

## Hexaborane(10) Derivatives: Relative Acidities of 2-CH<sub>3</sub>B<sub>6</sub>H<sub>9</sub> and 2-BrB<sub>6</sub>H<sub>9</sub> and NMR Spectra of 2-CH<sub>3</sub>B<sub>6</sub>H<sub>8</sub><sup>-</sup>, 2-BrB<sub>6</sub>H<sub>8</sub><sup>-</sup>, and (THF)<sub>2</sub>Mg(2-CH<sub>3</sub>B<sub>6</sub>H<sub>8</sub>)<sub>2</sub>

RANDALL J. REMMEL, DOUGLAS L. DENTON, JOHN B. LEACH, MARK A. TOFT, and SHELDON G. SHORE\*<sup>1</sup>

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Proton competition reactions show that the relative Brønsted acidities of substituted hexaborane(10) species are in the order 2-BrB<sub>6</sub>H<sub>9</sub> > B<sub>6</sub>H<sub>10</sub> > 2-CH<sub>3</sub>B<sub>6</sub>H<sub>9</sub>. Conjugate bases of the substituted acids, the anions 2-BrB<sub>6</sub>H<sub>8</sub><sup>-</sup> and 2-CH<sub>3</sub>B<sub>6</sub>H<sub>8</sub><sup>-</sup>, are obtained from the reaction of potassium hydride with the parent acid. The reaction of dimethylmagnesium with 2-methylhexaborane(10) in a 1:2 molar ratio in THF yields (THF)<sub>2</sub>Mg(2-CH<sub>3</sub>B<sub>6</sub>H<sub>8</sub>)<sub>2</sub>. Proton and boron-11 NMR spectra of these fluxional species are presented.

### Introduction

Many of the boron hydrides can function as Brønsted acids.<sup>2-9</sup> Proton removal has been generally achieved with bases such as alkali metal hydrides<sup>2-5,7</sup> and lithium alkyls.<sup>5,6,9</sup> In some cases ammonia<sup>5,8</sup> has also been used as a deprotonating agent. As a rule, the acidic site is a B-H-B bridge, and removal of a proton yields a B-B bond. From proton competition studies, relative acidities have been established for a number of boron hydrides. In general, within a class of hydrides (nido: B<sub>n</sub>H<sub>n+4</sub>; arachno: B<sub>n</sub>H<sub>n+6</sub>) acidity increases with increasing size of the boron framework.<sup>5b</sup>

The effect of substitution on relative acidities has been reported for pentaborane(9) derivatives.<sup>5c</sup> Methyl-substituted and halogen-substituted B<sub>5</sub>H<sub>9</sub> are respectively weaker and stronger Brønsted acids than B<sub>5</sub>H<sub>9</sub>. For the present study we have been concerned with the methyl and bromo derivatives of hexaborane(10): 2-CH<sub>3</sub>B<sub>6</sub>H<sub>9</sub> and 2-BrB<sub>6</sub>H<sub>9</sub>. These compounds are fluxional on the boron-11 and proton NMR scales.<sup>10</sup> The dynamic process consists of migration of bridge hydrogens among the basal boron-boron bond sites while terminally bonded groups remain at fixed positions. At low temperatures these systems are effectively quenched, and the structure of the preferred isomer of 2-CH<sub>3</sub>B<sub>6</sub>H<sub>9</sub> and 2-BrB<sub>6</sub>H<sub>9</sub> under the condition of slow exchange has been deduced from NMR spectra.<sup>10</sup> The static structures of these two molecules (Figure 1) differ in that the methyl-substituted boron in 2-CH<sub>3</sub>B<sub>6</sub>H<sub>9</sub> is associated with two B-H-B bridges while the bromo-substituted boron in 2-BrB<sub>6</sub>H<sub>9</sub> is associated with one B-H-B bond and one B-B bond. The low-temperature structure of 2-ClB<sub>6</sub>H<sub>9</sub> from X-ray crystallography<sup>19</sup> is in accord with this structure of 2-BrB<sub>6</sub>H<sub>9</sub>. That bridge hydrogens tend to move into positions adjacent to the methyl substituted

