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Ligand-centered reactivity of organometallic radicals

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Contents

Abstract

Due to the increasing number of odd-electron organometallic species implicated in catalytic processes, interest in such compounds has risen. Although the prior emphasis in the literature was on metal-centered reactivity, reports of radical reactivity within ligands have

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recently become more common and a wider variety of reactions have been observed. This review serves as an overview of ligand-centered reactions of organometallic radicals with emphasis on the recent literature.

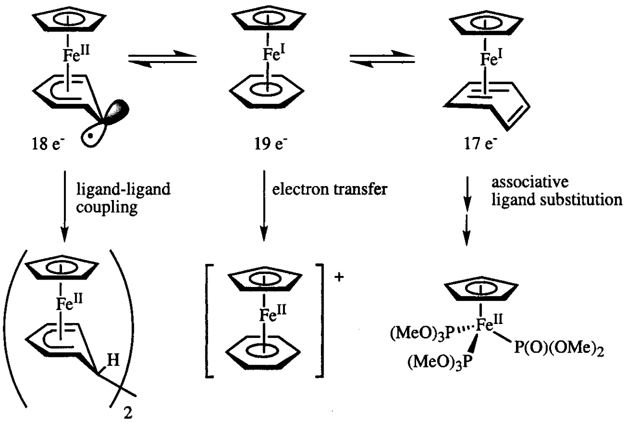
Keywords: Organometallic radicals; Free radical addition; Ligand–ligand coupling

1. Background

Organometallic radicals have been a topic of interest due to their reactivity and proposed involvement in catalysis [1–5]. Organometallic radicals can be generated from closed shell (18 e^-) transition metal complexes in the following ways: homolysis of metal–metal bonds or metal–ligand bonds, electron transfer, atom abstraction, or addition of organic radicals to closed shell complexes. The resulting species are described as 17 e^-, 19 e^-, or $(18+\delta)$ e^-, depending on the location of the unpaired electron with respect to the valence shell of the metal. In the simplest view, 17 e^- and 19 e^- complexes are produced by one-electron oxidation and reduction, respectively, of an 18 e^- complex at the metal. An $(18+\delta)$ e^- complex bears spin density primarily in the ligand orbitals [6].

From this simple view (and the assumption that the spin density determines the reactive site), it would be expected that reactivity would most likely occur at the metal for 17 e^- and 19 e^- complexes and at one or more sites within the ligand for $(18+\delta)$ e^- complexes. However, reactive sites may not correlate to the location of the spin density in the most stable form of the complex as determined spectroscopically. For complexes whose ligands provide variable bonding modes, changes in ligand geometry can alter the electron count at the metal so that several different radical species can be in equilibrium. Examples such as the iron sandwich complexes $CpFe(C_6R_6)$ where $R = H$, Me [1,7] undergo reactions characteristic of different radical types. Although the spectroscopic and structural data are consistent with formulation as Fe(I) 19 e^- complexes, various reaction modes suggest 17 e^-, 18 e^-, or 19 e^- species (Scheme 1) [7]. Both metal-centered and ligand-centered radical reactivity can occur in these ‘chameleon-like’ radicals.

The processes illustrated in Scheme 1 are a subset of the known reactions of organometallic radicals. These include radical coupling, atom transfer, associative substitution, electron transfer, metal-alkyl homolysis and migratory insertion. Although the literature contains extensive examples of metal-centered radical reactivity, there are relatively few examples of radical reactivity within the ligands. There are even fewer cases in which both metal-centered and ligand-centered radical reactivity are observed from the same molecule. The more common metal-centered reactions involve dimerization by formation of metal–metal bonds, halogen atom abstraction and hydrogen abstraction. These topics have been reviewed extensively and will not be discussed further [3]. Organic free radical reactions that are mediated by organometallic complexes have also been recently reviewed [8–11] and will not be covered within this discussion. Recently emphasis has also been placed



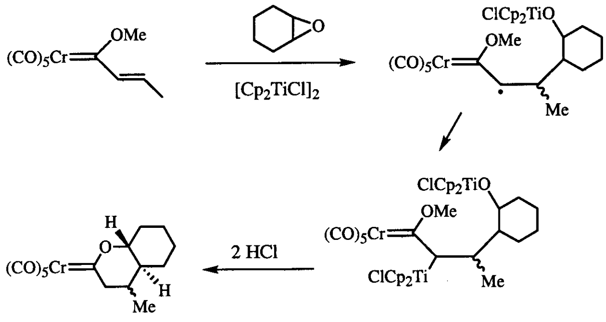
Scheme 1.

on the study of odd-electron organometallics and the design of electron reservoirs. Little consideration will be given to these systems here because they involve reversible electron transfer and do not result in permanent chemical reactions [12,13]. In addition, there are several examples of $18+\delta$ complexes that have significant spin density on the ligands as determined spectroscopically [6]. Inclusion of these complexes will be limited to cases that have demonstrated radical reactivity at the ligands.

This review will cover systems that display ligand-centered radical reactivity with emphasis on literature since the last major review of organometallic radicals in 1995 [1]. First, systems involving the addition of organic radicals to organometallic complexes will be considered. Next, reactions involving selective generation of ligand-centered radical species will be discussed. A survey of radical ligand–ligand coupling will be followed by an overview of organometallic radicals that show both ligand-centered and metal-centered reactivity due to the changing hapticity of the coordinated ligands. After short consideration of a few other ligand-centered radical reactions, a final discussion will be given to chemistry involving 17-electron cationic carbynes.

2. Free radical addition to organometallic complexes

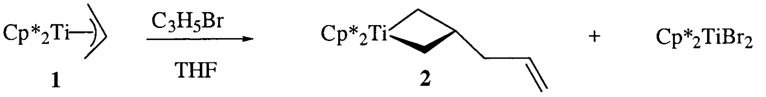
Recently, Elschenbroich and Agbaria described a system in which an organic radical ($R^\bullet$) is added to the chromium sandwich complex $(\eta^6\text{-}C_6H_6)_2Cr$ [14]. A paramagnetic adduct forms in which the R group ends up on the arene ring *endo* to the metal. ENDOR studies indicate a dynamic ring-to-ring migration mediated by the central metal atom. Thus, during the migration of the R group, the site of the radical moves back and forth between the metal center and the arene ring. Merlic also reported addition of organic radicals to 18-electron organometallic



Scheme 2.

species to generate organometallic radicals [15]. As shown in Scheme 2, the radical adds to the double bond of an unsaturated Fischer carbene resulting in an alkyl radical adjacent to the metal center. This species is then trapped by Cp_2TiCl and subsequent acidic workup leads to the cyclized product.

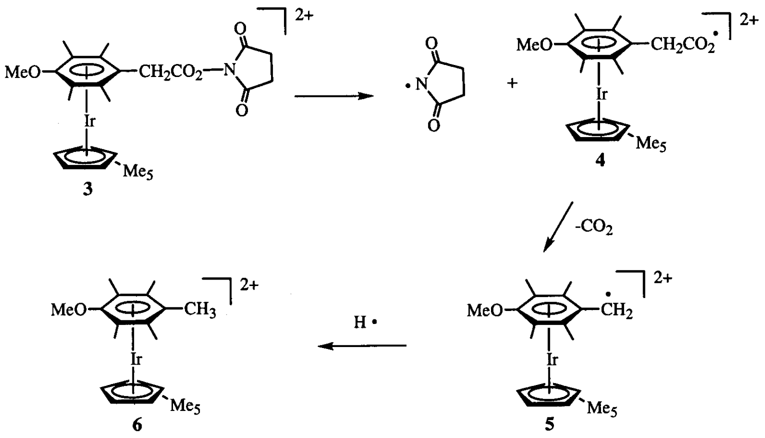
Demonstrating a slightly different reactivity, Stryker adds allyl radicals to the 17-electron organometallic allyl species **1** (Eq. (1)) [16]. Although metal-centered radical reactivity would be expected, the radical addition occurs solely at the central carbon of the allyl to produce the metallacyclic product **2**. This regiochemistry could be indicative of spin density at C2 in the original complex. Additions of radicals to analogous η^3-propargyl complexes exhibit a similar regioselectivity for addition at C2 [17].



