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Seventeen-Electron Metal-Centered Radicals

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Contents

I. Introduction

Although organotransition metal chemistry has long been dominated by compounds containing closed-shell electron configurations and obeying the 18-electron rule,[1] there has appeared increasing evidence in recent years for the existence of simple 17-electron organotransition metal compounds. While relatively few such species were mentioned in a review of paramagnetic organometallics published in 1976,[2] the situation has now changed drastically and it is well recognized that both electron-transfer reactions of mononuclear carbonyl complexes[3] (eq 1) and photoinduced homolysis of dimeric compounds containing metal–metal bonds[4] (eq 2) can result in the formation of the corresponding 17-electron monomeric compounds.

$$ML_n \rightarrow \{ML_n^{\bullet +}\} + e^- \qquad (1)$$

$$ML_n = \text{18-electron compound}$$

$$L_nM\text{–}ML_n \xrightarrow{h\nu} 2\{ML_n^{\bullet}\} \qquad (2)$$

$$L = \text{CO, tertiary phosphine, } \eta^5\text{-}C_5H_5\text{, etc.}$$

Presented below is an overview of publications dealing with the physical and chemical characterization of the more extensively studied classes of metal carbonyl 17-electron compounds. This overview will discuss the major groups of known compounds, their structures, and their more important chemistry, although discussion of paramagnetic sandwich complexes will be omitted as the electronic structures and relevant chemistry of this class of compounds have been amply dealt with elsewhere.[5]

Michael Baird was born in Hamilton, Canada, in 1940; he obtained an Hon. B.Sc. from McMaster University in 1962 and a Ph.D. from the University of Toronto in 1965 (with the late A. D. Allen). His interests in organometallic chemistry were largely stimulated during 18 months of postdoctoral research with Geoffrey Wilkinson at Imperial College, London, during which time he had the good fortune to synthesize the first transition-metal thiocarbonyl and carbon disulfide complexes. Baird joined the faculty of Queen's University, Kingston, in 1967, where he is currently Professor of Chemistry. He was Humboldt Fellow at the Technical University, Munich, in 1975, and won the Alcan Lecture Award of the Chemical Institute of Canada in 1986. His research interests have to do primarily with organotransition metal chemistry and catalysis, although he likes on occasion to dabble in other fields.

In order to clearly distinguish in the text 17-electron species from closed-shell compounds of similar structures, the chemical formulas of the former will henceforth be enclosed in brace brackets, as in eq 1 and 2.

II. Carbonyl and Substituted Carbonyl Complexes

A. Hexacoordinated Species

1. Complexes of Vanadium, Niobium, and Tantalum

Vanadium hexacarbonyl, $\{V(CO)_6\}$, is unique among the simple binary metal carbonyls in that it is a readily isolable, 17-electron compound that is thermally stable with respect to dimerization.[6] If the structure of $\{V(CO)_6\}$ were rigorously octahedral (O_h symmetry), the compound would have a $(t_{2g})^5$ electron configuration and a $^2T_{2g}$ electronic ground state. It should therefore be subject to a Jahn–Teller distortion, and considerable

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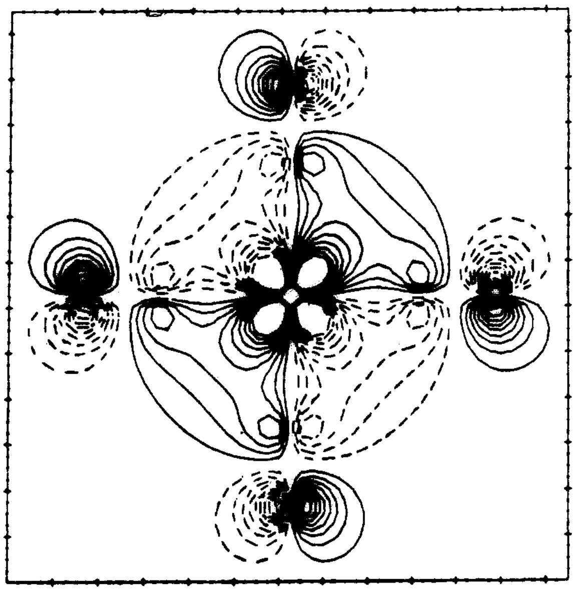


Figure 1. Contour plot of the singly occupied molecular orbital ($2t_{2g}$) of {V(CO)$_6$} in a V(CO)$_4$ plane.[9] (Reprinted from ref 9; copyright 1983 American Chemical Society.)

effort has been expended to detect evidence for such a distortion. Magnetic measurements in the temperature range 4.2–300 K,[7a] comparisons of the gas-phase IR spectrum with that of Cr(CO)$_6$,[7b] MCD spectroscopy of the compound in inert gas matrices at 5 K,[7c] and electron diffraction[7d] and X-ray crystallographic[7e] studies have, taken together, been interpreted in terms of a dynamic Jahn–Teller perturbation of the $^2T_{2g}$ state at moderate temperatures and a very small, static distortion at low temperatures. The exact nature of the distortion appears yet to remain ambiguous although low-temperatue ESR studies of {V(CO)$_6$},[8a,b] complemented by similar studies of derivatives,[8c,d] have been interpreted in terms of a nonaxial distortion, possible to D_{2h} symmetry,[8b] for the hexacarbonyl.

It would seem that the stability of {V(CO)$_6$} with respect to dimerization is to be attributed to very extensive π delocalization of the odd electron onto the ligands.[8b,9] Analyses of the hyperfine structure of the ESR spectra,[8b] complemented by SCF–Xα–DV calculations,[9] suggest that {V(CO)$_6$} is a π radical, as shown in a contour plot of the singly occupied molecular orbital (SOMO) (Figure 1). In contrast to the situation with other simple 17-electron species (see below), the unpaired spin of {V(CO)$_6$} has little directional character and the reorganization energy required for the compound to rearrange in order to interact with one-electron ligands must therefore be prohibitively high. Thus {V(CO)$_6$} does not dimerize, although [V(CO)$_6$]$_2$, with bridging carbonyls, may have been formed on cocondensation of vanadium atoms and carbon monoxide at low temperatures.[10]

Consistent with the above, compounds of the type V(CO)$_6$X (X = one-electron donor) are not known,[6] although many seven-coordinated phosphine-substituted derivatives of the type V(CO)$_{6-n}$L$_n$X (n = 1–6; X = H, alkyl, other metals, etc.) have been reported.[6] While it is not clear why the sterically more demanding tertiary phosphines would stabilize the higher coordination number, an ESR study of fac-V(CO)$_3$(PMe$_3$)$_3$[8d] has shown that the SOMO of this molecule has σ rather than π character. Thus the SOMO of substituted compounds may generally be hybridized in a manner more appropriate for σ bonding.

TABLE I. IR Data for Selected Mono- and Disubstituted Compounds of Vanadium(0)[12a]

compd	ν_{CO}, cm^{-1} (toluene)
{V(CO)$_5$PMe$_3$}	2040, 1922
{V(CO)$_5$P(n-Bu)$_3$}	2042, 1922
{V(CO)$_5$PMePh$_2$}	2041, 1930
{V(CO)$_5$P(OMe)$_3$}	2054, 1930
{V(CO)$_5$PPh$_3$}	2050, 1930
{V(CO)$_5$P(i-Pr)$_3$}	2040, 1920
{V(CO)$_5$AsPh$_3$}	2051, 1934
$trans$-{V(CO)$_4$(PBu$_3$)$_2$}	1981, 1860
cis-{V(CO)$_4$(PMePh$_2$)$_2$}	1990, 1895, 1867, 1845
cis-{V(CO)$_4$(P(OMe)$_3$)$_2$}	2007, 1905, 1885, 1865
$trans$-{V(CO)$_4$(PPh$_3$)$_2$}	1990, 1892, 1860

TABLE II. Second-Order Rate Constants and Activation Parameters for Selected Substitution and Disproportionation Reactions of {V(CO)$_6$} with Ligands L[11]

