Metal Vinylidenes and Allenylidenes in Catalysis

From Reactivity to Applications in Synthesis

Edited by
Christian Bruneau and Pierre Dixneuf

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Preface

Catalytic transformations of alkynes have recently led to tremendous developments of synthetic methods with useful applications in the synthesis of natural products and molecular materials. Among them, the selective activations of terminal alkynes and propargylic alcohols via vinylidene- and allenylidene-metal intermediates play an important role, and have opened new catalytic routes toward *anti*-Markovnikov additions to terminal alkynes, carbocyclizations or propargylations, in parallel to the production of new types of molecular catalysts.

After the discovery of the first terminal vinylidene-metal complex in 1972, it was established that the stoichiometric activation of terminal alkynes by a variety of suitable metal complexes led to 1,2-hydrogen transfer and the formation of metal-vinylidene species, which is now a classical organometallic reaction. A metal-vinylidene intermediate was proposed for the first time in 1986 to explain a catalytic *anti*-Markovnikov addition to terminal alkynes. Since then, possible metal-vinylidene intermediate formation has been researched to achieve catalytic regioselective formation of carbon–heteroatom and carbon–carbon bonds involving the alkyne terminal carbon.

In parallel, since the first preparation of allenylidene-metal complexes in 1976, the formation of these carbon-rich complexes developed rapidly after the discovery, in 1982, that allenylidene-metal intermediates could be easily formed directly from terminal propargylic alcohols via vinylidene-metal intermediates. This decisive step has led to regioselective catalytic transformations of propargylic derivatives via carbon(1)–atom bond formation or alternately to propargylation. Due to their rearrangement into indenylidene complexes, metal-allenylidene complexes were also found to be catalyst precursors for olefin and enyne metathesis.

Higher cumulenyl moieties stabilized by organometallic fragments were introduced in the eighties and have recently received much attention. Such linear unsaturated carbon-rich cumulenyl-metal complexes have allowed access to new molecular architectures and have revealed interesting properties in the field of electronics and molecular wires.

The activation of alkynes to metal-vinylidenes with transition metal complexes of Groups 6–9, essentially, provides reactive intermediates with an electrophilic terminal carbon atom, whereas allenylidene species present two electrophilic carbon centers. Advantage has been taken of this property for the rational design of new catalytic transformations, and useful atom-economical catalytic transformations have been brought to light. The new trends aim at the use of multifunctional acetylenic substrates with the objective of performing unprecedented cascade catalytic reactions.

The content of this book gathers in the same volume all aspects of vinylidene- and allenylidene-metal complexes, including the preparation of these organometallic carbon-rich systems with a metal–carbon double bond, their stoichiometric reactivity and theoretical aspects, and their applications in catalysis for the production of fine chemicals, mainly in the field of selective transformations of functional terminal alkynes. It provides essential general information on catalytic transformations of alkynes and their use in synthesis.

This book should be of interest to academic and industrial researchers involved in the fields of organometallic, coordination and bioinorganic chemistry, transition metal catalysis, and organic synthesis.

We are grateful to the team from Wiley-VCH who made this project possible and to all contributors to this book for their enthusiasm in writing a chapter on their favorite selected topic.

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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, $HC{\equiv}CH$, to which it is related by a 1,2-H shift (Equation 1.1):

$$HC{\equiv}CH \rightarrow :C{=}CH_2 \tag{1.1}$$

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):

$$ML_n + HC{\equiv}CR \rightarrow L_nM{=}C{=}CHR \tag{1.2}$$

The first vinylidene complex, $Fe_2(\mu\text{-}C{=}CPh_2)(CO)_8$, was obtained by Mills and Redhouse by irradiation of diphenylketene with $Fe(CO)_5$ [2]. The first terminal vinylidene complex, $MoCl\{{=}C{=}C(CN)_2\}(PPh_3)_2Cp$, was prepared by King and Saran from the reaction between $Mo\{CCl{=}C(CN)_2\}(CO)_3Cp$ and 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 vinylidenes 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 Tf_2O [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 η^2-alkyne → hydrido(η^1-alkynyl) → 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.
9. From alkenes.
10. Miscellaneous methods involving the use of other precursors.
11. Vinylvinylidenes.

