°C and at 0 °C did not bring about a further displacement of $N(CH_3)_3$ from IV.[9]

(d) $B_3H_6{\cdot}2N(CH_3)_3{}^+B_3H_8{}^-$ and $P(CH_3)_3$. A sample of $B_3H_6{\cdot}2N(CH_3)_3{}^+B_3H_8{}^-$ was treated with $P(CH_3)_3$ in a manner similar to that used for preparation c. Formation of $BH_3{\cdot}P(CH_3)_3$ was noted at −30 °C. The reaction was slow at −20 °C. Although the reaction proceeded with a moderate rate to completion at +10 °C, weak signals of decomposition products were noted in the ^{11}B spectrum of the final solution.

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Registry No. I, 113810-98-3; II, 113811-00-0; III, 113811-03-3; IV, 113811-02-2; $B_3H_6{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3{}^+B_3H_8{}^-$, 112925-44-7; $B_3H_6{\cdot}2N(CH_3)_3{}^+B_3H_8{}^-$, 113810-96-1; $N(CH_3)_3$, 75-50-3; $P(CH_3)_3$, 594-09-2; $BH_3{\cdot}N(CH_3)_3$, 75-22-9; $BH_3{\cdot}P(CH_3)_3$, 1898-77-7.

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(9) This observation was made by M. Kameda of this laboratory.

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Bis(μ-dimethylamino)tetraborane(10), (μ-$Me_2N)_2B_4H_8$

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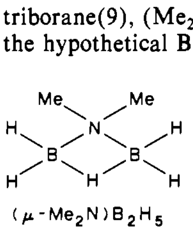
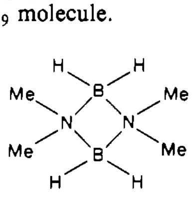
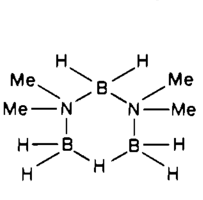
One of our synthetic interests is the incorporation of group V (group 15) atoms into intermediate-sized borane clusters. The paucity of such compounds has led us to consider a variety of previously unexplored routes to borane clusters having group V substituent atoms in terminal or bridging positions[1] and group V cluster heteroatoms.[2] As part of this study we have recently initiated studies of the reactions of the (dialkylamido)boron halides R_2NBX_2 and $(R_2N)_2BX$ with a variety of boron cluster anions. The insertion of dialkylamino groups into bridging locations between boron atoms of borane cluster molecules is well documented for the (μ-dialkylamino)diboranes, (μ-$R_2N)B_2H_5$,[3] in which the R_2N group replaces a bridge hydrogen atom in the parent diborane, B_2H_6. The dimeric (dialkylamino)boranes, $[R_2NBH_2]_2$,[4] may be considered to be the fully aminated class of bridging amino-substituted diboranes. The cyclic bis(μ-dimethylamino)triborane(9), $(Me_2N)_2B_3H_7$,[5] is a bridging amino derivative of the hypothetical B_3H_9 molecule.



(μ-$Me_2N)B_2H_5$



$(Me_2NBH_2)_2$



$(Me_2N)_2B_3H_7$

A bridging amino group and a terminal amine group occur in $(EtNH_2)B_8H_{11}(NHEt)$,[6] perhaps the only example of a larger amino-bridged borane cluster. Our investigations of the reactions of the (dialkylamido)boron halide $(Me_2N)_2BBr$ with the octahydrotriborate anion, $B_3H_8{}^-$, has resulted in the synthesis of the first example of an intermediate-sized bis(amino)-bridged borane cluster.

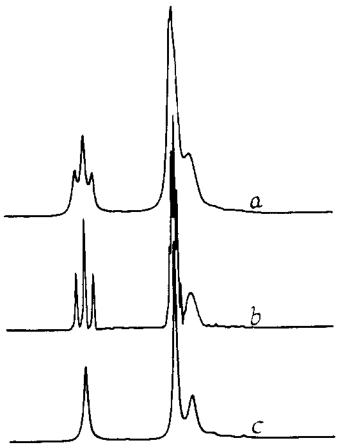


Figure 1. 86.7-MHz ^{11}B NMR spectra of neat (μ-$Me_2N)_2B_4H_8$: (a) normal; (b) line narrowed; (c) ^{1}H decoupled.

