[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Metallo Borohydrides. I. Aluminum Borohydride

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As has already been described in a brief preliminary communication,[2] trimethylaluminum and diborane react to form the compound AlB_3H_{12}, according to the equation

$$Al_2(CH_3)_6 + 4B_2H_6 \longrightarrow 2B(CH_3)_3 + 2AlB_3H_{12}$$

For satisfactory preparation, the diborane must be present in a quantity somewhat greater than indicated by the equation, since with smaller quantities there is obtained a complex mixture of compounds difficult to separate. The formula of the compound was established by determination of the vapor density, and by analyses based upon its reactions with water and with hydrogen chloride.

The substance has the physical characteristics of a non-polar compound; its colorless crystals melt at $-64.5°$, its vapor tension at 0° is 119.5 mm., and its boiling point (extrapolated) is 44.5°. In its chemical behavior, AlB_3H_{12} greatly resembles diborane. It reacts readily with air, as a matter of fact more readily than diborane, since it inflames spontaneously, giving a blue-white flash of unusual brilliance. It is rapidly hydrolyzed at ordinary temperatures, to give hydrogen, boric acid and aluminum hydroxide; with hydrogen chloride it reacts readily, even at $-80°$, to form aluminum chloride, hydrogen and diborane. Although the products of its interaction with excess trimethylaluminum have not yet been fully identified, it seems likely that this reaction is similar to that of diborane with trimethylboron.[3]

Three other properties are important because of their bearing on the structure of the compound. The first of these is its interaction with ethyllithium in benzene solution to give the compound $LiBH_4$.[4]

The second of these properties is the fact that with trimethylamine and with dimethyl ether, at low temperatures, AlB_3H_{12} forms the addition compounds, $AlB_3H_{12}{\cdot}N(CH_3)_3$ and $AlB_3H_{12}{\cdot}O(CH_3)_2$. These products, although moderately stable, are decomposed when the temperature is raised to 40 or 60°, but not into their parent substances. The etherate gives methane and unidentified products; the trimethylamminate undergoes a complex reaction, one of the products of which is borine trimethylammine, $BH_3{\cdot}N(CH_3)_3$.[5] Ammonia also reacts with AlB_3H_{12} to give an end-product of the composition $AlB_3H_{12}{\cdot}NH_3$, but there is evidence that the reaction is not one of simple addition; during the absorption of one mole of ammonia, the first product is an amorphous white solid, which changes to a colorless liquid, and finally goes over to colorless crystals.

The evidence for the existence of these "mono-addition" products is not, as yet, entirely satisfactory, since it has been impossible to determine their molecular weights. It has, however, been possible to demonstrate that an analogous beryllium compound, $BeB_2H_8{\cdot}N(CH_3)_3$[6] is homogeneous and this fact, together with the data presented in the experimental part of this paper, strongly supports the opinion that at least the etherate and the trimethylamminate are definite compounds.

The third property referred to is the reaction of AlB_3H_{12} with an *excess* of trimethylamine, as a result of which borine trimethylammine is obtained. The reaction appears to be very complex, leading to a number of products (aside from borine trimethylammine) which have similar degrees of volatility, and are very difficult to separate and identify. But the production of borine trimethylammine is in itself of sufficient interest to warrant the inclusion of these experiments in the present paper even though the reaction has not yet been fully elucidated.

The compound $LiBH_4$ has the properties of a polar compound containing the BH_4 group or ion[4]; its direct formation from the aluminum compound, therefore, suggests for the latter a structure roughly represented by the formula $Al(BH_4)_3$. Such a structure is also in accordance with the ability of the compound to add one molecule of dimethyl ether or of trimethylamine, thus producing molecules in which the coördination num-

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[1] The subject matter of this paper is taken almost wholly from a dissertation submitted by R. Thomas Sanderson to the Faculty of the Division of the Physical Sciences of the University of Chicago in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Schlesinger, Sanderson and Burg, THIS JOURNAL, **61**, 536 (1939).

[3] Schlesinger and Walker, *ibid.*, **57**, 622 (1935).

[4] Schlesinger and Brown, *ibid.*, **62**, 3429 (1940).

