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STUDIES ON BORON - NITROGEN AND BORON - GADOLINIUM COMPOUNDS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in the Graduate School of the Ohio State University

By

Allison Lynne DeGraffenreid, B.S.

* * * * *

The Ohio State University

1995

Dissertation Committee:
Dr. Bruce Bursten
Dr. Patrick Gallagher
Dr. Daniel Cox
Dr. Sheldon Shore

Approved By:

Advisor

Department of Chemistry
To My Family
ACKNOWLEDGEMENTS

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VITA

January 27, 1965  Born - Nashville, Tennessee

1987  B.S. (Chemistry),
University of Kentucky, Lexington, Kentucky

1988 - 1989  Laboratory Technician,
University of Kentucky Medical Center, Lexington, Kentucky

1989-1995  Graduate Fellow,
Department of Chemistry,
The Ohio State University, Columbus, Ohio

Publications

of the Type RR'B(p-pz)2BRR' and Related Studies."

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American Chemical Society, Atlanta, Georgia, April 1992: "Preparation of Boron Nitride
from the Molecular Precursor, Ammonia-Monochloroborane."

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Issued December 8, 1992: "Method for the Preparation of Boron Nitride Using Ammonia-
Monochloroborane."

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Session, The Ohio State University, October 21, 1994, Columbus, OH 43220: "The
Hydridic and Protonic Nature of Ammonia-Borane and Related Studies."
VITA CONTINUED

Fields of Study

Major Field: Chemistry

Studies in Non-Metal and Organometallic Chemistry: Professors Sheldon G. Shore, Andrew Wojicki and Associate Professor Eugene P. Schram.


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I. INTRODUCTION

A. The History of Ammonia-Borane

In 1923, Stock and Kuss first prepared the diammoniate of diborane. According to elemental analysis studies and molecular weight determinations, the compound had the molecular formula, \( B_2N_2H_{12} \), which had the corresponding empirical formula, BNH\(_6\). The diammoniate of diborane was produced from the reaction of diborane with 2 equivalents of ammonia.\(^1\)\(^2\)\(^3\)\(^4\)

\[
B_2H_6 + 2 \text{NH}_3 \rightarrow B_2\text{H}_6\cdot 2\text{NH}_3
\]  \hspace{1cm} (1)

For years, the structure and bonding of the material was debated as well as the existence of an elementary compound with the same empirical formula, \( \text{H}_3\text{NBH}_3 \). It was postulated that if the simpler compound could be produced and studied, it could give information about the connectivity of the double molecular weight compound.\(^5\)\(^6\)

In 1958, the structure of the diammoniate of diborane was shown to be the borohydride salt, \([\text{(NH}_3)_2\text{BH}_3][\text{BH}_4]\).\(^7\)\(^8\)\(^9\)\(^10\)\(^11\)\(^12\)\(^13\) Earlier, in 1955, Shore and Parry were able to synthesize ammonia-borane, \( \text{H}_3\text{NBH}_3 \), using the reaction of lithium borohydride
with ammonium chloride. 14

\[
\text{LiBH}_4 + \text{NH}_4\text{Cl} \xrightarrow{\text{Et}_2\text{O}} \text{H}_3\text{NBH}_4 + \text{LiCl} + \text{H}_2 \quad (2)
\]

Since its initial preparation, many methods for the synthesis of ammonia-borane have been established including its preparation from the diammoniate of diborane 7, 14, 15 and its synthesis using the reagents that originally produced the diammoniate of diborane. 16, 17

\[
\text{[\text{(NH}_3\text{)}_2\text{BH}_2][\text{BH}_4]} + \text{NH}_4\text{Cl} \xrightarrow{\text{Et}_2\text{O}, \text{trace NH}_3} \text{H}_3\text{NBH}_4 + [\text{(NH}_3\text{)}_2\text{BH}_2]\text{Cl} + \text{H}_2 \quad (3)
\]

\[
\text{B}_2\text{H}_6 + 2 \text{NH}_3 \xrightarrow{\text{ethers or dioxane}} 2 \text{H}_3\text{NBH}_3 \quad (4)
\]

\[
2 \text{LiBH}_4 + (\text{NH}_4)_2\text{SO}_4 \xrightarrow{\text{Et}_2\text{O}} 2 \text{H}_3\text{NBH}_3 + \text{Li}_2\text{SO}_4 + 2 \text{H}_2 \quad (5)
\]

\[
(\text{NH}_4)_2\text{CO}_3 + 2 \text{NaBH}_4 \xrightarrow{\text{THF}} 2 \text{H}_3\text{NBH}_3 + \text{Na}_2\text{CO}_3 + 2 \text{H}_2 \quad (6)
\]
The most popular routes of ammonia-borane synthesis involve the reaction of Lewis base borane adducts, $\text{LBH}_3$, with ammonia.

$\text{(CH}_3\text{)}_2\text{SBH}_3 + \text{NH}_3 \xrightarrow{-20 \degree\text{C}} \text{H}_3\text{NBH}_3 + (\text{CH}_3\text{)}_2\text{S} \quad (7)$

$\text{THF-BH}_3 + \text{NH}_3 \xrightarrow{\text{THF}} \text{H}_3\text{NBH}_3 + \text{THF} \quad (8)$

Though ammonia-borane is an extremely simple molecule and though the compound is isoelectronic with $\text{CH}_3\text{CH}_3$, surprisingly little is known about its chemical reactivity because very few studies of the chemistry of the compound have been undertaken. Studies have been mainly devoted to measuring the physical and spectroscopic properties of ammonia-borane or to calculating its energy levels. Other ammonia-borane studies have investigated its thermal decomposition as a solid or in solution. For example, during an attempt to identify and possibly isolate the unknown moiety aminoborane, $\text{H}_2\text{NBH}_2$, Kuznesof and co-workers studied the vapors above solid $\text{H}_3\text{NBH}_3$ at room temperature. Mass spectral analysis of the vapors gave evidence for $\text{H}_3\text{NBH}_3$, $\text{H}_2\text{NBH}_2$, and $\text{B}_2\text{H}_6$.\text{26}
In a 1963 reactivity study of H$_3$NBH$_3$, it was noted that the material could be heated above 500 °C to produce boron nitride according to equation 9.\(^{16}\)

\[
\text{H}_3\text{NBH}_3 \xrightarrow{\Delta} \text{BN} + 3\text{H}_2 \quad (9)
\]

In this paper, the first evidence that H$_3$NBH$_3$ is a reducing agent was also reported. It was shown that aqueous solutions of metal chlorides or sulfates and ammonia-borane could reduce the metal to its elemental form. The metals surveyed in this study included gold, palladium, silver, copper, iron and nickel.\(^{16}\) Andrews and Crawford also investigated the reducing properties of H$_3$NBH$_3$ when they discovered that it could stereoselectively reduce aldehydes and ketones in both protic and non-protic solvents.\(^{22,30}\) The reducing ability of ammonia-borane has been adapted to many industrial applications. The literature contains numerous patents utilizing the substance as a reducing agent within the process.\(^{23,24}\)

In a 1967 paper, Holliday and Pendlebury noted that ammonia-borane reacted with tetravinyl lead to produce trivinylplumbane and ammonia-monovinylborane.\(^{31}\)

\[
\text{H}_3\text{NBH}_3 + (\text{CH}_2=\text{CH})_4\text{Pb} \xrightarrow{\text{DME}} (\text{CH}_2=\text{CH})_3\text{PbH} + \text{H}_3\text{NBH}_2(\text{CH}=\text{CH}_2) \quad (10)
\]
It has also been shown that the ammonia adduct can be replaced by other amine
groups like trimethylamine.

$$\text{H}_3\text{NBH}_3 + (\text{CH}_3)_2\text{N} \longrightarrow (\text{CH}_3)_2\text{NBH}_3 + \text{NH}_3$$ (11)

Several crystal structures of 1:1 and 2:1 adducts of ammonia-borane with 18-
crown-6 and its methyl and anisyl derivatives have been published. Whether the isolated
adduct existed in a 1:1 or a 2:1 ratio depended upon the size and geometry within the
cavity of the ether. The 18-crown-6 version crystallized as a 1:1 complex and
was isolated from a methanol solution of H$_3$NBH$_3$ and the crown ether.

H$_3$NBH$_3$ is a colorless, crystalline solid that is purified by subliming below 60 °C.
Sublimation can be performed at higher temperatures but the rate of decomposition within
the bulk solid increases at these temperatures and thus decreases the yield. A second
method of purification requires recrystallization from diethylether.

The proton coupled boron-11 NMR spectrum of H$_3$NBH$_3$ obtained in THF shows
a quartet centered at -22.55 ppm (J = 95 Hz). Proton NMR spectroscopy in deuterated
THF consists of resonances at 3.97 ppm (triplet, J = 39 Hz) and at 1.44 ppm (quartet, J
= 95 Hz) for the NH$_3$ and BH$_3$ groups, respectively. Ammonia-borane has also been
characterized by infrared spectroscopy, mass spectroscopy, and X-ray powder
diffraction.
B. The History of Aminoborohydride Derivatives

1. [R₂NBH₃]⁻

Only two N-alkylated derivatives of the aminoborohydride anion had been discussed in the literature prior to 1992. They were dimethylaminoborohydride, M[Me₂NBH₃] where M = Li, Na, and K and sodium tert-butylaminoborohydride, Na[t-BuNBH₃].

The dimethylamine derivative was first produced in 1961 by the action of sodium hydride on dimethylamine borane.³⁸

\[ \text{NaH} + \text{Me}_2\text{NHBH}_3 \rightarrow \text{Na}[\text{Me}_2\text{NBH}_3] + \text{H}_2 \]  (12)

The product was isolated as the dioxanate and was characterized by ¹¹B NMR spectroscopy and elemental analysis. In 1968, a method for the production of the non-solvated form of sodium dimethylaminoborohydride was reported. This synthesis utilized elemental sodium rather than the hydride with liquid ammonia as the solvent.³⁹

\[ \text{Na} + \text{Me}_2\text{NHBH}_3 \rightarrow \text{Na}[\text{Me}_2\text{NBH}_3] + \frac{1}{2} \text{H}_2 \]  (13)

The hydrolysis of Na[Me₂NBH₃] in strong acid was reported as well as a listing of the proton NMR chemical shifts and IR frequencies for the compound.³⁹
In 1975, it was reported that lithium hydride reacts with the ring compound \([\text{Me}_2\text{NBH}_3]\) to produce \(\text{Li}[\text{Me}_2\text{NBH}_3]\). \(^{40}\)

\[
2 \text{LiH} + [\text{Me}_2\text{NBH}_3] \xrightarrow{25^\circ \text{C}, 2 \text{ months}} 2 \text{Li}[\text{Me}_2\text{NBH}_3]
\]  \hspace{1cm} (14)

A few reactivity studies have been performed on \([\text{Me}_2\text{NBH}_3]\). Diborane is unsymmetrically cleaved by \(\text{Na}[\text{Me}_2\text{NBH}_3]\) to form \(\mu\)-NMe_2B_2H_5 and NaBH_4. \(^{41,42}\) The reaction of Li[Me_2NBH_3] with LiNMe_2 produces B(NMe_2)_3 and LiH. \(^{43}\) Acid methanolysis studies compared the rate of solvolysis of K[Me_2NBH_3] to the solvolysis rates for Na[Me_2N2BH_3], \(\mu\)-NMe_2B_2H_5 and Me_2NHBH_2Cl. The study showed that the methanolysis of K[Me_2NBH_3] was slower and required higher temperatures than the solvolysis of the other three compounds. \(^{44}\)

The N-alkylated borohydride salts Na[Me_2NBH_3] and Na[t-BuNHBH_3] reduce aldehydes, ketones, esters and amides to the corresponding alcohol or amine. The reduction of amides was found to be selective for primary and tertiary amides. The product obtained for tertiary amides was dependent upon the steric bulk of the starting material. \(^{45}\) This study was the first to note that aminoborohydride salts can behave as reducing agents. The scientist's work took advantage of the fact that replacing a hydrogen atom of [BH_3] with an electron donating R_3N group increases the reducing properties of the reagent.
In a series of papers beginning in 1992, Singaram and co-workers continued with this type of research when they synthesized a large number of N-alkylated aminoborohydride compounds and used them as a reducing agents in organic chemistry. The cation chosen for the studies was lithium rather than sodium because the reduction capabilities of the alkali metal borohydrides decreases rapidly in the series LiBH₄ > NaBH₄ > KBH₄ and they were seeking the best reducing agent. The new compounds contained the N-functional groups listed in Figure 1.

Figure 1: Amine Functional Groups in Lithium Aminoborohydride, [R₂NBH₄]⁺; Studies
Singaram's compounds were produced by reacting the parent aminoborane with butyllithium at 0 °C.

\[
\text{R}_2\text{NHBH}_3 + \text{CH}_3\text{Li} \xrightarrow{0 \degree\text{C, THF}} \text{Li}[\text{R}_2\text{NBH}_3] + \text{CH}_4 \quad (15)
\]

Lithium pyrrolidinoborohydride, Li[\text{C}_6\text{H}_5\text{NBH}_3], was singled out as a representative compound for discussions but it was reported that the other [R_2NBH_3]^- compounds listed in Figure 1 could be used with equivalent success for the organic reductions. Li[\text{C}_6\text{H}_5\text{NBH}_3] is equal in hydride donating ability to LiAlH_4 but without the undesired safety and flammability problems. It can be used to selectively reduce many organic functional groups including \(\alpha,\beta\)-unsaturated carbonyl compounds, tertiary amides and alkylcyclohexanones.46, 47, 48, 49, 50

\[
\text{Li} \left[ \begin{array}{c} \text{NBH}_3 \\ \text{C}_6\text{H}_5 \end{array} \right] + \begin{array}{c} \text{O} \\ \text{\text{C}}^{65\degree, \text{THF}} \end{array} \rightarrow \begin{array}{c} \text{C} \\ \text{H}_6\text{C}_6 \text{CH}_3 \text{OH} \end{array} \quad 89 \% \quad (16)
\]

One criteria for determining whether an aminoborohydride compound will serve as a good reducing agent in organic synthesis was discussed. This criteria was vigorous exothermic reaction with methyl iodide with the production of methane and the parent aminoborane.
Boron-11 NMR chemical shifts of the parent, \( R_2\text{NBH}_3 \), and anionic, \([R_2\text{NBH}_3]^−\), derivative compounds remain relatively similar. The two species can be differentiated by \( ^{11}\text{B} \) NMR spectroscopy, however, due to the fact that aminoborohydride compounds have coupling constants in the area of 85 Hz while the parent amineborane compounds have values in the 95 Hz range.

2. \([\text{H}_2\text{NBH}_3]^−\)

Relatively little information is available concerning B-alkylated aminoborohydride derivatives. A 1933 study measured conductance values for \( \text{M}[\text{H}_2\text{NB(C}_6\text{H}_5)_3]\) (\( \text{M} = \text{Na}, \text{K} \)) which was produced from the alkali metal amide and triphenylboron (equation 17). The study compared the conductance of \([\text{NH}_2]^−\), \([\text{C}_6\text{H}_5\text{NH}]^−\), \([\text{C}_6\text{H}_5\text{H}_2\text{N}]^−\), and \([\text{H}_2\text{NB(C}_6\text{H}_5)_3]^−\) in liquid ammonia. It was found that the larger the anion, the greater the conductance due to greater dissociation in solution. 51

\[
\text{MNH}_2 + \text{B(C}_6\text{H}_5)_3 \xrightarrow{\text{NH}_3} \text{M[H}_2\text{NB(C}_6\text{H}_5)_3]\]

(17)

In 1951, it was reported that alkali metals react with trimethylborane, \( \text{B(\text{CH}_3)_3} \), or tributylborane, \( \text{B(C}_8\text{H}_9)_3 \), in liquid ammonia to produce sodium or potassium aminotrialkylborohydride, \( \text{M[H}_2\text{NBR}_3]\) (equation 18). These compounds were then found to be reactive with ammonium bromide with the production of \( \text{H}_3\text{NBR}_3, \text{NaBr}, \text{and NH}_3 \). 52
The only other B-alkylated aminoborohydride reagent study in the literature investigated K[H₂NBMe₃], prepared via the reaction of trimethylboron with potassium amide (equation 17). The reagent's response to aqueous hydrochloric acid and heat and its reactivity with the Lewis acid electron pair acceptors diborane, trimethylboron and boron trifluoride was investigated. The goal of the study was to produce new compounds with B-N-B linkages. Instead it was found that K[H₂NBMe₃] did not react with B(CH₃)₃ and produced mixed products with B₂H₆ and BF₃. ⁵³

3. [H₂NBH₄]⁻

The aminoborohydride anion was first mentioned in the literature during a discussion of the structure of the diammoniate of diborane in 1938. During attempts to prepare related compounds, Schlesinger and Burg reacted BH₃OMe₂ with sodium in ammonia and recovered one half of an equivalent of hydrogen gas. The reaction is given in equation 19 and was deduced based upon hydrogen evolution data and the fact that elemental analysis of the residue after ammonia evaporation indicated one equivalent of boron per equivalent of nitrogen. ⁵

\[
\text{Na} + \text{BH₃OMe₂} + \text{NH₃} \xrightarrow{\text{NH₃}} \text{Na[H₂NBH₄]} + 1/2 \text{H₂} + \text{Me₂O} \quad (19)
\]
A 1958 study reported that sodium hydride reacted with ammonia-borane to produce Na[H₂NBH₃] but again the reaction stoichiometry was deduced based upon gas evolution volumes. No effort was made to isolate or characterize the product. ⁷

In 1984, ab initio calculations compared the isoelectronic series [XNH₃]^+, XCH₃ and [XBH₃]^− where X = Li, BeH, BH₂, CH₃, NH₂, OH, or F. The calculations showed that [BH₃]^− should interact favorably with the σ-acceptors including NH₂, OH and F but unfavorably with the σ-donors BeH, BH₂, and CH₃. ⁵⁴ The interaction with NH₂ would produce [H₂NBH₃]^− which at the time was unknown. The calculation indicating a favorable interaction has been validated since [H₂NBH₃]^− has now been prepared.

In his 1990 dissertation, Niedenzu was the first to study [H₂NBH₃]^− and to characterize the sodium and potassium salts. He prepared the analogs by the reaction of sodium or potassium hydride with ammonia-borane. He also performed one reactivity study. That reaction being the interaction of Na[H₂NBH₃] with ammonium chloride forming ammonia-borane, sodium chloride and ammonia (equation 20). ⁵⁵

\[ \text{Na[H}_2\text{NBH}_3] + \text{NH}_3\text{Cl} \rightarrow \text{H}_2\text{NBH}_3 + \text{NH}_3 + \text{NaCl} \quad (20) \]

In 1993, Salupo reported the synthesis of the first lanthanide salts of the aminoborohydride anion. She reacted europium and ytterbium metal with ammonia-borane in liquid ammonia and recorded the IR spectra for both Yb(H₂NBH₃)_2 and Eu(H₂NBH₃)_2 and the ¹¹B NMR spectrum for the Yb compound. ⁵⁶
C. The History of Halogenated Derivatives

1. \(R_3NBH_xX\) and \(R_3NBHX_2\)

Mono and dihalogenated alkylamineborane compounds, \(R_{3-n}NH_BH_{3-m}X_m\), have been known since 1939 when Schlesinger, Flodin and Burg prepared the first examples.\(^{57}\) The literature is inundated with articles about this class of compounds with an overwhelming majority of the work being focused on the trimethylamine adducts, \(Me_3NBH_xX\) and \(Me_3NBHX_2\). The known compounds have been halogenated by fluorine, chlorine, bromine and iodine as Table 1 notes.

There are at least six methods for the production of the mono and dihalo alkylamineborane compounds with the most important methods being recorded below. Most of the syntheses also produce the dihalogenated compounds when stoichiometries and reaction times are adjusted.

\[
\begin{align*}
R_3NBH_3 + HX & \longrightarrow R_3NBH_2X + H_2 \quad (21) \\
R_3NBH_3 + X_2 & \longrightarrow R_3NBH_2X + HX \quad (22) \\
R_3NBH_3 + BX_3 & \longrightarrow R_3NBH_2X + BH_2X \quad (23) \\
R_3NBH_3 + R_3NBX_3 & \longrightarrow R_3NBH_2X + R_3NBHX_2 \quad (24)
\end{align*}
\]
\[ R_3NBH_3 + NaOCl \rightarrow R_3NBH_3Cl + NaOH \] (25)

\[ R_3NBH_3 + RX \rightarrow R_3NBH_2X + RH \] (26)

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The compounds have been compared to one another by IR spectroscopy, \(^{63, 64, 74}\) proton NMR spectroscopy, \(^{61, 75}\) and boron-11 NMR spectroscopy. \(^{58, 64}\)

\(^{75}\) R\(_3\)NBH\(_2\)X compounds have been shown to have useful reactivity. Their reactions with Lewis bases, L, produce the cations, [L\(_2\)BH\(_2\)]\(^+\) \(^{76-78}\) and [L\(_3\)BH]\(^+\). \(^{78}\) R\(_3\)NBH\(_2\)X compounds have been used in hydroboration studies. \(^{70}\) They have also been used extensively in the preparation of pyrazabole compounds. \(^{79-82}\)
TABLE 1

Known Mono and Dihalogenated Amine Boranes

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2. $H_3NB{R_2}X$ and $H_3NB{RX_2}$

The only known amineborane compounds for which the boron atom is functionalized with both an alkyl group and a halogen were prepared in the first study halogenating amineboranes. The boron di-functionalized compounds that were synthesized are $Me_3NBHMeCl$, $Me_3NBMe_2Cl$ and $Me_3NBMeCl_2$. They were prepared by the reaction of the parent B-methylated amineborane compound with hydrochloric acid. 57

3. $H_3NB{H_2}X$ and $H_3NB{HX_2}$

Ammonia-borane was first halogenated in 1979 by Hu and Geanangel in an $^{11}$B NMR spectroscopy study of mixtures of $H_3NBH_3$ and $BX_3$ in varying ratios. Inspection of the resultant spectra revealed that multiple species were present in all of the ether solutions but that the new compounds, $H_3NBH_2Cl$, $H_3NBHCl_2$ and $H_3NBH_2Br$ could be identified by the position of their proton decoupled boron-11 NMR resonances and by the multiplicity of the coupled spectra. The other compounds present in the $BCl_3$ / $H_3NBH_3$ mixtures included $(BHNH)_3$, $Et_2O BH_2 Cl$, $Et_2O B HCl_2$, $\mu$-$NH_2 B_2 H_5$ and $H_2 NBCl_3$. The $BBr_3$ / $H_3NBH_3$ mixtures contained the bromine analogs of the previously noted compounds along with $Et_2BH$ and $Et_3B$. The reaction with $BF_3$ produced an 80 % yield of $\mu$-$NH_2 B_2 H_5$ along with $H_3NBF_3$ and $B_2 H_6$. Some unreacted $H_3NBH_3$ and $Et_2O BF_3$ also remained in the solution. 57
H₃NBH₂Cl was isolated cleanly for the first time when ammonia-borane was reacted with hydrochloric acid. ⁵⁵

\[ \text{H₃NBH₃ + HCl} \xrightarrow{\text{Et₂O}} \text{H₃NBH₂Cl + H₂} \] (27)

The solid was characterized by \(^{11}\)B and \(^{1}\)H NMR spectroscopy. Its reaction with ammonia, which yielded \([\text{(NH₃)}₂BH₂]\text{Cl}\), was noted. The thermal decomposition of H₃NBH₂Cl was also studied. ⁵⁵ This thermal decomposition, which resulted in the formation of boron nitride, was investigated further in a 1992 patent by Shore, Niedenzu and DeGraffenreid. ⁹⁸

\[ \text{H₃NBH₂Cl} \xrightarrow{\Delta} \text{BN + 2 H₂ + HCl} \] (28)

That H₃NBH₂Cl can be used as a precursor compound for the preparation of carbon and oxygen free boron nitride is an exciting discovery. There is current research that is dedicated to developing lower temperature and lower pressure methods of synthesizing pure BN. ⁹⁹,¹⁰⁰

Boron nitride is a colorless ceramic material with many industrial uses due to its high thermal stability, anti-corrosive nature and its properties as a thermal conductor and an electrical insulator. BN is produced industrially as fibers, thin films, coatings or
powders which are then fabricated into sheets or pressed into molds. BN resists thermal
shock, has good machinability and can withstand high pressures. It is used as a solid
lubricant between metal parts in machinery and as a crucible for reactions involving molten
metals due to its non-wettability and chemical inertness.\textsuperscript{99-101}

Most of the methods for the production of BN involve high temperatures and high
pressures and lead to products containing carbon, oxygen and hydrogen impurities.
Lately, interest has turned to the search for methods of BN production which involve
simple molecular precursors. These precursors are often polymeric and can be heated
under milder conditions to produce BN.\textsuperscript{101-104}

D. Gadolinium Borohydrides

1. The Lanthanide Metals

The lanthanide and actinide elements have 4f and 5f electrons, respectively. These
elements are the so called "rare earth metals". The name rare earth was originally given
to the metals because they were thought to be scarce on the earth. Better separation and
identification techniques have shown, however, that most of them are quite common.\textsuperscript{105}

A particular property of the lanthanide metals is that they tend to have very similar
chemical reactivity and physical properties due to the fact that the f electrons are relatively
uninvolved in bonding. This lack of reactivity is prompted by the fact that f orbitals have
limited radial extension beyond the closed s shell of the preceding alkaline earth metal.\textsuperscript{106}

Because of this, lanthanide metals tend to exist as highly charged cations. They generally
form ionic compounds with +3 being the most stable oxidation state. In many cases, +3
is the only readily available oxidation state. A +2 oxidation state is accessible to only a few metals including Sm, Eu and Yb and the +4 state is only available to Ce.\textsuperscript{105,106} The lanthanides, due to their large radii, generally have coordination numbers of 7 to 9 atoms.\textsuperscript{105}

Gadolinium is the seventh element of the lanthanide series; it has the electronic configuration [Xe]6s\textsuperscript{2}4f\textsuperscript{7}. Due to its central position in the lanthanide series, many properties of the group including enthalpies of sublimation and crystal coordination geometries plateau at Gd.\textsuperscript{105} Gadolinium is paramagnetic which hampers the effectiveness of NMR spectroscopy as a technique for the characterization of its compounds.

