Synthesis of $B_2H_5FeCo(CO)_6$, $Fe_2Co(CO)_9(-CO)BH_2$, $FeCo_2(CO)_9(-CO)BH$, $FeCo_2(CO)_9(BH)_2$, and $HFe_3Co(CO)_{12}BH$. $Co(CO)_3$ Fragment Addition and Fragment Exchange in Ferraborane Clusters

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The reactions of $Co_2(CO)_8$ with the ferraboranes $B_2H_6Fe_2(CO)_6$, $HFe_3(CO)_9BH_4$, $HFe_3(CO)_{10}BH_2$, and $HFe_4(CO)_{12}BH_2$ lead to fragment addition and/or fragment exchange. Thus, the new mixed-metal metallaboranes $B_2H_5FeCo(CO)_6$ (**1**), $Fe_2Co(CO)_9(-CO)BH_2$ (**2**), $FeCo_2(CO)_9(-CO)BH$ (**3**), $FeCo_2(CO)_9(BH)_2$ (**4**), and $HFe_3Co(CO)_{12}BH$ (**5**) have been isolated in modest yields and characterized spectroscopically. Comparison of selected spectroscopic and chemical properties of isoelectronic pairs of hetero- and homometallaboranes defines the perturbation of the cluster network by the replacement of HFe by Co. Both direct effects due to the different metal atoms and indirect effects resulting from the differing number of skeletal hydrogen atoms are observed. Consistent with the radical mechanism suggested for $Co(CO)_x$ fragment addition to and exchange with organometallic clusters, a radical mechanism is proposed. However, the metallaborane reactions require neutral molecules and appear to be initiated by H atom transfer whereas the analogous anionic organometallic reactions proceed via electron transfer.

Introduction

The synthesis of main group element analogs of organometallic complexes provides an experimental platform for developing an understanding of the role of element variation in structure and reactivity.[1] A significant number of ferraboranes made up of $Fe(CO)_3$ and BH fragments have isoelectronic transition metal hydrocarbyl partners; i.e., a BH_2 or BH^- fragment in the former is replaced by a CH fragment in the latter.[2] The same type of interchange in terms of isolobal metal fragments is the replacement of a $HFe(CO)_3$ or $[Fe(CO)_3]^-$ fragment with a $Co(CO)_3$ fragment. Indeed we, and others, have explored the subtle changes induced by such an interchange in organometallic clusters.[3−6] An examination of the effects of metal variation on the structure and properties of a borane fragment in a metallaborane would complete the carbon−boron analogy. As there are numerous metallaboranes containing the ^{5}-C_5H_5Co fragment,[7−11] which is isolobal with the $Fe(CO)_3$ fragment, one might argue that this has already been accomplished. Indeed even a metallaborane containing both ^{5}-C_5H_5Co fragments and $Fe(CO)_3$ fragments is known.[12] But in comparing compounds containing isolobal $Fe(CO)_3$ vs ^{5}-C_5H_5Co fragments, it is not possible to separate the effects of the different metals from those of the different ligands on the metals. The electronic effects of a metal fragment, as opposed to its qualitative bonding tendencies, depend strongly on its ligands, and only by a comparison of compounds with identical ligands on the metal centers can the properties be directly related to the identity of the metal centers.[13,14]

The interchange of nuclei in isoelectronic systems is only realized indirectly, and the desired metallaboranes present a significant synthetic problem. There are only a few examples of metallaboranes containing cobalt carbonyl fragments in the literature.[15−18] However, metal carbonyl anions, including those of iron, are known to undergo metal fragment addition or exchange reactions with $Co_2(CO)_8$.[19−21] The seemingly straightforward extension of this chemistry to the ferraboranes, patterned after the anionic cluster chemistry, led only to complete degradation of the starting material. Further exploration showed that it is the neutral ferraboranes that permit the synthesis of a set of compounds containing one or two $Co(CO)_3$ fragments. In this manner the isoelectronic boron−carbon cluster analogy has been extended to mixed−metal systems and the solution of the synthetic problem suggests mechanistic connections between the organometallic and metallaborane systems. In retrospect, the presence of radical intermediates in the fragment addition or exchange chemistry of the organometallic clusters[20] is consistent with sensitivity of the reaction to charge on the reactant, solvent, and reaction conditions.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1996.

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Experimental Section

General Procedures. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk line or drybox techniques. Solvents were predried over KOH (hexanes, toluene), and purged with N_2 prior to distillation. Hexanes and toluene were distilled from sodium benzophenone ketyl. $Co_2(CO)_8$ was obtained from Strem and purified by recrystallization from hexanes. The ferraboranes were prepared and purified as described in the literature.[22] Carbon monoxide was used directly from the tank. Baker Silica gel was activated by heating at 110 °C for several hours before chromatography was carried out. Column chromatography was performed under N_2 at low temperatures. NMR spectra were obtained on 300-MHz FT- NMR spectrometers. Residual protons of solvent were used as the reference for ^1H NMR (‰, ppm: benzene, 7.15; dichloromethane, 5.32; toluene, 2.09). A sealed tube containing $[(NEt_4)(B_3H_8)]$ (‰ −29.7 ppm) was used as the external reference for ^{11}B NMR. Infrared spectra were obtained on a Nicolet 205 FT-IR spectrometer. Mass spectra were obtained on a Finnigan MAT Model 8400 mass spectrometer with EI ionization mode. Perfluorokerosene was used as the standard for the high-resolution EI mass spectra.

Reaction of $B_2H_6Fe_2(CO)_6$. To a CO- or N_2-saturated hexane solution of 0.9 g (2.6 mmol) of $Co_2(CO)_8$ in 30 mL of hexane in a 40 mm o.d. cylindrical Schlenk tube was added 0.4 g (1.3 mmol) of liquid $B_2H_6Fe_2(CO)_6$. The flask was heated to the reaction temperature and the progress of the reaction monitored periodically by ^{11}B NMR. The reaction was stopped at the optimal yield of the desired product (see below) by cooling the tube. After reduction of the solution volume to 10 mL, the bulk of the $Co_4(CO)_{12}$, which inevitably formed no matter what the conditions, could be precipitated by holding the tube at 0 °C for several hours. The supernatant was loaded onto a cold chromatography column (silica gel, 1.8   15 cm, −20 to −40 °C under N_2), and the products described below were eluted with hexanes. All of the compounds are air sensitive and rather unstable. Besides those described below, other products were formed but were formed in low yield and/or were too unstable to isolate as pure compounds.

