Reactions of Pentaborane(9) with Ammonia. Characterization of the Diammoniate of Pentaborane(9)

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Abstract: At −78° pentaborane(9) reacts rapidly with liquid ammonia through a reversible Brønsted–Lowry acid-base interaction to give $[NH_4]^+[B_5H_8]^-$. A competing slower reaction between B_5H_9 and ammonia gives the diammoniate of pentaborane(9), $B_5H_9 \cdot 2NH_3$. The latter compound is a stable solid below 0° but decomposes spectacularly at room temperature. It has been assigned the formula $[H_2B(NH_3)_2][B_4H_7]$. Evidence is presented to show that the newly characterized anion, $B_4H_7^-$, has four borons arranged in a trigonal pyramid with a hydrogen bridge bond along each basal edge of the pyramid. The nonsymmetrical cleavage pattern observed earlier for B_2H_6, B_4H_{10}, and B_5H_{11} is now extended to a borane which has no clearly recognizable BH_2 unit. The possible mechanism of such a reaction is discussed.

In an early summary[2] of the reactions of the boranes, it was suggested that pentaborane(9) should undergo a variety of reactions with Lewis bases. The postulated reaction to form $B_5H_8^-$ has been well established.[3-6] Symmetrical cleavage[7] reactions to produce BH_3 and B_4H_6 fragments have been reported[8] as have anomalous[7] cleavage reactions generating B_2H_4 and B_3H_5 fragments.[9] Addition reactions to give well-defined products containing two molecules of base, $B_5H_9 \cdot$2base, have also been described,[10,11] but no clear-cut example of a nonsymmetrical cleavage process involving B_5H_9 has been reported previously. Reactions with ammonia would be expected to favor such a process, if any base would.

Since Stock[12] first reported the formation of $B_5H_9 \cdot 4NH_3$ in 1924, the reaction between B_5H_9 and NH_3 has been studied extensively.[12,13] In general, literature reports have been conflicting or nondefinitive. Several ammoniates including a diammoniate, $B_5H_9 \cdot 2NH_3$, have been described[13] but in no case was the product ever well characterized. Recent work, described herein, shows that B_5H_9 can react with ammonia in at least two clearly defined ways, and the products generated are of low stability. Under carefully defined conditions B_5H_9 will react with NH_3 to give a diammoniate of pentaborane, $[H_2B(NH_3)_2][B_4H_7]$; under other conditions, NH_3 and B_5H_9 react to give $[NH_4][B_5H_8]$. It is now clear that most of the products described in the earlier literature were mixtures resulting from these competing reactions. Much of the chemistry of B_5H_9 can be clarified by an application of this information.

1. Preparation and Characterization of the Diammoniate of Pentaborane(9), $[H_2B(NH_3)_2][B_4H_7]$

In a typical reaction a 2-mmol quantity of B_5H_9 was dissolved in about 5 ml of diethyl ether. An 8-mmol quantity of ammonia gas was introduced slowly above the surface of the solution which was stirred continuously at −80°. After the ammonia had been absorbed, the reaction system, which contained a white precipitate, was aged at −80° for 1–3 weeks before removal of the ether and excess ammonia. The diammoniate of pentaborane(9) could be isolated by *careful* removal of the last trace of the volatile component at 0° under vacuum. The synthesis was described in an earlier communication.[14]

The structure $[H_2B(NH_3)_2][B_4H_7]$ for $B_5H_9 \cdot 2NH_3$ is supported by both chemical and physical evidence. If $B_5H_9 \cdot 2NH_3$, prepared as described above, is treated with an equal molar quantity of anhydrous HCl in dry diethyl ether, a precipitate of $H_2B(NH_3)_2Cl$ appears. The yield is quantitative in terms of the equation

$$[H_2B(NH_3)_2][B_4H_7] + HCl \xrightarrow[-80 \sim -40^\circ]{(C_2H_5)_2O} [H_2B(NH_3)_2]Cl + B_4H_8 \cdot O(C_2H_5)_2$$

Evidence for $B_4H_8 \cdot O(C_2H_5)_2$ in the products was obtained by treating the supernatant ether solution with $(CH_3)_2NPF_2$. The isolation of $(CH_3)_2NPF_2B_4H_8$ in good yield is consistent with the ether displacement reaction.

$$B_4H_8 \cdot O(C_2H_5)_2 + F_2PNR_2 \longrightarrow B_4H_8F_2PNR_2 + (C_2H_5)_2O$$

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[1] Correspondence should be directed to the University of Utah.

[2] R. W. Parry and L. J. Edwards, *J. Amer. Chem. Soc.*, **81**, 3554 (1959).

[3] (a) R. A. Geanangel and S. G. Shore, *ibid.*, **89**, 6771 (1967); (b) D. G. Gaines and T. V. Iorns, *ibid.*, **89**, 3375 (1967).

