fluxional. This is to be expected since all the bridging sites are occupied[20] and thus a mechanism for exchange of bridging hydrogen atoms is not available. Hexaborane(10) itself,[21] and the precursor, $K[Fe(CO)_4B_6H_9]$, are fluxional because there is one vacant site into which the bridging hydrogens and the Fe moiety may move.[22]

The species represents the first reported example of a rational synthesis of a heterobimetallaborane and is formally an *arachno*-dimetallaoctaborane.[23] There are two other known heterobimetallaboranes, and they are based on hexaborane(10) moieties in which a ligated metal moiety subrogates a BH group. $Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_3$[24] was prepared directly from $K[B_5H_8Fe(CO)_3]$ and $Cu[P(C_6H_5)_3]_3Cl$ and clearly represents a rational synthesis of a heterobimetallaheptaborane. The other, $\{[(C_6H_5)_3P]_2(CO)Os[C_6H_5(CH_3)_2P]ClHPtB_5H_7\}$,[25] is the somewhat unexpected product from the reaction between $\{[(C_6H_5)_3P]_2(CO)OsB_5H_8\}^-$ and $\{PtCl_2[P(CH_3)_2C_6H_5]_2\}$. This reaction was probably designed as a rational synthesis of a bimetallaheptaborane, but instead of simply replacing the missing proton in $\{[(C_6H_5)_3P]_2(CO)OsB_5H_8\}^-$ with the Pt moiety, $\{PtCl[P(CH_3)_2C_6H_5]_2\}^+$, 1 mol of $[P(CH_3)_2C_6H_5]$ is eliminated and the Pt bonds to the Os atom via the terminal H atom on Os, affording a species in which the electron count is 2 electrons short for a seven-vertex nido cluster.[25a,b] The structure of the latter is correct for a seven-vertex nido cluster, and the authors have explained the electron count in terms of the influence of the square-planar Pt^{2+} moiety.[24c,d] A metallaoctaborane, $[3,3,3,3\text{-}(CO)_4\text{-}arachno\text{-}WB_7H_{12}]^-$, was recently reported,[26] but our system represents the first report of a heterobimetallaoctaborane. The preparation of $Cu[P(C_6H_5)_3]_2B_6H_9Fe(CO)_4$ and the other examples we cite suggest that other dimetallaboranes may be accessible, and we have work in the area underway.

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Electron Transfer between Metal Cluster Complexes: Reaction of the Dianions $M_3(CO)_{11}^{2-}$ with the Dodecacarbonyltrimetal Clusters $M_3(CO)_{12}$ (M = Fe, Ru, Os)

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Summary: Electron-transfer reactions between trinuclear dianions $M_3(CO)_{11}^{2-}$ and neutral clusters $M'_3(CO)_{12}$ occur for M = Os, M′ = Fe and Ru and for M = Ru, M′ = Fe, producing the new clusters and cluster dianions $M'_3(CO)_{11}^{2-}$ and $M_3(CO)_{12}$. The reactions are consistent with the two-electron potentials obtained from reactions of the clusters with mononuclear anions. Isotopic labeling is inconsistent with a CO^{2+} transfer and indicates an outer-sphere electron-transfer mechanism through odd-electron intermediates.

Reaction of a metal carbonyl cluster with a metal carbonyl cluster dianion, redox condensation, is one of the most useful techniques for synthesis of high nuclearity metal clusters.[1] We have recently reported reactions of mononuclear metal carbonyl anions with the group 8 trinuclear clusters that provided an evaluation of the two-electron half-reaction potentials.[2]

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

In this note we describe the use of the half-reaction potentials to predict the electron transfer between metal cluster moieties.

Experimental Section

The details of the experimental procedure, syntheses, and kinetic procedure have been previously reported.[2] The infrared spectra of the $M_3(CO)_{11}^{2-}$ species are in good agreement with those previously reported.[3]

Reaction of $M_3(CO)_{11}^{2-}$ with $M'_3(CO)_{12}$. $M'_3(CO)_{12}$ (5 mg) was added to an excess of $[PPN]_2M_3(CO)_{11}$ (10–15 mg) in 15–20 mL of THF. The reaction mixture was allowed to stir for 10–15 min, and an IR spectrum in THF was taken. This spectrum showed that the reaction was complete and that $M_3(CO)_{12}$ and $M'_3(CO)_{11}^{2-}$ were formed. The THF was removed under reduced pressure and the solid extracted with hexanes. An IR spectrum in hexanes confirmed the presence of $M'_3(CO)_{12}$. These reactions were examined at 25 °C by using the 1.0-mm Irtran cell under pseudo-first-order conditions. The concentration of $(PPN)_2M_3(CO)_{11} = 1 \times 10^{-3}$ M, while $[M'_3(CO)_{12}] = 1 \times 10^{-2}$ M. Limited solubility of $M'_3(CO)_{12}$ precluded variation of the initial concentration of $M'_3(CO)_{12}$. However, the second-order rate constant can be calculated from $k_{obs} = k_2[M'_3(CO)_{12}]$. The de-

