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Reaction of Metal Carbonyl Anions with Metal Carbonyl Dimers: Thermodynamic and Kinetic Factors That Control the Reactions

M. Shauna Corraine and Jim D. Atwood*

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

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The reactions of mononuclear metal carbonyl anions, M^- (M^- = $Co(CO)_4^-$, $CpFe(CO)_2^-$, $Re(CO)_5^-$, $Mn(CO)_4L^-$, L = 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 $Cp_2Ru_2(CO)_4$)), are described:

$$2M^- + M'_2 \rightarrow M_2 + 2M'^-$$

To determine the thermodynamic parameters, we have derived values for the two-electron-reduction potentials ($M_2 + 2e^- \rightarrow 2M^-$) and shown that these values correctly predict the direction of reaction. The order of these reduction potentials is (all are negative) $Co_2(CO)_8 > Cp_2Cr_2(CO)_6 > Cp_2Mo_2(CO)_6 > Mn_2(CO)_{10} > Re_2(CO)_{10} > Cp_2Fe_2(CO)_4$. In each case a clean reaction is observed with only M_2 and $2M'^-$ produced. The kinetics show that the rate has a first-order dependence on $[M^-]$; rate = $k[M^-][M'_2]$. All dimers that contain a cyclopentadienyl ligand react more rapidly than expected from the potential. Product distributions for reactions of heterobimetallic complexes are also consistent with a different mechanism for dimers with a cyclopentadienyl ligand.

Metal carbonyl anions have been among the most important organometallic reagents.[1] Fundamental studies of metal carbonyl anions have included electrochemistry,[2] nucleophilicity,[3] and ion pairing.[4] One type of reaction exhibited by metal carbonyl anions is electron transfer, which has become an active area of investigation.[2i,5,6] Reactions of metal carbonyl anions with cations have been the focus of two groups.[2i,5,6] In many cases a two-electron process can be observed with a new cation and anion formed prior to the single-electron transfer that leads ultimately to dinuclear products.[2i,5b] Kochi and co-workers have been examining cation–anion annihilation reactions leading to dinuclear complexes.[6] These reactions appear to occur by single-electron transfer to form the corresponding 17- and 19-electron complexes.

Reactions of metal carbonyl anions with dimers and clusters have been used for many years to prepare new clusters.[7] These reactions proceed through direct addition of the anion to the dimer (cluster) or by electron transfer. Reactions of several anions with dimers were reported a few years ago.[7b] These reactions were reported to occur cleanly and to generate a dimer derived from the anion and new carbonyl anions derived from the original dimer. The clean product formation indicates that these reactions are reasonable to expand our mechanistic studies of the electron-transfer reactions of metal carbonyl anions. We have previously communicated the reaction of $Re(CO)_5^-$ with $Mn_2(CO)_{10}$, $Co_2(CO)_8$, and $Cp_2Mo_2(CO)_6$.[5c]

Table I. Kinetic Data Showing the Effect of Added $NaBPh_4$ on the Reaction of $Re(CO)_5^-$ with $Cp_2Mo_2(CO)_6$

$[Na^+]/[Re(CO)_5^-]$	k_{obs}, s^{-1}	$[Na^+]/[Re(CO)_5^-]$	k_{obs}, s^{-1}
0.50	0.149 ± 0.002	2.00	0.984 ± 0.002
1.00	0.580 ± 0.001	3.00	1.59 ± 0.03

In this paper we report the reactions of ten different metal carbonyl anions with nine homobimetallic and two heterobimetallic complexes. The direction of reaction is controlled by the two-electron-reduction potentials for the dimers. The values for these potentials are derived from the reduction potential of the 17-electron species and the metal–metal bond strength of the dimer. Kinetic and mechanistic studies are also reported.

