drogen bonding being an important factor in the determination of structure in **2**, as was intimated previously.[4] These structural generalizations above may provide insight into the bonding of four-coordinate 1,3,2,4-diazadiphosphetidine derivatives, which at this time can only be dealt with qualitatively. However, their identification can allow productive pursuit of further theoretical studies. Such studies are currently in progress in our laboratories and will be reported later.

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Registry No. **2**, 70160-66-6; **3**, 80631-62-5; **4**, 80631-63-6; **5**, 80631-64-7; $C_6H_5CH_2Br$, 100-39-0; CH_3I, 74-88-4; C_2H_5I, 75-03-6.

Supplementary Material Available: Tables listing structure factor amplitude data, anisotropic thermal parameters, nonessential intramolecular distances and angles, equations for least-squares planes, and data collection parameters (22 pages). Ordering information is given on any current masthead page.

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New, Systematic Syntheses of Boron Hydrides via Hydride Ion Abstraction Reactions: Preparation of B_2H_6, B_4H_{10}, B_5H_{11}, and $B_{10}H_{14}$

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The boron hydrides B_2H_6, B_4H_{10}, B_5H_{11}, and $B_{10}H_{14}$ are prepared in good yields through hydride ion abstraction reactions when the borane anions BH_4^-, $B_3H_8^-$, $B_4H_9^-$, and $B_9H_{14}^-$ respectively are treated with 1 molar equiv of a Lewis acid BX_3 (X = F, Cl, or Br), generally in the absence of a solvent, for reaction periods of 1–4 h. A high-yield (85–90%) method for the conversion of B_5H_9 to $B_9H_{14}^-$ is presented as the precursor to the practical conversion of B_5H_9 to $B_{10}H_{14}$ (45–50%). Additionally, treatment of the anion $BrB_3H_7^-$ with BBr_3 results in the formation of 2-BrB_4H_9 in low yield (15%). The hydride ion abstraction reactions by BBr_3 and BCl_3 lead to the new anions $HBBr_3^-$ and $HBCl_3^-$.

Introduction

One of the principal handicaps to the investigation of the chemistry of the intermediate boron hydrides B_4H_{10} and B_5H_{11} has been the absence of simple preparative procedures which would provide these materials in relatively large quantities and in good yield.[1,2]

Traditionally, B_4H_{10} and B_5H_{11} have been prepared by hot–cold reactor techniques,[3,4] thermolysis reactions,[5-8] and more recently from the protonation of $B_3H_8^-$ salts with HCl or polyphosphoric acid.[9-12] In addition, B_5H_{11} has been prepared[13] from the protonation of the hypho anion $B_5H_{12}^-$.

Hot–cold reactor methods,[3,4] although capable of providing B_4H_{10} and B_5H_{11} in reasonable quantities, have several experimental drawbacks. A glass hot–cold reactor requires the handling of relatively large quantities of potentially hazardous B_2H_6 at elevated temperature and high pressure. In addition, the technique is tedious, requiring several days of operation with constant attention to produce 10–20-mmol quantities of borane products, which then require separation by low-temperature vacuum-line fractionation. In general, the hot–cold reactor method also requires greater technical skill on the part of the investigator than the simpler techniques to be discussed in this paper.

Table I. Reactants, Conditions, and Yields (%) in the Preparation of B_2H_6 from [M][BH_4]

	M		
BX_3	Na^{+a}	$N(n\text{-}C_4H_9)_4^{+b}$	$(CH_3)P(C_6H_5)_3^{+b}$
BBr_3	0	94	90
BCl_3	0	98	94
BF_3	95	60	60

[a] No solvent, room temperature, 4–8 h (same results for 1:1 and 3:4 molar ratios of $NaBH_4$ and BF_3, respectively). [b] CH_2Cl_2, room temperature, 3 h.

The protonation of $B_3H_8^-$ salts[9-12] provides a laboratory method which eliminates the necessity of handling large quantities of B_2H_6 at high temperatures and pressures. This method, however, often requires tedious fractionation procedures before obtaining B_4H_{10} and B_5H_{11} in yields of 40% and 14%, respectively.[9-12] Pentaborane(11) may also be obtained in yields of up to 60% from the protonation of $B_5H_{12}^-$ salts by anhydrous HCl.[13] However, large quantities of B_5H_{11} are difficult to prepare by this method using standard vacuum-line techniques and the overall reaction requires much time as well as an available source of B_4H_{10}.

In a preliminary communication[14] we reported a new, systematic approach to boron hydride syntheses which not only

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(1) Onak, T.; Shore, S. G.; Yamauchi, M. "Gmelin Handbuch der Anorganischen Chemie"; Springer-Verlag: Berlin, 1978; Vol. 52, Chapter 6, pp 206–208.
(2) Onak, T.; Shore, S. G.; Yamauchi, M. "Gmelin Handbuch der Anorganischen Chemie"; Springer-Verlag: Berlin, 1979; Vol. 54, Chapter 1, pp 1–4.
(3) Stock, A.; Mathing, W. *Ber. Dtsch. Chem. Ges.* **1936**, 69, 1456.
(4) Klein, M. J.; Harrison, B. C.; Solomon, I. *J. Am. Chem. Soc.* **1958**, *80*, 4149.
(5) Hughes, R. L.; Smith, I. V.; Lawless, E. W. "R. T. Holtzman, Production of the Boranes and Related Research"; Academic Press: New York, 1967; p 65.
(6) Nigon, J. P. U.S. Patent 2864754, 1958; *Chem. Abstr.* **1959**, *53*, 5926.
(7) Cromwell, T. M. U.S. Patent 2967140, 1961; *Chem. Abstr.* **1961**, *55*, 9811.
(8) Kotlensky, W. V.; Shaeffer, R. *J. Am. Chem. Soc.* **1958**, *80*, 4517.
(9) Jeffers, W. British Patent 853727, 1960; *Chem. Abstr.* **1961**, *55*, 26835.
(10) Schaeffer, R.; Tebbe, F. *J. Am. Chem. Soc.* **1962**, *84*, 3974.
(11) Gaines, D. F.; Schaeffer, R. *Inorg. Chem.* **1964**, *3*, 438.
(12) Bond, A. C.; Pinsky, M. L. *J. Am. Chem. Soc.* **1970**, *92*, 32.
(13) Remmel, R. J.; Johnson, H. D., II; Jaworiwsky, I. S.; Shore, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 5395.
(14) Leach, J. B.; Toft, M. A.; Himpsl, F. L.; Shore, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 988.