2. \([\text{B}_3\text{H}_6]^-\)

The octahydrotriborate (1-) ion, \([\text{B}_3\text{H}_6]^-\), was first synthesized in 1956 by the reaction of sodium amalgam with diborane in diethylether solvent.\textsuperscript{107,108}

\[
2 \text{Na} / \text{Hg} + 2 \text{B}_2\text{H}_6 \xrightarrow{\text{Et}_2\text{O}} \text{Na[}\text{B}_3\text{H}_6\text{]} + \text{Na[BH}_4\text{]} \quad (29)
\]

Since this time, many procedures for the preparation of the arachno \([\text{B}_3\text{H}_6]^-\) anion have been reported in the literature. Most involve sodium borohydride, \(\text{Na[BH}_4\text{]}\), or diborane, \(\text{B}_2\text{H}_6\), as the starting material.\textsuperscript{107,109-112} A very simple preparation of \([\text{B}_3\text{H}_6]^-\) compounds was reported in 1991 by Shore and co-workers. It requires that an amalgam of the metal be stirred with \(\text{BH}_4\text{THF}\).\textsuperscript{113}
\[ 2 \text{M}/\text{Hg} + 4 \text{BH}_3 \cdot \text{THF} \xrightarrow{\text{THF}} \text{M[BH}_4] + \text{M[B}_3\text{H}_8] \] (30)

All of the alkali metal salts including Cs[B_3H_8] and Rb[B_3H_8] have been prepared using this procedure as well as the divalent lanthanide metal compound, Yb(B_3H_8)_2. \textsuperscript{113} Other cations that have been utilized with the [B_3H_8]^+ ion include alkyl and phenyl ammonium, phosphonium and arsonium ions as well as the alkaline earth metals and transition metals. \textsuperscript{107} The alkali metals form ionic compounds with [B_3H_8]^+. \textsuperscript{114} Transition metals bind [B_3H_8]^+ in a covalent manner.

The structure of the anion was first solved as the [(NH_4)_2BH_4]^+ salt and is shown in Figure 2. \textsuperscript{107,115} It is based upon an isosceles triangle with bridging B-H-B hydrogens constituting two sides of the triangle. In the compounds with transition metals, the ion combines with the metals via bridging M-H-B bonds. \textsuperscript{114} The majority of these transition metal compounds involve a [B_3H_8]^+ ligand which is bound in a bidentate manner. (CO)_3MnB_3H_8, however, contains a tridentate [B_3H_8] moiety (Figure 3). \textsuperscript{114,116-119}
Figure 2: Structure of the [B$_4$H$_8$]$^-$ Ion
Figure 3: Covalent Bonding Modes of \([\text{B}_3\text{H}_6]^+\)
The boron-11 NMR spectrum of the $[\text{B}_3\text{H}_8]^-$ ion in ionic compounds consists of a nonet centered near -30 ppm with a coupling constant of 33 Hz. The specific position of the peak varies somewhat depending upon the cation. The spectrum is a nonet due to the fluxionality of the molecule. All hydrogen atoms couple with all boron atoms.\textsuperscript{107} The multiplicity is given by the equation $2 \Sigma I + 1$ which predicts a nonet ($2[8(1/2)] + 1 = 9$).

The proton NMR spectrum of the $[\text{B}_3\text{H}_8]^-$ ion consists of a decet also with a coupling constant of 33 Hz centered at 0.3 ppm. The complicated spectrum is also due to the fluxionality of the molecule ($2[3(3/2)] + 1 = 10$).\textsuperscript{107} A possible mechanism for the fluxionality of the molecule has been discussed. The model involves two stages in which a bridge hydrogen first changes its coordination to become a terminal hydrogen. This forms a BH$_3$ group which rotates and allows a new B-H-B bridge to form.\textsuperscript{107,114} $[\text{B}_3\text{H}_8]^-$ salts are solids which are stable to air and moisture.\textsuperscript{107}
Figure 4: $^{11}$B and $^1$H NMR Spectra of the [B$_3$H$_6$]$^-$ ion
3. \([\text{B}_{10}\text{H}_{14}]^-\)

Tetradecahydononaborate (1-), \([\text{B}_{10}\text{H}_{14}]^-\), was first prepared in 1963 by Benjamin, Stafeij and Takacs.\(^{120}\) This arachno-boron hydride anion can be produced by the action of sodium hydride, \(\text{NaH}\) on pentaborane (9), \(\text{B}_5\text{H}_9\), in THF\(^{121}\) or by the base degradation of decaborane (14), \(\text{B}_{10}\text{H}_{14}\) (equations 31 - 33).\(^{122}\)

\[
\text{B}_{10}\text{H}_{14} + \text{[OH]}^- \rightarrow \text{[B}_{10}\text{H}_{13}]^- + \text{H}_2\text{O} \quad (31)
\]

\[
\text{[B}_{10}\text{H}_{13}]^- + \text{[OH]}^- \rightarrow \text{[B}_{10}\text{H}_{13}\text{OH}]^{2-} \quad (32)
\]

\[
\text{[B}_{10}\text{H}_{13}\text{OH}]^{2-} + \text{[H}_3\text{O}]^+ + \text{H}_2\text{O} \rightarrow \text{[B}_9\text{H}_{14}]^- + \text{B(OH)}_3 + \text{H}_2 \quad (33)
\]

Common cations for the \([\text{B}_9\text{H}_{14}]^-\) anion are alkali metals. These can be substituted by alkyl and phenyl ammonium and phosphonium ions using simple metathesis reactions.

The structure of the \([\text{B}_9\text{H}_{14}]^-\) ion is shown in Figure 5. It was first solved by the single crystal X-ray diffraction study of the cesium salt in 1970.\(^{123}\) The structure is based upon the nido-boron hydride molecule \(\text{B}_{10}\text{H}_{14}\) with boron number 6 removed.
Figure 5: Structure of the $\left[B_3H_{14}\right]^+$ ion
The boron-11 NMR spectrum of Cs[B$_3$H$_9$] in DMSO consists of three doublets of equal intensity at -8.17 ppm (J = 140 Hz), -20.37 ppm (J = 132 Hz), and -23.69 ppm (J = 140 Hz). The signals are due to boron groups 5, 7, 9; 4, 6, 8 and 1, 2, 3, respectively. Doublets are produced due to the interaction of each boron with a terminal hydrogen ($2[1/2]+1 = 2$). This coupling continues to be observed at low temperatures as the compound is fluxional down to -70 °C. Smaller coupling due to bridging hydrogens is not observed. $^{126-126}$

The proton NMR spectrum of Cs[B$_3$H$_9$] in D$_2$O consists of three overlapping quartets and a broad singlet centered at -1.50 ppm. The quartets lie at 2.10 ppm, 1.60 ppm, and 1.10 ppm and have coupling constants of 136, 124, and 140 Hz, respectively. The quartets are produced by the coupling of the terminal hydrogens to the borons and the broad singlet arises from the bridging hydrogens in the molecule. $^{123-126}$ [B$_3$H$_9$]$^-$ salts are air stable and can be stored in air for extended periods of time.
Figure 6: $^{11}$B and $^1$H NMR Spectra of the [B$_6$H$_6$]$^+$ ion
4. The History of the Gadolinium Boranes

Only a handful of gadolinium-boron compounds have been synthesized with much of the literature originating in Russia. Most of the known gadolinium-boron compounds are \([\text{BH}_4^-]\) salts but a few large cage borane salts are also known.

In 1975, Bernstein and Chen reported the synthesis of a variety of lanthanide borohydride salts with the formula \(\text{Ln(BH}_4\text{)}_3\text{solvent}\). They included two routes of synthesis. The first route took advantage of the reaction of \(\text{Al(BH}_4\text{)}_3\) with \(\text{Ln(OCH}_3\text{)}_3\) (equation 34). The second synthetic method, from which crystals were isolated, involved the reaction of \(\text{Ln(OCH}_3\text{)}_3\) with diborane (equation 35). The reaction with \(\text{B}_2\text{H}_6\) had also been previously reported by Zange.

\[
3 \text{Al(BH}_4\text{)}_3 + \text{Ln(OCH}_3\text{)}_3 \rightarrow \text{Ln(BH}_4\text{)}_3\text{3THF} + 3 \text{Al(BH}_4\text{)}_2(\text{OCH}_3) \tag{34}
\]

\[
2 \text{B}_2\text{H}_6 + \text{Ln(OCH}_3\text{)}_3 \rightarrow \text{Ln(BH}_4\text{)}_3\text{3THF} + \text{B(OCH}_3\text{)}_3 \tag{35}
\]

The isostructural single crystal structures of \(\text{Gd(BH}_4\text{)}_3\text{3THF}\), \(\text{Y(BH}_4\text{)}_3\text{3THF}\) and the mixed metal compound \((\text{Er, Y, Gd})(\text{BH}_4)_3\text{3THF}\) were reported. A later, more detailed investigation of the crystal structure noted that the crystals contain three inequivalent borohydride groups. One of the \([\text{BH}_4^-]\) groups is bidentate while the other
two are bound in a tridentate manner to the metal ion.\textsuperscript{130}

A new method for the synthesis of Gd(BH\textsubscript{4})\textsubscript{3}·3THF was published in 1978. It involved intense stirring in THF solution of anhydrous gadolinium trichloride and sodium borohydride.\textsuperscript{131}

\[
\text{GdCl}_3 + 3 \text{NaBH}_4 \xrightarrow{\text{THF}} \text{Gd(BH}_4)_3\text{THF} + 3 \text{NaCl} \tag{36}
\]

The solubility of Gd(BH\textsubscript{4})\textsubscript{3}·3THF and the double borohydride salt, (Li,Gd)(BH\textsubscript{4})\textsubscript{3}·6THF was discussed and the infrared spectrum for the former compound was reported.\textsuperscript{131,132} Upon increasing the temperature of a Gd(BH\textsubscript{4})\textsubscript{3} / THF solution from 0 to 40 °C, the solubility of the material increased from 2.07 to 3.41 mole %.

The borohydride compound containing one retained chloride ion, GdCl(BH\textsubscript{4})\textsubscript{2}·2THF, was prepared as the THF solvate by altering the stoichiometry of the GdCl\textsubscript{3} / [BH\textsubscript{4}]\textsuperscript{−} reaction from a molar ratio of 1:3 to 1:2 (equation 37).\textsuperscript{133-137}

\[
\text{GdCl}_3 + 2 \text{LiBH}_4 \xrightarrow{\text{THF}} \text{GdCl(BH}_4)_2\text{2THF} + 2 \text{LiCl} \tag{37}
\]

The monochlorobistetrahydroborate, GdCl(BH\textsubscript{4})\textsubscript{2}·2THF, compound's chemical behavior was studied. It was found that another new compound, GdCl(B\textsubscript{2}H\textsubscript{6}), could be formed by heating it for 2 hours at 186 °C. The product was isolated after both THF and H\textsubscript{2} had been
GdCl(BH$_4$)$_2$·2THF also reacts with NaOCH$_3$ to produce Gd(OCH$_3$)$_2$(BH$_4$)$_4$.$^{133,136}$

Mixed metal lanthanide / alkali metal complexes, MLn(BH$_4$)$_4$ were synthesized in DME via equation 38. This reaction involves a change in the ratio of reactants and another solvent system.

\[
\text{LnCl}_3 + 4 \text{NaBH}_4 \xrightarrow{\text{DME}} \text{NaLn(BH}_4)_4 \text{DME} + 3 \text{NaCl} \quad (38)
\]

The gadolinium analog, NaGd(BH$_4$)$_4$·4DME, is insoluble in ether. It was characterized by thermal analysis, elemental analysis and infrared spectroscopy.$^{138}$ In 1986, the study of this salt was expanded when it was discovered that heating it in a vacuum sublimator produced the new compound Gd(BH$_4$)$_3$·DME which sublimed out of the bulk solid (equation 39). This monoglyme solvated species was characterized by elemental analysis and infrared spectroscopy.$^{139}$

\[
\text{NaGd(BH}_4)_4 \cdot 4\text{DME} \xrightarrow{\Delta} \text{Gd(BH}_4)_3 \text{DME} + \text{NaBH}_4 + 3 \text{DME} \quad (39)
\]

The related THF solvated compound, LiGd(BH$_4$)$_4$·4THF, was produced by heating LiGd(BH$_4$)$_4$·6THF under vacuum at 50 °C. These materials were characterized by IR spectroscopy.$^{133,140}$
The ethylenediamine adduct of gadolinium borohydride, Gd(BH₄)₃·4en, was synthesized by adding ethylenediamine to Gd(BH₄)₃·3THF dissolved in THF, hexane, benzene or toluene. The reaction was violent and exothermic and so the ethylenediamine was only added very carefully to solid Gd(BH₄)₃·3THF. The resultant compound was characterized by elemental analysis and infrared spectroscopy. Thermal decomposition studies were also performed. ¹⁴¹

The first citation of a gadolinium borane compound other than a borohydride complex was included in a report on rare earth [B₁₂H₂₄]²⁺ salts including Gd₂(B₁₂H₂₄)₃·18H₂O. The IR spectra for the rare earth compounds as well as their rates of hydrolysis in water were compared. The similarity of the IR data indicated that the compounds were ionic in nature. ¹⁴²

A 1977 Russian paper compared the Raman and IR spectra of 35 salts of [B₁₀H₁₀]²⁻ including Gd₂(B₁₀H₁₀)₃. They found that the cation did not influence the IR spectrum of [B₁₀H₁₀]²⁻ due to the ionic nature of the species. ¹⁴³ In 1987, Itoh and co-workers employed an aqueous preparation of the Gd₂(B₁₀H₁₀)₃ as the precursor compound for the synthesis of gadolinium borides. The gadolinium boron cluster compound was prepared by the reaction of gadolinium oxide with H₂B₁₀H₁₀⁻.

\[
3 \text{H}_2\text{B}_{10}\text{H}_{10} + \text{Gd}_2\text{O}_3 \xrightarrow{\text{H}_2\text{O}, \text{pH} > 5} \text{Gd}_2(\text{B}_{10}\text{H}_{10})_3 + 3 \text{H}_2\text{O}
\] (40)
Once prepared, $\text{Gd}_2(\text{B}_{10}\text{H}_{10})_3$ was pyrolyzed to 1200 °C yielding $\text{GdB}_2$, $\text{GdB}_6$, and amorphous boron in varying ratios depending upon the specific reaction conditions.  

A 1989 report in a Chinese journal indicated the synthesis of $\text{Gd}_2(\text{B}_{20}\text{H}_{18})_3$ and $[\text{Gd(bpy)}]_2[\text{B}_{20}\text{H}_{18}]_3$ according to equations 41 and 42. Characterization was performed by elemental analysis, IR spectroscopy, TG-DTA and electrical conductivity.

\begin{equation}
3 \text{H}_2\text{B}_{20}\text{H}_{18} + \text{Gd}_2\text{O}_3 \rightarrow \text{Gd}_2(\text{B}_{20}\text{H}_{18})_3 + 3 \text{H}_2\text{O} \quad (41)
\end{equation}

\begin{equation}
\text{Gd}_2(\text{B}_{20}\text{H}_{18})_3 + 8 \text{bpy} \rightarrow [\text{Gd(bpy)}]_2[\text{B}_{20}\text{H}_{18}]_3 \quad (42)
\end{equation}

The first carborane / gadolinium compound was reported in 1992 by Hosmane and co-workers. The huge cluster complex, $[\{\eta^5-1-\text{Gd}-2,3-(\text{SiMe}_3)_2-2,3-\text{C}_2\text{B}_4\text{H}_4\}_3\{\mu_3-\text{OMe}\}{\mu_2-\text{Li}(\text{C}_4\text{H}_6\text{O})}_3]\{\mu_3-\text{O}\}$, was characterized by single crystal X-ray diffraction. It contained 6 carborane cages, 3 THF molecules, 3 Gd atoms and 6 Li atoms in approximately 3-fold symmetry.

\begin{equation}
\text{GdCl}_3 + \text{Li}_2[2,3-(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4] \rightarrow
[\{\eta^5-1-\text{Gd}-2,3-(\text{SiMe}_3)_2-2,3-\text{C}_2\text{B}_4\text{H}_4\}_3\{\mu_3-\text{OMe}\}{\mu_2-\text{Li}(\text{C}_4\text{H}_6\text{O})}_3]\{\mu_3-\text{O}\} \quad (43)
\end{equation}
E. Statement of the Problem

The initial goal of this study was to investigate the amphoteric nature of ammonia-borane. Though \( \text{H}_3\text{NBH}_3 \) had been known since 1955, very little of its chemical reactivity had been investigated. The molecule is very interesting, however, because opposite chemical reactivity is found at sites which are adjacent to each other in the relatively small molecule. Looking at a schematic diagram of \( \text{H}_3\text{NBH}_3 \) (Figure 7) and comparing electronegativity differences between boron and nitrogen, a partial positive charge resides on the boron atom and a partial negative charge resides on the nitrogen atom. The positive charge on boron should stimulate the attached hydrogen atoms to become negatively charged and hydridic in nature. The negative charge on nitrogen should encourage its attached hydrogens to become positively charged and protonic in nature. An initial guess would be that this opposite behavior could not be observed at sites which are on adjacent atoms.

![Schematic Diagram of Ammonia-Borane](image)

**Figure 7: Schematic Diagram of Ammonia-Borane**
In an effort to determine whether the compound was amphoteric, $\text{H}_3\text{NBH}_3$ was reacted under different conditions. The reaction of $\text{H}_3\text{NBH}_3$ with metal hydrides, $\text{MH}$, indicated that the hydrogens on nitrogen were indeed protonic in nature. The reaction of $\text{H}_3\text{NBH}_3$ with hydrohalic acids, $\text{HX}$, gave an opportunity to illustrate the fact that the hydrogens attached to boron were hydridic in nature.

Once amphotericism had been established, the reactivity of the derivative compounds $\text{H}_3\text{NBH}_2\text{X}$ and $\text{M}[\text{H}_2\text{NBH}_3]$ were to be investigated. Initially the goal was to utilize the hydridic and protonic sites as a window to bimetallic compounds. Further reactivity studies of the derivatives indicated that mixed metal B-N compounds would not be accessible. It was shown, however, that $\text{H}_3\text{NBH}_2\text{Cl}$ was an excellent molecular precursor compound for the production of BN. $\text{M}[\text{H}_2\text{NBH}_3]$ was found to behave as either a ligand or a powerful hydride donor in inorganic reactions. The method of reaction for $[\text{H}_2\text{NBH}_3]^-$ changed depending upon the reduction potential of the other inorganic reactant.

F. Gadolinium Project Goals

Several gadolinium-boron cluster compounds were to be synthesized and characterized in an effort to prepare molecular precursor compounds for thermal decomposition studies. Since the compounds would contain varying ratios of gadolinium atoms to boron atoms, different gadolinium boride phases could hopefully be isolated after pyrolysis. Facile lower temperature routes for the production of known borides are always in demand. They were $[\text{B}_3\text{H}_6]^-$ and $[\text{B}_3\text{H}_{14}]^+$. Two initial boron clusters were chosen. These anions were chosen due to the relative ease of preparation of the starting materials
and due to their long term stability and solubility characteristics.
II. RESULTS AND DISCUSSION

A. Ammonia-Borane's Protonic Nitrogen Hydrogens

1. Preparation of Alkali Metal Derivatives

The chemistry of the aminoborohydride anion, \([H_2NBH_3]^+\), has been expanded as new methods for its synthesis have been explored, new cations have been utilized and new reactivity studies have been performed.

a. Preparation From the Reaction of MH with H_3NBH_3

Three synthetic methods have been employed for the production of M[H_2NBH_3]. The first involves the action of a metal hydride on ammonia-borane. Originally sodium hydride or potassium hydride was employed. In the present study, lithium hydride was also utilized.

\[
\text{H}_3\text{NBH}_3 + \text{MH} \xrightarrow{\text{THF}} \text{M[H}_2\text{NBH}_3] + \text{H}_2 \tag{44}
\]

The three alkali metal hydrides, LiH, NaH, and KH must be reacted under different conditions due to stability and solubility differences of the final products. Li[H_2NBH_3] is the least difficult to synthesize because it requires no special conditions beyond the
exclusion of air. Stirring a solution of LiH and H₃NBH₃ for approximately 4 hours at room temperature produces Li[H₂NBH₃] in 95% yield. The salt is isolated by filtering the THF solution and removing the solvent. When the reaction is attempted at -78 °C, no appreciable reaction occurs after 54 hours. The production of Li[H₂NBH₃] using this method is always accompanied by the formation of small amounts of LiBH₄ and small amounts of an unknown compound that appears in the ¹¹B NMR spectrum as a triplet at -8.64 ppm (J = 101 Hz). The borohydride salt and unidentified triplet are not observed in any of the other reactions with metal hydrides.

The sodium salt, Na[H₂NBH₃], is unstable in THF at room temperature. It is prepared at -78 °C. This lower reaction temperature slows the rate of reaction so the solution must be stirred at least 24 hours to assure a yield over 92%. The Na[H₂NBH₃] is separated by filtering the solution and removing the THF from the filtrate. This reveals the colorless sodium salt, Na[H₂NBH₃].

K[H₂NBH₃] is insoluble in THF and forms a colorless precipitate as it is produced. The optimum reaction conditions for its production are -78 °C for 2 days to obtain a yield of 87%. Because K[H₂NBH₃] does not decompose in THF at room temperature, KH and H₃NBH₃ can be reacted at room temperature but the boron-11 NMR spectrum of the material reveals that several boron-containing species are produced under these conditions. For the synthesis of K[H₂NBH₃], it is best to use an excess of H₃NBH₃ to assure complete reaction of KH. KH is insoluble in THF and its separation from K[H₂NBH₃] is difficult. Care must also be taken that the potassium hydride is completely free of adhering mineral oil or solvent and that the KH and H₃NBH₃ are not shaken together in the absence of
solvent because an avenue exists for a solvent free detonation. The residue after
detonation always contains unreacted KH and H$_3$NBH$_3$, but consists primarily of an off-
white, THF insoluble material which is not K[H$_2$NBH$_3$] as indicated by X-ray powder
diffraction studies.

b. Preparation From the Reaction of M with H$_3$NBH$_3$

The second method for the production of M[H$_2$NBH$_3$] has also been previously
reported. In 1958, Shore and Parry reported that the reaction of elemental sodium with
H$_3$NBH$_3$ released 1/2 equivalent of H$_2$. Based upon the stoichiometry, they envisioned a
reaction like that of equation 45 but made no attempt to further isolate or characterize the
product.  

\[
\text{H}_3\text{NBH}_3 + \text{M} \xrightarrow{\text{NH}_3, \text{-78 C}} \text{M[H}_2\text{NBH}_3\text{]} + \text{1/2 H}_2 \quad (45)
\]

In 1993, Salupo reported that the Yb$^{2+}$ and Eu$^{2+}$ salts of [H$_2$NBH$_3$]$^-$ could be
produced in this ammonia reaction. She obtained IR spectra for the two compounds and
$^{11}$B NMR data for Yb(H$_2$NBH$_3$)$_2$.\textsuperscript{56} The method has now been extended to include
potassium and it has been shown by X-ray powder diffraction, $^{11}$B NMR spectroscopy and
IR spectroscopy that the reaction with elemental potassium produces the same compound
that the reaction with KH produced.
c. Preparation From the Reaction of RLi with H$_3$NBH$_3$

The third method for the production of the aminoborohydride ion is via the reaction of ammonia-borane with either methyllithium or butyllithium at temperatures below 0 °C.

\[
\text{H}_3\text{NBH}_3 + \text{RLi} \underset{0 \text{ °C}}{\xrightarrow{\text{THF}}} \text{Li[H}_2\text{NBH}_3] + \text{RH} \quad (46)
\]

The temperature must be kept low, H$_3$NBH$_3$ must be in excess and the alkylolithium reagent must be added slowly in order to obtain relatively pure Li[H$_2$NBH$_3$]. The reaction with methyllithium is always cleaner than the reaction with butyllithium. Side products in both reactions are probably alkylated and lithiated derivatives of H$_3$NBH$_3$ and M[H$_2$NBH$_3$].

Any Li[H$_2$NBH$_3$] synthesized in this manner must be used immediately. Within 12 hours of being produced when the alkylolithium reagent was CH$_3$Li, both solutions of Li[H$_2$NBH$_3$] and isolated solids decomposed. The boron-11 NMR spectrum of the decomposed solutions indicated the presence of three unknown compounds. These compounds were observed in the boron-11 NMR spectrum as a doublet at -21.27 ppm ($J = 63$ Hz), a triplet at -24.38 ppm ($J = 70$ Hz) and a very broad singlet at approximately -24 ppm as illustrated in Figure 8. A white precipitate was also produced during the decomposition process.
When C$_4$H$_7$Li was utilized in the production of Li[H$_2$NBH$_3$], a white precipitate was again obtained. The boron-11 NMR spectrum of the THF soluble fraction after decomposition consisted of the signal for Li[(B(n-Bu)$_2$)$_4$] (a sharp singlet at -17.93 ppm), two broad singlets at -10.11 ppm and at -24.24 ppm, a doublet at -14.43 ppm ($J = 59$ Hz) and a triplet at -19.63 ppm ($J = 70$ Hz) (Figure 9). Solution decomposition of Li[H$_2$NBH$_3$] synthesized from RLi does not involve the production of [BH$_4$]$^-$. It is possible that the white precipitate contains LiNH$_2$.

Figure 8: Decomposition $^{11}$B NMR Spectrum of Li[H$_2$NBH$_3$] Produced from CH$_3$Li and H$_3$NBH$_3$
Figure 9: Decomposition $^{11}$B NMR Spectrum of Li[H$_2$NBH$_3$] Produced from C$_5$H$_7$Li and H$_3$NBH$_3$. 