Experimental Section

$Cp_2Mo_2(CO)_6$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Co_2(CO)_8$, $Cp_2Fe_2(CO)_4$, $Cp_2Ru_2(CO)_4$, PPh_3, PBu_3, and $P(OPh)_3$ were purchased from Strem Chemical Co. and used as received. [PPN][Cl] (PPN = bis(triphenylphosphine)nitrogen(1+)) was purchased from either Strem Chemical Co. or Aldrich Chemical Corp. Infrared spectra were recorded on a Beckman 4240 infrared spectrophotometer. THF was first refluxed with CaH_2, distilled onto Na/benzophenone, and distilled from CaH_2 under N_2. Anhydrous diethyl ether was distilled from Na/benzophenone under N_2. The com-

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pounds [PPN][$Re(CO)_5$],[2i] [PPN][$Mn(CO)_4L$] (L = $P(OPh)_3$, PPh_3, PBu_3), [PPN][$CpFe(CO)_2$],[2i] [PPN][$Mn(CO)_5$],[2i] [PPN][$CpCr(CO)_3$],[3c] [PPN][$CpMo(CO)_3$],[3c] $Cp_2M_2(CO)_6$[8] (M = Cr, W), and $Cp(CO)_2FeMn(CO)_5$[9] were prepared by literature procedures. The infrared absorption frequencies are given in Table S1, and microanalytical results for the PPN salts of the anions are given in Table S2 (supplementary material).

Kinetics. All reactions were accomplished at 25 °C under pseudo-first-order conditions (10-fold excess of dimer) by following the disappearance of the anion absorption in the infrared spectrum. The solutions (THF) were prepared in an inert-atmosphere glovebox in septum-capped flasks and removed for analysis on our stopped-flow infrared spectrometer, which has been previously described.[5c] For the experiments reported in this paper, a cell with a 1.0-mm path length was used. All data were analyzed with use of the stopped-flow operating system (OLIS).

Because of the thermal sensitivity of $Co_2(CO)_8$, an alternate procedure was used. Samples of $Co_2(CO)_8$ were accurately weighed in the dry box and put into 50-mL flasks with 24/40 joints. The flasks were sealed with 24-mm rubber septa and stored in a freezer until needed. Each sample was taken from the freezer, and the appropriate amount of solvent was syringed into the flask. The flask was then attached to the stopped-flow instrument. This preparation was done as quickly as possible to prevent decomposition of the cobalt dimer.

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

Sodium Ion Effect. The effect of added sodium ion was examined for the reaction between $Re(CO)_5^-$ and $Cp_2Mo_2(CO)_6$. The rate for reaction of 5×10^{-4} M (PPN)$Re(CO)_5$ with 5.0×10^{-3} M $Cp_2Mo_2(CO)_6$ was examined with added $NaBPh_4$ (0.5, 1, 2, and 3 molar ratio with respect to $Re(CO)_5^-$) in THF at 25 °C. The rate constants are shown in Table I and plotted in Figure S1 (supplementary material).

Results and Discussion

Thermodynamic Considerations. Reactions of some metal carbonyl anions with metal carbonyl dimers result in electron transfer with formation of a new anion and dimer:[5c,7b]

$$2M^- + M'_2 \rightarrow M_2 + 2M'^- \qquad (1)$$

$$M = CpFe(CO)_2;\ M' = Re(CO)_5,\ Mn(CO)_5,\ CpMo(CO)_3,\ Co(CO)_4,\ CpRu(CO)_2$$

$$M = Re(CO)_5;\ M' = Mn(CO)_5,\ CpMo(CO)_3,\ Co(CO)_4,\ CpCr(CO)_3,\ CpW(CO)_3$$

$$M = Mn(CO)_5;\ M' = CpMo(CO)_3,\ Co(CO)_4$$

$$M = CpMo(CO)_3;\ M' = Co(CO)_4$$

Each reaction is clean, with no observed products other than M_2 and M'^-. In no case was a heterobimetallic complex observed. The direction of reaction 1 could be predicted from the relative potentials for the two reduction half-reactions

