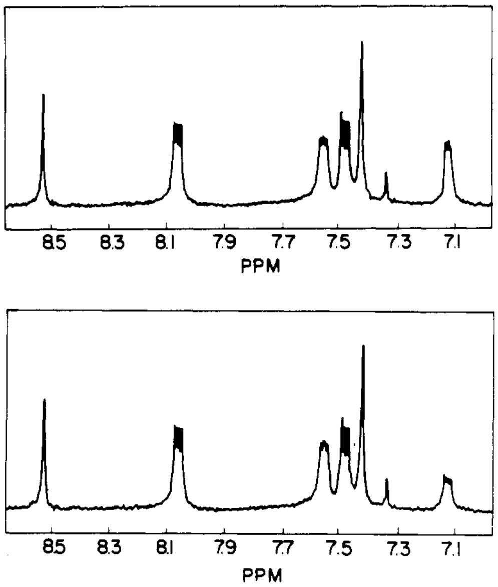

Figure 3. Mixture of bis(tributylphosphine)(anthracene)nickel (**3a**) and anthracene in THF-d_8 at -50 °C (a, top) without saturation and (b, bottom) with saturation of H_2 and H_3. See the assignment of the resonances in Figure 2.

same conditions but without saturation (Figure 3a). Thus, we conclude that *during the haptotropic process **1a** ⇄ **1b** intermolecular exchange of anthracene* (which is the most labile ligand) *does not take place, and the rearrangement is therefore intramolecular.*

The method's main limitations are that the complex under study has to be stable to excess ligand[10] and that the resonances which are exchanging must be sufficiently resolved to allow the specific saturation of only the desired resonance. In cases where the lines are poorly resolved, a 2D EXSY[8] experiment must be carried out. However, we want to emphasize that in many cases it is unnecessary to run the 2D experiment, which is far more time consuming and presents technical difficulties, especially when measurements at low temperature for prolonged times are required.

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(10) For example, **3** decomposes in the presence of Bu_3P to free anthracene and $(Bu_3P)_nNi$ (n = 3 or 4, depending on the amount of the phosphine introduced). Thus, a saturation-transfer experiment to determine a possible phosphine exchange (as suggested here) could not be performed.

$Cu[P(C_6H_5)_3]_2B_6H_9Fe(CO)_4$: Rational Synthesis of a Heterobimetallaborane from B_6H_{10}

Lawrence Barton* and Dileep K. Srivastava

Department of Chemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121

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Summary: The heterobimetallaborane $Cu[P(C_6H_5)_3]_2B_6H_9Fe(CO)_4$ is prepared by the reaction of $K[Fe(CO)_4B_6H_9]$ with $[P(C_6H_5)_3]_2CuBr\cdot0.5C_6H_6$. The species forms by insertion of the Cu(I) moiety into a basal boron-boron bond in the $Fe(CO)_4B_6H_{10}$ moiety generated by removal of a bridging hydrogen. This is the first report of a rational synthesis of a heterobimetallaborane from B_6H_{10}.

Hexaborane(10) and its conjugate base have several potential donor sites, but to date this aspect of its chemistry has not been exploited to any great extent,[1] and there are no known examples of simple dimetallaboranes in which a single hexaborane unit coordinates to two metal atoms. The direct basal B-B bond in B_6H_{10} is a basic site. This was demonstrated several years ago in proton affinity measurements,[2] and later, complexes of iron,[3,4] rhodium, iridium, nickel, and platinum,[4,5] in which this bond donates two electrons to the metal, were prepared. Also a bridging hydrogen atom in B_6H_{10} may be removed and replaced by electrophilic metal-containing moieties.[6] Thus complexes containing the metals Mg, Zn, Cd,[7] Ti,[8] Pt,[9] and Cu[10] have been prepared. The only example of a hexaborane(10)-based system in which these two bonding modes are found in a single B_6H_{10} moiety system is in the two related species $[(CO)_4FeB_7H_{12}]^-$ and $(CO)_4FeB_7H_{11}$. In these species,[11] a BH_3 moiety has been inserted into a site vacated by a proton and the B-B bond coordinates to a $Fe(CO)_4$ group. There do exist metallaboranes in which a $B_6H_9^-$ moiety coordinates to two metal atoms, but these examples, $\{[P(CH_3)_2C_6H_5)]_2Pt_2(\eta^3\text{-}B_6H_9)_2\}$,[9,12] $[Ti(B_6H_9)(C_5H_5)_2]_2$,[8,10b] and

