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MECHANISTIC STUDIES OF NINETEEN-ELECTRON ORGANOMETALLIC COMPLEXES; SYNTHESIS OF STABLE NINETEEN-ELECTRON COMPLEXES

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SUMMARY

Evidence for the existence of photochemically generated 19-electron complexes is reviewed. The synthesis of the stable 19-electron (18+δ) $Cp'Mo(CO)_2(L_2\text{-}P,P')$ complex is described ($Cp' = \eta^5\text{-}C_5Ph_4H$; L_2 = 2,3-bis(diphenylphosphino)maleic anhydride). The spectroscopic properties of this complex are reported and discussed.

INTRODUCTION

For the past ten years, our laboratory has been investigating the chemistry of organometallic radicals. The most important discovery to emerge from our research is that many 17-electron organometallic radicals can react with ligands to form adducts (ref. 1):

$$\underset{17e^-}{ML_n} + L' \overset{K_{eq}}{\rightleftharpoons} \underset{19e^-}{ML_nL'} \qquad (1)$$

ML_n = $CpMo(CO)_3$, $CpW(CO)_3$, $CpFe(CO)_2$, $Mn(CO)_5$, $Co(CO)_4$
L' = PR_3, $P(OR)_3$, NR_3, Cl^-, Br^-, I^-, CH_3CN, THF, and other coordinating solvents

For lack of a better name, we call the adducts that form in these reactions 19-electron adducts (or complexes) simply because the sum of 17 valence electrons from the metal radical and the two electrons from the ligand is nineteen. We state emphatically, however, that no implication about the electronic or geometric structures of these complexes is implied by this name (ref. 2). Nineteen-electron adducts are reactive intermediates, and they form only transiently in reactions involving organometallic radicals: we have never been able to observe them spectroscopically by flash photolysis or by other fast kinetics techniques. For these reasons, it was necessary for us to devote considerable effort to establishing the existence of these fleeting species.

In this paper, we briefly review the initial mechanistic evidence which led us to propose the formation and existence of 19-electron complexes. In the second part of the paper, we discuss the synthesis and characterization of a stable 19-electron adduct.

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EVIDENCE FOR PHOTOCHEMICALLY GENERATED NINETEEN-ELECTRON COMPLEXES

Disproportionation reactions of the $Cp_2Mo_2(CO)_6$ complex

The initial evidence that 17-electron radicals react with ligands to form 19-electron adducts came from an investigation of the mechanism of the photochemical disproportionation reactions of the $Cp_2Mo_2(CO)_6$ complex in benzene solution, eq 2 (ref. 3).

$$Cp_2Mo_2(CO)_6 + 2\ PR_3 \xrightarrow[\text{benzene}]{h\nu} CpMo(CO)_2(PR_3)_2^+ + CpMo(CO)_3^- + CO \qquad (2)$$

Our preliminary mechanistic studies established that the quantum yields for this disproportionation reaction are greater than one. (Under some conditions quantum yields as high as 100 were obtained (ref. 3).) This result, coupled with the fact that irradiation of metal-metal bonded dimers was known to homolyze the metal-metal bond (eq 3) (ref. 4), pointed to a radical chain mechanism.

$$M_2L_{2n} \overset{h\nu}{\rightleftharpoons} 2\ \underset{17e^-}{ML_n} \qquad (3)$$

ML_n = $Mn(CO)_5$, $Re(CO)_5$, $CpM(CO)_3$ (M = Cr, Mo, W),
$CpFe(CO)_2$, $Co(CO)_4$

One possible mechanism, involving only conventional elementary steps, is shown in Scheme I.

$$Cp_2Mo_2(CO)_6 \overset{h\nu}{\rightleftharpoons} 2\ CpMo(CO)_3 \qquad \text{initiation} \qquad (4)$$

$$CpMo(CO)_3 + L \longrightarrow CpMo(CO)_2L + CO \qquad (5)$$

$$CpMo(CO)_2L + Cp_2Mo_2(CO)_6 \longrightarrow \underset{16e^-}{CpMo(CO)_2L^+} + Cp_2Mo_2(CO)_6^- \qquad (6)$$

$$Cp_2Mo_2(CO)_6^- \longrightarrow CpMo(CO)_3^- + CpMo(CO)_3 \qquad (7)$$

$$\underset{16e^-}{CpMo(CO)_2L^+} + L \longrightarrow CpMo(CO)_2L_2^+ \qquad (8)$$

(Various radical coupling termination steps are not shown.)

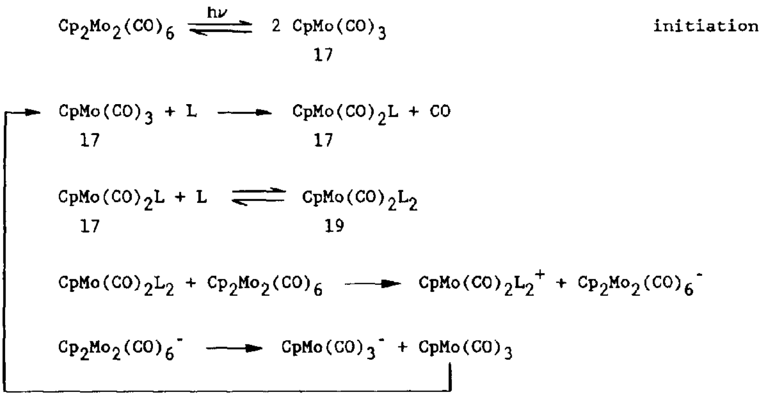
$$\text{Overall:}\quad Cp_2Mo_2(CO)_6 + 2\ L \xrightarrow{h\nu} CpMo(CO)_2L_2^+ + CpMo(CO)_3^- + CO \qquad (9)$$

Scheme I

Note that the primary photoprocess in this scheme is homolysis of the metal-metal bond with the subsequent formation of 17-electron metal radicals. Following substitution (eq 5), the next step is electron transfer from the substituted 17-electron radical to an unreacted dimer molecule (eq 6). Reduction of metal carbonyl dimers is known to cause fragmentation (eq 7) giving the anionic product of the reaction and the 17-electron radical (ref. 5). The latter species is recycled and the chain continues.

Despite its orthodox features, this mechanism was intuitively unsatisfying because the 17-electron complex is the reductant in the reaction. That a 17-electron complex would be the reductant seems unlikely because the dimers are difficult to reduce: their reduction potentials are usually on the order of -1.5 volts or lower vs. Ag/AgCl (ref. 6). Chemical intuition suggests that the 17-electron radicals are not strong reductants because they are electron deficient.

