Organometallics 1993, *12*, 4413-4419 4413

Electron and Bromine Transfer Reactions between Metal Carbonyl Anions and Metal Carbonyl Bromides. Crystal and Molecular Structure of Dimeric Indenyl Molybdenum Tricarbonyl

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Received March 26, 1993[⊗]

Reactions of metal carbonyl anions with metal carbonyl halides proceed by two separate paths. When the reactant anion is a strong nucleophile, the halogen is transferred, resulting in a new metal carbonyl halide and a new metal carbonyl anion as intermediates. The ultimate products, in this case, are the homobimetallic complexes. In cases where the reactant metal carbonyl anion is a poor nucleophile, a single electron transfer occurs, leading to the two homobimetallic complexes and to the heterobimetallic complex. Halide effects and possible indenyl effects are examined. The complex $[Mo(indenyl)(CO)_3]_2$ crystallizes in the noncentrosymmetric orthorhombic space group $P2_12_12_1$ (No. 19) with $a = 7.3572(7)$ Å, $b = 14.4539(12)$ Å, $c = 19.983(2)$ Å, $V = 2125.0(4)$ Å^3, and $Z = 4$. Diffraction data were collected on a Siemens R3m/V diffractometer for $2\theta = 5$–$45°$ (Mo Kα), and the structure was solved and refined to $R = 3.21\%$ and $R_w = 3.23\%$ for all 2786 independent reflections ($R = 2.26\%$ and $R_w = 2.81\%$ for those 2314 reflections with $|F_o| > 6\sigma(|F_o|)$. The complex is held together by a Mo–Mo single bond (Mo(1)–Mo(2) = 3.251(1) Å), and has Mo–CO distances ranging from 1.956(6) to 1.988(7) Å, averaging 1.970 ± 0.016 Å. Molybdenum–carbon distances to the η^5-indenyl rings range from 2.300(7) to 2.427(6) Å for Mo(1) and 2.306(7) to 2.430(6) Å for Mo(2).

Reactions of metal carbonyl anions with metal carbonyl halides have been a primary method for formation of metal–metal bonds.[1] Such reactions have been especially useful for preparation of heterobimetallic complexes.[2] In such reactions the yield of the heterobimetallic complex is quite dependent on the nature of the anion and on the nature of the metal carbonyl halide.[2] Examples are provided by the approach to $MnRe(CO)_{10}$.[3]

$$KMn(CO)_5 + Re(CO)_5(O_3SCF_3) \rightarrow \underset{86\%}{MnRe(CO)_{10}} \quad (1)$$

$$NaMn(CO)_5 + Re(CO)_5Br \rightarrow \underset{25\%}{Mn_2(CO)_{10}} + \underset{25\%}{Re_2(CO)_{10}} + \underset{50\%}{MnRe(CO)_{10}} \quad (2)$$

$$NaRe(CO)_5 + Mn(CO)_5Br \rightarrow \underset{\sim 50\%}{Mn_2(CO)_{10}} + \underset{\sim 50\%}{Re_2(CO)_{10}} + \underset{<10\%}{MnRe(CO)_{10}} \quad (3)$$

A satisfactory explanation of these reactions has remained elusive. Ingham and Coville have examined the product yields of heterobimetallic complex as the halide (or pseudohalide) is varied.[4] Only with the triflate derivative, $Re(CO)_5(O_3SCF_3)$, could high yields of the heterobimetallic complexes $Cp(CO)_3MRe(CO)_5$ (M = Mo, W) be obtained from reactions of group 6 derivatives with $Re(CO)_5$-containing species.[4]

Electron transfer reactions of halide containing species have proven very valuable for understanding mechanisms of reactions of coordination complexes.[5,6] Transfer of halide ions in electron transfer reactions was very important in defining the inner sphere mechanism. Such transfers have also been observed between metallocene complexes,[7,8]

$$Cp_2RuX^+ + Cp'_2Ru \rightarrow Cp_2Ru + Cp'_2RuX^+ \quad (4)$$

where the metal centers undergo two electron oxidation and reduction. These reactions have been interpreted as two electron transfer followed by transfer of bromine atoms in the other direction.[7] The dependence of the rate on halide, $I^- > Br^- > Cl^-$, is as expected for bridging halide ligands. Self-exchange reactions of halogens between group 6 metal carbonyl groups have also been reported.[9] The halogen dependence is also $I^- > Br^- > Cl^-$ for these exchanges between $CpM(CO)_3X$ and $CpM(CO)_3^-$, M = Mo, W.[9]

Reactions of the metal carbonyl anions with a variety of oxidants have demonstrated two paths:[10–13] (1) electron transfer by an outer sphere mechanism (single electron transfer in organic terminology) and (2) group transfer by

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[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1993.

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0276-7333/93/2312-4413$04.00/0

an inner sphere process (two electron changes or nucleophilic attack in organic nomenclature). The outer sphere electron transfer reactions occur with coordination complexes ($Co(o\text{-phen})_3^{3+}$ or $Co(o\text{-phen})_2Cl_2^+$), pyridinium ions, metal carbonyl dimers, and metal carbonyl clusters.[10] Group transfer reactions are observed when a transferable group (hydride,[12,14] alkyl,[12] or CO[11]) bound to a metal carbonyl group is reacted with a more nucleophilic metal carbonyl anion.

$$M^- + M'{-}X \rightarrow M{-}X + M'^- \qquad (5)$$

M, M′ = metal carbonyl anions with M more nucleophilic than M′

$$X = H^+, CH_3^+, CH_2Ph^+, CO^{2+}$$

In this manuscript reactions of metal carbonyl anions with metal carbonyl halides are reported that show both halide transfer and electron transfer pathways.