$B_2H_5FeCo(CO)_6$ (1). Reaction at 70 °C under 1 atm of CO for 7 h led to the total consumption of $B_2H_6Fe_2(CO)_6$. The first band from the column was a volatile, orange oil, which was purified by vacuum line fractionation (−20 °C). Compound **1** was isolated in 34% yield based on the ferraborane. This compound was formed under all reaction conditions but was easily removed from the reaction mixture under vacuum. MS/EI, *m*/*e*: P^+ 310 (2B − 6CO); calcd for $(P - 28)^+$, $^{12}C_5{}^1H_5{}^{16}O_5{}^{11}B_2{}^{56}Fe^{59}Co$, 281.9041, obsd 281.9021. NMR: ^{11}B (hexane, 22 °C, ‰) −13.5 br d (J_{BH} = 144 Hz), $\{^1H\}$ br s; ^1H (toluene-d_8, 22 °C, ‰) 2.24 br (2H), −2.68 br (1H), −15.17 br (2H). IR (hexane, cm^{-1}): (BH) 2530 vw; (CO) 2098 w, 2054 vs, 2034 s, 2007 m.

$Fe_2Co(CO)_9($ -CO$)BH_2$ (2). After reaction at room temperature under 1 atm of N_2 for 1 day with stirring (magnetic stirring bar), the concentrated reaction mixture was kept at 0 °C for 24 h to remove excess $Co_2(CO)_8$ and $Co_4(CO)_{12}$. The second band from the column was a nonvolatile, deep dull green compound. Minor volatile impurities were removed by extended time under vacuum giving pure **2** in 30% yield. MS/EI, *m*/*e*: P^+ 463.6 (1B − 10CO); calcd for $^{12}C_{10}{}^1H_2{}^{16}O_{10}{}^{11}B^{56}Fe_2{}^{59}Co$ 463.78. NMR: ^{11}B (hexane, 22 °C, ‰) 58.2 br d (J_{BH} = 120 Hz), $\{^1H\}$ br s; ^1H (toluene-d_8, 22 °C, ‰) 5.5 br d (partially collapsed q) (1H), −10.8 br s (1H). IR (hexane, cm^{-1}): (BH), 2496 vw; -(CO) 2102 m, 2059 vs, 2051 vs, 2039 s, 2020 s, 2019 sh, 2004 s, 1990 sh, 1973 vw, 1963, vw, 1896 m br.

$FeCo_2(CO)_9($ -CO$)BH$ (3) and $FeCo_2(CO)_9(BH)_2$ (4). Reaction at 70 °C under 1 atm of CO for 12 h optimized formation of **3**, which appeared as the major component of the second band (volatile, purple-brown compound). It was purified by vacuum sublimation and isolated in 30% yield. MS/EI, *m*/*e*: P^+ 466 (1B − 10CO), calcd for $^{12}C_{10}{}^1H^{16}O_{10}{}^{11}B^{56}Fe^{59}Co_2$ 465.7676, obsd 465.7624. NMR: ^{11}B (hexane, 22 °C, ‰) 85.6 br d (J_{BH} = 135 Hz), $\{^1H\}$ br s; ^1H (toluene-d_8, −55 °C, ‰) 6.76 br s (collapsed q). IR (hexane, cm^{-1}): (BH), 2533 vw; (CO) 2061 s, 2053 vs, 2037 s, 2023 m, 2001 s, 1866 w.

A reaction mixture, which was prepared under the same conditions just described, was crystallized (−5 °C for 1 week to precipitate $Co_2(CO)_8$ and $Co_4(CO)_{12}$; evacuation for 1 day to remove all volatile material; precipitation at −40 °C with minimum amount of hexanes) to obtain **4**. Although the compound was pure by NMR, the mass spectrum showed a significant amount of **3** formed, presumably during the MS procedures. Column chromatography of **4** resulted in the formation of **3**, which was not a major component of the reaction mixture before chromatography. MS/EI, *m*/*e*: P^+ 450 (2B − 9CO), calcd for $^{12}C_9{}^1H_2{}^{16}O_9{}^{11}B_2{}^{56}Fe^{59}Co_2$ 449.7898, obsd 449.790. NMR: ^{11}B (hexane, 22 °C, ‰) 102.3 br d (J_{BH} =160 Hz), $\{^1H\}$ br s; ^1H (toluene-d_8, −55 °C, ‰) 6.9 br s (collapsed q). IR (hexane, cm^{-1}): (BH), 2543 vw; (CO) 2078 w, 2061 s, 2054 vs, 2047 s, 2036 sh, 2023 s, 2000 s, 1985 w sh, 1886 w.

Reactions of $HFe_3(CO)_9BH_4$, $HFe_3(CO)_{10}BH_2$, and $HFe_4(CO)_{12}BH_2$. In contrast to $B_2H_6Fe_2(CO)_6$, these ferraboranes generated a single boron-containing product in good yield. Fragment addition to the three-metal clusters and fragment substitution of the four-metal cluster were observed.

