with $Cr(CO)_5(THF)$ with loss of the SO_3 unit to give a heterotrimetallic sulfido cluster. We in turn have found that the SO_3 moiety can be stripped off even by weak organic bases such as amines and alcohols to regenerate **1** under mild conditions. This suggests the possibility of a catalytic cycle wherein SO_2 is brought to react with bases [B] to give S^0 and S^{VI} products:

$$1.5SO_2 + M\text{–}S\text{–}M \rightarrow 0.5S + M\text{–}SSO_3\text{–}M$$

$$\underline{M\text{–}SSO_3\text{–}M + [B] \rightarrow M\text{–}S\text{–}M + [B]{\cdot}SO_3}$$

$$1.5SO_2 + [B] \rightarrow 0.5S + [B]{\cdot}SO_3$$

Assuming that [B] is an inexpensive organic compound (e.g., ROH), conversion of SO_2 to useful sulfonylated organics may be a feasible SO_2 recovery method. The chemistry of **2** will be investigated further to determine whether the above cycle can be catalytic and to survey the reactivity of **2** with hydride reducing agents and strong acids.

Summarizing, the oxygen-transfer chemistry of SO_2 and related thiosulfate formation is a promising area for future development. The facile reactions of $Cp^*{}_2Mo_2(S_2)(S)(S_2O_3)$ demonstrate that the thiosulfate ligand possesses versatile reactivity and is not merely a terminal end product of partial SO_2 reduction. The role of the metal center in this chemistry is undefined and conceivably the reaction sites are entirely ligand-based. Further examination of small molecule reactivity with the numerous known metal–sulfide clusters could lead to rich chemistry and excellent systems for catalytic conversion of SO_2 and other noxious small molecules (e.g., NO_x[32]).

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Supplementary Material Available: Fractional coordinates (Tables Is and IIs) and anisotropic thermal parameters (Tables IIIs and IVs) (4 pages); observed and calculated structure factors (Tables Vs and VIs) (23 pages). Ordering information is given on any current masthead page.

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[32] Preliminary results[29] show that $[Cp^*MoS(SH)]_2$ also catalyzes reduction of NO by H_2 to give N_2, N_2O, and H_2O, but at a much slower rate than for SO_2 reduction (amines did not appear to promote the reaction significantly). Equimolar $NO\text{–}SO_2$ mixtures were reduced to the latter products plus S_8 at a rate halfway between NO and SO_2 reduction.

Steric and Electronic Factors That Control Two-Electron Processes between Metal Carbonyl Cations and Anions

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Abstract: Reactions of metal carbonyl cations ($Mn(CO)_6^+$, $Re(CO)_6^+$, $Mn(CO)_5PPh_3^+$, $Mn(CO)_4(PPh_3)_2^+$, $Mn(CO)_5PEt_3^+$, $Mn(CO)_5PPh_2Me^+$, $Re(CO)_5PPh_3^+$, and $CpFe(CO)_3^+$) with metal carbonyl anions ($Co(CO)_3PPh_3^-$, $Co(CO)_4^-$, $Mn(CO)_5^-$, $Mn(CO)_4PPh_3^-$, $Mn(CO)_4PEt_3^-$, $Mn(CO)_4PPh_2Me^-$, $Mn(CO)_3(PPh_3)_2^-$, $CpFe(CO)_2^-$, $Re(CO)_5^-$, and $Re(CO)_4PPh_3^-$) are reported. Peak potentials are reported for all ions, and nucleophilicities (as measured by reaction with MeI) are reported for the anions. Reaction of any metal carbonyl cation with any metal carbonyl anion leads ultimately to binuclear products, which are the thermodynamic products. The binuclear products are formed by a single-electron transfer. In over half of the reactions between metal carbonyl cations and anions, a two-electron change results in a new metal carbonyl cation and anion. The two-electron change may be considered mechanistically as a CO^{2+} transfer with the more nucleophilic of the two anions retaining the CO^{2+}. The kinetic and thermodynamic driving forces and the suggested mechanism are examined.

Electron transfer is one of the fundamental reaction types in chemistry.[1,2] Through elegant studies, outer-sphere electron transfer,[1] inner-sphere electron transfer,[1] long-range electron transfer,[3] and single-electron-transfer reactions[2] are well understood. In our research, aimed at defining the mechanistic possibilities for organometallic electron-transfer reactions, we have found that in some cases reactions of metal carbonyl cations with metal carbonyl anions result in a single-event two-electron transfer (or a transfer of a CO^{2+} group).[4] In this manuscript we examine the scope of this reaction and the kinetic and thermodynamic driving forces for such a reaction.

The thermodynamic parameters for electron-transfer reactions are most easily assessed from the standard potential for the reaction. Most of the simple metal carbonyl cations and anions have been electrochemically examined a number of times,[5] but since the electrochemical reactions are irreversible, reliable values for E_0 are not known for most metal carbonyl complexes.

