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19-Electron Organometallic Adducts

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The most fundamental principle of organometallic chemistry is the 18-electron rule.[1,2] The rule, which is analogous to the octet rule in organic chemistry, simply states that stable organometallic complexes will have a total of 18 valence electrons. The origin of the rule is shown pictorially in Figure 1.[3] Note in this figure that a transition metal has nine valence orbitals. In a complex with n ligands, n of these valence orbitals will be used to form M–L σ bonding molecular orbitals, and $9 - n$ of the orbitals will form π bonds or be nonbonding. When the σ-bonding and π-bonding/nonbonding orbitals are filled (18 electrons total), any additional electrons (e.g., a "19th" electron) must occupy M–L antibonding orbitals, and that, of course, imparts instability to the complex.[4] Note that the 18-electron rule does not apply to classical coordination complexes because the nonbonding/antibonding energy gap is smaller than in organometallic complexes; therefore, it is not as energetically unfavorable to have additional electrons in the M–L antibonding orbitals.[1]

At one time, the 18-electron rule had a second clause.[1,2] This part of the rule stipulated that organometallic reactions occur via intermediates that have an even number of electrons (18 electrons or fewer). However, about 15 years ago, investigators like Brown,[6] Kochi,[7] Geiger,[8] Connelly,[8] Halpern,[9] Rieger,[10] and others started to develop the chemistry of organometallic radicals. These workers showed that many characteristic organometallic reactions can follow odd-electron pathways, typically involving 17- or 15-electron species. Because of their work, the existence of pathways involving odd-electron intermediates with fewer than 18 electrons is firmly established and accepted today.[11]

Although odd-electron intermediates with fewer than 18 electrons were firmly established by the late 1970s, the concept of intermediates with more than 18 valence electrons was not accepted. This disbelief persisted despite Astruc's emerging work with "19-electron reservoirs"[12] and the fact that cobaltocene was a well-known 19-electron complex.

19-Electron Complexes. In 1982, we reported the results of our study on the mechanism of the photochemical disproportionation reactions of the $Cp_2Mo_2(CO)_6$ complex (eq 1, Scheme I).[13] Reasonable mechanistic evidence led us to propose that a key, short-lived intermediate was a 19-electron adduct ($CpMo(CO)_3L$), formed by reaction of a 17-electron radical with a ligand (eq 3). Subsequent work showed that the formation of 19-electron adducts from a 17-electron species and a ligand was general, as depicted in eq 7. However, as became clear from reviewers' comments on our papers, many organometallic chemists remained skeptical about the existence of the 19-electron adducts. For that reason we embarked on a research program to definitively establish the existence of the 19-electron adducts and to explore their chemistry.

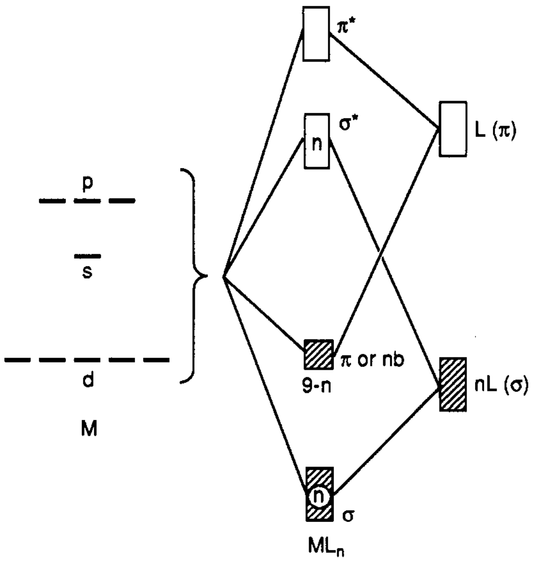

Figure 1. Simplified molecular orbital diagram for a transition-metal organometallic complex with n ligands; "nb" in the figure stands for "nonbonding".

The thrust of our efforts to establish the existence of the 19-electron adducts was two-pronged: First, we would establish that the adducts were thermodynamically reasonable. Establishing this point was crucial because the most common objection to the existence of the 19-electron adducts was that they were too high in energy to form under ordinary reaction conditions.

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(1) Elschenbroich, C.; Salzer, A. *Organometallics—A Concise Introduction*; VCH Publishers: New York, 1988; pp 186, 412.

(2) Tolman, C. A. *Chem. Soc. Rev.* **1972**, *1*, 337–353.

(3) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711–724.

(4) The only notable exceptions to the 18-electron rule are the so-called 16-electron complexes. The existence of these complexes, however, is not a matter for concern because it is well-understood why these complexes only have 16 valence electrons rather than 18.[5] In fact, to acknowledge the existence of these complexes, the 18-electron rule is frequently called the 18/16-electron rule.[2]

(5) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W. B. Saunders: Philadelphia, 1977; p 804.

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(9) (a) Halpern, J. *Pure Appl. Chem.* **1979**, *51*, 2171–2182. (b) Halpern, J. *Pure Appl. Chem.* **1986**, *58*, 575–584.

