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John P. Selegue
Department of Chemistry
University of Kentucky
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Metallacumulenes and Carbide Complexes
Final Performance Report

DOE support for our research on metallacumulenes and carbide complex began in September, 1985 and ended in December, 1992. We investigated many aspects of transition metal complexes of carbon-rich ligands. These included cumulated transition metal carbene complexes of the types vinylidene ($M=C=CR_2$), allenylidene ($M=C=C=CR_2$) and butatrienylidene ($M=C=C=CR_2$), as well as "naked" carbon ligands C_1, C_2 and C_3. In the last 3 years, we began to put some of our effort into studying the fullerenes, a series of newly discovered, molecular allotropes of carbon. Finally, we investigated initial aspects of the coordination chemistry of thiophenes, from the perspectives of (1) modeling the transition-metal-catalyzed hydrodesulfurization of fossil fuels, and (2) development of metal-doped, polythiophene-based polymers.

I. Vinylidenes

A. Iron, Ruthenium and Osmium

1. Alkyne to vinylidene rearrangements

The ethyne to vinylidene ($HC\equiv CH \rightarrow C=CH_2$) rearrangement is a fundamentally important transformation which is strongly endothermic in the gas phase. On certain metal surfaces and metal complexes, ethyne converts spontaneously to vinylidene. For example, reactions of $[M(PR_3)_2(Cp)]^+$ (M = Fe, Ru, Os) sources with 1-alkynes normally lead to vinylidene complexes $[M(C=CR'H)(PR_3)_2(Cp)]^+$ without observed $[M(\eta^2\text{-}R'C\equiv CH)(PR_3)_2(Cp)]^+$ intermediates, especially for large phosphine ancillary ligands such as PPh_3. However, we discovered that metastable η^2-ethyne complexes of certain sterically nondemanding $[M(PR_3)_2(Cp)]^+$ metal centers could be isolated, and the rearrangements of these complexes to their more stable vinylidene forms could be followed by NMR. This study was begun by Ph.D. student Kevin Frank and completed by Ph.D. student Jeffrey Lomprey. They found (Scheme 1) that the complexes $[MX(PR_3)_2(Cp)]$ (MX = FeI, RuCl; PR_3 = $P(OMe)_3$, PMe_3, PMe_2Ph, 1/2 *o*-$(PMe_2)_2C_6H_4$, 1/2 $Me_2PCH_2CH_2PMe_2$) react with ethyne in polar media to form metastable η^2-ethyne complexes (**1**, R = H) which gradually rearrange to the thermodynamically favored vinylidene form (**2**, R = H). For 1-alkynes such as propyne or phenylethyne, vinylidene complexes **2** were isolated with no trace of η^2-ethyne species.

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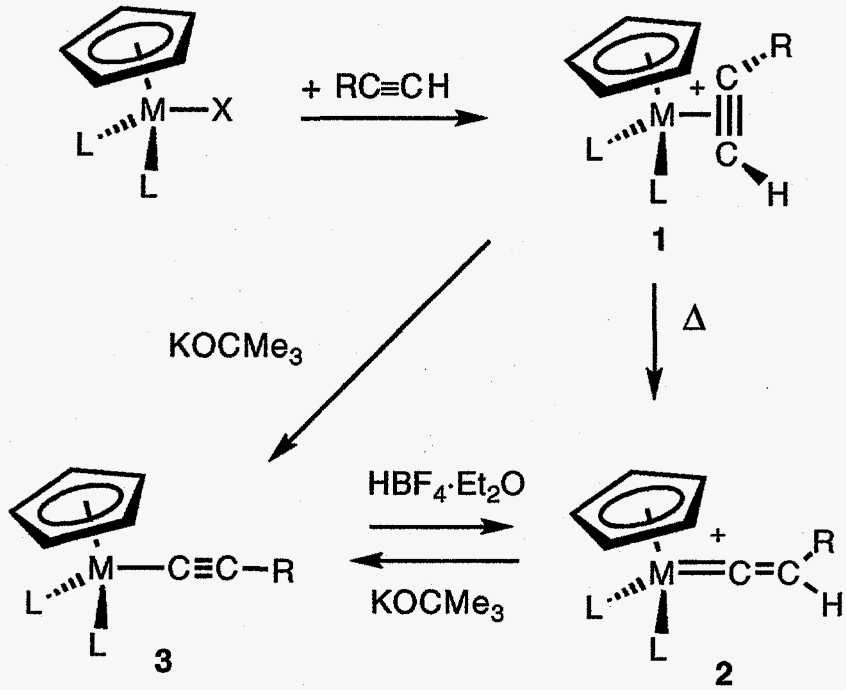


Scheme 1

The kinetics of conversion of the η^2-ethyne complexes **1** to their vinylidene isomers **2** were studied by using NMR spectroscopy. In Table 1, the size of the ligand is expressed as Θ_{cor}, a version of Tolman's original cone angles modified by Ernst to more accurately reflect the large volume swept out by flexible phosphine or phosphite ligands. The rates and activation parameters show that the rate of alkyne to vinylidene rearrangement is faster on iron than ruthenium, and is faster for larger ancillary ligands.

Table 1. η^2-Ethyne to Vinylidene Kinetics

M	L	Θ_{cor}	E_a (kcal·mol^{-1})	$\Delta H^‡$ (kcal·mol^{-1})	$\Delta S^‡$ (cal·mol^{-1})	$t_{1/2}$ (T)
Fe	$P(OMe)_3$	128°	21(2)	20(2)	-9(4)	21 min (38°C)
Ru	$P(OMe)_3$	128°	25(3)	21.5(9)	-2(5)	40 min (65°C)
Ru	PMe_2Ph	122°	18.8(7)	18.2(8)	-11(2)	18 min (60°C)
Ru	PMe_3	118°		20.5(6)[1]	-18(2)[1]	~5 h (60°C)[1]

We also studied the rates of displacement of the η^2-ethyne ligands from $[M(\eta^2\text{-}HC{\equiv}CH)(PR_3)_2(Cp)]^+$ complexes. Ethyne was displaced from $[Fe(\eta^2\text{-}HC{\equiv}CH)(PMe_3)_2(Cp)]^+$ by acetone more rapidly than rearrangement to the vinylidene form occurred. The displacement of the ethyne ligand from $[Fe(\eta^2\text{-}HC{\equiv}CH)L_2(Cp)]^+$ (L = $P(OMe)_3$, PMe_3, 1/2 pdmp) by acetonitrile occurs readily. The rates of displacement were monitored spectrophotometrically. Activation parameters obtained in this study along with similar results from an analogous system are presented in

Table 2. Similar to the rearrangement reactions, the rates and activation parameters show that ethyne displacement is faster from iron than ruthenium, and is faster for larger ancillary ligands.

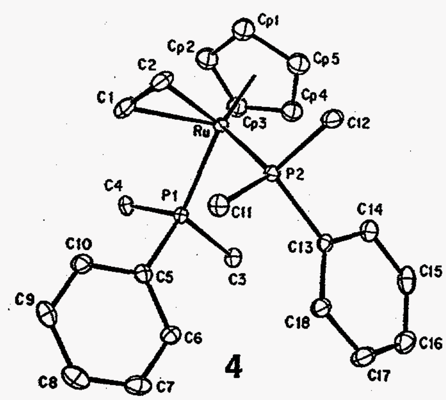
Table 2. Activation Parameters for
$[M(\eta^2\text{-}R'C{\equiv}CH)(PR_3)_2(Cp)]^+ + L \rightarrow [ML(PR_3)_2(Cp)]^+ + R'C{\equiv}CH$

M	R'	PR_3	L	E_a (kcal/mol)	$\Delta H^‡$ (kcal/mol)	$\Delta S^‡$ (cal/K·mol)
Fe	H	1/2 pdmp	CH_3CN	27.1(6)	28.7(4)	20(1)
Fe	H	$P(OMe)_3$	CH_3CN	29.6(6)	27.1(4)	13(1)
Fe	H	PMe_3	CH_3CN	a	a	a
Ru	H	PMe_3	CD_3CN		31(1)[1]	9(4)[1]

a. Too rapid to measure by NMR.

2. Structure

We have long been interested in whether there is any structural basis for the instability of η^2-alkyne complexes on d^6 metal centers. Structures of isomeric $[Ru(\eta^2\text{-}HC{\equiv}CH)(PMe_2Ph)_2(Cp)][BF_4]$ (**4**) and $[Ru(C{=}CH_2)(PMe_2Ph)_2(Cp)][BF_4]$ (**5**) were both determined by X-ray diffraction. Aside from the difference in the geometry of the carbon atoms of the C_2H_2 ligands , the structures are nearly identical.[2] (H atom positions were not determined.) The η^2-HC≡CH ligand of **4** is not "tilted" or distorted in any way which indicates that it is predisposed to arrange.



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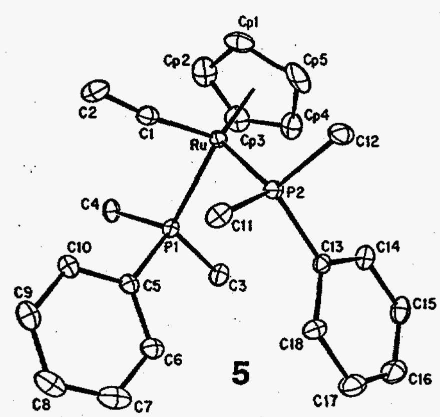

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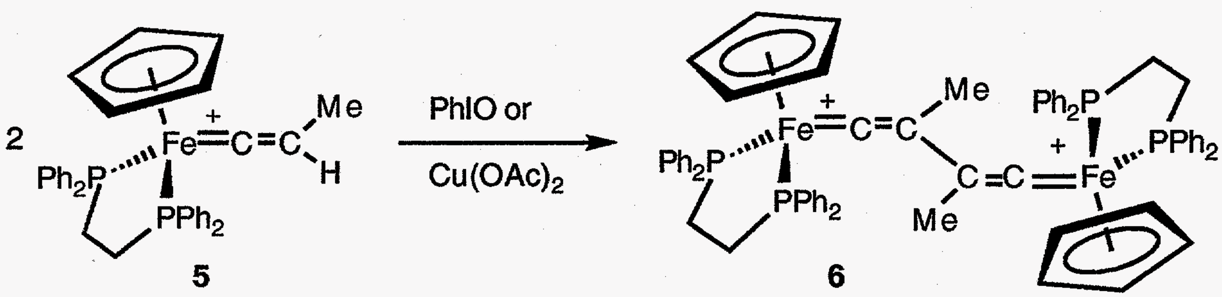
3. Reactions

a. Deprotonation. Both cationic η^2-ethyne and vinylidene complexes are readily deprotonated to give neutral ethynyl complexes (**3**, Scheme 1). $[Fe(C{\equiv}CH)\{P(OMe)_3\}_2(Cp)]$ (**7**) was structurally characterized by X-ray diffraction. The most important structural feature is the linear geometry of the ethynyl ligand; i.e., the Fe-C≡C angle is 176.9(2)° The Fe-C_α bond (1.909(2) Å) of **7** is very slightly shorter than the average Fe-C_α distance of 1.922 Å for three similar iron alkynyls

$[Fe(C{\equiv}CR)(CO)_2(\eta^5\text{-}C_5R'_5)]$ (R = H, Ph; R' = H, Me), which may indicate a stronger metal-carbon bond. The C≡C distance (1.199(3) Å) falls in the range of free acetylenes (1.20 Å), and organometallic alkynyls (1.18-1.25 Å). (The hydrogen atom on the ethynyl ligand was located during the difference Fourier but could not be refined.) The iron to phosphorus distances in $[Fe(C{\equiv}CH)\{P(OMe)_3\}_2(Cp)]$, 2.120(1) Å and 2.125(1) Å, are slightly shorter than the average of fourteen other iron trimethylphosphite complexes, 2.156 Å. We very recently completed the structure of $[Fe(C{\equiv}CH)(Ph_2PCH_2CH_2CH_2PPh_2)(Cp)]$. There are no significant differences in the bonding of the ethynyl ligand to iron; i.e., the donor ability of the phosphorus ancillary ligands is not reflected in the structures.

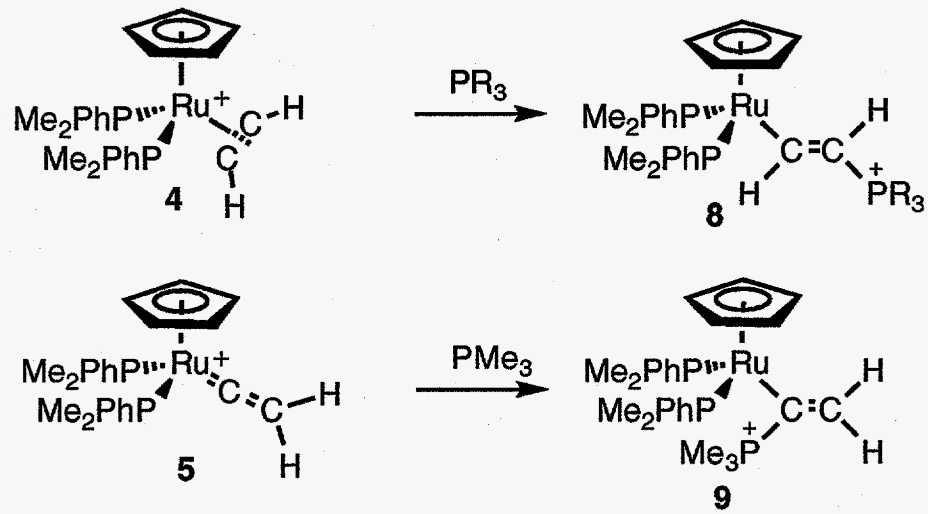
Protonation of the alkynyl complexes gave only vinylidene, never η^2-ethyne products (Scheme 1). The η^2-ethyne to vinylidene conversion can be carried out by stepwise deprotonation of **1** to give $[M(C{\equiv}CH)(PR_3)_2(Cp)]$ (**3**), followed by protonation to give exclusively vinylidene isomer **2**.

b. Coupling. Oxidatively coupling of the iron vinylidene complex **5** by either iodosobenzene or copper (II) acetate gave the diiron divinylidene complex **6** (Scheme 2). This novel carbon-carbon bond forming reaction reverses the usual regioselectivity of copper-promoted 1-alkyne couplings. Whereas normally an alkyne RC≡CH is oxidatively coupled in a tail-to-tail fashion to RC≡C-C≡CR, rearrangement of the alkyne to its vinylidene form on iron prior to coupling leads to a head-to-head coupling.[3]



Scheme 2

c. Nucleophilic additions. The reaction between $[Ru(\eta^2\text{-}HC{\equiv}CH)\text{-}(PMe_2Ph)_2(Cp)]^+$ (**4**, Scheme 3) and PR_3 results in the β-phosphonium vinyl complexes $[Ru(HC{=}CHPR_3)(PMe_2Ph)_2(Cp)]^+$ (R = Me (**8a**), Ph (**8b**)). An α-regioisomer of **8a**, $[Ru(C(PMe_3){=}CH_2)(PMe_2Ph)_2(Cp)]^+$ (**9**), is prepared by the reaction of $[Ru(C{=}CH_2)(PMe_2Ph)_2(Cp)]^+$ (**5**) and PMe_3. The structures of **8a** and **9** were confirmed by X-ray crystallography. ^{13}C NMR spectra of the phosphonium complexes **8** and **9** reveal unusually small coupling constants between C_α and the nuclei directly bonded to C_α. For C_α of **8a**, δ_C = 207.5 ppm and $^1J_{HC}$ = 121.5 Hz. This low value of $^1J_{HC}$ for C_α is in the normal range for a sp^3 hybridized carbon atom (114 to 130 Hz) without heteroatom attachment, rather than in the expected sp^2 range (148 to 160 Hz). For C_α of **9**, δ_C = 147.7 ppm and $^1J_{PC}$ = 11.4 Hz; *c.f.*, $^1J_{PC}$ = 70.4 Hz for C_β of **8a**. The unusual spectroscopic and structural properties of **8** and **9** lead us to conclude that the small $^1J_{HC}$ and $^1J_{PC}$ values of the C_α resonances are due to some alkylidene character at the ruthenium-C_α center.