1.2.1
From 1-Alkynes (Equation 1.3)

$$\mathrm{ML}_n + \mathrm{HC{\equiv}CR} \rightarrow \mathrm{L}_n\mathrm{M{=}C{=}CHRML}_n \tag{1.3}$$

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 d^6 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 η^2-alkyne complex which then undergoes either a 1,2-H migration with concomitant formation of the η^1-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 $RhCl(PPr^i_2R)_2$ ($R = C{=}NCBu^t{=}CHNMe$) 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 $ReCl(N_2)(dppe)_2$. 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 $RuCl_2(=C=CH_2)(L)_2$ from $\{RuCl_2(cod)\}_n$, H_2 and PPr^i_3 (L) in 2-butanol with C_2H_2 [34] or $RuCl_2(=C=CHBu^t)(PCy_3)(Imes)$ from $\{RuCl_2(p\text{-cymene})\}_2$, [ImesH]Cl, $NaOBu^t$ and $HC{\equiv}CBu^t$ [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 $RuCl(=C=CHR)(PPh_3)Cp'$ [36, 37]. Alternatively, complexes containing hemi-labile ligands, such as $PPr^i_2\{CH_2C(O)OMe\}$, $PPr^i_2(CH_2CH_2OMe$, and $PPr^i_2(CH_2CH_2NMe_2)$ ($=P \sim O$, $P \sim N$), can be used to generate a vacant coordination site for the incoming vinylidene [38]. Reactions of $[Ru(PPh_3)\{\kappa^2\text{-}PPh_2(CH_2CH{=}CH_2)\}(\eta^5\text{-}C_9H_7)]^+$ with $HC{\equiv}CAr$ give $[Ru(=C=CHAr)(PPh_3)\{\kappa^1\text{-}PPh_2(CH_2CH{=}CH_2)\}(\eta^5\text{-}C_9H_7)]^+$ [39]. In Group 9, other starting materials include $\{RhCl(L)_2\}_2$ and $IrH_2Cl(L)_2$ (the complex $IrCl(L)_2$ is inaccessible). Direct reaction of $Rh(C{\equiv}CH)(\eta\text{-}C_2H_4)(L)_2$ with $HC{\equiv}CH$ in

Table 1.1 Some metal-vinylidene complexes, $L_nM{=}C{=}CRR'$, prepared from 1-alkynes.

Metal	ML_n
Co	$Co(PBu^t_2CH_2CH_2\text{-}\eta\text{-}C_5H_4)$[56]
Fe	$Fe(CO)_2(PEt_3)_2$ [57], $Fe(PP)Cp*$ [58], $FeCl(PP)_2$ [59]
Ir	$Ir\{N(SiMe_2CH_2PPh_2)_2\}$[60]
Mn	$Mn(CO)_3(PP)$ [61], $Mn(CO)_2Cp$ [5, 6]
Mo	$Mo(PP)(\eta\text{-}C_7H_7)$[62]
Os	$Os(CO)(NO)(PMeBu^t_2)_2$ [63], $Os(CO)(L)Cp$ [64, 65], $OsX(pcp)$ [66, 67], $OsXP_2$ [68], $OsClPCp$ [69], $OsHX_2P_2$ [70–72], $OsP_2(\eta\text{-arene})$ [73, 74], OsP_2Cp' [75–77]
Re	$Re(CO)_3P_2$ [78], $Re(CO)_2\{MeC(CH_2PPh_2)_3\}$ [79–81], $Re(CO)_2Cp$ [82], $ReCl(PP)_2$ [42]
Rh	$RhX(L)_2$ [40, 52]
Ru	$RuXLP_2$ [83], $RuHXP_2$ [84–86], RuP_2L^{OEt} [87], $RuXP(N_3)$ [88], Ru(pnp) [89], $RuCl(NN)P_2$ [46, 47], $RuCl(P\sim O)_2$ [90–93], $RuClL_2$ [48–50, 94, 95], $RuCl(PP)_2$ [53, 54, 96–100], $Ru(CO)LCp'$ [101–104], $Ru(L)PCp$ [105, 106], RuL_2Cp' [39, 45, 107, 108], $RuClPCp'$ [109–111], RuP_2Cp' [112–120], RuP_2Cp* [44, 121, 122], RuL_2Cp* [123–125], $RuXPTp$ [111, 125], RuL_2Tp' [126, 127], RuP_2Tp' [127–130], $RuClP\{O_2CCH(dmpz)_2\}$ [47], $Ru(P\sim O)(\eta\text{-arene})$ [131], $RuClP(\eta\text{-arene})$[132]
Tc	$TcCl(PP)_2$ [133]
W	$W(CO)_3(PP)$[134]

the presence of NEt_3 affords *trans*-$Rh(C{\equiv}CH)({=}C{=}CH_2)(L)_2$ [40] while the more basic $[Rh(PMe_3)_4]Cl$ reacts directly with 1-alkynes by C–H activation and oxidative addition to give $[RhH(C{\equiv}CR)(PMe_3)_4]Cl$, no migration of H to the metal being observed [41].

