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The Preparation and Properties of 2- and μ-(Halosilyl)pentaboranes(9)

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Received March 16, 1970

The reactions of 2-$SiH_3B_5H_8$ and μ-$SiH_3B_5H_8$ with BCl_3 and BBr_3 produce 2-($ClSiH_2$)B_5H_8, μ-($ClSiH_2$)B_5H_8, and 2-($BrSiH_2$)-B_5H_8, in high yield. The 2-($ClSiH_2$)B_5H_8 and 2-($BrSiH_2$)B_5H_8 can also be prepared from the aluminum halide catalyzed reactions of 2-$SiH_3B_5H_8$ with HCl and HBr, respectively. In all cases, halogenation occurs exclusively at the silicon atom. The new compounds have been characterized by elemental analyses and infrared, ^{11}B nmr, ^1H nmr, and mass spectral data. Deuterium exchange between DCl and 2-$SiH_3B_5H_8$ or 2-($ClSiH_2$)B_5H_8, catalyzed by aluminum chloride, occurs at the apical, B(1), terminal position.

Introduction

Several examples of compounds containing boranes bonded to a silane or alkylsilane moiety have appeared.[1-3] However, very little chemistry of these compounds has been reported. Our interest in preparing silylboranes which have reactive functional groups on the silicon atom and in determining the effect of borane substitution on the reactivity of the SiH_3 moiety has led us to examine reactions of 2-$SiH_3B_5H_8$ and μ-$SiH_3B_5H_8$ with a variety of halogenating agents. During this study we have prepared and characterized the first examples of (halosilyl)pentaboranes: 2-($ClSiH_2$)B_5H_8, 2-($BrSiH_2$)B_5H_8, and μ-($ClSiH_2$)B_5H_8. The results of this work are given below.

Experimental Section

Apparatus and Techniques.—All work was carried out in a standard high-vacuum system.[4,5] Vapor pressure *vs.* temperature data were obtained using an all-glass immersible tensimeter which had been predried with SiH_3Br for a period of 12 hr. Samples were frozen to −196° between pressure measurements to minimize decomposition. Melting points were obtained by the Stock magnetic plunger technique. Infrared spectra were obtained with Beckman IR-12 and Perkin-Elmer Model 21 spectrometers on gaseous samples in a 10-cm cell fitted with KBr windows. Proton nuclear magnetic resonance spectra were recorded at 60 MHz using a Varian Associates A-60A spectrometer. Proton chemical shifts are reported relative to internal $(CH_3)_4Si$. Boron-11 spectra were obtained with a Varian HA-100 spectrometer equipped with standard probe and radiofrequency unit accessories. Boron-11 chemical shifts were measured relative to external $B(OCH_3)_3$ (δ −18.1 ppm from $BF_3 \cdot O(C_2H_5)_2$). Chemical shifts are reported relative to $BF_3 \cdot O(C_2H_5)_2$. Mass spectra were obtained on Varian MAT CH-5 and CH-5 and CH-7 spectrometers. Samples were introduced into the instrument in sealed glass capillaries.

Materials.—Bridge (μ-) and 2-$SiH_3B_5H_8$ were prepared as described previously.[2] Hydrogen bromide and BCl_3 were purified by fractional condensation. Deuterium chloride was prepared by the hydrolysis of $SiCl_4$ with D_2O.[6] Aluminum chloride and $AlBr_3$ (Matheson Coleman and Bell) were sublimed directly into the reaction vessel prior to use. Boron tribromide (Alfa Inorganics) was used without further purification.