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

$$M'_2 + 2e^- \rightarrow 2M'^- \qquad (3)$$

The half-reactions are comprised of two reactions:

$$M^\bullet + e^- \rightarrow M^- \qquad (4)$$

$$M_2 \rightarrow 2M^\bullet \qquad (5)$$

The energetics of these reactions have been evaluated separately—reaction 4 as the reduction potential[2j] and reaction 5 as the metal–metal bond energy.[10] These values are listed in Table II for the anions used in this study. Combining these values, one can determine the free energy and the potential for reactions 2 and 3. These values are given as the standard reduction potentials in Table II. While there are fairly large uncertainties in the bond energies[10] and some approximations in the values for the oxidation of the anions,[2j] and the reactions use THF instead of CH_3CN, the direction of the reaction observed is correctly predicted in almost every case. The exception is that $Re(CO)_5^-$ does react with $Cp_2W_2(CO)_6$ to produce $Re_2(CO)_{10}$ and $CpW(CO)_3^-$. The thermodynamic parameters in Table II are very close for the two half-reactions. Evidently one of the values is in error—probably an overestimate of the tungsten–tungsten bond energy for $Cp_2W_2(CO)_6$. The other reactions are correctly predicted: $CpFe(CO)_2^-$, formed with the most negative half-reaction reduction potential, reacts with $Re_2(CO)_{10}$, $Mn_2(CO)_{10}$, $Cp_2Mo_2(CO)_6$, and $Co_2(CO)_8$, $Re(CO)_5^-$ reacts with $Mn_2(CO)_{10}$, $Cp_2Mo_2(CO)_6$, and $Co_2(CO)_8$, $Mn(CO)_5^-$ reacts with $Cp_2Mo_2(CO)_6$ and $Co_2(CO)_8$, $CpMo(CO)_3^-$ reacts with $Co_2(CO)_8$, and $Co(CO)_4^-$ reacts with none of the dimers.

Table II. Thermodynamic Parameters for the Reduction Half-Reaction $M_2 + 2e^- \rightarrow 2M^-$ (M = Metal Carbonyl Anion)

M^-	E,[a] V	M–M bond energy, kcal[10]	$\Delta G(M_2 + 2e^- \rightarrow 2M^-)$, kcal[b]	$E(M_2 + 2e^- \rightarrow 2M)$, V
$Co(CO)_4^-$	−0.123	12	7	−0.15
$CpCr(CO)_3^-$	−0.639	15	34	−0.70
$CpMo(CO)_3^-$	−0.336	33	38	−0.79
$Mn(CO)_5^-$	−0.400	38	47	−0.97
$Re(CO)_5^-$	−0.523	45	60	−1.2
$CpW(CO)_3^-$	−0.330	56	61	−1.3[c]
$CpFe(CO)_2^-$	−1.186	22	80	−1.7

[a] These values are quoted as the standard reduction potentials (versus SHE) for formation from $M^\bullet$ (eq 4).[2j] [b] The bond energies that are reported as enthalpies were converted to free energies by using ΔS = 35 cal/(mol K) at 300 K.[10b] For $Mn_2(CO)_{10}$ this gave a ΔG value of 27 kcal/mol for the Mn–Mn bond formation. This may be compared to a value of ΔG = 25 kcal/mol evaluated from different data.[10d] [c] As discussed in the text, this value is probably not accurate.