A variety of substituents can be tolerated (usually H, alkyl, aryl, $SiMe_3$, CO_2R), but in some cases, intramolecular nucleophilic attack on a presumed intermediate vinylidene complex results in the formation of carbene complexes. Ready replacement of $SiMe_3$ by H makes $HC{\equiv}CSiMe_3$ an attractive precursor for the parent complexes containing ${=}C{=}CH_2$ ligands. However, the strongly nucleophilic character of the OH group in hydroxyalkyl-alkynes often results in rapid addition to C_α. 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 $[Re(CN)({=}C{=}CHPh)(dppe)_2]^+$ from aminocarbene $[ReCl(CNH_2)(dppe)_2]^+$ and $HC{\equiv}CR$ [42]; $[Ru\{{=}C{=}CHC{\equiv}C[RuCl(CO)_2(PPh_3)_2]\}(PPh_3)_2Cp]PF_6$, from $RuCl(C{\equiv}CC{\equiv}CH)(CO)_2(PPh_3)_2$ and $[Ru(thf)(PPh_3)_2Cp]PF_6$ [43]; the fullerene derivative RuCl{(*R*)-prophos}(η^5-$C_{60}Me_5$) can be converted to [Ru(=C=CHPh){(*R*)-prophos}(η^5-$C_{60}Me_5$)]$^+$ 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], $RuCl(Me_2bpy)(PPh_3)_2$ [46], RuCl(L) [L = $(dmpz)_2$-acetate [47], 2,6-$(dmpz)_2$-

pyridine [48], 2,6-$(NMe_2CH_2)_2C_5H_3N$ [49]] fragments. Structurally characterized macrocyclic ruthenium vinylidene complexes include RuCl{=C=CH(C_6H_4X-4)} (16-tmc) (R = H, Cl, Me, OMe; 16-tmc = tetramethyl-1,5,9,13-tetra-azacyclohexadecane) [50], while $[Ru(N_4Me_8)(=C=CHR)]^{2-}$ (N_4Me_8 = octamethylporphyrinogen; R = H, Ph) have been obtained from the anionic $[Ru(N_4Me_8)]^{2-}$ and ethyne or HC≡CPh, respectively [51]. In this case, formation of an intermediate η^2-alkyne complex is unlikely, the probable mechanism being deprotonation of the alkyne and coordination of the alkynyl 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-HOC_6H_4OH, 1,4-$C_6H_4$$\{CPh(OH)\}_2$] and $\{RhCl(L)_2\}_2$ [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^t, Ph) and {RuCl(η-C_2H_4)(PCy_3)}(μ-Cl)$_3${Ru(η^6-*p*-cymene)} afford {RuCl(=C=CHR)(PCy_3)}(μ-Cl)$_3${Ru (η^6-*p*-cymene)}; ethyne gives an unusual tetranuclear μ-carbido complex [55].

1.2.1.1 **Migration of Other Groups (SiR_3, SnR_3, 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 example, 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 $SiMe_3$ or $SnPh_3$, 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 [NBu_4]F.

An early example was provided by the reactions between $\{RhCl(L)_2\}_n$ and RC≡C$SiMe_3$ [R = Me, Ph, CO_2Et, CO_2SiMe_3, CH_2OH, C(O)$CHPh_2$] [135]. Kinetic studies carried out with FcC≡C$SiMe_3$ in the same reaction confirmed the 1,2-migration of the $SiMe_3$ group [136]. Similar silyl migration reactions have been found with $C_2(SiMe_3)_2$ and Ru(OTf)(NO)$(L)_2$ [137], Co(η-$C_5H_4CH_2CH_2PBu^t_2$) [56], $IrCl(N_2)(PPh_3)_2$ [138] and $IrPh_2(N_2)$Tp∗ [139]. For the former, Me_3SiC≡CC≡C$SiMe_3$ affords IrCl{=C=C($SiMe_3$)C≡C$SiMe_3$}(PPh_3). The reaction of an excess of $C_2(SiMe_3)_2$ with $Ru(NCMe)_2$$\{(C_2B_{10}H_{10})CMe_2$(η-$C_5H_4$)} afforded the first bis(vinylidene)ruthenium complex, Ru{=C=C$(SiMe_3)_2\}_2\{(C_2B_{10}H_{10})CMe_2$(η-$C_5H_4$)} [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 η^2-alkyne complexes M(η^2-$Me_3SiC_2SiMe_3$)$(CO)_2$(η-arene) (M = Cr, Mo) results in formation of the vinylidene cations $[M\{=C=C(SiMe_3)_2\}(CO)_2(\eta\text{-arene})]^+$.