Syntheses of (Halosilyl)pentaboranes. (A) 2-($ClSiH_2$)B_5H_8.—Boron trichloride (0.97 mmol) and 2-$SiH_3B_5H_8$ (3.34 mmol) were condensed at −196° into a Pyrex tube and allowed to react at 0° for 30 min with occasional shaking. Volatile materials from the reaction were removed and passed through a −95° trap into a −196° trap. The −196° trap collected B_2H_6 containing traces of $BHCl_2$ and B_2H_5Cl (0.53 mmol total; confirmed by ir spectrum).[7,8] High-vacuum column distillation[9] of the products in the −95° trap yielded 2-$SiH_3B_5H_8$ (0.59 mmol) and 2-($ClSiH_2$)B_5H_8 (2.62 mmol). The melting point of 2-($ClSiH_2$)B_5H_8 was found to be $-60.1 \pm 0.3°$. The solution molecular weight in pentane was 130; calcd, 127.7. A sharp cutoff in its mass spectrum was observed at *m/e* 132; calcd for $^{37}Cl^{30}Si^{11}B_5H_{10}$, 132. The vapor pressures, given in Table I, conform to the equation $\log P = (-2493.3/T) + 8.9576$. The extrapolated boiling point is 137°, the molar heat of vaporization is 11.4 kcal, and Trouton's constant is 27.8 cal mol^{-1} deg^{-1}. Infrared spectrum (cm^{-1}): 2610 (s), 2180 (s), 1845 (w), 1460 (sh), 1400 (m), 1345 (sh), 1105 (w), 940 (m), 855 (m), 830 (vs), 705 (w), 670 (w), 610 (w), 530 (m).

TABLE I

VAPOR PRESSURE *vs.* TEMPERATURE DATA

2-($ClSiH_2$)B_5H_8			μ-($ClSiH_2$)B_5H_8		
	P, mm			*P*, mm	
Temp, °C	Obsd	Calcd	Temp, °C	Obsd	Calcd
0.0	0.6	0.7	0.0	1.0	1.0
5.7	1.1	1.0	5.6	1.6	1.6
11.8	1.6	1.6	11.1	2.4	2.3
16.8	2.1	2.3	18.0	3.8	3.7
23.1	3.4	3.5	23.8	5.4	5.5
29.6	5.4	5.3	30.1[a]	8.0	8.1
35.9[a]	7.5	7.7			
31.8[b]	6.0	6.0			
26.2[b]	4.4	4.2			
9.5[b]	1.5	1.4			
0.0[b]	0.7	0.7			

[a] Above this temperature the rate of decomposition was appreciable. [b] Pressure observed while decreasing the temperature.

(B) 2-($BrSiH_2$)B_5H_8. BBr_3 Method.—Boron tribromide (2.55 mmol) and 2-$SiH_3B_5H_8$ (10.62 mmol) were condensed at −196° into a tube and slowly warmed to 0°. A rapid reaction occurred as the mixture melted (*ca.* −50°) as evidenced by frothing. The mixture was allowed to react at 0° for 2.5 hr. Diborane (1.28 mmol; confirmed by ir spectrum;[8] vapor tension at −112°: found, 220 mm; lit.,[10] 225 mm) was separated from the product mixture by fractional condensation through a −95° trap into a −196° trap. The material in the −95° trap was separated by high-vacuum fractional distillation and found to

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consist of 2-$SiH_3B_5H_8$ (5.45 mmol), 2-($BrSiH_2$)B_5H_8 (1.60 mmol, 31% yield based on 2-$SiH_3B_5H_8$ reacted), and an incompletely characterized product of low volatility (685 mg; vapor tension at 20° less than 0.3 mm).

In another experiment, BBr_3 (1.65 mmol) was condensed during a 30-min period onto stirred 2-$SiH_3B_5H_8$ (5.99 mmol) maintained at −45°. This mixture was then allowed to react at 0° for an additional 1.5 hr. Separation of the products as above yielded B_2H_6 (0.83 mmol), 2-$SiH_3B_5H_8$ (1.64 mmol), 2-($BrSiH_2$)B_5H_8 (2.52 mmol; 58% yield), and the low volatility fraction (332 mg). The melting point of 2-($BrSiH_2$)B_5H_8 was found to be −51.6 ± 0.1°. A sharp cutoff in its mass spectrum occurred at *m/e* 176 (calcd for $^{81}Br^{30}Si^{11}B_5H_{10}$, 176) This compound had a vapor pressure of 1.2 ± 0.3 mm at 20°. Attempts at obtaining accurate vapor pressure *vs.* temperature data resulted in decomposition of the sample during transfer to the tensimeter. Infrared spectrum (cm^{-1}): 2610 (s), 2180 (s), 1845 (w, b), 1460 (sh), 1400 (m), 1105 (w), 940 (m), 855 (m), 835 (vs), 830 (vs), 675 (w), 535 (m).

