1 Preparation and Stoichiometric Reactivity of Mononuclear Metal Vinylidene Complexes

Michael I. Bruce

1.1 Introduction

Vinylidene, \( :C=CH_2 \), is a tautomer of ethyne, \( HC≡CH \), to which it is related by a 1,2-H shift (Equation 1.1):

\[
HC≡CH \rightarrow :C=CH_2
\]  

Attempts to produce vinylidene in the free state result in rapid reversion to ethyne, with a lifetime of \( 10^{-10} \) s [1]. As with many reactive organic intermediates, however, vinylidene can be stabilized by complexation to a metal center, using the lone pair for coordination and thus preventing the reversion to ethyne. Most 1-alkynes can be converted into the analogous vinylidene complexes by simple reactions with appropriate transition metal substrates (Equation 1.2):

\[
ML_n + HC≡CR \rightarrow L_n M = C=CHR
\]  

The first vinylidene complex, \( \text{Fe}_2(\mu-C≡CPh_2)(\text{CO})_8 \), was obtained by Mills and Redhouse by irradiation of diphenylketene with \( \text{Fe} (\text{CO})_5 \) [2]. The first terminal vinylidene complex, \( \text{MoCl} = C≡C(\text{CN})_2(P\text{Ph}_3)_2\text{Cp} \), was prepared by King and Saran from the reaction between \( \text{Mo} \{\text{CCl}=C(\text{CN})_2\} (\text{CO})_3\text{Cp} \) and \( \text{PPh}_3 \) [3]. Several groups reported synthetic approaches to metal vinylidene complexes during the late seventies, including platinum-stabilized carbenium ions by Clark and Chisholm [4], manganese and rhenium vinylidens by Russian workers [5, 6], an iron vinylidene by Mays [7], and the present author’s work on ruthenium and osmium systems [8]. Further studies, including Hughes’s conversion of iron acyls to vinylidenes with \( \text{Tf}_2\text{O} \) [9] and Mansuy’s serendipitous synthesis of a vinylidene-iron porphyrin system [10] followed soon after.

Much of the chemistry of metal-vinylidene complexes has been summarized in several reviews [11–14] and the following will merely summarize the main preparative methods and survey the reactions of many of the metal complexes so obtained. Complexes of most transition metals have been described, although most work has been developed using electron-rich ruthenium derivatives, which have been used in
the multitude of catalytic reactions (either directly or prepared in situ) described in the main part of this volume. A special issue of *Coordination Chemistry Reviews* was devoted to the chemistry of vinylidene, allenylidene and cumulenylidene complexes [15]. Specific reviews of vinylidene complexes of elements of various Periodic groups have been published: Ti, [16] Mn [17, 18], W, [19] Fe, Ru, Os, [20–23] Rh, Ir, [24] and much chemistry is summarized in the particular Group volumes in the recently published COMC 3 [25]. Applications of metal vinylidene complexes to catalysis form the major part of this volume and have been previously reviewed [26–30].

There is not sufficient space to discuss all vinylidene complexes which have been reported, for example over 200 crystal structures are listed in the CCDC. Consequently, this article largely concentrates on the chemistry of metal vinylidene complexes which has been described since 1995. Vinylidene complexes are generally available for the metals of Groups 4–9, with several reactions of Group 10 alkynyls being supposed to proceed via intermediate vinylidenes. However, few of the latter compounds have yet been isolated. This chapter contains a summary of various preparative methods available, followed by a survey of stoichiometric reactions of vinylidene-metal complexes. A short section covers several non-catalytic reactions which are considered to proceed via vinylidene complexes. The latter, however, have been neither isolated nor detected under the prevailing conditions.

1.2
Preparative Methods

The main synthetic approaches to metal-vinylidene complexes will be discussed under the following headings:

1. From 1-alkynes via a 1,2-hydrogen shift.
2. The $\eta^2$-alkyne $\rightarrow$ hydrido($\eta^1$-alkynyl) $\rightarrow$ vinylidene transformation.
3. From metal alkynyls.
4. From metal allenylidenes via metal alkynyls.
5. By deprotonation of metal-carbyne complexes.
6. From metal-carbon complexes.
7. From acyl complexes.
8. From metal-vinyl complexes.
10. Miscellaneous methods involving the use of other precursors.
11. Vinylvinylidenes.

1.2.1
From 1-Alkynes (Equation 1.3)

\[
ML_n + HC\equiv CR \rightarrow L_nM=\equiv C=\equiv HRML_n
\]  

(1.3)
This is the most common route to vinylidene complexes and occurs in reactions of the 1-alkynes with metal complexes, preferably with labile neutral or anionic ligands, which give neutral or cationic complexes, respectively. In the latter case, halide is commonly extracted, either by spontaneous displacement by a polar solvent, or by using sodium, silver or thallium salts.

Isomerization of the 1-alkyne to vinylidene generally occurs at d⁶ metal centers which are coordinatively unsaturated. The relative stability of the vinylidene complex increases with rising electron density at the metal center. The kinetics and mechanisms of the various reactions have been studied extensively, commonly accepted mechanisms being initial formation of an η²-alkyne complex which then undergoes either a 1,2-H migration with concomitant formation of the η¹-vinylidene directly, or an oxidative addition to form a hydrido(alkynyl) complex, from which the vinylidene ligand is formed by a 1,3 H-shift. A variety of theoretical treatments of the course of this reaction have appeared, a recent comprehensive summary by Wakatsuki [31] providing a useful starting point for discussion.

The reactions on Rh/Ir usually proceed via oxidative addition to give hydrido (alkynyl) complexes, which then undergo 1,3-H shifts to form the vinylidene complexes. In general, a unimolecular mechanism has been considered to be operative. Recent studies of RhCl(PPr⁴₂R)₂ (R = CNCBuᵗ = CHNMe) complexes have shown a remarkable acceleration of the isomerization, with the =C=CHBu complex being formed within seconds [32]. Suitable cross-over experiments showed that a bimolecular mechanism, earlier suggested by some experimental and computational results [33], did not operate.

A range of metal-ligand centers has been shown to facilitate the formation of vinylidene complexes from 1-alkynes, a selection of recent examples being given in Table 1.1. In some cases, the preparation of the vinylidene is improved by deprotonation of the initial product to give the corresponding alkynyl compound, which can be reprotonated (see next section). Syntheses of both cationic and neutral vinylidene complexes can be achieved, the former by displacement of halide or triflate in a polar solvent, or of a labile neutral ligand, such as dinitrogen in ReCl(N₂)(dppe)₂. Neutral vinylidene complexes are obtained by the latter route and offer the opportunity of exchange of halide for other anionic ligands (for example).

Efficient syntheses of ruthenium complexes from readily available starting materials, such as RuCl₂(=C=CH₂)(L)₂ from {RuCl₂(cod)}ₙ, H₂ and PPr⁴₃ (L) in 2-butanol with C₂H₂ [34] or RuCl₂(=C=CHBu')(PCy₃)(Imes) from {RuCl₂(p-cymene)}₂, [ImesH]Cl, NaOBUᵗ and HC≡CBut [35], have been described. Reactions of allyl-Ru complexes with 1-alkynes in the presence of HCl result in ready displacement of the allyl group and formation of neutral complexes RuCl(=C=CHR)(PPh₃)Cp⁺ [36, 37]. Alternatively, complexes containing hemi-labile ligands, such as PPr⁴₂(CH₂C(O)OMe), PPr⁴₂(CH₂CH₂OMe, and PPr⁴₂(CH₂CH₂NMe₂) (=P ~ O, P ~ N), can be used to generate a vacant coordination site for the incoming vinylidene [38]. Reactions of {Ru[PPh₃]₂(η²-PPh₂(CH₂CH=CH₂)}(η⁵-C₅H₁₀) with HC≡Car give {Ru(=C=CHAr)[PPh₃]₂(η¹-PPh₂(CH₂CH=CH₂)}(η⁵-C₅H₁₀) [39]. In Group 9, other starting materials include {RhCl(L)₂} and IrH₂Cl(L)₂ (the complex IrCl(L)₂ is inaccessible). Direct reaction of Rh(C≡CH)(η-C₂H₄)(L)₂ with HC≡CH in

1.2 Preparative Methods
the presence of NEt₃ affords trans-Rh(C≡CH)(≡C=CH₂)(L)₂ [40] while the more basic [Rh(PMe₃)₄]Cl reacts directly with 1-alkynes by C–H activation and oxidative addition to give [RhH(C≡C≡CH)(PMe₃)₄]Cl, no migration of H to the metal being observed [41].

