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STUDIES OF GROUP V SUBSTITUTED BORANES

by

Lawrence David Schwartz

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DEPARTMENT OF CHEMISTRY

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1971

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ABSTRACT

The reaction of diborane with various lithium amides, phosphides, and arsenides has been investigated, and the products characterized.

When diborane reacts with lithium dimethyl- or diethylphosphide(1-) in ether solvents, only lithium bis(borane)dimethyl- or diethylphosphide(1-) is obtained. A study of the stepwise addition of diborane to lithium dimethylphosphide(1-) indicated no intermediates other than the final product, lithium bis(borane)dimethylphosphide(1-). $\text{Li}(\text{CH}_3)_2\text{P}(\text{BH}_3)_2$ is reasonably air, water and thermally stable, but is rapidly hydrolyzed in aqueous acid. It exchanges hydrogen with diborane and although no intermediates were identified, μ -dimethylphosphinodiborane is suggested as the exchanging species. Attempts to prepare μ - $(\text{CH}_3)_2\text{PB}_2\text{H}_5$ from lithium bis(borane)dimethylphosphide(1-), and hydrogen chloride or warm polyphosphoric acid failed. The infrared and nmr spectral properties of $\text{Li}(\text{CH}_3)_2\text{P}(\text{BH}_3)_2$ compare favorably with $\text{Na}(\text{CH}_3)_2\text{N}(\text{BH}_3)_2$, $\text{KH}_2\text{P}(\text{BH}_3)_2$, and other structurally related compounds.

Heating lithium bis(borane)dimethylphosphide(1-) with amine hydrochlorides, $(\text{CH}_3)_3\text{NHCl}$, $(\text{CH}_3)_2\text{NH}\cdot\text{HCl}$, $\text{CH}_3\text{NH}_2\cdot\text{HCl}$ and $\text{NH}_3\cdot\text{HCl}$, monoglyme yields a new series

of compounds with the N-B-P-B backbone, $R_3NBH_2P(CH_3)_2BH_3$. These volatile compounds are air and thermally stable, and are quite resistant to hydrolysis. Furthermore they are soluble in non-polar solvents; except for the ammonia derivative, they are insoluble in water. Pyrolysis of these derivatives at temperatures over 100° results in recovery of dimethylphosphinoborane trimer, a boron-nitrogen compound (whose nature is dependent upon the amine derivative), and hydrogen (except for the trimethylamine compound). The infrared, and nmr spectral properties of these compounds compare favorably with the structurally related N-B-N-B [$R_3NBH_2P(CH_3)_2BH_3$] compounds. However unlike the NBNB derivatives, no indication or dissociation into amine and μ -dimethylphosphinodiborane is found for the NBPB compounds as evidenced by the lack of reaction with amines and boron trifluoride.

Unlike lithium dimethyl- and diethylphosphide, N-alkyl substituted lithium amides ($LiNHR$, $R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, s-C_4H_9, t-C_4H_9, n-C_5H_{11}$, and $C_6H_5CH_2$; $LiNR'_2$, $R' = CH_3, C_2H_5, n-C_3H_7, \text{ and } i-C_3H_7$), do not yield lithium bis(borane)alkylamides, when diborane reacts with them. The study of the stepwise addition of diborane to solutions of the amides was undertaken with the aid of boron-11 nmr. With the exception of lithium monomethyl- and monoethylamide, the first products detected were a tri(amino)borane, and lithium borohydride; addition

of further diborane yielded a di(amino)borane and a μ -aminodiborane; additional diborane resulted in the final products, a μ -aminodiborane and an aminoborane. At 0° lithium monomethyl- and monoethylamide behave similarly, but at ambient temperatures the products include an amine-borane and a borazine. These products are a result of the decomposition of either the tri- or di(amino)borane. The study characterizes some new μ -aminodiboranes and suggests reasons for the differences between various amide and phosphide reactions.

The reaction of lithium dimethylarsenide(1-) with diborane yields lithium bis(borane)dimethylarsenide(1-). Although work is still incomplete, the new compound appears to be similar to the phosphorus analog, not only in its hydrolytic and air stabilities, but also in its spectral properties.

CHAPTER 1

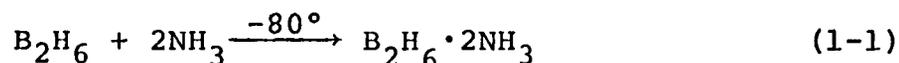
INTRODUCTION

During the first 30 years of this century, the chemistries of boron and silicon hydrides were investigated in a classic study by Alfred Stock of Germany. In order to handle these reactive compounds, Stock also developed high vacuum techniques, many of which are still in use today.^{1,2}

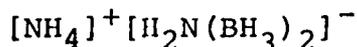
In the 1930's H.I. Schlesinger at the University of Chicago was attracted to Stock's work. Schlesinger and his co-workers further developed the reactions of the lower boron hydrides.

A.B. Burg, a Schlesinger student, among his studies, investigated the reactions of the lower boron hydrides with various derivatives of the group V elements. Many of these reactions are fundamental to this work.

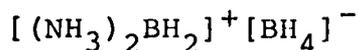
One of the most perplexing problems confronting boron chemists for many years was the reaction of ammonia with diborane. Stock originally found that 2 moles of ammonia were consumed per mole of diborane (eq 1-1).³



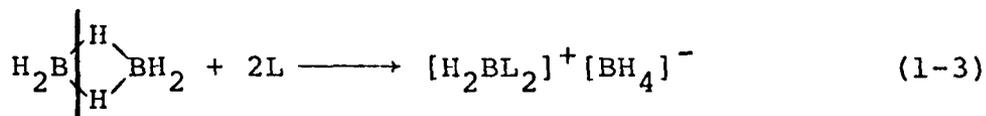
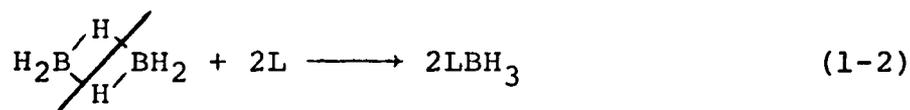
Schlesinger and Burg found this substance to be ionic and proposed a structure for the "diammoniate of diborane."⁴



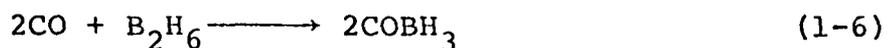
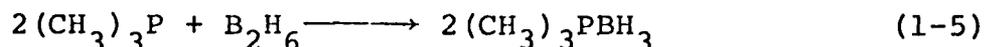
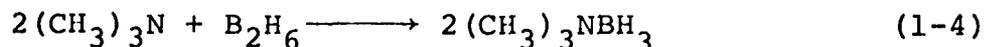
Nearly 30 years later other workers^{5,6,7} established the correct structure by chemical methods.