(C) 2-($BrSiH_2$)B_5H_8. HBr($AlBr_3$) Method.—Hydrogen bromide (1.53 mmol) and 2-$SiH_3B_5H_8$ (1.26 mmol) were condensed at −196° into a 1-l. flask containing $AlBr_3$. As the flask warmed, the 2-$SiH_3B_5H_8$ melted and frothed for about 30 sec. The mixture was allowed to react at room temperature for 15 min. Hydrogen (1.48 mmol) was removed from the reaction flask, and the volatile products passed through a −95° trap into a −196° trap. High-vacuum fractional distillation of the products condensing in the −95° trap yielded 2-$SiH_3B_5H_8$ (0.35 mmol), 2-($BrSiH_2$)B_5H_8 (0.22 mmol; 24% yield based on 2-$SiH_3B_5H_8$ consumed), and intractable products of low volatility which were not characterized.

(D) μ-($ClSiH_2$)B_5H_8.—Boron trichloride (*ca.* 3.5 mmol) and μ-$SiH_3B_5H_8$ (2.29 mmol) were allowed to react with stirring for 4.5 hr at room temperature. High-vacuum fractional distillation of the products which condensed in a −95° trap yielded μ-$SiH_3B_5H_8$ (0.46 mmol) and μ-($ClSiH_2$)B_5H_8 (1.59 mmol). A trace of H_2 was detected in the reaction mixture and a small amount of uncharacterized nonvolatile yellow liquid remained in the reaction tube. The μ-($ClSiH_2$)B_5H_8 melted at −77.1 ± 0.1°. The mass spectrum exhibited a sharp cutoff at *m/e* 132 (calcd for $^{37}Cl^{30}Si^{11}B_5H_{10}$, 132). Vapor pressures are given in Table I and conform to the equation $\log P = (-2452.9/T) + 8.9985$. The extrapolated boiling point is 128°, the molar heat of vaporization is 11.2 kcal, and Trouton's constant is 28.0 cal mol^{-1} deg^{-1}. Infrared spectrum (cm^{-1}): 2165 (vs), 2215 (sh), 2180 (s), 1845 (w), 1400 (m), 1105 (w), 930 (m), 910 (sh), 900 (sh), 860 (s), 835 (vs), 810 (sh), 745 (w), 675 (w), 615 (m), 530 (m), 460 (w).

In another experiment, boron trichloride (0.24 mmol) and μ-$SiH_3B_5H_8$ (1.02 mmol) were allowed to react for 20 min at 0°. The reaction mixture was passed through a −112° trap into a −196° trap. Condensed in the −112° trap was BCl_3 containing only traces of $BHCl_2$ and B_2H_5Cl (confirmed by ir spectrum), indicating only slight reduction of the BCl_3.

Exchange of 2-$SiH_3B_5H_8$ with DCl($AlCl_3$).—Deuterium chloride (2.69 mmol) and 2-$SiH_3B_5H_8$ (1.24 mmol) were allowed to react in a 1-l. flask for 3.5 hr at room temperature. The DCl and 2-$SiH_3B_5H_8$ were recovered quantitatively and separated by passage through a −112° trap into a −196° trap. No detectable deuterium exchange had occurred as evidenced by the lack of B–D[11] and Si–D[12] stretching absorptions in the infrared spectrum of the recovered 2-$SiH_3B_5H_8$. The DCl and 2-$SiH_3B_5H_8$ were then condensed into a 1-l. flask containing a small amount of $AlCl_3$. The contents of the flask were allowed to react for 1 hr at room temperature. The reaction materials were separated by successive passage into −45, −78, −112, and −196° traps. An unmeasured amount of hydrogen was obtained. The −45° trap contained 2-($ClSiH_2$)B_5H_8 (0.45 mmol) which had undergone appreciable deuterium exchange at terminal boron–hydrogen position(s) as evidenced by an absorption at 1980 cm^{-1} in its infrared spectrum.[11] The −78° trap contained 2-$SiH_3B_5H_8$ which also exhibited the B–D ir stretching absorption. Terminally deuterated pentaborane (0.01 mmol; confirmed by ir spectrum[11]) condensed in the −112° trap. The −196° trap contained DCl (HCl) and traces of SiH_4 and SiH_3Cl (2.42 mmol; confirmed by lack of ir absorption). The deuterated 2-$SiH_3B_5H_8$ (0.87 mmol) was again treated with DCl (6.77 mmol) in the presence of $AlCl_3$ at room temperature for 2 min. Fractional condensation of the products yielded additional deuterated 2-($ClSiH_2$)B_5H_8 (0.36 mmol).

