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Dr. Sheldon G. Shore

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13. ABSTRACT (Maximum 200 words)
The synthesis of B₁₀H₁₄ from B₅H₉ was modified to facilitate large scale production. Reductions of boranes by alkali and lanthanide metals were studied. Depending upon reaction conditions chosen, the anions [BH₃]²⁻, [B₂H₆]²⁻, and [B₃H₈]⁻ were produced. A simple procedure was developed for the preparation of the solvent free salts M[B₃H₈] (M = K, Rb, Cs). Borohydrides of the divalent lanthanides Yb, Eu were synthesized, structurally characterized, and then converted to lanthanide borides, YbB₄ and EuB₆. New procedures for the preparation of high purity boron nitride as powders and coatings were developed. An essentially instantaneous reaction between B₃N₃H₃Cl₃ and Cs can be initiated at temperatures as low as 135 °C to produce very finely divided amorphous boron nitride. The amorphous BN is converted to the turbostratic form by heating it at 1100 °C. H₃NBH₂Cl in solution form can be applied to a surface. Heating to 1100 °C in vacuum produces a coating of turbostratic BN.

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DERIVATIVES OF BORANES, POSSIBLE METAL BORIDE AND BORON NITRIDE PRECURSORS

Final Report

For the Period

August 1, 1988 - July 31, 1991

Dr. Sheldon G. Shore

September 27, 1991



**U. S. ARMY RESEARCH OFFICE
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FORWARD

The period in which this grant was in effect was one of transition in this laboratory. The focus of our program shifted from investigations of boron hydrides to a more general one that also encompasses investigations of boron nitrogen and lanthanide boron containing materials. While continuing with boron hydride syntheses, significant progress was made in these newer areas.

Our studies equally emphasize new, novel chemistry; efficient synthetic procedures adaptable to scale-up; and practical applications of results. Our earlier work under ARO support led to the syntheses of high purity electronics grade diboranes,^{1a} B_2H_6 and B_2D_6 , which are now commercially produced by the Voltaix Company. High purity deuterated diborane is receiving very favorable attention for applications in plasma fusion reactors. We also developed a number of practical syntheses of higher boranes,^{1b-8} including $B_{10}H_{14}$, using B_5H_9 as a feed stock, thus enabling the conversion of surplus B_5H_9 in U.S. Government stockpiles (ca. 200,000 lbs) to more useful materials.

During our present grant period we modified our procedure for the conversion of B_5H_9 to $B_{10}H_{14}$ in order to make it more convenient for large scale production. No longer commercially produced in the United States, $B_{10}H_{14}$ is in short supply. Strem Chemical Company has been able to duplicate our procedure and is currently working out details for production in kilo quantities. The Transbas Company is also interested in our procedure. Other examples of technology developed in this laboratory, during the period of this grant, are our preparations of high purity boron nitride powders³⁸ and coatings.³⁹ These procedures are presently under consideration by Union Carbide Corporation, Advanced Ceramics Division.

Our research activities are summarized in the following sections which are listed in the Table of Contents. Each section contains a preamble which provides a statement of the problem studied.

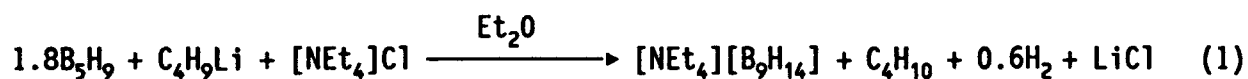
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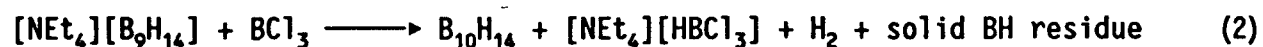
I. MODIFIED SYNTHESSES OF $[B_9H_{14}]^-$ SUITABLE FOR LARGE SCALE PRODUCTION OF $B_{10}H_{14}$

In earlier grants under ARO support we demonstrated that B_5H_9 ^{1b-4} can be successfully employed in close to quantitative preparation of either $[B_9H_{14}]^-$ or $[B_{11}H_{14}]^-$, depending upon the conditions chosen. We were able to convert these anions to $B_{10}H_{14}$ and a number of higher boron hydride derivatives. Thus the B_5H_9 presently in U.S. Government storage can be converted to potentially useful materials.

With the present shortage of $B_{10}H_{14}$ due to the absence of commercial production in the U.S., we developed a modification of our earlier synthesis of $[B_9H_{14}]^-$ that would be more suitable for large scale production of this anion, which in turn would facilitate large scale production of $B_{10}H_{14}$. In our earlier work we generated $[B_9H_{14}]^-$ by deprotonating B_5H_9 with NaH in the presence of $[NEt_4]Cl$ in THF. However, it is impractical to use NaH on a large scale since it must first be removed from its protective oil packing and then cleaned. We were able to substitute butyl lithium for NaH as the deprotonating agent as shown in Equation (1). The synthesis of $B_{10}H_{14}$ from $[B_9H_{14}]^-$ in about 60% yield was achieved



according to our usual procedure as indicated by Equation (2).



