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The Preparation and Some Properties of Dihydridobis(monomethylamine)- and Dihydridobis(dimethylamine)boron(III) Tetrahydridoborate(III)[1]

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Tetrahydridoborate(III) salts of $H_2B(CH_3NH_2)_2^+$ and $H_2B[(CH_3)_2NH]_2^+$ cations were prepared by metathetical reactions between the chlorides of the cations and $NaBH_4$ and by direct reactions between diborane and the amines. The *pure* BH_4^- salts are *stable, white solids in vacuo* at room temperature (mp 48° for $[H_2B(CH_3NH_2)_2]BH_4$ and 57° for $[H_2B\{(CH_3)_2NH\}_2]BH_4$). The ligand monomethylamine in the $H_2B(CH_3NH_2)_2^+$ ion can be replaced by ammonia or dimethylamine, and the ligand dimethylamine in the $H_2B[(CH_3)_2NH]_2^+$ ion can be replaced by ammonia or monomethylamine. Spontaneous direct conversion of these BH_4^- salts to the corresponding amine boranes was not observed. On the basis of observed stability of these salts, the process determining the formation of the unsymmetrical and symmetrical cleavage products of diborane was considered.

Shore, Hickam, and Cowles[2] found, by means of B^{11} nmr techniques, that both unsymmetrical and symmetrical cleavage products of diborane [*i.e.*, $[H_2B(amine)_2]BH_4$ and amine–BH_3, respectively], were formed when diborane reacted with excess monomethylamine or dimethylamine at low temperatures. Beachley[3] reported that the reaction of diborane with monomethylamine yielded a *liquid* product and demonstrated that the liquid could be represented as an ionic salt $[H_2B(CH_3NH_2)_2]BH_4$. Recently it was reported[4] that the salts $[H_2B(NH_3)_2]BH_4$ and $[H_2B(CH_3NH_2)_2]BH_4$ could be prepared indirectly from NH_3BH_3 and $CH_3NH_2BH_3$, respectively, and a mechanistic argument was presented to rationalize the cleavage pattern of diborane. When this work was initiated it too had as its objective elucidation of the nature of the reactions between diborane and mono- or dimethylamine.

Salts containing unusually stable cations of the form $H_2B(amine)_2^+$ have been reported.[5,6] Pure BH_4^- salts of these cations have not, however, been described in the literature except for the salts of $H_2B(NH_3)_2^+$ [7] and $H_2B(CH_3NH_2)_2^+$ [3] cations. Isolation and characterization of the BH_4^- salts of the cations $H_2B(CH_3NH_2)_2^+$ and $H_2B[(CH_3)_2NH]_2^+$ are described herein.

Results and Discussion

(1) Preparation of BH_4^- Salts by Metathesis.—

Tetrahydridoborate(III), BH_4^-, salts of the dihydridobis(monomethylamine)boron(III) cation, $H_2B(CH_3NH_2)_2^+$, and the dihydridobis(dimethylamine)boron(III) cation, $H_2B[(CH_3)_2NH]_2^+$, were prepared by metathetical reactions and by direct reactions of diborane with the corresponding amines. The pure compounds are *stable, white solids in vacuo* at room temperature.

The metathetical reactions between the chloride salts of $H_2B(amine)_2^+$ cations and $NaBH_4$ in appropriate solvents proceed to form the BH_4 salts

$$[H_2B(CH_3NH_2)_2]Cl + NaBH_4 \xrightarrow{\text{in liquid } CH_3NH_2} NaCl + [H_2B(CH_3NH_2)_2]BH_4$$

$$[H_2B\{(CH_3)_2NH\}_2]Cl + NaBH_4 \xrightarrow{\text{in liquid } (CH_3)_2NH} NaCl + [H_2B\{(CH_3)_2NH\}_2]BH_4$$

The cations $H_2B(CH_3NH_2)_2^+$ and $H_2B[(CH_3)_2NH]_2^+$ undergo ligand-exchange reactions when dissolved in liquid ammonia or in liquid amines. The general scheme is represented as

$$\begin{tikzcd}
{[H_2B(CH_3NH_2)_2]Cl} \arrow[rr, shift left, "\text{liquid } (CH_3)_2NH"] \arrow[dr, "\text{liquid } NH_3"'] & & {[H_2B\{(CH_3)_2NH\}_2]Cl} \arrow[ll, shift left, "\text{liquid } CH_3NH_2"] \arrow[dl, "\text{liquid } NH_3"] \\
 & {[H_2B(NH_3)_2]Cl} &
\end{tikzcd}$$