Elemental Analyses.—The decomposition of weighed samples of ($XSiH_2$)B_5H_8 (where X = Cl or Br) for elemental analysis was effected by hydrolysis for 12 hr at 95° with 2 ml of 2 *N* KOH followed by the addition of 1 ml of 6 *N* HNO_3 and an additional 12-hr hydrolysis at 95°. Hydrolytic hydrogen was calculated according to the equation

$$(XSiH_2)B_5H_8 + 17H_2O \longrightarrow SiO_2 + 5B(OH)_3 + HX + 14H_2$$

Anal. Calcd for 2-($ClSiH_2$)B_5H_8: Cl, 27.8%; H_2, 110 mmol/g. Found: Cl, 28.4%; H_2, 111 mmol/g. Calcd for μ-($ClSiH_2$)B_5H_8: Cl, 27.8%; H_2, 110 mmol/g. Found: Cl, 28.4%; H_2, 113 mmol/g. Calcd for 2-($BrSiH_2$)B_5H_8: B, 31.4%; Br, 46.4%; H_2, 81.4 mmol/g. Found: B, 32.5%; Br, 46.4%; H_2, 82.0 mmol/g.

Results and Discussion

Halogenation Reactions.—Halogenation of the SiH_3 group in 2-$SiH_3B_5H_8$ occurs smoothly upon reaction with BCl_3 and BBr_3, respectively (eq 1), or upon reaction with hydrogen halides in the presence of aluminum halide catalysts (eq 2) (X = Cl or Br; m = 2 or μ). Similarly, μ-$SiH_3B_5H_8$ is chlorinated in reactions with BCl_3 (eq 1). Halogenation occurred exclusively at the silicon atom in all reactions studied.

$$2BX_3 + 6\ m\text{-}SiH_3B_5H_8 \longrightarrow B_2H_6 + 6\ m\text{-}(XSiH_2)B_5H_8 \qquad (1)$$

$$HX + 2\text{-}SiH_3B_5H_8 \xrightarrow{AlX_3} H_2 + 2\text{-}(XSiH_2)B_5H_8 \qquad (2)$$

No evidence for halogenation of the pentaborane unit was obtained. When boron trihalides were used as the halogenating agents, no cleavage or decomposition products were detected. Chlorination of 2-$SiH_3B_5H_8$ with BCl_3 occurred quantitatively (within 5%) under the conditions studied. However, the reaction of DCl–$AlCl_3$ with 2-$SiH_3B_5H_8$ yielded traces of SiH_4, SiH_3Cl, and B_5H_9, presumably as a result of cleavage of the Si–B bond. Likewise, when a mixture of 2-$SiH_3B_5H_8$, HBr, and $AlBr_3$ was allowed to stand at room temperature for several hours, large amounts of SiH_4, SiH_3Br, SiH_2Br_2, $SiHBr_3$, and B_5H_9 were recovered, and only a trace of 2-($BrSiH_2$)B_5H_8 was found.

