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# Transition metal $\eta^2$-vinyl complexes

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## Contents

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*Abbreviations:* Cp, $\eta^5$-$C_5H_5$; Cp′, $\eta^5C_5H_4Me$; Cp*, $\eta^5$-$C_5Me_5$; $Cp^x$, Cp, Cp′ and/or Cp*; Ind, indenyl ($\eta^5$-$C_9H_7$); Tp, hydridotris(1-pyrazolyl)borate; Tp′, hydridotris(3,5-dimethylpyrazolyl)borate; $Tp^x$, Tp and/or Tp′; dtc, dithiocarbamate ($S_2CNR_2$); $H_4$-pia, $Me_2NCH_2CH_2N{=}CH(C_6H_4^-)$; $F_4$-pia, $Me_2NCH_2CH_2N{=}CH(C_6F_4^-)$; PBP, $\kappa^2$-$P(OMe)_2OBF_2OP(OMe)_2$; dppe, $Ph_2PCH_2CH_2PPh_2$; $N_3N$, $[(Me_3SiNCH_2CH_2)_3N]^{3-}$; MA, maleic anhydride; Tol, *para*-tolyl.

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## Abstract

Transition metal η$^2$-vinyl complexes, $L_nM(\eta^2\text{-CR=CR}_2)$, adopt structures in which both alkenyl carbons are bound to the metal. The $M(\text{–CR=CR}_2)$ unit is not planar in these 1-metallocyclopropene complexes. Instead, the $CR_2$ entity is twisted by ca. 90° away from planarity with the three-membered ring formed by M, $C_\alpha$, and $C_\beta$. The ring carbons of η$^2$-vinyl ligands are bound asymmetrically to the metal with one short metal–carbon bond and one long metal–carbon bond. These geometrical features reflect double bond character between $C_\alpha$ and the metal at the expense of the carbon–carbon double bond in the classic organic vinyl moiety. Coordination of both carbons of the four-electron donating η$^2$-vinyl ligand increases the electron count at the metal by two electrons relative to an η$^1$-bound vinyl ligand. This review summarizes synthetic methods which yield η$^2$-vinyl complexes, describes bonding and structural characteristics of η$^2$-vinyl ligands, tabulates NMR spectroscopic signatures of η$^2$-vinyl ligands, and outlines reactions of this growing class of compounds.

*Keywords:* η$^2$-Vinyl complexes; Alkenyl complexes; Metallacyclopropene complexes

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## 1. Introduction

Organic vinyl fragments, $[\text{CR=CR}_2]^-$, bound through both carbon atoms to a single metal center constitute an important subset of metal–alkenyl complexes. Transition metal alkenyl complexes, $L_nM\text{–CR=CR}_2$, have attracted attention because of their significance in organometallic synthesis and catalysis [1–3]. The discovery that alkenyl ligands could adopt η$^2$-structures in which both alkenyl carbons were bound to the metal led to speculation that η$^2$-vinyl, or 1-metallacyclopropene, complexes, $L_nM(\eta^2\text{-CR=CR}_2)$, might be involved along catalytic pathways involving coordinatively unsaturated alkenyl species. Coordination of both carbons of the vinyl unit increases the electron count at the metal by two electrons relative to a simple σ- or η$^1$-bound vinyl ligand. This review will describe synthetic methods which have produced isolable η$^2$-vinyl complexes, consider the bonding and structural characteristics coincident with the η$^2$-binding mode, and outline the reactivity patterns of this modestly populated class of compounds. Before systematically surveying η$^2$-vinyl ligands, a few points deserve to be highlighted.

Two prominent geometrical features define η$^2$-vinyl ligands. First, the ligand is bound asymmetrically to the metal through both carbons; either a ring description or an η$^2$ descriptor highlights this point (Fig. 1). Second, the $MCR\text{=}CR_2$ fragment is not planar in η$^2$-vinyl ligands. Rather, the $CR_2$ unit is rotated so that the carbon–carbon double bond characteristic of the vinyl unit is compromised in favor of double bond character between $C_\alpha$ and the metal. The net result is that the substituents on the β carbon are approximately orthogonal to the $MC_2$ plane and the distinction between *cis* and *trans* sites associated with organic vinyl fragments is lost.

The $[\eta^2\text{-C(R)=CR}_2)]^-$ ligand has been described as an $\eta^2$-vinyl ligand or as an $\eta^2$-alkenyl ligand, and the resulting product has been termed either an $\eta^2$-vinyl complex or a 1-metallacyclopropene complex. Why have we chosen the $\eta^2$-vinyl designation for the title of this article? The $\eta^2$-vinyl term has enjoyed widespread use in the literature, and the origin of the fragment and the reactivity patterns that yield and consume these ligands are intrinsically associated with the vinyl name. On the other hand, Casey has eloquently argued for adoption of the 1-metallacyclopropene nomenclature [4]. Indeed, the 1-metallacyclopropene nomenclature more accurately conveys the physical characteristics of the $\eta^2$-$\text{C(R)=CR}_2$ entity. The concurrent use of metallacyclopropene terminology for coordinated alkynes complicates differentiation of $\eta^2\text{-C(R)=CR}_2$ products from alkyne reagent precursors. In accord with our focus on synthesis and reactivity, we will utilize the $\eta^2$-vinyl nomenclature while conceding the hazards involved in misrepresenting the structural and spectroscopic properties with this terminology. The 1-metallacyclopropene structural representation will be used since it is congruent with the ground state structures and spectroscopic properties of these complexes.

Early work in this area was dominated by the research groups of Green and Davidson with each group focusing on nucleophilic addition to Group (VI) metal alkyne complexes. Despite the absence of a review article dedicated solely to $\eta^2$-vinyl chemistry, two relevant survey articles appeared in the 1980's that discussed $\eta^2$-vinyl complexes. A 1986 *J. Organomet. Chem.* article provided excellent coverage of extensive work on molybdenum $\eta^2$-vinyl complexes from the Michael Green laboratory [5]. A 1989 review of alkynes as π-donor ligands included $\eta^2$-vinyl chemistry derived from 4-electron donor alkyne ligands bound to molybdenum or tungsten [6]. During the past decade, new research groups have contributed exciting chemistry to this field. Our goal is to provide a survey of hydrocarbon $\eta^2$-vinyl chemistry in monomeric complexes, $L_nM(\eta^2\text{-CR=CR}_2)$. Heteroatom analogues, $L_nM(\eta^2\text{-C(R)=ER}_m)$ ($m = 0, 1, 2$) [7–16], are beyond the scope of this review.

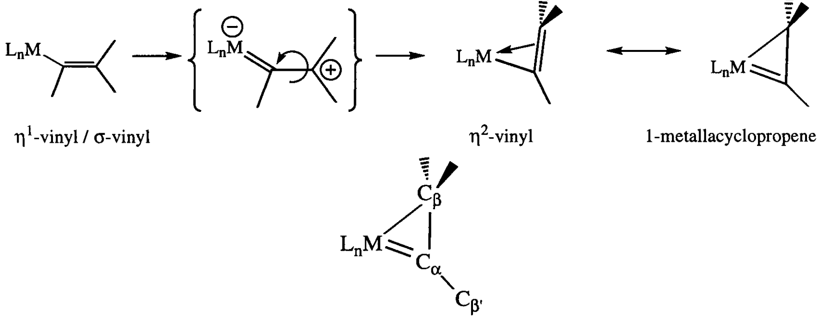


Fig. 1. Nomenclature and Labeling for $L_nM(\eta^2\text{-CR=CR}_2)$ complexes.

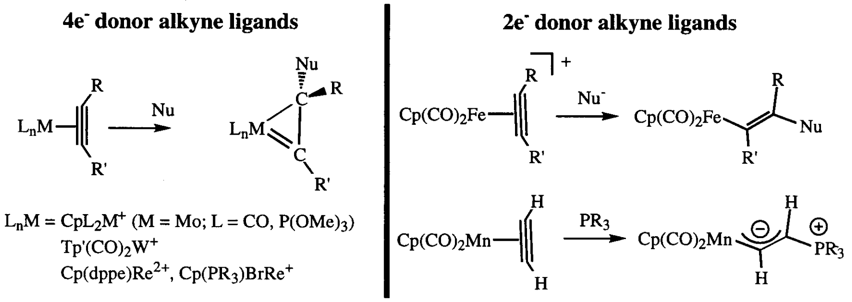


Fig. 2. Nucleophile addition to alkyne ligands.

## 2. Syntheses of $\eta^2$-vinyl complexes

### 2.1. Nucleophile addition to alkyne complexes

Nucleophile addition to unsaturated $d^4$ transition metal complexes, $L_nM(RC{\equiv}CR')^{m+}$ ($m = 0$, 1, 2), in which the alkyne acts as a four-electron donor ($4e^-$) is the most common route to $L_nM(\eta^2\text{-}C(R){=}CHR')$ complexes (Fig. 2). The valence electron count at the metal is crucial to $\eta^2$-vinyl formation. In contrast, addition of nucleophiles to two-electron donor ($2e^-$) alkyne ligands in coordinatively saturated Fe(II) $d^6$ alkyne complexes results in $\sigma$- or $\eta^1$-vinyl complexes [17–19]. Alt has reported phosphine addition to $2e^-$ donor acetylene ligands in Mn(I) complexes to yield ylidic carbene complexes [20a].

The issue of valence electron count in determining the binding mode for the vinyl ligand is highlighted by consideration of alternative $4e^-$ binding modes. Alkenylzirconocene complexes with bulky substituents, $Cp_2(Cl)Zr(CR{=}CR'H)$, exhibit $\beta$-C–H agostic interactions with the $16e^-$ Zr(IV) center (Fig. 3) [20b]. The $d^0$ electron count at the metal precludes $\eta^2$-vinyl formation since no backbonding electrons are available to stabilize the constrained ring geometry of the $\eta^2$-vinyl linkage. Theoretical studies of $\eta^2$-vinyl complexes have noted the importance of the backbonding interaction in determining $\eta^2$-vinyl ligand stability [21,22]. A ruthenium(II) $d^6$ alkenyl intermediate having a $\beta'$ C–H agostic interaction has been spectroscopically observed in coupling reactions between 2-butyne and terminal alkynes (Fig. 3) [23].

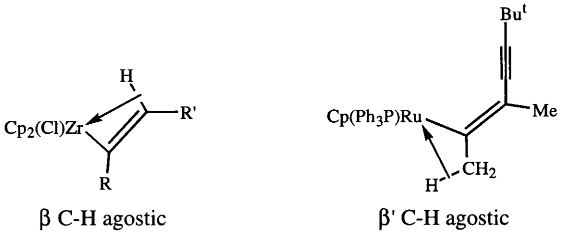


Fig. 3. Alternative $4e^-$ binding modes for vinyl ligands.

Coordination of the C–C double bond of the vinyl ligand is not possible owing to the lack of an empty dπ orbital which is necessary to form the M=C linkage.

Hydride, typically delivered from $KHB(s\text{-}Bu)_3$ or $LiHBEt_3$ to cationic alkyne complexes, is the most versatile nucleophile for generating $\eta^2$-vinyl complexes. Hydride addition to $CpL_2Mo(RC{\equiv}CR')^+$ ($L = P(OMe)_3$; $R = R' = Ph$; $R = Ph$, $R' = CH_2Ph$) [24], $IndL_2Mo(HCCSiMe_3)^+$ ($L = P(OMe)_3$) [25], $CpLL'Mo(PhC{\equiv}CPh)^+$ ($L = L' = P(OMe)_3$; $L = CO$, $L' = PMe_2Ph$) [26], $Cp(PBP)Mo(RC{\equiv}CR')$ ($R = Ph$, $R' = Me$, Ph) [27], $Tp'(CO)_2W(RC{\equiv}CR')^+$ ($R = H$, $R' = Me$, $Bu^n$, $Bu^t$, $CH_2Ph$, Ph, $SiMe_3$; $R = R' = Ph$) [28,29], $Cp(L)BrRe(PhC{\equiv}CPh)^+$ ($L = PPh_3$, $PMe_2Ph$) [30] and $Cp(dppe)Re(RC{\equiv}CR')^{2+}$ ($R = Ph$, $R' = Me$, Ph) [30] has produced $\eta^2$-vinyl complexes. For complexes with terminal alkyne ligands, hydride addition occurs regioselectively at the terminal carbon of the $4e^-$-donor alkyne ligand (Fig. 4). Green has rationalized this regioselectivity for terminal alkynes in terms of a frontier-orbital controlled attack on the alkyne portion of the LUMO of the metal alkyne complexes and steric accessibility to the terminal site [24].

In the case of internal alkynes, hydride prefers to add to aryl substituted alkyne carbons. A complicating factor for $\eta^2$-vinyl complexes having β′-alkyl groups is the tendency to isomerize into $\eta^3$-allyl complexes (see Section 5). For example, treatment of $[Cp(P(OMe)_3)_2Mo(\eta^2\text{-}PhC{\equiv}CCH_2Ph)]^+$ with $KHB(s\text{-}Bu)_3$ forms $Cp(P(OMe)_3)_2Mo(\eta^2\text{-}C(CH_2Ph){=}CHPh)$, which slowly rearranges into $Cp(P(OMe)_3)_2Mo(\eta^3\text{-}CHPhCHCHPh)$ in solution [24]. Reaction of the zwitterionic $Cp(PBP)Mo(\eta^2\text{-}PhC{\equiv}CMe)$ with $KHB(s\text{-}Bu)_3$ produces the anionic $\eta^2$-vinyl complex, $[K][Cp(PBP)Mo(\eta^2\text{-}C(Me){=}CHPh)]$ [27]. Addition of $KHBEt_3$ to $[Tp'(CO)_2W(\eta^2\text{-}PhC{\equiv}CMe)]^+$ results in the spectroscopic observation of $[Tp'(CO)_2W(\eta^2\text{-}C(Me){=}CHPh)]$ on the way to $Tp'(CO)_2W(\eta^3\text{-}CH_2CHCHPh)$ [28].

Does hydride addition occur directly at an alkyne carbon, or does the hydride first add to the metal and then migrate to an alkyne carbon? For the latter reaction pathway, the alkyne would need to retract an electron pair ($4e^- \rightarrow 2e^-$) in order to accommodate hydride addition at the metal center. No well-defined intermediate has been observed for hydride addition reactions, but Green's work in this area is

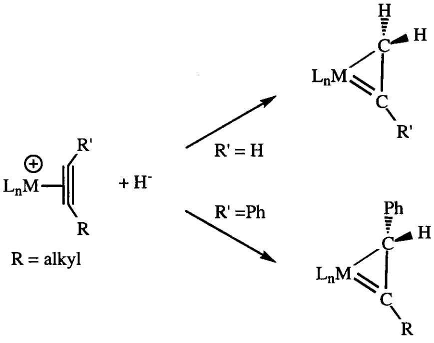
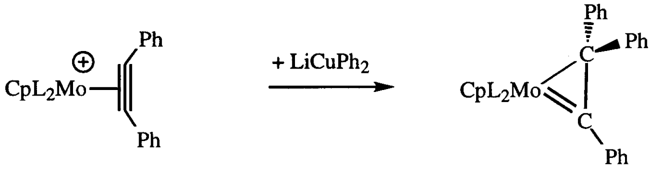


Fig. 4. Regioselectivity of hydride addition to $4e^-$ donor alkyne ligands.

noteworthy [5]. Reaction products of alkyl and aryl nucleophiles with alkyne complexes are relevant to this question.

Reaction of $LiCuPh_2$ with $[CpL_2Mo(\eta^2\text{-}PhC{\equiv}CPh)]^+$ ($L = P(OMe)_3$) produces the $\eta^2$-vinyl complex, $CpL_2Mo(\eta^2\text{-}C(Ph){=}CPh_2)$ (Eq. (1)) [24]. With $LiCuMe_2$ as the nucleophile, two products are isolated: the analogous $\eta^2$-vinyl product, $CpL_2Mo(\eta^2\text{-}C(Ph){=}CMePh)$, and the ligand substitution product, $CpL(Me)Mo(\eta^2\text{-}PhC{\equiv}CPh)$ (Eq. (2)). Reaction of the methyl alkyne product with $P(OMe)_3$ under a variety of conditions failed to convert it into the $\eta^2$-vinyl complex [24]. Only ligand substitution to produce $CpLRMo(\eta^2\text{-}R^2C{\equiv}CR^3)$ complexes was observed for the reaction of $LiCuR_2$ ($R = Me$, Ph) reagents with other internal alkyne complexes, $CpL_2Mo(\eta^2\text{-}R^2C{\equiv}CR^3)$ ($R^2 = Me$, $R^3 = Me$, $Bu^t$; $R^2 = Ph$, $R^3 = CH_2Ph$) [24]. Attempts to convert these $CpLRMo(\eta^2\text{-}RC{\equiv}CR)$ complexes into $\eta^2$-vinyl derivatives were unsuccessful. A rare halogen substituted $\eta^2$-vinyl complex, $CpL_2Mo(\eta^2\text{-}C(Br){=}CPh_2)$, was obtained via treatment of $CpL_2Mo(\eta^2\text{-}BrC{\equiv}CPh)^+$ with $LiCuPh_2$ [31]. In contrast, treatment of the cationic bromoalkyne complex with $KHB(s\text{-}Bu)_3$ results in a seven-coordinate vinylidene complex, $CpL_2(Br)Mo{=}C{=}CHPh$, in which the α-bromide substituent has migrated to the metal.



