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Transition Metal Complexes of Neutral η^1-Carbon Ligands

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30
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Transition Metal Complexes of Neutral η^1-Carbon Ligands

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The series *Topics in Organometallic Chemistry* presents critical overviews of research results in organometallic chemistry. As our understanding of organometallic structures, properties and mechanisms grows, new paths are opened for the design of organometallic compounds and reactions tailored to the needs of such diverse areas as organic synthesis, medical research, biology and materials science. Thus the scope of coverage includes a broad range of topics of pure and applied organometallic chemistry, where new breakthroughs are being made that are of significance to a larger scientific audience.

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Preface

Metal–carbon bonds are gems of the organic chemistry toolbox, serving to activate octet-covalent carbon centers, and stabilize their resulting non-octet covalent electronic structure in the jewel cases of diffuse transition metal orbitals. Whereas many criteria are used for general ligand classifications (coordinating function, donor/acceptor character,. . .), a further simple analogy among carbon ligands allows quite different classical representatives such as NHCs, ylides, and cumulenylidenes to be placed in the category of neutral η^1-carbon ligands. Their internal typology is based on the three fundamental hybridization states of covalent carbon atoms (sp3, sp2, sp), and is refined according to the number of conjugated heteroatoms, such as nitrogen or phosphorus. The three types and six subtypes of ligands are thus put together for the first time under the unifying heading of this volume. The seven chapters are not primarily dedicated to provide extensive reviews, but to illustrate synergetically how the cognate ligands share common features that could inspire the design of novel or mixed representatives for targeted applications. After the reign of sp2 and sp3 N and P ligands in the realm of catalysis, spectator C-ligands recently entered through the sp2 gate with the tremendous achievements of the NHC family. While other sp2, sp3, and sp families still remain as infant pretenders, the present categorization might help their advent in the design of future catalysts.

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Toulouse Remi Chauvin, Yves Canac

Contents

Part I *sp*^{3} -Hybridized Neutral η^1-Carbon Ligands

Part II *sp*^{2} -Hybridized Neutral η^1-Carbon Ligands

Part III *sp* -Hybridized Neutral η^1-Carbon Ligands

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Neutral η^1-Carbon Ligands: Beyond Carbon Monoxide

Yves Canac, Christine Lepetit, and Remi Chauvin

Abstract The Green formalism proposes a natural typology of the metal–carbon ligands. Among the neutral η^1 representatives satisfying the octet rule for the carbon atom in the free state, three types are distinguished depending on the hybridization state (or connectivity) of the coordinating carbon atom. Each type corresponds to a well identified class of ligands exhibiting remarkable stability as compared to "anionic" versions: the ylide-type ligands and associated carbodiphosphoranes (sp^3), the *N*-heterocyclic carbenes (NHCs) and other stabilized carbenes (sp^2), and the cumulenylidenes with an even number of consecutive digonal carbon atoms stabilized by either heteroatomic or simple π-conjugated substituents (*sp*).

Keywords Allenylidenes · Carbenes · Carbodiphosphoranes · Carbon ligands · Cumulenylidenes · NHCs · Ylides

Contents

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1 Introduction

In spite of its reactivity, the single metal-to-carbon bond is not a marriage against Nature: to last, it just requires to be nested in a soft environment. The softness is primarily provided by polarizable (late) transition metal centers, but the formal neutrality of the carbon ligand remains essential for maintaining the harmony. The history of the transition metal–carbon bond began accordingly in 1827 with the isolation by Zeise of the first stable complex containing a carbon ligand, $[\mathrm{Pt}(\eta^2\text{–}\mathrm{C_2H_4})\mathrm{Cl_2}]_2$ [1]. According to updated knowledge, the ethylene ligand is weakly η^2-coordinated, but the discovery of $\mathrm{Ni(CO)_4}$ in 1890 by Langer and Mond constituted the emergence of the organometallic chemistry of strongly bonded neutral η^1-carbon ligands, involving a hybrid single–double–triple metal–carbon bond ($\mathrm{M^-\text{–}{}^+C{=}O} \leftrightarrow \mathrm{M^-\text{–}C{\equiv}O^+} \leftrightarrow \mathrm{M{=}C{=}O} \leftrightarrow \mathrm{M^+{\equiv}C\text{–}O^-}$) [2].

Following the tremendous development of the organometallic chemistry of the carbonyl ligands, and later in the 1950s of stable "anionic" carbon ligands (a paradigm being the cyclopentadienyl ligand) [3, 4], the chemistry of the "neutral" versions first revived in 1964 with Fischer's discovery of stable carbene ligands, displaying a metal–carbon bond with a strong double character ($\mathrm{M = CR'(OR)}$) [5].

A second revival occurred in 1968 with the first isolation of *N*-heterocyclic carbene (NHC) ligands with a *quasi* simple character of the metal–carbon bond ($\mathrm{M^-\text{–}C(N^{+0.5}R_2)_2}$) [6, 7].

In a less highlighted, but – perhaps – not less promising, manner, the story proceeded with the first insights into the organometallic chemistry of ylide and related carbodiphosphorane ligands, involving a *pure* simple metal–carbon bond ($\mathrm{M^-\text{–}CR'_2P^+R_3}$) [8–13].

At last, the advent of the organometallic chemistry of cumulenylidene ligands could be regarded as a revival of one main feature of the "old" neutral carbonyl ligand: the *sp*-carbon–metal bond [14–19]. The number of cumulated *sp*-carbon atoms is either odd (with a partial triple metal–carbon bond of opposite polarity with respect to the carbonyl ligand: $\mathrm{M^-{\equiv}C\text{–}(C{\equiv}C)_{\mathit{n}}\text{–}C^+R_2}$) or even (without any triple character of the metal–carbon bond: $\mathrm{M^-\text{–}(C{\equiv}C)_{\mathit{n}}\text{–}C^+R_2}$). Due to this fundamental analogy with the carbonyl ligand, the latter category deserves special attention.

2 The Underlying Ligand Typology: A Basic Lewis Analysis

The preceding historical survey is actually underlying a fundamental – but simple – aspect of the Lewis theory. Given an $[(\mathrm{M})\cdots\mathrm{L}]^{\mathrm{Q}}$ complex ion (or complex if $Q = 0$),[1] where Q represents the sum of metal-conjugated charges, the $\mathrm{M}\cdots\mathrm{L}$ bond is dissected

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[1] The (M)…L symbol represents a set of bonding interactions between the metal atom M and $1 + n$ *adjacent* atoms in the ligand L. So it features one π-*conjugated* $\eta^{(1+n)}$ interaction, and not the global hapticity of the ligand that results from the combination of all σ-separated such interactions.

in such a way that the L fragment undergoes the minimal absolute ionization |q| to ensure an octet, duet, or resonance-allowed hypo/hypervalent stability of the coordinating atom in the so-defined "free ligand" L^q. And if opposite absolute ionizations $\pm q$ are possible, the VSEPR-consistent one is retained [20]. Following this definition, L is said to be "neutral" if $q = 0$ (PR_3, SR_2, BX_3, C=O, C=NR, $C(NR)_2$, $C{=}C_{2x+1}{=}E$, $^{-}CR_2{-}P^{+}R'_3$,...), "anionic" if $q < 0$ (Cl^-, CN^-, SCN^-, OH^-, O^{2-}, H^-, bent NO^-, $^{-}CR_3$, $^{-}C(R){=}E$, $^{-}C{\equiv}CR$,...), and "cationic" if $q > 0$ (H^+, linear NO^+). Although a few ambiguities require complementary information (e.g., for hydrides H^- vs protons H^+), in most cases (except e.g. the ylide case) this analysis meets the Green formalism ("neutral" ligands are of the L_n-type, "anionic" ones are of the L_nX-type) [21].

One hereafter focuses on the so-defined *neutral* η^1-*carbon*-centered ligands other than the carbonyl, thiocarbonyl, isocyanide (C=X, X = O, S, NR), and original Fischer carbenes derived thereof ($CR'{-}XR$) [22]. Beyond these, two broad categories of carbon-centered ligands are thus excluded, respectively constituted by the neutral η^n-coordinated ligands ($n \geq 2$: alkenes, butadienes, arenes, alkynes, aldehydes, and ketones...), and by the following anionic η^1-coordinated ligands, where E denotes either a single atom (e.g., O, S), an sp^2 substituent (e.g., NR', CR'_2), or an sp- or $sp^3\sigma^*$ substituent (e.g., CR', PR'_3):

- All the alkenyl, -aryl, -acyl, -iminoacyl, -alkynyl, cyanide ligands ($C(R){=}E$ or $C{\equiv}E$)
- All the alkenylidene ligands ($C{=}CR_2$)
- All the alkylidyne- or "carbyne-" ligands (CR)
- The nonylidic alkyl ligands (CR_3)
- The non-π-conjugated alkylidene- or Schrock-type "carbene-" ligands (CR_2)
- The odd-cumulenylidene ligands ($C{=}[C{=}C]_n{=}E$)[2]

The remaining cases are thus:

A. The ylidic alkyls or simply "ylides" and related carbodiphosphoranes ($CR_2{=}E \leftrightarrow {}^{-}CR_2{-}E^+$)
B. The π-conjugated alkylidenes or "π-conjugated carbenes" ($CR{-}E| \leftrightarrow {}^{-}CR{=}E^+$)
C. The even-cumulenylidenes ($C{=}[C]_{2n+1} = E \leftrightarrow {}^{-}C{\equiv}[C]_{2n+1}{-}E^+$)

where the nature of E must stabilize the development of a positive charge on it. While both the resonance forms satisfy the octet rule for case A, a single does for cases B and C. In all three cases, however, the formally anionic octet carbon of the zwitterionic form is a priori prevailing for describing the "free ligand" in a precoordinating situation. Each case A, B, or C corresponds to a specific hybridization state, namely sp^3, sp^2, or sp, respectively.

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[2] In the neutral form of the butatrienylidene ligand for example ($n = 1$), the first zwitterionic resonance structure ensuring the octet at the coordinating atom would be $^{-}C{\equiv}C{-}^{+}C{=}C{<}$, where the γ-carbon is not only hypovalent ($6e^-$) but also incompatible regarding its linear geometry (it should be trigonal according to the VSEPR). By contrast, in the neutral form of the allenylidene ligand, the corresponding resonance structure $^{-}C{\equiv}C{-}C^{+}{<}$ is fully compatible with the present trigonal geometry of the γ-carbon.

In a refined approach, however, ligands of given coordinating atom, given charge and given steric bulk, are usually compared through their electronic σ/π-/donor/acceptor characters. Referring to a formal hydrated equivalent (as done for defining the oxidation level in organic chemistry or the octahedral *d*-orbital splitting in crystal field theory), one might assume that the donating component of the M–C bond (i.e., the heterolytic M^+/C^- dissociation energy) grossly varies as the proton affinity of the C^- ligand and, consequently, that the less acidic the C–H bond, the more donating the C ligand. Since the average acidity of sp^x-C–H bonds varies in the sense $sp > sp^2 > sp^3$, one may infer that an sp^3-C ylide should be a stronger donor than an sp^2-C carbene, itself a stronger donor than an *sp*-C cumulenylidene.

In a more discriminating way, the promised accepting vs donating character of a free ligand can be tentatively analyzed through the weights of two kinds of resonances forms: those where the coordinating atom is octet-saturated and carries at least one lone pair, and those where this atom is hypovalent. Although resonance weighting is not univocally defined, various methods – from VB [23] and NRT [24–26] to ELF [27] analyses – were proposed, and generally agree, at least in general trends.

Carbon monoxide, the paradigm of neutral η^1–carbon ligands, was early recognized to be well described by three limiting forms: C=O, $^-C{\equiv}O^+$, and $^+C{-}O^-$, to which Pauling empirically assigned the respective weights 50%, 40%, and 10% [28]. This weighting was recently refined to 48%, 42%, and 10% respectively from ELF analysis of the electron density [27, 30]. A crude interpretation of theses results suggests that the bonding character of CO would thus be 40% σ-donating and 60% π-accepting. This was accurately confirmed by Frenking et al. who arrived at 46% σ-donating and 54% π-accepting contributions from an in situ energy decomposition analysis of the $Ni(CO)_4$ complex [29]. A recent analysis of the contributions of fragment orbitals to relevant ELF basins of $Ni(CO)_4$ suggested an even higher π-accepting character per CO ligand (79% vs 13% σ-donating and 8% π-donating), which is also fully consistent with a refined ELF-weighting of the resonance forms of CO [27, 30]. The metal-charge transfer effectiveness of each resonance form of the free ligand is indeed expected to depend continuously on the unsaturation level at the carbon atom.[3] More fundamentally, the ambivalence of the CO ligands results from a mixed HSAB character of the coordinating carbon: it was recently underlined that this ligand acts both as a soft base [31] and as a hard acid [32].

Once validated, a similar analysis can now be performed for the ligand types A, B and C. It is simplified here by taking into account two resonance forms only:

- A-type free ylidic alkyl ligands are thus described by resonance forms both obeying the octet rule at the coordinating carbon. In this approximation, no π-accepting character is available, and these ligands are expected to be purely σ-donating. In principle, residual π-acceptation could however operate through the $\sigma_{C-E}{}^*$ antibonding orbital of the C–E bond, itself featured by the additional

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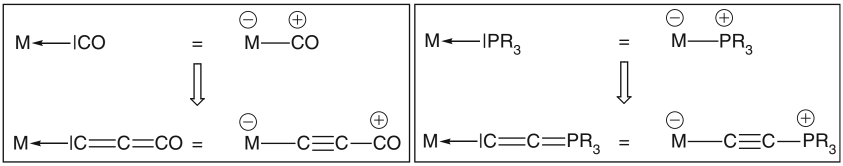
[3] The carbon unsaturation level is $u = 2$ and 4 electrons for the C=O and $^+C{-}O^-$ accepting forms, respectively, and $u = 0$ for the donating form $^-C{\equiv}O^+$. Assuming that the metal-charge transfer effectiveness varies as $1+\alpha u$, the latter result gives $\alpha \approx 1.25$.

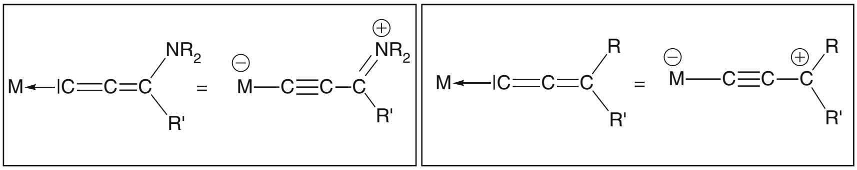
no-bond resonance form "R_2C, E" inspired by Bertrand's report on the cleavage of certain phosphonium ylides to phosphine and carbene moieties ($R_2C^-{-}P^+R'_3 \rightarrow R_2C| + |PR'_3$) [33, 34]. In the σ-coordinated situation $M^-{-}CR_2{-}^+PR'_3$, the $\sigma_{C-P+}*$ MO is predominantly located near the less electronegative carbon center. Although the spatial condition for π acceptation is thus a priori favorable, the energetic condition is not, and the π-accepting character of ylide ligands is definitely negligible (unless the P–C bond is cleaved). Residual π-acceptation of ylide ligands could also be taken over "through space" by empty orbitals located near the E^+ center. Although the ELF-derived resonance description of η^1-phosphonium ylide complexes indeed indicates a contribution of the η^2-haptomeric form, its weight is quite low (less than 20%), in accordance with the absence of example of η^2-coordination of the $CR_2{=}E$ form [35]. The ylide ligands are thus definitely anticipated to act almost exclusively as donors, and this was experimentally demonstrated in a systematic manner [36–38]. The coordinating nature of ylidic carbons is – both a priori and a posteriori – even more intriguing in the case of the carbodiphosphoranes that possess a doubly zwitterionic resonance form ($R'_3P{=}C{=}PR'_3 \leftrightarrow R'_3P^+{-}C^{2-}{-}P^+R'_3$). The question, tackled in 1983 [8], has been the matter of recent debates [39–42].

- B-type free β-conjugated carbene ligands involve resonance forms with either an octet or a 6-electron count at the coordinating carbon atom ($CR{-}E| \leftrightarrow {}^-CR{=}E^+$). If the substituents E and R are strongly π-donating, like alkylated nitrogen atoms, the octet form is prevailing. This is the case of the widely studied NHCs, which are today recognized as extremely donating soft ligands beyond the classical phosphane ligands (PR_nAr_{3-n}). The coordination mode of NHCs has been investigated in detail by several authors, but the first secondary effect indeed proves to be π-donation rather than π-acceptation [43–48].
- C-type free even cumulenylidene ligands also involve resonance forms with either an octet or a 6-electron count at the coordinating carbon atom ($C{=}[C]_{2n+1} = E \leftrightarrow {}^-C{\equiv}[C]_{2n+1}{-}E^+$) [14]. Whatever is the nature of E, they are cumulogue equivalents of the CO ligand and are thus pivotal in this context for being anticipated to be relatively less σ-donating than ylides and π-conjugated carbenes. The most obvious case (E = CO, $n = 0$) is C_3O, which has been theoretically investigated in nickel(0) complexes [30, 49]: the strong π-accepting properties of CO are uncovered, as qualitatively suggested by the functional *carbo*-mer principle [50]. The opposite prediction can be done for the phosphora analog (E = PPh_3, $n = 0$) [51, 52] if the corresponding complexes are regarded as functional *carbo*-mers of phosphine complexes (Scheme 1).

In the σ-donating (zwitterionic) resonance form of the latter heteroatom-cumulated free ligands, *all* the atoms satisfy the octet rule. Two kinds of all-carbon versions can be distinguished: those that are π-conjugated to a remote heteroatom and those that are not [14–19]. The former are largely exemplified by aminoallenylidenes, in which the σ-donating resonance form of the free ligand is also stabilized by the octet rule (they are functional *carbo*-mers of the Fischer-type aminocarbenes). The second kind is represented by C-substituted allenylidenes.



Scheme 1 *Carbo*-meric versions of carbonyl and phosphane ligands



Scheme 2 Octet-stabilized amino-allenylidene ligands (*left*), and non-octet-stabilized allenylidene ligands (*right*)

In this case the σ-donating resonance form does not formally obey the octet rule: the cationic center is however stabilized by either inductive effects of alkyl substituents, or by mesomeric effects of unsaturated alkenyl, aryl, or alkynyl substituents. This form is indeed "chemically active," since the complexes are obtained by protonation of the propargylic alkoxy group of the "anionic" alkynyl ligand precursor [53]. Finally, these ligands are functional *carbo*-mers of non- or weakly π-conjugated carbene ligands (CR_2) that are stabilized by conjugation through the inserted C_2 units: the *sp* (vs sp^2) hybridization state of the coordinating atom is thus essential (Scheme 2).

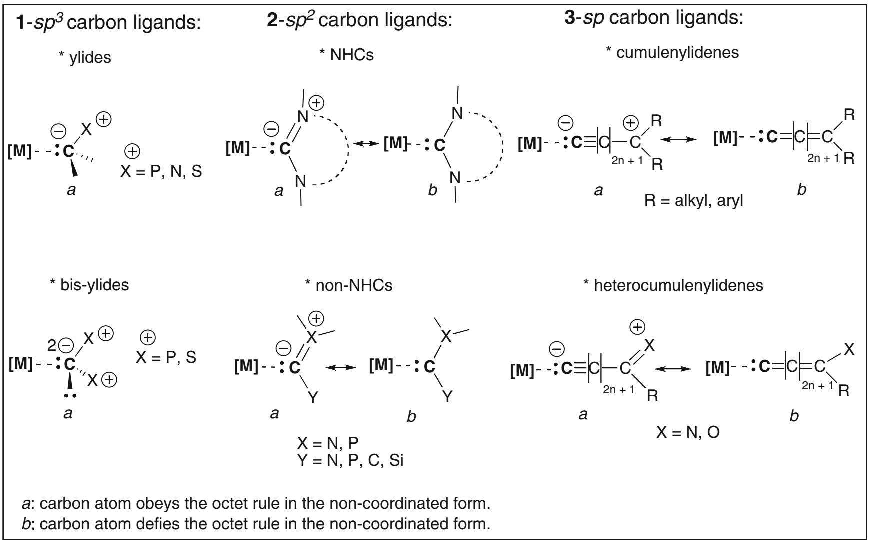
The category of "neutral η^1–carbon ligands" is thus not only defined from a historical perspective and a formal bonding typology (Scheme 3), but also in accordance with the current analysis of the bonding properties of ligands vs their σ/π-donating/accepting ability [54–57].

3 Descriptive Introduction of the Neutral sp*x*-Carbon Ligands, x = 3, 2, 1

The trends anticipated from basic Lewis and resonance theories are, of course, qualitative in nature. The three ligand types A, B, and C are now briefly described in decreasing order of their anticipated σ-donating vs π-accepting ability.

3.1 *Class A. Neutral* sp^3*-Carbon Ligands: Ylides and Carbodiphosphoranes*

Ylides are species in which a positively charged heteroatom X (such as P, S, N, or As) is connected to a negatively charged atom possessing an unshared electron



Scheme 3 Typology of neutral η1–carbon ligands. The coordinating carbon atom of the free ligand obeys the octet rule in one of its main resonance form (form a)

pair. The main class of ylides is constituted by the phosphonium ylides where an easily pyramidalized carbanion is stabilized by an adjacent tetrahedral phosphonium center.

The first representative, (diphenylmethylene)diphosphorane, was reported by Staudinger in 1919 [58] but their chemical value was only revealed in 1949 when Wittig showed that they can be used in a systematic manner for the formation of carbon–carbon double bonds in organic synthesis [59, 60].

Beyond their ubiquitous role in organic synthesis, "stabilized," "semistabilized," or "nonstabilized" phosphonium ylides are fascinating ligands of transition metals. Their coordination chemistry is dominated by C-coordination to the metal center: they are known to act exclusively as η^1- carbon-centered ligands rather than as η^2–C=P ligands.

Phosphonium ylides form complexes with almost every metal of the periodic table [8–13]. The first ylide complexes involved "carbonyl-stabilized" ylides at Pd (II) and Pt(II) metal centers. One early example was reported by Arnup and Baird in 1969 [61]. The scope of the ylide coordination chemistry was then extensively investigated by Schmidbaur [8].

Rather surprisingly, examples of catalytic use of phosphonium ylide complexes are still limited [62, 63], but chiral ylide complexes (Pd, Rh) were already used in enantioselective catalysis [64–66]. Since phosphonium ylides have recently been shown to act as extremely strong donor ligands, even stronger than NHCs [36–38], their wider use in transition metal catalysis surely deserves further attention. The continuous exploration of the fascinating structural features and bonding properties of ylide ligands makes them attractive candidates for organometallic applications.

These aspects will be detailed by E. P. Urriolabeitia in the second chapter of this volume.

Changing one of the two non-P^+ substituents of the ylidic carbon atom by a second positively charged heteroatom results in a bis-ylide. In this category, carbodiphosphoranes constitute the most studied representatives [8–13, 39–42]. The free ligands contain two cumulated ylide functions and a formally divalent central carbon(0) atom bearing two formal negative charges, stabilized by two phosphonio substituents. The presence of two lone pairs of electrons at the central carbon atom results in remarkable geometrical and electronic features: a bent structure and an anticipated strong nucleophilicity of the carbon(0). After having been described by Ramirez in 1961 [67], the first carbodiphosphorane complexes were reported by Kaska in 1973 (1:1 complex) [68], and by Schmidbaur in 1975 (1:2 complex) [69]. Related carbodiarsoranes ($R_3AsCAsR_3$) were exemplified in 1985 [70], and more recently, bis-ylides containing the $S^{VI}=C=S^{VI}$ sequence [71], and mixed phosphonium–sulfonium bis-ylides were also described [72, 73]. Both theoretical and experimental features of these highly electron-rich potential ligands are discussed by G. Frenking and W. Petz in the third chapter of this volume.

3.2 Class B. Neutral sp^2-Carbon Ligands: NHC and Non-NHC π-Conjugated Carbenes

Carbenes [74–76], and in particular *N*-heterocyclic carbenes (NHCs), are today the topics of very intense research [43–48]. Carbenes were originally considered as chemical curiosities before being introduced by Doering in organic chemistry in the 1950s [77], and by Fischer in organometallic chemistry in 1964 [5]. Later, it was shown that the stability of carbenes could be dramatically enhanced by the presence of heteroatom substituents. After the discovery of the first stable carbene, a (phosphino)(silyl)carbene, by Bertrand et al. in 1988 [78], a variety of stable acyclic and cyclic carbenes have been prepared. With the exception of bis(amino)cyclopropenylidenes [79], all these carbenes feature at least one amino or phosphino group directly bonded to the electron-deficient carbenic center.

Since their discovery by Arduengo et al. in 1991, cyclic diaminocarbenes (NHCs) have known a tremendous and still increasing success in both organic and organometallic chemistry [80]. In particular, they lend themselves to numerous applications as ligands in transition metal catalysts and more recently as organic catalysts [43–48]. Their efficiency is generally attributed to their unique combination of strongly σ-donating, poorly π-accepting, and locally C_2-symmetric steric properties. By comparison to the phosphine ligands, they are more strongly bound to the metal, and the resulting catalysts are less sensitive to air, moisture, and oxidation.

Analogs of NHCs such as cyclic diphosphinocarbenes [81] or alkyl-monoaminocarbenes (CAACs) [82, 83] were then designed. As compared to NHCs, their specific electronic and steric features allowed for specific applications, in particular as ligands of original catalysts [84–86]. Although many updated reviews on NHC ligands are available, salient aspects of their chemistry are presented by M. C. Jahnke and F. E. Hahn in the fourth chapter of this volume. An overview of the so-called “non-NHC carbenes” and associated ligand properties is then given by T. Kato, E. Maerten, and A. Baceiredo in the fifth chapter.

3.3 *Class C. Neutral* sp-*Carbon Ligands: Amino- and Nonamino-Cumulenylidenes*

Cumilogues of carbenes are allenylidenes ($n = 0$) and cumulenylidenes ($n \geq 1$) ligands. Recently, this class of neutral carbon ligands has attracted an increasing interest for theoretical and experimental purposes, particularly as ligands in catalysis and as building blocks in the design of new materials [14–19]. The two first examples of transition metal complexes containing allenylidene ligands were simultaneously reported by Huttner and Berke in 1976 [87, 88].

By analogy with the carbene ligands, substitution at the terminal sp^2 carbon atom (remote from the metal) exerts a considerable electronic influence and thus modifies the chemical reactivity of the complexes. Most metallacumulenes bear carbon substituents, mainly aryl groups, which protect the electron deficient carbon atoms from nucleophilic attacks by delocalization of the partial positive charge. By both contrast and analogy, metallacumulenes bearing heteroatom substituents, mainly amino- and alkoxy groups, are stabilized through an all-octet polyynyl resonance structure (Scheme 3) [14–19]. In other words, the cumulenylidene resonance form largely predominates in ligands possessing weakly donor substituents, while the zwitterionic alkynyl resonance form contributes more when the terminal substituents exhibit an enhanced π-donor character. The reactivity of allenylidene ligands is consequently characterized by nucleophilic attack at the C_α and C_γ carbon atoms and by electrophilic attack at the C_β carbon atom. In addition to their geometrical effect (change in the C–C bond lengths), the terminal donor groups induce an important electron transfer towards the metal center, thus increasing the global donor character of the carbon ligand.

Both categories of *sp*-hybridized neutral carbon ligands, namely the all-carbon-substituted and heteroatom-conjugated allenylidene and cumulenylidene ligands, are presented in great detail by V. Cadierno and S. E. García-Garrido in the sixth and seventh chapters of this volume, respectively.

4 Conclusion

This introductory part suggests that the following chapters are intended to be more than exhaustive reviews of the chemistry of the three kinds of ligands, which is indeed extensively and thoroughly covered elsewhere. The three types of ligands that have been rarely put under the same heading are gathered for the first time in a detailed manner. Their resemblances and differences can be traced within the same volume. An auxiliary guideline is also suggested for ligand design, in particular in catalysis where the efficiency of a complex is strongly correlated with the donating (vs accepting) properties of the "spectator" ligands. The neutral carbon ligand category is indeed entering a promising future.

References

1. Zeise WC (1827) Ann Phys 9:32
2. Mond L, Langer C, Quincke F (1890) J Chem Soc 749
3. Kealy TJ, Pauson PL (1951) Nature 168:1039
4. Wilkinson G, Rosenblum M, Whiting MC, Woodward RB (1952) J Am Chem Soc 74:2125
5. Fischer EO, Maasbol A (1964) Angew Chem Int Ed Engl 3:580
6. Öfele K (1968) J Organomet Chem 12:42
7. Wanzlick HW, Schönherr HJ (1968) Angew Chem Int Ed Engl 7:141
8. Schmidbaur H (1983) Angew Chem Int Ed Engl 22:907
9. Kaska WC, Ostoja Starzewski KA (1993) In: Johnson AW (eds) Ylides and imines of phosphorus, chap 14. Wiley, New York
10. Kolodiazhnyi OI (1996) Tetrahedron 52:1855
11. Vicente J, Chicote MT (1999) Coord Chem Rev 193–195:1143
12. Falvello LR, Ginés JC, Carbó JJ, Lledos A, Navarro R, Soler T, Urriolabeitia EP (2006) Inorg Chem 45:6803
13. Urriolabeitia EP (2008) Dalton Trans 42:5673
14. Cadierno V, Gimeno J (2009) Chem Rev 109:3512
15. Trost BM, McClory A (2008) Chem Asian J 3:164
16. Bruneau C, Dixneuf PH (2006) Angew Chem Int Ed Engl 45:2176
17. Bruce MI (2004) Coord Chem Rev 248:1603
18. Winter RF, Zális S (2004) Coord Chem Rev 248:1565
19. Bruce MI (1998) Chem Rev 98:2797
20. Gillespie RJ, Robinson EA (2005) Chem Soc Rev 34:396
21. Green MLH (1995) J Organomet Chem 500:127
22. Dötz KH, Tomuschat P (1999) Chem Soc Rev 28:187
23. Shaik S, Hiberty PC (2007) A chemist's guide to valence bond theory. Wiley, New York
24. Glendening ED, Weinhold F (1998) J Comp Chem 19:593
25. Glendening ED, Weinhold F (1998) J Comp Chem 19:610
26. Glendening ED, Badenhoop JK, Weinhold F (1998) J Comp Chem 19:628
27. Lepetit C, Silvi B, Chauvin R (2003) J Phys Chem A 107:464
28. Pauling L (1960) The Nature of the Chemical Bond, 3rd edn. Cornell University Press, Ithaca
29. Doerr M, Frenking G (2002) Z Anorg Allg Chem 628:843
30. Ducéré JM, Lepetit C, Silvi B, Chauvin R (2008) Organometallics 27:5263
31. Pearson RG (1968) J Chem Educ 45:581
32. Canac Y, Debono N, Vendier N, Chauvin R (2009) Inorg Chem 48:5562
33. Canac Y, Conejero S, Soleilhavoup M, Donnadieu B, Bertrand G (2006) J Am Chem Soc 128:459
34. Conejero S, Song M, Martin D, Canac Y, Soleilhavoup M, Bertrand G (2006) Chem Asian J 1/2:155
35. Lepetit C, Chauvin R, unpublished results
36. Canac Y, Lepetit C, Abdalilah M, Duhayon, C, Chauvin R (2008) J Am Chem Soc 130:8406

37. Canac Y, Duhayon C, Chauvin R (2007) Angew Chem Int Ed Engl 46:6313
38. Abdellah I, Debono N, Canac Y, Duhayon C, Chauvin R (2009) Dalton Trans 8493
39. Tonner R, Öxler F, Neumüller B, Petz W, Frenking G (2006) Angew Chem Int Ed Engl 45:8038
40. Schmidbaur H (2007) Angew Chem Int Ed Engl 46:2984
41. Frenking G, Neumüller B, Petz W, Tonner R, Öxler F (2007) Angew Chem Int Ed Engl 46:2986
42. Tonner R, Frenking G (2008) Chem Eur J 14:3260
43. Díez-González S, Marion N, Nolan SP (2009) Chem Rev 109:3612
44. Hahn FE, Jahnke MC (2008) Angew Chem Int Ed 47:3122
45. Wurtz S, Glorius F (2008) Acc Chem Res 41:1523
46. Nolan SP (2006) N-heterocyclic carbenes in synthesis. Wiley, Weinheim, Germany
47. Kirmse W (2004) Angew Chem Int Ed Engl 43:1767
48. Alder RW, Blake ME, Chaker ME, Harvey JN, Paolini F, Schütz J (2004) Angew Chem Int Ed 43:5896
49. Gicquel M, Heully JL, Lepetit C, Chauvin R (2008) Phys Chem Chem Phys 10:3578
50. Maraval V, Chauvin R (2007) New J Chem 31:1853
51. Dahlenburg L, Weiß A, Bock M, Zahl A (1997) J Organomet Chem 541:465
52. Sünkel K, Birk U (1999) Polyhedron 18:3187
53. Selegue JP (1982) Organometallics 1:217
54. Tolman CA (1970) J Am Chem Soc 92:2953
55. Dorta R, Stevens ED, Scott NM, Costabile C, Cavallo L, Hoff CD, Nolan SP (2005) J Am Chem Soc 127:2485
56. Frenking G (2001) J Organomet Chem 635:9 and references therein
57. Mitoraj M, Michalak A (2007) Organometallics 26:6576
58. Staudinger H, Meyer J (1919) Helv Chim Acta 2:635
59. Wittig G, Rieber M (1949) Liebigs Ann Chem 562:177
60. Wittig G, Geissler G (1953) Liebigs Ann Chem 580:44
61. Arnup PA, Baird MC (1969) Inorg Nucl Chem Lett 5:65
62. Grey RA, Anderson LR (1977) Inorg Chem 16:3187
63. Alexander Ostofa Starzewski K, Witte J (1985) Angew Chem Int Ed 24:599
64. Ohta T, Fujii T, Kurahashi N, Sasayama H, Furukawa I (1998) Sci Eng Rev Doshisha University 39:133
65. Viau L, Lepetit C, Commenges G, Chauvin R (2001) Organometallics 20:808
66. Canal C, Lepetit C, Soleilhavoup M, Chauvin R (2004) Afinidad 61:298
67. Ramirez F, Desai NB, Hansen B, McKelvie N (1961) J Am Chem Soc 83:3539
68. Kaska WC, Mitchell DK, Reichelderfer RF (1973) J Organomet Chem 47:391
69. Schmidbaur H, Gasser O (1975) J Am Chem Soc 97:6281
70. Schmidbaur H, Nuβstein P (1985) Organometallics 4:345
71. Fujii T, Ikeda T, Mikami T, Suzuki T, Yoshimura T (2002) Angew Chem Int Ed 41:2576
72. Pascual S, Asay M, Illa O, Kato T, Bertrand G, Saffon-Merceron N, Branchadell V, Baceiredo A (2007) Angew Chem Int Ed 46:9078
73. Zurawinski R, Lepetit C, Canac Y, Mikolajczyk M, Chauvin R (2009) Inorg Chem 48:2147
74. Vignolle J, Cattoen X, Bourissou D, (2009) Chem Rev 109:3333
75. Canac Y, Soleilhavoup M, Conejero S, Bertrand G (2004) J Organomet Chem 689:3857
76. Bourissou D, Guerret O, Gabbaï FP, Bertrand G (2000) Chem Rev 100:39
77. Doering WvE, Hoffmann AK (1954) J Am Chem Soc 76:6162
78. Igau A, Grützmacher H, Baceiredo A, Bertrand G (1988) J Am Chem Soc 110:6463
79. Lavallo V, Canac Y, Donnadieu B, Schoeller WW, Bertrand G (2006) Science 312:722
80. Arduengo AJIII, Harlow RL, Kline MJ (1991) J Am Chem Soc 113:361
81. Martin D, Baceiredo A, Gornitzka H, Schoeller WW, Bertrand G (2005) Angew Chem Int Ed 44:1700

82. Lavallo V, Canac Y, Präsang C, Donnadieu B, Bertrand G (2005) Angew Chem Int Ed 44:5705
83. Jazzar R, Dewhurst RD, Bourg JB, Donnadieu B, Canac Y, Bertrand G (2007) Angew Chem Int Ed 46:2899
84. Lavallo V, Canac Y, Dehope A, Donnadieu B, Bertrand G (2005) Angew Chem Int Ed 44:7236
85. Lavallo V, Frey GD, Donnadieu B, Soleilhavoup M, Bertrand G (2008) Angew Chem Int Ed 47:5224
86. Zeng X, Frey GD, Kinjo R, Donnadieu B, Bertrand G (2009) J Am Chem Soc 131:8690
87. Fischer EO, Kalder HJ, Frank A, Köhler FK, Huttner G (1976) Angew Chem Int Ed 15:623
88. Berke H (1976) Angew Chem Int Ed 15:624

Part I
sp^3 -Hybridized Neutral η^1-Carbon Ligands

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Ylide Ligands

Esteban P. Urriolabeitia

Abstract The use of ylides of P, N, As, or S as ligands toward transition metals is still a very active research area in organometallic chemistry. This fact is mainly due to the nucleophilic character of the ylides and to their particular bonding properties and coordination modes. They can behave as monodentate or bidentate – chelate or bridging – species, they can be used as chiral auxiliary reagents, and they are interesting reaction intermediates or useful starting materials in a wide variety of processes, etc. The most interesting bonding properties, structural features, and applications of these versatile compounds will be covered in this chapter.

Keywords Nitrogen · Phosphorus · Sulfur · Transition metal · Ylide

Contents

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Abbreviations

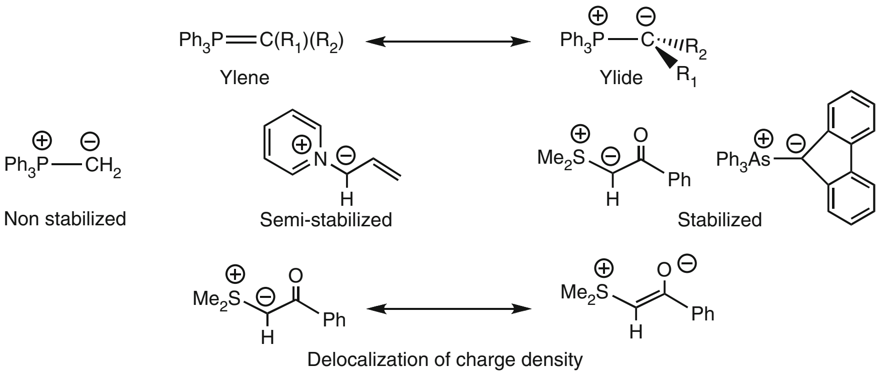
acac	Acetylacetonate
COD	1,5-Cyclooctadiene
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
dipp	Diisopropylphenyl
dmba	$C_6H_4CH_2NMe_2$–C^2,N
dmgH	Dimethylglyoxime mono anion
dppm	$Ph_2PCH_2PPh_2$, bis(diphenylphosphino)methane
dppe	$Ph_2PCH_2CH_2PPh_2$, bis(diphenylphosphino)ethane
napy	1,8-naphthyridine
NHC	*N*-Heterocyclic Carbenes
OAc	Acetate
PPN	Ph_3P=N=PPh_3
py	Pyridine
THF	Tetrahydrofuran
tht	Tetrahydrothiophene

1 Introduction

This chapter is devoted to the use of ylides as ligands. It is probably unnecessary to spend much time introducing the ylides; almost 6,000 papers indexed at the Web Of Knowledge© (2009 July), more than 81,000 citations and an "*h*" index of 82 are certainly good credentials to show the impressive importance of these compounds. The main part of this work concerns the chemistry performed on the Wittig reaction [1], but very important contributions have been developed around the use of ylides as ligands towards transition metals [2]. In this chapter we will show the most interesting aspects of the binomial ylides–ligands, applied to organometallic complexes. The different synthetic strategies to complexes with ylides in several bonding modes will be discussed, as well as their main structural features. Related aspects such as different reactivity patterns or applications (for instance, as source of other ligands or in catalytic processes) will also be covered.

2 Ylides: Basic Concepts

Ylides, by definition, are nucleophiles. Probably the most complete definition has been given by AW Johnson [2], who stated that "an ylide is a carbanion directly bonded to a heteroatom with a high degree of formal positive charge, this charge

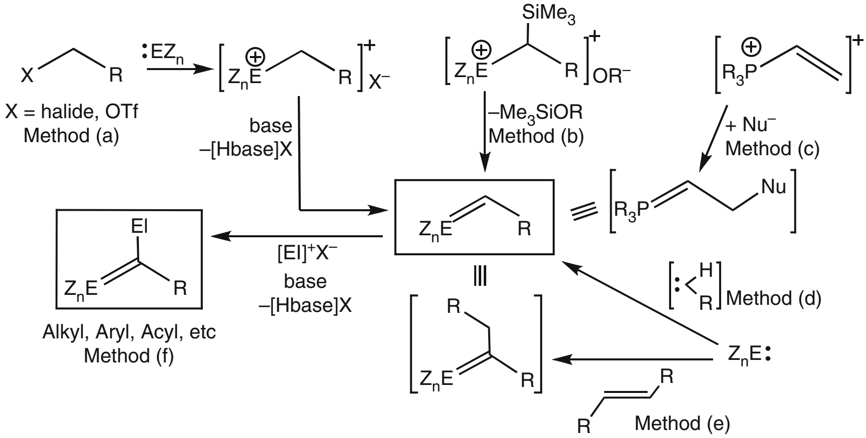


Scheme 1 General features of ylides

arising from the number of sigma bonds between the heteroatom and its substituents." Formally, ylides could be represented in two extreme canonical forms, one without formal charges (ylene) and one zwitterionic (ylide), both shown in Scheme 1. In practice, the chemical behavior of the ylides can be explained just considering the polar ylide form. The presence of a negative charge at the ylidic carbanionic center is the source of the nucleophilic behavior of the ylides and, hence, the origin of their ability to behave as ligands. The nature of the substituents R_1 and R_2 could allow the delocalization of the charge through auxiliary functional groups, and then the ylides can be classified in three main groups: nonstabilized, semistabilized, and stabilized.

This stability is referred to as the reactivity of the carbanionic center. It is clear that a keto (or a cyano) group is able to delocalize very efficiently the negative charge, this fact providing air- and moisture-stable ylides. In addition, these stabilized species are the less nucleophilic reagents. The opposite behavior is found when the two substituents are H atoms or alkyl groups: most of the ylidic charge resides at the carbon atom, and therefore these ylides are strong nucleophiles and very reactive species, and unstable towards air or moisture. Between the two extremes, as a function of R_1 and R_2, we find continuous more or less stabilized situations and, hence, more or less nucleophilic reagents, with allyl, vinyl or phenyl as substituents.

Ylides in which the heteroatom is N, P, As, S, or Se are well known. Other ylides containing Sb, Bi, O, Te, I, or Br are also known, but they are rarely used as ligands since they are very unstable, and they will not be treated here. The synthesis of the ylides is achieved through several preparative methods, most of which have been comprehensively reviewed [2–11]. The most relevant of these requires two steps, and involves the reaction of a halide with an EZ_n nucleophile (NR_3, PR_3, AsR_3, SR_2, etc.) and subsequent dehydrohalogenation of the "onium" salt (method a) as represented in Scheme 2 [2–6]. This process has been reported in a wide variety of experimental conditions, using virtually all kinds of solvents and bases (provided that they are compatible). The desilylation of some α-$SiMe_3$ onium salts (method b)

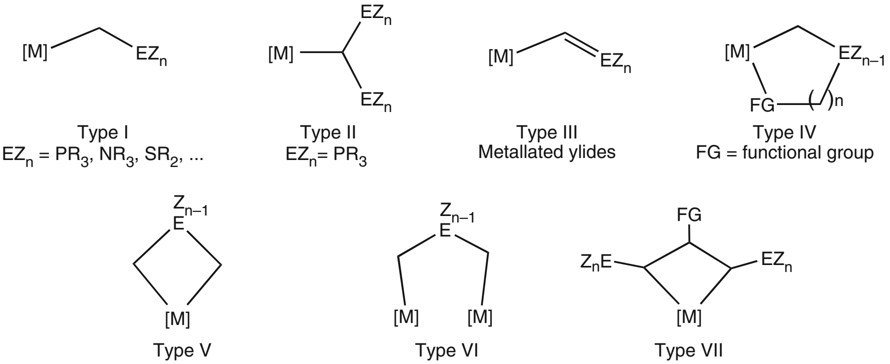


Scheme 2 Most common preparative methods for the synthesis of ylides

is a useful alternative to the deprotonation method when competitive pathways to ylide formation are operative [2, 3, 7]. The best desilylating agent seems to be the fluoride anion [7].

On the other hand, nucleophilic attack with Schweizer's reagent – a vinyl phosphonium salt, method c – is also a very efficient synthetic method to prepare P-ylides [2, 3, 5, 8]. Further reactivity of these ylides gives very interesting derivatives [2]. The homolytic cleavage of the Z_nE=C double bond should give, in principle, a singlet carbene and the nucleophile Z_nE. Therefore, it is not surprising that the reaction between a carbene and the corresponding nucleophile (R_3P, R_3N, R_2S, etc.) gives cleanly the expected ylide (method d) [2–4, 9]. The carbene is usually stabilized as a diazo derivative. This method is specially representative in the case of sulfur ylides, and allows one to consider the ylides as carbene transfer reagents. In fact, this is the case, as we will see later. Another useful method is the reaction of nucleophiles (phosphines, amines, sulfides, etc.) with unsaturated substrates. Amongst them, alkenes and alkynes are the best choices (method e) due to the availability of different substrates [2, 5, 8], which results in a large variety of possible structures. The cycloaddition reactions [10] and other more specific processes [11] have also been reviewed.

In addition, the functionalization of a preformed ylide is also a valuable synthetic procedure. The addition of an electrophile to single-substituted ylides (in other words, with an H atom at the ylidic Cα atom) gives the corresponding onium salts, which can be further deprotonated to give doubly-substituted ylides (method f) [2, 5]. Alkylation, arylation, or acylation processes at the Cα have been reported, amongst others, with the concomitant synthesis of the doubly substituted ylides. Not only the preparative methods specified, but also the bonding properties [12] of the ylides – mostly at the E=Cα bond – and some interesting organic applications [13, 14], have been the subject of detailed revision works. In summary, the chemistry



Scheme 3 Typology of the complexes described as a function of the ylide

shown in Scheme 2 constitutes a useful set of tools, able to provide tailored synthetic procedures for obtaining a given ylide, whatever its structure.

Ylides can also be behave as ligands towards transition metals due to the presence of the negative charge, which could either be centered at the Cα atom or more or less delocalized through the substituents. Ylides are not simply ligands; they are very good ligands and they have been frequently used as ancillary ligands in organometallic complexes. There are several reasons to explain this success. The deep knowledge of these systems, the variety of structural motifs and the number of different preparative methods, and results of the development of the Wittig reaction which provide a set of available ligands that can be customized, and in which the steric and electronic requirements can easily be tuned. Moreover, some ylides (mainly the stabilized ylides) have several potential donor atoms, this fact conferring on them a monodentated vs polydentate behavior. A very interesting fact is that, as a function of the substituents, the C bonding of the ylide transforms the prochiral center on the free ylide in a stereogenic center in the complex, being the source of asymmetry (the Cα atom) bonded directly to the metal (that is, where things happen, for instance, in catalytic processes).

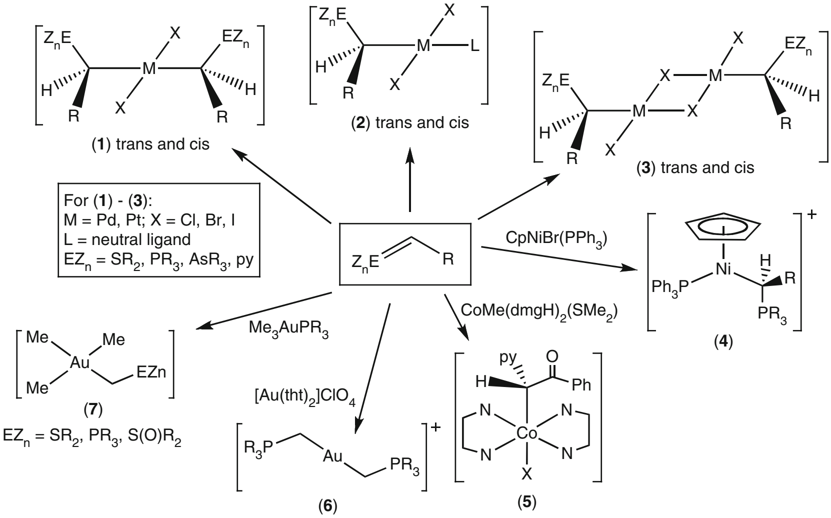
Although, in principle, the chemistry here reported should be centered on the "late" transition metals, sometimes we will jump the frontier between "late" and "middle" or "early" transition metal since this line could be more or less diffuse and could change as a function of the history. At least seven different coordination modes have been identified (I–VII, Scheme 3) as the main bonding modes. In modes I and II the ylide behaves as neutral and monodentate, bonded exclusively through the Cα atom (κC mode); this is the case for simple ylides and carbodiphosphoranes. Mode III covers the variants of a "metallated" ylide, that is, a situation in which the metal replaces a substituent of the ylide and transforms it into an anionic ligand.

Mode IV represents the well known chelating bonding mode, one donor atom being the ylidic C (κC) and the other a heteroatom (κE), while mode V presents the particular case of a chelate in which the two donor atoms are ylidic carbons of the same bisylide (κ^2-C,C). Mode VI is the bridging version of type V, and mode VII attempts to cover the chemistry of different types of bis-ylides. Both modes VI and VII are bonded through two ylidic carbon atoms.

Some particular aspects of the chemistry of ylides as ligands have been reviewed throughout the years [15–27]. The topics are quite specific in most cases, and are mainly treated comprehensively: nonstabilized ylides [15, 16], S-ylides [17], Au ylides and methanides [18], Li derivatives [19], Pd and Pt complexes [20–23], zwitterionic metallates [24], stabilized ylides [25], and applications [26, 27] have been reported upon. We will try in the following sections to give a basic complementary point of view about the chemistry of ylides as ligands.

3 Complexes with Ylides as Monodentate κ^1C Ligands

The simplest method to coordinate an ylide to a transition metal is the reaction between the free ylide and a metallic precursor with at least one coordinative vacant or a ligand easily removable. The greatest ability to coordinate to the metal is shown by the nonstabilized ylides, but even their stabilized counterparts behave as good ligands. The first examples of metal-bonded ylides were Pd(II) and Pt(II) complexes. The starting materials were simple complexes as MX_2L_2 or $Q_2[MCl_4]$ (X = halide; L = SMe_2, NCMe, NCPh; Q = Na, Li) or even the binary salts MCl_2 [28–34]. Mono and dinuclear complexes (**1**)–(**3**), with one or two ylides bonded to each metal center, and in different geometries, were prepared and characterized as shown in Scheme 4. Dinuclear Ni(II) and Co(II) derivatives similar

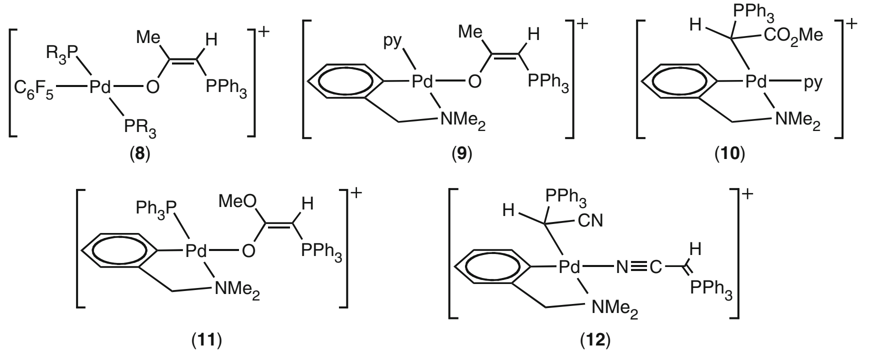


Scheme 4 Synthesis of C-bonded ylide complexes by ligand displacement

to (**3**) have also been reported [35]. The ylide displaces the bromide ligand from the coordination sphere of the Ni(II) center in [CpNiBrL], giving cationic cyclopentadienyl Ni(II) derivatives (**4**) [36]. Similarly, Co(III) complex (**5**) can be obtained from [CoMe(dmgH)$_2$(SMe$_2$)] by substitution of the sulfide group by the pyridinium ylide [37].

Complex (**5**) with X = Cl can be obtained by oxidative addition of the pyridinium salts [pyCH$_2$C(O)Ph]X to the Co(II) derivative [Co(dmgH)$_2$(OH$_2$)$_2$] [38]. We will discuss in some depth later the use of the stable onium salts as precursors of metal-bonded ylides. Further examples of ylide bonding by ligand displacement can be found in gold complexes. Au(I) and Au(III) derivatives (**6**) and (**7**) have been prepared by reaction of [Au(tht)$_2$]ClO$_4$ [39] or Me$_3$AuPR$_3$ [40] with nonstabilized ylides. In the first case the labile tht is removed, but in the second case a phosphine group, usually a strongly coordinated ligand, can be displaced.

The synthetic method outlined in the preceding paragraph has been by far the most employed preparative pathway, mainly in Pd(II) and Pt(II) complexes with stabilized ylides [41–47]. However, the C-bonding of the ylide could not be the final observed bonding mode in all cases. This fact is due to the presence of additional donor atoms, oxygen atoms in keto– or ester –stabilized ylides, or nitrogen atoms in cyano-stabilized ylides. The O-bonding of a keto-stabilized ylide to a soft metal in complex (**8**) (Scheme 5) was observed by Usón et al. in 1985 [48]. The O-bonding was also observed in hard metals (Ti, Zr, Nb) or in main group elements (Si, Sn) in high oxidation states, but this topic will not be treated here [21]. Further studies showed that stabilized ylides can behave as ambidentate ligands toward *soft* metals, bonding through the Cα atom *or* through the heteroatom (O or N) but not using the two donor atoms at the same time. The adoption of a particular bonding mode seemed to be dependent upon several parameters. The first is the nature of the ancillary ligands at the starting complex, mainly the ligand trans to the vacant site. The second is the nucleophilicity of the ylidic carbon and last, but not least, are the steric requirements [21]. The coordination of the poorly nucleophilic ylide [Ph$_3$P=CHC(O)Me] to the solvate complex [Pd(dmba)(py)(THF)]$^+$ yields complex (**9**), in which the ylide is O-bonded trans to the palladated carbon



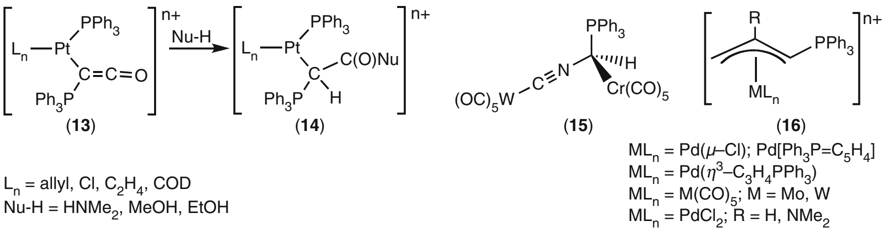
Scheme 5 Ambidentate (O vs C) behavior of stabilized ylides as ligands

[49], while the more nucleophilic ylide [$Ph_3P{=}CHCO_2Me$] coordinates through the carbon atom giving (**10**) [50] (Scheme 5). It is very remarkable that C-bonding in (**10**) occurs trans to the N atom of the NMe_2 group, with concomitant migration of the py ligand to the position trans to the palladated carbon. However, the same nucleophilic ylide [$Ph_3P{=}CHCO_2Me$] bonds through the oxygen atom when a phosphine ligand is blocking the position trans to the N atom, giving complex (**11**) [50]. A careful inspection of several examples [51–54] leads to the conclusion that the O-coordination is produced trans to a soft (C or P) atom, while C-coordination mainly occurs trans to a harder (N) atom. Complex (**12**) is the paradigm of this selectivity on bonding modes and sites [53]: the C-bonded ylide is found trans to the N atom while the N-bonded ylide is trans to the palladated C atom. In spite of this puzzling appearance (Scheme 5), the consideration of the nature of the donor atoms and the antisymbiotic behavior of the Pd center [55] provides a sensible explanation of the observed reactivity [21].

The introduction of a second stabilizing group changes dramatically the reactivity of the ylides, since the Cα atom is no longer coordinated to the metal. Examples of doubly stabilized ylides are $(Aryl)_3P{=}C[C(O)R_1][C(O)R_2]$ or $(Aryl)_3P{=}C[C(O)R_1][C({=}NR_2)R_3]$, which only bind to the metal through the heteroatoms, not just in Pd or Pt centers [56, 57] but also in other metals [58]. However, highly conjugated ketene ylide [$Ph_3P{=}C{=}C{=}O$] coordinates to Pd and Pt metallic centers through the Cα atom giving derivatives (**13**) [23, 59–63], which keep the ketene character and react with nucleophiles to give simple ylides (**14**) (Scheme 6). Another highly conjugated species, the Fehlhammer's ylide, bonds to Pt, Cr, or W using the isocyanide functional group, but can also acts as a C,C- bridging ligand, for instance in (**15**) [64].

A special case shown in Scheme 6 is constituted by ylides having the allyl functional group as substituent [65–71]. These semistabilized ylides bond η^3 to the metal, for instance in Pd, Mo, or W complexes. The Pd complexes have been prepared by reaction of the allyl-phosphonium salt with $Na_2[PdCl_4]$ in the presence of base [66, 68–70] or by direct treatment of the free ylide with $PdCl_2(COD)$ [71], while the Mo or W complexes have been synthesized by refluxing the free ylide with the corresponding hexacarbonyl derivative [65, 67]. In spite of the high reactivity of the allyl ylide, the resulting complexes (**16**) are very stable and, for instance, the bis(allyl) derivative does not eliminate the C,C coupling product.

When the starting ylide is very unstable, or when it is difficult to create vacant coordination sites, alternative synthetic methods have to be developed. One of the



(**13**) (**14**) (**15**) (**16**)

L_n = allyl, Cl, C_2H_4, COD
Nu-H = $HNMe_2$, MeOH, EtOH

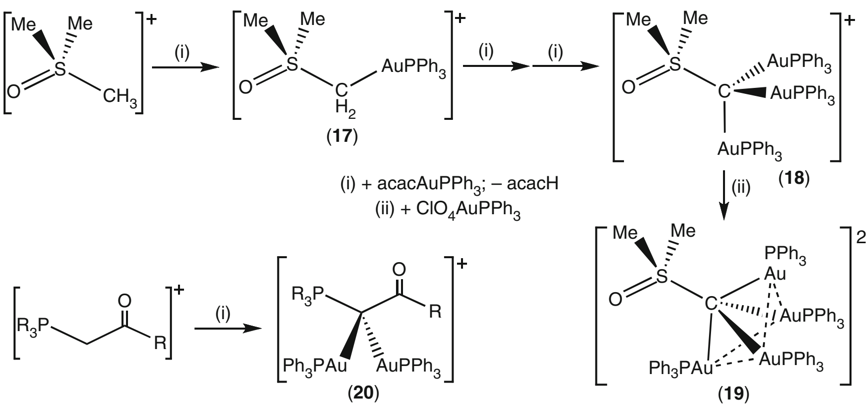
ML_n = Pd(μ-Cl); Pd[$Ph_3P{=}C_5H_4$]
ML_n = Pd(η^3-$C_3H_4PPh_3$)
ML_n = $M(CO)_5$; M = Mo, W
ML_n = $PdCl_2$; R = H, NMe_2

Scheme 6 Highly conjugated ylides and different bonding modes most popular is the so-called “acac method,” which is particularly useful in gold complexes with stabilized ylides [72]. This method implies the reaction of an “onium” salt with an acetylacetonate derivative of Au(I), for instance [acacAuL] (L = neutral ligand). The acid character of the methylene protons adjacent to the stabilizing group allows their easy extraction by the acetylacetonate, a weak base.

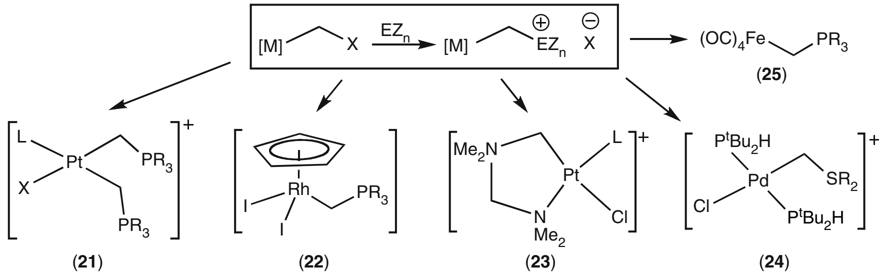
The “in situ” generated ylide binds to the metal center replacing the acac ligand, which is liberated under its protonated form. Examples are shown in Scheme 7. In some cases, even the methyl group can be sequentially deprotonated. Treatment of the sulfoxonium salt $[Me_3SO]ClO_4$ with $[acacAuPPh_3]$ gives a simple substitution product (**17**). Further reaction of (**17**) with $[acacAuPPh_3]$ allows the complete deprotonation of the methyl group and the synthesis of trinuclear (**18**), which can incorporate an additional $[AuPPh_3]^+$ cationic fragment and give an hypercoordinate ylidic Cα atom in (**19**) [73, 74]. This method also applies to phosphonium salts, allowing the synthesis of bridging carbene-like species (**20**) [75–77], although alternative methods have been reported [78].

A different approach to synthesize nonstabilized ylide complexes is the reaction of halomethyl-metallic precursors with the corresponding nucleophile EZ_n. This method is quite general and usually occurs in very mild reaction conditions. Platinum, rhodium, iron, and palladium complexes (**21**)–(**25**) (Scheme 8) have been prepared, using phosphines [79–83], amines [84], or sulfides [85] as nucleophiles. Some of the most representative examples are shown in Scheme 8.

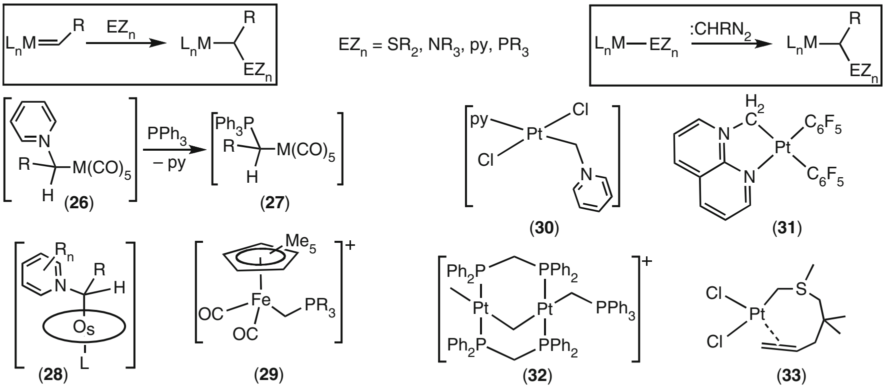
We have previously stated that an ylide could be considered the coupling product of a singlet carbene with a nucleophile. Therefore, it seems logical that the reaction of a metallic carbene with a nucleophile would give a metal bonded ylide and, in fact, this is a quite useful method to prepare metallated ylides. Even more, in some cases coordinated ylides have been used as masked carbenes [85]. Complexes (**26**) (Scheme 9, M = Cr, W), which contain a pyridinium ylide, are conveniently prepared by reaction of the corresponding carbenes $[(CO)_5M{=}C(OEt)R]$ with 1,2- or 1,4-dihydropyridines. During the reaction an unprecedented hydride



Scheme 7 Examples of ylide complexes obtained from the “acac method”



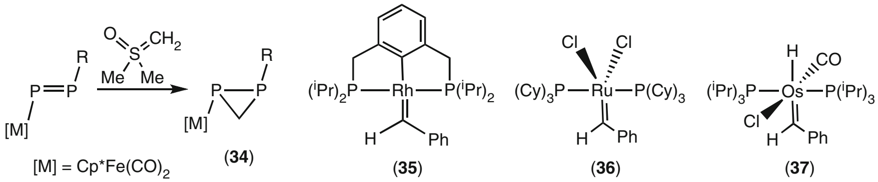
Scheme 8 Ylide complexes obtained from halomethyl derivatives



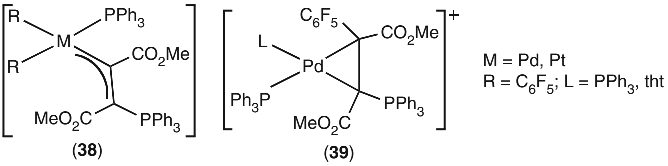
Scheme 9 Ylide complexes obtained from carbene derivatives

transfer occurred [86], with concomitant ethanol elimination. Interestingly, (**26**) reacted with PPh_3 giving (**27**) and free pyridine, in a clear example of exchange of nucleophiles and showing the reversibility of the ylide formation. In a similar way, pyridine reacts with rhenium carbenes [87] and with osmium porphyrin carbenes [88], the latter giving complexes (**28**). Stable iron ylide complexes (**29**) have been obtained by reaction of the very unstable carbene precursors $[CpFe(=CH_2)L_n]$ with PPh_3 [89, 90]. On the other hand, complexes (**30**)–(**33**) in (Scheme 9) have been prepared by insertion of a carbene fragment into a Pt-E bond, being E a nitrogen atom as in (**30**) or (**31**) [91, 92], a phosphorus atom as in (**32**) [93] or a sulfur atom as in (**33**) [94].

Closely related with the synthesis of ylides from carbenes is the use of ylides as carbene transfer reagents (CTR), that is processes in which the ylide is cleaved homolytically, liberating the nucleophile and the carbene, which could remain both coordinated to the metal or not (Scheme 10). Diphosphirane (**34**) can be obtained from the diphosphene by reaction with sulfur ylide $Me_2S(O)=CH_2$, which behave as a carrier of the CH_2 unit [95]. Recent work of Milstein et al. shows that sulfur ylides decompose in the presence of Rh derivatives with vacant coordination sites affording Rh(I)–carbene complexes [96, 97]. Complexes (**35**–**37**) can be obtained from



Scheme 10 Carbene complexes obtained from nonstabilized ylides as CTR



Scheme 11 Carbene complexes obtained from stabilized ylides as CTR

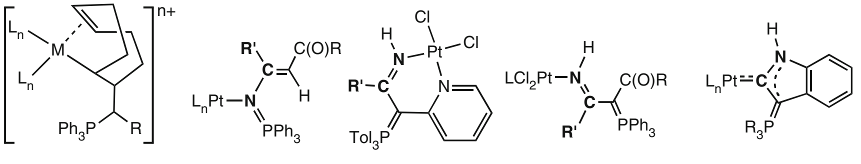
reaction of the ylide $Ph_2S{=}C(H)Ph$ with the adequate precursors [(pincer)RhN_2] [96], $RuCl_2(PCy_3)_3$ or $OsH(Cl)(CO)(P^iPr_3)_2$ respectively [97].

Examination of the ability of ylides to behave as carbene transfer reagents has been extended recently to stabilized bis-ylides in Pd(II) or Pt(II) complexes, as shown in Scheme 11 [98]. As a function of the auxiliary ligands in the starting material, the carbene (**38**) is stable (both R are C_6F_5 groups or a cyclometallated ligand) or evolves to the metallacyclopropane (**39**) (only one C_6F_5 ligand in the starting compound).

All synthetic methods described up to now (ligand displacement, acac or halomethyl precursors, metal-bonded carbene + nucleophile, metal-bonded nucleophile + carbene) result in a metal-bonded ylide through the Cα atom. The reactivity of ylides toward metallic systems is, however, greater than anticipated and other reaction pathways could compete with simple C-bonding.

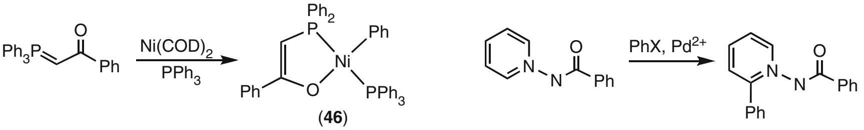
The first example is the clean reactivity of stabilized ylides towards simple palladium and platinum complexes containing alkene ligands, for instance COD. The COD ligand is easily removable from the coordination sphere of the Pd(II) or Pt (II) centers, and therefore the expected reactivity would be the displacement of the alkene by a more powerful ylidic nucleophile. However, the observed process is the addition of the ylide to the alkene giving σ-bonded alkyl derivatives (**40**) such as those presented in Scheme 12 [99, 100]. In the same way, platinum coordinated nitriles NCR′ react with stabilized ylides to give iminophosphoranes (**41**) [101], imidoyl-ylides (**42**) [102], and iminoylides (**43**) [103], while coordinated isonitriles CNR′ (where R′ is a functional group containing the ylide moiety) also react with ylides giving interesting carbenes (**44**) [104, 105].

Furthermore, there are a number of processes which are not strictly the coordination of ylides, but which are relevant enough to spend some paragraphs on describing them. This could probably give a better perspective of the potential of the ylides as versatile reagents.



(40) (41) (42) (43) (44)

Scheme 12 Alternative reactivity of stabilized ylides with coordinated ligands



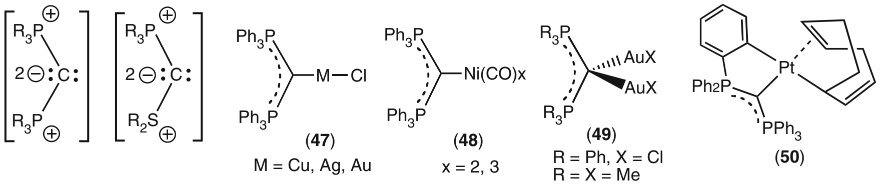
(46)

Scheme 13 Applied reactivity of stabilized ylides

An interesting reactivity is that provided by the redox behavior of the ylides. The firsts attempts to obtain stabilized ylides bonded to Pt(IV) were unsuccessful, since neutral complexes were employed and reduction to Pt(II) was observed instead [106]. The use of anionic Pt(IV) starting compounds avoided the redox process and stable (PPN)[$PtCl_4(NH_2R)$(ylide)] (**45**) complexes were prepared [107]. However, the observed redox behavior suggested the use of stabilized ylides as useful reducing agents under mild experimental conditions [108]. The coupling between Pt-coordinated nitriles and nucleophiles (oximes, for instance) is a reaction controlled by the oxidation state of the metal: the coupling is achieved at the Pt(IV) center, but not (or not so successfully) at the Pt(II) center. Then it is possible to propose a sensible synthetic pathway to obtain the coupling product starting from the more accessible Pt(II) complexes: (1) coordination of the nitrile to Pt(II); (2) oxidation with Cl_2; (3) coupling at the Pt(IV) center; (4) reduction with stabilized ylides [106]. This reaction scheme has been used very successfully.

Another impressive application of the keto-stabilized ylides is that derived from their reactivity towards Ni(0) complexes. The ylide [$Ph_3P{=}CHC(O)Ph$] reacts with $Ni(COD)_2$ in the presence of PPh_3 to give, through an oxidative addition reaction, the phosphino-enolate complexes (**46**) [109]. Compound (**46**) shows an outstanding activity in the oligo- and polymerization of olefins, and also in the copolymerization of ethylene and CO, and the reaction shown in the left part of Scheme 13 is a very easy and inexpensive synthesis of this type of complexes. Due to this exceptional activity and selectivity many variants of (**46**) have been prepared, in order to study the influence of the different reagents. Therefore, the phosphine, the substituents of the ylide, the solvent (and so on) have been changed. Far from being exhausted, the interest in this type of complexes has not ceased, as is evidenced by the number of contributions which still appear every year [26, 110–112].

Finally, it should also be noted that a renewed interest in ylides as starting materials to prepare more elaborated products in a catalytic way has emerged.



Scheme 14 Structures found for the carbodiphosphorane $Ph_3P{=}C{=}PPh_3$ (type II)

The process shown in the right half of Scheme 13 represents the selective ortho arylation of an iminopyridinium ylide, directed by the CO group, which affords adequate precursors of natural products [113, 114].

After this brief discussion of the reactivity and applications of ylides, we return to the κ^1C bonding mode, introducing new ligands: carbodiphosphoranes and cyclopentadienyl ylides.

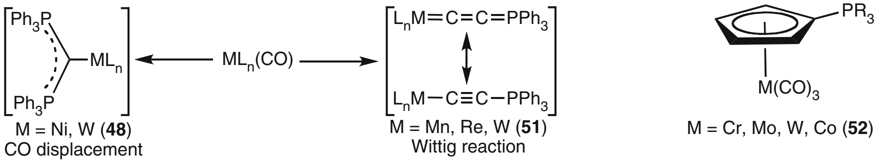
Carbodiphosphoranes [$R_3P{=}C{=}PR_3$] are a unique class of compounds for several reasons. The first noteworthy feature is that they have been described as “divalent carbon(0) compounds,” that is, having two lone pairs located over the central carbon [115]. Similarly, a detailed analysis of the mixed phosphonium–sulfonium bisylide [$R_3P{=}C{=}SR_2$] shows that the HOMO orbital corresponds to the in-plane lone pairs of the C atom [116]. The structures shown in Scheme 14 summarize this situation. These facts mean that the reactivity of these species would be strictly centered at the C center, which should behave as a strong nucleophile. In fact, the reaction of [Ph_3PCPPh_3], the best known carbodiphosphorane, with several transition metals always occurs through the central carbon atom, giving structures such as those shown in Scheme 14. Simple salts of coinage metals [CuCl or AgCl] or simple complexes [AuCl(CO)] react with [Ph_3PCPPh_3] giving derivatives (**47**) [117]. The substitution of the chloride ligand by other anionic ligands is easily achievable [118]. $Ni(CO)_4$ also reacts with [Ph_3PCPPh_3] giving two different complexes (**48**) – dicarbonyl and/or tricarbonyl – as a function of the reaction solvent [119]. The dicarbonyl derivative seems to be the first nickel complex with the $Ni(CO)_2$ fragment linked to only one additional ligand, the diphosphorane in this case, resulting in an unsaturated $16e^-$ species. The presence of a high excess of electron density at the ylidic Cα atom allows the incorporation of a second metal center in some cases, for instance in the gold derivatives (**49**). Complexes (**49**) have been prepared by reaction of [Ph_3PCPPh_3] with 2 equivalents of ClAu(tht) [120] or $MeAuPMe_3$ [121], respectively. The reactivity of [Ph_3PCPPh_3] with Pt(II) compounds is more complicated since, in addition to the simple κ^1C-bonding, additional CH bond activation occurs. The reaction of 3 equivalents of [Ph_3PCPPh_3] with $I_2Pt(COD)$ gives complex (**50**) through orthoplatination of one phenyl ring and further activation of the COD, which is transformed into a cyclooctadienyl ligand [122]. The own ylide acts as proton abstractor, forming [$Ph_3PC(H)PPh_3$]I. In spite of the clear reactivity of Pt (II) complexes, the reaction of Pt(IV) species is more complicated [123] and gives mixtures of different types of orthometallated Pt(II) materials.

The reaction of metallic carbonyl derivatives towards carbodiphosphoranes is not always as simple as represented by the synthesis of complex (**48**). A further degree of complexity is introduced by the Wittig processes observed between Mn or Re carbonyls and [Ph_3PCPPh_3]. The reaction occurs with elimination of $OPPh_3$ (typical residue of the Wittig reaction) and formation of a new phosphonium–alkynide ligand in complexes (**51**). This new ligand can be represented by two resonance forms, shown in Scheme 15, but the chemical behavior of (**51**) is better explained taking into account the alkynyl form [124]. The different behavior (Wittig vs substitution) seems to be strongly dependent of the reaction conditions, in addition to the nature of the metal center, since the same metal can show the two behaviors. Thus [$W(CO)_5(THF)$] reacts with [Ph_3PCPPh_3] to give the substitution complex (**48**), but photolysis of [$W(CO)_6$] and [Ph_3PCPPh_3] gives the Wittig product (**51**) (Scheme 15) [125].

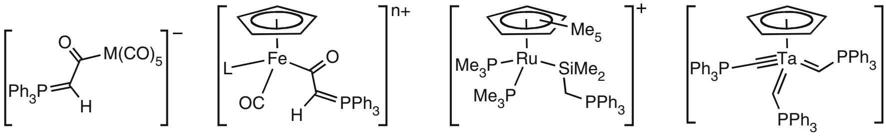
The cyclopentadienyl-ylide [$Ph_3P{=}C_5H_4$], most commonly called Ramirez Ylide [126], and its derivatives [$R_3P{=}C_5H_4$] are very stable species due to extensive delocalization of charge density through the C_5H_4 ring. Due to this fact they are almost chemically inert, and only recently a renewed interest allowed the synthesis and reactivity of a family of complexes (**52**), shown in Scheme 15 [127]. This is probably a very interesting field which merits developing.

The attack of nucleophiles on unsaturated ligands or functional groups bonded to metallic centers, exemplified in Scheme 9 (reaction of metallic carbenes with phosphines or pyridines) or in Scheme 15 (Wittig reaction) can be extended to a wide variety of reagents. Two main groups of reactions can be considered: (1) those in which the nucleophile is an ylide and (2) those in which the nucleophile is a phosphine (and less commonly other nucleophiles). Usually these reactions give metallated ylides (type III), that is, species in which the ylide substituents are metallic centers.

Examples of the first group of reactions are presented in Scheme 16. The ylide $Ph_3P{=}CH_2$ reacts with the metal hexacarbonyls $M(CO)_6$ (M = Cr, W) to give the metallated species (**53**) in two steps. The reaction begins with the addition of the nucleophilic ylidic Cα atom to the carbon atom of the CO ligand and subsequent CC coupling. The neutral intermediate [$(CO)_5MC(O)CH_2PPh_3$] reacts with a second equivalent of $Ph_3P{=}CH_2$, which deprotonates the $C(O)CH_2$ group and gives the metallated ylide (**53**) together with the corresponding phosphonium salt [124]. This reactivity represents an alternative pathway to the displacement of CO and to the Wittig reaction. The iron complex (**54**) is obtained strictly following the same procedure, from cationic [$CpFe(CO)_2L$]$^+$ and 2 equivalents of Ph_3PCH_2 [128].



Scheme 15 Reactivity of $Ph_3P{=}C{=}PPh_3$ and usual bonding modes of the Ramirez ylide



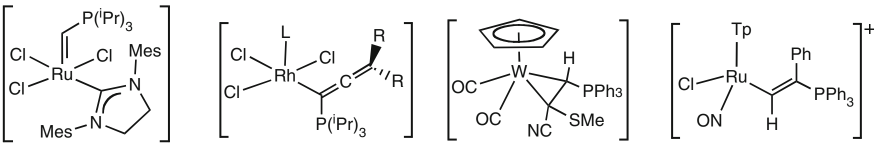
M = Cr, W (**53**) ylide + CO

(**54**) ylide + CO

(**55**) ylide + M=$SiMe_2$

(**56**) multiple deprotonation

Scheme 16 Reactivity of $Ph_3P{=}CH_2$ towards different unsaturated substrates

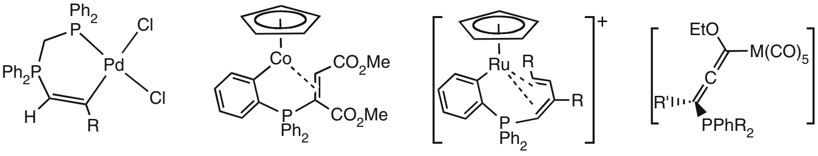


(**57**) phosphine + carbyne

(**58**) phosphine + allenylidene

(**59**) phosphine + σ-alkenyl

(**60**) phosphine + σ-alkynyl



(**61**) phosphine + π-alkyne

(**62**) phosphine + π-alkyne

(**63**) phosphine + 2 π-alkyne

(**64**)

Scheme 17 Reactivity of nucleophiles (ylides, PR_3) towards unsaturated substrates

In some cases the addition occurs without additional deprotonation, as is the case of the attack of Ph_3PCH_2 to silylene derivatives to give (**55**) [129], but the usual trend is that, once the first ylide coordinates to the metal center, the excess of basic ylide promotes further deprotonations giving different species. Li and Sundermeyer have developed a very rich chemistry in Ta, Nb, W, and Re derivatives [130, 131], and one example is shown in Scheme 16. The reaction of Ph_3PCH_2 with $CpTaCl_4$ starts with the coordination of the ylide and formation of $[CpTa(CH_2PPh_3)Cl_4]$, which in turn reacts with 6 equivalents of Ph_3PCH_2 to give several intermediates as $[CpTa(\equiv C–PPh_3)Cl_2]$ and $[CpTa(\equiv C–PPh_3)(=C(H)PPh_3)Cl]$, and finally the methylidyne complex (**56**).

Phosphines, as nucleophiles, add to many unsaturated substrates giving metallated ylides. Scheme 17 collects some representative examples of the addition of phosphines to carbyne complexes, giving (**57**) [132], to allenylidenes (**58**) [133], σ-alkenyls (**59**) [134], or σ-alkynyls (**60**) [135]. Moreover, reaction of phosphines with π-alkenes [136] and π-alkynes (**61**)–(**64**) [137–140] have also been reported. It is not possible to explain in depth each reaction, but the variety of resulting products provides an adequate perspective about the synthetic possibilities of this type of reactions.

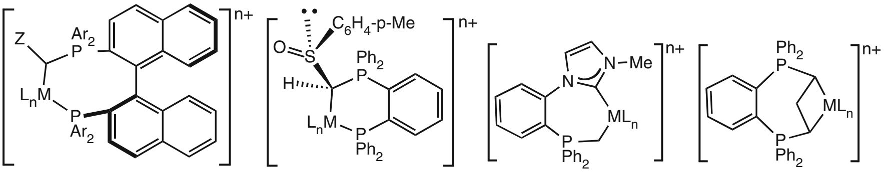
This first section has presented the most relevant preparative methods in order to obtain coordinated ylides. There are numerous possibilities, and the resulting compounds are fascinating and open new doors to future research. Now we will deal with complexes showing particular bonding modes – prepared following one of the reported methods or a slightly different variant – and which exhibit a particular feature.

4 Complexes with Ylides as Bidentate κ^1C–κ^1E Ligands

The κ^1C bonding mode includes most of the reported work on ylides. However, modifications of the structure of the ylide could be advantageous, in particular the introduction of additional donor atoms to form chelate ligands. The combination of the pure σ-donor properties of the ylide with those of the auxiliary donor atom could be used for tuning the steric and electronic properties of ylide complexes. There are reports of useful C,P- and C,C-chelates, which will be detailed here.

A very good example of this methodology is the recent application of the chiral properties of the ylides to enantioselective homogeneous catalysis. Chiral Rh complexes (**65**), prepared by ligand displacement (Scheme 18), has all chirality sources at the phosphine fragment, [141], while the Pd counterparts contain an additional stereogenic center at the ylidic carbon [142]. These Pd complexes are adequate catalysts for enantioselective allylic substitution reactions, achieving *ee* up to 90%. An improved chiral environment has been obtained in the more rigid six-membered ring of (**66**), which contains two adjacent stereogenic centers. In this case, the two diastereoisomers can be isolated separately, and both are configurationally stable [143, 144]. In spite of this, low *ee* were observed on hydrosilylation or hydrogenations catalyzed by Rh(I) complexes. Further studies show that the Rh–C bond is cleaved in acidic medium, while epimerization occurs in basic medium, these facts being responsible for the low *ee* values.

A different approach to the modulation of steric and electronic properties has been reported using NHC moieties as ancillary ligands. A very rich chemistry has been developed around this topic in the last few years [145–148]. Complexes (**67**) have been prepared by deprotonation of the corresponding phosphonium–imidazolonium salt. The analysis of several Rh^{I} derivatives (**67**) shows that the ylide behave as a very strong σ-donor, even more than the NHC ligand, and that Pd^{II} complexes



(**65**)
ML_n = Rh(COD), Z = H
ML_n = Pd(dba), Z = CN, CO_2Et

(**66**)
ML_n = Rh(COD), Pd(μ-Cl)

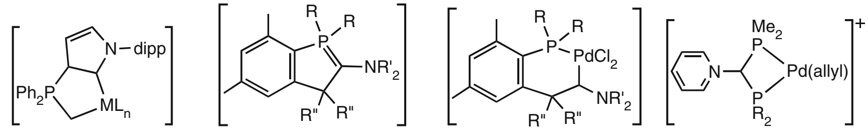
(**67**)
ML_n = $Rh(CO)_2$, Pd(η^3-allyl)

(**68**)
ML_n = $Rh(CO)_2$

Scheme 18 Chiral chelating P,C-ylide and C-ylide,C-carbene complexes are efficient catalysts in allylic substitution reactions [145, 146]. It is very worthy of note that the synthesis of the related bis-ylide complex (**68**) (Scheme 18) was not straightforward at all, and that many interesting species were isolated and characterized during its synthesis, finally achieved using cyclic bis-ylides.

Recent research on aminocarbenes has led to the development of a very fruitful field. The synthesis of relevant complexes (Scheme 19) such as aminobis(ylide) carbene species (**69**) [147], cyclic C-amino P-ylides (**70**) (easily transformed into carbenes) [148] and their corresponding complexes (**71**) [149], and special ylides (**72**), which also transform very easily into carbenes by loss of pyridinium group, has been reported. Emphasis has been made on the transformation between ylides and carbenes and on the donor properties of the ylides. From the results obtained the ylides have shown a stronger σ-donor behavior compared with the carbenes.

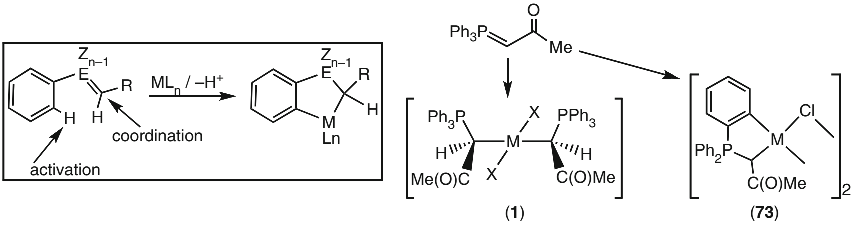
Ylides containing aryl substituents are specially prone to undergo activation of CH bonds when they reacts with electrophilic metal reagents. The outstanding importance of the metal-mediated CH bond activation as a tool for functionalization of organic substrates is of special interest [150]. When several CH bonds can be activated on the same molecule and in equivalent positions, then a problem of selectivity occurs. This is usually overcome by the introduction of a directing group, which also coordinates to the metal center. In the case of aromatic systems the metallation is thus directed to the ortho position with respect to the directing group, giving rise to orthometallated complexes. In the case of ylides, several studies have been devoted to the preparation of this type of compounds, as presented in Schemes 20–23. It seems more or less clear that the reaction consists of two different steps, the first being the coordination of the ylide (the directing group) and the second the CH bond activation itself. The first example of these reactions was reported by Burmeister et al. [151], correcting previous work [31]. The reaction



(**69**) (**70**) (**71**) (**72**)

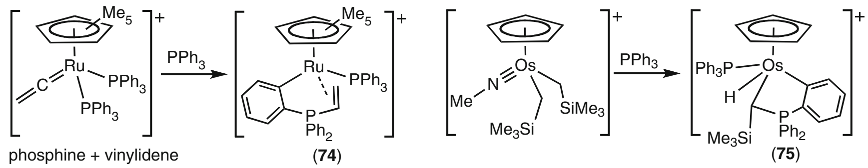
$ML_n = Rh(CO)_2, Pd(\eta^3\text{-allyl})$

Scheme 19 Different aminocarbene/ylide complexes

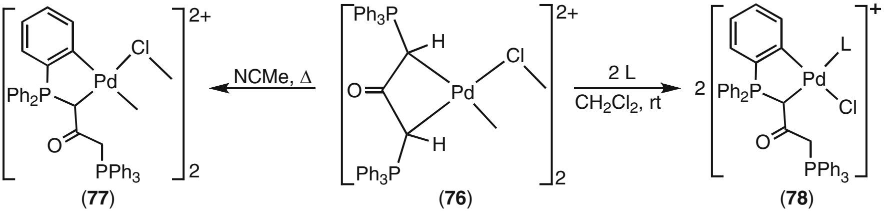


(**1**) (**73**)

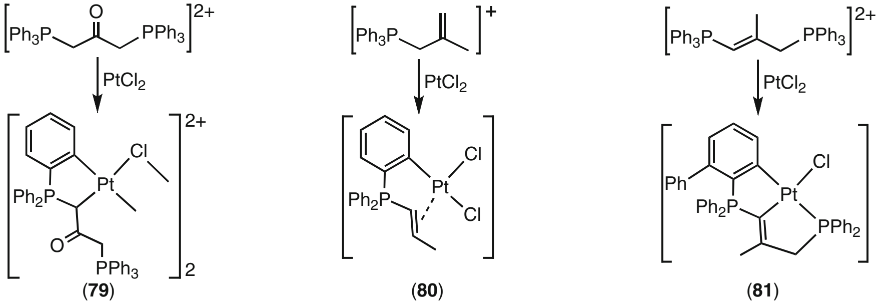
Scheme 20 Orthometallation of ylides; principles and first examples



Scheme 21 Orthometallation of ylides; ruthenium and osmium examples



Scheme 22 Different ways to promote orthometallation on Pd(bis-ylide) complexes



Scheme 23 Different orthoplatination reactions from ylide and phosphonium salts

of $PtCl_2$ with $Ph_3P{=}CHC(O)Me$ was expected to give the coordination product (**1**) [31], but the actual reaction product is the orthoplatinated (**73**) [151]. Further work of Vicente et al. on Pd complexes led to the preparation of either (**1**) or (**73**) as a function of the reaction conditions [152].

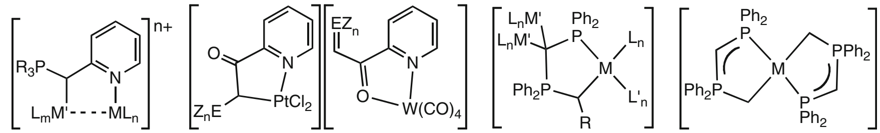
Most of the chemistry performed on orthometallated ylides has been carried out with Pd and Pt as metal centers. Few examples dealing with other metals (Co, Ru, and Os mainly, see **62** and **63**) have been reported. Complex (**74**) has been prepared by reaction of a Ru-vinylidene with PPh_3 [153] while Os^{IV} derivative (**75**) has been obtained after treatment of the methylimido complex with PPh_3 [154]. Orthoruthenated indenyl complexes [155] have been synthesized by reaction of the halomethyl precursors with PPh_3, and the oxidative addition of the ylide $Ph_3P{=}CHC(O)H$ to clusters of Ru^0 and/or Os^0 also allows the synthesis of orthometallated complexes

[156, 157]. In spite of the synthesis of very interesting compounds, the latter are not general preparative methods.

As stated in the preceding paragraph, the main part of the orthometallated derivatives are Pd^{II} and Pt^{II} complexes. Compounds structurally similar to (**73**) have been prepared by different authors [158–160]. In the reported examples, the CH bond activation step has been promoted by thermal activation. This is also the case for the rearrangement of bis-ylide complexes (**76**), which evolve to orthopalladated (**77**) after heating in NCMe for 8 h (Scheme 22). The chemistry of bis-ylides is richer than anticipated, as we will see in Sect. 3, and allows additional ways to promote CH bond activation, such as the addition of bulky ligands (regardless of the nature of the donor atom), and even a spontaneous reaction can occur [161]. The cleavage of the chloride bridging system in (**76**) allows one to obtain (**78**) in very mild conditions only when L is a bulky ligand (PPh_3).

The thermal promotion of the CH bond activation is largely the best preparative method if Pt^{II} derivatives are the target. Several complexes have been reported starting not only from ylides, but also from phosphonium salts, in very harsh conditions (refluxing 2-methoxyethanol). Scheme 23 resumes some recent contributions. While the synthesis of complexes (**79**) is conceptually very similar to that of (**77**) (an electrophilic substitution in aromatic ring followed by an intramolecular acid–base reaction) [162], the change of the carbonyl group by the olefin group promotes a 1,3-sigmatropic shift after metallation in (**80**), and the subsequent transformation of an allyl-phosphonium salt into a platinated vinyl phosphonium salt. The synthesis of (**81**) [163] represents quite a complicated process since it involves three CH and one CP bond activations, and one CC bond coupling. The structural diversity throughout all these situations is evident.

Additional types of κ^1C–κ^1E chelating ylide complexes merit mentioning here, in addition to the species already presented, and some of them are shown in Scheme 24. The first is formed by ylides containing a pyridine functionality as substituent of the ylidic carbon. This type of ligand has allowed the synthesis of many "loose clusters" (**82**) of Cu^I, Ag^I, and Au^I which show weak metal(d^{10})–metal(d^{10}) interactions. These facts have prompted the definition of a new phenomenon (*numismophilicity*) to account for these weak interactions, uniquely shared by the three coinage metals [164]. Nitrogen and sulfur keto-stabilized ylides have been reacted with Pt^{II} and W^0



(**82**) (**83**) (**84**) (**85**) (**86**)

ML_n, ML'_m = $AuPPh_3$, AuCl, Ag

EZ_n = SMe_2, NC_5H_5 PPh_3

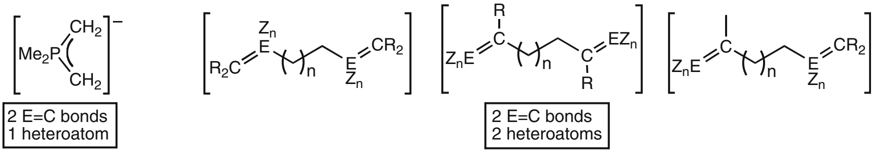
M = Pd, Pt; L_n = Cl, py, C_6F_5
M = Au, L_n = C_6F_5; $M'L_n$ = AuC_6F_5, AuCl, $AgPPh_3$

Scheme 24 Some possibilities of bidentate ylides and observed bonding modes derivatives and, while C-bonding is produced in the platinum case (**83**), O-bonding is observed for the tungsten derivatives (**84**) [165–168].

Complexes (**85**) with ylides derived from bis-phosphines, dppm, or dppe, have been more extensively developed than previous examples. First contributions start to appear in the mid-1970s using stabilized derivatives [169] and several authors have contributed throughout the years to this field [170, 171]. The methylenic protons between the two phosphorus atoms of these chelating ligands, even coordinated, are acidic and, therefore, can easily be removed and replaced by other electrophilic substrates. Using this concept, Laguna et al. have prepared a large series of mono-, di-, and trinuclear complexes of general structure (**85**), mixing a central square–planar Au^{III} center and peripheric Au^{I} or Ag^{I} metal centers [172–174]. In contrast with the numerous examples reported with stabilized ylides, very few representatives of nonstabilized ylides (**86**), shown in Scheme 24, appear in the literature [175–177]. Clearly, the combination of the strong σ-donating ability of the ylidic Cα atom with the properties (steric and/or electronic) of the ancillary heteroatoms in chelating ylides offers a huge variety of structural motifs. These can be fine tuned in order to obtain the desired results. Applications of these ylide complexes to catalytic processes or functionalization of molecules are of broad interest and show promising results. However, these systems are not yet completely explored and merit further development.

5 Complexes with Ylides as Bidentate κ²C,C Ligands

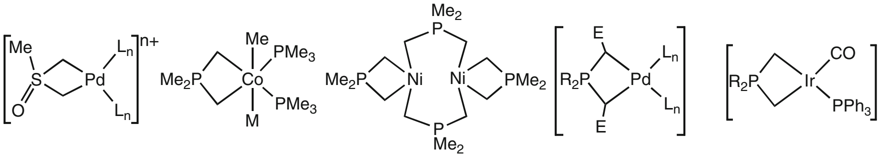
The last group of ylide complexes in this personal classification is devoted to bis-ylides, due to their particular bonding properties. Some main types of bis-ylides can easily be identified, and they are anionic or neutral species behaving as chelating or bridging ligands. These bonding modes correspond to classes V, VI, and VII in Scheme 3. On the other hand, some of the different strategies to build a bis-ylide are presented in Scheme 25. When the bis-ylide contains only one heteroatom bonded to the two ylidic carbons, an anionic species is obtained (Scheme 25, left), while neutral compounds are the consequence of the presence of one heteroatom for each ylidic Cα atom. In this second possibility (Scheme 25, right), three substructures can be envisaged: both terminal ylidic carbons, both terminal heteroatoms ("onium groups") and a mixed arrangement. The synthesis of both-terminal bis-ylides (for



Scheme 25 Different strategies to build bis-ylide skeletons

instance, from diphosphines) is quite difficult, as we have seen in the synthesis of (**67**) and (**68**), due to intramolecular rearrangements. This problem is circumvented using cyclic bis-ylides. The bis-terminal "onium group" is the most frequent arrangement, since it starts from readily available dihalide precursors. The mixed situation is barely represented.

The use of anionic bis-ylides acting as chelating ligands is also little developed. Different synthetic approximations can be found for synthesis of complexes type V, and the resulting complexes are shown in Scheme 26. Lin et al. have reported an extensive work on complexes (**87**) containing sulfur bis-ylides. The synthesis is carried out in aqueous media using phase transfer catalysis, starting from the sulfonium salt [Me_3SO]X and the metal salt in the presence of NaOH. This method tolerates the presence of a wide variety of functional groups and/or ancillary ligands L_n [178–182]. It is very worthy of note that both the ylide ligands and the resulting complexes are water soluble. Therefore they can be considered very promising candidates as palladium sources in Pd-catalyzed processes occurring in water. Phosphorus bis-ylides bonded to Co^{III} (**88**) and Ni^{II} (**89**) have been prepared [183] by reaction of the free ylide with the corresponding precursors [for instance, $Ni(CO)_4$ in the case of (**89**)]. However, Pd^{II} complexes (**90**) were obtained by different methods as a function of the substituents. In the case of the unsubstituted compound (E = H) the bis(methanide) [$Pd(Ph_2PCHPPh_2)_2$] reacts with the free ylide $Me_3P{=}CH_2$ [184], the deprotonated dppm acting as internal base and giving the mixed ylide–methanide (**90**), while the substituted complex (E = CO_2Me) is prepared by transmetallation from the corresponding Ag^I compound [185]. Only in the case of the synthesis of (**91**) is the nucleophilic lithium derivative Li[$R_2P(CH_2)_2$] needed [186].



(**87**)
$L_n = CH_2S(O)Me_2$, I, PPh_3, $(CH_2)_2S(O)Me$

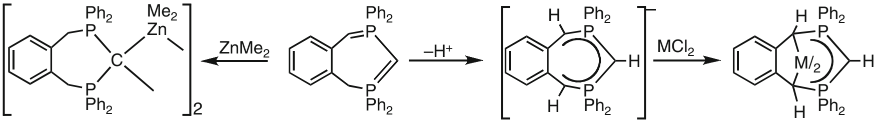
(**88**)

(**89**)

(**90**)
R = Me, E = H, $L_n = Ph_2PCHPPh_2$
R = Ph, E = CO_2Me
$L_n = (CHR)_2PR_2$, Cl, PPh_3, acac, py

(**91**)

Scheme 26 CC-chelating anionic bis-ylides in different transition metals



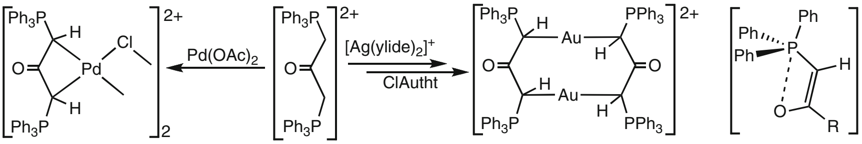
(**92**)

(**93**)
M = Mn, Fe, Co

Scheme 27 Cyclic bis-ylides in different transition metals

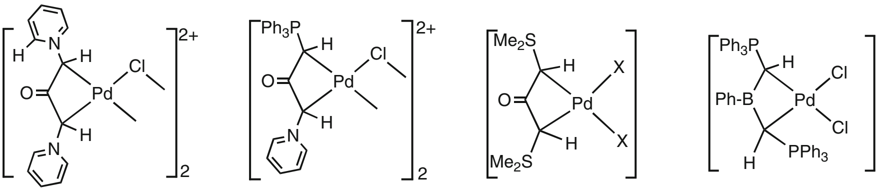
Examples of cyclic bis-ylide complexes are shown in Scheme 27. The neutral double ylide is easily prepared from dppm and 1,2-$(BrCH_2)_2C_6H_4$ and subsequent deprotonation with KH [187]. It is noteworthy that the second deprotonation is produced at the methylene group between the two P atoms. This unsymmetrical species reacts with $ZnMe_2$ giving (**92**), in which the central carbon atom is bonded to the Zn metal center. In addition, this unsymmetrical species can be further deprotonated at the remaining methylene group to give a symmetrical triple-ylide anion which coordinates to Co^{II}, Fe^{II}, or Mn^{II} complexes giving (**93**) [188] as shown in Scheme 27. Note the different bonding mode of the neutral (**92**) and the anionic (**93**) species. Stabilized cyclic bis-ylides have been reported for Pd^{II} [189, 190]. Complexes containing the anionic ligand $[H_2C{=}PPh_2CHPPh_2{=}CH_2]^-$ bonded to Ni^{II}, Pd^{II}, Pt^{II}, or Au^{III} through the two terminal ylidic carbons (see Scheme 25) have been prepared [191], but starting from the carbodiphosphorane $Me_3P{=}C{=}PMe_3$ and the corresponding metallic halide.