Under reaction conditions in which quantities of BCl_3 equal to or slightly greater than that required for monohalogenation were used, there was no evidence for the formation of di- or trichlorinated products of either μ-$SiH_3B_5H_8$ or 2-$SiH_3B_5H_8$. However, in the BBr_3 bromination of 2-$SiH_3B_5H_8$ large amounts of a low-volatility compound were obtained. Only limited data were obtained to characterize this compound because of its extremely low volatility. This species exhibited an ^{11}B nmr spectrum consistent with that expected for a 2-substituted pentaborane. Its ir spectrum exhibited strong Si–H and B–H stretching absorptions plus several peaks characteristic of a B_5 species.[11] From these data and the fact that it is formed along with 2-SiH_3-

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B_5H_8 upon the disproportionation of 2-$(BrSiH_2)B_5H_8$, the compound is presumed to be 2-$(Br_2SiH)B_5H_8$.

Insufficient data are available to allow a detailed assessment of the effect of pentaboranyl-group substitution on the rate of boron trihalide or hydrogen chloride–aluminum chloride chlorination of silane to be made. However, tentative conclusions concerning the BCl_3 chlorinations can be stated. The 2-$SiH_3B_5H_8$ reacts quantitatively within 30 min at 0°. In contrast, μ-$SiH_3B_5H_8$ is incompletely reacted after 4.5 hr at room temperature. Monosilane (SiH_4) reportedly undergoes no reaction with BCl_3 at 0°,[13] although, in the presence of a free-radical initiator reaction does occur.[14] These data suggest that pentaboranyl-group substitution markedly enhances the reactivity of the SiH_3 moiety toward BCl_3. The increased effectiveness of a 2-B_5H_8 group over a μ-B_5H_8 group is apparent also. However, until more data are available speculation into the basis of the reactivity differences seems unjustified.

Characterization of (Halosilyl)pentaboranes.—The 2-$(ClSiH_2)B_5H_8$ and μ-$(ClSiH_2)B_5H_8$ were characterized on the basis of elemental analyses, solution molecular weights, and infrared, ^1H nmr, ^{11}B nmr, and mass spectral data. Where possible, vapor tension data were obtained.

The mass spectra of the new compounds exhibited fragmentation patterns consistent with those expected for (halosilyl)pentaboranes. In each case a weak molecular ion was observed, providing confirmation of the molecular weight and compound stoichiometry.

The infrared spectra show characteristic Si–H, B–H (terminal), and B–H(bridge) stretching absorptions at 2180, 2610–2615, and 1845 cm^{-1}, respectively.[11,15,16] In addition, absorptions at 930 cm^{-1} in μ-$(ClSiH_2)$-B_5H_8 and 940 cm^{-1} in 2-$(ClSiH_2)B_5H_8$ and 2-$(BrSiH_2)$-B_5H_8 attributable to the SiH_2 bending vibration were observed.[15] Owing to the complexity of the spectra, no attempt was made to assign the remaining absorptions.

The nmr spectral parameters are given in Table II.

TABLE II

^{11}B AND ^1H NMR SPECTRAL RESULTS[a]

	^{11}B[b]				^1H[c]
Compound	B(1) (*J*)	B(2)	B(3, 5) (*J*)	B(4) (*J*)	$\delta(SiH_2)$ (*J*)
2-$(ClSiH_2)B_5H_8$	50.4 (178)	15.2	11.2 (184)	6.1 (150)	−4.67 (11.4)
2-$(BrSiH_2)B_5H_8$	40.3 (172)	16.5	11.4 (170)	6.5 (145)	−4.28 (8.4)
			B(2–5) (*J*)		
μ-$(ClSiH_2)B_5H_8$	44.7 (178)		9.5 (160)		−5.40

[a] Obtained on 20–50% (by volume) solutions in CS_2. [b] Chemical shifts in ppm relative to $BF_3 \cdot O(C_2H_5)_2$; coupling constants in Hz. [c] Chemical shifts in ppm relative to internal $(CH_3)_4Si$; apparent coupling constants in Hz.