An alternative mechanism for the disproportionation reactions was proposed by Tyler and Stiegman (Scheme II) (ref. 3). This mechanism is similar to the pathway in Scheme I but it differs in one important aspect: the electron transfer occurs not from a 17-electron complex but from a 19-electron complex. Note that the 19-electron complex is formed by association of a 17-electron complex with a ligand (eq 12). The 19-electron complex is electronically super-saturated, and it should be an excellent reductant, capable of reducing the dimer.



$$Cp_2Mo_2(CO)_6 \overset{h\nu}{\rightleftharpoons} 2\ \underset{17}{CpMo(CO)_3} \qquad \text{initiation} \qquad (10)$$

$$\underset{17}{CpMo(CO)_3} + L \longrightarrow \underset{17}{CpMo(CO)_2L} + CO \qquad (11)$$

$$\underset{17}{CpMo(CO)_2L} + L \rightleftharpoons \underset{19}{CpMo(CO)_2L_2} \qquad (12)$$

$$CpMo(CO)_2L_2 + Cp_2Mo_2(CO)_6 \longrightarrow CpMo(CO)_2L_2^+ + Cp_2Mo_2(CO)_6^- \qquad (13)$$

$$Cp_2Mo_2(CO)_6^- \longrightarrow CpMo(CO)_3^- + CpMo(CO)_3 \qquad (14)$$

(Various radical coupling and electron transfer chain termination steps are not shown.)

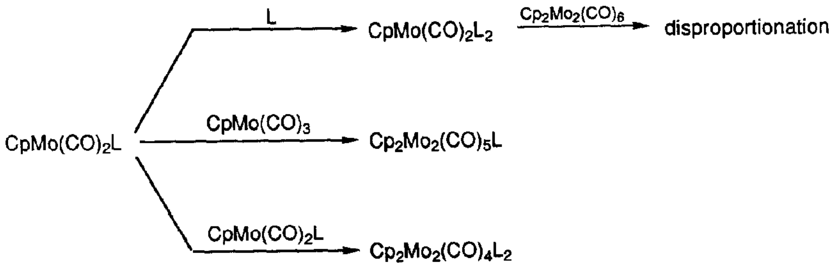
$$\text{Overall:} \quad Cp_2Mo_2(CO)_6 + 2\ L \xrightarrow{h\nu} CpMo(CO)_2L_2^+ + CpMo(CO)_3^- + CO \qquad (15)$$

Scheme II

Several studies in the literature supported our proposal that 19-electron intermediates formed in the disproportionation reactions. The first was a study by Poë showing that the ligand substitution reactions of the 17-electron $Re(CO)_5$ radical were associatively activated (ref. 7). No 19-electron intermediates were detected in these reactions (the 19-electron complex was proposed to be a transition state), but this study was the first to suggest the concept of associatively activated reactions of 17-electron complexes. Subsequent work by Trogler and Basolo showed that the 6-coordinate $V(CO)_6$ complex also substituted via an associatively activated pathway (ref. 8), and once again a 19-electron transition state was invoked.

Disproportionation reactions with dppe

Our initial evidence that 19-electron adducts formed in the disproportionation reactions and that these species were intermediates, not just transition states, came from experiments using dppe as the ligand (dppe = 1,2-bis(diphenylphosphino)ethane) (ref. 3). We used this ligand because we wanted to measure the quantum yields of the disproportionation reactions. With monodentate phosphine or phosphite ligands, there were problems making these measurements because the ionic disproportionation products were not the only products formed when the $Cp_2Mo_2(CO)_6$ complex is irradiated; $Cp_2Mo_2(CO)_5L$ and $Cp_2Mo_2(CO)_4L_2$ also formed, undoubtedly by the coupling of the $CpMo(CO)_2L$ radical with either the $CpMo(CO)_3$ or $CpMo(CO)_2L$ radical:



Thus, for most ligands it was impossible to measure the quantum yields for disproportionation because of the competing substitution side reactions. However, we found that disproportionation was the only reaction when dppe was the ligand. This is an expected result if the pathway in Scheme II is followed, but it is not expected for the pathway in Scheme I involving the 17-electron reductant. The reasoning is as follows: When L = dppe, the rate constant for attack by the second ligand (eq 12 in Scheme II) is expected to be faster than the initial substitution because the second attack is a ring closure step . (Ring closure steps are generally several orders of magnitude faster than the attack of the initial end of a chelate ligand.) The ring closure and subsequent electron transfer thus occur before combination of two 17-electron fragments gives the substitution products. Consequently, there are no competing substitution reactions when L is dppe, and the sole reaction is given by:

$$Cp_2Mo_2(CO)_6 + dppe \xrightarrow{h\nu} CpMo(CO)_2dppe^+ + CpMo(CO)_3^- + CO \qquad (16)$$

On the other hand, if the pathway in Scheme I is followed there is no particular reason why a bidentate ligand should prevent the substitution reactions. The efficiency of the formation of $CpMo(CO)_2$(dppe-P) should be independent of the denticity of the ligand and some substitution should occur (as well as disproportionation). The substitution products would presumably be $Cp_2Mo_2(CO)_5$(dppe-P), $Cp_2Mo_2(CO)_4$(dppe-P)$_2$, $Cp_2Mo_2(CO)_4$(dppe-P,P') or perhaps a dppe-bridged complex like $Cp_2Mo_2(CO)_5$(u-dppe)$Mo_2(CO)_5Cp_2$. (The dppe-P nomenclature indicates one P atom of dppe is coordinated; dppe-P,P' indicates two P atoms are coordinated.) The fact that no substitution products of any kind were observed was taken as evidence that 17-electron radicals were not involved in the disproportionation reactions because the ring closure reaction to make the 19-electron species was fast. Finally, also note that the quantum yields of the reactions with dppe are high, even at very low concentrations. As Table 1 shows (ref. 3), it takes concentrations of monodentate ligands that are one hundred- to a thousand-fold larger to give quantum yields that are comparable to those obtained with dppe at a lower concentration. This result is consistent with the proposal that two phosphines must coordinate to the metal center before electron transfer occurs, i.e. that a 19-electron intermediate must form.

TABLE 1

Quantum yields for the disproportionation of $Cp_2Mo_2(CO)_6$ with various ligands upon irradiation at 405 nm in benzene.

Ligand	Concentration	ϕ
dppe	0.001	1.63
dppe	0.01	7.8, 11.8, 6.6
$PPh_2(CH_3)$	0.2	2.0
$P(OCH_3)_3$	2.0	1.2

It is possible to formulate alternative explanations for the disproportionation reaction of $Cp_2Mo_2(CO)_6$ with dppe that do not involve 19-electron complexes. Our discussion and dismissal of these alternatives is found in ref. 1.

