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Metallacumulenes: from vinylidenes to metal polycarbides

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Abstract

Metallacumulenes and carbide complexes exhibit diverse structures and modes of reactivity. This review presents an overview of work in the author's research group on vinylidene complexes of group 6 and 8 metals, allenylidene and butatrienylidene complexes of group 8 metals, and metal carbide, bicarbide and tricarbide complexes of group 6, 7 and 8 metals.

Keywords: Metallacumulenes; Vinylidenes; Metal polycarbides; Allenylidenes; Metal carbides

1. Vinylidene complexes

Alan Davison, my PhD advisor at the Massachusetts Institute of Technology, has an amazing instinct for patterns of chemical reactivity. He was the first to realize that the reactivity of metal carbonyl and cyano ligands toward electrophiles at the β atom inferred that a metal alkynyl should react with an electrophile at Cβ to give a metal vinylidene complex. This project first fell to Willy Krusell in the Davison group, who attempted to react group 6 ethynyl anions, $[M(C{\equiv}CH)(CO)_5]^-$, with protonic acids to produce unsubstituted vinylidene complexes, $[M(C{=}CH_2)(CO)_5]$. After many unsuccessful,

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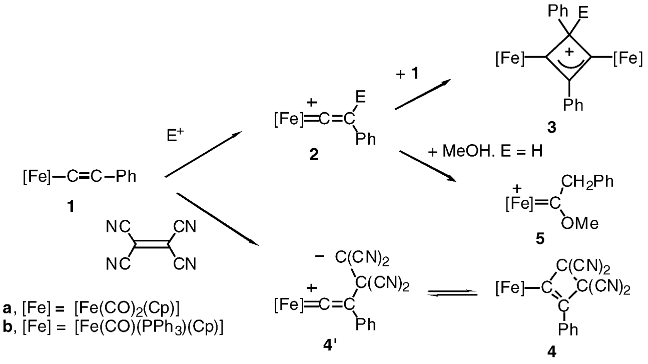
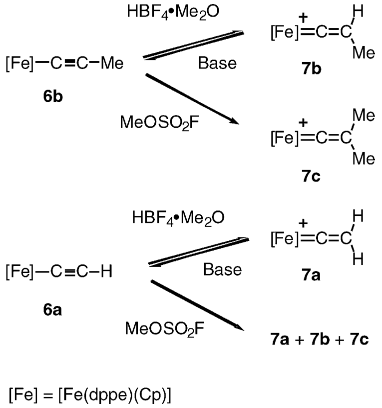


Scheme 1.

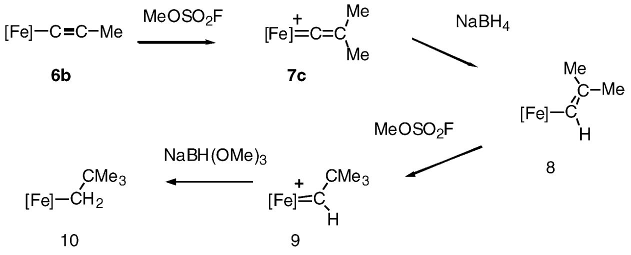
but chromatographically colorful, attempts, Willy moved on to other experiments. Jeff Solar inherited the project, shifting to the more robust $[\mathrm{Fe(C{\equiv}CR)L_2(Cp)}]$ system. He quickly produced evidence that $[\mathrm{Fe(C{\equiv}CPh)(CO)_2(Cp)}]$ (**1a**, Scheme 1) reacts with protonic acids or methyl fluorosulfonate at Cβ to form reactive vinylidene cations, $[\mathrm{Fe(C{=}CEPh)(CO)_2(Cp)}]^+$ (**2a**, E = H, Me), that are trapped by a second equivalent of **1** to give cyclobutenyl complexes, $[\{\mathrm{Fe(CO)_2(Cp)}\}_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-}\mathrm{C_4EPh_2})]^+$ (**3a**) [1]. Further, the alkynyl formed 1:1 or 2:1 adducts at Cβ with the electrophiles, tetracyanoethylene or trifluoroacetone (**4′**), followed by closure (to **4**) in a net [2 + 2] cycloaddition reaction. Replacing a carbonyl ligand with triphenylphosphine increased the electron richness of the alkynyl **1b** to the point that the vinylidene cation $[\mathrm{Fe(C{=}CHPh)(CO)(PPh_3)(Cp)}]^+$ was stable enough to isolate as a labile pink solid that reacted with a second equivalent of **1b** to give cyclobutenyl complex **3b**, or with methanol to give a Fischer carbene complex, $[\mathrm{Fe\{C(OMe)CH_2Ph\}(CO)_2(Cp)}]^+$ (**5b**) [2]. At this point, Jeff had completed his PhD research, so I set about making even more electron-rich $[\mathrm{Fe(C{\equiv}CR')(PR_3)_2(Cp)}]$ complexes to increase the nucleophilicity at Cβ. The requisite starting materials, $[\mathrm{FeX(PR_3)_2(Cp)}]$, were not conveniently available, so we developed a method of sequentially adding two equivalents of phosphine followed by cyclopentadienythallium(I) to $\mathrm{FeX_2}$ to give a range of starting materials with X = Cl, Br, I; $\mathrm{PR_3} = \mathrm{PMe_3}$, $\mathrm{P(OMe)_3}$, 1/2 $\mathrm{Ph_2PCH_2CH_2PPh_2}$ (dppe) and 1/2 $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_4PPh_2})_2]$. Reactions with lithium alkynyls gave $[\mathrm{Fe(C{\equiv}CR')(dppe)(Cp)}]$ (R = H (**6a**), Me (**6b**)) in sufficient yield to survey reactions with electrophiles. A straightforward reaction of $[\mathrm{Fe(C{\equiv}CMe)(dppe)(Cp)}]$ with methyl fluorosulfonate led to $[\mathrm{Fe(C{=}CMe_2)(dppe)(Cp)}][\mathrm{FSO_3}]$ (**7c**, Scheme 2), the first dialkylvinylidene complex [3]. Protonic acids added similarly and reversibly to give $[\mathrm{Fe(C{=}CHMe)(dppe)(Cp)}]^+$ (**7b**). A spectrophotometric titration in $\mathrm{THF/H_2O}$ established the $\mathrm{p}K_\mathrm{a}$ of **7b** as about 7.7, between a tertiary ammonium and pyridinium ion. We were also able to characterize $[\mathrm{Fe(C{=}CH_2)(dppe)(Cp)}]^+$ (**7a**), the first complex with a unsubstituted vinylidene (ethenylidene) ligand [3]. Alkynyl complexes with other phosphine ligands reacted similarly.



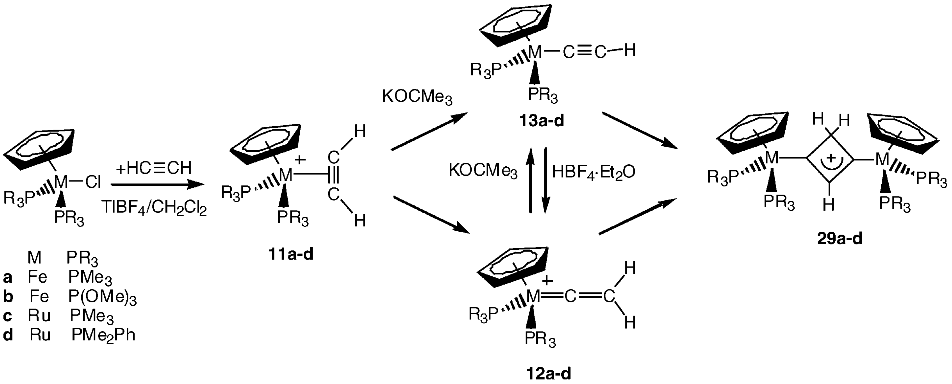
Scheme 2.

The only literature precedents for metal vinylidene complexes derived from alkynes were Clark and Chisholm's classic work on "platinum-stabilized carbenium ions," [4–8] Bellerby's and Mays' brief report on an η^2-alkyne to vinylidene rearrangement in the $[\mathrm{FeX_2(Et_2PCH_2CH_2PEt_2)_2}]$ system [9], and the initial work by Antonova and co-workers on manganese vinylidene complexes [10–14]. King's pioneering dicyanovinylidene complexes [15–22] had been obtained by a completely different method. Unknown to us, Bruce was about to publish his initial observations about vinylidene formation by both alkyne rearrangement and electrophilic addition in closely related ruthenium and osmium complexes [23–26]. Soon thereafter, Hughes reported the synthesis of cationic iron vinylidene complexes by reacting iron acyls with triflic anhydride [27–29], and Mansuy reported the novel formation of vinylidene ligand in the iron–porphyrin system [30–33].

Perhaps more importantly, the $[\mathrm{Fe(dppe)(Cp)}]^+$ system demonstrated unambiguously the positive polarity of Cα and negative polarity of Cβ of an unsaturated η^1-hydrocarbon ligand attached to an electron-rich metal. By using a series of alternating electrophilic additions to neutral compounds at Cα and nucleophilic additions to cations at Cβ, we carried out the stepwise conversion of metal alkynyl **6b** to a vinylidene cation **7c**, alkenyl **8**, alkylidene cation **9**, and finally a neopentyl complex **10** (Scheme 3) [34]. This report spurred many theoretical investigations of frontier orbital interactions in σ-bonded hydrocarbyl ligands



Scheme 3.



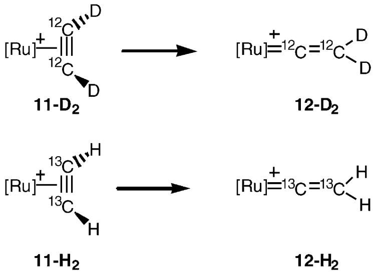
Scheme 4.

[35–37], as well as many experimental studies, including related studies in the $[Fe(dippe)(Cp)]^+$ (dippe = 1,2-bis(diisopropylphosphino)ethane) and $[Fe(dippe)(Cp^*)]^+$ (Cp* = η^5-C_5Me_5) system [38].

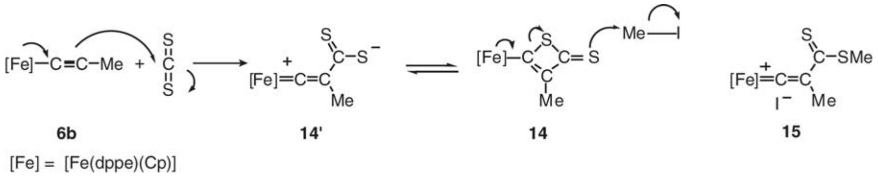
1.1. Alkyne to vinylidene rearrangements

In my own group, Jeff Lomprey investigated some details of the rearrangement of ethyne to vinylidene in the $[M(C_2H_2)(PR_3)_2(Cp)]^+$ system [39]. 1-Alkynes typically react with the d^6 iron(II) or ruthenium(II) centers $[M(PR_3)_2(Cp)]^+$ to give spontaneously vinylidene complexes, $[M(C{=}CHR')(PR_3)_2(Cp)]^+$. However, for ethyne itself we were able to isolate the initially formed η^2 isomers, $[M(\eta^2\text{-}HC{\equiv}CH)(PR_3)_2(Cp)]^+$, for small phosphine ancillary ligands (**11**, Scheme 4). The η^2 complexes rearrange to the more stable vinylidene isomers (**12**) above room temperature. The η^2-ethyne to vinylidene conversion can also be carried out by deprotonation of **11d** to give $[Ru(C{\equiv}CH)(PMe_2Ph)_2(Cp)]$ (**13d**), followed by protonation to give exclusively **12d**. We structurally characterized both isomers of $[Ru(C_2H_2)(PMe_2Ph)_2(Cp)][BF_4]$, **11d** and **12d**. Perhaps the most surprising aspect of the structures is how similar they are, differing significantly only in the bonding mode of the C_2H_2 ligand. In **11d**, the η^2-ethyne ligand is nearly symmetrically bound to Ru, with Ru–C distances of 2.20(2) and 2.21(2) Å and a C–C distance of 1.22(2) Å. The vinylidene ligand in **12d** is bound to Ru with a Ru–C distance of 1.84(1) Å, a C–C distance of 1.29(1) Å, and a Ru–C–C angle of 174.1(8)°. The η^2-ethyne ligand in **11d** occupies slightly more space on the coordination sphere, resulting in a slightly smaller P–Ru–P angle in **11d**, 91.6(1)°, than in **12d**, 92.8(1)°.