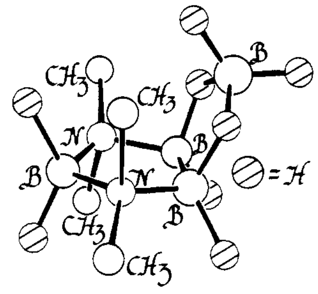


Figure 2. Proposed structure of (μ-$Me_2N)_2B_4H_8$.

Table I. Infrared Stretching Frequencies for Boron–Nitrogen Bonds in Selected Aminoboranes

aminoborane	BN(asym)[a]	BN(sym)[a]	ref
(μ-$Me_2N)B_2H_5$	1184 vs	1069 vs	17
$[(Me_2N)_2BH_2]_2$	1193 vs	*b*	18
$(Me_2N)_2BH$	1548 vs	1409 vs	19
$(Me_2N)_3B$	1507 vs	1383 vs	20
(μ-$Me_2N)_2B_4H_8$	1175 vs	1040 vs	*c*

[a] Frequencies reported in cm^{-1}. [b] Not assigned. [c] This work.

Results and Discussion

Bis(dimethylamido)boron bromide reacts readily with tetramethylammonium octahydrotriborate(1−), $Me_4NB_3H_8$, in CH_2Cl_2 solution to form bis(μ-dimethylamino)tetraborane(10), (μ-$Me_2N)_2B_4H_8$, in yields of ca. 10%. The other major volatile boron-containing products in this synthesis are (μ-$Me_2N)B_2H_5$ and $(Me_2NBH_2)_2$. In the absence of solvent, considerable $(Me_2NBH_2)_2$ is formed along with (μ-$Me_2N)B_2H_5$ but very little of the bis(μ-dimethylamino)tetraborane(10) is obtained.

The relatively volatile (μ-$Me_2N)_2B_4H_8$ is a clear liquid, melting at −3 to −4 °C. It appears to be stable when neat but slowly decomposes in solution over a period of weeks, primarily to $(Me_2NBH_2)_2$ and (μ-$Me_2N)B_2H_5$. The decomposition of (μ-$Me_2N)_2B_4H_8$ in air is rapid, producing a typical aminoborane odor but no spontaneous combustion.

The ^{11}B NMR spectrum of bis(μ-dimethylamino)tetraborane(10), Figure 1, consists of three resonances; a triplet at +5.97 ppm (J = 107 Hz) of unit intensity, which collapses to a singlet on broad-band ^{1}H decoupling; a multiplet of intensity 2

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at −7.49 ppm (J = 34 Hz), which resolves to an apparent septet on line narrowing and collapses to a singlet on ^{1}H decoupling; and a broad singlet of intensity 1 at −9.80 ppm, which narrows slightly on ^{1}H decoupling but shows no resolvable coupling even upon substantial line narrowing.

Two preliminary structural interpretations of the ^{11}B NMR spectra are possible. It would be mechanistically logical to expect the Me_2N groups to be terminally bound. If this were the case, the broad singlet at −9.80 would represent the boron atom, B(2), to which the two terminal amino groups are attached. The triplet would then arise from the BH_2 group opposite, B(4), and the intensity 2 multiplet at −7.49 ppm would correspond to the two equivalent boron atoms in the middle, B(1) and B(3), coupled equivalently to the six remaining hydrogen atoms. Exchange of hydrogens between B(1) and B(3) without involvement of hydrogens on B(4) is unprecedented, though intramolecular exchange of all the boron-bound hydrogen atoms associated with the B_3 triangle in $B_3H_8^-$ anion derivatives is well-known.[7,8]

