Table V. Structural Parameters in GeH_3X and $(CH_3)_3GeX$

	GeH_3X				$(CH_3)_3GeX$			
X	∠HGeH, deg	r(GeH), A	r(GeX), A	Ref	∠CGeC, deg	r(GeC), A	r(GeX), A	Ref
H	109.7	1.527 ± 0.003	1.527 ± 0.003	*a*	109.6 ± 0.1	1.947 ± 0.005	1.532 ± 0.001	*b*
Cl	110.9 ± 1.5	1.52 ± 0.03	2.148 ± 0.003	*c*	112.8 ± 0.08	1.9400 ± 0.0001	2.170 ± 0.001	*d*
Br	109.4 ± 4	1.44 ± 0.1	2.2970 ± 0.0002	*e*	112.4 ± 0.1	1.936 ± 0.006	2.323 ± 0.001	*f*

[a] Obtained by infrared contour analysis: L. P. Lindman and M. K. Wilson, *J. Chem. Phys.*, **22**, 1723 (1954). [b] J. R. Durig, M. M. Chen, and Y. S. Li, to be submitted for publication. [c] See ref 9. [d] See ref 8. [e] See ref 11 and A. H. Sharlaugh, B. S. Pritchard, V. G. Thomas, J. M. Mays, and B. P. Dailey, *Phys. Rev.*, **79**, 189 (1950). [f] Present work.

for all the molecules. There may appear to be some question about the longer GeX distance in trimethylgermane compared to germanium hydride, since the GeH distance in trimethylgermane is the r_s distance whereas in germane it is an r_0 value. The r_0 value is usually larger than the corresponding r_s value for the same molecule. For this reason, it is logical to conclude that the GeX distance is longer in trimethylgermane than in germane, which would be similar to the other cases listed in the same table. This longer GeX distance in trimethylgermyl compounds compared to the hydrides may arise from the increase in the amount of ionic bonding due to the methyl substitution. The absence of observable quadrupole splitting information has prevented us from calculating the percentage of the ionic bond.[9] However, from the GeBr bond distance, it is estimated that the GeBr bond has a double-bond character of only 7% which is small in comparison with the 15% for germyl bromide.

An examination of the structural parameters listed in Table V shows that the CGeC angle opens appreciably and the GeC distance decreases by the substitution of a chlorine or bromine atom for the hydrogen in trimethylgermane. Thus, it appears that the trimethylgermyl parameters are somewhat dependent on the substituents. However, the structures of the trimethylgermyl moiety in the chloride and bromide are quite similar to each other. Microwave work on $(CH_3)_3GeCN$ and $(CH_3)_3GeNC$ is currently in progress in this laboratory and the results will be reported later.

Registry No. $(CH_3)_3{}^{76}Ge^{81}Br$, 36965-95-4; $(CH_3)_3{}^{74}Ge^{81}Br$, 36926-72-4; $(CH_3)_3{}^{73}Ge^{81}Br$, 36926-73-5; $(CH_3)_3{}^{72}Ge^{81}Br$, 36926-74-6; $(CH_3)_3{}^{70}Ge^{81}Br$, 36926-75-7; $(CH_3)_3{}^{76}Ge^{79}Br$, 36926-76-8; $(CH_3)_3{}^{74}Ge^{79}Br$, 36926-77-9; $(CH_3)_3{}^{72}Ge^{79}Br$, 36926-78-0; $(CH_3)_3{}^{70}Ge^{79}Br$, 36926-79-1.

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Deprotonation of Pentaborane(9) Derivatives. Evidence for Tautomerism and Isomerization of Resulting Anions

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Deprotonation of $1\text{-}CH_3B_5H_8$, $2\text{-}CH_3B_5H_8$, $1\text{-}ClB_5H_8$, and $1\text{-}BrB_5H_8$ by potassium hydride yielded $1\text{-}CH_3B_5H_7^-$, $2\text{-}CH_3B_5H_7^-$, $1\text{-}ClB_5H_7^-$, and $1\text{-}BrB_5H_7^-$. Low-temperature pmr studies (−90 to −130°) gave evidence of partial quenching of tautomerism of the bridging protons in $2\text{-}CH_3B_5H_7^-$ but not in the case of the apically substituted anions. Boron-11 nmr studies showed evidence of isomerization of $1\text{-}CH_3B_5H_7^-$ to $2\text{-}CH_3B_5H_7^-$. The relative acidities of these boron hydrides was found to be in the order $1\text{-}ClB_5H_8 > B_5H_9 > 1\text{-}CH_3B_5H_8 \cong 2\text{-}CH_3B_5H_8$.