$HFe_3Co(CO)_{12}BH$ (5). In a typical reaction, 0.3 g (0.5 mmol) of $HFe_4(CO)_{12}BH_2$ and 2.0 g of $Co_2(CO)_8$ (6 mmol) were dissolved in 20 mL of hexanes in a 40 mm o.d. Schlenk flask under CO atmosphere. Reaction at 75 °C showed only a single new ^{11}B signal; however, after long reaction times when the reactant ferraborane was depleted, a shoulder appeared on the low-field side of the triplet at ‰ 114 due to $HFe_4(CO)_{12}BH_2$. Column chromatography yielded yellow bands of $Fe(CO)_5$ and $Co_2(CO)_8$, followed by a green-brown band of **5**, which was isolated in 20% yield. The actual yield was substantially higher (>50% by NMR), but much was lost during separation due to overlap of **5** with the closely following bands of $HFe_4(CO)_{12}BH_2$ and $Co_4(CO)_{12}$. MS/EI, *m*/*e*: P^+ 576 (1B − 12 CO); calcd for $^{12}C_{12}{}^1H_2{}^{16}O_{12}{}^{11}B^{56}Fe_3{}^{59}Co$ 575.7004, obsd 575.7020. NMR: ^{11}B (hexane, 22 °C, ‰) 147.8 br d (J_{BH} = 70 Hz), $\{^1H\}$ br s; ^1H (toluene-d_8, 20 °C, ‰) −9.9 br d (partially collapsed q) 1 H), −23.73 s (with long delay time, no broadening at low temperature) (1 H). IR (hexane, cm^{-1}): (CO) 2103 w, 2063 s, 2049 vs, 2042 vs, 2034 s, 2014 m, 1994 m.

Heating a pure sample of **5** in toluene-d_8 at 70 °C while the ^1H NMR spectrum was monitored gave rise to the appearance of a partially collapsed quartet at ‰ −11.8 ppm. The intensity of this signal increased to a plateau at 10% of that of **5**. Subsequent ^{11}B NMR showed the presence of **5** and a weak triplet at ‰ 115 (J_{BH} = 70 Hz). Unfortunately, this apparent isomer of **5**, **5′**, could not be isolated as a pure compound. Note that the ^{11}B NMR of the isomer is nearly identical to that of $HFe_4(CO)_{12}BH_2$ whereas the ^1H NMR is significantly different.

In a typical reaction, 44 mg (0.10 mmol) of $HFe_3(CO)_9BH_4$ in 1 mL of hexanes was added to 67 mg (0.20 mmol) of $Co_2(CO)_8$ in hexanes under N_2 or CO and the reaction was monitored by ^{11}B NMR at various temperatures. At a reaction temperature of 45 °C, the half-life of the ferraborane was 2 h and exclusive formation of **5** was observed by ^{11}B NMR in 40% NMR yield. Reaction at 70 °C led to the formation of **5** and **5′** in 60 and 4% yields, respectively. Reaction at 70 °C under CO gave the same results but slightly higher yields (73 and 4%, respectively).

Reaction of 80 mg (0.17 mmol) of $HFe_3(CO)_{10}BH_2$ in 2 mL of hexanes with excess $Co_2(CO)_8$ under N_2 was monitored by ^{11}B NMR at room temperature. The half-life of the ferraborane was 5.5 h, and exclusive formation of **5** was observed by ^{11}B NMR in 80% yield. The ^1H NMR at 80 °C showed the presence of **5** and **5′** in the ratio 8:1.

Proton Competition. The salt of the conjugate base of $B_2H_6Fe_2(CO)_6$, $[HNEt_3][B_2H_5Fe_2(CO)_6]$, was prepared by deprotonation of $B_2H_6Fe_2(CO)_6$ with NEt_3. Similarly, neat NEt_3 was added to a Schlenk flask containing 0.01 mmol of **1** in 5 mL of hexane at −78 °C until the orange color of the hexane solution completely disappeared. The red-brown precipitate that formed was washed with hexane to remove any slight excess of amine. Addition of CF_3CO_2H to the precipitate plus hexane led to its disappearance and the formation of an orange solution containing **1** (IR and NMR). The clean protonation of the solid to give **1** is chemical evidence that the precipitate is $[HNEt_3][B_2H_4FeCo(CO)_6]$. Dissolution of the precipitate in THF, SMe_2, or H_2O led to rapid, complete decomposition, thereby precluding direct spectroscopic characterization.

To a Schlenk flask containing an excess amount of $[HNEt_3][B_2H_5Fe_2(CO)_6]$ powder was added 0.01 mmol of **1** in 10 mL of hexane. The solution was stirred at room temperature with occasional shaking

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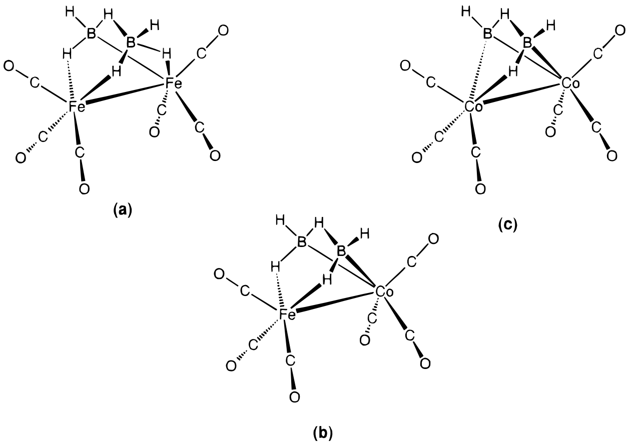

Figure 1. Schematic drawings of the proposed structures for (a) $B_2H_6Fe_2(CO)_6$, (b) $B_2H_5FeCo(CO)_6$, **1**, and (c) $B_2H_4Co_2(CO)_6$.

of the entire flask, and aliquots of the solution were examined by ^{11}B NMR at 2 h intervals. No $B_2H_6Fe_2(CO)_6$ was detected, and **1** remained undecomposed.

To a Schlenk flask containing 0.01 mmol of $[HNEt_3][B_2H_4FeCo(CO)_6]$ powder was added an approximately 2-fold excess of $B_2H_6Fe_2(CO)_6$ in 10 mL of hexane. The solution was stirred at room temperature, and aliquots of the solution were examined by ^{11}B NMR at 2 h intervals. The resonance characteristic of **1** was observed in an integrated intensity comparable to the loss in intensity in the signal due to $B_2H_6Fe_2(CO)_6$. Extraction of the hexane-insoluble solid with diethyl ether after completion of the reaction, followed by ^{11}B NMR of the solution, shows the presence of $[HNEt_3][B_2H_5Fe_2(CO)_6]$. The relative intensity of the signal due to $[HNEt_3][B_2H_5Fe_2(CO)_6]$ was comparable to that of **1** from which the sample of $[HNEt_3][B_2H_4FeCo(CO)_6]$ was prepared.