[4] W. V. Hough, L. J. Edwards, and A. F. Stang, *ibid.*, **85**, 831 (1963).

[5] T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, **6**, 1465 (1967).

[6] H. D. Johnson, R. A. Geanangel, and S. G. Shore, *ibid.*, **9**, 908 (1970).

[7] Symmetrical cleavage as applied to the B_5H_9 molecule is that reaction in which the products contain the BH_3 fragment; nonsymmetrical cleavage is that reaction in which the products contain the H_2B^+ fragment. Anomalous cleavage is that combination of these processes or a separate process which generates products containing other borane fragments.

[8] W. V. Hough, M. D. Ford, and L. J. Edwards, Abstracts, 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959, p 38M.

[9] E. R. Lory and D. M. Ritter, *Inorg. Chem.*, **9**, 1847 (1970).

[10] A. B. Burg, *J. Amer. Chem. Soc.*, **79**, 2129 (1957).

[11] M. L. Denniston and S. G. Shore, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. INOR 104.

[12] A. Stock and W. Siecke, *Chem. Ber.*, **57**, 562 (1924); A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p 126.

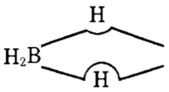
[13] R. T. Holzman, "Production of the Boranes and Related Research," Academic Press, New York, N. Y., 1967, pp 258–260.

[14] G. Kodama, *J. Amer. Chem. Soc.*, **92**, 3482 (1970).

The compound $[H_2B(NH_3)_2][B_4H_7]$ is a white, powdery solid which decomposes spectacularly when warmed to 25°. For a minute or two after warming to 25° the solid appears to be stable under vacuum; then, suddenly, without warning, it puffs quietly to fill the container with its decomposition products. These include hydrogen (identified by its molecular weight), diborane(6), tetraborane(10), pentaborane(9), hexaborane(10), μ-aminodiborane(6), borazine, and an unidentified viscous liquid. The boron compounds, identified in the products, were recognized by their infrared and/or ^{11}B nmr spectra.

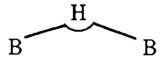
2. Mechanism of the Formation of $[H_2B(NH_3)_2][B_4H_7]$

Although nonsymmetrical cleavage of a double bridge bond to give a product containing an H_2B^+ unit was suggested[1] as a reaction common to all boron hydrides, the process has been observed only with B_2H_6, B_4H_{10}, and B_5H_{11}, all of which have an $H_2B<$ unit fastened to the remainder of the molecule by two hydrogen bridge bonds. It had been supposed[15] that this structural feature was essential for the generation of the $[H_2B(NH_3)_2]^+$ ion. Since B_5H_9 does not contain a

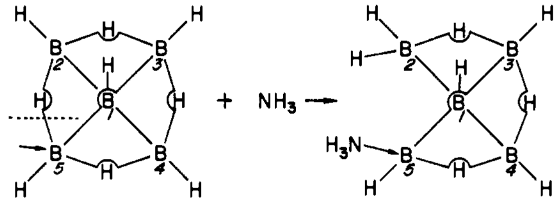


unit, the mechanism by which $[H_2B(NH_3)_2][B_4H_7]$ forms is worthy of consideration. The following model is consistent with all currently available information.

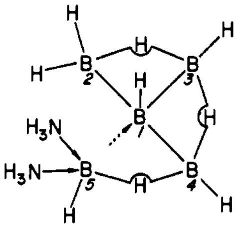
The reaction is considered to be similar in its initial stages to that already suggested for the reactions of B_2H_6,[16,17] B_4H_{10},[18,19] and B_5H_{11}[20] with bases. Initial base attack presumably involves breaking of a bridge



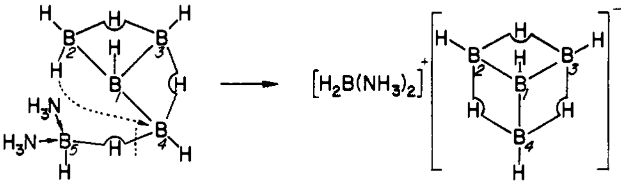
bond with the hydride moiety going to one boron and the attacking base going to the second.[21] The intermediate can be visualized now as an H_3NBH unit (boron 5) fastened to the remainder of the molecule by



both a three-center BBB bond and by a three-center BHB bridge bond. Attack of a second ammonia molecule on boron 5 would increase electron density at this boron with a consequent withdrawal of the electrons in the three-center $B_5B_1B_3$ bridge. Charge would move from boron atom 5 toward boron atom 1, thus generating a two-center bond between boron atoms 1 and 3.[22] The resulting structure can be visualized as



Moving one of the hydrogens attached to boron atom 2 toward boron atom 4 would permit formation of a hydrogen bridge bond between boron atoms 2 and 4 with a resultant closing up of the tetrahedral boron framework. A deficiency of orbitals on boron atom 4 would then require that the BHB bridge bond between boron atoms 5 and 4 would break near boron 4. The appropriate model is



This model suggests a structure for $B_4H_7^-$ which is identical with the structure predicted by Lipscomb in 1958 from molecular orbital theory.[23] Evidence in

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(15) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, p 171.