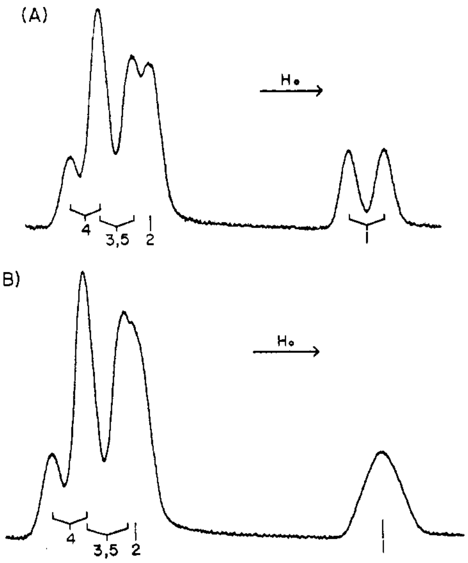

Figure 1.—The 32.1-MHz ^{11}B nmr spectra of 2-$(BrSiH_2)B_5H_8$ (A) and apically deuterated (B(1)) 2-$(ClSiH_2)B_5H_7D$ (B).

The ^{11}B nmr spectrum of 2-$(BrSiH_2)B_5H_8$, shown in Figure 1A, is representative of that observed for 2-$(BrSiH_2)B_5H_8$ and 2-$(ClSiH_2)B_5H_8$. The upfield doublet (area 1) occurs in the region typical for the apical boron of a pentaborane derivative. The group of peaks in the low-field region of the spectra (area 4) consists of an overlapped doublet of intensity 1, B(4), a doublet of intensity 2, B(3,5), and a singlet of intensity 1, B(2). The peak at highest field in the group for both spectra was assigned to the boron bonded to the halosilyl group, B(2). This assignment agrees with that made for the 2-$SiH_3B_5H_8$ spectrum in which the B(2) resonance is at highest field in the group.[2] This assignment also gives a reasonable value for the B–H coupling constant for the doublet assigned to the borons in the 3,5 positions.[17]

The ^{11}B nmr spectrum of μ-$(ClSiH_2)B_5H_8$ is similar to that of B_5H_9[18] and μ-$SiH_3B_5H_8$.[2] The spectrum consists of a high-field doublet of intensity 1 (apical boron) and a low-field doublet of intensity 4 (basal borons). Thus, although the B(2)–B(3) borons are bridged by the SiH_2Cl group and the B(4)–B(5) borons are bridged by a proton, all four basal borons appear magnetically equivalent.

The ^1H nmr spectra of 2-$(ClSiH_2)B_5H_8$, 2-$(BrSiH_2)$-B_5H_8, and μ-$(ClSiH_2)B_5H_8$ are particularly interesting because the resonance arising from the SiH_2 protons is temperature dependent. Representative ^1H nmr data obtained for 2-$(BrSiH_2)B_5H_8$ are shown in Figure 2. At ambient probe temperature (34°) the SiH_2 resonance appears as a broad, poorly resolved doublet (Figure 2A). The line width at half-peak intensity ($\nu_{1/2}$) is 27 Hz. At −13°, the doublet collapses to a broad singlet of $\nu_{1/2}$ = 19 Hz (Figure 2B). Upon further cooling to −85° a sharp singlet resonance of $\nu_{1/2}$ = 4.5 Hz (Figure 2C) is obtained. Within experimental error, the chemical shift of the resonance is temperature independent. Owing to the marginal stability of the

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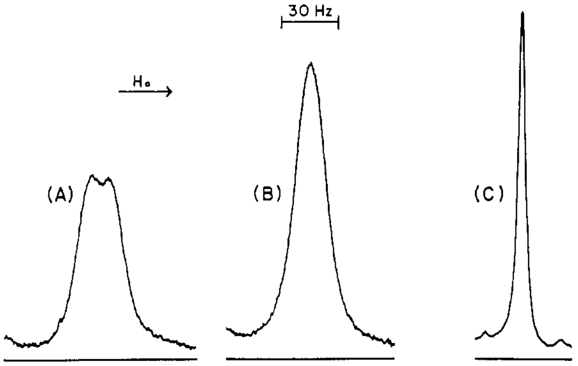

Figure 2.—The SiH$_2$ resonance in the ^{1}H nmr spectrum of 2-(BrSiH$_2$)B$_5$H$_8$ at 34° (A), −13° (B), and −85° (C).