L	k, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}
	Substitution		
PMe$_3$	132	7.6 ± 0.7	−23.4 ± 3.4
PBu$_3$	50.2	7.6 ± 0.4	−25.2 ± 1.7
PMePh$_2$	3.99	8.9 ± 0.3	−25.9 ± 1.1
P(OMe)$_3$	0.70	10.9 ± 0.2	−22.6 ± 0.8
PPh$_3$	0.25	10.0 ± 0.4	−27.8 ● 1.6
	Disproportionation		
pyridine	1.22		
NEt$_3$	0.77		
MeCN	0.28		
acetone	1.93×10^{-2}		
THF	4.35×10^{-3}	14.2 ± 1.2	−21.5 ± 4.2
Et$_2$O	9.63×10^{-5}		

In striking contrast to the analogous chemistry of the closed-shell, 18-electron compound Cr(CO)$_6$, carbon monoxide substitution reactions of {V(CO)$_6$} and its derivatives apparently proceed via associative pathways and are significantly more rapid (by several orders of magnitude) than are the corresponding reactions of Cr(CO)$_6$.[11] The reactions give either the products of mono- and disubstitution (with soft bases such as tertiary phosphines, L) (eq 3)[11a] or the products of disproportionation (hard bases, with oxygen or nitrogen donor atoms, B) (eq 4).[11b] IR data for a number of substituted derivatives are presented in Table I.

$$\{V(CO)_6\} + L \rightarrow \{V(CO)_5L\} + CO \xrightarrow{+L'} \{V(CO)_4LL'\} + CO \quad (3)$$

$$2\{V(CO)_6\} + 6B \rightarrow [VB_6][V(CO)_6]_2 + 6CO \quad (4)$$

Both substitution and disproportionation reactions proceed solely via second-order processes according to rate laws that are first order in both {V(CO)$_6$} and incoming ligand. The rates are unchanged under an atmosphere of carbon monoxide but are highly dependent on both the basicity and the size of the ligand. Also consistent with the postulate of associative pathways is the observation of negative entropies of activation[11] (Table II).

It would seem that reactions are facilitated by two-center, three-electron interactions between the ligand lone pairs and the electron "hole" in the SOMO, possibly via a 19-electron intermediate.[12] The essentials of the interaction are shown in a general fashion in the molecular orbital diagram of Figure 2.[12a] Here the SOMO of a 17-electron compound overlaps with the

TABLE III. IR and ESR Data for Selected Chromium(I) Complexes and Their 18-Electron Analogues

complexes	ν_{CO}, cm^{-1}	g_{av}	ref
$\{Cr(CO)_6^+\}$		1.982, A_{Cr} = 21.6 G	14c
$\{$*trans*-$Cr(CO)_4(PPh_3)_2^+\}$	1990	2.027, A_p = 18 G	15c
trans-$Cr(CO)_4(PPh_3)_2$	1880		
$\{$*cis*-$Cr(CO)_4(dppm)^+\}$	2084, 2033, 1969	2.009, A_p = 6.9 G	15a,g[a]
cis-$Cr(CO)_4(dppm)$	2006, 1915, 1897, 1875		
$\{$*mer*-$Cr(CO)_3(P(OMe_3))_3^+\}$	2051, 1988, 1935	2.002, A_p = 40 G (av)	15d
mer-$Cr(CO)_3(P(OMe_3))_3$	1981, 1900, 1878		
$\{$*mer*-$Cr(CO)_3(PMe_2Ph)_3^+\}$	2010, 1940, 1904	2.019, A_p = 20 G (t), 36 G (d)[a]	15d
$\{Cr(CO)_3(dmpe)(L^{Et})^+\}$	2010, 1930, 1890	2.019, A_p = 22.3 G	15f[a]
$Cr(CO)_3(dmpe)(L^{Et})$	1901, 1806		

[a] dppm = $Ph_2PCH_2PPh_2$, L^{Et} = carbenoid ligand, dmpe = $Me_2PCH_2CH_2PMe_2$, d = doublet, t = triplet.

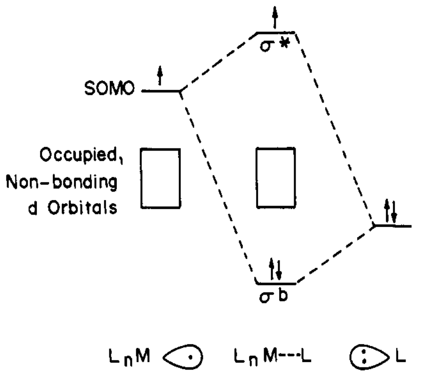


Figure 2. Qualitative molecular orbital scheme illustrating the nature of the interactions between the singly occupied molecular orbital of a 17-electron species $\{ML_n\}$ and a two-electron donor L.

lone pair of the incoming nucleophile L, the net effect being stabilizing because of the concomitant formation of a *filled* σ orbital of lower energy and a *half-filled* σ* orbital of higher energy. As the latter orbital is of metal–ligand σ* character, a carbonyl ligand is thus normally labilized and is readily lost. This type of associative process is not generally available to 18-electron compounds because the net effect of the type of interaction illustrated in Figure 2 would be destabilizing. Recent SCF-Xα-DV calculations suggest that attack by a nucleophile on $\{V(CO)_6\}$ would occur preferentially at an octahedral face rather than at an edge.[12c]

The neutral hexacarbonyls of tantalum and niobium have not been unambiguously characterized, although $Ta(CO)_6$ may have been formed via cocondensation of tantalum atoms in a carbon monoxide matrix at low temperatures.[13]

2. Complexes of Chromium, Molybdenum, and Tungsten

The closed-shell compound $Cr(CO)_6$ undergoes electrochemical oxidation to yield $\{Cr(CO)_6^+\}$, isoelectronic with $\{V(CO)_6\}$.[14] This cation is stable on a time scale of seconds, in contrast to the analogous complexes of molybdenum and tungsten,[14a,b] but does not as yet appear to be well characterized. Published ESR spectral data[14a,c] differ sufficiently that they may well be attributable to different species. While neither appears to implicate the type of orbital degeneracy noted above for $\{V(CO)_6\}$, it has been noted that the *g* value reported in ref 14c is much more similar to the *g* values of other octahedral chromium(I) complexes (Table III). Interestingly, observation of vibrational fine structure on photoionization bands of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ has resulted in the reasonable conclusion that the metal–carbon bond lengths of the corresponding 17-electron cations are about 0.1 Å longer than in the neutral, electronically saturated molecules.[14e]

Substituted 17-electron complexes of the types $\{M(CO)_{6-n}L_n^+\}$, $\{M(CO)_4(L\text{-}L)^+\}$, and $\{M(CO)_2(L\text{-}L)_2^+\}$ (M = Cr, Mo, W; n = 1–3; L = monodentate tertiary phosphine; L–L = bidentate tertiary phosphine) have long been known and are much more stable thermally than are the corresponding hexacarbonyl cations.[15] Many of the ions are sufficiently stable, in fact, that IR and ESR spectra can be readily obtained, and cases of geometrical isomerism have been identified on the basis of carbonyl stretching modes and/or hyperfine coupling to phosphorus (Table III). As can be seen, the *g* values are normally significantly larger than the free electron value, while the ν_{CO} of the 17-electron complexes are generally about 100 cm^{-1} higher than are the ν_{CO} of the corresponding 18-electron compounds.

As with the isoelectronic vanadium(0) complexes, the 17-electron complexes of chromium, molybdenum, and tungsten are much more labile with respect to ligand substitution and isomerization reactions than are the parent 18-electron compounds. Thus it has been shown that *cis*–*trans* or *fac*–*mer* isomerization reactions are far more facile than are the same processes for the electronically saturated analogues. In agreement with theory,[16] the *trans* and *mer* isomers are generally more stable and, as electron transfer between 17- and 18-electron analogues is often facile, *cis* → *trans* and *fac* → *mer* isomerization of 18-electron compounds can be catalyzed by traces of the 17-electron complex (or of an appropriate oxidant).