[5] Burg and Schlesinger, *ibid.*, **59**, 780 (1937).

[6] Burg and Schlesinger, *ibid.*, **62**, 3425 (1940).

ber of aluminum is four. Furthermore, such a formula is in agreement with a study of the electron diffraction of the compound, the results of which were kindly communicated to us by Dr. J. Y. Beach and Dr. S. H. Bauer.[6a]

On the other hand, the relatively low melting and boiling points of the compound, and its relatively high vapor tension at 0°, are not consistent with the assumption of a high degree of polarity. Furthermore, the facts that it closely resembles diborane in its chemical behavior and that it gives borine trimethylammine, $BH_3 \cdot N(CH_3)_3$, are more suggestive of the presence of BH_3 groups than of BH_4 groups or ions.

As will be discussed in more detail in the third paper of this series, the most satisfactory way to reconcile these contradictory properties and to interpret the structure of the compound is to assume that it contains three BH_4 groups. These are, however, to be considered so extensively distorted by the small, highly charged aluminum ion, that ionic character of the molecule has largely, if not completely, been lost, and that, under appropriate conditions, the BH_4 group readily breaks down into a BH_3 group.

Although AlB_3H_{12} is not to be thought of as a salt, nor indeed as a compound of a high degree of polarity, its probable structure has led us to adopt the name aluminum borohydride, and to use the corresponding nomenclature for the beryllium and lithium compounds.

The fact that excess of trimethylamine extracts BH_3 groups in the form of their trimethylamine complex from the aluminum compound, led us to attempt to remove all of the boron from the compound and thus to prepare aluminum hydride or its trimethylamine complex. Direct experiments produced inseparable mixtures of several products. An indirect mode of attack in which the ammoniate was treated with trimethylamine led to the removal of 93% of the boron, but some loss of hydrogen occurred. Although no pure end-products have been obtained, there is some indication that a substance of the composition $(AlH_2N)_x$ is an intermediate product. This might possibly be an analog of the ring compound triborine triamine, $B_3N_3H_6$.

Experimental Part

Apparatus and Technique.—The vacuum apparatus and technical methods required for this investigation have been described by Stock[7] and in papers by Schlesinger and his collaborators.[8]

Preparation of Aluminum Borohydride.—About 10 millimoles of trimethylaluminum[9] was heated a few hours at 60° with a total of 13.39 millimoles of diborane in successive portions of about 2.2 millimoles each. After reaction of each portion, products volatile at −95° were removed, before addition of the next portion of diborane. The final products were chiefly about 6.7 millimoles of trimethylboron (probably mixed with smaller portions of methyldiboranes[10]) and 5.354 millimoles of the new compound, trapped at −95°, but slowly volatile at −80°.

The compound so prepared was purified readily by repeated distillation at −80°, through a trap cooled to −95°. All fractions had the same vapor tension, namely, 119.5 mm. at 0°.

The only non-volatile product of this reaction was a glassy liquid, which gave off 0.009 millimole of the new compound in twenty hours at 25°. After contact with 2.744 millimoles of nearly pure diborane for three days at ordinary temperature, the liquid had changed to solid, having taken up 0.143 millimole of diborane and having evolved 0.080 millimole of the new compound. The solid did not react further with diborane in six hours of heating from 40 to 60°.

The reaction of diborane with trimethylaluminum is not confined to the dimeric form of the latter, for reaction occurs also with the ethyl etherate, $Al(CH_3)_3 \cdot O(C_2H_5)_2$. As in the reaction with $Al_2(CH_3)_6$, trimethylboron is produced; the other products were not identified.

Several experiments were tried in which smaller proportions of diborane were allowed to react with trimethylaluminum. The reaction products were complex mixtures of as yet unknown compounds. While the new compound here considered may have been present among them, it is doubtful whether a practical separation from some of the other substances could have been effected, because there seemed to be several compounds of very closely similar volatility.

Determination of Formula.—The composition of aluminum borohydride was established by the results of hydrolysis and confirmed by the study of the reaction with hydrogen chloride.

