$[Cu^{2+}]$ in excess at all pHs (Table I), conforming to the relationship (2), where $X = [Cu^{2+}]$ or $[LH_2]$. Usually Cu^{2+} was used in excess. This behavior resembles closely that shown by the Cu^{2+}–DOTA system,[8] where "saturation kinetics" were observed. A similar treatment and explanation of the results were adopted. The reaction of Cu^{2+} with Ia or Ib was therefore interpreted in terms of eq 3–6. The overall reaction can proceed by a combination of (4) and (5), in which a rapidly formed adduct (formation constant K) is more slowly transformed into the final complex (k_1). With this mechanism, $A = k_1K$ and $B = K$.[8] Alternatively, the adduct is rapidly formed in (4) but is not on the reaction pathway to the final product, which results only from step 6, where $A = k_2$.[8] The values of K_1, k_1, and k_2 are collected in Table II. We formulate the adduct and its breakdown as in (4) and (5) because of the invariance of K with pH and the dependence of k_1 on $[H^+]^{-1}$ (Table II). This latter point means that the breakdown of the adducts $Cu^{2+}{\cdot}LH_2$ in (5) must involve several steps, including a preequilibrium in which one proton features in the product. The variation of k_2 with pH (Table II) indicates that, for Ia and Ib, LH_2 is much less reactive than LH^-. It is easily shown[8] then that $k_2 = k_{LH^-}[1 + K_3^{-1}[H^+]]^{-1}$. From the appropriate plot and a knowledge of K_3,[17] the value of k_{LH^-} for Ia can be calculated as 1.6×10^8 M^{-1} s^{-1}. A similar behavior for the fast step of Id (see below) allows an estimate for the reactivity of LH^-.

$$k_{\text{obsd}} = \frac{A[X]}{1 + B[X]} \tag{2}$$

$$LH_2 \rightleftarrows LH^- + H^+ \quad K_3 \tag{3}$$

$$Cu^{2+} + LH_2 \rightleftarrows Cu^{2+}{\cdot}LH_2 \quad K \tag{4}$$

$$Cu^{2+}{\cdot}LH_2 \rightarrow CuL + 2H^+ \quad k_1 \tag{5}$$

$$Cu^{2+} + LH_2 \rightarrow CuL + 2H^+ \quad k_2 \tag{6}$$

Ic. Again, a single first-order reaction using excess metal ion was observed, with characteristics similar to those of Ia and Ib and explainable in terms of (3)–(6). An adduct with formation constant $K \sim 10^2$ M^{-1}, approximately independent of pH (Table II), was deduced. Either the breakdown of this adduct (k_1) or the second-order formation rate constant (k_2) was inversely dependent on $[H^+]$ (Table II). The constancy of absorbance changes with changing Cu^{2+} and H^+ concentrations indicated that formation of a complex was complete, despite the presence of only one pendent $-CH_2CO_2^-$ group in the ligand. It was assumed that this group was present as the diprotonated $^+HNCH_2COOH$ moiety in the pH region examined. When ligand was used in excess, two reactions were observed, both of which showed increasing and comparable absorbance changes at 330 nm. The two stages were sufficiently different in rates to be easily resolvable. The fast reaction appeared very similar to that observed when excess copper ion was used, both in absorbance changes and in rate constant/Cu^{2+}/pH characteristics. The slower reaction rate was independent of Cu^{2+} concentrations and pH and was 1.1 ± 0.1 s^{-1}. Unlike those for the other three ligands examined therefore, the absorbance changes were different when ligand instead of copper ion was used in excess. The slower step probably arises from the formation of higher species (ligand:Cu^{2+} = 2), since such complexes have been isolated.[18] It is apparent that the formation of this higher species is controlled by a first-order process, probably involving some necessary rearrangement of the macrocycle after the mono complex has formed and before the bis species can arise.

Id. The behavior of this ligand was the most interesting of the four examined. Two reactions were observed that were identical in characteristics regardless of whether copper ion or ligand (examined only at pH 4.25) was used in excess (Table I). The constancy of the total absorbance changes with differing Cu^{2+} and H^+ concentrations, as well as considerations of stability constants,[11,13,17] showed that complex formation was complete and that the same species resulted from use of either reactant in excess. The predominant ligand species at pH 3.75–4.75 is the dizwitterion LH_2 (II, R = H, n = 1).