(10) See, for example: Bezemo, G. J.; Rieger, P. H.; Visco, S. *J. Chem. Soc., Chem. Commun.* **1981**, 265–266.

(11) Tyler, D. R. *Prog. Inorg. Chem.* **1988**, *36*, 125–194.

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Scheme I
Mechanism for the Photochemical Disproportionation of $Cp_2Mo_2(CO)_6$

$$Cp_2Mo_2(CO)_6 + L \xrightarrow{h\nu} CpMo(CO)_3L^+ + CpMo(CO)_3^- \quad \textit{overall reaction} \quad (1)$$

$$CpMo_2(CO)_6 \underset{}{\overset{h\nu}{\rightleftharpoons}} 2\ \underset{17}{CpMo(CO)_3} \quad \textit{initiation} \quad (2)$$

$$\underset{17}{CpMo(CO)_3} + L \overset{K_{eq}}{\rightleftharpoons} \underset{19}{CpMo(CO)_3L} \quad \textit{propagation} \quad (3)$$

$$\underset{19}{CpMo(CO)_3L} + Cp_2Mo_2(CO)_6 \longrightarrow \underset{18}{CpMo(CO)_3L^+} + Cp_2Mo_2(CO)_6^- \quad (4)$$

$$Cp_2Mo_2(CO)_6^- \longrightarrow \underset{18}{CpMo(CO)_3^-} + \underset{17}{CpMo(CO)_3} \quad (5)$$

$$\underset{19}{CpMo(CO)_3L} + \underset{17}{CpMo(CO)_3} \longrightarrow \underset{18}{CpMo(CO)_3L^+} + \underset{18}{CpMo(CO)_3^-} \quad \textit{termination} \quad (6)$$

Table I
$\Delta G°$ and K_{eq} Values for the Formation of 19-Electron Complexes

$$\underset{17}{ML_n} + L' \overset{K_{eq}}{\rightleftharpoons} \underset{19}{ML_nL'}$$

ML_n	L'	K_{eq} (298 K)	$\Delta G°$, kcal/mol	ref
$CpMo(CO)_3$	Cl^-	>34	≤-2.1	14
$CpMo(CO)_3$	Br^-	>66	≤-2.5	14
$CpMo(CO)_3$	I^-	>180	≤-3.1	14
$CpMo(CO)_3$	dppe-*P,P'*[a,b]	>1.4 × 10^8	≤-11.2	*c*
$CpFe(CO)_2$	dppe-*P*[d,e]	0.9	0.06	15
$CpFe(CO)_2$(dppe-*P*)[d]	dppe-*P,P'*[a,f]	10^8	-10	15
$CpFe(CO)(PPh_3)CH_3^+$	py	7	-1	16
(mesitylene)$W(CO)_3^+$	$P(O\text{-}nBu)_3$	3000	-5	17
(mesitylene)$W(CO)_3^+$	CH_3CN	~10^{-1}	1	17
$Mn(CO)_2$(dppe-*P,P'*)(dppe-*P*)	chelate ring closure	10^{-6}	8	18

[a] The -*P,P'* notation indicates that both P atoms are coordinated. [b] The 19-electron product is $CpMo(CO)_2$(dppe-*P,P'*). [c] Philbin, C. E.; Tyler, D. R., unpublished work. [d] The -*P* notation indicates that only one P atom is coordinate. [e] The 19-electron product is $CpFe(CO)_2$(dppe-*P*). [f] The 19-electron product is CpFe(CO)(dppe-*P,P'*).

Second, we would attempt to synthesize a long-lived 19-electron adduct. A successful synthesis would, of course, demonstrate beyond all doubt that such adducts could exist.

Thermodynamics of 19-Electron Adduct Formation.[14] Standard free energies of formation for the 19-electron adducts were obtained by measuring the equilibrium constants for reaction 7. The equilibrium constants were measured by studying the quantum yields for metal–metal bond disproportionation reactions (e.g., eq 1) as a function of ligand concentration and curve-fitting the results to the predicted relationship.[14] Results of the measurements are summarized in Table I. (The nature of the measurements is such that lower limits for K_{eq} are obtained. Thus, the method gives upper limits for $\Delta G°$.) In every case we examined, the 19-electron complex is thermodynamically downhill (or thermochemically neutral: see the fifth entry in Table I) with respect to the 17-electron complex and the ligand.