Neutral bis-ylides with both terminal "onium groups" have been prepared with different heteroatoms and stabilizing groups, and have been coordinated to different metals (Schemes 28 and 29). Bridging (**94**) [192] and chelating (**76**) [193–200] bonding modes have been reported. The most widely employed system is $[Ph_3P{=}CHC(O)CH{=}PPh_3]$, a keto-stabilized phosphorus bis-ylide. In contrast to the stabilized ylides $R_3P{=}CHC(O)R'$ (usually air – and moisture – stable for months), this bis-ylide is quite unstable, and different synthetic alternatives to the simple ligand displacement have been developed. Complex (**76**) is obtained by reaction of the phosphonium salt with $[Pd(OAc)_2]$, while gold complex (**94**) is synthesized by transmetallation from the corresponding Ag^I complex, prepared in turn from the bis-phosphonium through a transylidation process [192].



(**76**) (**94**)

Scheme 28 Different bonding modes of $[Ph_3PCHC(O)CHPPh_3]$



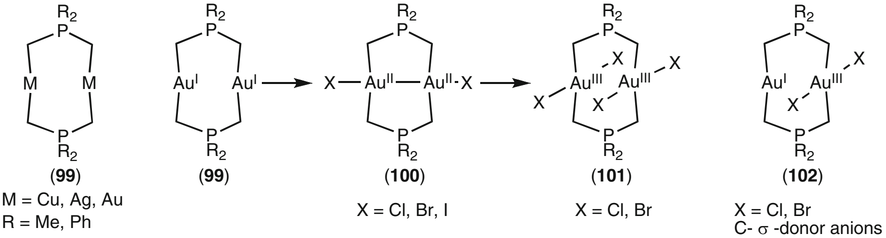
(**95**) (**96**) (**97**) (**98**)

Scheme 29 Conformational preferences on Pd complexes

The coordination of this ligand, either to Au [192] or to Pd or Pt metals [162, 193], in chelating or bridging modes, reveals an extremely important fact. In spite of the presence of two prochiral centers in the starting free ligand, the bonding of the bis-ylide occurs with complete diastereoselectivity and only one of the two possible diastereoisomers – the meso form, with configurations *RS*/*SR* – is obtained. This empirical observation was related to structural features: the cationic phosphonium groups are always in cisoid form with respect to the carbonyl C=O bond, the phosphorus–oxygen intramolecular nonbonding distance is always shorter than the sum of the van der Waals radii, and the dihedral angle P–Cα–C=O is always close to zero. All this experimental evidence, already noted by other authors [194], points to the existence of conformational preferences in stabilized P ylides. These conformational preferences were studied by DFT methods [195] in model compounds, which showed that the cisoid form is energetically more stable than the transoid form (about 10 kcal mol^{-1}), that the interconversion cisoid–transoid needs more than 20 kcal mol^{-1} to be reached, and that the presence of one oxygen (C=O group) or one strongly electronegative atom is critical for the establishment of these preferences. The topological study (AIM) of the electron density [195] showed the existence of bond critical points between the positively charged P atom and the negatively charged O atom, and also the presence of ring critical points involving the P–Cα–C=O ring. Therefore, there is a true interaction between P and O atoms (Scheme 28, right), this interaction is of electrostatic nature and is the final responsible of the conformational preferences. These preferences are transferred to the metallic complexes, since it has been shown that the energy difference between the two metallic diastereoisomers comes mainly from the difference between geometric isomers (cisoid–transoid) in the free ligands [196].

Interestingly, the existence of conformational preferences on bis-ylides is not limited to phosphorus ylides, and recent work has extended this study to nitrogen, arsenic, and sulfur ylides [197–200]. Complexes derived from pyridinium (**95**) [197] or imidazolium [198] show strictly the same conformational preferences, since only the meso form is obtained (Scheme 29). However, the phenomenon which originates the conformational preferences in these cases are not the predictable nitrogen–oxygen electrostatic interactions, but the presence of hydrogen bonds between the ortho pyridinium (or the imidazolium) protons and the carbonyl oxygen. The hydrogen bonds have also been studied in model systems and characterized using AIM tools [197]. Moreover, the presence of two different "onium groups" in the same molecule has been studied in complexes (**96**), showing that the two sources of conformational preferences are not mutually exclusive and, once again, producing this type of complex with total diastereoselectivity [199]. A recent report describes a similar situation in sulfur ylides (**97**) without characterization of the source of preferences [200]. Complex (**98**) does not have a carbonyl group and, according to previous DFT studies, must not show conformational preferences. In fact, complex (**98**) has been obtained as the dl-pair, but in a similar Zr^{IV} complex the ylide bonds as the meso form show that the two forms are isoenergetic [201].

The anionic bis-ylide compounds $[\text{R}_2\text{P}(\text{CH}_2)_2]^-$ bonded as bridging ligands (mode VI) have been extensively studied in complexes of coinage metals, mainly

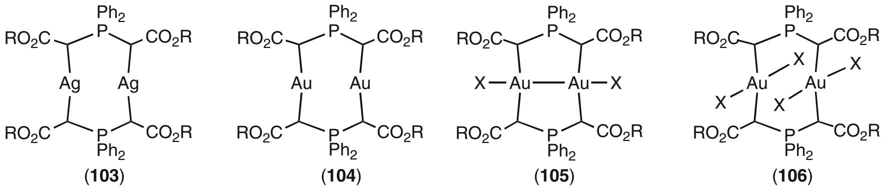


Scheme 30 Dinuclear complexes of coinage metals with the bis-ylide $[R_2P(CH_2)_2]$

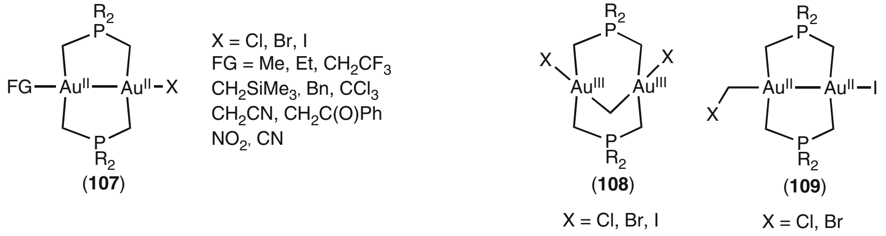
in gold derivatives. Several reasons can be given for this interest, but the most evident is the close proximity of the gold centers in these derivatives, a structural arrangement of exceptional stability provided by the bis-ylide ligands. Moreover, this close proximity favors redox processes in which metal–metal bonds can be formed and cleaved, these facts resulting in rich and fruitful reactivity.

The bis-ylide ligands $[R_2P(CH_2)_2]^-$ can easily be prepared by treatment of the phosphonium salts $[R_2PMe_2]^+$ (R = Me, Ph) with strong deprotonating reagents such as lithium derivatives, $NaNH_2$, or non stabilized ylides $R_3P{=}CH_2$. However, Au^I, Ag^I, and Cu^I complexes (**99**) were prepared by reaction of $ClMPMe_3$ (M = Ag, Au) or CuCl with excess of $R_3P{=}CH_2$ [202, 203] (Scheme 30).

Dimers (**99**), containing the $[Au^IAu^I]$ moiety, undergo two stepwise oxidative additions of halogens X_2 to give the corresponding $[Au^{II}–Au^{II}]$ (**100**) and $[Au^{III}Au^{III}]$ (**101**) derivatives. The gold–gold intramolecular separation decreases notably from (**99**) [about 3.0 Å] to (**100**) [about 2.6 Å], in keeping with the presence of a metal–metal bond in the latter, and further increases in (**101**) [about 3.1 Å] according to the cleavage of the gold–gold bond [204]. Complexes (**101**) are shown in Scheme 30 as *trans–trans*, but they could also be obtained in other isomeric forms [204]. Although no formal gold–gold bonds are present in (**99**) or (**101**), short metal–metal separations are found (*numismophilicity*) and, in the case of (**101**), very unusual structures have been obtained [205]. The oxidative additions to (**99**) always occur in the same way, giving complexes (**100**), which are very stable. Complexes (**100**) can also be obtained by comproportionation of (**99**) and (**101**). However, the $2e^-$ oxidation of a single center in dimer (**99**) to give the mixed derivative $[Au^IAu^{III}]$ (**102**) is not possible at all but, curiously, the $2e^-$ reduction of (**101**) (for instance, with AgCN) affords (**102**) cleanly [206]. Complexes (**102**) can also be obtained by disproportionation of (**100**), induced by strong σ-donors such as lithium derivatives [207–209] or $R_3P{=}CH_2$ [210]. The high trans influence of these ligands seems to destabilize the $Au^{II}–Au^{II}$ bond and promotes the disproportionation. In fact, recent work [209] has shown how complexes (**100**) and (**102**) containing acetylide ligands can be related by processes of comproportionation and disproportionation. DFT studies of model complexes containing $[Au^IAu^I]$, $[Au^{II}–Au^{II}]$, $[Au^{III}Au^{III}]$, and $[Au^IAu^{III}]$ metallic cores have been published very recently [211].



Scheme 31 Dinuclear complexes with the stabilized bis-ylide $[R_2P(CHCO_2R)_2]$



Scheme 32 Asymmetric dinuclear complexes with the ligand $[R_2P(CH_2)_2]$

The stabilized versions of (**99**)–(**101**) have easily been obtained from the silver derivative (**103**), shown in Scheme 31 [212]. Treatment of (**103**) with ClAu(tht) gives (**104**), which can be oxidized to give the dinuclear complexes (**105**) and (**106**) [213]. Interestingly, treatment of (**103**) with Pd^{II} precursors gives complexes in which the bis-ylide is always behaving as a chelate [214].

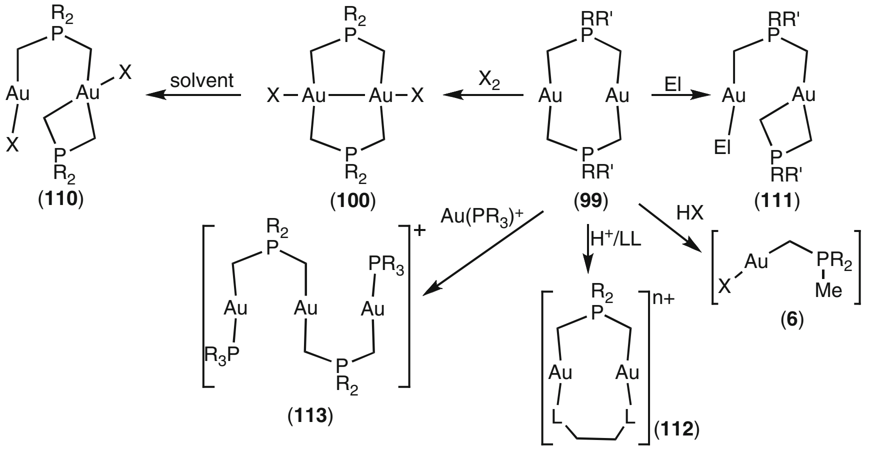
Due to the ability of the $[Au^{I}Au^{I}]$ core to undergo oxidative additions, many other substrates have been used. Asymmetric $[Au^{II}–Au^{II}]$ complexes (**107**) have been obtained by oxidative addition of a large variety of alkyl halides RX, as summarized in Scheme 32. Amongst them we have to mention MeI [207, 215], EtI [216], Me_3SiCH_2I, $PhCH_2Br$ [217], CCl_4 [218], or $NCCH_2Br$ [219]. In some cases [217], the addition of the alkyl halide is reversible. In this respect, the presence of a strongly electron-withdrawing group helps to stabilize the dimer $[Au^{II}–Au^{II}]$. The dimers (**107**) with a nitro ligand at both sides of the Au–Au bond have been prepared by oxidative addition of $MeNO_2$ to (**99**) [220], while those having CN ligands [221] have been obtained by treatment of (**99**) with $Hg(CN)_2$.

Dihalomethylenes CH_2X_2, and related species, also add oxidatively to (**99**), but the final products are quite different from those already presented. In general, the reaction of (**99**) with CH_2X_2 affords complexes (**108**), in which both C–X bonds add to the gold centers [222]. Complexes (**108**) show both gold centers in the (+III) oxidation state, and are very stable. A proof of this stability is the lack of reactivity of the methylene bridge toward different reagents. A synthetic alternative for (**108**) is the reaction of (**100**) with CH_2N_2 [223], or other unexpected sources of CHR groups [224]. Soon after the first synthesis of (**108**) an intermediate (**109**), containing a haloalkyl ligand, was isolated and characterized [223]. The isolation of (**109**) allowed the proposal of a reaction mechanism based on carbene species [225]. The reactivity of (**108**) has been studied in some depth [226].

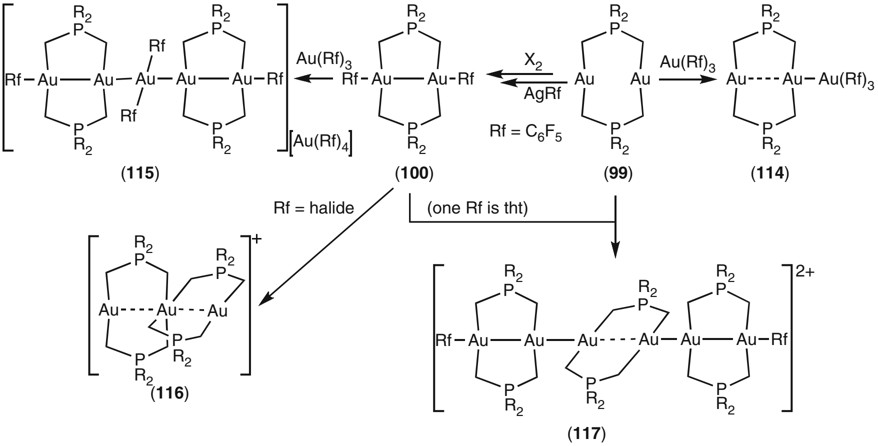
Each species (**99**), (**100**), (**101**), (**102**), or (**108**) has been subjected to a wide variety of substitution processes of the ylide ligand by other anionic ligands, or of the X ligand by other anionic or neutral L ligands, acting as monodentate, chelate or bridge. This results in a plethora of complexes with very diverse structural features, whose complete description falls outside the remit of this chapter. However, there are some noteworthy processes which merit mentioning here.

The first is the solvent-promoted ($MeNO_2$, acetone) isomerization of (**100**) into an [Au^IAu^{III}] mixed complex (**110**) (Scheme 33) [227], related to the synthesis of (**102**). The critical step in this process is the cleavage of the dimer. Here the strong σ-donor is not necessary, since a weak donor solvent promotes the reaction, but it should be noted that the final structure contains one of the bis-ylides acting as a chelating ligand. This cleavage seems to be involved in other relevant reactions. For instance, the dimer $[Au(CH_2)_2PPhMe]_2$, type (**99**), is obtained in *trans* form, that is, with the two Ph groups on opposites sides of the molecular plane. The addition of Lewis acids to (**99**) (even the reaction solvent) promotes its isomerization to the *cis* form through species (**111**) [228]. The addition of a very strong Lewis acid (hydrogen halides) results in the cleavage of (**99**) and protonation of the bis-ylide, giving C-bonded ylides (**6**) [229], or in the formation of dimers (**112**) if protonation is performed in the presence of chelating ligands LL [230]. Dimer (**99**) can also be cleaved by metallic electrophiles. In this case, a further transylidation from (**99**) to the incoming metallic electrophile is observed, giving trinuclear species (**113**) [231].

The reactivity of the electron rich dimeric Au^I derivative (**99**) towards electrophiles (metallic or not) seems to begin by direct attack of the electrophile on the



Scheme 33 Representative reactivity of complexes with the ligand $[R_2P(CH_2)_2]$



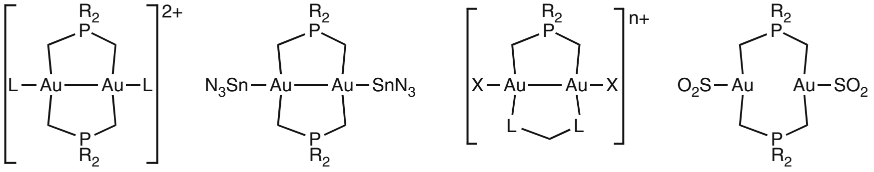
Scheme 34 Synthesis of polynuclear complexes with the ligand [$R_2P(CH_2)_2$]

gold center, forming a direct Au^I–El bond. This concept has been used to build polynuclear gold complexes in various oxidation states, starting from (**99**) and with different reagents. Some outstanding results are shown in Scheme 34.

The reaction of (**99**) with $(C_6F_5)_3AuOEt_2$ cleanly produces trimer (**114**) through an acid–base Lewis process. However, the assignation of the individual oxidation states for the gold atoms is not evident from the X-ray data [232]. A very different process is observed when (**100**) is reacted with $(C_6F_5)_3AuOEt_2$, since the pentanuclear complex (**115**) is obtained, together with the byproduct F_5C_6–C_6F_5.

The assignation of oxidation states in (**115**) is even less evident than in (**114**), and it has been proposed as $\{[Au^{II}Au^{II}][Au^I][Au^{II}Au^{II}]\}^+$ (giving the first Au^I center in a square–planar environment) or, alternatively, $\{[Au^{II}Au^I][Au^{III}][Au^IAu^{II}]\}^+$, which is also an unprecedented situation [233]. Complexes (**116**) are obtained in the disproportionation of (**100**), induced by strong σ-donors as $R_3P{=}CH_2$ [210], regardless of the nature of the halide. In this case there is no doubt about the oxidation state since a chain $[Au^IAu^{III}Au^I]$ is clearly identified. Au^{II} dimers (**100**) behave as nucleophiles when reacting with the highly electrophilic $Au(Rf)_3$ derivatives, giving (**115**), but they can also behave as electrophiles towards highly nucleophilic compounds (**99**). In this respect, (**117**) is a very good example of this versatility [234].

Finally, a more classical reactivity dealing with simple ligand substitution has been developed. Some notable contributions must be mentioned here such as the synthesis of water-soluble Au^{II} dimers (**118**) [235] (Scheme 35) using common procedures [236], the synthesis of very large rings using polysulfide anions [237], the synthesis of heteropolymetallic derivatives (**119**) [238], the synthesis of complexes with mixed ligands (one ylide and another different anionic ligand) (**120**) either by ligand substitution in Au^{II} precursors or by oxidation of preformed mixed



(**118**) (**119**) (**120**) (**121**)

L = water soluble phosphine

N_3 = MeSi(Me$_2$SiN(p-tol))$_3$

L = xanthate, dppm

Scheme 35 Miscellaneous reactivity with the anionic bridging ligand [$R_2P(CH_2)_2$]

Au^I complexes [239, 240], or the coordination of very elusive ligands, such as the adducts with SO_2 (**121**) [241].

6 Summary

Complexes of transition metals containing ylides as ligands have been known for more than 30 years. During this time, a wide range of preparative methods, unusual chemical structures, unexpected reactivity and fascinating applications, even in the industrial field and regardless of the transition metal, have been developed. In this chapter a brief summary of the behavior of ylides with *late* transition metals has been presented, covering examples of ylides as monodentate species, as bidentate chelating or bridging ligands, precursors of carbenes, chiral ancillary moieties, hemilabile ligands or stabilizing unusual structures or oxidations states. The importance of the ylides is evident in all areas where they are present, from the merely organic point of view to the organometallic one. Because of this, new applications can be expected, and additional efforts are necessary to improve and further develop this rich field of chemistry.

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References

1. Hoffmann RW (2001) Angew Chem Int Ed 40:1411
2. Johnson AW (1993) Ylides and imines of phosphorus. Wiley, New York, USA
3. Coyne EJ, Gilheany DG (1995) In: Katritzky AR, Meth-Cohn O, Rees CW (eds) Pattenden G (vol ed) Comprehensive organic functional group transformation, Vol 3, Chap 3.13. Pergamon, Oxford, UK
4. Whittingham WG (1995) In: Katritzky AR, Meth-Cohn O, Rees CW (eds) Pattenden G (vol ed) Comprehensive organic functional group transformations, Vol 3, Chap 3.08. Pergamon, Oxford, UK

5. Kolodiazhnyi OI (1999) Phosphorus ylides. Wiley, Weinheim, Germany
6. Clark JS (2002) Nitrogen, oxygen and sulfur ylide chemistry. Oxford University Press, Oxford, UK
7. Vedejs E, West FG (1986) Chem Rev 86:941
8. Kolodiazhnyi OI (1996) Tetrahedron 52:1855
9. Padwa A, Hornbuckle SF (1991) Chem Rev 91:263
10. Coldham I, Hufton R (2005) Chem Rev 105:2765
11. Burton DJ, Yang Z-Y, Qiu W (1996) Chem Rev 96:1641
12. Gilheany DG (1994) Chem Rev 94:1339
13. Li A-H, Dai L-X, Aggarwal VK (1997) Chem Rev 97:2341
14. Sun X-L, Tang Y (2008) Acc Chem Res 41:937
15. Schmidbaur H (1975) Acc Chem Res 8:62
16. Schmidbaur H (1983) Angew Chem Int Ed Engl 22:907
17. Weber L (1983) Angew Chem Int Ed Engl 22:516
18. Laguna A, Laguna M (1990) J Organomet Chem 394:743
19. Cristau HJ (1994) Chem Rev 94:1299
20. Belluco U, Michelin RA, Mozzon M, Bertani R, Facchin G, Zanotto L, Pandolfo L (1998) J Organomet Chem 557:37
21. Navarro R, Urriolabeitia EP (1999) J Chem Soc Dalton Trans:4111
22. Urriolabeitia EP (2008) Dalton Trans 5673
23. Bertani R, Casarin M, Pandolfo L (2003) Coord Chem Rev 236:15
24. Chauvin R (2000) Eur J Inorg Chem 577
25. Taillefer M, Cristau HJ (2003) Top Curr Chem 229:41
26. Kuhn P, Sémeril D, Matt D, Chetcuti MJ, Lutz P (2007) Dalton Trans 515
27. Cantat T, Mézailles N, Auffrant A, Le Floch P (2008) Dalton Trans 1957
28. Koezuka H, Matsubayashi G-E, Tanaka T (1974) Inorg Chem 13:443
29. Bravo P, Fronza G, Ticozzi C, Gaudiano G (1974) J Organomet Chem 74:143
30. Nishiyama H, Itoh K, Ishii Y (1975) J Organomet Chem 87:129
31. Weleski ET Jr, Silver JL, Jansson MD, Burmeister JL (1975) J Organomet Chem 102:365
32. Bravo P, Fronza G, Ticozzi C (1976) J Organomet Chem 111:361
33. Koezuka H, Matsubayashi G-E, Tanaka T (1976) Inorg Chem 15:417
34. Seno M, Tsuchiya S (1977) J Chem Soc Dalton Trans 751
35. Tewari RS, Awasthi AK (1984) J Organomet Chem 271:403
36. Booth BL, Smith KG (1981) J Organomet Chem 220:219
37. Saito T, Urabe H, Sasaki Y (1980) Transition Met Chem 5:35
38. Saito T (1978) Bull Chem Soc Jpn 51:169
39. Usón R, Laguna A, Laguna M, Usón A, Jones PG, Erdbrügger CF (1987) Organometallics 6:1778
40. Stein J, Fackler JP Jr, Paparizos C, Chen H-W (1981) J Am Chem Soc 103:2192
41. Facchin G, Bertani R, Calligaris M, Nardin G, Mari M (1987) J Chem Soc Dalton Trans:1381
42. Facchin G, Bertani R, Zanotto L, Calligaris M, Nardin G (1989) J Organomet Chem 366:409
43. Albanese JA, Rheingold AL, Burmeister JL (1988) Inorg Chim Acta 150:213
44. Albanese JA, Staley DL, Rheingold AL, Burmeister JL (1989) J Organomet Chem 375:265
45. Barco IC, Falvello LR, Fernández S, Navarro R, Urriolabeitia EP (1998) J Chem Soc Dalton Trans 1699
46. Fernández S, García MM, Navarro R, Urriolabeitia EP (1998) J Organomet Chem 561:67
47. Carbó M, Falvello LR, Navarro R, Soler T, Urriolabeitia EP (2004) Eur J Inorg Chem 2338
48. Usón R, Forniés J, Navarro R, Espinet P, Mendívil C (1985) J Organomet Chem 290:125
49. Falvello LR, Fernández S, Navarro R, Urriolabeitia EP (1997) Inorg Chem 36:1136
50. Falvello LR, Fernández S, Navarro R, Pascual I, Urriolabeitia EP (1997) J Chem Soc Dalton Trans 763
51. Facchin G, Zanotto L, Bertani R, Canovese L, Uguagliati P (1993) J Chem Soc Dalton Trans 2871

52. Belluco U, Michelin RA, Bertani R, Facchin G, Pace G, Zanotto L, Mozzon M, Furlan M, Zangrando E (1996) Inorg Chim Acta 252:355
53. Falvello LR, Fernández S, Navarro R, Urriolabeitia EP (1996) Inorg Chem 35:3064
54. Soulivong D, Wieser C, Marcellin M, Matt D, Harriman A, Toupet L (1997) J Chem Soc Dalton Trans 2257
55. Pearson RG (1973) Inorg Chem 12:712
56. Falvello LR, Ginés JC, Carbó JJ, Lledós A, Navarro R, Soler T, Urriolabeitia EP (2006) Inorg Chem 45:6803
57. Carbó M, Marín N, Navarro R, Soler T, Urriolabeitia EP (2006) Eur J Inorg Chem 4629
58. Laavanya P, Venkatasubramanian U, Panchanatheswaran K, Krause Bauer JA (2001) Chem Commun 1660
59. Pandolfo L, Paiaro G, Dragani LK, Maccato C, Bertani R, Facchin G, Zanotto L, Ganis P, Valle G (1996) Organometallics 15:3250
60. Bertani R, Meneghetti F, Pandolfo L, Scarmagnan A, Zanotto L (1999) J Organomet Chem 583:146
61. Bertani R, Casarin M, Ganis P, Maccato C, Pandolfo L, Venzo A, Vittadini A, Zanotto L (2000) Organometallics 19:1373
62. Benetollo F, Bertani R, Ganis P, Pandolfo L, Zanotto L (2001) J Organomet Chem 629:201
63. Bertani R, Pandolfo L, Zanotto L (2002) Inorg Chim Acta 330:213
64. Zinner G, Fehlhammer WP (1985) Angew Chem Int Ed Engl 24:979
65. Greco A (1972) J Organomet Chem 43:351
66. Itoh K, Nishiyama H, Ohnishi T, Ishii Y (1974) J Organomet Chem 76:401
67. Starzewski KAO, Dieck HT, Franz KD, Hohmann F (1972) J Organomet Chem 42:C35
68. Hirai M-F, Miyasaka M, Itoh K, Ishii Y (1978) J Organomet Chem 160:25
69. Hirai M-F, Miyasaka M, Itoh K, Ishii Y (1979) J Organomet Chem 165:391
70. Hirai M-F, Miyasaka M, Itoh K, Ishii Y (1979) J Chem Soc Dalton Trans 1200
71. Spannenberg A, Baumann W, Rosenthal U (2000) Organometallics 19:3991
72. Vicente J, Chicote MT (1999) Coord Chem Rev 193/195:1143
73. Vicente J, Chicote MT, Guerrero R, Jones PG (1996) J Am Chem Soc 118:699
74. Vicente J, Chicote MT, Abrisqueta MD, González-Herrero P, Guerrero R (1998) Gold Bull 31:126
75. Vicente J, Chicote MT, Cayuelas JA, Fernández-Baeza J, Jones PG, Sheldrick GM, Espinet P (1985) J Chem Soc Dalton Trans 1163
76. Vicente J, Chicote MT, Saura-Llamas I, Lagunas MC (1992) J Chem Soc Chem Commun 915
77. Vicente J, Chicote MT, Abrisqueta MD, Alvarez-Falcón MM, Ramírez de Arellano MC, Jones PG (2003) Organometallics 22:4327
78. Schmidbaur H, Gabbaï FP, Schier A, Riede J (1995) Organometallics 14:4969
79. Kermode NJ, Lappert MF, Skelton BW, White AH, Holton J (1982) J Organomet Chem 228:C71
80. Engelbert C, Moss JR, Niven ML, Nassimbeni LR, Reid G (1982) J Organomet Chem 232:C78
81. Hoover JF, Stryker JM (1988) Organometallics 7:2082
82. Werner H, Hofmann L, Paul W, Schubert U (1988) Organometallics 7:1106
83. Toupet L, Weinberger B, Des Abbayes H, Gross U (1984) Acta Crystallogr C40:2056
84. Ferguson G, Li Y, McAlees AJ, McCrindle R, Xiang K (1999) Organometallics 18:2428
85. Leoni P, Marchetti F, Paoletti M (1997) Organometallics 16:2146
86. Rudler H, Audouin M, Parlier A, Martin-Vaca B, Goumont R, Durand-Réville T, Vaiseermann J (1996) J Am Chem Soc 118:12045
87. Zhang C, Guzei IA, Espenson JH (2000) Organometallics 19:5257
88. Djukic JP, Young VG Jr, Woo LK (1994) Organometallics 13:3995
89. Guerchais V, Astruc D, Nunn CM, Cowley AH (1990) Organometallics 9:1036

90. Nakazawa H, Yamaguchi Y, Mizuta T, Ichimura S, Miyoshi K (1995) Organometallics 14:4635
91. Hanks TW, Ekeland RA, Emerson K, Larsen RD, Jennings PW (1987) Organometallics 6:28
92. Casas JM, Diosdado B, Falvello LR, Forniés J, Martín A, Rueda A (2004) Dalton Trans 2773
93. Azam KA, Frew AA, Lloyd BR, Manojlovic-Muir L, Muir KW, Puddephatt RJ (1985) Organometallics 4:1400
94. McCrindle R, Ferguson G, Arsenault GJ, McAlees AJ, Ruhl BL, Sneddon DW (1986) Organometallics 5:1171
95. Weber L, Lücke E, Boese R (1988) Organometallics 7:978
96. Gandelman M, Rybtchinski B, Ashkenazi N, Gauvin RM, Mistein D (2001) J Am Chem Soc 123:5372
97. Gandelman M, Naing KM, Rybtchinski B, Poverenov E, Ben-David Y, Ashkenazi N, Gauvin RM, Milstein D (2005) J Am Chem Soc 127:15265
98. Falvello LR, Llusar R, Margalejo ME, Navarro R, Urriolabeitia EP (2003) Organometallics 22:1132
99. Vicente J, Chicote MT, MacBeath C, Fernández-Baeza J, Bautista D (1999) Organometallics 18:2677
100. Vicente J, Chicote MT, MacBeath C, Jones PG (2003) Organometallics 22:1843
101. Vicente J, Chicote MT, Fernández-Baeza J, Lahoz FJ, López JA (1991) Inorg Chem 30:3617
102. Vicente J, Chicote MT, Lagunas MC, Jones PG (1995) Inorg Chem 34:5441
103. Vicente J, Chicote MT, Beswick MA, Ramírez de Arellano MC (1996) Inorg Chem 35:6592
104. Facchin G, Campostrani R, Michelin RA (1985) J Organomet Chem 294:C21
105. Michelin RA, Facchin G, Braga D, Sabatino P (1986) Organometallics 5:2265
106. Wagner G, Pakhomova TB, Bokach NA, Frausto da Silva JJR, Vicente J, Pombeiro AJL, Kukushkin VY (2001) Inorg Chem 40:1683
107. Bokach NA, Selivanov SI, Kukushkin VY, Vicente J, Haukka M, Pombeiro AJL (2002) Organometallics 21:3744
108. Bokach NA, Kukushkin VY, Haukka M, Fraústo da Silva JJR, Pombeiro AJL (2003) Inorg Chem 42:3602
109. Keim W, Kowaldt FH, Goddard R, Krügger C (1978) Angew Chem Int Ed Engl 17:466
110. Kermagoret A, Braunstein P (2008) Dalton Trans 822 and references cited therein
111. Lee P-Y, Liang L-C (2008) Inorg Chem 47:749
112. Kuhn P, Sémeril D, Jeunesse C, Matt D, Lutz PJ, Louis R, Neuburger M (2006) Dalton Trans 3647
113. Larivée A, Mousseau JJ, Charette AB (2008) J Am Chem Soc 130:52
114. Mousseau JJ, Larivée C, Charette AB (2008) Org Lett 10:1641
115. Tonner R, Öxler F, Neumüller B, Petz W, Frenking G (2006) Angew Chem Int Ed 45:8038
116. Pascual S, Asay M, Illa O, Kato T, Bertrand G, Saffon-Merceron N, Branchadell V, Baceiredo A (2007) Angew Chem Int Ed 46:9078
117. Schmidbaur H, Zybill CE, Müller G, Krüger C (1983) Angew Chem Int Ed Engl 22:729
118. Zybill C, Müller G (1987) Organometallics 6:2489
119. Petz W, Weller F, Uddin J, Frenking G (1999) Organometallics 18:619
120. Vicente J, Singhal AR, Jones PG (2002) Organometallics 21:5887 and references therein
121. Schmidbaur H, Gasser O (1976) Angew Chem Int Ed Engl 15:502
122. Petz W, Kutschera C, Neumüller B (2005) Organometallics 24:5038
123. Baldwin JC, Kaska WC (1979) Inorg Chem 18:686
124. Kaska WC, Mitchell DK, Reichelderfer RF, Korte WD (1974) J Am Chem Soc 96:2847
125. Kaska WC, Mitchell DK, Reichelderfer RF (1973) J Organomet Chem 47:391
126. Ramirez F, Levy S (1956) J Org Chem 21:488
127. Brownie JH, Baird MC, Schmider H (2007) Organometallics 26:1433 and references therein
128. Nakazawa H, Ueda Y, Nakamura K, Miyoshi K (1997) Organometallics 16:1562

129. Grumbine SK, Mitchell GP, Straus DA, Tilley TD, Rheingold AL (1998) Organometallics 17:5607
130. Li X, Wang A, Wang L, Sun H, Harms K, Sundermeyer J (2007) Organometallics 26:1411
131. Li X, Schopf M, Stephan J, Kipke J, Harms K, Sundermeyer J (2006) Organometallics 25:528
132. van der Eide EF, Romero PE, Piers WE (2008) J Am Chem Soc 130:4485
133. Werner H, Wiedemann R, Laubender M, Windmüller B, Steinert P, Gevert O, Wolf J (2002) J Am Chem Soc 124:6966
134. Kubicki MM, Kergoat R, Scordia H, Gomes de Lima LC, Guerchais JE, L'Haridon P (1988) J Organomet Chem 340:41
135. Nishimura Y, Arikawa Y, Inoue T, Onishi M (2005) Dalton Trans 930
136. Du S, Ellis DD, Jellis PA, Kautz JA, Malget JM, Stone FGA (2000) Organometallics 19:1983
137. Allen A Jr, Lin W (1999) Organometallics 18:2922
138. O'Connor JM, Bunker KD (2003) J Organomet Chem 671:1
139. Rüba E, Mereiter K, Schmid R, Kirchner K, Bustelo E, Puerta MC, Valerga P (2002) Organometallics 21:2912
140. Aumann R, Jasper B, Läge M, Krebs B (1994) Chem Ber 127:2475
141. Viau L, Lepetit C, Commenges G, Chauvin R (2001) Organometallics 20:808
142. Ohta T, Sasayama H, Nakajima O, Kurahashi N, Fujii T, Furukawa I (2003) Tetrahedron Asymm 14:537
143. Zurawinski R, Donnadieu B, Mikolajczyk M, Chauvin R (2003) Organometallics 22:4810
144. Zurawinski R, Donnadieu B, Mikolajczyk M, Chauvin R (2004) J Organomet Chem 689:380
145. Canac Y, Lepetit C, Abdalilah M, Duhayon C, Chauvin R (2008) J Am Chem Soc 130:8406
146. Canac Y, Duhayon C, Chauvin R (2007) Angew Chem Int Ed 46:6313
147. Asay M, Donnadieu B, Baceiredo A, Soleilhavoup M, Bertrand G (2008) Inorg Chem 47:3949
148. Canac Y, Conejero S, Soleilhavoup M, Donnadieu B, Bertrand G (2006) J Am Chem Soc 128:459
149. Vignolle J, Donnadieu B, Bourissou D, Soleilhavoup M, Bertrand G (2006) J Am Chem Soc 128:14810
150. Dyker G (2005) Handbook of C-H transformations: applications in organic synthesis. Wiley, Weinheim, Germany
151. Illingsworth ML, Teagle JA, Burmeister JL, Fultz WC, Rheingold AL (1983) Organometallics 2:1364
152. Vicente J, Chicote MT, Fernández-Baeza J (1989) J Organomet Chem 364:407
153. Onitsuka K, Nishii M, Matsushima Y, Takahashi S (2004) Organometallics 23:5630
154. Koch JL, Shapley PA (1999) Organometallics 18:814
155. Park JH, Koh JH, Park J (2001) Organometallics 20:1892
156. Heineke D, Bohle DS, Vahrenkamp H (1993) Chem Ber 126:355
157. Deeming AJ, Nuel D, Powell NI, Whittaker C (1992) J Chem Soc Dalton Trans 757
158. Vicente J, Chicote MT, Lagunas MC, Jones PG, Bembenek E (1994) Organometallics 13:1243
159. Facchin G, Zanotto L, Bertani R, Nardin G (1996) Inorg Chim Acta 245:157
160. Aguilar D, Aragüés MA, Bielsa R, Serrano E, Navarro R, Urriolabeitia EP (2007) Organometallics 26:3541
161. Falvello LR, Fernández S, Navarro R, Rueda A, Urriolabeitia EP (1998) Organometallics 18:5887
162. Falvello LR, Fernández S, Larraz C, Llusar R, Navarro R, Urriolabeitia EP (2001) Organometallics 20:1424
163. Gracia C, Marco G, Navarro R, Romero P, Soler T, Urriolabeitia EP (2003) Organometallics 22:4910
164. Vicente J, Chicote MT, Lagunas MC (1993) Inorg Chem 32:3748
165. Matsubayashi G-E, Kondo Y, Tanaka T, Nishigaki S, Nakatsu K (1979) Chem Lett 375

166. Matsubayashi G-E, Kawafune I, Tanaka T, Nishigaki S, Nakatsu K (1980) J Organomet Chem 187:113
167. Matsubayashi G-E, Ueyama K, Nakatsu K (1982) J Organomet Chem 240:103
168. Kawafune I, Matsubayashi G-E (1983) Inorg Chim Acta 70:1
169. Oosawa Y, Urabe H, Saito T, Sasaki Y (1976) J Organomet Chem 122:113
170. Holy N, Deschler U, Schmidbaur H (1982) Chem Ber 115:1379
171. Usón R, Forniés J, Navarro R, Ortega AM (1987) J Organomet Chem 334:389
172. Usón R, Laguna A, Laguna M, Lázaro I, Jones PG (1987) Organometallics 6:2326
173. Gimeno MC, Jones PG, Laguna A, Laguna M, Lázaro I (1993) J Chem Soc Dalton Trans 2223
174. Gimeno MC, Jones PG, Laguna A, Villacampa MD (1995) J Chem Soc Dalton Trans 805
175. Schmidbaur H, Deschler U, Milewski-Mahrla B (1981) Angew Chem Int Ed Engl 20:586
176. Gong JK, Peters TB, Fanwick PE, Kubiak CP (1992) Organometallics 11:1392
177. Alcock NW, Pringle PG, Bergamini P, Sostero S, Traverso O (1990) J Chem Soc Dalton Trans 1553
178. Lin IJB, Lai HYC, Wu SC, Hwan L (1986) J Organomet Chem 306:C24
179. Lin IJB, Hwan L, Shy HC, Chen MC, Wang Y (1986) J Organomet Chem 315:135
180. Cheng MC, Peng SM, Lin IJB, Meng BHH, Liu CH (1987) J Organomet Chem 327:275
181. Lin IJB, Shy HC, Liu CW, Liu L-K, Yeh S-K (1990) J Chem Soc Dalton Trans 2509
182. Wu RF, Lee LIJB, GH CMC, Wang Y (1990) Organometallics 9:126
183. Brauer DJ, Krüger C, Roberts PJ, Tsay Y-H (1974) Chem Ber 107:3706
184. Basset JM, Mandl JR, Schmidbaur H (1980) Chem Ber 113:1145
185. Vicente J, Chicote MT, Saura-Llamas I, López-Muñoz MJ, Jones PG (1990) J Chem Soc Dalton Trans 3683
186. Hostetler MJ, Butts MD, Bergman RG (1992) Inorg Chim Acta 198–200:377
187. Schmidbaur H, Costa T, Milewski-Mahrla B (1981) Chem Ber 114:1428
188. Schmidbaur H, Costa T, Milewski-Mahrla B, Köhler FH, Tsay Y-H, Krüger C, Abart J, Wagner FE (1982) Organometallics 1:1266
189. Fluck E, Bieger K, Heckmann G, Neumüller B (1993) J Organomet Chem 459:73
190. Falvello LR, Margalejo ME, Navarro R, Urriolabeitia EP (2003) Inorg Chim Acta 347:75
191. Schmidbaur H, Gasser O, Krüger C, Sekutowski JC (1977) Chem Ber 110:3517
192. Vicente J, Chicote MT, Saura-Llamas I, Jones PG, Meyer-Bäse K, Erdbrügger CF (1988) Organometallics 7:997
193. Falvello LR, Fernández S, Navarro R, Rueda A, Urriolabeitia EP (1998) Inorg Chem 37:6007
194. Aitken RA, Karodia N, Lightfoot P (2000) J Chem Soc Perkin Trans 2:333
195. Lledós A, Carbó JJ, Urriolabeitia EP (2001) Inorg Chem 40:4913
196. Lledós A, Carbó JJ, Navarro R, Urriolabeitia EP (2004) Inorg Chim Acta 357:1444
197. Lledós A, Carbó JJ, Navarro R, Serrano E, Urriolabeitia EP (2004) Inorg Chem 43:7622
198. Nielsen DJ, Cavell KJ, Skelton BW, White AH (2001) Organometallics 20:995
199. Serrano E, Vallés C, Carbó JJ, Lledós A, Soler T, Navarro R, Urriolabeitia EP (2006) Organometallics 25:4653
200. Serrano E, Soler T, Navarro R, Urriolabeitia EP (2008) J Mol Struct 890:57
201. Jiang F, Shapiro PJ, Fahs F, Twamley B (2003) Angew Chem Int Ed 42:2651
202. Schmidbaur H, Franke R (1973) Angew Chem Int Ed Engl 12:416
203. Schmidbaur H, Adlkofer J, Buchner W (1973) Angew Chem Int Ed Engl 12:415
204. Dudis DS, Fackler JP Jr (1985) Inorg Chem 24:3758
205. Raptis RG, Fackler JP Jr, Murray HH, Porter LC (1989) Inorg Chem 28:4057
206. Raptis RG, Porter LC, Emrich RJ, Murray HH, Fackler JP Jr (1990) Inorg Chem 29:4408
207. Schmidbaur H, Franke R (1975) Inorg Chim Acta 13:85
208. Neitling DC, Staples RJ, Fackler JP Jr (1997) Inorg Chim Acta 263:35
209. Méndez LA, Jiménez J, Cerrada E, Mohr F, Laguna M (2004) J Am Chem Soc 127:852
210. Schmidbaur H, Hartmann C, Reber G, Müller G (1987) Angew Chem Int Ed Engl 26:1146

211. Pan Q-J, Zhou X, Fu H-G, Zhang H-X (2008) Organometallics 27:2474
212. Vicente J, Chicote MT, Saura-Llamas I, Jones PG (1989) Organometallics 8:767
213. Vicente J, Chicote MT, Saura-Llamas I (1990) J Chem Soc Dalton Trans 1941
214. Vicente J, Chicote MT, Saura-Llamas I, López-Muñoz MJ, Jones PG (1990) J Chem Soc Dalton Trans 3683
215. Fackler JP Jr, Basil JD (1982) Organometallics 1:871
216. Murray HH, Fackler JP Jr, Trczinska-Bancroft B (1985) Organometallics 4:1633
217. Basil JD, Murray HH, Fackler JP Jr, Tocher J, Mazany AM, Trzcinska-Bancroft B, Knachel H, Dudis D, Delord TJ, Marler D (1985) J Am Chem Soc 107:6908
218. Murray III HH, Fackler Jr JP, Porter LC, Mazany AM (1986) J Chem Soc Chem Commun 321
219. Murray HH, Fackler JP Jr, Mazany AM, Porter LC, Shain J, Falvello LR (1986) Inorg Chim Acta 114:171
220. Trzcinska-Bancroft B, Khan MNI, Fackler JP Jr (1988) Organometallics 7:993
221. Murray HH, Mazany AM, Fackler JP Jr (1985) Organometallics 4:154
222. Jandik P, Schubert U, Schmidbaur H (1982) Angew Chem Int Ed Engl 21:73, 74
223. Murray HH, Fackler JP Jr, Mazany AM (1984) Organometallics 3:1310
224. Knachel HC, Dudis DS, Fackler JP Jr (1984) Organometallics 3:1312
225. Murray HH III, Fackler JP Jr, Tocher DA (1985) J Chem Soc Chem Commun 1278
226. Schmidbaur H, Hartmann C, Riede J, Huber B, Müller G (1986) Organometallics 5:1652
227. Fackler JP Jr, Trczinska-Bancroft B (1985) Organometallics 4:1891
228. Heinrich DD, Staples RJ, Fackler JP Jr (1995) Inorg Chim Acta 229:61
229. Knachel HC, Dettorre CA, Galaska HJ, Salupo TA, Fackler JP Jr, Murray HH (1987) Inorg Chim Acta 126:7
230. Bardají M, Cerrada E, Jones PG, Laguna A, Laguna M (1997) J Chem Soc Dalton Trans 2263
231. Cerrada E, Gimeno MC, Jiménez J, Laguna A, Laguna M, Jones PG (1994) Organometallics 13:1470
232. Usón R, Laguna A, Laguna M, Tartón MT, Jones PG (1988) J Chem Soc Chem Commun 740
233. Usón R, Laguna A, Laguna M, Jiménez J, Jones PG (1991) Angew Chem Int Ed Engl 30:198
234. Laguna A, Laguna M, Jiménez J, Lahoz FJ, Olmos E (1994) Organometallics 13:253
235. Mohr F, Sanz S, Tiekink ERT, Laguna M (2006) Organometallics 25:3084
236. Usón R, Laguna A, Laguna M, Jiménez J, Jones PG (1991) J Chem Soc Dalton Trans 1361
237. Fackler JP Jr, Porter LC (1986) J Am Chem Soc 108:2750
238. Findeis B, Contel M, Gade LH, Laguna M, Gimeno MC, Scowen IJ, McPartlin M (1997) Inorg Chem 36:2386
239. Bardají M, Gimeno MC, Jones PG, Laguna A, Laguna M (1994) Organometallics 13:3415
240. Bardají M, Jones PG, Laguna A, Laguna M (1995) Organometallics 14:1310
241. King C, Heinrich DD, Wang JC, Fackler JP Jr, Garzon G (1989) J Am Chem Soc 111:2300

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Carbodiphosphoranes and Related Ligands

Wolfgang Petz and Gernot Frenking

Abstract The theoretical and experimental research on carbodiphosphoranes $C(PR_3)_2$ and related compounds CL_2, both as free molecules and as ligands in transition metal complexes, is reviewed. Carbodiphosphoranes are examples of divalent carbon(0) compounds CL_2 which have peculiar donor properties that are due to the fact that the central carbon atom has two lone electron pairs. The bonding situation is best described in terms of L→C←L donor acceptor interactions which distinguishes CL_2 compounds (carbones) from divalent carbon(II) compounds (carbenes) through the number of lone electron pairs. The structures and stabilities of transition metal complexes with ligands CL_2 can be understood and predictions can be made considering the double donor ability of the carbone compounds.

Keywords Carbodicarbene · Carbodiphosphorane · Divalent carbon(0) · DFT calculations · Transition metal complex

Contents

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Abbreviations

cod	Cyclooctadiene
CDP	Carbodiphosphorane
DFT	Density functional theory
DME	Dimethoxyethane
DMSO	Dimethylsulfoxide
KHMDS	Potassium hexamethyl disilazide
LDA	Lithium diisopropylamide
nbd	Norbornadiene
NHC	*N*-Heterocyclic carbene
PA	Proton affinity
TAA	Tetraaminoallene
TfO	Trifluoromethanesulfonate
THF	Tetrahydrofuran
tht	Tetrahydrothiophene

1 Introduction

Carbodiphosphoranes $C(PR_3)_2$ and related ligands CL_2 which are also termed double ylides differ from the other carbon ligands which are discussed in this volume in the number of lone electron pairs at the carbon donor atom. Ylides, carbenes, allenylidenes, and cumulenylidenes have *one* lone electron pair but carbodiphosphoranes have *two* lone electron pairs with σ and π symmetry. The bonding situation in a carbodiphosphorane (a special class of CL_2 compounds, abbreviated as CDP) is best described in terms of donor–acceptor bonding between the phosphane ligands which serve as σ donor and a naked carbon atom in an

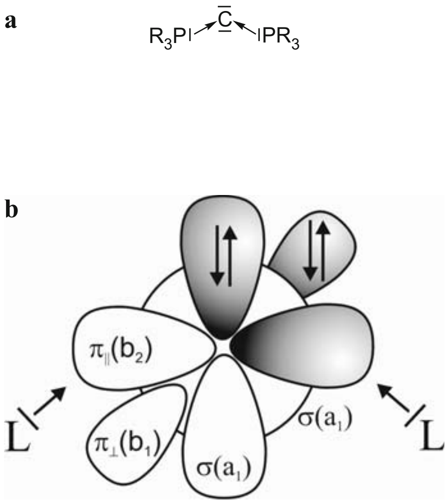


Fig. 1 (**a**) Schematic representation of the bonding situation in carbodiphosphoranes. (**b**) Schematic representation of the donor–acceptor interaction in a divalent C(0) compound CL_2 between a carbon atom in the electronic ^1D state with the electron configuration $2p_{\sigma}^2\ 2p_{\pi\perp}^2\ 2s^0\ 2p_{\pi\|}^0$ and the ligands L

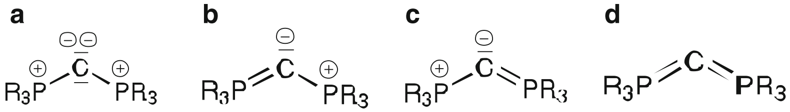


Fig. 2 Schematic representation of the bonding situation in carbodiphosphoranes using Lewis structures

excited singlet (^1D) state which serves as an acceptor. Figure 1a schematically shows the chemical bonding in CDP compounds. Figure 1b displays in more detail the electron configuration at the central carbon atom and the donor–acceptor interaction between the σ lone electron pairs of the donor ligands L and the carbon atom. Since none of the electrons of carbon is involved in the L→C←L bonds, the central atom in CL_2 is a divalent carbon(0) atom. The bonding situation in divalent carbon(0) compounds is thus different from carbenes CR_2 which possess electron sharing bonds where the carbon atom contributes two electrons to the R–C–R bonds. The former compounds have been termed carbones [1] in order to distinguish them from carbenes. Note that carbones have an electron octet at the carbon atom while carbenes formally possess only an electron sextet. Carbenes which are stable in a condensed phase like NHCs are electronically stabilized by π donation from the lone electron pairs of nitrogen into the formally empty p(π) atomic orbital of carbon. Carbones CL_2 are thus π donors whereas carbenes are π acceptors.

The bonding situation in carbodiphosphoranes may also be described using Lewis structures as shown in Fig. 2. The most appropriate form is shown in Fig. 2a where the carbon atom has two formal negative charges while each phosphane ligand carries a positive charge. Figures 2b, c exhibits structures with only one negative charge at carbon and one C=P double bond while Fig. 2d shows a Lewis structure with two double bonds P=C=P and no formal charge. The latter structure is often found in the literature. It is in agreement with the frequently stated rule that the best Lewis structure is one which has the least formal charges. This is not correct. The best Lewis structure for main group compounds is one which obeys the octet rule.

2 Theoretical Studies of Free Ligands CL_2

Quantum chemical calculations using DFT methods have been carried out for the experimentally unknown parent CDP $C(PH_3)_2$ (**1**) and for the trimethyl and triphenyl substituted systems $C(PMe_3)_2$ (**2**) and $C(PPh_3)_2$ (**3**) [2–4]. Figure 3 shows the optimized geometries of **1**–**3** and the most important bond lengths and angles. Experimental values which have been determined by electron diffraction for **2** [5] and by X-ray structure analysis for **3** [6] are in good agreement with the calculated data.

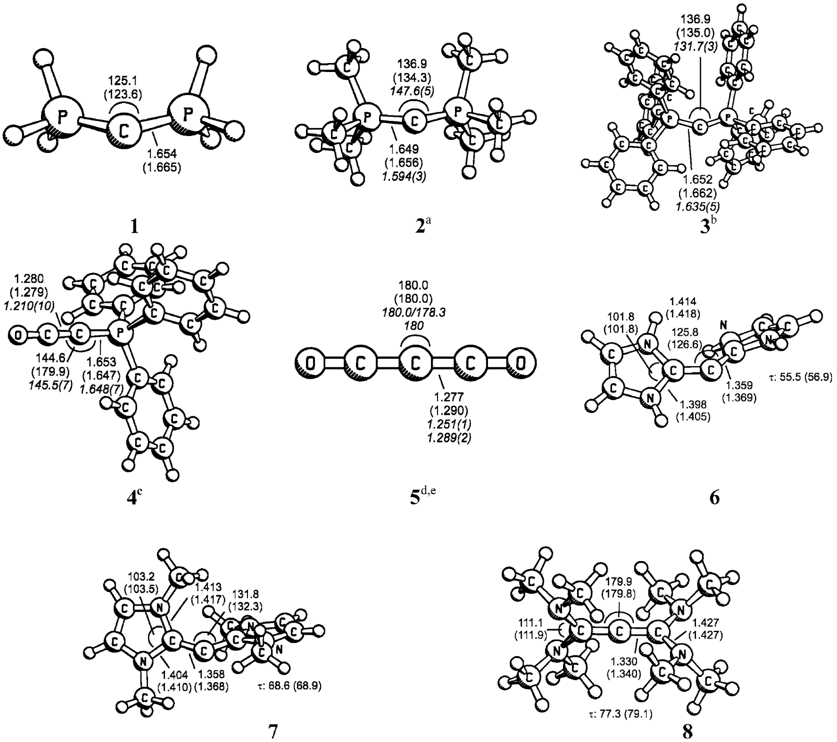


Fig. 3 Optimized geometries at BP86/TZ2P (BP86/SVP) of ligands **1**–**8**. Experimental values are given *in italics*. Bond lengths in Å, angles in degrees. [a]Experimental values from electron diffraction taken from [5]. [b]Experimental values from X-ray analysis taken from [6]. [c]Experimental values from X-ray analysis taken from [7]. [d]Experimental values (*top*) from X-ray analysis taken from [18]. [e]Experimental values (*bottom*) from electron diffraction taken from [19]

The CDPs are strongly bent at the central carbon atom. The bending angle in **1** ($\alpha = 125.1^{\circ}$) becomes significantly wider in **2** ($\alpha = 136.9^{\circ}$) and **3** ($\alpha = 136.9^{\circ}$). It is noteworthy that the energy which is necessary to stretch the P–C–P angle of **1**–**3** to 180° is not very large. The calculations predict that the energy difference between the equilibrium geometries and the linear structures are only 2.0 kcal/mol for **1**, 0.9 kcal/mol for **2**, and 3.1 kcal/mol for **3** [4].

Calculations have also been carried out for compounds CL_2 where one or both PPh_3 ligands of **3** are substituted by CO. Figure 3 shows the optimized geometries of $C(PPh_3)(CO)$ (**4**) and $C(CO)_2$ (**5**) which are experimentally known compounds. Carbon monoxide is a good π acceptor which has a strong impact on the electronic structure and the geometry of **4** and **5**. The bending potential of **4** is extremely shallow. Figure 3 shows that the calculated bending angle for **4** (144.6°) which is larger than in **3** is in very good agreement with the experimental result (145.5°) that was obtained from X-ray structure analysis [7]. The energy difference at BP86/TZ2P between the equilibrium geometry of **4** and the structure where the OC–C–P angle is frozen at 180.0° is only 0.3 kcal/mol. The linear form resembles the structure of a ketene and compound **4** is actually introduced as phosphoranylideneketene [7]. The analysis of the bonding situation suggests that **4** should better be termed either carbonylcarbophosphorane or carbocarbonylphosphorane [4]. The electron diffraction and X-ray measurements show that **5** has a linear (180.0°) or nearly linear (178.3°) OC–C–CO angle. The calculations also give a linear ($D_{\infty h}$) geometry for C_3O_2 but the bending potential is very shallow. The energy which is necessary to distort the linear form of **5** to an OC–C–CO angle of 136.9° (which is the L–C–L equilibrium angle of **3**) is only 1.9 kcal/mol. The π acceptor strength of CO explains the change of the geometry toward a more linear form from **3** → **4** → **5**. The bonding situation in linear **5** may thus be described as a cumulene O=C=C=C=O which upon bending changes towards the description $O{\equiv}C{\rightarrow}C{\leftarrow}C{\equiv}O$.

The bonding properties of phosphanes are frequently compared with NHC ligands which are both considered as mainly σ donors. Divalent carbon(0) compounds with carbene ligands $C(NHC)_2$ were unknown until recently. Figure 3 shows the calculated geometries of the parent system **6** and the *N*-methyl substituted derivative **7**. Both dicarbodicarbenes have a bent geometry where the bending angles of **6** ($\alpha = 125.8^{\circ}$) and **7** ($\alpha = 131.8^{\circ}$) are similar to the values in the CDPs **1**–**3**. The planes of the NHC ligands are twisted with respect to the central C3 plane. The potential energy surface for rotation of the NHC ligands and for the bending potential is very shallow. The calculations predict that the structures with a linear C3 moiety are only 3.6 kcal/mol (**6**) and 3.2 kcal/mol (**7**) higher in energy than the equilibrium structures. Shortly after the theoretical study of **6** and **7** was published [8, 9] the first synthesis and X-ray structure analysis of a carbodicarbene were reported [10, 11]. The experimental geometry of the benzoannelated homologue of **7** is in excellent agreement with the calculated data. Calculations have also been performed for compounds where the central carbon atom is bonded to acyclic carbene ligands. Figure 3 shows that the optimized geometry of $C\{C(NMe_2)_2\}_2$ (**8**) has a nearly linear arrangement of the ligands at the central carbon atom. The geometry thus suggests that **8** should be considered as a tetraaminoallene (TAA) rather than a carbodicarbene. Calculated data which are described below and experimental observations [12, 13] provide strong evidence that TAAs are very strong carbon donor ligands which react like carbodicarbenes $(Me_2N)_2C{\rightarrow}C{\leftarrow}C(NMe_2)_2$.

The schematic representation of the bonding situation of carbones shown in Figs. 1 and 2 suggests that the central carbon(0) atom should carry a large negative partial charge. Table 1 shows the calculated charges of the C(0) atom and the directly bonded atoms E. It becomes obvious that the central carbon(0) atom has a large negative charge particularly in compounds **1–3**. Note that the negative charge concentration at the central carbon atom significantly decreases from **3** (−1.43) to **4** (−0.96) to **5** (−0.55). The smallest value is calculated for the TAA **8** (−0.21). The donor atoms which are bonded to the divalent C(0) atom always carry a positive charge.

A physical probe which may be used to measure the claimed (double) donor ability of divalent carbon(0) compounds is the first and second proton affinity (PA). Table 1 gives the calculated values for the first and second PAs of **1–8**. The first PA of the CDPs are very large, particularly for the substituted compounds **2** and **3**. Note that the second PAs of the latter compounds are also rather high. It is important to recognize that the change in the first PA can be quite different from the change in the second PA. The first PAs of **2** and **3** are very similar to each other but the second PA of **3** is much higher than that of **2** (Table 1). Substitution of the phosphane groups PPh_3 in **3** by CO yields a large drop in the first and second PA for **4** and **5**. The calculated PAs of **6–8** provide important information. The atomic partial charges at the divalent C(0) atom let one expect that the proton affinities of the latter compounds should not be very large. The results in Table 1 indicate that **6–8** have the largest first PAs of the compounds investigated here and that the second PAs are also very large! It becomes obvious that the atomic partial charges are no reliable indicators for the PA. The value for the second PA has been suggested as an experimentally available probe for the divalent C(0) character of a CL_2 compound [1, 4]. The calculated data in Table 1 indicate that the carbodicarbenes **6** and **7** and also the TAA **8** should be classified as divalent carbon(0) compounds. Since the bonding situation in the linear equilibrium geometry is best described with two

Table 1 Partial charges *q* and first and second proton affinities PA (kcal/mol) of **1–8**

L	L′	No.	q(C[a])	q(E[b])	1. PA	2. PA
PH_3	PH_3	**1**	−1.32	0.78	259.4	119.2
PMe_3	PMe_3	**2**	−1.47	1.53	285.4	165.2
PPh_3	PPh_3	**3**	−1.43	1.52	286.0	193.4
PPh_3	CO	**4**	−0.96	1.54/0.58	252.5	129.7
CO	CO	**5**	−0.55	0.65	181.6	23.6
NHC_H	NHC_H	**6**	−0.51	0.28	297.3	155.7
NHC_{Me}	NHC_{Me}	**7**	−0.50	0.29	297.5	170.3
$C(NMe_2)_2$	$C(NMe_2)_2$	**8**	−0.21	0.25	292.2	158.5

[a] Central carbon atom

[b] Atom E which is directly bonded to the central carbon atom. For **1–3**: E = P, for **4**: E = P/C; for **5–8**: E = C

double bonds at the central carbon atom while the donor–acceptor bonding comes only to the fore in the bent geometry, tetraaminoallenes have been termed “hidden divalent C(0) compounds” [4].

The bonding situation for divalent C(0) compounds given in Figs. 1 and 2 lead one to expect that carbones have two high-lying lone-pair orbitals which have σ and π symmetry. Figure 4 shows the HOMO and the HOMO-1 of **1–8**. The shape of the two highest lying occupied orbitals of the CDPs **1–3** are easily classified as lone-pair MOs which have π (HOMO) and σ symmetry (HOMO-1), respectively. Figure 4 shows that the orbital contributions from CO to the degenerate HOMO and HOMO-1 of **4** and **5** are clearly larger than the ligand atom contributions in **1–3** but the largest coefficients are still calculated for the central carbon atom. Note that the energy levels of the occupied frontier orbitals of **4** and **5** are clearly lower than those of the HOMO and HOMO-1 of **1–3**. A systematic study of the first and second proton affinities of carbon bases showed that there is a very high correlation between the energies of the frontier orbitals and the calculated PA [1]. The energetically rather low-lying frontier orbitals of **4** and **5** explain the small values of the calculated proton affinities of the compounds.

The HOMO and HOMO-1 orbitals of the carbodicarbenes **6** and **7** also have the largest coefficients at the divalent C(0) atom (Fig. 4) but the π-type HOMO exhibits some delocalization in the NHC ring (Fig. 4). The energy levels of the frontier

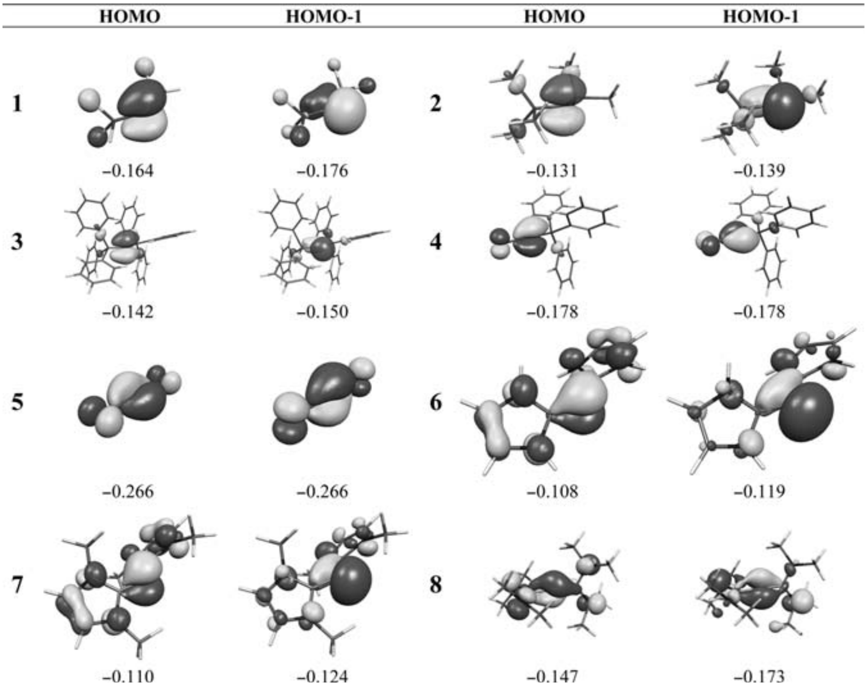


Fig. 4 Shape and eigenvalues (in eV) of the two highest lying occupied orbitals HOMO and HOMO-1 of **1**– **8** at BP86/SVP

orbitals of **6** and **7** are clearly higher than the HOMO and HOMO-1 of the CDPs **1**–**3**. This explains the larger values for the first PAs of **6** and **7** compared with **1**–**3**. The second PAs of the former compounds are also very large but the numerical values do not exactly follow the trend of the HOMO-1 nor do they exhibit the same trend as the HOMO. The second PA of the carbon bases should actually be compared with the HOMO of the singly protonated species. The correlation of the latter variables is very good [1]. It should be noted, however, that the PA is not only determined by the energy level of the HOMO but also by the charge accumulation q and by the relaxation energy of the protonated species.

Figure 4 shows that the HOMO and HOMO-1 of the TAA **8** can be identified as π bonding orbitals of the central C=C=C moiety but the largest contribution to the highest lying occupied orbitals comes from the dicoordinated carbon atom. The calculated large values for the first and second PAs which come from protonation at the central carbon atom rather than the nitrogen atoms points towards the "hidden double lone-pair character" of the TAA [4].

The theoretical studies of carbodiphosphoranes and related divalent carbon(0) compounds suggest that the CL_2 species should be very strong σ donors but they should also possess a decent π donor strength. The theoretical and experimental investigations which are discussed below agree with the classification.

3 Experimental Studies of Free Ligands CL_2

In the following section we discuss the present knowledge about divalent carbon(0) compounds which has been gained from experimental work.

3.1 General Remarks

The theoretical section introduced divalent carbon(0) compounds as molecules CL_2 where the ligand L is a σ donor. In principle this task can be fulfilled by various neutral group 15 compounds (N_2, nitriles, amines, phosphanes, arsanes, etc.), neutral group 16 compounds (sulfides, selenides, etc.) as well as by divalent C(II) with a free pair of electrons at a carbon atom, such as isonitriles, NHCs, carbenes, CO, ylides, etc. The neutral and isolable compound C_2PPh_3 [14, 15] may also serve as a donor L to stabilize a carbon atom.

The bonding situation in carbones CL_2 is presented in Fig. 2 in terms of Lewis structures. For simplification and for better readability we use in the experimental part the description shown in Fig. 5 where we omit the partial charges.

Among the possible CL_2 compositions the number of compounds is limited and the chemistry of most compounds still remains undeveloped. The nucleophilic behavior is more pronounced in double ylide structures in which more negative charge is located at the carbon atom which favors the bent structure. Thus, less stable carbenes as donors L, such as $C(NMe_2)_2$ or CF_2, give structures CL_2 which

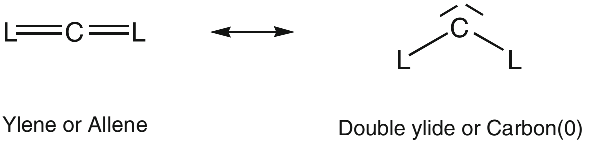


Fig. 5 Schematic representation of the ylene/allene form vs double ylide structure of CL_2 compounds which is used for the formulas of the experimentally observed compounds

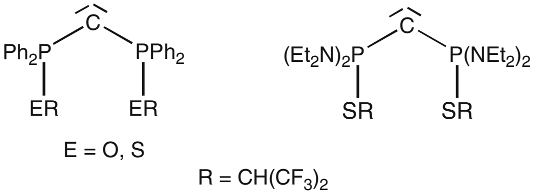


Fig. 6 Various substituted carbodiphosphoranes which have been synthesized

appear as typical allenes whereas NHC ligands prefer the bent structure [4]. Similarly, carbon suboxide C_3O_2 has a linear cumulene structure rather than an ylidic form [16–19]. The transition from a linear ylene to a bent ylide structure can be induced by an appropriate Lewis acidic transition metal fragment A [20, 21]; see the formulation of allenes with a "hidden carbon(0)" atom.

The first experimentally known divalent carbon(0) compounds are the double ylides $C(PR_3)_2$ or carbodiphosphoranes where the most prominent and most frequently studied example is hexaphenylcarbodiphosphorane $C(PPh_3)_2$. Other carbodiphosphoranes with L = PMe_3, $PPhMe_2$ [22], PPh_2Me [23] were reported by Schmidbaur but no reactions with transition metal Lewis acids are known. The hexamethyl analog $C(PMe_3)_2$ was intensively studied by the same group; however its chemistry is governed by the acidity of the methyl groups and not by the lone electron pairs at the carbon atom [24].

A series of heteroatom substituted carbodiphosphoranes $C\{PR_2ECH(CF_3)_2\}_2$ have been prepared in the last 10 years by various groups as shown in Fig. 6. The main synthetic approach consists of the reaction of hexafluoroacetone or thioacetone with the related diphosphines $R_2P–CH_2–PR_2$ [25, 26]. The bent structure with a P–C–P angle (140°) confirms the double ylidic nature [27] and a related chemistry to $C(PPh_3)_2$ is expected; however, no reports about coordination activities were reported so far. Theoretically, double alkylation at the heteroatoms of the dianion in Fig. 9 would lead to the substituted carbodiphosphoranes. The amino derivative $C(P\{NMe_2\}_3)_2$ has a linear structure and was not investigated further [28].

The symmetrically halogenated species $C(PClPh_2)_2$ for which only reactions with HCl or ROH were published was obtained by reacting CCl_4 with $Ph_2P–CH(SiMe_3)–PPh_2$ [29, 30]. The carbodiphosphorane $C(PH\{NR_2\}_2)_2$ with a P–H bond (R = *i*Pr) was also recently reported [31, 32]. A series of CLL′ compounds with

L = $PMe(NMe_2)_2$ and L′ = $POR(NMe_2)_2$ (R = Me, Et, Pr, Bu, Ph) were presented by Fluck but structural details were not given [33]. As further asymmetric carbodiphosphoranes were mentioned $C(P\{NMe_2\}_3)(PCl\{NMe_2\}_2)$ [28], $C(PPh_2Cl)(PPh_3)$ [34], and $C(PH\{NR_2\}_2)(PFNR_2)$ with one P–H and one P–F bond (R = *i*Pr) [31, 32].

Cyclic derivatives of $C(PR_3)_2$ compounds with five-, six-, and seven-membered rings were also described by Schmidbaur but they are very unstable. Formally, the carbon(0) atom is stabilized by the chelating ligands $Ph_2P–(CH_2)_n–PPh_2$ ($n = 2, 3, 4$) [35–37]. A list of all known cyclic and acyclic $C(PR_3)_2$ compounds up to 1983 is summarized in a publication of Schmidbaur [38]. A particular class of cyclic PCP's with a five membered CNPCP ring, which exhibit unusual stability, were presented in 2006 by the group of Baceiredo [39–42]. All known cyclic carbodiphosphoranes are depicted in Fig. 7.

The number of bisylides, in which the carbon atom is stabilized by two neutral sulfur compounds, is restricted so far to one example, $C(S\{NMe\}Ph_2)_2$, with sulfur (IV). The proton of the conjugated acid $(HC(S\{NMe\}Ph_2)_2)^+$ can be reversibly removed on an ion exchange resin loaded with OH^-; protonation is achieved with 10% $HClO_4$ in methanol as shown in Fig. 8. The bent structure with an S–C–S angle of 117° and bond shortening of the C–S bond upon deprotonation of the related cation proves this compound as a typical carbon(0) compound stabilized by the Lewis base $S(NMe)Ph_2$. Although the compound was reported to be stable even

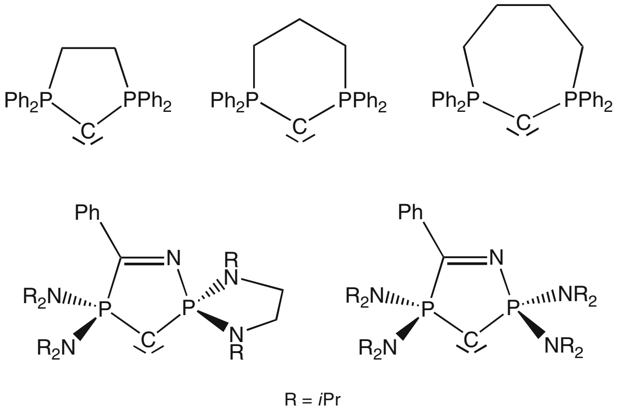


Fig. 7 Experimentally known cyclic carbodiphosphoranes

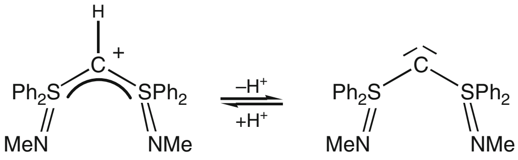


Fig. 8 Preparation of the unique carbodisulfurane

against water, no subsequent attempts have been made to study the complex chemical behavior. Ab initio molecular calculations of the molecule have been published [43, 44].

The first persistent mixed phosphorus sulfur bisylide $C(PPh_3)(SMe_2)$ was presented recently by the group of Baceiredo; preparation and coordination ability are shown in Fig. 12 [45, 46]. The diazomethylenetriphenylphosphorane $C(PPh_3)N_2$ was suggested to be an intermediate during the formation of a heterocycle composed of two molecules of $C(PPh_3)N_2$ and Me_3PX_2; however, it could not be isolated but the existence was deduced from consecutive reactions [47]. Later, the first stable diazomethylenephosphoranes, $C(PX\{NMe_2\}_2)(N_2)$, with X = Cl, Br were reported by the group of Bertrand [48].

A series of dianionic compounds (E = O, S, Se, NR) with two pairs of electrons at the carbon atom as in the neutral carbodiphosphoranes has been described. The dianions act as pincer ligands towards various metal fragments donating four electrons via the carbon atom and two pairs of electrons via the heteroatoms as depicted in Fig. 9. According to theoretical calculations these species can be regarded either as "a coordinated dianion with a strong delocalization of the charge onto the two P–C bonds or as nucleophilic carbene complexes" [49, 50]. A series of such compounds were reported by the groups of Cavell [51], LeFloch [49, 50, 52, 53], and Caulton [54], but they will not be treated here.

Table 2 shows those double ylides or related compounds for which transition metal complexes $A \leftarrow CL_2$ or $A \leftarrow CLL'$ are known. A more detailed description of the divalent carbon(0) compounds in Table 2 which act as ligands in transition metal chemistry are given in the following sections.

Figure 10 shows the possible coordination modes **I–IV** of a divalent carbon (0) compound to a Lewis acid A. The Lewis acid binds in most cases to the σ electron lone pair which yields the planar arrangement **I**. Complexes where the Lewis acid binds to the π lone electron pair of the carbone ligand as shown in coordination mode **II** are not known so far. However, such a binding mode has been predicted for the heavier group-14 species EL_2 where E = Si to Sn [55, 56]; coordination mode **II′** should also be taken into account. The double complexation mode **III** is known for several compounds which are discussed in the sections below. The same holds true for some ligands CL_2 such as C_3O_2 [57] and the ketenyliden ylide $C(PPh_2Me)(CO)$ [58, 59] which bind through the π orbital yielding the structural motif **IV**.

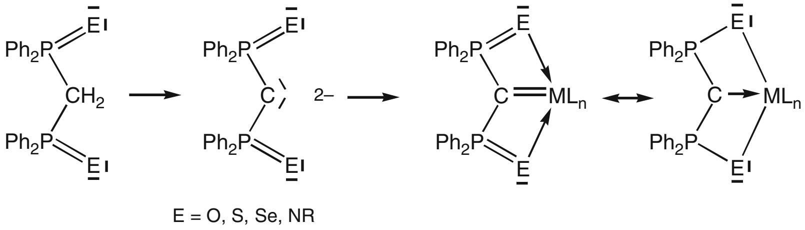


Fig. 9 Dianionic carbodiphosphoranes

Table 2 List of carbodiphosphosphoranes and related ligands CL_2 and CLL' for which transition metal complexes have been synthesized

CL_2 or CLL'		
L	L′	TM
PPh_3	PPh_3	W, Ni, Cu, Ag, Au, Re, Pt, Hg
$(iPr_2N)_2P–C(Ph)=N–PR_2$		Cu, Au, Rh, Pd
$PMePh_2$	SPh_2	Cu
PPh_3	CO	Cr, Mo, W, Fe, Pt, Pd, Mn, Re
CO	CO	Theory
NHC	NHC	Rh
$C(NMe_2)_2$	$C(NMe_2)_2$	Au
$ArOC(NPh)_2COAr$		Rh
$R_2N–C(C_6H_{10})C–NR_2$		Rh, Ir

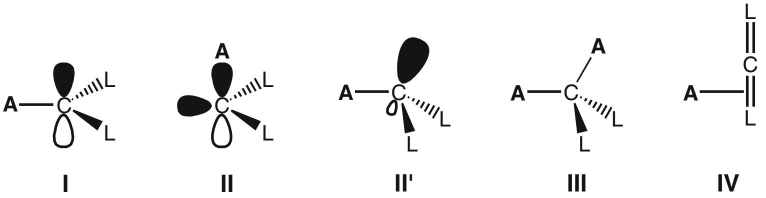


Fig. 10 Possible coordination modes of CL_2 ligands as ligands in complexes

3.2 *Carbodiphosphoranes $C(PR_3)_2$*

In this section we describe $C(PR_3)_2$ compounds for which transition metal complexes $[M]\leftarrow C(PR_3)_2$ have been reported in experimental studies. The most prominent $C(PR_3)_2$ double ylide is the hexaphenylcarbodiphosphorane, $C(PPh_3)_2$. The story of the first divalent carbon(0) compound began in 1961 with a short note about the preparation of $C(PPh_3)_2$ from $(HC\{PPh_3\}_2)Br$ and elemental potassium in diglyme [60]; NaH can also be used [61]. Furthermore, starting with the dibromide $(H_2C\{PPh_3\}_2)Br_2$, dehydrohalogenation was achieved with potassium [61] or $NaNH_2$ in THF [62]. An improved method was reported later and implicates the dehalogenation of the easily available salt $(ClC\{PPh_3\}_2)Cl$ by $P(NMe_2)_3$ [63, 64]. $C(PPh_3)_2$ forms bright yellow crystals which are soluble in hot toluene and in THF and are very sensitive to moisture. Figure 11 shows the methods which were employed to synthesize $C(PPh_3)_2$.

Some years after the first synthesis of $C(PPh_3)_2$ an X-ray analysis revealed the bent nature of the compound which surprisingly crystallizes with two different molecules in the unit cell [65, 66]. A more precise structure analysis of the toluene solvate of $C(PPh_3)_2$ was carried out recently [67]. The most remarkable feature is the flexibility of the P–C–P skeleton with angles amounting to 130° and 144° in the two molecules and unusual short P–C bond lengths being 0.2 Å shorter than a normal single bond [65–67]. Moreover, $C(PPh_3)_2$ shows triboluminescence, which means that it reacts with emission of light upon mechanical treatment [68, 69].

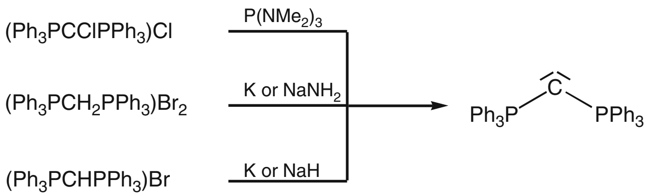


Fig. 11 Methods for the preparation of $C(PPh_3)_2$

The chemistry of $C(PPh_3)_2$ remained rather unexplored for a long time. If $C(PPh_3)_2$ is brought into contact with wet air the hydrolysis product $Ph_3P{=}CH{-}P(O)Ph_2$ is produced quantitatively (1) [70, 71]; however, the action of excess water leads to decomposition of $C(PPh_3)_2$:

$$C(PPh_3)_2 + H_2O \rightarrow \; Ph_3P = CH - P(O)Ph_2 + C_6H_6 \qquad (1)$$

$Ph_3P{=}CH{-}P(O)Ph_2$ can also be considered as an ylide-like compound where the central sp^2 carbon atom is endowed with a free pair of electrons, prone to add a Lewis acid under formation of an sp^3 carbon atom. Reactions of $C(PPh_3)_2$ with organic compounds were reported by Bestmann [72–75]. It is a strong and hard nucleophile which reacts with the heterocumulenes Y=C=X (X, Y=O, S, NR) to produce the betain-like compounds $(Ph_3P)_2C{-}CXY$ [76–78] as show in (2). The compounds $(Ph_3P)_2C{-}CXY$ are sources for the heterocumulenes $E{=}C{=}C{=}PPh_3$ (E = O, S) of the type CLL′ with L = PPh_3 and L′ = CO (see below):

$$C(PPh_3)_2 + CXY \rightarrow (Ph_3P)_2C{-}CXY \qquad (2)$$

Various adducts with Lewis acidic elements or ions of the coordination mode **I** were also described [61], but the first structural proofs were reported by the group of Schmidbaur with the Lewis acids L = S, Se [79, 80], and I^+ [81, 82]. Further adducts of the type **I** with the main group Lewis acids $AlBr_3$ and $InMe_3$ were reported recently and confirmed by X-ray analyses [71].

Under special conditions, $C(PPh_3)_2$ can be protonated to form the cations $(HC\{PPh_3\}_2)^+$ and $(H_2C\{PPh_3\}_2)^{2+}$, respectively by deprotonation of solvents like halogenated hydrocarbons, THF, DMSO, etc. ((3) and (4)). No reports are known about protonation in aqueous solution [83]:

$$C(PPh_3)_2 + H^+ \rightarrow (HC\{PPh_3\}_2)^+ \qquad (3)$$

$$(HC\{PPh_3\}_2)^+ + H^+ \rightarrow (H_2C\{PPh_3\}_2)^{2+} \qquad (4)$$

The latest results including theoretical calculations about the base strength of $C(PPh_3)_2$ are presented in the preceding theoretical part. The chemistry of carbodiphosphoranes with particular emphasis on $C(PPh_3)_2$ has been thoroughly reviewed in the past by various groups [84–89].

3.3 *Mixed Double Ylides CLL′*

From mixed double ylides CLL′ only one compound has been prepared so far. The mixed phosphonium–sulfonium double ylide, $C(PMeR_2)(SPh_2)$, is highly reactive and similar species have never been isolated or observed by spectroscopic methods. The compound was obtained according to the reaction sequence shown in Fig. 12. The conjugated acid $(HC\{PMeR_2\}\{SPh_2\})TfO$ was deprotonated at low temperature (−78°C) in THF by KHMDS. The compound is stable at −20°C and decomposes at room temperature to give a mixture of products. NBO analyses were performed on a model compound [45, 46].

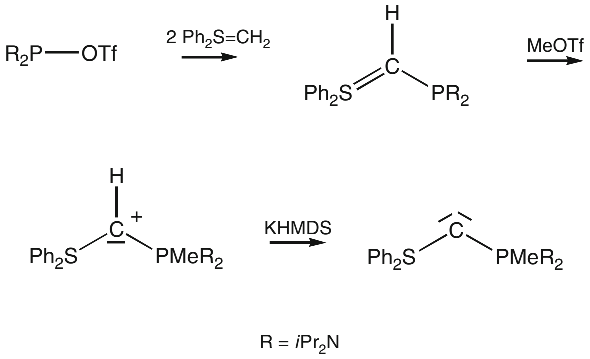


Fig. 12 Preparation of the double ylide $C(PMeR_2)(SPh_2)$

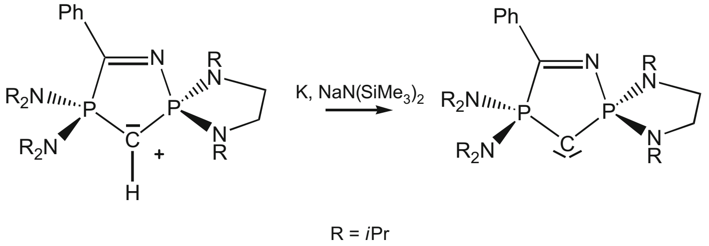


Fig. 13 Preparation of *P*-heterocyclic carbodiphosphoranes

3.4 Cyclic Carbodiphosphoranes

Besides a series of thermally unstable cyclic carbodiphosphoranes presented by Schmidbaur [35–37], two new *P*-heterocyclic carbodiphosphoranes (PHCP) were described recently by the group of Baceiredo [39–42]. One example is shown in Fig. 13, the second bears two $P(NR_2)_2$ groups instead of the PNCCP five membered ring. The cation, obtained by cycloaddition of a phosphonio diazomethane precursor and benzonitrile, can be deprotonated with sodium or potassium hexamethyldisilazide or KO*t*-Bu to produce the carbodiphosphorane. The P–C bond lengths are short, amounting to 1.65(1) Å (mean value) and the fixed P–C–P angle of 105° is much more acute than those of other known $C(PR_3)_2$ compounds [39–42].

3.5 Ketenylidenephosphoranes $C(PR_3)(CO)$

Ketenylidenephosphoranes or ketene ylides are extremely rare and mainly concentrate on $C(PPh_3)(CO)$, which can also be seen as a carbon atom stabilized by the neutral molecules PPh_3 and CO. The bent structure with a P–C–C angle of 145.5° establishes the nucleophilic behavior and the emphasis is on the ylidic form rather than on the ylene form [90]. The P–C bond length is short (1.648(7) Å), but is slightly longer than that in $C(PPh_3)_2$; the C–C bond length (1.210(10) Å) is close to that of a triple bond, which means that the occupied p orbital is more involved in back bonding to the carbonyl group [90]. As mentioned above, the heterocumulene adducts $(Ph_3P)_2C{-}CXY$ are the sources for the ketenylidenephosphoranes $(Ph_3P)C{=}C{=}O$ and $(Ph_3P)C{=}C{=}S$ (5) [72–78]. $(Ph_3P)C{=}C{=}O$ is also obtained by the reaction of bases with $Ph_3P{=}CHC(O)OMe$ (6) [91]:

$$(Ph_3P)_2C-CE_2 \rightarrow (Ph_3P)C=C=E+Ph_3PE \ (E=S,\ O) \tag{5}$$

$$Ph_3P=CHC(O)OMe+NaNH_2 \rightarrow (Ph_3P)C=C=O+NaOMe \tag{6}$$

The organic chemistry of $(Ph_3P)C{=}C{=}O$ is covered by various articles and reviews [72–75, 91–94]. A review concerning the organometallic chemistry of $(Ph_3P)C{=}C{=}O$ has appeared recently [95].

3.6 Carbon Suboxide

Carbon suboxide ($C(CO)_2$) can be prepared according to the method of dehydrating malonic acid with P_2O_5 [96]. The molecule has a linear geometry but the bending potential is remarkably shallow and it was therefore suggested that carbon suboxide is a quasi-linear molecule [16–19]. Calculations on the DFT level on $[(CO)_5W(C\{CO\}_2)]$, $[(CO)_3Ni(C\{CO\}_2)]$, and $[(CO)_2Ni(C\{CO\}_2)]$ with η^1 coordination have been presented [97]; however, as yet only compounds with η^2 (C,C) coordination could be synthesized with platinum [98, 99] and nickel [100].

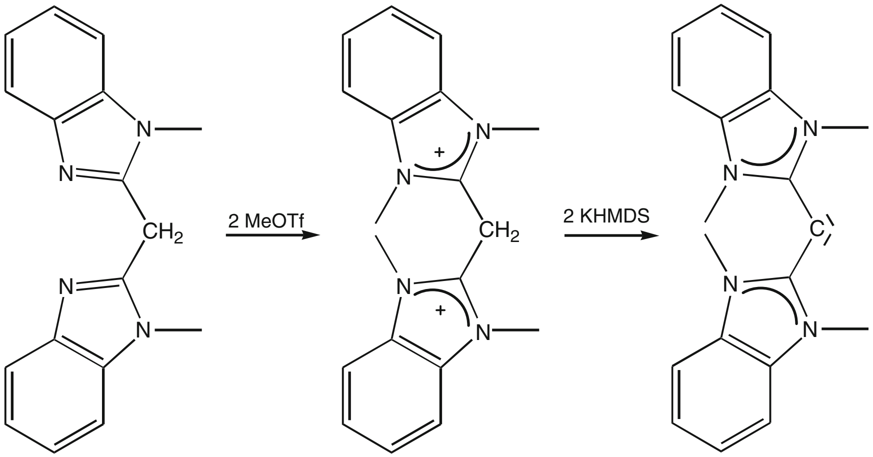


Fig. 14 Synthesis of carbodicarbenes $C(NHC)_2$

3.7 Carbodicarbenes

The carbodicarbenes $C(NHC)_2$ constitute a new class of compounds, first theoretically predicted [8, 9] and shortly after synthesized and characterized by X-ray analyses [10, 11]. Carbon(0) atoms stabilized by two NHC ligands behave similar to carbodiphosphoranes and are also equipped with HOMO and HOMO-1 orbitals of σ and π symmetry. The first carbodicarbene was prepared in a two-step reaction as depicted in Fig. 14.

The C–C–C angle amounts to 134.8(2)°, a value which is closely related to the P–C–P angle in the carbodiphosphorane $C(PPh_3)_2$. Thus, the structure can more likely be described with two lone pairs of electrons. The C–C bond lengths are only slightly longer (1.343(2) Å) than the standard bond length for allenes (1.31 Å) but shorter than a C–C single bond, indicating some back bonding of electron density into the empty NHC carbon p orbital, similar to the negative hyperconjugation effect in double ylides [10, 11]; the preparative findings are supported by theoretical calculations [8, 9].

The potential carbodicarbene $C\{C(NMe_2)_2\}_2$ has been known for a long time but no complex has been reported [101, 102]. It adopts a linear allene geometry in the free state but according to theoretical analysis exhibits a strong nucleophilic central carbon atom [4, 97] and can be seen as an allene with a “hidden” divalent carbon(0) character emerging in the presence of electron deficient electrophiles. Based on these findings a new field of chemistry will be opened and the number of compounds with a η^1 coordination mode should increase in the future.

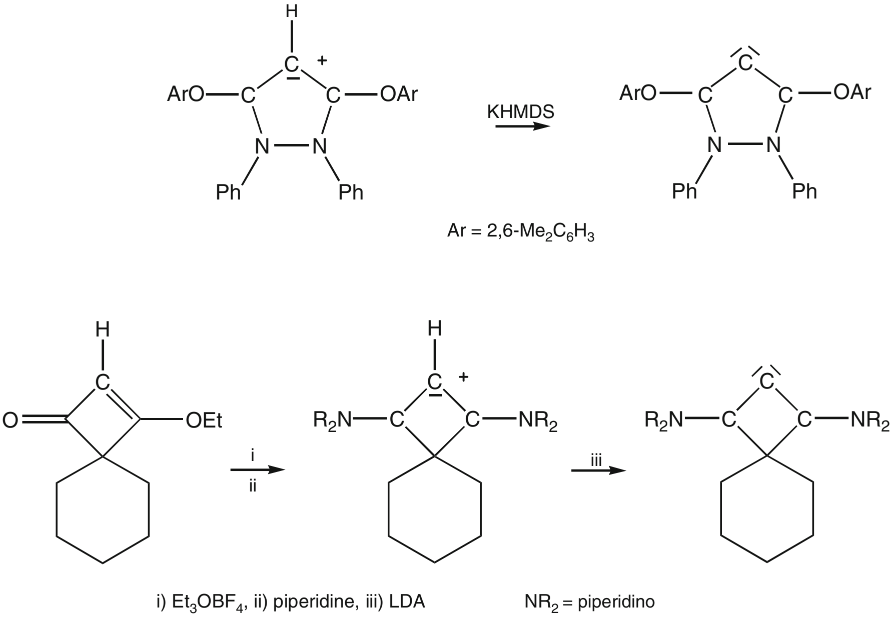
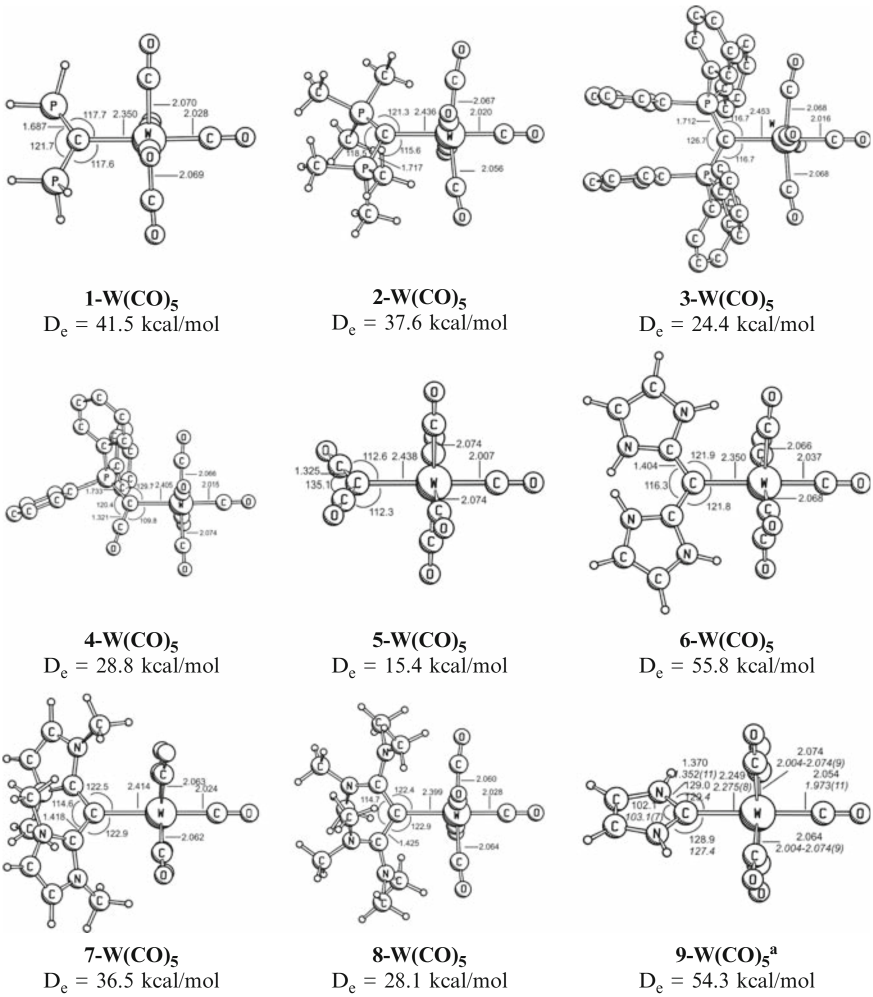


Fig. 15 Syntheses of heterocyclic and all carbon cyclic bent allenes

3.8 Cyclic Divalent C(0) Compounds ("Bent Allenes")

As described above, carbodicarbenes such as $C(NHC)_2$ adopt a bent structure or the bent structure is induced upon complex formation as in $C\{C(NMe_2)_2\}_2$. Deviation from linearity of the cumulene CCC fragment can also be achieved upon cyclization and the sp character of the central carbon atom changes to sp^2 with decreasing ring size and increasing ring strain. The latest results in this field of chemistry were presented by Bertrand with the isolation and characterization of a stable cyclic compound which has a cumulene CCC moiety confined in a five-membered heterocyclic ring [103, 104]. This molecule, shown in Fig. 15, is an example of a cyclic divalent carbon(0) compound which is also known as a "bent allene." A similar analog exhibiting a four-membered all carbon ring was also synthesized [105, 106]. Both compounds can be regarded as a carbon(0) ligated by chelating biscarbenes. Other than in related all carbon cyclic "allenes," which are only identified as intermediates, the N atoms of the heterocycle and the OAr as well as the electron donating NR_2 substituents (NR_2 = piperidino) in the four membered all carbon ring support the stability of the molecules. The crystal structure of the heterocyclic carbon(0) compound shows a C–C–C angle of 97.7° and C–C distances to the carbon(0) atom of 1.370(4) and 1.386(3) Å. The compound is prepared by treatment of the related cation with KHMDS as shown in Fig. 15 and is obtained as a racemic mixture as a result of pyramidalization of the N atoms with a trans arrangement of the phenyl rings.



1-W(CO)$_5$
D$_e$ = 41.5 kcal/mol

2-W(CO)$_5$
D$_e$ = 37.6 kcal/mol

3-W(CO)$_5$
D$_e$ = 24.4 kcal/mol

4-W(CO)$_5$
D$_e$ = 28.8 kcal/mol

5-W(CO)$_5$
D$_e$ = 15.4 kcal/mol

6-W(CO)$_5$
D$_e$ = 55.8 kcal/mol

7-W(CO)$_5$
D$_e$ = 36.5 kcal/mol

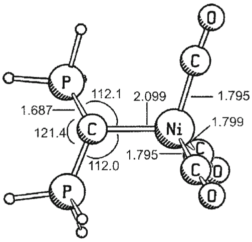
8-W(CO)$_5$
D$_e$ = 28.1 kcal/mol

9-W(CO)$_5$^{a}
D$_e$ = 54.3 kcal/mol

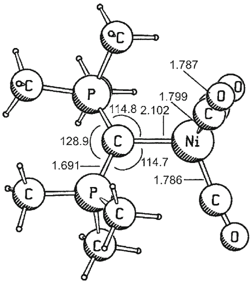
Fig. 16 Optimized geometries at BP86/SVP of the wolfram complexes **N–W(CO)$_5$**, (N = **1**–**9**). Experimental values are given *in italics*. Bond lengths in Å, angles in degrees. Hydrogen atoms of the phenyl rings are omitted for clarity. ^{a}Experimental values from X-ray analysis taken from [147]

4 Theoretical Studies of Metal Complexes with Carbodiphosphoranes and Related Ligands

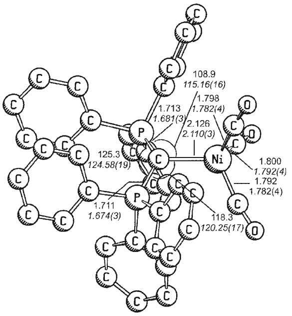
The number of theoretical investigations of transition metal complexes with carbodiphosphoranes and related divalent carbon(0) ligands is rather small. Quantum chemical calculations of the nickel complexes $(CO)_nNi–C(PPh_3)_2$ with $n = 2$, 3 have been published together with experimental work which describes the synthesis and X-ray structure analyses of the compounds [107]. The first systematic theoretical investigation of complexes [TM]–CL_2 comprises the divalent C(0) compounds **1**–**8** as ligands in complexes with $W(CO)_5$ and $Ni(CO)_3$ (n = 2, 3) [97]. The work was complemented by calculations of the related complexes with the NHC **9** as ligand. Figure 16 shows the optimized geometries and the bond dissociation energies (BDEs) of the complexes **N–W(CO)$_5$** where N = **1**–**9**.



