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Preparation and Nuclear Magnetic Resonance Studies of the Stereochemically Nonrigid Anions $B_4H_9^-$, $B_5H_{12}^-$, $B_6H_{11}^-$, and $B_7H_{12}^-$ Improved Syntheses of B_5H_{11} and B_6H_{12}

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Received January 27, 1975

Abstract: Using KH or NH_3 as a deprotonating agent, $B_4H_9^-$ is prepared on a practical basis from B_4H_{10}. Addition of BH_3 to $B_4H_9^-$, $B_5H_8^-$, and $B_6H_9^-$ results in polyhedral expansion, yielding $B_5H_{12}^-$, $B_6H_{11}^-$, and $B_7H_{12}^-$. The $B_5H_{12}^-$ ion is the only known binary hydride species that is a member of the newly recognized class of hypho boranes. Variable temperature boron-11 and proton NMR spectra are presented and discussed in terms of dynamic properties of the anions and their static structures. Syntheses of B_5H_{11} and B_6H_{12} in 60-70% yield are achieved by addition of liquid HCl to $B_5H_{12}^-$ and $B_6H_{11}^-$. Relative Brönsted acidities of B_4H_{10} and B_6H_{12} are established by proton competition reactions.

Although the Brönsted acidity of $B_{10}H_{14}$ was first demonstrated in 1956,[1] leading to the prediction[2] that lower boron hydrides could also function as Brönsted acids, it was not until 1967 that definitive evidence for the Brönsted acidity of a lower boron hydride, B_5H_9,[3a-c] was offered. Over the past several years evidence has been accumulated which shows that many of the lower boron hydrides can function as monoprotic Brönsted acids with a bridging hydrogen serving as the proton source.[4-6] Each of the resulting conjugate bases possesses a boron-boron bond which is susceptible to insertion of an electrophillic reagent.[3b,7-9] Thus deprotonation of B_4H_{10}, B_5H_9, and B_6H_{10} yields conjugate bases to which the electrophile BH_3 can be added, resulting in polyhedral expansion of the boron frameworks to give the new anions $B_5H_{12}^-$, $B_6H_{11}^-$, and $B_7H_{12}^-$.

In the present article we consider the acidities of B_4H_{10} and B_6H_{12} and provide detailed boron-11 and proton NMR spectra of the anions $B_4H_9^-$, $B_5H_{12}^-$, and $B_6H_{11}^-$, and $B_7H_{12}^-$, which allow consideration of static and dynamic forms. Detailed procedures are provided for good yield syntheses of B_5H_{11} from $B_5H_{12}^-$ and B_6H_{12} from $B_6H_{11}^-$. Observations and procedures which were not discussed in detail in earlier communications[4d,7b] are fully presented herein.

Results and Discussion

Reactions of Tetraborane(10). At −78° deprotonation of B_4H_{10} in ether solvents can occur according to the following reaction. The $B_4H_9^-$ ion is formed in essentially quantitative yield.[4d,5]

$$B_4H_{10} + ML \rightarrow M^+ \, B_4H_9^- + LH \qquad (1)$$

where ML = KH,[4d] NaH,[10] and $LiCH_3$.[5] We have found the reaction to be very sensitive to solvent, deprotonating agent, and concentration of reactants. The cleanest reactions were consistently obtained in dimethyl ether using potassium hydride as the deprotonating agent with concentrations of reactants being at least 1 *M*. Solutions of KB_4H_9 in ether solvents are colorless and appear to be stable for periods of several months at −78°. At room temperature the solutions indicate decomposition after 30-40 min. A white, unidentified solid precipitates and new, unidentified resonances appear in the boron-11 NMR spectrum, but $B_4H_9^-$ is still visible in the boron-11 NMR spectrum even after the solution has been at room temperature for 12-14 hr. Ether solutions of LiB_4H_9 give evidence for much more rapid decomposition than those of KB_4H_9 under equivalent conditions.

Table I. NMR Data for KB_4H_9

100-MHz $^1H^a$		Assignments^b		32.1-MHz $^{11}B^c$	
−16°	−100°	H	B	+20°	−90°
	12.73	μ			
	11.71	1a			
9.58	$(9.63)^d$	all H	1		54.4 (J = 101)
	9.33	1e	1, 3	27.0	(26.8)
	8.20	2, 4	2, 4	10.4	10.2 (J = 99)
	7.37	3	3		−0.8 (J = 113)

^{a} Chemical shifts expressed in ppm relative to tetramethylsilane = 10.00. Values are accurate to $\tau \pm 0.03$. The solvent is $(CD_3)_2O$. ^{b} The number, n, denotes B_n or the terminal hydrogen attached to B_n. The letter, a, denotes axial hydrogen atom; e denotes equatorial hydrogen atom. ^{c} Chemical shifts expressed in ppm relative to $BF_3 \cdot O(C_2H_5)_2$ = 0.0. Deviations: δ, ±0.2 ppm; J, ±5 Hz. The solvent is $(CD_3)_2O$. ^{d} Values in parentheses are appropriately weighted averages.

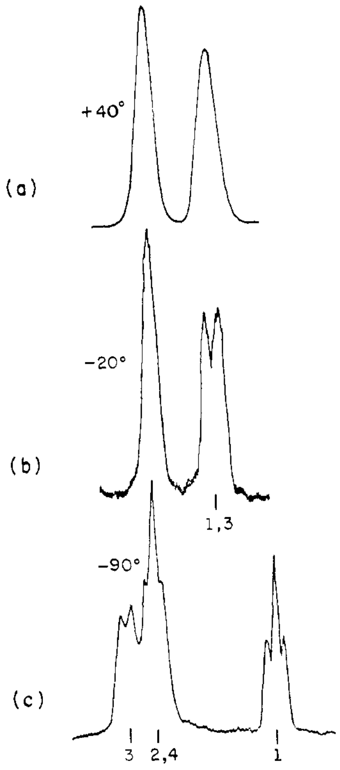


Figure 1. The 32.1-MHz boron-11 NMR spectrum of $B_4H_9^-$: (a) $[(C_6H_5)_3PCD_3][B_4H_9]$ in CD_2Cl_2 at +40°, (b) $[(C_6H_5)_3PCD_3][B_4H_9]$ in CD_2Cl_2 at −20°, (c) $NH_4^+B_4H_9^-$ in $(CH_3)_2O$ at −90°

Tetra-n-butylammonium and triphenylmethylphosphonium salts of $B_4H_9^-$ were conveniently prepared by the following metathesis reactions

$$KB_4H_9 + (n\text{-}C_4H_9)_4NI \xrightarrow{(CH_3)_2O} [(n\text{-}C_4H_9)_4N][B_4H_9] + KI \quad (2)$$

$$KB_4H_9 + [(C_6H_5)_3PCH_3]I \xrightarrow{THF\text{-}CH_2Cl_2} [(C_6H_5)_3PCH_3][B_4H_9] + KI \quad (3)$$

These salts can be isolated as white solids and appear to be more stable than KB_4H_9.

At −78°, NH_3 rapidly deprotonates B_4H_{10} to yield $NH_4B_4H_9$. Evidence for this reaction was offered by boron-11 NMR spectra which showed the exclusive presence of $B_4H_9^-$ as the initial reaction product at temperatures below −65°. A metathesis reaction demonstrated that NH_4^+ was the counterion present in this system.