Table I. Boron-11 NMR Data<sup>a</sup>

| K[2-BrB <sub>6</sub> H <sub>8</sub> ]<br>(-22 °C) |                                 | K[2-CH <sub>3</sub> B <sub>6</sub> H <sub>8</sub> ]<br>(0 °C) |                                 | (THF) <sub>2</sub> Mg(2-CH <sub>3</sub> B <sub>6</sub> H <sub>8</sub> ) <sub>2</sub> (25 °C) |                                 |
|---|---------------------------------|---|---------------------------------|--|---------------------------------|
| δ (J, Hz)   | assignt                         | δ (J, Hz)   | assignt                         | δ (J, Hz)  | assignt                         |
| -48.9 (142)                                       | B <sub>1</sub>                  | -48.0 (133)   | B <sub>1</sub>                  | -46.5 (142)  | B <sub>1</sub>                  |
| 22.5  | B <sub>2</sub>                  | 32.5 <sup>b</sup>   | B <sub>2</sub>                  | 32.7 <sup>b</sup>  | B <sub>2</sub>                  |
| 6.6 (130)   | B <sub>3</sub> , B <sub>6</sub> | -6.1 <sup>b</sup>   | B <sub>4</sub> , B <sub>5</sub> | -4.2 <sup>b</sup>  | B <sub>4</sub> , B <sub>5</sub> |
|   | B <sub>4</sub> , B <sub>5</sub> | 18.6 <sup>b</sup>   | B <sub>3</sub> , B <sub>6</sub> | 17.7 <sup>b</sup>  | B <sub>3</sub> , B <sub>6</sub> |

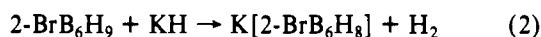
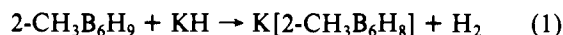
<sup>a</sup> Chemical shifts are relative to BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (δ 0.00) determined by assignment relative to BCl<sub>3</sub> (δ 46.8) as an external standard. Deviations: δ, ±0.2; J, ±5 Hz. <sup>b</sup> The coupling constant was not determined because of poor resolution of the signal.

boron atom, when the fluxional system is quenched in 2-CH<sub>3</sub>B<sub>6</sub>H<sub>9</sub>, is also observed<sup>20</sup> in the case of 1-CH<sub>3</sub>B<sub>4</sub>H<sub>8</sub><sup>-</sup>.

We report here the deprotonation of 2-CH<sub>3</sub>B<sub>6</sub>H<sub>9</sub> and 2-BrB<sub>6</sub>H<sub>9</sub> and their relative acidities. Fluxional behavior of the conjugate base anions of these derivatives have been examined by variable-temperature NMR spectroscopy. In addition, deprotonation of 2-CH<sub>3</sub>B<sub>6</sub>H<sub>9</sub> by (CH<sub>3</sub>)<sub>2</sub>Mg in THF yields the metalloborane (THF)<sub>2</sub>Mg(2-CH<sub>3</sub>B<sub>6</sub>H<sub>8</sub>)<sub>2</sub>.

### Results and Discussion

**Deprotonation Reactions.** Potassium hydride deprotonates 2-CH<sub>3</sub>B<sub>6</sub>H<sub>9</sub> and 2-BrB<sub>6</sub>H<sub>9</sub> quantitatively in dimethyl ether at -78 °C (eq 1 and 2). Dimethylmagnesium deprotonates

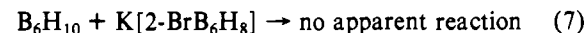
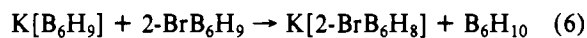
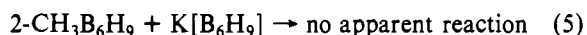
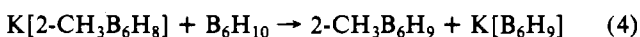


2-CH<sub>3</sub>B<sub>6</sub>H<sub>9</sub> in THF at -78 °C (eq 3). Reactions are complete

$$2\text{-CH}_3\text{B}_6\text{H}_9 + (\text{CH}_3)_2\text{Mg} + 2\text{THF} \rightarrow \text{Mg}(2\text{-CH}_3\text{B}_6\text{H}_8)_2(\text{THF})_2 + 2\text{CH}_4 \quad (3)$$

in about 15 min for 1 M solutions. Solid K[2-CH<sub>3</sub>B<sub>6</sub>H<sub>8</sub>] and Mg(2-CH<sub>3</sub>B<sub>6</sub>H<sub>8</sub>)<sub>2</sub>(THF)<sub>2</sub> are stable at room temperature under vacuum, while K[2-BrB<sub>6</sub>H<sub>8</sub>] decomposes significantly at room temperature over a period of 24 h.

