

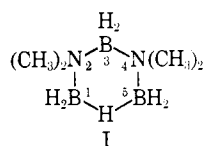
# Bis( $\mu$ -dimethylamino)triborane(9). Synthesis by Stepwise Boron-Nitrogen Chain Buildup and from Tris- and Bis(dimethylamino)borane. Spectroscopic, Chemical, and Isotopic Studies

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**Abstract:** Bis( $\mu$ -dimethylamino)triborane(9) (I) can be prepared in low yield by the action of excess diborane on  $\text{Al}[\text{N}(\text{CH}_3)_2]_3$  in diethyl ether. Spectroscopic studies show the compound to have a cyclic hydrogen bridged structure. Reaction of  $(\text{CH}_3)_2\text{NHBH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$  with potassium in ether solvents affords the unstable salt  $\text{K}[(\text{CH}_3)_2\text{NBH}_2\text{N}(\text{CH}_3)_2\text{BH}_3]$  which reacts with excess diborane to generate I and  $\text{KBH}_4$ . Treatment of  $\text{HB}[\text{N}(\text{CH}_3)_2]_2$  with 0.5 mol of diborane produces only  $[(\text{CH}_3)_2\text{NBH}_2]_2$ . The reaction of  $\text{B}[\text{N}(\text{CH}_3)_2]_3$  with excess diborane in diethyl ether produces a mixture of I,  $[(\text{CH}_3)_2\text{NBH}_2]_2$ , and  $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$ . The first step in this reaction has been shown to be exchange of a dimethylamino group for hydrogen to form  $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$  and  $\text{HB}[\text{N}(\text{CH}_3)_2]_2$ . The action of diborane upon I slowly affords  $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$ ; thermal decomposition of I yields  $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$  and  $[(\text{CH}_3)_2\text{NBH}_2]_2$ . The reaction of  $\text{HB}[\text{N}(\text{CH}_3)_2]_2$  with  $^{10}\text{B}_2\text{H}_6$  in diethyl ether produces bis( $\mu$ -dimethylamino)triborane(9)- $I,5\text{-}^{10}\text{B}$  ( $I,5\text{-}^{10}\text{B}$ ). Reaction of I with trimethylamine or dimethylamine produces  $[(\text{CH}_3)_2\text{NBH}_2]_2$  and the appropriate amine adduct of  $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$ . Low temperature boron-11 nmr studies of this reaction gave no evidence for intermediate species. The action of dimethylamine on  $I,5\text{-}^{10}\text{B}$  affords  $[(\text{CH}_3)_2\text{N}^{10}\text{BH}_2]_2$  and  $(\text{CH}_3)_2\text{NH}^n\text{BH}_2\text{N}(\text{CH}_3)_2^{10}\text{BH}_3$ . The boron-10 label on the latter is lost by isotopic scrambling upon standing at room temperature. Reaction of I with sodium hydride yields  $[(\text{CH}_3)_2\text{NBH}_2]_2$  and  $\text{Na}[(\text{CH}_3)_2\text{N}(\text{BH}_3)_2]$ . Repetition of this experiment using  $I,5\text{-}^{10}\text{B}$  generates  $[(\text{CH}_3)_2\text{N}^{10}\text{BH}_2]_2$  and sodium bis(borane)dimethylamide containing both  $^{11}\text{B}$  and  $^{10}\text{B}$ .

In 1972<sup>1</sup> we reported the isolation and characterization of bis-( $\mu$ -dimethylamino)triborane(9) (I)



formed as a low yield by-product from the reaction of excess diborane with  $\text{Al}[\text{N}(\text{CH}_3)_2]_3$  in diethyl ether. Our interest in this new type of boron-nitrogen compound and our desire to compare its properties with those of structurally related substances like  $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$  and  $[(\text{CH}_3)_2\text{NBH}_2]_2$  gave impetus to a search for more convenient and efficient synthetic methods, two of which are detailed in this article.

The synthesis problem was attacked first by attempting to build up a boron-nitrogen chain in a stepwise fashion starting with the easily available  $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$ .<sup>2</sup> This technique proved successful and in addition gave new information and insight on the synthesis, stability, and behavior of extended boron-nitrogen chains.

The second synthetic approach evolved from the re-examination of some unpublished and previously unexplained results of an earlier study on the lithium dimethylamide-diborane reaction,<sup>3</sup> which indicated that some I possibly formed from the action of excess diborane on  $\text{B}[\text{N}(\text{CH}_3)_2]_3$ . Accordingly, the reaction of diborane with  $\text{B}[\text{N}(\text{CH}_3)_2]_3$  or  $\text{HB}[\text{N}(\text{CH}_3)_2]_2$  under controlled conditions was found to be an excellent preparative method for I. These studies give new information on steric effects in  $\text{B}[\text{NR}_2]_3$ -diborane

reactions and shed new light on some much earlier observations on dimethylamino boron hydride systems by Burg and Randolph.<sup>4</sup> The use of  $^{10}\text{B}_2\text{H}_6$  in this synthesis produces a specifically labeled product which carries strong implications on its mode of formation and has provided a rare opportunity to probe some of the mechanistic behavior of boron-nitrogen chain compounds.

## Results and Discussion

**Spectroscopic and Synthetic Studies. Nmr Spectra.** The boron-11 nmr spectra of a toluene solution of I at temperatures between  $-30$  and  $60^\circ$  are illustrated in Figure 1. The spectrum at  $-30^\circ$  consists of a superimposed triplet ( $-6.7$  ppm;  $J = 109$  Hz) and triplet of doublets (1.6 ppm;  $J_{\text{BH}} = 120$  Hz,  $J_{\text{BHB}} = 30$  Hz). The general line shape and appearance of the overlapping signals are close to those of the structurally related compounds  $[(\text{CH}_3)_2\text{NBH}_2]_2$  (triplet  $-5.4$  ppm;  $J = 110$  Hz) and  $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$  (triplet of doublets at low temperatures 17.0 ppm;  $J_{\text{BH}} = 130$  Hz,  $J_{\text{BHB}} = 30$  Hz). The line widths of the triplets arising from I and  $[(\text{CH}_3)_2\text{NBH}_2]_2$  are sufficiently narrow to distinguish easily separate signals in mixtures of the two (see, for example, Figures 4 and 5).

The low field triplet portion of the spectrum does not change shape with temperature. The triplet of doublets shows the typical temperature dependence of the  $-\text{H}_2\text{B}-\text{HBH}_2-$  group in  $\mu$ -aminodiboranes<sup>5</sup> in showing increasingly rapid intramolecular bridge-terminal hydrogen exchange with temperature. It is interesting that comparison of line shapes at different temperatures shows that the intramolecular exchange is consider-

(1) P. C. Keller, *J. Amer. Chem. Soc.*, **94**, 4020 (1972).

(2) P. C. Keller, *Syn. Inorg. Metal-Org. Chem.*, **3**, 307 (1973).

(3) L. D. Schwartz and P. C. Keller, *J. Amer. Chem. Soc.*, **94**, 3015 (1972).

(4) A. B. Burg and C. L. Randolph, Jr., *J. Amer. Chem. Soc.*, **73**, 953 (1951).

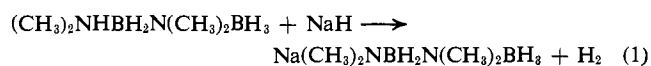
(5) D. F. Gaines and R. Schaeffer, *J. Amer. Chem. Soc.*, **86**, 1505 (1964).

ably faster in I than in  $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5^6$  and that the exchange rate is less sensitive to solvent (toluene, diethyl ether, and monoglyme) than  $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$ . The greatest structural difference between I and  $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$  that might affect the exchange rate is ring strain. In  $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$  the BNB angle is  $76.4 \pm 5.5^\circ$  with a relatively long  $1.92 \pm 0.11 \text{ \AA}$  B...B distance,<sup>7</sup> while in I the six-membered ring may be relatively strain free.

