

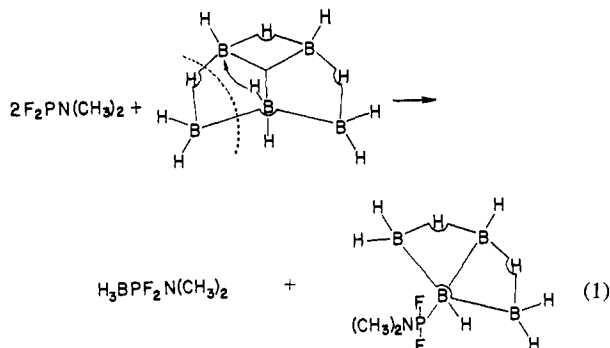
# Preparation and Properties of the Diammoniate of Pentaborane(11)

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**Abstract:** Pentaborane(11) and ammonia, if mixed in a 1:2 molar ratio at  $-112^\circ$ , react at low temperatures in an ether solvent to form a diammoniate of pentaborane(11),  $B_5H_{11} \cdot 2NH_3$ . The diammoniate is an unstable solid at room temperature, decomposing to a viscous liquid. The reaction of the diammoniate with HBr in ether at  $-112^\circ$  gives  $[H_2B(NH_3)_2]^+Br^-$  and  $B_4H_{10}$  quantitatively. Chemical and nmr evidence thus supports the formula  $[H_2B(NH_3)_2]^+[B_4H_9]^-$ . The nonsymmetrical cleavage pattern, observed in the reactions of  $B_2H_6$  and  $B_4H_{10}$  with ammonia, is thus extended to the reaction of  $B_5H_{11}$  with ammonia. Properties of the  $B_4H_9^-$  ion are described;  $B_4H_{10}$ , the conjugate protic acid of  $B_4H_9^-$ , is a weaker protic acid than  $B_5H_{11}$ .

Diborane(6) and tetraborane(10) are known<sup>3</sup> to react with ammonia through nonsymmetrical cleavage of the double bridge bond to give  $[H_2B(NH_3)_2]^+[BH_4]^-$  and  $[H_2B(NH_3)_2]^+[B_3H_8]^-$ , respectively. Bases such as  $F_2PN(CH_3)_2$  will react with diborane(6) and tetraborane(10) by symmetrical cleavage of the double bridge to give  $H_3BPF_2N(CH_3)_2$  and  $H_7B_3PF_2N(CH_3)_2$ , respectively.<sup>4</sup> Pentaborane(11), like diborane(6) and tetraborane(10), is known<sup>5</sup> to react with  $F_2PN(CH_3)_2$  to give  $H_5B_4PF_2N(CH_3)_2$  by a symmetrical cleavage process (eq 1). In contrast, the reaction of  $B_5H_{11}$  with



ammonia was not clearly defined in earlier studies. In his original work, Stock<sup>6</sup> reported that ammonia adds to  $B_5H_{11}$  to give  $B_5H_{11} \cdot 2.7NH_3$ , while an excess of  $NH_3$  was reported to give  $B_5H_9 \cdot 4NH_3$  plus 1 mol of hydrogen gas/mol of  $B_5H_{11}$ . Neither of Stock's pentaborane(11)-ammonia reaction products was ever characterized or studied further.

An extrapolation<sup>3</sup> of the nonsymmetrical cleavage argument cited earlier for  $B_4H_{10}$  and  $B_2H_6$  indicated that  $B_5H_{11}$  should pick up two molecules of ammonia to give  $[H_2B(NH_3)_2]^+[B_4H_9]^-$ . In this publication the successful isolation of  $B_5H_{11} \cdot 2NH_3$  and its characterization as  $[H_2B(NH_3)_2]^+[B_4H_9]^-$  are reported along with some properties of the  $B_4H_9^-$  ion.

(1) Portion of work done as Visiting Professor at the University of Michigan.

(2) University of Utah.

(3) (a) R. W. Parry and L. J. Edwards, *J. Amer. Chem. Soc.*, **81**, 3554 (1959); (b) G. Kodama and R. W. Parry, *ibid.*, **82**, 6250 (1960).

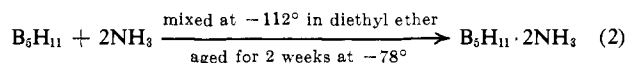
(4) M. A. Fleming, Ph.D. Dissertation, University of Michigan, 1963.

(5) L. F. Centofanti, G. Kodama, and R. W. Parry, *Inorg. Chem.*, **8**, 2072 (1969); E. R. Lory and D. M. Ritter, *ibid.*, **9**, 1847 (1970).

(6) A. Stock and E. Pohland, *Chem. Ber.*, **59**, 2210 (1926); A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p 126.

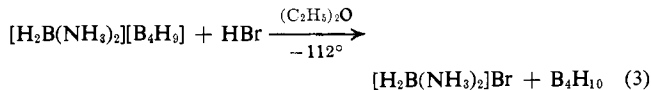
## Results

(1) **The Synthesis of  $B_5H_{11} \cdot 2NH_3$ .** When a known quantity of pentaborane(11) was dissolved in diethyl ether at  $-112^\circ$ , then mixed slowly with *exactly twice* that quantity of  $NH_3$ , a clear solution was formed. No  $H_2$  gas evolution was detected. After the system had been held for 2 weeks at  $-78^\circ$ , the solvent ether was pumped off under vacuum. A white, clearly crystalline solid remained in the reaction tube. Since only pure ether solvent was removed and the product was homogeneous, the reaction is properly characterized by the equation



The diammoniate of pentaborane(11) is stable indefinitely below  $-23^\circ$ , but evolves hydrogen gas at higher temperatures to produce a yellow liquid. Washing the solid with dry methylene chloride at temperatures below  $-23^\circ$  improved the stability of the product, but slow decomposition was still observed at room temperature.

