

placement of amine governs the rate. Such solvent attack does not obtain in the hydrolysis of I, where carboxylate and then hydroxide are the attacking species.

The steric restrictions to approach for cations of primary and secondary amine are usually less than that for tertiary amines (except for π bases like pyridine) and may account for the observed differences in lability. The facile loss of trimethylamine from Z, which is not sterically much different from inert $[(\text{CH}_3)_3\text{N}]_2\text{BH}_2^+$, would then require explanation. An attractive possibility is that the linkage of the attacking carboxylate to the substrate in Z permits a configuration with close oxygen-boron approach in the absence of solvent cage. Simple aquated ions and water, in this view, are inoperative because of large size or insufficient nucleophilicity to displace amine from the cations. One would expect attack only by small anions with good nucleophilic power and weak solvation. Some supportive evidence is found in the pyrolysis of $[(\text{CH}_3)_3\text{N}]_2\text{BH}_2^+\text{X}^-$ salts.¹¹ Whereas the halide ions require

(11) N. E. Miller, B. L. Chamberland, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1064 (1964).

temperatures near 200° for amine replacement, the more nucleophilic azide and carbonate react at 100° or below.

A structural factor also of importance in hydrolysis of I is the location of the carboxylate group such that cyclization can proceed to give a five-membered ring. The similar cation $(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5^+$ ¹² loses the ester moiety in base but is not hydrolyzed. A cyclization *via* the carboxylate did not occur either because of a different electronic environment at boron, or more likely because of the additional strain that the six-membered ring closure would produce.

The results of this study of the first hydrolytically unstable bistertiary amine-borane cation, then, implicate steric effects as the primary source of the chemical inertness of bistertiary amine-borane cations.

Acknowledgment. Support by a grant from the National Science Foundation is gratefully acknowledged. Assistance in calculation of trial exponential functions from Mr. Lanny Hoffman is also appreciated.

(12) N. E. Miller and D. L. Reznicek, *ibid.*, **8**, 275 (1969).

Boron Insertion Reactions. II. The Preparation of μ -Dimethylborylpentaborane(9) and 4,5-Dimethylhexaborane(10)¹

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Abstract: Lithium octahydropentaborate(1-), LiB_5H_8 , reacts with dimethylboron chloride at low temperatures to produce μ -dimethylborylpentaborane(9), in which the dimethylboryl moiety appears to occupy a bridging position between two boron atoms in the base of the pentaborane(9) tetragonal pyramid. This unusual compound is considered to be a stable intermediate in the formation of a B_6 pentagonal pyramid structure from a B_5 tetragonal pyramid precursor *via* a rational boron insertion reaction. This hypothesis is supported by the observation that μ -dimethylborylpentaborane(9) isomerizes in the presence of diethyl ether to 4,5-dimethylhexaborane(10).

The preparation of the octahydropentaborate(1-) anion, B_5H_8^- , and several group IV derivatives of pentaborane(9) has been described in previous papers.² In related research, other workers have reported that the octahydropentaborate(1-) anion reacts with dialkylchlorophosphines to form phosphinopentaborane(9)'s³ and with diborane(6) to yield hexaborane(10) as the end product.⁴

Several explicit examples of boron insertion reactions have been reported in which phenylboron dichloride reacts with the (3)-1,2-dicarbollide ion to form 3-phenyl-1,2-dicarbalo-dodecaborane(12)⁵

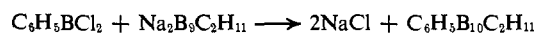
(1) For the previous paper see D. F. Gaines, *J. Amer. Chem. Soc.*, **91**, 6503 (1969).

(2) D. F. Gaines and T. V. Iorns, *ibid.*, **90**, 6617 (1968), and references therein.

(3) A. B. Burg and H. Heinen, *Inorg. Chem.*, **7**, 1021 (1968).

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

(5) M. F. Hawthorne and P. A. Wegner, *ibid.*, **90**, 896 (1968).