Table III. Second-Order Rate Constants ($s^{-1}\ M^{-1}$) for the Reaction of Metal Carbonyl Anions with Metal Carbonyl Dimers at 27 °C in THF

	dimer				
anion	$Cp_2Fe_2(CO)_4$	$Re_2(CO)_{10}$	$Mn_2(CO)_{10}$	$Cp_2Mo_2(CO)_6$	$Co_2(CO)_8$
$CpFe(CO)_2^-$		0.56 ± 0.26	70 ± 12	500 ± 20	80 ± 8
$Re(CO)_5^-$	NR		2.8 ± 0.8	40 ± 4	26 ± 2
$Mn(CO)_5^-$	NR	NR		30 ± 6	68 ± 6
$CpMo(CO)_3^-$	NR	NR	NR		20 ± 4
$Co(CO)_4^-$	NR	NR	NR	NR	

Isotopic exchange occurs between $Mn(CO)_5^-$ and $Mn_2(CO)_{10}$ when either $Mn(^*CO)_5^-$ or $Mn_2(^*CO)_{10}$ is used as a reactant. The label is rapidly equilibrated between the anion and the dimer. Thus, the reaction occurs even in the absence of an electrochemical driving force.

Kinetic Considerations. All of the reactions have been examined by infrared stopped-flow kinetic studies.[5c] The rate law for each is first order in metal carbonyl anion and in dimer, as shown in eq 6. The rate constants were

$$\text{rate} = k[M^-][M'_2] \qquad (6)$$

evaluated under pseudo-first-order conditions with the

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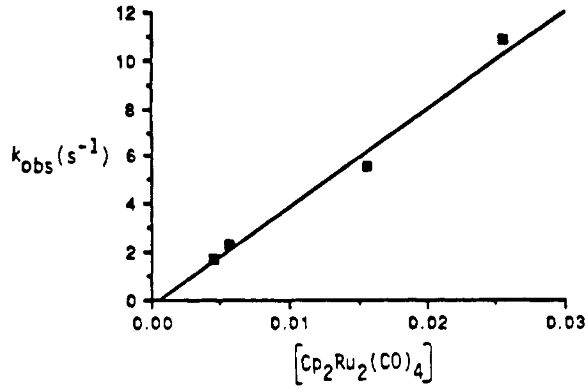


Figure 1. Typical plot of k_{obs} versus concentration of the dimer that gives the rate constant as the slope. The data are for reaction of $CpFe(CO)_2^-$ with $Cp_2Ru_2(CO)_4$.

Table IV. Relative Rates of Reaction of Metal Carbonyl Anions, $Mn(CO)_4L^-$, with $Cp_2Mo_2(CO)_6$ and CH_3I in THF

	rel rate	
anion	$Cp_2Mo_2(CO)_6$	CH_3I
$Mn(CO)_5^-$	1.0	1.0
$Mn(CO)_4P(OPh)_3^-$	0.5	1.3
$Mn(CO)_4PPh_3^-$	5.1	5.2
$Mn(CO)_4PBu_3^-$	20.0	59.0

dimer in at least 10-fold excess. A representative trace of absorption change with time is shown in Figure S2 (supplementary material). The initial concentration of the dimer was varied to allow determination of k_2 from plots of k_{obs} versus $[M'_2]$. A representative plot is shown in Figure 1. In this manner the second-order rate constants shown in Table III were evaluated. These rate constants show that the reaction rate depends on the nature of the anion and the dimer.

The effect of changing the ligand environment on the anion was examined by reactions of $Mn(CO)_4L^-$ with $Cp_2Mo_2(CO)_6$:

$$2Mn(CO)_4L^- + Cp_2Mo_2(CO)_6 \rightarrow Mn_2(CO)_8L_2 + 2CpMo(CO)_3^- \quad (7)$$

$$L = CO, P(OPh)_3, PPh_3, PBu_3$$

In these reactions the ligand L remains bound to the manganese in the product. The dependence of the second-order rate constant on the nature of L is shown by the data in Tables IV and S3 (Table S3 is in the supplementary material). These data indicate that ligand σ donation ability has a significant influence on the rate of the electron-transfer reaction. This is shown by the reactivity order $L = PBu_3 > PPh_3 > P(OPh)_3$. That $Mn(CO)_4P(OPh)_3^-$ reacts more slowly than $Mn(CO)_5^-$ indicates steric interactions impede the reaction, as expected for a second-order process. Thus, phosphine ligand substitution on the anion results in an increased reactivity that is only partially offset by an increase in steric interactions. Substitution on the dimer has a larger inhibiting effect on the rate of reactions represented by eq 8. These reactions