(16) S. G. Shore, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1956, p 29.

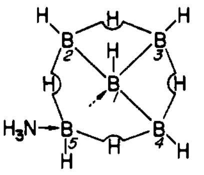
(17) (a) R. W. Parry and S. G. Shore, *J. Amer. Chem. Soc.*, **80**, 15 (1958); (b) B. Z. Egan and S. G. Shore, *ibid.*, **83**, 4717 (1961).

(18) G. Kodama, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1957.

(19) R. W. Parry, R. W. Rudolph, and D. F. Shriver, *Inorg. Chem.*, **3**, 1479 (1964).

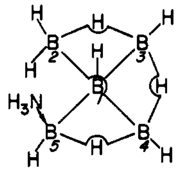
(20) G. Kodama, J. E. Dunning, and R. W. Parry, Abstracts, 25th Annual Northwest Regional Meeting of the American Chemical Society, Seattle, Wash., June 1970, Paper No. 98; G. Kodama, J. E. Dunning, and R. W. Parry, *J. Amer. Chem. Soc.*, **93**, 3372 (1971).

(21) It is not clear that a BHB bond must break before the BBB three-center bond when the first molecule of base attacks the B_5H_9 molecule. If the BBB three-center bond breaks first, the alternative intermediate would be



Experiments to try to identify the intermediates are in progress. Similar questions exist for B_5H_{11}.

(22) Use of the three-center bond to represent structure is simply for convenience. Although a model which contains a $B_5B_1B_3$ three-center bond was employed in the argument presented above, use of other models is equally valid. For example, if a representation containing a $B_2B_1B_4$ three-center bond is used, the structure of the intermediate would be

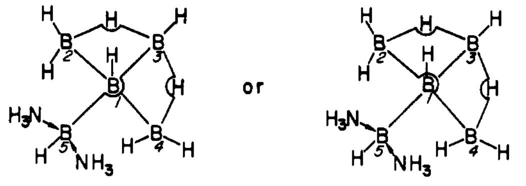


The second ammonia attack would shift electron charge from B_5 to B_1 to form B_1B_2 and B_1B_4 two-center bonds. As long as the *remainder of the molecule* is capable of withdrawing electrons, the same arguments would be applicable regardless of the bond type involving B_1 and B_5.

(23) W. N. Lipscomb, *J. Chem. Phys.*, **28**, 170 (1958).

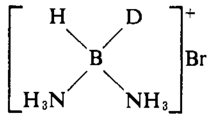
support of this structure will be summarized in a later section.

In considering the mechanism of the process and the identity of the reacting species in ether solution one other possibility was important. If during the second ammonia attack on boron 5, the B_5HB_4 bridge bond of the intermediate broke instead of the $B_5B_1B_3$ bond, a product as shown below could result.



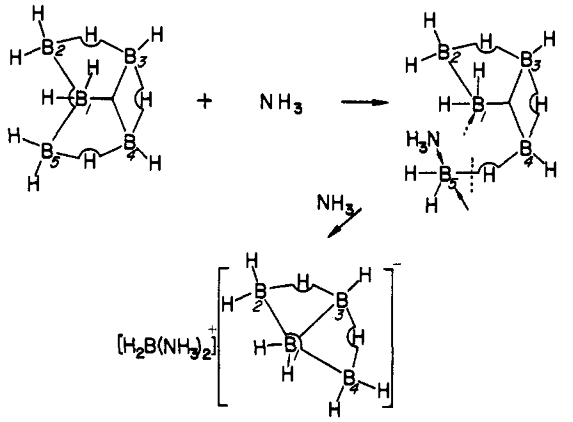
The species, as well as the ionic form of $B_5H_9\cdot 2NH_3$, could also generate $[H_2B(NH_3)_2]X$ (X = halogens) and $B_4H_8\cdot O(C_2H_5)$ upon treatment with ethereal hydrogen halides. To check this point the product ($B_5H_9\cdot 2NH_3$ in ether) was treated with DBr.