Several samples of the compound (measured as a gas) were treated with an excess of water.[11] The reaction proceeds in accordance with the equation

$$AlB_3H_{12} + 12H_2O \longrightarrow 12H_2 + 3H_3BO_3 + Al(OH)_3$$

The hydrogen evolved was removed by means of a Töpler

[6a] Beach and Bauer, THIS JOURNAL, **62**, 3440 (1940).

[7] Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933; *Ber.*, **54A**, 142 (1921).

[8] Schlesinger and Walker, THIS JOURNAL, **57**, 622 (1935); Burg, *ibid.*, **56**, 499 (1934); Burg and Schlesinger, *ibid.*, **59**, 780 (1937).

[9] Trimethylaluminum, $Al_2(CH_3)_6$, was prepared from aluminum and dimethylmercury (Buckton and Odling, *Ann. Spl.*, **4**, 109 (1865)) and purified by distillation *in vacuo*. Its melting point was 15°. The melting point given by Buckton and Odling, as well as by Quincke (*Z. physik. Chem.*, **3**, 164 (1889)), as "about 0°" seems to be an error.

[10] For methyldiboranes see Schlesinger and Walker, *loc. cit.*

[11] Aluminum borohydride reacts instantly with the minute traces of water present on the inner walls of an evacuated apparatus. It also attacks the stopcock grease. It is important, therefore, that the apparatus used in working with the compound be thoroughly dried by heating it in high vacuum and that no stopcocks be present.

pump and measured in a gasometer; its identity was checked by combustion. Boric acid was distilled from the hydrolysis products as methyl borate,[12] converted back to boric acid, and titrated in the usual manner with barium hydroxide in the presence of mannitol. The aluminum hydroxide was dissolved in dilute hydrochloric acid, and subsequently precipitated and weighed as the 8-hydroxyquinolinate, $Al(C_9H_6ON)_3$.[13]

The analysis yielded the following result: 0.201 millimole of the compound produced 2.39 millimoles hydrogen and 0.199 millimole aluminum 8-hydroxyquinolinate; another sample (0.141 millimole) yielded 0.450 millimole boric acid. Calculated for AlB_3H_{12} is 2.41, 0.201 and 0.423, respectively.

The formula of the new compound was established definitely as AlB_3H_{12} by measurement of its **molecular weight.** The average of three determinations by vapor density measurements was 71.4 (71.7, 71.0, 71.5); the calculated value is 71.5.

Physical Properties of Aluminum Borohydride.—Aluminum borohydride seems to be a normal liquid: the plot of vapor tension data as log P *versus* $1/T$ gives a straight line, represented by the equation: $\log P = 7.808 - (1565/T)$.

The average heat of vaporization, calculated from these data, is 7160 calories per mole, and the Trouton constant, 22.5.

TABLE OF VAPOR TENSION DATA

T, °C.	P(obsd.)	P(calcd.)	T, °C.	P(obsd.)	P(calcd.)
−41.9	11.0	10.9	0°	119.5	119.5
−34.1	18.0	18.2	7.6	171.0	171.0
−28.5	25.3	25.7	9.9	190.0	189.7
−18.4	46.1	46.1	11.5	203.0	203.7
−11.9	65.5	65.5	13.5	220.0	222.8
− 8.4	80.0	79.1	14.1	226.0	228.6
− 4.7	95.0	94.8	16.9	257.0	258.2
− 2.0	108.6	108.4			

The melting point, −64.5 ± 0.5°, was determined as the average of three readings: −65.0, −64.2 and −64.7; the observed melting range was about 0.5°.

Reaction with Hydrogen Chloride.—The reaction takes place readily at −80°, according to the equation

$$2AlB_3H_{12} + 6HCl \longrightarrow 6H_2 + 3B_2H_6 + Al_2Cl_6$$

Secondary to the main reaction, the following seems to take place to a slight extent

$$B_2H_6 + HCl \longrightarrow H_2 + B_2H_5Cl$$

The total hydrogen, therefore, was obtained as the sum of hydrogen formed by the hydrogen chloride reaction plus that formed by subsequent hydrolysis of the mixture of diborane and chlorodiborane. Titration of the hydrolysis product gave the boron as boric acid. The final results show that 0.236 millimole of aluminum borohydride yielded 2.851 millimoles of hydrogen and 0.705 millimole of boric acid (theoretical: 2.832 and 0.708, respectively).

