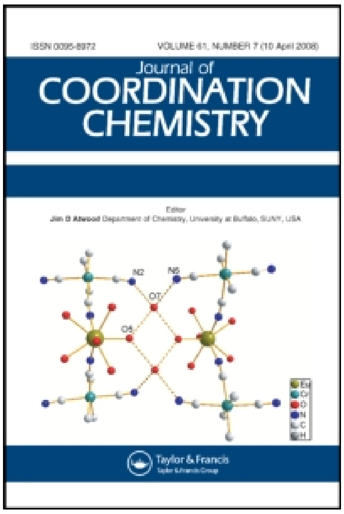


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

ELECTRON TRANSFER REACTIONS OF METAL CARBONYL ANIONS

Jim D. Atwood[a]; M. Shauna Corraine-pandolfino[a]; Yueqian Zhen[a]; William S. Striejewske[a]; C. K. Lai[a]; Ping Wang[a]
[a] Department of Chemistry, University at Buffalo, State University of New York, Buffalo, NY

To cite this Article Atwood, Jim D. , Corraine-pandolfino, M. Shauna , Zhen, Yueqian , Striejewske, William S. , Lai, C. K. and Wang, Ping(1994) 'ELECTRON TRANSFER REACTIONS OF METAL CARBONYL ANIONS', Journal of Coordination Chemistry, 32: 1, 65 — 78

To link to this Article: DOI: 10.1080/00958979408024238

URL: http://dx.doi.org/10.1080/00958979408024238

J. Coord. Chem., 1994, Vol 32, pp. 65–78
Reprints available directly from the publisher
Photocopying permitted by license only

ELECTRON TRANSFER REACTIONS OF METAL CARBONYL ANIONS[†]

JIM D. ATWOOD,* M. SHAUNA CORRAINE-PANDOLFINO, YUEQIAN ZHEN, WILLIAM S. STRIEJEWSKE, C.K. LAI and PING WANG

Department of Chemistry, University at Buffalo, State University of New York, Buffalo, NY 14214

(Received November 22, 1993)

Metal carbonyl anions exhibit one- and two-electron reactions. The two-electron processes involving transfer of groups (hydrogen, alkyl, and halogen) between metal centers are related to the nucleophilicity. The one-electron processes are primarily outer-sphere electron transfer for the metal carbonyl anions. These reactions are observed in the presence of oxidants such as coordination complexes, pyridinium salts, metal carbonyl dimers and metal carbonyl clusters. However, in contrast to organic reactions, the metal carbonyl anions may undergo inner-sphere electron transfer. Reactions of metal carbonyl anions of low nucleophilicity with metal carbonyl cations or halides are best interpreted as inner-sphere, one-electron transfer.

KEYWORDS: metal carbonyl anions, electron transfer, outer sphere

INTRODUCTION

Electron transfer is a primary reaction in chemistry and of ultimate importance in biological systems. A number of very elegant theoretical and experimental studies have focused on the mechanism of electron transfer in coordination complexes.[1–10] Although electron transfer is commonly observed in organometallic complexes, relatively few studies of electron transfer by organometallic complexes have been accomplished.[11–13] A basic description of the factors affecting rates of electron transfer by organometallic complexes should enhance understanding of electron transfer reactions in synthesis and catalysis.

Electron transfer has been frequently observed in catalytic and synthetic reactions of organometallic complexes. Simple reduction[14,15] and oxidation[14] reactions are commonly observed and utilized. Disproportionation reactions provide another example of electron transfer.[16] Reactions between cationic and anionic carbonyls to form metal-metal bonds also involve a formal electron transfer.[17,18]

$$\mathrm{Mn(CO)_6^+ + Mn(CO)_5^- \rightarrow Mn_2(CO)_{10} + CO} \qquad (1)$$

$$\mathrm{[Co(CO)_3(PPh_3)_2][Co(CO)_4] \xrightarrow{\Delta} Co_2(CO)_6(PPh_3)_2 + CO} \qquad (2)$$

The primary method of synthesis of heterobimetallic complexes may involve electron transfer[19] between metal halides and metal carbonyl anions.[20–23]

---

* Author for correspondence.

[†] In honour of Professor Theodore L. Brown's 65th birthday and retirement.

$$\mathrm{CpFe(CO)_2I + NaMn(CO)_5 \rightarrow Cp(CO)_2FeMn(CO)_5 + NaI} \tag{3}$$

$$\mathrm{Re(CO)_5Cl + NaMn(CO)_5 \rightarrow MnRe(CO)_{10} + NaCl} \tag{4}$$

$$\mathrm{Mn(CO)_5Cl + NaCo(CO)_4 \rightarrow MnCo(CO)_9 + NaCl} \tag{5}$$

$$\mathrm{Pt(Py)_2Cl_2 + 2NaCo(CO)_4 \rightarrow Pt(Py)_2[Co(CO)_4]_2 + 2NaCl} \tag{6}$$

This type of reaction sometimes leads to formation of homobimetallic complexes. Indeed a rather simple change from reaction 3

$$\mathrm{2CpFe(CO)_2^- + 2Mn(CO)_5Br \rightarrow Cp_2Fe_2(CO)_4 + Mn_2(CO)_{10}} \tag{7}$$

gives a different product distribution.[24] Redox condensation is an important method of synthesis for metal clusters, especially for mixed metal clusters.[23-25] An interesting example of electron transfer from $Mn(CO)_5^-$ to $Cr(\eta^6 - C_6H_6)_2^+$ is shown below.[14]

$$\mathrm{2[Cr(\eta^6 - C_6H_6)_2][Mn(CO)_5] \rightarrow 2Cr(\eta^6 - C_6H_6)_2] + Mn_2(CO)_{10}} \tag{8}$$

Synthetic applications of organometallic electron transfer reactions have been reviewed.[26]

Metal Carbonyl Anions

The most significant advances in organometallic reactions have come in electron transfer reactions of metal carbonyl anions. The utility of metal carbonyl anions in synthesis of organometallic complexes have been recognized for many years.[15,16] Metal carbonyl anions such as $CpFe(CO)_2^-$, $HFe(CO)_4^-$,$Fe(CO)_4^{2-}$ and $Co(CO)_4^-$ have shown great utility for organic synthetic reactions.[14,27] In addition, metal carbonyl anions have been implicated as the catalysts for a number of reactions: (1) $HRu(CO)_4^-$ and $Rh(CO)_4^-$ have been shown to be active in CO hydrogenation reactions;[28] (2) $Rh(CO)_2I_2^-$ apparently is the active catalyst for methanol carbonylation to acetic acid in the Monsanto process;[29] (3) $Fe(CO)_4^{2-}$ has been suggested as the catalyst for methanol homologation;[30] (4) $Rh(CO)_4^-$ was shown to be active for the carbonylation of nitrobenzenes;[31] and (5) $W(CO)_5X^-$ was demonstrated as an active catalyst for olefin metathesis.[32]

