Organometallics **1991,** *10,* 2647-2651

case of heteronuclear clusters, where each term is, in the strict sense, a summation over a number of possible reaction pathways.

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Supplementary Material Available: Tables of $[CoRh(CO)_7]_t$ versus time data and a table of $k_{obs}(T,x_{H_2})$ data (4 pages). Ordering information is given on any current masthead page.

Electron Transfer between Mononuclear Metal Carbonyl Anions ($M(CO)_5^-$, M = Mn, Re; $CpFe(CO)_2^-$; $CpM(CO)_3^-$, M = Cr, Mo) and Trinuclear Clusters ($M_3(CO)_{12}$, M = Fe, Ru, Os) and between Trinuclear Dianions ($M_3(CO)_{11}^{2-}$, M = Fe, Ru, Os) and Metal Carbonyl Dimers ($Mn_2(CO)_{10}$ and $Cp_2M_2(CO)_6$, M = Cr, Mo, W)

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

Reaction of anionic carbonyl species with metal cluster complexes has been among the most useful synthetic procedures to high nuclearity and mixed-metal clusters.[1,2] The reaction of cluster anions with cluster complexes to generate high nuclearity clusters has been termed redox condensation.[1]

$$Rh_6(CO)_{15}^{2-} + Rh_6(CO)_{16} \rightarrow Rh_{12}(CO)_{30}^{2-} \rightarrow CO \quad (1)$$

Such reactions are used synthetically, but the mechanisms have not been investigated.

Several reactions of mononuclear carbonyl anions with metal clusters have been examined for synthetic applications. The reaction of $Fe(CO)_4^{2-}$ with $M_3(CO)_{12}$ (M = Fe, Ru, Os) is a synthetic route to the mixed-metal tetranuclear cluster dianions.[2] The reaction of monoanions, $M(CO)_5^-$ (M = Mn, Re), with $M_3(CO)_{12}$ (M = Fe, Ru, Os) leads to a wide mixture of products.[3]

$$Re(CO)_5^- + Os_3(CO)_{12} \rightarrow [\;] \xrightarrow{H^+} H_3ReOs_3(CO)_{13} + HReOs_3(CO)_{15} + HReOs_2(CO)_{12} + HReOs_3(CO)_{16} \quad (2)$$

Similar reactions are observed for $Mn(CO)_5^-$ as anion or for $Ru_3(CO)_{12}$ as the cluster.[3] The reactions of $M_3(CO)_{12}$ with $Co(CO)_4^-$ have also been reported.[4]

$$Co(CO)_4^- + M_3(CO)_{12} \rightarrow \xrightarrow{H^+} HCoM_3(CO)_{13} \quad (3)$$

$$M = Ru, Os$$

$$Co(CO)_4^- + Fe_3(CO)_{12} \rightarrow \xrightarrow{H^+} HCo_3Fe(CO)_{12} + Co_4(CO)_{12} \quad (4)$$

The use of manganese carbonylate as a reducing agent (not incorporated in the product) has also been reported[5]

$$Ru_3(CO)_{12} \xrightarrow{Mn(CO)_5^-} \xrightarrow{H^+} HRu_6(CO)_{18}^- + H_3Ru_4(CO)_{12}^- \quad (5)$$

although a mixed-metal cluster may be an intermediate as in the formation of $Fe_6(CO)_{16}C^{-2}$ from $Fe(CO)_5$ and $Mn(CO)_5^-$. Alkali-metal reductions of $Ru_3(CO)_{12}$ have been reported to generate a variety of anions.[6] While reactions such as 1–9 have proven synthetically useful, there have been no kinetic or mechanistic studies of the reduction of cluster complexes.

As a continuation of our exploration of the mechanisms of reaction of metal carbonyl anions with various oxidizing agents,[7] we now report on the reactions of metal carbonyl

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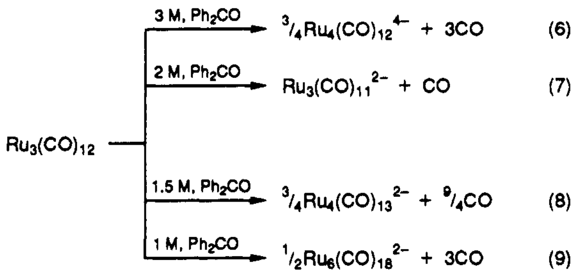

$$Ru_3(CO)_{12} \xrightarrow{3\ M,\ Ph_2CO} {}^3/_4Ru_4(CO)_{12}^{4-} + 3CO \quad (6)$$
$$\xrightarrow{2\ M,\ Ph_2CO} Ru_3(CO)_{11}^{2-} + CO \quad (7)$$
$$\xrightarrow{1.5\ M,\ Ph_2CO} {}^3/_4Ru_4(CO)_{13}^{2-} + {}^9/_4CO \quad (8)$$
$$\xrightarrow{1\ M,\ Ph_2CO} {}^1/_2Ru_6(CO)_{18}^{2-} + 3CO \quad (9)$$

anions with the group 8 dodecacarbonyltrimetallic clusters, $M_3(CO)_{12}$ (M = Fe, Ru, Os).

