

Protonation of the Neutral Boron Hydrides

 B_6H_{10} and $2-CH_3B_6H_9$ ¹

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Abstract: The Brønsted basicity of the basal boron-boron bond of B_6H_{10} and of $2-CH_3B_6H_9$ has been demonstrated. Protonation of this site by liquid hydrogen bromide and in the reactions, $B_6H_{10} + HCl + BCl_3 \rightarrow [B_6H_{11}^+][BCl_4^-](CH_2Cl_2)$ and $2-CH_3B_6H_9 + HCl + BCl_3 \rightarrow [2-CH_3B_6H_{10}^+][BCl_4^-](CH_2Cl_2)$, has been established by boron-11 and proton nmr. The salts, $[B_6H_{11}^+][BCl_4^-]$ and $[2-CH_3B_6H_{10}^+][BCl_4^-]$, have been isolated at low temperature as white solids. The tetrachloroborate ion has been identified in the solid state by Raman spectroscopy and in solution by boron-11 nmr. The bridging hydrogens of B_6H_{10} exchange rapidly with deuterium chloride in the absence of a catalyst.

The boron-boron bond in the base of the pentagonal-pyramidal structure of hexaborane(10) (Figure 1) is the shortest boron-boron bond found among the boron hydrides (1.60 Å).² The potential Brønsted basicity of this site has been suggested by Lipscomb; indeed he predicted³ the existence of $B_6H_{11}^+$ (Figure 1), noting formal similarities to B_5H_9 , which is of high thermal stability. The existence of such a species in at least a transitory state can be inferred from the fact that B_6H_{10} undergoes deuterium exchange with deuterium chloride⁴ and also with deuterium oxide⁵ exclusively at bridge sites. More recently,⁶ chemical ionization mass spectrometry of B_6H_{10} has revealed the formation of $B_6H_{11}^+$ in the gas phase. However, the site of attachment of the proton is not revealed by this technique.

We report herein the formation, isolation, and nmr spectral study of the undecahydrohexaboronium ion, $B_6H_{11}^+$, the first example of a polyhedral boron cation, and its derivative, the 2-methyldecahydrohexaboronium ion, $2-CH_3B_6H_{10}^+$.

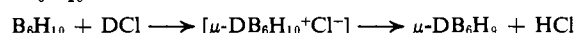
Results and Discussion

Bridge Deuteration. Within 2 min of warming a frozen mixture of DCl and B_6H_{10} (2.5:1 molar ratio) to room temperature in a gas-phase infrared cell (42 mm total pressure), the infrared spectrum yielded evidence of significant deuterium exchange with bridge protons, while there was no apparent exchange of terminal hydrogens. In this 2-min period the system had apparently reached equilibrium since there was no further change in the infrared spectrum over a period of 1 hr. Decomposition was evident some 12 hr later.

The infrared spectrum of the gas-phase mixture (before decomposition was detected) contained characteristic HCl bands which were much stronger than those of DCl. Evidence for exchange of bridge protons was based upon changes in the two strongest ab-

sorptions assigned^{5,7} to the hydrogen bridge system, 1940 and 1490 cm^{-1} . Marked attenuation of the B-H-B band at 1940 cm^{-1} was observed. The reported isotope shift,⁶ 1.33, would put the corresponding B-D-B band at about 1470 cm^{-1} which is close to the second strongest B-H-B bond at 1490 cm^{-1} . Thus this isotope shift was not observed, but the band at 1490 cm^{-1} was noticeably attenuated. The B-D-B absorption corresponding to the B-H-B band at 1490 cm^{-1} was clearly identified as a band of medium intensity at 1125 cm^{-1} . Samples of approximate composition $\mu-D_3B_6H_7$ showed noticeable evidence of bridge-terminal exchange, in the gas phase, after a period of 1 day at room temperature as shown by the growth of a B-D stretch at 1950 cm^{-1} and the decrease of B-D-B band at 1125 cm^{-1} . This exchange was complete in 4 days.

The rapid exchange of bridge hydrogens of B_6H_{10} with DCl in the absence of a catalyst or basic solvent has no precedent in boron hydride chemistry.⁸ This exchange is undoubtedly due to the basicity of the unique boron-boron bond giving rise to the intermediate $\mu-DB_6H_{10}^+$.