The 17-electron cationic complexes have been shown both to behave as oxidizing agents and to undergo disproportionation, reactions that are exemplified in eq 5 and 6 for $\{$*trans*-$Cr(CO)_4(PPh_3)_2^+\}$.[15c]

$$2\{trans\text{-}Cr(CO)_4(PPh_3)_2^+\} + 2X^- \rightarrow 2trans\text{-}Cr(CO)_4(PPh_3)_2 + X_2 \quad (5)$$

$$X = Br, I$$

$$2\{trans\text{-}Cr(CO)_4(PPh_3)_2^+\} \rightarrow trans\text{-}Cr(CO)_4(PPh_3)_2 + Cr(II) + 2PPh_3 + 4CO \quad (6)$$

B. Pentacoordinated Species

1. Complexes of Manganese and Rhenium

The earlier literature on the binary carbonyls of manganese and rhenium has been reviewed.[17] The simplest stable species are of the stoichiometry $M_2(CO)_{10}$, with metal–metal bonds joining two essentially square-pyramidal $M(CO)_5$ units as shown in Figure 3

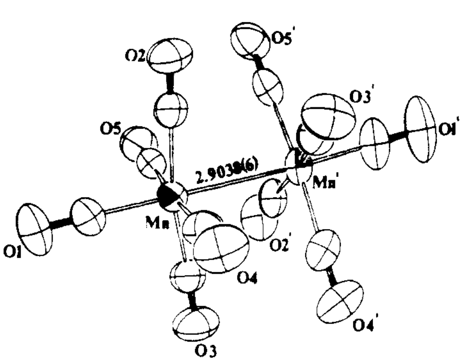
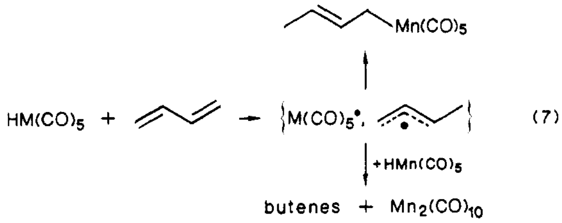


Figure 3. Molecular structure of $Mn_2(CO)_{10}$.[18] (Reprinted from ref 18; copyright 1981 American Chemical Society.)

for $Mn_2(CO)_{10}$.[18] While it is clear that equilibrium concentrations of the monomeric species $\{M(CO)_5\}$ in solutions at room temperatures are very low,[17] $\{Mn(CO)_5\}$ and substituted derivatives, formed via thermal homolysis of the metal–metal bonds, have been implicated in substitution reactions of the corresponding dimers.[19a–c] Similarly, $\{Mn(CO)_5\}$ appears as one component of a radical pair intermediate during olefin hydrogenation and insertion reactions of the hydride, $HMn(CO)_5$.[19d] The latter reactions proceed as in eq 7.



(7)

However, it has long been known that photolysis of the dimers at appropriate wavelengths can lead to homolytic dissociation and generation of the corresponding 17-electron monomeric species $\{M(CO)_5\}$, apparently via population of the metal–metal σ^* orbital (eq 8).[20,21] Substituted analogues can be made in the same way[20b,21a,22] (eq 9), and both the substituted and the unsubstituted compounds can also be prepared via electron-transfer processes (as in eq 10–12).[21c,23,24]

$$M_2(CO)_{10} \xrightarrow{h\nu} 2\{M(CO)_5\} \quad (8)$$

$$M_2(CO)_8L_2 \xrightarrow{h\nu} 2\{M(CO)_4L\} \quad (9)$$

$$M_2(CO)_{10} + e^- \rightarrow \{M(CO)_5\} + [M(CO)_5]^- \quad (10)$$

$$[M(CO)_5]^- \rightarrow \{M(CO)_5\} + e^- \quad (11)$$

$$[M(CO)_6]^+ + e^- \rightarrow \{M(CO)_5\} + CO \quad (12)$$

There is evidence for short-lived 19-electron intermediates in reactions similar to (12), which apparently involves initial electron addition followed by ligand loss.[24a,b]

The compound $\{Mn(CO)_5\}$ has been characterized by IR,[21e,25a] ESR,[25b,c] and electronic spectroscopy.[20a,21d,e] It appears to assume an essentially square-pyramidal (C_{4v}) structure, and ν_{CO} have been reported at 1987.6 cm^{-1} (e) and 1978.4 cm^{-1} (a_1) (CO matrix at 10–20 K).[25a] On the basis of the IR intensity data, an axial–equatorial bond angle of 96 ± 3° has been calculated.[25a] The ESR spectra have been obtained at low temperatures and in inert matrices, and are axial, with $g_{\parallel} = 2.00$ and $g_{\perp} = 2.04$, and manganese hyperfine splitting constants $A_{\parallel} = 65$ G and $A_{\perp} = -33.5$ G.[25c] The odd electron is largely localized on the C_4 axis in an orbital of a_1 symmetry ($3d_{z^2}$), as predicted by theory[26] (Figure 4).

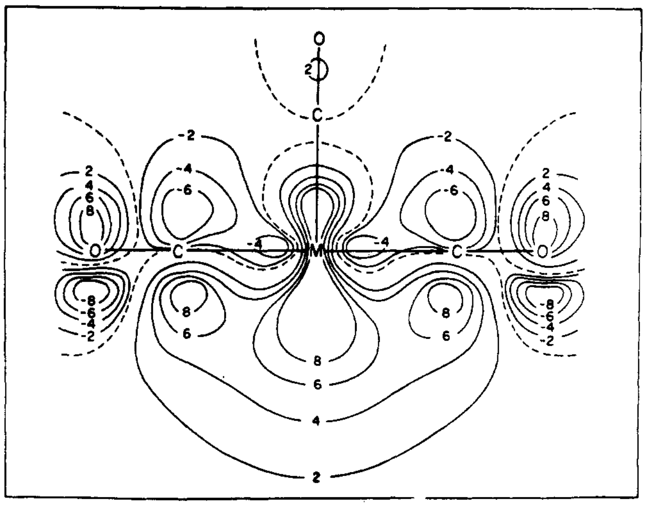


Figure 4. Contour plot of the singly occupied molecular orbital (a_1) of square-pyramidal $\{M(CO)_5\}$.[26] (Reprinted from ref 26; copyright 1975 American Chemical Society.)

TABLE IV. Second-Order Rate Constants k_2 for Dimerization Reactions of Selected 17-Electron Compounds $\{M(CO)_4L\}$[20]

compd	k_2, M^{-1} s^{-1}	cone angle of L, deg
$\{Mn(CO)_5\}$	9×10^8	95
$\{Mn(CO)_4P(n\text{-}Bu)_3\}$	1×10^8	132
$\{Mn(CO)_4P(i\text{-}Bu)_3\}$	2×10^7	143
$\{Mn(CO)_4P(i\text{-}Pr)_3\}$	4×10^6	160
$\{Mn(CO)_4P(OPh)_3\}$	9×10^7	128
$\{Mn(CO)_4PPh_3\}$	1×10^7	145
$\{Re(CO)_5\}$	4×10^9	95

The rhenium analogue $\{Re(CO)_5\}$ has also been similarly characterized,[21c,f,g] as have substituted manganese and rhenium compounds.[22a–d] All are believed to have structures similar to $\{Mn(CO)_5\}$ and thus, in contrast to $\{V(CO)_6\}$ (see above), the SOMO in these compounds is oriented appropriately for attack by a σ radical. Furthermore, and again in contrast to the situation with $\{V(CO)_6\}$, little reorganization of the ligands would be required during coupling to either a radical or to another $\{M(CO)_5\}$ species to form the coupled products (Figure 3).

Indeed, combination reactions of two molecules of $\{Mn(CO)_5\}$, of $\{Re(CO)_5\}$, or of their phosphine-substituted derivatives at room temperature to form the corresponding 18-electron dimers (reverse of eq 8 and 9) proceed via second-order processes at rates approaching the diffusion limit[20,21b–h,22d,23a] (Table IV). The apparent correlation of second-order rate constants for dimerization with cone angles of L suggests that steric effects are more important than electronic effects in controlling the dimerization reactions.[20b]

Similar chemistry apparently pertains in "ion-pair annihilation" reactions of manganese(I) cations with manganate(-I) anions, which are believed to proceed via initial electron transfer followed by coupling of the ensuing 17-electron species (eq 13).[27]

$$[Mn(CO)_6]^+ + [Mn(CO)_5]^- \xrightarrow{-CO} 2\{Mn(CO)_5\} \rightarrow Mn_2(CO)_{10} \quad (13)$$

This proclivity toward dimerization stands in direct contrast with the behavior of $\{V(CO)_6\}$, consistent with the very significant differences in the nature of the SOMOs of the two compounds (see above and Figures 1 and 2), and suggests that the 17-electron manganese and rhenium compounds are best considered to be metal-centered radicals. As can be seen in Table IV, dimerization is faster for $\{Re(CO)_5\}$ than for the smaller $\{Mn(CO)_5\}$[21b] and is less facile for compounds in which carbon monoxide has been substituted by tertiary phosphines, especially sterically demanding phosphines.[22a,b,d,28]