Parry and Edwards classified diborane - base fragmentation reactions into two categories, symmetrical (eq 1-2) and unsymmetrical (eq 1-3) cleavage.⁸ Classification is based on the nature of the products and makes no implication as to the reaction mechanism.



Most diborane - Lewis base reactions follow the symmetrical cleavage route (eq 1-4 through 1-6).



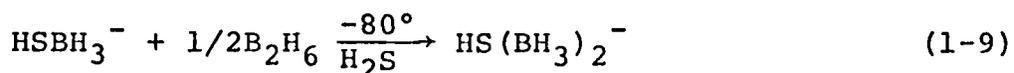
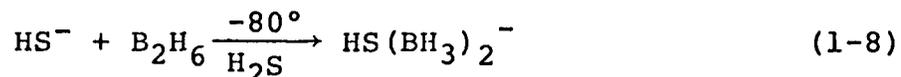
A few bases, notably primary and secondary amines yield both the symmetrical and unsymmetrical fragmentation products. However relatively few bases give exclusively unsymmetrical cleavage (ionic) products. These bases include ammonia, dimethylsulfoxide, and hydroxide and methoxide ions.⁹ In 1955 Schaeffer and

Basile¹⁰ reported that the reaction of lithium amide and diborane in diethyl ether yielded only the unsymmetrical cleavage product (eq 1-7). This reaction discouraged

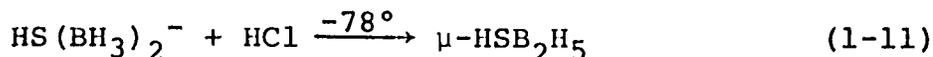
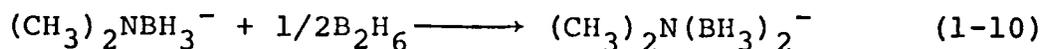


the investigations of the reactions between diborane and substituted amides, phosphides and arsenides.

Recently P.C. Keller^{11,12} has investigated reactions of diborane with HS^- and HSBH_3^- (eq 1-8 and 1-9). These compounds cleave diborane symmetrically:



Keller has also reported that $(\text{CH}_3)_2\text{NBH}_3^-$ resembles HSBH_3^- in its reaction with diborane (eq 1-10). However unlike the sulfur analog, addition of more diborane generates a bridge substituted diborane, μ -dimethylaminodiborane.^{13,14} The analogous μ -mercaptodiborane, μ - HSB_2H_5 is prepared by treating $\text{HS}(\text{BH}_3)_2^-$ with anhydrous hydrogen chloride at -78° (eq 1-11).



Some question was raised as to whether the μ -mercaptodiborane produced was a result of eq 1-11 or actually due to other unidentified species reacting with HCl.^{12,15}

The preparation of $\text{HS}(\text{BH}_3)_2^-$ 11,12,15 and $(\text{CH}_3)_2\text{N}(\text{BH}_3)_2^-$ 14,16 by Keller and $\text{H}_2\text{P}(\text{BH}_3)_2^-$ 17,18,19 by others is quite interesting since these compounds are related to the originally proposed structure of the diammoniate of diborane.

Reactions 1-8 through 1-11 have led to the problem which concerns the reaction of various amides, phosphides and arsenides with diborane, and the characterization of these products. The study is presented in chronological order of investigation with the understanding of each system complementing the next.

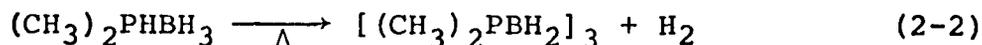
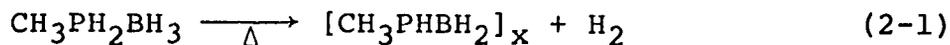
CHAPTER 2

THE PREPARATION AND PROPERTIES OF LITHIUM BIS(BORANE)DIMETHYLPHOSPHIDE(1-)

Although a considerable number of boron - phosphorus compounds have been characterized, most are either complexes of the type R_3PBH_3 or associated phosphinoboranes $(R_2PBH_2)_x$. The complexes are similar to the nitrogen analogs already discussed in chapter one; phosphine yielding the symmetrical cleavage product exclusively. Phosphinoboranes are nearly exclusively associated.²⁰ Depending on the substituent on boron or phosphorus ($R_2PBR'_2$), these compounds are dimers, trimers, tetramers or higher polymers. The monomeric phosphinoboranes appear to be a result of steric hindrance.²⁰

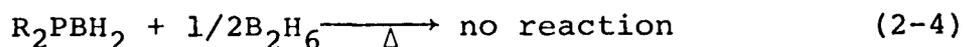
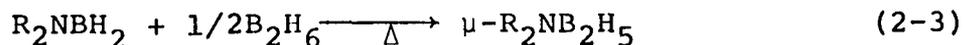
Burg and Wagner²¹ first prepared the P-methyl derivatives of phosphinoboranes, CH_3PHBH_2 and $(CH_3)_2PHBH_2$, by the pyrolysis of the corresponding phosphine-borane.

The $CH_3PH_2BH_3$ (2-1) reaction yields a



viscous oil, apparently a high polymer, while $(CH_3)_2PHBH_3$ (2-2) yields primarily a trimer, although a tetramer and a higher polymer were also identified. These compounds, especially $[(CH_3)_2PBH_2]_3$ had very low reactivity. Unlike

their nitrogen analogs, they did not react with diborane at elevated temperatures to form μ -phosphinodiboranes (eq 2-3, 2-4); they were thermally stable when heated over



200°, and were resistant to all but the most extreme hydrolytic conditions (300° for 12 days in concentrated hydrochloric acid).