Relative Brønsted acidities of 2-CH<sub>3</sub>B<sub>6</sub>H<sub>9</sub> and 2-BrB<sub>6</sub>H<sub>9</sub> with respect to B<sub>6</sub>H<sub>10</sub> were determined by means of the proton competition reactions (4)–(7) in dimethyl ether at -78 °C.



Significant differences in the chemical shifts of the boranes and their respective anions allowed straightforward identification of the species in solution. These systems establish the following order of relative acidities: 2-BrB<sub>6</sub>H<sub>9</sub> > B<sub>6</sub>H<sub>10</sub> > 2-CH<sub>3</sub>B<sub>6</sub>H<sub>9</sub>. This trend is similar to that observed for pentaborane(9) derivatives. It also parallels the recently reported order of Lewis basicity of the basal boron-boron bond in

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Table II. Proton NMR Data

| K[2-BrB <sub>6</sub> H <sub>8</sub> ] <sup>a</sup> (-30 °C) |                                 | K[2-CH <sub>3</sub> B <sub>6</sub> H <sub>8</sub> ] <sup>a</sup> |                      |                                 | (THF) <sub>2</sub> Mg(2-CH <sub>3</sub> B <sub>6</sub> H <sub>8</sub> ) <sub>2</sub> <sup>b</sup> |                     |   |
|---|---------------------------------|--|----------------------|---------------------------------|---|---------------------|---|
| δ   | assignt                         | δ  |                      | assignt                         | δ   |                     | assignt   |
|   |                                 | -30 °C   | -130 °C              |                                 | 25 °C   | -120 °C             |   |
| 12.84   | H <sub>μ</sub>                  | 13.18 {  | 14.46                | H <sub>1</sub>                  | 12.87 {   | 14.20               | H <sub>μ</sub> <sub>23</sub> , H <sub>μ</sub> <sub>26</sub> |
|   |                                 |  | (13.08) <sup>c</sup> |                                 |   |                     |   |
| 11.27   | H <sub>1</sub>                  | 11.83  | 11.84                |                                 | 11.43   | 11.51               | H <sub>1</sub>  |
|   | H <sub>3</sub> , H <sub>6</sub> |  |                      |                                 |   | 7.14                | H <sub>6</sub>  |
| 6.54  | H <sub>4</sub> , H <sub>5</sub> | 7.68   | 7.68                 | H <sub>3</sub> , H <sub>6</sub> | 7.43 {  | (7.52) <sup>c</sup> |   |
|   |                                 |  |                      |                                 |   |                     | 7.90  |
|   |                                 | 5.65   | 5.63                 | H <sub>4</sub> , H <sub>5</sub> | 5.55  | 5.64                | H <sub>4</sub> , H <sub>5</sub>                             |
|   |                                 | 9.19   | 9.16                 | CH <sub>3</sub>                 | 9.13  | 9.18                | CH <sub>3</sub>   |

<sup>a</sup> Chemical shifts are relative to Me<sub>4</sub>Si (δ 10.00) with (CH<sub>3</sub>)<sub>2</sub>O (δ 6.76) as an internal standard. Deviations: δ, ±0.03. <sup>b</sup> Chemical shifts are relative to Me<sub>4</sub>Si (δ 10.00) with CHCl<sub>3</sub> (δ 2.75) as an internal standard. Deviations: δ, ±0.03. <sup>c</sup> Weighted average.

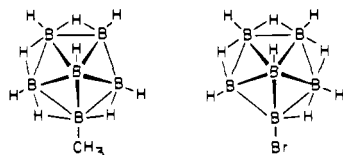


Figure 1. Topological structures.

methyl- and halogen-substituted hexaborane(10).<sup>11</sup> The basal boron-boron bond (Figure 1) can function as a Brønsted base (proton acceptor<sup>14</sup>) and as a Lewis base.<sup>11, 13, 14</sup>