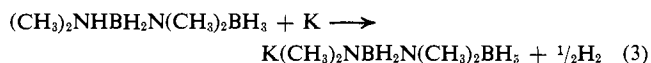
The proton spectrum of I at  $-20^\circ$  (toluene- $d_6$ ) consists of a single *N*-methyl signal at  $\tau$  8.20 superimposed upon two overlapping 1:1:1:1  $^{11}\text{B-H}$  quartets in 2:1 intensity ratio at  $\tau$  7.43,  $J = 118 \text{ Hz}$ , and  $\tau$  8.07,  $J = 109 \text{ Hz}$ , respectively. The bridge hydrogen resonance is clearly observable at  $\tau$  11.54. Owing to the superposition of signals from thermal decomposition products, unambiguous high temperature spectra could not be obtained.

#### Formation of I by Boron-Nitrogen Chain Buildup.

The formation of amine adducts of  $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$  is a well-established route to BNB chain compounds. The key step in chain extension beyond this point in our technique is the removal of the NH proton from  $(\text{CH}_3)_2\text{NHBH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$  to form a Lewis base capable of an addition reaction with diborane. The deprotonation can be brought about by using sodium hydride (eq 1), but chain cleavage by excess reagent is a serious competing reaction (eq 2) rendering this method of little value.



In practice deprotonation is accomplished effectively by reduction with potassium metal (eq 3); the reaction with sodium is inconveniently slow.



The salt could not be isolated in a pure form, apparently owing to instability and decomposition upon solvent removal. However, the circumstantial evidence of the hydrogen and potassium stoichiometry and the boron-11 nmr and the reaction products with diborane leave minimal doubt concerning the constitution of the product. The boron-11 nmr spectrum of a fresh solution of deprotonated product shows the expected triplet ( $-2.4 \text{ ppm}$ ,  $J = 92 \text{ Hz}$ ) and quartet (slightly asymmetric,  $13.1 \text{ ppm}$ ,  $J = 81 \text{ Hz}$ ). The chemical shifts of these signals are close to their counterparts in the spectrum of the parent compound, but the coupling constants are sufficiently diminished to allow a clear distinction to be made between the two substances. The diminution of the coupling constant, at least in the case of the triplet, can be correlated with the effect of the nitrogen lone pair on the BH coupling constant.<sup>8,9</sup> In fresh samples the signals are of nearly equal intensity; after 17 hr at ambient temperature the triplet intensity diminished to *ca.* one-fourth that of the quartet. No new signals appeared.

(6) R. E. Schirmer, J. H. Noggle, and D. F. Gaines, *J. Amer. Chem. Soc.*, **91**, 6240 (1969).

(7) K. Hedberg and A. J. Stosick, *J. Amer. Chem. Soc.*, **74**, 954 (1952).

(8) V. M. S. Gil and J. J. C. Teixeira-Dias, *Mol. Phys.*, **15**, 47 (1968).

(9) V. M. S. Gil and A. C. P. Alves, *Mol. Phys.*, **16**, 527 (1969).

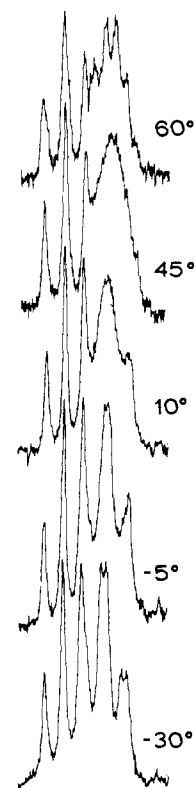
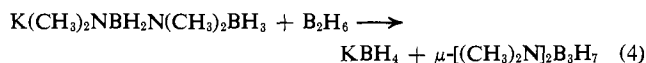
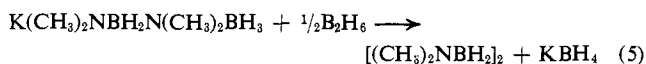


Figure 1. Temperature variation of the boron-11 nmr spectrum of I in toluene. Magnetic field increases from left to right.

The addition of diborane to monoglyme or diethyl ether solutions of  $\text{K}(\text{CH}_3)_2\text{NBH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$  occurs smoothly at room temperature in agreement with eq 4.

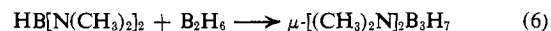


Since the same reaction occurs with a monoglyme solution of the sodium salt, the formation of an insoluble metal borohydride is not the driving force for the process. It is interesting that transfer of hydride ion to diborane and subsequent ring closure (eq 5) do



not occur. At least two explanations for the absence of reaction 5 can be proposed. First, bond strain may control the ring size of the product; the six-membered ring structure of I should be less strained than the four-membered ring of  $[(\text{CH}_3)_2\text{NBH}_2]_2$ . Alternatively, the formation of the dimeric aminoborane may require the intermediacy of monomeric  $(\text{CH}_3)_2\text{NBH}_2$ , which would not be expected to form under the conditions of this reaction.

**Formation of I from  $\text{HB}[\text{N}(\text{CH}_3)_2]_2$ .** Diethyl ether solutions of  $\text{HB}[\text{N}(\text{CH}_3)_2]_2$  react with equimolar quantities of diborane according to eq 6. Addition of more



diborane merely results in the appearance of a signal characteristic of this reactant at low field. The reaction generates no by-products other than small easily removed amounts of  $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$ , probably formed by the action of diborane on I (see below), and is the most straightforward and convenient laboratory synthesis of I.

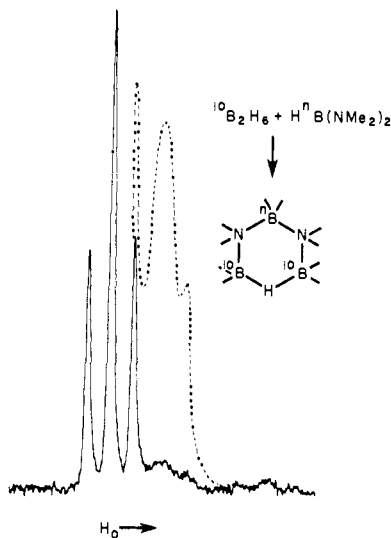


Figure 2. Boron-11 nmr spectrum of the products of the reaction of  $\text{H}^n\text{B}[\text{N}(\text{CH}_3)_2]_2$  with excess  $^{10}\text{B}_2\text{H}_6$  in diethyl ether. The dotted curve outlines the missing part of the spectrum of I with a normal isotope distribution.

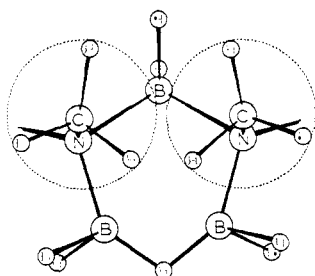
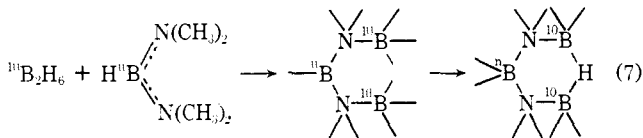


Figure 3. Approximate geometry of I showing axial crowding of *N*-methyl groups.

Reaction of  $^{10}\text{B}_2\text{H}_6$  with isotopically normal  $\text{HB}[\text{N}(\text{CH}_3)_2]_2$  generates I selectively labeled with boron-10 in the 1,5 positions as demonstrated by the nmr spectrum in Figure 2 (compare  $10^\circ$  spectrum in Figure 1). The dotted curve outlines the missing part of the isotopically normal spectrum. This result suggests a reaction mechanism similar to that shown in eq 7.<sup>10</sup>



The loss of (p → p)π stabilization of the three-coordinate boron in the intermediate double borane adduct would provide the driving force for the rearrangement of the hydrogen atoms.