Recent results of other investigators are consistent with our finding that the formation of 19-electron adducts can be thermodynamically favorable. For example, the formation of the 19-electron complex is spontaneous in both eq 8[16] and eq 9.[17]

$$\underset{17}{ML_n} + \underset{2}{L'} \overset{K_{eq}}{\rightleftharpoons} \underset{19}{ML_nL'} \quad (7)$$

ML_n =
$^{\bullet}Mn(CO)_5$, $^{\bullet}Co(CO)_4$, $CpMo^{\bullet}(CO)_3$, $CpFe^{\bullet}(CO)_2$

L' = phosphines, amines, O donors, halides, pseudohalides

$$\underset{17}{CpFe(CO)(PPh_3)CH_3^+} + py \overset{K_{eq}}{\rightleftharpoons} \underset{19}{CpFe(CO)(PPh_3)(CH_3)py^+} \quad (8)$$

$$\underset{17}{(mesitylene)W(CO)_3^+} + P(O\text{-}nBu)_3 \overset{K_{eq}}{\rightleftharpoons} \underset{19}{(mesitylene)W(CO)_3(P(O\text{-}nBu)_3)^+} \quad (9)$$

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(15) Castellani, M. P.; Tyler, D. R. *Organometallics* **1989**, *8*, 2113–2120.

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(17) Zhang, Y.; Gosser, D. K.; Rieger, P. H.; Sweigart, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 4062–4068.

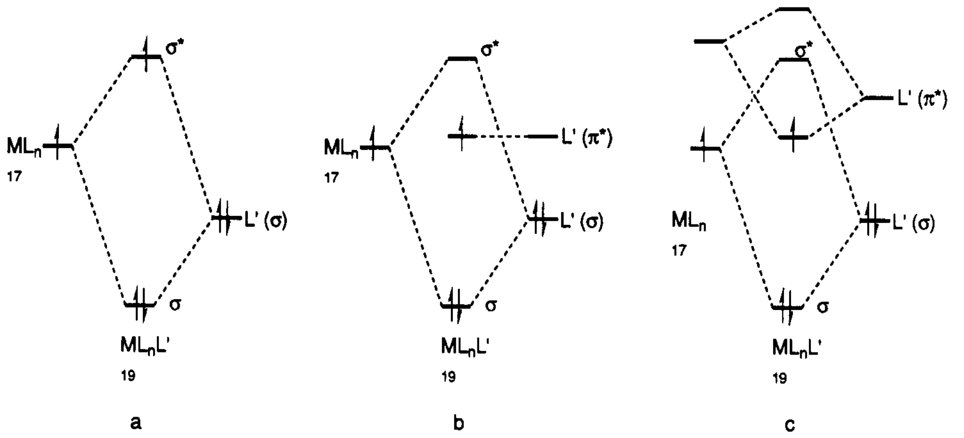

Figure 2. (a) Simplified molecular orbital scheme showing the interaction of the singly occupied orbital on a 17-electron organometallic radical with a ligand orbital to form a 19-electron complex. Note that the unpaired ("19th") electron occupies a M–L antibonding orbital. (b) Same as part a except that the ligand has a low-energy π^* orbital. This scheme is applicable to "18 + δ" complexes. The unpaired electron now occupies the π^* orbital. (c) Same as part b except that an additional orbital on the metal is shown interacting with the ligand π^* orbital. This latter interaction leads to delocalization of the unpaired electron onto the metal.

Note, however, that the formation of 19-electron complexes from 17-electron radicals and a ligand need not always be spontaneous. One nonspontaneous reaction is eq 10, for which $K_{eq} = 10^{-6}$.[18] In this case, the

$$\mathrm{Mn(CO)_2(\eta^2\text{-dppe})(\eta^1\text{-dppe})} \xrightleftharpoons{K_{eq}} \mathrm{Mn(CO)_2(\eta^2\text{-dppe})_2} \quad (10)$$

buildup of electron density on the metal is apparently enough such that ring closure is not favorable.

In conclusion, the formation of 19-electron complexes from 17-electron complexes and a ligand can be slightly thermodynamically downhill. (The reason the reactions are downhill will be discussed in a later section.) *Thus, unfavorable thermodynamics cannot be an objection to the existence of the 19-electron adducts.*

Electron-Transfer Chemistry of the 19-Electron Adducts. The origin of the misconception that 19-electron complexes are high in energy no doubt arose because the reference point used in defining what was high in energy was the corresponding 18-electron complex, rather than the photogenerated 17-electron radicals. In fact, the 19-electron complexes are high in energy *relative to the 18-electron complexes.* This fact is reflected in the chemistry of the 19-electron complexes; their predominant mode of reactivity is electron transfer:[19]

$$\underset{19}{\mathrm{CpFe(CO)dppe}} + \tfrac{1}{2}\mathrm{Mn_2(CO)_{10}} \rightarrow \mathrm{Mn(CO)_5^-} + \underset{18}{\mathrm{CpFe(CO)dppe^+}} \quad (11)$$

$$E^\circ_{\mathrm{Mn_2(CO)_{10}}} < -1.5 \text{ V vs SCE}$$

$$\underset{19}{\mathrm{CpFe(CO)dppe}} + \mathrm{Cp_2Co^+} \rightarrow \mathrm{Cp_2Co} + \underset{18}{\mathrm{CpFe(CO)dppe^+}} \quad (12)$$

$$E^\circ_{\mathrm{Cp_2Co^+}} = -0.88 \text{ V vs SCE}$$

$$\underset{19}{\mathrm{CpFe(CO)dppe}} + \mathrm{MV^{2+}} \rightarrow \mathrm{MV^+} + \underset{18}{\mathrm{CpFe(CO)dppe^+}} \quad (13)$$

$$E^\circ_{\mathrm{MV^{2+}}} = -0.46 \text{ V vs SCE; } \mathrm{MV^{2+}} = \text{methylviologen dication}$$