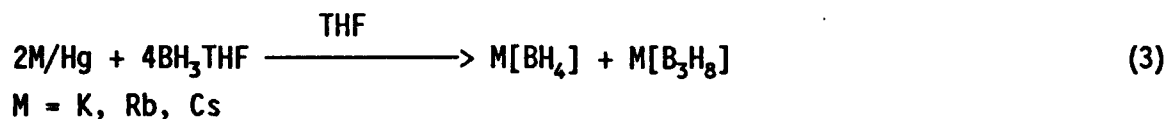
The Strem Chemical Company has repeated our modified procedure and is scaling it up with a view to commercial production. The Transbas Company of Billings, Montana is also interested in our procedure. The modified synthesis of $[B_9H_{14}]^-$ can also lead to the scaled up syntheses of higher borane derivatives that we have prepared from this anion.^{1b-8}

II. FORMATION OF SOLVENT FREE ALKALI METAL (K, Rb, Cs) SALTS OF $[B_3H_8]^-$

Applications of the octahydrotriborate(1-) ion, $[B_3H_8]^-$, include: explosive and propellant technology;⁹ preparation of electrode coatings¹⁰; neutron capture therapy;¹¹ serum triglyceride and serum cholesterol biological studies;¹² syntheses of metallaboranes,¹³ higher borane¹⁴ heteroatom boranes¹⁵ and carborane cluster compounds;¹⁶ and reduction of a number of organic compounds.¹⁷

Prior to our work, no *simple* route to solvent free alkali metal salts of $[B_3H_8]^-$ was reported. $Na[B_3H_8]$ is highly solvated by ether,¹⁸ making it difficult to accurately measure amounts of this salt to be used for chemical reactions. It is generally converted to more tractable alkylammonium,^{19,20} alkylphosphonium,²¹ other alkali metal¹⁹ or thallium^{19b} salts by metathesis reactions.

We obtained the salts $M[B_3H_8]$ ($M = K, Rb, Cs$) through the reduction of BH_3THF by alkali metal amalgams.²² This procedure provides a solvent free



product, and provides simpler routes to these salts than previously described.¹⁹ Furthermore, for most, if not all applications, $Tl[B_3H_8]$ can be replaced by one of the alkali metal $[B_3H_8]^-$ salts described here. $Tl[B_3H_8]$ is a useful material in the preparation of derivatives of $[B_3H_8]^-$ through metathesis reactions,¹⁹ but because of the toxicity of thallium,²³ this salt presents a hazard.

In the present grant period we took advantage of our synthesis of solvent free $K[B_3H_8]$ by simplifying our procedure for the synthesis of B_4H_{10} by substituting $K[B_3H_8]$ ²² for $[NEt_4][B_3H_8]$ (Equation (4)). Our earlier procedure³

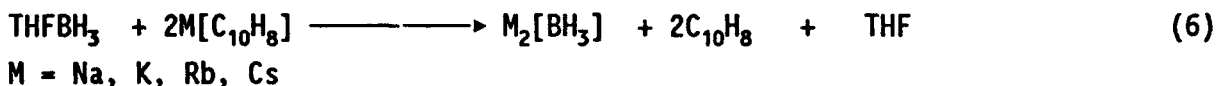
$$K[B_3H_8] + BCl_3 \longrightarrow B_4H_{10} + K[HBCl_3] + \text{solid BH residue} \quad (4)$$

required the preparation of $[NEt_4][B_3H_8]$ from $Na[B_3H_8]$ because Equation (4) is not

effective with $\text{Na}[\text{B}_3\text{H}_8]$ due to retained ether interfering with the desired reaction between the $[\text{B}_3\text{H}_8]^-$ anion and the boron halide. Prior to this reaction, solvent free alkali metal salts of $[\text{B}_3\text{H}_8]^-$ required multi-step procedures.¹⁹

III. FORMATION OF $[\text{BH}_3]^{2-}$ AND $[\text{B}_2\text{H}_6]^{2-}$

In the preceding grant period we showed that the homogeneous reduction of BH_3THF by an alkali metal, in the presence of naphthalene as an electron carrier, can produce $[\text{BH}_3]^{2-}$, the analogue of the carbanion $[\text{CH}_3]^-$. This is in contrast to the synthesis of $[\text{B}_3\text{H}_8]^-$ described above which is a heterogeneous reaction involving alkali metal amalgams. In the present grant period studies of the homogeneous reduction reaction were continued. Addition of BH_3THF to $[\text{BH}_3]^{2-}$ gives $[\text{B}_2\text{H}_6]^{2-}$, the analogue of C_2H_6 . The $[\text{B}_2\text{H}_6]^{2-}$ dianion is converted to $[\text{B}_3\text{H}_8]^-$ and $[\text{BH}_4]^-$ upon addition of two moles of BH_3THF . The following reaction sequence was studied. The anions produced in these reactions are stable in the absence of air.



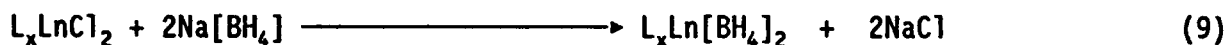
IV. LANTHANIDE-BORANE COMPLEXES AS PRECURSORS TO LANTHANIDE BORIDES

Borides of the lanthanides, transition metals, and actinides are extremely hard, wear resistant materials that can possess desirable magnetic, electronic, thermal, and mechanical properties.²⁴ During the present grant period we studied borane derivatives of divalent lanthanides that are potential precursors to lanthanide borides. We produced new materials and demonstrated that several of them are readily converted to lanthanide borides and coatings. Described below

is a summary of our work.

A. Syntheses of Borohydride Complexes of Eu(II) and Yb(II)

We find²⁵ that CH_3CN and $\text{C}_5\text{H}_5\text{N}$ are exceptionally good ligands for promoting formation of complexes of Ln(II) with boron hydride anions. A series of Eu(II) and Yb(II) borohydride complexes were synthesized, isolated, and characterized: $(\text{CH}_3\text{CN})_4\text{Yb}[(\mu\text{-H})_3\text{BH}]_2$, $(\text{C}_5\text{H}_5\text{N})_4\text{Yb}[\text{BH}_4]_2$, $(\text{CH}_3\text{CN})_2\text{Eu}[\text{BH}_4]_2$, and $(\text{C}_5\text{H}_5\text{N})_{1.8}\text{Eu}[\text{BH}_4]_2$. Equation (9) represents the general reaction employed. Not only are coordination



Ln = Eu, Yb; L = CH_3CN , $\text{C}_5\text{H}_5\text{N}$

geometries of the metals of interest, but these complexes also serve as precursors to the formation of lanthanide borides (see section IV.C.).