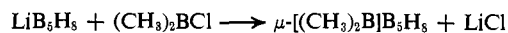


and with $\text{B}_{10}\text{H}_{10}\text{S}^{2-}$ to form the icosahedral species $\text{C}_6\text{H}_5\text{B}_{11}\text{H}_{10}\text{S}$.⁶ The recently reported preparation of 1,1-dimethyldiborane(6) and 2,2-dimethyltetraborane(10) from the reaction of dimethylboron chloride with sodium borohydride and sodium triborohydride, respectively, represents another type of boron insertion reaction.¹ We wish to describe here a boron insertion reaction involving the octahydropentaborate(1-) anion and the subsequent characterization and some chemical properties of the product of this reaction.

Results and Discussion

Lithium octahydropentaborate(1-) reacts readily with dimethylboron chloride to form a bridge-substituted pentaborane(9) derivative

(6) W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1696 (1967).



The reaction is carried out in diethyl ether solution at low temperature and yields have generally been in the range of 65–85%. The product, μ -dimethylborylpentaborane(9), was characterized by its infrared, ^{11}B nmr, ^1H nmr, and mass spectra.

The ^{11}B nmr spectrum of μ -dimethylborylpentaborane(9) (Figure 1) consists of a high-field doublet, a low-field triplet-like group, and a singlet at very low field. These peaks have relative area ratios of 1:4:1, and except for the singlet, the spectrum is similar to that of μ -trimethylsilylpentaborane(9), described in previous papers.² On the basis of this similarity, the same resonance assignments are proposed for this compound. Thus the high-field doublet is assigned to the apex boron atom, B(1), though it is at con-

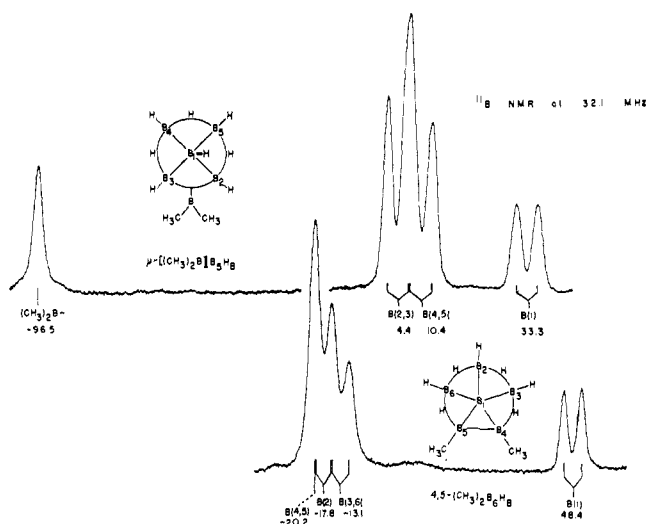


Figure 1. The 32.1-MHz ^{11}B nmr spectra of μ -dimethylborylpentaborane(9) and 4,5-dimethylhexaborane(10). Chemical shifts (ppm) are relative to $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2 \pm 0.5$. Observed coupling constants (Hz ± 10) for μ -dimethylborylpentaborane(9) are B(2,3)-H, 170; B(4,5)-H, 202; B(1)-H, 181; and for 4,5-dimethylhexaborane(10) are B(2)-H, 160; B(3,6)-H, 152; B(1)-H, 152.

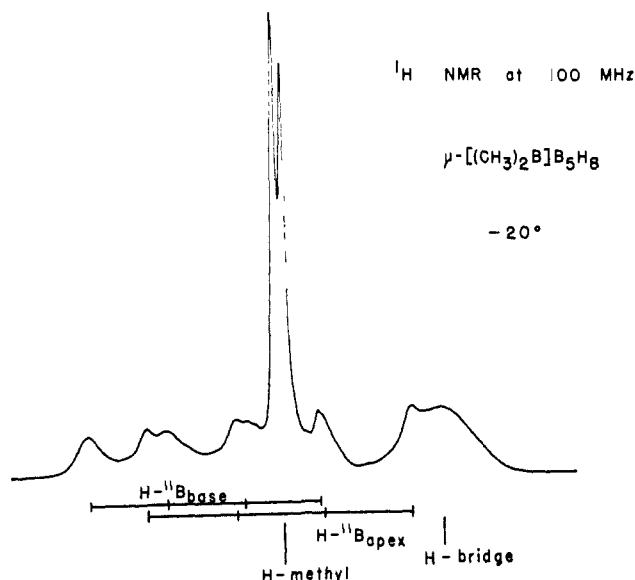


Figure 2. The 100-MHz ^1H nmr spectrum of μ -dimethylborylpentaborane(9) at -20° .