Protonation of B_6H_{10} and $2-CH_3B_6H_9$. Formation of $B_6H_{11}^+$ and $2-CH_3B_6H_{10}^+$. Evidence consistent with the formation of protonated species was obtained from tensimetric titration curves in which it was shown that 1 mol of HCl reacts with 1:1 molar ratios of $BCl_3:B_6H_{10}$ in CH_2Cl_2 at -78° and 1:1 molar ratios of $BCl_3:2-CH_3B_6H_9$ in CH_2Cl_2 at -78° .

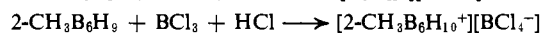
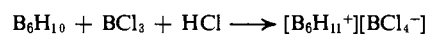


Figure 2 shows typical tensimetric titration curves for the systems HCl- B_6H_{10} , HCl- BCl_3 , and HCl- $BCl_3-B_6H_{10}$. In the first two cases no evidence for stoichiometric interaction was observed.¹⁰ However, a

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(2) G. W. Pawley, *Acta Crystallogr.*, **30**, 631 (1966); F. L. Hershfield, K. Eriks, R. E. Dickerson, E. L. Lippert, and W. N. Lipscomb, *J. Chem. Phys.*, **28**, 56 (1958).

(3) W. N. Lipscomb, *ibid.*, **28**, 170 (1958).

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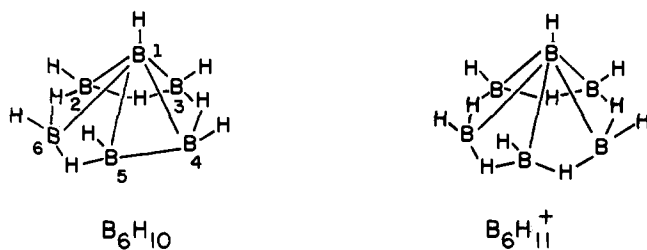
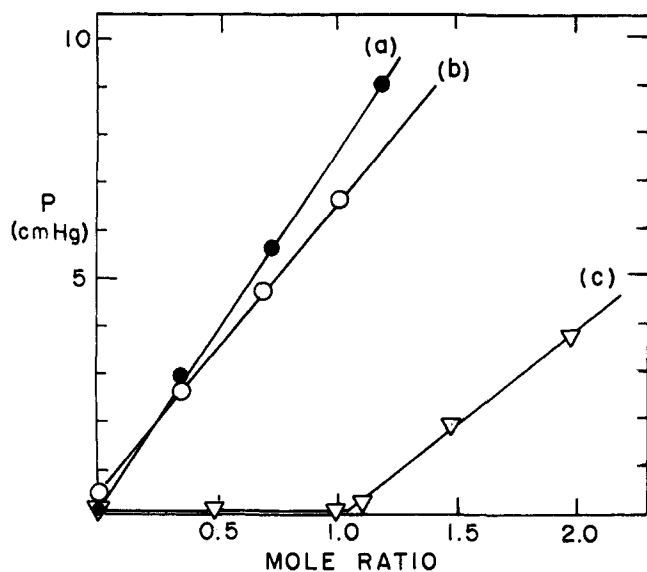
(6) J. J. Solomon and R. F. Porter, *J. Amer. Chem. Soc.*, **94**, 1443 (1972).

(7) S. G. Gibbons and I. Shapiro, *J. Chem. Phys.*, **30**, 1483 (1959).

(8) Although the bridge hydrogens of $B_{10}H_{14}$ do exchange with DCl, a basic solvent is required and a dissociative mechanism has been proposed.⁹

(9) M. F. Hawthorne and J. J. Miller, *J. Amer. Chem. Soc.*, **80**, 754 (1958); J. J. Miller and M. F. Hawthorne, *ibid.*, **81**, 4501 (1959); I. Shapiro, M. Lusty, and R. E. Williams, *ibid.*, **81**, 838 (1959).

(10) While tensimetric titrations and boron-11 nmr spectra show no apparent reaction between BCl_3 and B_6H_{10} in CH_2Cl_2 at low temperature, the addition of B_6H_{10} to BCl_3 (neat) at -78° results in the formation of a white crystalline solid, the stoichiometry of which we have not yet determined.