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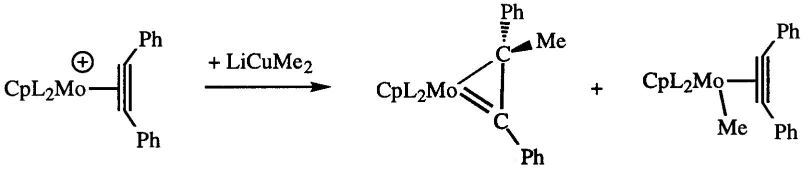
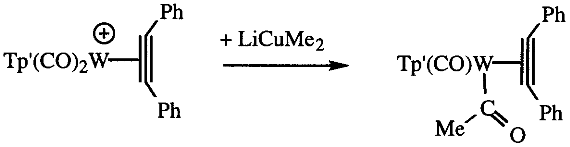


(2)

Attempts to utilize Grignard nucleophiles, RMgBr ($R = Me$, Et, $CH_2Ph$), with $[CpL_2Mo(\eta^2\text{-}PhC{\equiv}CPh)][BF_4]$ complexes uniformly resulted in ligand substitution to form $CpLRMo(\eta^2\text{-}PhC{\equiv}CPh)$ complexes [27]. In a related dicarbonyl system, addition of $LiCuR_2$ ($R = Me$, $n$-Bu) reagents to $[Tp'(CO)_2W(\eta^2\text{-}PhC{\equiv}CMe)]^+$ resulted in attack at a carbonyl ligand to produce $\eta^1$-acyl alkyne complexes, $Tp'(CO)(\eta^1\text{-}C(O)R)W(\eta^2\text{-}PhC{\equiv}CMe)$ (Eq. (3)) [28,32]. Modification of the ancillary ligand set to include an isocyanide ligand, $Tp'(CO)(CNMe)W(\eta^2\text{-}PhC{\equiv}CMe)^+$, led to $\eta^2$-vinyl formation, $Tp'(CO)(CNMe)W(\eta^2\text{-}C(Ph){=}CMe_2)$, from an alkyl cuprate reagent (Eq. (4)) [33]. Use of MeLi and a more reactive terminal alkyne ligand, $PhC{\equiv}CH$, promoted $\eta^2$-vinyl formation in the synthesis of $Tp'(CO)_2W(\eta^2\text{-}C(Ph){=}CHMe)$ (Eq. (5)) [28].



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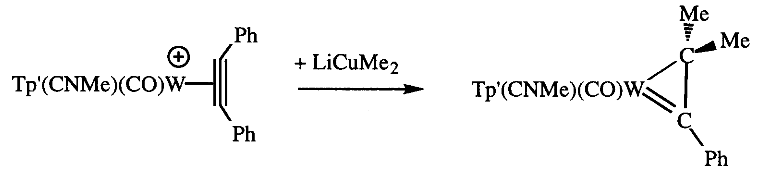

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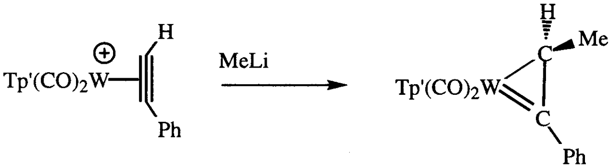
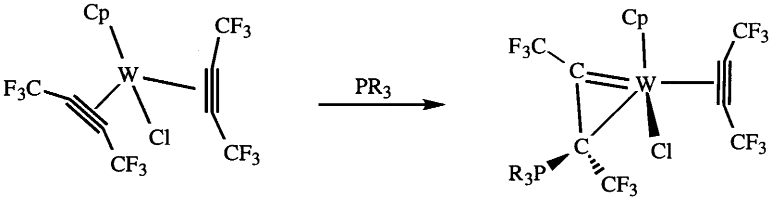


(5)

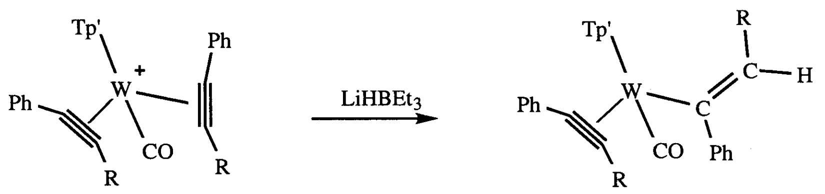
Both direct attack at an alkyne carbon and initial attack at the metal are viable reaction pathways for alkyl nucleophiles. Although hydride migrations from metal to ligand are surely more facile than alkyl migrations, direct attack of hydride at an alkyne carbon seems likely, especially for sterically hindered metal centers.

Davidson and co-workers have capitalized on the variable electron donating properties of alkyne ligands in bis-hexafluoro-2-butyne complexes. Attack of phosphorus nucleophiles ($PEt_3$, $P(C_6H_{11})_3$, $PMe_2Ph$, $PMePh_2$, $PPh_3$, $P(OMe)_3$, $P(OEt)_3$, $P(OPh_3)_3$) on a formally $3e^-$ donating perfluoro-2-butyne ligand in $CpXM(\eta^2\text{-}CF_3C{\equiv}CCF_3)_2$ complexes converts it into an $\eta^2$-vinyl ligand (Eq. (6)) [34–36]. The remaining perfluoro-2-butyne ligand adopts a $2e^-$ binding mode in deference to the more π-basic $\eta^2$-vinyl group. For phosphines and phosphites with relatively small cone angles ($PEt_3$, $PMe_2Ph$, $P(OMe)_3$, $P(OEt)_3$)) a kinetic isomer of $CpCl(\eta^2\text{-}CF_3C{\equiv}CCF_3)Mo(\eta^2\text{-}C(CF_3){=}C(CF_3)PX_3)$ is isolable, which differs from the thermodynamic isomer only in the relative position of the $\eta^2$-vinyl β-substituents. These results will be discussed further in Section 5.



(6)

It is worthwhile to contrast the perfluoro alkyne results, driven by the preference of the electron poor alkyne to serve as a $2e^-$ donor, with hydride addition to $[Tp'(CO)W(\eta^2\text{-}PhC{\equiv}CR)_2]^+$ complexes to form $\eta^1$-vinyl complexes, $Tp'(CO)(\eta^2\text{-}PhC{\equiv}CR)W(\eta^1\text{-}C(Ph){=}CHR)$, in which the strongly π-donating alkyne remaining in the coordination sphere forces the vinyl ligand to adopt an $\eta^1$ ($2e^-$) binding mode rather than an $\eta^2$ ($4e^-$) binding mode (Eq. (7)) [37]. Lithium dimethyl cuprate addition to $[Cp(CO)Mo(MeC{\equiv}CMe)_2]^+$ also results in an $\eta^1$-vinyl complex, $Cp(CO)(\eta^2\text{-}MeC{\equiv}CMe)Mo(\eta^1\text{-}C(Me){=}CMe_2)$ for similar electronic reasons [38].

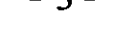


(7)

Treatment of monoalkyne complexes with phosphorus nucleophiles has also resulted in $\eta^2$-vinyl formation. Addition of $PMe_3$ or $P(OR)_3$ (R = Me, Et) to bis-dithiocarbamate complexes, $(dtc)_2(MA)W(\eta^2\text{-}PhC{\equiv}CH)$, results in nucleophilic addition to the terminal carbon of the phenylacetylene ligand to form $\eta^2$-vinyl products, $(dtc)_2(MA)W(\eta^2\text{-}C(Ph){=}CHPR_3)$ [39]. Facile dissociation of phosphite occurs from $(S_2CNMe_2)_2(MA)W(\eta^2\text{-}C(Ph){=}CHP(OEt)_3)$ at room temperature (r.t.) to regenerate the alkyne reagent. Attempts to add phosphorus nucleophiles to internal alkyne analogues were unsuccessful.

Reaction of $[Tp'(CO)_2W(\eta^2\text{-}PhC{\equiv}CH)][BF_4]$ with $P(OMe)_3$ in THF produced the neutral $\eta^2$-vinyl complex, $Tp'(CO)_2W(\eta^2\text{-}C(Ph){=}CHP(O)(OMe)_2)$, in which an Arbuzov elimination had occurred from the phosphite substituent [28]. Notably, more electron-rich $CpL_2Mo(\eta^2\text{-}RC{\equiv}CR)$ complexes do not react with $P(OMe)_3$ [5]. Use of a more stabilizing counterion ($O_3SCF_3^-$) and a less Lewis basic solvent ($CH_2Cl_2$) suppressed the Arbuzov elimination and allowed the isolation of the cationic $\eta^2$-vinyl complex, $[Tp'(CO)_2W(\eta^2\text{-}C(Ph){=}CHP(OMe)_3)][O_3SCF_3]$, as well as other phosphite substituted $\eta^2$-vinyl complexes, $Tp'(CO)(L)W(\eta^2\text{-}C(R){=}CH(P(OMe)_3)$ (L = CO, R = Me, $SiMe_3$; L = CNMe, $O_3SCF_3$, R = $SiMe_3$) [40].

The electron deficient nature of the hexafluoro-2-butyne ligands in $CpClM(\eta^2\text{-}CF_3C{\equiv}CCF_3)_2$ (M = Mo, W) complexes renders them susceptible to attack by other nucleophiles as well; isonitrile [34], alkyl thiolates [41,42] and heterocyclic nitrogen thiolates [35,43] have been used to produce $\eta^2$-vinyl products from $CpClM(\eta^2\text{-}CF_3C{\equiv}CCF_3)_2$ (M = Mo, W) complexes. Reaction of thallium thiolates, TlSR (R = Me, Et, ${}^i$Pr,) with $CpClM(\eta^2\text{-}CF_3C{\equiv}CCF_3)_2$ yields $Cp(\eta^2\text{-}CF_3C{\equiv}CCF_3)M(\eta^3\text{-}C(CF_3){=}C(CF_3)SR)$ (M = Mo, R = Me; M = W, R = Me, Et, $Pr^i$) complexes in which the thiolate sulfur is bound to both an $\eta^2$-vinyl β-carbon and to the metal (Eq. (8)). The comparable reaction with electron-poor aryl thiolates (R = $C_6F_5$, Ph, $C_6H_4Me$ in TlSR) results in chloride substitution at metal to produce bis-alkyne thiolate complexes, $Cp(\eta^2\text{-}CF_3C{\equiv}CCF_3)_2M\text{–}SR$, providing additional evidence for two pathways for nucleophile addition to alkyne complexes (Eq. (9)). Other examples of chelating $\eta^2$-vinyl ligands were obtained via treatment of $CpClM(\eta^2\text{-}CF_3C{\equiv}CCF_3)_2$ (M = Mo, W) complexes with heterocyclic nitrogen thiolates, Tl(LL) (LL = 2-$SC_5H_4N$, 2-$SC_4H_3N_2$) [35,43]. The resulting $\eta^2$-vinyl complexes, $Cp(\eta^2\text{-}CF_3C{\equiv}CF_3)M(\eta^3\text{-}C(CF_3){=}C(CF_3)LL)$ result from displacement of $Cl^-$ with $SR^-$ and nitrogen attack at a bound alkyne carbon.



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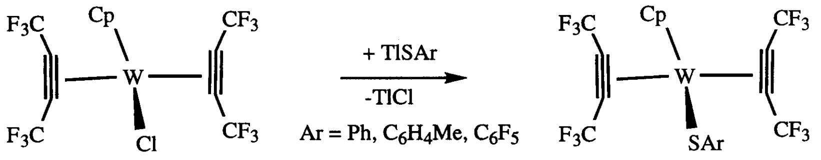
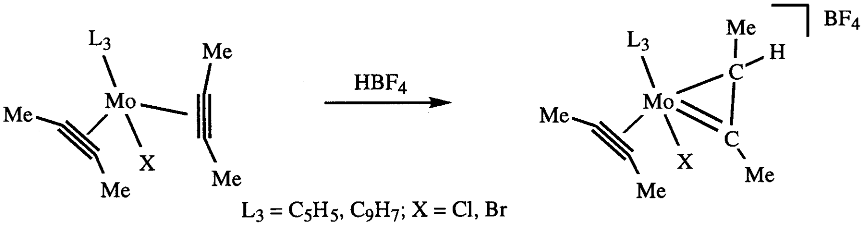


(9)

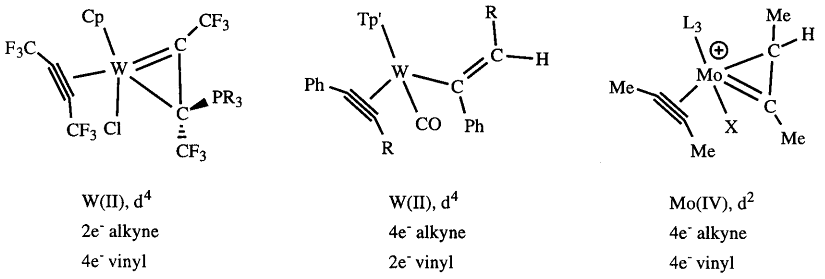
## 2.2. Protonation of alkyne and allene complexes

Treatment of neutral bis-alkyne $L_3XMo(\eta^2\text{-MeC}{\equiv}\text{CMe})_2$ ($L_3 = C_5H_5$, $C_9H_7$; X = Cl, Br) complexes with $HBF_4$ yields cationic $\eta^2$-vinyl complexes, $[L_3X(\eta^2\text{-MeC}{\equiv}\text{CMe})Mo(\eta^2\text{-C(Me)}{=}\text{CHMe})][BF_4]$ (Eq. (10)) [44]. In contrast to the vinyl–alkyne complexes above, both the vinyl ligand and the remaining 2-butyne ligand are required to donate $4e^-$ each owing to the formal two-electron oxidation of the metal, Mo(II) → Mo(IV), which accompanies alkyne protonation. A series of complimentary vinyl–alkyne complexes are presented in Fig. 5 for comparative purposes. Reaction of the cationic vinyl alkyne complexes with LiX (X = Cl, Br) results in neutral bis-halide complexes in which the vinyl ligand retains the $\eta^2$-binding mode and the 2-butyne ligand only donates $2e^-$ to the metal center [44].



(10)

Casey, et al. have recently observed $\eta^2$-vinyl intermediates in the acid catalyzed rearrangement of alkyne ligands into $\eta^3$-allyl and $\eta^2$-allene ligands in $Cp^*(CO)_2Re(\eta^2\text{-alkyne})$ complexes. Protonation of $Cp^*(CO)_2Re(\eta^2\text{-RC}{\equiv}\text{CR})$ (R = Me, *i*-Pr, Ph) yields $[Cp^*(CO)_2Re(\eta^2\text{-C(R)}{=}\text{CHR})][X]$ species [4,45,46]. Monitoring



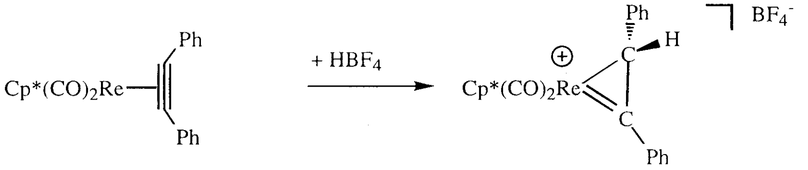
W(II), $d^4$
$2e^-$ alkyne
$4e^-$ vinyl

W(II), $d^4$
$4e^-$ alkyne
$2e^-$ vinyl

Mo(IV), $d^2$
$4e^-$ alkyne
$4e^-$ vinyl

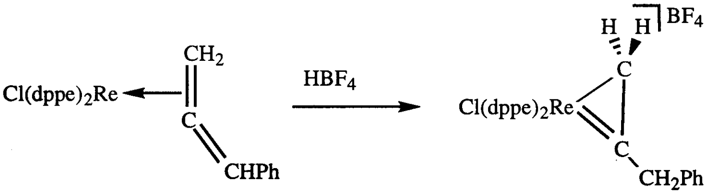
Fig. 5. Comparison of vinyl–alkyne complexes derived from addition reactions of bis-alkyne complexes.

of these reactions via $^1$H-NMR allowed the observation of rhenium–hydride complexes from kinetic protonation at the metal prior to migratory insertion to yield the $\eta^2$-vinyl intermediates. A formal oxidation of Re(I) $d^6$ to Re(III) $d^4$ accompanies the protonation reaction and necessitates the $\eta^2$ ($4e^-$) binding mode for the vinyl ligand. For R = Me, slow isomerization to the $\eta^3$-allyl isomer ($X = BF_4^-$) competes with reversible addition of conjugate bases ($X = Cl^-$, $O_2CCF_3^-$) on the way to the methyl allene complex, $Cp^*(CO)_2Re(\eta^2\text{-}MeHC{=}C{=}CH_2)$ [4,46]. For R = Ph, the $\eta^2$-vinyl intermediate has been isolated and structurally characterized (Eq. (11)) [46]. Similar results were reported for trityl ($Ph_3C^+$) addition to $Cp^*(CO)_2Re(\eta^2\text{-}MeC{\equiv}CH)$ where trityl addition to the terminal site of the propyne ligand to form $Cp^*(CO)_2Re(\eta^2\text{-}C(Me){=}CHCPh_3)^+$ was followed by a 1,2-Ph shift to yield $Cp^*(CO)_2Re(\eta^3\text{-}Ph_2CC(Ph)CHMe)$ [47].