(1)

3. Radical generation at the ligand

In addition to reactions in which an organic radical is added to a closed shell organometallic system to generate an organometallic radical (vide supra), there are also a few cases in which a radical has been generated intentionally at the ligand. Although the aryl ligand of the dicationic iridium compound **3** (Scheme 3) is stable by itself, decomposition ensues upon complexation to the metal [18]. It is proposed that the O–N bond undergoes homolysis to produce carboxyl radical **4**, which then loses CO_2 to produce the alkyl radical **5**. Hydrogen abstraction at the ligand produces the final product **6**. Other cases involve generation of samarium ketyls from chromium complexed aryl ketones [19–21]. As an example, the complexed ketyl **7** undergoes an intermolecular radical addition to an alkene to yield alkyl radical **8** (Scheme 4). Reduction by samarium(II) then produces the corresponding anion. After protic workup, cyclization yields the lactone **9**. Related intramolecular

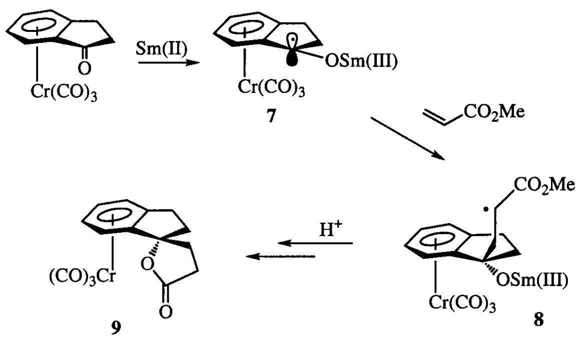


Scheme 3.

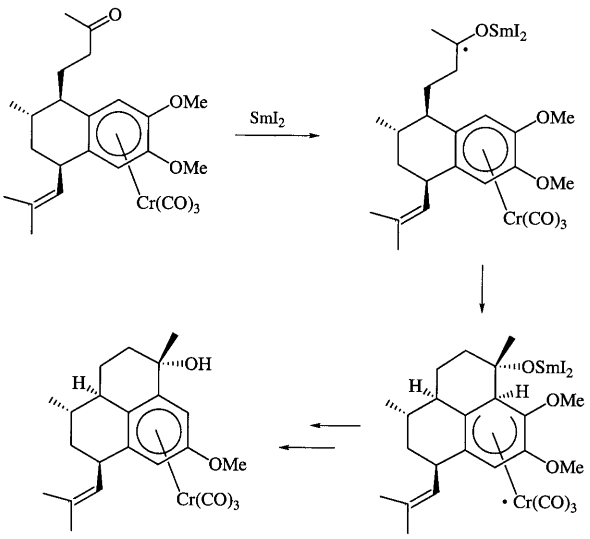
reactions of remote ketones have been used to assemble polycyclic structures (Scheme 5) [22]. Iron diene complexes have also been utilized as substrates for intramolecular attack of ketyl radicals (Scheme 6) [23].

4. Ligand–ligand coupling

A more common mode for ligand-centered reactivity of odd-electron organometallics is ligand–ligand coupling. Metal-centered radical reactivity is typical for neutral 17 e^- organometallic complexes such as $CpM(CO)_3$ [M = Cr, Mo, W] [3]. However, ligand-centered radical reactivity is often observed in 19 e^- or cationic 17 e^- systems [24]. Since aspects of this topic have been discussed [1], this section of the review focuses on the most recent literature although some earlier reports will be covered as well. These reactions will be grouped according to the coupling process. Dimerization through polyhapto ligands will be examined first



Scheme 4.

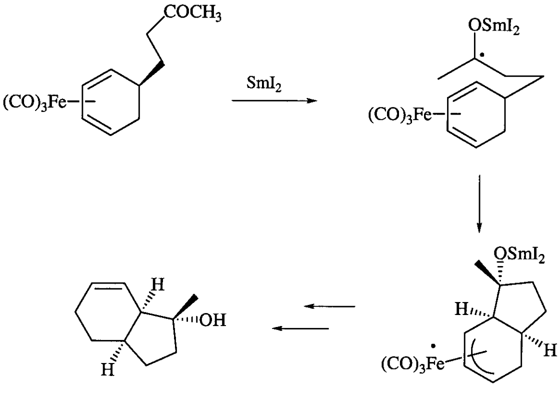


Scheme 5.

followed by coupling through monohapto ligands. Finally, miscellaneous reactions involving coupling of other molecules to the ligand radical will be considered.

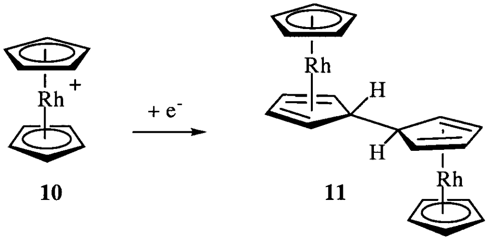
4.1. Coupling through polyhapto ligands in 19 e^- complexes

By all accounts, 19 e^- systems tend to have more radical density located on the ligand than 17 e^- complexes. This is a consequence of the nineteenth electron on the metal (if any) needing to occupy a high-energy metal-centered orbital. Therefore, the most stable 19 e^- complexes tend to have polyhapto ligands in which the radical density can be evenly spread over a large number of atoms. The most



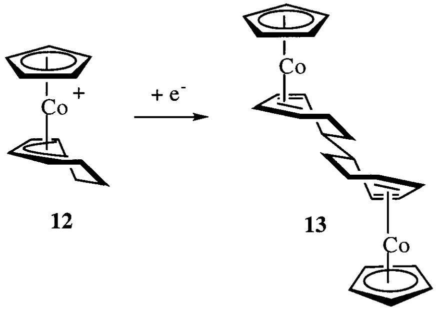
Scheme 6.

common reaction for 19 e^- systems is dimerization through polyhapto ligands. Dimerization results in a lowering of the electron count by decreasing the hapticity of the perturbed ligand. For example, upon one electron reduction, rhodocenium cation **10** dimerizes through the Cp ring to form complex **11** (Eq. (2)) [25]. A more recent example involves the reduction of the mixed Cp rhodocenium complex $[(\eta^5\text{-}C_5Me_5)Rh(\eta^5\text{-}C_5H_5)]^+$ [26]. Dimerization occurs as above; however, only one isomer is observed in which one of the Cp ligands dimerizes with a Cp* ligand of another rhodocene.



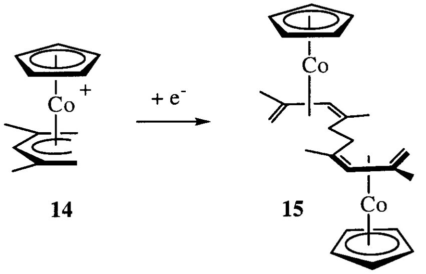
10 **11** (2)

Dimerization through ligands other than Cp can also be observed in cobaltocenium complexes. For example, $[CpCo(\eta^5\text{-}C_7H_9)]^+$ (**12**) can be reduced chemically and electrochemically to produce complex **13** (Eq. (3)) [24].