(2) **The Reaction of  $B_5H_{11} \cdot 2NH_3$  with HBr.** When an ether solution of  $B_5H_{11} \cdot 2NH_3$  was treated with an equivalent quantity of HBr at  $-112^\circ$ , the products were  $[H_2B(NH_3)_2]Br^+$  and  $B_4H_{10}$ . The  $B_4H_{10}$  in the ether solution was identified by its  $^{11}B$  nmr spectrum<sup>8</sup> and by its reaction with  $(CH_3)_3N$  to give stoichiometric yields of  $(CH_3)_3NBH_3$  and  $(CH_3)_3NB_3H_7$ .<sup>9</sup> All of the foregoing facts support the formula  $[H_2B(NH_3)_2][B_4H_9]$  for  $B_5H_{11} \cdot 2NH_3$ . The following equations are appropriate.



(3) **The Protic Acid Behavior of  $B_5H_{11}$  and Conditions for the Synthesis of  $B_5H_{11} \cdot 2NH_3$ .** The successful synthesis of  $[H_2B(NH_3)_2][B_4H_9]$  is dependent upon mixing ammonia and pentaborane(11) in a ratio approach-

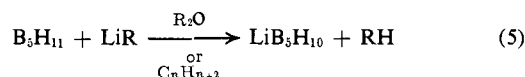
(7) D. R. Schultz and R. W. Parry, *J. Amer. Chem. Soc.*, **80**, 4 (1958).

(8) T. P. Onak, H. Landerman, R. E. Williams, and I. Shapire, *J. Phys. Chem.*, **63**, 1533 (1959).

(9) L. J. Edwards and W. V. Hough, *Proc. Int. Congr. Pure Appl. Chem.*, 1957, **16**, 475 (1958).

ing 2 as closely as possible. Some explanation for this observation is found in the protic acid behavior of  $B_5H_{11}$  and in the reaction between excess  $B_5H_{11}$  and the  $B_4H_9^-$  anion.

Pentaborane(11) is a Brønsted acid under some conditions; it reacts with an equimolar amount of alkyl-lithium in ethers or hydrocarbons to liberate the theoretical amount of the corresponding alkane. The pertinent equation is

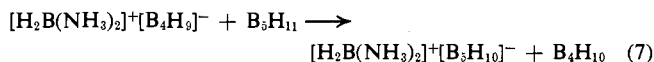


When the ether solution of  $LiB_5H_{10}$ , obtained as a product in our studies, was treated with an equivalent amount of  $HBr$ ,  $LiBr$  and  $B_5H_{11}$  were obtained in a yield above 87%. The pertinent equation is



Solutions of  $LiB_5H_{10}$  in diethyl ether or pentane were stable at  $0^\circ$  for at least 24 hr. At room temperature hydrogen was evolved slowly. When an attempt was made to remove the solvent from  $LiB_5H_{10}$  at a temperature of  $0^\circ$ , decomposition took place to give  $B_5H_9$ ,  $H_2$ , and an uncharacterized white solid.

When  $NH_3$  and  $B_5H_{11}$  were mixed in a ratio below 2 (1:1, for example), the nmr spectrum of the product mixture gave unequivocal evidence for the presence of  $B_4H_{10}$ . The known reaction of  $B_4H_9^-$  with a proton donor to give  $B_4H_{10}$  (see  $HBr$  reaction, eq 3) and the proton donor properties of  $B_5H_{11}$  (indicated above in eq 5) provide an explanation of the sensitivity of the diammoniate of pentaborane(11) to excess pentaborane(11). It also explains the appearance of  $B_4H_{10}$  in the system. The pertinent equation is



This observation indicates that  $B_5H_{11}$  is a stronger acid than  $B_4H_{10}$ . This fact and other recent observations of Shore<sup>10</sup> support an earlier suggestion from this laboratory that the proton acid strength of comparable boron hydrides increases with an increase in the size of the boron framework.<sup>3a</sup>

When  $NH_3$  and  $B_5H_{11}$  were mixed in a ratio above 2 and/or when the temperature of the initial mixing was  $-78^\circ$  instead of  $-112^\circ$ , a white precipitate gradually formed in the originally clear solution as the system stood at  $-78^\circ$ . Apparently a further reaction occurred between  $B_5H_{11} \cdot 2NH_3$  and excess  $NH_3$ , rendering the isolation of  $B_5H_{11} \cdot 2NH_3$  impossible. The nature of this interaction was not studied in detail, but it probably involves attack by  $NH_3$  on the  $B_4H_9^-$  framework.

## Discussion

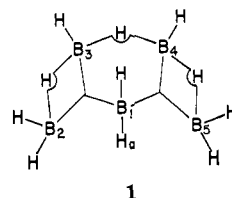
(1) **Observations on Symmetrical and Nonsymmetrical Cleavage of the Double Bridge Bond.** The terms symmetrical and nonsymmetrical cleavage of the double bridge bonds were originally used<sup>11</sup> to describe the reactions of diborane(6). The  $BH_2^+$  unit appears in the products of a nonsymmetrical cleavage process,

(10) H. D. Johnson, II, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, **9**, 908 (1970).

