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Directive Effects in Bridge Cleavage Reactions of Methyl-Substituted Boron Hydrides. 1. Preparation and Nuclear Magnetic Resonance Spectra of 3-$CH_3B_6H_{11}$, 3-$CH_3B_6H_{10}$, and 1-$CH_3B_4H_9$

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Procedures have been developed for preparing certain specifically methyl-substituted boron hydrides: 3-$CH_3B_6H_{11}$, 3-$CH_3B_5H_{10}$, and 1-$CH_3B_4H_9$. The methyl-substituted derivative of B_6H_{12}, 3-$CH_3B_6H_{11}$, is prepared by adding BH_3 to 1-$CH_3B_5H_7^-$ followed by protonation with HCl. Starting with 3-$CH_3B_6H_{11}$, the lower hydrides are prepared through the following sequence of steps: (1) cleavage of the bridge system with ammonia yielding $[BH_2(NH_3)_2^+][3\text{-}CH_3B_5H_9^-]$; (2) protonation of the anion with liquid HCl yielding 3-$CH_3B_5H_{10}$. The same sequence applied to 3-$CH_3B_5H_{10}$ yields 1-$CH_3B_4H_9$. A directive effect appears to be operative in the cleavage reactions. In each case, boron atoms farthest from the methyl group are split off from the framework. The methyl-substituted boron hydrides 3-$CH_3B_6H_{11}$, 3-$CH_3B_5H_{10}$, and 1-$CH_3B_4H_9$ appear to be more stable than the parent hydrides B_6H_{12}, B_5H_{11}, and B_4H_{10}.

Introduction

In conjunction with the development in this laboratory of practical preparations of B_6H_{10},[2] B_6H_{12}, and B_5H_{11},[3] we have been concerned with the development of principles for the syntheses of specific methyl-substituted derivatives of the boron hydrides. Our preparation of 2-$CH_3B_6H_9$[2] using a procedure similar to that of the preparation of B_6H_{10}[2] suggested that the procedure for the preparation of B_6H_{12}[3] might be similarly adapted for high-yield synthesis of methyl-substituted derivatives of B_6H_{12}. In the present paper, we describe the preparation of 3-$CH_3B_6H_{11}$ and then show how this compound is the starting material for a sequence of steps which effectively involve selective degradation of the B_6 framework using ammonia as the cleaving agent, to yield 3-$CH_3B_5H_{10}$ and 1-$CH_3B_4H_9$. Assignments of structures are based upon boron-11 and proton NMR spectra.

Results and Discussion

Preparative Reactions. 3-Methylhexaborane(12), 3-$CH_3B_6H_{11}$, was prepared in 80–90% yields using the sequence of steps in eq 1–3.

$$1\text{-}CH_3B_5H_8 + KH \xrightarrow[-78\ ^\circ C]{(CH_3)_2O} K[1\text{-}CH_3B_5H_7] + H_2 \quad (1)$$

$$K[1\text{-}CH_3B_5H_7] + {}^1/_2B_2H_6 \xrightarrow[-78\ ^\circ C]{(CH_3)_2O} K[CH_3B_6H_{10}] \quad (2)$$

$$K[CH_3B_6H_{10}] + HCl \xrightarrow{-110\ ^\circ C} 3\text{-}CH_3B_6H_{11} + KCl \quad (3)$$

Starting with 3-$CH_3B_6H_{11}$, the lower hydrides 3-$CH_3B_5H_{10}$ and 1-$CH_3B_4H_9$ were prepared in 70–80% yields via the sequence of steps in eq 4–7.

$$3\text{-}CH_3B_6H_{11} + 2NH_3 \xrightarrow[-78\ ^\circ C]{CH_2Cl_2} [BH_2(NH_3)_2][CH_3B_5H_9] \quad (4)$$

$$[BH_2(NH_3)_2][CH_3B_5H_9] + HCl \xrightarrow{-110\ ^\circ C} BH_2(NH_3)_2Cl + 3\text{-}CH_3B_5H_{10} \quad (5)$$

$$CH_3B_5H_{10} + 2NH_3 \xrightarrow[-78\ ^\circ C]{CH_2Cl_2} [BH_2(NH_3)_2][CH_3B_4H_8] \quad (6)$$

$$[BH_2(NH_3)_2][CH_3B_4H_8] + HCl \xrightarrow{-110\ ^\circ C} BH_2(NH_3)_2Cl + 1\text{-}CH_3B_4H_9 \quad (7)$$