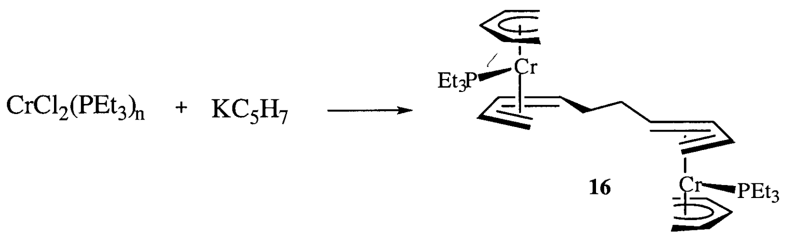
12 **13** (3)

There are a few cases of dimerization through open polyhapto ligands as well. For example, reduction of cobaltocenium complex **14** results in dimerization through the pentadiene ligand to produce **15** (Eq. (4)) [27].



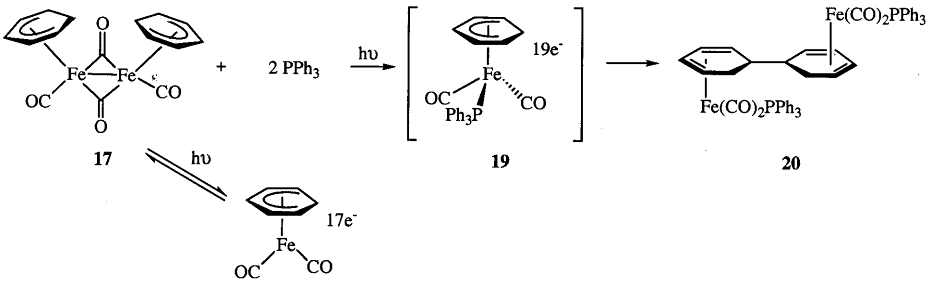
14 **15** (4)

Dimerization was also observed upon reaction of $CrCl_2(PEt_3)_n$ with two equivalents of KC_5H_7. Reaction occurs through the pentadienyl ligand of an odd-electron intermediate to yield the chromium dimer **16** (Eq. (5)) with spontaneous reduction of the metal from Cr(II) to Cr(I) [28].



16 (5)

As discussed above, neutral 17 e^- complexes tend to undergo metal-centered reactions while 19 e^- complexes are dominated by ligand-centered reactivity. The example in Scheme 7 demonstrates these differences within the same system [29].



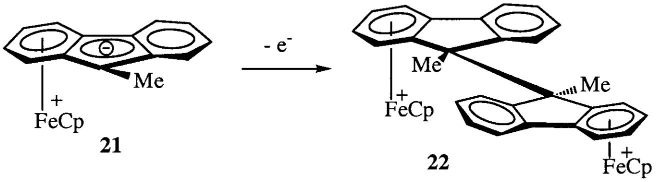
17 **18** **19** **20**

Scheme 7.

Upon photolysis, the iron dimer **17** undergoes homolysis of the iron–iron bond to form the 17 e^- neutral radical species **18,** which dimerizes at the metal to regenerate the starting material. Photolysis in the presence of a ligand such as PPh_3 results in a dimerization at the ligand to produce **20** following addition of phosphine to yield the intermediate 19 e^- radical **19**.

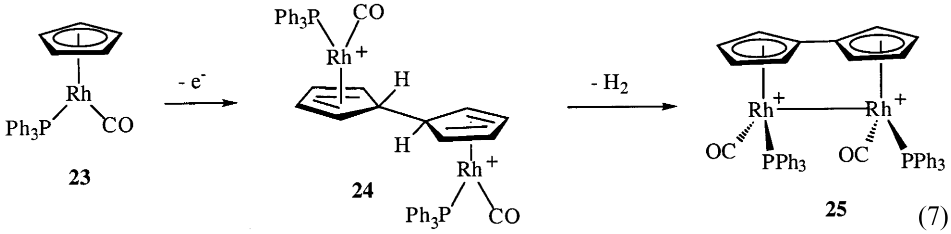
4.2. Coupling through polyhapto ligands in 17 e^- complexes

Unlike their neutral counterparts, 17 e^- cationic complexes often demonstrate ligand-centered reactivity. For example, formation of dimer **22** occurs upon one-electron oxidation of the iron fluorenyl complex **21** (Eq. (6)) [30].



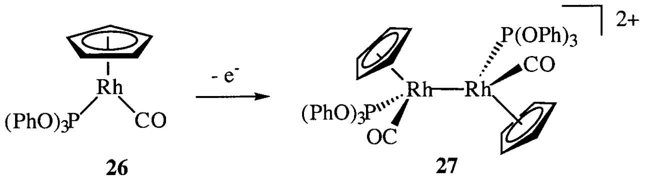
21 **22** (6)

In a related reaction, oxidation of the rhodium half-sandwich complex **23** produces dimer **25**, formally by loss of H_2 from the expected dimerization product **24** (Eq. (7)) [31,32]. The driving force for the reaction is the regeneration of the η^5-Cp ligand.



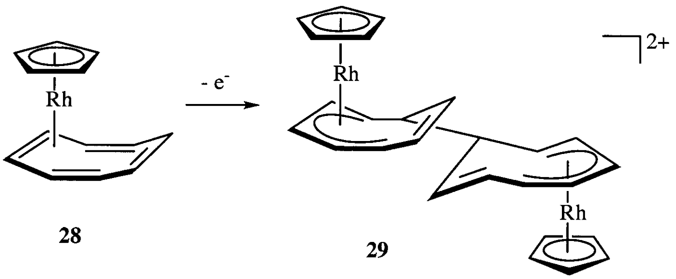
(7)

Surprisingly, it was found that exchanging the phosphine ligand in complex **23** for either $P(OPh)_3$ or PMe_3 resulted in entirely different chemistry. As shown in Eq. (8), the 17 e^- radical cation generated from phosphite complex **26** reacts as a metal-centered radical to form the metal–metal bonded dimer **27** [33].



(8)

Like the 19 e^- systems, there are also a few cationic 17 e^- systems which exhibit coupling reactions involving polyhapto ligands other than Cp. Geiger has shown that the rhodium cyclooctatetraene complex **28** yields the ligand-coupled dimer **29** upon oxidation (Eq. (9)) [34]. The proposed intermediate bears a cyclooctatetraene ring that is bound η^5, with the remaining carbons comprising an allyl radical. Connelly observed an analogous dimer when $Ru(CO)_2(PPh_3)(\eta^4\text{-}C_8H_8)$ was oxidized with ferrocenium tetrafluoroborate [35].