**NMR Spectra.** Boron-11 and proton NMR data are presented in Tables I and II. Relative areas and peak multiplicities assisted in making assignments of boron-11 NMR spectra. Peak areas and selective narrow-line decoupling assisted in assigning <sup>1</sup>H NMR spectra. A feature common to all of the boron spectra is that with lowering temperature the basal boron signals broadened, generally becoming featureless below -70 °C. Such behavior appears to be a general characteristic of pyramidal borane species which contain one or more basal boron-boron bonds.<sup>5d, h, 10, 15</sup>

The anions 2-CH<sub>3</sub>B<sub>6</sub>H<sub>8</sub><sup>-</sup> and 2-BrB<sub>6</sub>H<sub>8</sub><sup>-</sup> are fluxional on the boron-11 and proton NMR time scales. The fluxional process is considered to be analogous to that described above for the parent molecules 2-CH<sub>3</sub>B<sub>6</sub>H<sub>9</sub> and 2-BrB<sub>6</sub>H<sub>9</sub><sup>10</sup> with the additional feature that the anions possess two basal boron-boron bond sites which are available for insertion of a bridge hydrogen during the fluxional process.

**1. 2-CH<sub>3</sub>B<sub>6</sub>H<sub>8</sub><sup>-</sup>.** The boron-11 NMR spectrum of 2-CH<sub>3</sub>B<sub>6</sub>H<sub>8</sub><sup>-</sup> at 0 °C is depicted in Figure 2a. Assignments of basal boron-11 signals reflect earlier assignments of the neutral parent molecule 2-CH<sub>3</sub>B<sub>6</sub>H<sub>9</sub><sup>10</sup> and 2,3-(CH<sub>3</sub>)<sub>2</sub>B<sub>6</sub>H<sub>8</sub>.<sup>16</sup>

Proton NMR spectra (broad-band <sup>11</sup>B decoupled) at -100 and -130 °C are shown in Figure 2b. In the spectrum taken at -100 °C all of the proton signals are sufficiently decoupled to be readily visible. In the spectrum taken at -130 °C the apical signal is undecoupled and is not readily visible. However, selective, narrow-line decoupling does bring out this resonance.

At -100 °C the <sup>1</sup>H NMR spectrum reveals only a single averaged bridge proton signal. But at lower temperatures it splits into two signals in the ratio 2:1, which indicates at least partial quenching of the fluxional process. The weighted average of the chemical shifts of these new bridge proton

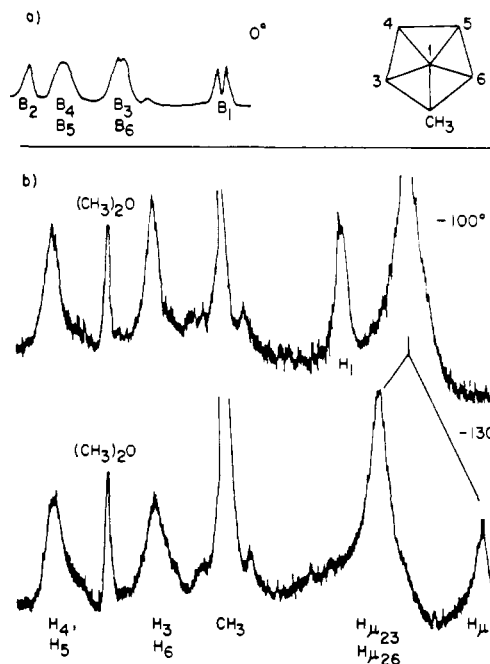
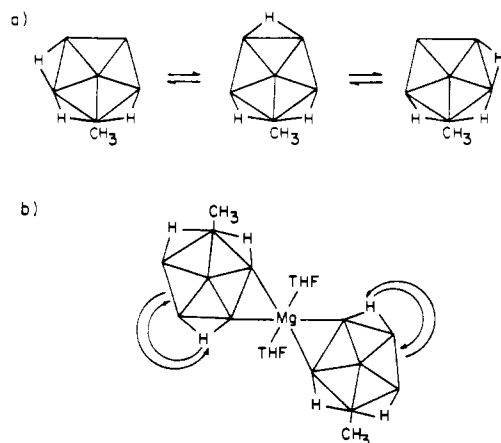


Figure 2. NMR spectra of 2-CH<sub>3</sub>B<sub>6</sub>H<sub>8</sub><sup>-</sup>: (a) boron-11 NMR spectrum in (CD<sub>3</sub>)<sub>2</sub>O; (b) proton NMR spectrum in (CD<sub>3</sub>)<sub>2</sub>O/CHClF<sub>2</sub> (<sup>11</sup>B decoupled).