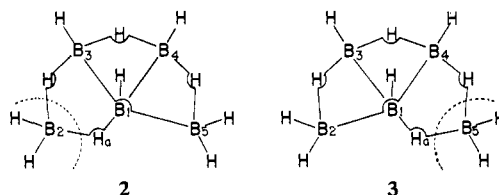
(11) (a) S. G. Shore, Ph.D. Dissertation, University of Michigan, 1956; (b) R. W. Parry and S. G. Shore, *J. Amer. Chem. Soc.*, **80**, 15 (1958).

while the  $H_3B$  unit appears in the products of a symmetrical cleavage process. Later, a close parallel between the chemistry of  $B_4H_{10}$  and that of  $B_2H_6$  was found, and it seemed logical to use the same terms in describing the reactions of  $B_4H_{10}$ .<sup>9,12</sup> It was then suggested<sup>3a</sup> that these two cleavage processes might appear in the reactions of other boron hydrides as well.

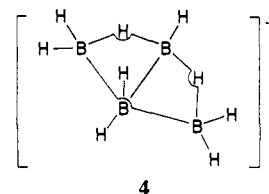
Both  $B_2H_6$  and  $B_4H_{10}$  have a distinct  $BH_2$  unit fastened to the remainder of the molecule by two hydrogen bridge bonds. In  $B_5H_{11}$  such a  $BH_2^+$  unit is much less obvious. The usual structure assigned to  $B_5H_{11}$ <sup>13</sup> is 1. However, careful inspection of the model for



$B_5H_{11}$  indicates that by some bond readjustment the required  $BH_2$  unit, fastened to the remainder of the molecule by two hydrogen bridge bonds, can be seen. Some special features of the  $B_5H_{11}$  molecule are important. The hydrogen atom represented as  $H_a$  is positioned in the molecule such that it can be considered to occupy a bridging position between either boron atoms 1 and 2 or 1 and 5. Thus either of the bonding representations in 2 or 3 is equally appropriate. Non-



symmetrical cleavage is then represented easily by the dashed lines shown above. A similar view was taken by Lipscomb and others.<sup>14</sup> Subjecting this structure to a nonsymmetrical cleavage process then delineates the most probable structure for the  $B_4H_9^-$  anion. It is the fragment left after removal of a  $BH_2^+$  from  $B_5H_{11}$  (4). This structure is identical with that ob-



tained from the known structure of  $B_4H_8PF_2NR_2$ <sup>15</sup> if one replaces the base  $PF_2NR_2$  with a hydride ion.

The actual mechanism of the reaction between  $B_5H_{11}$  and ammonia is considered to be similar to that proposed for the reactions of diborane(6)<sup>11</sup> and of tetraborane(10)<sup>12a</sup> with ammonia. It has been suggested<sup>3a</sup> that the base originally attacks a bridge hydrogen

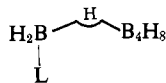
(12) (a) G. Kodama, Ph.D. Dissertation, University of Michigan, 1957; (b) G. Kodama and R. W. Parry, *Proc. Int. Congr. Pure Appl. Chem.*, 1957, **16**, 483 (1958).

(13) (a) L. Lavine and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 614 (1954); (b) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, p 5.

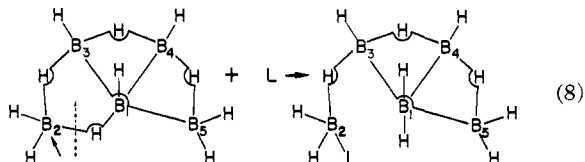
(14) See, for example, ref 13b, p 169.

(15) M. D. La Prade and C. E. Nordman, *Inorg. Chem.*, **8**, 1669 (1969).

in a reversible step under very mild conditions. Under somewhat more vigorous conditions base attack on boron 2 of  $B_5H_{11}$  would break one bridge bond to give the intermediate



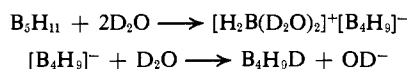
as shown in eq 8. This intermediate could give either a



symmetrical or nonsymmetrical cleavage product, the nature of the product being determined by whether the second molecule of the base attacks boron 1 or boron 2.<sup>16</sup>

While the term nonsymmetrical cleavage of the *double bridge bond* can be applied to the reaction of  $B_5H_{11}$  and ammonia, as a direct extension of the cleavage pattern in  $B_2H_6$  and  $B_4H_{10}$ , its geometric meaning is less obvious here than with either  $B_2H_6$  or  $B_4H_{10}$ . Finally, the observation<sup>17</sup> by one of us that  $B_5H_9$  will react with ammonia to give  $[H_2B(NH_3)_2][B_4H_7]$  shows that a  $-BH_2$  group can be split from a boron hydride molecule even when no *geometrically distinct*  $BH_2$  group is present. In the original discussion on systematics it was suggested that *reactions giving  $BH_2^+$  be classed as nonsymmetrical cleavage processes* even though the original geometric implications for the symmetrical and nonsymmetrical cleavage of the diborane molecule are no longer appropriate. In higher hydrides such as  $B_3H_9$  and  $B_5H_{11}$ , removal of the  $BH_2^+$  unit involves breaking of delocalized partial boron-boron bonds as well as hydrogen bridge bonds. The nature of the intermediate in the  $B_5H_9$  case will be considered as a logical extension of the cleavage process in a paper devoted to this topic.

