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Notes

Deprotonation of Ferraborane Clusters and Their Relative Acidities

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Introduction

The Brønsted acidities of transition metal hydrides and metal carbonyl hydrides is of general interest because of their importance in a variety of preparative reactions and theoretical studies.[1,2] The relative acidities of metal carbonyl cluster hydrides[3] and those of borane clusters[4,5] have been related to the structural arrangements and the relative sizes of the cluster cores. The only reported comparisons of Brønsted acidities in metallaborane clusters[6] found that the Brønsted acidity of B_2H_5-$FeCo(CO)_9$ is less than that of $B_2H_6Fe_2(CO)_9$, contrary to prediction based on the relative acidities of isoelectronic monometallic analogues. The authors concluded that the number of endo-bridging hydrogens in $B_2H_6Fe_2(CO)_9$ must have a greater effect on the protic nature of a hydrogen atom than the more subtle change in metal identities. We continue this work using proton competition reactions between neutral and anionic cluster pairs to determine the relative Brønsted acidities of four closely related metalloboranes, $HFe_4(CO)_{12}BH_2$ **(a)**,[7c] $HFe_3(CO)_9BH_4$ **(b)**,[7b] $HFe_3(CO)_{10}BH_2$ **(c)**,[7d] and $B_2H_6Fe_2(CO)_6$ **(d)**,[7a] (Figure 1).

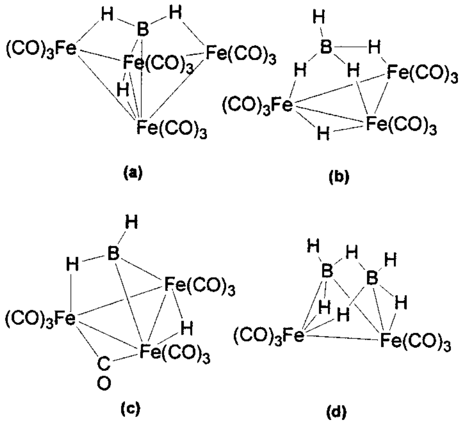

Figure 1. Molecular structures of (**a**) $HFe_4(CO)_{12}BH_2$, (**b**) $HFe_3(CO)_9$-BH_4, (**c**) $HFe_3(CO)_{10}BH_2$, and (**d**) $B_2H_6Fe_2(CO)_6$.

Experimental Section

Under a nitrogen atmosphere, the reagent solvents tetrahydrofuran, acetonitrile, diethyl ether, toluene, and hexane were stirred over benzophenone ketyl, methanol was stirred over calcium chloride, and dichloromethane was stirred over molecular sieves. All these solvents were distilled before use. Solvents for chromatographic separations were stirred over molecular sieves and deoxygenated with N_2. The reactants $Fe(CO)_5$, $Fe_2(CO)_9$, and $BH_3S(CH_3)_2$ [10 M] were purchased from Aldrich and used as received. CF_3COOH and $N(C_2H_5)_3$ were alsopurchased from Aldrich and deoxygenated with nitrogen before use. Chromatography was performed under nitrogen at reduced temperature on 60−200 mesh dried silica gel (Baker). Infrared spectra were recorded on a Nicolet 205 FT-IR spectrometer. ^{11}B NMR spectra were obtained on a Bruker 300 MHz spectrometer [external reference: $NEt_4B_3H_8$ ($\delta = -29.7$ ppm)]. $HFe_4(CO)_{12}BH_2$ (**a**),[7c] $HFe_3(CO)_9BH_4$ (**b**),[7b] $HFe_3(CO)_{10}$-BH_2 (**c**),[7d] and $B_2H_6Fe_2(CO)_6$ (**d**)[7a] were prepared using published methods and standard glovebag and Schlenk line techniques.

Deprotonation of $B_2H_6Fe_2(CO)_6$, $HFe_3(CO)_9BH_4$, $HFe_4(CO)_{12}BH_2$, and $HFe_3(CO)_{10}BH_2$. $[HNEt_3][B_2H_5Fe_2(CO)_6]$ (**d′**) was prepared in a 250 mL Schlenk flask from ca. 10 mL of concentrated hexane solution of $B_2H_6Fe_2(CO)_6$ (**d**) by adding NEt_3 slowly by drops from a syringe with stirring. The bright-yellow color diminished immediately, forming a brown precipitate that was washed with fresh hexanes and was evaporated to dryness, leaving solid **d′** in the flask:

$$B_2H_6Fe_2(CO)_6\ (\mathbf{d}) + NEt_3 \rightarrow [HNEt_3][B_2H_5Fe_2(CO)_6]\ (\mathbf{d'}) \qquad (1)$$

In similar reactions, deprotonation of $HFe_4(CO)_{12}BH_2$ (**a**), $HFe_3(CO)_9$-BH_4 (**b**), and $HFe_3(CO)_{10}BH_2$ (**c**) produced $[HNEt_3][HFe_4(CO)_{12}BH]$ (**a′**), $[HNEt_3][HFe_3(CO)_9BH_3]$ (**b′**), and $[HNEt_3][Fe_3(CO)_{10}BH_2]$ (**c′**), respectively.