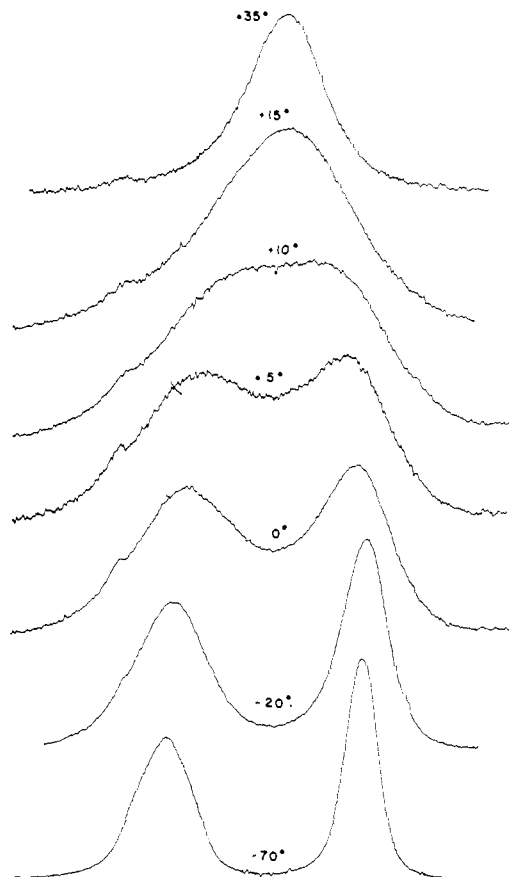


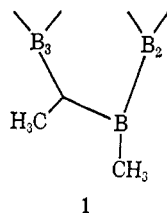
Figure 3. The temperature dependence of the 100-MHz ^1H nmr spectrum of μ -dimethylborylpentaborane(9). The peak separation at -70° is 19.3 Hz.

siderably lower field than is usually observed for pentaborane(9) derivatives; the triplet-like group is assigned to a composite of two overlapping doublets of equal intensity arising from two sets of two equivalent basal boron atoms, B(2,3) and B(4,5), and the singlet at very low field is assigned to the dimethylboryl moiety. The assignment of B(4,5) to the high-field doublet of the triplet-like group is based on the fact that the chemical shift is very close to that of the basal borons, B(2-5), of pentaborane(9). The extremely low-field position of the dimethylboryl singlet suggests that this boron is sp^2 hybridized. The chemical shift (-96.5 ppm) is lower than that observed for trimethylboron (-85 ppm) and boron trichloride (-48 ppm), both of which have trigonal planar structures. When boron is sp^3 hybridized, the chemical shift is always at much higher field—usually above -20 ppm.

The ^1H nmr spectrum of μ -dimethylborylpentaborane(9) is similar to that of other pentaborane(9) derivatives (Figure 2). Integration of the appropriate peak areas confirms the presence of five terminal hydrogens and three bridging hydrogens, as required for a bridge-substituted pentaborane(9) derivative.

The structure of μ -dimethylborylpentaborane(9) is undoubtedly very similar to that of 1-Br- μ -(CH_3)₃-SiB₅H₇. The structure of the latter has been confirmed by X-ray analysis in the laboratories of Professor L. F. Dahl, which showed that the trimethylsilyl moiety is in a bridging position, with the methyl groups in a