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$\{Pt_2[P(CH_3)_2C_6H_5)]_2(\eta^3\text{-}B_2H_5)(\eta^3\text{-}B_6H_9)\}$,[13] involve complex dimeric species in the case of the first two and the latter involves a complex system involving the coordination of an adjacent pair of Pt atoms to both a $[B_6H_9]$ and a $[B_2H_5]$ moiety. A more complex example is the species $\{[P(CH_3)_2C_6H_5)]_4Pt_3B_{14}H_{16}\}$.[13b,c] In the case of the Pt species, the products result from either degradative processes involving higher boranes or thermolysis of similar species. Herein we report the first rational synthesis and characterization of a heterobimetallaborane based on B_6H_{10}.

Experimental Section

Materials. Hexaborane(10)[14] and $[(C_6H_5)_3P]_2CuBr{\cdot}0.5C_6H_6$[15] were synthesized by using standard literature procedures. $(C_6H_5)_3P$ and $CuBr_2$ were obtained from Alfa and used without further purification. KH, obtained as a mineral oil suspension from Research Organic/Inorganic Chemical Corp., was washed repeatedly with anhydrous pentane on the vacuum line before use until it was a free-flowing white powder. The activity of the powder in reactions with methanol was 85–95%. All solvents were reagent grade and were dried and distilled prior to use and stored in Pyrex vessels with Teflon stopcocks.

Apparatus. Standard high-vacuum line and drybox techniques were employed in this work.[16] NMR spectra were obtained on a Varian XL-300 high-resolution spectrometer operating at 300.1, 121.5, 96.3, and 76.6 MHz to observe ^1H, ^{31}P, ^{11}B, and ^{13}C resonances, respectively. ^{11}B chemical shifts are reported in ppm, positive signs denoting a shift at a lower field with respect to the $(C_2H_5)_2O{\cdot}BF_3$ reference (0 ppm). ^1H, ^{13}C, and ^{31}P chemical shifts were measured relative to $Si(CH_3)_4$, $CDCl_3$, and H_3PO_4, respectively. IR spectra were run as Nujol mulls prepared in the drybox or as KBr pellets on a Perkin-Elmer 1604 FT-IR spectrometer. Analyses were performed by Schwarzkopf Microanalytical Laboratories.

Synthesis. In a typical reaction, a vessel was charged with $Fe_2(CO)_9$ (0.66 g, 1.82 mmol) in the drybox. After evacuation on the vacuum line, 0.2 mL of B_6H_{10} (1.82 mmol) and 5 mL of pentane were condensed onto the solid. The mixture was allowed to stir at room temperature overnight (12 h). When all the solid dissolved, the solution was filtered into a two-necked reaction vessel and cooled to −35 °C. The pentane was distilled out of the vessel. Upon warming to 0 °C, excess B_6H_{10} and $Fe(CO)_5$ were removed under vacuum. The vessel was attached to an extractor and sealed with a rotatable solid addition tube containing 0.08 g (1.82 mmol, 90% active) of KH with utilization of a standard inert-atmosphere box. After evacuation on the vacuum line, the vessel was cooled to −35 °C and pumped for 2 h. Following prolonged evacuation, 0.4 mL of THF was condensed in at −196 °C. Deprotonation, under continual stirring, proceeded at −70 ± 10 °C. When H_2 evolution ceased, 1.3 mmol of H_2 was recovered on a Toepler pump. The flask was cooled to −196 °C, and under positive nitrogen flow, the vessel was sealed with a tipper tube side-arm containing $[(C_6H_5)_3P]_2CuBr{\cdot}0.5C_6H_6$ (0.92 g, 1.3 mmol). After evacuation, 7 mL of CH_2Cl_2 was distilled into the solution. The mixture was stirred at −78 °C and $[(C_6H_5)_3P]_2CuBr{\cdot}0.5C_6H_6$ was added. After stirring vigorously at −78 °C for 2 h, the mixture was allowed to warm and stirred for 1 h at −35 °C and overnight at −78 °C. The contents of the flask were filtered at −78 °C in a vacuum extractor to remove KBr. The orange yellow filtrate obtained was frozen at −196 °C, and under positive flow of nitrogen, the flask was transferred to a clean extractor on the vacuum line. After the volume of the filtrate was reduced (at −45 °C), 5 mL of $(C_2H_5)_2O$ was condensed at −196 °C. The solution was allowed to warm to −78 °C without stirring. Standing overnight at −78 °C under a blanket of nitrogen resulted in precipitation of the product, which was isolated by filtration at −78 °C and repeatedly washed with cold $(C_2H_5)_2O$ and C_5H_{12}. The product was dried under vacuum for several days. A pale yellow solid, which melts at 76–78 °C with decomposition, is obtained in 50% yield. It is soluble in CH_2Cl_2 and $CHCl_3$, slightly soluble in THF and $(C_2H_5)_2O$, and insoluble in pentane and hexane. Anal. Calcd for $C_{40}H_{39}B_6CuFeO_4P_2$: C, 57.8; H, 4.7. Found: C, 56.6; H, 4.9. The compound appears to be air and light sensitive, but in the dark it is stable for several days at room temperature and several months in a refrigerator in vacuo. Attempts to grow crystals from CH_2Cl_2/C_5H_{12} and also $C_6H_5CH_3/C_5H_{12}$ at low temperatures resulted in decomposition either in solution or upon removal of the solvent.