Further evidence for a 19-electron reductant in the disproportionation reactions of the $Cp_2Mo_2(CO)_6$ complex

A consideration of all the mechanistic possibilities for the disproportionation reactions led us to the conclusion that there are only three reasonable species that can act as photogenerated reductants in these reactions (in benzene solution). As discussed above, two of these species are the 17-electron $CpMo(CO)_2L$ complex (Scheme I) and the other is the 19-electron $CpMo(CO)_2L_2$ complex (Scheme II). The third possibility is the 17-electron $CpMo(CO)L_2$ species; a mechanism showing how this species could form and how it could be involved in the disproportionation reaction is shown in Scheme III (ref. 9).

$$Cp_2Mo_2(CO)_6 \underset{}{\overset{h\nu}{\rightleftharpoons}} \underset{17}{2\ CpMo(CO)_3} \qquad \text{initiation} \qquad (17)$$

$$\underset{17}{CpMo(CO)_3} + L \longrightarrow \underset{17}{CpMo(CO)_2L} + CO \qquad (18)$$

$$\underset{17}{CpMo(CO)_2L} + L \longrightarrow \underset{17}{CpMo(CO)L_2} + CO \qquad (19)$$

$$CpMo(CO)L_2 + Cp_2Mo_2(CO)_6 \longrightarrow CpMo(CO)L_2^+ + Cp_2Mo_2(CO)_6^- \qquad (20)$$

$$Cp_2Mo_2(CO)_6^- \longrightarrow CpMo(CO)_3^- + CpMo(CO)_3 \qquad (21)$$

$$\underset{16e^-}{CpMo(CO)_2L^+} + CO \longrightarrow CpMo(CO)_2L_2^+ \qquad (22)$$

(Various radical coupling and electron transfer chain
termination steps are not shown.)

$$\text{Overall:}\quad Cp_2Mo_2(CO)_6 + 2\ L \xrightarrow{h\nu} CpMo(CO)_2L_2^+ + CpMo(CO)_3^- + CO \qquad (23)$$

Scheme III

We were able to eliminate the pathway in Scheme III by using a tridentate ligand (ref 9). The logic of the experiment was as follows. If $CpMo(CO)L_2$ is the reductant then electron transfer from this species yields the 16-electron $CpMo(CO)L_2^+$ species, as shown in eq 20; this cation then reacts with CO to form the $CpMo(CO)_2L_2^+$ complex (eq 22). However, if the ligand is tridentate then the $CpMo(CO)L_2^+$ species has a dangling, uncoordinated ligand end that can coordinate to the vacant coordination site to form the $CpMo(CO)L_3^+$ complex. The coordination of the dangling end of the tridentate ligand ought to be faster than the reaction with CO (eq 22) because this is a ring-closure step and such steps are usually fast.

The experiment was carried out with the tridentate triphos ligand (triphos - bis(2-(diphenylphosphino)ethyl)phenylphosphine). Irradiation of $Cp_2Mo_2(CO)_6$ and triphos gave the products shown in the following equation:

$$Cp_2Mo_2(CO)_6 + \text{triphos} \xrightarrow{h\nu} CpMo(CO)_2(\text{triphos-P,P}')^+ + CpMo(CO)_3^- + CO \qquad (24)$$

Note that the only cationic product formed was the $CpMo(CO)(\text{triphos-P,P}')^+$ species, where the P,P′ nomenclature indicates that two of the phosphorus atoms in the triphos ligand are coordinated. Because no $CpMo(CO)(\text{triphos-P,P}',\text{P}'')^+$ formed, it was concluded that 17-electron intermediates of the form $CpMo(CO)L_2$ are not important in the disproportionation reactions of the Mo complex. Nineteen-electron reductants are the only species consistent with the results using dppe and triphos.

Initial evidence for 19-electron intermediates (continued): disproportionation reactions of the $Mn_2(CO)_{10}$ complex

Following our finding that 19-electron species are important intermediates in the disproportionation reactions of the $Cp_2Mo_2(CO)_6$ complex, we turned our attention to the disproportionation reactions of other metal-metal bonded dimers to see if 19-electron complexes were also important in these reactions (ref 10). We did this because we wanted to generalize the concept that 17-electron metal radicals react with ligands to form 19-electron adducts, and the disproportionation reactions provided a convenient way to study this problem. In particular, our work with the $Cp_2Mo_2(CO)_6$ complex provided us with a clever trick to test for 19-electron complexes: use multidentate ligands and check for (1) an increased efficiency of the reaction, (2) the absence of substitution products, and (3) the absence of ring-closure products in experiments analogous to the one with triphos.

$Mn_2(CO)_{10}$ disproportionates with amine ligands as follows (refs. 10 and 11):

$$Mn_2(CO)_{10} + 3\ NR_3 \xrightarrow{h\nu} Mn(CO)_3(NR_3)_3^+ + Mn(CO)_5^- + 2\ CO \qquad (25)$$

The following mechanism is suggested by comparison to the mechanism of $Cp_2Mo_2(CO)_6$ disproportionation.

$$Mn_2(CO)_{10} \xrightarrow{h\nu} 2\ Mn(CO)_5 \tag{26}$$

$$Mn(CO)_5 + NR_3 \longrightarrow Mn(CO)_4NR_3 + CO \tag{27}$$

$$Mn(CO)_4NR_3 + NR_3 \longrightarrow Mn(CO)_3(NR_3)_2 + CO \tag{28}$$

$$Mn(CO)_3(NR_3)_2 + NR_3 \longrightarrow Mn(CO)_3(NR_3)_3 \tag{29}$$

$$Mn(CO)_3(NR_3)_3 + Mn_2(CO)_{10} \longrightarrow Mn(CO)_3(NR_3)_3^+ + Mn_2(CO)_{10}^- \tag{30}$$

$$Mn_2(CO)_{10}^- \longrightarrow Mn(CO)_5^- + Mn(CO)_5 \tag{31}$$

(Various radical coupling termination steps are not shown.)

$$\text{Overall:}\quad Mn_2(CO)_{10} + 3\ NR_3 \longrightarrow Mn(CO)_3(NR_3)_3^+ + Mn(CO)_5^- + 2\ CO \tag{32}$$

Scheme IV

Note that our trick of using a bidentate ligand will not work with this reaction because the 19-electron species is of the form $Mn(CO)_3(NR_3)_3$. However, a <u>tridentate</u> ligand should form this 19-electron species efficiently. In fact, that is what we found (ref. 10). The quantum yield results for the disproportionation of $Mn_2(CO)_{10}$ with amine ligands of different denticities are shown in Table 2. These data show that disproportionation is inefficient with monodentate amines, slightly more efficient with the bidentate amine Me_3en (especially when the Me_3en is concentrated), and very efficient with the tridentate dien ligand (even at very low concentrations). Our proposed explanation for this increased efficiency was identical to the explanation for the increased efficiency using the bidentate ligands in the $Cp_2Mo_2(CO)_6$ reactions. Analogous to the disproportionation reactions of $Cp_2Mo_2(CO)_6$ with bidentate ligands, we also found that no substitution products were formed in the disproportionation reactions of $Mn_2(CO)_{10}$ with tridentate ligands.