In earlier arguments describing nonsymmetrical cleavage,<sup>3a,12a,18</sup> it was noted that water, like ammonia, should give nonsymmetrical cleavage of the double bridge bond. Norman and Schaeffer<sup>19</sup> interpreted the reaction between  $B_5H_{11}$  and  $D_2O$  to produce  $\mu$ -monodeuterated tetraborane(10) in terms of a  $B_4H_9^-$  intermediate.



The observations reported here on the nonsymmetrical cleavage of  $B_5H_{11}$  by ammonia and on the reaction of the  $B_4H_9^-$  ion with a proton donor to give  $B_4H_{10}$  provide support for the mechanistic suggestion of Norman and Schaeffer.

(16) When the second base molecule attacks boron 1, one of the hydrogen atoms attached to boron 1 may shift to boron 3 to form the symmetrical cleavage product  $B_4H_9L$ . (The base L is bonded to boron 1 in the known derivatives of  $B_4H_9$ .) Alternatively, initial cleavage of the  $B_2HB_3$  bridge bond at the  $B_2$  side, followed by the cleavage of the  $B_2HB_1$  bond, is equally appropriate. This process does not involve the shift of a hydrogen atom to give the symmetrical cleavage product. Data to permit choice of these processes are not available at the present time.

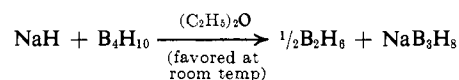
(17) G. Kodama, *J. Amer. Chem. Soc.*, **92**, 3482 (1970).

(18) G. Kodama and R. W. Parry, presented at the 17th Congress of the International Union of Pure and Applied Chemistry, Munich, Sept 1959.

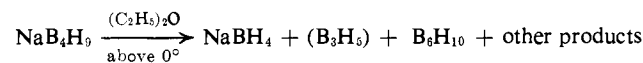
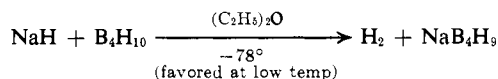
(19) A. D. Norman and R. Schaeffer, *Inorg. Chem.*, **4**, 1225 (1965).

(2) **Observations on the Nonanhydrotetraborate(-1) Ion,  $B_4H_9^-$ .** In recent months the  $B_4H_9^-$  ion has been prepared independently in two laboratories besides this one. Johnson and Shore<sup>20</sup> prepared it by the reaction of potassium hydride with  $B_4H_{10}$  and by the low-temperature reversible reaction of  $B_4H_{10}$  and ammonia. Bond and Pinsky<sup>21</sup> have prepared it by the reaction of  $B_4H_{10}$  with alkyl lithium.

The alkali metal hydride-tetraborane(10) reaction is of special interest. In 1957 Edwards and Hough<sup>9</sup> reported that  $B_4H_{10}$  and NaH react in diethyl ether at room temperature to give almost quantitative yields of  $NaB_3H_8$  and  $B_2H_6$ . The same synthesis of  $NaB_3H_8$  in our laboratory in the late 1950's indicated that the reaction is very sensitive to experimental conditions.<sup>22</sup> Hydrogen gas was always produced in variable amounts and small amounts of  $B_6H_{10}$  were usually identified. The amount of hydrogen evolved and the yield of  $NaB_3H_8$  were dependent upon the source of the sodium hydride used as well as upon the temperature of the system. When the reaction was run at  $-78^\circ$ , 1 mol of hydrogen gas was produced per mole of tetraborane(10),<sup>22b</sup> and no diborane(6) could be detected in the reaction products. After the mixture had been filtered at  $0^\circ$ , a precipitate of  $NaBH_4$  separated slowly from the clear filtrate. Data now available indicate that the reaction between NaH and  $B_4H_{10}$  proceeds in two ways. The first reaction involves symmetrical cleavage of the double bridge bond of  $B_4H_{10}$  to give  $NaB_3H_8$ .



The second reaction involves the acidic bridge hydrogen of  $B_4H_{10}$  and the hydridic hydrogen of NaH;  $NaB_4H_9$  is the product.  $NaB_4H_9$  then decomposes on standing at temperatures above  $0^\circ$  to give  $NaBH_4$  and  $B_3H_5$ . The  $B_3H_5$  fragment reacts to give other products.



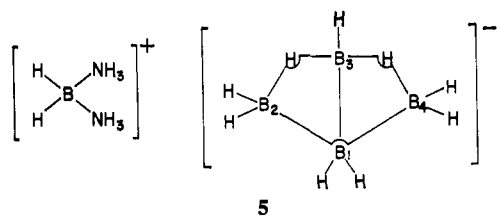
As yet, all factors determining the relative yields of  $NaB_3H_8$  and  $NaB_4H_9$  are not completely defined.

(3) **The  $^{11}B$  Nmr Spectrum of the System  $B_5H_{11}-2NH_3$ .** The  $^{11}B$  nmr spectrum of the pentaborane(11)-ammonia system taken at 32.1 MHz is strongly temperature dependent. The curves at various temperature values are shown in Figure 1. At  $-80^\circ$  two broad, overlapping peaks at 86 and 97 ppm appear along with a well-defined triplet at 139 ppm ( $J_{BH} = 100$  Hz). At  $-40^\circ$  the broad peak at 86 ppm and the triplet at 139 ppm disappear while the peak at 97 ppm becomes sharper and a very broad band centering at 110-120 ppm develops. This change is reversible when the temperature is lowered again. These nmr spectra provide limited information in support of the proposed structure 5. The resonance due to the cation  $[H_2B-$

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

(21) A. C. Bond and M. L. Pinsky, *ibid.*, **92**, 7585 (1970).