Electrophilic attack of DBr on boron 5 would shift the electron cloud toward the boron atom and would rupture the B_5–B_1 portion of the bond to give


Br^- and $B_4H_8O(C_2H_5)_2$

When DBr was added to the slurry of $B_5H_9\cdot 2NH_3$ in ether, the precipitate obtained was identified as $[H_2B(NH_3)_2]^+Br^-$ by its ^{11}B nmr spectrum in liquid ammonia. The foregoing observations support the existence of preformed $[H_2B(NH_3)_2]^+$ and $[B_4H_7]^-$ ions in the diammoniate solution *before* addition of the acid.

The previously supported idea of base attack on boron as a means of breaking a BBB bridge bond can also be applied to the reaction between B_5H_{11} and NH_3. If one uses the usual bonding representation for B_5H_{11}, the initial molecule can be looked upon as having an $H_2B<$ unit fastened to the boron framework by both BHB and BBB three-center bonds. (In $B_5H_9\cdot NH_3$ one assumes that an H_3NBH unit is fastened to the remaining boron framework by both BHB and BBB three-center bonds; see above.)



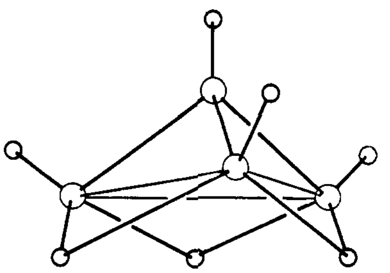
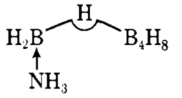


Figure 1. Structure suggested for the $B_4H_7^-$ anion: ○, boron; o, hydrogen.

Initial ammonia attack on boron atom 5 would convert the three-center $B_2B_1B_5$ bond into a two-center B_2B_1 linkage.[21] Subsequent attack of ammonia on boron 5 of the



intermediate would give the observed $[H_2B(NH_3)_2][B_4H_9]$.

Since B_5H_{11} could also be interpreted satisfactorily in terms of the double hydrogen bridge bond used for B_2H_6 and B_4H_{10}, its current treatment in terms of BBB and BHB linkages makes the B_5H_{11} molecule appear as a bridge between the chemistry of B_5H_9 and B_4H_{10}. It is then significant that the concept of bridge cleavage can be expanded in a logical fashion to encompass the formerly unexpected reaction between B_5H_9 and NH_3.

3. Boron-11 Nmr Spectrum of $[H_2B(NH_3)_2][B_4H_7]$. Structure of the $[B_4H_7^-]$ Anion

In liquid ammonia the ^{11}B nmr spectrum of a sample of $[H_2B(NH_3)_2][B_4H_7]$, measured over the temperature range −70 to −40°, consists of a broad low-field band (relative area 4) and a somewhat sharper high-field singlet (relative area 1) (see Figure 2c). The low-field band can be resolved into a triplet (δ 102 ppm from $B(CH_3)_3$, peak separation and *ca.* $J_{B-H} = 117 \pm 3$ Hz, relative area = 1) and a singlet (δ 108 ppm, relative area 3). The triplet is attributed to the $[H_2B(NH_3)_2]^+$ cation (literature δ 101–103 ppm from $B(CH_3)_3$, J_{B-H} = 110–120 Hz[24]). The singlet at 108 ppm is attributed to the three basal boron atoms in the $B_4H_7^-$ anion (see Figure 1). The singlet at 128 ppm is assigned to the apex boron atom of the $B_4B_7^-$ pyramid. It is significant that the B–H coupling for protons attached directly to boron atoms could not be resolved at −40°. Decomposition of $B_4H_7^-$ complicated measurements at higher temperatures. The slight shoulder appearing on the right hand side of the lower field band at about 117 ppm corresponds to the $B_3H_8^-$ ion which is being formed from $B_4H_7^-$ decomposition. The decomposition process is being studied.

(24) T. P. Onak and J. Shapiro, *J. Chem. Phys.*, **32**, 952 (1960); C. W. Heitsch, *Inorg. Chem.*, **4**, 1019 (1965).