At  $-30^\circ$  the boron-11 nmr spectrum of the products of the reaction of  $\text{HB}[\text{N}(\text{CH}_3)_2]_2$  with a half molar quantity of diborane consists of an undecipherable complex of at least 15 lines resulting from a number of overlapping signals which grow or diminish with time. After raising the probe temperature to  $25^\circ$  the many lines rapidly disappear and signals due to  $[(\text{CH}_3)_2\text{NBH}_2]_2$  and  $\text{HB}[\text{N}(\text{CH}_3)_2]_2$  grow in. The net reaction is summarized by eq 8. In view of the cleanness and

(10) The symbol  $^n\text{B}$  represents boron with normal  $^{10}\text{B}$ - $^{11}\text{B}$  isotopic distribution.

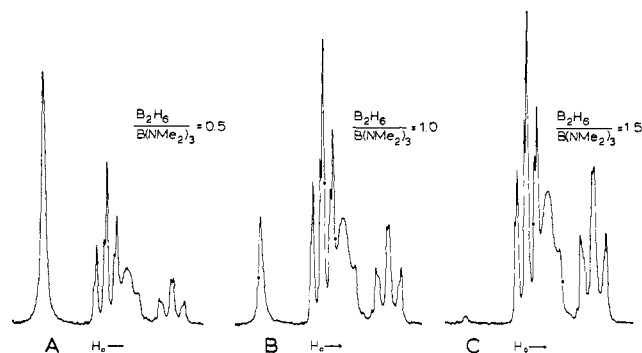
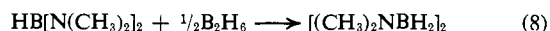
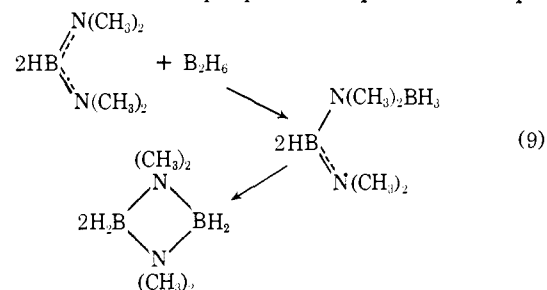


Figure 4. Boron-11 nmr study of the stepwise addition of  $\text{B}_2\text{H}_6$  to a diethyl ether solution of  $\text{B}[\text{N}(\text{CH}_3)_2]_3$ . The signals are assigned (low to high field) to  $\text{B}[\text{N}(\text{CH}_3)_2]_2$ ,  $[(\text{CH}_3)_2\text{NBH}_2]_2$  overlapping with I, and  $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$ .



selectivity exhibited in the isotopic labeling studies above, it is attractive to propose a sequence like eq 9



to account for these results. Unfortunately, the apparent complexity of the low temperature boron nmr spectrum of 2:1  $\text{HB}[\text{N}(\text{CH}_3)_2]_2$ -diborane solution in diethyl ether may indicate a more complex pathway.

It is interesting that in 1954 Burg and Randolph noted in passing that a mixture of "metastable" solid and liquid intermediates could be seen in the low temperature reaction of diborane with  $\text{HB}[\text{N}(\text{CH}_3)_2]_2$  (and  $\text{B}[\text{N}(\text{CH}_3)_2]_3$ ) in the absence of solvent.<sup>4</sup> The results outlined here probably explain part of these observations.

Another intriguing aspect of these systems is that no evidence has been found for the formation of compounds like I when nitrogen bears substituents larger than a methyl group. The only detected products of the reactions of diborane with bulkier bis- and tris-(dialkylamino)boranes are dimeric dialkylaminoboranes and  $\mu$ -dialkylaminodiboranes.<sup>3</sup> The origin of this selectivity can be ascribed to the steric interference of axial groups in the six-membered ring structure of I. Figure 3 illustrates an approximate molecular model of I constructed using the bond distances enumerated in ref 7. The dotted circles outline the rotational circumference of the axial methyl groups; the equatorial methyl groups are omitted for reasons of clarity. It is evident from the figure that the presence of nitrogen substituents larger than methyl results in complete obstruction of free rotation of the axial groups. Even *N*-methyl substituents evidence some crowding reminiscent of the situation in  $[(\text{CH}_3)_2\text{NBH}_2]_3$ ,<sup>11</sup> which may contribute to the sparing thermal stability of I.

**The  $\text{B}[\text{N}(\text{CH}_3)_2]_3$ -Diborane System.** The boron-11 nmr spectra in Figure 4A-C show that the stepwise

(11) L. M. Trefonas, F. S. Mathews, and W. N. Lipscomb, *Acta Crystallogr.*, **14**, 273 (1961).

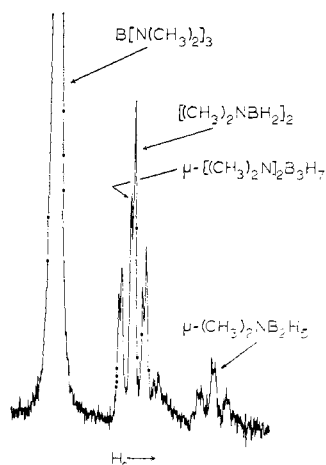
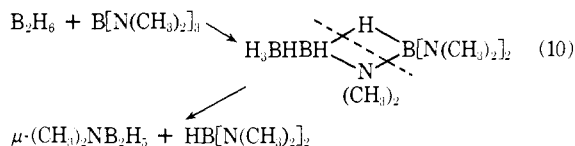


Figure 5. Boron-11 nmr spectrum of the products of the reaction of 1.22 mmol  $B[N(CH_3)_2]_3$  with 0.84 mmol  $^{10}B_2H_6$  in diethyl ether.

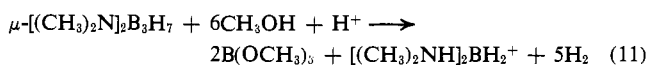
addition of diborane to an ether solution of  $B[N(CH_3)_2]_3$  generates a mixture containing substantial amounts of I,  $\mu-(CH_3)_2NB_2H_5$ , and  $[(CH_3)_2NBH_2]_2$ . When this experiment is repeated using  $^{10}B_2H_6$  and isotopically normal  $B[N(CH_3)_2]_3$ , I is again formed with boron-10 exclusively in the 1,5 positions. Figure 5 shows the spectrum recorded a few minutes after the first addition of  $^{10}B_2H_6$  ( $^{10}B_2H_6$  to  $B[N(CH_3)_2]_3$  ratio 0.68). The weakness of the high field signal shows that  $\mu-(CH_3)_2NB_2H_5$  forms in the early stages of the reaction containing a high percentage of boron-10. The presence of boron-11 in this product probably results from the action of diborane on I (see below).

All the above information and the results of previous work<sup>3</sup> indicate that the first step in the diborane- $B[N(CH_3)_2]_3$  reaction is formation of  $\mu-(CH_3)_2NB_2H_5$  and  $HB[N(CH_3)_2]_2$  by simple hydride-dimethylamino group exchange (eq 10). Note that this interchange



preserves all isotopic labels. The next step would be rapid interaction of the product  $HB[N(CH_3)_2]_2$  with any remaining diborane. As shown above, this process can follow two possible routes. First, with a local shortage of diborane, the product would be  $[(CH_3)_2NBH_2]_2$ . Second, with a local excess of diborane, I would be generated containing boron atoms from the diborane in the 1,5 positions *via* a mechanism like reaction 7. Substantial quantities of  $[(CH_3)_2NBH_2]_2$  would be expected to form, as observed, when diborane is added to the  $B[N(CH_3)_2]_3$  only in limited quantities.