Experimental Section

$Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Cp_2Fe_2(CO)_4$, and $Cp_2Mo_2(CO)_6$ were purchased from Strem Chemical Co. and used as received. [PPN][Cl] (PPN = bis(triphenylphosphine)nitrogen(1+)) and indene were purchased from Aldrich Chemical Corp. Bromine was purchased from Mallinckrodt Specialty Chemical Co., iodine from Fisher Scientific, and chlorine from Matheson Gas Products, Inc. Infrared spectra were recorded on a Mattson Polaris FTIR. THF was refluxed with Na/benzophenone and distilled under N_2. Hexane was refluxed with CaH_2 and distilled under N_2. The compounds $[PPN][Re(CO)_5]$,[11c] $[PPN][Mn(CO)_5]$,[11c] $[PPN][CpFe(CO)_2]$,[11c] $[PPN][CpMo(CO)_3]$,[11c] $Re(CO)_5X$[15] (X = Cl, Br, I), $Mn(CO)_5Br$,[16] $CpMo(CO)_3X$ (X = Cl, Br, I),[17] $CpFe(CO)_2X$ (X = Cl,[18] Br,[19] I[19,20]), $(C_9H_7)_2Mo(CO)_6$,[21,22] and $(C_9H_7)Mo(CO)_3Br$[23] were prepared by literature procedures. The infrared absorption frequencies are given in Table S1, and microanalytical results are given in Table S2 (supplementary material).

Product Studies. For determination of products, equal volumes of 1×10^{-3} M THF solutions of metal carbonyl anion and metal carbonyl halide were mixed at ambient conditions in an inert atmosphere glovebox. The reactions were followed by infrared spectroscopy. After completion, the THF was removed by vacuum and the solids were extracted with hexanes. After extraction the residue was redissolved in THF. All product determinations were done by infrared spectroscopy.

Reactions of $Mn(CO)_5^-$ with $Mn(CO)_5Br$, $CpMo(CO)_3^-$ with $CpMo(CO)_3Br$, $Re(CO)_5^-$ with $Re(CO)_5Br$, and $CpFe(CO)_2^-$ with $CpFe(CO)_2Br$ resulted in the homobimetallic complexes quantitatively.

Reaction of $Re(CO)_5^-$ with $CpFe(CO)_2I$ produced $Cp_2Fe_2(CO)_4$ and $Re_2(CO)_9I^-$ [24] as major products while $Re(CO)_5^-$ with $CpFe(CO)_2Cl$ produced, primarily, $Cp_2Fe_2(CO)_4$ and $Re_2(CO)_{10}$.

Kinetics. All reactions were accomplished at 25 °C under pseudo-first-order conditions (at least a 10-fold excess of halide complex) by following the disappearance of a metal carbonyl anion absorption in the infrared spectrum.

THF solutions were prepared in volumetric flasks in an inert-atmosphere glovebox. Concentrations of the metal carbonyl anions were $\sim 1 \times 10^{-3}$ M (between 0.7 and 1.3×10^{-3} M). Concentrations of the metal carbonyl halides ranged from 1×10^{-2} to 5×10^{-2} M. One of two methods of analysis was used, depending on the rate of the reaction:

(1) The reactions of $CpMo(CO)_3^-$ with $Re(CO)_5Br$, $Mn(CO)_5Br$, and $CpFe(CO)_2Br$ and the reaction of $Mn(CO)_5^-$ with $Re(CO)_5Cl$ were too slow to be monitored on our infrared stopped-flow spectrometer, which has been described previously.[25] As a result, these reactions were monitored as follows: with anion solution stirring in a vial, a solution of halide was added, and the time of addition was noted. After a short mixing time, a cell with a path length of 0.5 mm was filled and removed from the glovebox to our Mattson Polaris FTIR. Spectra were recorded periodically from the same sample.

(2) For all other reactions the solutions were prepared in the same way, transferred to septum-capped vials, and removed for analysis on our stopped-flow instrument. The data collected were analyzed using the stopped-flow operating system (OLIS).

All rate constants are averages of multiple reactions of independently prepared solutions. Error limits are standard deviations for k_{obs}, and 95% confidence limits for second-order rate constants.

Collection of X-ray Diffraction Data for [Mo(indenyl)(CO)$_3$]$_2$. The crystal selected for the X-ray diffraction study had approximate dimensions of 0.4 × 0.25 × 0.1 mm. It was centered on a Siemens R3m/V diffractometer. Determination of Laue symmetry (D_{2h}; *mmm*), crystal class, and unit cell parameters was carried out as described previously.[26] Details are provided in Table I.

The crystal belongs to the orthorhombic system and crystallizes in the noncentrosymmetric space group $P2_12_12_1$ (D_2^4; No. 19) as indicated unequivocally by the systematic absences $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $00l$ for $l = 2n + 1$. A total of 6084 data were collected for the octants $\bar{h}kl$, $\bar{h}k\bar{l}$, $\bar{h}\bar{k}l$, and $\bar{h}\bar{k}\bar{l}$ and were averaged ($R_{int} = 1.35\%$) to provide 2786 point-group independent data.