$^{11}$B{$^1$H}
d. Characterization

The alkali metal aminoborohydride salts were characterized by NMR spectroscopy, IR spectroscopy, X-ray powder diffraction, and elemental analysis. The $^{11}\text{B}$ and $^1\text{H}$ NMR spectra of $\text{Na[H}_2\text{NBH}_4]$ in THF-$d_8$ are displayed in Figure 10. The other compounds yield similar spectra. Table 2 lists the $^7\text{Li}$, $^1\text{H}$ and $^{11}\text{B}$ NMR chemical shifts of the lithium, sodium and potassium salts. The $^1\text{H}$ NMR spectrum of $\text{K[H}_2\text{NBH}_4]$ is recorded as chemical shift downfield with respect to the solvent $\text{NH}_2$. The proton signal for the $\text{NH}_2$ group lies beneath that of the solvent.

<table>
<thead>
<tr>
<th>M</th>
<th>$^7\text{Li}$ δ (ppm), mult</th>
<th>$^1\text{H}$ δ (ppm), mult, J (Hz)</th>
<th>$^{11}\text{B}$ δ (ppm), mult, J (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>varies s</td>
<td>1.46 q</td>
<td>-22.33 q 87.1</td>
</tr>
<tr>
<td></td>
<td>varies</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>-</td>
<td>1.52 q</td>
<td>-21.96 q 84.2</td>
</tr>
<tr>
<td></td>
<td>varies</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>-</td>
<td>0.77 q</td>
<td>-18.97 q 81.8</td>
</tr>
<tr>
<td></td>
<td>0.00 s</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The NMR spectra of the lithium and sodium salts are recorded in THF-$d_8$. The spectrum of the potassium salt is recorded in ND$_3$. 
Figure 10: $^{11}\text{B}$ and $^1\text{H}$ NMR Spectra of Na[$\text{H}_2\text{NBH}_3$]
The chemical shifts reported in the proton NMR spectrum of the NH$_2$ group and in the lithium-7 NMR spectrum of the lithium ion vary because it has been discovered that the position of the peak can be shifted due to changes in concentration. The signals are shifted upfield as the solution becomes more concentrated. The $^{11}$B NMR chemical shifts for the compounds are also shifted by concentration changes but the boron signal is the least perturbed. Figure 11 illustrates this point with a plot of concentration versus chemical shift for the three nuclei.

![Figure 11: NMR Spectroscopy: Chemical Shift Versus Concentration](image-url)
Change in chemical shift as a function of concentration is attributed to shifts in the equilibrium involving ion-pairing (Figure 12). In very dilute solutions, a solvent separated species would predominate whereas in concentrated solutions, an associated species would be in the majority. The ion pairing of the lithium ion with the nitrogen atom in the ion-paired complex drains electron density from the nitrogen and shifts its resonance upfield. The affect on the boron is the same though to a lesser degree because the boron atom is removed one atom from the lithium. LeChatlier's Principle dictates in which direction the equilibrium lies.

Solvent Separated

![Solvent Separated](image)

Ion-Paired

![Ion-Paired](image)

Figure 12: Equilibrium Involving Solvent Separated and Ion-Paired Complexes
The three alkali metal salts were also characterized by infrared spectroscopy in KBr pellets. Figure 13 and Table 3 compare the NH and BH stretching regions for the three compounds which contain strong, broad BH absorbances and medium intensity, sharp NH stretches.

**TABLE 3**

Infrared Data for $\text{M[H}_2\text{NBH}_3]$

<table>
<thead>
<tr>
<th>$\nu (\text{cm}^{-1})$, intensity</th>
<th>$\text{Li[H}_2\text{NBH}_3]$</th>
<th>$\text{Na[H}_2\text{NBH}_3]$</th>
<th>$\text{K[H}_2\text{NBH}_3]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_{\text{NH}}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3359, m</td>
<td>3369, m</td>
<td>3504, w</td>
<td></td>
</tr>
<tr>
<td>3310, vs</td>
<td>3317, s</td>
<td>3346, m</td>
<td></td>
</tr>
<tr>
<td>3273, m</td>
<td>3303, s</td>
<td>3299, w</td>
<td></td>
</tr>
<tr>
<td>3246, sh</td>
<td>3254, m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_{\text{BH}}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2510, sh</td>
<td>2359, sh</td>
<td>2332, sh</td>
<td></td>
</tr>
<tr>
<td>2349, vs</td>
<td>2329, vs</td>
<td>2250, sh</td>
<td></td>
</tr>
<tr>
<td>2325, vs</td>
<td>2278, s</td>
<td>2182, vs</td>
<td></td>
</tr>
<tr>
<td>2281, vs</td>
<td>2210, s</td>
<td>2169, vs</td>
<td></td>
</tr>
<tr>
<td>2246, vs</td>
<td>2175, vs</td>
<td>2123, sh</td>
<td></td>
</tr>
<tr>
<td>2194, vs</td>
<td>2115, s</td>
<td>2081, s</td>
<td></td>
</tr>
<tr>
<td>2153, vs</td>
<td>2071, s</td>
<td>2021, sh</td>
<td></td>
</tr>
<tr>
<td>2037, sh</td>
<td>2010, sh</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 13: Infrared Spectra of $M[H_2NBH_3]$
X-ray powder diffraction of the three alkali metal salts indicates that they are crystalline materials but attempts to grow single crystals using crown ethers and amine reagents to encapsulate the alkali metal atom failed due largely to long term stability problems in solution.

Lithium aminoborohydride is extremely soluble in THF. It always redissolves when it is reconstituted from a powder. It is insoluble, on the other hand, in other common solvents including Et₂O. Sodium aminoborohydride is initially soluble in THF but loses some solubility once the solvent has been removed. It, unlike Li[H₂NBH₃], is also soluble in Et₂O. As previously stated, K[H₂NBH₃] is insoluble in THF and other common organic solvents. The only solvent located in which it was soluble was ammonia.

All three alkali metal salts show good stability when stored under vacuum or in the nitrogen atmosphere of the glove box. The sodium salt gives no evidence by X-ray powder diffraction of decomposition after 15 days. Samples of K[H₂NBH₃] which have been allowed to age 5 months do show by IR and NMR spectroscopy that decomposition has occurred. These K[H₂NBH₃] samples will also flame when water is added to them. Fresh M[H₂NBH₃] compounds do not flame in water.

e. Solution Decomposition

The decomposition properties of the alkali metal compounds in solution differ extensively. Li[H₂NBH₃] decomposes more slowly in solution than Na[H₂NBH₃]. After several months in THF solution, the once clear solution of Li[H₂NBH₃] becomes thick with large amounts of off-white precipitate as hydrogen gas is evolved. ¹¹B NMR
spectroscopy after complete decomposition reveals only $[\text{BH}_4]^-$ . Boron-11 NMR spectra as the solution is aging show other peaks growing in and then diminishing in intensity as the decomposition nears completion. The intermediate compounds include a very broad singlet at -24 ppm underlying a multiplet (either a doublet or a quartet) at -24.30 ppm ($J = 82$ Hz) and a quartet centered at -21.42 ppm ($J = 83$ Hz) (Figure 14). Li[H$_2$NBH$_3$] also decomposes in the presence of 12-crown-4 and TMEDA.

Figure 14: $^{11}$B NMR Spectrum of Intermediates in THF Decomposition of Li[H$_2$NBH$_3$]
Na[H₂NBH₃] begins to decompose in THF within 8 hours of being warmed to room temperature with the formation of an off-white precipitate and H₂ gas. None of the residue remains THF soluble. No [BH₄]⁻ is seen in the process as the boron-11 NMR spectrum shows no signal from the sample. Na[H₂NBH₃] produces a material which is amorphous to X-rays as it decomposes. It does not re-precipitate NaH as a part of its decomposition process.

A possible explanation for the fact that the Li[H₂NBH₃] decomposition pathway produces [BH₄]⁻ and the Na[H₂NBH₃] decomposition pathway does not could be the fact that the lithium salt already contained a small amount of LiBH₄ from its initial synthesis. This [BH₄]⁻ could catalyze a somewhat different decomposition path which includes its own production.

The intermediates obtained from the THF decomposition of Li[H₂NBH₃] are extremely similar, according to ¹¹B NMR spectroscopy, to those obtained from the THF decomposition of Li[H₂NBH₃] prepared from the reaction of CH₃Li with H₃NBH₃. The differences are that [BH₄]⁻ is not produced in the CH₃Li decomposition process and the multiplicity and coupling constants of the peaks at -21 ppm and -24 ppm are different in the two cases. For the CH₃Li reaction, the coupling constants are 63 Hz (d) and 70 Hz (t), respectively. Here the coupling constants are 83 Hz (d or q) and 82 Hz (q), respectively.

This result gives credence to the theory that long term THF decomposition of Li[H₂NBH₃] produces [BH₄]⁻ because the borohydride ion is already present in the solution. The Li[H₂NBH₃] produced from CH₃Li does not originally contain [BH₄]⁻ in its
solution and it does not decompose to form $[\text{BH}_4]$.

Previous work on the solution phase decomposition of $\text{Na}[\text{H}_2\text{NBH}_3]$ reported that 1/2 of an equivalent of $\text{H}_2$ was lost in the process and that the gas loss was complete after 7 days. Further long term investigation has shown that the process continues to evolve hydrogen through at least 26 days though the rate of gas loss decreases rapidly after 2 weeks. The percentage of $\text{H}_2$ that is released is also considerably greater than 50 %. Values over 100 % were routinely obtained with 193 % for 26 days being the largest volume collected. The loss of two equivalents of $\text{H}_2$ would result in a compound with the formula $\text{M}[\text{NBH}]$. This material would be required to be polymeric in nature in order to satisfy the coordination sites of the boron and nitrogen atoms. The production of similar polymeric compounds with the theoretical formula, $\text{M}[\text{NBR}]$, have been proposed in the literature from the thermal decomposition of $\text{M}[\text{R}_2\text{NBH}_3]$.\textsuperscript{53}

Attempts were made to sublime $(\text{H}_2\text{NBH}_3)_n$ ring compounds from the amorphous residue obtained from the THF decomposition of the sodium salt by heating to 80 °C. At this temperature, $(\text{H}_2\text{NBH}_3)_n$ rings would readily migrate to the cold finger if they were present.\textsuperscript{147} No material was ever found to sublime with temperatures up to 95 °C. The X-ray powder pattern of the heated material remained amorphous.

$\text{K}[\text{H}_2\text{NBH}_3]$ does not decompose in THF because it is insoluble in the solvent. Samples of $\text{K}[\text{H}_2\text{NBH}_3]$ which were left in THF solution for 7 days showed no evidence of change by $^{11}\text{B}$ and $^1\text{H}$ NMR spectroscopy or by X-ray powder diffraction.
f. Thermal Decomposition

Attempts were made to decompose both Na[H₂NBH₃] and K[H₂NBH₃] thermally and to characterize the products. Na[H₂NBH₃] appears to be slightly more thermally stable than K[H₂NBH₃]. It begins to evolve H₂ gas between 80 and 90 °C but only releases a small amount. With an increase in temperature, the rate of gas evolution increases but only slightly. When heated to 103 °C for 3 days, only 38.3 mole % of hydrogen was evolved.

The potassium salt gave off slightly more hydrogen. When heated from 66 to 110 °C for 2 days, 42.0 % of H₂ was evolved with the rate of release again increasing with the increase in temperature. X-ray powder diffraction of the residue showed that it had become an amorphous material which was free of KH.

With neither the sodium or potassium salts, did application of heat encourage the sublimation of (H₂NBH₃)ₙ rings from the amorphous residue or the reformation of the starting metal hydride.

It has been reported in the literature that heating [R₂NBH₃] compounds produces polyanion salts which are polymeric and difficult to analyze. Holliday and Thompson reported that heating K[H₂NBMe₃] at 140 °C for several hours caused the salt to lose 2 moles of methane and to become a sticky amorphous material. ³³

\[
\text{K[H₂NBMe₃]} \rightarrow \text{K[NBMe]} + 2 \text{CH}_₄
\] (47)
The aminoborohydride anion is the hydrogen analog of these \([R_2NBH_3]^+\) compounds and so would be likely to behave in a similar manner.

2. Reactivity of Alkali Metal Derivatives

a. Reactivity As a Hydride Source

Before being able to attempt reactivity studies of the \([H_2NBH_3]^-\) ion, a form of it had to be synthesized with enhanced stability and solubility. It was decided that large alkyl or phenyl ammonium or phosphonium cations might produce salts with this enhanced stability. Many metathesis reactions were attempted with the same failed results. The \(^{11}\) B and \(^1\) H NMR spectra were extremely complicated due to reaction and decomposition within the system.

\[
M[H_2NBH_3] + [R_4A]X \xrightarrow{\text{Decomposition}} (48)
\]

\[
\begin{align*}
R_4A &= \text{Bu}_4N, \text{Et}_4N, \text{BzMe}_3P, \text{MePh}_3P, \text{Ph}_4As \\
X &= \text{Cl}, \text{Br}, \text{I} \\
\text{solvent} &= \text{CHCl}_3, \text{CH}_2\text{Cl}_2, \text{THF}, \text{CH}_3\text{CN}, \text{NH}_3
\end{align*}
\]

These disappointing experiments led to the realization that \([H_2NBH_3]^-\) was attacking the salts. A test reaction was performed with the Lewis acid, BH₃THF, to determine what type of properties the anion had as a base. This reaction led to the discovery that \([H_2NBH_3]^-\) is a powerful hydride donor.
1. Reaction With BH\textsubscript{3} THF

When lithium or sodium aminoborohydride is reacted with borane tetrahydrofuran complex in THF, a clear colorless solution is obtained. The primary boron containing product of the reaction is [BH\textsubscript{4}\textsuperscript{-}] which can be seen clearly in the boron-11 NMR spectrum as a quintet with a coupling constant of 81 Hz at -42 ppm.\textsuperscript{148}

\[
\text{MBH}_4 + \text{THF} + "\text{H}_2\text{NBH}_2" \quad (49)
\]

The stoichiometry of the equation dictates that aminoborane, H\textsubscript{2}NBH\textsubscript{2}, would be the other major product of the reaction. H\textsubscript{2}NBH\textsubscript{2} monomer was never observed in any spectra recorded for [H\textsubscript{2}NBH\textsubscript{3}]\textsuperscript{-} reactions. This is expected, however, because the monomer is an unstable compound and is known to quickly polymerize into an intractable polymeric solid, (H\textsubscript{2}NBH\textsubscript{3})\textsubscript{n}, or to (H\textsubscript{2}NBH\textsubscript{2})\textsubscript{n} ring compounds.\textsuperscript{26, 28, 29, 147, 130, 151} In this reaction, no precipitate of (H\textsubscript{2}NBH\textsubscript{3})\textsubscript{n} was formed but evidence for the production and subsequent reaction of H\textsubscript{2}NBH\textsubscript{2} was obtained. Boron-11 NMR spectroscopy revealed the presence of \(\mu\)-NH\textsubscript{2}B\textsubscript{2}H\textsubscript{5}. The formation of \(\mu\)-NH\textsubscript{2}B\textsubscript{2}H\textsubscript{5} has been theorized to be the result of the reaction of H\textsubscript{2}NBH\textsubscript{2} with one half of a B\textsubscript{2}H\textsubscript{6} molecule. The reaction in equation 50 was interpreted.\textsuperscript{152}

\[
\text{H}_2\text{NBH}_2^{+} + 1/2 \text{B}_2\text{H}_6 \quad \longrightarrow \quad \mu\text{-NH}_2\text{B}_2\text{H}_5 \quad (50)
\]
In the current system, the \( \text{H}_2\text{NBH}_2 \) moiety, once produced, would react with \( \text{BH}_3\text{THF} \) in the solution.

The other major product of the reaction was \( \text{H}_3\text{NBH}_3 \). Boric acid, \( \text{B(OH)}_3 \), and another organylborane compound with the \( ^{11}\text{B} \) NMR spectrum of 26.7 ppm (d, \( J = 163 \) Hz) were also present in the reaction mixture to a lesser degree. The \( ^{11}\text{B} \) NMR chemical shift and coupling constant of the latter compound is indicative of \( \text{BH(OR)}_2 \) compounds including \( \text{BH(OMe)}_2 \), \( \text{BH(OEt)}_2 \), \( \text{BH(OPr)}_2 \) and \( \text{BH(OBu)}_2 \). Lastly, trace quantities of \( [\text{B}_3\text{H}_8]^+ \) and \( \text{BH}_3\text{THF} \) were present in the solution.

2. Reaction With Metal Carbonyl Compounds

When it was established that \( [\text{H}_2\text{NBH}_3]^+ \) is a hydride source, several inorganic hydride transfer reactions were carried out in order to determine the level of hydride donating ability. The first was the reaction with the ruthenium cluster compound ruthenium dodecacarbonyl, \( \text{Ru}_3(\text{CO})_{12} \).

\[
\text{M[}\text{H}_2\text{NBH}_3] + \text{Ru}_3(\text{CO})_{12} \xrightarrow{\text{nrg}} \text{M[Ru}_3(\text{CO})_{11}\text{] + CO + }\text{"H}_2\text{NBH}_2\text{"} (51)
\]

Carbon monoxide bubbled out of the clear, orange solution and the metal hydride signal for \( [\text{HRu}_3(\text{CO})_{11}]^+ \) was observed in the proton NMR spectrum as a singlet at -12.68 ppm. \(^{153}\) Again the \( \text{H}_2\text{NBH}_2 \) monomer was not observed directly but evidence for its production was obtained. The \( ^{11}\text{B} \) NMR spectrum showed that ammonia-borane and
(H₂NBH₃)₂ were produced. (H₂NBH₃)₂ is detected as a triplet in the ¹¹B NMR spectrum at -11.72 ppm with a coupling constant of 101 Hz. This signal is tentatively assigned to the trimer but the literature indicates that the dimer is known to have the same chemical shift and the tetramer and pentamer are calculated to have signals in the same region of the boron spectrum. The presence of this signal indicates that rather than polymerizing and precipitating, some of the H₂NBH₃ produced oligomers.

The second set of hydride transfer experiments involved the reaction with the iron and chromium carbonyl compounds, M(CO)ₙ, to produce the alkali metal salts of the metal formyl anions, [M(CO)ₙ₊₁CHO]:

\[
\text{M[H₂NBH₃] + M'(CO)ₙ} \quad \text{---} \quad \text{M[M'(CO)ₙ₊₁CHO]}
\]

\[
\begin{align*}
\text{M'} & = \text{Fe, Cr} \\
n & = 5, 6
\end{align*}
\]

For the reactions, the Li[Fe(CO)₅CHO] and Li[Cr(CO)₅CHO] were observed in the ¹H NMR spectra as singlets at 14.6 ppm and 14.9 ppm respectively. The boron-¹¹ NMR spectra were very complex with numerous unidentified resonances.

The transformation of iron pentacarbonyl to its formyl derivative has been used by scientists to investigate the reducing ability of other hydride sources. Winter, Cornett and Thompson reported that trialkoxyborohydride and triethylborohydride salts produced the formyl compound, [Fe(CO)₄CHO], in yields of 98 and 69 % while sodium borohydride,
lithium aluminum hydride and potassium hydride resulted in yields of 5, 5 and 0 %, respectively. As an initial estimation, \([\text{H}_2\text{NBH}_3]^+\), which easily produces the formyl ion, can be placed in the listing along with the stronger hydride sources, \(\text{M}[\text{HB(OR)}_3]\) and \(\text{M}[\text{HBR}_3]\). \([\text{H}_2\text{NBH}_3]^+\) has the great advantage over the other hydridic compounds studied based upon the fact that it is safe to use and does not flame in air or water.

3. Reaction With \(\text{ZnCl}_2\)

\(\text{M}[\text{H}_2\text{NBH}_3]\) also reacted with \(\text{ZnCl}_2\) in a temperature sensitive reaction that originally produced \(\text{Zn}(\text{H}_2\text{NBH}_3)_2\) but which, upon warming, precipitated elemental zinc as the zinc compound was reduced.

\[
2 \text{M}[\text{H}_2\text{NBH}_3] + \text{ZnCl}_2 \xrightarrow{\text{THF} \atop -78 \degree \text{C}} \text{Zn}(\text{H}_2\text{NBH}_3)_2 + 2 \text{MCl} \quad (53)
\]

\[
\text{Zn}(\text{H}_2\text{NBH}_3)_2 \xrightarrow{\text{r.t.}} \text{Zn} + [\text{BH}_4]^+ + \text{H}_3\text{NBH}_3 + \text{H}_2 \quad (54)
\]

Initial low temperature \(^{11}\text{B}\) NMR spectroscopy of the \(\text{Zn}(\text{H}_2\text{NBH}_3)_2\) revealed a broad singlet centered at -20.78 ppm. The signal appeared as a broad singlet due to high solvent viscosity. When the NMR tube was warmed above 0 °C, large amounts of white precipitate appeared in the tube and the boron-11 NMR spectrum became complicated.
with numerous signals. The X-ray powder diffraction pattern of the white precipitate indicated that it was sodium chloride. When the counterion was lithium, the LiCl remained dissolved in the THF solvent and was characterized by its X-ray powder diffraction pattern in the final product.

Though complicated, the boron-11 NMR spectrum consistently contained the resonance for Zn(H₂NBH₄)₂ as a quartet at -20.49 ppm with a coupling constant of 89 Hz. Upon aging at room temperature for 4 to 8 hours, hydrogen gas was released and a black precipitate of elemental zinc formed as the Zn(H₂NBH₄)₂ was reduced. After 20 hours at room temperature, 0.78 equivalents of H₂ gas were collected. Continued room temperature decomposition produced more H₂ but the rate of gas release slowed considerably. During the next 24 hours, 0.33 more equivalents of H₂ gas were evolved. After 22 days at room temperature, a total of 1.65 molar equivalents of hydrogen gas (based upon initial moles of ZnCl₂) were collected.

The boron-11 NMR spectrum of the THF soluble fraction after the redox reaction had occurred indicated the presence of [BH₄]⁻ and H₃NBH₃. These two ¹¹B NMR signals increased with time, becoming the strongest signals. For the reaction with Li[H₂NBH₄], the [BH₄]⁻ signal appeared as a sharp quintet at -43.39 ppm with a coupling constant of 82 Hz. For Na[H₂NBH₄], it occurred at -44.76 ppm (quint, J = 83 Hz). These chemical shifts and coupling constants do not agree with the literature values of LiBH₄, NaBH₄ or Zn(BH₄)₂.¹⁴⁸ They are much more likely to result from M[Zn(BH₄)] where M = Li, Na or from Li₂[Zn(BH₄)]. The boron-11 NMR signals for these appear in THF as quintets at -42.0 ppm (J = 83 Hz), -43.5 ppm (J = 84 Hz) and -42.0 ppm (J = 84 Hz),
respectively.$^{148}$

X-ray powder diffraction of the black residue indicated the presence of elemental zinc. According to the boron-11 NMR spectrum, other boron containing species included (BHNH)$_3$.

4. Reaction With $\text{H}_2\text{O}$

$\text{M[H}_2\text{NBH}_3]$ reacts with water according to equation 55.

$$\text{M[H}_2\text{NBH}_3] + \text{H}_2\text{O} \rightarrow \text{H}_2\text{NBH}_3 + \text{MOH} \quad (55)$$

The ammonia-borane was characterized by boron-11 and proton NMR spectroscopy and LiOH was identified by X-ray powder diffraction. In this reaction, the aminoborohydride anion accepts a proton from water in a typical Brønstead-Lowery acid-base reaction.

b. Reactivity As a Ligand

1. Reaction With MgI$_2$

In other reactions of the alkali metal aminoborohydride compounds, the anion behaved as a ligand rather than a hydride source. One example was the reaction with MgI$_2$. 
2 M[H₂NBH₃] + MgI₂ → Mg(H₂NBH₃)₂ + 2 MI (56)

Four products were isolated after the relatively slow reaction was complete. Completion of the reaction was indicated by monitoring the intensity of the resonances for the starting material and product in the boron-11 NMR spectrum. Figure 15 depicts the boron-11 NMR spectrum of a typical reaction after 2 days. Both Li[H₂NBH₃] and Mg(H₂NBH₃)₂ are present in the solution. Figure 16 demonstrates the boron-11 NMR spectrum of Mg(H₂NBH₃)₂ after the reaction is complete. It consists of a quartet at -20.15 ppm with a coupling constant of 89 Hz. Three equivalents of hydrogen gas are released during the reaction as secondary products are produced along with Mg(H₂NBH₃)₂.

The proton NMR spectrum of Mg(H₂NBH₃)₂ after complete reaction and isolation consists of a quartet at 1.25 ppm with a coupling constant of 89 Hz for the BH₃ groups and a broad singlet for the NH₂ group. The position of the resonance for the NH₂ group varies from spectrum to spectrum as a function of concentration. The boron decoupled proton NMR spectrum indicates that the quartet collapses to a singlet when boron is decoupled from hydrogen. This signifies that the quartet is due to the BH₃ group.
Figure 15: $^{11}$B NMR Spectrum of a $\text{M[H}_2\text{NBH}_3]$ / $\text{Mg(H}_2\text{NBH}_3)_2$ Mixture
$^{11}\text{B}'$ NMR Spectrum of Mg(H$_2$NBH$_3$)$_2$

Figure 16: $^{11}\text{B}$ NMR Spectrum of Mg(H$_2$NBH$_3$)$_2$
The infrared spectrum of Mg(H$_2$NBH$_3$)$_2$ consists of 2 very sharp NH stretches and several strong overlapping BH absorbances (Figure 17).
Mg(H₂NBH₃)₂ is soluble in both THF and Et₂O. It shows good stability when stored under nitrogen. Boron-11 NMR spectroscopy of samples aged for 8 months remained unchanged. Mg(H₂NBH₃)₂ is crystalline according to its X-ray powder diffraction pattern but attempts to grow good crystals failed.

The secondary products produced along with Mg(H₂NBH₃)₂ included a colorless precipitate which was insoluble in THF. It was therefore separated by washing it with THF. The infrared spectrum of the THF insoluble solid is depicted in Figure 18. The weak BH absorbances diminished upon repeated washes with THF. This suggests that their source is contamination with impurities. In one experiment, the solid was determined to contain NH₄I by its X-ray powder diffraction pattern. Based upon this result and the IR spectrum of the solid in the NH stretching region, an ammonium salt is suggested.