Scheme 3

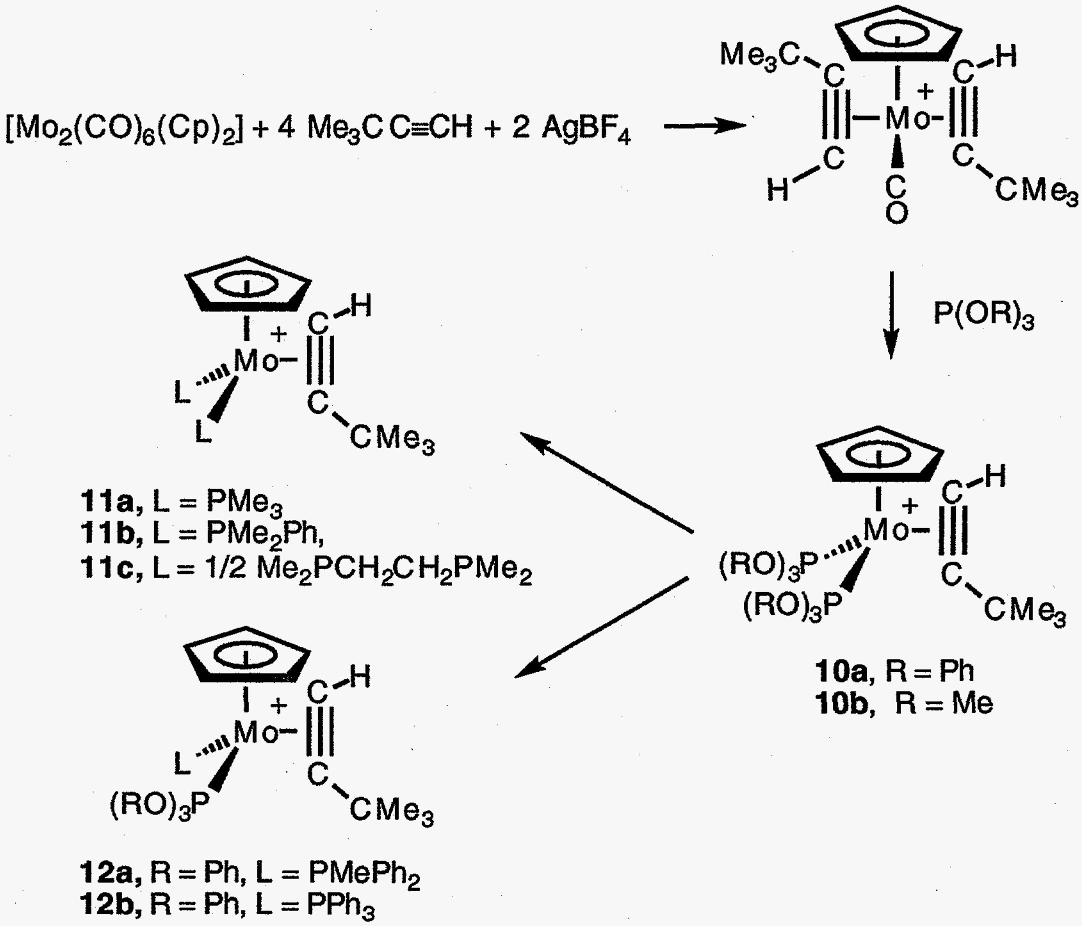
B. Molybdenum and tungsten.

1. η^2-Alkyne, alkynyl and vinylidene complexes

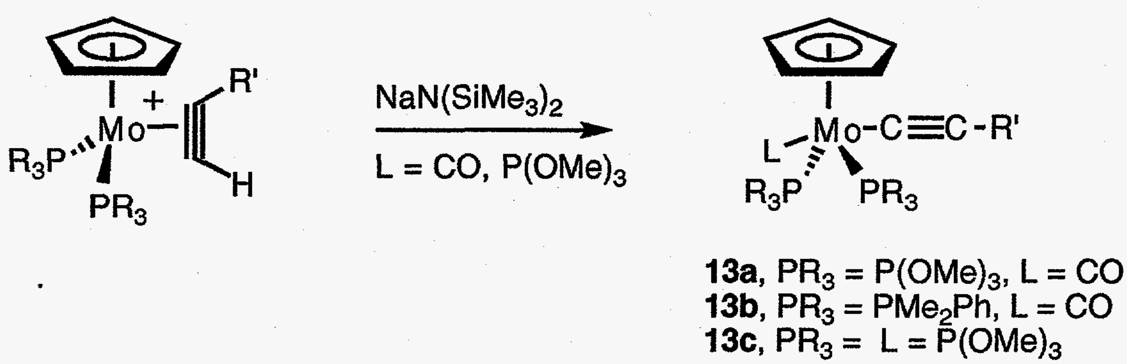
Beginning in about 1986, we turned our attention to the vinylidene chemistry of the group 6 metals. We developed methods for the synthesis of a variety of electron-rich molybdenum and tungsten alkynyls Scheme 4). $[Mo(HC{\equiv}CCMe_3)\{P(OPh)_3\}_2(Cp)][BF_4]$ (**10a**), which can be prepared in nearly quantitative yield from $[Mo(HC{\equiv}CCMe_3)_2(CO)(Cp)][BF_4]$ and $P(OPh)_3$, proved to be a key intermediate in the preparation of several molybdenum alkyne complexes. Simple substitution reactions give $[Mo(HC{\equiv}CCMe_3)(PR_3)_2(Cp)][BF_4]$ (**11**, $PR_3 = PMe_3$, PMe_2Ph 1/2 $Me_2PCH_2CH_2PMe_2$) in excellent yield. Larger phosphines give mixtures with $[Mo(HC{\equiv}CCMe_3)(PR_3)\{P(OPh)_3\}(Cp)][BF_4]$ (**12**, $PR_3 = PMePh_2$, PPh_3) as the principal component.

Molybdenum alkynyls *trans*-$[Mo(C{\equiv}CCMe_3)L(PR_3)_2(Cp)]$ (**13a-c**, Scheme 5) were prepared by deprotonation of $[Mo(HC{\equiv}CCMe_3)(PR_3)_2(Cp)]^+$ (**10** and **11**) using $NaN(SiMe_3)_2$ in the presence of CO or $P(OMe)_3$. The chelate complex *cis*-$[Mo(C{\equiv}CCMe_3)(CO)(Ph2PCH{=}CHPPh2)(Cp)]$ (**14**) was prepared similarly. Attempts to prepare mixed η^2-alkyne/alkynyl complexes $[M(C{\equiv}CCMe_3)(\eta^2\text{-}RC{\equiv}CR)\{P(OMe)_3\}_2(Cp)]$ by deprotonation of $[Mo(HC{\equiv}CCMe_3)\{P(OMe)_3\}_2(Cp)][BF_4]$ in the presence of alkynes $MeC{\equiv}CMe$ or $Me_3COC{\equiv}COCMe_3$ failed. Two electron-rich tungsten alkynyls *trans*-$[W(C{\equiv}CPh)(CO)\{P(OMe)_3\}_2(Cp)]$ (**15**) and *cis*-$[W(C{\equiv}CPh)(CO)(Ph_2PCH_2PPh_2)(Cp)]$ (**16**) were prepared by photolytic substitution of $[W(C{\equiv}CPh)(CO)_3(Cp)]$.

Electron-rich metal alkynyls $[M(C{\equiv}CR)(CO)L_2(Cp)]$ (**13 – 16**, Scheme 6) react with $HBF_4{\cdot}Et_2O$ or methyl triflate to give stable vinylidene complexes $[M(C{=}CRE)(CO)L_2(Cp)]^+$ (**17 – 20**) in the same manner as iron group alkynyls. The molybdenum complexes are much more labile than their tungsten congeners; e.g., the molybdenum analogs of **18a** and **18b** were unstable above about 0°C. The structure of *trans*-[W(C=CMePh)(CO){$P(OMe)_3\}_2$(Cp)][PF_6] (**18b**) was determined by X-ray



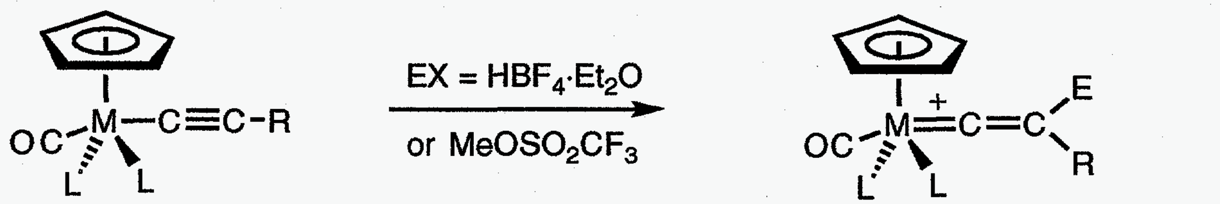
Scheme 4



Scheme 5

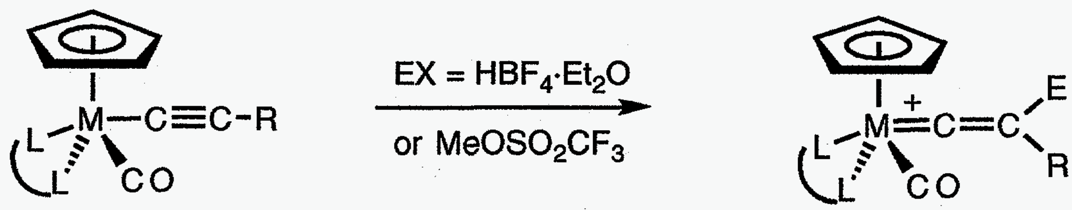
diffraction . The W-C(vinylidene) bond is short (1.947(6) /) and the planar vinylidene ligand lies in the symmetry plane of the $[W(CO)\{P(OMe)_3\}_2(Cp)]^+$ moiety.

Molybdenum alkynyls without carbonyl ancillary ligands, i.e. $[Mo(C{\equiv}CCMe_3)(PR_3)_3(Cp)]$, are so basic that it is more convenient to isolate them in



13b, M = Mo, L = PMe_2Ph, R = CMe_3
15, M = W, L = $P(OMe)_3$, R = Ph

17c, M = Mo, L = PMe_2Ph, E = H
17d, M = Mo, L = PMe_2Ph, E = Me
18a, M = W, L = $P(OMe)_3$, E = H
18b, M = W, L = $P(OMe)_3$, E = Me



14, M = Mo, L_2 = $Ph_2PCH{=}CHPPh_2$, R = CMe_3
16, M = W, L_2 = $Ph_2PCH_2PPh_2$, R = Ph

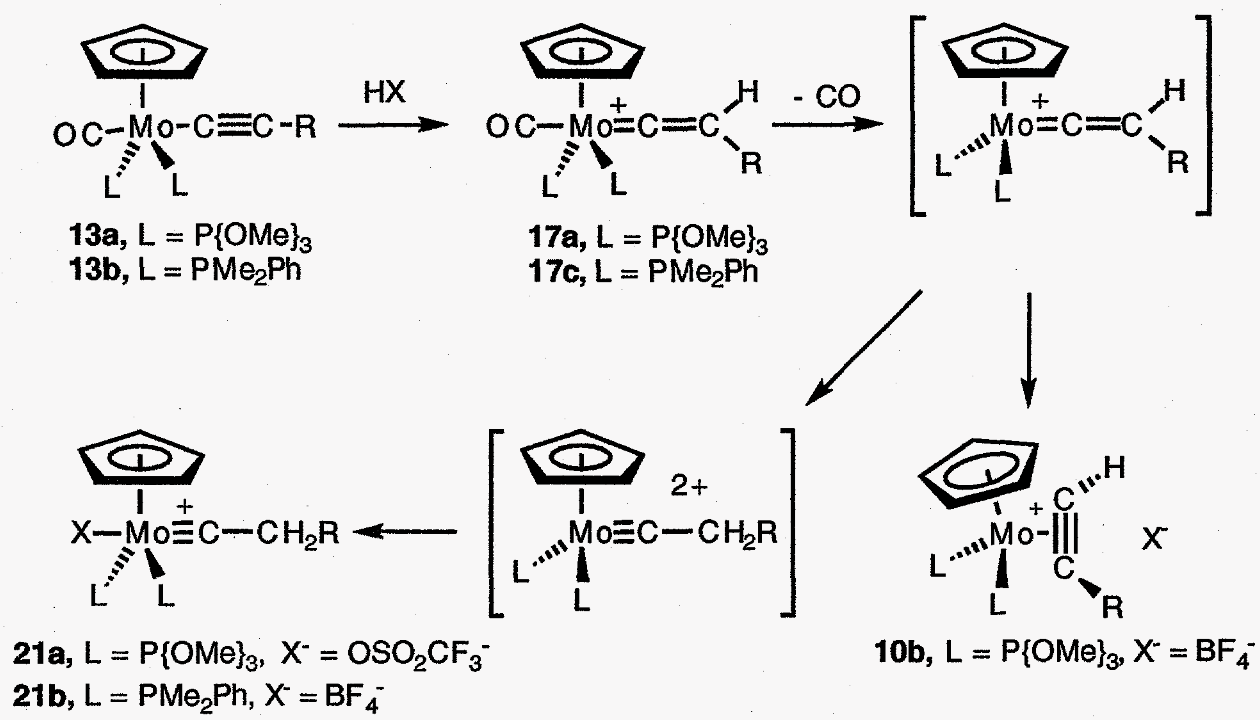
19, M = Mo, E = Me
20, M = W, E = Me

Scheme 6

their protonated (vinylidene) form. For example, the crude reaction mixture from the deprotonation of $[Mo(HC{\equiv}CCMe_3)\{P(OMe)_3\}_2(Cp)][BF_4]$ in the presence of PMe_3 gives *trans*-$[Mo(C{=}CHCMe_3)(PMe_3)\{P(OMe)_3\}_2(Cp)][PF_6]$ in 63% yield when worked up by chromatography on alumina/NH_4PF_6. Incoming $P(OMe)_3$ behaves similarly to give [Mo(C=CHCMe3)$\{P(OMe)_3\}_3(Cp)][PF_6]$.

Cationic molybdenum vinylidenes $[Mo(C{=}CHCMe_3)LL'_2(Cp)]^+$ are stable only when the ancillary ligand set LL'_2 is strongly electron donating; e.g., the PMe_2Ph complexes **17c** and **17d** in Scheme 6 are stable at room temperature. When the ancillary ligand set LL'_2 includes only CO and phosphites, the vinylidene complexes are labile but can be observed by NMR at low temperature. Protonation of $[Mo(C{\equiv}CCMe_3)(CO)\{P(OMe)_3\}_2(Cp)]$ (**13a**, Scheme 7) with $HBF_4{\cdot}Et_2O$ at -78°C gives *trans*-$[Mo(C{=}CHCMe_3)(CO)\{P(OMe)_3\}_2(Cp)][BF_4]$ (**17a**), which decarbonylates to $[Mo(HC{\equiv}CCMe_3)\{P(OMe)_3\}_2(Cp)][BF_4]$ (**10b**) above 0°C. The departing CO ligand can be replaced by an anionic ligand *before* rearrangement of the vinylidene ligand back to its η^2-alkyne form. Specifically, protonation of $[Mo(C{\equiv}CCMe_3)(CO)\{P(OMe)_3\}_2(Cp)]$ (**13a**) with excess triflic acid (HOTf) at -78°C gives the alkylidyne complex *trans*-$[Mo({\equiv}CCH_2CMe_3)(OTf)\{P(OMe)_3\}_2(Cp)][OTf]$ (**21a**). Protonation of $[Mo(C$ʃ$CCMe)(CO)(PMe_2Ph)_2(Cp)]$ (**21b**) with excess $HBF_4{\cdot}Et_2O$ similarly gives *trans*-$[Mo({\equiv}CCH_2CMe_3)(BF_4)(PMe_2Ph)_2(Cp)][BF_4]$ (**21b**). This result is surprising, since the probable intermediate *trans*-[Mo(C=CHCMe$_3$)-

$(CO)(PMe_2Ph)_2(Cp)]^+$ (**17c**) is stable at room temperature. Evidently, a second protonation occurs at C_β (or possibly at Mo) which renders the CO ligand labile, leading to its replacement by the very weak, anionic ligand BF_4^-.