Because of such base replacement reactions the metathetical reactions to prepare $[H_2B(CH_3NH_2)_2]BH_4$ and $[H_2B\{(CH_3)_2NH\}_2]BH_4$ had to be carried out in liquid monomethylamine and in liquid dimethylamine, respectively. The compound $[H_2B(CH_3NH_2)_2]BH_4$ thus obtained was reasonably pure and showed the same stability as that prepared by the direct reaction of diborane with monomethylamine. The metathesis product obtained for the dimethylamine system, however, was unstable and began to lose hydrogen slowly near 0° to give a viscous liquid, from which $(CH_3)_2NHBH_3$ could be sublimed. Treatment of the unstable product with liquid ammonia yielded the diammoniate of diborane, $[H_2B(NH_3)_2]BH_4$

$$[H_2B\{(CH_3)_2NH\}_2]BH_4 + 2NH_3 \xrightarrow{\text{in liquid } NH_3} [H_2B(NH_3)_2]BH_4 + 2(CH_3)_2NH$$

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(1) Based in part on an M.S. Thesis submitted by M. Inoue to the Graduate School of the Tokyo College of Science, Feb 1965. Presented in part at the 18th annual meeting of the Chemical Society of Japan, April 1965, Paper No. 6307.

(2) S. G. Shore, C. W. Hickam, Jr., and D. Cowles, *J. Am. Chem. Soc.*, **87**, 2755 (1965).

(3) O. T. Beachley, *Inorg. Chem.*, **4**, 1823 (1965).

(4) S. G. Shore and C. L. Hall, *J. Am. Chem. Soc.*, **88**, 5346 (1966).

(5) (a) H. Nöth and H. Beyer, *Angew. Chem.*, **71**, 383 (1959); H. Nöth and H. J. Vetter, *Ber.*, **97**, 110 (1964); (b) H. Nöth and H. Beyer, *ibid.*, **93**, 1078 (1960); H. Nöth, *Angew. Chem.*, **72**, 638 (1960).

(6) H. C. Miller, N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **85**, 3885 (1963); N. E. Miller and E. L. Muetterties, *ibid.*, **86**, 1033 (1964); N. E. Miller, B. L. Chamberland, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1064 (1964).

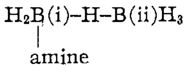
(7) (a) D. R. Schultz and R. W. Parry, *J. Am. Chem. Soc.*, **80**, 4 (1958); (b) R. W. Parry and S. G. Shore, *ibid.*, **80**, 15 (1958); (c) S. G. Shore and R. W. Parry, *ibid.*, **80**, 8, 12 (1958); S. G. Shore, P. R. Girardot, and R. W. Parry, *ibid.*, **80**, 20 (1958); R. C. Taylor, D. R. Schultz, and A. R. Emery, *ibid.*, **80**, 27 (1958).

(2) **Direct Reactions of Diborane with Mono- or Dimethylamine.**—Diborane was allowed to react with these amines at low temperatures and, as suggested by Shore,[2] both amine boranes and $[H_2B(amine)_2]BH_4$ salts could be isolated from the products. As reported earlier[8] the crude product mixtures decomposed at room temperature to give hydrogen and viscous liquid. If the products, however, had been washed extensively with ether in the cold and thus ether-soluble components had been removed, the BH_4^- salts of the cations could be obtained as stable solids. The ether-soluble components were mainly amine boranes contaminated with unidentified liquid. Relative quantities of the BH_4^- salts and the amine boranes (or the ether-soluble components) produced in the reactions were affected by the reaction conditions. Under comparable conditions, the ratio of the BH_4^- salt to amine borane produced in the reactions is higher for the monomethylamine system than for dimethylamine, which is in agreement with the results from the nmr spectra.[2] It was noted that the direct reaction of diborane with the amine sometimes gave only a viscous liquid from which the solid BH_4^- salt could not be isolated. Use of diethyl ether as a reaction medium always resulted in the formation of the BH_4^- salt as a solid precipitate and thus appeared to assure formation of some salt despite lower yields. It was reported that treatment of diborane with ammonia in tetrahydrofuran[9] or dimethyl ether[10] solution resulted in simultaneous formation of the diammoniate of diborane, $H_2B(NH_3)_2BH_4$, and ammonia borane, H_3NBH_3. In all of these cases the role of the ethers as Lewis bases as well as reaction moderators is apparent.