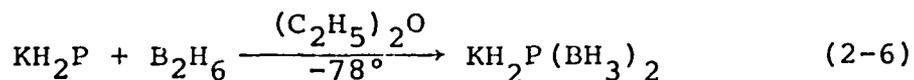
The stability of the phosphinoboranes may be due in part to the fact that unlike aminoboranes, these compounds show no tendency to dissociate into monomeric species.²² Phosphorus, unlike nitrogen does not form strong $P_{\pi} - P_{\pi}$ bonds.²³ This lack of π -bonding prohibits stabilization of three coordinate phosphorus bonded to boron ($R_2P-BR'_2$); the associated structures of phosphinoboranes are a result of phosphorus increasing its coordination to at least four.

Despite the stability of phosphinoboranes, other phosphorus - boron compounds have been prepared. In 1961 Muettterties and co-workers²⁴ reported the synthesis of $Na(CH_3)_2PBH_3$ by the sodium hydride deprotonation of dimethylphosphine-borane in monoglyme. In 1965 Thompson¹⁷ (eq 2-6)

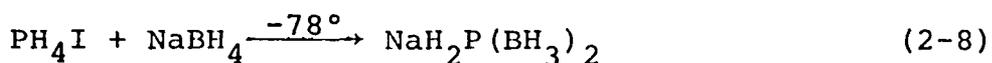
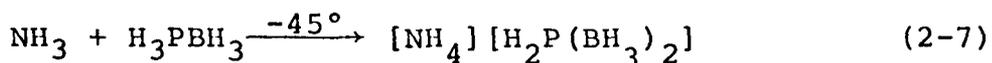


reported the preparation of $KH_2P(BH_3)_2$ by reacting potassium dihydrogen phosphide with diborane in ether at -78°, although the product was poorly characterized. Two years

later two groups independently prepared and characterized

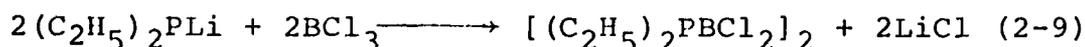


the bis(borane)dihydrogenphosphide(1-) anion. Gilje, Morse and Parry¹⁸ synthesized $[\text{NH}_4][\text{H}_2\text{P}(\text{BH}_3)_2]$ by the reaction of ammonia and phosphine-borane (H_3PBH_3) at low temperatures (eq 2-7). Mayer and Hester,¹⁹ on the other hand obtained the sodium salt by the reaction of phosphonium iodide and sodium borohydride at -78° (eq 2-8). The research groups found the resulting compounds to be

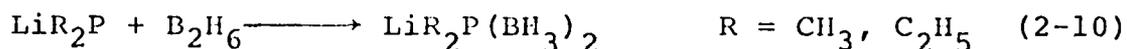


hydrolytically and thermally stable, but not to the extent found for most phosphinoboranes.

Considering the stability of phosphinoboranes, one would expect the Schaeffer - Basile reaction¹⁰ discussed in chapter 1 (eq 1-7) to predominate when an ionic dialkylphosphide reacts with a borane. This is the case when lithium diethylphosphide reacts with boron trichloride.²⁵



However we have found that unlike lithium amide, lithium dimethylphosphide reacts with diborane in ether to produce lithium bis(borane)dimethylphosphide(1-).²⁶ A similar reaction occurs with lithium diethylphosphide.



Experimental Section

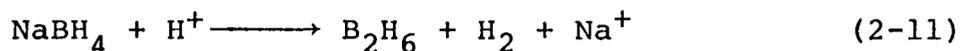
General Data

Reactions were carried out with the aid of a standard high vacuum system as described in the appendix. Air-sensitive materials were manipulated in nitrogen-filled drybags, also discussed in the appendix, or in the vacuum line. Diethyl ether, monoglyme (1,2 dimethoxyethane) and dioxane were stored in evacuated bulbs over lithium aluminum hydride, and when needed, were condensed directly into the reaction vessel. Boron-11 nmr spectra were obtained using a Varian HA-100 spectrometer operating at 32.1 MHz; proton nmr spectra were obtained with Varian HA-100 and A-60 instruments. Boron-11 and proton chemical shifts are in parts per million (ppm) relative to diethyl ether - boron trifluoride and tetramethylsilane (TMS), respectively. Infrared spectra were obtained using Perkin-Elmer 137 and 337 spectrophotometers.

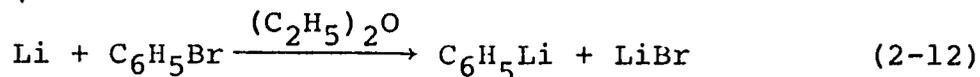
Reagents

Diborane and B_2D_6 were prepared by the reaction of warm polyphosphoric acid with sodium borohydride and $NaBD_4$, respectively. Generally 20 mmol samples of diborane were prepared and stored in vessels maintained at -196° . Typically, a one liter three-necked flask, equipped with a motor stirrer, an addition side-arm, and a connection to the vacuum line, was charged with about 100 ml of viscous

polyphosphoric acid. A quantity of sodium borohydride was placed in the side-arm, and the entire system evacuated. After heating the flask to about 60° with a heating mantle, the acid became more fluid and was stirred vigorously while sodium borohydride was slowly added from the side-arm. The generated diborane was collected in traps cooled to -196°. Yields were generally over 90%. The B₂D₆ reaction essentially paralleled the diborane reaction; smaller samples, about 1 mmol, were prepared.



