

position. This is equivalent to 105 g of sample per mole of carbon monoxide liberated. The solid obtained from decomposition was shown by its molecular weight and its low temperature infrared spectrum to be trimethylamine-borane. Carbon monoxide was identified by its molecular weight and its infrared spectrum. No other products were observed. The infrared spectrum of the solid obtained by direct reaction was identical with that obtained when the reaction was allowed to take place in methyl ether. The composition of the adduct was also demonstrated by using excess trimethylamine in the reaction and analyzing the recovered excess by formation of trimethylammonium halides.

**Evidence for Dissociation of  $H_3BC(O)N(CH_3)_3$ .** A sample of  $H_3BC(O)N(CH_3)_3$  was warmed very rapidly to room temperature, its pressure measured quickly, and the sample immediately cooled to  $-196^\circ$ . The carbon monoxide which had formed was removed and the remainder of the sample was transferred to a weighing bulb. The apparent molecular weight of the gas was 51.1. If the sample had not been dissociated, the molecular weight expected for  $H_3-$

$BCO \cdot N(CH_3)_3$  would be 101.0. If it had dissociated into two particles, the apparent molecular weight would then be 50.5. It is concluded that the dissociation products are  $H_3BCO$  and trimethylamine. If dissociation had occurred to yield trimethylamine-borane and carbon monoxide directly, the very low vapor pressure of the trimethylamine-borane at room temperature would have resulted in only half the total pressure observed. When a sample was warmed very rapidly and allowed to stand, the pressure reached a maximum and then dropped to approximately half of the value as a reaction took place with the visible formation of trimethylamine-borane in the reaction tube.

**Acknowledgment.** We wish to acknowledge financial support of this research by the American Cancer Society (Grant T-325) and the National Institutes of Health (Grant CA-08222). George W. Luther III also acknowledges support by an NDEA Fellowship.

## A Study of the Reactions of Diborane with Several Polydimethylaminoalanes and Related Compounds. The Synthesis and Chemistry of $H_2B(NMe_2)_2Al(BH_4)_2$

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**Abstract:** Excess  $B_2H_6$  reacts with  $Et_2O$  solutions of  $Al(NMe_2)_3$ ,  $HAl(NMe_2)_2$ , or  $[H_2B(NMe_2)_2]_2AlH$  to form the new compounds  $H_2B(NMe_2)_2Al(BH_4)_2$  and  $\mu-[Me_2N]_2B_3H_7$  in addition to  $Me_2NAl(BH_4)_2$ ,  $Et_2OAl(BH_4)_3$ ,  $(Me_2NBH_2)_2$ , and  $\mu-Me_2NB_2H_5$ . The compound  $H_2B(NMe_2)_2Al(BH_4)_2$  reacts slowly with  $B_2H_6$  in  $Et_2O$  to form  $\mu-Me_2NB_2H_5$  and  $Et_2O \cdot Al(BH_4)_3$ . Reaction with 1 mol of  $P(C_6H_5)_3$  affords  $H_2B(NMe_2)_2AlH(BH_4)$  and  $(C_6H_5)_3PBH_3$ , while excess  $Me_3N$  gives  $[H_2B(NMe_2)_2]_2AlH$ ,  $Me_3NBH_3$ , and an inseparable mixture of  $Me_3N$  complexes of aluminum hydridoborohydrides. A study of the stepwise addition of  $B_2H_6$  to  $Al(NMe_2)_3$  shows that treatment with 0.5 mol of  $B_2H_6$  yields approximately equal quantities of  $HAl(NMe_2)_2$  and  $[H_2B(NMe_2)_2]_2AlH$ . Reaction of  $HAl(NMe_2)_2$  with 1 mol of  $B_2H_6$  produces  $H_2B(NMe_2)_2AlH(BH_4)$ , while reaction of  $[H_2B(NMe_2)_2]_2AlH$  with 1 mol of  $B_2H_6$  gives  $H_2B(NMe_2)_2AlH(BH_4)$  and  $(Me_2NBH_2)_2$ . Diborane and  $H_2B(NMe_2)_2AlH(BH_4)$  form  $H_2B(NMe_2)_2Al(BH_4)_2$ ,  $\mu-Me_2NB_2H_5$ ,  $Me_2NAl(BH_4)_2$ , and a small quantity of  $\mu-(Me_2N)_2B_3H_7$ .