The kinetic $[M(\eta^2\text{-}C_2H_2)(PR_3)_2(Cp)]^+$ isomers rearrange to the thermodynamic vinylidene isomers at temperatures from room temperature to 80 °C. In general, rearrangements are faster for iron than ruthenium, and for larger rather than smaller ancillary ligands. Activation energies decrease in the order $[Ru\{P(OMe)_3\}_2(Cp)]^+ > [Fe\{P(OMe)_3\}_2(Cp)]^+ \geq [Ru(PMe_3)_2(Cp)]^+ > [Ru(PMe_2Ph)_2(Cp)]^+$. The isomerization proceeds more slowly, with higher activation parameters, in acetone compared to dichloromethane. Deuteration of the ethyne ligand significantly raises the activation parameters, with E_a increasing from about 79 kJ mol^{-1} for $[Ru(C_2H_2)(PMe_2Ph)_2(Cp)]^+$ to 113 kJ mol^{-1} for $[Ru(C_2D_2)(PMe_2Ph)_2(Cp)]^+$. Enthalpy and entropy of activation parameters are consistent with an associative (intramolecular) mechanism. An isotopic crossover experiment further established that the rearrangement is intramolecular. A 1:1 mixture of $[Ru(\eta^2\text{-}H^{13}C{\equiv}^{13}CH)(PMe_2Ph)_2(Cp)]^+$ and $[Ru(\eta^2\text{-}D^{12}C{\equiv}^{12}CD)(PMe_2Ph)_2(Cp)]^+$ heated to 64.5 °C in CD_2Cl_2 rearranged to $[Ru(^{13}C{=}^{13}CH_2)(PMe_2Ph)_2(Cp)]^+$ and $[Ru(^{12}C{=}^{12}CD_2)(PMe_2Ph)_2(Cp)]^+$ with virtually no crossover of D to the ^{13}C-labeled complex (Scheme 5). In $(CD_3)_2CO$, a small amount of crossover occurred, but no more than was observed for the rearrangement of pure $[Ru(\eta^2\text{-}H^{13}C{\equiv}^{13}CH)(PMe_2Ph)_2(Cp)]^+$ in $(CD_3)_2CO$. Although an intermolecular proton transfer is ruled out, the detailed intramolecular mechanism is still in question. Calculations of Silvestre and Hoffmann suggest that a 1,2-hydrogen shift concerted with a metal η^2 to η^1 migration should be the minimum energy pathway [40]. However, some experimental and theoretical results suggest that isomerization to an alkynyl hydride followed by subsequent 1,3-hydrogen migration of the hydrogen to Cβ is a viable mechanistic alternative [41–54]. In the electron-rich, sterically crowded $[Ru(PR_3)_2(Cp^*)]^+$ system, Puerta and co-workers isolated metastable alkynyl hydrides, $[RuH(C{\equiv}CR)(dippe)(Cp^*)]^+$ R = H, Ph, $SiMe_3$, CO_2Me) by ionizing $[RuCl(dippe)(Cp^*)]$ with $NaBPh_4$ in methanol prior to



Scheme 5.



Scheme 6.

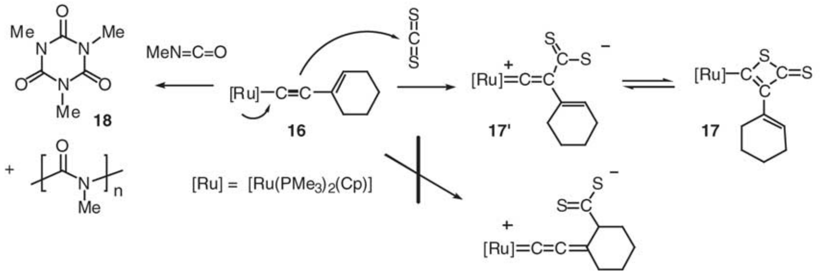
addition of alkyne. The alkynyl hydrides rearrange to their vinylidene isomers in both the solution and solid state. In solution, the reaction proceeds via a dissociative, non-concerted mechanism, apparently involving intermolecular proton transfer, since the reaction inhibited by addition of acid [51,55]. Monitoring the solid-state rearrangement by using infrared spectroscopy shows that the reaction proceeds rapidly at room temperature for R = Ph and $SiMe_3$, slowly at 50 °C for R = H, and more slowly than decomposition for R = CO_2Me. Like the solution rearrangement, the data are consistent with an intermolecular movement of H^+ in the solid-state reaction [56]. Remarkably, Puerta and coworkers have isolated and crystallographically characterized metastable η^2-ethyne and ethynyl hydride forms as well as the stable vinylidene product in the $[Ru(PEt_3)_2(Cp^*)]^+ + C_2H_2$ system [57]. A theoretical analysis showed that a combination of steric and electronic effects makes the η^2-ethyne and ethynyl hydride isomers close in energy in this system.

1.2. *Reactions of alkynyls with heteroallenes*

Among the interesting electrophiles to react with metal alkynyls are the heteroallenes. In particular, we found that carbon disulfide reacts with $[Fe(C\equiv CMe)(dppe)(Cp)]$ to give a deep purple, insoluble adduct (Scheme 6). Attempts to grow single crystals were not successful, because the adduct is too insoluble to recrystallize, and heat causes it to dissociate to its starting materials. Spectroscopic evidence, including an infrared stretch at $1275\,cm^{-1}$ attributed to $\nu(C{=}S)$ and intense visible absorptions at 564 and 402 nm (ε = 9420, 8810), are more consistent with a closed *2H*-thiete-2-thione (**14**) rather than an open, zwitterionic dithiocarboxylate (**14′**). Adduct **14** reacts with a variety of electrophiles to give more soluble derivatives. We crystallographically characterized the iodomethane product **15**. The open dithioester structure of **15** suggests that electrophilic attack on the thione sulfur atom of **14** is accompanied by ring opening [58]. Surprisingly, photochemical reactions of carbon disulfide with $[Fe(C\equiv CR)LL'(Cp)]$ (L, L′ = dppm or L = CO, L′ = PPh_3; R = Ph, CMe_3) [59], as well as thermal reactions with $[Ru(C\equiv CPh)(PPh_3)_2(Cp)]$ [60] or unsaturated $[Ru(C\equiv CCMe_3)(PPh_3)(Cp^*)]$ (generated in situ from $[RuCl(C{=}CHCMe_3)(PPh_3)(Cp^*)]$) [61], give dithiopropiolate insertion products $[M(\kappa^2 S,S\text{-}S_2CC\equiv CR)(PR_3)(Cp)]$, rather than cycloadducts.

$[Fe(C\equiv CMe)(dppe)(Cp)]$ is inert to CO_2, and evidence for reaction with OCS was ambiguous at best. However, Templeton later found that Cβ of the anionic tungsten alkynyls Li[*fac*-$W(C\equiv CR)(CO)_3(dppe)$] react with CO_2 to give the vinylidene adducts Li[*mer*-$W(C{=}CRCO_2)(CO)_3(dppe)$], which were O-methylated with Me_3OBF_4 to give vinylidene esters [62]. Probably, the greater nucleophilicity of the anionic alkynyls and some degree of assistance by the Lewis acidic counterion promote the CO_2 reaction.

Bruce Young later studied reactions of several other heteroallenes with the nucleophilic alkynyl [Ru(C≡C-*cyclo*-$C_6H_9)(PMe_3)_2(Cp)$] (**16**, Scheme 19). This compound reacts similarly to $[Fe(C\equiv CMe)(dppe)(Cp)]$, giving a very insoluble *2H*-thiete-2-thione (Scheme 7, **17**). There is no evidence for reaction at Cδ rather than Cβ. Unlike **14**, we were not able to obtain a tractable, soluble derivative by subsequent reaction of **17** with iodomethane. Rather than forming a discrete cycloadduct, **16** catalyzes the polymerization of MeN=C=O into a mixture of its cyclic trimer, trimethylisocyanurate (**18**), and an oligomer. Alkynyl **16** did not react with CO_2 or OCS; reaction with MeN=C=S gave an intractable mixture [63]. Similar reactions of heteroallenes with $[Ni(C\equiv CR)(PR_3)(Cp)]$ [64,65] and iron alkynyls [66] have been reported.



Scheme 7.

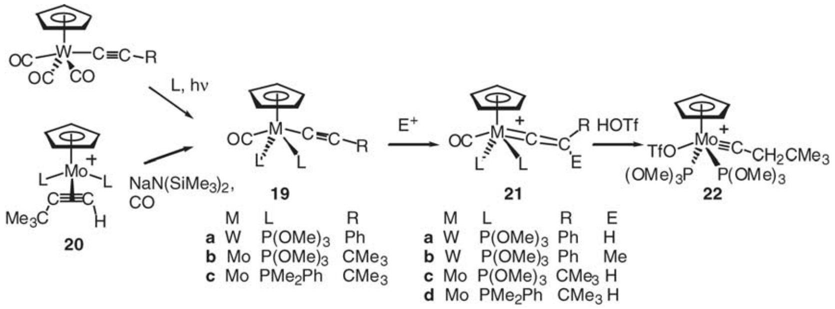
1.3. Group 6 vinylidene complexes

The mid-1980s were a period of rapid growth of new methods for studying structure and dynamics by NMR. In particular, our attention was drawn to using the two-dimensional NOESY experiment to study the rearrangements of fluxional organometallic complexes. Our ongoing interest in alkyne complexes led us to the intriguing bis(alkyne) complexes $[M(CO)(\eta^2\text{-}RC{\equiv}CH)_2(Cp)]^+$ (M = Mo, W). Electron-counting rules suggest that the complexes contain a pair of three-electron alkyne ligands. Our study, by Peter Nickias along with Prof. Stan Smith and his student Alan Kook, of the rotation of these alkyne ligands was one of the first applications of 2D NMR to study a dynamic process in organometallic chemistry [67]. Along with the NMR phenomena, our interest was drawn to the reactivity of group 6 alkyne complexes.

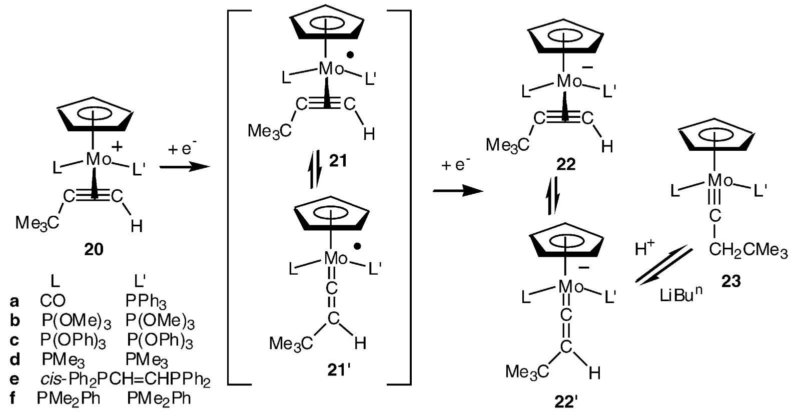
The different electron count of the otherwise identical group 6 and group 8 alkyne complexes, $[M(RC{\equiv}CH)(PR'_3)_2(Cp)]^+$, leads to different ground state structures. For M = Mo or W, the η^2-alkyne isomer is more stable; for M = Fe, Ru, Os, the η^1-vinylidene isomer is more stable. The major electronic difference is the presence of a *d*-based π-acceptor orbital on the d^4, group 6 metal center, as opposed to a *d*-based π-donor orbital on the d^6, group 8 metal center. As pointed out by Templeton [68], donation from an alkyne ligand's full $\pi_\perp$ orbital to a metal π-acceptor orbital leads to a very stable 4-electron metal-alkyne interaction, whereas conflict between the same alkyne orbital and a metal π-donor orbital tends to destabilize a metal-alkyne interaction. Indeed, the latter interaction helps to explain why iron-group $[M(RC{\equiv}CH)(PR'_3)_2(Cp)]^+$ complexes rearrange spontaneously to their vinylidene isomers.