Table I. 32.1-MHz Boron-11 NMR Data[a-c]

atom	δ	J_{BH}	atom	δ	J_{BH}	atom	δ	J_{BH}	J_{BH} br[d]
B_6H_{12}			B_5H_{11}			B_4H_{10}			
B_3,B_6	+22.6	156	B_2,B_5	+7.44	132	B_2,B_4	−5.16	132	~30
B_1,B_4	+7.9	133	B_3,B_4	+0.47	160	B_1,B_3	−4.7	160	~23
B_2,B_5	−22.6	158	B_1	−55.2	152				
3-$CH_3B_6H_{11}$			3-$CH_3B_5H_{10}$			1-$CH_3B_4H_9$			
B_3	+35.2		B_3	+20.4		B_2,B_4	−4.7	129	~26
B_6	+20.5	150	B_5	+8.78	122	B_1	−29		~40
B_4 or B_1	+9.8	124	B_2	−2.36	127	B_3	−41.1	161	
B_1 or B_4	+6.2	114	B_4	−7.77	179				
B_2 or B_5	−19.1	162	B_1	−52.02	142				
B_5 or B_2	−24.0	151							

[a] Chemical shifts are expressed in ppm relative to $\delta[BF_3\cdot O(C_2H_5)_2] = 0.0$. [b] Deviations: δ, ±0.2 ppm; *J*, ±5 Hz. A positive sign denotes a shift downfield from the reference.[19] [c] Coupling constants are in hertz. [d] Bridging hydrogen.

At room temperature 3-$CH_3B_6H_{11}$, 3-$CH_3B_5H_{10}$, and 1-$CH_3B_4H_9$ are clear liquids which display greater thermal stabilities than the parent hydrides B_6H_{12}, B_5H_{11}, and B_4H_{10}. Samples of 3-$CH_3B_6H_{11}$, 3-$CH_3B_5H_{10}$, and 1-$CH_3B_4H_9$ which have been purified either by fractional distillation or by gas chromatography can be handled at room temperature on the order of 20 min without apparent decomposition, based upon vapor pressure and NMR data. Vapor pressure data for these compounds are given in the Experimental Section.

The results of the reactions cited above clearly indicate a directive effect produced by the presence of a methyl group. The reactant boranes 3-$CH_3B_6H_{11}$ and 3-$CH_3B_5H_{10}$ each have two BH_2 groups, one of which is adjacent to the methylated boron atom. In each case, only the removal of the *distant* BH_2 group accounts for the observed products without necessitating extensive skeletal rearrangement or methyl-group migration. Figure 1 depicts the topological relationship between 3-$CH_3B_6H_{11}$ and 3-$CH_3B_5H_{10}$ and between 3-$CH_3B_5H_{10}$ and 1-$CH_3B_4H_9$. It seems unlikely that steric considerations are primarily responsible for these apparent directive effects. More likely an inductive effect is the principal factor. It is reasonable to assume that the splitting off of boron from the framework occurs through nucleophilic attack by ammonia at the more positive H_2B boron site in the structure.[4] Since this site appears to be the boron atom farthest removed from the methyl group, a simple rationalization of this result is to assume that the methyl group is releasing electron density, thereby causing the BH_2 boron adjacent to it to be less positive than the farthest removed BH_2 boron. Such an "explanation" is consistent with observations of Brice and Shore[5] and Fehlner and Ulman[6] on 1-$CH_3B_5H_8$, 2-$CH_3B_5H_8$, and 2-$CH_3B_6H_9$.

NMR Spectra. 3-$CH_3B_6H_{11}$. Boron-11 NMR spectra of 3-$CH_3B_6H_{11}$ (proton-coupled and proton-decoupled) are compared with the boron-11 NMR spectrum of B_6H_{12}[7] in Figure 2 (see Table I). In the proton-coupled spectrum of B_6H_{12}, the B_3,B_6 resonances are a single doublet of area 2. In

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Table II. 100-MHz Proton NMR Data[a,b]

atom	τ	atom	τ	atom	τ
B_6H_{12}		B_5H_{11}		B_4H_{10}	
H_3,H_6	4.9	H_{2e},H_{5e}	6.5	H_{2e},H_{4e}	7.54
H_{1a},H_{4a} or H_{1e},H_{4e}	5.8	H_3,H_4	6.6	H_{2a},H_{4a}	7.74
H_{1e},H_{4e} or H_{1a},H_{4a}	6.1	H_{2a},H_{5a}	6.9	H_1,H_3	8.66
H_2,H_5	7.9	H_μ	8.2	μ	11.38
μ	10.2	$\mu_{2,3},\mu_{4,5},H_1$	10.6		
		$\mu_{3,4}$	12.0		
$3\text{-}CH_3B_6H_{11}$		$3\text{-}CH_3B_5H_{10}$		$1\text{-}CH_3B_4H_9$	
H_6	5.55	$H_{2a},H_{2e},H_{5a},H_{5e}$[c]	6.65, 6.87	H_{2e},H_{4e}	7.41
$H_{1a},H_{1e},H_{4a},H_{4e}$[c]	6.45, 6.55, 6.63, 6.83	H_4	7.24	H_{2a},H_{4a}	7.57
H_2 or H_5	8.46	H_μ	8.13	CH_3	9.68
H_5 or H_2	8.58	CH_3	9.27	H_3	9.85
CH_3	9.2	μ,[d] H_1	10.44	μ	10.82
μ	10.32, 10.54, 10.75[c]	μ[d]	10.03, 11.32		