Introduction

The reported deprotonation of pentaborane(9),[1-3] hexaborane(10),[3-5] and tetraborane(10)[6,7] by alkali metal hydrides, methyllithium, or ammonia has demonstrated the ability of the intermediate boron hydrides to act as Bronsted acids. The relative acidities of these boron hydrides has been shown to increase with increasing size of polyhedral frameworks[3] of composition B_nH_{n+4}: $B_{10}H_{14} > B_6H_{10} > B_5H_9$. In the cases of B_5H_9[1] and B_6H_{10}[4] the proton is removed from a bridging site in the base of the pyramidal framework. Rapid tautomerism of the remaining bridge protons in $B_5H_8^-$ and $B_6H_9^-$ has been invoked[2,3] to explain the apparent magnetic equivalence of the boron atoms observed in the boron-11 nmr spectra. To date accompanying pmr spectral studies to support such evidence has not been cited.

We report in this paper a study of the effects of methyl, chloro, and bromo substituents on the B_5H_9 framework with regard to relative Bronsted acidities and properties of the resulting anions as studied by proton and boron-11 nmr spectra. Pmr evidence for tautomerism of the bridging protons is presented as well as partial quenching of tautomerism in $2\text{-}CH_3B_5H_7^-$ at low temperatures.

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(1) D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, **89**, 3375 (1967).

(2) R. A. Geanangel and S. G. Shore, *J. Amer. Chem. Soc.*, **89**, 6771 (1967).

(3) H. D. Johnson, II, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, **9**, 908 (1970).

(4) H. D. Johnson, II, S. G. Shore, N. L. Mock, and J. C. Carter, *J. Amer. Chem. Soc.*, **91**, 2131 (1969).

(5) G. L. Brubaker, M. L. Denniston, S. G. Shore, J. C. Carter, and F. Swicker, *J. Amer. Chem. Soc.*, **92**, 7216 (1970).

(6) A. C. Bond and M. L. Pinsky, *J. Amer. Chem. Soc.*, **92**, 7585 (1970).

(7) H. D. Johnson, II, and S. G. Shore, *J. Amer. Chem. Soc.*, **92**, 7586 (1970).

Table I. Pmr Chemical Shifts of the Anions[a]

Compd	H_{base}	H_{bridge}	H_{apex}	CH_3
$B_5H_8^-$	8.53	13.51	10.41	
B_5H_9[b]	7.51	12.28	9.47	
$1\text{-}CH_3B_5H_7^-$	8.52	13.10		9.91
$1\text{-}CH_3B_5H_8$[b]	7.58	12.06		9.96
$1\text{-}ClB_5H_7^-$	8.12	12.68		
$1\text{-}ClB_5H_8$[b]	7.22	11.65		
$1\text{-}BrB_5H_7^-$	8.10	12.73		
$1\text{-}BrB_5H_8$[b]	7.17	11.55		
$2\text{-}CH_3B_5H_7^-$ (−50°)	8.52, 9.23	13.14	10.44	9.70
(−110°)	8.50, 9.17	12.76, 13.85	10.44	9.68
$2\text{-}CH_3B_5H_8$[b]	7.73	11.66, 12.43	9.54	9.54

[a] Chemical shifts are with respect to $(CH_3)_4Si$ (TMS), τ 10.00, at −50° in $(CD_3)_2O$. Values are good to τ ±0.03. [b] P. M. Tucker, T. Onak, and J. B. Leach, *Inorg. Chem.*, **9**, 1430 (1970).

Results and Discussion

Deprotonation Reactions. Potassium hydride deprotonates $1\text{-}CH_3B_5H_8$, $2\text{-}CH_3B_5H_8$, $1\text{-}ClB_5H_8$, and $1\text{-}BrB_5H_8$ in tetrahydrofuran (THF) and dimethyl ether. Reactions are quantitative at −78°; *i.e.*

$$1\text{-}RB_5H_8 + KH \rightarrow K^+[1\text{-}RB_5H_7^-] + H_2 \quad (R = CH_3, Cl, Br)$$

$$2\text{-}CH_3B_5H_8 + KH \rightarrow K^+[2\text{-}CH_3B_5H_7^-] + H_2$$

The rate of reaction is dependent on the concentration of the solution. For 1 *M* solutions on a 0.5-mmol scale in THF, $1\text{-}ClB_5H_8$ and $1\text{-}BrB_5H_8$ react completely within a matter of minutes; $1\text{-}CH_3B_5H_8$ reacts in about 30 min; and $2\text{-}CH_3B_5H_8$ requires slightly over 1 hr for completion of the reaction. In $(CH_3)_2O$ the reactions appear to be faster. In solution $K^+[1\text{-}CH_3B_5H_7^-]$, $K^+[1\text{-}ClB_5H_7^-]$, and $K^+[1\text{-}BrB_5H_7^-]$ are stable to +10° and $K^+[2\text{-}CH_3B_5H_7^-]$ is stable up to ambient temperature.