$$2Re(CO)_5^- + Mn_2(CO)_8L_2 \rightarrow Re_2(CO)_{10} + 2Mn(CO)_4L^- \quad (8)$$

are too slow for examination by the stopped-flow spectrometer, with second-order rate constants of $\sim 10^{-2}$ s^{-1} M^{-1}. In this case either electronic or steric interactions would be expected to slow the electron transfer.

Heterobimetallic species were not observed in any of the reactions of anions and dimers. To probe the significance of this, we have examined the reaction of $Re(CO)_5^-$ with $MnRe(CO)_{10}$:

$$Re(CO)_5^- + MnRe(CO)_{10} \rightarrow Re_2(CO)_{10} + Mn(CO)_5^- \quad (9)$$

The rate constant for reaction 9 is 70 ± 14 s^{-1} M^{-1}, more than 20 times that for reaction of $Re(CO)_5^-$ with $Mn_2(CO)_{10}$. Thus, one is not able to observe $MnRe(CO)_{10}$ in the reaction of $Re(CO)_5^-$ with $Mn_2(CO)_{10}$ for kinetic reasons.

To provide more examples of cyclopentadienyl-containing dimers, we have also examined the reaction of $Re(CO)_5^-$ with $Cp_2Cr_2(CO)_6$ and $Cp_2W_2(CO)_6$ and the reaction of $CpFe(CO)_2^-$ with $Cp_2Ru_2(CO)_4$. These reactions proceed as in reaction 1 with the rate law described by eq 6. The second-order rate constants are 1200 ± 100 and 14 ± 2 s^{-1} M^{-1} for $Cp_2Cr_2(CO)_6$ and $Cp_2W_2(CO)_6$, respectively, reacting with $Re(CO)_5^-$. The reaction of $CpFe(CO)_2^-$ with $Cp_2Ru_2(CO)_4$ occurs with a second-order rate constant of 420 ± 140 s^{-1} M^{-1}. The dependence on the metal carbonyl dimer is as follows: $Cp_2Cr(CO)_6 > Cp_2Mo_2(CO)_6 \approx Cp_2Ru_2(CO)_4 > Co_2(CO)_8 > Mn_2(CO)_{10} > Cp_2W_2(CO)_6 > Re_2(CO)_{10}$.

We have used the reaction of $Re(CO)_5^-$ with $Cp_2Mo_2(CO)_6$ to examine the effect of countercation and solvent:

$$2Re(CO)_5^- + Cp_2Mo_2(CO)_6 \rightarrow Re_2(CO)_{10} + 2CpMo(CO)_3^-$$

The rate depends linearly on the concentration of added Na^+, as shown in Figure S1. Addition of a 1:1 ratio of $NaBPh_4$ to $(PPN)Re(CO)_5^-$ leads to a rate constant (120 s^{-1} M^{-1}) for reaction with $Cp_2Mo_2(CO)_6$ that is nearly as large as the rate constant for reaction of $NaRe(CO)_5$ (k = 150 s^{-1} M^{-1}). The more strongly interacting cation leads to a somewhat more rapid reaction, although the magnitude of the change is small. The presence of Na^+ must provide a small stabilization of the transition state. To avoid complications from such interactions, our studies have focused on the PPN^+ salts. Changes in the solvent show the dielectric constant to be completely unrelated to the reactivity, as shown by the similarity of the rate constants in THF and CH_3CN. The reaction in chlorobenzene is considerably more rapid, but reaction of $Re(CO)_5^-$ with other chlorinated solvents precludes a more extensive examination.