In some cases inner-sphere electron-transfer reactions are accompanied by transfer of an atom between the redox-active centers. This often results when the substitutional reactivity of the two centers is markedly affected by the oxidation or reduction as in

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the classic reduction of $Co(NH_3)_5Cl^{2+}$ by $Cr(H_2O)_6^{2+}$ resulting in $Cr(H_2O)_5Cl^{2+}$ and $Co(H_2O)_6^{2+}$.[1k] Oxide transfer is observed between main-group complexes, although in most cases the mechanism appears to involve one-electron transfer.[6]

Electron-transfer reactions have been utilized in organometallic chemistry through disproportionation, redox condensation, and electron-transfer catalysis.[7] Only recently have there been significant efforts to define the mechanisms of organometallic electron-transfer reactions. Two studies have shown that oxidation of $M_2(CO)_{10}$ (M_2 = Mn_2, Re_2, MnRe) occurs by an outer-sphere process.[8] A similar conclusion was reached for oxidation of $Cp_2Fe_2(CO)_4$.[9] Self-exchange rates have been determined for three complexes with phosphorus donor ligands, $M(dmpe)_3^{+/2+}$ (M = Tc, Re) and $Co(P(OMe)_3)_4^{-/0}$.[10] Several papers describing the annihilation of metal carbonyl cations and anions have appeared.[11] Our approach to mechanisms of electron transfer in organometallic reactions has centered on oxidation of metal carbonyl anions with metal carbonyl cations, with metal carbonyl dimers and with inorganic oxidants of known electron-transfer mechanisms.[4,12] Preliminary studies indicate three separate mechanisms: (1) two-electron transfer accompanied by CO transfer, (2) single-electron transfer through a nucleophilic attack mechanism, and (3) outer-sphere electron transfer.

Experimental Section

$Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Co_2(CO)_8$, $Cp_2Fe_2(CO)_4$, PPh_3, PEt_3, and PPh_2Me were purchased from Strem Chemical Co. and used as received. [PPN][Cl] (PPN = bis(triphenylphosphine)iminium) was purchased from either Strem Chemical Co. or Aldrich Chemical Corp. CH_3I (Aldrich) was purified on an alumina column before use. ^{13}CO gas (99%) was purchased from Icon Service, Inc. Infrared spectra were recorded on a Beckman 4240 infrared spectrophotometer. Mass spectra were recorded on a VG 70-SE mass spectrometer.

THF was first refluxed with CaH_2, distilled onto Na–benzophenone and distilled from Na–benzophenone under N_2. Hexanes and CH_3CN were distilled from CaH_2 under N_2. Anhydrous diethyl ether was distilled from Na–benzophenone under N_2. Acetone was fractionally distilled from P_2O_5 three times and distilled again under N_2.

Substituted dimers, $M_2(CO)_8L_2$, were prepared thermally (L = PPh_3, M = Mn, Re) or photolytically (L = PPh_2Me, PEt_3; M = Mn) according to literature procedures; infrared spectra were consistent with those previously reported.[13] Compounds enriched with ^{13}CO were prepared as described below: $Mn_2(^{13}CO)_{10}$ was prepared by photolyzing (100-W Ace-Hanovia high-pressure mercury lamp) 0.9 g of $Mn_2(CO)_{10}$ in 30 mL of benzene under 40 psi of ^{13}CO in a 90-mL pressure tube (Fisher-Porter). After 24 h the gas was removed and fresh ^{13}CO added. Repeating four times resulted in 78% enrichment, calculated from the mass spectrum. $Re_2(CO)_{10}$ was enriched similarly at 40 psi but only once in a 275-mL pressure tube. The resulting enrichment was shown by a mass spectrum to be 68%.

Preparation of Anions. The complexes $[PPN][Co(CO)_4]$, $[PPN][Mn(CO)_5]$, $[PPN][Mn(^{13}CO)_5]$, $[PPN][Mn(CO)_4PPh_3]$, $[PPN][Mn(CO)_4PPh_2Me]$, $[PPN][Mn(CO)_4PEt_3]$, $[PPN][Co(CO)_3PPh_3]$, and $[PPN][CpFe(CO)_2]$ were prepared through reduction of the corresponding dimer by modification of the procedure reported for $[PPN][Co(CO)_4]$.[14] A THF solution (30 mL) containing $Co_2(CO)_8$ (2.0 g) was stirred over excess Na (Hg) for 2 h. The supernatant was poured away from the amalgam and the solvent removed under vacuum. [PPN][Cl] (3.3 g) dissolved in a minimum of CH_3CN was added to the solid and stirred for 15 min. The CH_3CN was removed, and the $[PPN][Co(CO)_4]$ was extracted with THF. The THF extract was filtered (at least twice) through a medium-fritted glass filter with Celite filter aid until a clear solution was obtained. The volume of THF was reduced to 10 mL and diethyl ether slowly added to induce crystallization. The yields were all nearly quantitative.

Table I. Infrared Spectra of the Metal Carbonyl Anions

compd	solvent	ν_{CO}
$[PPN][Co(CO)_3PPh_3]$	CH_3CN	1926 m, 1830 br, vs
$[PPN][Co(CO)_4]$	CH_3CN	1890 s
$[PPN][Mn(CO)_5]$	THF	1887 m, 1856 s
	CH_3CN	1897 m, 1860 s
$[PPN][Mn(CO)_4PPh_3]$	CH_3CN	1938 s, 1838 w, 1806 vs
$[PPN][Mn(CO)_4PEt_3]$	CH_3CN	1928 s, 1823 w, 1790 vs
$[PPN][Mn(CO)_4PPh_2Me]$	CH_3CN	1936 s, 1836 w, 1802 vs,
$[PPN][Mn(CO)_3(PPh_3)_2]$	CH_3CN	1747
$[PPN][CpFe(CO)_2]$	CH_3CN	1860 vs, 1784 vs
$[PPN][Re(CO)_5]$	THF	1902 m, 1857 s
	CH_3CN	1914 m, 1860 s
$[PPN][Re(CO)_4PPh_3]$	CH_3CN	1947 m, 1845 w, 1807 s

Table II. Infrared Spectra of the Metal Carbonyl Cations in CH_3CN

compd	ν_{CO}
$[Mn(CO)_6][BF_4]$	2092
$[Re(CO)_6][BF_4]$	2082
$[Mn(CO)_5PPh_3][ClO_4]$	2141 m, 2051 vs
$[Mn(CO)_4(PPh_3)_2][ClO_4]$	2002
$[Mn(CO)_5PEt_3][ClO_4]$	2140 m, 2045 vs
$[Mn(CO)_5PPh_2Me][ClO_4]$	2143 m, 2053 s
$[Re(CO)_5PPh_3][ClO_4]$	2157 m, 2048 s
$[CpFe(CO)_3][BF_4]$	2122 s, 2073 s

$[PPN][Re(CO)_5]$ and $[PPN][Re(^{13}CO)_5]$ are more easily prepared by reduction of the dimers in diethyl ether.[15] The remainder of the procedure was analogous to that described for $[PPN][Co(CO)_4]$.

