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Review

Bridging vinylalkylidene transition metal complexes☆

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ABSTRACT

Vinylalkylidene transition metal complexes have been extensively used as 'multitalent tools' in organic synthesis, covering a broad field of applications. The vinylalkylidene ligands can be monodentate; alternatively they can adopt a bridging coordination mode in complexes with two adjacent metal atoms. As for other unsaturated organic ligands which can bond in both mono- and di-nuclear modes, the bridging coordination can give rise to new and different chemical properties from those found when the ligand is bound to a single metal centre. Likewise, the synthetic routes to bridging vinylalkylidene complexes offer a broader range of possibilities compared to those used to make mononuclear vinylalkylidenes. In spite of the fact that bridging vinylalkylidene complexes have been known for about 40 years, their synthetic potential as C_3 activated fragments has so far been under-exploited. Comparison with other C_3 bridged ligands (allenyls and allyls) indicates that vinylalkylidene ligands are reactive and versatile species. This review article gives an overview of the chemistry of bridging vinylalkylidene complexes to focus attention on their potential as synthetic tools.

☆ Dedicated to Professor Fausto Calderazzo, a great scientist, a superb teacher, and an excellent friend.

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1. Introduction

Vinylalkylidene complexes (α,β-unsaturated Fischer carbene complexes, also known as alkenyl carbenes) play a special role in the field of metal–carbene complexes, as they have strongly contributed to the enormous development of metal–carbene chemistry that has arisen in catalysis and organic synthesis [1–9]. Indeed, since the discovery of the Dötz benzannulation reactions [10–12] vinylalkylidene complexes have been explored as multitalent tools in organic synthesis, and major applications have been covered in review articles [13–15].

Most vinylalkylidene complexes are mononuclear displaying a η^1 coordination; η^3 coordinated complexes are also known but have been less investigated. A review of the chemistry of η^3 vinylcarbene complexes [16] showed that the coordination of the vinyl moiety has a significant influence on the reactivity, as the conjugated vinyl substituent stabilizes the electron-deficient carbene center. Theoretical studies have also supported η^3 vinylcarbene complexes as important reaction intermediates in the Dötz benzannulation [17,18], in acetylene [19] and olefin polymerization [20] and in the alkyne metathesis [21].

Although vinylalkylidene ligands can also coordinate metal centres in a bridging mode, information concerning di- and polymetallic complexes containing carbene ligands is more limited than for the corresponding mononuclear compounds [22,23]; however, di- and polynuclear complexes represent an area of great interest in the development of new reagents and catalysts because of the potential advantage of cooperative effects due to the presence of two or more metal atoms [24–28]. An additional reason which makes this area attractive is the possibility that bridging coordination might produce new reaction patterns, different from those found when the same ligand is coordinated to a single metal atom [29–32]. Such new activation modes, and the stabilization of intermediate species, unattainable in mononuclear complexes, are the subject of this review.

The chemistry of bridging vinylalkylidenes complements the picture offered by other C_3 bridged unsaturated ligands such as allyl [33,34], allenyl [35–37], and allenylidene [38,39], which have been more extensively described in the literature. The aim of the present review is to stimulate interest in this class of complexes for their possible use in metal-assisted synthesis and catalysis.

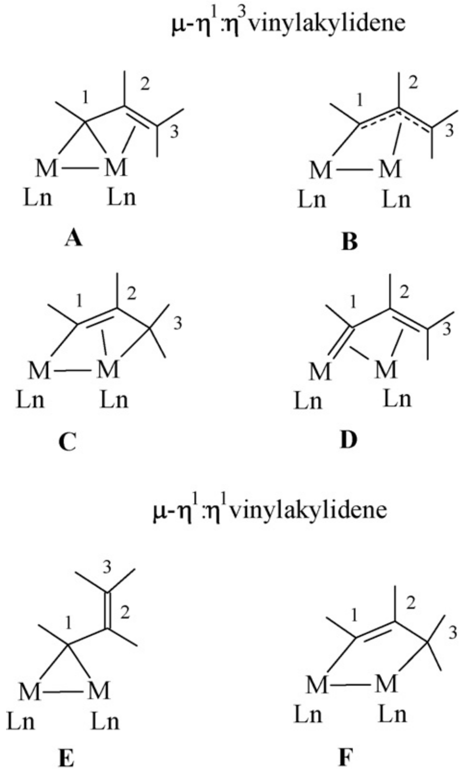
2. Mode of coordination

2.1. Dinuclear complexes

The coordination possibilities of the bridging η^1:η^3-vinylcarbene ligand can be described in different ways as illustrated in Scheme 1. In the most common representations, **A**, **B** and **C**, the ligand acts as a four electron donor, and the C^1 carbon assumes an alkylidene, allyl or vinyl character, respectively. The **D** form, corresponding to a “metallabutadiene” is less common [40,41]. Most authors regard these forms as extreme representations, and a full description of the bonding necessarily involves taking into consideration different contributions of each.

Bridging vinylalkylidene ligands can also act as two electron donors, when the vinyl moiety is uncoordinated, as in the structures **E** [42] and **F** [43,44]. These are less common and are not described in detail here. However the bridging coordination mode **E** is important as it probably represents the structure of intermediates in the displacement of the vinyl coordination in an early step in many reactions involving bridging vinylalkylidenes.

Structural data for a number of vinylalkylidene complexes are available in the literature and they have been taken as evidence to indicate which, of the **A**–**D** formulations, better represents each compound. Several structural data can be used to designate the predominant form. The bond angles and the deviations from planarity of the bridging frame are indicative of the hybridization assumed by the bridging carbons: for example, carbon C^1 is mainly sp^2 in **B**, **C**, **D** and sp^3 in **A** while C^3 is sp^3 hybridized in **C**, and sp^2 in **A**. (Scheme 1). Differences in the C^1–M bond distances are also indicative, as are the C^1–C^2 and C^2–C^3 bond distances, and their comparison has been frequently considered in assigning the predominant contributions to the resonance forms. In Table 1 we have collected the literature data concerning the C^1–C^2 and C^2–C^3 bond distances. A more careful look at the bond distances reveals that only in a very few cases are the C^1–C^2 and C^2–C^3 significantly different. Indeed, if we consider the experimental errors, and assume a reasonably high probability level to describe bond lengths accurately, many of the differences between C^1–C^2 and C^2–C^3 listed in Table 1 are negligible. This indicates that in all cases the π bond is largely delocalized over the C_3 unit.

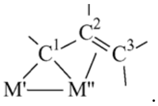


Scheme 1.

The delocalized bond character of the bridging ligand and the lack of a unique and simple representation leads also to some ambiguity in naming the ligand: vinylalkylidene and allylidene are often used synonymously, although they apparently refer to the **A** and **B** forms, respectively. Likewise, the coordination modes **C** and **D** are mostly indicated as dimetallacyclobutene and metallabutadiene, respectively. For simplicity, we will describe the bridging C_3 as “vinylalkylidene”, even though this might not be a strictly accurate description.

In addition, ^1H and ^{13}C NMR spectroscopic data provide a useful indication of the bonding mode in that changes in the alkyl, alkylidene, vinyl or allyl characters of the bridging carbon atoms are accompanied by changes in the chemical shifts and coupling constants. In particular, downfield shifted resonances are found in the ^{13}C spectra for the C^1 carbon when it has alkylidene character, form **A** or **D** [45,40], and also in the ^1H spectra for any hydrogen substituents that are present.

Table 1
C–C bond distances (Å) within the bridging C_3 chain in vinylalkylidene ligands.

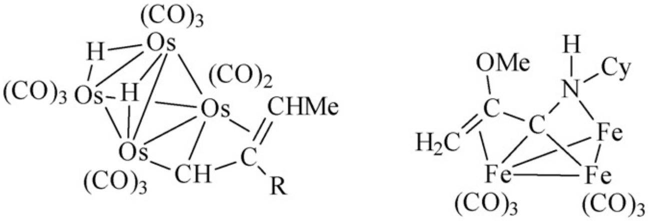


M′–M″	C^1–C^2	C^2–C^3	Reference
Fe–Fe	1.457(17)	1.433(18)	[46]
Fe–Fe	1.434(4)	1.432(4)	[48]
Fe–Fe	1.416(3)	1.435(3)	[48]
Fe–Fe	1.415(4)	1.422(4)	[47]
Fe–Fe	1.396(4)	1.415(4)	[47]
Fe–Fe	1.441(8)	1.408(9)	[99]
Fe–Fe	1.422(2)	1.425(2)	[44]
Fe–Fe	1.430(10)	1.430(10)	[123]
Ho–Ho	1.410(7)	1.425(7)	[76]
Ir–Ir	1.43(2)	1.47(2)	[64]
Ir–Ir	1.440(10)	1.431(9)	[70]
Mo–Mo	1.397(8)	1.418(9)	[40]
Mo–Mo	1.426(4)	1.420.4	[40]
Mo–Mo	1.397(8)	1.418(9)	[80]
Re–Re	1.378(14)	1.426(18)	[41]
Re–Re	1.441(16)	1.385(18)	[45]
Rh–Rh	1.425(6)	1.445(6)	[63]
Rh–Rh	1.344(4)	1.505(4)	[43]
Ru–Fe	1.401(6)	1.453(6)	[91]
Ru–Fe	1.43(2)	1.46(2)	[91]
Ru–Ru	1.429(3)	1.425(5)	[73]
Ru–Ru	1.425(10)	1.490(10)	[59]
Ru–Ru	1.47(3)	1.51(3)	[30]
Ru–Ru	1.51(1)	1.43(1)	[30]
Ru–Ru	1.431(10)	1.439(11)	[68]
Ru–Ru	1.425(10)	1.490(10)	[59]
Ru–Ru	1.432(14)	1.417(13)	[60]
Ru–Ru	1.421(9)	1.427(10)	[60]
Ru–Ru	1.378(6)	1.457(4)	[69]
Ru–Ru	1.431(10)	1.439(10)	[67]
W–Fe	1.44(1)	1.35(1)	[92]
W–W	1.24	1.44	[86]
W–W	1.44(1)	1.42(1)	[88]
W–W	1.40(2)	1.33(2)	[42]
W–W	1.44(5)	1.45(5)	[106]

The spectroscopic and structural data show that bridging C_3 ligands shown in Scheme 1 are very versatile in that they can easily undergo small modifications of the bonding mode. Presumably these adjustments of the geometry and hybridization of the bridging carbon chain allow a better response to the steric and electronic requirements of the ancillary ligands and of the M–M interaction. However this versatility and flexibility has sometimes (and erroneously) been interpreted in terms of fluxional behaviour, or of a lability of the bridging ligand. This is not the case, as the μ-vinylalkylidenes are very stereochemically rigid. Thus stereoisomers with different substituents on the C_3 carbon do not isomerize even upon heating [46–48]. Likewise, no isomerization is observed in heterodinuclear vinylalkylidene complexes, where isomers arise from coordination of the vinyl moiety to different metal atoms [49].