Table II. Reactants, Conditions, and Yields (%) in the Preparation of B_4H_{10} from [M][B_3H_8]

	M			M	
BX_3	$N(n\text{-}C_4H_9)_4{}^+$	$N(CH_3)_4{}^+$	BX_3	$N(n\text{-}C_4H_9)_4{}^+$	$N(CH_3)_4{}^+$
BF_3	43[c]	65[b]	BBr_3	65[a]	5,[a] 30[d]
BCl_3	65[a]	5,[a] 30[d]			

[a] No solvent, 0 °C, 1 h. [b] No solvent, 0 °C, 3 h. [c] No solvent, 0 °C, 3 h. [d] No solvent, room temperature, 3 h.

provides the boranes B_4H_{10} and B_5H_{11} in relatively large quantities and in good yield but which has also been extended to the preparation of 2-BrB_4H_9 and has produced a simple conversion of pentaborane(9) to $B_{10}H_{14}$. We wish to report now, in detail, this new systematic approach to boron hydride syntheses, the important features of which are (1) only a simple vacuum-line apparatus is required, (2) reaction times are brief, and (3) in most cases no solvent is required and the products obtained require little purification. The basis for this synthetic method relates to our observation that hydride ion can be abstracted from certain borane anions using the Lewis acids BBr_3, BCl_3, and BF_3 to yield as one of the final products a neutral borane which contains one more boron atom than the anionic starting material.

Results and Discussion

B_2H_6 from BH_4^-. The simplest reaction observed (1) in-

$$[M][BH_4] + BX_3 \xrightarrow[\text{room temp}]{CH_2Cl_2} {}^1/_2B_2H_6 + [M][HBX_3] \qquad (1)$$

$$M = N(n\text{-}C_4H_9)_4{}^+, (CH_3)P(C_6H_5)_3{}^+; BX_3 = BCl_3, BBr_3$$

volves the abstraction of hydride ion from BH_4^- ions to generate BH_3 units which combine to form B_2H_6. Yields of B_2H_6 and reaction conditions are summarized in Table I. This procedure for the synthesis of B_2H_6 differs from the traditional synthesis in which the B_2H_6 is generated through hydride–halide exchange in reactions of metal borohydrides with group 3 halides in ethereal solvents.[15,16] In addition to reaction 1, reactions 2 and 3 were also observed to generate B_2H_6, but

$$NaBH_4 + BF_3^- \xrightarrow{\text{room temp}} {}^1/_2B_2H_6 + {}^3/_4NaBF_4 + {}^1/_4NaBH_4 \qquad (2)$$

$$3NaBH_4 + 4BF_3 \xrightarrow[\text{room temp}]{} 2B_2H_6 + 3NaBF_4 \qquad (3)$$

in the absence of any solvent. These results are also summarized in Table I. Of particular interest are those reactions which are close to being quantitative in the production of B_2H_6. The reaction of BF_3 with $NaBH_4$ occurs in the absence of a solvent, producing essentially pure B_2H_6, while the reactions of the metathesized borohydride salts are best carried out in CH_2Cl_2.

Another point of interest concerning reaction 1 is that the anions unknown previous to this work, $[HBCl_3]^-$ and $[HBBr_3]^-$, are prepared in nearly quantitative yields. The $[N(n\text{-}C_4H_9)_4]^+$ and $[(CH_3)P(C_6H_5)_3]^+$ salts of $[HBCl_3]^-$ and $[HBBr_3]^-$ are stable in CH_2Cl_2 solution for several hours at room temperature. The solids are free-flowing materials which are stable at room temperature under dry N_2. The ^{11}B NMR spectrum of each anion in CH_2Cl_2 at ambient temperature consists of a doublet which collapses to a single resonance upon proton decoupling. ^{11}B NMR data: $[HBCl_3]^-$ 3.0 ppm ($J_{^{11}B-^1H} = 158$ Hz); $[HBBr_3]^-$ −13.0 ppm ($J_{^{11}B-^1H} = 176$ Hz). The infrared spectra of the $[N(n\text{-}C_4H_9)_4]^+$ and $[(CH_3)P(C_6H_5)_3]^+$ salts of $[HBCl_3]^-$ and $[HBBr_3]^-$ in CH_2Cl_2 have B–H stretches at 2480 and 2520 cm^{-1}, respectively. Acid hydrolysis of the anions produces 1 equiv of H_2 based on 1 $H^-/[HBX_3]^-$.

Table III. Reactants, Conditions, and Yields in the Preparation of B_5H_{11} from K[B_4H_9]

BX_3	yield, %	BX_3	yield, %
BF_3	48[a]	BBr_3	45[b]
BCl_3	60[a]		

[a] No solvent, −35 °C, 3 h. [b] No solvent, 0 °C, 1 h.

B_4H_{10} from $B_3H_8^-$. Tetraborane(10) is readily prepared in up to 25-mmol quantities in yields up to 65% (based on boron in $B_3H_8^-$) from the hydride abstraction reaction (4). Table

$$[M][B_3H_8] + BX_3 \rightarrow B_4H_{10} + [M][HBX_3] + [\text{solid BH residue}] \qquad (4)$$

$$M = N(CH_3)_4{}^+, N(n\text{-}C_4H_9)_4{}^+; BX_3 = BF_3, BCl_3, BBr_3$$

II summarizes the yields of B_4H_{10} and the reaction conditions. Note that the conditions reported in Table II do not require use of a solvent.

In those reactions that produce 65% yields of B_4H_{10} all of the reactants are consumed and the gaseous products are at least 95% pure B_4H_{10}. The small amounts of impurities present are B_5H_9 and B_2H_6, which are easily separated from the B_4H_{10} by standard methods.[8]

The reaction of $[B_3H_8]^-$ with BX_3 (reaction 4) can be viewed as involving an initial step which generates unstable B_3H_7 through hydride ion abstraction. It is reasonable to assume that transfer of a BH_3 unit from one B_3H_7 to another is responsible for the production of B_4H_{10} and a residue of empirical composition BH_2. Thus the following sequence with resulting stoichiometry, reaction 4′, can be envisioned:

$$\begin{array}{c}
[B_3H_8]^- + BX_3 \rightarrow B_3H_7 + [HBX_3]^- \\
{}^1/_2[B_3H_7] + {}^1/_2[B_3H_7] \rightarrow {}^1/_2B_4H_{10} + (1/x)(BH_2)_x \\
\hline
[B_3H_8]^- + BX_3 \rightarrow {}^1/_2B_4H_{10} + (1/x)(BH_2)_x + [HBX_3]^-
\end{array} \qquad (4')$$

In the overall reaction of (4′), 67% of the boron in $[B_3H_8]^-$ is converted to B_4H_{10}. That this percent conversion agrees closely with the maximum yields of B_4H_{10} (65%) obtained experimentally suggests that in these cases the amount of B_4H_{10} obtained is close to quantitative with respect to the theoretical limit.