Experimental Section

The metal carbonyl compounds ($Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Cp_2Fe_2(CO)_4$, $Cp_2Mo_2(CO)_6$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, and $Fe(CO)_5$) were purchased from Strem Chemical Inc. and used without further purification. Triphenylphosphineimminium chloride, PPN^+Cl^-, was purchased frrom Aldrich and used as received. All solvents were dried before use and stored under argon. All operations were performed under an inert atmosphere. Infrared spectra were recorded on a Beckman 4240 infrared spectrophotometer or a Mattson Polaris FTIR. The carbonyl stretching frequencies of all reactants and products are given in Table I. The mononuclear metal carbonyl anions were prepared as previously described.[7] For all anions only the PPN salts were used. Triiron dodecacarbonyl, $Fe_3(CO)_{12}$, was prepared as previously described, as was the undecacarbonyl dianion, $Fe_3(CO)_{11}^{2-}$.[8]

$M_3(CO)_{11}^{2-}$, M = Ru, Os. These compounds were prepared by a method similar to that previously reported.[9] A 50-mL round-bottom flask was loaded with benzophenone (0.105 g), sodium (0.014 g), and THF (4 mL). The mixture was stirred for 5 h, resulting in a dark blue solution (no metallic sodium remained). The trimetallic cluster (M = Ru, 0.166 g; M = Os, 0.236 g) was added in 20-mg quantities every 20 min and then allowed to stir for 2 h. The THF was removed by vacuum leaving an oily residue of $Na_2M_3(CO)_{11}$. Redissolving in a minimum of THF and precipitation with pentane resulted in the sodium salt as a solid. The Na^+ was exchanged for PPN^+ by dissolving the $Na_2M_3(CO)_{11}$ in a minimum of THF and adding PPNCl dissolved in CH_3CN. The solvents were removed by vacuum, the solid extracted by a minimum of THF and the $[PPN]_2[M_3(CO)_{11}]$ precipitated by addition of Et_2O.

Reaction of M^- with $Os_3(CO)_{12}$ (M^- = $CpFe(CO)_2^-$ and $Re(CO)_5^-$). The cluster $Os_3(CO)_{12}$ was added to a slight molar excess of the metal carbonyl anion in THF. A typical reaction would use 50 mg of M^- and 80 mg of $Os_3(CO)_{12}$ in 15 mL of THF. After 30 min an infrared spectrum was taken; for $CpFe(CO)_2^-$ as the reactant anion, the reaction was complete with $Cp_2Fe_2(CO)_4$ and $Os_3(CO)_{11}^{2-}$ present; for $Re(CO)_5^-$, no reaction had occurred and the solution was stirred for a week when only $Re_2(CO)_{10}$ and $Os_3(CO)_{11}^{2-}$ were present. After the reactions had gone to completion, the THF was removed and the dimer separated by extraction into hexanes to confirm the reaction stoichiometry.

Reaction of M^- with $Ru_3(CO)_{12}$ (M^- = $CpFe(CO)_2^-$, $Re(CO)_5^-$, and $Mn(CO)_5^-$). The triruthenium complex was added to a slight molar excess of M^- (typically 50 mg of M^- and 60 mg of $Ru_3(CO)_{12}$) in 15 mL of THF and stirred for times from 30 min ($CpFe(CO)_2^-$) to 3 h ($Mn(CO)_5^-$ and $Re(CO)_5^-$). The THF was removed by vacuum and the solid extracted with hexanes to effect separation of the neutral products. Infrared spectra of the hexane extract in hexanes and the remaining solid in THF gave the product distribution shown in Table II. For $Re(CO)_5^-$ the mixed-metal cluster product of the addition, $ReRu_3(CO)_{16}^-$, is observed.[3] For addition of $CpFe(CO)_2^-$, unidentified absorptions at 1933 and 2030 cm^{-1} were observed. The addition product $CpFeRu_3(CO)_{13}^-$ has not been previously reported and we made no attempt to further identify the source of these absorptions.

Table I. Infrared Data of Metal Carbonyl Complexes in THF[a]

