The synthesis of $\text{B}_{10}\text{H}_{14}$ from $\text{B}_2\text{H}_6$ was modified to facilitate large scale production. Reductions of boranes by alkali and lanthanide metals were studied. Depending upon reaction conditions chosen, the anions $[\text{BH}_3]^{2-}$, $[\text{B}_2\text{H}_6]^{2-}$, and $[\text{B}_3\text{H}_8]^{-}$ were produced. A simple procedure was developed for the preparation of the solvent free salts $\text{M}[\text{B}_3\text{H}_8]$ ($\text{M} = \text{K, Rb, Cs}$). Borohydrides of the divalent lanthanides $\text{Yb}$, $\text{Eu}$ were synthesized, structurally characterized, and then converted to lanthanide borides $\text{YbB}_4$ and $\text{EuB}_6$. New procedures for the preparation of high purity boron nitride as powders and coatings were developed. An essentially instantaneous reaction between $\text{B}_3\text{N}_3\text{H}_3\text{Cl}_3$ 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. $\text{H}_3\text{NBHCl}$ in solution form can be applied to a surface. Heating to 1100 °C in vacuum produces a coating of turbostratic BN.
DERIVATIVES OF BORANES, POSSIBLE METAL BORIDE AND BORON NITRIDE PRECURSORS

Final Report
For the Period
August 1, 1988 - July 31, 1991

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September 27, 1991

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ARO Proposal No. 26145-CH
Grant No. DAAL03-88-K-0176

The Ohio State University Research Foundation
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,\textsuperscript{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,\textsuperscript{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 powders\textsuperscript{38} and coatings.\textsuperscript{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 SYNTHESES 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).

\[
1.8B_5H_9 + C_4H_9Li + [NEt_4]Cl \xrightarrow{Et_2O} [NEt_4][B_9H_{14}] + C_4H_{10} + 0.6H_2 + LiCl \quad (1)
\]

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 coatings\(^10\); neutron capture therapy;\(^11\) serum triglyceride and serum cholesterol biological studies;\(^12\) syntheses of metallaboranes,\(^13\) higher borane\(^14\) heteroatom boranes\(^15\) 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 metal\(^19\) or thallium\(^19,22\) salts by metathesis reactions.

We obtained the salts \(M[B_3H_8]\) \((M = K, \text{Rb}, \text{Cs})\) through the reduction of \(BH_3\text{THF}\) by alkali metal amalgams.\(^22\) This procedure provides a solvent free

\[
2M/Hg + 4BH_3\text{THF} \xrightarrow{\text{THF}} M[BH_4] + M[B_3H_8]
\]

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 procedure\(^3\)

\[
K[B_3H_8] + \text{BCl}_3 \longrightarrow B_4H_{10} + K[\text{HBCl}_3] + \text{solid BH residue}
\]

required the preparation of \([NEt_4][B_3H_8]\) from \(Na[B_3H_8]\) because Equation \((4))\) is not
Effective with Na[B₂H₆] due to retained ether interfering with the desired reaction between the [B₃H₈]⁻ anion and the boron halide. Prior to this reaction, solvent free alkali metal salts of [B₃H₈]⁻ 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 BH₃THF by an alkali metal, in the presence of naphthalene as an electron carrier, can produce \([\text{BH}_3]^{2−}\), the analogue of the carbanion [CH₃]⁻. 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 BH₃THF to \([\text{BH}_3]^{2−}\) gives \([\text{B}_2\text{H}_6]^{2−}\), the analogue of \(\text{C}_2\text{H}_6\). 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 BH₃THF. The following reaction sequence was studied. The anions produced in these reactions are stable in the absence of air.

\[
\begin{align*}
\text{THFBH}_3 + 2\text{M[C}_1\text{H}_8] & \rightarrow \text{M}_2[\text{BH}_3] + 2\text{C}_1\text{H}_8 + \text{THF} \\
\text{M} & = \text{Na, K, Rb, Cs} \\
\text{THFBH}_3 + \text{Rb}_2[\text{BH}_3] & \rightarrow \text{Rb}_2[\text{B}_2\text{H}_6] + \text{THF} \\
\text{THFBH}_3 + \text{Rb}_2[\text{B}_2\text{H}_6] & \rightarrow \text{Rb}[\text{B}_3\text{H}_8] + \text{Rb}[\text{BH}_4] + \text{THF}
\end{align*}
\]