Figure 1 shows structures of $(\text{CH}_3\text{CN})_4\text{Yb}[(\mu\text{-H})_3\text{BH}]_2$ and $(\text{C}_5\text{H}_5\text{N})_4\text{Yb}[\text{BH}_4]_2$.

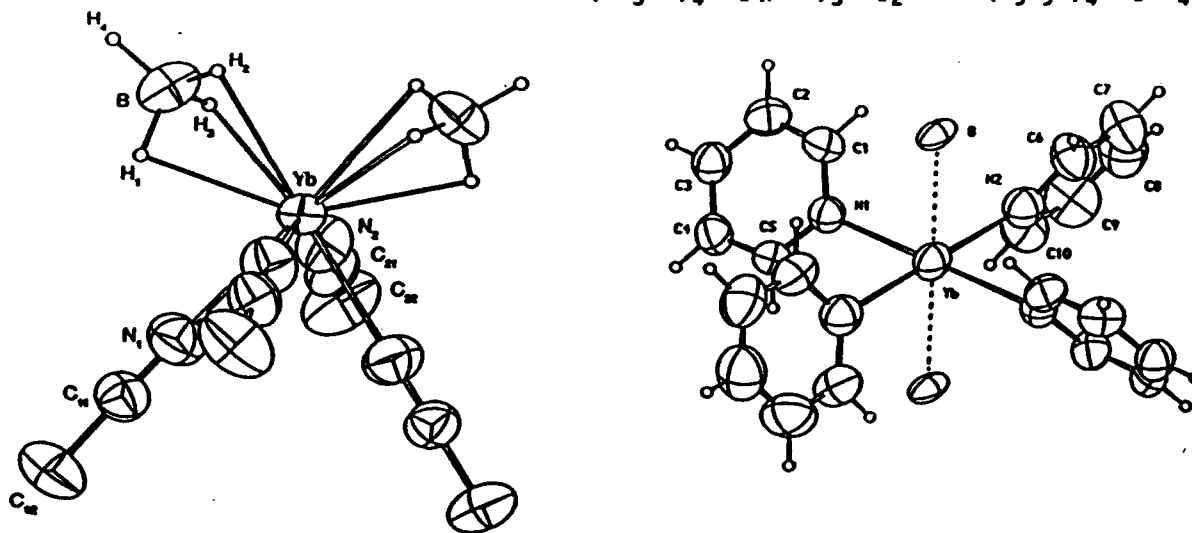


Figure 1. Molecular structures of $(\text{CH}_3\text{CN})_4\text{Yb}[(\mu\text{-H})_3\text{BH}]_2$ and $(\text{C}_5\text{H}_5\text{N})_4\text{Yb}[\text{BH}_4]_2$.

Each borohydride unit in $(\text{CH}_3\text{CN})_4\text{Yb}[(\mu\text{-H})_3\text{BH}]_2$ is bound to Yb through three Yb-H-B bridges and the four CH_3CN ligands are arranged in a "see-saw" configuration with respect to the central Yb atom.

The structure of $(\text{C}_5\text{H}_5\text{N})_4\text{Yb}[\text{BH}_4]_2$ contains an axially distorted octahedral arrangement of ligands around Yb(II). Borohydride ligands are *trans* to each other

along the elongated axis. Pyridine ligands are arranged in the shape of a "four-bladed propeller". Hydrogens on the borohydride could not be located in the X-ray structure determination; however, the bonding mode of $[\text{BH}_4]^-$ is believed to be the same, η^3 , in this compound as in $(\text{CH}_3\text{CN})_4\text{Yb}[(\mu\text{-H})_3\text{BH}]$ since their Yb-B distances agree within 0.026(11) Å. Different hapticity of the borohydride ligand is expected to cause a significant difference in metal-boron distances.²⁶

B. Reduction of Decaborane(14) by Lanthanide-Ammonia Solutions

We found^{25b} that liquid NH_3 solutions of Eu and Yb, like liquid NH_3 solutions of Na^{27} , reduce $\text{B}_{10}\text{H}_{14}$ to $[\text{B}_{10}\text{H}_{14}]^{2-}$. The decaborate complexes $(\text{NH}_3)_3\text{Yb}[\text{B}_{10}\text{H}_{14}]$, $(\text{CH}_3\text{CN})_6\text{Yb}[\text{B}_{10}\text{H}_{14}]$, $[(\text{CH}_3\text{CN})_x\text{Yb}][\text{B}_{10}\text{H}_{13}][\text{B}_{10}\text{H}_{15}]$, $(\text{NH}_3)_x\text{Eu}[\text{B}_{10}\text{H}_{14}]$, $(\text{CH}_3\text{CN})_x\text{Eu}[\text{B}_{10}\text{H}_{14}]$, and $[(\text{CH}_3\text{CN})_x\text{Eu}][\text{B}_{10}\text{H}_{13}][\text{B}_{10}\text{H}_{15}]$ were synthesized from reduction products of $\text{B}_{10}\text{H}_{14}$ in liquid ammonia by the elemental lanthanides. Reduction products in these reactions were ammonia-solvated powders, insoluble in saturated amines and ethers. Components of these solids were extracted with CH_3CN .