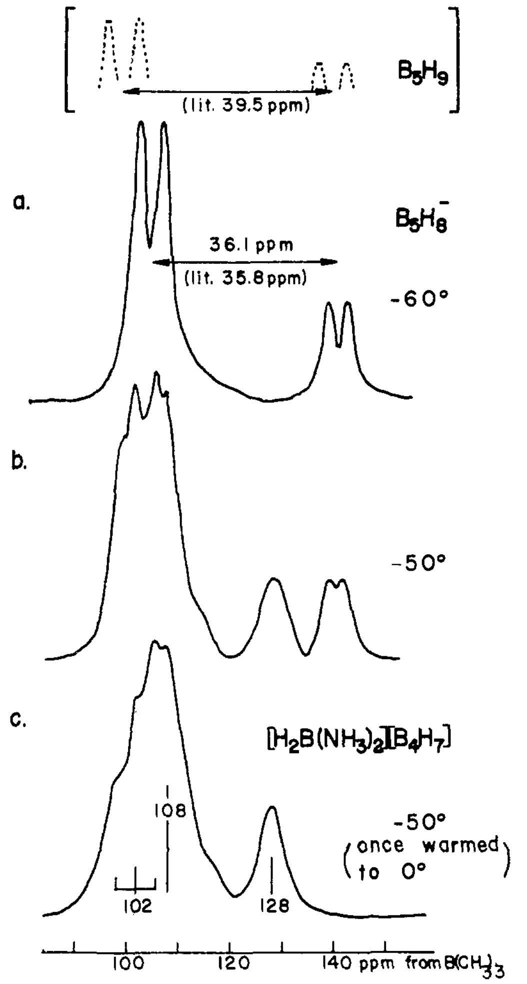


Figure 2. ^{11}B nmr spectra of the B_5H_9 solution in liquid ammonia.

4. General Behavior of B_5H_9 in Liquid Ammonia

The foregoing isolation and characterization of $[H_2B(NH_3)_2][B_4H_7]$, coupled with Shore's[6] characterization of the $B_5H_8^-$ anion, have made it possible to follow the reactions of B_5H_9 in liquid ammonia using nmr as a probe. The successive ^{11}B spectra of the B_5H_9–liquid ammonia system are shown in Figure 2. At −60° the fresh solution of B_5H_9 in liquid ammonia (Figure 2a) shows only the $B_5H_8^-$ anion which is clearly characterized by the chemical shift difference between the two sets of doublets [$\Delta\delta$ obsd 36.1 ppm (lit.[6] 35.8 ppm)]. On standing the system develops new peaks which are seen in Figure 2b. The presence of the compound $[H_2B(NH_3)_2][B_4H_7]$ is indicated (*cf.* Figure 2c). The appearance of the $B_4H_7^-$ anion could be accelerated if the sample tube were allowed to warm to 0° for a few minutes after digesting the solution for several hours at −60°.

At temperatures above 0° the $B_3H_8^-$ ion begins to appear in the spectrum. If the liquid ammonia solution is warmed abruptly to room temperature, or if the solution is held at room temperature after gradual warming, a small bulge, attributable to the $B_3H_8^-$ ion, develops on the upfield side of the low-field peak.

From the foregoing observations the solution of B_5H_9 in liquid ammonia can be described in terms of several equations. The first is a Brønsted–Lowry acid–base process.

$$B_5H_9 + NH_3 \rightleftharpoons [NH_4]^+[B_5H_8]^-$$

The process is apparently fast and reversible.

By a second process the compound $[H_2B(NH_3)_2][B_4H_7]$ is formed. This process is slower and irreversible.

$$B_5H_9 + 2NH_3 \longrightarrow [H_2B(NH_3)_2][B_4H_7]$$

It is not yet completely clear whether the reacting boron species in the last equation is the $B_5H_8^-$ ion or the B_5H_9 molecule, but present arguments strongly favor the B_5H_9 molecule. For example, preliminary data indicate that those boranes which are stronger Brønsted–Lowry acids react with ammonia to give the $[H_2B(NH_3)_2]^+$ cation more slowly. Specifically the B_6H_{10} unit is known[25] to be a stronger Brønsted–Lowry acid than B_5H_9. Significantly B_6H_{10} produces the $[H_2B(NH_3)_2]^+$ cation much more slowly than does B_5H_9.[26] The 2,3-dicarbohexaborane(8), $C_2B_4H_8$, is isoelectronic with the B_6H_{10} molecule but is a significantly stronger acid than hexaborane(10). When treated with ammonia in ether under conditions known to give $[H_2B(NH_3)_2]^+$ from B_6H_{10}, only ammonium salts are formed.[26]

Finally by a still incompletely defined third process the compound $[H_2B(NH_3)_2][B_4H_7]$ undergoes conversion at temperatures near 25° to $[H_2B(NH_3)_2][B_3H_8]$ and other products. The incomplete equation is

$$[H_2B(NH_3)_2][B_4H_7] \xrightarrow{25^\circ} [H_2B(NH_3)_2][B_3H_8] + \text{other products}$$

Very similar processes have been observed and described by Johnson and Shore in the reactions of B_4H_{10} with NH_3 in liquid ammonia.[27]

$$B_4H_{10} + NH_3 \rightleftharpoons [NH_4]^+[B_4H_9]^-$$

$$B_4H_{10} + 2NH_3 \longrightarrow [H_2B(NH_3)_2]^+[B_3H_8]^-$$

5. Review of Earlier Reports on the B_5N_9–NH_3 System in the Light of Present Evidence

The formation of a diammoniate of pentaborane(9) was reported earlier by Hough, *et al.*,[28] as a product prepared from NH_3 and B_5H_9 at −80°. On the other hand, this material exhibited properties which contrast sharply with those reported here for $[H_2B(NH_3)_2][B_4H_7]$. The −80° adduct underwent decomposition to NH_3 and B_5H_9 when it was placed under vacuum at −65 to −45°. These properties suggest that the −80° material is either a molecular compound with two ammonia molecules bound loosely to bridge protons or a monoammonia solvate of the compound $[NH_4][B_5H_8]$. Indeed it was observed in the course of this study that a

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(25) H. D. Johnson, S. G. Shore, N. L. Mock, and J. C. Carter, *J. Amer. Chem. Soc.*, **91**, 2131 (1969).