The more attractive proposed structure for $(\mu\text{-}Me_2N)_2B_4H_8$, shown in Figure 2, is consistent with prior IR (Table I) and NMR data obtained for aminoboranes and for borane derivatives having a B_3H_8 group attached to some other moiety. The details of the substantial rearrangements necessary for the formation of this structure are not yet established, but the requirements are no more complex than those observed for many reactions involving iminoboranes.[9] The chemical shift of the lower field triplet in the ^{11}B NMR spectrum of $(\mu\text{-}Me_2N)_2B_4H_8$ is similar to that for $(Me_2NBH_2)_2$ (+5.3 ppm, J = 110 Hz).[10] This suggests similar chemical environments for the BH_2 groups in $(Me_2NBH_2)_2$ and $(\mu\text{-}Me_2N)_2B_4H_8$, and the triplet is therefore assigned to B(2), to which the two bridging dimethylamino groups are attached. The septet that emerges upon line narrowing of the −7.49 ppm resonance must be the result of facile internal exchange of the hydrogens on the B(1), B(3), and B(4) triangle, a fluxional process that does not exchange boron atoms. The activation energy barrier for the overall hydrogen exchange is low as it was not attenuated on the NMR time scale even at −110 °C. That the hydrogen coupling is not observed on the high-field resonance is unusual but not unprecedented in triborohydride chemistry.[8] The ^{11}B NMR spectrum of $(CO)_4MnB_3H_8$, for example, shows a high field multiplet of intensity 2 while the unique boron atom at lower field remains a broad singlet. A 2-D COSY ^{11}B–^{11}B NMR experiment has shown coupling between the two high-field resonances, B(1), B(3) and B(4), but not between these resonances and the low-field triplet resonance, B(2).[11] The quadrupole moment of ^{14}N should curtail its ability to act as a spin-transfer agent and prevent observation of ^{11}B–^{11}B coupling between its adjacent boron atoms by using the COSY pulse sequence. These data are consistent with those for several substituted B_3H_8 anions[8] and, when taken with the line narrowing experiments and chemical shift similarities indicated above, strongly supports the proposed structure for $(\mu\text{-}Me_2N)_2B_4H_8$.

The ^{1}H NMR spectrum of $(\mu\text{-}Me_2N)_2B_4H_8$ in CD_2Cl_2 solution exhibits two large singlets, at +2.55 and +2.48 ppm, corresponding to the methyl groups on nitrogen, superimposed on a quartet (+2.05 ppm, J = 105 Hz) and an overlaping broad resonance centered at ca. +1.88 ppm. Exo and endo methyl groups are expected for a rigid tetraborane(10) butterfly molecular shape. At least one of the hydrogens of the isolated BH_2 group is observed as the quartet. Since these hydrogens are stereochemically different, a second quartet might be expected to be chemically shifted from the first as in B_4H_{10} or 2,2-$Me_2B_4H_8$.[12] However, it may be coincident or broadened and submerged in the broad resonance attributed to the remaining six fluxional BH hydrogens.

In an attempt to force the production of a terminally substituted aminotetraborane(10) for comparison with $(\mu\text{-}Me_2N)_2B_4H_8$, the reaction of 1,3-dimethyl-2-chloro-1,3,2-diazaboracyclopentane with $Me_4NB_3H_8$ was attempted. No reaction was observed, however, and only starting materials were recovered. That no reaction was observed suggests that facile formation of a bridging amino functionality is important in the very early stages of the reaction sequence, and blocking this process inhibits even the initial metathesis. Further studies of synthetic routes to new nitrogen derivatives of borane clusters are in progress.

