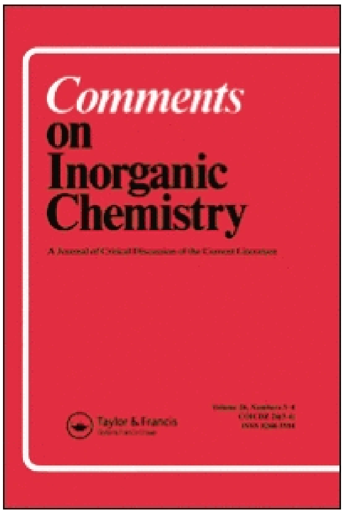

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Reactivity of Seventeen- and Nineteen-Valence Electron Complexes in Organometallic Chemistry

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Reactivity of Seventeen- and Nineteen-Valence Electron Complexes in Organometallic Chemistry

Organometallic chemistry has traditionally been the domain of diamagnetic complexes and the powerful 16- and 18-electron rule.[1] This rule, as set forth by Tolman,[1(a)] states that ". . . diamagnetic organometallic complexes of transition metals may exist in a significant concentration at moderate temperature only if the metal's valence shell contains 16 or 18 electrons." Furthermore, the rule states that "organometallic reactions, including catalytic ones, proceed by elementary steps involving only intermediates with 16 or 18 metal valence electrons." Although the rule is enormously useful for predicting the stability and reactivity of diamagnetic complexes, the range of organometallic chemistry has expanded in recent years to include numerous paramagnetic 17-valence electron complexes, which exist as both stable complexes and short-lived intermediates.[2,3,4] These species, essentially metal-centered radicals, are typified by complexes such as $Mn(CO)_5$, $Mn(CO)_3(PR_3)_2$, $Co(CO)_4$, and $CpMo(CO)_3$ ($Cp = \eta^5\text{-}C_5H_5$).

Unfortunately, the 16- and 18-electron rule provides no insights into the stability or reactivity of the odd-electron species. It would clearly be useful, both to mechanistic and synthetic chemists, to have guidelines that describe the chemistry of these species. This Comment, therefore, will propose and justify one guideline which we feel dominates all others concerning the reactivity of 17-electron species. Specifically, it is our primary thesis that the reactions of

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17-electron metal radicals are associatively activated with the reactions proceeding through a (formally) 19-valence electron species:

$$\underset{17}{ML_n} + Y \longrightarrow \underset{19}{ML_nY} \longrightarrow \text{products} \qquad (1)$$

It is the intent of this Comment to unify the disparate reaction chemistry of the 17-electron metal radicals in terms of this associative reaction pathway and to discuss the intermediacy of 19-valence electron complexes in producing the observed products. It is also our purpose to suggest that related associatively activated pathways need to be considered in some reactions that are thought to occur by more conventional routes involving 16- and 18-electron intermediates. Because the 19-electron complexes of the type we are discussing here are rather new to organometallic chemistry, we also briefly discuss the basic reaction chemistry and electronic structures of these species.

REACTIONS OF SEVENTEEN-VALENCE ELECTRON COMPLEXES: THE GENERAL INTERMEDIACY OF NINETEEN-VALENCE ELECTRON SPECIES

The reactivity of 17-electron organometallic radical complexes consists primarily of substitution, ligand association (adduct formation), inner-sphere electron transfer, and halogen atom abstraction (and, of course, radical coupling reactions). These types of reactivities were first observed for the $Co(CN)_5^{3-}$ complex, a species that serves as the prototype for all metal radicals,[5] and it is useful to describe organometallic radical reactivity based on the models for $Co(CN)_5^{3-}$ reactivity.

Substitution. The most thoroughly studied reactions of 17-electron complexes are the substitution reactions.[2,6] It was recognized early that substitution of 17-electron radicals was extremely facile, but there was considerable confusion for some time as to whether the process was associatively (Eq. (2)) or dissociatively (Eq. (3)) activated.

$$\underset{17}{ML_n} + L' \longrightarrow \underset{19}{ML_nL'} \longrightarrow \underset{17}{ML_{n-1}L'} + L \quad (2)$$

$$\underset{17}{ML_n} \xrightarrow{-L} \underset{15}{ML_{n-1}} \xrightarrow{L'} \underset{17}{ML_{n-1}L'} \quad (3)$$

Recent studies, however, have established the generality of the associatively activated pathway and have thereby established the principle that 17-electron species are susceptible to nucleophilic attack. In the earliest study supporting this conclusion, Poë, Fox and Malito studied the substitution reactions of photogenerated 17-electron $Re(CO)_5$ radicals.[7]

$$Re(CO)_5 + PR_3 \longrightarrow Re(CO)_4PR_3 + CO \quad (4)$$

$$PR_3 = PPh_3,\ P(n\text{-butyl})_3$$

No 19-electron intermediates were observed, but the reaction kinetics were consistent with a rate law for substitution that is first order in PR_3, implying an associatively activated mechanism. A second thorough study of the substitution mechanisms of 17-electron radicals was reported by Shi, Richmond, Trogler and Basolo[8] using the $V(CO)_6$ complex.

$$V(CO)_6 + PR_3 \longrightarrow V(CO)_5PR_3 + CO \quad (5)$$

The rate laws and activation parameters [$\Delta H^{\ddagger} = 10.0 \pm 0.4$ kcal/mol, $\Delta S^{\ddagger} = -27.8 \pm 1.6$ cal/(mol K); $PR_3 = PPh_3$] for substitution of $V(CO)_6$ by various phosphines (Eq. (5)) are consistent with an associatively activated mechanism, but once again, no intermediate of higher coordination number was observed or implied.

In a related study, McCullen, Walker and Brown studied the substitution reactions of the 17-electron $M(CO)_3L_2$ complexes (M = Mn, Re).[9] In previous work, Brown and co-workers had shown that 17-electron species of this type (L = a bulky phosphine) were stable with respect to radical recombination because of the steric bulk of the phosphines.[10] The $M(CO)_3L_2$ complexes thus provided an ideal opportunity to study in a straightforward fashion the reactivity of 17-electron species that were coordinatively unsaturated (as opposed to $V(CO)_6$, say, which is nominally coordinatively saturated). In their study, Brown and co-workers established that these complexes substituted via an associatively activated mechanism.[9] In subsequent work, Brown also repeated his earlier study of the substitution reactions of the $Mn(CO)_5$ species and found that this species also substituted via an associatively activated mechanism.[11] This latter study is especially important because in an earlier study, Brown had proposed that substitution reactions of $Mn(CO)_5$ were dissociatively activated.[6] This claim, accepted by chemists until Poë's[7] and Trogler and Basolo's[8] work cited above, hindered for several years the acceptance of associative activation as a general pathway.