The molecular structure of $(\text{CH}_3\text{CN})_6\text{Yb}[\text{B}_{10}\text{H}_{14}]$ is shown in Figure 2. It crystallizes as $(\text{CH}_3\text{CN})_6\text{Yb}[(\mu\text{-H})_2\text{B}_{10}\text{H}_{12}]$ with two additional molecules of CH_3CN

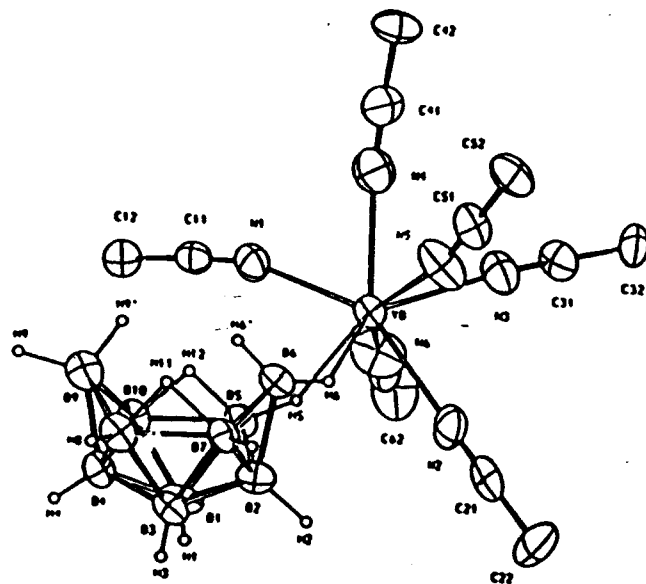


Figure 2. The molecular structure of $(\text{CH}_3\text{CN})_6\text{Yb}[\text{B}_{10}\text{H}_{14}]$.

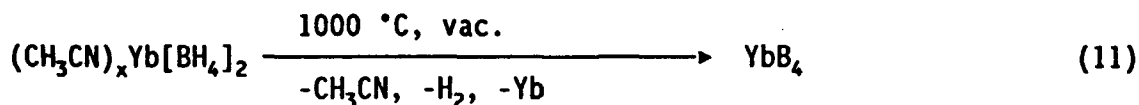
of solvation.^{25b} This X-ray structure confirms the presence of the Yb-H-B bridge bonding inferred from ¹¹B NMR spectra.

C. Formation of Lanthanide Borides.

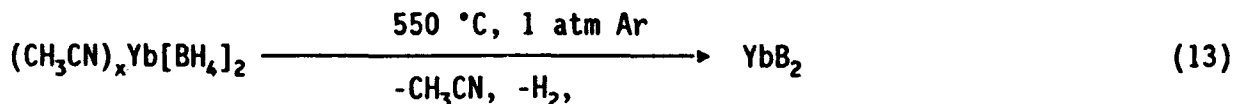
1. Thermal Decomposition of Ln(II) Borohydrides.^{25a} When (CH₃CN)₄Yb[(μ-H)₃BH]₂ and (CH₃CN)₂Eu[BH₄]₂ are heated in vacuum at 200 °C, CH₃CN and H₂ are evolved, but no boron hydride is produced (Equation (10)). IR spectra



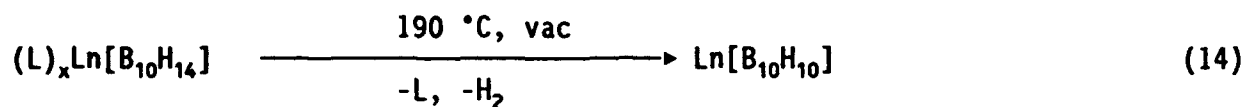
of the resulting solids reveal no ligand stretches. These solids represent an intimate mixture of elemental lanthanide and boron in a precise 1:2 ratio, an ideal starting point for producing a metal boride. Dry solids from the complexes (CH₃CN)₄Yb[(μ-H)₃BH]₂ and (CH₃CN)₂Eu[BH₄]₂ were heated to 1000 °C in a quartz tube maintained at 10⁻⁵ Torr (Equations (11) and (12)). At 100 °C CH₃CN is given off; above 150 °C H₂ evolution occurs; above 450 °C, lanthanide metal sublimes out of both solids.



The resulting materials are shiny-grey solids with a metallic luster. Their X-ray powder patterns revealed YbB₄ and EuB₆ to be the only crystalline phases present. We were able to prepare a crystalline YbB₂ phase by referring to the phase diagram to choose conditions under which YbB₂ is stable (Equation (13)).²⁸



2. Thermal Decomposition of Ln(II) Decaborates. Controlled pyrolyses of $(\text{CH}_3\text{CN})_6\text{Yb}[\text{B}_{10}\text{H}_{14}]$ and $(\text{NH}_3)_x\text{Eu}[\text{B}_{10}\text{H}_{14}]$ in vacuum produces Ln(II) complexes of the *closo*-anion $[\text{B}_{10}\text{H}_{10}]^{2-}$ (Equation (14)).^{27b} These *closo*-complexes



Ln = Eu, Yb L = NH_3 , CH_3CN

are soluble in CH_3CN or $\text{C}_5\text{H}_5\text{N}$. The ^{11}B -NMR spectrum of $\text{Yb}[\text{B}_{10}\text{H}_{10}]$ in $\text{C}_5\text{H}_5\text{N}$ is very similar to that of alkali metal salts of $[\text{B}_{10}\text{H}_{10}]^{2-}$, indicating that this ion is solvent separated in solution. To further investigate the thermal stability of this compound it was heated in a quartz tube. The $\text{Yb}[\text{B}_{10}\text{H}_{10}]$ slowly evolved H_2 from 300-500 $^\circ\text{C}$; no further volatiles were evolved up to 1000 $^\circ\text{C}$. The X-ray powder pattern of the resulting black powder showed it to be YbB_6 . Amorphous B was probably present as well. $\text{M}(\text{B}_{10}\text{H}_{10})_3$ complexes (M = Ce, Gd) have been thermally decomposed at 1000 -1200 $^\circ\text{C}$ to form CeB_6 and GdB_6 and amorphous boron.²⁹