2.2. Polynuclear complexes

Bridging vinylalkylidene ligands occur also in tri- and tetranuclear complexes, although they are less common than dinuclear complexes. Two examples are shown in Scheme 2. In the tetraosmium complex $[Os_4H_2(CO)_{11}(CHCRCHMe)]$ [50] the vinylalkylidene ligand simply bridges two metal atoms, therefore the coordination is unchanged with respect to the modes previously described. A very similar bonding mode is found in the tri-heteronuclear complexes $[WFe_2(\mu_3\text{-CR})\{\mu\text{-C(OH)CMeCHMe}\}(\mu\text{-PR'})_2(CO)_5(Cp)][BF_4]$ [51]. In the tri-iron compound shown in Scheme 2, the bridging frame is bound to all three Fe atoms; nevertheless the bridging coordination mode remains that typical for dinuclear complexes, in that a third Fe atom is coordinated simply through a N-containing substituent of the C_3 ligand [52].



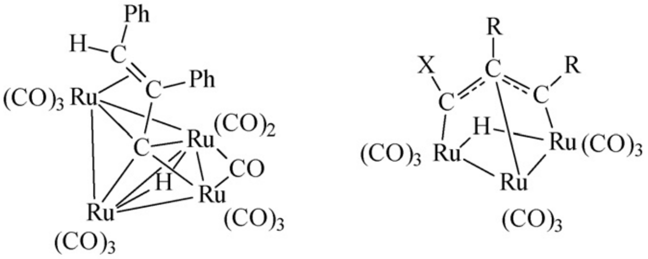
Scheme 2.

Other polynuclear complexes contain bridging C_3 fragments that can be formally derived-from vinylalkylidene ligands (:CRCR=CR$_2$), by replacement of a R substituent with a metal carbon interaction. Examples are shown in Scheme 3. Strictly speaking, these bridging C_3 frames are not vinylalkylidene ligands, although they display some analogies. In other words, any extension of the multisite coordination requires loss of substituents on the C_3 ligands that consequently become more unsaturated fragments. In the ruthenium cluster $[Ru_4H(CO)_{12}(CCPhCHPh)]$ one terminal end of the C_3 frame consists of a η^4-coordinated C atom [53]. Likewise, a series of triruthenium complexes of the type shown in Scheme 3, exhibit a bridging C(X)CRCR ligand (X = OMe, NEt$_2$; R = Me, Ph) in a μ_3–η^3 coordination mode, that can be formally related to vinylalkylidene ligands [54–57]. The analogy, in this case, is also in the synthesis of the C_3 ligand, which is obtained by alkyne–alkylidyne coupling (see Sections 3.5 and 3.6).

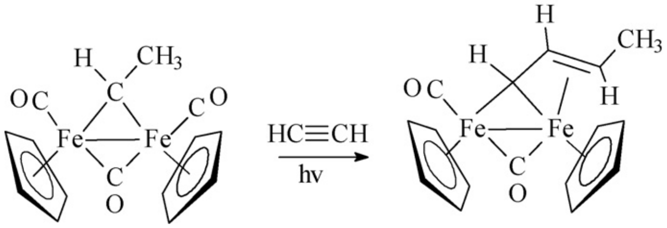
3. Synthesis of bridging vinylalkylidene complexes

Dinuclear complexes containing μ–η^1:η^3-vinylalkylidene ligands have been obtained by a variety of synthetic methods, which we briefly summarize here. The number of possible routes is impressive and indicates the ease of formation of this class of compounds.

Two major approaches can be seen, one consists of the metal-assisted assembly of smaller coordinated coordinated units, typically C_1 (methyl, methylidene or methylidyne) and C_2 (alkene, or alkyne) ligands. A second general route involves the transformations of C_3 ligands (such as allyl, allenes, and cyclopropyl species). Therefore, in most cases, bridging vinylalkylidene ligands are assembled or generated by exploiting the activation effects of multisite coordination.



Scheme 3.



Scheme 4.

3.1. Reactions of μ-alkylidene (methylidene) complexes with alkynes

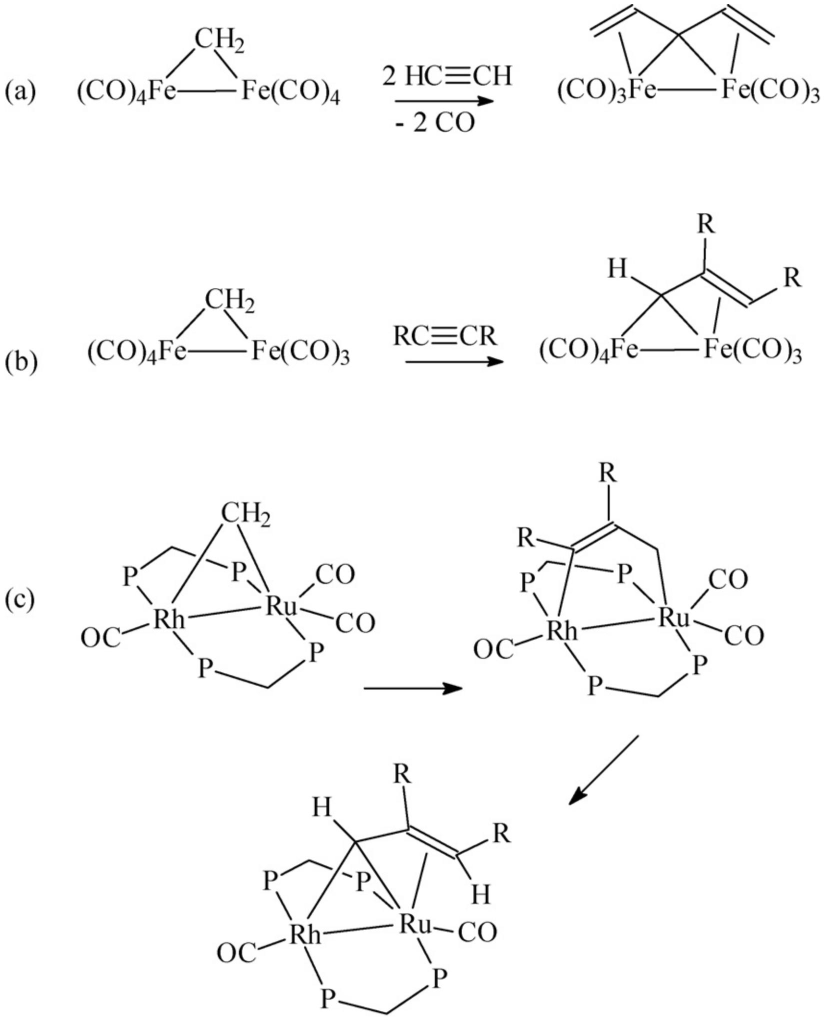
The coupling of bridging alkylidene (methylidene) ligands and alkynes provides a rather general approach to the formation of bridging vinylalkylidene complexes. As an example, the complexes [$M_2\{\mu$-η^1:η^3-C(R)C(R)CHMe}(μ-CO)(CO)(Cp)$_2$] (M = Fe, Ru, R = H, COOEt) have been obtained from the corresponding bridging ethylidene precursors (Scheme 4) [46].

A number of other μ-vinylalkylidene complexes have been similarly obtained from alkynes and dinuclear bridged methylidene species, including: [Fe Fe] [58], [Ru Ru] [59–62], [Fe Ru] [49], [Rh Rh] [63], and [Ir Ir] [64]. Many of these complexes have been structurally characterized (see Table 1).

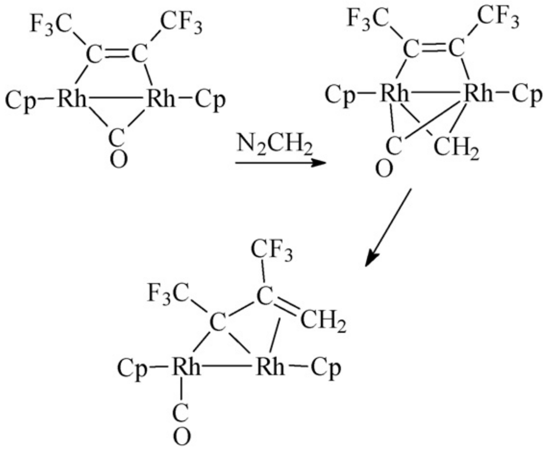
Alkyne insertion in the metal–alkylidene bond, shows analogies to the reactions of terminally bonded carbene complexes with acetylenes, which is a key step in the Dötz benzannulation. However bridging alkylidene (methylidene) ligands are usually less reactive than alkylidenes bonded to a single metal centre. Thus the observed acetylene insertion in dinuclear complexes is presumably the result of an intramolecular activation via the preliminary coordination of the alkyne to one of the metal atoms. This is consistent with the fact that the reactions usually take place under photolytic conditions that remove a CO and generate a vacant coordination site. Alternatively the presence of labile ligands (usually acetonitrile) is required as the equivalent of coordinative unsaturation [59].

In spite of the generality of the reaction slightly different reactions have been found in a few cases:

(i) Multiple alkyne insertion is occasionally observed, leading to the formation of more complex hydrocarbyl bridging chains (Scheme 5a) [63,65].
(ii) Alkyne (RCCR') insertion into the metal-methylidene (CH_2) can produce a bridging C_3 frame of the type (CHCRCR'H) instead of (CRCR'CH_2), which implies that a 1,3 hydrogen shift has occurred (Scheme 5b) [58].
(iii) In the heterodinuclear complex [RhRu(CO)$_3$(μ-CH_2)(dppm)$_2$][CF_3SO_3] the reaction with alkynes proceeds through an intermediate species in which the η^1:η^1-CH_2CRCR ligand acts as a two electron donor (Scheme 5c) [30,43]. The subsequent



Scheme 5.



Scheme 6.

transformation into a (bridging η^1:η^3) four electron donor requires both loss of CO, and a 1,3 hydrogen shift. Moreover the transformation is accompanied by a shift from Rh to Ru of the fragment originally generated by the alkyne insertion.

3.2. Reactions of μ-alkyne complexes and diazo-compounds

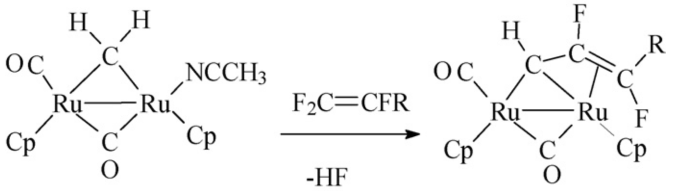
This method is closely related to the previous in that bridging vinylalkylidene ligands again result from alkyne–alkylidene intramolecular coupling, though with a reversed sequence in the coordination of the C_1 and C_2 fragments, and without CO displacement. As an example, in the reaction of complex $[Rh_2(\mu\text{–}\eta^1\text{:}\eta^1 CF_3C{=}CCF_3)(\mu\text{-}CO)(Cp)_2]$ with N_2CH_2 the alkyne is coordinated in the dirhodium precursor and the methylidene is provided externally in the form of a diazo-compound [66]. The bridging methylidene is generated 'in situ' and coupling with the bridging alkyne occurs as shown in Scheme 6.

A very similar reaction occurs when $[Ru_2(\mu\text{–}PhC{\equiv}CPh)(\mu\text{-}CO)(Cp)_2]$ is treated with $RCHN_2$ (Scheme 7) [67,68].