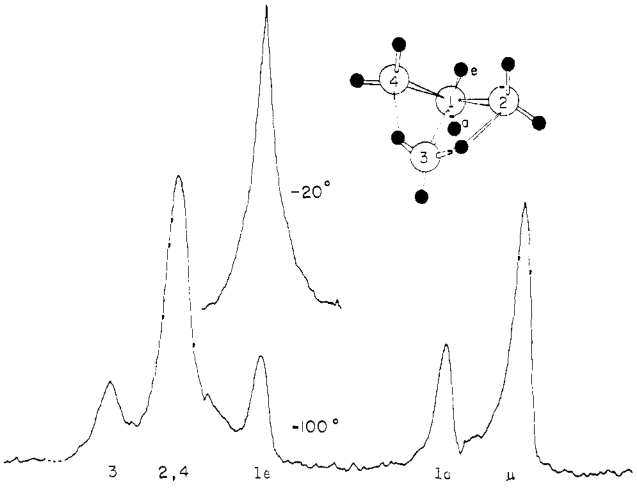


Figure 2. The 100-MHz proton NMR spectrum of KB_4H_9 in $(CD_3)_2O$ at −100 and −20°, boron-11 atoms spin decoupled. The letters a and e represent the axial and equatorial hydrogens, respectively. The protium impurity in the $(CD_3)_2O$ is not shown (dashed line).

$$NH_4B_4H_9 + (n\text{-}C_4H_9)_4NI \xrightarrow{CH_2Cl_2\text{-}(C_2H_5)_2O} (n\text{-}C_4H_9)_4NB_4H_9 + NH_4I \quad (4)$$

The deprotonation of B_4H_{10} by NH_3 is of special interest since NH_3 was previously reported to cleave B_4H_{10} in $(C_2H_5)_2O$ solution to give $[BH_2(NH_3)_2][B_3H_8]$.[11] In actuality both reactions occur. The deprotonation reaction is, however, much more rapid at −78° and is therefore the reaction which is observed initially when boron-11 NMR spectroscopy is used to observe the system. However, on allowing the solutions to stand for extended periods of time (several days at temperatures below −65°) the cleavage product $[BH_2(NH_3)_2][B_3H_8]$ plus B_4H_{10} appeared simultaneously in apparently equal amounts based upon boron-11 NMR spectra, while $NH_4B_4H_9$ diminished in concentration. On raising the temperature above −65° the process accelerated and went to completion. No H_2 was given off. The final products were separated and their identities further established (see Experimental Section). We interpret these results in terms of two competing reactions represented in the following way.

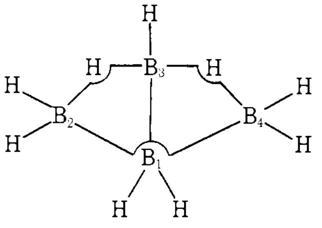
$$NH_3 + B_4H_{10} \rightleftarrows NH_4B_4H_9 \quad (5)$$

$$\downarrow$$

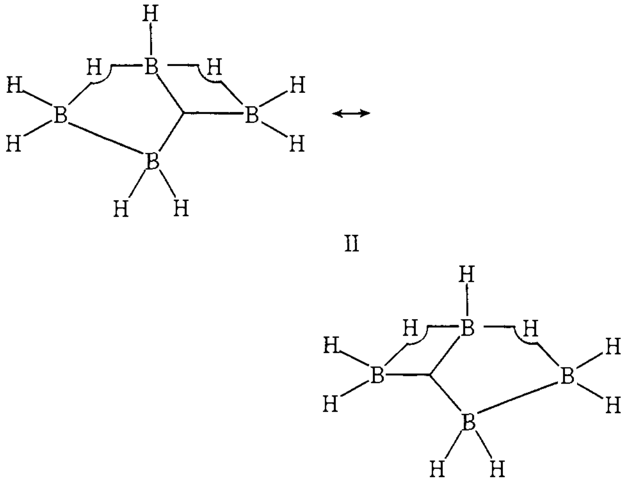
$$\tfrac{1}{2}[BH_2(NH_3)_2][B_3H_8] + \tfrac{1}{2}B_4H_{10} \quad (6)$$

The deprotonation reaction represents a rapidly established equilibrium while the cleavage reaction which is irreversible, but slow by comparison, eventually predominates. This accounts for the observation given in the early accounts of the preparation of $[BH_2(NH_3)_2][B_3H_8]$ that good yields were obtained only when the systems were aged over extended periods.[11] Similar competing reactions involving ammonia and a boron hydride have been noted for other systems as well. The best other documented case is that of the reaction of NH_3 with B_5H_9 giving initially $NH_4B_5H_8$ but finally going to $[BH_2(NH_3)_2][B_4H_7]$.[3d,12]

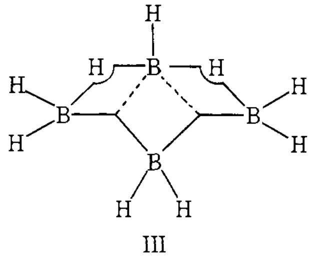
NMR Spectra of $B_4H_9^-$. The boron-11 and ^1H NMR spectra of $B_4H_9^-$ are temperature dependent (Table I, Figures 1 and 2), reflecting the dynamic behavior of this anion on the NMR time scale. The low temperature spectra are fully consistent with a static structure, first proposed by Lipscomb,[13] which in *styx* notation is a 2113 topological valence structure. This structure has been observed for the isoelectronic analog of $B_4H_9^-$, $B_4H_8PF_2N(CH_3)_2$.[14] The simplest 2113 representation consistent with the C_s symmetry implied by the low temperature spectra has an open three-center B-B-B bond, I. However, recent theoretical studies indicate that open three-center B-B-B bonds are not favored in the boron hydrides.[15] Two symmetry equivalent resonance forms are required in order to preserve C_s symmetry when the valence structure is drawn using a closed three-center B-B-B bond (II). More recent considerations by Lipscomb[16] introduce the concept of a pair of fractional three-center B-B-B bonds in place of adjacent two-center B-B and three-center B-B-B bonds. Thus $B_4H_9^-$ can be represented in terms of fractional three-center bonds in a single structure with C_s symmetry, III.



I



II



III

Based on peak multiplicities and relative areas the assignment of resonances in the boron-11 NMR spectrum of $B_4H_9^-$ at −90° is self-evident (Figure 1c). On warming the sample, the triplet assigned to B_2 and B_4 becomes a singlet, but does not shift position. On the other hand, warming causes the triplet assigned to B_1 and the doublet assigned to B_3 to first collapse to singlets and upon further warming disappear while a doublet appears at a position which is equal to the average of the chemical shifts of B_1 and B_3 (Table I and Figure 1b). Still further warming, up to about 40°, causes the doublet which is designated 1,3 to collapse to a singlet without changing position (Figure 1a). These spectral changes are reversible and are indicative at higher temperatures of rapid hydrogen exchange on the boron-11 NMR time scale, thereby causing an averaging of the B_1 and B_3 resonances and apparent eventual loss of spin-spin correlation. The doublet which is designated 1,3 at −20° (Figure 1b) is indicative of a terminal hydrogen on B_1 and a terminal hydrogen on B_3 which are migrating sufficiently slowly on the boron-11 NMR time scale so that spin-spin correlation with B_1 and B_3, respectively, is maintained. Thus these terminal hydrogens appear to be static. Interestingly, however, the proton spectrum at that temperature consists of a single resonance (Figure 2) which is indicative of exchange averaging of all of the protons on the ^1H NMR scale.