The fast step had the characteristics of the first step in binding by Ia–Ic. The associated formation and rate constants are shown in Table II. The slow step had a constant rate (3.0 ± 0.2 s^{-1}) independent of Cu^{2+} concentration above 2.0 mM in the pH range 4.0–4.75. There was some indication from absorbance changes of an equilibrium for the first step at lower Cu^{2+} concentration and pH (3.75) but not for the overall reaction, and these data were not used in calculating the results in Table II.

Conclusions

Even one carboxylate arm in Ic is sufficient to promote copper complexing. No interaction is observed spectrally when 10 mM Kryptofix 22 (I, R = R′ = H, n = 2) is mixed with copper ion (2 mM) at pH 4.75. The reported stability constants for Cu^{2+} complexing with Kryptofix 22 are quite low, $10^{6.2}$ or $10^{7.6}$ at 25 °C in 0.1 M Et_4NClO_4.[19,20] The kinetic data indicate that in the reaction of excess Cu^{2+} with Ia–Id, there is a common first step in which there is a rapidly formed adduct between the metal ion and the zwitterionic forms of the ligand. If the formation of the final complex circumvents this adduct, then the process involves a second-order reaction of Cu^{2+} with LH^- (Ia, Ib, Id), which contains one $>NCHRCO_2^-$ and one $>N^+HCHRCO_2^-$ residue, or with LH (Ic), which has one $>N^+H_2$ and one $>NCH_2CO_2^-$ entity. From the known ionization constants for ligands Ia and Id and the approach outlined previously,[8] the rate constant for the reaction of Cu^{2+} with LH^- can be calculated as 1.6×10^8 and 3.0×10^8 M^{-1} s^{-1} for Ia and Id, respectively.[21] These values are close to those measured for Cu^{2+} with $NH_2CH_2CO_2^-$ and with the monoprotonated forms of DOTA and TETA.[8] The diprotonated forms LH_2 (II) and LH_2^+ (Ic) are unreactive.[22] The binding of the $>NCH_2CO_2^-$ residue in LH^- (Ia, Ib) or LH (Ic) to Cu^{2+} is followed by a rapid, intramolecular completion of complexing, with the remaining $>N^+HCH_2CO_2^-$ (Ia, Ib) or $>N^+H_2$ (Ic) groups aided perhaps by the ether oxygens. With the less flexible 15-membered ligand (Id) it appears that, after the initial binding to the $>NCH_2CO_2^-$ residue, the completion of complexing is controlled by a first-order process, $k = 3.0$ s^{-1}, which may be a conformational change in the macrocycle so as to orient the $>N^+HCH_2CO_2^-$ group in the correct position.

Acknowledgment. This work was supported by a National Science Foundation grant, which is gratefully acknowledged.

Registry No. Ia, 82353-42-2; Ib, 72912-01-7; Ic, 86952-04-7; Id, 81963-61-3; Cu^{2+}, 15158-11-9.

---

(18) Kasprzyk, S. P., unpublished results.

(19) Arnaud-Neu, F.; Spiess, B.; Schwing-Weill, M. J. *Helv. Chim. Acta* **1977**, *60*, 2633.

(20) Luboch, E.; Cygan, A.; Biernat, J. F. *Inorg. Chim. Acta* **1983**, *68*, 201.

(21) The ionization constants for Ib and Ic can be assumed to be similar to those for Ia and Id; therefore, it is assumed that $k_{LH} \sim 10^8$ M^{-1} s^{-1} for these also.

(22) The data in Table II indicate that there is a small contribution to the rate from the LH_2 species for Id with $k \sim 10^4$ M^{-1} s^{-1}.