V. New Syntheses of Boron Nitride

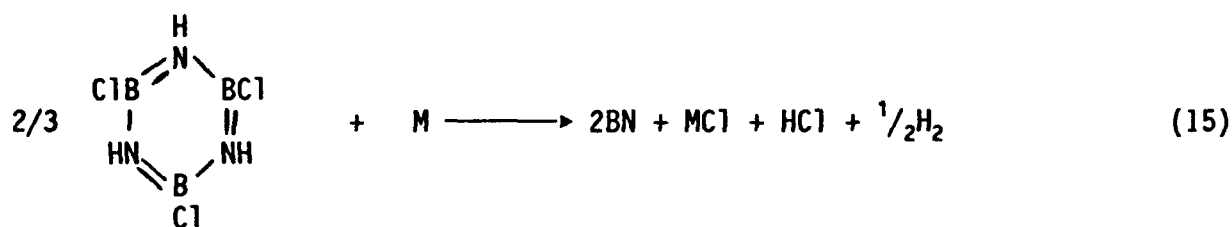
Boron nitride is a well-known ceramic, possessing a number of useful properties.^{30,31} Articles composed (wholly or in part) of BN are finding an increasing number of applications. Consequently there is great interest in finding new and improved methods for its production³¹.

Traditional³¹⁻³³ routes to boron nitride involve high temperature syntheses. A common method for commercial BN production involves carbothermal reduction of boric acid³¹ at temperatures in excess of 1500 $^\circ\text{C}$, under an atmosphere of N_2 . For production of BN thin films of exceptionally high purity, chemical vapor deposition (CVD) is employed^{30,31,34}, with the most widely-used precursors being

BCl_3/NH_3 and $\text{BCl}_3/\text{NH}_3/\text{H}_2$ mixtures. Additionally, there has been much recent interest in polymeric preceramic compounds^{31,35-37}, where the boron and nitrogen-containing polymer may then undergo thermolysis to yield BN. Described are syntheses that provide high purity boron nitride in potentially useful forms.

A. Formation of Boron Nitride from $\text{B}_3\text{Cl}_3\text{N}_3\text{H}_3$

We produced amorphous boron nitride in an unprecedented procedure that involves the reaction of $\text{B}_3\text{Cl}_3\text{N}_3\text{H}_3$ with the alkali metals (Cs, Rb, K) in the absence of a solvent.³⁸ The reaction is initiated at 130 - 160 °C; it is vigorous



(M = Cs, Rb, K)

and virtually instantaneous, proceeding with a flash of light. Effectively hydrogen and chlorine are stripped from the B_3N_3 core to give amorphous BN. Higher temperatures are required in the reactions of $\text{B}_3\text{Cl}_3\text{N}_3\text{H}_3$ with K and Rb than with Cs. This method is the most energy efficient preparation of amorphous boron nitride yet devised. The BN is a very finely divided powder. The amorphous product, after removal of alkali metal halide and unreacted $\text{B}_3\text{Cl}_3\text{N}_3\text{H}_3$, was converted to the turbostratic form of boron nitride upon heating to 1100 °C. The experimental density of the turbostratic BN is 1.7 g/cm³, in good agreement with the accepted value of 1.7-1.8 g/cm³. Chemical analyses and XPS spectra confirm the composition BN. Our present maximum yield of BN is about 60%.

Figure (3) shows the X-ray powder pattern of the amorphous BN after removal of CsCl and unreacted $\text{B}_3\text{Cl}_3\text{N}_3\text{H}_3$, and the powder pattern of turbostratic BN obtained by heating the amorphous BN to 1100 °C. Figure (4) is the infrared

spectrum of turbostratic BN indicating a clean product with no residual OH bonds or BCl bonds.

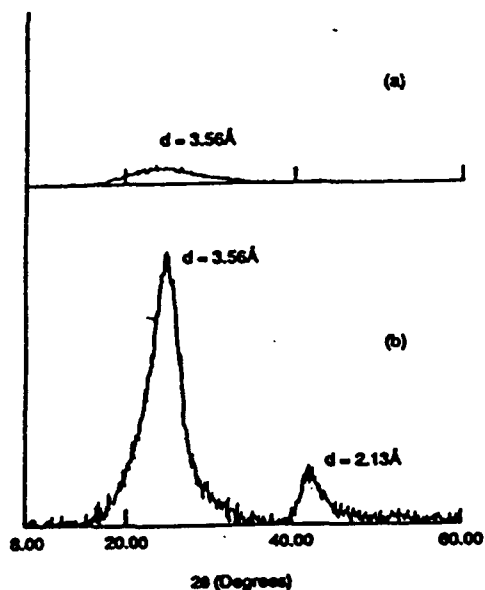


Figure 3. X-ray Powder Patterns:
a) amorphous boron nitride;
b) turbostratic boron nitride.

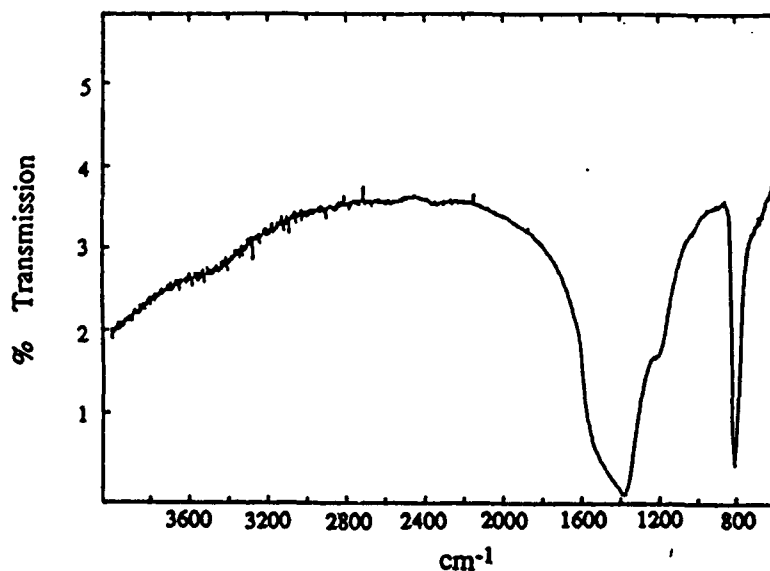
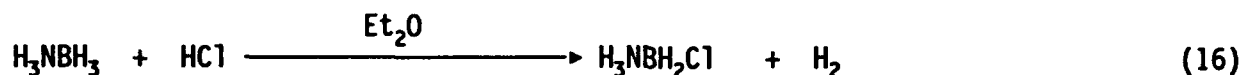


Figure 4. Infrared spectrum of turbostratic boron nitride.