The normal ^1H NMR spectrum of $B_4H_9^-$ at low temperature contains little detail. Although the bridge hydrogen resonance is observed, only broad unresolved resonances represent the terminal hydrogens. However, by spin decoupling all of the boron-11 atoms, using a broad band noise decoupler, the spectrum at −100° shown in Figure 2 was obtained. This spectrum was assigned to the static structure of $B_4H_9^-$. Assignment of terminal hydrogen resonances was deduced by employing narrow line spin decoupling at boron-11 resonance frequencies which correspond to the single resonances shown in Figure 1c. The large difference in chemical shift between the axial and equatorial hydrogens on B_1 (Figure 2) is noteworthy since the boron-11 NMR spectrum (Figure 1c) shows that spin coupling of boron with these hydrogens must be essentially the same since the triplet which is observed for B_1 is sharp and symmetrical. The decision as to which of these hydrogens is axial and which is equatorial is based upon assignments from other studies.[17]

The single proton resonance observed at −20° (Figure 2) has a chemical shift which is in accord with the weighted average of the shifts (Table I) of the resonances observed in the limiting spectrum observed at −100° (Figure 2) thus providing evidence for exchange averaging of all of the protons in the anion.

Polyhedral Expansion through BH_3 Addition. The boron-boron bond of a boron hydride anion which is derived by removal of a bridge proton is potentially a basic site that is available for insertion of an electrophile.[3b,7-9] We have observed facile addition of BH_3 to the anions $B_4H_9^-$, $B_5H_8^-$, and $B_6H_9^-$ resulting in expanded anion structures (eq 7, 8, and 9). Anions of such composition were postulated by Muetterties and Knoth in a "formalistic view" of a sequential pathway leading to the closo anion $B_{12}H_{12}^{2-}$.[18]

$$B_4H_9^- + \tfrac{1}{2}B_2H_6 \xrightarrow{-35°} B_5H_{12}^- \qquad (7)$$

$$B_5H_8^- + \tfrac{1}{2}B_2H_6 \xrightarrow{-78°} B_6H_{11}^- \qquad (8)$$

$$B_6H_9^- + \tfrac{1}{2}B_2H_6 \xrightarrow{-78°} B_7H_{12}^- \qquad (9)$$

The stoichiometry of reaction 7 was established by recovery of excess B_2H_6 from solutions at −78°. Determination of the stoichiometry of reaction 8 and reaction 9 was complicated by the fact that excess B_2H_6 reacts with $B_6H_{11}^-$ and $B_7H_{12}^-$. However, these secondary reactions proceed significantly more slowly than the primary reactions to produce the anions. Thus it was possible to employ tensimetric titrations of $B_5H_8^-$ and $B_6H_9^-$ by B_2H_6 to support the formulation of $B_6H_{11}^-$ and $B_7H_{12}^-$. We have described these titrations previously.[7a] The rate of reaction of B_2H_6 with $B_6H_{11}^-$ and with $B_7H_{12}^-$ is dependent upon the counterion present, being significantly faster for lithium salts than for potassium, tetra-*n*-butylammonium, or triphenylmethylphosphonium salts. The reactions are also quite complex.

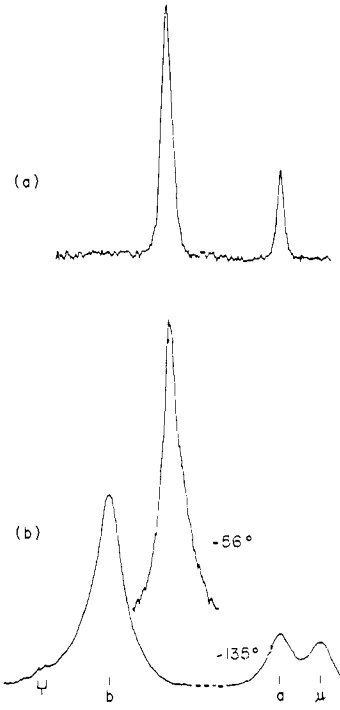


Figure 3. NMR spectra of [$(C_6H_5)_3PCD_3$][B_5H_{12}]: (a) 32.1-MHz boron-11 NMR spectrum in CD_2Cl_2 at −25°, 100-MHz proton NMR spectrum in CD_2Cl_2 and $CHClF_2$ at −135° and at −56°, boron-11 atoms spin decoupled. The doublet at low field is due to the protium impurity in the cation. An impurity resonance is not shown (dashed line).

The final products of the reaction of $B_6H_{11}^-$ with B_2H_6 include H_2, B_2H_6, B_5H_9, B_6H_{10}, and $B_{10}H_{14}$.[7b] The reaction of $B_7H_{12}^-$ with B_2H_6 produces $B_{10}H_{14}$ (ca. 15% of the total boron).

Stabilities of $B_5H_{12}^-$ Salts. The tetra-*n*-butylammonium and triphenylmethylphosphonium salts of dodecahydropentaborate(1−) are white solids which were isolated by pumping away CH_2Cl_2 solvent at −78°. They can be warmed to room temperature for 10-15 min without significant decomposition. The potassium salt on the other hand is difficult to isolate from the ether solutions in which it is prepared. Complete removal of ether requires warming to about −35° which causes reversal of eq 7 above. In a closed system, KB_5H_{12} is stable in ethyl ether to about −10°. Decomposition is indicated by the appearance of an unidentified white solid and B_5H_9.

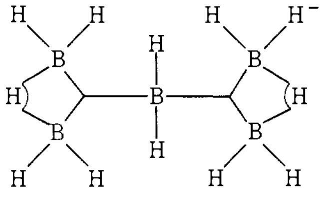
NMR Spectra of $B_5H_{12}^-$. A typical boron-11 NMR spectrum of $B_5H_{12}^-$ is shown in Figure 3a. Over the temperature range studied (−25° to −105°) the spectrum shows only two invariant resonances in an area ratio of 4:1 with chemical shifts at 15.9 and 57.6 ppm (respectively) relative to $BF_3O(C_2H_5)_2$. The high field resonance is typical for that of a pyramidal boron hydride[19] and the spectrum can be considered to be consistent with a structure which is a pyramid that contains four basal boron atoms. The apparent absence of ^{11}B-^{1}H spin coupling at low temperatures may be due to rapid nuclear quadrupolar relaxation ("thermal decoupling").[20] At higher temperatures the dynamic character of this anion is clearly reflected in its boron-11 spin decoupled proton NMR spectrum at −56° (Figure 3b) which shows only a single resonance which is the weighted average (Table II) of the resonances observed in the limiting proton spectrum at −135°. This single averaged resonance was observed at temperatures above about −90°.

Table II. NMR Data for [$(C_6H_5)_3PCD_3$] [B_5H_{12}]

100-MHz $^1H^a$			32.1-MHz $^{11}B^c$	
0°	−135°	Assignments^b	−25°	−105°
9.41	11.85	μ		
	(9.46)^d			
	11.20	a	57.6	57.6
	8.42	b	15.9	15.9

^{a} Chemical shifts are expressed in ppm relative to tetramethylsilane = 10.00. Values are accurate to τ ±0.03. The solvent is a mixture of $CHClF_2$ and CD_2Cl_2. ^{b} The letter a denotes apical boron atom, or hydrogens attached to it. The letter b denotes basal boron atoms, or terminal hydrogens attached to them. ^{c} Chemical shifts are expressed in ppm relative to $BF_3{\cdot}O(C_2H_5)_2$ = 0.0. Deviations: δ, ±0.2 ppm; *J*, ±5 Hz. The solvent is CH_2Cl_2. ^{d} Values in parentheses are appropriately weighted averages.

The boron-11 spin decoupled proton NMR spectrum observed at −135° (Figure 3b) is believed to be the limiting spectrum with dynamic character being sufficiently retarded so that the spectrum reflects the static structure of the anion. The three resonances observed are in the area ratio of 8:2:2. From narrow line boron-11 spin decoupling the resonance of relative area 8 is decoupled at an irradiating frequency related to the resonance assigned to the basal boron atoms in the boron-11 NMR spectrum. The middle resonance in the ^1H NMR spectrum is decoupled at an irradiating frequency which represents the apical boron in the boron-11 NMR spectrum. The remaining resonance in the proton resonance spectrum is insensitive to variation in the boron-11 decoupling frequency and is therefore assigned to bridging hydrogens since bridging hydrogens generally do not spin couple strongly with boron. The 2205 topological representation shown below, IV, is consistent with the



IV

NMR data. Other topological representations are also possible, but we will use the depicted structure until a definitive X-ray structure becomes available.