B_5H_{11} from $B_4H_9^-$. The preparation of B_5H_{11}, in up to 10-mmol quantities, in yields up to 60% (based upon boron in $B_4H_9^-$) was readily achieved from the hydride ion abstraction reaction (5). Table III summarizes yields of B_5H_{11} and reaction conditions.

$$K[B_4H_9] + BX_3 \rightarrow B_5H_{11} + K[HBX_3] + [\text{solid BH residue}] \qquad (5)$$

$$BX_3 = BF_3, BCl_3, BBr_3$$

In addition to the reactions indicated in Table III, the reaction of $[N(n\text{-}C_4H_9)_4][B_4H_9]$ with BBr_3 at 0 °C was also observed, and a 58% yield of B_5H_{11} was obtained. In those reactions which produce B_5H_{11} in better than 55% yields, all of the reactants appear to be consumed and the gaseous products are at least 95% B_5H_{11}. The impurities present are B_5H_9, B_2H_6, and B_9H_{15}. They are readily separated from the B_5H_{11} by standard methods.[8]

Reaction 5 is analogous to reactions 1 and 4 and can be viewed as involving an initial hydride ion abstraction from $B_4H_9^-$ to form as an unstable intermediate B_4H_8. Formation of B_5H_{11} is believed to occur through a second step in which BH_3 is transferred from one B_4H_8 to another B_4H_8 unit. The

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(15) Brown, H. D.; Tierney, P. A. *J. Am. Chem. Soc.* **1958**, *80*, 1552.

(16) Brown, H. C.; Murray, K. J.; Murray, L. J.; Snover, J. A.; Zweifel, G. *J. Am. Chem. Soc.* **1960**, *82*, 4233.

Table IV. Reactants, Conditions, and Yields (%) in the Preparation of $B_{10}H_{14}$ from $[M][B_9H_{14}]$[a]

	M			M	
BX_3	$N(CH_3)_4{}^+$	$N(n\text{-}C_4H_9)_4{}^+$	BX_3	$N(CH_3)_4{}^+$	$N(n\text{-}C_4H_9)_4{}^+$
BF_3	<1	<1	BBr_3	30	50
BCl_3	50	50			

[a] Room temperature, 3-6 h, no solvent, $B_{10}H_{14}$ sublimed from reaction flask at 110 °C.

following sequence with resulting stoichiometry (5′) is suggested:

$$[B_4H_9]^- + BX_3 \rightarrow B_4H_8 + [HBX_3]^-$$

$$^1/_2B_4H_8 + {}^1/_2B_4H_8 \rightarrow {}^1/_2B_5H_{11} + (1/2x)(B_3H_5)_x$$

$$[B_4H_9]^- + BX_3 \rightarrow {}^1/_2B_5H_{11} + [HBX_3]^- + (1/2x)(B_3H_5)_x \quad (5')$$

In reaction 5′, 63% of the boron available in the $B_4H_9{}^-$ is converted to B_5H_{11}. The results reported in Table III suggest that those reactions which produce B_5H_{11} in greater than 55% yields approach the theoretical limit of available B_5H_{11} as defined by reaction 5′.

$B_{10}H_{14}$ from B_5H_9 via $B_9H_{14}{}^-$. In a reaction analogous to the preparations of B_4H_{10} and B_5H_{11}, decaborane(14) was prepared in yields up to 50% from $[B_9H_{14}]^-$ (based on the boron in $[B_9H_{14}{}^-]$) through the hydride ion abstraction reaction (6). Table IV summarizes the yields of $B_{10}H_{14}$ and the reaction conditions employed. In those reactions in which 50% yields of $B_{10}H_{14}$ are obtained, all of the reactants appear to be consumed and the $B_{10}H_{14}$ produced is quite pure. The small amount of liquid borane impurities present are readily removed in the sublimation process.

$$[M][B_9H_{14}] + BX_3 \rightarrow B_{10}H_{14} + H_2 + [M][HBX_3] + [\text{solid BH residue}] \quad (6)$$

$$M = [N(CH_3)_4]^+, [N(n\text{-}C_4H_9)_4]^+$$

$$BX_3 = BF_3, BCl_3, BBr_3$$

The reaction of $[B_9H_{14}{}^-]$ with BX_3 is believed to proceed in a manner analogous to reaction 1, 4′, and 5′. It should be noted, however, that while hydride ion abstraction from the arachno[17] borane anions $[B_3H_8]^-$ and $[B_4H_9]^-$ results in the formation of the neutral arachno species B_4H_{10} and B_5H_{11}, respectively, the abstraction of hydride ion from the *arachno*-$[B_9H_{14}]^-$ ion leads to the isolation of the neutral nido[17] borane $B_{10}H_{14}$. This result is rationalized by assuming that *arachno*-$B_{10}H_{16}$ is formed initially, but it eliminates H_2 to form *nido*-$B_{10}H_{14}$. Thus the reaction scheme of (6′) consistent with (1), (4′), and (5′) is proposed. In the overall reaction of (6′), 56% of the boron in $[B_9H_{14}]^-$ is converted to $B_{10}H_{14}$. The results listed in Table IV suggest that the reactions which produce $B_{10}H_{14}$ in 50% yield approach the theoretical limit defined by (6′).

$$[B_9H_{14}]^- + BX_3 \rightarrow B_9H_{13} + [HBX_3]^-$$

$$^1/_2B_9H_{13} + {}^1/_2B_9H_{13} \rightarrow {}^1/_2B_{10}H_{16} + (1/2x)(B_8H_{10})_x$$

$$^1/_2B_{10}H_{16} \rightarrow {}^1/_2B_{10}H_{14} + {}^1/_2H_2$$

$$[B_9H_{14}]^- + BX_3 \rightarrow {}^1\!/_2B_{10}H_{14} + {}^1\!/_2H_2 + (1/2x)(B_8H_{10})_x + [HBX_3]^- \quad (6')$$

That $B_{10}H_{14}$ can be readily prepared from $[B_9H_{14}]^-$ is of no practical consequence without the availability of a convenient high-yield preparation of this anion. The traditional synthesis has involved degradation of $B_{10}H_{14}$,[18] a route which is of no use in the present case. More recently, however, the decomposition of $[B_5H_8]^-$ to $[B_9H_{14}]^-$ in yields up to 60% has been recognized as a potential source of this anion,[19-22] the $[B_5H_8]^-$ ion being generated through the deprotonation of B_5H_9. Our initial studies along these lines involved reactions of $[N(n\text{-}C_4H_9)_4][B_5H_8]$ with $AlCl_3$ and with BBr_3 under conditions in which $[B_5H_8]^-$ could decompose to give $[B_9H_{14}]^-$ (see eq 7 and 8).