Solution and Refinement of the Structure. All crystallographic calculations were performed under the SHELXTL PLUS program set.[27] The analytical scattering factors for neutral atoms were corrected for both the $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion.[28] The structure was solved by direct methods. Hydrogen atoms were included in idealized positions, based upon $d(C{-}H) = 0.96$ Å,[29] and their isotropic thermal parameters were refined. Refinement converged with $R = 3.21\%$ and $R_w = 3.23\%$ for 304 variables refined against 2786 independent reflections ($R = 2.26\%$ and $R_w = 2.81\%$ for those 2314 data with $|F_o| > 6\sigma(|F_o|)$).

The chirality of the crystal studied is correctly defined, as indicated by refinement of η to a value of +1.23(12). (Note that the bulk sample is presumably composed of a 50:50 mixture of

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Table I. Experimental Data for the X-ray Diffraction Study of [Mo(indenyl)(CO)$_3$]$_2$

	Crystal Data
empirical formula	$C_{24}H_{14}Mo_2O_6$
color; habit	dark red crystal
cryst size (mm)	0.40 × 0.25 × 0.10
cryst syst	orthorhombic
space group	$P2_12_12_1$
unit cell dimens	
a (Å)	7.3572(7)
b (Å)	14.4539(12)
c (Å)	19.983(2)
vol (Å^3)	2125.0(4)
Z	4
fw	590.2
dens(calc) (Mg/m^3)	1.845
abs/coeff (mm^{-1})	1.190
F(000)	1160
	Data Collection
diffractometer used	Siemens R3m/V
radiation; λ (Å)	Mo Kα; 0.710 73
temp (K)	295
monochromator	highly oriented graphite crystal
2θ range (deg)	5.0–45.0
scan type	2θ–θ
scan speed (deg/min)	constant; 2.00 in ω
scan range (ω) (deg)	0.75 plus Kα separation
backgd measmt	stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
no. of std reflns	3 measured every 97 reflns
no. of index ranges	$-7 \leq h \leq 0, -15 \leq k \leq 15, -21 \leq l \leq 21$
no. reflns collcd	6084
no. of ind reflns; R_{int} (%)	2786; 1.35
no. of reflns >6σ	2314
abs correction	semiempirical
min/max trans	0.5967/0.6728
	Solution and Refinement
system used	Siemens SHELXTL PLUS (VMS)
solution	direct methods
refinement method	full-matrix least squares
quantity minimized	$\sum w(F_o - F_c)^2$
absolute structure	$\eta = 1.23(12)$
extinction correction	$\chi = 0.00014(4)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
H atoms	riding model, refined isotropic U
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0008F^2$
no. of params refined	304
final R indices (all data) (%)	$R = 3.21$, $R_w = 3.23$
R indices (6σ data) (%)	$R = 2.26$, $R_w = 2.81$
goodness-of-fit	0.76
largest and mean Δ/σ	0.001, 0.000
data-to-param ratio	9.2:1
largest diff peak (e Å^{-3})	0.56
largest diff hole (e Å^{-3})	–0.56

the two possible enantiomeric crystal forms.) Features on a final difference-Fourier map range from +0.56 to –0.56 e/Å^3.

Final positional parameters are collected in Table II.

Table II. Atomic Coordinates (×10^4) and Equivalent Displacement Coefficients (Å × 10^3) for [Mo(indenyl)(CO)$_3$]$_2$

	x	y	z	U(eq)[a]
Mo(1)	506(1)	3851(1)	7273(1)	31(1)
Mo(2)	1788(1)	3772(1)	8828(1)	32(1)
C(1)	2957(10)	4420(5)	7347(3)	52(2)
O(1)	4379(8)	4756(5)	7310(3)	95(3)
C(2)	3374(9)	2951(5)	8308(3)	46(2)
O(2)	4375(8)	2447(4)	8056(2)	71(2)
C(3)	−1075(9)	4630(4)	7830(3)	41(2)
O(3)	−2113(7)	5094(3)	8101(2)	58(2)
C(4)	1924(10)	2680(4)	9409(3)	47(2)
O(4)	2001(10)	2044(3)	9756(3)	81(2)
C(5)	137(9)	4949(4)	6717(3)	46(2)
O(5)	−119(8)	5590(3)	6394(2)	69(2)
C(6)	−669(10)	3223(4)	8754(3)	46(2)
O(6)	−2082(7)	2900(4)	8776(3)	81(2)
C(11)	1421(8)	2418(4)	6737(3)	35(2)
C(12)	310(9)	2207(4)	7309(3)	40(2)
C(13)	−1423(9)	2579(4)	7176(3)	49(2)
C(14)	−1406(9)	3053(4)	6568(3)	47(2)
C(15)	347(8)	2941(4)	6280(3)	36(2)
C(16)	1134(10)	3216(4)	5658(3)	47(2)
C(17)	2833(10)	2948(4)	5507(3)	49(2)
C(18)	3903(9)	2435(5)	5960(3)	46(2)
C(19)	3249(9)	2179(4)	6558(3)	41(2)
C(21)	972(9)	5200(4)	9395(3)	40(2)
C(22)	2067(10)	5404(4)	8833(3)	48(2)
C(23)	3809(9)	5022(5)	8935(3)	52(3)
C(24)	3776(9)	4529(5)	9533(3)	48(2)
C(25)	2044(9)	4648(4)	9837(3)	38(2)
C(26)	1282(10)	4350(5)	10460(3)	51(2)
C(27)	−394(12)	4641(5)	10629(3)	58(3)
C(28)	−1436(10)	5178(5)	10194(4)	59(3)
C(29)	−823(10)	5451(4)	9585(3)	52(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Products of the Reaction of M$^-$ with M′Br (M, M′ = CpFe(CO)$_2$, Re(CO)$_5$, Mn(CO)$_5$, CpMo(CO)$_3$)