In summary, our study of the $Mn_2(CO)_{10}$ complex provided additional evidence for 19-electron complexes, and most important, it provided the first evidence that the reaction of 17-electron radicals with ligands to form 19-electron adducts may be a general reaction type.

TABLE 2

Quantum yields of disappearance for $Mn_2(CO)_{10}$ in the disproportionation of $Mn_2(CO)_{10}$[a] with various ligands upon irradiation at 366 nm.

Ligand	Concentration[b]	ϕ[c]
pyridine	neat (≈12 M)	0.10, 0.10
$N(CH_2CH_3)_3$	neat (≈7 M)	0.11, 0.10, 0.20
$(CH_3)_2NCH_2CH_2N(H)(CH_3)$	neat (≈8 M)	1.2
	2.0 M	0.17, 0.28
$NH(CH_2CH_2NH_2)_2$	0.1 M	6.3, 7.8
	0.2 M	10.7, 19.1

[a] The concentration of $Mn_2(CO)_{10}$ is 1.4×10^{-4} M. The disappearance of $Mn_2(CO)_{10}$ was monitored at 343 nm.

[b] In benzene solution.

[c] Each number represents an independent determination of the quantum yield. The error for each measurement is approximately 10%.

Summary of the expected disproportionation products

At this point it is appropriate to systematize the various intermediate species that could be acting as reducing agents in the disproportionation reactions. The example is given for the case of the $Cp_2Mo_2(CO)_6$ dimer because it is the most thoroughly studied of the dimers. A similar analysis could be applied to the other dimers, however. As discussed previously (ref. 3), three possible species in benzene solution are the 17-electron $CpMo(CO)_2L$ and $CpMo(CO)L_2$ complexes (Schemes I and III) and the 19-electron $CpMo(CO)_2L_2$ species (Scheme II). Slightly different reductants are proposed in CH_2Cl_2 solution because the cationic product is $CpMo(CO)_3L^+$ (ref. 13):

$$Cp_2Mo_2(CO)_6 + L \xrightarrow[CH_2Cl_2]{h\nu} CpMo(CO)_3L^+ + CpMo(CO)_3^- \qquad (33)$$

Thus, possible reductants in CH_2CH_2 include the 17-electron $CpMo(CO)_2L$ (Scheme V) and $CpMo(CO)_3$ (scheme not shown) species and the 19-electron $CpMo(CO)_3L$ (Scheme VI) complex. Each of these reductants will give different products depending on the denticity of the ligand. The predicted and actual products are shown in Table 3.

$$\mathrm{Cp_2Mo_2(CO)_6} \xrightleftharpoons{h\nu} 2\ \underset{17}{\mathrm{CpMo(CO)_3}} \qquad \text{initiation} \tag{34}$$

$$\underset{17}{\mathrm{CpMo(CO)_3}} + \mathrm{L} \longrightarrow \underset{17}{\mathrm{CpMo(CO)_2L}} + \mathrm{CO} \tag{35}$$

$$\underset{17}{\mathrm{CpMo(CO)_2L}} + \mathrm{Cp_2Mo_2(CO)_6} \longrightarrow \underset{16}{\mathrm{CpMo(CO)_2L^+}} + \mathrm{Cp_2Mo_2(CO)_6^-} \tag{36}$$

$$\mathrm{CpMo_2(CO)_6^-} \longrightarrow \mathrm{CpMo(CO)_3^-} + \mathrm{CpMo(CO)_3} \tag{37}$$

$$\underset{16}{\mathrm{CpMo(CO)_2L^+}} + \mathrm{CO} \longrightarrow \mathrm{CpMo(CO)_3L^+} \tag{38}$$

(Various radical coupling and electron transfer chain termination steps are not shown.)

$$\text{Overall:}\quad \mathrm{Cp_2Mo_2(CO)_6} + \mathrm{L} \xrightarrow{h\nu} \mathrm{CpMo(CO)_3L^+} + \mathrm{CpMo(CO)_3^-} \tag{39}$$

Scheme V

$$\mathrm{Cp_2Mo_2(CO)_6} \xrightleftharpoons[k_{-1}]{h\nu} 2\ \underset{17}{\mathrm{CpMo(CO)_3}} \qquad \text{initiation} \tag{40}$$

$$\underset{17}{\mathrm{CpMo(CO)_3}} + \mathrm{L} \xrightleftharpoons[k_{-2}]{k_2(K_{eq})} \underset{19}{\mathrm{CpMo(CO)_3L}} \tag{41}$$

$$\underset{19}{\mathrm{CpMo(CO)_3L}} + \mathrm{Cp_2Mo_2(CO)_6} \xrightarrow{k_3} \mathrm{CpMo(CO)_3L^+} + \mathrm{Cp_2Mo_2(CO)_6^-} \tag{42}$$

$$\mathrm{Cp_2Mo_2(CO)_6^-} \xrightarrow{k_4} \mathrm{CpMo(CO)_3^-} + \mathrm{CpMo(CO)_3} \tag{43}$$

One of several termination steps:

$$\underset{19}{\mathrm{CpMo(CO)_3L}} + \underset{17}{\mathrm{CpMo(CO)_3}} \xrightarrow{k_5} \mathrm{CpMo(CO)_3L^+} + \mathrm{CpMo(CO)_3^-} \tag{44}$$

$$\text{Overall:}\quad \mathrm{Cp_2Mo_2(CO)_6} + \mathrm{L} \xrightarrow{h\nu} \mathrm{CpMo(CO)_3L^+} + \mathrm{CpMo(CO)_3^-} \tag{45}$$

Scheme VI

TABLE 3

Predicted and actual products from the disproportionation of $Cp_2Mo(CO)_6$ with monodentate, bidentate, and tridentate ligands.