We first needed to establish whether group 6 "piano-stool" vinylidene complexes, $[M(C{=}CHR)L_3(Cp)]^+$, are stable. King's pioneering *trans*-$[MoCl\{C{=}C(CN)_2\}(PR_3)_2(Cp)]$ compounds [17–20] and Green's *trans*-$[MoBr(C{=}CHPh)\{P(OMe)_3\}_2(Cp)]$ [69] provided some support, but they differed in charge and ligand set. Peter Nickias and Bruce Young found two convenient routes to the requisite alkynyls, *trans*-$[M(C{\equiv}CR)(CO)L_2(Cp)]$ (**19a–c**, Scheme 8). Photolytic substitution of $[W(C{\equiv}CPh)(CO)_3(Cp)]$ gives *trans*-$[W(C{\equiv}CPh)(CO)\{P(OMe)_3\}_2(Cp)]$ (**19a**) and a similar *cis*-alkynyl with $Ph_2PCH_2PPh_2$. Alternatively, facile substitution of the precursor $[Mo(\eta^2\text{-}Me_3CC{\equiv}CH)\{P(OPh)_3\}_2(Cp)]^+$ gives $[Mo(\eta^2\text{-}Me_3CC{\equiv}CH)L_2(Cp)]^+$ (**20**, Schemes 8 and 9) containing phosphorus ancillary ligands with a broad range of electronic and steric properties [70–72]. Subsequent deprotonation of **20** under a CO atmosphere gives molybdenum alkynyls $[Mo(C{\equiv}CCMe_3)(CO)L_2(Cp)]$ (**19b–c**). The molybdenum and tungsten alkynyls **19** react at −78 °C with electrophiles $HBF_4{\cdot}Et_2O$, HOTf or MeOTf to give cationic vinylidene complexes, $[M(C{=}CER)(CO)L_2(Cp)]^+$ (**21a–d**). Stability of the complexes is generally higher for tungsten than molybdenum, for stronger electron-donor ancillary ligands L, and for E = Me rather than H. The structure of tungsten vinylidene complex **21a** establishes the *trans*-geometry of the vinylidene and carbonyl ligands. The vinylidene ligand lies in a "vertical" orientation, with the vinylidene plane nearly coincident with the $[W(CO)L_2(Cp)]$ symmetry plane. The phenyl substituent is *syn* to the cyclopentadienyl ligand, presumably minimizing steric interactions with the $P(OMe)_3$ ligands. The W–C(vinylidene) bond, 1.947(6) Å, is shorter than the W–CO bond, 1.990(7) Å, suggesting very strong W-vinylidene π-backbonding. ^{13}C NMR spectra of complexes **21a–d** show low-field phosphorus-coupled triplets for vinylidene Cα at ca. δ_C 320–340. Infrared spectra show a characteristic $\nu(C{=}C)$ at 1605–1632 cm^{-1}. The vinylidene ligand exerts a very strong *trans*-labilizing effect. Warming a solution of the BF_4^- salt of **21c** from −78 °C to 0 °C causes it to lose CO, regenerating **19b**. Warming the triflate salt of **21c** in the presence of excess triflic acid leads to the stable alkylidyne complex *trans*-$[Mo(OTf)({\equiv}CCH_2CMe_3)\{P(OMe)_3\}_2(Cp)]^+$ OTf^- (**22**). Evidently the decarbonylation product of **21c** is trapped by triflate to give *trans*-$[Mo(OTf)(C{=}CHCMe_3)\{P(OMe)_3\}_2(Cp)]$, which is subsequently protonated at Cβ by triflic acid to give **22**. The ^{13}C NMR spectrum of **22** shows a ^{31}P-coupled triplet at δ_C 390.4.

Peter Nickias and Bruce Young next set out to investigate whether the two-electron reduction of $[M(\eta^2\text{-}RC{\equiv}CH)L_2(Cp)]^+$ (M = Mo, W) would promote an alkyne to vinylidene rearrangement. Green and co-workers had already reported



Scheme 8.

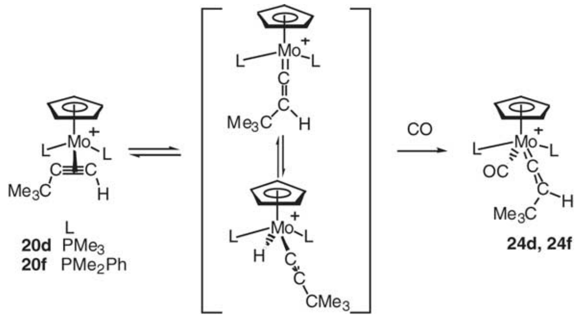


Scheme 9.

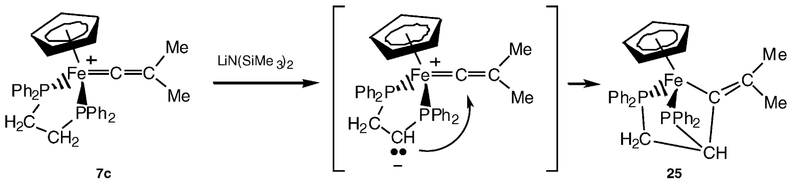
that deprotonation of $[Mo(\equiv CCH_2CMe_3)\{P(OMe)_3)\}_2(Cp)]$ (Scheme 9, **23b**) led to the anionic vinylidene complex $[Mo(C{=}CHCMe_3)\{P(OMe)_3)\}_2(Cp)]^-$ (**22′b**), which was spectroscopically characterized, trapped with electrophiles, and coupled with one-electron oxidants [73–75]. Thus, the targeted anionic vinylidene complexes would be likely be at least stable enough to observe spectroscopically and trap in solution. Reduction of $[Mo(\eta^2\text{-}Me_3CC\equiv CH)(CO)(PPh_3)(Cp)]^+$ (**20a**) with sodium naphthalenide at −78 °C followed by protonation gave $[Mo(\equiv CCH_2CMe_3)(CO)(PPh_3)(Cp)]$ (**23a**) in a disappointing 4% yield (Scheme 9). $[Mo(\eta^2\text{-}Me_3CC\equiv CH)\{P(OMe)_3\}_2(Cp)]^+$ (**20b**) was similarly reduced by lithium or sodium naphthalenide, but we were unable to isolate or trap putative vinylidene anion **22′b**. Attempts to trap single-electron reduction products (**21a–b**) with $SnHBu_3$, a hydrogen atom-donor, also failed [70,72].

Cyclic voltammetry of $[Mo(Me_3CC\equiv CH)L_2(Cp)]^+$ (Scheme 9, **20b–e**, L = $P(OMe)_3$, $P(OPh)_3$, PMe_3; L_2 = *cis*-$Ph_2PCH{=}CHPPh_2$) showed two one-electron reduction waves. The first reduction at −1.1 to −1.2 V (versus Ag/AgCl) is reversible even at scan rates as slow as $10\,mV\,s^{-1}$, but the second reduction at −1.8 to −2.0 V is only quasi-reversible even at scan rates above $500\,mV\,s^{-1}$. For **20e**, the second reduction is irreversible at all scan rates when the reduction is carried out under one atm of CO. Apparently the second reduction is followed by a rapid chemical step. If this chemical step is the rearrangement of the alkyne ligand, it is puzzling that we have not been able to trap the putative anionic vinylidene product. We carried out one-electron electrochemical reduction of **20b** in the presence of the spin trap phenyl-α-*tert*-butylnitrone. The EPR spectrum of the resulting spin adduct was a triplet of doublets with a_N = 14.27 G and a_H = 2.79 G (a_N is the triplet splitting by nitrogen; a_H is the doublet splitting by hydrogen). The multiplet was centered at a *g*-value of approximately 2.025. The lack of additional coupling in the spin adduct is consistent with attachment to a radical centered on carbon, not molybdenum or any other spin-active nucleus, but we have no additional data to suggest which carbon atom attaches to the spin trap [72].

An alternative to explicit addition of two electrons to a d^4 alkyne complex is addition of an additional two-electron ligand. We found that the alkyne complexes $[Mo(\eta^2\text{-}HC\equiv CCMe_3)(PR_3)_2(Cp)][BF_4]$ (Scheme 10, **20d** and **20f**, $PR_3 = PMe_3, PMe_2Ph$) are driven to the vinylidene complexes $[Mo(C{=}CHCMe_3)(CO)(PR_3)_2(Cp)][BF_4]$ (**24d** and **24f**) by straightforward treatment with 1 atm of carbon monoxide [70]. For poorly electron-donating ancillary ligands, such as carbonyl and phosphites (i.e., **20a–c**), the η^2-alkyne complexes do not react with CO. We were not able to distinguish among possible mechanisms for the formation of **24**. Perhaps strong electron-donor ancillary ligands promote an equilibrium between $[Mo(\eta^2\text{-}HC\equiv CCMe_3)(PR_3)_2(Cp)]^+$ (**20d** and **20f**) and $[Mo(C{=}CHCMe_3)(PR_3)_2(Cp)]^+$, with the latter being intercepted by CO. Alternatively, the CO addition itself could promote the hydrogen migration. Later work suggests that oxidative addition of the alkyne ligand to form an alkynyl hydride, $[MoH(C\equiv CCMe_3)(CO)(PR_3)_2(Cp)]^+$, may precede formation of the vinylidene complex [41–44,46–54]. Yang et al. have also reported vinylidene complexes in the $[Mo(CO)(dppe)(Cp)]^+$ system [76], and Whiteley et al. have worked with the complementary $[Mo(PR_3)_2(\eta\text{-}C_7H_7)]^+$ system [77–81].



Scheme 10.

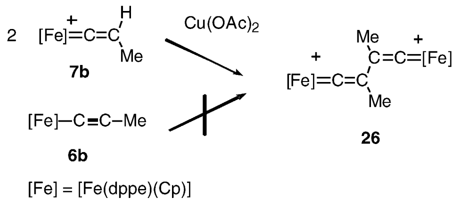


Scheme 11.

2. Reactions of vinylidene ligands

2.1. Intramolecular reactions

Surprisingly, despite important developments in the structural characterization of inorganic compounds at MIT, in the late 1970s there were no facilities for X-ray diffraction. When I took a postdoctoral position with Rick Adams at Yale University in late 1978, I carried along a puzzling compound in the iron vinylidene series. $[Fe(C{=}CMe_2)(dppe)(Cp)]^+$ (**7c**, Scheme 11) is deprotonated by strong, non-nucleophilic bases. With the help of NMR spectroscopy, we had made a few wild, incorrect structural guesses. X-ray crystallography revealed that removal of a proton from the bridge of the dppe ligand, followed by intermolecular attack of $Ph_2PCHCH_2PPh_2^-$ on the electrophilic Cα of the vinylidene ligand, resulted in $[Fe\{\kappa^3 P,P,C\text{-}PPh_2CH_2CH(PPh_2)C{=}CMe_2\}(Cp)]$ (**25**), an unusual 1-ferra-2,5-diphosphabicyclo[2.1.1]hexane [82]. The structure shows the effects of appreciable strain in a four-membered ring system, in particular a long Fe–C bond (2.030(7) Å), an abnormally long C–C bond (1.649(9) Å) and an acute Fe–C–C angle (99.0(4)°). Bruce et al. later reported an identical deprotonation of $[Ru(C{=}CMePh)(dppe)(Cp)]^+$ [83]. The larger metal atom relieves some of the strain in the bicyclic ring; in particular the C–C bond in the four-membered ring is closer to normal (1.534(7) Å). Most of our later follow-up studies on the acidity of coordinated phosphine ligands came too late to avoid being scooped by other groups. Activation by two PPh_2 groups makes coordinated $PPh_2CH_2PPh_2$ (dppm) even more acidic than coordinated dppe. The resulting $Ph_2PCHPPh_2^-$ complexes can be stable without closure; e.g., deprotonated dppm does not attack a coordinated carbonyl, but rather gives the “open” bisphosphinomethanide complex $[Fe(CO)(\kappa^2 P,P\text{-}Ph_2PCHPPh_2)(Cp)]$ [84]. With James Goodrich, we characterized similarly stable deprotonated phosphine complexes $[Fe(\kappa^3 P,P,P\text{-}(PPh_2)_3C\}(Cp)]$ and $[Ni(\kappa^2 P,P\text{-}Ph_2PCHPPh_2)(Cp)]$ [85].