The very appropriate analogy with radical chemistry is also underlined by the proclivity of the manganese and rhenium 17-electron species toward reactions typical of organic radicals. Thus spin trapping by nitroso compounds has been observed, yielding metal-substituted nitroxide radicals, which have been characterized by their ESR spectra (eq 14).[29] A variety of α,β-diketones have also been found to react with the manganese- and rhenium-centered radicals to form paramagnetic compounds of the type $\{M(CO)_4(\text{diketone})\}$.[29e] On the basis of ESR data, however, it has been suggested that these compounds are best regarded as being 18-electron complexes with a radical anion ligand.[29e] Similar conclusions have been reached concerning analogous compounds containing α,β-diimines.[29f]

$$\{M(CO)_4L\} + RN{=}O \rightarrow R\dot{N}(O)M(CO)_4L \quad (14)$$

$$R = \text{alkyl, aryl}$$

The metal-centered radicals also participate in a variety of atom abstraction reactions, for instance of halogen atoms from alkyl halides (eq 15) and of the hydride hydrogen atom from compounds such as Bu_3SnH (eq 16).[20b,21a,c,22b,c,e,23a,24c,28c,30]

$$\{M(CO)_4L\} + RX \rightarrow XM(CO)_4L + R^\bullet \quad (15)$$

$$\{M(CO)_4L\} + R_3SnH \rightarrow HM(CO)_4L + R_3Sn^\bullet \quad (16)$$

It has been found that atom abstraction reactions are generally bimolecular[20b,22b,e,24c,30c–g] and are more facile for compounds of rhenium than of the smaller manganese.[22c] For substituted radicals, rates are enhanced by increased electron donation by the phosphine but are retarded by increased steric requirements of the phosphine.[20b,22b,c,30c,d] Rates of halogen atom abstraction increase as the C–X bond dissociation energies decrease for some systems,[30c,f,h] but not for others, where there appears to be a correlation with the reduction potentials of the alkyl halides.[22e] It has been suggested that reactions such as that depicted in eq 15 may proceed either via direct atom transfer, as in eq 17, or via electron transfer, as in eq 18.[22e] The mechanism of eq 17 would correspond essentially to a classical inner-sphere process, and that of eq 18 to a classical outer-sphere process. The former probably applies also to hydrogen abstraction reactions (eq 16) and presumably involves a stabilizing, two-center, three-electron interaction between electrons on the atom being abstracted and the SOMO of the metal-centered radical,[12] of the type noted above for substitutions of $\{V(CO)_6\}$.

$$\{M(CO)_4L\} + RX \rightarrow [R\text{---}X\text{---}M(CO)_4L] \rightarrow R^\bullet + XM(CO)_4L \quad (17)$$

$$\{M(CO)_4L\} + RX \rightarrow [RX^- + M(CO)_4L^+] \rightarrow R^\bullet + XM(CO)_4L \quad (18)$$

TABLE V. IR and ESR Data for Selected Complexes $\{$*trans*-$Fe(CO)_3L_2^+\}$ and Their 18-Electron Analogues[32a,d,h]

L	ν_{CO}, cm^{-1}	g_{av} (A_P, G)
$\{Fe(CO)_5^+\}$		2.054
$\{Fe(CO)_3(PMe_3)_2^+\}$	1990	2.056 (18.2)
$Fe(CO)_3(PMe_3)_2$	1863	
$\{Fe(CO)_3(PBu_3)_2^+\}$	1980	2.057 (18.5)
$Fe(CO)_3(PBu_3)_2$	1955	
$\{Fe(CO)_3(PMePh_2)_2^+\}$	1993	2.052 (18.8)
$Fe(CO)_3(PMePh_2)_2$	1878	
$\{Fe(CO)_3(PPh_3)_2^+\}$	1999	2.053 (18.7)
$Fe(CO)_3(PPh_3)_2$	1878	
$\{Fe(CO)_3(P(OPh)_3)_2^+\}$	2029	2.053 (25.0)
$Fe(CO)_3(P(OPh)_3)_2$	1923	
$\{Fe(CO)_3(AsPh_3)_2^+\}$	1992	2.054
$Fe(CO)_3(AsPh_3)_2$	1876	

The fate of the alkyl group radical in eq 15 has been determined in only a very few cases, as normally the steady-state concentrations of the photochemically generated metal radicals are small, and thus coupling of the metal and the organic radicals has very low probability. However, the formation of bibenzyl and the triphenylmethyl radical when $Mn_2(CO)_{10}$ is photolyzed in the presence of benzyl chloride and trityl chloride, respectively, has been reported,[21a] as has the apparent formation of $Mn(CO)_3(Et_2PCH_2CH_2PEt_2)(n\text{-}Pr)$ from the reaction of the partially dissociated $[Mn(CO)_3(Et_2PCH_2CH_2PEt_2)]_2$ with n-PrBr.[28c]

Interestingly, the pentacoordinated radicals of manganese and rhenium are much more labile with respect to ligand substitution reactions than are the analogous pentacoordinated, closed-shell compounds of iron. The radical substitution reactions are also associative rather than dissociative in nature,[19,21d,28a,b,30b] as has been noted above for $\{V(CO)_6\}$, and presumably involve the same type of two-center, three-electron interaction postulated for substitution reactions of that compound. Photochemical disproportionation reactions of $Mn_2(CO)_{10}$ with amines also appear to involve facile substitution of CO in the radical species.[31]

2. *Complexes of Iron and Osmium*

The species $\{M(CO)_5^+\}$ (M = Fe, Os) have been prepared by γ irradiation of the corresponding neutral species in various matrices at low temperatures[32a–c] and appear from their ESR parameters to have C_{4v} symmetry, similar to the isoelectronic $\{Mn(CO)_5\}$ (see above). Substituted complexes of the types $\{Fe(CO)_{5-n}L_n^+\}$ (n = 1, 2; L = CO, tertiary phosphines) have also been synthesized by controlled oxidation of the parent 18-electron compounds.[32d–h] Although reactive in ways not yet fully elucidated, several of the iron-centered radicals are sufficiently stable that IR and ESR spectra have been obtained (Table V). Unlike $\{Fe(CO)_5^+\}$ and the isoelectronic manganese analogues, compounds of the type $\{Fe(CO)_3L_2^+\}$ appear to assume trigonal-bipyramidal (D_{3h}) structures.

Few studies have yet been reported of the chemistry of the cationic 17-electron compounds, but one carbonyl group of complexes of the type $\{Fe(CO)_3L_2^+\}$ is readily substituted by pyridine via an associative process that is far more rapid than the analogous reactions of the neutral $Fe(CO)_3L_2$. Subsequent steps then involve disproportionation to complexes of iron(II) and iron(0).[32g]

3. Complexes of Chromium, Molybdenum, and Tungsten

Cocondensation of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ with alkali-metal atoms in inert gas matrices results in the formation of the species $\{M(CO)_5^-\}$ (M = Cr, Mo, W). Careful analysis of the IR spectrum of the chromium analogue, obtained with $^{13}C^{16}O/^{12}C^{16}O$ mixtures, resulted in the conclusion that the radical has a square-pyramidal (C_{4v}) structure,[33] similar to the structures of the isoelectronic $\{Mn(CO)_5\}$ and $\{Fe(CO)_5^+\}$ but in contrast to the trigonal-bipyramidal structures of the isoelectronic iron complexes $\{Fe(CO)_3L_2^+\}$.