Contribution from the Department of Chemistry,
University of Utah, Salt Lake City, Utah 84112

Formation of Diboron Complex Cations

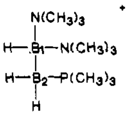
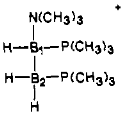
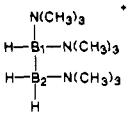
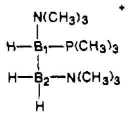
Rosemarie E. DePoy and Goji Kodama*

Received October 16, 1987

Earlier, we reported briefly that the reaction of bis(trimethylamine)hexahydrotriboron(1+) octahydrotriborate(1−), $B_3H_6{\cdot}2N(CH_3)_3^+$ $B_3H_8^-$, with trimethylamine resulted in the cleavage of the triboron cation framework to produce a new

0020-1669/88/1327-1836$01.50/0

Table I. Chemical Shift Values for the Diboron Complex Cations[a]

		 I	 II	 III	 IV
^{11}B	B(1)	+11.4	-5.8	+12.5	-5.4
	B(2)	-34.7	-35.8	-3.9	-5.4
^{31}P	P(1)		-14.2		-13.0
	P(2)	+1.9	+0.5		
^{1}H	$H_{NMe}(1)$	2.68	2.67	2.75	2.72
	$H_{NMe}(2)$			2.51	2.54
	$H_{PMe}(1)$		1.39[b]		1.44[b]
	$H_{PMe}(2)$	1.20[b]	1.22[c]		

[a] The shift values are expressed in ppm. Standards for the shifts: ^{11}B, $BF_3{\cdot}O(C_2H_5)_2$; ^{31}P, 85% orthophosphoric acid; ^{1}H, CH_2Cl_2 signal at 5.28 ppm. Low-field shifts are taken as positive. [b] Doublet, J_{HP} = 10 Hz. [c] Doublet, J_{HP} = 11 Hz.

diboron complex cation, tris(trimethylamine)trihydrodiboron(1+), as indicated in eq 1.[1] This reaction contrasted sharply with our

$$B_3H_6{\cdot}2N(CH_3)_3{}^+B_3H_8{}^- + 2N(CH_3)_3 \rightarrow B_2H_3{\cdot}3N(CH_3)_3{}^+B_3H_8{}^- + BH_3{\cdot}N(CH_3)_3 \quad (1)$$

earlier observation[2] on the reaction of $B_3H_6{\cdot}2P(CH_3)_3{}^+B_3H_8{}^-$ with $N(CH_3)_3$, which produced the tetraborane(8) adduct according to eq 2. The reaction of $B_3H_6{\cdot}2P(CH_3)_3{}^+B_3H_8{}^-$ with $P(CH_3)_3$

$$B_3H_6{\cdot}2P(CH_3)_3{}^+B_3H_8{}^- + 2N(CH_3)_3 \rightarrow B_4H_8{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3 + BH_3{\cdot}P(CH_3)_3 + BH_3{\cdot}N(CH_3)_3 \quad (2)$$

proceeded similarly to give $B_4H_8{\cdot}2P(CH_3)_3$.[2]

As a result of the recent, successful isolation of $B_2H_4{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3$ in pure form, another triboron complex cation, $B_3H_6{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3{}^+$, became available.[3] It was of interest to see how the $B_3H_8{}^-$ salt of this "hybrid" cation would respond to the treatment with $N(CH_3)_3$ or $P(CH_3)_3$. In this paper, results of the reaction studies of $B_3H_6{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3{}^+B_3H_8{}^-$ are described and are compared with corresponding reactions of $B_3H_6{\cdot}2N(CH_3)_3{}^+B_3H_8{}^-$ and $B_3H_6{\cdot}2P(CH_3)_3{}^+B_3H_8{}^-$.

Results

Reactions of $B_3H_6{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3{}^+B_3H_8{}^-$ and $B_3H_6{\cdot}2N(CH_3)_3{}^+B_3H_8{}^-$ with $N(CH_3)_3$ or $P(CH_3)_3$ proceeded according to eq 3–6.