$[PPN][Re(CO)_4PPh_3]$ and $[PPN][Mn(CO)_3(PPh_3)_2]$ could not be prepared by reduction of the dimers but were conveniently prepared by reduction of the bromides $Re(CO)_4PPh_3Br$[16] and $Mn(CO)_3(PPh_3)_2Br$.[17] The remainder of the procedure was analogous to that of $[PPN][Co(CO)_4]$.

The infrared spectra of the anions are given in Table I; microanalyses are given in Table S1 of the supplementary material.

Preparation of Cations. The cations $[Mn(CO)_6][BF_4]$, $[Mn(^{13}CO)_6][BF_4]$, $[Re(CO)_6][BF_4]$, $[Mn(CO)_5(CH_3CN)][BF_4]$, $[Mn(CO)_5PPh_3][ClO_4]$, $[Mn(CO)_5PPh_2Me][ClO_4]$, and $[Mn(CO)_5PEt_3][ClO_4]$ were prepared by literature procedures.[18] $[CpFe(CO)_3][BF_4]$ was prepared by the same procedure used for $[Re(CO)_6][BF_4]$.[18a]

$[Re(CO)_5PPh_3][ClO_4]$ was prepared by modification of the procedure used for $[Mn(CO)_5PPh_3][ClO_4]$. A solution of 0.5 g of $Re(CO)_5Br$ in 40 mL of CH_2Cl_2 was stirred with 0.52 g of $AgClO_4$ in a foil-wrapped flask under N_2 for 10 h. The solution was filtered under N_2 and 0.35 g of PPh_3 was added. After stirring for 5 h the solvent was reduced to 5 mL under vacuum and 20 mL of diethyl ether added to induce precipitation of $[Re(CO)_5PPh_3][ClO_4]$. The product was recrystallized from CH_3CN/Et_2O to give white crystals.

$[Mn(CO)_4(PPh_3)_2][ClO_4]$ was prepared by the same procedure as $[Re(CO)_5PPh_3][ClO_4]$ using $Mn(CO)_4(PPh_3)Br$. The product was recrystallized from CH_3CN/Et_2O.

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The infrared spectra of the cations are given in Table II; microanalyses are reported in Table S1 of the supplementary material.

Reactions between Cations and Anions. For each reaction a known molar ratio of the two reactants (typically 20–30 mg) was mixed in 5–10 mL of CH_3CN. An infrared spectrum was immediately recorded, and the reaction was followed by infrared until completion. The solvent was removed, and the binuclear products were extracted into hexanes or benzene, separated by column or thin-layer chromatography, and characterized by infrared spectroscopy. The infrared spectra of the binuclear products are given in the supplemental data (Table S2 of the supplementary material). The remaining solid was dissolved in CH_3CN and also characterized by infrared spectra.

Labeling Studies. The reaction of $Re(CO)_5^-$ with $Mn(CO)_6^+$ was examined in the presence of ^{13}CO by the following procedure. In an inert-atmosphere glovebox [PPN][$Re(CO)_5$] (56 mg) was dissolved in 6 mL of CH_3CN in a pressure tube. The tube was evacuated by three freeze–pump–thaw cycles, and 0.6 atm of ^{13}CO was added. The solution was thawed and stirred for 10 min to dissolve the ^{13}CO. The tube was frozen in N_2(l), and an equimolar quantity of [$Mn(CO)_6$][BF_4] was added. The tube was evacuated and refilled with ^{13}CO. After stirring for 5 min the solvent was removed by vacuum. The solid was washed with benzene and THF to remove any binuclear product and the formed $Mn(CO)_5^-$ and then dissolved in CH_3CN. An infrared spectrum was recorded, and NaI was added to form $Re(CO)_5I$, suitable for mass spectroscopic analysis. The mass spectrum and the infrared spectrum showed no incorporation of ^{13}CO into $Re(CO)_6^+$.

Reaction of [PPN][$CpFe(CO)_2$] (20 mg) with [$Mn(^{13}CO)_6$][BF_4] (20 mg) in 5 mL of CH_3CN for 5 min and solvent removal gave a solid, which when extracted with hexanes, gave only $Cp_2Fe_2(CO)_4$. The mass spectrum showed 12% ^{13}C enrichment in $Cp_2Fe_2(CO)_4$.[19]

We have found that CH_3I functions very effectively to quench these reactions and to prepare for mass spectra. CH_3I reacts with the anion forming a methyl complex and generates I^- that reacts with the cation to form the iodide. This reaction has shown the enrichment in [PPN][$Re(CO)_5$]. [PPN][$Re(^{13}CO)_5$] (20 mg) was dissolved in 5 mL of CH_3CN in a pressure tube in an inert-atmosphere glovebox. The tube was sealed, removed from the glovebox, and evacuated on the high-vacuum line (three freeze–pump–thaw cycles). CH_3I was vacuum distilled onto the frozen solution, and the solution was warmed and stirred for 10 min. Mass spectral analysis of $CH_3Re(^{13}CO)_5$ showed 66% enrichment.[19]

Reaction with CH_3I was also used to determine the enrichment transferred to the cations in reaction of $Re(^{13}CO)_5^-$ with $Re(CO)_6^+$. Equimolar quantities of [PPN][$Re(^{13}CO)_5$] and [$Re(CO)_6$][BF_4] were added to a pressure tube, which was removed from the inert-atmosphere glovebox and attached to the high-vacuum line. CH_3CN was vacuum distilled onto the solid. The solution was thawed, stirred for 10 s, and frozen in N_2(l). CH_3I (1 mL) was vacuum distilled onto the solution. Mass spectral analysis showed 34% enrichment in the $Re(CO)_5I$ derived from the cation.[19]

A similar procedure was used to examine the reaction of $Re(^{13}CO)_5^-$ with $Mn(CO)_6^+$. After a reaction time of 5 min, addition of CH_3I and mass spectral analysis showed 50% enrichment in $Re(CO)_5I$.