Relatively little is known of the chemistry of mixed boron-aluminum compounds, and their systematic preparation is a challenging synthetic problem. The recent studies by Schram and his colleagues<sup>1</sup> and the earlier work by Ruff<sup>2,3</sup> on aminoboron-aluminum hydrides have amply demonstrated the chemical and structural complexity of this field. In this laboratory the study of boron-aluminum chemistry commenced with the investigation of the action of  $B_2H_6$  on amine- and aminoalanes,<sup>4</sup> which took form as a supplement to an investigation of the reactions of  $B_2H_6$  with tris-(amino)boranes<sup>5</sup> and as part of a general interest in the synthesis and study of heteroatom substituted boranes. An account of the early phase of this work appeared in 1972 which detailed the reactions of  $B_2H_6$  with  $Me_3NAIH_3$  and  $(Me_2NAIH_2)_3$ .<sup>4</sup> In these relatively

simple systems the rapid formation of aluminum borohydride derivatives by addition of diborane to the Al-H bond was followed by slow aluminum-nitrogen bond cleavage to afford  $Et_2OAl(BH_4)_3$  and  $Me_3NBH_3$  and  $\mu-Me_2NB_2H_5$ , respectively, on prolonged exposure to excess  $B_2H_6$ . It was anticipated that the reactions of  $HAl(NMe_2)_2$  and  $Al(NMe_2)_3$ <sup>6</sup> with  $B_2H_6$  would be more complex and would provide an illuminating comparison with the analogous reactions of  $HB(NMe_2)_2$  and  $B(NMe_2)_3$  with  $B_2H_6$ .<sup>7</sup> The action of excess  $B_2H_6$  on  $Al(NMe_2)_3$  in  $Et_2O$  produces, among other products, the new B-N-Al heterocycle  $H_2B(NMe_2)_2Al(BH_4)_2$ ,<sup>8</sup> the chemistry of which is partly the subject of this paper. The discovery that  $HAl(NMe_2)_2$  and  $[H_2B(NMe_2)_2]_2-$

(1) R. E. Hall and E. P. Schram, *Inorg. Chem.*, **10**, 192 (1971), and earlier papers.

(2) J. K. Ruff, *Inorg. Chem.*, **2**, 515 (1963).

(3) J. K. Ruff, *Inorg. Chem.*, **1**, 612 (1962).

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

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

(6) In  $Et_2O$  tris(dimethylamino)alane is reported to be monomeric, while bis(dimethylamino)alane was suggested to be in monomer-dimer equilibrium: E. Wiberg and A. May, *Z. Naturforsch.*, **106**, 234 (1955). Similarly, dimethylaminoaluminum borohydride is known to be associated in benzene (ref 2) but its state of aggregation in  $Et_2O$  is uncertain. In this paper these compounds will be written as monomers.

(7) P. C. Keller, *J. Amer. Chem. Soc.*, **96**, 3078 (1974)

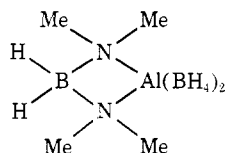
(8) P. C. Keller, *J. Amer. Chem. Soc.*, **94**, 4020 (1972).

$\text{AlH}^9$  also afford exactly the same set of products with excess  $\text{B}_2\text{H}_6$  stimulated the more careful and thorough examination of these systems described in this paper.

## Results

**Characterization of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$ . General Properties.** The compound  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$  is produced in yields as high as 81% along with the by-products  $\text{Me}_2\text{NAl}(\text{BH}_4)_2$ ,  $\text{Et}_2\text{OAl}(\text{BH}_4)_3$ ,  $\mu\text{-(Me}_2\text{N)}_2\text{B}_3\text{H}_7$ ,  $(\text{Me}_2\text{NBH}_2)_2$ , and  $\mu\text{-Me}_2\text{NB}_2\text{H}_5$  by the action of excess  $\text{B}_2\text{H}_6$  on  $\text{Et}_2\text{O}$  solutions of  $\text{Al}(\text{NMe}_2)_3$ ,  $\text{HAl}(\text{NMe}_2)_2$ , or  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$ . The pure product, a volatile, colorless, crystalline solid melting at  $39\text{--}41^\circ$ , is readily soluble without reaction in ethers and aromatic and saturated hydrocarbons. Although thermally stable for several days when kept in clean evacuated vessels, the compound is acutely sensitive to air and protic materials.

The boron-11 nmr spectrum consists of a triplet ( $\delta -1.6$  ppm,  $J = 115$  Hz) and a quintet ( $\delta 37.6$  ppm,  $J = 89$  Hz) in 1:2 ratio, respectively. The chemical shifts, coupling constants, and line widths are nearly coincident with those of  $(\text{Me}_2\text{NBH}_2)_2$  ( $\delta -5.4$  ppm,  $J = 116$  Hz) and  $\text{Al}(\text{BH}_4)_3$  in  $\text{Et}_2\text{O}$  ( $\delta 35.7$  ppm,  $J = 85$  Hz). The proton nmr spectrum shows a single N-CH<sub>3</sub> signal ( $\tau 1.41$ ), implying equivalence of all methyl groups, and a 1:1:1:1 quartet assigned to the  $^{11}\text{BH}_2$  protons ( $\tau 1.60$ ,  $J = 113$  Hz). The signal associated with the  $\text{BH}_4$  protons was not observed, probably owing to extreme quadrupolar broadening resulting from interaction with the aluminum-27 and nitrogen-14 nuclei. These nmr data imply the cyclic structure shown

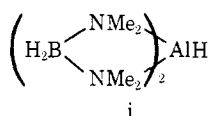


The polyisotopic mass spectrum contains no peaks higher than the parent ion at  $m/e 158$ ;<sup>10</sup> prominent metastable peaks and their assigned reactions are listed in Table I. The major peak groupings and the identi-