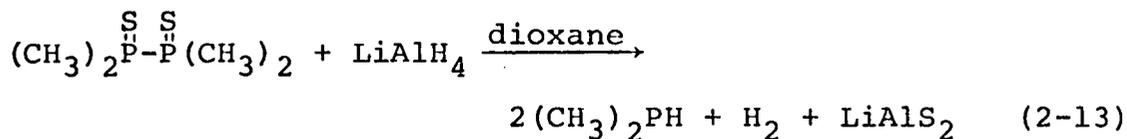
Phenyllithium was prepared in diethyl ether from bromobenzene and lithium wire containing 1% sodium (Alpha Inorganics, Inc.) by the method of Gilman and Morton.²⁷ Because of side reactions, decomposition, and incomplete separation, the phenyllithium contained small quantities of diphenyl, lithium ethoxide and lithium bromide. Older samples became increasingly contaminated with lithium ethoxide,



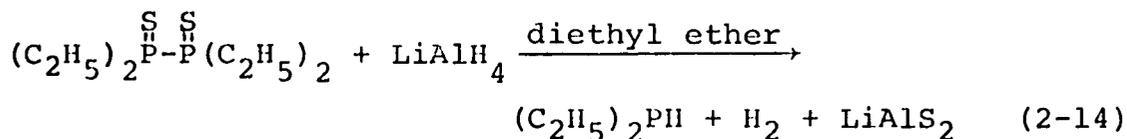
N-butyllithium in hexane, approximately 1.6 M (Foote Chemical Co.) was used without purification. All samples were contaminated with lithium bromide, while older samples contained appreciable quantities of lithium butoxide due to decomposition. Both phenyllithium and n-butyllithium were always handled in drybags and stored

in refrigerators to retard decomposition, when not in use.

The Preparation of Dimethylphosphine. Dimethylphosphine was prepared from the reaction of tetramethyldiphosphinedisulfide with lithium aluminium hydride in dioxane.²⁸ Typically 20 mmol of tetramethyldiphosphinedisulfide and 22 mmol of lithium aluminium hydride were placed in a 200 ml flask. After evacuation, dry dioxane was condensed in the vessel which was then heated to about 50° with an oil bath. The vessel was opened to the vacuum line manometer in order to monitor the course of the reaction. When 300 or 400 mm of pressure developed, the dimethylphosphine was removed and the reaction allowed to continue. Yields up to 30 mmol, 70%, were obtained when the reaction was allowed to continue over a 24 hour period. Dimethylphosphine was purified by fractionation through



a -78° trap to remove the dioxane. Its purity was determined by comparison of its 0° vapor pressure with the literature value of 339 mm.²⁹ Diethylphosphine was prepared in a similar manner using tetraethyldiphosphinedisulfide, lithium aluminium hydride and diethyl ether.³⁰



The Preparation of Lithium Dimethylphosphide(1-).

Lithium dimethylphosphide was prepared from the reaction of phenyllithium and dimethylphosphide in diethyl ether.³¹ In a drybag, a known amount of phenyllithium was injected into a flask. The vessel was quickly transferred to the vacuum line where it was evacuated. A slight excess of dimethylphosphine was condensed in the flask which was then warmed to room temperature and stirred magnetically. After about 15 minutes the pale pink solution turned cloudy and a white precipitate of lithium dimethylphosphide settled out when stirring was discontinued. After 1 hour, all volatiles were removed by vacuum pumping; the amount of phosphide formed was determined by the dimethylphosphine consumption, and the lithium phosphide was used without further purification. Lithium diethylphosphide was pre-



pared analogously. In some reactions n-butyllithium was used in place of phenyllithium.

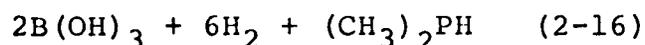
The Reaction of Lithium

Dimethylphosphide with Diborane

In a typical reaction, a 200 ml reaction vessel was charged with 2.69 mmol of lithium dimethylphosphide in 5 ml of monoglyme. A 3.10 mmol sample of diborane was condensed into the evacuated vessel, which was then warmed to room temperature and stirred magnetically for one hour. Separation of the volatile products produced

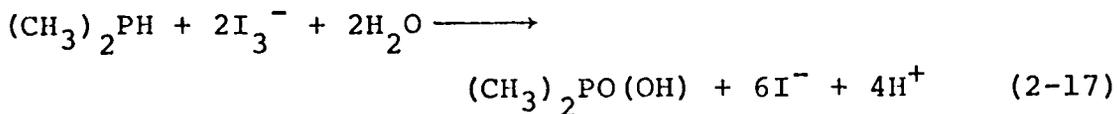
only monoglyme and 0.32 mmol of diborane, implying a 2.78 mmol consumption of diborane. The involatile residue consisted of a viscous oil which, after treatment with 5 ml of anhydrous dioxane and evaporation of the solution under vacuum, yielded a colorless crystalline solid which was then washed with heptane and cold dioxane and dried under vacuum.

Analysis. Analysis of the product, $\text{Li}(\text{CH}_3)_2\text{P}(\text{BH}_3)_2$. $\text{C}_4\text{H}_8\text{O}_2$, (I), presented a problem because the material contained an appreciable, though evidently nonstoichiometric, quantity of lithium bromide³² introduced from the phenyllithium preparation. Analysis was accomplished by acid hydrolysis according to eq 2-16. Sulfuric acid, 1 M,

$$(\text{CH}_3)_2\text{P}(\text{BH}_3)_2^- + \text{H}^+ + 6\text{H}_2\text{O} \longrightarrow$$


was added through the stopcock of an evacuated vessel containing a weighed amount to I. Vigorous bubbling occurred instantly and lasted for several minutes. After about one hour, the vessel was frozen with liquid nitrogen and the hydrogen removed and measured with a Toepler pump. Boric acid was determined by complexing with D-mannitol and titration with standard base. Dimethylphosphine was determined by distilling the hydrolyzed solution into excess I_3^- followed by back titration with thiosulfate

(eq 2-17). The dioxane of crystallization was recovered



quantitatively by heating the solid to 80° under vacuum. Absolute percentages varied considerably between samples, but the elemental ratios remained essentially constant. In a typical analysis, the B:H:P ratio was found to be 1.9:5.8:1.0, compared to the calculated ratio of 2.0:6.0:1.0. In a separate experiment 0.96 mmol of dioxane was recovered per mmol of I.