A variety of substituents can be tolerated (usually H, alkyl, aryl, SiMe₃, CO₂R), but in some cases, intramolecular nucleophilic attack on a presumed intermediate vinylidene complex results in the formation of carbene complexes. Ready replacement of SiMe₃ by H makes HC≡CSiMe₃ an attractive precursor for the parent complexes containing ≡C=CH₂ ligands. However, the strongly nucleophilic character of the OH group in hydroxyalkyl-alkynes often results in rapid addition to Cα. If the alkyl chain is long enough, cyclic oxacarbenes can be formed; if not, then intermolecular attack on a second molecule results in binuclear derivatives, which may contain both carbene and vinylidene functions (see Section 1.5).

Some notable complexes which have been reported include [Re(CN)(≡C=CHPh)(dppe)]⁺ from aminocarbene [ReCl(CNH₂)(dppe)]⁺ and HC≡CR [42]; [Ru(≡C=CHC≡C[RuCl(CO)₆(PPh₃)₂])(PPh₃)₂CP]{PF₆}, from RuCl(C≡CC≡C)[(PPh₃)₂CP]{PF₆}, [Ru(thf)(PPh₃)₂CP]{PF₆}[43]; the fullerenic derivative RuCl[(R)-prophos]{(η⁵-C₆₀Me₅)} can be converted to [Ru(≡C=CHPh){(R)-prophos}{(η⁵-C₆₀Me₅)}]⁺ with good diastereoselectivity [44].

Although the majority of ruthenium complexes contain tertiary phosphines as co-ligands, N-donor ligands are present in complexes obtained with Ru(tmeda) Cp [45], RuCl(Me₂bpy)(PPh₃)₂ [46], RuCl(L) [L = (dmpz)₂-acetate [47], 2,6-(dmpz)₂-

<table>
<thead>
<tr>
<th>Metal</th>
<th>Metal-vinylidene complexes, LₙM≡C≡CRR', prepared from 1-alkynes.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>Co(PBu₃CH₂CH₂CH₂·η-C₅H₄)[56]</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe(CO)₂(PEt₃)₂ [57], Fe(PPh₃)Cp⁺ [58], FeCl(PPh₂)₂ [59]</td>
</tr>
<tr>
<td>Ir</td>
<td>Ir[N(SiMe₂)₂CH₂PPb₂]₂[60]</td>
</tr>
<tr>
<td>Mn</td>
<td>Mn(u)(CO)₃(P) [61], Mn(CO)₃Cl [5, 6]</td>
</tr>
<tr>
<td>Mo</td>
<td>Mo(P)(η-C₅H₅)</td>
</tr>
<tr>
<td>Os</td>
<td>Os(CO)(NO)(PMe₃)₂, Os(CO)LCl [64, 65], OsX(pcp) [66, 67], OsXP₂ [68], OsClPcp [69], OsHX₂P₂ [70–72], OsP₂(η-arene) [73, 74], OsP₂CP [75–77]</td>
</tr>
<tr>
<td>Re</td>
<td>Re(CO)₂P₂ [78], Re(CO)₂[MeC(CH₂PPh₂)₂] [79–81], Re(CO)₂ClP [82], ReCl(PPh₂) [42]</td>
</tr>
<tr>
<td>Rh</td>
<td>RhX(L)₂ [40, 52]</td>
</tr>
<tr>
<td>Ru</td>
<td>RuXL(P)₂ [83], RuHXP₂ [84–86], RuP₂L₄[87], RuXP(N₃) [88], Ru(pup) [89], RuCl(NN)P₂ [46, 47], RuCl(P = O)₂ [90–93], RuClL₂ [48–50, 94, 95], RuCl(PPh₂) [53, 54, 96–100], Ru(u)(CO)LP [101–104], Ru(L)PCP [105, 106], RuL₂P [39, 45, 107, 108], RuClPcp [109–111], RuP₂P [112–120], RuP₂P⁺ [111, 121, 122], RuL₂P⁺ [123–125], RuXP₃ [111, 125], RuL₂P₃ [126, 127], RuP₂P₃⁺ [127–130], RuClP₂O₂C(dpmpz₂) [47], Ru(P = O)(η-arene) [131], RuClP(η-arene) [132]</td>
</tr>
<tr>
<td>Tc</td>
<td>TcCl(PPh₂) [133]</td>
</tr>
<tr>
<td>W</td>
<td>W(CO)₃(PPh) [134]</td>
</tr>
</tbody>
</table>

References:
1. Preparation and Stoichiometric Reactivity of Mononuclear Metal Vinylidene Complexes
pyridine [48], 2,6-(NMMe₂CH₂)₂C₅H₃N [49]] fragments. Structurally characterized macrocyclic ruthenium vinylidene complexes include RuCl{=C=CH(C₆H₄X-4)} (16-tmc) (R = H, Cl, Me, OMe; 16-tmc = tetramethyl-1,5,9,13-tetra-azacyclohexadecane) [50], while [Ru(N₃Me₈)≡C=CHR]²⁻ (N₃Me₈ = octamethylporphyrinogen; R = H, Ph) have been obtained from the anionic [Ru(N₃Me₈)]²⁻ and ethyne or HC≡CPh, respectively [51]. In this case, formation of an intermediate η²-alkyne complex is unlikely, the probable mechanism being deprotonation of the alkyne and coordination of the alkylnyl anion followed by proton transfer.

Complexes containing several vinylidene-ruthenium fragments attached to branching organic centers are formed from suitable poly(ethynyl) precursors containing branching organic centers, such as HC≡C─X─C≡CH (X = 1, 4-HOC₆H₄OH, 1,4-C₆H₄(CPh(OH))₂) and {RhCl(L)₂} [52], or from 1,3,5-tri(alkynyl)benzenes (triskela) [53], while convergent syntheses of polynuclear dendrimer complexes have also been described [54]. Reactions between HC≡CR (R = Bu, Ph) and {RuCl(η-C₂H₄)PCy₃}(μ-Cl)₂{Ru(η⁶-p-cymene)} afford {RuCl(=C=CHR)(PCy₃)}(μ-Cl)₃{Ru(η⁶-p-cymene)}; ethyne gives an unusual tetranuclear μ-carbido complex [55].

1.2 Preparative Methods

1.2.1 Migration of Other Groups (SiR₃, SnR₃, SR, SeR)

Although the vast majority of the reactions involving 1-alkynes proceed by 1,2-migration of the terminal H atom, other groups have been found to participate in this transfer. The nature of the other substituent on the 1-alkyne is often crucial, in some cases, for the presence of H providing a high kinetic barrier to the alkyne/vinylidene rearrangement. This barrier is lowered by the presence of Group 14 substituents, such as SiMe₃ or SnPh₃, with well-documented examples of facile 1,2-migration of the heavier groups. The Group 14 substituent may be replaced by H in situ by conventional means, such as treatment with [NBu₄]F.

An early example was provided by the reactions between {RhCl(L)₂}n and RC≡CSiMe₃ ([R = Me, Ph, CO₂Et, CO₂SiMe₃, CH₂OH, C(O)CHPh] [135]. Kinetic studies carried out with FcC≡CSiMe₃ in the same reaction confirmed the 1,2-migration of the SiMe₃ group [136]. Similar silyl migration reactions have been found with C₂(SiMe₃)₂ and Ru(OTf)(NO)(L)₂ [137], Co{(η-C₅H₄C₂H₂CH₂)₂PBu₃} [56], IrCl(N₂)(PPh₃)₂ [138] and IrPh₂(N₂)Tp⁺ [139]. For the former, Me₃SiC≡CC≡CSiMe₃, affords IrCl{(≡C=CSiMe₃)C≡CSiMe₃}(PPh₃). The reaction of an excess of C₂(SiMe₃)₂ with Ru(NCMe)₂{(C₂B₁₀H₁₀)CMe₂(η-C₅H₄)} afforded the first bis(vinylidene)ruthenium complex, Ru{(≡C=CSiMe₃)₂}{(C₂B₁₀H₁₀)CMe₂(η-C₅H₄)} [108].