Pyrolysis.—A thorough investigation of the thermal decomposition of the borohydride has not yet been made. Elevation of temperature causes the evolution of hydrogen and ultimately the formation of a mixture of dark metallic crystals (possibly AlB_2) and an amorphous black solid which reacts with water to liberate hydrogen.

Reaction with Dimethyl Ether.—A slightly volatile liquid of empirical formula $AlB_3H_{12}{\cdot}O(CH_3)_2$ is formed rapidly by interaction at 25° of equimolar quantities (*e. g.*, 0.705 millimole) of dimethyl ether and the borohydride. The reaction proceeds equally well at much lower temperatures, for example, −80°. The product does not react further with an excess of ether. At room temperature the vapor tension is only about 0.5 mm., at 67° it is 3.2 mm. and at 85°, 7.5 mm. At temperatures as low as 50° slow decomposition takes place, resulting in the formation of methane and other as yet unidentified products. Because of these reactions it was impossible to determine the vapor density of the pure compound.

Reaction of Aluminum Borohydride with Trimethylamine.—Since this study is not yet completed, the observations thus far made will be reported very briefly.

A. What appears to be the white crystalline compound, $AlB_3H_{12}{\cdot}N(CH_3)_3$ (m. p. 79°), is formed when equimolecular quantities of aluminum borohydride (*e. g.*, 0.991 millimole) and of trimethylamine react at −80°. The solid, although only very slightly volatile at 25°, can be sublimed readily *in vacuo*. It was impossible, however, to determine whether the vapor is homogeneous; at room temperature, the vapor tension of the compound is too low for precise work, whereas at temperatures near 100° the vapor is at least partially dissociated, a reaction which is apparently reversible. One of the dissociation products is borine trimethylammine, the other is an oily liquid which may be AlB_2H_9, but which has not yet been obtained in pure condition.

B. When aluminum borohydride was treated with a large excess of trimethylamine (ratios approximately 1:5.5 and 1:6.5 moles in two experiments) at −80°, and the unchanged trimethylamine was distilled away from the reaction product at the same temperature, approximately 3 moles (2.98 moles in one and 3.16 moles in the second experiment) were retained per mole of aluminum compound. As the product was slowly warmed to room temperatures, it separated into a mixture of a crystalline solid and a liquid.

From this mixture, borine trimethylammine is removed by continued evacuation at room temperature, but there is also a loss of trimethylamine. For example, in one experiment 0.742 mole of trimethylamine and 1.225 moles of borine trimethylammine were removed per mole of aluminum compound originally used. If, however, the removal of borine trimethylammine is carried out in a stream of trimethylamine, approximately 1 mole (more precisely 0.85 mole) of the former is given up.[14] The reaction is very complex. There is evidence that with the borine trimethylammine there escapes a slightly more volatile substance, solid at ordinary temperature, which decomposes into trimethylamine and an oily liquid, too involatile to investigate in the vacuum apparatus. These substances may be $(AlB_2H_9)_x$, the non-volatile liquid, and $AlB_2H_9{\cdot}N(CH_3)_3$, the slightly volatile solid capable of losing tri-

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[12] Gooch, *Am. Chem. J.*, **9**, 23 (1887); and others.

[13] Lundell and Knowles, *Bur. Standards J. Research*, **3**, 92 (1929).

[14] The removal of the last traces of borine trimethylammine is very slow and difficult. It is to be noted that a small loss of hydrogen also occurred.

methylamine. In this connection, it is interesting to note that when a reaction between 3 moles of trimethylamine per mole of aluminum borohydride is carried out in a sealed tube (thus avoiding loss of the amine) there is obtained a product which absorbs nearly 1 mole (0.925) of diborane. Such a result could be explained by the reaction

$$AlB_2H_9{\cdot}N(CH_3)_3 + B_2H_6 \longrightarrow AlB_3H_{12} + BH_3{\cdot}N(CH_3)_3$$

Other interpretations are, however, possible; the data are not yet adequate for a definite conclusion.[15]

Reaction of Aluminum Borohydride with Ammonia.—A mixture of 0.705 millimole of pure AlB_3H_{12} and 0.709 millimole of pure ammonia were condensed together in a tube, which was sealed and kept for fourteen hours at −80°. The mixture then consisted partly of clear crystals, like those observed as a final product, and partly of amorphous white solid. After half an hour at 0°, the crystals had disappeared entirely, leaving only the amorphous white solid, with some vapor, which underwent no noticeable change in three hours more at 0°.