Table I. Prominent Metastable Ions in the Mass Spectrum of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$

$m^*(\text{obsd})$	$m^*(\text{calcd})$	Assignment
116.3	116.2	$143^+ \rightarrow 129^+ + 14$
75.0	74.9	$101^+ \rightarrow 87^+ + 14$
61.3	61.2	$87^+ \rightarrow 73^+ + 14$

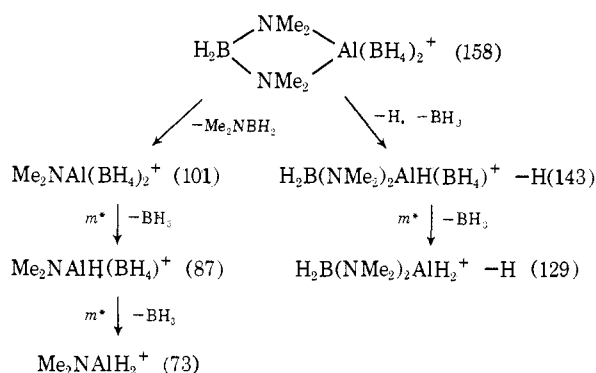
(9) This compound was described in ref 3 as "bis(dimethylamino-borane)-bis-(dimethylamino)alane,"  $(\text{Me}_2\text{N})_2\text{AlH} \cdot (\text{Me}_2\text{NBH}_2)_2$ , in reference to its antecedent reactants. Although the molecular structure has not been determined by X-ray crystallographic methods, the author feels that the bicyclic form proposed by Ruff (i) used throughout this



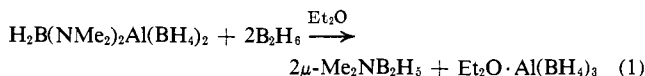
paper is the structure most consistent with all reported physical and spectral data. Other suggested structures are seemingly less satisfactory arrangements with three- or four-coordinate aluminum and uncoordinated  $\text{-NMe}_2$  groups.

(10) See paragraph at end of paper regarding supplementary material.

fication of all "metastable" transitions with loss of a mass 14 fragment suggest the decomposition pathway shown below involving sequential loss of  $\text{BH}_3$  from the  $\text{P1}^-$  ion and from  $\text{Me}_2\text{NAl}(\text{BH}_4)_2^+$ . The general absence of ions in the  $m/e 102\text{--}124$  region argues against successive loss of  $\text{CH}_3$  rather than  $\text{BH}_3$  from the parent ion.

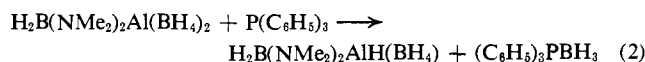


**Reaction with  $\text{B}_2\text{H}_6$ .** Over a period of weeks  $\text{B}_2\text{H}_6$  reacts with an  $\text{Et}_2\text{O}$  solution of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$  at  $25^\circ$  in agreement with eq 1. It is likely that  $\text{Me}_2\text{-}$



$\text{NAl}(\text{BH}_4)_2$  could be an intermediate in this process, since it has been shown to react with  $\text{B}_2\text{H}_6$  at a qualitatively similar rate to give the same products.<sup>4</sup> The appearance of  $\mu\text{-Me}_2\text{NB}_2\text{H}_5$  seems to be the ultimate fate of dimethylamino groups bound to aluminum when subjected to reaction with  $\text{B}_2\text{H}_6$  in ether solvents for extended periods of time.

**The Compound  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{AlH}(\text{BH}_4)$ .** Reaction of equimolar quantities of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$  and  $\text{P}(\text{C}_6\text{H}_5)_3$  affords  $(\text{C}_6\text{H}_5)_3\text{PBH}_3$  and a colorless liquid of a volatility sufficiently similar to that of the starting material to prevent satisfactory separation by standard high vacuum methods. The infrared spectrum (liquid film) was virtually superimposable with that of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$  but in addition exhibited a strong relatively sharp band at  $1870\text{ cm}^{-1}$  characteristic of terminal Al-H stretching. The mass spectrum of the liquid showed only peaks previously observed for  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$ . The boron-11 nmr spectrum (toluene) exhibited the triplet and quintet signals characteristic of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$ , but the integrated intensity of the quintet was considerably less than twice that of the triplet. The isolation of a sample of this material completely free of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$  was never realized, although characterization was fully in accord with the properties expected for a  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2\text{-H}_2\text{B}(\text{NMe}_2)_2\text{AlH}(\text{BH}_4)$  mixture. The reaction with  $\text{P}(\text{C}_6\text{H}_5)_3$  may be regarded as an example of the well-documented displacement of  $\text{BH}_3$  from an aluminum borohydride derivative (eq 2) by a strong Lewis base.<sup>11</sup>



**Reaction with Excess  $\text{NMe}_3$ .** Work-up of this more complex reaction produces  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$  as an

(11) P. H. Bird and M. G. H. Wallbridge, *J. Chem. Soc.*, 3923 (1965).