A sub-set of these reactions is provided by the redox rearrangements of several complexes which have been extensively studied by Connelly and coworkers [140]. Oxidation of the η²-alkyne complexes M{(η²-Me₃SiC₂SiMe₃)(CO)}₂{η-arene} (M = Cr, Mo) results in formation of the vinylidene cations [M{(≡C=CSiMe₃)₂}(CO)}₂{η-arene}]+.

Reactions of RC≡CSnMe₃ with MnCp’{(η⁶-C₇H₈)} in the presence of dmpe give Mn{(≡C=CR(SnMe₃))}{(dppe)Cp’}, while with Ph₃SnC≡CC≡CSnPh₃, the alkylnylvinylidene Mn{(≡C=CSnPh₃}C≡CSnPh₃}{(dmpe)Cp’} is first formed. Subsequent irradiation then affords butatrienyliyldene Mn{(≡C=CSnPh₃)₂}{(dmpe)Cp’}
Stannylalkynes and \([\text{RhCl}(\text{L})_2]_2\) afford many Rh\(\{\text{=C=CR(SnPh}_3\}\}(\text{L})_2\) complexes directly, which react with \(\text{H}^+\) to cleave the SnPh\(_3\) group [144].

The reaction of \(\text{C}_2\text{(SMe)}_2\) with \(\text{RuCl(PPMe}_3\text{)}_2\text{Cp}\) gives \([\text{Ru}\{\text{=C=C(SMe)}_2\}\text{(PPMe}_3\text{)}_2\text{Cp}]^+\) via the \(\eta^2\text{-C}_2\text{(SMe)}_2\) complex [145]. A 1,2-shift of SeR occurs in the reaction between \(\text{RuCl(PPPh}_3\text{)}_2\) and PhC\(\equiv\text{CSePr}_i\) in the presence of Na[BPh\(_4\)], which affords \([\text{Ru}\{\text{=C=CPh(SePr}_i\}\}(\text{PPPh}_3\text{)}_2\text{Cp}]^+\) [146].

1,2-Halogen shifts have been found for tungsten, with assumed formation of iodoxyvinylides in reactions of 1-iodo-1-alkynes with W(CO)\(_5\)\((\text{thf})\) en route to cyclization of 2-(iodoethynyl)styrenes to naphthalenes and of iodo-alkynyl silyl enol ethers [147], while more substantial confirmation is found in Mn\{\(\text{=C=C(I)CH(OR)}_2\text{(CO)}_2\text{Cp}\)\(\text{[R}\equiv\text{Me, Et; (OR)}_2\equiv\text{O(CH}_2\text{)}_3\text{O}\)]\], of which the XRD structure of Mn\{\(\text{=C=C(I)CH(OMe)}_2\text{(CO)}_2\text{Cp}\)\] was determined [148].

1.2.2

The \(\eta^2\text{-Alkyne} \rightarrow \text{Hydrido(}\eta^1\text{-Alkynyl}) \rightarrow \text{Vinylidene Transformation (Equation 1.4)}\)

\[
\text{ML}_n + \text{CH}≡\text{CR} \rightarrow \text{L}_n\text{M} \rightarrow \text{ML}_n\text{C}≡\text{CHR}
\]

Formation of the intermediate \(\eta^2\text{-alkyne complex has been reported in some reactions of 1-alkynes with metal centers, followed by rearrangement to the } \eta^1\text{-vinylidene. This occurs but rarely in the ruthenium series, for example, with Ru(PPMe}_2\text{Ph}_2\text{Cp}, where both } \eta^2\text{-alkyne and vinylidene isomers of the product from C}_2\text{H}_2\text{ have been structurally characterized [149], and Ru(dippe)Cp}^+, \text{ where metastable } [\text{RuH(C≡CR)(dippe)Cp}^+]^+ (R = \text{Ph, CO}_2\text{Me, SiMe}_3) \text{ transform into } [\text{Ru(=C=CHR)(dippe)Cp}^+]^+ \text{ in solution or the solid state [123]. Direct conversion of } [\text{Ru(}\eta^2\text{-HC}_2\text{Ph})(\text{CO})\text{(PPMe}_2\text{)}_2\text{Cp}]^+, \text{ prepared at } −40 °\text{C, to } [\text{Ru(=C=CHPh})(\text{CO})(\text{PPMe}_2\text{)}_2\text{Cp}^+]^+ \text{ occurs upon warming to 25 °C [104]. In contrast, the alkynyl complex predominates in the room temperature solution equilibrium of the PPh}_3\text{ analog [150].}}

The transformation predominates in Group 9 (Rh, Ir) chemistry. Reactions of \{\text{RhCl}(\text{L})_2\}_2\text{ with 1-alkynes give the } \eta^2\text{-alkyne complexes which slowly convert to the hydrido(alkynyl)s at room temperature. The latter are sensitive to air and not often isolated. Addition of pyridine affords RhHCl(=C=CR)(py)\text{(L)}_2\text{, which readily lose pyridine in hydrocarbon solvents to give square-planar trans-RhCl(=C=CHR)(\text{L})_2.}}

Alternatively, the Cp complexes Rh\(\{\text{=C=CHR}\}(\text{L})\text{Cp can be obtained by reaction of the chloro complexes with TlCp. In the iridium series, heating for 36 h in refluxing toluene afforded the vinylidenes in 80–90% yields. Table 1.2 lists several examples of reactions in which the } \eta^2\text{-alkyne complexes have been detected.}

1.2.3

From Metal Alkynyls

In contrast to the alkynyl anion, coordination to a metal center results in C\(_2\) being electron-poor and subject to frontier-orbital controlled nucleophilic attack, while the
metal center and Cβ are electron-rich and electrophilic attack is charge controlled. Consequently, a common route to vinylidene complexes is addition of electrophiles (E+) to pre-formed neutral alkynyl-metal complexes, taking advantage of the polarization of the M≡C≡C⁻ fragment so that Cβ is the preferred site of attack (Equation 1.5):

\[
L_nM = C≡CR + E^+ \rightarrow [L_nM = C≡C(E)R]^+
\]  

(1.5)

The alkynyl-metal complexes are strong carbon bases, with measured pKa values for M(C≡CBut)LaCp being 13.6 [ML2 = Fe(CO)(PMe3)] and 20.8 [ML2 = Ru(PMe3)2] [170].

Table 1.3 lists several examples of MLn groups supporting this reaction.

While protonation affords the vinylidene expected by H migration from the original 1-alkyne, use of other electrophiles provides a convenient route to disubstituted vinylidenes. The stereospecificity of this reaction with Re(C≡C[Re(NO)(PPh3)])  

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### Table 1.2 Some vinylidene complexes, LₙM≡C=CRR', obtained by η²-alkyne → hydrido(η¹-alkynyl) → vinylidene transformations.

<table>
<thead>
<tr>
<th>Metal</th>
<th>MLₙ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>Co[PP(CH₂CH₂PPPh₂)] [151]</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe(CO)₂P(PEt₃)₂ [152]</td>
</tr>
<tr>
<td>Ir</td>
<td>IrCl[PPr₃CH₂CH₂OMe/NMe₂]₂ [153], IrCl₂ [138, 154–156]</td>
</tr>
<tr>
<td>Mn</td>
<td>Mn(CO)₂Cp [157]</td>
</tr>
<tr>
<td>Os</td>
<td>Os(CO)(NO)P₂ [63], OsHX(L)₂ [158], OsXPCp [159], OsP₂Cp [160]</td>
</tr>
<tr>
<td>Rh</td>
<td>RhCl[PPr₃CH₂CH₂OMe/NMe₂]₂ [161, 162], RhXP₂ [32, 40, 163–166]</td>
</tr>
<tr>
<td>Ru</td>
<td>Ru(tmeda)Cp [45], RuCl(P)Cp [36], RuHCl(CO)P₂ [158], RuP₂Cp [149, 167]</td>
</tr>
<tr>
<td>W</td>
<td>W(CO)₅ [168], W(CO)_₄(P) [169]</td>
</tr>
</tbody>
</table>

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### Table 1.3 Some metal vinylidene complexes, LₙM≡C=CRR', obtained from alkynyl-metal systems.