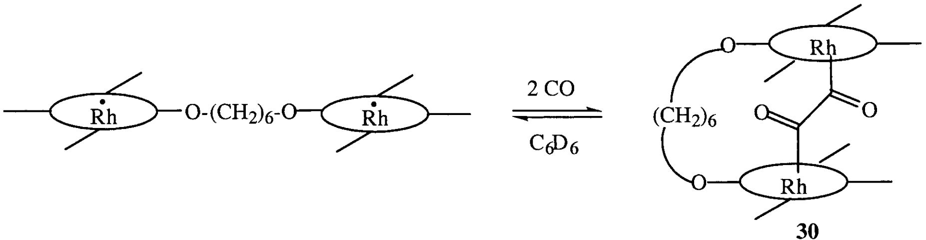


(9)

4.3. Coupling through monohapto ligands

Although early examples of dimerization chemistry involved polyhapto ligands, there is a growing body of literature on the coupling of monohapto ligands. One way to ensure ligand-centered radical reactivity is to increase the steric bulk around the metal center. Metalloporphyrin systems have become popular for these studies. The odd-electron complex (TMP)RhCO (TMP = tetramesitylporphyrin) behaves as an acyl radical, coupling through the carbonyl ligands to form the diketone dimer

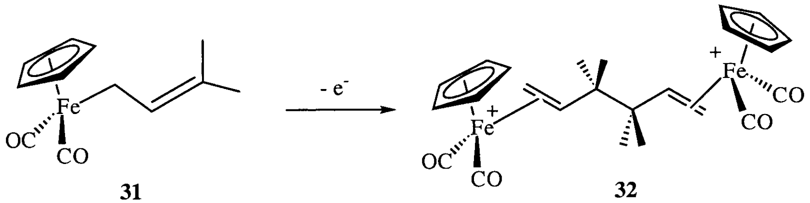
(TMP)RhC(O)C(O)Rh(TMP) in the absence of good H-donors [36]. More recently, Wayland examined the reactivity of a rhodium(II) porphyrin bimetalloradical complex, $^{\bullet}RhO(CH_2)_6ORh^{\bullet}$, in which two trimesitylphenylporphyrin units are bridged by a diether $(O–(CH_2)_6–O)$ spacer. This bimetalloradical complex reacts reversibly with CO to form the diketone complex **30** (Eq. (10)) [37].



30

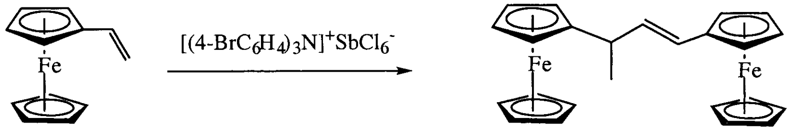
(10)

In a more common type of organometallic system, Waterman observed coupling of allyl fragments to produce **32** upon one-electron oxidation of the iron allyl complex **31** (Eq. (11)) [38]. Along similar lines, coupling of two allyl ligands on the same metal to produce 1,5-hexadiene has been noted following one-electron oxidation of $CpMo(\eta^3-C_3H_5)_2$ [39].



31 **32** (11)

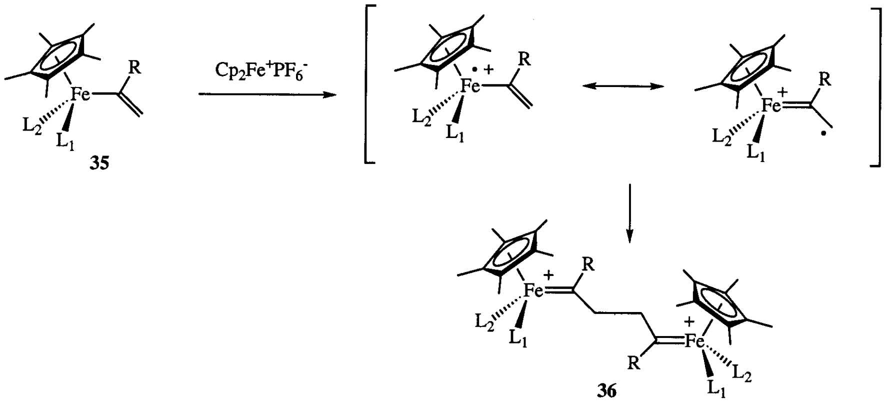
Although the mechanism has not been elucidated, the reaction proceeds very quickly without loss of propene, which suggests an intramolecular radical coupling reaction. Oxidation of vinyl ferrocene **33** with the aminium salt $(4-BrC_6H_4)_3N^+$ $SbCl_6^-$ was found to result in coupling at the vinyl ligand to produce complex **34** (Eq. (12)) [40].



33 **34** (12)

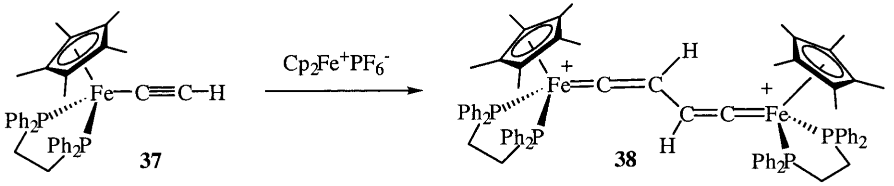
Iron vinyl complexes such as **35** have been shown to couple readily upon oxidation to yield bis(alkylidene) dimers **36** (Scheme 8) [41–43]. The resonance structures in Scheme 8 provide a rationale for the observed reactivity.

Due to recent interest in molecular wires [42,44,45], there has been rapid development of oxidative coupling chemistry for the synthesis of conjugated carbon linkers between two metals. Although a discussion of the redox chemistry of the molecular wires is outside the scope of this review, the oxidative reactions used to construct the dimers will be presented.



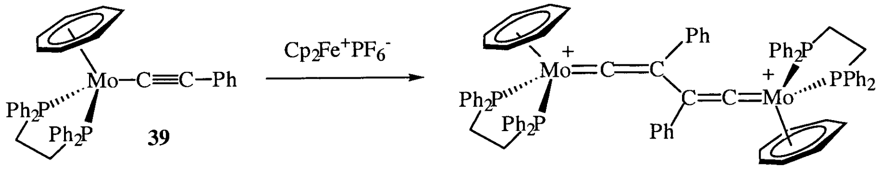
Scheme 8.

Lapinte has reported oxidation of the iron-alkynyl complex **37** with ferrocenium hexafluorophosphate to yield the dicationic vinylidene dimer **38** (Eq. (13)) [46,47].



(13)

A similar dimerization for molybdenum alkynyl complex **39** was described by Beddoes (Eq. (14)) [48]. An analogous reaction was found to occur upon one-electron oxidation of $Cp(CO)_3Cr(C{\equiv}C{-}Ph)$ to produce $[Cp(CO)_3Cr{=}C{=}C(Ph)C(Ph){=}C{=}Cr(CO)_3Cp]^{2+}$ [49].



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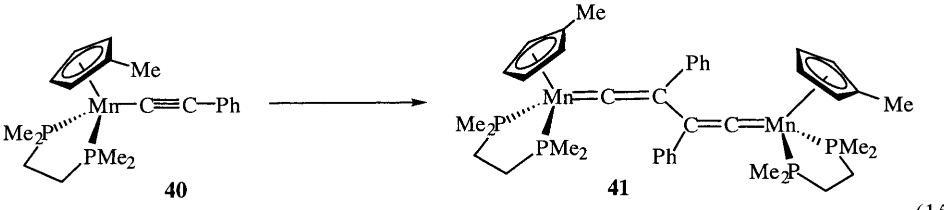
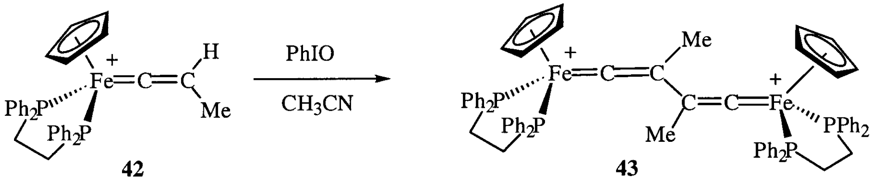
Unlike most 17-electron neutral systems which display metal-centered reactivity, manganese alkyne complex **40** produces vinylidene dimer **41** upon warming (Eq. (15)).