**Chemical and Isotopic Studies. Solvolysis and Thermal Stability.** Solvolysis in acidic anhydrous methanol proceeds according to eq 11. The boronium



salt is highly resistant to acid solvolysis. Formation of this product suggests that solvolytic attack in acidic methanol occurs first at the 1,5-boron atoms, leaving the N-B-N portion of the molecule intact. Identification of the product as  $[(CH_3)_2NH]_2BH_2Cl$  had to be

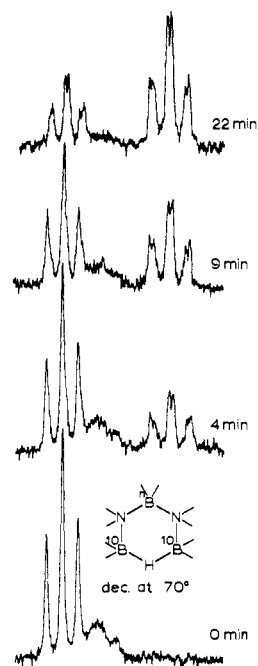


Figure 6. Boron-11 nmr study of the thermal decomposition of I-1,5- $^{10}B$  in toluene solution at  $70^\circ$ . Spectra were scanned at normal probe temperature.

accomplished by comparison with an authentic sample, since the boron-11 nmr parameters of this compound could not be found in the literature. The chemical shift and coupling constant presented in Table I fit

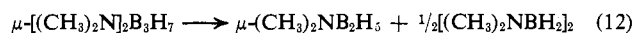
Table I. Boron-11 Nmr Parameters of Bis(amine)boronium(1+) Ions

Ion	$\delta$ , ppm	$J_{BH}$ , Hz
$(H_3N)_2BH_2^+$ <sup>a</sup>	14.3	110
$(CH_3NH_2)_2BH_2^+$ <sup>b</sup>	9.2	104
$[(CH_3)_2NH]_2BH_2^+$ <sup>c</sup>	1.8	110
$[(CH_3)_3N]_2BH_2^+$ <sup>d</sup>	-3.6	120

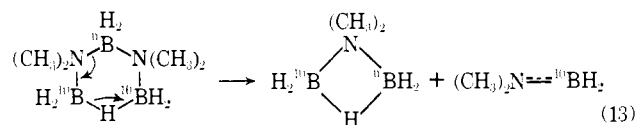
<sup>a</sup> C. W. Heitsch, *Inorg. Chem.*, **4**, 1019 (1965). <sup>b</sup> S. G. Shore, C. W. Hickam, Jr., and D. Cowles, *J. Amer. Chem. Soc.*, **87**, 2755 (1965). <sup>c</sup> This work. <sup>d</sup> N. E. Miller and E. L. Muettterties, *J. Amer. Chem. Soc.*, **86**, 1033 (1964).

with the trend in values of these parameters for varying *N*-methyl substitution in bis(amine)boronium(1+) ions.

Thermal decomposition of I to  $[(CH_3)_2NBH_2]_2$  and  $\mu-(CH_3)_2NB_2H_5$  (eq 12) is complete within 15 min at



$75^\circ$  in toluene solution; decomposition of neat samples occurs similarly. Decomposition studies with I-1,5- $^{10}B$  show that boron in  $[(CH_3)_2NBH_2]_2$  comes largely from the 1,5 atoms (Figure 6). If the decomposition is unimolecular, which has not been experimentally demonstrated here, the process could occur by selective loss of a (p  $\rightarrow$  p) $\pi$  stabilized monomeric  $(CH_3)_2NBH_2$  fragment (eq 13).



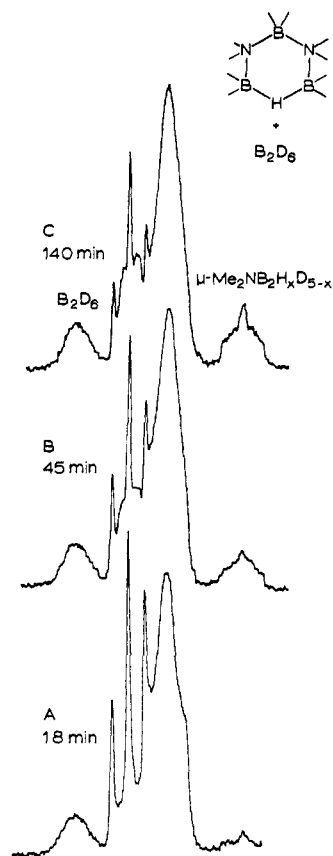
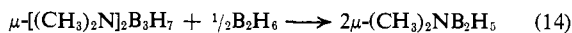


Figure 7. Boron-11 nmr study of the hydrogen isotope exchange between I and  $B_2D_6$ .

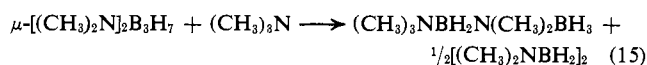
**Reaction with  $B_2H_6$  and  $B_2D_6$ .** Reaction between diborane and I in diethyl ether occurs slowly at  $25^\circ$  in agreement with eq 14. Since the rates of thermal de-



composition and the diborane reaction are of the same order of magnitude, diborane could simply act as a scavenger for monomeric  $(CH_3)_2NBH_2$ , if formed, converting it to  $\mu\text{-}(CH_3)_2NB_2H_5$ .

As shown in Figure 7, I exchanges all BH hydrogens with  $B_2D_6$ . The exchange is much faster than the reaction with diborane that produces  $\mu\text{-}(CH_3)_2NB_2H_5$ ; qualitatively the  $-H_2BHBH_2-$  hydrogens seem to exchange at a greater rate than the  $NBH_2N$  hydrogens.

**Reaction with  $(CH_3)_3N$  and  $(CH_3)_2NH$ .** At first these experiments were an attempt to form linear NBNBNB chains by analogy with the amine addition reactions of  $\mu\text{-}(CH_3)_2NB_2H_5$ .<sup>12</sup> Treatment of I with  $(CH_3)_3N$  affords the chain cleavage products summarized in eq 15.



The study of the reaction of  $(CH_3)_2NH$  with I-1,5- $^{10}B$  presented the opportunity not only to get a more direct identification of the less dissociated  $(CH_3)_2NH$  complex with  $\mu\text{-}(CH_3)_2NB_2H_5$  but also to observe the distribution of boron isotopes in the products. Figure 8A shows the boron-11 nmr spectrum of this system within 5 min of mixing. The isotope distribution

(12) G. A. Hahn and R. Schaeffer, *J. Amer. Chem. Soc.*, **86**, 1503 (1964).

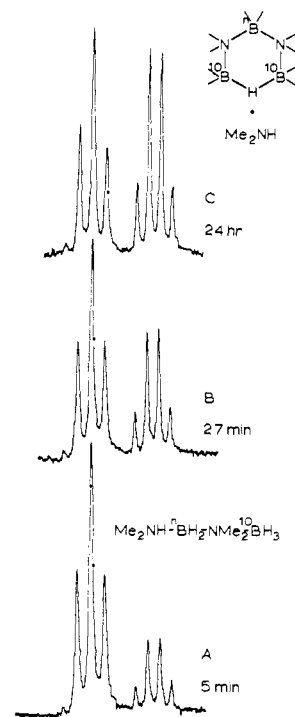
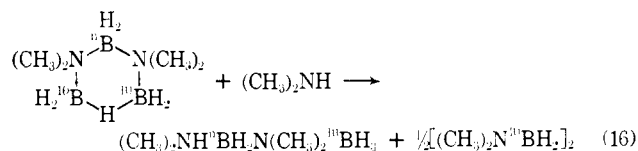
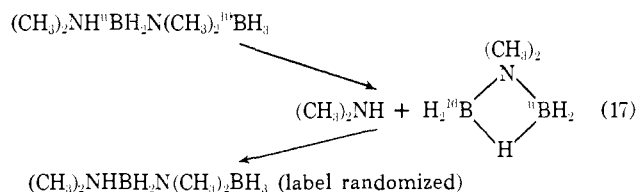