<table>
<thead>
<tr>
<th>Metal</th>
<th>MLₙ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr, Mo, W</td>
<td>M(CO)(NO)Cp [173–177]</td>
</tr>
<tr>
<td>Fe</td>
<td>FeP₄ [178], Fe(P)Cp [179–183]</td>
</tr>
<tr>
<td>Ir</td>
<td>IrCl(L)₂ [154]</td>
</tr>
<tr>
<td>Mn</td>
<td>Mn(CO)₂Cp [184], Mn(P)Cp [185]</td>
</tr>
<tr>
<td>Mo</td>
<td>Mo(CO)₂P₂Cp [186], MoH₃(P)P₂ [187]</td>
</tr>
<tr>
<td>Nb</td>
<td>NbLCP₄ [188]</td>
</tr>
<tr>
<td>Os</td>
<td>OsH(GePh₃)(L)Cp [189]</td>
</tr>
<tr>
<td>Pt</td>
<td>PtMeP₂ [190]</td>
</tr>
<tr>
<td>Re</td>
<td>Re(NO)(PPh₃)Cp [191, 192]</td>
</tr>
<tr>
<td>Rh</td>
<td>RhCl[N(CH₂CH₂PPPh₂)₃] [193, 194], RhClP₂ [195]</td>
</tr>
<tr>
<td>Ru</td>
<td>Ru(P)₄ [196], RuP₂Cp' [171, 197–201], RuP₂Tp [202, 203]</td>
</tr>
<tr>
<td>W</td>
<td>W(CO)₅ [204, 205], W(CO)₂Cp [186], W(O)Tp [206]</td>
</tr>
</tbody>
</table>
Cp has been discussed [170b]. Alkylation with haloalkanes (often iodoalkanes), triflates (alkyl, benzyl, cyclopropyl), or [R₂O]⁺ (R = Me, Et) is often the best entry to vinylidenes of any particular system. Other common electrophiles, such as halogens (Cl, Br, I), acylium ([RCO]⁺), azoarenes ([ArN₂]⁺), tropylum ([C₇H₇]⁺), triphenylcarbenium (trityl, [C₆H₅]+), arylthio (ArS) and arylseleno (ArSe) have also been used.

Several complexes have been obtained from reactions of alkynyl anions, such as [M(C≡CR)(CO)₂]⁻ or [M(C≡CR)(CO)(NO)Cp]⁻ (M = Cr, Mo, W), obtained from M(CO)₅[R] and LiC≡CR, or [Mn(C≡CR)(CO)₃Cp]⁺, under charge-control.

Alkylation may sometimes afford unusual complexes as a result of subsequent reactions (see also below). Reactions of Ru(C≡CR)(PPh₃)(POMe₃)Cp with halides XCH₂R (R = CN, Ph, C₆F₅, C₆H₄CN-4, C₆H₄CF₃-4, 1-nap, CO₂Me) give Ru[P(O)(OMe)]₂{[C≡CPhCH₂R] (PPH₃)Cp via an initial cationic vinylidene which loses MeX in an Arbusov-like reaction [171]. A similar reaction with RNCS gives Ru[P(O)(OMe)]₂{[C≡CPhSH=NR]} (PPH₃)Cp with low yields, which can be improved by working at higher temperatures [172].

1.2.3.1 Some Specific Examples
An interesting series of bimetallic vinylidene complexes is formed in reactions of [W(C≡CBu¹)(CO)₃]⁻ with cationic hydrocarbon-metal carbonyls, such as [M(C≡CR)(CO)₅]⁺ (M = Cr, W), [Mn(C≡CPh)(NO)Cp]⁺, or [Re(C≡CMe)(C≡CPh)(NO)Cp]⁺, under charge-control.

Reactions of Ru(C≡CPh)(PPh₃)(POMe₃)Cp with halides XCH₂R (R = CN, Ph, C₆F₅, C₆H₄CN-4, C₆H₄CF₃-4, 1-nap, CO₂Me) give Ru[P(O)(OMe)]₂{[C≡CPhCH₂R] (PPH₃)Cp via an initial cationic vinylidene which loses MeX in an Arbusov-like reaction [171]. A similar reaction with RNCS gives Ru[P(O)(OMe)]₂{[C≡CPhSH=NR]} (PPH₃)Cp with low yields, which can be improved by working at higher temperatures [172].

Reactions of Mn(C≡CMe)(CO)(PPh₃)Cp with electrophiles such as H⁺, RI (R = Me, Et, Bu¹), MeOTf, [Et₃O]⁺, RC(O)Cl (R = Me, Ph), (tol)NCO, Ph₂C≡C=O, CO₂ and PhCH=CHCOMe give directly the neutral complexes Mn(C≡CMe)(CO)(PPh₃)CpMo⁺ [E = H, alkyl, RC(O), C(O)NH(tol), C(O)CHPh₂, C(O)OMe (after treatment with MeOTf) and CHPCH₂C(O)Me, respectively] (Scheme 1.1) [184, 210]. Aldehydes and ketones react with the propynyl anion to give vinylcarbyne cations after hydroxide elimination, which react with bulky nucleophiles (PPh₃) to give vinylidenes [211]. Similarly, the BF₃ adducts of epoxides react with [Mn(C≡CMe)(CO)(PPh₃)CpMo⁺] to afford anionic [Mn
{eq}C≡CMeCH₂CMe₂(CH₂)nO(BF₃)}(CO)(PPh₃)Cₚ⁻ (n = 0, 1, respectively), possibly via intermediate hydroxyalkyl-vinylidenes Mn{eq}C≡CMeCH₂CMe₂(OH)}(CO)(PPh₃)Cₚ⁺ which undergo intramolecular attack at Cα [210].

Protonation of Ru{eq}C≡CPh₂(C₂H₄)[Co₂(CO)₆]}(PPh₃)₂(η⁵-C₅H₇) and (E,Z)-Ru{eq}C≡CCH=CH(C₂Ph₂[Co₂(CO)₆]}(PPh₃)₂(η⁵-C₅H₇) gives the corresponding vinylidenes [212]. The complex trans-Rh(C≡CH)(η-C₅H₄)(L)₂ is protonated with [pyH]BF₄ to give trans-Rh(=C≡CH₂)(py)(L)₂⁺ and reacts with cyclopentadiene to give Rh(=C≡CH₂)(L)Cₚ [40].

1.2.3.2 Redox Rearrangements of Metal Alkynes and Vinylidenes

Oxidative coupling of metal alkynes to give binuclear bis(vinylidene) complexes is exemplified by MLₙ = Nb(C≡CPh)CₚS₂ [213], Fe(P)CP⁺ [214] or Ru(P)CP⁺ (Equation 1.6): [215]

\[ 2LₙM − C≡CR → [LₙM=C−CR=C=MLₙ]^{2+} \] (1.6)

Suitable oxidizing agents are [FeCP₂]⁺ or Ag⁺, while the cationic species may be reduced back to the alkyne complexes using CoCP₂. Some of this chemistry has been reviewed [216].