$$B_3H_6{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3{}^+B_3H_8{}^- + 2N(CH_3)_3 \rightarrow \underset{\text{I}}{[N(CH_3)_3]_2{\cdot}BHBH_2{\cdot}P(CH_3)_3{}^+}B_3H_8{}^- + BH_3{\cdot}N(CH_3)_3 \quad (3)$$

$$B_3H_6{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3{}^+B_3H_8{}^- + 2P(CH_3)_3 \rightarrow \underset{\text{II}}{N(CH_3)_3{\cdot}P(CH_3)_3{\cdot}BHBH_2{\cdot}P(CH_3)_3{}^+}B_3H_8{}^- + BH_3{\cdot}P(CH_3)_3 \quad (4)$$

$$B_3H_6{\cdot}2N(CH_3)_3{}^+B_3H_8{}^- + 2N(CH_3)_3 \rightarrow \underset{\text{III}}{[N(CH_3)_3]_2{\cdot}BHBH_2{\cdot}N(CH_3)_3{}^+}B_3H_8{}^- + BH_3{\cdot}N(CH_3)_3 \quad (5)$$

$$B_3H_6{\cdot}2N(CH_3)_3{}^+B_3H_8{}^- + 2P(CH_3)_3 \rightarrow \underset{\text{IV}}{N(CH_3)_3{\cdot}P(CH_3)_3{\cdot}BHBH_2{\cdot}N(CH_3)_3{}^+}B_3H_8{}^- + BH_3{\cdot}P(CH_3)_3 \quad (6)$$

Generally, these reactions are clean and virtually quantitative as long as the reaction solutions are kept below the decomposition temperatures of the respective products. As the reaction proceeded, the signals of the $N(CH_3)_3$ or $P(CH_3)_3$ adduct of BH_3 and the diboron complex cation grew in the ^{11}B NMR spectrum of each reaction solution while the signals of the triboron complex cation diminished and that of $B_3H_8{}^-$ remained unchanged. Compound IV is the most stable of the four diboron cations, and most of the coproduct, $BH_3{\cdot}P(CH_3)_3$, can be sublimed out at 0 °C. Above 0 °C, however, this salt decomposes slowly. This compound can also be prepared from III by a ligand displacement reaction (eq 7).

$$[N(CH_3)_3]_2{\cdot}BHBH_2{\cdot}N(CH_3)_3{}^+B_3H_8{}^- + P(CH_3)_3 \rightarrow N(CH_3)_3{\cdot}P(CH_3)_3{\cdot}BHBH_2{\cdot}N(CH_3)_3{}^+B_3H_8{}^- + N(CH_3)_3 \quad (7)$$

Salt III is the least stable and undergoes decomposition at -40 °C. Compounds I and II decompose slowly at -30 °C. Because of their limited stabilities, the salts were characterized by their NMR spectra as they were formed, in the presence of the coproducts $BH_3{\cdot}N(CH_3)_3$ or $BH_3{\cdot}P(CH_3)_3$.

NMR Spectra and Structures of the Diboron Complex Cations. The chemical shift data for the four diboron cations, I–IV, are listed in Table I.

(a) 1,1-Bis(trimethylamine)-2-(trimethylphosphine)trihydrodiboron(1+) Cation, $[N(CH_3)_3]_2{\cdot}BHBH_2{\cdot}P(CH_3)_3{}^+$ (I). The two broad signals at +11.4 and -34.7 ppm in the $^{11}B\{^1H\}$ NMR spectrum could readily be assigned to the two-amine-attached boron and the phosphine-attached boron atoms, respectively. Furthermore, the presence of only one amine methyl proton signal and its intensity 2 relative to that of the phosphine methyl proton signal supported the designated structure of this cation.

(b) 1-(Trimethylamine)-1,2-bis(trimethylphosphine)trihydrodiboron(1+) Cation, $N(CH_3)_3{\cdot}P(CH_3)_3{\cdot}BHBH_2{\cdot}P(CH_3)_3{}^+$ (II). The broad signal at -5.8 ppm in the $^{11}B\{^1H\}$ spectrum was attributed to the boron atom attached to both an amine group and a phosphine group, and the signal at -35.8 ppm could be attributed to the phosphine-attached boron atom. The presence of two phosphine methyl proton signals was also consistent with the structure assigned to this cation.