Properties of metal carbonyl anions that are necessary to interpret reactions are the oxidation potentials, the pK_a of the conjugate hydride and the nucleophilicity. Values for several metal carbonyl anions are summarized in Table 1.[33-35] Reliable

Table 1 Properties of Metal Carbonyl Anions

Metal anion	$E(\cdot M \rightarrow M^-)$ in mV[33]	$pK_a(MH)$[34]	$\ln k_2(CH_3I)$
$CpFe(CO)_2^-$	-1.186	19.4	14
$Re(CO)_5^-$	-0.523	21.1	4.3
$Mn(CO)_4PEt_3^-$	-0.854[a]	–	4.1
$Mn(CO)_3(PPh_3)_2^-$	-1.029[a]	–	3.8
$Mn(CO)_4PPh_2Me^-$	-0.800[a]	–	2.9
$Mn(Co)_4PPh_3^-$	-0.754	–	2.1
$Mn(CO)_4P(OPh)_3^-$	-0.525[a]	–	0.64
$Mn(CO)_5^-$	-0.400	15.1	0.41
$CpMo(CO)_3^-$	-0.336	13.9	-.94
$CpCr(CO)_3^-$	-0.639	13.3	-2.8
$Co(CO)_3PPh_3^-$	-0.607	15.4	-1.0
$Co(CO)_4^-$	-0.123	8.3	-4.7

[a] Correction assumed to be that for $Mn(CO)_4PPh_3^-$.

quantitative electrochemical treatment of metal carbonyl anions has been limited by the irreversibility of oxidation of the anions and reduction of the dimers. Tilset and Parker applied a kinetic correction to the electrode potential to obtain the reduction potential for the radical.[33]

$$M\cdot + e^- \rightarrow M^- \qquad (9)$$

Parker and his coworkers used these potentials to generate thermochemical cycles. In most electron transfer reactions, the end product of oxidation of the anion is not the odd-electron species but the dimer. We used the Tilset and Parker values for reaction 9 coupled with the best estimates of the metal-metal bond energy to derive the two-electron reduction potential for the dimer.[36]

$$M_2 + 2e^- \rightarrow 2M^- \qquad (10)$$

The values for the potential of these reactions correctly predict the observed direction of reactions,

$$2M^- + M_2' \rightarrow M_2 + 2M'^- \qquad (11)$$

between metal carbonyl anions and dimers.[36] (Note the similarity to reactions of halogens $2X^- + X_2' \rightarrow X_2 + 2X'^-$.) We have also estimated the two-electron potentials for trinuclear clusters by chemical reactivity studies.[37]

The potentials for all of these reactions are shown in Table 2.

$$M_3(CO)_{12} + 2e^- \rightarrow M_3(CO)^{2-}_{11} + CO \qquad (12)$$

Meyer and Pugh have provided an electrochemical route to determine metal-metal bond strengths in solution.[38] Their values are in the order estimated from our reactivity studies and in moderate quantitative agreement. For the first time, reliable thermodynamic data are available for electron transfer reactions of metal carbonyl complexes.

Several studies have expanded on the acidity of the metal carbonyl hydrides reported by Jordan and Norton.[34] The gas phase acidities of $HMn(CO)_5$,

Table 2 Half-Reaction Reduction Potentials[a] For Two-Electron Transition of Metal Carbonyl Species[36-38]

	Dimers
Metal carbonyl, M_2	$M_2 + 2e^- \rightarrow 2M^-$
$Co_2(CO)_8$	-0.123
$Cp_2Cr_2(CO)_6$	-0.639
$Cp_2Mo_2(Co)_6$	-0.336
$Cp_2W_2(CO)_6$[b]	-0.330
$Mn_2(CO)_{10}$	-0.400
$Re_2(CO)_{10}$	-0.523
$Cp_2Fe_2(CO)_4$	-1.186
	Clusters
Metal carbonyl, M_3	$M_3 + 2e^- \; 2M_3^{2-} + CO$
$Fe_3(CO)_{12}$	-0.8V
$Ru_3(CO)_{12}$	-0.9V
$Os_3(CO)_{12}$	-1.1V

[a] Potentials are quoted *versus* SHE in volts.

[b] This is an estimated value based on the reactions observed. The calculated value is too large.

$H_2Fe(CO)_4$ and $HCo(CO)_4$ demonstrated that these species are strong acids in the gas phase.[39] Ryan, Tilset and Parker have also examined the acidity and/or proton transfer reactions of transition metal hydride species.[40]

Nucleophilicity of the metal carbonyl anions, as measured by reactions with CH_3I, has been examined by three separate groups with good agreement between the values.[27] Replacing CO's by better donor/weaker acceptor ligands results in an increase in nucleophilicity that is somewhat attenuated if the ligand is large.[27a] Usually anions based on 2nd or 3rd row metals are more nucleophilic than their 1st row analogues. Five-coordinate anions are more nucleophilic than four- or six-coordinate anions,[27c] presumably because of more favorable bonding to CO for four- and six-coordinate metals. Ion-pairing[41] can have a significant effect on the nucleophilicity with a more interacting cation decreasing the nucleophility. Ion-pairing was evidently responsible for the similar nucleophilicities of $Na_2Fe(CO)_4$ and $PPNCpFe(CO)_2$.[42]

Organometallic Electron Transfer

While electron transfer is a common reaction of organometallic complexes, mechanistic studies of electron transfer between organometallic complexes are not as common.[11,12,43–46] Creating coordination sites through electron transfer catalysis has generated increasing interest.[47–52] Electron transfer catalysis has been implicated in substitution reactions, cycloadditions, isomerization, polymerization, oxidative addition, reductive elimination, Diels-Alder reactions, chelation and stereoisomerizations.[47–53] Applications to organometallic chemistry center on the greatly enhanced reactivity of 17- and 19-electron complexes over 16- and 18-electron species.[54–56] A communication has described the use of electron transfer catalysis to effect the polymerization of terminal alkynes.[52] Treatment of the non-catalytically active complex $W(CO)_3(CH_3CN)_3$ with a small quantity of $[Cp_2Fe^+]PF_6$ generates the active catalyst, $W(CO)_3(CH_3CN)_3{}^+$.[52]