The salts $[H_2B(CH_3NH_2)_2]BH_4$ and particularly $[H_2B\{(CH_3)_2NH\}_2]BH_4$ frequently melt and decompose when impure. Undoubtedly, discrepancies in properties described for the same salt by Beachley[3] must be due to the lack of complete elimination of the ether-soluble component in his preparation.

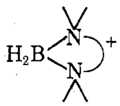
The results of this study show conclusively that earlier molecular weight determinations on amine boranes made by Parry and co-workers[8b] were seriously complicated (1) by the fact that the original amine borane, made by direct reaction of diborane and amine, was a mixture and (2) by the fact that amine-exchange reactions occurred when compounds such as $[H_2B(CH_3NH_2)_2]BH_4$, etc., were dissolved in liquid ammonia.

The BH_4^- salts obtained in this work do not transform to amine boranes in liquid amines or in diethyl ether. When they do change to form amine boranes, evolution of hydrogen is always observed. Therefore, the idea[3] that donor molecules might initiate the *unsymmetrical* cleavage at low temperatures, followed by rearrangement to form the symmetrical cleavage product if the latter were more stable, is not applicable to the system described here. Clearly, the presence of amine boranes in the products of amine–diborane reactions is not due to the conversion of $[H_2B(amine)_2]BH_4$. The results reported here give support to the mechanistic argument that was first proposed by Parry and Shore[7b] for the reaction of diborane with ammonia and recently extended[4] to systems involving diborane with amines. That is, the cleavage pattern of diborane, unsymmetrical or symmetrical, is determined by the site of the second amine attack in the intermediate



$$\underset{\text{amine}}{H_2\overset{}{B}}(i){-}H{-}B(ii)H_3$$

The relative yields of the BH_4^- salt and the amine borane may be taken as a rough measure of the extent to which the second amine molecule attacks boron i and ii. The greater extent of attack on boron ii by dimethylamine thus deduced from experimental results is that expected if one of the dominant factors determining the site of the attack is steric interaction. Under comparable conditions trimethylamine and diborane react to form trimethylamine borane alone. It was reported,[11] however, that certain bidentate *tertiary* amine ligands such as tetrakis(dimethylamino)ethylene and *o*-bis(dimethylamino)benzene reacted with diborane to give BH_4^- salts of



cations. In such cases the course of the reaction mechanism appears to be influenced strongly by the chelating effect of the ligand amines.

It is noted that the behavior of the system described here differs sharply from that proposed for the tetrahydrofuran–tetraborane system in which conversion of $[H_2B(THF)_2]B_3H_8$ to $(THF)B_3H_7$ was postulated as the temperature was raised.[12]

Experimental Section

General Material.—Volatile compounds for reaction studies were handled in a standard high-vacuum line apparatus, and moisture-sensitive solids were handled in a plastic bag filled with dry nitrogen.

Amines were liberated from hydrochlorides of monomethylamine and dimethylamine by adding concentrated NaOH solution. The free amines were dried over KOH pellets, stored in small steel cylinders, and dried again before use by treating with sodium metal until the blue color due to the dissolved sodium persisted in the liquid amines. Diborane was prepared from $BF_3\cdot(C_2H_5)_2O$ and $LiAlH_4$ by the literature method.[13] Ether was kept over sodium ribbon, and freshly distilled ether was used for the diborane preparation. Ether for other purposes was stored over $LiAlH_4$ and distilled directly in the vacuum line. Commercial $NaBH_4$ was purified by leaching with liquid ammonia.

Chloride salts of $H_2B(CH_3NH_2)_2^+$ and $H_2B[(CH_3)_2NH]_2^+$ ions were prepared by the reactions of amine–BH_2Cl with amines in

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[8] (a) E. Wiberg, A. Bolz, and P. Buchheit, *Z. Anorg. Chem.*, **256**, 285 (1948); R. E. McCoy and S. H. Bauer, *J. Am. Chem. Soc.*, **78**, 2061 (1956); (b) R. W. Parry, G. Kodama, and D. R. Schultz, *ibid.*, **80**, 24 (1958).