$$[N(n\text{-}C_4H_9)_4][B_5H_8] + AlCl_3 \xrightarrow{100\ °C} B_{10}H_{14}\ (25\%\ \text{yield based on}\ [B_5H_8]^-) \quad (7)$$

$$[N(n\text{-}C_4H_9)_4][B_5H_8] \xrightarrow[\text{24 h, room temp}]{CH_2Cl_2} [N(n\text{-}C_4H_9)_4][B_9H_{14}] + BBr_3 \rightarrow B_{10}H_{14}\ (30\%\ \text{yield based on}\ [B_5H_8]^-) \quad (8)$$

Further investigations in this laboratory led to the development of a simple high-yield (85-90%) conversion of B_5H_9 to $[NR_4][B_9H_{14}]$, where $NR_4 = [N(CH_3)_4]^+$ or $[N(n\text{-}C_4H_9)_4]^+$. This was accomplished by allowing B_5H_9 to react with either NaH or KH in a 2:1 molar ratio in THF at room temperature in the presence of a 1 molar equiv of $[N(CH_3)_4]Cl$ or $[N(n\text{-}C_4H_9)_4]Br$. In a period of less than 1 h, 1 mol of H_2 is given off/mol of alkali-metal hydride. The initial borane anion formed is $[B_5H_8]^-$, which then undergoes subsequent reaction[23] with the remaining B_5H_9 to give $[B_9H_{14}]^-$. The primary resulting products are a mixture of $[NR_4][B_9H_{14}]$ and alkali-metal halide which is isolated as a free-flowing solid by pumping away the volatiles. Separation of $[NR_4][B_9H_{14}]$ from the alkali-metal halide is achieved by extracting it with THF or CH_2Cl_2. Yields up to 85% of $[NR_4][B_9H_{14}]$ (based upon boron in B_5H_9) of 95% purity were obtained. However, for the preparation of $B_{10}H_{14}$, $[NR_4][B_9H_{14}]$ need not be separated from the alkali-metal halide. After this mixture is isolated as a solid, a 1 molar equiv of boron halide is added to generate $B_{10}H_{14}$ according to reaction 6 to give the yields reported in Table IV for specific reactants and conditions. While the conversion of $NaBH_4$ to $B_{10}H_{14}$, another nonpyrolytic method, offers comparable yields[24,25] (based upon boron in $[BH_4]^-$), the present procedure is simpler and requires a solvent for only the first step.

2-BrB_4H_9 from $B_3H_7Br^-$. When $[N(n\text{-}C_4H_9)_4][B_3H_7Br]$,[26] prepared from the reaction of $[N(n\text{-}C_4H_9)_4][B_3H_8]$ with HBr, is reacted with BBr_3 in a 1:1 molar ratio in CH_2Cl_2 at -78 °C, the principal products are 2-BrB_4H_9, B_4H_{10}, 2-BrB_5H_8, and B_2H_6 (each in 10-15% yields based upon boron in $[B_3H_7Br]^-$. Other volatile products in smaller amounts (1-5%) are BrB_2H_5, B_2H_6, 1-BrB_5H_8, and B_5H_9. The total amount of boron in the volatile products is 60-65% of the boron in $[B_3H_7Br]^-$. This is consistent with the stoichiometry (eq 4′) suggested for the

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[17] Williams, R. E. *Inorg. Chem.* **1971**, *10*, 210.

[18] Benjamin, L. E.; Stafiej, S. F.; Tackacs, E. A. *J. Am. Chem. Soc.* **1963**, *85*, 2674.

[19] Brice, V. T.; Johnson, H. D., II; Denton, D. L.; Shore, S. G. *Inorg. Chem.* **1972**, *11*, 1135.

[20] Savory, C. G.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1973**, 179.

[21] Denton, D. L.; Clayton, W. R.; Mangion, M.; Shore, S. G.; Meyers, E. A. *Inorg. Chem.* **1976**, *15*, 541.

[22] Barton, L.; Onak, T.; Shore, S. G.; "Gmelin Handbuck der Anorganischen Chemis"; Springer-Verlag: Berlin, 1979; Vol. 54, Chapter 4, pp 113-114.

[23] Keller, P. C.; Himpsl, F. L.; Toft, M. A.; Boocock, S. K.; Shore, S. G. "Abstracts of Papers", 181st National Meeting of the American Chemical Society, Atlanta, GA, March-April 1981; American Chemical Society: Washington, D.C., 1981; INOR 195.

[24] Dunks, G. B.; Ordonez, K. P. *J. Am. Chem. Soc.* **1978**, *100*, 2555.

[25] Dunks, G. B.; Barker, K.; Hedaya, E.; Hefner, C.; Ordonez, K. P.; Remec, P. *Inorg. Chem.* **1981**, *20*, 1692.

[26] Ryschkewitsch, G. E.; Miller, V. H. *J. Am. Chem. Soc.* **1975**, *97*, 6258.

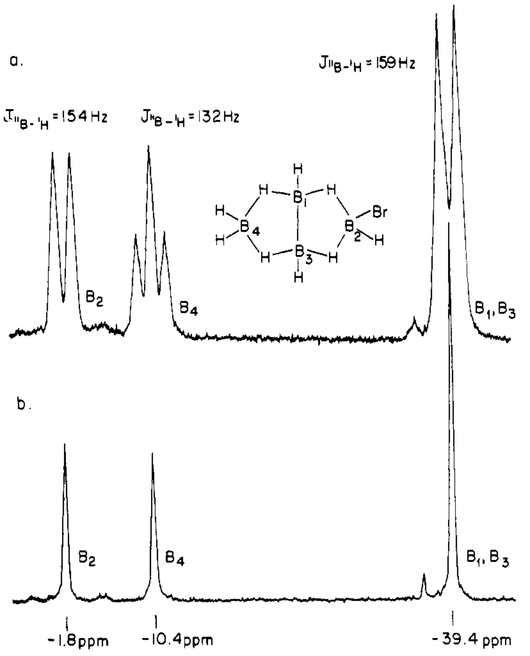

Figure 1. 96.27-MHz boron-11 NMR spectra of $2\text{-}BrB_4H_9$ in CD_2Cl_2 at −20 °C: (a) proton coupled; (b) proton decoupled.

reaction of $[B_3H_8]^-$ with a boron halide. The salts $[N(n\text{-}C_4H_9)_4][BBr_4]$ and $[N(n\text{-}C_4H_9)_4][HBBr_3]$ are present in the solid products. Apparently both Br^- and H^- are susceptible to abstraction by BBr_3 in the reaction with $[B_3H_7Br]^-$, thereby allowing the formation of B_3H_7 and B_3H_6Br initially. The formation of the numerous volatile products formed suggests that transfer and recombination involving BH_3 and BH_2Br may be occurring. There is also, undoubtedly, some decomposition which results in the formation of the B_5 species.