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 find\textsuperscript{25} that CH\textsubscript{3}CN and C\textsubscript{5}H\textsubscript{5}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: (CH\textsubscript{3}CN)\textsubscript{4}Yb[(μ-H)\textsubscript{3}BH\textsubscript{2}], (C\textsubscript{5}H\textsubscript{5}N)\textsubscript{4}Yb[BH\textsubscript{4}])\textsubscript{2}, (CH\textsubscript{3}CN)\textsubscript{2}Eu[BH\textsubscript{4}]\textsubscript{2}, and (C\textsubscript{5}H\textsubscript{5}N)\textsubscript{1.8}Eu[BH\textsubscript{4}]\textsubscript{2}. Equation (9 represents the general reaction employed. Not only are coordination 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 (CH\textsubscript{3}CN)\textsubscript{4}Yb[(μ-H)\textsubscript{3}BH\textsubscript{2}] and (C\textsubscript{5}H\textsubscript{5}N)\textsubscript{4}Yb[BH\textsubscript{4}]\textsubscript{2}.

Figure 1. Molecular structures of (CH\textsubscript{3}CN)\textsubscript{4}Yb[(μ-H)\textsubscript{3}BH\textsubscript{2}] and (C\textsubscript{5}H\textsubscript{5}N)\textsubscript{4}Yb[BH\textsubscript{4}]\textsubscript{2}. Each borohydride unit in (CH\textsubscript{3}CN)\textsubscript{4}Yb[(μ-H)\textsubscript{3}BH\textsubscript{2}] is bound to Yb through three Yb-H-B bridges and the four CH\textsubscript{3}CN ligands are arranged in a "see-saw" configuration with respect to the central Yb atom.

The structure of (C\textsubscript{5}H\textsubscript{5}N)\textsubscript{4}Yb[BH\textsubscript{4}]\textsubscript{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, $\eta^3$, 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 found²⁵ that liquid NH₃ solutions of Eu and Yb, like liquid NH₃ solutions of Na²⁷, 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 CH₃CN.

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 CH₃CN.

![Figure 2. The molecular structure of $(\text{CH}_3\text{CN})_6\text{Yb}[\text{B}_{10}\text{H}_{14}]$.](image)
of solvation. This X-ray structure confirms the presence of the Yb-H-B bridge bonding inferred from $^{11}$B NMR spectra.

C. Formation of Lanthanide Borides.

1. Thermal Decomposition of Ln(II) Borohydrides. When $(\text{CH}_3\text{CN})_4\text{Yb}[(\mu-\text{H})_3\text{BH}]_2$ and $(\text{CH}_3\text{CN})_2\text{Eu}[\text{BH}_4]_2$ are heated in vacuum at 200 °C, CH$_3$CN and H$_2$ are evolved, but no boron hydride is produced (Equation (10)). IR spectra

$$\text{(CH}_3\text{CN)}_x\text{Ln[BH}_4\text{]}_2 \xrightarrow{200 \, ^\circ\text{C}, \text{vac.}} \text{"LnB}_2\text{"}$$

$\text{Ln} = \text{Eu, Yb}$

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 $(\text{CH}_3\text{CN})_4\text{Yb}[(\mu-\text{H})_3\text{BH}]_2$ and $(\text{CH}_3\text{CN})_2\text{Eu}[\text{BH}_4]_2$ were heated to 1000 °C in a quartz tube maintained at 10$^{-5}$ Torr (Equations (11) and (12)). At 100 °C CH$_3$CN is given off; above 150 °C H$_2$ evolution occurs; above 450 °C, lanthanide metal sublimes out of both solids.

$$\text{(CH}_3\text{CN)}_x\text{Yb[BH}_4\text{]}_2 \xrightarrow{1000 \, ^\circ\text{C}, \text{vac.}} \text{YbB}_4$$

$$\text{(CH}_3\text{CN)}_x\text{Eu[BH}_4\text{]}_2 \xrightarrow{1000 \, ^\circ\text{C}, \text{vac.}} \text{EuB}_6$$

The resulting materials are shiny-grey solids with a metallic luster. Their X-ray powder patterns revealed YbB$_4$ and EuB$_6$ to be the only crystalline phases present. We were able to prepare a crystalline YbB$_2$ phase by referring to the phase diagram to choose conditions under which YbB$_2$ is stable (Equation (13)).

$$\text{(CH}_3\text{CN)}_x\text{Yb[BH}_4\text{]}_2 \xrightarrow{550 \, ^\circ\text{C}, 1 \text{ atm Ar}} \text{YbB}_2$$

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

\[
\begin{align*}
(\text{L})_x\text{Ln}[\text{BoH}_{14}] & \xrightarrow{190 ^\circ \text{C}, \text{vac}} \text{Ln}[\text{BoH}_{10}] \\
-\text{L}, -\text{H}_2
\end{align*}
\]

