Formation of $[BH_3]^{2-}$ and $[B_2H_6]^{2-}$ from the Homogeneous Reduction of B_2H_6

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The $[BH_3]^{2-}$ dianion is isoelectronic with $[CH_3]^-$ and NH_3, while $[B_2H_6]^{2-}$ is isoelectronic with C_2H_6. Such species, as possibly generated in the reduction of diborane,[1−8] have been the subjects of discussion and speculation since the work of Stock[1] in 1935. An earlier attempt to detect $[BH_3]^{2-}$ and $[B_2H_6]^{2-}$ in the heterogeneous reduction of B_2H_6 was unsuccessful.[8] We now report boron-11 NMR evidence for the stepwise generation of $[BH_3]^{2-}$ and $[B_2H_6]^{2-}$ as discrete, stable intermediates in the reduction of B_2H_6 by alkali metal naphthalides[9] in THF to form $[B_3H_8]^-$ and $[BH_4]^-$ as the final products (eqs 1a−c).[10] These species were observed upon addition of increments of B_2H_6 to alkali metal naphthalide in THF solutions.[11] NMR spectra and NMR data are given in Figure 1 and Table 1.

$$^{1}/_{2}B_2H_6 + 2M^+/C_{10}H_8^- \xrightarrow{\text{THF}} M_2[BH_3] + 2C_{10}H_8 \quad \text{(1a)}$$

$$M_2[BH_3] + {}^{1}/_{2}B_2H_6 \xrightarrow{\text{THF}} M_2[B_2H_6] \quad \text{(1b)}$$

$$M_2[B_2H_6] + B_2H_6 \xrightarrow{\text{THF}} M[B_3H_8] + M[BH_4]\downarrow \quad \text{(1c)}$$
$$M = K, Rb$$

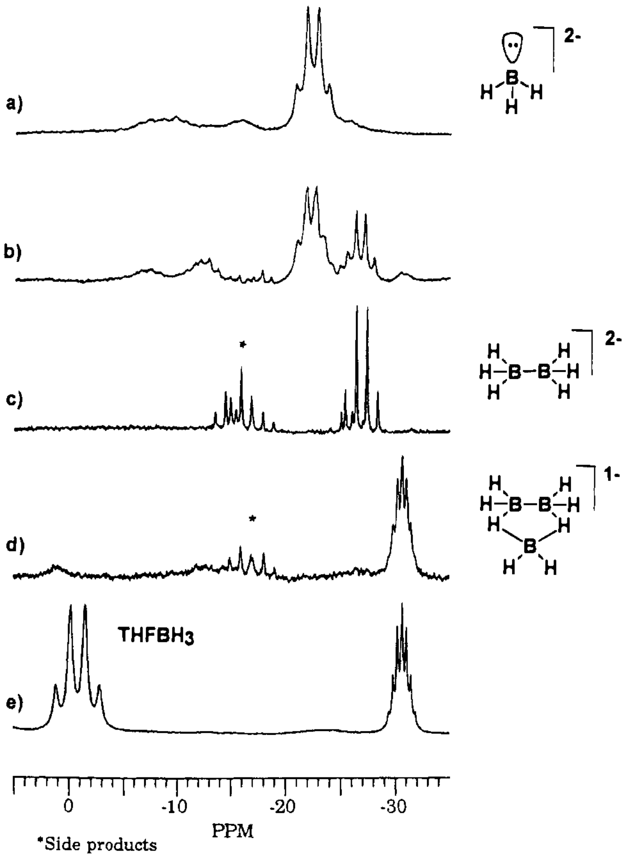

Figure 1. Boron-11 NMR spectra in THF at 303 K. The asterisks (*) indicate side products.

Table 1. Experimental ^1H and ^{11}B and Calculated ^{11}B Chemical Shifts for $[BH_3]^{2-}$ and $[B_2H_6]^{2-}$

	shift, ppm		
	$^1H^a$	$^{11}B^b$	IGLO, ^{11}B
$K_2[BH_3]$	0.5	−22.3	
$Rb_2[BH_3]$	0.5	−22.1	
$K_2[B_2H_6]$	1.6	−26.8	
$Rb_2[B_2H_6]$	1.6	−26.8	
$[BH_3]^{2-}$			−23.9
$[B_2H_6]^{2-}$			−31.4

[a] Chemical shifts referenced to TMS, $\delta = 0.00$ ppm. $J(^1H-^{11}B) = 80$ Hz. [b] Chemical shifts referenced to Et_2OBF_3, $\delta = 0.00$ ppm. $J(^{11}B-^1H) = 80$ Hz.