Experimental Section

Standard high-vaccum-line techniques were employed.[13] $Me_4NB_3H_8$ was prepared by a published procedure[14] and was dried overnight on a standard high-vacuum line at room temperature. The $(Me_2N)_2BBr$[15] was synthesized by reaction of $(Me_2N)_3B$ with BBr_3, and was purified by distillation. 1,3-Dimethyl-2-chloro-1,3,2-diazaboracyclopentane was formed by reaction of excess *N,N'*-dimethylethylenediamine with BCl_3.[16] The BCl_3 (Matheson Chemical Co., technical grade), BBr_3, and *N,N'*-dimethylethylenediamine (Alfa Products) were used without further purification. Methylene chloride was dried over P_2O_5 and distilled immediately prior to use. All starting materials were identified by their ^{11}B or ^{1}H NMR and IR spectra. The ^{11}B and ^{1}H NMR data were acquired by using an IBM WP-270 NMR spectrometer at 86.7 and 270.1 MHz, respectively. The IR spectra were collected on a Beckman 4250 IR spectrophotometer. Mass spectral data were obtained on a KRATOS MS80 spectrometer at 30 eV. ^{11}B–^{11}B 2D COSY NMR spectra were obtained on a Bruker AM 500 spectrometer at 160.4 MHz.[11]

Reaction of $(Me_2N)_2BBr$ and $Me_4NB_3H_8$. In a typical experiment, 2.218 g (12.4 mmol) of $(Me_2N)_2BBr$ and 1.42 g (12.4 mmol) of $Me_4NB_3H_8$ were stirred in 50 mL dry CH_2Cl_2 at ambient temperature for 3 days in a 100-mL high-vaccum reaction vessel. Volatile products were separated on a high-vacuum line by distillation through a −45 °C U-trap twice (to remove CH_2Cl_2). The materials condensed in the −45 °C trap were repeatedly distilled into a 0 °C U-trap. The purified product, $(\mu\text{-}Me_2N)_2B_4H_8$, which condensed in the 0 °C trap, melts at −3 and −4 °C and shows a parent ion peak in the mass spectrum at m/e 140.1995. Calculated for $^{12}C_4{}^{14}N_2{}^{11}B_4{}^{1}H_{20}$: m/e 140.1999. The most intense peak at the parent envelope occurs at m/e 138.1960, corresponding to $^{12}C_4{}^{14}N_2{}^{11}B_3{}^{10}B{}^{1}H_{19}$ (calculated: m/e 138.1957). The IR spectrum has major absorbances as follows: 3020 (s), 2980 (s), 2950 (s), 2900 (m), 2525 (s), 2470 (s), 2400 (s, sh), 2325 (m), 1475 (s), 1450 (s), 1443 (m), 1410 (m), 1235 (m), 1200 (s), 1175 (s), 1149 (s), 1110 (s), 1040 (s), 1000 (s), 970 (s), 930 (s), 898 (m), 835 (m), 780 (m) cm^{-1}. The ^{11}B NMR spectrum (measured neat) shows the following resonances: 5.97 (t, J = 107 Hz), −7.49 (septet, J = 34 Hz), −9.80 ppm (s, br). All resonances sharpen on broad-band ^{1}H decoupling. The ^{1}H NMR spectrum (measured in CD_2Cl_2) exhibits the following resonances: +2.55 (s), +2.48 (s), +2.06 (q, J = 105 Hz), +1.88 ppm (br). The yield of purified $(\mu\text{-}Me_2N)_2B_4H_8$ was 13% based on starting $Me_4NB_3H_8$.

Reaction of 1,3,2-Diazaboracyclopentane with $Me_4NB_3H_8$. In a 100-mL high-vacuum reaction vessel equipped with a magnetic stir bar were mixed 1.17 g (10.2 mmol) of $Me_4NB_3H_8$, 1.36 g (10.3 mmol) of 1,3-dimethyl-2-chloro-1,3,2-diazaboracyclopentane, and 20 mL of CH_2Cl_2. After 5 days, no reaction was discerned. Starting materials were recovered unchanged.

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Registry No. $(\mu\text{-}Me_2N)_2B_4H_8$, 108083-02-9; $Me_4NB_3H_8$, 12386-10-6; bis(dimethylamido)boron bromide, 6990-27-8; 1,3-dimethyl-2-chloro-1,3,2-diazaboracyclopentane, 113810-94-9.

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