A couple of studies have explored the application of Marcus relationships to organometallic electron transfer reactions.[57-61] Burke and Brown studied the transfer of an electron from $Re(CO)_4L\cdot$ to N-methylpyridinium cations.[57] Treatment by Marcus equations led to an intrinsic barrier of 3 kcal/mole for the rhenium radical.[57] Meyer and coworkers found that some substituted rhenium carbonyl complexes undergo intramolecular electron transfer in the inverted region predicted by Marcus.[58] Theopold and coworkers have examined self-exchange rate constants for several systems.[58-61] Gas phase kinetics have been used to evaluate self-exchange between the metallocenes of manganese, iron, cobalt and ruthenium.[12] The much lower efficiency for manganocene indicates a substantial barrier from internal rearrangement, as expected from a d^5 high-spin complex. Metallocene self-exchange has been examined with correlation of the rate constants to electronic structure and to the nuclear frequency factor.[62,63] Disproportionation of $V(CO)_6$ was examined with the possibility of electron transfer through an isocarbonyl.[46] The observation that $V(CO)_5PBu_3$ disproportionates 10^5 more slowly suggests large ligand effects are possible in organometallic electron transfer. The kinetics of the oxidation of $Cp_2Fe_2(CO)_4$ by $Ru(bipy)_2Cl_2{}^+$ and by $[CpFe(CO)]_4{}^+$ have been reported.[43]

$$Cp_2Fe_2(CO)_4 + 2Ru(bipy)_2Cl_2{}^+ \xrightarrow{CH_3CN} 2CpFe(CO)_2(NCCH_3)^+ + 2Ru(bipy)_2Cl_2 \tag{13}$$

$$Cp_2Fe_2(CO)_4 + 2[CpFe(CO)]_4^+ + \xrightarrow{CH_3CN} 2CpFe(CO)_2(NCCH_3)^+ + 2[CpFe(CO)]_4 \quad (14)$$

As usual for oxidation-reduction reactions, the rate is first order in $Cp_2Fe_2(CO)_4$ and the oxidant. The rates were rapid ($k \cong 5 \times 10^4 s^{-1}$), requiring stopped-flow techniques. Very low activation enthalpies (2–6 kcal/mole) and negative entropies of activation ($\Delta S^\ddagger = -25$ eu) were found.[43] The initial step was suggested as transfer of an electron from the Fe-Fe bond to the oxidant. For both oxidants the mechanism involved outer-sphere electron transfer. In contrast, the reactions of $Mo(N_2)_2(dppe)_2$ with alkyl halides were shown to proceed by inner-sphere processes.[44]

Both inner- and outer-sphere mechanisms of electron transfer are possible in organometallic complexes. Similar techniques to those used for coordination complexes may be used to distinguish between outer-sphere and inner-sphere mechanisms if applied carefully. In coordination complexes the higher oxidation state metal has the shorter M-L bond lengths, while for metal carbonyls the lower oxidation state metal has shorter M-CO bonds. The vanadium hexacarbonyls, $V(CO)_6$ and $V(CO)_6^-$, with V-C bond distances of 2.001 and 1.931 Å, respectively, serve as an example.[64,65] The bond distance difference of 0.07 Å should be readily accommodated in vibrational modes, and one would assume that the self-exchange would be rapid. The small structural change is as expected for removal of a t_{2g} electron in conversion between t_{2g}^6 and t_{2g}^5. An example from coordination complexes of removal of a t_{2g} electron is self-exchange for $Fe(bipy)_3^{+2,+3}$,

$$*Fe(bipy)_3^{+2} + Fe(bipy)_3^{+3} \rightleftarrows *Fe(bipy)_3^{+3} + Fe(bipy)_3^{+2} \quad (15)$$

which is a very rapid outer-sphere reaction. The difference in bond distances is 0.01 Å between the +2 and +3 ions.[66]

Two separate studies of reactions between organometallic cations and anions have been reported.[67–74] These studies show that concurrent single-electron and two-electron processes are possible, very similar to reactions of organic anions which may be nucleophilic-electrophilic or single-electron transfer. Disproportionation of a dimeric species is the reverse of a single-electron transfer reaction between cationic and anionic species. Tyler has continued his studies of disproportionation of metal carbonyl dimers.[75] Castellani and Tyler demonstrated that photochemical and thermal disproportionation of $Cp_2Fe_2(CO)_4$ in the presence of a phosphine occur by the same mechanism.[75]

$$Cp_2Fe_2(CO)_4 \rightleftarrows 2CpFe(CO)_2\cdot \quad (16)$$

$$CpFe(CO)_2\cdot + L \rightleftarrows CpFe(CO)_2L\cdot \quad (17)$$

$$CpFe(CO)_2L\cdot + Cp_2Fe_2(CO)_4 \rightarrow CpFe(CO)_2L^+ + Cp_2Fe_2(CO)_4^{\dot-} \quad (18)$$

$$Cp_2Fe_2(CO)_4^{\dot-} \rightarrow CpFe(CO)_2^- + CpFe(CO)_2\cdot \quad (19)$$

$$CpFe(CO)_2L\cdot + CpFe(CO)_2\cdot \rightarrow CpFe(CO)_2L^+ + CpFe(CO)_2^- \quad (20)$$

For L = CO we can observe the reaction in the opposite direction ($CpFe(CO)_3^+ + CpFe(CO)_2^- \rightarrow Cp_2Fe_2(CO)_4 + CO$).[74] Obviously, subtle electronic factors can change the potential enough to change the direction of reaction. Photochemical activation of $(CO)_5MnMn(CO)_3$(α-diimine) resulted in $Mn(CO)_5^-$ and $Mn(CO)_3$(α-diimine)L^+ (L = a donor ligand) by an ETC process.[76] Reactions of

$Mn_2(CO)_8(PBu_3)_2$ with alkyl halides have been reported to occur by an outer-sphere electron transfer mechanism.[77] The products are $Mn(R)(CO)_4PBu_3$ and $Mn(CO)_4(PBu_3)X$.[77]

Explorations of the reactivity of odd electron complexes continue to attract attention from organometallic chemists. Interconversions between $17e^-$, $18e^-$ and $19e^-$ tungsten complexes were reported.[78] Oxidation of $W(CO)_3$ (mesitylene) led to the $17e^-$ complex which reacted with solvent or phosphine to give the $19e^-$ adduct which was further oxidized to the $18e^-$ complex. Rate constants for reactions of $17e^-$ complexes usually fall in the 10^5 - 10^8 s^{-1} M^{-1} range.[78,79] In solution the $17e^-$ complexes react by associative routes; a gas phase study of $Cr(CO)_5^-$ suggested an electron transfer mechanism for reaction with ligands.[80] Oxidation of $Ru(CO)_3(PR_3)_2$ to the $17e^-$ complex $Ru(CO)_3(PR_3)_2{}^+$, which is suggested to be important in catalytic carbonylation of nitroaromatics, was recently demonstrated.[81] A number of reactions were reported.