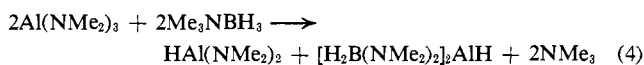
involatile residue in the reaction vessel and a colorless volatile solid-liquid mixture consisting of  $\text{Me}_3\text{NBH}_3$  and unstable and labile aluminum compounds which deposit more  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$  during trap to trap fractionation. No other aluminum-containing substance could be positively identified in this system.

**Stepwise Addition of  $\text{B}_2\text{H}_6$  to  $\text{Al}(\text{NMe}_2)_3$ .** In an effort to understand the processes involved in the conversion of  $\text{Al}(\text{NMe}_2)_3$  to the numerous identified products, a study of the reactions resulting from the stepwise addition of  $\text{B}_2\text{H}_6$  was undertaken. The reactions described here were seldom quantitative and can only be regarded as an approximation to the detailed workings of this system.

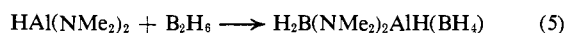
One mole of  $\text{Al}(\text{NMe}_2)_3$  reacts with 0.5 mol of  $\text{B}_2\text{H}_6$  according to eq 3. The products are apparently formed



in equal quantity and no evidence for other boron- or aluminum-containing substances was discovered. This initial step clearly demonstrates why the  $\text{B}_2\text{H}_6$  chemistry of  $\text{Al}(\text{NMe}_2)_3$  resembles that of  $\text{HAl}(\text{NMe}_2)_2$  and  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$ . Indeed, with the perspicacity afforded by hindsight, reaction 3 might have been expected, since Ruff showed that the same products form when  $\text{Al}(\text{NMe}_2)_3$  and  $\text{Me}_3\text{NBH}_3$  react (eq 4).<sup>3</sup>

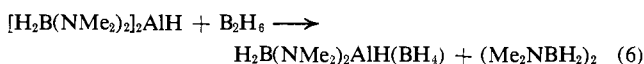


The next steps in the investigation of the  $\text{B}_2\text{H}_6$ - $\text{Al}(\text{NMe}_2)_3$  system are the addition of  $\text{B}_2\text{H}_6$  to the products of reaction 3. A stoichiometric quantity of  $\text{B}_2\text{H}_6$  reacts with  $\text{HAl}(\text{NMe}_2)_2$  (eq 5) to yield the intermediate  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{AlH}(\text{BH}_4)$  together with considerably smaller quantities of the other products of the general  $\text{Al}(\text{NMe}_2)_3$  plus excess  $\text{B}_2\text{H}_6$  reaction. Equation 5 probably represents the primary step



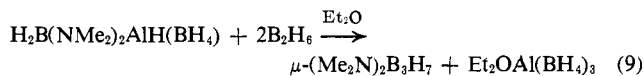
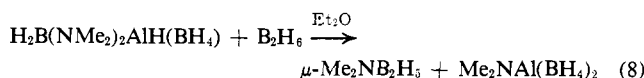
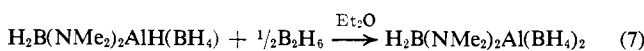
all other products can be ascribed to the further action of  $\text{B}_2\text{H}_6$  upon  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{AlH}(\text{BH}_4)$  (see below).

The action of a stoichiometric amount of  $\text{B}_2\text{H}_6$  on  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$  is summarized by eq 6. As above,



the formation of these materials is accompanied by the appearance of lesser quantities of substances resulting from the reactions of  $\text{B}_2\text{H}_6$  with  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{AlH}(\text{BH}_4)$ . Reaction 6 represents the first appearance of a boron-nitrogen compound in this system. The formation of the common intermediate  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{AlH}(\text{BH}_4)$  explains why  $\text{HAl}(\text{NMe}_2)_2$  and  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$  give identical products when treated with an excess of  $\text{B}_2\text{H}_6$ .

Most of the final products of the  $\text{Al}(\text{NMe}_2)_3$ -excess  $\text{B}_2\text{H}_6$  system result from the action of  $\text{B}_2\text{H}_6$  on  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{AlH}(\text{BH}_4)$ . Based on the materials formed, at least three distinct reactions can be recognized in the terminal step. Only in this last step do the products of reactions 8 and 9 appear in significant quantity.



Judged by product distribution, simple addition of  $\text{BH}_3$  to an Al-H bond (eq 7) represents the main pathway in this system.