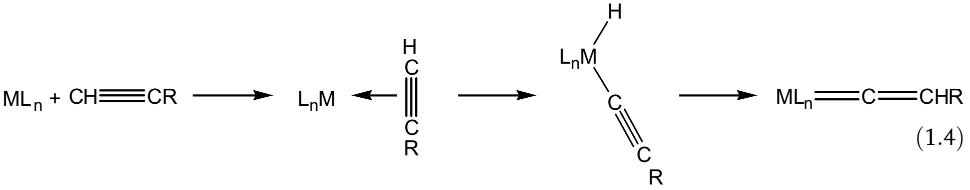
Reactions of RC≡C$SnMe_3$ with MnCp′(η^6-C_7H_8) in the presence of dmpe give Mn{=C=CR($SnMe_3$)}(dppe)Cp′, while with Ph_3SnC≡CC≡C$SnPh_3$, the alkynylvinylidene Mn{=C=C($SnPh_3$)C≡C$SnPh_3$}(dmpe)Cp′ is first formed. Subsequent irradiation then affords butatrienylidene Mn{=C=C=C=C$(SnPh_3)_2$}(dmpe)Cp′

[141–143]. Stannylalkynes and $\{RhCl(L)_2\}_2$ afford many $Rh\{=C=CR(SnPh_3)\}(L)_2$ complexes directly, which react with H^+ to cleave the $SnPh_3$ group [144].

The reaction of $C_2(SMe)_2$ with $RuCl(PMe_3)_2Cp$ gives $[Ru\{=C=C(SMe)_2\}(PMe_3)_2Cp]^+$ via the η^2-$C_2(SMe)_2$ complex [145]. A 1,2-shift of SeR occurs in the reaction between $RuCl(PPh_3)_2Cp$ and $PhC{\equiv}CSePr^i$ in the presence of $Na[BPh_4]$, which affords $[Ru\{=C=CPh(SePr^i)\}(PPh_3)_2Cp]^+$ [146].

1,2-Halogen shifts have been found for tungsten, with assumed formation of iodovinylidenes in reactions of 1-iodo-1-alkynes with $W(CO)_5(thf)$ 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 $Mn\{=C=C(I)CH(OR)_2\}(CO)_2Cp$ [$R = Me, Et$; $(OR)_2 = O(CH_2)_3O$], of which the XRD structure of $Mn\{=C=C(I)CH(OMe)_2\}(CO)_2Cp$ was determined [148].

1.2.2
The η^2-Alkyne → Hydrido(η^1-Alkynyl) → Vinylidene Transformation (Equation 1.4)



(1.4)

Formation of the intermediate η^2-alkyne complex has been reported in some reactions of 1-alkynes with metal centers, followed by rearrangement to the η^1-vinylidene. This occurs but rarely in the ruthenium series, for example, with $Ru(PMe_2Ph)_2Cp$, where both η^2-alkyne and vinylidene isomers of the product from C_2H_2 have been structurally characterized [149], and Ru(dippe)Cp∗, where metastable $[RuH(C{\equiv}CR)(dippe)Cp*]^+$ ($R = Ph, CO_2Me, SiMe_3$) transform into $[Ru(=C=CHR)(dippe)Cp*]^+$ in solution or the solid state [123]. Direct conversion of $[Ru(\eta^2\text{-}HC_2Ph)(CO)(PMePr^i_2)Cp*]^+$, prepared at −40 °C, to $[Ru(=C=CHPh)(CO)(PMePr^i_2)Cp*]^+$ occurs upon warming to 25 °C [104]. In contrast, the alkyne complex predominates in the room temperature solution equilibrium of the PPh_3 analog [150].