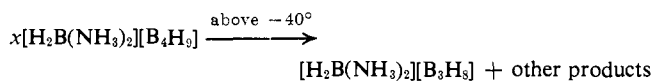
(22) (a) Reference 12a, p 77; (b) R. W. Parry, *et al.*, "The Chemistry of Boron Hydrides and Related Hydrides," University of Michigan, Quarterly Report No. 1, Contract No. AF 33(616)-3343, May 1956, p 10.



$(NH_3)_2]^+$  should appear at around 102 ppm.<sup>23</sup> A broad peak in this position would be overlapped and buried under the broad peak at 97 ppm. Asymmetry in the broad peak at 97 ppm suggests the presence of the  $[H_2B(NH_3)_2]^+$  resonance.

At  $-80^\circ$  the two broad peaks appearing at 86 and 97 ppm and the triplet at 139 ppm must be due to the  $B_4H_9^-$  ion. Because of the breadth of the peaks and the resulting uncertainty in the base line, area measurements are of limited accuracy. The total area under the two broad peaks is 2.6 times the area under the triplet. The triplet is assigned to the  $BH_2$  unit at position 1; this assignment is also consistent with that for  $B_4H_8L$ ,<sup>5,24</sup> in which the resonance for the boron at position 1 always appears at the highest field. If this assignment is accepted, the reversible disappearance of both the triplet at 139 ppm and the band at 86 ppm, concurrent with the appearance of the very broad band centering at 110–120 ppm and the sharpening of the peak at 97 ppm, can indicate shifting of hydrogen within the ion. Hydrogen atoms in the  $B_4H_9^-$  ion must be undergoing rapid enough motion between bridge and nonbridge positions at  $-40^\circ$  to place boron atoms 1 and 3 within a common magnetic environment. Thus the very broad band centering at 110–120 ppm can be attributed to boron atoms at positions 1 and 3, and the peak at 97 ppm must be assigned to boron atoms at positions 2 and 4. The concept of hydrogen tautomerism in boron hydride anions is not new, having been suggested first by Lipscomb for the  $B_3H_8^-$  ion.<sup>25</sup>

As the temperature of the  $B_5H_{11} \cdot 2NH_3$  system was raised from  $-40$  to  $-10^\circ$ , extra peaks began to grow in at 102, 111, and 117, and a sharpening and shrinking of the peak at 97 ppm was noted (Figure 1). The peaks at 102 and 117 ppm remained in the spectrum when the sample was cooled back down to  $-80^\circ$ . At room temperature ( $30^\circ$ ) the irreversible peaks at 102 and 117 ppm continued to grow bigger at the expense of the 97-ppm peak. A white precipitate formed as the sample stood. The peak at 102 ppm is quite clearly associated with the  $[H_2B(NH_3)_2]^+$  cation, while the peak at 117 corresponds to the unresolved multiplet of the  $[B_3H_8]^-$  ion. Since the peak at 97 ppm is associated with the  $B_4H_9^-$  ion, a change characterized, at least in part, by the following incomplete equation is indicated.<sup>26</sup>



The peak appearing at 111 ppm as the temperature

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

(24) A. D. Norman and R. Schaeffer, *J. Phys. Chem.*, **70**, 1662 (1966); R. T. Paine and R. W. Parry, unpublished results for  $B_4H_8PF_2X$  ( $X = Cl, Br, \text{ and } I$ ).

(25) W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, **1**, 132 (1959).

(26) A number of possible equations for the conversion can be written, but the exact nature of the process can be established only after more work.

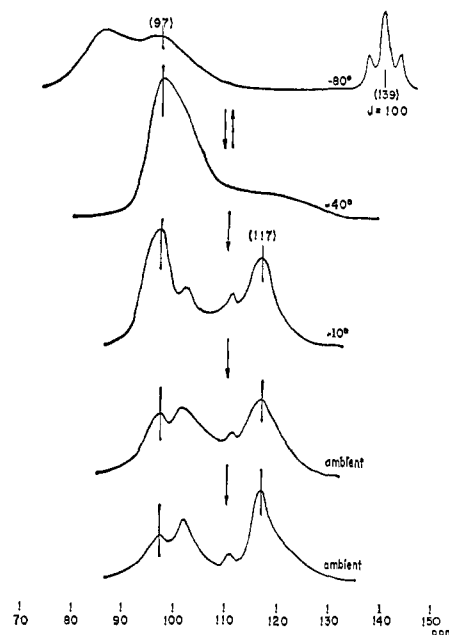


Figure 1. The  $^{11}B$  nmr spectrum of the system  $B_5H_{11} \cdot 2NH_3$  taken at various temperatures, 32.1 MHz. The change between  $-40$  and  $-80^\circ$  is reversible. The solvent is diethyl ether and the standard for chemical shift is  $B(CH_3)_3$ .

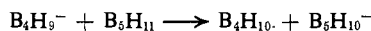
was raised above  $-40^\circ$  became undetectable again as the temperature was lowered to  $-80^\circ$ . The precise nature of the species giving this signal at 111 ppm is not defined.<sup>27</sup> Besides the uncertainty in the identity of the decomposition products, the intensity of the signal which they generate cannot be estimated because of the presence of other overlapping peaks. A quantitative estimate of the number of borons involved is thus made uncertain. The system is now being studied further.