## Discussion

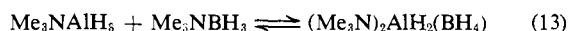
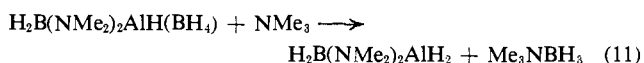
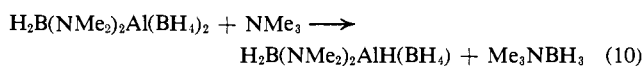
In considering the complex interconversions brought to light here it is instructive to compare the  $\text{B}_2\text{H}_6$  reactions of  $\text{HAl}(\text{NMe}_2)_2$  and  $\text{Al}(\text{NMe}_2)_3$  with those of  $\text{HB}(\text{NMe}_2)_2$  and  $\text{B}(\text{NMe}_2)_3$ .<sup>7</sup> The formation of a four-membered ring by the action of  $\text{B}_2\text{H}_6$  on  $\text{HAl}(\text{NMe}_2)_2$  bears a strong formal resemblance to the reaction of  $\text{HB}(\text{NMe}_2)_2$  with a deficiency of  $\text{B}_2\text{H}_6$ . The facility with which aluminum increases its coordination number may in part explain the preference for eq 5 rather than the duplication of the  $\text{HB}(\text{NMe}_2)_2$  plus excess  $\text{B}_2\text{H}_6$  reaction.

The first step in the  $\text{Al}(\text{NMe}_2)_3$ - $\text{B}_2\text{H}_6$  reaction is dominated by the formation of a compound for which no boron analog exists,  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$ . Ruff demonstrated that this material forms in a remarkable variety of systems whenever boron and aluminum are free to exchange hydride and dimethylamino groups.<sup>3</sup>

The chemical ubiquity of  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$  suggests an enhanced stability which is probably related to a unique molecular geometry. The bicyclic structure suggested here is the simplest arrangement of hydride and dimethylamino groups between boron and aluminum that allows both boron and nitrogen to be four coordinate while simultaneously permitting aluminum to surround itself with five electron pairs. Examples of aluminum compounds in which the metal is formally surrounded by five or six electron pairs are relatively rare and are usually limited to coordination complexes with sterically small ligands.

Although  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$  is reported to be inert to attack by  $\text{NMe}_3$ ,<sup>3</sup> possibly by virtue of its electron-rich structure, it reacts readily with the electrophile  $\text{B}_2\text{H}_6$  to generate compounds with higher coordination numbers but with fewer electron pairs about aluminum as displayed in Table II.

The electron deficiency of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$  and  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{AlH}(\text{BH}_4)$  is reduced by the action of  $\text{NMe}_3$  with the partial regeneration of  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$ . The following reactions may explain these observations.



A moderate quantity of the proposed intermediate  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{AlH}_2$  apparently survives the first stages of separation, as evidenced by the deposition of  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$  during later fractionation. The equilibrium of eq 13, first investigated by Ruff, is complex and resistant to clean separation;<sup>12</sup> reactions of this type, probably including all species of eq 12 and 13, may be operative in this system. The electron de-

(12) J. K. Ruff, *Advan. Chem. Ser.*, No. 42, 139 (1964).

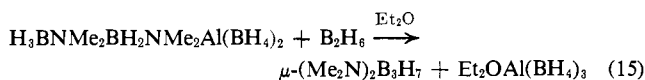
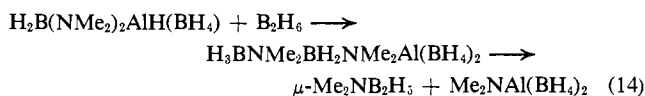
**Table II.** Electron Deficiency of the  $\text{Al}(\text{NMe}_2)_3\text{-B}_2\text{H}_6$  System of Compounds

Compound	Al coordn no.	Electron pairs about Al	Average no. of electrons per bond about Al
$\text{Al}(\text{NMe}_2)_3$	4 <sup>a</sup>	4	2
$\text{HAl}(\text{NMe}_2)_2$	4 <sup>a</sup>	4	2
$[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$	5	5	2
$\text{H}_2\text{B}(\text{NMe}_2)_2\text{AlH}(\text{BH}_4)$	5	4	1.6
$\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$	6	4	1.33
$\text{Et}_2\text{OAl}(\text{BH}_4)_3$	7	4	1.125

<sup>a</sup> These compounds will have four coordinate aluminum owing either to dimerization or to complexation by  $\text{Et}_2\text{O}$ .

deficiency of  $\text{Et}_2\text{OAl}(\text{BH}_4)_3$  is similarly decreased by  $\text{NMe}_3$ , giving  $(\text{Me}_3\text{N})_2\text{AlH}_3$  which also has five electron pairs about aluminum.

The overall distribution of products resulting from the addition of  $\text{B}_2\text{H}_6$  to  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{AlH}(\text{BH}_4)$  (reactions 7, 8, and 9) is probably a function of the extent of diborane promoted aluminum-nitrogen bond cleavage required for each step. Reactions 8 and 9 must proceed by opening the B-N-Al heterocycle before formation of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$ , since further reaction of this product with  $\text{B}_2\text{H}_6$  is slow. In speculation we suggest the following sequence of reactions to explain the results.