compound	ν_{CO}, cm^{-1}
$Mn(CO)_5^-$	1893 (m), 1860 (s), 1827 (sh)
$Re(CO)_5^-$	1906 (m), 1860 (s)
$CpFe(CO)_2^-$	1860 (m), 1875 (m)
$CpMo(CO)_3^-$	1893 (s), 1780 (s)
$Cp_2Fe_2(CO)_4$	1987 (s), 1945 (m), 1780 (s)
$Cp_2Fe_2(CO)_4$[b]	2010 (s), 1965 (m), 1793 (s)
$Mn_2(CO)_{10}$	2050 (m), 2015 (s), 1985 (w)
$Re_2(CO)_{10}$	2070 (m), 2010 (s), 1965 (m)
$Re_2(CO)_{10}$[b]	2073 (w), 2017 (s), 1977 (m)
$Cp_2Mo_2(CO)_6$	1950 (m), 1910 (m), 1775 (w)
$Cp_2Mo_2(CO)_6$[b]	1964 (m), 1920 (m), 1915 (sh)
$Cp_2Cr_2(CO)_6$	2005 (m), 1937 (s), 1912 (s), 1897 (sh)
$Cp_2Cr_2(CO)_6$[b]	2020 (m), 1954 (s), 1926 (s), 1912 (m)
$Cp_2W_2(CO)_6$	1943 (s), 1898 (s), 1888 (sh)
$Ru_3(CO)_{12}$	2065 (s), 2030 (m), 2015 (sh)
$Os_3(CO)_{12}$	2070 (s), 2035 (s), 1995–2010 (br)
$Os_3(CO)_{12}$[b]	2070 (s), 2036 (s), 2015 (m), 2003 (m)
$Fe_3(CO)_{12}$[b]	2045 (vs), 2015 (m), 1850 (br, w)
$Ru_3(CO)_{11}^{2-}$	1995 (m), 1975 (sh), 1945 (s), 1930 (w, sh), 1875 (sh), 1757 (w)
$Os_3(CO)_{11}^{2-}$	2015 (m), 2010 (sh), 1987 (s), 1975 (sh), 1945 (m), 1915 (sh)
$Fe_3(CO)_{11}^{2-}$	1975 (sh), 1937 (sh), 1920 (m), 1870 (s)
$ReRu_3(CO)_{16}^-$[c]	2095 (vw), 2010 (s), 1995 (sh, s), 1985 (sh), 1955 (sh), 1935 (sh, m), 1890 (w)

[a] All anions are the PPN^+ salts. Each compound was prepared or purchased as described in the Experimental Section and the spectrum recorded on the pure compound. [b] In hexane. [c] Reference 3.

Table II. Product Characterization of the Reactions of Metal Carbonyl Anions with Metal Carbonyl Clusters

reactants	products
$CpFe(CO)_2^- + Fe_3(CO)_{12}$[a]	$Fe_3(CO)_{11}^{2-}$, $Cp_2Fe_2(CO)_4$
$CpFe(CO)_2^- + Ru_3(CO)_{12}$	$Cp_2Fe_2(CO)_4$[b]
$CpFe(CO)_2^- + Os_3(CO)_{12}$	$Os_3(CO)_{11}^{2-}$, $Cp_2Fe_2(CO)_4$
$Re(CO)_5^- + Fe_3(CO)_{12}$[a]	$Fe_3(CO)_{11}^{2-}$, $Re_2(CO)_{10}$, $ReFe_2(CO)_{12}^-$, $Fe(CO)_5$
$Re(CO)_5^- + Fe_3(CO)_{12}$[c]	$ReFe_2(CO)_{12}^-$, $Fe(CO)_5$
$Re(CO)_5^- + Ru_3(CO)_{12}$	$Re_2(CO)_{10}$, $ReRu_3(CO)_{16}^-$
$Re(CO)_5^- + Os_3(CO)_{12}$	$Os_3(CO)_{11}^{2-}$, $Re_2(CO)_{10}$[d]
$Mn(CO)_5^- + Fe_3(CO)_{12}$[a]	$Fe_3(CO)_{11}^{2-}$, $Mn_2(CO)_{10}$ $MnFe_2(CO)_{12}^-$, $Fe(CO)_5$
$Mn(CO)_5^- + Fe_3(CO)_{12}$[c]	$MnFe_2(CO)_{12}^-$, $Fe(CO)_5$
$Mn(CO)_5^- + Ru_3(CO)_{12}$	$Ru_3(CO)_{11}^{2-}$, $Mn_2(CO)_{10}$
$CpMo(CO)_3^- + Fe_3(CO)_{12}$[a]	$Fe_3(CO)_{11}^{2-}$, $Cp_2Mo_2(CO)_6$ $CpMoFe_2(CO)_{10}^-$, $Fe(CO)_5$
$CpMo(CO)_3^- + Fe(CO)_{12}$[b]	$CpMoFe_2(CO)_{10}^-$, $Fe(CO)_5$

[a] Excess anion in solution. The products are formed in approximately equal amounts based on infrared intensities. [b] Also a product with absorbances at 2030 and 1933 cm^{-1} that was not identified. [c] Excess cluster in solution. [d] This reaction is very slow; after one week it had not reached completion.

Reaction of M^- with $Fe_3(CO)_{12}$ (M^- = $CpFe(CO)_2^-$, $Re(CO)_5^-$, $Mn(CO)_5^-$, and $CpMo(CO)_3^-$). Dodecacarbonyltriiron (40 mg) was added to an excess of the metal carbonyl anion (usually ~50 mg) in 20 mL of THF. After times ranging from a few minutes to a couple of hours, the THF was removed and the neutral products were separated by hexane extraction. Infrared analysis of the solid and the extractant gave the products shown in Table II. For these reactions, in addition to the products observed for reactions of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$, and mixed-metal ionic product resulting from displacement of $Fe(CO)_5$ by M^- is observed.