The second unidentified side product was insoluble in Et₂O; it was separated from Mg(H₂NBH₃)₂ with an Et₂O wash. The infrared spectrum of the THF soluble solid is reproduced in Figure 19. The unknown colorless solid was no longer soluble in THF after having been washed with Et₂O. Based upon the strong broad absorbances in the NH and BH stretching regions of the IR spectrum, it is possible that this solid is some sort of BN polymer or ring compound. Sublimation, however, did not cause the known ring compounds to sublime from the residue. The second solid reacted with water in a vigorous reaction that evolved gas and produced H₂NBH₃. A secondary product of the reaction with water was indicated by a broad singlet in the boron-11 NMR spectrum at 3.11 ppm.
X-ray powder diffraction studies of the two unknown solids showed that the majority of the bands repeated from X-ray pattern to X-ray pattern but that the complete profile was not reproducible. Upon comparing the patterns of the 2 solids to each other, it was noted that they had some X-ray powder diffraction d spacings in common but the majority of the bands were dissimilar. The similarities were likely to be the result of cross contamination of the samples.

![Infrared Spectrum of the THF Insoluble Precipitate](image)

**Figure 18: Infrared Spectrum of the THF Insoluble Precipitate**
Figure 19: Infrared Spectrum of the THF Soluble Solid
As isolated samples of Mg(H₂NBH₃)₂ age in THF solution, a white precipitate forms and the boron-11 and proton NMR spectra indicate the presence of small amounts of ammonia-borane in solution. Since the original reaction can take 5 to 8 days to reach completion, it is reasonable to assume that this decomposition process is occurring during the reaction and causing the formation of the secondary products.

The fourth product of the reaction, LiCl, is soluble in both THF and Et₂O. It was identified by its characteristic X-ray powder diffraction pattern in the final product.

2. Reaction With (C₅H₅)₂ZrCl₂

Mg[H₂NBH₃] reacts with zirconocene dichloride in a reaction that produces two products in varying ratios depending upon the reaction stoichiometry and the alkali metal used.

\[ 3 \text{Mg[H₂NBH₃]} + 2 (\text{C₅H₅})₂\text{ZrCl₂} \xrightarrow{\text{THF}} (\text{C₅H₅})₂\text{ZrCl}(\text{H₂NBH₃}) + (\text{C₅H₅})₂\text{Zr[H₂NBH₃]₂} + 3 \text{MCl} \]  

(57)

In the reaction of Li[H₂NBH₃] with (C₅H₅)₂ZrCl₂ in a 2:1 molar ratio, both (C₅H₅)₂Zr[H₂NBH₃]₂ and (C₅H₅)₂ZrCl(H₂NBH₃) were produced along with other minor secondary products. When the stoichiometry was reduced to 1:1, the zirconium monochloride compound, (C₅H₅)₂ZrCl(H₂NBH₃), began to predominate. Attempts to force the reaction toward the production of (C₅H₅)₂Zr(H₂NBH₃)₂ exclusively using a 3:1
molar ratio were unsuccessful as hydrogen was given off and H\textsubscript{3}NBH\textsubscript{3} and NH\textsubscript{4}Cl were produced. Unreacted (C\textsubscript{3}H\textsubscript{5})\textsubscript{2}ZrCl\textsubscript{2} and unknown boron containing materials were also present though in the minority.

Figure 20 presents the boron-11 NMR spectrum of a mixture of (C\textsubscript{3}H\textsubscript{5})\textsubscript{2}ZrCl(H\textsubscript{2}NBH\textsubscript{3}) and (C\textsubscript{3}H\textsubscript{5})\textsubscript{2}Zr(H\textsubscript{2}NBH\textsubscript{3})\textsubscript{2}. The compound containing one chloride ion has a signal downfield (-23.08 ppm) from the compound containing no chlorine which appears at -34.12 ppm.

Potassium aminoborohydride reacting in a 1:1 molar ratio with (C\textsubscript{3}H\textsubscript{5})\textsubscript{2}ZrCl\textsubscript{2} produced only (C\textsubscript{3}H\textsubscript{5})\textsubscript{2}ZrCl(H\textsubscript{2}NBH\textsubscript{3}) but K[H\textsubscript{2}NBH\textsubscript{3}] is THF insoluble and so the yield was minuscule. Even after reacting 11 days, \textsuperscript{1}H NMR spectroscopy and X-ray powder diffraction revealed that K[H\textsubscript{2}NBH\textsubscript{3}] and (C\textsubscript{3}H\textsubscript{5})\textsubscript{2}ZrCl\textsubscript{2} were the major components of the solution.
Figure 20: $^{11}$B NMR Spectrum of a $(\text{C}_2\text{H}_5)_2\text{ZrCl}((\text{H}_2\text{NBH}_3)_2 / (\text{C}_2\text{H}_5)_2\text{Zr}((\text{H}_2\text{NBH}_3)_2)_2$ Mixture
Differences in reaction products with changing ratios of reactants were also noted when the alkali metal counterion was varied. Reactions involving sodium as the counterion to [H\textsubscript{2}NBH\textsubscript{3}\textsuperscript{-}] tended to produce a larger ratio of (C\textsubscript{3}H\textsubscript{5})\textsubscript{2}ZrCl(H\textsubscript{2}NBH\textsubscript{3}) to (C\textsubscript{3}H\textsubscript{5})\textsubscript{2}Zr(H\textsubscript{2}NBH\textsubscript{3})\textsubscript{2} than reactions utilizing the lithium ion. These reactivity differences are likely to be related to the equilibrium reactions which are established in the lithium system. LiCl is soluble in THF and therefore remains ionized and ready to shift the equilibria (equations 58 and 59) in either direction. When Na[H\textsubscript{2}NBH\textsubscript{3}] is the reactant, NaCl precipitates from solution and prohibits the formation of any equilibria in the solution.

\[
\text{M[}H\textsubscript{2}NBH\textsubscript{3}] + (C\textsubscript{3}H\textsubscript{5})\textsubscript{2}ZrCl_2 \rightleftharpoons (C\textsubscript{3}H\textsubscript{5})\textsubscript{2}ZrCl(H\textsubscript{2}NBH\textsubscript{3}) + \text{MCl} \quad (58)
\]

\[
\text{M[}H\textsubscript{2}NBH\textsubscript{3}] + (C\textsubscript{3}H\textsubscript{5})\textsubscript{2}ZrCl(H\textsubscript{2}NBH\textsubscript{3}) \rightleftharpoons (C\textsubscript{3}H\textsubscript{5})\textsubscript{2}Zr(H\textsubscript{2}NBH\textsubscript{3})\textsubscript{2} + \text{MCl} \quad (59)
\]

The reaction of Na[H\textsubscript{2}NBH\textsubscript{3}] with (C\textsubscript{3}H\textsubscript{5})\textsubscript{2}ZrCl\textsubscript{2} at -78 °C produced no evidence of NaCl formation after 24 hours. After warming the solution, a precipitate eventually formed but boron-11 NMR spectra of the sample indicated the presence of only H\textsubscript{3}NBH\textsubscript{3}. Proton NMR spectra indicated that unreacted (C\textsubscript{3}H\textsubscript{5})\textsubscript{2}ZrCl\textsubscript{2} was also present. X-ray powder diffraction studies of the isolated solid after solvent evaporation gave evidence for NH\textsubscript{4}Cl.
Figure 21 depicts the infrared spectrum of \((\text{C}_5\text{H}_5)_2\text{ZrCl(H}_2\text{NBH}_3)\) and Figure 22 illustrates the IR spectrum of a mixture of \((\text{C}_5\text{H}_5)_2\text{ZrCl(H}_2\text{NBH}_3)\) and \((\text{C}_5\text{H}_5)_2\text{Zr(H}_2\text{NBH}_3)_2\). The NH and BH stretches of \((\text{C}_5\text{H}_5)_2\text{ZrCl(H}_2\text{NBH}_3)_2\) (3395, 3304, 2376 and 2304 cm\(^{-1}\)) lie adjacent to those of \((\text{C}_5\text{H}_5)_2\text{ZrCl(H}_2\text{NBH}_3)\) which appear at 3383, 3280, 2405, 2393 and 2319 cm\(^{-1}\). The absorbances for \((\text{C}_5\text{H}_5)_2\text{Zr(H}_2\text{NBH}_3)_2\) appear at higher wavenumbers in the NH stretching region and at lower energy in the BH stretching region.

![Infrared Spectrum of \((\text{C}_5\text{H}_5)_2\text{ZrCl(H}_2\text{NBH}_3)\)](image)

**Figure 21:** Infrared Spectrum of \((\text{C}_5\text{H}_5)_2\text{ZrCl(H}_2\text{NBH}_3)\)
Figure 22: Infrared Spectrum of a (C₅H₅)₂ZrCl(H₂NBH₃) / (C₅H₅)₂Zr(H₂NBH₃)₂ Mixture
Addition of acetone to a mixture containing \((\text{C}_5\text{H}_5)_2\text{Zr(H}_2\text{NBH}_3)_2\) and \((\text{C}_5\text{H}_5)_2\text{ZrCl(H}_2\text{NBH}_3)\) produced \(\text{B(OMe)}_3\) and metallic zirconium.

c. Conclusion

Differences in the reactivity of the \([\text{H}_2\text{NBH}_3]^+\) anion with inorganic metal compounds can best be explained by comparing the reduction potentials of the metals involved (Table 4).

<p>| TABLE 4 |
|-----------------|-----------------|
| <strong>Reduction Potentials of Selected Metals</strong> |</p>
<table>
<thead>
<tr>
<th>Metal</th>
<th>Reduction Potential (V) $^{105}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>-3.0401</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>-2.71</td>
</tr>
<tr>
<td>K$^+$</td>
<td>-2.931</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>-2.372</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>-2.407</td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>-2.22 $^{157}$</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>-0.7618</td>
</tr>
<tr>
<td>Cu$^+$</td>
<td>+0.521</td>
</tr>
</tbody>
</table>
Copper is included in the list because the reaction of \( \text{P(C}_6\text{H}_5)_3\text{CuBr} \) with \( \text{M[H}_2\text{NBH}_3] \) was performed. An orange-red color indicative of copper hydride was immediately observed in the reaction flask but \(^{11}\text{B} \) and \(^1\text{H} \) NMR spectroscopy, IR spectroscopy and X-ray powder diffraction studies of the reaction mixture could not conclusively identify any of the products.

In the cases where the reduction potential is large and negative, \([\text{H}_2\text{NBH}_3]^-\) behaves as a ligand. For example, the alkali metals have large negative reduction potentials ranging from -3.04 to -2.71 V. These values indicate that the reduction of these metals in aqueous media is difficult. This redox stabilization allows the \( \text{M[H}_2\text{NBH}_3] \) compounds to resist reduction.

In instances where the value is positive, hydride transfer occurs. Zinc's reduction potential is intermediate and with \([\text{H}_2\text{NBH}_3]^-\) it behaves in an intermediate manner. At low temperatures, \([\text{H}_2\text{NBH}_3]^-\) is a ligand to zinc forming \( \text{Zn(H}_2\text{NBH}_3)_2 \). Upon warming, \([\text{H}_2\text{NBH}_3]^-\) reduces the zinc to its elemental form as several boron containing species are produced.
B. Ammonia-Borane's Hydridic Boron Hydrogens

1. Preparation of Halide Derivatives

a. $\text{H}_3\text{NBH}_2\text{Cl}$

As noted in an earlier work in the Shore group, ammonia-borane reacts with anhydrous hydrochloric acid in ethereal solvent to produce the monochlorinated derivative, $\text{H}_3\text{NBH}_2\text{Cl}$, in a 97% yield. This synthesis has been expanded to include reaction with hydrobromic acid which produces $\text{H}_3\text{NBH}_2\text{Br}$ in a 92% yield. The reaction is given in equation 59. $X$ can be substituted by Cl or Br.

\[
\text{Et}_2\text{O} \quad \text{room temp.} \quad \text{H}_3\text{NBH}_2 + \text{HX} \rightarrow \text{H}_3\text{NBH}_2\text{X} + \text{H}_2 \quad (59)
\]

The boron-11 NMR spectrum of ammonia-monochloroborane in deuterated acetonitrile is a 1:2:1 triplet centered at -8.87 ppm. The proton NMR spectrum of the compound exhibits a 1:1:1:1 quartet at 2.58 ppm for the hydrogens in the BH$_2$Cl unit and a 1:2:1 triplet at 4.35 ppm for the NH$_3$ unit (Figure 23).
Figure 23: $^{11}$B and $^1$H NMR of H$_3$NBH$_2$Cl
The infrared spectrum of H$_3$NBH$_2$Cl has been recorded in a KBr pellet. The NH and BH stretching regions for it are depicted in Figure 24. The NH stretches at 3295, 3232, 3189 and 3142 cm$^{-1}$ are very similar in position and overall peak shape to those obtained at 3313, 3252, 3195 and 3175 cm$^{-1}$ for H$_3$NBH$_3$ in a KBr pellet. The BH stretching regions of H$_3$NBH$_2$Cl and H$_3$NBH$_3$ are not similar.
H$_3$NBH$_2$Cl is soluble in Et$_2$O and THF and it is partially soluble in CH$_3$CN. It decomposes with the evolution of gas and the production of an insoluble material in CHCl$_3$ and pyridine.

b. H$_3$NBH$_2$Br

The appearance of the boron-11 and proton NMR spectra of ammonia-monobromoborane is the same as the spectra for the analogous chlorinated species except that the peak positions are different. The similarity between the two compounds ends here, however. Ammonia-monobromoborane exhibits very different chemical behavior. Whereas H$_3$NBH$_2$Cl is soluble in Et$_2$O and THF, H$_3$NBH$_2$Br is only slightly soluble in both and forms a precipitate as it is produced. H$_3$NBH$_2$Br is also unstable when solvent is removed from its environment. It decomposes, first to an oil and with consistent evacuation, to an off-white solid. The decomposition of H$_3$NBH$_2$Br involves effervescence but the gas is shown by gas mass spectral analysis to be Et$_2$O. It is not H$_2$, HBr or any other substance which was originally a part of the H$_3$NBH$_2$Br molecule. The decomposition residue contains H$_2$NBH$_3$Br, H$_3$NBH$_3$, (BHNH)$_3$, $\mu$-NH$_2$B$_2$H$_5$, Et$_2$OBH$_3$ and Et$_2$BH. All of these compounds were identified by their $^{11}$B NMR spectra in diethyl ether. The residue also contains large amounts of an Et$_2$O insoluble material which was not characterized by the $^{11}$B NMR spectrum.

The presence of these boron compounds in a Et$_2$O solution containing H$_3$NBH$_2$Br has been noted before. When Geanangel reacted H$_3$NBH$_3$ and BBr$_3$ in Et$_2$O solution for 18 hours, the resulting $^{11}$B NMR spectrum indicated the presence of all of the above
compounds except $\text{H}_3\text{NBH}_3$. 97

As stated before, $\text{H}_3\text{NBH}_2\text{Br}$ is slightly soluble in $\text{Et}_2\text{O}$ and THF. It decomposes in both solvents upon standing. The products of the decomposition in $\text{Et}_2\text{O}$ include a white precipitate along with $\mu$-NH$_2$B$_2$H$_6$, $\text{H}_3\text{NBH}_3$, B(OEt)$_3$, (H$_2$NBH$_3$)$_3$, (BHNNH)$_3$, BH(OEt)$_2$, Et$_2$OBH$_2$Br, and Et$_2$O-BH$_2$. $\text{H}_3\text{NBH}_2\text{Br}$ is insoluble in methylene chloride and hexane and decomposes with effervescence in chloroform, acetonitrile and pyridine.

c. $\text{H}_3\text{NBHCl}_2$

Unlike previously recorded, 55 $\text{H}_3\text{NBHCl}_2$ can be produced from the conditions used for the production of the monochloro compound if an excess of hydrochloric acid is added to the ammonia-borane. This $\text{H}_3\text{NBHCl}_2$ can be seen clearly in the boron-11 NMR spectrum as a doublet at -1.21 ppm with a coupling constant of 147 Hz. The NH$_3$ group is observed in the proton NMR spectrum as a triplet at 4.99 ppm ($J = 47$ Hz). The BHCl$_2$ unit cannot be seen in the proton NMR spectrum due to overlap with the BH$_2$Cl signal of the monochloro compound. $\text{H}_3\text{NBHCl}_2$ is always accompanied by $\text{H}_3\text{NBH}_2\text{Cl}$ and so cannot be studied beyond NMR spectroscopy. The solubility of $\text{H}_3\text{NBH}_2\text{Cl}$ and $\text{H}_3\text{NBHCl}_2$ in $\text{Et}_2\text{O}$, THF and $\text{CH}_3\text{CN}$ is the same so separation is not feasible. Figure 25 demonstrates the $^{11}$B and $^1$H NMR spectra of a $\text{H}_3\text{NBH}_2\text{Cl} / \text{H}_3\text{NBHCl}_2$ mixture.

It is likely that Niedenzu was not able to synthesize $\text{H}_3\text{NBHCl}_2$ from the procedure because he attempted to add a second equivalent of HCl to $\text{H}_3\text{NBH}_2\text{Cl}$ after it had already been produced and isolated. This method utilizes an excess of HCl initially in the experiment.
H₂NBHCl₂ is much less stable than H₂NBH₂Cl. It decomposes within 24 hours of production. H₂NBH₂Cl on the other hand, begins to decompose soon after production but is only completely decomposed after several weeks in solution.

2. Reactivity of the Halide Derivatives

a. Reaction With H₂O

Ammonia-monochloroborane reacts with water according to equation 60.

\[
\text{H}_2\text{NBH}_2\text{Cl} + 3 \text{H}_2\text{O} \rightarrow \text{B(OH)}_3 + \text{NH}_4\text{Cl} + 2 \text{H}_2
\]  

(60)

The products of the reaction were identified using several techniques. \(^{11}\) B NMR spectroscopy identified boric acid. X-ray powder diffraction identified ammonium chloride and hydrogen was identified by its gas mass spectrum. The reaction is exothermic, animated and rapid.
Figure 25: $^{11}$B and $^1$H NMR Spectra of a H$_3$NBH$_2$Cl / H$_3$NBHCl$_2$ Mixture
b. Vacuum Decomposition

Solid $\text{H}_3\text{NBH}_2\text{Cl}$, if allowed to decompose under vacuum, releases one equivalent of $\text{H}_2$ gas and produces a white residue. Based upon the stoichiometry of gas evolution, the following reaction is suggested:

$$\text{H}_3\text{NBH}_2\text{Cl} \xrightarrow{\text{vacuum}} \text{H}_2\text{NBHCl} + \text{H}_2$$  \hspace{1cm} (61)

In an earlier work, Niedenzu produced a compound with the same composition from the thermal decomposition of $\text{H}_3\text{NBH}_2\text{Cl}$ at 58 °C. Elemental analysis confirmed the empirical formula. The X-ray powder data for $\text{H}_2\text{NBHCl}$ produced in the two manners agree with one another.

c. Thermal Decomposition to BN

The most interesting reactivity of $\text{H}_3\text{NBH}_2\text{Cl}$ is observed in thermal decomposition studies of the compound. When heated to 58 °C, $\text{H}_3\text{NBH}_2\text{Cl}$ begins to decompose in a flurry of activity and with the release of 1.58 equivalents of hydrogen gas. If pyrolysis is continued to 1100 °C, turbostratic boron nitride is recovered as more $\text{H}_2$ gas is released along with HCl gas according to equation 62. This procedure for BN production has been patented by our group.
Turbostratic boron nitride is the semi-crystalline form of BN that is generally obtained at temperatures as low as 1100 °C. In this morphology, the BN planes have formed but have not lined up to form ordered layers.\textsuperscript{97,101,138}

The pyrolysis was performed in a step-wise manner and the gases at each temperature were collected, measured, and identified by their gas mass spectra. The increments for the pyrolysis followed the temperature profile: 58 - 116 - 200 - 400 - 600 - 800 - 1100 °C. Residence times for each temperature of 6 - 24 hours were maintained.

Hydrogen gas began to evolve at 58 °C and continued to be released up to approximately 800 °C. HCl was first emitted above 100 °C and continued to be released throughout the procedure. Several experiments were run where the condensible and non-condensible gases were separated and measured at each temperature of the profile. While this data was not reproducible from one temperature to another, the overall profile was reproducible. A optimum total gas yield of 94.3 % was obtained.
Figure 26 presents a typical gas evolution profile with a large gas loss at 58 °C, an increase in gas production at 400 °C, and the emissions tapering off after that.

The increase in the gas evolution at 400 °C is primarily the result of a surge in HCl production. This is an interesting result because previous thermogravimetric data of the pyrolysis gave no evidence of a gas increase at this temperature. 
The sublimed residue and bulk material were also analyzed at each temperature by X-ray powder diffraction and FAB mass spectra. The powder data were not reproducible. They also did not agree with published patterns for \((H_2NBH_2)_n\) rings or polymer. FAB mass spectra for all of the bulk samples indicated the presence of a substance with a very high molecular weight. This FAB data suggests that the residues were being converted to BN within the instrument. The major accomplishment of these experiments was the knowledge that NH\(_4\)Cl sublimes out of the furnace beginning at approximately 100 °C. It sublimes in varying amounts depending upon reaction conditions. It was also discovered that turbostratic BN begins to appear in the bulk powder at about 400 °C which is also the temperature at which the majority of the gas has been released. The X-ray powder pattern for turbostratic BN grows in intensity with each temperature increase from 400 to 1100 °C.

The sublimation of ammonium chloride from the furnace as the reaction proceeds indicates that the reaction in equation 63 could also be occurring.

\[
n\text{H}_2\text{NBH}_2\text{Cl} \xrightarrow{\Delta} \text{NH}_4\text{Cl} + (\text{BH})_n
\]

No direct evidence for the production of BH polymer was obtained from X-ray powder diffraction studies. It may also have sublimed out of the furnace but it was never detected.
The pyrolysis of $\text{H}_3\text{NBH}_2\text{Br}$ follows a very different process than that of $\text{H}_3\text{NBH}_2\text{Cl}$ due to the fact that a mixture of substances is being heated. The same temperature profile was followed for the monobromo case as for the monochloro case in an effort to keep one variable constant. By 58 °C under vacuum, the ammonia-monobromoborane residue also undergoes an animated decomposition process but it decomposes with the evolution of both $\text{H}_2$ and $\text{HBr}$ gas. The loss of these two gases continues to 200 °C for $\text{H}_2$ and to 400 °C for $\text{HBr}$. This is different from $\text{H}_3\text{NBH}_2\text{Cl}$ pyrolysis. Beginning at 200 °C, the two systems really begin to diverge. In the bromine system, at 200 °C, hydrocarbon fragments begin to emerge as condensible gas. This continues to 1100 °C. At 400 °C, non-condensible $\text{N}_2$ gas is also evolved and continues throughout the pyrolysis procedure.

When $\text{H}_3\text{NBH}_2\text{Cl}$ is pyrolyzed to 1100 °C, BN is produced. The BN synthesized in the pyrolysis was characterized by several techniques including X-ray powder diffraction (Figure 27) and diffuse reflectance infrared spectroscopy (Figure 28). The results of both of these techniques agree with published values.\textsuperscript{101, 104, 158, 159} The diffuse reflectance IR spectrum especially indicates that the BN is free of the extraneous CH and OH stretches that are often found in commercial BN sources.\textsuperscript{101}

As with $\text{H}_3\text{NBH}_2\text{Cl}$ pyrolysis, the production of BN in the $\text{H}_3\text{NBH}_2\text{Br}$ system is accompanied by sublimation. $\text{NH}_3\text{Br}$ and unknown crystalline substances sublime out of the furnace beginning at 58 °C. X-ray powder diffraction and infrared spectroscopy studies of the bulk product indicate that BN is produced but that it is contaminated with $\text{NH}_3\text{Br}$ and other unknown crystalline materials.
Figure 27: X-ray Powder Diffraction Pattern of BN at 1100 °C
Figure 28: Diffuse Reflectance IR Spectrum of BN at 1100 °C
Two methods were attempted to obtain a yield for the BN system. They were by mass and by gas evolution volumes. Both failed due to the fact that at 58 °C, the powder becomes very mobile during its decomposition and scatters all over the tube. During this movement, some of the solid splatters out of the furnace. Several sizes and shapes of boats, crucibles and tubes with out-gassing holes fabricated from quartz, platinum and stainless steel were manufactured to try to resolve the problem. The result was the same in all instances. The out-gassing at 58 °C forced the lid off of the vessels and caused the powder to be spilled into the outer quartz tube. NH₄Cl, of course, was also able to sublime in these experiments. The scattering made impossible a yield by mass and also made attempts to obtain a yield by gas evolution difficult. Since all of the solid did not remain within the furnace, it was not all pyrolyzed to BN. The best yield obtained by measuring H₂ and HCl gas volumes was 94.3 %.

The molecular precursor compound, H₃NBH₂Cl, was often somewhat solvated when pyrolysis began. This also made a yield by weight difficult to obtain. The solvation persisted even though the solid had been continuously evacuated overnight. The degree of solvation varied and was unknown. This uncertainty precluded obtaining an accurate mass of the precursor compound.

An accurate yield by gas evolution was also obstructed by the fact that at 800 and 1100 °C, the volume of H₂ and HCl gas that is released is extremely small. These volumes were difficult to quantify using the Töpler system which is geared to larger volumes of gases.
Scanning electron microscopy photomicrographs were taken of pieces of BN at many different magnifications. Figures 29 and 30 display the BN topology at magnifications of 60 X, 300 X and 1000 X. From the photo at 60 X, one can see that the surface is very rough and that out-gassing tunnels riddle the surface. At 300 X, one can see the holes more clearly. At 1,000 X, the camera zooms down to explicitly show that the surface has a layered texture to it. This layering is indicative of turbostratic boron nitride.

Attempts were made to measure the density of this light, airy BN material. All attempts failed due to the fact that it was impossible to remove all of the entrapped air for an accurate volume measurement. In one experiment, the BN was thoroughly ground to assure that it would not float on the surface of the chlorobenzene solvent but after 12 hours, gas bubbles were still escaping the system. Of course after this amount of time, the chlorobenzene had evaporated to an unknown extent.