Results

Mixed-metal Co−Fe metallaboranes are prepared by $Co(CO)_3$ fragment addition or exchange with known ferraboranes. With one exception, each of these new compounds is isoelectronic with a structurally characterized ferraborane. Hence, the geometric structures can be established from the spectroscopic data as follows.

$B_2H_5FeCo(CO)_6$ (1). Composition of this volatile liquid is defined by precise mass measurement, an isotope distribution pattern characteristic of two boron atoms, and fragments corresponding to six CO losses of the parent cation in the mass spectrum. The IR spectrum is characteristic of a "sawhorse" $M_2(CO)_2$ fragment[23] and very similar to that of $[B_2H_5Fe_2(CO)_6]^-$ except that the frequencies lie 50 cm^{-1} to higher energy.[24] The ^{11}B NMR spectrum shows the presence of equivalent BH fragments in accord with the IR in the BH stretching region. The ^1H NMR is consistent with two equivalent BH terminal protons, one B−H−B bridge proton and two equivalent B−H−M protons. Below −60 °C, the signal at ‰ −15.2 is split by 12 Hz into two signals of equal intensity. This splitting is assigned to geminal $H_{term}-H_{bridge}$ coupling[25] rather than fortuitous near overlap of B−H−Fe and B−H−Co resonances. The proposed structure of **1**, shown in Figure 1b, is consistent with the spectroscopic data. Note that the postulated structure of $B_2H_6Fe_2(CO)_6$ is supported by solid state structure determinations on two geometric isomers of the dimer $\{B_2H_4Fe_2(CO)_6\}_2$[26] as well as the structure of a closely related tantalum compound.[27]

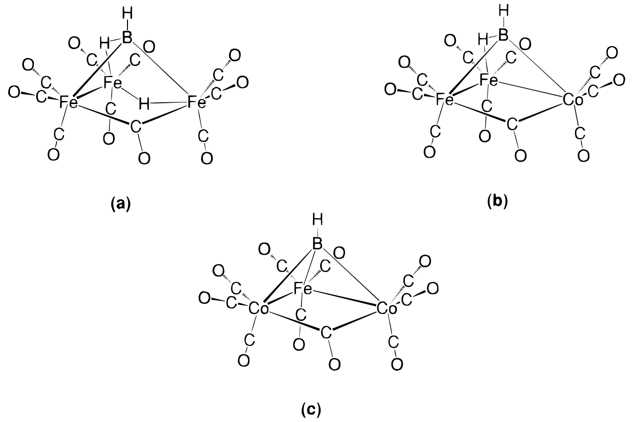

Figure 2. Schematic drawings of the proposed structures for (a) $HFe_3(CO)_{10}BH_2$, (b) $Fe_2Co(CO)_{10}BH_2$, **2**, and (c) $FeCo_2(CO)_{10}BH$, **3**.

$Fe_2Co(CO)_9$(-CO)BH_2 (2). Composition of this volatile solid compound is defined by the mass, an isotope distribution pattern characteristic of one boron atom, and fragments corresponding to 10 CO losses of the parent cation in the mass spectrum. The IR spectrum is very similar to that of $HFe_3(CO)_{10}BH_2$ (Figure 2a)[28] and is distinguished by the presence of a strong absorption due to a bridging CO ligand. It has the same number of hydrogen atoms as $[Fe_3(CO)_{10}BH_2]^-$, the structure of which has been verified by a crystal structure of $[Fe_3(CO)_{10}HBCl]^-$.[29] The chemical shift and ^1H coupling exhibited by the ^{11}B NMR resonance are very similar to those of $HFe_3(CO)_{10}BH_2$, and the two ^1H resonances are similar to the terminal BH and bridging B−H−M proton resonances of the same compound. Thus, the postulated structure of **2** is that shown in Figure 2b.

$FeCo_2(CO)_9$(-CO)BH (3). Composition of this solid compound is defined by precise mass measurement, an isotope distribution pattern characteristic of one boron atom, and fragments corresponding to 10 CO losses of the parent cation in the mass spectrum. As with **2**, the IR spectrum is similar to that of $HFe_3(CO)_{10}BH_2$ and exhibits a band due to a bridging CO ligand. The ^{11}B NMR resonance is further downfield (see below) and the BH terminal coupling is larger, consistent with the loss of a B−H−M bridge.[25] The ^1H NMR spectrum shows only a BH terminal resonance, and the postulated structure of **3** is shown in Figure 2c.

$FeCo_2(CO)_9(BH)_2$ (4). The composition of this solid compound is suggested by the parent ion *m*/*e* measurement, an isotope distribution pattern characteristic of two boron atoms, and fragment ions corresponding to nine consecutive CO losses from the parent radical cation in the mass spectrum. **3** is a prominent impurity in the mass spectrum despite the fact that solution spectra suggested a relatively pure sample. The high volatility of **3** and the tendency of **4** to be converted into **3** are undoubtedly responsible for this observation. The low-field ^{11}B resonance, large J_{BH}, and single ^1H terminal BH resonance are consistent with BH fragments capping a M_3 triangle. The closest structural analog is $Cp^*{}_3Co_3B_2H_4$,[30,31] and its structure and the postulated structure of **4** are shown in Figure 3 .

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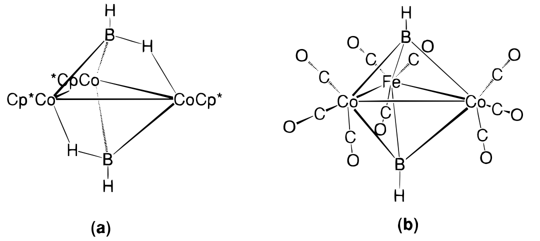

Figure 3. Schematic drawings of (a) the structure for $Cp*_3Co_3B_2H_4$ and (b) the proposed structure of $FeCo_2(CO)_9B_2H_2$, **4**.