Figure 8. Boron-11 nmr study of the time loss of isotope labels in the products of the reaction of  $(CH_3)_2NH$  with I-1,5- $^{10}B$  in diethyl ether.

implied by this result is summarized in eq 16. The

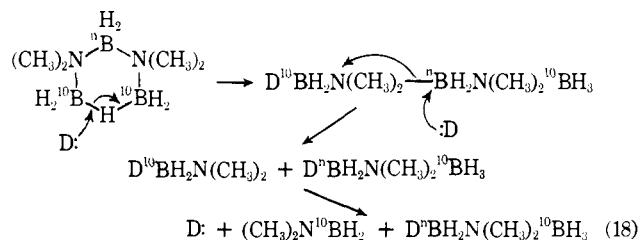


product of reaction 16 is the first example of a boron labeled NBNB chain compound. The spectra in Figures 8B and C follow the loss of the boron label in solution with time. The isotope randomization most probably arises from the reversible dissociation of the complex (eq 17) to form a symmetrical intermediate.

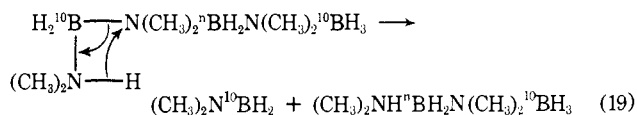


The discovery that the attacking base emerges from the reaction joined to the boron originally occupying the 3-position was completely unexpected. Based on the many known donor-acceptor reactions in boron hydride chemistry, attack by dimethylamine would have been naively predicted to occur at the hydrogen bridged end of the molecule, ultimately giving a product with the amine connected to one of the 1,5 borons.

A plausible explanation for these observations may lie in the base catalyzed scheme outlined in eq 18. The viability of this mechanism hinges upon the easy dissociation of the base- $(CH_3)_2NBH_2$  adduct to afford the experimentally observed products. If the donor is an amine, this prerequisite is satisfied;<sup>4</sup> if the donor is a hydride ion (see below), it is not.

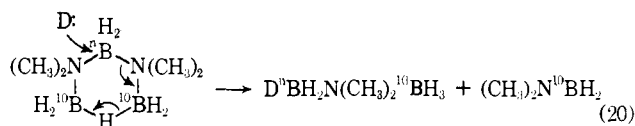


A second possibility is represented by the hydrogen transfer mechanism shown in eq 19. It should be



noted, however, that this process cannot explain the products of the reaction between I and  $(\text{CH}_3)_3\text{N}$ .

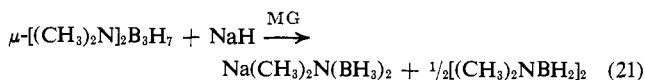
From the available data the alternative of direct base attack on the boron in the 3 position cannot be ruled out. The elimination of a  $(p \rightarrow p)\pi$  stabilized monomeric  $(\text{CH}_3)_2\text{NBH}_2$  could facilitate such a reaction (eq 20). Although this pathway seems without



precedent, it is important to realize that I is the first example of a boron-nitrogen compound with these two chemically distinct kinds of boron present in the same molecule.

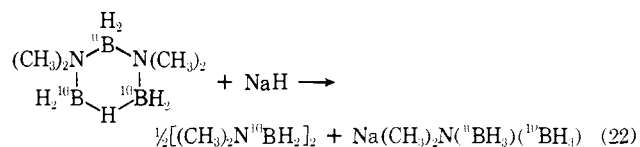
Attempts to detect intermediates by low temperature nmr studies on the  $(\text{CH}_3)_2\text{NH}-\text{I}$  system were unsuccessful. Although the spectra were complicated owing to overlapping signals, at no time could the spectra not be interpreted in terms of a diminishing signal due to I and growing signals due to  $[(\text{CH}_3)_2\text{NBH}_2]_2$  and  $(\text{CH}_3)_2\text{NHBH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$ .

**Reaction with Sodium Hydride.** As above, the original purpose of this experiment was the synthesis of the hydride ion addition compound  $\text{H}_3\text{BN}(\text{CH}_3)_2\text{BH}_2\text{N}(\text{CH}_3)_2\text{BH}_3^-$ . The actual reaction is slow and follows the course indicated by eq 21. In addition to



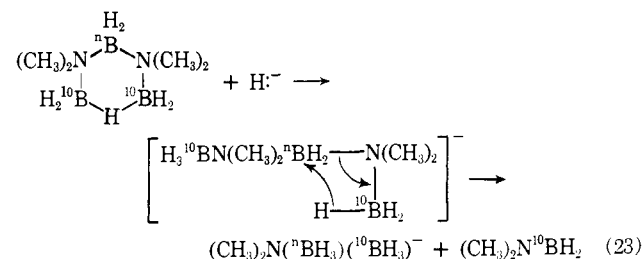
the materials indicated, a small amount of an involatile unidentified by-product also forms (boron-11 nmr, triplet  $-2.9$  ppm,  $J = 106$  Hz).

The product isotope distribution from the reaction of sodium hydride with I-1,5- $^{10}\text{B}$  in monoglyme is summarized by eq 22. Again, the  $[(\text{CH}_3)_2\text{NBH}_2]_2$  is

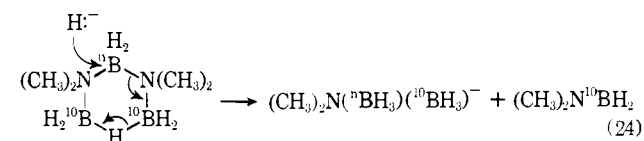


formed only from the boron-10 labeled portion of the substrate. Owing to the symmetry of the  $(\text{CH}_3)_2\text{N}(\text{BH}_3)_2^-$  ion, no more mechanistic information can be extracted from this particular experiment. The isotope distribution is consistent either with the formation of

$\text{H}_3^{10}\text{BN}(\text{CH}_3)_2^n\text{BH}_2\text{N}(\text{CH}_3)_2^{10}\text{BH}_3^-$  and its decomposition by hydride ion shift and elimination of monomeric  $(\text{CH}_3)_2\text{N}^{10}\text{BH}_2$  (eq 23) or with direct attack by



hydride ion on the 3 position of the substrate (eq 24).



It is important to recognize that the observed products are not consistent with a base catalyzed scheme like reaction 18, since the  $(\text{CH}_3)_2\text{NBH}_2$ -hydride ion complex,  $\text{Na}(\text{CH}_3)_2\text{NBH}_3$ , is a stable substance at room temperature.

## Experimental Section

**General Procedure.** Standard inert atmosphere and high vacuum techniques were followed for routine manipulations throughout this investigation. Special nmr reaction vessels<sup>13</sup> and weighing vessels<sup>14</sup> for low volatility air sensitive compounds have been described in other papers. Boron-11 nmr studies were performed with a Varian HA-100 instrument operating at 32.1 MHz equipped with standard variable temperature accessories. Boron chemical shifts were determined by the substitution method and are expressed in ppm relative to diethyl ether-boron trifluoride. Proton spectra were obtained with Varian HA-100 and T-60 instruments. Infrared spectra were obtained for gaseous samples using a 10-cm cell with KBr windows. Solid infrared samples were run in a KBr matrix; low volatility liquids were run as liquid films between KBr disks. Spectra were obtained with a Perkin-Elmer 337 spectrophotometer. Mass spectra were obtained using a Hitachi-Perkin-Elmer RMU-6E double focusing spectrometer operating with all inlet heaters off to minimize sample pyrolysis.