[a] Chemical shifts are expressed in ppm relative to $\tau(Me_4Si) = 10.00$. [b] Values are accurate to $\tau \pm 0.04$. The solvent is $CHCl_3$. The letters e and a denote the equatorial and axial hydrogens on the BH_2 groups. [c] Individual basal terminal hydrogen resonances were not assigned. [d] Hydrogen bridges $\mu_{2,3}$, $\mu_{3,4}$, and $\mu_{4,5}$ were not assigned.

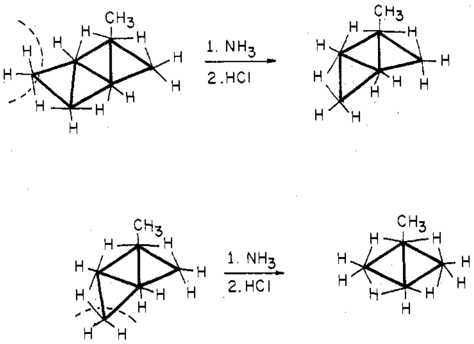

Figure 1. Topological relationships of organoboranes derived from cleavage reactions.

the proton-coupled spectrum of the organoborane, the corresponding resonance is approximately halved and is assigned to B_6. The low-field singlet in this spectrum is assigned to B_3, the methyl-substituted boron. The large downfield shift of this resonance is in accord with general observations of methyl-substituted boron hydrides.[5,8,9] The triplet which is assigned to B_1 and B_4 in the B_6H_{12} spectrum is replaced by an apparent quartet in the spectrum of $3\text{-}CH_3B_6H_{11}$. This is the result of partial overlap of the B_1 and B_4 triplets. The high-field doublet in the B_6H_{12} spectrum assigned to B_2 and B_5 is replaced by an apparent triplet in the spectrum of $3\text{-}CH_3B_6H_{11}$. This is the result of partial overlap of the B_2 and B_5 doublets. The broad-band proton-decoupled boron-11 NMR spectrum of $3\text{-}CH_3B_6H_{11}$ (Figure 2c) clearly indicates the asymmetry of the molecule by showing the six separate boron resonances. The only assignments which can be made with any certainty are the obvious ones, i.e., B_3 and B_6. Trends which indicate the influence of methyl-substituted boron on the chemical shift of other boron atoms in *nido*-alkylboranes[10] have not been shown to necessarily apply for *arachno*-alkylboranes. Therefore we choose not to make assignments of *arachno*-$3\text{-}CH_3B_6H_{11}$ based upon such trends.

The broad-band boron-11-decoupled proton NMR spectrum of $3\text{-}CH_3B_6H_{11}$ is compared with that of B_6H_{12} in Figure 3 (see Table II). Assignments to B_6H_{12} were made in an earlier work.[7] Selective boron-11 decoupling was used to make assignments. However, the hydrogens on the pairs B_1,B_4 and B_2,B_5 could not be individually assigned since the individual boron resonances in each pair could not be assigned. For the same reason bridging resonances could not be individually assigned.

$3\text{-}CH_3B_5H_{10}$. Boron-11 NMR spectra of $3\text{-}CH_3B_5H_{10}$ (proton-coupled and proton-decoupled) are compared with the

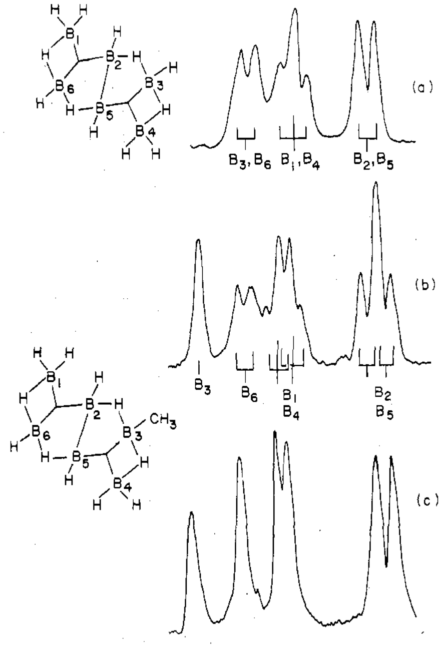

Figure 2. Boron-11 NMR specta at 32.1 MHz in $CHCl_3$ at −20 °C: (a) B_6H_{12}, (b) $3\text{-}CH_3B_6H_{11}$, (c) $3\text{-}CH_3B_6H_{11}$, proton decoupled.