Reactions of Organic Anions

Development of the concept of electron transfer in organic reactions has continued.[82–88] A couple of studies have discussed the distinctions between SET (single electron transfer) and S_n2 mechanisms in methyl transfer.[82,83] Lewis has concluded that agreement with the Marcus equation is insufficient evidence to assign a SET mechanism. Despite the correlation of rates of methyl transfer with the Marcus equation, Lewis concludes that simple SET mechanisms cannot be operative.[82] Bordwell and Harrelson have also concluded that most substitution reactions of organic anions with alkyl halides do not involve SET.[83] Organic electron transfer has developed enough to accommodate quantitative treatment of the possible reactions.[84–86] Arnett and coworkers have continued their studies of reactions of carbocations and carbanions by measuring/calculating the energies of bond heterolysis, electron transfer and bond homolysis.[84,85] Knowledge of two of these energies allows calculation of the third. A somewhat more theoretical approach to the solution thermochemistry of organic molecules, ions and radicals has also appeared.[86] The cycle to define all homolytic and heterolytic cleavage reactions was shown to depend on seven parameters: the oxidation and reduction potentials of R-R′, R·, R·′ and the bond homolysis energy R-R′.[86]

Electron Transfer Reactions of Metal Carbonyl Anions

Outer-sphere electron transfer reactions (single electron transfer in organic terminology) are observed between metal carbonyl anions and many oxidants. These reactions lead, ultimately, to metal carbonyl dimers through seventeen electron complexes. The seventeen electron complexes formed by oxidation of the metal carbonyl anions show ligand lability and other reactions typical for organometallic radical complexes.[54–56]

Outer-sphere reactions must show a dependence on the driving force. For a given oxidant the driving force is determined by the potential;

$$M^- \rightarrow M\cdot + e^- \qquad (21)$$

these potentials are given in Table 1.[33] The rates of outer-sphere electron transfer reactions should show a dependence on the nature of the metal carbonyl anion.

$$CpFe(CO)_2^- > Re(CO)_5^- > Mn(CO)_5^- > CpMo(CO)_3^- > Co(CO)_4^- \qquad (22)$$

Outer-sphere electron transfer reactions have a rate law

$$\text{rate} = k[\text{reductant}][\text{oxidant}] \qquad (23)$$

or for reactions of metal carbonyl anions

$$\text{rate} = k[M^-][\text{oxidant}] \qquad (24)$$

All of the reactions examined in this manuscript show this rate law and all rate constants quoted are the second-order rate constants.

Reactions with Known Outer-Sphere Oxidants

To ascertain the characteristics expected for outer-sphere electron transfer reactions of the metal carbonyl anions, reactions were examined with $Co(o\text{-}phen)_3^{3+}$ and 3-acetoxy-N-methylpyridinium.[89]

$$2M^- + 2Co(o\text{-}phen)_3^{3+} \rightarrow M_2 + 2Co(o\text{-}phen)_3^{2+} \qquad (25)$$

These reactions were first order in $[M^-]$ and $[Co(o\text{-}phen)_3^{3+}]$ or $[Py^+]$ as expected for electron transfer. The iron complex, $Fe(o\text{-}phen)_3^{3+}$ reacted too rapidly for kinetic examination. The order for the rates of different metal carbonyl anions in reaction 25 was as expected from potentials, $CpFe(CO)_2^- > Re(CO)_5^- > Mn(CO)_5^- > CpMo(CO)_3^-$, but the rates are within a factor of 3. The 3-acetoxy-N-methylpyridinium reactions show the same order for different metal carbonyl anions with the rates spanning a factor of 30. For the same anions, reactions with MeI (used to define the nucleophilicity) span rates of 10^6.[35] Thus the outer-sphere reaction is much less dependent on the nature of M^-. The effect of the ligand in $Mn(CO)_4L^-$ (L = CO, PPh_3, PEt_3) is also reversed for reaction with $Co(o\text{-}phen)_3^{3+}$ (rate decreases by a factor of 6, L = CO > PEt_3 > PPh_3) in comparison to reaction with MeI (rate increases by factor of 50, L = PEt_3 > PPh_3 > CO).[1,2] The reason for the ligand dependence for the outer-sphere reactions of $Mn(CO)_4L^-$ (L = CO, PEt_3, PPh_3) has not been examined in detail, but are in an order that suggests steric effects offset the expected increase in potential. Structural studies of $Mn(CO)_4L^-$ (L = CO, PEt_3 and PPh_3) show a shortening of all Mn-CO bonds for the L = PEt_3 complex. Since oxidation would lead to bond lengthening, an increase in the intrinsic barrier may contribute to the slower reaction for the L = PEt_3 complex.

Reactions of the anions with $Co(o\text{-}phen)_2Cl_2^+$ and $CrCl_3 \cdot 3CH_3CN$ also occur by outer-sphere reactions with the dimers, M_2 as the initial products.[90] Reactions of $Co(o\text{-}phen)_2Cl_2^+$ are more rapid than reactions of $Co(o\text{-}phen)_3^{3+}$ as expected from reduction potential data. Reactions of these chloride-containing coordination complexes indicate the importance of determining initial products. The ultimate products involved mixtures of metal carbonyl dimers and metal carbonyl chlorides.[90] The dimers were shown to form initially and undergo further reaction with the coordination complex to give the metal carbonyl chloride. The dependence on the metal carbonyl anion is shown for reaction with $CrCl_3 \cdot 3CH_3CN$ in Table 3. A good correlation coefficient (0.98) for the driving force *versus* ln(k) as shown in Table 3 provides further support for an outer-sphere reaction.[90]

Table 3 Rate Constants of Reactions Between Metal Carbonyl Anions and $CrCl_3 \cdot 3THF$ excess in CH_3CN at 25°C[90]

Anion	$k(s^{-1}M^{-1})$	Anion	$k(s^{-1}M^{-1})$
$CpFe(CO)_2^-$	$2500^a \pm 100$	$CpMo(CO)_3^-$	7 ± 2
$(\eta^5\text{-}C_5Me_5)Fe(CO)_2^-$	$1500^a \pm 30$	$CpCr(CO)_3^-$	6 ± 0.5
$Re(CO)_5^-$	280 ± 20	$Co(CO)_4^-$	NR
$Mn(CO)_5^-$	19 ± 1		

[a] The rate was too rapid to measure accurately by IR stopped-flow, but instead was obtained by dividing the k_{obs} value for the reaction between 0.001 M anion and 0.005 M $CrCl_3 \cdot 3THF$ by the concentration of $CrCl_3 \cdot 3THF$ used.