**Reagents.** Dimethylamine and trimethylamine were purchased from the Matheson Gas Co. Diborane- $d_6$  was prepared from  $\text{NaBD}_4$  purchased from Alfa Inorganics. Diborane- $^{10}\text{B}$  was prepared by reaction of a diethyl ether solution of  $\text{LiAlH}_4$  with  $(\text{C}_2\text{H}_5)_2\text{O} \cdot ^{10}\text{BF}_3$ ,<sup>15</sup> which was generated from a sample of  $\text{CaF}_2 \cdot ^{10}\text{BF}_3$  purchased from Oak Ridge National Laboratory. Tris(dimethylamino)borane and tris(diethylamino)borane were purchased from Alfred Bader Chemicals and Research Organic/Inorganic Chemical Corp., respectively. The compound  $(\text{CH}_3)_2\text{NHBH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$  was formed by the action of dimethylamine upon  $\mu-[(\text{CH}_3)_2\text{NBH}_2]_2$ ,<sup>12</sup> which had been prepared by the dimethylamine-borane-sodium borohydride-iodine method.<sup>2</sup> Tris(dimethylamino)alane was generated by the method of Ruff.<sup>16</sup> Bis(dimethylamino)borane was prepared by heating a 500-ml bulb containing 3.95 mmol of  $\text{B}[\text{N}(\text{CH}_3)_2]_3$  and 0.79 mmol of diborane at  $185^\circ$  for 24 hr. A small sample of  $^{10}\text{B}[\text{N}(\text{CH}_3)_2]_3$  was prepared by treating  $^{10}\text{B}_2\text{H}_6$  with an excess of  $\text{LiN}(\text{CH}_3)_2$ .<sup>3</sup> Sodium hydride was purchased as a 50% dispersion in mineral oil from Research Organic/Inorganic Chemical Corp.; prior to use the compound was freed of oil by washing with dry cyclohexane under nitrogen. Toluene- $d_8$  was purchased from Stohler Isotope Chemicals and was dried before use. Diethyl ether and monoglyme (1,2-dimethoxyethane) were stored in evacuated bulbs over  $\text{LiAlH}_4$  and when needed were vacuum transferred directly into the reaction vessel.

(13) P. C. Keller, *Inorg. Chem.*, **11**, 256 (1972).

(14) P. C. Keller, *J. Amer. Chem. Soc.*, **96**, 3073 (1974).

(15) I. Shapiro, H. G. Weiss, M. Schmick, S. Skolnik, and G. B. L. Smith, *J. Amer. Chem. Soc.*, **74**, 901 (1952).

(16) J. K. Ruff, *J. Amer. Chem. Soc.*, **83**, 2835 (1961).

**Studies on the Deprotonation of  $(\text{CH}_3)_2\text{NHBH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$ .** A magnetically stirred monoglyme solution of 0.198 g (1.71 mmol) of  $(\text{CH}_3)_2\text{NHBH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$  was allowed to react in a vacuum filter apparatus for 2.5 hr at 25° with a 0.225-g (5.77 mmol) piece of freshly cut potassium metal. Evolution of hydrogen from the potassium surface was brisk, commencing well below room temperature. After collection of the hydrogen (0.885 mmol), the clear colorless solution was filtered to recover the remaining very shiny piece of unreacted potassium, which weighed 0.159 g, implying a consumption of 0.066 g (1.69 mmol) in excellent agreement with the quantity of  $(\text{CH}_3)_2\text{NHBH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$  used.

Attempts to isolate a pure tractable product by evaporation of the solvent, either monoglyme or diethyl ether, proved unsuccessful. Long periods of time were required to achieve complete dryness, and a solid product with a reproducible infrared spectrum could not be isolated. In a similar experiment, treatment of  $(\text{CH}_3)_2\text{NHBH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$  with excess sodium hydride in monoglyme resulted in exclusive formation of  $\text{Na}(\text{CH}_3)_2\text{NBH}_3$ . A boron-11 nmr monitored experiment using equimolar quantities of these reactants showed the formation of roughly equal quantities of  $\text{Na}(\text{CH}_3)_2\text{NBH}_3$  and  $\text{Na}(\text{CH}_3)_2\text{NBH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$ .

**Synthesis of I from  $(\text{CH}_3)_2\text{NHBH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$ .** A magnetically stirred solution of 0.272 g (2.34 mmol) of  $(\text{CH}_3)_2\text{NHBH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$  in 15 ml of diethyl ether was allowed to react with a 0.5-g piece of freshly cut potassium metal for 5 hr at 25°. Over this period a colorless solid and hydrogen gas (1.16 mmol) slowly appeared. A 3.15 mmol sample of diborane was condensed into the vessel which was then stirred at 25° for 10 min and recooled to -196°. Volatile products were pumped through traps maintained at -63, -126, and -196° as the vessel slowly warmed to ambient temperature. The -196° trap retained 0.57 mmol of diborane, implying a consumption of 2.58 mmol. The crude product in the -63° trap was purified by slow fractionation through -17.5 into -30.6°. The latter trap contained 0.175 g (1.37 mmol, 59%) of pure I. The colorless nonvolatile residue in the reaction was identified as  $\text{KBH}_4$  by its boron-11 nmr spectrum (water solution).

**Synthesis of I from  $\text{HB}[\text{N}(\text{CH}_3)_2]_2$  and Excess Diborane.** Owing to the cleanness of this reaction, preparation of I for chemical studies was often carried out *in situ*. As shown below, the isolation of the pure product is easy and, if carried out promptly, can afford very high yields.

A 1.50-mmol sample of  $\text{HB}[\text{N}(\text{CH}_3)_2]_2$  and 0.5 ml of diethyl ether were condensed into an nmr reaction vessel. After addition of 1.54 mmol of diborane, the boron-11 nmr spectrum consisted of a strong signal due to I and a very weak  $\mu\text{-}(\text{CH}_3)_2\text{NB}_2\text{H}_5$  signal. Addition of another 0.82 mmol of diborane resulted only in the appearance of a signal characteristic of this reagent in the appropriate part of the spectrum. At this point, rather than isolating the products, it was decided to allow the solution to remain at room temperature for 24 hr to carry out a preliminary observation of the effect of excess diborane on I (this reaction is detailed below). At the end of this period the boron-11 nmr spectrum indicated about 50% conversion to  $\mu\text{-}(\text{CH}_3)_2\text{NB}_2\text{H}_5$ . The volatile materials were then fractionated through a trap maintained at -45°; the trap retained 0.102 g (0.79 mmol) of pure I for a yield of 53%.

**Reaction of  $\text{HB}[\text{N}(\text{CH}_3)_2]_2$  with a Deficiency of Diborane.** In an nmr reaction vessel 1.29 mmol of  $\text{HB}[\text{N}(\text{CH}_3)_2]_2$  and 0.63 mmol of diborane were allowed to react in 0.4 ml of diethyl ether at -78°. After 10 min the tube was placed in the nmr probe maintained at -30°. After obtaining spectra at this temperature and at 25°,  $[(\text{CH}_3)_2\text{NBH}_2]_2$  and  $\text{HB}[\text{N}(\text{CH}_3)_2]_2$  were isolated and identified by their infrared spectra.

**Synthesis of I from  $\text{B}[\text{N}(\text{CH}_3)_2]_3$  and Diborane.** In an nmr reaction vessel a 0.403-g (2.81 mmol) sample of  $\text{B}[\text{N}(\text{CH}_3)_2]_3$  in 1 ml of diethyl ether was treated with successive incremental additions of 1.42, 1.40, and 1.43 mmol of diborane. The boron-11 nmr spectrum of the resulting solution was obtained after each addition (Figure 4A-C). Standard vacuum line work-up and infrared spectroscopic identification confirmed the nmr assignment of the signals to (from low to high field)  $\text{B}[\text{N}(\text{CH}_3)_2]_3$ ,  $[(\text{CH}_3)_2\text{NBH}_2]_2$  overlapping I, and  $\mu\text{-}(\text{CH}_3)_2\text{NB}_2\text{H}_5$ . The trap to trap vacuum line separation of I from appreciable quantities of  $[(\text{CH}_3)_2\text{NBH}_2]_2$  is tedious, and exact yield data were not obtained for this synthesis.