In addition to the above observations, two more interesting and significant points were noted. First it was found that the spectrum of a  $B_5H_{11} \cdot 2NH_3$  mixture in diethyl ether, taken 3 days after mixing, was almost identical with the spectrum taken 7 days after mixing. This point seems to be in conflict with the valid observation that the mixture had to be aged for weeks before a product sufficiently stable for isolation of  $[H_2B(NH_3)_2][B_4H_9]$  could be obtained. The data reported herein suggest that very sizable quantities of  $[H_2B(NH_3)_2][B_4H_9]$  form within the initial 3-day period, but unless essentially all of the  $B_5H_{11}$  or the reactive intermediate<sup>28</sup> has been removed, reaction with  $B_4H_9^-$  occurs on warming.

(27) In a recent, independent work on  $B_4H_9^-$  ion by Johnson and Shore,<sup>20</sup> the presence of a doublet at 26.5 ppm from  $BF_3 \cdot O(C_2H_5)_2$  (or 113 ppm if the chemical shift of  $B(CH_3)_3$  is taken as 86.5 ppm), which was assigned to boron atoms at positions 1 and 3, was noted in their room-temperature spectrum of  $B_4H_9^-$ . This may well correspond to the signal at 111 ppm in our spectra.

(28) A similar set of observations<sup>12</sup> was made in the preparation of  $B_4H_{10} \cdot 2NH_3$ . It was noted and reported that unless the system was digested long enough, some  $B_4H_{10}$  was distilled out of the system when the solvent ether was removed by pumping. Kodama and Parry interpreted these observations as suggesting low-temperature addition of ammonia to the very weakly acidic bridge hydrogens without bridge rupture.<sup>3</sup> This suggestion is made more reasonable by a recent observation by Johnson and Shore,<sup>20</sup> who report that ammonia and tetraborane undergo a fast equilibrium reaction to form  $[NH_4^+][B_4H_8^-]$ . Johnson and Shore<sup>20</sup> also have recently observed a similar reaction between  $B_5H_{11}$  and  $NH_3$ .

A second point in the nmr spectra which is worthy of comment involves the acidic character of  $B_5H_{11}$ . This point has been mentioned briefly in earlier discussion. When  $NH_3$  and  $B_5H_{11}$  were mixed at  $-112^\circ$  in a 1:1 molar ratio and allowed to stand for 3 days at  $-78^\circ$ , the triplet of  $B_4H_9^-$ , appearing at 139 ppm, was replaced by a singlet at 140 ppm. The doublet of  $B_4H_{10}$  ( $\delta$  128 ppm,  $J_{BH} = 155$  Hz) also appeared clearly; the triplet of  $B_4H_{10}$  was somewhat obscured by overlapping peaks. (The new singlet at 140 ppm corresponds to one of the peaks of the  $B_5H_{10}^-$  ion.) These data provide the basis for the suggestion that  $B_5H_{11}$  transfers a proton to  $B_4H_9^-$  to give  $B_5H_{10}^-$  and  $B_4H_{10}$ .



## Experimental Section

**Apparatus.** 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.

**Materials.** Commercial anhydrous diethyl ether was stored in a flask with  $LiAlH_4$  and distilled into the reaction vessel attached to the vacuum system. Anhydrous liquid ammonia (Matheson Co.) was dried by dissolving Na metal in the liquid. The methyl lithium used was a 1 M ether solution of the LiBr complex, a product of Foote Mineral Co. The *n*-butyllithium used was a 2.25 M solution in hexane and was obtained from Alfa Inorganics, Inc. Pentaborane(11) was prepared by the pyrolysis of diborane(6) in a hot-cold reactor. Temperatures of outer and inner walls at the steady running state were kept at  $-78$  and  $+160^\circ$ , respectively, and a total pressure of 1500 mm was maintained. The annular space was 17 mm. The crude product was freed from side products (mainly  $B_4H_{10}$ ) by a trap-to-trap fractionation. A sample of pentaborane(11) thus obtained showed a vapor pressure of 52–53 mm at  $0^\circ$ , and no  $B_5H_9$  could be detected in it by either  $^{11}B$  nmr or infrared spectra.

**Preparation of  $B_5H_{11} \cdot 2NH_3$ .** In a typical run, a 1.34-mmol sample of  $B_5H_{11}$  and a 5-ml sample of diethyl ether were condensed at  $-196^\circ$  in a reaction tube (made of 22-mm diameter Pyrex tubing). The nitrogen bath was then replaced by a  $-112^\circ$  bath, and the liquid in the reactor was stirred with a magnetically energized hopper stirrer. A 2.66-mmol sample of ammonia was measured out and introduced into the reaction system slowly (20 min to complete the addition) by opening the connecting stopcock very slightly while the solution was stirred at  $-112^\circ$ . The ammonia was completely absorbed by the solution. The system was allowed to warm to  $-78^\circ$  and kept at this temperature for 25 days. During the 25-day period the solution remained clear and no pressure buildup was detected. Most of the solvent ether was removed at  $-78^\circ$  by pumping it into the vacuum fractionation system. The reactor was allowed to warm to  $-23$  and to  $0^\circ$  for 1 or 2 min to remove the solvent completely. During this solvent removal process, infrared spectra of the distillate were taken from time to time. No signal originating from N–H or B–H could be detected in any part of the distillate. A white crystalline solid remained in the tube.