Retention of the pyramidal framework of the anions is indicated by the fact that addition of HCl to $1\text{-}CH_3B_5H_7^-$, $2\text{-}CH_3B_5H_7^-$, $1\text{-}ClB_5H_7^-$, and $1\text{-}BrB_5H_7^-$ in solution produces the parent, neutral hydrides $1\text{-}CH_3B_5H_8$, $2\text{-}CH_3B_5H_8$, $1\text{-}ClB_5H_8$, and $1\text{-}BrB_5H_8$, respectively, in yields of greater than 90%.

Attempted deprotonation of $2\text{-}ClB_5H_8$ yielded excess hydrogen indicating decomposition of $2\text{-}ClB_5H_7^-$. No attempt was made to deprotonate $2\text{-}BrB_5H_8$.

Pmr Spectra of the Anions. Proton chemical shifts of $B_5H_8^-$, $1\text{-}CH_3B_5H_7^-$, $2\text{-}CH_3B_5H_7^-$, $1\text{-}ClB_5H_7^-$, and $1\text{-}BrB_5H_7^-$ are presented in Table I.

The chemical shifts of the basal terminal protons and the bridge protons in the case of all the anions are upfield from the values of their conjugate acids. This might be due to the increased electron density in the basal positions due to the removal of a proton. The apical proton resonances of $2\text{-}CH_3B_5H_7^-$ and $B_5H_8^-$ also shift slightly upfield from their original values. Assignments of resonances are based on comparison with the chemical shift values and areas and multiplicities of resonances of the neutral parent species.

From 0 to −90° the boron-11 decoupled proton nmr spectrum of $2\text{-}CH_3B_5H_7^-$ consists of an apical resonance, a methyl resonance, two basal terminal proton resonances in the area ratio of 2:1, and a single bridge resonance (see Table I for chemical shifts). Apparent equivalence of the bridging hydrogens favors a tautomerism of the bridge protons placing them in an averaged magnetic environment which yields only one resonance. Basal terminal hydrogens are considered to be static during the exchange process to account for the two resonances observed.

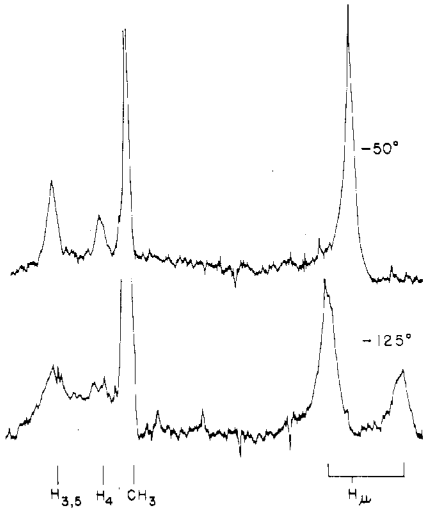

Figure 1. Pmr spectra at 100 MHz of $2\text{-}CH_3B_5H_7^-$ with the boron-11 nuclei in the base spin decoupled.

This model for exchange is that applied[3] to $B_5H_8^-$ and $B_6H_9^-$ which in turn stems from the model suggested[8] for B_6H_{10}. A test for such exchange is to quench the system at low temperature and observe splitting of the bridge resonance thereby confirming the presence of nonequivalent bridge sites in the static structures. To date, successful quenching of exchange in $B_5H_8^-$ and $B_6H_9^-$ has not been observed in this laboratory. However, for $2\text{-}CH_3B_5H_7^-$ we have obtained evidence which suggests partial quenching of exchange from −90 to −130°, the lowest temperature at which spectra were recorded. The evidence is presented in Figure 1.