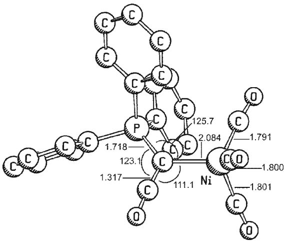
1-Ni(CO)$_3$
D_e = 25.5 kcal/mol



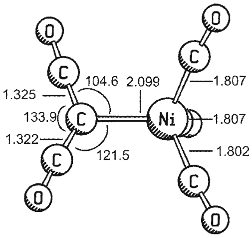
2-Ni(CO)$_3$
D_e = 26.0 kcal/mol



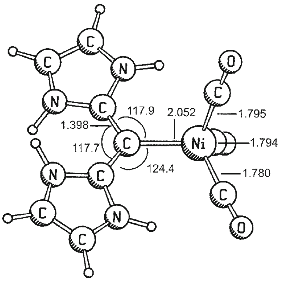
3-Ni(CO)$_3$[a]
D_e = 13.4 kcal/mol



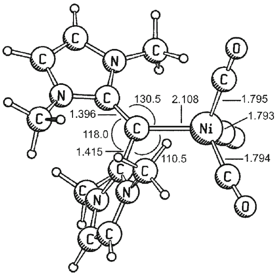
4-Ni(CO)$_3$
D_e = 16.8 kcal/mol



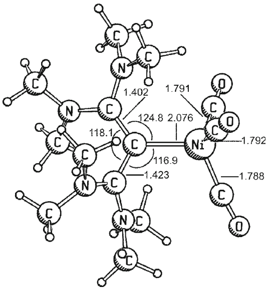
5-Ni(CO)$_3$
D_e = 6.4 kcal/mol



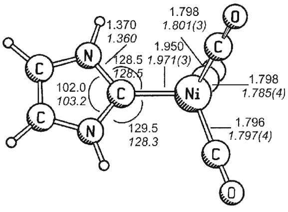
6-Ni(CO)$_3$
D_e = 38.6 kcal/mol



7-Ni(CO)$_3$
D_e = 22.9 kcal/mol



8-Ni(CO)$_3$
D_e = 13.7 kcal/mol



9-Ni(CO)$_3$[b]
D_e = 36.6 kcal/mol

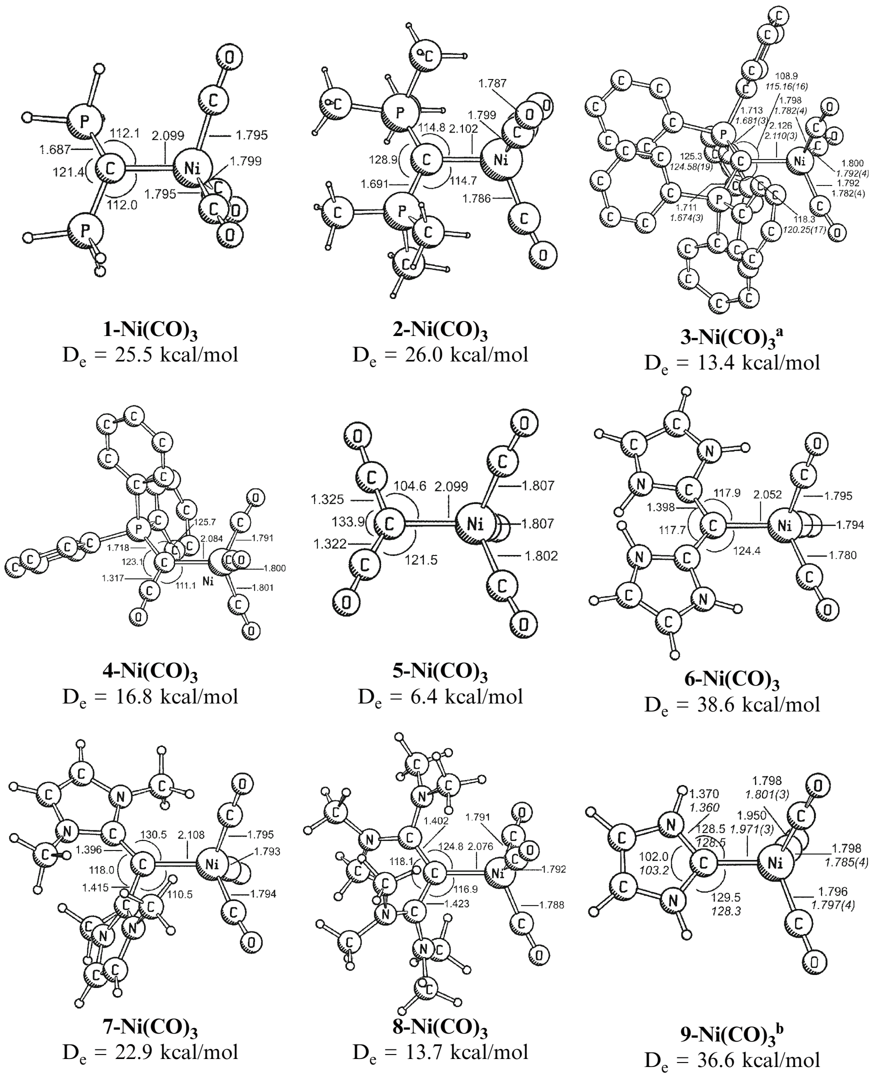
Fig. 17 Optimized geometries at BP86/SVP of the nickel complexes **N–Ni(CO)$_3$** (N = **1**–**9**). Experimental values are given *in italics*. Bond lengths in Å, angles in degrees. Hydrogen atoms of the phenyl rings are omitted for clarity. [a]Experimental values from X-ray analysis taken from [107]. [b]Experimental values from X-ray analysis of a substituted analog taken from [111]

The calculated BDE values shown in Fig. 16 exhibit a range between D_e = 55.8 kcal/mol for the strongest bond which is found for **6-W(CO)$_5$**) and D_e = 15.4 kcal/mol for the weakest bond which is calculated for **5-W(CO)$_5$**. The BDE values for **N–W(CO)$_5$** may be compared with the calculated result for $W(CO)_6$ (D_e = 44.5 kcal/mol) obtained at the same level of theory. The latter value gives a theoretical BDE of D_0^{298} = 43.0 kcal/mol after correction for thermal and ZPE contributions which is in excellent agreement with the experimental value of 46 ± 2 kcal/mol [108]. The data suggest that the carbodicarbene ligand **6** and the NHC ligand **9** yield stronger bonds with $W(CO)_5$ than CO, while the other carbon donor ligands have weaker bonds. The only complex for which an experimental geometry of a substituted homologue is available is the NHC complex **9-W(CO)$_5$**. The experimental bond lengths of the *N*-methyl derivative are in reasonable agreement with the calculated values. The synthesis of the CDP complex **3-W(CO)$_5$** was reported more than 30 years ago by Kaska et al. [109] but attempts to obtain crystals which are suitable for X-ray diffraction analysis were unsuccessful [109, 110].

The theoretically predicted BDE values for **N–Ni(CO)$_3$** (Fig. 17) and **N–Ni(CO)$_2$** (Fig. 18) suggest that the L_2C–Ni bonds are weaker than the respective L_2C–W bonds and that the L_2C–$Ni(CO)_2$ bonds are always stronger than the particular L_2C–$Ni(CO)_3$ bond. The calculated trend of the bond energies is thus L_2C–$W(CO)_5$ > L_2C–$Ni(CO)_2$ > L_2C–$Ni(CO)_3$. The theoretical bond energies for **9-Ni(CO)$_3$** and **9-Ni(CO)$_2$** may be compared with experimentally estimated values for *N*-substituted analogs that were published by Nolan et al. [111]. The bond strength of the NHC_{Ad}–$Ni(CO)_2$– and $NHC_{t\text{-Bu}}$–$Ni(CO)_2$–complexes (Ad = adamantyl; *t*-Bu = *tert*-butyl) was given as 42 and 37 kcal/mol, respectively. This is in very good agreement with the value D_0^{298} = 41.7 kcal/mol which was calculated for the parent system **9-Ni(CO)$_2$** [97]. The calculated value for **9-Ni(CO)$_3$** of D_0^{298} = 34.7 kcal/mol [97] is somewhat larger than the experimental estimate NHC_{Mes}–$Ni(CO)_3 \geq 24$ kcal/mol $\geq NHC_{Ad}$–$Ni(CO)_3$ (Mes = mesityl) [111] but the difference may come from the bulky substituents in the experimentally investigated compounds.

The calculated bond lengths of **3-Ni(CO)$_3$**, **9-Ni(CO)$_3$**, **3-Ni(CO)$_2$** and **9-Ni(CO)$_2$** are in very good agreement with the experimental values where the latter data for the NHC complexes come from *N*-alkyl substituted homologues. The optimized geometry of **5-Ni(CO)$_2$** (Fig. 18) suggests that the complex exhibits an η^2 binding mode of the C_3O_2 ligand across the C=C double bond rather than an η^1 binding mode through the lone pair MO of the central carbon atom as in **5-Ni(CO)$_3$** (Fig. 17).

The nature of the bonding situation in the complexes **N–W(CO)$_5$**, **N–Ni(CO)$_3$** and **N–Ni(CO)$_2$** has been investigated with charge and energy decomposition analyses [97]. Table 3 gives the atomic partial charges for the transition metal complexes. The most interesting result is that the carbon donor atom retains its negative partial charge in the divalent carbon(0) complexes **1-TM(CO)$_n$** – **8-TM(CO)$_n$** which become even slightly more negative in some complexes compared with the free ligands (Table 1). This was explained with the enhanced charge donation $L_2 \rightarrow C$ which compensates for the $L_2C \rightarrow M(CO)_n$ donation [97]. The overall partial charges of the CL_2 ligands have positive values except for the C_3O_2 ligand



1-Ni(CO)$_3$
D$_e$ = 25.5 kcal/mol

2-Ni(CO)$_3$
D$_e$ = 26.0 kcal/mol

3-Ni(CO)$_3$^{a}
D$_e$ = 13.4 kcal/mol

4-Ni(CO)$_3$
D$_e$ = 16.8 kcal/mol

5-Ni(CO)$_3$
D$_e$ = 6.4 kcal/mol

6-Ni(CO)$_3$
D$_e$ = 38.6 kcal/mol

7-Ni(CO)$_3$
D$_e$ = 22.9 kcal/mol

8-Ni(CO)$_3$
D$_e$ = 13.7 kcal/mol

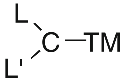
9-Ni(CO)$_3$^{b}
D$_e$ = 36.6 kcal/mol

Fig. 18 Optimized geometries at BP86/SVP of the nickel complexes **N–Ni(CO)$_2$** (N = **1**–**9**). Experimental values are given *in italics*. Bond lengths in Å, angles in degrees. Hydrogen atoms of the phenyl rings are omitted for clarity. ^{a}Experimental values from X-ray analysis taken from [107]. ^{b}Experimental values from X-ray analysis of a substituted analog taken from [111]

in **5-Ni(CO)$_3$** and **5-Ni(CO)$_2$** and the mixed Ph$_3$P–C–CO ligand in **4-Ni(CO)$_2$** (Table 3). The negative value for q(CL$_2$) may be caused by L$_2$C←[TM] π-back-donation when L = CO.

It is noteworthy that the tungsten atom in the complexes always carries a significant negative charge while the nickel atom is always positively charged in **N–Ni(CO)$_n$**. Atomic partial charges must not be used as indicators for the

Table 3 NBO results (BP86/TZVPP//BP86/SVP) for **N–W(CO)$_5$**, **N–Ni(CO)$_3$**, **N–Ni(CO)$_2$** (**N** = **1**–**9**). Atomic partial charges (in e) are given for the central carbon atom (q(C)), the metal atom (q(M)) and the whole CL$_2$-fragment (q(CL$_2$))



TM

			W(CO)$_5$			Ni(CO)$_3$			Ni(CO)$_2$		
	L	L′	q(C)	q(CL$_2$)	q(M)	q(C)	q(CL$_2$)	q(M)	q(C)	q(CL$_2$)	q(M)
1-TM	PH$_3$	PH$_3$	−1.34	+0.30	−0.66	−1.41	+0.11	+0.41	−1.47	+0.06	+0.34
2-TM	PMe$_3$	PMe$_3$	−1.41	+0.34	−0.60	−1.52	+0.17	+0.44	−1.59	+0.12	+0.37
3-TM	PPh$_3$	PPh$_3$	−1.41	+0.27	−0.59	−1.47	+0.08	+0.46	−1.55	+0.03	+0.35
4-TM	PPh$_3$	CO	−0.95	+0.24	−0.63	−1.04	+0.07	+0.41	−1.09	−0.01	+0.35
5-TM	CO	CO	−0.64	+0.12	−0.64	−0.68	−0.10	+0.31	−0.68	−0.32	+0.39
6-TM	NHC$_H$	NHC$_H$	−0.45	+0.41	−0.65	−0.54	+0.22	+0.43	−0.63	+0.18	+0.35
7-TM	NHC$_{Me}$	NHC$_{Me}$	−0.53	+0.37	−0.62	−0.59	+0.17	+0.43	−0.64	+0.15	+0.29
8-TM	C(NMe$_2$)$_2$	C(NMe$_2$)$_2$	−0.45	+0.38	−0.61	−0.53	+0.19	+0.44	−0.57	+0.13	+0.31
9-TM	HN=CH–CH=NH		+0.19	+0.32	−0.72	0.04	+0.13	+0.41	+0.01	+0.13	+0.27

electrostatic interaction between bonded atoms, because they do not give any information about the spatial distribution of the electronic charge. The $L_2C \rightarrow [TM]$ bond mainly comes from the carbon σ lone-pair which induces strong electrostatic attraction due to overlap with the metal nucleus. A much better insight into the nature of the metal–ligand bonding can be obtained from an energy decomposition analysis (EDA) [112–114] of the chemical bond. The EDA decomposes the instantaneous interaction energy ΔE_{int} of a bond A–B between two fragments A and B into three main components $\Delta E_{\mathrm{int}} = \Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{orb}}$ which can be interpreted in a physically meaningful way. The term $\Delta E_{\mathrm{elstat}}$ corresponds to the quasiclassical electrostatic interaction between the unperturbed charge distributions of the prepared atoms and is usually attractive. $\Delta E_{\mathrm{Pauli}}$ comprises the destabilizing interactions between electrons of the same spin on either fragment. The orbital interaction ΔE_{orb} accounts for mixing between occupied and vacant orbitals and for polarization effects. The ΔE_{orb} term can be broken down into contributions from each irreducible representation of the point group of the interacting system. Since the molecules in our study have at least C_s symmetry, it is possible to estimate the intrinsic strength of orbital interactions from orbitals having a′ (σ) and a″ (π) symmetry quantitatively. This directly gives the contributions of the σ and π orbital interactions to the ΔE_{orb} term. To obtain the bond dissociation energy D_e the preparation energy ΔE_{prep}, which gives the relaxation of the fragments into their electronic and geometrical ground states, must be added to the interaction energy: $-D_e = \Delta E_{\mathrm{int}} + \Delta E_{\mathrm{prep}}$. Further details on the EDA can be found in the literature [115, 116].

Table 4 gives the EDA results for the metal complexes **N–W(CO)$_5$**, **N–Ni(CO)$_3$**, and **N–Ni(CO)$_2$** for **N** = **1**, **5**, **6**, **9** which have been published [97]. The EDA results for the metal–CO bonds of $[W(CO)_6]$ and $[Ni(CO)_4]$ are given for comparison [117, 118]. The calculated energy terms suggest that the **N–W(CO)$_5$** bonds have a larger electrostatic than covalent character. The $\Delta E_{\mathrm{elstat}}$ values are always bigger than the ΔE_{orb} term. The orbital interactions in **N–W(CO)$_5$** mainly come from the σ orbitals which contribute 73–75% to the ΔE_{orb} term. The rather small π-bonding contribution distinguishes the bonds of the divalent carbon ligands from the OC–W(CO)$_5$ bond which has a stronger π-bonding contribution than σ-bonding contribution (Table 4). The π-contribution to the ΔE_{orb} term in the nickel complexes **N–Ni(CO)$_3$** is even smaller than in the tungsten analogs **N–W(CO)$_5$**. This is also the main difference between the **N–Ni(CO)$_3$** and the **OC–Ni(CO)$_3$** bonds. The latter has a stronger π-bonding contribution than σ-bonding contribution. Note that the electrostatic attraction in the nickel complexes **N–Ni(CO)$_3$** is very similar to the tungsten analogs **N–W(CO)$_5$** although the atomic partial charges at the *N*–Ni bonds have opposite signs while the *N*–W bonds have the same sign (Table 4).

Are the shorter and stronger N–Ni bonds in the 16-electron complexes **N–Ni(CO)$_2$** due to a larger contribution from $L_2C \rightarrow Ni$ π-donation from the second lone-pair orbital of the carbon donor atom? Is there a qualitative difference in the bonding situation between the **N–Ni(CO)$_2$** complexes and the 18-electron complexes **N–Ni(CO)$_3$**? The comparison of the $\Delta E_{\pi\perp}(b_1)$ values in the divalent C(0) 16-electron complexes **1-Ni(CO)$_2$** and **6-Ni(CO)$_2$** with the data for $\Delta E_{\pi}(a'')$ in the 18-electron homologues indeed shows an increase from 7.4% to 15.0% for the CDP complexes

Table 4 EDA results (BP86/TZ2P) of **N–W(CO)$_5$**, **N–Ni(CO)$_3$** and **N–Ni(CO)$_2$** where N = **1**, **5**, **6**, **9**, CO. The **N–W(CO)$_5$** and **N–Ni(CO)$_3$** complexes (except **5-Ni(CO)$_2$**) have been optimized under C_{2v}-symmetry constraints, for **N–Ni(CO)$_3$** and **5-Ni(CO)$_2$**) C_s-symmetry was applied. Energy values are given in kcal/mol

	1-W(CO)$_5$		**5-W(CO)$_5$**		**6-W(CO)$_5$**		**9-W(CO)$_5$**		**OC-W(CO)$_5$**	
ΔE_{int}	−47.0		−20.0		−60.9		−57.8		−49.6	
ΔE_{Pauli}	95.4		51.1		128.6		123.3		118.6	
$\Delta E_{\text{elstat}}{}^{a}$	−95.0	(66.7%)	−38.4	(54.0%)	−132.7	(70.0%)	−128.5	(70.9%)	−89.7	(53.3%)
$\Delta E_{\text{orb}}{}^{a}$	−47.5	(33.3%)	−32.7	(46.0%)	−56.9	(30.0%)	−52.6	(29.1%)	−78.6	(46.7%)
$\Delta E_{\sigma}(\text{a}_1)^{b}$	−35.4	(74.6%)	−23.8	(72.7%)	−42.1	(74.0%)	−38.6	(73.3%)	−36.3	(46.1%)
$\Delta E_{\delta}(\text{a}_2)^{b}$	−0.6	(1.2%)	−0.4	(1.3%)	−1.2	(2.1%)	−0.5	(0.9%)	0.0	(0.0%)
$\Delta E_{\pi\perp}(\text{b}_1)^{b}$	−6.0	(12.7%)	−3.0	(9.0%)	−7.3	(12.9%)	−9.1	(17.3%)	−21.2	(26.9%)
$\Delta E_{\pi\parallel}(\text{b}_2)^{b}$	−5.5	(11.6%)	−5.6	(17.0%)	−6.3	(11.0%)	−4.5	(8.5%)	−21.2	(26.9%)
ΔE_{prep}	3.9		4.0		8.4		2.4		3.9	
$\Delta E_{\text{prep}}(\text{N})$	2.4		3.1		5.8		0.4		0.4	
$\Delta E_{\text{prep}}(\text{TM})$	1.5		0.9		2.6		2.0		3.5	
$\Delta E(=-D_e)$	−43.1		−16.0		−52.5		−55.5		−45.7	
$d(N\text{–TM})$	2.335		2.411		2.357		2.230		2.060	
	1-Ni(CO)$_3$		**5-Ni(CO)$_3$**		**6-Ni(CO)$_3$**		**9-Ni(CO)$_3$**		**CO–Ni(CO)$_3$**	
ΔE_{int}	−35.5		−14.4		−50.1		−47.0		−40.4	
ΔE_{Pauli}	95.7		59.3		122.8		129.3		129.0	
$\Delta E_{\text{elstat}}{}^{a}$	−89.7	(68.4%)	−44.7	(60.8%)	−120.9	(69.9%)	−127.1	(72.1%)	−101.7	(60.0%)
$\Delta E_{\text{orb}}{}^{a}$	−41.5	(31.6%)	−28.9	(39.2%)	−52.0	(30.1%)	−49.2	(27.9%)	−67.7	(40.0%)
$\Delta E_{\sigma}(\text{a}')^{b}$	−38.4	(92.6%)	−26.8	(92.8%)	−48.4	(93.2%)	−41.4	(84.1%)	−49.6	(73.2%)
$\Delta E_{\pi}(\text{a}'')^{b}$	−3.1	(7.4%)	−2.1	(7.2%)	−3.6	(6.8%)	−7.8	(15.9%)	−18.1	(26.8%)
ΔE_{prep}	8.7		7.6		13.6		8.8		11.1	
$\Delta E_{\text{prep}}(\text{N})$	1.9		3.2		5.0		0.4		0.2	
$\Delta E_{\text{prep}}(\text{TM})$	6.8		4.4		8.6		8.4		10.9	
$\Delta E(=-D_e)$	−26.8		−6.7		−36.4		−38.1		−29.3	
$d(\text{N–TM})$	2.068		2.137		2.083		1.954		1.815	

	1-Ni(CO)$_2$		**5-Ni(CO)$_2$**		**6-Ni(CO)$_2$**		**9-Ni(CO)$_2$**	
ΔE_{int}	−43.5		−46.4		−61.8		−50.4	
$\Delta E_{\mathrm{Pauli}}$	103.4		130.7		129.7		125.6	
$\Delta E_{\mathrm{elstat}}{}^{a}$	−101.8	(69.3%)	−88.8	(50.1%)	−141.2	(73.7%)	−131.9	(74.9%)
$\Delta E_{\mathrm{orb}}{}^{a}$	−45.1	(30.7%)	−88.4	(49.9%)	−50.3	(26.3%)	−44.1	(25.1%)
$\Delta E_{\sigma}(\mathrm{a}_1)^{b}$	−32.0	(70.9%)			−34.4	(68.3%)	−31.3	(70.9%)
$\Delta E_{\delta}(\mathrm{a}_2)^{b}$	−0.2	(0.5%)			−0.4	(0.8%)	0.1	−(0.3%)
$\Delta E_{\pi\perp}(\mathrm{b}_1)^{b}$	−6.8	(15.0%)			−6.9	(13.6%)	−8.1	(18.2%)
$\Delta E_{\pi\parallel}(\mathrm{b}_2)^{b}$	−6.1	(13.6%)			−8.7	(17.4%)	−4.9	(11.1%)
$\Delta E_{\sigma}(\mathrm{a}')^{b}$			−78.8	(89.2%)				
$\Delta E_{\pi}(\mathrm{a}'')^{b}$			−9.5	(10.8%)				
ΔE_{prep}	6.8		27.1		14.3		5.8	
$\Delta E_{\mathrm{prep}}(\mathrm{N})$	1.7		15.9		5.7		0.3	
$\Delta E_{\mathrm{prep}}(\mathrm{TM})$	5.1		11.2		8.5		5.5	
$\Delta E(=-D_{\mathrm{e}})$	−36.7		−19.3		−47.5		−44.6	
$d(N\text{–TM})$	1.953		1.919		2.001		1.927	

[a] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{orb}}$

[b] The percentage values in parentheses give the contribution to the total orbital interactions ΔE_{orb}

1-Ni(CO)$_n$ and from 6.8% to 13.6% for the carbodicarbene complexes **6-Ni(CO)$_n$**. The change in the π-bonding contribution in the carbon suboxide complexes **5-Ni(CO)$_n$** is not really meaningful because the nature of the $(CO)_2C–Ni(CO)_n$ bond significantly changes from $n = 3$ where the carbon suboxide ligand is η^1-bonded to $n = 2$ where it is η^2-bonded. The latter species has a significantly more covalent bond ($\Delta E_{orb} = 49.9\%$) than the former complex ($\Delta E_{orb} = 39.1\%$) which comes mainly from the in-plane (a′) orbital interactions. The π-bonding contributions in **1-Ni(CO)$_2$** (15.0%) and **6-Ni(CO)$_2$** (13.6%) are still significantly smaller than the 26.8% π-bonding which is calculated for the $OC–Ni(CO)_3$ bond (Table 4). However, the latter value refers to the $OC \leftarrow Ni(CO)_3$ π backdonation whereas the former values come from $L_2C \rightarrow Ni(CO)_2$ π donation. The stability of the experimentally observed [107] 16-electron complex **3-Ni(CO)$_2$** may be caused by the steric interactions between the bulky $C(PPh_3)_2$ ligand and the metal fragment. Steric interactions are most likely the reason that the homologue of the 16-electron NHC complex **9-Ni(CO)$_2$** which has very bulky substituents at nitrogen could becomes isolated [111].

5 Experimental Studies of Metal Complexes with Carbodiphosphoranes and Related Ligands

In this section we review experimental work about transition metal complexes bearing divalent carbon(0) ligands $[M]–CL_2$.

5.1 Transition Metal Complexes of $C(PPh_3)_2$

The majority of transition metal complexes $[M]–CL_2$ are known with $C(PPh_3)_2$ as ligand CL_2 while the coordination ability of other symmetrical carbodiphosphoranes remains unexplored as yet. General preparation methods to introduce this ligand consists in a reaction between the free double ylide and a transition metal complex with a labile bonded ligand or compounds with a vacant coordination site.

Earlier reports on carbonyl adducts of $C(PPh_3)_2$, especially on the carbene-like complex $[(CO)_5W(C\{PPh_3\}_2)]$ (**11**), were presented by the group of Kaska but without presenting sufficient characterization or structural proof [119, 120]. The results of our own experiments with tungsten carbonyl compounds are quite different. If the photochemically generated $[(CO)_5W(THF)]$ was reacted with a THF solution of $C(PPh_3)_2$, quantitative precipitation of the salt like compound $(HC\{PPh_3\}_2)_2[W_2(CO)_{10}]$ was obtained under deprotonation of the solvent; however, the initial formation of **11** cannot be excluded but also cannot be evidenced. In benzene or toluene solution the reaction is much more complicated and leads to several products which can be traced by ^{31}P NMR spectroscopy. Thus, in benzene solution $[W(CO)_6]$ and $C(PPh_3)_2$ slowly form the Wittig product $[(CO)_5W(C\{PPh_3\}_2)]$ along with the CO_2 insertion product $[(CO)_5WOC(O)C(PPh_3)_2]$; the latter originates from $OPPh_3$ according to (7)–(10). Free CO_2 is immediately consumed by $C(PPh_3)_2$ to give the addition compound $O_2C–C(PPh_3)_2$. The origin of CO_2 is due to the oxidation of CO by $OPPh_3$ according to (8) [121]:

$$[W(CO)_6] + C(PPh_3)_2 \rightarrow \left[(CO)_5W(C_2PPh_3)\right] + OPPh_3 \tag{7}$$

$$[W(CO)_6] + OPPh_3 \rightarrow \text{``}W(CO)_5\text{''} + CO_2 + PPh_3 \tag{8}$$

$$C(PPh_3)_2 + CO_2 \rightarrow O_2C-C(PPh_3)_2 \tag{9}$$

$$\text{``}W(CO)_5\text{''} + O_2C-C(PPh_3)_2 \rightarrow \left[(CO)_5WOC(O)C(PPh_3)_2\right] \tag{10}$$

The carbonyl compounds $[Fe(CO)_5]$, $[Mn_2(CO)_{10}]$, and $[Co_2(CO)_8]$ react in the same manner and no traces of a neutral or cationic carbodiphosphorane complex can be detected. In the case of these earlier and middle carbonyls in non-polar solvents, apparently the hard nature of $C(PPh_3)_2$ comes into force upon attacking a carbonyl carbon atom and formation of the C_2PPh_3 ligand [122]; in THF, DME, quantitatively the related salts $(HC\{PPh_3\}_2)[M(CO)_x]$ ($M = Mn$, $x = 5$; $M = Co$, $x = 4$) were formed upon deprotonation of the solvent [123, 124].

Furthermore, a red nickel carbonyl complex was mentioned and formulated as $[(CO)_3Ni(C\{PPh_3\}_2)]$ [120], but no crystal structure was presented. The group of Petz found that the outcome of the reaction of $C(PPh_3)_2$ with $Ni(CO)_4$ depends on the choice of the solvent. In toluene, beautiful bright yellow crystals were obtained which turned out to be the complex $[(CO)_3Ni(C\{PPh_3\}_2)]$ (**12**); however, if THF is used as the solvent, mainly dark red crystals of the dicarbonyl complex $[(CO)_2Ni(C\{PPh_3\}_2)]$ (**13**) were formed. Compound **12** can reversibly be converted into **13** upon attachment to the vacuum line while addition of gaseous CO reconverts the tricarbonyl complex [107]. In this late nickel carbonyl complex the CO groups are more labile and displacement occurs prior to carbonyl C attack. The crystal data of **12** and **13** allows a better understanding of the bonding situation in carbonyl complexes of $C(PPh_3)_2$. In **12** and **13** the donating carbon atom is exactly planar coordinated according to conformation mode **I**. In **13** the C–Ni–C and P–C–P planes are twisted by about 9° [107]. The carbonyl complexes are collected in Fig. 19.

A quite different situation is found in the cationic Re(VII) complex **14** with ReO_4^- as counter ion which is obtained from Re_2O_7 and $C(PPh_3)_2$ as shown in Fig. 20. The long P–C bonds to the ylidic carbon atom suggest a strong reduction of the negative p–σ* hyperconjugation in favor of an Re=C double bond in which the

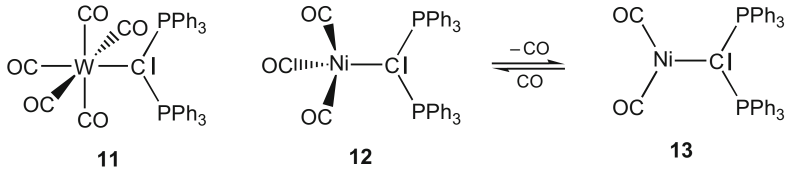
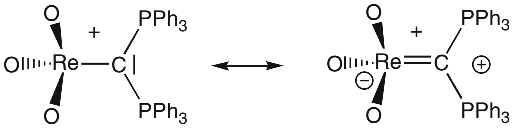


Fig. 19 Complexes of $C(PPh_3)_2$ with low valent transition metal carbonyls

Fig. 20 Cationic complex of $C(PPh_3)_2$ with a high valent Re transition metal fragments



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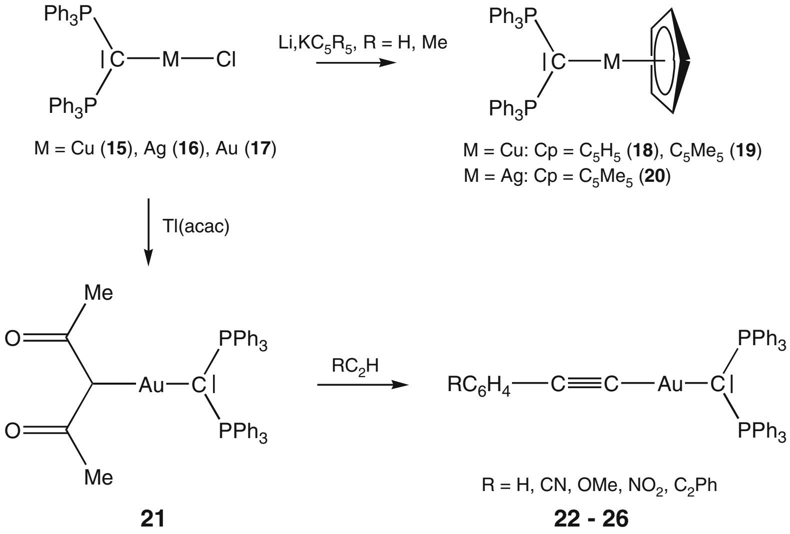
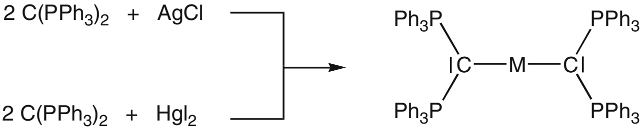


Fig. 21 Various compounds of Cu, Ag, and Au with one $C(PPh_3)_2$ ligand

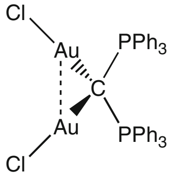
ligand acts as a four electron donor by σ and π interaction with the metal atom [125]; in **12** and **13** these bond lengths are about 0.1 Å shorter. An iridium cod complex with $C(PPh_3)_2$ as ligand, mentioned in [126], is highly speculative because neither spectroscopic nor structural proofs were presented.

Various Group 11 and group 12 compounds have been published containing the intact $C(PPh_3)_2$ ligand. A series of $ClMC(PPh_3)_2$ with M = Cu (**15**) [127–129], Ag (**16**) [127–129], Au (**17**) [127–130] were reported; for the gold complex **17** [(CO)AuCl] can also be used as source. The compounds were prepared by addition of the appropriate MCl to one equivalent of $C(PPh_3)_2$ in THF; the sterically demanding PPh_3 groups favor the linear Cl–M–C arrangement; a crystal structure for **15** is provided. Ligand exchange of the chloride ion of **15** and **17** with $(C_5H_5)^-$ or $(C_5Me_5)^-$ or the reaction of the radical $[\mathbf{CpCu}]^{\cdot}$ with $C(PPh_3)_2$ leads to the copper cyclopentadienide complexes **18** and **19**, respectively; similar exchange of **16** gives **20** [62]. Ligand exchange in the gold complex **17** with Tl(acac) gives **21** from which the acac group can be removed by monosubstituted alkynes and formation of the compounds **22–26** [130]; the group 11 transition metal complexes with one intact $C(PPh_3)_2$ ligand are collected in Fig. 21.



M = Ag$^+$ (**27**), Hg^{2+} (**28**)

Fig. 22 Preparation and structures of the cations $[Ag(C\{PPh_3\}_2)_2]^+$ (**27**) and $[Hg(C\{PPh_3\}_2)_2]^{2+}$ (**28**)



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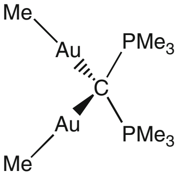

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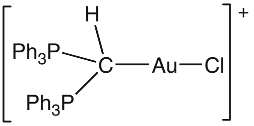
Fig. 23 Structures of $[(ClAu)_2C(PPh_3)_2]$ (**29**) and $[(MeAu)_2C(PPh_3)_2]$ (**30**) obeying coordination mode **III**

New outstanding results were obtained in the preparation of compounds with either two $C(PPh_3)_2$ ligands at the same metal (Fig. 22) or of a complex with one carbodiphosphorane coordinated to two metal fragments as shown in Fig. 23.

The first compounds containing two $C(PPh_3)_2$ ligands are cationic adducts with Ag^+ and Hg^{2+} ions and were synthesized in the group of Petz from AgCl or $AgBF_4$ and HgI_2 and $C(PPh_3)_2$ in THF solution; Cl^- and $BF_4{}^-$ act as counterions of **27** whereas $Hg_2I_6{}^{2-}$ is formed as counterion of **28**. X ray analyses show that the metal atoms are linearly coordinated and both PCP planes are twisted by 67° (Ag) and 77° (Hg), respectively. The Ag–C and Hg–C bond lengths amount to 2.115(8) Å and 2.070(6) Å, respectively. In the mercury compound **28** a slight pyramidization at the coordinating carbon atoms is observed. The sum of the angles at the carbon atom of 358° and 356° can be interpreted either in terms of packing effects or of a slight tendency to coordination mode **II′**. The carbon atoms are extended by 0.13 Å and 0.11 Å out of the P_2Hg plane [131].

In transition metal complexes with the intact $C(PPh_3)_2$ ligand of coordination mode **I** (Fig. 10) only two parameters, such as the P–C distances and P–C–P angles, can be influenced upon coordination to the metal, depending on the interaction of the filled p orbital at the carbon atom with metal orbitals. The free ligand exhibits an extremely short P–C bond distance of 1.635 Å. The P–C–P angle is very flexible and values between 130° and 140° were measured. Based on about five crystal structures of compounds with Cu(I), Ag(I) and Ni(0) metals, a mean P–C value of 1.674 Å is estimated. The bond elongation is indicative of a medium reduction of the p–σ*(P–C) interaction. In the case of high valent metal such as Re(VII) the P–C bond length has increase to 1.770(8) Å which can be interpreted in terms of a Re=C double bond with a σ/π 4 electron donor ability. The P–C–P angles are less sensitive to coordination but drop down in most cases below 130° and no dependence from the Lewis acid attached can be seen.



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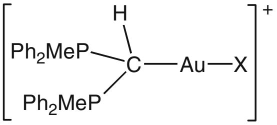

X = Cl (**32**), C_6F_5 (**33**)

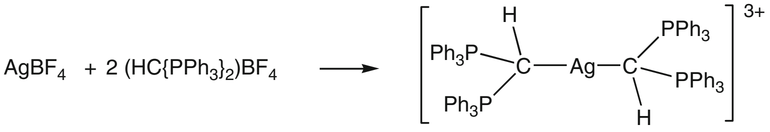

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Fig. 24 Type III complexes with the ylide $(HC\{PPh_3\}_2)^+$

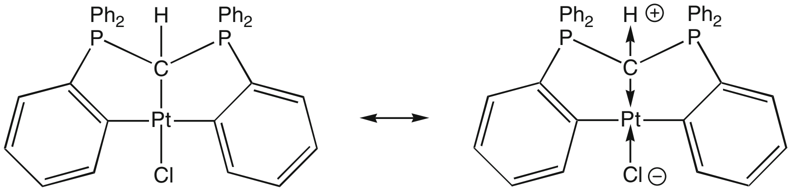

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Fig. 25 Pt(II) complex **36** as the first and unique example of a doubly *ortho* metalated complex with coordination mode **III**

A unique transition metal complex which represents the coordination mode **III** (Fig. 10) was also presented by the group of Vicente. They obtained the first example with two Lewis acids coordinated at the ylidic carbon atom by treating the gold complex **17** with 0.5 equivalent of $C(PPh_3)_2$ in CH_2Cl_2 solution. The structure was determined by X ray analysis (Fig. 23). The resulting complex **29** has an sp^3 carbon atom and the PCP plane is nearly perpendicular to the AuCAu plane. Both gold atoms are connected by an aurophilic contact amounting to 3.1432(2) Å, which is probably responsible or even prerequisite for this unusual coordination mode [130]. The related compound **30** with the double ylide $C(PMe_3)_2$ was formulated without an aurophilic interaction; however no structural prove is given [132, 133].

In principle coordination mode **III** (Fig. 10) can also be viewed in the few known compounds containing the cation $(HC\{PPh_3\}_2)^+$ or $(HC\{PMePh_2\}_2)^+$ as complex ligands as shown in Figs. 24 and 25. The cationic compounds can be regarded as complexes between one transition metal fragment A and the proton H^+ as a second Lewis acid to give $A \leftarrow C(PPh_3)_2 \rightarrow H^+$ compounds. Although these cations possess one pair of electrons the positive charge gives them the character of only a weak nucleophile. Thus, $[ClAu(HC\{PPh_3\}_2)]TfO$ (**31**) is obtained from ClAu(tht)

(tht = tetrahydrothiophene) and $(HC\{PPh_3\}_2)TfO$ [130]. The compounds **32** and **33** containing the cation $(HC\{PMePh_2\}_2)^+$ as ligand were obtained similarly; the X ray structure of **33** shows an almost linear C–Au–C array of 176° [134]. Preparation and crystal structure of the unusual trication $[Ag(HC\{PPh_3\}_2)_2][BF_4]_3$ (**34**) was reported recently. Based on coordination mode **II′** the ions H^+ and Ag^+ play the role of the two Lewis acids at the ylidic carbon atom of $C(PPh_3)_2$. In the presence of other than weakly coordinating anions such as BF_4^-, removal of $(HC\{PPh_3\}_2)^+$ occurs. The Ag–C bond lengths in **34** are about 0.1 Å longer than those found in **27** and belong to the longest values ever described [2, 3]. The related gold trication **35** (as the TfO salt, not shown in Fig. 24) was mentioned but without being established by a crystal structure analysis [130].

An unusual combination between a coordination mode **III** complex and doubly *ortho* metalation (see below) is found in the unique complex **36** in Fig. 25. If we consider the coordination of the CHP_2 unit as a cationic carbon donor, like the cation $(HC\{PPh_3\}_2)^+$ in Fig. 24 for the metal the oxidation state Pt(II) is more likely rather than Pt(IV) [135].

The sum of the angles P–C–P, P–C–Pt, and P–C–Pt in **36** amounts to 342° which is larger than for a tetrahedral arrangement but agrees well with an sp^3 carbon atom. The Pt–C bond length amounts to 2.051(6) Å and is closely related to those in **41** and **42**. As expected, the relevant P–C distances in **36** are very long (1.800(6) Å) and correspond to a pure single bond [135]. Similar long distances were measured for compounds **33** [134] and **34** (1.785(6) Å) [2, 3]. The P–C–P angles in **33**, **34**, and **36** are more acute than those in $C(PPh_3)_2$ complexes and are close together, amounting to 119°, 119°, and 123°, respectively, reflecting the proximity to sp^3 hybridization at the donating carbon atom.

Unusual *ortho* metallation of one or two phenyl groups of $C(PPh_3)_2$ is observed by reacting with some second and third row group 9 and 10 transition metal compounds. As mentioned before, transition metal precursors were compounds with either vacant coordination sites or easily removable ligands. Doubly *ortho* metalated compounds can also be seen as pincer carbodiphosphoranes.

A first report about an ortho metalation of a phenyl group of $C(PPh_3)_2$ was presented in 1979. As the results of the reaction with $[Me_3Pt]PF_6$ or $[Me_3PtTfO]_4$ complex **37** was formulated (Fig. 26). Depending on the molar ratio of the reactants, a Pt(II) complex was obtained for which formula **38** was suggested; a methyl transfer to one phenyl ring was deduced from spectroscopic data [70, 71]. The platinum complex **39** was obtained through reaction of the Pt(II) complex $[Me_2Pt(SMe_2)]_2$ with $C(PPh_3)_2$ via double metalation and evolution of methane [136]. The allyl palladium complex **40** with unilateral *ortho*-metalation was obtained upon reaction of $C(PPh_3)_2$ with $[\{ClPd(allyl)\}_2]$ [39–42]. The first Pt compound established by an X ray analysis was **41** which formed upon ortho platination of one phenyl ring and additional CH activation of the cod ligand by reacting three equivalents of $C(PPh_3)_2$ with $[X_2Pt(cod)]$ (X = Cl, I) in THF solution; THF insoluble $(HC\{PPh_3\}_2)X$ could be separated [137]. Compound **41** is not stable in halogenated hydrocarbons and is quantitatively converted into the type **III** complex **36**. Surprisingly, crystals of the doubly orthoplatinated pincer carbonyl complex **42**

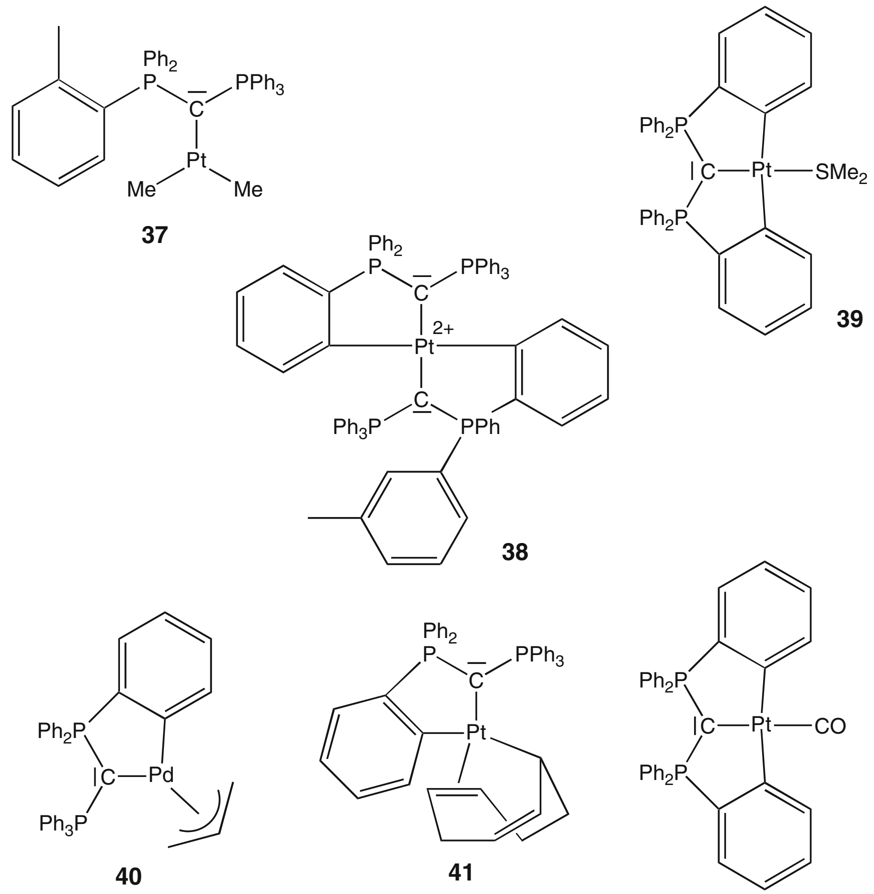
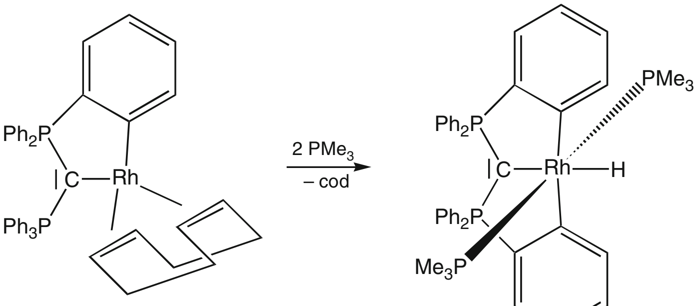


Fig. 26 Singly and doubly *ortho*-metalated Pt and Pd complexes of $C(PPh_3)_2$

were obtained from a solution of **41** in $CDCl_3$ upon standing of the solution for several weeks. The formation of an intermediate dichlorocarbene complex was suggested in which the CCl_2 ligand was hydrolyzed under formation of the CO ligand upon contact with traces of water introduced via a leaking stopcock. The central unit of **42** is planar and the P–C–P angle amounts to 128.4(3)°. The P–C bond distance (1.706(3) Å) is longer than the mean value in other complexes with the intact $C(PPh_3)_2$ ligand indicating lower bond order [135].

Besides Pt and Pd *ortho*-metalated species, related Rh complexes were also prepared which are shown in Fig. 27. Thus, the reaction of four equivalents of $C(PPh_3)_2$ with $[ClRh(cod)]_2$ produces the complex **43**; as with the Pt compounds the *ortho* proton of the phenyl group is removed with formation of the salt $(HC\{PPh_3\}_2)Cl$. Addition of two equivalents of PMe_3 to **43** causes a second *ortho*-metallation with loss of cod and H transfer to the metal to give the Rh(III)



43 **44**

Fig. 27 Preparation of the Rh(I) and Rh(III) cyclometalated $C(PPh_3)_2$ compounds **43** and **44**

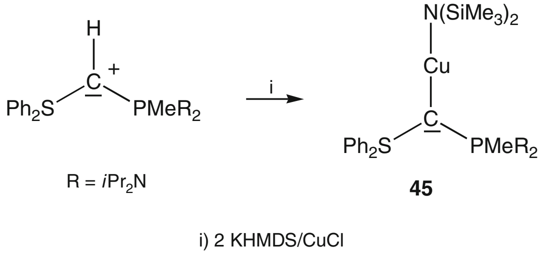
hydride complex **44**. This can also be seen as an insertion of Rh into the ortho phenyl C–H bond or oxidative addition of this bond to Rh; the crystal structure exhibits a planar arrangement with the PMe_3 groups completing the octahedral coordination [136].

For the semi and doubly *ortho* metalated **41**, **42**, **43**, and **44** crystal structures were presented which allow a comparison of the parameters with those containing the intact $C(PPh_3)_2$ ligand. The P–C bond lengths in the unilateral metalated compounds **41** and **43** and in the bis metalated Pt(II) complex **42** are slightly elongated, whereas the P–C bond length in the octahedral Rh(III) complex **44** joins the mean values of compounds with the intact ligand. The P–C–P angles normally range between 121° and 128° with the exception of that of **43** being, at 138.3°, the greatest throughout the carbodiphosphorane Complexes.

An interesting variant of a carbodiphosphorane $C(L)_2$ compound is $C(PPh_2CH_2PPh_2)_2$ containing two functional CH_2PPh_2 groups [148]. The cationic pincer complex 77 (counterion is Cl^-) of coordination mode **I** (Fig. 10) was the direct result of a three component reaction between $PdCl_2$, CS_2 and the chelating ligand $Ph_2PCH_2PPh_2$ (dppm) as depicted in Fig. 36. The free ligand was not yet isolated and the mechanism of its formation is unclear so far. The ylidic carbon atom stems from CS_2 and dppm acts as desulfurization agent to give $Ph_2PCH_2P(S)Ph_2$. Further addition of HCl to 77 produced the dicationic compound **78** of coordination mode **III** in good yields.

Treatment of 77 with one equivalent of [AuCl(tht)] (tht = tetrahydrothiophene) leads to the type **III** AuCl bridged pincer complex **79** in high yield (counterion is Cl^-) [149]. The unique complex **79** is the only heterodimetallic compound with two metal atoms attached at a carbodiphosphorane carbon(0) atom. The environment at the central carbon atom is planar in **77** and pyramidal in **78** and **79**. P–C bond lengths and P–C–P angles in the dication **78** are closely related to those in the neutral Pt complex **36** (Fig. 25). The two metals of **79** attached to the carbon atom are connected via a very short d^8-d^{10} pseudo closed shell interaction with a Pd-Au bond length of 2.8900(3) Å; a similar bonding situation (aurophilic attraction) is found in the gold complex **29** shown in Fig. 23.

Fig. 28 Preparation of complex **45** containing the double ylide $C(PMeR_2)(SPh_2)$ as ligand



5.2 Transition Metal Complex of the CLL′ Double Ylide C(PMeR₂)(SPh₂)

The mixed double ylide copper complex **45** was not obtained by reacting the ylide with a copper complex but upon deprotonation of its conjugated acid $(HC\{PMeR_2\}\{SPh_2\})TfO$ in the presence of CuCl as depicted in Fig. 28. The X ray analysis of **45** shows a similar geometry to that of a related carbodiphosphorane copper complex; the P–C–S angle is rather acute amounting to 115.3° and the P–C and S–C bond lengths are slightly shorter than those of the related cation $[HC(PMeR_2)(SPh_2)]^+$ [45, 46].

5.3 Transition Metal Complexes with Cyclic Carbodiphosphoranes

Transition metal complexes of coordination mode **I** with the cyclic carbodiphosphorane shown in Fig. 13 were obtained upon reacting the ligand with CuCl (**46**), $[AuCl(SMe)_2]$ (Cl exchange by O*t*-Bu gives (**47**) and (**48**)) [138], $[ClRh(CO)_2]_2$ (**49**), $[ClRh(nbd)]_2$ (**50**), or $[ClPd(allyl)]_2$ (**51**) [39–42]. A collection of the metal complexes is presented in Fig. 29.

The structures of six complexes were established by X-ray analyses. The copper and gold compounds **46–48** show a linear arrangement of the ligands about the metal. As expected, the rigidity of the five membered ligand skeleton does not allow strong variations in the P–C–P angles; in all compounds a slight opening of about 1°–4° is observed upon complex formation. The P–C distances, showing the degree of hyperconjugation, are also slightly elongated as reported for related complexes of $C(PPh_3)_2$. Long C–M bonds are indicative for the presence of a metal to carbon single bond with weaker back donation as to NHC ligands [39–42, 138].

5.4 Transition Metal Complexes with C(PPh₃)(CO) as η¹ Bonded Ligand

There are only very few transition metal complexes with $C(PPh_3)(CO)$ ligands which have been synthesized so far. In general an η^1 coordination at Lewis acids

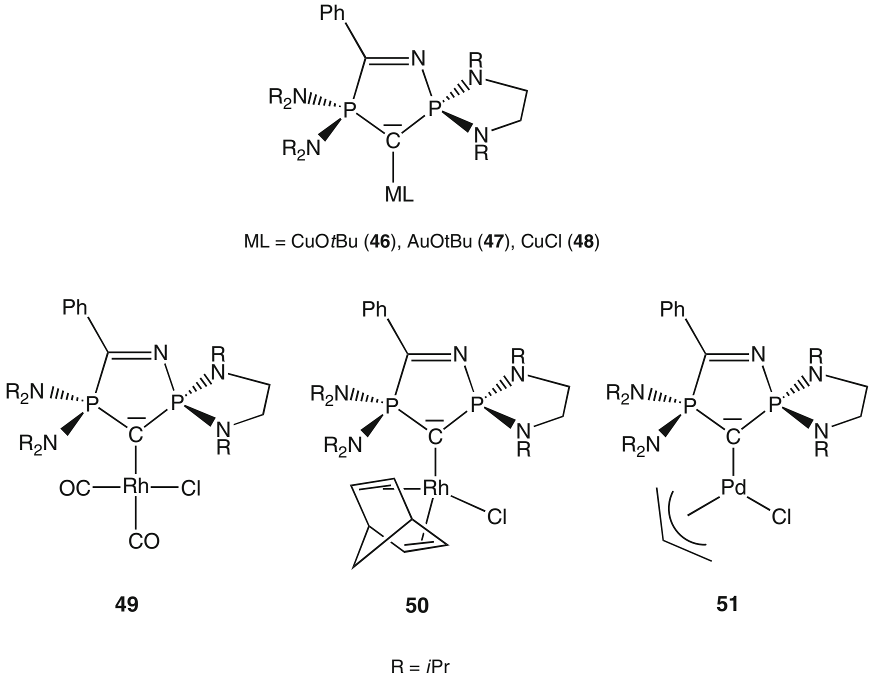
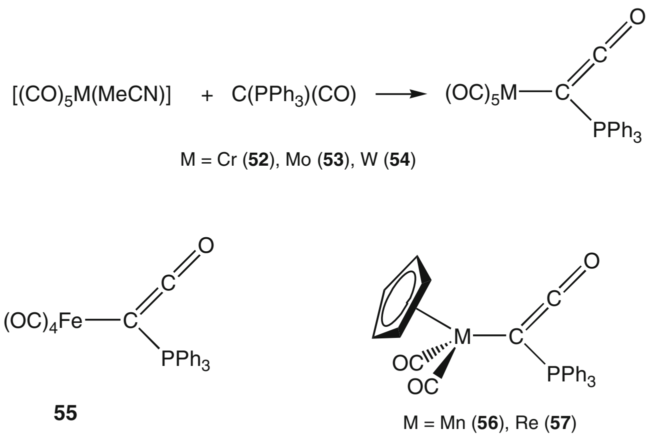


Fig. 29 Transition metal complexes of *P*-heterocyclic carbodiphosphoranes

via the carbon atom is observed. However, in the case of the ylide C(PPh$_2$Me)(CO) an η^2-(C,C) coordination to tungsten was reported [58, 59]; such compounds will not be considered here. For the preparation of carbonyl derivatives to introduce the C(PPh$_3$)(CO) ligand usually precursors with weakly bonded ligands are used. The first examples of metal bonded C(PPh$_3$)(CO) were derivatives of group 6 carbonyl compounds and as starting materials the photochemically generated acetonitrile complexes [(CO)$_5$M(MeCN)] were used to give **52**–**54**. For **54** the pure hexacarbonyl was reacted [139–141].

The related iron carbonyl complex **55** was obtained by the reaction of [Fe$_3$(CO)$_{12}$] with C(PPh$_3$)(CO); however, according to [95] it is questionable because the spectroscopic data do not match with those of related compounds. The Mn and Re complexes [Cp(CO)$_2$M{C(PPh$_3$)(CO)}] (M = Mn (**56**), Re (**57**)) have also been reported; the ylide replaces the labile ether ligand in [Cp(CO)$_2$M (OEt$_2$)] [142]. The examples with the η^1 bonded ketenylidene ligand C(PPh$_3$)(CO) are summarized in Fig. 30.

A series of Pt(II) compounds including one Pd(II) complex were synthesized by the group of Pandolfo [95]. With the Zeise's salt K[PtCl$_3$(C$_2$H$_4$)] or [PtCl$_2$(C$_2$H$_4$)]$_2$ as sources and one equivalent of C(PPh$_3$)(CO) the complex **58** is formed (Fig. 31); further addition of the ligand to **58** or to [{PtCl$_2$(C$_2$H$_4$)}$_2$] replaces all ethylene molecules to generate the bis-ylide complex **59** in high yields; the Pt atom in **59** is located on an inversion center and coordination about Pt is exactly planar [143].

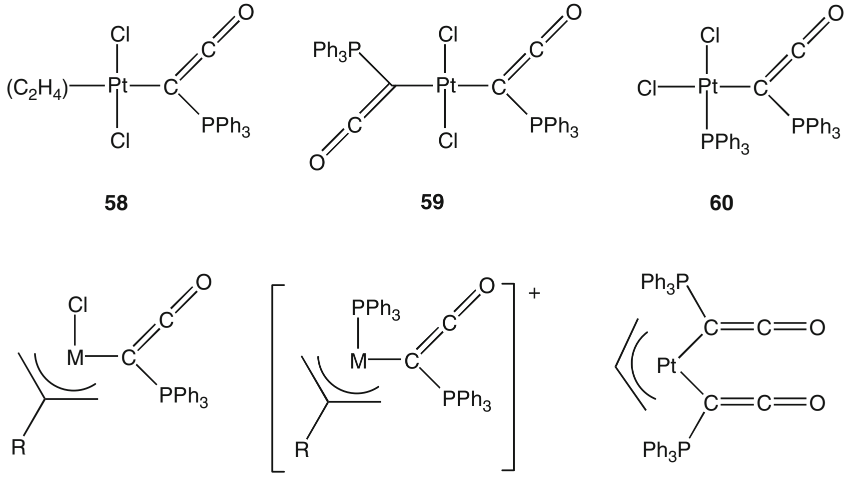


M = Cr (**52**), Mo (**53**), W (**54**)

55

M = Mn (**56**), Re (**57**)

Fig. 30 $C(PPh_3)(CO)$ complexes from group 6, 7 and 8 carbonyl complexes



58 **59** **60**

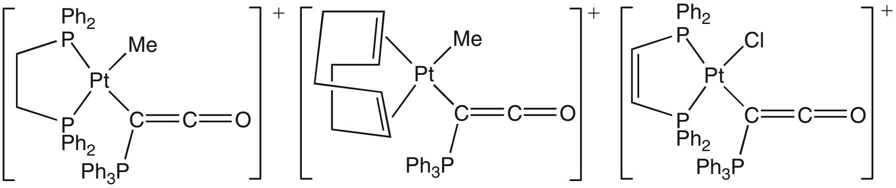
M = Pt, R = H (**61**)
M = Pd, R = H (**62**); R = Me (**63**)

M = Pt, R = H (**65**)
M = Pd; R = Me (**66**)

64

Fig. 31 Pt and Pd compounds with one or two η^1 bonded $C(PPh_3)(CO)$ ligands

The nucleophilicity of the ketenyl ylide is strong enough to break the chlorine bond in dimeric $[PtCl_2(PPh_3)]_2$ to give **60** and similarly, in the tetrameric allyl complex $[Pt(C_3H_5)Cl]_4$ with **61** resulting; the dimeric Pd analog gives **62** and **63**. Consecutive reaction of **61** with $AgBF_4$ (to remove Cl as AgCl) and with a further molecule of the ketenyl ylide produces the *cis*-bis-η^1-ketenyl ylide complex **64** [144, 145]. The same group was also successful in the preparation of cationic complexes with the ylide ligand. The related $[(allyl)M(PPh_3)Cl]$ was first treated with $AgBF_4$ followed by addition of the ketenyl ligand to produce **65** and **66** with the BF_4 anion [145].



67 **68** **69**

Fig. 32 Pt compounds with additional chelating ligands and one η^1 bonded C(PPh$_3$)(CO) ligand

The cationic compounds **67** and **68** containing chelating ligands were synthesized as the BF$_4$ salts following standard procedures involving the formation of a coordinative vacancy on the related [(chel)PtMeCl] with Ag$^+$ followed by addition of C(PPh$_3$)(CO). Splitting of the cation [(diphos)PtCl]$_2$(BF$_4$)$_2$ with the ligand generates complex **69** as shown in Fig. 32 [146].

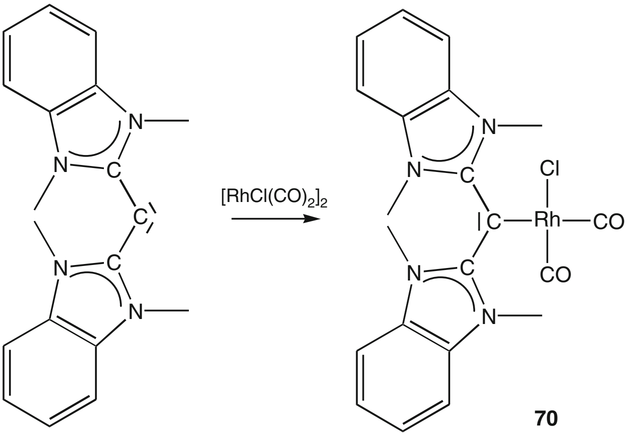
From two crystal structure determinations (compounds **59** and **65**) some trends in ligand parameters upon coordination of C(PPh$_3$)(CO) to the metal become apparent. The P–C and C–C bond lengths increase by about 0.11 and 0.07 Å, respectively, relative to those of the free ligand, indicating electron release from the donating carbon atom; the P–C–C angles are more acute, ranging about 116° which supports the increased ylidic character of the ligand when bonded to the metal [95, 145].

5.5 Transition Metal Complexes with C(NHC)$_2$ and with C{C(NMe$_2$)$_2$}$_2$ as Ligands

As yet, with regard to both ligands C(NHC)$_2$ and C{C(NMe$_2$)$_2$}$_2$, each is only represented by one transition metal complex. The two complexes are confirmed by X-ray analyses. The carbodicarbene C(NHC)$_2$ was allowed to react with [Rh(μ-Cl)(CO)$_2$]$_2$ to afford complex **70** in benzene solution. The carbon is able to split the chlorine bridge in the starting Rh complex and the vacant coordination site is occupied by the ligand, a very common synthetic route [10, 11].

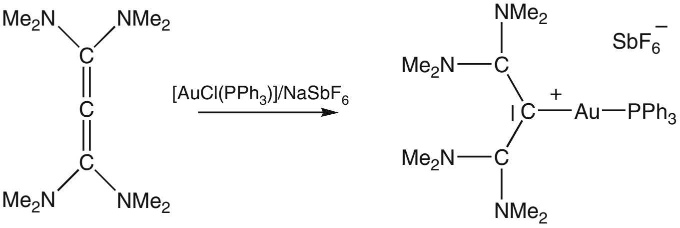
Upon complex formation, the changes of ligand parameters in C(NHC)$_2$ are similar to that with C(PPh$_3$)$_2$. The C–C–C bond angle becomes more acute changing from 134.8° in the free ligand to 121.2° in the complex, thus gaining more *sp*^{2} character and the C–C bond lengths are elongated by about 0.05 Å according to a weakening of the "negative hyperconjugation." Low carbonyl stretching frequencies were taken as indicative for a σ and π donor ability of the ligand [10, 11] (see Fig. 33).

The very early reported allene (NMe$_2$)$_2$C=C=C(NMe$_2$)$_2$ [12, 13] can also be considered as a push–push allene and the bent structure is activated upon complex formation as shown in Fig. 34. Reaction with [ClAu(PPh$_3$)] and Cl$^-$ exchange by the weakly coordinating anion SbF$_6$$^-$ results in the formation of **71** in good yields [20, 21].



70

Fig. 33 Preparation of the first complex of a carbodicarbene coordinated to Rh



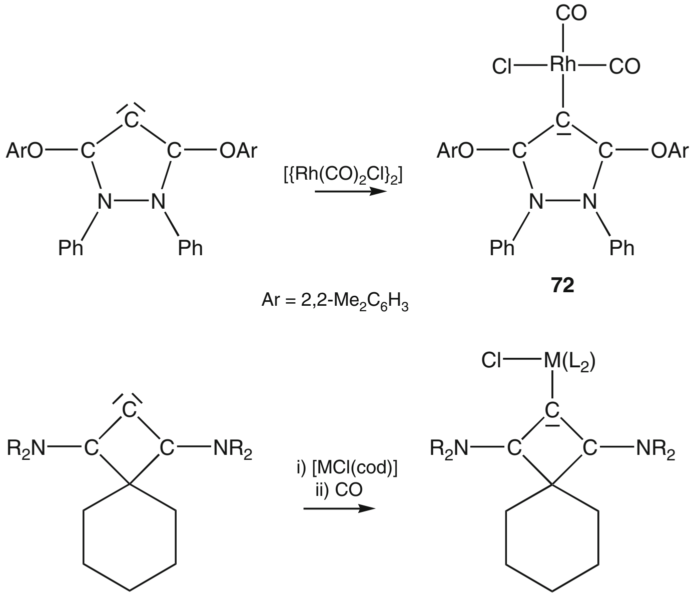
71

Fig. 34 Synthesis of the first complex with $C(C\{NMe_2\}_2)_2$ as ligand

As expected, for the metalated carbon atom a trigonal planar coordination geometry is achieved. Both lateral carbene moieties which stabilize the carbon(0) atom are planar but are tilted relative to each other to relieve allylic strain [20, 21].

5.6 Transition Metal Complexes with Heterocyclic and Cyclic Divalent Carbon(0) Compounds as Ligands

The Rh complex **72** shown in Fig. 35 was obtained by simple addition of the *N*-heterocyclic carbon(0) ligand to $[Rh(\mu\text{-}Cl)(CO)_2]_2$ in THF solution [103, 104]. The transition metal complexes **73** and **74** of the all carbon four-membered cyclic ligand shown in Fig. 15 were prepared by adding the rhodium or iridium compounds $[M(\mu\text{-}Cl)(cod)]_2$ to the freshly generated allene at −20° C in THF solution [105, 106]. The cod ligand can easily be replaced by admitting CO at room temperature to THF solutions of the complexes to give **75** and **76**, respectively, as shown in Fig. 35.



72

M = Rh, L_2 = cod (**73**)
M = Ir, L_2 = cod (**74**)
M = Rh, L = CO (**75**)
M = Ir, L = CO (**76**)

Fig. 35 Synthesis of Rh and Ir complexes containing η^1 coordinated cyclic allene ligands

The X ray diffraction analysis of **72** shows a slight opening of the CCC angle to 100.6(2)° upon complex formation. The two C–C distances to the carbon(0) atom are only minimally elongated to 1.384(3) and 1.400(2) Å, respectively. The structures of compounds **73**–**76** were confirmed by an X-ray analysis of **73**. The sum of C–C–C angles in the four membered ring is 360°, indicating strong planarity; the angle at the central donor carbon atom amounts to 88.4(3)° and the mean C–C distances of 1.405(6) Å to the donor carbon atom are closely related to those in the carbodicarbene complex **70**. The two other C–C distances in the four membered ring are typical single bonds. From carbonyl stretching frequencies in the IR spectra of the carbonyl compounds **75** and **76** it was deduced that the cyclic carbon(0) ligand belongs to the strongest donor ligands known.

6 Summary and Outlook

Theoretical studies on carbodiphosphoranes and related divalent carbon(0) compounds (carbones) of the type CL_2 and the collection of “forgotten” CL_2 compounds show that there is a class of molecules which has a unique bonding situation that is clearly different from divalent carbon(II) compounds (carbenes).

The divalent carbon(0) atom in L→C←L has two lone electron pairs which makes CL_2 a particular class of ligands which may bind as a bidentate Lewis base to one and to two monodentate Lewis acids. The nature of the ligand L determines whether a divalent carbon atom behaves as a carbone or as a carbene. The newly gained insight into the electronic structure of carbones opens a large field for theoretical and experimental research.

From a preparative point of view the access to new CL_2 or CLL' compounds and the study of their coordination ability is a challenge for the chemical community. In most cases the carbon(0) atom is stabilized by simple and well known Lewis bases but the uptake as well as the removal of this carbon(0) atom is not trivial. The latter reaction, the transformation of a single carbon atom to other substrates, has not been observed as yet. The access to a variety of stable bisylides or bent allenes often proceeds upon deprotonation of related $(HCL_2)^+$ cations or $(H_2C\{L\}_2)^{2+}$ dications by appropriate strong Lewis bases.

The activation of “hidden carbon(0)” atoms for donor properties in electron rich allenes is not fully recognized as yet and could lead to new and surprising donor acceptor compounds with electron deficient transition metal, group 13 compound, or heteroallenes, such as CE_2 ($E = O$, S, Se, NR, etc.); adducts of tetramethyl allene with CE_2 with an interesting star-like C_4 arrangement was mentioned very early but without experimental details [12, 13]. Thus, the coordination chemistry of bent allenes may be a promising concept for synthetic working chemists. Such compounds could also find entrance into catalytic activities. As yet only η^1 bonded complexes according to coordination mode **I** could be established by preparative methods, although **II** and **III** were possible according to theoretical considerations.

For complex formation, simple and well established techniques are brought into action. Splitting of halogen bridged dimers or replacement of weakly bonded ligands such as THF would be successful; the presence of only weakly coordinating anions could support the transition from a linear (ylene) arrangement into a bent structure to form $L_nM{\leftarrow}CL_2$ compounds.

7 Additions in Proof

A further $C(L)_2$ compound and its complexes should be added to chapter ***5.1***. An interesting variant of a carbodiphosphorane $C(L)_2$ compound is $C(PPh_2CH_2PPh_2)$ 2 containing two functional CH2PPh2 groups [148]. The cationic pincer complex **77** (counterion is Cl^-) of coordination mode **I** (Fig. 10) was the direct result of a three component reaction between PdCl2, CS2 and the chelating ligand $Ph_2PCH_2PPh_2$ (dppm) as depicted in Fig. 36. The free ligand was not yet isolated and the mechanism of its formation is unclear so far. The ylidic carbon atom stems from CS_2 and dppm acts as desulfurization agent to give $Ph_2PCH_2P(S)Ph_2$. Further addition of HCl to **77** produced the dicationic compound **78** of coordination mode **III** in good yields. Treatment of **77** with one equivalent of [AuCl(tht)] (tht = tetrahydrothiophene) leads to the type **III** AuCl bridged pincer complex **79**

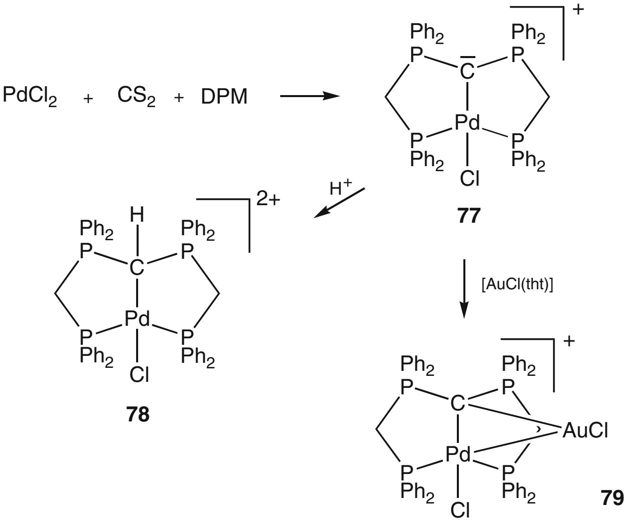


Fig. 36 Complexes with the carbodiphosphorane ligand C(dppm)$_2$

in high yield (counterion is Cl$^-$) [149]. The unique complex **79** is the only heterodimetallic compound with two metal atoms attached at a carbodiphosphorane carbon(0) atom. The environment at the central carbon atom is planar in **77** and pyramidal in **78** and **79**. P–C bond lengths and P–C–P angles in the dication **78** are closely related to those in the neutral Pt complex **36** (Fig. 25). The two metals of **79** attached to the carbon atom are connected via a very short d^8–d^{10} pseudo closed shell interaction with a Pd–Au bond length of 2.8900(3) Å; a similar bonding situation (aurophilic attraction) is found in the gold complex **29** shown in Fig. 23.

Acknowledgements This work was supported by the Deutsche Forschungsgemeinschaft.

References

1. Tonner R, Heydenrych G, Frenking G (2008) Chem Phys Chem 9:1474
2. Tonner R, Öxler F, Neumüller B, Petz W, Frenking G (2006) Angew Chem 118:8206
3. Tonner R, Öxler F, Neumüller B, Petz W, Frenking G (2006) Angew Chem Int Ed 45:8038
4. Tonner R, Frenking G (2008) Chem Eur J 14:3260
5. Ebsworth EVA, Fraser TE, Rankin DWH, Gasser O, Schmidbaur H (1977) Chem Ber 110:3508
6. Hardy GE, Zink JI, Kaska WC, Baldwin JC (1978) J Am Chem Soc 100:8002
7. Daly JJ, Wheatley PJ (1966) J Chem Soc 1703
8. Tonner R, Frenking G (2007) Angew Chem 119:8850
9. Tonner R, Frenking G (2007) Angew Chem Int Ed 46:8695
10. Dyker CA, Lavallo V, Donnadieu B, Bertrand G (2008) Angew Chem 120:3250
11. Dyker CA, Lavallo V, Donnadieu B, Bertrand G (2008) Angew Chem Int Ed 47:3206
12. Viehe HG, Janousek Z, Gompper R, Lach D (1973) Angew Chem 85:581
13. Viehe HG, Janousek Z, Gompper R, Lach D (1973) Angew Chem Int Ed Engl 12:566

14. Bestmann HJ, Frank W, Moll C, Pohlschmidt A, Clark T, Göller A (1998) Angew Chem 110:347
15. Bestmann HJ, Frank W, Moll C, Pohlschmidt A, Clark T, Göller A (1998) Angew Chem Int Ed 22:729
16. Vander Auwera J, Johns JWC, Polyansky OL (1999) J Chem Phys 99:2299
17. Koput J (2000) Chem Phys Lett 320:237
18. Ellern A, Drews T, Seppelt K (2001) Z Anorg Allg Chem 627:73
19. Tanimoto M, Kuchitsu K, Morino (1970) Bull Chem Soc Jpn 43:2776
20. Fürstner A, Alcarazo M, Goddard R, Lehmann CW (2008) Angew Chem 120:3254
21. Fürstner A, Alcarazo M, Goddard R, Lehmann CW (2008) Angew Chem Int Ed Engl 47:3210
22. Schmidbaur H, Gasser O, Hussain MS (1977) Chem Ber 110:3501
23. Schubert U, Kappenstein C, Milewsky-Mahrla B, Schmidbaur H (1981) Chem Ber 114:3070
24. Gasser O, Schmidbaur H (1975) J Am Chem Soc 97:6281
25. Shevchenko IV, Mikolenko RN, Loss S, Grützmacher H (1999) Eur J Inorg Chem 1665
26. Shevchenko IV (1998) J Chem Soc Chem Commun 1203
27. Shevchenko IV, Mikolenko RN, Lork E, Röschenthaler GV (2001) Eur J Inorg Chem 2377
28. Appel R, Baumeister U, Knoch F (1983) Chem Ber 116:2257
29. Appel R, Waid K (1979) Angew Chem 91:177
30. Appel R, Waid K (1979) Angew Chem Int Ed 18:169
31. Soleilhavoup M, Baceiredo A, Bertrand G (1993) Angew Chem 105:1245
32. Soleilhavoup M, Baceiredo A, Bertrand G (1993) Angew Chem Int Ed Engl 32:1161
33. Fluck E, Lange K, Heckmann G (1992) Phosphorus Sulfur Silicon 72:59
34. Appel R, Wihler HD (1978) Chem Ber 111:2054
35. Schmidbaur H, Costa T, Milewsky-Mahrla B, Schubert U (1980) Angew Chem 92:557
36. Schmidbaur H, Costa T, Milewsky-Mahrla B, Schubert U (1980) Angew Chem Int Ed 19:555
37. Schmidbaur H, Costa T (1981) Chem Ber 114:3063
38. Schmidbaur H, Herr R, Zybill C (1984) Chem Ber 117:3374
39. Marrot S, Kato T, Gornitzka H, Baceiredo A (2006) Angew Chem 118:2660
40. Marrot S, Kato T, Gornitzka H, Baceiredo A (2006) Angew Chem Int Ed Engl 45:2598
41. Marrot S, Kato T, Cossio FP, Gornitzka H, Baceiredo A (2006) Angew Chem 118:7607
42. Marrot S, Kato T, Cossio FP, Gornitzka H, Baceiredo A (2006) Angew Chem Int Ed Engl 45:7447
43. Fujii T, Ikeda T, Mikami T, Suzuki T, Yoshimura T (2002) Angew Chem 114:2688
44. Fujii T, Ikeda T, Mikami T, Suzuki T, Yoshimura T (2002) Angew Chem Int Ed 41:2576
45. Pascual S, Asay M, Illa O, Kato T, Bertrand G, Saffon-Merceron N, Branchadell V, Baceiredo A (2007) Angew Chem 119:9236
46. Pascual S, Asay M, Illa O, Kato T, Bertrand G, Saffon-Merceron N, Branchadell V, Baceiredo A (2007) Angew Chem Int Ed 46:9078
47. Zinner G, Beck G, Fehlhammer WP, Wiberg N (1989) J Organomet Chem 368:23
48. Sotiropoulos J-M, Babeiredo A, Bertrand G (1987) J Am Chem Soc 109:4711
49. Cantat T, Mezailles N, Ricard L, Jean Y, Le Floch P (2004) Angew Chem 116:6542
50. Cantat T, Mezailles N, Ricard L, Jean Y, Le Floch P (2004) Angew Chem Int Ed 43:6382
51. Fang M, Jones ND, Friesen K, Lin G, Ferguson MJ, McDonald R, Lukowsky R, Cavell RG (2009) Organometallics 28:1652
52. Cantat T, Ricard L, Mezailles N, Le Floch P (2006) Organometallics 25:6030
53. Cantat T, Jaroschik F, Ricard L, Le Floch P, Nief F, Mezailles N (2006) Organometallics 25:1329
54. Smurnyy Y, Bibal C, Pink M, Caulton KG (2005) Organometallics 24:3849
55. Takagi N, Shimizu T, Frenking G (2009) Chem Eur J 15:3448
56. Takagi N, Shimizu T, Frenking G (2009) Chem Eur J 15:8593
57. Casarin M, Pandolfo L, Sassi A (2002) Organometallics 21:2235
58. Stone KC, Jamison GM, White PS, Templeton JL (2002) Inorg Chim Acta 330:161

59. List AK, Hillhouse GL, Rheingold LA (1989) Organometallics 8:2010
60. Ramirez F, Desai NB, Hansen B, McKelvie NJ (1961) J Am Chem Soc 83:3539
61. Driscoll JS, Grisley DW Jr, Pustinger JV, Harris JE, Matthews CN (1964) J Org Chem 29:2427
62. Zybill C, Müller G (1987) Organometallics 6:2489
63. Appel R, Knoll F, Schöler H, Wihler HD (1976) Angew Chem 88:769
64. Appel R, Knoll F, Schöler H, Wihler HD (1976) Angew Chem Int Ed Engl 15:701
65. Vincent AT, Wheatley PJJ (1972) J Chem Soc Dalton Trans 617
66. Hardy GE, Zink JI, Kaska WC, Baldwin JC (1978) J Am Chem Soc 100:8001
67. Funk M, Univ Marburg, Personal communication
68. Zink JI, Kaska WC (1973) J Am Chem Soc 95:7510
69. Hardy GE, Baldwin JC, Zink JI, Kaska WC, Liu PH, Dubois L (1977) J Am Chem Soc 99:3552
70. Baldwin JC, Kaska WC (1979) Inorg Chem 18:686
71. Petz W, Kutschera C, Tschan S, Weller F, Neumüller B (2003) Z Anorg Allg Chem 629:1235
72. Bestmann HJ (1977) Angew Chem 89:351
73. Bestmann HJ (1977) Angew Chem Int Ed Engl 16:349
74. Bestmann HJ, Sandmeier D (1980) Chem Ber 113:274
75. Bestmann HJ, Oechsner H (1983) Z Naturforsch 38b:861
76. Matthews CN, Driscoll JS, Birum GH (1966) J Chem Soc Chem Commun 736
77. Petz W, Weller F, Kutschera C, Heitbaum M, Frenking G, Tonner R, Neumüller B (2005) Inorg Chem 44:1263
78. Matthews CN, Birum GH (1966) Tetrahedron Lett 46:5707
79. Schmidbaur H, Zybill CE, Neugebauer D (1982) Angew Chem 94:321
80. Schmidbaur H, Zybill CE, Neugebauer D (1982) Angew Chem Int Ed Engl 21:310
81. Schmidbaur H, Zybill C, Neugebauer D, Müller G (1985) Z Naturforsch 40b:1293
82. Petz W, Heimann S, Öxler F, Neumüller B (2007) Z Anorg Allg Chem 633:365
83. Petz W, Neumüller B unpublished results
84. Kaska WC (1983) Coord Chem Rev 48:1
85. Schmidbaur H (1983) Angew Chem 95:980
86. Schmidbaur H (1983) Angew Chem Int Ed Engl 22:907
87. Schmidbaur H (1979) Nachr Chem Tech Lab 27:620
88. Kaska W, Starzewski KAO (1993) Ylides and Imines of Phosphorus. Wiley, New York, USA
89. Kolodiazhnyi OI (1996) Tetrahedron 52:1855
90. Daly JJ, Wheatley PJ (1966) J Chem Soc A:1703
91. Bestmann HJ, Schmidt M, Shobert R (1988) Synthesis 49
92. Johnson AW, Kaska WC, Starzewski KAO, Dixon DA (1993) Ylides and imines of phosphorus. Wiley, New York
93. Kolodiazhnyi OI (1999) Phosphorus ylides. Wiley, Weinheim
94. Benetollo F, Bertani R, Ganis P, Pace G, Pandolfo L, Zanotto L (2002) J Organomet Chem 642:64
95. Bertani R, Casarin M, Pandolfo L (2003) Coord Chem Rev 236:15
96. Diels O, Meyerheim G (1907) Ber Deut Chem Ges 40:355
97. Tonner R, Frenking G (2008) Chem Eur J 14:3273
98. Paiaro G, Pandolfo L (1981) Angew Chem 93:294
99. Paiaro G, Pandolfo L (1981) Angew Chem Int Ed 20:285
100. List AK, Milton R, Smith R III, Hillhouse GL (1991) Organometallics 10:361
101. Viehe HG, Janousek Z, Gomper R, Lach D (1973) Angew Chem 85:581
102. Viehe HG, Janousek Z, Gomper R, Lach D (1973) Angew Chem Int Ed Engl 12:566
103. Lavallo V, Dyker CA, Donnadieu B, Bertrand G (2008) Angew Chem 120:5491
104. Lavallo V, Dyker CA, Donnadieu B, Bertrand G (2008) Angew Chem Int Ed 47:5411
105. Melaimi M, Parameswaran P, Donnadieu B, Frenking G, Bertrand G (2009) Angew Chem 121:4886
106. Melaimi M, Parameswaran P, Donnadieu B, Frenking G, Bertrand G (2009) Angew Chem Int Ed 48:4792

107. Petz W, Weller F, Uddin J, Frenking G (1999) Organometallics 18:619
108. Lewis KE, Golden DM, Smith GP (1984) J Am Chem Soc 106:3905
109. Kaska WC, Mitchell WK, Reichelderfer RF (1973) J Organomet Chem 47:391
110. Goldberg SZ, Raymond KN (1973) Inorg Chem 12:2923
111. Dorta R, Stevens ED, Scott NM, Costabile C, Cavallo L, Hoff CD, Nolan SP (1977) J Am Chem Soc 127:2485
112. Ziegler T, Rauk A (1979) Inorg Chem 18:1755
113. Ziegler T, Rauk A (1979) Inorg Chem 18:1558
114. Morokuma K (1971) J Chem Phys 5:1236
115. Bickelhaupt FM, Baerends EJ (2000) Reviews in computational chemistry, vol 15. Wiley, New York, p 1
116. Te Velde G, Bickelhaupt FM, Baerends EJ, Fonseca Guerra C, Van Gisbergen SDJA, Snijders J, Ziegler T (2001) J Comp Chem 22:931
117. Diefenbach A, Bickelhaupt FM, Frenking G (2000) J Am Chem Soc 122:6449
118. Dörr M, Frenking G (2002) Z Allg Anorg Chem 628:843
119. Kaska WC, Mitchell DK, Reichelderfer RF (1973) J Organomet Chem 47:391
120. Kaska WC, Mitchell DK, Reichelderfer RF, Korte WD (1974) J Am Chem Soc 96:2847
121. Petz W, Neumüller B, Tonner R (2009) (to be published)
122. Petz W, Weller F (1996) Z Naturforsch 51b:1598
123. Petz W, Wenck K, Neumüller B (2007) Z Naturforsch 62b:413
124. Petz W, Öxler F, Ronge R, Neumüller B (2008) Z Anorg Allg Chem 634:1415
125. Sundermeyer J, Weber K, Peters K, von Schnering HG (1994) Organometallics 13:2560
126. Kaska WC, Reichelderfer RF (1974) J Organomet Chem 78:C47
127. Schmidbaur H, Zybill CE, Müller G, Krüger C (1983) Angew Chem 95:753
128. Schmidbaur H, Zybill CE, Müller G, Krüger C (1983) Angew Chem Int Ed Engl 22:729
129. Müller G, Krüger K, Zybill C, Schmidbaur H (1986) Acta Cryst C42:1141
130. Vicente J, Singhal AR, Jones PG (2002) Organometallics 21:5887
131. Petz W, Öxler F, Neumüller B (2009) J Organomet Chem 694:4094
132. Schmidbaur H, Gasser O (1976) Angew Chem 88:542
133. Schmidbaur H, Gasser O (1976) Angew Chem Int Ed Engl 15:502
134. Romeo I, BardaJi M, Gimeno MC, Laguna M (2000) Polyhedron 19:1873
135. Petz W, Neumüller B (to be published)
136. Kubo K, Jones ND, Ferguson MJ, McDonald R, Cavell RG (2005) J Am Chem Soc 127:5314
137. Petz W, Kutschera C, Neumüller B (2005) Organometallics 24:5038
138. Coberan R, Marrot S, Dellus N, Merceron-Saffon N, Kato T, Peris E, Baceiredo A (2009) Organometallics 28:326
139. Berke H, Lindner E (1973) Angew Chem 85:668
140. Berke H, Lindner E (1973) Angew Chem Int Ed Engl 12:667
141. Lindner E (1975) J Organomet Chem 94:229
142. Lindenberger H, Birk R, Orama O, Huttner G, Berke H (1988) Z Naturforsch 43b:749
143. Bertani R, Casarin M, Ganis P, Maccato C, Pandolfo L, Venzo A, Vittadini A, Zanotto L (2000) Organometallics 19:1373
144. Bertani R, Meneghetti F, Pandolfo L, Scarmagnan A, Zanotto L (1999) J Organomet Chem 583:146
145. Pandolfo L, Paiaro G, Dragani LK, Maccato C, Bertani R, Facchin C, Zanotto L, Ganis P, Valle G (1996) Organometallics 15:3250
146. Bertani R, Pandolfo L, Zanotto L (2002) Inorg Chim Acta 330:213
147. Kuhn N, Kratz T, Boese R, Bläser D (1994) J Organomet Chem 470:C8
148. Stallinger S, Reitsamer C, Schuh W, Kopacka H, Wurst K, Peringer P (2007) Chem Commun 510
149. Reitsamer C, Schuh W, Kopacka H, Wurst K, Peringer P (2009) Organometallics DOI:10,1021/om900686r

Part II

sp^2 -Hybridized Neutral η^1-Carbon Ligands

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Chemistry of *N*-Heterocyclic Carbene Ligands

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Abstract *N*-Heterocyclic carbenes (NHCs) have developed into an important class of ligands in transition metal coordination chemistry. They have been employed successfully as spectator ligands in various catalytically active metal complexes and as organocatalysts. In this chapter we present some important synthetic methods for the preparation of various NHCs and their metal complexes.

Keywords *N*-Heterocyclic carbene · Synthetic procedures · Transition metal complexes

Contents

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1 Introduction

N-Heterocyclic carbenes (NHCs) are defined as neutral compounds with a divalent carbon atom possessing only six valence electrons and being part of a nitrogen containing heterocycle [1, 2]. The interest in this class of ligands and their use in coordination chemistry was only marginal over several decades, although first investigations on NHCs were reported by Wanzlick as early as 1960 [3, 4]. However, no stable *N*-heterocyclic carbenes emerged from these studies. Wanzlick [5] and Öfele [6] later reported the preparation of the first metal complexes bearing NHC ligands (Fig. 1, top and middle). This was followed by some reports from Lappert et al. who prepared complexes with NHC ligands from electron-rich enetetramines [7]. The chemistry of NHCs has experienced tremendous development since 1991 when Arduengo et al. isolated the first stable *N*-heterocyclic carbene (Fig. 1, bottom) [8].

Stable NHCs are singlet carbenes featuring an sp^2-hybridized carbene carbon(II) atom. The two nonbonding electrons occupy the sp^2-orbital with an antiparallel spin orientation, while the p-orbital is empty ($\sigma^2 p_\pi^0$, $^1A_1$-state). Thus NHCs should, in principle, display an ambiphilic behavior, but in reality they behave mostly as σ-donor ligands [1, 2]. The singlet ground state in NHCs is stabilized by σ-electron withdrawing, electronegative substituents at the carbene carbon atom. In addition, mesomeric effects play a crucial role for the stabilization of NHCs. If the carbene carbon atom is substituted with σ-donor substituents X, the nonbonding electron pairs of the σ-donors can effectively interact with the empty p_π-orbital at the carbene

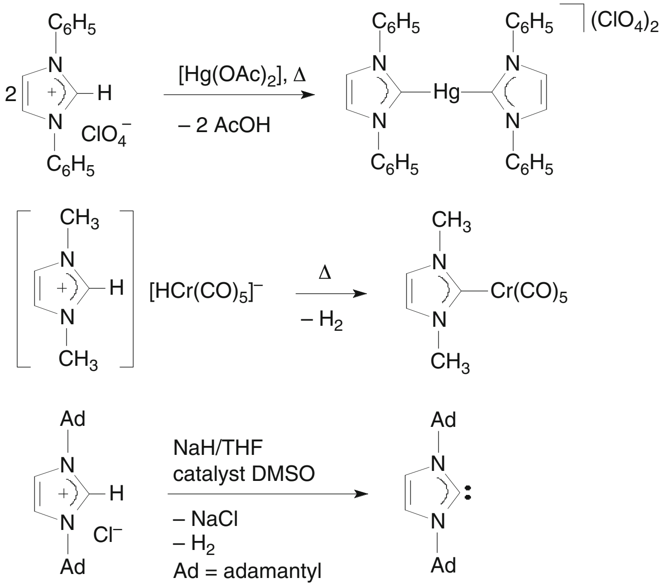


Fig. 1 Synthesis of the first NHC complexes (*top*, *middle*) and of the first stable NHC (*bottom*)

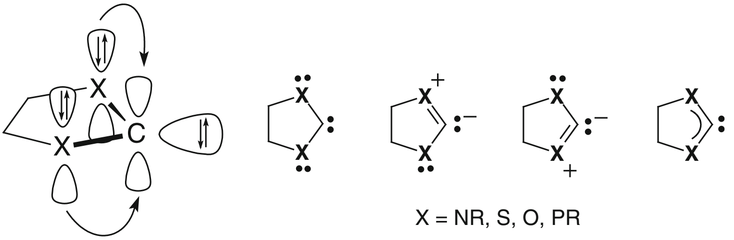


Fig. 2 Electronic configuration and resonance structures of heterocyclic carbenes containing an X_2C: carbene center

carbon atom resulting in the formation of a four-electron-three-center π-system, where the X–C bonds acquire partial double bond character (Fig. 2). Consequently, planar nitrogen substituents which are more electronegative than carbon and which possess a free electron pair with π-symmetry are perfectly suited to stabilize a singlet carbene carbon atom.

Several features make NHCs superior spectator ligands in metal catalysts when compared to phosphines. NHCs are known to form stable bonds with metals which are surprisingly resistant against heat, moisture, and even acids [9]. The NHCs are electron-rich, neutral σ-donor ligands with no or negligible π-acceptor properties, although this latter feature is still debated [10–13]. The CO stretching frequencies of complexes of the type $[MClL(CO)_2]$ (M = Rh, Ir) [14, 15] or $[NiL(CO)_3]$ [16] (L = NHC) revealed that the electron donating ability of different NHC ligands are quite similar and that they are all more electron-rich ligands than the most basic phosphines. Although the electron donating properties of different NHCs are quite similar, small changes in the nature of the heterocyclic ring can still influence the electronic properties of the carbene. While NHC complexes with almost all transition metals and a large number of main group metals are known [1], decomposition of carbene complexes by reductive elimination of azolium salts is a standard decomposition pathway for complexes with alkyl or aryl groups as coligand next to the carbene donor function (see Sect. 3.3).

2 *N*-Heterocyclic Carbene Ligands

NHCs have become popular ligands in coordination chemistry owing to the facile access to this type of ligands and to metal–NHC complexes. Most NHC ligands are prepared from azolium compounds such as imidazolium, triazolium, benzimidazolium, imidazolidinium, or thiazolium salts [1]. Alternatively, the reductive desulfurization of imidazolin-, benzimidazolin-, and imidazolidin-2-thiones to yield a variety of NHCs has been described. The preparation of suitable azolium salts and imidazolin-2-thiones is presented in Sect. 2.1. This is followed by the description of methods to liberate the free NHCs from these compounds. Today, stable singlet carbene centers embedded in three- [17, 18], four- [19], five- [1], six- [20–22], and seven-membered heterocyclic rings [23, 24] are known. Those derived from five-membered heterocycles are by far the most popular NHCs and only their synthesis will be discussed in detail.

2.1 Synthesis of the Parent Azolium Salts and 2-Thiones

The most common methods suitable for the synthesis of different azolium compounds will be discussed here. Two routes are particularly useful for the preparation of the imidazolium salts: (1) substitution reactions at the nitrogen atoms of imidazole [25] and (2) multicomponent reactions for the generation of an *N*,*N*′-substituted heterocycle which are particularly useful for the synthesis of imidazolium salts bearing aromatic, very bulky, or particularly reactive *N*,*N*′-substituents (Fig. 3a,b) [26]. Both methods offer the opportunity to produce unsymmetrically substituted imidazolium salts of type **1** either by stepwise alkylation of imidazole or by the synthesis of an *N*-arylated imidazole derivative followed by *N*′-alkylation [27]. Nevertheless, the method of choice for the preparation of the imidazolium salts **1** is the *N*,*N*′-substitution of imidazole. Several other methods for the preparation of imidazolium salts with previously unattainable substitution patterns have also been described [28, 29].

The saturated imidazolidinium salts can be obtained by alkylation of dihydroimidazole or by selected cyclization reactions [22]. A multicomponent reaction leading to unsymmetric derivatives of type **2** has also been reported (Fig. 3c) [30].

Alternative precursors for the synthesis of NHCs are thiourea derivatives of type **3**. The preparation of such thiones with a symmetrical substitution pattern is achieved by the reaction of α-hydroxyketones like 3-hydroxy-2-butanone with suitable 2-thiones (Fig. 3d) [31] or by reaction of a diamine with thiophosgene [32, 33]. Unsymmetrically substituted thiones **4** possessing a saturated heterocycle have also been described (Fig. 3e) [34, 35].

In addition to the compounds listed above, a number of triazolium [36], thiazolium [37], and benzimidazolin-2-thione [32] derivatives as well as five-membered heterocycles with only one nitrogen atom [38, 39] or two phosphorus atoms [40] within the heterocycle, all of which are suitable for the generation of heterocyclic carbenes, have been described.

2.2 Preparation of the Free N-Heterocyclic Carbenes

Two general routes are normally employed for the generation of free *N*-heterocyclic carbenes **5**. These are (1) the deprotonation of azolium salts of types **1** and **2** or (2) the reductive desulfurization of thiones **3** and **4** (Fig. 4) [1]. Most of the free NHCs are obtained by deprotonation of the azolium salts at the C2 position of the heterocycle with a suitable base like NaH, KO*t*-Bu, or DMSO/NaH in THF [8] or liquid ammonia

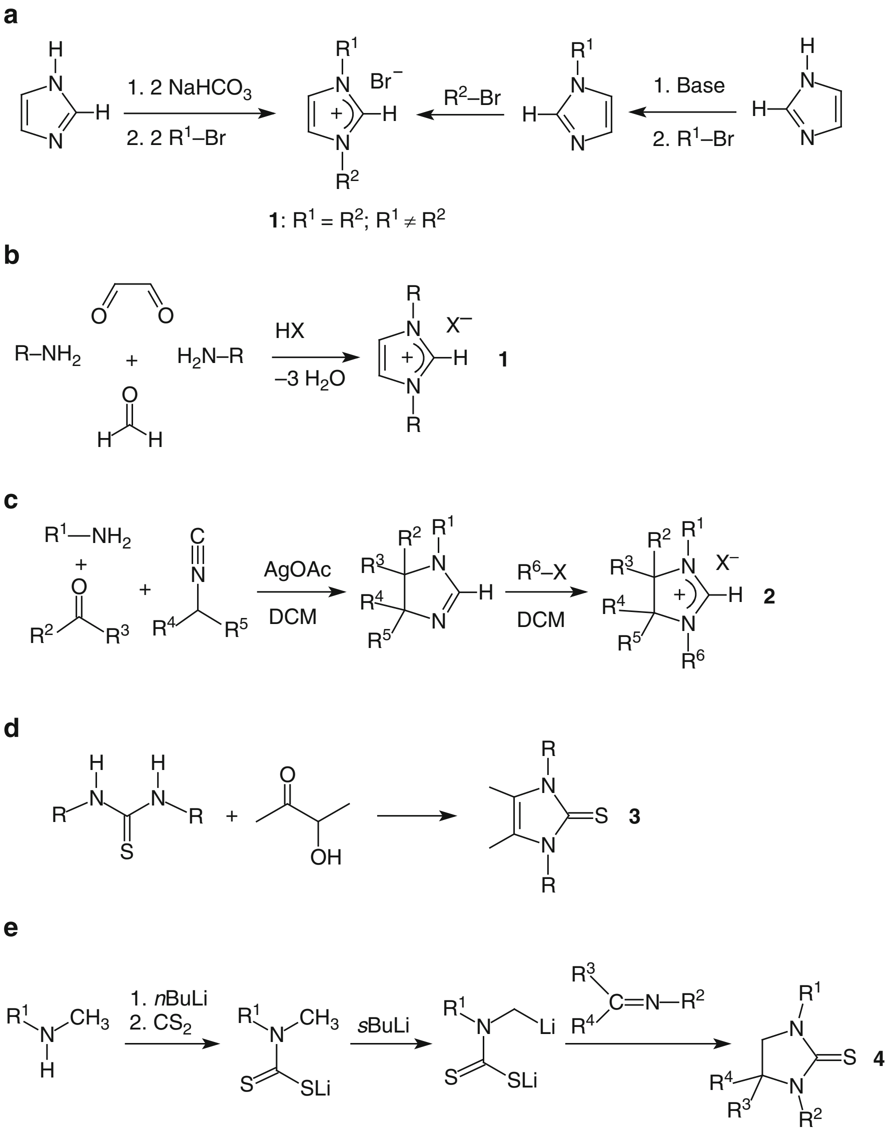


Fig. 3 Syntheses of imidazolium salts **1** (**a**, **b**), unsymmetrically substituted imidazolidinium salts **2** (**c**) and of cyclic 2-thiones **3** and **4** (**d**, **e**)

[41]. In the case of azolium salts with acidic substituents the use of a sterically demanding base like KHMDS is required for a selective deprotonation at C2.

The reductive desulfurization of thiones was first described by Kuhn et al. in 1993 [31] and has become an alternative method for the preparation of saturated [34, 35, 42, 43] and unsaturated NHCs [31, 32] (Fig. 4). The reducing agent of choice depends on the thiones to be desulfurized. Imidazolin-2-thiones **3** are reduced to the free carbenes **5** with potassium within 4 h in boiling THF, while benzimidazolin-2-thiones can be reduced with an Na/K-alloy in toluene [32] requiring a reaction time of up to 3 weeks.

Although these two methods have found widespread application for the synthesis of free carbenes, they failed for selected saturated imidazolidin-2-ylidenes and especially in the preparation of triazolin-5-ylidenes. In these cases the free carbene species **7** can be obtained from 2-alkoxyimidazolidines **6** [44] or 5-alkoxytriazoles [36] by thermally induced α-elimination of an alcohol (Fig. 5). In addition to 2-alkoxyimidazolidines, 2-(pentafluorophenyl)imidazolidines [45, 46] have also been used for the generation of NHCs by α-elimination. The adduct **8** eliminates acetonitrile upon heating [47] to yield the benzimidazolin-2-ylidene **9**. In a more exotic procedure, imidazolium salts have been reduced electrochemically to give the free imidazolin-2-ylidenes [48].

2.3 *Comparison of Different N*-Heterocyclic Carbenes

Imidazolin-2-ylidenes of type **5** are normally obtained as colorless, diamagnetic, crystalline solids with surprisingly high melting points. In the absence of air and moisture, they exhibit a remarkable stability and even some air-stable derivatives are known [49]. The characteristic ^{13}C NMR signal for the C2 carbon atom is

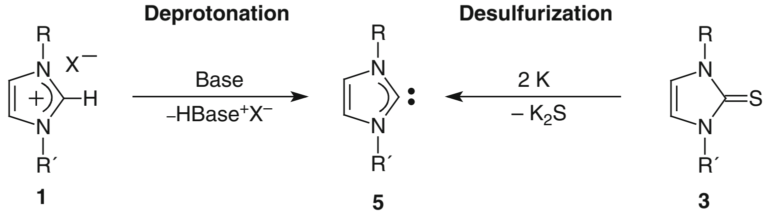


Fig. 4 Preparation of free *N*-heterocyclic carbenes by deprotonation of azolium salts or by desulfurization of the corresponding thiones

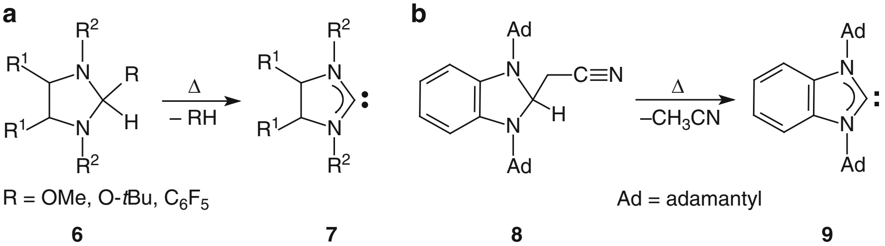


Fig. 5 NHC synthesis by thermally induced α-elimination

detected in the range of δ 210–220 ppm. Dimerization of imidazolin-2-ylidenes of type **5** to the electron-rich tetraazafulvalenes is normally not observed but can be enforced in certain cases by suitable bridges between two imidazolin-2-ylidenes [50]. Theoretical and experimental studies led to the conclusion that thermodynamic factors (electronic structure) contribute mostly to the stabilization of imidazolin-2-ylidenes, while kinetic factors (steric protection of the carbene carbon atom) are less important [51–54].