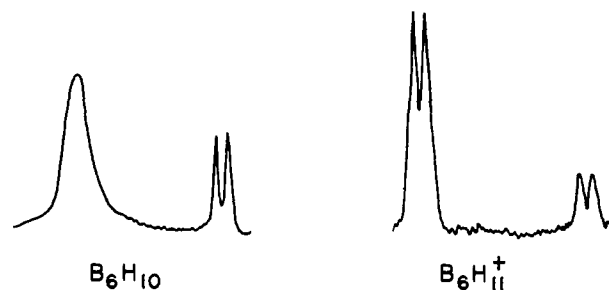
Figure 1. Structure of B_6H_{10} and $B_6H_{11}^+$.Figure 2. Tensimetric titrations at -78° in CH_2Cl_2 with HCl of (a) BCl_3 , (b) B_6H_{10} , and (c) B_6H_{10} and BCl_3 in equimolar quantities.

sharp break occurred in the titration curve at a molar ratio of 1:1:1 when HCl was added to a 1:1 molar ratio of BCl_3 and B_6H_{10} in CH_2Cl_2 at -78° (Figure 2). For the systems HCl- $2-CH_3B_6H_9$ and HCl- BCl_3 - $2-CH_3B_6H_9$, tensimetric titrations in methylene chloride at -78° produced results which were identical with those shown in Figure 2 for the analogous systems.

The products $[B_6H_{11}^+][BCl_4^-]$ and $[2-CH_3B_6H_{10}^+][BCl_4^-]$ precipitated from solution and were isolated as white crystalline solids. Raman spectra of these solids at -40 to -50° provided evidence for the presence of BCl_4^- in that a band which can be assigned to the totally symmetric stretch, a_1 , was observed at 407 cm^{-1} (reported^{11,12} 404 and 405 cm^{-1}) in the respective solids, but, due to problems of light scattering, weaker vibrational modes could not be definitely accounted for. However, $[2-CH_3B_6H_{10}^+][BCl_4^-]$ is sufficiently stable and soluble in CH_2Cl_2 for identification of a boron-11 resonance which can be assigned to BCl_4^- . Based upon boron-11 nmr which is discussed in the next section, $[2-CH_3B_6H_{10}^+][BCl_4^-]$ appears to be significantly more stable in CH_2Cl_2 solution than $[B_6H_{11}^+][BCl_4^-]$. It is also more stable in the solid state. Respective decomposition of the solids occurred at around 0 and -40° . Initial decomposition products appeared to be the reactants HCl, BCl_3 , and hexaborane(10) or its 2-methyl derivative.

The difference in stability between $[B_6H_{11}^+][BCl_4^-]$ and $[2-CH_3B_6H_{10}^+][BCl_4^-]$ is believed to be due to

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 (12) J. A. Creighton, *J. Chem. Soc.*, 6589 (1954).

Figure 3. Boron-11 nmr spectrum of B_6H_{10} in CH_2Cl_2 at -80° and $B_6H_{11}^+$ in liquid HBr at -80° .

enhanced basicity of the boron hydride through methyl substitution on the framework. In the analogous pyramidal systems which contain a basal boron-boron bond which can function as a basic site with respect to protonation, it was found¹³ that $2-CH_3B_5H_7^-$ is a stronger base than $B_5H_8^-$.

Boron-11 Nmr. Tensimetric titrations in methylene chloride at -78° failed to establish the formation of stoichiometric entities in the reaction of HBr with B_6H_{10} and with $2-CH_3B_6H_9$. Low-temperature boron-11 nmr spectra of these solutions revealed the presence of only free B_6H_{10} and $2-CH_3B_6H_9$ based upon chemical shifts and coupling constants. However, when B_6H_{10} and $2-CH_3B_6H_9$ were dissolved in liquid HBr, significant downfield shifts of basal resonances occurred in the boron-11 nmr spectra (Table I). These shifts are