Figure 1 is the pmr spectrum of $2\text{-}CH_3B_5H_7^-$ with the basal boron-11 nuclei spin decoupled. A transmitter power setting was chosen to enhance the bridge resonance. At this particular power setting the undecoupled apical resonance (a quartet) is not visible above the base line. Below −90°, the bridge resonance splits into two peaks in the area ratio of 2:1; the terminal proton resonances are still apparent although broadened (Figure 1). The temperature dependence of the spectrum is fully reversible and the weighted average of the chemical shifts of the two peaks (τ 13.12 ppm) is in good agreement with the chemical shift of the single bridge peak (τ 13.14 ppm) which occurs above −90°. This indicates that the bridging system had undergone tautomerism at higher temperatures to give magnetic equivalence of bridge sites but has now been at least partially quenched resulting in nonequivalent bridge hydrogen environments. Two possibilities for static structures are shown in Figure 2a. Equivalent mixtures of these structures would not account for the observed spectrum. If one of these structures predominates, then the area ratio of 2:1 for bridge protons would be the result of two of the three hydrogens having overlapping resonances since each static structure requires three nonequivalent bridging protons.

Another possibility to account for the 2:1 area ratio is that the system is partially quenched with two of the hydrogens static on the nmr time scale and the third hydrogen exchanging at an adjacent B–B bond site. At the present time we favor this concept of partial exchange involving the structures shown in Figure 2b. Such exchange is assumed to cause apparent equivalence of $H_{bridge}(2,3)$ and $H_{bridge}(2,5)$. This choice of structure which places static bridge hydrogens adjacent to methyl-substituted boron is based on assignments

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(8) R. E. Williams, *J. Inorg. Nucl. Chem.*, **20**, 198 (1961); W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, p 173.

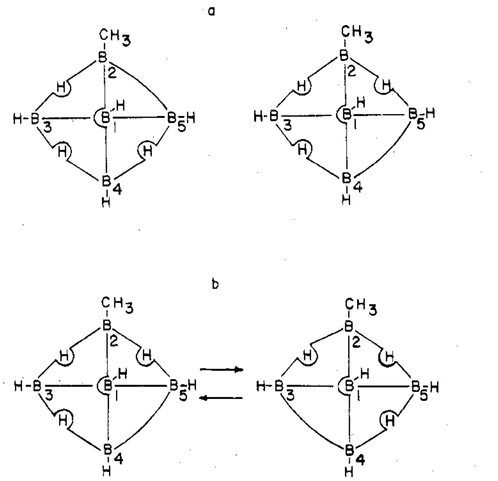

Figure 2. (a) Possible static structures for $2\text{-}CH_3B_5H_7^-$. (b) Possible exchange in a partially quenched system.

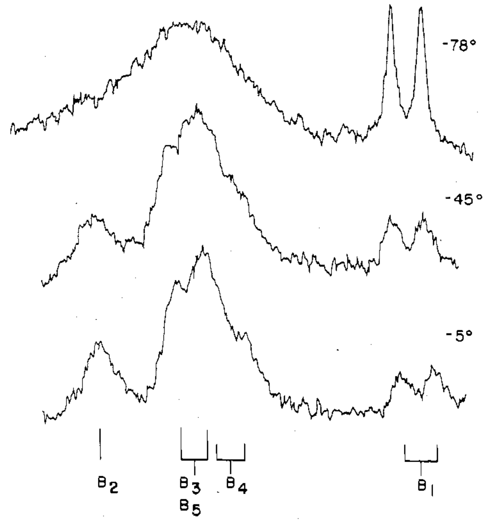

Figure 3. Variable-temperature boron-11 nmr spectra at 32.1 MHz of $2\text{-}CH_3B_5H_7^-$

of the pmr spectra of $2\text{-}CH_3B_5H_8$[9] and $2\text{-}CH_3B_6H_9$.[10] In these compounds, resonances of bridge hydrogens which occur at lowest field are assigned to bridge hydrogens adjacent to the methyl-substituted boron. Of the two bridge resonances of $2\text{-}CH_3B_5H_7^-$ which appear below −90°, the resonance of relative area 2 occurs at lower field (Figure 1).

In view of the apparent partial quenching of tautomerism in $2\text{-}CH_3B_5H_7^-$, it appears that a basally substituted methyl group in some manner aids in slowing the mechanism for bridge proton tautomerism since no such change in the magnetic environment of the bridge protons is observed for $B_5H_8^-$ or the apically substituted derivatives. The boron-11 decoupled proton nmr of $1\text{-}CH_3B_5H_7^-$, $1\text{-}ClB_5H_7^-$, and $1\text{-}BrB_5H_7^-$ from 0 to −125° reveals only one resonance for the basal terminal protons and one resonance for the bridge protons. Thus tautomerism in these species appears to be rapid on the nmr time scale even to −125°.

