

fluxional. This is to be expected since all the bridging sites are occupied²⁰ 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*-dimetallaheptaborane.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 $Cu[P(C_6H_5)_3]Cl$ 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 unex-

pected 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 metallaheptaborane, $[3,3,3,3-(CO)_4\text{-arachno-WB}_7H_{12}]^-$, was recently reported,²⁶ but our system represents the first report of a heterobimetallaheptaborane. The preparation of $Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_4$ and the other examples we cite suggest that other dimetallaboranes may be accessible, and we have work in the area underway.

Acknowledgment. We acknowledge the support of the Monsanto Co. in the form of a postdoctoral fellowship to D.K.S., the Missouri Research Assistance Act and UM—St. Louis for financial support, and the National Science Foundation for the grant for the NMR spectrometer (CHE-8506671).

(26) Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; Macpherson, I.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* 1987, 476.

- (20) Rush, P. K.; Barton, L. *Polyhedron* 1985, 4, 1741.
 (21) (a) Brice, V. T.; Johnson, H. D.; Shore, S. G. *J. Am. Chem. Soc.* 1973, 95, 6629. (b) Brice, V. T.; Johnson, H. D.; Shore, S. G. *J. Chem. Soc., Chem. Commun.* 1972, 1128.
 (22) Ragaini, J. D. Ph.D. Thesis, The Ohio State University, 1977.
 (23) (a) Williams, R. E. *Inorg. Chem.* 1971, 10, 210. (b) Wade, K. *Adv. Inorg. Chem. Radiochem.* 1971, 18, 1. (c) Mingos, D. M. P. *Acc. Chem. Res.* 1984, 17, 311.
 (24) Mangion, M.; Ragaini, J. D.; Schmitkons, T. A.; Shore, S. G. *J. Am. Chem. Soc.* 1979, 101, 754.
 (25) (a) Bould, J.; Crook, J. E.; Greenwood, N. N.; Kennedy, J. D. *J. Chem. Soc., Chem. Commun.* 1983, 951. (b) Kennedy, J. D. *Prog. Inorg. Chem.* 1986, 34, 211. (c) Kennedy, J. D. *Main Group Met. Chem.* 1989, 12, 149. (d) Bould, J.; Crook, J. E.; Greenwood, N. N.; Kennedy, J. D. *J. Chem. Soc., Dalton Trans.* 1991, 185.

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

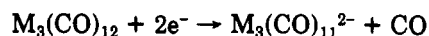
M. Shauna Corraine and Jim D. Atwood*

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

Received April 19, 1991

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



- (1) (a) Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* 1976, 14, 285. (b) Chini, P.; Cavalieri, A.; Maritengo, S. *Coord. Chem. Rev.* 1972, 8, 3. (c) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* 1980, 18, 207. (d) Geoffroy, G. L.; Gladfelter, W. L. *J. Am. Chem. Soc.* 1977, 99, 304. (e) Geoffroy, G. L.; Gladfelter, W. L. *J. Am. Chem. Soc.* 1977, 99, 7565.

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-

- (2) Corraine, M. S.; Atwood, J. D. *Organometallics*, in press.
 (3) (a) Strong, H.; Krusic, P. J.; San Filippo, J., Jr. *Inorg. Synth.* 1988, 24, 157. (b) Nagel, C. C.; Bricker, J. C.; Alway, D. G.; Shore, S. G. *J. Organomet. Chem.* 1981, 219, C9.

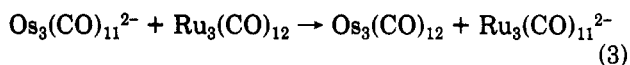
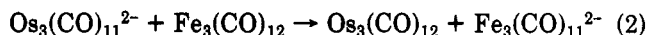
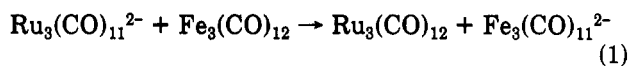
Table I. Second-Order Rate Constants ($s^{-1} M^{-1}$) for the Reaction of Metal Carbonyl Cluster Dianions with Metal Carbonyl Clusters at 25 °C in THF

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
$Os_3(CO)_{11}^{2-}$	$211 \bullet 7$	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.



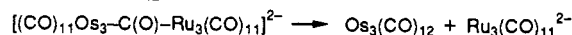
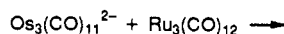
The half-reaction reduction potentials ($M_3(CO)_{12} + 2e^- \rightarrow M_3(CO)_{11}^{2-} + CO$) have been previously evaluated:² $M = Fe$, -0.8 V ; $M = Ru$, -0.9 V ; $M = Os$, -1.1 V . The reactions observed (eqs 1–3) are consistent with these values for the reduction potentials.

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 $\sim 80\%$) led to $Os_3(CO)_{12}$ highly enriched ($\sim 60\%$). Thus a simple CO^{2+} transfer can be excluded

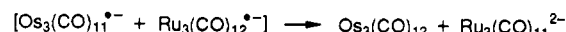
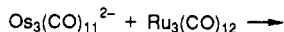
(4) (a) Atwood, J. D. *Inorg. Chem.* **1987**, *26*, 2918. (b) Zhen, Y.; Atwood, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 1506. (c) Zhen, Y. Q.; Feighery, W. G.; Lai, C. K.; Atwood, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 7832.

Scheme I

CO^{2+} transfer



outer sphere (single-electron transfer)



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.

Acknowledgment. We are grateful to the Department of Energy, Office of Basic Energy Sciences (Grant DE-FG02-87ER13775.A004), for support of this research. The VG 70-SE Mass Spectrometer was purchased by an instrument grant from the National Science Foundation (Grant CHE-850962).

(5) (a) Downard, A. J.; Robinson, B. H.; Simpson, J.; Bond, A. M. *J. Organomet. Chem.* **1987**, *320*, 363. (b) Dawson, P. A.; Peake, B. M.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1980**, *19*, 465. (c) Bond, A. M.; Dawson, P. A.; Peake, B. M.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1977**, *16*, 2199.

(6) Cyr, J. C.; DeGray, J. A.; Gosser, D. K.; Lee, E. S.; Rieger, P. H. *Organometallics* **1985**, *4*, 950.

(7) Troglor, W. C., Ed. *Organometallic Radical Processes*; Elsevier: Amsterdam, 1990.