tetrahedral arrangement around the silicon.⁷ The bonding in μ -dimethylborylpentaborane(9) is probably very similar to that of pentaborane(9) itself, with a bridge hydrogen replaced by a dimethylboryl group which contributes an sp^2 hybrid orbital to a three-center two-electron bond with B(2) and B(3). Of special interest in this regard is the temperature dependence of the methyl resonance in the ^1H nmr spectrum of μ -dimethylborylpentaborane(9) shown in Figure 3. Above room temperature a single resonance is observed. As the temperature is lowered, however, this resonance broadens and finally separates into two peaks of apparently equal area, but with different half-height widths. This phenomenon is attributed to rotation of the dimethylboryl moiety about the axis of the sp^2 -hybridized orbital which bonds it to the pentaborane(9) framework. As the temperature is lowered, the energy available is no longer sufficient to overcome the barrier to rotation, and the dimethylboryl moiety may be aligned so that one methyl group is under the pentaborane(9) pyramid and in a substantially different environment from the other methyl group, which is oriented away from the molecule. The difference in half-height widths of the two methyl peaks may be due to a difference in the quadrupolar environments of the methyl groups, since one is substantially closer to several boron atoms than the other. It is not clear whether the barrier to rotation is steric; however, a model constructed on the basis of estimated bond lengths and bond angles indicates that the bridging hydrogens are close enough to the hydrogens on the interior methyl group to interact. Interaction of the p_z orbital of the dimethylboryl boron with a pair of nonbonding orbitals from the adjacent boron atoms may also contribute to the rotational barrier. An alternate but less favored explanation of the nonequivalent methyl groups at low temperatures is that a methyl bridge and a boron-boron bond are formed, as shown in 1. As a consequence, however, the boron



atoms B₂ and B₃ would also be nonequivalent, and some temperature-dependent changes in the ^{11}B nmr spectra should be observed. Although the barrier to internal rotation cannot be accurately determined from the available data, rough calculations indicate a value of 3–5 kcal/mol.⁸ Precise analysis is not feasible at this time because of the instability of the compound at higher temperatures, the broadness of the peaks, the difference in the half-height widths, and the overlap of the methyl resonances with the other resonances in the ^1H nmr spectrum.

While the infrared spectrum of μ -dimethylborylpentaborane(9) is similar to that of most other pentaborane(9) derivatives, the presence of two absorptions in the B–H stretching region (2600 cm^{-1}) is of interest. This extends a trend apparent in the bridge-substituted

group IV derivatives of pentaborane(9), where a shoulder was noted. Most other pentaborane(9) derivatives, in contrast, have a single sharp absorption at this frequency.

The mass spectrum of μ -dimethylborylpentaborane(9) reveals successive loss of hydrogens and methyl groups in a manner typical of substituted boron hydrides. A sharp cutoff occurs at m/e 104, as required for the expected parent peak, and the most intense peak occurs at m/e 40–41, $(\text{CH}_3)_2\text{B}^+$, indicating that the substituent is rather weakly bound to the pentaborane(9) pyramid.

Liquid samples of μ -dimethylborylpentaborane(9) turn yellow fairly rapidly at room temperature, indicating that the compound is thermally unstable. Heating in the gas phase to 100° for a few hours results in the deposit of a yellowish, resinous material on the walls of the flask, and fractionation of the volatile species yields pentaborane(9), several methyl-diboranes, 2-methylpentaborane, a trace of starting material, and several unidentified materials.

Reaction of μ -dimethylborylpentaborane(9) with bromine at low temperature, even with BBr_3 as a solvent, is rapid and sometimes violent. Although there was some evidence for the formation of 1-bromo- μ -dimethylborylpentaborane(9), the product mixture was very complex and a pure product was not isolated.

Dimethylhexaborane(10) is the major product (yields range from 50 to 85%) when μ -dimethylborylpentaborane(9) isomerizes in the presence of diethyl ether at room temperature. The characterization of the structural framework of this new hexaborane(10) derivative is based primarily on ^{11}B and ^1H nmr and infrared spectral data.

The ^{11}B nmr spectrum of dimethylhexaborane(10) (Figure 1) consists of a high-field doublet of relative area 1 and a low-field multiplet of relative area 5. The low-field multiplet has been shown by ^1H decoupling to consist of a singlet of relative area 2, a doublet of relative area 2, and a doublet of relative area 1. The chemical shift region of this multiplet is close to that of the basal borons in hexaborane(10), which is about 25 ppm below the shift of the basal borons of pentaborane(9). The disappearance of all resonances having chemical shifts close to those of the starting material and the appearance of resonances having chemical shifts close to those of hexaborane(10) indicate that this isomerization involves a change from a formal pentaborane(9) derivative to a hexaborane(10) derivative. The ^{11}B nmr spectrum is compatible with either 3,6-dimethylhexaborane(10) or 4,5-dimethylhexaborane(10), but it seems more probable, from a consideration of the starting material, that the methyl groups are on adjacent borons. For this reason, the assignments given are based on 4,5-dimethylhexaborane(10).