Reactions with Metal Carbonyl Dimers and Clusters

Reactions of mononuclear metal carbonyl anions, M^- ($M^- = Co(CO)_4^-$, $CpFe(CO)_2^-$, $Re(CO)_5^-$, $Mn(CO)_4L^-$; L = CO, PPh_3, PBu_3, $P(OPh)_3$, $CpM''(CO)_3$; M'' = Cr, Mo, W) with metal carbonyl dimers, M'_2($M'_2 = Co_2(CO)_8$, $Cp_2Fe_2(CO)_4$, $Re_2(CO)_{10}$,$Mn_2(CO)_{10}$,$Cp_2M_2''(CO)_6$; M'' = Cr, Mo, W, and $Cp_2Ru_2(CO)_4$) were examined.[36]

$$2M^- + M'_2 \rightarrow M_2 + 2M'^- \tag{26}$$

The direction of these reactions is correctly predicted from the two-electron reduction potentials for the dimers ($M_2 + 2e^- \rightarrow 2M^-$ (see Table 2)). The anion of any dimer with a more negative two electron potential will react by reaction 26. Thus, for instance, $CpFe(CO)_2^-$ reacts with all dimers by reaction 26. Each reaction is clean with only M_2 and M^- formed. The kinetics show the rate to have a first order dependence on $[M^-]$ and $[M'_2]$.[36] For a given M'_2 the nature of M^- has a relatively small effect on the rate of the reaction, consistent with an outer-sphere process. All dimers that contain a cyclopentadienyl group are more reactive than expected from the potential. An initial suggestion of ring-slippage for the cyclopentadienyl complexes could not be confirmed from reactions of $(\eta^5\text{-indenyl})_2Mo_2(CO)_6$ which was only marginally more rapid than the cyclopentadienyl complex.[91] Product distributions for reactions of heterobimetallic complexes were also consistent with a different mechanism for dimers containing a cyclopentadienyl ligand, although the nature of the difference in mechanism is not yet established.[36]

Reaction of mononuclear metal carbonyl anions with trinuclear clusters of Group 8 ($M_3(CO)_{12}$, M = Fe, Ru, Os) at ambient conditions leads to four separate outcomes:[37] (1) formation of the metal carbonyl dimer and the trinuclear dianion which occurs whenever the two-electron reduction potential for the dimer is more negative than for the trinuclear cluster; (2) formation of $MFe_2(CO)_7^-$ by elimination of $Fe(CO)_5$ from $Fe_3(CO)_{12}$ which occurs for M = $Re(CO)_5$, $Mn(CO)_5$, and $CpMo(CO)_3$; (3) formation of the adduct, $MRu_3(CO)_{11}^-$, from $Ru_3(CO)_{12}$ which occurs for $Re(CO)_5$; and (4) no reaction when the two-electron reduction potential for the trinuclear complex is more negative than for the dimer. For complexes where the two-electron potential for the cluster is more negative than for the dimer, reaction of $M_3'(CO)_{11}^{2-}$ with M_2 to give $M'_3(CO)_{12}$ and $2M^-$ is observed. The observed reactions allow an estimate of the two-electron reduction potentials for the trinuclear clusters which are given in Table 2.[57] The kinetics of all of these reactions indicate a first-order dependence on the oxidant and on the reductant and are most consistent with outer-sphere electron transfer.

To verify the two-electron reduction potentials for $M_3(CO)_{12}$, reactions between the trinuclear clusters and dianions were examined.[92]

$$M_3(CO)_{11}^{2-} + M'_3(CO)_{12} \rightarrow M_3(CO)_{12} + M'_3(CO)_{11}^{2-}$$

$$M = Os;\ M' = Fe, Ru \qquad (27)$$

$$M = Ru;\ M' = Fe$$

Thus these reactions occur as expected from the estimated potentials. Isotopic labeling shows the CO's to become scrambled, consistent with an initial single electron transfer to the radical anions, $M_3(CO)^{\cdot-}_{11\text{ or }12}$ where CO scrambling occurs, followed by a second electron transfer.[92]

Other Electron Transfer Reactions

In several other reactions of metal carbonyl anions, electron transfer has been observed. In the following sections, electron transfer reactions: (1) of $Fe(CO)_4{}^{2-}$ with $Mn_2(CO)_{10}$, (2) metal carbonyl anions with cations, (3) metal carbonyl anions with metal carbonyl halides; and (4) $CpFe(CO)_2{}^-$ with acetyl complexes of manganese and molybdenum will be discussed.

Reaction of $Fe(CO)_4{}^{2-}$ with $Mn_2(CO)_{10}$. I have chosen to highlight this reaction to emphasize that $Fe(CO)_4{}^{2-}$ which has been termed a "super nucleophile", may also react by an outer-sphere electron transfer.[93]

$$2Fe(CO)_4{}^{2-} + Mn_2(CO)_{10} \rightarrow Fe_2(CO)_8{}^{2-} + 2Mn(CO)_5{}^- \qquad (28)$$

The $Fe_2(CO)_8{}^{2-}$ could form from reaction of $Fe(CO)_4{}^{2-}$ with $Fe(CO)_5$ or by dimerization of $Fe(CO)_4{}^{\cdot-}$. However, reaction of $Fe(CO)_4{}^{2-}$ with $Fe(CO)_5$ occurs two orders of magnitude more slowly than reaction of $Fe(CO)_4{}^{2-}$ with $Mn_2(CO)_{10}$, implicating $Fe(CO)_4{}^{\cdot-}$ in the reaction.[93] Slow addition of $Fe(CO)_4{}^{2-}$ prohibits the generation of sufficient quantities of $Fe(CO)_4{}^{\cdot-}$ to dimerize and $MnFe(CO)_9{}^-$ becomes a significant product from coupling of $Fe(CO)_4{}^{\cdot-}$ and $Mn(CO)_5$.[93] Product and rate studies provide strong support for an outer-sphere electron transfer mechanism for reaction of $Fe(CO)_4{}^{2-}$ with $Mn_2(CO)_{10}$.