Table I. Boron-11 Nmr Data at 32.1 MHz

	$B_6H_{11}^+{}^a$	$B_6H_{10}{}^b$	$B_6H_9{}^c$
$\delta(\text{apex})$, ppm ^d	48.7	50.9	49.3
J_{BH} , Hz	173	155	137
$\delta(\text{base})$, ppm	-20.9	-16.5	-10.1
J_{BH} , Hz	179		
		$2-CH_3B_6H_{10}{}^{+e}$	$2-CH_3B_6H_9{}^f$
$\delta B(1)$, ppm ^d		48.3	49.4
J_{BH} , Hz		162	153
$\delta B(2)$, ppm		-34.1	-29.4
$\delta B(3,6)$ or $B(4,5)$, ppm			-17.7
J_{BH} , Hz		-17.6	
$\delta B(4,5)$ or $B(3,6)$, ppm			149
J_{BH} , Hz			

^a In liquid HBr at -80° . ^b In CH_2Cl_2 at -80° . Chemical shifts are temperature dependent: V. T. Brice, H. D. Johnson, II, and S. G. Shore, *Inorg. Chem.*, submitted for publication. ^c In $(CH_3)_2O$ at -80° . The basal doublet is unresolved at -80° . ^d $BF_3O(C_2H_5)_2 = 0$ ppm. ^e In liquid HBr at -80° . ^f In CH_2Cl_2 at -80° . Chemical shifts are temperature dependent: see reference in footnote b. The basal doublets are unresolved at -80° .

consistent with proton addition on the basis of the expected inductive effect. It is of interest to note that the boron-11 nmr spectra of B_5H_9 and $2-CH_3B_5H_8$ in liquid HBr were unaltered with respect to chemical shift and coupling constants. Neither of these compounds has available a basal boron-boron bond for protonation. In addition to the downfield shift, the basal resonance of B_6H_{10} dissolved in liquid HBr was markedly sharper at equivalent temperatures than that of B_6H_{10} in CH_2Cl_2 (Figure 3). The boron-11 nmr evidence discussed below and the proton nmr discussed

- (13) V. T. Brice and S. G. Shore, *Inorg. Chem.*, submitted for publication.

in the following section strongly indicate the formation of $B_6H_{11}^+$ and $2-CH_3B_6H_{10}^+$ in liquid HBr.

Boron-11 nmr spectra of $[2-CH_3B_6H_{10}^+][BCl_4^-]$ in CH_2Cl_2 and the boron-11 nmr spectrum of $2-CH_3B_6H_{10}^+$ in liquid HBr are presented in Figure 4. As noted above, the existence of BCl_4^- in solution at -50° was established on the basis of the observed chemical shift. The remainder of the spectrum is identical with that of Figure 4b, the spectrum of $2-CH_3B_6H_{10}^+$ in liquid HBr. Assignments, chemical shifts, and coupling constants are given in Table I. It should be noted that unambiguous assignments could not be made to all of the basal borons in $2-CH_3B_6H_9$. Thus the resonance at -17.6 ppm is assigned to the pair of equivalent boron atoms B_3, B_6 or B_4, B_5 , while the resonance at $+5.8$ ppm is assigned to the equivalent pair B_4, B_5 or B_3, B_6 . In the protonated species $2-CH_3B_6H_{10}^+$, the upfield resonance at $+5.8$ ppm is shifted downfield to overlap the resonance at 17.7 ppm. The area of the resulting resonance which is assigned to B_3, B_4, B_5, B_6 compared to the area of the apical resonance B_1 , in Figure 4b is in the ratio 3.95:1. The area of the B_2 resonance is markedly sensitive to temperature and transmitter power settings. The signal line width increases with decreasing temperature. At $+5^\circ$ a 1:1 area ratio was observed at low power settings which were chosen to minimize saturation of the B_2 signal. Such line broadening upon substitution has been observed by Leach and Onak.¹⁴