(halosilyl)pentaboranes no attempt was made to examine the spectra above 34°.

Electric quadrupole relaxation of a nucleus of $I = {}^3/_2$ coupled to a nucleus of $I = {}^1/_2$ has been examined theoretically and experimentally by Bacon, Gillespie, and Quail.[19] These workers have shown that quadrupolar relaxation can produce spectral effects analogous to those observed for the (halosilyl)pentaboranes examined in this study. However, for boron compounds, this effect has been reported only for the ^{19}F nmr spectra of compounds in which the fluorine atom is directly bonded to the boron atom. The (halosilyl)pentaboranes appear to be the first examples of molecules in which the temperature dependence is observed to affect a two-bond coupling constant between hydrogen and boron.

Evidence to support the interpretation that the splitting of the SiH$_2$ resonance arises due to coupling with the 2-boron atom and not from coupling to other nuclei in the system was obtained from a heteronuclear spin decoupling, ^{1}H–^{11}B, experiment. Irradiation of the ^{11}B nuclei at a nominal frequency of 32.1 MHz using a "noise" decoupler while scanning the 100-MHz ^{1}H spectrum caused the broad doublet resonance to collapse to a sharp singlet of $\nu_{1/2} = 3$ Hz.

Deuteration Reactions.—The deuteration of 2-SiH$_3$B$_5$H$_8$ and 2-(ClSiH$_2$)B$_5$H$_8$ by DCl–AlCl$_3$ appears to occur in a manner analogous to that reported for B$_5$H$_9$.[20] The infrared and ^{11}B nmr spectra of the 2-silylpentaborane which is recovered and the 2-(chlorosilyl)pentaborane which is formed from the 2-SiH$_3$-B$_5$H$_8$–DCl(AlCl$_3$) reaction indicate that specific deuteration at the 1 position of both compounds occurs. Ir absorptions at 1980 cm^{-1} for 2-silylpentaborane and 2-(chlorosilyl)pentaborane indicate the presence of deuterium in terminal positions. The collapse of only the upfield doublets to singlets in the ^{11}B nmr spectra (Figure 1B) suggests that, within experimental error, deuteration has occurred specifically at the 1 position. The presence of deuterium in bridging positions cannot be unambiguously excluded, since both 2-SiH$_3$B$_5$H$_8$ and 2-(ClSiH$_2$)B$_5$H$_8$ have broad infrared absorptions in the region where bridge-deuterium absorptions are expected to occur.

Acknowledgment.—Support of this work by the National Science Foundation (GP-8090) is gratefully acknowledged.

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Magnetic Resonance Spectra of Tetraborane(10), Pentaborane(11), Hexaborane(10), and Hexaborane(12)

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Received May 14, 1970

The 220-MHz ^{1}H and 70.6-MHz ^{11}B nmr spectra of B$_4$H$_{10}$, B$_5$H$_{11}$, B$_6$H$_{10}$, and B$_6$H$_{12}$ have been recorded and confirm the previously accepted structures. Further elucidation of basal and apical signals of B$_4$H$_{10}$, B$_5$H$_{11}$, and B$_6$H$_{10}$ was obtained by multiple decoupling experiments at 100 MHz. In the pmr spectra at 51.680 kG two magnetically nonequivalent sets of protons are resolved for the –BH$_2$ groups of B$_4$H$_{10}$, B$_5$H$_{11}$, and B$_6$H$_{12}$. Distinct bridge resonance signals are found in B$_5$H$_{11}$. In addition, the apically attached anomalous proton and the single-bridge proton lying on the symmetry plane display additional fine structure.

Introduction

Proton magnetic resonance spectra of boron hydrides obtained at lower field strength have proved to be less informative in chemical and structural studies than the more easily interpreted ^{11}B nmr spectra.[2] The complexity of the pmr spectra arises from the coupling of each distinct proton with both boron isotopes (80% ^{11}B,

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[2] (a) R. Schaeffer, "Progress in Boron Chemistry," Vol. 1, H. Steinberg and A. L. McCloskey, Ed., Macmillan, New York, N. Y., 1964, p 422; (b) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.