Occasionally during a pyrolysis experiment, the resultant BN powder would be off-white or tan colored rather than white with the color change generally beginning at 600 °C. Attempts were made to determine what was causing the discoloration and to determine the identity of the impurity. Several samples were sent off for elemental analysis for the presence of elemental carbon but the results showed that the carbon content was less than 0.1 %. A very low carbon content is expected for this system due to the fact that the only carbon containing species in the procedure is Et_2O which has been volatilized by 58 °C and lacks the opportunity to be pyrolyzed to black elemental carbon.
Figure 29: SEM Photomicrograph of BN Powder at 60 X and 300 X
Figure 30: SEM Photomicrograph of BN Powder at 1000 X
Energy dispersive X-ray spectroscopy (EDS) was performed on tan and brown BN samples to analyze for trace impurities. Both samples contained silicon and chlorine as impurities that could originate from the preparation. The silicon could have been leached from the quartz tubing during pyrolysis and the chlorine would come from Cl that was not removed from the sample as HCl gas or sublimed out as NH₄Cl. The spectra also indicated the presence of oxygen and aluminum. These contaminants are artifacts of the atmosphere within the instrument and the aluminum stage upon which the sample sits, respectively.

Figure 31: EDS Plot of a BN Sample
An ESCA survey was also obtained of the BN powder as shown in Figure 32. The profile only indicated the presence of boron and nitrogen in the sample. Carbon and oxygen are present in the spectrum as background atmosphere contaminants.

Figure 32: ESCA Survey of BN Powder
In an effort to maximize the quality and quantity of the BN produced, a host of variables were targeted sequentially to determine which could be causing the brown discoloration. The following discussion includes some of the variables not previously mentioned.

Neither a dynamic nor static vacuum forced the BN to remain white. A dynamic vacuum, however, had the unfortunate drawback of reducing the yield. This lowered productivity occurred because the incessant evacuation encouraged the sublimation of \( \text{NH}_4\text{Cl} \). Though constant evacuation is not recommended, the tube must be evacuated occasionally due to the immense volume of gas that is evolved as the sample is heated. If the tube is not vented, the large pressure would cause the tube to explode. Evacuating frequently is preferred to sporadically but both result in tan BN samples.

The volume of the tube also did not alter the BN color but did play a part in determining the amount of sublimation that occurred. The volume influenced sublimation in the same manner that a dynamic vacuum increased sublimation. A larger volume allowed for greater sublimation. It also was not important whether the tubes were new or had been cleaned out and were being re-used. Both could produce samples of BN that were tan.

As previously stated, residence times of 6 to 24 hours at temperature were used with the preparation though these times could probably be lowered even further. Residence time did not affect BN color. One exception was noted. Ramping the temperature from 25 to 1100 °C as quickly as the instrument could go always produced a BN sample that was brown.
Samples that contained \( \text{H}_3\text{NBHCl}_2 \) prior to pyrolysis had no greater likelihood of producing tan BN than precursor without the impurity. The results did indicate, however, the possibility that samples including the dichloride sublimed more ammonium chloride.

All attempts to alter the method of heating including: cooling between temperatures, maintaining the temperature during gas measurement, bringing the furnace to temperature prior to insertion of the tube and allowing the tube to warm along with the furnace showed no change in the color of the BN. All could be tan.

The source of the \( \text{H}_3\text{NBH}_3 \) also did not seem to be a factor. Both starting materials purchased from Aldrich and samples produced in the laboratory on occasion led to tan BN samples.

Attempts were made to heat the \( \text{H}_3\text{NBH}_2\text{Cl} \) to 200 °C in one vessel and then to transfer the bulk material to a second vessel for continued pyrolysis. This allowed separation of BN precursor from sublimed material in case the sublimed material was somehow linked to the discoloration. This procedure also allowed the isolated BN powder to be discolored.

It is possible that the sublimation of \( \text{NH}_4\text{Cl} \) is a key to the question. If \( \text{NH}_4\text{Cl} \) does sublime due to the reaction in equation 63, then possibly the tan color is due to the other product, \((\text{BH})_n\) polymer. This material could be pyrolyzed in the furnace to black elemental boron. All attempts to detect excess boron in the BN samples by EELS, elemental analysis, solid state boron-11 NMR spectroscopy and EDS spectroscopy did not produce conclusive evidence for its existence.
d. Thermal Decomposition Under NH₃ Flow

Based upon work reported by Sneddon and co-workers on the related compound Me₂SBHBr₂, the pyrolysis of H₃NBH₄Cl was carried out under a constant flow of ammonia gas. The BN produced in this manner was never discolored. The flow of gas, however, did cause the draw back of a reduced yield as the sample was blown out of the furnace by the gas sweeping through.

As a control reaction, a sample was pyrolyzed under a flow of argon gas to determine whether the important factor was a flowing gas or whether it was NH₃ that made the difference. The resultant product consisted of a few shiny brown kernels of material that was not BN according to X-ray powder diffraction studies. Large amounts of shiny sublimed solid were also produced.

Samples of BN produced with NH₃ flow were analyzed along with samples produced under vacuum by both serial EELS (SEELS) and parallel EELS (PEELS). In the SEELS experiment, the data were ± 10 - 12 % in accuracy. When the NH₃ flow sample was compared to the vacuum sample, the sample formed under NH₃ flow seemed to contain excess nitrogen and the one produced under vacuum seemed to be nitrogen deficient.

In the PEELS experiments no systematic variation could be observed upon comparing BN produced under NH₃ flow to samples produced under vacuum. The accuracy of these experiments was also ± 10 - 15 relative percent. Figure 33 exhibits a representative plot obtained in the PEELS experiments. The lower energy loss absorbances at 200 eV are due to boron and the higher energy ones at 400 eV originate
from nitrogen. The areas under the curves were used for the calculation of the elemental ratios. That the samples are carbon free is indicated by the absence of a series of peaks at approximately 290 eV.

Figure 33: Parallel EELS Spectrum
A sample of BN that was produced under ammonia was sent off for elemental analysis with poor results. The analyst reported that the sample was contaminated with oxygen and hydrogen but that carbon impurity was less than 1%. The infusion of oxygen and hydrogen into the experiment is understandable since the pyrolysis conditions are not rigorous in the exclusion of air. There is a large length of rubber tubing and the system is only separated from air via a mercury / mineral oil bubbler. It is reasonable to think that in this system, air could leak in and create oxides.

Solid state boron-11 NMR spectra of the BN produced under NH₃ flow also indicate that oxygen is present in the sample as B₂O₃ (Figure 34). The shoulder at 13 ppm and the increased height of the peak at 4.5 ppm are probably the result of the overlap of the solid state ¹¹B NMR spectrum of B₂O₃ with that of BN.

Figure 34: Solid State ¹¹B NMR Spectrum of BN Produced Under NH₃ Flow
e. Coatings

In his dissertation, Niedenzu discussed some preliminary coating experiments using an ethereal slurry of H$_3$NBH$_2$Cl and pieces of quartz and a silicon chip. This work has been expanded to include other substrates and coating with much more dilute solutions. The present work has also determined that BN is not the substance which coats the substrates after pyrolysis to 1100 °C. EDS spectroscopy of coated pieces of quartz indicated the presence of boron and oxygen but no nitrogen was found in the sample. Pieces of tantalum foil which were coated had a covering of a tantalum boride. In another experiment, a stainless steel tube with a screw on cap and an out-gassing hole drilled into the lid was produced to keep a sample H$_3$NBH$_2$Cl out of contact with the quartz tube and to keep the solid within the furnace during pyrolysis. In this experiment, the resultant product was a jet black solid that could not be identified as BN. It was an iron boride though the composition was never determined.

For the coating experiments, the variables studied were varying the substrate, varying the percent H$_3$NBH$_2$Cl, and heating in an oil vs dipping, drying and heating without the presence of the oil.

By varying the concentration of the H$_3$NBH$_2$Cl slurry, the thickness and morphology of the coating on the end product could be controlled somewhat. When a piece of silicon was dipped in a solution with the consistency of oil and pyrolyzed in that oil, a thick coating was obtained. The surface was very rough and jagged with deep out-gassing tunnels as demonstrated in Figure 35. When pieces were dipped in an oil and heated without the oil, a similar morphology was obtained. The deep out-gassing tunnels
raised the question of whether the surface was fully coated with ceramic or whether surface metal was exposed at the end of the tunnels.

Figure 35: SEM Photo of a Si Wafer With Coating from a Concentrated Solution
In another set of coating experiments, pieces of tantalum foil were dipped in a slurry with a 1 weight percent composition. With the dilute solution, a much thinner coating could be laid down on the substrate. This would eliminate the need for large, deep out-gassing tunnels.

Some pieces were dipped once and heated following the regular temperature profile to 1100 °C. Others were dipped, heated sequentially to 400 °C, re-dipped and re-heated. Four hundred degrees was chosen as the separation temperature because previous gas evolution studies had shown that by this temperature, most of the gases had been evolved. Several dips were employed based upon industrial coating applications. Each layer should cover the out-gassing tunnels of the last layer and assure a product that contains no exposed surface metal. In these experiments, the pieces of tantalum foil were held at each temperature for 6 hours rather than 24. Past experience had shown that this was more than adequate time.

When the first coat of H₂NBH₂Cl was applied, it was not visible to the naked eye. The second coat of precursor compound could not be seen until the surface was scratched and then a difference could be noted. The third coat was clearly visible and looked uneven and patchy where the sample had been held in tweezers as it was dipped and dried.

SEM photos were taken of the dipped pieces. At a magnification of 200 X, the Ta square is covered by light and dark areas (Figure 38). When the lens zooms down to magnifications of 5,000 X; 10,000 X; and 40,000 X, the light areas appear to have a jagged "cottage cheese" appearance reminiscent of the samples dipped in a concentrated slurry. The gas evolution tunnels are obvious. The dark areas at the same magnifications,
on the other hand, have a much more lamellar appearance. The gas tunnels look like tiny
facial pores (Figures 36 and 37). Other photos show that it is also possible that the rough,
jagged areas are melting together to form the layered areas. This opens the possibility that
longer, high temperature pyrolyses could produce samples containing only the layered
areas.

Comparing samples with 1, 2, and 3 dips, few differences are noted. Dark and
light areas are noted in all three systems. The morphology within each type of area
remains the same. It does appear, however, that the space between dark areas decreases
as the number of coatings increases (Figure 38). It is also possible that light areas are laid
down on light areas and dark areas are laid down on dark areas.

All of the substrates used in the coating experiments were successfully coated with
the exception of Al₂O₃. Aluminum oxide rods and disks were originally coated but the
covering was lost during subsequent handling. Auger spectroscopy of a coated disk
revealed only aluminum and oxygen with no boron or nitrogen in the sample. Later
inspection of the sample vial revealed that the coated powder was there.
Figure 36: SEM Photos of Ta Foil Dipped in a 1% Slurry

Light versus Dark Areas at 10,000 X
Figure 37: SEM Photos of Ta Foil Dipped in a 1 % Slurry

Light versus Dark Areas at 40,000 X
Figure 38: SEM Photos of Ta Foil Dipped in a 1% Slurry
C. The Synthesis and Characterization of Gadolinium Borohydrides

Two novel gadolinium boron hydride compounds, Gd(B₃H₈)₃nsolvent and Gd(B₄H₁₄)₃nsolvent have been produced by the action of anhydrous GdCl₃ on the potassium salt of the boron anion, KBₓHᵧ, in either dimethylformamide or dimethylacetamide solution. The reactions proceed according to equation 64.

\[
GdCl₃ + 3 KBₓHᵧ \xrightarrow{\text{DMF or DMAC}} Gd(BₓHᵧ)₃nsolvent + 3 KCl \quad (64)
\]

In both cases, the reaction is instantaneous. Immediately upon pouring a solution of GdCl₃ into a solution of KBₓHᵧ, a white precipitate, which is shown by its X-ray powder diffraction pattern to be KCl, is produced. The KCl precipitate is extremely fine and filters through the frit during attempted extractions. In order to avert this, the solutions are centrifuged and decanted for isolation purposes.

1. Gadolinium Octahydrotriborate (1-)

Though the two compounds are produced in an analogous manner, their stability and spectroscopy vary with Gd(B₃H₈)₃nsolvent being the most interesting. When dissolved in DMF, the stability of Gd(B₄H₁₄)₃ is limited. If allowed to remain in DMF solution, it begins to decompose within 12 hours to produce Me₃NBH₃. In fact, even
when the DMF is evaporated from the Gd compound, it continues to decompose, though more slowly, and the $^{11}\text{B}$ NMR spectrum indicates only $\text{Me}_3\text{NBH}_3$ when $\text{Gd(B}_3\text{H}_8)_3$ is redissolved in DMF or DMAC. Figure 39 depicts the boron-11 NMR spectra of a sample of $\text{Gd(B}_3\text{H}_8)_3\text{nDMF}$ as it decomposes in DMF. The spectra show time progression from a fresh sample to complete decomposition at 3 months.

The infrared spectrum of the decomposed substance shows medium intensity BH stretches (Figure 40).
Figure 39: Decomposition of $\text{Gd(B}_3\text{H}_5)_2\text{nDMF}$ in DMF by $^{11}$B NMR Spectroscopy
Figure 40: Decomposition IR Spectrum of Gd(BiHg)_{n}DMF
This degradation to $\text{Me}_3\text{NBH}_3$ by solvent is not observed in samples of $\text{Gd}(\text{B}_3\text{H}_4)_3$ produced in DMAC or in samples of $\text{KB}_3\text{H}_6$ dissolved in DMF. Peters and co-workers found that $\text{Bu}_3\text{N}[\text{B}_3\text{H}_6]$ reacted with hydrochloric acid in DMF to produce $\text{Me}_3\text{NBH}_3$.\(^{160}\)

\[
\text{B}_2\text{H}_6 + 2 \text{H}^+ + \text{Me}_2\text{NCOH} \rightarrow 3 \text{Me}_3\text{NBH}_3 + \text{borates} \quad (65)
\]

The postulated mechanism of the $[\text{B}_3\text{H}_6]^-$ reaction with DMF is analogous to that of diborane with DMF. It involves, as a first step, the reduction of DMF. The product of the reduction, $\text{Me}_2\text{NCH}_2\text{OB}_2\text{H}_5$, then disproportionates to form $\text{Me}_3\text{N}$ and $\text{B}_2\text{H}_4\text{O}$. The borate compound then decomposes to other borates and diborane which is then free to react with the previously formed trimethylamine (equations 66 - 69).\(^{160}\)

\[
\text{B}_2\text{H}_6 + \text{Me}_2\text{NCOH} \rightarrow \text{Me}_2\text{NCH}_2\text{OB}_2\text{H}_5 \quad (66)
\]

\[
\text{Me}_2\text{NCH}_2\text{OB}_2\text{H}_5 \rightarrow \text{Me}_3\text{N} + \text{B}_2\text{H}_4\text{O} \quad (67)
\]

\[
\text{B}_2\text{H}_4\text{O} \rightarrow \text{B}_2\text{H}_6 + \text{borates} \quad (68)
\]

\[
2 \text{Me}_3\text{N} + \text{B}_2\text{H}_6 \rightarrow 2 \text{Me}_3\text{NBH}_3 \quad (69)
\]
The cation used in the DMF / B$_2$H$_6$ studies was [Bu$_4$N]$^+$ rather than [Me$_3$N]$^+$ so that it could be shown conclusively that the methyl groups originated from DMF. The present Gd(B$_3$H$_6$)$_n$THF system does not contain HCl but it is possible that the highly electropositive Gd$^{3+}$ ion causes the solution to become acidic enough to catalyze the disintegration of the [B$_3$H$_6$]$^-$ cage. Even the solid decomposes because though solidified, the compound remains highly solvated. This allows the mechanism for deterioration to persist. The decomposition does not occur in dimethylacetamide because DMAC is a bulkier base than DMF and probably cannot be reduced as readily. The analogous acid catalyzed DMAC decomposition reactions would produce EtMe$_2$NBH$_3$. This compound, however, is not observed in DMAC NMR spectra.

The boron-11 NMR spectrum of Gd(B$_3$H$_6$)$_3$ consists of a broad singlet with a chemical shift that varies widely depending upon concentration. This behavior points toward a compound with good Gd to boron interaction. Gadolinium is paramagnetic and in NMR spectroscopy, close interaction with paramagnetic substances erases BH coupling and causes peaks to shift from their natural positions. The value recorded for the $^{11}$B chemical shift of -29.0 ppm is obtained by referencing internally to the Me$_3$NBH$_3$ that is produced as the decomposition proceeds. Me$_3$NBH$_3$ is also shifted from its natural position by the presence of Gd in the system but the separation between it and the signal for Gd(B$_3$H$_6$)$_3$ remains constant.

Fluxionality cannot be argued as an explanation for the lack of coupling of the boron-11 NMR signal. It has already been shown that the [B$_3$H$_6$]$^-$ ion is fluxional and that this fluxionality prompts the signal to appear as a decet.
Figure 41 displays the IR spectrum of a sample of Gd(B₂H₆)₃nDMF in a KBr pellet. This IR spectrum in the BH stretching region is identical to that of the DMAC solvated moiety.
The IR spectrum of Gd(B₃H₆)₃ is similar to that of KB₃H₆. Table 5 compares the BH stretching region of Gd(B₃H₆)₃·nDMF and KB₃H₆. In these spectra, the two low wavenumber absorbances at approximately 2100 cm⁻¹ are in the region that is characteristic of bridging B-H-B hydrogens in ionic [B₃H₆]⁺ compounds. The IR stretching frequencies for the B-H-B bridge in transition metal [B₃H₆]⁺ compounds occur in the region of 1820 cm⁻¹. These frequencies are somewhat different due to the covalent nature of the transition metal compounds.

### TABLE 5

Comparison of IR Spectra of Gd(B₃H₆)₃·nDMF and KB₃H₆

<table>
<thead>
<tr>
<th>ν (cm⁻¹), intensity</th>
<th>Gd(B₃H₆)₃·nDMF</th>
<th>KB₃H₆ ¹¹³</th>
</tr>
</thead>
<tbody>
<tr>
<td>2525, sh</td>
<td></td>
<td>2432, vs</td>
</tr>
<tr>
<td>2392, s</td>
<td></td>
<td>2475, s</td>
</tr>
<tr>
<td>2442, s</td>
<td></td>
<td>2376, s</td>
</tr>
<tr>
<td>2312, m</td>
<td></td>
<td>2338, s</td>
</tr>
<tr>
<td>2279, sh</td>
<td></td>
<td>2226, vw</td>
</tr>
<tr>
<td>2223, vw</td>
<td></td>
<td>2212, vw</td>
</tr>
<tr>
<td>2122, m</td>
<td></td>
<td>2134, w</td>
</tr>
<tr>
<td>2076, w</td>
<td></td>
<td>2100, w</td>
</tr>
</tbody>
</table>
Based upon the similar IR spectrum for Gd(B$_3$H$_9$)$_3$ nDMF and KB$_3$H$_6$, a similar bonding interaction can be proposed. The crystal structure of [(NH$_3$)$_2$BH$_3$]B$_3$H$_6$ was solved in 1960. It showed that the molecule is ionic in nature. It is reasonable to assume that Gd(B$_3$H$_9$)$_3$ nDMF is also ionic in nature.

2. Gadolinium Tetradecahydrononaborate (1-)

NMR and IR spectroscopy of the [B$_3$H$_9$]$^-$ and [B$_9$H$_{14}$]$^-$ compounds indicate interesting differences in the manner that the two boron cages interact with the gadolinium ion. The boron-11 NMR spectrum of Gd(B$_9$H$_{14}$)$_3$ nDMF includes the three characteristic 1:1:1 doublets for [B$_9$H$_{14}$]$^-$ though their positions have changed from that of the alkali metal salts. This type of pattern points to a solvent separated ionic species in which the gadolinium ion and the boron cage are isolated from one another in such a manner that the lanthanide metal's paramagnetic nature is not able to influence the position or multiplicity of the peaks. Table 6 compares the boron-11 NMR spectra of Gd(B$_9$H$_{14}$)$_3$ and KB$_3$H$_6$ in dimethylformamide solution. Figure 42 illustrates the boron-11 NMR spectrum of Gd(B$_9$H$_{14}$)$_3$ nDMF in DMF and Figure 43 depicts the proton NMR spectrum of the substance in deuterated acetonitrile. The boron and proton spectra are also only slightly perturbed from that of the alkali metal salts. The spectra indicate that the bridge and terminal hydrogens on the boron cage continue to retain their separate spectroscopic identities. The large singlet in the proton NMR spectrum arises from the solvent, CH$_3$CN.
**TABLE 6**

Boron NMR Spectra of [B₃H₁₄]⁻ Species in DMF *

<table>
<thead>
<tr>
<th></th>
<th>Gd(B₃H₁₄)₃nDMF</th>
<th>KB₃H₁₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ (ppm), mult, J (Hz)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-21.30</td>
<td>d 123 Hz</td>
<td>-23.76</td>
</tr>
<tr>
<td>-18.06</td>
<td>d 119 Hz</td>
<td>-20.47</td>
</tr>
<tr>
<td>-5.76</td>
<td>d 132 Hz</td>
<td>-8.25</td>
</tr>
</tbody>
</table>

* The NMR spectra were obtained on a Bruker AM-250 FT spectrometer.

![NMR Spectrum](image)

**Figure 42: **¹¹B NMR Spectrum of Gd(B₃H₁₄)₃nDMF
Figure 43: $^1$H NMR Spectrum of Gd(B$_2$H$_{12}$)$_3$ nDMF
The large separation of the cation and the boron cage has been observed in the crystal structure of CsB₉H₁₄. In this structure, the Cs ion has inter ion distances which are too long to allow significant covalent bonding. It is reasonable to assume that with the significantly larger radius of gadolinium, ion separation would increase even further.

X-ray powder diffraction studies of the Gd(B₉H₁₄)ₓnDMF compound revealed that the substance is crystalline but isolated single crystals diffracted too weakly for the structure to be solved.

Unlike the [B₃H₄]⁺ salts, the infrared spectra of the potassium salt and the gadolinium salt of [B₉H₁₄]⁺ do not show similarities and so assumptions on structure cannot be made based upon infrared spectroscopy. Figure 44 illustrates the infrared spectrum in a KBr pellet of Gd(B₉H₁₄)ₓnDMF. Table 7 lists the numerical data for the boron stretching region of this IR spectrum and compares it to KB₉H₁₄.

<table>
<thead>
<tr>
<th>Gd(B₉H₁₄)ₓnDMF</th>
<th>KB₉H₁₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>2515, s</td>
<td>2579, s</td>
</tr>
<tr>
<td>2462, sh</td>
<td>2550, s</td>
</tr>
<tr>
<td>2426, sh</td>
<td>2520, vs</td>
</tr>
<tr>
<td>2390, sh</td>
<td>2492, sh</td>
</tr>
<tr>
<td>2329, sh</td>
<td>2471, vs</td>
</tr>
</tbody>
</table>

* The IR spectra were obtained on a Mattson-Polaris FT-IR Spectrometer
Figure 44: Infrared Spectrum of Gd(B$_2$H$_6$)$_3$·nDMF
3. Crystal Structure of GdCl$_3$2DME

The single crystal X-ray diffraction structure of GdCl$_3$2DME was determined at -60 °C. The material crystallizes in a monoclinic unit cell with 4 molecules per unit cell. Figure 45 shows ortep plots of two different views of the molecular structure. The room temperature structure of the molecule had been previously reported.

Tables 8 through 10 list pertinent crystallographic data as well as selected bond lengths and bond angles.