The metal–metal double-bond incorporates two methylidene units one of which undergoes a coupling reaction with the bridging alkyne ligand.

3.3. Reactions of μ-methylidene complexes with alkenes

The coupling of bridging alkylidene ligands with alkenes aimed at generating μ-vinylalkylidenes necessitates the elimination of a substituent from both the alkylidene and the alkene, which is not easy to accomplish. Consequently, this approach is of limited application. Knox reported that the complex $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(NCMe)(CO)(Cp)_2]$ undergoes a methylidene–alkene combination, which occurs under mild conditions *via* HF elimination [69] (Scheme 8).



Scheme 8.

3.4. Reactions of dinuclear alkyl complexes with alkynes

The formation of bridging vinylalkylidene di-iridium complexes $[Ir_2H(CO)_2(\mu\text{-}CHCRC(H)R)(dppm)_2][CF_3SO_3]$, by reaction of the methyl di-iridium precursor with internal, unactivated alkynes was reported by Cowie [70,71] (Scheme 9). The reaction formally requires the cleavage of two C–H bonds of the methyl ligand, accompanied by condensation of the resulting methylidyne group at one end of alkyne and transfer of a hydrogen to the other end.

The authors suggested a reasonable sequence to explain the formation of the observed vinylalkylidene product based on C–H activation of the methyl and formation of methylidene-bridged intermediates. This route can therefore be related to the alkylidene–alkyne coupling reactions.

3.5. Coupling between μ-alkylidyne and alkenyl ligands

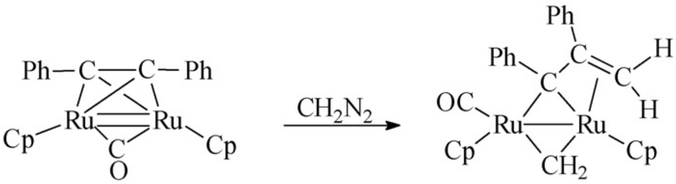
Coupling between a bridging alkylidyne (>CR) and an alkenyl ligand (–CH=CHR′) also provides a direct route to the formation of bridging vinylalkylidenes (>CRCH=CHR). This method is potentially more efficient than the alkylidene–alkyne coupling since both the alkylidyne and the alkenyl ligands are generally more reactive than the alkylidenes and alkynes.

On the other hand, for the same reasons it is more difficult to obtain dinuclear complexes containing both μ-alkylidyne and alkenyl ligands. Consequently, the method lacks general applicability; however an interesting example is shown in Scheme 10 [72].

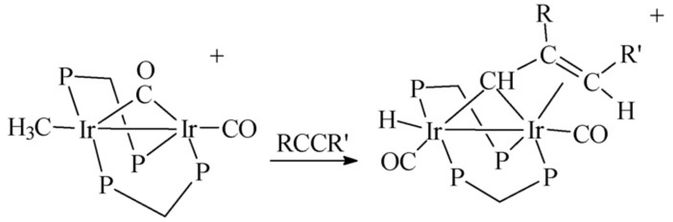
A bridging methylidyne intermediate complex is generated by protonation and loss of HOR from a μ-alkylidene precursor. The bridging methylidyne promptly reacts with the diphenylethenyl ligand to give a bridging vinylalkylidene in which one phenyl group is coordinated to a Fe atom. A different bridging vinylalkylidene complex is formed when the reaction is conducted in the presence of PPh_3. In this case the Ph groups are not on adjacent carbons of the hydrocarbyl bridging chain, which implies some further rearrangement. The authors suggested that this isomerization occurs via a diphenylcyclopropene intermediate.

3.6. Reactions of bridging carbynes with alkenes

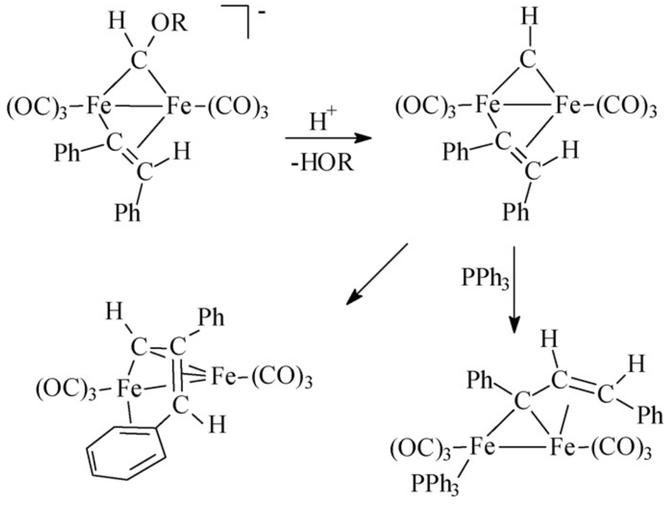
Under photolytic conditions the ethylidyne complex $[Ru_2(\mu\text{-}CMe)(\mu\text{-}CO)(CO)(Cp)_2][BF_4]$ reacts with ethene to give $[Ru_2\{\mu\text{–}\eta^1\text{:}\eta^3\text{-}C(Me)C(Me)CH_2\}(\mu\text{-}CO)(CO)(Cp)]$ [73] (Scheme 11); propene reacts similarly.



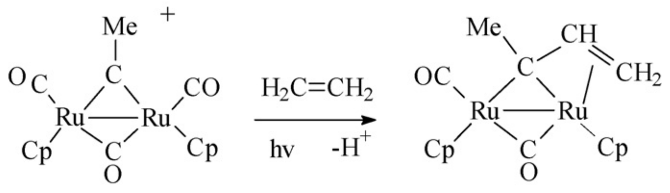
Scheme 7.



Scheme 9.



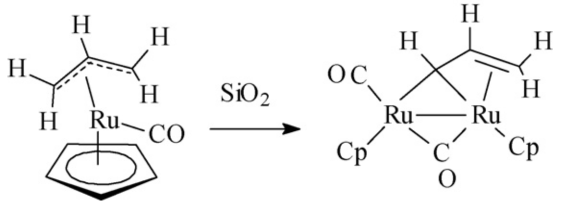
Scheme 10.



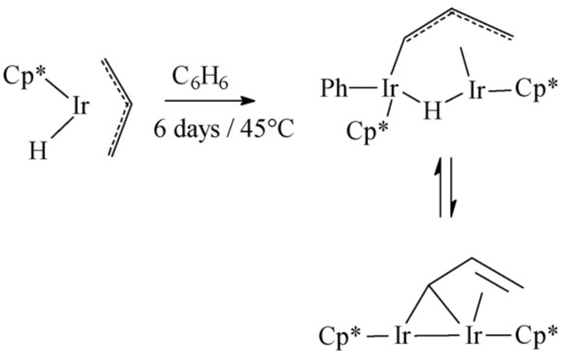
Scheme 11.

The same vinylalkylidene product can be also obtained upon treatment of $[Ru_2(CO)_4Cp_2]$ with MeLi, HBF_4 and $NaBH_4$, in succession; the μ-CO is converted to μ-CMe^+ by MeLi–HBF_4, whereas deprotonation is achieved by $NaBH_4$. Knox proposed that the olefin–carbyne coupling proceeded via the formation of a metallacyclobutane intermediate, which undergoes β-elimination.

More recently, a number of heteroatom functionalized bridging vinylalkylidene complexes have been obtained by analogous reactions involving the coupling of bridging thio- or amino–alkylidyne ligands and activated alkenes in diiron and diruthenium complexes [47,48]. Some of the reactions of bridging thio- and amino-carbyne diiron complexes are shown in Scheme 12.



Scheme 13.

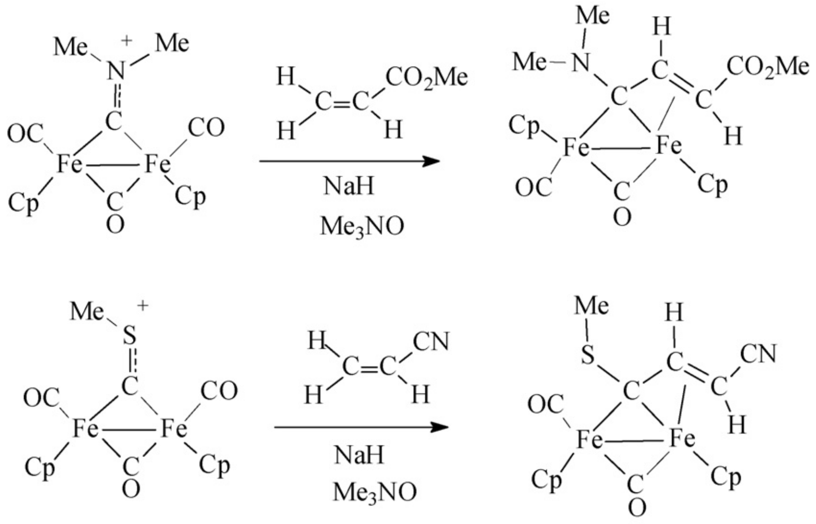


Scheme 14.

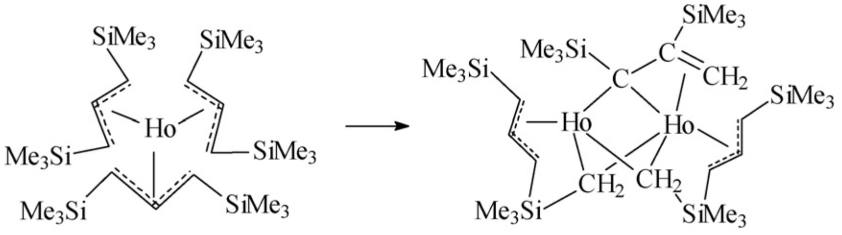
The reaction of alkylidynes and olefins occurs only in the presence of Me_3NO and NaH. The former labilizes a CO to generate a coordinatively unsaturated metal center to which the olefin can coordinate, while the treatment with NaH accomplishes the deprotonation. A further requirement is the use of olefins activated by electron-withdrawing groups (e.g. CN, COOMe). An interesting point is that the olefin incorporation is regioselective: olefins such as CH_2CHR ($R = CN$, CO_2Me) are combined as shown in Scheme 12, with the olefin CH_2 linked to the alkylidyne carbon.

3.7. Transformations of bridging-allyl, -allenyl, and -allene complexes

An effective and rather obvious approach to the synthesis of bridging vinylalkylidene complexes involves the modification of closely related bridging C_3 ligands, such as allyl ($CH_2CH{=}CH_2$) or allenyl ($CH{=}C{=}CH_2$). The transformations are



Scheme 12.



Scheme 15.

most frequently accomplished through protonation/deprotonation reactions. Indeed, allyls require hydrogen abstraction to be transformed into vinylalkylidenes. Conversely, hydrogen addition is necessary to convert the allenyls into vinylalkylidenes.

As an example, Efraty described a facile transformation of a η^3-allyl ruthenium complex into a diruthenium μ-vinylalkylidene by passing an acetone-hexane solution of [Ru(CO)(η^3-C_3H_5)(Cp)] through a deactivated silica gel column (Scheme 13) [74].