Kochi and co-workers also studied the substitution reactions of 17-electron species.[12] Their approach was to generate the 17-electron species by electrochemically oxidizing stable 18-electron complexes. Using cyclic voltammetry and curve-fitting techniques, it was possible to study the substitution kinetics of the 17-electron species. Complexes studied by this technique include $CpMn(CO)_2L$ where L is a variety of ligands. In each case, the substitution of the 17-electron species was associatively activated, consistent with the results discussed above for other 17-electron species. From a mechanistic viewpoint, the reactions are interesting because they are examples of electron-transfer catalyzed reactions.[13] A sample pathway is shown below:

$$\underset{18}{CpMn(CO)_2L} \xrightarrow{-e^-} \underset{17}{CpMn(CO)_2L^+} \quad \text{initiation} \tag{6}$$

$$CpMn(CO)_2L^+ + L' \longrightarrow CpMn(CO)_2L'^+ + L \quad \text{propagation} \tag{7}$$

$$CpMn(CO)_2L'^+ + CpMn(CO)_2L \longrightarrow CpMn(CO)_2L' + CpMn(CO)_2L^+ \tag{8}$$

$$CpMn(CO)_2L'^+ \xrightarrow{+e^-} CpMn(CO)_2L' \quad \text{termination} \tag{9}$$

SCHEME I

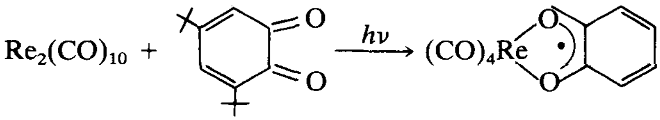
This mechanism is common for organometallic radicals and will be discussed further below.

The work cited above is largely responsible for demonstrating that the substitution reactions of 17-electron species are associatively activated and, in a more general sense, that these species are susceptible to nucleophilic attack. It is noteworthy that in none of the papers cited above was a discreet 19-electron intermediate spectroscopically observed, intercepted, or trapped. (For that matter, the term "19-electron" was not even used.) The substitution process is apparently a concerted process with no evidence of a local minimum in the energy surface corresponding to an intermediate.

Definitive evidence that 17-electron metal radicals can react with nucleophiles to form 19-electron species comes directly from experiments in which the 19-electron complexes are stable products of the reaction. The following reactions provide examples:

$$W_2(CO)_{10}^{2-} \xrightarrow{h\nu} W(CO)_5^- \xrightarrow{\text{4-pyCN}} W(CO)_5(\text{4-pyCN})^- \quad (10)[14]$$

4-pyCN = 4-cyanopyridine



(11)[15]

isolated

(and various substituted derivatives)

$$Co_2(CO)_8 + P_2 \xrightarrow{h\nu} Co(CO)_3P_2 \quad (12)[16]$$

$$Mn_2(CO)_{10} + P_2 \xrightarrow{h\nu} Mn(CO)_4P_2 \quad (13)[16]$$

(isolated and characterized)

P_2 = 2,3-bis(diphenylphosphino)maleic anhydride

$$Mn_2(CO)_{10} + \text{t-butyl-DAB} \xrightarrow{h\nu} Mn(CO)_4(\text{t-Bu-DAB}) \quad (14)[17]$$

(not isolated)

DAB = 1,4-diaza-1,3-butadiene

In each case, irradiation of the dimer cleaves the M–M bond to yield the 17-electron radicals which then react with the ligands to form the 19-electron species. As discussed below, the stability of these 19-valence electron products can be attributed to the special ligands involved—the 19th valence electron is thought to reside primarily in low-energy orbitals on these ligands. These 19-electron complexes thus might be better described as 18-electron complexes with radical anion ligands. Nevertheless, these reactions clearly demonstrate that 17-electron radicals will react with Lewis bases to give "19-electron" adducts. Evidence for 19-electron species with the 19th electron more metal-localized was provided by the electron-transfer studies discussed in the next section.

Inner-Sphere Electron-Transfer Reactions. There are very few examples of inner-sphere electron-transfer reactions of organometallic radicals, but the well-studied reactions of $Co(CN)_5^{3-}$ provide a model for this type of reactivity. The inner-sphere electron-transfer reactions of $Co(CN)_5^{3-}$ were studied by Halpern and co-workers and a typical reaction is shown in Eq. (15).[18]

$$Co(CN)_5^{3-} + Co(NH_3)_5X^{2+} \longrightarrow Co(CN)_5X^{3-} + Co(NH_3)_5^{2+} \qquad (15)$$

$$(X = Cl^-, Br^-, I^-, N_3^-, NCS^-, OH^-)$$

(Reaction (15) is the first step in the $Co(CN)_5^{3-}$ catalyzed CN^--substitution of $Co(NH_3)_5X^{2+}$.[18(b)] Reaction (16) completes the catalysis.)

$$Co(NH_3)_5^{2+} + 5\,CN^- \longrightarrow Co(CN)_5^{3-} + 5\,NH_3 \qquad (16)$$

The mechanism of reaction (15) involves an inner-sphere electron-transfer via the bridged intermediate $[(CN)_5Co\text{–}X\text{–}Co(NH_3)_5]^-$. Evidence for the bridged intermediate in reaction (15) was obtained by spectroscopic detection of the transient intermediates $[Co(CN)_5ONO]^{3-}$ and $Co(CN)_5NC^{3-}$. These species indicate a reaction between $Co(CN)_5^{3-}$ and a lone pair on the O in NO_2 or N in CN in the $Co(NH_3)_5X^{2+}$ species.[18(a)] The importance of reaction (15) is that it demonstrates that inner-sphere electron transfer can occur following the associative reaction of a metal radical with an appropriate Lewis base. In this sense, reaction (15) provides a model for the inner-sphere electron-transfer reactions of organometallic radicals.

In the best characterized inner-sphere electron-transfer involving an organometallic radical, Trogler and Basolo showed an inner-sphere mechanism (Eq. (18)) for the base-induced disproportionation of $V(CO)_6$[19]:

$$V(CO)_6 + B \longrightarrow V(CO)_5B + CO \qquad (17)$$

$$V(CO)_5B + V(CO)_6 \rightleftharpoons \underset{\textstyle I}{(CO)_5V^+\text{-}O\text{-}C\text{-}V^-(CO)_5} + B \qquad (18)$$

$$V(CO)_6 + I \xrightarrow{B} (CO)_5V\text{-}C\text{-}O\text{-}V(B)_4\text{-}O\text{-}C\text{-}V(CO)_5 \qquad (19)$$

Electron transfer in reaction (18) is proposed to occur through a bridging isocarbonyl. The formation of the isocarbonyl product is consistent with this interpretation. In a related reaction, as yet *unpublished*,[20] *it was found that* $CpFe(CO)_2$ reacts with $Fe(CN)_6^{3-}$ to give the CN bridged $[Cp(CO)_2Fe\text{-}N{\equiv}C\text{-}Fe^{II}(CN)_5]^{3-}$ complex. In both the $V(CO)_6$ and $CpFe(CO)_2$ reactions, the key feature is the ability of the metal radical to react with a Lewis base to form a metal center with 19 electrons; the ligand bridge facilitates electron transfer from this electron-rich metal.

Atom Abstraction Reactions. Metal radicals react readily with halocarbons to produce metal halides and an organic radical[2,21]:

$$\underset{17}{ML_n} + RX \longrightarrow ML_nX + \dot{R} \qquad (20)$$

$$ML_n = Mn(CO)_5,\ Re(CO)_5,\ CpMo(CO)_3,\ \text{etc.}$$

(The organometallic radicals are conveniently generated by irradiation of metal–metal bonded dimers.) In this section, we demonstrate that these reactions can, once again, be interpreted in terms of a 19-valence-electron intermediate formed via an associative reaction of the 17-valence-electron metal radical with the halocarbon. And, once again, the $Co(CN)_5^{3-}$ complex provides a model for the reactions of the organometallic radicals.