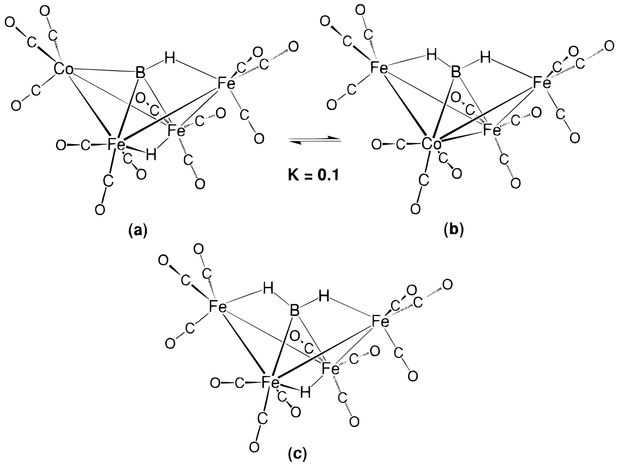

Figure 4. Schematic drawings of the proposed structures for (a) $HFe_3Co(CO)_{10}BH$, **5**, and (b) $Fe_3Co(CO)_{12}BH_2$, isomer of **5**, and the structure of (c) $HFe_4(CO)_{12}BH_2$.

$HFe_3Co(CO)_{12}BH$ (5). Composition of this solid compound is defined by precise mass measurement, an isotope distribution pattern characteristic of one boron atom, and fragments corresponding to 12 CO losses of the parent cation in the mass spectrum. The IR spectrum of **5** is very similar to that of the crystallographically characterized $HFe_4(CO)_{12}BH_2$. No BH terminal stretch is observed, which suggests an open "butterfly" structure similar to that of the parent ferraborane.[32] The doublet observed in the ^{11}B NMR at a chemical shift similar to that of $[HFe_4(CO)_{12}BH]^-$[33] suggests a like distribution of hydrogen atoms on the cluster framework. Consistent with this assumption, the value of J_{BH} is similar to that observed for $HFe_4(CO)_{12}BH_2$ and the chemical shifts and widths of the two signals observed in the ^1H NMR spectrum are characteristic of B−H−M and M−H−M protons, respectively. Variable-temperature ^1H NMR showed no change in the M−H−M resonance with temperature (fwhm = 7 Hz), consistent with a Fe−H−Fe bridge. Thus, the postulated structure for **5** is that shown in Figure 4a, i.e., the same as that of $[HFe_4(CO)_{12}BH]^-$ with a $Co(CO)_3$ fragment replacing a $Fe(CO)_3$ fragment in a "wing-tip" position.

The isomer of **5**, **5′**, was not isolated as a pure compound; however, the formation of **5′** from three independent routes to **5** confirms that it is indeed an isomer. The NMR data give a clear picture of the structure of **5′**. The ^1H NMR shows no M−H−M resonance and a single B−H−M resonance shifted upfield from that of **5** to a chemical shift similar to, but measurably different from, those of the B−H−Fe protons of $HFe_4(CO)_{12}BH_2$. Consistent with this observation, the ^{11}B NMR resonance appears at a chemical shift nearly equal to that of $HFe_4(CO)_{12}BH_2$. Thus, the postulated structure (Figure 4b) has a $Co(CO)_3$ fragment replacing a "hinge" $Fe(CO)_3$ fragment and the Fe−H−Fe bridging hydrogen of the $HFe_4(CO)_{12}BH_2$ structure. Although equilibrium between **5** and **5′** at 70 °C appears to be established (pure **5** yields 10% of **5′**), the conversion of the isomer into the equilibrium mixture could not be investigated. Nonetheless, the exclusive formation of **5** from either $HFe_3(CO)_9BH_4$ or $HFe_3(CO)_{10}BH_2$ at room temperature suggests that **5** is the first formed product and rearrangement to the slightly less stable isomer occurs subsequently and only at elevated temperatures. Note that in the organometallic analog of this reaction the product observed inevitably shows the heterometal in the "hinge" position. Presumably the more accessible "wing-tip" position is replaced first in the organometallic cluster. This kinetic product must rearrange rapidly into the more stable "hinge" isomer under the reaction conditions.[19]

Proton Competition. The relative acidities of a pair of molecules can be determined by reacting the conjugate base of one molecule with the other and vice versa.[34,35] For an unambiguous result, both anions (conjugate bases) are required. The anions of all the ferraboranes dealt with here are easily obtained by deprotonation with a variety of bases.[36] However, deprotonation of a metallaborane with one or more $Co(CO)_x$ fragments gives an anion of limited stability, particularly in polar solvents. Consequently, we were only successful in defining the Brønsted acidity of **1** relative to $B_2H_6Fe_2(CO)_6$. The experiments demonstrate that the equilibrium constant for (1)

$$[HNEt_3][B_2H_4FeCo(CO)_6] + B_2H_6Fe_2(CO)_6 = [HNEt_3][B_2H_5Fe_2(CO)_6] + B_2H_5FeCo(CO)_6 \quad (1)$$

is greater than 1. Thus, $B_2H_6Fe_2(CO)_6$ is a stronger Brønsted acid than $B_2H_5FeCo(CO)_6$, showing that the replacement of a $HFe(CO)_3$ fragment by a $Co(CO)_3$ fragment results in a decrease in acidity.

Mechanistic Observations. Additional observations that have mechanistic relevance are as follows. Non-boron-containing products included the ubiquitous $Co_4(CO)_{12}$, $HCo(CO)_4$, and $Fe(CO)_5$, which were identified by their physical properties and characteristic IR spectra during product separation. In contrast to related substitution reactions with anionic organometallic clusters,[20] neither $[B_2H_5Fe_2(CO)_6]^-$ nor $[B_2H_4Fe_2(CO)_6]^{2-}$ yields any new boron-containing products on reaction with $Co_2(CO)_8$. Although the anions of the ferraboranes are both stable and useful synthetically, attempts to deprotonate the mixed-metal compounds were largely unsuccessful. In fact, all the mixed-metal compounds had limited stability in polar solvents like THF, which partially deprotonates $B_2H_6Fe_2(CO)_6$. Finally, **1** reacts with $Co_2(CO)_8$ to yield **3**, **4**, $B_2H_4Co_2(CO)_6$, and substantial amounts of $Co_5(CO)_{14}B_2H$.[37]