Table I. 96-MHz ^{11}B NMR Data[a]

$[(C_6H_5)_3P]_2CuB_6H_9Fe(CO)_4$[c]		$B_6H_{10}Fe(CO)_4$[d]	
atom	δ^b (J_{BH})	atom	δ^b (J_{BH})
B^1	−51.9 (159)	B^1	−52.19 (159)
B^2, B^3	−4.23[e]	B^4, B^5	2.05 (138)
B^4 or B^5	0.38[e]	B^3, B^6	6.79 (159)
B^5 or B^4	9.1[e]	B^2	12.6 (148)
B^6	12.89[e]		

[a] For numbering scheme, see Figure 1. [b] Chemical shifts are relative to $BF_3{\cdot}O(C_2H_5)_2$ (δ 0.00) determined by assignment relative to BCl_3 (δ 46.8) as an external standard. Uncertainties: δ, ±0.2 ppm; J, ±5 Hz. [c] In CD_2Cl_2 at 0 °C. [d] In $CDCl_3$ at 22 °C. [e] The coupling constant was not determined owing to the broad signals.

Infrared Data. The IR spectrum, run as a KBr pellet, showed the following absorbances (cm^{-1}): 3052 (m), 2960 (m), 2926 (m), 2860 (w), 2580 (m), 2518 (m), 2417 (w), 2058 (s), 1999 (s), 1948 (s), 1866 (s), 1481 (s), 1435 (m), 1261 (w), 1155 (w), 1092 (m), 1027 (w), 994 (w), 740 (m), 695 (m), 638 (m), 621 (m), 512 (m), 488 (m).

NMR Data. NMR spectral data (^1H, ^{11}B) and assignments for $[(C_6H_5)_3P]_2CuB_6H_9Fe(CO)_4$ and $B_6H_{10}Fe(CO)_4$ are summarized in Tables I and II, respectively.

Results and Discussion

The bimetallic species $Cu[P(C_6H_5)_3]_2B_6H_9Fe(CO)_4$, I, is prepared in 50% yield from B_6H_{10} as follows:

$$B_6H_{10} + Fe_2(CO)_9 \xrightarrow[25\ °C]{\text{pentane}} Fe(CO)_4B_6H_{10} + Fe(CO)_5 \qquad (1)$$

$$Fe(CO)_4B_6H_{10} + KH \xrightarrow[-78\ °C]{\text{THF}} K[Fe(CO)_4B_6H_9] + H_2 \qquad (2)$$

$$K[Fe(CO)_4B_6H_9] + [P(C_6H_5)_3]_2CuBr{\cdot}0.5C_6H_6 \xrightarrow[-35\ °C]{CH_2Cl_2} Cu[P(C_6H_5)_3]_2B_6H_9Fe(CO)_4 + KBr + 0.5C_6H_6 \qquad (3)$$

$Fe(CO)_4B_6H_{10}$, prepared by stirring B_6H_{10} and $Fe_2(CO)_9$ in pentane for 12 h, filtering off the insoluble materials, and removing excess B_6H_{10}, $Fe(CO)_5$, and pentane from the filtrate in vacuo,[17] is deprotonated with KH in THF at −78 °C to afford $K[Fe(CO)_4B_6H_9]$. Treatment with $[(C_6H_5)_3P]_2CuBr{\cdot}0.5C_6H_6$ in CH_2Cl_2 at −35 °C, gives an orange/yellow solid, which after workup affords a pale yellow powder that melts at 76–78 °C with decomposition and is slightly soluble in $(C_2H_5)_2O$ and insoluble in hydrocarbons. The compound appears to be air and light