The undecoupled pmr spectra of these anions reveal that as the temperature is lowered, the bridge resonance sharpens while the terminal basal multiplet collapses and slowly appears as a broad singlet below −100°. The sharpening of the bridge resonance and the collapse of the basal terminal multiplet to a singlet is an example of thermal decoupling which has been attributed to more rapid relaxation of the boron nuclei.[11,12] The apical quartet in $B_5H_8^-$ and $2\text{-}CH_3B_5H_7^-$ is still in evidence at −90° although it is broadened. These observations provide supporting evidence that basal borons appear to undergo relaxation more rapidly than apical borons.[13]

Boron-11 Nmr Spectra of the Anions. Qualitatively the spectra of $1\text{-}CH_3B_5H_7^-$, $1\text{-}ClB_5H_7^-$, and $1\text{-}BrB_5H_7^-$ are similar to those of their parent compounds exhibiting a low-field doublet due to the basal borons and a high-field singlet due to the apical boron. The spectrum of $2\text{-}CH_3B_5H_7^-$ at −5° (Figure 3) shows a high-field doublet due to the apical boron, lower field multiplets due to the three unsubstituted borons, and a low-field singlet due to the methylated boron. The area ratios of these peaks at −5° from low field to high field is 1:3:1.

From 0 to −60° for $1\text{-}CH_3B_5H_7^-$ and from 0 to −50° for $1\text{-}ClB_5H_7^-$ and $1\text{-}BrB_5H_7^-$ the basal doublets remain resolved in 1 *M* solutions in THF. Below these temperatures resolution is lost and broadening of the resonance continues to increase. However, only one resonance which is symmetric in appearance is observed. Similar broadening has been observed and attributed to rapid relaxation of the boron nuclei at these low temperatures. The possibility of broadening being due to a slowing of the rate of tautomerism can be dismissed on the basis of pmr data discussed above. Severe broadening and loss of resolution of the basal resonances is observed in the spectrum of $2\text{-}CH_3B_5H_7^-$ below −50° (Figure 3). The presence of a methyl group in a basal position appears to enhance line broadening and loss of resolution at higher temperatures. Leach and Onak have observed analogous broadening in pmr spectra of basally substituted boron hydrides in their studies.[14]

The apical singlet of $1\text{-}CH_3B_5H_7^-$ and the apical doublet of $2\text{-}CH_3B_5H_7^-$ sharpen considerably as the temperature of the samples is lowered. This sharpening has been reported for $B_5H_8^-$ [3] and $2\text{-}CH_3B_5H_8$.[10] It has been suggested that thermal decoupling of the basal borons from the apical boron might be the cause of such observations.[14] Low-temperature spectra of B_5H_9, $1\text{-}CH_3B_5H_8$, and $2\text{-}CH_3B_5H_8$ do not reveal such significant sharpening of the apical resonances at least to −80°. On the other hand, the apical resonances of $1\text{-}ClB_5H_7^-$ and $1\text{-}BrB_5H_7^-$ broaden at lower temperatures. This broadening might be due to interaction of boron with the nuclear quadrupolar moment of the halogen or to unresolved couplings between boron and the halogen.

Chemical shifts (Table II) of the basal resonances of these anions are upfield from those of the neutral parent hydride which might be expected on the basis of increased electron density in the base. There is, however, a downfield shift in the apical resonances which cannot be accounted for in such a simple manner.

Isomerization of $1\text{-}CH_3B_5H_7^-$. At +10° a rapid change was noted in the appearance of the boron-11 nmr spectrum of $1\text{-}CH_3B_5H_7^-$ in THF. Within 10 min the upfield singlet disappeared. A high-field doublet, a low-field singlet, and a multiplet centered at ~18 ppm grew in. The boron-11 nmr spectrum matched that of $2\text{-}CH_3B_5H_7^-$.

$$1\text{-}CH_3B_5H_7^- \xrightarrow[+10°]{\text{THF}} 2\text{-}CH_3B_5H_7^-$$

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(9) See footnote *b* of Table I.

(10) V. T. Brice, H. D. Johnson, II, and S. G. Shore, submitted for publication.

(11) D. Marynick and T. Onak, *J. Chem. Soc. A*, 1170 (1970).

(12) H. Beall, C. M. Buschweller, W. J. Dewkett, and M. Grace, *J. Amer. Chem. Soc.*, **92**, 3484 (1970).

(13) J. D. Odom and R. Schaeffer, *Inorg. Chem.*, **9**, 2151 (1970).

(14) J. B. Leach and T. Onak, *J. Magn. Resonance*, **4**, 30 (1971).

