There then would be a 50–50 chance of a boat or chair distortion depending on the more favorable crystal-packing conformation. We were, therefore, fortunate that our first structure of this type turned out to be of the boat form as the significance of the π interaction would have not been apparent if the chair geometry was found. These results suggest that mixed-ligand complexes should be useful templates for altering the aromatic chemistry of a particular ligand.

Registry No. Cu(acac)(hfac), 21429-77-6.

Supplementary Material Available: Tables of anisotropic thermal parameters and calculated hydrogen atom positions (2 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of New Hampshire,
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Characterization of $[Fe_2(CO)_6B_3H_6]^-$: A Comment on the Dynamic Structure of $Fe_2(CO)_6B_3H_7$

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One of the interesting aspects of metal cluster chemistry is the positioning of skeletal endo hydrogens and their susceptibility toward fluxional processes on the cluster surface.[2] The association of metal and main-group fragments (e.g. borane) in a cluster environment can produce a significant effect on some or all of the skeletal protons.[3,4] One simple chemical change that a hydrido cluster often readily undergoes is deprotonation. The action of removing an endo hydrogen can induce proton mobility among hydrogens remaining in the anion when such mobility required a greater activation energy in the conjugate acid. This is commonly the case in borane anions.[5] Among the ferraboranes, examples of the lowering of the activation barrier for hydrogen scrambling are found in going from $HFe(CO)_3B_5H_9$ to $[HFe(CO)_3B_5H_8]^-$,[6] from $HFe_3(CO)_9BH_4$ to $[HFe_3(CO)_9BH_3]^-$,[7] and from $HFe_4(CO)_{12}BH_2$[8] to $[HFe_4(CO)_{12}BH]^-$.[9] The latter two anions are distinct from the former one because they exhibit fluxionality between Fe–H–B and Fe–H–Fe hydrogens rather than simply between B–H–B hydrogens in different environments. $Fe_2(CO)_6B_3H_7$ (II) has previously been characterized,[10,11] but a study of its conjugate base $[Fe_2(CO)_6B_3H_6]^-$ (I) is reported here for the first time. What made I seemingly unusual was the fact that, at room temperature and on the 300-MHz NMR time scale, it possessed a static structure, whereas II had been reported to be fluxional at the same temperature and on the 100-MHz time scale,[10] i.e. the reverse trend for the conjugate ferraborane acid–base pairs mentioned above. The present work presents spectroscopic data and an analysis of I, along with a reanalysis of II. In addition, the Fenske–Hall quantum chemical approach is used to suggest reasons why II deprotonates via loss of an Fe–H–B rather than a B–H–B proton.

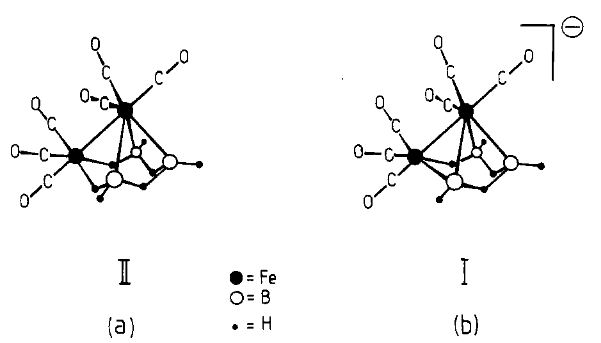
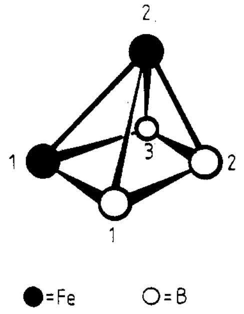


Figure 1. Structural representations of (a) $Fe_2(CO)_6B_3H_7$ (II) and (b) $[Fe_2(CO)_6B_3H_6]^-$ (I).

Chart I



Experimental Section

General Methods. All manipulations were carried out under inert atmospheres by using standard techniques.[12] Hexane was dried over molecular sieves, degassed, and distilled from sodium/benzophenone; methanol was dried over molecular sieves and degassed before use; anhydrous diethyl ether (Fisher) was distilled from sodium/benzophenone. [PPN]Cl (PPN = bis(triphenylphosphine)nitrogen(1+)) (Aldrich) was used as received.

^{11}B and ^1H FT NMR spectra were obtained on a Nicolet 300-MHz spectrometer; infrared spectra were recorded on a Perkin-Elmer 983 spectrometer. ^{11}B NMR shifts are reported with respect to $BF_3{\cdot}Et_2O$ ($\delta = 0$) and ^1H shifts, with respect to Me_4Si ($\delta = 0$).