Reduction potentials for typical photogenerated 19-electron complexes are estimated to be <1.5 V vs SCE.[19] *The 19-electron complexes are thus excellent photogenerated reducing agents.*

Why the Formation of 19-Electron Adducts Is Downhill with Respect to 17-Electron Radicals and a Ligand. A simple molecular orbital scheme showing the interaction of the singly ocupied metal radical orbital with the donor orbital on the ligand is shown in Figure 2a. Note that one electron must occupy the metal–ligand antibonding molecular orbital. This situation is the classic 3-electron bond,[20] resulting in a net metal–ligand bond order of $^1/_2$. Thus, the driving force for the formation of 19-electron adducts is the formation of one-half of a metal–ligand bond.

Some simple calculations lead to the conclusion that reaction 7 should be slightly downhill. A typical metal–ligand bond is worth about 30 kcal/mol,[1] so $^1/_2$ of this value is approximately 15 kcal/mol. The decrease in entropy for two particles associating is usually taken as about 10–15 kcal/mol ($T\Delta S$ at 298 K).[21] Therefore, ΔG° is about 0 to −5 kcal/mol for the formation of the adduct, as reflected in many of the measurements in Table I.

Alternative Electronic Structures for the 19-Electron Adducts That Avoid a 19-Electron Configuration. One objection to the concept of 19-electron adducts is that they might not actually have a 19-electron configuration at the metal because the extra electron might be primarily ligand localized. This is an important point because the phrase "19-electron complex" conveys the concept of a 19th electron in an orbital that has substantial metal character. Unfortunately, the electronic structures of 19-electron adducts have only been studied for a few species because the complexes are too reactive for detailed spectroscopic analyses. However, one example of a complex that was

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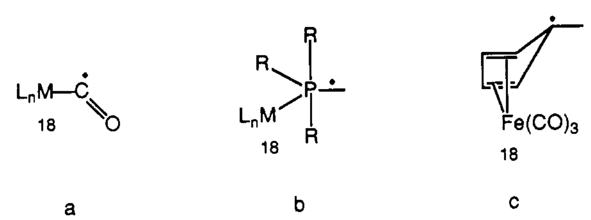
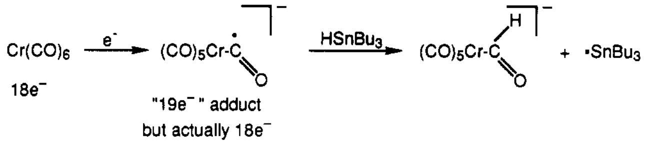


Figure 3. Alternative structures for 19-electron adducts in which the unpaired electron is ligand localized: (a) a molecule with a bent CO (1-electron donor) ligand; (b) a phosphoranyl radical type structure; (c) a "slipped" Cp ring.

Scheme II
A Reaction That Suggests Some 19-Electron Adducts May Have Bent CO Ligands



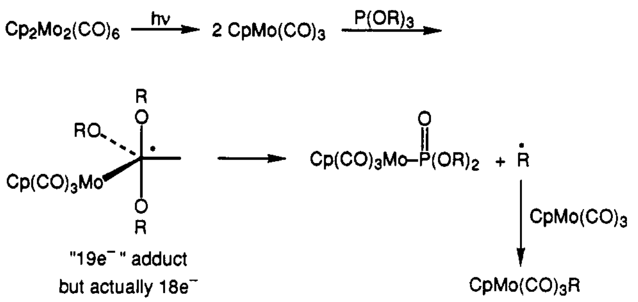
stabilized at low temperature is $Mn(CO)_5Cl^-$.[22,23] ESR spectroscopy of this species (formed by pulse radiolysis of $Mn(CO)_5Cl$ doped in a single crystal of $Cr(CO)_6$) indicated that the unpaired electron does indeed occupy the Mn–Cl σ^* orbital, as indicated in Figure 2a.

Indirect evidence suggests that other 19-electron adducts avoid the occupation of a high-energy M–L orbital by changing the geometry of a ligand. Thus, CO ligands can bend (Figure 3a), phosphine or phosphite ligands can adopt a phosphoranyl radical type structure (Figure 3b), and Cp rings can slip (e.g., Figure 3c) in order to avoid a 19-electron configuration at the metal. Conceptually, these distortions stabilize the 19-electron adducts by removing the unpaired electron from the high-energy metal–ligand antibonding orbital and putting it in a lower energy ligand orbital.