The reaction described above provides an alternative route to the preparation of $2\text{-}BrB_4H_9$. The only other procedure reported gives comparable yields and involves the reaction of excess B_4H_{10} with Br_2 over an 18-h period at −15 °C.[27] The present procedure offers advantages in that it does not require B_4H_{10} as a starting material and the reaction temperature of −78 °C is much easier to maintain than −15 °C over an extended time period.

Boron-11 and proton NMR spectra of $2\text{-}BrB_4H_9$ at 96.2 and 300 MHz, respectively, are shown in Figures 1 and 2. The boron-11 NMR spectra given in Figure 1 are consistent with the previously assigned 19.3 MHz spectra,[27] with the exceptions that the resonances due to B_2 and B_4 no longer overlap in the coupled spectrum, and that those for $B_{1,3}$ are found at −39.4 ppm instead of −34.7 ppm. The broad-band boron-11 decoupled proton spectrum of $2\text{-}BrB_4H_9$ (Figure 2) has been assigned with the assistance of narrow-band boron-11 spin-decoupling at frequencies which can be correlated to the individual boron resonances found in Figure 1. The peak assigned to H_2 has been given a relative area of 1 (the remaining resonances have all been assigned relative areas of 2). The resonance assigned to H_1 and H_3 is somewhat reduced in intensity in the broad band boron-11 decoupled spectrum (Figure 2) because at the optimum average frequency for decoupling all of the boron resonances, insufficient power is distributed to decouple H_1 and H_3 completely. However, narrow band decoupling markedly enhances this resonance, and a relative area of 2 is therefore assigned.

Experimental Section

Materials. $[N(n\text{-}C_4H_9)_4][B_3H_8]$, $[N(n\text{-}C_4H_9)_4N][BH_4]$, and $[(CH_3)P(C_6H_5)_3][BH_4]$ were prepared according to previous literature reports.[28,29] $[N(CH_3)_4][B_3H_8]$ (Alfa), $Na[BH_4]$ (Matheson Coleman Bell), $Li[BH_4]$ (Alfa), B_5H_9 (Callery Chemical Co.), and BBr_3 (Aldrich) were used as received. BF_3 and BCl_3 (Matheson) were fractionated through a −95 °C U-trap prior to use. $[N(CH_3)_4]Cl$ and $[N(n\text{-}C_4H_9)_4]Br$ (Alfa) were heated to 200 °C under dynamic vacuum and stored under dry nitrogen until used. KH (Alfa) and NaH (Metal Hydrides Inc.) in 50% mineral oil suspensions were washed repeatedly with dry pentane to remove the oil and then stored under dry nitrogen. Activities of the KH and NaH used were 95% and 98%, respectively, as determined by methanolysis and measurement of H_2 evolved with a Toepler pump. CH_2Cl_2 and CD_2Cl_2 were distilled from P_2O_5 and stored under vacuum. $(CH_3)_2O$ was dried over KH at −78 °C and stored at −78 °C under vacuum. THF was distilled from and stored over Na/benzophenone in vacuo.

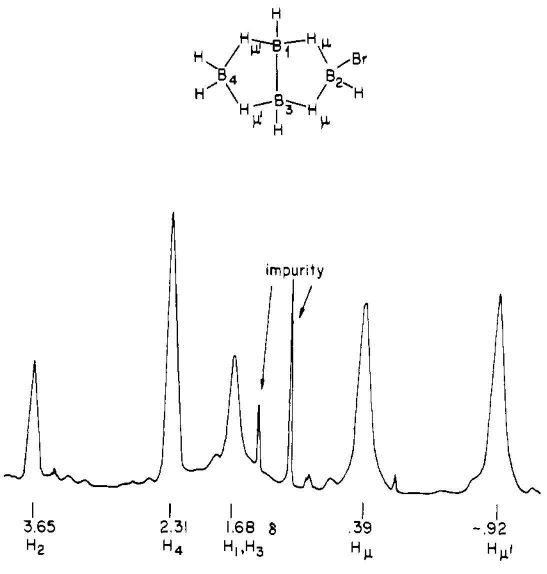

Figure 2. 300-MHz proton NMR spectrum of $2\text{-}BrB_4H_9$ in CD_2Cl_2 at −20 °C, with the boron-11 broad band decoupled.

General Method for Acid Hydrolysis. The solid to be analyzed for H_2 by hydrolysis (a 200–500-mg sample) was placed in a 15-mm × 250-mm hydrolysis tube sealed at one end and equipped with a 9-mm Fischer-Porter Solv-Seal joint at the other end. A stopcock adapter was then attached to the hydrolysis tube (all manipulations being carried out in a nitrogen filled glovebox), and 4–6 cm^3 of degassed aqueous 6 M HCl was condensed in at −196 °C. The hydrolysis tube was then placed in a sand bath and heated to ~100 °C for 24 h. After being cooled to −196 °C, the hydrolysis tube was opened to a Toepler pump and the quantity of H_2 gas measured.

Apparatus. All manipulations were carried out on a standard high-vacuum line or in a glovebox under an atmosphere of dry, pure nitrogen. Infrared spectra were obtained with a Perkin-Elmer 457 infrared spectrometer. ^1H and ^{11}B NMR spectra were recorded with a Varian HA-100 NMR spectrometer operating at 100 MHz and 32.1 MHz, respectively, a Bruker HX-90 NMR spectrometer operating at 90 and 28.87 MHz, respectively, and a Bruker WM-300 NMR spectrometer operating at 300 and 96.27 MHz, respectively. Chemical shifts for ^{11}B NMR spectra were referenced to $BF_3\cdot Et_2O$ = 0.00 ppm) with BCl_3 at +46.8 ppm as an external standard. Chemical shifts for ^1H NMR were referenced to Me_4Si (= δ 0.00). Mass spectra were obtained with an AEI mass spectrometer equipped with modified MS10 electronics and capable of unit mass resolution in the range of 2–200 amu.

Preparation of B_2H_6 and HBX_3^- (Where X = Cl, Br). Reaction of $[N(n\text{-}C_4H_9)_4][BH_4]$ with BBr_3. In a nitrogen-filled glovebox, $[N(n\text{-}C_4H_9)_4][BH_4]$ (590 mg, 2.30 mmol) was weighed into a 30-cm^3 reaction flask containing a Teflon-coated magnetic stir bar and fitted with a stopcock adapter. Boron tribromide (2.35 mmol) and CH_2Cl_2 (5 cm^3) were condensed into the vessel at −196 °C. The reaction mixture was warmed to room temperature with stirring for 2 h. The flask was then cooled to −78 °C and the volatiles fractionated through

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[27] Dobson, J.; Schaeffer, R. *Inorg. Chem.* **1965**, *4*, 593.

[28] Ryschkewitsch, G. E.; Nainan, K. C. *Inorg. Synth.* **1974**, *15*, 111.