Preparation of [I]PPN. I was formed as a byproduct during the preparation of $[HFe_3(CO)_9BH_3]PPN$.[7] I was readily separated from other anionic products of the reaction[7] by selective protonation using 40% phosphoric acid followed by hexane extraction. The yellow-orange hexane extract containing II[13] was transferred into a flask containing a solution of [PPN]Cl dissolved in methanol. After 20 min of vigorous stirring, the color of the hexane layer diminished and the methanol layer turned dark red, indicating that deprotonation of II to I had occurred. II could be regenerated by treating I with H_3PO_4. [I]PPN: ^{11}B NMR ($CD_3C(O)CD_3$, 20 °C) δ +2.4 (m, 1 B), +8.6 (m, 1 B), +33.9 (m, 1 B); $^{11}B\{^1H\}$ J_{BH}(Fe–H–B) = 60 Hz, J_{BH}(B–H–B) < 40 Hz, J_{BH}(term) = 125 Hz; ^1H NMR ($CD_3C(O)CD_3$, 20 °C) δ 7.7–7.5 (m, 30 H, PPN^+),

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[1] Laboratory experimental and spectroscopic work was carried out at the University of Notre Dame; calculational work was carried out at the University of New Hampshire.

[2] See, for example: Johnson, B. F. G.; Benfield, R. E. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980; p 471.

[3] See, for example: Gilbert, K. B.; Boocock, S. K.; Shore, S. G. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 6, p 879.

[4] See, for example: Gaines, D. F.; Hildebrandt, S. J. In *Metal Interactions with Boron Clusters*; Grimes, R. N., Ed.; Plenum: New York, 1982, p 119.

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[13] In most reactions II was accompanied by a smaller amount of $Fe_2(CO)_6B_2H_6$.[14]

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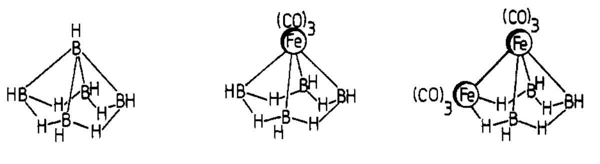

(a) (b) (c)

Figure 2. Schematic representations of the structures of (a) B_5H_9, (b) $Fe(CO)_3B_4H_8$, and (c) $Fe_2(CO)_6B_3H_7$.

3.8–3.6 (br, 3 H, terminal H), −2.0 (br, 1 H, B–H–B), −3.0 (br, 1 H, B–H–B), −17.0 (br, 1 H, Fe–H–B); IR (acetone, cm^{-1}) ν_{CO} 2026 w, 1998 s, 1973 vs, and 1950 m, ν_{BH} 2470 vw.

Fenske–Hall Calculational Parameters. Fenske–Hall calculations[15] were carried out on II[16] and two isomers of I; Ia had one Fe–H–B proton from II removed and Ib had a B–H–B proton removed. The cluster geometries were all based on a symmetry optimized geometry with atomic coordinates taken from the crystallographically determined structure of II.[11] Protons were removed directly as appropriate. Distances used were Fe–Fe = 2.55 Å, Fe(apex)–B = 2.07, 2.07, and 2.05 Å, Fe(base)–B = 2.26 Å, B–B = 1.78 Å, Fe–CO = 1.78 Å, C–O = 1.15 Å, Fe–HB = 1.54 Å, B–HFe = 1.30 Å, B–H(term) = 1.17 Å, and B–HB = 1.32 Å. The basis functions for the calculations were as previously reported.[17,18]

Results and Discussion

Structural Features of I and II: Proton Nonmobility. The crystal structure of the neutral ferraborane II has been reported.[10,11] The cluster core possesses a square-pyramidal arrangement with one iron in the apical position and one in the base (Figure 1a). On deprotonation of II to I, the ^{11}B NMR spectrum shows that, of the three borons originally in two distinct positions (+12.4 (1 B), +4.2 (2 B) ppm), one boron resonance is shifted almost 30 ppm downfield,[19] while the remaining two boron signals shift marginally upfield. The fact that a boron originally attached to both Fe–H–B and B–H–B protons (ie. B(1) or B(3) in Chart I) alone undergoes a significant change in environment indicates that deprotonation occurs at an Fe–H–B site (Figure 1b).[20] This conclusion is supported by the appearance in the ^1H NMR spectrum of two midfield proton resonances assigned to 2B–H–B and one highfield resonance assigned to 1Fe–H–B, in addition to a broad lower field signal due to 3H(terminal). All resonances sharpen at lower temperatures due to thermal B-H spin decoupling.[21] The room-temperature solution structure of I therefore shows no proton mobility on the NMR time scale. Previously it had been reported that, on the grounds of ^1H NMR integral data, the parent neutral compound (II) exhibited some degree of fluxionality, involving the three protons associated with B(2)[10] (Chart I). In the light of the present results obtained for I, a reinvestigation of II was called for.