With a 1:4 ratio of B_2H_6 to potassium or rubidium naphthalide (eq 1a), a quartet (1:3:3:1) is observed in the ^{11}B NMR spectrum (Figure 1a) that is assigned to $[BH_3]^{2-}$. Addition of B_2H_6 to $[BH_3]^{2-}$ in THF (eq 1b) results in the appearance of a second quartet (1:3:3:1) at higher field in the ^{11}B NMR spectrum of the solution (Figure 1b) that is assigned to $[B_2H_6]^{2-}$. In the ^1H NMR spectrum, a quartet (1:1:1:1) assigned to $[B_2H_6]^{2-}$ occurs at lower field than the quartet (1:1:1:1) assigned to $[BH_3]^{2-}$. Complete consumption of $[BH_3]^{2-}$ to form $[B_2H_6]^{2-}$ is best achieved by titration of the solution containing $[BH_3]^{2-}$ with B_2H_6. Spectra b and c of Figure 1 illustrate this conversion. Addition of B_2H_6 to a solution of $[B_2H_6]^{2-}$ (eq 1c) results in the formation of $M[B_3H_8]$, identified by its characteristic ^{11}B NMR signal at −30.1 ppm[12] (Figure 1d), and $M[BH_4]$, which forms as a precipitate. There is no evidence in the NMR spectra for intermediate species during the conversion of $[B_2H_6]^{2-}$ to $[B_3H_8]^-$ and $[BH_4]^-$. Addition of excess B_2H_6 at any point during the reaction series shown in eqs 1a−c results in

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(9) Reductions have been carried out heterogeneously employing alkali metal amalgams[1−6,8] as well as the homogeneous reductions discussed here.

(10) A 2.5 mmol quantity of B_2H_6 was added to a solution contining 10 mmol of $M[C_{10}H_8]$ in 25 mL of THF at −196 °C. Warming the mixture to −78 °C and then to room temperature with continuous stirring resulted in a rapid color change from green to brown. A precipitate consisting predominately of $M[BH_4]$ was removed from the solution by filtration. $K[BH_4]$ IR, cm^{-1} (intensity): 2376 (m), 2280 (s), 2213 (m), 1119 (s). X-ray powder diffraction: *d* (Å) (intensity): 3.90 (s), 3.54 (vs), 2.37 (s), 2.03 (ms), 1.94 (m), 1.68 (vw), 1.54 (w), 1.50 (m), 1.37 (w), 1.28 (vw), 1.89 (vw). The solution contains predominately $[BH_3]^{2-}$, as evidenced by ^{11}B NMR spectroscopy. Soluble side products appear to be formed from the reaction of naphthalene with borane, leaving some unreacted alkali metal naphthalide in solution that is identified from its ESR spectrum.[24] Conversion of $[BH_3]^{2-}$ to $[B_2H_6]^{2-}$ (eq 1b) required the addition of a total of 2.7−3.0 mmol of B_2H_6 to the solution. After addition of 1.5 mmol of B_2H_6, additional precipitate was removed and the remainder of the B_2H_6 was added in 0.25 mmol increments. Consumption of $[BH_3]^{2-}$ was monitored by ^{11}B NMR spectroscopy. Solutions of $[B_2H_6]^{2-}$ were light yellow. Conversion of $[B_2H_6]^{2-}$ to form $[B_3H_8]^-$ and solid $[BH_4]^-$ typically required 1−2 mmol of B_2H_6. Solutions of $[B_3H_8]^-$ prepared in these experiments were light yellow.

(11) **CAUTION!** The use of 1,4-dioxane as a solvent in these reactions resulted in solid precipitates that detonated upon contact with a spatula in the absence of oxygen.