Extensive studies of the reactions of $Co(CN)_5^{3-}$ with organic halides (Eq. (21)) were carried out in the 1960s by Halpern, Kwiatek, and others.[5(a),22]

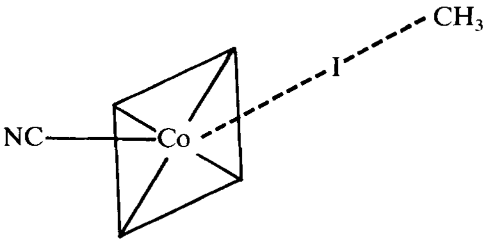
$$2\ Co(CN)_5^{3-} + RX \longrightarrow Co(CN)_5X^{3-} + Co(CN)_5R^{3-} \qquad (21)$$

The reaction takes place in two steps (Eqs. (22) and (23)) with the first being the halogen atom abstraction.

$$Co(CN)_5^{3-} + RX \longrightarrow Co(CN)_5X^{3-} + R \qquad (22)$$

$$Co(CN)_5^{3-} + \dot{R} \longrightarrow Co(CN)_5R^{3-} \qquad (23)$$

The overall reaction follows a second-order rate law $(-d[Co(CN)_5^{3-}]/dt = 2\,k[Co(CN)_5^{3-}][RX])$, and calculations on the transition state of reaction (22) for the case of CH_3I indicated a minimum energy for the bent structure II.[23]



II

A more detailed description of the abstraction process is given in the section on electronic structures, but the important point is that the transition state complex is analogous to the 19-electron species formed by associative activation in the substitution and inner-sphere electron-transfer reactions discussed above. Because the metal center is oxidized and the carbon center reduced, the halogen atom abstraction is mechanistically related to an inner-sphere electron transfer:

$$\underset{17}{M^nL_n} + R^{+1}\text{–}X \longrightarrow [L_nM\text{–}X\text{–}R] \longrightarrow L_nM^{n+1}\text{–}X + \cdot R^0 \qquad (24)$$

Less is known about the process of halogen atom abstraction by organometallic radicals but the mechanism is undoubtedly very similar to that described above for $Co(CN)_5^{3-}$.[24]

For halogen abstraction by $Co(CN)_5^{3-}$ and by organometallic radicals, systematic studies have noted a positive correlation between bimolecular reaction rates (or activation enthalpies) and the carbon–halogen bond strength.[24,25] The rate constants follow the pattern $k_{RCl} < k_{RBr} < k_{RI}$, a trend which correlates with the general bond energy trend RCl > RBr > RI. It is important to note, however, that in almost all cases reduction potentials for halocarbons parallel the carbon–halogen bond energies.[26] A comparison of rate constants with reduction potentials for the halocarbons will result in an equally convincing correlation. Thus, the facility of the abstraction reaction is directly related to the ability of the 19-electron intermediate (or transition state) $L_nM{-}X{-}R$ to reduce the substrate. Brown's observation that for a given halocarbon, the phosphine-substituted manganese carbonyl radicals $Mn(CO)_4PR_3$ reacted faster than $Mn(CO)_5$ is consistent with this interpretation.[24] Phosphine-substituted metal centers are more electron-rich than their carbonyl analogs and, therefore, the 19-electron metal center formed by reaction of $Mn(CO)_4PR_3$ with RX will be a more potent reductant than the 19-electron center formed with $Mn(CO)_5$. It should be made clear that the reduction potentials and bond energies for halocarbons are not separable quantities. Recent work by Eberson on the reduction of halocarbons at electrode surfaces suggests a large reorganization energy consistent with a largely broken carbon–halogen bond at the time of electron transfer.[26] Thus, correlation of the rate constants with R–X bond strength and the reduction potential of RX are both valid. However, the correlation with reduction potentials is most easily interpreted in terms of 19-electron intermediate species using the model provided by $Co(CN)_5^{3-}$.

REACTIVITY OF NINETEEN-ELECTRON COMPLEXES

Having established that the principle reactions of 17-electron species are associatively activated with 19-electron intermediates or transition states, we next turn to a discussion of the reactivity of the 19-electron complexes. Because of their relative instability, there have been very few studies of the reaction chemistry of

19-electron complexes. However, it is possible to glean from the literature that 19-electron complexes exhibit the following reactivities: outer-sphere electron-transfer, ligand dissociation, substitution, and ligand coupling reactions.

Outer-Sphere Electron-Transfer Reactions. Not unexpectedly, the dominant chemistry of many 19-electron complexes is electron transfer to reducible substrates. Again, the precedent for this type of reactivity with organometallic 19-electron species comes from studies of the $\mathrm{Co(CN)_5^{3-}}$ complex. Thus, the reaction of $\mathrm{CN^-}$ with $\mathrm{Co(CN)_5^{3-}}$ forms the electron-rich 19-electron $\mathrm{Co(CN)_6^{4-}}$ species which is a potent reductant[5(a)]:

$$\mathrm{Co(CN)_5^{3-} + CN^- \longrightarrow Co(CN)_6^{4-}} \tag{25}$$

$$\mathrm{Co(CN)_6^{4-} + S \longrightarrow Co(CN)_6^{3-} + S^-} \tag{26}$$

$$\mathrm{S = Co^{III}(NH_3)_5X; \quad X = PO_4^{3-}, CO_3^{2-}, SO_4^{2-}, NH_3, OAc^-}$$

Organometallic chemists studying electron-transfer catalyzed (ETC) reactions[13] have appreciated the reducing ability of 19-electron complexes for years. A typical example, provided by Jones, Huggins and Bergman, is the electron-transfer catalyzed substitution of several metal carbonyl complexes by $\mathrm{CpV(CO)_3H^-}$ [27]:

$$\underset{18}{\mathrm{CpV(CO)_3H^-}} + \underset{18}{\mathrm{ML}_n} \longrightarrow \underset{17}{\mathrm{CpV(CO)_3H}} + \underset{19}{\mathrm{ML}_n^-} \tag{27}$$

$$\underset{19}{\mathrm{ML}_n^-} \longrightarrow \underset{17}{\mathrm{ML}_{n-1}^-} + \mathrm{L} \tag{28}$$

$$\underset{17}{\mathrm{ML}_{n-1}^-} + \mathrm{L'} \longrightarrow \underset{19}{\mathrm{ML}_{n-1}\mathrm{L'}^-} \tag{29}$$

$$\underset{19}{\mathrm{ML}_{n-1}\mathrm{L'}^-} + \underset{17}{\mathrm{CpV(CO)_3H}} \longrightarrow \underset{18}{\mathrm{ML}_{n-1}\mathrm{L'}} + \underset{18}{\mathrm{CpV(CO)_3H^-}} \tag{30}$$

The key concept in this reaction scheme, as it relates to our topic, is that coordination of a Lewis base to a 17-electron species (Eq. (29)) will form an electron-rich metal center which is an outer-sphere reductant (Eq. (30)).