A competition reaction between $Re(CO)_6^+$ and CH_3I for $Re(^{13}CO)_5^-$ was examined by mixing $Re(CO)_6BF_4$ and $PPNRe(^{13}CO)_5$ as solids in a pressure tube in an inert-atmosphere glovebox. The tube was attached to a high-vacuum line; a mixture of CH_3CN and CH_3I was vacuum distilled onto the solids. The reactants were thawed and stirred, and the products were analyzed for ^{13}CO enrichment. The ^{13}C was randomized between the rhenium products.

To ascertain that ^{13}CO from solution was not incorporated into the products during the quenching procedure, the reaction of $Re(CO)_6^+$ with $Mn(CO)_5^-$ was examined in the presence of ^{13}CO. [PPN][$Mn(CO)_5$] (33 mg) was dissolved in CH_3CN in a pressure tube. This tube was removed from the inert-atmosphere glovebox and attached to the high-vacuum line. The solution was freeze–pump–thawed (3×) and 0.6 atm of ^{13}CO introduced. The mixture was stirred for 10 min to allow dissolution of ^{13}CO and the solution frozen in N_2(l). [$Re(CO)_6$][BF_4] (20 mg) was added to the frozen solution and the vessel reevacuated. CH_3I (0.5 mL) was vacuum distilled onto the solution, and the ^{13}CO atmosphere was added. The solution was stirred for 20 min. Infrared and mass spectral analysis indicated no incorporation of ^{13}CO into $CH_3Mn(CO)_5$ or $Re(CO)_5I$.

Electrochemistry. Cyclic voltammetric measurements were performed on a BAS 100 electrochemical analyzer, in our modified Vacuum Atmospheres glovebox, under an atmosphere of argon. All measurements were made in acetonitrile, which was freshly distilled from P_2O_5 and stored under N_2. The supporting electrolyte was 0.1 M tetrabutylammonium tetrafluoroborate (Kodak), TBATFB, which was recrystallized three times from an ethanol solution and vacuum dried before use. The working electrode was a 3-mm platinum disk electrode, and the auxiliary electrode was a platinum wire. The reference electrode was a Ag/Ag^+ (0.01 M $AgNO_3$/0.25 M TBATFB in acetonitrile) separated from the cell by a Vycor tip. All potentials were measured and are reported versus this electrode. The cell was set up to minimize the effects of solution resistance; however, no *iR* compensation was employed in the measurements. The concentration of analyte was 10^{-3} M in all cases. All measurements were recorded at a scan speed of 100 mV/s. Under these conditions ferrocene exhibited a reversible couple at $E_{1/2}$ = 84 mV.

Table III. Peak Potentials for the Oxidation of Anions and Reduction of Cations

metal anion	E_p^-, mV	metal cation	E_p^+, mV	$E(M^+ \rightarrow M^-)$
$Co(CO)_4^-$	−206			
$Co(CO)_3PPh_3^-$	−642			
$Mn(CO)_5^-$	−480	$Mn(CO)_6^+$	−1296	−890
$Mn(CO)_4PPh_3^-$	−851	$Mn(CO)_5PPh_3^+$	−1384	−1120
$Re(CO)_5^-$	−646	$Re(CO)_6^+$	−1611	−1130
$Mn(CO)_4PEt_3^-$	−951	$Mn(CO)_5PEt_3^+$	−1666	−1310
$Mn(CO)_4PPh_2Me^-$	−895	$Mn(CO)_5PPh_2Me^+$	−1578	−1240
$Mn(CO)_3(PPh_3)_2^-$	−1133	$Mn(CO)_4(PPh_3)_2^+$	−1592	−1360
$Re(CO)_4PPh_3^-$	−923	$Re(CO)_5PPh_3^+$	−1784	−1350
$CpFe(CO)_2^-$	−1303	$CpFe(CO)_3^+$	−921	−1110

Table IV. Rates of Reactions of Metal Carbonyl Anions in CH_3CN with MeI as a Measure of Nucleophilicity[a]

complex	k_2, M^{-1} s^{-1}
$CpFe(CO)_2^-$	>1000 M^{-1} s^{-1}
$Re(CO)_5^-$	74 ± 7
$Mn(CO)_4PEt_3^-$	62 ± 4
$Mn(CO)_3(PPh_3)_2^-$	44 ± 5
$Mn(CO)_4PPh_2Me^-$	19.2 ± 0.9
$Mn(CO)_4PPh_3^-$	7.8 ± 0.4
$Mn(CO)_5^-$	1.5 ± 0.2
$Co(CO)_4^-$	0.009 ± 0.001

[a] All are the PPN^+ salts.