The resonances assigned to BCl_4^- in Figures 4a and 4b are reversibly temperature dependent. We believe that this effect arises from dissociation of BCl_4^- into BCl_3 , leading to exchange averaging of the chemical shift as a function of temperature. Exchange averaging as a function of concentration at ambient temperature has been reported¹⁵ for BCl_4^- . A "limiting value" of -6.74 ppm was observed in methylene chloride in the presence of excess chloride ion. At -30° the resonance we assign to BCl_4^- occurs at -8.6 ppm. Since the chemical shift of BCl_3 (-46.8 ppm) occurs some 40 ppm downfield of the reported¹⁵ "limiting value" of BCl_4^- , this indicates that our sample at -30° contained better than 90% BCl_4^- in the exchange equilibrium. Because of limited solubility below -30° we were unable to conveniently observe the spectrum below -30° . At $+5^\circ$, the resonance labeled BCl_4^- in Figure 4a occurred at -15 ppm which indicates that the sample contained about 80% BCl_4^- in the BCl_4^- - BCl_3 exchange equilibrium. The chemical shifts of $2-CH_3B_6H_{10}^+$ at $+5^\circ$ remained constant within ± 0.3 ppm of the values in Table I at -80° .

In the case of $[B_6H_{11}^+][BCl_4^-]$, its solubility in CH_2Cl_2 was insufficient below -45° to obtain spectra. However, at -45° the basal doublet of $B_6H_{11}^+$ was visible. Also visible was the much smaller partly overlapping basal doublet of free B_6H_{10} . This indicates that significant dissociation occurred. The presence of both $B_6H_{11}^+$ and B_6H_{10} shows that on the nmr time scale proton exchange between these moieties is slow. The presence of a signal which could be assigned to the BCl_4^- - BCl_3 exchange could not be detected, presumably because it overlapped the area which is obscured by the $B_6H_{11}^+$ and B_6H_{10} basal doublets (-12 to -24

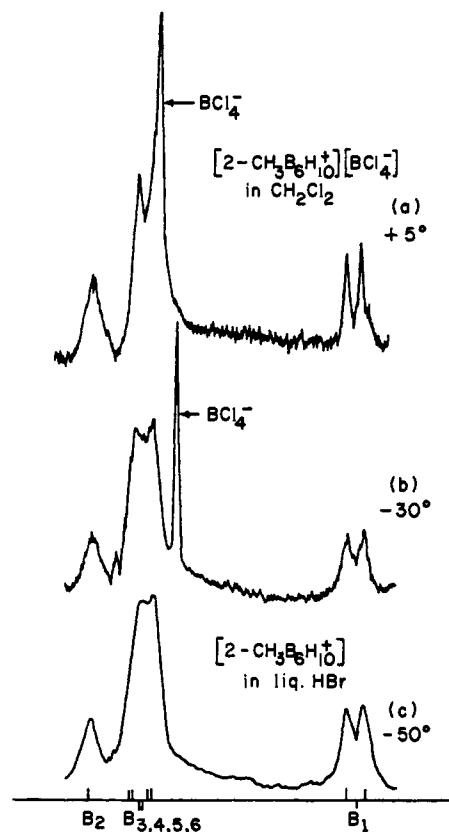


Figure 4. Boron-11 nmr spectra of $2-CH_3B_6H_{10}^+$ salts.

ppm). At higher temperatures, however, this signal was observed and the position of resonance could be correlated with extent of dissociation. Thus at -15° the area ratio of $B_6H_{11}^+$ to B_6H_{10} basal doublets was about 1:2. The resonance assigned to the BCl_4^- - BCl_3 exchange occurred at -33 ppm, which is indicative of 1:2 BCl_4^- : BCl_3 in the exchange equilibrium. At 0° the area ratio of basal doublets of $B_6H_{11}^+$: B_6H_{10} was 1:4 while the resonance due to BCl_4^- - BCl_3 exchange averaging occurred at -39 ppm which is consistent with 1:4 BCl_4^- : BCl_3 . Cooling of the sample to -45° regenerated the original spectrum.

Proton Nmr of $B_6H_{11}^+$ and $2-CH_3B_6H_{10}^+$. Heteronuclear decoupling of boron-11 nuclei allowed the determination of meaningful area ratios from the 100-MHz proton nmr spectra of $B_6H_{11}^+$, B_6H_{10} , and $B_6H_9^-$ when the spectra were recorded at power levels low enough to avoid saturation effects. As shown in Table II, with the basal boron-11 nuclei decoupled, the experimental values of the area ratios of the bridge hydrogens relative to the basal terminal hydrogens were in good agreement with the values calculated assuming five, four, and three bridge hydrogens for $B_6H_{11}^+$, B_6H_{10} , and $B_6H_9^-$, respectively. These area ratios have been corrected for contributions due to hydrogen attached to boron-10 ($I = 3$). The necessity of the double resonance technique is shown in Figure 5 [$B_6H_{11}^+$, 5a; $B_6H_{11}^+$ with basal boron nuclei decoupled, 5b]. The apical terminal resonance is not visible at the low power settings employed for obtaining integrated areas.