Table II. Boron-11 Nmr Chemical Shifts of the Anions[a]

Compd	$\delta(1)$ (J^b)	$\delta(2)$	$\delta(3,5)$ (J^b)	$\delta(4)$ (J^b)
2-$CH_3B_5H_7^-$	50.4 (148)	2.5	16.9[c]	22.5[c]
2-$CH_3B_5H_8$[d]	51.5 (176)	−1.6	13.5 (169)	19.1 (165)
1-$CH_3B_5H_7^-$	44.0		16.2 (127)	
1-$CH_3B_5H_8$[d]	45.3		13.3 (167)	
1-$ClB_5H_7^-$	26.4		15.6 (128)	
1-ClB_5H_8[d]	28.7		11.9 (164)	
1-$BrB_5H_7^-$	35.2		16.1 (130)	
1-BrB_5H_8[d]	37.3		12.4 (165)	
$B_5H_8^-$	52.9 (150)		17.1 (130)	
B_5H_9[d]	53.1 (178)		13.4 (162)	

[a] Chemical shifts are relative to $BF_3 \cdot (C_2H_5)_2O$. Deviations: δ, ±0.2 ppm; J, ±5 Hz. [b] Coupling constant in Hz. [c] Chemical shift values determined from proton-decoupled boron-11 nmr spectra provided by Dr. G. Kodama of the University of Utah. [d] Footnote *b*, Table I.

Addition of HCl produced 2-$CH_3B_5H_8$ in low yields. This isomerization of 1-$CH_3B_5H_7^-$ to 2-$CH_3B_5H_7^-$ is not clean as is evidenced by the low yields and the immediate appearance of a white precipitate indicative of decomposition. In order to determine if the rearrangement of the anion might be assisted by the basicity of the solvent, the tetrabutylammonium salt[15] $[(n\text{-}C_4H_9)_4N^+][1\text{-}CH_3B_5H_7^-]$ was prepared and dissolved in CH_2Cl_2. This salt was also observed to rearrange in the boron-11 nmr spectrum at +10°. The anion thus appears to rearrange without the aid of a basic solvent. On the other hand, a sample of 1-$CH_3B_5H_8$ in THF at room temperature for 1 year showed no rearrangement.

The rearrangement of 1-alkylpentaboranes(9) in the presence of amines has been studied.[16] Rearrangements facilitated by tautomerism,[17-19] ionic intermediates,[20-22] and base adduct or associated species[16] have been proposed.

The evidence presented here shows that an ionic 1-$CH_3B_5H_7^-$ intermediate, if formed, can rearrange to 2-$CH_3B_5H_7^-$. However, the low yield of isomer favors adduct formation as a more viable competing mechanism. Pentaborane(9) forms adducts with trimethylamine[23] whereas it is deprotonated by NH_3.[5] Therefore it might depend on the base used as to whether deprotonation or adduct formation is the intermediate step.

The variable-temperature boron-11 nmr spectra of 1-$ClB_5H_7^-$ and 1-$BrB_5H_8^-$ showed that both of these species rapidly decompose at +10°. No evidence was seen for the formation of 2-halopentaborane anion in either case. The tetrabutylammonium salt of 1-$ClB_5H_7^-$ was prepared and dissolved in CH_2Cl_2. The same observations as for the potassium salt were noted in the boron-11 nmr. The isomerization of 1-ClB_5H_8 to 2-ClB_5H_8 has been reported[24,25] in diethyl ether at room temperature. It was proposed that the intermediate to rearrangement is a solvent attack on the basal boron. An ionic intermediate would not be expected and the evidence presented here supports this contention since 1-$ClB_5H_7^-$ does not produce 2-$ClB_5H_7^-$. While 1-$ClB_5H_7^-$ is stable up to +10°, 1-ClB_5H_8 begins isomerizing to 2-ClB_5H_8 at −35°.

Relative Acidities of the Boranes. Relative acidities of B_5H_9, 1-$CH_3B_5H_8$, 2-$CH_3B_5H_8$, and 1-ClB_5H_8 were determined by proton competition reactions between a neutral species and an anion at −78° in THF

$$B_5H_9 + RB_5H_7^- \rightarrow B_5H_8^- + RB_5H_8 \ (R = CH_3 \text{ or Cl})$$

Reaction conditions are presented in the Experimental Section. From the boron-11 nmr chemical shifts and from the shapes of the apical resonances (at low temperature this resonance sharpens in the anion but remains broad in the neutral moiety) the respective species in solution could be determined. The relative acidities appear to be in the order 1-ClB_5H_8 > B_5H_9 > 1-$CH_3B_5H_8$ ≅ 2-$CH_3B_5H_8$. Reactions between pentaborane(9) and each of these derivatives always appeared to be complete. However, the reactions between 1- and 2-methylpentaboranes were not complete. Chemical shifts of the apical resonances were about midway between the values for those of the anion and the neutral species. Fractionation of these mixtures at low temperature and collection of the volatile boranes yielded about 1:1 mixtures of 1-$CH_3B_5H_8$ and 2-$CH_3B_5H_8$ as determined by the area ratios of the apical resonances in the boron-11 nmr.