[9] S. G. Shore and K. W. Böddeker, *Inorg. Chem.*, **3**, 914 (1964).

[10] G. Kodama, Ph.D. Dissertation, University of Michigan, 1957, p 90. The compound described as "the mistreated diammoniate of diborane" has been shown to be identical with the compound $H_2B(NH_3)_2BH_4$ by means of its X-ray powder pattern.

[11] N. Wiberg and J. W. Buchler, *Ber.*, **96**, 3000 (1963).

[12] R. Schaeffer, F. Tebbe, and C. Phillips, *Inorg. Chem.*, **3**, 1475 (1964).

[13] I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik, and G. B. L. Smith, *J. Am. Chem. Soc.*, **74**, 901 (1952).

TABLE I

DATA FOR DIRECT REACTIONS BETWEEN B_2H_6 AND AMINES

$[B_2H_6]$, mmoles	[Amines], mmoles	Solvent	$[H_2B(amine)_2BH_4]$, mmoles	$[Amine{-}BH_3]$,[a] mmoles	% yield of the BH_4 salt based on B_2H_6 used
2.69	CH_3NH_2, excess	CH_3NH_2	1.56	...	58.2[c]
2.00	CH_3NH_2, excess	CH_3NH_2	...	0.29	92.7[b]
2.00	CH_3NH_2, excess	CH_3NH_2	...	0.67	83.3[b]
1.56	CH_3NH_2, 3.14	$(C_2H_5)_2O$	0.24	...	15.4[c]
3.45	CH_3NH_2, 13.7	$(C_2H_5)_2O$	...	1.91	72.3[b]
7.22	CH_3NH_2, 15.1	$(C_2H_5)_2O$	...	4.24	70.7[b]
2.99	$(CH_3)_2NH$, excess	$(CH_3)_2NH$	1.36	...	45.5
2.00	$(CH_3)_2NH$, excess	$(CH_3)_2NH$	...	2.32	42.0[b]
2.37	$(CH_3)_2NH$, 5.50	$(C_2H_5)_2O$	0.69	...	28.9
2.59	$(CH_3)_2NH$, 5.18	$(C_2H_5)_2O$	0.79	...	30.5
4.62	$(CH_3)_2NH$, 9.30	$(C_2H_5)_2O$	1.08	...	25.8

[a] The ether-soluble component was assumed here to have been all in the form of amine borane. [b] The yield of the BH_4 salt was calculated from the yield of the amine borane. [c] Estimated loss due to incomplete recovery from the filter unit was large.

diethyl ether as described by Nöth.[5b] The solid products were washed thoroughly with dry ether. *Anal.* Calcd for $[H_2B(CH_3NH_2)_2]Cl$: B, 9.8; N, 25.4; Cl, 32.1. Found: B, 9.7; N, 24.8; Cl, 31.8. Calcd for $[H_2B\{(CH_3)_2NH\}_2]Cl$: B, 7.8; N, 20.2. Found: B, 7.7; N, 20.7.

Ligand-Exchange Reactions of the Chloride Salts.—A sample of the salt was treated with an excess of liquid ammonia or one of the liquid methylamines. After the removal of the solvent by pumping, the identity of the residue was checked by means of its X-ray powder pattern. In each case the presence of a single solid phase was indicated. The X-ray powder pattern for $[H_2B(NH_3)_2]Cl$ was identical with that reported earlier.[7a] The patterns for $[H_2B(CH_3NH_2)_2]Cl$ and $[H_2B\{(CH_3)_2NH\}_2]Cl$ are given at the end of this section.

Metathetical Preparation of $[H_2B(CH_3NH_2)_2]BH_4$.—A 1.54-mmole sample of $[H_2B(CH_3NH_2)_2]Cl$ and a 1.52-mmole sample of $NaBH_4$ were dissolved in 8 ml of liquid CH_3NH_2 at −78°. The solution was stirred and the temperature was raised slowly. A white precipitate began to form near −40°. The system was held at −10° for 1.5 hr. The NaCl precipitate was filtered off using a filtration unit[14] attached to the vacuum line and the solvent amine was removed from the filtrate by pumping. The white solid obtained as residue gave a distinctive X-ray powder pattern in which only a few lines of the NaCl powder pattern were barely detected. The solid is stable at room temperature *in vacuo*.