The associative formation of 19-electron complexes from 17-electron species and the subsequent electron-transfer chemistry of the 19-electron species is beautifully illustrated by the photochemical disproportionation reactions of metal–metal bonded dimers.[28–32] The mechanism for the disproportionation of $Cp_2Mo_2(CO)_6$ by PR_3 in CH_2Cl_2 is shown in Scheme II.[28,31] Related mechanisms apply to the disproportionation of the other metal–metal bonded dimers.[32,33] The key steps in this pathway are the formation of a 19-electron species from the 17-electron radical (Eq. (32)) and the electron-transfer reaction of the 19-electron species (Eq. (33)).

$$Cp_2Mo_2(CO)_6 \xrightarrow{h\nu} 2\ \underset{17}{CpMo(CO)_3} \tag{31}$$

$$\underset{17}{CpMo(CO)_3} + PR_3 \longrightarrow \underset{19}{CpMo(CO)_3PR_3} \tag{32}$$

$$\underset{19}{CpMo(CO)_3PR_3} + Cp_2Mo_2(CO)_6 \longrightarrow \underset{18}{CpMo(CO)_3PR_3^+} + Cp_2Mo_2(CO)_6^- \tag{33}$$

$$Cp_2Mo_2(CO)_6^- \longrightarrow CpMo(CO)_3^- + CpMo(CO)_3 \tag{34}$$

$$\text{Overall:}\quad Cp_2Mo_2(CO)_6 + PR_3 \xrightarrow{h\nu} CpMo(CO)_3PR_3^+ + CpMo(CO)_3^- \tag{35}$$

SCHEME II

Equation (33) is an interesting step because the reduction potentials (E_{pc}) of the $Cp_2Mo_2(CO)_6$ complex and other related dimers are quite high: −1.4 V (vs. Ag/Ag^+) for $Cp_2Mo_2(CO)_6$ to −2.2 V for $Cp_2Fe_2(CO)_4$.[34] Thus, the 19-valence electron species are quite powerful reducing agents. One would expect the 19-electron intermediates to be capable of reducing substrates other than metal–metal bonded dimers and indeed they do. Simply by adding the substrates to a solution of the dimer with an appropriate ligand and irradiating will in general give the reduced substrate.

The reactions below are examples of substrate reductions by 19-electron species.[33]

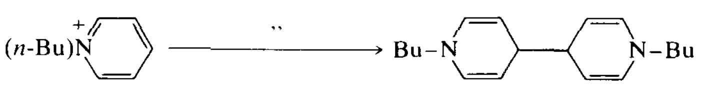
$$CpMo(CO)_3Cl \xrightarrow[h\nu]{Cp_2Fe_2(CO)_4/dppe} CpMo(CO)_3^- \quad (36)$$

$$Mn_2(CO)_{10} \xrightarrow{\text{''}} Mn(CO)_5^- \quad (37)$$

$$Cp_2Mo_2(CO)_6 \xrightarrow{\text{''}} CpMo(CO)_3^- \quad (38)$$

$$Fe(CN)_6^{3-} \xrightarrow{\text{''}} Fe(CN)_6^{4-} \quad (39)$$

$$Cp_2Co^+ \xrightarrow{\text{''}} Cp_2Co \quad (40)$$



(41)

$$PQ^{2+} \xrightarrow{\text{''}} PQ^+ \quad (42)$$

$(PQ^{2+}$ = paraquat$)$

The reducing agent in each case is the 19-electron CpFe(CO)dppe complex formed by irradiation of $Cp_2Fe_2(CO)_4$ with dppe (dppe = 1,2-bis-(diphenyl)phosphinoethane):

$$Cp_2Fe_2(CO)_4 \xrightarrow{h\nu} \underset{17}{2\ CpFe(CO)_2} \xrightarrow{dppe} \underset{19}{CpFe(CO)dppe} \quad (43)$$

This 19-electron species then reduces the substrate, presumably by an outer-sphere electron-transfer mechanism:

$$\underset{19}{\mathrm{CpFe(CO)dppe}} + \mathrm{substrate} \longrightarrow \underset{18}{\mathrm{CpFe(CO)dppe}^+} + \mathrm{substrate}^-$$

(The other product in each of the reactions above is the $\mathrm{CpFe(CO)dppe}^+$ complex.) One point to note in the reactions above is the variety of complexes that are reducible; organometallic, organic, and coordination complexes can all be reduced by the 19-electron intermediates. It is also noteworthy that the 19-electron species formed in these reactions are *discrete* complexes with sufficient lifetimes to undergo bimolecular reactions. Because many of the ligands that react with 17-electron species to form 19-electron species will also substitute the 17-electron complex, it is clear that substitution and electron transfer are competitive reaction pathways.

A question of considerable importance concerning the 19-electron species is, what is their oxidation potential? These numbers have not been measured for 19-electron species of the type formed as intermediates in the reactions above. However, the photochemical disproportionation reactions of the $\mathrm{Cp_2Mo_2(CO)_6}$, $\mathrm{Cp_2Fe_2(CO)_6}$, and $\mathrm{Mn_2(CO)_{10}}$ dimers all proceed via the general mechanism in Scheme II so we can put a lower limit on the oxidation potentials for the 19-electron species that is equal to the negative of the reduction potential of the corresponding dimers (i.e., $\mathrm{CpFe(CO)L_2}$: +2.2 V vs. $\mathrm{Ag/Ag^+}$; $\mathrm{CpMo(CO)_3L}$: +1.4 V vs. $\mathrm{Ag/Ag^+}$; $\mathrm{Mn(CO)_3(NR_3)_3}$: +1.7 V vs. $\mathrm{Ag/Ag^+}$).[34]

Nineteen-electron complexes with oxidation potentials considerably higher than those above are obtained from the $\mathrm{W_2(CO)_{10}^{2-}}$ dimer. Thus, irradiation of $\mathrm{W_2(CO)_{10}^{2-}}$ with $\mathrm{PPh_3}$ produces $\mathrm{W(CO)_5PPh_3^-}$, a species with an oxidation potential greater than 2 V.[35] This complex will transfer an electron to $\mathrm{CO_2}$, producing formate and CO.[36] Acetophenone is also reduced by the $\mathrm{W(CO)_5PPh_3^-}$ complex.

Ligand Dissociation. Numerous studies have demonstrated that 19-electron complexes dissociate a ligand rapidly to yield a 17-electron complex. Electrochemical studies, in particular, provide abundant examples of this type of reactivity, e.g.:

$$\mathrm{Fe(CO)_5} \xrightarrow{e^-} [\mathrm{Fe(CO)_5^-}] \longrightarrow \mathrm{Fe(CO)_4^-} + \mathrm{CO} \qquad (44)^{37}$$

$$\mathrm{W(CO)_6} \xrightarrow{e^-} [\mathrm{W(CO)_6^-}] \longrightarrow \mathrm{W(CO)_5^-} + \mathrm{CO} \qquad (45)^{38}$$

Further examples come from studies of the substitution reactions of 17-electron complexes (see above). Recall that species of higher coordination number have never been detected in these reactions. This result implies that *if* 19-electron species are forming as *intermediates* in these reactions, then they are quite labile.

A further example of ligand dissociation is provided by the work of Lapinte, Catheline and Astruc.[39] These workers found that the $\mathrm{LiAlH_4}$ reduction of $\mathrm{Cp^*Fe(CO)dppe^+}$ ($\mathrm{Cp^*} = \mathrm{(CH_3)_5C_5}$) proceeded in some instances by the following pathway:

$$\begin{tikzcd}
\mathrm{Cp^*Fe(CO)dppe^+} \arrow[r, "\mathrm{LiAlH_4}"] & \mathrm{Cp^*Fe(CO)dppe} \\
18 & 19 \arrow[d] \\
\mathrm{Cp^*Fe(CO)(dppe\text{-}P)H} & \mathrm{Cp^*Fe(CO)(dppe\text{-}P)} \arrow[l, "\dot{\mathrm{H}}"'] \\
18 & 17
\end{tikzcd}$$

(dppe-P indicates monodentate dppe)

SCHEME III

The ligand lability in 19-electron complexes is undoubtedly related to the electronic configuration. When the 19th electron occupies an M–L antibonding orbital, the M–L bond will be weakened. Further details are found below in the discussion of the electronic structures of the 19-electron complexes.