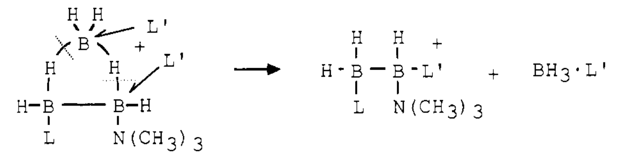
(c) 1,1,2-Tris(trimethylamine)trihydrodiboron(1+) Cation, $[N(CH_3)_3]_2{\cdot}BHBH_2{\cdot}N(CH_3)_3{}^+$ (III). As reported earlier[1] the ^{11}B resonance signals appeared at +12.5 and -3.9 ppm, which were assigned to the two-amine-attached boron and one-amine-attached boron atom, respectively. The presence of the two amine methyl proton signals in a 2:1 intensity ratio is consistent with the designated structure of this cation.

(d) 1,2-Bis(trimethylamine)-1-(trimethylphosphine)trihydrodiboron(1+) Cation, $N(CH_3)_3{\cdot}P(CH_3)_3{\cdot}BHBH_2{\cdot}N(CH_3)_3{}^+$ (IV). The $^{11}B\{^1H\}$ spectrum showed only one broad signal at -5.4 ppm, which is due to the overlapping of signals arising from the two nonequivalent boron atoms in the cation. This assignment is made on the basis of the relative intensities of the signals present in the spectrum of the reaction solution: the signal at -5.4 ppm; intensity 2, $B_3H_8{}^-$ signal; intensity 3, and $BH_3{\cdot}P(CH_3)_3$ signal; intensity 1. These two coincidental signals at -5.4 ppm could not be resolved even on a Varian XL-400 instrument (^{11}B observation frequency, 128 MHz). However, on this high-field instrument the application of resolution enhancement techniques did indicate a dissymmetry attributable to the overlapping of these two signals. Furthermore, the presence of two trimethylamine proton signals in a 1:1 intensity ratio verified the identity of this cation.

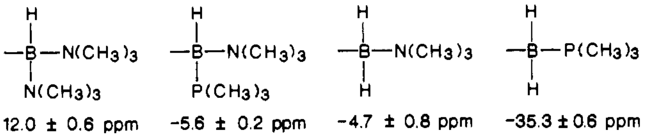
---

(1) DePoy, R. E.; Kodama, G. *Inorg. Chem.* **1985**, *24*, 2871.
(2) Kameda, M.; Kodama, G. *Inorg. Chem.* **1984**, *23*, 3710.
(3) DePoy, R. E.; Kodama, G. *Inorg. Chem.* **1988**, *27*, 1116.

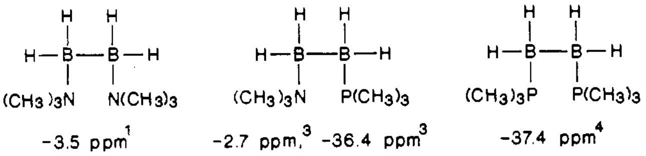
Scheme I



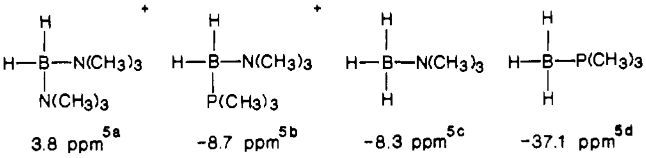
Summary of ^{11}B Shift Values. The following ^{11}B group shift values are found for the diboron complex cations:



When trimethylamine is replaced by trimethylphosphine on the adjacent boron atom, the ^{11}B resonance moves upfield only slightly. For example, in going from $[N(CH_3)_3]_2·BHBH_2·N(CH_3)_3^+$ to $[N(CH_3)_3]_2·BHBH_2·P(CH_3)_3^+$, the ^{11}B shift value of the $[N(CH_3)_3]_2·BH$ group decreases by 1.1 ppm. Thus, each of the ^{11}B shift values for these groups is essentially constant regardless of the type of ligands ($N(CH_3)_3$ or $P(CH_3)_3$) attached to the adjacent boron atom. Furthermore, the values listed above are comparable with those for $B_2H_4·L·L'$:



The values further compare with those reported for the following monoborane species:



