4 coordination sphere to that found in the known hydrogen cleavage catalyst $Ni(NHPPr^n_3S'_3)$ [S′ = bis(2-sulfanylphenyl)sulfide(2-)]. Complex **93** undergoes a reversible reduction to generate an EPR-active monoanion that shows a nickel



91
M = Pd, Pt
M' = $Fe(CO)_3$; $M(PBu^t_3)$



92

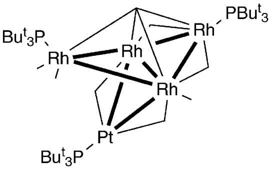


93 R = H, Me

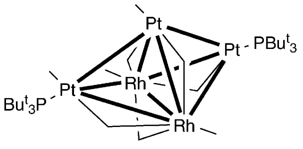
contribution to the SOMO, suggesting a delocalization of spin-density across the Fe_2Ni cluster; this is in contrast to other forms of [NiFe] hydrogenase, which show considerable S content in the SOMO.[91]

11.4 Group 9

The cyanoamido-bridged bimetallic complex $Ir_2(\mu\text{-}NCN)_2Cp^*{}_2$ has been reacted with a range of Lewis acid metal fragments to afford a series of NCN-capped heterotrinuclear complexes $Ir_2M(\mu_3\text{-}NCN)_2(L)Cp^*{}_2$ [M(L) = Rh(COD), RuCp, $Pd(\eta^3\text{-}C_3H_5)$].[92] The bis(imido)- bridged complex $[Rh_3(\mu_3\text{-}NC_6H_4\text{-}4\text{-}Me)_2(CO)_6]^-$ reacts with $AuCl(PPh_3)$ to give a butterfly cluster addition product $Rh_3Au(\mu_3\text{-}NC_6H_4\text{-}4\text{-}Me)_2(CO)_6(PPh_3)$ *via* Rh–Rh and Rh–Au bond formation, whereas reaction with $[Rh(NCMe)_2(COD)]^+$ gives the opened-triangular complex $Rh_3(\mu_3\text{-}NC_6H_4\text{-}4\text{-}Me)(CO)_6\{(\mu_4\text{-}\eta^1\text{:}\eta^5\text{-}NC_6H_4\text{-}4\text{-}Me)Rh(COD)\}$, containing a Rh(COD) fragment coordinated to the arene ring of one imido ligand. Interestingly, a similar reaction with $PdCl_2(COD)$ affords a vertex replacement product $Rh_2Pd(\mu_3\text{-}NC_6H_4\text{-}4\text{-}Me)_2(CO)_4(COD)$.[93] $Rh_4(CO)_{12}$ reacts with $Pt(PBu^t{}_3)_2$ to give a mixture of **94–96**, while reaction at higher temperatures affords decanuclear **4** in very low yield. Complex **94** contains an unusual $\mu_4\text{-}\eta^1$-CO ligand with one wing-tip Rh–C bond slightly longer than the others, and **95** is two electrons deficient for a trigonal bipyramidal cluster. Cluster **96** undergoes dynamic behaviour involving exchange of the (phosphine)platinum groups.[17]



94



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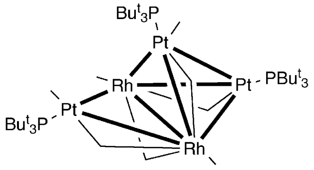
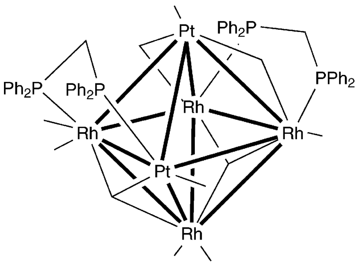
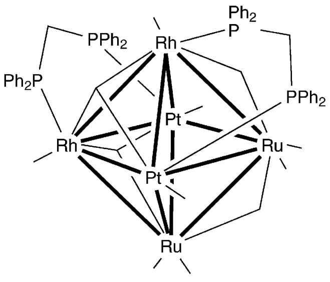