## Experimental Section

**General Procedure.** Most routine manipulations involving air- or moisture-sensitive materials were carried out using standard inert atmosphere and high vacuum techniques. All joints and stopcocks coming in contact with aluminum compounds were lubricated with Apiezon-N grease. Boron-11 nmr studies were performed in reaction vessels described previously.<sup>4</sup> Boron-11 nmr spectra were obtained with a Varian HA-100 spectrometer with a 32.1-MHz probe and standard accessories; proton spectra were obtained with Varian HA-100 and T-60 instruments. Boron chemical shifts are in ppm relative to  $\text{Et}_2\text{OBF}_3$ . Infrared spectra were obtained with a Perkin-Elmer 337 spectrophotometer. Spectra of solid aluminum compounds were run as Nujol mulls, since aluminum borohydride derivatives were found to react with KBr during pellet formation, resulting in a spectrum showing only bands characteristic of ionic borohydride in the BH stretching region. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6E spectrometer operating with all inlet heaters off to minimize sample pyrolysis.

The solvents diethyl ether and toluene were stored in evacuated bulbs over  $\text{LiAlH}_4$  and were vacuum transferred directly into reaction vessels when needed. Trimethylamine was generated by treating  $\text{Me}_3\text{N}\cdot\text{HCl}$  with concentrated aqueous  $\text{NaOH}$  and was purified by high vacuum methods. Triphenylphosphine was purchased from Orgmet, Inc., and was used without further purification. The  $\text{Al}(\text{NMe}_2)_3$  and  $\text{HAl}(\text{NMe}_2)_2$  were prepared by the method of Ruff.<sup>13</sup> The compound  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$  was prepared from  $(\text{Me}_2\text{NBH}_2)_2$  and  $(\text{Me}_2\text{N})_2\text{AlH}^3$  or was recovered as a by-product from experiments described below. Routine identification of these and other known compounds was usually accomplished by determination of melting points and infrared spectra.

In order to minimize physical handling during the weighing and transfer of compounds of low volatility and extreme air sensitivity, a special small u-trap, separable from the vacuum line, equipped with

Teflon vacuum stopcocks was employed. In practice samples were trapped at  $-30^\circ$  in this container and, after weighing, were condensed into a special u-shape reaction tube. One u-arm terminated with a constriction and a standard taper joint to accommodate the transfer tube; the other arm was fitted with a Teflon vacuum stopcock and a standard taper joint for attachment to the vacuum manifold. After transfer of the volatile reactant, the u-arm was sealed at the constriction and the transfer vessel was reweighed. Solvent and other reactants were then condensed into the reaction vessel through the stopcock. Nonvolatile products could be recovered easily under inert atmosphere by breaking open the vessel below the stopcock. The transfer vessel was also used as a sample holder for mass spectrometric studies.

For analysis the compounds in this work were completely solvolyzed in anhydrous methanol. Because of the vigor of this reaction, samples were dissolved in toluene prior to treatment. To ensure complete solvolysis, anhydrous hydrogen chloride was condensed into the vessel after collection of the first batch of hydrogen with a Toepler pump-gas buret assembly and the procedure was repeated. Boron was first separated from aluminum by vacuum evaporation of  $\text{B}(\text{OMe})_3$  which was then hydrolyzed to  $\text{B}(\text{OH})_3$  and titrated as the D-mannitol complex. Nitrogen was determined as  $\text{Me}_2\text{NH}$  by a Kjeldahl-type procedure. Aluminum was determined either gravimetrically as the 8-hydroxyquinoline complex or by atomic absorption spectrophotometry.

**Reaction of  $\text{Al}(\text{NMe}_2)_3$  with Excess  $\text{B}_2\text{H}_6$ .** During the course of this work many reactions of this type were carried out, and the product distribution varied considerably for reasons that are not apparent. The reaction described here can be regarded as typical. In a 500-ml reaction vessel a magnetically stirred solution of 0.963 g (6.06 mmol) of  $\text{Al}(\text{NMe}_2)_3$  in 20 ml of  $\text{Et}_2\text{O}$  was treated with 18.0 mmol of  $\text{B}_2\text{H}_6$  for 3 hr at  $25^\circ$ . Following cooling with liquid nitrogen, all volatile products were evaporated from the vessel over a 12-hr period. The inner walls of the reaction bulb were coated with  $\text{Me}_2\text{NAl}(\text{BH}_4)_2$ . Separation of the volatile products was effected by stepwise vacuum line fractionation through traps maintained at 0,  $-17.5$ ,  $-30.6$ ,  $-63$ ,  $-126$ , and  $-196^\circ$ . A total of 3.50 mmol of  $\text{B}_2\text{H}_6$  was recovered, implying a consumption of 14.5 mmol by 6.06 mmol of  $\text{Al}(\text{NMe}_2)_3$ . In this particular experiment no attempt was made to separate  $\text{Et}_2\text{O}$  and  $\mu\text{-Me}_2\text{NB}_2\text{H}_5$ ; in other runs the latter was isolated as the  $\text{Me}_2\text{NH}$  complex<sup>14</sup> or was estimated by acid hydrolysis of the  $\text{Et}_2\text{O}$  fraction. The  $0^\circ$  trap retained a small amount of  $\text{Et}_2\text{O}\cdot\text{Al}(\text{BH}_4)_3$ . The principal aluminum-containing product,  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$ , stops at  $-17.5^\circ$ . This reaction produced 0.489 g (3.10 mmol or 51% yield based on aluminum). Other experiments run under seemingly identical conditions have given yields of up to 81%. Stopping at  $-30.6^\circ$  was 0.058 g (0.453 mmol) of  $\mu\text{-}[(\text{CH}_3)_2\text{N}]_2\text{B}_3\text{H}_7$ .<sup>7</sup> The low yield is typical. The trap at  $-63^\circ$  retained 0.127 g (1.12 mmol) of  $(\text{Me}_2\text{NBH}_2)_2$ .