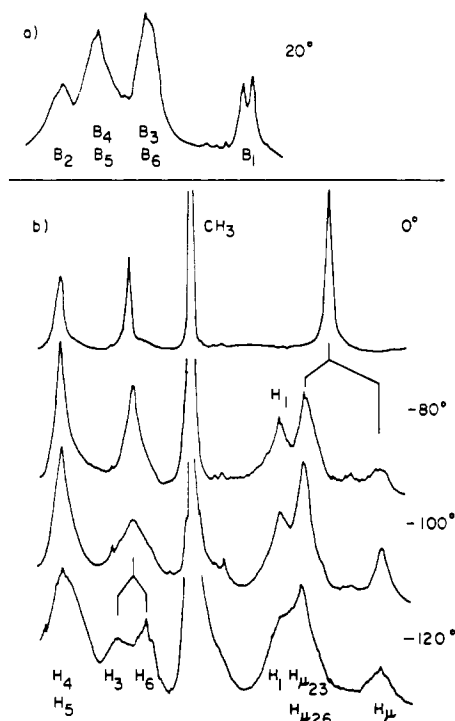
signals is in accord with that of the single bridge proton signal at higher temperatures. From selective decoupling experiments, terminal hydrogens and the bridge signal of area 2 are assigned in the spectrum at -130 °C. This spectrum represents a system in which two bridge hydrogens are effectively static on the proton NMR scale and are in bridge sites which are adjacent to the methyl-substituted boron. Assignment of the remaining bridge hydrogen depends upon whether it is fluxional or not on the proton NMR time scale. If it is not fluxional, this hydrogen is μ<sub>4,5</sub> and the static molecule possesses C<sub>s</sub> symmetry. If this hydrogen is fluxional, it is moving among the bridge sites shown in Figure 3a.

**2. (THF)<sub>2</sub>Mg(2-CH<sub>3</sub>B<sub>6</sub>H<sub>8</sub>)<sub>2</sub>.** Boron-11 and proton (broad-band <sup>11</sup>B decoupled) NMR spectra are shown in Figure 4. From earlier studies of the unsubstituted compound (THF)<sub>2</sub>Mg(B<sub>6</sub>H<sub>9</sub>)<sub>2</sub>, which included an X-ray structure determination,<sup>15</sup> the present compound is considered to be covalent with magnesium inserted into a bridge basal site. The molecule (THF)<sub>2</sub>Mg(B<sub>6</sub>H<sub>9</sub>)<sub>2</sub> is fluxional on the NMR time scale, with bridge hydrogens and bridge magnesium effectively moving into and out of available basal boron-boron bond sites. The boron-11 NMR spectrum at 20 °C and the proton NMR spectrum at 0 °C of (THF)<sub>2</sub>Mg(2-CH<sub>3</sub>B<sub>6</sub>H<sub>8</sub>)<sub>2</sub> are consistent with such fluxional character. While the apical terminal hydrogen signal is undecoupled and not visible in the particular

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**Figure 3.** (a) Partially quenched fluxional  $2\text{-CH}_3\text{B}_6\text{H}_8^-$ . (b) Partially quenched fluxional  $(\text{THF})_2\text{Mg}(2\text{-CH}_3\text{B}_6\text{H}_8)_2$ .



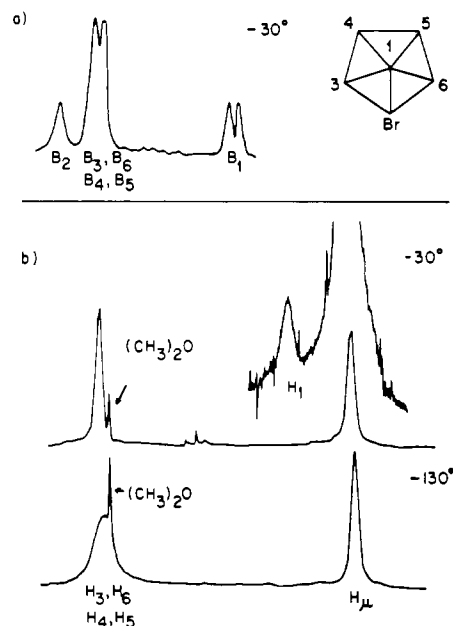
**Figure 4.** NMR spectra of  $(\text{THF-}d_6)_2\text{Mg}(2\text{-CH}_3\text{B}_6\text{H}_8)_2$ : (a) boron-11 NMR spectrum in  $\text{CD}_2\text{Cl}_2/\text{CHCl}_3$ ; (b) proton NMR spectra in  $\text{CD}_2\text{Cl}_2/\text{CHCl}_3$  ( $^{11}\text{B}$  decoupled).