Reducing Species	Ligand	Predicted Product	Actual Product
In CH_2Cl_2			
$CpMo(CO)_3$	L	$CpMo(CO)_3L^+$	$CpMo(CO)_3L^+$
	$\overset{\frown}{L\,L}$	$CpMo(CO)_3\underset{L}{L}^{+}$ [a]	$CpMo(CO)_2(L_2)^+$
$CpMo(CO)_2L$	L	$CpMo(CO)_2{L_2}^+$	$CpMo(CO)_3L^+$
	$\overset{\frown}{L\,L}$	$CpMo(CO)_2(L_2)^+$	$CpMo(CO)_2(L_2)^+$
$CpMo(CO)_3L$	L	$CpMo(CO)_3L^+$	$CpMo(CO)_3L^+$
	$\overset{\frown}{L\,L}$	$CpMo(CO)_2(L_2)^+$ [b]	$CpMo(CO)_2(L_2)^+$
In Benzene			
$CpMo(CO)_2L$	L	$CpMo(CO)_2{L_2}^+$	$CpMo(CO)_2{L_2}^+$
	$\overset{\frown}{L\,L}$	$CpMo(CO)_2(L_2)^+$	$CpMo(CO)_2(L_2)^+$
	$\overset{\frown\frown}{L\,L\,L}$	$CpMo(CO)_2\underset{L}{(L_2)}^{+}$ [b]	$CpMo(CO)_2\underset{L}{(L_2)}^{+}$
$CpMo(CO)L_2$	L	$CpMo(CO){L_3}^+$	$CpMo(CO)_2{L_2}^+$
	$\overset{\frown}{L\,L}$	$CpMo(CO)(L_2)\underset{L}{L}^{+}$	$CpMo(CO)_2(L_2)^+$
	$\overset{\frown\frown}{L\,L\,L}$	$CpMo(CO)(L_3)^+$	$CpMo(CO)_2\underset{L}{(L_2)}^{+}$
$CpMo(CO)_2L_2$	L	$CpMo(CO)_2{L_2}^+$	$CpMo(CO)_2{L_2}^+$
	$\overset{\frown}{L\,L}$	$CpMo(CO)_2(L_2)^+$	$CpMo(CO)_2(L_2)^+$
	$\overset{\frown\frown}{L\,L\,L}$	$CpMo(CO)_2\underset{L}{(L_2)}^{+}$	$CpMo(CO)_2\underset{L}{(L_2)}^{+}$

[a] The $\underset{L}{(L_2)}$ or $\underset{L}{L}$ nomenclature indicates one atom in the chelating ligand is uncoordinated.

[b] The $CpMo(CO)_3\underset{L}{L}^{+}$ product is not predicted because the 19-electron $CpMo(CO)_3\underset{L}{L}$ complex will substitute rapidly.

The products were predicted by using the appropriate denticity of ligand in the appropriate reaction scheme. For example, if a bidentate ligand is used and the reductant in CH_2Cl_2 is the $CpMo(CO)_3$ complex then the species formed after electron transfer is ${CpMo(CO)_3}^+$; subsequent reaction with the ligand would yield the $CpMo(CO)_3(L_2\text{-}P)^+$ species. A comparison of the actual and predicted products shows that only in the case of the 19-electron $CpMo(CO)_3L$ reductant do the predicted and actual products match up. This result was taken as evidence for a 19-electron reductant in CH_2Cl_2 solution. The one subtlety associated with this conclusion is that the $CpMo(CO)_3(L_2\text{-}P)^+$ might be the predicted product rather than $CpMo(CO)_2(L_2\text{-}P,P')^+$ when using a chelating ligand in CH_2Cl_2 solution. However, 19-electron complexes substitute rapidly, particularly when an uncoordinated end of a chelating ligand is dangling nearby, and thus $CpMo(CO)_2(L_2\text{-}P,P')^+$ is the predicted product.

A similar comparison of the predicted and actual products in benzene solution is also shown in Table 3. Note that in this case it was not possible to differentiate between the 17-electron $CpMo(CO)_2L$ and 19-electron $CpMo(CO)_2L_2$ reductants simply on the basis of the cationic product. However, as described previously, that differentiation could be made on the basis of other reactivity factors.

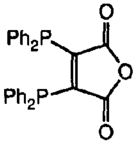
SYNTHESIS OF STABLE NINETEEN-ELECTRON COMPLEXES

Additional evidence for the 19-electron adducts

In addition to the early experiments discussed above, the results of other experiments now provide additional evidence for the existence of 19-electron complexes. In particular, the work of Kochi, Basolo and Trogler, and others provides strong evidence for the existence of these species (ref 15). Perhaps the strongest evidence is the isolation of adducts formed by the reaction of 17-electron radicals with ligands. An example is shown in the equation below (ref. 16 and 17):

$$\underset{}{Co_2(CO)_8} \rightleftharpoons \underset{17e^-}{2\ Co(CO)_4} \xrightarrow{L_2} \underset{19e^-}{Co(CO)_3L_2} + CO \qquad (46)$$

$L_2 =$



In discussing why this particular 19-electron complex is stable, it is important to point out that the stability of the 19-electron adducts depends critically on their electronic structure. At one extreme of the stability range are 19-electron species where the 19th electron is primarily metal-localized in a M-L antibonding orbital. Adducts such as this are believed to be involved in many of the associatively activated substitution reactions of

17-electron species (refs. 7 and 8). At the other extreme of stability are the relatively stable adducts, such as the $Co(CO)_3L_2$ (L_2= 2,3-bis(diphenylphosphino)maleic anhydride) species shown above, that are perhaps best described as 18-electron complexes with reduced ligands. (T.L. Brown coined the term $18+\delta$ complexes for these species.) The relative stability of the $18+\delta$ complexes is attributed to the fact that the extra electron is not in a metal-ligand antibonding orbital but rather in a ligand-based orbital (usually a π^* orbital). For example, ESR studies showed that the odd electron in the $Co(CO)_3L_2$ molecule is in an orbital that is primarily localized on the L_2 ligand (refs. 16 and 17). Because of their relative stability, most of the synthetic and reactivity studies of 19-electron adducts have focused on the $18+\delta$ type species. [It is important to emphasize that, although most of the work has been done with molecules of the $18+\delta$ type, other types of 19-electron complexes have now been spectroscopically detected and characterized (refs. 18-20).]

In molecular orbital terms the stability of the $18+\delta$ complexes is explained by the diagram in Fig. 1.