96

Octahedral clusters **97** and **98** are formed from reaction between electron-rich $Rh_2Pt_2(\mu\text{-}dppm)_2(CO)_6$ and $Rh_6(CO)_{14}(NCMe)_2$ or $Ru_3(CO)_{12}$, respectively. The difference in the metal constitution of the resulting products is likely due to the differences in the stability of the reactant clusters, with the $Ru_3(CO)_{12}$ easily degrading to mononuclear fragments, whereas the more stable hexarhodium complex requires harsher reaction conditions to promote fragmentation.[94]



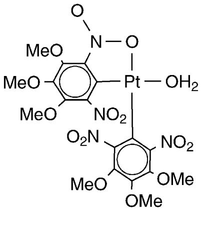
97



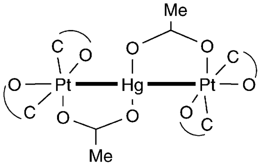
98

11.5 Group 10

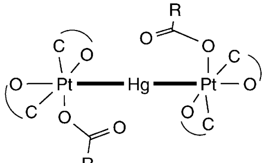
Oxidative addition of $Hg(O_2CR)_2$ to two equivalents of *cis*-$Pt(\kappa^2\text{-}Ar)(\kappa^1\text{-}Ar)(O_2H)$ [**99**, Ar = C_6-2,6-$(NO_2)_2$-3,4,5-$(OMe)_3$] affords **100** (R = Me) or **101** (R = Ph, C_6F_5, CF_3). Complex **100** contains a bridging carboxylato ligand and ^{195}Pt NMR data suggest the formal oxidation state of the platinum to be $Pt^{2.5+}$–Hg^{+}–$Pt^{2.5+}$, whereas the unbridged complex **101** is formally Pt^{3+}–Hg^{0}–Pt^{3+}.[95]



99

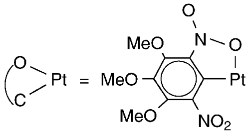


100



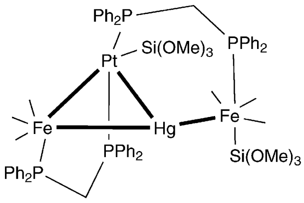
101

R = C_6F_5, CF_3,
$C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5

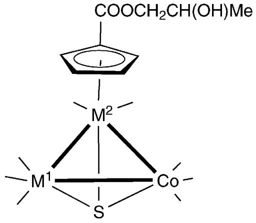


12 Clusters containing three different metals

Treatment of the trinuclear linear cluster $\{Fe[Si(OMe)_3](CO)_3(dppm\text{-}P)_2\}_2Hg$ with the labile Pt(0) complex $Pt(C_7H_{10})_3$ affords **102**, resulting from coordination of the

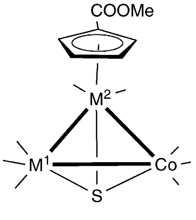


102



103

M^1 = Fe, Ru
M^2 = Mo, W

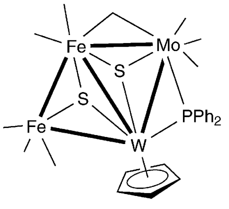


104

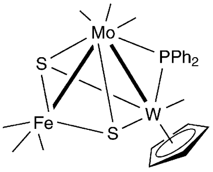
M^1 = Fe, Ru
M^2 = Mo, W

free phosphorus atom and unprecedented transfer of a silyl ligand to the incoming platinum unit. Previous reactions using Cu(I) or Pd(0) reagents have given products in which the silyl ligand remains coordinated to the iron centre and a comparative DFT study shows that this is mostly due to the greater electronegative character of the Pt.[96] Lipase-catalyzed ester exchange reactions utilizing functional groups on the cyclopentadienyl ligand of **103** has been used to produce chiral cluster derivatives **104**.[97]