The saturated imidazolidin-2-ylidenes **7** [34, 35, 43, 55] and the benzimidazolin-2-ylidenes **9** [32, 56, 57] also belong to the intensely studied NHCs. In contrast to the imidazolin-2-ylidene **5**, both the imidazolidin-2-ylidenes **7** and the benzimidazolin-2-ylidenes **9** dimerize rapidly to the corresponding enetetramines **7=7** or **9=9** if the nitrogen atoms are substituted with sterically less demanding substituents (Fig. 6). For these NHCs the kinetic stabilization of the carbene center by sterically demanding *N*,*N*′-substituents is much more important than for the unsaturated imidazolin-2-ylidenes of type **5** [51]. The resonance for the carbene carbon atom of imidazolidin-2-ylidenes **7** is observed around δ 240 ppm and the enetetramines **7=7** give rise to a resonance at δ 130 ppm in the ^{13}C NMR spectra. Typical resonances for the carbene carbon atom of **9** (δ ≈ 230 ppm) are observed at chemical

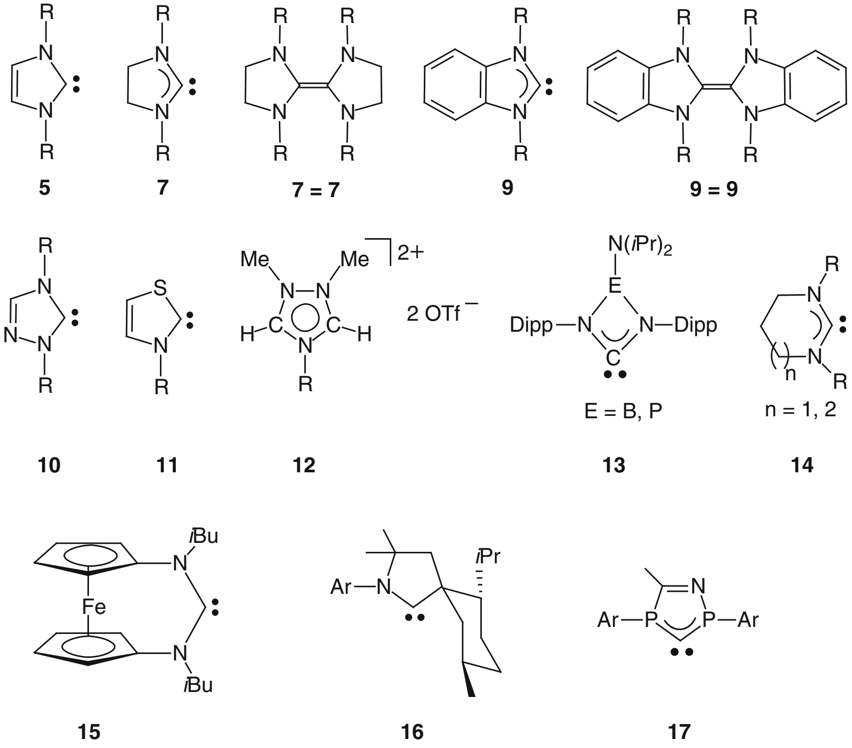


Fig. 6 Different types of NHCs

shifts which lie in between the typical values for the C2 resonance of saturated imidazolidin-2-ylidenes **7** and unsaturated imidazolin-2-ylidenes **5**.

In order to vary the electronic situation at the carbene carbon atom a number of carbo- and heterocycle-annulated imidazolin-2-ylidenes like the benzobis(imidazolin-2-ylidenes) [58–60] and the singly or doubly pyrido-annulated *N*-heterocyclic carbenes [61–63] have been prepared and studied. Additional carbenes derived from a five-membered heterocycle like triazolin-5-ylidenes **10** [36], which reveals properties similar to the imidazolin-2-ylidenes **5** and thiazolin-2-ylidene **11** [37] exhibiting characteristic properties comparable to the saturated imidazolidin-2ylidenes **7** have also been prepared. Bertrand reported the 1,2,4-triazolium dication **12** [64]. Although all attempts to isolate the free dicarbene species from this dication have failed so far, silver complexes [65] as well as homo- and heterobimetallic iridium and rhodium complexes of the triazolin-3,5-diylidene have been prepared [66]. The 1,2,4-triazolium salts and the thiazolium salts have been used successfully as precatalysts for inter- [67] and intramolecular benzoin condensations [68].

Stable free carbenes derived from four- (**13**), six-, or seven-membered heterocycles **14** are also known. Carbenes of type **13** can possess a phosphorus [19] or a boron atom [69] within the heterocycle. These carbenes exhibit extreme values regarding their ^{13}C NMR spectroscopic ($\delta_{\text{carbene–C}}$ 285 and 312.6 ppm) and structural properties (angle N–$\text{C}_{\text{carbene}}$–N 96.72(13) and 94.0(2)°).

The carbenes derived from six- [20–22] and seven-membered heterocycles [22–24, 70] of type **14** can be obtained both with an aliphatic or an aromatic backbone. The characteristic ^{13}C NMR resonances for the C2 carbon atoms in six-membered carbene heterocycles (δ 236–248 ppm) [20, 21] have been recorded in the same range as the $\text{C}_{\text{carbene}}$ resonances for saturated imidazolidin-2-ylidenes of type **7**. Dimerization to enetetramines occurs for some carbenes derived from a six-membered heterocycle [21] and this behavior is independent from the nature of the backbone (saturated or unsaturated), but depends strongly on the steric bulk of the *N*,*N*´-substituents.

No enetetramine formation has been observed with NHCs derived from seven-membered heterocycles. The C2 resonance in these derivatives is shifted further downfield (δ 250–260 ppm) in the ^{13}C NMR spectra. The most striking difference in comparison to all NHCs discussed previously is the twisted, nonplanar conformation of the seven-membered heterocycle both in the azolium precursor and in the carbene ligand. The twisted conformation appears to be essential to accommodate the strain within the seven-membered heterocycle.

Bielawski et al. described the synthesis and properties of NHC **15** introducing a novel carbene architecture incorporating a 1,1′-disubstituted ferrocene moiety as backbone [71]. In its metal complexes [71, 72] this carbene ligand supported a long-range electronic communication between the iron center and the carbene coordinated transition metal.

Bertrand et al. demonstrated with the stable cyclic (alkyl)(amino)carbenes (CAACs) **16** that only one nitrogen atom is sufficient for the stabilization of the carbene center. The resonance of the carbene carbon atom in carbenes of type **16** is significantly shifted downfield (δ 304.2–319.0 ppm) [38, 39] compared to cyclic diaminocarbenes. Even the *P*-heterocyclic carbene **17** has been prepared by Bertrand et al., who used extremely bulky substituents to planarize the phosphorus atoms [40]. Compared to the unsaturated NHCs of type **5**, the resonance of the carbene carbon atom of the PHC **17** is shifted upfield (δ 184 ppm).

2.4 Functionalized and Polydentate Carbene Ligands

Almost immediately after the isolation of the first stable carbene [8], reports about polydentate NHC ligands appeared. Meanwhile the number of these derivatives such as linked poly-NHCs and donor-functionalized NHC ligands or their protonated azolium precursors has grown significantly, largely due to applications of complexes with polydentate NHC ligands in catalytic transformations [9, 73, 74]. Owing to the large variety of such ligands only a selection will be presented here (Fig. 7).

Some bidentate bis(imidazolin-2-ylidene)s **18** have been used for the preparation of complexes with chelating dicarbene ligands [75–80]. The synthesis, properties, and coordination chemistry of tripodal tris(imidazolin-2-ylidene) ligands like **19**

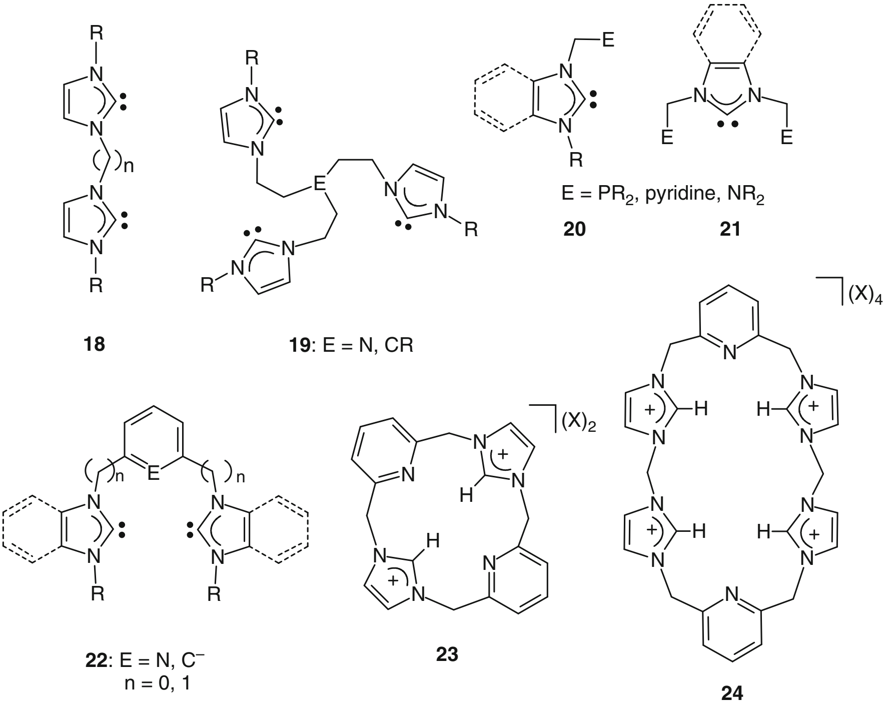


Fig. 7 Polydentate NHC ligands and ligand precursors

have recently been summarized [81]. Much effort has been directed towards the preparation of donor-functionalized bidentate as well as tridentate carbene ligands combining the carbene donor moiety with additional heteroatom donors [82]. Heteroatom donor functions in such bidentate ligands of type **20** are, for example, nitrogen [83] or phosphorus [84].

Furthermore, the rigid “pincer” topology [85] has been transferred to carbene coordination chemistry. Tridentate ligands containing one (**21**) or two (**22**) NHC groups, including derivatives with benzimidazolin-2-ylidene donors [86] and their metal complexes, have been prepared [87] and used in homogeneous catalysis [88]. Often, the free NHC ligands have not been isolated, but the polyimidazolium salts were used directly for the generation of NHC complexes.

Among the polydentate carbene ligands, particular interest has recently been placed on cyclic polycarbenes. Imidazolium precursors like **23** [89] or **24** [90, 91], which upon C2 deprotonation would lead to tetradentate or even hexadentate double-pincer NHC ligands, have been prepared. Their interesting coordination chemistry will be discussed in Sect. 4. Finally, Arnold et al. developed and reviewed NHC ligands which are functionalized with additional anionic (alkoxide or amido) donor groups [92].

3 Late Transition Metal Complexes with NHC Ligands

Over the last few years the number of complexes with heterocyclic carbene ligands has rapidly increased. Next to complexes of all transition metals [1, 2, 9, 73, 74], NHCs have been used as ligands for more exotic metals such as the *f*-block elements [92] and various technetium isotopes [93]. The search for NHC complexes is still driven by the need for new and selective catalysts [94].

3.1 Common Routes to NHC Complexes

The two most common methods for the synthesis of complexes with NHC ligands are the reaction of a free carbene (**a**) or its enetetramine dimer (**b**) with a suitable metal precursor or the in situ deprotonation of an azolium salt (**c**) depicted in Fig. 8 using diaminocarbenes with five-membered heterocycles as examples.

The reaction of the free carbene with a suitable metal complex is the simplest method for the preparation of an NHC complex (Fig. 8a). In addition, the cleavage of electron-rich enetetramines in the presence of coordinatively unsaturated metal complexes followed by coordination and stabilization of the NHC also constitutes an established method for the preparation of NHC complexes (Fig. 8b) [7, 95], which works particularly well for the preparation of complexes with benzimidazolin-2-ylidene ligands [56, 80, 96].

Metal complexes with *N*-heterocyclic carbene ligands were known long before the first stable NHCs were isolated. Wanzlick [5] and Öfele [6] demonstrated as early as 1968 that NHC complexes can be obtained by in situ deprotonation of azolium salts in the presence of a suitable metal complex without prior isolation of the free NHC ligand (Fig. 1). In these cases a ligand of the metal complex precursor (acetate or hydride) acted as a base for the deprotonation of the imidazolium cation. This method has been successfully transferred to other metal precursors containing basic ligands like $[Pd(OAc)_2]$ [97] and $[(cod)Ir(\mu\text{-}OR)_2Ir(cod)]$ [98, 99]. Alternatively, an external base such as NaOAc, KO*t*-Bu or MHMDS (M = Li, Na, K) can be added for the deprotonation of the azolium salt [100]. In general, the in situ deprotonation of azolium salts appears as the most attractive method for the preparation of NHC complexes as it does not require the isolation of the reactive free carbene or its enetetramine dimer.

The preparation of NHC complexes according to the methods shown in Fig. 8 and the properties of such complexes have been the subject of a number of reviews [1, 94, 100, 101]. Selected new methods for the preparation of NHC complexes will be presented in the following sections.

3.2 *Carbene Transfer Reactions*

The carbene transfer reaction from silver NHC complexes has developed into a standard procedure for the synthesis of NHC complexes. This versatile procedure was introduced by Lin et al. in 1998 [102]. It is based on the preparation of silver NHC complexes which are obtained in good yield by the in situ deprotonation of azolium salts with silver oxide (Fig. 9). Depending on the counter ions present in the azolium salt and the steric demand of the *N*,*N*′-substituents, complexes **25a**–**25c**

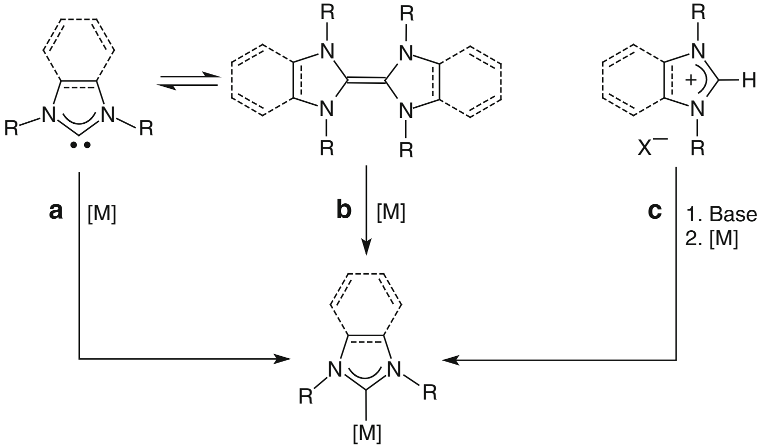


Fig. 8 Standard methods for the preparation of NHC complexes

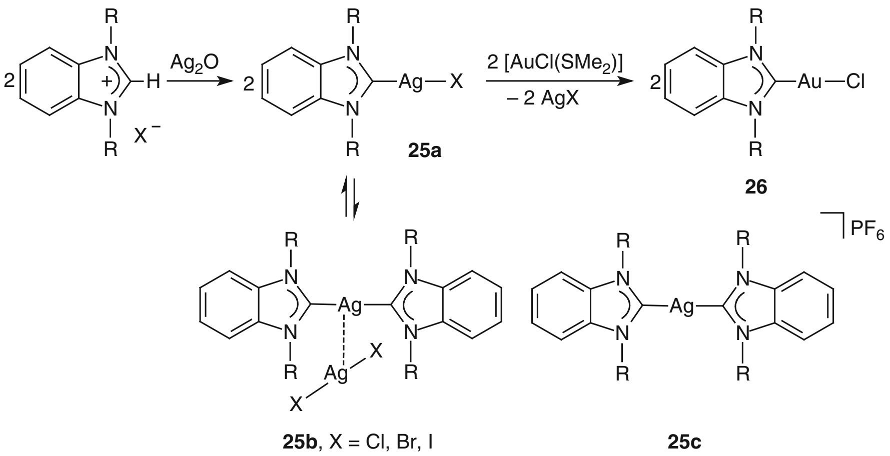


Fig. 9 Synthesis of silver NHC complexes by the Ag_2O method and carbene transfer to gold

are obtained. A large number of silver NHC complexes has been obtained by the reaction of azolium salts with Ag_2O. The Ag_2O method offers a number of advantages since the silver NHC complexes can be prepared in air and the deprotonation of the azolium salts normally occurs at the C2 position with other acidic protons in the azolium salts being generally no factor.

Due to the lability of the $Ag–C_{carbene}$ bond, silver NHC complexes of type **25** are useful agents for the NHC transfer reactions to transition metals. The preparation of silver NHC complexes using the Ag_2O method and the transfer of the NHC ligand to other metal centers like gold(I) has become a standard procedure in NHC complex synthesis. The Ag_2O method often gives access to NHC complexes where alternative syntheses are tedious or not successful.

Alternatively, NHC ligands can also be transferred from triethylborane–carbene adducts [103] or complexes of the type $[M(NHC)(CO)_5]$ (M = Cr, Mo, W) [104], but these procedures are limited to special cases and are of less importance. The coordination chemistry of silver NHC complexes [105] and the advantages and applications of the Ag_2O method [106] have recently been reviewed.

3.3 Oxidative Addition vs Reductive Elimination Reactions

The first examples for the oxidative addition of 2-chloro thiazoles to complexes of d^8 or d^{10} metal centers were reported by Roper et al. more than 30 years ago [107, 108]. In 2001 Cavell and Yates showed by detailed experimental studies supported by DFT calculations that the oxidative addition of the C2–X bond of imidazolium cations **27** to electron-rich d^{10} metals under formation of the carbene complexes **28** is energetically feasible (Fig. 10) [109–111]. The DFT calculations indicated that

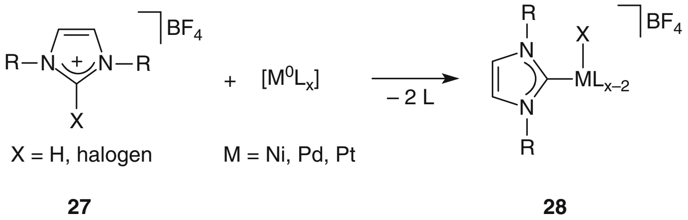


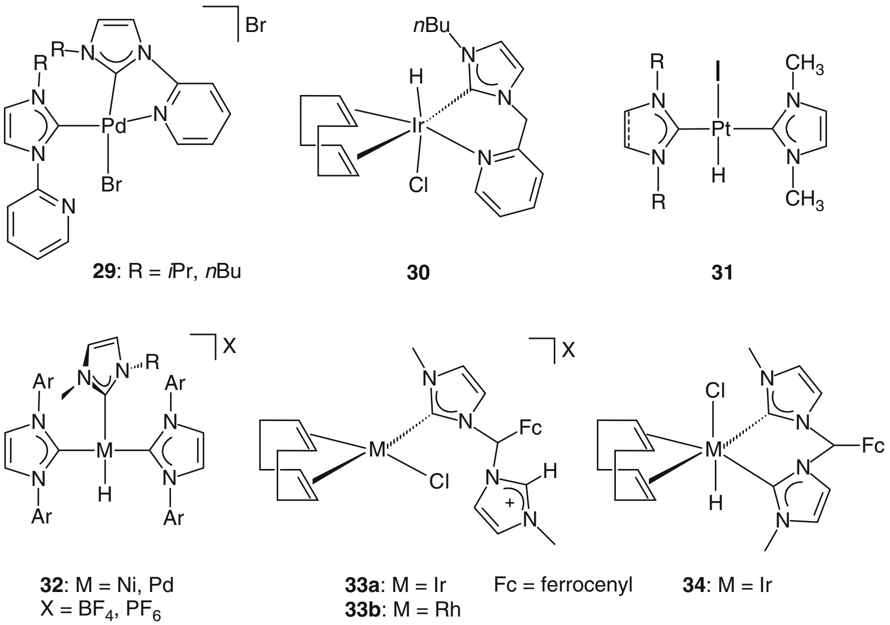
Fig. 10 Oxidative addition of azolium salts to M^0 precursors

the oxidative addition of the 1,2,3-trimethylimidazolium cation to the model compound H_3P–M–PH_3 is an exothermic reaction for M = Pt^0 and Ni^0, while it is slightly endothermic (3.7 kcal mol^{-1}) for M = Pd^0. The activation barrier for the oxidative addition of imidazolium cations (C2–X; X = CH_3, H, halogen) is lower for complexes with *cis*-coordinated basic chelate ligands compared to those with monodentate phosphine ligands. Furthermore, the exothermic character of the oxidative addition to Pd^0 increases in the order X = alkyl < H < halogen while the activation barrier decreases in the same order. These predictions were confirmed experimentally by the oxidative addition of C2–H and C2–I bonds to Pt^0, while the oxidative addition of the 1,2,3-trimethylimidazolium cation was not observed.

First attempts to isolate monocarbene-hydrido complexes by oxidative addition of *N*-(2-pyridyl)imidazolium cations to Pd^0 with utilization of the chelate effect of the donor-functionalized carbene ligand failed and only the dicarbene complexes such as **29** were isolated [112]. The iridium hydrido complex **30** was obtained in the oxidative addition of an *N*-(2-pyridylmethyl)imidazolium cation to iridium(I) (Fig. 11) [113]. This reaction proceeds most likely via the initial coordination of the nitrogen donor which brings the imidazolium C2–H bond in close proximity to the metal center. No reaction was observed with Rh^I under these conditions.

Monocarbene complexes of Pt^0 [114] as well as dicarbene complexes of Ni^0 and Pd^0 [115] activate the C2–H bond of imidazolium salts under formation of the thermally stable bis (**31**) and triscarbene hydrido complexes **32** (Fig. 11). The superb donor properties of the NHC ligands in the precursor complexes most likely support the oxidative addition of the imidazolium salt.

The oxidative addition of a ferrocenyl-bridged diimidazolium salt to $[MCl(cod)]_2$ (M = Rh^I, Ir^I) in the presence of the weak base triethylamine [116, 117] has also been studied. The two metal precursor complexes react differently. Complex **33b** was isolated for M = Rh^I, while the analogous Ir^I complex **33a** could not be isolated due to the subsequent oxidative addition of the second imidazolium unit to give **34**. While the formation of the octahedral iridium hydrido complex **34** is clearly an oxidative addition, an oxidative addition–reductive elimination mechanism has been proposed for the generation of complex **33b**. The length of the bridge between the imidazolin-2-ylidene groups in complexes of type **34** is of importance for their stability. Longer alkyl chains facilitate a reductive elimination of HCl under formation of square-planar dicarbene complexes [117].



29: R = *i*Pr, *n*Bu

30

31

32: M = Ni, Pd
X = BF_4, PF_6

33a: M = Ir
33b: M = Rh

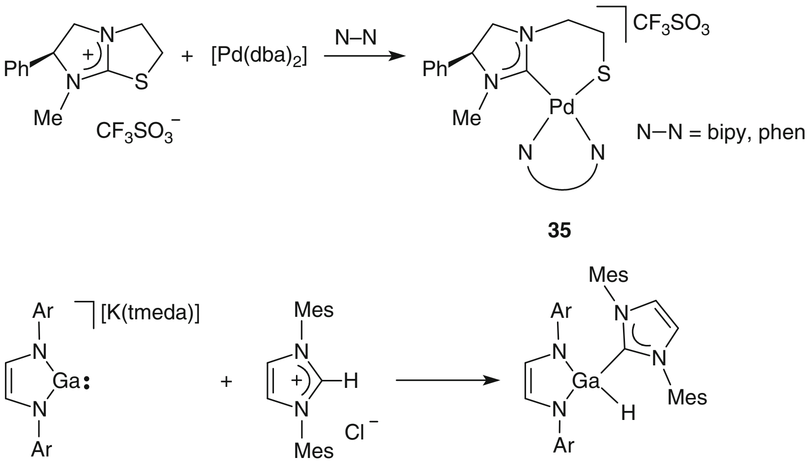
34: M = Ir

Fig. 11 Products of the oxidative addition of imidazolium salts to transition metals

In accord with calculations performed by Cavell et al. [110], the oxidative addition of C2–X functionalized azolium cations (X = halogen) to d^{10} metal centers proceeds faster and with a more favorable reaction enthalpy than the oxidative addition of the C2–H substituted imidazolium cations [118, 119]. The former reaction was applied successfully for the preparation of nickel and palladium complexes bearing a variety of different ylidene ligands [119].

Recently, the oxidative addition of C2–S bond to Pd^0 has been described. Methyl levamisolium triflate reacts with $[Pd(dba)_2]$ to give the cationic palladium complex **35** bearing a chiral bidentate imidazolidin-2-ylidene ligand [120]. The oxidative addition of the levamisolium cation to triruthenium or triosmium carbonyl compounds proceeds also readily to yield the carbene complexes [121]. The oxidative addition of imidazolium salts is not limited to d^8 or d^{10} transition metals but has also been observed in main group chemistry. The reaction of a 1,3-dimesitylimidazolium salt with an anionic gallium(I) heterocycle proceeds under formation of the gallium(III) hydrido complex **36** (Fig. 12) [122].

A large number of NHC complexes tolerate moisture, air, and elevated temperatures [1, 2]. The stability of these compounds is, however, still limited. One of the most important decomposition route for these complexes is the reductive elimination of 2-alkyl or 2-aryl substituted azolium salts from NHC complexes with alkyl or aryl groups in *cis*-position to the NHC ligand. This route can be considered as the reverse reaction of the previously discussed oxidative addition of C2–X bonds to transition metals and has been reviewed [94, 123].

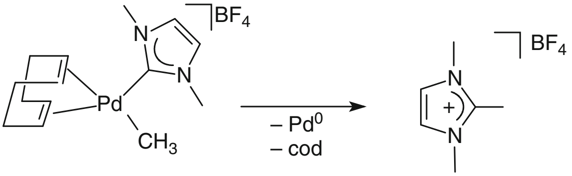


35

R = 2,6–(iPr$_2$)$_2$C$_6$H$_3$

36

Fig. 12 Oxidative addition of the levamisolium cation to Pd^0 and an imidazolium cation to Ga^I



37

38

Fig. 13 Reductive elimination of azolium salts from a palladium NHC complex

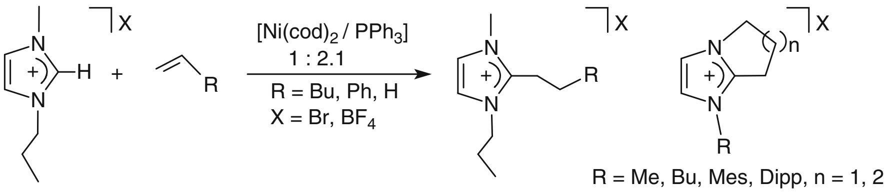
For example, complex **37** with an imidazolin-2-ylidene and a methyl ligand in *cis*-position to each other decomposes to yield the 1,2,3-trimethylimidazolium salt **38**, Pd^0, and cod (Fig. 13) [124]. Additional examples for the reductive elimination of 2-alkyl and 2-aryl substituted azolium salts from palladium or nickel NHC complexes have been reported [125, 126]. Today, reductive elimination reactions have been established as one important reaction pathway for the deactivation of catalytically active metal NHC complexes [126, 127].

Important features favoring the reductive elimination reaction have been discussed based on theoretical and experimental studies [128–130]. The reductive elimination of an azolium salt from a palladium NHC alkyl complex (Fig. 13) proceeds under direct formation of Pd^0 in an exothermic process with a low activation barrier [128]. The coligands at the palladium atom play an important role. It has been shown that the C_{alkyl}–Pd–C_{NHC} angle becomes more acute during the reductive elimination to allow for an optimal orbital overlap of the groups to be eliminated, while the angle L–Pd–L involving the coligands becomes larger. These geometry changes are best accommodated if the coligands L are monodentate donors, while bidentate chelating phosphines, for example, effectively prevent such geometric changes. Consequently, palladium NHC alkyl complexes bearing chelating diphosphines are significantly more stable against reductive elimination than their analogs with two monodentate phosphine ligands [128]. Similar observations have been made with complexes bearing bidentate carbene ligands (donor functionalized NHCs and di-NHCs) which are more stable against reductive elimination than their analogs with monodentate NHC ligands. Square-planar palladium complexes with bidentate NHC ligands gain additional stability from the coplanar arrangement of the NHC ligand with the coordination plane at the metal center which prevents an optimal orbital overlap of the groups to be eliminated [131, 132]. One dimethyl palladium complex with a pincer-NHC ligand does not undergo reductive elimination altogether, but instead reacts under migration of one methyl group from Pd^{II} to a coordinated NHC donor [133].

Additional factors which lead to an increased stability of the carbene complexes towards reductive elimination are the type of NHC ligand and the *N*,*N*′-substitution pattern. The stability of NHC complexes depends strongly on the electronic situation at the carbene center. The oxidative addition of *p*-tolyl chloride to linear Pd^0 complexes bearing two unsaturated imidazolin-2-ylidenes (type **5**, Fig. 6) or two saturated imidazolidin-2-ylidenes (type **7**, Fig. 6) proceeds readily. The Pd^{II} complex with the imidazolin-2-ylidene ligands is stable, while the one with the imidazolidin-2-ylidene ligands reductively eliminates the C2-arylated imidazolidinium salt [134].

The influence of the *N*-substituents at the carbene ligands on the course of the reductive elimination is largely based on electronic rather than steric effects if their influence on the orientation of the carbene ligand relative to the metal coordination plane in square-planar metal complexes is neglected. *N*-Substituents with a strong (+I)-effect like neopentyl or *tert*-butyl lead to electron-rich NHC ligands reducing the positive charge at the metal center and thus stabilize the complex against reductive elimination. Aromatic *N*-substituents, on the other hand, can interact with the π-system of the heterocycle leading to a reduction of the electron density at the carbene carbon atom and thus at the metal center which facilitates the reductive elimination [123, 130].

While the reductive elimination is a major pathway for the deactivation of catalytically active NHC complexes [127, 128], it can also be utilized for selective transformations. Cavell et al. [135] described an interesting combination of oxidative addition and reductive elimination for the preparation of C2-alkylated imidazolium salts. The in situ generated nickel catalyst $[Ni(PPh_3)_2]$ oxidatively added the C2–H bond of an imidazolium salt to form a Ni^{II} hydrido complex. This complex reacts under alkene insertion into the Ni–H bond followed by reductive elimination of the 2-alkylimidazolium salt **39** (Fig. 14). Treatment of *N*-alkenyl functionalized azolium salts with $[NiL_2]$ (L = carbene or phosphine) resulted in the formation of five- and six-membered ring-fused azolium (type **40**) and thiazolium salts [136, 137].



39 **40**

Fig. 14 Nickel catalyzed C–C coupling reactions

3.4 Remote Carbenes

Recently a new type of metal bonded *N*-heterocyclic carbenes named remote *N*-heterocyclic carbenes (*r*NHCs) has been described [138]. In contrast to "normal" NHCs, *r*NHCs possess no heteroatom adjacent to the carbene carbon atom. The less efficient stabilization of the carbene carbon atom has so far prevented the isolation of a free *r*NHC which consequently have to be stabilized by coordination to a suitable metal center.

Complexes with *r*NHC ligands such as **41** are normally obtained by oxidative addition of a C–X (X = halide) bond to a d^{10} metal center [138]. Compounds like **42** with no heteroatom within the cycle containing the carbene carbon atom are also known [139] together with complexes of type **43** containing *r*NHCs derived from pyrazole [140]. Quantum chemical calculations revealed M–C$_{\text{carbene}}$ bonds that are stronger than those observed in complexes with "normal" NHC ligands [141] and in recent studies complexes bearing *r*NHCs were shown to exhibit a superior performance in catalytic C–C coupling reactions compared to complexes with classical NHC ligands [142].

3.5 Abnormal Carbenes

In addition to complexes of type **44** with a C2 coordinated NHC ligand, complexes of type **45** with abnormal C4 or C5 bound carbene ligands have recently been described (Fig. 16) [143, 144]. The carbene carbon atom in these complexes is stabilized by only one nitrogen atom. A similar situation has been observed for the cyclic (alkyl)(amino)carbene (type **16**, Fig. 6) [38, 39].

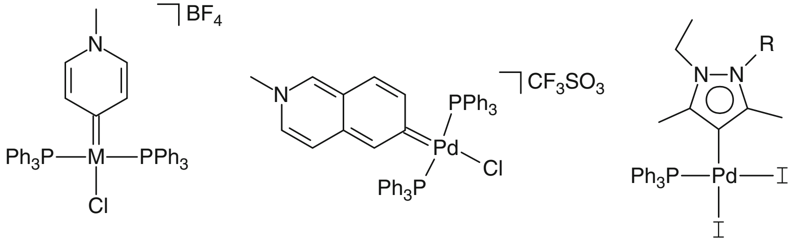
The formation of complexes with abnormal carbene ligands is controlled by steric, electronic, and kinetic effects as well as by the counter ion present in the azolium salt [145–148]. In selected cases the base used for the deprotonation of the azolium salt [149, 150] also plays a significant role. Crabtree et al. demonstrated in a detailed study that *N*-pyridyl functionalized imidazolium salts react with

$[IrH_5(PPh_3)_2]$ under formation of the complexes with C2 (**46**) or C5 (**47**) metalated NHC ligand depending on the type of *N*′-substituent and the counter ion present (Fig. 17) [148].

The exclusive coordination of the C5 carbon atom in complex **48** was achieved by a reduction of the bite angle [147]. Blocking of the C4 and C5 positions as seen in benzimidazolin-2-ylidenes led to the complex with the C2-metalated NHC ligand **49** [147]. No transformation of a C5-coordinated NHC ligand into a C2-coordinated one, i.e., conversion of **46** to **47** or vice versa, has been observed so far.

Not only donor-functionalized but also simple *N*,*N*′-dialkyl or *N*,*N*′-diaryl functionalized imidazolium salts can lead to complexes with abnormal NHC ligands. The iridium complex **50**, for example, is formed by selective metalation of the sterically least-hindered ring carbon atom (Fig. 18) [151]. Blocking of the C2 position of the heterocycle with an alkyl or aryl group also leads to the formation of C4 or C5 bound carbene ligands in **51** [151] and **52** [152]. Albrecht et al. have shown that this method is suitable for the preparation of complexes like **53** bearing methylene bridged dicarbene ligands where both carbene donors are metalated at the C5 position (Fig. 18) [153, 154].

Alternatively, complexes **54** and **55** with abnormally bound NHC ligands have been obtained by oxidative addition of a C–H bond to Pd^0 and Pt^0 while blocking the C2 position of the azolium salt [155] or even without any blocking of the C2 position by oxidative addition of a C5–I bond of a donor-functionalized imidazolium cation (Fig. 19) [156].



41, M = Ni, Pd, Pt

42

43, R = Me, Ph

Fig. 15 Complexes with *r*NHC ligands

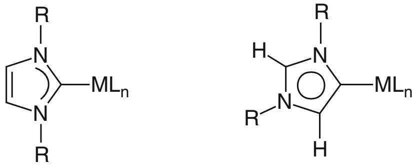


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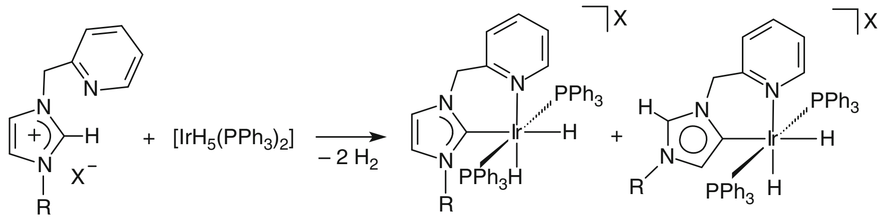
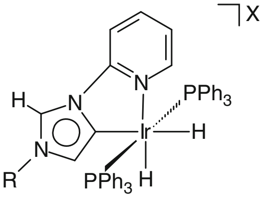
Fig. 16 Complex with "normal" and abnormal bound carbene ligands

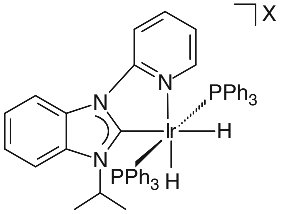


R	X	**46** [%]	**47** [%]
Me	Br	91	9
Me	BF_4	45	55
*i*Pr	Br	84	16
*i*Pr	BF_4	0	100



X = Br, BF_4
R = Mes, *i*Pr, *n*Bu, Me

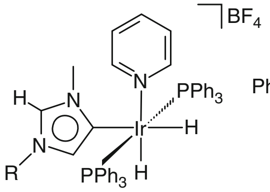
48



X = Br, BF_4

49

Fig. 17 Iridium complexes with normally and abnormally coordinated NHC ligands



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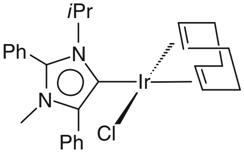

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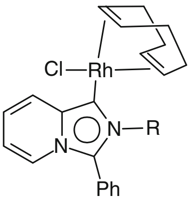

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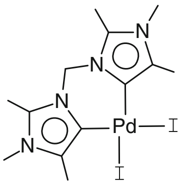


53

Fig. 18 Complexes with mono and bidentate abnormally coordinated NHC ligands

3.6 Template Synthesis of NHC Complexes

The majority of *N*-heterocyclic carbenes and their metal complexes are obtained from cyclic azolium derivatives (Fig. 8). Nevertheless, the first complex with a heteroatom stabilized carbene ligand, although it was not recognized as such, was prepared by Tschugajeff et al. as early as 1925 [157]. It was later identified as a heterocarbene complex [158]. Tschugajeff reacted the nucleophilic proton base

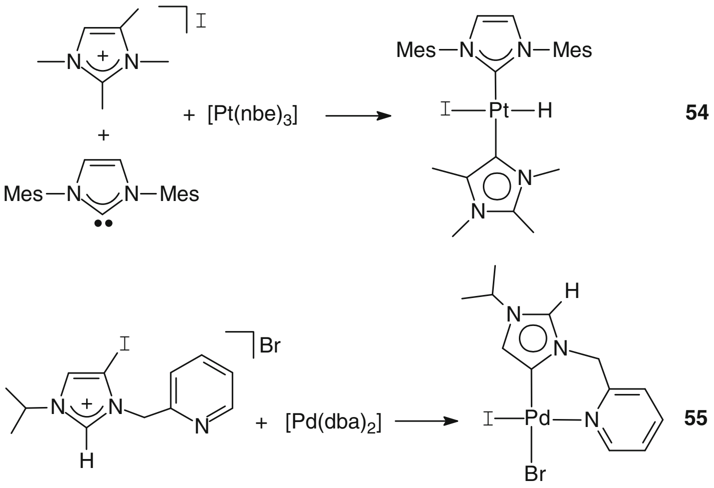


Fig. 19 Synthesis of complexes with abnormal NHC ligands by oxidative addition

hydrazine with a diisocyanide complex [157] under formation of the heterocarbene complex.

The use of functionalized isocyanides containing both the isocyanide function and the nucleophile in the same molecule leads to complexes with heterocyclic carbene ligands via a 1,2-addition across the C≡N triple bond. Complexes with functionalized isocyanide ligands can be generated in template reactions or a nucleophile functionalized isocyanide can be reacted directly with a suitable metal complex.

The template-controlled generation of nucleophile functionalized isocyanides is achieved by the reaction of coordinated isocyanic acid with epoxides or aziridine (Fig. 20a) [159–163]. Liu et al. reacted an amine phosphinimine with a metal carbonyl complex and obtained the complex with the β-amine functionalized isocyanide ligand. Subsequent spontaneous cyclization led to the carbene complexes of type **56** (Fig. 20b) [164, 165]. Additional templates syntheses of complexes with cyclic heterocarbene ligands using isocyanide [166] or carbonyl complexes [167] as starting material have been described. Unsaturated imidazolin-2-ylidenes have been generated by the nucleophilic attack of the diacetal protected amino acetaldehyde at a tetraisocyanide palladium complex followed by an acid-catalyzed cyclization reaction resulting in the formation of the tetracarbene complex **57** with four NH,NR-stabilized imidazolin-2-ylidene ligands (Fig. 20c) [168, 169]. Another method for the synthesis of complexes with imidazolin-2-ylidenes ligands is the template-controlled coupling of a propargyl amine with a phenylisocyanide leading to complex **58** (Fig. 20d) [170, 171].

Much simpler than the template-controlled generation of β-functionalized isocyanides is their direct use. 2-Hydroxyalkyl isocyanide **59**, where the nucleophilic group and the isocyanide are linked together, spontaneously cyclizes upon activation of the isocyanide by coordination to an electron-poor metal center under

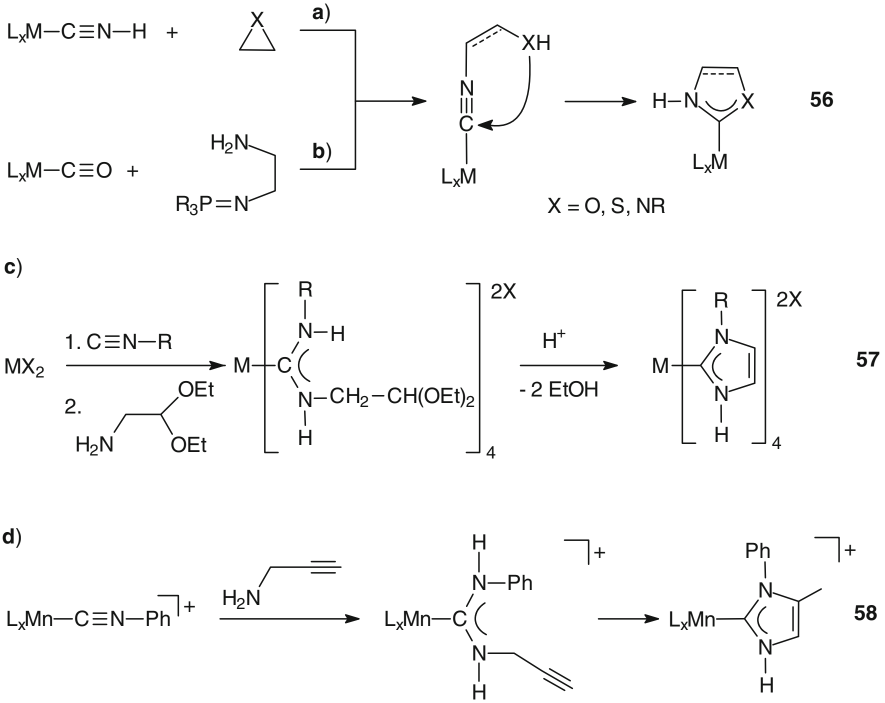


Fig. 20 Template-synthesis of β-functionalized isocyanides followed by cyclization

formation of the heterocarbene complex **60** (Fig. 21) [172, 173]. This cyclization is obstructed, however, if the ligand coordinates to an electron-rich metal center which deactivates the isocyanide for an intramolecular nucleophilic attack by strong μ→CNR π-backbonding [174]. The analogous 2-aminoethyl isocyanide is not stable in the free state, but it can be generated in a Staudinger reaction from coordinated 2-azidoethyl isocyanide at a suitable metal center. The in situ generated 2-aminoethyl isocyanide then cyclizes to yield complex **61** with an NH,NH-stabilized cyclic heterocarbene ligand [175]. The same cyclization has been observed starting from $[W(CO)_6]$ and an amine phosphinimine (Fig. 20b) [164, 165]. The *N*,*N′*-dialkylation of **61** proceeds readily (Fig. 21) [175].

The β-functionalized 2-hydroxyphenyl isocyanide not only contains the isocyanide and the nucleophile within the same molecule, but both functional groups are also arranged in one plane for an intramolecular nucleophilic attack [176]. This arrangement, in addition to the aromaticity of the five-membered ring obtained after cyclization to the carbene ligand, particularly favors the intramolecular nucleophilic attack. In contrast to 2-hydroxyethyl isocyanide, free 2-hydroxyphenyl isocyanide is not stable [177]. The stable 2-trimethylsiloxyphenyl isocyanide [178] can serve as a synthon for 2-hydroxyphenyl isocyanide. Carbene complexes **63** with an NH,O-stabilized NHC ligand can be obtained from the complexes **62** with the

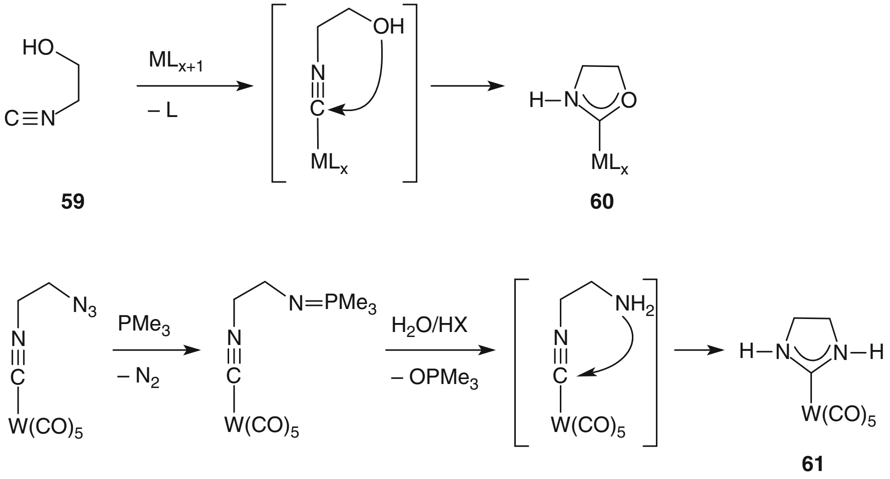


Fig. 21 Template-controlled synthesis of NH,O and NH,NH-stabilized heterocarbene ligands

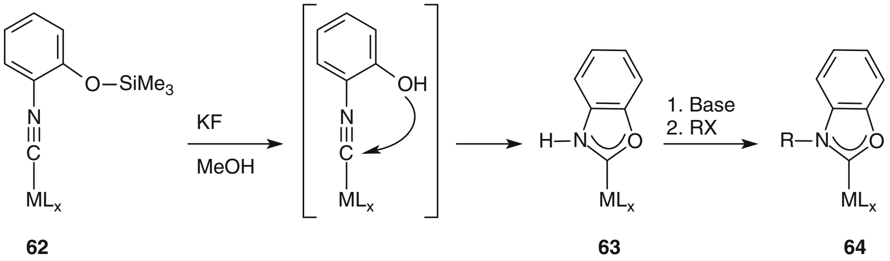


Fig. 22 Template-controlled synthesis of NH,O- and NR,O-stabilized heterocarbene ligands

2-trimethylsiloxyphenyl isocyanide ligand by cleavage of the O–$SiMe_3$ bond with potassium fluoride followed by intramolecular cyclization (Fig. 22) [179]. The *N*-alkylation of the heterocycle to give **64** proceeds readily [179, 180].

The cyclization reaction of coordinated 2-hydroxyphenyl isocyanide is obstructed, when the isocyanide is coordinated to an electron-rich transition metal complex where the isocyanide ligand is deactivated by strong d→π* backbonding from the metal center to the isocyanide. Very strong μ→CNR backbonding can lead to an umpolung of the reactivity of the coordinated isocyanide ligand, which is then attacked by electrophiles at the isocyanide nitrogen atom [181]. The reactivity of β-hydroxy functionalized isocyanide ligands has been reviewed [182, 183].

Both 2-azido [184] and 2-nitrophenyl isocyanides [185] are suitable synthons for the generation of the freely unstable 2-aminophenyl isocyanide and they have been used (Fig. 23) in the template-controlled preparation of NH,NH-stabilized benzimidazolin-2-ylidene ligands. Both phenyl isocyanides coordinate readily to transition metal centers. The isocyanide ligand in complex **65** reacts with PPh_3 and the resulting iminophosphine group in complex **66** can be hydrolyzed with HBr/H_2O leading via cyclization of the intermediate 2-aminophenyl isocyanide derivative to **67** with an NH,NH-stabilized benzimidazolin-2-ylidene ligand.

Complex **67** is also accessible from the 2-nitrophenyl isocyanide complex **68** by reduction of the nitro group with Sn/HCl. Incomplete reduction of the nitro group in **68** with Raney-Nickel/hydrazine yields, after intramolecular cyclization, the complex **70** with the NH,NOH-stabilized benzimidazolin-2-ylidene ligand. Complex **69** with the 2-hydoxylamin-substituted phenyl isocyanide ligand presumably occurs as an intermediate in this reaction. The alkylation of both the NH,NH- and the NH, NOH-stabilized NHC ligands in **67** and **70**, respectively, proceeds readily (Fig. 23) [184, 185].

The template-controlled generation of ylidene ligands from β-functionalized isocyanides constitutes an alternative access to complexes with cyclic diaminocarbenes. It proceeds via the complexes with NH,NH-stabilized ylidene ligands which are easily alkylated at the heteroatoms. Such complexes are valuable and reactive intermediates for the generation of complexes with macrocyclic ligands possessing NHC donors (see Sect. 4).

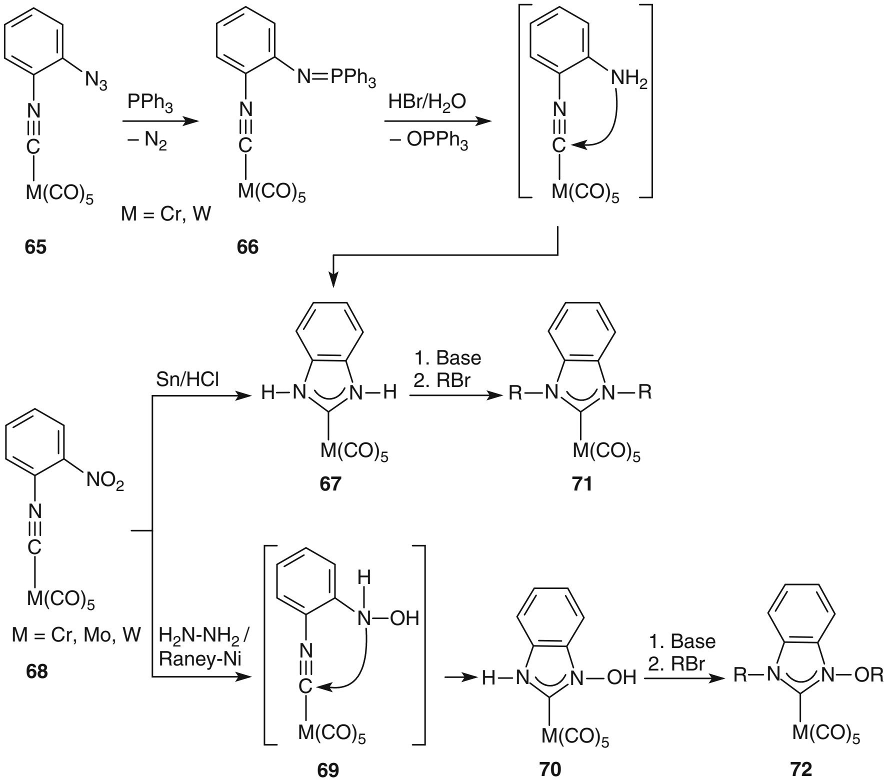


Fig. 23 Template-controlled synthesis of benzimidazolin-2-ylidene ligands

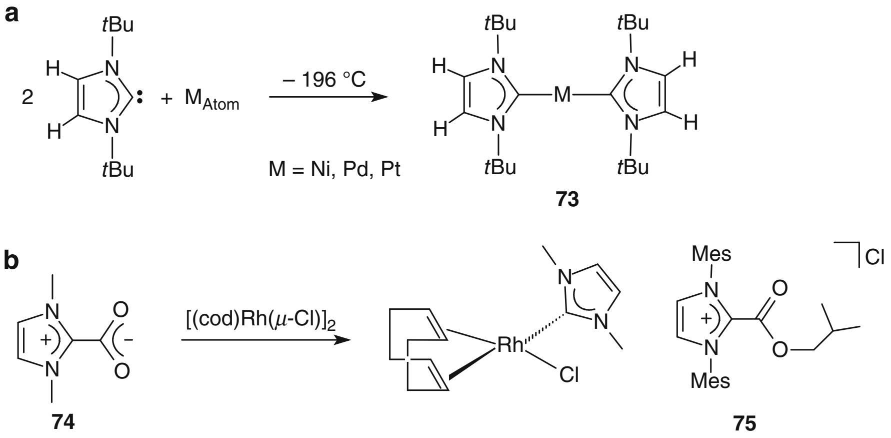


Fig. 24 Alternative methods for the preparation of NHC complexes

3.7 Additional Methods for the Preparation of NHC Complexes

Cloke et al. presented the elegant metal-vapor synthesis for the preparation of linear 14 valence-electron complexes [M^0(NHC)$_2$] **73** (M = Ni, Pd, Pt) (Fig. 24a) [186]. The method was subsequently improved [187] and the interesting electronic and catalytic properties of Pd^0 and Pt^0 biscarbene complexes have been studied in detail [188–191].

The air and moisture stable zwitterionic *N*,*N*′-dimethylimidazolium-2-carboxylate **74** has been shown to be an efficient carbene transfer agent for various metals (Rh, Ir, Ru, Pd, Pt) (Fig. 24b) [192]. Since the access to derivatives of type **74** is of limited generality, the imidazolium-2-isobutylester salt **75** has been developed and used in the preparation of NHC complexes [193].

N-Alkylimidazole and various thiazoles can be deprotonated with *n*-butyl lithium at the C2 carbon atom [194, 195]. The lithiated species **76** obtained from *N*-methylimidazole is readily metalated by transition metals at the C2 ring atom to yield the unstable intermediate **77** [196]. *N*-Methylation of compound **77** yields complex **78** with the *N*,*N*′-dimethylimidazolin-2-ylidene ligand, while all attempts to protonate the ring nitrogen atom in **77** failed and resulted in formation of the imido complex **79** (Fig. 25a) [196]. In contrast to this observation, lithiated *N*-ethylbenzimidazole reacts regioselectively with [W(CO)$_5$(THF)] to give the C2 metalated anionic tungsten complex **80** which was subsequently protonated exclusively at the ring nitrogen atom to yield complex **81** with an NH,NR-stabilized benzimidazolin-2-ylidene ligand (Fig. 25b) [197].

Recently the synthesis of NHC complexes by a base catalyzed tautomeric rearrangement has been introduced. *N*-Phenylimidazole coordinates via the unsubstituted nitrogen atom to Mn$^{\mathrm{I}}$ to give complex **82** (Fig. 26a) [198]. Subsequent attempts to deprotonate the C2 carbon atom in complex **82** led to the intermediate

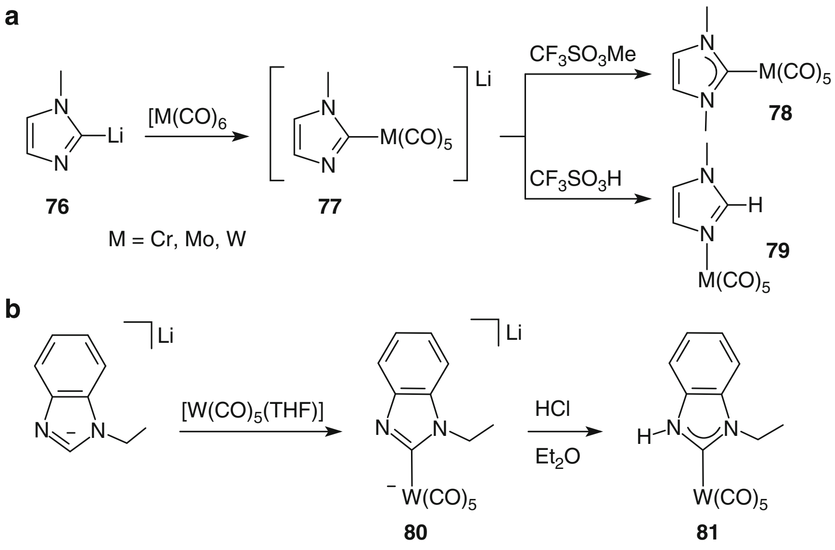


Fig. 25 Metalation of azoles

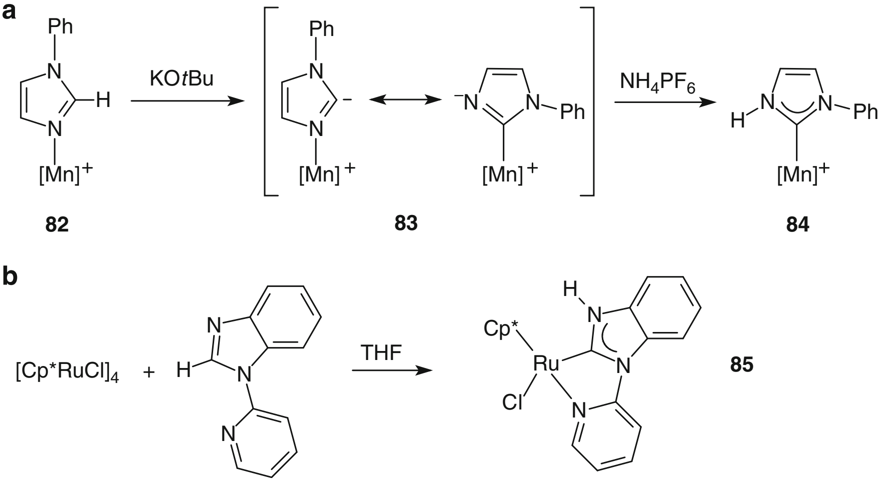


Fig. 26 Synthesis of NHC complexes by tautomeric rearrangements

83, which upon protonation with NH_4PF_6 gave complex **84** with a C2 metalated NH,NPh-stabilized imidazolin-2-ylidene ligand [198]. A direct tautomerization was observed with *N*-pyridylbenzimidazole which upon reaction with $[Cp^*RuCl]_4$ gave the complex with the C2 metalated, chelating coordinated bidentate benzimidazolin-2-ylidene **85** (Fig. 26b) [199]. The formation of related, catalytically active

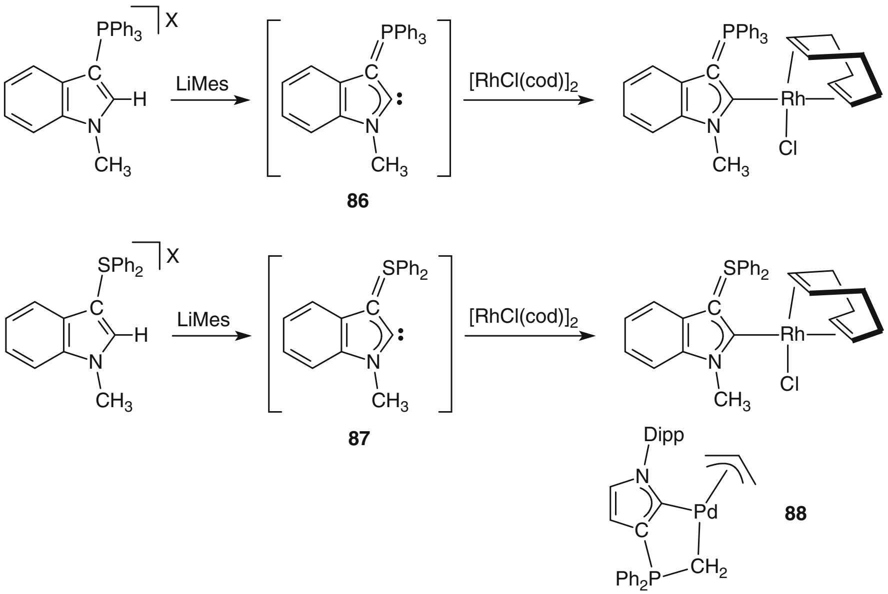


Fig. 27 Synthesis of complexes with (amino)(ylidene)carbenes

rhodium(I) complexes with NH,NR-stabilized benzimidazolin-2-ylidene ligands has been described by Bergman et al. [200–202].

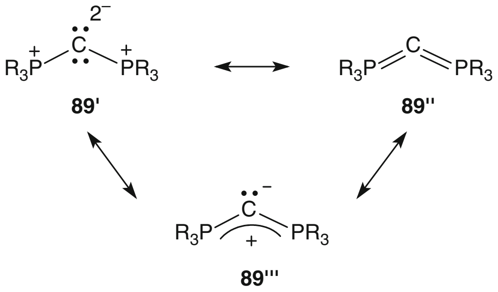
4 New Trends in the Chemistry of NHC Ligands

In spite of the large number of *N*-heterocyclic carbenes known to date, new NHC ligands are regularly introduced. A selection of most recent developments is presented in this section.

The most recent development concerns the heterocyclic (amino)(ylide)carbenes AYC. Such compounds have been known for some years [203] but so far had little impact compared to their diamino stabilized relatives. Both phosphorus ylide (**86**) and sulfur ylide (**87**) stabilized AYC ligands have been generated in situ and were stabilized at suitable metal centers (Fig. 27) [204, 205]. The palladium complex **88** with an anionic (amino)[bis(ylide)]carbene is also known [206].

Iminio–phosphonio dications have been obtained by *N*- and *P*-methylation of (imidazolylphenyl)diphenylphosphine. These dications are suitable precursors for C,C-chelating ligands. Deprotonation of the *N*-heterocycle leads to an NHC carbene which can be coordinated to a suitable metal center like Pd^{II}. The subsequent deprotonation of the phosphonio moiety gave the complex with a bidentate chelating coordinated NHC–ylide ligand [207, 208].

Fig. 28 Resonance structures for carbodiphosphoranes



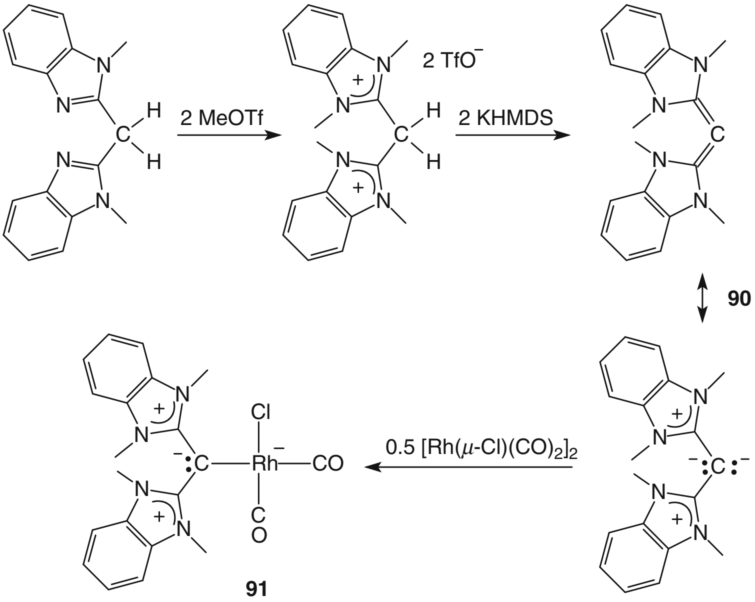


Fig. 29 Synthesis and coordination chemistry of the first carbodicarbene

Carbodiphosphoranes of type **89** [209] have been known for many years. The bonding parameters and the reactivity indicate that the electronic situation in these compounds is reasonably described by the polar structure **89**′ with two electron pairs at the central carbon atom, although alternative representations (**89**″ and **89**‴) are also possible (Fig. 28) [210].

NHCs are often compared to phosphines and theoretical studies by Frenking et al. [211–213] showed that the substitution of the phosphines in **89** for two NHCs leads to compounds with a carbon(0) atom that is formally stabilized by two NHC→C donor–acceptor bonds. The first carbodicarbene **90** was prepared by Bertrand et al. who selected benzimidazolin-2-ylidenes as carbene donors and the deprotonation of the conjugated acid of an allene as the synthetic strategy (Fig. 29)

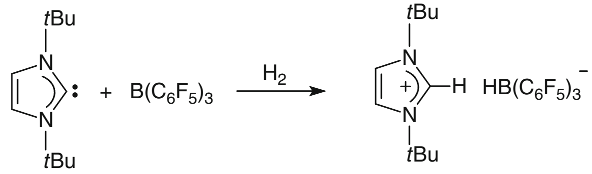
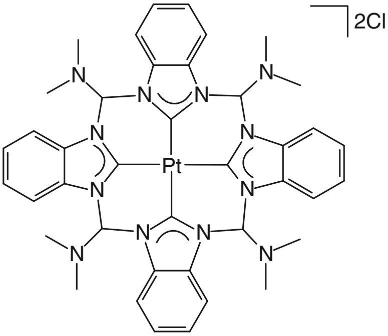


Fig. 30 Reaction of the frustrated Lewis acid/Lewis base pair NHC/$B(C_6F_5)_3$ with H_2



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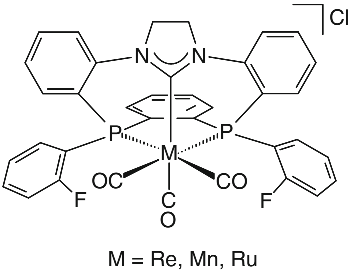

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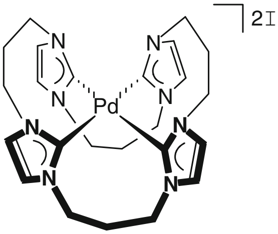

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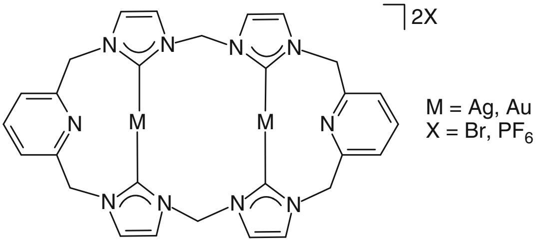


95

Fig. 31 Complexes with macrocyclic ligands containing NHC donor groups

[214]. Alternatively, compound **90** can be described as a strongly bent allene (angle C–C–C 134.8(2)°). The monometalation of **90** to give complex **91** has also been demonstrated.

Fürstner et al. studied the polarized C–C bond in 2-methyl substituted imidazolium salts and were able to metalate the terminal carbon atom in these compounds [215]. A very recent report on a five-membered-ring allene [216] has initiated a discussion about the type of bonding these derivatives [217, 218].

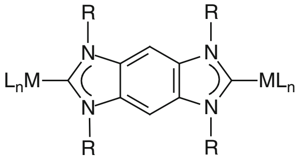
NHCs possess a lone pair of electrons and an accessible vacant orbital. This combination resembles the situation in many transition metal centers and could thus mimic their chemical behavior. While cyclic diaminocarbenes are inert towards hydrogen, it has been demonstrated that cyclic (alkyl)(amino)carbenes of type **16**

(Fig. 6) can activate hydrogen under mild conditions [219]. In contrast to transition metals, that act as electrophiles towards hydrogen, the (alkyl)(amino)carbenes mainly behave as nucleophiles initially creating a hydride like species, which then attacks the positively polarized carbene carbon atom.

Even more effective in hydrogen activation are frustrated Lewis pairs [220] containing NHCs as Lewis bases. In 2008 two research groups reported the activation of hydrogen by frustrated Lewis pairs made up from a suitably *N*,*N*′-substituted NHC and $B(C_6F_5)_3$ (Fig. 30) [221, 222]. The corresponding reaction of the frustrated Lewis pair with primary and secondary alkyl amines resulted in the formation of aminoboranes [222].

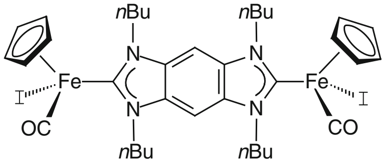
Complexes with cyclic polydentate ligands containing NHC donor groups like **92** and **93** have been obtained in metal template-controlled reactions [223–225]. Related complexes (**94** and **95**) have been synthesized directly from polyimidazolium salts [226, 227] (Fig. 31).

Bielawski et al. have developed “Janus-head” dicarbene ligands which are able to act as a bridge between two metal centers, thereby leading to dinuclear complexes of type **96** [58–60] (Fig. 32). More recently homonuclear bimetallic ruthenium(II) and iron(II) complexes **97** have been synthesized. It was hoped that the dicarbene ligand would interconnect the redox-active metal centers, but the



M = Ag, Rh, Ru

96



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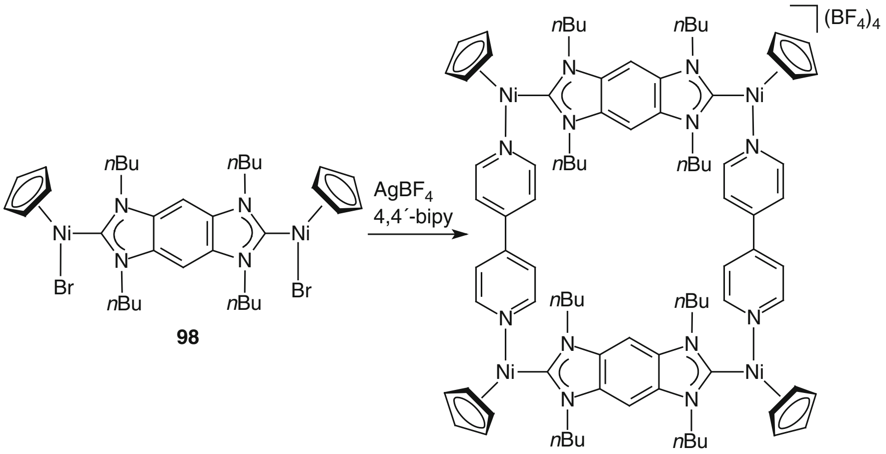

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Fig. 32 Coordination compounds of rigid dicarbene ligands observed metal–metal interactions are only very weak or modest [228]. Nevertheless, rigid dicarbene ligands are useful building blocks for the synthesis of supramolecular structures. The dinuclear nickel complex **98** reacts with 4,4′-bipyridine after abstraction of the bromo ligands with $AgBF_4$ to give the molecular rectangular **99** (Fig. 32) [229].

References

1. Hahn FE, Jahnke MC (2008) Angew Chem Int Ed 47:3122
2. Bourissou D, Guerret O, Gabbaï FP, Bertrand G (2000) Chem Rev 100:39
3. Wanzlick H-W, Schikora E (1960) Angew Chem 72:494
4. Wanzlick H-W, Kleiner H-J (1961) Angew Chem 73:493
5. Wanzlick H-W, Schönherr H-J (1968) Angew Chem Int Ed 7:141
6. Öfele K (1968) J Organomet Chem 12:P42
7. Lappert MF (2005) J Organomet Chem 690:5467
8. Arduengo AJ III, Harlow RL, Kline M (1991) J Am Chem Soc 113:361
9. Herrmann WA (2002) Angew Chem Int Ed 41:1291
10. Lee M-T, Hu C-H (2004) Organometallics 23:976
11. Hu X, Castro-Rodriguez I, Olsen K, Meyer K (2004) Organometallics 23:755
12. Cavallo L, Correa A, Costabile C, Jacobsen H (2005) J Organomet Chem 690:5407
13. Tonner R, Heydenrych G, Frenking G (2007) Chem Asian J 2:1555
14. Chianese AR, Li X, Janzen MC, Faller JW, Crabtree RH (2003) Organometallics 22:1663
15. Kelly RA III, Clavier H, Guidice S, Scott NM, Stevens ED, Bordner J, Samardjiev I, Hoff CD, Cavallo L, Nolan SP (2008) Organometallics 27:202
16. Dorta R, Stevens ED, Scott NM, Costabile C, Cavallo L, Hoff CD, Nolan SP (2005) J Am Chem Soc 127:2485
17. Lavallo V, Canac Y, Donnadieu B, Schoeller WW, Bertrand G (2006) Science 312:722
18. Holschumacher D, Hrib CG, Jones PG, Tamm M (2007) Chem Commun 3661
19. Despagnet-Ayoub E, Grubbs RH (2004) J Am Chem Soc 126:10198
20. Alder RW, Blake ME, Bortolotti C, Bufali S, Butts CP, Linehan E, Oliva JM, Orpen AG, Quayle MJ (1999) Chem Commun 241
21. Bazinet P, Ong T-G, O´Brien JS, Lavoie N, Bell E, Yap GPA, Korobkov I, Richeson DS (2007) Organometallics 26:2885
22. Jazzar R, Liang H, Donnadieu B, Bertrand G (2006) J Organomet Chem 691:3201
23. Scarborough CC, Grady MJW, Guzei IA, Gandhi BA, Bunel EE, Stahl SS (2005) Angew Chem Int Ed 44:5269
24. Iglesias M, Beetstra DJ, Knight JC, Ooi L-L, Stasch A, Coles S, Male L, Hursthouse MB, Cavell KJ, Dervisi A, Fallis IA (2008) Organometallics 27:3279
25. Herrmann WA, Gooßen LJ, Spiegler M (1997) J Organomet Chem 547:357
26. Böhm VPW, Weskamp T, Gstöttmayr CWK, Herrmann WA (2000) Angew Chem Int Ed 39:1602
27. Gridnev AA, Mihaltseva IM (1994) Synth Commun 24:1547
28. Altenhoff G, Goddard R, Lehmann CW, Glorius F (2003) Angew Chem Int Ed 42:3690
29. Fürstner A, Alcarazo M, César V, Lehmann CW (2006) Chem Commun 2176
30. Bon RS, de Kanter FJJ, Lutz M, Spek AL, Jahnke MC, Hahn FE, Groen MB, Orru RVA (2007) Organometallics 26:3639
31. Kuhn N, Kratz T (1993) Synthesis 561
32. Hahn FE, Wittenbecher L, Boese R, Bläser D (1999) Chem Eur J 5:1931
33. Denk MK, Gupta S, Brownie J, Tajammul S, Lough AJ (2001) Chem Eur J 7:4477

34. Hahn FE, Paas M, Le Van D, Lügger T (2003) Angew Chem Int Ed 42:5243
35. Hahn FE, Paas M, Le Van D, Fröhlich R (2005) Chem Eur J 11:5080
36. Enders D, Breuer K, Raabe G, Runsink J, Teles JH, Melder J-P, Ebel K, Brode S (1995) Angew Chem Int Ed Engl 34:1021
37. Arduengo AJ III, Goerlich JR, Marshall WJ (1997) Liebigs Ann Recueil 365
38. Lavallo V, Canac Y, Präsang C, Donnadieu B, Bertrand G (2005) Angew Chem Int Ed 44:5705
39. Lavallo V, Canac Y, DeHope A, Donnadieu B, Bertrand G (2005) Angew Chem Int Ed 44:7236
40. Martin D, Baceiredo A, Gornitzka H, Schoeller WW, Bertrand G (2005) Angew Chem Int Ed 44:1700
41. Herrmann WA, Elison M, Fischer J, Köcher C, Artus GRJ (1996) Chem Eur J 2:772
42. Denk MK, Hatano K, Ma M (1999) Tetrahedron Lett 40:2057
43. Denk MK, Thadani A, Hatano K, Lough AJ (1997) Angew Chem Int Ed Engl 36:2607
44. Scholl M, Ding S, Lee CW, Grubbs RH (1999) Org Lett 1:953
45. Blum AP, Ritter T, Grubbs RH (2007) Organometallics 26:2122
46. Nyce GW, Csihony S, Waymouth RW, Hedrick JL (2004) Chem Eur J 10:4073
47. Korotkikh NI, Raenko GF, Pekhtereva TM, Shvaika OP, Cowley AH, Jones JN (2006) Russ J Org Chem 42:1822
48. Gorodetsky B, Ramnial T, Branda NR, Clyburne JAC (2004) Chem Commun 1972
49. Arduengo AJ III, Davidson F, Dias HVR, Goerlich JR, Khasnis D, Marshall WJ, Prakasha TK (1997) J Am Chem Soc 119:12742
50. Taton TA, Chen P (1996) Angew Chem Int Ed Engl 35:1011
51. Alder RW, Blake ME, Chaker L, Harvey JN, Paolini F, Schütz J (2004) Angew Chem Int Ed 43:5896
52. Arduengo AJ III, Dias HVR, Dixon DA, Harlow RL, Klooster WT, Koetzle TF (1994) J Am Chem Soc 116:6812
53. Heinemann C, Müller T, Apeloig Y, Schwarz H (1996) J Am Chem Soc 118:2023
54. Boehme C, Frenking G (1996) J Am Chem Soc 118:2039
55. Arduengo AJ III, Goerlich JR, Marshall WJ (1995) J Am Chem Soc 117:11027
56. Hahn FE, Wittenbecher L, Le Van D, Fröhlich R (2000) Angew Chem Int Ed 39:541
57. Liu Y, Lindner PE, Lemal DM (1999) J Am Chem Soc 121:10626
58. Boydston AJ, Williams KA, Bielawski CW (2005) J Am Chem Soc 127:12496
59. Khramov DM, Boydston AJ, Bielawski CW (2006) Angew Chem Int Ed 45:6186
60. Boydston AJ, Bielawski CW (2006) Dalton Trans 4073
61. Weiss R, Reichel S (2000) Eur J Inorg Chem 1935
62. Nonnenmacher M, Kunz D, Romminger F, Oeser T (2005) J Organomet Chem 690:5647
63. Alcarazo M, Roseblade SJ, Cowley AR, Fernández R, Brown JM, Lassaletta JM (2005) J Am Chem Soc 127:3290
64. Guerret O, Solé S, Gornitzka H, Teichert M, Trinquier G, Bertrand G (1997) J Am Chem Soc 119:6668
65. Guerret O, Solé S, Gornitzka H, Trinquier G, Bertrand G (2000) J Organomet Chem 600:112
66. Mas-Marzá E, Mata JA, Peris E (2007) Angew Chem Int Ed 46:3729
67. Enders D, Balensiefer T (2004) Acc Chem Res 37:534
68. Enders D, Niemeier O, Henseler A (2007) Chem Rev 107:5606
69. Ishida Y, Donnadieu B, Bertrand G (2006) Proc Natl Acad Sci USA 103:13585
70. Iglesias M, Beetstra DJ, Stasch A, Horton PN, Hursthouse MB, Coles SJ, Cavell KJ, Dervisi A, Fallis IA (2007) Organometallics 26:4800
71. Khramov DM, Rosen EL, Lynch VM, Bielawski CW (2008) Angew Chem Int Ed 47:2267
72. Siemeling U, Färber C, Bruhn C (2009) Chem Commun 98
73. Nolan SP (2006) *N*-Heterocyclic carbenes in synthesis. Wiley, New York
74. Glorius F (2007) Top Organomet Chem 21:1
75. Herrmann WA, Köcher C, Gooßen LJ, Artus GRJ (1996) Chem Eur J 2:1627

76. Douthwaite RE, Haüssinger D, Green MLH, Silcock PJ, Gomes PT, Martins AM, Danopoulos AA (1999) Organometallics 18:4584
77. Herrmann WA, Schwarz J, Gardiner MG (1999) Organometallics 18:4082
78. Mata JA, Chianese AR, Miecznikowski JR, Poyatas M, Peris E, Faller JW, Crabtree RH (2004) Organometallics 23:1253
79. Hahn FE, Foth M (1999) J Organomet Chem 585:241
80. Hahn FE, von Fehren T, Wittenbecher L, Fröhlich R (2004) Z Naturforsch 59b:541
81. Hu X, Meyer K (2005) J Organomet Chem 690:5474
82. Normand AT, Cavell KJ (2008) Eur J Inorg Chem 2781
83. Jahnke MC, Pape T, Hahn FE (2009) Eur J Inorg Chem 1960
84. Lee C-C, Ke W-C, Chan K-T, Lai C-L, Hu C-H, Lee HM (2007) Chem Eur J 13:582
85. Albrecht M, van Koten G (2001) Angew Chem Int Ed 40:3750
86. Hahn FE, Jahnke MC, Pape T (2007) Organometallics 26:150
87. Pugh D, Danopoulos AA (2007) Coord Chem Rev 251:610
88. Peris E, Crabtree RH (2004) Coord Chem Rev 248:2239
89. Baker MV, Skelton BW, White AH, Williams CC (2002) Organometallics 21:2674
90. Wong WWH, Vickers MS, Cowley AR, Paul RL, Beer PD (2005) Org Biomol Chem 3:4201
91. Chellappan K, Singh NJ, Hwang I-C, Lee JW, Kim KS (2005) Angew Chem Int Ed 44:2899
92. Arnold PL, Liddle ST (2006) Chem Commun 3959
93. Braband H, Kückmann TI, Abram U (2005) J Organomet Chem 690:5421
94. Crudden CM, Allen DP (2004) Coord Chem Rev 248:2247
95. Lappert MF (1988) J Organomet Chem 358:185
96. Hahn FE, von Fehren T, Lügger T (2005) Inorg Chim Acta 358:4137
97. Herrmann WA, Elison M, Fischer J, Köcher C, Artus GRJ (1995) Angew Chem Int Ed Engl 34:2371
98. Köcher C, Herrmann WA (1997) J Organomet Chem 532:261
99. Hahn FE, Holtgrewe C, Pape T, Martin M, Sola E, Oro LA (2005) Organometallics 24:2203
100. Weskamp T, Böhm VPW, Herrmann WA (2000) J Organomet Chem 600:12
101. Herrmann WA, Köcher C (1997) Angew Chem Int Ed Engl 36:2162
102. Wang HMJ, Lin IJB (1998) Organometallics 17:972
103. Yamaguchi Y, Kashiwabara T, Ogata K, Miura Y, Nakamura Y, Kobayashi K, Ito T (2004) Chem Commun 2160
104. Liu S-T, Reddy KR (1999) Chem Soc Rev 28:315
105. Garrison JC, Youngs WJ (2005) Chem Rev 105:3978
106. Lin IJB, Vasam CS (2007) Coord Chem Rev 251:642
107. Fraser PJ, Roper WR, Stone FGA (1973) J Organomet Chem 50:C54
108. Fraser PJ, Roper WR, Stone FGA (1974) J Chem Soc Dalton Trans 102
109. McGuinness DS, Cavell KJ, Yates BF (2001) Chem Commun 355
110. McGuinness DS, Cavell KJ, Yates BF, Skelton BW, White AH (2001) J Am Chem Soc 123:8317
111. Graham DC, Cavell KJ, Yates BF (2007) Dalton Trans 4650
112. Gründemann S, Albrecht M, Kovacevic A, Faller JW, Crabtree RH (2002) J Chem Soc Dalton Trans 2163
113. Mas-Marzá E, Sanaú M, Peris E (2005) Inorg Chem 44:9961
114. Duin MA, Clement ND, Cavell KJ, Elsevier CJ (2003) Chem Commun 400
115. Clement ND, Cavell KJ, Jones C, Elsevier CJ (2004) Angew Chem Int Ed 43:1277
116. Viciano M, Mas-Marzá E, Poyatos E, Sanaú M, Crabtree RH, Peris E (2005) Angew Chem Int Ed 44:444
117. Viciano M, Poyatos M, Sanaú M, Peris E, Rossin A, Ujaque G, Lledos A (2006) Organometallics 25:1120
118. Fürstner A, Seidel G, Kremzow D, Lehmann CW (2003) Organometallics 22:907
119. Kremzow D, Seidel G, Lehmann CW, Fürstner A (2005) Chem Eur J 11:1833
120. Cabeza JA, del Rio I, Sánchez-Vega MG, Suárez M (2006) Organometallics 25:1831

121. Cabeza JA, da Silva I, del Rio I, Sánchez-Vega MG (2006) Dalton Trans 3966
122. Jones C, Mills DP, Rose RP (2006) J Organomet Chem 691:3060
123. Cavell KJ, McGuinness DS (2004) Coord Chem Rev 248:671
124. McGuinness DS, Green MJ, Cavell KJ, Skelton BW, White AH (1998) J Organomet Chem 565:165
125. McGuinness DS, Cavell KJ, Skelton BW, White AH (1999) Organometallics 18:1596
126. McGuinness DS, Cavell KJ (2000) Organometallics 19:4918
127. McGuinness DS, Mueller W, Wasserscheid P, Cavell KJ, Skelton BW, White AH, Englert U (2002) Organometallics 21:175
128. McGuinness DS, Saendig N, Yates BF, Cavell KJ (2001) J Am Chem Soc 123:4029
129. Graham DC, Cavell KJ, Yates BF (2005) Dalton Trans 1093
130. Graham DC, Cavell KJ, Yates BF (2006) Dalton Trans 1768
131. Tulloch AAD, Winston S, Danopoulos AA, Eastham G, Hursthouse MB (2003) Dalton Trans 699
132. Nielsen DJ, Cavell KJ, Skelton BW, White AH (2006) Inorg Chim Acta 359:1855
133. Danopoulos AA, Tsoureas N, Green JC, Hursthouse MB (2003) Chem Commun 756
134. Caddick S, Cloke FGN, Hitchcock PB, Leonard J, de K. Lewis AK, McKerrecher D, Titcomb LR (2002) Organometallics 21:4318
135. Clement ND, Cavell KJ (2004) Angew Chem Int Ed 43:3845
136. Normand AT, Hawkes KJ, Clement ND, Cavell KJ, Yates BF (2007) Organometallics 26:5352
137. Normand AT, Yen SK, Huynh HV, Hor TSA, Cavell KJ (2008) Organometallics 27:3153
138. Raubenheimer HG, Cronje S (2008) Dalton Trans 1265
139. Schuster O, Raubenheimer HG (2006) Inorg Chem 45:7997
140. Han Y, Huynh HV, Tan GK (2007) Organometallics 26:6581
141. Schneider SK, Julius GR, Loschen C, Raubenheimer HG, Frenking G, Herrmann WA (2006) Dalton Trans 1226
142. Schneider SK, Rentzsch CF, Krüger A, Raubenheimer HG, Herrmann WA (2007) J Mol Catal A Chem 265:50
143. Arnold PL, Pearson S (2007) Coord Chem Rev 251:596
144. Albrecht M (2008) Chem Commun 3601
145. Gründemann S, Kovacevic A, Albrecht M, Faller JW, Crabtree RH (2001) Chem Commun 2274
146. Kovacevic A, Gründemann S, Miecznikowski JR, Clot E, Eisenstein O, Crabtree RH (2002) Chem Commun 2580
147. Gründemann S, Kovacevic A, Albrecht M, Faller JW, Crabtree RH (2002) J Am Chem Soc 124:10473
148. Appelhans LN, Zuccaccia D, Kovacevic A, Chianese AR, Miecznikowski JR, Macchioni A, Clot E, Eisenstein O, Crabtree RH (2005) J Am Chem Soc 127:16299
149. Lebel H, Janes MK, Charette AB, Nolan SP (2004) J Am Chem Soc 126:5046
150. Campeau L-C, Thansandote P, Fagnou K (2005) Org Lett 7:1857
151. Chianese AR, Kovacevic A, Zeglis BM, Faller JW, Crabtree RH (2004) Organometallics 23:2461
152. Alcarazo M, Roseblade SJ, Cowley AR, Fernández R, Brown JM, Lassaletta JM (2005) J Am Chem Soc 127:3290
153. Heckenroth M, Kluser E, Neels A, Albrecht M (2007) Angew Chem Int Ed 46:6293
154. Yang L, Krüger A, Neels A, Albrecht M (2008) Organometallics 27:3161
155. Bacciu D, Cavell KJ, Fallis IA, Oui L-I (2005) Angew Chem Int Ed 44:5282
156. Kluser E, Neels A, Albrecht M (2006) Chem Commun 4495
157. Tschugajeff L, Skanawy-Grigorjewa M, Posnjak A (1925) Z Anorg Allg Chem 148:37
158. Burke A, Balch AL, Enemark JH (1970) J Am Chem Soc 92:2555
159. Beck W, Weigand W, Nagel U, Schaal M (1984) Angew Chem Int Ed Engl 23:377
160. Bär E, Völkl A, Beck F, Fehlhammer WP, Robert A (1986) J Chem Soc Dalton Trans 863

161. Kunz R, Le Grel P, Fehlhammer WP (1996) J Chem Soc Dalton Trans 3231
162. Bertani R, Mozzon M, Michelin RA (1988) Inorg Chem 27:2809
163. Bertani R, Mozzon M, Michelin RA, Benetollo F, Bombieri G, Castilho TJ, Pombeiro AJL (1991) Inorg Chim Acta 189:175
164. Liu C-Y, Chen D-Y, Lee G-H, Peng S-M, Liu S-T (1996) Organometallics 15:1055
165. Ku R-Z, Chen D-Y, Lee G-H, Peng S-M, Liu S-T (1997) Angew Chem Int Ed Engl 36:2631
166. Motschi H, Angelici RJ (1982) Organometallics 1:343
167. Michelin RA, Zanotto L, Braga D, Sabatino P, Angelici RJ (1988) Inorg Chem 27:93
168. Ito Y, Hirao T, Tsubata K, Saegusa T (1978) Tetrahedron Lett 19:1535
169. Fehlhammer WP, Bliß T, Fuchs J, Holzmann G (1992) Z Naturforsch 47b:79
170. Ruiz J, García G, Mosquera MEG, Perandones BF, Gonzalo MP, Vivanco M (2005) J Am Chem Soc 127:8584
171. Ruiz J, Perandones BF, García G, Mosquera MEG (2007) Organometallics 26:5687
172. Bartel K, Fehlhammer WP (1974) Angew Chem Int Ed 13:599
173. Kernbach U, Fehlhammer WP (1995) Inorg Chim Acta 235:299
174. Fehlhammer WP, Bartel K, Weinberger B, Plaia U (1985) Chem Ber 118:2220
175. Hahn FE, Langenhahn V, Pape T (2005) Chem Commun 5390
176. Hahn FE (1993) Angew Chem Int Ed Engl 32:650
177. Ferris JP, Antonucci FR, Trimmer RW (1973) J Am Chem Soc 95:919
178. Jutzi P, Gilge U (1983) J Organomet Chem 246:159
179. Hahn FE, Tamm M (1993) J Organomet Chem 456:C11
180. Hahn FE, Tamm M, Lügger T (1994) Angew Chem Int Ed Engl 33:1356
181. Glaser M, Spies H, Lügger T, Hahn FE (1995) J Organomet Chem 503:C32
182. Tamm M, Hahn FE (1999) Coord Chem Rev 182:175
183. Michelin RA, Pombeiro AJL, Guedes da Silva MFC (2001) Coord Chem Rev 218:75
184. Hahn FE, Langenhahn V, Meier N, Lügger T, Fehlhammer WP (2003) Chem Eur J 9:704
185. Hahn FE, García Plumed C, Münder M, Lügger T (2004) Chem Eur J 10:6285
186. Arnold PL, Cloke FGN, Geldbach T, Hitchcock PB (1999) Organometallics 18:3228
187. Caddick S, Cloke FGN, Clentsmith GKB, Hitchcock PB, McKerrecher D, Titcomb LR, Williams MRV (2001) J Organomet Chem 617–618:635
188. Green JC, Scurr RG, Arnold PL, Cloke FGN (1997) Chem Commun 1963
189. Titcomb LR, Caddick S, Cloke FGN, Wilson DJ, McKerrecher D (2001) Chem Commun 1388
190. Buisine O, Berthon-Gelloz G, Brière J-F, Stérin S, Mignani G, Branlard P, Tinant B, Declercq J-P, Markó IE (2005) Chem Commun 3856
191. Esposito O, de K. Lewis AK, Hitchcock PB, Caddick S, Cloke FGN (2007) Chem Commun 1157
192. Voutchkova AM, Appelhans LN, Chianese AR, Crabtree RH (2005) J Am Chem Soc 127:17624
193. Voutchkova AM, Feliz M, Clot E, Eisenstein O, Crabtree RH (2007) J Am Chem Soc 129:12834
194. Raubenheimer HG, Cronje S (2001) J Organomet Chem 617–618:170
195. Raubenheimer HG, Scott F, Cronje S, van Rooyen PH, Psotta K (1992) J Chem Soc Dalton Trans 1009
196. Raubenheimer HG, Stander Y, Marais EK, Thompson C, Kruger GJ, Cronje S, Deetlefs M (1999) J Organomet Chem 590:158
197. Meier N, Hahn FE, Pape T, Siering C, Waldvogel SR (2007) Eur J Inorg Chem 1210
198. Ruiz J, Perandones BF (2007) J Am Chem Soc 129:9298
199. Araki K, Kuwata S, Ikariya T (2008) Organometallics 27:2176
200. Tan KL, Bergman RG, Ellman JA (2002) J Am Chem Soc 124:3202
201. Tan KL, Bergman RG, Ellman JA (2002) J Am Chem Soc 124:13964
202. Wiedemann SH, Lewis JC, Ellman JA, Bergman RG (2006) J Am Chem Soc 128:2452

203. Facchin G, Mozzon M, Michelin RA, Ribeiro MTA, Pombeiro DJL (1992) J Chem Soc Dalton Trans 2827
204. Nakafuji S-y, Kobayashi J, Kawashima T (2008) Angew Chem Int Ed 47:1141
205. Fürstner A, Alcarazo M, Radkowski K, Lehmann CW (2008) Angew Chem Int Ed 47:8302
206. Asay M, Donnadieu B, Baceiredo A, Soleilhavoup M, Bertrand G (2008) Inorg Chem 47:3949
207. Canac Y, Duhayon C, Chauvin R (2007) Angew Chem Int Ed 46:6313
208. Canac Y, Lepetit C, Abdalilah M, Duhayon C, Chauvin R (2008) J Am Chem Soc 130:8406
209. Schmidbaur H (1983) Angew Chem Int Ed Engl 22:907
210. Kaufhold O, Hahn FE (2008) Angew Chem Int Ed 47:4057
211. Tonner R, Frenking G (2007) Angew Chem Int Ed 46:8695
212. Tonner R, Frenking G (2008) Chem Eur J 14:3260
213. Tonner R, Frenking G (2008) Chem Eur J 14:3273
214. Dyker CA, Lavallo V, Donnadieu B, Bertrand G (2008) Angew Chem Int Ed 47:3206
215. Fürstner A, Alcarazo M, Goddard R, Lehmann CW (2008) Angew Chem Int Ed 47:3210
216. Lavallo V, Dyker CA, Donnadieu B, Bertrand G (2008) Angew Chem Int Ed 47:5411
217. Christl M, Engels B (2009) Angew Chem Int Ed 48:1538
218. Lavallo V, Dyker CA, Donnadieu B, Bertrand G (2009) Angew Chem Int Ed 48:1540
219. Frey GD, Lavallo V, Donnadieu B, Schoeller W, Bertrand G (2007) Science 316:439
220. Stephan DW (2009) Dalton Trans 3129
221. Holschumacher D, Bannenberg T, Hrib CG, Jones PG, Tamm M (2008) Angew Chem Int Ed 47:7428
222. Chase PA, Stephan DW (2008) Angew Chem Int Ed 47:7433
223. Hahn FE, Langenhahn V, Lügger T, Pape T, Le Van D (2005) Angew Chem Int Ed 44:3759
224. Kaufhold O, Stasch A, Edwards PG, Hahn FE (2007) Chem Commun 1822
225. Kaufhold O, Stasch A, Pape T, Hepp A, Edwards PG, Newman PD, Hahn FE (2009) J Am Chem Soc 131:306
226. McKie R, Murphy JA, Park SR, Spicer MD, Zhou S-z (2007) Angew Chem Int Ed 46:6525
227. Hahn FE, Radloff C, Pape T, Hepp A (2008) Chem Eur J 14:10900
228. Mercs L, Neels A, Albrecht M (2008) Dalton Trans 5570
229. Hahn FE, Radloff C, Pape T, Hepp A (2008) Organometallics 27:6408

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Non-NHCs Stable Singlet Carbene Ligands

Tsuyoshi Kato, Eddy Maerten, and Antoine Baceiredo

Abstract Carbene chemistry has been tremendously developed during the last 20 years. NHC carbenes have found many applications as ligands in organometallic chemistry or as catalysts in organocatalysis. On the other hand, the so-called "non-NHC stable carbenes" have had a restrained development to date in spite of the high potential of this family of carbenes which offers many more possibilities in structure modifications, resulting in original reactivities. This chapter gives an overview over non-NHC stable singlet carbenes and their properties as ligands.

Keywords Carbene · Stable carbene · Non-NHC · NHC · Ligand · Catalysis

Contents

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1 Introduction

Since the first reports of stable nucleophilic carbenes, the phosphino(silyl) carbenes in the late 1980s [1, 2], and the cyclic diaminocarbenes (NHCs) in the early 1990s [3], their chemistry has been impressively developed, gaining better comprehension of their electronic and chemical properties [4]. These two families of carbenes possess at least one stabilizing electron donating substituent, but the variation in their stabilization modes induces different chemical behaviors. The phosphino (silyl)carbenes, stabilized by a "push–pull" effect with an electron-withdrawing substituent (Me_3Si–) and a π-donating group (R_2P–), present a very small singlet–triplet gap and exhibit the typical transient carbene reactivity. In marked contrast, the cyclic diaminocarbenes, stabilized by a "push–push" effect with two very strong π-donating amino substituents, exhibit a highly perturbed carbene reactivity, being strong nucleophiles and very poor electrophiles, due to their very large singlet–triplet energy gap. These unique properties make them resistant ligands and their resulting transition metals complexes are highly electron rich [5–7]. In addition, their stability leads to simplicity in carbene complex synthesis, providing a large choice over the types of metal complex employed, which allowed one to synthesize various NHC-transition complexes. Today, numerous stable carbenes with different stabilization modes and, as a consequence, with different properties are available [8, 9]. This variety should make their use as ligands in catalysis, a field of growing interest.

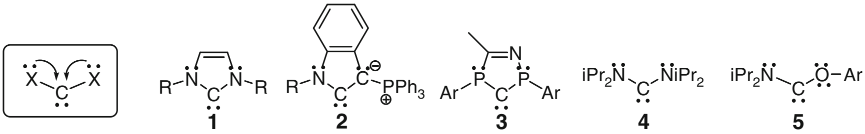
In this chapter we present the different types of non-NHC stable carbenes and their properties as ligands. Here, by *N*-heterocyclic carbenes (NHCs), we mean carbenes with two π-donating substituents (N, S, O) connected to the carbene center.

2 Non-NHC Stable Carbenes and Their Properties

Different types of stabilization modes are known to provide a range of stable carbenes with different electronic and steric properties. In this section, we categorize the stable non-NHC carbenes by the type of stabilization mode involved, in order to highlight their effect on the properties of the carbene as ligand.

2.1 Push–Push System

In the "push–push" stabilization mode, the central carbon atom is substituted by two π-donating groups which compensate the electronic deficiency of the carbene center. As is well known with highly stable NHCs, due to the strong π-donation of the two amino substituents, the singlet–triplet energy gaps are very large (67–90 kcal/mol) and, as a consequence, NHCs present a very poor carbenic character in general [10, 11]. Moreover, due to the high electronegativity of the nitrogen atom as compared to



Scheme 1 Stable "push–push" carbenes

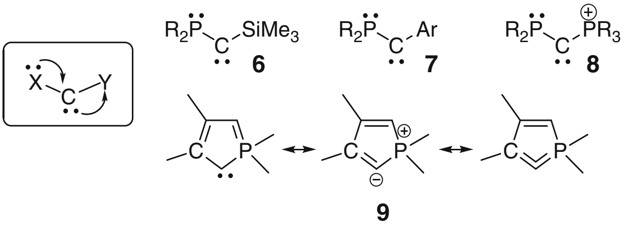
that of the carbon atom, the amino substituents present a σ-withdrawing character, and therefore the HOMO level of classical NHCs **1** (−5.1 to −5.2 eV) are less elevated compared to other non-NHC carbenes. In order to increase the nucleophilicity of the carbene, replacement of the amino group by a more electropositive π-donating substituent has been considered. Indeed, the recently reported amino-ylide carbenes **2** (Scheme 1), in which one of the amino groups has been replaced by a phosphonium ylide function, acting as a stronger carbon-based π-donating substituent, exhibit a very high HOMO level (−4.4 eV) and the strongest electron-donating ability among carbenes known to date [12–14].

In the same vein, the synthesis of cyclic diphosphinocarbenes (PHCs) **3**, with two electropositive π-electron donating groups has been considered [15]. In this case, because of the weak π-donating character of phosphine substituents due to their high planarization energy (35 kcal/mol) as compared to that of amino groups (5 kcal/mol), the synthesis of the corresponding carbenes appeared to be more difficult. Bertrand et al. showed that the use of very bulky substituents at the phosphorus atoms, such as 2,4,6-tri-*tert*-butylphenyl groups, forces the phosphine in the cyclic structure to be planar, allowing the synthesis of **3**, a stable diphosphorus analog of Enders' NHC [16]. The HOMO of this nucleophilic carbene (−5.0 eV) is higher in energy than that calculated at the same level of theory for Enders' NHC (−5.1 eV) [17]. As a consequence of the weak P=C π-bond energy, the singlet–triplet energy gap of PHC **3** is smaller (41.4 kcal/mol).