Reaction of $Os_3(CO)_{11}^{2-}$ with M_2 (M = $Mn(CO)_5$, $CpW(CO)_3$, $CpMo(CO)_3$, and $CpCr(CO)_3$). The reactants (M_2, 20 mg; $Os_3(CO)_{11}^{2-}$, 20 mg) were mixed in 10 mL of THF and stirred for 10 min. An infrared spectrum showed complete reaction to

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Table III. Product Characterization of the Reactions of Metal Carbonyl Cluster Dianions with Metal Carbonyl Dimers

reactants	products
$Fe_3(CO)_{11}^{2-} + Mn_2(CO)_{10}$	$Mn(CO)_5^-$, $Fe_3(CO)_{12}$
$Fe_3(CO)_{11}^{2-} + Cp_2W_2(CO)_6$	$CpW(CO)_3^-$, $Fe_3(CO)_{12}$
$Fe_3(CO)_{11}^{2-} + Cp_2Mo_2(CO)_6$	$CpMo(CO)_3^-$, $Fe_3(CO)_{12}$
$Fe_3(CO)_{11}^{2-} + Cp_2Cr_2(CO)_6$	$CpCr(CO)_3^-$, $Fe_3(CO)_{12}$
$Ru_3(CO)_{11}^{2-} + Mn_2(CO)_{10}$	$Mn(CO)_5^-$, $Ru_3(CO)_{12}$
$Ru_3(CO)_{11}^{2-} + Cp_2W_2(CO)_6$	$CpW(CO)_3^-$, $Ru_3(CO)_{12}$
$Ru_3(CO)_{11}^{2-} + Cp_2Mo_2(CO)_6$	$CpMo(CO)_3^-$, $Ru_3(CO)_{12}$
$Ru_3(CO)_{11}^{2-} + Cp_2Cr_2(CO)_6$	$CpCr(CO)_3^-$, $Ru_3(CO)_{12}$
$Os_3(CO)_{11}^{2-} + Mn_2(CO)_{10}$	$Mn(CO)_5^-$, $Os_3(CO)_{12}$
$Os_3(CO)_{11}^{2-} + Cp_2W_2(CO)_6$	$CpW(CO)_3^-$, $Os_3(CO)_{12}$
$Os_3(CO)_{11}^{2-} + Cp_2Mo_2(CO)_6$	$CpMo(CO)_3^-$, $Os_3(CO)_{12}$
$Os_3(CO)_{11}^{2-} + Cp_2Cr_2(CO)_6$	$CpCr(CO)_3^-$, $Os_3(CO)_{12}$

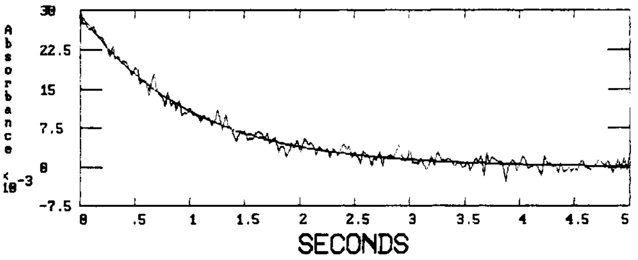

Figure 1. Sample plot of the absorbance change with time for reaction of $Re(CO)_5^-$ with $Fe_3(CO)_{12}$.

$Os_3(CO)_{12}$ and M^-. The products are shown in Table III.

Reaction of $Ru_3(CO)_{11}^{2-}$ with M_2 (M = $CpCr(CO)_3$, $CpMo(CO)_3$, and $CpW(CO)_3$). The metal carbonyl dimer and $Ru_3(CO)_{11}^{2-}$ (15 mg) were added in a stoichiometric ratio to 15 mL of THF and allowed to stir for 5 min. The infrared spectrum showed conversion to $Ru_3(CO)_{12}$ and M^-. The THF was removed to allow dissolution into hexanes. The hexane spectrum confirmed the presence of $Ru_3(CO)_{12}$.

Reaction of $Fe_3(CO)_{11}^{2-}$ with M_2 (M = $Mn(CO)_5$, $CpCr(CO)_3$, and $CpMo(CO)_3$). Molar equivalents of M_2 and $Fe_3(CO)_{11}^{2-}$ (15 mg) were mixed in 15 mL of THF. An infrared spectrum taken after a few minutes indicated that reaction had occurred resulting in $Fe_3(CO)_{12}$ and M^-.

Kinetic Studies. Most of the reactions were examined by infrared stopped-flow kinetics by using our previously described apparatus.[7c] Reactions were run under pseudo-first-orrder conditions with the neutral dimer or cluster in excess. The disappearance of the anions was followed; a typical plot is shown in Figure 1. The anion concentrations were usually 5×10^{-4} M. The rates of reaction were obtained at 25 °C in THF with use of the 1.0-mm cell. For most reactions the second-order rate constants were obtained from plots of the observed pseudo-first-order rate constant versus the concentration of the neutral dimer or trimer. A sample plot is shown in Figure 2. For reactions of $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$, limited solubility precluded such plots. For these species the k_2 values were calculated from the known concentration of cluster. The observed pseudo-first-order rate constants were obtained from best fits to the stopped-flow data by using the OLIS stopped-flow operating system. Error limits for k_{obs} values are standard deviations; error limits for k_2 values are 95% confidence limits. Values of k_2 are given in Tables IV and V.