broad-band  $^{11}\text{B}$  decoupled proton spectrum shown at  $0^\circ\text{C}$ , selective, narrow-line  $^{11}\text{B}$  decoupling did produce the apical signal. This signal is visible in the remaining broad-band  $^{11}\text{B}$  decoupled spectra shown in Figure 4b.

When the temperature is lowered, two bridge proton signals are present in the  $^1\text{H}$  NMR spectrum. At this temperature the fluxional character of the system is partially quenched. Effectively, two bridge protons are fixed in positions adjacent to the substituted boron while the remaining bridge hydrogen and the magnesium are still involved in the fluxional process. Note: for the anion  $2\text{-CH}_3\text{B}_6\text{H}_8^-$ , partial quenching of bridge hydrogen motion occurs at a temperature below  $-100^\circ\text{C}$ .

At  $-120^\circ\text{C}$  distinct  $\text{H}_3$  and  $\text{H}_6$  signals are present, and the  $\text{H}_4$ ,  $\text{H}_5$  signal is at the initial stage of splitting while the bridge signal  $\mu_{23}$ ,  $\mu_{26}$  is broadened. At this temperature the magnesium is effectively in a fixed position, and the remaining bridge hydrogen is probably moving between two sites as shown in Figure 3b.

**3.  $2\text{-BrB}_6\text{H}_8^-$ .** Boron-11 and proton (broad-band  $^{11}\text{B}$  decoupled) NMR spectra are shown in Figure 5. In the proton



**Figure 5.** NMR spectra of  $2\text{-BrB}_6\text{H}_8^-$ : (a) boron-11 NMR spectrum in  $(\text{CD}_3)_2\text{O}$ ; (b) proton NMR spectrum in  $(\text{CD}_3)_2\text{O}/\text{CHClF}_2$  ( $^{11}\text{B}$  decoupled).

spectra, the apical terminal resonance was not observed under the condition of broad-band boron-11 decoupling. However, the apical signal was observed when selective, narrow-line decoupling was employed.

While  $2\text{-BrB}_6\text{H}_8^-$  is undoubtedly fluxional with respect to the bridge hydrogens, the single signal which represents  $\text{B}_3$ ,  $\text{B}_4$ ,  $\text{B}_5$ ,  $\text{B}_6$  in the boron-11 spectrum and the single signal which represents  $\text{H}_3$ ,  $\text{H}_4$ ,  $\text{H}_5$ ,  $\text{H}_6$  in the proton spectrum are unexpected. The expected arrangement is two sets of averaged boron signals ( $\text{B}_3$ ,  $\text{B}_6$  and  $\text{B}_4$ ,  $\text{B}_5$ ) and two sets of averaged proton signals ( $\text{H}_3$ ,  $\text{H}_6$  and  $\text{H}_4$ ,  $\text{H}_5$ ) as observed for  $2\text{-CH}_3\text{B}_6\text{H}_8$  above  $-100^\circ\text{C}$ . At the lowest temperature available,  $-140^\circ\text{C}$ , there is no apparent splitting of the  $\text{H}_3$ ,  $\text{H}_4$ ,  $\text{H}_5$ ,  $\text{H}_6$  signal or the  $\text{H}_\mu$  signal.