C. Tetra- and Tricoordinated Species

1. Complexes of Cobalt

Although the simplest stable binary carbonyl of cobalt is $Co_2(CO)_8$,[34] monomeric $\{Co(CO)_4\}$ has been formed in a variety of matrices at low temperature and has been characterized by IR and ESR spectroscopy.[35] In a CO matrix at 6–15 K, the ESR spectrum is typical of a molecule with axial symmetry, with $g_\parallel = 2.007$, $g_\perp = 2.128$, $A_\parallel(Co) = 58 \times 10^{-4}$ cm^{-1}, and $A_\perp(Co) = 55 \times 10^{-4}$ cm^{-1}. Interestingly, with ^{13}CO-labeled compound, a large hyperfine coupling to only one carbonyl group is observed, suggesting C_{3v} symmetry. The IR spectrum is consistent with this conclusion, as three ν_{CO} are observed at 2010.7 (e), 2028.8 (a_1), and 2107.0 (a_1) cm^{-1}. The analogous tetracarbonyls of rhodium and iridium have been studied by IR spectroscopy and probably also have C_{3v} symmetry.[35c]

As with other metal–metal-bonded systems, photolysis of $Co_2(CO)_8$ and its substituted derivatives yields the metal radicals $\{Co(CO)_3L\}$ (L = CO, tertiary phosphine) (eq 19),[36a–c] while $\{Co(CO)_4\}$ has also been generated via hydrogen atom abstraction from $HCo(CO)_4$ by the trityl radical (eq 20)[36e] and by photoinduced (via excitation of the charge-transfer bands) electron transfer within the contact ion pairs $[(\eta^5\text{-}C_5H_5)_2Co^+][Co(CO)_3L^-]$ (eq 21)[36f] and $[Co(CO)_3(PPh_3)_2^+][Co(CO)_4^-]$ (eq 22).[36g] The cobalt radicals can be detected by using spin traps[29c] (eq 23).

$$[Co(CO)_3L]_2 \xrightarrow{h\nu} 2\{Co(CO)_3L\} \quad (19)$$

$$HCo(CO)_4 + \{Ph_3C^\bullet\} \rightarrow \{Co(CO)_4\} + Ph_3CH \quad (20)$$

$$[(\eta^5\text{-}C_5H_5)_2Co^+][Co(CO)_3L^-] \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)_2Co + \{Co(CO)_3L\} \rightarrow 0.5[Co(CO)_3L]_2 \quad (21)$$

$$[Co(CO)_3(PPh_3)_2^+][Co(CO)_4^-] \xrightarrow{h\nu} \{Co(CO)_3(PPh_3)_2\} + \{Co(CO)_4\} \rightarrow [Co(CO)_3PPh_3]_2 + CO \quad (22)$$

$$\{Co(CO)_3L\} + RN{=}O \rightarrow R\dot{N}(O)M(CO)_3L \quad (23)$$

$$R = \text{alkyl}$$

Photoinitiated hydrogen abstraction reactions of the cobalt-centered radicals with silanes and stannanes have also been investigated.[36b–d] Interestingly, the reactions are believed not to involve simple atom abstraction (as in eq 16), but rather a series of steps as in eq 24–27.

$$[Co(CO)_3L]_2 \xrightarrow{h\nu} 2\{Co(CO)_3L\} \quad (24)$$

$$\{Co(CO)_3L\} + R_3SnH \rightarrow Co(CO)_2LH(SnR_3) + CO \quad (25)$$

$$Co(CO)_2LH(SnR_3) + R_3SnH \rightarrow Co(CO)_2LH_2(SnR_3) + R_3Sn^\bullet \quad (26)$$

$$Co(CO)_2LH_2(SnR_2) + CO \rightarrow Co(CO)_3L(SnR_3) + H_2 \quad (27)$$

Step 25 would involve formal oxidative addition of stannane to the radical intermediate.

Reaction of $Co_2(CO)_8$ with nitrogen and phosphorus donors results in a variety of substitution (eq 28) and

$$Co_2(CO)_8 + L \rightarrow Co_2(CO)_7L + Co_2(CO)_6L_2 \quad (28)$$

disproportionation (eq 29) products, and radical chain

$$Co_2(CO)_8 + 2L \rightarrow [Co(CO)_3L_2][Co(CO)_4] + CO \quad (29)$$

processes, in competition with a dissociative process have been invoked to rationalize the rather complicated kinetics (eq 30–37).[37]

$$Co_2(CO)_8 + L \rightarrow Co_2(CO)_8L \quad (30)$$

$$Co_2(CO)_8L \rightarrow \{Co(CO)_4\}\{Co(CO)_3L\} + CO \quad (31)$$

$$\{Co(CO)_3L\} + Co_2(CO)_8 \rightarrow [Co(CO)_3L]^+ + [Co_2(CO)_8]^- \quad (32)$$

$$[Co_2(CO)_8]^- \rightarrow [Co(CO)_4]^- + \{Co(CO)_4\} \quad (33)$$

$$[Co(CO)_3L]^+ + L \rightarrow [Co(CO)_3L_2]^+ \quad (34)$$

$$\{Co(CO)_4\} + L \rightarrow \{Co(CO)_3L\} + CO \quad (35)$$

$$\{Co(CO)_3L\} + \{Co(CO)_4\} \rightarrow Co_2(CO)_7L \quad (36)$$

$$2\{Co(CO)_3L\} \rightarrow [Co(CO)_3L]_2 \quad (37)$$

The $\{Co(CO)_4\}$ radical has also been implicated in a variety of hydrogenation and insertion reactions of $HCo(CO)_4$ with conjugated diolefins.[38] See eq 7 for analogous chemistry of $HMn(CO)_5$.

2. Complexes of Iron, Nickel, and Copper

Treatment of $Fe(CO)_5$ and $Ni(CO)_4$ with alkali-metal atoms in inert gas matrices results in the species $\{Fe(CO)_4^-\}$ and $\{Ni(CO)_3^-\}$, respectively.[33a] Analyses of the IR spectra suggest a C_{3v} structure for $\{Fe(CO)_4^-\}$ and a D_{3h} structure for $\{Ni(CO)_3^-\}$, although ESR data for the former have also been interpreted in terms of a D_{2d} structure.[32b] However, little is known of these complexes. The compounds $Cu(CO)_3$[33b–d] and $Ag(CO)_3$[33d] have also been detected at low temperatures and have been characterized by IR and ESR spectroscopy. While the former appears to be a trigonal planar π radical, the latter may exist in both planar and pyramidal forms.

III. Complexes with One Polyhapto Ligand

A. Cyclopentadienyl and Arene Complexes of Chromium, Molybdenum, and Tungsten

The compound $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ has been shown to have a very long metal–metal bond,[39a] and the apparent weakness[39b] of this bond has been invoked to rationalize the high chemical reactivity of $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ relative to the molybdenum and tungsten analogues.[40] (The compound $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ actually has a shorter metal–metal bond than does $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$.[39a]) In addition, ESR, UV–visible, and IR studies have shown that $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ dissociates somewhat to the paramagnetic monomer

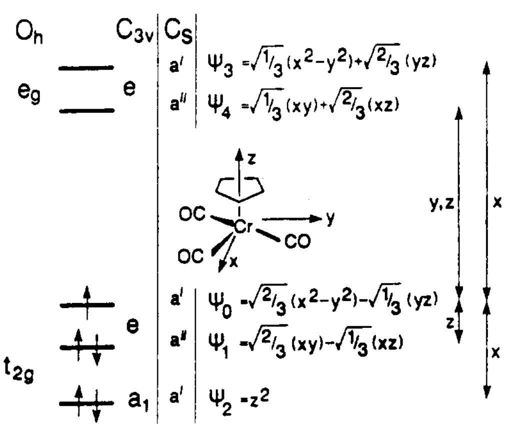


Figure 5. The 3d levels of $\{(\eta^5\text{-}C_5H_5)Cr(CO)_3\}$ in C_s symmetry.[41a] (Reprinted from ref 41a; copyright 1987 Academic Press.)

$\{(\eta^5\text{-}C_5H_5)Cr(CO)_3\}$ on sublimation and dissolution,[40e–g] and an equilibrium constant and thermodynamic parameters for the homolytic dissociation have been measured.[40g] Although $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ dissociates only to the extent of a few percent at room temperature, homolysis is far more extensive as higher temperatures, and the carbonyl stretching modes have been assigned by IR difference spectroscopy at 92 °C.[40g] Interestingly, the related compound $[(\eta^5\text{-}C_5Me_5)Cr(CO)_3]_2$ is also dimeric in the solid state but dissociates completely in solution, presumably because of the steric requirement of the $\eta^5\text{-}C_5Me_5$ ligand.[40i] The solution chemistry of this radical strongly resembles that of the $\eta^5\text{-}C_5H_5$ compound.