Proton Competition Reactions: Reaction of $HFe_3(CO)_9BH_4$ with $[HNEt_3][B_2H_5Fe_2(CO)_6]$ and of $B_2H_6Fe_2(CO)_6$ with $[HNEt_3][HFe_3$-$(CO)_9BH_3]$. A dilute hexane solution (ca.10 mL) of $HFe_3(CO)_9BH_4$ (**b**) was added to a flask containing a large excess of solid $[HNEt_3][B_2H_5$-$Fe_2(CO)_6]$ (**d′**). After an initial infrared spectrum of the hexane solution was obtained, the mixture was stirred. Infrared spectra were taken of aliquots (0.1 mL) at 10 min intervals until the spectral characteristics (Table 1) indicated that (1) proton transfer had occurred, (2) reactions other than proton transfer had occurred, or (3) no reaction had occurred after 2−3 h. The hexane phase was removed by cannula, and the anion phase was washed with hexane, evaporated, dissolved in diethyl ether, and analyzed by ^{11}B NMR spectroscopy (Table 2). The proton competition reaction of the complementary pair **d** and **b′** was done in a similar manner. By use of similar reaction conditions, proton competition reactions of pairs of neutral and anionic clusters of **d** with **a** and **b** with **a** were studied.

Reactions between $HFe_4(CO)_{12}BH_2$ (a) and $HFe_3(CO)_9BH_4$ (b) Studied by ^{11}B NMR Spectroscopy. A concentrated diethyl ether

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solution (ca. 4 mL) of $[HFe_4(CO)_{12}BH]^-$ (**a′**) was cannula-transferred to an NMR tube attached to a Schlenk flask and evaporated to dryness. A concentrated hexane solution (ca. 4 mL) of $HFe_3(CO)_9BH_4$ (**b**) was transferred via cannula into the NMR tube, which was then sealed. ^{11}B NMR spectra were obtained on the mixture over ca. 4 h, collecting 3000 scans for each spectrum. In a similar manner **b′** was reacted with **a**, and the reaction was followed by ^{11}B NMR spectroscopy.

Results

When **a** was mixed with **b′**,

$$HFe_4(CO)_{12}BH_2\ (\mathbf{a}) + [HFe_3(CO)_9BH_3]^-\ (\mathbf{b'}) \rightarrow [HFe_4(CO)_{12}BH]^-\ (\mathbf{a'}) + \text{other products} \quad (2)$$

the characteristic infrared signals for **a** disappeared over time. After 2 h only very low-intensity bands attributed to $Fe_3(CO)_{12}$ and no bands corresponding to the presence of **b** were observed in the hexane-phase infrared spectrum. The presence of **a′** in the products was indicated by observation of its characteristic signal in the ^{11}B NMR spectrum of the solid phase. When **b** was mixed with **a′**, the infrared spectrum did not change over a 3 h period. The ^{11}B NMR spectrum of the solid phase indicated the presence of **a′** and **c′**.[8]

When **b** was reacted with **a′** in an NMR tube,

$$HFe_3(CO)_9BH_4\ (\mathbf{b}) + [HFe_4(CO)_{12}BH]^-\ (\mathbf{a'}) \rightarrow HFe_4(CO)_{12}BH_2\ (\mathbf{a}) + [HFe_3(CO)_9BH_3]^-\ (\mathbf{b'}) \quad (3)$$

a very small signal characteristic of **a** was observed growing in over a 3 h time period. An ^{11}B NMR spectrum of a diethyl ether solution of the solid phase indicated the presence of both the original **a′** and small amounts of the anion **b′**. In attempts to react the opposing pair of clusters, when **a** was mixed with **b′** in an NMR tube, only the signal attributed to **a** was observed in the ^{11}B NMR spectra obtained after 3 h. The ^{11}B NMR spectrum of a diethyl ether solution of the solid phase contained only the signal attributed to the original reactant **b′**.