Discussion

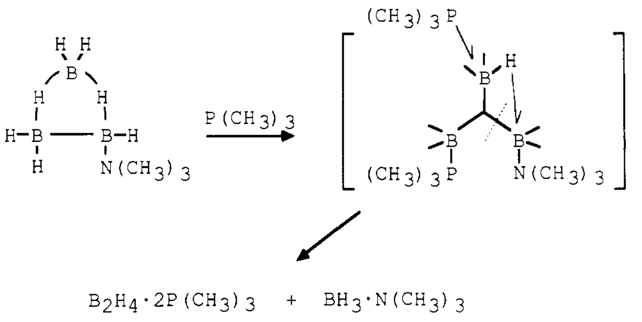
There are two important features that are common to the reactions represented by eq 3–6: (1) In the diboron complex cations produced, the attacking Lewis base is always bonded to the amine-attached boron atom, and (2) the BH_3 adduct that is formed always contains the attacking Lewis base. Thus, the four reactions can be summarized by eq 8, where L and L′ are $N(CH_3)_3$

$$B_3H_6·L·N(CH_3)_3{}^+B_3H_8{}^- + 2L' \rightarrow L·BH_2–BH·N(CH_3)_3·L'^+B_3H_8{}^- + BH_3·L' \quad (8)$$

or $P(CH_3)_3$ and L′ is the attacking base. Apparently, the bond cleavages occur as indicated in Scheme I. This observation immediately provides a "partial" explanation for the behavior of $B_3H_6·2P(CH_3)_3{}^+B_3H_8{}^-$ toward $P(CH_3)_3$ or $N(CH_3)_3$ (eq 2). Because of the absence of a trimethylamine-attached boron atom in the $B_3H_6·2P(CH_3)_3{}^+$ cation, the attacking base, L′, cannot find an effective site of attack on the $(CH_3)_3P–B–B–P(CH_3)_3$ moiety to produce a $B_2H_3·2P(CH_3)_3·L'^+$ cation.

The Lewis base adducts of triborane(7) are isoelectronic and isostructural with the triboron complex cations. Interestingly, however, the above pattern of triboron cation cleavage contrasts with those observed for the cleavage of $B_3H_7·N(CH_3)_3$ and $B_3H_7·P(CH_3)_3$ with $N(CH_3)_3$ or $P(CH_3)_3$, where the BH_3 adducts produced contain $N(CH_3)_3$ whenever $N(CH_3)_3$ is involved in the reaction system.[3] For example, $B_3H_7·N(CH_3)_3 + 2P(CH_3)_3 \rightarrow B_2H_4·2P(CH_3)_3 + BH_3·N(CH_3)_3$. This observation was explained[3] by extending the mechanism proposed by Ritter and co-workers[6] and by Paine and Parry,[7] as a result of favorable elimination of $BH_3·N(CH_3)_3$ from the reaction intermediate "$B_3H_7·P(CH_3)_3·N(CH_3)_3$". Upon further $P(CH_3)_3$ attack on the intermediate, $BH_3·N(CH_3)_3$ splits off from the intermediate and the attacking base $P(CH_3)_3$ is combined with the B_2H_4 fragment as illustrated in Scheme II. This mechanistic model for the triborane(7) adduct cleavage does not explain the observed cleavage pattern of the triboron cations. Reactivity variation due to the presence of charge and the nature of ligand is demonstrated in these triboron framework cleavages. Further studies are being pursued to elucidate the triboron framework cleavage processes, in which Lewis bases play subtle, but important roles.

Scheme II



Experimental Section

General Procedures for the Reaction Studies. A dichloromethane solution (ca. 2 mL) of the triboron complex cation was prepared in a 10 mm o.d. Pyrex tube or a 10 mm o.d. resealable NMR sample tube (product of Young Ltd.). A measured amount of $N(CH_3)_3$ or $P(CH_3)_3$ was condensed onto the solution at liquid-nitrogen temperature. The solution was mixed well at −80 °C, and then the tube was placed in the precooled probe of a Varian XL-300 NMR spectrometer to monitor the reaction as the temperature of the probe was raised stepwise.