Attempted Metathetical Preparation of $[H_2B\{(CH_3)_2NH\}_2]BH_4$.—A procedure similar to that described above for the monomethylamine system was followed. However, the chloride salt $[H_2B\{(CH_3)_2NH\}_2]Cl$ is only slightly soluble in liquid dimethylamine, and hydrogen gas evolves slowly from the reaction mixture when the system is warmed near 0°. Therefore, the reaction mixture was stirred at −45° for 2 hr and at −35° for 25 hr to ensure complete reaction. It was then filtered at about −35°. The white solid residue obtained from the filtrate after removing the solvent was stable below −23°, but began to evolve hydrogen near 0°. When a freshly prepared sample of this unstable solid was treated with liquid ammonia and all of the volatiles were removed at room temperature by pumping, a solid residue contaminated with a viscous liquid resulted. The X-ray powder pattern of the residue was identical with the pattern of $[H_2B(NH_3)_2]BH_4$ reported earlier,[9] and no other lines could be detected in it.

Isolation of $[H_2B(CH_3NH_2)_2]BH_4$ and $[H_2B\{(CH_3)_2NH\}_2]BH_4$ from the Products Obtained by Direct Reaction between B_2H_6 and Amines.—Data of typical runs are summarized in Table I.

(1) **The Reaction with a Large Excess of Amine.**—Liquid CH_3NH_2 (about a 5-ml sample) was distilled into a reaction tube (22-mm diameter); on top of the amine a sample of B_2H_6 and about 2 ml of liquid CH_3NH_2 were condensed in several alternating layers at −196°. The system was allowed to warm gradually to −85° over a period of 5 hr. The resulting clear solution was stirred well and held at −78° for a few days. The solvent amine was then distilled out at −23°; a solid and a viscous liquid remained; no noncondensable gas was found. A few milliliters of diethyl ether was then condensed into the reaction tube, and the mixture was stirred at −35°. On vaporization of the ether at −35°, only a crystalline solid remained in the reaction tube. The solid was washed quickly with several 8-ml portions of cold ether (below 0°) in the filtration unit. The X-ray powder pattern of this solid was identical with that of $[H_2B(CH_3NH_2)_2]BH_4$ obtained by the metathetical reaction except for the absence of lines due to NaCl. *Anal.* Calcd for $[H_2B(CH_3NH_2)_2]BH_4$: N, 27.6. Found: N, 26.9, 28.5.

The reaction of diborane with dimethylamine was carried out in the manner described above for the monomethylamine reaction, except that the solvent amine was distilled out at −40° and the filtration and washing were performed at about −30° to avoid the decomposition of the product at higher temperatures. The ether-insoluble solid thus obtained was quite stable *in vacuo* when warmed to room temperature and no sign of decomposition was observed over a period of 2 days. *Anal.* Calcd for $[H_2B\{(CH_3)_2NH\}_2]BH_4$: N, 23.8. Found: N, 23.6, 23.9.

(2) **The Reaction in Ether Solution.**—A sample of B_2H_6 (see Table I) and a 5- to 8-ml sample of diethyl ether were condensed in a reaction tube; when the temperature was raised to −78° a diethyl ether solution of B_2H_6 resulted. The solution was frozen again; then an approximately 2-mole equivalent of CH_3NH_2 or $(CH_3)_2NH$ per mole of the B_2H_6 was condensed into the tube. The system was allowed to warm slowly to −112°, at which temperature the solution began to become turbid. The solution was stirred for several hours at −112°; then the reaction vessel was immersed in a −78° bath and held at that temperature for a few days. The tube was then attached to the filtration unit and the solid product was quickly filtered and washed with fresh, dry diethyl ether. Temperature during the filtration and washing process was maintained below 0° for the monomethylamine system and below −23° for the dimethylamine system; the decompositions that take place at higher temperatures were thus avoided. The ether-insoluble solids thus obtained were stable, dry powders at room temperature. Identification of these solids as $[H_2B(CH_3NH_2)_2]BH_4$ and $[H_2B\{(CH_3)_2NH\}_2]BH_4$ was accomplished by their X-ray powder patterns.

From both the ether washings in (1) and the ether filtrate in (2), a solid residue could be obtained when the ether was removed at low temperatures by vaporization. On warming to room temperature the system produced small quantities of hydrogen and amine, and a part of the solid changed to a liquid of low volatility. Monomethylamine borane or dimethylamine borane could be sublimed from such a mixture, but a significant fraction of the nonvolatile liquid was left behind.