In addition to the area ratios provided in Table II, another noteworthy point is the large downfield shift in the position of the hydrogen bridges of $B_6H_{11}^+$ and

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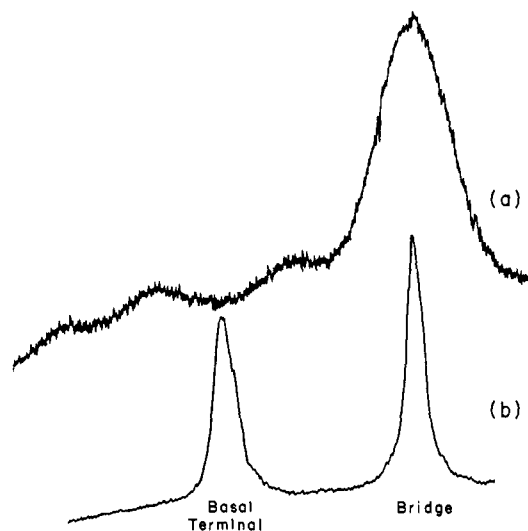


Figure 5. $B_6H_{11}^+$ bridge and terminal resonance: (a) normal spectrum, (b) same spectrum with basal boron-11 nuclei spin decoupled.

Table II. 100-MHz Pmr Data: $B_6H_{11}^+$, B_6H_{10} , $B_6H_9^-$

	$B_6H_{11}^+$ ^b	B_6H_{10} ^c	$B_6H_9^-$ ^d
Bridge area ^e	5.0	4.2	2.9
No. of bridges	5	4	3
τ (bridge), ppm ^f	7.9	11.1	14.2
τ (apical), ppm	9.9	11.2	12.4
τ (basal), ppm	5.1	5.8	6.9

^a Topological representations are not intended to imply framework bonds; $B=BH$. ^b In liquid HBr, -80° . ^c In $CHCl_3$, -80° . Results are consistent with earlier proton spectra.^b ^d In $(CD_3)_2O$, -80° . ^e Experimental value corrected for boron-10 attached hydrogens and expressed relative to five basal terminal hydrogens. ^f TMS = 10 ppm.

the upfield shift of the bridge hydrogens of $B_6H_9^-$ relative to B_6H_{10} . Such shifts are expected on adding or removing a bridge proton if inductive effects are operative.

Table III. 100-MHz Pmr Data: $2-CH_3B_6H_{10}^+$ and $2-CH_3B_6H_9$

	$2-CH_3B_6H_{10}^+$ ^a	$2-CH_3B_6H_9$ ^b
τH_{B_1} , ppm ^c	9.85	11.17
τCH_3	8.78	9.18
$\tau H_{B_3}, H_{B_5}$ or H_{B_4}, H_{B_6}	5.32	5.73
$\tau H_{B_4}, H_{B_5}$ or H_{B_3}, H_{B_6}	5.20	6.52
τH_μ	7.45, 8.10	10.57, 11.09

^a In liquid HBr, -60° . ^b In CH_2Cl_2 , -60° . ^c TMS = 10.00 ppm.

Table III presents proton nmr data for $2-CH_3B_6H_{10}^+$ and $2-CH_3B_6H_9$. The addition of a proton to $2-CH_3B_6H_9$ resulted in a downfield shift in all the resonances and an especially large downfield shift in the bridge resonance. Two bridge resonances in the approximate area ratio 3:2 are observed in the spectrum of $2-CH_3B_6H_{10}^+$ due to the three nonequivalent types of bridging protons. Apparently two of these reso-

nances coincidentally overlap. The pmr spectrum of $[2-CH_3B_6H_{10}^+][BCl_4^-]$ in CH_2Cl_2 was identical with that of $2-CH_3B_6H_{10}^+$ prepared by adding $2-CH_3B_6H_9$ to liquid HBr.