Oxidation of trans-RuCl(C≡CCHPh₂)(dppe)₂ favors hydrogen atom transfer leading to trans-[RuCl(=C≡CCHCHPh₂)(dppe)₂]⁺ [217]. Chemical oxidation of Ru(C≡CRc)(PPh₃)₂Cₚ (Rc = ruthenocenyl) gives the cyclopentadienyldiene-ethylidene
Scheme 1.2 [Ru] = Ru(PPh$_3$)Cp. Reagents: (i) [FeCp$_2$]$^+$; (ii) p-benzoquinone.

complex [Ru{$^1$:η$^5$:η$^6$:C=C=C$_5$H$_4$}RuCp]{$^{+}$PPh$_3$$_2$Cp}$^+$, while Ru{$^1$:C=C=C$_5$H$_4$}RuCp$^+$) gives successively [Ru{$^1$:C=C=C$_5$H$_4$}RuCp]{$^{+}$PPh$_3$$_2$Cp}$^+$ and the fulvene-vinylidene [Ru{$^1$:C=C=C$_5$H$_4$}Ru($^1$:C$_5$Me$_4$CH$_2$)]{$^{+}$PPh$_3$$_2$Cp}$^+$ (Scheme 1.2) [218].

Examples of oxidative dehydro-dimerisation of vinylidenes are found with Mo(PP)($^1$:η$^6$:C$_7$H$_7$) [219], M(CO)$_2$Cp (M = Mn, Re) [220, 221] or Mn(PP)Cp$_2$Me$_4$ [185] centers (Equation 1.7):

\[ 2L_nM=C=CHR \rightarrow L_nM=C=CR-CR=C=ML_n \] (1.7)

For M(CO)$_2$Cp, this reaction proceeds via a 16-e alkynyl cation radical [M(C=CPh)(CO)$_2$]$^+$, which, for M = Mn, couples at C$_\beta$ to give the bis(carbony) dication [220]. For M = Re, a similar cation radical is formed, which with NEt$_3$ affords a mixture of {Cp(OC)$^2$Re}=$^1$:C=CPhCPh=C={Re(CO)$_2$Cp} and the isomeric μ-vinylidene {Cp(OC)$_2$Re}$_2$μ-C=CPhC=CPh by competitive C$_\beta$–C$_\beta$ and C$_\beta$–M coupling [221]. With an alternative ligand set, the Mn{$^1$:C=C(R(SnMe$_3$)$_3$)} complexes can be destannylated with[NBu$_4$]F before oxidative coupling to the bis(vinylidene). Reductive uncoupling also occurs, making these systems of interest as potential energy sinks [142].

Oxidation [PhIO or Cu(OAc)$_2$] of [Fe{$^1$:C=CHMe}(dppe)Cp]$^+$ affords bis(vinylidene) [{Fe(dppe)Cp}$_2$(μ-$^1$:C$_4$Me$_2$)]$^{2+}$, possibly via an intermediate radical cation [222]. Similar oxidative coupling of cyclopropenyl Ru{$^1$:C=CPHCH(CN)}{$^{+}$PPh$_3$$_2$Cp affords bis(vinylidene) [{Cp(Ph$_3$P)$_2$Ru}=C=CPHCH(CN)$_2$]$_{2}^+$ which, in turn, can be deprotonated to the bis(cyclopropenyl) [223]. Oxidation of [Ru(N$_4$Me$_8$)(=C=CH$_2$)]$^{2-}$ with PhN$_3$ or [FeCp$_2$]$^+$ affords [{Ru(N$_4$Me$_8$)$_2$}(μ-$^1$:C=CHCH=C)=C]$_{2}^+$ [51].
1.2.4

From Metal Allenylidenes via Metal Alkynyls

Ready addition of nucleophiles (Nu⁻) to metal-allenylidene complexes affords alkynyl derivatives. Subsequent protonation or alkylation, as described in Section 1.2.3 above, then gives the corresponding vinylidene complexes (Equation 1.8):

\[ \text{L}_n\text{M}=\text{C}=\text{C}=(\text{Nu})\text{RR'} \quad + \quad \text{Nu}^- \quad \rightarrow \quad \text{L}_n\text{M}=\text{C}=\text{C}(\text{Nu})=\text{C}=\text{C}=(\text{Nu})\text{RR'} \]

(1.8)

For example, addition of LiBu\(^t\) to Mn(=C=CPh\(_2\))(CO)\(_2\)Cp, followed by protonation or methylation gives Mn{=C=CR(CPh\(_2\)Bu\(^t\))}(CO)\(_2\)CpMe (R = H, Me) [224]. This is a method which has not been employed generally, and could perhaps be exploited to produce more unusual derivatives.

In the ruthenium series, more success has been reported, particularly with Ru\(_2\)Cp’ (Cp’ = Cp* [225], \(\eta^5\)-C\(_9\)H\(_7\) [115, 226–232], Tp [130]). This can be rationalized in terms of a high contribution from the vinylidene to the structure of the alkenylcarbyne formed by protonation of the allenylidene (Equation 1.9):

\[ [\text{Ru}]^{2+} = \text{C} = \text{C} = \text{C} = \text{C} \quad \rightarrow \quad [\text{Ru}]^+ = \text{C} = \text{C} = \text{C} = \text{C} \]  

(1.9)

Thus, protonation of the intermediate formed from RuCl(dippe)Cp* and HC≡CCHPh(OH), followed by addition of ketones, aldehydes, thiophene, dicarbonyl and related compounds affords [Ru{=C=CHCHPh(E)}(dippe)Cp*]\(^+\) [E = CH\(_2\)C(O)Me, CH(CH\(_2\))\(_2\)CO, CH\(_2\)(O)Ph, C=CHCH=CMeS, CH(COR)C(O)R (R = Me, OMe), CH(CN)\(_2\), CH(COMe)C(O)Et] (Scheme 1.3) [225].

Regioselective Diels–Alder addition of 1,3-dienes (isoprene, cyclopentadiene, 1,3-cyclohexadiene) to C=C..C in [Ru(=C=C=CPh\(_2\))(CO)(PPr\(_i\)\(_3\))\(_2\)]\(^+\) affords vinylidenes (Scheme 1.4) [232], while [Ru(=C=CHPh)(dippe)Cp*]\(^+\) adds nucleophiles such as pyrazole, PhSH, pyrrole or 2-methylfuran (the latter two in the presence of acid) to give [Ru(=C=CHCHPhR)(dippe)Cp*]\(^+\) (R = pz, SPh, pyr, fur) [228]. In the presence of base, acetone adds to C=C, to give alkynes which afford [Ru(=C=HCRPhCH\(_2\)C(O)Me)(dippe)Cp*]\(^+\) with HBF\(_4\) (Scheme 1.5). Regiospecific addition of [M{=CCH\(_2\)O(OMe)}(CO)\(_3\)]\(^-\) (M = Cr, Mo, W) to [Ru{=C=CHPh(R)}(PPh\(_3\))\(_2\)(\(\eta^5\)-C\(_9\)H\(_7\))\(_2\)]\(^+\), followed by protonation, gives bimetallic {[(\(\eta^5\)-C\(_9\)H\(_7\))(Ph\(_3\)P)\(_2\)Ru]=C=CHCPh(R)CH\(_2\)C(O)Me}=M(CO)\(_3\)}\(^{+\text{BH}}\), containing vinylidene-carbene bridges [115].

1.2.5

From Metal-Carbyne Complexes

The deprotonation of carbyne complexes is the formal reverse of the addition of a proton to the vinylidene (Equation 1.10, Table 1.4):

\[ [\text{L}_n\text{M}=\text{C}=\text{C}=\text{C}]=\text{C} \quad + \quad \text{B} \quad \rightarrow \quad [\text{L}_n\text{M}=\text{C}=\text{C}=\text{C}]=\text{C} \quad + \quad [\text{BH}]^{+} \]

(1.10)
Scheme 1.3 $[\text{Ru}^{*}] = \text{Ru(dippe)}\text{Cp}$. Reagents: (i) MeC(O)R ($R = \text{Me, Ph}$); (ii) cyclopentanone; (iii) 2-Me-thiophene; (iv) CH$_2$(CN)$_2$; (v) RC(O)CH$_2$C(O)R ($R = \text{Me, OMe}$); (vi) MeC(O)CH$_2$CO$_2$Et. All reactions run in the presence of HBF$_4$. 
Deprotonation may be achieved by reaction with alkyllithiums, but has also been found in other circumstances. A reaction between CF$_3$I and Mo{\(\equiv\)C(CH$_2$Bu$_t$)}{P(OMe)$_3$}$_2$Cp afforded MoI{\(\equiv\)C(CH$_2$Bu$_t$)}{P(OMe)$_3$}$_2$Cp in a reaction suggested to proceed via electron transfer from the carbyne to CF$_3$I, followed by abstraction of H by the CF$_3$ radical. A related reaction occurs with [4-FC$_6$H$_4$N$_2$]BF$_4$ [233].