M$^-$	M′–Br	products
$CpFe(CO)_2^-$	$Re(CO)_5Br$	$CpFe(CO)_2Br$,[a] $Re(CO)_5^-$,[a] $Cp_2Fe_2(CO)_4$, $Re_2(CO)_{10}$
$CpFe(CO)_2^-$	$Mn(CO)_5Br$	$Mn(CO)_5^-$, $Cp_2Fe_2(CO)_4$, $Mn_2(CO)_{10}$
$CpFe(CO)_2^-$	$CpMo(CO)_3Br$	$CpMo(CO)_3^-$, $Cp_2Fe_2(CO)_4$, $Cp_2Mo_2(CO)_6$
$Re(CO)_5^-$	$CpFe(CO)_2Br$	$Re_2(CO)_{10}$, $Cp_2Fe_2(CO)_4$, $Cp(CO)_2FeRe(CO)_5$
$Re(CO)_5^-$	$Mn(CO)_5Br$	$Re(CO)_5Br$,[a] $Mn(CO)_5^-$,[a] $Re_2(CO)_{10}$, $Mn_2(CO)_{10}$
$Re(CO)_5^-$	$CpMo(CO)_3Br$	$Re(CO)_5Br$,[a] $CpMo(CO)_3^-$,[a] $Re_2(CO)_{10}$, $Cp_2Mo_2(CO)_6$
$Mn(CO)_5^-$	$CpFe(CO)_2Br$	$Cp(CO)_2FeMn(CO)_5$, $Cp_2Fe_2(CO)_4$, $Mn_2(CO)_{10}$
$Mn(CO)_5^-$	$Re(CO)_5Br$	$MnRe(CO)_{10}$, $Re_2(CO)_{10}$, $Mn_2(CO)_{10}$
$Mn(CO)_5^-$	$CpMo(CO)_3Br$	$CpMo(CO)_3^-$, $Mn_2(CO)_{10}$, $Cp_2Mo_2(CO)_6$
$CpMo(CO)_3^-$	$CpFe(CO)_2Br$	$Cp_2Fe_2(CO)_4$, $Cp_2Mo_2(CO)_6$
$CpMo(CO)_3^-$	$Re(CO)_5Br$	$Cp_2Mo_2(CO)_6$, $Re_2(CO)_{10}$, $CpMoRe(CO)_7$
$CpMo(CO)_3^-$	$Mn(CO)_5Br$	$Cp_2Mo_2(CO)_6$, $Mn_2(CO)_{10}$, $CpMoMn(CO)_7$

[a] Observed as intermediates.

Results

Products. The products of the reactions are given in Table III. These products can be generalized into two categories: (1) When M$^-$ is more nucleophilic than M′$^-$ (reaction 5), the halide M–X and M′$^-$ are formed; subsequent single electron reactions produce M$_2$ and M′$_2$, with no evidence for the mixed-metal MM′. (2) When M$^-$ is less nucleophilic than M′$^-$, no M–X is formed and the mixed-metal dimer is observed along with M$_2$ and M′$_2$.

Kinetics. All reactions were first order in metal carbonyl anion, M$^-$, and metal carbonyl halide, M′X, with a rate law typical for electron transfer reactions.

$$\text{rate} = k[\text{M}^-][\text{M}'\text{–X}]$$

The second-order rate constants were obtained under pseudo-first-order conditions with M′–X in excess. A sample plot is shown in Figure 1. The rate constants obtained are listed in Table IV. The reactions of CpFe(CO)$_2^-$ with the other metal carbonyl bromides were too rapid for accurate evaluation but may be estimated as ~10^4 s^{-1} M^{-1}. These were the most rapid of the reactions examined. Reactions of Mn(CO)$_5^-$ and Re(CO)$_5^-$ occurred

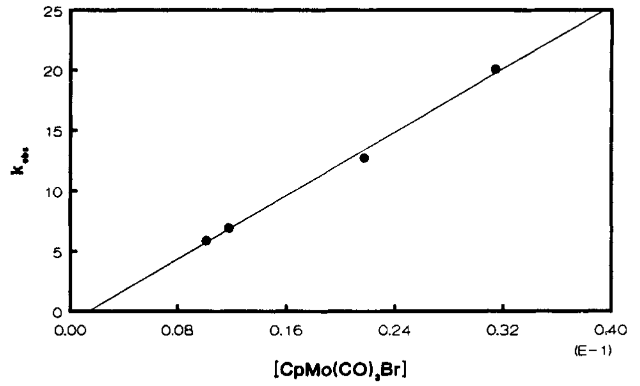

Figure 1. Plot of k_{obs} versus [CpMo(CO)$_3$Br] for reaction with 1×10^{-3} M $Mn(CO)_5^-$ at 27 °C in THF solution. The k_{obs} values are in s^{-1}.

at rates appropriate for examination by infrared stopped-flow spectroscopy. Reactions of $CpMo(CO)_3^-$ were sufficiently slow for standard absorption techniques. Reactions that occur by Br^+ transfer are very rapid, while the reactions involving electron transfer are considerably slower. The halide dependence is shown for three reactions in Table V.