Reactions under an Atmosphere of CO. Two reactions were accomplished under 1 atm of CO. Reaction of 20 mg of PPN-$Mn(CO)_5$ with 8 mg of $Ru_3(CO)_{12}$ in 10 mL of THF gave the same products ($Mn_2(CO)_{10}$ and $Ru_3(CO)_{11}^{2-}$) in the same amounts in the presence and absence of CO. Similarly the presence of CO (1 atm) had no effect on k_2 for reaction of $Ru_3(CO)_{11}^{2-}$ with $Cp_2Mo_2(CO)_6$ (k = 590 s^{-1} M^{-1} versus k_{CO} = 600 s^{-1} M^{-1}).

Results and Discussion

The reactions under consideration are reactions of metal carbonyl anions, M^-, with trinuclear clusters M_3'. These reactions may, in general, be represented as reaction 10.

$$2M^- + M_3' \rightleftharpoons M_2 + M_3'^{2-} \qquad (10)$$

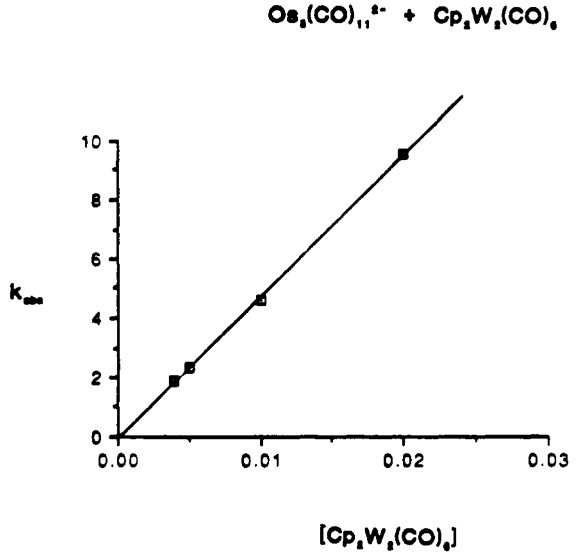

Figure 2. Sample plot of k_{obs} versus concentration of neutral carbonyl. This plot is for reaction of $[PPN]_2Os_3(CO)_{11}$ with $Cp_2W_2(CO)_6$.

Table IV. Second-Order Rate Constants (s^{-1} M^{-1}) for the Reaction of Metal Carbonyl Anions with Metal Carbonyl Clusters at 25 °C in THF

anion/cluster	$Fe_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Os_3(CO)_{12}$
$CpFe(CO)_2^-$	290 ± 20	440 ± 20	108 ± 2
$Re(CO)_5^-$	200 ± 20	168 ± 8	slow
$Mn(CO)_5^-$	106 ± 6	104 ± 4	NR
$CpMo(CO)_3^-$	100 ± 4	NR	NR

Table V. Second-Order Rate Constants (s^{-1} M^{-1}) for the Reactions of Metal Carbonyl Cluster Dianions with Metal Carbonyl Dimers at 25 °C in THF

dianion/ dimer	$Mn_2(CO)_{10}$	Cp_2W_2-$(CO)_6$	Cp_2Mo_2-$(CO)_6$	Cp_2Cr_2-$(CO)_6$
$Fe_3(CO)_{11}^{2-}$	350 ± 10	880 ± 20	220 ± 20	460 ± 20
$Ru_3(CO)_{11}^{2-}$	230 ± 10	640 ± 20	590 ± 20	194 ± 16
$Os_3(CO)_{11}^{2-}$	96 ± 6	480 ± 20	310 ± 10	82 ± 6

Depending on M and M′[7,10–13] the reaction may proceed in either direction. In three cases the reaction could be observed from both directions. The mononuclear anions examined are $CpFe(CO)_2^-$, $Re(CO)_5^-$, $Mn(CO)_5^-$, and $CpMo(CO)_3^-$; the clusters are $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$.

Reaction of the mononuclear metal carbonyl anions with $M_3(CO)_{12}$ are not all clean with three different types of products formed depending on M^-, M_3', and the conditions. The reactions observed are listed in Tables II and III with the products.[14] With only a few exceptions, the reaction of M^- with $M_3'(CO)_{12}$ leads to M_2 and $M_3'(CO)_{11}^{2-}$.