The single peak for the 3,6 and 4,5 pairs probably arises from coincidental overlap of the two sets of signals. Partially relaxed FT boron-11 and proton FT NMR spectra do not reveal the separate 3,6 and 4,5 pairs. Relaxation times ( $T_1$ ) at  $-80^\circ\text{C}$  observed in these spectra are as follows:  $\text{B}_1$ ,  $0.020 \pm 0.002$ ;  $\text{B}_3$ ,  $\text{B}_4$ ,  $\text{B}_5$ ,  $\text{B}_6$ ,  $0.0019 \pm 0.0001$ ;  $\text{H}_1$ ,  $0.44 \pm 0.02$ ;  $\text{H}_3$ ,  $\text{H}_4$ ,  $\text{H}_5$ ,  $\text{H}_6$ ,  $0.32 \pm 0.02$  s. It is not likely that there is a fundamental structural difference between  $2\text{-BrB}_6\text{H}_8^-$  and  $2\text{-BrB}_6\text{H}_9$ . Protonation of the anion in liquid  $\text{HBr}$  at  $-78^\circ\text{C}$  readily produced  $2\text{-BrB}_6\text{H}_9$  in high yield.

### Experimental Section

**Materials.** Hexaborane(10) and  $2\text{-CH}_3\text{B}_6\text{H}_9$  were prepared according to previous reports<sup>17</sup> from this laboratory. Boron tribromide and  $\text{CHClF}_2$  (Matheson Co.) were used as received. Potassium hydride (RIC/ROC Co.) in a 50% mineral oil suspension was washed repeatedly with pentane to remove the oil. Dimethylmagnesium was prepared according to a literature report. All solvents including methylene- $d_2$  chloride and tetrahydrofuran- $d_8$  (Mallinckrodt Nuclear Co.) were distilled from  $\text{LiAlH}_4$  and stored under vacuum. Dimethyl- $d_6$  ether was prepared<sup>16</sup> from the reaction of methanol- $d_4$  and

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 (20) (a) Jaworinsky, I. S.; Barton, L.; Shore, S. G., in preparation. (b) Jaworinsky, I. S. Ph.D. Thesis, The Ohio State University, 1975.

methyl- $d_3$  iodide (Stohler Isotopes Co.)

**Apparatus.** All manipulations were carried out on a standard high-vacuum line or in a glovebox under an atmosphere of dry pure nitrogen. Boron-11 and proton magnetic resonance spectra were obtained with use of a Bruker HX-90 NMR spectrometer (28.87 and 90 MHz) operating in the FT mode and a Varian HA-100 NMR spectrometer (32.1 and 100 MHz).

**Preparation of 2-BrB<sub>6</sub>H<sub>9</sub>.**<sup>11,18</sup> Hexaborane(10) (4.24 mmol) and BBr<sub>3</sub> (6.36 mmol) were condensed into a 25-mL reaction vessel containing a Teflon covered magnetic stirring bar. The vessel was warmed to room temperature and stirred for 60 h. Initially a white solid precipitated, but it disappeared after about 10 h, at which time the solution was an intense yellow color. After 60 h had elapsed, an ice bath was placed around the reaction vessel, and the volatiles were pumped through U traps maintained at -35 and -196 °C while the reaction vessel slowly warmed to room temperature. The fractionation was terminated after 8 h. Isolated in the -35 °C U trap was 2-BrB<sub>6</sub>H<sub>9</sub> (2.49 mmol, 59% yield). Boron-11 and proton NMR spectra were identical with the literature report.<sup>11</sup>

**Preparation of (THF)<sub>2</sub>Mg(2-CH<sub>3</sub>B<sub>6</sub>H<sub>8</sub>)<sub>2</sub>.** In a nitrogen-filled glovebox 1.00 mL of a 0.43 M solution of (CH<sub>3</sub>)<sub>2</sub>Mg in THF was syringed into a reaction bulb which was fitted to a vacuum-line extractor. On the vacuum line the solution was cooled to -196 °C. The bulb was evacuated, and 0.85 mmol of 2-CH<sub>3</sub>B<sub>6</sub>H<sub>9</sub> was condensed on top of the (CH<sub>3</sub>)<sub>2</sub>Mg solution. The bulb was then warmed to -78 °C briefly to allow the 2-CH<sub>3</sub>B<sub>6</sub>H<sub>9</sub> to melt into the solution. Rapid methane evolution commenced immediately, accompanied by the precipitation of a white solid. The mixture was stirred at -78 °C until the evolution of methane nearly ceased (about 15 min). The mixture was cooled to -196 °C, and 0.43 mmol of methane was measured. Upon warming of the vessel to 0 °C gas evolution resumed rapidly. An additional 0.4 mmol of methane was evolved. Thus a total of 0.85 mmol of methane was evolved, 100% of the theoretical amount.