The transformation predominates in Group 9 (Rh, Ir) chemistry. Reactions of $\{RhCl(L)_2\}_2$ with 1-alkynes give the η^2-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 $RhHCl(C{\equiv}CR)(py)(L)_2$, which readily lose pyridine in hydrocarbon solvents to give square-planar *trans*-$RhCl(=C=CHR)(L)_2$. Alternatively, the Cp complexes $Rh(=C=CHR)(L)Cp$ 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 η^2-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_α being electron-poor and subject to frontier-orbital controlled nucleophilic attack, while the

Table 1.2 Some vinylidene complexes, $L_nM{=}C{=}CRR'$, obtained by η^2-alkyne → hydrido(η^1-alkynyl) → vinylidene transformations.

Metal	ML_n
Co	$Co\{P(CH_2CH_2PPh_2)_2\}$[151]
Fe	$Fe(CO)_2(PEt_3)_2$ [152]
Ir	$IrCl(PPr^i{}_2CH_2CH_2OMe/NMe_2)_2$ [153], $IrClP_2$ [138, 154–156]
Mn	$Mn(CO)_2Cp$ [157]
Os	$Os(CO)(NO)P_2$ [63], $OsHX(L)P_2$ [158], $OsXPCp$ [159], OsP_2Cp [160]
Rh	$RhCl(PPr^i{}_2CH_2CH_2OMe/NMe_2)_2$ [161, 162], $RhXP_2$ [32, 40, 163–166]
Ru	Ru(tmeda)Cp [45], RuCl(P)Cp [36], $RuHCl(CO)P_2$ [158], RuP_2Cp [149, 167]
W	$W(CO)_5$ [168], $W(CO)_3(PP)$[169]

metal center and C_β 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 $M{-}C{\equiv}C{-}$ fragment so that C_β is the preferred site of attack (Equation 1.5):

$$L_nM-C{\equiv}CR+E^+ \rightarrow [L_nM{=}C{=}C(E)R]^+ \tag{1.5}$$

The alkynyl-metal complexes are strong carbon bases, with measured pK_a values for $M(C{\equiv}CBu^t)L_2Cp$ being 13.6 [$ML_2 = Fe(CO)(PMe_3)$] and 20.8 [$ML_2 = Ru(PMe_3)_2$] [170].

Table 1.3 lists several examples of ML_n 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 $Re(C{\equiv}CR)(NO)(PPh_3)$

Table 1.3 Some metal vinylidene complexes, $L_nM{=}C{=}CRR'$, obtained from alkynyl-metal systems.

Metal	ML_n
Cr, Mo, W	M(CO)(NO)Cp [173–177]
Fe	FeP_4 [178], Fe(PP)Cp [179–183]
Ir	$IrCl(L)_2$ [154]
Mn	$Mn(CO)_2Cp$ [184], Mn(PP)Cp [185]
Mo	$Mo(CO)(P)_2Cp$ [186], $MoH_3(PP)_2$ [187]
Nb	$NbLCp^{Si}{}_2$ [188]
Os	$OsH(GePh_3)(L)Cp$ [189]
Pt	$PtMeP_2$ [190]
Re	$Re(NO)(PPh_3)Cp{*}$ [191, 192]
Rh	$RhCl\{N(CH_2CH_2PPh_2)_3\}$ [193, 194], $RhClP_2$ [195]
Ru	$Ru(PO)_4$ [196], RuP_2Cp' [171, 197–201], RuP_2Tp [202, 203]
W	$W(CO)_5$ [204, 205], $W(CO)_2Cp$ [186], WI(O)Tp [206]

Cp has been discussed [170b]. Alkylation with haloalkanes (often iodoalkanes), triflates (alkyl, benzyl, cyclopropyl), or $[R_3O]^+$ (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 ($[ArN_2]^+$), tropylium ($[C_7H_7]^+$), triphenylcarbenium (trityl, $[CPh_3]^+$), arylthio (ArS) and arylseleno (ArSe) have also been used.

Several complexes have been obtained from reactions of alkynyl anions, such as $[M(C{\equiv}CR)(CO)_5]^-$ or $[M(C{\equiv}CR)(CO)(NO)Cp]^-$ (M = Cr, Mo, W), obtained from $M(CO)_2(NO)Cp$ and $LiC{\equiv}CR$, or $[Mn(C{\equiv}CR)(CO)_2Cp]^-$, under charge-control.