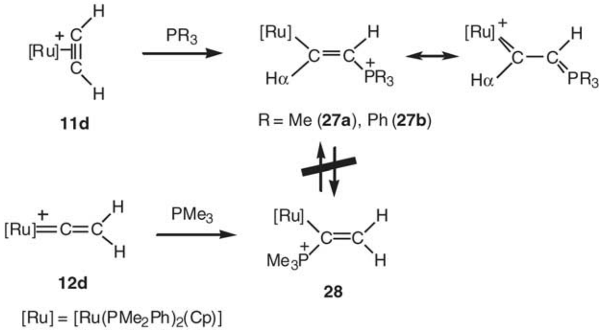
Scheme 12.

The higher electrophilicity of vinylidene compared to carbonyl is reflected by the fact that in an isoelectronic complex, deprotonated dppm does attack vinylidene to form $[Fe\{\kappa^3 P,P,C\text{-}PPh_2CH(PPh_2)C{=}CMeCMe_3\}(Cp)]$, a strained 1-ferra-2,4-diphosphabicyclo[1.1.1]pentane [86].

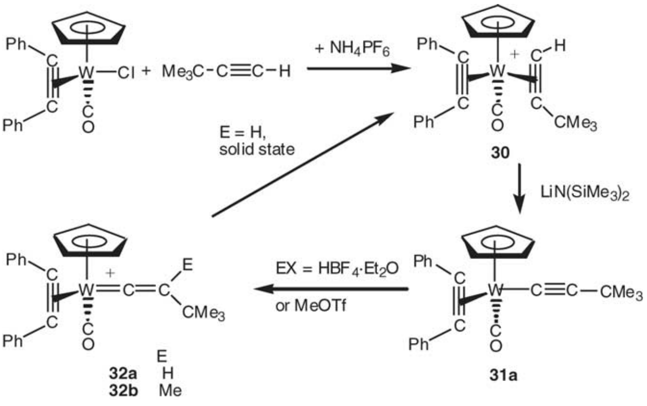
2.2. Intermolecular reactions

Postdoc Ramnath Iyer accidentally discovered an intriguing coupling reaction of the vinylidene complex $[Fe(C{=}CHMe)(dppe)(Cp)]^+$ (Scheme 12, **7b**) [87]. Oxidation of **7b** with a copper(II) salt, typically copper(II) acetate, leads to dimerization to $[\{Fe(dppe)(Cp)\}_2(\mu\text{-}C{=}CMeCMe{=}C)]^{2+}$ (**26**) via formation of a C–C bond between two Cβ atoms with concomitant loss of two protons. The structure of **26** shows a μ-divinylidene dication with a typical C–C single bond (1.50(1) Å) between the two Cβ atoms, with a roughly s-trans configuration about the C–C bond; the C=C–C=C torsion angle is 150.7°. Steric interaction between the two [Fe(dppe)(Cp)] groups causes one of the vinylidene ligands to twist slightly from its ideal geometry. Normally, vinylidenes are perpendicular to the symmetry plane of a $[ML_2(Cp)]^+$ metal center; the dihedral angles in **26** are 90.0° and 117.2°. Although, in principle, the oxidation of propynyl **6b** should lead to **26**, in our hands the dimerization only worked for the vinylidene cation. Since our initial report, the oxidative Cβ–Cβ coupling of metal alkynyls has been used to great benefit in synthetic chemistry. Similar oxidative dimerization reactions of manganese vinylidene complexes [88–90] have been reported. Whiteley et al. later examined quantitatively the electrochemical oxidation of iron and ruthenium alkynyls [91] and also observed similar oxidative coupling reactions of molybdenum alkynyls [77,78] Green reported a similar oxidative coupling of an *anionic* group 6 vinylidene complex (**22′a**, Scheme 9) to give a neutral bisalkylidyne complex [73,75]. Gladysz [92–95], Lapinte [96,97] and others [98] coupled vinylidene or ethynyl ligands, e.g., $[L_nM(C{\equiv}C)_xH]$ to $[L_nM(C{\equiv}C)_{2x}L_n]$, by using oxidative coupling reactions, typically under copper-promoted Glaser, Hay or Cadiot–Chodkiewicz conditions.

Jeff Lomprey investigated reactions of both $[Ru(C_2H_2)(PMe_2Ph)_2(Cp)]^+$ isomers, **11d** and **12d**, with nucleophiles. With the alkyne isomer **11d**, trimethylphosphine gives $[Ru(\eta^1\text{-}E\text{-}CH{=}CHPMe_3)(PMe_2Ph)_2(Cp)]^+$ (**27a**, Scheme 13). The structure of **27a** shows a resonance hybrid of a ruthenium alkenyl complex with a phosphonium substituent and a ruthenium alkylidene complex



Scheme 13.



Scheme 14.

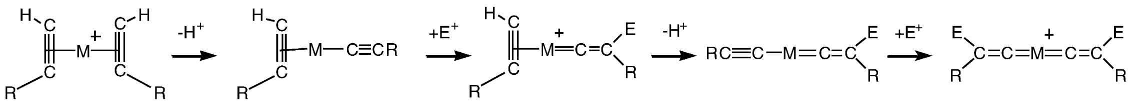
with an phosphorus ylide substituent. The reaction of trimethylphosphine with ethenylidene isomer **12** gives $[Ru\{C(PMe_3){=}CH_2\}(PMe_2Ph)_2(Cp)]^+$ (**28**), which we also structurally characterized. A vinylphosphonium is the only reasonable formulation for **28**, unlike **27**. The structure shows evidence of steric crowding around Cα. Accordingly, triphenylphosphine forms a phosphine adduct **27b** with **11d** but not **12d**. Because, **11d** and **12d** give different adducts, phosphine addition must occurs more rapidly than hydrogen migration. Similar structures of phosphine adducts of cationic iron [27] and rhenium [99] as well as neutral manganese [100] vinylidene complexes had been previously reported.

Generally, deprotonation of either **11** or **12** (Scheme 4) gives thermally stable, air-sensitive ethynyl complexes, $[M(C{\equiv}CH)L_2(Cp)]$ (**13**). The ruthenium PMe_2Ph complex **13d** is particularly well behaved. Reactions of vinylidenes **12a–d** with alkynyls **13a–d** lead to cyclobutenyl complexes, $[\{Ru(PR_3)_2(Cp)\}_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-}C_4H_3)]^+$ (**29a–d**, Scheme 4), similar to the iron complexes (**3**) discussed above.

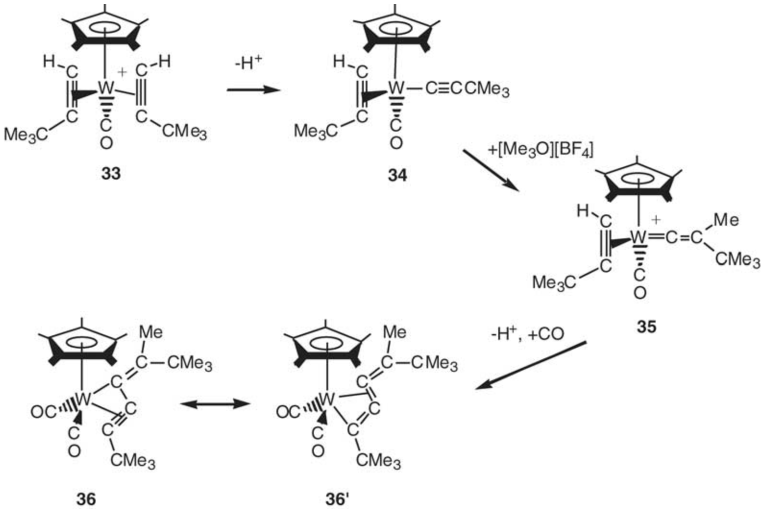
2.3. Group 6 vinylidene reactions

Continuing our study of group 6 alkyne and vinylidene complexes, postdoc Matthew Stainer developed a method for the synthesis of cyclopentadienyl tungsten compounds with both a 1-alkyne and a diarylalkyne ligand (**30**, Scheme 14) [101]. Deprotonation of the 1-alkyne ligand of **30** by $LiN(SiMe_3)_2$ gives alkynyl **31**, which in turn reacts with $HBF_4{\cdot}Et_2O$ or MeOTf to give vinylidene complexes **32a–b**. The *tert*-butyl vinylidene ligand of **32a** slowly reverts to a *tert*-butyl acetylene ligand (**30**) in the solid state at room temperature. Because of their asymmetry, **30**–**32** exist as pairs of enantiomers. In addition, bis(alkyne) complex **30** is produced as a mixture of *syn* and *anti* alkyne orientation isomers that interconvert slowly at room temperature (monitored by ^1H NMR). X-ray crystal structure analysis of alkyne/vinylidene complex **32b** established its structure, but was complicated by the existence of two independent molecules in the unit cell with orientationally disordered vinylidene ligands. However, the stability of **32a–b** confirmed that alkyne and vinylidene ligands could coexist.

We devised a preparative route to the first complex containing two vinylidene ligands by isomerization of both of the alkyne ligands of $[M(CO)(\eta^2\text{-}RC{\equiv}CH)_2(Cp)]^+$ in a stepwise sequence of deprotonation and electrophilic addition steps (Scheme 15) [102]. Postdocs, Anne McMullen and Jin-Guu Wang, carried out this chemistry, encountering an unexpectedly facile C–C coupling reaction along the way (Scheme 16). Deprotonation of $[W(CO)(\eta^2\text{-}HC{\equiv}CCMe_3)_2(Cp)]^+$ (**33**) proceeds smoothly to the alkynyl $[W(CO)(C{\equiv}CCMe_3)(\eta^2\text{-}HC{\equiv}CCMe_3)(Cp)]$ (**34**). In this transformation, one of a pair of three-electron alkyne ligands becomes a four-electron donor. Electrophilic methylation with trimethyloxonium gives $[W(CO)(C{=}CMeCMe_3)(\eta^2\text{-}HC{\equiv}CCMe_3)(Cp)]^+$ (**35**), a stable alkyne/vinylidene complex. Deprotonation of the second alkyne apparently generates a transient alkynyl–vinylidene complex $[W(CO)(C{=}CMeCMe_3)(C{\equiv}CCMe_3)(Cp)]$. Insertion of the vinylidene ligand into the tungsten–alkynyl bond with concomitant addition of a CO ligand resulted in the unusual η^3-enynyl complex, $[W(CO)_2\{\eta^3\text{-}C(C{\equiv}CCMe_3){=}CMeCMe_3\}(Cp)]$ (**36**). A few other η^3-enynyl structures have been reported [103–110]. The structure of **36** is intermediate between the η^3-enynyl form **36** and η^3-butatrienyl form **36′**, with the coordinated C≡C bond 1.27(11) Å long and the adjacent C–C bond 1.369(9) Å. To accommodate η^3-binding, the central alkyne carbon bends to a surprisingly acute 145.0(6)° angle. The facile formation of **36** suggests that vinylidene ligands are very prone



Scheme 15.



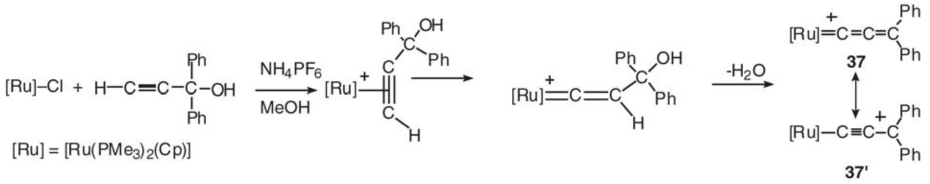
Scheme 16.

toward migratory insertion into metal–carbon bonds. Although discrete examples are scarce [111], similar insertion steps are implicated in many organometallic-catalyzed reactions of alkynes [112–115]. In particular, Puerta and co-workers have isolated η^3-enynyl complexes in the $[Ru(PR_3)_2(Tp)]^+$ (Tp = hydrotris(pyrazolyl)borate) system, which are involved in stoichiometric and catalytic alkyne coupling reactions [116].