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(14) R. W. Parry, D. R. Schultz, and P. R. Giradot, *J. Am. Chem. Soc.*, **80**, 1 (1958)

Properties of $[H_2B(CH_3NH_2)_2]BH_4$ and $[H_2B\{(CH_3)_2NH\}_2BH_4$. (1) **General Characteristics.**—An evacuated glass tube containing a sample of the compound was placed in a water bath and the temperature of the bath was raised at a rate of about 1°/min. The monomethylamine compound turned to a liquid containing bubbles at 48°. For the dimethylamine compound, the evolution of gas could be detected at 50° by means of a manometer attached to the system, and the solid melted very sharply at 57°.

The compounds are soluble in water. Hydrogen gas evolved very slowly from neutral aqueous solutions, but very rapidly when the solution was acidified. The monomethylamine compound is very deliquescent. Although the dimethylamine compound was stable when stored *in vacuo*, it changed to a liquid in a few days, and a gas was evolved if it was transferred to a glass vial with a polyethylene cap. On standing further, well-defined crystals of $(CH_3)_2NHBH_3$ formed slowly in the vial.

(2) **Ligand-Exchange Reactions.**[15] (a) **With Ammonia.**—A sample of $[H_2B(CH_3NH_2)_2]BH_4$ was dissolved in liquid ammonia and then the volatiles were removed by pumping. The residual solid was identified as $[H_2B(NH_3)_2]BH_4$ by means of its X-ray powder pattern.[9] The same treatment of $[H_2B\{(CH_3)_2NH\}_2]BH_4$ also resulted in the formation of $[H_2B(NH_3)_2]BH_4$. The chloride salts also underwent similar exchange as described earlier in this section.

(b) **With Methylamines.**—A 2-mmole sample of $[H_2B(CH_3NH_2)_2]BH_4$ was dissolved in liquid $(CH_3)_2NH$ at −78°, and the solution was allowed to warm gradually to −23° over a period of 4 hr. Most of the amine was then distilled out at −23°. In order to remove the amine retained in the system, a 3-ml sample of diethyl ether was condensed in; the mixture was stirred, and the volatiles were removed by pumping without warming the system above −23°. After several such treatments, the solid residue was washed with *cold* ether in the filtration unit. The solid, however, decomposed to give hydrogen when allowed to warm to room temperature and turned to a mixture of solid and liquid. The solid component resulting from this decomposition was identified by its melting point (35°) and X-ray powder pattern as $(CH_3)_2NHBH_3$. The foregoing observation suggests that the ligand-exchange reaction takes place in the system

$$[H_2B(CH_3NH_2)_2]BH_4 + 2(CH_3)_2NH \longrightarrow [H_2B\{(CH_3)_2NH\}_2]BH_4 + 2CH_3NH_2$$

$$[H_2B\{(CH_3)_2NH\}_2]BH_4 \xrightarrow{\text{decomposition}} (CH_3)_2NHBH_3,\ H_2,\ \text{and others}$$

A 2-mmole sample of $[H_2B\{(CH_3)_2NH\}_2]BH_4$ was treated with liquid CH_3NH_2 in the same manner as described above. The solid product obtained on the frit was stable at room temperature and was identified as $[H_2B(CH_3NH_2)_2]BH_4$ by means of its X-ray powder pattern.

Infrared Spectra and X-Ray Powder Patterns.—Infrared spectra of the samples were taken in KBr pellets at room temperature using NaCl optics. The pellets were prepared in an atmosphere of dry nitrogen and were placed in a stream of dry nitrogen during the recording. The X-ray powder patterns were recorded photographically with a 114.6-mm diameter camera using Cu Kα or Fe Kα radiation. The X-ray powder pattern of $[H_2B(CH_3NH_2)_2]Cl$ differs somewhat from that reported by Beachley.[3]

(1) **$[H_2B(CH_3NH_2)_2]Cl$.**—*d* values (Å): 7.80 (vs), 7.27 (vw), 5.95 (s), 5.05 (w), 4.52 (s), 4.29 (vw), 4.13 (w), 3.96 (s), 3.77 (m), 3.65 (vs), 3.59 (vw), 3.50 (vw), 3.34 (vs), 3.27 (m), 3.01 (m), 2.91 (w), 2.83 (vw), 2.79 (w), 2.72 (vw), 2.66 (w), 2.60 (vw), 2.53 (m), 2.41 (s), 2.33 (w), 2.26 (m), 2.21 (s), 2.169 (w), 2.135 (vw), 1.984 (vw), 1.836 (vw), 1.783 (w), 1.752 (w), 1.642 (vw), 1.616 (vw), 1.591 (vw). Cu Kα radiation was used.