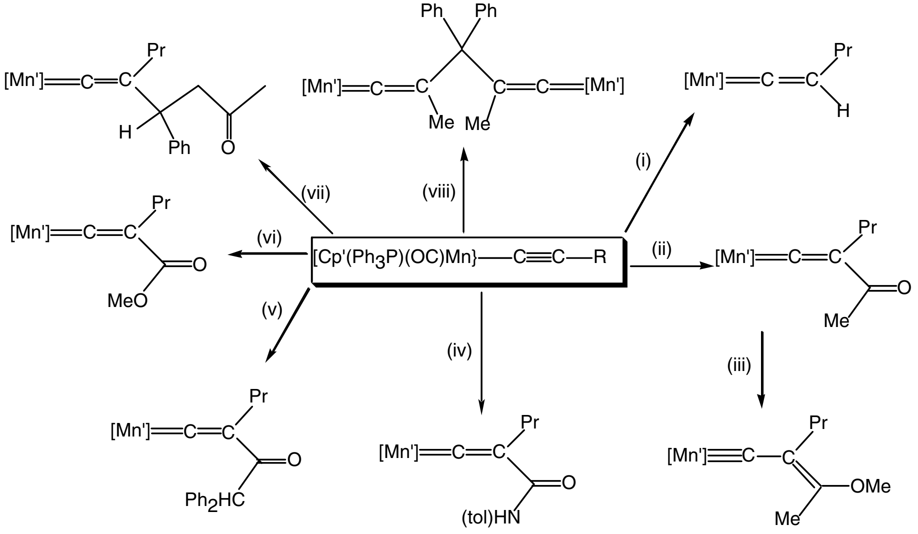
Alkylation may sometimes afford unusual complexes as a result of subsequent reactions (see also below). Reactions of $Ru(C{\equiv}CPh)(PPh_3)\{P(OMe)_3\}Cp$ with halides XCH_2R (R = CN, Ph, C_6F_5, C_6H_4CN-4, $C_6H_4CF_3$-4, 1-nap, CO_2Me) give $Ru\{P(O)(OMe)_2\}(=C=CPhCH_2R)(PPh_3)Cp$ via an initial cationic vinylidene which loses MeX in an Arbuzov-like reaction [171]. A similar reaction with RNCS gives $Ru\{P(O)(OMe)_2\}\{=C=CPh(SH=NR)\}(PPh_3)Cp$ 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 $[W(C{\equiv}CBu^t)(CO)_5]^-$ with cationic hydrocarbon-metal carbonyls, such as $[M(CO)_3(\eta\text{-}C_7H_7)]^+$ (M = Cr, W), $[Mn(CO)_3(\eta\text{-}C_6H_6)]^+$, $[Re(CO)_4(\eta\text{-}C_2H_4)]^+$, $[Fe(CO)_3(\eta^5\text{-}C_6H_6R)]^+$ or $[Fe(CO)_3(\eta^5\text{-}C_7H_9)]^+$ [207]. Reaction of the heterocumulene CO_2 with $[W(C{\equiv}CR)(CO)_3(dppe)]^-$ gives $Li[W(=C=CRCO_2)(CO)_3(dppe)]$ which can be alkylated with $[Me_3O]^+$ to neutral $W\{=C=CR(CO_2Me)\}(CO)_3(dppe)$ [208].

Reactions of $M(CO)_2(NO)Cp$ (M = Mo, W) with $LiC{\equiv}CR$ [R = Ph, Bu^t, $CH_2OCH_2CH{=}CH_2$, $(CH_2)_2OSiMe_2Bu^t$] give $Li[M(C{\equiv}CR)(CO)(NO)Cp]$ which react further with electrophiles to give either vinylidene or η^2-alkyne complexes. The former are obtained when aqueous acids (HCl) or MeOTf (hard electrophiles) are used [174]. The parent complex $W(=C=CH_2)(CO)(NO)Cp$ was formed when the product from $LiC{\equiv}CSiMe_3$ was quenched with aqueous $NaHCO_3$. Treatment of the vinylidene with LiBu reforms the alkynyl anion [174, 175]. η^2-Alkyne complexes are formed with soft electrophiles, such as $SiClMe_3$, their formation resulting from the initial product by thermal isomerization [209]. In the case of $Mo(=C=CHBu^t)(CO)(NO)Cp$, depending on solvent, tautomerization may occur via either a 1,2-H shift (non-polar) or by a multi-step route involving deprotonation/protonation and reductive elimination (in EtOH).