![Scheme 1.4](image)

**Scheme 1.4** [Ru] = Ru(CO)(PP$_i$)$_3$Cp; R = Me, n = 0; R = H, n = 1,2.

![Scheme 1.5](image)

**Scheme 1.5** [Ru$^{\bullet}$] = Ru(dippe)Cp$^{\bullet}$. Reagents: (i) (X = pzH, dmpzH, HSPh); (ii) pyrrole (X = NH, R = H), 2-Me-furan (X = O, R = Me); (iii) Me$_2$CO; (iv) H$^+$. 

Table 1.4 Some vinylidene complexes, L$_n$M{\(\equiv\)CRR$'$}, obtained from carbynes.

<table>
<thead>
<tr>
<th>Metal</th>
<th>ML$_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>Mn(CO)(PP$_i$)$_3$Cp [211, 234]</td>
</tr>
<tr>
<td>Mo</td>
<td>Mo(CO)$_2$(PP)$_2$ [235], Mo(CO)$_2$Tp$^*$ [236], MoP$_2$Cp [233, 237]</td>
</tr>
<tr>
<td>Os</td>
<td>Os(CO)$_2$P$_2$ [238], OsXP_Cp [239], OsXP$_2$ [240, 241], OsHLP$_2$ [242], OsHXLP$_2$ [71, 243–245]</td>
</tr>
<tr>
<td>Re</td>
<td>Re(CO)$_2$(pz) [81], Re(CO)$_2$Cp [234], ReCl(PP)$_2$ [246]</td>
</tr>
<tr>
<td>W</td>
<td>W(CO)(PP)$_2$ [235, 247]</td>
</tr>
</tbody>
</table>
Highly nucleophilic anions \[\text{M(\text{C=CR})(CO)(PPh}_3\text{)Cp}\]^{\text{--}} \ (\text{M = Mn, Re}) \text{ are obtained from M(CO)}_2\text{(PPh}_3\text{)Cp} \text{ and LiC=CR} [211, 234]. \text{ These add to aldehydes and ketones to give vinylicarbynes [Mn(\text{CCMe=CPH}_2\text{)(CO)(PPh}_3\text{)Cp}]}^{\text{+}}. \text{ Subsequent addition of nucleophiles to C}\gamma \text{ gives neutral vinyldiene complexes Mn}\text{[\text{C}}_\text{=C}\text{MeCPh}_2\text{](Nu)}\text{(CO)(PPh}_3\text{)Cp)} \text{ for Nu = H or alkyl; with LiC=CBu}_3\text{, only attack at C}\alpha \text{ to give a carbene complex was observed [211]. Coupling of the carbyne with Mn(\text{CCMe})(CO)(PPh}_3\text{)Cp]}\text{ gave the binuclear bis(vinyldiene) }\{\text{[Mn(CO)}\text{(PPh}_3\text{)Cp}\text{)}\text{=C=CMe}\}_2\text{CPH}_2\text{.}

1.2.6
\text{From Metal-Carbon Complexes}

\text{The reaction of Ru(\text{≡C})Cl}_2\text{(PCy}_3\text{)(L}^1\text{, L}^\text{= Imes; Scheme 1.6}) \text{ with CH(C}_6\text{H}_4\text{NO}_2\text{-4)}\text{(CO}_2\text{Me)}_2 \text{ in the presence of 4-Bu'}\text{C}_2\text{H}_4\text{N (Bu'}\text{py) gives Ru}\text{[\text{C}=\text{C}}(\text{C}_6\text{H}_4\text{NO}_2\text{-4) CH(CO}_2\text{Me)}_2\text{]}\text{Cl}_2\text{(Imes)(Bu'}\text{py)}_2\text{[248]. Similar complexes were obtained from Feist's acid dimethyl ester in the presence of malonate, while Ru(\text{≡CHPh})Cl}_2\text{(Imes)(Bu'}\text{py)}_2 \text{ reacts with the ester to give Ru}\text{[\text{C}=\text{C}}(\text{CO}_2\text{Me)(CHCO}_2\text{Me}_2\text{)}\text{Cl}_2\text{(Imes)(Bu'}\text{py)}_2\text{, probably via an intermediate carbide complex. A related reaction is that between Ru(\text{≡C})Cl}_2\text{(PCy}_3\text{)}_2 \text{ (I, I} = \text{PCy}_3\text{ and C}_2\text{(CO}_2\text{Me)}_2 \text{ to give cyclopropenylidene Ru}\text{[\text{C}}_\text{=C}\text{C}}(\text{CO}_2\text{Me})_2\text{Cl}_2\text{(PCy}_3\text{)}_2, \text{ which ring-opens with HX to give Ru}\text{[\text{C}=\text{C}}(\text{CO}_2\text{Me})_2\text{]}\text{X}_2\text{(PCy}_3\text{)}_2 [249].}

\text{Scheme 1.6 Reagents: (i) }\text{C}_2\text{(CO}_2\text{Me)}_2\text{; (ii) HX [X = NHAr, OH, OPh, B(pin)]; (iii) py-N-oxide.}
1.2.7
From Acyl Complexes (Equation 1.11)

\[
\text{L}_n\text{M} = \text{C} = \text{O} \quad + \quad \text{H}^+ \quad \rightarrow \quad \text{L}_n\text{M} = \text{C} = \text{C} \quad \stackrel{-\text{H}_2\text{O}}{\longrightarrow} \quad \text{L}_n\text{M} = \text{C} = \text{C} = \text{H} \\
(1.11)
\]

An early approach to vinylidenes was by the formal dehydration of metal acyls, which is best achieved by treatment with an electrophile, often the proton in the form of a non- or weakly-coordinating strong acid. The reaction appears to proceed stepwise via a hydroxycarbene formed by protonation of the acyl, subsequent dehydration of which affords the vinylidene. Occasionally, mixtures of the two complexes are obtained, again suggesting the intermediacy of the carbene.

This reaction was first described for the conversion of Fe\{(O)Me\}(CO)(PPh\text{₃})\text{Cp} to [Fe(=C=CH\text{₂})(CO)(PPh\text{₃})\text{Cp}]\text{BF₄} by treatment with a HBF₄·OEt₂/triflic anhydride mixture [9a]. Transformations on Re(NO)PCp [170b] and Fe(PP)\text{Cp} [9b, 250] centers have also been reported. The complexes [Mn\{(O)CH\text{₂}R\}(CO)\text{CpMe}]/C₀ and [M(SnPh\text{₃})\{(O)CH\text{₂}R\}(CO)\text{Cp}]/C₀ (M = Fe, Ru), obtained from reactions of Mn(CO)₃\text{CpMe} or M(SnPh\text{₃})(CO)\text{Cp} with Li\text{CH₂R}, could be converted to the corresponding vinylidene complexes by treatment with AcCl [251]. More recently, lithiated diarylmethanes and M(CO)₆ (M = Cr, W) have given anionic Li [M\{(O)CAr\text{₂}\}(CO)\text{S}₅] which with (CF₃CO)₂O gave reactive M(=C=CAr\text{₂}) (CO)₅ [252].

1.2.8
From Vinlys

Treatment of TaCl₂\text{Cp}*₂ with (CH\text{₂}=CH)MgBr afforded TaH(=C=CH\text{₂})\text{Cp}*₂ directly in 75% yield, presumably by an α-H shift from an intermediate Ta (CH=CH\text{₂})₂\text{Cp}*₂; the vinyl Ta(CH=CH\text{₂})(CO)\text{Cp}*₂ was formed by a formal reversal of this shift on treatment with CO. UV irradiation of this vinyl reformed the vinylidene [253].