Mechanistic Considerations. Correlation of the rate parameters for reaction 1 with the thermodynamic parameters (shown in Figure 2) shows that reactions involving a dimer that contains a cyclopentadienyl ligand occur more rapidly than might be expected from thermodynamic parameters. On the basis of this and the products of the two reactions outlined below different mechanisms may be operative for dimers with and without cyclopentadienyl groups.

To probe further the nature of the interaction of metal carbonyl anions with binuclear complexes, we have examined two different approaches to formation of the adduct $[Re(CO)_5CpFe(CO)_2Mn(CO)_5]^-$:

$$Re(CO)_5^- + Cp(CO)_2FeMn(CO)_5 \rightarrow Cp(CO)_2FeRe(CO)_5 + Mn(CO)_5^- + Cp_2Fe_2(CO)_4 \quad (10)$$

$$CpFe(CO)_2^- + MnRe(CO)_{10} \rightarrow Mn(CO)_5^- + Cp_2Fe_2(CO)_4 + Mn_2(CO)_{10} + Re_2(CO)_{10} + CpFe(CO)_2Re(CO)_5 \quad (11)$$

In the reaction of $Re(CO)_5^-$ with $Cp(CO)_2FeMn(CO)_5$ the predominant products are $Cp(CO)_2FeRe(CO)_5$ and $Mn(CO)_5^-$ with formation of a small amount of $Cp_2Fe_2(CO)_4$ and traces of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. Reaction of $CpFe(CO)_2^-$ with $MnRe(CO)_{10}$ results in a mixture of binuclear products, $Cp_2Fe_2(CO)_4$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $Cp(CO)_2FeRe(CO)_5$, in the approximate ratio of 1.5:1:1:0.5,

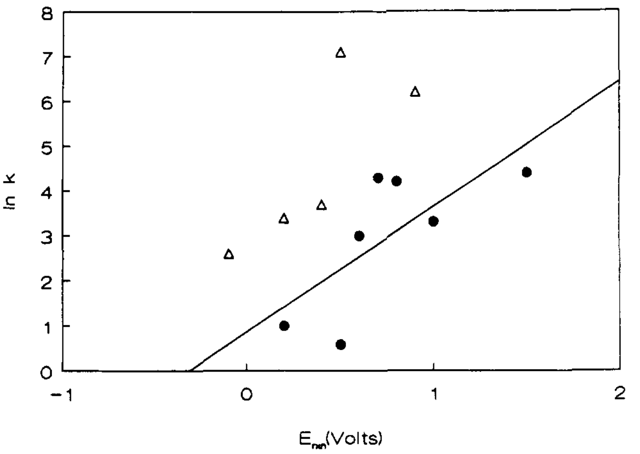


Figure 2. Plot of ln *k* vs the potentials for reaction 1. Dimers containing only CO are the closed circles; dimers containing a cyclopentadienyl group are open triangles. The line is a least-squares fit to the data for dimers that do not contain cyclopentadienyl ligands. Note that all dimers containing Cp lie above the line.

Scheme I

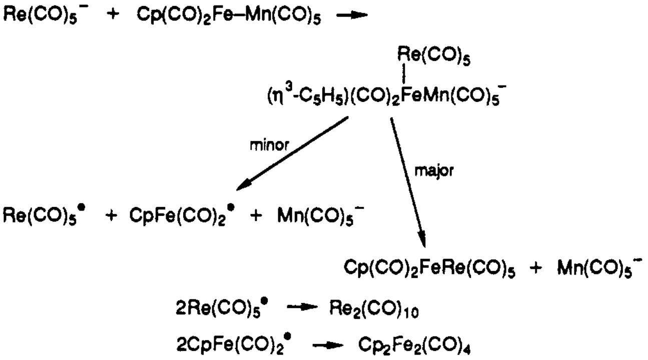
$$\mathrm{CpFe(CO)_2^- + MnRe(CO)_{10} \rightarrow CpFe(CO)_2^{\bullet} + MnRe(CO)_{10}^{\bullet -}}$$