(26) G. Kodama, unpublished results.

(27) H. D. Johnson, II, and S. G. Shore, *J. Amer. Chem. Soc.*, **92**, 7586 (1970).

(28) W. V. Hough, *et al.*, "Research and Development of Advanced Solid Propellant System," Callery Chemical Co., Quarterly Report No. 3, Contract No. NOr 60-0168-C, Oct 26, 1960. Cited in ref 13, p 259.

mixture of NH_3 and B_5H_9 in ether undergoes partial decomposition to B_5H_9 and NH_3 if exposed to high vacuum at −80° without proper aging. When the foregoing −80° mixture was treated with HCl before aging, a portion of the original B_5H_9 could be recovered from the system leaving NH_4Cl behind. The proposed equilibria are represented by the equations

$$\begin{array}{l} \mathrm{HCl} \\ + \\ \mathrm{NH_3} + \mathrm{B_5H_9} \rightleftharpoons \mathrm{NH_4^+} + \mathrm{B_5H_8^-} \\ \downarrow \\ \mathrm{NH_4Cl} \end{array}$$

It has been clearly established in recent months that other boron hydrides serve as Brønsted–Lowry acids; Johnson and Shore[27] have established that B_4H_{10} and NH_3 react to give $[NH_4][B_4H_9]$, while Brubaker, *et al.*,[29] identified the $B_6H_9^-$ anion in liquid ammonia.

Although the precise identity of Stock's $B_5H_9 \cdot 4NH_3$ was not investigated in this study, a tensimetric titration of B_5H_9 with ammonia in ether at −80° gave some evidence for the formation of a species with the empirical formula $B_5H_9 \cdot 4NH_3$. The data from the titration are displayed in Figure 3. The break in the curve near a mole ratio of 4:1 NH_3–B_5H_9 is significant. When the volatile components were removed from this system first at −45° and then at above 0° by exposure to the high vacuum pumps, ammonia was removed and the diammoniate of pentaborane $[H_2B(NH_3)_2][B_4H_7]$ remained in the vessel. These data indicate that this tetrammoniate is a solvate, $[H_2B(NH_3)_2][B_4H_7] \cdot 2NH_3$. In view of the facts that the Stock's tetrammoniate was prepared through the reaction of gaseous B_5H_9 and ammonia at room temperature and that it did not split off ammonia to give a diammoniate at room temperature, the tetrammoniate observed in this study is considered different from that of Stock.

It now seems clear that many of the products reported earlier from the reaction of NH_3 and B_5H_9 were rather complex mixtures resulting from different competing reactions of B_5H_9 and NH_3 and from decomposition reactions involving these products.

Experimental Section

General Procedures. Standard high-vacuum techniques were used throughout. Boron nmr spectra were determined with a Varian HR-100 nmr spectrometer at 32.1 MHz. Chemical shifts were obtained by tube interchange.

Pentaborane(9) was obtained from Callery Chemical Co. It was purified by a trap-to-trap fractionation in the vacuum line. Anhydrous hydrogen chloride, hydrogen bromide, and ammonia were obtained from Matheson Co. Deuterium bromide was prepared by the reaction of PBr_3 and D_2O. Commercial anhydrous ether was stored in a flask with $LiAlH_4$ and distilled into the reaction vessels attached to the vacuum system. A sample of $(CH_3)_2NPF_2$ was available in our laboratory.

Preparation of $B_5H_9 \cdot 2NH_3$. The reaction vessel was a 20-mm o.d. tube equipped with ₸ 24/40 inner joint. The solution was stirred with a solenoid-operated hopper-type stirrer. The actual synthesis is described in section 1. Because the sample decomposes at room temperature, an aliquot for Kjeldahl nitrogen analysis was weighed in a cold room held at −10°. The sample for nmr study in liquid ammonia was also placed in the nmr tube in the cold room and kept at low temperature (below 0°) prior to condensation of liquid ammonia in the tube and sealing. *Anal.* Calcd for $B_5H_9 \cdot 2NH_3$: N, 28.8. Found: N, 29.1. Composition also established by ratios used in synthesis.