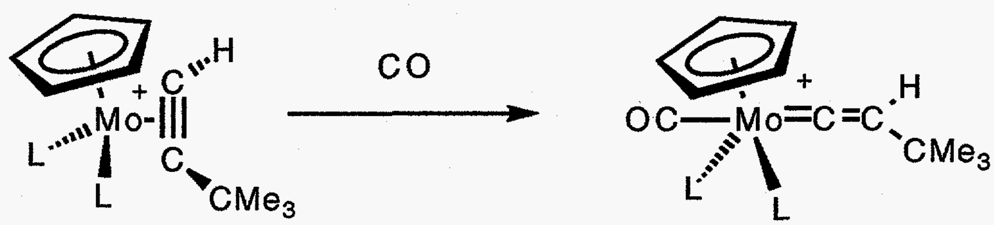


Scheme 7

The stable alkyne complexes $[M(HC{\equiv}CR)L_2(Cp)]^+$ (M = Cr, Mo, W) are "isomeric" with, but have two fewer metal-based electrons than, the stable vinylidene complexes $[M'(HC{\equiv}CR)L_2(Cp)]^+$ (M' = Fe, Ru, Os). We decided to try to "pump" two extra electrons into the Mo and W complexes, to see whether this would induce rearrangement to the vinylidene form.[4] Exposure of $[Mo(\eta^2\text{-}HC{\equiv}CCMe_3)L_2(Cp)][BF_4]$ (**11a**, **11b**, Scheme 8) to one atm of CO effects conversion to *trans*-$[Mo(C{=}CHCMe_3)(CO)L_2(Cp)][BF_4]$ (**22a, 22b**) in 70-84% yield. The reaction is not very general, failing for ancillary phosphites ($P(OMe)_3$, $P(OPh)_3$), bulkier phosphines ($PMePh_2$) and a chelating diphosphine ($Me_2PCH_2CH_2PMe_2$). Similarly, only CO as incoming ligand cleanly induces the alkyne to vinylidene rearrangement. PF_3 reacts with $[Mo(HC{\equiv}CCMe_3)\{P(OMe)_3\}_2(Cp)][BF_4]$ to give a mixture of *trans*-[Mo-$(C{=}CHCMe_3)(PF_3)\{P(OMe)_3\}_2(Cp)][BF_4]$ and $[Mo(HC{\equiv}CCMe_3)(PF_3)\{P(OMe)_3\}$-$(Cp)][BF_4]$ (NMR characterization). Isonitriles $RN{\equiv}C$: (R = CMe_3, 2,6-$C_6H_3Me_2$) react with $[Mo(HC{\equiv}CCMe_3)\{P(OMe)_3\}_2(Cp)][BF_4]$ to give a mixtures containing little to no vinylidene products (by NMR). The complexes $[Mo(HC{\equiv}CCMe_3)L_2(Cp)][BF_4]$ (L = $P(OMe)_3$ or PMe_2Ph) do not react with KCN.

2. Electrochemical and chemical reductions of d^4 alkyne complexes

We attempted to convert d^4 alkyne complexes $[M(HC{\equiv}CR)L_2(Cp)]^+$ (M = Mo, W) to d^6 vinylidene complexes $[M(C{=}CHR)L_2(Cp)]^-$ by direct two-electron reduction reactions. Green and coworkers had independently produced vinylidene anions of this type by the deprotonation of alkylidynes $[M({\equiv}CCH_2R)L_2(Cp)]$, and trapped them with electrophiles.[5] Cyclic voltammetry of the alkyne complexes $[Mo(HC{\equiv}CCMe_3)$



11a, L = PMe_3
11b, L = PMe_2Ph

22a, L = PMe_3
22b, L = PMe_2Ph

Scheme 8

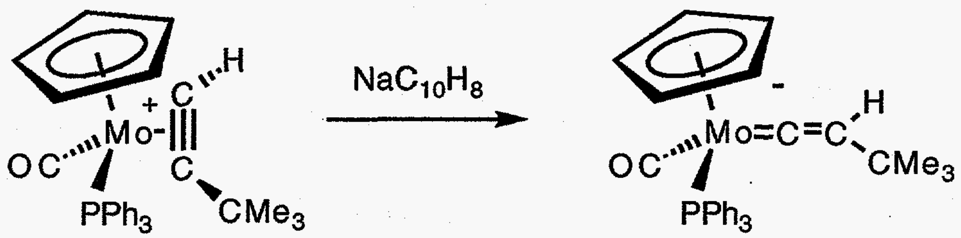
$L_2(Cp)][BF_4]$ (**10a**, L = $P(OPh)_3$; **10b,** L = $P(OMe)_3$; **11a**, L = PMe_3; and L_2 = dpe) shows two one-electron reduction waves. In each case, the first reduction (*ca.* -1.1 V *vs.* Ag/AgCl) is completely reversible at scan rates as low as 10 mV/s, but the second reduction (*ca.* -1.9 V *vs.* Ag/AgCl) is reversible only at high scan rates (above 500 mV/s). This second reduction never becomes completely reversible because of the chemical step that follows. For the relatively electron-deficient complex $[Mo(HC{\equiv}CCMe_3)(CO)(PPh_3)(Cp)][BF_4]$, three irreversible reduction waves are seen at -0.6, -1.4, and -1.8 volts *vs.* Ag/AgCl.

Controlled-potential electrolysis of $[Mo(HC{\equiv}CCMe_3)\{P(OMe)_3\}_2(Cp)][BF_4]$ (**10b**) slightly below its first reduction potential in the presence of the spin trap phenyl-α-*tert*-butylnitrone (PBN) produces an adduct whose ESR spectrum displays a triplet of doublets due to splitting by ^{14}N (S = 1) and ^1H (S = 1/2). The absence of additional coupling suggests that the electrochemically produced radical is carbon-based. This data, combined with the reversible nature of the electrochemical reduction even at slow scan rates, leads us to suggest that the radical produced by one-electron reduction is $[Mo(HC{\equiv}CCMe_3)\{P(OMe)_3\}_2(Cp)]^\bullet$. (Preliminary studies by Vernon Parker of Utah State University suggest that the radical rapidly and reversibly dimerizes, but the study was complicated by adsorption on the electrode.) The site of PBN trapping is probably at the alkyne ligand. Attempts to trap the radical with a hydrogen atom using $SnHBu_3$ failed.

Cyclic voltammetry suggested that the anions produced by two-electron reduction of $[Mo(HC{\equiv}CCMe_3)L_2(Cp)]^+$ rearranged to vinylidenes $[Mo(HC{\equiv}CCMe_3)L_2(Cp)]^-$. Reduction of $[Mo(HC{\equiv}CCMe_3)(CO)(PPh_3)(Cp)][BF_4]$ with excess sodium naphthalenide, followed by protonation with H_2O and chromatography, led to a disappointing 4% yield of $[Mo({\equiv}CCH2CMe_3)(CO)(PPh_3)(Cp)][BF_4]$ (Scheme 9). Attempts to improve this yield, and to prepare solutions of

$[Mo(C{=}CHCMe_3)\{P(OMe)_3\}_2(Cp)]^-$ by controlled-potential electrolysis or by chemical reduction using sodium or lithium naphthalenide failed.

Several other physical studies of the $[Mo(HC{\equiv}CR)L_2(Cp)]^+$ system were carried out, including ^{95}Mo NMR spectra and ESCA measurements on several species. ASED calculations (a modified extended Hückel method) on the cation, neutral radical, and anion in both alkyne and vinylidene forms supported the idea that the cation should be more stable in the η^2-alkyne form, the radical should be marginally



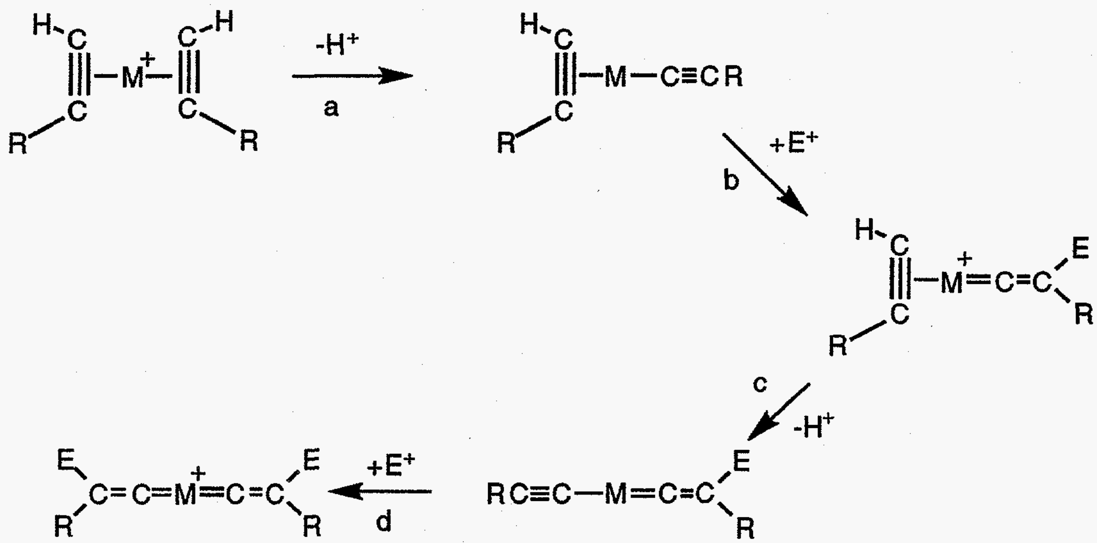
Scheme 9

more stable in the η^2-alkyne form, and the anion should be more stable in the vinylidene form.

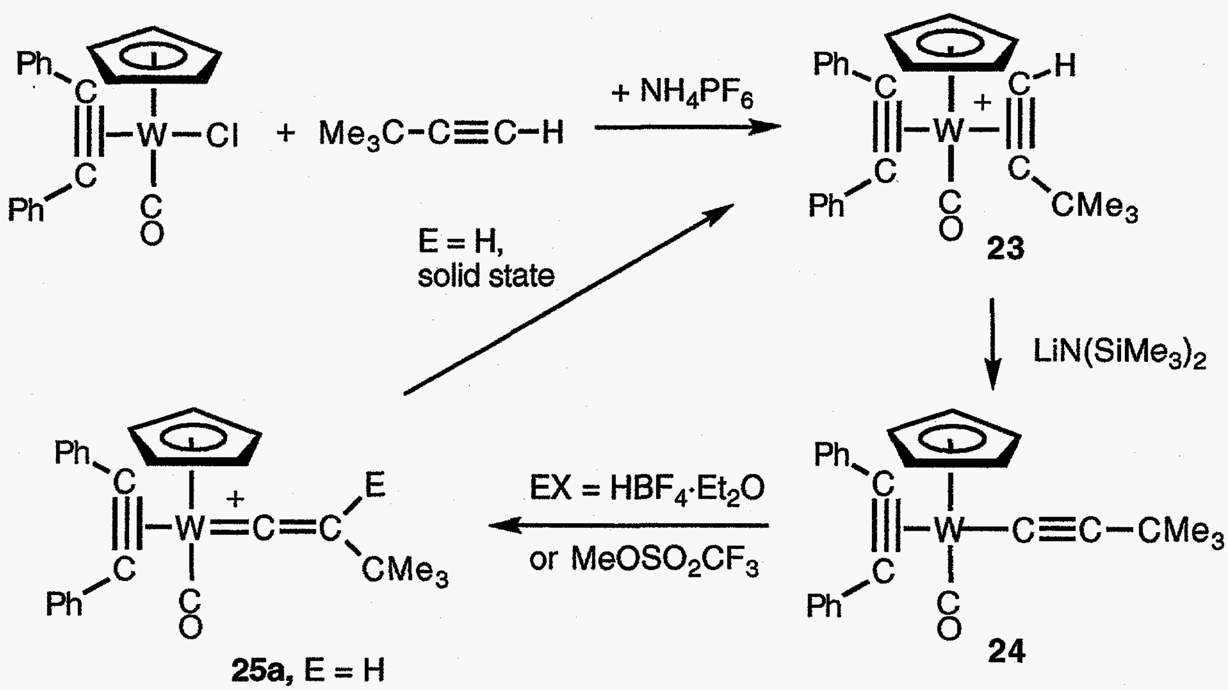
3. Tungsten vinylidene complexes with alkyne ancillary ligands

We are interested in generating a complex with more than one vinylidene ligand on a single metal center. Lippard and coworkers have shown that two carbonyl ligands may be reductively coupled with difficulty the possibility, but that two isocyanides are significantly easier to couple;[6,7] periodicity suggests that two vinylidenes should be even easier to couple. Optimistically, two 1-alkynes could be coupled in a unique fashion on a metal by rearrangement to two vinylidenes, followed by reductive coupling in a "head-to-head" fashion.

A logical approach to a bis(vinylidene) complex is to coordinate two 1-alkynes to a metal center, followed by their sequential conversion to vinylidenes *via* deprotonation and electrophilic addition (Scheme 10). We first needed to develop a method for the preparation of a complex with both an alkyne and a vinylidene ligand. To simplify the chemistry, we initially "locked" the alkyne ligand in η^2-form by using a diarylalkyne ancillary ligand. Scheme 11 shows our method for the preparation of asymmetric tungsten 1-alkyne/diarylalkyne complexes. Stepwise conversion of the 1-alkyne ligand of **23** to a vinylidene proceeds satisfactorily *via* deprotonation with $LiN(SiMe_3)_2$ followed by reaction of the resulting alkynyl complex **24** with $HBF_4{\cdot}Et_2O$ or MeOTf. The low symmetry of these compounds introduces stereochemical complexity to their chemistry. For example, bis(alkyne) complex **23** is produced as a mixture of *syn* and *anti* alkyne orientation isomers, which interconvert slowly at room temperature (observed by ^1H NMR). X-ray crystal structure analysis of alkyne/vinylidene complex **25b** established its structure, but was complicated by the existence of two independent molecules in the unit cell, with orientationally disordered vinylidene ligands.

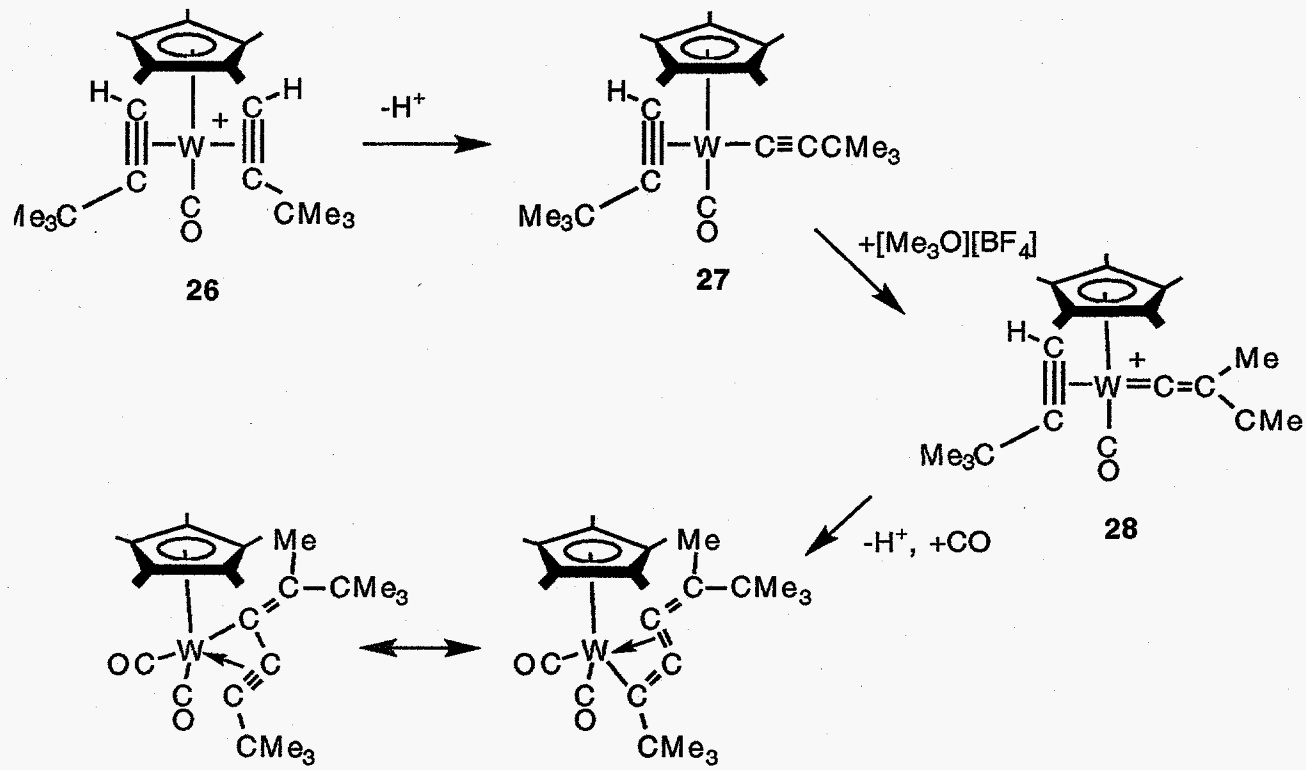


Scheme 10



Scheme 11

Extending this chemistry to bis(1-alkyne) complexes was not straightforward (Scheme 12). $[W(BF_4)(CO)_3(Cp^*)]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) reacts with *tert*-butyl acetylene to give the tungsten bis(alkyne) complex $[W(CO)(\eta^2\text{-}HC{\equiv}CCMe_3)_2(Cp^*)][BF_4]$ (**26**). Deprotonation of **26** with KH gives alkynyl/alkyne complex $[W(C{\equiv}CCMe_3)(CO)(\eta^2\text{-}HC{\equiv}CCMe_3)(Cp^*)]$ (**27**). Methylation of **27** with $[Me_3O][BF_4]$ gives alkyne/vinylidene cation $[W(C{=}CMeCMe_3)(CO)(\eta^2\text{-}HC{\equiv}CCMe_3)(Cp^*)][BF_4]$ (**28**). Deprotonation of **28** with $NaN(SiMe_3)_2$ under one atm of CO at -78°C gives $[W(CO)_2(\eta^3\text{-}Me_3CC{\equiv}CC{=}CMeCMe_3)(Cp^*)]$ (**29**), containing an unusual η^3-enynyl ligand. X-ray crystallographic characterization of **29** was consistent with spectroscopic data suggesting that a η^3-enynyl description (resonance form **29a**) is more appropriate than an alternative η^3-trienyl description (**29b**). The facility of the insertion of a coordinated vinylidene into an adjacent metal-carbon bond is surprising. This finding suggests that any method for the synthesis of a bis(vinylidene) complex in which a vinylidene ligand is *cis* to a σ-bonded carbon ligand will fail.[8]



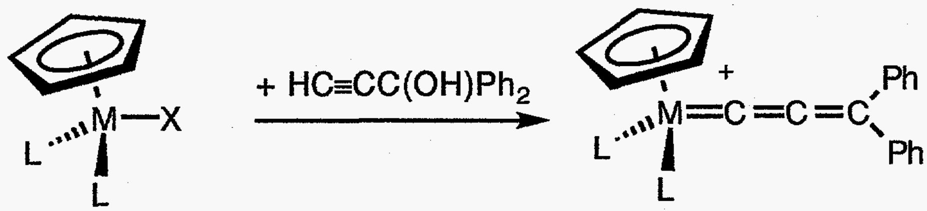
Scheme 12

Attempts to enter related group 6 alkyne-vinylidene systems were not successful. For example, we could not prepare chromium bis(alkyne) complexes $[Cr(CO)(\eta^2\text{-}RC{\equiv}CR)_2(Cp^*)]^+$. Tungsten bis(alkyne) complexes $[WX(\eta^2\text{-}RC{\equiv}CR)_2(Cp)]^+$ (X = Cl, I) were amazingly inert, resisting several efforts to convert them to alkynyls $[W(C{\equiv}CR')(\eta^2\text{-}RC{\equiv}CR)_2(Cp)]$.