The $B_5H_{12}^-$ ion is of special significance since it is the only binary hydride species to be prepared that is a member of the newly recognized class of hypho (Greek for net) boranes containing $2n + 8$ framework electrons.[21,22] The commonly recognized classes are closo ($2n + 2$), nido ($2n + 4$), and arachno ($2n + 6$).[23] For a given number of framework boron atoms, *n*, the structural arrangement opens from a cage structure ($2n + 2$) to an increasingly open structure as framework electrons are added.[24,25] Thus we expect $B_5H_{12}^-$ to be more open than the respective nido and arachno pentaboranes B_5H_9 and B_5H_{11}. The adduct $B_5H_9[P(CH_3)_3]_2$ is also a member of the hypho class of boranes. It is presumably isostructural with the hypothetical $B_5H_{11}^{2-}$ ion (H^- replaces $P(CH_3)_3$) and is isoelectronic with $B_5H_{12}^-$ and the hypothetical B_5H_{13}. The structure is that of a shallow pyramid which is highly fluxional on the NMR time scale.[22] A third member of the hypho class is also known: $B_6H_{10}[P(CH_3)_3]_2$. The boron arrangement has been shown to be an open structure which is not a pentagonal pyramid as in B_6H_{10} but is a fragment of the equatorial belt of an icosahedron.[27]

Stabilities of $B_6H_{11}^-$ Salts. Ether solutions of LiB_6H_{11} are stable to about −15°. Above this temperature an unidentified white solid precipitates and decomposition becomes evident through the appearance of a complex, as yet

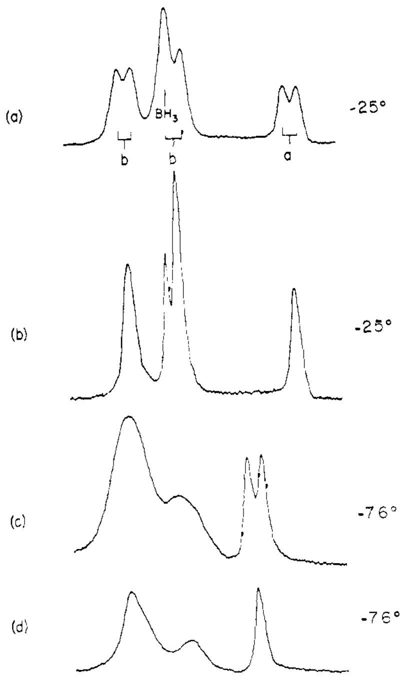


Figure 4. The 28.87-MHz boron-11 NMR spectrum of KB_6H_{11} in $(CD_3)_2O$: (a) −25°, basal and apical resonances are designated b and a; (b) −25°, protons spin decoupled; (c) −76°; (d) −76°, protons spin decoupled.

Table III. NMR Data for KB_6H_{11}

100-MHz $^1H^a$			28.87-MHz $^{11}B^c$	
−25°	−125°	Assignments^b	−25°	−76°
	12.35	$\mu_{3,4}$		
	11.16	$\mu_{2,3}$ and $\mu_{4,5}$		
9.29	(9.25)^d	all μ and BH_3		
	7.89	$\mu_{2,6}$		
	6.47	BH_2	−1.6	*e*
	8.57	2 or 5, or 3 or 4		
6.68	(6.69)	2 and 5 or 3 and 4	−14.0 (J = 117)	−15.2
	4.81	3 or 4, or 2 or 5		
	7.89	3 or 4, or 2 or 5		
7.23	(7.18)	3 and 4 or 2 and 5	0.9 (J = 125)	−1.0
	6.47	2 or 5, or 3 or 4		
9.66	9.58	1	34.6 (J = 117)	21.7 (J = 117)

[a] Chemical shifts are expressed in ppm relative to tetramethylsilane = 10.00. Values are accurate to τ ±0.03. The solvent is $(CD_3)_2O$. [b] The number, n, denotes B_n or the terminal hydrogen attached to B_n. [c] Chemical shifts expressed in ppm relative to $BF_3{\cdot}O(C_2H_5)_2 = 0.0$ Deviations: δ, ±0.2 ppm; J, ±5 Hz. The solvent is $(CD_3)_2O$. [d] Values in parentheses are appropriately weighted averages. [e] The resonance due to B_6 overlaps the resonance due to B_2 and B_5 (or B_3 and B_4) at −76°. See Figure 4.

uninterpreted, boron-11 NMR spectrum. Ether solutions of KB_6H_{11} appear to be stable at −15° and can be handled at room temperature for short periods of time (ca. 1 hr) without significant decomposition. The salts LiB_6H_{11} and KB_6H_{11} are so strongly solvated by ethers that they cannot be isolated free of these solvents. On the other hand the salts $[(C_6H_5)_3PCH_3][B_6H_{11}]$ and $[(n\text{-}C_4H_9)_4N][B_6H_{11}]$ prepared in CH_2Cl_2 solution show no sign of decomposition in solution at room temperature after 2-3 hr. After 12-14 hr $B_6H_9^-$ appears as a major decomposition product (identified by its boron-11 NMR spectrum) in solution. These salts can be isolated as crystalline solids which can be handled at room temperature for several hours before significant decomposition occurs.

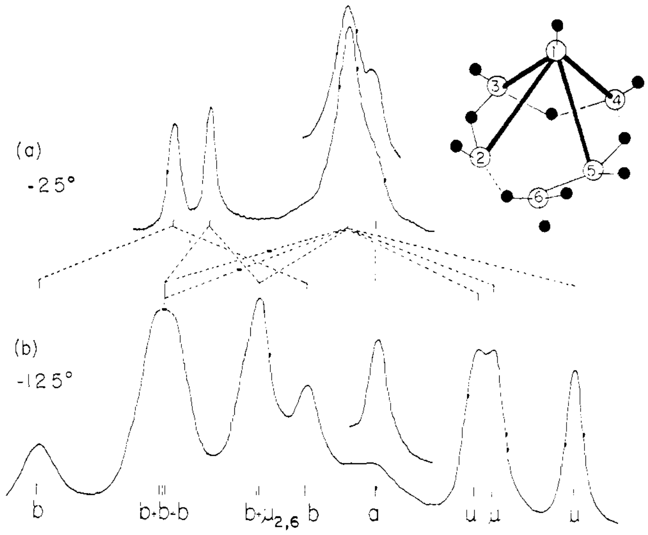


Figure 5. Proton NMR spectrum of KB_6H_{11} in $(CD_3)_2O$, boron-11 atoms spin decoupled. The letters b, a, and μ denote basal terminal, apical, and bridging hydrogens, respectively: (a) 100 MHz at −25°; (b) 90 MHz at −125°C, this spectrum is to scale with (a) with respect to ppm.