Characterization. I dissolves without reaction in glyme ethers, ethanol, toluene, neutral water, and aqueous base, but is insoluble in diethyl ether, benzene, heptane, and chloroform. After nine months, a solution of I in neutral D₂O had undergone only slight decomposition and exchange as indicated by its boron-11 nmr spectrum. Acidification of an aqueous solution of I results in rapid hydrolysis (eq 2-17). Although I is reasonably air stable, it is quite hygroscopic. The proton nmr spectrum of I in D₂O (fig 1) shows chemical shifts of $\delta(\text{BH}) = -0.47$ ppm and $\delta(\text{CH}) = -1.08$ ppm with coupling constants $J_{\text{BH}} = 88$ Hz, $J_{\text{PCH}} = 8$ Hz, and $J_{\text{PBH}} = 12$ Hz. The boron-11 nmr spectrum of I in D₂O (fig 2) shows a chemical shift of +34.5 ppm with coupling constants of $J_{\text{BH}} = 88$ Hz and $J_{\text{BP}} = 107$ Hz. The coupling constants and line widths are solvent dependent as indicated by the boron-11 nmr of I in monoglyme

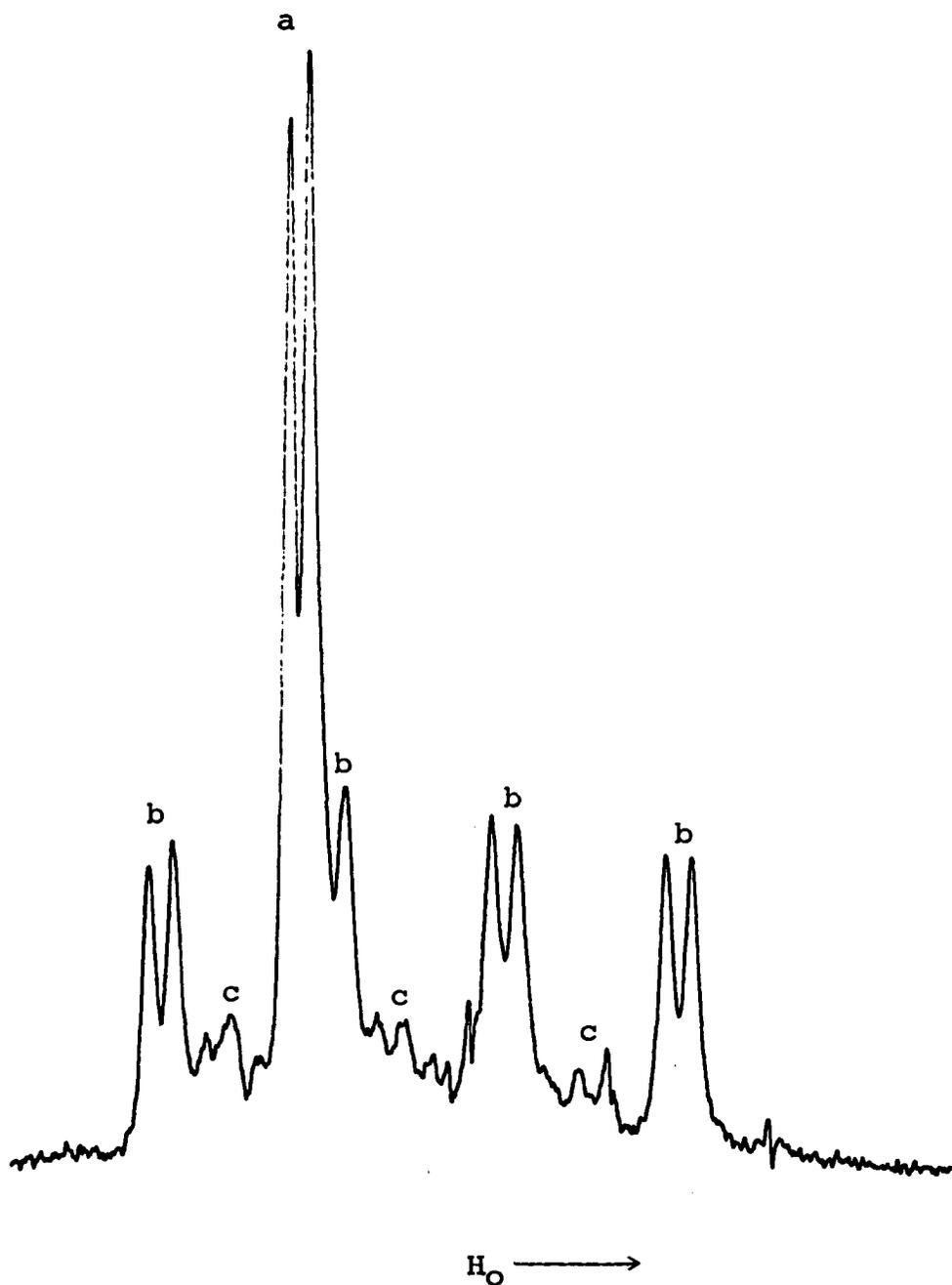
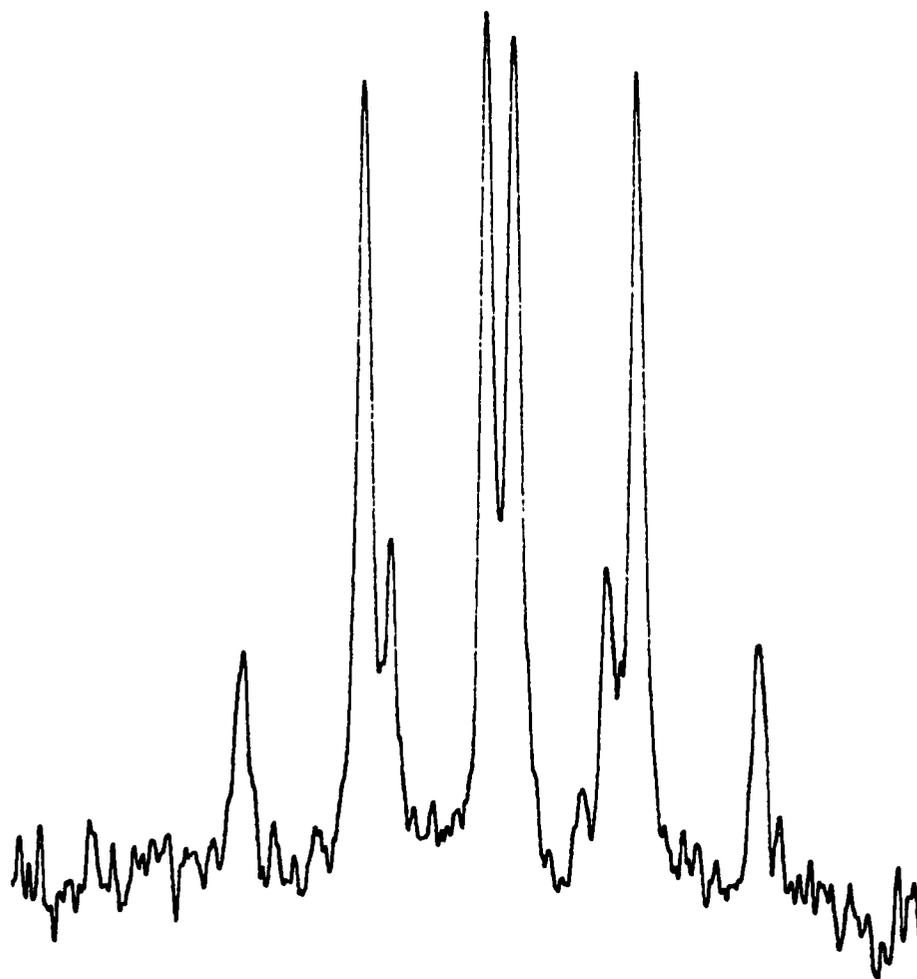