There are very few examples of "push–push" type acyclic stable carbenes and their utilization as ligands are rare. This is probably due to their decreased stability and coordinating ability as compared with that of NHCs. In fact, there are only two types of stable carbenes (diamino carbene **4** [18] and amino-alkoxy carbene **5** [19], Scheme 1) which were employed and evaluated as ligands. The acyclic diaminocarbene **4** mainly presents a much smaller S/T energy gap and a stronger nucleophilicity than the cyclic ones [20]. The replacement of one amino group by an alkoxy substituent (electronegative π-donating group) in **5**, drastically diminishes the nucleophilic character of the carbene [21].

2.2 *Push–Pull System*

The first isolated singlet carbenes were "push–pull" systems featuring both an electron-donating and an electron-withdrawing group that interact directly with the carbene center (Scheme 2). Phosphinocarbenes **6–8** are perfect in this category,



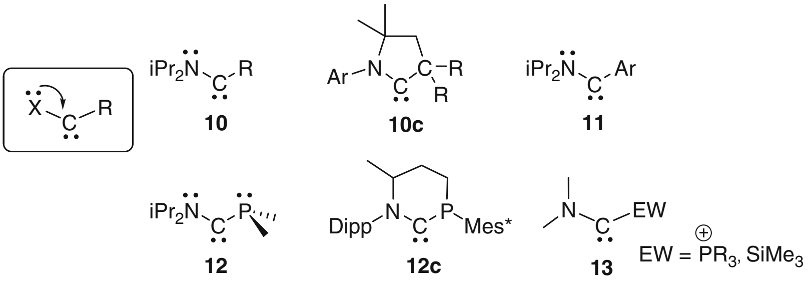
Scheme 2 Stable "push–pull" carbenes

in which the carbene center is stabilized by the π-donating phosphine group and electron-withdrawing groups (trimethylsilyl, aryl, phosphonio) [22, 23]. Because of this stabilization, these carbenes exhibit very wide carbene angles [24]. As already mentioned, the weak π-donating ability of phosphino group dramatically decreases the S/T energy gap (4–7 kcal/mol) [25], which is the origin of their unique reactivity like transient singlet carbenes [2, 26, 27]. Despite their early discovery, the coordination chemistry of phosphinocarbenes remained poorly developed because of their reluctance to act as ligands. Indeed, their widened valence angles at the central carbon require a geometrical modification to a bent carbene structure during the coordination onto the metallic center, which significantly increases the distortion energy [28, 29].

Another carbene formally stabilized by a push–pull system is the recently reported vinylidenephosphorane **9** (Scheme 2), which presents a unique cyclic structure [30]. This carbene is formally stabilized by a conjugated ylide as a π-donating group and phosphonio fragment as a π-withdrawing substituent. Here the phosphonio group presents a double π-withdrawing function both for the carbene lone pair and for the cyclic π-conjugated system. The presence of only one π-electron donating substituent and the strong π-accepting character of the phosphonio group considerably decrease the S/T energy gap of the carbene. Moreover, this carbene **9** shows a very high nucleophilic character, due to the presence of a substituent more electropositive than nitrogen directly connected to the carbene center. In addition, its structural study revealed that the ylidic π-bond is extremely polarized due to a very weak or even absent interaction between the carbene lone pair and the phosphonio group. As a consequence, the carbene lone pair is fully available for coordination to the transition metal center. In fact, this cyclic carbene was thus found to be a strongly nucleophilic ligand. Closely related, a highly polarized cyclic bent allene has recently been synthesized [31–33].

2.3 Push–Spectator System

In 2001, Bertrand et al. reported that in fact only one π-electron donating substituent such as an amino group is sufficient to obtain stable carbenes. In this case, the



Scheme 3 Stable “push–spectator” carbenes

other substituent, which does not participate in the stabilization, can be considered as a spectator substituent (Scheme 3) [34]. This stabilization system is particularly efficient with an amino group which is not only a π-donating substituent but also a σ-electron withdrawing group. This stabilization mode provides a large choice of substituents allowing an easy functionalization of the corresponding stable monoaminocarbenes. In fact, several types of acyclic and cyclic amino carbenes have been already synthesized [8, 9].

Acyclic amino-alkyl carbenes **10** in particular exhibit a typical feature of monoamino carbene. The presence of only one stabilizing π-donating substituent decreases the S/T energy gap (26.7 kcal/mol), and replacement of an amino group by a more electropositive alkyl substituent (*t*-Bu) significantly increases the HOMO level (−4.3 eV) [35]. Therefore, this mono-alkyl carbene **10** is both more nucleophilic and more electrophilic than diaminocarbenes, and it shows the typical reactivity of transient nucleophilic carbenes in cyclopropanation reactions with olefins. As can be expected on the basis of the high HOMO level, the alkyl aminocarbene behaves as a strong electron donating ligand.

The cyclic version of alkylaminocarbenes, the cyclic alkyl aminocarbenes **10c** (CAACs), have also been reported [36]. The rigid cyclic structure with very bulky substituents at the nitrogen atom increases the S/T energy gap (45.1 kcal/mol) [37]. Due to this electronic effect as well as to the more resistant substituent pattern, CAACs are much more resistant than the acyclic ones.

A very unique molecule in this category is the amino-phosphinocarbene **12** [38]. Here, due to the high planarization energy of the phosphine center [39], the phosphino group remains pyramidal although the amino group exhibits a planar geometry. As a consequence, the phosphine part is available for further coordination to a metal center, and these carbenes behave as α,β-bidentate carbene ligands. Very recently, the cyclic version of the phosphino-amino carbene **12c** has also been synthesized [40].

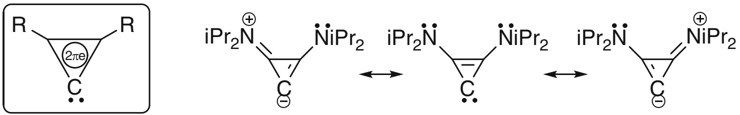
Aminocarbenes possessing a π-accepting substituent such as trimethylsilyl group **13** also behave as strong σ-donating ligand probably due to the much smaller carbene angle (133° for **13**-PR_3, 127° for **13**-$SiMe_3$) [41] as compared to those of corresponding push–pull type phosphino-silyl carbenes (152–165°) which are reluctant to act as a ligand [24, 42].

2.4 Cyclopropenylidene Carbene

Cyclopropenylidene (R=H) is a cyclic carbene that was first detected in interstellar space [43]. This small three membered cyclic and aromatic carbene **14**, bearing two bulky π-donating diisopropylamino substituents, has been very recently isolated in the solid state (Scheme 4) [44].

This carbene exhibits a very strong nucleophilic character (HOMO: −4.6 eV) probably due to the absence of electronegative substituents directly connected to the carbene center [45]. In addition, the strong π-donation of the two amino substituents induces a large S/T energy gap (59.4 kcal/mol) comparable to that of the acyclic bis(amino)carbenes [46]. Considering these electronic properties and the very peculiar geometry with a very acute carbene angle (57.2°) as compared to those of other stable carbenes, this type of carbene presents unique coordination properties [47–49].

After this brief presentation of stable carbenes with different stabilization modes, we can understand and predict the effect of substituent changes on the carbene properties. In Fig. 1 the HOMO level and S/T energy gap for each family of carbenes are detailed.



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Scheme 4 Cyclopropenylidene carbene

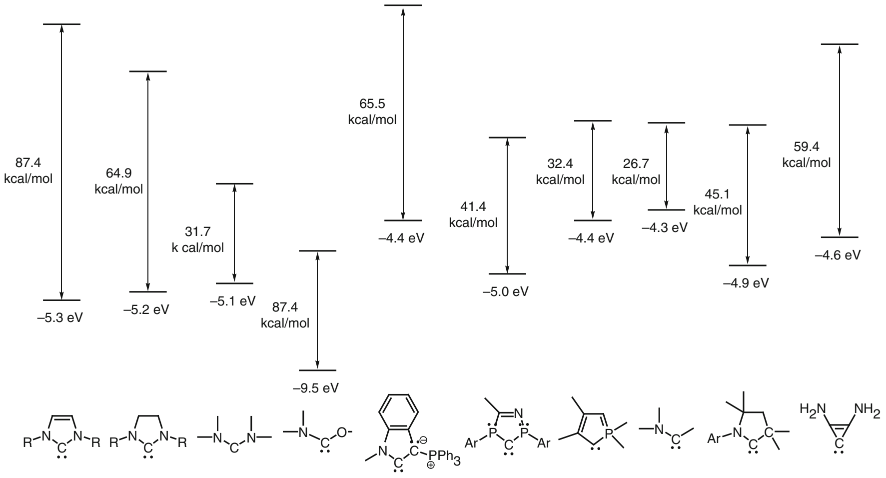


Fig. 1 HOMO level and S/T gap of stable carbenes

First of all, the introduction of an electropositive substituent onto the carbene center increases its nucleophilicity. In particular, the effect of a strong π-donating and electropositive ylide substituent is efficient as can be seen in the case of amino (ylide) carbenes and of cyclic vinylidenephosphorane type carbenes. Acyclic structures also increase the HOMO level but they also significantly diminish the S/T energy gap.

The carbonyl stretching frequencies of *cis*-$[RhCl(CO)_2L]$ complexes are recognized to give an excellent measure of the σ-donor vs π-acceptor properties of the carbene ligand L [50]. Stronger donating ligands shift down the frequency of the absorption bands for the COs in the corresponding complexes (Table 1).

Carbenes with stronger π- and σ- donating substituents with a high HOMO level are found to be strongly donating ligands. However, the π-accepting character is also important, as can be seen, particularly, in the case of amino(alkyl)carbenes or PHCs, less strongly electron-donating substituents in spite of their very high HOMO level. They present a small S/T energy gap (low LUMO level) with an enhanced π-acceptor character.

3 Coordination Chemistry of Non-NHC Stable Carbenes

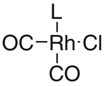
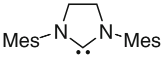
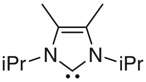
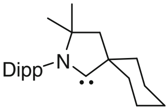
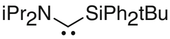
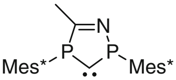
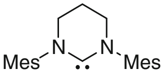
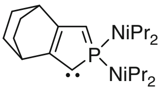
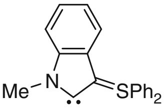
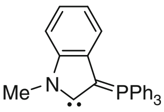
Almost all stable carbenes behave as 2-electron-σ-donating ligands with a few exceptions. In particular, in almost all cases corresponding Rh(I) complexes were targeted due to the easy synthetic method. An exception is the cyclopropenylidene carbene, with an extremely acute carbene angle. In this case, a second equivalent of carbene squeezes into the rhodium center, eliminating a chloride anion, giving the cationic dicarbenic rhodium(I) complex [51] (Scheme 5).

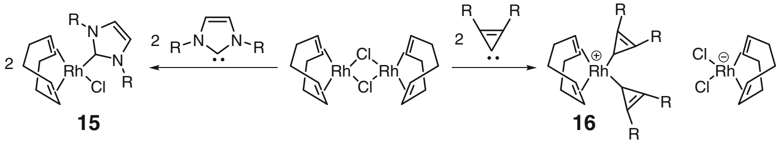
In order to compare the ligand properties of non-NHC carbenes, several spectroscopic (^{13}C-NMR chemical shift of the carbene center) and structural parameters (carbene angle) of Rh(I)-carbene complexes, as well as those of the corresponding free carbenes, are listed in Table 2. In all cases, the Rh–C bond length remains in the range of 1.99–2.10 Å corresponding to that of a Rh–C single bond presenting a very weak π-back-donation from the metal to the carbene center. Only very minor structural changes were observed for the carbene ligand upon coordination, except in the case of phosphinocarbenes. In this case, the very large carbene angle (162°) significantly decreases to 119°, which is one of the main reasons for their reluctance to act as ligands.

Although a large proportion of stable carbenes behaves as strongly 2-electron donating ligands, several carbenes are known to show a different coordination mode, coming from their unique electronic and geometric properties. This is illustrated by the case of acyclic structures which allow the free rotation of the substituents in contrast to the cyclic ones. In this section we will present several particular coordination modes of non-NHCs stable carbenes.

Much less coordination chemistry of acyclic diaminocarbenes **4** as compared to that of cyclic ones has been described (Scheme 6). Interestingly, in the case of

Table 1 Carbonyl stretching frequencies of Rh–carbene complexes

L	*v*(co)l		L = carbene ligand	
		v(co)2	Average	Ref.
	2,081	1,996	2,039	[74]
	2,076	1,996	2,036	[75]
	2,077	1,994	2,035	[56]
	2,072	1,989	2,030	[76]
	2,070	1,989	2,030	[35]
	2,059	1,985	2,022	[15]
	2,057	1,984	2,021	[74]
	2,062	1,976	2,018	[77]
	2,058	1,976	2,017	[30]
	2,052	1,975	2,014	[13]
	2,062	1,962	2,012	[12]



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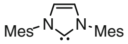
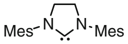
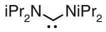
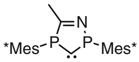
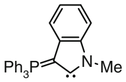
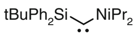
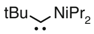
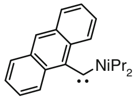
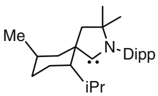
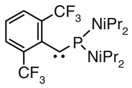
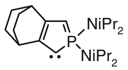
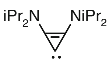
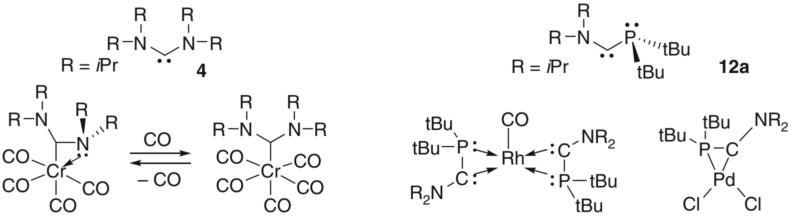
Scheme 5 Carbene–Rh(I) complexes

Table 2 Spectroscopic data and structural parameters of Rh–carbene complexes [2]

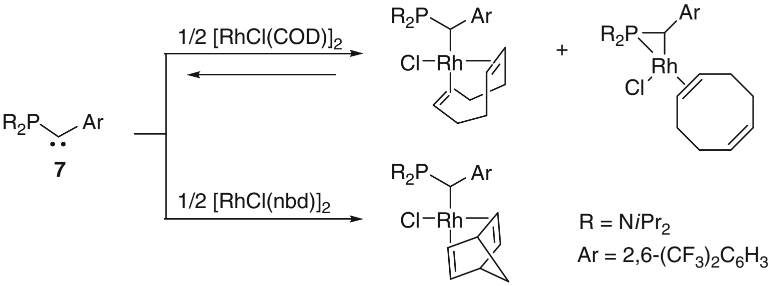
	13C-NMR(ppm)		Carbene angle(°)		Rh–C(A)	Ref.
	Carbene	Complex	Carbene	Complex		
	220	184 (53 Hz)	101.9	103.5	2.069	[72]
	245	212 (49.0 Hz)	100.7	107.3	2.064	[73]
	256	234 (68 Hz)	121.0	118.0	2.041	[74]
	184	171 (41.0 Hz)	98.2	100.7	2.064	[15]
	218	201 (41 Hz)	–	105.0	2.036	[12]
	377	306 (33 Hz)	133.1	124.0	1.994	[76]
	326	279 (40 Hz)	120.5	121.1	2.039	[35]
	315	249 (45 Hz)	–	114.8	2.043	[78]
	319	249 (49 Hz)	106.5	108.7	1.940[a]	[56]
	146	121 (59 Hz)	162.1	119.0	2.096[b]	[34, 55]
	184	148 (42 Hz)	99.9	103.2	2.089	[30]
	189	–	54.2	–	–	[51]

[a] Data from LRh(CO)Cl complexes

[b] Data from LRh(nbd)Cl complexes



Scheme 6 α,β-Bidentate ligands and their complexations



Scheme 7 Coordination modes of phosphinoarylcarbenes

carbene–Cr(0) carbonyl complexes of the acyclic bis(diisopropylamino)carbene, an equilibrium was observed between monodentate and bidentate coordination modes involving dissociation/association of a CO ligand [52]. This behavior can be explained by the strong donation of an amino group to the carbene center and by the acyclic structure ensuring a relatively small rotation barrier of the amino groups (12.7 Kcal/mol for the carbene, 13.1 Kcal/mol for the corresponding iminium salt) [46] and allowing one of the amino groups to rotate and behave as a second coordination site.

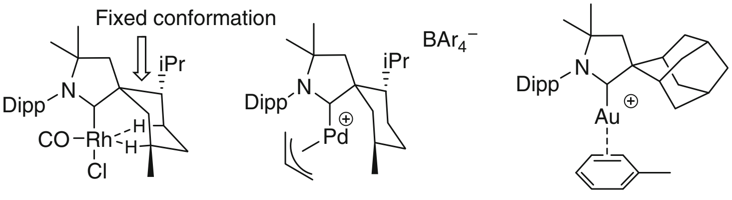
The amino(phosphino)carbene **12a** with a pyramidalized phosphino substituent behaves as α,β-bidentate ligand to give highly stable Rh(I) [53] and Pd(II) [54] complexes.

The reaction of phosphino(aryl)carbenes **7** with $[RhCl(COD)]_2$ leads to a mixture of Rh(I) complexes, one with a monodentate C-phosphinocarbene ligand and the other one with a η^2-coordination mode (Scheme 7) [55]. In addition, because of the bulky cyclooctadiene ligand at the Rh center, the coordination of the carbene moiety is not favored and, in consequence, the two Rh(I)-complexes are in equilibrium with the free phosphino(aryl)carbene. In the case of the less sterically demanding Rh(I) complex with a norbornadiene ligand, only the η^1-phosphinocarbene complex was observed. The structural study of this complex showed that the phosphinocarbene complex can be regarded as a Fischer-type complex with a long Rh–C bond (2.096 Å) and short P–C bond (1.673 Å) indicating a strong π-donation of the phosphino group to the carbene center, in spite of the very small S/T energy gap of the phosphinocarbene.

Recently a unique stabilizing technique for the low-coordinate transition metal complexes using a rigid cyclic (alkyl)(amino)carbene (CAAC) with a substituted cyclohexyl substituent whose conformation is completely fixed has been proposed to achieve the first synthesis of 14-electron Rh(I) and cationic Pd(II) complexes (**17** and **18** respectively, Scheme 8) [56]. Due to the fixed conformation of the bulky menthyl group, the metal center is efficiently protected. In addition, this fixed conformation provides an efficient agostic interaction between the metallic center and the axial cyclohexyl protons. Using a similar stabilization technique, a highly robust cationic gold complex **19** has also been successfully synthesized [57–60].

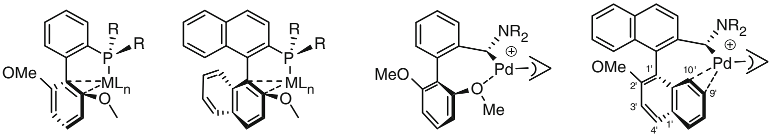
The weak metal–arene interaction (π-aryl interaction) is known to be a very important interaction providing stability for the metal center during a catalytic process (Scheme 9). This is particularly well known for the very efficient Pd-catalyzed cross-coupling reactions using phosphinobiaryl ligands [61–63]. In contrast, formal replacement of the phosphine center by an aminocarbene moiety influences markedly the relative position of the metal fragment and the biaryl skeleton, so that unusual Pd–O and Pd–arene interactions involving remote ring of the binaphthyl skeleton (at the position 9′ and 10′) were found for **22** and **23** respectively [64].

Several unique synthetic strategies for bidentate(amino)(oxy)- and (amino)(aryl) carbenes have been described (Scheme 10). For the former, the reaction of the amino(phosphino)carbene with an *ortho*-quinone leads to the transient formation of a zwitterionic species featuring both a phosphonio nucleofuge and an aryloxide nucleophile that allow for a subsequent intramolecular substitution process. The



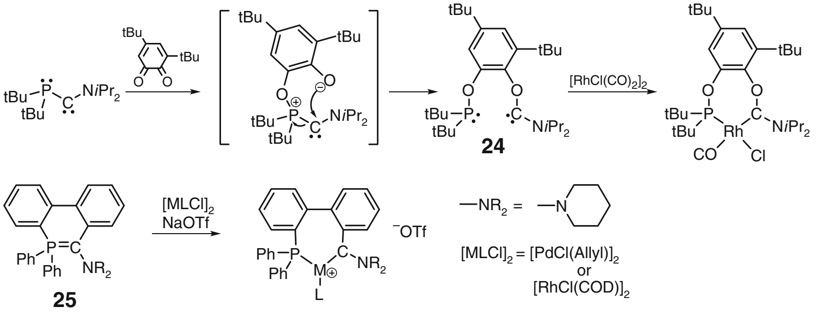
17 **18** **19**

Scheme 8 Metal complexes stabilized by CAAC ligands

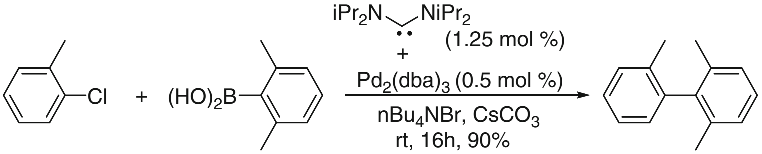


20 **21** **22** **23**

Scheme 9 Metal–arene interactions in biaryl ligands



Scheme 10 Synthesis of 1,6-bidentate carbene ligands and complexes



Scheme 11 Suzuki reaction catalyzed by acyclic diaminocarbenes–Pd complexes

corresponding amino(oxy)carbene was isolated in nearly quantitative yield [65]. This bidentate ligand **24** featuring a phosphino group in position-6 respect to the carbene center was used to prepare the corresponding Rh(I) complex [53].

Another unique synthetic methodology for the carbene phosphine bidentate ligand is the utilization of destabilized *C*-amino phosphorus ylides **25** as carbene source [66]. Due to the electrostatic repulsion between the two lone pairs on the nitrogen and on the ylidic carbon, the ylidic bond is very labile. Thus, these *C*-amino phosphorus ylides readily act as 1,6-bidentate ligand precursors by insertion of the metal fragment between the phosphine and carbene centers.

4 Catalytic Reactions

Very few catalytic reactions using complexes with stable non-NHC carbenes have been reported yet. Nevertheless, taking advantage of the specific properties of non-NHC carbenes, several catalytic reactions have been described, especially using CAACs.

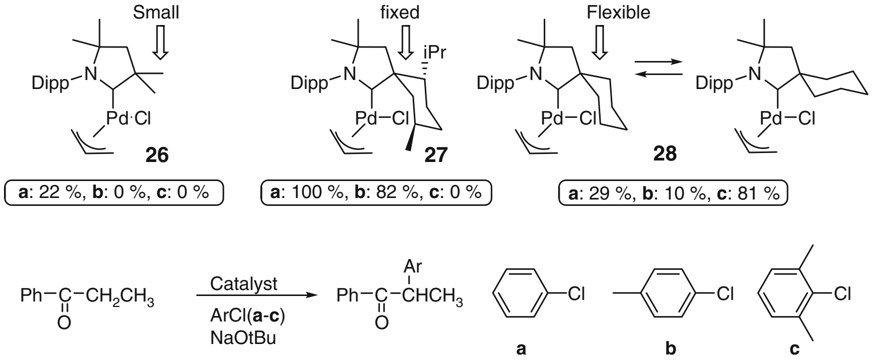
The Suzuki–Miyaura reactions with relatively inert arylchloride are known to require palladium complexes possessing highly electron-rich ligands which favor the oxidative addition of the arylchloride into Pd(0)-complex (Scheme 11) [67–69]. Herrmann et al. showed that the utilization of NHC ligands with bulky substituents is particularly efficient for this type of reactions [70]. However this system shows limitations when bulky aryl halides and boronic acids are used. In marked contrast, the acyclic bis(diisopropylamino)carbene **4** is reported to improve the reaction even in the case of sterically hindered aryl substrates [71].

This is probably due to the high electron donating character of the acyclic bis (amino)carbene as compared to the NHCs, and to its structural flexibility which could liberate the reaction site on the metal center.

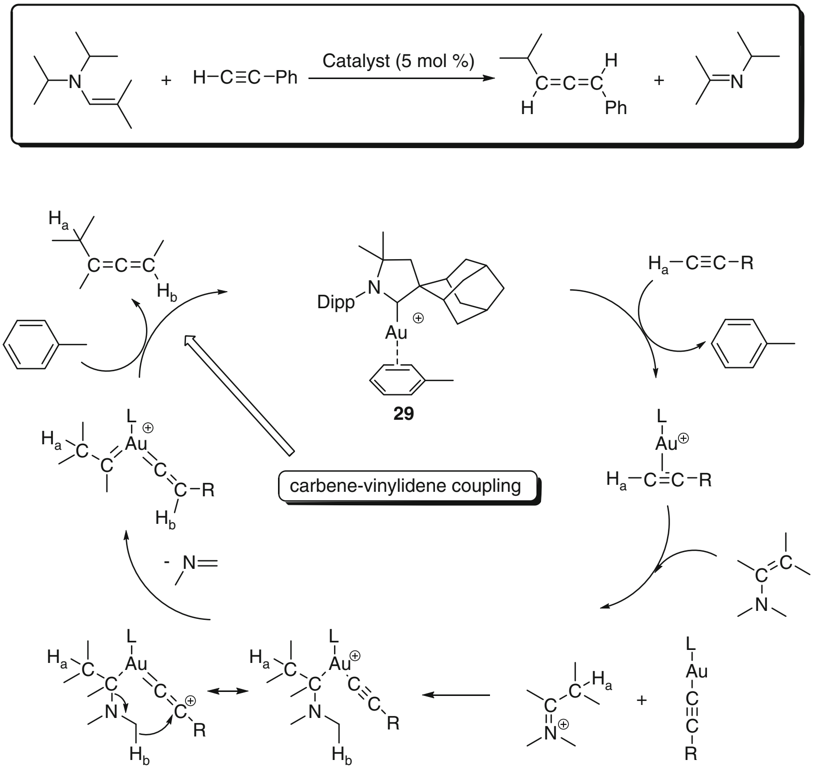
The *push–spectator* stabilization system enables one to employ various alkyl groups with different types of steric environment, which differentiate amino(alkyl) carbenes dramatically from the NHCs as ligands. Taking advantage of their steric and electronic properties, Bertrand et al. nicely demonstrated the utility of CAACs as ligands in the palladium catalyzed α-arylation of ketones. Depending on the nature of the aryl chloride used, dramatic differences were observed in the catalytic activity of Pd-complexes with CAACs featuring different types of steric environment [36].

Although CAACs with a small substituent do not favor the reductive elimination step in the catalytic cycle, those with bulky substituents and fixed conformations can easily promote this step. This can be clearly seen by the efficient catalytic activity of catalyst **27** in the reactions with the aryl chlorides **a** and **b** (Scheme 12). However, this complex is not effective in the case of the sterically hindered aryl chloride **c**. In marked contrast, the complex with a CAAC possessing a cyclohexyl substituent **28** catalyzes efficiently the reaction with **c**. This can be explained by the flexibility of cyclohexane moiety which undergoes a ring flip in solution leading to a steric environment similar to that of **26**. This flexibility explains the superiority of **28** over **27** in accommodating sterically demanding substrates in the coupling process.

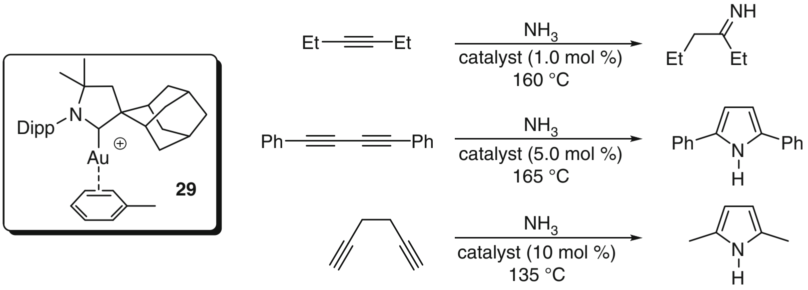
As already mentioned, CAAC ligands can stabilize electron-deficient metal centers such as in cationic gold complexes. Complex **29** catalyzes a very unique reaction of enamines with acetylene, which produces a cumulene and an imine



Scheme 12 α-Arylation of ketones catalyzed by CAAC–Pd complexes



Scheme 13 Cumulene formation catalyzed by CAAC–Au complexes



Scheme 14 Hydroamination reactions catalyzed by CAAC–Au complexes

fragment (Scheme 13) [57]. After a detailed mechanistic study using deuterated substrates, the authors concluded that the formation of the cumulene is due to an unusual carbene–vinylidene coupling during the catalytic cycle.

The cationic gold complex with CAAC ligand **29** can also catalyze the unprecedented hydroamination reaction of alkynes and allenes using ammonia [59, 60]. It was also demonstrated that it can catalyze the simple hydroamination reaction. It also catalyzes regioselectively the cyclizing double hydroamination of diynes, to give the corresponding pyrroles (Scheme 14). It is worth noting that the highly efficient stabilization of cationic complexes by CAACs allows the reaction to take place under harsh conditions, namely by heating at 130–165 °C.

5 Conclusion

It is clear that the variation in the carbene stabilization modes dramatically modify the carbene properties in terms of steric and electronic factors, which is very essential in the design of new ligands for transition metals. In comparison to classical NHCs, non-NHC carbenes offer a large range of possible structural variations, which should rapidly enhance the interest in non-NHC-based complexes. We can anticipate that the fine tuning of the properties of stable non-NHC carbenes makes these ligands very promising for the development of novel and efficient catalysts.

References

1. Igau A, Grützmacher H, Baceiredo A, Bertrand G (1988) J Am Chem Soc 110:6463
2. Igau A, Baceiredo A, Trinquier G, Bertrand G (1989) Angew Chem Int Ed 28:621
3. Arduengo AJ III, Harlow RL, Kline M (1991) J Am Chem Soc 113:361
4. Bourissou D, Guerret O, Gabbaï FP, Bertrand G (2000) Chem Rev 100:39
5. Crudden CM, Allen DP (2004) Coord Chem Rev 248:2247
6. Peris E (2007) Top Organomet Chem 21:83
7. Kantchev EAB, O'Brien CJ, Organ MG (2007) Angew Chem Int Ed 46:2768
8. Canac Y, Soleilhavoup M, Conejero S, Bertrand G (2004) J Organomet Chem 689:3857
9. Vignolle J, Cattoën X, Bourissou D (2009) Chem Rev 109:3333
10. Heinemann C, Thiel W (1994) Chem Phys Lett 217:11
11. Olsson MHM, Borowski P, Roos BO (1993) Theor Chim Acta 93:17
12. Nakafuji S, Kobayashi J, Kawashima T (2008) Angew Chem Int Ed 47:1141
13. Fürstner A, Alcarazo M, Radkowski K, Lehmann CW (2008) Angew Chem Int Ed 47:8302
14. Asay M, Donnadieu B, Baceiredo A, Soleilhavoup M, Bertrand G (2008) Inorg Chem 47:3949
15. Martin D, Baceiredo A, Gornitzka H, Schoeller WW, Bertrand G (2005) Angew Chem Int Ed 44:1700
16. Enders D, Breuer K, Raabe G, Runsink J, Teles J, Melder JP, Ebel K, Brode S (1995) Angew Chem Int Ed 34:1021
17. Raabe G, Breuer K, Enders D, Teles JH (1996) Z Naturforsch A Phys Sci 51:95
18. Alder RW, Allen PR, Murray M, Orpen AG (1996) Angew Chem Int Ed 35:1121
19. Alder RW, Butts CP, Orpen AG (1998) J Am Chem Soc 120:11526
20. Lee M-T, Hu C-H (2004) Organometallics 23:976
21. Rondan NG, Houk KN, Moss RA (1980) J Am Chem Soc 102:1770
22. Buron C, Gornitzka H, Romanenko V, Bertrand G (2000) Science 288:834
23. Despagnet-Ayoub E, Solé S, Gornitzka H, Rozhenko AB, Shoeller WW, Bourissou D, Bertrand G (2003) J Am Chem Soc 125:124
24. Kato T, Gornitzka H, Baceiredo A, Savin A, Bertrand G (2000) J Am Chem Soc 122:998

25. Dixon DA, Dobbs KD, Arduengo AJ, Bertrand G (1991) J Am Chem Soc 113:8782
26. Goumri-Magnet S, Kato T, Gornitzka H, Baceiredo A, Bertrand G (2000) J Am Chem Soc 122:4464
27. Krysiak J, Kato T, Gornitzka H, Baceiredo A, Mikolajczyk M, Bertrand G (2001) J Org Chem 66:8242
28. Schoeller WW, Eisner D, Grigoleit S, Rozhenko AB, Alijah A (2000) J Am Chem Soc 122:10115
29. Schoeller WW, Rozhenko AJB, Alijah A (2001) J Organomet Chem 617:435
30. Asay M, Kato T, Saffon-Merceron N, Cossío FP, Baceiredo A, Bertrand G (2008) Angew Chem Int Ed 47:7530
31. Similar behavior is known: Lavallo V, Dyker, CA, Donnadieu B, Bertrand G (2008) Angew Chem Int Ed 47:5411
32. Christl M, Engels B (2009) Angew Chem Int Ed 48:1538
33. Lavallo V, Dyker CA, Donnadieu B, Bertrand G (2009) Angew Chem Int Ed 48:1540
34. Solé S, Gornitzka H, Schoeller WW, Bourissou D, Bertrand G (2001) Science 292:1901
35. Lavallo V, Mafhouz J, Canac Y, Donnadieu B, Schoeller WW, Bertrand G (2004) J Am Chem Soc 126:8670
36. Lavallo V, Canac Y, Präsang C, Donnadieu B, Bertrand G (2005) Angew Chem Int Ed 44:5705
37. Frey GD, Lavallo V, Donnadieu B, Schoeller WW, Bertrand G (2007) Science 316:439
38. Merceron N, Miqueu K, Baceiredo A, Bertrand G (2002) J Am Chem Soc 124:6806
39. Kapp J, Schade C, El-Nahasa AM, Schleyer PvR (1996) Angew Chem Int Ed 35:2236
40. Frey GD, Song M, Bourg J-B, Donnadieu B, Soleihavoup M, Bertrand G (2008) Chem Commun 4711
41. Conejero S, Canac Y, Tham FS, Bertrand G (2004) Angew Chem Int Ed 43:4089
42. Soleilhavoup M, Baceiredo A, Treutler O, Ahlrichs R, Nieger M, Bertrand G (1992) J Am Chem Soc 114:10959
43. Kaiser RI (2002) Chem Rev 102:1309
44. Lavallo V, Canac Y, Donnadieu B, Schoeller WW, Bertrand G (2006) Science 312:722
45. Schoeller WW, Frey GD, Bertrand G (2008) Chem Eur J 14:4711
46. Alder RW, Blake ME, Oliva JM (1999) J Phys Chem A 103:11200
47. Wass D, Haddow M, Hey T, Orpen A, Russell C, Shishkov I, Wingad R, Green M (2007) Chem Commun 2704
48. Herrmann WA, Ofele K, Taubmann C, Herdtweck E, Hoffmann S (2007) J Organomet Chem 692:3846
49. Wass D, Hey T, Rodriguez-Castro J, Russell C, Shishkov I, Wingad R, Green M (2007) Organometallics 26:4702
50. Kelly RA III, Clavier H, Giudice S, Scott NM, Stevens ED, Bordner J, Samardjiev I, Hoff CD, Cavallo L, Nolan SP (2008) Organometallics 27:202
51. Kuchenbeiser G, Donnadieu B, Bertrand G (2008) J Organomet Chem 693:899
52. Herrmann WA, Öfele K, v. Preysing D, Herdtweck E (2003) J Organomet Chem 684:235
53. Merceron-Saffon N, Gornitzka H, Baceiredo A, Bertrand G (2004) J Organomet Chem 689:1431
54. Teuma E, Lyon-Saunier C, Gornitzka H, Mignani G, Baceiredo A, Bertrand G (2005) J Organomet Chem 690:5541
55. Despagnet E, Miqueu K, Gornitzka H, Dyer PW, Bourissou D, Bertrand G (2002) J Am Chem Soc 124:11834
56. Lavallo V, Canac Y, DeHope A, Donnadieu B, Bertrand G (2005) Angew Chem Int Ed 44:7236
57. Lavallo V, Frey GD, Kousar S, Donnadieu B, Bertrand G (2007) Proc Natl Acad Sci USA 104:13569
58. Frey GD, Dewhurst RD, Kousar S, Donnadieu B, Bertrand G (2008) J Organomet Chem 693:1674

59. Lavallo V, Frey GD, Donnadieu B, Soleilhavoup M, Bertrand G (2008) Angew Chem Int Ed 47:5224
60. Zeng X, Frey GD, Kinjo R, Donnadieu B, Bertrand G (2009) J Am Chem Soc 131:8690
61. Barder TE, Walker SD, Martinelli JR, Buchwald SL (2005) J Am Chem Soc 127:4685
62. Walker SD, Barder TE, Martinelli JR, Buchwald SL (2004) Angew Chem Int Ed 43:1871
63. Huang X, Anderson KW, Zim D, Jiang L, Klapars A, Buchwald SL (2003) J Am Chem Soc 125:6653
64. Vignolle J, Gornitzka H, Donnadieu B, Bourissou D, Bertrand G (2008) Angew Chem Int Ed 47:2271
65. Merceron-Saffon N, Baceiredo A, Gornitzka H, Bertrand G (2003) Science 301:1223
66. Vignolle J, Donnadieu B, Soleilhavoup M, Bourissou D, Bertrand G (2006) J Am Chem Soc 128:14810
67. Stürmer R (1999) Angew Chem Int Ed 38:3307
68. Riermeier TH, Zapf A, Beller M (1997) Top Catal 4:301
69. Zapf A, Ehrentraut A, Beller M (2000) Angew Chem Int Ed 39:4153
70. Gstöttmayr CWK, Böhm VPW, Herdtweck E, Grosche M, Hermann WA (2002) Angew Chem Int Ed 41:1363
71. Dhudshia B, Thadani AN (2006) Chem Commun 668
72. Ahmed M, Buch C, Routaboul L, Jackstell R, Klein H, Spannenberg A, Beller M (2007) Chem Eur J 13:1594
73. Blum AP, Ritter T, Grubbs RH (2007) Organometallics 26:2122
74. Denk K, Sirsch P, Herrmann WA (2002) J Organomet Chem 649:219
75. Neveling A, Julius GR, Cronje S, Esterhuysen C, Raubenheimer HG (2005) Dalton Trans 181
76. Canac Y, Conejero S, Donnadieu B, Schoeller WW, Bertrand G (2005) J Am Chem Soc 127:7312
77. Mayr M, Wurst K, Ongania K-H, Buchmeiser MR (2004) Chem Eur J 10:1256
78. Cattoën X, Gornitzka H, Bourissou D, Bertrand G (2004) J Am Chem Soc 126:1342

Part III

sp -Hybridized Neutral η^1-Carbon Ligands

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All-Carbon-Substituted Allenylidene and Related Cumulenylidene Ligands

Victorio Cadierno and Sergio E. García-Garrido

Abstract Allenylidene complexes have gained considerable significance in the context of transition-metal carbene chemistry due to their potential applications in organic synthesis. The aim of this chapter is to draw together a general presentation of the most efficient synthetic routes, the main structural features and reactivity patterns, as well as current applications in homogeneous catalysis, of all-carbon-substituted allenylidenes and related cumulenylidene complexes containing an odd number of carbon atoms.

Keywords Allenylidene ligands · Carbene complexes · Cumulenylidene ligands · Pentatetraenylidene ligands · Propargylic alcohols

Contents

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Dedicated to Prof. Pierre H. Dixneuf in recognition of his outstanding contributions to this field

List of Abbreviations

16-TCM	1,5,9,13-Tetramethyl-1,5,9,13-tetraazacyclohexadecane
Ad	1-Adamantyl
Ar_F	3,5-Bis(trifluoromethyl)phenyl
bdmpza	Bis(3,5-dimethylpyrazol-1-yl)acetate
BINAP	2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl
depe	1,2-Bis(diethylphosphino)ethane
dippe	1,2-Bis(diisopropylphosphino)ethane
dmpe	1,2-Bis(dimethylphosphino)ethane
dmPy	Dimethylpyrazole
dppe	1,2-Bis(diphenylphosphino)ethane
dppf	1,1′-Bis(diphenylphosphino)ferrocene
dppm	Bis(diphenylphosphino)methane
Fc	Ferrocenyl
H_2IMes	1,3-Dimesityl-4,5-dihydroimidazol-2-ylidene
IMes	1,3-Dimesitylimidazol-2-ylidene
IPr	1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene
i-Pr-pybox	2,6-Bis[4′-isopropyloxazolin-2′-yl]pyridine
prophos	1,2-Bis(diphenylphosphino)propane
TFB	Tetrafluorobenzobarrelene
Tp	Tris(pyrazolyl)borate
TPPMS	(3-Sulfonatophenyl)diphenylphosphine sodium salt
triphos	1,1,1-Tris(diphenylphosphinomethyl)ethane

1 Introduction

The cumulene carbenes $:C(=C)_n=CH_2$ ($n \geq 0$) comprise an important series of extremely reactive molecules. The simplest member of this family, i.e., vinylidene ($:C=CH_2$), represents a paradigm in chemistry teetering on the edge of existence because it rapidly rearranges to acetylene [1]. Although vinylidene has an extremely short lifetime, both experimental and theoretical studies confirm that higher unsaturated carbenes ($n > 0$) are relatively more stable. Indeed, propadienylidene ($:C=C=CH_2$), the next member of this family commonly referred to as allenylidene, was discovered in the Taurus molecular cloud by microwave radioastronomy [2] and can be generated in the laboratory (and trapped in cold matrixes) by photolysis, flash vacuum pyrolysis, or electrical discharge of suitable precursors such as cyclopropenylidene [3, 4], diazopropyne [5–7], or acetylene [8]. Similarly, the higher cumulenylidenes butatrienylidene ($n = 2$) [9–12], pentatetraenylidene ($n = 3$) [13, 14], hexapentaenylidene ($n = 4$) [13–16], heptahexaenylidene ($n = 5$) [17, 18], octaheptaenylidene ($n = 6$) [17, 18], and nonaoctaenylidene ($n = 7$) [17, 18] have also been detected in interstellar clouds and in the laboratory. Extensive theoretical studies on the electronic structure of these cumulene carbenes have been performed, predicting in all cases a singlet character in the ground state [3, 13, 16, 18, 19]. Contributions from zwitterionic forms have also been evaluated, the calculations showing that stabilization by charge separation is effective with odd numbers of carbon atoms (e.g., $:C{=}C{=}CH_2 \leftrightarrow {}^{-}:C{\equiv}C{-}C^{+}H_2$) [20]. Considering these zwitterionic alkynyl resonance forms, the carbenic carbon atom of odd cumulenylidenes obeys the Lewis octet rule, a fact impossible to be achieved by their even counterparts.

After the discovery by Fischer and Maasböl of the first stable carbene complexes in 1964, i.e., $[(CO)_5W\{{=}C(OMe)R\}]$ [21], generation of related metallacumulene derivatives $[M]{=}C({=}C)_n{=}CR_2$ ($n \geq 0$) was obviously envisaged. Thus, it is presently well-established that stabilization of these neutral unsaturated carbenes by coordination to a transition metal center is possible by the use of the lone pair of electrons on the carbenic carbon atom, via formation of a metal–carbon σ-bond (electron back-donation from the metal fragment to the carbon ligand may strengthen this bond). This has allowed the development of a rich chemistry of current intense interest due to the potential applications of the resulting metallacumulenic species in organic synthesis, as well as in the construction of molecular wires and other nanoelectronic devices [22].

In this chapter we will concentrate on the chemistry of metallacumulene complexes containing odd carbon chains, i.e., those derived from cumulene–carbene ligands in which the coordinating carbon atom obeys the octet rule by mesomery. Within this family of compounds, allenylidene complexes $[M]{=}C{=}C{=}CR_2$ are the simplest and most widely studied representatives. Their synthesis was achieved for the first time in 1976, with the simultaneous isolation of the allenylidene derivatives $[M\{{=}C{=}C{=}CPh(NMe_2)\}(CO)_5]$ (M = Cr, W) [23] and $[MnCp\{{=}C{=}C{=}C(t\text{-}Bu)_2\}(CO)_2]$ (Cp = η^5-cyclopentadienyl) [24] by Fischer and Berke's groups, respectively. Some years later (1982), Selegue reported a systematic approach to allenylidene complexes based on the dehydration reaction of propargylic alcohols $HC{\equiv}CCR^1R^2(OH)$ in the coordination sphere of a metal [25]. Since then, the application of Selegue's methodology to a wide variety of electron-rich metal fragments, as well as the subsequent availability of a number of alternative routes, has allowed easy access to these derivatives. This has triggered reactivity studies disclosing not only a rich and versatile chemical behavior in stoichiometric processes but also important applications in homogeneous catalysis which launched the modern interest in the chemistry of metal allenylidenes.

In contrast, the chemistry of higher metallacumulenylidene complexes containing longer odd carbon chains has been comparatively less studied due to the synthetic difficulties in preparing such species. This fact relies on the increased reactivity of the unsaturated carbon chains towards electrophilic and nucleophilic attacks. In fact, only a limited number of stable pentatetraenylidene complexes have been described, while others have been proposed as highly reactive transient intermediates.

The aim of this chapter is to draw together a general presentation of the most efficient synthetic routes, the main structural features and reactivity patterns, as well as current applications in homogeneous catalysis, of all-carbon-substituted

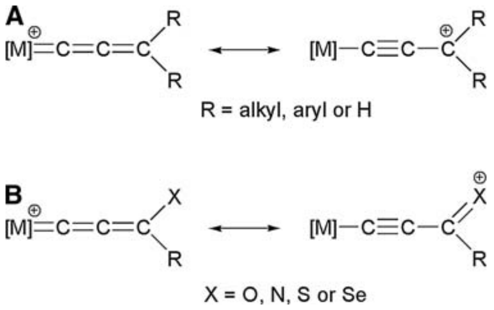


Fig. 1 Major mesomeric forms of allenylidene complexes of types **A** and **B**

allenylidenes **A** (Fig. 1) and related cumulenylidene complexes. Another article in this volume will cover the chemistry of the related species **B** bearing heteroatomic substituents. Marked differences in chemical behavior between **A** and **B** exist, due to the extensive π-conjugation present in the latter, supporting this fragmentation. Since no comprehensive information will be provided, for this purpose, we draw the attention of the reader to the general reviews [26–29], accounts [22, 30–39], and a recent book [40] available on this topic.

2 Allenylidene Complexes

The allenylidene group usually acts as a terminal η^1 ligand featuring an almost linear coordination (see below). Accordingly, in the following sections we will discuss exclusively the chemistry of allenylidene complexes showing this typical terminal coordination. However, we note that the allenylidene group can also act as a bridging ligand, in both homo- and hetero-binuclear complexes, adopting two well-established μ–η^1:η^1 (2e$^-$ donor) [41–52] and μ–η^1:η^2 (4e$^-$ donor) [53–59] coordination modes (**C** and **D**, respectively, in Fig. 2). Bonding of allenylidene ligands to metal clusters offers the possibility of attachment to more than two metal centers and of interaction of all three carbons of the unsaturated C_3 fragment with the cluster. Thus, besides the most common μ_3-(4e$^-$) coordination **E** [60–69], an atypical μ_3–η^1:η^2:η^3 (6e$^-$) bridging mode has been described in complexes **F** [70], confirming the electronic richness and coordinative versatility of the allenylidene chain.

2.1 *Preparation of Allenylidene Complexes*

As commented in the introduction of this chapter, the most general synthetic approach to allenylidene complexes employs propargylic alcohols $HC{\equiv}CCR^1R^2(OH)$ as source of the unsaturated C_3 skeleton. In 1982, Selegue introduced for the first time this synthetic strategy for the high yield preparation of the cationic Ru(II)

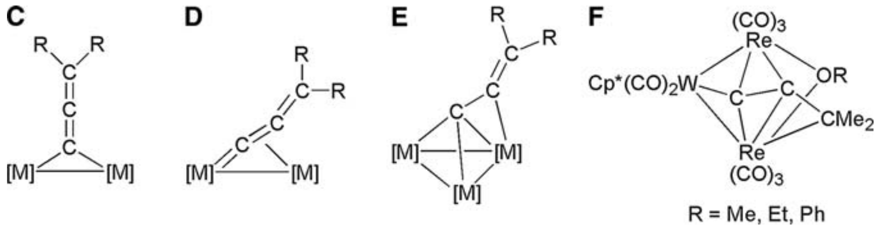
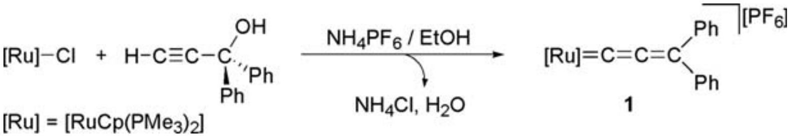
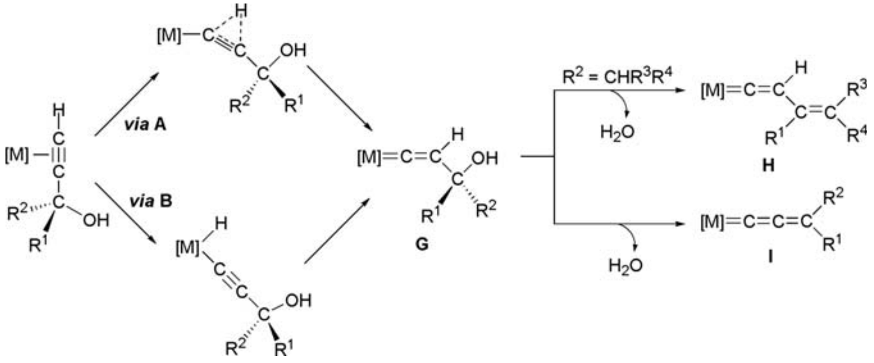


Fig. 2 Coordination modes adopted by allenylidene ligands in bi- and trinuclear complexes



Scheme 1 Synthesis of the allenylidene complex **1** from 1,1-diphenyl-2-propyn-1-ol



Scheme 2 Reaction pathways for the dehydration of terminal propargylic alcohols

complex $[RuCp(=C=C=CPh_2)(PMe_3)_2][PF_6]$ (**1**) starting from $[RuClCp(PMe_3)_2]$ and 1,1-diphenyl-2-propyn-1-ol [25]. The alkynol is converted into the allenylidene unit via elimination of a molecule of water (Scheme 1).

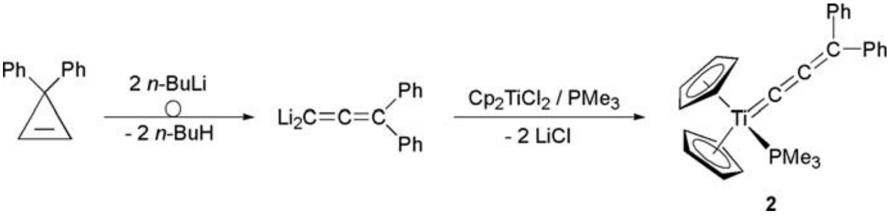
The reaction mechanism is now well-established and involves the dehydration of intermediate 3-hydroxyvinylidene species **G** generated, either via **A** or via **B** (Scheme 2), after coordination of the C≡C bond of the alkynol at the metal center [26–40]. Limitations of this synthetic route mainly stem from (1) the reluctance of intermediates **G** to undergo dehydration, specially when strong electron-releasing metal fragments are used, and (2) the competitive formation of alkenyl–vinylidene isomers **H** vs the expected allenylidenes **I**, arising from the activation of propargylic alcohols containing a C–H bond in β-position with respect to the OH group (Scheme 2) [71–75]. Thus, although spontaneous dehydration of **G** usually occurs, eventually these 3-hydroxyvinylidene intermediates are stable and conversion into the allenylidenes **I** requires treatment with acidic Al_2O_3 or catalytic amounts of CF_3CO_2H [76–82]. In this context, recent theoretical calculations on the propargylic alcohol–allenylidene transformation, using the half-sandwich ruthenium fragments $[RuCp(PH_3)_2]^+$ and $[CpRuCl(\mu\text{-}SMe)_2RuCp]^+$ as models, have pointed out the important role played by protic solvents (e.g., MeOH) in the dehydration process [83]. Ab initio molecular orbital calculations on the models $[RuCp\{=C=C=C(H)CH_3\}(PH_3)_2]^+$ and $[RuCp\{=C=C(H)CH=CH_2\}(PH_3)_2]^+$ also showed that the alkenyl–vinylidene tautomer is 2.1 kcal mol^{-1} more stable than the allenylidene, explaining the competitive formation of these species when terminal alkynols containing C–H bonds in β-position with respect to the alcohol functionality are used as substrates [74]. Consequently, most of the allenylidene complexes reported to date in the literature bear phenyl or related aromatic groups as substituents at the C_γ carbon atom [26–40].

Selegue's route has been widely used during the last two decades for the preparation of transition-metal allenylidene complexes, its efficiency allowing the access to a huge number of representatives. Although other synthetic alternatives of allenylidenes are presently known, their applications have been comparatively less developed. In the following subsections updated syntheses of allenylidene complexes are presented by Periodic Group.

It is worth mentioning that, to date, no Group 5 and 11 allenylidenes have been described [84, 85] and only a few heteroatom-substituted Group 10 representatives are known [86].

2.1.1 Group 4 Metals

The mononuclear complex $[TiCp_2(=C=C=CPh_2)(PMe_3)]$ (**2**), generated by reacting 1,1-dilithio-3,3-diphenylallenylidene with dichlorotitanocene in the presence of trimethylphosphine (Scheme 3) [87], and the dinuclear derivative $[(ZrCp_2Et)_2(\mu\text{–}\eta^1\text{:}\eta^2\text{–}C=C=CMe_2)]$ [52] are the only Group 4 allenylidenes described to date in the literature.



Scheme 3 Synthesis of the titanium–allenylidene complex **2**

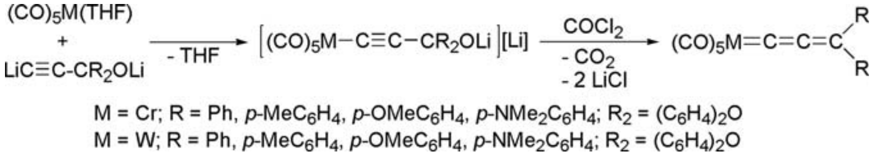
2.1.2 Group 6 Metals

Most of the reported examples of Group 6 allenylidenes are substituted derivatives bearing heteroatomic π-donor groups at the terminal C_γ atom of the cumulenic chain [88]. This is due to the thermal instability of their all-carbon-substituted counterparts. In fact, only the presence of electron-rich substituents (generally aryl-substituted groups) allows stable crystalline compounds to be isolated. Concerning their syntheses, although the classical Selegue's protocol was successfully applied in the preparation of $[M\{=C=C=C(p\text{-}RC_6H_4)_2\}(CO)_5]$ (M = Cr, W; R = OMe, NMe_2) [89–91] and $[Mo(\eta^7\text{-}C_7H_7)\{=C=C=C(R)Ph\}(dppe)][PF_6]$ (R = Me, Ph) [92], the most employed route involves the reaction of tetrahydrofuran solvates $[(CO)_5M(THF)]$ with the corresponding dianion $[C{\equiv}CCR_2O]^{2-}$ and subsequent deoxygenation of the resulting metal–acetylide with phosgene (Scheme 4) [89–91].

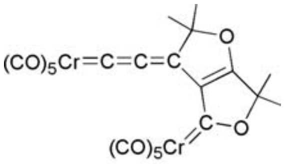
Related reactions have also been performed starting directly from $M(CO)_6$ precursors, via decarbonylation (UV irradation) of the corresponding intermediate $[M\{=C(OLi)C{\equiv}CCR_2OLi]$ and subsequent treatment with $COCl_2$ [43, 90, 93]. However, these reactions are not always straightforward and, in some cases, different types of products derived from subsequent cyclization or addition reactions have been obtained. As an example, reaction of the intermediate chromium complex obtained from $Cr(CO)_6$ and $[C{\equiv}CCMe_2O]^{2-}$ with MeCOCl led to the bicyclic dinuclear allenylidene–carbene complex **3** (see Fig. 3) [94].

2.1.3 Group 7 Metals

Preparation of the pioneering manganese(I) allenylidene derivatives $[MnCp(=C=C=CR_2)(CO)_2]$ (**5**) was accomplished by treatment of the π-alkyne complex $[MnCp(\eta^2\text{-}HC{\equiv}CCO_2Me)(CO)_2]$ (**4**) with excess of an organolithium reagent, followed by deoxygenation with HCl or $COCl_2$ (Scheme 5) [24, 42, 95]. In essence, this reaction

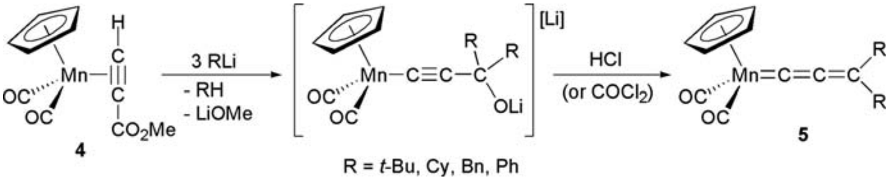


Scheme 4 Synthesis of Group 6 allenylidenes from dianions of propargylic alcohols



3

Fig. 3 Structure of the bicyclic allenylidene–chromium complex **3**



Scheme 5 Synthesis of manganese allenylidenes **5** from π-alkyne complex **4**

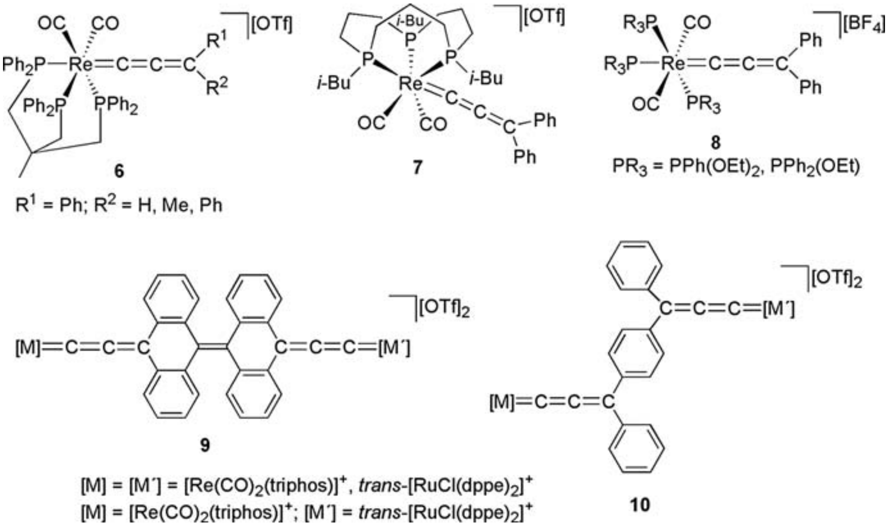
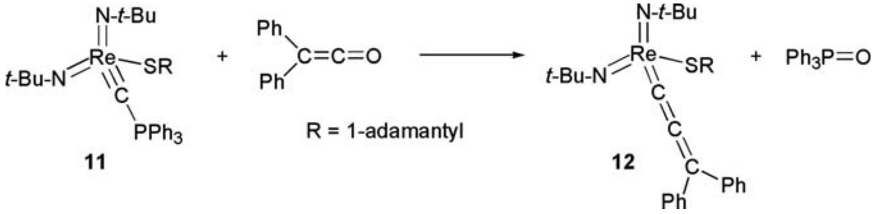


Fig. 4 Structure of the rhenium(I) allenylidenes **6–10**

is closely related to those involving addition of dianions $[C{\equiv}CCR_2O]^{2-}$ to metal carbonyls (Scheme 4). Related species bearing methylcyclopentadienyl instead of the cyclopentadienyl ligand were similarly synthesized [96]. Alternatively, complexes $[MnCp(=C=C=CR^1R^2)(CO)_2]$ ($R^1 = R^2 =$ Me, Ph; $R^1 =$ Me, $R^2 =$ Ph) could also be generated from $[MnCp\{\eta^2\text{-}HC{\equiv}CCR^1R^2(OH)\}(CO)_2]$ upon treatment with base and subsequent acid-promoted dehydration [97].

After these initial studies, the most recent developments in Group 7 allenylidene chemistry concern rhenium. Thus, the cationic octahedral Re(I) derivatives **6** [98, 99], **7** [100], and **8** [101] have been conveniently prepared by following the Selegue's synthetic approach (Fig. 4). In addition, starting from appropriate bis-alkynols, several homo- and hetero-bimetallic derivatives **9**–**10**, in which two allenylidene groups are held together by an organic spacer, could also be synthesized [102].

In contrast, the tetrahedral rhenium(VII) derivative $[Re(N\text{-}t\text{-}Bu)_2(SR)(=C=C=CPh_2)]$ (**12**), which represents the only d^0-allenylidene complex characterized crystallographically to date, was obtained through a rather unusual synthetic



Scheme 6 Synthesis of the tetrahedral rhenium(VII) allenylidene **12**

strategy, involving the reaction of the phosphonioalkylidyne rhenium complex **11** with diphenylketene (Scheme 6) [103].

2.1.4 Group 8 Metals

The chemistry of allenylidene complexes is dominated by these metals, mainly due to the efficiency and versatility of Selegue's synthetic approach (Scheme 2). In fact, although the first examples were synthesized by reacting carbonylic precursors with dianions $[C{\equiv}CCR_2O]^{2-}$, e.g., [Fe{=C=C=C(*t*-Bu)$_2$}(CO)$_4$] [46], this route did not find further utility. Only the application of Selegue's protocol has given rise to the systematic synthesis of stable Group 8 allenylidenes. The reactions usually proceed in a one-pot manner by reacting halide precursors with the appropriate propargylic alcohol in the presence of an halide abstractor ($NaBF_4$, KPF_6, $AgSbF_6$, etc.). In some cases, precursors containing labile ligands, such as acetonitrile, acetone, dinitrogen, or olefins, have been employed. Addition of nucleophiles to allenylidenes dominates the reactivity of these electrophilic groups (see below). Therefore, the use of nucleophilic solvents such as methanol or ethanol (or sometimes the molecule of water resulting from the spontaneous dehydration of the alkynol) often leads to the isolation of a Fischer-type alkoxy- or hydroxy-carbenes [M]=C(OR)CH=CR^{1}R^2 instead of the desired allenylidenes. The use of silver(I) salts AgX (X^- = PF_6^-, TfO^-, BF_4^-) partially soluble in chlorinated solvents avoids this drawback. The synthetic methodology turns out to be quite general regardless of the precursor metal complex used, including octahedral, five-coordinate and half-sandwich metal fragments.

Iron

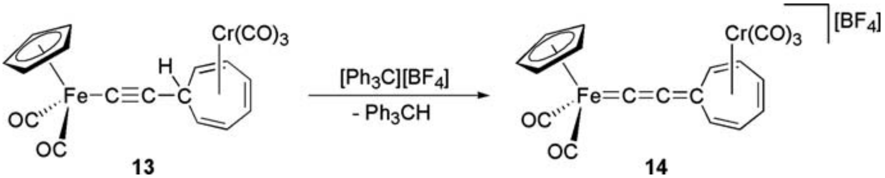
Neutral five-coordinate species [Fe(=C=C=CR^{1}R^2)(CO)$_2${P(OMe)$_3$}$_2$] (R^1 = R^2 = Ph, *t*-Bu; R^1 = Me, R^2 = *t*-Bu) [104], cationic and dicationic octahedral complexes [Fe(=C=C=CR^{1}R^2)(depe)$_2$][BF$_4$] (R^1 = R^2 = Ph, Et; R^1 = Me, R^2 = Ph; R^{1}R^2 = –(CH$_2$)$_5$–) [105–107], and [Fe(=C=C=CPh$_2$){P(OEt)$_3$}$_5$][BPh$_4$]$_2$ [108], respectively, as well as the half-sandwich derivatives [FeCp(=C=C=CPh$_2$)(dppe)][BF$_4$] [109], [FeCp*(=C=C=CR^{1}R^2)(dppe)][PF$_6$] (R^1 = R^2 = Ph; R^1 = Me,

R^2 = Ph, Et) [110] and [FeCp{=C=C=C(H)C≡CFeCp(dppe)}(dppe)][BPh_4] [111], have been synthesized using the Selegue's route. In contrast, the heterobimetallic iron(II)–chromium(0) complex **14**, containing a bridging allenylidene ligand, has been obtained through a completely different strategy involving hydride abstraction from the neutral cycloheptatrienylacetylide complex **13** (Scheme 7) [112].

Ruthenium

Following the seminal preparation of [RuCp(=C=C=CPh_2)(PMe_3)$_2$][PF_6] (**1**) (Scheme 1) [25], extensive series of analogous half-sandwich allenylidenes have been prepared from the appropriate propargylic alcohol. Typical metal fragments include not only the classical η^5-cyclopentadienyl and η^6-arene derivatives but also tethered-type ligands in which the rings are linked to the metal also through an ancillary κ^1-coordinated donor atom (Fig. 5).

The most common are cationic complexes of general composition [Ru(η^5-Ring)(=C=C=CR^1R^2)(L^1)(L^2)][X] (R^1/R^2 = aryl or alkyl groups; L^1/L^2 = mono- or bidentate phosphines, CO or mixed *P,O*-donor ligands) involving both cyclopentadienyl (C_5H_5) [113–117], pentamethylcyclopentadienyl (C_5Me_5) [75, 79, 80, 118–122], or indenyl (C_9H_7 or 1,2,3-$C_9H_4Me_3$) rings [74, 113, 123–131]. For the latter, some examples containing chiral phosphines, such as (*R*)-BINAP [130, 131], or chiral substituents in the allenylidene chain (**15–17** in Fig. 6) have been described [126, 127]. Recently, allenylidene complexes bearing a fullerene-cyclopentadienyl ligand have been synthesized starting from [RuCl(η^5-$C_{60}Me_5$){(*R*)-prophos}] and



13 **14**

Scheme 7 Synthesis of the heterobimetallic allenylidene complex **14**

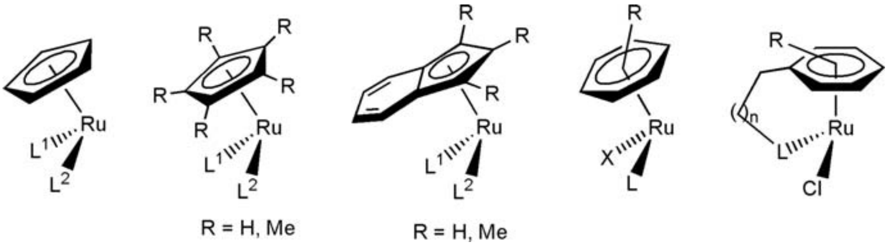


Fig. 5 Typical half-sandwich ruthenium fragments used in the preparation of allenylidene complexes. Ancillary ligands include CO, mono- and bidentate phosphines or *N*-heterocyclic carbenes

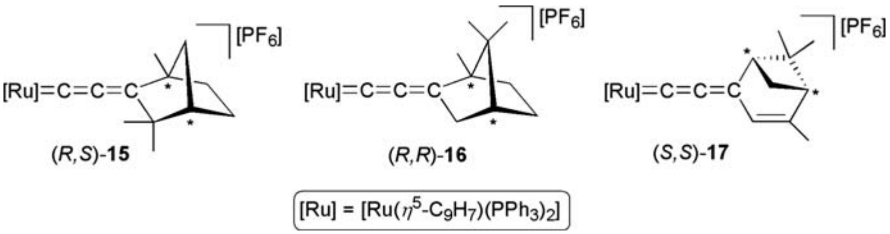


Fig. 6 Indenyl-ruthenium(II) complexes containing chiral allenylidene chains

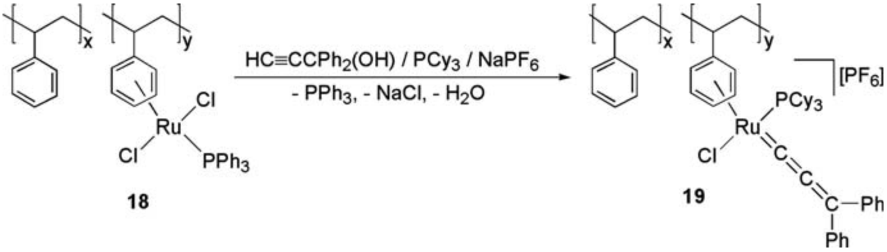
the appropriate alkynol [132]. Selegue's route has also been successfully applied in the preparation of the cyclopentadienyl-bisphosphine tethered derivative $[\mathrm{Ru}\{\eta^5{:}\kappa^2(P,P)\text{-}\mathrm{C_5H_4CH_2CMe(CH_2PPh_2)_2}\}(\mathrm{=C=C=CPh_2})][\mathrm{PF_6}]$ [133].

Atypical dinuclear allenylidene complexes $[\mathrm{Cp^*RuCl(\mu\text{-}SMe)_2Ru\{=C=C=C(H)Ph\}Cp^*}][\mathrm{BF_4}]$ and $[\mathrm{Cp^*RuCl(\mu\text{-}EMe)_2RuCp^*\{=C=C=C(}p\text{-}\mathrm{MeC_6H_4)_2\}}][\mathrm{OTf}]$ (E = S, Se, Te) have been synthesized by reaction of the chalcogenolate-bridged diruthenium(III) precursors $[\{\mathrm{Cp^*RuCl(\mu\text{-}SMe)}\}_2]$ or $[\mathrm{Cp^*RuCl(\mu\text{-}ER)_2RuCp^*(OH_2)}][\mathrm{OTf}]$ with the corresponding alkynol [134–136]. These species, which are the only ruthenium(III) allenylidenes reported to date, have been widely used in catalytic transformations of propargylic alcohols (see below).

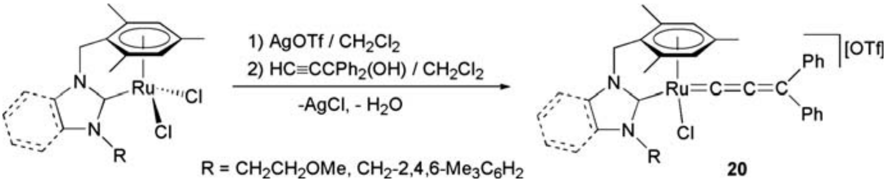
In contrast to their cationic counterparts, neutral η^5-$\mathrm{C_5R_5}$-based ruthenium–allenylidenes are scarce. Thus, only complexes $[\mathrm{RuClCp(=C=C=CPh_2)(PPh_3)}]$, resulting from the treatment of the η^3-allyl derivative $[\mathrm{Ru}(\eta^3\text{-}2\text{-}\mathrm{C_3H_4Me})\mathrm{Cp(PPh_3)}]$ with $\mathrm{HC{\equiv}CCPh_2(OH)/HCl}$ [118], and $[\mathrm{RuClCp^*(=C=C=CPh_2)}\{\kappa^1(P)\text{-}i\text{-}\mathrm{Pr_2PCH_2CO_2Me}\}]$, generated from $[\mathrm{RuClCp^*}\{\kappa^2(P,O)\text{-}i\text{-}\mathrm{Pr_2PCH_2CO_2Me}\}]$ and $\mathrm{HC{\equiv}CCPh_2(OH)}$ [137], have been described. The use of acidic $\mathrm{Al_2O_3}$ as dehydrating agent was in both cases required.

Ruthenium-allenylidene complexes bearing η^6-arene auxiliary ligands are also well documented. Most of the reported examples belong to the series of cationic complexes with general formula $[\mathrm{RuCl(=C=C=CR^1R^2)}(\eta^6\text{-arene})(\mathrm{L})][\mathrm{X}]$ (arene = p-cymene, $\mathrm{C_6Me_6}$, 1,3,5-$\mathrm{C_6H_3Me_3}$, 1,2,4,5-$\mathrm{C_6H_2Me_4}$; L = monodentate phosphine or *N*-heterocyclic carbene) [138–151]. These species have attracted a great deal of attention in recent years since they can act as efficient precatalysts for olefin metathesis (see below). The synthesis of the polystyrene-supported allenylidene **19**, which can be recovered quantitatively and reused in catalytic RCM reactions, could also be successfully achieved starting from the immobilized dichloride precursor **18** (Scheme 8) [152].

Ruthenium fragments bearing tethered-type arene–phosphine ligands have also been employed for the preparation of stable allenylidene complexes. Representative examples are the cationic diphenylallenylidenes $[\mathrm{RuCl(=C=C=CPh_2)}\{\eta^6{:}\kappa^1(P)\text{-}\mathrm{C_6H_5O(CH_2)_2P}t\text{-}\mathrm{Bu_2}\}][\mathrm{PF_6}]$ [153] and $[\mathrm{RuCl(=C=C=CPh_2)}\{\eta^6{:}\kappa^1(P)\text{-}\mathrm{C_6H_5(CH_2)}_n\mathrm{PR_2}\}][\mathrm{X}]$ (R = Cy, $n = 3$, $\mathrm{X^-} = \mathrm{TfO^-}$, $\mathrm{PF_6^-}$; R = t-Bu, $n = 2$, $\mathrm{X^-} = \mathrm{PF_6^-}$) [143, 153]. Related tethered species **20** containing NHC-carbenes as side arms have also been described (Scheme 9) [154, 155].



Scheme 8 Synthesis of the polystyrene-supported allenylidene complex **19**



Scheme 9 Synthesis of allenylidene complexes **20** bearing a tethered arene/NHC ligand

Extensive studies on octahedral and five-coordinate ruthenium allenylidenes have been published. Illustrative examples in which the cumulenic chain was generated from propargylic alcohols, through the classical Selegue's synthetic route, are shown in Fig. 7. As expected, the use of bulky ligands (such as IMes, PCy_3, or Sb*i*-Pr_3) is usually required to stabilize $16e^-$ five-coordinate allenylidenes. In addition to these examples, large series of cationic derivatives of general composition *trans*-$[RuCl(=C=C=CR^1R^2)(P\text{–}P)_2]^+$ and *trans*-$[Ru(C\equiv CR^1)(=C=C=CR^2R^3)(P\text{–}P)_2]^+$ (P–P = chelating diphosphine), including bis- and tris(allenylidene) species derived from the activation of bis- and tris(alkynols), are known [148, 169–180]. In some cases, the presence of coordinating substituents in the allenylidene chain has been exploited for the preparation of redox-active dimetallic derivatives such as complexes **21** [166], **22** [166], **23** [180], and **24** [180] (Fig. 8).

Formation of complex **26** by oxidation of the allenylidene–acetylide derivative **25** with cerium(IV) ammonium nitrate merits to be highlighted since **26** represents a unique example in which two allenylidene ligands are bonded to a metal (Scheme 10) [181].

Dinuclear bis(allenylidene) complexes containing bridging halide ligands, such as complexes **27–29** (Fig. 9), are more common [182–184]. Thus, while complexes **27** and **28** were formed through direct activation of the appropriate alkynol with $[RuCl_2(PPh_3)_3]$ and $[\{RuCl_2(TPPMS)_2\}_2]$, respectively, complexes **29** were obtained by treatment of the corresponding alkenyl–carbyne complex $[RuX_3\{\equiv CC(H)=CR_2\}(dppf)]$ with $AgSbF_6$, abstraction of the halide ligand being accompanied by the spontaneous deprotonation of the carbyne group.

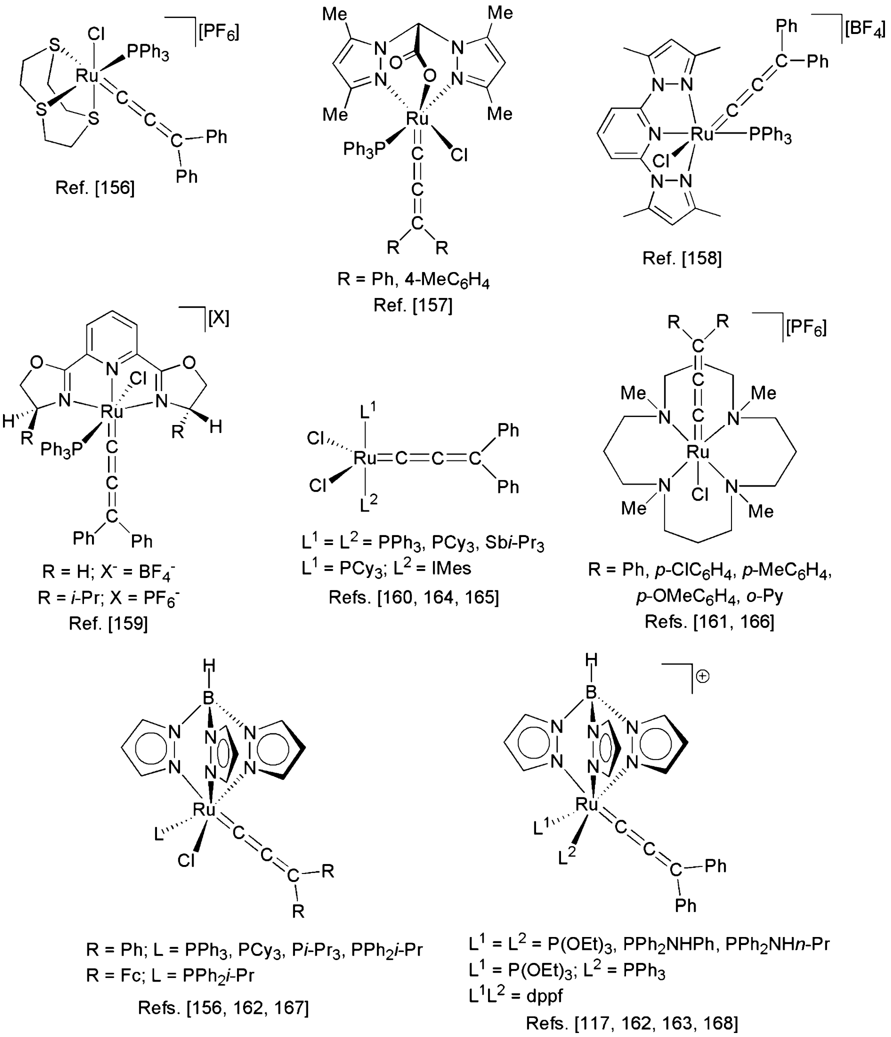


Fig. 7 Some examples of six- and five-coordinate ruthenium allenylidenes

Besides Selegue's methodology, several synthetic alternatives of ruthenium allenylidene complexes have been reported. The most popular involves trapping of transient butatrienylidene or pentatetraenylidene intermediates with nucleophiles [26–29]. Although alcohols, amines, or thiols have been usually employed in these reactions leading to the corresponding heteroatom-substituted allenylidenes, in some cases the use of carbon-centred nucleophiles, such as pyrroles, has been described [185, 186]. Quite recently, a systematic route to prepare sequentially polyalkenyl–allenylidene complexes has also been discovered (Scheme 11) [187–189]. The first step consists of the insertion of the ynamine $MeC{\equiv}CNEt_2$ into the

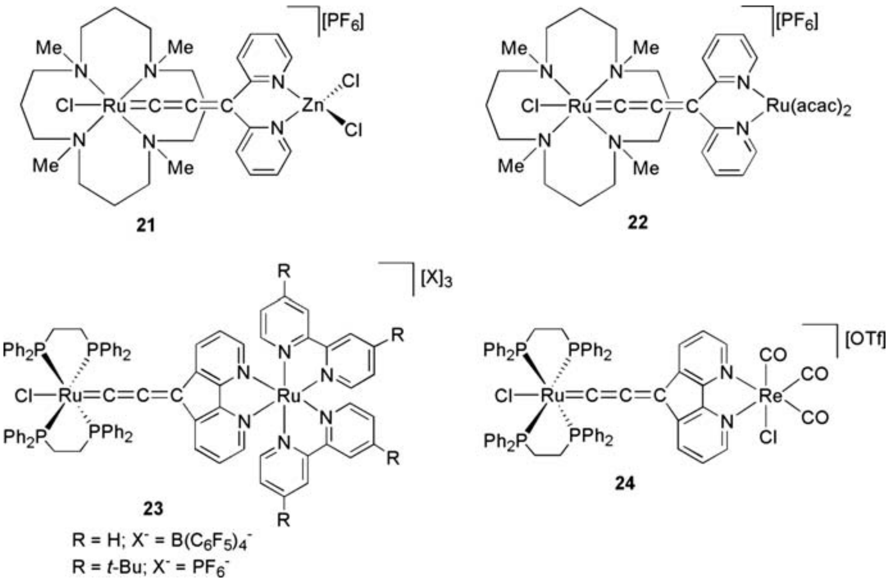
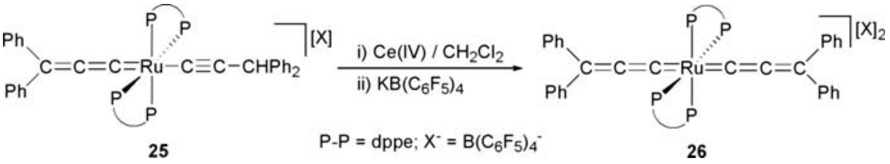


Fig. 8 Structure of some mixed bimetallic allenylidene complexes



Scheme 10 Synthesis of the bis(allenylidene) complex **26**

C_β=C_γ bond of indenyl–allenylidene complexes **30** which leads to the stereoselective formation of cationic amino-allenylidenes **31**. When R = Ph, complexes **31** can be transformed into the secondary derivatives **32** via treatment with $LiBHEt_3$ and subsequent purification on silica-gel column. Further insertions of MeC≡$CNEt_2$ into **32** allow the preparation of polyunsaturated cumulene chains (related insertion reactions will be discussed in the reactivity section).

More elaborated examples of ruthenium allenylidenes include the diruthenium(II) derivatives **33** (Fig. 10) containing a planar "W" shaped π-conjugated C_7 bridge. They were formed by coupling the cationic allenylidenes *trans*-[RuCl{=C=C=C(R^1)CH_2R^2}$(dppe)_2$][BF_4], featuring an acidic methylenic unit, with the neutral diynyl complex *trans*-[RuCl{$(C{\equiv}C)_2H$}$(dppe)_2$]. The process involves the initial protonation of the latter by the methylenic unit of the former and subsequent C–C coupling between the resulting organometallic species [190]. Similar C_9-bridged species were synthesized using the triynyl derivative *trans*-[RuCl{$(C{\equiv}C)_3SiMe_3$}$(dppe)_2$]. Oxidation or protonation of the diynyl complex *trans*-[RuCl{$(C{\equiv}C)_2H$}

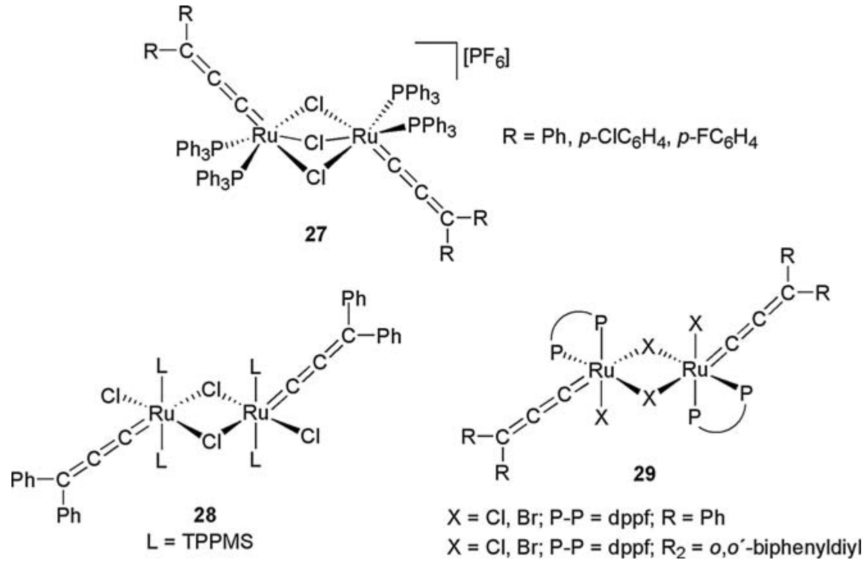
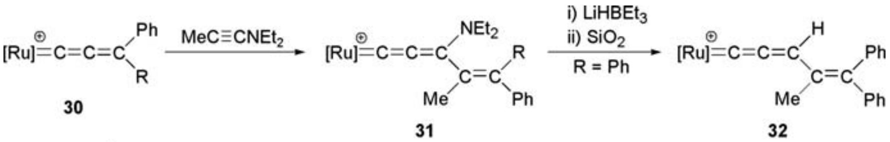


Fig. 9 Structure of the dinuclear bis(allenylidene) complexes **27–29**



$[Ru] = [Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]$; R = Ph, H

$[Ru] = [Ru(\eta^5\text{-}C_9H_7)(PPh_3)\{\kappa^1(P)\text{-}Ph_2PCH_2CH{=}CH_2\}]$; R = Ph

Scheme 11 Procedure for the preparation of unsaturated allenylidene complexes

$(dppe)_2]$ was reported to yield the related C_7-anelated complex **34** (Fig. 10), the process involving a highly reactive butatrienylidene intermediate $[Ru]^+{=}C{=}C{=}C{=}CH_2$ [190]. Allenylidene complex **35**, containing a spirobicyclic organic skeleton, is also known. It was unexpectedly formed in the reaction of $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ with 1-ethynyl-1-cyclohexanol [191, 192].

Osmium

Several half-sandwich-type derivatives, in which the allenylidene unit is generated from propargylic alcohols following the Selegue's protocol, are known. Representative examples include (1) the cationic cyclopentadienyl complexes $[CpOs({=}C{=}C{=}CPh_2)(L^1)(L^2)][PF_6]$ ($L^1 = L^2 = PPh_3$, $Pi\text{-}Pr_3$; $L^1 = Pi\text{-}Pr_3$, $L^2 = CO$, $PHPh_2$) [193–195] and $[Os({=}C{=}C{=}CPh_2)\{\eta^5{:}\kappa^1(P)\text{–}C_5H_4CH_2CH_2PPh_2\}(Pi\text{–}Pr_3)]$

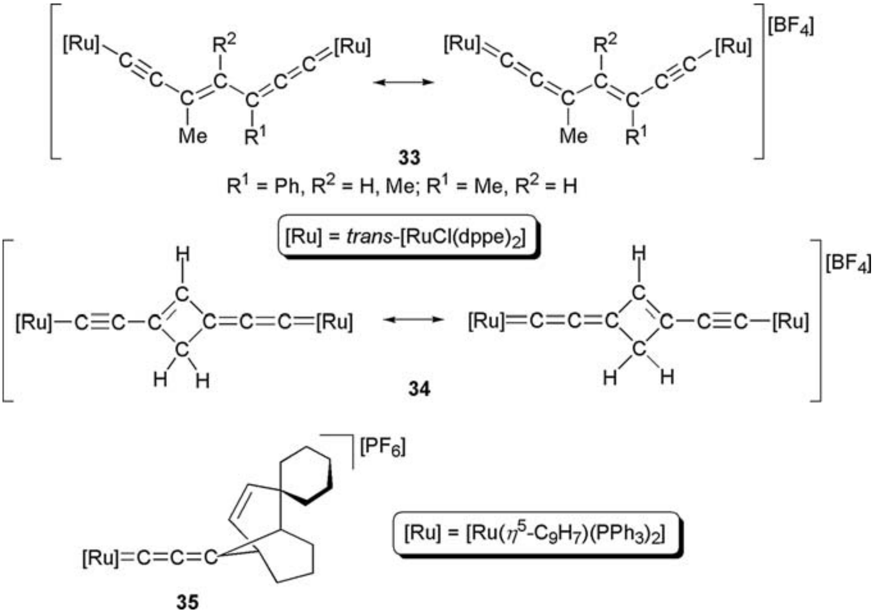


Fig. 10 Structure of complexes **33–35**

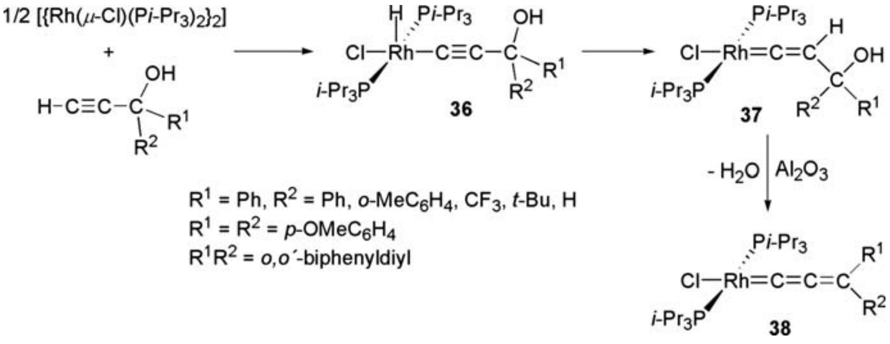
$[PF_6]$ [196], (2) the neutral derivative $[OsClCp(=C=C=CPh_2)(P\textit{i}\text{–}Pr_3)]$ [197], (3) the indenyl complexes $[Os(\eta^5\text{-}C_9H_7)(=C=C=CR_2)(PPh_3)_2][PF_6]$ (R = Ph; R_2 = *o*,*o*′-biphenyldiyl) [123], and (4) the cationic η^6-arene derivatives $[OsX(=C=C=CPh_2)(\eta^6\text{-arene})(PR_3)][PF_6]$ (arene = mesitylene, X = Cl, $PR_3 = PMe_3, PPh_3, PCy_3$; arene = C_6H_6, X = I, $PR_3 = PCy_3$; arene = *p*-cymene, X = Cl, $PR_3 = PCy_3$) [198] and $[OsCl(=C=C=CPh_2)(\eta^6\text{-}p\text{-cymene})(IPr)][BF_4]$ [199].

Octahedral Os(II) allenylidenes are also well-known. Thus, the cationic complexes *trans*-$[OsCl(=C=C=CR^1R^2)(dppm)_2][PF_6]$ ($R^1 = R^2$ = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4; R^1 = Ph, R^2 = H; CR^1R^2 = 4,5-diazafluoren-9-yl) have been obtained in high yields by reacting *cis*-$[OsCl_2(dppm)_2]$ with the appropriate alkynol in the presence of $NaPF_6$ [161, 175, 179]. Similarly, displacement of the labile acetone ligand in $[Os\{\kappa^2(C,O)\text{–}C(=CH_2)CO_2Me\}(acetone)(CO)(P\textit{i}\text{-}Pr_3)_2][BF_4]$ by $HC\equiv CCPh_2(OH)$ led to the selective formation of $[Os\{\kappa^2(C,O)\text{–}C(=CH_2)CO_2Me\}(C=C=CPh_2)(CO)(P\textit{i}\text{–}Pr_3)_2][BF_4]$ [200]. The neutral complex $[OsCl_2(=C=C=CPh_2)(CO)(PPh_3)_2]$ [201] and the dicationic derivative $[Os(=C=C=CPh_2)\{P(OEt)_3\}_5][BPh_4]_2$ [202] have also been synthesized using the Selegue's route. In contrast, the diphenylallenylidene species $[OsH(=C=C=CPh_2)(CH_3CN)_2(P\textit{i}\text{–}Pr_3)_2][BF_4]$ has been obtained by deprotonation of the dicationic alkenyl–carbyne $[OsH\{\equiv CC(H)=CPh_2\}(CH_3CN)_2(P\textit{i}\text{–}Pr_3)_2][BF_4]_2$ with *t*-BuOK [203]. Complex $[Os(=C=C=CPh_2)(IPr)(CH_3CN)_3(P\textit{i}\text{–}Pr_3)][BF_4]_2$ is also known [199]. It was generated from the half-sandwich derivative $[OsCl(=C=C=CPh_2)(\eta^6\text{-}p\text{-cymene})(IPr)][BF_4]$, via chloride abstraction with $AgBF_4$ and concomitant displacement of the coordinated arene ligand by acetonitrile, followed by substitution of one of the solvent molecules of the tetrakis(solvento) intermediate [Os(=C=C=CPh$_2$)(IPr)(CH$_3$CN)$_4$][BF$_4$]$_2$ by P*i*–Pr$_3$.

2.1.5 Group 9 Metals

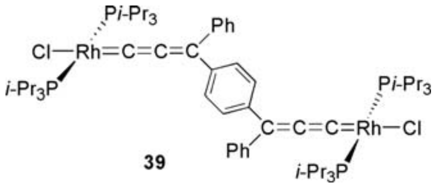
While no cobalt allenylidene complexes have been reported to date, wide series of square-planar Rh(I) and Ir(I) derivatives are known. Thus, the neutral rhodium derivatives *trans*-[RhCl(=C=C=CR^{1}R^2)(P*i*–Pr$_3$)$_2$] (**38**) have been synthesized in high yields by treatment of dimer [{Rh(μ-Cl)(P*i*–Pr$_3$)$_2$}$_2$] with the appropriate alkynol, via acidic-Al$_2$O$_3$-promoted dehydration of the corresponding 3-hydroxyvinylidene intermediates **37** (Scheme 12) [76, 204–206]. Working at low temperature (ca. −60 °C), the initially formed alkynyl(hydrido)rhodium(III) species **36** could be in some cases isolated and characterized. It is worth noting that complex [{Rh(μ-Cl)(P*i*–Pr$_3$)$_2$}$_2$] was found to be extremely sensitive to the nature of the alkynol, the activation of alkyl-substituted derivatives HC≡CCMePh(OH), HC≡CCMe$_2$(OH) and HC≡CC(*i*-Pr)$_2$(OH) affording mixtures containing the expected allenylidenes along with their tautomeric alkenyl–vinylidene isomers [76, 204].

Activation of 1,1-diphenyl-2-propyn-1-ol by [{Rh(μ-Cl)(*i*-Pr$_2$PCH$_2$CH$_2$Ph)$_2$}$_2$], [RhCl{κ^1(*P*)-*i*-Pr$_2$PCH$_2$CH$_2$OMe}{κ^2(*P,O*)-*i*-Pr$_2$PCH$_2$CH$_2$OMe}] and *trans*-[RhCl{κ^1(As)-*i*-Pr$_2$AsCH$_2$CH$_2$OMe}$_2$(C$_2$H$_4$)] gave the related neutral diphenylallenylidene complexes *trans*-[RhCl(=C=C=CPh$_2$)L$_2$] (L = *i*-Pr$_2$PCH$_2$CH$_2$Ph [207], *i*-Pr$_2$PCH$_2$CH$_2$OMe [208], *i*-Pr$_2$AsCH$_2$CH$_2$OMe [209]), the use of acidic alumina as dehydrating agent also being required. In contrast, dehydration of the cationic 3-hydroxyvinylidene [Rh{=C=C(H)CPh$_2$(OH)}(acetone)(P*i*–Pr$_3$)$_2$][PF$_6$], generated by displacement of acetone in [Rh(acetone)$_2$(P*i*–Pr$_3$)$_2$][PF$_6$] by HC≡CCPh$_2$(OH), takes place spontaneously at room temperature affording the corresponding cationic Rh(I) allenylidene [Rh(=C=C=CPh$_2$)(acetone)(P*i*–Pr$_3$)$_2$][BF$_4$] [210]. Interestingly, the phenylene-bridged bis-allenylidene complex **39** (Fig. 11) could also be



Scheme 12 Activation of alkynols by the rhodium(I) dimer [{Rh(μ-Cl)(P*i*–Pr$_3$)$_2$}$_2$]

Fig. 11 Structure of the dinuclear bis(allenylidene) – Rh(I) complex **39**



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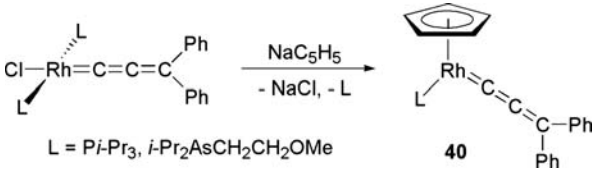


40

Scheme 13 Synthesis of the cyclopentadienyl-Rh(I) allenylidenes **40**

synthesized starting from $[\{Rh(\mu\text{-}Cl)(Pi\text{–}Pr_3)_2\}_2]$ and the bis-alkynol 1,4-$[HC{\equiv}CC(OH)Ph]_2C_6H_4$ [82].

The lower reactivity of iridium complexes requires the use of more activated precursors. Thus, the neutral square-planar derivatives *trans*-$[IrCl\{{=}C{=}C{=}C(R)Ph\}(Pi\text{–}Pr_3)_2]$ (R = Ph, *t*-Bu) have been prepared from $[IrH_2Cl(Pi\text{–}Pr_3)_2]$ and the appropriate alkynol, via UV-promoted or CF_3CO_2H-catalyzed dehydration of the initially formed hydride-alkynyl intermediates $[IrHCl\{C{\equiv}CC(R)Ph(OH)\}(Pi\text{–}Pr_3)_2]$ [78, 81]. The cationic species $[Ir({=}C{=}C{=}CPh_2)(\eta^4\text{-diene})(PR_3)][BF_4]$ (diene = COD, PR_3 = PCy_3; diene = TFB, PR_3 = PCy_3, $Pi\text{–}Pr_3$) are also known [211]. They were synthesized by reacting the methoxo compounds $[Ir(OMe)(\eta^4\text{-diene})(PR_3)]$ with 1,1-diphenyl-2-propyn-1-ol, followed by dehydration of the resulting alkynyl derivatives $[Ir\{C{\equiv}CCPh_2(OH)\}(\eta^4\text{-diene})(PR_3)]$ with stoichiometric amounts of HBF_4.

In accord with the expected *trans* influence of the π-acceptor allenylidene unit [212], substitution of the chloride ligand by different anionic nucleophiles in complexes *trans*-$[MCl({=}C{=}C{=}CR^1R^2)(Pi\text{–}Pr_3)_2]$ (M = Rh, Ir) is favored, affording new allenylidene derivatives *trans*-$[MX({=}C{=}C{=}CR^1R^2)(Pi\text{–}Pr_3)_2]$ (X = I, F, OH, N_3, etc.) (see reactivity studies below). Of particular interest is the behavior of the Rh(I) species *trans*-$[RhCl({=}C{=}C{=}CPh_2)L_2]$ (L = $Pi\text{–}Pr_3$, *i*-$Pr_2AsCH_2CH_2OMe$) towards NaC_5H_5 since the reactions lead to the clean formation of complexes **40** (Scheme 13), the only half-sandwich-type Group 9 allenylidenes presently known [206, 209].