NMR Spectra of $B_6H_{11}^-$. Boron-11 NMR spectra of KB_6H_{11} are depicted in Figure 4. They strongly support a structure in which a borane group has entered the vacant bridging site in the $B_5H_8^-$ ion, leaving the boron framework intact (in a topological sense). The high field doublet of relative area 1 is assigned to an apical boron. There are two sets of low field doublets one of which is overlapped by a single resonance which represents the boron of the added BH_3 group. These points are confirmed in Figure 4b which shows the proton decoupled boron-11 NMR spectrum at −25°. Collapse of the multiplet structure clearly reveals the resonance of the inserted boron. The doublet character of the apical and basal resonances is consistent with a single terminal hydrogen on each of these boron atoms and is characteristic of the $B_5H_8^-$ spectrum. The apparent absence of spin coupling of terminal hydrogens with the inserted boron is suggestive of dynamic character for the anion. On lowering the temperature, the apical resonance is markedly shifted downfield and the basal resonances show a small shift which is slightly larger than the experimental uncertainty in the chemical shift measurement (See Table III). Furthermore, on cooling the system to low temperature (−76°) the apical resonance maintains its doublet character, but the basal resonances broaden and become thermally decoupled. This is typical behavior for a stereochemically nonrigid pyramidal species.[3b,4b,e,9a,c,28]

^1H NMR spectra of KB_6H_{11} with boron-11 atoms spin decoupled are shown in Figure 5 and presented in Table III. From narrow line decoupling experiments, assignments of terminal hydrogens, consistent with the assignments of boron resonances in the B_5 framework, were made. The large, apparently single resonance, which partially overlaps the apical resonance is assigned to bridging hydrogens from the $B_5H_8^-$ and terminal hydrogens from the BH_3 group. While spin coupling with boron indicates that the terminal hydrogens are static on the ^1H NMR and boron-11 NMR time scales at −25°, we believe that the bridging hydrogens and the hydrogens from the BH_3 group undergo exchange averaging, thereby accounting for the single resonance. Evidence for such a dynamic system is provided by temperature-dependent ^1H NMR spectra. As the temperature is lowered the resonances shown in Figure 5a broaden until very low temperatures (ca. −125°), where eight relatively sharp resonances can be discerned in the boron-11 spin

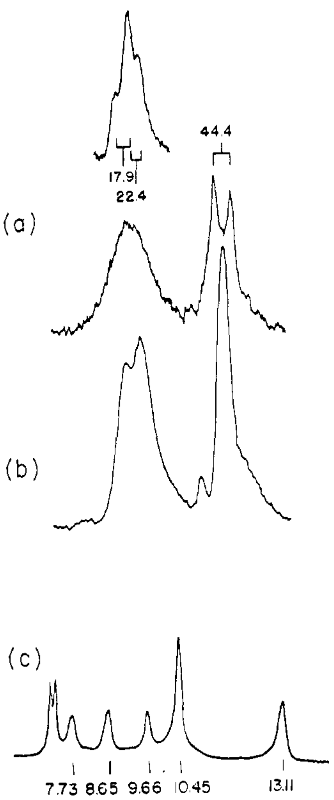
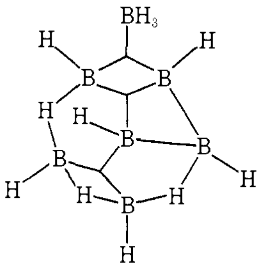


Figure 6. NMR spectra of $B_7H_{12}^-$: (a) 32.1-MHz boron-11 NMR spectrum of $[(n\text{-}C_4H_9)_4N][B_7H_{12}]$ at −80° with a mixture of CH_2Cl_2, CH_3Cl, and $CHClF_2$ as the solvent (The inset shows the salt $[(C_6H_5)_3PCH_3][B_7H_{12}]$ under identical conditions. Chemical shifts are expressed in ppm relative to $BF_3O(C_2H_5)_2 = 0.0$.); (b) 32.1-MHz boron-11 NMR spectrum of $[(n\text{-}C_4H_9)_4N][B_7H_{12}]$ at −70° with a mixture of CH_2Cl_2, CH_3Cl, and $CHClF_2$ as the solvent (The protons are spin decoupled. Some decomposition at this temperature is indicated by the small impurity peak and the shoulder on the upfield resonance.); (c) 100-MHz proton NMR spectrum of $[(C_6H_5)_3PCH_3][B_7H_{12}]$ in CD_2Cl_2 at −80°, boron-11 atoms spin decoupled. (The doublet at low field is due to $(C_6H_5)_3PCH_3^+$ Chemical shifts are expressed in ppm relative to TMS = 10.00.)

decoupled ^1H NMR spectrum (with relative areas toward increasing τ of 1:3:2:1:1:1:1:1). In Figure 5b the resonances observed at −125° are believed to represent an effectively static structure on the ^1H NMR time scale. The relationships (dashed lines) between these resonances and the resonances at −25° are demonstrated in Table III in which the weighted averages of the low temperature resonances are shown to be in agreement with the exchange averaged resonances observed at −25°. The framework appears to remain pyramidal. The assignment of the apical resonance was once again confirmed by narrow line decoupling. The resonances assigned to bridging hydrogens are relatively insensitive to boron-11 spin decoupling and have τ values which are in the range observed for pyramidal borane anions. That there are three separate bridge resonances and four separate terminal resonances implies that the static structure of $B_6H_{11}^-$ is asymmetric. Two of the hydrogens of the inserted BH_3 group have the same resonance position, τ 6.47, while the unique one resonates at τ 7.89. It is conceivable that in the static structure the symmetry of the ion has been reduced by the act of the borane group assuming a static position such that one of its hydrogen atoms is in what is nearly a bridging position (Figure 5) analogous to the equatorial hydrogen on the apex of B_5H_{11} which resonates at τ 8.2.[29] The two remaining borane group hydrogens are therefore stereochemically nonequivalent but their resonances nontheless overlap.

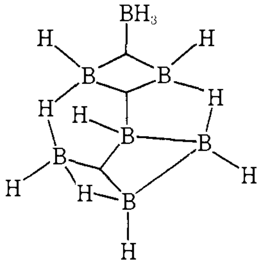
Stabilities of $B_7H_{12}^-$ Salts. The anion decomposes in ethereal solutions of KB_7H_{12} and methylene chloride solutions of $[(n\text{-}C_4H_9)_4N][B_7H_{12}]$ and $[(C_6H_5)_3PCH_3][B_7H_{12}]$ at temperatures above −70°. The solid salts decompose upon warming to room temperature; a major decomposition product is the $B_6H_9^-$ ion which is identified by its boron-11 and proton NMR spectra.

NMR Spectra of $B_7H_{12}^-$. Boron-11 spectra shown in Figure 6a and 6b are undecoupled (−80°) and proton decoupled (−70°), respectively. The appearance of the undecoupled spectrum is highly dependent upon the concentration of the salt, the temperature, counterion, and the solvent. The high-field doublet is always observed, but the lower field portion of the spectrum is unresolved when the solution is too concentrated, $(n\text{-}C_4H_9)_4N^+$ is the counterion, the temperature is below −70°, or only CH_2Cl_2 is used as the solvent. The decoupled spectra always show a pair of low field resonances and a single high field resonance with the area ratio of the low-field pair to the high-field resonance being 4:3. The simplicity of the spectrum may be due to exchange averaging of resonances as well as coincidental overlap of resonances. We cannot easily account for this spectrum in terms of what might be considered to be the most likely structure of $B_7H_{12}^-$. Based upon the recently determined structure of the $\mu\text{-Fe(CO)}_4\text{-}B_7H_{12}^-$ ion,[9b] the static structure of $B_7H_{12}^-$ might be expected to consist of a pentagonal pyramid of the $B_6H_9^-$ structure with a BH_3 group inserted into a basal boron–boron bond as indicated by the two structures drawn below. It was recently shown by J. Ragaini in this laboratory that the isoelectronic analog of $B_7H_{12}^-$, $C_2B_5H_{10}^-$ (obtained by the addition of $\frac{1}{2}B_2H_6$ to $C_2B_4H_7^-$), contains an inserted BH_3 group as evidenced by spin coupling of hydrogens to the inserted boron atom.