Infrared spectra taken of samples of **b** mixed with **d′**,

$$HFe_3(CO)_9BH_4\ (\mathbf{b}) + [B_2H_5Fe_2(CO)_6]^-\ (\mathbf{d'}) \rightarrow [HFe_3(CO)_9BH_3]^-\ (\mathbf{b'}) + B_2H_6Fe_2(CO)_6\ (\mathbf{d}) \quad (4)$$

afforded a new band at 2092 cm^{-1} due to **d** while the band at 2097 cm^{-1} due to **b** was diminished. When **d** was reacted with **b′**, the infrared spectrum remained unchanged over a 2 h time period.

Mixtures of **a** with **d′**,

$$HFe_4(CO)_{12}BH_2\ (\mathbf{a}) + [B_2H_5Fe_2(CO)_6]^-\ (\mathbf{d'}) \rightarrow [HFe_4(CO)_{12}BH]^-\ (\mathbf{a'}) + B_2H_6Fe_2(CO)_6\ (\mathbf{d}) \quad (5)$$

showed the presence of **d** by the growth of a new band in the infrared spectrum at 2092 cm^{-1} as the band due to **a** at 2059 cm^{-1} simultaneously diminished. The final infrared spectrum contained only peaks due to **d**. When the opposite pair of clusters were mixed (**d** with **a′**), no changes were observed in the infrared spectra.

Table 1. Neutral Ferraborane Infrared Spectral Bands (ν_{CO}, cm^{-1})

$HFe_4(CO)_{12}BH_2$ (**a**)	$HFe_3(CO)_9BH_4$ (**b**)	$HFe_3(CO)_{10}BH_2$ (**c**)	$B_2H_6Fe_2(CO)_6$ (**d**)
	2095[a] m	2106 w	2090[a] s
2059 s	2058 vs	2054 vs	
2047[a] vs		2041 sh	2046 vs
2034[a] s	2038 vs	2031 m	
	2026 vs		2026 s
		2022 m	2022 s
	2017 m sh		
2013 m		2010 m	
	2008 m sh		
		1995 m	1996 s
1988 m	1984 m	1990 s	
		1868[a] m	

[a] Bands used for compound identification.

Table 2. Ferraborane ^{11}B NMR Spectral Data (ppm)

$HFe_4(CO)_{12}BH_2$ (**a**)	106 (t)	$HFe_4(CO)_{12}BH^-$ (**a′**)	149 (br)
$HFe_3(CO)_9BH_4$ (**b**)	1.5 (m)	$HFe_3(CO)_9BH_3^-$ (**b′**)	6.2 (br, q)
$HFe_3(CO)_{10}BH_2$ (**c**)	56.5 (d) (20 °C)	$Fe_3(CO)_{10}BH_2^-$ (**c′**)	57.4 (br, d)
$B_2H_6Fe_2(CO)_6$ (**d**)	−24 (q)	$B_2H_5Fe_2(CO)_6^-$ (**d′**)	−17.4 (br)

We found $HFe_3(CO)_{10}BH_2$ difficult to prepare and keep in quantities sufficient for this study. We never were able to perform direct proton competition reactions under the conditions we desired.

Discussion

From the results of the reaction shown in eq 4, it is clear that $HFe_3(CO)_9BH_4$ (**b**) transferred a proton to $[B_2H_5Fe_2(CO)_6]^-$ (**d′**). No proton transfer occurred when the opposing pair of clusters, $[HFe_3(CO)_9BH_3]^-$ (**b′**) and $B_2H_6Fe_2(CO)_6$ (**d**), were mixed. We conclude that **b** is more acidic than **d** under these reaction conditions. Likewise, proton transfer from reaction of $HFe_4(CO)_{12}BH_2$ (**a**) with $[B_2H_5Fe_2(CO)_6]^-$ (**d′**) [eq 5] and no proton transfer from mixing $B_2H_6Fe_2(CO)_6$ (**d**) with $[HFe_4(CO)_{12}BH]^-$ (**a′**) indicate that **a** is a stronger Brønsted acid than **d** under these conditions.

The reactions involving $HFe_4(CO)_{12}BH_2$ (**a**) with $[HFe_3(CO)_9BH_3]^-$ (**b′**) and $HFe_3(CO)_9BH_4$ (**b**) with $[HFe_4(CO)_{12}BH]^-$ (**a′**) are less straightforward and appear to be very dependent on the relative physical states and the concentrations of the two reacting species. The reactions were studied under different conditions of relative concentration and were monitored by two different methods. In the reactions monitored by infrared spectroscopy, the anion was present in large excess. When the reactions were monitored by ^{11}B NMR spectroscopy, the clusters were present in approximately equimolar amounts. Under conditions of excess anion, **b′** deprotonated **a** but without concomitant protonation of **b′** to form **b** (eq 2). Under equimolar reaction conditions **b′** did not deprotonate **a**. Under conditions of excess anion, **a′** did not react with **b**. But when present in approximately equimolar amounts, **a′** did deprotonate **b** to a small extent, producing very small amounts of both **a** and **b′** (eq 3). It is clear that each anionic cluster is capable of deprotonating the neutral cluster in certain circumstances. It appears that the basicity of the anions in the solid state drives these reactions. We never observe that **a** is capable of protonating **b′**, but we do observe **b** protonating **a′**. From these results it appears that **a** may be slightly less acidic than **b**. Without further studies we can only conclude that the relative Brønsted acidities of the clusters $HFe_4(CO)_{12}BH_2$ (**a**) and $HFe_3(CO)_9BH_4$ (**b**) are nearly identical under these conditions.