[29] Hertz, R. K.; Johnson, H. D., II; Shore, S. G. *Inorg. Synth.* **1977**, *17*, 21–24.

U-traps maintained at −140 and −196 °C. Diborane (1.10 mmol, 94%) was obtained in the −196 °C trap and was identified by its infrared spectrum.[30] The creamy-white $[N(n\text{-}C_4H_9)_4][HBBr_3]$ was freed of remaining solvent by pumping at room temperature for 1 h and isolated in a yield of 85%.

Reaction of $[N(n\text{-}C_4H_9)_4][BH_4]$ with BCl_3. $[N(n\text{-}C_4H_9)_4][BH_4]$ (578 mg, 2.25 mmol) and BCl_3 (2.25 mmol) were reacted in CH_2Cl_2 (5 cm^3) under conditions identical with those above, producing B_2H_6 (1.10 mmol, 98%) and $[N(n\text{-}C_4H_9)_4][HBCl_3]$ (86% isolated).

Reaction of $[(CH_3)P(C_6H_5)_3][BH_4]$ with BBr_3. $[(CH_3)P(C_6H_5)_3][BH_4]$ (738 mg, 2.53 mmol) and BBr_3 (2.55 mmol) were reacted in CH_2Cl_2 (5 cm^3) under the conditions listed above. Diborane (1.15 mmol, 90%) and $[(CH_3)P(C_6H_5)_3][HBBr_3]$ (85%) were readily isolated.

Reaction of $[(CH_3)P(C_6H_5)_3][BH_4]$ with BCl_3. $[(CH_3)P(C_6H_5)_3][BH_4]$ (683 mg, 2.34 mmol) and BCl_3 (2.35 mmol) were reacted in CH_2Cl_2 (5 cm^3) under the same conditions employed above. Diborane (1.10 mmol, 94%) and $[(CH_3)P(C_6H_5)_3][HBCl_3]$ (84%) were isolated.

Reaction of $NaBH_4$ with BF_3 in a 1:1 Molar Ratio. $NaBH_4$ (980 mg, 26.3 mmol) was weighed into a 100-cm^3 reaction vessel containing a Teflon-coated magnetic stir bar and fitted with a stopcock adapter. BF_3 (26.3 mmol) was condensed onto the $NaBH_4$ at −196 °C, followed by slow warming to room temperature with vigorous stir bar action for 4 h. The flask was then opened to a U-trap maintained at −196 °C, and the B_2H_6 (13.0 mmol, 95% based on $[BH_4]^-$ and reaction 1) produced was collected and identified by its infrared spectrum[30] and vapor pressure at −111.6 °C (experimental 224 torr; literature 225 torr).[44] The solid remaining in the reaction flask was determined to be a 3:1 mixture of $NaBF_4$ and $NaBH_4$ by analysis of the ^{11}B NMR spectrum in 0.1 M aqueous NaOH.

Reaction of $NaBH_4$ with BF_3 in a 3:4 Molar Ratio. Sodium borohydride (342 mg, 9.05 mmol) and BF_3 (12.1 mmol) were reacted under the conditions stated above. Diborane (5.75 mmol, 95%) was obtained in a purity of approximately 95%. The solid remaining in the reaction flask consisted entirely of $NaBF_4$.

Preparation of B_4H_{10}. Reaction of $[N(n\text{-}C_4H_9)_4][B_3H_8]$ with BBr_3. BBr_3 (13.041 g, 52.1 mmol) was condensed at −196 °C into a 500-cm^3 reaction vessel containing a Teflon-coated magnetic stir bar and $[N(n\text{-}C_4H_9)_4][B_3H_8]$ (14.6855 g, 52.0 mmol) and fitted with a stopcock adapter. The reaction mixture was warmed slowly from −196 to 0 °C with vigorous stirring for 1 h. The flask was then cooled to −196 °C and allowed to slowly warm to room temperature while pumping the volatile products through U-traps maintained at −95, −140, and −196 °C. B_4H_{10} (25.1 mmol, 64% based on $B_3H_8^-$) was obtained in the −140 °C U-trap and identified by its infrared and ^{11}B NMR spectra.[31,32] Pentaborane(9) (1.5 mmol) was obtained in the −95 °C U-trap and was identified by its infrared spectrum.[33] A trace of B_2H_6 (1 mmol)[30] was trapped at −196 °C. Acid hydrolysis of a portion of the solid remaining in the reaction flask produces H_2 equivalent to the presence of $[HBBr_3]^-$ and a residue of empirical formula BH_2. The ^{11}B NMR spectrum of the solid reaction product shows only the presence of $[HBBr_3^-]$: −13.1 ppm, $J_{^{11}B-^{1}H} = 175$ Hz.

Reaction of $[N(n\text{-}C_4H_9)_4][B_3H_8]$ with BCl_3. BCl_3 (1.70 mmol) was condensed at −196 °C into a 30-cm^3 reaction flask containing a Teflon-coated magnetic stir bar and $[N(n\text{-}C_4H_9)_4][B_3H_8]$ (0.4687 g = 1.66 mmol) and fitted with a stopcock adapter. The reaction mixture was warmed slowly to 0 °C with vigorous stirring for 1 h. The flask was then cooled to −196 °C and allowed to warm slowly to room temperature while the volatile products were pumped through U-traps maintained at −95, −140, and −196 °C. B_4H_{10} (0.80 mmol, 65% based on $B_3H_8^-$) was obtained in the −140 °C U-trap and identified by its infrared spectra.[31]

Reaction of $[N(CH_3)_4][B_3H_8]$ with BF_3. In a typical reaction, BF_3 (36.0 mmol) was condensed at −196 °C into a 500-cm^3 reaction flask containing a Teflon-coated magnetic stir bar and $[N(CH_3)_4][B_3H_8]$ (4.1710 g, 36.4 mmol) and fitted with an appropriate stopcock adapter. The flask was then warmed to 0 °C, and the reactants were stirred vigorously for 3 h, followed by cooling to −196 °C and fractionation of the volatile products through U-traps maintained at −95, −140, and −196 °C while the reaction flask warmed to room temperature. B_4H_{10} (16.3 mmol, 60%) was obtained in the −140 °C U-trap and identified by its infrared spectra.[31] A mixture of B_2H_6/BF_3 (1.5 mmol) was isolated in the −196 °C U-trap and identified by infrared spectroscopy.[30]