Cosublimation of $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ and $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ results in a sample of $\{(\eta^5\text{-}C_5H_5)Cr(CO)_3\}$ doped into the crystals of the diamagnetic host, thus permitting a single-crystal ESR study.[41a,b] In C_{3v} symmetry, the d orbitals of a $M(CO)_3$ moiety transform as a_1 ($3d_{z^2}$) + e ($3d_{x^2-y^2}$, $3d_{xy}$), and, in spite of considerable theoretical considerations of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$,[42] it is not a priori clear what should be the nature of the SOMO of $\{(\eta^5\text{-}C_5H_5)Cr(CO)_3\}$. In fact, the chromium radical is subject to a Jahn–Teller distortion such that the unpaired electron is in an a′ orbital in C_s symmetry (Figure 5). Thus the ordering of d orbitals is as postulated for $(\eta^5\text{-}C_5H_5)Mn(CO)_3$,[42] and the SOMO of $\{(\eta^5\text{-}C_5H_5)Cr(CO)_3\}$ is largely of $3d_{x^2-y^2}$ character. Interestingly, the paramagnetic tris(pyrazolyl)borate complex $TpMo(CO)_3$ appears to have a rather similar electronic structure, although low-temperature ESR data are not yet available.[43]

A variety of atom abstraction reactions of $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ appear to actually reflect the chemistry of the monomer $\{(\eta^5\text{-}C_5H_5)Cr(CO)_3\}$ (eq 38–40), including exchange of the iodine and of the hydridic hydrogen of $(\eta^5\text{-}C_5H_5)Cr(CO)_3X$ (X = H, I) (eq 41).[40d]

$$[CpCr(CO)_3]_2 \rightarrow 2\{CpCr(CO)_3\} \qquad (38)$$

$$2\{CpCr(CO)_3\} + MeI \rightarrow CpCr(CO)_3Me + CpCr(CO)_3I \qquad (39)$$

$$2\{CpCr(CO)_3\} + n\text{-}Bu_3SnH \rightarrow CpCr(CO)_3SnBu_3 + CpCr(CO)_3H \qquad (40)$$

$$\{CpCr(CO)_3\} + XCr'(CO)_3Cp \rightarrow \text{“}CpCr(CO)_3\text{---}X\text{---}Cr'(CO)_3Cp\text{”} \rightarrow CpCr(CO)_3X + \{Cr'(CO)_3Cp\} \qquad (41)$$

$$Cp = \eta^5\text{-}C_5H_5$$

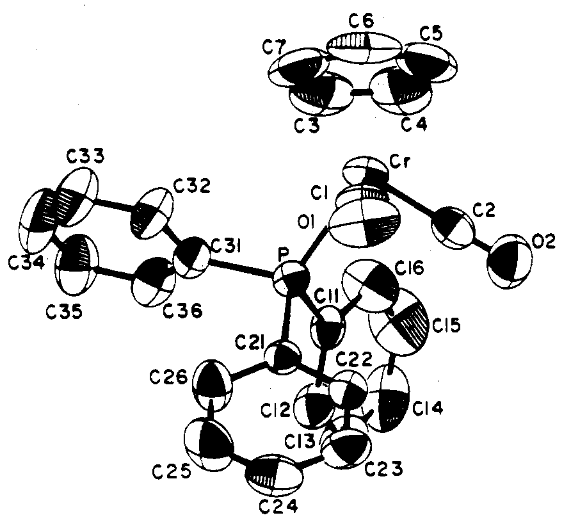


Figure 6. Molecular structure of $\{(\eta^5\text{-}C_5H_5)Cr(CO)_2PPh_3\}$.[40d]

TABLE VI. IR Data (CH_2Cl_2) for Complexes of the Type $\{\eta^5\text{-}C_5H_5)Cr(CO)_2L\}$[40h]

compd	ν_{CO}, cm^{-1}
$\{(\eta^5\text{-}C_5H_5)Cr(CO)_2(PEt_3)\}$	1924, 1805
$\{(\eta^5\text{-}C_5H_5)Cr(CO)_2(PBu_3)\}$	1921, 1803
$\{(\eta^5\text{-}C_5H_5)Cr(CO)_2(PCy_3)\}$	1919, 1802
$\{(\eta^5\text{-}C_5H_5)Cr(CO)_2(PPh_3)\}$	1920, 1800
$\{(\eta^5\text{-}C_5H_5)Cr(CO)_2(PMe_2Ph)\}$	1925, 1807
$\{(\eta^5\text{-}C_5H_5)Cr(CO)_2(PEt_2Ph)\}$	1923, 1807
$\{[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2(\mu\text{-dppb})\}$	1915, 1806
$\{[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2(\mu\text{-dpph})\}$	1915, 1795

Consistent with spontaneous homolysis of $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ in solution at room temperatue to form the presumed substitution-labile $\{(\eta^5\text{-}C_5H_5)Cr(CO)_3\}$, treatment of $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ with a variety of tertiary phosphines L results both in the facile formation of compounds of the stoichiometry $\{(\eta^5\text{-}C_5H_5)Cr(CO)_2L\}$ (eq 42), for which IR data are presented in Table VI,[40c,d,g,h] and in disproportionation (eq 43).[40h]

$$[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2 + 2L \rightarrow 2\{(\eta^5\text{-}C_5H_5)Cr(CO)_2L\} \qquad (42)$$

$$[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2 + 2L \rightarrow [(\eta^5\text{-}C_5H_5)Cr(CO)_2L_2]^+ + [(\eta^5\text{-}C_5H_5)Cr(CO)_3]^- \qquad (43)$$

The ease of substitution decreases as the steric requirements of L increase, as does the proclivity of $\{(\eta^5\text{-}C_5H_5)Cr(CO)_2L\}$ to dimerize. Thus $[(\eta^5\text{-}C_5H_5)Cr(CO)_2P(OMe)_3]_2$ is dimeric and diamagnetic in the solid state but with an even longer chromium–chromium bond than in $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$, but is extensively dissociated in solution to substituted monomer.[40c] Complexes with bulkier phosphines are completely dissociated in solution and in the solid state, and the X-ray crystal structure has been determined in one case, $\{(\eta^5\text{-}C_5H_5)Cr(CO)_2PPh_3\}$[40d] (Figure 6).

This compound is isostructural with the 18-electron manganese analogue, but with one subtle difference; the OC–Cr–CO bond angle is, at 80.9°, much less than the 90–92° normally found for such "piano stool" compounds. It was suggested, and confirmed by a single-crystal ESR spectrum of $\{(\eta^5\text{-}C_5H_5)Cr(CO)_2PPh_3\}$ doped into the diamagnetic manganese analogue,[41b,c] that the SOMO is of largely $3d_{xy}$ character such that the "hole" is localized between the carbonyl ligands.

Photolysis of $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$[44a–c] and $(\eta^5\text{-}C_5H_5)M(CO)_3H$[44d] (M = Mo, W) has been shown to yield the

TABLE VII. IR and ESR Data for Selected Compounds $\{(\eta^6\text{-}C_6Me_6)Cr(CO)_2L^+\}$ and Their 18-Electron Analogues[47a,b]

complex	ν_{CO}, cm^{-1}	g_{av} (A_P, G)
$\{(\eta^6\text{-}C_6Me_6)Cr(CO)_2PPh_3^+\}$	1969, 1853	2.041 (31.3)
$(\eta^6\text{-}C_6Me_6)Cr(CO)_2PPh_3$	1857, 1796	
$\{(\eta^6\text{-}C_6Me_6)Cr(CO)_2PMePh_2^+\}$	1965, 1849	
$(\eta^6\text{-}C_6Me_6)Cr(CO)_2PMePh_2$	1853, 1793	
$\{(\eta^6\text{-}C_6Me_6)Cr(CO)_2PMe_2Ph^+\}$	1961, 1849	
$(\eta^6\text{-}C_6Me_6)Cr(CO)_2PMe_2Ph$	1850, 1787	
$\{(\eta^6\text{-biphenyl})Cr(CO)_2PPh_3^+\}$	1993, 1886	2.043 (30.6)
$(\eta^6\text{-biphenyl})Cr(CO)_2PPh_3$	1887, 1833	