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[17] Since $Fe(CO)_4B_6H_{10}$ is thermally and photolytically unstable at room temperature, we chose to use this method of isolation, rather than that suggested in ref 4, since it reduces the extent of decomposition into B_6H_{10} and iron carbonyls. We found that sublimation followed by handling at room temperature in the drybox, for extended periods, resulted in decomposition.

Table II. 300-MHz ^1H NMR Data[a]

$[(C_6H_5)_3P]_2CuB_6H_9Fe(CO)_4$[b]			$B_6H_{10}Fe(CO)_4$[c]		
atom	peak[d] (area)	δ	atom	peak (area)	δ (J)
C_6H_5 H atoms	m	7.25	H^5 or H^4	br s (1)	4.73
H^2, H^3 or H^4, H^5	br s (2)	3.62	H^4 or H^5	br s (1)	4.25
H^4, H^5 or H^2, H^3	br s (2)	3.02	H^3 or H^2	br s (1)	3.69
H^6	br s (1)	2.16	H^2 or H^3	br s (1)	3.18
H^1	q (1)	−0.95[e]	H^6	br s (1)	2.36
$H_{\mu 5,6}$ or $H_{\mu 2,6}$	br s (1)	−0.43	H^1	q (1)	−0.25[e] (165)
$H_{\mu 2,6}$ or $H_{\mu 5,6}$	br s (1)	−1.61	$H_{\mu 3,4}$, $H_{\mu 5,6}$	br s (2)	−1.35
$H_{\mu 3,4}$	br s (1)	−2.07	$H_{\mu 2,3}$, $H_{\mu 2,6}$	br s (2)	−0.2

[a] Chemical shifts expressed relative to $\delta(Me_4Si)$ = 0 ppm; values are accurate to $\delta = \pm 0.04$; for numbering scheme, see Figure 1; J in Hz. [b] In CD_2Cl_2 at −60 °C. [c] In $CDCl_3$ at 22 °C. [d] br = broad, s = singlet, q = quartet. [e] Center of quartet.

sensitive, but in the dark it is stable for several days at ambient temperature and for several months in a refrigerator under vacuum. The IR spectrum shows absorbances (KBr, cm^{-1}) at 2580 (m), 2518 (m), and 2417 (m), assigned to ν_{BHt}, and at 2058 (s), 1999 (s), 1948 (s), and 1866 (s), assigned to ν_{CO}. These latter data suggest that the $Fe(CO)_4$ group is intact and that the presence of possible B–H–Cu bonds is not confirmed. We have been unable to grow crystals suitable for crystal structure determination by X-ray diffraction.

NMR spectra are consistent with the pyramidal structure whose valence represenatation is given in the inset in Figure 1b. In this species, the anion $[B_6H_9]^-$ utilizes two donor sites involving basal B–B bonds. The ^{11}B spectrum is shown in Figure 1b, and Figure 1a contains the ^{11}B spectrum for $B_6H_{10}Fe(CO)_4$ that we recorded for comparison purposes. The ^{11}B spectrum of $Cu[P(C_6H_5)_3]_2B_6H_9Fe(CO)_4$ exhibits four broad resonances of approximate area ratio 1:1:1:2 at 12.89, 9.1, 0.38, and −4.23, and a sharp doublet at −51.9 ppm (J = 159 Hz) of area ratio 1. The resonances sharpen substantially on decoupling; the latter appearing as a sharp singlet. We assign the four broad resonances to basal boron atoms and the doublet to the apical boron. ^{11}B resonances for basal boron atoms in copper(I) boranes are observed to be typically broad, especially at lower temperatures,[10a,18] and this has been ascribed to the influence of quadrupolar relaxation of the copper nuclei.[18a]