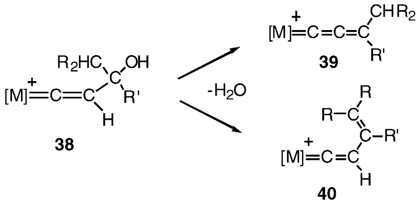
3. Allenylidene complexes

Soon after arriving at University of Kentucky, I decided to try to extend the vinylidene series to longer cumulenylidenes–allenylidenes ($C{=}C{=}CR_2$), butatrienylidenes ($C{=}C{=}C{=}CR_2$) and beyond. Little was known about these complexes, with the first two allenylidenes reported just a few years earlier [117,118], but the syntheses were rather complicated and not very general. We reasoned that rearrangement of a η^2-3-alkyn-1-ol on an electron-rich d^6 metal center to a hydroxyvinylidene ligand would be followed by spontaneous dehydration to an allenylidene complex, promoted by the demonstrated acidity of a proton on vinylidene Cβ. The first reaction we tried, $[RuCl(PMe_3)_2(Cp)]$ plus $HC{\equiv}CC(OH)Ph_2$ and NH_4PF_6 (Scheme 17), was a rare treat. On the first run, the reaction gave the desired product in essentially quantitative yield, including huge, abundant X-ray quality crystals! The product, $[Ru(C{=}C{=}CPh_2)(PMe_3)_2(Cp)][PF_6]$ (**37**), was the first allenylidene complex of a group 8 metal [119].

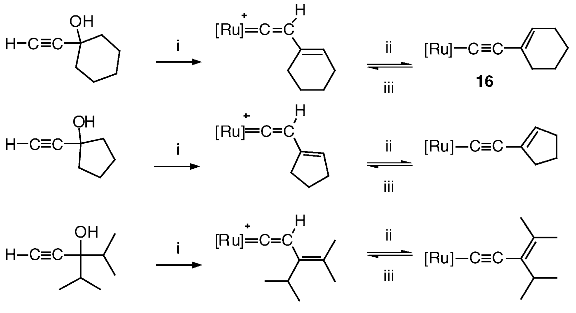
The allenylidene cations are hybrids of two resonance forms, a cumulated carbene complex with the charge localized on ruthenium (**37**), and a propargyl cation with an alkynylruthenium substituent (**37′**). The relative importance of each form depends on the nature of the metal center and the allenylidene substituents. Strong electron-donor ligands on the metal center favor the allenylidene form, whereas substituents good at stabilizing a carbenium ion at Cγ favor the propargyl cation form. The structure of **37** clearly indicates that both forms are important, with bond distances along the linear chain Ru–Cα–Cβ–Cγ being 1.884(5), 1.255(8) and 1.329(9) Å. The structure of $[Ru(C{=}C{=}CPh_2)\{P(OMe)_3\}_2(Cp)][PF_6]$ [120] is very similar, but shows slightly more contribution from a propargyl cation rather than an allenylidene form (Ru–Cα–Cβ–Cγ distances are 1.895(7), 1.248(9) and 1.344(9) Å), because of the more weakly donating $P(OMe)_3$ ancillary ligands. The crystal structure of **37** was the first to show for a group 8 metal the now well-established "vertical" allenylidene configuration, in which the allenylidene plane and the $[ML_2(Cp)]^+$ are nearly coincident as predicted by Hoffmann [36] and Fenske [37]. Puerta and co-workers later were able to characterize metastable η^2-alkynol complexes in the $[RuCl(PR_3)_2(Cp^*)]^+$ system. They rearrange competitively to 3-hydroxyalkynyl hydride and 3-hydroxyvinylidene complexes [121–124].



Scheme 17.



Scheme 18.

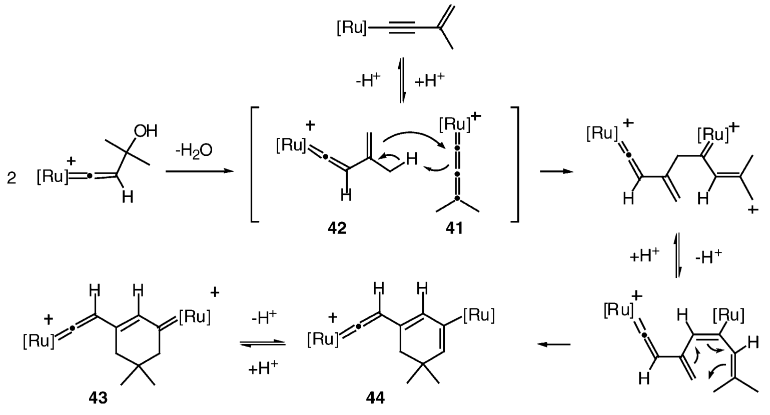


$[Ru] = [Ru(PMe_3)_2(Cp)]$, i = $[Ru–Cl, NH_4PF_6, MeOH$; ii = $NaOMe, C_5H_{12}$; iii = $HBF_4{\bullet}Et_2O$

Scheme 19.

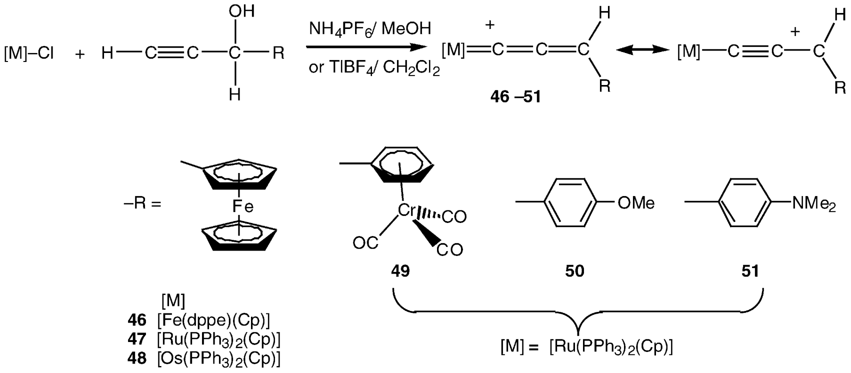
For aliphatic rather than aromatic alkyn-1-ols, dehydration of the hydroxyvinylidene intermediate (**38**, Scheme 18) can proceed two different ways. Dehydration across Cβ–Cγ gives an allenylidene complex (**39**), whereas dehydration across Cγ–Cδ gives a vinylvinylidene complex (**40**). Ramnath Iyer found that for [M] = [Fe(dppe)(Cp)] or $[Ru(PPh_3)_2(Cp)]$, NMR spectra showed that vinylvinylidene was favored over allenylidene for several alkyn-1-ols, including HC≡CC(OH)MePh. The product mixtures were generally intractable. Bruce Young and Stanley Logan had better success investigating reactions of $[RuCl(PMe_3)_2(Cp)]$ with 1-ethynylcyclohexanol, 1-ethynylcyclopentanol and 3-isopropyl-4-methyl-1-pentyn-3-ol (Scheme 19) [63,72]. The high-yield products are exclusively vinylvinylidene cations, which are smoothly and reversibly deprotonated to neutral σ-enynyls. Because, the cyclohexenyl complex **16** is especially well behaved, we studied its reactions with many electrophiles (*vide supra*). Puerta and co-workers have demonstrated the competitive dehydration of 3-hydroxyvinylidene complexes (and their 3-hydroxyalkynyl hydride precursors) to vinylvinylidene, allenylidene, or novel enynyl hydrido complexes [121–123]. Other workers have also studied extensively the chemistry of vinylvinylidene complexes [41,42,44,125–137].

Before we had encountered the competition between dehydration of hydroxyvinylidene intermediates to give allenylidenes and vinylvinylidenes (Scheme 18), we allowed $[RuCl(PPh_3)_2(Cp)]$ to react with $HC{\equiv}CC(OH)Me_2$ and NH_4PF_6, intending simply to extend the scope of the allenylidene series to $[CpRu(C{=}C{=}CMe_2)(PPh_3)_2]^+$ (**41**, Scheme 20) with substituents less able to stabilize a carbenium center at C_3. The product obtained in nearly quantitative yield is an intensely deep red-violet ($\lambda_{max} = 498\,nm$, $\varepsilon = 1.2 \times 10^4$) compound [138]. "Sporting methods" were not enough to nail down a definite structure, although it was clear from ^1H, ^{13}C and ^{31}P NMR spectra that the complex had a complicated structure with two quite different $[Ru(carbene)(PPh_3)_2(Cp)]^+$ centers. With the X-ray diffraction and computing facilities available at the time, solving and refining the structure proved to be a challenge. With 112 non-hydrogen atoms, the structure was at the limit of the dimensions of our crystallographic programs—a disordered solvent molecule put it over the top. I recall pleading with a dean for more mainframe computer time to finish refining the structure, back in the bad old days of scarce computer resources! The structure of $[\{Ru(PPh_3)_2(Cp)\}_2(\mu\text{-}C_{10}H_{12})]^{2+}$ (**43**, Scheme 20) shows a surprising dimerization of two dimethylallenylidene ligands. We postulate that the initially formed hydroxyvinylidene complex dehydrates to a mixture of allenylidene (**41**) and vinylvinylidene (**42**) isomers. An ene reaction between the allenylidene and vinylvinylidene ligands creates a bond between Cδ of the vinylvinylidene and Cα of the allenylidene. (Alternatively, that bond may be formed by deprotonation of either form to give a neutral enynyl, followed by attack of its nucleophilic Cδ on electrophilic Cα



$[Ru] = [Ru(PPh_3)_2(Cp)]$

Scheme 20.



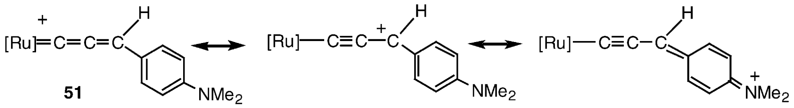
Scheme 21.

of **41** or **42**.) Subsequent proton loss, electrocyclic closure of the six-membered ring, and reprotonation result in the alkylidene–vinylidene product **43**, which is reversibly deprotonated to a deep blue-violet (λ_{max} = 575 nm, $\varepsilon = 1.9 \times 10^4$) alkynyl–alkylidene cation **44**. The same μ-$C_{10}H_{12}$ ligand is formed from $[RuCl(dippe)_2(Tp)]$ and $HC{\equiv}CC(OH)Me_2$ [139]. Formation of **43** presaged some of the applications of metallacumulene chemistry in organic synthesis developed by Trost [113,140,141], Dixneuf [114,115], Puerta [45] and Gimeno [142].

We became interested in preparing allenylidene complexes with a single cation-stabilizing substituent at Cγ, i.e., $[M(C{=}C{=}CHR)L_2(Cp)]^+$ (M = Fe, Ru, Os). We first took advantage of the well-known stability of ferrocenyl carbenium ions. Straightforward reactions of $[MXL_2(Cp)]$ with the alkynol HC≡CCH(OH)Fc (**45**, Scheme 21, Fc = ferrocenyl) and $TlBF_4$ in CH_2Cl_2 or NH_4PF_6 in MeOH gave the monosubstituted allenylidene complexes $[M(C{=}C{=}CHFc)L_2(Cp)]^+$ (**46**, Fe; **47**, Ru; **48**, Os) [143]. The colors of these compounds, deep purple for iron and deep green for ruthenium and osmium, indicate a high degree of electron delocalization. The PF_6^- salt of **47** was crystallographically characterized, revealing typical allenylidene geometry. The allenylidene chain is roughly linear, and the allenylidene lies in a vertical conformation (dihedral angle of 8.90° between the allenylidene plane and $[RuL_2(Cp)]$ symmetry plane); the ferrocenyl substituent is oriented *syn* to the cyclopentadienyl ring on ruthenium. The NMR spectra of **2b** show complex behavior at low temperature, attributed to temperature-dependent chemical shifts and correlated motions of the allenylidene ligand and the ferrocenyl substituent. In their ^{1}H NMR spectra, the allenylidene hydrogens on Cγ resonate at low field (**46**, 7.90 (*t*, $^5J_{HP}$ = 2.4 Hz), **47**, 8.96 (s), **48**10.98 (s)) in the region typical of hydrogens on carbenium ions [144,145] or metal alkylidene ligands [146]. The downfield trend from iron to osmium may reflect the decreasing π-donating ability of the $[ML_2(Cp)]$ fragments on descending the group, with the propargyl cation resonance form decreasing in importance from osmium to iron. ^{13}C NMR spectra show phosphorus-coupled triplets for Cα at low field (**46**, 280.1 (*t*, 38 Hz); **47**, 271.5 (*t*, 20 Hz); **48**, 246.5 (*t*, 13 Hz). The upfield trend from Fe to Os is typical of group 8 carbene complexes. Carbon atoms Cβ resonate between δ_C 180 and 200 ppm, characteristic of the internal, sp-hybridized carbon atoms of allenes [147] and other allenylidene complexes [41,42]. Carbon atoms Cγ resonate between δ_C 145 and 155 ppm, downfield of the usual δ_C from 75 to 120 ppm range for terminal allene carbons [147], again reflecting a significant contribution from the propargyl cation resonance form. Cyclic voltammograms of **46**–**48** in MeCN show a reversible ferrocenyl-based one-electron oxidation, in addition to irreversible $[ML_2(Cp)]$-based oxidation and reduction waves.