**The Reaction of  $B_5H_{11} \cdot 2NH_3$  with HBr.** The diammoniate of  $B_5H_{11}$  obtained above (presumably 1.34 mmol) was dissolved in a 5-ml sample of diethyl ether. The solution was cooled to  $-112^\circ$  and a 1.32-mmol sample of HBr was introduced into the reactor in the same manner as described above for the ammonia addition. A white precipitate formed immediately, and the HBr was absorbed by the solution completely. No hydrogen gas was evolved under these conditions. (The system, however, gave off hydrogen gas very slowly if the reaction was run at  $-78^\circ$ .) A 2.63-mmol sample of  $N(CH_3)_3$  was then added to the system at  $-112^\circ$ ; the mixture was stirred for 30 min after the completion of the amine addition and kept at  $-78^\circ$  for 12 hr. The temperature of the system was then raised to  $-45^\circ$  for 20 min and the mixture was filtered on the vacuum-line filtration assembly. The precipitate collected on the filter disk was washed with ether several times and was identified as  $H_2B(NH_3)_2Br$  by its X-ray powder pattern. The

yield (as scraped out of the filtration unit) was 139.7 mg or 1.10 mmol (83.7% recovery based on the HBr used). From the filtrate a mixture of  $(CH_3)_3NBH_3$  and  $(CH_3)_3NB_3H_7$  was recovered by removal of the ether. These were separated by fractional sublimation. Yields were 98.0 mg or 1.34 mmol of  $(CH_3)_3NBH_3$  and 114.2 mg of 1.16 mmol of  $(CH_3)_3NB_3H_7$ . These correspond to 102.1 and 86.8% recovery, respectively, based on the  $(CH_3)_3N$  used.

**Preparation of Nmr Samples.** Solutions of the diammoniate of  $B_5H_{11}$  were prepared in the standard 5-mm diameter nmr sample tubes. A 0.3-mmol quantity of  $B_5H_{11}$ , a 0.5-ml sample of ether, and a 0.6-mmol quantity of  $NH_3$  were used. A stirring rod with long stem was inserted in the tube and was magnetically operated to stir the solution. When the mixing was completed, the rod was pulled out and the tube was sealed before removal from the vacuum line. Other conditions were the same as described for the routine preparation. The reaction with HBr was also run in an nmr tube to detect  $B_4H_{10}$ . The spectrum of the supernatant solution was taken without removing the precipitate of  $H_2B(NH_3)_2Br$ .

**Reactions of  $B_5H_{11}$  with Alkyl lithium.** A 1-ml sample of methyl lithium solution (1 M with ether as the solvent) was injected into a well-dried, nitrogen-filled reaction tube by means of a hypodermic syringe. The tube was then attached to the vacuum line, frozen with liquid nitrogen, and evacuated. A sample of diethyl ether was condensed in the tube to make about 7 ml of solution and the solution was refrozen. A measured amount of pentaborane(11) was condensed in the tube and the tube was warmed to  $-112^\circ$ . The amount of gas evolved, the molecular weight of which was determined to be that of methane by a gas density measurement, was equal to that of pentaborane(11) or methyl lithium, whichever was present in limiting amount. When an excess of methyl lithium was used, however, the solution became yellow quickly at higher temperatures. A reaction of  $LiB_3H_{10}$  with  $LiCH_3$  was indicated.

The reaction of  $LiB_3H_{10}$  with HBr was run by starting with stoichiometric amounts of the reactants. After the evolution of  $CH_4$  gas ceased, a slight excess of HBr was condensed into the system and the solution was stirred at  $-112^\circ$ . The volatile components were carefully fractionated and an 0.87-mmol quantity of  $B_5H_{11}$  could be recovered. The identity of the  $B_5H_{11}$  was checked by its vapor pressure and infrared spectrum.

Prior to performing these reactions, a 1.00-ml aliquot of the methyl lithium solution was transferred by a syringe into a reaction tube where it was hydrolyzed by condensing excess water into the tube. Reproducibility of the methyl lithium transfer technique was indicated by the consistent amounts of methane evolved. They ranged from 0.95 to 1.03 mmol/1 ml of the original methyl lithium solution.

The use of *n*-butyllithium gave similar results with  $B_5H_{11}$ . Other solvents such as pentane, hexane, and dimethyl ether gave similar results.

**Reactions of  $B_4H_{10}$  with NaH.** (a) **Room-Temperature Reaction.** Data summarized in ref 12a, pp 78–79, indicate that the reaction is not strictly definable. In these experiments, NaH was placed in a reaction vessel of 60–200 ml volume which was equipped with a break-off tip. The vessel was attached to the vacuum line and dry diethyl ether and  $B_4H_{10}$  were distilled in. The tube was sealed off; then the system was warmed to room temperature while the contents were agitated on a shaking machine. The tube was frozen, attached to the vacuum line, and opened. After the removal of volatile components from the vessel, the residue was leached with ether in a vacuum-line extraction system. The crystalline  $NaB_3H_8$  could be obtained by removal of the solvent ether from the filtrate. Besides the products listed earlier ( $B_2H_6$ ,  $H_2$ ,  $NaB_3H_8$ ), hexaborane (6), identified by its vapor pressure (7.5 mm at  $0^\circ$ ), by its molecular weight (vapor density gives value of 75), and by the analysis ( $H_2$  on hydrolysis/B = 2.33), was always detected in small amounts.