V

or



VI

The boron-11 decoupled ^1H NMR spectrum shown in Figure 6c is difficult to rationalize in terms of the boron-11 NMR spectrum. We were unable to obtain NMR spectra at temperatures lower than −80° because of the low solubilities of the salts of the $B_7H_{12}^-$ ion and the tendency for solutions to become viscous. We believe that this ion is stereochemically nonrigid and that the spectra were not obtained at sufficiently low temperature to adequately reflect its static structure.

Protonation Reactions. Removal of the solvent from ethereal solutions of KB_5H_{12} and KB_6H_{11} followed by treatment with HCl resulted in the following reactions.

$$KB_5H_{12} + HCl \xrightarrow{-110^\circ} B_5H_{11} + H_2 + KCl \qquad (10)$$

$$KB_6H_{11} + HCl \xrightarrow{-110^\circ} B_6H_{12} + KCl \qquad (11)$$

Pentaborane(11) and hexaborane(12) were obtained in 60–70 and 60–65% yields, respectively. The preparation of B_5H_{11} is a practical alternative to other reported procedures while the preparation of B_6H_{12} is vastly superior to any previously reported method.[10,30,31] Thus B_6H_{12} can now be made available in quantities large enough for extensive studies.

Treatment of solutions of the $B_7H_{12}^-$ ion with stoichiometric amounts of HCl or removal of the bulk of the solvent and treatment with excess liquid HCl produce, as the major product, B_6H_{10}. Hydrogen is also produced and from one reaction mixture, small amounts of B_8H_{12} and n-B_9H_{15} were identified by boron-11 NMR spectra. While no direct evidence was obtained for B_7H_{11} in the protonation reaction cited above, this highly unstable hydride has been stabilized as the μ-$Fe(CO)_4$-B_7H_{11} adduct.[9b] It is prepared by treatment of μ-$Fe(CO)_4$-$B_7H_{12}^-$ with HCl. The adduct $B_7H_{11}O(CH_3)_2$[32] which is isoelectronic with $B_7H_{12}^-$ may reflect the structure of this anion rather than neutral B_7H_{11}.

Brönsted Acidities. From proton competition reactions we have shown that *arachno*-B_4H_{10} is a stronger Brönsted acid than *nido*-B_6H_{10} and B_5H_9.[4d]

$$B_4H_{10} + B_5H_8^- \rightarrow B_4H_9^- + B_5H_9 \qquad (12)$$

$$B_4H_{10} + B_6H_9^- \rightarrow B_4H_9^- + B_6H_{10} \qquad (13)$$

From boron-11 NMR spectra these reactions appear to go to completion. An earlier proton competition study[5] showed that $B_{10}H_{14}$ is a stronger Brönsted acid than B_4H_{10}.

On the basis of previously studied acidities, the relative acidities of the *nido* and *arachno* boron hydrides are:[1i,33,34,35] *nido*-$B_5H_9 < B_6H_{10} < B_{10}H_{14} < B_{16}H_{20} <$ n-$B_{18}H_{22}$ = i-$B_{18}H_{22}$, *arachno*-$B_4H_{10} < B_5H_{11}$.[10] These results provide strong support for the prediction of Parry and Edwards[2] that within a given class of boron hydrides, the Brönsted acidity increases with increase in size of the boron framework. We have not yet examined the acidity of B_6H_{12} relative to B_5H_{11}, but the former is probably the stronger acid. We have, however, observed the following proton competition reaction which appears to be complete.

$$B_6H_{12} + B_5H_8^- \rightarrow B_6H_{11}^- + B_5H_9 \qquad (14)$$

The NMR spectrum of $B_6H_{11}^-$ is identical with that of the $B_6H_{11}^-$ prepared according to eq 8.

Attempted deprotonation of B_6H_{12} by H^- (KH) was not successful. Hydrogen given off was only 50-70% of theory and the NMR spectra gave no indication of the formation of $B_6H_{11}^-$ even though B_6H_{12} had been consumed. Attempted deprotonation of B_5H_{11} by H^- (KH) was partially successful; hydrogen was given off in 55-77% of theory. The boron-11 NMR spectrum showed the presence of $B_5H_{10}^-$ and $B_5H_{12}^-$. It is likely that the H^- ion can react with B_5H_{11} in two ways: (1) react with protonic bridge hydrogens to eliminate H_2 giving $B_5H_{10}^-$, (2) add to B_5H_{11} to form the previously reported $B_5H_{12}^-$. The $B_5H_{10}^-$ was identified from its boron-11 NMR spectrum obtained from $[BH_2(NH_3)_2][B_5H_{10}]$[17b,36] formed by the reaction of B_6H_{12} with NH_3. The anion appears to be unstable at temperatures much above −80°. The spectrum consists of two doublets (δ 13.2 ppm, J = 162 Hz; δ 52.0 ppm, J = 175 Hz) in the area ratio 4:1. This ion and the preparation of $[BH_2(NH_3)_2][B_5H_{10}]$ will be discussed elsewhere. We were able to confirm that H^- can add to B_5H_{11} by observing the following reaction

$$B_5H_{11} + B_6H_{11}^- \xrightarrow{(CH_3)_2O} B_5H_{12}^- + B_6H_{10} \qquad (15)$$

in which the products were identified from their boron-11 NMR spectra.

Experimental Section

Methods. Volatile materials were manipulated by standard vacuum techniques. Air sensitive, nonvolatile substances were handled in an inert atmosphere enclosure.

Materials. Potassium hydride was obtained from ROC/RIC, Sun Valley, Calif., and was freed of oil by washing under vacuum with anhydrous pentane. The freely flowing, fine white powder thus obtained showed an activity of 95-98% on methanolysis. Pentaborane(9) and B_2H_6 were purchased from Callery Chemical Co. Published methods were used for the preparation of B_4H_{10},[37] B_6H_{10},[7b,38] and $(C_6H_5)_3CD_3PI$.[39]

NMR Spectra. ^1H NMR and boron-11 NMR spectra were obtained with a Varian HA-100 high resolution spectrometer at 100 MHz in the HA mode and at 32.1 MHz in the HR mode, respectively. All ^1H NMR chemical shifts are given in τ units relative to $(CH_3)_4Si = \tau$ 10.00 using the internal standards $CHClF_2$ = 2.76, $(CH_3)_2O = \tau$ 6.76, $CH_2Cl_2 = \tau$ 4.67, $CHCl_3 = \tau$ 2.75, or $(C_6H_5)_3CD_3P^+ = \tau$ 2.30. Boron-11 NMR shifts are reported in parts per million relative to $BF_3 \cdot O(C_2H_5)_2$ and were obtained by use of the external standard BCl_3 (δ −46.8[40]). Decoupling experiments were carried out using a General Radio Co. 1164A frequency synthesizer, a Hewlett Packard 3722A noise generator, and an Electronic Navigation Laboratories 3100L power amplifier. For boron-11 decoupling, additional amplification was obtained with a Heathkit Co. Model SB-220 RF amplifier. NMR spectra of KB_6H_{11} were also obtained at 90 MHz (^1H) and 28.87 MHz (^{11}B) with a Bruker HX-90 NMR spectrometer. Heteronuclear broad band decoupling was accomplished by using the B-SV3-B noise decoupler set at maximum width. Spectra were obtained in the FT mode using 100 pulses per spectrum.