Discussion

The reactions of metal carbonyl anions with metal carbonyl halides follow two paths, depending on the nature of the metal carbonyl moieties. An outer sphere electron transfer is observed when the reactant anion is less nucleophilic than an anion derived from the metal carbonyl halide. This reaction can be illustrated by the reaction of $Mn(CO)_5^-$ with $Re(CO)_5Br$ ($Mn(CO)_5^-$ is less nucleophilic than $Re(CO)_5^-$).

$$Mn(CO)_5^- + Re(CO)_5Br \rightarrow Mn_2(CO)_{10} + Re_2(CO)_{10} + MnRe(CO)_{10} + Br^- \quad (6)$$

For reactions occurring by electron transfer, the heterobimetallic complex is observed in reasonable yield. In cases where the reactant metal carbonyl anion is more nucleophilic than an anion derived from the metal carbonyl bromide, a transfer of the bromine is observed. This can be illustrated for reaction of $Re(CO)_5^-$ with $Mn(CO)_5Br$.

$$Re(CO)_5^- + Mn(CO)_5Br \rightarrow [Re(CO)_5Br + Mn(CO)_5^-] \rightarrow Re_2(CO)_{10} + Mn_2(CO)_{10} \quad (7)$$

Both $Re(CO)_5Br$ and $Mn(CO)_5^-$ are observed by infrared spectra before subsequent reactions lead to the dimers. The heterobimetallic complex is not formed because reaction of $Re(CO)_5^-$ with $Re(CO)_5Br$ producing $Re_2(CO)_{10}$ occurs rapidly, consuming the rhenium carbonyl species. Reaction of $Re(CO)_5^-$ with $Mn(CO)_5Br$ in a 2:1 ratio produces $Mn(CO)_5^-$ and $Re_2(CO)_9$ (THF)[30] with no evidence for $Mn_2(CO)_{10}$ or $MnRe(CO)_{10}$. Thus two features of the products of reactions 6 and 7 distinguish the two pathways: (1) Substantial amounts of the heterobimetallic complex are formed in the electron transfer reaction (eq 6), and (2) the new metal carbonyl anion and bromide are observed with the bromide transfer (eq 7). As shown in Table III, reaction 7 is observed when a more nucleophilic anion is the reactant. For the anions used here the nucleophilicity order is[32]

$$CpFe(CO)_2^- > Re(CO)_5^- > Mn(CO)_5^- > CpMo(CO)_3^-$$

Thus, to prepare the heterobimetallic complex, the least nucleophilic anion should be reacted with a metal carbonyl containing an excellent anionic leaving group.

The reactions are first-order in oxidant and in reductant, typical for electron transfer processes. The rates of reaction provide another difference for the bromide transfer versus the electron transfer in that bromine transfer occurs much more rapidly with rate constants $>10^3$ s^{-1} M^{-1}. The rates of electron transfer are slower, with $CpMo(CO)_3^-$ reactions with $CpFe(CO)_2Br$ and $Re(CO)_5Br$ occurring with rate constants of $\sim 10^{-4}$ s^{-1} M^{-1}. The other rates are between 0.1 and 200 s^{-1} M^{-1} with no clear pattern for different metal carbonyl anions or metal carbonyl halides.

Electron Transfer Reactions. In addition to group transfer, both inner and outer sphere electron transfer mechanisms have been reported for the metal carbonyl anions. Outer sphere reactions are more common,[10] but attack at a carbonyl[11] and ring-slippage[10c] have been suggested preceding an inner sphere electron transfer.[10]

The dependence on the halide is not straightforward for the electron transfer reactions reported herein (Table V). For outer sphere electron transfer the rate should depend on the driving force for the reaction. Unfortunately, the electrochemical processes are irreversible and the potentials are not accurately known. Potentials that have been published indicate a dependence

$$I < Br < Cl$$

for the driving force for reduction of $CpFe(CO)_2X$ and $Re(CO)_5X$.[33] If these potentials are accurate, an outer sphere mechanism should show this dependence; the electron transfer reactions reported in this manuscript show the opposite dependence. Dependences of the rate, I > Br > Cl, have been observed for self-exchange reactions of Cp_2RuX^+ with Cp_2Ru and $CpM(CO)_3X$ with $CpM(CO)_3^-$.[7,9] This dependence is typically associated with inner sphere electron transfer involving a bridging halide. The kinetic data presented in Table V show that the order is I > Br > Cl for reaction of metal carbonyl halides with metal carbonyl anions. While the ordering is constant, the magnitude of the effect of halide on rate is quite different. For the previous inner sphere organometallic self-exchange reactions,[7,9] the rates have usually covered about 6 orders of magnitude from iodide to chloride. In the reactions of metal carbonyl anions with metal carbonyl halides, only for reaction of $Mn(CO)_5^-$ with $Re(CO)_5X$ is the rate difference large enough to apply the detailed mechanistic considerations used for $CpM(CO)_3/CpM(CO)_3X$ self-exchange reactions.[9] The other two reactions show a halide dependence of less than a factor of 10,