Discussion

Comparison of selected spectroscopic and chemical properties of these five new compounds with those of known isoelectronic ferraboranes reveals the role of the heterometal in cluster properties. A comparison of the ferraboranes with isoelectronic hydrocarbyl complexes has been done previously.[36]

Vibrational Frequencies. As already noted above, the carbonyl bands of isoelectronic Fe and FeCo pairs have similar frequencies and intensities. The well-resolved, simple pattern

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of the "sawhorse" $M_2(CO)_6$ fragment in $B_2H_6Fe_2(CO)_6$,[24] **1**, and $B_2H_4Co_2(CO)_6$[37] permits a more precise comparison. On average, the CO stretching frequencies of these three compounds differ by 5 cm^{-1} with $B_2H_4Co_2(CO)_6 > B_2H_5FeCo(CO)_6 > B_2H_6Fe_2(CO)_6$, suggesting increasing negative charge at the metal center in the same order. For calibration, note that in going from $B_2H_6Fe_2(CO)_6$ to $[B_2H_5Fe_2(CO)_6]^-$ there is a decrease in (CO) of 75 cm^{-1}.

The effect of metal change on the BH_{term} stretching frequencies is considerably greater. The average change is 30 cm^{-1}, and the frequencies decrease in the same order as observed for (CO) ($B_2H_4Co_2(CO)_6$ 2582.0, 2524.4, $B_2H_5FeCo(CO)_6$ 2530.3, and $B_2H_6Fe_2(CO)_6$ 2526.0, 2444.4 cm^{-1}, where the two stretches observed for the first and last compounds are thought to reflect asymmetric boron environments). The same is true for the BM_3 skeletal systems ($FeCo_2(CO)_{10}BH$ 2533.3, $Fe_2Co(CO)_{10}BH_2$ 2495.7, $HFe_3(CO)_{10}BH_2$ 2471.1 cm^{-1}). The number of hydrogens bound to a given boron atom is expected to have a greater effect on the BH_{term} frequencies than on the CO frequencies simply in terms of proximity, i.e., change of effective boron hybridization.

Brønsted Acidity. Hydrogen atoms that bridge two atoms have an enhanced Brønsted acidity relative to terminal hydrogens. Thus M−H−M, B−H−B, and B−H−M bridging hydrogens can be significantly acidic despite being bound to atoms of lower electronegativity. The question addressed here is how the FeH−Co fragment interchange affects the Brønsted acidity of the cluster-bound hydrogen atoms.

For mononuclear compounds, the trend in acidities with metal is well established in that the acidity decreases as one goes down a column of the periodic table and increases upon going from left to right, e.g., $HMn(CO)_5 < H_2Fe(CO)_4 < HCo(CO)_4$.[38−40] Note that the number of hydrogen atoms attached to the metal atom is not qualitatively important and that, although ancillary ligands have a significant effect on the absolute acidity, for a given ligand set trends with metal identity are consistent.

Thus, the observation that the equilibrium constant for reaction 1 is greater than 1 is counterintuitive. Replacement of an Fe and H atom pair by a Co atom should increase rather than decrease the Brønsted acidity. In a recent communication,[41] we argued that the effect of the change in metal atom was small with respect to the effect of the change in the number of skeletal hydrogen atoms. This explanation conflicts with the trend in CO frequencies described above if ground state charge at the metal centers is the determining factor. On the other hand, the BH_{term} stretch increases as FeH is replaced by Co, implying an increased s character of the BH_{term} bond and a concomitant increased p character of the BH_{bridge} interaction. The latter would be consistent with decreased Brønsted acidity of the BHM hydrogen atoms as the number of Co atoms increases. Although ground state effects must be important, it is likely that the relative anion stabilities are equally so in that the greater the number of skeletal hydrogens, the more stable the anion will be. Thus, the additional skeletal proton of $B_2H_6Fe_2(CO)_6$ relative to **1** produces a preferential stabilization of $[B_2H_5Fe_2(CO)_6]^-$ relative to the anion of **1**.

Chemical Shifts. The ^{11}B chemical shifts observed for metallaboranes are strongly affected by the presence or absence of direct interactions with transition metals. A connection between electronic structure and the chemical shift exists and constitutes another probe of the effect of the metal on cluster properties.[42] We have described an empirical correlation between the nearest neighbors of a boron atom in a ferraborane and its chemical shift. Later we described the connection between chemical shift and a molecular orbital description of the electronic structures.[43,44]

Table 1. Observed and Estimated ^{11}B NMR Chemical Shifts for Isoelectronic Ferraboranes and Ferracobaltaboranes

compound	‰$_{obsd}$	‰$_{obsd}$	n^a	‰$_{calcd}{}^b$
$B_2H_6Fe_2(CO)_6$	−24	(0)	$1^1/_2$	(0)
$B_2H_5FeCo(CO)_6$, **1**	−13	+11	1	+17
$B_2H_4Co_2(CO)_6$	−1	+23	$^1/_2$	+34
$HFe_3(CO)_{10}BH_2$	56	(0)	1	(0)
$Fe_2Co(CO)_{10}BH_2$, **2**	58	+2	1	0
$FeCo_2(CO)_{10}BH$, **3**	85	+29	0	+34
$HFe_4(CO)_{12}BH_2$	116	(0)	2	(0)
$[HFe_4(CO)_{12}BH]^-$	150	+34	1	+34
$HFe_3Co(CO)_{10}BH$, **5**	148	+32	1	+34
$Fe_3Co(CO)_{10}BH_2$, **5′**	115	−1	2	0

[a] For $H_{term}BH_n$, where *n* is the number of hydrogens bridging to metal atoms and is averaged for fluxional molecules. [b] See text.

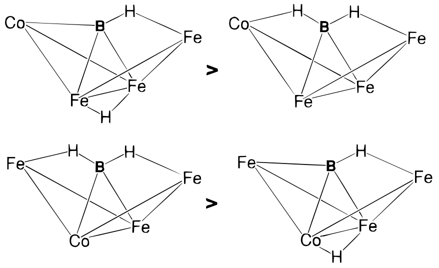

Figure 5. Relative stability of the isomers of $HFe_3Co(CO)_{10}BH$, **5**.