$$\mathrm{2CpFe(CO)_2^{\bullet} \rightarrow Cp_2Fe_2(CO)_4}$$

$$\mathrm{MnRe(CO)_{10}^{\bullet -} \rightarrow Re(CO)_5^{\bullet} + Mn(CO)_5^-}$$

$$\mathrm{2Re(CO)_5^{\bullet} \rightarrow Re_2(CO)_{10}}$$

Scheme II



respectively. Infrared spectra are shown in Figure 3. The variety of products in reaction 11 is consistent with radical reactions resulting from an outer-sphere reaction. The more specific reaction products from reaction 10 indicate that the Fe–Re bond is formed and maintained. This could occur by rhenium attack on the iron, resulting in ring slippage.[11] These possibilities are shown in Scheme I and II.

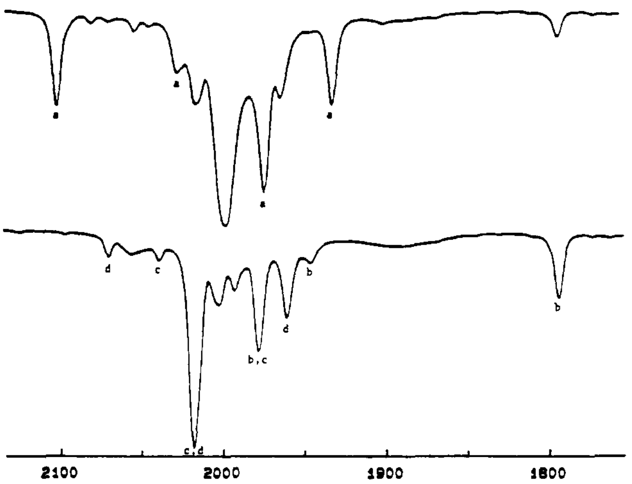


Figure 3. Spectra of the products of reaction 10 (top) and reaction 11 (bottom). The spectrum shows $\mathrm{Cp(CO)_2FeRe(CO)_5}$ (peaks labeled (a) at 2110, 2025, 1975, 1930 cm^{-1}) as a primary product in the top spectrum and not in the lower spectrum from reaction 10. The lower spectrum is composed of (b) $\mathrm{Cp_2Fe_2(CO)_4}$, (c) $\mathrm{Mn_2(CO)_{10}}$, and (d) $\mathrm{Re_2(CO)_{10}}$, primarily.[7] Peaks not assigned are due to reactants.

Thus, rate dependences and the nature of the products are consistent with two mechanisms for the reaction of metal carbonyl anions with dimers: (1) an outer-sphere transfer through odd-electron species for dimers that have only carbonyl ligands and (2) nucleophilic attack through a ring-slipped transition state for dimers containing a cyclopentadienyl ligand.

Conclusion. These results on the reaction of metal carbonyl anions with metal carbonyl dimers show the following: (1) The reactions are thermodynamically controlled; derived potentials for the half-reactions ($\mathrm{2M^- \rightarrow M_2 + 2e^-}$) provide a measure of the energy. (2) The reactions have a first-order dependence on the anion and on the dimer. (3) The nucleophilicity of the anions appears to be important in the rate of the reaction for dimers containing a cyclopentadienyl group. (4) The rate increases with added alkali-metal cation. (5) Dimers with a cyclopentadienyl group are more reactive. (6) Different schemes are required for dimers with a cyclopentadienyl group (ring slippage is suggested) or without a cyclopentadienyl group (outer-sphere addition to the metal–metal antibonding orbital to form a radical anion is suggested).

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Supplementary Material Available: Tables of carbonyl stretching frequencies, microanalytical results, and effects of various parameters on *k* values and figures showing a *k* vs [Na$^+$] plot and stopped-flow IR data (5 pages). Ordering information is given on any current masthead page.

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