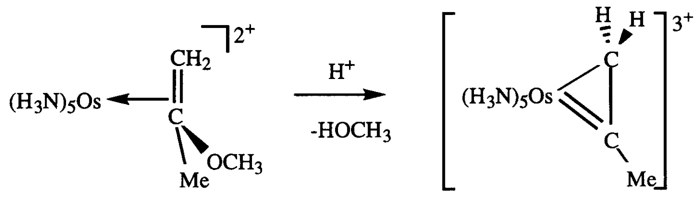
(11)

What ligands in addition to alkynes can serve as precursors to $\eta^2$-vinyl complexes? Pombeiro and co-workers reported the first $\eta^2$-vinyl complex of rhenium, $[(dppe)_2(Cl)Re(\eta^2\text{-}C(CH_2Ph){=}CH_2)][BF_4]$ via protonation of an allene complex, $(dppe)_2(Cl)Re(\eta^2\text{-}CH_2{=}C{=}CHPh)$ with $HBF_4$ (Eq. (12)) [48,49]. Subsequent mechanistic studies have revealed that the initial site of protonation with HCl as the acid source is the metal and not an allene carbon [50]. Transformation of the hydrido allene species to the final product, $[(dppe)_2(Cl)Re(\eta^2\text{-}C(CH_2Ph){=}CH_2)]^+$ occurs by two pathways; intramolecular H migration from the metal to the allene ligand and an acid–base catalyzed route involving a dicationic hydrido vinyl species, $[(dppe)_2(Cl)(H)Re(\text{–}C(Me){=}CH_2)]^{2+}$; the hapticity of the vinyl ligand in the dicationic species is unclear.



(12)

In a study of alkene ligands bound to the $(NH_3)_5Os^{2+}$ fragment, Harman and Chen discovered a unique route to osmium $\eta^2$-vinyl complexes. Protonation of vinyl ether complexes, $[(NH_3)Os(\eta^2\text{-}CH_2{=}CR(OR'))]^{2+}$, yields tricationic $\eta^2$-vinyl species following loss of HOR′ (Eq. (13)) [51]. Addition of nucleophiles to the α-carbon of the $\eta^2$-vinyl intermediates generates new alkene complexes. Vinyl $[(NH_3)_5Os(\eta^2\text{-}C(R){=}CHR')]^{3+}$ species are assumed to be intermediates in these transformations, and for R = Me, R′ = H, Me spectral characterization data were obtained.

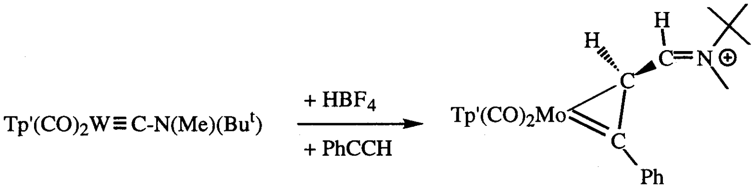


(13)

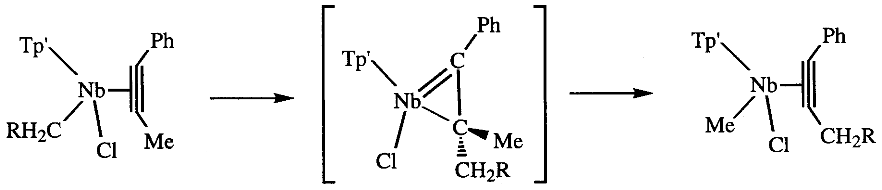
## 2.3. Alkyne insertion into metal–ligand bonds

Despite the postulated involvement of $\eta^2$-vinyl species in alkyne polymerization routes, few concrete examples involving insertion of an alkyne into a metal ligand bond exist. Studies by Alt and co-workers on the photoreactivity of $Cp^*(CO)_3WH$ ($Cp^* = C_5Me_5$) in the presence of alkynes ($CH_3C{\equiv}CR$; R = H, $CH_3$) implicated vinyl intermediates on the pathway to $\eta^3$-allyl complexes, although it is unknown whether the vinyl intermediates adopt the $\eta^2$-binding mode prior to isomerization [52]. Addition of hexafluoro-2-butyne to $Cp(CO)_3W{-}SR$ (R = Me, Et) complexes forms $\eta^2$-vinyl complexes, $Cp(CO)_2W(\eta^2\text{-}C(CF_3){=}C(CF_3)C(O)SR)$, with insertion of CO between carbon and sulfur [53–55]. Formation of these $\eta^2$-vinyl complexes has been interpreted in terms of initial metallacycle formation followed by a 1,3 sulfur shift.

Protonation of an aminocarbyne complex, $Tp'(CO)_2Mo \equiv CN(Me)(Bu^t)$, in the presence of free phenylacetylene yields $[Tp'(CO)_2Mo(\eta^2\text{-}C(Ph){=}CHCH{=}N(Me)\text{-}(Bu^t)][BF_4]$, presumably via reaction of phenylacetylene with an intermediate aminocarbene complex (Eq. (14)) [56]. Etienne et al. have proposed that $\eta^2$-vinyl intermediates form in the intramolecular exchange of niobium alkyl groups and alkyne substituents in $Tp'(Cl)(CH_2R)Nb(\eta^2\text{-}PhC{\equiv}CR')$ complexes via a migratory insertion/β-alkyl elimination pathway (Eq. (15)) [57]. Trapping of intermediate $\eta^1$-vinyl complexes, $Tp'(Cl)(\eta^1\text{-}C(Ph){=}C(Et)_2)Nb{=}E$ ($E = NP(NPr^i_2)_2$, O, S) was reported.



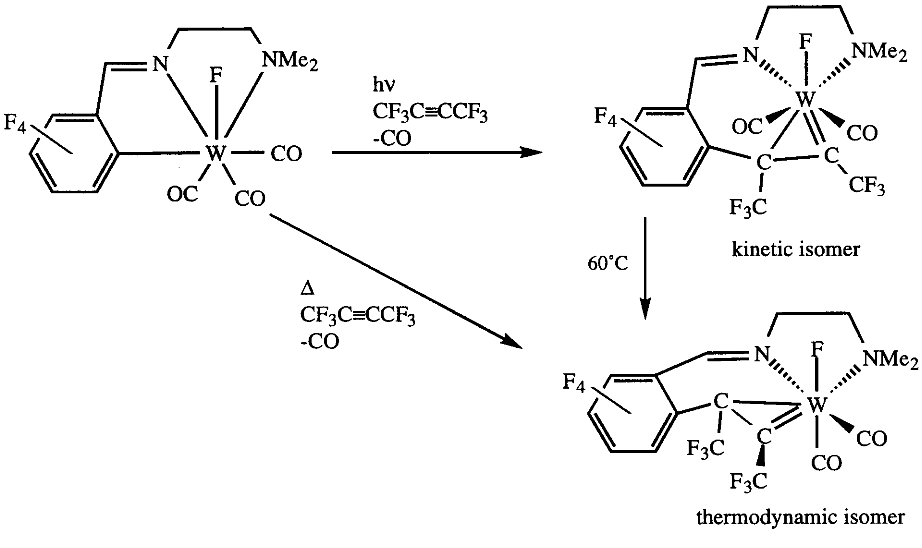
(14)



(15)

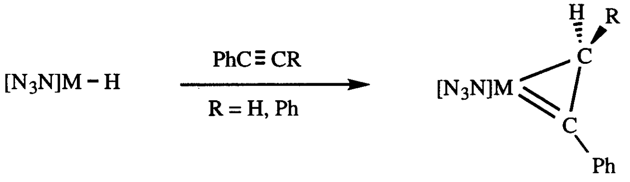
Although late transition metal $\eta^2$-vinyl chemistry is largely unrealized, $\eta^2$-vinyl species formed via alkyne insertions have been proposed for some late transition metal systems. Mechanistic studies and ab initio calculations of vinylidene formation from terminal alkyne ligands in ruthenium and osmium hydrido alkyne complexes support vinyl intermediates; $\eta^1$-vinyl in the case of ruthenium and $\eta^2$-vinyl for osmium that are formed via initial alkyne insertion into an M–H bond [58]. Ungváry et al. have postulated that $\eta^2$-vinyl intermediates may be involved in the reaction of phenylacetylene with $HCo(CO)_4$ to yield styrene and 2-phenylpropanal [59]. A theoretical investigation of acetylene insertion into square planar Pd(II) identified an $\eta^2$-vinyl transition state that is energetically accessible [60].

Richmond and co-workers achieved $\eta^2$-vinyl ligand formation via migratory insertion of alkyne into a metal ligand bond. Treatment of $(F_4\text{-pia})FW(CO)_3$ with perfluoro-2-butyne in toluene at 80°C results in the thermodynamically preferred isomer of the $\eta^2$-vinyl complex, $F(CO)_2W(\eta^2\text{-}C,C\text{-}\kappa^2\text{-}N,N\text{-}C(CF_3){=}C(CF_3)(F_4\text{-pia}))$, which has the $\eta^2$-vinyl fragment located *cis* to the CO and fluoride ligands (Eq. (16)) [61,62]. A kinetic isomer of $F(CO)_2W(\eta^2\text{-}C,C\text{-}\kappa^2\text{-}N,N\text{–}C(CF_3){=}C(CF_3)(F_4\text{-pia}))$ which has the $\eta^2$-vinyl ligand *cis* to the CO ligands and *trans* to the fluoride ligand was isolated following photolysis of $(F_4\text{-pia})FW(CO)_3$ in the presence of $CF_3C{\equiv}CCF_3$. Conversion of the kinetic isomer into the thermodynamic isomer occurs above 60°C. Additional examples of $\eta^2$-vinyl complexes utilizing other activated alkynes, the non-fluorinated $H_4$-pia ligand and molybdenum as the metal have been reported [63,64]. Alkynes (2-butyne, 3-hexyne) without electron withdrawing groups result in ligand substitution of two CO ligands to produce $(X_4\text{-pia})(CO)(F)W(\eta^2\text{-}RC{\equiv}CR)$ $(X = H, F;\ R = Me, Et)$ complexes [63].

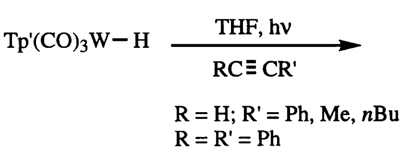


(16)

Alkyne insertion into tungsten–hydride bonds has produced isolable $\eta^2$-vinyl complexes in both $d^2$ and $d^4$ systems. Reaction of $[N_3N]WH$ with phenylacetylene or diphenylacetylene results in rare $d^2$ $\eta^2$-vinyl complexes, $[N_3N]W(\eta^2\text{-}C(Ph){=}CHR)$ (R = H, Ph) (Eq. (17)) [65]. The diphenyl $\eta^2$-vinyl derivative has been structurally characterized. The balance between steric and electronic properties may be important in this system as the related paramagnetic complex $[N_3N]W$(1-cyclopentene) adopts an $\eta^1$-structure [66]. Photolysis of $Tp'(CO)_3WH$ with alkynes yields $\eta^2$-vinyl, $\eta^3$-allyl, carbyne, $\eta^2$-acyl and metallafuran complexes [67,68]. Competing 1,2 and 2,1 alkyne insertion pathways dictate product outcome in this system. Photolysis of $Tp'(CO)_3WH$ with aryl alkynes ($RC{\equiv}CPh$; R = H, Ph) produces only $\eta^2$-vinyl products, $Tp'(CO)_2W(\eta^2\text{-}C(Ph){=}CHR)$ (Eq. (18)). For linear, terminal alkyl alkynes ($HC{\equiv}CR$; R = Me, $Bu^n$), the α-substituted $\eta^2$-vinyl products, $Tp'(CO)_2W(\eta^2\text{-}C(R){=}CH_2)$, are favored [68].



(17)



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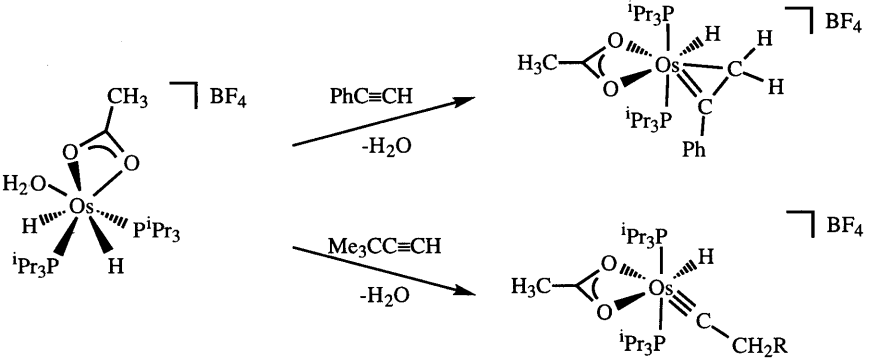
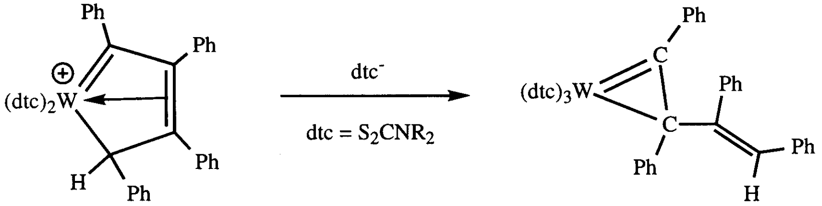


(19)

During the revision of this manuscript, Esteruelas, Eisenstein and co-workers published a report describing the chemistry between bis-hydride osmium complexes and alkynes. Reaction of $[(\kappa^2\text{-}OCOCH_3)(P(i\text{-}Pr)_3)_2(H_2O)Os(H)_2]^+$ with phenylacetylene results in an $\eta^2$-vinyl complex, while reaction with *tert*-butylacetylene results in a carbyne complex (Eq. (19)) [115]. Subtle electronic features control the product outcome in these reactions. Electron poor alkynes such as phenylacetylene or 1,1-diphenyl-2-propyn-1-ol form $\eta^2$-vinyl complexes via a bis hydride alkyne intermediate. With electron rich alkynes such as *tert*-butylacetylene or trimethylsilylacetylene a $d^6$ dihydrogen alkyne intermediate is accessed which isomerizes to a dihydrogen vinylidene complex prior to formation of the hydrido-carbyne.

### 2.4. Miscellaneous syntheses

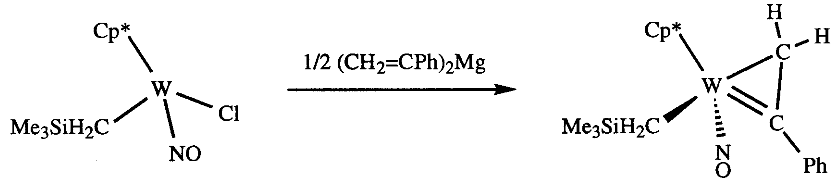
Vinyl substituted $\eta^2$-vinyl complexes, $(dtc)_3W(\eta^2\text{-}C(Ph){=}C(Ph)C(Ph){=}CHPh)$ have been produced via dechelation of a $\eta^4$-butadienyl ligand in bis-dithiocarbamate tungsten complexes, $(dtc)_2W(\eta^4\text{-}C_4Ph_4H)$, following addition of free dithiocarbamate anion (Eq. (20)) [69]. These complexes are unusual among isolated $\eta^2$-vinyl complexes in having both seven-coordination and a $d^2$ metal center. With the exception of the Schrock complexes noted above [65], all other isolated $\eta^2$-vinyl complexes are effectively pseudo-octahedral $d^4$ metal complexes (e.g. Mo(II), W(II), Re(III), Os(IV)). The putative $\eta^2$-vinyl intermediates postulated by Etienne et al., $Tp'(Cl)Nb(\eta^2\text{-}C(Ph){=}CRR')$, are formally $d^2$ Nb(II) complexes [57].



(20)

Traditional organometallic routes to introducing hydrocarbon fragments to transition metal complexes have had only limited success. Oxidative addition of a 2-bromopropene to $W(CO)_6$ in refluxing THF followed by addition of KTp′ results in a poor yield (6%) of $Tp'(CO)_2W(\eta^2\text{-}C(Me){=}CH_2)$ [29]. An unusual route to $Tp'(CO)_2W(\eta^2\text{-}C(Me){=}CH_2)$ via $LiCuMe_2$ addition to $Tp'(CO)_2W{\equiv}CCl$ has been reported and it is assumed that $Tp'(CO)_2W{\equiv}CMe$ is an intermediate in this reaction [70].

Legzdins et al. have recently reported the synthesis of an atypical vinyl complex, $Cp^*(Me_3SiCH_2)(NO)W(\eta^2\text{-}C(Ph){=}CH_2)$ in which the bonding is intermediate between the $\eta^1$- and $\eta^2$-binding modes (Eq. (21)) [71,72]. Access to the chloro derivative, $Cp^*(Cl)(NO)W(\eta^2\text{-}C(Ph){=}CH_2)$, was also obtained via a Grignard reaction using $Cp^*(Cl)_2W(NO)$ as the metal substrate and $Mg(CPh{=}CH_2)\cdot x$(dioxane) as the vinyl source [71,72]. The chloro derivative is amenable to ligand exchange via halogen abstraction with silver salts, AgX, to produce $Cp^*(X)(NO)W(C(Ph){=}CH_2)$ complexes and either $\eta^1$-vinyl ($X = O_2CPh$) or $\eta^2$-vinyl ($X = O_3SCF_3$) complexes result depending on the donor properties of the incoming ligand. Reaction of $Cp^*(Cl)(NO)W(\eta^2\text{-}C(Ph){=}CH_2)$ with two equivalents of *tert*-butylamine also results in chloride displacement to yield an $\eta^1$-vinyl complex, $Cp^*(NO)(\eta^1\text{-}C(Ph){=}CH_2)W{=}NHBu^t$ owing to the strongly donating amido ligand. Reaction of $Cp^*(SiMe_3CH_2)(NO)W(\eta^2\text{-}C(Ph){=}CH_2)$ with $H_2$ in the presence of $PPh_3$ results in the formation of a seven-coordinate $\eta^1$-vinyl complex, $Cp^*(H)(PPh_3)(NO)W(\eta^1\text{-}C(Ph){=}CH_2)$.