Experimental Section

Materials. Solvents were dried over $LiAlH_4$ and stored in glass vessels having Teflon valves. Boron trichloride and HCl were purchased from the Matheson Co. Hydrogen chloride was used as obtained from the tank and boron trichloride was purified by fractional condensation. Hexaborane(10) and $2-CH_3B_6H_9$ were prepared from B_6H_9 (Callery Chemical Co.).¹⁶ Potassium nonahydrohexaborate, KB_6H_9 , was prepared in $(CD_3)_2O$ by methods previously reported.¹⁷ Deuterium chloride was prepared from the reaction of D_2O with BCl_3 .

Apparatus. Proton magnetic resonance spectra were obtained at 100 MHz and boron-11 nmr spectra were obtained at 32.1 MHz using a Varian high-resolution HA-100 spectrometer. Heteronuclear decoupling was accomplished with a General Radio Co. 1164A coherent decade frequency synthesizer and an Electronic Navigation Instrument Co. Model 320L RF power amplifier. Chemical shifts for boron-11 nmr spectra were measured relative to an external $BF_3 \cdot Et_2O$ standard enclosed in a capillary within the nmr tube. Proton nmr spectra were run using $CHCl_3$ or CH_2Cl_2 as the lock signal. Chemical shifts are given with reference to $Si(CH_3)_4$ using a value of $\tau = 4.67$ for CH_2Cl_2 and $\tau = 2.75$ for $CHCl_3$. Infrared spectra were obtained on a Perkin-Elmer 457 spectrometer using a 10-cm cell with KBr windows. Raman spectra were recorded on a Jarrell-Ash 25-300 Raman spectrometer using a specially constructed cell jacket made of styrofoam with glass windows for low-temperature work.

Tensimetric Titrations. A solution of 0.92 mmol of B_6H_{10} , 0.92 mmol of BCl_3 , and 1.00 ml of CH_2Cl_2 was prepared at -78° in a reaction vessel attached to the vacuum line and opened to a mercury manometer. Hydrogen chloride was added in increments to the well-stirred reaction mixture and allowed to react completely (a few minutes) before the pressure in the system was recorded. In this manner, a total of 1.83 mmol of HCl was added and a white solid formed at -78° . Unreacted HCl, 0.90 mmol, was recovered by fractionation thru a -111° trap yielding a reaction ratio of 1.01 HCl to 1.00 $B_6H_{10}-BCl_3$ in good agreement with the tensimetric plot shown in Figure 2. The product was isolated as a free-flowing white solid by pumping away the bulk of the solvent from -78° and then warming to -45° for a few minutes to remove the remainder. The titration of 0.50 mmol of $2-CH_3B_6H_9$ and 0.50 mmol of BCl_3 in 0.5 ml of CH_2Cl_2 at -78° with HCl was carried out in the same way. The tensimetric plot showed the reaction ratio to be 0.95 HCl to 1.0 $2-CH_3B_6H_9$ to 1.0 BCl_3 . The product, which precipitated from solution, was isolated as described above for $[B_6H_{11}^+][BCl_4^-]$. Boron trichloride in CH_2Cl_2 , B_6H_{10} in CH_2Cl_2 , and $2-CH_3B_6H_9$ in CH_2Cl_2 were titrated with HCl in separate experiments like those described above. No precipitate was produced and no inflection point was evident in any of the tensimetric plots.

Preparation of Nmr Samples. Solvent and reactants were condensed at -196° into standard 5-mm nmr tubes in the vacuum line and were sealed and stored under vacuum at this temperature. Samples were allowed to react at -78° before recording spectra. Concentrations were about 1 mol/l. of solvent.

Preparation of Raman Samples. Sample tubes, 3-mm o.d. by 5 cm long, were attached to the bottom of small reaction vessels in which approximately 0.5-mmol quantities of $[B_6H_{11}^+][BCl_4^-]$ and $[2-CH_3B_6H_{10}^+][BCl_4^-]$ were prepared at low temperature in CH_2Cl_2 as described above. The bulk of solvent was removed at -78° and the remainder at -35° . The products were packed in the bottom of the sample tubes by gentle tapping and cooled to -196° and the tubes were sealed with a torch.

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