**Reaction of  $\text{B}[\text{N}(\text{C}_2\text{H}_5)_2]_3$  with Diborane.** A 0.140-g (0.616 mmol) sample of  $\text{B}[\text{N}(\text{C}_2\text{H}_5)_2]_3$  was transferred using a hypodermic syringe to an nmr reaction vessel. A 0.5-ml sample of diethyl ether was condensed and followed by 1.53 mmol of diborane. The boron-11 nmr spectrum was run immediately and showed signals characteristic of unreacted  $\text{B}[\text{N}(\text{C}_2\text{H}_5)_2]_3$  and  $\mu\text{-}(\text{C}_2\text{H}_5)_2\text{NB}_2\text{H}_5$  only.

**Acid Methanolysis, Analysis, and Characterization of I.** In an

early attempt at analysis a 0.0648-g (0.507 mmol) sample of I was condensed into a bulb containing a 1 N solution of hydrogen chloride in anhydrous methanol. After a suitable reaction time, the evolved hydrogen was collected and the methanol solution was vacuum transferred into a bulb containing water to convert the methyl borate to boric acid, which was then titrated in the usual manner as the D-mannitol complex. Calcd for eq 11 (mmol from 0.0648 g of I):  $\text{B}(\text{OH})_3$ , 1.01;  $\text{H}_2$ , 2.53. Found:  $\text{B}(\text{OH})_3$ , 1.00;  $\text{H}_2$ , 2.51. Boron-11 nmr data for solid residue (water)  $\delta$  1.7 ppm,  $J = 112$  Hz; authentic  $[(\text{CH}_3)_2\text{NH}]_2\text{BH}_2\text{I}$  (water)  $\delta$  1.8 ppm,  $J = 110$  Hz.

For complete analysis a second sample was allowed to undergo thermal decomposition to  $\mu\text{-}(\text{CH}_3)_2\text{NB}_2\text{H}_5$  and  $[(\text{CH}_3)_2\text{NBH}_2]_2$ , and these products were solvolyzed as described above. Nitrogen was determined as dimethylamine by a Kjeldahl-type procedure. *Anal.* Calcd (weight per cent) for  $[(\text{CH}_3)_2\text{N}]_2\text{B}_2\text{H}_4$ : B, 25.4; H (hydrolytic), 5.46;  $(\text{CH}_3)_2\text{N}$ , 68.7. Infrared spectrum (liquid film; frequency in  $\text{cm}^{-1}$ ): 3020 (m), 2985 (m), 2945 (m), 2890 (w), 2850 (vw), 2800 (vww), 2500 (vs), 2420 (vs), 2350 (m, sh), 2320 (m, sh), 2110 (m), 2050 (m, sh), 1965 (s), 1610 (vww), 1465 (s), 1445 (s), 1430 (m), 1400 (w), 1234 (s), 1205 (s), 1175 (vs), 1140 (m), 1105 (m), 1050 (s), 1018 (vs), 995 (s), 940 (s), 888 (vw), 829 (m), 783 (m). Other properties: mp 10-11°; vapor pressure 0° (0.38 mm), 23° (3.28 mm).

**Thermal Decomposition of I.** A toluene solution of I in an nmr tube was kept at 75° for 15 min, then cooled to 25° to run the boron-11 nmr spectrum. The assignment of the signals to  $[(\text{CH}_3)_2\text{NBH}_2]_2$  and  $\mu\text{-}(\text{CH}_3)_2\text{NB}_2\text{H}_5$  was confirmed by separation on the vacuum line and infrared spectroscopic identification.

**Reaction of  $\text{H}^a\text{B}[\text{N}(\text{CH}_3)_2]_2$  with  $^{10}\text{B}_2\text{H}_6$ . Formation of I-1,5- $^{10}\text{B}$ .** A 0.705-mmol sample of  $\text{H}^a\text{B}[\text{N}(\text{CH}_3)_2]_2$  was condensed into an nmr reaction vessel followed by 0.3 ml of diethyl ether. A 1.32-mmol sample of  $^{10}\text{B}_2\text{H}_6$  was then condensed into the vessel and the nmr spectrum was run (Figure 2). Samples of I-1,5- $^{10}\text{B}$  used in experiments described below were generated in this manner.

**Reaction of  $^n\text{B}[\text{N}(\text{CH}_3)_2]_3$  with  $^{10}\text{B}_2\text{H}_6$ .** Successive 0.84, 0.78, and 0.45 mmol portions of  $^{10}\text{B}_2\text{H}_6$  were added to 0.175 g (1.22 mmol) of  $^n\text{B}[\text{N}(\text{CH}_3)_2]_3$  in 1 ml of diethyl ether in a boron-11 nmr monitored experiment similar to that associated with Figure 4A-C.

**Reaction of  $^{10}\text{B}[\text{N}(\text{CH}_3)_2]_3$  with  $^n\text{B}_2\text{H}_6$ .** A 0.29-mmol sample of  $^{10}\text{B}[\text{N}(\text{CH}_3)_2]_3$  dissolved in 0.5 ml of diethyl ether was treated with 0.48 mmol of  $^n\text{B}_2\text{H}_6$  in an nmr reaction vessel. The spectrum of the resulting solution showed boron-11 signals resulting from  $\mu\text{-}(\text{CH}_3)_2\text{NB}_2\text{H}_5$ ,  $[(\text{CH}_3)_2\text{NBH}_2]_2$ , and the  $-\text{H}_2\text{BHBH}_2-$  portion of I. The triplet associated with the  $\text{BH}_2$  group in the 3 position was absent.

**Thermal Decomposition of I-1,5- $^{10}\text{B}$ .** A toluene solution of I-1,5- $^{10}\text{B}$  in an nmr reaction vessel was immersed in a water bath at 70° for periods of 1, 3, 5, and 13 min (total exposure 22 min). The boron-11 nmr spectrum was recorded after each immersion (Figure 6).

**Exchange of I with  $\text{B}_2\text{D}_6$ .** A 0.108-g (0.794 mmol) sample of I was condensed into an nmr reaction vessel followed by 0.3 ml of diethyl ether. A 0.455-mmol sample of  $\text{B}_2\text{D}_6$  was then added and the nmr spectrum was recorded after elapsed times of 14, 30, and 140 min (Figure 7).

**Extended Reaction of I with Diborane.** A diethyl ether solution of I in the presence of excess diborane was generated in an nmr reaction vessel by combining 0.750 mmol of  $\text{HB}[\text{N}(\text{CH}_3)_2]_2$  with 1.52 mmol of diborane in 0.4 ml of diethyl ether. After 48 hr the boron-11 nmr spectrum showed ca. 75% conversion of I to  $\mu\text{-}(\text{CH}_3)_2\text{NB}_2\text{H}_5$ .