The ^1H nmr spectrum of 4,5-dimethylhexaborane(10) (Figure 4) is quite similar to that of hexaborane(10). A distinguishing characteristic is the appearance of two peaks from a ^1H – ^{11}B quartet at a higher field than that of the broad resonance due to the bridging hydrogens. Integration of this spectrum confirms the presence of four terminal hydrogens and four bridge hydrogens.

The infrared spectrum of 4,5-dimethylhexaborane(10) has only one distinguishing feature: the absorptions

(7) We thank L. F. Dahl and J. C. Calabrese for permission to quote these results prior to their publication.

(8) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 6 (1956).

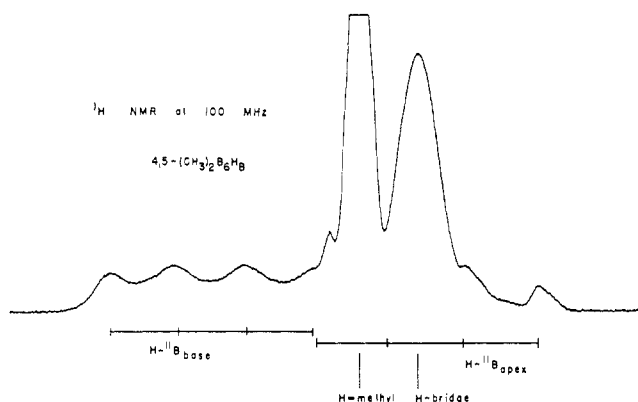


Figure 4. The 100-MHz nmr spectrum of 4,5-dimethylhexaborane(10).

normally associated with bridge hydrogens are found at 1950 cm^{-1} , quite close to those of hexaborane(10) and considerably shifted from those of pentaborane(9), which are found at about 1800 cm^{-1} .

The mass spectrum of 4,5-dimethylhexaborane(10) has been obtained at several voltages, and unfortunately the fragmentation pattern is very similar to that found for μ -dimethylborylpentaborane(9). The cutoff occurs at m/e 104 as expected, but the data could not be interpreted on the basis of any particular isomer of dimethylhexaborane(10).

Experimental Section

Standard high-vacuum techniques were used for manipulation and purification of volatile materials. Infrared spectra were recorded using a Beckman IR-10 or a Perkin-Elmer 700 spectrometer and quoted frequencies are $\pm 10\text{ cm}^{-1}$. Nmr spectra were obtained using Varian HA-100, A-60, and A-60A spectrometers equipped with standard Varian accessories. Integrations of nmr spectra were measured using a planimeter.

Diethyl ether was dried over lithium aluminum hydride and distilled in the vacuum line immediately prior to use. Dimethylboron chloride was prepared by the general method proposed⁹ and used by Stone^{10,11} and others.^{12,13} Other reagents were used as received.

μ -Dimethylborylpentaborane(9), μ -[(CH₃)₂B]B₅H₈. Dimethylboron chloride (16 mmol) was condensed at -196° into a reaction flask containing lithium octahydropentaborate(1-) (13.3 mmol) dissolved in diethyl ether.² The contents of the flask were warmed to -78° and then, with continuous stirring, from -78° to -40°

over a period of 1 hr. At this point, the solution was slightly yellow and a white precipitate was present. The product was isolated from the rest of the volatile components by distillation through a U-tube trap at -37° and condensation in a trap -63° . A white solid remained in the reaction flask. The product was liquid, having a vapor pressure of $4.5 \pm 0.5\text{ mm}$ at 0° ; yield, 81% (10.6 mmol). Yields were variable, but generally fell in the range of 65–85%.