A related reaction, reported by Bergman, concerned the transformation of a mononuclear iridium allyl compound into a dinuclear species with a bridging C_3 unit Scheme 14 [75]. The reaction is remarkable in that it proceeds through C–H oxidative addition/reductive elimination steps under surprisingly mild conditions (Scheme 14).

A bridging vinylalkylidene di-holmium complex was obtained upon treatment of holmium triflate with the bis(1,3-trimethylsilyl)allyl anion in the presence of traces of water. Under these condition the trimethylsilylated allyl complexes initially formed were transformed into the product vinylalkylidene diholmium complex (Scheme 15). Several steps are involved, including protonation, C–H activation, hydrogen abstraction and dimerization [76].

Bridging allyl complexes can also be transformed into μ-vinylalkylidenes: the μ-allyl complex [(Cp)Mo(CO)(μ-C_4H_7)Mn(CO)] can be deprotonated with LiBu giving anionic species which are postulated to contain bridging–vinylalkylidene ligands [77].

Conversion of μ-allenyl ligands into μ-vinylalkylidenes was shown to occur in di-palladium complexes upon reaction with HCl (Scheme 16) [78].

The reaction is not limited to the protonation of the bridging ligand, and displays a more general character: treatment with acetyl chloride in the place of HCl also gave vinylalkylidene complexes. In these complexes, electrophilic addition and carbon–carbon bond formation both occur at the central carbon of the allenyl ligand (Scheme 16).

Allenes represent a further type of C_3 unsaturated ligand which can display bridging coordination and provide a suitable source of μ-vinylalkylidene complexes Compared to the reactions mentioned above in which hydrogen addition or abstraction is necessary in order to generate vinylalkylidenes, the conversions of allenes simply require an intramolecular rearrangement (hydrogen shift). Nevertheless, the transformation is relatively uncommon and apparently difficult to accomplish.

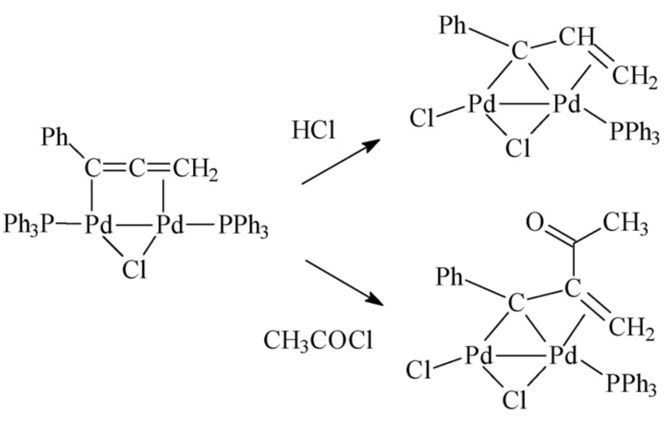
Cowie reported the formation of the bridging vinylalkylidene complexes [$Ir_2(CO)_2${μ-η^1:η^3-HCC(CH_3)C(H)R}$(dppm)_2$][CF_3SO_3] from the reaction of [$Ir_2(CH_3)(CO)$(μ-CO)$(dppm)_2$][CF_3SO_3] with allenes [79]. In this case, the bridging vinylalkylidenes are generated by the rearrangement of an intermediate allene (Scheme 17).

Migration of the methyl ligand to the central cumulene carbon, followed by activation of a cumulene C–H bond was proposed as a reaction sequence to account for the formation of the vinylalkylidene.

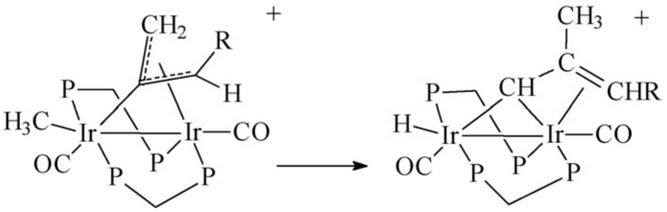
3.8. Cyclopropene opening reactions

Cyclopropenes are valuable sources of vinylalkylidene complexes for two main reasons: (i) their composition (e.g. C_3H_4) exactly corresponds to that of a vinylalkylidene, thus neither addition, cleavage nor rearrangement of substituents is required to produce a vinylalkylidene ligand, but only ring opening; (ii) cyclopropenes are reactive molecules and the three-membered ring is susceptible to cleavage upon treatment with appropriate metal fragments. As an example, the reaction of 3,3-dimethylcyclopropene with [$Mo_2L_2(CO)_4$] gave the corresponding bridging vinylalkylidene complexes (Scheme 18) [80,40].

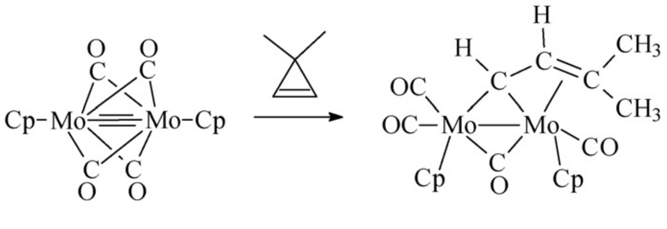
It should be emphasised that cleavage of the cyclopropene presumably occurs upon coordination to a metal centre, and that a



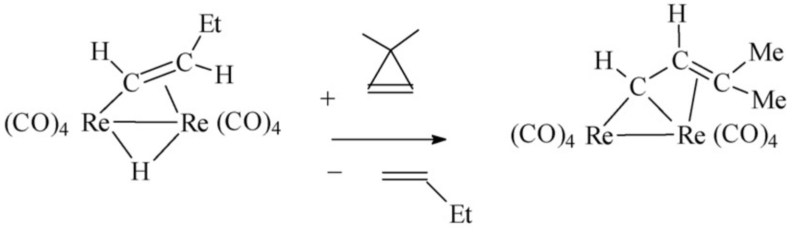
Scheme 16.



Scheme 17.



Scheme 18.



Scheme 19.

second adjacent unsaturated metal centre largely contributes to the stabilization of the resulting C_3 fragment by π-interaction.

In a similar reaction, the dirhenium complex $[Re_2(\mu\text{-H})(\mu\text{-CH=CHEt})(CO)_8]$ was treated with 3,3-dimethylcyclopropene to form the μ-vinylalkylidene complex $[Re_2(\mu-\eta^1{:}\eta^3\text{-CHCHCMe}_2)(CO)_8]$ [41].

Interestingly, in this case, the coordination site that is necessary to bind the C_3 fragment generated by ring opening is provided by elimination of alkenyl and hydride bridging ligand, here as 1-butene (Scheme 19).

A reaction which models a ring-opening step closely similar to that which must occur in the above-mentioned reactions of cyclopropenes, is shown by the reactions of Pd(0) and Pt(0) with triarylcyclopropenium bromide to give the dinuclear complexes, and isolated as their acac derivatives as shown in Scheme 20 [81–83].

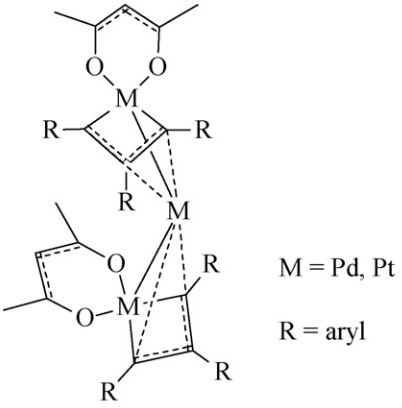
3.9. *Reactions of mononuclear vinylcarbene ligands with metal fragments*

A common feature of the synthetic approaches so far described arises from the observation that bridging vinylalkylidene ligands are obtained by the assembly or modification of various ligands or molecular units coordinated to the metal centres. A different strategy consists in reacting mononuclear complexes which already contain vinylalkylidene ligands with other metal fragments to give di- or polynuclear complexes with bridging vinylalkylidenes. In this case, the synthetic effort is more focused on the assembly of different mononuclear metal species.

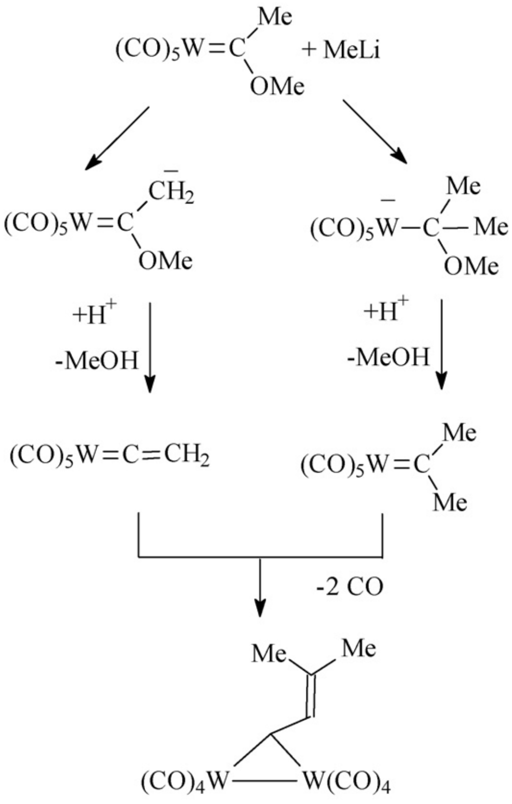
Pioneering work by Rudler described the formation of the bridging vinylalkylidene di-tungsten complexes obtained from classical Fischer type mononuclear carbene complexes $[W\{C(Me)OR\}(CO_5)]$ upon treatment with RLi (R = Me, Bu^t), followed by addition of CF_3CO_2H. The complexes obtained using this approach included $[W_2(\mu\text{–}\eta^1{:}\eta^1\ \text{CHCH=CMe}_2)(CO)_8]$ [84,42] $[W_2(\mu-\eta^1{:}\eta^1\text{CHCH=CMe}_2)(CO)_{10}]$ [85], in which the vinylalkylidene act as a two electron donor and adopts the coordination mode **E** (Scheme 1), and also the complexes $[W_2(\mu\text{–}\eta^1{:}\eta^3\text{-CHCH=CMe}_2)(CO)_9]$ [86] and $[W_2(\mu\text{–}\eta^1{:}\eta^3\text{C(OR)CH=CHMe})(CO)_9]$ [85]. The formation of the vinylalkylidene ligand was proposed to occur through several steps involving the coupling of vinylidene and alkylidene mononuclear intermediates derived from the alkoxycarbene precursor (Scheme 21) [42].

A more linear and general synthesis was accomplished by reacting the α,β-unsaturated alkoxycarbene complex $[W\{C(OMe)CH=CHR\}(CO)_5]$ (R = H, Me, Ph) with $[W(CPh_2)(CO)_5]$ or with $[W(CO)_6]$ under $h\nu$ irradiation [87]. Further improvements have been devised by using $[W(CO)_5(THF)]$ as a better source of the coordinatively unsaturated metal fragment (Scheme 22) [88].