Experiments involving treatment of  $\text{HAl}(\text{NMe}_2)_2$  or  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$  with excess  $\text{B}_2\text{H}_6$  followed by separation as described above resulted in the isolation of the same set of products.

**Characterization of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$ .** *Anal.* Calcd for  $(\text{Me}_2\text{N})_2\text{AlB}_3\text{H}_{10}$ : Al, 17.1; B, 20.9; H(hydrolytic), 6.33;  $\text{Me}_2\text{N}$ , 55.7. Found: Al, 17.5; B, 20.2; H(hydrolytic), 6.20;  $\text{Me}_2\text{N}$ , 55.7. Several attempts were made to determine the solution molecular weight in  $\text{Et}_2\text{O}$  by vapor pressure lowering. The values obtained, 165, 174, 181, and 242, are not as good as might be desired owing to the difficulty in manipulating the compound, but all values except the highest are close to the monomer weight (158). *Caution!* Disposal of this substance requires care since direct reaction with even sterically hindered alcohols is violent. Destruction of unwanted material is best accomplished by the careful addition of isopropyl alcohol to a dilute toluene solution.

**Thermal Decomposition of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$ .** A 0.0482 g (0.305 mmol) sample of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$  in an evacuated Pyrex vessel was allowed to stand at  $25^\circ$  for 28 days. At the end of this period 0.0286 g (0.180 mmol) of starting material was recovered (60%). The decomposition products were hydrogen, 0.06 mmol, nonvolatile colorless solid, and about 0.01 mmol each of  $\text{B}_2\text{H}_6$ ,  $(\text{Me}_2\text{NBH}_2)_2$ , and  $\mu\text{-Me}_2\text{NB}_2\text{H}_5$ . In a separate experiment using a similar vessel and sample size, about 50% of the starting material was recovered after 90 min at  $80^\circ$ . The decomposition products were the same.

**Reaction of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$  with  $\text{B}_2\text{H}_6$ .** Several experiments of varying duration were ultimately performed in which  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{-}$

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

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

$\text{Al}(\text{BH}_4)_2$  was allowed to react with  $\text{B}_2\text{H}_6$  in  $\text{Et}_2\text{O}$  at room temperature. About 1 month is required for complete conversion. In all cases  $\mu\text{-Me}_2\text{NB}_2\text{H}_5$  and  $\text{Et}_2\text{OAl}(\text{BH}_4)_3$  were the only products isolated.

**Reaction of  $\text{Al}(\text{NMe}_2)_3$  with  $\text{B}_2\text{H}_6$ , 2:1.** A stirred solution of 0.891 g (5.60 mmol) of  $\text{Al}(\text{NMe}_2)_3$  in 10 ml of  $\text{Et}_2\text{O}$  at  $25^\circ$  was allowed to react with 2.82 mmol of  $\text{B}_2\text{H}_6$  for 90 min. Work-up of the volatile fraction on the vacuum line produced only  $\text{Et}_2\text{O}$ . The non-volatile colorless solid residue was extracted with *n*-hexane in a vacuum filtration apparatus. The insoluble fraction was identified as  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$ ; the solid extracted by *n*-hexane was  $\text{HAl}(\text{NMe}_2)_2$  contaminated with a small amount of  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$ .

**Reaction of  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$  with  $\text{B}_2\text{H}_6$ , 1:1. The Compound  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{AlH}(\text{BH}_4)$ .** A stirred solution of 0.297 g (1.29 mmol) of  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$  in 10 ml of  $\text{Et}_2\text{O}$  at  $0^\circ$  was treated with 1.20 mmol of  $\text{B}_2\text{H}_6$  for 75 min. The volatile products were separated on the vacuum line as described above. A small amount of starting material remained in the vessel. No  $\text{B}_2\text{H}_6$  was recovered; acid hydrolysis of the  $\text{Et}_2\text{O}$  fraction produced 0.894 mmol of hydrogen, implying the presence of 0.179 mmol of  $\mu\text{-Me}_2\text{NB}_2\text{H}_5$ . A crystalline solid passing  $-30^\circ$  and stopping at  $-63^\circ$  was identified as  $(\text{Me}_2\text{NBH}_2)_2$ . The  $-30^\circ$  trap contained the bulk of the product, a colorless material melting well below room temperature to an oily liquid. Analysis of a 0.1096-g sample of the liquid gave the following results: Al, 0.725 mmol;  $\text{B}(\text{OH})_3$ , 1.77 mmol;  $\text{H}_2$ (hydrolytic), 6.04 mmol;  $\text{Me}_2\text{NH}$ , 1.47 mmol. Calcd for a 0.1096-g mixture of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$  (0.304 mmol, 42%) and  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{-AlH}(\text{BH}_4)$  (0.427 mmol, 58%): Al, 0.731 mmol;  $\text{B}(\text{OH})_3$ , 1.77 mmol;  $\text{H}_2$ (hydrolytic), 6.03 mmol;  $\text{Me}_2\text{NH}$ , 1.46 mmol.