**Reaction of I with Trimethylamine.** A 0.111-g (0.869 mmol) sample of I was transferred to an nmr reaction vessel followed by 1 ml of diethyl ether and a 0.770-mmol sample of trimethylamine (amine to substrate ratio 0.885). The nmr spectrum showed only signals characteristic of the products of eq 15. Addition of another portion of trimethylamine (0.542 mmol; amine to substrate ratio 1.51) produced no change in the spectrum. Product separation on the vacuum line easily gave  $[(\text{CH}_3)_2\text{NBH}_2]_2$  for identification by infrared spectroscopy, but, owing to the highly dissociated nature of  $(\text{CH}_3)_2\text{NBH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$  in the gas phase,<sup>17</sup> a definitive sample could not be obtained. A mass spectrum of the material appropriately stopping in a -63° trap showed peaks diagnostic of the presence of trimethylamine and  $\mu\text{-}(\text{CH}_3)_2\text{NB}_2\text{H}_5$ , but no parent ion was observed. The boron-11 nmr peaks at -4.1 ppm (110 Hz) and 11.4 ppm (95 Hz) assigned to this compound are in good agree-

(17) A. B. Burg and J. S. Sandhu, *Inorg. Chem.*, **4**, 1467 (1965).

ment with the literature values<sup>12</sup> of  $-3.5$  ppm (108 Hz) and  $11.7$  ppm (95 Hz) for  $(\text{CH}_3)_3\text{NBH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$ .

**Reaction of I-1,5-<sup>10</sup>B with Dimethylamine.** The solution resulting from the addition of  $1.32$  mmol of  $^{10}\text{B}_2\text{H}_6$  to  $0.705$  mmol of  $\text{H}^n\text{B}[\text{N}(\text{CH}_3)_2]_2$  in  $0.3$  ml of diethyl ether was freed of excess  $^{10}\text{B}_2\text{H}_6$  by cooling to  $-78^\circ$  and pumping for  $15$  min. A  $1.19$ -mmol sample of dimethylamine was then added and the boron-11 nmr spectrum was recorded within  $5$  min. The spectrum was rerun after periods of  $22$  min and  $24$  hr (Figure 8A-C). Product separation and characterization by infrared spectroscopy unequivocally identified the products as  $[(\text{CH}_3)_2\text{NBH}_2]_2$  and  $(\text{CH}_3)_2\text{NHBH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$ .

**Low Temperature Nmr Study of the Reaction of I with Dimethylamine.** A solution of I in  $0.5$  ml of diethyl ether was generated as detailed above from  $0.671$  mmol of  $\text{HB}[\text{N}(\text{CH}_3)_2]_2$  and  $0.798$  mmol of diborane. After pumping off excess diborane,  $0.623$  mmol of dimethylamine was introduced and the system was warmed to  $-78^\circ$  and agitated at this temperature for  $5$  min. The sample was then transferred to the nmr probe which was maintained at  $-50^\circ$ . The temperature was slowly increased from  $-50$  to  $25^\circ$  and over a  $60$ -min period; the nmr spectrum was scanned intermittently during the warming process.

**Reaction of I with Sodium Hydride.** A  $0.101$ -g ( $0.792$  mmol) sample of I and  $2$  ml of monoglyme were combined with  $0.043$  g ( $1.8$  mmol) of oil-free sodium hydride in an nmr reaction vessel. The boron-11 nmr spectrum of the solution run immediately after mixing showed only starting materials. After  $21$  hr at room temperature, the reaction was complete. Assignment of nmr signals to  $[(\text{CH}_3)_2\text{NBH}_2]_2$  and  $\text{Na}(\text{CH}_3)_2\text{N}(\text{BH}_3)_2$  was confirmed by product isolation and identification by infrared spectroscopy.

**Reaction of I-1,5-<sup>10</sup>B with Sodium Hydride.** A  $0.5$ -ml mono-

glyme solution of I-1,5-<sup>10</sup>B prepared from  $0.60$  mmol of  $\text{H}^n\text{B}[\text{N}(\text{CH}_3)_2]_2$  and  $1.25$  mmol of  $^{10}\text{B}_2\text{H}_6$  was condensed into an nmr reaction vessel charged with  $0.054$  g ( $2.25$  mmol) of oil-free sodium hydride. The boron-11 nmr spectrum recorded immediately afterwards showed only unreacted boron-10 labeled substrate. After  $24$  hr the nmr spectrum showed a quartet at  $10.7$  ppm,  $J = 85$  Hz, characteristic of  $\text{Na}(\text{CH}_3)_2\text{N}(\text{BH}_3)_2$ ,<sup>18</sup> but no boron-11 signal due to  $[(\text{CH}_3)_2\text{NBH}_2]_2$ . The triplet arising from an unidentified by-product, noted above, was also present in this spectrum.

The mass spectrum of I together with those of  $[(\text{CH}_3)_2\text{NBH}_2]_2$  and  $\mu\text{-}(\text{CH}_3)_2\text{NB}_2\text{H}_5$  for comparison will appear following these pages in the microfilm edition of the journal. See paragraph at end of paper regarding supplementary material.

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**Supplementary Material Available.** The mass spectrum of I will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche ( $105 \times 148$  mm,  $24\times$  reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for  $\$3.00$  for photocopy or  $\$2.00$  for microfiche, referring to code number JACS-74-3078.

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## Thermal Rearrangements of Nonicosahedral Cobaltacarboranes

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**Abstract:** The thermal rearrangements which isomerize the known isomers of nonicosahedral cobaltacarboranes of the type  $(\eta\text{-C}_5\text{H}_5)\text{CoC}_2\text{B}_n\text{H}_{n+2}$ ,  $n = 6, 7, 8,$  and  $10$ , are discussed. A summary of conclusions regarding these rearrangements is presented as a set of empirical rules which seem to govern the migration of heteroatoms during thermal isomerizations. Kinetic data of some representative rearrangements are also discussed.

The thermally induced migration of carbon atoms over the surfaces of polyhedral cobaltacarboranes is a well-established phenomenon.<sup>1-5</sup> However, only for the icosahedral complexes,  $(\eta\text{-C}_5\text{H}_5)\text{CoC}_2\text{B}_9\text{H}_{11}$ , and its carbon substituted derivatives have all possible isomers been isolated.<sup>3</sup> If the metal atom is used as a point of reference within the complex, the migration of carbon atoms produces nine possible isomers—all of which have been characterized.

We now wish to report a study of the thermal rearrangements of nonicosahedral cobaltacarboranes. Such a study is inherently limited, however, since all possible isomers of a given polyhedral geometry are not presently available either by direct synthesis or by other means. Nevertheless, an investigation of the rearrange-

ments of the compounds which are presently known does reveal some basic principles which govern the manner in which the heteroatoms are distributed over the surface of a polyhedral metallocarborane. Although these principles will be invaluable in identifying isomers that may be synthesized in the future, the main objective of this work was to establish an understanding of the systematics which govern heteroatom migrations on polyhedral surfaces. The results are set forth as a list of empirical rules regarding the thermal rearrangements of polyhedral cobaltacarboranes. Subsequently, the investigation of carbon atom migration modes may be extended to include bi- and trimetallic systems.

**Rearrangement of  $(\eta\text{-C}_5\text{H}_5)\text{CoC}_2\text{B}_8\text{H}_{10}$ .**  $1\text{-}(\eta\text{-C}_5\text{H}_5)\text{-}1\text{-Co-}2,4\text{-C}_2\text{B}_8\text{H}_{10}$ <sup>6,7</sup> rearranged to  $1\text{-}(\eta\text{-C}_5\text{H}_5)\text{-}1\text{-Co-}$

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(7) Numbers accompanying formulas refer to the positions of the heteroatoms within the *closo*-metallocarborane framework and to the location of the exopolyhedral substituents, if any. Lowest numbers consistent with the molecular geometry are given to carbon in accordance with the inverse periodic order adhered to by the IUPAC Inorganic Nomenclature Committee [see R. M. Adams, *Pure Appl. Chem.*, **30**, 683 (1972)]. For example, in  $1\text{-}(\eta\text{-C}_5\text{H}_5)\text{-}1\text{-Co-}2,4\text{-C}_2\text{B}_8\text{H}_{10}$ , cobalt occupies position 1 while carbon atoms are located at vertices 2 and 4. The cyclopentadienyl ring is  $\pi$  bonded to the cobalt.

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