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(8) Clusters **a**, **c**, and **d** are formed in the same synthesis and separated using column chromatography on silica. While most of compound **c** produced in these reactions is deprotonated during the chromatographic separation, residual amounts are often detected by NMR spectroscopy in solutions of **a** as a result of incomplete separation. We have noted the presence of **c** in very small quantities in solutions of **a** due to incomplete separation under the conditions employed. Thus, it is likely that the **c′** we find in products of reactions involving **a′** is the result of its presence in the initial solution when **a** was deprotonated.

As was noted in the Experimental Section, the placement of $HFe_3(CO)_{10}BH_2$ (**c**) in the series could not be determined using proton competition reactions. We place it as the most acidic of all the clusters as the result of two observations. First, in the attempted reaction of $HFe_3(CO)_9BH_4$ (**b**) with $[HFe_4(CO)_{12}BH]^-$ (**a′**) we find $[Fe_3(CO)_{10}BH_2]^-$ (**c′**) is also present in the products, indicating that **c′** is not protonated by **b**.[8] Second, since **c** is largely deprotonated to **c′** under chromatographic separation conditions on basic silica where **a** and **d** remain protonated, it is reasonable to conclude that **c** is the most acidic of these three clusters.

On the basis of the all these results, we propose that the relative order of acidity for the four ferraboranes studied is

$$B_2H_6Fe_2(CO)_6\ (\mathbf{d}) < HFe_4(CO)_{12}BH_2\ (\mathbf{a}) = HFe_3(CO)_9BH_4\ (\mathbf{b}) < HFe_3(CO)_{10}BH_2\ (\mathbf{c})$$

Quantitative studies of metal carbonyl cluster hydrides[3] and qualitative studies of boranes[6] have demonstrated that their acidities can be related to the size and structure of the metal or boron core, respectively. For example $H_2Os_3(CO)_{12}$ was found to be 3 orders of magnitude less acidic than $H_4Os_4(CO)_{12}$.[3] For borane clusters the relative Brønsted acidity also increases with size.[5] This relationship does not strictly hold with these four ferraboranes. The tetranuclear cluster, $HFe_4(CO)_{12}BH_2$, is definitely less acidic than at least one of the trinuclear clusters, $HFe_3(CO)_{10}BH_2$, and it may be equally or slightly less acidic than the other trinuclear cluster, $HFe_3(CO)_9BH_4$. The smallest cluster, $B_2H_6Fe_2(CO)_6$, is the least acidic.

The monoanion of $HFe_3(CO)_{10}BH_2$ is formed by loss of the M−H−M bridging hydrogen. Monoanions of every other reported metallaborane cluster including those in this study, $HFe_4(CO)_{12}BH_2$, $HFe_3(CO)_9BH_4$, and $B_2H_6Fe_2(CO)_6$, occur through loss of the B−H−M bridging hydrogen. The competition for electron density between the M−H−M bridging hydrogen and the bridging CO group in the cluster core may have the strongest influence on the relative acidity of $HFe_3(CO)_{10}BH_2$ compared to either $HFe_4(CO)_{12}BH_2$ or $HFe_3(CO)_9BH_4$.

It is not clear what most influences the relative acidities of clusters $HFe_4(CO)_{12}BH_2$ and $HFe_3(CO)_9BH_4$. The earlier comparison of the dinuclear clusters attributed the greater acidity of $B_2H_6Fe_2(CO)_9$ compared to $B_2H_5FeCo(CO)_9$ to be the result of the larger number of endo-bridging hydrogens.[6] In our studies the greater number of endo-bridging hydrogens in trinuclear $HFe_3(CO)_9BH_4$ (**b**) compared to $HFe_4(CO)_{12}BH_2$ (**a**) may be mitigating the greater acidity of the tetranuclear cluster under certain conditions. As always, reaction conditions dictate which compounds are found as products in these proton competition reactions. We were interested in studying these compounds under the same conditions used for the previously reported study of the isoelectronic metalloboranes $B_2H_5FeCo(CO)_9$ and $B_2H_6Fe_2(CO)_9$.

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