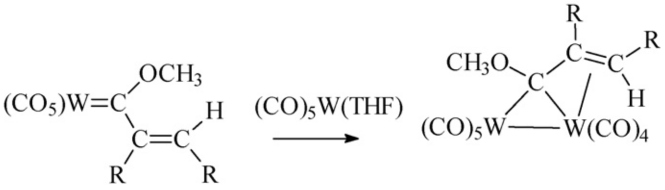
η^3 Vinylcarbene complexes, such as $[Fe\{\eta^3\text{-C(OMe)CR=CHR}'\}(CO)_3]$, have also been used to form dinuclear complexes containing bridging vinylalkylidene ligands [16,89–91] as shown in Scheme 23. Since the synthetic approach is modular and allows the assembly of two different metal complexes, one containing the vinylcarbene ligand, it is very useful for the preparation of heterodinuclear species, such as the complexes



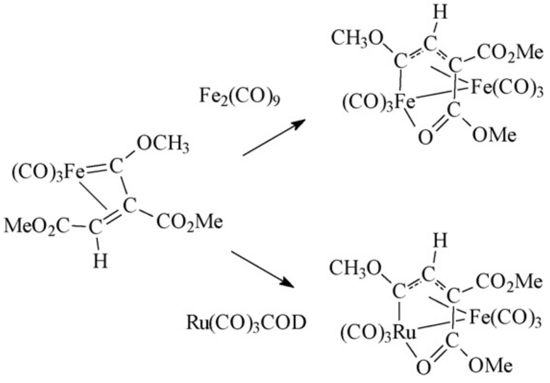
Scheme 20.



Scheme 21.



Scheme 22.



Scheme 23.

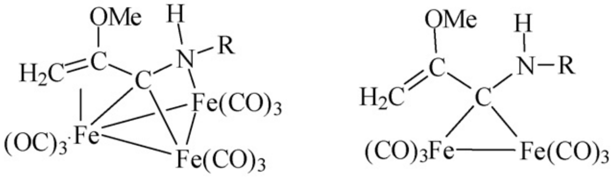
[FeRu{μ–η^1:η^3C(OMe)C(CO_2Me)CH(CO_2Me)}$(CO)_6$] [91], and [WFe (μ–η^1:η^3C(OR)CH=CHR′)] [92].

The reactions described above almost exclusively involve α,β-unsaturated alkoxycarbene ligands. However, the more stable aminocarbene ligands can also act as a source of bridging vinylalkylidene complexes. Aumann reported that the aminocarbene complex [Cr{C(NHCy)C(OCH_3)=CH_2}$(CO)_5$] (Cy = cyclohexyl) reacts with [$Fe_2(CO)_9$] to give, among other products, the di- and trinuclear iron complexes illustrated in Scheme 24. The reaction leads to a transmetalation of the vinylalkylidene ligand. The chromium complex simply delivers the C_3 ligand and is not incorporated into the resulting polynuclear product [52].

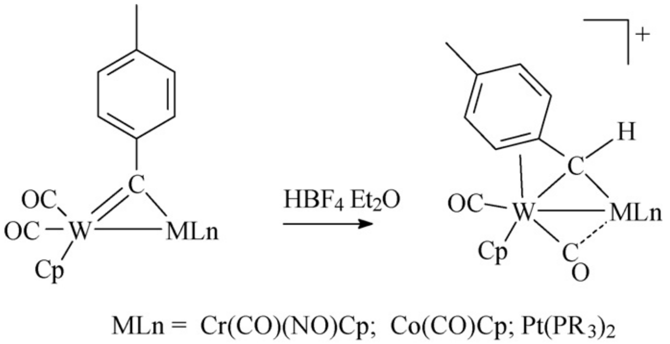
3.10. Other methods

A very fruitful and systematic approach to the synthesis of di- and polynuclear complexes with bridging carbyne and carbene ligands was developed by Stone [93]. In particular, a number of heterodinuclear bridging carbyne complexes containing a p-tolyl (C_6H_4Me-4) group on the carbyne carbon were transformed into the corresponding α,β-unsaturated carbene ligands upon protonation [94–96] (Scheme 25).

Bridging vinylalkylidene complexes can be also produced through a variety of rather unpredictable rearrangements of coordinated species, under forcing reaction conditions, such as prolonged heating or photolysis. This is not surprising in view of the high stability associated with the μ–η^1:η^3 coordination mode. As an example, Knox reported that prolonged UV irradiation of the pentamethylcyclopentadienyl dirutheniumcarbonyl complex [$Ru_2(CO)_4(C_5Me_5)_2$] in toluene for 3 days, in the presence of ethene led to the formation of a variety of species including, as predominant final product, the bridging [Ru_2(μ-CMeCHCH_2)(μ-CO)(CO)$(C_5Me_5)_2$] [97]. Knox also demonstrated that dimetallacyclopentenone complexes of the type [Ru_2{μ-C(O)C(R)C(R)}(μ-CO)(CO)$(Cp)_2$] are a good source of bridging vinylalkylidene complexes, by a range of different transformations. One example is the photolysis of [Ru_2{μ-C(O)C(Me)C(CO_2Me)}(μ-CO)(CO)$(Cp)_2$] (Scheme 26) [98]. The transformation involves loss of CO and H-migration from the methyl group to the adjacent carbon, leading to the coordination of the vinyl group.

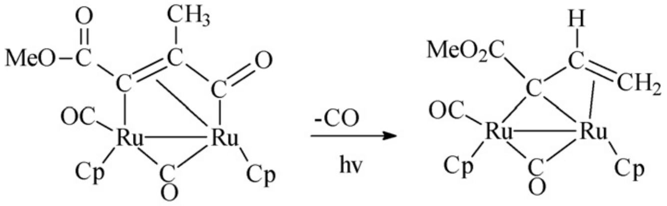


Scheme 24.

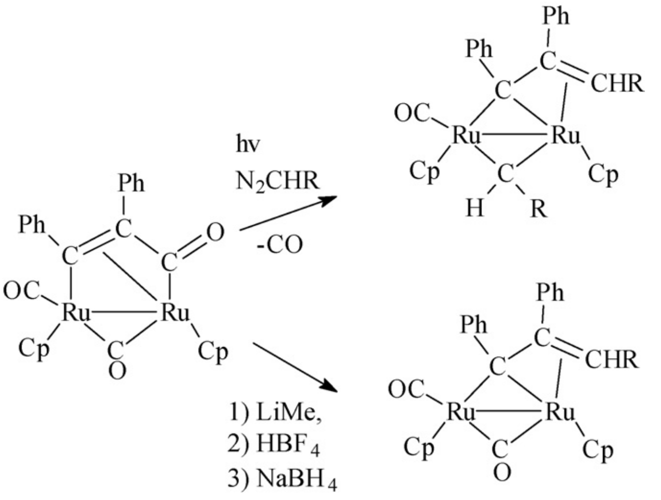


Scheme 25.

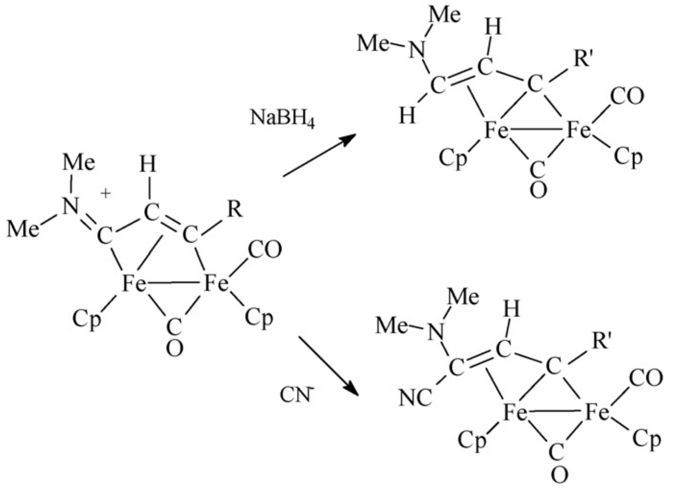
In a related reaction, the dirutheniumcyclopentenone [Ru_2(μ-CO){μ-C(O)C(Ph)C(Ph)}(CO)$(Cp)_2$] forms bridging vinylalkylidene complexes upon treatment with diazoalkanes (N_2CHR); a second alkylidene unit is incorporated as bridging ligand [67]. The cyclopentenone complex also produces a bridging vinylalkylidene product through a sequence of treatments with LiMe, HBF_4 and $NaBH_4$ reagents (Scheme 27).



Scheme 26.



Scheme 27.



Scheme 28.

Common features in these reactions are the C–C cleavage and replacement of the CO group in the bridging ligand with an alkylidene unit.

Diiron vinyliminium complexes exhibit some analogies to the dimetallacyclopentenone complexes mentioned above, in that the bridging ligand displays the same coordination mode, with an iminium group ($Me_2N{=}C<$) in the place of the carbonyl ($O{=}C<$). A noteworthy difference is that the diiron complexes are positively charged and the bridging C_3 ligand displays a significant electrophilic character. Therefore, nucleophilic additions take place easily at the vinyliminium ligand with a variety of reagents including hydride [99,100], carbon nucleophiles, such as cyanide [101] and acetylides [102], and lead to the formation of vinylalkylidene complexes (Scheme 28).

Diruthenium vinyliminium complexes analogous to those shown in Scheme 28 are also known. Replacement of iron with ruthenium does not affect the reactivity, in that reactions of the vinyliminium diruthenium species with $NaBH_4$ closely parallel those of the corresponding diiron complexes, affording bridging vinylalkylidene products [103].

Nucleophilic additions directed to the iminium carbon are limited to complexes in which the N substituents are methyls, like those shown in Scheme 28. Replacement of a methyl with more sterically demanding substituents, such as a xylyl group, exerts a controlling influence over the reaction and direct the nucleophilic attack to the central carbon of the C_3 frame. In this latter case the reaction products are bis-alkylidene complexes, instead of vinylalkylidenes.

Two aspects make the reactions shown in Scheme 28 particularly interesting: (i) the additions are stereoselective and produce the isomeric forms in which the NMe_2 group is *trans* with respect to the μ alkylidene carbon; and (ii) the synthetic method affords bridging C_3 ligands containing different functional groups which can be exploited to promote further reactions and transformations.

A further observation is that the stability of the bridging vinylalkylidene complexes act as a sort of 'driving force' promoting and directing intramolecular rearrangement. Thus nucleophilic additions directed to sites other than the iminium group, such as the Cp, can be followed by intramolecular rearrangement, with hydrogen transfer from the cyclopentadiene to the bridging C_3 ligand, ultimately affording vinylalkylidene products (Scheme 29) [104].