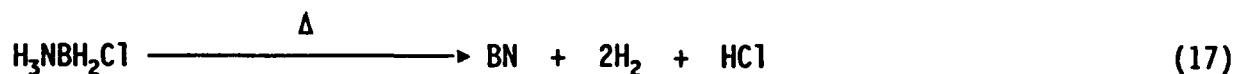
The boron nitride produced need never come in contact with carbon-containing materials, as no solvent is required for the reaction to proceed. Impurities formed in the reaction may be removed by heating and/or washing with water. The main impurity to be removed is the byproduct, CsCl, which is removed by washing with water. It may also be removed by vacuum sublimation at the appropriate temperature (above ca. 600 °C), enabling BN to be prepared which has not been exposed to either water or oxygen. Samples prepared by this procedure are finely divided powders.

B. Formation of Boron Nitride from H_3NBH_2Cl

We prepared H_3NBH_2Cl , a simple molecular precursor for boron nitride coatings, through the following reaction. Thermolysis of H_3NBH_2Cl at 1100 °C



produces turbostratic boron nitride.³⁹ Its X-ray powder pattern and infrared



spectrum are virtually identical to those shown in Figures (3b and 4). Chemical analyses and XPS spectra verify the composition as BN.

Preparation of boron nitride from the thermal decomposition of H_3NBH_2Cl represents a simple, viable approach to forming BN coatings and possibly thin films through a CVD process. Our synthesis of H_3NBH_2Cl is much simpler than syntheses of many other precursors that have been employed to produce BN coatings. Furthermore, an ammonia atmosphere is not required during the firing process. Coatings are formed by dipping the object to be coated into an ethereal solution of H_3NBH_2Cl or by brushing the solution onto the object to be coated. After the solvent has evaporated, firing at 1100 °C produces the turbostratic form of BN. Quartz plates and silicon chips were coated in this manner.

We have found that in the thermal decomposition of H_3NBH_2Cl only H_2 is given off below 80 °C. A sample of H_3NBH_2Cl heated to 60 °C for 7 hours eliminated only H_2 gas. The resulting boron-nitrogen containing product analyzed closely for $B_3N_3Cl_3H_9$. It appears to be principally two linked cycloborazane rings as indicated on the next page.

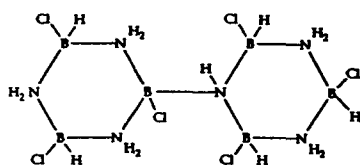


Figure 5. Proposed structure of $B_3N_3Cl_3H_8$.

Treatment of this compound with $LiBH_4$ produces cyclotriborazane, $B_3H_6N_3H_6$. Heating of $B_3N_3Cl_3H_8$ at 88 °C produced additional H_2 but no HCl . At higher temperatures HCl was produced.

We obtained a polymeric boron-nitrogen containing material with a parent mass of about 900 by heating H_3NBH_2Cl in vacuum at a temperature above 150 °C. It is not highly sensitive to moisture and it sublimes in vacuum at elevated temperature. When this material is heated at 1100 °C, BN is formed. This material might be useful for the formation of thin films of BN CVD or for forming films by means of laser ablation.

VI. A New Boron-Nitrogen-Aluminum Complex

We have observed that the reaction between $LiAlH_4$ and H_3NBH_3 in a 1:1 molar ratio in THF produces two moles of hydrogen gas and a salt that is assigned the formula $Li[AlH_2(\mu-NH)(\mu-H)BH_2]$ based on chemical analyses and NMR spectra. The proposed structure of the anion is shown on the next page. The lithium salt is isolated as the thermally stable solid $Li[AlH_2(\mu-NH)(\mu-H)BH_2] \cdot 0.5THF$.