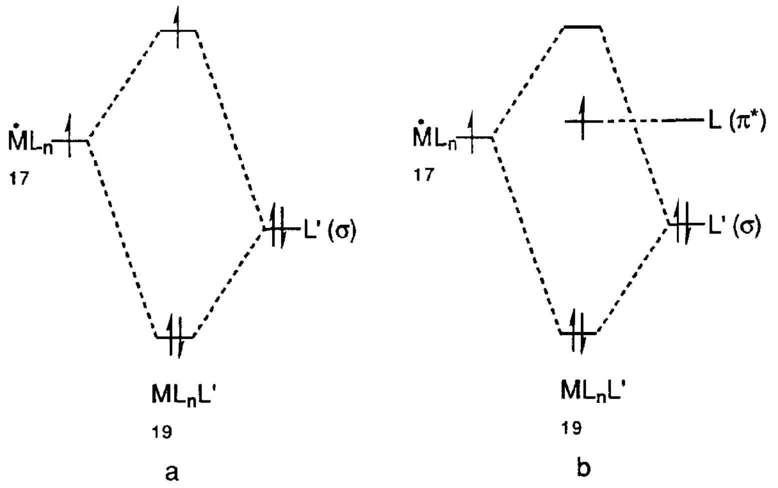


Fig. 1. (a) A simplified molecular orbital scheme for the interaction of a ligand with a 17-electron metal radical. (b) The molecular orbital scheme for the case in which the ligand also has a low energy π^* orbital.

The scheme in Fig. 1a shows the interaction of a 17-electron metal radical with a ligand to form a 19-electron complex. Note that the three electrons are distributed such that the bonding orbital is fully occupied and the metal-ligand antibonding orbital is occupied by a single electron. To a first approximation, half of a metal ligand bond is formed, and this bond formation is the driving force for the formation of the 19-electron complex (ref. 21). If the ligand (or any ligand) has a low energy π^* orbital, then the MO diagram for the 19-electron adduct is that shown in Fig. 1b. Note that the unpaired electron now occupies the π^* orbital; this is the predicted situation for an 18+δ complex. Because of Fenske's success in using the L_2 ligand to synthesize the $Co(CO)_3L_2$ complex, we decided to use the L_2 ligand to synthesize other stable 19-electron (18+δ) complexes. In the remainder of this paper I will focus on the synthesis of the $Cp'Mo(CO)_2(L_2\text{-}P,P')$ complex ($Cp' = \eta^5\text{-}C_5Ph_4H$) (refs. 22 and 23).

Synthesis of the $Cp'Mo(CO)_2L_2$ complex

The $Cp'Mo(CO)_2(L_2\text{-}P,P')$ complex was synthesized by irradiation of a THF solution of $Cp_2'Mo_2(CO)_6$ and L_2 (ref. 23):

$$Cp_2'Mo_2(CO)_6 + 2\ L_2 \xrightarrow{h\nu} 2\ Cp'Mo(CO)_2(L_2\text{-}P,P') + 2\ CO \qquad (47)$$

During the irradiation, the $Cp_2'Mo_2(CO)_6$ bands at 2007, 1950, 1924, and 1903 cm^{-1} disappeared and new product bands appeared at 1958 and 1886 cm^{-1}. The product from this reaction was stable enough to isolate, and the elemental analysis is consistent with the formulation $Cp'Mo(CO)_2(L_2\text{-}P,P')$. A crystal structure confirmed this assignment (see Fig. 2) (ref. 23).

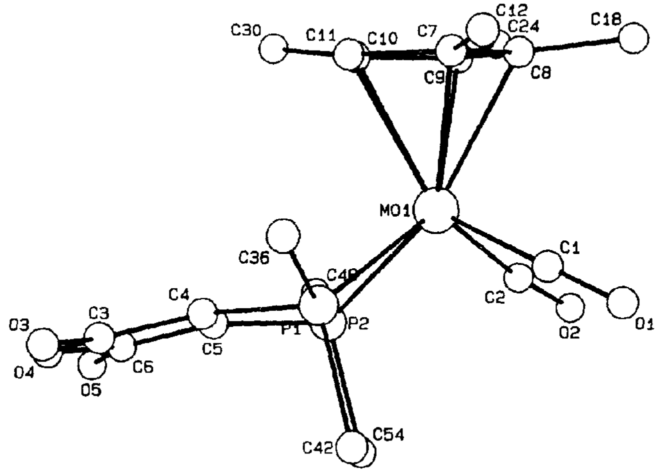


Fig. 2. Crystal structure of the 19-electron $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2L_2$ complex. The molecule has a four-legged piano stool structure. The phenyl rings on the C_5 ring and phosphorus atoms have been omitted for clarity.

The infrared spectrum of the complex (1958 and 1886 cm^{-1}) is similar to the spectra of related $CpMo(CO)_2(PR_3)_2^+$ complexes (Table 4). This result strongly suggests that the $CpMo(CO)_2(L_2\text{-}P,P')$ complex contains Mo in the +2 oxidation state and a reduced, radical anion L_2 ligand, i.e. the complex is an 18+δ complex.

TABLE 4

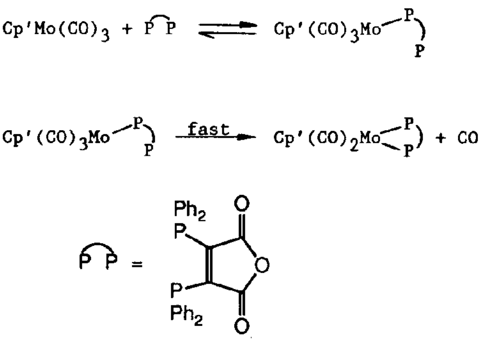
Infrared data for $CpMo(CO)_2L_2^{+/o}$ complexes.

Complex	$\nu(C{\equiv}O)$, cm^{-1}	Solvent	Reference
$Cp'Mo(CO)_2(L_2\text{-}P,P')^a$	1958 s, 1886 s	CH_2Cl_2	this work
$CpMo(CO)_2(PPh_3)_2^{+b}$	1978 s, 1901 vs		24, 25
$CpMo(CO)_2(PEt_3)_2^{+b}$	1961 s, 1883 s	CH_2Cl_2	26
$CpMo(CO)_2(dppe)^{+b}$	1980 s, 1915 s	CH_2Cl_2	26

[a]Cp' = $\eta^5\text{-}C_5Ph_4H$.
[b]Cp = $\eta^5\text{-}C_5H_5$.