(21)

# 3. Characterization of η$^2$-vinyl complexes

## 3.1. Structural characterization

The geometric consequences of the metal–(η$^2$-vinyl) linkage are readily apparent in X-ray studies of η$^2$-vinyl complexes. The important metrical features include (1) short M–C$_\alpha$ bond distances (1.90–2.0 Å) appropriate for metal–carbon double bonds, (2) longer M–C$_\beta$ bond distances (2.10–2.30 Å) in the M–C single bond range, and (3) C$_\alpha$–C$_\beta$ bond distances of 1.40–1.46 Å which are intermediate between typical C–C single and C=C double bonds (Table 1). The remaining feature defining an η$^2$-vinyl, or 1-metallocyclopropene, ligand is the location of C$_\beta$ substituents in a plane roughly orthogonal to the MC$_\alpha$C$_\beta$ plane. In discussions of coordination sphere geometries, the small bite angle of the η$^2$-vinyl ligand effectively confines it to a single coordination site.

The geometries of Cp$^x$L$_2$M(η$^2$-vinyl) (Cp$^x$ = Cp, Cp*) are typically described in terms of the familiar ‘piano-stool’. A variety of ground state η$^2$-vinyl orientations have been observed and representative geometries are illustrated in Fig. 6. The most common structural type here is alignment of the η$^2$-vinyl ligand along a ligand axis such that the carbenic C$_\alpha$ is oriented either towards the Cp ligand ($\theta = 0°$) or away from the Cp ligand ($\theta = 180°$). This preference for alignment along a ligand axis has been rationalized on an electronic basis [22]. However, alignments approaching $\theta = 45°$ are also common.

Notable exceptions to these generalities are Legzdins’ Cp*(X)(NO)W(η$^2$-C(Ph)=CH$_2$) complexes, which feature physical parameters intermediate between those of η$^1$- and η$^2$-vinyl ligands. The vinyl orientations in Legzdins’ complexes approximately correspond to $\theta = 270°$ with the η$^2$-vinyl lying along the W–NO axis and having C$_\alpha$ towards the nitrosyl ligand [72].

For the two Tp′(CO)$_2$M(η$^2$-vinyl) structures [28,29], the η$^2$-vinyl ligand bisects the OC–M–CO angle and has the carbenoid C$_\alpha$ carbon proximal to the carbonyl ligands ($\theta = 225°$ relative to CpL$_2$M complexes). EHMO calculations on H$_3$(CO)$_2$W(η$^2$-CH=CH$_2$)$^{2-}$ suggest that this orientation is preferred by ca. 11 kcal mol$^{-1}$ over the opposite rotamer which has C$_\alpha$ directed away from the CO ligands [73]. Comparison of the structure of Tp′(CO)$_2$W(η$^2$-C(Ph)=CHPh) [29] to that of the isoelectronic [Cp*(CO)$_2$Re(η$^2$-C(Ph)=CHPh)]$^+$ [4] hints that ground state structural preferences may have a large steric component. The orientation of the η$^2$-vinyl ligand in the Tp′W system is orthogonal to that adopted in the Cp*Re system in which the C$_\alpha$–C$_\beta$ vector of the η$^2$-vinyl ligand lies parallel to the Cp* ligand plane

($\theta = 135°$). In the Tp′W system, the $\eta^2$-vinyl ligand lies in the cleft formed by the two *cis*-3,5-dimethyl pyrazole rings, while the $\eta^2$-vinyl ligand in the Cp*Re system follows the steric profile of the planar Cp* ligand.

Few structures of $\eta^2$-vinyl complexes lacking a capping tridentate ligand such as Cp, Cp*, or Tp′ have been reported. Pombeiro et al. have published the structure

Table 1
Structural parameters for $\eta^2$-vinyl complexes[a]

| Complex | M–C$_\alpha$ | M–C$_\beta$ | C$_\alpha$–C$_\beta$ | Ref. |
|---|---|---|---|---|
| Cp[P(OMe)$_3$]$_2$Mo($\eta^2$-C(Ph)=CHPh) | 1.95 | 2.30 | 1.43 | [24,26] |
| Cp[P(OMe)$_3$]$_2$Mo($\eta^2$-C(Bu$^t$)=CHPh) | 1.94 | 2.29 | 1.44 | [24] |
| Cp[P(OMe)$_3$]$_2$Mo($\eta^2$-C(Me)=CPh$_2$) | 1.96 | 2.25 | 1.46 | [24] |
| ($\eta^5$-C$_9$H$_7$)[P(OMe)$_3$]$_2$Mo($\eta^2$-C(SiMe$_3$)=CH$_2$) | 1.96 | 2.26 | 1.44 | [25] |
| Cp(Cl)(CF$_3$C$\equiv$CCF$_3$)Mo($\eta^2$-C(CF$_3$)=C-(CF$_3$)(PEt$_3$))[b] | 1.92; 1.91 | 2.29; 2.32 | 1.43; 1.42 | [36] |
| Cp(Cl)(CF$_3$C$\equiv$CCF$_3$)W($\eta^2$-C(CF$_3$)=C-(CF$_3$)(CNBu$^t$)) | 1.89 | 2.30 | 1.41 | [35] |
| Cp(SC$_6$H$_4$Me)(CF$_3$C$\equiv$CCF$_3$)W($\eta^2$-C(CF$_3$)=C-(CF$_3$)(PEt$_3$))) | 1.91 | 2.33 | 1.45 | [35] |
| Cp(CO)$_2$W($\eta^2$-C(CF$_3$)=C(CF$_3$)(C(O)SMe)) | 1.96 | 2.19 | 1.44 | [53,55] |
| Cp(CF$_3$C$\equiv$CCF$_3$)Mo($\eta^3$-C(CF$_3$)=C(CF$_3$)-(NC$_5$H$_4$S)) | 1.91 | 2.12 | 1.39 | [74] |
| Cp(CF$_3$C$\equiv$CCF$_3$)W($\eta^2$-C(CF$_3$)=C(CF$_3$)(SPr$^i$)) | 1.91 | 2.18 | 1.42 | [41] |
| CpMo[$\eta^5$-C(CF$_3$)=C(CF$_3$)(C(CF$_3$))$_2$-(C(CO$_2$Me))$_2$(SPr$^i$)] | 1.92 | 2.18 | 1.41 | [75] |
| CpMo[$\eta^6$-C(CF$_3$)=C(CF$_3$)(C(CF$_3$))$_2$C(CO$_2$Me)-C(SPr$^i$)(CO$_2$Me)] | 1.92 | 2.20 | 1.41 | [75] |
| (dtc–Me)$_3$W($\eta^2$-C(Ph)=CPh(CPh=CHPh) | 1.94 | 2.32 | 1.43 | [69] |
| [N$_3$N]W($\eta^2$-C(Ph)=CHPh) | 1.98 | 2.12 | 1.26 | [65] |
| [Tp′(CO)$_2$Mo($\eta^2$-C(Ph)=CH(CH=N(Bu$^t$)(Me))]-[BF$_4$] | 1.97 | 2.28 | 1.45 | [56] |
| Tp′(CO)$_2$W($\eta^2$-C(Ph)=CHPh) | 1.99 | 2.26 | 1.41 | [29] |
| Cp*(CH$_2$SiMe$_3$)(NO)W($\eta^2$-C(Ph)=CH$_2$) | 2.08 | 2.62 | 1.34 | [71,72] |
| Cp*(Cl)(NO)W($\eta^2$-C(Ph)=CH$_2$) | 2.07 | 2.58 | 1.33 | [72] |
| (F)(CO)$_2$W($\eta^2$-*C*,*C*-$\kappa^2$-*N*,*N*-C(Ph)=CPh(H$_4$-pia)) | 1.98 | 2.21 | 1.45 | [63] |
| (F)(CO)$_2$W($\eta^2$-*C*,*C*-$\kappa^2$-*N*,*N*-C(Me)=CPh-(H$_4$-pia)) | 1.97 | 2.21 | 1.44 | [63] |
| (F)(CO)$_2$W($\eta^2$–*C*,*C*–$\kappa^2$–*N*,*N*–C(CF$_3$)=CCF$_3$-(F$_4$-pia))[b] | 1.94; 1.95 | 2.20; 2.21 | 1.45; 1.41 | [61,62] |
| [(dppe)$_2$ClRe($\eta^2$-C(CH$_2$Ph)=CH$_2$)][BF$_4$] | 1.95 | 2.19 | 1.41 | [48] |
| Cp(Br)(PMePh$_2$)Re($\eta^2$-C(Ph)=CHPh) | 1.91 | 2.13 | 1.39 | [30] |
| [Cp(dppe)Re($\eta^2$-C(Ph)=CHPh)][BF$_4$] | 1.93 | 2.26 | 1.43 | [30] |
| [Cp*(CO)$_2$Re($\eta^2$-C(Ph)=CHPh)][BF$_4$] | 1.98 | 2.26 | 1.43 | [4] |
| [($\kappa^2$-OCOCH$_3$)(P(*i*-Pr)$_3$)$_2$(H)Os($\eta^2$-C(Ph)=CH$_2$)]-[BF$_4$] | 1.90 | 2.14 | 1.40 | [115] |

[a] Bond distances in Å.

[b] Two isomers.

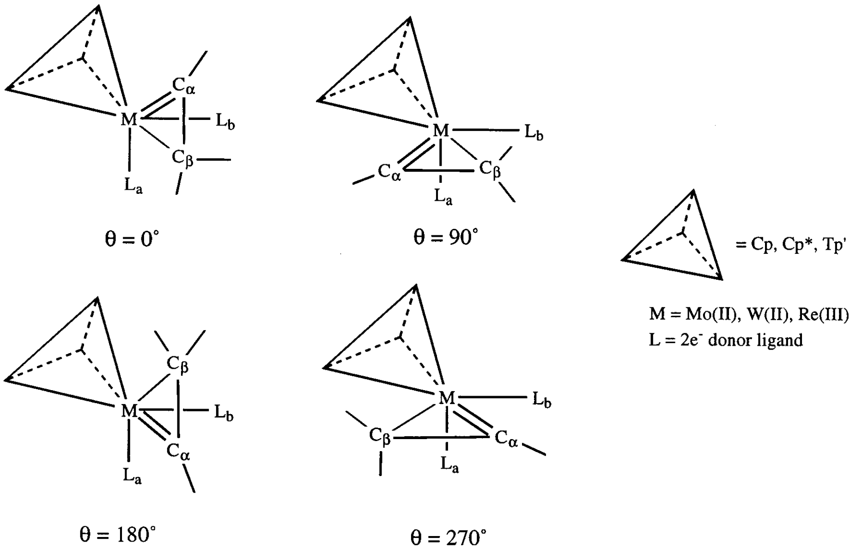


Fig. 6. Representative structural types for $\eta^2$-vinyl complexes with capping ligands. $\theta$ is the $C_\alpha$–$C_\beta$–M–$L_a$ dihedral angle.

of $(dppe)_2ClRe(\eta^2\text{-}C(CH_2Ph){=}CH_2)$, which adopts an octahedral geometry having both dppe ligands in the equatorial plane [48]. The $\eta^2$-vinyl ligand is *trans* to the chloride ligand and is oriented about 20° from coincidence with a P–Re–P vector, presumably for steric reasons. The geometry of the osmium $\eta^2$-vinyl complex, $[(\kappa^2\text{-}OCOCH_3)(P(i\text{-}Pr)_3)_2(H)Os(\eta^2\text{-}C(Ph){=}CH_2)][BF_4]$, is roughly distorted octahedral with the $P(i\text{-}Pr)_3$ ligands *trans* to each other with the hydride and acetate ligands in the equatorial plane [115]. The geometry of the osmium complex can alternatively be described as a distorted pentagonal bipyramidal if the $\eta^2$-vinyl is considered to occupy two coordination sites.

Schrock's five-coordinate, $d^2$ $\eta^2$-vinyl complex, $[N_3N]W(\eta^2\text{-}C(Ph){=}CHPh)$, adopts a slightly distorted trigonal bipyramidal geometry with the $\eta^2$-vinyl ligand in an axial site [65]. The $\eta^2$-vinyl ligand is orthogonal to one of the equatorial M–N axes rather than along any of the M–N axes in the equatorial plane. The seven-coordinate $d^2$ $\eta^2$-vinyl complex, $(dtc)_3W(\eta^2\text{-}C(Ph){=}CPh(CPh{=}CHPh)$, exhibits a distorted pentagonal bipyramidal geometry with an equatorial plane comprised of two dtc ligands and an additional sulfur atom from the third dtc ligand [69]. The $\eta^2$-vinyl ligand is aligned with the M–S bond axis of the dtc ligand with only one sulfur atom in the equatorial plane. The net effect of this orientation is to maximize π-acceptance from the only filled dπ orbital. The substituents of the $\eta^2$-vinyl ligand are well-removed from the dtc ligands in the equatorial plane.

The remaining class of complexes which lack a facial tridentate ligand is Richmond's $(X)(CO)_2M(\eta^2 - C,C,\text{-}\kappa^2\text{-}N,\ N\text{–}C(R){=}C(R)(Y_4\text{-pia})$ complexes. The kinetic isomer of $(F)(CO)_2M(\eta^2 - C,C,\text{-}\kappa^2\text{-}N,\ N\text{–}C(CF_3){=}C(CF_3)(F_4\text{-pia}))$[62] can be mapped to the Cp and Tp′ structural classes above for $\theta = 180$ if the amide and

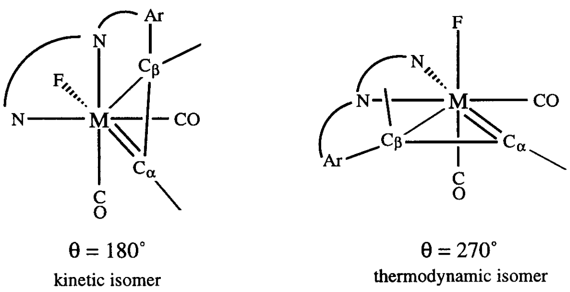


Fig. 7. Structural preferences in (X)$(CO)_2$M($\eta^2$- *C*,*C*,-$\kappa^2$-*N*, *N*–C(R)=C(R)($Y_4$-pia) complexes.

imine nitrogens of the chelating $F^4$-pia $\eta^2$-vinyl substituents and the fluoride are considered to form a three-atom capping group (Fig. 7). The thermodynamic isomer of this complex and other fluorinated and non-fluorinated analogs [63] can be mapped to a 270° vinyl orientation with the requirement that the three atom grouping is positioned to place the fluoride in a meridional arrangement with the carbonyl ligands.

### *3.2. NMR characterization*

The preferred spectroscopic method for identifying $\eta^2$-vinyl ligands in solution is $^{13}$C-NMR spectroscopy. The effective double bond character of the M=$C_\alpha$ linkage is reflected in low-field chemical shifts for Cα carbons of 220–300 ppm (Table 2), although α-carbons in fluorinated derivatives resonate near 200 ppm. The tetra-coordinate β-carbons appear at much higher fields, typically 10–80 ppm, consistent with $sp^3$-hybridization. Coupling constant values between the β-carbons and β-protons is typically on the order of 150–160 Hz, which is consistent with a strained ring geometry. One caveat here is that complexes may deviate from the $\eta^2$-vinyl bonding paradigm, yet still show similar spectroscopic properties. Notable here are Alt's zwitterionic Cp*$(CO)_2$Mn(CH=$CHPR_3$) complexes ($C_\alpha = 240$ ppm; $C_\beta = 97$ ppm), which do not contain $\eta^2$-vinyl ligands [20a]. Legzdins' Cp*(X)(NO)W($\eta^2$-C(Ph)=$CH_2$) complexes (see Table 1) show substantial structural distortions from optimal $\eta^2$-binding even though both carbons are coordinated to the metal [72].

Dynamic processes on the NMR timescale are often observed for $\eta^2$-vinyl complexes. Ground state structures for $CpL_2Mo(\eta^2\text{-vinyl})$ ($L = P(OMe)_3$) generally have the vinyl ligand aligned along one of the metal–phosphite axes creating inequivalent phosphite groups (Fig. 6; $\theta = 0$ or 90°). For $CpL_2Mo(\eta^2\text{-}C(Me) = CPh_2$, with identical substituents on $C_\beta$, a low energy fluxional process renders the phosphorus nuclei equivalent [24]. A similar process was indicated for the related $IndL_2Mo(\eta^2\text{-}C(SiMe_3) = CH_2)$ complex which shows an effective mirror plane in solution [25]. For complexes with different substituents on $C_\beta$, diastereomers result and the $L_2$ phosphorus nuclei are inequivalent.