Deprotation of B_4H_{10} by KH. In the drybox, an excess of KH, 2.0 mmol, was placed in a 20 mm diameter reaction tube containing a Teflon covered magnetic stirring bar. The tube was fitted with a stopcock adapter, taken to the vacuum line, and evacuated. Two milliliters of $(CH_3)_2O$ and 1.50 mmol of B_4H_{10} were condensed in at −196°. The liquid nitrogen bath was replaced by a Dry Ice-isopropyl alcohol bath. Gas evolution commenced on melting of the solvent and the vigorous reaction was complete in minutes. The hydrogen was collected with a Töpler pump and measured, yield 1.41 mmol, 94% of theory. The bulk of the solvent could be removed at −78° and the remainder at −35° leaving a fine white powder. Larger scale reactions, 8-10 mmol, were carried out at −126° but were still vigorous. With $(C_2H_5)_2O$ as the solvent, large scale reactions, 8-10 mmol, were run at −110° and smaller scale reactions, up to about 4 mmol, at −78°. However, induction periods of variable duration were observed when $(C_2H_5)_2O$ was used, and with some samples of KH, no reaction occurred. These same samples of KH did react satisfactorily in $(CH_3)_2O$. Yields of H_2 ranged from 88 to 98%.

Regeneration of B_4H_{10} from KB_4H_9. Treatment of solid KB_4H_9 obtained as above with liquid HCl at −110° followed by fractionation through U traps maintained at −78, −126, and −196° allowed isolation of pure B_4H_{10} at −126°, vapor tension at 0°, 388 mm (lit. 388 mm[41]), in 96% yield based on the H_2 evolved in the deprotonation reaction.

Preparation of $[(C_6H_5)_3PCD_3][B_4H_9]$. In the drybox, the reaction vessel was loaded with 0.366 g of $(C_6H_5)_3CD_3PI$, 0.90 mmol, and 1.0 mmol of KH. The vessel was fitted with a stopcock adapter, taken to the vacuum line, and evacuated. One milliliter of $(CH_3)_2O$ and 0.89 mmol of B_4H_{10} were added and 0.85 mmol of H_2 was generated at −78°. The solvent was removed as described above and CH_2Cl_2, 2.6 ml, and THF, 1.3 ml, were added at −78°. The mixture was vigorously stirred at −35° until the crystals of $(C_6H_5)_3CD_3PI$ disappeared (approximately 1 hr) and a white precipitate formed. The bulk of the solvent was removed at −35°, then the vessel was warmed to ambient temperature and opened to dynamic vacuum for an additional 20 min; $[(C_6H_5)_3PCD_3][B_4H_9]$ was extracted with 1 ml of CD_2Cl_2 and identified by its boron-11 NMR spectrum which was identical with that of KB_4H_9 prepared as described above.

Preparation of $[(n\text{-}C_4H_9)_4N][B_4H_9]$. Potassium nonahydrotetraborate(1−) was prepared in $(CH_3)_2O$ in the presence of an equimolar quantity of $(n\text{-}C_4H_9)_4NI$ and freed from solvent as described above. The metathesis reaction was conducted and $[(n\text{-}C_4H_9)_4N][B_4H_9]$ was isolated by a previously reported method.[42] Potassium iodide was identified by its X-ray powder diffraction pattern. The boron-11 NMR spectrum of $[(n\text{-}C_4H_9)_4N][B_4H_9]$ is identical with that of KB_4H_9.

Deprotonation of B_4H_{10} by NH_3. An NMR tube was attached to the vacuum line and 0.40 mmol of B_4H_{10} and 0.3 ml of $(C_2H_5)_2O$

were condensed in and mixed at −78°. The sample was frozen at −196° and 0.40 mmol of NH_3 was added. The NMR tube was sealed off with a torch and stored at −196°. Immediately before commencing the boron-11 NMR study, the sample was placed in a −78° bath briefly (ca. 1 min) then placed in the probe at −100°. The initial spectrum showed only B_4H_{10} (doublet, 40 ppm; poorly resolved broad triplet, 7 ppm) and $B_4H_9^-$ (triplet, 53 ppm; broad, unresolved peak, 3–5 ppm) in approximately equal concentrations. The probe temperature was slowly raised and at −80° B_4H_{10} began to disappear and at −65° only $B_4H_9^-$ was visible. No further change in the spectrum was observed over a period of approximately 30 min at −65° and recooling the sample did not alter the spectrum except to broaden all resonances. At −50°, B_4H_{10} and $B_3H_8^-$ (δ 29 ppm) appeared, and the temperature was held at −45° as $B_4H_9^-$ disappeared completely. At this point, a broad unresolved peak assigned to $BH_2(NH_3)_2^+$ was visible at 14.8 ± 0.5 ppm. By measurement of relative peak areas, the mole ratio of $B_3H_8^-$ to B_4H_{10} was determined to be 1.0. The NMR tube was reattached to the vacuum line and opened under vacuum and the volatile material (B_4H_{10} and ether) was vapor transferred to a vessel containing an excess of KH. On warming, a total of 0.06 mmol of H_2 ($B_4H_{10} + KH \rightarrow KB_4H_9 + H_2$) and 0.05 mmol of B_2H_6 ($B_4H_{10} + KH \rightarrow KB_3H_8 + \frac{1}{2}B_2H_6$) was formed indicating the recovery of 0.16 mmol of B_4H_{10}, 80% of theory. The white solid remaining in the NMR tube was 0.22 mmol of $[BH_2(NH_3)_2][B_3H_8]$, identified by its X-ray powder diffraction pattern.

The $B_4H_9^-$ ion was also prepared by the reaction of B_4H_{10} with NH_3 in $(CH_3)_2O$, and with CH_3NH_2 in $(C_2H_5)_2O$. Trimethylamine does not react in $(C_2H_5)_2O$ under these conditions (below −40°, 1 hr reaction time). Dissolving B_4H_{10} in liquid ammonia at −70° produces $NH_4^+B_4H_9^-$ as shown by boron-11 NMR; however, decomposition occurs steadily at this temperature.

No $NH_4^+B_4H_9^-$ is detectable in the reaction of NH_3 with B_4H_{10} in CH_2Cl_2; $BH_2(NH_3)_2^+B_3H_8^-$ is very rapidly produced. A 1:1 mixture of CH_2Cl_2 and $(C_2H_5)_2O$ containing equimolar amounts of B_4H_{10} and $(n\text{-}C_4H_9)_4NI$ does absorb gaseous NH_3 at −78° to produce NH_4I and $(n\text{-}C_4H_9)_4NB_4H_9$, but these products are contaminated by $(n\text{-}C_4H_9)_4NB_3H_8$ as shown by boron-11 NMR. Ammonium iodide was identified from its X-ray powder diffraction pattern.

Preparation of $B_5H_{12}^-$. A 1.59 mmol quantity of KB_4H_9 was prepared in 1.8 ml of $(C_2H_5)_2O$ as described above and 1.18 mmol of B_2H_6 was added at −196° and allowed to react at −35° as the solution was continuously stirred. The reaction was complete in about 4 hr as determined by monitoring the pressure in the system. The sample was cooled to −78° and the bulk of the volatile material was removed by distillation. The sample was then warmed to −35° for about 5 min and additional solvent was removed leaving a white powder which retains ether. Slow fractional distillation of the volatile fraction from −78° through U traps maintained at −140 and −196° yielded 0.41 mmol of B_2H_6 at −196°. The molar reaction ratio was thus 0.97 BH_3:1.00 $B_4H_9^-$. The product was found to dissociate to B_2H_6 and KB_4H_9 on prolonged pumping at −35°. Dimethyl ether was also used for the preparation of KB_5H_{12}.

In an analogous fashion, samples of $[(C_6H_5)_3PCD_3][B_5H_{12}]$ and $[(n\text{-}C_4H_9)_4N][B_5H_{12}]$ were prepared in CH_2Cl_2 or CD_2Cl_2 by reaction of B_2H_6 at −35° with the corresponding $B_4H_9^-$ salt. The boron-11 NMR spectra are the same for each $B_5H_{12}^-$ salt.