The chloro derivative is more acidic than B_5H_9 which is expected on the basis of the electron-withdrawing character of the chlorine atom. The methyl groups appear to be electron releasing resulting in these derivatives being less acidic than B_5H_9. The position of the methyl group in the framework does not appear to affect greatly the relative acidity with respect to B_5H_9. The greater basicity of the methyl anions compares favorably with the evidence of the apparent greater stability of the protonated 2-methylhexaborane(10) salt $[2\text{-}CH_3B_6H_{10}^+]BCl_4^-$ as compared to the $[B_6H_{11}^+]BCl_4^-$ salt.[26]

Experimental Section

Materials. Pentaborane(9) was obtained from the Callery Chemical Co. and used directly from the cylinder. 1-Methylpentaborane(9),[27] 2-methylpentaborane(9),[16] 1-chloropentaborane(9),[25] and 1-bromopentaborane(9)[28] were prepared according to the literature. Potassium hydride was obtained from RIC/ROC as a 50% mineral oil suspension. The oil was removed by repeated washings with pentane. Hydrogen chloride was obtained from the Matheson Co. Perdeuteriodimethyl ether was prepared from CD_3I and $KOCD_3$. The CD_3I and CD_3OD were purchased from Stohler Isotope Chemicals. Dimethyl ether was purchased from the Matheson Co. Solvents were dried over $LiAlH_4$. The KB_5H_8 salt was prepared according to the literature in quantities as needed.[3]

Apparatus. Proton magnetic resonance spectra were recorded on a Varian HA-100 high-resolution nmr spectrometer. Decoupling experiments were carried out employing an Electronic Navigation Laboratories 320L power amplifier, a Hewlett-Packard 3722A noise generator, and a General Radio frequency synthesizer. Chemical shifts were measured relative to $(CH_3)_2O$ and corrected to $(CH_3)_4Si$ using τ 6.76 for $(CH_3)_2O$. Boron-11 nmr were recorded on the same instrument in the HR mode at 32.1 MHz. Chemical shifts were measured relative to $BF_3 \cdot (C_2H_5)_2O$ as an external standard. Relative peak areas were measured using a polar planimeter.

Deprotonation of Pentaborane(9) Derivatives. For pmr studies a vessel was constructed from 13-mm glass tubing containing a medium frit and a 14/35 ground-glass joint side arm. The reaction portion of this vessel (containing the side arm) was sealed into a test tube bottom. An nmr tube was connected to the other side of the frit. In

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a standard drybox an excess of KH was loaded into the reaction side of the vessel through the ground-glass joint. Under nitrogen this vessel was removed to the vacuum line and evacuated. At −196° 0.4 mmol of 1-$CH_3B_5H_8$ and 0.3 ml of $(CD_3)_2O$ were condensed into the reaction tube. The tube was then warmed to −78° and the reaction was allowed to proceed until evolution of gas ceased. The vessel was immersed in liquid nitrogen, the hydrogen was removed, and 0.1 ml of $CHCl_3$ was condensed into the flask. The vessel was inverted. A −78° bath covered the nmr tube and an area above the frit. As the solution melted, it dropped to the frit. At no time was the solution above −78°. After filtration the solution in the nmr tube was frozen and the tube was sealed with a torch and removed.

For 1.0-mmol samples or larger a test tube type apparatus containing a magnetic stirring bar and fitted with an nmr tube side arm was employed. The sample was prepared as above. When the reaction stopped, the entire vessel including side arm was immersed in a −78° bath. The necessary amount of solution was then tipped into the nmr tube. The vessel was frozen and the nmr tube was sealed with a torch and removed.

For boron-11 nmr studies both tetrahydrofuran and dimethyl ether were used as solvents.

The hydrogen from samples was Toepler-pumped and measured. Yields were in excess of 97% of the theoretical value.

The deprotonation reactions of 2-$CH_3B_5H_8$, 1-ClB_5H_8, and 1-BrB_5H_8 were carried out in a similar manner as above.