II. Allenylidenes

For several years, we have utilized reactions of 1-alkyn-3-ols $HC{\equiv}C(OH)RR'$ with $[MXL_2(\eta\text{-}C_5H_5)]$ (M = Fe, Ru, Os; X = halide) to prepare cationic allenylidene complexes $[M(C{=}C{=}CRR')L_2(\eta\text{-}C_5H_5)]^+$ *via* the dehydration of intermediate hydroxyvinylidene complexes [M{C=CHC(OH)RR'}L_2(η-C_5H_5)]$^+$. We investigated the scope of this reaction at both the metal and the organic end.

The reported reaction of [RuCl(PMe_3)$_2$(Cp)] with HC≡CC(OH)Ph_2/NH_4PF_6 gives the allenylidene cation [Ru(C=C=CPh_2)(PMe_3)$_2$(Cp)][PF_6] (**30a**, Scheme 13), which is very stable by virtue of the strong electron-donor ability of the [Ru(PMe_3)$_2$(Cp)] group.[9] The less electron-rich [RuCl{P(OMe)$_3$}$_2$(Cp)] also reacts smoothly with HC≡CC(OH)Ph_2/NH_4PF_6 to give stable [Ru(C=C=CPh_2)-{P(OMe)$_3$}$_2$(Cp)][PF_6] (**30b**). Comparison of the crystal structures of **30a** and **30b** shows *little* difference in bond distances and angles, despite the much lower donor ability of P(OMe)$_3$ compared to PMe_3. This finding suggests that the propargylic resonance form, with the cationic charge localized at C_γ, is so dominant in these complexes that the electron-donor ability of the metal group is only of minor importance. However, there is a limit to how electron-deficient the metal center may be. The reaction of [RuCl(CO)$_2$(Cp*)] with HC≡CC(OH)Ph_2/$AgBF_4$ produces a deep purple complex, presumably [Ru(C=C=CPh_2)(CO)$_2$(Cp)][BF_4], which decomposes during workup to [Ru(CO)$_3$(Cp*)][BF_4]. Either the complex is extremely air- or water-sensitive and the allenylidene ligand is oxidized to a carbonyl, or intermolecular ligand exchange is very rapid, leading to a buildup of the very stable tricarbonyl complex plus unidentified byproducts.



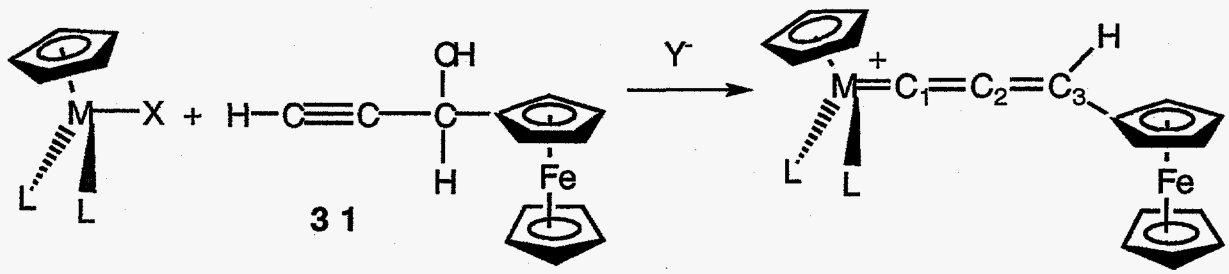
30a, L = PMe_3
30b, L = P(OMe)$_3$

Scheme 13

Utilizing strongly electron-releasing organic substituents at C_3 has enabled us to prepare several stable *monosubstituted* allenylidene complexes. Reactions of the transition metal halide complexes [MXL_2(η-C_5H_5)] (M = Fe, X = I, L_2 = dppe; M = Ru, X = Cl, L = PPh_3; M = Os, X = Br, L = PPh_3) with the alkynol HC≡C(OH)(H)(Fc) (**31**, Scheme 14, Fc = ferrocenyl) in the presence of $TlBF_4$ gave the first monosubstituted allenylidene complexes [M(C=C=CHFc)L_2(η-C_5H_5)][BF_4] (**32a**: M = Ru, L = PPh_3; **33**: M = Fe, L_2 = dppe; **34**: M = Os, L = PPh_3). Similarly the reaction of **31** with [RuCl(PPh_3)$_2$(η-C_5H_5)] and NH_4PF_6 in methanol gave [Ru(C=C=CHFc)(PPh_3)$_2$(η-C_5H_5)][PF_6] (**32b**). These highly colored compounds were characterized by spectroscopic and electrochemical techniques and in the case of **32b** by a single crystal X-ray structure determination. Cyclic voltammetry in MeCN in the presence of [Bu^n_4N][ClO_4] at 100 mV·s^{-1} shows a reversible ferrocenyl-based one-electron oxidation. Also observed are irreversible oxidation and reduction processes. The latter may be a result of reductive, intermolecular carbon-carbon coupling.

Similarly, reactions of [RuCl(PPh_3)$_2$(η-C_5H_5)] with HC≡C(OH)(H)(*p*-C_6H_4R)/NH_4PF_6 gave [Ru(C=C=CH-*p*-C_6H_4R)(PPh_3)$_2$(η-C_5H_5)][PF_6] (Scheme 15:

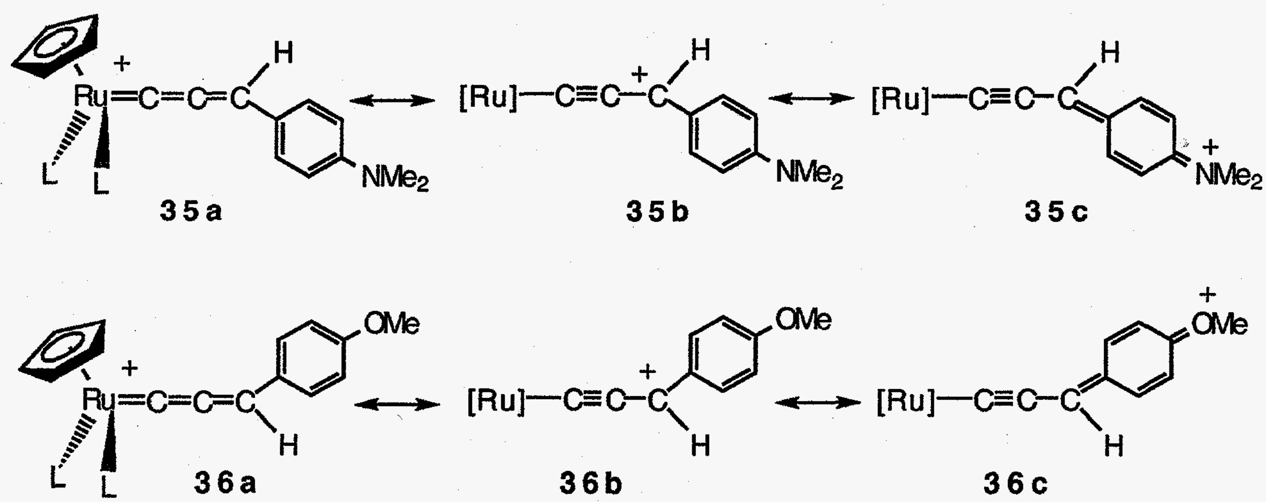
35, R = NMe_2; **36**, R = OMe). These allenylidene complexes are brilliantly colored; the dimethylamino complex is brilliant blue, and the methoxy compound is deep rose-red. Both compounds were characterized spectroscopically and by an X-ray structure determination. Clearly, the propargylic resonance forms are major contributors to the compounds' stability. The bond length alternation in the allenylidene chains is most consistent with the descriptions [Ru–C≡C–C^+H-*p*-C_6H_4R] (**35b** and **36b**). The dimethylamino group in **35** is planar, suggesting that the electron lone pair on nitrogen is conjugated into the aromatic ring, i.e., the quinoid forms **35c** and **36c** are



Complex	M	L_2	Y^-
32a	Ru	$(PPh_3)_2$	BF_4^-
32b	Ru	$(PPh_3)_2$	PF_6^-
33	Fe	dppe	BF_4^-
34	Os	$(PPh_3)_2$	BF_4^-

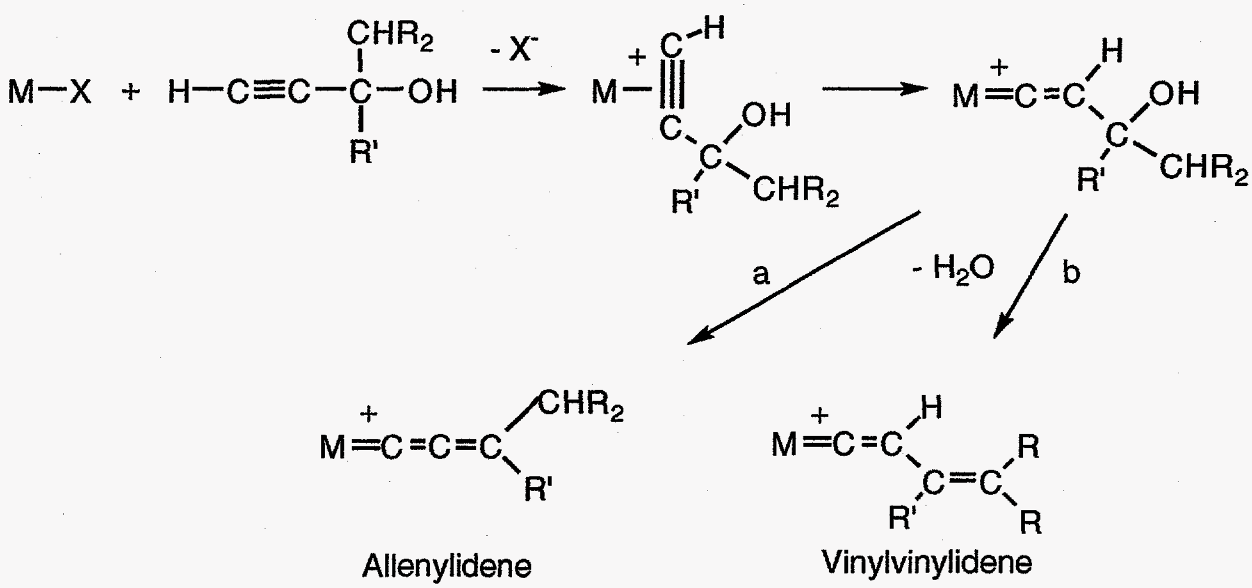
Scheme 14

also significant resonance contributors. In both compounds, the allenylidene plane is roughly coincident with the $[RuL_2(Cp)]$ symmetry plane, but in **35** the aryl group is *anti* to the cyclopentadienyl ligand (like the ferrocenyl compound), whereas in **36** the aryl group is *syn* to the cyclopentadienyl ligand.



Scheme 15

In forming complexes **30** and **32–36**, there are no hydrogen atoms on C_δ, so there is only one possible direction of dehydration of putative 3-hydroxyvinylidene intermediates, leading to allenylidenes. We were interested in establishing whether dehydration of a hydroxyvinylidene intermediate **37** (Scheme 16) would give an allenylidene (path a) or a vinylvinylidene (path b) product when there is a choice between two dehydration directions. Reactions of $[RuCl(PMe_3)_2(Cp)]$ with 1-ethynylcyclohexanol or 1-ethynylcyclopentanol and NH_4PF_6 lead to cationic *cycloalkenylvinylidene* complexes $[Ru\{C{=}CH\text{-}cyclo\text{-}C{=}CH(CH_2)_n\}(PMe_3)_2(Cp)][PF_6]$

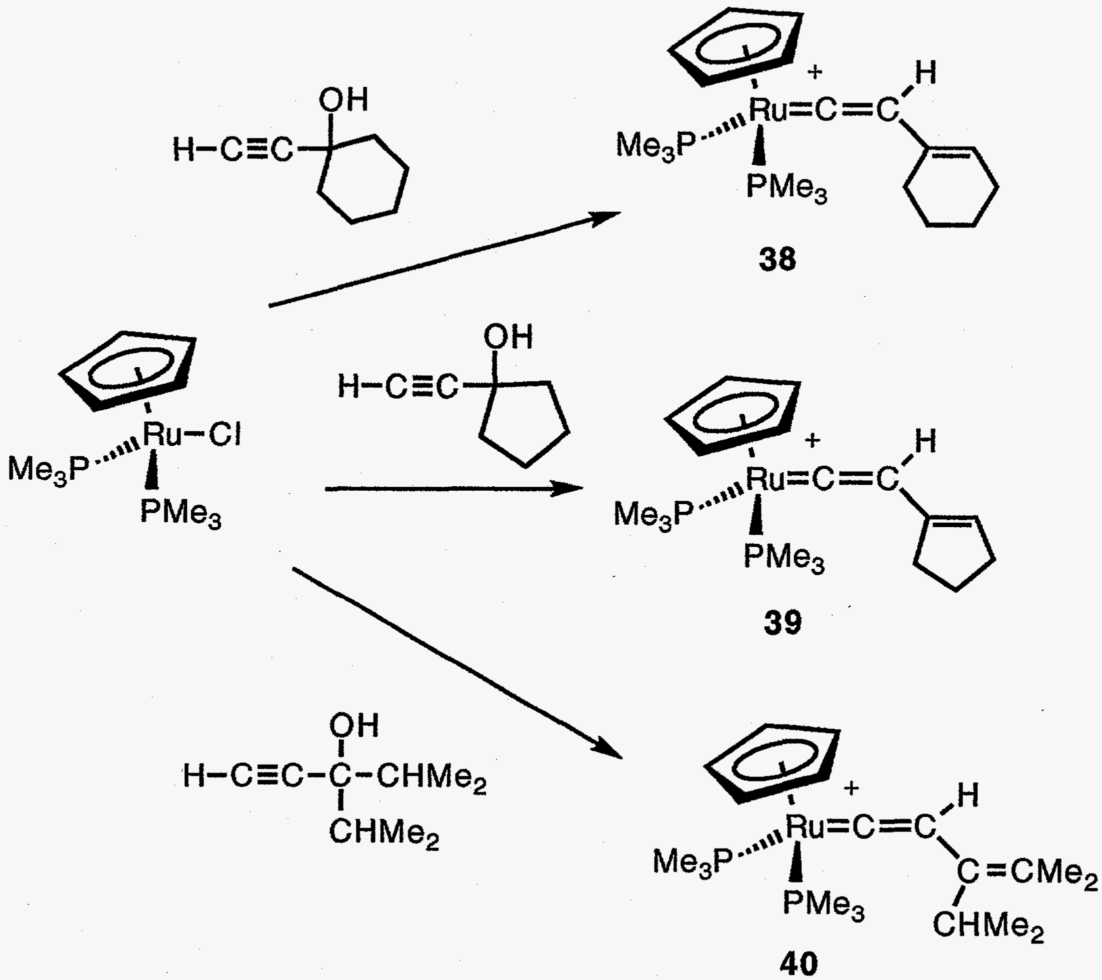


Scheme 16

(Scheme 17: **38**, n = 4, and **39**, n = 3) in *ca.* 80% yield. Similarly, 3-isopropyl-4-methyl-1-pentyn-3-ol ($HC{\equiv}CC(OH)(CHMe_2)_2$) produces $[Ru\{C{=}CHC(CHMe_2)\text{-}({=}CMe_2)\}(PMe_3)_2(Cp)][PF_6]$ (**40**) in 77% yield. The structure of **38** was determined by X-ray diffraction. The molecule contains a cyclohexenylvinylidene ligand bonded to the ruthenium atom by a short Ru-C bond (1.843(7) Å). The vinylvinylidene products were spectroscopically characterized; the C_α signals at very low field (δ_C = 346 to 356 ppm) are especially diagnostic. There is a clear preference for *vinylvinylidene,* rather than allenylidene, formation in this system.