TABLE VIII. IR and ESR Data for Selected Compounds $\{(\eta^5\text{-}C_{5-x}Me_x)Mn(CO)_{3-y}L_y^+\}$ and Their 18-Electron Analogues[48a]

complex	ν_{CO}, cm^{-1}	g_{av}
$\{(\eta^5\text{-}C_5H_5)Mn(CO)_2PPh_3^+\}$	2045, 1965	
$(\eta^5\text{-}C_5H_5)Mn(CO)_2PPh_3$	1931, 1863	
$\{(\eta^5\text{-}C_5H_5)Mn(CO)_2PEt_3^+\}$	2037, 1951	
$(\eta^5\text{-}C_5H_5)Mn(CO)_2PEt_3$	1922, 1851	
$\{(\eta^5\text{-}C_5H_4Me)Mn(CO)_2PPh_3^+\}$	2041, 1961	
$(\eta^5\text{-}C_5H_4Me)Mn(CO)_2PPh_3$	1927, 1861	
$\{(\eta^5\text{-}C_5H_4Me)Mn(CO)_2PEt_3^+\}$	2029, 1945	
$(\eta^5\text{-}C_5H_4Me)Mn(CO)_2PEt_3$	1919, 1845	
$\{(\eta^5\text{-}C_5H_4Me)Mn(CO)_2PMe_2Ph^+\}$	2039, 1953	
$(\eta^5\text{-}C_5H_4Me)Mn(CO)_2PMe_2Ph$	1923, 1852	
$\{(\eta^5\text{-}C_5H_4Me)MnCO(PPh_3)_2^+\}$	1913	2.02 (A_{Mn} = 93.2 G, A_P = 24.5 G)
$(\eta^5\text{-}C_5H_4Me)MnCO(PPh_3)_2$	1816	
$\{(\eta^5\text{-}C_5H_4Me)MnCO(MePPh_2)_2^+\}$	1912	2.02 (A_{Mn} = 93.2 G, A_P = 24.5 G)
$(\eta^5\text{-}C_5H_4Me)MnCO(MePPh_2)_2$	1815	

monomeric species $\{(\eta^5\text{-}C_5H_5)M(CO)_3\}$, which may also be obtained electrochemically from the dimers.[44e] The IR spectra[44d] of the molybdenum- and tungsten-centered radicals in CO matrices at low temperature are very similar to the solution spectrum of the chromium analogue, mentioned above.[40g]

The metal-centered radicals have been investigated by utilizing spin traps (eq 44).[29c,d,30g]

$$\{\eta^5\text{-}C_5H_5M(CO)_3\} + RN{=}O \rightarrow R\dot{N}(O)M(CO)_3(\eta^5\text{-}C_5H_5) \quad (44)$$

$$R = \text{alkyl, aryl}$$

They take part in disproportionation reactions (eq 45)[13a] and also abstract halogen atoms from halocarbons

$$[(\eta^5\text{-}C_5H_5)M(CO)_3]_2 + 2L \xrightarrow{h\nu} [(\eta^5\text{-}C_5H_5)M(CO)_2L_2^+] + [(\eta^5\text{-}C_5H_5)M(CO)_3^-] \quad (45)$$

(eq 46)[30i,44a-c,f] and the hydrogen atom from $HMn(CO)_5$

$$[(\eta^5\text{-}C_5H_5)M(CO)_3]_2 + 2RX \xrightarrow{h\nu} 2(\eta^5\text{-}C_5H_5)M(CO)_3X \quad (46)$$

(eq 47).[36c] The radicals $\{(\eta^5\text{-}C_5H_5)M(CO)_3\}$ have been

$$[(\eta^5\text{-}C_5H_5)M(CO)_3]_2 + 2HMn(CO)_5 \xrightarrow{h\nu} 2(\eta^5\text{-}C_5H_5)M(CO)_3H + Mn_2(CO)_{10} \quad (47)$$

implicated in thermal and photochemical substitution reactions of $(\eta^5\text{-}C_5H_5)M(CO)_3H$[45a] and in olefin hydrogenation reactions of the hydrides,[45b] as in eq 7 for $HMn(CO)_5$. Substitution reactions of the tungsten radical, formed via hydrogen atom abstraction from $(\eta^5\text{-}C_5H_5)W(CO)_3H$, have also been studied and found to be associative in nature.[46]

Complexes $\{(\eta^6\text{-arene})Cr(CO)_2L^+\}$ (L = CO, tertiary phosphine) can be prepared by chemical and electrochemical oxidation of the corresponding 18-electron compounds and, although the tricarbonyl species appear to be too unstable to isolate, the substituted complexes are sufficiently robust that several have been isolated and characterized by IR and ESR spectroscopy (Table VII).[47]

The cationic, diphosphine-bridged bis(arene) complex $\{(\mu\text{-biphenyl})[Cr(CO)_2]_2(\mu\text{-dppm})^+\}$ displays IR and ESR spectra indicative of a charge- and spin-localized mixed-valent complex.[47b]

B. Cyclopentadienyl Complexes of Manganese and Rhenium

A large number of complexes of the type $\{(\eta^5\text{-}C_5H_{5-x}Me_x)M(CO)_{3-y}L_y^+\}$ (M = Mn, Re; L = nitrogen, phosphorus donor; x = 0, 1, 5; y = 0, 1) have been prepared via oxidation of the 18-electron neutral precursors.[48] Many of the 17-electron species are sufficiently stable that they have been characterized by and their reactions monitored by IR and ESR spectroscopy and electrochemistry (Table VIII).

Substitution reactions are associative in nature and are much more facile, with significantly (>10^6 faster) higher rates, than are reactions of the closed-shell parent compounds. It has thus been shown that substitution reactions of 18-electron compounds of the type $(\eta^5\text{-}C_5H_5)Mn(CO)_2L$ can undergo electrocatalyzed substitution reactions. The species $\{(\eta^5\text{-}C_5H_5)Mn(CO)_2L^+\}$, produced initially at the anode, undergoes rapid exchange with a ligand L′ to form the substituted 17-electron intermediate $\{(\eta^5\text{-}C_5H_5)Mn(CO)LL'^+\}$. The latter then abstracts an electron from a molecule of $(\eta^5\text{-}C_5H_5)Mn(CO)_2L$ to form the substituted product $(\eta^5\text{-}C_5H_5)Mn(CO)LL'$ and to regenerate the cationic $\{(\eta^5\text{-}C_5H_5)Mn(CO)_2L^+\}$, thus completing the chain propagation sequence.[48c]

The related compounds $(\eta^5\text{-}C_5H_5)Mn(CO)_2ER$ (E = S, Se) have also been reported.[48f]

C. Cyclopentadienyl Complexes of Iron and Ruthenium

The compound $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}$ has been generated photochemically from the corresponding dimer[49a-g] and is an intermediate in conjugated diolefin hydrogenation and insertion reactions of the hydride, $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$[49h] (see eq 7 for a description of similar chemistry of $HMn(CO)_5$).

The radical $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}$ has been shown to abstract halogen atoms from halocarbons (eq 48)[49a-c] and to react with spin traps (eq 49).[29c,d,30g]

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 + RX \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)Fe(CO)_2X \quad (48)$$

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 + RNO \xrightarrow{h\nu} R\dot{N}(O)Fe(CO)_2(\eta^5\text{-}C_5H_5) \quad (49)$$

Use of very fast time-resolved IR spectroscopy has permitted the observation of the carbonyl stretching modes of the very short-lived iron-centered radical, as well as the monitoring of its dimerization reaction and of its substitution reactions with various ligands L to form $\{(\eta^5\text{-}C_5H_5)Fe(CO)L\}$.[49d-f] The dimerization proceeds with a rate constant near the diffusion-controlled

TABLE IX. IR and ESR Data for Selected Compounds $\{(\eta^3\text{-}C_3H_5)Fe(CO)_2L\}$[49i,51a,e,g]

complex	ν_{CO}, cm^{-1}	g_{av}
$\{(\eta^3\text{-}C_3H_5)Fe(CO)_3\}$	2046, 1968–1960	2.0421
$\{(\eta^3\text{-}C_3H_5)Fe(CO)_2P(n\text{-}Bu)_3\}$	1945, 1884	2.0423
$\{(\eta^3\text{-}C_3H_5)Fe(CO)_2PPh_3\}$	1956, 1893	2.0462 (A_P = 17.1 G)
$\{(\eta^3\text{-}C_3H_5)Fe(CO)_2PMe_3\}$	1960, 1884	2.0449
$\{(\eta^3\text{-}C_3H_5)Fe(CO)_2PEt_3\}$	1960, 1885	2.0463
$\{(\eta^3\text{-}C_3H_5)Fe(CO)_2PMe_2Ph\}$	1961, 1895	2.0473
$\{(\eta^3\text{-}C_3H_5)Fe(CO)_2PMePh_2\}$	1963, 1899	2.0482
$\{(\eta^3\text{-indenyl})Fe(CO)_3$	2038, 1970, 1962	2.1013
$\{(\eta^3\text{-indenyl})Fe(CO)_2PPh_3\}$	1975, 1968, 1918, 1911	2.0054 (A_P = 68 G)

limit, while the substitution reactions are associative but less rapid.