Green has aptly described this process as a 'windscreen-wiper' motion which consists of an oscillation of about 90° from $\theta = 0°$ through $\theta = 45°$ to $\theta = 90°$ (Fig.

8) [5,24]. Rotation in the opposite direction ($\theta = 0° \rightarrow 315° \rightarrow 270°$) does not interconvert degenerate isomers, but reverses the relative positions of $C_\alpha$ and $C_\beta$ to form a distinct isomer. EHMO calculations on $Cp(P(OH)_3)_2Mo(\eta^2\text{-}CH{=}CH_2)$ indicated that the barrier to full rotation ($\theta = 0° \rightarrow 180° \rightarrow 0°$) is about 4 times greater than is the barrier to 90° oscillation (ca. 5 kcal $mol^{-1}$) [24]. Additional support for the windscreen wiper motion was found in the isolation of two diastereomers of $CpL_2Mo(\eta^2\text{-}C(CH_2Ph){=}CHPh)$ via hydride addition to $[CpL_2Mo(PhC{\equiv}CCH_2Ph)]^+$ [24]. Upon standing, slow conversion reflecting a net 90° rotation to the thermodynamically favored isomer occurs.

β-Substituent exchange on the NMR timescale has been observed for some $\eta^2$-vinyl complexes. A 16.2 kcal $mol^{-1}$ barrier for interconversion of enantiomers of the vinyliminium complex, $[Tp'(CO)_2Mo(\eta^2\text{-}C(Ph){=}CHCH{=}N(Bu^t)(Me)]^+$ was calculated for a process postulated to involve degenerate closure from an $\eta^1$-vinyl intermediate possessing a mirror plane (Fig. 8) [56]. Hydride addition to $[Tp'(CO)_2Mo(\eta^2\text{-}C(Ph){=}CHCH{=}N(Bu^t)(Me)]^+$ occurs at the carbon of the iminium substituent to yield a neutral $\eta^2$-vinyl complex which is rigid on the NMR timescale. The chiral-at-metal $\eta^2$-vinyl complex, $Tp'(CO)(CNMe)W(\eta^2\text{-}C(Ph){=}CMe_2)$ shows a single broad resonance for the β-methyl groups at r.t. which reflects a 15 kcal $mol^{-1}$ barrier for exchange of these two β-methyl groups [33].

Schrock's $d^2$ $\eta^2$-vinyl complex $[N_3N]W(\eta^2\text{-}C(Ph){=}CH_2)$ has mirror plane symmetry on the NMR timescale [65]. Warming the complex to 80°C results in apparent rotation of the $\eta^2$-vinyl ligand to produce a species with effective $C_3$ symmetry. Either simple rotation of the $\eta^2$-vinyl ligand with both carbons remaining bound to the metal or an $\eta^2 \rightarrow \eta^1 \rightarrow \eta^2$ process with rotation about the metal–carbon single bond in the $\eta^1$-form are consistent with the observed behavior.

Higher barriers to β-substituent exchange are indicated for $CpCl(\eta^2\text{-}CF_3C{\equiv}CCF_3)M(\eta^2\text{-}C(CF_3){=}CCF_3(PR_3))$ complexes. Both the kinetic and thermodynamic isomers of $CpCl(\eta^2\text{-}CF_3C{\equiv}CCF_3)Mo(\eta^2\text{-}C(CF_3){=}CCF_3(PEt_3))$ have been isolated and structurally characterized [36]. The kinetic isomer is structurally similar to the precursor bis-alkyne complex, perhaps reflecting direct nucleophilic attack at an alkyne carbon, and has the alkyne and $\eta^2$-vinyl ligands aligned nearly parallel to the M–Cl axis with the phosphine of the $\eta^2$-vinyl group located opposite the Cp group (pseudo-axial position) (Fig. 9). The geometry of the thermodynamic isomer can be obtained from that of the kinetic isomer by exchanging the vinyl β-substituents such that the phosphine occupies the position closer to the Cp ligand (pseudo-equatorial) and by tilting the $\eta^2$-vinyl unit by 30° away from the Cp ligand. Interconversion is presumed to occur by an $\eta^2 \rightarrow \eta^1 \rightarrow \eta^2$ process. Note that the $18e^-$ valence count at the metal could be retained throughout the process by a $2e^- \rightarrow 4e^-$ switch in electron donation by the perfluoro-2-butyne ligand.

## 4. Theoretical studies of $\eta^2$-vinyl complexes

Molecular orbital descriptions of $\eta^2$-vinyl complexes have stressed the isolobality of $\eta^2$-vinyl and $4e^-$ donor alkyne ligands. Although the relative energies differ,

Table 2
$^{13}$C-NMR data for $\eta^2$-vinyl complexes$^a$

| Complex | $C_\alpha$ | $C_\beta$ | Ref. |
|---|---|---|---|
| Cp[P(OMe)$_3$]$_2$Mo($\eta^2$-C(Ph)=CHPh)$^b$ | 255.5 | 26.8 | [24] |
| Cp[P(OMe)$_3$]$_2$Mo($\eta^2$-C(Bu$^t$)=CHPh)$^b$ | 286.5 | 29.9 | [24] |
| Cp[P(OMe)$_3$]$_2$Mo($\eta^2$-C(Bu$^t$)=CH(C$_6$H$_4$Me-4))$^b$ | 286.9 | 29.3 | [24] |
| Cp[P(OMe)$_3$]$_2$Mo($\eta^2$-C(Pr$^i$)=CH(C$_6$H$_4$Me-4))$^b$ | 276.2 | 26.1 | [24] |
| Cp[P(OMe)$_3$]$_2$Mo($\eta^2$-C(Me)=CPh$_2$)$^b$ | 237.4 | 35.7 | [24] |
| Cp[P(OMe)$_3$]$_2$Mo($\eta^2$-C(CH$_2$Ph)=CHPh)$^{b,c}$ | 260.4; 260.3 | 24.6; 24.6 | [24] |
| Cp[P(OMe)$_3$]$_2$Mo($\eta^2$-C(Ph)=CPh$_2$)$^b$ | 230.0 | n.r. | [24] |
| Cp[P(OMe)$_3$]$_2$Mo($\eta^2$-C(Ph)=CMePh)$^c$ | 259.4 | n.r. | [24] |
| ($\eta^5$-C$_9$H$_7$)[P(OMe)$_3$]$_2$Mo($\eta^2$-C(SiMe$_3$)=CH$_2$)$^d$ | 276.5 | 23.9 | [25] |
| Cp(PMe$_2$Ph)(CO)Mo($\eta^2$-C(Ph)=CHPh)$^b$ | 245.8 | 37.6 | [76] |
| Cp[P(OMe)$_3$]$_2$Mo($\eta^2$-C(Br)=CPh$_2$)$^e$ | 230.5 | n.r. | [31] |
| Cp(Cl$_2$)($\eta^2$-MeC≡CMe)Mo($\eta^2$-C(Me)=CHMe)$^f$ | 291.3 | 70.0 | [44] |
| [Cp(Br)($\eta^2$-MeC≡CMe)Mo($\eta^2$-C(Me)=CHMe)][BF$_4$]$^g$ | 297.6 | 73.6 | [44] |
| [K][Cp(pbp)Mo($\eta^2$-C(Me)=CHPh)$^f$ | 242.3 | 49.4 | [27] |
| [K][Cp(pbp)Mo($\eta^2$-C(Ph)=CHPh)$^f$ | 240.8 | 31.0 | [27] |
| (dtc–Et)$_2$($\eta^2$-MA)W($\eta^2$-C(Ph)=CH(P(Me)$_3$)$^e$ | 226.8 | n.r. | [39] |
| (dtc-Et)$_2$($\eta^2$-MA)W($\eta^2$-C(Ph)=CH(P(OMe)$_3$)$^e$ | 222.2 | 11.6 | [39] |
| (dtc-Me)$_3$W($\eta^2$-C(Ph)=CPh(CPh=CHPh)$^f$ | 260.6 | 62.1 | [69] |
| (dtc–Et)$_3$W($\eta^2$-C(Ph)=CPh(CPh=CHPh)$^f$ | 262.2 | 62.3 | [69] |
| [N$_3$N]W($\eta^2$-C(Ph)=CHPh)$^e$ | 246.1 | 56.6 | [65] |
| [N$_3$N]W($\eta^2$-C(Ph)=CH$_2$)$^e$ | 242.5 | 56.6 | [65] |
| [Tp′(CO)$_2$Mo($\eta^2$-C(Ph)=CH(CH=N(Bu$^t$)(Me))][BF$_4$]$^f$ | 242.6 | 40.7 | [56] |
| Tp′(CO)$_2$Mo($\eta^2$-C(Ph)=CH(CH$_2$N(Bu$^t$)(Me))$^f$ | 285.3 | 44.3 | [56] |
| Tp′(CO)$_2$W($\eta^2$-C(Me)=CH$_2$)$^e$ | 248.0 | 17.5 | [29] |
| Tp′(CO)$_2$W($\eta^2$-C(Et)=CH$_2$)$^e$ | 252.7 | 15.0 | [29] |
| Tp′(CO)$_2$W($\eta^2$-C(Bu$^n$)=CH$_2$)$^e$ | 260.4 | 15.6 | [29] |
| Tp′(CO)$_2$W($\eta^2$-C(Bu$^t$)=CH$_2$)$^e$ | 260.4 | 15.2 | [68] |
| Tp′(CO)$_2$W($\eta^2$-C(CH$_2$Ph)=CH$_2$)$^e$ | 247.5 | 16.7 | [29] |
| Tp′(CO)$_2$W($\eta^2$-C(CH$_2$CH$_2$Ph)=CH$_2$)$^e$ | 247.4 | 13.9 | [33] |
| Tp′(CO)$_2$W($\eta^2$-C(CH(Me)(Pr$^n$))=CH$_2$)$^e$ | 254.3 | 31.6 | [29] |
| Tp′(CO)$_2$W($\eta^2$-C(CH(CH(OH)Ph)(Pr$^n$)=CH$_2$)$^e$ | 246.0 | 15.7 | [29] |
| Tp′(CO)$_2$W($\eta^2$-C(SiMe$_3$)=CH$_2$)$^e$ | 252.6 | 30.6 | [68] |
| Tp′(CO)$_2$W($\eta^2$-C(Ph)=CH$_2$)$^f$ | 234.4 | 17.3 | [28] |
| Tp′(CO)$_2$W($\eta^2$-C(Ph)=CHMe)$^f$ | 264.5 | 38.0 | [28] |
| Tp′(CO)$_2$W($\eta^2$-C(Ph)=CHPh)$^{c,f}$ | 255.7; 241.0 | 41.3; 39.8 | [28] |
| Tp′(CO)(CNMe)W($\eta^2$-C(Ph)=CHMe)$^{f,h}$ | 247.3 | n.r. | [33] |
| [Tp′(CO)$_2$W($\eta^2$-C(Me)=CHP(OMe)$_3$)][O$_3$SCF$_3$]$^f$ | 221.3 | 8.67 | [40] |
| [Tp′(CO)$_2$W($\eta^2$-C(SiMe$_3$)=CHP(OMe)$_3$)][O$_3$SCF$_3$]$^f$ | 240.8 | 16.2 | [40] |
| [Tp′(CO)$_2$W($\eta^2$-C(Ph)=CHP(OMe)$_3$)][O$_3$SCF$_3$]$^f$ | 233.6 | 7.47 | [40] |
| Tp′(CO)$_2$W($\eta^2$-C(Ph)=CHPO(OMe)$_2$)$^f$ | 229.6 | 17.3 | [28] |
| [Tp′(CO)$_2$W($\eta^2$-C(Ph)=CHP(OH)(OMe)$_2$)][BF$_4$]$^f$ | 225.5 | 13.9 | [28] |
| [Tp′(CO)(CNMe)W($\eta^2$-C(Ph)=CH(P(OMe)$_3$)][O$_3$SCF$_3$]$^{c,f}$ | 234.4; 233.4 | 8.73; 5.67 | [40] |
| (Cl)(CO)$_2$Mo($\eta^2$-*C*,*C*-$\kappa^2$-*N*,*N*–C(Ph)=CPh(H$_4$-pia))$^f$ | 258.1 | 46.1 | [64] |
| (Cl)(CO)$_2$Mo($\eta^2$-*C*,*C*-$\kappa^2$-*N*,*N*–C(Me)=CPh(H$_4$-pia))$^f$ | 264.2 | 41.2 | [64] |
| (F)(CO)$_2$W($\eta^2$-*C*,*C*-$\kappa^2$-*N*,*N*–C(CF$_3$)=CCF$_3$(H$_4$-pia))$^f$ | 203.2 | 37.6 | [63] |
| (F)(CO)$_2$W($\eta^2$-*C*,*C*-$\kappa^2$-*N*,*N*–C(Ph)=CCPh(H$_4$-pia))$^f$ | 228.4 | 43.4 | [63] |
| (F)(CO)$_2$W($\eta^2$-*C*,*C*-$\kappa^2$-*N*,*N*–C(Me)=CPh(H$_4$-pia))$^f$ | 237.2 | 41.9 | [63] |
| (F)(CO)$_2$W($\eta^2$-*C*,*C*-$\kappa^2$-*N*,*N*–C(4-C$_6$H$_4$-CF$_3$)=CPh-(H$_4$-pia))$^f$ | 225.2 | 44.3 | [63] |

Table 2 (*Continued*)

| Complex | C$_\alpha$ | C$_\beta$ | Ref. |
|---|---|---|---|
| (F)(CO)$_2$W($\eta^2$-*C*,*C*-$\kappa^2$-*N*,*N*–C(Ph)=C(4-C$_6$H$_4$-CF$_3$)-(H$_4$-pia))$^f$ | 227.5 | 42.9 | [63] |
| (F)(CO)$_2$W($\eta^2$-*C*,*C*-$\kappa^2$-*N*,*N*–C(CF$_3$)=CCF$_3$(F$_4$-pia))$^{c,f}$ | 202.8; 196.8 | 31.5; 32.4 | [61,62] |
| (F)(CO)$_2$W($\eta^2$-*C*,*C*-$\kappa^2$-*N*,*N*–C(Ph)=CPh(F$_4$-pia))$^f$ | 230.1 | 25.7 | [63] |
| Cp*(Me$_3$SiCH$_2$)(NO)W($\eta^2$-C(Ph)=CH$_2$)$^b$ | 227.9 | 83.1 | [71,72] |
| Cp*(Cl)(NO)W($\eta^2$-C(Ph)=CH$_2$)$^e$ | 220.8 | 83.6 | [72] |
| Cp*(O$_3$SCF$_3$)(NO)W($\eta^2$-C(Ph)=CH$_2$)$^e$ | 258.0 | 77.6 | [72] |
| Cp*(Ph)(NO)W($\eta^2$-C(Ph)=CH$_2$)$^e$ | 225.1 | 78.6 | [77] |
| Cp*(MeC$_5$H$_4$)(NO)W($\eta^2$-C(Ph)=CH$_2$)$^{c,e}$ | 233.6; 234.6 | 79.6; 80.3 | [77] |
| Cp*(CH$_2$Ph)(NO)W($\eta^2$-C(Ph)=CH$_2$)$^e$ | 207.8 | 78.6 | [77] |
| Cp*(3,5-Me$_2$C$_6$H$_3$)(NO)W($\eta^2$-C(Ph)=CH$_2$)$^e$ | 233.5 | 80.9 | [77] |
| Cp*(3,4-Me$_2$C$_6$H$_3$)(NO)W($\eta^2$-C(Ph)=CH$_2$)$^e$ | 232.8 | 82.2 | [77] |
| Cp*(Me$_3$SiOSi(Me)$_2$CH$_2$)(NO)W($\eta^2$-C(Ph)=CH$_2$)$^e$ | 228.0 | 82.1 | [77] |
| [(dppe)$_2$ClRe($\eta^2$-C(CH$_2$Ph)=CH$_2$)][BF$_4$]$^f$ | 258.2 | n.r. | [48] |
| Cp(Br)(PPh$_3$)Re($\eta^2$-C(Ph)=CHPh)$^i$ | 258.3 | 15.5 | [30] |
| Cp(Br)(PMePh$_2$)Re($\eta^2$-C(Ph)=CHPh)$^f$ | 253.6 | 16.7 | [30] |
| [Cp(dppe)Re($\eta^2$-C(Ph)=CHPh)][BF$_4$]$^f$ | 260.9 | 25.2 | [30] |
| [Cp(dppe)Re($\eta^2$-C(Me)=CHPh)][BF$_4$]$^f$ | 258.1 | 33.3 | [30] |
| [Cp*(CO)$_2$Re($\eta^2$C(Me)=CHMe)][BF$_4$]$^{f,h}$ | 302.6 | 18.4 | [4] |
| [Cp*(CO)$_2$Re($\eta^2$C(Ph)=CHPh)][BF$_4$]$^f$ | 280.3 | 23.6 | [4] |
| [(NH$_3$)$_5$Os($\eta^2$-C(Me)=CH$_2$)][O$_3$SCF$_3$]$_3$$^j$ | 299.9 | 29.2 | [51] |
| [(NH$_3$)$_5$Os($\eta^2$-C(Me)=CHMe)[O$_3$SCF$_3$]$_3$$^k$ | 299.4 | 44.0 | [51] |
| ($\kappa^2$-OCOCH$_3$)(P(*i*-Pr)$_3$)$_2$(H)Os($\eta^2$-C(Ph)=CH$_2$)][BF$_4$]$^f$ | 263.2 | −0.7 | [115] |
| ($\kappa^2$-OCOCH$_3$)(P(*i*-Pr)$_3$)$_2$(H)Os($\eta^2$-C(C(OH)(Ph)$_2$)=CH$_2$)]-[BF$_4$]$^f$ | 279.8 | 9.6 | [115] |

[a] Chemical shifts in ppm; n.r. = not reported.