The tube was then warmed to 25°. After one hour, the solid appeared somewhat moist, and after two hours drops of liquid, from which the colorless, bar-shaped crystals were beginning to form, were visible on the tube walls. After twenty hours at 25°, the material was all crystalline.

At the same time secondary reactions produced a small amount of volatile material: 0.031 millimole of hydrogen and 0.053 millimole of diborane (tentatively identified as such by the ratio of boric acid to hydrogen formed upon hydrolysis).

Three more moles of ammonia could be taken up by the crystalline material mentioned above, but the reaction appeared to be complex and was not studied further.

Reaction of aluminum borohydride with trimethylaluminum forms trimethylboron and other volatile products, as yet unidentified because they are very difficult to separate by fractional distillation. This observation explains the difficulties encountered in isolating the pure borohydride from the products of interaction of trimethylaluminum and diborane, unless an excess of the latter is used.

Other Reactions.—All of the following experiments were carried out with the purpose of preparing a compound of the type $AlH_3{\cdot}X$ ($X = N(CH_3)_3$ or NH_3) as mentioned in the introduction. Since none of them led to the desired result, they are but briefly recounted.[16]

A. Trimethylamine completely liberates dimethyl ether from the etherate $AlB_3H_{12}{\cdot}O(CH_3)_2$, and leaves behind a mixture of liquid and solid material like that obtained by interaction of aluminum borohydride and an excess of trimethylamine.

B. Treatment of the compound $AlB_3H_{12}{\cdot}N(CH_3)_3$ with an excess of ammonia, first at −80° and then at −16°, results in the formation of trimethylamine, borine trimethylammine and an unidentified non-volatile residue from which hydrogen was slowly evolved. Only about one-sixth of the boron was removed from the material by this procedure.

C. The reaction between trimethylamine and the material of the composition $AlB_3H_{12}{\cdot}NH_3$ removed a larger percentage of the borine from the borohydride than any other procedure. Thus a mixture of 2.093 millimoles of trimethylamine and 0.705 millimole of the "ammoniate" was kept in a sealed tube for two and one-half hours at −80° and for an hour longer at 0°, in darkness to decrease the rate of hydrogen evolution. During this time 1.254 millimoles of hydrogen were evolved. After another hour at room temperature an additional 0.062 millimole of hydrogen, together with borine trimethylammine and trimethylamine, were obtained. At this point the amount of hydrogen evolved corresponded to within 9% of 2 moles per mole of aluminum compound. But 2 moles of hydrogen is the quantity to be expected if the reaction produces borine trimethylammine and the compound $(AlNH_2)_x$, as mentioned in the introduction. The evidence is, however, far from convincing, since not all of the boron had been removed from the residue. Further treatment with additional trimethylamine led to the removal of additional borine trimethylammine, but also to further loss of hydrogen. Finally, heating of the residue to 500° brought the amount of hydrogen liberated to that expected if decomposition into aluminum nitride had been complete.

Summary

1. The preparation and some of the physical and chemical properties of the new compound, aluminum borohydride, AlB_3H_{12}, are described. It is shown to react vigorously with oxygen, water, and hydrogen chloride, much as does diborane.

2. One mole of dimethyl ether, as well as one mole of trimethylamine, form "addition products" with one mole of the compound. When these compounds are warmed, complex reactions occur, since the original constituents are not regenerated. The reaction between ammonia and the borohydride leads to a product of the empirical formula $AlB_3H_{12}{\cdot}NH_3$ but the reaction seems to be complex.

3. The reaction of aluminum borohydride with an excess of trimethylamine has been studied at various temperatures under varying conditions. Warming the reaction product to 25° *in vacuo* results in the liberation of trimethylamine and of borine trimethylammine. The reaction is discussed both from the point of view of the possible nature of the resulting aluminum compound and in terms of its bearing on the structure of the borohydride.