III. Butatrienylidenes

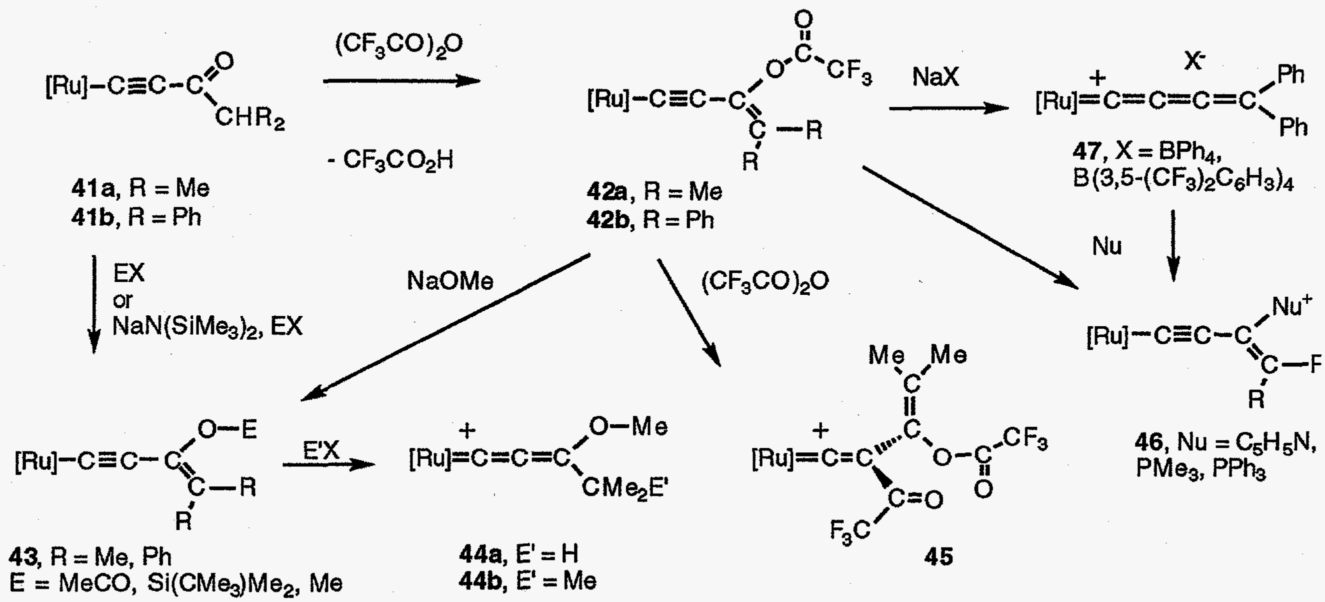
Having investigated aspects of vinylidene and allenylidene complexes, we trained our sights on the next higher cumulogs, butatrienylidene complexes ($M{=}C{=}C{=}C{=}CR_2$). Reactions of $[RuCl(PPh_3)_2(Cp)]$ ($Cp = \eta\text{-}C_5H_5$) with $Me_3SiC{\equiv}CCOCR_2H$ and KF in methanol result in the formation of ketoalkynyl complexes $[Ru(C{\equiv}CCOCHMe_2)(PPh_3)_2(Cp)]$ (Scheme 18, **41a**, R = Me; **41b**, R = Ph) in about 80% yield. **41a** and **41b** react with trifluoroacetic anhydride at ambient temperature to give enynyls $[Ru\{C{\equiv}CC(OCOCF_3)CR_2\}(PPh_3)_2(Cp)]$ (**42 a** and **42b**), whose structures were determined by X-ray crystallography. They displayed unusually long C_γ-O bond lengths, suggestive of partial ionization in the solid state.. **42a** and **42b** may be considered as cationic ruthenium butatrienylidene complexes trapped by the attachment of a trifluoroacetate anion to C_γ of the $[Ru{=}C{=}C{=}C{=}CR_2]^+$ chain. Several related enynyl complexes $[Ru\{C{\equiv}CC(OE)({=}CR_2)\}(PPh_3)_2(Cp)]$ (**43**) were prepared by reactions of **41a**, **41b** or their acylate anions obtained by deprotonation with $NaN(SiMe_3)_2$, with MeCOCl, $SiCl(CMe_3)Me_2$ or $MeOSO_2CF_3$. The enynyl complexes **42** and **43** exhibit ambiphilic behavior in additions of



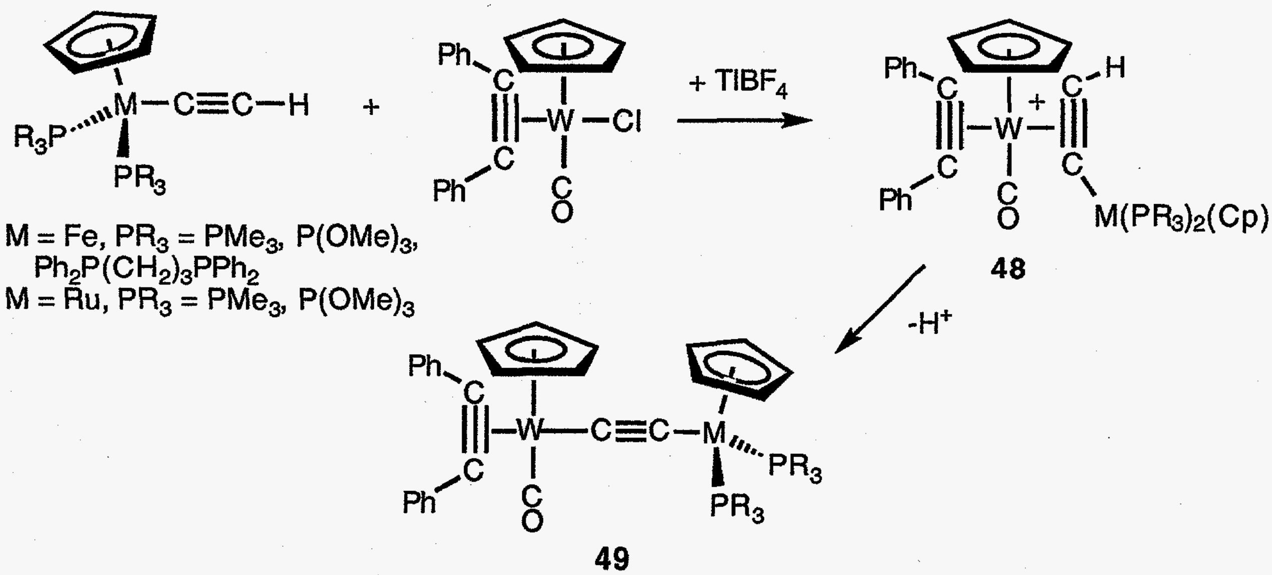
Scheme 17

electrophiles and nucleophiles. The regiochemistry of electrophilic addition reactions depends on the nature of the OE group. The electron-donating methoxide group of $[Ru\{C∫CC(OMe)({=}CMe_2)\}(PPh_3)_2(Cp)]$ (**43**) directs the electrophiles $HBF_4{\cdot}Et_2O$ and methyl triflate to the δ-carbon, forming allenylidene complexes **44a** and **44b**. The electron-withdrawing trifluoroacetate group of **42a** directs trifluoroacetic anhydride to the β-carbon, forming the vinylidene complex **45**. Trifluoroacetate is readily displaced from **42a** and **42b** by nucleophiles, giving $[Ru\{C{\equiv}CC(OMe)({=}CMe_2)\}(PPh_3)_2(Cp)]$ (**43**) with methoxide or adducts $[Ru\{C{\equiv}CC(Nu)({=}CR_2)\}(PPh_3)_2(Cp)]^+$ (**46**, Nu =

C_5H_5N, PMe_3). The novel "naked" butatrienylidene cation [Ru{=C=C=C=CPh_2}(PPh_3)$_2$(Cp)]$^+$ (**47**) was generated in reactions of enynyl complexes [Ru{C≡CC(OE)(=CPh_2)}(PPh_3)$_2$(Cp)] (**43b** or **43**, R = Ph) with Lewis acids. The sodium salts Na[BPh_4] and Na[B(3,5-(CF_3)$_2C_6H_3$)$_4$] are sufficiently Lewis acidic to effect ionization of complexes bearing labile leaving groups (OE = $OCOCF_3$, OCOMe), whereas complexes bearing less labile leaving groups (OE = OMe, OSiBu^{t}Me$_2$) require the use of the stronger Lewis acid boron trifluoride. These [Ru{=C=C=C=CPh_2}(PPh_3)$_2$(Cp)]$^+$ salts were too reactive to isolate, but were



Scheme 18, [Ru] = [Ru(PPh_3)$_2$(Cp)]



Scheme 19

characterized by ^1H NMR and ^{13}C NMR spectroscopy, and by trapping with triphenylphosphine and pyridine to give [Ru{C≡CC(L)(=CPh-$_2$)}$(PPh_3)_2$(Cp)][X] (**46**, R = Ph, L = PPh_3, NC_5H_5).

IV. Carbides

1. C_1 and μ-C_2 complexes

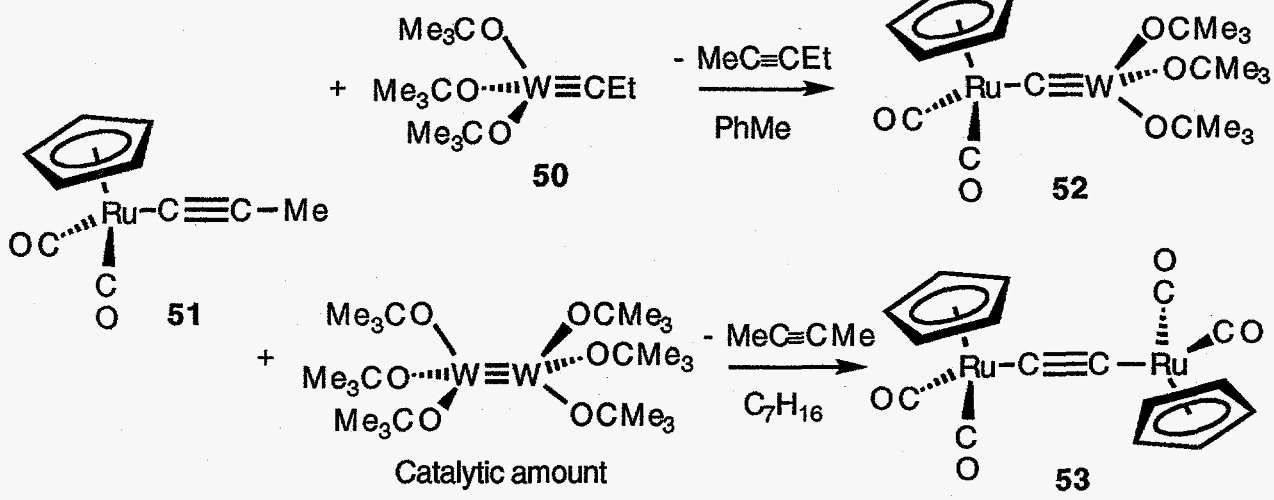
Reactions of the ethynyl complexes [M(C≡CH)$(PR_3)_2$(Cp)] with the transition metal electrophile, [WCl(CO)(PhC≡CPh)(Cp)]/$TlBF_4$, gave a series of heterobimetallic μ-ethynyl complexes (**48**, Scheme 19). A X-ray crystal structure determination of [(Cp)$(PMe_3)_2$Ru(μ-C≡CH)W(CO)(PhC≡CPh)(Cp)][BF_4] revealed a geometry in which the ethynyl bridge is σ-bonded to ruthenium, but distinctly distorted from η^2 geometry at tungsten. The nearly linear Ru-C1-C2 angle of 163(1)° combined with the long W-C1 distance of 2.53(1) Å suggest that the solid-state structure more closely resembles a cationic ruthenium complex with a tungsten-substituted vinylidene ligand, rather than a cationic tungsten complex with a ruthenium-substituted alkyne ligand as suggested by spectroscopic evidence

Deprotonation of the μ-ethynyl complexes at low temperature gave the heterobimetallic ethynediyl complexes [(Cp)$(PR_3)_2$M(μ-C≡C)W(CO)(PhC≡CPh)(Cp)] (**49**). Attempts to make heterobimetallic bicarbide complexes $[M{=}C{=}C{=}M']^{2+}$ *via* chemical and electrochemical oxidations of the complexes **49** were not successful.

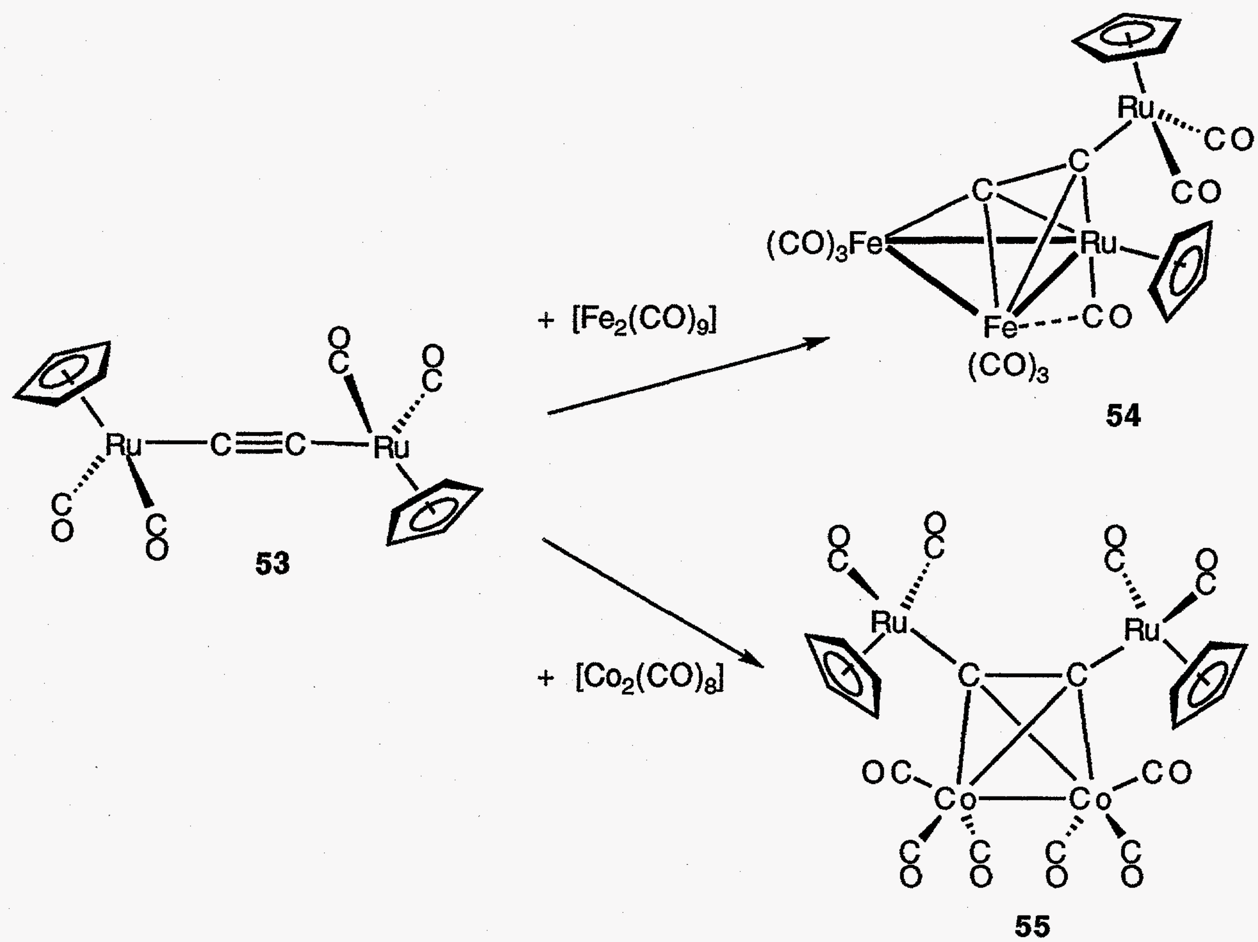
The tungsten propylidyne complex **50**, developed by Schrock and Chisholm,[10,11] metathesizes alkynes efficiently. The ruthenium propynyl complex **51** reacts with a stoichiometric amount of **50** in toluene solution to give the ruthenium-substituted alkylidyne complex **52** (Scheme 20). The crystal structure of **52** shows a single carbon atom bridging ruthenium and tungsten atoms in a linear fashion (177(2)°), with a short, triple W-C bond (1.75(2) Å) and a long, single Ru-C bond (2.09(2) Å).