Results

Reaction of any of the anions listed in Table I with any of the cations listed in Table II results in formation of binuclear products.[20]

$$M^+ + M'^- \rightarrow M_2 + M'_2 + MM' \qquad (1)$$

$$M^+ = \text{a metal carbonyl cation as listed in Table II}$$

$$M'^- = \text{a metal carbonyl anion as listed in Table I}$$

The ratio of products depends on the nature and relative amounts of M^+ and M'^-. Since these reactions are irreversible (the binuclear complexes do not disproportionate in the presence of CO), the binuclear complexes may be considered as the *thermodynamic* products. The binuclear products are characterized by infrared spectroscopy; the infrared spectra are given as Table S2 in the supplementary data. The rates of reaction 1 vary from quite rapid ($CpFe(CO)_3^+$ reacts with $CpFe(CO)_2^-$ with k_2 > 2000 M^{-1} s^{-1}) to very slow ($Mn(CO)_5^-$ reacts with $Mn(CO)_5PEt_3^+$ with k_2 = 5.3×10^{-4} M^{-1} s^{-1}).

We have evaluated the oxidation of the anions and the reduction of the cations electrochemically. The electrochemistry of several of these species has been previously reported.[5] However, since the reactions are not reversible, reliable values of $E_{1/2}$ are not available. The peak potentials for the anions and cations are reported in Table III. In no case was there evidence of reverse current under these conditions. Therefore, in the absence of other information, it is not possible to relate the peak potential to the standard potentials for the charge-transfer process. However, since the potentials are all recorded under comparable conditions, these

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(19) The percent enrichment was calculated from the mass spectrum using the program MSCAL 2.0 devised by Dr. J. B. Keister.

(20) Reactions that involve formation of $Mn(CO)_3(PPh_3)_2$ and sometimes $Mn(CO)_4L$ also produce hydrides, presumably by abstraction of hydrogen from the solvent.

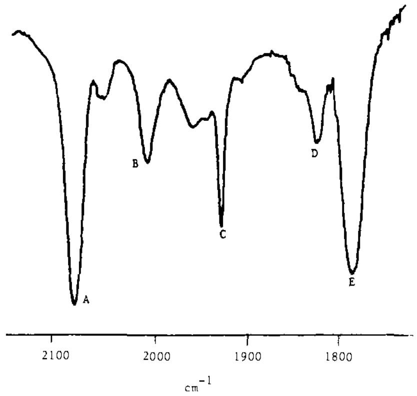

Figure 1. Infrared spectrum of the reaction between $Re(CO)_5^-$ and $Mn(CO)_5PPh_3^+$ in acetonitrile after 5 min shows $Re(CO)_6^+$ (A) and $Mn(CO)_4PPh_3^-$ (C–E). The absorptions between these arise from the binuclear products from the subsequent single-electron transfer.

values may be correlated with the observed reactivity.

We have evaluated the nucleophilicity of the metal carbonyl anions by their rates of reaction with MeI. Those rates are shown in Table IV. Values for $NaCo(CO)_4$ and $NaMn(CO)_5$ have been previously reported.[21] The values in glyme ($NaCo(CO)_4$, 0.01; $NaMn(CO)_5$, 0.77) and THF ($NaCo(CO)_4$, 0.0437; $NaMn(CO)_5$, 7.4) are in moderate agreement with our values ($PPNCo(CO)_4$, 0.009; $PPNMn(CO)_5$, 1.5) considering the difference in counterion and solvent.

For many reactions a two-electron transfer is observed prior to the single-electron transfer

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

An infrared spectrum illustrating such a reaction is shown in Figure 1. Reaction 2 is observed when the nucleophilicity of M^- is greater than the nucleophilicity of M'^-. The few exceptions will be discussed in a later section. The reduction potential for a two-electron half-reaction may be given by consideration of the process

$$M^+ \xrightarrow{E^+} M^0 \xrightarrow{E^-} M^- \tag{3}$$

where E^+ and E^- are the formal potentials for the individual one-electron steps. Thus the potential for a two-electron half-reaction

$$M^+ + 2e^- \rightarrow M^- \tag{4}$$

would be

$$E(M) = (E^+ + E^-)/2 \tag{5}$$

Realizing that in the irreversible limit the experimental peak potentials of Table I for the cathodic reactions are shifted positively and that the peak potentials for the anodic reactions are shifted negatively, we use the sum of these peak potentials as an approximation for the sum of formal potentials in eq 5. The values of E thus calculated are provided in Table III. For reaction 2 the potential can be evaluated as E_{rxn}.

$$E_{rxn} = E(M) - E(M') \tag{6}$$

With a few exceptions (all reactions involving $CpFe(CO)_2^-$, for instance), the E_{rxn} values provide a useful measure of the direction of the two-electron reaction ($+E_{rxn}$ occurs).

The two-electron-transfer reaction can be illustrated by the reaction of $Re(CO)_5^-$ with $Mn(CO)_6^+$.

$$Re(CO)_5^- + Mn(CO)_6^+ \rightarrow Re(CO)_6^+ + Mn(CO)_5^- \tag{7}$$

From Table III the driving force for this reaction is estimated to be +240 mV. Reaction 7 occurs in a few seconds to the kinetic products, $Re(CO)_6^+$ and $Mn(CO)_5^-$; the formed $Re(CO)_6^+$ and $Mn(CO)_5^-$ undergo reactions to binuclear species. Reaction 7 has been carefully examined by isotopic labeling. With $Re(^*CO)_5^-$ as reactant in reaction 7, quenching with CH_3I gave $Re(CO)_5I$ with ^{13}C enrichment of 50%. Considering the 68% starting enrichment in $Re(CO)_5^-$ and addition of one ^{12}CO, the expected value would be 56%. The reaction products are shown by infrared spectra illustrated in Figure 2. No gaseous CO was found incorporated from reaction 7 or from the quenching and analysis. There is no evidence that the reverse of reaction 7 occurs. $Re(CO)_6^+$ and $Mn(CO)_5^-$ react to give binuclear products but do not give the two-electron transfer (as expected from the potentials).