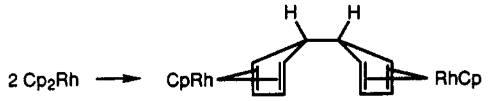
Evidence for these alternative structures comes primarily from reactivity studies. For example, electrochemical reduction of $Cr(CO)_6$ in the presence of a hydrogen atom donor gave $Cr(CO)_5CHO^-$.[24] The pathway in Scheme II was proposed. Note that the "19-electron complex" has a bent CO ligand (formally a one-electron donor), and this gives the metal center an 18-electron count.

Another example is provided by the 19-electron $CpMo(CO)_3(P(OR)_3)$ complex. Evidence for a phosphoranyl radical type structure in this molecule comes from studies which showed that irradiation of $Cp_2Mo_2(CO)_6$ in the presene of $P(OR)_3$ led to small amounts of $CpMo(CO)_3(P(O)(OR)_2)$ and $CpMo(CO)_3R$.[25] The Arbuzov pathway depicted in Scheme III was suggested.[26,27]

Scheme III
A Reaction That Suggests Some 19-Electron Adducts May Have Phosphoranyl Radical Type Structures



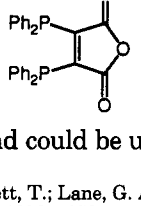
Finally, electrochemical studies have shown that, when many 19-electron complexes couple, they couple through the ligands, presumably because the unpaired electron is ligand localized. This result is so common that it is one of Geiger's rules[28] for predicting the chemistry of organometallic radicals. The classic example of two 19-electron complexes coupling through their ligands in rhodocene:



(14)

The examples above are cited as evidence that many 19-electron complexes may have 18-electron metal centers with a ligand-localized unpaired electron. However, Astruc has warned that it is unwise to draw conclusions about the location of the unpaired electron on metal radicals based on the structure of coupling-reaction products.[12] He showed that the location of the spin density in the transition state of a coupling reaction can be very different from that in the ground state.[12] If this is the case, then reliable information about the location of the unpaired electron in 19-electron adducts would seem to be available only by direct spectroscopic measurements. In conclusion, the electronic structures of 19-electron adducts await further study.

Synthesis of Stable 19-Electron Adducts. Any attempt to synthesize a stable 19-electron adduct must stabilize the "19th" valence electron in the M–L antibonding orbital. The discussion in the preceding section suggests that the way to do this is to shift the electron onto a lower energy ligand orbital. In particular, our strategy for the synthesis of stable 19-electron complexes has been to use ligands that have a vacant π^* orbital lower in energy than the metal–ligand antibonding orbital (Figure 2b).[29] The chelating phosphine 2,3-bis(diphenylphosphino)maleic anhydride is an excellent ligand for this purpose.[29-31] Fenske previously



showed that this ligand could be used to synthesize the

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$Co(CO)_3L_2$ and $Mn(CO)_4L_2$ complexes.[32] These complexes are nominally 19-electron complexes, but ESR studies showed that the unpaired electron was ligand localized, and hence they are better described as 18-electron complexes with reduced ligands.[29,32] We showed that irradiation of metal–metal bonded dimers in the presence of this ligand led to the formation of long-lived adducts.[29,30]

$$Cp_2Mo_2(CO)_6 + 2L_2 \xrightarrow{h\nu} \underset{\text{“19”}}{2CpMo(CO)_2L_2} + 2CO \quad (15)$$

$$Co_2(CO)_8 + 2L_2 \xrightarrow{h\nu} \underset{\text{“19”}}{2Co(CO)_3L_2} + 2CO \quad (16)$$

L_2 = 2,3-bis(diphenylphosphino)maleic anhydride

Thus, we confirmed the hypothesis that 17-electron metal radicals will react with ligands to form adducts.

Amount of 19-Electron Character in the Stable 19-Electron Adducts. The reason the 19-electron adducts with the L_2 ligand are stable is that the 19th valence electron is primarily localized in a π^* orbital on the ligand and not in a metal–ligand antibonding orbital. The name “19-electron complex” is thus a misnomer. Professor Ted Brown at the University of Illinois recommended the name “18+δ complexes” for these species, where the δ nomenclature is intended to indicate the fraction of the unpaired electronic charge that is delocalized onto the metal. (Thus, “authentic” 19-electron complexes (Figure 2a) would have $\delta > \simeq 0.5$, and complexes with no electron delocalization onto the metal from the ligand would have $\delta \simeq 0$.) The determination of δ values in the adducts is, in general, not straightforward, but ESR spectroscopy was used to show that $\delta = 0.015$ in the $Co(CO)_3L_2$ complex.[33] (SCF-Xα-SW calculations give a similar value.[33]) Clearly, the unpaired electron is primarily L_2 localized in this complex. (Techniques for the determination of δ in 19-electron metallocene complexes have been reviewed.[12])

Manipulation of the Amount of 19-Electron Character in 18+δ Complexes. One reason for synthesizing the 18+δ complexes is that they may act as model complexes for the short-lived, and thus less easily studied, 19-electron adducts formed in reactions such as eq 1. However, the small values of δ call into question the ability of the 18+δ complexes to mimic the short-lived adducts, which almost certainly have substantial 19-electron character. For that reason, it was necessary to find ways to manipulate δ and to increase it.