Figure 1. ^1H NMR of $(\text{CH}_3)_2\text{P}(\text{BH}_3)_2^-$ in D_2O



$H_0 \longrightarrow$

Figure 2. ^{11}B NMR of $(\text{CH}_3)_2\text{P}(\text{BH}_3)_2^-$ in D_2O

(fig 3). The ^{11}B nmr of lithium bis(borane)diethylphosphide(1-), shown in fig 4, shows a chemical shift of +34.7 ppm and an apparent coupling constant of $J = 93$ Hz. Because of accidental overlap, the relative J_{BH} and J_{BP} coupling constants are undeterminable.

The infrared spectrum (KBr matrix) is recorded in Table 1 along with some probable vibrational assignments.

Attempt to Detect $[(\text{CH}_3)_2\text{PBH}_2]_3$. To determine whether any dimethylphosphinoborane is formed in the preparation of lithium bis(borane)dimethylphosphide(1-) (eq 2-10), via a Schaeffer-Basile type reaction¹⁰ (eq 2-18),



a sample of the crude reaction product in monoglyme was hydrolyzed with a small amount of aqueous acid. The boron-11 nmr spectrum of this solution showed only a single peak due to boric acid. Any significant quantity of dimethylphosphinoborane would have been detected, since this compound is highly resistant to hydrolysis.²¹

Reactions of I. The reaction of I with warm polyphosphoric acid yields only dioxane and hydrogen as volatile products. The experimental procedure was identical to that used to make diborane and discussed earlier in this chapter.

The reaction of I with hydrogen chloride in monoglyme yields methyl chloride, indicating probable cleavage