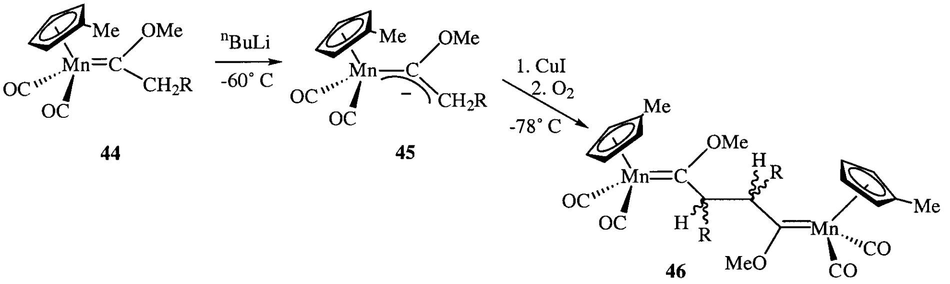
(15)

One-electron oxidation of iron vinylidene **42** with iodosylbenzene yields the dicationic vinylidene dimer **43** (Eq. (16)) [50]. This complex is proposed to result from dimerization of the 17 e^- radical cation $[Cp(dppe)Fe^-C{\equiv}CMe]^+$ produced after deprotonation of the oxidized vinylidene. In a similar reaction $[Ru_2(\mu\text{-}C_4TMS_2)(PMe_3)_4Cp_2]^{2+}$ was produced after air oxidation of the cationic ruthenium vinylidene $[Cp(PMe_3)_2Ru{=}C{=}CH(TMS)]^+$ [51].



(16)

Coupling by deprotonation/oxidation sequences has also been reported. Deprotonation of manganese carbene **44** yields anion **45**, which couples via the carbene ligand to yield **46** upon oxidation with CuI (Eq. (17)) [52]. Templeton developed a similar route for oxidative coupling of carbyne complexes [53]. Deprotonation of the Tp′ carbyne **47** (Tp′ = hydridotris(3,5-dimethyl-1-pyrazolyl)borate; M = Mo, W) with ^{n}BuLi followed by two-electron oxidation results in the coupled product **48** (Eq. (18)). Analogously, deprotonation of $Cp\{P(OMe)_3\}_2Mo{\equiv}CCH_2^tBu$ with ^{n}BuLi followed by oxidation with ferrocenium tetrafluoroborate yields $Cp\{P(OMe)_3\}_2\text{-}Mo{\equiv}CCH^tBuCH^tBuC{\equiv}Mo\{P(OMe)_3\}_2Cp$ [54].



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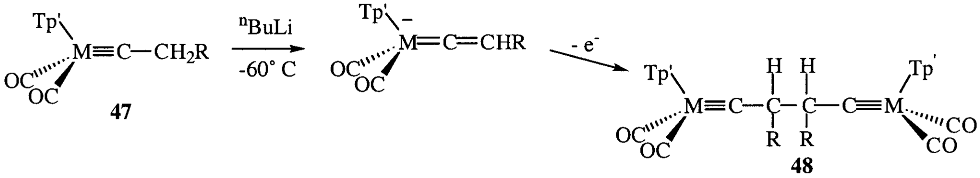
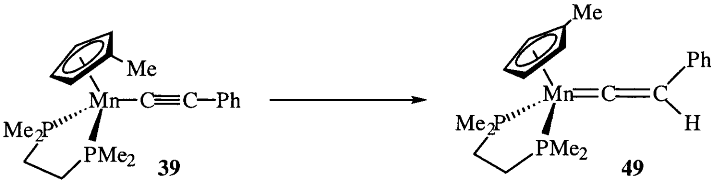


(18)

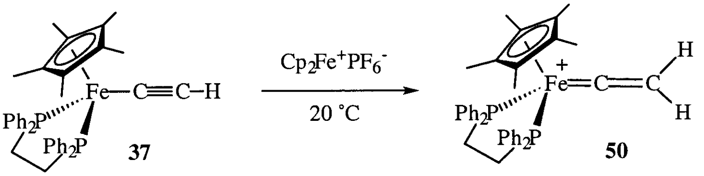
5. Hydrogen-atom abstraction

Although ligand–ligand coupling is the most common ligand-centered reaction for organometallic radical complexes, these radicals can also react intermolecularly with other species in solution. For example, some of the above dimerization reactions occur in competition with hydrogen atom abstraction. In the case of the manganese alkyne complex (η^5-C_5H_4Me)(dmpe)Mn–C≡CPh, hydrogen atom abstraction resulted in formation of vinylidene **49** (Eq. (19)) [55].



(19)

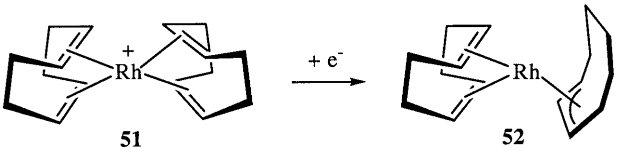
This reaction competed with dimerization to the extent that the resulting mixtures were difficult to purify. In the presence of better hydrogen atom donors, such as ^{n}Bu$_3$SnH, the vinylidene could be prepared directly from the manganese alkyne complex without any detectable amounts of dimerization products. In a related process, Lapinte found that if the iron alkyne complex **37** were oxidized at 20°C instead of at temperatures below − 50°C, H atom abstraction at C2 of the alkyne to yield vinylidene **50** became the dominant reaction pathway (Eq. (20)) [47].



(20)

As discussed above, one-electron oxidation of (η^7-C_7H_7)(dppe)Mo(C≡CPh) with ferrocenium hexafluorophosphate results in dimerization at C2 of the alkyne [48]. However, when the alkyne is substituted with a *tert*-butyl group instead of a phenyl group, oxidation results in the corresponding cationic vinylidene complex via hydrogen atom abstraction [56]. In this case dimerization is prevented by the steric bulk of the *tert*-butyl group. Similarly, Wayland found that the metalloporphyrin complex (TMP)RhCO reacted with the good H-donor ^{n}Bu$_3$SnH by hydrogen atom abstraction at the carbonyl ligand to form the formyl species (TMP)RhC(O)H [36].

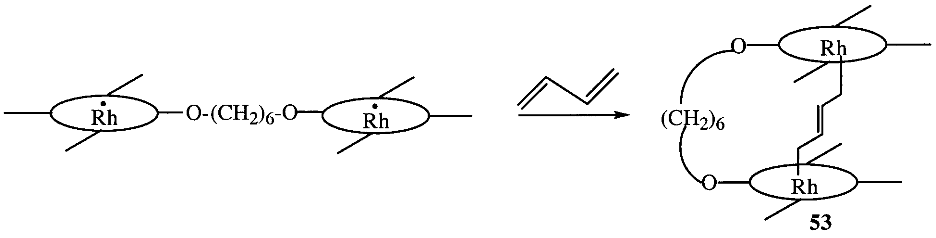
As would be expected for 17 e^- neutral radicals, reduction of $(COD)_2Rh^+$ (COD = cyclooctadiene) in CH_2Cl_2 resulted in halogen atom abstraction from the solvent at the metal center to produce [(COD)Rh(μ-Cl)]$_2$ [57]. Unexpectedly, reduction at − 45°C in the absence of a halogenated solvent resulted in hydrogen atom abstraction at the ligand to produce **52** (Eq. (21)). It should be noted that the exact isomer of the product is not known.