This empirical correlation does not take into account effects such as change of skeletal structure. That this factor is important is seen from a comparison of **4** and **5**. In Table 1, the pertinent observed chemical shifts are compiled along with estimated shift changes as the number of B−H−M interactions with a given boron atom changes. For this purpose, the previous empirical parameters[43] are used without optimization for the new compounds. Comparison of these numbers establishes two points. First, the replacement of FeH by Co does not result in a change in chemical shift unless there is also a change in the number of B−H−M bridging hydrogens attached to the boron atom observed. Second, the parameter used in the previous correlation for each B−H−M interaction, which was derived for the BM_4 "butterfly" skeleton, must be reduced for the BM_3 skeleton and further reduced for the B_2M_2 skeleton. That is, increasing the number of metal atoms in the cluster increases the magnitude of the shift change on changing the number of B−H−M interactions but for a given skeletal size the metal itself has little effect. Note that this conclusion does not apply to a comparison of compounds containing CpM and $(CO)_3M$ fragments, showing the large effect of ancillary ligands on isolobal metal fragment properties.

Skeletal Hydrogen Position and Mobility. As described previously, the distribution of H atoms on a set of isoelectronic main group−transition element clusters can be correlated with the difference in the electronegativities between the cluster atoms.[2] That is, in going from a CFe_3 skeleton to a BFe_3 skeleton, E−H−M bridges (E = main group atom) are favored

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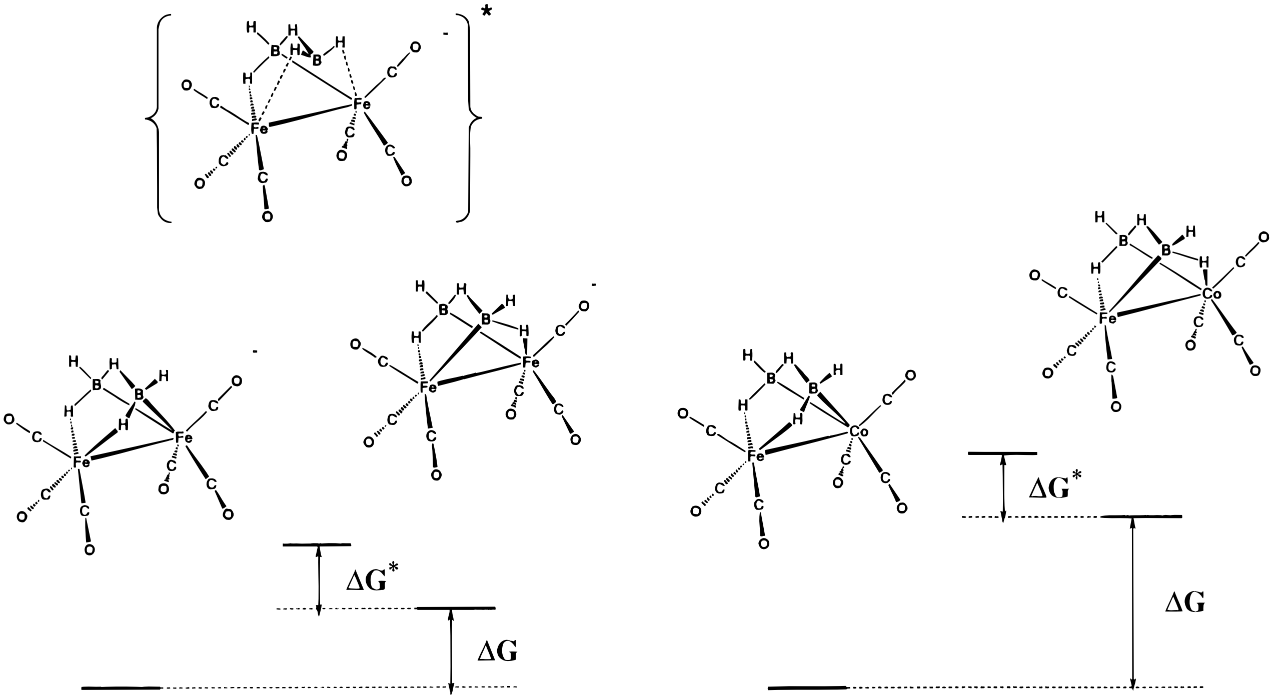

Figure 6. Comparison of schematic potential energy surfaces for the interchange of BH_{term} and B−H−M protons of $[B_2H_5Fe_2(CO)_6]^-$ and $B_2H_5FeCo(CO)_6$, **1**.

over M−H−M bridges. Likewise, in going from CFe_3 to $CFeCo_2$, E−H−M bridges are favored over M−H−M bridges. The bridging H atoms are distributed so as to maximize interactions with the skeletal atoms of lowest electronegativity. Compound **5** and its isomer provide new expression of the same phenomenon. Thus, as shown schematically in Figure 5, the skeletal hydrogens tend to avoid the more electronegative cobalt atom relative to the iron atom.

The decrease in mobility of the skeletal hydrogens that accompanies the replacement of FeH by Co is consistent with the existence of a difference in stability between B−H−Fe and B−H−Co bridging hydrogens. This is best illustrated in the B_2M_2 skeleton. $B_2H_6Fe_2(CO)_6$ exhibits a complex fluxional behavior, and that of $[B_2H_5Fe_2(CO)_6]^-$, illustrated in Figure 6, is much easier to understand. $[B_2H_5Fe_2(CO)_6]^-$ exists in two forms, the more stable of the two being that with both B−H−Fe bridges to the same Fe atom. It undergoes a BH_{term}−BH_{bridge} fluxional process on the NMR time scale below room temperature via “rotation” of the BH_2 groups as shown in the figure. **1** has the same structure as the predominant form of $[B_2H_5Fe_2(CO)_6]^-$ with two B−H−Fe bridges. However, the NMR measurements show that the fluxional process has a higher barrier in **1**. The higher barrier can be ascribed in part to a difference in energy between the two structural forms due to a difference in stability of B−H−Fe and B−H−Co interactions. This difference adds to the intrinsic barrier for the fluxional process. Note, however, that the intrinsic barrier for BH_{term}−BH_{bridge} exchange also depends on the metal (or the number of skeletal hydrogen atoms) in that this process has a higher barrier for $B_2H_4Co_2(CO)_6$ than for $[B_2H_5Fe_2(CO)_6]^-$.[37]

Mechanistic Considerations. The addition and loss of CO and H_2 diatomic molecules to transition metal clusters are well documented.[3] It follows that the formal loss of CO as $Fe(CO)_5$ in a cluster-building process[20,45,46] is mechanistically significant. Further, the facile formation of radical species in metal carbonyl systems[47−50] and evidence for radical participation in cluster fragment addition and exchange reactions in metal carbonyl systems have been reported.[20] We have suggested that ferraborane cluster-building reactions with $Fe_2(CO)_9$ proceed via a radical mechanism.[46] Consistent with “the apparent necessity of employing dianion clusters...”,[20] we found a dependence of reactivity on the charge of the anionic ferraborane precursor in this system.