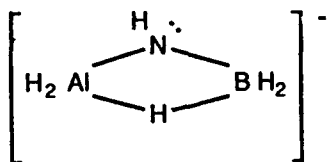


Figure 6. Proposed structure of $[AlH_2(\mu-NH)(\mu-H)BH_2]^-$

VII. Bibliography

1. a) Shore, S. G.; Toft, M. A. U. S. 4,388,284, 1983. b) Shore, S. G.; Toft, M. A.; Himpsl, F. L. U. S. 4,338,289, 1982.
2. Lawrence, S. H.; Wermer, J. R.; Boocock, S. J.; Banks, M. A.; Keller, P. C.; Shore, S. G. *Inorg. Chem.*, 1986, 25, 367.
3. a) Toft, M. A.; Leach, J. B.; Himpsl, F. L.; Shore, S. G. *Inorg. Chem.* 1982, 21, 1952. b) Leach, J. B.; Toft, M. A.; Himpsl, E. L.; Shore, S. G. *J. Am. Chem. Soc.* 1981, 103, 988.
4. Hosmane, N. S.; Wermer, J. R.; Hong, Z.; Getman, T. D.; Shore, S. G. *Inorg. Chem.* 1987, 26, 3638.
5. Getman, T. D.; Krause, J. A. Niedenzu, P. M.; Shore, S. G. *Inorg. Chem.* 1989, 28, 1507.
6. Getman, T. D.; Krause, J. A.; Shore, S. G. *Inorg. Chem.* 1988, 27, 2398.
7. Getman, T. D.; Shore, S. G. *Inorg. Chem.* 1988, 27, 3439.
8. Getman, T. D.; Deng, H.-B.; Hsu, L.-Y.; Shore, S. G. *Inorg. Chem.* 1989, 28, 3612.
9. a) Walker, F. E.; Wasley, R. J. U.S. 4304,614, 1981. b) Capellos, C.; Iyer, S. *NATO Adv. Study Inst. Ser.; Ser. C* 1981, C 71, 401. (c) Walker, F. E.; Wasley, R. J. U.S. 4,196,05, 1980.
10. a) Tamblyn, W. H.; Aquadro, R. E.; Deluca, O. D.; Weingold, D. H.; Dao, T. V. *Tett. Lett.* 1983, 24, 4955. b) Tamblyn, W. H.; Weingold, D. H.; Snell, E. D.; Waltermire, R. E. *Tett. Lett.* 1982, 23, 3337.
11. Komura, M.; Anon, K.; Nagasawa, K.; Sumimoto, S. *Chem. Express* 1987, 2, 173.
12. Hall, I. H.; Brotherton, R. H. U.S. 4,672,060, 1987.

13. a) Gilbert, K. B.; Boocock, S. K.; Shore, *Comprehensive Organometallic Chemistry*, Eds, Wilkinson, G.; Stone, F. G. A.; Abel, E. 1982, Chapt 41.1, and references therein.
14. a) Brellochs, B.; Binder, H. *Z. Naturforsch. B Chem. Sci.* 1988, 43, 648. b) Brellochs, B.; Binder, H. *Angew. Chem.* 1988, 100, 270. c) Wolfer, K.; Hausen, H. D.; Binder, H. *Z. Naturforsch. B Anorg. Chem, Org. Chem.* 1985, 40B, 235. d) Dunks, G. B.; Ordonez, K. D. *Inorg. Chem.* 1978, 17, 1514. e) Ryschkewitsch, G. E.; Miller, V. H. *J. Am. Chem. Soc.* 1975, 97, 6258.
15. a) Gaines, D. F.; Kunz, J. C. *Inorg. Chem.* 1988, 27, 1893. b) Gaines, D. F.; Coons, D. E. *Inorg. Chem.* 1986, 25, 364.
16. a) Hosmane, N. S.; Grimes, R. N. *Inorg. Chem.* 1980, 19, 3482. b) Hosmane, N. S.; Grimes, R. N. *Inorg. Chem.* 1979, 18, 3294.
17. Shevchenko, Y. N.; Fesenko, A. V.; Nazarova, T. M.; Biryukovich, O. K.; Yatsimirskii, K. B.; Ogenko, U. M.; Slesarenko, Y. N.; Naprasnaya, S. V.; Larikov, E. I.; Svitsyn, R. A. *Otkrytiya, Izobret., Prom. Obrazttsy, Tovarnye Zhaki* 1984, (31), 78.
18. Hough, W.V.; Edwards, L.J.; McElroy, A. D. *J. Am. Chem. Soc.* 1956, 78, 689.
19. a) Dewkett, W. J.; Grace, M.; Beall, H. *Inorg. Syn.* 1974, 15, 115. b) Amberger, E.; Gut, E. *Chem. Ber.* 1968, 101, 1200.23.
20. Kodama, G.; Parry, R. W. *J. Am. Chem. Soc.* 1960, 82, 6250.
21. a) Depoy, R. E.; Kodama, G. *Inorg. Chem.* 1988, 27, 1836. b) Toft, M. A.; Leach, J. B.; Himpsl, F. L.; Shore, S. G. *Inorg. Chem.* 1982, 21, 1952.
22. Hill, T. G.; Godfroid, R. A.; White, J. P. III; Shore, S. G. *Inorg. Chem.* 1991, 30, 2952.
23. Browning, E. *Toxicity of Industrial Metals*, 2nd ed., Appleton-Century-Crofts, NY, 1969, pp. 317-322.
24. Matkovich, V. I. Ed. *Boron and Refractory Borides* Springer-Verlag New York, 1977.
25. a) White, J. P. III; Deng, H.-B.; Shore, S. G. *Inorg. Chem.* 1991, 30, 2337. b) White, J. P. III; Deng, H.-B.; Shore, S. G. *J. Am. Chem. Soc.* 1989, 111, 8946.
26. Marks, T. J.; Kolb, J. R. *Chem. Rev.* 1977, 77, 263.
27. Toeniskoetter, R.H. Ph.D. Dissertation, St. Louis University 1958, St. Louis, Mo. (Diss. Abstr. 1959, 20, 879).
28. *Binary Alloy Phase Diagrams* Massalski, T. B., Ed., 1986, American Society for Metals, Vol. 1, 354.