One way to manipulate δ is to vary the solvent.[33] The solvent dependence arises from the relationship between the dipole moment of the molecule and the solvent polarity. This relationship is illustrated using the $Co(CO)_3L_2$ molecule, the dipole moment of which is shown in Figure 4. In polar solvents, it is energetically advantageous to maintain a large dipole (to maximize dipolar interactions with the solvent), and so the unpaired electron is primarily localized in a π^* orbital on the L_2 ligand. In less polar solvents, there is no compelling energetic reason to maintain the dipole, and delocalization of the unpaired electron onto the $Co(CO)_3$ portion of the molecule leads to net stabilization. The varying extent of delocalization onto the $Co(CO)_3$ fragment was detected spectroscopically.[33] For example, the Co hyperfine coupling constant increased as the solvent polarity decreased. Similarly, plots of the LMCT frequency vs solvent polarity and $\nu(C{\equiv}O)$ (or $\nu(C{=}O)$) frequencies vs solvent polarity also indicated increased delocalization onto $Co(CO)_3$ in nonpolar solvents.[33] Although the increase of δ is not expected to be dramatic, it did affect the reactivity of the molecule.

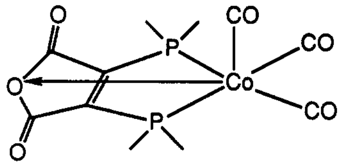

Figure 4. The dipole direction (in the basal plane) for the $Co(CO)_3L_2$ molecule.

Correlation of the Amount of 19-Electron Character with the Reactivity of 18+δ Complexes. In fact, there is a correlation between the amount of 19-electron character and the reactivity of the 18+δ complexes.[33] The correlation is illustrated using the substitution chemistry of $Co(CO)_3L_2$. This molecule substitutes via a dissociatively activated pathway, as shown in Scheme IV.[29,33] The rate constant (25 °C) for substitution by PPh_3 is 7.46 (±0.04) × 10^{-2} in benzene and 5.47 (±0.03) × 10^{-3} in CH_2Cl_2. As discussed in the preceding section, the complex has more 19-electron character in benzene (the less polar solvent) than in CH_2Cl_2. Thus, the complex is more reactive toward substitution when the metal has more 19-electron character. The reason the complex is more reactive is explained by Figure 2c: the metal orbital that is mixed with the L_2 π^* orbital must be M–L antibonding (recall that all of the bonding and nonbonding orbitals are already filled). Occupation of this orbital will weaken the M–L bond, rendering the complex more labile.

Scheme IV

Dissociatively Activated Substitution of $Co(CO)_3L_2$

$$Co(CO)_3L_2 \xrightleftharpoons{-CO,\ slow} Co(CO)_2L_2 \xrightarrow[L']{fast} Co(CO)_2L_2L'$$

L_2 = 2,3-bis(diphenylphosphino)maleic anhydride

The Importance of 19-Electron Adducts in Organometallic Chemistry. The discussion above summarizes the wealth of data which supports the hypothesis that 19-electron complexes form readily from 17-electron radicals and nucleophiles. Given the prevalence of radical intermediates in many organometallic reaction systems, it is logical to suggest that 19-electron species may be important in these reactions. In particular, because 19-electron species are powerful reductants, we feel that many radical chain pathways may in fact be electron-transfer-chain (ETC) catalyzed pathways. For example, the radical chain mechanism depicted in Scheme V was proposed for the $Cp_2Mo_2(CO)_6$-catalyzed substitution of $CpMo(CO)_3I$.[34] An alternative mechanism for these substitution reactions, however, is the ETC pathway depicted in Scheme VI,

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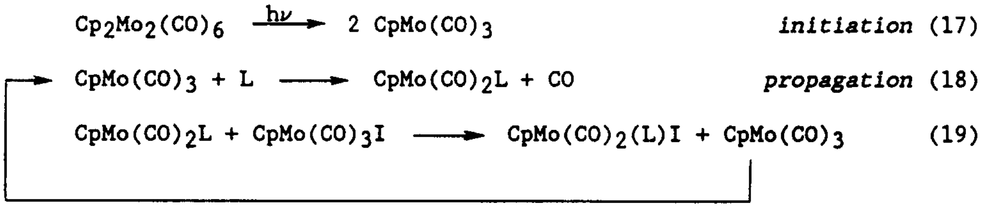
(32) Fenske, D. *Chem. Ber.* **1979**, *112*, 363–375.

(33) Mao, F.; Tyler, D. R.; Rieger, A. L.; Rieger, P. H. *J. Chem. Soc., Faraday Trans.*, accepted for publication.