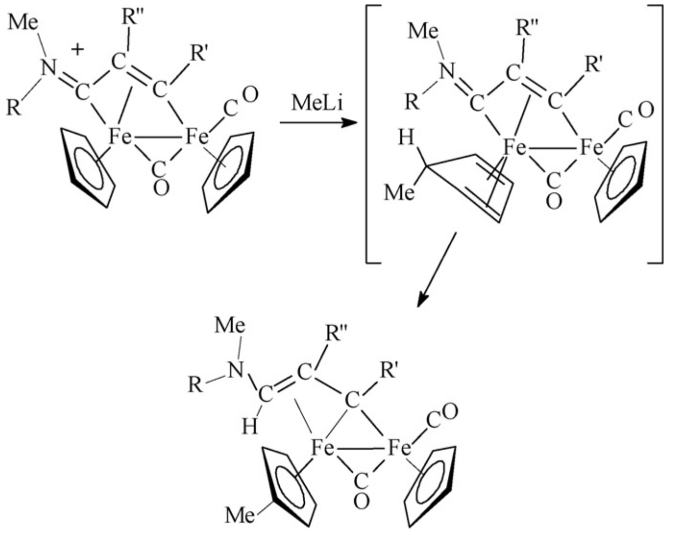
4. Reactions of μ-vinylalkylidene complexes

As the μ-η^1:η^3 coordination provides strong stabilization of the vinylalkylidene ligand, the dinuclear complexes do not easily release the bridging C_3 ligand, nor do they decompose upon mild heating [65]. However, in spite of their stability, dinuclear complexes with bridging vinylalkylidene ligands exhibit a remarkable reactivity and undergo a variety of transformations which we now briefly summarize. One major aspect is C–C bond formation which involves the bridging C_3 ligand and leads to the formation of hydrocarbyl frames of increased length and complexity.

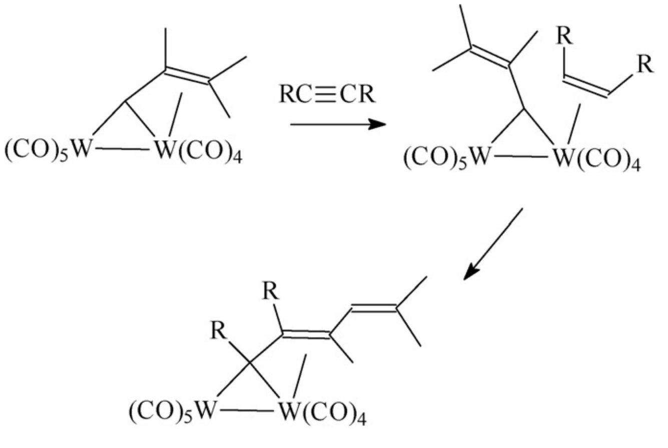
4.1. Reactions with alkynes

Among the reactions which have been investigated, the incorporation of alkynes resulting in the formation of unsaturated bridging hydrocarbyl chains, displaying dienylalkylidene character, is certainly one of the most important, as these reactions have implications for metathesis and alkyne polymerization. Rudler reported that bridging vinylalkylidenes behave as initiators and carriers of the carbon chain growth in 2-butyne polymerization [105–107]. The products formed by the insertion of stoichiometric amounts of alkynes are shown in Scheme 30.

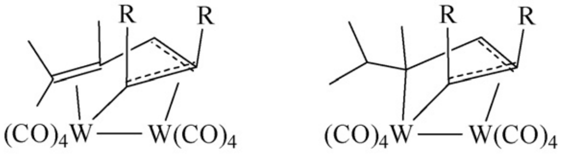
Rudler also reported that the complexes formed by alkyne addition to the bridging C_3 ligand can rearrange, producing bridging fragments of the type shown in Scheme 31 [108].



Scheme 29.



Scheme 30.



Scheme 31.

Other possible outcomes in the reaction with alkynes arise from the presence of specific functionalities. As an example, the incorporation of alkynes containing phosphino groups leads to the formation of dinuclear species with bridging phosphido and allenyl ligands (Scheme 32) [109].

In addition to the ditungsten complexes described above, diruthenium vinylalkylidene complexes undergo similar reactions with alkynes, as reported by Knox [60,64,46] (Scheme 33).

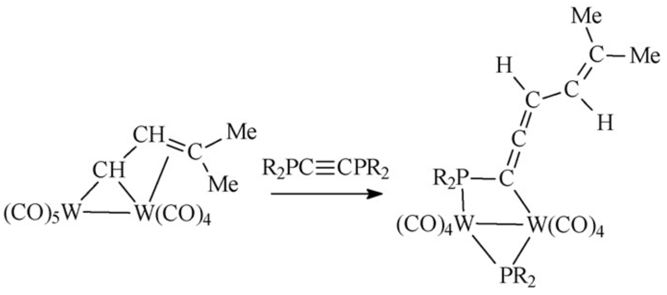
In the diruthenium complexes the double alkyne insertion leads to bridging five-carbon chains of differing stereochemistry: the incorporated olefinic units can adopt a *cis* or *trans* configuration depending on steric crowding of the alkyne substituents. This observation suggests that stereoregular polyalkynes can be obtained from bridging dinuclear alkylidene complexes through controlled manipulation of steric constraints.

The structures of the complexes illustrated in Schemes 30–33 show the complexity of these reactions and the various reaction paths that are readily available to these systems.

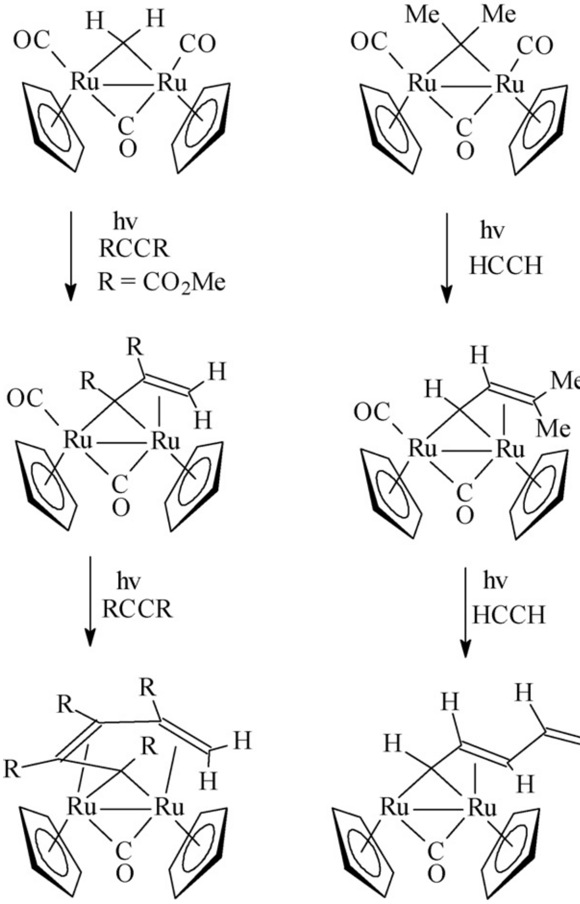
This point is better substantiated by the reaction of vinylalkylidene dimolybdenum complexes with alkynes, investigated by Green. In addition to the insertion of one acetylene unit in a way similar to that described above the reaction can proceed with the incorporation of CO leading to the cleavage of the Mo–Mo bond. The resulting metal frameworks remain connected through an unsaturated ligand formed by the coupling of the C_3 (vinylalkylidene) and C_2 (acetylene) units and a CO [110,111] (Scheme 34).

The di-molybdenum vinylalkylidene complexes also react with 1,3-dienes and allenes, generating a range of dinuclear products with different bridging hydrocarbyl ligands [111]. In particular the reaction with allenes cleaves the Mo–Mo bond, and to couple with the vinylalkylidene ligand forming bis allylic derivatives (Scheme 35).

Alkyne oligomerization follows a different route in the case of the di-rhodium complex $[Rh_2(\mu\text{-}CH_2)_2(NCMe)_2(Cp^*)_2][PF_6]_2$ containing two bridging methylidene ligands, shown in Scheme 36 (Here and elsewhere $Cp^* = \eta^5\text{-}C_5Me_5$). A first phenylacetylene unit is coupled with the methylidene yielding a bridging vinylalkylidene intermediate. A second phenylacetylene unit is incorporated forming C–C bonds with both the C_3 ligand and the methylidene. The overall result consists in the formation of a bridging C_6 hydrocarbyl ligand [63] (Scheme 36).



Scheme 32.



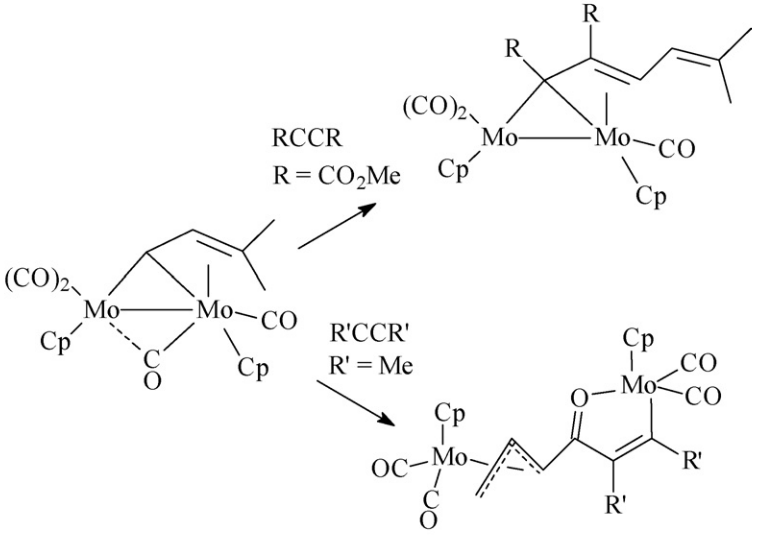
Scheme 33.

A related reaction occurs upon treatment of the di-alkynyl-di-μ-methylidene–dirhodium complexes $[\{Cp^*Rh(\mu\text{-}CH_2)(C_2Ar)\}_2]$ with HBF_4, as shown in Scheme 37 [112]. Here the proton induced coupling of the alkynyl and methylidene units takes place before the two C_3 units are linked. The resulting C_6 frame is therefore different from that shown in Scheme 36, obtained by a different coupling sequence. Moreover, the two rhodium atoms give rise to two separated and symmetric units and products displaying both *syn-* and *anti*-geometry are observed.

4.2. Cyclization reactions

As mentioned in Section 1, an important application of mononuclear vinylcarbene complexes is in the field of cyclization reactions. The most typical is the Dötz benzannulation of vinyl (or aryl) metal–carbene complexes in which classic Fischer alkoxycarbene complexes, like $[Cr(CO)_5C(OMe)R]$, undergo a [3+2+1] cycloaddition, combining the vinylcarbene, alkyne and CO. The benzannulation provides a one-pot access to substituted oxygenated arenes (Scheme 38).

The mechanism of the benzannulation [113–122] is believed to consist of a stepwise alkyne–carbene–CO coupling sequence. The rate determining step is thought to be the decarbonylation of the carbene complex precursor allowing alkyne coordination. Insertion of the alkyne into the metal–carbene bond producing a η^3-vinylacarbene intermediate, is followed by CO insertion that results in the formation of a η^4-vinyl ketene species. Subsequent ring closure generates a cyclohexadienone complex which rearranges to a $M(CO)_3$ coordinated hydroquinone complex.



Scheme 34.

In principle, the sequence described above should take place also with bridging vinylalkylidenes. Alkyne insertion is feasible, as discussed in the previous paragraph, but CO insertion is apparently unfavourable and this might explain the absence of cyclization reactions equivalent to the benzannulation in the case of bridging vinylalkylidenes.

One significant exception is the reaction reported in Scheme 39 [110] which to the best of our knowledge represents a unique example of cyclization involving a bridging vinylalkylidene ligand, that has some analogies with the benzannulation. The coordination mode of the dienone ligands, investigated by an X-ray diffraction study, also shows some complexity due to the considerable delocalization of the diene fragment.