First, ^1H NMR shifts for the three types of proton in II were as reported,[10] but relative integrals differed: viz. $\simeq$+3.0 (br, 3 H), −2.6 (2 H), −16.6 (2 H) ppm. These data in themselves suggest a static structure in accordance with the observed solid-state structure. Further evidence for a static solution structure comes from $^{11}B\{^1H\}$ selective decoupling experiments on II not previously carried out. The crucial information is found in the results of selective decoupling of the terminal proton for B(2); the ^{11}B resonance (δ 12.4) shows a well-resolved triplet due to residual proton coupling, indicating that two equivalent protons remain associated with the boron: $J_{BH}(BHB) \simeq 40$ Hz. Conversely, selective decoupling of the BHB protons produces a well-defined doublet ($J_{BH(term)} = 140$ Hz).[22] Thus, it is concluded that, at 20 °C, both I and II exhibit no proton mobility on the NMR time scale and that the ^1H resonance integrals previously reported were incorrect.

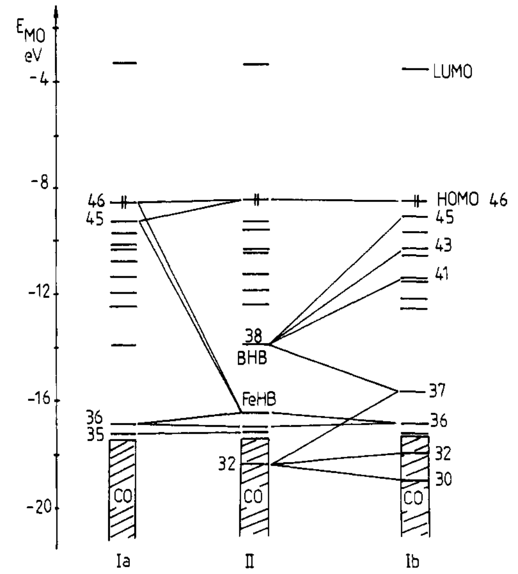

Figure 3. MO correlation diagram for the deprotonation of II to Ia or Ib. The orbital energies of II vs. I are affected by total charge; a realistic comparison is made by taking the anion orbital energies from the Fock matrix of the neutral complex.[32]

It is worth comparing these results with those of related compounds. First, II is derived from B_5H_9 by replacing two BH vertices each by $Fe(CO)_3$. The intermediate cluster $Fe(CO)_3B_4H_8$ is also known,[23] although, as with II, only one isomer is known, viz. that in which the borane fragment resides in the basal plane and, in the case of II, remains as complete an entity as possible (Figure 2). All three neutral compounds exhibit structures that, at room temperature and on the NMR time scale, are static, or, at least, do not show exchange between different types of protons. The anions, on the other hand, present a contrast. From NMR evidence, B_5H_9 deprotonates by loss of a B–H–B proton, but the $[B_5H_8]^-$ anion exhibits an average B–H–B ^1H NMR resonance indicating basal bridge hydrogen equivalence through fluxionality.[24] Deprotonation of $Fe(CO)_3B_4H_8$ by KH or LiMe is reported to yield the anion, which on reprotonation with DCl gives the basally deuterated $Fe(CO)_3B_4H_4(\mu\text{-}H)_3(\mu\text{-}D)$,[25] but no spectroscopic evidence is cited. Hence, whether or not the basally bridging protons in $[Fe(CO)_3B_4H_7]^-$ are fluxional at room temperature is not known. It seems, however, that it is the introduction of M–H–B in place of B–H–B interactions which tends to raise the activation barrier to hydrogen mobility and thus sets I apart from the isolobal anion $[B_5H_8]^-$ and, perhaps, from $[Fe(CO)_3B_4H_7]^-$ as well. For instance, in related complexes of $[B_3H_8]^-$,[4,21] such as $[Cr(CO)_4B_3H_8]^-$,[26] $Cu(Ph_3P)_2B_3H_8$,[27] and $Mn(CO)_4B_3H_8$,[28] the borane ligand coordinates to a metal center through two terminal hydrogens, forming M–H–B bridges in the complex. This results in a marked slowing of the pseudorotation of the borane hydrogens[4,21] compared to that in the free ligand which exhibits total proton equivalence at room temperature. We have previously shown[29] that the properties of the B_3H_7 moiety change from those

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(16) A detailed discussion of the electronic structure of II has previously appeared and will not be dealt with here: Andersen, E. L.; DeKock, R. L.; Fehlner, T. P. *Inorg. Chem.* **1981**, *20*, 3291.