Reaction of $Fe_2(\mu\text{-}S_2)(CO)_6$ with $WMo(\mu\text{-}PPh_2)(CO)_8Cp$ affords a range of Mo–W–Fe clusters **105–109**, including a product resulting from fragmentation of the diiron species.[98] The trimetallic octahedral cluster $Ru_2Rh_2Pt_2(\mu_3\text{-}CO)_2(\mu\text{-}CO)_2(\mu\text{-}dppm)_2(CO)_8$ (**98**) is formed in good yield from $Rh_2Pt_2(\mu\text{-}dppm)_2(CO)_6$ and $Ru_3(CO)_{12}$.[94] Cluster core expansion of $WIr_3(CO)_{11}(\eta^5\text{-}C_5R_5)$ (R = H, Me) and $W_2Ir_2(CO)_2Cp_2$ with the ethyndiyl complex $\{Ru(CO)_2Cp\}_2(\mu\text{-}C{\equiv}C)$ affords **110** and **111**, the former *via* W–Ir and Ru–C bond cleavage, and the latter by Ru–C cleavage, formal insertion of the C_2 unit into a W–Ir bond, and dimerization to give a C_4 ligand, the first synthesis of C_4 from a dimetalated precursor.[75]



105



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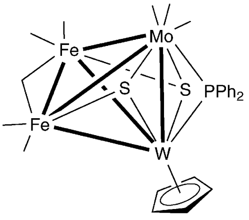
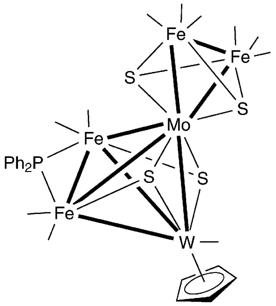
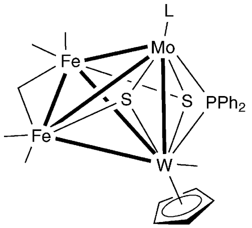


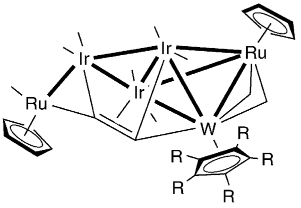
107



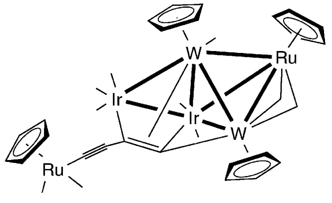
108



109 L = (nbd)(CO), η^6-C_6H_6



110 R = H, Me



111

Abbreviations

Ac	Acetyl
ccp	Cubic close-packed
COD	1,5-Cyclooctadiene
COE	Cyclooctene
Cp	η^5-Cyclopentadienyl
Cp′	η^5-Methylcyclopentadienyl
Cp*	η^5-Pentamethylcyclopentadienyl
c.v.e.	Cluster valence electrons
Cy	Cyclohexyl
dba	Dibenzylideneacetone
DFT	Density functional theory
dmad	Dimethyl acetylenedicarboxylate
dpmp	Bis(diphenylphosphinomethyl)phenylphosphine
dppm	Bis(diphenylphosphino)methane
eV	Electron volts
FMO	Frontier molecular orbital
H_2abqH	2-Amino-6-methylpyridine
H_2ampy	2-Amino-6-phenylpyridine
H_2apyPh	2-Amino-7,8-benzoquinoline
Hapyr	2-Aminopyridine
hcp	Hexagonal close-packed
ITO	Indium tin oxide
MV	Methyl viologen
nbd	Norbornadiene
PNNP	3,5-Bis{(diphenylphosphino)methyl}pyrazolato
Py	Pyridyl
Pyz	Pyrazine
Tol	4-C_6H_4Me
Xyl	2,6-$C_6H_3Me_2$

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