Table 8: Crystallographic Data for GdCl$_3$2DME

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Observed Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>C$<em>5$H$</em>{20}$Cl$_3$GdO$_4$</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>443.85</td>
</tr>
<tr>
<td>Crystal Description</td>
<td>Colorless</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space Group</td>
<td>P2$_1$/c</td>
</tr>
<tr>
<td>a, Å</td>
<td>11.452(2)</td>
</tr>
<tr>
<td>b, Å</td>
<td>8.889(3)</td>
</tr>
<tr>
<td>c, Å</td>
<td>15.611(3)</td>
</tr>
<tr>
<td>β, deg</td>
<td>104.89(2)</td>
</tr>
<tr>
<td>Volume, Å$^3$</td>
<td>1535.7(6)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calc), g/cm$^3$</td>
<td>2.049</td>
</tr>
<tr>
<td>Absorption Coefficient</td>
<td>46.9</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα ($\lambda = 0.71073$ Å)</td>
</tr>
<tr>
<td>Temperature of Collection (°C)</td>
<td>-60</td>
</tr>
<tr>
<td>R$_f$</td>
<td>0.018</td>
</tr>
<tr>
<td>R$_w$</td>
<td>0.848</td>
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</table>
Figure 45: Molecular Structure of GdCl$_2$2DME
Table 9: Selected Bond Distances (Å) for GdCl$_2$2DME

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Distance</th>
<th>Atoms</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd - Cl (1)</td>
<td>2.6249(9)</td>
<td>O (1) - C (2)</td>
<td>1.443(5)</td>
</tr>
<tr>
<td>Gd - Cl (2)</td>
<td>2.6210(9)</td>
<td>O (2) - C (3)</td>
<td>1.431(4)</td>
</tr>
<tr>
<td>Gd - Cl (3)</td>
<td>2.6252(9)</td>
<td>O (3) - C (6)</td>
<td>1.451(4)</td>
</tr>
<tr>
<td>Gd - O (1)</td>
<td>2.467(2)</td>
<td>O (4) - C (7)</td>
<td>1.436(4)</td>
</tr>
<tr>
<td>Gd - O (2)</td>
<td>2.458(2)</td>
<td>O (1) - C (1)</td>
<td>1.442(5)</td>
</tr>
<tr>
<td>Gd - O (3)</td>
<td>2.416(2)</td>
<td>O (2) - C (4)</td>
<td>1.459(5)</td>
</tr>
<tr>
<td>Gd - O (4)</td>
<td>2.500(2)</td>
<td>O (3) - C (5)</td>
<td>1.440(5)</td>
</tr>
<tr>
<td>C (2) - C (3)</td>
<td>1.482(6)</td>
<td>O (4) - C (8)</td>
<td>1.424(5)</td>
</tr>
<tr>
<td>C (6) - C (7)</td>
<td>1.485(6)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 10: Selected Bond Angles (deg) for GdCl$_2$2DME

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Angle</th>
<th>Atoms</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl (1) - Gd - Cl (2)</td>
<td>91.88(3)</td>
<td>O (1) - Gd - O (2)</td>
<td>66.04(8)</td>
</tr>
<tr>
<td>Cl (1) - Gd - Cl (3)</td>
<td>168.24(3)</td>
<td>O (1) - Gd - O (3)</td>
<td>157.45(9)</td>
</tr>
<tr>
<td>Cl (2) - Gd - Cl (3)</td>
<td>97.33(3)</td>
<td>O (1) - Gd - O (4)</td>
<td>130.45(8)</td>
</tr>
<tr>
<td>Cl (1) - Gd - O (1)</td>
<td>107.22(7)</td>
<td>Cl (3) - Gd - O (1)</td>
<td>81.63(6)</td>
</tr>
<tr>
<td>Cl (1) - Gd - O (2)</td>
<td>79.39(7)</td>
<td>Cl (3) - Gd - O (2)</td>
<td>97.82(7)</td>
</tr>
<tr>
<td>Cl (1) - Gd - O (3)</td>
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<td>89.24(6)</td>
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<td>Cl (1) - Gd - O (4)</td>
<td>89.96(6)</td>
<td>Cl (3) - Gd - O (4)</td>
<td>78.33(6)</td>
</tr>
<tr>
<td>Cl (2) - Gd - O (1)</td>
<td>80.39(6)</td>
<td>O (2) - Gd - O (3)</td>
<td>136.04(9)</td>
</tr>
<tr>
<td>Cl (2) - Gd - O (2)</td>
<td>140.44(7)</td>
<td>O (2) - Gd - O (4)</td>
<td>72.46(8)</td>
</tr>
<tr>
<td>Cl (2) - Gd - O (3)</td>
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<td>O (3) - Gd - O (4)</td>
<td>66.61(9)</td>
</tr>
<tr>
<td>Cl (2) - Gd - O (4)</td>
<td>146.66(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd - O (1) - C (2)</td>
<td>113.3(2)</td>
<td>Gd - O (3) - C (6)</td>
<td>112.0(2)</td>
</tr>
<tr>
<td>Gd - O (2) - C (3)</td>
<td>118.6(3)</td>
<td>Gd - O (4) - C (7)</td>
<td>117.4(2)</td>
</tr>
</tbody>
</table>
The molecule crystallizes in a distorted pentagonal bipyramid with a coordination number of seven. Two DME molecules are coordinated to gadolinium through their oxygen atoms. The three chlorine atoms complete the inner coordination sphere. Chlorine atoms 1 and 3 form the apexes of the pentagonal bipyramid. The other chlorine atom and the four oxygen atoms of the two DME molecules form the 5 membered ring which is buckled out of a planar position (Figure 46).

The effective ionic radius for seven coordinate Gd$^{3+}$ is 1.00 Å. The covalent radius of O is 1.40 Å. These numbers give calculated bond distances of 2.40 Å for gadolinium - oxygen linkages. Zachariasen has reported gadolinium - chlorine bond distances to be 2.412 Å. Experimental determined gadolinium - chlorine bond distances range from 2.6210 to 2.6252 Å. The experimentally determined gadolinium - oxygen bond lengths vary from 2.146 to 2.500 Å. Both of these sets of distances agree with the expected values.
Figure 46: Simplified Molecular Structure of GdCl$_2$2DME
D. Conclusion

The chemical reactivity of ammonia-borane, \( \text{H}_3\text{NBH}_3 \), has been studied and it has been found that \( \text{H}_3\text{NBH}_3 \) contains both protonic and hydridic sites within its framework. The hydrogen atoms which are bound to the nitrogen are protonic in nature and the hydrogens attached to the boron atom are hydridic in nature.

The protonic nature of the nitrogen hydrogens was investigated by the preparation of alkali metal aminoborohydride salts, \( \text{M[H}_2\text{NBH}_3] \) where \( \text{M} = \text{Li, Na or K} \). \( \text{M[H}_2\text{NBH}_3] \) can be synthesized from \( \text{H}_3\text{NBH}_3 \) in three manners:

1. Reaction of \( \text{H}_3\text{NBH}_3 \) with the alkali metal hydrides LiH, NaH or KH.
2. Reaction of \( \text{H}_3\text{NBH}_3 \) with elemental sodium or potassium in liquid ammonia.
3. Reaction of \( \text{H}_3\text{NBH}_3 \) with methyl or butyllithium.

The alkali metal aminoborohydride salts were characterized by \( ^1\text{H} \), \( ^7\text{Li} \), and \( ^11\text{B} \) NMR spectroscopy, IR spectroscopy and X-ray powder diffraction. Their stability and solubility under vacuum and in THF was investigated. The thermal decomposition of \( \text{M[H}_2\text{NBH}_3] \) was also studied.

\( \text{M[H}_2\text{NBH}_3] \) behaves as a hydride donor in some reactions with inorganic reagents. In a reaction with \( \text{BH}_3\text{THF} \), \( \text{M[H}_2\text{NBH}_3] \) transferred a \( \text{H}^+ \) forming \( [\text{BH}_3]^+ \). In reactions with \( \text{Fe(CO)}_5 \) and \( \text{Cr(CO)}_6 \), the formyl compounds \( [\text{Fe(CO)}_4\text{CHO}]^- \) and \( [\text{Cr(CO)}_4\text{CHO}]^- \) were produced. Reaction of \( \text{M[H}_2\text{NBH}_3] \) with \( \text{Ru}_3(\text{CO})_{12} \) produced the metal hydride
compound $[\text{HRu}_3(\text{CO})_{11}]^+$. The reaction of $\text{M}[\text{H}_2\text{NBH}_3]$ with $\text{ZnCl}_2$ was temperature sensitive. At -78 °C, $\text{Zn}(\text{H}_2\text{NBH}_3)_2$ was formed. Upon warming the solution above 0 °C, the zinc compound was reduced to metallic zinc. $[\text{H}_2\text{NBH}_3]^+$ has the advantage over commercial hydride sources that it does not flame in the presence of air or water. This increased stability makes $[\text{H}_2\text{NBH}_3]^+$ a safer hydride source.

In other reactions, $\text{M}[\text{H}_2\text{NBH}_3]$ behaved as a ligand. $\text{Mg}(\text{H}_2\text{NBH}_3)_2$ was formed from the reaction of $\text{M}[\text{H}_2\text{NBH}_3]$ with $\text{MgI}_2$. $(\text{C}_2\text{H}_5)_2\text{ZrCl}(\text{H}_2\text{NBH}_3)$ and $(\text{C}_3\text{H}_5)_2\text{Zr}(\text{H}_2\text{NBH}_3)_2$ were formed when $\text{M}[\text{H}_2\text{NBH}_3]$ and $(\text{C}_2\text{H}_5)_2\text{ZrCl}_2$ were reacted in THF.

The hydridic nature of the boron hydrogens of $\text{H}_3\text{NBH}_3$ was investigated by reaction of $\text{H}_3\text{NBH}_3$ with hydrohalic acids, $\text{HX}$ ($\text{X} = \text{Cl, Br}$). Ammonia-monohaloborane, $\text{H}_3\text{NBH}_2\text{X}$, and ammonia-dichloroborane, $\text{H}_3\text{NBHCl}_2$, were synthesized and characterized by $^1\text{H}$ and $^{11}\text{B}$ NMR spectroscopy, IR spectroscopy and X-ray powder diffraction.

The thermal decomposition of $\text{H}_3\text{NBH}_2\text{Cl}$ was studied under vacuum conditions. It was discovered that turbostratic boron nitride, $\text{BN}$, is produced upon heating to 1100 °C. The thermal decomposition was also studied under NH$_3$ flow. The BN was analyzed by X-ray powder diffraction, diffuse reflectance IR spectroscopy, elemental analysis, solid state $^{11}\text{B}$ NMR spectroscopy, SEM, EELS, ESCA, EDS. All of these techniques indicated that turbostratic BN with a carbon content of less than 0.1 % and with low oxygen impurities had been formed.
A ceramic coating was also laid down on pieces of quartz and tantalum foil by immersing the substrate in an ethereal solution of $\text{H}_3\text{NBH}_2\text{Cl}$ and heating to 1100 °C under vacuum. The coating which was obtained was not BN according to EDS spectroscopy but rather a boron oxide on the pieces of quartz and a tantalum boride on the pieces of tantalum.

Two gadolinium boron hydride compounds, $\text{Gd(B}_2\text{H}_6)_3\text{nsolvent}$ and $\text{Gd(B}_9\text{H}_{14})_3\text{nsolvent}$ were also synthesized and characterized by $^{11}\text{B}$ NMR spectroscopy. The compounds were produced by the reaction of anhydrous GdCl$_3$ with KB$_x$H$_y$ in either dimethylformamide or dimethylacetamide solution.

Boron-11 NMR spectroscopy suggests that the Gd$^{3+}$ - $[\text{B}_3\text{H}_6]^{-}$ compound is a solvent separated species. The $^{11}\text{B}$ NMR spectrum consists of 3 doublets of equal intensity. The fact that the signals remain coupled indicates that the cluster is not in close proximity to the paramagnetic Gd$^{3+}$ ion.
III. EXPERIMENTAL

A. Vacuum Line

Due to the fact that many of the compounds used in this study are air and moisture sensitive, manipulations were carried out using a standard vacuum system. The vacuum system consisted of five major components: a calibrated distillation train, calibrated Töppler pump, McCloed gauge, and two reaction manifolds. The different portions of the system were interconnected via Pyrex glass tubing and connected to the pumping station via 45 mm outer diameter Pyrex glass tubing.

The distillation train was calibrated using known volumes of carbon dioxide so that measured volumes of gas could be added to reactions. It consisted of four U-tubes connected to a mercury manometer. At each side of the distillation train, there were inlet ports. One port accepted 9 mm solv-seal greaseless joints, and the other was sized for 14/35 ground glass outer joints. There was also, at a 90 degree angle, a port that would accept the 14/35 inner joint of an extractor. All were equipped with Kontes Teflon valves.

The Töppler pump was used to measure the volume of non-condensible gas that was evolved during reactions. It was also calibrated against known quantities of CO₂.
The reaction manifolds consisted of inlet ports for reaction vessels having 9 mm solv-seal joints or 14/35 ground glass female or male joints. One set of inlet ports was equipped with 18/9 outer ball joints for the addition of a removable solvent trap. All reaction ports were isolated from the vacuum system using either Kontes or Fischer-Porter greaseless stopcocks. Many of these reaction ports were equipped with mercury blow out tubes in an effort to maintain safe limits on pressure.

The McCloed gauge was employed in the measurement of the vacuum in the system. Pressures ranging from $1 \times 10^{-3}$ to $5 \times 10^{-4}$ mm Hg could be monitored.

The entire system was evacuated using a Welch Duo-Seal rotary pump as a rough pump and a two stage mercury diffusion pump to attain high vacuum. A liquid nitrogen trap (-196 °C) and a dry ice/isopropanol trap (-78 °C) were used between the vacuum system and the pumps in an effort to protect the pumps from harmful volatile and corrosive gases. An ultimate vacuum of $10^{-5}$ mm Hg could be obtained using this system.

B. Glove Box

Manipulations such as the weighing and transferring of non-volatile air and moisture sensitive compounds were carried out in one of two Vacuum Atmospheres glove boxes. A dry nitrogen atmosphere with an oxygen content of less than 10 ppm was maintained at all times by circulating the atmosphere over a catalyst tower containing Linde 13-X molecular sieves with a copper based oxygen scavenger (Rid-Ox). The oxygen levels in the box were monitored using a titanocene (III) chloride solution. This solution changed to yellow from green when the oxygen level exceeded 10 ppm. The
oxygen content of the atmosphere was sometimes checked by cutting a fresh piece of cesium metal and determining the rate at which it tarnished. The box was entered or exited through a side port which was evacuated, filled with dry nitrogen and re-evacuated. The two systems required that the port be evacuated for 20 and 15 minutes or for 15 and 10 minutes prior to opening the door to the inner chamber. Evacuations were accomplished using a high speed Welch Dou-Seal mechanical pump.

C. Specialty Glassware

Many different sizes and shapes of glassware were used in the reactions described in this document. Most involved Pyrex glass flasks and vacuum line adapters that were fitted with 9 or 15 mm solv-seal joints (Figure 47). Stirring was accomplished with glass encapsulated or Teflon coated magnetic stir bars which were rotated by external stir plates and stir motors. Cleaning of glassware was performed by soaking it overnight in either an isopropanol / potassium hydroxide bath or in aqua regia (3 HCl : 1 HNO₃) before leaving it overnight in slightly acidic water. The following morning, the glassware was rinsed first in distilled water and then in acetone before being put in an 80 °C oven to dry.

Extractor:

Reactions involving filtration were carried out using 9 or 15 mm solv-seal extractors as shown in Figure 48. Once the reaction was complete, the entire apparatus was rotated 180° to allow the reaction mixture to fall onto the frit and be filtered. For difficult separations, either the collection flask was cooled or stopcock B was opened to the vacuum line to force the liquid through the frit. Any solid residue on the frit was
washed by opening valve A, and using a cotton wand saturated with liquid nitrogen to cause some solvent to condense above the frit. This upper area was then thawed, the stopcock closed and the solvent re-filtered through the solid.

For ammonia filtrations, a modified extractor was used. This vessel contained a glass jacket around the frit in which dry ice could be poured. This allowed the temperature to remain low and the pressure to remain within safe levels during the extraction and washing process.

**Side-Arm NMR Tube Reactor:**

Reactions in which an NMR spectrum was obtained on thermally unstable materials were performed using a special flask which was equipped with a side-arm NMR tube (Figure 49). After the reaction had progressed, the NMR tube was cooled and the reaction mixture tipped into it. The NMR tube was quickly sealed using a glass blowers torch and the spectrum was run.

**NMR Tube Reactor:**

Very small scale reactions were performed in vessels produced by attaching a standard 5 mm NMR tube onto a 9 mm solv-seal joint which could then be connected to the vacuum line via an adapter (Figure 50). NMR spectra were run after separating the NMR tube from the 9 mm joint with a torch.

**Tip Tube Flask Reactor:**

For reactions where it was necessary to isolate the starting materials until solvent had been added or until a special temperature had been reached, a tip tube flask (Figure 51) was added to the reaction flask. When proper conditions had been reached, the tip
tube was rotated to allow its contents to flow into the reaction flask.

**Pyrolysis Tube:**

For high temperature pyrolyses, a quartz tube of 15 or 25 mm outer diameter was closed off on one end and sealed via temperature gradient glass to a 15 or 20 mm solv-seal joint at the other end (Figure 52). For pyrolysis involving gas flowing over the substrate, both ends of the quartz tube were fitted with 20 mm solv-seal joints.

**Screw Cap / Septum Stoppered NMR Tube:**

Seven or eight inch NMR tubes with screw on lids were purchased from Wilmad Glass Company. The lids had a whole in the center through which a PTFE / Silicone septum was accessible for syringing in solvents and reagents.

**Water Cooled Sublimator:**

All purifications by sublimation and some thermal decomposition studies were performed using a water cooled sublimation apparatus (Figure 53). This vessel consisted of a thick walled Pyrex flask with an attachment that included a finger onto which substances could adhere and a 14/35 ground glass joint for attachment to the vacuum line. Cold tap water was circulated through the projected finger while the apparatus was heated in an oil or sand bath.
Figure 47: Vacuum Line Flask and Adaptor
Figure 48: Extractor
Figure 49: Side-Arm NMR Tube Reactor
Figure 50: NMR Tube Reactor
Figure 51: Tip Tube Flask Reactor
Figure 52: Pyrolysis Tube and Adapter
Figure 53: Water Cooled Sublimator
SOLVENTS:

**Acetonitrile**, \( \text{CH}_3\text{CN} \) (Mallinckrodt), was dried and degassed by stirring it for several days over phosphorous pentoxide, \( \text{P}_4\text{O}_{10} \), prior to transferring it under vacuum to a storage flask.

**Benzene**, \( \text{C}_6\text{H}_6 \), was purchased from various chemical sources and dried by stirring it at elevated temperatures with sodium-benzophenone ketyl until the dark blue or purple color persisted. The solution was then transferred to a Teflon stoppered storage bulb containing sodium-benzophenone ketyl.

**Chloroform**, \( \text{CHCl}_3 \), was purchased from several sources and dried in the same manner as acetonitrile.

**Dichloromethane**, \( \text{CH}_2\text{Cl}_2 \), was obtained from various chemical companies and dried similarly to acetonitrile.

**Diethylether**, \( \text{Et}_2\text{O} \), was purchased from J. T. Baker and treated in an analogous manner to benzene.

**1,2-Dimethoxyethane**, DME, was purchased from Aldrich Chemical Company and purified analogously to benzene.

**N, N-Dimethylacetamide**, DMAC, was dried by stirring for several days over 4A molecular sieves and filtering prior to storage in the glove box until used. It was purchased from Aldrich Chemical Company.

**N, N-Dimethylformamide**, DMF, was purchased from Mallinckrodt Chemical Company and treated analogously to dimethylacetamide.
**Ethanol**, absolute CH₂CH₂OH, was ordered from Midwest Grain Products and degassed in a Pyrex storage tube by freezing it, evacuating the bulb and thawing it. It was taken through this freeze-thaw cycle several times.

**Hexane**, C₆H₁₄ (Mallinckrodt), was stirred overnight first with concentrated sulfuric acid and then with anhydrous magnesium sulfate before being washed with several portions of water and distilled from CaH₂ to a storage flask containing 4A molecular sieves. It was degassed using numerous freeze-thaw cycles.

**Methanol**, CH₃OH, was purchased from various vendors and treated analogously to ethanol.

**2-Methoxyethylether**, DIME, was purchased from Aldrich and was dried and stored over sodium metal.

**Pyridine**, C₅H₅N, was purchased from various sources and degassed and stored over sodium metal.

**Tetrahydrofuran**, THF, was purchased from Mallinckrodt Chemical Company and purified in the same manner as benzene.

**Deuterated solvents**: D₂O, THF-d₆, Et₂O-d₁₀, CD₃CN, CD₂Cl₂, C₆D₆, and CDCl₃ were purchased from Aldrich Chemical Company, Isotec Isotope Labs and Cambridge Isotope Labs and stored over the same reagents as their protonated counterparts.
GASES:

Ammonia, \( \text{NH}_3 \), Hydrochloric Acid, HCl, Hydrobromic Acid, HBr, and Boron Trichloride, \( \text{BCl}_3 \) were purchased in gas cylinders from Matheson Gas Company and transferred to thick walled Pyrex flasks for storage at -78 °C prior to use. The HCl, HBr, and \( \text{BCl}_3 \) were purified by multiple fractionations through a U-trap maintained at -126 °C for HCl and -78 °C for the others. The \( \text{NH}_3 \) was stored over sodium metal to keep it free of water.

Dry Ice, \( \text{CO}_2 \), was purchased through laboratory stores as a solid and purified by subliming and fractionating it at -78 °C. It was also stored in a Teflon stoppered storage flask at -78 °C.

REAGENTS:

Ammonia-Borane:

Most of the \( \text{H}_3\text{NBH}_3 \) was purchased from either Callery Chemical Company or from Aldrich Chemical Company and sublimed onto a water cooled finger from a 60 °C oil bath for purification. The rest was prepared following the literature procedures of Adams and co-workers and purified by sublimation.\(^{15}\)

Borane Tetrahydrofuran Complex:

The \( \text{BH}_3\text{THF} \) used in the preparation of ammonia-borane and diethylamine-borane was 10 M in THF from Aldrich Chemical Company. The substance used in the reactions with the aminoborohydride anion was 1 M in THF from the same company.
**Chromium Hexacarbonyl:**

The Cr(CO)$_6$ was purchased from Aldrich Chemical Company and sublimed by Glenn Jordan at room temperature onto a water cooled finger prior to use. It was stored in a vial in the glove box.

**Diethylamine:**

(CH$_3$CH$_2$)$_2$NH was purchased from Fischer Scientific and degassed and distilled from 4A molecular sieves to a storage flask containing the same size sieves.

**Potassium:**

K metal was purchased from Aldrich and stored in mineral oil. When needed, pieces were cut, washed with hexane and stored in the glove box under nitrogen.

**Potassium Hydride:**

KH was purchased from Aldrich as a mineral oil emulsion and washed with several portions of hexane prior to storage under nitrogen. The activity of the lithium, sodium and potassium hydrides was assayed by reaction with methanol or ethanol and measurement of the volume of hydrogen gas evolved.

**Sodium:**

Na metal was purchased from Aldrich and treated in an analogous fashion to the potassium metal.

**Tantalum:**

Ta metal was purchased from Johnson Matthey as 50 mm X 50 mm sheets and cut into 10 mm X 10 mm pieces for coating experiments. The foil was 99.95 % purity and 0.25 mm thick.
**N, N, N, N-Tetramethylethlenediammine**

TMEDA from Aldrich Chemical Co. was purified by stirring and storing over 4A molecular sieves.

**Literature Preparations:**

The following table lists chemicals that were prepared using known literature methods.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Reference No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis(triphenylphosphine)copper (I) bromide</td>
<td>(PPh₃)₂CuBr</td>
<td>165</td>
</tr>
<tr>
<td>Deuteroammonia</td>
<td>ND₃</td>
<td>166</td>
</tr>
<tr>
<td>Diethylammine-borane</td>
<td>Et₂NHBH₃</td>
<td>15</td>
</tr>
<tr>
<td>Potassium octahydrotriborate (1-)</td>
<td>KB₃H₈</td>
<td>113</td>
</tr>
<tr>
<td>Potassium tetradecahydonaborate (1-)</td>
<td>KB₉H₁₄</td>
<td>122</td>
</tr>
<tr>
<td>Ruthenium dodecacarbonyl</td>
<td>Ru₆(CO)₁₂</td>
<td>167</td>
</tr>
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</table>

**Commercial Chemicals:**

The reagents in Table 12 were purchased from the associated company and used as received. In most cases, the purest grade available was purchased.
<table>
<thead>
<tr>
<th>Chemical</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>4A Molecular Sieves</td>
<td>Union Carbide</td>
</tr>
<tr>
<td>Aluminum Oxide Disks and Rods, $A_2O_3$</td>
<td>Materials Research Corp.</td>
</tr>
<tr>
<td>Apiezon Grease</td>
<td>VWR Scientific</td>
</tr>
<tr>
<td>Benzophenone, $C_6H_5COC_6H_5$</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Benzyltrimethylammonium bromide, $C_6H_5CH_2N(CH_3)_2Br$</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>Butyllithium, $C_4H_9Li$ (10 M in hexanes)</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>Calcium Hydride, CaH$_2$</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>Carbon Fiber, C</td>
<td>Union Carbide</td>
</tr>
<tr>
<td>12-crown-4, $C_8H_{16}O_4$</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>Gadolinium trichloride, GdCl$_3$</td>
<td>Strem Chemicals</td>
</tr>
<tr>
<td>Iron pentacarbonyl, Fe(CO)$_5$</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>Lithium hydride, LiH</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>Magnesium iodide, MgI$_2$</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>Magnesium Sulfate, MgSO$_4$</td>
<td>EM Science</td>
</tr>
<tr>
<td>Mercury, Hg</td>
<td>Bethlehem Instruments</td>
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<tr>
<td>Methyllithium, $CH_3Li$ (1.4 M in ether)</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>Methyltriphenylphosphonium bromide, $CH_3PPh_3Br$</td>
<td>Aldrich Chemical Co.</td>
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<tr>
<td>Nujol</td>
<td>Aldrich Chemical Co.</td>
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<tr>
<td>Potassium Bromide, KBr</td>
<td>Mallinckrodt Chemicals</td>
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</table>
Table 12 (continued)

<table>
<thead>
<tr>
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<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorous Pentoxide, (P_2O_{10})</td>
<td>Mallinckrodt Chemicals</td>
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<tr>
<td>Sodium Hydride, NaH</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>Sulfuric Acid, (H_2SO_4)</td>
<td>EM Science</td>
</tr>
<tr>
<td>Tetra-n-butylammonium bromide, ((n-C_4H_{10})_4NBr)</td>
<td>Aldrich Chemical Co.</td>
</tr>
<tr>
<td>Zinc (II) chloride, (ZnCl_2)</td>
<td>Strem Chemicals</td>
</tr>
<tr>
<td>Zirconocene dichloride, ((C_5H_5)_2ZrCl_2)</td>
<td>Aldrich Chemical Co.</td>
</tr>
</tbody>
</table>

E. Nuclear Magnetic Resonance (NMR) Spectra

All proton, boron-11, lithium-7 and variable temperature NMR spectra were recorded on a Bruker AM-250 or a MSL-300 FT spectrometer. Boron decoupled proton NMR spectra were recorded on the 300 MHz spectrometer only. These instruments were utilized at the following frequencies for the designated isotopes: \(^1H\) at 250 and 300 MHz, \(^{11}B\) at 80.25 and 96.3 MHz and \(^7Li\) at 97.21 MHz on the AM-250 spectrometer. If no notation is given, the spectra were recorded at 303 K (30 °C). When lower temperatures were required, they were achieved by cooling the variable temperature probe with liquid nitrogen.

Chemical shift values in ppm are recorded with positive values being downfield (left) of the standard. The standard for boron-11 NMR spectroscopy is BF\(_3\)Et\(_2\)O dissolved in \(C_6D_6\). The proton NMR standard is tetramethylsilane, \((CH_3)_4Si\), and the
lithium-7 NMR standard is LiCl. All of these standards have been set to 0.00 ppm. For low temperature applications due to the freezing point of C₆D₆, the actual boron standard utilized was BCl₃ in CD₂Cl₂ which has a shift of 46.8 ppm relative to the primary standard, BF₃ etherate. ⁷Li NMR spectra were obtained by Dr. Ron Grinsted and ¹H(¹¹B) spectra were recorded by Dr. Charles Cottrell at Ohio State University.

Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, b = broad.

Solid State NMR

Solid state boron-11 NMR spectra were obtained on a CMX 400 (9.4 T) by Dr. Pierre Florian in Dr. Phillip Grandinetti's group at The Ohio State University. The boron standard utilized was BF₃Et₂O in C₆D₆ as in the solution ¹¹B NMR spectra.

F. Infrared (IR) Spectra

All IR spectra were recorded with 2 cm⁻¹ resolution on a Mattson-Polaris FT-IR or a Mattson-Cygnus 100 FT-IR spectrometer. Samples were prepared in many ways including KBr pellets, nujol mulls, solutions, gases or diffuse reflectance powders.

The pellets were formed by finely grinding a small amount of the sample with dry potassium bromide and pressing it into a pellet using a stainless steel press. The samples in nujol mulls were pressed between solid NaCl windows and enclosed in an airtight cell with o-rings as gaskets. The solution IR samples were contained in a sealed liquid IR cell between matched NaCl, KBr or KCl plates. The liquid IR cell had Teflon spacers giving
a 0.10 mm path length. Gaseous samples were expanded into a gas IR cell with matched salt plates sealed by epoxy onto the ends. Diffuse reflectance IR spectra were observed for powdered samples in a KBr matrix and were recorded as KM function versus wavenumbers.

In spectra containing BH stretches, the instrument was purged with nitrogen for 10 to 15 minutes prior to analysis in an effort to remove CO$_2$ stretches which overlap the BH region of the IR spectrum.

Abbreviations: vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

G. Mass Spectra

Gas Mass Spectra

Mass spectra of gaseous samples were obtained on a Balzers QME 112 Quadrupole mass spectrometer. The system was pumped down to $10^{-7}$ mbar before the sample was admitted. Gas masses up to approximately 200 amu could be detected with this unit. Routine scans were to 35 or 45 amu. Unless otherwise noted, all evolved gases were identified using this method.

Electron Impact (EI) Mass Spectra

Routine mass spectra of solid substances were obtained on a VG-70-250S or Kratos MS-30 mass spectrometer at the Campus Chemical Instrumentation Center at Ohio State University by David Chang.
Fast Atom Bombardment (FAB) Mass Spectra

FAB mass spectra in DMSO were recorded at the Ohio State University using a VG-70-250S or Kratos MS-30 mass spectrometer by David Chang.

H. X-ray Powder Diffraction

Photographic

Photographic X-ray powder diffraction patterns were produced using a Debye-Scherrer camera from Phillips Electronics, Inc. and an Enraf-Nonius-Delft Diffractus 582 X-ray generator. The generator provided Kα radiation from a copper target. Exposure times were 4 or 6 hours depending upon whether the instrument was set at a voltage of 40 KV and a current of 18 mA or at power settings of 32 KV and 15 mA. Samples were prepared by finely grinding the unknown solid in the glove box and loading it into a 0.3, 0.5, or 0.7 mm glass capillary tube which was temporarily sealed with grease before being flame sealed to keep out air and moisture. The film used in all photographic patterns was Kodak DEF-392. Data was interpreted by measuring bands to 0.05 cm on a General Electric Fluoroline illuminator and calculating 2Θ by hand.

Diffractometer

Diffraction patterns of air stable substances were obtained on a Rigaku Geigerflex powder diffractometer with a copper target. Samples were loaded onto a glass slide which was positioned vertically in front of the beam. The computer performed all calculations and plotted the diffraction pattern as 2Θ versus intensity.
Abbreviations: vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak, b = broad.

I. Single Crystal X-ray Diffraction

Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer. Crystallographic computations were performed using a Digital 3100 VAX Station. Crystal structures were solved by Glenn Jordan using SDP (Structure Determination Package) software.¹⁶⁸

The crystals were isolated in the glove box and transferred to 0.3 or 0.5 mm glass capillary tubes which were temporarily plugged with stopcock grease prior to being flame sealed and prepared for mounting onto the instrument.

J. Elemental Analysis (EA)

Chemical analyses were performed by the companies listed in Table 13.
TABLE 13
Elemental Analysis Sources

<table>
<thead>
<tr>
<th>Company</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analytische Laboratorien, Engelskirchen, Germany</td>
<td>BN</td>
</tr>
<tr>
<td>Galbraith Laboratories, Inc., Knoxville, TN. USA</td>
<td>Li[H₂NBH₃], BN</td>
</tr>
<tr>
<td>Mikroanalytisches Labor Pascher, Remagen, Germany</td>
<td>BN</td>
</tr>
<tr>
<td>Schwarzkopf Microanalytical Laboratory, Woodside, NY. USA</td>
<td>H₃NBH₂Cl, BN</td>
</tr>
</tbody>
</table>

K. Scanning Electron Microscopy (SEM) and Tunneling Electron Microscopy (TEM)

SEM and TEM were the microscopic techniques chosen to view boron nitride particles and to study their topology. Scanning electron microscopy was carried out on a Hitachi S-510 or a Philips XL-30 SEM with FEG and was performed by Clare MacDonald or Cameron Begg at the Electron Optics Facility at The Ohio State University. TEM was performed by Hendrik Colijn on a Philips CM-200 FEG TEM. The pieces of BN were gold coated prior to analysis in order to make them conductive.

L. X-ray Photoelectron Spectroscopy (XPS)

XPS, also known as Electron Spectroscopy for Chemical Analysis (ESCA), was recorded on a Perkin Elmer Model 550 ESCA / Auger spectrometer by Roy Tucker, previously of the Shared Analytical Instrumentation Laboratory at Ohio State. The
experiments were analyzed in an effort to determine the elemental ratio of materials with respect to sample depth and to differentiate surface adsorbed contaminants from the bulk material.

M. Electron Energy Loss Spectroscopy (EELS)

Parallel EELS was performed in an effort to determine the relative abundance of boron to nitrogen in samples of boron nitride. It was performed by Hendrik Colijn at the Electron Optics Facility at The Ohio State University on a Philips CM-200 FEG TEM with Gatan Imaging Filter (GIF) and a power setting of 200 KV.

N. Energy Dispersive X-Ray Spectroscopy (EDS)

EDS was performed by Hendrik Colijn or Cameron Begg on a Philips XL-30 SEM with EDAX DX-4 light element X-ray detector. EDS is a technique used to determine the elemental composition of a sample and can be used to ferret out trace impurities.

O. Pyrolysis

All samples heated above 200 °C were heated in a Lindberg furnace model number 551221 or 55055. Some lower temperature pyrolyses were performed using a sand bath made from a heating mantle filled with sand and attached to a variac for temperature control.
P. Reactions:

1. Preparation of \( \text{H}_3\text{NBH}_2\text{X} \) from \( \text{HX} \) and \( \text{H}_3\text{NBH}_3 \)

\( \text{H}_3\text{NBH}_2\text{Cl} \):

A flask was charged with 0.3086 g (10.0 mmole) \( \text{H}_3\text{NBH}_3 \) and evacuated. Seventy mL of anhydrous diethylether and ten mmoles of gaseous HCl were condensed into the flask at -196 °C. The vessel was warmed to room temperature. Hydrogen gas formed and the reaction was complete within 5 minutes. The \( \text{H}_3\text{NBH}_2\text{Cl} \) is colorless. It is soluble in Et\(_2\)O and it is isolated by filtration and evaporation of the ether. The 97 % yield was determined by measuring the hydrogen gas volume. The hydrogen was identified by its gas mass spectrum.

\(^{11}\text{B NMR} \) (CD\(_3\)CN): -8.87 ppm, t, \( J = 119 \) Hz. \(^1\text{H NMR} \) (CD\(_3\)CN): 4.35 ppm, t, \( J = 46 \) Hz (3 H); 2.58 ppm, q, \( J = 118 \) Hz (2H). \textbf{IR (KBr pellet): } \nu_{\text{NH}} \text{ cm}^{-1} \text{ (intensity): } 3295 (vs), 3232 (s), 3189 (sh), 3142 (m). \nu_{\text{BH}}: 2462 (vs), 2386 (s). \nu: 2111 (w), 2028 (vw), 1812 (w), 1640 (m), 1577 (s), 1388 (vs), 1209 (s), 1131 (vs), 1082 (vs), 903 (s), 797 (s), 718 (m), 546 (s). \textbf{X-ray powder diffraction (photographic): } d(\text{Å}) \text{ (intensity): } 4.19 (vs), 3.95 (vs), 3.40 (vs), 3.06 (s), 2.98 (vw), 2.80 (s), 2.64 (s), 2.37 (ms), 2.16 (ms), 2.09 (vw), 2.04 (m, b), 1.98 (w), 1.89 (m), 1.78 (vw), 1.74 (m, b), 1.69 (vw), 1.57 (w), 1.53 (vww), 1.49 (vw), 1.46 (vw), 1.41 (vw), 1.36 (vww), 1.34 (vw), 1.31 (vw), 1.30 (vww), 1.23 (vww), 1.22 (vww), 1.16 (vww), 1.12 (vww), 1.08 (vww), 1.06 (vww), 1.04 (vww), 0.99 (vww), 0.96 (vww), plus other very faint lines.
H₂NBH₂Cl is soluble in Et₂O and THF. It is slightly soluble in CH₃CN. It decomposes in CHCl₃ and C₅H₅N. The EI mass spectrum, elemental analysis and NMR spectra of H₂NBH₂Cl in Et₂O have been recorded elsewhere.⁵⁵

**H₂NBH₂Br:**

Ammonia-monobromoborane was produced under reaction conditions similar to those employed in the preparation of the monochloroborane except that the H₂NBH₂Br is only slightly soluble in Et₂O and THF. It formed a colorless precipitate as the HBr was consumed. The yield was 92% based upon evolved hydrogen. The H₂ was identified by its gas mass spectrum.

\[ ^{11} \text{B NMR (Et}_2\text{O-d}_{10}) : -12.12 \text{ ppm, t, J} = 122 \text{ Hz.} \]

\[ ^{1} \text{H NMR (Et}_2\text{O-d}_{10}) : 5.06 \text{ ppm, t, J} = 38 \text{ Hz; q, J} = 121 \text{ Hz} \]

(The exact chemical shift of the BH₂Br signal could not be determined due to partial overlap with a solvent peak).

H₂NBH₂Br could not be characterized in detail because it decomposed to a paste when the solvent was evaporated. The gas evolved during this decomposition was identified as Et₂O by its gas mass spectrum. Boron-11 NMR spectroscopy in Et₂O of the decomposition residue showed that the Et₂O soluble fraction contained H₂NBH₂Br, \( \mu \)-NH₂BH₂H₅, H₃NBH₅, BH₂Et₂O and Et₂BH. A significant portion of the residue remained insoluble in ether. IR spectroscopy of the residue also attested to the fact that it contained NH and BH stretches.
H₃NBH₂Br is slightly soluble in Et₂O and THF. It is insoluble in CH₂Cl₂ and C₆H₁₄ and it decomposes in CHCl₃, CH₃CN and C₃H₅N. If allowed to remain in ethereal solution at room temperature for 12 hours, it decomposes to μ-NH₂B₂H₅, H₃NBH₃, B(OEt)₃, (H₂NBH₂)₃, (BHNH)₃, BH(OEt)₂, Et₂OBH₂Br, and Et₂OBH₃. These compounds were identified by their ¹¹B NMR spectra. A white precipitate was also formed during the solution phase decomposition.

2. Preparation of H₃NBHCl₂

To prepare ammonia-dichloroborane, the conditions for the formation of ammonia-monochloroborane were followed except that an excess of HCl was used. This increased ratio resulted in the formation of both ammonia-monochloroborane and ammonia-dichloroborane which can be detected in the proton and boron-11 NMR spectra.

¹¹B NMR (CD₃CN): -1.21 ppm, d, J = 147 Hz. ¹H NMR (CD₃CN): 4.99 ppm, t, J = 47 Hz. The proton NMR signal for the BHCl₂ moiety is buried beneath that of BH₂Cl.

Ammonia-dichloroborane is extremely unstable. It decomposes within 24 hours. It could not be separated or characterized further.

3. Reaction of H₃NBH₂Cl with H₂O: Formation of H₃BO₃ and NH₄Cl

A tip tube reaction flask was charged with H₃NBH₂Cl and evacuated before D₂O was tipped into the flask onto the solid. This addition of D₂O caused the flask to become warm as white smoke was emitted from the reaction mixture. Boron-11 NMR spectroscopy demonstrated that the only boron containing product was B(OH)₃. X-ray
powder diffraction of samples aged in moist air indicated the presence of NH₄Cl. Mass spectral analysis of the evolved gas showed it to be H₂. No attempt was made to measure the yield.

4. Decomposition of H₃NBH₂Cl in Vacuum: Formation of H₂NBHCl

In a typical experiment, 0.3961 g (6.065 mmole) of freshly prepared H₃NBH₂Cl was placed in a flask and set aside for 1 month to allow complete decomposition to occur. 6.10 mmole of gas was collected and identified as hydrogen. Based upon the ratio of evolved H₂, the molecular formula H₂NBHCl is obtained. The residue reacted with water. It was soluble in ethanol and insoluble in acetone. X-ray powder diffraction (photographic): d(Å) (intensity): 4.63 (vw), 4.23 (s), 3.90 (vs), 3.35 (vs), 2.86 (w), 2.76 (ww), 2.60 (vs), 2.31 (vw), 1.98 (vw), 1.80 (vw), 1.61 (vw). Elemental analysis of H₂NBHCl prepared from the low temperature pyrolysis of H₃NBH₂Cl has been recorded previously. 55

5. Formation of Boron Nitride From the Pyrolysis of H₃NBH₂Cl

Dynamic or Static Vacuum

A 0.6531 g (10.0 mmole) sample of H₃NBH₂Cl was weighed into a quartz tube which was evacuated and put into a furnace. The tube was slowly heated to 58 °C under either dynamic or static vacuum depending upon the variables being studied. At 58 °C, the H₃NBH₂Cl began to decompose with the evolution of H₂ gas. Occasionally, decomposition began prior to 58 °C. This proved to be due to the loss of adhering solvent
which was identified by gas mass spectral analysis.

At regular intervals, the temperature was raised by doubling it up to a maximum temperature of 1100 °C. Each temperature was held for 6 to 24 hours. A general residence time of 48 hours was maintained for the highest temperature.

After 24 hours at temperature, in experiments where the gas at each stage was measured, the tube was opened to the vacuum line and the gas measured using the Töppler system. The hydrochloric acid was separated from the hydrogen by positioning a liquid nitrogen trap before the valve to the Töppler system. This trap condensed the HCl but allowed H₂ to continue through. The H₂ and HCl were identified by their gas mass spectra. The yield based upon the total volume of gas obtained was 94.3 %. All attempts to obtain a yield by weighing the final product failed because the H₂ loss at 58 °C caused the powder to expand and scatter throughout the tube.

The product was identified as turbostratic BN by X-ray powder diffraction (photographic and diffractometer): d (Å) (intensity): 2.13 (m, vb), 3.57 (s, b) and by diffuse reflectance IR: v cm⁻¹ (intensity): 1403 (vs), 1287 (m, sh), 801 (s). Elemental analyses of BN samples produced in this manner have been previously recorded but new samples were prepared and analyzed for carbon content. Anal. Calc. for BN: C, 0.00. Found; C, <0.1. An attempt was made to measure the density of the BN powder but the solid was so porous that it proved to be impossible to remove all of the trapped air.

Continuous evacuation of the system encouraged the production of a side product which sublimed out of the furnace and was characterized as NH₄Cl by its X-ray powder diffraction pattern.
**Gas Flow**

In experiments where ammonia or argon gas was allowed to flow over the powder during pyrolysis, the same procedure was followed except that one end of the quartz tube was connected to a gas cylinder and the other to a mineral oil / mercury bubbler. The gas flow rate was kept low by monitoring the number of gas bubbles that escaped the system.

**Coating Experiments**

In coating experiments, the surface of the metal substrate to be coated was first etched by submerging it for one minute in 3% HF, rinsing with distilled water and air drying. Under an inert atmosphere, the pieces were dipped in solutions of $\text{H}_3\text{NBH}_2\text{Cl}$ in ether. The most dilute solution was 1% w/w but other solutions were much more concentrated up to the consistency of oil. After being emersed in the solution, the ether was allowed to evaporate and the pieces were placed in a quartz tube and into the furnace. Some pieces were dipped once and heated in stages to 1100 °C. Other pieces were dipped, heated sequentially to 400 °C, dipped again in the slurry and reheated to 400 °C. Numbers of dippings varied from one to three before complete step-wise pyrolysis to 1100 °C.

Pieces of quartz, silicon, aluminum oxide, tantalum foil and carbon fiber were coated and analyzed by SEM photomicrographs, EDS analysis and auger depth profiles.
6. Pyrolysis of $\text{H}_3\text{NBH}_2\text{Br}$

The residue from the decomposition of ammonia-monobromoborane due to solvent removal was pyrolyzed in a quartz tube utilizing the same temperature scheme that was employed with ammonia-monochloroborane. In this experiment, $\text{H}_2$ and $\text{HBr}$ were both evolved at 58 °C and at 116 °C. Hydrogen continued to be released to 200 °C after which another non-condensable gas with a mass of 28 amu ($\text{N}_2$) began to be released. $\text{HBr}$ was produced up to 400 °C. It was joined at 58 °C by a hydrocarbon fragment with a mass of 36 amu and at 600 °C by another hydrocarbon fragment with a mass of 43 amu.

Infrared spectroscopy and X-ray powder diffraction of the bulk solid obtained after complete pyrolysis to 1100 °C indicated that it contained BN and $\text{NH}_4\text{Br}$ along with other crystalline materials.

Sublimation of $\text{NH}_4\text{Br}$ from the furnace began at 58 °C and continued throughout the heating process. X-ray powder diffraction of the sublimed solid showed the same impurity bands that appeared in the bulk solid along with the characteristic bands for $\text{NH}_4\text{Br}$.

7. Preparation of $\text{M[H}_2\text{NBH}_3]$ from $\text{MH}$ and $\text{H}_3\text{NBH}_3$

$\text{Li[H}_2\text{NBH}_3]$:

In a typical experiment, 0.0397 g (5.0 mmole) of LiH and 0.1543 g (5.0 mmole) of $\text{H}_3\text{NBH}_3$ were placed in a flask. The flask was evacuated and approximately 50 mL of THF was condensed in at -196 °C. The flask was warmed and the contents stirred at room temperature for approximately 4 hours or until the obvious evolution of gas had ceased.
The clear, colorless mixture was filtered to remove small quantities of unreacted LiH and the solvent was evaporated to reveal the colorless solid Li[H₂NBH₃]. The yield was 95% based upon the amount of hydrogen gas that was formed and was identified by its gas mass spectrum.

**B NMR (THF-d₈):** -22.33 ppm, q, J = 87.1 Hz. **H NMR (THF-d₈):** 1.46 ppm, q, J = 87.1 Hz (3 H); variable ppm, s (2 H). **Li NMR (THF):** The chemical shift of the lithium ion varies as a function of concentration. **IR (KBr pellet):** ν_{NH} cm⁻¹ (intensity): 3359 (m), 3310 (vs), 3273 (m), 3246 (sh). ν_{NH}: 2510 (sh), 2349 (vs), 2325 (vs), 2281 (vs), 2246 (vs), 2194 (vs), 2153 (vs), 2037 (sh). ν: 1378 (s), 1261 (s), 1178 (vs), 1160 (vs), 1066 (m), 1016 (m), 902 (w), 843 (w), 799 (m), 785 (sh), 467 (s), 452 (sh).

Li[H₂NBH₃] is soluble in THF. It is insoluble in Et₂O, CH₂Cl₂, DME and C₆H₁₄ and it decomposes in CH₃CN.

**Na[H₂NBH₃]:**

The colorless sodium salt of the aminoborohydride anion was prepared in a manner analogous to the preparation of the lithium salt except that the reaction was performed at -78 °C in an effort to avoid decomposition. Due to this lower temperature, the reaction required 24 hours to produce a yield of 92%. The yield was based upon H₂ evolution.

**B NMR (THF-d₈):** -21.96 ppm, q, J = 84.2 Hz. **H NMR (THF-d₈):** 1.52 ppm, q, J = 84.3 Hz (3 H); variable ppm, s (2 H). The NMR data obtained here differ slightly from previously recorded values. **IR (KBr pellet):** ν_{NH} cm⁻¹ (intensity): 3369 (m), 3317 (s),...
$\nu_{BH}: 2359$ (sh), $2329$ (vs), $2278$ (s), $2216$ (s), $2175$ (s), $2115$ (s), $2071$ (s), $2010$ (sh). $\nu$: $1604$ (w), $1381$ (m), $1182$ (s), $1064$ (w), $1000$ (w), $902$ (w), $824$ (w), $742$ (w). X-ray powder diffraction (photographic): $d(\AA)$ (intensity): 4.48 (m), 4.31 (m), 3.85 (m), 3.72 (s), 3.63 (s), 3.48 (m), 3.31 (s), 3.07 (s), 2.97 (m), 2.85 (mw), 2.62 (s), 2.46 (w), 2.38 (mw), 2.34 (vw), 2.19 (mw), 2.17 (mw), 2.06 (mw), 1.96 (mw), 1.93 (vw), 1.85 (mw), 1.83 (w), 1.79 (vw), 1.76 (vw), 1.73 (vw), 1.64 (mw), 1.58 (vw), 1.53 (vw), 1.48 (vw), 1.46 (vw), 1.38 (w), 1.28 (vw).

$Na[H_2NBH_3]$ is soluble in $Et_2O$ and THF. It is insoluble in $CH_2Cl_2$, $CH_3CN$ and $CHCl_3$. Elemental Analysis and EI mass spectra of $Na[H_2NBH_3]$ have been reported elsewhere. 35

$K[H_2NBH_3]$:  

The potassium salt was produced by employing a method analogous to the preparation of the lithium and sodium salts. Variations included performing the reaction at -78 °C, a two day reaction time and the need to keep the ammonia-borane in excess. Low temperature was required in order to stop the formation of secondary products. The excess $H_2NBH_3$ was used to assure that there was no unreacted KH leftover as was the longer reaction time. The potassium salt was not THF soluble. It formed a colorless precipitate as the reaction proceeded. It was therefore isolated by filtering and washing several times with THF. $K[H_2NBH_3]$ could be further purified by dissolving it in $NH_3$ and filtering the solution. An 87 % yield was determined by measuring hydrogen evolution.
$^{11}$B NMR (ND$_3$, -63 °C): -18.97 ppm, q, J = 81.8 Hz. $^1$H NMR (ND$_3$, -63 °C): 0.77 ppm, q, J = 82.7 Hz; 0.00 ppm, s. The $^1$H NMR spectrum is recorded as chemical shift downfield with respect to the solvent NH$_3$. The NH$_2$ signal lies beneath the signal for the solvent ammonia. IR (KBr pellet): $\nu_{\text{NH}}$ cm$^{-1}$ (intensity): 3504 (w), 3346 (m), 3299 (w).

$v_{\text{BH}}$: 2332 (sh), 2250 (sh), 2182 (vs), 2169 (vs), 2123 (sh), 2081 (s), 2021 (sh). $v$: 1243 (sh), 1224 (sh), 1201 (s), 1179 (sh), 1128 (w), 1006 (m), 886 (w), 827 (m), 792 (m), 750 (m), 453 (w). X-ray powder diffraction (photographic): d(Å) (intensity): 5.06 (s), 4.72 (m), 4.33 (mw), 3.95 (m), 3.70 (s), 3.54 (m), 3.45 (vw), 3.32 (s), 3.17 (s), 3.05 (m), 2.97 (s), 2.77 (s), 2.55 (ms), 2.47 (w), 2.40 (m), 2.36 (m), 2.30 (m), 2.24 (mw), 2.19 (mw), 2.12 (s), 1.98 (vwv), 1.84 (mw), 1.60 (vw), 1.54 (w), 1.46 (vw).

K[H$_2$NBH$_3$] is soluble in NH$_3$. It is insoluble in Et$_2$O, THF, CH$_2$Cl$_2$, CH$_3$CN, C$_6$H$_5$N and CHCl$_3$ and it decomposes in DMF and C$_6$H$_5$N. Elemental Analysis of K[H$_2$NBH$_3$] has been previously recorded.

8. Preparation of K[H$_2$NBH$_3$] from K and H$_3$NBH$_3$

A flask was charged in a nitrogen atmosphere with 0.154 g (5.0 mmole) of H$_3$NBH$_3$ and 0.195 g (5.0 mmole) of potassium metal. The nitrogen was pumped away and 50 mL of NH$_3$ was condensed in at -196 °C. The reaction mixture was warmed to -78 °C and stirred approximately 3 days until the blue color of the solvated electron dissipated signalling the completion of the reaction. The flask was cooled to -196 °C and hydrogen evolved measured to give a yield of 100 % (2.5 mmole H$_2$). The ammonia solvent was evaporated leaving behind the colorless product which was washed with THF.
to remove residual H$_3$BNH$_3$. $^{11}$B NMR spectra, IR spectra and X-ray powder diffraction patterns of the product agreed with previously observed values.

9. Preparation of Li[H$_2$NBH$_3$] from RLi and H$_3$NBH$_3$

CH$_3$Li:

A 3-neck round-bottom flask was fitted with nitrogen inlet and outlet adapters and a pressure equalizing dropping funnel. The funnel was equipped with a rubber septum for the addition of CH$_3$Li by syringe. 0.1534 g (4.970 mmole) of H$_3$NBH$_3$ was added to the flask before THF was pipetted in. The flask was submerged in an ice bath and N$_2$ was circulated through the system for approximately 15 minutes. This reaction was very temperature and stoichiometry sensitive so care was taken to keep the ammonia-borane in excess. The CH$_3$Li was added drop-wise to the stirred solution and an immediate reaction occurred with the evolution of methane gas. The boron-11 NMR spectrum indicated that the product of the reaction was Li[H$_2$NBH$_3$].

Attempts to perform this reaction using methods that involved rapid addition of the methyllithium (i.e. syringing directly into a reaction solution maintained at -78 °C or using a tip tube apparatus) failed due to the production of at least 6 side products.