Preparation of B_5H_{11}. Reaction of KB_4H_9 with BCl_3. In a typical preparation of B_5H_{11}, KH (560 mg, 12.8 mmol) was weighed into a 250-cm^3 reaction flask, containing a Teflon-coated magnetic stir bar and fitted with a stopcock adapter, in a nitrogen filled glovebox. $(CH_3)_2O$ (14 cm^3) and B_4H_{10} (12.8 mmol) were condensed into the flask at −196 °C. The flask was then warmed to −78 °C with stirring for 1 h. After the flask was cooled to −196 °C, the H_2 (12.6 mmol) produced in the deprotonation[34,35] was measured with a Toepler pump and pumped away. The $(CH_3)_2O$ was removed by pumping at −78 °C for 1–2 h followed by pumping at −45 °C for 1 h to remove the last traces of solvent since if all of the $(CH_3)_2O$ is not removed it will react with the boron trihalide to be used in the following step of the reaction sequence. BCl_3 (12.9 mmol) was condensed onto the dry $K[B_4H_9]$ at −196 °C followed by warming to −35 °C with stirring for 2.5–3 h. The vessel was cooled to −196 °C, and a trace of H_2 (1 mmol) was pumped away. Fractionation of the volatile products was accomplished by warming the reaction flask to −45 °C while pumping through U-traps maintained at −78 and −196 °C. The B_5H_{11} produced was collected together with trace B_5H_9 and B_2H_6 in the −196 °C trap. The contents of this trap were fractionated (under a static vacuum) through a −78 and a −196 °C trap while slowly warming this trap to room temperature. The −78 °C trap contained B_5H_{11} (6.0 mmol, 59% based on $B_4H_9^-$), which was identified by its ^{11}B NMR[36] and infrared spectra.[37]

Reaction of $[N(n\text{-}C_4H_9)_4][B_4H_9]$ with BBr_3. KH (188 mg, 4.45 mmol) and $[N(n\text{-}C_4H_9)_4]I$ (1.65 g, 4.45 mmol) were weighed into a 100-cm^3 reaction vessel containing a Teflon-coated magnetic stir bar and fitted with an appropriate stopcock adapter in a nitrogen-filled glovebox. Dimethyl ether (4 cm^3) and B_4H_{10} (4.45 mmol) were condensed into the flask at −196 °C. $[N(n\text{-}C_4H_9)_4][B_4H_9]$ was then prepared as described elsewhere.[34] BBr_3 (1.0821 g, 4.32 mmol) was warming to 0 °C with vigorous stirring for 1 h. Fractionation of volatile products through U-traps maintained at −78 and −196 °C under dynamic vacuum followed by a second fractionation of the material collected in the −196 °C U-trap through −78 and −196 °C U-traps under static vacuum led to the isolation of 2.0 mmol B_5H_{11} in the −78 °C U-trap. The B_5H_{11} was identified by its gas-phase infrared spectrum.[37] The solid remaining in the reaction vessel, $[N(n\text{-}C_4H_9)_4][HBBr_3]$, was identified by its ^{11}B NMR spectrum: −13.0 ppm, $J_{^{11}B-^{1}H} = 173$ Hz.

Conversion of B_5H_9 to $B_{10}H_{14}$. Reaction of $[N(CH_3)_4][B_9H_{14}]$ (Prepared in Situ) with BCl_3. NaH (5.8 mg, 21.6 mmol) and $[N(CH_3)_4]Cl$ (2.41 g, 22 mmol) were weighed into a 500-cm^3 reaction flask, containing a Teflon-coated magnetic stir bar and fitted with a stopcock adapter, in a nitrogen-filled glovebox. THF (15–20 cm^3) and B_5H_9 (43.2 mmol, 4.30 cm^3, $d_0° = 0.66$ g/cm^3) were condensed into the reaction vessel at −196 °C. The flask was slowly warmed to room temperature with stirring for 12 h. H_2 (22 mmol) was measured by Toepler pump and pumped away. The THF was removed by pumping, leaving behind a dry, slightly yellow solid which was shown to be a mixture of almost pure $[N(CH_3)_4][B_9H_{14}]$ (by ^{11}B NMR)[38] and NaCl. BCl_3 (22.0 mmol) was then condensed onto the solid reaction products at −196 °C, followed by warming of the reaction flask to room temperature with vigorous stirring for 6 h. After the flask was cooled to −196 °C, H_2 (10.0 mmol) was measured by Toepler pump and removed. The reaction vessel was then heated with an oil bath to ~100 °C and the $B_{10}H_{14}$ (1.18 g, 9.57 mmol) (46% based on B_5H_9)) sublimed into a removable U-trap at 0 °C under dynamic vacuum. The $B_{10}H_{14}$ prepared was identified by its ^{11}B NMR spectrum.[39]

Reaction of $[N(n\text{-}C_4H_9)_4][B_9H_{14}]$ (Prepared in Situ) with BBr_3. In a nitrogen-filled glovebox, KH (215 mg, 4.94 mmol) and [N(*n*-

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(30) Lord, R. C.; Nielsen, E. *J. Chem. Phys.* **1951**, *19*, 1.

(31) Lutz, C. A.; Ritter, D. M. *Can. J. Chem.* **1963**, *41*, 1344.

(32) Leach, J. B.; Onak, T.; Spielman, J.; Rietz, R. R.; Schaeffer, R.; Sneddon, L. G. *Inorg. Chem.* **1970**, *9*, 2170.

(33) Hrostowski, H. J.; Pimentel, G. C. *J. Am. Chem. Soc.* **1954**, *76*, 1003.

(34) Remmel, R. J.; Johnson, H. D., II; Jaworinsky, I. S.; Shore, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 5395.

(35) Johnson, H. D., II; Shore, S. G. *J. Am. Chem. Soc.* **1970**, *92*, 7586.

(36) Rietz, R. R.; Schaeffer, R.; Sneddon, L. G. *J. Am. Chem. Soc.* **1970**, *92*, 3514.

(37) Spielman, J. R.; Burg, A. B. *Inorg. Chem.* **1963**, *2*, 1139.

(38) Schaeffer, R.; Sneddon, L. G. *Inorg. Chem.* **1972**, *11*, 3102.

(39) Williams, R. E. *Inorg. Chem.* **1965**, *4*, 1504.

$C_4H_9)_4$]I (2.0 g, 5.4 mmol) were weighed into a 100-cm^3 reaction flask containing a Teflon-coated magnetic stir bar and fitted with a stopcock adapter. Tetrahydrofuran (10 cm^3) and B_5H_9 (1.0 cm^3, 10.0 mmol, d_0° = 0.66 g/cm^3) were condensed into the flask at -196 °C, followed by warming to room temperature with stirring for 15 h. H_2 (4.97 mmol) was removed with a Toepler pump, and the THF was pumped away under dynamic vacuum, leaving behind a dry, light yellow solid. BBr_3 (1.2206 g, 4.90 mmol) was condensed onto the solid products at -196 °C, and the reaction flask and contents were then warmed to room temperature, forming a "melt" that was slowly stirred for 8 h. H_2 (1.83 mmol) was then removed via a Toepler pump, followed by sublimation of the $B_{10}H_{14}$ (0.24 g, 2.0 mmol). This quantity represents a yield of 40% based upon B_5H_9 and approximately 47% based upon [N(*n*-$C_4H_9)_4$][B_9H_{14}]. Trace quantities of additional volatile liquid boranes were not investigated.