2.2 *Structure of Allenylidene Complexes*

Structural parameters of several mononuclear complexes containing terminal allenylidene ligands are summarized in Table 1. In addition to the expected short M–C_α

Table 1 Structural data of selected mononuclear allenylidene complexes

Compound	M=C$_\alpha$(Å)	C$_\alpha$=C$_\beta$(Å)	C$_\beta$=C$_\gamma$(Å)	M–C$_\alpha$–C$_\beta$(°)	C$_\alpha$–C$_\beta$–C$_\gamma$(°)	[Ref]
[Cr(=C=C=CPh$_2$)(CO)$_5$]	1.931(2)	1.249(3)	1.358(3)	176.7(2)	179.5(3)	[89–91]
[Mo(η^7-C$_7$H$_7$)(=C=C=CPh$_2$)(dppe)][PF$_6$]	1.994(3)	1.258(5)	1.354(5)	176.1(3)	174.4(4)	[92]
[MnCp(=C=C=CCy$_2$)(CO)$_2$]	1.806(6)	1.252(8)	1.342(8)	177.9(5)	175.1(6)	[213]
[Re(=C=C=CPh$_2$)(N*t*–Bu)$_2$(S-Ad)]	1.898(13)	1.275(16)	1.339(15)	171.4(10)	177.0(12)	[103]
[Re(=C=C=CPh$_2$)(CO)$_2$(triphos)][BPh$_4$]	1.996(4)	1.237(6)	1.359(6)	171.7(4)	172.1(5)	[214]
[FeCp*(=C=C=CPh$_2$)(dppe)][PF$_6$]	1.785(5)	1.257(7)	1.361(7)	177.4(4)	177.6(5)	[110]
[Fe{=C=C=C(*t*-Bu)$_2$}(CO)$_2${P(OMe)$_3$}$_2$]	1.833(4)	1.266(5)	1.344(6)	179.1(2)	177.8(3)	[104]
[RuCp(=C=C=CPh$_2$)(PMe$_3$)$_2$][PF$_6$]	1.884(5)	1.255(8)	1.329(9)	175.9(5)	175.1(7)	[25]
[RuCp{=C=C=CPh(*p*-NO$_2$C$_6$H$_4$)}(PMe$_3$)$_2$][PF$_6$]	1.889(3)	1.246(4)	1.358(3)	176.3(2)	176.6(3)	[116]
[RuCp{=C=C=C(Me)(1-Me-pyrrol-2-yl)}(PPh$_3$)$_2$][PF$_6$]	1.92(1)	1.24(2)	1.37(2)	173.5(8)	172(1)	[185]
[RuCp{=C=C=C(C$_{12}$H$_{12}$)}(PPh$_3$)$_2$][PF$_6$][a]	1.94(1)	1.23(2)	1.42(2)	170(1)	174(1)	[215]
[RuCp{=C=C=C(C$_{14}$H$_{10}$)}(PPh$_3$)$_2$][PF$_6$][b]	1.895(3)	1.267(4)	1.352(4)	171.3(3)	172.4(3)	[215]
[RuCp(=C=C=CPh$_2$){PPh$_2$(NHPh)}$_2$][OTf]	1.889(6)	1.270(8)	1.356(8)	175.5(5)	172.9(7)	[117]
[RuCp{=C=C=C(Me)Ph}(dippe)][BPh$_4$]	1.884(5)	1.257(6)	1.338(7)	169.3(4)	175.9(5)	[119]
[RuCp*(=C=C=CPh$_2$)(PEt$_3$)$_2$][BPh$_4$]	1.876(5)	1.245(7)	1.352(8)	172.1(5)	170.8(6)	[79]
[RuCp*{=C=C=C(H)Ph}(PEt$_3$)$_2$][BF$_4$]	1.884(8)	1.244(13)	1.353(14)	175.2(7)	169.6(10)	[122]
[RuCp*{=C=C=C(H)Ph}(dippe)][BPh$_4$]	1.865(8)	1.249(10)	1.320(12)	172.8(7)	177.5(9)	[80]
[Ru{η^5:κ^2(*P*,*P*)-C$_5$H$_4$CH$_2$CMe(CH$_2$PPh$_2$)$_2$}(=C=C=CPh$_2$)][PF$_6$]	1.907(6)	1.270(8)	1.358(8)	173.4(5)	175.9(6)	[133]
[Ru(η^5-C$_{60}$Me$_5$){=C=C=CH(*p*-NMe$_2$C$_6$H$_4$)}{(*R*)-prophos}][PF$_6$]	1.75(2)	1.37(3)	1.40(3)	175.6(19)	170(2)	[132]
[Ru(η^5-C$_9$H$_7$)(=C=C=CPh$_2$)(PPh$_3$)$_2$][PF$_6$]	1.878(5)	1.260(7)	1.353(7)	168.5(5)	168.2(7)	[123]
[Ru(η^5-C$_9$H$_7$){=C=C=C(C$_{13}$H$_{20}$)}(PPh$_3$)$_2$][PF$_6$][c]	1.889(5)	1.256(7)	1.339(7)	173.6(4)	173.2(5)	[191]
[Ru(η^5-1,2,3-C$_9$H$_4$Me$_3$)(=C=C=CPh$_2$)(CO)(PPh$_3$)][BF$_4$]	1.92(1)	1.26(1)	1.35(2)	172(1)	176(1)	[124]
[RuCl(=C=C=CPh$_2$)(η^6-*p*-cymene)(P*i*–Pr$_3$)][PF$_6$]	1.894(3)	1.253(5)	1.361(5)	174.6(3)	168.8(4)	[143]
[RuCl(=C=C=CPh$_2$)(η^6-*p*-cymene)(IMes)][PF$_6$]	1.890(4)	1.255(5)	1.353(6)	166.6(3)	171.8(4)	[142]
[RuCl(=C=C=CPh$_2$)(η^6-1,3,5-C$_6$H$_3$Me$_3$)(κ^1(*P*)-Ph$_2$PCH$_2$P{=N(C$_5$F$_4$N)}Ph$_2$)][SbF$_6$]	1.896(7)	1.242(9)	1.366(10)	178.7(6)	176.6(8)	[149]
[RuCl(=C=C=CPh$_2$){η^6:κ^1(*P*)–C$_6$H$_5$–(CH$_2$)$_3$–PCy$_2$}][OTf]	1.903(4)	1.244(5)	1.364(5)	170.9(4)	178.4(5)	[143]
[RuCl{=C=C=C(H)Ph}(dppm)$_2$][PF$_6$]	1.886(10)	1.254(14)	1.34(2)	177.0(8)	174.1(11)	[175]
[RuCl{=C=C=C(C$_{10}$H$_6$N$_2$)}(dppm)$_2$][PF$_6$][d]	1.868(6)	1.255(9)	1.352(9)	179.5(6)	178.0(7)	[180]
[RuCl{=C=C=C(C$_{14}$H$_{10}$)}(dppm)$_2$][PF$_6$][e]	1.85(2)	1.29(3)	1.39(3)	179(2)	177(2)	[216]

(*continued*)

Table 1 (continued)

Compound	M=C$_\alpha$(Å)	C$_\alpha$=C$_\beta$(Å)	C$_\beta$=C$_\gamma$(Å)	M–C$_\alpha$–C$_\beta$(°)	C$_\alpha$–C$_\beta$–C$_\gamma$(°)	[Ref]
[RuCl{=C=C=CMe(1-Me-pyrrol-2-yl)}(dppm)$_2$][SbF$_6$]	1.911(5)	1.245(7)	1.378(7)	179.5(4)	174.7(5)	[186]
[RuCl{=C=C=C(C$_{10}$H$_6$N$_2$)}(dppe)$_2$][PF$_6$]^d	1.875(11)	1.268(7)	1.348(6)	177.8(9)	172(3)	[180]
[Ru(C≡CPh)(=C=C=CPh$_2$)(dppe)$_2$][PF$_6$]	1.91(1)	1.28(2)	1.35(2)	173.9(9)	177(1)	[174]
[RuCl{=C=C=C(C$_{10}$H$_6$N$_2$)}(dmpe)$_2$][PF$_6$]^d	1.84(5)	1.28(5)	1.34(4)	175(3)	176.5(17)	[179]
[RuCl(=C=C=CPh$_2$){κ^2(*P*,*O*)-*i*-Pr$_2$PCH$_2$CH$_2$OMe}$_2$][OTf]	1.829(6)	1.259(9)	1.352(9)	170.9(4)	171.8(6)	[77]
[RuCl(=C=C=CPh$_2$){κ^2(*P*,*O*)-Cy$_2$PCH$_2$CH$_2$OMe}$_2$][PF$_6$]	1.840(3)	1.273(4)	1.357(4)	178.7(3)	176.7(4)	[217]
[RuCl(=C=C=CPh$_2$){κ^4(*N*,*N*,*N*,*N*)-16-TMC}][PF$_6$]	1.849(4)	1.262(7)	1.339(7)	177.6(4)	170.1(5)	[161]
[RuCl(=C=C=CPh$_2$){κ^3(*N*,*N*,*N*)–(*S*,*S*)-*i*-Pr-pybox}(PPh$_3$)][PF$_6$]	1.868(11)	1.266(14)	1.353(14)	168.9(10)	173.1(12)	[159]
[RuCl(=C=C=CPh$_2$){κ^2(*P*,*N*)–Ph$_2$PCH$_2$CH$_2$-3,5-dmPy}$_2$][BPh$_4$]	1.877(6)	1.252(9)	1.364(9)	178.1(5)	176.5(7)	[218]
[RuCl$_2$(=C=C=CPh$_2$)(CO)(Sb*i*–Pr$_3$)$_2$]	1.88(2)	1.24(2)	1.34(2)	177(2)	174(2)	[160]
[RuCl$_2$(=C=C=CPh$_2$)(EtOH)(PPh$_3$)$_2$]	1.836(4)	1.250(4)	1.354(5)	177.8(3)	176.5(4)	[165]
[RuCl$_2$(=C=C=CPh$_2$)(MeOH)(PPh$_3$)$_2$]	1.833(6)	1.236(7)	1.384(8)	177.1(5)	178.9(6)	[165]
[RuCl$_2$(=C=C=CPh$_2$)(H$_2$O)(PPh$_3$)$_2$]	1.848(9)	1.244(11)	1.345(11)	179.1(8)	177.8(9)	[165]
[RuCl$_2$(=C=C=CPh$_2$)(*p*-NMe$_2$C$_5$H$_4$N)(PPh$_3$)$_2$]	1.902(4)	1.190(5)	1.397(5)	179.3(4)	175.3(4)	[165]
[RuCl(=C=C=CPh$_2$){κ^3(*N*,*N*,*O*)-bdmpza}(PPh$_3$)]	1.886(5)	1.266(7)	1.362(7)	175.9(4)	176.3(6)	[157]
[RuCl$_2$(=C=C=CPh$_2$){κ^3(*P*,*N*,*P*)–N(*n*-Pr)(CH$_2$CH$_2$PPh$_2$)$_2$}]	1.858(7)	1.221(9)	1.376(10)	175.8(6)	171.1(7)	[219]
[RuCl$_2$(=C=C=CPh$_2$)(IMes)(PCy$_3$)]	1.7932(13)	1.2605(17)	1.3447(17)	175.36(11)	175.29(13)	[164]
[RuCl$_2$(=C=C=CPh$_2$)(PCy$_3$)$_2$]	1.794(11)	1.273(12)	1.346(12)	169.20(12)	167.20(18)	[164]
[RuTp(=C=C=CPh$_2$)(PPh$_3$)$_2$][PF$_6$]	1.889(3)	1.248(4)	1.357(4)	167.6(3)	169.0(3)	[162]
[RuTp(=C=C=CPh$_2$)(dppf)][SbF$_6$]	1.88(4)	1.32(5)	1.26(5)	168(3)	168(4)	[163]
[RuClTp(=C=C=CPh$_2$)(PPh$_2$*i*-Pr)]	1.862(2)	1.259(3)	1.349(3)	163.6(2)	171.9(2)	[167]
[RuClTp(=C=C=CFc$_2$)(PPh$_2$*i*–Pr)]	1.889(2)	1.254(2)	1.365(2)	168.8(2)	175.0(2)	[167]
[OsCp(=C=C=CPh$_2$)(PPh$_3$)$_2$][PF$_6$]	1.897(4)	1.258(6)	1.350(6)	170.2(4)	172.4(5)	[194]
[OsCp(=C=C=CPh$_2$)(PHPh$_2$)(P*i*–Pr$_3$)][PF$_6$]	1.890(2)	1.266(3)	1.349(4)	169.2(2)	175.7(3)	[195]
[OsCp(=C=C=CPh$_2$)(CO)(P*i*–Pr$_3$)][PF$_6$]	1.913(5)	1.246(7)	1.358(7)	174.4(5)	175.4(6)	[195]
[OsClCp(=C=C=CPh$_2$)(P*i*–Pr$_3$)]	1.875(6)	1.222(9)	1.344(9)	171.6(6)	172.0(7)	[197]
[Os(η^5-C$_9$H$_7$)(=C=C=CPh$_2$)(PPh$_3$)$_2$][PF$_6$]	1.895(4)	1.265(6)	1.349(7)	169.3(4)	168.0(5)	[123]
[OsCl(=C=C=CPh$_2$)(η^6-1,3,5-C$_6$H$_3$Me$_3$)(PMe$_3$)][PF$_6$]	1.90(1)	1.27(1)	1.37(1)	172.5(9)	177(1)	[198]
[OsCl{=C=C=C(C$_{10}$H$_6$N$_2$)}(dppm)$_2$][PF$_6$]^d	1.875(2)	1.268(3)	1.343(3)	179.4(2)	177.3(2)	[179]
[OsH(=C=C=CPh$_2$)(CH$_3$CN)$_2$(P*i*–Pr$_3$)$_2$][BF$_4$]	1.854(6)	1.275(8)	1.347(8)	177.5(5)	173.2(7)	[203]
[Os{(*E*)-CH=CHPh}(=C=C=CPh$_2$)(CH$_3$CN)$_2$(P*i*–Pr$_3$)$_2$][BF$_4$]	1.866(3)	1.274(4)	1.351(4)	171.9(2)	172.3(3)	[203]

$[\mathrm{Os}\{\kappa^2(C,O)\text{-}\mathrm{C}(=\mathrm{CH_2})\mathrm{CO_2Me}\}(=\mathrm{C}=\mathrm{C}=\mathrm{CPh_2})(\mathrm{CO})(\mathrm{P}i\text{–}\mathrm{Pr_3})_2][\mathrm{BF_4}]$	1.947(6)	1.250(8)	1.376(9)	173.5(6)	171.2(7)	[200]
$[\mathrm{Os}(=\mathrm{C}=\mathrm{C}=\mathrm{CPh_2})(\mathrm{IPr})(\mathrm{CH_3CN})_3(\mathrm{P}i\text{–}\mathrm{Pr_3})][\mathrm{BF_4}]_2$	1.882(6)	1.246(8)	1.362(9)	168.2(5)	172.6(7)	[199]
$[\mathrm{OsCl_2}(=\mathrm{C}=\mathrm{C}=\mathrm{CPh_2})(\mathrm{CO})(\mathrm{PPh_3})_2]$	1.898(4)	1.235(6)	1.356(6)	173.4(4)	172.0(5)	[201]
$[\mathrm{RhCl}\{=\mathrm{C}=\mathrm{C}=\mathrm{CPh}(o\text{-}\mathrm{MeC_6H_4})\}(\mathrm{P}i\text{–}\mathrm{Pr_3})_2]$	1.855(5)	1.239(8)	1.370(9)	176.0(5)	170.9(1)	[76]
$[\mathrm{Rh}(\mathrm{N_3})\{=\mathrm{C}=\mathrm{C}=\mathrm{CPh}(t\text{-}\mathrm{Bu})\}(\mathrm{P}i\text{–}\mathrm{Pr_3})_2]$	1.849(5)	1.269(7)	1.348(7)	177.6(5)	169.1(6)	[205]
$[\mathrm{Rh}(=\mathrm{C}=\mathrm{C}=\mathrm{CPh_2})(\mathrm{acetone})(\mathrm{P}i\text{–}\mathrm{Pr_3})_2][\mathrm{PF_6}]$	1.822(2)	1.267(3)	1.343(3)	178.1(2)	172.6(2)	[210]
$[\mathrm{RhCp}(=\mathrm{C}=\mathrm{C}=\mathrm{CPh_2})(\mathrm{P}i\text{–}\mathrm{Pr_3})]$	1.880(6)	1.255(7)	1.350(7)	177.1(5)	176.5(6)	[206]
$[\mathrm{IrCl}(=\mathrm{C}=\mathrm{C}=\mathrm{CPh_2})(\mathrm{P}i\text{–}\mathrm{Pr_3})_2]$	1.862(7)	1.247(11)	1.360(11)	178.5(14)	176.7(14)	[81]
$[\mathrm{IrF}(=\mathrm{C}=\mathrm{C}=\mathrm{CPh_2})(\mathrm{P}i\text{–}\mathrm{Pr_3})_2]$	1.85(2)	1.22(2)	1.37(2)	177.1(17)	173(2)	[81]
$[\mathrm{IrCl_2H}(=\mathrm{C}=\mathrm{C}=\mathrm{CPh_2})(\mathrm{P}i\text{–}\mathrm{Pr_3})_2]$	1.877(15)	1.249(19)	1.349(19)	178.7(13)	176.0(15)	[220]

[a] $\mathrm{C}(\mathrm{C_{12}H_{12}})$ = 6,8-dimethyl-7*H*-benzocycloheptene-7,7-diyl

[b] $\mathrm{C}(\mathrm{C_{14}H_{10}})$ = 5*H*-dibenzo[*a*,*d*]cycloheptene-5,5-diyl

[c] $\mathrm{C}(\mathrm{C_{13}H_{20}})$ = spiro(bicyclo[3.3.1]non-2-en-9-ylidene-4-cyclohexane)

[d] $\mathrm{C}(\mathrm{C_{10}H_6N_2})$ = 4,5-diazafluoren-9-yl

[e] $\mathrm{C}(\mathrm{C_{14}H_{10}})$ = 3-phenylindenylidene

bond lengths, the most remarkable feature is that, within the unsaturated three-carbon chain, the C_α–C_β distances are in all cases shorter than the C_β–C_γ distances (ca. 0.1 Å). These data are consistent with a description of bonding as a resonance of metal–carbene and metal–alkynyl mesomers (Fig. 12), the latter being the dominant contribution to the observed structures (zwitterionic species $[M]^-$–C≡C–$C^+R^1R^2$ for neutral allenylidenes). A slightly bent linear arrangement of the allenylidene chain is also observed in all the X-ray crystal structures reported.

The conformational orientation adopted by the allenylidene group =C=C=CR^1R^2 also merits comment. Thus, in half-sandwich complexes, mainly derived from $[M(\eta^5\text{-}C_xH_y)L_2]^+$ (M = Fe, Ru, Os) metal fragments, a marked preference of the allenylidene group to adopt a "vertical" orientation in which the *ipso* carbon atoms of the R^1/R^2 substituents are contained in the molecular plane (pseudo mirror plane bisecting the half-sandwich metal fragment) is observed. Preference for this conformation arises from the dominant metal d_{xy}–$C_{p\pi}$ back donation of the metal–HOMO into the allenylidene–LUMO π* orbital (see Fig. 13). In contrast to this general trend, an unusual "horizontal" orientation of the allenylidene group was

Fig. 12 The allenylidene/alkynyl resonance

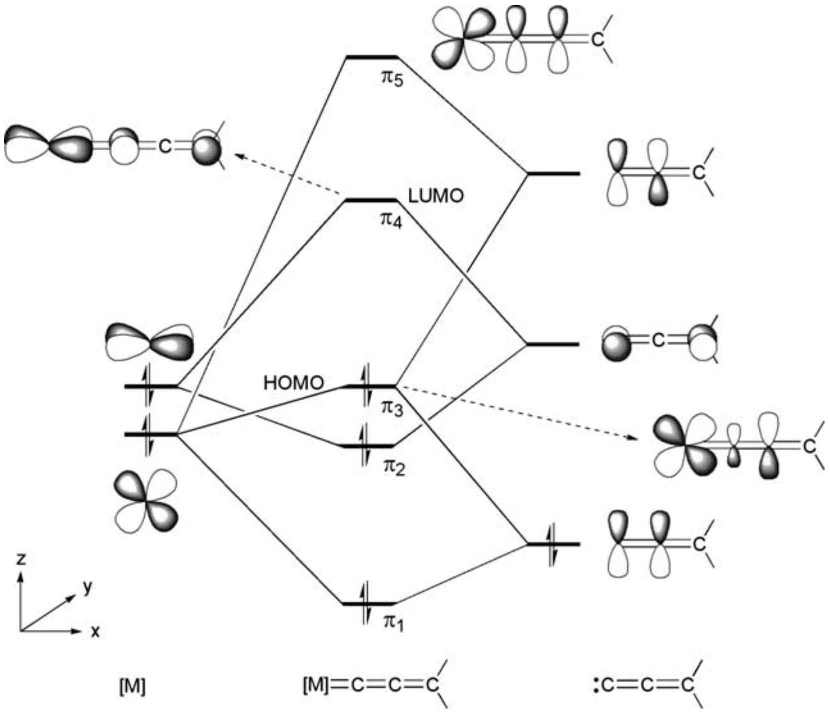


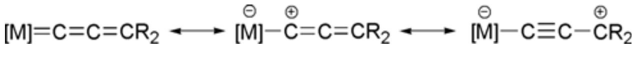
Fig. 13 Simplified π-orbital diagram for metal–allenylidene complexes

found in complex [Mo(η^7-C_7H_7)(=C=C=CPh_2)(dppe)][PF_6] [92]. DFT calculations on the fragments [Mo(η^7-C_7H_7)(dppe)]$^+$ and [Ru(η^5-C_5H_5)(dppe)]$^+$ revealed significant differences in the energy ordering of the respective MO manifolds. Thus, while the HOMO of the molybdenum system has substantial $d_z{}^2$ character, the HOMO of the [Ru(η^5-C_5H_5)(dppe)]$^+$ fragment is based on a metal d_{xy} orbital, orthogonal to the HOMO of the [Mo(η^7-C_7H_7)(dppe)]$^+$ unit. Interaction between this $d_z{}^2$-based HOMO and the vacant LUMO of the cumulenylidene ligand seems to be linked to the unusual horizontal arrangement observed [92].

2.3 Reactivity of Allenylidene Complexes

Based on a large number of stoichiometric studies, the main trends of allenylidene reactivity are presently well established [26–40]. They are governed by the electron deficient character of the C_α and C_γ carbon atoms in the cumulenic chain, the C_β being a nucleophilic center. This can also be rationalized by considering the mesomeric forms depicted in Fig. 14. However, it should be noted that, as commented on previously, only contribution from the alkynyl resonance form is supported by X-ray diffraction.

In order to rationalize the observed reactivity, theoretical calculations on the electronic structure of allenylidene complexes have been extensively developed [92, 157, 161, 166, 179, 193, 213, 221–228]. They clearly establish that the allenylidene fragment is a σ-donor π-acceptor ligand with a dominant contribution to the bonding of the latter component. Concerning the regioselectivity of both electrophilic and nucleophilic additions, it is frontier orbital controlled with the LUMO, mainly localized at the C_α and C_γ carbon atoms, while the HOMO is centred on the metal and C_β atoms (breakdowns of the contributions from the cumulenic carbon atoms to the HOMO and LUMO orbitals of several allenylidene model complexes are shown in Table 2). This alternating array of electrophilic/nucleophilic carbon sites makes allenylidene complexes unique organometallic reagents for C–C and C–heteroatom couplings via simple addition reactions. Thus, while electrophiles add selectively to C_β yielding alkenyl-carbyne derivatives **J**, the nucleophilic attacks can take place both at the C_α or C_γ atoms affording metal-allenyl **K** or metal-alkynyl **L** complexes, respectively (Scheme 14). Moreover, the unsaturated character of the allenylidene chain makes also possible cyclization processes, allowing the construction of original carbo- and heterocyclic compounds.



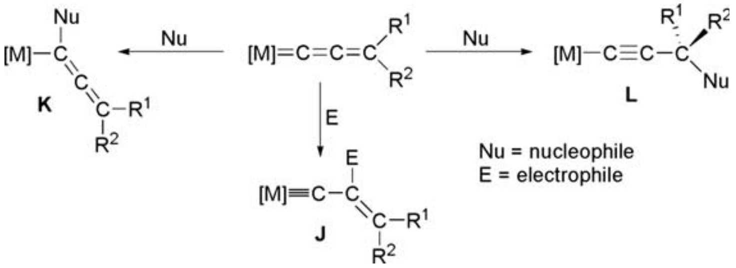
$$[M]{=}C{=}C{=}CR_2 \longleftrightarrow \overset{\ominus}{[M]}{-}\overset{\oplus}{C}{=}C{=}CR_2 \longleftrightarrow \overset{\ominus}{[M]}{-}C{\equiv}C{-}\overset{\oplus}{C}R_2$$

Fig. 14 Canonical forms of allenylidene complexes

Table 2 HOMO and LUMO distribution along the cumulenic chain on several allenylidene model complexes

Model		C_α(%)	C_β(%)	C_γ(%)	[Ref]
$[Cr(=C=C=CH_2)(CO)_5]$	HOMO	5.8	20.1	0.8	[224]
	LUMO	15	4	35.7	
$[Cr\{=C=C=C(CH=CH_2)_2\}(CO)_5]$	HOMO	3.3	17.1	0	[225]
	LUMO	15.4	5.5	20.5	
$[Cr(=C=C=CPh_2)(CO)_5]$	HOMO	[a]	[a]	[a]	[227]
	LUMO	20	5	25	
$[RuCl(=C=C=CH_2)(PH_3)_4]^+$	HOMO	6	20	0	[226]
	LUMO	32	6	37	
$[RuCp(=C=C=CH_2)(CO)(PH_3)]^+$	HOMO	[b]	20	[b]	[223]
	LUMO	23	6	31	
$[Ru(\eta^5\text{-}C_9H_7)(=C=C=CH_2)(CO)(PH_3)]^+$	HOMO	4	21	0	[28]
	LUMO	24	4	37	
$[Ru(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)(=C=C=CH_2)(CO)(PH_3)]^+$	HOMO[c]	4	21	0	[28]
	LUMO	23	4	36	
$[Ru(\eta^5\text{-}C_9H_7)(=C=C=CH_2)(PH_3)_2]^+$	HOMO	3	21	0	[28]
	LUMO	20	6	34	
$[OsCp(=C=C=CH_2)(CO)(PH_3)]^+$	HOMO	5	23	0	[193]
	LUMO	28	3	33	
$[OsCp(=C=C=CH_2)(PH_3)_2]^+$	HOMO	4	25	0	[193]
	LUMO	24	5	31	
$[OsClCp(=C=C=CH_2)(PH_3)]$	HOMO	4	22	0	[193]
	LUMO	24	5	30	

[a] No data available
[b] $C_\alpha + C_\gamma = 6\%$
[c] Next HOMO



Scheme 14 Typical nucleophilic and electrophilic additions on metal-allenylidenes

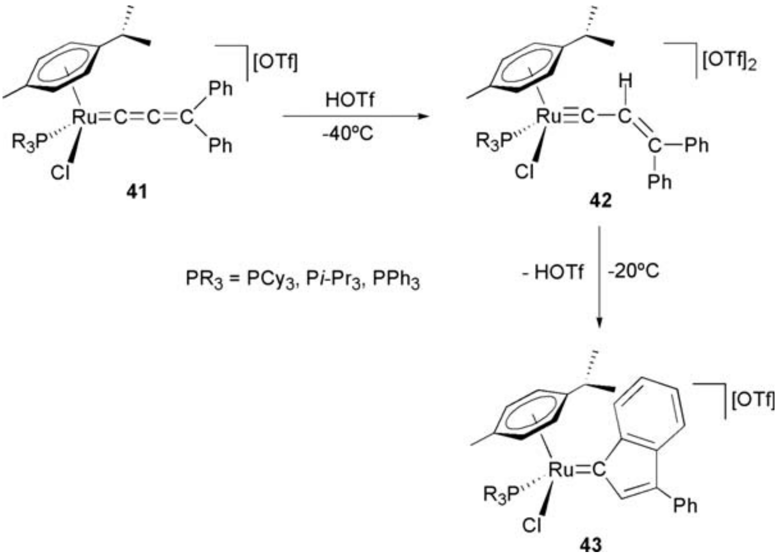
2.3.1 Electrophilic Additions

The nucleophilic character of the allenylidene C_β was experimentally demonstrated for the first time by N. E. Kolobova and co-workers in 1984, who obtained alkenyl-carbyne complexes $[MnCp\{\equiv CC(H)=CR_2\}(CO)_2][X]$ (R = *t*-Bu, Ph; $X^- = Cl^-$, BF_4^-, $CF_3CO_2^-$) by treatment of the corresponding neutral manganese(I) allenylidenes $[MnCp(=C=C=CR_2)(CO)_2]$ with Brønsted acids HX [229]. Since then, a large variety of neutral and cationic transition-metal allenylidenes have been selectively protonated (Brønsted acids) or methylated (methyl triflate) at the C_β atom to afford stable alkenyl-carbyne species $[M]{\equiv}CC(E){=}CR^1R^2$ (E = H, Me). Representative examples are: $[OsCpCl(=C=C=CPh_2)(P\textit{i}{-}Pr_3)]$ [197], $[OsCp(=C=C=CPh_2)(P\textit{i}{-}Pr_3)(L)][PF_6]$ (L = $P\textit{i}{-}Pr_3$ [193], $PHPh_2$ [195]), $[Os\{\eta^5{:}\kappa^1(P){-}C_5H_4CH_2CH_2PPh_2\}(=C=C=CPh_2)(P\textit{i}{-}Pr_3)][PF_6]$ [196], $[OsX(=C=C=CPh_2)(NCMe)_2(P\textit{i}{-}Pr_3)_2][BF_4]$ (X = H [230], (*E*)–CH=CHPh [231]), $[RuTpCl(=C=C=CR_2)(PR_3)]$ (PR_3 = PPh_3, $PPh_2(\textit{i}{-}Pr)$; R = Ph, Fc) [167], $[\{RuX(\mu{-}X)(=C=C=CR_2)(dppf)\}_2]$ (R = Ph, *i*-Pr; X = Cl, Br) [184], $[RuCl(=C=C=CPh_2)\{\kappa^2(P,O){-}Cy_2PCH_2CH_2OMe\}_2][PF_6]$ [217], *trans*-$[RuCl\{=C=C=C(Me)R\}(dppe)_2][BF_4]$ (R = Me, Ph) [232], $[RuCp^*\{=C=C=C(R)Ph\}(dippe)][B(Ar_F)_4]$ (R = H, Ph) [233], $[RuCp^*(=C=C=CR^1R^2)(PEt_3)_2][BF_4]$ (R^1 = R^2 = Ph; R^1 = H, R^2 = Ph, *p*-FC_6H_4, *p*-$OMeC_6H_4$) [122], and $[Re(=C=C=CPh_2)(CO)_2(triphos)][OTf]$ [234].

In contrast, treatment of the neutral allenylidene complexes $[RuCl_2(=C=C=CPh_2)\{\kappa^2(P,O){-}\textit{i}{-}Pr_2PCH_2CO_2Me\}\{\kappa^1(P){-}\textit{i}{-}Pr_2PCH_2CO_2Me\}]$ and *trans*-$[IrCl\{=C=C=C(R)Ph\}(P\textit{i}{-}Pr_3)_2]$ (R = Ph, *t*-Bu) with HX has been reported to yield the α,β-unsaturated carbenes $[RuCl_2\{=C(X)C(H)=CPh_2\}\{\kappa^2(P,O){-}\textit{i}{-}Pr_2PCH_2CO_2Me\}\{\kappa^1(P){-}\textit{i}{-}Pr_2PCH_2CO_2Me\}]$ (X = Cl) [235] and *trans*-$[IrCl\{=C(X)C(H)=C(R)Ph\}(P\textit{i}{-}Pr_3)_2]$ (R = Ph, *t*-Bu; X = OTf, CF_3CO_2) [220], respectively, via HX-addition across the $C_\alpha{=}C_\beta$ double bond, the Brønsted acids acting like classical NuH nucleophiles (see below). Nevertheless, it should be noted that the iridium derivatives (X = CF_3CO_2) readily evolved into the expected carbynes *trans*-$[IrCl\{{\equiv}CC(H)=C(R)Ph\}(P\textit{i}Pr_3)_2][OTf]$ when dissolved in polar solvents [220]. Interestingly, the Rh(I) allenylidenes *trans*-$[RhCl\{=C=C=C(R)Ph\}(P\textit{i}{-}Pr_3)_2]$ (R = Ph, *o*-MeC_6H_4) have been found to react with HCl to afford the allenyl-Rh(III) species $[RhCl_2\{C(H)=C=C(R)Ph\}(P\textit{i}Pr_3)_2]$, via formal HCl-addition across the $Rh{=}C_\alpha$ bond [206]. The course of this unexpected reaction involves an initial oxidative addition of HCl at the rhodium center followed by insertion of the allenylidene unit into the Rh–H bond.

Probably the most striking discovery related to this chemistry is the evidence that allenylidene–ruthenium complexes **41** rearrange, upon treatment with HOTf, into indenylidene complexes **43** which display an extremely high catalytic activity in alkene metathesis (Scheme 15) [145, 147, 150]. The process involves the initial formation of alkenyl-carbynes **42** which evolve into **43** through a formal electrophilic substitution of an *ortho*-proton of one of the phenyl groups by the C_α-atom of the carbyne moiety, with concomitant elimination of HOTf. A related acid-promoted allenylidene to indenylidene rearrangement has been observed for the osmium derivative $[OsCp(=C=C=CPh_2)(CO)(P\textit{i}{-}Pr_3)][PF_6]$ [195]. Remarkably, the direct activation of $HC{\equiv}CCPh_2(OH)$ by $[RuCl_2(PPh_3)_4]$ also led to the formation of an indenylidene complex, in this case an acidic medium not being required to promote the intramolecular allenylidene rearrangement [164]. The chemistry and catalytic applications in olefin metathesis of ruthenium indenylidenes has been reviewed [40, 236, 237].

Quite recently it has also been reported that the neutral Mn(I) allenylidene $[MnCp(=C=C=CPh_2)(CO)(PPh_3)]$ catalyzes the reduction of protons from HBF_4 into dihydrogen via initial formation of the corresponding alkenyl-carbyne [MnCp



Scheme 15 Acid-promoted allenylidene to indenylidene rearrangement

$\{\equiv CC(H)=CPh_2\}(CO)(PPh_3)]^+$, followed by reduction to the 19-electron radical $[MnCp\{\equiv CC(H)=CPh_2\}(CO)(PPh_3)]^\bullet$. This radical undergoes a rapid homolytic cleavage of the C_β–H bond generating a free H-radical, which produces the molecular hydrogen, with concomitant recovery of the neutral metallacumulene catalyst [238].

2.3.2 Nucleophilic Additions

The regioselectivity of the nucleophilic additions on allenylidene complexes (C_α vs C_γ) is subtly controlled by the electronic and steric properties both of the substituents on the unsaturated hydrocarbon chain and the ancillary ligands on the metal atom, as well as by the nucleophile employed. In this section we will summarize the nucleophilic reactivity of mononuclear Group 6–9 allenylidenes.

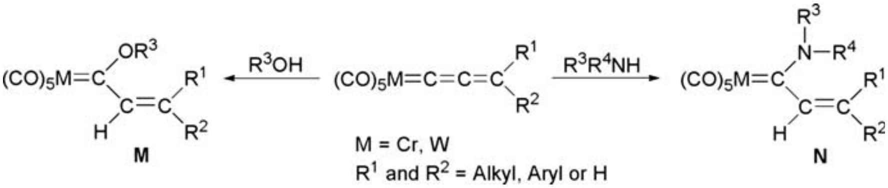
Group 6 Allenylidenes

The reactivity of Group 6 allenylidenes $[M(=C=C=CR^1R^2)(CO)_5]$ (M = Cr, W; R^1 and R^2 = alkyl, aryl or H) towards nucleophiles is clearly dominated by the additions at the electrophilic α-carbon. In this sense, the most common reaction of these complexes (usually generated in situ) is the addition of alcohols R^3OH across the $C_\alpha=C_\beta$ bond to afford Fischer-type α,β-unsaturated alkoxycarbene derivatives $[M\{=C(OR^3)CH=CR^1R^2\}(CO)_5]$ (**M**) via nucleophilic attack of the alcohol at the electrophilic C_α and subsequent migration of the hydrogen atom to C_β (Scheme 16) [239–242]. Related N–H additions of amines (as well as imines and hydrazines) to afford α,β-unsaturated aminocarbenes **N** have also been reported [89, 243, 244].

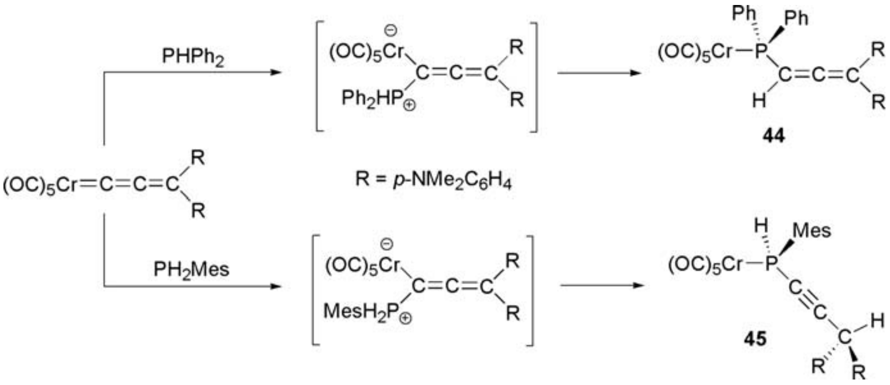
Similarly, complexes $[M\{=C=C=C(i\text{-}Pr)_2\}(CO)_5]$ (M = Cr, W) selectively add PPh_3 at C_α to afford the stable zwitterionic phosphonio-allenyl derivatives $[M\{C(PPh_3)=C=C(i\text{-}Pr)_2\}(CO)_5]$ [93]. The related species $[Cr\{C(PR_3)=C=C(p\text{-}NMe_2C_6H_4)_2\}(CO)_5]$ (PR_3 = PMe_3, $PHPh_2$, PH_2Mes; Mes = 2,4,6-$Me_3C_6H_2$) are also formed starting from $[Cr\{=C=C=C(p\text{-}NMe_2C_6H_4)_2\}(CO)_5]$. However, while the $PHPh_2$ adduct evolves slowly into the allenylphosphine complex **44** by migration of the $Cr(CO)_5$ group from the allenyl C_α atom to P and synchronous H migration along the carbon chain, the PH_2Mes adduct immediately isomerizes into **45** (Scheme 17) [245].

Group 7 Allenylidenes

Only the reactivity of complexes $[Mn(\eta^5\text{-}C_5R_5)(=C=C=CPh_2)(CO)_2]$ (C_5R_5 = Cp or C_5H_4Me) and $[Re(=C=C=CR^1R^2)(CO)_2(triphos)][OTf]$ towards nucleophiles has been described in detail. Thus, the former react with MeO^- and Me_2N^- to generate



Scheme 16 Nucleophilic addition of alcohols and amines to Group 6 allenylidene complexes



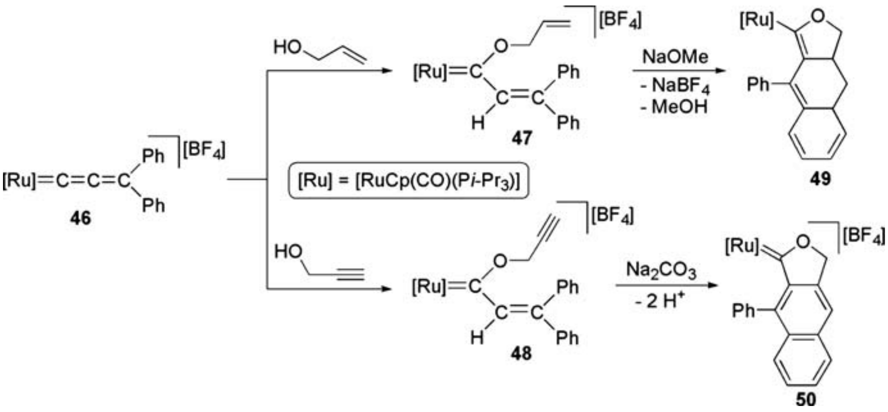
Scheme 17 Some reactions of chromium allenylidenes with phosphines

unstable anionic allenyl complexes $[Mn(\eta^5\text{-}C_5R_5)\{C(X)=C=CPh_2\}(CO)_2]^-$ which on protonation can be transformed into the isolable alkenyl-carbenes $[Mn(\eta^5\text{-}C_5R_5)\{=C(X)CH=CPh_2\}(CO)_2]$ (X = OMe, NMe_2) [213]. Related C_α-additions take place with PPh_3 affording stable phosphonio-allenyl derivatives $[Mn(\eta^5\text{-}C_5R_5)\{C(PPh_3)=C=CPh_2\}(CO)_2]$ [213, 246]. In contrast, addition of the carbanion $t\text{-Bu}^-$ to $[Mn(\eta^5\text{-}C_5H_4Me)(=C=C=CPh_2)(CO)_2]$ occurs selectively at C_γ leading after protonation to the isolation of the vinylidene complex $[Mn(\eta^5\text{-}C_5H_4Me)\{=C=C(H)CPh_2t\text{-Bu}\}(CO)_2]$ [96]. Mixtures of C_γ and C_α adducts are formed when $t\text{-BuS}^-$ is used as nucleophile [213]. On the basis of these results a rationalization of the C_γ vs C_α preference is not possible in this case.

Concerning the reactivity of the cationic Re(I) complexes, it was found that while the diphenylallenylidene $[Re(=C=C=CPh_2)(CO)_2(triphos)][OTf]$ is unreactive towards alcohols, its monosubstituted counterparts $[Re(=C=C=CHR)(CO)_2(triphos)][OTf]$ (R = Me, Ph) undergo O–H additions of methanol or water across the $C_\alpha=C_\beta$ bond to afford the corresponding carbenes $[Re\{=C(OR')CH=CHR\}(CO)_2(triphos)][OTf]$ (R′ = Me, H) [98, 99]. These results are in accord with the well-known stabilizing effect associated with the presence of aryl groups on the terminal position of cumulenic chains. In contrast to its behavior towards alcohols, complex $[Re(=C=C=CPh_2)(CO)_2(triphos)][OTf]$ readily adds thiols RSH and primary amines RNH_2 to give thiocarbenes $[Re\{=C(SR)CH=CPh_2\}(CO)_2(triphos)][OTf]$ (R = Ph, 1-naphthyl, allyl) and azoniabutadienyl compounds $[Re\{C(=NHR)CH=CPh_2\}(CO)_2(triphos)][OTf]$ (R = H, Ph, $CH_2C\equiv CH$), respectively [247]. The reactivity of this diphenylallenylidene towards anionic nucleophiles (MeO^-, HO^-, Me^-, H^-, enolates, etc.) has also been described, leading to the formation of neutral σ-alkynyl compounds via regioselective addition at the electrophilic C_γ [234]. Phosphines also attack the allenylidene-C_γ atom to give kinetic phosphonio-alkynyl products which are transformed thermally into thermodynamically more stable phosphonio-allenyl derivatives [214]. On the basis of these results we can conclude that the fragment $[Re(CO)_2(triphos)]^+$ orients the addition of hard nucleophiles to the C_γ atom, soft nucleophiles giving thermodynamically stable C_α-adducts.

Group 8 Allenylidenes

The reactivity of cationic half-sandwich ruthenium(II) allenylidenes towards nucleophiles has been extensively investigated, the results pointing out that the C_γ vs C_α preference is strongly dependent on the steric and electronic properties of the ancillary ligands in the metal fragment. This is clearly exemplified by the behavior towards alcohols. Thus, while allenylidene ligands attached to the fragments $[RuCl(\eta^6\text{-arene})(L)]^+$ (L = PR_3 or CNR) [138, 242, 248–253], $[RuCp(CO)(PR_3)]^+$ (PR_3 = PPh_3, $Pi\text{–}Pr_3$) [242, 254], $[Ru(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)(CO)(PPh_3)]^+$ [124] and $[Ru(\eta^5\text{-}C_9H_7)L_2]^+$ (L_2 = dppe, dppm) [123] are able to add alcohols across the $C_\alpha=C_\beta$ bond to yield Fischer-type α,β-unsaturated alkoxycarbenes, the more sterically demanding and/or electron-rich units $[RuCl(L_2)_2]^+$ (L_2 = dppm, dppe) [148, 169–180, 190], $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ [123], $[RuCp(PPh_3)_2]^+$ [115],

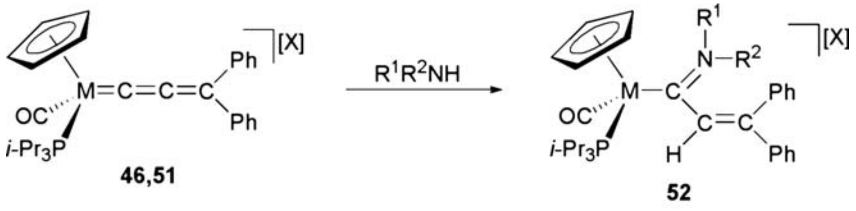


Scheme 18 Coupling of an allenylidene ligand with allyl and propargyl alcohol

$[RuCp^*(dippe)]^+$ [119], and $[RuCp^*(PR_3)_2]^+$ (PR_3 = PEt_3, $PMePh_2$) [122, 255] make the allenylidene ligand resistant to alcohols or, in some cases, orient the addition across the C_β=C_γ to generate vinylidene complexes [Ru]=C=C(H) $CR_2(OR')$ [123, 255]. In this context, of particular interest are the reactions of complex **46** with allyl and propargyl alcohol (Scheme 18), the resulting alkoxycarbenes **47** and **48** serving as intermediates for the construction, among others, of the polycyclic derivatives **49** and **50** via intramolecular cycloaddition processes [256, 257]. Addition of water across the C_α=C_β of complex **46**, to afford the stable hydroxycarbene $[RuCp\{=C(OH)CH=CPh_2\}(CO)(Pi\text{–}Pr_3)][BF_4]$, has also been described [254]. In contrast, the hydroxycarbenes formed by addition of water to $[RuCl(=C=C=CHPh)(\eta^6\text{-}p\text{-cymene})(PR_3)][OTf]$ (PR_3 = PPh_3, PCy_3) are not stable evolving into the carbonyl derivatives $[RuCl(\eta^6\text{-}p\text{-cymene})(CO)(PR_3)][OTf]$ by releasing styrene [258].

Likewise to alcohols and water, the ruthenium allenylidene complex **46** and its osmium counterpart $[OsCp(=C=C=CPh_2)(CO)(Pi\text{–}Pr_3)][PF_6]$ (**51**) also add the N–H bond of primary and secondary amines across the C_α=C_β generating azoniabutadienyl ruthenium and osmium complexes **52** (Scheme 19) [195, 259–261]. Azoniabutadienyl species were also formed in the reactions of $[RuCp^*(=C=C=CPh_2\}(CO)(PMei\text{–}Pr_2)][B(Ar_F)_4]$ (**53**) with amines [262]. The closely related α,β-unsaturated-2-azaallenyl complexes $[RuCp\{C(=N=CPh_2)C(H)=CPh_2\}(CO)(Pi\text{–}Pr_3)][BF_4]$ and $[RuCp^*\{C(=N=CPh_2)C(H)=CPh_2\}(CO)(PMei\text{–}Pr_2)][B(Ar_F)_4]$ were similarly obtained by reacting the allenylidene precursors **46** and **53**, respectively, with benzophenoneimine [254, 262]. In contrast, the product resulting from the addition of $MeNH_2$ to the neutral heteroscorpionato allenylidene complex $[RuCl\{=C=C=C(p\text{-}MeC_6H_4)_2\}\{\kappa^3(N,N,O)\text{-bdmpza}\}(PPh_3)]$ has been better described as a Fischer-type aminocarbene $[RuCl\{=C(NHMe)C(H)=C(p\text{-}MeC_6H_4)_2\}\{\kappa^3(N,N,O)\text{-bdmpza}\}(PPh_3)]$ rather than an azoniabutadienyl complex [263].

The utility of these N–H addition reactions for the construction of complex molecular architectures was nicely illustrated in the behavior of **46** towards



M = Os; X^- = PF_6^-; R^1 = H; R^2 = Ph
M = Ru; X^- = BF_4^-; R^1 = H; R^2 = Ph, *n*-Pr, $CH_2CH{=}CH_2$, $CH_2C{\equiv}CH$, *o*-C_5H_4N
M = Ru; X^- = BF_4^-; R^1 = Me; R^2 = $CH_2C{\equiv}CH$
M = Ru; X^- = BF_4^-; R^1 = R^2 = Et
M = Ru; X^- = BF_4^-; R^1R^2 = -$(CH_2)_5$-

Scheme 19 Formation of azoniabutadienyl complexes from Ru- and Os-allenylidenes

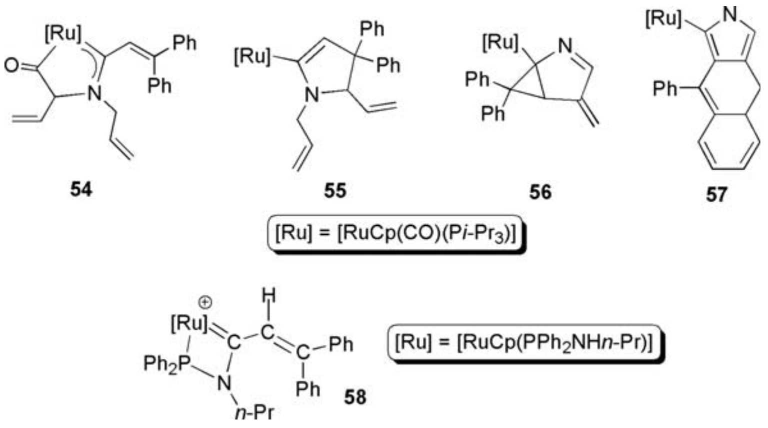


Fig. 15 Structure of the ruthenium(II) complexes **54–58**

N,N-diallylamine and *N*-propargylamine, the reactions leading to the formation of the heterocyclic derivatives **54, 55** and **56, 57** (Fig. 15), respectively, via base-promoted intramolecular cyclization of the corresponding azoniabutadienyl intermediates [260, 261]. It is also worth noting that an intramolecular version of these N–H additions occurred in the reaction of the propargylic alcohol $HC{\equiv}CCPh_2(OH)$ with complex $[RuClCp(PPh_2NH\textit{n}{-}Pr)_2]$, which afforded the azaphosphacarbene **58** (Fig. 15). This complex is formed through an intramolecular N–H addition of one of the phosphinoamine ligands to the $C_\alpha{=}C_\beta$ on the allenylidene chain of the intermediate species $[RuCp({=}C{=}C{=}CPh_2)(PPh_2NH\textit{n}{-}Pr)_2][OTf]$ [117].

Thiols also react with allenylidenes **46** and **53** to afford α,β-unsaturated thiocarbenes, i.e., $[RuCp\{{=}C(S\textit{n}{-}Pr)CH{=}CPh_2\}(CO)(P\textit{i}{-}Pr_3)][BF_4]$ [254] and $[RuCp^*\{{=}C(S\textit{n}{-}Pr)CH{=}CPh_2\}(CO)(PMe\textit{i}{-}Pr_2)][B(Ar_F)_4]$ [262], via S–H addition across the $C_\alpha{=}C_\beta$ double bond of the cumulenic chain. Single-crystal X-ray diffraction studies on the latter point out the existence of an important contribution of the tautomeric thiabutadienyl resonance form $[\mathrm{RuCp^*\{C(=S}n\text{–}\mathrm{Pr)CH{=}CPh_2\}(CO)(PMe}i\text{–}\mathrm{Pr_2)][B(Ar_F)_4]}$.

The crucial role of the ancillary ligands on the C_γ vs C_α preference is also reflected in the behavior of half-sandwich Ru(II) allenylidenes towards phosphines. Thus, while complexes **46** and **53** add phosphines at the C_α atom to yield cationic phosphonio-allenyl derivatives $[\mathrm{RuCp\{C(PR_3){=}C{=}CPh_2\}(CO)(P}i\text{–}\mathrm{Pr_3)][BF_4]}$ ($\mathrm{PR_3} = \mathrm{PPh_3}$, $\mathrm{PMePh_2}$, $\mathrm{PHPh_2}$) [264] and $[\mathrm{RuCp^*\{C(PR_3){=}C{=}CPh_2\}(CO)(PMe}i\text{–}\mathrm{Pr_2)][B(Ar_F)_4]}$ ($\mathrm{PR_3} = \mathrm{PMe_3}$, $\mathrm{PMe}i\text{–}\mathrm{Pr_2}$) [262], respectively, allenylidenes $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{{=}C{=}C{=}CR^1R^2})(\mathrm{PPh_3})_2][\mathrm{PF_6}]$ containing the bulkier bis(triphenylphosphine)indenyl fragment react selectively at the C_γ affording phosphonio-alkynyl species $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_9H_7})\{\mathrm{C{\equiv}CCR^1R^2(PR_3)}\}(\mathrm{PPh_3})_2][\mathrm{PF_6}]$ ($\mathrm{R^1}$, $\mathrm{R^2}$ = alkyl, aryl or H; $\mathrm{PR_3} = \mathrm{PPh_3}$, $\mathrm{PMePh_2}$, $\mathrm{PMe_2Ph}$, $\mathrm{PMe_3}$) [72, 74, 265, 266]. A related C_γ-attack occurs in the reaction of $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{{=}C{=}C{=}CPh_2})(\mathrm{dppm})][\mathrm{PF_6}]$ with $\mathrm{PMe_3}$. Nevertheless, the resulting phosphonio-alkynyl derivative $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_9H_7})\{\mathrm{C{\equiv}CCPh_2(PMe_3)}\}(\mathrm{dppm})][\mathrm{PF_6}]$ is unstable, evolving spontaneously into the allenyl isomer $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_9H_7})\{\mathrm{C(PMe_3){=}C{=}CPh_2}\}(\mathrm{dppm})][\mathrm{PF_6}]$ via $\mathrm{PMe_3}$-migration from C_γ to C_α. This is favored by the presence of the less sterically demanding bis(diphenylphosphino)methane ligand and the steric congestion on the C_γ atom due to the presence of phenyl groups [265]. In this context, it should be noted that the phosphonio-alkynyl derivatives $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_9H_7})\{\mathrm{C{\equiv}CCH(R^1)(PR_3)}\}(\mathrm{PPh_3})_2][\mathrm{PF_6}]$ ($\mathrm{R^1} = \mathrm{H}$, $\mathrm{PR_3} = \mathrm{PPh_3}$; $\mathrm{R^1} = \mathrm{Ph}$, $\mathrm{PR_3} = \mathrm{PMe_3}$), all containing an acidic hydrogen atom at C_γ, have proven to be excellent substrates for Wittig-type reactions. Thus, by deprotonation they generate the highly unstable ylide-alkynyl derivatives $[\mathrm{Ru\{C{\equiv}CC(R^1){=}PR_3\}}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{PPh_3})_2]$ which readily react with carbonyl compounds, leading to wide series of neutral σ-enynyl and polyenynyl complexes (representative examples are shown in Fig. 16) [266–270].

The addition of anionic heteroatom-centered nucleophiles ($\mathrm{HO^-}$, $\mathrm{MeO^-}$, pyrazolate, etc.) and carbanions ($\mathrm{CN^-}$, enolates, alkyl or alkynyl reagents) to the cationic allenylidenes $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{{=}C{=}C{=}CR^1R^2})(\mathrm{PPh_3})_2][\mathrm{PF_6}]$ [125–128, 192, 265, 269, 271–273], $[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{{=}C{=}C{=}CHPh})\{(R)\text{-BINAP}\}][\mathrm{PF_6}]$ [130], $[\mathrm{Ru}(\eta^5\text{-}1,2,3\text{-}\mathrm{Me_3C_9H_4})(\mathrm{{=}C{=}C{=}CPh_2})(\mathrm{CO})(\mathrm{PPh_3})][\mathrm{BF_4}]$ [124], $[\mathrm{RuCp^*(=C{=}C{=}CR^1R^2)(dippe)][BPh_4]}$ [233], $[\mathrm{RuCp(=C{=}C{=}CPh_2)(PPh_3)_2][PF_6]}$ [115], [RuCp

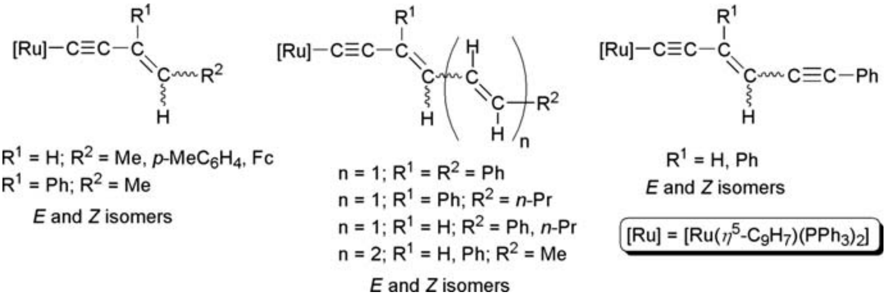


Fig. 16 Structure of σ-enynyl and polyenynyl complexes generated via Wittig-type reactions

$(=C=C=CPh_2)(CO)(P\textit{i}{-}Pr_3)][BF_4]$ (**46**) [223, 264] and $[Ru(\eta^5\text{-}C_{60}Me_5)(=C=C=CR^1R^2)\{(R)\text{-prophos}\}][PF_6]$ [132] has also been extensively studied, the regioselectivity of the attack differing slightly from the trends observed with neutral (soft) nucleophiles. Thus, the steric protection of the C_α atom, together with the extensive contribution of the metal-alkynyl resonance form $[Ru]{-}C{\equiv}C{-}C^+R^1R^2$ in these species, make the C_γ-additions highly favored and neutral σ-alkynyl species are in all cases selectively formed. Only in the case of complex **46** have simultaneous C_α and C_γ attacks been observed [223]. This behavior was exploited in the chemistry of the indenyl–ruthenium complexes for the preparation of wide series of functionalized alkynyl derivatives, including several optically active representatives (Fig. 17) [125–128, 192, 265, 269, 271–273].

Moreover, taking advantage of the regioselectivity shown by the indenyl–ruthenium(II) complexes $[Ru(\eta^5\text{-}C_9H_7)(=C=C=CR^1R^2)(PPh_3)_2][PF_6]$, an efficient

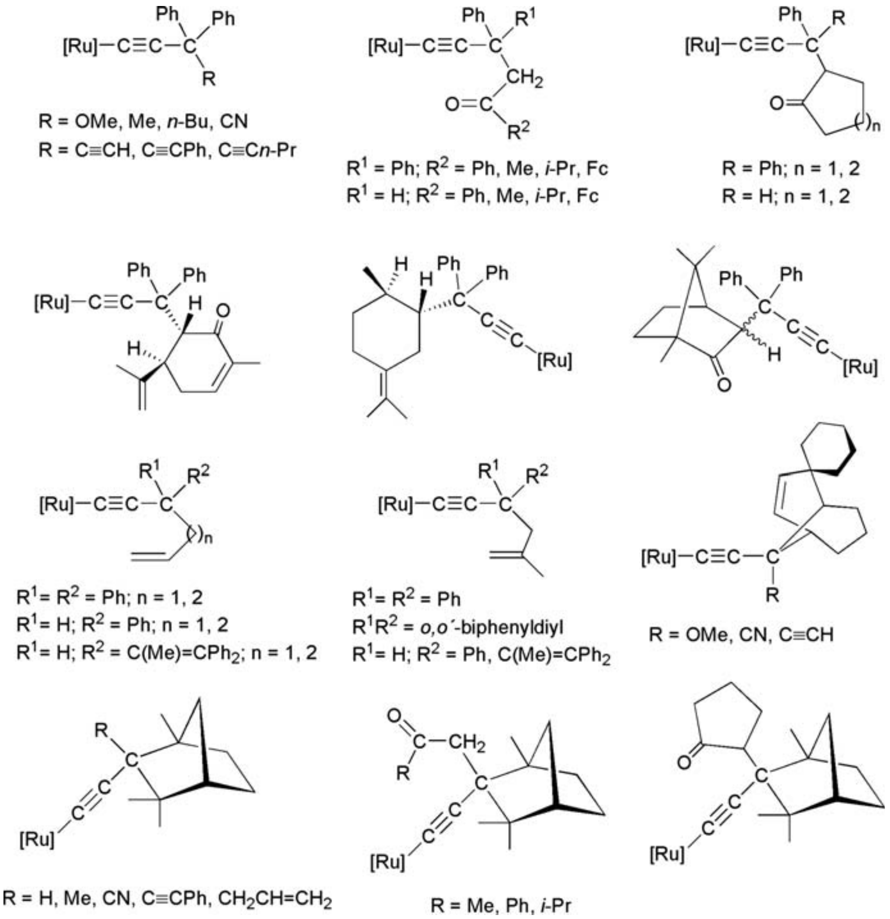
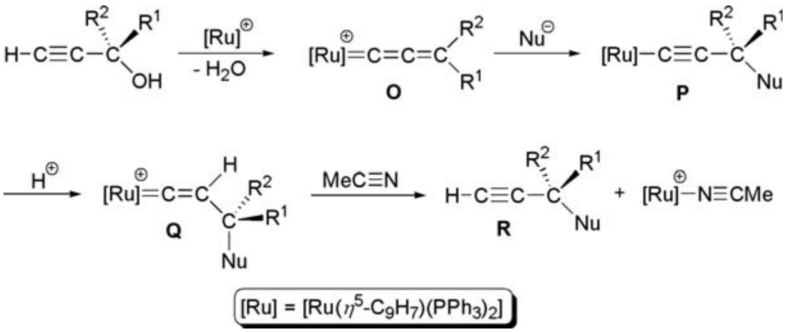


Fig. 17 Indenyl-ruthenium(II) σ-alkynyl complexes generated from allenylidenes

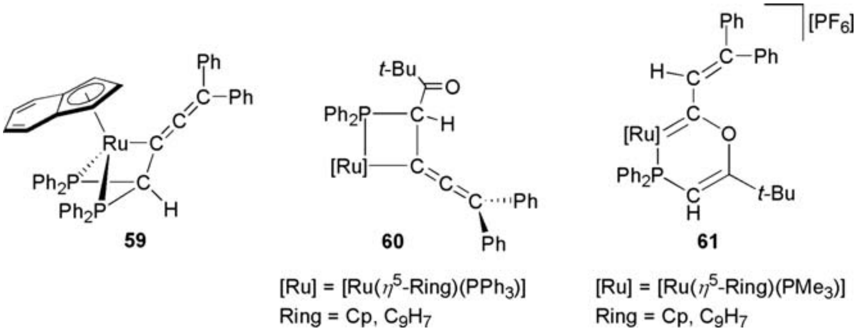


Scheme 20 $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$-mediated propargylic substitution of alkynols

synthetic procedure for the propargylic substitution of 2-propyn-1-ols mediated by the metallic fragment $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ was developed (Scheme 20). Thus, in a first step allenylidene complexes **O** were formed and subsequently transformed into the corresponding σ-alkynyl derivatives **P** which undergo a selective C_β protonation to afford the vinylidene complexes **Q**. Finally, demetallation of **Q** with acetonitrile led to the functionalized terminal alkynes **R** in excellent yields. Following this route, a large variety of γ-ketoalkynes [126, 127, 271], 1,4-diynes [128, 269, 274], and 1,5- and 1,6-enynes [272, 273] could be synthesized. Related processes have also been described starting from the chiral allenylidene $[Ru(\eta^5\text{-}C_9H_7)(=C=C=CHPh)\{(R)\text{-BINAP}\}][PF_6]$, allowing the preparation of propargylic-substituted compounds with complete enantioselectivity [130]. In all cases the metal is recovered as the corresponding acetonitrile solvate.

Although rare, regioselective nucleophilic additions of anions at the α-carbon of cationic ruthenium allenylidenes are also known, involving in all cases intramolecular processes. Thus, treatment of $[Ru(\eta^5\text{-}C_9H_7)(=C=C=CPh_2)(dppm)][PF_6]$ and $[Ru(\eta^5\text{-Ring})(=C=C=CPh_2)\{\kappa^1(P)\text{-}Ph_2PCH_2C(=O)t\text{-Bu}\}(PPh_3)][PF_6]$ (Ring = Cp or C_9H_7) with K_2CO_3 or Li*t*-Bu generates the allenylmetallacyclic species **59** and **60** formed by monodeprotonation of the methylenic unit of the phosphine ligand and subsequent attack of the resulting carbanion to the electrophilic C_α (Fig. 18) [113, 265]. Related base-promoted intramolecular coupling processes starting from the more basic derivatives $[Ru(\eta^5\text{-Ring})(=C=C=CPh_2)\{\kappa^1(P)\text{–}Ph_2PCH_2C(=O)t\text{-Bu}\}(PMe_3)][PF_6]$ have also been described [275]. However, no C–C coupling between the phosphine backbone and the allenylidene ligand takes place in this case, the metallacycles **61** being selectively formed instead. Addition of the enolic form of the keto-phosphine ligand $Ph_2PCH_2C(=O)t$-Bu at the C_α atom of the cumulenic chain through the oxygen atom explains the formation of **61**.

The behavior of osmium-allenylidenes towards nucleophiles follows similar trends to those observed for their analogous ruthenium counterparts. Thus, while the electron-rich bis-phosphine complexes $[Os(\eta^5\text{-Ring})(=C=C=CPh_2)(PR_3)_2][PF_6]$ (Ring = Cp, PR_3 = P*i*–Pr_3; Ring = C_9H_7, PR_3 = PPh_3) are inert towards alcohols and amines [123, 193], as commented previously the more electrophilic carbonyl derivative $[OsCp(=C=C=CPh_2)(CO)(Pi\text{–}Pr_3)][PF_6]$ (**51**) readily reacts



[Ru] = [Ru(η^5-Ring)(PPh$_3$)]
Ring = Cp, C$_9$H$_7$

[Ru] = [Ru(η^5-Ring)(PMe$_3$)]
Ring = Cp, C$_9$H$_7$

Fig. 18 Structure of the metallacyclic compounds **59–61**

with methanol and aniline to afford [OsCp{=C(OMe)CH=CPh$_2$}(CO)(P*i*–Pr$_3$)][PF$_6$] and [OsCp{C(=NHPh)CH=CPh$_2$}(CO)(P*i*–Pr$_3$)][PF$_6$] (**52** in Scheme 19), respectively [195]. C$_\alpha$-additions of alcohols and phosphines to the (η^6-arene)-Os(II) allenylidene [OsCl(=C=C=CPh$_2$)(η^6-1,3,5-C$_6$H$_3$Me$_3$)(PMe$_3$)][PF$_6$] have also been described, allowing the preparation of [OsCl{=C(OR)CH=CPh$_2$}(η^6-1,3,5-C$_6$H$_3$Me$_3$)(PMe$_3$)][PF$_6$] (R = Me, Et) and [OsCl{C(PR$_3$)=C=CPh$_2$}(η^6-1,3,5-C$_6$H$_3$Me$_3$)(PMe$_3$)][PF$_6$] (PR$_3$ = PMe$_3$, PPh$_3$), respectively [198]. As expected, due to the presence of two coordinated bulky P*i*–Pr$_3$ ligands, the addition of anionic nucleophiles (Me$^-$, MeO$^-$, MeC(=O)CH$_2$$^-$) to [OsCp(=C=C=CPh$_2$)(P*i*–Pr$_3$)$_2$][PF$_6$] takes place selectively on the sterically less congested C$_\gamma$ generating neutral alkynyl species [OsCp{C≡CCPh$_2$(Nu)}(P*i*–Pr$_3$)$_2$] [193]. Related C$_\gamma$-additions of anions have also been observed starting from the octahedral derivative [Os{κ^2(*C*,*O*)-C(CO$_2$Me)=CH$_2$}(=C=C=CPh$_2$)(CO)(P*i*–Pr$_3$)$_2$][BF$_4$] [200].

In contrast to ruthenium and osmium, the reactivity of iron allenylidenes remains almost unexplored. Only the behavior of the cationic diphenylallenylidene–Fe(II) derivative *trans*-[FeBr(=C=C=CPh$_2$)(depe)$_2$]$^+$ has been studied in detail. Thus, it has been found that this complex reacts exclusively at C$_\gamma$ with both neutral (amines, phosphines) and anionic (H$^-$, MeO$^-$, CN$^-$) nucleophiles [105–107]. This behavior contrasts with that of the neutral Fe(0) derivative [Fe{=C=C=C(*t*-Bu)$_2$}(CO)$_5$] which undergoes PPh$_3$-attack at C$_\alpha$ to afford the zwitterionic phosphonio-allenyl species [Fe{C(PPh$_3$)=C=C(*t*-Bu)$_2$}(CO)$_5$] [104].

Group 9 Allenylidenes

As mentioned previously, the reactivity of the square-planar Rh(I) and Ir(I) allenylidenes *trans*-[MCl(=C=C=CR^{1}R^2)(P*i*–Pr$_3$)$_2$] towards nucleophiles is governed by the strong *trans* influence of the π-acceptor allenylidene group, allowing the easy exchange of the chloride ligand by a large variety of anions (I$^-$, HO$^-$, RO$^-$, RCO$_2$$^-$, N$_3$$^-$, SCN$^-$, etc.) [76, 78, 81, 204–210, 220, 276, 277]. Among the different products formed, compounds *trans*-[M(OPh)(=C=C=CR^{1}R^2)(P*i*–Pr$_3$)$_2$]

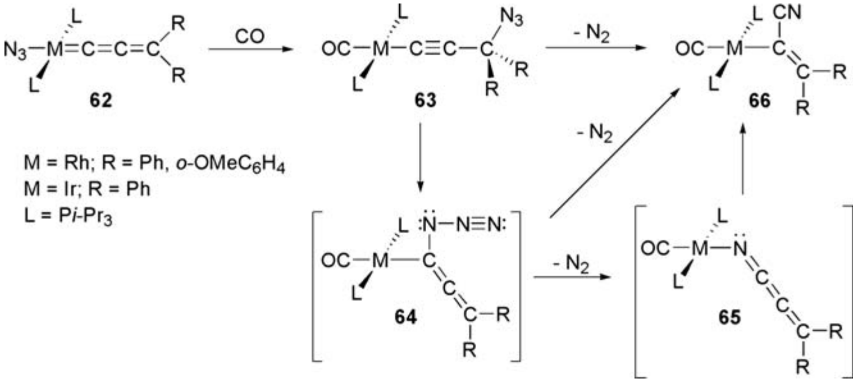
(M = Rh, R^1 = Ph, R^2 = Ph, *o*-MeC_6H_4; M = Ir, R^1 = Ph, R^2 = *t*-Bu) and *trans*-[Rh{κ^1-(*O*)-O_2CMe}(=C=C=CR^1R^2)(P*i*–Pr_3)$_2$] (R^1 = Ph, R^2 = Ph, *o*-MeC_6H_4) are of particular interest since, upon treatment with carbon monoxide, they undergo migratory insertion of the allenylidene unit into the M–O bond to generate the σ-alkynyl complexes *trans*-[M{C≡CR^1R^2(OPh)}(CO)(P*i*–Pr_3)$_2$] and *trans*-[Rh{C≡CR^1R^2(O_2CMe)}(CO)(P*i*–Pr_3)$_2$], respectively [81, 277]. Similarly, the reactions of the hydroxo compounds *trans*-[Rh(OH)(=C=C=CR^1R^2)(P*i*–Pr_3)$_2$] (R^1 = R^2 = Ph, *o*-$OMeC_6H_4$; R^1 = Ph, R^2 = *t*-Bu) with $CH_2(CN)_2$ and either CO or CNMe yielded *trans*-[Rh{C≡$CR^1R^2CH(CN)_2$}(L)(P*i*–Pr_3)$_2$] (L = CO, CNMe), via highly unstable allenylidene intermediates *trans*-[Rh{$CH(CN)_2$}(=C=C=CR^1R^2)(P*i*–Pr_3)$_2$] [277].

Treatment of the azido complexes **62** with CO also leads to the migration of the N_3^- ligand to the allenylidene unit (Scheme 21). Nevertheless, the initially formed azido-alkynyl compounds **63** are in this case thermally unstable, evolving slowly into the metallated acrylonitrile derivatives **66** via extrusion of N_2. The mechanism of formation of **66** involves the migration of the azido moiety from C_γ to the C_α atom of the alkynyl ligand to generate the allenyl intermediates **64**, which by elimination of N_2 and shifting of the metal fragment (directly or via intermediate **65**) affords **66** [81, 205].

In this context, it should also be noted that an oxidatively induced C_α–P coupling has been described in the oxidation reactions of complexes *trans*-[RhCl(=C=C=CR_2)(P*i*–Pr_3)$_2$] (R = Ph, *o*-$OMeC_6H_4$) with Cl_2 or $PhICl_2$, affording phosphonio-allenyl products [$RhCl_3${C(P*i*–Pr_3)=C=CR_2}(P*i*–Pr_3)]. They are formed by migration of one P*i*–Pr_3 group from the metal to the allenylidene α-carbon in the six-coordinate Rh(III) intermediates [$RhCl_3$(=C=C=CR_2)(P*i*–Pr_3)$_2$] [205].

2.3.3 C–C Coupling Reactions

Besides the classical additions of carbon-centered nucleophiles to the electrophilic sites of the cumulenic chain, transition-metal allenylidenes are able to promote



Scheme 21 Allenylidene–azide couplings promoted by CO

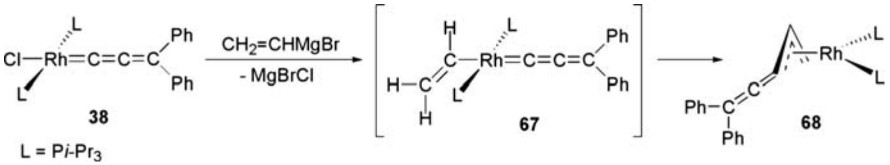
a number of original carbon–carbon coupling processes. Reported processes include:

(1) Insertion of the methylene unit $:CH_2$ into the Rh=C bond of *trans*-[RhCl(=C=C=CR^{1}R^2)(P*i*–Pr$_3$)$_2$] (R^1 = R^2 = Ph, *p*-OMeC$_6$H$_4$; R^1 = Ph, R^2 = CF$_3$, *t*-Bu) upon treatment with diazomethane, which allowed the isolation of stable butatriene–Rh(I) compounds *trans*-[RhCl(η^2–H$_2$C=C=C=CR^{1}R^2)(P*i*–Pr$_3$)$_2$] [205]. Noteworthy, their iodide counterparts *trans*-[RhI(η^2-H$_2$C=C=C=CR$_2$)(P*i*–Pr$_3$)$_2$] (R = Ph, *p*-OMeC$_6$H$_4$) were generated by reacting the corresponding allenylidene complexes *trans*-[RhI(=C=C=CR$_2$)(P*i*–Pr$_3$)$_2$] with MeI [205]. This unusual C–C coupling reaction, in which MeI behaves as a $:CH_2$ source, involves oxidative addition of MeI at the rhodium center followed by insertion of the allenylidene unit into the Rh–Me bond. The resulting allenyl–Rh(III) intermediates [RhI$_2${η^1-C(Me)C=C=CR$_2$}(P*i*–Pr$_3$)$_2$] evolve through a β–H shift to give [RhHI$_2$(η^2–H$_2$C=C=C=CR$_2$)(P*i*–Pr$_3$)$_2$] which upon reductive elimination of HI generate the final butatriene–Rh(I) complexes. The same reactivity pattern was observed in the reaction of *trans*-[IrI(=C=C=CPh$_2$)(P*i*–Pr$_3$)$_2$] with MeI [220]. A related insertion of *tert*-butyl isocyanide into the Mn=C bond of [MnCp(=C=C=CPh$_2$)(CO)$_2$], giving rise to the unstable species [MnCp(η^2-*t*-BuN=C=C=C=CPh$_2$)(CO)$_2$], has also been described [278].

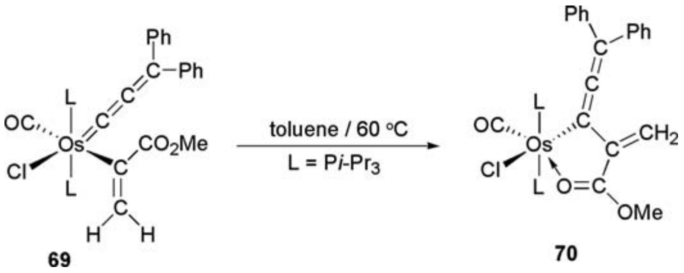
(2) A C$_3$ + C$_2$ coupling process observed in the reactions of the square-planar Rh(I)-allenylidenes **38** with the Grignard reagent CH$_2$=CHMgBr to yield η^3-pentatrienyl derivatives [205]. An example is shown in Scheme 22. This C–C coupling takes place through an initial substitution of the chloride ligand, leading to the vinyl-metal intermediate **67** which rearranges, by migratory insertion of the allenylidene unit into the Rh–CH=CH$_2$ bond, to give the final product **68**.

Related η^3-pentatrienyl compounds are also formed in the reactions of [OsClCp(=C=C=CPh$_2$)(P*i*–Pr$_3$)] and [RuClCp*(=C=C=CPh$_2$){κ^1(*P*)-*i*-Pr$_2$PCH$_2$CO$_2$Me}] with CH$_2$=CHMgBr [197, 279]. In contrast, the insertion of the allenylidene ligand into the Os–C(alkenyl) bond of **69** has been reported to yield the five-membered metallacyclic compound **70** instead of the expected η^3-pentatrienyl isomer (Scheme 23) [200].

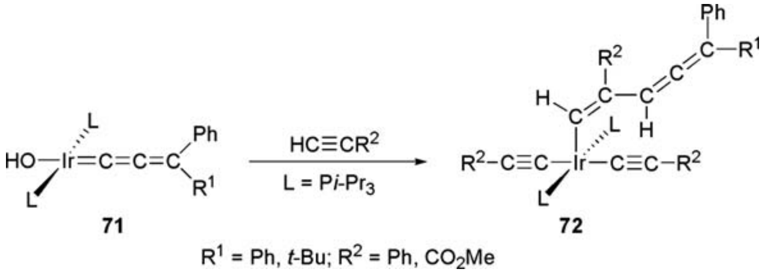
(3) C–C couplings with alkynes. An unprecedented coupling of this type was found in the reaction of the Ir(I) hydroxo-allenylidenes **71** with excess of HC≡CR (R = Ph, CO$_2$Me) to afford, under remarkably mild conditions (r.t.), the novel five-coordinate compounds **72** (Scheme 24). The proposed mechanism involves an initial HO$^-$/R^{2}C≡C$^-$ ligand exchange followed by the oxidative addition of a



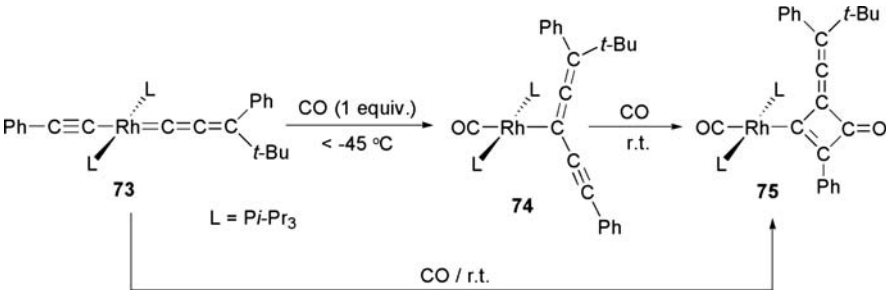
Scheme 22 Coupling of an allenylidene ligand with a vinyl group at rhodium



Scheme 23 Coupling of an allenylidene ligand with a vinyl group at osmium



Scheme 24 Coupling of allenylidene ligands with terminal alkynes at iridium



Scheme 25 CO-promoted intramolecular allenylidene-alkynyl coupling

second molecule of the alkyne to generate the hydride Ir(III) intermediate $[\mathrm{IrH(C{\equiv}CR^2)_2\{{=}C{=}C{=}C(R^1)Ph\}(P\mathit{i}{-}Pr_3)_2}]$. The rearrangement to an allenyl species followed by the C–C coupling with a third alkyne molecule gives the final product [81].

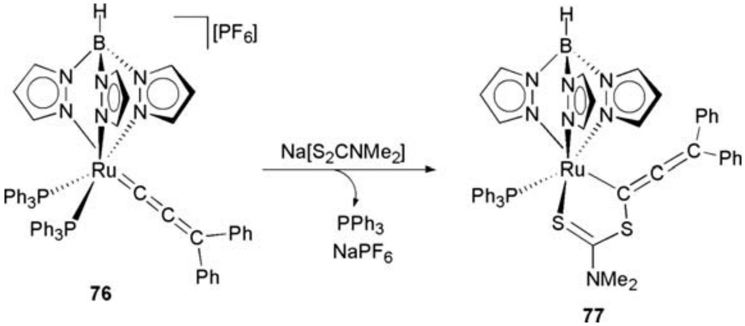
An intramolecular allenylidene–alkynyl coupling was also observed in the reaction of the mixed alkynyl-allenylidene rhodium(I) complex **73** with carbon monoxide (Scheme 25). In this case, the initially formed thermally unstable allenyl derivative **74** evolved into the metallated cyclobutenone **75** when an excess of CO was present [276].

(4) C–C couplings by linkage of two allenylidene moieties have also been described. For example, treatment of the bis(hydroxyalkynyl)-rhodium(III) complex [RhH{C≡CCPh$_2$(OH)}$_2$(P*i*–Pr$_3$)$_2$] with Al$_2$O$_3$, in the presence of chloride ions, yielded the hexapentaene–Rh(I) derivative *trans*-[RhCl(η^2-Ph$_2$C=C=C=C=C=CPh$_2$)(P*i*–Pr$_3$)$_2$], via the initial formation of a cationic bis(allenylidene) intermediate *trans*-[Rh(=C=C=CPh$_2$)$_2$(P*i*–Pr$_3$)$_2$]$^+$ which undergoes a chloride-promoted coupling of the two cumulenic groups [280]. Alternatively, this hexapentaene complex can be generated by thermolysis of *trans*-[RhCl(=C=C=CPh$_2$)(P*i*–Pr$_3$)$_2$] [205]. Remarkably, the organic fragment Ph$_2$C=C=C=C=C=CPh$_2$ can be easily decoordinated by ligand displacement with CO, demonstrating the synthetic utility of transition-metal allenylidenes for the construction of elaborated organic compounds [280]. Linkage of two allenylidene moieties has also been observed in the thermal decomposition of [MnCp(=C=C=C(*t*-Bu)$_2$)(CO)$_2$], which generates small quantities of the free tetrasubstituted hexapentaene *t*-Bu$_2$C=C=C=C=C=C*t*-Bu$_2$ [24], as well as in the photolysis of [Cr(=C=C=CPh$_2$)(CO)$_5$] which affords Ph$_2$C=C=C=C=C=CPh$_2$ in high yield [281].

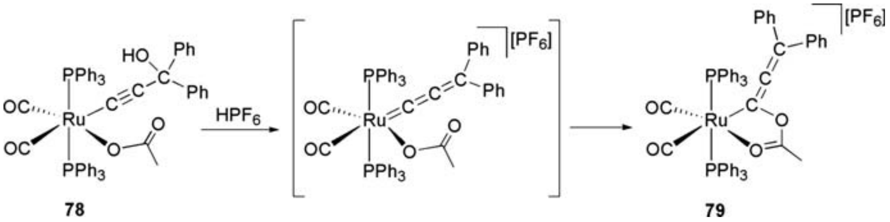
2.3.4 Cycloaddition and Cyclization Reactions

Transition-metal allenylidenes are prone to undergo cycloaddition and related cyclization reactions involving both M=C$_\alpha$, C$_\alpha$=C$_\beta$, and C$_\beta$=C$_\gamma$ bonds of the cumulenic chain. In some cases, cyclization/cycloreversion pathways have been observed leading to the final isolation of acyclic products.

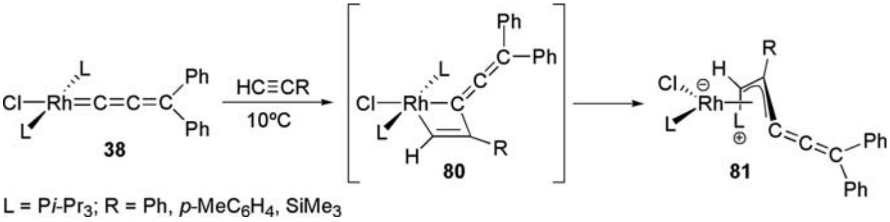
Concerning the M=C$_\alpha$ bond, most of the reported examples result from inter- or intramolecular additions of anionic nucleophiles containing at least two reactive heteroatoms. Thus, sodium dimethyldithiocarbamate was found to react with the cationic allenylidene [RuTp(=C=C=CPh$_2$)(PPh$_3$)$_2$][PF$_6$] (**76**) to generate the allenyl-metallacycle **77** (Scheme 26) as the result of the nucleophilic addition of one of the sulfur atoms at the C$_\alpha$ carbon and subsequent coordination of the second sulfur to the ruthenium center, with concomitant release of a triphenylphosphine ligand [282]. Complex **77** could also be synthesized by treatment of the neutral derivative



Scheme 26 Addition of dimethyldithiocarbamate to an allenylidene ligand



Scheme 27 Intramolecular cyclization between acetate and allenylidene ligands



Scheme 28 Reactivity of complex **38** towards terminal alkynes

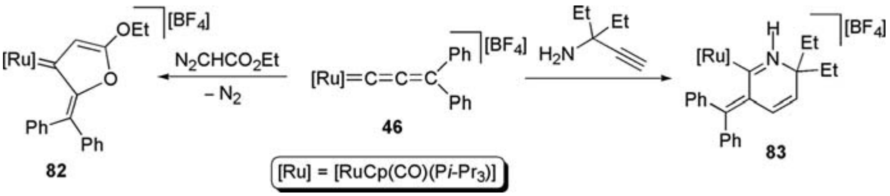
[RuTpCl(=C=C=CPh$_2$)(PPh$_3$)] with Na[S$_2$CNMe$_2$]. The cycloaddition of the dimethyldithiocarbamate anion to the Ru=C$_\alpha$ bond of [Ru{κ^2(S,S)-S$_2$CNMe$_2$}(=C=C=CPh$_2$)(CO)(PPh$_3$)$_2$][PF$_6$] has also been described [282].

A related intramolecular coupling between a monodentate acetate ligand and a transient diphenylallenylidene moiety was observed when the hydroxo-alkynyl derivative **78** was treated with HPF$_6$, affording the ruthenacycle **79** (Scheme 27) [283].

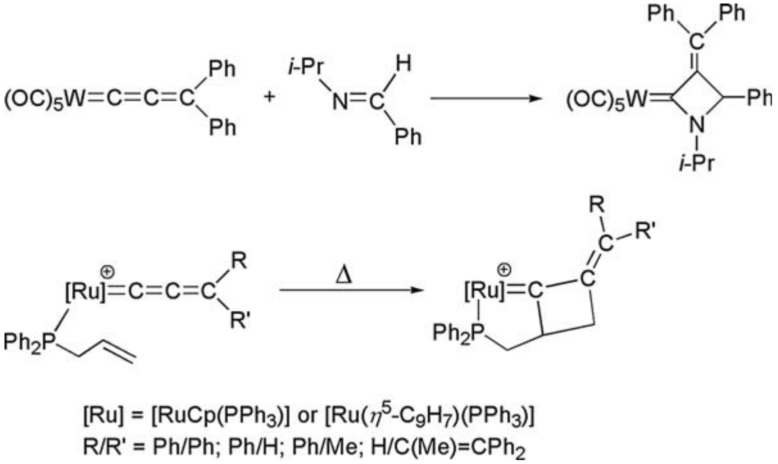
A cycloaddition process between the Rh=C$_\alpha$ bond of the allenylidene derivative **38** and the C≡C bond of the terminal alkyne has been evoked in the formation of the zwitterionic π-allyl-allenyl complexes **81** (Scheme 28), the initially formed metallacyclobutenes **80** evolving into **81** by formation of carbene intermediate [RhCl(P*i*–Pr$_3$)$_2$(=CHCR=C=C=CPh$_2$)] (R = Ph, *p*-MeC$_6$H$_4$, SiMe$_3$) and subsequent migration of one of the phosphine ligands from the metal to the carbene carbon atom [205].

The central C$_\alpha$=C$_\beta$ double bond of an allenylidene backbone can also react with a variety of dipolar organic substrates to yield cyclic adducts. Most of the cyclization processes reported occur in a stepwise manner via an initial nucleophilic attack at the C$_\alpha$ atom and further rearrangement of the molecule involving a coupling with the C$_\beta$ carbon. Representative examples are the reactions of the electron-poor ruthenium–allenylidene complex **46** with ethyl diazoacetate and 1,1-diethylpropargylamine to yield the five- and six-membered heterocyclic compounds **82** and **83**, respectively (Scheme 29) [260, 284].

As exemplified in Scheme 30, the formation of four-membered ring systems via inter- or intramolecular [2+2] cycloadditions between the C$_\alpha$=C$_\beta$ moiety and C=N or C=C double bonds have also been described [89, 129, 189].



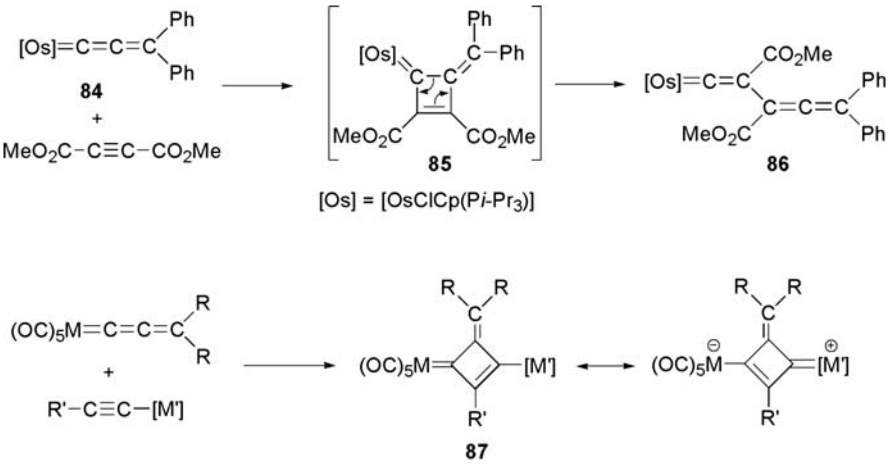
Scheme 29 Formation of the five- and six-membered heterocyclic compounds **82** and **83**



Scheme 30 [2+2]-Cycloadditions involving allenylidene $C_\alpha=C_\beta$ bonds

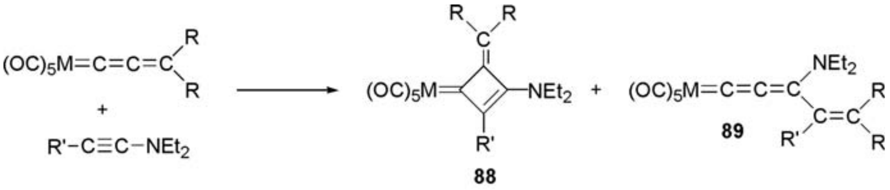
Related cycloadditions involving alkynes have been documented. Thus, it was found that heating a toluene solution of the neutral osmium complex **84** in the presence of dimethylacetylenedicarboxylate (DMAD) leads to the selective formation of the allenyl-vinylidene **86** (Scheme 31). The formal insertion of the alkyne into the $C_\alpha=C_\beta$ double bond has been rationalized in terms of an initial cycloaddition followed by the ring-opening of the cyclic intermediate **85** [197]. In contrast to **85**, the cyclobutylidene derivatives **87**, resulting from a [2+2] cycloaddition between Group 6 allenylidenes and organometallic alkynyl species, were found to be stable not evolving through cycloreversion [285].

Group 6 allenylidenes also react with the carbon–carbon triple bond of ynamines to yield similar cyclobutenylidene derivatives **88** along with the corresponding alkenyl-aminoallenylidenes **89** (Scheme 32) [286]. These aminoallenylidene complexes result from a formal [2+2] cycloaddition between the ynamine C≡C and allenylidene $C_\beta=C_\gamma$ bonds followed by cycloreversion. A stepwise cyclization initiated by the addition of the nucleophilic $R'C\equiv CNEt_2$ carbon at the C_α or C_γ position has been proposed in the formation of these isomeric products. As commented previously, unlike their Cr and W counterparts, the reactions of



M = Cr, W; R = *p*-MeC$_6$H$_4$, *p*-OMeC$_6$H$_4$; R' = Ph, *n*-Bu
[M'] = [FeCp(CO)$_2$], [FeCp*(CO)$_2$], [FeCp(CO){P(OMe)$_3$}], [NiCp(PPh$_3$)]
(not all combinations)

Scheme 31 [2+2]-Cycloadditions of allenylidenes with alkynes

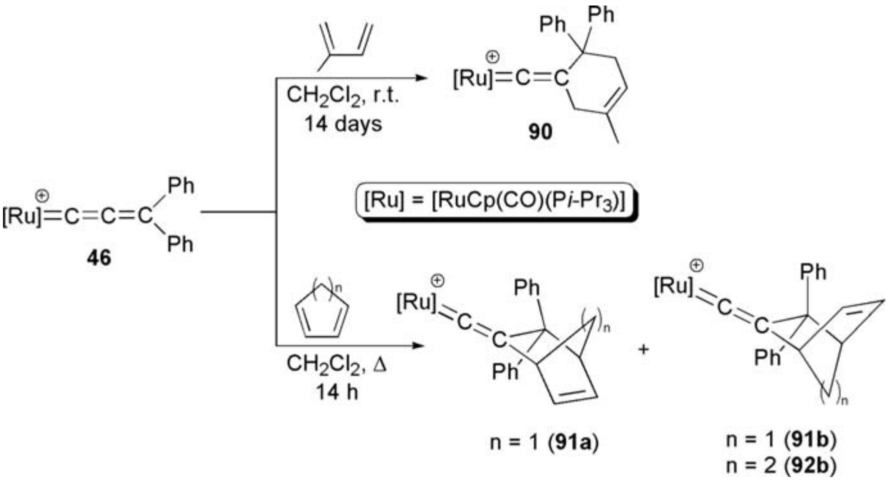


M = Cr, W; R = Ph, *p*-MeC$_6$H$_4$, *p*-OMeC$_6$H$_4$, *p*-NMe$_2$C$_6$H$_4$; R' = Me, Ph
(not all combinations)

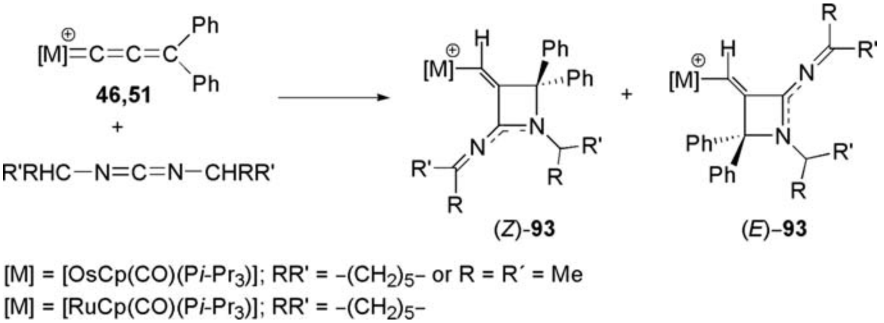
Scheme 32 Coupling between Group 6 allenylidene complexes and ynamines

indenyl-ruthenium(II) allenylidenes **30** with ynamines take place regioselectively at the C$_\beta$=C$_\gamma$ unit furnishing exclusively the alkenyl-aminoallenylidene complexes **31** (see Scheme 11) [187–189].

An unusual Diels–Alder cycloaddition involving the C$_\beta$=C$_\gamma$ bond has been described. The reaction took place by treatment of the electron-deficient allenylidene moiety in complex [RuCp(=C=C=CPh$_2$)(CO)(P*i*–Pr$_3$)][BF$_4$] (**46**) with a 20-fold excess of isoprene at room temperature affording the cycloadduct **90** (Scheme 33) [287]. This Diels–Alder cycloaddition in which the allenylidene moiety acts as a dienophile was completely regioselective, only the C$_\beta$=C$_\gamma$ bond of the allenylidene skeleton being implicated. Furthermore, it was also regioselective with regard to the orientation of the diene with the exclusive attack of C(1) and C(4) carbons at the C$_\beta$ and C$_\gamma$ positions, respectively. Allenylidene **46** also underwent Diels–Alder reactions with cyclopentadiene and cyclohexadiene to afford the



Scheme 33 Diels–Alder-type cycloadditions involving an allenylidene ligand



Scheme 34 Coupling of Ru(II) and Os(II) diphenylallenylidenes with carbodiimides

bicyclic products **91** and **92**, respectively, as a mixture of diastereomers for the former and as a sole diastereomer for the latter (Scheme 33) [287].

The activation of the allenylidene group by an electron-deficient organometallic fragment was also evidenced when allenylidene complex **46** and its osmium counterpart **51** were treated with carbodiimides in dichloromethane at room temperature. Under these mild conditions, the reactions yielded *Z*- and *E*-iminiumazetidinylidenemethyl species **93** (Scheme 34), while the related bis(phosphine) complex $[OsCp(=C=C=CPh_2)(PHPh_2)(P\textit{i}{-}Pr_3)][PF_6]$ remained inert [195, 288]. The formation of cycloadducts **93** was rationalized in terms of a stepwise [2+2] cycloaddition between the allenylidene $C_\beta=C_\gamma$ and one of the two C=N bonds of the carbodiimide, followed by an Alder-ene rearrangement.

A wide range of dinucleophiles are prone to undergo cyclization processes by addition on both $C_\alpha=C_\beta$ and $C_\beta=C_\gamma$ bonds of an allenylidene moiety (1,2,3-heterocyclizations). The structure of the products generated depends mainly on the number

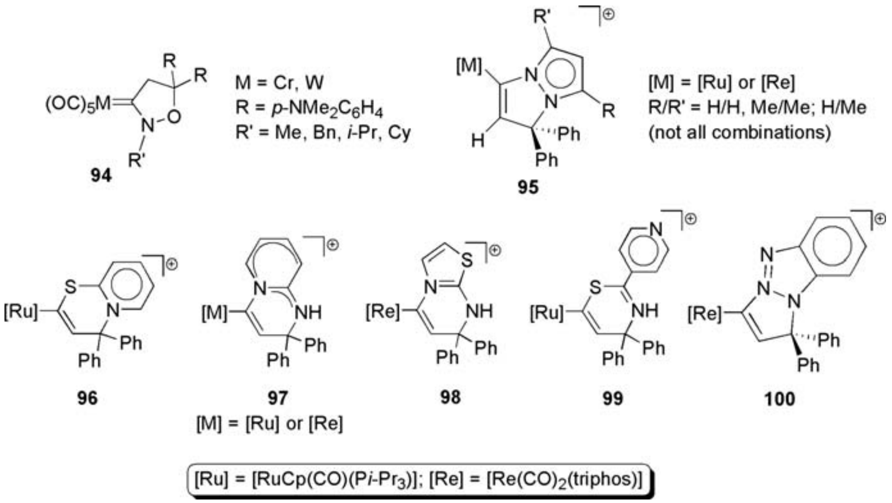


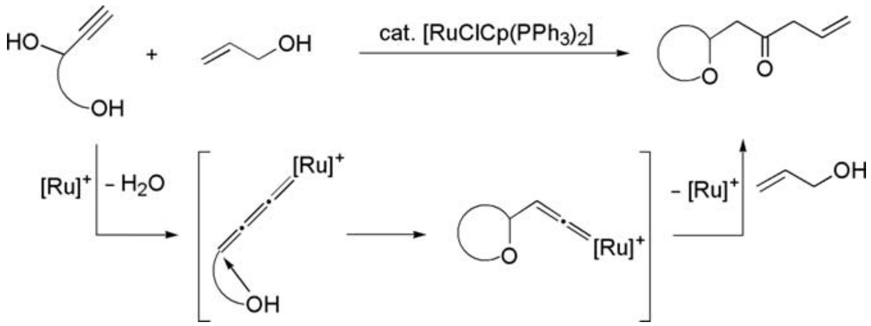
Fig. 19 Products derived from 1,2,3-diheterocyclization reactions of allenylidenes

of hydrogen atoms that the organic dinucleophile can deliver. For example, while the reactions of chromium and tungsten diarylallenylidene compounds $[M(=C=C=CR_2)(CO)_5]$ with hydroxylamines yield the cyclic amino-carbene derivatives **94** [244], treatment of complexes $[RuCp(=C=C=CPh_2)(CO)(Pi\text{–}Pr_3)][BF_4]$ (**46**) and $[Re(=C=C=CPh_2)(CO)_2(triphos)][OTf]$ (**6**) with dinucleophiles possessing only one heteroatom-hydrogen bond, such as pyrazoles, leads to the heterocyclic alkenyl derivatives **95** (Fig. 19) [289, 290]. Complexes **94** result formally from the addition of the nitrogen and oxygen atoms to C_α and C_γ, respectively, and the transfer of two hydrogen atoms to the C_β position. In the case of **95**, a related addition of the two nitrogen nuclei at the C_α and C_γ and a hydrogen atom at C_β takes place.

Similar 1,2,3-diheterocyclizations have been performed by addition of other *N,N*- or *N,S*-dinucleophiles, such as pyridine-2-thiol, 2-aminopyridine, 2-aminothiazole, thioisonicotinamide, and 1*H*-benzotriazole, to complexes **6** and **46** giving rise to the formation of the five- and six-membered cyclic alkenyl derivatives **96–100** (Fig. 19) [289, 291, 292].

2.4 Catalytic Reactions Involving Allenylidene Complexes

The involvement of transition-metal allenylidene complexes in homogeneous catalysis was reported for the first time by B. M. Trost and co-workers in 1992 (Scheme 35) [293–295]. The catalytic reactions allowed the preparation of a wide variety of tetrahydropyranyl and furanyl β,γ-unsaturated ketones starting from hydroxy-functionalized alkynols and allylic alcohols, the key step in the catalytic



Scheme 35 The first catalytic reaction via allenylidene complexes as key intermediates

cycle involving the intramolecular nucleophilic attack of the hydroxy group on the C_γ atom of allenylidene–ruthenium intermediates.

Despite this seminal work, it has only been recently that these metallacumulenes have really emerged as useful catalyst precursors or catalyst intermediates in organic synthesis. In particular, significant advances have been made in the field of alkene metathesis and propargylation reactions using mainly ruthenium complexes. A survey of this chemistry is presented in the following section.