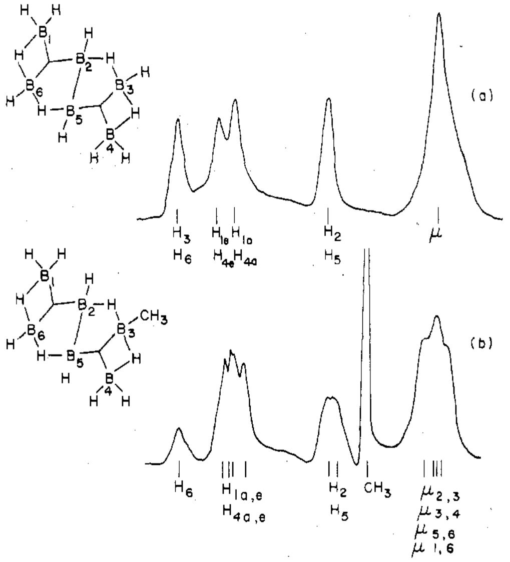

Figure 3. Proton NMR spectra at 100 MHz, boron-11-decoupled, in $CHCl_3$ at −20 °C: (a) B_6H_{12}, (b) $3\text{-}CH_3B_6H_{11}$.

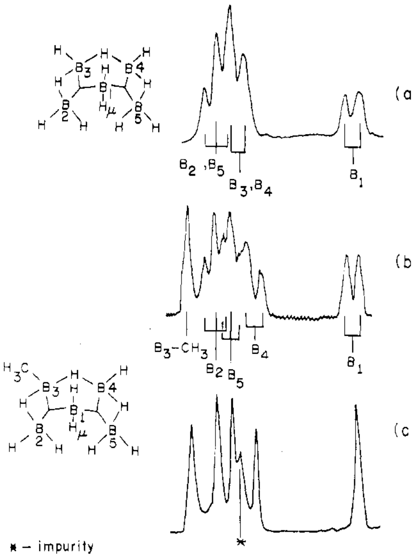

Figure 4. Boron-11 NMR spectra at 32.1 MHz in CH_2Cl_2 at −35 °C: (a) B_5H_{11}, (b) 3-$CH_3B_5H_{10}$, (c) 3-$CH_3B_5H_{10}$, proton decoupled.

proton-coupled spectrum of B_5H_{11}[7,11–13] in Figure 4 (see Table I). Assignments are straightforward. In this proton-coupled spectrum of B_5H_{11} the B_3,B_4 resonances are a single doublet of area 2. In the proton-coupled spectrum of the organoborane, the corresponding resonance is approximately halved and is assigned to B_4. The low-field singlet in this spectrum is assigned to B_3, the methyl-substituted boron. The absence of doublet character for this resonance suggests that no terminal hydrogen is bound to this boron, thereby eliminating B_2 as a possible assignment. For the pair of atoms B_2,B_5 in 3-$CH_3B_5H_{10}$, we assume that B_2 will show the larger change in chemical shift from the B_2,B_5 pair in B_5H_{11} (see Table I) since it is adjacent to the the methyl-substituted boron. On this basis we have assigned B_2 and B_5. As with the parent hydride,[7] the apical (B_1) resonance of 3-$CH_3B_5H_{10}$ is a doublet. There is apparent spin coupling with only one of its two hydrogens. The second hydrogen is believed to function more as a bridging hydrogen, alternately between B_2 and B_5.

The broad-band proton-decoupled spectrum in Figure 4 reveals the five separate resonances of 3-$CH_3B_5H_{11}$ plus the resonance of an impurity (−0.74 ppm). Careful gas chromatographic separation reduced the concentration of this impurity, but it could not be completely removed. The undecoupled impurity resonance (obtained by selectively decoupling adjacent B_4 and B_5 resonances) is either a doublet or a quartet. We have been unable to identify the impurity. However, it is not an obvious decomposition product such as 2-$CH_3B_5H_8$ or 1-$CH_3B_5H_8$.

The broad-band boron-11-decoupled proton NMR spectrum of 3-$CH_3B_5H_{10}$ is compared with that of B_5H_{11} in Figure 5 (see Table II). An earlier investigation reported the hydrogen assignments for B_5H_{11}.[7] Selective decoupling was used to make assignments for all hydrogens which are terminally bound to boron atoms, including H_μ. Although not visible in the spectrum shown in Figure 5, selective decoupling experiments revealed the separate resonances assigned to H_1 and μ. Bridging hydrogens were less sensitive to selective decoupling than terminal hydrogens; therefore the assignments of bridging hydrogens were not made.