(21)

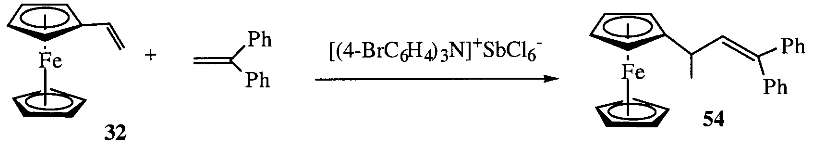
6. Intermolecular radical additions to unsaturated substrates

Another type of intermolecular reaction involves the addition of organometallic radicals to unsaturated species. (TMP)RhCO was found to form the adduct (TMP)RhC(O)CH_2CH(Ph)C(O)Rh(TMP) in the presence of styrene. This product results from radical addition to the alkene followed by coupling to a second equivalent of (TMP)Rh(CO) [36]. The bimetalloradical complex depicted in Eq. (10) also reacts with alkenes to produce species such as **53**, in which the metal atoms are bridged by carbon chains (Eq. (22)) [37].

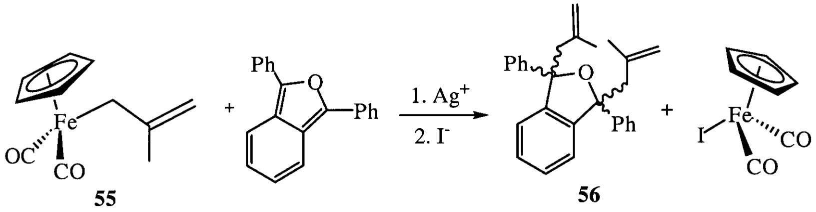


(22)

Oxidation of vinyl ferrocene (**32**) with $(4\text{-BrC}_6H_4)_3N^+SbCl_6^-$ in the presence of 1,1-diphenylethylene results in formation of the adduct **54** (Eq. (23)) [40]. A similar coupling was noted upon oxidation of the iron allyl complex **55** in the presence of 1,3-diphenylisobenzofuran. In this case oxidation was followed by treatment with I^- to remove the metal from the benzofuran product **56** (Eq. (24)) [38].



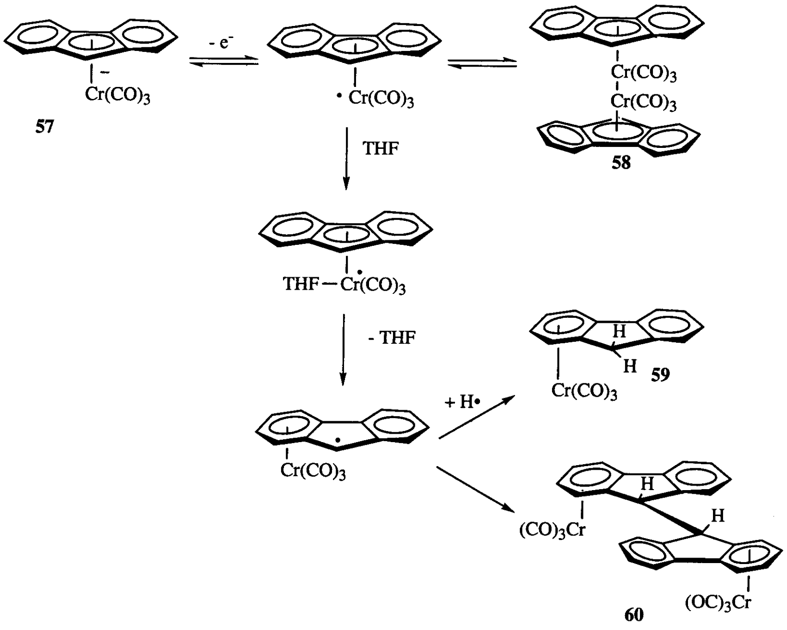
(23)



(24)

7. Metal and ligand reactivity–hapticity changes

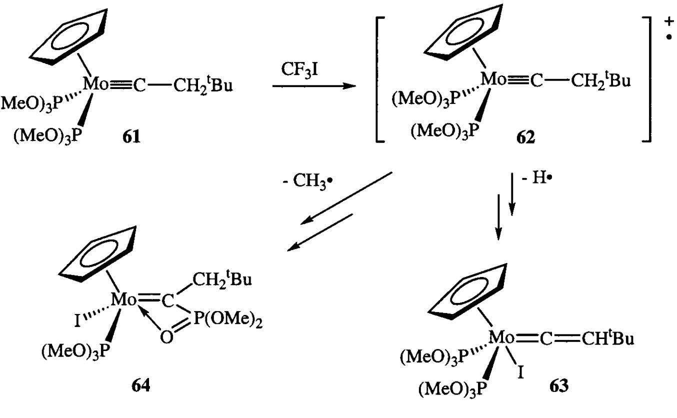
Because metal-centered organometallic radicals are generally more reactive than ligand-centered organometallic radicals, a system that displays metal radical behavior rarely exhibits ligand-centered reactivity as well. A recent example by Strelets involves chromium tricarbonyl anions complexed to fluorenyl systems via the central Cp ring [58]. One-electron oxidation of **57** leads to generation of the corresponding radical which is in equilibrium with metal–metal bonded dimer **58** (Scheme 9). The major product **59** results from H atom abstraction at the fluorenyl ligand, with the minor product resulting from dimerization at the fluorenyl ligand to yield **60**. The product distribution can be explained by a facile haptotropic shift of the chromium tricarbonyl complex from η^5 to η^6.



Scheme 9.

8. Miscellaneous ligand-centered reactions

Green observed that addition of CF_3I to the carbyne Cp{P(OMe)$_3$}$_2$-Mo≡CCH$_2^t$Bu results in formation of two different organometallic products (Scheme 10) [59]. These products are proposed to arise via initial electron transfer from the carbyne **61** to CF_3I to produce the 17-electron radical cation **62**. H-atom abstraction from the carbyne ligand followed by addition of I^- to the metal gives rise to the vinylidene **63**. The second product results from Arbuzov-type



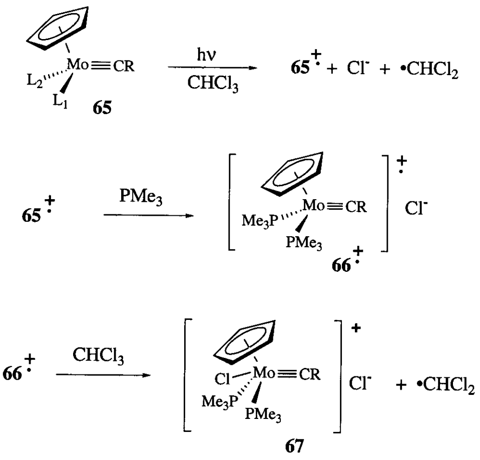
Scheme 10.

abstraction of $CH_3^{\bullet}$ from one of the coordinated phosphite groups. The resulting complex adds I^- followed by migration of the phosphite to the carbyne carbon. Coordination of the oxygen to the metal results in the final product **64**. Thus, although radical reactivity is implicated in these processes, the radical reactions are different from any of those previously described.