29. Itoh, H.; Tsuzuki, Y.; Yogo, T.; Naka, S. *Mat. Res. Bull.* 1987, 22, 1259.
30. a) Meller, A. *Gmelin Handbuch der Anorganische Chemie, Boron Compounds*, 2nd Suppl. 1983, 1, 304. b) Meller, A. *Gmelin Handbuch der Anorganische Chemie, Boron Compounds*, 3rd Suppl. 1988, 3, 1.
31. Paine, R. T.; Narula, C. K. *Chem. Rev.* 1990, 90, 73 and references therein.
32. O'Connor, T. E. *J. Am. Chem. Soc.* 1962, 84, 1753.
33. Economy, J.; Anderson, R. *Inorg. Chem.* 1966, 5, 989.
34. Singh, R. N. *Proc. Electrochem. Soc.* 1987, 87-88, 543.
35. Fazen, P. J.; Beck, J. S.; Lynch, A. T.; Remsen, E. E.; Sneddon, L. G. *Chem. Mater.* 1990, 2, 96.
36. Narula, C. K.; Lindquist, D. A.; Fan, M.-F.; Borek, T. T.; Duesler, E. N.; Datye, A. K.; Schaeffer, R.; Paine, R. T. *Chem. Mater.* 1990, 2, 377.
37. a) Narula, C. K.; Schaeffer, R.; Datye, A. K.; Borek, T. T.; Rapko, B. M.; Paine, R. T. *Chem. Mater.* 1990, 2, 384. b) Beck, J. S.; Albani, C. R.; McGhie; McGhie, A. R.; Rothman, J. B.; Sneddon, L. G. *Chem. Mater.* 1989, 1, 433.; c) Kazimiera, J. L. Paciorek; Masuda, S. R.; Kratzer, R. H.; Schmidt, W. R. *Chem. Mater.* 1991, 3, 88.
38. Shore, S. G.; Dolan, S. E. U. S. 5,053,365, 1991.
39. Shore, S. G., Niedenzu, P. M.; Degrafenried, A. L. U. S. Pending.

VIII. PUBLICATIONS, PATENTS, DISSERTATIONS

A. Publications

"Synthesis of the New Boron Hydride *nido*-Undecaborane(15), $B_{11}H_{15}$, and the X-Ray Structure of its Conjugate Base Tetradecahydroundecaborate(1-), $[B_{11}H_{14}]^-$ " Getman, T. D.; Krause, J. A.; Shore, S. G. *Inorg. Chem.* 1988, 27, 2398.

" $[B_9H_{13}]^{2-}$ an *arachno*- $[B_nH_{n+4}]^{2-}$ Dianion; Synthesis, Characterization, and Molecular Structure" Getman, T. D.; Krause, J. A.; Niedenzu, P. M.; Shore, S. G. *Inorg. Chem.* 1989, 28, 1507.

"Syntheses of *closo*-Methylphosphadodecaborane(11), $B_{11}H_{11}PCH_3$ and *nido*-7-methylphosphaundecaborane(12), $B_{10}H_{12}PCH_3$, from the $[B_{11}H_{13}]^{2-}$ Anion and their Molecular Structures" Getman, T. D.; Deng, H.-B.; Hsu, L.-Y.; Shore, S. G. *Inorg. Chem.* 1989, 28, 3612.

"Synthesis of Divalent Lanthanide Tetradecahydrodeca- and Decahydrodeca-borates: The X-Ray Crystal Structure of $(\text{CH}_3\text{CN})_6\text{Yb}(\mu\text{-H})_2\text{-B}_{10}\text{H}_{12}\cdot\text{CH}_3\text{CN}$ " White, J. P. III; Deng H.-B.; Shore, S. G. *J. Am. Chem. Soc.* 1989, *111*, 8946.

"Borohydride Complexes of Eu(II) and Yb(II) and Their Conversion to Metal Borides; Structure of $(\text{L})_4\text{Yb}[\text{BH}_4]_2$ (L = CH_3CN , $\text{C}_5\text{H}_5\text{N}$)" White, J. P. III; Deng, H.-B.; Shore, S. G. *Inorg. Chem.* 1991, *30*, 2337.

"Reduction of BH_3THF by Alkali (K, Rb, Cs) and Ytterbium Amalgams to Form Salts of $[\text{B}_3\text{H}_8]^-$; A Simple Procedure for the Synthesis of Tetraborane(10)" Hill, T. G.; Godfroid, R. A.; White, J. P. III; Shore, S. G. *Inorg. Chem.* 1991, *30*, 2952.

"Coordination Complexes of Divalent Lanthanides (Sm(II), Eu(II), Yb(II)) with Decaborates; Evidence for Lanthanide Hydrides En Route to Lanthanide Borides" White, J. P. III; Shore, S. G. *Inorg. Chem.* Submitted.

B. Patents

"Method for the Low Temperature Preparation of Amorphous Boron Nitride Using Alkali Metal and Haloborazines" Shore, S. G.; Dolan, S. E. U. S. 5,053,365, 1991.

"Method for the Preparation of Boron Nitride Using Ammonia-Monohaloborane" Shore, S. G.; Niedenzu, P. M.; DeGraffenreid, A. L. U. S. Pending.

C. Dissertations

"The Reaction of Alkali Metals and Trihaloborazines. A New Method to Produce Amorphous Boron Nitride and the Preparation of Boron-Nitride Polymers" by Shawn Dolan. M.S. Dissertation, 1989.

"Studies of Polyboron Hydride Anions and Amine-Borane" by Phillip Niedenzu. Ph.D. Dissertation, 1990.

"Synthesis and Characterization of Divalent Lanthanide (Ln^{2+} = Sm, Eu, Yb) Coordination Complexes with Boron Hydride and Transition Metal Carbonyl Anions; The Formation of Metallic Films and Metal Borides from Complex Precursors" by James White. Ph. D. Dissertation, 1990.

"Alkali and Lanthanide Metal Salts of the Octahydrotriborate(1-) Ion" by Robert A. Godfroid. M.S. Dissertation 1991.

IX. PARTICIPATING SCIENTIFIC PERSONNEL

Dr. Sheldon Shore
Aillison Degrafenried
Shawn Dolan (MS, 1989)
Robert Godfroid (MS, 1991)
Dr. Ewan Hamilton
Dr. Tara Hill
Dr. William Quintana
Dr. Charles Mann
Dr. Phillip Niedenzu (PhD, 1990)
Terrece Salupo
Dr. James White (PhD, 1990)

X. INVENTIONS

"Method for the Low Temperature Preparation of Amorphous Boron Nitride Using Alkali Metal and Haloborazines"

"Method for the Preparation of Boron Nitride Using Ammonia-Monohaloborane"