In several of the μ -dimethylborylpentaborane(9) preparations, the reaction solution turned varying shades of red in a totally irreproducible manner. Although the red color had no observable effect on the product yield, small amounts of a yellow solid of low volatility were produced. The yield of this solid was less than 1%, and before it could be purified, the yellow color disappeared; the ¹¹B nmr of the resulting white solid was identical with that of decaborane(14). The formation of the yellow solid may be related to the reaction of diborane(6) with lithium octahydropentaborate(1-) that produces decaborane(14) in about 30% yield.⁴

4,5-Dimethylhexaborane(10), 4,5-(CH₃)₂B₆H₈. About 6 mmol of μ -dimethylborylpentaborane(9) was condensed at -196° into a reaction flask containing several milliliters of diethyl ether. The flask was warmed to room temperature for several hours. The product was isolated from the rest of the volatile materials by condensation in a U-tube trap at -45° . At this point, the 4,5-dimethylhexaborane(10) is contaminated (about 10–20%) by side products. Yields are generally in the range of 50–85%. Pure 4,5-dimethylhexaborane(10) can be obtained using a high-vacuum low-temperature spinning-band distillation column. The optimum temperature for the top of the column is about -40° . The product is a liquid having a vapor pressure of $3.5 \pm 0.5\text{ mm}$ at 19° .

Analysis of 4,5-(CH₃)₂B₆H₈. A sample purified in the manner described was analyzed by the Schwarzkopf Microanalytical Laboratory. *Anal.* Calcd for C₂B₆H₁₄: C, 23.32; H, 13.70; B, 62.98. Found: C, 23.42; H, 13.64; B, 62.45.

Reaction of Bromine with μ -Dimethylborylpentaborane(9). Excess μ -[(CH₃)₂B]B₅H₈ and about 0.1 ml of liquid bromine were condensed into a reaction flask at -196° and warmed to -78° . The flask was warmed to -25° over a period of 1 hr. At this time all the bromine color had disappeared. Fractionation yielded pentaborane(9), methyl diboranes, hydrogen bromide, and a small amount of an unstable compound, believed to be 1-bromo- μ -dimethylborylpentaborane(9), 1-Br- μ -[(CH₃)₂B]B₅H₈, on the basis of its ¹¹B nmr spectrum.

Nmr Spectra. The ¹¹B nmr spectra of μ -[(CH₃)₂B]B₅H₈ and 4,5-(CH₃)₂B₆H₈ are shown in Figure 1. Chemical shift data are included in the figure. The ¹H nmr spectra of these compounds at 100 MHz are shown in Figures 2 and 3. Chemical shift and coupling constant data were obtained from the 60-MHz nmr spectra. μ -[(CH₃)₂B]B₅H₈: H_{base} δ -1.45 ppm , $J = 162\text{ cps}$; H_{apex} δ -0.97 ppm , $J = 175\text{ cps}$; H_{bridge} δ $+2.23\text{ ppm}$; H_{methyl} δ -0.88 ppm . 4,5-(CH₃)₂B₆H₈: H_{base} δ -3.60 ppm , $J = 145\text{ cps}$; H_{apex} δ $+1.27\text{ ppm}$, $J = 153\text{ cps}$; H_{bridge} δ $+0.80\text{ ppm}$; H_{methyl} δ -0.40 ppm .

Infrared Spectra. The infrared spectra of μ -[(CH₃)₂B]B₅H₈ and 4,5-(CH₃)₂B₆H₈, respectively, are (cm^{-1}) as follows. μ -[(CH₃)₂B]B₅H₈: 3000 (m), 2630 (s), 2580 (m), 1820 (b, w), 1450 (m, b), 1320 (s), 1240 (m), 960 (m), 900 (w), 840 (m), 770 (vw), and 690 (vw). 4,5-(CH₃)₂B₆H₈: 2990 (m), 2940 (w), 2860 (vw), 2600 (s), 1950 (w), 1860 (vw, b), 1460 (s), 1330 (m), 1150 (w), 1120 (w), 1090 (w), 1000 (vw), 950 (m), 910 (m), 850 (m), 790 (vw), and 700 (vw).

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(12) W. Gerrard, E. F. Mooney, and R. G. Rees, *J. Chem. Soc.*, 740 (1964).

(13) P. M. Trelchel, private communication.