Preparation of B_5H_{11} from $B_5H_{12}^-$. The 1.54 mmol sample of KB_5H_{12} prepared in $(C_2H_5)_2O$ and isolated as described in the preceding section was cooled to −196° and about 2 ml of HCl was added. The mixture was warmed to −110° and stirred until H_2 evolution ceased (approximately 20 min). The quantity of H_2 collected with the Töpler pump and measured was 1.47 mmol, 96% of theory. The HCl was removed at −110° and discarded. The reaction mixture was then opened to U traps maintained at −126 and −196° and held at −78° for several hours. To ensure complete removal of B_5H_{11} the reaction vessel was finally warmed to room temperature over a period of approximately 30 min. The B_5H_{11} thus produced and collected at −126° was further purified by additional fractionation from −35 to −110°. Isolated was 1.08 mmol of B_5H_{11}. Infrared spectra and boron-11 NMR spectra showed traces of B_4H_{10} and B_5H_9.

In another reaction, 7.65 mmol of KB_5H_{12} was prepared in $(CH_3)_2O$ and 4.4 mmol of B_5H_{11} was obtained by the method described above.

Tensimetric Titration of $B_5H_8^-$ with B_2H_6. Solutions containing LiB_5H_8 or KB_5H_8 in $(C_2H_5)_2O$ were maintained at −78° and stirred magnetically as measured increments of B_2H_6 were allowed to expand into the reaction vessel. After each addition the equilibrium pressure was measured on an absolute reading mercury manometer using a cathetometer. Up to a mole ratio, $B_2H_6/B_5H_8^-$ of 0.5, the absorption of B_2H_6 is rapid, and equilibrium pressures are obtained in 3–5 min. However, subsequent increments of B_2H_6 required 1–2 days to react completely in the case of lithium salt and even longer for the potassium salt.

In an experiment illustrating the first step in this reaction, 10.2 mmol of KB_5H_8 was prepared in $(CH_3)_2O$,[4b] the solvent was removed at low temperature,[4b] and 10 ml of $(C_2H_5)_2O$ was added. KB_5H_8 is only slightly soluble in this solvent and in the course of the titration gradually dissolves to give a clear colorless solution at the apparent equivalence point, $B_2H_6/B_5H_8^- = 0.54$. This titration was completed in 1 day.

The final overall stoichiometry is shown by the titration of a 4.79 mmol sample of LiB_5H_8 in 10 ml of $(C_2H_5)_2O$.[4b] At the end of the titration the reaction mixture was warmed to −35° and the unreacted B_2H_6 was recovered and separated from $(C_2H_5)_2O$ by slow passage through a trap at −140°. The reaction ratio thus determined, $B_2H_6/B_5H_8^- = 1.02$, agrees well with that indicated by the tensimetric plot.

Preparation of $B_6H_{11}^-$. Solutions of 2–6 mmol of LiB_5H_8 or KB_5H_8 in $(C_2H_5)_2O$, $(CH_3)_2O$, or THF and solutions of $(n\text{-}C_4H_9)_4NB_5H_8$[42] in CH_2Cl_2 were stirred at −78° and 0.50 mol of B_2H_6 per mole of $B_5H_8^-$ was added and allowed to react for 30–45 min. The boron-11 NMR spectra of these salts are the same in each case.

Preparation of B_6H_{12}. In 2 ml of $(CH_3)_2O$, a 1.94 mmol sample of KB_6H_{11} was prepared at −78° as described above. As much solvent as possible was removed by pumping first at −78°, then −35°. The solvated salt remaining at this point is clear, colorless, and very viscous. Sufficient HCl was then added at −196° so that on warming to −110° the liquid HCl (2–3 ml) completely covered the KB_6H_{11}. The mixture was then stirred at −110° until the viscous residue dissolved and a white solid formed. The HCl was removed by distillation and discarded. The reaction mixture was opened to U traps maintained at −97 and −196° and warmed first to −78, −35, and 0° as the products distilled into the fractionation train under dynamic vacuum. The fraction collecting at −97° was found by boron-11 NMR and infrared spectroscopy to be nearly pure B_6H_{12}, 1.4 mmol. The major contaminants, less than 5 mole %, were B_5H_9 and B_4H_{10}. Final purification was effected by rapid distillation into a −63° U trap.

Preparation of $[(C_6H_5)_3PCH_3][B_6H_9]$. In the drybox, a reaction vessel equipped with a rotatable side arm was loaded with 4.12 mmol of KH. The side arm was loaded with 4.12 mmol of $(C_6H_5)_3PCH_3I$. The vessel was then fitted onto an extractor and removed to the vacuum line and evacuated. Dimethyl ether, 3.5 ml, and 4.14 mmol of B_6H_{10} were condensed into the vessel, and hydrogen was quantitatively liberated at −78°. An additional 6.5 ml of $(CH_3)_2O$ was then condensed onto the clear solution and the $(C_6H_5)_3PCH_3I$ was tipped into the reaction vessel which remained at −196°. The mixture was stirred for 1 hr at −30° before the dimethyl ether was removed at −78°. The white solid was then extracted with 7.0 ml of CH_2Cl_2 while warming to ambient temperature. The boron-11 NMR spectrum of the product is identical with that of KB_6H_9.[43]

Preparation of $[(n\text{-}C_4H_9)_4N][B_6H_9]$. The preparation of tetra-*n*-butylammonium nonahydrohexaborate(1−) is analogous to that of $[(C_6H_5)_3PCH_3][B_6H_9]$. The boron-11 NMR spectrum of this salt is identical with that of KB_6H_9.

Tensimetric Titration of $B_6H_9^-$ with B_2H_6. A dichloromethane solution of $[(n\text{-}C_4H_9)_4N][B_6H_9]$ was titrated tensimetrically with B_2H_6 at −78°. The equilibrium pressure was measured on an absolute reading mercury manometer using a cathetometer after each measured increment of B_2H_6 was allowed to expand into the reaction vessel. The titration curve shows a sharp break at 0.54 mol of B_2H_6 per mole of $B_6H_9^-$.

Preparation of $B_7H_{12}^-$. In the drybox, 0.47 mmol of $[(C_6H_5)_3PCH_3][B_6H_9]$ was loaded into a reaction vessel containing a Teflon covered stirring bar and equipped with an NMR tube side arm. The vessel was fitted with a stopcock adapter and removed to the vacuum line and evacuated. Dichloromethane-d_2, 0.45 ml, was condensed into the vessel. Diborane, 0.23 mmol, was allowed to expand into the reaction vessel at −78°. The clear solution was poured into the NMR side arm taking care to maintain the entire vessel and side arm at −78°. The NMR sample was removed with the torch and stored at −78°.

In an analogous fashion, samples of $[(n\text{-}C_4H_9)_4N][B_7H_{12}]$ were prepared in a mixture of CH_2Cl_2, CH_3Cl, and $CHClF_2$. The salt $[(C_6H_5)_3PCH_3][B_7H_{12}]$ was also prepared in the above mixed solvent system.

Proton Competition Reactions. The relative acidities of the boron hydride anions discussed here were determined as previously described.[4e] The following pairs of reactions were carried out: B_4H_{10} and $[(n\text{-}C_4H_9)_4N][B_5H_8]$; B_4H_{10} and $[(n\text{-}C_4H_9)_4N][B_6H_9]$; KB_5H_8 and B_6H_{12}.

Acknowledgment. We wish to acknowledge, gratefully, the support of this work by the National Science Foundation. We also wish to thank Mr. John Kelley for constructing the spin decoupling apparatus and for aiding in spin decoupling experiments.

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