Substitution Reactions. Despite the propensity of 19-electron complexes to transfer an electron or dissociate a ligand to give a

17-electron complex, several substitution reactions of 19-electron complexes have been reported. Examples are shown in Eqs. (46)–(49).

$$\mathrm{Mn(CO)_4(DBOQ)} + \text{t-Bu-DAB}$$

$$\xrightarrow{\text{RT, dark}} \mathrm{Mn(CO)_3(DBOQ)(t\text{-}Bu\text{-}DAB\text{-}N')} + \mathrm{CO} \quad (46)^{17}$$

(DBOQ = 3,5-di-t-butyl-ortho-benzoquinone; the -N′ nomenclature for the DAB ligand indicates only one N atom is coordinated to the Mn)

$$\mathrm{Mn(CO)_4(bpy)^-} + \mathrm{PPh_3} \xrightarrow{\text{RT}} \mathrm{M(CO)_3PPh_3(bpy)^-} + \mathrm{CO} \quad (47)^{40}$$

$$\mathrm{Mn(CO)_3(CH_3CN)_3} \xrightarrow[\text{RT}]{\text{L}} \mathrm{Mn(CO)_3(CH_3CN)_2L}$$

$$\xrightarrow{\text{L}} \mathrm{Mn(CO)_3(CH_3CN)L_2} \quad (48)^{41}$$

$$\text{L} = \mathrm{PPh_3} \text{ or } \mathrm{PMe_2Ph}$$

$$\mathrm{CpMo(CO)_2(c\text{-}hex\text{-}DAB)}$$

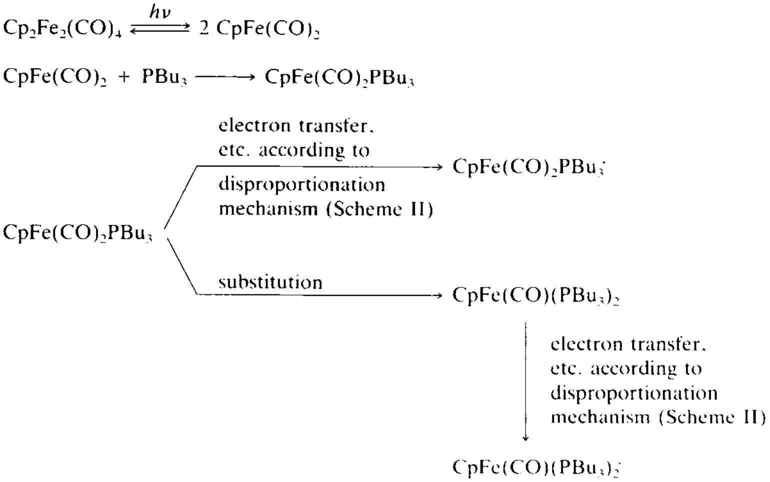
$$\xrightarrow[\text{RT}]{\mathrm{PPh_3}} \mathrm{CpMo(CO)(PPh_3)(c\text{-}hex\text{-}DAB)} + \mathrm{CO} \quad (49)^{42}$$

It is logical to propose that these reactions proceed via a dissociatively activated mechanism. However, one must be careful. For example, the 19-electron complex $\mathrm{Cp_2MnPR_3}$ is known, as is the "21-electron" $\mathrm{Cp_2Mn(dppm)}$ (dppm = 1,2-bis(diphenylphosphino)methane).[43] The existence of the latter complex suggests that the phosphine substitution reactions of the former could proceed via an associatively activated mechanism. Admittedly, this is an extreme case because the $\mathrm{Cp_2MnPR_3}$ complex is decidedly ionic; nevertheless, it serves to caution us about the possibility of associatively activated reactions.

As mentioned previously, electron transfer is in competition with ligand dissociation. This competition is clearly illustrated in the photochemical disproportionation of $Cp_2Fe_2(CO)_4$ with PBu_3[33]:

$$Cp_2Fe_2(CO)_4 \xrightarrow[h\nu]{PBu_3} CpFe(CO)_2PBu_3^+ + CpFe(CO)(PBu_3)_2^+ + CpFe(CO)_2^- \qquad (50)$$

Two different cations form because $CpFe(CO)_2PBu_3$ can either electron transfer or substitute, as the following mechanism for reaction (50) illustrates.



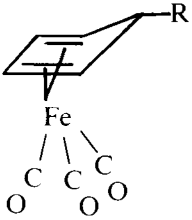
SCHEME IV

Reactions of Ligands in 19-Electron Complexes. As discussed in more detail below, in many 19-electron complexes the 19th electron is in an orbital that is primarily ligand in character. In some instances, the reactivity of the complex reflects the location of the extra electron. Thus, Kochi and Narayanan observed that $Cr(CO)_6^-$, $Fe(CO)_5^-$, and $Mn(CO)_4(PPh_3)_2$ (all 19-electron complexes generated electrochemically from the stable 18-electron complexes) will abstract a hydrogen atom from $HSnR_3$ to give formyl complexes; e.g.,[44]

$$\mathrm{Fe(CO)_5^-} + \mathrm{HSnR_3} \longrightarrow \mathrm{(CO)_4Fe(COH)^-} + \mathrm{SnR_3} \quad (51)$$

It was suggested that these reactions are consistent with considerable spin density on the C atoms of the CO ligands. In a conceptually similar reaction, Wrighton and Blaha reported the photochemical reaction of $\mathrm{CpFe(CO)_2R}$ ($R = \mathrm{CH_2C_6H_5}$) with CO[45]:

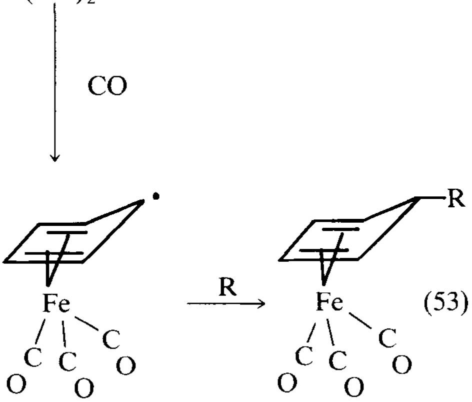
$$\mathrm{CpFe(CO)_2R} + \mathrm{CO} \xrightarrow{h\nu}$$



(52)

The following mechanism was suggested:

$$\mathrm{CpFe(CO)_2R} \xrightarrow{h\nu} \mathrm{CpFe(CO)_2} + \mathrm{R}$$



(53)

The key point here is that the Cp ring has slipped in the 19-electron $\mathrm{CpFe(CO)_3}$ complex so as to give a more stable 18-electron configuration at the Fe center. A coupling reaction of the (radical) ring and the R radical is therefore possible.