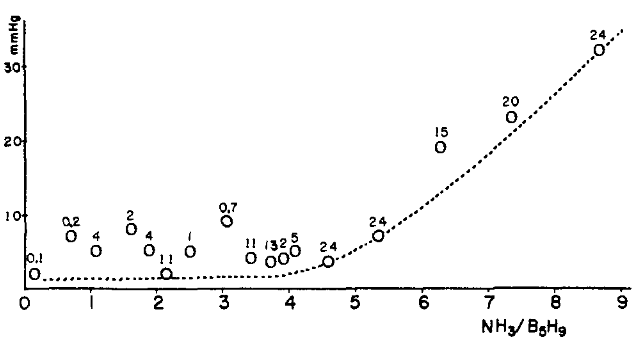

Figure 3. Tensimetric titration curve for the system B_5H_9–NH_3 in diethyl ether at −80°. Numbers above the circles indicate the hours the system was held at the composition before the pressure readings were made.

Reaction of $B_5H_9 \cdot 2NH_3$ with Hydrogen Chloride. A slurry of freshly prepared $B_5H_9 \cdot 2NH_3$ (0.70 mmol) in 5 ml of diethyl ether was allowed to react while being stirred with hydrogen chloride (1.29 mmol) at −80° for 12 hr. Only a trace of hydrogen gas was evolved during the reaction. The powdery precipitate which formed was filtered quickly in a vacuum line filtration apparatus and washed with ether at room temperature. An X-ray powder pattern showed $H_2B(NH_3)_2Cl$ as the only detectable solid product. The solid on the filter disk was dissolved in water and the amount of $H_2B(NH_3)_2Cl$ was determined by precipitating Cl^- ion as AgCl. The silver chloride weighed 93.4 mg or the amount of $H_2B(NH_3)_2Cl$ recovered was 0.65 mmol (93% yield).

Reaction of $B_4H_8 \cdot O(C_2H_5)_2$ with $(CH_3)_4NPF_3$. A 2.2-mmol sample of freshly prepared $B_5H_9 \cdot 2NH_3$ in 5 ml of diethyl ether was treated with a 2.0-mmol sample of hydrogen chloride as described above. The reaction mixture was frozen at −197° and a 2.15-mmol sample of $(CH_3)_2NPF_2$ was condensed on it. The tube was warmed to −80° and held for 12 hr and then warmed to room temperature for a few minutes. No hydrogen gas evolved during these operations. Volatile components were removed and fractionated through a −80° trap. The component retained in the −80° trap was then distilled through traps cooled at −23, −35, and −197°. A small amount of $(CH_3)_2NPF_2BH_3$ (identified by its vapor pressure and ir spectrum[30]) was found in the −197° trap. About 0.3 g or 1.8 mmol of $(CH_3)_2NPF_2B_4H_8$ was obtained from the −35° trap. The compound was identified by its ^{19}F and ^{11}B nmr spectra.[31]

Reaction with $B_5H_9 \cdot 2NH_3$ with Deuterium Bromide. A 0.43-mmol sample of $B_5H_9 \cdot 2NH_3$ in 5 ml of diethyl ether was treated with a 0.62-mmol sample of DBr in the same manner as for the HCl reaction. After the system had been held at −80° for 12 hr, the tube was allowed to warm to −45° for 0.5 hr. The new precipitate was filtered and washed with diethyl ether. The X-ray powder pattern of the solid was identical with that of $H_2B(NH_3)_2Br$ and its ^{11}B nmr spectrum at −40∼−55° gave a well-resolved triplet of 102 ppm from $B(C_2H_5)_3$ with a peak separation of 97 ± 3 Hz. Thus the solid was considered essentially pure $H_2B(NH_3)_2Br$.

Tensimetric Titration of B_5H_9 with NH_3. In ether solutions of B_5H_9 (5 ml of $(C_2H_5)_2O$ with 2.19 mmol of B_5H_9), known amounts of ammonia were condensed. The solution was stirred constantly while the temperature was held at −80° (Dry Ice–2-propanol mixture). Pressure above the solution was read at intervals. Equilibria were not reached rapidly and sometimes the subsequent portions of ammonia were added to the system before the equilibria were attained. Therefore, lowest limiting pressures were taken as the closest to the equilibrium pressures in drawing a line in Figure 3.

After the titration was completed (10 days after the beginning of the titration), volatile components were pumped out of the sys-

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(30) G. Kodama and R. W. Parry, *Inorg. Chem.*, 4, 410 (1965).

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tem at −45°. The system was pumped further at room temperature for 2 min. The volatile components were ether and ammonia; no boron hydride compound was detected in volatiles. Ammonia retained in the solid residue was 4.8 mmol or the ratio NH_3(retained)/B_5H_9 was 2.2.