9. 17-electron cationic carbynes

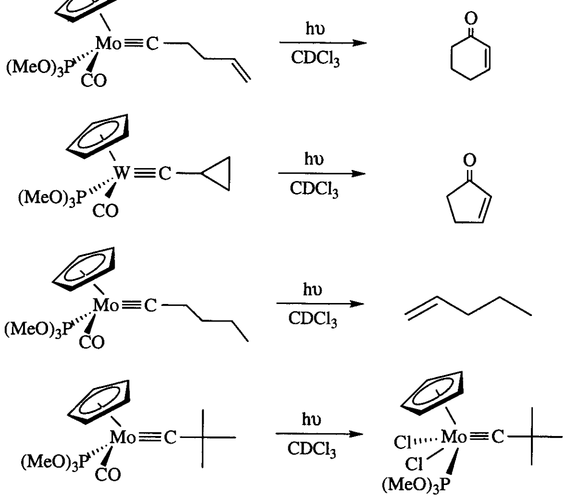
Over the past several years, we have studied activation of low-valence carbyne complexes by photochemical electron transfer. In the presence of halocarbons, the complexes $CpL_2M{\equiv}CR$ [M = Mo, W; L = $P(OMe)_3$, CO and R = alkyl, aryl] undergo photooxidation to give 17-electron cation radicals. Unlike the majority of the complexes described above in which reaction occurs either at the metal atom or within a ligand, the 17-electron carbyne complexes exhibit both metal-centered and ligand-centered reactivity without changing ligand binding modes. In the metal-centered mode, ligand exchange and halogen abstraction (characteristic reactions of metal radicals) yield new carbyne complexes. In the ligand-centered mode, hydrogen abstraction at the carbyne carbon yields highly reactive cationic carbene complexes whose further rearrangements lead ultimately to organic products.

The initial investigations of this system involved irradiation of $CHCl_3$ solutions of the carbynes **65**. When the reactions were run in the presence of PMe_3 to stabilize any unsaturated intermediates, new cationic carbyne complexes resulted as shown in Scheme 11 [60,61]. Mechanistic studies showed the primary photoprocess to be electron transfer from the excited state of the carbyne to the chloroform solvent. Upon reduction, the solvent undergoes fragmentation to form chloride ion and dichloromethyl radical ensuring an irreversible electron transfer. The resulting 17-electron cationic carbyne $\mathbf{65}^{+\bullet}$ then undergoes ligand exchange $\mathbf{66}^{+\bullet}$ and halogen-atom abstraction to yield the final cationic carbyne **67**.



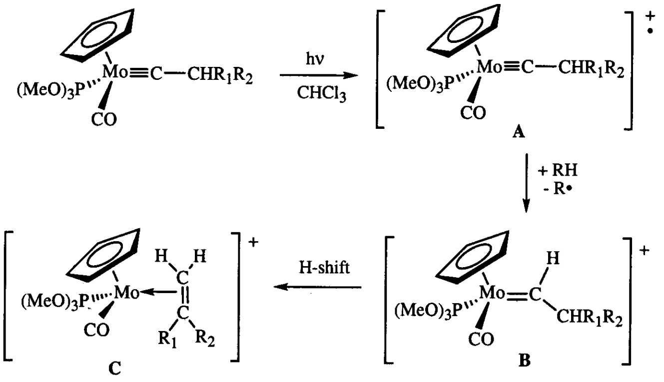
Scheme 11.

In the absence of strongly nucleophilic species such as PMe$_3$, the results of the photooxidation are quite different. For the complexes Cp(CO)LM$\equiv$CR, where R is a primary or secondary alkyl group, photooxidation results in organic products derived from the carbyne substituent [62]. If R is a tertiary alkyl group, a new carbyne species is the product (Scheme 12).



Scheme 12.

Mechanistic studies have revealed that these products are derived from similar intermediates. As shown in the proposed mechanism for the formation of olefins from carbynes bearing primary alkyl substituents (Scheme 13), the first step is



Scheme 13.

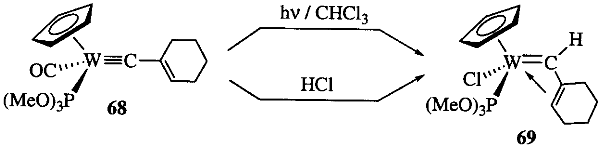
one-electron oxidation of the carbyne to form the 17-electron radical cationic carbyne **A**. H-atom abstraction at the carbyne carbon results in an electrophilic carbene **B** which undergoes a 1,2-hydride shift to yield the final olefin complex **C**. Under the oxidative conditions, the olefin is released from **C**. In general, the fate of the carbyne radical **A** depends on the steric bulk of the carbyne substituent. For primary and secondary substituents on the carbyne, hydrogen atom abstraction is standard. For tertiary substituents, the 17-electron cationic carbyne undergoes ligand exchange with chloride followed by halogen atom abstraction to form the new carbyne via metal-centered radical reactions.

Because of the electronic structure of the neutral carbyne complexes, hydrogen abstraction at the carbyne carbon was unexpected. Extended Hückel and INDO calculations on the neutral carbyne complexes indicate that their HOMOs are nonbonding metal d orbitals ($d_{x^2-y^2}$) [63]. This suggests that one-electron oxidation should yield radical cations whose spin density and positive charge are on the metal, not the carbyne ligand. However, INDO calculations on the carbyne radical cation $[Cp(CO)\{P(OMe)_3\}Mo{\equiv}CCH_2CH_3]^{+\bullet}$ indicate stabilization upon bending the Mo≡C–C angle from 180 to 120°. This change in geometry places spin density on the carbyne carbon in the radical cation although the initial oxidation occurs from an orbital that is primarily nonbonding metal d in character. The oxidized carbyne is thus able to function as a carbon-centered radical and abstract a hydrogen atom at the carbyne carbon.

As mentioned above, complexes with tertiary substituents on the carbyne yielded new carbyne species via metal-centered radical reactions. This is consistent with the additional steric hindrance at the carbyne carbon rendering H abstraction at that site too slow to compete with reaction at the metal atom of the radical cation. An alternative view is that the steric bulk of the *tert*-butyl group hinders the bending of the Mo≡C–C angle, preventing the shift of spin density onto the carbyne carbon. The *tert*-butyl carbyne thus behaves as a typical metal-centered 17-electron radical.

Although proposed as an intermediate in several carbyne photooxidation reactions, the electrophilic carbene **B** generated upon hydrogen abstraction by the

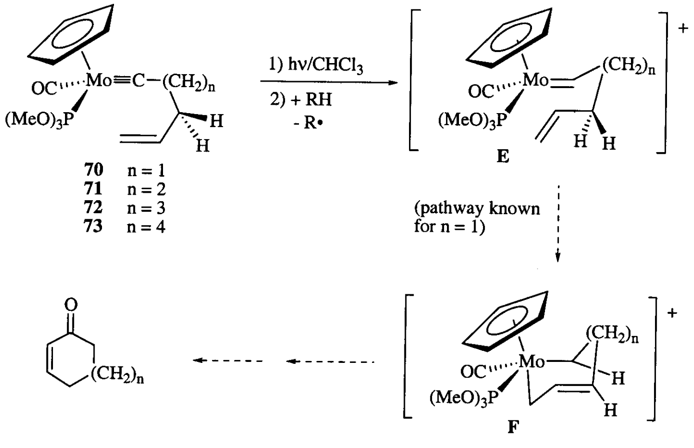
17-electron radical cation had not been directly observed. However, it was recently found that photooxidation of the cyclohexenyl carbyne **68** in $CHCl_3$ produced carbene complex **69** (Scheme 14) [64]. The carbene moiety is proposed to form via electron transfer and hydrogen atom abstraction as with other carbynes. In this particular case, the alkene moiety then coordinates to the metal and Cl^- exchanges for the carbonyl ligand to yield the final product. Carbene **69** is stable at −40°C and has been characterized spectroscopically (^{1}H-, ^{13}C-NMR, IR and electrospray MS). These results are significant because they represent the first direct observation of a carbene complex in one of our photooxidation reaction mixtures. This provides corroborating evidence that the carbyne radical cation produced upon oxidation does indeed undergo the highly unusual hydrogen abstraction process we have postulated on the basis of mechanistic studies.