$[Cr(C_6H_5)(CO)_3]$ also has a remarkable ability to stabilize an adjacent carbenium ion center. $[Cr\{\eta^6\text{-}C_6H_5CH(OH)\text{-}C{\equiv}CH\}(CO)_3]$ reacts with $[RuCl(PPh_3)_2(Cp)]$ in NH_4PF_6/MeOH to give a stable allenylidene complex, $[Ru\{C{=}C{=}CH(\eta^6\text{-}C_6H_5)Cr(CO)_3\}(PPh_3)_2(Cp)][PF_6]$ (**49**, Scheme 21). This deep green complex shows properties similar to **47**, including a characteristic allenylidene resonance at δ 8.31 in its ^{1}H NMR spectrum [148].

Strongly electron-donating aryl groups also stabilize monosubstituted allenylidene complexes. Reactions of $[RuCl(PPh_3)_2(Cp)]$ in NH_4PF_6/MeOH with $HC{\equiv}CCH(OH)\text{-}4\text{-}C_6H_4X$ (X = OMe, NMe_2) give very stable allenylidene complexes, $[Ru(C{=}C{=}CH\text{-}4\text{-}C_6H_4X)(PPh_3)_2(Cp)][PF_6]$ (**50** and **51**, Scheme 21) [149]. The complexes are highly crystalline and intensely colored, deep rose-red (**50**) and deep blue (**51**). Their ^{1}H NMR spectra showed characteristic allenylidene signals at δ 8.93 (**50**) and 8.28 (**51**). Crystal



Scheme 22.

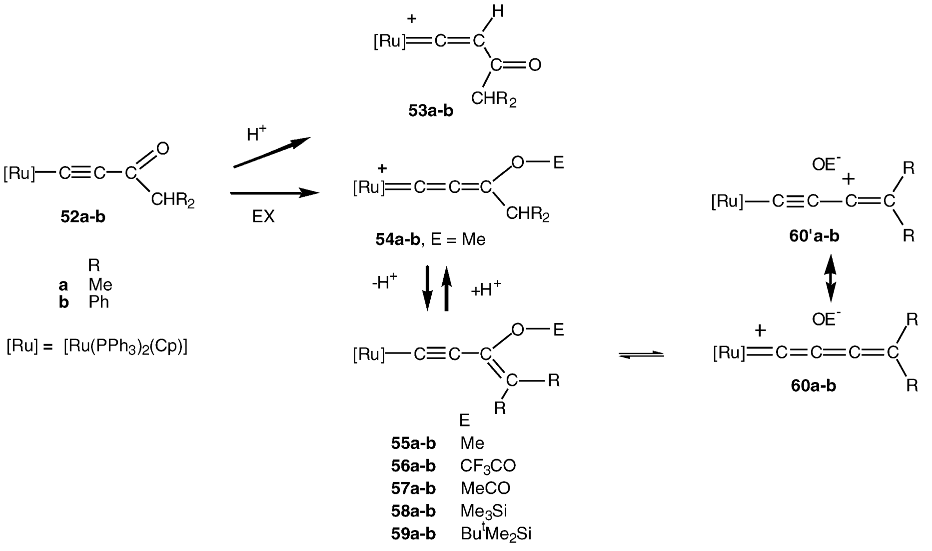
structure analyses showed that, as usual, the allenylidene plane lies roughly in [RuL$_2$(Cp)] symmetry plane. Surprisingly, the 4-methoxyphenyl substituent lies *syn* to the Cp group, whereas the dimethylaminophenyl group lies *anti* to Cp. Both structures show significant contributions from allenylidene, propargyl cation and quinoid resonance forms (Scheme 22); e.g., the dimethylaminophenyl group is nearly planar; distances along the Ru–Cα–Cβ–Cγ–C$_{aryl}$ chain being 1.95, 1.24, 1.38 and 1.40 Å. Puerta and co-workers have structurally characterized an allenylidene complex with a single phenyl substituent, [Ru(C=C=CHPh)(dippe)(Cp*)][BPh$_4$] [121].

Although, we did not investigate the reaction chemistry of allenylidene complexes, other groups have carried out extensive studies [45]. In particular, Puerta and co-workers have shown that the strongly electron-donating metal moiety [Ru(dippe)(Cp*)]$^+$ direct nucleophiles to Cγ of the allenylidene chain [150], whereas weaker donors, such as [Ru(CO)(PR$_3$)(Cp)]$^+$ allow attack at Cα [151–153]. Remarkably, allenylidene cations of the [Ru(dippe)(Cp*)]$^+$ group react with H$^+$ at Cβ to give dicationic carbyne complexes, [Ru{≡CCH=CRPh)(dippe)(Cp*)]$^{2+}$ (R = H, Ph), which react with weak nucleophiles at Cγ [150].

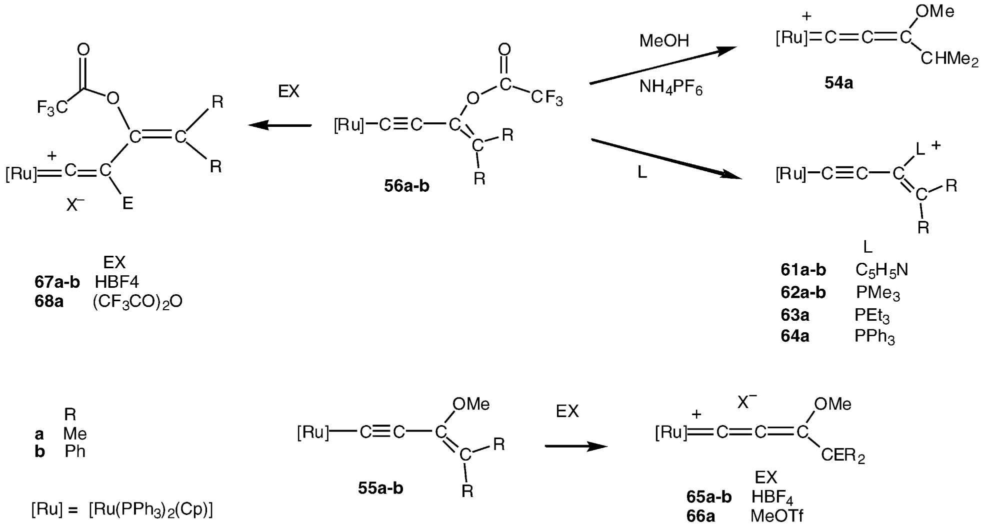
4. Butatrienylidene complexes

Extending allenylidene by one more carbon atom to butatrienylidene posed an interesting synthetic challenge. We chose to approach the problem by using the cumulog of Hughes' vinylidene synthesis, the electrophilic abstraction of OH$^-$ from an acyl ligand [27–29]. Jeff Lomprey and postdoc James Wakefield prepared [Ru(C≡CCOCHR$_2$)(PPh$_3$)$_2$(Cp)] (Scheme 23; R = Me (**52a**), Ph (**52b**)) from [RuCl(PPh$_3$)$_2$(Cp)], Me$_3$SiC≡CCOCHR$_2$ and KF. Although these enynyls react normally at Cβ with protonic acids to give vinylidene complexes, [Ru(C=CHCOCHR$_2$)(PPh$_3$)$_2$(Cp)]$^+$ (**53a–b**) methylation with methyl triflate takes place at the ketone oxygen atom to give methoxyallenylidene complexes, [Ru{C=C=C(OMe)CHR$_2$}(PPh$_3$)$_2$(Cp)]$^+$ (**54a–b**). Reactions with electrophiles (CF$_3$CO)$_2$O, (MeCO)$_2$O, MeOTf, Me$_3$SiOTf, Bu^{t}Me$_2$SiCl (EX in Scheme 23) in the presence of base gave enynyls [Ru{C≡CC(OE)=CR$_2$}(PPh$_3$)$_2$(Cp)] (**55–59**) with potential leaving groups on Cγ. Prior formation of the enolate of **52a–b**, Na$^+$ [Ru(C≡CCOCR$_2$)(PPh$_3$)$_2$(Cp)]$^-$ by using NaN(SiMe$_3$)$_2$ improved the yield in several cases [154,155].

The enynyl complexes **55–59** exhibit ambiphilic behavior. The structures of **56a** and **56b** resemble trifluoroacetate-trapped forms of the butatrienylidene cations (i.e., **60** ↔ **60′**). The unusually long Cγ–O bonds (**56a**, 1.42(2) and 1.66(2) Å in 70% and 30% occupied disordered trifluoroacetate orientations; **56b**, 1.461(6) Å; cf. a typical enol ester, 1.35(2) Å) suggest slight ionization in the solid state. However, NMR spectra of **56a** and **56b** show no evidence for dissociation in solution. Spectra of **56a** show two well-separated methyl resonances (δ 1.86 and 1.67 in CD$_2$Cl$_2$) that do not interchange up to 25 °C in CD$_2$Cl$_2$ or 60 °C in THF-d_8; reversible ionization to the "free" symmetric butatrienylidene cation [Ru{C=C=C=CMe$_2$}(PPh$_3$)$_2$(Cp)]$^+$ (**59a**) would equilibrate the two methyl groups. Trifluoroacetate loss is promoted by additions of Lewis acids, especially for phenyl-substituted **55b–59b**. Fully ionized [Ru{=C=C=C=CPh$_2$}(PPh$_3$)$_2$(Cp)]$^+$ is generated in solution by allowing carboxylate complexes **56a–b** and **57a–b** to react with weak Lewis acids salts of non-coordinating anions, Na[BPh$_4$] or Na[B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$]. The stronger Lewis acid BF$_3$ abstracts methoxide or siloxide from **55a–b**, **58a–b** and **59a–b**. ^{1}H NMR spectra of [Ru{=C=C=C=CPh$_2$}(PPh$_3$)$_2$(Cp)]$^+$ (**60b**)



Scheme 23.



Scheme 24.

generated in this way in CD_2Cl_2 show a downfield shift of the cyclopentadienyl resonance from δ 4.2–4.4 for **55b**–**59b** to δ 5.17 for **60b**, consistent with formation of a cationic complex. ^{13}C NMR signals for the butatrienylidene chain of **60b** are observed at δ_C 335.0 (Cα), 212.9 (Cγ), 155.3 (C_β) and 112.7 (C_δ). Although, single crystals of **60a** or **60b** salts could not be grown, trapping with nucleophiles gives $[Ru\{C{\equiv}CC(L)(=CPh_2)\}(PPh_3)_2(Cp)]^+$ (Scheme 24, L = pyridine (**61b**); PMe_3 (**62b**)). Even without added Lewis acid, trifluoroacetate is displaced from Cγ of **56a–b** by pyridine and PMe_3 to give **61a–b** and **62a–b** (Scheme 24). The methyl-substituted trifluoroacetate **56a** similarly reacts with the larger nucleophiles triethylphosphine and triphenylphosphine to give adducts **63a** and **64a**, and is solvolyzed by methanol to give the methoxyallenylidene complex **54a**.

The enynyls **55a–b** and **56a–b** also exhibit nucleophilic behavior. The regioselectivity of their electrophilic addition reactions depends on the nature of the OE group. The electron-donating methoxide group directs electrophiles to Cδ of **55a–b** (Scheme 24), with HBF_4 giving methoxyallenyldenes **65a–b**. Methyl triflate reacts only with the less crowded methyl compound **55a** to give *tert*-butyl methoxyallenylidene **66a**. The electron-withdrawing trifluoroacetate group directs HBF_4 to Cβ of **56a–b** to give vinylvinylidene complexes **67a–b**. The reaction of **56a** with excess trifluoroacetic anhydride poses a problem during its synthesis. If the amount of trifluoroacetic anhydride added to ketone **52a** (Scheme 23) is not rigorously limited, a mixture of **56a** and **68a**, resulting from trifluoroacetylation of **56a** at Cβ, is obtained. The mixture is spectroscopically confusing and inseparable. Cation **68a** crystallizes as its $[H(CF_3CO_2)_2]^-$ salt, further complicating the spectroscopic properties of the mixture. The structure of **68a**$[H(CF_3CO_2)_2]$ shows that it is a trifluoroacetyl vinylvinylidene salt. Steric crowding around the vinylidene ligand is evidenced by several intramolecular contacts shorter than 3.5 Å. Restricted rotation of the bulky vinylidene ligand accounts for the observation of two PPh_3 resonances in its ^{31}P NMR spectrum at room temperature [154].