4. Unsuccessful attempts to prepare aluminum hydride or addition products of this substance are described.

5. To complete the description of the chemical

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(15) For results in experiments in which the reactions were carried out at higher temperatures or with different proportions of the two reactants the original thesis must be consulted. One additional fact may be briefly mentioned: if an excess of the amine is allowed to react with the borohydride at 25° (instead of −80°) 4 moles of the former (instead of 3) are retained per mole of the latter. The product, as in the cases described in the text, is a mixture of solid and liquid products.

(16) For details, consult the original thesis.

behavior of aluminum borohydride, its reaction with ethyllithium to form lithium borohydride, $LiBH_4$, is mentioned, as is also the existence of the beryllium borohydride, BeB_2H_8, although detailed discussion of these substances is deferred to papers about to be published.

6. The possible structure of aluminum borohydride is discussed in preliminary fashion in the light of the facts presented. More detailed discussion of this matter is likewise deferred to the later papers to which reference has been made.

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Metallo Borohydrides. II. Beryllium Borohydride

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The similarity between aluminum and beryllium suggests that diborane, which reacts with trimethylaluminum to produce aluminum borohydride, AlB_3H_{12}, might behave in similar fashion toward dimethylberyllium. Not only does the reaction in question actually lead to the formation of a stable compound of molecular formula BeB_2H_8, but it proceeds in such a way that it is possible to recognize the existence of intermediate steps and to isolate by-products which are of importance in elucidating the chemical character of these metallo borohydrides.

The first product of the reaction between diborane and dimethylberyllium is a glassy material rich in methyl groups. The next stage is a non-volatile, mobile liquid. Further treatment with diborane leads to an unstable, easily sublimable solid which has a composition approximating the formula CH_3BeBH_4. This material reacts vigorously with additional diborane to give the volatile final product BeB_2H_8 and a small amount of a non-volatile by-product which appears to be $(BeBH_5)_x$. In addition to these substances, boron trimethyl or methyl derivatives of diborane (or both) are obtained.

One might represent the series of reactions by the scheme

$$[Be(CH_3)_2]_x \xrightarrow{B_2H_6} (CH_3)BeBH_4 \xrightarrow{B_2H_6} HBeBH_4 \xrightarrow{B_2H_6} (BH_4)Be(BH_4)$$

This scheme, however, is merely a summary of products obtained, and is not intended to suggest either a mechanism of the reaction or structures of the compounds involved.

The final product of the reaction, beryllium borohydride, BeB_2H_8, exhibits many properties which indicate its close relationship to aluminum borohydride. Like the latter, the beryllium compound inflames violently in air and reacts vigorously with water. Its reaction with hydrogen chloride, to give hydrogen, diborane, and beryllium chloride, is rapid even at −80°, and was found useful for analytical purposes. In physical properties it differs more decidedly from the aluminum compound; although both are readily vaporized at room temperatures, the beryllium compound is less volatile than the aluminum compound and its melting point is at least 180° higher. These differences suggest that the beryllium compound may be more highly polar in character than the aluminum compound. It should be mentioned also that the beryllium compound may be obtained as an unstable glass by rapid condensation at low temperatures. Possibly the crystalline variety of high melting point may represent a polymeric modification.

Of particular interest is the reaction of BeB_2H_8 with trimethylamine. In this respect also the beryllium compound shows marked similarity with the aluminum analog, except that the results with beryllium borohydride are more clearly interpretable. At −80° beryllium borohydride reacts with trimethylamine to form the relatively stable substance, $BeB_2H_8 \cdot N(CH_3)_3$. Although the substance begins to decompose irreversibly at 140°, it is sufficiently volatile that its purity can be demonstrated by measurement of its vapor tensions in the range 65–140°, and that its molecular weight can be confirmed by a determination of its vapor density.

On heating it to 100° with trimethylamine (present in excess) the compound $BeB_2H_8 \cdot N(CH_3)_3$ reacts further, yielding borine trimethylamine, $BH_3N(CH_3)_3$, and the compound $BeBH_5 \cdot N(CH_3)_3$. The latter is a solid which loses trimethylamine reversibly. It was not possible, however, to re-

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