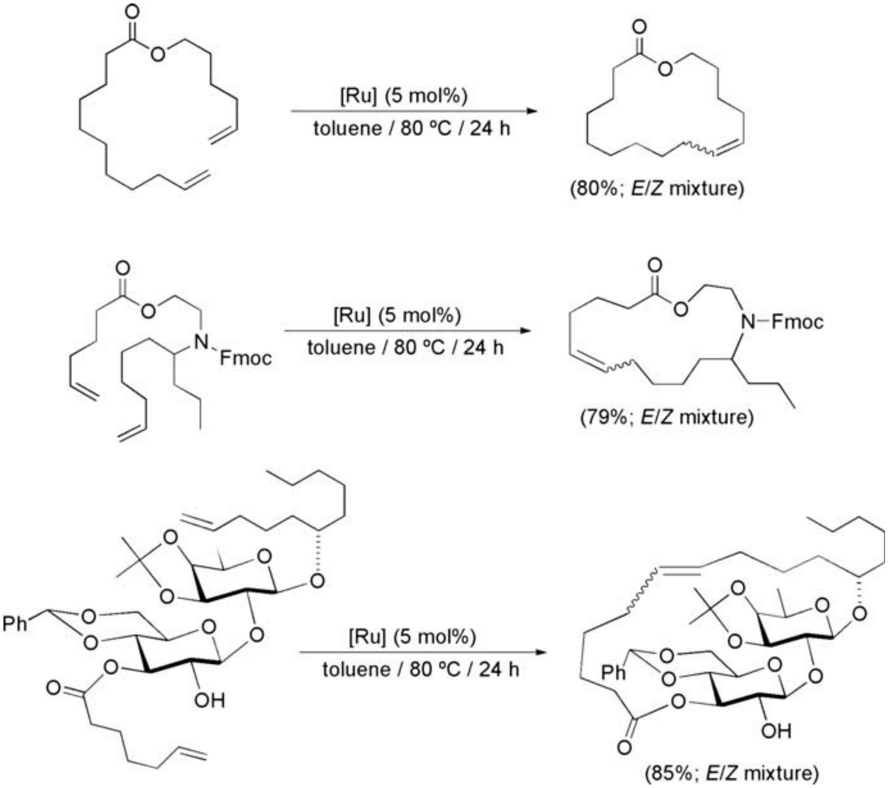
2.4.1 Olefin Metathesis

Alkene metathesis constitutes nowadays a powerful synthetic tool in organic, material, and polymer chemistry [296, 297]. In this context, ruthenium–allenylidene complexes, easy to prepare and handle, have recently emerged as a valid alternative to the widely used alkylidene derivatives $[L_nRu]=CHR$ (the Grubbs catalysts family) [33, 36, 37, 40]. The first studies were described in 1998 by Dixneuf's and Fürstner's groups, evaluating the catalytic potential of several well-defined 18-electron ruthenium–allenylidene complexes $[RuCl(=C=C=CR_2)(\eta^6\text{-}p\text{-cymene})(PR_3)][X]$ in RCM, using the transformation of *N*,*N*-diallyltosylamide **101** into *N*-tosyldihydropyrrole **102** as model reaction (Scheme 36) [140, 141, 143]. Among them, the best catalytic performances were observed with complex $[RuCl(=C=C=CPh_2)(\eta^6\text{-}p\text{-cymene})(PCy_3)][PF_6]$, which was able to convert quantitatively **101** into **102** after only 4 h at 80 °C.

Remarkably, this precatalyst could also be successfully applied in the RCM of several representative diene substrates, allowing the synthesis of essentially all ring sizes greater than four, including mono- and bicyclic compounds, in good to excellent yields, as well as a set of uncommon macrocyclic compounds (representative examples are shown in Scheme 37) [140, 141, 143, 298–300].

The catalytic activity of $[RuCl(=C=C=CPh_2)(\eta^6\text{-}p\text{-cymene})(PCy_3)][PF_6]$ under controlled microwave irradiation was also studied and similar conversions were obtained in lower reaction times than classical thermal protocols [301]. This

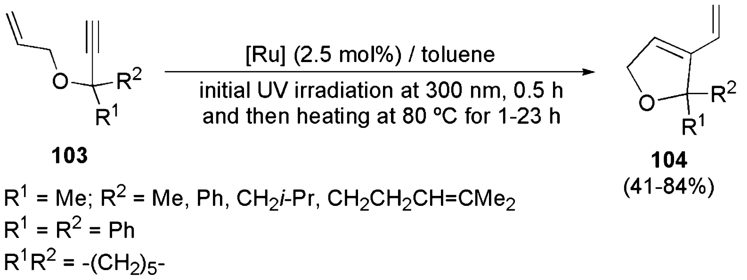
Scheme 36 The RCM of *N*,*N*-diallyltosylamide



Scheme 37 Some RCM reactions catalyzed by [RuCl(=C=C=CPh$_2$)(η^6-*p*-cymene)(PCy$_3$)][PF$_6$]

complex is also able to promote RCM of dienes using ionic liquids as solvents [302]. Although the activity in this medium was slower than in classical organic solvents, the catalyst could be recycled twice owing to its moderate stability. As commented previously, the attachment of this catalyst to the benzene rings of polystyrene was also described, allowing its recovery and reuse up to three times with a good catalytic activity (Scheme 8) [152].

Complex [RuCl(=C=C=CPh$_2$)(η^6-*p*-cymene)(PCy$_3$)][PF$_6$] (or its triflate salt) was also effective in the RCM of enynes. Thus, as shown in Scheme 38, the straightforward synthesis of 3-vinyl-2,5-dihydrofurans **104** from enynes **103**



Scheme 38 RCM of enynes **103** catalyzed by $[RuCl(=C=C=CPh_2)(\eta^6\text{-}p\text{-cymene})(PCy_3)][X]$

could be achieved in moderate to good yields after initial UV activation of the catalyst [303, 304]. Following the same procedure, a variety of vinyl cyclic amino acid derivatives have been also synthesized [305].

The ring opening metathesis polymerization (ROMP) of cyclic olefins constitutes an excellent method to synthesize linear polymers with regularly disposed CH=CH bonds [296, 297]. In this context, it was demonstrated that complex $[RuCl(=C=C=CPh_2)(\eta^6\text{-}p\text{-cymene})(PCy_3)][OTf]$ is also able to promote the ROMP of both norbornene and cyclooctene [306]. With norbornene, the reaction was also carried out in a biphasic medium, consisting of the ionic liquid $[bdmin][PF_6]$ and toluene, maintaining a good catalytic activity within four consecutive cycles, and better recycling ability than the standard Grubbs-type first and second generation catalysts $[RuCl_2(=CHPh)(PCy_3)_2]$ and $[RuCl_2(=CHPh)(PCy_3)(H_2IMes)]$, respectively [307]. Moreover, the rate of polymerization could be dramatically accelerated by adding strong acids to the reaction media, obtaining impressive TOF values of 1,096,000 and 44,444 h^{-1} in the room temperature ROMP of cyclooctene and cyclopentadiene, respectively [145, 150]. In this context, based on kinetic studies and stoichiometric reactions [145, 147, 150], it could be demonstrated that the real active catalytic species involved in the metathesis reactions promoted by $[RuCl(=C=C=CPh_2)(\eta^6\text{-}p\text{-cymene})(PCy_3)][X]$ ($X^- = PF_6^-$, TfO^-) is the corresponding indenylidene derivative **43** (see Scheme 15), whose formation is favored in acidic media via intramolecular rearrangement of the initially formed alkenyl-carbyne intermediate.

Although several other ruthenium–allenylidene complexes, including half-sandwich, five- and six-coordinate species, have proven to be active in RCM and ROMP of olefins, their efficiencies are in general lower than that showed by $[RuCl(=C=C=CPh_2)(\eta^6\text{-}p\text{-cymene})(PCy_3)][X]$ ($X^- = PF_6^-$, TfO^-) and will not be commented on [142, 146, 154, 155, 164, 217, 308–310]. The cross-olefin metathesis of cyclopentene with methyl acrylate using as catalyst the water soluble allenylidene–ruthenium(II) complex **28** (see Fig. 9) has also been described [183]. Otherwise, the acyclic diene metathesis polymerization of decadiene could be efficiently performed with allenylidene $[RuCl(=C=C=CPh_2)(\eta^6\text{-}p\text{-cymene})(PCy_3)][OTf]$ after activation with HOTf [145, 150].

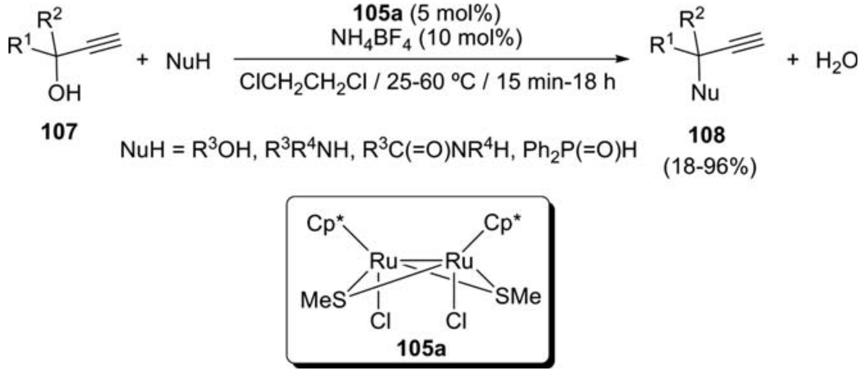
2.4.2 Propargylic Substitution Reactions

Metal-catalyzed substitution reactions involving propargylic derivatives have not been studied in much detail until recently [311, 312]. In this context, the ability shown by transition-metal allenylidenes to undergo nucleophilic additions at the C_γ atom of the cumulenic chain has allowed the development of efficient catalytic processes for the direct substitution of the hydroxyl group in propargylic alcohols [313]. These transformations represent an appealing alternative to the well-known and extensively investigated Nicholas reaction, in which stoichiometric amounts of $[Co_2(CO)_8]$ are employed [314–317].

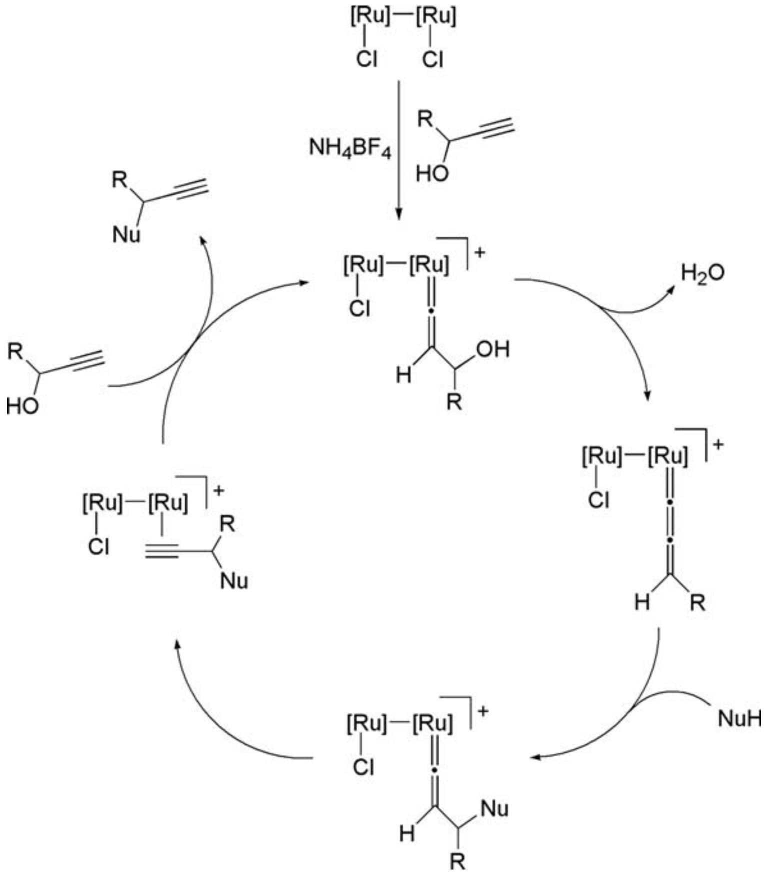
Studies of propargylic substitution reactions, through metal allenylidene intermediates, were initiated in 2000 by Nishibayashi in cooperation with both Hidai and Uemura using as catalyst precursors the thiolate-bridged diruthenium(III) complexes $[\{Cp^*RuCl(\mu\text{-}SR)\}_2]$ (R = Me (**105a**), Et (**105b**), *n*-Pr (**105c**), *i*-Pr (**105d**)) and $[Cp^*RuCl(\mu\text{-}SR)_2RuCp^*(OH_2)][OTf]$ (R = Me (**106a**), *i*-Pr (**106b**)). Thus, in the presence of catalytic amounts of complex **105a** and NH_4BF_4, reactions of propargylic alcohols bearing a terminal C≡C unit **107** with a variety of heteroatom-centered nucleophiles, such as alcohols, amines, amides, or diphenylphosphine oxide, gave the corresponding propargylic substituted products **108** in moderate to high yields with complete selectivity (Scheme 39) [134, 318].

The nature of the bridging thiolate ligands or the replacement of a terminal chloride ligand by water did not have much effect on the catalytic activity, complexes **105b–d** and **106a,b** being also operative in these transformations. In contrast, conventional monometallic ruthenium derivatives, as well as diruthenium complexes having no Ru–Ru bond, did not work at all.

Stoichiometric reactions of isolated allenylidenes such as $[Cp^*RuCl(\mu\text{-}SMe)_2Ru\{=C=C=C(H)Ph\}Cp^*][BF_4]$ or $[Cp^*RuCl(\mu\text{-}SMe)_2Ru\{=C=C=C(p\text{-}MeC_6H_4)_2\}Cp^*][BF_4]$, prepared by treatment of **105a** with propargylic alcohols in the presence of NH_4BF_4, gave the corresponding propargylic substituted products confirming the involvement of allenylidene–ruthenium intermediates in these catalytic



Scheme 39 Propargylic substitution reactions catalyzed by complex **105a**



Scheme 40 Proposed catalytic cycle for the Ru-catalyzed propargylic substitution reactions

transformations [134, 318]. The proposed catalytic cycle is shown in Scheme 40. The reason why only the diruthenium complexes **105a–d** and **106a,b** are effective catalysts for these reactions is believed to be governed by the ruthenium moiety not involved in the allenylidene formation. In this regard, it was established that this ruthenium partner acts as an electron pool, facilitating the exchange of the coordinated propargylic substituted product by the incoming alkynol in the last step of the catalytic cycle.

The intramolecular version of these propargylic substitution processes to obtain the cyclic adducts **109–111** could be developed by treatment of appropriate propargylic alcohols, bearing an additional hydroxyl group at a suitable position on the molecule, with **105a** (Fig. 20) [318]. Moreover, a set of rotaxanes **112** has also been described starting from an ammonium functionalized alkynol and several heteroatom-centered nucleophiles, by performing the catalytic reactions with **105a** in the presence of dibenzo[24]crown-8 (Fig. 20) [319].

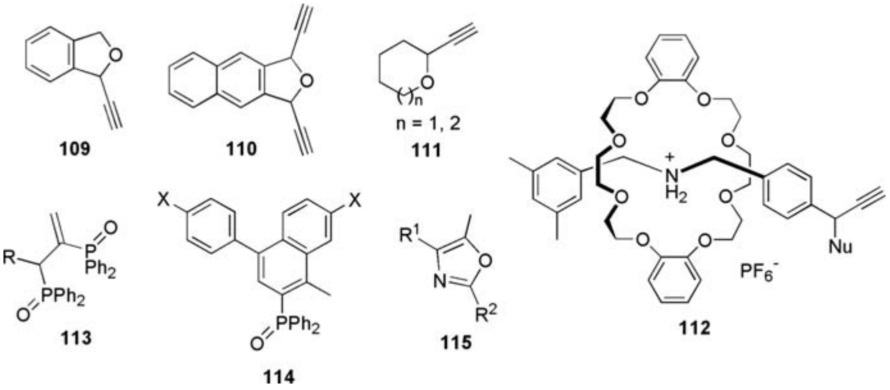
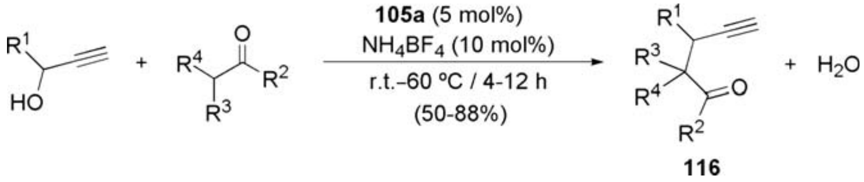


Fig. 20 Series of products obtained through propargylic substitution reactions



Scheme 41 Propargylic substitution reactions with enolizable ketones

Interestingly, the unexpected and highly efficient formation of various 2,3-bis(diphenylphosphinyl)-1-propenes **113** and aryl(diphenyl)phosphine oxides **114** could be performed by treatment of $Ph_2P(=O)H$ with the corresponding alkynols in the presence of **105a** (Fig. 20) [320, 321]. These processes involve the formation of an allenyldiphenylphosphine oxide intermediate, resulting from a Ru-catalyzed tautomerization of the initially formed propargylic substituted derivatives, which evolves into the final products by subsequent addition of $Ph_2P(=O)H$ or by intramolecular cyclization and aromatization, respectively. In a similar way, an elegant and straightforward route for the synthesis of oxazoles **115** starting from secondary alkynols and amides by the sequential action of complex **105a** and $AuCl_3$ has also been described (Fig. 20) [322].

Propargylic substitutions catalyzed by the thiolate-bridged diruthenium complexes **105a–d** and **106a,b** also take place with carbon-centered nucleophiles. Thus, reactions of secondary propargylic alcohols with enolizable ketones, as well as silyl enol ethers, in the presence of **105a** proceeded quite smoothly to give the corresponding alkylated products **116** in high yields (Scheme 41) [323, 324]. The asymmetric version of this reaction, through the incorporation of a bridging chiral thiolate ligand into the diruthenium catalyst, has also been investigated [325, 326]. Moreover, based on this alkylation process, an original synthetic route to a large series of furans and *N*-aryl pyrroles was developed, via ruthenium- and platinum-promoted sequential reactions [327].

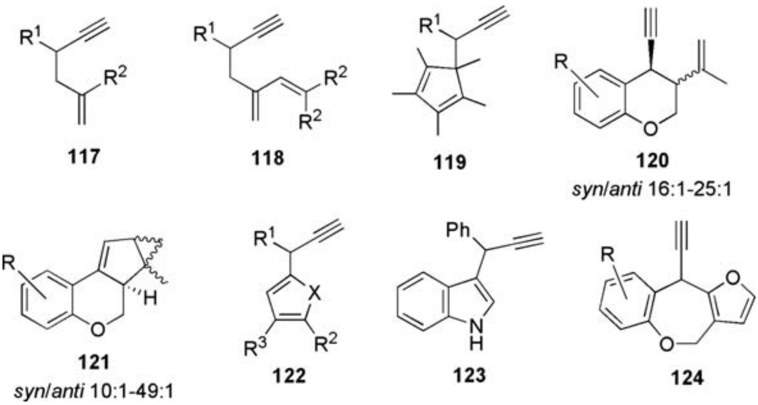


Fig. 21 Products obtained through propargylic substitution reactions with carbon-centred nucleophiles

The diruthenium complexes **105a–d** also catalyze the substitution reactions of terminal secondary alkynols with simple alkenes and 1,3-conjugated dienes, in 1,2-dichloroethane, leading to the selective formation of 1,5-enynes **117** and dienynes **118** and **119**, respectively (Fig. 21) [328, 329]. Moreover, changing the reaction solvent from 1,2-dichloroethane to alcohols, oxypropargylation of the alkene was observed [330]. The intramolecular version of these C–C bond-forming reactions to obtain a set of substituted chromanes **120**, isolated as a mixture of two diastereoisomers, has also been described (Fig. 21) [328]. As an extension of this work, related enantioselective intramolecular cyclizations were reported quite recently using suitable chiral diruthenium complexes [331]. Interestingly, when the cyclizations were performed in the presence of $PtCl_2$, the fused polycyclic compounds **121**, containing a bicyclo[3,1,0]hex-2-ene framework (Fig. 21), could be synthesized in good to excellent yields via a Pt-catalyzed cycloisomerization of the in situ generated chromenes **120** [332].

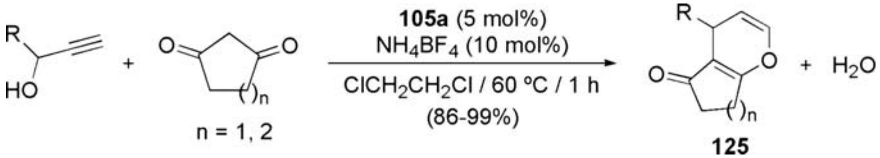
Propargylation of aromatic compounds can also be performed with Nishibayashi's catalysts [333, 334]. Thus, reactions of secondary propargylic alcohols with heteroaromatic compounds such as furans, thiophenes, pyrroles, and indoles in the presence of **105a** proceeded smoothly to afford the corresponding propargylated products **122** and **123** in high yields with complete regioselectivity (Fig. 21). Intramolecular cyclization reactions were also operative leading to the tricyclic species **124** (Fig. 21) [334]. Once again, the involvement of allenylidene intermediates was demonstrated through the stoichiometric reaction of isolated $[Cp^*RuCl(\mu\text{-}SMe)_2Ru\{=C=C=C(H)Ph\}Cp^*][BF_4]$ with 2-methylfuran, which led to the expected propargylated species 2-methyl-5-(1-phenyl-2-propynyl)furan as the sole reaction product. Electron-rich arenes, such as anilines, 1,3,5-trimethoxybenzene, 3,5-dimethylacetanilide, and azulene, could also be propargylated using **105a** as catalyst, the corresponding aromatic products being generated in moderate yields [333, 334]. The asymmetric version of these reactions, using as catalyst a chiral diruthenium derivative, has recently been described [335–337].

2.4.3 Other Catalytic Reactions

In sharp contrast to the alkylation reactions of propargylic alcohols with simple ketones catalyzed by complexes **105a–d** and **106a,b** (Scheme 41), related reactions with 6- and 5-membered ring cyclic 1,3-diketones led to the unexpected formation of chromenone and pyranone derivatives **125** (Scheme 42) [338]. The stoichiometric reaction of the isolated allenylidene complex [Cp*RuCl(μ-SMe)$_2$Ru{=C=C=C(H)Ph}Cp*][BF$_4$] with 1,3-cyclohexanedione gave the corresponding chromenone, confirming the involvement of the cumulenic species in this cyclizative coupling process. Related cycloaddition reactions of secondary alkynols with 2-naphthols and phenols bearing electron-donating groups to afford the corresponding 1*H*-naphtho[2,1-*b*]pyrans and 4*H*-1-benzopyrans, respectively, have also been described [339].

In addition to the propargylic substitution and cycloaddition processes discussed above, the thiolate-bridged diruthenium(III) complexes **105a–d** and **106a,b** were found to promote other catalytic transformations of alkynols via ruthenium-allenylidenes as key intermediates; these include (1) the formation of 1,5-hexadiynes **126** (Fig. 22) by reaction of monoaryl-substituted propargylic alcohols with pinacolborane (H-Bpin) [340], (2) the generation of conjugated enynes **127** through the addition of nitrogen- and oxygen-centered nucleophiles to tertiary alkynols bearing a cyclopropyl group at the propargylic position [341], and (3) the intramolecular cyclization of 3-butyne-1,2-diols to yield the corresponding substituted furans **128** [342].

Otherwise, the involvement of ruthenium–allenylidene intermediates has been evoked in the Meyer–Schuster-type rearrangement of terminal propargylic alcohols (Scheme 43) catalyzed by complexes [RuClCp(PMe$_3$)$_2$] [343], [Ru(η^3-2-C$_3$H$_4$Me)(CO)(dppf)][SbF$_6$] [344–346], and [Cp*Ru(μ-SMe)$_2$RuCp*(OH$_2$)][OTf]$_2$ (**106a**)



Scheme 42 Formation of chromenone and pyranone derivatives catalyzed by complex **105a**

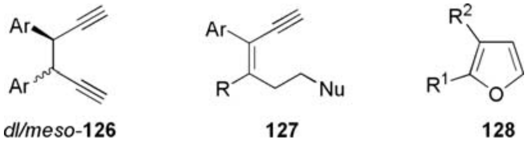
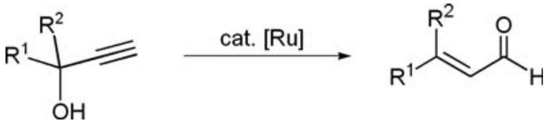
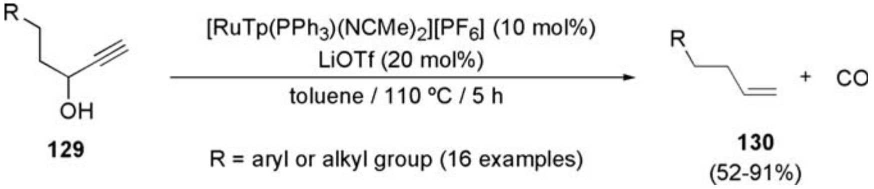


Fig. 22 Structure of compounds **126–128**



Scheme 43 Ru-catalyzed Meyer–Schuster rearrangement of terminal alkynols



Scheme 44 Catalytic transformation of alkynols into alkenes and CO

[347]. Addition of water to the electrophilic C_α of the cumulenic chain explains the formation of the α,β-unsaturated aldehydes.

The ability of the tris(pyrazolyl)borate complex $[RuTp(PPh_3)(NCMe)_2][PF_6]$ to promote catalytic transformations of alkynes is presently well-known [348], the involvement of allenylidene intermediates being proposed in some cases. Thus, in the presence of a catalytic amount of this complex and LiOTf, propargylic alcohols **129** were split into alkenes **130** and carbon monoxide (Scheme 44). This C≡C bond cleavage reaction seems to proceed via a cationic ruthenium–allenylidene intermediate, which traps the formed water molecule at C_α to generate an acyl complex that decomposes through decarbonylation [349]. This catalyst was also employed for the catalytic fragmentation of propargylic ethers into ketones, ethylene, carbon monoxide, and hydrogen [350], as well as for the conversion of 3-benzyl but-1-ynyl ethers into 1,3-dienes and benzaldehyde [351, 352].

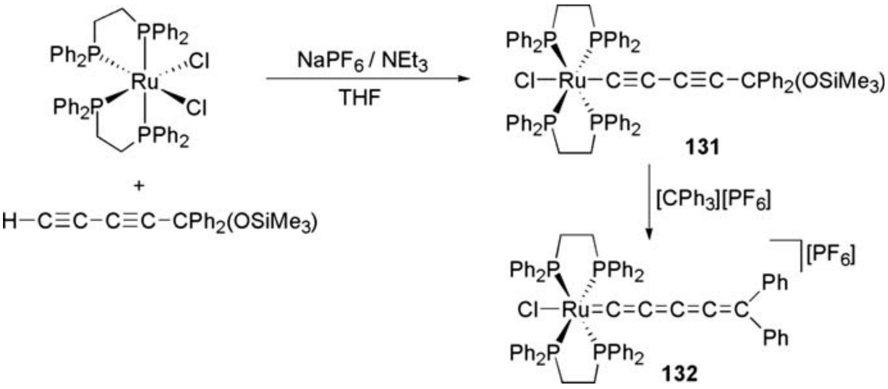
Other catalytic reactions involving a transition-metal allenylidene complex, as catalyst precursor or intermediate, include (1) the dehydrogenative dimerization of tributyltin hydride [116], (2) the controlled atom-transfer radical polymerization of vinyl monomers [144], (3) the selective transetherification of linear and cyclic vinyl ethers under non acidic conditions [353], (4) the cycloisomerization of *N*,*N*-diallyltosylamide into 3-methyl-4-methylene-*N*-tosylpyrrolidine [354, 355], and (5) the reduction of protons from HBF_4 into dihydrogen [238].

3 Higher Cumulenylidene Complexes

As commented previously, higher metallacumulenylidene complexes containing longer odd carbon chains $[M]{=}C{=}(C)_n{=}CR_2$ ($n = 3, 5$) are scarce mainly due to the synthetic difficulties in preparing such species, a fact associated with their intrinsic high reactivity. Most of the reported examples contain heteroatom-based substituents at the final carbon atom, allowing the stabilization of the cumulenic chain through polyynyl resonance structures [356]. In this sense, the only isolated heptahexaenylidene complexes, which constitute the longest metallacumulenylidenes reported to date, are the amino-substituted chromium and tungsten derivatives [M{=C=C=C=C=C=C=C(NMe$_2$)$_2$}(CO)$_5$] (M = W, Cr) described by Fischer and co-workers [357]. Concerning the all-carbon-substituted species, only a limited number of stable pentatetraenylidene complexes have been described, being generally proposed as highly reactive transient intermediates. A survey of the synthesis, structural studies, and reactivity of these complexes is presented in the following sections.

3.1 Preparation of Pentatetraenylidene Complexes

By analogy to the well-known syntheses of allenylidene derivatives from substituted propargylic alcohols, the most fruitful approaches to pentatetraenylidene complexes stem from the reactions of metallic precursors with penta-1,3-diynols HC≡CC≡CCR$_2$(OH) and related diynes. In this sense, the first isolated pentatetraenylidene complex, namely *trans*-[RuCl(=C=C=C=C=CPh$_2$)(dppe)$_2$][PF$_6$] (**132**), was synthesized by Dixneuf and co-workers in 1994 through the reaction of *cis*-[RuCl$_2$(dppe)$_2$] with 5,5-diphenylpentadiynyl trimethylsilylether in the presence of NaPF$_6$/NEt$_3$, followed by [CPh$_3$][PF$_6$]-induced elimination of [OSiMe$_3$]$^-$ in the resulting butadiynyl intermediate **131** (Scheme 45) [358]. In contrast, all attempts to obtain related pentatetraenylidene derivatives by direct activation of diynes XC≡CC≡CCPh$_2$(OR) (X = H, SiMe$_3$, SnBu$_3$; R = H, SiMe$_3$) with complexes [RuCl$_2$(η^6-C$_6$Me$_6$)(PR$_3$)] (PR$_3$ = PMe$_3$, PMe$_2$Ph, PMePh$_2$) [359–361], [RuCl$_2${κ^4(*N*,*P*,*P*,*P*)-N(CH$_2$CH$_2$PPh$_2$)$_3$}] [362], and [RuCl$_2$(dppm)$_2$] [169, 216, 363] failed,

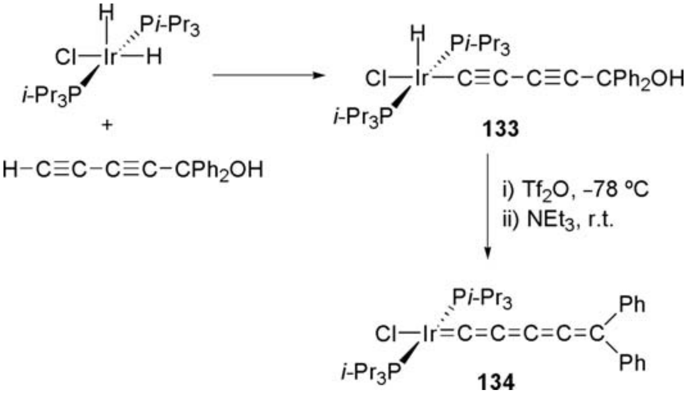


Scheme 45 Synthesis of the first isolated pentatetraenylidene complex

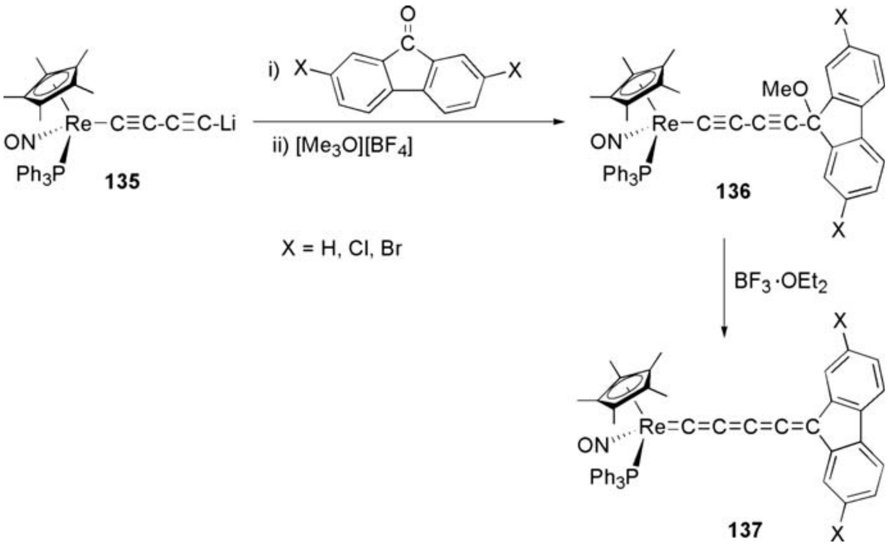
the formation of different alkenyl-allenylidenes or butatrienyl-carbenes, via nucleophilic addition of the alcohols or amines used as solvents to the cumulenic chain, being observed instead (see reactivity studies below). Only the hexamethylbenzene derivative [RuCl{=C=C=C=C=C(*p*-$NMe_2C_6H_4)_2$}(η^6-C_6Me_6)(PMe_3)][PF_6] could be synthesized and fully characterized by activation of $Me_3SiC{\equiv}CC{\equiv}CC$(*p*-$NMe_2$-$C_6H_4)_2(OSiMe_3)$ [364]. The remarkable stability of this complex is attributed to presence of the π-electron-donating amino groups in *para* position of the aromatic substituents.

Stable Group 9 pentatetraenylidene complexes are known. Thus, the neutral square-planar Ir(I) derivative *trans*-[IrCl(=C=C=C=C=CPh_2)(P*i*–$Pr_3)_2$] (**134**) was synthesized by treatment of [IrH_2Cl(P*i*–$Pr_3)_2$] with $HC{\equiv}CC{\equiv}CCPh_2(OH)$ and subsequent dehydration of the resulting hydrido(diynyl) complex [IrHCl{$C{\equiv}CC{\equiv}CCPh_2(OH)$}(P*i*–$Pr_3)_2$] (**133**) through sequential reactions with triflic anhydride and NEt_3 at low temperature [78, 365] (Scheme 46). Its rhodium(I) counterpart *trans*-[RhCl(=C=C=C=C=CPh_2)(P*i*–$Pr_3)_2$] was prepared following the same methodology starting from [{Rh(μ-Cl)(P*i*–$Pr_3)_2\}_2$] and $HC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ [366].

An alternative approach to pentatetraenylidene complexes was used by Gladysz and co-workers in the preparation of the rhenium(I) derivatives [ReCp*{=C=C=C=C=C($C_{12}H_6X_2$)}(NO)(PPh_3)][BF_4] (**137**) (Scheme 47) [367]. It is based on the initial deprotonation of the diynyl complex [ReCp*($C{\equiv}CC{\equiv}CH$)(NO)(PPh_3)] to afford the lithiated species [ReCp*($C{\equiv}CC{\equiv}CLi$)(NO)(PPh_3)] (**135**) which, after sequential treatment with different 9-fluorenone derivatives and [Me_3O][BF_4], is transformed into the methoxy adducts **136**. Final treatment of **136** with $BF_3{\cdot}OEt_2$ leads to the thermally labile pentatetraenylidenes **137**. Following a similar approach, the binuclear C_5-bridged complex [{(PPh_3)(NO)Cp*Re}=C=C=C=C=C={Mn(η^5-C_5Cl_5)$(CO)_2$}][BF_4] could be synthesized starting from **135** and [Mn(η^5-C_5Cl_5)$(CO)_3$] [368, 369].



Scheme 46 Synthesis of the pentatetraenylidene–iridium(I) complex **134**



Scheme 47 Synthesis of the pentatetraenylidene–rhenium(I) complexes **137**

Table 3 Structural data of pentatetraenylidene complexes **132** and **134**

Comp.	$M{=}C_{\alpha}$[a]	$C_{\alpha}{=}C_{\beta}$[a]	$C_{\beta}{=}C_{\gamma}$[a]	$C_{\gamma}{=}C_{\delta}$[a]	$C_{\delta}{=}C_{\varepsilon}$[a]	$M–C_{\alpha}–C_{\beta}$[b]	$C_{\alpha}–C_{\beta}–C_{\gamma}$[b]	$C_{\beta}–C_{\gamma}–C_{\delta}$[b]	$C_{\gamma}–C_{\delta}–C_{\varepsilon}$[b]
132	1.891(9)	1.25(1)	1.30(1)	1.24(1)	1.36(1)	179.0(1)	178.0(1)	179.0(1)	178.0(1)
134	1.834(5)	1.261(6)	1.296(6)	1.259(6)	1.344(6)	176.8(4)	175.8(5)	177.1(5)	174.8(5)

[a] Expressed in Angstroms
[b] Expressed in degrees

3.2 Structure of Pentatetraenylidene Complexes

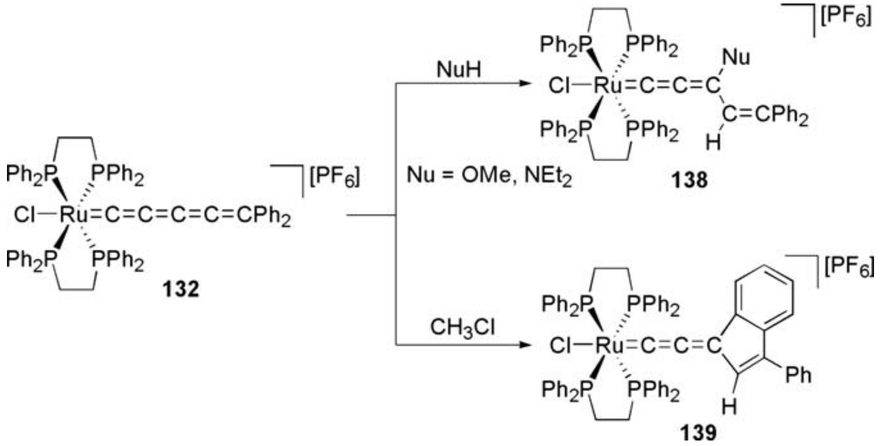
Only the structure of the pentatetraenylidene complexes *trans*-[RuCl(=C=C=C=C=CPh$_2$)(dppe)$_2$][PF$_6$] (**132**) [358] and *trans*-[IrCl(=C=C=C=C=CPh$_2$)(P*i*–Pr$_3$)$_2$] (**134**) [365] could be unambiguously established by single-crystal X-ray diffraction techniques. Structural parameters are summarized in Table 3, showing that, within the unsaturated five-carbon chain, the C_{α}–C_{β} and C_{γ}–C_{δ} distances are in both cases shorter than the C_{β}–C_{γ} and C_{δ}–C_{ε} distances (ca. 0.05 Å). Moreover, the terminal C_{δ}–C_{ε} bond is significantly longer than the internal ones. All these data are consistent with a description of bonding as a small but significant polyyne-like carbon–carbon bond lengths alternation superimposed onto an average cumulenic structure. As observed for allenylidene complexes, the metallacumulenic chain deviates only slightly from linearity (with M=C=C and C=C=C angles varying between 174.8° and 179°), being most pronounced in the case of the iridium derivative.

Extensive DFT calculations have also been carried out in order to establish the basic knowledge on the electronic structures and bonding patterns of these metallacumulenes [224–226, 370, 371]. Remarkable features are (1) the electronic structure is described on the basis of the synergetic σ-donation π-back-donation model with a slightly higher contribution of the latter component and (2) regardless of the substituents of the chain and the metal fragment used in the models, the LUMO is mostly localized on the odd carbon atoms whereas the HOMO has contributions mainly from the metal fragment and the even carbon atoms of the chain. Hence, electrophilic and nucleophilic sites are alternately localized along the metallacumulenic chain.

3.3 *Reactivity of Pentatetraenylidene Complexes*

Although the chemistry of pentatetraenylidene complexes $[M]{=}C({=}C)_3{=}CR^1R^2$ has not received as much attention as that of allenylidenes, there is ample experimental evidence to confirm the electrophilic character of the C_α, C_γ and C_ε carbons of the cumulenic chain [26–29, 31]. Thus, treatment of *trans*-$[RuCl({=}C{=}C{=}C{=}C{=}CPh_2)(dppe)_2][PF_6]$ (**132**) with alcohols or secondary amines resulted in addition of the nucleophilic solvent across the $C_\gamma{=}C_\delta$ double bond to give alkenyl-allenylidenes **138** (Scheme 48) [358]. In chloroform, electrophilic cyclization with one of the Ph groups occurred to give **139**. This transformation is actually the parent of the later observed allenylidene to indenylidene intramolecular rearrangement (Scheme 15).

Related reactivity patterns have been described for the in situ formed complexes $[RuCl({=}C{=}C{=}C{=}C{=}CPh_2)(\eta^6\text{-}C_6Me_6)(PR_3)][PF_6]$ (PR_3 = PMe_3, PMe_2Ph, $PMePh_2$) [359, 360], $[RuCl({=}C{=}C{=}C{=}C{=}CPh_2)\{\kappa^4(N,P,P,P)\text{–}N(CH_2CH_2PPh_2)_3\}][PF_6]$ [362], or *trans*-$[RuCl({=}C{=}C{=}C{=}C{=}CPh_2)(dppm)_2][PF_6]$ [169, 216, 363], which readily add alcohols and amines (used as solvents) across the $C_\gamma{=}C_\delta$ bond. However, in the former case a competitive nucleophilic addition across the $C_\alpha{=}C_\beta$ double bond was also observed with methanol.



Scheme 48 Reactivity of the pentatetraenylidene–ruthenium complex **132**

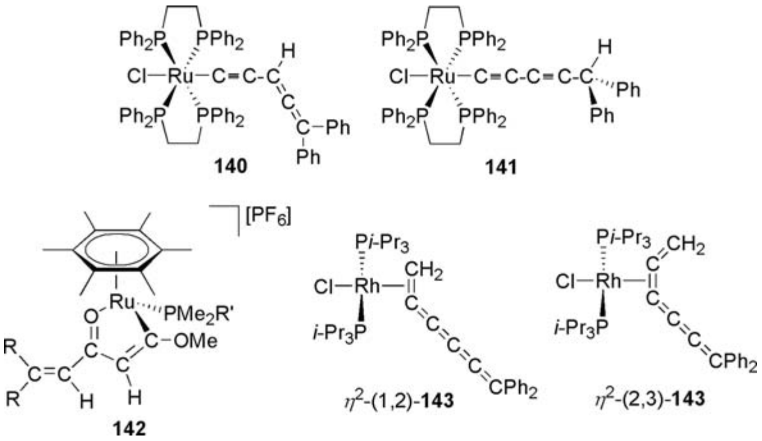


Fig. 23 Structure of compounds **140–143**

Otherwise, reaction of **132** with a hydride source such as $NaBH_4$ afforded the neutral allenylethynyl complex **140** by regioselective addition at the C_γ atom (Fig. 23) [372]. In contrast, reduction with one equivalent of cobaltocene, and subsequent trapping of the resulting radical with Ph_3SnH, yielded the isomeric 5,5-diphenylpenta-1,3-diynyl complex **141**, suggesting that the unpaired electron of the pentatetraenylidene radical is predominantly localized on the C_ε atom [372].

Formation of the chelated 3-oxapentadienyl ruthenium(II) complexes **142** (Fig. 23) merits highlighting since they result from a double nucleophilic addition on the transient pentatetraenylidene complexes $[RuCl(=C=C=C=C=CR_2)(\eta^6\text{-}C_6Me_6)(PMe_2R')][PF_6]$ (R = Me, Ph; R′ = Me, Ph) [359]. Thus, an initial nucleophilic addition of MeOH across the $C_\alpha=C_\beta$ double bond generates the corresponding butatrienyl(methoxy)carbenes which further react with water to afford **142**. Insertion of the methylene unit $:CH_2$ into the Rh=C bond of *trans*-$[RhCl(=C=C=C=C=CPh_2)(P\textit{i}\text{–}Pr_3)_2]$ upon treatment with diazomethane has also been described, affording a mixture of the η^2-(1,2)- and η^2-(2,3)-coordinated diphenylhexapentaene complexes **143** [366]. Finally, it has also been reported that the bimetallic complex $[\{(PPh_3)(NO)Cp^*Re\}=C=C=C=C=C=\{Mn(\eta^5\text{-}C_5Cl_5)(CO)_2\}][BF_4]$ is stable towards dimethyl sulfide, ethylene, or tetracyanoethylene but readily reacts with trimethylphosphine, even at −80°C, to afford complicated mixtures of products which have not been identified [368].

4 Conclusions

In this chapter an updated "state of the art" of the chemistry of allenylidene and higher cumulenylidene complexes has been presented. The spectacular growth of this chemistry seen in recent years stems mainly from the versatile reactivity of these complexes. This is associated with the presence of unsaturated carbon chains which provide multifaceted reactive sites (nucleophilic and electrophilic) of interest in organic synthesis. As a consequence, remarkable developments on the use of metal allenylidenes as catalytic precursors or as intermediates in selective transformations of propargylic alcohols, propargylic derivatives and other multifunctional alkynes have been made. Probably the most remarkable discovery is the catalytic activity of ruthenium–allenylidenes in olefin and enyne metathesis via their rearranged indenylidene complexes. The ready accessibility of these catalysts has triggered the increasing importance of metal allenylidenes.

Overall, it is shown that the chemistry of metal allenylidenes and higher cumulenylidenes has not only reached a remarkable level of conceptual and experimental knowledge but also brought to light new perspectives with potential synthetic utility. It is apparent that these achievements will enhance the rapid growth of new developments, challenging the interest of those working in metal promoted organic synthesis. In addition, the search for missing Group 5 and 11 allenylidenes, as well as for non-heteroatom-stabilized Group 10 and cobalt representatives, still remains a synthetic challenge.

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References

1. Stanton JF, Gauss J (1994) J Chem Phys 101:3001–3005 and references therein
2. Cernicharo J, Gottlieb CA, Guelin M, Killian TC, Paubert G, Thaddeus P, Vrtilek JM (1991) Astrophys J 368:L39–L41
3. Maier G, Reisenauer HP, Schwab W, Čársky P, Hess BA, Schaad LJ (1987) J Am Chem Soc 109:5183–5188
4. Vrtilek JM, Gottlieb CA, Gottlieb EW, Killian TC, Thaddeus P (1990) Astrophys J 364:L53–L56
5. Seburg RA, Patterson EV, Stanton JF, McMahon RJ (1997) J Am Chem Soc 119:5847–5856
6. Stanton JF (1997) J Am Chem Soc 119:429–430
7. Hodges JA, McMahon RJ, Stanton JF, Sattelmeyer KW (2000) Astrophys J 544:838–842
8. Birza P, Chirokolava A, Araki M, Kolek P, Maier JP (2005) J Mol Spectrosc 229:276–282
9. Stang PJ, Fisk TE (1979) J Am Chem Soc 101:4772–4773
10. Killian TC, Vrtilek JM, Gottlieb CA, Gottlieb EW, Thaddeus P (1990) Astrophys J 365: L89–L92
11. Cernicharo J, Gottlieb CA, Guelin M, Killian TC, Thaddeus P, Vrtilek JM (1991) Astrophys J 368:L43–L45
12. Goldberg N, Sülzle D, Schwarz H (1993) Chem Phys Chem 213:593–596
13. McCarthy MC, Travers MJ, Kovács A, Chen W, Novick SE, Gottlieb CA, Thaddeus P (1997) Science 275:518–520
14. McCarthy MC, Travers MJ, Kovács A, Gottlieb CA, Thaddeus P (1997) Astrophys J Suppl Ser 113:105–120

15. Langer WD, Velusamy T, Kuiper TBH, Peng R, McCarthy MC, Travers MJ, Kovács A, Gottlieb CA, Thaddeus P (1997) Astrophys J 480:L63–L66
16. Dua S (1998) Chem Commun 1767–1768
17. Thaddeus P, McCarthy MC, Travers MJ, Gottlieb CA, Chen W (1998) Faraday Discuss 109:121–125
18. Apponi AJ, McCarthy MC, Gottlieb CA, Thaddeus P (2000) Astrophys J 530:357–361
19. Fischer G, Maier JP (1997) Chem Phys 223:149–158
20. Dykstra CE, Parsons CA, Oates CL (1979) J Am Chem Soc 101:1962–1965
21. Fischer EO, Maasböl A (1964) Angew Chem Int Ed Engl 3:580–581
22. Special issue devoted to the chemistry of vinylidene, allenylidene and metallacumulene complexes (2004) Coord Chem Rev 248:1531–1716
23. Fischer EO, Kalder HJ, Frank A, Köhler FH, Huttner G (1976) Angew Chem Int Ed Engl 15:623–624
24. Berke H (1976) Angew Chem Int Ed Engl 15:624
25. Selegue JP (1982) Organometallics 1:217–218
26. Bruce MI (1991) Chem Rev 91:197–257
27. Bruce MI (1998) Chem Rev 98:2797–2858
28. Cadierno V, Gamasa MP, Gimeno J (2001) Eur J Inorg Chem 571–591
29. Cadierno V, Gimeno J (2009) Chem Rev 109:3512–3560
30. Werner H (1997) Chem Commun 903–910
31. Touchard D, Dixneuf PH (1998) Coord Chem Rev 178–180:409–429
32. Werner H, Ilg K, Lass R, Wolf J (2002) J Organomet Chem 661:137–147
33. Castarlenas R, Fischmeister C, Bruneau C, Dixneuf PH (2004) J Mol Catal A Chem 213:31–37
34. Pombeiro AJL (2005) J Organomet Chem 690:6021–6040
35. Esteruelas MA, López AM (2005) Organometallics 24:3584–3613
36. Dragutan I, Dragutan V (2006) Platinum Met Rev 50:81–94
37. Bruneau C, Dixneuf PH (2006) Angew Chem Int Ed 45:2176–2203
38. Esteruelas MA, López AM, Oliván M (2007) Coord Chem Rev 251:795–840
39. Che C-M, Ho C-M, Huang J-S (2007) Coord Chem Rev 251:2145–2166
40. Bruneau C, Dixneuf PH (eds) (2008) Metal vinylidenes and allenylidenes in catalysis: from reactivity to applications in synthesis. Wiley, Weinheim
41. Berke H (1980) J Organomet Chem 150:75–78
42. Berke H (1980) Chem Ber 113:1370–1376
43. Berke H, Härter P, Huttner G, Zsolnai L (1982) Chem Ber 115:695–705
44. Kolobova NE, Ivanov LL, Zhvanko OS, Aleksandrov GG, Struchkov YT (1982) J Organomet Chem 228:265–272
45. Berke H, Härter P, Huttner G, Zsolnai L (1984) Chem Ber 117:3423–3431
46. Berke H, Gröβmann U, Huttner G, Zsolnai L (1984) Chem Ber 117:3432–3442
47. Etienne M, Toupet L (1989) J Chem Soc Chem Commun 1110–1111
48. Etienne M, Talarmin J, Toupet L (1992) Organometallics 11:2058–2068
49. Terada M, Masaki Y, Tanaka M, Akita M, Moro-oka Y (1995) J Chem Soc Chem Commun 1611–1612
50. Edwards AJ, Esteruelas MA, Lahoz FJ, Modrego J, Oro LA, Schrickel J (1996) Organometallics 15:3556–3562
51. Akita M, Kato S, Terada M, Masaki Y, Tanaka M, Moro-oka Y (1997) Organometallics 16:2392–2412
52. Binger P, Langhauser F, Gabor B, Mynott R, Herrmann AT, Krüger C (1992) J Chem Soc Chem Commun 505–506
53. Froom SFT, Green M, Mercer RJ, Nagle KR, Orpen AG, Schwiegk S (1986) J Chem Soc Chem Commun 1666–1668
54. Froom SFT, Green M, Mercer RJ, Nagle KR, Orpen AG, Rodrigues RA (1991) J Chem Soc Dalton Trans 3171–3183

55. Capon JF, Le Berre-Cosquer N, Bernier S, Pichon R, Kergoat R, L´Haridon P (1995) J Organomet Chem 487:201–208
56. Capon JF, Le Berre-Cosquer N, Leblanc B, Kergoat R (1996) J Organomet Chem 508:31–37
57. Capon JF, Le Berre-Cosquer N, Chuburu F, Kergoat R, Saillard J-Y (1996) Inorg Chim Acta 250:119–127
58. Ojo W-S, Pétillon FY, Schollhammer P, Talarmin J, Muir KW (2006) Organometallics 25:5503–5505
59. Ojo W-S, Capon J-F, Le Goff A, Pétillon FY, Schollhammer P, Talarmin J, Muir KW (2007) J Organomet Chem 692:5351–5367
60. Aime S, Deeming AJ, Hursthouse MB, Backer-Dirks JDJ (1982) J Chem Soc Dalton Trans 1625–1629
61. Iyoda M, Kuwatani Y, Oda M (1992) J Chem Soc Chem Commun 399–400
62. Sappa E, Predieri G, Tiripicchio A, Ugozzoli F (1995) Gazz Chim Ital 125:51–56
63. Gervasio G, Marabello D, Sappa E (1997) J Chem Soc Dalton Trans 1851–1855
64. Gervasio G, Gobetto R, King PJ, Marabello D, Sappa E (1998) Polyhedron 17:2937–2955
65. Bruce MI, Skelton BW, White AH, Zaitseva NN (1999) Inorg Chem Commun 2:17–20
66. Bruce MI, Skelton BW, White AH, Zaitseva NN (2000) J Chem Soc Dalton Trans 881–890
67. Charmant JPH, Crawford P, King PJ, Quesada-Pato R, Sappa E (2000) J Chem Soc Dalton Trans 4390–4397
68. Gatto E, Gervasio G, Marabello D, Sappa E (2001) J Chem Soc Dalton Trans 1485–1491
69. Gervasio G, Marabello D, Sappa E, Secco A (2005) J Organomet Chem 690:3755–3764
70. Peng J-J, Horng K-M, Cheng P-S, Chi Y, Peng S-M, Lee G-H (1994) Organometallics 13:2365–2374
71. Selegue JP, Young BA, Logan SL (1991) Organometallics 10:1972–1980
72. Cadierno V, Gamasa MP, Gimeno J, Borge J, García-Granda S (1997) Organometallics 16:3178–3187
73. Esteruelas MA, López AM, Ruiz N, Tolosa JI (1997) Organometallics 16:4657–4667
74. Cadierno V, Conejero S, Gamasa MP, Gimeno J, Rodríguez MA (2002) Organometallics 21:203–209
75. Aneetha H, Jiménez-Tenorio M, Puerta MC, Valerga P, Mereiter K (2003) Organometallics 22:2001–2013
76. Werner H, Rappert T, Wiedemann R, Wolf J, Mahr N (1994) Organometallics 13:2721–2727
77. Martín M, Gevert O, Werner H (1996) J Chem Soc Dalton Trans 2275–2283
78. Werner H, Lass RW, Gevert O, Wolf J (1997) Organometallics 16:4077–4088
79. Bustelo E, Tenorio MJ, Puerta MC, Valerga P (1999) Organometallics 18:4563–4573
80. Bustelo E, Jiménez-Tenorio M, Puerta MC, Valerga P (2001) Eur J Inorg Chem 2391–2398
81. Ilg K, Werner H (2001) Organometallics 20:3782–3794
82. Callejas-Gaspar B, Laubender M, Werner H (2003) J Organomet Chem 684:144–152
83. Ammal SC, Yoshikai N, Inada Y, Nishibayashi Y, Nakamura E (2005) J Am Chem Soc 127:9428–9438
84. Although no experimental evidences have been furnished, involvement of copper allenylidenes in catalytic propargylic substitution processes has been recently proposed: Detz RJ, Delville MME, Hiemstra H, van Maarseveen JH (2008) Angew Chem Int Ed 47:3777–3780
85. Hattori G, Matsuzawa H, Miyake Y, Nishibayashi Y (2008) Angew Chem Int Ed 47:3781–3783
86. Kessler K, Szesni N, Põhako K, Weibert B, Fischer H (2009) Organometallics 28:348–354
87. Binger P, Müller P, Wenz R, Mynott R (1990) Angew Chem Int Ed Engl 29:1037–1038
88. Fischer H, Szesni N (2004) Coord Chem Rev 248:1659–1677 and references cited therein
89. Fischer H, Roth G, Reindl D, Troll C (1993) J Organomet Chem 454:133–149
90. Fischer H, Reindl D, Roth G (1994) Z Naturforsch 49b:1207–1214
91. Haas T, Oswald S, Niederwieser A, Bildstein B, Kessler F, Fischer H (2009) Inorg Chim Acta 362:845–854

92. Grime RW, Helliwell M, Hussain ZI, Lancashire HN, Mason CR, McDouall JJW, Mydlowski CM, Whiteley MW (2008) Organometallics 27:857–871
93. Berke H, Härter P, Huttner G, Zsolnai L (1981) Z Naturforsch 36b:929–937
94. Berke H, Härter P, Huttner G, von Seyerl J (1981) J Organomet Chem 219:317–327
95. Berke H (1986) Organomet Synth 3:239–240
96. Berke H, Huttner G, von Seyerl J (1981) J Organomet Chem 218:193–200
97. Kolobova NE, Ivanov LL, Zhvanko OS, Derunov VV, Chechulina IN (1982) Izv Akad Nauk SSSR Khim 2632–2633
98. Bianchini C, Mantovani N, Marchi A, Marvelli L, Masi D, Peruzzini M, Rossi R, Romerosa A (1999) Organometallics 18:4501–4508
99. Bianchini C, Mantovani N, Marvelli L, Peruzzini M, Rossi R, Romerosa A (2001) J Organomet Chem 617–618:233–241
100. Baker RJ, Edwards PG, Gracia-Mora J, Ingold F, Malik KMA (2002) J Chem Soc Dalton Trans 3985–3992
101. Albertin G, Antoniutti S, Bordignon E, Bresolin D (2000) J Organomet Chem 609:10–20
102. Mantovani N, Brugnati M, Gonsalvi L, Grigiotti E, Laschi F, Marvelli L, Peruzzini M, Reginato G, Rossi R, Zanello P (2005) Organometallics 24:405–418
103. Li X, Schopf M, Stephan J, Kippe J, Harms K, Sundermeyer J (2004) J Am Chem Soc 126:8660–8661
104. Gauss C, Veghini D, Orama O, Berke H (1997) J Organomet Chem 541:19–38
105. Venâncio AIF, Martins LMDRS, Pombeiro AJL (2003) J Organomet Chem 684:315–321
106. Venâncio AIF, Martins LMDRS, Fraústo da Silva JJR, Pombeiro AJL (2003) Inorg Chem Commun 6:94–96
107. Venâncio AIF, Guedes da Silva MFC, Martins LMDRS, Fraústo da Silva JJR, Pombeiro AJL (2005) Organometallics 24:4654–4665
108. Albertin G, Agnoletto P, Antoniutti S (2002) Polyhedron 21:1755–1760
109. Nakanishi S, Goda K, Uchiyama S, Otsuji Y (1992) Bull Chem Soc Jpn 65:2560–2561
110. Argouarch G, Thominot P, Paul F, Toupet L, Lapinte C (2003) C R Chimie 6:209–222
111. Xia HP, Ng WS, Ye JS, Li X-Y, Wong WT, Lin Z, Yang C, Jia G (1999) Organometallics 18:4552–4557
112. Tamm M, Grzegorzewski A, Brüdgam I, Hartl H (1998) J Chem Soc Dalton Trans 3523–3528
113. Crochet P, Demerseman B, Vallejo MI, Gamasa MP, Gimeno J, Borge J, García-Granda S (1997) Organometallics 16:5406–5415
114. Xia HP, Wu WF, Ng WS, Williams ID, Jia G (1997) Organometallics 16:2940–2947
115. Bruce MI, Low PJ, Tiekink ERT (1999) J Organomet Chem 572:3–10
116. Maddock SM, Finn MG (2001) Angew Chem Int Ed 40:2138–2141
117. Pavlik S, Mereiter K, Puchberger M, Kirchner K (2005) Organometallics 24:3561–3575
118. Braun T, Steinert P, Werner H (1995) J Organomet Chem 488:169–176
119. de los Rios I, Tenorio MJ, Puerta MC, Valerga P (1997) J Organomet Chem 549:221–232
120. Bustelo E, Jiménez-Tenorio M, Puerta MC, Valerga P (1999) Organometallics 18:950–951
121. Jiménez-Tenorio M, Palacios MD, Puerta MC, Valerga P (2004) J Organomet Chem 689:2853–2859
122. Pino-Chamorro JA, Bustelo E, Puerta MC, Valerga P (2009) Organometallics 28:1546-1557
123. Cadierno V, Gamasa MP, Gimeno J, González-Cueva M, Lastra E, Borge J, García-Granda S, Pérez-Carreño E (1996) Organometallics 15:2137–2147
124. Gamasa MP, Gimeno J, González-Bernardo C, Borge J, García-Granda S (1997) Organometallics 16:2483–2485
125. Cadierno V, Conejero S, Gamasa MP, Gimeno J (2000) J Chem Soc Dalton Trans 451–457
126. Cadierno V, Conejero S, Gamasa MP, Gimeno J, Pérez-Carreño E, García-Granda S (2001) Organometallics 20:3175–3189

127. Cadierno V, Conejero S, Gamasa MP, Gimeno J, Falvello LR, Llusar RM (2002) Organometallics 21:3716–3726
128. Cadierno V, Conejero S, Gamasa MP, Gimeno J (2003) Dalton Trans 3060–3066
129. Díez J, Gamasa MP, Gimeno J, Lastra E, Villar A (2005) Organometallics 24:1410–1418
130. Nishibayashi Y, Imajima H, Onodera G, Uemura S (2005) Organometallics 24:4106–4109
131. García-Fernández A, Gimeno J, Lastra E, Madrigal CA, Graiff C, Tiripicchio A (2007) Eur J Inorg Chem 732–741
132. Zhong Y-W, Matsuo Y, Nakamura E (2007) Chem Asian J 2:358–366
133. Urtel K, Frick A, Huttner G, Zsolnai L, Kircher P, Rutsch P, Kaifer E, Jacobi A (2000) Eur J Inorg Chem 33–50
134. Nishibayashi Y, Wakiji I, Hidai M (2000) J Am Chem Soc 122:11019–11020
135. Nishibayashi Y, Imajima H, Onodera G, Hidai M, Uemura S (2004) Organometallics 23:26–30
136. Miyake Y, Endo S, Yuki M, Tanabe Y, Nishibayashi Y (2008) Organometallics 27:6039–6042
137. Braun T, Münch G, Windmüller B, Gevert O, Laubender M, Werner H (2003) Chem Eur J 9:2516–2530
138. Pilette D, Ouzzine K, Le Bozec H, Dixneuf PH, Rickard CEF, Roper WR (1992) Organometallics 11:809–817
139. den Reijer CJ, Drago D, Pregosin PS (2001) Organometallics 20:2982–2989
140. Fürstner A, Picquet M, Bruneau C, Dixneuf PH (1998) Chem Commun 1315–1316
141. Picquet M, Touchard D, Bruneau C, Dixneuf PH (1999) New J Chem 23:141–143
142. Jafarpour L, Huang J, Stevens ED, Nolan SP (1999) Organometallics 18:3760–3763
143. Fürstner A, Liebl M, Lehmann CW, Picquet M, Kunz R, Bruneau C, Touchard D, Dixneuf PH (2000) Chem Eur J 6:1847–1857
144. Opstal T, Verpoort F (2003) Polym Bull 50:17–23
145. Castarlenas R, Dixneuf PH (2003) Angew Chem Int Ed 42:4524–4527
146. Le Grende P, Picquet M, Richard P, Moïse C (2002) J Organomet Chem 643–644:231–236
147. Bassetti M, Centola F, Sémeril D, Bruneau C, Dixneuf H (2003) Organometallics 22:4459–4466
148. Weiss D, Dixneuf PH (2003) Organometallics 22:2209–2216
149. Cadierno V, Díez J, García-Álvarez J, Gimeno J (2004) Chem Commun 1820–1821
150. Castarlenas R, Vovard C, Fischmeister C, Dixneuf PH (2006) J Am Chem Soc 128:4079–4089
151. Govindaswamy P, Mozharivskyj YA, Kollipara MR (2004) Polyhedron 23:3115–3123
152. Akiyama R, Kobayashi S (2002) Angew Chem Int Ed 41:2602–2604
153. Jung S, Ilg K, Brandt CD, Wolf J, Werner H (2002) J Chem Soc Dalton Trans 318–327
154. Çetinkaya B, Demir S, Özdemir I, Toupet L, Sémeril D, Bruneau C, Dixneuf PH (2001) New J Chem 25:519–521
155. Çetinkaya B, Demir S, Özdemir I, Toupet L, Sémeril D, Bruneau C, Dixneuf PH (2003) Chem Eur J 9:2323–2330
156. Harlow KJ, Hill AF, Wilton-Ely JDET (1999) J Chem Soc Dalton Trans 285–292
157. Kopf H, Pietraszuk C, Hübner E, Burzlaff N (2006) Organometallics 25:2533–2546
158. Beach NJ, Spivak GJ (2003) Inorg Chim Acta 343:244–252
159. Cadierno V, Gamasa MP, Gimeno J, Iglesias L, García-Granda S (1999) Inorg Chem 38:2874–2879
160. Werner H, Grünwald C, Steinert P, Gevert O, Wolf J (1998) J Organomet Chem 565:231–241
161. Wong C-Y, Che C-M, Chan MCW, Leung K-H, Phillips DL, Zhu N (2004) J Am Chem Soc 126:2501–2514
162. Buriez B, Burns ID, Hill AF, White AJP, Williams DJ, Wilton-Ely JEDT (1999) Organometallics 18:1504–1516

163. Hartmann S, Winter RF, Brunner BM, Sarkar B, Knödler A, Hartenbach I (2003) Eur J Inorg Chem 876–891
164. Schanz H-J, Jafarpour L, Stevens ED, Nolan SP (1999) Organometallics 18:5187–5190
165. Shaffer EA, Chen CL, Beatty AM, Valente EJ, Schanz H-J (2007) J Organomet Chem 692:5221–5233
166. Wong C-Y, Tong GSM, Che C-M, Zhu N (2006) Angew Chem Int Ed 45:2694–2698
167. Pavlik S, Mereiter K, Puchberger M, Kirchner K (2005) J Organomet Chem 690:5497–5507
168. Albertin G, Antoniutti S, Bortoluzzi M, Zanardo G (2005) J Organomet Chem 690:1726–1738
169. Pirio N, Touchard D, Toupet L, Dixneuf PH (1991) J Chem Soc Chem Commun 980–982
170. Pirio N, Touchard D, Dixneuf PH (1993) J Organomet Chem 462:C18–C20
171. Touchard D, Morice C, Cadierno V, Haquette P, Toupet L, Dixneuf PH (1994) J Chem Soc Chem Commun 839–860
172. Touchard D, Pirio N, Dixneuf PH (1995) Organometallics 14:4920–4928
173. Guesmi S, Touchard D, Dixneuf PH (1996) Chem Commun 2773–2774
174. Touchard D, Haquette P, Daridor A, Romero A, Dixneuf PH (1998) Organometallics 17:3844–3852
175. Colbert MCB, Lewis J, Long NJ, Raithby PR, Younus M, White AJP, Williams DJ, Payne NN, Yellowlees L, Beljonne D, Chawdhury N, Friend RH (1998) Organometallics 17:3034–3043
176. de los Ríos I, Tenorio MJ, Puerta MC, Valerga P (1998) Organometallics 17:3356–3363
177. Díez J, Gamasa MP, Gimeno J, Rodríguez Y, García-Granda S (2004) Eur J Inorg Chem 2078–2085
178. Rigaut S, Perruchon J, Guesmi S, Fave C, Touchard D, Dixneuf PH (2005) Eur J Inorg Chem 447–460
179. Cifuentes MP, Humphrey MG, Koutsantonis GA, Lengkeek NA, Petrie S, Sanford V, Schauer PA, Skelton BW, Stranger R, White AH (2008) Organometallics 27:1716–1726
180. Pélerin O, Olivier C, Roisnel T, Touchard D, Rigaut S (2008) J Organomet Chem 693:2153–2158
181. Rigaut S, Costuas K, Touchard D, Saillard J-Y, Golhen S, Dixneuf PH (2004) J Am Chem Soc 126:4072–4073
182. Touchard D, Guesmi S, Bouchaib M, Haquette P, Daridor A, Dixneuf PH (1996) Organometallics 15:2579–2581
183. Saoud M, Romerosa A, Peruzzini M (2000) Organometallics 19:4005–4007
184. Cadierno V, Díez J, García-Garrido SE, Gimeno J (2005) Organometallics 24:3111–3117
185. Bruce MI, Hinterding P, Low PJ, Skelton BW, White AH (1998) J Chem Soc Dalton Trans 467–473
186. Hartmann S, Winter RF, Sakar B, Lissner F (2004) J Chem Soc Dalton Trans 3273–3282
187. Conejero S, Díez J, Gamasa MP, Gimeno J, García-Granda S (2002) Angew Chem Int Ed 41:3439–3442
188. Conejero S, Díez J, Gamasa MP, Gimeno J (2004) Organometallics 23:6299–6310
189. Díez J, Gamasa MP, Gimeno J, Lastra E, Villar A (2006) J Organomet Chem 691:4092–4099
190. Rigaut S, Olivier C, Costuas K, Choua S, Fadhel O, Massue J, Turek P, Saillard J-Y, Dixneuf PH, Touchard D (2006) J Am Chem Soc 128:5859–5876
191. Cadierno V, Gamasa MP, Gimeno J, Lastra E, Borge J, García-Granda S (1994) Organometallics 13:745–747
192. Cadierno V, Gamasa MP, Gimeno J, Lastra E (1999) J Chem Soc Dalton Trans 3235–3243
193. Baya M, Crochet P, Esteruelas MA, Gutiérrez-Puebla E, López AM, Modrego J, Oñate E, Vela N (2000) Organometallics 19:2585–2596
194. Lalrempuia R, Yennawar H, Mozharivskyj YA, Kollipara MR (2004) J Organomet Chem 689:539–543
195. Asensio A, Buil ML, Esteruelas MA, Oñate E (2004) Organometallics 23:5787–5798
196. Esteruelas MA, López AM, Oñate E, Royo E (2004) Organometallics 23:3021–3030

197. Crochet P, Esteruelas MA, López AM, Ruiz N, Tolosa JI (1998) Organometallics 17:3479–3486
198. Weberndörfer B, Werner H (2002) J Chem Soc Dalton Trans 1479–1486
199. Castarlenas R, Esteruelas MA, Lalrempuia R, Oliván M, Oñate E (2008) Organometallics 27:795–798
200. Bohanna C, Callejas B, Edwards AJ, Esteruelas MA, Lahoz FJ, Oro LA, Ruiz N, Valero C (1998) Organometallics 17:373–381
201. Wen TB, Zhou ZY, Lo MF, Williams ID, Jia G (2003) Organometallics 22:5217–5225
202. Albertin G, Antoniutti S, Bacchi A, Pelizzi G, Zanardo G (2008) Eur J Inorg Chem 1913–1920
203. Bolaño T, Castarlenas R, Esteruelas MA, Oñate E (2006) J Am Chem Soc 128:3965–3973
204. Werner H, Rappert T (1993) Chem Ber 126:669–678
205. Laubender M, Werner H (1999) Chem Eur J 5:2937–2946
206. Werner H, Wiedemann R, Laubender M, Windmüller B, Steinert P, Gevert O, Wolf J (2002) J Am Chem Soc 124:6966–6980
207. Canepa G, Brandt CD, Ilg K, Wolf J, Werner H (2003) Chem Eur J 9:2502–2515
208. Windmüller B, Wolf J, Werner H (1995) J Organomet Chem 502:147–161
209. Schwab P, Werner H (1994) J Chem Soc Dalton Trans 3415–3425
210. Windmüller B, Nürnberg O, Wolf J, Werner H (1999) Eur J Inorg Chem 613–619
211. Esteruelas MA, Oro LA, Schrickel J (1997) Organometallics 16:796–799
212. Kovacik I, Gevert O, Werner H, Schmittel M, Söllner R (1998) Inorg Chim Acta 275–276:435–439
213. Berke H, Huttner G, von Seyerl J (1981) Z Naturforsch 36b:1277–1288
214. Peruzzini M, Barbaro P, Bertolasi V, Bianchini C, de los Rios I, Mantovani N, Marvelli L, Rossi R (2003) Dalton Trans 4121–4131
215. Tamm M, Jentzsch T, Werncke W (1997) Organometallics 16:1418–1424
216. Touchard D, Pirio N, Toupet L, Fettouhi M, Ouahab L, Dixneuf PH (1995) Organometallics 14:5263–5272
217. Jung S, Brandt CD, Werner H (2001) New J Chem 25:1101–1103
218. Esquius G, Pons J, Yáñez R, Ros J, Mathieu R, Lugan N, Donnadieu B (2003) J Organomet Chem 667:126–134
219. Bianchini C, Peruzzini M, Zanobini F, Lopez C, de los Rios I, Romerosa A (1999) Chem Commun 443–444
220. Ilg K, Werner H (2001) Chem Eur J 7:4633–4639
221. Schilling BER, Hoffmann R, Lichtenberger DL (1979) J Am Chem Soc 101:585–591
222. Schilling BER, Hoffmann R, Faller JV (1979) J Am Chem Soc 101:592–598
223. Esteruelas MA, Gómez AV, López AM, Modrego J, Oñate E (1997) Organometallics 16:5826–5835
224. Re N, Sgamellotti A, Floriani C (2000) Organometallics 19:1115–1122
225. Marrone A, Re N (2002) Organometallics 21:3562–3571
226. Auger N, Touchard D, Rigaut S, Halet J-F, Saillard J-Y (2003) Organometallics 22:1638–1644
227. Drexler M, Haas T, Yu S-M, Beckmann HSG, Weibert B, Fischer H (2005) J Organomet Chem 690:3700–3713
228. Wong C-Y, Lai L-M, Lam C-Y, Zhu N (2008) Organometallics 27:5806–5814
229. Kolobova NE, Ivanov LL, Zhvanko OS, Khitrova OM, Batsanov AS, Struchkov YT (1984) J Organomet Chem 262:39–47
230. Bolaño T, Castarlenas R, Esteruelas MA, Oñate E (2007) Organometallics 26:2037–2041
231. Bolaño T, Castarlenas R, Esteruelas MA, Oñate E (2008) Organometallics 27:6367–6370
232. Rigaut S, Touchard D, Dixneuf PH (2003) Organometallics 22:3980–3984
233. Bustelo E, Jiménez-Tenorio M, Mereiter K, Puerta MC, Valerga P (2002) Organometallics 21:1903–1911
234. Mantovani N, Marvelli L, Rossi R, Bianchini C, de los Rios I, Romerosa A, Peruzzini M (2001) J Chem Soc Dalton Trans 2353–2361

235. Werner H, Stark A, Steinert P, Grünwald C, Wolf J (1995) Chem Ber 128:49–62
236. Dragutan V, Dragutan I, Verpoort F (2005) Platinum Met Rev 49:33–40
237. Boeda F, Clavier H, Nolan SP (2008) Chem Commun 2726–2740
238. Valyaev DA, Peterleitner MG, Semeikin OV, Utegenov KI, Ustynyuk NA, Sournia-Saquet A, Lugan N, Lavigne G (2007) J Organomet Chem 692:3207–3211
239. Cosset C, del Río I, Le Bozec H (1995) Organometallics 14:1938–1944
240. Cosset C, del Río I, Péron V, Windmüller B, Le Bozec H (1996) Synlett 435–436
241. Dötz KH, Paetsch D, Le Bozec H (1999) J Organomet Chem 589:11–20
242. Ulrich K, Porhiel E, Péron V, Ferrand V, Le Bozec H (2000) J Organomet Chem 601:78–86
243. Fischer H, Roth G (1995) J Organomet Chem 490:229–237
244. Roth G, Fischer H (1996) J Organomet Chem 507:125–136
245. Fischer H, Reindl D, Troll C, Leroux F (1995) J Organomet Chem 490:221–227
246. Kolobova NE, Ivanov LL, Zhvanko OS, Khitrova OM, Batsanov AS, Struchkov YT (1984) J Organomet Chem 265:271–281
247. Mantovani N, Marvelli L, Rossi R, Bertolasi V, Bianchini C, de los Rios I, Peruzzini M (2002) Organometallics 21:2382–2394
248. Devanne D, Dixneuf PH (1990) J Chem Soc Chem Commun 641–643
249. Dussel R, Pilette D, Dixneuf PH, Fehlhammer WP (1991) Organometallics 10:3287–3291
250. Ruiz N, Péron D, Dixneuf PH (1995) Organometallics 14:1095–1097
251. Ruiz N, Péron D, Sinbandith S, Dixneuf PH, Baldoli C, Maiorana S (1997) J Organomet Chem 533:213–218
252. Ulrich K, Guerchais V, Toupet L, Le Bozec H (2002) J Organomet Chem 643–644:498–500
253. Ghebreyessus KY, Nelson JH (2003) Inorg Chem Commun 6:1044–1047
254. Esteruelas MA, Gómez AV, Lahoz FJ, López AM, Oñate E, Oro LA (1996) Organometallics 15:3423–3435
255. Le Lagadec R, Roman E, Toupet L, Müller U, Dixneuf PH (1994) Organometallics 13:5030–5039
256. Esteruelas MA, Gómez AV, López AM, Oñate E, Ruiz N (1998) Organometallics 17:2297–2306
257. Esteruelas MA, Gómez AV, López AM, Oliván M, Oñate E, Ruiz N (2000) Organometallics 19:4–14
258. Bustelo E, Dixneuf PH (2007) Adv Synth Catal 349:933–942
259. Bernad DJ, Esteruelas MA, López AM, Modrego J, Puerta MC, Valerga P (1999) Organometallics 18:4995–5003
260. Buil ML, Esteruelas MA, López AM, Oñate E (2003) Organometallics 22:162–171
261. Buil ML, Esteruelas MA, López AM, Oñate E (2003) Organometallics 22:5274–5284
262. Jiménez-Tenorio M, Palacios MD, Puerta MC, Valerga P (2004) J Organomet Chem 689:2776–2785
263. Kopf H, Holzberger B, Pietraszuk C, Hübner E, Burzlaff N (2008) Organometallics 27:5894–5905
264. Esteruelas MA, Gómez AV, López AM, Modrego J, Oñate E (1998) Organometallics 17:5434–5436
265. Cadierno V, Gamasa MP, Gimeno J, López-González MC, Borge J, García-Granda S (1997) Organometallics 16:4453–4463
266. Cadierno V, Conejero S, Gamasa MP, Gimeno J, Asselberghs I, Houbrechts S, Clays K, Persoons A, Borge J, García-Granda S (1999) Organometallics 18:582–597
267. Cadierno V, Gamasa MP, Gimeno J, Moretó JM, Ricart S, Roig A, Molins E (1998) Organometallics 17:697–706
268. Cadierno V, Gamasa MP, Gimeno J (1999) J Chem Soc Dalton Trans 1857–1865
269. Cadierno V, Gamasa MP, Gimeno J, Pérez-Carreño E, García-Granda S (1999) Organometallics 18:2821–2832
270. Cadierno V, Gamasa MP, Gimeno J (2001) J Organomet Chem 621:39–45

271. Cadierno V, Gamasa MP, Gimeno J, Pérez-Carreño E, García-Granda S (2003) J Organomet Chem 670:75–83
272. Cadierno V, Conejero S, Gamasa MP, Gimeno J (2002) Organometallics 21:3837–3840
273. Cadierno V, Conejero S, Díez J, Gamasa MP, Gimeno J, García-Granda S (2003) Chem Commun 840–841
274. Maraval V, Duhayon C, Coppel Y, Chauvin R (2008) Eur J Org Chem 5144–5156
275. Demerseman B, Toupet L (2006) Eur J Inorg Chem 1573–1581
276. Gil-Rubio J, Weberndörfer B, Werner H (2000) Angew Chem Int Ed 39:786–789
277. Werner H, Wiedemann R, Laubender M, Windmüller B, Wolf J (2001) Chem Eur J 7:1959–1967
278. Kalinin VN, Derunov VV, Lusenkova MA, Petrovsky PV, Kolobova NE (1989) J Organomet Chem 379:303–309
279. Braun T, Meuer P, Werner H (1996) Organometallics 15:4075–4077
280. Werner H, Wiedemann R, Mahr N, Steinert P, Wolf J (1996) Chem Eur J 2:561–569
281. Abd-Elzaher MM, Weibert B, Fischer H (2005) Organometallics 24:1050–1052
282. Buriez B, Cook DJ, Harlow KJ, Hill AF, Welton T, White AJP, Williams DJ, Wilton-Ely JDET (1999) J Organomet Chem 578:264–267
283. Harlow KJ, Hill AF, Welton T (1999) J Chem Soc Dalton Trans 1911–1912
284. Esteruelas MA, Gómez AV, López AM, Puerta MC, Valerga P (1998) Organometallics 17:4959–4965
285. Fischer H, Leroux F, Stumpf R, Roth G (1996) Chem Ber 129:1475–1482
286. Roth G, Reindl D, Gockel M, Troll C, Fischer H (1998) Organometallics 17:1393–1401
287. Baya M, Buil ML, Esteruelas MA, López AM, Oñate E, Rodríguez JR (2002) Organometallics 21:1841–1848
288. Esteruelas MA, Gómez AV, López AM, Oñate E, Ruiz N (1999) Organometallics 18:1606–1614
289. Esteruelas MA, Gómez AV, López AM, Oñate E (1998) Organometallics 17:3567–3573
290. Bertolasi V, Mantovani N, Marvelli L, Rossi R, Bianchini C, de los Rios I, Peruzzini M, Akbayeva DN (2003) Inorg Chim Acta 344:207–213
291. Bernad DJ, Esteruelas MA, López AM, Oliván M, Oñate E, Puerta MC, Valerga P (2000) Organometallics 19:4327–4335
292. Mantovani N, Bergamini P, Marchi A, Marvelli L, Rossi R, Bertolasi V, Ferretti V, de los Rios I, Peruzzini M (2006) Organometallics 25:416–426
293. Trost BM, Flygare JA (1992) J Am Chem Soc 114:5476–5477
294. Trost BM, Kulawiec RJ, Hammes A (1993) Tetrahedron Lett 34:587–590
295. Trost BM, Flygare JA (1994) Tetrahedron Lett 35:4059–4062
296. Grubbs RH (ed) (2003) Handbook of metathesis. Wiley, Weinheim
297. Grubbs RH (2006) Angew Chem Int Ed 45:3760–3765 (The Nobel Lecture)
298. Fürstner A, Müller T (1999) J Am Chem Soc 121:7814–7821
299. Osipov SN, Artyushin OI, Kolomiets AF, Bruneau C, Dixneuf PH (2000) Synlett 1031–1033
300. Osipov SN, Artyushin OI, Kolomiets AF, Bruneau C, Picquet M, Dixneuf PH (2001) Eur J Org Chem 3891–3897
301. Garbacia S, Desai B, Lavastre O, Kappe CO (2003) J Org Chem 68:9136–9139
302. Sémeril D, Olivier-Bourbigou H, Bruneau C, Dixneuf PH (2002) Chem Commun 146–147
303. Picquet M, Bruneau C, Dixneuf PH (1998) Chem Commun 2249–2250
304. Le Nôtre J, Bruneau C, Dixneuf PH (2002) Eur J Org Chem 3816–3820
305. Sémeril D, Le Nôtre J, Bruneau C, Dixneuf PH, Kolomiets AF, Osipov SN (2001) New J Chem 25:16–18
306. Castarlenas R, Sémeril D, Noels AF, Demonceau A, Dixneuf PH (2002) J Organomet Chem 663:235–238
307. Csihony S, Fischmeister C, Bruneau C, Horváth IT, Dixneuf PH (2002) New J Chem 26:1667–1670
308. Abdallaoui IA, Sémeril D, Dixneuf PH (2002) J Mol Catal A Chem 182–183:577–583

309. Ledoux N, Drozdzak R, Allaert B, Linden A, Van der Voort P, Verpoort F (2007) Dalton Trans 5201–5210
310. Özdemir I, Demir S, Çetinkaya B, Toupet L, Castarlenas R, Fischmeister C, Dixneuf PH (2007) Eur J Inorg Chem 2862–2869
311. Kabalka GW, Yao M-L (2008) Curr Org Synth 5:28–32
312. Ljungdahl N, Kann N (2009) Angew Chem Int Ed 48:642–644
313. Nishibayashi Y, Uemura S (2006) Curr Org Chem 10:135–150
314. Nicholas KM (1987) Acc Chem Res 20:207–214
315. Green JR (2001) Curr Org Chem 5:809–826
316. Teobald BJ (2002) Tetrahedron 58:4133–4170
317. Díaz DD, Betancort JM, Martín VS (2007) Synlett 343–359
318. Nishibayashi Y, Milton MD, Inada Y, Yoshikawa M, Wakiji I, Hidai M, Uemura S (2005) Chem Eur J 11:1433–1451
319. Tokunaga Y, Kawai N, Shimomura Y (2007) Tetrahedron Lett 48:4995–4998
320. Milton MD, Onodera G, Nishibayashi Y, Uemura S (2004) Org Lett 6:3993–3995
321. Onodera G, Matsumoto H, Milton MD, Nishibayashi Y, Uemura S (2005) Org Lett 7:4029–4032
322. Milton MD, Inada Y, Nishibayashi Y, Uemura S (2004) Chem Commun 2712–2713
323. Nishibayashi Y, Wakiji I, Ishii Y, Uemura S, Hidai M (2001) J Am Chem Soc 123:3393–3394
324. Nishibayashi Y, Imajima H, Onodera G, Inada Y, Hidai M, Uemura S (2004) Organometallics 23:5100–5103
325. Nishibayashi Y, Onodera G, Inada Y, Hidai M, Uemura S (2003) Organometallics 22:873–876
326. Inada Y, Nishibayashi Y, Uemura S (2005) Angew Chem Int Ed 44:7715–7717
327. Nishibayashi Y, Yoshikawa M, Inada Y, Milton MD, Hidai M, Uemura S (2003) Angew Chem Int Ed 42:2681–2684
328. Nishibayashi Y, Inada Y, Hidai M, Uemura S (2003) J Am Chem Soc 125:6060–6061
329. Daini M, Yoshikawa M, Inada Y, Uemura S, Sakata K, Kanao K, Miyake Y, Nishibayashi Y (2008) Organometallics 27:2046–2051
330. Yamauchi Y, Miyake Y, Nishibayashi Y (2009) Organometallics 28:48–50
331. Fukamizu K, Miyake Y, Nishibayashi Y (2008) J Am Chem Soc 130:10498–10499
332. Nishibayashi Y, Yoshikawa M, Inada Y, Hidai M, Uemura S (2004) J Am Chem Soc 126:16066–16072
333. Nishibayashi Y, Yoshikawa M, Inada Y, Hidai M, Uemura S (2002) J Am Chem Soc 124:11846–11847
334. Inada Y, Yoshikawa M, Milton MD, Nishibayashi Y, Uemura S (2006) Eur J Org Chem 881–890
335. Matsuzawa H, Miyake Y, Nishibayashi Y (2007) Angew Chem Int Ed 46:6488–6491
336. Matsuzawa H, Kanao K, Miyake Y, Nishibayashi Y (2007) Org Lett 9:5561–5564
337. Kanao K, Matsuzawa H, Miyake Y, Nishibayashi Y (2008) Synthesis 3869–3873
338. Nishibayashi Y, Yoshikawa M, Inada Y, Hidai M, Uemura S (2004) J Org Chem 69:3408–3412
339. Nishibayashi Y, Inada Y, Hidai M, Uemura S (2002) J Am Chem Soc 124:7900–7901
340. Onodera G, Nishibayashi Y, Uemura S (2006) Organometallics 25:35–37
341. Yamauchi Y, Onodera G, Sakata K, Yuki M, Miyake Y, Uemura S, Nishibayashi Y (2007) J Am Chem Soc 129:5175–5179
342. Yada Y, Miyake Y, Nishibayashi Y (2008) Organometallics 27:3614–3617
343. Suzuki T, Tokunaga M, Wakatsuki Y (2002) Tetrahedron Lett 43:7531–7533
344. Cadierno V, Díez J, García-Garrido SE, Gimeno J (2004) Chem Commun 2716–2717
345. Cadierno V, García-Garrido SE, Gimeno J (2006) Adv Synth Catal 348:101–110
346. Cadierno V, Díez J, García-Garrido SE, Gimeno J, Nebra N (2006) Adv Synth Catal 348:2125–2132

347. Onodera G, Matsumoto H, Nishibayashi Y, Uemura S (2005) Organometallics 24:5799–5801
348. Liu R-S (2008) Synlett 6:801–812 and references cited therein
349. Datta S, Chang C-L, Yeh K-L, Liu R-S (2003) J Am Chem Soc 125:9294–9295
350. Shen H-C, Su H-L, Hsueh Y-C, Liu R-S (2004) Organometallics 23:4332–4334
351. Yeh K-L, Liu B, Lo C-Y, Huang H-L, Liu R-S (2002) J Am Chem Soc 124:6510–6511
352. Yeh K-L, Liu B, Lai Y-T, Li C-W, Liu R-S (2004) J Org Chem 69:4692–4694
353. Saoud M, Romerosa A, Carpio SM, Gonsalvi L, Peruzzini M (2003) Eur J Inorg Chem 1614–1619
354. Özdemir I, Çetinkaya E, Çetinkaya B, Çiçek M, Sémeril D, Bruneau C, Dixneuf PH (2004) Eur J Inorg Chem 418–422
355. Özdemir I, Çetinkaya B, Demir S, Çetinkaya E, Gürbüz N, Çiçek M (2004) Appl Organomet Chem 18:15–18
356. Bruce MI (2004) Coord Chem Rev 248:1603–1625
357. Dede M, Drexler M, Fischer H (2007) Organometallics 26:4294–4299
358. Touchard D, Haquette P, Daridor A, Toupet L, Dixneuf PH (1994) J Am Chem Soc 116:11157–11158
359. Romero A, Vegas A, Dixneuf PH (1990) Angew Chem Int Ed Engl 29:215–216
360. Romero A, Péron D, Dixneuf PH (1990) J Chem Soc Chem Commun 1410–1412
361. Péron D, Romero A, Dixneuf PH (1995) Organometallics 14:3319–3326
362. Wolinska A, Touchard D, Dixneuf PA (1991) J Organomet Chem 420:217–226
363. Pirio N, Touchard D, Dixneuf PH, Fettouhi M, Ouahab L (1992) Angew Chem Int Ed Engl 31:651–653
364. Péron D, Romero A, Dixneuf PH (1994) Gazz Chim Ital 124:497–502
365. Lass RW, Steinert P, Wolf J, Werner H (1996) Chem Eur J 2:19–23
366. Kovacik I, Laubender M, Werner H (1997) Organometallics 16:5607–5609
367. Szafert S, Haquette P, Falloon SB, Gladysz JA (2000) J Organomet Chem 604:52–58
368. Bartik T, Weng W, Ramsden JA, Szafert S, Falloon SB, Arif AM, Gladysz JA (1998) J Am Chem Soc 120:11071–11081
369. For a review that summarize the chemistry of complexes containing unsaturated carbon chains end-capped by various metal–ligand combinations, see: Bruce MI, Low PJ (2004) Adv Organomet Chem 50:179–444
370. Jiao H, Gladysz JA (2001) New J Chem 25:551–562
371. Marrone A, Colletti C, Re N (2004) Organometallics 23:4952–4963
372. Rigaut S, Maury O, Touchard D, Dixneuf PH (2001) Chem Commun 373–374

Top Organomet Chem (2010) 30: 219–252
DOI 10.1007/978-3-642-04722-0_7

Heteroatom-Conjugated Allenylidene and Related Cumulenylidene Ligands

Victorio Cadierno and Sergio E. García-Garrido

Abstract In this chapter, aspects related to the synthesis, structure, and reactivity of metallacumulenes $[M]{=}C({=}C)_n{=}CR^1R^2$ (n = 1, 3, 5) in which one or both substituents R^1/R^2 are heteroatomic π-donor groups (NR_2, OR, SR, SeR) are discussed. The coordination chemistry of related heteroatom-cumulated ligands, i.e., phosphonioacetylides and tricarbon monoxide, is also presented.

Keywords Allenylidene ligands · Carbene complexes · Cumulenylidene ligands · Phosphonioacetylide ligands · Tricarbon monoxide

Contents

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Abbreviations

Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
depe	1,2-Bis(diethylphosphino)ethane
DFT	Density functional theory
dhpm	Bis(dihydrophosphino)methane
dppe	1,2-Bis(diphenylphosphino)ethane
dppm	Bis(diphenylphosphino)methane
Fc	Ferrocenyl
MO	Molecular orbital
NLO	Nonlinear optics
tppe	1,1,2-Tris(diphenylphosphino)ethane

1 Introduction

Since their discovery in 1964 [1], tremendous progress has been made in the chemistry of the so-called Fischer-type carbene complexes $[M]{=}C(XR)R'$ due to their outstanding applications as stoichiometric reagents in organic synthesis [2–4]. Fischer-carbenes generally contain a low oxidation state metal and bear a heteroatomic substituent on the carbenic carbon ($XR = NR_2$, OR, SR, SeR, etc), which makes it electrophilic. In addition, their reactivity and physico-chemical properties can be modulated by simple variation of the nature of this heteroatomic substituent, a fact intimately tied with the respective weighting of the canonical forms **A–C** (Fig. 1). In terms of the classical description of the metal–ligand multiple bonds (σ-donor/π-acceptor synergism), the canonical structure **A** delineates the M–C "σ-bond" and **B** the "π-back-bond," the latter being strongly reinforced by a further π contribution **C**.

Heteroatom-substituted allenylidene and higher odd-chain cumulenylidene complexes $[M]{=}C({=}C)_n{=}CR^1R^2$ ($n = 1, 3, 5$; $R^1/R^2 = NR_2$, OR, SR, SeR) are directly related to the classical Fischer-type carbene complexes, being regarded as their functional *carbo*-mers [5–7]. However, although two of the first allenylidene complexes synthesized were the amino-allenylidene derivatives $[M\{{=}C{=}C{=}CPh(NMe_2)\}(CO)_5]$ (M = Cr, W) [8], the chemistry of these compounds has been much less developed [9, 10]. In fact, as already discussed in Chapter 6 the chemistry of metallacumulenes is largely dominated by the all-carbon substituted representatives

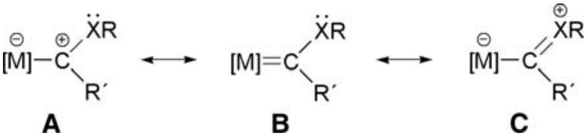


Fig. 1 Canonical forms of Fischer-type carbene complexes

[11–15]. In a recent study, the effects of the terminal substituents on the electronic structure of metallacumulene complexes $[Cr\{=C(=C)_n=CR_2\}(CO)_5]$ ($n = 0$–6; R = F, SiH_3, $CH=CH_2$, NH_2, NO_2) have been evaluated by means of DFT calculations [16]. HOMO and LUMO distribution in these substituted metallacumulenes follow qualitatively similar trends to those obtained for their unsubstituted counterparts $[Cr\{=C(=C)_n=CH_2\}(CO)_5]$ [17], i.e., the LUMO is mostly localized on the odd carbon atoms whereas the HOMO has contributions mainly from the metal fragment and the even carbon atoms of the chain. However, the electronic properties of the substituents strongly affect the frontier-orbital energies in a markedly different way, i.e., an increased LUMO energy for π-donor amino groups vs a decreased LUMO energy for π-acceptor nitro substituents. Therefore, while the nitro substituents lead to a favored reactivity towards nucleophiles, the presence of π-donor groups results in a significant stability of the cumulenic chains. This effect of the amino groups, which was found to be much more pronounced for odd-chain metallacumulenes, is in complete accord with the experimental evidences presently available indicating a high stability of amino-substituted allenylidene ($n = 1$), pentatetraenylidene ($n = 3$) and heptahexaenylidene ($n = 5$) complexes [9–15]. Using a simple Lewis analysis, the resonance effects (exemplified in Fig. 2 for the allenylidene case) derived from the electron transfer from the amino-substituents to the unsaturated carbon chain are responsible of the observed stability. In addition, the extensive π-conjugation present in these metallacumulenes results in marked differences in chemical behavior with respect to their all-carbon substituted counterparts.

In this chapter, the most efficient synthetic routes, the main structural features as well as reactivity patterns of odd-chain metallacumulene complexes bearing π-donor substituents, i.e., $[M]=C(=C)_n=CR^1R^2$ ($n = 1, 3, 5$; $R^1/R^2 = NR_2$, OR, SR, SeR), are reviewed. In addition, the coordination chemistry of phosphonioacetylides ($R_3P^+C\equiv C^-$) and tricarbon monoxide (C_3O) will also be discussed since these heteroatom-containing η^1-carbon ligands lead to closely related bonding situations, with participation of both neutral cumulenic and zwitterionic alkynyl-type mesomeric forms (Fig. 3).

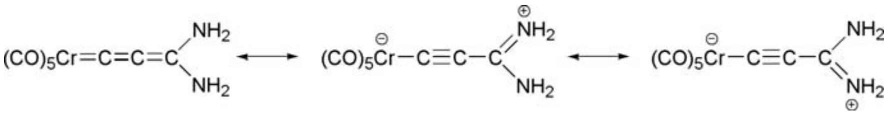


Fig. 2 Resonance effects associated to the amino-allenylidene $[Cr\{=C=C=C(NH_2)_2\}(CO)_5]$

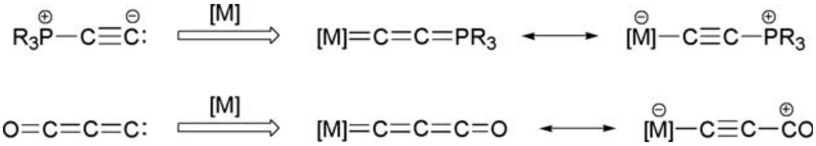


Fig. 3 Mesomeric forms of metal complexes derived from phosphonioacetylides and tricarbon monoxide

2 Allenylidene Complexes

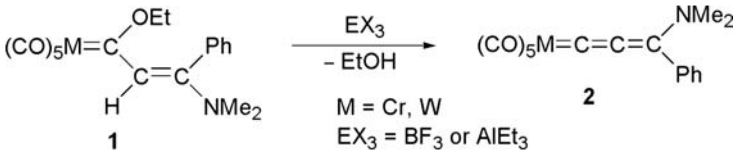
Despite the stabilizing effect of π-donor substituents on metallacumulenes, as mentioned above, the chemistry of allenylidene complexes containing heteroatomic units at the terminal C_γ atom of the unsaturated chain is much less developed than that of their all-carbon-substituted counterparts. The most powerful route to allenylidene complexes involves the use of propargylic alcohols $HC{\equiv}CCR^1R^2(OH)$ as sources of the C_3 fragment, a synthetic methodology introduced in 1982 by Selegue [18] and discussed in detail in our preceding chapter. Nevertheless, the synthesis of π-donor-substituted allenylidene complexes cannot be tackled following this general and classical methodology, slowing down the development of their chemistry. Although some alternative routes to this type of complexes are presently available, they are only of limited scope when compared to Selegue's methodology. In fact, to date, only π-donor-substituted allenylidenes of Groups 6 and 8 metals [9, 10] and a very reduced number of Group 10 representatives are known. In the following sections a general presentation of these synthetic routes, as well as the main characteristic structural features and reactivity patterns of the resulting complexes, is given. For detailed information on the spectroscopic and electrochemical properties of these heteroatom substituted allenylidene complexes, we refer the reader to other specific reviews [9, 10].

2.1 Preparation of Allenylidene Complexes

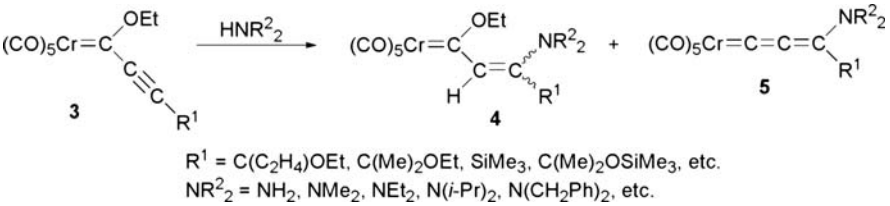
Main routes to π-donor-substituted allenylidene complexes include (1) the nucleophilic addition of secondary amines to Fischer-type carbenes $[M\{{=}C(OR^1)C{\equiv}CR^2\}(CO)_5]$ (M = Cr, W) [9], (2) the Lewis-acid induced abstraction of NR_2 groups from anionic complexes $[M\{C{\equiv}CC(NMe_2)_3\}(CO)_5]^-$ (M = Cr, W) [9], and (3) the regioselective addition of protic nucleophiles to metallacumulenylidenes with more extended unsaturated carbon chains, such as butatrienylidenes or pentatetraenylidenes [10]. In the following sections updated syntheses are presented by Periodic Group.

2.1.1 Group 6 Metals

In sharp contrast with the remaining transition metals, Group 6 allenylidenes $[M({=}C{=}C{=}CR^1R^2)(CO)_5]$ (M = Cr, Mo, W) containing non-donnor substituents at C_γ are in general thermally unstable [11–15]. For this reason, most of the reported examples are substituted derivatives bearing heteroatomic π-donor groups [9]. In this sense, the first stable Group 6 allenylidenes reported in the literature were the amino-allenylidene complexes **2**, prepared by E. O. Fischer and coworkers by a Lewis-acid induced elimination of ethanol from the 3-dimethylamino-1-ethoxy-3-



Scheme 1 Synthesis of the first amino-allenylidene complexes **2**

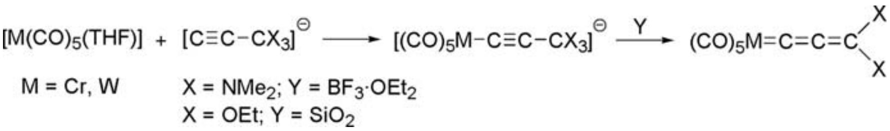


Scheme 2 Synthesis of amino-allenylidene chromium complexes **5**

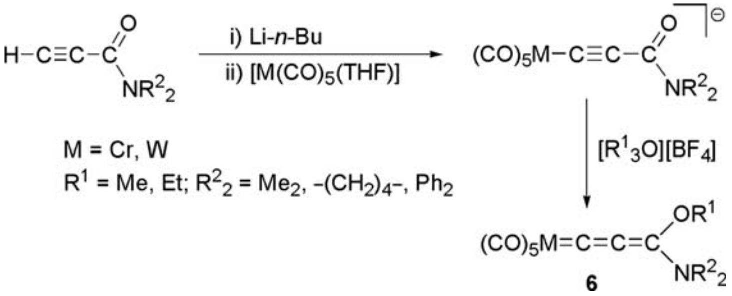
phenylpropenylidene derivatives **1** (Scheme 1) [8]. Following this seminal work, Aumann and coworkers also obtained related amino(phenyl)allenylidene chromium (0) complexes containing dimethylamino, methylphenylamino, ethylphenylamino, or indolino substituents, starting from the appropriate ethoxy-carbene via $AlCl_3$-promoted ethanol elimination [19].