Overnight, the product decomposed and a white precipitate formed. This decomposition occurred whether the product was a dry powder or dissolved in THF. The $^{11}$B NMR spectrum of the decomposition products contained a doublet at -21.27 ppm with a coupling constant of 63 Hz, a triplet at -24.38 ppm with a coupling constant of 70 Hz and a very broad singlet underlying the triplet in the -24 ppm range.
\textbf{C}_4\text{H}_5\text{Li:}

The reaction of \text{H}_3\text{NBH}_3 with \text{C}_4\text{H}_5\text{Li} was analogous to reaction with \text{CH}_3\text{Li}. The initial boron spectrum of the Li[\text{H}_2\text{NBH}_3] produced in this manner, however, always showed evidence for the production of small quantities of secondary products. Within 8 hours, the Li[\text{H}_2\text{NBH}_3] completely decomposed to unknown products. The decomposition products of the \text{C}_4\text{H}_5\text{Li} reaction were not the same as the decomposition products of the \text{CH}_3\text{Li} reaction. The THF soluble \text{C}_4\text{H}_5\text{Li} reaction products included Li[B(n-Bu)_4] and other unidentified boron containing compounds. The unidentified species were observed in the boron-11 NMR spectrum as two very broad resonances at -24.24 ppm and -10.00 ppm, a triplet at -19.63 ppm (\(J = 70\) Hz) and a doublet at -14.43 ppm (\(J = 59\) Hz). There was also a THF insoluble white precipitate present after decomposition had occurred.

10. Decomposition of \text{M}[\text{H}_2\text{NBH}_3]

\textbf{Decomposition Under a Nitrogen Atmosphere or in a Vacuum}

Weighed samples of \text{M}[\text{H}_2\text{NBH}_3] were placed in a flask and set aside at room temperature to allow decomposition to occur. After a specified amount of time, the flask was connected to the vacuum line and the condensible and non-condensible gases were separated, measured and identified. Hydrogen gas was produced along with an unknown amorphous solid.
Thermal Decomposition

A water cooled sublimation apparatus was filled with 2.50 mmole of Na[H₂NBH₃] or K[H₂NBH₃] and evacuated. The apparatus was submerged in an oil bath which was heated on a stirrer/hot plate. The temperature was increased to 80 °C and at regular intervals, the evolved gas was collected and measured. Mass spectral analysis showed the gas to be hydrogen. The amount given off differed for Na[H₂NBH₃] and K[H₂NBH₃]. Na[H₂NBH₃] released 38.3 mole % of H₂ after being heated for 3 days. K[H₂NBH₃] released 42.0 mole % after 2 days of pyrolysis. An unknown amorphous material (based upon X-ray powder diffraction) was also obtained.

Solution Decomposition

A flask was charged in an inert atmosphere with 2.50 mmole of Li[H₂NBH₃], Na[H₂NBH₃] or K[H₂NBH₃] and evacuated. Seventy milliliters of anhydrous THF was added at -196 °C and the vessel was allowed to warm to room temperature for decomposition to occur.

At regular intervals, the flask was cooled to -196 °C so that the gas could be measured. This gas was shown to be H₂ upon analysis. After decomposing for 26 days in THF, 1.93 equivalents of H₂ gas were evolved from a sample of Na[H₂NBH₃].

During and after decomposition of the compound, ¹¹B NMR spectra were recorded for the solutions. Li[H₂NBH₃] decomposes after a month to produce [BH₄]⁻; H₂ gas and large amounts of THF insoluble off-white precipitate. Boron-11 NMR spectra indicate that the intermediates in the solution phase decomposition of Li[H₂NBH₃] include a broad
resonance at -24 ppm, a quartet at -21.42 ppm ($J = 83$ Hz) and another multiplet which is either a doublet or a quartet at -24.30 ppm ($J = 82$ Hz).

$Na[H_2NBH_3]$ decomposes to a THF insoluble amorphous off-white precipitate and $H_2$ gas. The only species observed in the $^{11}$B NMR spectrum during its decomposition is $Na[H_2NBH_3]$. $K[H_2NBH_3]$ does not decompose in THF due to its low solubility.

11. Reaction of $Li[H_2NBH_3]$ with $D_2O$: Formation of $H_3NBH_3$

A screw cap NMR tube with a PTFE / silicone rubber septum was charged with 0.0250 g (0.679 mmole) $Li[H_2NBH_3]$ before $D_2O$ was syringed into the tube. An immediate reaction occurred and a clear, colorless solution was obtained. Boron-11 NMR spectroscopy in $D_2O$ indicated that the boron containing species was ammonia-borane. X-ray powder diffraction of the residue after solvent evaporation indicated $LiCl$.

12. Reaction of $M[H_2NBH_3]$ with $BH_3THF$: Formation of $[BH_4]^-$

A flask with a tip tube was charged with 0.0350 g (0.95 mmole) $Li[H_2NBH_3]$ and THF. The attached tip tube was subsequently filled with 1.00 mL (1.0 mmole) of 1 M $BH_3THF$ in THF. Both solutions were cooled to -196 °C before nitrogen was pumped away in order to minimize solvent or reagent loss. The solutions were warmed to room temperature and the $BH_3THF$ solution was poured into the other causing a rapid reaction with bubbling and the production of a clear and colorless solution. When the reaction was performed at 0 °C, no bubbling occurred and the products were identical.
The major product of the reaction was \([\text{BH}_3]^+\) which was identified by its boron-11 and proton NMR spectra. Secondary products included \(\text{H}_3\text{NBH}_3\), \(\mu\text{-NH}_2\text{B}_2\text{H}_5\), \(\text{B(OH)}_3\), an unidentified \(\text{BH}(\text{OR})_2\) compound and trace quantities of \([\text{B}_3\text{H}_6]^+\) and \(\text{BH}_3\text{THF}\). All of the products were identified by their boron-11 NMR spectra.

13. Reaction of \(\text{M[H}_2\text{NBH}_3]\) with \(\text{M(CO)}_n\): Formation of \([\text{M(CO)}_n\text{CHO}]^-\)

\(\text{Cr(CO)}_6\):

An NMR tube was charged with 0.0203 g (0.552 mmole) \(\text{Li[H}_2\text{NBH}_3]\) and 0.123 g (0.559 mmole) \(\text{Cr(CO)}_6\). THF was condensed in at -196 °C. As the NMR tube warmed to room temperature, the solution immediately turned maroon-rust in color. The proton NMR spectrum in THF indicated the formation of the formyl compound, \([\text{Cr(CO)}_6\text{CHO}]^-\), with a singlet at 14.9 ppm. Boron-11 NMR spectroscopy of the product indicated that numerous unidentified boron containing species were present.

\(\text{Fe(CO)}_5\):

A septum stoppered NMR tube was filled with 0.0280 g (0.761 mmole) \(\text{Li[H}_2\text{NBH}_3]\). THF was pipetted into the tube while it was still in the glove box and the cap was screwed on. Immediately before putting the tube into the NMR probe, 0.1 mL (0.761 mmole) of \(\text{Fe(CO)}_5\) was syringed into the tube and a dark red-brown solution formed. Formation of the formyl anion, \([\text{Fe(CO)}_5\text{CHO}]^-\), was confirmed by the \(^1\text{H}\) NMR spectrum with a singlet at 14.6 ppm. This reaction was also carried out using a 3 neck flask, dropping funnel and nitrogen flow for slow addition of \(\text{Fe(CO)}_5\). Both methods
gave the same results. Ammonia-borane was also produced along with several unidentified boron containing compounds.

14. Reaction of $\text{M[H}_2\text{NBH}_3]$ with $\text{Ru}_3(\text{CO})_{12}$: Formation of $[\text{HRu}_3(\text{CO})_{11}]^-$

To an NMR tube was measured 0.0491 g (0.077 mmole) of $\text{Ru}_3(\text{CO})_{12}$ and 0.0029 g (0.079 mmole) of $\text{Li[H}_2\text{NBH}_3]$. The NMR tube was evacuated and 30 mm of deuterated THF was condensed in at -196 °C. The NMR tube was sealed under vacuum and thawed. The clear solution became orange-red and CO gas was evolved as the reaction proceeded. The formation of $[\text{HRu}_3(\text{CO})_{11}]^-$ was indicated by the presence of a signal in the proton NMR spectrum with a chemical shift in the hydride region at -12.68 ppm. 151

Boron-11 NMR spectroscopy indicated the presence of large amounts of $\text{H}_2\text{NBH}_3$ and some $\text{(H}_2\text{NBH}_3)_n$ in the mixture. The $\text{(H}_2\text{NBH}_3)_n$ was observed as a triplet at -11.72 ppm with a coupling constant of 101 Hz. This chemical shift has been assigned to several BN ring compounds including $\text{(H}_2\text{NBH}_3)_2$ and $\text{(H}_2\text{NBH}_3)_3$. 29

15. Reaction of $\text{M[H}_2\text{NBH}_3]$ with $\text{ZnCl}_2$

This reaction is temperature sensitive so it was performed by charging a side-arm NMR tube flask with 1.89 mmole of $\text{Li[H}_2\text{NBH}_3]$ or $\text{Na[H}_2\text{NBH}_3]$ and 0.1301 g (0.9546 mmole) of $\text{ZnCl}_2$. The system was evacuated and THF added at -196 °C. The solution was warmed to -78 °C and stirred. A low temperature NMR sample was obtained by tipping some of the reaction solution into the NMR tube and then sealing it. $\text{Zn(H}_2\text{NBH}_3)_2$ was the only THF soluble material in the tube.
 Upon warming the solution to room temperature, large amounts of precipitate were formed in the colorless solution and the $^{11}$B NMR spectrum of the solution became complicated. Included with the other resonances was that of $\text{Zn(H}_2\text{NBH}_3)_2$. 

$^{11}$B NMR (THF): -20.49 ppm, q, $J = 89$ Hz.

The precipitate and solution were separated by filtration and the precipitate was shown to be NaCl from its X-ray powder diffraction pattern.

When the THF was removed from the soluble fraction, an off white solid was recovered. This solid decomposed within 4 to 8 hours to a black precipitate. This black precipitate also formed when solutions of $\text{Zn(H}_2\text{NBH}_3)_2$ in THF were allowed to age 4 to 8 hours. 1.5 equivalents of $\text{H}_2$ gas was evolved during the initial decomposition process. X-ray powder diffraction of the black solid indicated the presence of elemental Zn and the $^{11}$B NMR spectrum of the THF soluble fraction indicated the presence of $[$BH$_4]$ and H$_2$NBH$_3$ as the major identifiable components. A large portion of the boron signal was contained in broad featureless humps in the $^{11}$B NMR spectrum. Due to the $^{11}$B NMR chemical shift and coupling constants of the species (-44 ppm, quint, $J = -82$ Hz), the identity of the [BH$_4$]$^-$ species is probably M[Zn(BH$_4$)$_3$] where M = Li or Na or Li$_2$[Zn(BH$_4$)$_4$]. LiBH$_6$, NaBH$_6$, and Zn(BH$_4$)$_2$ resonate at -41.6, -42.2, and -46.8 ppm with coupling constants of 82, 81 and 84.3 ppm, respectively. The proton NMR spectrum proved to be too complex for analysis due to numerous overlapping multiplets.
The infrared spectrum of the residue after it decomposed at room temperature showed very broad featureless absorbances in both the NH and BH stretching regions.

16. Reaction of M[H₂NBH₄] with MgI₂

A reaction flask and extractor was charged with 0.184 g (5 mmole) of Li[H₂NBH₄] and 0.697 g (2.5 mmole) of MgI₂. Anhydrous THF was added at -196 °C and the apparatus was warmed to room temperature and stirred. Within minutes of warming, the solution began to look like milk with a white precipitate of MgI₂ in the colorless solution. The relatively slow reaction could be monitored by ¹¹B NMR spectroscopy. As the reaction progressed the intensity of the signal of the starting material decreased and the ¹¹B NMR spectroscopy signal of the product increased. The reaction involved the loss of 3 equivalents (7.5 mmole) of H₂ gas.

After 3 to 5 days of reaction Mg(H₂NBH₄)₂ was separated from three side products by THF and Et₂O washes. The first side product was insoluble in THF and collected on the frit during the first extraction. The second unknown product was soluble in THF but insoluble in Et₂O. It was separated by washing with ether. This second compound could not be redissolved in THF after being washed with ether. Lil was the third side product. It was both THF and Et₂O soluble and remained with Mg(H₂NBH₄)₂ after the washes. X-ray powder diffraction studies identified the Lil.
Characterization of Mg(H$_2$NBH$_3$)$_2$:

$^1$B NMR (THF): -20.15 ppm, q, J = 89 Hz. $^1$H NMR (THF): 1.25 ppm, q, J = 89 Hz. The NH$_2$ signal appears as a broad singlet with a position that varies from sample to sample. IR (KBr pellet): $\nu_{NH}$ cm$^{-1}$ (intensity): 3482 (sh), 3413 (vs, b), 3314 (m), 3281 (m). $\nu_{BH}$: 2340 (sh), 2328 (sh), 2285 (vs), 2245 (s), 2226 (s). $\nu$: 1562 (m), 1242 (w), 1160 (w), 1140 (w), 1038 (w), 891 (w).

Mg(H$_2$NBH$_3$)$_2$ is soluble in THF, Et$_2$O, H$_2$O and pyridine. It is insoluble in CH$_2$Cl$_2$, benzene and n-heptane and it decomposes in acetonitrile.

IR spectrum of the THF insoluble solid (KBr pellet): $\nu_{NH}$ cm$^{-1}$ (intensity): 3408 (m, vvb), 3208 (m, vvb). $\nu_{CH}$: 2980 (s), 2965 (sh), 2933 (sh), 2895 (s). $\nu_{BH}$: 2375 (sh), 2347 (sh), 2320 (w), 2217 (sh). $\nu$: 1022 (vs), 867 (s).

IR spectrum of the Et$_2$O insoluble solid (KBr pellet): $\nu_{NH}$ cm$^{-1}$ (intensity): 3532 (sh), 3403 (sh), 3308 (s, vb). $\nu_{CH}$: 2979 (s), 2935 (sh), 2885 (s). $\nu_{BH}$: 2327 (vs, vvb), 2219 (sh), 2120 (sh). $\nu$: 1472 (s), 1377 (s), 1261 (vw), 1164 (m), 1040 (m), 875 (m).

17. Reaction of M[H$_2$NBH$_3$] with (C$_5$H$_5$)$_2$ZrCl$_2$

1:1 Reaction

In the glove box, a flask and extractor were charged with 2.5 mmole of M[H$_2$NBH$_3$] (M = Li, Na, K) and 0.7308 g (2.5 mmole) of (C$_5$H$_5$)$_2$ZrCl$_2$. After the flask
was evacuated, 60 mL of anhydrous THF was added at -78 °C. The solutions were warmed and stirred. Those solutions containing lithium or sodium salts immediately began to turn yellow in color. With the sodium salt, the appearance of a white precipitate was also noted. The precipitate was shown to be NaCl by its X-ray powder diffraction pattern.

After filtration and solvent evaporation, the boron-11 and proton NMR spectra indicated that the product contained a mixture of substances including \((C_5H_5)_2ZrCl(NH_2BH_3)\), \((C_5H_5)_2Zr(NH_2BH_3)_2\), \((C_3H_3)_2ZrCl_2\), and \(H_3NBH_3\). For the reaction with Li\([H_2NBH_3]\), LiCl was also present. It was identified by its characteristic X-ray powder diffraction pattern. In this 1:1 reaction, the ratio of \((C_5H_5)_2ZrCl(NH_2BH_3)\) to \((C_3H_3)_2Zr(NH_2BH_3)_2\) in the final product was approximately 26 to 1 (as determined to the integration of the boron-11 NMR spectrum).

Because of the insolubility of K\([H_2NBH_3]\), the reaction between it and \((C_3H_3)_2ZrCl_2\) is extremely slow. A yellow color to the solution is noted only after weeks of stirring. The only product produced is \((C_5H_5)_2ZrCl(NH_2BH_3)\) but the yield is very low and the starting materials K\([H_2NBH_3]\) and \((C_3H_3)_2ZrCl_2\) predominate.

2:1 Reaction

The reaction in a 2:1 molar ratio was performed in the same manner as previously noted except that 2.95 mmole of Li\([H_2NBH_3]\) or Na\([H_2NBH_3]\) were used with 0.4310 g (1.48 mmole) \((C_2H_2)_2ZrCl_2\).
Again the yellow color and NaCl precipitate were noted as the reaction progressed. Boron-11 NMR spectroscopy demonstrated that the products were \((\text{C}_5\text{H}_5)_2\text{ZrCl(NH}_2\text{BH}_3)\) and \((\text{C}_5\text{H}_5)_2\text{Zr(NH}_2\text{BH}_3)_2\) but their molar ratios were more equal. Attempts to perform the reaction at -78 °C in an effort to drive the equilibrium to favor one species or the other failed. The reaction did not proceed at that temperature and analysis of the final mixture indicated the presence of ammonia-borane, \(\text{H}_2\) gas and \(\text{NH}_4\text{Cl}\) along with the starting material \((\text{C}_5\text{H}_5)_2\text{ZrCl}_2\).

Characterization of \((\text{C}_5\text{H}_5)_2\text{ZrCl(NH}_2\text{BH}_3)\):

\(^{11}\text{B NMR (THF): -23.08 ppm, q, } J = 89 \text{ Hz.}^{1}\text{H NMR (THF): 6.06 ppm, s; 2.74 ppm, bs; 0.21 ppm, q, } J = 89 \text{ Hz. IR (KBr pellet): } \nu_{\text{NH}} \text{ cm}^{-1} \text{ (intensity): 3383 (m), 3280 (s).} \nu_{\text{CH}} : 3097 \text{ (m).} \nu_{\text{BH}} : 2405 \text{ (s), 2393 (s), 2319 (ms).} \nu : 1437 \text{ (m), 1177 (s), 1014 (s), 984 (m), 813 (vs), 737 (m).}

Characterization of \((\text{C}_5\text{H}_5)_2\text{Zr(NH}_2\text{BH}_3)_2\):

\(^{11}\text{B NMR (THF): -34.12 ppm, q, } J = 91 \text{ Hz.} \text{ IR (KBr pellet): } \nu_{\text{NH}} \text{ cm}^{-1} \text{ (intensity): 3395 (m), 3303 (m).} \nu_{\text{CH}} : 3088 \text{ (w).} \nu_{\text{BH}} : 2376 \text{ (s), 2304 (m).}

\((\text{C}_5\text{H}_5)_2\text{Zr(NH}_2\text{BH}_3)_2\) was never isolated separately for detailed characterization. \((\text{C}_5\text{H}_5)_2\text{ZrCl(NH}_2\text{BH}_3)\) and \((\text{C}_5\text{H}_5)_2\text{Zr(NH}_2\text{BH}_3)_2\) are soluble in THF. They decompose to \(\text{B(OMe)}_3\) in acetone.
3:1 Reaction

Reactions in the molar ratio of three Li[H₂NBH₃] or Na[H₂NBH₃] to one (C₄H₉)₂ZrCl₂ were attempted in an effort to maximize the production of (C₄H₉)₂Zr(NH₂BH₃)₂. In both of these types of reactions, the products were predominantly H₂NBH₄ according to ¹¹B NMR spectroscopy. NH₄Cl was also obtained in these reactions.

18. Reaction of M[H₂NBH₃] with 12-crown-4

In an effort to grow crystals, 0.0460 g (1.25 mmole) Li[H₂NBH₃] was produced from LiH and H₂NBH₃ in THF. The volume of solvent was reduced under vacuum and 0.404 mL (2.50 mmole) of 12-crown-4 was syringed in. Small crystals immediately appeared in the solution but the structure could not be solved from the data obtained. Even when a 1:1 molar ratio of 12-crown-4 was added to dilute solutions of Li[H₂NBH₃], crystals immediately formed but their structures could not be solved. Attempts were made to grow larger crystals by allowing the solution to sit at room temperature or at -4 °C but both of these procedures led to the formation of large amounts of precipitate.

Initial ¹¹B NMR spectroscopy of Li[H₂NBH₃] in the presence of 12-crown-4 shows a broadened unsymmetrical quartet with the same chemical shift as pure Li[H₂NBH₃] in THF. However, within a few days, decomposition was evident in the crystal growing apparatus by the production of large amounts of off-white solid. IR spectroscopy indicated weak NH and strong BH bands but the absorbances had lost most of their fine structure.
19. Reaction of $M[H_2NBH_3]$ with TMEDA

Attempts to grow crystals from TMEDA were also attempted by synthesizing Li$[H_2NBH_3]$ as before and reducing the THF volume by solvent evaporation or by adding DME to solid Li$[H_2NBH_3]$ (0.0906 g = 2.462 mmole). To these solutions was added by syringe 0.37 mL (2.45 mmole) of TMEDA. No isolable crystals were detected in the solution after allowing it to sit at room temperature for several days. Initial $^{11}$B NMR spectroscopy indicated no perturbation of the signal for Li$[H_2NBH_3]$ by TMEDA. Within 10 days, noticeable decomposition had occurred in the flask and the boron-11 NMR spectrum showed the typical decomposition pattern of Li$[NH_2BH_3]$ in THF. IR spectroscopy of the solid residue from the decomposition indicated weak NH and strong BH absorptions with the loss of individual peak identities.

Neat TMEDA was also added to solid Li$[NH_2BH_3]$ and maintained at -4 °C in an effort to obtain crystals. No crystals were formed. After several weeks a precipitate was discovered in the tube.

20. Preparation of Gd($B_3H_8$)$_3$nsolvent

In the glove box, a flask was filled with 0.2111 g (0.8008 mmole) of anhydrous GdCl$_3$ and 0.1933 g (2.429 mmole) of KB$_3$H$_8$. Approximately 75 mL of dry DMF or DMAC was also added to the flask by pipette while in the glove box. An immediate reaction occurred with the production of a white precipitate which was later identified as KCl by its X-ray powder diffraction pattern. Attempts to filter the solution by gravity failed due to the fact that the KCl powder was very fine and filtered through the frit along
with the solution. Instead, the products were separated by centrifuging and decanting.

$^{11}$ B NMR (DMF): -29.0 ppm, bs. IR (KBr pellet): ν<sub>CH</sub> cm<sup>-1</sup> (intensity): 2966 (sh), 2936 (m), 2876 (sh), 2817 (w). ν<sub>BH</sub>: 2525 (sh), 2442 (s), 2392 (s), 2312 (m), 2279 (sh), 2122 (m), 2076 (w). ν: 1656 (vs).

The actual positioning of the boron-11 NMR signal varied from spectrum to spectrum but when referenced internally to Me<sub>3</sub>NBH<sub>3</sub>, the above value was obtained. The quantitative yield is based upon the fact that no starting material remained in the $^{11}$ B NMR spectrum or in the IR spectrum after the reaction had occurred. If prepared in DMF, the Gd(B<sub>9</sub>H<sub>14</sub>)<sub>3</sub> product began to decompose within 1 day to form Me<sub>3</sub>NBH<sub>3</sub>. This decomposition occurred rapidly if in solution but also occurred with the isolated powder though much more slowly. The decomposition did not occur in DMAC.

The compound is soluble in DMF, DMAC, CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub>. It is slightly soluble in THF and DME and it is insoluble in C<sub>6</sub>H<sub>14</sub>, C<sub>6</sub>H<sub>5</sub>, and Et<sub>2</sub>O.

21. Preparation of Gd(B<sub>9</sub>H<sub>14</sub>)<sub>3</sub>nDMF

The [B<sub>3</sub>H<sub>14</sub>]<sup>-</sup> salt was prepared in an analogous manner to the above compound except that 0.1012 g (0.6724 mmole) of KB<sub>9</sub>H<sub>14</sub> and 0.0590 g (0.224 mmole) of GdCl<sub>3</sub> were used instead. The boron-11 NMR spectrum of the gadolinium [B<sub>3</sub>H<sub>14</sub>]<sup>-</sup> compound, unlike that of the [B<sub>3</sub>H<sub>9</sub>]<sup>-</sup> compound, showed coupling. The reaction yield was quantitative based upon the absence of starting material in the boron-11 NMR or in the IR spectra after reaction. The KCl was identified by X-ray powder diffraction.
$^{11}$ B NMR (DMF): -21.30 ppm, d, J = 123 Hz (3 B); -18.06 ppm, d, J = 119 Hz (3 B); -5.76 ppm, d, J = 132 Hz (3 B).

IR (KBr pellet): $\nu_{\text{CH}}$ cm$^{-1}$ (intensity): 2965 (sh), 2935 (m), 2895 (sh), 2813 (w). $\nu_{\text{BH}}$: 2515 (s), 2462 (sh), 2426 (sh), 2390 (sh), 2329 (w). $\nu$: 1656 (vs). $\nu$: 1496 (m), 1438 (s), 1421 (sh), 1379 (s), 1253 (m), 1174 (m), 1170 (sh), 1113 (s), 1060 (w), 1018 (m), 946 (w), 864 (w), 679 (vs).

mass spec: Gd(B$_3$H$_{14}$)$_3$ DMF (calc.): 569 m/e. GdCl(B$_3$H$_{14}$)$_2$ DMF (calc.): 564 m/e. Found: 566 m/e.

The solvated salt is soluble in DMF, DMAC and CH$_3$CN. It is insoluble in Et$_2$O, THF, C$_6$H$_{14}$, C$_6$H$_6$ and CH$_2$Cl$_2$.

22. Crystal Structure of GdCl$_3$ 2DME

GdCl$_3$ 2DME was crystallized from a concentrated mixture of GdCl$_3$ and the potassium salt of a boron hydride in DME into which hexane was allowed to slowly diffuse. The crystals formed overnight at -4 °C, but formed much more quickly at room temperature. The crystals produced at room temperature, however, remained small and difficult to isolate. This structure had previously been solved using room temperature. Our X-ray data were collected at -60 °C.

The crystals were isolated in the glove box and transferred to 0.3 or 0.5 mm glass capillary tubes which were temporarily sealed with grease prior to being flame sealed and prepared for mounting onto the X-ray diffractometer.
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