Reaction of [N(*n*-$C_4H_9)_4$][B_9H_{14}] (Prepared in Situ) with BCl_3. In a nitrogen-filled glovebox, NaH (192 mg, 8.0 mmol) and [N(*n*-$C_4H_9)_4$]Br (2.6 g, 8.1 mmol) were weighed into a 100-cm^3 reaction flask containing a Teflon-coated magnetic stir bar and fitted with a stopcock adapter. Tetrahydrofuran (10 cm^3) and B_5H_9 (1.6 cm^3, 16 mmol, d_0° = 0.66 g/cm^3) were condensed into the flask at -196 °C, followed by warming to room temperature with stirring for 15–18 h. H_2 (7.4 mmol) was removed with a Toepler pump, and the THF was pumped away under dynamic vacuum, leaving behind a dry, light yellow solid. BCl_3 (8.0 mmol) was condensed onto the solid products at -196 °C, and the reaction flask and contents were then warmed to room temperature, forming a "melt" that was slowly stirred for 3 h. H_2 (4.12 mmol) was then removed via a Toepler pump, followed by sublimation of the $B_{10}H_{14}$ (0.47 g, 3.85 mmol). This is a yield of 48% based upon B_5H_9 and approximately 53% based upon [N(*n*-$C_4H_9)_4$][B_9H_{14}].

Reaction of [N($CH_3)_4$][B_9H_{14}] (Prepared from $B_{10}H_{14}$) with BCl_3. [N($CH_3)_4$][B_9H_{14}] (2.948 g, 15.9 mmol) was weighed into a 100-cm^3 reaction flask containing a Teflon-coated magnetic stir bar and fitted with a stopcock adapter. BCl_3 (16.0 mmol) was condensed into the flask at -196 °C, followed by warming to room temperature with vigorous stirring for 3 h. After the flask was cooled to -196 °C, H_2 (6.6 mmol) was measured by Toepler pump and removed. The reaction vessel was then heated with an oil bath to ~100 °C, and the $B_{10}H_{14}$ (0.802 g, 6.6 mmol) sublimed into a removable U-trap at 0 °C under dynamic vacuum. This represented a yield of 46% based on $B_9H_{14}^-$. The $B_{10}H_{14}$ isolated was identified by its ^{11}B NMR spectrum.[39]

Preparation of 2-BrB_4H_9. Reaction of [N(*n*-C_4H_9)][B_3H_7Br] with BBr_3. [N(*n*-$C_4H_9)_4$][B_3H_8] (5.60 g, 19.8 mmol) was weighed into a 200-cm^3 reaction flask, containing a Teflon-coated magnetic stir bar and fitted with a stopcock adapter. CH_2Cl_2 (8–10 cm^3) and HBr (19.6 mmol) were condensed into the flask at -196 °C. The flask was warmed with stirring to -78 °C for 1 h, followed by stirring at room temperature for several minutes. H_2 (19.7 mmol) evolved was measured with a Toepler pump and then pumped away. Further CH_2Cl_2 (2 cm^3) and BBr_3 (19.8 mmol) were condensed into the flask at -196 °C, and the reactants were warmed to -78 °C with stirring for ~12 h. The reaction vessel was allowed to warm slowly to room temperature while the volatile products and CH_2Cl_2 were pumped out through U-traps maintained at -78, -126, and -196 °C. The CH_2Cl_2 was allowed to pass completely through the -78 °C trap. The products and solvent in the -126 and -196 °C traps were refractionated through -95, -126, and -196 °C U-traps. B_4H_{10} (2–2.5 mmol, 15–20%) and trace CH_2Cl_2 were isolated in the -126 °C trap and identified by their infrared spectra.[31] B_2H_6 (1.5 mmol) was obtained in the -196 °C trap and identified by its infrared spectrum.[30] The lower volatility products isolated in the original -78 °C trap were separated with a low-temperature fractionation column.[40] 2-BrB_4H_9 (1.6–2.0 mmol, 11–14%) was taken off the column between -60 and -56 °C and was identified by its infrared,[41] ^{11}B NMR,[27] and ^1H NMR spectra. 2-BrB_5H_8 (1.8 mmol) was taken off the column between -53 and -31 °C and was identified by its ^{11}B NMR spectrum.[42] The light yellow solid remaining in the reaction flask was identified as being primarily a mixture of [N(*n*-$C_4H_9)_4$][BBr_4] and [N(*n*-C_4H_9)][$HBBr_3$] by their ^{11}B NMR spectra.[43]

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Registry No. B_2H_6, 19287-45-7; B_4H_{10}, 18283-93-7; B_5H_{11}, 18433-84-6; $B_{10}H_{14}$, 17702-41-9; 2-BrB_4H_9, 36730-91-3; [N(*n*-$C_4H_9)_4$][$HBBr_3$], 76522-06-0; [(CH_3)P($C_6H_5)_3$][$HBBr_3$], 80679-89-6; [N(*n*-$C_4H_9)_4$][$HBCl_3$], 69969-98-8; [(CH_3)P($C_6H_5)_3$][$HBCl_3$], 80679-90-9; [N(*n*-$C_4H_9)_4$][BH_4], 33725-74-5; [(CH_3)P($C_6H_5)_3$][BH_4], 40001-26-1; $NaBH_4$, 16940-66-2; [N(*n*-$C_4H_9)_4$][B_3H_8], 53451-55-1; [N($CH_3)_4$][B_3H_8], 12386-10-6; K[B_4H_9], 57406-39-0; [N(*n*-$C_4H_9)_4$][B_4H_9], 57472-84-1; [N($CH_3)_4$][B_9H_{14}], 12545-93-6; [N(*n*-$C_4H_9)_4$][B_9H_{14}], 80664-91-1; BBr_3, 10294-33-4; BCl_3, 10294-34-5; BF_3, 7637-07-2; B_5H_9, 19624-22-7; [N(*n*-$C_4H_9)_4$][B_3H_7Br], 57472-92-1; 2-BrB_5H_8, 23753-64-2.

---

(40) Dobson, J. E.; Schaeffer, R. *Inorg. Chem.* **1970**, *9*, 2183.

(41) Dazord, J.; Mongeot, H. *Bull. Soc. Chim. Fr.* **1972**, *3*, 950.

(42) Onak, T.; Dunks, G. B.; Searcy, I. W.; Spielman, J. *Inorg. Chem.* **1967**, *6*, 1465.

(43) Landesman, H.; Williams, R. E. *J. Am. Chem. Soc.* **1961**, *83*, 2663.

(44) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969; Appendix V, p 267.