Scheme 14.

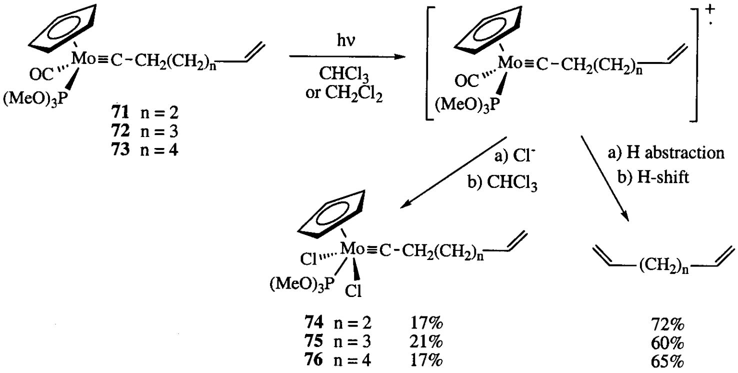
A further extension of this chemistry involved the examination of the ring size dependence of the cyclization reaction **E** → **F** (Scheme 15) [65]. The intramolecular ene reaction, carbonylation and reductive elimination sequence that forms a cycloalkenone had already been established for carbyne **70** [66]. Since intramolecular ene reactions of this type leading to 7, 8 and 9-membered rings are known in organic systems, the question of whether or not carbynes **71**–**73** would undergo cyclization of the intermediate carbene **E** was an interesting one.

For this study, the alkenyl carbyne complexes Cp(CO){P(OMe)$_3$}-Mo≡C–CH$_2$(CH$_2$)$_n$CH=CH$_2$ [$n=2$ (**71**), 3 (**72**), and 4 (**73**)] were prepared and



Scheme 15.

characterized. Photolysis of **71**–**73** in chlorinated solvents resulted in the formation of the corresponding α,ω-dienes $CH_2{=}CH(CH_2)_nCH{=}CH_2$ (Scheme 16) instead of cycloalkenones. Also produced were the dichloromolybdenum carbynes $Cp\{P(OMe)_3\}Cl_2Mo{\equiv}C{-}CH_2(CH_2)_nCH{=}CH_2$ (**74**–**76**).

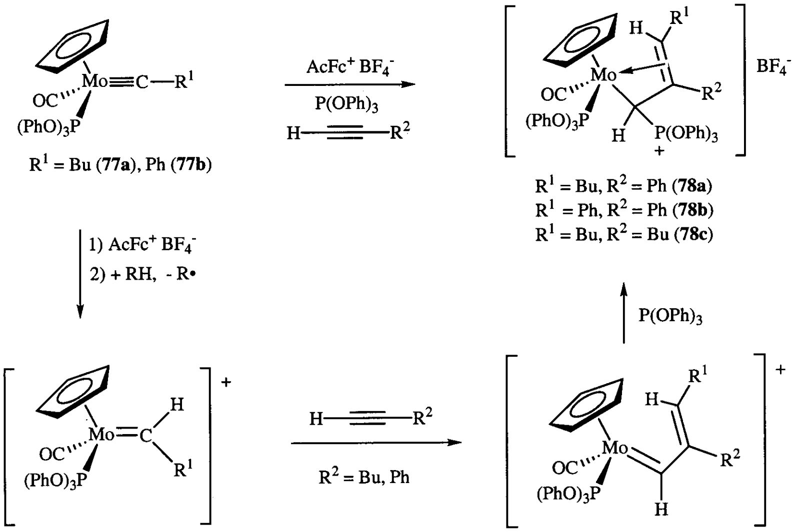


Scheme 16.

Although no cyclic products were formed, it should be noted that both sets of products arise from the highly reactive 17-electron species produced upon photooxidation. The dichloromolybdenum carbynes **74**–**76** are formed by exchange of Cl^- for the CO ligand and Cl abstraction at the metal. The dienes are produced from the radical cations by the mechanistic pathway shown in Scheme 13: H-abstraction at the carbyne carbon followed by H-shift. For the longer alkenyl chains ($n = 3$–5), the H-shift process is faster than intramolecular ene reaction, and no cyclization occurs. However, the product ratios allow us to evaluate the relative reactivity of the carbyne radical cation at the carbyne carbon (leading to olefins) versus its reactivity at the metal center (leading to dichloromolybdenum carbynes) in a case where the primary alkyl substituent provides minimal steric hindrance. In these sterically unbiased cases, the preference for radical reactivity in the carbyne ligand is in the range 3:1 to 4:1. Thus, a unique system has been developed in which metal and ligand radical reactivity are observed within the same molecule and an unusual preference for ligand-centered reactivity is observed.

Although photooxidation has been successful in yielding products derived from ligand-centered radical reactivity, there are aspects of this method that make it difficult to obtain organic products in high yield. Upon reduction, $CHCl_3$ fragments to Cl^- and $^{\bullet}CHCl_2$ [67]. Evidence for side reactions involving the $^{\bullet}CHCl_2$ radical can be found in the formation of CH_3Cl [68] by the Arbuzov reaction [69] of $P(OMe)_3$ ligands. The use of outer sphere chemical oxidants at low temperatures provides an alternative approach in which side reactions from $^{\bullet}CHCl_2$ can be avoided. One-electron oxidation of the carbyne complex $(\eta^5\text{-}C_5H_5)(CO)\{P(OPh)_3\}Mo{\equiv}C{-}CH_2CH_2CH_2CH_3$ (**77a**) in the presence of phenylacetylene results in H-abstraction and addition of the alkyne to the resulting metal carbene. The final product of the addition is the $\eta^1\eta^2$-allyl complex (η^5-

$C_5H_5)(CO)\{P(OPh)_3\}Mo[\eta^1\eta^2\text{-}CH\{P(OPh)_3\}C(Ph)=CH(CH_2CH_2CH_2CH_3)]$ (**78a**) (Scheme 17) [70]. Chemical oxidation generates the same intermediates as photooxidation as can be seen by the production of 1-pentene upon reaction of **77a** with acetylferrocenium tetrafluoroborate ($AcFc^+BF_4$) in the absence of alkyne. However, when the reaction is carried out in the presence of phenylacetylene, the expected H-shift to yield olefin is suppressed and compound **78a** is isolated in 25% yield. In previous cases where we have generated intermediates of the type (η^5-$C_5H_5)(CO)\{P(OR)_3\}M{=}CHR^+$ via oxidation of carbyne complexes, intramolecular rearrangement of the carbene ligand has been the dominant process. These examples are the first where the carbene could be intercepted in a bimolecular reaction.



Scheme 17.

10. Concluding remarks

Odd electron organometallic compounds have been the subject of intensive study. However, there is still much to learn about these species. The majority of the literature has focused on the more common metal-centered radical reactions, yet there is growing interest in ligand-centered radical reactivity. In the future, selectively accessing these reaction modes of organometallic radicals, which generally have no counterpart in the traditional reactions of even-electron species, could greatly enhance our ability to utilize organometallic chemistry in synthesis and catalysis.

Acknowledgements

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