\(\text{Ln} = \text{Eu}, \text{Yb} \quad \text{L} = \text{NH}_3, \text{CH}_3\text{CN}\)

are soluble in CH\(_3\)CN or C\(_5\)H\(_5\)N. The \(^{11}\text{B}\)-NMR spectrum of Yb[BoH\(_{10}\)] in C\(_5\)H\(_5\)N is very similar to that of alkali metal salts of \([\text{BoH}_{10}]^{2-}\), 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 Yb[BoH\(_{10}\)] slowly evolved H\(_2\) from 300-500 °C; no further volatiles were evolved up to 1000 °C. The X-ray powder pattern of the resulting black powder showed it to be YbB\(_6\). Amorphous B was probably present as well. \(\text{M}(\text{BoH}_{10})_3\) complexes \((\text{M} = \text{Ce}, \text{Gd})\) have been thermally decomposed at 1000 -1200 °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 production\(^{31}\).

Traditional\(^{31-33}\) routes to boron nitride involve high temperature syntheses. A common method for commercial BN production involves carbothermal reduction of boric acid\(^{31}\) at temperatures in excess of 1500 °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
BCl₃/NH₃ and BCl₃/NH₃/H₂ mixtures. Additionally, there has been much recent interest in polymeric preceramic compounds\textsuperscript{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 B₃Cl₃N₃H₃

We produced amorphous boron nitride in an unprecedented procedure that involves the reaction of B₃Cl₃N₃H₃ with the alkali metals (Cs, Rb, K) in the absence of a solvent.\textsuperscript{38} The reaction is initiated at 130 - 160 °C; it is vigorous

\[
\begin{array}{c}
\text{ClB} \quad \text{N} \\
\text{HN} \quad \text{B} \quad \text{NH} \\
\text{Cl}
\end{array}
\quad \begin{array}{c}
\text{M} \quad \longrightarrow \quad \text{2BN + MCl + HCl + } \frac{1}{2} \text{H}_2
\end{array}
\]

(M = Cs, Rb, K)

and virtually instantaneous, proceeding with a flash of light. Effectively hydrogen and chlorine are stripped from the B₃N₃ core to give amorphous BN. Higher temperatures are required in the reactions of B₃Cl₃N₃H₃ 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 B₃Cl₃N₃H₃, 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/cm\textsuperscript{3}, in good agreement with the accepted value of 1.7-1.8 g/cm\textsuperscript{3}. 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 B₃Cl₃N₃H₃, 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.

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

$$H_3NBH_3 + HCl \xrightarrow{Et_2O} H_2NBH_2Cl + H_2$$

(16)

produces turbostratic boron nitride. 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 $B_3N_3Cl_3H_8$. It appears to be principally two linked cycloborazane rings as indicated on the next page.
Figure 5. Proposed structure of $\text{B}_3\text{N}_3\text{Cl}_3\text{H}_6$.

Treatment of this compound with $\text{LiBH}_4$ produces cyclotriborazane, $\text{B}_3\text{H}_6\text{N}_3\text{H}_6$. Heating of $\text{B}_3\text{N}_3\text{Cl}_3\text{H}_6$ at 88 °C produced additional $\text{H}_2$ but no $\text{HCl}$. At higher temperatures $\text{HCl}$ was produced.

We obtained a polymeric boron-nitrogen containing material with a parent mass of about 900 by heating $\text{H}_3\text{NBH}_2\text{Cl}$ 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 $\text{LiAlH}_4$ and $\text{H}_3\text{NBH}_3$ in a 1:1 molar ratio in THF produces two moles of hydrogen gas and a salt that is assigned the formula $\text{Li}[\text{AlH}_2(\mu-\text{NH})(\mu-\text{H})\text{BH}_2]$ 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 $\text{Li}[\text{AlH}_2(\mu-\text{NH})(\mu-\text{H})\text{BH}_2] \cdot 0.5\text{THF}$. 
VII. Bibliography


VIII. Publications, Patents, Dissertations

A. Publications


"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.

14
"Synthesis of Divalent Lanthanide Tetradecahydrodeca- and Decahydrodeca-

"Borohydride Complexes of Eu(II) and Yb(II) and Their Conversion to Metal Borides; Structure of (L)₄Yb[BH₄]₂ (L = CH₃CN, C₅H₅N)" White, J. P. III; Deng, H.-B.; Shore, S. G. Inorg. Chem. 1991, 30, 2337.


"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


C. Dissertations


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"