Several investigators have since taken up the challenge of preparing longer metallacumulenes, e.g., mononuclear butatrienylidenes [98,129,142,156–159], pentatetraenylidenes [142,160–162] and hexapentaenylidenes [163] Nonetheless, many synthetic challenges remain in this field.

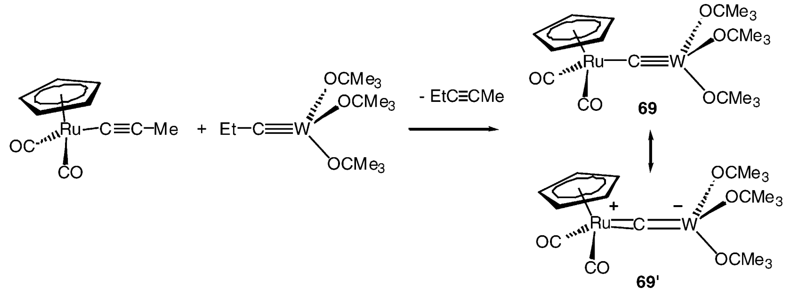
5. Metal carbide complexes

In the 1980s, we realized that the methods for preparing metallacumulenes with a metal at one end of a cumulated carbon chain might also allow us to approach metal carbide complexes, compounds with all-carbon ligands bearing only metal substituents.

Carbide-containing metal cluster complexes with one or two carbon atoms bonded to six, five and even four metal atoms were already well established [164–168], and the first report of a C_2 bridge between two metal atoms had just appeared [169]. The simplest possible carbide complex, a single carbon atom bonded to a mononuclear metal center seemed unlikely at the time, although terminal carbide complexes have more recently been prepared by the deprotonation of molybdenum and tungsten methylidyne complexes [170–172].

5.1. Heteronuclear μ_2-carbide complex

We decided to approach the simpler target of a C_1 ligand bridging two metal centers. By using methods developed in the synthesis of early-late transition metal complexes, such as $[(RO)_3TiRu(CO)_2(Cp)]$ [173–175], we set out to make mixed-metal μ_2-carbide complexes, $[L_nM{\equiv}C{-}M'L'_n]$. The use of Schrock's alkyne metathesis chemistry [176] provided a logical synthetic route

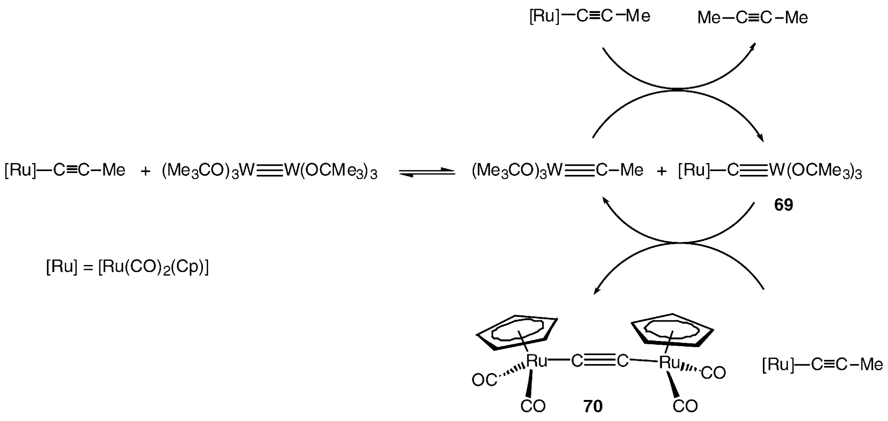


Scheme 25.

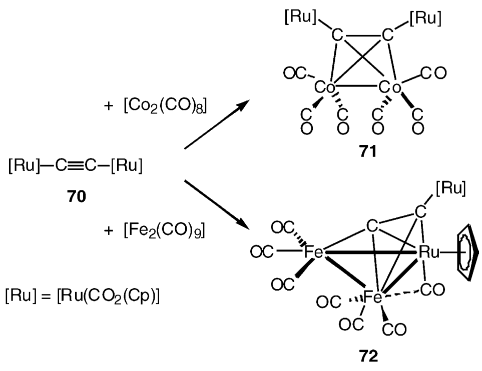
(Scheme 25). Postdoc Stan Latesky found that the Schrock alkylidyne, $[W(\equiv CEt)(OCMe_3)_3]$, reacted smoothly with the ruthenium alkynyl, $[Ru(C\equiv CMe)(CO)_2(Cp)]$, to give $[(Me_3CO)_3W\equiv C{-}Ru(CO)_2(Cp)]$ (**69**) a heteronuclear, μ_2-carbide complex [177]. A ^{13}C NMR resonance for the carbide ligand at δ_C 237.3 ($^1J_{CW}$ = 290.1 Hz) ppm and its crystal structure were more consistent with its description as a ruthenium-substituted alkylidyne (**69**) than a polar bisalkylidene (**69′**). The tungsten-carbon bond length of 1.75(2) Å in **69** is similar to related tungsten–alkylidyne bonds in other $[W(\equiv CR)(OCMe_3)_3]$ complexes (1.75–1.77 Å) [176,178–180], and the Ru–C bond length of 2.09(2) Å is in the range of a typical ruthenium-alkynyl σ-bond (2.0–2.1 Å) [181]. The W–C–Ru bond angle is essentially linear, 177(2)°, and the three ligands on each metal are staggered with respect to those on the other metal. Similar reactions with iron alkynyls, $[Fe(C\equiv CR)(CO)_2(Cp)]$, appeared to give an iron-tungsten carbide like **69**, but it was not stable enough to fully characterize. A few years later, Templeton and co-workers prepared a stable molybdenum–iron carbide complex, $[(Tp)(CO)_2Mo\equiv CFe(CO)_2(Cp)]$ by the reaction of $[(Tp)(CO)_2Mo\equiv CCl]$ (Tp = tris(3,5-dimethylpyrazolyl)borate) with $K[Fe(CO)_2(Cp)]$ [182]. Gladysz has made similar bimetallic compounds with C_3 and C_5 bridges, in some cases by using alkyne metathesis reactions [183–189].

5.2. *Diruthenium μ_2-ethynediyl complex*

Postdoc George Koutsantonis inherited the carbide project from Stan Latesky. In trying to optimize the synthesis of **69**, George discovered that the reaction is very solvent dependent. Whereas, in toluene the principal product is carbide **69**, a second product precipitates in high yield when the reaction is carried out in heptane. This product is $[\{Ru(CO)_2(Cp)\}_2(\mu\text{-}C\equiv C)]$ (**70**, Scheme 26), one of the first transition metal ethynediyl complexes to be fully characterized [190]. Although, a few ethynediyl complexes had been previously reported, they had generally been obtained by salt-elimination reactions [191–203]. The low solubility of **70** in saturated hydrocarbons leads to its isolation in good yield. As volatile 2-butyne is lost (Scheme 26), precipitation of **70** perturbs the alkyne metathesis equilibrium that otherwise would yield more soluble μ_2-carbide **69**. Accordingly, only a catalytic amount of $[W(\equiv CEt)(OCMe_3)_3]$, or more conveniently its tungsten–tungsten-bonded precursor $[W_2(OCMe_3)_6]$, is needed to make ethynediyl **70**. Unfortunately, this alkyne metathesis route to ethynediyls has very narrow scope. Even the small change from $[Ru(C\equiv CMe)(CO)_2(Cp)]$ to $[Fe(C\equiv CMe)(CO)_2(Cp)]$ failed, perhaps because of the instability of the putative intermediate, $[(Me_3CO)_3W\equiv C{-}Fe(CO)_2(Cp)]$. Phosphine-substituted alkynyls $[M(C\equiv CR)(CO)(PR'_3)(Cp)]$ and



Scheme 26.



Scheme 27.

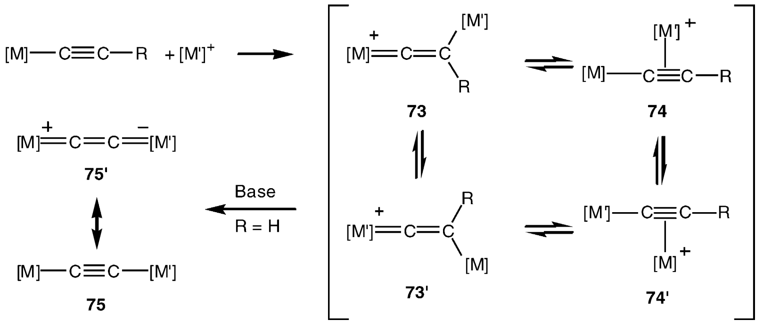
$[M(C{\equiv}CR)(PR'_3)_2(Cp)]$ also failed to give ethynediyl products. The structure of **70** shows a linear Ru–C≡C–Ru chain with typical Ru–C (2.04(1), 2.05(1) Å) and C≡C (1.19(1) Å) bond lengths. Cyclic voltammetry of **70** in MeCN shows two irreversible oxidation waves at 308 and 834 mV versus ferrocene, probably arising from oxidation of the C_2 bridge. Many ethynediyl and longer polyynediyl complexes have since been prepared by other methods. Their physical properties, in particular electron transfer between metal centers, as well as their chemistry have been extensively investigated by Gladysz [93–95,187,204–212], Lapinte [96,97,208,213,214], Akita [215], Koutsantonis [216–218] and others. μ_2-Bicarbide complexes with binding motifs [M=C=C=M] [169,219,220] and [M≡C–C≡M] [221] have also been investigated.

Ethynediyl complexes provide a useful core for the construction of carbon-based metal cluster complexes. We investigated reactions of (**70**) with the cluster-building metal carbonyls, $[Co_2(CO)_8]$ and $[Fe_2(CO)_9]$ [222]. $[Co_2(CO)_8]$ gives a classic alkyne adduct, $[Co_2(\mu_2\text{-}\eta^2\text{-}\{Ru(CO)_2(Cp)\}_2C_2)(CO)_6]$ (**71**, Scheme 27), with a typical, tetrahedral Co_2C_2 core. The two $[Ru(CO)_2(Cp)]$ centers remain bonded to the C_2 ligand in a η^1–η^1 fashion. The reaction of **79** with $[Fe_2(CO)_9]$ forms $[Fe_2Ru_2(\eta^1{:}\mu_4,\eta^2\text{–}C{\equiv}C)(\mu\text{–}CO)(CO)_8(\eta\text{–}C_5H_5)_2]$ (**72**), a bicarbide-centered metal cluster. Its structure shows that one of the ruthenium atoms migrates to become η^2-bonded to the ethynediyl unit in **72**. One ruthenium, two irons and the bicarbide ligand adopt a closed, trigonal–bipyramidal arrangement. A semibridging carbonyl spans the bond between the ruthenium atom in the core and one of the iron atoms. The other $[Ru(CO)_2(Cp)]$ group remains σ-bonded to the ethynediyl bridge.