Samples of sodium hydride used were the products of Metal Hydride, Inc., of Callery Chemical Co., and of our laboratory at the University of Michigan. The latter was prepared by the reaction of hydrogen and sodium dispersion in mineral oil at  $300^\circ$ .

(b) **Low-Temperature Reaction.** In one of the runs, samples of NaH (0.5 g, commercial product),  $B_4H_{10}$  (0.94 mmol), and diethyl ether (1.5 ml) were taken in a reaction tube and the system was held at  $-78^\circ$  while the contents were agitated with a stirrer. The rate of hydrogen gas evolution was recorded: 0.31 mmol in 2 hr, 0.89 mmol in 12 hr, 0.92 mmol in 20 hr, and 0.95 mmol in 34 hr. After this, the gas evolution was not noticed. The ratio  $H_2/B_4H_{10}$  was thus 1.01. The volatile component was pumped out while the reaction tube was held at  $-63^\circ$ . No evidence was found for the presence of any boron hydride in the distillate.

The rate of hydrogen evolution varied according to the source of the NaH used. In one run with NaH from a commercial source, 75% of the theoretical hydrogen gas was evolved in 30 min at  $-78^{\circ}$ . In another case, with the NaH made in our laboratory, 60% of the total hydrogen was evolved in 1.5 hr. Factors controlling this reaction are still under study.

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## Stabilities, Rates of Formation, and Rates of Transimination in Aqueous Solutions of Some Zinc(II)-Schiff Base Complexes Derived from Salicylaldehyde<sup>1,2</sup>

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**Abstract:** The rates of formation of Schiff bases with salicylaldehyde and ethylamine,  $\alpha$ -alaninate, or  $\beta$ -alaninate have been determined in the presence and absence of Zn(II). Rate laws identical with that previously reported for the formation of *N*-salicylidene-glycinate have been found. Rate constants for the reaction  $\text{sal}^- + \text{RNH}_2 \rightarrow \text{Schiff base}$  increase with increasing basicity of the amine. On the other hand, rate constants for the Zn(II)-catalyzed path,  $\text{Zn}^{2+} + \text{sal}^- + \text{RNH}_2 \rightarrow \text{Schiff base}$ , are almost independent of the amine, consistent with a promnastic model. Amine-exchange (transimination) reactions of Schiff bases have also been investigated. Proton-catalyzed, Zn(II)-dependent and -independent paths have been uncovered. Exchange reactions of the type  $\text{H}(\text{sal-NR}) + \text{H}_2\text{NR}' \rightleftharpoons \text{H}(\text{sal-NR}') + \text{H}_2\text{NR}$ , as well as those which involve Zn(II), proceed at considerably faster rates than does the formation of the Schiff bases by the reaction of  $\text{R}'\text{NH}_2$  with salicylaldehyde. The stabilities of the free and protonated Schiff bases correlate with the basicities of the parent amines. The stabilities of the Zn(II)-Schiff base complexes are also strongly influenced by structural factors.

Schiff bases and their metal-ion complexes find interest in organic chemistry, biochemistry, and inorganic chemistry. A program in these laboratories has been devoted to the investigation of the behavior of these substances in the presence of metal ions in aqueous media. Of particular interest has been the effect of metal ions on the rates of formation. The rate of the reaction of salicylaldehyde and glycinate to give *N*-salicylidene-glycinate has been studied in the presence and absence of various divalent metal ions.<sup>3,4</sup> To account for the interesting pattern of metal-ion reactivities wherein polarizing metal ions such as  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$  were found to be kinetically inactive, but where others,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ , in particular, but also  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Zn}^{2+}$ , were found to be active, the promnastic effect<sup>4</sup> was postulated. It was proposed that in essence the metal ion principally serves to lower the order of the reaction from the second-order reaction which is observed between the free ligands to a first-order reaction occurring within a mixed complex in which the reactants (at least the amine donor) are loosely bound to the metal ion. The highly dynamic situation in which various metal-donor atom bonds are frequently broken and re-formed in chelate<sup>5</sup> rings is visualized to give a sufficiently high concentration of uncoordinated amine electron pairs to enable the

addition of amine to carbonyl. The lower the inherent strength of the metal-nitrogen bond, the higher the activity of the mixed complex. Furthermore, in the reaction with glycinate variation of the carbonyl compound from salicylaldehyde to pyruvate<sup>6,7</sup> has little effect on the rate law except to introduce a change which quantitatively arises from the difference between the binding of these two ligands to the metal ion [Zn(II)] in the mixed complex.

In the present study the nature of the amine was varied. The amines investigated were ethylamine,  $\alpha$ -alanine, and  $\beta$ -alanine, which permitted the examination of the effect on the kinetics of (a) monodentate binding, (b) an alkyl side chain, and (c) six-membered chelate ring formation by the amine moiety.

It was also anticipated that *N*-salicylideneethylamine forms weaker Schiff base-metal ion complexes than Schiff bases derived from the bidentate amino acids, and this difference could be employed to study amine-exchange (transimination) processes in these systems. It has been reported<sup>8</sup> that Cu(II)-5-sulfosalicylaldehyde solutions containing ethylamine and glycinate first exhibit the absorption spectrum of the Cu(II) complex of the ethylamine Schiff base, but after 96 hr the spectrum goes over to that of the more stable glycinate Schiff base complex. This result shows that thermodynamic control determines the final distribution of species in these systems, although kinetics determine the initial distribution.

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