The reaction of the $Cp_2'Mo_2(CO)_6$ dimer with L_2 to form $Cp'Mo(CO)_2(L_2\text{-}P,P')$ likely follows the pathway in Scheme VII.

$$Cp_2'Mo_2(CO)_6 \overset{h\nu}{\rightleftharpoons} 2\ Cp'Mo(CO)_3 \qquad (48)$$



$$Cp'Mo(CO)_3 + \widehat{P\ P} \rightleftharpoons Cp'(CO)_3Mo\text{—}\overset{P}{\underset{P}{\rangle}} \qquad (49)$$

$$Cp'(CO)_3Mo\text{—}\overset{P}{\underset{P}{\rangle}} \xrightarrow{fast} Cp'(CO)_2Mo\overset{P}{\underset{P}{\lessgtr}} + CO \qquad (50)$$

Scheme VII

Note that the reaction of $Cp'Mo(CO)_3(L_2\text{-}P)$ to give $Cp'Mo(CO)_2(L_2\text{-}P,P')$ (eq 50) should be facile. Substitution reactions of 19-electron complexes are known to follow dissociatively activated pathways (ref. 17), and the rates of such pathways increase as the steric bulk of the complex increases (ref. 27). Therefore, the conversion of Cp'Mo(CO)$_3$(L$_2$-P) to Cp'Mo(CO)$_2$(L$_2$-P,P') is facilitated by the steric bulk of the Cp' ligand. The rapidity of the ring closure reaction (eq 50) apparently accounts for the failure to observe spectroscopically the Cp'Mo(CO)$_3$(L$_2$-P) species at room temperature and also for the absence of a back-reaction to reform the Cp$_2$'Mo$_2$(CO)$_6$ dimer.

It was possible to observe spectroscopically the intermediate Cp'Mo(CO)$_3$(L$_2$-P) species by irradiating a CH$_2$Cl$_2$ solution of Cp$_2$'Mo$_2$(CO)$_6$ and L$_2$ at -20° C. The four-line ESR spectrum of the product, suggested to be Cp'Mo(CO)$_3$(L$_2$-P), is shown in Fig. 3a. This spectrum is slowly converted to that of the Cp'Mo(CO)$_2$(L$_2$-P,P') complex, even at -20° (Fig. 3b-e).

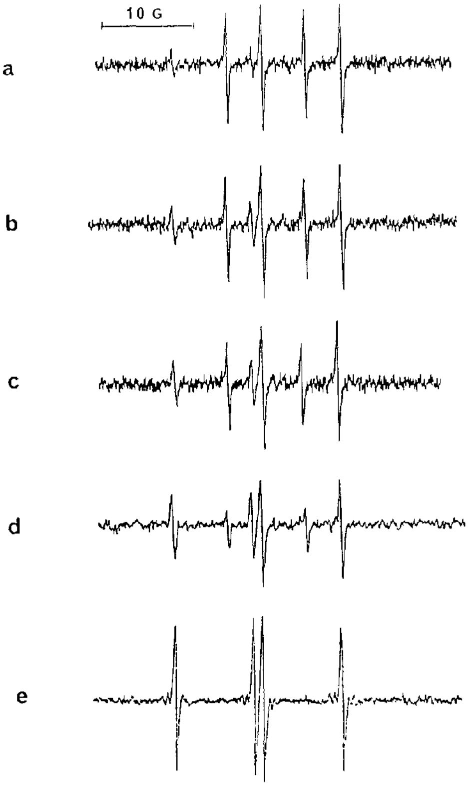


Fig. 3. ESR spectra following the irradiation (λ > 520 nm) of (η^5-C$_5$Ph$_4$H)$_2$-Mo$_2$(CO)$_6$ and L$_2$ in THF at -20 °C. The spectrum in (a) was taken immediately after irradiation. Spectra (b)-(e) follow at 10 min intervals.

The ESR spectrum of the $Cp'Mo(CO)_2(L_2\text{-}P,P')$ complex should be a 1:2:1 triplet if the two phosphorus atoms are equivalent. However, the room temperature ESR spectrum of $Cp'Mo(CO)_2(L_2\text{-}P,P')$ showed four major lines (Fig. 4a). [The small lines in the Figure are due to the coupling with ^{95}Mo ($I = 5/2$, 15.78%) and ^{97}Mo ($I = 5/2$, 9.60%).] When the temperature of the solution was increased, the two major signals in the middle of the spectrum merged, and eventually (at T = 185 °C) a three-line signal formed with an intensity ratio of 1:2:1 (Fig. 4f). The spectral changes are reversible, and the four-line spectrum reappeared when the temperature was lowered to room temperature.

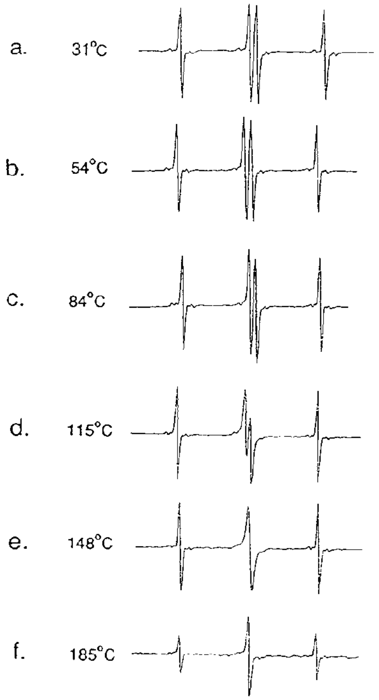


Fig. 4. ESR spectra of the 19-electron $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2L_2$ complex at various temperatures.

The four-line spectrum arises because the C_5Ph_4H ring is unsymmetrically substituted, and therefore the phosphorus atoms are magnetically inequivalent (see the structure in Fig. 2). Rotation of the ring will "exchange" the phosphorus atoms, and fast rotation of the ring will make the two phosphorus atoms magnetically equivalent. Therefore, we attribute the dynamic ESR spectrum to rotation of the C_5Ph_4H ring. By approximating the effect of the ring rotation as a "two-site exchange" case (ref. 22), we calculated the rate constants for the ring rotation. A plot of ln(k/T) vs 1/T yielded the following activation parameters: $\Delta H^{\ddagger} = 2.2 \pm 0.1$ kcal mol^{-1}, $\Delta S^{\ddagger} = -22.9 \pm 0.3$ cal K^{-1} mol^{-1}.

To confirm our assumption that ring rotation caused the dynamic ESR spectrum of the $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2(L_2\text{-}P,P')$ complex, we synthesized the 19-electron $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ complex. (Note the symmetrically substituted phenyl ring.) The ESR spectrum of this complex was a 1:2:1 triplet, consistent with a structure in which the two phosphorus atoms are magnetically equivalent because the ring is symmetrically substituted. Further details of the fluxional process can be found in ref. 22.