In contrast, reactions of propynyl **51** with a catalytic amount of either **50** or its precursor, [$W_2(OCMe_3)_6$], in *saturated hydrocarbon* solvent leads to a yellow precipitate of the ethynediyl complex [(Cp)$(CO)_2$Ru-C≡W$(OCMe_3)_3$] **53** in good yield. The structure of **53** shows a linear Ru–C≡C–Ru chain (angles at C are 178.1(9)° and 179,6(9)°) with Ru–C single bonds (1.87(1) Å, 1.88(1) Å) and a typical C≡C triple bond (1.19(1) Å). Attempts to make other μ-ethynediyl complexes by means of tungsten alkyne metathesis catalysts were not successful. We remain puzzled at the lack of generality of this reaction.

The ethynediyl ligand of **53** is reactive. It reacts with diiron nonacarbonyl to form [Fe_2Ru_2(η^1:μ_4,η^2-C≡C)(μ-CO)$(CO)_8$(η-C_5H_5)$_2$] (**54**, Scheme 21), a bicarbide-centered metal cluster. An X-ray crystal structure shows that one of the ruthenium atoms migrates from a position where it is σ-bonded to a single ethynediyl carbon in **53** to become η^2-bonded to the ethynediyl unit in **54**. A similar reaction of **53** with dicobalt octacarbonyl gives [Co_2Ru_2(μ_4-C≡C)$(CO)_{10}$(η-C_5H_5)$_2$] (**55**), which structurally resembles many other [$Co_2(CO)_6$]–alkyne complexes.



Scheme 20

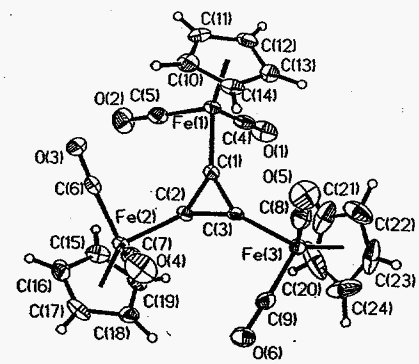


Scheme 21

2. Tricarbide complexes

We have prepared the first trimetallic complexes of the *cyclo*-C_3 ligand. This work complements efforts by Gladysz, who has prepared bimetallic complexes of linear C_2,[12] C_3,[13] and C_4,[14,15] and a trimetallic complex of linear C_3.[16] Other complexes of pure carbon ligands include metal complexes of the fullerenes (C_{60}, C_{70}, etc.) prepared by Fagan,[17] Balch[18] and others.

The reaction of three equivalents of $Na[Fe(CO)_2(Cp)]$ with $[C_3Cl_3][SbF_6]$, generated from C_3Cl_4 and $AgSbF_6$, $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**56**). The X-ray crystal structure of **1** shows a nearly equilateral C_3 ring with an iron center bonded to each vertex (significant distances (Å): Fe1–C1, 1.913 (6); Fe2–C2,1.917 (6); Fe3–C3, 1.919 (7); C1–C2, 1.388 (9); C1–C3, 1.394 (9); C2–C3, 1.375 (9)). The compound is fully characterized spectroscopically, including ^{13}C NMR with $\delta_{C\alpha} = 256.6$. We have prepared analogous C_3 compounds with three $[Ru(CO)_2(Cp)]$ or $[Re(CO)_5]$ groups. The tri-iron complex consistently analyzes for three fewer carbon atoms than are present in the molecule, which may indicate that an FeC phase survives combustion at about 1000°C.



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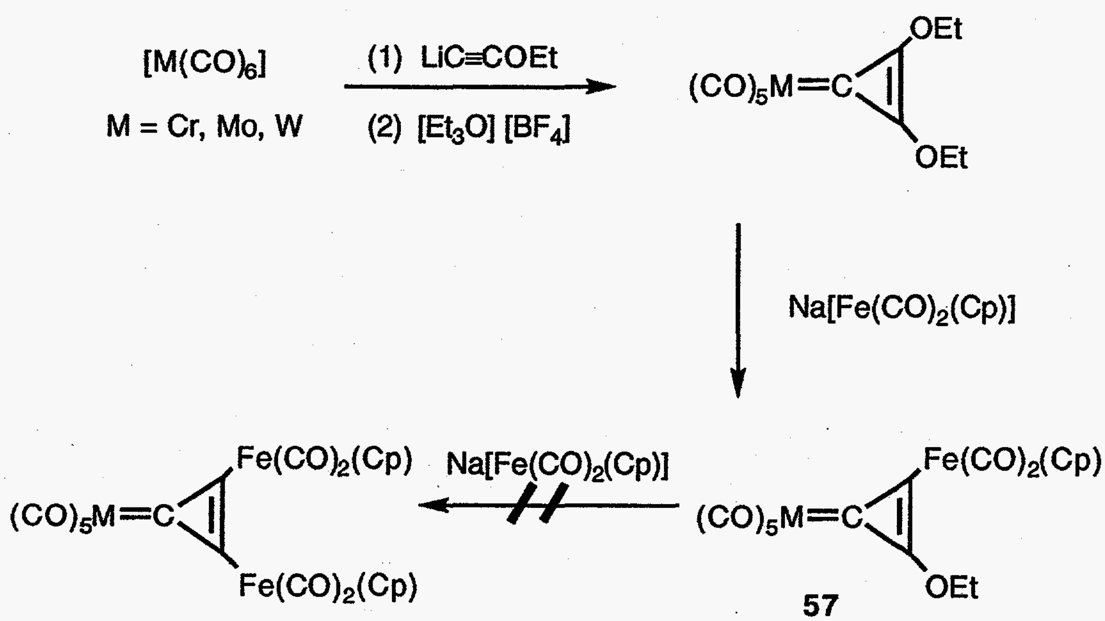


Scheme 22

Similar *neutral* C_3 complexes are being prepared *via* the reactions in Scheme 22. We have characterized the cyclopropenylidene complexes **57** with one iron attached, but have *not* been able to drive the addition of a second iron center.

V. Other topics

Our DOE project led us in a few new directions which were pursued briefly with DOE funding. New sources of funding were sought when the new projects had diverged from our DOE interests.

1. Fullerenes

Our interest in all-carbon ligands naturally attracted us to the fullerenes, which became available during the period of DOE support. With Prof. Mark Meier, we discovered that it is possible to separate C_{60} from C_{70} on gel permeation chromatography (GPC) columns with 100% toluene as the mobile phase. This method allowed a *substantial* scaleup of fullerene purification from the labor- and solvent-intensive open alumina column chromatography which was in use up to our report. The GPC method allowed us to process *kilograms* of fullerene-rich soot, and provided us with pure fullerenes for many chemical studies.

We were also able to apply the GPC method to the purification of the higher fullerene C_{84}. At 95°C on Waters Ultrastyragel (500 Å) columns, the chromatographic bandshape is sharp enough to allow "shaving" of a pure C_{84} fraction. The identity and purity of the sample were confirmed by HPLC analysis on a C_{18}-silica column, UV-visible spectroscopy, and Fourier Transform mass spectrometry (FT-MS).

The electrochemistry of C_{84} was successfully examined in both benzonitrile and ortho-dichlorobenzene (ODCB). Five couples can be clearly observed at potentials more negative than the rest potential. The first three of these are particularly well-behaved, representing the chemically and electrochemically reversible formation of C_{84}^{-}, C_{84}^{2-}, and C_{84}^{3-}. The fourth and fifth reductions were less well-behaved. Our larger fullerene work continues with other sources of funding.

2. Cyclopentadienyl metal complexes

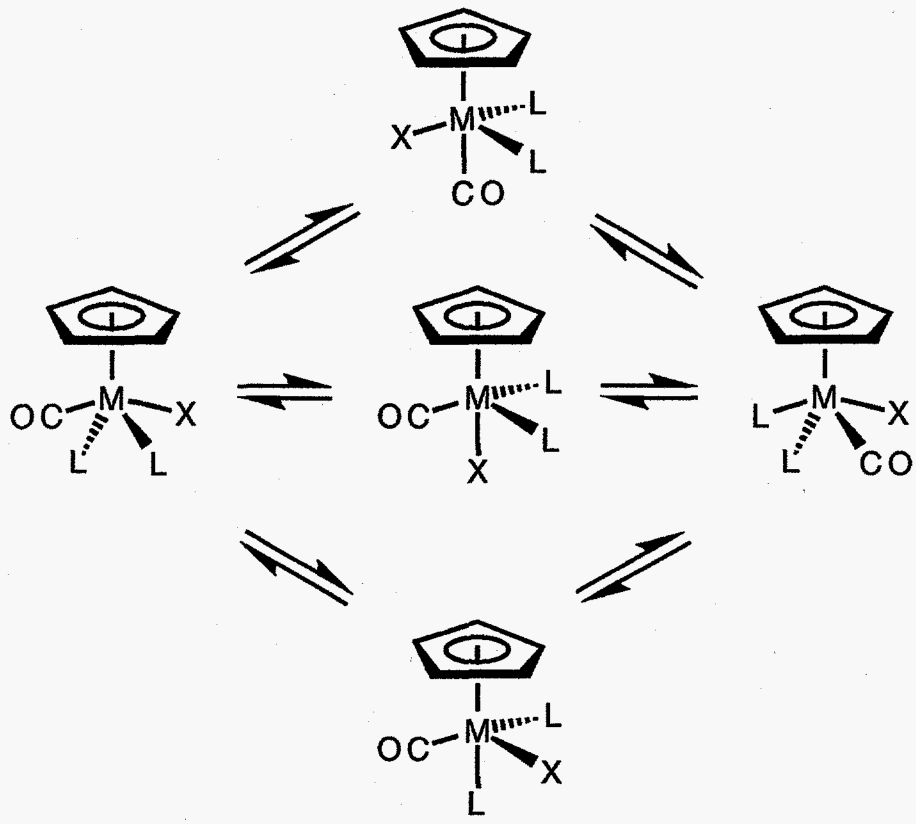
The metallacumulene studies described above required us to develop new or improved preparations of several transition metal starting materials. The ruthenium and osmium complexes $[MCl(CO)_2(Cp)]$ had been studied in much less detail than their iron analog because of inefficient syntheses and higher cost. We obtained $[RuCl(CO)_2(Cp)]$ (**58**) in two simple steps from $[RuCl_3(H_2O)_x]$. $[RuCl_2(CO)_3]_2$, produced by refluxing $[RuCl_3(H_2O)_x]$ in hydrochloric and formic acids, reacts cleanly with $[SiMe_3(C_5H_5)]$ to give **58** in 74% overall yield from $[RuCl_3(H_2O)_x]$. $[OsCl(CO)_2(Cp)]$ (**59**) is similarly obtained in four steps from $[OsO_4]$. Known conversion of $[OsO_4]$ to $[NH_4]_2[OsCl_6]$, reduction to $[OsCl_3]$ and carbonylation to $[OsCl_2(CO)_3]_2$ in a tube furnace, and finally reaction with $[SiMe_3(C_5H_5)]$ give **59** in 26% overall yield from $[OsO_4]$. These preparations are a significant improvement over previous published methods, avoiding the intermediacy of $[M_3(CO)_{12}]$.

Also in the iron group, we prepared several new electron-rich metal halides $[MX(PR_3)_2(Cp)]$ (M = Fe, Ru; X = Cl, Br, I). Most of the iron compounds (L = $P(OMe)_3$, PMe_3, PMe_2Ph, $PMePh_2$, 1/2 $Ph_2PCH_2CH_2PPh_2$, 1/2 $Ph_2PCH_2CH_2CH_2PPh_2$) were conveniently prepared in a "one-pot" procedure by the reaction of anhydrous FeX_2 with the phosphine ligand followed by [Tl(Cp)]. The interesting new iron halide [FeI{*o*-$C_6H_4(PMe_2)_2$}(Cp)] could not be obtained in this way, but rather required the stepwise reaction of $[FeI(CO)_2(Cp)]$ with *o*-$C_6H_4(PMe_2)_2$ (pdmp) to give [Fe(CO)(pdmp)(Cp)]I, photolysis in MeCN to give [Fe(MeCN)(pdmp)(Cp)]I, and finally reaction with $[NBu_4]I$. [FeI{*o*-$C_6H_4(PMe_2)_2$}(Cp)] was crystallographically characterized. The ruthenium complex [RuCl{*o*-$C_6H_4(PMe_2)_2$}(Cp)] could not be made by the "normal" displacement of PPh_3 from $[RuCl(PPh_3)_2(Cp)]$, but instead was made by reacting [RuCl(η^4-cyclooctadiene)(Cp)] with pdmp. The pdmp ligand is "non-innocent", supporting unusually high-valent complexes of transition metals. Indeed, the [FeX{*o*-$C_6H_4(PMe_2)_2$}(Cp)] complexes we have examined are reversibly oxidized at potentials *ca.* 200–300 mV less positive than complexes with most other phosphine ligands, and the ruthenium compounds behave similarly. These halides were essential starting materials in the studies of alkynyl and vinylidene complexes described above.

Several electron-rich group 6 complexes $[MX(CO)(PR_3)_2(Cp)]$ (M = Mo, W; X = Cl, Br, I) were prepared by straightforward thermal or photolytic substitution reactions of $[MX(CO)_3(Cp)]$. A range of phosphorus ligands including (in order of decreasing Tolman cone angle) PPh_3, $PMePh_2$, $P(OMe)Ph_2$, PEt_3, PBu_3, $P(OCHMe_2)_3$, $P(OPh)_3$, PMe_2Ph, PMe_3 and $P(OMe)_3$. The $PMePh_2$ and $P(OMe)Ph_2$ complexes displayed temperature dependent ^1H and ^{13}P NMR spectra. For example, $[MoCl(CO)\{P(OMe)Ph_2\}_2(Cp)]$ displays a single cyclopentadienyl resonance in its ^1H NMR spectrum at room temperature, but two resonances at 173 K. Similarly, $[MoCl(CO)(PMePh_2)_2(Cp)]$ (M = Mo, W) display single ^1H cyclopentadienyl resonances at room temperature, but five resonances at 173 K. ^{31}P NMR spectra are more complicated, showing several inequivalent species at low temperature. Evidently, several isomers or conformers are of nearly equal energy. We favor the explanation that two square pyramidal and three trigonal bipyramidal isomers (Scheme 23) are freely interconverting at room temperature, but "locked" at 173 K. ^{31}P–^{31}P coupling patterns are consistent with this explanation. Alternatively, the asymmetric phosphorus ligands may be "meshing" with one another, and at low temperature certain conformers may be freezing out.

3. Metal-thiophene complexes

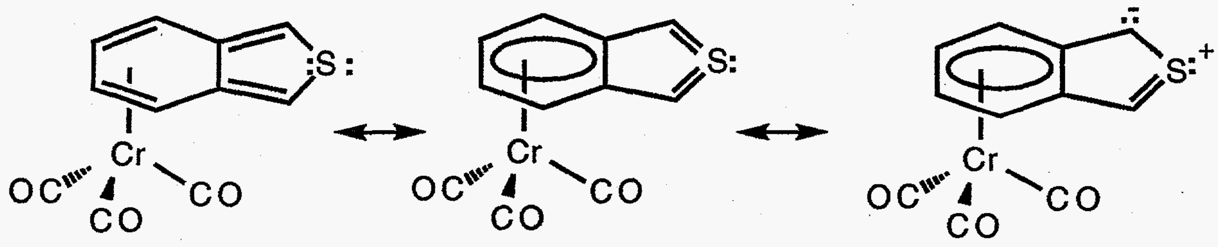
Metal-catalyzed hydrodesulfurization of fossil fuels is an area of DOE interest. We initiated an investigation of certain aspects of metal-thiophene interactions. We began by searching for simple S-bonded thiophene-metal complexes, which are scarce. We prepared a series of simple [Fe(η^1-S-thiophene)$(CO)_2$(Cp)][BF_4] complexes, including [Fe(η^1-S-dibenzothiophene)-$(CO)_2$(Cp)][BF_4] which we structurally characterized. The dibenzothiophene ligand is tipped away from iron with pyramidal geometry at sulfur. The dynamics of inversion at sulfur were probed by



Scheme 23

examining the temperature dependence of the ^{13}C NMR spectrum of [Fe(η^1-S-benzo-[*b*]-thiophene)$(CO)_2$(Cp)][BF_4]. The carbonyl ligands of this complex are nonequivalent at 170 K, coalescing at 249 K with $\Delta G^{\ddagger}$ = 39 kJ·mol^{-1}. This inversion barrier is about 10 kJ·mol^{-1} lower than the barrier in [Fe(η^1-S-PhSMe)$(CO)_2$(Cp)][BF_4].