(34) Alway, D. G.; Barnett, K. W. *Inorg. Chem.* **1980**, *19*, 1533–1543.

Scheme V

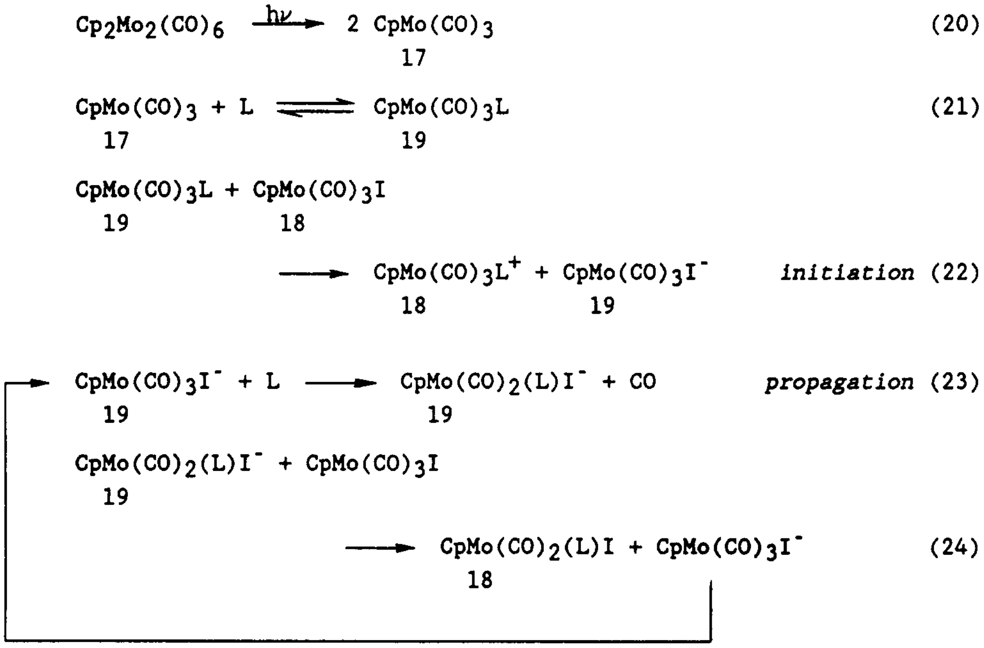


$$Cp_2Mo_2(CO)_6 \xrightarrow{h\nu} 2\ CpMo(CO)_3 \quad \textit{initiation} \quad (17)$$

$$CpMo(CO)_3 + L \longrightarrow CpMo(CO)_2L + CO \quad \textit{propagation} \quad (18)$$

$$CpMo(CO)_2L + CpMo(CO)_3I \longrightarrow CpMo(CO)_2(L)I + CpMo(CO)_3 \quad (19)$$

Scheme VI



$$\underset{}{Cp_2Mo_2(CO)_6} \xrightarrow{h\nu} 2\ \underset{17}{CpMo(CO)_3} \quad (20)$$

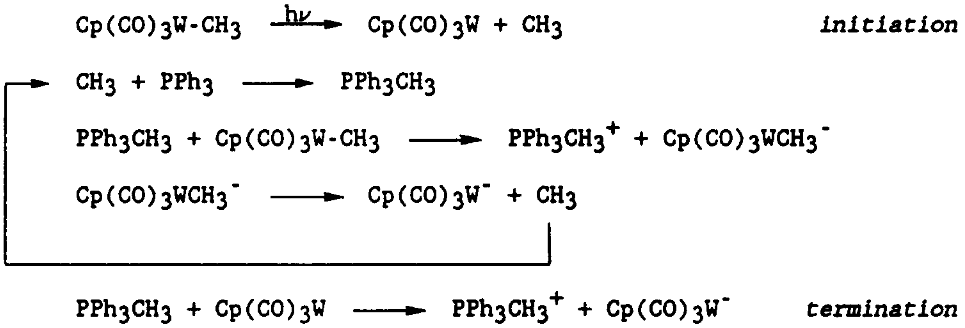
$$\underset{17}{CpMo(CO)_3} + L \rightleftharpoons \underset{19}{CpMo(CO)_3L} \quad (21)$$

$$\underset{19}{CpMo(CO)_3L} + \underset{18}{CpMo(CO)_3I} \longrightarrow \underset{18}{CpMo(CO)_3L^+} + \underset{19}{CpMo(CO)_3I^-} \quad \textit{initiation} \quad (22)$$

$$\underset{19}{CpMo(CO)_3I^-} + L \longrightarrow \underset{19}{CpMo(CO)_2(L)I^-} + CO \quad \textit{propagation} \quad (23)$$

$$\underset{19}{CpMo(CO)_2(L)I^-} + CpMo(CO)_3I \longrightarrow \underset{18}{CpMo(CO)_2(L)I} + CpMo(CO)_3I^- \quad (24)$$