**Reaction of  $\text{HAl}(\text{NMe}_2)_2$  with  $\text{B}_2\text{H}_6$ , 1:1.** A 0.217-g (1.87 mmol) sample of  $\text{HAl}(\text{NMe}_2)_2$  was allowed to react with 1.87 mmol of  $\text{B}_2\text{H}_6$  in 10 ml of  $\text{Et}_2\text{O}$  at  $0^\circ$  for 60 min and work-up was then effected as described above. No hydrogen,  $\text{B}_2\text{H}_6$ , or  $\mu\text{-Me}_2\text{NB}_2\text{H}_5$  was found. The trap at  $-63^\circ$  retained only a trace of  $(\text{Me}_2\text{NBH}_2)_2$ . The  $-30^\circ$  trap contained the main product, which was the same liquid material characterized in the preceding experiment (liquid film infrared spectrum). A small amount of  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{-AlH}$  remained in the reaction flask.

**Reaction of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{AlH}(\text{BH}_4)$  with  $\text{B}_2\text{H}_6$ .** A 0.146-g sample of the liquid  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{AlH}(\text{BH}_4)\text{-H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$  mixture, isolated from a reaction of  $\text{B}_2\text{H}_6$  with  $\text{HAl}(\text{NMe}_2)_2$ , was dissolved in 10 ml of  $\text{Et}_2\text{O}$  and treated with 2.99 mmol of  $\text{B}_2\text{H}_6$  for 2 hr at  $25^\circ$ . A small quantity of  $\text{Me}_2\text{NAl}(\text{BH}_4)_2$  remained in the reaction vessel after the removal of volatile products, which were separated as described above. A 2.50-mmol quantity of  $\text{B}_2\text{H}_6$  was recovered, demonstrating a consumption of 0.49 mmol. The  $\text{Et}_2\text{O}$  fraction

was subjected to acid hydrolysis and produced 0.973 mmol of hydrogen implying the presence of 0.195 mmol of  $\mu\text{-Me}_2\text{NB}_2\text{H}_5$ . Only a trace of material, presumably  $(\text{Me}_2\text{NBH}_2)_2$ , was found in the  $-63^\circ$  trap. The  $-30^\circ$  trap contained only enough material to give a weak gas-phase infrared spectrum which was, however, sufficient to identify this fraction as mainly  $\mu\text{-}(\text{Me}_2\text{N})_2\text{B}_3\text{H}_7$ .<sup>7</sup> The bulk of the product was retained in the  $-17.5^\circ$  trap, which contained 0.118 g (0.746 mmol) of crystalline  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$ .

**Reaction of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$  with  $\text{P}(\text{C}_6\text{H}_5)_3$ , 1:1.** A 0.499-g (3.16 mmol) sample of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$  was allowed to react with 0.832 g (3.18 mmol) of  $\text{P}(\text{C}_6\text{H}_5)_3$  in 10 ml of  $\text{Et}_2\text{O}$  for 15 min at  $25^\circ$ . The volatile products were distilled through a  $-30^\circ$  trap which retained a colorless material melting well below room temperature. The infrared spectrum (liquid film) of this substance was identical with that of the  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{AlH}(\text{BH}_4)\text{-H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$  mixture described above. The reactor contained 0.82 g (2.97 mmol, 93%) of  $(\text{C}_6\text{H}_5)_3\text{PBH}_3$ .

**Reaction of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$  with Excess  $\text{NMe}_3$ .** A stirred solution of 0.333 g (2.11 mmol) of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$  in 5 ml of  $\text{Et}_2\text{O}$  was treated with 6 mmol of  $\text{NMe}_3$  at  $25^\circ$  for 1 hr. The volatile products were separated from solvent and excess  $\text{NMe}_3$  by a  $-45^\circ$  trap. Remaining in the reaction tube was  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{-AlH}$  (0.140 g, 0.609 mmol). Separation of the materials retained at  $-45^\circ$  proved to be extremely difficult. With each attempted fractionation, a colorless solid deposit remained in the u-tube even after prolonged pumping. A trap containing some of this substance was removed from the vacuum line without exposing the contents to air and was transferred to a glove bag wherein the tube was opened. The solid was found to be  $[\text{H}_2\text{B}(\text{NMe}_2)_2]_2\text{AlH}$ . The only identifiable volatile product was  $\text{Me}_3\text{NBH}_3$ ; no tractable aluminum-containing material could be isolated in a state suitable for characterization.

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**Supplementary Material Available.** The mass spectrum of  $\text{H}_2\text{B}(\text{NMe}_2)_2\text{Al}(\text{BH}_4)_2$  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-74-3073.