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

dianion/cluster	$Fe_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Os_3(CO)_{12}$
$Fe_3(CO)_{11}^{2-}$		NR	NR
$Ru_3(CO)_{11}^{2-}$	181 ± 5		NR
$Os_3(CO)_{11}^{2-}$	211 ● 7	263 ± 7	

crease in absorbance due to $M_3(CO)_{11}^{2-}$ (1757 cm^{-1} for M = Ru; 1923 cm^{-1} for M = Os) was monitored. The pseudo-first-order rate constant was calculated from the average of four runs.

Results and Discussion

A net transfer of two electrons (and a CO) between two trinuclear clusters has been observed in three cases.

$$Ru_3(CO)_{11}^{2-} + Fe_3(CO)_{12} \rightarrow Ru_3(CO)_{12} + Fe_3(CO)_{11}^{2-} \quad (1)$$

$$Os_3(CO)_{11}^{2-} + Fe_3(CO)_{12} \rightarrow Os_3(CO)_{12} + Fe_3(CO)_{11}^{2-} \quad (2)$$

$$Os_3(CO)_{11}^{2-} + Ru_3(CO)_{12} \rightarrow Os_3(CO)_{12} + Ru_3(CO)_{11}^{2-} \quad (3)$$

The half-reaction reduction potentials ($M'_3(CO)_{12} + 2e^- \rightarrow M_3(CO)_{11}^{2-} + CO$) have been previously evaluated:[2] M = Fe, −0.8 V; M = Ru, −0.9 V; M = Os, −1.1 V. The reactions observed (eqs 1–3) are consistent with these values for the reduction potentials.

The kinetic studies (Table I) show only a very small dependence of the rate constants on the nature of the reactants for all three reactions within a factor of 2. Such a small dependence would be consistent with an outer-sphere process, as suggested for reaction of mononuclear anions with trinuclear clusters. However, reactions 1–3 could also be considered as a CO^{2+} transfer, a reaction that we have previously demonstrated for some metal carbonyl anions with metal carbonyl cations.[4] These two possibilities, shown in Scheme I, can be tested by a ^{13}CO-labeling experiment. A CO^{2+} transfer involves only one CO, while an outer-sphere process through odd-electron complexes would completely scramble the label through the products. Reaction of $Os_3(CO)_{11}^{2-}$ with $Ru_3(CO)_{12}$ (enriched to ~80%) led to $Os_3(CO)_{12}$ highly enriched (~60%). Thus a simple CO^{2+} transfer can be excluded

Scheme I

CO^{2+} transfer

$$Os_3(CO)_{11}^{2-} + Ru_3(CO)_{12} \longrightarrow [(CO)_{11}Os_3\text{–}C(O)\text{–}Ru_3(CO)_{11}]^{2-} \longrightarrow Os_3(CO)_{12} + Ru_3(CO)_{11}^{2-}$$

outer sphere (single-electron transfer)

$$Os_3(CO)_{11}^{2-} + Ru_3(CO)_{12} \longrightarrow [Os_3(CO)_{11}^{\bullet-} + Ru_3(CO)_{12}^{\bullet-}] \longrightarrow Os_3(CO)_{12} + Ru_3(CO)_{11}^{2-}$$

and the result is consistent with an outer-sphere electron transfer.

Electrochemical studies of the group 8 trinuclear clusters have been reported.[5,6] Detailed studies of the reduction of $Ru_3(CO)_{12}$ and the oxidation of $Ru_3(CO)_{11}^{2-}$ offer several possibilities for electron-transfer intermediates. Single-electron reduction of $Ru_3(CO)_{12}$ produces $Ru_3(CO)_{12}^{\bullet-}$; from the electrochemical study it was suggested that metal–metal bond opening occurred prior to a second reduction and CO loss. For reaction 3, where complete scrambling of labeled ^{13}CO occurs, a scheme producing $Ru_3(CO)_{12}^{2-}$ is not likely. Loss of a CO would produce $Ru_3(CO)_{11}^{2-}$, which does not readily exchange with free CO. The complete scrambling of ^{13}CO is most consistent with CO-exchange reactions of $Ru_3(CO)_{12}^{\bullet-}$ and $Os_3(CO)_{11}^{\bullet-}$. Odd-electron complexes are known to rapidly exchange ligands.[7]

The direction of reactions 1–3 is consistent with the two-electron potentials previously evaluated.[2] The kinetics for each and labeling for reaction 3 are most consistent with a single-electron transfer to the odd-electron complexes. These studies provide an indication that redox condensation reactions also proceed through odd-electron complexes that then couple.

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