Although OsI\{(C=CHPh)\text{L}(\text{η}-\text{C₆H₆})\} cannot be protonated to the corresponding vinylidene, reaction with NaBH₄ to give OsH(CH=CHPh)\text{L}(\text{η}-\text{C₆H₆}) followed by halogenation (CCl₄ or CH₂I₂) and reaction with LiBu⁺ gives Os(=C=CHPh)\text{L}(\text{η}-\text{C₆H₆}) [73, 74].

Several vinylidene complexes have been obtained from cyclopropenyl-ruthenium complexes Ru\{(C=CHPhR\text{₂})(PPh\text{₃})\text{Cp}, themselves obtained by intramolecular cyclization of [Ru\{(C=CHPhR\text{₂})(PPh\text{₃})\text{Cp}]}⁺ upon deprotonation [197, 223, 254]. Thus, ring-opening occurs when the neutral cyclopropenyls are treated with electrophiles such as CPh₃⁺, HgCl₂, H⁺ or tcnq (Section 1.3.2).
1.2.9
From Alkenes

Oxidative addition of α-chlorovinylsilanes to Cr(CO)$_3$(η-arene) or Mn(CO)$_3$C$_\text{Me}^\text{Me}$ afforded mono- or di-substituted vinylidenes by elimination of Me$_3$SiX across the M–C bond: intermediate η$^2$-alkene complexes were detected in the Mn system, slow conversion of Mn{η$^2$-CB$_2$CMe(SiMe$_3$)}(CO)$_2$C$_\text{Me}^\text{Me}$ to Mn{η=C=CM$_2$}(CO)$_2$C$_\text{Me}^\text{Me}$ occurring [255]. The reaction is solvent dependent, the major product from Me$_2$C=CCl(SiMe$_3$) being the vinylidene in pentane, but butatriene Mn{η$^2$-Me$_2$C=CC=CM$_2$}(CO)$_2$C$_\text{Me}^\text{Me}$ in thf [256].

Irradiation of M{η=C$_2$H$_4$}(L)C$_\text{Me}^\text{Me}$ (M = Rh, Ir, L = PMe$_3$; M = Ir, L = η-C$_2$H$_4$) in a matrix initially affords MH(CH=CH$_2$)(L)C$_\text{Me}^\text{Me}$ and then the dihydride MH$_2$(=C=CH$_2$)C$_\text{Me}^\text{Me}$ [257]. Treatment of {RhCl(L)$_2$}$_n$ or IrCl(coe)(L)$_2$ with RR'C=CHCl [RR' = Me$_2$, MePh, Ph$_2$, (CH$_2$)$_5$] and Na in benzene gives trans-MCl{η=C=CR'R}(L)$_2$, although the major product from IrCl(coe)(L)$_2$ and Ph$_2$C=CHCl is trans-IrCl(η-PhC$_2$Ph) (L)$_2$ [258]. The reaction probably involves formation of an intermediate vinyl radical and Ph group migration. Addition of norbornadiene (nbd) to {IrCl(coe)$_2$}$_2$ gives a polymer which with PR$_3$ affords trans-IrCl{η=C=CH(C$_7$H$_9$)}(PR$_3$)$_2$ (PR$_3$ = PPr$_3$, PMeBu$_1$) which, on heating, loses cyclopentadiene to give trans-IrCl{η=C=CHR} (PR$_3$)$_2$ (R = 5-norbornen-2-yl). It is thought that steric congestion afforded by the tertiary phosphines results in rearrangement of an initially-formed nbd-dimer complex 2 [259].

\[ \text{Ir} \quad \text{R}_3\text{P} \quad \text{Cl} \quad \text{R}_3\text{P} \]

1.2.10
Miscellaneous Reactions Affording Vinylidenes

The following are some examples of reactions which have produced vinylidene complexes but are either not of general application or have not been further developed. Oxygen atom transfer occurs in reactions of NbH(η$^2$ – OC – CPh$_2$)Cp'$_2$ with nitriles or isonitriles to give isocyanates and Nb(=C=CPh)$_2$Cp'$_2$ [260]. Metathesis of Ph(R) C=–C=NP$_2$ (R = Me, aryl) with W(=CHPh)(CO)$_5$ proceeds via W{C(NPh=CHPh)=C (R)Ph} (CO)$_5$, which is converted to W{η=C=CRPh} (CO)$_5$ by treatment with BF$_3$. OMe$_2$ [261].
Vinylidene 3 was obtained from Mn(CO)$_2$Cp and the cyclic alkynes SiMe$_2$C≡CSiMe$_2$(SiMe$_2$)$_n$SiMe$_2$ [262, 263]; formation of 4 from Fe$_2$(CO)$_9$ and (C≡CSiMe$_2$OSiMe$_2$OSiMe$_2$)$_2$ may involve intramolecular addition of an iron-vinylidene (formed by SiMe$_3$ migration) to the second C≡C triple bond [262].

![Vinylidene 3](image1)

![Vinylidene 4](image2)

Unusual iron-porphyrin vinylidene complexes were obtained from DDT [1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane] and Fe(tpp) [tpp = meso-tetraphenylporphinato (2-) in the presence of a reducing agent [10a, 264]. The derived N,N'-vinylene-bridged porphyrin reacts with metal carbonyls [Fe$_3$(CO)$_{12}$, Ru$_3$(CO)$_{12}$] to break one or both N=C bonds with insertion of the vinylidene into an M–N bond. While the iron complex was formed in 90% yield, the reaction with Ru$_3$(CO)$_{12}$ afforded three products, the vinylidene being formed in only 40% yield [265].

Isomerization of η$^2$-vinyl ether complexes of OsHCl(L)$_2$ to carbenes OsHCl{≡CMe(OR)}(L)$_2$ may be followed by C–OR bond cleavage to give either vinylidene OsHCl≡C=CH$_2$(L)$_2$ (R = Et) or carbyne OsHCl{≡CMe(OPh)(L)$_2$ (R = Ph) [266]. Rearrangement of [OsCl$_2$(CH=CHPh)(N=CR$_2$)(L)$_2$]$^+$ [CR$_2$ = CMe$_2$, C(CH$_2$)$_3$] with $L' = $ MeCN or H$_2$O gives [OsCl≡C=CHPh)(NH=CR$_2$)(L')(L)$_2$]$^+$, or in the absence of another ligand, neutral OsCl$_2$(≡C=CHPh)(NH=CR$_2$)(L)$_2$ [267].

1.2.11 Vinylvinylidene Complexes

An important sub-set of vinylidenes are those containing further unsaturation in conjugation with the metalla-allene system. Vinylvinylidene complexes have been obtained from methylated propargyl alcohols, where the normal dehydration to give allenylidene complexes does not occur. Thus, reactions of HC≡CCMe$_2$(OH) with metal halide complexes in the presence of [NH$_4$]PF$_6$ afford binuclear complexes such as 5 containing the vinylidene-alkylidene ligand, C$_{10}$H$_{12}$, which has been described for ML$_n$ = Ru(PPh$_3$)$_2$Cp [268, 269], Ru(dippe)Tp [127] and Os(PPh$_3$)$_2$Cp [77]. A related reaction is the formation of allenylidene [Ru{≡C=C=C(C$_{13}$H$_{20}$)}(PPh$_3$)$_2$(η$^5$-C$_5$H$_7$)]$^+$ (6) from [Ru{≡C=CH(C$_6$H$_9$)}(PPh$_3$)$_2$(η$^5$-C$_5$H$_7$)]$^+$ and HC≡C(C$_6$H$_9$) or HC≡C(C$_6$H$_{10}$)(OH); it can also be obtained directly from RuCl(PPh$_3$)$_2$(η$^5$-C$_5$H$_7$) and an excess of HC≡C(C$_6$H$_{10}$)OH [270].
Z and E isomers of W{C≡C(CO₂Me)₂C(CO₂Me)=CHPh}(CO)₃(dppe) are formed from C₂(CO₂Me)₂ and W=C=CHPh(CO)₅ by [2 + 2]-cycloaddition of the alkyne to the vinylidene, followed by ring-opening of the cyclobutenyl so formed, corresponding to a formal insertion of the alkyne into the C₂-C bond. The first-formed Z isomer is photo-converted to the E isomer (Z/E = 1/8) [271]. Similar reactions are found with RuCl(C≡C=CHCO₂Me)(PET₃)Tp and HC≡CCO₂Me [129], and with the neutral allenylidene OsCl(C≡C(C₆H₉))(PPr₃)Cp and C₂(CO₂Me)₂ to give OsCl(C≡C(CO₂Me)C(CO₂Me)=C=CH₂) (PPr₃)Cp [272].