About 10 mL of THF was condensed on the solid to form a slurry. The extractor was inverted to filter the solid, which was then washed several times with THF. The product was dried under vacuum for several days. The solid isolated represented a 95% yield. Anal. Calcd for (THF)<sub>2</sub>Mg(2-CH<sub>3</sub>B<sub>6</sub>H<sub>8</sub>)<sub>2</sub>: Mg, 7.06; B, 37.66; C, 34.87; H, 11.22. Found: Mg, 7.05; B, 37.0; C, 34.5; H, 11.0.

**Deprotonation of Hexaborane(10) Derivatives.** For NMR studies a reaction vessel was constructed from 16-mm glass tubing. One end was sealed into a test-tube bottom while the other end was connected

to a stopcock. The vessel, containing a Teflon-coated magnetic stirring bar, was equipped with a side arm made of 6-mm glass tubing attached to an NMR tube.

In a typical reaction an excess of KH was placed in the vessel with utilization of a standard inert-atmosphere box. The vessel was removed to the vacuum line, under nitrogen, and evacuated. At -196 °C 0.40 mmol of 2-CH<sub>3</sub>B<sub>6</sub>H<sub>9</sub>, 0.36 mL of (CD<sub>3</sub>)<sub>2</sub>O, and 0.04 mL of CHClF<sub>2</sub> were condensed into the vessel, which was then warmed to -78 °C. The reaction was allowed to proceed with stirring until the evolution of hydrogen ceased. The hydrogen was measured with a Toeppler pump. Yields were in excess of 95% of the theoretical amount. The solution was then decanted into the NMR tube taking care to maintain the vessel and the side arm at -78 °C. The vessel was then frozen, and the NMR tube was sealed with a torch and removed. Deprotonation of 2-BrB<sub>6</sub>H<sub>9</sub> was carried out in similar fashion.

<sup>1</sup>H NMR spectra at temperatures below -110 °C were obtained with use of samples which were 1:1 (CD<sub>3</sub>)<sub>2</sub>O/CHClF<sub>2</sub> (by volume at -78 °C). These samples were prepared by removing half of the (CD<sub>3</sub>)<sub>2</sub>O from a 1 M solution of the appropriate hexaborane(10) salt at -78 °C and replacing it with a like amount of CHClF<sub>2</sub>.

**Relative Acidities of the Boranes.** Proton competition reactions were carried out in dimethyl ether at -78 °C between various pairs of neutral boranes and anions. An anion was prepared on a 0.35-mmol scale at -78 °C as described above. The appropriate neutral species was then condensed in at -196 °C in an equivalent amount. The reaction was allowed to proceed for 1 h at -78 °C before the solution was decanted and the NMR tube removed. The following pairs of reactions were carried out and followed by boron-11 NMR spectroscopy in the temperature range -78 to -20 °C: 2-BrB<sub>6</sub>H<sub>9</sub> and KB<sub>6</sub>H<sub>9</sub>; K<sup>+</sup>[2-BrB<sub>6</sub>H<sub>8</sub><sup>-</sup>] and B<sub>6</sub>H<sub>10</sub>; B<sub>6</sub>H<sub>10</sub> and K<sup>+</sup>[2-CH<sub>3</sub>B<sub>6</sub>H<sub>8</sub><sup>-</sup>]; KB<sub>6</sub>H<sub>9</sub> and 2-CH<sub>3</sub>B<sub>6</sub>H<sub>9</sub>. The species present in the resulting solutions were identified by the chemical shifts of the resonances observed.

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**Registry No.** 2-BrB<sub>6</sub>H<sub>9</sub>, 76466-46-1; 2-CH<sub>3</sub>B<sub>6</sub>H<sub>9</sub>, 39733-37-4; (THF)<sub>2</sub>Mg(2-CH<sub>3</sub>B<sub>6</sub>H<sub>8</sub>)<sub>2</sub>, 76466-43-8; K[2-BrB<sub>6</sub>H<sub>8</sub>], 76466-41-6; K[2-CH<sub>3</sub>B<sub>6</sub>H<sub>8</sub>], 76466-40-5; B<sub>6</sub>H<sub>10</sub>, 23777-80-2; (CH<sub>3</sub>)<sub>2</sub>Mg, 2999-74-8; KH, 7693-26-7; BBr<sub>3</sub>, 10294-33-4.