Reagents. The $B_3H_8{}^-$ salts of the triboron complex cations were prepared in the reaction tubes according to the reported methods.[1,3] The salt was isolated as a solid in the tube, and then a fresh portion of the solvent was condensed into the tube to prepare the solution. The trimethylamine, trimethylphosphine, and dichloromethane used were from our laboratory stock.[8]

Reactions. (a) $B_3H_6·N(CH_3)_3·P(CH_3)_3{}^+B_3H_8{}^-$ and $N(CH_3)_3$. A 0.65-mmol sample of $B_3H_6·N(CH_3)_3·P(CH_3)_3{}^+B_3H_8{}^-$ was treated with 1.45 mmol of $N(CH_3)_3$. The signals of the products (the diboron cation (I) and $BH_3·N(CH_3)_3$) were detected at −80 °C. The reaction was complete as the probe temperatue was raised to −60 °C. At −20 °C, signals due to decomposition products began to appear slowly in the spectrum.

(b) $B_3H_6·N(CH_3)_3·P(CH_3)_3{}^+B_3H_8{}^-$ and $P(CH_3)_3$. A 0.49-mmol sample of $B_3H_6·N(CH_3)_3·P(CH_3)_3{}^+B_3H_8{}^-$ was treated with 0.98 mmol of $P(CH_3)_3$. When the reaction mixture was allowed to warm to −30 °C, the reactants had been changed to a 1:1 molar mixture of $N(CH_3)_3·P(CH_3)_3·BHBH_2·P(CH_3)_3{}^+B_3H_8{}^-$ (II) and $BH_3·P(CH_3)_3$. At this temperature, slow decomposition of the salt occurred as evidenced by the appearance of the $BH_3·N(CH_3)_3$ signal in the spectrum of the solution.

(c) $B_3H_6·2N(CH_3)_3{}^+B_3H_8{}^-$ and $N(CH_3)_3$. A sample (normally about 0.5 mmol) of $B_3H_6·2N(CH_3)_3{}^+B_3H_8{}^-$ was treated with 2 molar equiv or more of $N(CH_3)_3$. Conversion of the reactants to $[N(CH_3)_3]_2·BHBH_2·N(CH_3)_3{}^+B_3H_8{}^-$ (III) and $BH_3·N(CH_3)_3$ was complete at −60 °C. Above −40 °C (or even at −50 °C, upon irradiation of the solution with the ^{1}H resonance frequencies for decoupling the ^{1}H spins), decomposition of the diboron cation occurred. The decomposition product(s) had its characteristic ^{11}B signals at −2.9 and 13.3 ppm, and the $B_3H_8{}^-$ signal was present. The nature of the decomposition product has not been elucidated.

Conversion of III to IV. A sample containing III, which had been prepared as above, was mixed with 1 molar equiv of $P(CH_3)_3$ at −80 °C in CH_2Cl_2. At −45 °C changes in the spectrum were noted. After the mixture was stored for 2.5 h at −30 °C, III had been converted completely to IV. Treatment of III with a 3-fold excess of $P(CH_3)_3$ at −30

---

(4) Hertz, R. K.; Denniston, M. L.; Shore, S. G. *Inorg. Chem.* **1978**, *17*, 2673.

(5) Nöth, H.; Wrackmeyer, B. In *NMR, Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds. Springer-Verlag: West Berlin, Heidelberg, FRG, 1978; Vol. 14: (a) p 377; (b) p 380; (c) p 285; (d) p 341.

(6) Deever, W. R.; Lory, E. R.; Ritter, D. M. *Inorg. Chem.* **1969**, *8*, 1263.

(7) Paine, R. T.; Parry, R. W. *Inorg. Chem.* **1975**, *14*, 689.

(8) Kameda, M.; Kodama, G. *Inorg. Chem.* **1984**, *23*, 3710.

°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.

Acknowledgment. This work was supported by the U.S. Army Research Office through Grant DAAG 29-85-K-0034. The NMR instrument was acquired with the use of instrumentation funds that were provided by the National Science Foundation and the Department of Defense. Financial support to R.E.D. from the National Science Foundation (Minority Graduate Fellowship, 1981–1984) is appreciated.

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.