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[14] For the most part products were determined by comparison of infrared spectra to authentic compounds or to reference values. The infrared spectra are listed in Table I for all compounds prepared.

$$2M^- + M_3'(CO)_{12} \rightarrow M_2 + M_3'(CO)_{11}^{2-} + CO \quad (11)$$

$$\begin{aligned} M^- &= CpFe(CO)_2^-, M' = Fe, Ru, Os \\ &= Re(CO)_5^-, M' = Fe, Ru, Os \\ &= Mn(CO)_5^-, M' = Fe, Ru \\ &= CpMo(CO)_3^-, M' = Fe \end{aligned}$$

A second reaction involves attack of the anion on $Fe_3(CO)_{12}$ and extrusion of $Fe(CO)_5$.[15]

$$Re(CO)_5^- + Fe_3(CO)_{12} \rightarrow ReFe_2(CO)_{12}^- + Fe(CO)_5 \quad (12)$$

$$Mn(CO)_5^- + Fe_3(CO)_{12} \rightarrow MnFe_2(CO)_{12}^- + Fe(CO)_5 \quad (13)$$

$$CpMo(CO)_3^- + Fe_3(CO)_{12} \rightarrow CpMoFe_2(CO)_{10}^- + Fe(CO)_5 \quad (14)$$

When the $Fe_3(CO)_{12}$ is present in excess these became the dominant reactions. Reaction of $Re(CO)_5^-$ with $Ru_3(CO)_{12}$ leads to the addition product in addition to the electron transfer (reaction 11).[3,16a]

$$Re(CO)_5^- + Ru_3(CO)_{12} \rightarrow ReRu_3(CO)_{16}^- + CO \quad (15)$$

Reactions of the trinuclear dianions with dimers occur relatively cleanly to the neutral cluster and the mononuclear anions; no other products are observed.

$$M_3'(CO)_{11}^{2-} + M_2 + CO \rightarrow M_3'(CO)_{12} + 2M^- \quad (16)$$

$$M_2 = Mn_2(CO)_{10}, Cp_2Mo_2(CO)_6, Cp_2Cr_2(CO)_6, Cp_2W_2(CO)_6; M' = Fe, Ru, Os$$

Three of the reactions may be approached from either direction.

$$2Mn(CO)_5^- + Ru_3(CO)_{12} \rightleftarrows Mn_2(CO)_{10} + Ru_3(CO)_{11}^{2-} + CO \quad (17)$$

$$2Mn(CO)_5^- + Fe_3(CO)_{12} \rightleftarrows Mn_2(CO)_{10} + Fe_3(CO)_{11}^{2-} + CO \quad (18)$$

$$2CpMo(CO)_3^- + Fe_3(CO)_{12} \rightleftarrows Cp_2Mo_2(CO)_6 + Fe_3(CO)_{11}^{2-} + CO \quad (19)$$

The presence of CO (1 atm) has no significant effect on the kinetics or the product distribution indicating that reactions 17–19 are not simple equilibria. The reaction of $Fe_3(CO)_{11}^{2-}$ with $Co_2(CO)_8$ has previously been reported as a complicated reaction producing the heterometallic anion, $Fe_3Co(CO)_{13}^-$, with $Co(CO)_4^-$ and $Fe(CO)_5$.[17]

The kinetics of each reaction have been evaluated with a rate law

$$\text{rate} = k[\text{oxidant}][\text{reductant}] \quad (20)$$

typical for electron-transfer reactions. We utilize pseudo-first-order conditions with the oxidant in at least 10-fold excess. Fits to the stopped-flow data yield the pseudo-first-order rate constants, k_{obs}. Use of different initial concentrations of the oxidant give linear plots of k_{obs} versus initial concentration of oxidant with the second-order rate constant, k, given as the slope. These constants are listed in Tables IV and V. The second-order rate constants show relatively small dependences on the nature of the oxidant and the reductant. For the reactions represented by equation 11 the dependence of the rate on the nature of M^- varies with the nucleophilicity. However the nucleophilicity of the anions (as measured by the second-order rate constant for reaction with CH_3I) varies by 3 orders of magnitude for those anions listed in Table IV,[7e] but the rate changes only by a factor of 3–4 for reaction with the trinuclear clusters. Reactions of $M_3(CO)_{12}$ (M = Fe, Ru, Os) with the same anion show that $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ have similar reactivity and $Os_3(CO)_{12}$ is slower. For reaction of $Re(CO)_5^-$ with $Os_3(CO)_{12}$ the reaction takes place over several hours and we have not evaluated the rate constant.

Table VI. Comparison of the Trinuclear Anions, $M_3(CO)_{11}^{2-}$ (M = Fe, Ru), with $Re(CO)_5^-$ in Reaction with Dimers[7f]

	anion		
dimer	$Re(CO)_5^-$	$Ru_3(CO)_{11}^{2-}$	$Fe_3(CO)_{11}^{2-}$
$Mn_2(CO)_{10}$	1.4	114	176
$Cp_2Cr_2(CO)_6$	580	97	230
$Cp_2Mo_2(CO)_6$	20	290	110
$Cp_2W_2(CO)_6$	7	320	440