When several other investigators, notably Angelici[19] and Rauchfuss,[20] began making rapid progress in the modeling of metal-catalyzed thiophene hydrodesulfurization, we decided to shift our emphasis to less common thiophenes. Benzo[3,4-*c*]thiophene (isothianaphthene) is interesting from the perspective of its materials chemistry. The oxidized form of its polymer (PITN) has a small, <1 eV, bandgap. The reaction of benzo[3,4-*c*]thiophene with photolytically generated [Cr(thf)$(CO)_5$] in THF at room temperature leads to the formation of [Cr(η^6-C_8H_6S)$(CO)_3$] (**60**, Scheme 24) in up to 62% yield. No pentacarbonyl complex could be isolated. The loss of CO from the chromium pentacarbonyl fragment is unusually facile. Rational syntheses of **60** from benzo[3,4-*c*]thiophene and various [Cr$(CO)_3$] synthons failed. X-ray crystal structure analysis of **60** shows slightly asymmetric η^6-coordination of the benzo ring to chromium and unusually short S–C bond lengths in the planar thiophene ligand. The structure suggests that all three resonance forms, **60a**, **b** and **c**, contribute to the stability of **60**, which is thermally more stable than free benzo[*c*]thiophene.



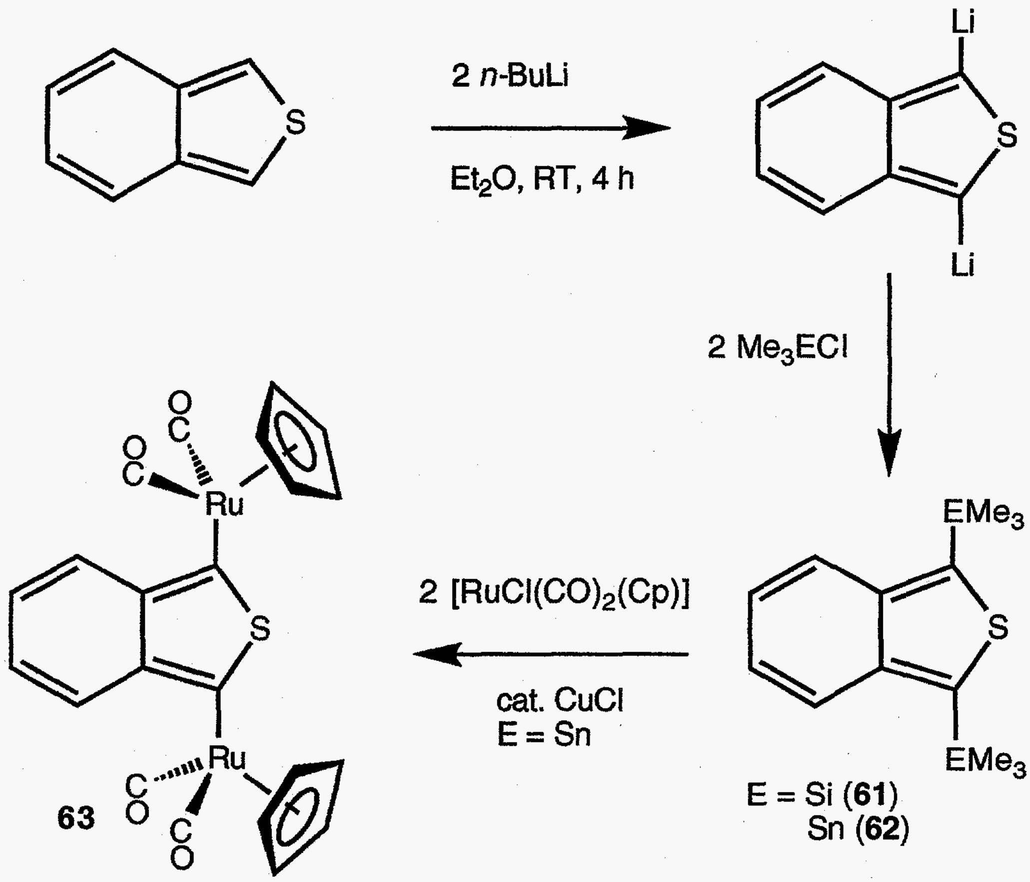
60a **60b** **60c**

Scheme 24

We have yet not been able to characterize any other π- or S-bonded metal complexes of benzo[*c*]thiophene. However, we have had some recent success in preparing new derivatives of benzo[*c*]thiophene by deprotonation with two equivalents of *n*-butyllithium, followed by reaction of the thienyllithium reagent with a metal or nonmetal halide. This procedure works nicely for preparing trimethylsilyl and trimethyltin compounds **61** and **62** (Scheme 25). The tin reagent **62** is a crystalline, white solid which is much more stable and polymerization resistant than benzo[*c*]thiophene itself. Thus, it can be used to prepare $[Cr\{\eta^6\text{-}(SnMe_3)_2C_8H_4S\}(CO)_3]$ from $[Cr(NH_3)(CO)_3]$ in refluxing dioxane. The reaction of **62** with $[RuCl(CO)_2(Cp)]$ and CuCl catalyst leads to $[\{Ru(CO)_2(Cp)\}_2(\mu_2\text{-}C_8H_4S)]$ (**63**), characterized by X-ray crystallography. Notable features include a *syn* orientation of the cyclopentadienyl groups on ruthenium atoms, and a very definite bond length alternation (*i.e.*, lack of aromaticity) in the benzo[*c*]thiophene rings.

VI. Summary

We investigated many aspects of metallacumulenes and carbide chemistry under grant DE-FG05-85ER13432. Our understanding of the fundamentals of the alkyne-to-vinylidene rearrangement on a metal center was improved. Many unsaturated, carbon-rich metal carbene complexes were prepared and characterized. The complexes offer reasonable models for the carbon-rich species which may be present on the surfaces of metal catalysts during metal-catalyzed synthesis gas and acetylene conversion reactions. In particular, a pattern of facile carbon-carbon bond formation steps is beginning to emerge. The intermolecular carbon-carbon coupling in the formation of **6** models a possible step in which two growing carbon chains encounter one another and couple. The *extreme* facility of the intramolecular carbon-carbon coupling in the formation of **29** demonstrates that vinylidene ligands have a great propensity to undergo insertion reactions, greater than isoelectronic carbonyl or isonitrile ligands. Vinylidene insertions into metal-carbon bonds may indeed be important steps in carbon chain growth. Additional reactivity studies on these unsaturated, carbon-rich complexes will be of interest in determining their relevance to the chemistry of carbon species on catalyst surfaces.



Scheme 25

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VIII. Accomplishments resulting from DOE-funded research

1. Publications

1. R. S. Iyer and J. P. Selegue, "Synthesis of a Diiron Divinylidene Complex by Oxidatively Induced Carbon-Carbon Coupling," *J. Am. Chem. Soc.*, **109**, 910-911 (1987).
2. S. L. Latesky and J. P. Selegue, "Preparation and Structure of [$(Me_3CO)_3W{\equiv}C$-$Ru(CO)_2(Cp)$], a Heteronuclear, μ_2-Carbide Complex," *J. Am. Chem. Soc.*, **109**, 4731-4733 (1987).
3. J. D. Goodrich, P. N. Nickias and J. P. Selegue, "Synthesis, Structure and Reactivity of [$Fe(dibenzothiophene)(CO)_2(Cp)$][$BF_4$] and Related S-Bonded Thiophene Complexes," *Inorg. Chem.*, **26**, 3424 (1987).
4. P. N. Nickias, B. A. Young and J. P. Selegue, "Facile Interconversions of Alkyne and Vinylidene Ligands on Divalent Molybdenum and Tungsten," *Organometallics,* **7**, 2248-2250 (1988).
5. K. G. Frank and J. P. Selegue, "Ruthenium-Tungsten and Iron-Tungsten Complexes with Ethynyl or Ethynediyl Bridges," *J. Am. Chem. Soc.*, **112**, 6414-6416 (1990).
6. K. G. Frank and J. P. Selegue, "Carbonyl(η5-cyclopentadienyl)bis--(trimethylphosphite)ruthenium(II) Tetrafluoroborate," *Acta Cryst.*, **C47**, 35-37 (1990).
7. G. A. Koutsantonis and J. P. Selegue, "Synthesis and Structure of [$\{Ru(CO)_2(Cp)\}_2(\mu{-}C{\equiv}C)$], an Ethynediyl Complex Formed During Tungsten-Catalyzed Alkyne Metathesis," *J. Am. Chem. Soc.*, **113**, 2316-2317 (1991).
8. J. P. Selegue, B. A. Young and S. L. Logan, "Reactions of [$RuCl(PMe_3)_2(Cp)$] With Aliphatic Alkynols Leading to Cationic Vinylvinylidene and Neutral Alkynyl Complexes, and Reactions of the Enynyls with Heteroallenes," *Organometallics,* **10**, 1972-1980 (1991).
9. A. K. McMullen, J. P. Selegue and J.-G. Wang, "Synthesis and Structure of a Tungsten η^3-Enynyl Complex Resulting from Facile Alkynyl-Vinylidene Coupling," *Organometallics,* **10**, 3421-3423 (1991).

10. M. S. Meier and J. P. Selegue, "Efficient Separation of C_{60} and C_{70}. Gel Permeation Chromatography of Fullerenes Using 100% Toluene as Mobile Phase," *J. Org. Chem.*, **57**, 1924-1926 (1992).
11. J. R. Lomprey and J. P. Selegue, "Structural Characterization of Alkyne and Vinylidene Isomers of $[Ru(C_2H_2)(PMe_2Ph)_2(Cp)][BF_4]$," *J. Am. Chem. Soc.*, **114**, 5518-5523 (1992).
12. G. A. Koutsantonis, J. P. Selegue and J.-G. Wang, "Cluster Building on a Bicarbide Fragment: Synthesis and Structure of $[Fe_2Ru_2(\mu^4\text{-}C{\equiv}C)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)_2]$," *Organometallics*, **11**, 2704-2708 (1992).
13. M. S. Meier, T. F. Guarr, J. P. Selegue and V. K. Vance, "Elevated Temperature Gel Permeation Chromatography and Electrochemical Behavior of the C_{84} Fullerene," *J. Chem. Soc., Chem. Commun.*, 63-65 (1993).
14. J. R. Lomprey and J. P. Selegue, "Syntheses and Structures of Two Trifluoroacetate-Trapped Derivatives of a Ruthenium Butatrienylidene Complex," *Organometallics*, **12**, 616-617 (1993).
15. J. P. Selegue and K. A. Swarat, "Preparation and Structure of $[Cr(\eta^6\text{-}C_8H_6S)(CO)_3]$, the First Transition Metal Complex of Benzo[3,4-*c*]thiophene," *J. Am. Chem. Soc.*, **115**, 6448-6449 (1993).
16. S. Dev and J. P. Selegue, "Convenient Syntheses of $[RuCl(CO)_2(Cp)]$ and $[OsCl(CO)_2(Cp)]$," *J. Organometal. Chem.*, **469**, 107-110 (1994).

2. Manuscripts in preparation:

1. G. A. Koutsantonis, R. S. Iyer and J. P. Selegue, "Synthesis and Characterization of Ferrocenyl Allenylidene Complexes of Iron, Ruthenium and Osmium: Crystal Structure of $[Ru(C{=}C{=}CHFc)(PPh_3)_2(Cp)][PF_6]{\bullet}CH_2Cl_2$."
2. J. R. Lomprey, J. P. Selegue and J. B. Wakefield, "Preparation of Masked Butatrienylidene Complexes of Ruthenium and Their Conversion to Butatrienylidene Complexes."
3. J. R. Lomprey and J. P. Selegue, "Regioisomers of $[Ru(C_2H_2PR_3)(PMe_2Ph)_2(Cp)]^+$."
4. M. S. Morton and J. P. Selegue, "Synthesis and Structure of the First Tri-Metal Substituted Cyclopropenium Salt: $[\{Fe(CO)_2(Cp)\}_3(\mu^3\text{-}C_3)][SbF_6]$."

3. Personnel supported at least partially with DOE funds, 1985-1993

a. Postdoctoral and Visiting Scholars

Ramnath S. Iyer, Postdoctoral Associate, 1985-87, (Sandoz Corporation, India)

Stanley L. Latesky, Postdoctoral Associate, 1986-87, (Missouri Western State College)

Matthew V. R. Stainer, Postdoctoral Associate, 1987-88, (Hughes Display Products, Lexington, KY)

Anne K. McMullen, Postdoctoral Associate, 1989-90, (Union Carbide, Sistersville, WV)

George A. Koutsantonis, Postdoctoral Associate, 1989-90, (Research Associate, Griffith University, Brisbane, Queensland, Australia)

Jin-Guu Wang, Postdoctoral Associate, 1989-90, (Industrial Chemical Employment in Taiwan)

Pamela A. Wexler, Postdoctoral Associate, 1990-91, (Employment Unknown) Karsten A. Swarat, Postdoctoral Associate, 1991-93, (seeking industrial employment in Germany following Postdoctoral Associateship at Illinois State University, Normal, IL)

Somanath Dev, Postdoctoral Associate, 1991-1994, (College of Pharmacy, University of Kentucky)

James B. Wakefield, Postdoctoral Associate, 1991-1993, (Seeking academic position)

b. Ph.D. Students

P. N. Nickias, "NMR Studies and Synthesis of Mo and W Organometallic Complexes," 1987, (Employed by Dow Chemical, Midland, MI).

B. A. Young, "Synthesis and Physical Studies of Transition Metal Vinylidene, Alkyne and Alkynyl Complexes," 1989, (Seeking Industrial Employment).

K. G. Frank, "Syntheses and Physical Studies of Transitional Metal Vinylidene, Alkyne and Ethynediyl Complexes," 1990, (Employed by Mobay Chemical, Parkersburg, WV).

Jeffrey R. Lomprey, "The Synthesis, Characterization, and Reactivity of Some Alkyne, Vinylidene, and Butatrienylidene Complexes of Ruthenium," 1993, (Postdoctoral Associate at Dartmouth College, NH).

Michael S. Morton, 1991-present, in progress.

c. M.S. students

James D. Goodrich, M.S. Thesis Unfinished, 1984-87, (Computing Company in North Carolina).

John F. Davis, M.S. Thesis Unfinished, 1985-87, (Employment Unknown).

Jonathan P. Shaw, 1991-present, in progress.

Temba Maqubela, 1992-1994, (Chemistry faculty, Phillips Academy, Andover, MA)

d. Undergraduates

Mark Huff, 1985-86, (Completed Ph.D. at University of South Carolina)

Stanley Logan, 1987-88, (Law School, Creighton University)

Azlan Zakaria, 1990-91, (Returned to Malaysia, Current Position Unknown)

Tab Farthing, Centre College, 1987-88, (Analytical chemist, Highbridge Spring Water Co., Wilmore, KY)

Reed Brodsky, Duke University, Summer 1989, (Planned to enter medical school, current employment unknown)

Charles Rader, Ohio University, Summer 1990, (Graduated from Ohio University in 1992, touring with a theater troupe but plans to enter graduate school in chemistry in Fall, 1993)

Efrem McAdoo, University of Dayton, Summer 1989, (Current employment unknown)

Jason Overby, University of Tennessee, Martin, Summer 1991

Tammy Metroke, Evangel College, Summer 1992, (Ph.D. Program at Oklahoma State University, Fall, 1993)

Janet Asper, Ohio University, Summer 1993, (Ph.D. Program at the University of Pittsburgh)

Andrew Kunev, Sayre High School, Summer 1986

Jennifer Crank, Dunbar High School, Spring 1992, Summer 1992, Fall 1992

4. Invited presentations based on DOE-supported research, 1985-1994

"Metallacumulenes and Alkyne Complexes," West Virginia University, November 6, 1985, Morgantown, WV.

"Metallacumulenes: Unsaturated Transition Metal Carbene Complexes," Indiana University, March 11, 1986, Bloomington, IN.

"Metallacumulenes: Unsaturated Transition Metal Carbene Complexes," Ohio State University, April 24, 1986, Columbus, OH.

"Metallacumulenes and Alkyne Complexes," University of Cincinnati, November 18, 1986, Cincinnati, OH.

"Metallacumulenes and Carbides: Carbon-Rich Organotransition Metal Complexes," Eidgenossische Technische Hochschule (Swiss Federal Institute of Technology), February 17, 1988, Zurich, Switzerland.

"Metallacumulenes and Carbides: Carbon-Rich Organotransition Metal Complexes," University of Freiburg, February 18, 1988, Freiburg, West Germany.

"Metallacumulenes and Carbides: Carbon-Rich Organotransition Metal Complexes," University of Bayreuth, June 21, 1988, Bayreuth, West Germany.