The two impurity resonances (9.62 and 11.78 ppm) were reduced when the sample was carefully chromatographed but they could not be eliminated. The more intense resonance shows no apparent spin coupling to boron. Although the impurity or impurities could not be removed, a carefully fractionated sample had a mass spectrum which showed no peaks above the parent mass of 3-$CH_3B_5H_{10}$ and had a vapor density which gave a molecular weight that agreed within 3% of the theoretical value.

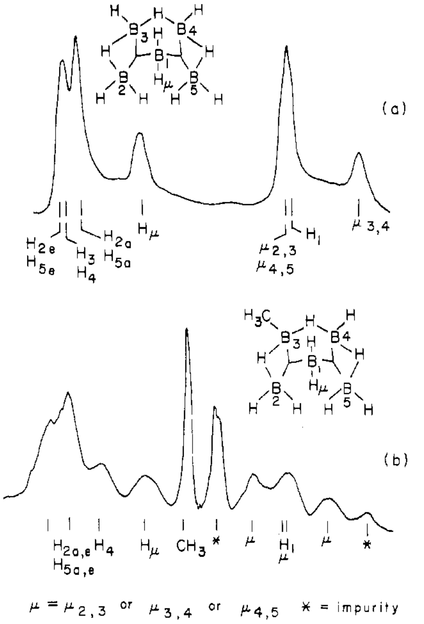

Figure 5. Proton NMR spectra at 100 MHz, boron-11-decoupled, in CH_2Cl_2 at −35 °C: (a) B_5H_{11}, (b) 3-$CH_3B_5H_{10}$.

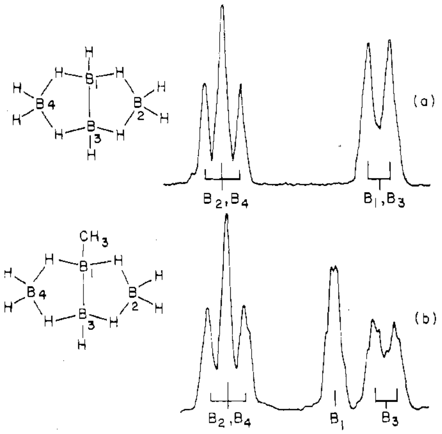

Figure 6. Boron-11 NMR spectra at 32.1 MHz in $CHCl_3$ at −30 °C: (a) B_4H_{10}, (b) 1-$CH_3B_4H_9$.

1-$CH_3B_4H_9$. Figure 6 compares the boron-11 NMR spectrum of 1-$CH_3B_4H_9$ with that of B_4H_{10} (see Table I). The spectrum is readily interpreted in terms of a structure in which the methyl group resides on B_1. The triplet assigned to B_2 and B_4 arises from spin coupling of terminal hydrogens with each boron atom. The doublet assigned to B_3 arises from spin coupling with the single terminal hydrogen. Fine structure appears on all of the resonances. In the case of B_4H_{10} such fine structure has been interpreted in terms of spin coupling with bridge[14–17] hydrogen plus long-range coupling. By expanding the individual resonances of 1-$CH_3B_4H_9$, sufficient resolution was attained to allow estimation of bridge hydrogen spin coupling with boron (Table I).

Figure 7 compares the boron-11-decoupled proton NMR spectrum of 1-$CH_3B_4H_9$ with that of B_4H_{10} (see Table II). The assignments for B_4H_{10} are based on earlier studies.[18]

Experimental Section

Apparatus. All manipulations were carried out in a standard high-vaccum line or in a glovebox under a nitrogen atmosphere. Proton NMR spectra were recorded on a Varian HA-100 high-resolution spectrometer operating at 100 MHz. Boron-11 NMR spectra were recorded on the same instrument at 32.1 MHz in the HR mode.

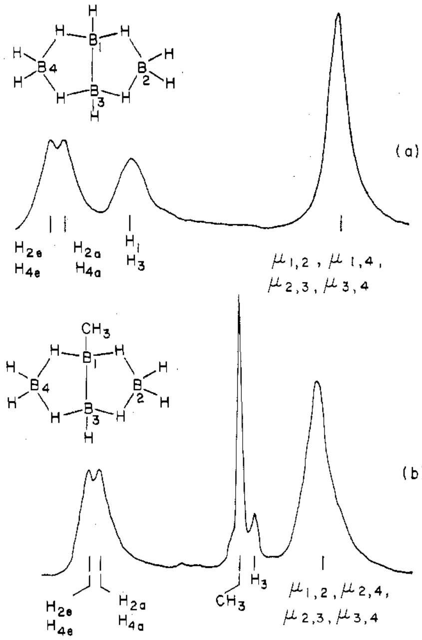

Figure 7. Proton NMR spectra at 100 MHz, boron-11-decoupled, in $CHCl_3$ at −30 °C: (a) B_4H_{10}, (b) 1-$CH_3B_4H_9$.