Reactions of $[Mn(C{\equiv}CR)(CO)(PPh_3)Cp^{Me}]^-$ (R = Me, Pr) with electrophiles such as H^+, RI (R = Me, Et, Bu^t), MeOTf, $[Et_3O]^+$, RC(O)Cl (R = Me, Ph), (tol)NCO, $Ph_2C{=}C{=}O$, CO_2 and $PhCH{=}CHCOMe$ give directly the neutral complexes $Mn(=C=CEMe)(CO)(PPh_3)Cp^{Me}$ [E = H, alkyl, RC(O), C(O)NH(tol), $C(O)CHPh_2$, C(O)OMe (after treatment with MeOTf) and $CHPhCH_2C(O)Me$, 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 (PPh_3) to give vinylidenes [211]. Similarly, the BF_3 adducts of epoxides react with $[Mn(C{\equiv}CMe)(CO)(PPh_3)Cp^{Me}]^-$ to afford anionic [Mn



Scheme 1.1 [Mn′] = Mn(CO)(PPh$_3$)Cp′. Reagents: (for R = Pr, Cp′ = Cp^{Me}) (i) H$^+$; (ii) MeC(O)Cl; (iii) MeOTf; (iv) NCO, then H$^+$; (v) Ph$_2$C=C=O, then H$^+$; (vi) CO$_2$, then MeOTf; (vii) PhCH = CHC(O)Me; (viii) (for R = Me,Cp′ = Cp) [Mn(≡CCMe=CPh$_2$)(CO)(PPh$_3$)Cp]$^+$.

$\{=C=CMeCH_2CMe_2(CH_2)_nO(BF_3)\}(CO)(PPh_3)Cp^{Me}]^-$ ($n = 0$, 1, respectively), possibly via intermediate hydroxyalkyl-vinylidenes Mn$\{=C=CMeCH_2CMe_2(OH)\}$(CO)(PPh$_3$)Cp^{Me} which undergo intramolecular attack at C$_\alpha$ [210].

Protonation of Ru$\{C{\equiv}CCPh_2(C_2H[Co_2(CO)_6])\}$(PPh$_3$)$_2$($\eta^5$-C$_9H_7$) and (*E*,*Z*)-Ru$\{C{\equiv}CCH{=}CH(C_2Ph[Co_2(CO)_6])\}$(PPh$_3$)$_2$($\eta^5$-C$_9H_7$) gives the corresponding vinylidenes [212]. The complex *trans*-Rh(C≡CH)(η-C$_2$H$_4$)(L)$_2$ is protonated with [pyH]BF$_4$ to give *trans*-[Rh(=C=CH$_2$)(py)(L)$_2$]$^+$ and reacts with cyclopentadiene to give Rh(=C=CH$_2$)(L)Cp [40].

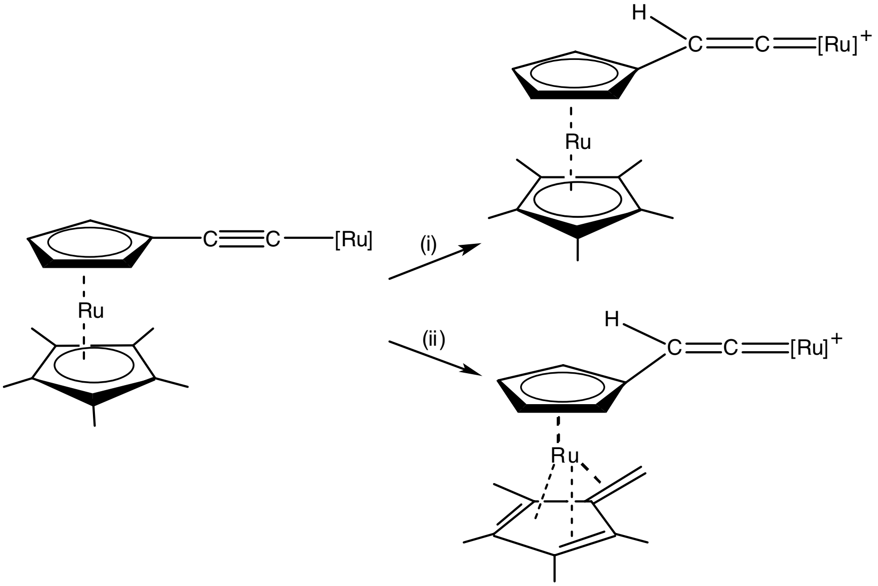
1.2.3.2 Redox Rearrangements of Metal Alkynyls and Vinylidenes