Metal carbonyl cations

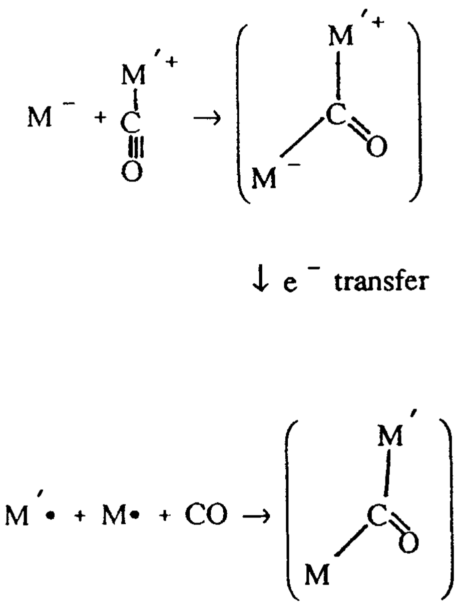
Reactions of metal carbonyl anions with metal carbonyl cations take two paths depending on the nature of the metal carbonyl moieties:[73,74,94,95] (1) When the reactant anion is more nucleophilic than the product anion in a CO^{2+} transfer reaction, transfer of CO^{2+} occurs; and (2) When the reactant anion is less nucleophilic, an electron transfer occurs. It is this latter reaction that is germane to our discussion. The reaction can be illustrated by reaction of $Mn(CO)_5{}^-$ with $Re(CO)_6{}^+$.[74]

$$Mn(CO)_5{}^- + Re(CO)_6{}^+ \rightarrow MnRe(CO)_{10} + Mn_2(CO)_{10} + Re_2(CO)_{10} + CO \qquad (29)$$

The characteristics of these reactions are as expected for odd-electron intermediates with a nearly statistical mixture of bimetallic complexes. For phosphine substituted species, where metal-metal bond formation doesn't readily occur, abstraction of hydrogen from solvent produces hydride complexes.[94]

$$2Mn(CO)_5^- + 2Mn(CO)_4(PPh_3)_2^+ \rightarrow Mn_2(CO)_{10} + 2HMn(CO)_4(PPh_3) + CO \quad (30)$$

This is also typical for odd-electron complexes. Except for unusual results when labeled CO is used, these would be readily interpreted as outer-sphere electron transfer. Reaction 29 is slowed under an atmosphere of ^{13}CO and provides selective enrichment of the $Mn(CO)_5^-$ (essentially no enrichment of $Re(CO)_6^+$).[95] These results cannot be accommodated by an outer-sphere mechanism and indicate an inner-sphere electron transfer. The most reasonable interpretation involves nucleophilic attack of the metal carbonyl anion on a carbon of the metal carbonyl cation.[95] The scheme below illustrates a mechanism to accommodate these results.



(31)

(32)

(33)

$$2M'\cdot \rightarrow M'_2 \quad (34)$$

$$2M\cdot \rightarrow M_2 \quad (35)$$

$$M\cdot + M'\cdot \rightarrow MM' \quad (36)$$

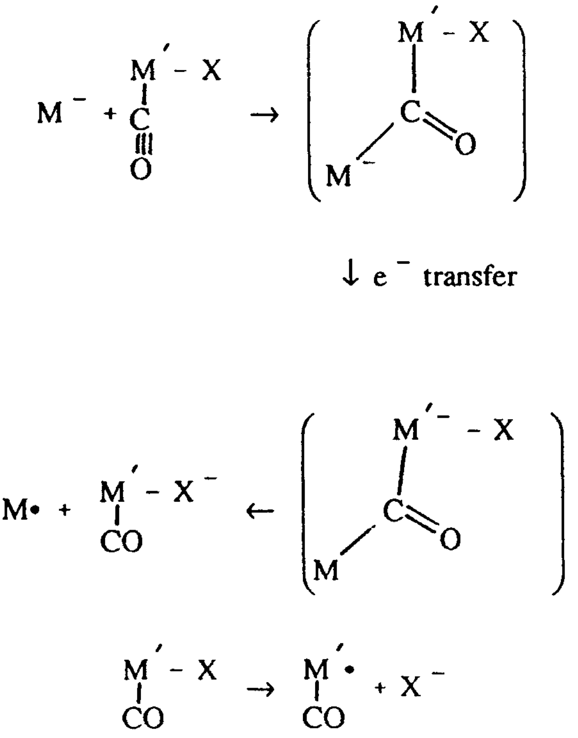
Selective enrichment of the anion occurs through the precursor complex formed in the initial reaction (reaction 31).

Reaction with metal carbonyl halides

Reactions of metal carbonyl anions with metal carbonyl halides are very similar to those with metal carbonyl cations.[91] When the reactant anion is less nucleophilic than the product anion in a halogen transfer, an electron transfer occurs.

$$Re(CO)_5^- + CpFe(CO)_2Br \rightarrow Re_2(CO)_{10} + Cp_2Fe_2(CO)_4 + Cp(CO)_2FeRe(CO)_5 + Br^- \quad (37)$$

The dependence of the rate on the nature of the halide is opposite to that expected from potentials indicating that outer-sphere electron transfer is probably not occurring.[91] The magnitude of the rate effect on the halogen (~ a factor of 10) is too small for a halogen-bridge mechanism. As for the reaction of metal carbonyl anions with metal carbonyl cations, a nucleophilic attack by the anion on a carbonyl was suggested as the mechanism for the electron transfer. A suggested scheme is shown below.



(38)

(39)

(40)

(41)

Reaction of $CpFe(CO)_2^-$ with acetyl complexes

Reaction of $CpFe(CO)_2^-$ with $CH_3C(O)Mn(CO)_5$ results in $CpFe(CO)_2Me$, $Cp_2Fe_2(CO)_4$ and $Mn(CO)_5^-$.[96]

$$CpFe(CO)_2^- + CH_3C(O)Mn(CO)_5 \rightarrow CH_3FeCp(CO)_2 + Cp_2Fe_2(CO)_4 + Mn(CO)_5^- \qquad (42)$$

Use of a ^{13}C label on the carbonyl of the acetyl gives label only on the carbonyl of $CH_3FeCp(CO)_2$. This indicates transfer of the acetyl from manganese to the iron, but to a complex activated for CO dissociation because $CH_3C(O)FeCp(CO)_2$ does not decarbonylate under the experimental conditions. The products were best accommodated by the following outer-sphere, electron transfer mechanism.

$$CpFe(CO)_2^- + CH_3C(O)Mn(CO)_5 \rightarrow CpFe(CO)_2\cdot + CH_3C(O)Mn(CO)_5^{\dot{-}} \quad (43)$$

$$2\ CpFe(CO)_2\cdot \rightarrow Cp_2Fe_2(CO)_4 \quad (44)$$

$$CH_3C(O)Mn(CO)_5^{\dot{-}} \rightarrow Mn(CO)_5^- + CH_3C(O)\cdot \quad (45)$$

$$CpFe(CO)_2^- + CH_3C(O)\cdot \rightarrow CH_3C(O)FeCp(CO)_2^{\dot{-}} \quad (46)$$

$$CH_3C(O)FeCp(CO)_2^{\dot{-}} \rightarrow CH_3FeCp(CO)_2 + CO + e^- \quad (47)$$

SUMMARY

Similar to the organic reactions of carbanions, metal carbonyl anions exhibit one- and two-electron reactions. The two-electron processes involving transfer of groups between metal centers are related to the nucleophilicity. The one-electron processes are primarily outer-sphere electron transfer for the metal carbonyl anions. However, in contrast to organic reactions, the metal carbonyl anions may undergo inner-sphere electron transfer. Reactions of metal carbonyl anions of low nucleophilicity with metal carbonyl cations or halides are best interpreted as inner-sphere, one-electron transfer.