An interesting feature of the dynamic ESR spectra in Fig. 4 is that the ^{31}P coupling constant (8.92 G) at high temperature is not the average of the two coupling constants (9.01 and 9.94) at the low temperature limit. Ideally, the high-temperature coupling constant should be the average. We attribute the non-ideal behavior observed with this molecule to a decrease in the electron withdrawing ability of the $\eta^5\text{-}C_5Ph_4H$ ligand as the temperature is increased. We suggest that, as the temperature is increased, the electron withdrawing ability decreases because rapid dynamic rotation of the phenyl rings destroys the extensive conjugation in the ligand. The decreased electron-withdrawing ability of the $\eta^5\text{-}C_5Ph_4H$ ligand will polarize the odd electron toward the oxygen atoms of the L_2 ligand. Consequently, there will be less unpaired electron spin density on the two phosphorus atoms at higher temperatures and the ^{31}P coupling constants will be smaller than at lower temperatures. In support of this proposal, we note that our previous study of the 19-electron $Co(CO)_3L_2$ complex and its CO-substituted derivatives showed that the phosphorus coupling constants decreased as the electron-donating ability of the substituting ligands increased (e.g. $Co(CO)_3L_2$, $a_P = 9.72$; $Co(CO)_2L_2(PPh_3)$, $a_P = 8.22$) (ref. 17). In addition, NMR spectroscopic results on diamagnetic complexes containing the $\eta^5\text{-}C_5Ph_4H$ ligand are consistent with the proposal that phenyl ring rotation increases with increasing temperature. Thus, Castellani and Trogler (ref. 28) showed that the proton signal in the $\eta^5\text{-}C_5Ph_4H$ ligand shifted upfield as the temperature increased. The upfield shift was attributed to rapid phenyl ring rotation; the rotation caused the loss of deshielding from the ring currents of adjacent coplanar phenyl rings.

Concluding remarks: speculation on the electronic spectra of the 19-electron complexes

The electronic spectrum of the $Co(CO)_3L_2$ complex in CH_2Cl_2 is shown in Fig. 5.

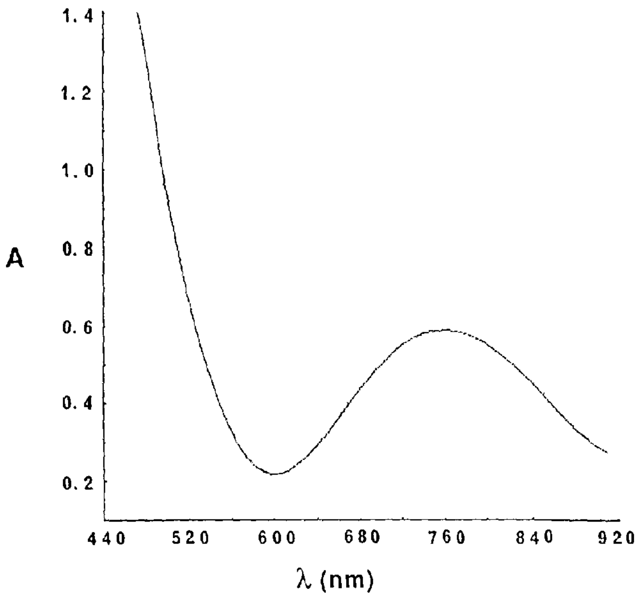


Fig. 5. Electronic absorption spectrum of the $Co(CO)_3L_2$ complex (2.0×10^{-3} M) in CH_2Cl_2.

The spectrum shows a weak, broad, low energy band that is typical of the electronic spectra of the 18+δ complexes containing the L_2 ligand. ($CpMo(CO)_2$-(L_2-P,P') exhibits a similar band at 665 nm (ϵ = 270).) According to the MO scheme in Fig. 1, the lowest energy band in 18+δ complexes is a $\pi^*(L_2) \rightarrow \sigma^*$(Mo-P) transition. However, the MO scheme in Fig. 1 may be a simplification in that if the $\sigma*$ molecular orbital is high in energy then CO π^* orbitals may lie to lower energy, as shown in Fig. 6. If this is the case then the lowest energy transition would be an *interligand* charge-transfer transition (ref. 29).

Distinguishing between the transitions is not straightforward. An Xα calculation (ref. 30) on the $Co(CO)_3L_2$ complex showed that the σ^* and CO π^* orbitals had nearly the same energies, and it could not therefore distinguish between the two possibilities. The band is solvatochromic (Fig. 7), but both the $\pi^* \rightarrow \sigma^*$ and ILCT transitions should exhibit this behavior. ILCT bands are generally weak (ref. 29), and the small extinction coefficient is consistent with this assignment.

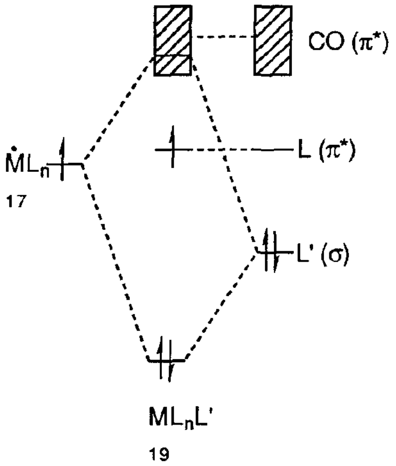


Fig. 6. Molecular orbital scheme for the interaction of a 17-electron metal radical with a ligand showing how a lowest energy $L_2(\pi^*) \rightarrow CO(\pi^*)$ transition could arise.

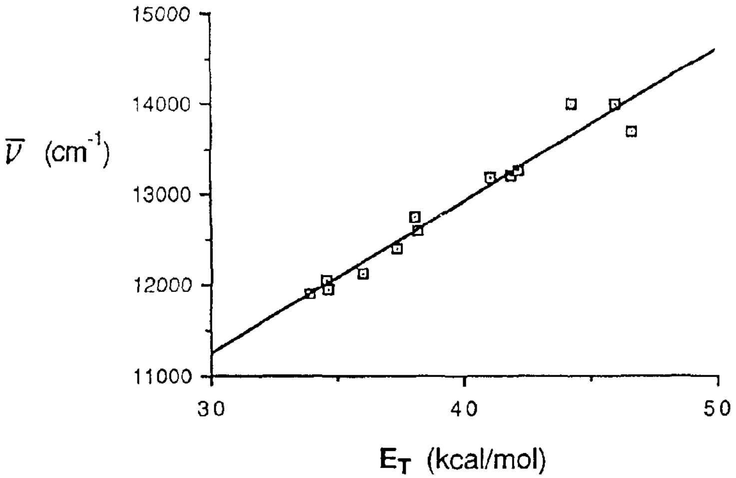


Fig. 7. Plot of $\bar{\nu}$(max) vs. the Reichardt E_T solvent parameter for the lowest energy band in the $Co(CO)_3L_2$ complex.

Work is continuing in our lab on the identification of the low energy bands in these and other 18+δ complexes.

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