[b] $C_6D_6$.

[c] Two isomers exist.

[d] Toluene-$d_8$.

[e] $CDCl_3$.

[f] $CD_2Cl_2$.

[g] $CD_3NO_2$.

[h] Low temperature data.

[i] $CD_3CN$.

[j] $DO_3SCF_3$–$CD_2Cl_2$.

[k] $HO_3SCF_3$–$CD_3CN$.

both ligands are characterized by a filled donor orbital of σ-symmetry ($\sigma_d$); a filled π-donor orbital ($\pi_d$), and an empty π-acceptor orbital ($\pi_a^*$). Fig. 10 depicts the frontier orbitals of an $L_5M$ fragment, an $\eta^2$-vinyl ligand, and an alkyne ligand. Although the shapes and origins of the relevant metal-based orbitals in molecules of lower symmetry vary from this idealized case, frontier orbitals of like symmetry exist for various $L_3X_2M$ metal fragments [78,79], including the special cases of $XL_4M$ [22], $CpL_2M$ [24,80,81] and $Tp^xL_2M$ [82]. Only a qualitative treatment of the theoretical aspects of $\eta^2$-vinyl ligands is presented here; sophisticated treatments have been published [4,22].

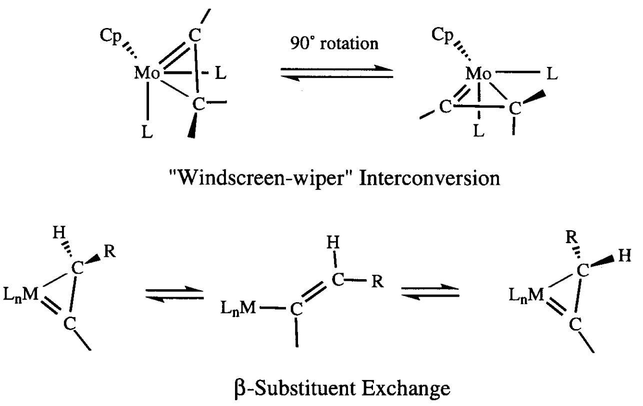


Fig. 8. Dynamic isomerization in $\eta^2$-vinyl complexes.

Fig. 11 shows the relative ordering in the frontier orbital region for metal–alkyne and metal–($\eta^2$-vinyl) combinations [21]. One feature to note here is the higher energy $\pi_d$ orbital of $[CH{=}CH_2]^-$ which renders the $\eta^2$-vinyl ligand a better π donor than HC≡CH. Although the energies of the $\pi_a^*$ orbitals of the two ligands are comparable, the acetylene ligand is a stronger π-acid than the $\eta^2$-vinyl owing to better overlap between $d_{xy}$ and $\pi_a^*$. The LUMO in each case is the antibonding combination of $d_{yz}$ and $\pi_d$ with roughly equal contributions from metal and ligand orbitals [4,21,22,24,30]. This orbital accounts for the susceptibility to nucleophilic addition seen for both alkynes and $\eta^2$-vinyl ligands. The bonding mate of this LUMO orbital of the metal–($\eta^2$-vinyl) interaction accounts for the localized double bond between the metal and $C_\alpha$.

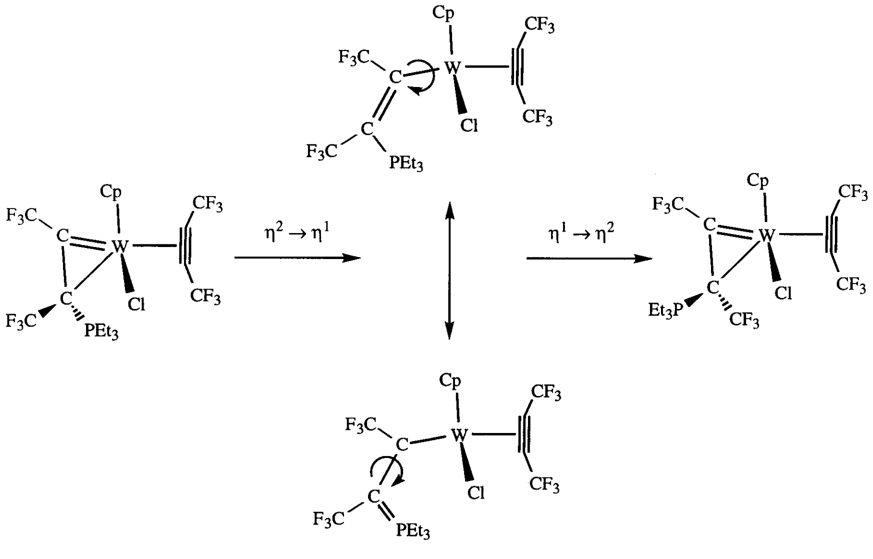


Fig. 9. β-substituent exchange in $Cp(Cl)(CF_3C{\equiv}CCF_3)W(\eta^2\text{-}C(CF_3){=}C(CF_3)PEt_3)$.

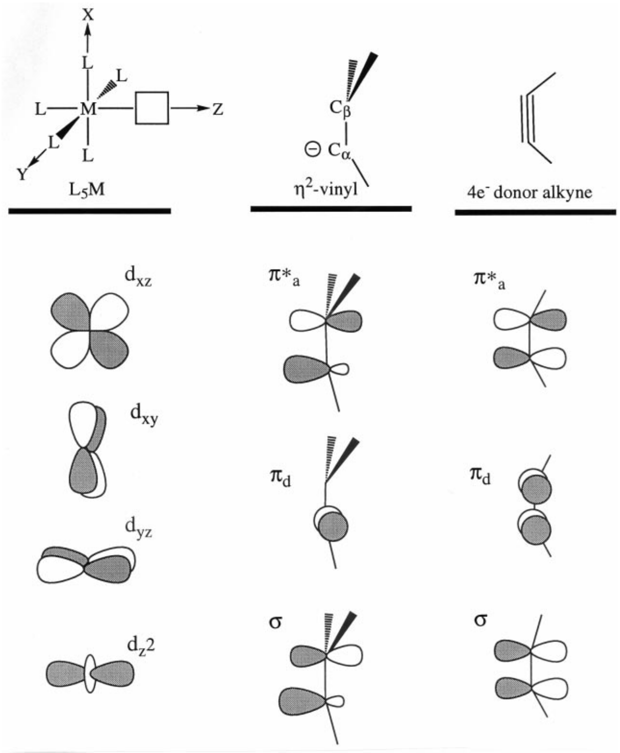


Fig. 10. Frontier orbitals for $L_5M$, $\eta^2$-vinyl, and $4e^-$ donor alkyne fragments.

Prediction of $\eta^2$-vinyl ligand reactivity with electrophiles is more difficult; both protonation at metal and at $C_\beta$ have been seen (Section 5). In the idealized case, the HOMO is essentially $d_{xy}$ in nature and frontier orbital controlled electrophile addition would be expected at the metal. However, the donor properties of real ligands will affect the energy of this orbital and it is important to take into account the ancillary ligand set of the complex in question. In relatively electron rich $\eta^2$-vinyl complexes, $CpL_2Mo(\eta^2\text{-}C(Ph){=}CHPh)^{n\pm}$ (M = Mo, L = $P(OMe)_3$, $n = 0$; M = Mo, $L_2$ = PBP, $n = -1$; M = Re, $L_2$ = $(Br)PPh_3$; $n = 0$), net protonation at $C_\alpha$ yields free stilbene [26,27,30]. Green has suggested that protonation occurs first at the metal and is followed by migratory insertion of vinyl group to give stilbene. Calculation of the effective charge distributions in $Cp(P(OH)_3)_2Mo(CH{=}CH_2)$ [24] and $CpBr(PH)_3Re(\eta^2\text{-}CH{=}CH_2)$ [30] reveal effective charges on the metal centers of ca. $-0.5$ which also supports charge controlled attack at the metal.

Protonation of $Tp'(CO)_2W(\eta^2\text{-}CR{=}CHR)$ complexes occurs at $C_\beta$ to produce β-agostic carbene complexes [28,73,83]. EHMO calculations on a simple model, $[H_3(CO)_2W(\eta^2\text{-}CH{=}CH_2)]^{2-}$, suggest that protonation at $C_\beta$ is favored both on a frontier orbital basis and from a charge controlled viewpoint [73]. The HOMO of $H_3(CO)_2W(\eta^2\text{-}CH{=}CH_2)$ is primarily the bonding combination between $d_{xz}$ and the

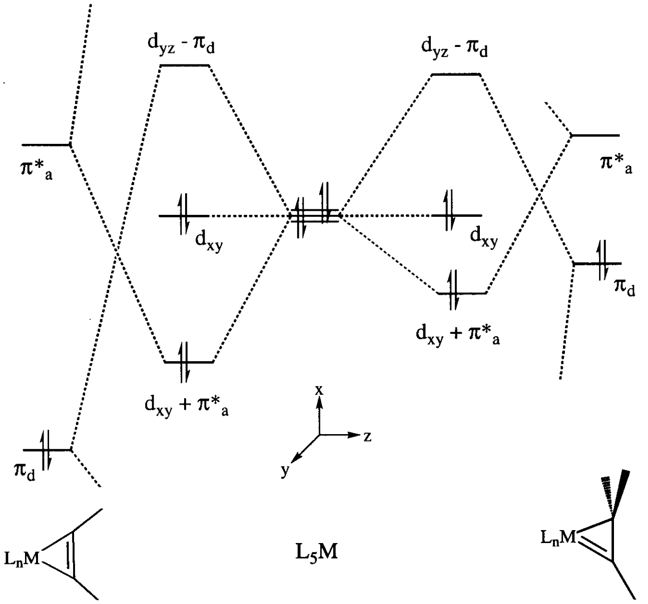


Fig. 11. Frontier orbital region of $\eta^2$-vinyl and 4e$^-$ donor alkyne ligands.

appropriate carbonyl ligand π* orbitals and protonation at metal is a possibility. However, second order mixing of $d_{xy}$ and $d_{yz}$ via the common agency of the strong π-acid CO ligands [84] allows a 10% contribution from $\pi^*_a$ of the $\eta^2$-vinyl ligand to become mixed into the HOMO of the complex. The incoming electrophile may prefer the highly directed and accessible orbital component on $C_\beta$ to the diffuse and sterically hindered (via Tp′) metal component. This second order mixing of dπ orbitals is not available to non-carbonyl containing complexes; spatial plots of $[(PH_3)_4ClRe(\eta^2\text{-}CH{=}CH_2)]^+$ obtained via B3LYP calculations show no $C_\beta$ component in the HOMO [22]. The calculated net atomic charges for $[H_3(CO)_2W(\eta^2\text{-}CH{=}CH_2)$ also support direct electrophilic attack at $C_\beta$ ( − 0.45 at $C_\beta$ versus W = + 0.87). A similar charge distribution via NBO analysis of the related model complex, $[Cp(CO)_2Re(\eta^2\text{-}C(Me){=}CHMe)]^+$, has been reported [4].

The rotational properties and orientational preferences of $\eta^2$-vinyl ligands have also been examined via calculational methods. Barriers to complete 180° rotation of 10–20 kcal mol$^{-1}$ have been reported with lower energies being calculated for species either having auxiliary π-acids or for which the complex geometry was allowed to relax during ligand rotation [21,22,24,73]. Choi and Lin have ascribed the preference for $\eta^2$-vinyl ligands in Cp-based complexes to align along a ligand axis to increased backbonding interactions between a filled metal dπ orbital and $\pi^*_a$ of the $\eta^2$-vinyl ligand and due to increased p character in the dπ manifold induced by ‘bending-back’ of the ancillary ligands [22]. A similar dependence on the amount of dπ backbonding has been noted in $[H_3(CO)_2W(\eta^2\text{-}CH{=}CH_2)]^{2-}$, although here the interactions between the metal and the carbonyl ligands control the relevant orbital occupancies [73].

## 5. Chemistry of $\eta^2$-vinyl complexes

### 5.1. Isomerization to form $\eta^3$-allyl complexes

Examination of common substituents located at the β′ site of $\eta^2$-vinyl ligands reveals an abundance of phenyl groups. Relatively few simple alkyl substituents are found in deference to numerous *tert*-butyl, trimethylsilyl, and trifluoromethyl groups [6,22]. In general, isomerization of $L_nM(\eta^2\text{-}C(CH_2R')=CR_2)$ complexes into $\eta^3$-allyl isomers, $L_nM(\eta^3\text{-}CR_2CHCHR')$, is facile. Addition of hydride to $CpL_2Mo(\eta^2\text{-}MeC{\equiv}CR)^+$ (R = Me, Et, $Pr^i$) [85] complexes or addition of $LiCuMe_2$ to $CpL_2Mo(\eta^2\text{-}RC{\equiv}CH)$ (R = $Pr^i$, $Bu^t$) [24] yields *anti*-$\eta^3$-allyl complexes, $CpL_2Mo(\eta^3\text{-}CH_2CHCHR)$, without detection of vinyl intermediates. The isomerization of $CpL_2Mo(\eta^2\text{-}C(Me)=CPh_2)$ into $CpL_2Mo(\eta^3\text{-}CH_2CHCPh_2)$ is much slower and occurs over a period of days [24].

Green has proposed a mechanism for the $\eta^2$-vinyl → $\eta^3$-allyl conversion of $L_nM(\eta^2\text{-}C(CH_3){=}CHR)$ complexes (Fig. 12) [5,85,86]. An $\eta^2 \rightarrow \eta^1$ change in coordination mode for the vinyl ligand is followed by β-hydrogen abstraction to form an allene–hydride species. Rotation of the allene ligand followed by hydrogen migration to the central allene carbon forms an $\eta^1$-allyl species which then closes to the kinetic *anti*-$\eta^3$-allyl product. Deuterium labeling studies of $L_nM(\eta^2\text{-}C(Me){=}CHR)$ ($L_nM{=}Cp(P(OMe)_3)_2Mo$, $Tp'(CO)_2W$) complexes are consistent with this mechanism [85,87].

Isomerization to $\eta^3$-allyl complexes for $Tp'(CO)_2W(\eta^2\text{-}C(CH_2R){=}CH_2)$ complexes is slower than for related $CpL_2Mo(\eta^2\text{-}C(CH_2R){=}CHR')$ species. A number of $Tp'(CO)_2W(\eta^2\text{-}C(CH_2R){=}CH_2)$ (R = H, Me, $Pr^n$, Ph, $CH_2Ph$) complexes having β′-hydrogens have been isolated [29,33]. It may be that the reluctance of Tp′ complexes to form the required seven-coordinate allene hydride intermediates compared to analogous Cp complexes plays a role [88]. Some of the difference in

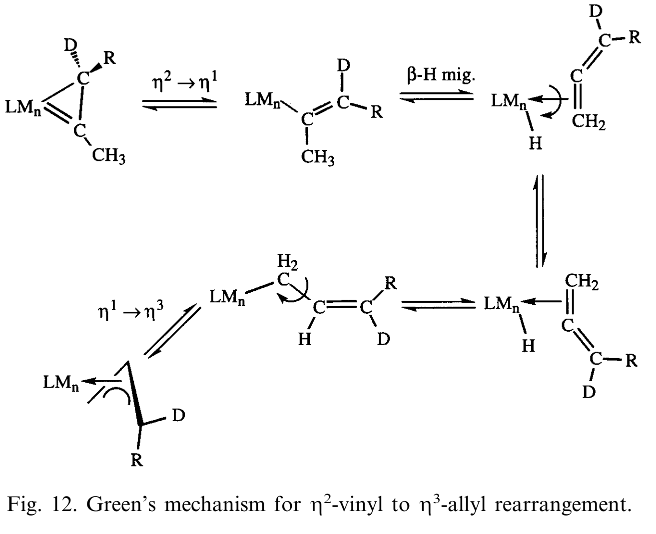


Fig. 12. Green's mechanism for $\eta^2$-vinyl to $\eta^3$-allyl rearrangement.

isomerization rates may also be credited to the generic increase in activation barriers for third row transition metals relative to those of the second row: $Tp'(CO)_2Mo(\eta^2\text{-}C(Me){=}CH_2)$ rearranges to the $\eta^3$-allyl isomer overnight [70], whereas the tungsten analog requires more than a week [68]. A 25 kcal mol$^{-1}$ activation barrier has been measured for the isomerization of $Tp'(CO)_2W(\eta^2\text{-}C(CH_2Pr_n){=}CH_2)$ into $Tp'(CO)_2W(\textit{anti}\text{-}\eta^3\text{-}CH_2CHCHPr_n)$ [33].