The cycloaddition product is only obtained in modest yield, among other products. Therefore the reaction is not selective and the major reaction product results from the cleavage of the Mo–Mo bond. The two Mo atoms are connected through a bridging ligand obtained from the assembly of the μ-C_3, the alkyne and CO, but without cyclization.

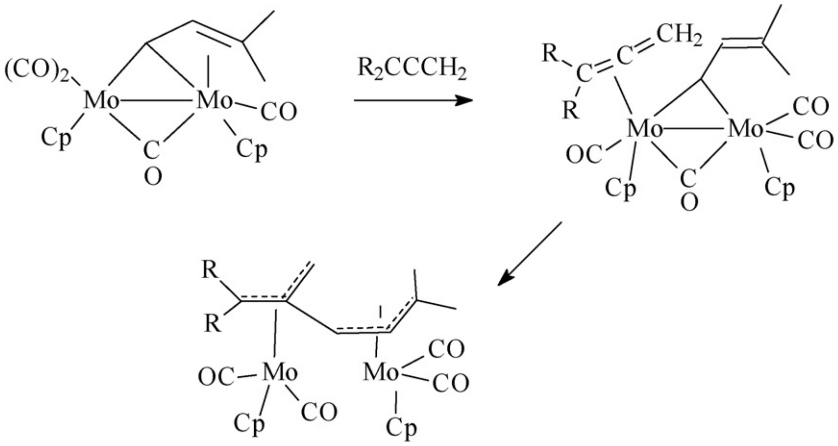
In spite of its unique and rather unpredictable character, the cyclization shown in Scheme 39 is of great interest because it is related to the Dötz benzannulation, in that it produces a cyclohexadienone derivative by the combination of a vinyl alkylidene ligand, a CO and an alkyne.

An example of cycloaddition that involves a bridging vinylalkylidene and an alkyne without CO insertion is offered by the reactions of the diiron complexes shown in Scheme 40. The noteworthy feature of these reactions is the “one-pot” formation of substituted ferrocenes [123].

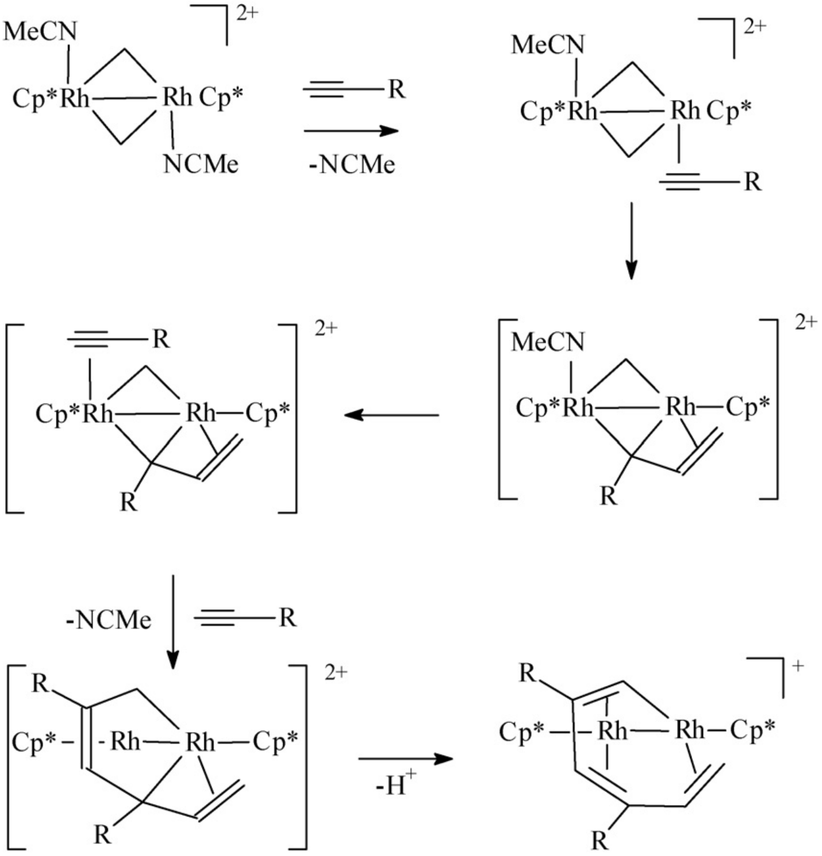
The tetrasubstituted Cp ligands arise from the cycloaddition of the vinylalkylidene ligand and the alkyne, and must arise from the cleavage of a C–H bond in the vinyl moiety of the bridging C_3 ligand. Since this latter contains several functionalities, these are transferred as substituents in the Cp ring as a consequence of the cycloaddition. The reaction also fragments the diiron precursor: one Fe and a C_5H_5 ring, together with the C_3 ligand and the alkyne give rise to the observed ferrocene, while the remainder of the diiron precursor generates some $[Fe_2(CO)_4(Cp)_2]$. This reaction provides a useful route to the formation of ferrocenes containing one Cp ring with different substituents. These are normally difficult to make by the usual lithiation/substitution methods.

4.3. Nucleophilic and electrophilic additions

Vinylalkylidene ligands are unsaturated species potentially susceptible to both nucleophilic and electrophilic additions, probably controlled by factors such as the nature and size of the substituents and the overall charge of the complex.



Scheme 35.



Scheme 36.

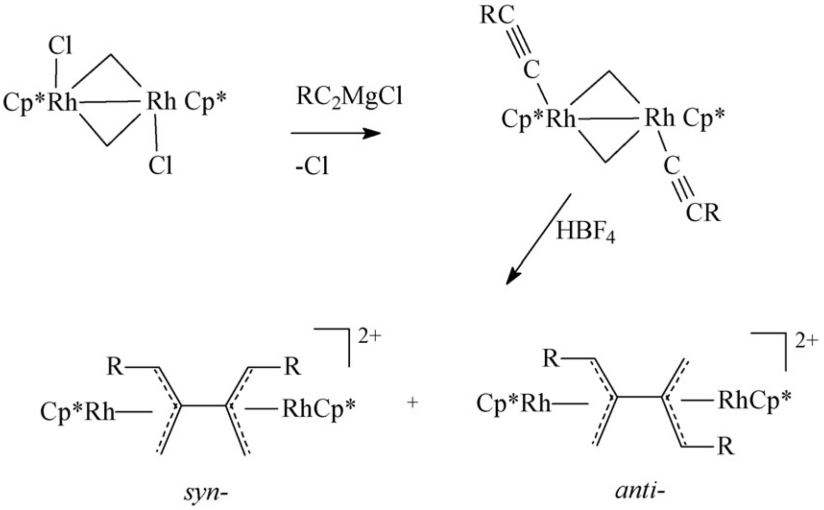
Examples of nuclephilic/electrophilic additions are so far relatively scarce.

The treatment of di-tungsten vinylalkylidene complexes with tertiary phosphines (Scheme 41) exhibits two possible outcomes: addition can be directed to the metal leading to the displacement of the vinyl coordination, or it can produce a zwitterionic derivative by phosphine addition at the vinyl moiety of the C_3 ligand [124].

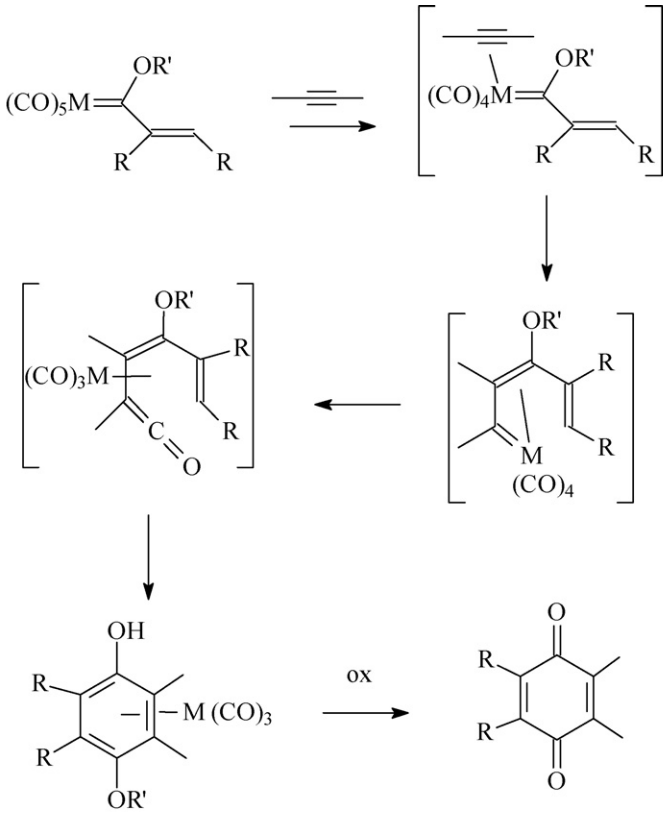
Diruthenium complexes containing bridging vinylalkylidene ligands, derived from propargyl alcohols, undergo protonation and H_2O elimination (Scheme 42), leading to the formation of a butadienyl complex adopting a μ–η^2:η^3 coordination mode [59].

Interestingly, the vinylalkylidene–butadienyl transformation can be reversed in that cationic diruthenium butadienyl complexes are susceptible to nucleophilic addition (e.g. by H^- or MeLi) which transforms the bridging C_4 frame into a vinylalkylidene ligand [59] (Scheme 43).

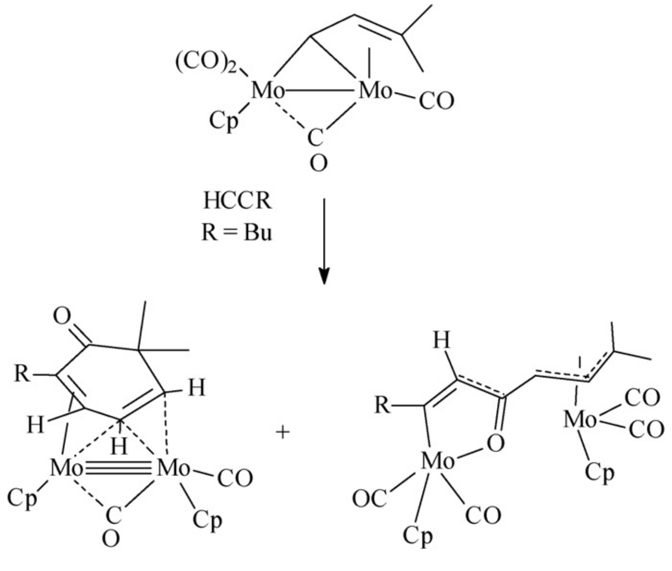
Bridging vinylalkylidene ligands in anionic complexes obviously undergo protonation more easily. The anionic [(Cp)Mo(CO)(μ–η^1:η^3-$CH_3CHCHCH$)(μ-PPh_2)Mn(CO)$_3$]$^-$, is believed to be the



Scheme 37.



Scheme 38.