Heteronuclear decoupling was accomplished by means of accessories which have been previously described.[3a] Proton chemical shifts are reported in τ units relative to $\tau[(CH_3)_4Si] = 10$ using $\tau(CHCl_3) = 2.75$ or $\tau(CH_2Cl_2) = 4.68$ as the internal standard. Boron-11 NMR shifts are given in ppm relative to $BF_3{\cdot}O(C_2H_5)_2$ using BCl_3 (δ +46.8) as an external standard.[19] Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer. Gaseous samples were run in a 10-cm cell equipped with KBr windows. Mass spectra were obtained on an AEI MS-9 mass spectrometer. X-ray powder patterns were obtained using a North American Philips X-ray generator employing a copper target and a nickel filter. A Debye-Scherrer camera with a diameter of 11.46 cm was used. Gas chromatographic separation was performed using previously described procedures.[20] A series 1700 Varian Aerograph chromatograph, fitted with 250-cm columns of glass (6 mm o.d.) or stainless steel (0.25 in. o.d.) packed with 20% Apiezon L on 60/80 mesh chromosorb P, was used at ambient temperature. A variable effluent splitter, with a ratio of approximately 50:1, was used to minimize decomposition in the detector.

Starting Materials. Diborane(6) and B_5H_9 were purchased from Callery Chemical Co., Callery, Pa. Hydrogen chloride was obtained from the J. T. Baker Co., Phillipsburg, N.J. Potassium hydride was obtained from ROC/RIC, Sun Valley, Calif., and was freed of oil by washing under vacuum with anhydrous pentane. 1-Methylpentaborane(9) and 2-methylpentaborane(9) were prepared according to literature methods.[21,22]

Preparation of 3-$CH_3B_6H_{11}$. In a typical preparation 11.8 mmol of 1-$CH_3B_5H_8$ was deprotonated by KH in dimethyl ether solvent at −78 °C. After the hydrogen had been pumped away, 6 mmol of B_2H_6 was added, and the mixture was allowed to stir for 2 h at −78 °C. The solvent was then removed by pumping at −78 °C for 14 h and at −45 °C for an additional 3 h. It is important that no dimethyl ether remain in the reaction vessel during the protonation because $CH_3B_6H_{11}$ may undergo a cleavage reaction with the ether. After all of the solvent had been removed, 8 mL of anhydrous HCl was condensed onto the residue, and the protonation was allowed to proceed at −110 °C for 30 s. Methylhexaborane(12) was separated from the reaction mixture by passing the products through a series of cold traps at −45, −78, and −196 °C. Methylhexaborane(12) is stopped at −78 °C. Some unidentified volatile material remained in the −45 °C trap. Purification was achieved by repeated fractional condensation from a −45 °C trap into a −78 °C trap until the vapor pressure at 0 °C remained constant at 6 torr. The yield of 3-$CH_3B_6H_{11}$ was 10.75 mmol or 91%. The product was stored at −78 °C in a tube fitted with a Teflon stopcock.

Infrared spectrum of 3-$CH_3B_6H_{11}$ (cm^{-1}): 2973 (w), 2921 (w), 2593 (s), 2508 (s), 2000 (m, br), 1941 (m, br), 1860 (w), 1628 (w), 1518 (s), 1438 (m, br), 1387 (m), 1329 (m), 1170 (m), 1130 (w), 1097 (w), 1049 (s), 1030 (s), 965 (m), 940 (m), 900 (m), 813 (w), 746 (m), 705 (m), 597 (w), 539 (m), 461 (m).

The normal boiling point (124 ± 2 °C) of 3-$CH_3B_6H_{11}$ was estimated from an extrapolated plot of log P vs. $1/T$, and the heat of vaporization (8.5 ± 0.1 kcal/mol) was calculated from the slope of the plot using the Clausius–Clapeyron equation. The experimental vapor pressures are as follows: 0 °C, 6 torr; 14 °C, 13.0 torr; 21 °C, 18.2 torr.

The molecular weight of 3-$CH_3B_6H_{11}$ was determined by the vapor-density method. A 0.0276-g sample of 3-$CH_3B_6H_{11}$ exerted a pressure of 18.2 torr in a volume of 291.39 mL at 21.0 °C. The molecular weight was calculated to be 95.5. A second determination gave a value of 87.2 (theoretical 90.8). The mass spectrum shows a cutoff at the expected mass to charge ratio of 92 for $CH_3{}^{11}B_6H_{11}$.