Finally, with one last example, we note that radical coupling of two rings is possible with certain 19-electron complexes, e.g.,[46]

$$\begin{tikzcd} (\eta^7\text{-}C_7H_7)Mo(CO)_3^+ \arrow[r, "e^-"] & \underset{19}{(C_7H_7)Mo(CO)_3} \arrow[d] \\ & (CO)_3Mo(\eta^6\text{-}C_7H_7\text{-}\eta^6\text{-}C_7H_7)Mo(CO)_3 \end{tikzcd} \qquad (54)$$

Cp_2Rh will also ring-couple in a similar fashion.[47]

Electron-Transfer Catalysis (*ETC*). This type of reactivity and related reactivities have been extensively reviewed recently,[13] so it is worthwhile only to point out that 19-electron complexes are frequently formed as intermediates in electron-transfer catalyzed reactions. A typical ETC substitution mechanism is shown below (also see Scheme I and Eqs. (27)–(30)):

$$\underset{18}{Fe(CO)_5} + e^- \longrightarrow \underset{19}{Fe(CO)_5^-} \quad \text{initiation} \qquad (55)$$

$$\begin{tikzcd}[column sep=small] \underset{19}{Fe(CO)_5^-} + L \arrow[r] & \underset{19}{Fe(CO)_4L^-} + CO \quad \text{propagation} \qquad (56) \\ \underset{19}{Fe(CO)_4L^-} + \underset{18}{Fe(CO)_5} \arrow[r] & \underset{18}{Fe(CO)_4L} + Fe(CO)_5^- \qquad (57) \arrow[u, bend right, to path={-| (\tikztotarget)}] \end{tikzcd}$$

SCHEME V

These reactions take advantage of the lability of the 19-electron complexes compared to the 18-electron precursors; presumably the intimate mechanism of reaction (56) is dissociative loss of CO, followed by reaction of the 17-electron $Fe(CO)_4^-$ species with L.

Note that both the electron-transfer reactivity and ligand lability are key steps in any ETC substitution mechanism.

ELECTRONIC STRUCTURES OF NINETEEN-ELECTRON COMPLEXES

Nineteen-electron complexes are commonly assumed to be so unstable that their formation in an associative reaction of a 17-electron species is considered unlikely. However, the driving force for the formation of these complexes can be seen qualitatively in the simple molecular orbital diagram in Fig. 1. This scheme depicts

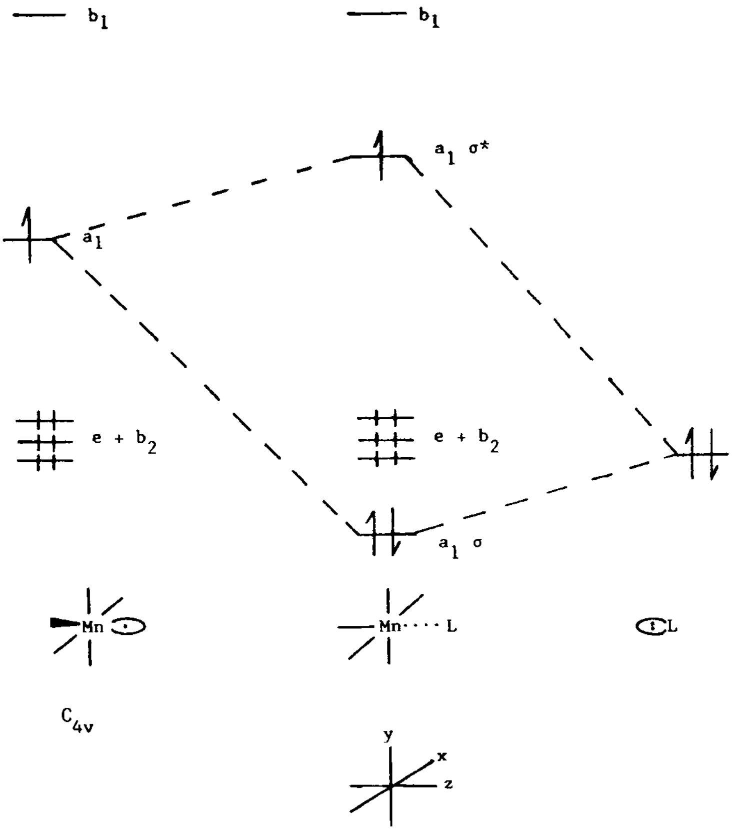


FIGURE 1 Molecular orbital scheme for the interaction of an $Mn(CO)_5$ fragment with a Lewis base.

the bonding of a square pyramidal $Mn(CO)_5$ radical to a Lewis base. In the following discussion, we will restrict our attention to bonding along the z axis (see the coordinate system in Fig. 1) and we will assume that the odd electron in the $Mn(CO)_5$ fragment resides in a pure d_{z^2} orbital (although the orbital is actually a mixture of d_{z^2}, p_z and s character[48]). This orbital is antibonding with respect to the apical CO ligand and, as it is half-occupied, gives a formal bond order of 1/2 to the $M-CO_{apical}$ bond.

Interaction of a ligand orbital containing a lone pair with the d_{z^2} orbital on the fragment results in the formation of a bonding–antibonding pair with the odd electron now in the high-energy antibonding orbital (Fig. 1).

The pair of electrons contributed by the base will compete with the apical CO for overlap with the d_{z^2}. The overall bond order along the z axis is still 1/2 but it will be split between the base and the apical ligand, i.e., each bond now has a formal bond order of 1/4. The net result is that there is still net bonding but the apical ligand bond is weakened. This explains the facile substitution chemistry that is observed with 17-electron species.

As previously stated, the half-occupied orbital in the fragment is not purely d_{z^2} but a mixture of higher-energy orbitals including the 4s and $4p_z$ orbitals. Mixing of these higher-energy components into the singly occupied orbital will result in the stabilization of the singly occupied orbital with the result that the overall bond order along the z axis is higher in the 19-electron species than in the 17-electron fragment. The degree of stability depends on the metal as well as on the ligand field strength of the entering base. Pi back-bonding from the d_{z^2} orbital to the equatorial ligands also lowers the energy of the bonding orbital causing additional stabilization of the species. This accounts for the formation of 19-electron species primarily by carbonyl, isocyanide, and cyanide containing species.

In summary, the driving force for the formation of 19-valence electron complexes from 17-electron species is the additional stability gained by the formation of the M–ligand bond. Although the discussion above used $Mn(CO)_5$ as an example, similar molecular orbital arguments will apply to other 17-electron fragments.[49] Also note that a similar conclusion is reached from the valence bond viewpoint, i.e., a half-filled hybrid orbital interacts with the donor pair on the ligand to give a metal–ligand "half-bond."

This general description of the structure and bonding in 19-electron species as well as their inherent stability compared to 17-electron fragments and a ligand is convincingly illustrated in the crystal structure of $[Co(CNPh)_5][ClO_4]_2$ reported by Raymond and co-workers.[50] In this complex the isocyanide ligands form a square-based pyramid and the oxygen atom of a perchlorate anion occupies a sixth coordination site so that the molecule is pseudo-octahedral with a formal 19-valence electron count.

Consistent with a bonding description involving a weak bond between the entering base and the 17-electron fragment, the cobalt-to-perchlorate oxygen bond length is 2.59 Å, too long to be a single bond but much shorter than would be predicted for a pure van der Waals interaction (2.77 Å). Raymond[50] calculated a Co–O bond order of 0.1 using the Pauling equation and a value of 1.97 Å as the Co–O single bond length.

Based on the bonding interaction previously described, there is an expected weakening of the metal–ligand bond *trans* to the entering base due to the formal reduction in the bond order for that ligand. Consistent with this prediction, the crystal structure shows a *trans* carbon–cobalt bond length of 1.95 Å. This distance is considerably longer than 1.83 Å, which is the average cobalt–carbon bond length of the basal isocyanide ligands. Because perchlorate is such a poor ligand, the fact that this complex forms at all strongly suggests that formation of the 19-electron species does provide a degree of electronic stability over the 17-electron fragment.