Scheme 39.

intermediate species obtained from a μ-allyl precursor upon deprotonation with LiBu. Here protonation of the anionic product simply reverses the reaction and regenerates the allyl precursor [77].

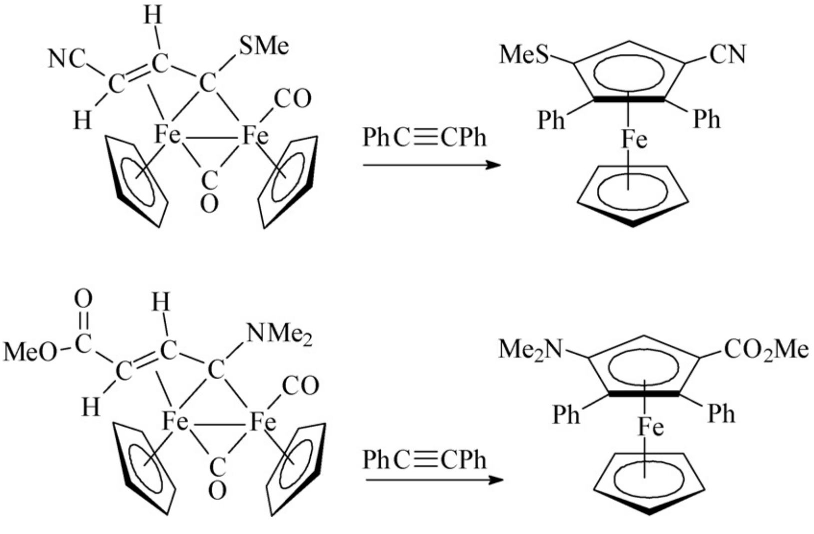
4.4. Carbonylation and decarbonylation reactions

Addition of CO (100 atm at 50 °C for 17 h) displaces the vinyl moiety from metal coordination in the diruthenium complex reported in Scheme 33. The change of coordination from a four to a two electron donor (corresponding to **A** and **E** type coordination, respectively, in Scheme 1) required vigorous reaction conditions which are indicative of the stability of the olefinic coordination [46]. The reverse transformation (from **E** to **A** coordination) is obviously promoted by CO removal and is easily accomplished on photolysis or by heating at 100 °C (Scheme 44).

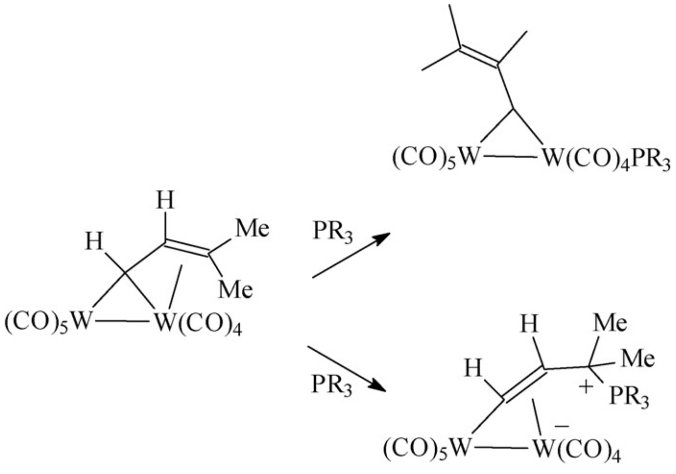
The reversible transformation between four and two electron donor coordination modes is not limited to the **A** and **E** configurations. Thus the dimetallacyclopentene coordination mode (**F**, Scheme 1) also generates a four electron donor bridging vinylalkylidene ligand upon CO loss by heating [44] (Scheme 45).

In this reaction the dimetallacyclopentene results from the addition of a phosphine to a bridging allenyl ligand. The dimetallacyclopentene character of the bridging C_3 ligand (HC–C(P) and CH_2–C(P) bonds are 1.379(6) and 1.446(6) Å, respectively) does not represent an obstacle to the conversion to bridging vinylcarbene and the reaction once again shows how easily the μ-C_3 frame can adjust to changes in the coordination sphere.

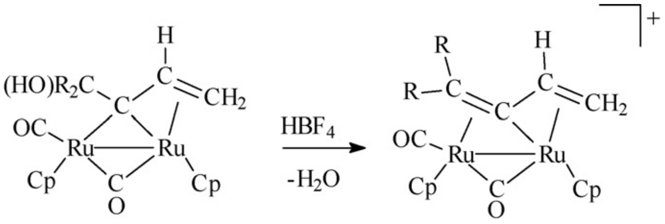
A different carbonylation pattern is observed in the reaction described in Scheme 46 [125].



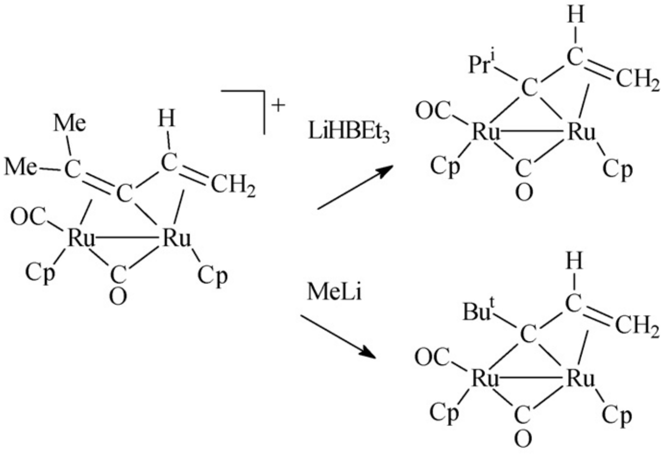
Scheme 40.



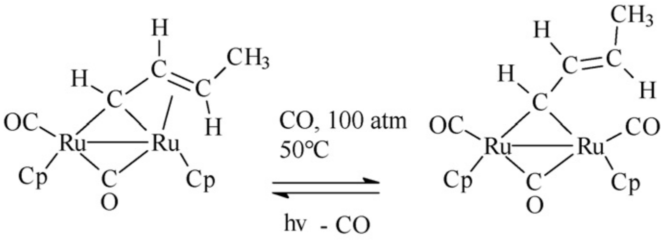
Scheme 41.



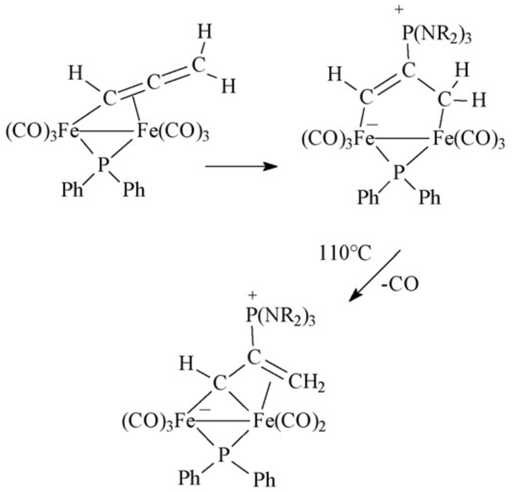
Scheme 42.



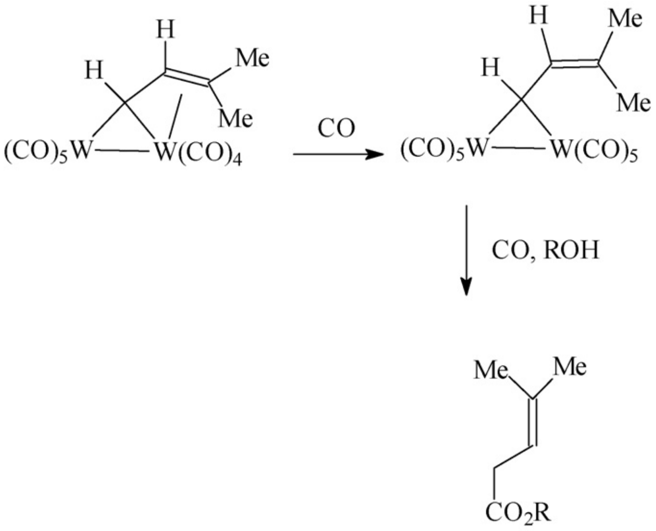
Scheme 43.



Scheme 44.



Scheme 45.

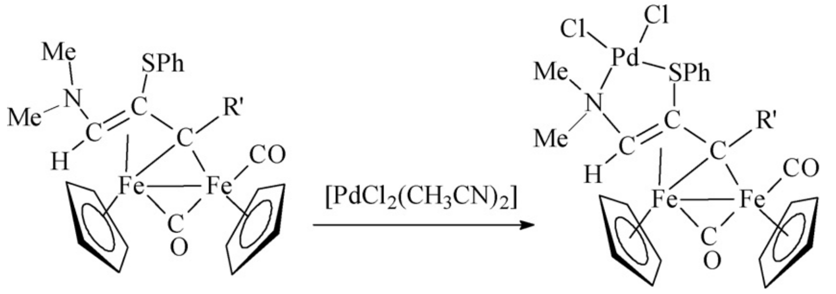


Scheme 46.

The addition of CO again releases the vinyl coordination, but in this case further carbonylation takes place at the bridging ligand and leads to the release of the bridging unit as a carboxylate derivative in the presence of ROH. This is an interesting example of the transformation and release of a bridging vinylalkylidene ligand.

4.5. Coordination of metal fragments

Bridging vinylalkylidene complexes in which the C_3 ligands contain donor heteroatoms (e.g. N, O, S) not directly involved in the coordination, have the potential to exploit these functionalities to coordinate further (external) metal centers. Therefore these species can overall act, as 'organometallic ligands'. An example is shown in Scheme 47 [126], from which it can be seen that, as coordination of the C_3 ligand to a further metal centre does not directly involve the C_3 carbon chain, only very limited changes occur in the coordination modes of the iron atoms.



Scheme 47.

5. Summary and conclusions

Bridging vinylalkylidene ligands display some distinctive features with respect to both vinylalkylidenes bound to a single metal center and other bridging C_3 ligands (e.g. allenyls, allyls). In particular, the μ–η^1:η^3 coordination allows the vinylalkylidene ligand to firmly bind to the adjacent metal atoms. At the same time, the unsaturated and highly delocalized character of the C_3 ligand, makes it 'flexible' and able to respond, even to major changes in the dinuclear frame, without affecting its binding properties. As a consequence bridging vinylalkylidenes are able to participate in a variety of homo and heterodinuclear complexes, with different charges, oxidation states, and ancillary ligand arrays. Bridging vinylalkylidenens can be obtained by a number of synthetic methods, for example by assembling and combining C_1 and C_2 coordinated ligands directly on the dinuclear framework. This can also extend the number and type of substituents and functional groups that can be placed on the bridging C_3 ligand. These potential advantages indicate that the use of bridging vinylalkylidene ligands in the synthesis of more complex molecular architecture has a bright future and should be exploited. Although, following the initial intense research efforts, in the eighties, interest in bridging C_3 hydrocarbyl ligands later declined, more recently there has been a resurgence of activity, due to the need for new metal promoted synthetic processes, and the use of complexes based on cheaper and environmentally safer metals. We anticipate important future developments in the chemistry of dinuclear bridging vinylalkylidenes that will lead to new metal-mediated syntheses and catalyses.

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