Deprotonation of vinylcarbyne complexes affords vinylvinylidenes in a reaction reversed by addition of HOTf. Reactions of Mn(C≡CMe=CHPh)(CO)(PPh₃)Cp with nucleophiles resulting in addition to Cγ occur with larger groups such as PPh₃ [211]. If Cγ bears a proton, however, facile deprotonation of the vinylcarbynes occurs to give Mn=C=CMε=CR=CR₂)(CO)(PPh₃)Cp (R' = H, R = tol, Bu'; R' = Me, R = H). The alkynylvinylidene [Re{C≡C=CHC₆H₉}(NO)(PPh₃)Cp]⁺ is obtained by protonation (HBF₄) of Re{(C₆H₉)}(NO)(PPh₃)Cp [192].

Vinylvinylidenes FeC≡C=CHR₁=CH₂)(CO)₂(PET₃)₂ (R₁ = Me, Et, Pr, Bu) are obtained by dehydration (silylated silica) of FeH{C≡CMeR₁(=CH₂)}(CO)₂(PET₃)₂ [273]. Rapid dehydration occurs in the reactions of RuCl(cod)Tp with HC≡CCMePh(OH) (in the presence of PPr₃Ph₂) resulting in the formation of RuCl(C≡C=CH(C₆H₉)=CH₂)(PPr₃Ph₂)Tp [130], or of OsCl₂(PPh₃)₃ with HC≡CCMe₂(OH) to give the η²-alkyne-Os complex, which is dehydrated at 85°C to OsCl(C≡C=CHCMe=CH₂)(PPh₃)Cp [159]. Reaction of OsCl(CO)(L)Cp with Ag[BF₄]⁺ followed by 1-ethynyl-1-cyclohexanol affords [Os{C≡C=CH(C₆H₉)}(CO)L]Cp⁺ [64].

Alkylation of Ru{C≡C(C₆H₉)}(PPh₃)₂Cp with BrCH₂CO₂Me affords [Ru{C≡C=CH(C₆H₉)}(CH₂CO₂Me)](PPh₃)Cp⁺ [199]. The reaction between Ru(NCMe)₂{(C₂B₁₀H₁₀)CMe₂(η-C₅H₄)} and HC≡CSiMe₃ gives the binuclear vinylvinylidene {C₂B₁₀H₁₀}CMe₂(η-C₅H₄)Ru{C≡C=CH(SiMe₃)}(C₆H₉)SiMe₃{Ru(C₂B₁₀H₁₀)CMe₂(η-C₅H₄)} (7) [108].
Enynes HC≡CCR=CHR’ (R = R’ = H; R = Me, R’ = H; R = H, R’ = OMe) react with \{RhCl(coe)\}_2 in the presence of PPr_i3 to give the expected η²-alkyne or hydrido (alkynyl) complexes, which rearrange in toluene at 25–45°C to give vinylnvinylidene complexes trans-RhCl(=C=CHCR=CHR’)(L)_2 [274]. Similar reactions with HC≡CCHMe(X) (X = OH, NH₂) afford trans-RhCl(=C=CHCHMe(X))(L)_2, which dehydrate or deaminate with acidic alumina or traces of acid to give the parent complex RhCl(=C=CHCH=CH_2)(L)_2 [274, 275]. Phenyl-substituted alkynols give allenylidenes [276]. While formation of hydrido(alkynyl)s occurs on treatment with py, carbonylation of the =C=CHCMe=CH_2 complex gives trans-RhCl(CO)(L)_2 and free enyne HC≡CMe=CH_2. Protonation (HBF_4) gives carbyne trans-[Rh (≡CCH=CMMe_2)(L)_2]^⁺, a reaction which is reversed with NaH. Addition of HOTf to the C₆–C₇ bond of trans-IrCl(≡C≡C≡CPh_2)(L)_2 affords trans-IrCl(≡C=CHC=CH(OTf)=CPh_2)(L)_2 [277].

1.3 Stoichiometric Reactions

The vinyldene ligand is polarized so that C₇ is electron poor (δ⁺) and the C₁ is electron rich (δ⁻). The HOMO is located on the metal and C₁, while the LUMO is found on C₇. This provides a ready distinction between the modes of reaction, although the presence of both electrophilic and nucleophilic centers in the same molecule can lead to the formation of cyclic products. Although C₁ is electron-rich, reactions with electrophiles are often limited by the positively charged metal complex and are more commonly found with the neutral species. Conversely, addition of nucleophiles to C₇ is facilitated by the positive charge. Many vinylenes are based on electron-rich metal-ligand fragments, one common feature being the presence of bulky phosphines. Many early studies used phenylphosphines, often PPh₃, and the kinetic stability afforded to the unsaturated ligand may result from steric shielding of C₁ by the phenyl groups. However, smaller tertiary phosphines, such as PMe₃ or dmpe, can also be used and result in increased reactivity.
Much of the chemistry of vinylidene complexes has been developed with catalytic applications in mind, as detailed later in this volume. Early examples had low activity for alkene metathesis, although complexes containing imidazolylidene ligands showed improved efficiencies [35]. However, in many cases, reactions of the vinylidene ligand have resulted in transformation to other carbon-based ligands which have not been released from the metal fragment.

The stoichiometric reactivity of metal-vinylidene complexes will be covered in the following sequence:

1. Addition to Cα – reactions of nucleophiles
2. Addition to Cβ – reactions with electrophiles
3. Cycloaddition reactions.

To some extent, the reactivity varies with the metal-ligand combination. Consequently, extensive studies of vinylidenes attached to a few specific MLn fragments have been reported, with those containing TiCp2, M(CO)5 (M = Cr, Mo, W), M(CO)(NO)Cp (M = Cr, Mo, W), [M(L')(P)Cp]+ (M = Fe, Ru; L' = CO, P) [Ru{=C=C(SMe)2}(PMe3)2Cp]+, and MCl(L)2 (M = Rh, Ir) fragments being summarized in Section 1.4.

1.3.1 Reactions at Cα

Addition of neutral nucleophiles to Cα affords the corresponding vinyl complexes, whereas anionic nucleophiles usually give carbene complexes.

1.3.1.1 Deprotonation

Nucleophilic attack resulting in deprotonation of Cβ has been reported for a range of metal centers (Equation 1.12):

\[ [\text{L}_n \text{M} = \text{C} = \text{CHR}]^+ + \text{B} \rightarrow \text{L}_n \text{M} = \text{C} \equiv \text{CR} + [\text{BH}]^+ \]  

MLn is exemplified by Fe(dppe)Cp [250a], Fe(CO)(PPh3)Cp [9], Fe(dppe)Cp+ [278], Ru(CO)(PMePr2)2Cp+ [104], trans-Ru(dppe)2 [96], Ru(dppe)Tp [127], Ru(CO)(PR3)\(\eta^5\)-arene [73, 74, 280].

Double deprotonation of Ru(=C=CH2)(PPh3)2Cp with LiBu' affords the lithioalkynyl Ru(C≡C(\text{Li})C(PPh3)2Cp [281]. Reversal of the intramolecular reductive elimination leading to vinylidene is found on treatment of trans-IrCl(=C=CHR)(L)2 with CO to give IrH(CO)(C≡CR)(L)2 [154].

1.3.1.2 Group 16 Nucleophiles, Oxygen

A commonly used nucleophile has been water. Although initial attack affords a hydroxy-carbene derivative, ready cleavage of the Cα–Cβ bond resulting from formal keto–enol tautomerism occurs to give either the acyl or the metal carbonyl (usually cationic) and the corresponding organic fragment (Equation 1.13):