Proton spectra are quite broad unless run at low temperatures. As indicated in Figure 1c, the −60 °C spectrum exhibits broad resonances at 3.62, 3.02, and 2.16 ppm in the approximate area ratio 2:2:1 and we have highlighted them in Figure 1c for clarity. These resonances broaden on warming and are indistinguishable at room temperature. They fall in the region expected for terminal hydrogens bonded to basal boron atoms and we assign them as H^4 and H^5, or H^2 and H^3; H^2 and H^3, or H^4 and H^5; and H^6, respectively. In the upfield region, broad resonances are observed at −0.43, −1.61, and −2.07 ppm, presumably arising from the three bridging hydrogen atoms. These resonances broaden somewhat as the sample is warmed but are still distinct at 0 °C. The hydrogen bonded to the apical boron atom (H^1) is not clearly observed, although weak members of a 1:1:1:1 quartet (J = 130 Hz) are visible centered at −0.95 ppm. At −60 °C, the terminal hydrogens bonded to the basal borons are presumably thermally decoupled but, as expected, the hydrogen bonded to the apical boron appears as a quartet. $^{31}P\{^1H\}$ NMR spectra at 1.3 °C exhibit a single resonance at −2.46 ppm, but as the temperature is lowered, it splits into two resonances at −20 °C and, at −80 °C, several species are observed, consistent with previous observations that dissociative equilibria exist for such systems.[19] The CO ligands are observed in ^{13}C NMR spectra at 210 ppm. Proton NMR data indicate that $Cu[P(C_6H_5)_3]_2B_6H_9Fe(CO)_4$ is not

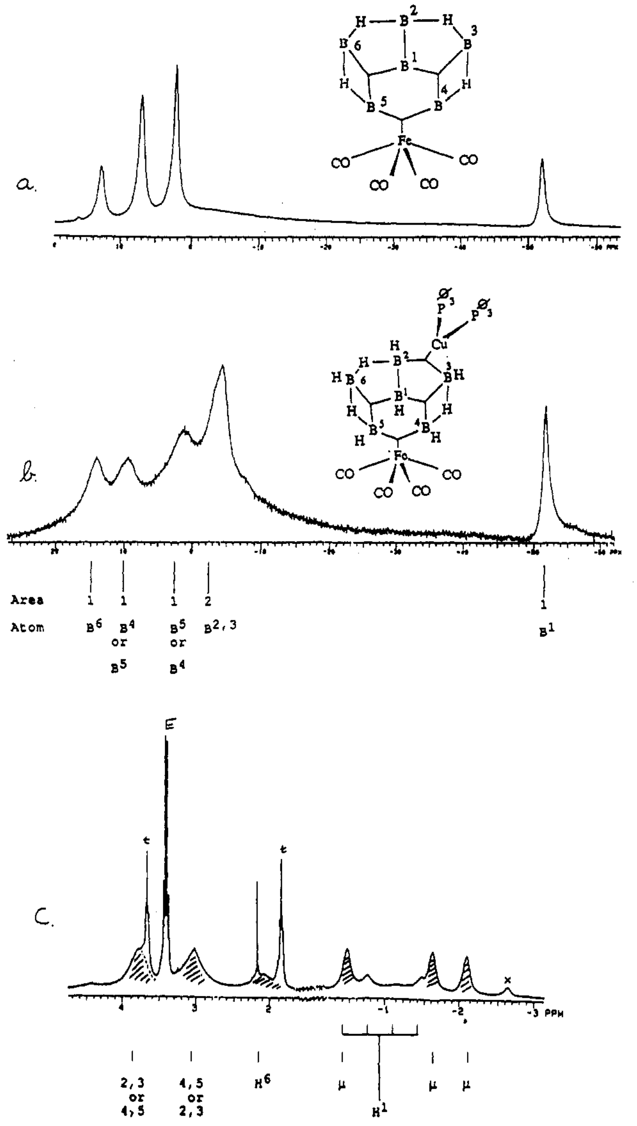

Figure 1. (a) $^{11}B\{^1H\}$ NMR spectrum of $B_6H_{10}Fe(CO)_4$ in CD_2Cl_2 at 0 °C with the structure of $B_6H_{10}Fe(CO)_4$ inset. (b) $^{11}B\{^1H\}$ NMR spectrum in CD_2Cl_2 at 0 °C with the proposed valence structure of $[(C_6H_5)_3P]_2CuB_6H_9Fe(CO)_4$ inset. (c) Proton NMR spectrum of $[(C_6H_5)_3P]_2CuB_6H_9Fe(CO)_4$ at −60 °C in CD_2Cl_2. (x = $K[B_6H_9Fe(CO)_4]$ impurity, t = THF, E = Et_2O).

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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)

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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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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