(2) **$[H_2B\{(CH_3)_2NH\}_2]Cl$.**—*d* values (Å): 5.80 (vs), 5.43 (m), 5.15 (w), 4.59 (vw), 4.44 (s), 4.25 (vw), 4.08 (vw), 3.94 (s), 3.84 (vw), 3.69 (s), 3.61 (m), 3.44 (vw), 3.18 (s), 3.07 (m), 2.94 (w), 2.84 (w), 2.75 (w), 2.71 (vw), 2.65 (vw), 2.45 (vw), 2.37 (w), 2.27 (vw), 2.093 (vw), 2.035 (vw), 1.970 (vw), 1.928 (vw), 1.840 (vw). Cu Kα radiation was used.

(3) **$[H_2B(CH_3NH_2)_2]BH_4$.**—*d* values (Å): 7.20 (vw), 5.79 (s), 5.52 (m), 5.03 (m), 4.77 (vs), 4.17 (vs), 4.04 (w), 3.86 (m), 3.65 (vw), 3.50 (m), 3.39 (s), 3.17 (s), 3.08 (w), 2.93 (vw), 2.86 (vw), 2.524 (m), 2.404 (vw), 2.338 (vw), 2.255 (vw), 2.083 (vw), 2.013 (vw), 1.959 (vw), 1.875 (vw). Fe Kα radiation was used. Infrared spectrum (cm^{-1}): 3460 (m, b), 3160 (sh), 3095 (vs), 3025 (sh), 2965 (m), 2715 (m), 2695 (m), 2425 (s), 2380 (m), 2295 (vs), 2232 (s), 1610 (m), 1602 (m), 1467 (m), 1422 (w), 1368 (s), 1353 (sh), 1336 (m), 1260 (w), 1197 (m), 1183 (s), 1148 (sh), 1133 (sh), 1126 (vs), 1064 (m), 1026 (m), 1018 (sh), 973 (w), 928 (sh), 919 (w), 858 (sh), 848 (m), 803 (w). The spectrum was recorded with a Japan Spectroscopic IR-S spectrometer.

(4) **$[H_2B\{(CH_3)_2NH\}_2]BH_4$.**—*d* values (Å): 9.98 (w), 6.51 (vw), 6.23 (w), 5.88 (vs), 5.61 (s), 5.36 (s), 5.15 (s), 4.82 (vw), 4.67 (vs), 4.53 (vw), 4.36 (w), 4.26 (m), 4.21 (m), 3.86 (s), 3.79 (m), 3.63 (vw), 3.44 (vw), 3.37 (vw), 3.29 (m), 3.15 (vw), 3.06 (m), 2.95 (vw), 2.80 (m), 2.72 (w), 2.66 (vw), 2.553 (w), 2.52 (vw), 2.460 (w), 2.384 (vw), 2.347 (vw), 2.310 (w), 2.254 (vw), 2.168 (vw). Fe Kα radiation was used. Infrared spectrum (cm^{-1}): 3400 (w, b), 3090 (s), 3020 (s), 2955 (sh), 2845 (m), 2685 (m), 2430 (s), 2380 (sh), 2340 (sh), 2285 (vs), 2215 (s), 2165 (sh), 1478 (m), 1463 (s), 1452 (sh), 1441 (m), 1435 (sh), 1410 (m), 1358 (s), 1341 (sh), 1229 (m), 1186 (vs), 1165 (m), 1155 (m), 1125 (s), 1100 (m), 1051 (w), 1031 (m), 1017 (m), 996 (m), 920 (s), 891 (w), 879 (s), 773 (w), 767 (w). The spectrum was recorded with a Hitachi EPI-S2 spectrometer.

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[15] Although details are not given here, it has been found that $[H_2B(NH_3)_2]BH_4$ can also be converted to the solid $[H_2B(CH_3NH_2)_2]BH_4$ by treating with liquid CH_3NH_2.