Other experimental verification of this electronic structure comes from EPR spectroscopy of the 19-electron $Mn(CO)_5Cl^-$ species, formed by pulse radiolysis of $Mn(CO)_5Cl$ doped in a single crystal of $Cr(CO)_6$.[51] The odd electron was found to reside in a σ^* orbital oriented along the Mn–Cl bond. Analysis of the manganese and chlorine hyperfine splittings indicates that the major contribution to the spin density is from the chlorine p_z and manganese d_{z^2} orbitals, a result consistent with the bonding scheme presented above. Note that this particular 19-electron species is a relevant model for 19-electron species found in solution as Cl^- has been shown to react with $CpMo(CO)_3$ to form the 19-electron

$CpMo(CO)_3Cl^-$ complex[29]:

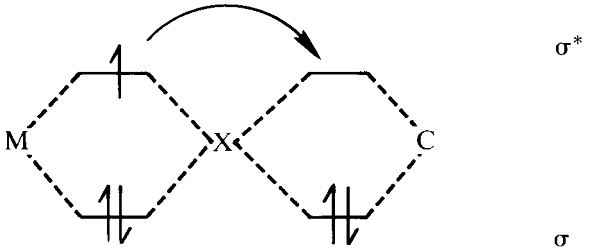
$$CpMo(CO)_3 + X^- \underset{}{\overset{K_{eq}}{\rightleftharpoons}} CpMo(CO)_3X^- \qquad (58)$$

$$X = Cl^-, Br^-$$

Recently, the equilibrium constant for reaction (58) was measured.[52] For $X^- = Cl^-$, $K_{eq} \geq 34\ M^{-1}$ and therefore $\Delta G^0_{17\rightarrow19} \leq -2.1$ kcal/mol; similarly, for $X^- = Br^-$, $K_{eq} \geq 65$ and $\Delta G^0_{17\rightarrow19} \leq -2.5$ kcal/mol. Thus, at least in these instances, the formation of the 19-electron species from a 17-electron radical and a halide is *thermodynamically favorable.* It should be made clear that while these species are favored relative to the metal radical and a ligand, they are still high-energy species that readily react to attain a more favorable electronic configuration.

As previously discussed, 19-electron species are frequently potent reducing agents. The origin of this high oxidation potential is easily inferred from the molecular orbital diagram. The odd electron resides in a high-energy orbital and loss of that electron results in a more stable 18-electron species. It follows that as the donor ability of the entering base increases, the 19-electron species should become a better reductant because the energy of the σ^* orbital is increased. In fact, this prediction has been verified experimentally: it was observed that phosphine ligands photochemically disproportionated $Cp_2Mo_2(CO)_6$ (Scheme II) more efficiently than phosphites.[28] This result was attributed to the better reducing abilities of the 19-electron $CpMo(CO)_3(PR_3)_2$ complex compared to $CpMo(CO)_2(P(OR)_3)_2$. Similarly, $Mn_2(CO)_{10}$ is photochemically disproportionated with amines but not with phosphines or phosphites.[53]

Atom abstraction reactions are also explained by the qualitative molecular orbital scheme in Fig. 1. As RX interacts with the metal radical to form the 19-electron complex, there is a flow of electron density that can be viewed as movement of the odd electron in the M–X σ^* orbital into the C–X σ^* orbital. This electron transfer simultaneously increases the M–X bond order to one and destabilizes the C–X bond.



Semi-empirical molecular orbital calculations provide a more detailed but qualitatively similar description of halide abstraction. Using the extended Hückel method, Ohkubo, Kanaeda and Tsuchihashi looked at the transition state for I-abstraction from CH_3I by $Co(CN)_5^{3-}$.[23] They found that the p_z lone pair on I interacts with the Co d_{z^2} orbital and the C–I σ* bond interacts with the d_{xy} orbital. [These interactions were determined for a transition state with the methyl iodide at a 45° angle to the basal plane of the $Co(CN)_5^{3-}$ species (see Structure II).] The predominant electron flow was calculated to be from the lone pair (p_z) on the iodine to the d_{z^2} on cobalt, forming a strong Co–I bond, and from the cobalt d_{xy} orbital into the pσ* of the C–X bond, which acts to break this latter bond.

A further discussion of transition states and intermediates is appropriate at this point. While there are many reactions in which 19-electron species are stable intermediates, we do not mean to imply that all reactions involving radicals and bases go through a true intermediate represented by a minimum in the reaction coordinate diagram. Reactions such as halogen abstraction can, and probably do, proceed through a smooth reaction path with the associated complex representing a transition state. However, the fundamental electronic characteristics found for a 19-electron "transition state" are analogous to those of an intermediate which results from association of a Lewis base with a metal radical. Hence, we believe that the generalized construct of a 19-electron species is useful and valid for a broad range of reactions.

Finally, it should be noted that in some 19-electron complexes, ligand orbitals (generally π* orbitals) will be lower in energy than the M–L σ* orbital. The 19-electron complexes formed in reactions (10)–(14) are examples of this type of complex. Ligand coupling reactions are sometimes observed under these circumstances (Eq. (54)).

WHY NINETEEN-ELECTRON COMPLEXES ARE IMPORTANT IN ORGANOMETALLIC CHEMISTRY

The discussion above demonstrates that 19-electron complexes form readily from 17-electron radicals and nucleophiles. Given the prevalence of radical intermediates in many organometallic reaction systems,[54] it is logical to suggest that 19-electron species may be important in these reactions. At the very least, pathways involving 19-electron species must be considered as viable alternatives in any mechanistic discussions. In particular, given the propensity of 19-electron species to act as powerful reductants, we feel that many "radical chain" pathways may in fact be ETC pathways. For example, the following chain mechanism was proposed for the $Cp_2Mo_2(CO)_6$-catalyzed substitution of $CpW(CO)_3I$ by various L.[55]

$$Cp_2Mo_2(CO)_6 \xrightarrow{h\nu} CpMo(CO)_3 \quad \text{initiation} \tag{59}$$

$$CpMo(CO)_3 + L \longrightarrow CpMo(CO)_2L + CO \quad \text{propagation} \tag{60}$$

$$CpMo(CO)_2L + CpMo(CO)_3X \longrightarrow CpMo(CO)_2LX + CpMo(CO)_3 \tag{61}$$

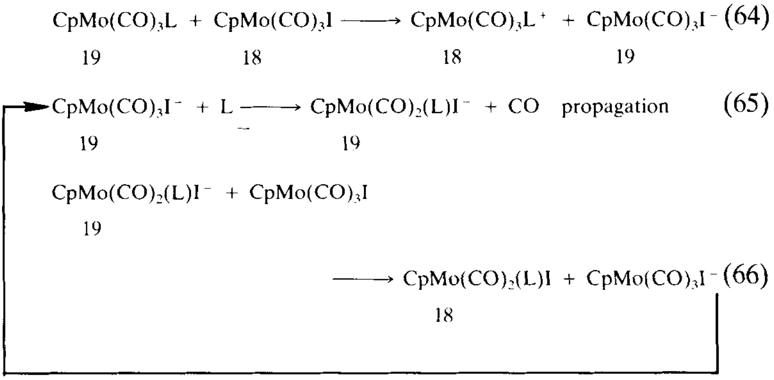
SCHEME VI

Similar radical chain substitution mechanisms have been proposed for numerous other complexes, including: $CpFe(CO)_2R$ (R = η^1-Cp, η^1-allyl),[56] $CpFe(CO)_2X$ (X = a halide),[57] and $CpMo(CO)_3R$.[58]