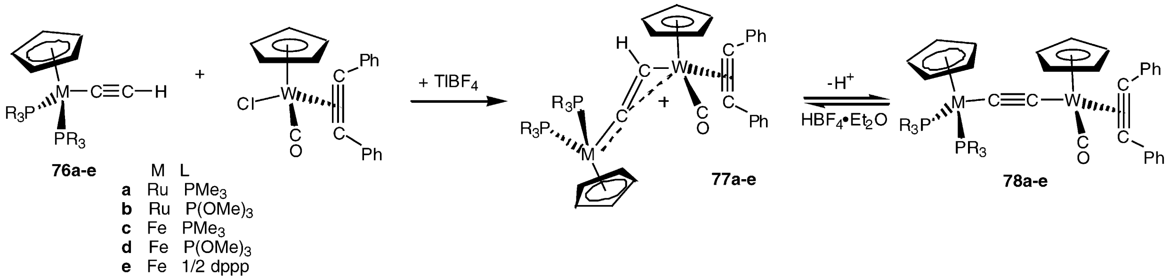
5.3. Mixed-metal ethynediyl complexes

Kevin Frank pursued another approach to the synthesis of heterometallic ethynediyl complexes. The facile reactions of electron-rich metal alkynyls with electrophiles at Cβ led us to consider reactions with transition-metal electrophiles (Scheme 28). An electrophilic addition like that of an organic electrophile would lead to a vinylidene complex with a metal substituent (**73**); alternatively, the metal center could form a η^2-complex with the alkynyl ligand (**74**). Depending on the relative electron-donor/acceptor character of the two metal centers, the two metal centers could exchange positions to **73′** and **74′** via a σ–π–σ–π pathway, like the well-studied rearrangement of alkyne to vinylidene. Finally, for an ethynyl bridge, deprotonation could lead to a heteronuclear ethynediyl complex (**75**), which could be strongly polarized to a cumulated form (**75′**) if one metal is a much stronger electron donor than the other.

We investigated this system by allowing electron-rich iron and ruthenium alkynyls, $[M(C{\equiv}CH)L_2(Cp)]$ (**76a–e**, Scheme 29) to react with electrophilic $[W(CO)(PhC{\equiv}CPh)(Cp)]^+$, generated in situ from $[WCl(CO)(PhC{\equiv}CPh)(Cp)]$ and $TlBF_4$ [223,224]. The products, $[(Cp)L_2M(\mu_2\text{-}C{\equiv}CH)W(CO)(PhC{\equiv}CPh)(Cp)][BF_4]$ (**77a–e**), contain μ_2-ethynyl ligands with unusual spectroscopic properties: δ_H = 8.90–11.20, δ_C = 186.0–198.6 (C≡CH) and 134.2–162.3 (C≡CH) and a weak ν(C≡C) = 1721–1800 cm^{-1}. NMR data are consistent with η^2-coordination of the ethynyl ligand to tungsten as one of a pair of three-electron alkyne ligands. However, the structure of $[(Cp)(PMe_3)_2Ru(\mu_2\text{-}C{\equiv}CH)W(CO)(PhC{\equiv}CPh)(Cp)][BF_4]$ (**77a**) shows significant distortion from normal η^2-coordination. The ethynyl ligand is η^1-bonded to ruthenium with a bond distance slightly shorter than a typical Ru-alkynyl



Scheme 28.



Scheme 29.

bond but longer than a Ru-vinylidene bond. η^2-Coordination to tungsten is very unusual with a 2.05(1) Å distance from W to Cβ of the ethynyl ligand, typical of a η^2-alkyne ligand, but a very long W–Cα distance, 2.53(1) Å. Comparable W–C bonds to the η^2-PhC≡CPh ligand are 2.10(2) and 2.21(2) Å. The very acute C–C–W angle of 97.3(8)° suggests that there is some bonding interaction between W and the Ru-bonded carbon; otherwise this angle would open up to minimize steric contact between the bulky ancillary ligands. The large distortion from normal η^2-alkyne geometry may be caused by a combination of steric interference by the bulky $[Ru(PMe_3)_2(Cp)]$ substituent and electronic distortion toward a tungsten-substituted vinylidene complex induced by the strong electron-donor character of the ruthenium center.

Reversible deprotonation of the μ-ethynyl complexes **77a–e** gives a series of μ-ethynediyl complexes, **78a–e**. ^{13}C NMR spectra of the μ-ethynediyl ligands show δ_C = 168.4–211.2 (M*C*≡C) and 144.5–165.1 (C≡CW), assigned by observing ^{13}C–^{31}P coupling to the phosphorus ligands on iron or ruthenium. Weak ν(C≡C) = 1666–1785 cm^{-1} may be due to the ethynediyl bridge or the η^2-PhC≡CPh ligand. Cyclic voltammograms of **78a–e** show reversible one-electron oxidation potentials (versus ferrocene) between −0.45 V (**78c**) and 0.10 V (**78d**). Irreversible second oxidation waves were observed for most of the compounds between 0.20 V and 1.09 V. Attempts to isolate the cationic radicals and dicationic μ-bicarbides failed.

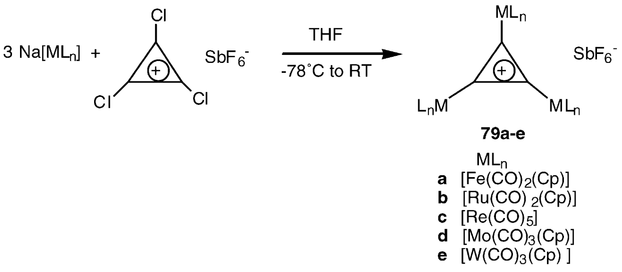
5.4. Tricarbides

The Doering–Moore–Skattebøl reaction is a method for converting an alkene to an allene. The two-step sequence is carried out by adding a dihalocarbene to an alkene, followed by dehalogenation of the resulting dihalocyclopropane. Unfortunately, numerous attempts by Michael Morton and Jeffrey Lomprey to add dihalocarbene to metal vinylidene and metal alkynyl complexes as a means of "growing" the ligand by one carbon atom did not pan out. We devised an alternative route to similar chemistry. Trichlorocyclopropenium ion, accessible by chloride abstraction from tetrachlorocyclopropene, is susceptible to substitution by a variety of nucleophiles. Michael Morton found that $[C_3Cl_3][SbF_6]$ reacts smoothly with the metallates $[Fe(CO)_2(Cp)]^-$, $[Ru(CO)_2(Cp)]^-$, $[Re(CO)_5]^-$, $[Mo(CO)_3(Cp)]^-$ and $[W(CO)_3(Cp)]^-$ to give $[\{ML_n\}_3(\mu_3\text{-}C_3)][SbF_6]$ (Scheme 30, **79a–e**) in about 20–80% yields [225,226]. The structure of the iron complex **79a** reveals a nearly equilateral C_3 ring with a $[Fe(CO)_2(Cp)]$ moiety σ-bonded to each vertex. The lengths of the Fe–C bonds to the cyclopropenyl ring, 1.913–1.919 Å, and the lack of a preferred orientation of the three $[Fe(CO)_2(Cp)]$ symmetry planes with respect to the C_3 plane suggest that Fe to cyclopropenyl π-donation is of minor importance. The spectroscopic properties of cyclopropenium complexes **79a–e** are also consistent with a μ_3-cyclopropenylidene description. Because of their threefold symmetry, NMR spectra display a single *cyclo*-C_3 ring carbon resonance and a single set of resonances for the metal moiety. The ^{13}C NMR shifts of the *cyclo*-C_3 ring range from 224.4 for W (**79e**) to 256.6 for Fe (**79a**).

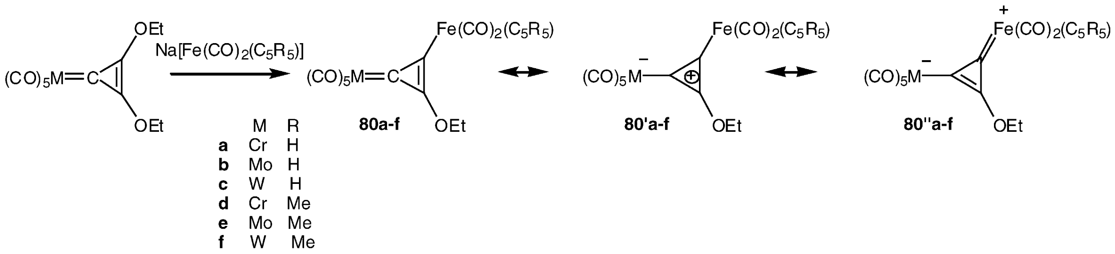
We were not able to develop significant reaction chemistry for iron complex **79a**. It reacts with $Li[BHEt_3]$ and LiMe to give complicated mixtures. It would not add a fourth metal center to the C_3 ring of **79a**, neither by adding a nucleophilic metallate nor by forming a η^3-complex to the C_3 ring.

A spectroscopically characterized C_9 complex, $[\{Fe(CO)_2(Cp)\}_3\{\mu_3\text{-}C_3(C{\equiv}C)_3\}][SbF_6]$, was similarly prepared by the reaction of three equivalents of $[Fe(C{\equiv}CSiMe_3)(CO)_2(Cp)]$ with $[C_3Cl_3][SbF_6]$, but it was not stable enough to isolate in analytically pure form.

We were also able to assemble two different metals around a C_3 kernel. The nucleophilic metallates $[Fe(CO)_2(Cp')]^-$ (Cp' = C_5H_5 or C_5Me_5) displace one of the ethoxides



Scheme 30.

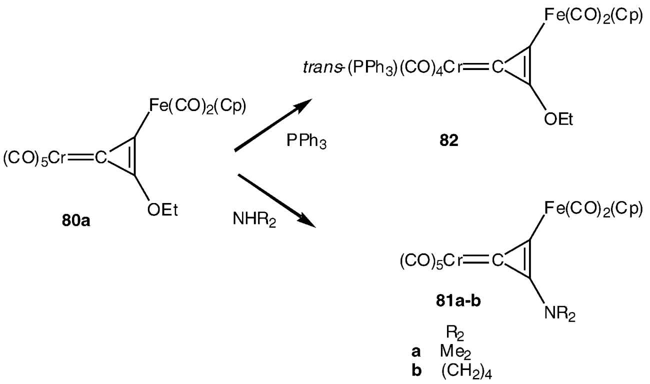


Scheme 31.

from [M(CO)$_5${η^1-*cyclo*-C$_3$(OEt)$_2$}] (M = Cr, Mo, W) [227] to give [M(CO)$_5${μ$_2$-η^1:η^1-C$_3$(OEt)}Fe(CO)$_2$(Cp')] (**80a–f**, Scheme 31) [228,229]. Spectroscopic evidence and structure determinations of **80a** and **80c** suggest that the central C$_3$ ring has a great deal of cyclopropenium character (resonance form **80**$'$). The Cr–C$_3$ (2.066(3) Å) and W–C$_3$ (2.194(5) Å) bonds are slightly longer than those in typical Fischer carbene complexes. The Fe–C$_3$ bonds (**80a**, 1.911(2) Å; **80c**, 1.907(5) Å) fall in the range of Fe–C bonds with partial multiple bonding character as in compound **3a** (resonance from 79$''$). In their ^{13}C NMR spectra, the cyclopropenium carbons of **80a–f** fall at fairly low field. The carbene carbon atom shift depends on the identity of M, resonating at δ_C 226.13 (Cr), 219.33 (Mo) and 207.22 (W). The upfield trend from Cr to W is typical of group 6 carbene complexes. The Fe–C resonance is found at δ_C 200–211 and the O–C resonance at δ_C 212–216, regardless of the identity of M.

We were unable to displace the remaining ethoxide from **80a–f** with a metallate anion, although dissolving **80a** in dimethylamine or pyrrolidine at room temperature replaces ethoxide by an amide (**81a–b**, Scheme 32). Apparently nucleophilic substitution of ethoxide only proceeds when accompanied by a proton transfer. Triphenylphosphine reacts with **80a** in refluxing hexane by replacing the chromium carbonyl *trans* to cyclopropenylidene to give **82**, but leaves the iron center untouched. Compound **80a** is inert to Me$_3$SiI and [Ni(η^4-cycloctadiene)$_2$].

For comparison, reports of a few linear tricarbide complexes have appeared in the literature, including examples from Templeton [230] and Gladysz [183–189]. We are not aware of other studies of *cyclo*-C$_3$ complexes.



Scheme 32.

6. Closing Remarks

Over the years, metallacumulene research provided us with satisfaction and surprises. To my regret, no one in my research group is working on them now, but there are clearly many challenges left in the field. Our interest in carbide complexes ultimately encouraged me to study fullerenes [231–237], carbon nanotubes [238–240] and carbon nano-onions [241], and research in those areas is ongoing.

I am astonished at how metallacumulene chemistry has progressed, since its beginnings about thirty years ago. In this brief, personal overview, the important advances made by many research groups were glossed over. I apologize to those whose work was given short shrift, but a thorough review of the field would fill an entire book.

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