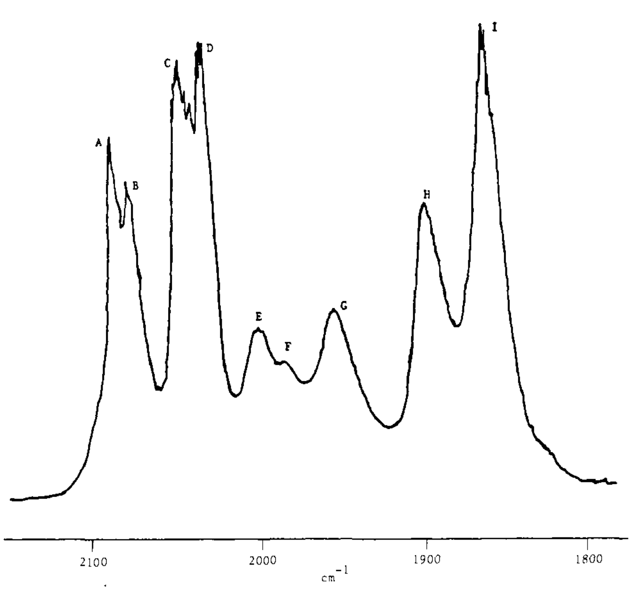

Figure 2. Infrared spectrum of the reaction between $Re(^{13}CO)_5^-$ and $Mn(CO)_6^+$ in CH_3CN shows the formation of $Re(^{13}CO)_6^+$ (B–D) and $Mn(CO)_5^-$ (I and H). A is excess $Mn(CO)_6^+$ and E–G are binuclear products.

Isotopic labeling has also been used to show that self-exchange reactions occur.

$$Re(CO)_6^+ + Re(^{13}CO)_5^- \rightleftarrows Re(^{13}CO)_5CO^+ + Re(CO)_5^- \tag{8}$$

$$Mn(CO)_6^+ + Mn(^{13}CO)_5^- \rightleftarrows Mn(^{13}CO)_5CO^+ + Mn(CO)_5^- \tag{9}$$

In reaction 9 both infrared analysis (strong absorption at 2050 cm^{-1}) and mass spectral analysis after 5 min indicated significant enrichment in the cation. The infrared spectrum also shows the enrichment.[4] The level of enrichment declined steadily until the labeled CO was equilibrated through the cation and anion after 20 min. Reaction 8 has the labeled CO randomized through the cation and anion after only 10 s. Clearly, the potential difference between reactants and products is zero for these self-exchange reactions.

All reactions of $CpFe(CO)_2^-$ with the cations listed in Table II appear to involve two-electron transfer. In these reactions $CpFe(CO)_3^+$ is not observed, presumably due to the very rapid reaction of $CpFe(CO)_3^+$ with $CpFe(CO)_2^-$ to generate $Cp_2Fe_2(CO)_4$. Reaction of $CpFe(CO)_2^-$ with $Mn(CO)_6^+$ can illustrate the reactions of $CpFe(CO)_2^-$ with cations.

$$CpFe(CO)_2^- + Mn(CO)_6^+ \rightarrow Cp_2Fe_2(CO)_4 + Mn(CO)_5^- + Mn(CO)_6^+ \rightarrow Cp_2Fe_2(CO)_4 + Mn_2(CO)_{10} \tag{10}$$

If the reaction is examined immediately after mixing, $Cp_2Fe_2(CO)_4$, $Mn(CO)_5^-$, and $Mn(CO)_6^+$ are observed. After further stirring $Mn(CO)_5^-$ and $Mn(CO)_6^+$ combine to give $Mn_2(CO)_{10}$. (Some $Mn_2(CO)_9(CH_3CN)$ is also observed.) Use of $Mn(^{13}CO)_6^+$ (65%) gives $Cp_2Fe_2(CO)_4$ that is 12% enriched, as expected for transfer of one CO in the formation of $CpFe(CO)_3^+$. Reaction of $CpFe(CO)_3^+$ with $Mn(CO)_5^-$ gave $Cp(CO)_2FeMn(CO)_5$ as the major product with some $Cp_2Fe_2(CO)_4$, $Mn_2(CO)_{10}$, and $Mn_2(CO)_9(CH_3CN)$.

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[21] (a) Dessy, R. E.; Pohl, R. L.; King, R. B. *J. Am. Chem. Soc.* **1966**, *88*, 5121. (b) Pearson, R. G.; Figdore, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 1541.

In two reactions an equilibrium appears to form as illustrated below.

$$Re(CO)_5^- + Mn(CO)_5PPh_3^+ \rightleftarrows Re(CO)_6^+ + Mn(CO)_4PPh_3^- \quad (11)$$

$$Re(CO)_5^- + Mn(CO)_5PPh_2Me^+ \rightleftarrows Re(CO)_6^+ + Mn(CO)_4PPh_3Me^- \quad (12)$$

Equilibrium 11 favors the right-hand side while reaction 12 generates almost equal amounts of reactants and products. The E_{rxn} value for reaction 11 is nearly zero (10 mV) as expected for an equilibrium; however, the value for reaction 12 of 110 mV indicates that this may be a fortuitous agreement. Subsequent reactions to binuclear products made determination of the equilibrium constants impossible. Note, however, that change to PEt_3 as the ligand on manganese causes the favorable reaction for a two-electron transfer to reverse.

$$Re(CO)_6^+ + Mn(CO)_4PEt_3^- \rightarrow Re(CO)_5^- + Mn(CO)_5PEt_3^+ \quad (13)$$

In combination with reaction 7, this shows a significant ligand effect on the reactivity toward two-electron transfer.