"Metallacumulenes and Carbides: Carbon-Rich Organotransition Metal Complexes," University of Munich, June 22, 1988, Munich, West Germany.

"Metallacumulenes and Carbides: Carbon-Rich Organotransition Metal Complexes," Max-Planck-Institut fur Kohlenforschung, July 14, 1988, Mülheim a.d. Ruhr, West Germany.

"Transition-Metal-Promoted Tautomerization of Alkynes to Vinylidenes: Which Factors Favor 'Iso-Acetylene'?", University of Utah, May 9, 1989, Salt Lake City, UT.

"Transition-Metal-Promoted Tautomerization of Alkynes to Vinylidenes: Which Factors Favor 'Iso-Acetylene'?", Utah State University, May 10, 1989, Logan, UT.

"Metallacumulenes and Carbides: Unsaturated Transition-Metal Carbene Complexes," Marshall University, April 10, 1990, Huntington, WV.

"Transition-Metal Promoted Tautomerization of Alkynes to Vinylidenes: Which Factors Favor 'Iso-Acetylene'?", June 4, 1990, Toledo, OH.

"Metallacumulenes and Carbide Complexes: New Chemistry of Carbon-Rich Ligands," October 5, 1990, Cleveland State University, Cleveland OH.

"Development of Organometallic Chemistry," November 14, 1990, Fisk University, Nashville, TN.

"Metallacumulenes and Carbide Complexes: New Chemistry of Carbon-Rich Ligands," November 15, 1990, Vanderbilt University, Nashville, TN.

"Metallacumulenes and Carbide Complexes: Carbon-Rich Transition Metal Complexes," September 10, 1991, Department of Chemistry, University of Illinois, Urbana, IL.

"Metallacumulenes and Carbide Complexes: Carbon-Rich Transition Metal Complexes," November 21, 1991, Department of Chemistry, University of Minnesota, Minneapolis, MN.

"Who Needs All Those Hydrogens Anyway?: New Carbon-Rich Organotransition Metal Chemistry," February 6, 1992, Department of Chemistry, Indiana University, Bloomington, IN.

"Chemistry of the Fullerenes: Discovery, Development and Work in Progress at the University of Kentucky," March 25, 1992, Paul L. Dunbar High School, Lexington, KY.

"They're Big and Round, They're All Around: New Fullerene Chemistry," October 6, 1992, Department of Chemistry, University of Cincinnati, Cincinnati, OH.

"They're Big and Round, They're All Around: New Fullerene Chemistry," November 19, 1993, Department of Chemistry, University of Louisville, Louisville, KY.

"They're Big and Round, They're All Around: New Fullerene Chemistry," February 21, 1994, Department of Chemistry, Transylvania University, Lexington, KY.

"Metallacumulenes and Carbides: Carbon-Rich Organotransition Metal Complexes," February 24, 1994, Miami University, Oxford, OH.

5. Contributed presentations based on DOE-supported research

"Preparation and Characterization of $[Ru\{C{=}CHC{=}CH(CH_2)_4\}\text{-}(PMe_3)_2(Cp)]\text{-}[PF_6]$, a Cationic Vinylvinylidene Complex," J. P. Selegue and B. A. Young, September 12, 1985, American Chemical Society National Meeting, Chicago, IL.

"New Vinylidene and Allenylidene Complexes of Iron and Ruthenium," (Poster) J. F. Davis, K. G. Frank, R. S. Iyer, J. P. Selegue and B. A. Young, August 10-15, 1986, Gordon Research Conference on Organometallic Chemistry, Andover, NH.

"Trigonal Bipyramidal Intermediates In the Stereochemical Rearrangement of Cyclopentadienyl Molybdenum and Tungsten 'Piano Stool' Complexes," P. N. Nickias and J. P. Selegue, September 8, 1986, American Chemical Society National Meeting, Anaheim, CA.

"Synthesis of a Diiron Divinylidene Complex by Oxidatively Induced Carbon-Carbon Coupling," R. S. Iyer and J. P. Selegue, September 10, 1986, American Chemical Society National Meeting, Anaheim, CA.

"Organotransition Metal Chemistry of Thiophene and Benzothiophenes," (Poster) J. P. Selegue, J. D. Goodrich and S. L. Latesky, September 18-19, 1986, University of Kentucky Energy and Minerals Conference, Lexington, KY.

"Synthesis and Reactivity of Mo and W Alkynyl Complexes," P. N. Nickias and J. P. Selegue, November 3, 1986, American Chemical Society Southeast Regional Meeting, Louisville, KY.

"Synthesis of Monosubstituted Allenylidene Complexes of Ruthenium," R. S. Iyer and J. P. Selegue, November 3, 1986, American Chemical Society Southeast Regional Meeting, Louisville, KY.

"Synthesis, Structure and Reactivity of Some Iron Thiophene Complexes," J. D. Goodrich and J. P. Selegue, November 3, 1986, American Chemical Society Southeast Regional Meeting, Louisville, KY.

"Synthesis and Reactivity of Ruthenium Cumulene and Alkynyl Complexes," J. P. Selegue and B. A. Young, November 3, 1986, American Chemical Society Southeast Regional Meeting, Louisville, KY.

"Preparation, Structure, and Reactivity of Organoruthenium Fluoride Complexes," J. F. Davis and J. P. Selegue, November 3, 1986, American Chemical Society Southeast Regional Meeting, Louisville, KY.

"2D NMR Applied to Organometallic Complexes," J. P. Selegue and P. N. Nickias, November 21, 1986, Kentucky Academy of Science Annual Meeting, Lexington, KY.

"Syntheses of Metallacumulenes of Ruthenium," R. S. Iyer and J. P. Selegue, November 21, 1986, Kentucky Academy of Science Annual Meeting,
Lexington, KY.

"Synthesis and Reactivity of Ruthenium Alkynyl and Vinylidene Complexes," J. P. Selegue and B. A. Young, November 21, 1986, Kentucky Academy of Science Annual Meeting, Lexington, KY.

"Synthesis and Reactivity of Electron-Rich Iron Phosphine Complexes," Kevin G. Frank and John P. Selegue, November 21, 1986, Kentucky Academy of Science Annual Meeting, Lexington, KY.

"Synthesis and Reactivity of Early-Late Transition Metal Organometallic Complexes," Stanley L. Latesky and John P. Selegue, November 21, 1986, Kentucky Academy of Science Annual Meeting, Lexington, KY.

"Attempted Syntheses of Ruthenium Butatrienylidene Complexes," John F. Davis and John P. Selegue, November 21, 1986, Kentucky Academy of Science Annual Meeting, Lexington, KY.

"Preparation, Structure and Dynamics of S-Bonded Iron Thiophene Complexes," J. D. Goodrich, P. N. Nickias and J. P. Selegue, April 7, 1987, American Chemical Society National Meeting, Denver, CO.

"Interconversion of Alkyne and Vinylidene Complexes of Molybdenum and Tungsten," P. N. Nickias and J. P. Selegue, April 8, 1987, American Chemical Society National Meeting, Denver, CO.

"Cyclopentadienyl Molybdenum Vinylidene and Alkylidyne Complexes," P. N. Nickias, J. P. Selegue and B. A. Young, June 26, 1987, American Chemical Society Central Regional Meeting, Columbus, OH.

"Preparation and Structure of $[(Me_3CO)_3W{\equiv}C\text{-}Ru(CO)_2(Cp)]$, A Heteronuclear, μ_2-Carbide Complex," S. L. Latesky and J. P. Selegue, June 26, 1987, American Chemical Society Central Regional Meeting, Columbus, OH.

"Transition Metal Thiophene Complexes: Models for Coal Desulfurization," J. D. Goodrich, S. L. Latesky, P. N. Nickias and J. P. Selegue, July 1, 1987, Consortium for Fossil Fuel Liquefaction Science First Annual Technical Meeting, Lexington, KY.

"New Ethyne and Ethynyl Complexes of Iron and Ruthenium, and Their Reactions with Transition-Metal Electrophiles," Kevin G. Frank and John P. Selegue, April 13, 1989, American Chemical Society National Meeting, Dallas, TX.

"Reduction and Ligand-Induced Tautomerization of Molybdenum Alkyne Complexes," John P. Selegue and Bruce A. Young, April 13, 1989, American Chemical Society National Meeting, Dallas, TX.

"Metal-Promoted Tautomerization of Alkynes to Vinylidenes: Which Factors Favor 'Iso-Acetylene'?" (Poster), John P. Selegue, April 18, 1989, NSF Site Visit, Kentucky EPSCoR Program, Louisville, KY.

"Transition-Metal-Promoted Tautomerization of Alkynes to Vinylidenes: Which Factors Favor 'Iso-Acetylene'?", Kevin G. Frank, Peter N. Nickias, John P. Selegue, Matthew V. R. Stainer and Bruce A. Young, April 19, 1989, Tri-State Catalyst Club Symposium '89 (Invited Contribution), Lexington, KY.

"Transition-Metal-Promoted Tautomerization of Alkynes to Vinylidenes: Which Factors Favor 'Iso-Acetylene'?", Kevin G. Frank, Peter N. Nickias, John P. Selegue and Bruce A. Young, May 26, 1989, Minisymposium on Chemical Catalysis (Invited Contribution), University of Louisville, Louisville, KY.

"Tungsten Vinylidene, Alkyne and Alkynyl Complexes with Alkyne Ancillary Ligands," (Poster), K. G. Frank, J. P. Selegue, and M. V. R. Stainer, July 18, 1989, Gordon Research Conference on Organometallic Chemistry, Newport, RI.

"Recent Developments in Metallacumulene Chemistry: Which Factors Favor Vinylidenes Over Alkynes?", October 9, 1989, Southeast Regional American Chemical Society Meeting (Invited Contribution), Winston-Salem, NC.

"Reactions Between Metal Ethynyls and Metal Electrophiles to Stabilize New Heterobimetallic Ethynediyl Complexes," (Poster), Kevin G. Frank and John P. Selegue, November 2, 1989, American Chemical Society Midwest Regional Meeting, St. Louis, MO.

"Metal-Promoted Tautomerization of Alkynes to Vinylidenes: Which Factors Favor 'Iso-Acetylene'?" (Poster), John P. Selegue, November 16-18, 1989, Kentucky Academy of Science Annual Meeting, Lexington, KY.

"Approaches to the Formation of a Bis-Vinylidene Complex of Tungsten," Anne K. McMullen and John P. Selegue, November 17, 1989, Kentucky Academy of Science Annual Meeting, Lexington, KY.

"Synthesis and Characterization of Ferrocenyl-Stabilized Metal Allenylidene Complexes," George A. Koutsantonis and John P. Selegue, November 17, 1989, Kentucky Academy of Science Annual Meeting, Lexington, KY.

"Preparation, Structure and Dynamics of S-Bonded Iron and Chromium Complexes of Thiophenes and Related Ligands," (Invited Contribution), J. D. Goodrich, P. N. Nickias and J. P. Selegue, April 26, 1990, American Chemical Society National Meeting, Boston, MA.

"Alkyne and Vinylidene Chemistry on Cyclopentadienyl Molybdenum and Tungsten Centers, J. P. Selegue, May 21, 1990, National Science Foundation Organometallic Chemistry Workshop, Lexington, KY.

"Chemistry of Metallacumulenes. Synthesis and Characterization of Some Monosubstituted Ferrocenyl Allenylidene Complexes," G. A. Koutsantonis and J. P. Selegue, August 23, 1990, International Conference on Organometallic Chemistry, Detroit, MI.

"Facile Alkynyl-Vinylidene Coupling Encountered on the Trail of a Tungsten Bis(vinylidene) Complex," A. K. McMullen, J. P. Selegue and J.-G. Wang, August 24, 1990, International Conference on Organometallic Chemistry, Detroit, MI.

"Facile Alkynyl-Vinylidene Coupling Encountered on the Trail of a Tungsten Bis(vinylidene) Complex," A. K. McMullen, J. P. Selegue, J.-G. Wang, August 26, 1990, American Chemical Society National Meeting, Washington, DC.

"Redox Chemistry of Metallacumulenes, Alkynyls and Alkyne Complexes," (Invited Contribution), K. G. Frank, G. A. Koutsantonis, J. P. Selegue and B. A. Young, August 29, 1990, American Chemical Society National Meeting, Washington, DC.

"Synthesis of an Ethynediyl Complex by Tungsten-Catalyzed Alkyne Metathesis, and its Use in the Formation of Bicarbide Clusters,"(Poster), May 5-9, 1991, The Catalysis Society, 12th North American Meeting, Lexington, KY.

"Metallacumulenes and Carbide Complexes: New Aspects of Carbon-Rich Ligands," (Poster), June 3-5, 1991, John P. Selegue, U. S. Department of Energy, Office of Basic Energy Sciences Program Review, Madison, WI.

"Metallacumulenes and Carbide Complexes: New Chemistry of Carbon-Rich Ligands," (Invited Lecture), July 16, 1991, Gordon Conference on Organometallic Chemistry, Newport, RI.

"Preparation, Structure and Reactivity of a Trapped Ruthenium Butatrienylidene Complex," Jeffrey R. Lomprey and John P. Selegue, April 6, 1992, American Chemical Society National Meeting, San Francisco, CA.

"Preparation, Structure and Reactivity of a Chromium Complex of Benzo[c]thiophene," (Poster), Karsten A. Swarat and John P. Selegue, April 7, 1992, American Chemical Society National Meeting, San Francisco, CA.

"Gel Permeation Based Separation of Higher Fullerenes," (Poster), M. S. Meier and John P. Selegue, April 8, 1992, American Chemical Society National Meeting, San Francisco, CA.

"Early/Late Transition Metal Compounds with Direct Metal-Metal Bonds or Carbide Bridges," (Invited Lecture), John P. Selegue, May 27-29, 1992, Symposium on Polynuclear Compounds, American Chemical Society Great Lakes Regional Meeting, Cincinnati, OH.

"Preparation, Structure and Reactivity of a Trapped Butatrienylidene Complex," Jeffrey R. Lomprey and John P. Selegue, May 29, 1992, 24th Central Regional Meeting of the American Chemical Society, Cincinnati, OH.

"Early/Late Transition Metal Compounds with Direct Metal-Metal Bonds or Carbide Bridges," (Invited Lecture), John P. Selegue, May 31 to June 4, 1992, Symposium on Heterobimetallic Compounds and Complexes of Disparate Metals, 75th Canadian Chemical Conference, Edmonton, Alberta, Canada.

"Preparation, Structure and Reactivity of a Chromium Complex of Benzo[c]thiophene," Karsten A. Swarat and John P. Selegue, May 31 to June 4, 1992, 75th Canadian Chemical Conference, Edmonton, Alberta, Canada.

"Chemically Modified Fullerenes and Fullerene Anions," J. P. Selegue, W. B. Barnhill, S. Dev, T. F. Guarr, M. S. Meier, T. Metroke, M. S. Morton, J. P. Shaw, K. A. Swarat and J. W. Wakefield, November 12, 1992, Southeast Regional Meeting of the American Physical Society, Oak Ridge, TN.

"Reactions of the Trapped Butatrienylidene Complex $[Ru\{C{\equiv}CC(O_2CCF_3){=}CPh_2\}\text{-}(PPh_3)_2(Cp)]$ with Lewis Acids," (Poster), J. B. Wakefield and J. P. Selegue, March 28, 1993, American Chemical Society National Meeting, Denver, CO.

"Mechanistic Insights Into the Transformation of Alkyne to Vinylidene Isomers on a Ruthenium (II) Center," J. L. Lomprey and J. P. Selegue, March 29, 1993, American Chemical Society National Meeting, Denver, CO.

"Gel-Permeation and Reverse-Phase Chromatographic Separations of C60, C70 and the Higher Fullerenes," J. P. Selegue, M. S. Meier, T. F. Guarr, V. K. Vance and J. P. Shaw, June 10, 1993, American Vacuum Society Meeting, Oak Ridge, TN.

"Approaching Ruthenium Butatrienylidene Complexes: Enolate Chemistry, Generation and Nucleophilic Trapping," (Poster), J. R. Lomprey, J. P. Selegue and J. B. Wakefield, July 11-16, 1993, Gordon Conference on Organometallic Chemistry, Newport, RI.

"Organometallic Chemistry of Benzo[c]thiophene and Linear Oligothiophenes," (Poster), E. L. Ross, J. P. Selegue and K. A. Swarat, July 11-16, 1993, Gordon Conference on Organometallic Chemistry, Newport, RI.

"Investigation of Ligand-Metal π-Conjugation in $CpRu(CO)_2L$, ($L = Cl$, $C{\equiv}CH_3$) and $[CpRu(CO)_2]_2(\mu\text{-}C{\equiv}C)$ Complexes Through Photoelectron Spectroscopy," (Poster), D. L. Lichtenberger, S. K. Renshaw A. B. Uplinger, J. P. Selegue and J. R. Lomprey, March 13, 1994, The 207th American Chemical Society National Meeting, San Diego, CA.