An alternative mechanism for these substitution reactions, however, is the following ETC pathway, initiated by electron transfer from a 19-electron species:

$$Cp_2Mo_2(CO)_6 \xrightarrow{h\nu} \underset{17}{2\,CpMo(CO)_3} \quad \text{initiation} \tag{62}$$

$$\underset{17}{CpMo(CO)_3} + L \longrightarrow \underset{19}{CpMo(CO)_3L} \tag{63}$$



$$\underset{19}{\mathrm{CpMo(CO)_3L}} + \underset{18}{\mathrm{CpMo(CO)_3I}} \longrightarrow \underset{18}{\mathrm{CpMo(CO)_3L^+}} + \underset{19}{\mathrm{CpMo(CO)_3I^-}} \quad (64)$$

$$\underset{19}{\mathrm{CpMo(CO)_3I^-}} + \mathrm{L} \longrightarrow \underset{19}{\mathrm{CpMo(CO)_2(L)I^-}} + \mathrm{CO} \quad \text{propagation} \quad (65)$$

$$\underset{19}{\mathrm{CpMo(CO)_2(L)I^-}} + \mathrm{CpMo(CO)_3I} \longrightarrow \underset{18}{\mathrm{CpMo(CO)_2(L)I}} + \mathrm{CpMo(CO)_3I^-} \quad (66)$$

SCHEME VII

Obviously, similar ETC mechanisms can be written for the substitution reactions of the other complexes proposed to substitute via the radical chain mechanism (Scheme VI).

It is not easy to distinguish mechanistically between the two pathways. Both mechanisms can be initiated by irradiation of added metal–metal bonded dimer, and quantum yields greater than one are possible. "Crossover" experiments in which metal radicals are shown to abstract halides from metal–halide complexes are frequently advanced as evidence for the radical chain mechanism. The following are examples:

$$\mathrm{(MeCp)_2Mo_2(CO)_6} + 2\ \mathrm{CpMo(CO)_3I} \longrightarrow \mathrm{(MeCp)Mo(CO)_3I} + \mathrm{(CpMo(CO)_3)_2} \quad (67)$$

$$\mathrm{(MeFp)_2} + 2\ \mathrm{FpCp} \longrightarrow 2\ \mathrm{(MeFp)Cp} + \mathrm{Fp_2} \quad (68)$$

$$\mathrm{Fp} = \mathrm{CpFe(CO)_2}$$

While such experiments suggest that Eq. (61) in the radical chain mechanism can occur, they do not demonstrate the occurrence of the pathway; i.e., in the absence of ligand, the 19-electron species cannot form so the ETC pathway is shut down; ligand or group abstraction by the radical is the only reaction available to the radical. Obviously, to differentiate between the two mechanisms, one must study the rates of the propagating steps in each pathway and then compare these to the actual rate of the reaction. Unfortunately, these experiments are usually more easily said than done. Electrochemical potentials can sometimes distinguish between the two pathways. In the ETC mechanism, the 19-electron species must have the potential to reduce the unsubstituted complex. Clearly, if electron transfer is unfavorable, then the ETC pathway is not viable.

We are not suggesting that all of the substitution reactions of the complexes mentioned above proceed via an ETC mechanism rather than the radical chain mechanism. We are simply pointing out that because 17-electron radicals are involved in these reactions and because 19-electron species form so easily from 17-electron species that the ETC mechanism must be considered as a viable alternative.

The principles pertaining to the formation of 19-electron species from 17-electron complexes can be generalized to include the formation of other odd-electron, but not necessarily 19-electron, complexes. Examples are known from coordination chemistry, main-group chemistry, and organic chemistry. Thus, Halpern *et al.* reported the following reaction between the 15-electron Rh(OEP) (OEP = octaethylporphyrin) and CO[59]:

$$Rh_2(OEP)_2 \rightleftharpoons \underset{15}{2\ Rh(OEP)} \xrightarrow{CO} \underset{17}{Rh(OEP)CO} \qquad (69)$$

Organic radicals can react with two-electron donor nucleophiles to form "hypervalent" species. The formation of phosphoranyl radicals by reaction of $\dot{R}'$ with PR_3 is an excellent example[49,60]:

$$\dot{R} + PR_3 \longrightarrow PR_4 \qquad (70)$$

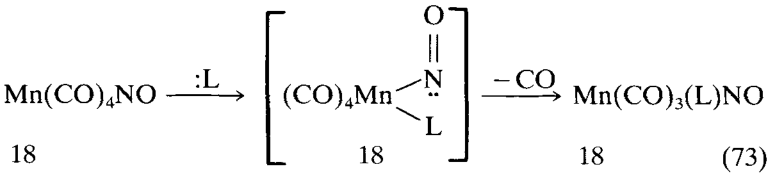
As with their 19-electron organometallic counterparts, the chemistry of phosphoranyl radicals is primarily ligand dissociation (yielding a net substitution) and electron transfer. Finally, in one last example, note that the formation of 19-electron species via reaction of an organic radical with an organometallic nucleophile has been suggested. The reaction in Eq. (71) was proposed as a key step in the $NaCo(CO)_4$ catalyzed reaction in Eq. (72).[61]

$$C_6H_5 + Co(CO)_4^- \longrightarrow \underset{19}{C_6H_5Co(CO)_4^-} \qquad (71)$$

$$C_6H_5Br + CO + NaOC(CH_3)_2CH_2CH_3 \xrightarrow[\substack{NaCo(CO)_4 \\ (2)\ H^+}]{(1)\ h\nu} C_6H_5COOR \qquad (72)$$

$$R = C(CH_3)_2CH_2CH_3\ (70\%);\ R = H\ (17\%)$$

Basolo has recently reviewed the associative substitution chemistry of 18-electron organometallic complexes.[62] He concluded that associatively activated substitution of 18-electron species will occur if an electron pair can be delocalized upon association with the entering ligand. In short, associative substitution can occur if a pathway that obeys the 18-electron rule can be found. For example, associative substitution of metal nitrosyl complexes such as $Mn(CO)_4NO$ is proposed to go through a high-coordination number intermediate which preserves the 18-electron count by the delocalization of an electron pair onto the nitrosyl ligand. The intermediate thus has a "bent" nitrosyl.



$$\underset{18}{Mn(CO)_4NO} \xrightarrow{:L} \underset{18}{\left[(CO)_4Mn\overset{O}{\underset{L}{<}}N\right]} \xrightarrow{-CO} \underset{18}{Mn(CO)_3(L)NO} \qquad (73)$$

While this is an entirely likely and plausible mechanism, it is formulated on the notion of obedience to the 18-electron rule. We suggest that an alternative and equally plausible mechanism can be proposed involving odd-electron species. The fact that the substitution chemistry of $Mn(CO)_4NO$ is identical to that of $Mn(CO)_5$ leads to the proposal that *one* electron is delocalized onto the nitrosyl, creating a species that is isoelectronic with $Mn(CO)_5$. Association of the entering base to form the 19-electron species leads to substitution:

$$\underset{18}{\mathrm{Mn(CO)_4NO}} \xrightarrow{:\mathrm{L}} \underset{19}{\mathrm{Mn(CO)_4(L)(NO)}} \xrightarrow{-\mathrm{CO}} \underset{18}{\mathrm{Mn(CO)_3(L)NO}} \tag{74}$$

Reasonable mechanisms involving odd-electron intermediates can be written for other associative substitution reactions. Our principal assertion here is not that the proposed mechanisms are incorrect but that alternative mechanisms that deviate from the 18-electron rule formalism are equally plausible and worthy of consideration.

Acknowledgments

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