Discussion

Of the many reactions between metal carbonyl cations and anions that we have examined, over half exhibit a two-electron-transfer product. All of the "self-exchange" reactions illustrated by eq 8 and 9 occur. Then, for any possible reaction

$$MCO^+ + M'^- \rightarrow M^- + M'CO \quad (14)$$

the two-electron transfer occurs in one direction.[22] Although there are some exceptions, there appears to be a correlation of the two-electron reactivity with E_{rxn}, as defined by reaction 6. Thus, there may be a thermodynamic driving force for reaction 2, even though the final thermodynamic products are the neutral, binuclear products.

Reaction 14 is very ligand specific with transfer of one CO. This indicates that both electrons are transferred in one event, not as two successive single-electron transfers since single-electron transfer would lead to odd-electron centers, which are known to very rapidly scramble the ligands.[23] It is also very difficult to rationalize two single-electron transfers past the thermodynamic odd-electron species and then a back-transfer of one electron. Thus the reaction must incorporate a single-event two-electron change.

Nucleophilic attack on the carbon of a carbonyl is very well-known for nucleophiles that are weaker than the metal carbonyl anions.[24] Attack by metal carbonyl anions on the ethylene of a cation $M(CO)_5(C_2H_4)^+$ (M = Mn, Re) led to the ethylene-bridged complexes, $M(CO)_5{-}C_2H_4{-}M(CO)_5$.[25] These complexes are very useful models for a mechanism involving nucleophilic attack of the anion on a carbonyl of the cation with an intermediate, MC(O)M′. If one considers the CO to be a CO^{2+}, then the product may arise from a competition of the two nucleophiles, M and M′ (M,M′ = metal carbonyl anions as shown in Table I) for the CO^{2+}. The stronger nucleophile retains the CO^{2+} forming the cation while the weaker nucleophile is eliminated as the anion. Our values for the nucleophilicities of the anions as determined by the rates of reaction with CH_3I are in reasonable agreement with those values previously reported.[21] The nucleophilicities of the two competing anions correctly predict the two-electron change for every reaction except those involving $Re(CO)_5^-$ competing with $Mn(CO)_4L^-$. Thus, as for reactions 7 and 10, reaction of a strong nucleophile M'^- with the CO^{2+} adduct of a weaker nucleophile M^- results in a two-electron process. The exceptions to this generalization lie in reactions such as eq 11–13. Reaction of $Re(CO)_5^-$ with CH_3I suggests that it is a stronger nucleophile than the $Mn(CO)_4L^-$ anions. However, the oxidation potential data suggest that the $Mn(CO)_4L^-$ species are stronger reducing agents. This difference between the oxidation potential data and the data for reaction with CH_3I suggests that steric interactions may be interfering with the $Mn(CO)_4L^-$ anions in their reactions with CH_3I. The reactions that we observe (reactions 11–13) indicate that competition for the CO^{2+} falls intermediate between reaction with CH_3I and oxidation in its steric requirements. For competitions between $Mn(CO)_4L^-$ species, the nucleophilicity correctly predicts the two-electron reactivity.

$$Mn(CO)_4PEt_3^- + Mn(CO)_5PPh_3^+ \rightarrow Mn(CO)_5PEt_3^+ + Mn(CO)_4PPh_3^- \quad (15)$$

$$Mn(CO)_4PEt_3^- + Mn(CO)_5PPh_2Me^+ \rightarrow Mn(CO)_5PEt_3^+ + Mn(CO)_4PPh_2Me^- \quad (16)$$

$$Mn(CO)_4PPh_2Me^- + Mn(CO)_5PPh_3^+ \rightarrow Mn(CO)_5PPh_2Me^+ + Mn(CO)_4PPh_3^- \quad (17)$$

Regardless of the driving force for the two-electron-transfer reactions, the rate of the two-electron processes appear to be unrelated to thermodynamic considerations. For the two self-exchange reactions shown in reactions 8 and 9, the thermodynamic change must be zero, yet the rates are markedly different. Reaction 9 has a half-life of ~10 min. Reaction 8 occurs very rapidly; we can obtain an estimate of the rate of CO scrambling between the cation and anion from a competitive reaction with CH_3I.

$$Re(^{13}CO)_5^- + CH_3I \rightarrow CH_3Re(^{13}CO)_5 + I^- \quad (18)$$

$$Re(^{13}CO)_5^- + Re(CO)_6^+ \rightleftarrows Re(^{13}CO)_5(CO)^+ + Re(CO)_5^- \quad (19)$$

The rate constant of reaction 18 has been evaluated as 74 $M^{-1}\,s^{-1}$. When $Re(^{13}CO)_5^-$ (68% ^{13}C), $Re(CO)_6^+$, and CH_3I were mixed in CH_3CN, the ^{13}CO content in $CH_3Re(CO)_5$ (29%) showed that the CO had completely scrambled before reaction with CH_3I. Thus reaction 8 occurs with a rate constant larger than 500 $M^{-1}\,s^{-1}$.

In addition to the two-electron transfer observed between metal carbonyl anions and cations, there is also a one-electron transfer that leads ultimately to the observed binuclear products. The single-electron transfer is most straightforward in the absence of a two-electron reaction. Two examples are shown below:

$$Co(CO)_4^- + Mn(CO)_6^+ \rightarrow Co_2(CO)_8 + Mn_2(CO)_{10} + CoMn(CO)_9 \quad (20)$$

$$Mn(CO)_5^- + Re(CO)_6^+ \rightarrow Mn_2(CO)_{10} + Re_2(CO)_{10} + MnRe(CO)_{10} \quad (21)$$

Often these reactions lead to a substantial amount of the heterobimetallic product. This is expected since formation of the radical species should lead to binuclear products with very low activation barriers and very little discrimination in the recombination reactions.[21,26] As expected from the known ligand lability of odd-electron species,[21] when labeled CO was present in either reactant or in solution, substantial incorporation into all binuclear products was observed. In contrast to the very rapid exchange of one CO between the cation and anion in the two-electron process, only a very slow ($t_{1/2}$ of several hours) exchange of CO

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(22) For two reactions (eq 11 and 12) an equilibrium is established.