For the reactions represented by eq 16 the rate constants are reported in Table V. The rate constants change smoothly $Fe_3(CO)_{11}^{2-} > Ru_3(CO)_{11}^{2-} > Os_3(CO)_{11}^{2-}$ for reaction with all dimers except $Cp_2Mo_2(CO)_6$. For $Cp_2Mo_2(CO)_6$, reaction with $Fe_3(CO)_{11}^{2-}$ is slower than would be expected. The dependence of rate on the dimer is rather small and in a completely different order than observed for reaction of the dimers with mononuclear anions. Table VI shows the comparison for the reaction of three anions, $Fe_3(CO)_{11}^{2-}$, $Ru_3(CO)_{11}^{2-}$, and $Re(CO)_5^-$, with different dimers. The reaction with $Re(CO)_5^-$ shows more variation in rate and a completely different order of reactivity than for $Fe_3(CO)_{11}^{2-}$ and $Ru_3(CO)_{11}^{2-}$. A ring slippage mechanism was suggested for reaction of mononuclear anions with dimers containing cyclopentadienyl.[7f] This would seem to be ruled out by the rate constant order for reactions with cluster anions (reaction 16). The presence of a CO atmosphere has no effect on the rate.

The reactions represented by eq 10 involve transfer of electrons between the monomers/dimers and the clusters. The observation of reactions in either direction depending on the nature of the cluster and the monomer/dimer suggests a thermodynamic driving force related to the oxidation potentials. On the basis of the reactions observed the oxidation potential order is

$$CpFe(CO)_2^- > Re(CO)_5^- > Os_3(CO)_{11}^{2-} > Mn(CO)_5^- \approx Ru_3(CO)_{11}^{2-} > CpMo(CO)_3^- \approx Fe_3(CO)_{11}^{2-} > CpCr(CO)_3^-, CpW(CO)_3^-$$

Thus $CpFe(CO)_2^-$ and $Re(CO)_5^-$ drive reaction 10 to the right for all three clusters $M_3(CO)_{12}$, $Mn(CO)_5^-$ does not react with $Os_3(CO)_{12}$, and $CpMo(CO)_3^-$ does not react with $Os_3(CO)_{12}$ or $Ru_3(CO)_{12}$. Reactions proceeding to the left for eq 10 are also consistent with this order. The order for the oxidation potentials of the mononuclear anions above is completely consistent with the order observed from reaction of mononuclear anions with metal carbonyl dimers.[7f] We have previously evaluated the potential for the two-electron oxidation of the metal carbonyl anions to the dimer

$$2M^- \rightarrow M_2 + 2e^- \quad (21)$$

as composed of the oxidation potential of the anion and the metal–metal bond strength.[7f] The values (shown in Table VII) correctly predict the direction of reaction of

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[15] The products, $MFe_2(CO)_7^-$, were identified by comparison of IR spectra to previously reported values.[16]

[16] (a) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organomet. Chem.* **1982**, *6*, 856 (Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.). (b) Anders, U.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1966**, 291.

[17] Horwitz, C. P.; Holt, E. M.; Shriver, D. F. *Organometallics* **1985**, *4*, 1117.

Table VII. Two-Electron Reduction Potentials for Selected Dimers[7f] and Trinuclear Clusters[a]

compound	product	potential, V
$Co_2(CO)_8$	$2Co(CO)_4^-$	−0.15
$Cp_2Cr_2(CO)_6$	$2CpCr(CO)_3^-$	−0.70
$Cp_2Mo_2(CO)_6$	$2CpMo(CO)_3^-$	−0.79
$Fe_3(CO)_{12}$	$Fe_3(CO)_{11}^{2-}$	−0.8
$Cp_2W_2(CO)_6$[b]	$2CpW(CO)_3^-$	−0.8
$Ru_3(CO)_{12}$	$Ru_3(CO)_{11}^{2-}$	−0.9
$Mn_2(CO)_{10}$	$2Mn(CO)_5^-$	−0.97
$Os_3(CO)_{12}$	$Os_3(CO)_{11}^{2-}$	−1.1
$Re_2(CO)_{10}$	$2Re(CO)_5^-$	−1.2
$Cp_2Fe_2(CO)_4$	$2CpFe(CO)_2^-$	−1.7

[a] The values for the clusters are estimates based on the reactivity order. [b] This value is a correction to the previously reported value[7f] based on the observed reactions in this manuscript.

an anion with a dimer.[7f] Since we know that the reactions represented by eq 10 have positive potentials we can approximate the two-electron half-reaction potentials for the clusters

$$M_3(CO)_{12} + 2e^- \rightarrow M_3(CO)_{11}^{2-} + CO \qquad (22)$$

as $Fe_3(CO)_{11}^{2-}$, ~−0.8 V; $Ru_3(CO)_{11}^{2-}$, ~−0.9 V; and $Os_3(CO)_{11}^{2-}$, ~−1.1 V by comparison to the potentials for two-electron oxidations of reaction 21. These values are in complete agreement with the reactivity shown for all reactions reported in this manuscript. As discussed previously,[7f] the value for the two-electron oxidation potential of $CpW(CO)_3^-$ to the dimer is too large for the observed reactions. The current study confirms this observation and indicates a value of ~−0.8 V would be more accurate.