Oxidative coupling of metal alkynyls to give binuclear bis(vinylidene) complexes is exemplified by ML$_n$ = Nb(C≡CPh)Cp$^{Si}{}_2$ [213], Fe(PP)Cp∗[214] or Ru(PP)Cp∗ (Equation 1.6): [215]

$$2L_nM-C{\equiv}CR \rightarrow [L_nM{=}C{=}CR-CR{=}C{=}ML_n]^{2+} \qquad (1.6)$$

Suitable oxidizing agents are [FeCp$_2$]$^+$ or Ag$^+$, while the cationic species may be reduced back to the alkyne complexes using CoCp$_2$. Some of this chemistry has been reviewed [216].

Oxidation of *trans*-RuCl(C≡CCHPh$_2$)(dppe)$_2$ favors hydrogen atom transfer leading to *trans*-[RuCl(=C=CHCHPh$_2$)(dppe)$_2$]$^+$ [217]. Chemical oxidation of Ru(C≡CRc)(PPh$_3$)$_2$Cp (Rc = ruthenocenyl) gives the cyclopentadienylidene-ethylidene



Scheme 1.2 [Ru] = $Ru(PPh_3)Cp$. Reagents: (i) $[FeCp_2]^+$; (ii) *p*-benzoquinone.

complex $[Ru\{\eta^1{:}\eta^6\text{-}(=C=C=C_5H_4)RuCp\}(PPh_3)_2Cp]^+$, while $Ru\{C{\equiv}C\text{-}\eta\text{-}C_5H_4)RuCp{*}\}(PPh_3)_2Cp$ gives successively $[Ru\{=C=CH(\eta\text{-}C_5H_4)RuCp{*}\}(PPh_3)_2Cp]^+$ and the fulvene-vinylidene $[Ru\{=C=CH(\eta\text{-}C_5H_4)Ru(\eta^6\text{-}C_5Me_4CH_2)\}(PPh_3)_2Cp]^{2+}$ (Scheme 1.2) [218].

Examples of oxidative dehydro-dimerisation of vinylidenes are found with $Mo(PP)(\eta\text{-}C_7H_7)$ [219], $M(CO)_2Cp$ (M = Mn, Re) [220, 221] or $Mn(PP)Cp^{Me}$ [185] centers (Equation 1.7):

$$2L_nM{=}C{=}CHR \rightarrow L_nM{=}C{=}CR{-}CR{=}C{=}ML_n \tag{1.7}$$

For $M(CO)_2Cp$, this reaction proceeds via a 16-e alkynyl cation radical $[M(C{\equiv}CPh)(CO)_2]^+$, which, for M = Mn, couples at C_β to give the bis(carbyne) dication [220]. For M = Re, a similar cation radical is formed, which with NEt_3 affords a mixture of $\{Cp(OC)_2Re\}{=}C{=}CPhCPh{=}C{=}\{Re(CO)_2Cp\}$ and the isomeric μ-vinylidene $\{Cp(OC)_2Re\}_2\{\mu\text{-}C{=}CPh(C{\equiv}CPh)\}$ by competitive $C_\beta{-}C_\beta$ and $C_\beta{-}M$ coupling [221]. With an alternative ligand set, the $Mn\{=C=CR(SnMe_3)\}$ 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 $[Fe(=C=CHMe)(dppe)Cp]^+$ affords bis(vinylidene) $[\{Fe(dppe)Cp\}_2(\mu\text{-}C_4Me_2)]^{2+}$, possibly via an intermediate radical cation [222]. Similar oxidative coupling of cyclopropenyl $Ru\{C{=}CPhCH(CN)\}(PPh_3)_2Cp$ affords bis(vinylidene) $[\{Cp(Ph_3P)_2Ru\}{=}C{=}CPhCH(CN)_2\}_2]^{2+}$ which, in turn, can be deprotonated to the bis(cyclopropenyl) [223]. Oxidation of $[Ru(N_4Me_8)(=C=CH_2)]^{2-}$ with PhN_3 or $[FeCp_2]^+$ affords $[\{Ru(N_4Me_8)\}_2(\mu\text{-}C{=}CHCH{=}C)]^{4-}$ [51].