---

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

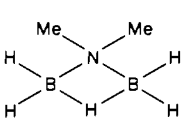
Contribution from the Department of Chemistry,
University of Wisconsin, Madison, Wisconsin 53706

Bis(μ-dimethylamino)tetraborane(10), $(\mu\text{-}Me_2N)_2B_4H_8$

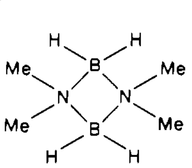
Donald F. Gaines* and Joan C. Kunz

Received December 1, 1987

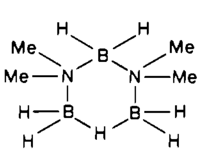
One of our synthetic interests is the incorporation of group V (group 15) atoms into intermediate-sized borane clusters. The paucity of such compounds has led us to consider a variety of previously unexplored routes to borane clusters having group V substituent atoms in terminal or bridging positions[1] 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, $(\mu\text{-}R_2N)B_2H_5$,[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.



$(\mu\text{-}Me_2N)B_2H_5$



$(Me_2NBH_2)_2$



$(Me_2N)_2B_3H_7$

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.

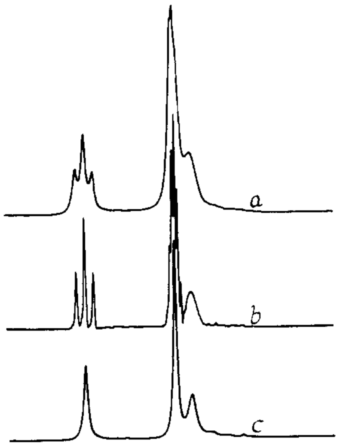


Figure 1. 86.7-MHz ^{11}B NMR spectra of neat $(\mu\text{-}Me_2N)_2B_4H_8$: (a) normal; (b) line narrowed; (c) ^1H decoupled.

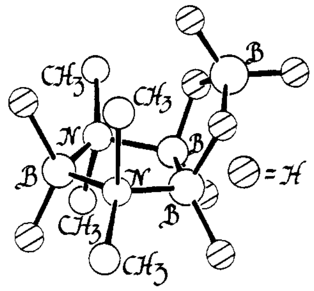


Figure 2. Proposed structure of $(\mu\text{-}Me_2N)_2B_4H_8$.

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

aminoborane	BN(asym)[a]	BN(sym)[a]	ref
$(\mu\text{-}Me_2N)B_2H_5$	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
$(\mu\text{-}Me_2N)_2B_4H_8$	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), $(\mu\text{-}Me_2N)_2B_4H_8$, in yields of ca. 10%. The other major volatile boron-containing products in this synthesis are $(\mu\text{-}Me_2N)B_2H_5$ and $(Me_2NBH_2)_2$. In the absence of solvent, considerable $(Me_2NBH_2)_2$ is formed along with $(\mu\text{-}Me_2N)B_2H_5$ but very little of the bis(μ-dimethylamino)tetraborane(10) is obtained.

The relatively volatile $(\mu\text{-}Me_2N)_2B_4H_8$ 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 $(\mu\text{-}Me_2N)B_2H_5$. The decomposition of $(\mu\text{-}Me_2N)_2B_4H_8$ 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 ^1H decoupling; a multiplet of intensity 2

---

(1) Gaines, D. F.; Coons, D. E. *Inorg. Chem.* **1986**, *25*, 364–367.
(2) Coons, D. E.; Gaines, D. F. *Inorg. Chem.* **1987**, *26*, 1985–1988.
(3) Schwartz, L. D.; Keller, P. D. *J. Am. Chem. Soc.* **1972**, *94*, 3015–3018 and references therein.
(4) *Gmelins Handbuch der Anorganischen Chemie*, 8th ed.; Springer Verlag: West Berlin, 1983, Vol. 1, 2nd Supplement, Boron Compounds, pp 409–414; 1980, Vol. 2, 1st Supplement, Boron Compounds, pp 142–163 and references therein.
(5) Keller, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 3078–3085.
(6) Lipscomb, W. N.; Lewis, R. In *Boron-Nitrogen Chemistry*; Gould, R. F., Ed.; American Chemical Society: Washington, DC, 1964, pp 312–322.

0020-1669/88/1327-1839$01.50/0