Scheme VII
The Mechanism of Reaction 26



$$Cp(CO)_3W\text{-}CH_3 \xrightarrow{h\nu} Cp(CO)_3W + CH_3 \quad \textit{initiation}$$

$$CH_3 + PPh_3 \longrightarrow PPh_3CH_3$$

$$PPh_3CH_3 + Cp(CO)_3W\text{-}CH_3 \longrightarrow PPh_3CH_3^+ + Cp(CO)_3WCH_3^-$$

$$Cp(CO)_3WCH_3^- \longrightarrow Cp(CO)_3W^- + CH_3$$

$$PPh_3CH_3 + Cp(CO)_3W \longrightarrow PPh_3CH_3^+ + Cp(CO)_3W^- \quad \textit{termination}$$

initiated by electron transfer from a 19-electron species. Similar ETC reactions, initiated by electron transfer from a 19-electron complex, can be proposed for virtually any metal radical chain mechanism.[35] In fact, it has been shown that in the decarbonylation of $Re_2(CO)_9CHO^-$ (eq 25) the traditional radical chain mechanism operates side by side with an ETC mechanism. (See Schemes I–III in ref 36.)

$$Re_2(CO)_9CHO^- \rightarrow Re_2(CO)_9H^- + CO \quad (25)$$

Of course, not all radical mechanisms which take place in the presence of a nucleophile involve a 19-electron intermediate. I am simply pointing out that, because 19-electron complexes form from 17-electron species and a ligand so readily, ETC mechanisms must be considered as viable alternatives.

Generalization of the 19-Electron Adduct Concept beyond Organometallic Chemistry. Do "hypervalent" species also form when nonorganometallic radicals react with nucleophiles? To study this question, we examined reactions that were "isolobal"[3] to the photochemical disproportionation reactions of the metal–metal-bonded dimers.[37] An example is shown in eq 26 for comparison to the disproportionation reaction in eq 27:

$$Cp(CO)_3WCH_3 + PPh_3 \xrightarrow{h\nu} Cp(CO)_3W^- + CH_3PPh_3^+ \quad (26)$$

$$Cp(CO)_3WW(CO)_3Cp + PPh_3 \xrightarrow{h\nu} Cp(CO)_3W^- + Cp(CO)_3WPPh_3^+ \quad (27)$$

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[35] Stiegman, A. E.; Tyler, D. R. *Comments Inorg. Chem.* **1986**, *5*, 215–245.

[36] Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* **1986**, *5*, 926–935.

[37] Goldman, A. S.; Tyler, D. R. *J. Am. Chem. Soc.* **1986**, *108*, 89–94.

The CH_3 radical is isolobal to 17-electron organometallic radicals ($\mathrm{Cp(CO)_3W} \underset{\circ}{\longleftrightarrow} \mathrm{CH_3}$); thus eq 26 is analogous to reaction 27 except that one of the $\mathrm{CpW(CO)_3}$ radicals has been replaced by a CH_3 radical. Work in our laboratory[37] established that the mechanism of reaction 26 (Scheme VII) is indeed "isolobal" to the disproportionation mechanism in Scheme I (compare Scheme VII to Scheme I). Note that a key intermediate in Scheme VII is a phosphoranyl radical, a species analogous to the 19-electron adducts. (In fact, it is well-established that organic radicals react with phosphines to form phosphoranyl radicals.[38] As with their 19-electron adduct counterparts, the chemistry of phosphoranyl radicals is primarily ligand dissociation and electron transfer.)

"Disproportionation" reactions analogous to eq 26 occur with other metal complexes, e.g.,[39]

$$\mathrm{Me_3SiCo(CO)_4} + \mathrm{NR_3} \xrightarrow{h\nu} \mathrm{Co(CO)_4}^- + \mathrm{Me_3SiNMe_3}^+ \tag{28}$$

These reactions probably also occur by a mechanism analogous to those in Schemes I and VII. If so, it can be concluded that radical species such as phenyl, $SnCl_3$, and $SiMe_3$ also react with nucleophiles to form hypervalent species which can undergo electron transfer.

In summary, the reaction of radicals with nucleophiles to form hypervalent species which can then undergo electron transfer appears to be a general phenomenon, occurring not only in organometallic chemistry but in coordination, main-group, and organic chemistry as well.

Concluding Remarks. The existence of the 19-electron adducts has now been convincingly demonstrated, and these species are generally accepted by the organometallic community. Numerous workers have shown that the interconversion of 17- and 19-electron species plays a major role in organometallic radical reactivity, including substitution reactions, insertion reactions, and electron-transfer reactions.[26,40] In fact, it has been suggested that the facile conversion between 17- and 19-electron species is as important in radical chemistry as the 18/16-electron conversion in traditional organometallic chemistry.[26,40]

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[39] Stiegman, A. E.; Tyler, D. R. *Coord. Chem. Rev.* 1985, *63*, 217–140.

[40] Trogler, W. C. In *Organometallics Radical Processes*; Trogler, W. C.; Ed.; Elsevier: New York, 1990.