Preparation of $CH_3B_5H_{10}$. In a typical preparation, 10 mmol of 3-$CH_3B_6H_{11}$ and 15 mL of CH_2Cl_2 were condensed into a 50-mL bulb containing a Teflon-covered stirring bar. The contents were warmed to −78 °C and 20 mmol of NH_3 was allowed to expand into the vigorously stirred reaction mixture. Within 15 min, a gummy precipitate formed which severely impeded the stirring of the system. Several hours later, the gum started to break up and a white precipitate began to appear. After 2 days of constant stirring, the gum disappeared completely and only the white precipitate remained. After the solvent was removed by pumping at −78 °C for 2 days and at −45 °C for an additional 6 h, 6 mL of anhydrous HCl was condensed onto the white residue and protonation allowed to proceed at liquid HCl temperature for 30 s. The volatiles were removed and fractionated through a series of traps at −63, −95, and −196 °C. 3-Methylpentaborane(10) distills slowly through a −78 °C trap and stops at −95 °C. The fractionations were repeated until the vapor pressure of the product at 0 °C achieved a constant value of 16 torr. The sample, at this point, contained traces of an impurity whose volatility was very similar to that of 3-$CH_3B_5H_{10}$. Complete elimination was impossible; however, its concentration, as indicated by the ^{11}B NMR spectrum, was reduced further by gas chromatography. The identity of the impurity was undetermined. The yield of 3-$CH_3B_5H_{10}$ was 76%. Storage was maintained at liquid nitrogen temperature.

The residue remaining in the flask after the protonation was identified as $[BH_2(NH_3)_2{}^+][Cl^-]$ by its X-ray powder pattern.[23]

Infrared spectrum of 3-$CH_3B_5H_{10}$ (cm^{-1}): 2972 (w), 2928 (w), 2580 (s), 2495 (s), 2060 (w), 1940 (w, br), 1480 (m, br), 1410 (m, br), 1323 (m), 1168 (m), 1122 (m), 1090 (m), 1020 (m), 961 (m), 891 (m), 710 (w), 580 (w), 482 (w).

The normal boiling point (99 ± 4 °C) of 3-$CH_3B_5H_{10}$ was estimated from an extrapolated plot of log P vs. $1/T$. The heat of vaporization (7.9 ± 0.1 kcal/mol) was calculated from the slope of the plot using the Clausius–Clapeyron equation. The experimental vapor pressures are as follows: 0 °C, 16 torr; 14.1 °C, 32.4 torr; 21.1 °C, 45.2 torr.

The molecular weight of 3-$CH_3B_5H_{10}$ was determined by the vapor-density method. A 0.0591-g sample of 3-$CH_3B_5H_{10}$ exerted a pressure of 45.5 torr in a 291.39-mL bulb at 26.8 °C. The molecular weight was calculated to be 83.4. A second determination gave a value of 79.0 (theoretical 79.0). The mass spectrum cuts off at a mass to charge ratio of 80 as expected for $CH_3{}^{11}B_5H_{10}$. Spectra run with the ion source at temperatures higher than ambient indicated the presence of B_4H_{10} and larger amounts of $CH_3B_2H_5$. These same impurities, along with traces of B_2H_6 and H_2, were shown to be present, by gas chromatography, in samples which had been stored at −78 °C for about 20 months indicating that B_4H_{10} and $CH_3B_2H_5$ are the major thermal decomposition products.

Preparation of 1-$CH_3B_4H_9$. A 7.6-mmol quantity of $CH_3B_5H_{10}$ and 10 mL of CH_2Cl_2 were condensed into a 50-mL vessel containing a Teflon-covered stirring bar. The contents were warmed to −78 °C, and 15.2 mmol of NH_3 was allowed to expand into the stirred reaction mixture. Within 15 min, a gummy residue formed which gradually broke up and turned into a white precipitate as the reaction proceeded. After all of the ammonia had been absorbed, the vessel was isolated from the vacuum line and the contents were stirred at −78 °C for 2 days. The CH_2Cl_2 was then removed by pumping at −78 °C for 3 days, and for an additional 8 h with the mixture at −45 °C. It was important to remove as much of the solvent as possible because it was very difficult to separate $CH_3B_4H_9$ from CH_2Cl_2. The white residue remaining in the bulb was then protonated with 5 mL of anhydrous HCl at −110 °C. 1-Methyltetraborane(10) was isolated by passing the volatile products through a −126 °C trap. Purification was achieved by fractionating the product through a −78 °C trap into a −111 °C trap until the vapor pressure remained constant at 111 torr at 0 °C.

The yield of 1-$CH_3B_4H_9$ was 75%. It was stored at −196 °C.

The residue which remained in the reaction vessel after protonation was identified as $[BH_2(NH_3)_2^+][Cl^-]$ by its X-ray powder pattern.[23]

Infrared spectrum of 1-$CH_3B_4H_9$ (cm^{-1}): 2977 (m), 2938 (w), 2856 (w), 2580 (s), 2492 (s), 2278 (w), 2170 (m), 2063 (m), 1505 (w, br), 1438 (w, br), 1386 (w), 1335 (w), 1321 (w), 1278 (w), 1278 (w), 1263 (w), 1145 (m, br), 1050 (m), 972 (m), 939 (m), 855 (w), 765 (m), 751 (s), 496 (w).