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(19) This shift is consistent with the change in number of direct vs. H-bridged Fe–B contacts and is predicted from a correlation of ^{11}B NMR shift vs. such contacts: Fehlner, T. P., personnal communication.

(20) The related compound 2-$CpCoB_4H_8$ also deprotonates at an M–H–B rather than at a B–H–B site: Weiss, R.; Bowser, J. R.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 1522.

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(22) For the Fe–H–B bridge hydrogen, $J_{BH} = 80$ Hz.

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Table I. Atomic Charges in $[Fe_2(CO)_6B_3H_{7-x}]^{x-}$ (x = 1, 0)

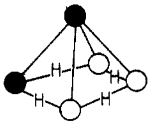
	cluster atom[b]				
structure	Fe(1)	Fe(2)	B(1)	B(2)	B(3)
Ia	+0.259	+0.300	−0.592	−0.079	−0.380
Ib	+0.425	+0.324	−0.338	−0.293	−0.553
II[a]	+0.434	+0.284	−0.350	−0.112	−0.350

[a] See also ref 16. [b] Atomic numbering is according to Chart I.

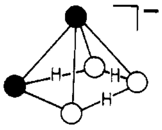
of a "borallyl" ligand in, e.g., $Pt(PhMe_2P)_2B_3H_7$[30] or $IrH(B_3H_7)(CO)(PPh_3)$[31] to a cluster fragment in II via an intermediate role in $Mn(CO)_4B_3H_8$. Clearly, in these metal–triborane compounds, the close association (viz. endo bridging) of a hydrogen with a metal imparts distinct properties upon the former.

Molecular Orbital Calculations. From a theoretical standpoint, the preference for Fe–H–B over B–H–B deprotonation in II (i.e. the formation of Ia rather than Ib) is examined first by consideration of molecular orbital perturbation and then by charge analysis.

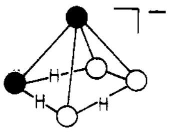
A comparison of the Fenske–Hall eigenvalue spectra for isomers Ia and Ib (Figure 3, right and left columns) sheds little light on the reason for their observed relative stabilities; the HOMO–LUMO separation shows only a marginal preference for Ia over Ib (Ia = 4.89 eV; Ib = 4.77 eV). The only significant difference in filled MO energies is a stabilization of MO 37 (B–H–B bonding MO) in going from Ia to Ib (Figure 3) (viz. in favor of the experimentally unobserved structure).



II



Ia



Ib

The molecular orbital changes that occur as II is deprotonated are shown in Figure 3. In II, the Fe–H–B bonding character is located mainly in MO 37 (with smaller contributions in MO's 34–36) while the B–H–B bonding character is found predominantly in MO's 38 and 32, the latter being embedded in the "CO band". (This apparent stabilization of the BH orbitals is considered to be an artifact of the calculations.[16]) Figure 3 shows that, in forming Ia, the only major orbital perturbation involves MO 37; its character, now lacking the stabilizing influence of one Fe-B bridge proton, is spread through three MO's in Ia. Deprotonating II to Ib perturbs both MO 32 and MO 38, distributing the non-H-bridge orbital characteristics to MO's 45, 43, and 41 while the remaining B–H–B bonding character moves to MO 37. Although the latter is 1.73 eV more stable than the B–H–B bonding MO in II, this stabilization is clearly not important enough in practice to allow Ib to persist over Ia. It is noteworthy too that what appears to be a favorable delocalization of B–B character in Ib vs. a lesser delocalization of Fe–B character in Ia does not swing the relative stabilization of the two isomers toward the experimentally favored structure.

In terms of the cage atomic charges shown in Table I, only Fe(1) and B(2) (Chart I) are significantly affected in going from Ia to Ib. The question is, relative to II, can Fe(1) bear a lower positive charge (II to Ia) more easily than B(2) bear a higher negative charge (II to Ib)? Indeed, in Ia, Fe(1) bears only a marginally smaller positive charge than Fe(2) bears in II. With respect to the boron, the metal center has the added capacity of offloading excess negative charge onto the carbonyl ligands. It is noted that the CO π-populations of Fe(1) increase by 0.307 electron in going from II to Ia, and only by 0.164 electron in going from II to Ib. Hence, charge considerations appear to be an important controlling factor in dictating which anion is formed.

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Registry No. [I]PPN, 102942-25-6; II, 102942-26-7.

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