Protonation of the Anions. The appropriate anion was prepared on the vacuum line on a 1.00-mmol scale in $(CH_3)_2O$ according to procedures described in the previous section. An excess of HCl was introduced at −196°. The reaction tube was warmed to −78° and stirred for 1 hr. The mixture was fractionated, and the boron hydride was isolated. The vessel was maintained at −78° until the solvent had been removed. Yields for the neutral boranes varied from 85 to 96%.

Preparation of $(n\text{-}C_4H_9)_4N[1\text{-}CH_3B_5H_7]$ and $(n\text{-}C_4H_9)_4N[1\text{-}ClB_5H_7]$. A 1.00-mmol sample of $(n\text{-}C_4H_9)_4NI$ and 1.00 mmol of KH were weighed into a reaction vessel in the drybox. The vessel was removed to the vacuum line and evacuated. About 2.0 ml of THF and 1.00 mmol of either 1-$CH_3B_5H_8$ or 1-ClB_5H_8 were condensed into the reaction tube. The vessel was warmed to −78°. When the reaction was completed, the hydrogen was removed and 4.0 ml of CH_2Cl_2 was condensed in at −196°. The vessel was warmed to −35° and stirred for 1 hr. Approximately 8–10 ml of diethyl ether was then introduced. Under nitrogen at −196° the vessel was attached to a filtration extractor on the line and evacuated. The solution was filtered at −78°. Again under nitrogen the bottom vessel containing the filtrate was removed and replaced with a test tube vessel fitted with an nmr tube side arm. The system was evacuated and pumped on for 1 hr. About 1 ml of methylene chloride was condensed in onto the frit at −78° and the tetra-*n*-butylammonium salt was allowed to wash through to the lower vessel. A portion of the sample was tipped at −78° into the nmr tube. The tube was frozen and removed. The solid on the frit was identified as KI by its X-ray powder pattern.

Relative Acidities of the Boranes. In reaction procedures described above proton competition reactions in THF were prepared between the various pairs of neutral boranes and anions. The appropriate anion was prepared on a 0.50-mmol scale at −78°. The neutral borane was introduced in an equivalent amount and the mixture was allowed to equilibrate at −78° for 1 hr before the nmr sample was removed. The following pairs of reactions were carried out and the resulting boron-11 nmr spectra were studied from −78° to ambient temperature: B_5H_9 and K[1-$CH_3B_5H_7$]; 1-$CH_3B_5H_8$ and KB_5H_8; B_5H_9 and K[2-$CH_3B_5H_7$]; 2-$CH_3B_5H_8$ and KB_5H_8; 1-$CH_3B_5H_8$ and K[2-$CH_3B_5H_7$]; 2-$CH_3B_5H_8$ and K[1-$CH_3B_5H_7$]; B_5H_9 and K[1-ClB_5H_7]; 1-ClB_5H_8 and KB_5H_8. The respective species in solution could be determined by the chemical shifts of the resonances observed. Solutions containing 1-$CH_3B_5H_8$ and 2-$CH_3B_5H_8$ and their corresponding anions were fractionated. Boron-11 nmr spectra revealed the presence of both neutral species in solution for this mixture.

Registry No. $B_5H_8^-$, 31426-87-6; 1-$CH_3B_5H_7^-$, 36900-66-0; 1-$ClB_5H_7^-$, 36900-67-1; 1-$BrB_5H_7^-$, 36900-68-2; 2-$CH_3B_5H_7^-$, 37035-65-7.

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Nuclear Magnetic Resonance Spectroscopy. Spin-Spin Coupling of Carbon to Phosphorus, Mercury, Nitrogen, and Other Elements[1a,b]

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Spin-spin coupling between carbon and phosphorus, mercury, nitrogen, and boron has been observed in proton-decoupled ^{13}C spectra. One-bond couplings involving carbon are generally positive and two-bond couplings are negative; however, if unhybridized p orbitals are used in the bonding, such as with phosphorus(III) or fluorine, one-bond couplings are negative and two-bond couplings are positive. A comparison of the magnitudes of carbon–phosphorus and carbon–nitrogen couplings with carbon–carbon couplings shows a significant negative contribution to the coupling constants which suggests that average energy approximation should not be used for this kind of comparison. Carbon–mercury couplings correlate well with carbon–carbon or proton–mercury couplings in similar bonding situations.

Prior to the advent of field frequency controlled spectrometers, studies of coupling between carbon and nuclei other than hydrogen and fluorine were rare.[2] Indor techniques could be used to study the couplings involving methyl carbons,[3] and carbon enrichment allowed observation of the couplings in the carbon spectrum,[4] but with the requirement of simple molecules or inconvenience of labeled

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