The second-order rate constants for reaction of the mononuclear anions with $M_3(CO)_{12}$ show a small dependence on the nucleophilicity of the anion as shown by the data in Table V.[7e,10] The magnitude of the change in rate is less than observed for reaction of the mononuclear anions with metal carbonyl dimers.[7f] The dependence on the neutral cluster shows that $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ react at comparable rates and somewhat more rapidly than $Os_3(CO)_{12}$. Reaction of the trinuclear cluster anions, $M_3(CO)_{11}^{2-}$, with the metal carbonyl dimers show remarkably similar rate constants (Table V). The order of rates $Fe_3^{2-} > Ru_3^{2-} > Os_3^{2-}$ appears consistent, but only different by less than 1 order of magnitude. Such a small difference is much less than that observed for other types of cluster reactions.[18] The dependence of the second-order rate constant on the nature of the dimer is much smaller and in a different order than observed for reactions of mononuclear metal carbonyl anions with the dimers.

The kinetic data for reaction 10 are most consistent with an outer-sphere mechanism. Reaction of mononuclear anions with the neutral trimetallic clusters show small dependences on the metal carbonyl anion and the cluster. The mechanism is illustrated for reaction of $Re(CO)_5^-$ with $M_3(CO)_{12}$ in Figure 3. The mononuclear anion reacts with $M_3(CO)_{12}$ to generate $[Re(CO)_5, M_3(CO)_{12}]^-$. Depending on M_3 this complex may produce three different sets of products. For M = Ru, a CO may dissociate leading to $ReRu_3(CO)_{16}^-$. For M = Fe, an $Fe(CO)_5$ may be extruded resulting in $ReFe_2(CO)_{12}^-$. For all three metals (M = Fe, Ru, Os) an electron may be transferred resulting in $Re(CO)_5$ and $M_3(CO)_{12}^{\bullet-}$, the species suggested in the electrochemical reduction of $M_3(CO)_{12}$.[13] On the basis of the lability of many odd-electron complexes, we suggest that CO dissociation from $M_3(CO)_{12}^{\bullet-}$ occurs to $M_3(CO)_{11}^{\bullet-}$. This is also the species that would be formed in the outer-sphere electron transfer from $M_3(CO)_{11}^{2-}$ to the metal carbonyl dimer. Reduction of $M_3(CO)_{11}^{\bullet-}$ could arise from either $Re(CO)_5^-$ or $Re_2(CO)_9^{\bullet-}$, depending on the relative rates and concentrations.

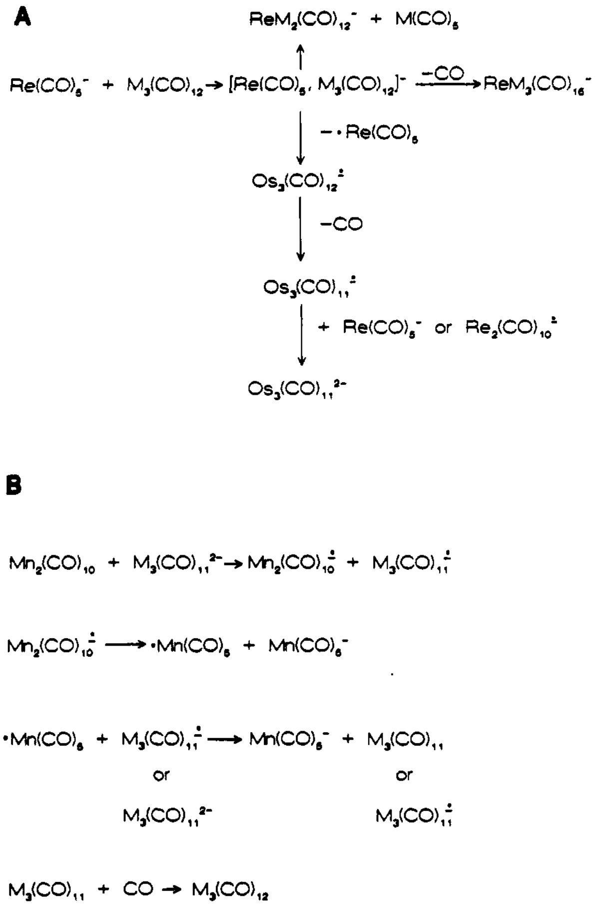

Figure 3. Scheme for the reaction of a mononuclear carbonyl anion, represented for $Re(CO)_5^-$, with a group 8 trinuclear cluster in the upper part of the figure. The lower portion represents the scheme for reaction of a trinuclear dianion with a metal carbonyl dimer, represented by $Mn_2(CO)_{10}$.

It seems likely that reactions of the polynuclear metal carbonyl species reported in this manuscript occur by an outer sphere mechanism. The larger size and more diffuse electron density may prevent direct nucleophilic attack. Reactions such as redox condensation used to build high nuclearity metal clusters[1,2] probably occur by an outer-sphere electron transfer and then coupling of the odd-electron fragments. Further studies are in progress to better define the reaction between a cluster anion and a neutral cluster complex.

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(18) Shojaie, A.; Atwood, J. D. *Organometallics* **1985**, *4*, 187.