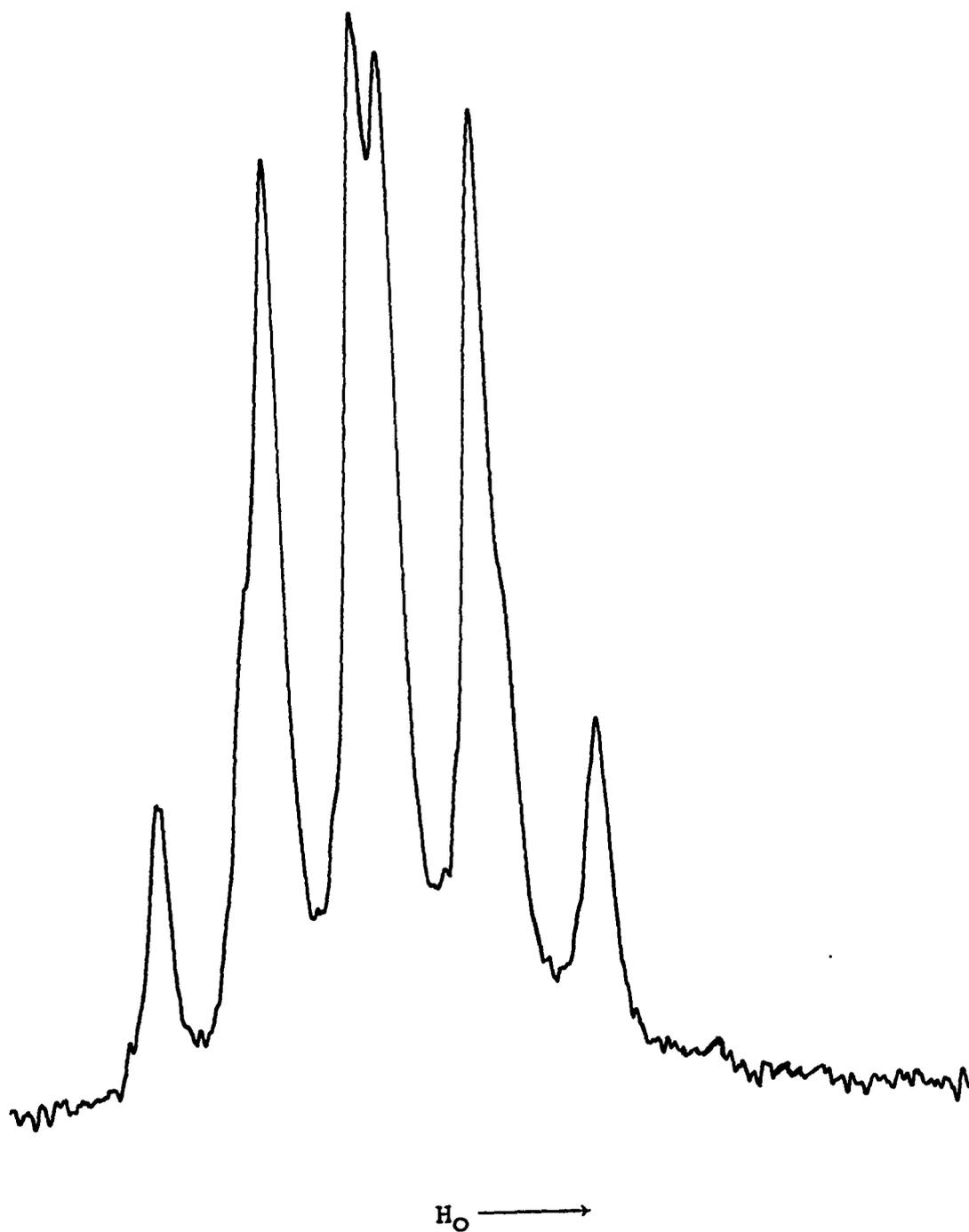


Figure 3. ^{11}B NMR of $(\text{CH}_3)_2\text{P}(\text{BH}_3)_2^-$ in Monoglyme

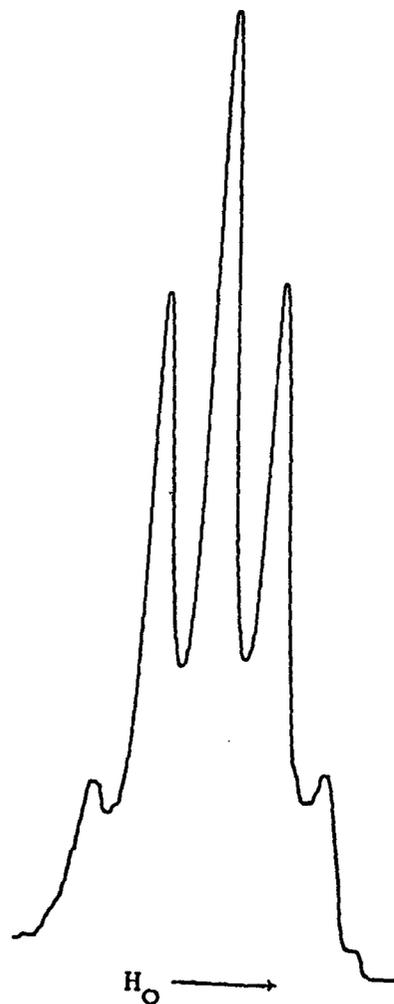


Figure 4. ^{11}B NMR of $\text{Li}(\text{C}_2\text{H}_5)_2\text{P}(\text{BH}_3)_2$ in Diethyl Ether

of the solvent, and hydrogen. No volatile boron containing material was detected. In a typical experiment, a weighed sample of I was placed in a vessel and evacuated. After condensing in monoglyme, anhydrous hydrogen chloride was added and the boron-11 nmr spectrum recorded. Initially the hydrogen chloride appeared to chlorinate the boron as indicated by the collapse of the multiplet. Upon standing several weeks, further reaction yielded methyl chloride which was isolated and identified.

Attempts to Detect the Intermediate Formation of $\text{Li}(\text{CH}_3)_2\text{PBH}_3$. The stepwise addition of diborane to a monoglyme solution of lithium dimethylphosphide was studied in an nmr vessel equipped with a Kontes high-vacuum stopcock (see Appendix). A 2.0 ml sample of 0.5 M phenyllithium in diethyl ether was injected into the vessel followed by 1.0 mmol of dimethylphosphine. The vessel was agitated occasionally, and after 2 hours all volatile products were removed. Diborane, 0.5 mmol, and about 1 ml of monoglyme were condensed into the vessel and the boron-11 nmr spectrum recorded. The resultant spectrum resembled figure 3. Addition of another 0.5 mmol of diborane produced a stronger spectrum identical with the first. Addition of another 0.5 mmol of diborane resulted in a slight loss of resolution and the appearance of a broad peak at low field due to diborane. Removal

of the volatiles and the addition of fresh monoglyme regenerated the original well-resolved spectrum.

In an attempt to detect the intermediate formation of $\text{Li}(\text{CH}_3)_2\text{PBH}_3$ by conversion to dimethylphosphineborane, 1 mmol of anhydrous methanol was condensed into an nmr reaction vessel containing the products of the reaction of 1 mmol of lithium dimethylphosphide and 0.5 mmol of diborane. No signal other than that assigned to I was detected in the boron-11 nmr spectrum. Attempts to isolate $(\text{CH}_3)_2\text{PHBH}_3$ using vacuum line techniques also failed.

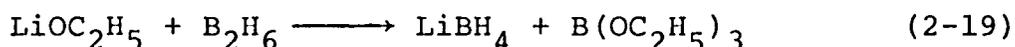
Deuterium Exchange Between I and B_2D_6 . A 2.0 mmol sample of I was placed in a 200 ml reaction vessel. The vessel was evacuated and 2 ml of monoglyme was condensed in the flask, followed by 0.5 mmol of B_2D_6 . The solution was warmed to room temperature and stirred magnetically for about 2 hours. The infrared spectra of the recovered diborane and the solid residue clearly indicated deuterium exchange had occurred. The solid residue showed new peaks at 1748, 1720 and 1700 cm^{-1} resulting from deuterium exchange. 33

Results and Discussion

Formation of I

The reaction of lithium dimethylphosphide with diborane in monoglyme or diethyl ether yields only lithium

bis(borane)dimethylphosphide(1-). No evidence for the presence of dimethylphosphinoborane could be found. In some isolated cases lithium borohydride was detected among the reaction products, but this was attributed to the reaction of diborane with lithium ethoxide,^{9,34} an impurity in the phenyllithium. Since no $\text{Li}(\text{CH}_3)_2\text{PBH}_3$



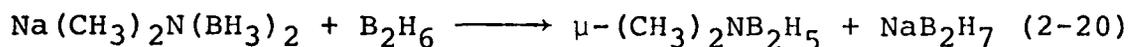
was found, even when lithium dimethylphosphide was in excess, diborane may add to lithium dimethylphosphide as a unit to produce I directly. The reported low reactivity of dimethylphosphinoborane²¹ makes its participation in this reaction as an intermediate very unlikely.