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[30] We cannot find a literature report for the infrared spectrum of $Re_2(CO)_9(THF)$, but the similarity to other equatorially substituted complexes[31] allows assignment to this product. $Re_2(CO)_9(THF)$: 2092 (w), 2030 (m), 2002 (m), 1977 (s), 1932 (m). $Re_2(CO)_9(CH_3CN)$: 2099 (w), 2042 (m), 2012 (m), 1980 (s), 1963 (m), 1942 (s). $Re_2(CO)_9$(picoline): 2102 (m), 2038 (s), 2014 (s), 1985 (s), 1961 (s), 1933 (s). $Re_2(CO)_9(Py)$: 2099 (w), 2039 (m), 2011 (m), 1980 (s), 1960 (m), 1933 (m).

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Table IV. Second-Order Rate Constants (s^{-1} M^{-1}) for the Reactions of Metal Carbonyl Anions with Metal Carbonyl Bromides

	M′X			
M^-	$CpFe(CO)_2Br$	$Re(CO)_5Br$	$Mn(CO)_5Br$	$CpMo(CO)_3Br$
$CpFe(CO)_2^-$	1400 ± 400	$>5 \times 10^3$	$>5 \times 10^3$	$>5 \times 10^3$
$Re(CO)_5^-$	180 ± 20	2000 ± 1000	$>5 \times 10^3$	280 ± 50
$Mn(CO)_5^-$	3.8 ± 1.0	80 ± 30	0.4 ± 0.1	660 ± 100
$CpMo(CO)_3^-$	$(8.3 \pm 0.8) \times 10^{-4}$	$(1.9 \pm 0.2) \times 10^{-4}$	0.14 ± 0.07	9×10^{-3}

Table V. Halide Dependence for Reaction of Metal Carbonyl Anions with Metal Carbonyl Halides

anion	metal carbonyl halide	k (s^{-1} M^{-1})
$Mn(CO)_5^-$	$Re(CO)_5I$	180 ± 20
	$Re(CO)_5Br$	80 ± 30
	$Re(CO)_5Cl$	$(5 \pm 5) \times 10^{-3}$
$Re(CO)_5^-$	$CpFe(CO)_2I$	1250 ± 30
	$CpFe(CO)_2Br$	180 ± 20
	$CpFe(CO)_2Cl$	130 ± 30
$CpFe(CO)_2^-$	$CpFe(CO)_2I$	1500 ± 60
	$CpFe(CO)_2Br$	1400 ± 60
	$CpFe(CO)_2Cl$	1000 ± 40

Table VI. Selected Bond Distances and Angles for $[Mo(indenyl)(CO)_3]_2$

Bond Distances (Å)			
Mo(1)–Mo(2)	3.251(1)	Mo(2)–C(21)	2.430(6)
Mo(1)–C(11)	2.427(6)	Mo(2)–C(22)	2.368(6)
Mo(1)–C(12)	2.381(5)	Mo(2)–C(23)	2.350(7)
Mo(1)–C(13)	2.331(6)	Mo(2)–C(24)	2.306(7)
Mo(1)–C(14)	2.300(7)	Mo(2)–C(25)	2.388(6)
Mo(1)–C(15)	2.383(6)		
Bond Angles			
Mo(2)–Mo(1)–C(1)	71.3(2)	Mo(1)–Mo(2)–C(2)	71.8(2)
Mo(2)–Mo(1)–C(3)	69.5(2)	Mo(1)–Mo(2)–C(4)	127.5(2)
Mo(2)–Mo(1)–C(5)	127.7(2)	Mo(1)–Mo(2)–C(6)	71.1(2)
C(1)–Mo(1)–C(5)	80.4(3)	C(2)–Mo(2)–C(6)	105.1(3)
C(3)–Mo(1)–C(5)	76.9(3)	C(4)–Mo(2)–C(6)	76.7(3)

indicating that other mechanistic possibilities must be considered.

To examine the possibility of ring-slippage in reactions of metal carbonyl anions with $CpMo(CO)_3Br$, we studied the reactions of the indenyl analogue $(\eta^5\text{-}C_9H_7)Mo(CO)_3Br$. The resonance stabilization of the transition state for ring-slippage mechanisms involving the $\eta^3\text{-}C_9H_7$ species leads to dramatic rate enhancements which are termed the "indenyl effect".[34] Reaction of $Re(CO)_5^-$ with $(\eta^5\text{-}C_9H_7)Mo(CO)_3Br$ occurred with a factor of 3 increase over the cyclopentadienyl analogue. This is too small an effect for a ring-slippage mechanism unless the ring was already slipped in the ground state. The dimer $(\eta^5\text{-}C_9H_7)_2Mo_2(CO)_6$ showed a similar very small rate enhancement, and we determined the structure to check for possible ground state ring-slippage.

The compound $[Mo(indenyl)(CO)_3]_2$ crystallizes as discrete dimeric molecular units which are separated by normal van der Waals distances. The atomic labeling is illustrated by Figure 2. Interatomic distances and angles are collected in Table VI.