The starting Fischer-type carbene complexes **1** were obtained by Michael addition of dimethylamine to the carbon–carbon triple bond of the corresponding ethoxy-(phenylethynyl)carbenes. In this regard, de Meijere and co-workers observed that the reactions of several primary and secondary amines with this sort of carbenes, in particular chromium derivatives **3** containing bulky substituents at the terminal carbon of the acetylenic unit, result in formation of the aminoallenylidene derivatives **5** as by-products of the expected Michael adducts **4** (Scheme 2) [20–24].

In some cases, replacement of the amines by the corresponding lithium amides turned out to be advantageous, increasing the yields of the aminoallenylidenes (up to 96%) [22]. Following this protocol, galactopyranosylamino-substituted allenylidene complexes of chromium and tungsten could also be prepared [25]. Otherwise, substitution of the corresponding amine by sodium ethoxide in the reactions with $[M\{=C(OEt)C{\equiv}CPh\}(CO)_5]$ (M = Cr, W) yielded the O/C-substituted ethoxy-(phenyl)allenylidene derivatives $[M\{=C{=}C{=}C(OEt)Ph\}(CO)_5]$ (M = Cr, W), albeit in very low yields (ca. 10%) [26]. In general, the **4**:**5** ratios observed were strongly dependent on the steric requirements of R^1 and the reaction conditions employed, reducing considerably the synthetic utility of this methodology. For example, when alkynylcarbene complexes **3** with less bulky substituents R^1 (Me, *i*-Pr, *n*-Pr, etc.) were employed as substrates, only the Fischer-type alkenylcarbene derivatives **4** could be isolated [26]. Moreover, the synthetic approaches depicted in Schemes 1 and 2 drag in another inconvenience since bis(π-donor)-substituted allenylidene complexes cannot be prepared by these routes, their scope being



Scheme 3 Synthesis of Group 6 allenylidenes from deprotonated tris-amino or alkoxo prop-1-ynes



Scheme 4 Access to mixed N/O-substituted allenylidenes **6** starting from propynoic acid amides

confined to allenylidene derivatives with N/C- or N/Si-substitution patterns (R^1 = alkyl, aryl, and $SiMe_3$).

In order to overcome all these synthetic drawbacks, an alternative methodology using tetrahydrofuran solvates $[M(CO)_5(THF)]$ and deprotonated tris-amino or alkoxo prop-1-ynes was developed by H. Fischer and co-workers (Scheme 3), which allowed the preparation of the bis(amino)- and bis(ethoxy)-allenylidene complexes $[M\{=C=C=C(NMe_2)_2\}(CO)_5]$ (M = Cr, W) [27] and $[M\{=C=C=C(OEt)_2\}(CO)_5]$ (M = Cr, W) [28], respectively. Although the latter could not be isolated in pure form, they were conveniently employed as starting materials for further transformations (see below).

As shown in Scheme 4, alkynyl metallates derived from propynoic acid amides can also be used as source of the allenylidene C_3 unit, their reactions with the tetrahydrofuran solvates $[M(CO)_5(THF)]$ affording the N/O-substituted allenylidene complexes **6** after selective *O*-alkylation with $[R_3O][BF_4]$ [29].

The same synthetic approach is also applicable for the preparation of analogous N/N- and N/C-substituted allenylidenes **7–10** (Fig. 4) by using *C*-ethynylimines, such as $HC{\equiv}CC(=NMe)Ph$, 2-ethynylpyridines, 2-ethynylquinoline, or 2-ethynylpyrimidine, instead of propynoic acid amides [29, 30].

Allenylidenes **8** containing six-membered *N*-heterocyclic substituents brominated at 3- and 4-positions were used to introduce various alkynyl groups through classical Pd-catalyzed coupling processes with terminal alkynes, yielding complexes **11–13** (Fig. 4) in moderate to good yields [31]. Desilylation of the $SiMe_3$-containing chromium-allenylidene **11** led to the corresponding ethynyl-terminated derivative, which was used to prepare hetero-binuclear Cr–Ru and Cr–Fe complexes through CuI-catalyzed coupling reactions of the generated terminal $C{\equiv}CH$ unit with $[RuBrCp(CO)_2]$ and $[FeBrCp^*(CO)_2]$, respectively. Oxidative

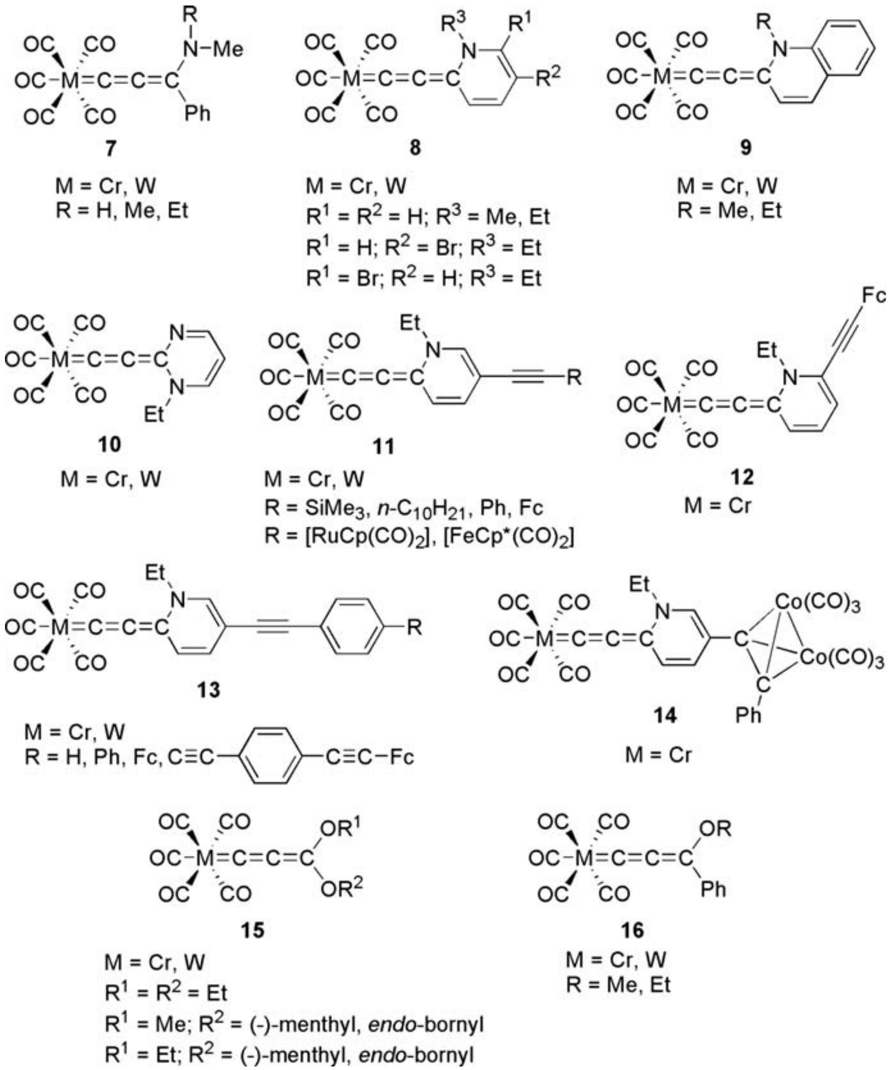
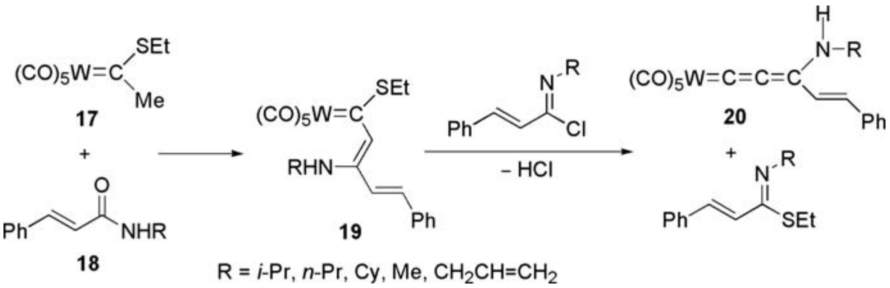


Fig. 4 Structure of chromium and tungsten allenylidenes **7**–**16**

coupling of this ethynyl-terminated allenylidene with $Cu(OAc)_2$ was described affording an unusual homo-binuclear bis(allenylidene) [31]. The addition of $Co_2(CO)_8$ to the terminal carbon–carbon triple bond of the phenylethynyl chromium complex **11** (R = Ph) was also performed, leading to the heterotrinuclear complex **14** [31]. In addition, bimetallic Cr–Cr and W–W species were prepared starting from allenylidenes **10** after coordination of $[M(CO)_5]$ units to the nonalkylated nitrogen atom of the pyrimidyl unit [30].

O/O- and O/C-substituted allenylidene complexes **15** and **16** (Fig. 4) were also accessible starting from ethynyl ketones HC≡CC(=O)R and propynoic acid



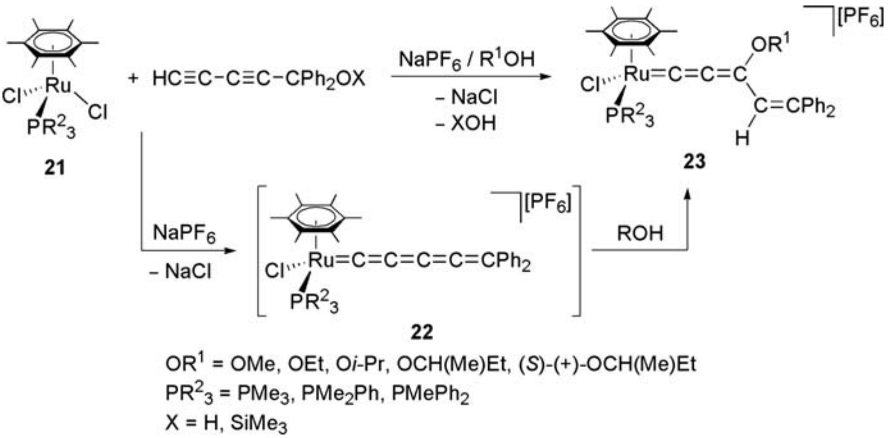
Scheme 5 Synthesis of the tungsten allenylidene complexes **20**

esters HC≡CC(=O)OR, respectively, after sequential deprotonation, coordination to [M(CO)$_5$] units, and final alkylation [9, 28]. Some of these complexes were subsequently used as suitable precursors of related allenylidenes via substitution, insertion and carbene transfer reactions (see reactivity studies below). Quite recently, a further series of allenylidene tungsten derivatives **20** has been synthesized through condensation of the (methyl)thiocarbene complex **17** with α,β-unsaturated secondary amides **18**, followed by imidoyl chloride-promoted thiol elimination (Scheme 5) [32]. However, the yields were low due to the extensive formation of by-products derived from the intramolecular cyclization of intermediates **19**.

2.1.2 Group 8 Metals

In the course of early studies directed to the preparation of stable pentatetraenylidene–ruthenium(II) complexes, Dixneuf and co-workers have described the synthesis and characterization of several alkoxy-substituted alkenyl-allenylidenes **23** through the activation of diynes HC≡C–C≡C–CPh$_2$OX (X = H, SiMe$_3$) by the hexamethylbenzene–ruthenium(II) precursors **21** in the presence of NaPF$_6$ (Scheme 6) [33–35]. The reactions involve the transient formation of highly reactive pentatetraenylidenes [RuCl(=C=C=C=C=CPh$_2$)(η^6-C$_6$Me$_6$)(PR$^2_3$)][PF$_6$] (**22**) via dehydration (or trimethylsilanol elimination) of the diyne upon coordination to the 16-electron intermediates [RuCl(η^6-C$_6$Me$_6$)(PR$^2_3$)]$^+$. Pentatetraenylidenes **22** were not stable enough to be isolated, being instead trapped as the corresponding allenylidenes **23** which result from the nucleophilic addition of alcohols across the C_γ=C_δ double bond of the cumulenic chain. Analogously, the related diphenylamino-substituted allenylidenes [RuCl{=C=C=C(NPh$_2$)CH=CPh$_2$}(η^6-C$_6$Me$_6$)(PR$^2_3$)][PF$_6$] (PR$^2_3$ = PMe$_3$, PMe$_2$Ph, PMePh$_2$) could be isolated using NHPh$_2$ as trapping agent [33–35].

Extension of these studies to other ruthenium fragments, such as [RuCl$_2${κ^4(*N*,*P*,*P*,*P*)–N(CH$_2$CH$_2$PPh$_2$)$_3$}] [36], *cis*-[RuCl$_2$(dppe)$_2$] [37] and *cis*-[RuCl$_2$(dppm)$_2$] [38, 39], led to the related mono(alkenyl-allenylidenes) **24–26** and the bis(alkenyl-allenylidene) **27** (Fig. 5). Pentatetraenylidene derivatives were in all cases



Scheme 6 Synthesis of the alkenyl-allenylidene ruthenium complexes **23**

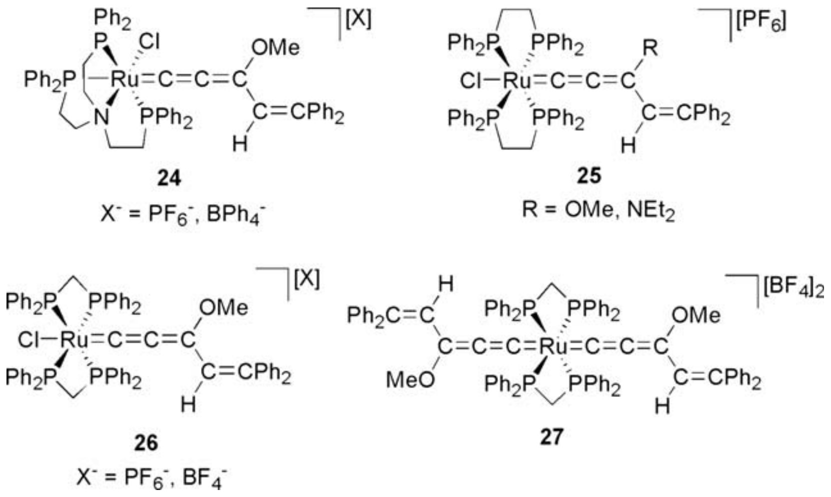
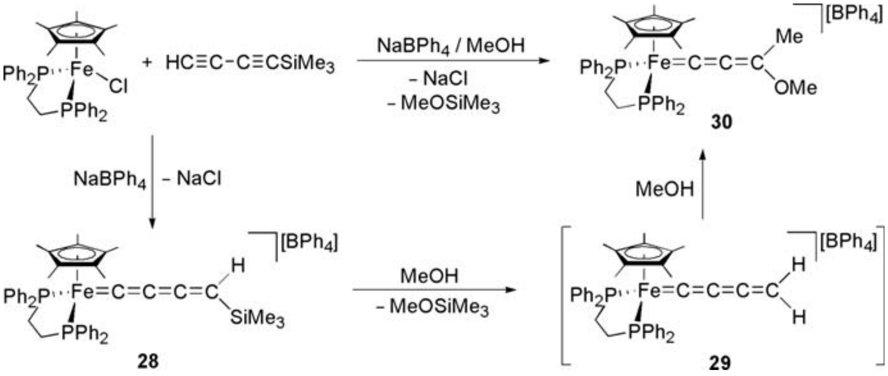


Fig. 5 Structure of mono- and bis-allenylidene ruthenium complexes **24–27**

proposed as transient intermediates, their involvement being unambiguously confirmed by the isolation of *trans*-[RuCl{=C=C=C=C=CPh$_2$}(dppe)$_2$] during the synthesis of complexes **25** [37].

Nucleophilic additions of alcohols, amines, thiols, and selenols to Group 8 butatrienylidene intermediates [M]=C=C=C=CR$_2$ have also been used in the preparation of stable heteroatom-conjugated allenylidene complexes. Thus, activation of trimethylsilyl-1,3-butadiyne HC≡C–C≡CSiMe$_3$ by the iron(II) complex [FeClCp*(dppe)], in methanol and in the presence of NaBPh$_4$, resulted in the high-yield formation of the methoxy-allenylidene [FeCp*{=C=C=C(OMe)Me}



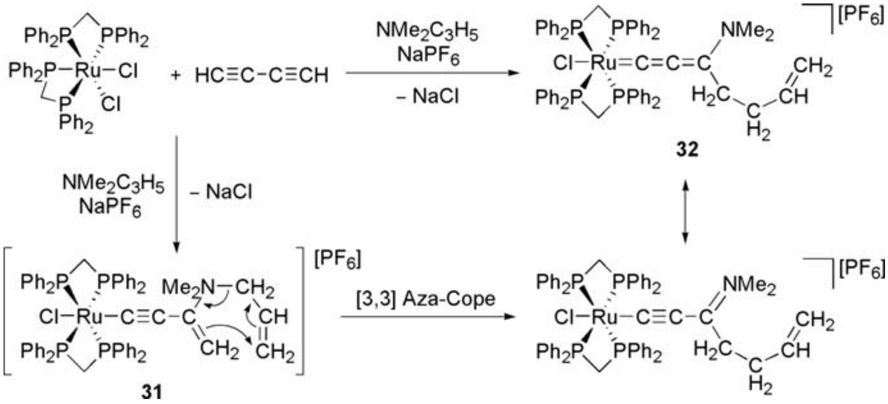
Scheme 7 Synthesis of methoxy-allenylidene iron(II) complex **30**

(dppe)][BPh$_4$] (**30**) via methanol addition across the C$_\gamma$=C$_\delta$ double bond of **29** (Scheme 7) [40]. The unstable butatrienylidene complex **29** is generated from HC≡C–C≡CSiMe$_3$ by means of an initial 1,4-H shift and subsequent desilylation of the intermediate **28**. Similarly, the amino-allenylidene [RuCp*{=C=C=C(NH$_2$)Me}(dppe)][PF$_6$] could be generated by activation of Me$_3$SiC≡C–C≡CSiMe$_3$ with [RuClCp*(dppe)] in the presence of KF/NH$_4$PF$_6$. It results from the addition of NH$_3$ to the butatrienylidene intermediate [RuCp*(=C=C=C=CH$_2$)(dppe)][PF$_6$] [41].

Synthesis of the methoxy-allenylidene ruthenium(II) complex *trans*-[RuCl{=C=C=C(OMe)CH$_2$Ph}(dppe)$_2$][PF$_6$] by addition of methanol to *trans*-[RuCl{=C=C=C=C(H)Ph}(dppe)$_2$][PF$_6$], generated in situ by protonation of the neutral diynyl complex *trans*-[RuCl(C≡C–C≡CPh)(dppe)$_2$] or by direct activation of phenyl-1,3-butadiyne HC≡C–C≡CPh with *cis*-[RuCl$_2$(dppe)$_2$] in presence of NaPF$_6$, has also been described [42]. Other transient butatrienylidene ruthenium (II) complexes, namely *trans*-[RuCl(=C=C=C=CH$_2$)(dppm)$_2$][SbF$_6$] and [RuCp(=C=C=C=CH$_2$)(PPh$_3$)$_2$][PF$_6$], generated by activation of HC≡C–C≡CH could also be trapped by addition of NuH nucleophiles across the C$_\gamma$=C$_\delta$ double bond to yield stable allenylidenes *trans*-[RuCl{=C=C=C(Nu)Me}(dppm)$_2$][SbF$_6$] (Nu = NR^{1}R^2 (several examples) [43], SEt [44]) and [RuCp{=C=C=C(NPh$_2$)Me}(PPh$_3$)$_2$][PF$_6$] [45, 46], respectively.

The behavior of *trans*-[RuCl(=C=C=C=CH$_2$)(dppm)$_2$][PF$_6$] towards the tertiary amine allyldimethylamine merits to be highlighted since the reaction led to the dimethylamino-allenylidene complex **32** through an Aza-Cope (or Claisen) rearrangement of the initially generated quaternary vinyl-allyl-ammonium salt [RuCl{C≡CC(NMe$_2$CH$_2$CH=CH$_2$)=CH$_2$}(dppm)$_2$][PF$_6$] (**31**) (Scheme 8) [47].

This unusual reactivity was subsequently extended to a broad variety of allylic and propargylic amines, in combination with other ruthenium(II) metal fragments, allowing the isolation of aminoallenylidene complexes **33–35** [47–49] (Fig. 6). In addition, the synthesis of the thio-allenylidene [44] and seleno-allenylidene [50] derivatives **36** from the in situ generated butatrienylidene *trans*-[RuCl(=C=C=C=CH$_2$)(L$_2$)$_2$]$^+$ (L$_2$ = dppm, dppe) and the corresponding allyl sulfides



Scheme 8 Synthesis of the amino-allenylidene complex **32** through a [3,3] Aza-Cope rearrangement

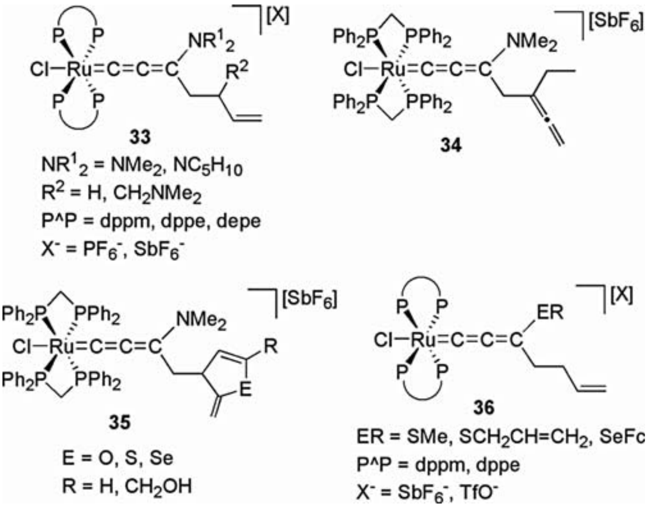
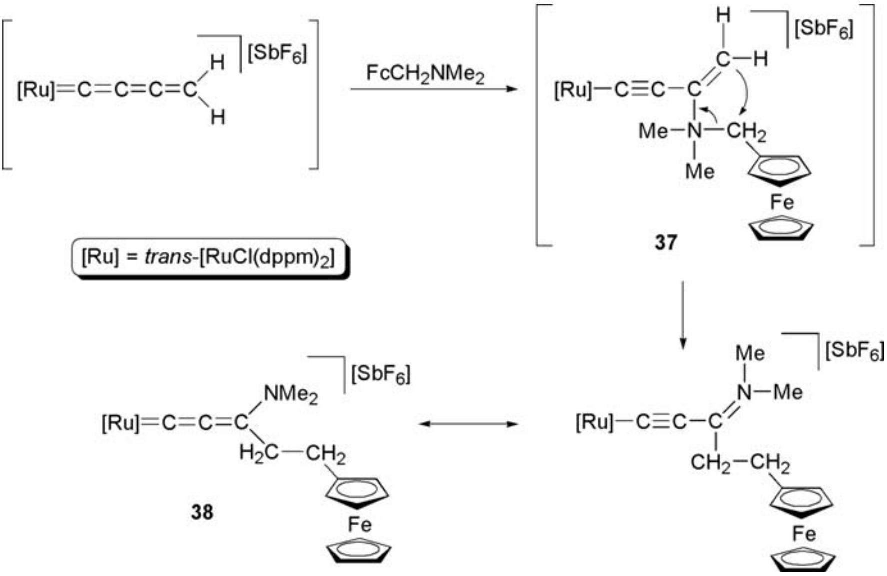


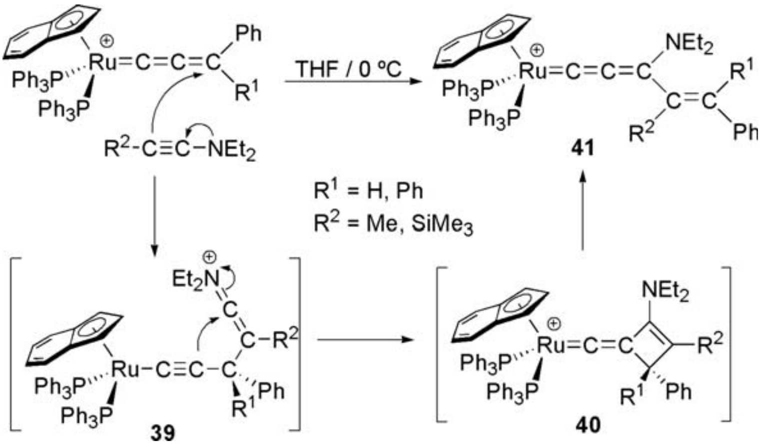
Fig. 6 Structure of the amino-, thio-, and seleno-allenylidenes **33–36**

or allyl selenides, respectively, has also been described (Fig. 6). As observed for **32** (see Scheme 8), the resulting cationic complexes showed structures intermediate between allenylidenes and the mesomeric alkynyl forms, the contribution of the latter being enhanced with the increasing donor properties of the heteroatom.

Formation of *trans*-$[RuCl\{=C=C=C(NMe_2)CH_2CH_2Fc\}(dppm)_2][SbF_6]$ (**38**) by treatment of transient *trans*-$[RuCl(=C=C=C=CH_2)(dppm)_2][SbF_6]$ with $FcCH_2NMe_2$ has also been described [51]. In this case, the initially generated 2-ammoniobutenynyl derivative **37** evolved into **38** through the migration of the resonance stabilized ferrocenylcarbenium ion from the quaternary nitrogen atom to the neighboring nucleophilic C_δ (Scheme 9).



Scheme 9 Synthesis of amino-allenylidene ruthenium(II) complex **38**



Scheme 10 Synthesis of alkenyl(amino)allenylidene ruthenium(II) complexes **41**

Otherwise, the reactions of indenyl-ruthenium(II) allenylidenes [Ru(η^5-C_9H_7){=C=C=C(R^1)Ph}(PPh_3)$_2$][PF_6] (R^1 = H, Ph) with ynamines $R^2C{\equiv}CNEt_2$ (R^2 = Me, $SiMe_3$) have been reported to yield the alkenyl(amino)allenylidene complexes **41** via insertion of the ynamine into the $C_\beta{=}C_\gamma$ allenylidene bond (Scheme 10) [52, 53]. This insertion process involves an initial nucleophilic addition of the ynamine at C_γ atom of the cumulene, which leads to the cationic alkynyl intermediate complexes **39**. Further ring closing, involving the C_β atom, generates the [2+2]

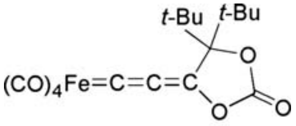

42

Fig. 7 Structure of the iron–allenylidene complex **42**

vinylidene cycloadducts **40** which, in a final cycloreversion step, evolves into allenylidenes **41**. Likewise, the analogous complex [Ru(η^5-C_9H_7){=C=C=C(NEt$_2$)C(Me)=CPh$_2$}{κ^1(P)-Ph$_2$PCH$_2$CH=CH$_2$}(PPh$_3$)][PF$_6$] could be prepared by the reaction of the allyldiphenylphosphine derivative [Ru(η^5-C_9H_7)(=C=C=CPh$_2$){κ^1(P)-Ph$_2$PCH$_2$CH=CH$_2$}(PPh$_3$)][PF$_6$] with MeC≡CNEt$_2$ [54]. Based on these insertion reactions, a systematic route to prepare sequentially polyalkenyl-allenylidene complexes has been reported (details are given in the reactivity section below).

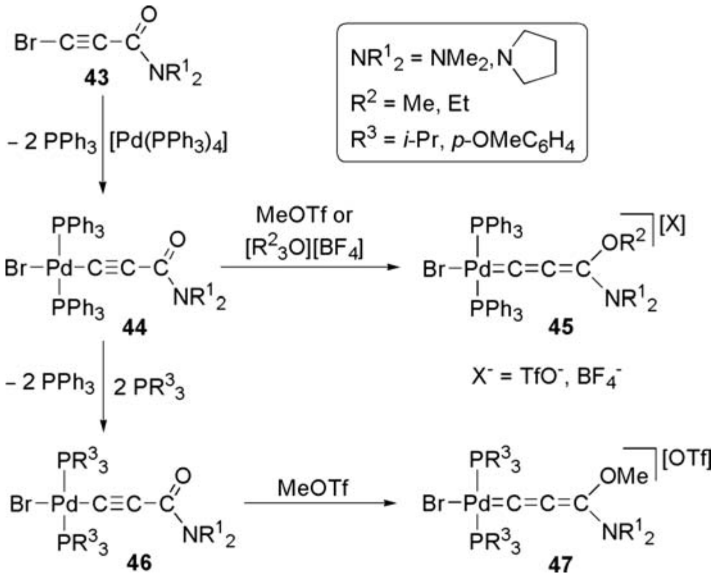
Finally, it should be mentioned that the reaction of the dianion derived from alkynol HC≡CC(OH)*t*-Bu$_2$ with [Fe(CO)$_4$(NMe$_3$)] led to a complex mixture of mono- and polynuclear products, from which the iron(0)-allenylidene complex **42** (Fig. 7) could be isolated [55].

2.1.3 Group 10 Metals

Palladium complexes *trans*-[PdBr{=C=C=C(NR$^1_2$)OR^2}(PPh$_3$)$_2$][X] (NR$^1_2$ = NMe$_2$, dipyrrolidin-1-ylamine; R^2 = Me, Et; X$^-$ = TfO$^-$, BF$_4^-$; **45**) and *trans*-[PdBr{=C=C=C(NR$^1_2$)OMe}(PR$^3_3$)$_2$][OTf] (NR$^1_2$ = NMe$_2$, dipyrrolidin-1-ylamine; R^3 = *i*-Pr, *p*-OMeC$_6$H$_4$; **47**), recently described by H. Fischer and co-workers, constitute the only Group 10 allenylidenes reported to date in the literature [56]. The syntheses of cationic compounds **45** proceeded smoothly through the initial oxidative addition of bromoalkynes **43** to [Pd(PPh$_3$)$_4$] and subsequent *O*-alkylation of the resulting neutral alkynyl complexes **44** (Scheme 11). Otherwise, exchange of PPh$_3$ in **44** by the more basic phosphines P(*i*-Pr)$_3$ and P(*p*-OMeC$_6$H$_4$)$_3$ gave the alkynyl complexes **46** which, after treatment with MeOTf, afforded allenylidenes **47** (Scheme 11).

2.2 Structure of Allenylidene Complexes

Structural parameters of selected mononuclear complexes containing heteroatomic π-donor-substituted allenylidene ligands are summarized in Table 1. When these data are compared to those reported for related complexes bearing conventional alkyl or aryl substituents (see Table 1 of chapter "All-Carbon-Substituted Allenylidene and Related Cumulenylidene Ligands"), a lengthening of the M=C$_\alpha$ bond



Scheme 11 Synthesis of the palladium allenylidene complexes **45** and **47**

distances, accompanied by a tendency toward shorter $C_\alpha{=}C_\beta$ and longer $C_\beta{=}C_\gamma$ bonds, becomes evident. These observations provide further support for a significant or even dominating contribution of the alkynyl-type resonance forms **E** and **F** vs the cumulenic one **D**. The former are favored by the ability of the heteroatom lone pair to stabilize a positive charge on the carbon chain (Fig. 8).

The structure of amino-substituted allenylidene complexes merits special attention since those compounds derived from unsymmetrically substituted amines usually give rise to isomeric mixtures in solution (C–N bond rotamers) [19–24, 27, 43]. For complexes *trans*-$[\mathrm{RuCl}\{{=}\mathrm{C}{=}\mathrm{C}{=}\mathrm{C}(\mathrm{NR}^1\mathrm{R}^2)\mathrm{Me}\}(\mathrm{dppm})_2]^+$ the rotational energy barriers around the C–N bond could be experimentally determined by dynamic $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectroscopy, the high values observed (ca. 85 kJ mol^{-1}) pointing to a dominant contribution of the iminium-alkynyl resonance forms *trans*-$[\mathrm{RuCl}\{\mathrm{C}{\equiv}\mathrm{C}{-}\mathrm{C}({=}\mathrm{NR}^1\mathrm{R}^2)\mathrm{Me}\}(\mathrm{dppm})_2]^+$ (**F** in Fig. 8) [43]. Quantum chemical calculations on the model complex *trans*-$[\mathrm{RuCl}\{{=}\mathrm{C}{=}\mathrm{C}{=}\mathrm{C}(\mathrm{NMe}_2)\mathrm{Me}\}(\mathrm{dhpm})_2]^+$ (dhpm = $H_2PCH_2PH_2$) confirmed that these high barriers are electronic rather than steric in origin [43]. Thus, in good qualitative agreement with the experimental values, the energy difference between the optimized structures for a parallel and an orthogonal orientation of the NMe_2 entity with respect to the allenylidene π-system amounted to 109 kJ mol^{-1}. Moreover, upon rotation around the iminium-type CN bond from the parallel to the orthogonal orientation, a decoupling of the nitrogen lone pair and the π-system of the allenylidene ligand was observed, resulting in a significantly longer C–N bond distance and a tetrahedrally coordinated nitrogen atom.

Table 1 Structural data of selected mononuclear π-donor-substituted allenylidene complexes

Compound	$M{=}C_\alpha$(Å)	$C_\alpha{=}C_\beta$(Å)	$C_\beta{=}C_\gamma$(Å)	$M–C_\alpha–C_\beta$(°)	$C_\alpha–C_\beta–C_\gamma$(°)	[Ref]
$[Cr(=C=C=C\{N(Et)CH=CHCH=CH\})(CO)_5]$	2.042(2)	1.225(2)	1.409(2)	176.9(2)	175.0(2)	[29???]
$[Cr(=C=C=C\{N(H)CH_2CH_2N(CH_2CH_2NH_2)\})(CO)_5]$	2.030(3)	1.214(4)	1.411(4)	175.8(2)	173.1(3)	[61???]
$[Cr\{=C=C=C(NEt_2)C(Me)=C(p\text{-}NMe_2C_6H_4)_2\}(CO)_5]$	2.019(5)	1.221(7)	1.392(7)	175.5(5)	173.8(5)	[64???]
$[Cr\{=C=C=C(NMe_2)Ph\}(CO)_4(PPh_3)]$	2.000(3)	1.236(4)	1.398(4)	177.4(2)	172.5(3)	[57???]
$[Cr\{=C=C=C(NMe_2)O–(-)–menthyl\}(CO)_5]$	1.996(6)	1.228(8)	1.366(7)	176.1(5)	171.1(6)	[28]
$[Cr\{=C=C=C(NBn_2)CMe_2OEt\}(CO)_5]$	1.993(2)	1.222(2)	1.388(2)	177.2(1)	173.5(2)	[22]
$[W\{=C=C=C(NMe_2)_2\}(CO)_5]$	2.185(8)	1.205(11)	1.386(11)	180.0(1)	180.0(1)	[27]
$[W\{=C=C=C(NMe_2)CH=C(NMe_2)_2\}(CO)_5]$	2.178(5)	1.216(7)	1.427(6)	178.8(4)	172.8(5)	[27]
$[W\{=C=C=C(NMe_2)N=C(NH_2)Ph\}(CO)_5]$	2.173(6)	1.207(8)	1.426(8)	176.1(5)	179.3(6)	[62???]
$[W\{=C=C=C(NMe_2)NHPh\}(CO)_5]$	2.158(9)	1.179(13)	1.420(12)	179.3(9)	179.0(10)	[61???]
$[W\{=C=C=C(NMe_2)Ph\}(CO)_5]$	2.150(6)	1.228(8)	1.399(8)	175.3(5)	174.0(6)	[29???]
$[W\{=C=C=C(NMe_2)OMe\}(CO)_5]$	2.142(10)	1.253(13)	1.408(12)	176.7(7)	179.5(9)	[29???]
$[Fe(=C=C=C\{OC(=O)OC(t\text{-}Bu)_2\})(CO)_4]$	1.803(5)	1.255(6)	1.315(6)	177.9(5)	177.2(5)	[55???]
$[Ru\{=C=C=C(OCH_3)CH=CPh_2\}_2(dppm)_2][BF_4]_2$	1.997(7)	1.22(1)	1.39(1)	175.0(7)	171.4(9)	[38, 39???]
$[RuCp\{=C=C=C(NPh_2)Me\}(PPh_3)_2][PF_6]$	1.97(1)	1.18(2)	1.41(2)	171(1)	178(2)	[63???]
$[Ru(\eta^5\text{-}C_9H_7)\{=C=C=C(NEt_2)C(Me)=CPh_2\}(PPh_3)_2][PF_6]$	1.956(5)	1.235(6)	1.392(6)	168.0(4)	174.7(5)	[52, 53???]
$[RuCl\{=C=C=C(Me)NMeBn\}(dppm)_2][SbF_6]$	1.947(6)	1.217(9)	1.398(9)	175.6(6)	170.8(8)	[43???]
$[Ru(\eta^5\text{-}C_9H_7)\{=C=C=C(NEt_2)C(Me)=CHC(Me)=CPh_2\}(PPh_3)_2][PF_6]$	1.946(4)	1.229(5)	1.390(5)	174.6(3)	177.8(4)	[52, 53???]
$[RuCp^*\{=C=C=C(NH_2)Me\}(dppe)][PF_6]$	1.942(3)	1.238(4)	1.382(4)	178.4(3)	167.6(3)	[41???]
$[RuCl\{=C=C=C(NMe_2)CH_2CH_2CH=CH_2\}(dppe)_2][SbF_6]$	1.934(8)	1.232(13)	1.393(13)	177.8(7)	168.7(9)	[48???]
$[RuCl\{=C=C=C(OMe)CH=CPh_2\}\{\kappa^4(N,P,P,P)–N(CH_2CH_2PPh_2)_3\}][PF_6]$	1.921(5)	1.254(7)	1.369(7)	174.1(3)	170.2(6)	[36???]
$[Pd(O_2CCF_3)\{=C=C=C(NMe_2)OMe\}(PPh_3)_2][BF_4]$	1.925(3)	1.217(4)	1.420(4)	176.7(2)	172.6(3)	[56???]

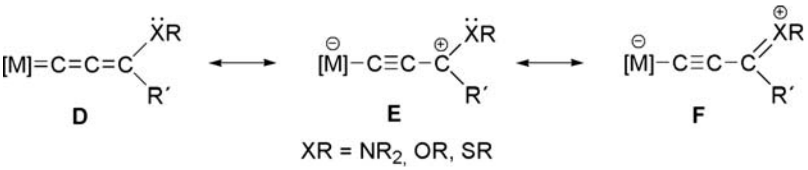


Fig. 8 Canonical forms of heteroatom-substituted allenylidene complexes

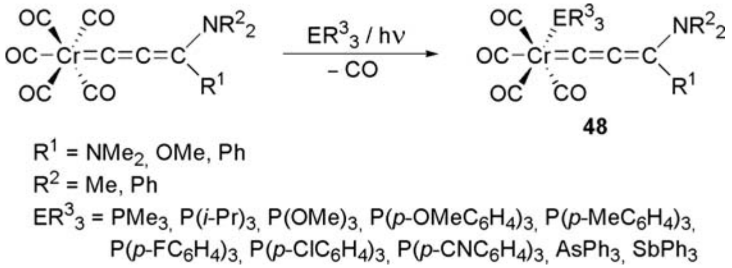
2.3 *Reactivity of Allenylidene Complexes*

As already commented in the introduction of this chapter, regardless of its substitution pattern, the main trends of allenylidene reactivity are governed by the electron deficient character of the C_α and C_γ carbon atoms of the cumulenic chain, the C_β being a nucleophilic center [9–15]. Thus, as occurs with their all-carbon substituted counterparts, electrophilic additions on π-donor-substituted allenylidene complexes are expected to take place selectively at C_β, while nucleophiles can add to both C_α and C_γ atoms. However, the extensive π-conjugation present in these molecules results in a reduced reactivity of the cumulenic chain and, in some cases, in marked differences in the regioselectivity of the nucleophilic additions when compared to the all-carbon substituted allenylidenes. In the following subsections updated reactivity studies on π-donor-substituted allenylidene complexes are presented by Periodic Group.

2.3.1 Group 6 Metals

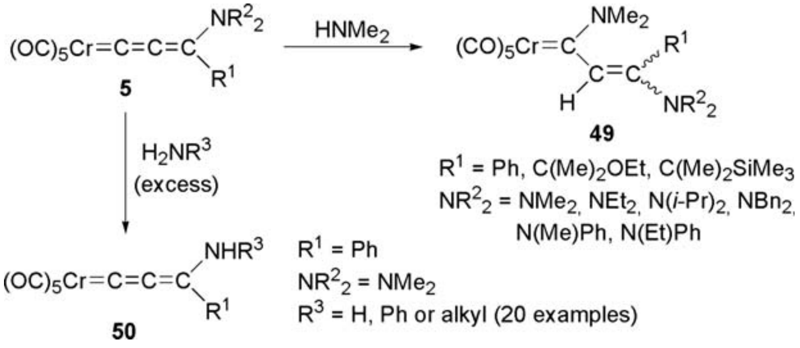
As it was extensively discussed in Our Preceding Chapter 6 the reactivity of Group 6 allenylidene complexes $[M({=}C{=}C{=}CR^1R^2)(CO)_5]$ ($M = Cr, W$; R^1 and R^2 = alkyl or aryl group) towards nucleophiles (alcohols, phosphines and amines) is clearly dominated by the regioselective additions at the electrophilic α-carbon. However, the behavior of amino-substituted chromium-allenylidenes differs from this general reactivity pattern and nucleophiles such as phosphines, phosphites, arsines, or stibines do not add to the cumulenic chain. Instead, the reactions lead, upon UV-irradiation, to the substitution of one CO ligand to afford *cis*-allenylidene tetracarbonyl complexes **48** (Scheme 12) [29, 57]. This behavior is in agreement with the expected lowering of reactivity of the allenylidene chain upon introduction of π-donor substituents due to the increase of the LUMO energy. Similarly, the photo-induced reaction of the bis(alkoxy)-substituted allenylidene $[Cr\{{=}C{=}C{=}C(OEt)OR\}(CO)_5]$ (R = *endo*-bornyl) with excess of PPh_3 generated a mixture of the corresponding tetra- and tri-carbonyl allenylidenes, which could be separated after chromatographic workup [28].

Otherwise, while the reactions of chromium mono(amino)allenylidene complexes **5** with dimethylamine afforded the alkenyl(amino)carbene derivatives **49** by means of the expected N–H addition across the $C_\alpha{=}C_\beta$ double bond (Scheme 13)



R^1 = NMe$_2$, OMe, Ph
R^2 = Me, Ph
ER^3_3 = PMe$_3$, P(i-Pr)$_3$, P(OMe)$_3$, P(p-OMeC$_6$H$_4$)$_3$, P(p-MeC$_6$H$_4$)$_3$, P(p-FC$_6$H$_4$)$_3$, P(p-ClC$_6$H$_4$)$_3$, P(p-CNC$_6$H$_4$)$_3$, AsPh$_3$, SbPh$_3$

Scheme 12 Synthesis of tetracarbonyl-chromium allenylidene complexes **48**



R^1 = Ph, C(Me)$_2$OEt, C(Me)$_2$SiMe$_3$
NR^2_2 = NMe$_2$, NEt$_2$, N(i-Pr)$_2$, NBn$_2$, N(Me)Ph, N(Et)Ph

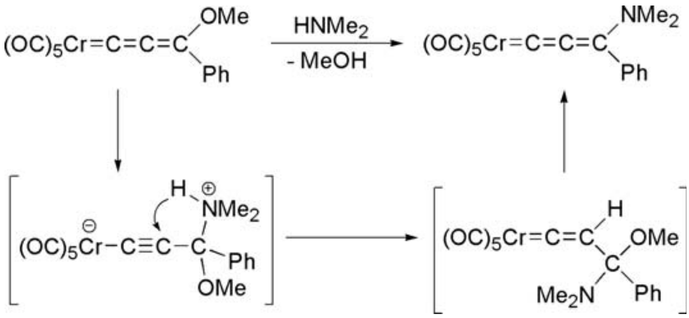
R^1 = Ph
NR^2_2 = NMe$_2$
R^3 = H, Ph or alkyl (20 examples)

Scheme 13 Reactivity of chromium allenylidene complexes **5** towards amines

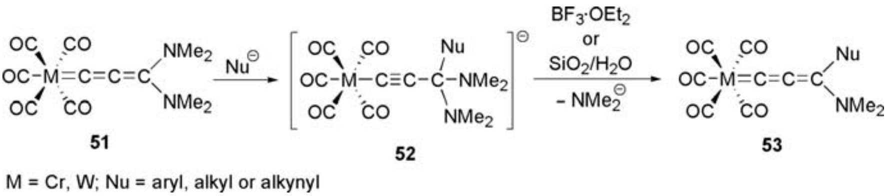
[22, 24, 28, 29, 58], treatment of **5** (R^1 = Ph; R^2 = Me) with a large excess of ammonia or primary amines R^3NH_2 gave rise to the substitution of the dimethylamino group and formation of the derivatized chromium allenylidenes **50** [58].

Exchange instead of addition reactions were also observed starting from alkoxy-substituted allenylidenes. For example, treatment of the chromium derivative [Cr{=C=C=C(OMe)Ph}(CO)$_5$] with one equivalent of Me$_2$NH resulted in the high-yield formation of the amino-allenylidene complex [Cr{=C=C=C(NMe$_2$)Ph}(CO)$_5$] [28]. This unexpected substitution process, which is initiated by the nucleophilic attack of dimethylamine to the C_γ atom of the allenylidene chain followed by elimination of methanol (Scheme 14), can be considered as the “allenylidene version” of the classical aminolysis of Fischer-type alkoxycarbene complexes [59, 60]. Exchange reactions of the alkoxy groups by primary and secondary amines in complexes [Cr{=C=C=C(NMe$_2$)OMe}(CO)$_5$] [9, 29, 61, 62] and [M{=C=C=C(OR)OEt}(CO)$_5$] (M = Cr, W; R = Et, (−)-menthyl, *endo*-bornyl) [28] have also been described, allowing the preparation of a large variety of novel mono- and di-amino substituted Group 6 allenylidenes.

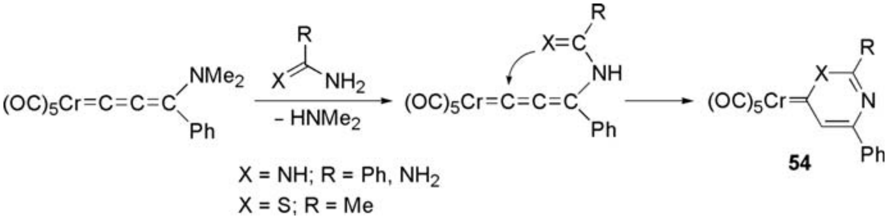
Substitution of one dimethylamino group by alkyl, aryl, or alkynyl groups in complexes [M{=C=C=C(NMe$_2$)$_2$}(CO)$_5$] (M = Cr, W; **51**) has also been described [9]. The process occurs through an initial addition of the anionic carbon nucleophile to the C_γ atom of **51** and subsequent abstraction of one dimethylamido



Scheme 14 Substitution of the methoxy group in complex [Cr{=C=C=C(OMe)Ph}(CO)$_5$]



Scheme 15 Synthesis of dimethylamino(organyl)allenylidene complexes **53**



Scheme 16 Synthesis of *N*- and *S*-heterocyclic chromium carbenes **54**

group in the resulting metallate **52** upon treatment with $BF_3{\cdot}OEt_2$ or SiO_2/H_2O (Scheme 15). Such a transformation of the bis(dimethylamino)allenylidene ligand offers a facile access to a great variety of N/C-substituted allenylidene derivatives **53**. All these results clearly indicate a marked preference of the heteroatom-substituted Group 6 allenylidenes for the C_γ vs C_α additions opposite to their alkyl or aryl-substituted counterparts.

Going one step beyond, the reaction of these π-donor-substituted Group 6 allenylidenes with bifunctional *N*,*N*- or *N*,*S*-dinucleophiles opened up a fruitful route for the synthesis of an extensive family of *N*- or *S*-heterocyclic carbenes. Thus, treatment of complex [Cr{=C=C=C(NMe$_2$)Ph}(CO)$_5$] with benzamidine, guanidine or thioacetamide has been reported to yield the α,β-unsaturated carbenes **54** (Scheme 16) [62], arising from nitrogen attack at C_γ, subsequent $HNMe_2$

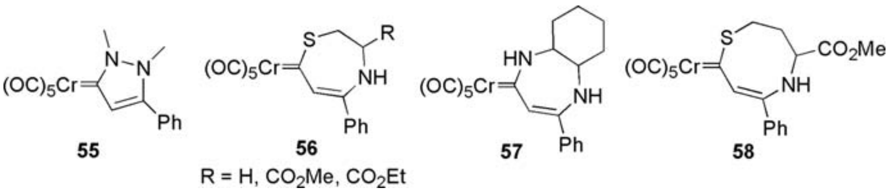
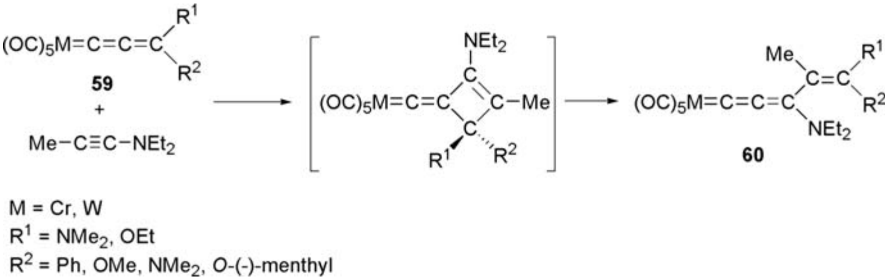


Fig. 9 Five-, seven-, and eight-membered heterocyclic carbene species **55–58**



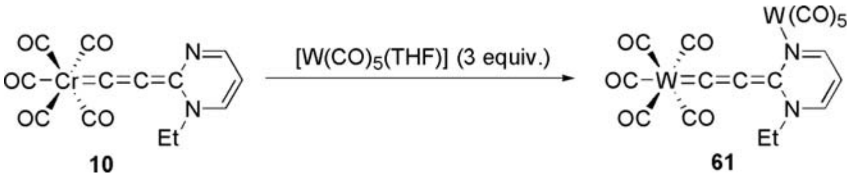
Scheme 17 Synthesis of alkenyl(amino)allenylidenes **60**

elimination, and further reorganization of the molecule through a ring-closing process.

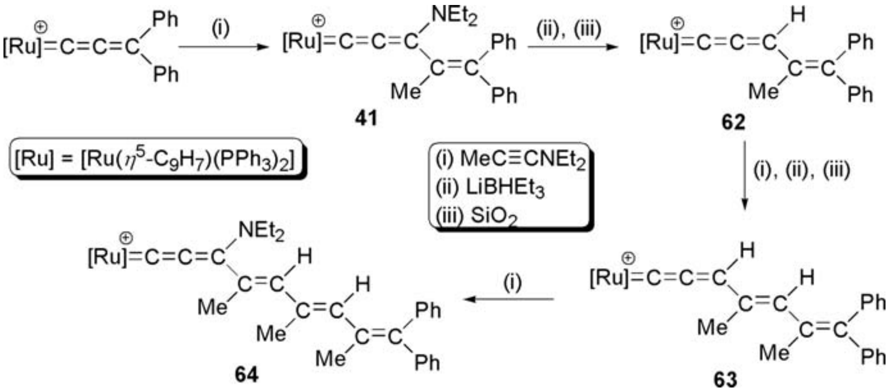
The addition of other bifunctional nucleophiles also allowed the preparation, in moderate to high yields, of the five-, seven-, and eight-membered heterocyclic carbene species **55–58** (Fig. 9) which, in some cases, were formed along with minor amounts of other derivatives [63]. Related 1,2,3-diheterocyclizations involving (ethoxy)allenylidene complexes have been described, ethanol instead of $HNMe_2$ being released in this case [62].

Insertion of ynamine $MeC{\equiv}CNEt_2$ into the $C_\beta{=}C_\gamma$ bond of allenylidenes **59** has also been described and constitutes an interesting approximation to prepare alkenyl(amino)allenylidenes **60** (Scheme 17) [9, 28]. Analogously, the bis(aryl) allenylidene complexes $[M(=C=C=CR^1_2)(CO)_5]$ (M = Cr, W; R^1 = Ph, p-MeC_6H_4, p-$OMeC_6H_4$, p-$NMe_2C_6H_4$) also react with different ynamines R^2-$C{\equiv}C{-}NEt_2$ (R^2 = Me, Ph), affording the corresponding alkenyl(amino) allenylidenes $[M\{=C=C=C(NEt_2)C(R^2)=CR^1_2\}(CO_5)]$ (M = Cr, W; R^1 = Ph, p-MeC_6H_4, p-$OMeC_6H_4$, p-$NMe_2C_6H_4$; R^2 = Me, Ph). However, in these cases, the reactions are not regioselective and mixtures with other compounds are formed [64].

Otherwise, treatment of the chromium complex **10** with an excess of $[W(CO)_5(THF)]$ afforded the tungsten allenylidene **61** by transmetallation of the cumulenic ligand and further addition of $W(CO)_5$ to the N-atom of the heterocyclic substituent (Scheme 18) [30]. The related chromium complexes $[Cr(=C=C=CR^1R^2)(CO)_5]$ (R^1 = NMe_2, R^2 = NMe_2, OMe, Ph; R^1 = N(Et)Me, R^2



Scheme 18 Transmetallation of an allenylidene ligand from chromium to tungsten



Scheme 19 Synthesis of the trienyl(amino)allenylidene complex **64**

= Ph; $R^1 = N(n\text{-Bu})Me$, $R^2 = Ph$; $R^1 = NPh_2$, $R^2 = OMe$) were also able to transfer the allenylidene ligand to tungsten. In contrast, the reverse transmetallation from tungsten to chromium could not be achieved. DFT analysis on the reaction pathway indicated that it proceeds by means of an associative rather than a dissociative mechanism, coordination of a $[W(CO)_5]$ fragment to the $C_\alpha{=}C_\beta$ bond of the chromium allenylidene ligand being the initial step [30].

2.3.2 Group 8 Metals

As commented previously, alkenyl(amino)allenylidene ruthenium(II) complexes **41** are easily accessible through the reaction of indenyl-Ru(II) precursors with ynamines (Scheme 10) [52–54]. Based on this reactivity, an original synthetic route to polyunsaturated allenylidene species could be developed (Scheme 19) [52, 53]. Thus, after the first ynamine insertion, complex **41** could be transformed into the secondary derivative **62** by treatment with $LiBHEt_3$ and subsequent purification on silica–gel column. Complex **62** is able to insert a second ynamine molecule, via the cyclization/cycloreversion pathway discussed above, to generate the corresponding dienyl(amino)allenylidene species. Further transformations of this intermediate in the presence of $LiBHEt_3$ and SiO_2

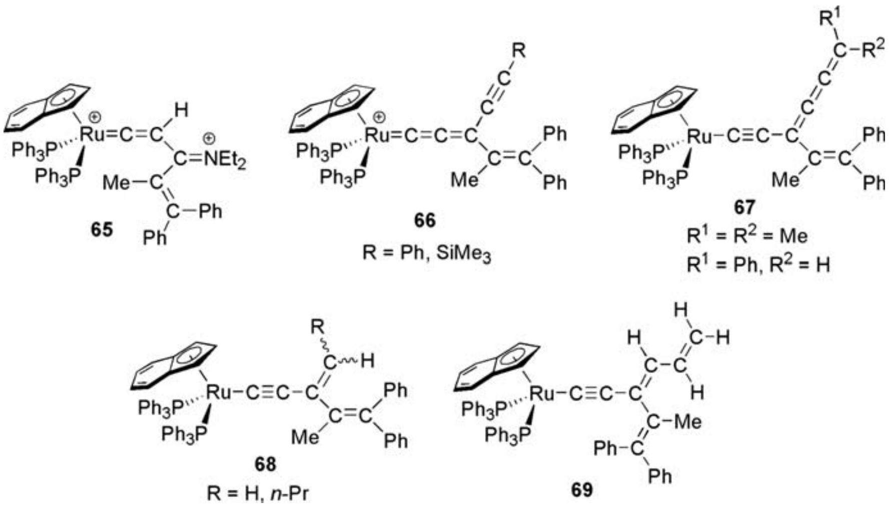


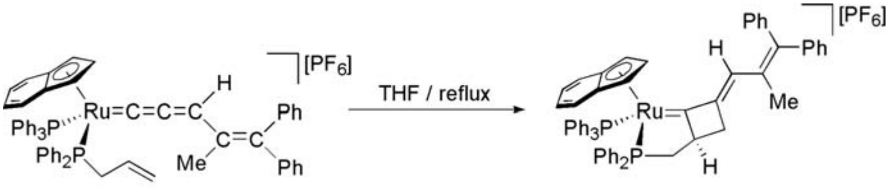
Fig. 10 Structure of the indenyl-ruthenium(II) complexes **65–69**

furnished the monosubstituted dienylallenylidene complex **63**. Finally, a third ynamine insertion provided the highly unsaturated trienyl(amino)allenylidene compound **64**. All the processes involved in this synthetic methodology were regio- and stereoselective giving rise to the formation of **64** as the *trans*,*trans* isomer exclusively.

The alkenyl(amino)allenylidene complex **41** is also prone to undergo electrophilic additions at the C_β atom of the cumulenic chain. Thus, treatment of **41** with $HBF_4{\cdot}OEt_2$ led to the spectroscopically characterized dicationic vinylidene complex **65** (Fig. 10) [52, 53]. Related C_β-protonations of complexes **35** (Fig. 6) have also been described [49].

Nucleophilic additions of acetylides and other carbanions at the C_γ atom of the alkenyl(amino)allenylidene **41** have been described. Thus, the reaction of compound **41** with an excess of $LiC{\equiv}CR$ ($R = Ph, SiMe_3$) or $LiC{\equiv}CCHR^1R^2$ ($R^1 = R^2 = Me$; $R^1 = Ph$, $R^2 = H$) afforded, after treatment with $HBF_4{\cdot}OEt_2$ or Al_2O_3, the disubstituted alkynylalkenylallenylidenes **66** and 3-alkenyl-3,4,5-hexatrienynyl derivatives **67**, respectively (Fig. 10) [52, 53]. Otherwise, the addition of LiR ($R = Me$, *n*-Bu) or allylmagnesium bromide ($BrMgCH_2CH{=}CH_2$) to a THF solution of **41** led, after treatment with Al_2O_3, to the butadiene- and hexadiene–alkynyl complexes **68** and **69**, respectively (Fig. 10) [52, 53].

Analogously to what has been observed for complex **41**, treatment of the related allyldiphenylphosphine derivative $[Ru(\eta^5\text{-}C_9H_7)\{{=}C{=}C{=}C(NEt_2)C(Me){=}CPh_2\}\{\kappa^1(P)\text{-}Ph_2PCH_2CH{=}CH_2\}(PPh_3)][PF_6]$ with $LiBHEt_3$ and subsequent purification on a silica-gel column afforded the mono-substituted alkenylallenylidene **70** which, upon warming, evolves into the cyclobutylidene complex **71** via intramolecular [2+2] cycloaddition of the allylic C=C bond of the allylphosphine with the $C_\alpha{=}C_\beta$ bond of the allenylidene moiety (Scheme 20) [54].



70

71

Scheme 20 Synthesis of the cyclobutylidene complex **71**

3 Higher Cumulenylidene Complexes

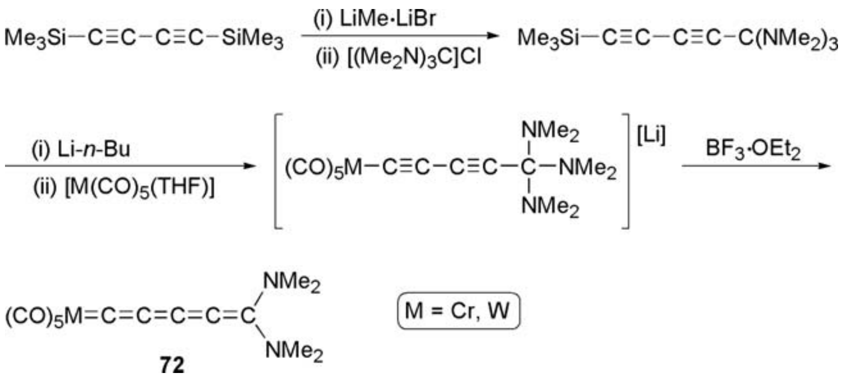
As already commented in the introduction of this article, theoretical calculations have suggested an increased stability of odd-chain metallacumulenes bearing π-donor substituents when compared to their all-carbon substituted counterparts [16]. However, despite this theoretical prediction, synthetic efforts directed to the preparation of heteroatom-substituted metallacumulenes longer than allenylidenes have been scarce till now. All the reported examples belong to the family of amino-substituted Group 6 cumulenylidenes. In this section a survey of their chemistry is presented.

3.1 Pentatetraenylidene Complexes

Following a synthetic strategy related to that used in the preparation of the diamino-substituted allenylidenes $[M\{=C=C=C(NMe_2)_2\}(CO)_5]$ (M = Cr, W), the pentatetraenylidene complexes **72** could be synthesized in moderate yield (36–42%) starting from diyne $Me_3Si(C{\equiv}C)_2SiMe_3$ (Scheme 21) [27]. Key steps are the treatment of solvates $[M(CO)_5(THF)]$ with lithium 5,5,5-tris(dimethylamino) penta-1,3-diyne, generated in situ from Li-*n*-Bu and $Me_3SiC{\equiv}CC{\equiv}CC(NMe_2)_3$, and the subsequent abstraction of one dimethylamino group on the resulting metallates $[M\{C{\equiv}CC{\equiv}CC(NMe_2)_3\}(CO)_5][Li]$ upon treatment with $BF_3{\cdot}OEt_2$.

Essentially six resonance structures (**G–L** in Fig. 11) have to be taken into account for complexes **72**, their spectroscopic data, as well as the X-ray structural analysis performed on the tungsten derivative, suggesting that strongly dipolar ylidic structures **J–L** are the most important contributions to the overall bonding situation.

On the basis of the resonance forms depicted in Fig. 11, nucleophilic attacks on complexes **72** are expected to occur at the metal-bound C_α at C_γ or at the terminal C_ε atom of the carbon chain where positive charges are located along the different structures. As already discussed in our preceding chapter, this prediction is in complete accord with the extensive theoretical calculations performed in metallacumulenes which, regardless of the substituents of the chain and the metal fragment



Scheme 21 Synthesis of the pentatetraenylidene complexes **72**

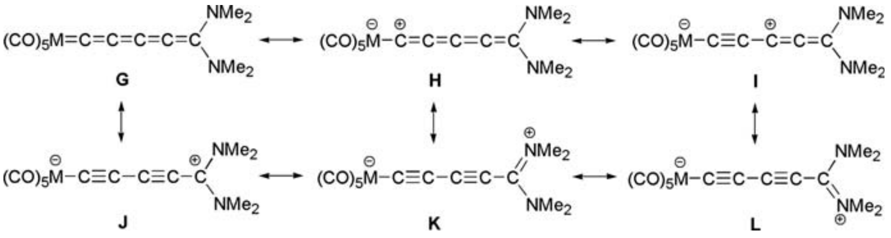
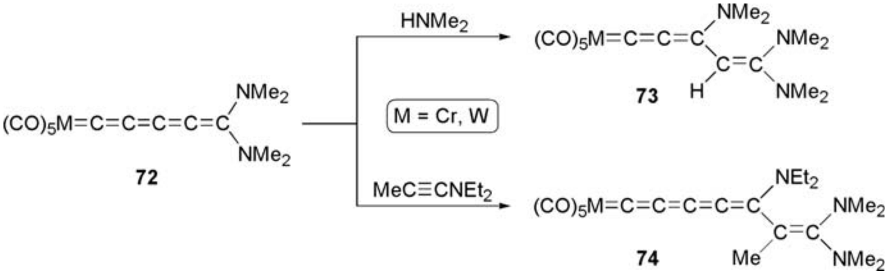


Fig. 11 Resonance structures of the pentatetraenylidene complexes **72**



Scheme 22 Reactivity of complexes **72** towards $HNMe_2$ and $MeC{\equiv}CNEt_2$

used in the models, point out that the LUMO is mostly localized on the odd carbon atoms, whereas the HOMO is on the even carbons [16, 17, 65–67]. Experimentally, it has been found that complexes **72** quantitatively add dimethylamine across the $C_\gamma{=}C_\delta$ bond to afford exclusively the α,β-unsaturated amino-allenylidenes **73** (Scheme 22) [27], and that they undergo selective insertion of the ynamine $MeC{\equiv}CNEt_2$ into the $C_\delta{=}C_\varepsilon$ bond to yield the α,β-unsaturated pentatetraenylidene complexes **74** [68]. The latter process involves an initial cycloaddition reaction between $MeC{\equiv}CNEt_2$ and the $C_\delta{=}C_\varepsilon$ bond of **72**, via attack of the nucleophilic

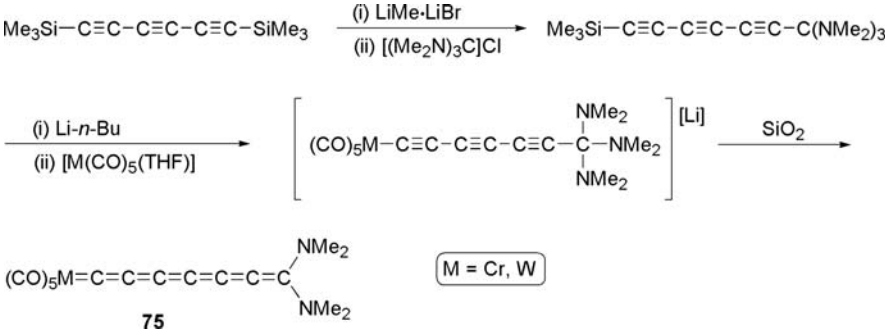
C_β carbon atom of the ynamine at the electrophilic terminal pentatetraenylidene C_ε atom, followed by cycloreversion. These observations seem to indicate a marked preference of soft nucleophiles for the C_ε carbon atom and hard nucleophiles for the central carbon of the unsaturated chain.

It is also worth noting that, due to their dipolar and conjugated donor–acceptor nature, all these amino-terminated Group 6 metallacumulenes exhibit a strong negative solvatochromic effect and they show significant second-order NLO properties [68].

3.2 Heptahexaenylidene Complexes

The stabilizing effect of the π-donor dimethylamino group is clearly reflected in the preparation of the heptahexaenylidene complexes $[M\{=C=C=C=C=C=C=C(NMe_2)_2\}(CO)_5]$ (M = Cr, W) (**75**), which represent the longest metallacumulenylidenes isolated to date (Scheme 23) [69, 70]. They were synthesized from triyne $Me_3Si(C\equiv C)_3SiMe_3$ by a sequential five step reaction (overall yield 3%), analogous to that discussed previously in the preparation of their pentatetraenylidene counterparts **72**.

Complexes **75** are remarkably stable at room temperature in the solid state and, when heated, they start to decompose only at about 130 °C (Cr) or 145 °C (W). Such a thermal stability is undoubtedly associated with their strongly dipolar nature, in which six possible ylide-type resonance forms contribute to the bonding (Fig. 12). As expected, analysis of the electronic structure of complex $[W\{=C=C=C=C=C=C=C(NMe_2)_2\}(CO)_5]$ by DFT methods showed that the LUMO is mostly localized on the odd carbon atoms of the chain, whereas the HOMO is on the even carbons. In accord with these electronic features, it was found that $[W\{=C=C=C=C=C=C=C(NMe_2)_2\}(CO)_5]$ readily adds dimethylamine across the $C_5=C_6$ bond, to give the isolable alkenyl-pentatetraenylidene derivative $[W\{=C=C=C=C=C(NMe_2)CH=C(NMe_2)_2\}(CO)_5]$ [69, 70].



Scheme 23 Synthesis of the heptahexaenylidene complexes **75**

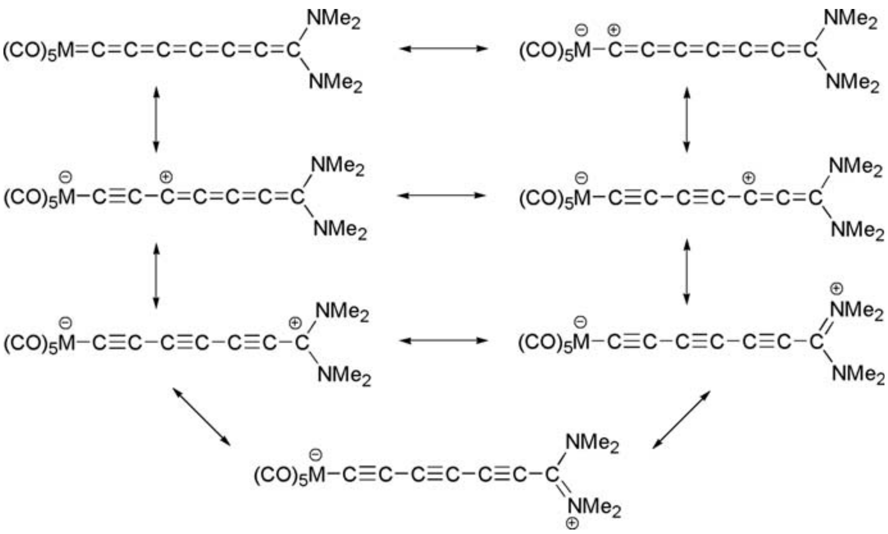


Fig. 12 Resonance structures of the heptahexaenylidene complexes **75**

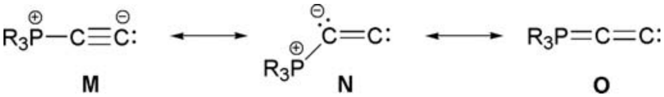
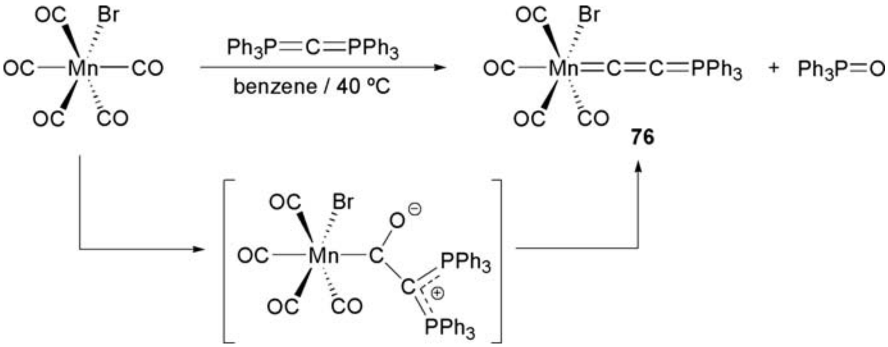


Fig. 13 Mesomeric forms of phosphonioacetylides

4 Complexes Containing Phosphonioacetylide Ligands

Phosphonioacetylides, which can be formally described by the limit mesomeric structures **M–O** (Fig. 13), are isoelectronic species with the well-known and widely employed isocyanide ligands [71]. However, in contrast to isocyanides, they are thermally unstable, e.g., triphenylphosphonioacetylide $Ph_3P^+C{\equiv}C^-$, generated by desilylation of $[R_3PC{\equiv}CSiMe_3][OTf]$ with $[PhCH_2NMe_3][F]$ at −90 °C, readily decomposes at temperatures above −40 °C [71].

Stabilization of these zwitterionic species has been commonly achieved through the formation of donor–acceptor borate adducts ($R_3P^+C{\equiv}CBR_3{}^-$) [72, 73] or by coordination to transition-metal fragments, the latter studies confirming the partial cumulenic character of these heteroatomic C-donor ligands (resonance form **O** in Fig. 13). In this sense, the manganese(I) derivative **76**, originally formulated as *cis*-$[MnBr(CO)_4({=}C{=}C{=}PPh_3)]$, was the first example described of a metal-complex containing a coordinated phosphonioacetylide ligand (Scheme 24) [74, 75]. It was obtained through the thermal treatment of $[Mn(CO)_5Br]$ with hexaphenylcarbodiphosphorane $Ph_3P{=}C{=}PPh_3$, via a Wittig-type reaction of the ylide with one of the coordinated carbonyl ligands.



Scheme 24 Synthesis of the Mn(I)-phosphonioacetylide complex **76**

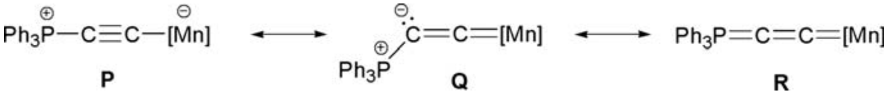
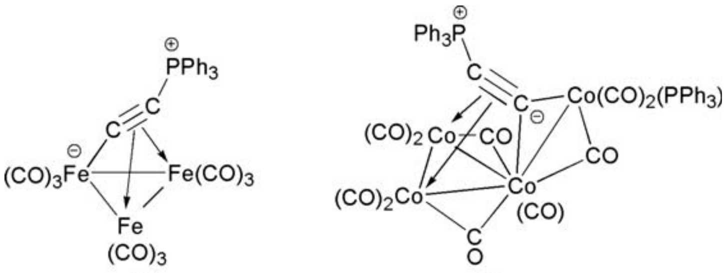


Fig. 14 Possible resonance forms for complex **76**

Single crystal X-ray diffraction studies on complex **76** were performed and its structure compared to that of triphenylphosphoranylideneketene $Ph_3P{=}C{=}C{=}O$ [76]. The observed linearity of the Mn–C–C–P linkage (Mn–C–C = 176.3(12)°; C–C–P = 164.0°) confirmed that, of the three resonance forms which may be used to describe the bonding in **76** (Fig. 14), contributions of **P** and **R** are the most important. The observed Mn–C (1.981(14) Å), C–C (1.216(14) Å) and C–P (1.679 (13) Å) bond distances were also in accord with this bonding description, pointing out that, in contrast to $Ph_3P{=}C{=}C{=}O$, the acetylenic form **P** predominates over the heterocumulenic one **R**. From this structural study, it was also concluded that the phosphonioacetylide ligand is a good σ-donor with poorer π-accepting properties than CO.

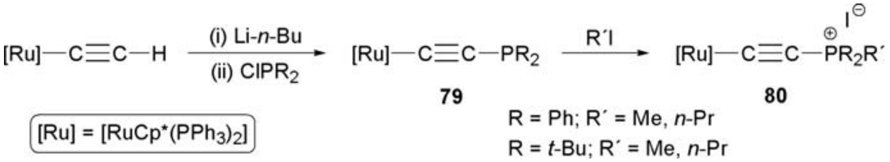
Following this seminal work, the related mononuclear derivatives *cis*-[ReBr $(CO)_4(C{\equiv}CPPh_3)$] [75], [$W(C{\equiv}CPPh_3)(CO)_5$] [77] and [$Fe(C{\equiv}CPPh_3)(CO)_4$] [78], as well as the cluster compounds **77** and **78** in which the bridging phosphonioacetylide ligand acts as a five- or six-electron donor (Fig. 15) [78, 79], were synthesized by treatment of the appropriate metal-carbonyl precursor with $Ph_3P{=}C{=}PPh_3$. Interestingly, the X-ray data obtained for the mononuclear iron(0) derivative showed a preferent contribution of the metallacumulenic structure [Fe $({=}C{=}C{=}PPh_3)(CO)_4$] vs the acetylide one [$Fe(C{\equiv}CPPh_3)(CO)_4$] commonly proposed in all the other cases [78].

Despite the apparent generality of this Wittig-type process, it must be noted that the reactions of $Ph_3P{=}C{=}PPh_3$ with transition-metal carbonyl compounds do not always result in the formation of phosphonioacetylide moieties. Thus, replacement of, instead of addition to (see Scheme 24), the CO group has been observed in some



77 **78**

Fig. 15 Structure of the cluster compounds **77** and **78**

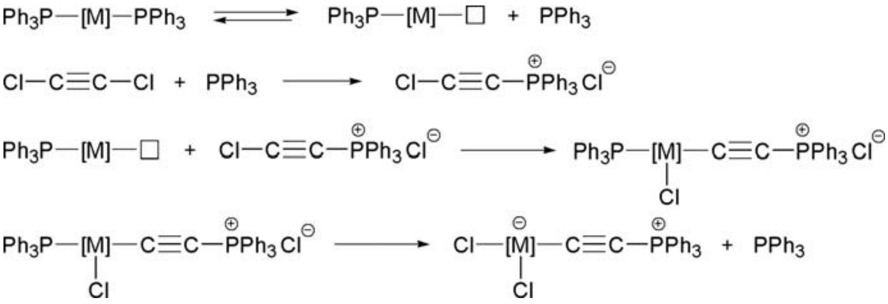


Scheme 25 Synthesis of the phosphonioacetylide–ruthenium(II) complexes **80**

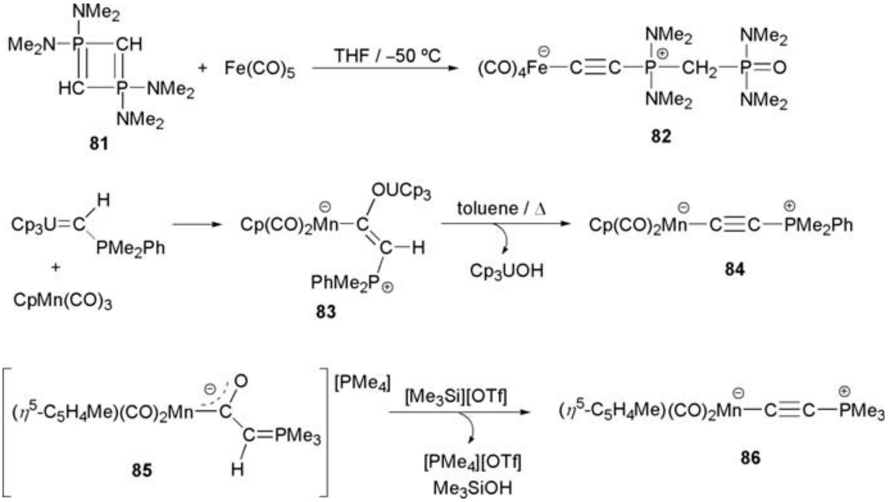
cases (e.g., $Ni(CO)_4$) leading to $[M]\leftarrow:C(PPh_3)_2$ adducts in which the metal–carbon interaction can be described as a dative two-electron σ-bond [75, 80], a reactivity extensively studied with noncarbonylic metal fragments [81, 82].

As shown in Scheme 25, an alternative approach to phosphonioacetylide complexes consists of the selective *P*-alkylation of a phosphinoacetylide precursor. Following this route, the half-sandwich ruthenium(II) derivatives **80** could be generated in excellent yields (>80%) and remarkable mild conditions (r.t. or 0 °C) starting from complexes **79** [83]. The related iron(II) derivative $[FeCp^*(C{\equiv}CPPh_2Me)\{\kappa^2(P,P)\text{-tppe}\}][I]$ was also synthesized by quaternization of $[FeCp^*(C{\equiv}CPPh_2)(tppe)]$ with MeI [84]. Although no X-ray structural data were obtained for these electron-rich Group 8 complexes, extensive contribution of the corresponding heterocumulenic form $[M]^+{=}C{=}C{=}PR_3$ could be deduced by ^{13}C-NMR spectroscopy.

Alternatively, phosphonioacetylide complexes have also been generated by reacting dichloroethyne with metallic precursors containing labile auxiliary phosphine ligands. Thus, treatment of $[Pd(PPh_3)_4]$ and $[RhCl(PPh_3)_3]$ with $ClC{\equiv}CCl$ resulted in the formation of $[PdCl_2(C{\equiv}CPPh_3)(PPh_3)]$ and $[RhCl_3(C{\equiv}CPPh_3)(PPh_3)_2]$, respectively, the process involving the initial in situ formation of $[Ph_3PC{\equiv}CCl][Cl]$ from one released PPh_3 ligand, followed by oxidative addition of the remaining Cl–C≡ bond of the alkyne to the metal. In the case of palladium complex, a subsequent displacement of a second PPh_3 molecule by the chloride anion affords the final product (see Scheme 26) [85]. In accord with this reaction pathway, the related platinum complex $[PtCl_2(C{\equiv}CPPh_3)(PPh_3)]$ could be prepared by reaction of $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ with isolated $[Ph_3PC{\equiv}CCl][Cl]$ [85]. The crystal



Scheme 26 Access to phosphonioacetylide complexes from dichloroethyne



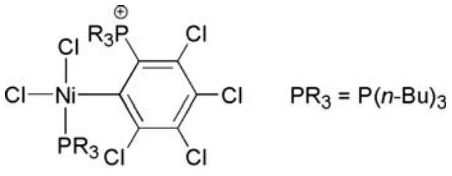
Scheme 27 Synthesis of the phosphonioacetylide complexes **82**, **84**, and **86**

structure of the Pd derivative was determined by X-ray diffraction methods and the bonding described as a hybrid of the two major resonance forms $Ph_3P^+–C\equiv C–[Pd]^-$ $Ph_3P=C=C=[Pd]$. Extension of these studies to nickel(0) phosphine complexes $[Ni(PR_3)_2(\eta^2\text{-}C_2H_4)]$ (R = *n*-Bu, Me, *n*-Pr) also allowed the isolation of the cationic monophosphonioacetylide complexes $[NiCl(C\equiv CPR_3)(PR_3)_2]^+$ (R = Bu, Me, *n*-Pr), as well as the structurally characterized dicationic bis-phosphonioacetylide derivative $[Ni\{C\equiv CP(n\text{-}Bu)_3\}_2\{P(n\text{-}Bu)_3\}_2]^{2+}$ [86].

Other phosphonioacetylide complexes described to date in the literature are (Scheme 27):

1. The iron derivative **82**, isolated in the reaction of 1,1,3,3-tetrakis(dimethylamino)-1λ^5,3λ^5-diphosphete **81** with $Fe(CO)_5$ [87]
2. The manganese derivative **84**, generated from the reaction of the uranium–carbene complex $[UCp_3\{=C(H)PMe_2Ph\}]$ with $[MnCp(CO)_3]$, via initial

Fig. 16 Structure of the cyclotrimerization product **87**



87

insertion of a carbonyl group into the uranium–carbon double bond, followed by thermal carbon–oxygen bond cleavage in the resulting intermediate **83** [88]

3. The closely related manganese complex **86**, resulting from the treatment of the acylate derivative **85** with [Me_3Si][OTf] [89]

It must also be noted that alternative synthetic approaches to the trinuclear cluster [$Fe_3(CO)_9(\mu^3\text{-}\eta^2\text{-}C{\equiv}CPPh_3)$] (**77** in Fig. 15) and its congeners [$Fe_3(CO)_9(\mu^3\text{-}\eta^2\text{-}C{\equiv}CPMePh_2)$], [$Fe_3(CO)_9(\mu^3\text{-}\eta^2\text{-}C{\equiv}CPMe_3)$] and [$Fe_3(CO)_9(\mu^3\text{-}\eta^2\text{-}C{\equiv}CAsPh_3)$] have also been described [90–92]. They are based on the nucleophilic attack of the appropriate phosphine or arsine ligand on anionic acetylide clusters [$Fe_3(CO)_9(\mu^3\text{-}\eta^2\text{-}C{\equiv}CX)$]$^-$, in which X is a good leaving group (OAc, SMe, OEt).

Finally, it merits to be highlighted that, despite the relatively large number of phosphonioacetylide complexes reported to date, the reactivity of these species remains almost unexplored, the scarce data presently available preventing any conclusion on the chemical behavior of the coordinated $R_3P^+C{\equiv}C^-$ framework. Thus, while the $Ph_3P^+C{\equiv}C^-$ unit remained unaltered after treatment of the manganese complex **76** with bromine, an unusual behavior for acetylenic compounds that confirms the heterocumulenic [$MnBr(CO)_4({=}C{=}CPPh_3)$] character of this complex [75], the in situ formed nickel derivative [$NiCl_2\{C{\equiv}CP(n\text{-}Bu)_3\}\{P(n\text{-}Bu)_3\}$] readily reacted with an excess of dichloroethyne to afford **87** (Fig. 16) through a classical [2+2+2] alkyne-cyclotrimerization process [86].

5 Complexes Containing Tricarbon Monoxide

Carbon monoxide *carbo*-mers [5–7], i.e., monoxides of linear odd carbon chains longer than one C_nO ($n = 3, 5, 7, 9...$), are highly reactive molecules suggested as potential constituents of interstellar and circumstellar gas clouds. Considerations based on MO theory and quantum chemical calculations indicate that, similar to pure odd carbon chains, all these heterocumulenes are singlet carbenes in the ground state [93]. Since its matrix isolation in 1971 [94] and its synthesis in gas phase in 1983 [95], the simplest member of this family, i.e., tricarbon monoxide C_3O, has been extensively studied both experimentally and theoretically [96–102], and its interstellar presence fully confirmed [103]. In particular, on the basis of computational studies, the coordinating properties of C_3O have been recently evaluated and compared to those of CO using the nickel(0) complexes $[Ni(C_3O)(CO)_3]$ and $[Ni(CO)_4]$ as models [104]. The calculations predicted the $Ni{-}C_3O$ bond to be stronger than the corresponding Ni–CO bond. Electron localization function (ELF) and atoms-in-molecules (AIM) analyses were used to estimate the donation and back-donation contributions to the net charge transfer involved in both complexes. The σ-donating and π-accepting properties of C_3O toward $Ni(CO)_3$ are slightly stronger than for its CO parent. In both cases, however, π-back-donation is the prevailing electron transfer process. In the same work, the weighted combination of Lewis structures for the free C_3O molecule were also estimated by ELF analyses (Fig. 17), the large overall contribution of polarized structures observed being consistent with the experimental dipole moment of C_3O ($\mu = 2.391$ D).

On the basis of the above-mentioned calculations it seems that coordination chemistry is a viable alternative to stabilize this heterocumulene. However, the experimental access to metal complexes containing the tricarbon monoxide ligand remains a challenge. Thus, to date, the coordination chemistry of C_3O is confined to $[Cr({=}C{=}C{=}C{=}O)(CO)_5]$ (**89**), obtained by treatment of $[n\text{-}Bu_4N][CrI(CO)_5]$ with the silver acetylide derived of sodium propiolate in the presence of Ag^+ (Scheme 28) [105]. Reaction of the presumed π-alkyne intermediate complex **88** with thiophosgene generates the heterocumulene **89**. Neither structural nor reactivity studies were undertaken with this complex.

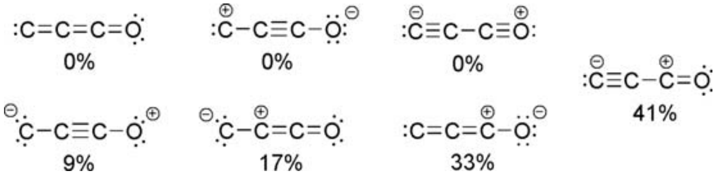
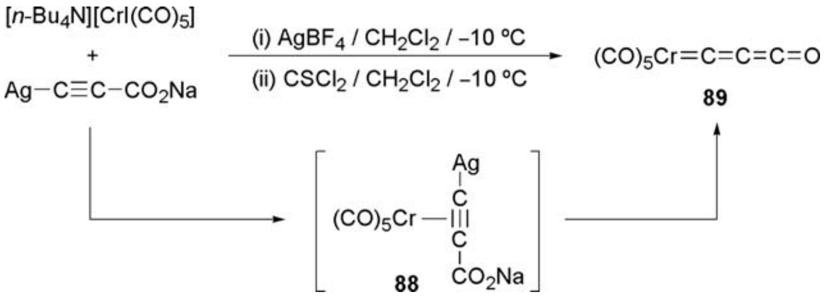


Fig. 17 Weights of Lewis structures of C_3O



Scheme 28 Synthesis of the chromium complex **89**

6 Conclusions

In this chapter, preparative routes and reactivity studies of π-donor substituted metallacumulenes have been presented. In contrast to their all-carbon substituted counterparts, the chemistry of these heteroatom-conjugated cumulenylidene complexes remains almost confined to Groups 6 and 8 metals due to the lack of general and straightforward routes of access. However, recent efforts from Fischer's and Winter's groups have led to the isolation of a large number of allenylidene complexes with a broad spectrum of substitution patterns. The presence of heteroatomic π-donor groups at the terminal allenylidene carbon atom results in an increased stability of these metallacumulenes, which is associated with the resonance effects derived from the electron transfer from the heteroatom to the unsaturated allenylidene chain. Taking advantage of this stabilizing effect, the longest cumulenylidene complexes reported to date, i.e., the heptahexaenylidene derivatives $[M\{=C=C=C=C=C=C=C(NMe_2)_2\}(CO)_5]$, has been recently isolated.

Aspects related to the chemistry of the heteroatom-terminated η^1-carbon ligands $R_3P^+C{\equiv}C^-$ and C_3O have also been discussed. Thus, upon coordination, the former seem to present a partial cumulenic character $[M]=C=C=PR_3$, but little is known about the chemical behavior of this coordinated unit. In the case of the tricarbon monoxide ligand, recent theoretical calculations have shown that coordination chemistry could be an alternative to stabilize this highly unstable heterocumulene. However, the access to metal complexes containing the C_3O unit represents an exciting experimental challenge for the near future.

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References

1. Fischer EO, Maasböl A (1964) Angew Chem Int Ed Engl 3:580–581
2. Zaragoza Dörwald F (1998) Metal carbenes in organic synthesis. Wiley, Weinheim
3. Bertrand G (ed) (2002) Carbene chemistry: from fleeting intermediates to powerful reagents. Marcel Dekker, New York
4. Dötz KH (ed) (2004) Metal carbenes in organic synthesis. Springer, Berlin
5. Chauvin R (1995) Tetrahedron Lett 36:397–400
6. Maraval V, Chauvin R (2006) Chem Rev 106:5317–5343
7. Maraval V, Chauvin R (2007) New J Chem 31:1853–1873
8. Fischer EO, Kalder HJ, Frank A, Köhler FH, Huttner G (1976) Angew Chem Int Ed Engl 15:623–624
9. Fischer H, Szesni N (2004) Coord Chem Rev 248:1659–1677
10. Winter RF, Záliš S (2004) Coord Chem Rev 248:1565–1583
11. Bruce MI (1991) Chem Rev 91:197–257

12. Bruce MI (1998) Chem Rev 98:2797–2858
13. Cadierno V, Gamasa MP, Gimeno J (2001) Eur J Inorg Chem 571–591
14. Bruneau C, Dixneuf PH (eds) (2008) Metal vinylidenes and allenylidenes in catalysis: from reactivity to applications in synthesis. Wiley, Weinheim
15. Cadierno V, Gimeno J (2009) Chem Rev 109:3512–3560
16. Marrone A, Re N (2002) Organometallics 21:3562–3571
17. Re N, Sgamellotti A, Floriani C (2000) Organometallics 19:1115–1122
18. Selegue JP (1982) Organometallics 1:217–218
19. Aumann R, Jasper B, Fröhlich R (1995) Organometallics 14:3173–3177
20. Duetsch M, Stein F, Lackmann R, Pohl E, Herbst-Irmer R, de Meijere A (1992) Chem Ber 125:2051–2065
21. Stein F, Duetsch M, Noltemeyer M, de Meijere A (1993) Syn Lett 486–488
22. Stein F, Duetsch M, Pohl E, Herbst-Irmer R, de Meijere A (1993) Organometallics 12:2556–2564
23. Wu Y-T, Flynn B, Schirmer H, Funke F, Müller S, Labahn T, Nötzel M, de Meijere A (2004) Eur J Org Chem 724–748
24. de Meijere A, Schirmer H, Stein F, Funke F, Duetsch M, Wu Y-T, Noltemeyer M, Belgardt T, Knieriem B (2005) Chem Eur J 11:4132–4148
25. Aumann R (1994) Chem Ber 127:725–729
26. Aumann R (1992) Chem Ber 125:2773–2778
27. Roth G, Fischer H (1996) Organometallics 15:1139–1145
28. Szesni N, Weibert B, Fischer H (2006) Inorg Chim Acta 359:617–632
29. Fischer H, Szesni N, Roth G, Burzlaff N, Weibert B (2003) J Organomet Chem 683:301–312
30. Szesni N, Drexler M, Fischer H (2006) Organometallics 25:3989–3995
31. Szesni N, Drexler M, Maurer J, Winter RF, de Montigny F, Lapinte C, Steffens S, Heck J, Weibert B, Fischer H (2006) Organometallics 25:5774–5787
32. Nitsche F, Aumann R, Fröhlich R (2007) J Organomet Chem 692:2971–2989
33. Romero A, Peron D, Dixneuf PH (1990) J Chem Soc Chem Commun 1410–1412
34. Péron D, Romero A, Dixneuf PH (1994) Gazz Chim Ital 124:497–502
35. Péron D, Romero A, Dixneuf PH (1995) Organometallics 14:3319–3326
36. Wolinska A, Touchard D, Dixneuf PH (1991) J Organomet Chem 420:217–226
37. Touchard D, Haquette P, Daridor A, Toupet L, Dixneuf PH (1994) J Am Chem Soc 116:11157–11158
38. Pirio N, Touchard D, Dixneuf PH, Fettouhi M, Ouahab L (1992) Angew Chem Int Ed Engl 31:651–653
39. Touchard D, Pirio N, Toupet L, Fettouhi M, Ouahab L, Dixneuf PH (1995) Organometallics 14:5263–5272
40. Guillaume V, Thominot P, Coat F, Mari A, Lapinte C (1998) J Organomet Chem 565:75–80
41. Bruce MI, Ellis BG, Skelton BW, White AH (2005) J Organomet Chem 690:1772–1783
42. Haquette P, Touchard D, Toupet L, Dixneuf P (1998) J Organomet Chem 565:63–73
43. Winter RF, Hartmann S, Záliš S, Klinkhammer KW (2003) Dalton Trans 2342–2352
44. Winter RF (1999) Eur J Inorg Chem 2121–2126
45. Bruce MI, Hinterding P, Low PJ, Skelton BW, White AH (1996) Chem Commun 1009–1010
46. Bruce MI, Hinterding P, Low PJ, Skelton BW, White AH (1998) J Chem Soc Dalton Trans 467–473
47. Winter RF, Hornung FM (1997) Organometallics 16:4248–4250
48. Winter RF, Klinkhammer K-W, Záliš S (2001) Organometallics 20:1317–1333
49. Harbort R-C, Hartmann S, Winter RF, Klinkhammer KW (2003) Organometallics 16:3171–3174
50. Hartmann S, Winter RF, Scheiring M, Wanner J (2001) J Organomet Chem 637–639: 240–250
51. Winter RF (1998) Chem Commun 2209–2210
52. Conejero S, Díez J, Gamasa MP, Gimeno J, García-Granda S (2002) Angew Chem Int Ed 41:3439–3442

53. Conejero S, Díez J, Gamasa MP, Gimeno J (2004) Organometallics 23:6299–6310
54. Díez J, Gamasa MP, Gimeno J, Lastra E, Villar A (2006) J Organomet Chem 691:4092–4099
55. Berke H, Größmann U, Huttner G, Zsolnai L (1984) Chem Ber 117:3432–3442
56. Kessler F, Szesni N, Põhako K, Weibert B, Fischer H (2009) Organometallics 28:348–354
57. Szesni N, Weibert B, Fischer H (2004) Inorg Chim Acta 357:1789–1798
58. Szesni N, Weibert B, Fischer H (2005) Inorg Chim Acta 358:1645–1656
59. Bernasconi CF, Stronach MW (1993) J Am Chem Soc 115:1341–1346
60. Bernasconi CF, Bhattacharya S (2004) Organometallics 23:1722–1729
61. Drexler M, Haas T, Yu S-M, Beckmann HSG, Weibert B, Fischer H (2005) J Organomet Chem 690:3700–3713
62. Szesni N, Drexler M, Weibert B, Fischer H (2005) J Organomet Chem 690:5597–5608
63. Szesni N, Hohberger C, Mohamed GG, Burzlaff N, Weibert B, Fischer H (2006) J Organomet Chem 691:5753–5766
64. Roth G, Reindl D, Gockel M, Troll C, Fischer H (1998) Organometallics 17:1393–1401
65. Jiao H, Gladysz JA (2001) New J Chem 25:551–562
66. Auger N, Touchard D, Rigaut S, Halet J-F, Saillard J-Y (2003) Organometallics 22: 1638–1644
67. Marrone A, Colletti C, Re N (2004) Organometallics 23:4952–4963
68. Roth G, Fischer H, Meyer-Friedrichsen T, Heck J, Houbrechts S, Persoons A (1998) Organometallics 17:1511–1516
69. Roth G, Fischer H (1996) Organometallics 15:5766–5768
70. Dede M, Drexler M, Fischer H (2007) Organometallics 26:4294–4299
71. Bestmann HJ, Frank W, Moll C, Pohlschmidt A, Clark T, Göller A (1998) Angew Chem Int Ed 37:338–342
72. Bestmann HJ, Behl H, Bremer M (1989) Angew Chem Int Ed 28:1219–1221
73. Bestmann HJ, Hadawi D, Behl H, Bremer M, Hampel F (1993) Angew Chem Int Ed 32:1205–1208
74. Mitchell DK, Korte WD, Kaska WC (1970) J Chem Soc D 1384–1385
75. Kaska WC, Mitchell DK, Reichelderfer RF, Korte WD (1974) J Am Chem Soc 96:2847–2854
76. Goldberg SZ, Duesler EN, Raymond KD (1972) Inorg Chem 11:1397–1401
77. Kaska WC, Mitchell DK, Reichelderfer RF (1973) J Organomet Chem 47:391–402
78. Petz W, Weller F (1996) Z Naturforsch 51b:1598–1604
79. Petz W, Wenck K, Neumüller B (2007) Z Naturforsch 62b:413–418
80. Petz W, Weller F, Uddin J, Frenking G (1999) Organometallics 18:619–626
81. Petz W, Kutschera C, Neumüller B (2005) Organometallics 24:5038–5043 and references therein
82. Jones ND, Cavell RG (2005) J Organomet Chem 690:5485–5496 and references therein
83. Dahlenburg L, Weiβ A, Moll M (1997) J Organomet Chem 535:195–200
84. Dahlenburg L, Weiβ A, Bock M, Zahl A (1997) J Organomet Chem 541:465–471
85. Sünkel K (1992) J Organomet Chem 436:101–108
86. Sünkel K, Birk U (1999) Polyhedron 18:3187–3197
87. Rosche F, Heckmann G, Fluck E, Weller F (1996) Z Anorg Allg Chem 622:974–980
88. Cramer RE, Higa KT, Gilje JW (1985) Organometallics 4:1140–1141
89. Blau H, Griessmann K-H, Malisch W (1984) J Organomet Chem 263:C5–C9
90. Jensen MP, Sabat M, Shriver DF (1990) J Cluster Sci 1:75–91
91. Jensen MP, Sabat M, Johnston DH, Jones LM, Shriver DF (1990) J Organomet Chem 383:279–294
92. Jensen MP, Shriver DF (1992) Organometallics 11:3385–3389
93. Janoschek R (1999) Sulfur Reports 21:373–400
94. DeKock RL, Weltner W (1971) J Am Chem Soc 93:7106–7107
95. Brown RD, Eastwood FW, Elmer PS, Godfrey PD (1983) J Am Chem Soc 105:6496–6497
96. Brown RD, Pullin DE, Rice EHN, Rodler M (1985) J Am Chem Soc 107:7877–7880

97. Brown RD, Godfrey PD, Elmes PS, Rodler M, Tack LM (1985) J Am Chem Soc 107: 4112–4115
98. Moazzen-Ahmadi N, Zerbetto F (1995) J Chem Phys 103:6343–6349
99. Strelnikov D, Reusch R, Krätschmer W (2007) J Mol Spectrosc 243:189–193
100. Eichelberger B, Snow TP, Barckholtz C, Bierbaum VM (2007) Astrophys J 667:1283–1289
101. Gicquel M, Heully J-L, Lepetit C, Chauvin R (2008) Phys Chem Chem Phys 10:3578–3589
102. Ogata T, Tatamitani Y (2008) J Phys Chem A 112:10713–10715
103. Palumbo ME, Leto P, Siringo C, Trigilio C (2008) Astrophys J 685:1033–1038 and references cited therein
104. Ducéré J-M, Lepetit C, Silvi B, Chauvin R (2008) Organometallics 27:5263–5272
105. Berke H, Härter P (1980) Angew Chem Int Ed Engl 19:225–226

Index