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Synthesis, Structure, and Reactions of 1,2-Dicarbapentaborane(7)[1]

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Abstract: The carborane 1,2-dicarba-*nido*-pentaborane(7) has been obtained from the reaction of tetraborane(10) with acetylene and structurally characterized. The compound is stable in the vapor phase at 50° and in dilute hydrocarbon solutions, but the neat liquid rapidly and irreversibly polymerizes without evolution of hydrogen. Polymerization is also induced by ethereal solvents, hydrogen chloride, and certain other reagents. The carborane is highly reactive toward B_4H_{10} or B_2H_6 in the absence of acetylene. Reaction with acetylene yields 2,3,4,5-$C_4B_2H_6$ and with ethylene produces alkylboranes. The carborane forms a stable 1:1 adduct with triethylamine. Bromine apparently adds to the C–C bond of $C_2B_3H_7$, while excess Br_2 attacks the boron portion of the molecule and destroys the cage. Iron pentacarbonyl and $C_2B_3H_7$ react under ultraviolet light to produce the complex (π-$C_2B_3H_7$)Fe(CO)$_3$ which contains the planar dicarbacyclopentaboranyl(2−) ligand, an isoelectronic analog of $C_5H_5^-$.

Of the many known carborane cage systems, most represent isoelectronic and isostructural analogs of known boron hydrides or polyhedral borane anions. For example, the entire hexaborane series (B_6H_{10}, 2-CB_5H_9, 2,3-$C_2B_4H_8$, 2,3,4-$C_3B_3H_7$, and 2,3,4,5-$C_4B_2H_6$) has been characterized, each species having a pentagonal-pyramidal structure with 0–4 bridge hydrogen atoms.[2] Carborane analogs of smaller boron hydrides were unknown prior to the present work, although Lipscomb has predicted,[3] from MO arguments, the existence of square-pyramidal carboranes isoelectronic with B_5H_9. A preliminary communication[4] from this laboratory reported the isolation and structural characterization of the first such molecule, 1,2-$C_2B_3H_7$. In this paper we describe the preparation of this compound and some of the most significant aspects of its chemistry as it has developed thus far.

Results and Discussion

Synthesis. The reaction of tetraborane(10) with acetylene in the gas phase at 50° has been described in detail, and the formation of the methyl derivatives of 2,3,4-$C_3B_3H_7$ in this system has been examined kinetically.[5] In our early studies of this reaction it was allowed to run to completion, which at 50° requires 4–5 hr when the C_2H_2:B_4H_{10} ratio is 1:1, but several days for a 10:1 mixture. More recent work has disclosed that a substantially different product mixture is obtained when the reaction is quenched well before completion. The major difference, in comparison with reactions over longer periods, is the recovery of 1,2-$C_2B_3H_7$ in substantial yield. This new compound is actually the predominant volatile product (10% yield[6] based on boron consumed) obtained from a 10:1 C_2H_2–B_4H_{10} mixture after 24 hr at 50°. These observations are explained by the subsequent findings that pure $C_2B_3H_7$ reacts readily with B_4H_{10} and B_2H_6 at 50° (see Experimental Section) and much more slowly with C_2H_2, as discussed below. In the presence of a large excess of C_2H_2, the rapid C_2H_2–B_4H_{10} interaction[7] dominates the system, in effect protecting the $C_2B_3H_7$ from attack by B_4H_{10}. Consequently, a prerequisite to the synthesis of $C_2B_3H_7$ in reasonable yield is a C_2H_2:B_4H_{10} mole ratio of at least 2:1, with optimum conditions depending on a complex interrelationship between partial pressures of reactants, temperature, and reaction time.

Structure. A square-pyramidal structure analogous to B_5H_9 (Figure 1) has been postulated from spectroscopic evidence,[4] and the preliminary results of a microwave study in progress elsewhere are consistent with this structure.[8] The ^{11}B and ^1H nmr spectra of

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(1) Abstracted in part from the Ph.D. Dissertation of D. A. F., University of Virginia, 1970, and presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstract INOR 8.

(2) For a recent review, see R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970.

(3) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

(4) D. A. Franz and R. N. Grimes, *J. Amer. Chem. Soc.*, **92**, 1438 (1970).

(5) D. A. Franz and R. N. Grimes, *ibid.*, **93**, 387 (1971), and references cited therein.

(6) Actual yields of $C_2B_3H_7$ have ranged as high as 20% at low partial pressures of reactants. However, under these conditions the absolute quantity of $C_2B_3H_7$ produced is inconveniently small.

(7) Kinetic studies[5] have indicated that the actual species reacting with C_2H_2 is B_4H_8, a highly reactive intermediate produced from B_4H_{10} in the gas phase.

(8) R. A. Beaudet, private communication. We thank Professor Beaudet for permission to quote these results prior to publiction.