The molybdenum–molybdenum bond distance is 3.251(1) Å. The Mo–C(carbonyl) distances are as follows: Mo(1)–C(1) = 1.988(7) Å, Mo(1)–C(3) = 1.965(6) Å, Mo(1)–C(5) = 1.956(6) Å, Mo(2)–C(2) = 1.962(7) Å, Mo(2)–C(4) = 1.961(6) Å, and Mo(2)–C(6) = 1.979(7) Å. The average of the Mo–C(carbonyl) distances is 1.970 ± 0.016 Å. The C–O distances within the carbonyl ligands range from 1.141(9) to 1.155(10) Å, averaging 1.150 ± 0.005 Å.

The Mo–Mo–C(carbonyl) angles about both molybdenum atoms show a pattern of two acute angles and one obtuse angle. Specifically, about Mo(1), Mo(2)–Mo(1)–C(1) = 71.3(2)°, Mo(2)–Mo(1)–C(3) = 69.5(2)°, and Mo(2)–Mo(1)–C(5) = 127.7(2)°; and for those angles about Mo(2), Mo(1)–Mo(2)–C(2) = 71.8(2)°, Mo(1)–Mo(2)–C(4) = 127.5(2)°, and Mo(1)–Mo(2)–C(6) = 71.1(2)°. The C(carbonyl)–Mo–C(carbonyl) angles show a similar pattern, with C(1)–Mo(1)–C(3) = 104.9(3)°, C(1)–Mo(1)–C(5) = 80.4(3)°, C(3)–Mo(1)–C(5) = 76.9(3)°, C(2)–Mo(2)–C(4) = 78.3(3)°, C(2)–Mo(2)–C(6) = 105.1(3)°, and C(4)–Mo(2)–C(6) = 76.7(3)°. Thus, that carbonyl ligand associated with the obtuse Mo–Mo–C angles is involved with acute angles to the other carbonyl ligands.

The bond distances between the molybdenum atoms and the carbon atoms of the five-membered rings of the indenyl ligand show considerable variation. For Mo(1), distances are (cyclically) Mo(1)–C(11) = 2.427(6) Å, Mo(1)–C(12) = 2.381(5) Å, Mo(1)–C(13) = 2.331(6) Å, Mo(1)–C(14) = 2.300(7) Å, and Mo(1)–C(15) = 2.383(6) Å, with the average Mo–C distance for this group being 2.364

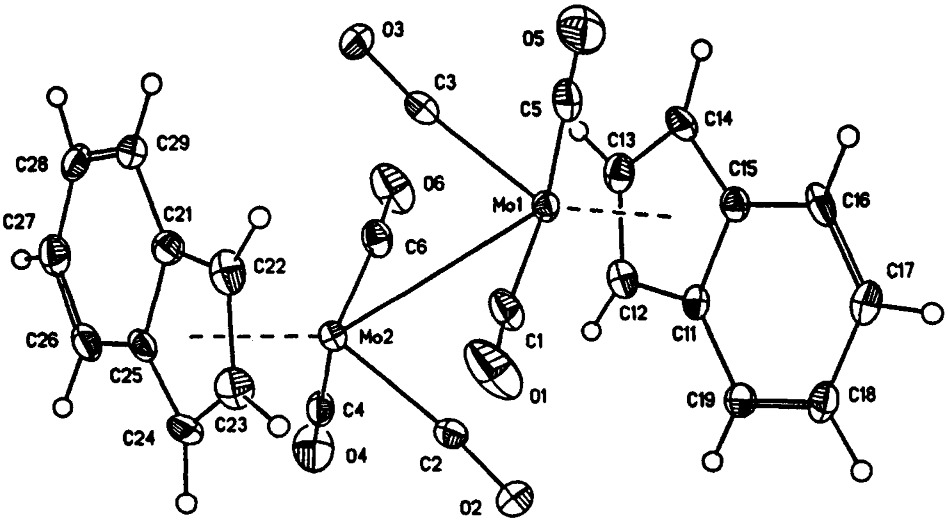


Figure 2. Labeling diagram for $[Mo(indenyl)(CO)_3]_2$.

Å. Distances involving Mo(2) are Mo(2)–C(21) = 2.430(6) Å, Mo(2)–C(22) = 2.368(6) Å, Mo(2)–C(23) = 2.350(7) Å, Mo(2)–C(24) = 2.306(7) Å and Mo(2)–C(25) = 2.388(6) Å, the average being 2.368 Å. The average Mo–C distance to the η^5-ring is thus very similar for Mo(1) and Mo(2). The average C–C bond distance in the five-membered ring associated with Mo(1) is 1.405 ± 0.035 Å, while for that associated with Mo(2) the average C–C distance is 1.402 ± 0.030 Å.