The products observed in the present work originate in the following two reaction types. (i) Metal fragment exchange: $Co(CO)_3$ replacement of $HFe(CO)_3$; formation of **1** from $B_2H_6Fe_2(CO)_6$, formation of **5** from $HFe_4(CO)_{12}BH_2$, conversion of **2** to **3**. (ii) Metal fragment addition: $Co(CO)_3$ addition with loss of 3H; formation of **5** from $HFe_3(CO)_9BH_4$, conversion of **1** to **4**. Note that **4** appears to be the precursor of **2** which is formed during chromatography. (Base-facilitated BH vertex loss has considerable precedent and has been reported in another system during chromatography.[7,51]). $Co(CO)_3$ addition with loss of CO; formation of **5** from $HFe_3(CO)_{10}BH_2$.

Formation of $HCo(CO)_4$ and $Fe(CO)_5$ as coproducts suggests sinks for cobalt and iron fragments as well as for H and CO; however, in contrast to the very clean stoichiometry of the $[HFe_3(CO)_9BH_3]^- + Fe_2(CO)_9$ reaction, the situation here is far from clear-cut; e.g., $Co_4(CO)_{12}$ is a prominent product as well.

Facile reaction of the ferraborane anions with $Co_2(CO)_8$ takes place, but no FeCo metallaboranes are observed under varied reaction conditions. Therefore, in contrast to conclusions suggested by observations on the analogous organometallic clusters,[20] anionic clusters do not necessarily foster $Co(CO)_x$

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fragment addition and substitution reactions. Clearly these reactions are very sensitive to the donor properties of the cluster as well as other reaction conditions.

The following mechanism, based on reactions of neutral species, is proposed to account for the cluster fragment addition and fragment substitution reactions. Radical initiation is followed by fragment addition. Competition between deactivation of the adduct and base-facilitated loss of $Fe(CO)_5$ determines whether net addition or substitution is observed. This mechanism is very similar to those proposed earlier for related systems except that H atom transfer rather than electron transfer plays the prominent role although $Co(CO)_4^{\bullet}$ is the radical carrier in both cases.[20,46,36]

initiation

$$B_xH_yFe_z(CO)_n + Co_2(CO)_8 \rightarrow B_xH_{y-1}Fe_z(CO)_n^{\bullet} + HCo(CO)_4 + Co(CO)_4^{\bullet}$$

or $$Co_2(CO)_8 \rightarrow 2Co(CO)_4^{\bullet}$$

propagation

$$B_xH_yFe_z(CO)_n + Co(CO)_4^{\bullet} \rightarrow B_xH_yFe_zCo(CO)_{n+4}^{\bullet}$$

fragment addition

$$B_xH_yFe_zCo(CO)_{n+4}^{\bullet} + Co_2(CO)_8 \rightarrow B_xH_{y-1}Fe_zCo(CO)_{n+3} + HCo(CO)_4 + CO + Co(CO)_4^{\bullet}$$

or $$B_xH_yFe_zCo(CO)_{n+4}^{\bullet} + Co_2(CO)_8 \rightarrow B_xH_{y-1}Fe_zCo(CO)_{n+2} + HCo(CO)_4 + 2CO + Co(CO)_4^{\bullet}$$

$$B_xH_{y-1}Fe_zCo(CO)_{n+3}^{\bullet} + Co_2(CO)_8 \rightarrow B_xH_{y-3}Fe_zCo(CO)_{n+3}^{\bullet} + 2HCo(CO)_4$$

fragment substitution

$$B_xH_yFe_zCo(CO)_{n+4}^{\bullet} + CO \rightarrow B_xH_yFe_{z-1}Co(CO)_n^{\bullet} + Fe(CO)_5$$

$$B_xH_yFe_{z-1}Co(CO)_n^{\bullet} + Co_2(CO)_8 \rightarrow B_xH_{y-1}Fe_{z-1}Co(CO)_n + HCo(CO)_4 + Co(CO)_4^{\bullet}$$

A successful synthetic reaction thus depends on several factors. Radical initiation and addition to the reactant cluster must have a convenient rate, but subsequent reaction of the desired product with the radical carrier, $Co(CO)_4$,$^{\bullet}$ must be sufficiently slow so product accumulates in the system. Presumably, with anionic ferraboranes, the reaction of the product with $Co(CO)_4^{\bullet}$ is so fast that rapid conversion to intractable material takes place. The electron or H atom donor ability of the parent cluster (hence anionic charge) or the ability of the fragment source to spontaneously generate radicals is important if initiation begins with H atom transfer as we suggest. Competition between the addition and substitution reactions depends on the relative rates of continued H atom transfer vs CO-assisted $Fe(CO)_5$ loss. Thus, dependence of product yield on the partial pressure of CO in the $B_2H_6Fe_2(CO)_6$ reaction system becomes understandable.

Conclusions

The change in the identity of a transition metal in a strictly isoelectronic series does not affect gross properties such as geometric structure. However, it does perturb both directly (change in metal atom properties) and indirectly (change in number of skeletal hydrogen atoms) the electronic structure to a significant extent as demonstrated by differences in spectroscopic, dynamic, and chemical reaction properties. These results complement our previous comparison of the organometallic clusters $Co_3(CO)_9CCH_3$ and $HFeCo_2(CO)_9CCH_3$.[6]

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