Acknowledgement

Ted Brown introduced me to metal carbonyl complexes and the utility of isotopic labeling for mechanistic interpretation. His guidance is greatly appreciated. The Department of Energy (ER 13775) has supported our electron transfer research.

References

1. H. Taube, *J. Chem. Ed.* **45**, 452 (1968).
2. L.E. Bennett, *Prog. Inorg. Chem.* **18**, 2 (1973).
3. J.E. Earley, *Prog. Inorg. Chem.* **13**, 243 (1970).
4. N. Sutin, *Acc. Chem. Res.* **1**, 225 (1968).
5. H. Taube and E.S. Gould, *Acc. Chem. Res.* **2**, 321 (1969).
6. A. Haim, *Acc. Chem. Res.* **8**, 264 (1975).
7. F. Moattar, J.R. Walton and L.E. Bennett, *Inorg. Chem.* **22**, 550 (1983).
8. N. Sutin, *Prog. Inorg. Chem.* **36**, 441 (1983).
9. R.A. Marcus, *Ann. Rev. Phys. Chem.* **15**, 155 (1964).
10. T.J. Meyer, *Prog. Inorg. Chem.* **30**, 389 (1983).
11. J.K. Kochi, *J. Organomet, Chem.* **300**, 139 (1986).
12. J.R. Eyler and D.E. Richardson, *J. Am. Chem. Soc.* **107**, 6130 (1985).
13. W.E. Geiger and N.G. Connelly, *Adv. Organomet. Chem.* **24**, 87 (1985).
14. I. Wender and P. Pino, *Metal Carbonyls in Organic Synthesis,* Vol. 1, Interscience (John Wiley and Sons, New York, 1968).
15. R.B. King, *Adv. Organometal. Chem.* **2**, 157 (1964).
16. J.E. Ellis, *J. Organomet. Chem.* **86**, 1 (1975).
17. T. Kruck and M. Hoffer, *Chem. Ber.* **97**, 2289 (1964).
18. M.' Absi-Halabi, J.D. Atwood, N.P. Forbus and T.L. Brown, *J. Am. Chem. Soc.* **102**, 6248 (1980).
19. The mechanism of these reactions are not meant to be indicated, merely the result. If the dimer is considered composed of two 17-electron metal centers, a net electron transfer has taken place. This is most correct for reaction 4 and least valid for reaction 6.
20. R.B. King, P.M. Treichel and F.G.A. Stone, *Chem. Ind.,* 747 (1961).

21. N. Flitcroft, D.K. Huggins and H.D. Kaesz, *Inorg. Chem.* **3**, 1123 (1964).
22. G. Sbrignaldello, *Inorg. Chim. Acta* **48**, 237 (1981).
23. P. Chini, G. Longoni and V.G. Albano, *Adv. Organomet. Chem.* **14**, 285 (1976).
24. D.J. Maltbie and J.D. Atwood, unpublished results.
25. W.L. Gladfelter and G.L. Geoffroy, *Adv. Organomet. Chem.* **18**, 207 (1980).
26. N.G. Connelly, *Chem. Soc. Rev.* **18**, 153 (1989).
27. (a) J.P. Collman, *Acc. Chem. Res.* **8**, 342 (1975) and references therein; (b) J.P. Collman, R.G. Finke, J.N. Cawse and J.I. Brauman, *J. Am. Chem. Soc.* **99**, 2515 (1977); (c) R.G. Teller, R.G. Finke, J.P. Collman, H.B. Chin and R. Bau, *J. Am. Chem. Soc.* **99**, 1104 (1977).
28. B.D. Dombek, *J. Organomet. Chem.* **372**, 151 (1989).
29. D. Forster, *Adv. Organomet. Chem.* **17**, 255 (1979).
30. S.A. Roth, G.D. Stucky, H.M. Feder, M.J. Chen and J.W. Rathke, *Organometallics* **3**, 708 (1984).
31. C.-H. Liu and C.-H. Chung, *J. Organomet. Chem.* **420**, 119 (1991).
32. T. Szymańska-Buzar, *J. Mol. Catal.* **68**, 177 (1991).
33. M. Tilset and V.D. Parker, *J. Am. Chem. Soc.* **111**, 6711 (1989).
34. R.F. Jordan and J.R. Norton, *J. Am. Chem. Soc.* **104**, 1255 (1982).
35. (a) C.-K. Lai, W.G. Feighery, Y. Zhen, J.D. Atwood, *Inorg. Chem.* **28**, 3929 (1989); (b) R.E. Dessy, R.L. Pohl, R.B. King, *J. Am. Chem. Soc.* **88**, 5121 (1966); (c) R.G. Pearson, P.E. Figdore, *J. Am. Chem. Soc.* **102**, 1541 (1980).
36. M.S. Corraine and J.D. Atwood, *Organometallics* **10**, 2315 (1991).
37. M.S. Corraine and J.D. Atwood, *Organometallics* **10**, 2647 (1991).
38. (a) J.R. Pugh and T.J. Meyer, *J. Am. Chem. Soc.* **110**, 8245 (1988); (b) J.R. Pugh and T.J. Meyer, *J. Am. Chem. Soc.* **114**, 3784 (1992).
39. A.E.S. Miller and J.L. Beauchamp, *J. Am. Chem. Soc.* **113**, 8765 (1991).
40. (a) O.B. Ryan, M. Tilset and V.D. Parker, *Organometallics* **10**, 298 (1991); (b) O.B. Ryan, M. Tilset and V.D. Parker, *J. Am. Chem. Soc.* **112**, 2618 (1990); (c) M. Tilset and V.D. Parker, *J. Am. Chem. Soc.* **111**, 6711 (1989).
41. M.Y. Darensbourg, *Prog. Inorg. Chem.* **33**, 221 (1985).
42. P. Wang and J.D. Atwood, *Organometallics*, in press.
43. J.N. Braddock and T.J. Meyer, *Inorg. Chem.* **12**, 723 (1973).
44. J. Chatt, G.J. Leigh, H. Neukomm, C.J. Pickett and D.R. Stanley, *J. Chem. Soc. Dalton*, **121** (1980).
45. F. Calderazzo and G. Pampaloni, *J. Chem. Soc. Chem. Comm.* 1249 (1984).
46. T.G. Richmond, Q.Z. Shi, W.C. Trogler and F. Basolo, *J. Am. Chem. Soc.* **106**, 76 (1984).
47. D. Astruc, *Angew Chem. Int. Ed. Engl.* **27**, 643 (1988) and references therein.
48. M. Julliard and M. Chanon, *Chem. Rev.* **83**, 425 (1983) and references therein.
49. M. Chanon, *Bull. Soc. Chim. Fr.* 197 (1982).
50. M. Chanon, *Bull. Soc. Chim. Fr.* 209 (1985).
51. M. Chanon, *Acc. Chem. Res.* **20**, 214 (1987).
52. M.-H. Desbois and D. Astruc. *J. Chem. Soc. Comm.* 472 (1988).
53. J.-N. Verpeaux, M.-H. Desbois, A. Madonik, C. Amatore and D. Astruc, *Organometallics* **9**, 630 (1990).
54. A.E. Stiegman and D.R. Tyler, *Comments Inorg. Chem.* **5**, 215 (1986).
55. W.C. Trogler, *Int. J. Chem. Kinetics* **19**, 1025 (1987).
56. S.B. McCullen, H.W. Walker and TL.. Brown, *J. Am. Chem. Soc.* **104**, 4007 (1982).
57. M.R. Burke and T.L. Brown, *J. Am. Chem. Soc.* **111**, 5185 (1989).
58. P. Chen, R. Duesing, G. Tapolsky and T.J. Meyer, *J. Am. Chem. Soc.* **111**, 8305 (1989).
59. J.D. Prolasiewicz, K.H. Theopold and G. Schulte, *Inorg. Chem.* **27**, 1133 (1988).
60. E.K. Byrne and K.H. Theopold, *J. Am. Chem. Soc.* **109**, 1282 (1987).
61. E.K. Byrne and K.H. Theopold, *J. Am. Chem. Soc.* **111**, 3887 (1989).
62. R.M. Nielson, M.N. Golovin, G.E. McManis and M.J. Weaver, *J. Am. Chem. Soc.* **110**, 1745 (1988).
63. G.E. McManis, R.M. Nielson, A. Gochev and M.J. Weaver, *J. Am. Chem. Soc.* **111**, 5533 (1989).
64. S. Bellard, K.A. Rubinson and G.M. Sheldrik, *Acta Cryst.* **B35**, 271 (1979).
65. R.D. Wilson and R. Bau, *J. Am. Chem. Soc.* **96**, 7601 (1974).
66. D.Z. Szalada, C. Creutz, D. Mahajan and N. Sutin, *Inorg. Chem.* **22** 2372 (1983).
67. K.Y. Lee and J.K. Kochi, *Inorg. Chem.* **28**, 567(1989).
68. K.Y. Lee, D.J. Kuchynka and J.K. Kochi, *Organometallics* **6**, 1886 (1987).