The normal boiling point (45 ± 0.6 °C) and heat of vaporization (7.1 ± 0.02 kcal/mol) of 1-$CH_3B_4H_9$ were estimated from an extrapolated plot of log P vs. $1/T$ and the Clausius–Clapeyron equation. The experimental values are as follows: −45.2 °C, 9.3 torr; −22.9 °C, 37.3 torr; 0 °C, 120.0 torr.

A 0.1281-g sample of 1-$CH_3B_4H_9$ exerted a pressure of 111 torr in a 291.39-mL bulb at 0 °C. The calculated molecular weight is 64.5 (theoretical 67.2). The cutoff in the mass spectrum occurs at a mass to charge ratio of 68 as expected for $CH_3{}^{11}B_4H_9$.

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Registry No. 3-$CH_3B_6H_{11}$, 68070-89-3; 3-$CH_3B_5H_{10}$, 68051-06-9; 1-$CH_3B_4H_9$, 68051-07-0; 1-$CH_3B_5H_8$, 23753-74-4; B_2H_6, 19287-45-7; B_6H_{12}, 12008-19-4; B_5H_{11}, 18433-84-6; B_4H_{10}, 18283-93-7.

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A Novel Diphosphorus Zwitterion

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A novel acyclic diphosphorus zwitterion $F_5P^-CH_2P^+F(NMe_2)_2$ (**1**) featuring hexa- and tetracoordinate phosphorus atoms has been synthesized by the action of Me_3SiNMe_2 on methylenebis(tetrafluorophosphorane). Compound **1** was characterized by means of ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectroscopy at ambient temperature. The ^1H and ^{19}F resonances were found to collapse at higher temperatures. Possible causes for these spectral changes are discussed. Some unsuccessful attempts to synthesize new F_4PXPF_4 compounds, X = NMe, O, and S, are described.

Introduction

Over the past few years a large number of interesting compounds featuring the difluorophosphino moiety (PF_2) have been reported.[1] By contrast, far less is known about species bearing the tetrafluorophosphoranyl (PF_4) substituent. While several compounds of the type XPF_4, X = H, NR_2, OR, SR, halogen, etc., have been characterized,[2] we are aware of only four materials involving more than one PF_4 group, namely, $F_4PCH_2PF_4$,[3,4] $F_4PCH_2CH_2PF_4$,[4] $F_4PCH{=}CHPF_4$,[4] and $F_4PN(Me)N(Me)PF_4$.[5] Our initial aim was to expand significantly the range of derivatives of this type by incorporating new bridging groups between two or more PF_4 moieties. An aspect of particular interest in structures of this kind is that they represent cases where two or more pentacoordinate geometries are interconnected, thereby raising intriguing questions about the nature of the ligand permutation process(es).

Unfortunately, our attempts to prepare new derivatives of the type F_4PXPF_4 were not successful. However, in the course of exploring the reactivity of $F_4PCH_2PF_4$ toward silyl reagents we discovered that this compound reacts with Me_2NSiMe_3 to afford a novel acyclic zwitterion featuring tetra- and hexacoordinate phosphorus atoms.

Experimental Section

General Procedures. Essentially all the materials described herein are moisture- and/or oxygen-sensitive. Accordingly, volatile compounds were manipulated in a high-vacuum system of conventional design and less volatile materials were handled in a helium-filled drybox. The various reaction vessels were flame-dried several times prior to use.

Materials. The compounds $MeN(PF_2)_2$,[6] $F_2PN(Me)PF_4$,[7] F_2POPF_2,[8] F_2PSPF_2,[9] $F_4PCH_2PF_4$,[3] and Me_3SiNMe_2[10] were prepared and purified according to published procedures. Sulfur tetrafluoride was procured commercially and used as supplied. Xenon difluoride was kindly donated by Mr. Timothy Juhlke of Professor R. J. Lagow's research group.

Reaction of $MeN(PF_2)_2$ with SF_4. In a typical reaction, SF_4 (1.7 mmol) and $MeN(PF_2)_2$ (1.5 mmol) were condensed in a heavy-walled Pyrex tube reactor at −196 °C. The reactor and its contents were allowed to warm to −78 °C and were maintained at this temperature for 2 days. Following this, the reactor was attached to the vacuum system and arranged so that the contents were maintained at −20 °C. The volatile materials which emerged were subjected to fractional vacuum condensation with U-traps held at −78, −90, and −196 °C. The −196 °C trap was found to contain PF_5 (identified by IR spectroscopy[11]), and mass spectral/NMR analysis indicated that the −78 °C trap retained $MeN[P(S)F_2]_2$[12] and trace amounts of $(MeNPF_3)_2$.[13] The same products were observed when reaction

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