The structure is related to that of the single-bonded (Mo—Mo) complex $[CpMo(CO)_3]_2$[35] in which Mo—Mo = 3.235(1) Å (cf. 3.251(1) Å in $[Mo(indenyl)(CO)_3]_2$). The Mo—Mo single bonds in these species are about 0.75 Å longer than the Mo≡Mo triple bond length of 2.500(1) Å found in $[Mo(indenyl)(CO)_2]_2$ (Mo≡Mo).[36]

The most intriguing facet of any metal—indenyl structure may well be the pattern of distances from the metal center to the η^5-ring. These metal—carbon distances may indicate ring-slippage toward an η^3-coordination mode[37] or may simply result from the trans influence of the ligand trans to a metal—carbon bond.[38] The average of the Mo—C distances for $[Mo(indenyl)(CO)_3]_2$ to the bridgehead carbons of the indenyl system (2.405 Å) is longer than the average distance to the remaining three carbon atoms in the five-membered ring (2.337 Å). These averages are very similar to the averages observed for the Mo≡Mo complex $[Mo(indenyl)_2(CO)_2]_2$—2.339 Å for the three shorter and 2.399 Å for the two longer M—C distances. For $[Mo(indenyl)(CO)_3]_2$ one Mo—C distance is considerably longer than the other four for each five-membered ring (Mo(1)—C(11) = 2.427(6) Å; Mo(2)—C(21) = 2.430(6) Å). These two long Mo—C bonds are each trans to a carbonyl ligand, as with previous structures.[38] The differences between the bridgehead and other three Mo—C bond distances are not sufficiently large to indicate ring-slippage.[38] Thus, we conclude that the $[Mo(indenyl)(CO)_3]_2$ structure shows no evidence of ring slippage.

Atom and Group Transfer Reactions. Reaction of metal carbonyl anions with a number of metal carbonyl species results in transfer of an atom or group.

$$M^- + M'\text{–}X \rightarrow M\text{–}X + M'^- \qquad (8)$$

$$X = H^+, CH_3^+, CO^{2+}, Cl^+, Br^+, I^+$$

For the halides these transfer reactions are much more rapid than single electron transfer to generate bimetallic species. These transfer reactions may be considered (with no mechanistic implications) as simultaneous two-electron transfer with atom transfer in the opposite direction or as X^+ transfer. The transfer reactions occur when M^- is more nucleophilic than M'^-, and we prefer the simplicity of referring to these as X^+ transfer. The transfer reactions occur very rapidly in the order

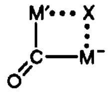
$$H^+ > Br^+ \sim CO^{2+} > CH_3^+$$

The rapidity of the X^+ transfer precludes a full kinetic treatment of the reactions. Only for reaction of $Re(CO)_5^-$ with $CpMo(CO)_3X$ could the halide dependence be evaluated for the halide transfer reactions. The rate constants (X = I, $k = 380 \pm 60\ s^{-1}\ M^{-1}$; X = Br, $k = 280 \pm 50\ s^{-1}\ M^{-1}$; X = Cl, $k = 150 \pm 50\ s^{-1}\ M^{-1}$) show a dependence that is very similar to those shown in Table V for electron transfer reactions. This similarity may indicate a similar mechanism.

Mechanism of the Reaction of Metal Carbonyl Anions with Metal Carbonyl Halides. The dependence of the rate constants on the metal carbonyl anion indicates that nucleophilicity of the metal carbonyl anion is important to the rate.[32] The lack of dependence on the driving force as the halide is changed makes an outer sphere reaction unlikely. A metal carbonyl halide offers several possible sites for nucleophilic attack. The small rate enhancements for indenyl complexes relative to cyclopentadienyl complexes coupled with no evidence for ground state ring-slippage indicates that ring-slippage is not important for these complexes. Nucleophilic attack at the metal center for a cyclopentadienyl complex would probably show an indenyl effect. Nucleophilic attack of a metal carbonyl anion on the metal center of a metal carbonyl halide complex would produce a good yield (>50%) of heterobimetallic complex which is not observed for the reactions reported in this manuscript. Nucleophilic attack at the metal is likely for reactions where a good leaving group allows yields of up to 90% for the heterobimetallic complex.[39]

Nucleophilic attack at the halide would be expected to have a large dependence on the halide, as observed for X^+ self-exchange reactions,[7,9] although alternate mechanisms may be operative for the self-exchange reactions.[9] Reaction of $Mn(CO)_5^-$ with $Re(CO)_5X$ where the rates span 4 orders of magnitude as the halide is changed *may* occur by such a mechanism. The halide dependence is too small for nucleophilic attack at the halogen for the other reactions examined.

The remaining site for nucleophilic attack on a metal carbonyl halide is the carbon of a cis carbonyl. Nucleophilic attack on the carbon of a carbonyl is well precedented,[40] and attack on the carbonyl has been implicated in CO^{2+} transfer reactions.[11] For the metal carbonyl halides, nucleophilic attack at the cis CO is probably accompanied by an interaction of the halide as shown in I. In this scheme the halide would be acting as a Lewis base. The dependence on halide observed in reactions reported in this manuscript is very similar to that observed in coordination complexes where the halide is a Lewis base toward two transition metal centers.[6] The interaction with the halide would also facilitate the elimination of M–X in the halide transfer reactions. Nucleophilic attack of the metal carbonyl anion on a CO cis to the halide



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provides a mechanism most consistent with the data described in this manuscript. Self-exchange reactions previously reported[7,9] and the very rapid halide transfer reactions may follow a different mechanistic path.

Acknowledgment. We are grateful to the Department of Energy (Grant No. ER13775) for support of this research. Purchase of the diffractometer was made possible by Grant 89-13733 from the Chemical Instrumentation Program of the National Science Foundation.

Supplementary Material Available: Tables of carbonyl stretching frequencies, microanalytical results, bond distances and angles, anisotropic thermal parameters, and calculated positions of hydrogen atoms for [Mo(indenyl)$(CO)_3]_2$ (6 pages). Ordering information is given on any current masthead page.

OM930193H