69. D.J. Kuchynka, C. Amatore and J.K. Kochi, *Inorg. Chem.* **27**, 2574 (1988).
70. D.J. Kuchynka and J.K. Kochi, *Inorg. Chem.* **28**, 855 (1989).
71. T.M. Bockman and J.K. Kochi, *J. Am. Chem. Soc.* **111**, 4669 (1989).
72. R.E. Lehman, T.M. Bockman and J.K. Kochi, *J. Am. Chem. Soc.* **112**, 458 (1990).
73. Y. Zhen and J.D. Atwood, *J. Am. Chem. Soc.* **111**, 1506 (1989).
74. Y.Q. Zhen, W.G. Feighery, C.K. Lai and J.D. Atwood, *J. Am. Chem. Soc.* **111**, 7832 (1989).
75. M.P. Castellani and D.R. Tyler. *Organometallics* **8**, 2113 (1989) and reference therein.
76. T. van der Graff, R.M.J. Hofstra, P.G.M. Schilder, M. Rijkhoff, D.J. Stufkens and J.G.M. van der Linden, *Organometallics* **10**, 3668 (1991).
77. R. Davis and F.I.C. Wilson, *J. Organomet. Chem.* **396**, 55 (1990).
78. Y. Zhang, D.K. Gosser, P.H. Rieger and D.A. Sweigart, *J. Am. Chem. Soc.* **113**, 4062 (1991).
79. K.-W. Lee and T.L. Brown, *J. Am. Chem. Soc.* **109**, 3269 (1987).
80. Y.H. Pan and D.P. Ridge, *J. Am. Chem. Soc.* **111**, 1150 (1989).
81. S.J. Sherlock, D.C. Boyd, B. Moarser and W.L. Gladfelter, *Inorg. Chem.* **30**, 3636 (1991).
82. E.S. Lewis, *J. Am. Chem. Soc.* **111**, 7576 (1989).
83. F.G. Bordwell and J.A. Harrelson, Jr., *J. Org. Chem.* **54**, 4893 (1989).
84. E.M. Arnett, K. Amarnath, N.G. Harvey and J.-P. Cheng, *Science* **247**, 423 (1990) and references therein.
85. E.M. Arnett, N.G. Harvey, K. Amarnath and J.-P. Cheng, *J. Am. Chem. Soc.* **111**, 4143 (1989).
86. D. Griller, J.A.M. Simoes, P. Mulder, B.A. Sim and D.D.M. Wayner, *J. Am Chem. Soc.* **111**, 7872 (1989).
87. (a) L. Eberson and S.S. Shaik, *J. Am. Chem. Soc.* **112**, 4484 (1990);(b) B. Reitstoen and V.D. Parker, *J. Am. Chem. Soc.* **113**, 6954 (1991); (c) V. D. Parker, Y. Chao and B. Reitstoen, *J. Am. Chem. Soc.* **113**, 2337 (1991); (d) C. Zou, J.B. Miers, R.M. Ballew, D.D. Dlott and G.B. Schuster, *J. Am. Chem. Soc.* **113**, 7823 (1991).
88. (a) C.D. Ritchie and S. Lu, *J. Am. Chem. Soc.* **112**, 7748 (1990); (b) J.A. Dodd, S. Baer, C.R. Moylan and J.I. Brauman, *J. Am. Chem. Soc.* **113**, 5942 (1991).
89. M.S. Corraine, C.K. Lai, Y. Zhen, M.R. Churchill, L.A. Buttrey, J.W. Ziller and J.D. Atwood, *Organometallics* **11**, 35 (1992).
90. C.K. Lai, M.S. Corraine and J.D. Atwood *Organometallics* **11**, 582 (1992).
91. W.S. Striejewske, R.F. See, M.R. Churchill and J.D. Atwood, *Organometallics* **12**, 4413 (1993).
92. M.S. Corraine and J.D. Atwood *Organometallics* **10**, 2985 (1991).
93. Y. Zhen and J.D. Atwood, *Organometallics* **10**, 2778 (1991).
94. Y. Zhen and J.D. Atwood, *J. Coord. Chem.*, **25**, 229 (1992).
95. Y. Zhen, W.G. Feighery and J.D. Atwood, *J. Am. Chem. Soc.* **113**, 3616 (1991).
96. P. Wang and J.D. Atwood, *J. Coord. Chem.*, in press.