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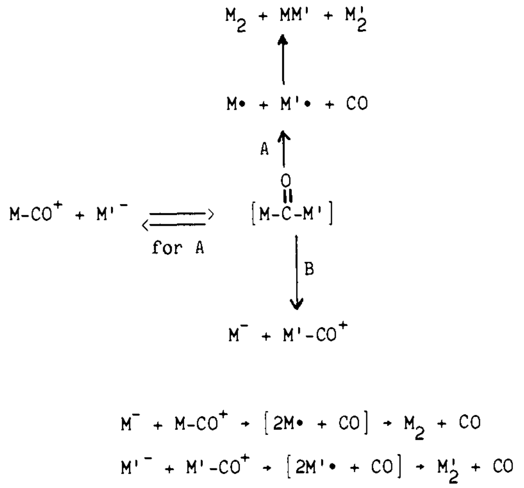

Figure 3. Suggested scheme for the reaction of metal carbonyl anions with metal carbonyl cations. A is observed for M more nucleophilic than M′. B is observed for M less nucleophilic than M′.

between the cation and anion is observed for the single-electron process.

$$Mn(^{13}CO)_5^- + Re(CO)_6^+ \rightarrow \text{binuclear products} + Re(^{13}CO)_6^+ \quad (22)$$

The labeling appears in the $Re(CO)_6^+$ at about the same rate as formation of the binuclear products, suggesting a common step. We suggest a sequence as shown below to account for the ^{13}CO in the $Re(CO)_6^+$.

$$Re(CO)_6^+ + Mn(^{13}CO)_5^- \rightarrow Re(CO)_6 + Mn(^{13}CO)_5 \quad (23)$$

$$Re(CO)_6 + Mn(^{13}CO)_5 \rightarrow Re(^*CO)_6 + Mn(^*CO)_5 \quad (24)$$

$$Re(CO)_6^+ + Re(^*CO)_6 \rightleftarrows Re(^*CO)_6^+ + Re(CO)_6 \quad (25)$$

An asterisk indicates a randomization of the ^{13}CO. The substitutional lability of $Re(CO)_6^+$ is known to be low.[27] All of the characteristics of the single-electron transfer are consistent with the formation of 17- and 19-electron species.[21]

The single-electron reactions that accompany a two-electron transfer often give different ratios of binuclear products than reactions that do not proceed through a two-electron step. Usually no heterobimetallic complex is observed. Reactions of $Mn(CO)_{6/5}^{+/-}$ with $CpFe(CO)_{2/3}^{-/+}$ illustrate the different bimetallic products.

$$CpFe(CO)_2^- + Mn(CO)_6^+ \rightarrow Cp_2Fe_2(CO)_4 + Mn_2(CO)_{10} \quad (26)$$

$$Mn(CO)_5^- + CpFe(CO)_3^+ \rightarrow Cp(CO)_2FeMn(CO)_5 + Cp_2Fe_2(CO)_4 + Mn_2(CO)_{10} \quad (27)$$

Reaction 26 occurs first by a two-electron transfer generating $CpFe(CO)_2^-$, $Mn(CO)_6^+$, $CpFe(CO)_3^+$, and $Mn(CO)_5^-$ in the same solution. Reaction of $CpFe(CO)_2^-$ with $CpFe(CO)_3^+$ occurs rapidly ($k_2 > 2000\ M^{-1}\ s^{-1}$), much more rapidly than $Mn(CO)_5^-$ with $Mn(CO)_6^+$ ($k_2 = 2.3\ M^{-1}\ s^{-1}$). Thus at no time in reaction 26 are the iron and manganese odd-electron complexes present at the same time. In reaction 27 $Mn(CO)_5^-$ reacts with $CpFe(CO)_3^+$ generating $Mn(CO)_5$ and $CpFe(CO)_3$, which react together to give the heterobimetallic product $Cp(CO)_2FeMn(CO)_5$ as the primary product.

The suggested mechanism for these electron-transfer reactions is shown in Figure 3. Given the ease of nucleophilic attack on carbonyls at cationic centers,[24] it is very likely that the first step is nucleophilic attack of the anion on the cation for either the single- or two-electron transfer. Most often this intermediate undergoes heterolytic fission, with CO^{2+} remaining with the more nucleophilic metal carbonylate. Thus, in the scheme shown in Figure 3, the intermediate reverts to reactants for M^- more nucleophilic than M'^- or progresses on path B to a new cation and anion. More slowly, a single-electron transfer occurs leading to $M^\bullet$ and $M'^\bullet$ for path A, which undergo radical recombination to give all possible products M_2, MM′, and M'_2. For path B usually one of the reactions of cation with anion is more rapid and only M_2 and M'_2 are observed. That nucleophilic attack is the first step is supported by qualitative observations of rates with $Co(CO)_4^-$ reacting much more slowly than other anions[28] and that more substituted cations also react more slowly.

Conclusion

In the reactions of metal carbonyl anions with metal carbonyl cations we have observed two distinct reaction pathways: (1) an unprecedented two-electron transfer that may mechanistically be described as a CO^{2+} transfer (This reaction leads to one CO transferred (no ligand scrambling), giving a new cation and anion. The eventual bimetallic products are the homobimetallic complexes.); (2) the expected single-electron transfer (This reaction leads to odd-electron species that undergo ligand scrambling and form substantial yields of the heterobimetallic complexes in addition to the homobimetallic complexes.).

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Supplementary Material Available: Tables of microanalyses, infrared spectra of binuclear complexes, and observed reactions (6 pages). Ordering information is given on any current masthead page.

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