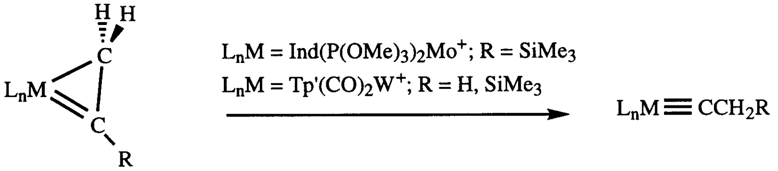
Additional insight into the $\eta^2$-vinyl → $\eta^3$-allyl process is available by further consideration of the $Tp'(CO)_2W$ system. The primary determinant of isomerization rate for $Tp'(CO)_2W(\eta^2\text{-}C(CH_2R){=}CHR')$ complexes appears to be substitution at the β-position. Complexes having a substituent on the β-carbon, $Tp'(CO)_2W(\eta^2\text{-}C(CH_2R){=}CHR')$ isomerize to $\eta^3$-allyl complexes within a few hours at r.t., while β-methylene analogues, $Tp'(CO)_2W(\eta^2\text{-}C(CH_2R){=}CH_2)$ ($R = H$, Me, $Pr^n$), require more than a week [28,67,68]. In general, the β-substituted $\eta^2$-vinyl complexes display $\nu_{CO}$ bands 15 cm$^{-1}$ lower on average than the less-substituted $Tp'(CO)_2W(\eta^2\text{-}C(R){=}CH_2)$ complexes. A similar drop in CO stretching energies is seen when going from $Tp'(CO)_2W(\eta^2\text{-}CPh{=}CHPh)$ ($\nu_{CO}$ (KBr) = 1949, 1857 cm$^{-1}$; $\nu_{CO}$ (avg.) = 1903 cm$^{-1}$) to $Tp'(CO)_2W(\eta^2\text{-}CPh{=}CHMe)$ ($\nu_{CO}$ (KBr) = 1938, 1838 cm$^{-1}$; $\nu_{CO}$ (avg.) = 1887 cm$^{-1}$) [28]. The lower energy $\nu_{CO}$ signatures of the β-substituted $\eta^2$-vinyl species are consistent with both increased electron density in the vinyl ligand owing to the additional alkyl substituent, and also a weaker backbonding interaction between the π-acidic $\eta^2$-vinyl ligand and the $Tp'(CO)_2W$ metal center owing to unfavorable steric interactions between the β-substituent and the prominent $CH_3$ groups of the Tp′ pyrazole rings. A dependence on the strength of the backbonding interaction in determining $\eta^2$-vinyl stability has been noted in theoretical studies [21,22].

A kinetic preference for *anti*-substitution in the isomerization of $[Cp^*(CO)_2Re(\eta^2\text{-}C(Me){=}CHMe)]^+$ to $[Cp^*(CO)_2Re(\eta^3\text{-}CH_2CHCHMe)]^+$ has also been seen [4]. An activation barrier of 20.1 kcal mol$^{-1}$ has been measured for this isomerization. Interestingly, a 1:1 mixture of *anti*:*syn* products of $[Cp^*(CO)_2Re(\eta^2\text{-}Me_2CCHCHPr^i)]^+$ was obtained upon protonation of $Cp^*(CO)_2Re(\eta^2\text{-}Pr^iC{\equiv}CPr^i)$ [4,45]. Monitoring of the reaction via low temperature $^1$H-NMR allowed the detection of an $\eta^2$-vinyl intermediate, $[Cp^*(CO)_2Re(\eta^2\text{-}C(Pr^i){=}CHPr^i)]^+$ [4]. Casey has suggested that the $\eta^2$-vinyl → $\eta^3$-allyl transformation may be accomplished via simple 1,2 hydride migration from the β′ carbon to $C_\alpha$ [4,46]. However, allene hydride intermediates have been detected in related systems [50,89].

### 5.2. Isomerization to form carbyne complexes

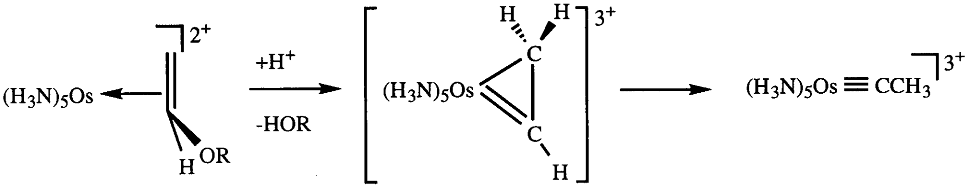
Isomerization of $\eta^2$-vinyl complexes to carbyne complexes represents a second important class of $\eta^2$-vinyl ligand transformations. Heating the $\eta^1$-vinyl complex, $CpL_3Mo(\eta^1\text{-}CH{=}CHBu^t)$ ($L = P(OMe)_3$) induces conversion into a carbyne complex, $CpL_2Mo{\equiv}CCH_2Bu^t$ [5,86]. The transformation is inhibited by excess phosphine indicating that either a vacant coordination site is necessary, or that an $\eta^2$-vinyl species could be involved. Attempts to probe the two mechanistic possibilities led to the discovery of a vinylidene intermediate, which underwent reversible protonation at $C_\beta$ to yield the carbyne product indicating that initial hydride migration to metal to form a hydrido vinylidene was feasible [90,91].

Evidence for intermediate $\eta^2$-vinyl complexes has also been gathered. Hydride addition to $[IndL_2Mo(\eta^2\text{-}Me_3SiC{\equiv}CH)]^+$ forms an $\eta^2$-vinyl complex, $IndL_2Mo(\eta^2\text{-}C(SiMe_3){=}CH_2)$, which was structurally characterized [25]. Heating the trimethylsilylvinyl complex results in apparent 1,2 $SiMe_3$ migration to form a carbyne product, $IndL_2Mo \equiv CCH_2SiMe_3$ (Eq. (22)). Room temperature addition of $NaBH_4$ to $[CpL_2Mo(\eta^2\text{-}Pr^iC{\equiv}CH)]^+$ with excess $P(OMe)_3$ present allows direct access to the carbyne product, $CpL_2Mo \equiv CCH_2Pr^i$ [5]. Reaction of $[Tp'(CO)_2W(\eta^2\text{-}HC{\equiv}CH)]^+$ with $LiHBEt_3$ at −78°C in THF forms a spectroscopically observable $\eta^2$-vinyl intermediate before forming the ethylidyne complex, $Tp'(CO)_2W{\equiv}CMe$ [68]. Trimethylsilyl migration for $Tp'(CO)_2W(\eta^2\text{-}C(SiMe_3){=}CH_2)$ to form $Tp'(CO)_2W{\equiv}CCH_2SiMe_3$ has also been documented [68]. Treatment of $CpL(CO)Mo(\eta^2\text{-}C(Ph){=}CHPh)$ with PhIO in $CH_2Cl_2$ results in a 1,2-Ph shift to form $CpL(CO)Mo{\equiv}CCHPh_2$, presumably via a radical cation intermediate [76].



(22)

Harman and Chen have reported that protonation of osmium vinylether complexes in the absence of nucleophiles results in the isolation of $[(NH_3)_5Os{\equiv}CMe]^{3+}$, presumably via formation of the parent $\eta^2$-vinyl complex, $[(NH_3)_5Os(\eta^2\text{-}C(H){=}CH_2]^{3+}$, followed by a 1,2 H shift (Eq. (23)) [51]. Notably, dissolution of $[(NH_3)_5Os(\eta^2\text{-}CH_2{=}CH(OEt)]^{2+}$ in neat $DO_3SCF_3$ results in a carbyne product lacking deuterium incorporation indicating that the net 1,2-H shift is intramolecular for the osmium system.



(23)

### 5.3. Isomerization to form $\eta^2$-vinyl isomers

Rotation of an $\eta^2$-vinyl ligand in the coordination sphere and β-substituent exchange are isomerization reactions which have been discussed earlier in connection with the NMR behavior of $\eta^2$-vinyl ligands (Section 3). An additional pathway for interconversion of distinct $\eta^2$-vinyl isomers is net 1,2 H migration from $C_\beta$ to $C_\alpha$. This process was first inferred from the observation that some $\eta^2$-vinyl ligands which lack β′-hydrogens could also rearrange into $\eta^2$-allyl isomers. For example, reaction of $CpL_2Mo(Bu^tC{\equiv}CH)^+$ with $LiCuMe_2$ produces only the allyl isomer, $CpL_2Mo(\eta^3\text{-}CHBu^tCHCH_2)$, presumably via initial $CpL_2Mo(\eta^2\text{-}C(Bu^t){=}CHMe)$ formation [24]. The related $\eta^2$-vinyl complex, $Tp'(CO)_2W(\eta^2\text{-}C(Ph){=}CHMe)$, is isolable and isomerization to the $\eta^3$-allyl isomer, $Tp'(CO)_2W(\eta^2\text{-}CHPhCHCH_2)$, occurs over a period of months [28]. It is assumed in each case that a net 1,2-H migration from $C_\beta$ to $C_\alpha$ occurs to form an $\eta^2$-vinyl isomer with abstractable $\beta'$-hydrogens which then rearranges into the $\eta^3$-allyl isomer.

An elegant experiment by Casey et al. has recently shed light on this intriguing process. Low temperature addition ($-78°C$) of $CF_3CO_2D$ to $Cp^*(CO)_2Re(\eta^2\text{-}MeHC{=}C{=}CH_2)$ forms $[Cp^*(CO)_2Re(\eta^2\text{-}C(CH_2D){=}CHMe)]$, which is selectively deuterated on the $\beta'$-carbon [4]. Warming of the solution to $-32°C$ results in incorporation of deuterium into both methyl groups with an activation barrier of 18.5 kcal $mol^{-1}$. An intermediate hydride alkyne species was ruled out by a lack of deuterium incorporation into the *syn* position of the substituted allyl terminus in the final product, $Cp^*(CO)_2Re(\eta^3\text{-}CH_2^DCH^DCH(Me^D))$ ($^D$ indicates partially labeled site). These results have been interpreted in terms of degenerate $1,2\text{-}H(C_\beta \rightarrow C_\alpha)$ migration between the $\eta^2$-vinyl carbons occurring simultaneously with reversible deprotonation of the $\beta'$-site of the two isomeric $\eta^2$-vinyl species which incorporates deuterium into the methyl groups (Fig. 13). Protonation of $Cp^*(CO)_2Re(\eta^2\text{-}PhC{\equiv}CTol)$ allowed the NMR observation of non-degenerate $1,2\text{-}H(C_\beta \rightarrow C_\alpha)$ migration between $Cp^*(CO)_2Re(\eta^2\text{-}C(Ph){=}CHTol)$ and $Cp^*(CO)_2Re(\eta^2\text{-}C(Tol){=}CHPh)$ [4].

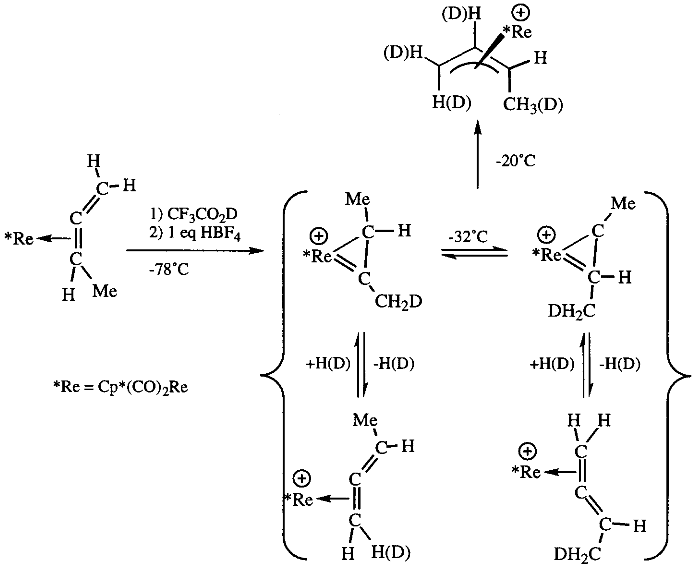
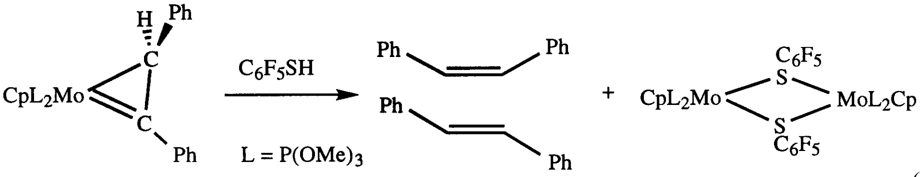


Fig. 13. 1,2 H ($C_\beta \rightarrow C_\alpha$) migration in $[Cp^*(CO)_2Re(\eta^2\text{-}C(CH_2D){=}CH_2)]^+$.

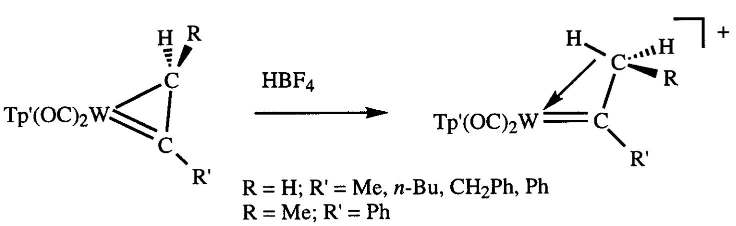
### 5.4. Reactions with electrophiles

The reactivity of $\eta^2$-vinyl complexes with electrophiles is presently limited to reactions with protic reagents. Reaction of $CpL_2Mo(\eta^2\text{-}C(Ph){=}CHPh)$ with the weak acid $C_6F_5SH$ results in net protonation at the vinyl ligand to produce a mixture of *cis*- and *trans*-stilbene along with a dimeric metal product (Eq. (24)) [26]. In similar fashion, protonation of $[K][Cp(PBP)Mo(\eta^2\text{-}C(Ph){=}CHPh)]$ liberates *trans*-stilbene [27] and addition of $HBF_4$ to $Cp(PPh_3)BrRe(\eta^2\text{-}C(Ph){=}CHPh)$ also results in stilbene loss [30]. These results are compatible with either direct protonation at $C_\alpha$ or protonation at metal followed by migratory insertion to yield the alkene product. EHMO calculations on Mo [27] and Re [30] models indicate a relatively large negative charge buildup at the metal consistent with kinetic protonation at metal. Casey's detection of hydrido alkyne complexes in the protonation of related $Cp^*(CO)_2Re(\eta^2\text{-}RC{\equiv}CR)$ complexes [4,46] supports initial protonation at metal given the electronic similarities between alkyne and $\eta^2$-vinyl ligands.



(24)

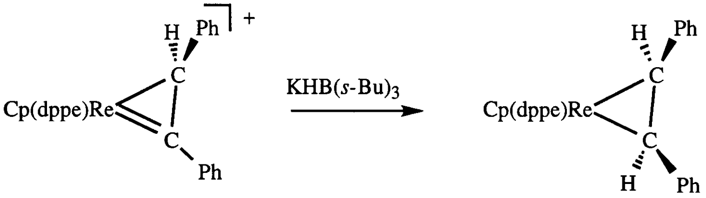
In contrast, $HBF_4$ addition to $Tp'(CO)_2W(\eta^2\text{-}C(R){=}CHR')$ ($R = Me$, Bu, $CH_2Ph$, Ph, $R' = H$; $R = Ph$, $R' = Me$) results in the delivery of a proton to $C_\beta$ forming β-agostic carbene complexes, $[Tp'(CO)_2W{=}C(R)(\mu\text{-}CH_2R')]^+$ (Eq. (25)) [33,37,73,83]. Chemical shifts of ca. $-20$ ppm for the carbons of the bridging C–H group characterize the agostic interaction. For $[Tp'(CO)_2W({=}C(Ph)(\mu\text{-}CH_2Me)]^+$, the β-agostic interaction for the ethyl substituent was unambiguously established by low-temperature $^1$H-NMR which revealed diastereotopic methylene protons [37]. Addition of $NEt_3$ readily regenerates the parent $\eta^2$-vinyl complexes. This reactivity is reminiscent of electrophile addition to the β-carbon of $\eta^1$-vinyl complexes to yield carbene complexes [92–97]. Note that conversion of the $\eta^2$-vinyl into a carbene ligand reduces the metal valence electron count by two, while protonation of an $\eta^1$-vinyl ligand leaves the count unchanged. Direct proton addition to the β-carbon is compatible with steric expectations for the hindered system and with EHMO calculations on $[H_3(CO)_2W(\eta^2\text{-}CH{=}CH_2]^{2-}$ [73].



(25)

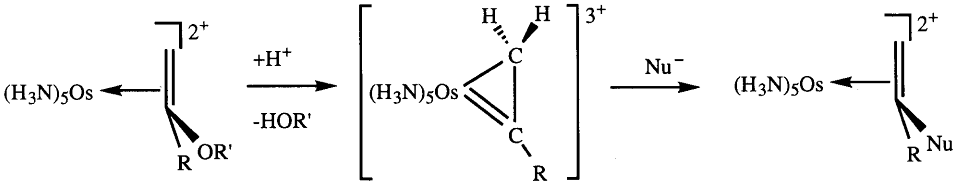
### 5.5. Reactions with nucleophiles

Recent reports have explored the reactivity of $\eta^2$-vinyl ligands with nucleophiles. Addition of hydride to $[Cp(dppe)Re(\eta^2\text{-}C(Ph){=}CHPh)]^+$ yields a *cis*-stilbene complex, $Cp(dppe)Re(\eta^2\text{-}PhHC{=}CHPh)$, which was structurally characterized (Eq. (26)) [30]. This provides an interesting contrast to previous reports of stilbene formation upon protonation of electron-rich $CpL_2Mo(\eta^2\text{-}C(Ph){=}CHPh)$ complexes [26,27,30]. It may be that the positive charge on the rhenium complex facilitates nucleophile addition. Recall that the diphenylvinyl complex is itself formed from hydride addition to a diphenylacetylene complex. The net result of the sequential $H^-/H^-$ addition is reduction of an alkyne via double hydride addition across the carbon–carbon triple bond of the original alkyne.