The analogous radicals $\{(\eta^5\text{-}C_5H_5)Ru(CO)_2\}$[49a] and $\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}$[49g] have also been studied and shown to have properties similar to those of $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}$. Interestingly, photolysis of the compound $[(\eta^5\text{-indenyl})Fe(CO)_2]_2$ in the presence of ligand L (L = CO, PPh_3, $PHPh_2$) results in the formation of compounds of the type $\{(\text{indenyl})Fe(CO)_2L\}$;[49i] as the indenyl ligand is presumably bound in η^3-fashion, these compounds will be discussed below in section IIID.

A related series of 17-electron iron complexes, albeit of a higher formal oxidation state, are formed on one-electron oxidation of compounds of the type $(\eta^5\text{-}C_5H_5)FeLL'R$ (L, L′ = CO, tertiary phosphines; R = alkyl). Oxidized species $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2R^+\}$ and $\{(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R^+\}$ are believed to be intermediates in many oxidative cleavage reactions of the neutral, 18-electron alkyl analogues but are generally too unstable to detect.[50a] However, many similar species have been stabilized via substitution of acetyl,[50b,c] cyano,[50d] or chelating ligands,[50e] and reactions of the radicals have been studied electrochemically and spectroscopically. The analogous complexes $\{(\eta^5\text{-}C_5H_5)FeLL'(SPh)^+\}$ (L = CO, phosphites, isonitriles) have also been reported.[50f]

D. Allyliron Complexes

Rather similar to the (polyhapto ligand)metal carbonyl radicals discussed above is a class of allyliron carbonyl compounds. It has long been known that reduction of $(\eta^3\text{-}C_3H_5)Fe(CO)_3Br$ gives the red, dimeric $[(\eta^3\text{-}C_3H_5)Fe(CO)_3]_2$,[51a,b] with a very long iron–iron bond.[51c] Consistent with the implied weakness of the metal–metal bond, the dimer exists in solution in equilibrium with the green, monomeric $\{(\eta^3\text{-}C_3H_5)Fe(CO)_3\}$,[51a–c] a type of radical that has also been obtained via the low-temperature UV irradiation of solutions of $Fe(CO)_5$ and olefins.[51d]

As is the case with other metal radicals, $\{(\eta^3\text{-}C_3H_5)Fe(CO)_3\}$ is very substitution labile, and several phosphine derivatives of the type $\{(\eta^3\text{-}C_3H_5)Fe(CO)_2L\}$ have also been prepared by treating the dimer with the phosphine in nonpolar solvents.[51a,e] In polar solvents, disproportionation also occurs (eq 50).[51g]

$$[(\eta^3\text{-}C_3H_5)Fe(CO)_3]_2 + 2L \rightarrow [(\eta^3\text{-}C_3H_5)Fe(CO)_2L_2]^+ + [(\eta^3\text{-}C_3H_5)Fe(CO)_3]^- \quad (50)$$

The IR and ESR spectra of several of the monomeric radicals have been reported (Table IX),[51a,e] but several of the monomer–dimer equilibrium constants reported for substituted compounds[51e] have been shown to be in error, as the significant presence of disproportionation products was not taken into account.[51g]

TABLE X. Data for Selected Compounds $\{(\eta^5\text{-}C_5R_5)VL\}$ (R = H, Me)[53c,e]

compd	g_{av}
$\{(\eta^5\text{-}C_5H_5)_2V(CO)\}$	2.005 (A_V = 28.8 G)
$\{(\eta^5\text{-}C_5Me_5)_2V(CO)\}$	2.000 (A_V = 18.6 G)
$\{(\eta^5\text{-}C_5H_5)_2V(CF_3C_2CF_3)\}$	1.997 (A_V = 47.3 G)

Little is known of the chemistry of this class of metal compounds except that $\{(\eta^3\text{-}C_3H_5)Fe(CO)_2(PPh_3)\}$ does effect the debromination of vicinal dibromides.[51f] The fluxional compound $\{(\eta^3\text{-cyclooctenyl})Fe[P(OMe)_3]\}$ has also been reported.[52]

IV. Complexes with Two Polyhapto Ligands

The 15-electron compound vanadocene, $(\eta^5\text{-}C_5H_5)_2V$, readily combines with a variety of π-acid ligands L (L = CO, olefins, alkynes, but not tertiary phosphines) to form 17-electron complexes of the type $\{(\eta^5\text{-}C_5H_5)_2VL\}$.[53] Similar compounds of stoichiometry $\{(\eta^5\text{-}C_5H_7)_2VL\}$ are formed with the acyclic pentadienyl ligand.[53d–f]

ESR (Table X) and SCF–Xα–DV molecular orbital calculations have been carried out for several of the compounds, and it has been shown that the SOMO for the $\eta^5\text{-}C_5H_5$ compounds is of a_1 character and is largely localized between the cyclopentadienyl planes and hence accessible for bimolecular nucleophilic attack.[53e] As a result, CO exchange reactions of $\{(\eta^5\text{-}C_5H_5)_2VCO\}$ and $\{(\eta^5\text{-}C_5Me_5)_2VCO\}$ are associative, with $\Delta S^\ddagger \approx -21$ cal mol^{-1} K^{-1} for the latter. In addition, the second-order rate constants for the former at various temperatures are about 3 times those of the more crowded $\eta^5\text{-}C_5Me_5$ complex.[53d]

In contrast, the SOMOs of the pentadienyl and mixed cyclopentadienyl–pentadienyl complexes, although also of a_1 symmetry, appear to be oriented toward the centers of the polyhapto ligands and thus are much less accessible toward nucleophiles.[53e] As a result, CO exchange reactions are several orders of magnitude slower and appear to be associative in nature.[53d]

V. Relative Reactivities of Metal-Centered Radicals

Photolysis of mixtures of homonuclear metal–metal-bonded species results in largely random coupling of the thus generated radicals to form various heterodinuclear compounds, which have been isolated and characterized.[54] In order to gain information concerning the relative reactivities of many of the various radicals, competition experiments, in which heterodinuclear compounds have been photolyzed in the presence of alkyl halides, have been carried out.[54a,b] On the basis of these studies, and including what is known of the chemistry of $\{V(CO)_6\}$, the ordering of metal radical reactivity with respect to halogen atom abstraction is $\{Re(CO)_5\} > \{Mn(CO)_5\} > \{(\eta^5\text{-}C_5H_5)W(CO)_3\} > \{(\eta^5\text{-}C_5H_5)Mo(CO)_3\} > \{(\eta^5\text{-}C_5H_5)Fe(CO)_2\} > \{Co(CO)_4\} > \{V(CO)_6\}$.

VI. Summary

While a variety of 17-electron metal-centered radicals, many of them persistent, are known, the total number which has been well-characterized either structurally or chemically is as yet rather small. Common synthetic routes to radicals include photolytic homolysis of compounds containing metal–hydrogen or metal–metal bonds and electron-transfer processes of 18-electron compounds. Other synthetic routes, such as atom abstraction reactions, are as yet relatively unexploited, and the number of bimetallic compounds for which the metal–metal bond is sufficiently weak that homolytic dissociation occurs spontaneously in the dark at room temperature is small.

Metal radicals exhibit much of the chemistry of the much better studied carbon-centered radicals, and thus dimerization generally occurs readily although the process is often subject to severe steric constraints. Many metal radicals also react with spin traps and readily abstract halogen and hydrogen atoms from various sources.

Substitution reactions of metal radicals differ strikingly from the corresponding reactions of similar 18-electron compounds, generally reacting much more quickly, via associative (19-electron intermediates or transition states) rather than dissociative processes. Although no general theoretical studies of this phenomenon have yet been reported, it would seem that S_N2-type reactions are made possible because of stabilizing two-orbital three-electron interactions between the SOMO of the complex and the lone pair of the incoming radical. Ligand-induced disproportionation reactions appear to proceed via similar steps.

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