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consumption of the intermediate species and the formation of $M[B_3H_8]$, $M[BH_4]$ as a precipitate, and the excess B_2H_6 as $THFBH_3$ (Figure 1e).

IGLO calculations, used to predict ^{11}B NMR chemical shifts, were performed on $[BH_3]^{2-}$ and $[B_2H_6]^{2-}$. The predicted and experimental chemical shift values are shown in Table 1. The IGLO[21] calculations were carried out at the double-ζ level on structures that were geometry optimized using the Gaussian-90 code at the MP2/6-31G* level; HF = $-26.051\,71$ AU for $[BH_3]^{2-}$ and $-52.775\,44$ AU for the $[B_2H_6]^{2-}$ anion. The vibrationally stable forms of the two ions have symmetry assignments of C_{3v} for the $[BH_3]^{2-}$ ion and D_{3d} for $[B_2H_6]^{2-}$. In any comparison between experimental and calculated boron chemical shifts (at the levels of theory used in the present study) it is reasonable, on the basis of previous work,[13] to expect errors to be small and within 5 ppm. Solvent effects on the chemical shifts of ionic species cannot be easily calculated and could account for much of any chemical shift differences.

While the main soluble product of the reaction between B_2H_6 and alkali metal naphthalide is $[BH_3]^{2-}$ (eq 1a), a red precipitate is formed and the solution contains soluble side products and unreacted alkali metal naphthalide. The precipitate consists predominately of $M[BH_4]$, as determined by its IR spectrum and X-ray powder diffraction pattern, whereas the component giving rise to the red color in the precipitate is unidentified. The presence of unreacted naphthalide in solutions of $[BH_3]^{2-}$ was confirmed by ESR spectroscopy.[10,24] The soluble side products in solution produce ^{11}B NMR signals downfield of $[BH_3]^{2-}$. As additional B_2H_6 is added to the solution, $[B_2H_6]^{2-}$ is formed (eq 1b), and the signals from the soluble side products sharpen to triplets, $J(^{11}B-^{1}H) = 77$ Hz at 14–18 ppm (Figure 1c). The ^{11}B NMR chemical shifts of these species are consistent with the formation of naphthyl-substituted borohydrides.[14] They are not involved in the formation of $[B_3H_8]^-$, as evidenced by their presence after the conversion of $[B_2H_6]^{2-}$ to $[B_3H_8]^-$ and $[BH_4]^-$ (eq 1c, Figure 1d). The direct addition of B_2H_6 to alkali metal naphthalides in amounts sufficient to fulfill eq 1 also gives rise to similar side products.

Approximately 40 years ago Burg and Campbell reported[15] the synthesis of $Na_2[HB(CH_3)_2]$ by the reaction of $HB(CH_3)_2$ and sodium, in liquid ammonia. Campbell later proposed[16] the formation of $Ca[HB(CH_3)_2]$ and $Ca[B_2H_2(CH_3)_4]_2$. However, characterization of the ammonia-solvated products was limited to chemical analyses which showed significant scatter. Their attempts to form $Na_2[BH_3]$ from the reaction of diborane with sodium in liquid ammonia were unsuccessful. Presumably the formation of the diammoniate of diborane, $[H_2B(NH_3)_2][BH_4]$,[17] is so rapid as to preclude the formation of $[BH_3]^{2-}$ by this method. Some success, however, has been reported in the alkali metal reduction of $B(aryl)_3$. Tri-1-naphthylboron,[18] triphenylboron,[19] and trimesitylboron[20] react with sodium in ether solutions to form monoanions. The anions of tri-1-naphthylboron and triphenylboron were found to be diamagnetic in ether solution, possibly indicating dimerization to form $[(aryl)_3BB(aryl)_3]^{2-}$. The trimesitylborate(1−) anion is monomeric in solution, possibly due to the steric bulk of the substituents.[21] These triarylboron compounds also react with excess sodium in ethers to form the respective monomeric diamagnetic dianions, $[B(aryl)_3]^{2-}$.[21-23] Reported characterization of these mono- and dianions consists of analyses for Na and B, solution conductivity studies, and magnetic susceptibility and ESR experiments.

Attempts to probe further the chemistry of $[BH_3]^{2-}$ and $[B_2H_6]^{2-}$ are currently underway.

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