(26)

As noted in Section 2, protonation of osmium vinylether complexes, $[(NH_3)_5Os(\eta^2\text{-}CH_2{=}CR(OR'))]^{2+}$, (R = H, Me) results in loss of HOR′ to yield reactive $\eta^2$-vinyl intermediates [51]. Protonation in the presence of a nucleophile yields nucleophilic substitution products, $[(NH_3)_5Os(\eta^2\text{-}CH_2{=}CR(Nu)]^{2+}$ (Eq. (27)). This system adds a variety of nucleophiles such as phosphine, sulfide, amine, alkoxy, and hydroxide. These results have been interpreted in terms of initial $\eta^2$-vinyl formation followed by nucleophilic attack at $C_\alpha$ of the $\eta^2$-vinyl intermediate. In cases where the vinyl ligand bears a stabilizing alkyl group, $[(NH_3)_5Os(\eta^2\text{-}C(R){=}CHR']^{3+}$ (R = Me; R′ = H, Me), the $\eta^2$-vinyl complexes have been spectroscopically observed. Electrophile addition to $\eta^2$-furan complexes of osmium is an analogous reaction that involves ring opening of the furan olefin analogue, possibly through an $\eta^2$-vinyl intermediate which then adds a nucleophile [98]. Nucleophilic substitution of osmium coordinated $\eta^2$-thiophenium complexes are proposed to follow a similar ring opening mechanism involving $\eta^2$-vinyl intermediates [99].



(27)

Casey and co-workers have noted HX (X = Cl, $O_2CCF_3$) addition across the triple bond of rhenium bound 2-butyne in Cp- and $Cp^*(CO)_2Re(\eta^2\text{-}MeC{\equiv}CMe)$ to produce alkene intermediates, $Cp^x(CO)_2Re(\eta^2\text{-MeHC=CMeX})$ [46]. Based on complimentary studies with $HBF_4$ as the acid source [4], these results have been interpreted in terms of initial $\eta^2$-vinyl formation followed by nucleophilic addition of the conjugate base to $C_\alpha$ of the $\eta^2$-vinyl intermediate. The stereochemistry of $O_2CCF_3^-$ addition is reversed for Cp versus Cp* as the capping ligand; for Cp the *E* isomer of the alkene ligand is kinetically preferred, while the *Z* isomer is favored for Cp*. Regardless of kinetic control, interconversion of the *E* and *Z* alkene isomers occurs to produce thermodynamic ratios consistent with the steric profiles of the capping ligand. Casey et al. have made the interesting suggestion that interconversion of the alkene isomers occurs via reversible addition of $O_2CCF_3^-$ to opposite faces of an $\eta^2$-vinyl intermediate. Addition of 2,6-dimethylpyridine to solutions of $Cp^x(CO)_2Re(\eta^2\text{-MeHC=CMeX})$ facilitates net removal of HX to yield allene complexes, $Cp^*(CO)_2Re(\eta^2\text{-MeHC=C=CH}_2)$.

Treatment of $Tp'(CO)_2W(\eta^2\text{-C(R)=CH}_2)$ (R = Me, Bu$^n$) with $PMe_3$ results in $Tp'(CO)_2W(\eta^2\text{-CH}_2\text{=CRPMe}_3)$ complexes via addition to $C_\alpha$ (Fig. 14) [33]. The phosphine addition is reversible and $PMe_3$ readily dissociates at r.t. in solution to reform the $\eta^2$-vinyl complexes. Legzdins et al. have reported $PMe_3$ addition to $Cp^*(NO)(Me_3SiCH_2)W(\eta^2\text{-C(Ph)=CH}_2)$ to produce $Cp^*(NO)(Me_3SiCH_2)W(\eta^2\text{-CH}_2\text{=C(Ph)PMe}_3)$, which has been structurally characterized [72]. Protonation of Alt's ylide carbene complexes, $Cp^x(CO)_2Mn(CHCHPEt_3)$ results in isoelectronic manganese products, $[Cp^x(CO)_2Mn(CH_2\text{=CHPEt}_3)]^+$ [100]. These results are reminiscent of phosphine addition to metallafuran complexes, $Cp^x(CO)_2M(\text{=CHCHC(O)R})$ ($Cp^x$ = Cp, Cp*, $C_5H_4Me$; M = Mo, W), to yield $Cp^x(CO)_2M(\eta^2\text{-PMe}_3\text{HC=CHC(O)R})]$ complexes via phosphine attack at $C_\alpha$ of the

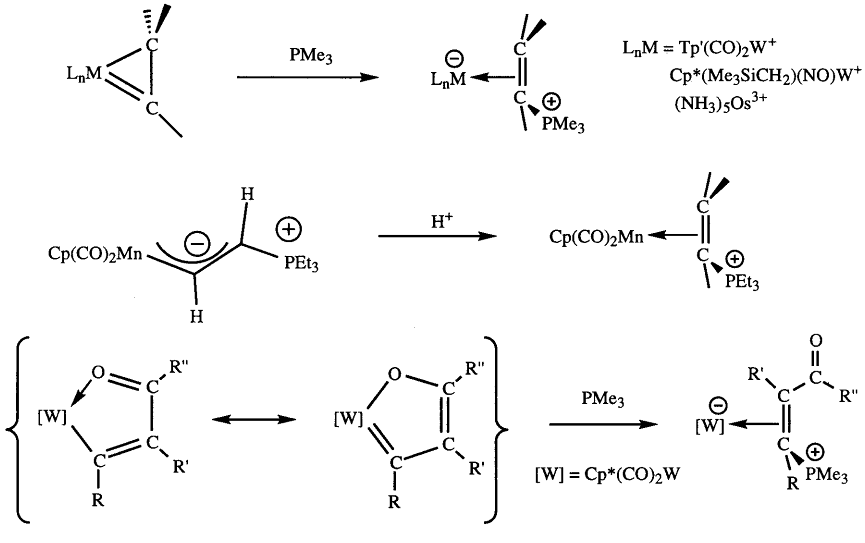


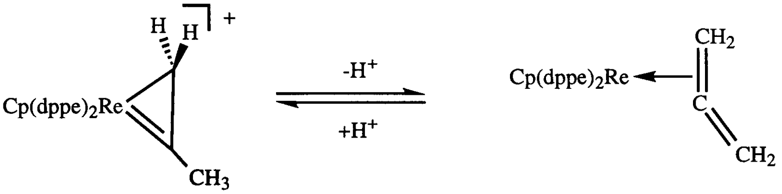
Fig. 14. Reaction of phosphine nucleophiles with $\eta^2$-vinyl and related complexes.

metallafuran ring and dechelation of the ketone oxygen [101]. The common feature linking the $\eta^2$-vinyl complexes with the metallafuran complexes is the presence of the carbenoid linkage between the electron poor metal center and $C_\alpha$ which activates the $\alpha$ carbon towards nucleophilic attack.

## *5.6. Reactivity at the β′ site*

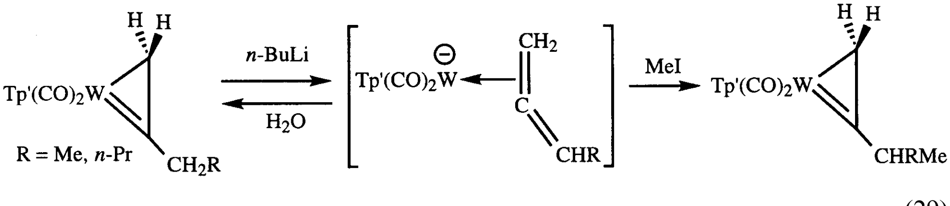
The protonation of allene ligands to yield $\eta^2$-vinyl ligands [48–50] suggests that these two ligands may be linked in the same fashion as $4e^-$ donor alkynes and $\eta^2$-allenyl ligands. Deprotonation of propargyl hydrogens from $4e^-$ donor alkyne ligands to yield reactive $\eta^2$-allenyl intermediates which undergo alkylation to form new alkyne ligands is well established [102–104]. The deprotonation of $[CpL_2Mo(PhC{\equiv}CCH_2Ph)]^+$ with KH to yield a stable $\eta^2$-allenyl complex, $CpL_2Mo(\eta^2\text{-}PhC{=}C{=}CHPh)$ has been reported [105]. Similar chemistry has also been reported for $\eta^2$-acyl ligands which are also isolobal with $\eta^2$-vinyl ligands [82,106,107].

Green et al. have reported reversible deprotonation of $[Cp(dppe)Re(\eta^2\text{-}C(CH_3){=}CHPh)][BF_4]$ to yield an allene complex, $Cp(dppe)Re(\eta^2\text{-}CH_2{=}C{=}CHPh)$ (Eq. (28)) [30]. The isolation of allene complexes via 2,6-dimethylpyridine addition to $Cp^x(CO)_2Re(\eta^2\text{-}MeHC{=}CMeX)$ [46] also represents deprotonation of a β′-hydrogen of an $\eta^2$-vinyl ligand.



(28)

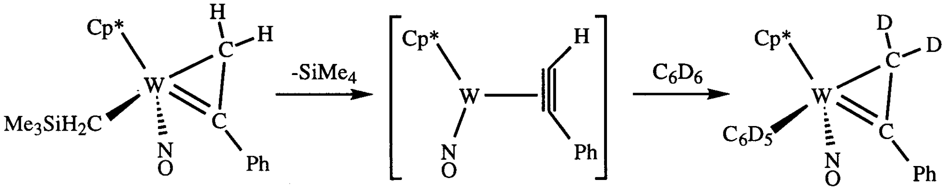
Low temperature addition of *n*-BuLi to $Tp'(CO)_2W(C(CH_2R){=}CH_2)$ ($R = H, Pr^n$) complexes results in deprotonation to yield anionic $\eta^2$-allene complexes, $[Li][Tp'(CO)_2W(\eta^2\text{-}CH_2{=}C{=}CHR)]$ which have been observed via IR spectroscopy [29]. Quenching of the allene complexes with MeI results in new derivative $\eta^2$-vinyl complexes, $Tp'(CO)_2W(\eta^2\text{-}C(CHRMe){=}CH_2)$ (Eq. (29)). For $R = Pr^n$, reaction of the allene intermediate with benzaldehyde followed by acidification produced a racemic mixture of $\eta^2$-vinyl diastereomers incorporating an alcohol substituent, $Tp'(CO)_2W(\eta^2\text{-}C(CHPr^n(CH(OH)Ph)){=}CH_2)$.



(29)

### 5.7. Miscellaneous reactivity

The novel $\eta^2$-vinyl complex, Cp*(NO)($Me_3SiCH_2$)W($\eta^2$-C(Ph)=$CH_2$), synthesized by Legzdins et al. shows unusual reactivity. Upon heating to 45°C, this complex readily undergoes β-hydrogen elimination from the vinyl group and expels $SiMe_4$ to produce a coordinatively unsaturated phenylacetylene complex, Cp*(NO)W($\eta^2$-PhC≡CH) [108]. The phenylacetylene complex is reactive and undergoes both C–H activation of alkanes and reductive coupling with small unsaturated molecules to produce metallacyclic products under mild conditions [71,77]. Thermolysis of Cp*(NO)($Me_3SiCH_2$)W($\eta^2$-C(Ph)=$CH_2$) in aromatic solvents yields new $\eta^2$-vinyl complexes, Cp(CO)(Ar)W($\eta^2$-C(Ph)=$CH_2$) (Eq. (30)) [77]. Mechanistic studies with labeled aromatics result in incorporation of deuterium into both positions on $C_\beta$ suggesting facile equilibria between free arene and σ and π bound arenes. This reaction is only partially selective for aromatic hydrogens; with toluene or xylenes (*o*, *m*, *p*), C–H activation of the alkyl groups occurs to produce benzyl groups in varying amounts depending on the substrate.



(30)

Ligand coupling reactions involving $\eta^2$-vinyl complexes have also been reported and examples prior to 1988 have been discussed in earlier reviews [5,6]. We limit our treatment to a few recent examples. Davidson et al. have reported that reaction of Cp($CF_3C{\equiv}CCF_3$)M($\eta^3$-C($CF_3$)=C($CF_3$)SR) (M = Mo, W; R = Me, Et, $Pr^i$) complexes with $MeO_2CC{\equiv}CCO_2Me$ (dmad) leads to alkyne oligomerization to yield metal diene and triene complexes [75]. The reaction pathways in these coupling reactions are highly complex, but in each case the initial step is apparent insertion of dmad into the carbon–sulfur bond to yield $\eta^2$-vinyl intermediates, Cp($CF_3C{\equiv}CCF_3$)M($\eta^3$-C($CF_3$)=C($CF_3$)CR′=CR′SR) (R′ = $CO_2Me$), which then isomerize to diene products or couple with the perfluoro butyne ligand to ultimately produce triene products. An earlier report of the reaction of the bis-alkyne thiolate complex, Cp($CF_3C{\equiv}CCF_3$)$_2$Mo–$SC_6F_5$, with alkynes to produce an $\eta^4$-butadienyl complex [109] suggested that the $\eta^2$-vinyl complexes first underwent migration of the thiolate substituent to the metal to form bis-alkyne thiolate complexes prior to reaction with dmad.

Green et al. have reported ligand coupling for $L_3X$(MeC≡CMe)Mo($\eta^2$-C(Me)=CHMe)$^+$ ($L_3$ = Cp, Ind; X = Cl, Br) upon $P(OMe)_3$ or $PMe_3$ addition to yield cationic $\eta^4$-butadienyl complexes [44]. Interestingly, the coupling reaction also occurs in the presence of trace water with $H_2O$ acting as the incoming nucleophile [110]. Reduction of the neutral bis-halide derivative, $CpBr_2$(MeC≡CMe)Mo($\eta^2$-C(Me)=CHMe), in the presence of carbon monoxide results in ligand coupling and halogen abstraction to produce a neutral $\eta^4$-butadiene complex, CpBr(CO)Mo($\eta^4$-MeHC=C(Me)C(Me)=CHMe) [44]. $\eta^2$-Vinyl intermediates have also been postulated in the coupling of alkyne ligands to form $\eta^3$-1,4-pentadienyl and $\eta^3$-cyclopropenyl complexes following treatment of $[Cp(P(OMe)_3)_2Mo(\eta^2\text{-}PhC\equiv CPh)]^+$ with allyl– and vinyl–Grignard reagents, respectively [27].

Schrock et al. have proposed $\eta^2$-vinyl intermediates in the coupling of alkylidyne ligands to form an alkyne ligand in osmium(VI) bis-alkylidyne complexes [111]. An analogous process here would be the coupling of alkylidyne and carbonyl ligands to yield $\eta^2$-ketenyl ligands [112–114]. $\eta^2$-Ketenyl ligands are also isolobal with $\eta^2$-vinyl ligands [21].

## 6. Conclusions

The inaugural postulate that $\eta^2$-vinyl species might serve as intermediates in alkyne polymerization reactions has yet to be realized. The requirements for rehybridization and rotation of the vinyl $CR_2$ fragment are substantial and may limit interconversion of $\eta^1$- and $\eta^2$-vinyl ligands to relatively high-energy pathways. The demand that the vinyl ligand sacrifice the carbon–carbon double bond in order to donate a second pair of electrons to the metal distinguishes it from other ligands which exhibit facile variable electron donation such as nitrosyl, allyl or alkyne. It may even be that $\eta^2$-vinyl complexes inhibit catalysis either by formation of a stable $\eta^2$-vinyl linkage or through conversion to other ligands such as allene, allyl, or carbyne. Caulton and Spivak have noted that formation of the $\eta^2$-vinyl linkage is likely to be counterproductive to catalysis since it reflects a preference for formation of new bonds between metal and carbon rather than between ligands [58].

Multiple synthetic routes to $\eta^2$-vinyl ligands or 1-metallacyclopropene complexes now exist. Although dominated by addition of nucleophiles to four-electron donor alkyne ligands, other methods of preparation have been reported, including examples of (1) alkyne insertion into metal–ligand bonds and (2) substituent loss from coordinated olefins to leave behind an $\eta^2$-vinyl ligand. These preparative methods reflect the accuracy of the half-alkyne/half-alkene description of $\eta^2$-vinyl ligands presented by Casey [4]. The non-planar structures of these metallacycles and the defining spectroscopic properties of this class of ligands are also congruent with the half-alkyne/half-alkene description.

Isomerization reactions to form isomeric $\eta^2$-vinyl ligands, $\eta^3$-allyl ligands, or $\eta^1$-carbynes are relatively common and reflect the difficulties in exploring the chemistry available to $\eta^2$-vinyl ligands. Both nucleophilic addition reactions and protonation have produced alkene products from $\eta^2$-vinyl complexes. As reflected in this review and the accompanying references, the chemistry of $\eta^2$-vinyl ligands is now firmly established, yet abundant opportunities remain for additional exploration of this fledgling field.

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