Properties of I

The boron-11 and proton nmr are consistent with the assigned structure. In the proton nmr spectrum (fig 1), (a) is assigned to the methyl protons which are split into a doublet of relative intensity six by ^{31}P ($I = 1/2$); (b) arises from the BH_3 protons which are split by ^{11}B ($I = 3/2$) into a 1:1:1:1 quartet, each member of which is further split into a doublet by ^{31}P . The fine structure (c) is due to ^{10}B . The ^{11}B nmr spectrum of I (fig 2 and 3) consists of two overlapping quartets created by a similarity in the B-P and B-H coupling constants. In lithium bis(borane)diethylphosphide(1-) these coupling constants appear to be nearly identical hence the apparent quintet.

The infrared spectrum of I is shown and partially assigned in table 1. It compares favorably to the structurally related compounds $\text{Na}(\text{CH}_3)_2\text{N}(\text{BH}_3)_2$,¹⁴ and $\text{NaH}_2\text{P}(\text{BH}_3)_2$.^{17,18,33}

The thermal and hydrolytic stability of I is similar to that reported for $\text{KH}_2\text{P}(\text{BH}_3)_2$.^{17,18} Attempts to prepare μ -dimethylphosphinodiborane from I and either polyphosphoric acid or hydrogen chloride failed. The compound $\text{Na}(\text{CH}_3)_2\text{N}(\text{BH}_3)_2$ has been shown to react with diborane in monoglyme to form μ -dimethylaminodiborane and sodium heptahydrodiborate (eq 2-20).¹⁶ Treatment of



I with diborane results only in recovery of the starting materials. The deuterium exchange of I with B_2D_6 may possibly be explained by a process similar to eq 2-20. In this case (2-21) the equilibrium may lie well to the left, while in the nitrogen compound, product formation is favored, perhaps owing to steric effects. The

$\text{Li}(\text{CH}_3)_2\text{P}(\text{BH}_3)_2 + \text{B}_2\text{H}_6 \rightleftharpoons \mu\text{-(CH}_3)_2\text{PB}_2\text{H}_5 + \text{LiB}_2\text{H}_4$ (2-21)

possibility that deuterium exchange results from interchange of borane groups (2-22) is unlikely in light of the stability of I in aqueous solution for extended periods of time.

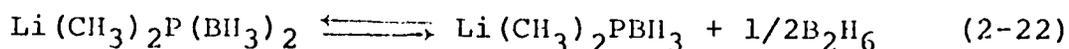


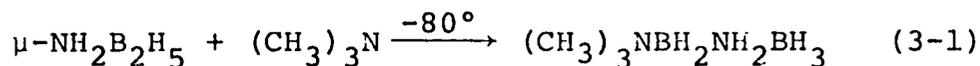
Table 1. Infrared Spectrum of $\text{Li}(\text{CH}_3)_2\text{P}(\text{BH}_3)_2$,
Dioxane-Free

Frequency (cm^{-1})	Intensity	Assignment
2970	weak	vas C-H
2905	weak	vs C-H
2865	weak	combination
2350	strong	vas B-H
2280	strong	vs B-H
2255	strong	combination
1420	medium	δ as CH_3
1280	medium	δ s CH_3
1060	medium	δ as BH_3
940	medium	{ ν P-C δ BH_3
920	medium	
708	medium	ν B-P?

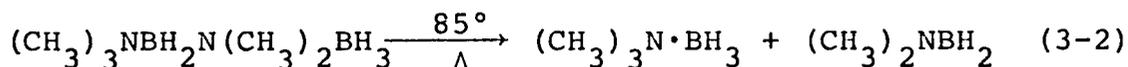
CHAPTER 3

THE PREPARATION AND PROPERTIES OF AMINE DERIVATIVES OF μ -DIMETHYLPHOSPHINODIBORANE: COMPOUNDS WITH A N-B-P-B SKELETON

In a detailed study of μ -aminodiborane reported in 1938, Schlesinger, Ritter and Burg³⁵ found that this compound exhibited Lewis acid character. When μ -aminodiborane was condensed together with either ammonia or trimethylamine, a stable adduct was formed.



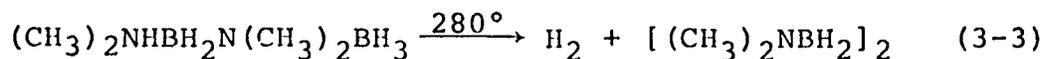
Twenty-one years later Burg and Randolph³⁶ found that the methyl derivatives of μ -aminodiborane acted similarly with trimethylamine. These amine complexes appeared reasonably stable at room temperature, but decomposed when heated (eq 3-2).



In a more recent report, Burg and Sandhu³⁷ investigated the complexes formed with μ -dimethylaminodiborane and various bases. The strong bases pyridine, trimethylphosphine, 2-methylpyridine and trimethylamine formed stable complexes at room temperature while the weaker bases dimethylphosphine, methylphosphine and $(\text{CH}_3)_2\text{PCF}_3$ were partially or wholly dissociated at room temperature.

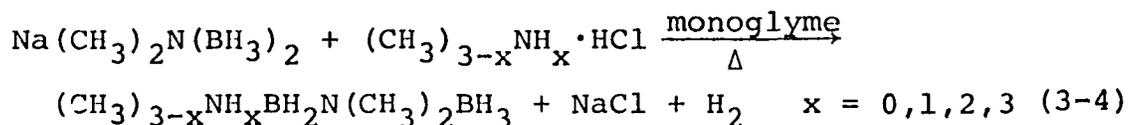
This study indicated that diborane was a much stronger Lewis acid than μ -dimethylaminodiborane.

In 1964 Hahn and Schaeffer³⁸ reported the synthesis of $(\text{CH}_3)_2\text{NHBH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$ which was isolated in small yields from the reaction of sodium borohydride with dimethylammonium chloride. The major product of this reaction was dimethylaminoborane but yields of the other compound were enhanced if refluxing of the reaction mixture was eliminated. (This compound has a N-B-N-B skeleton; derivatives with this backbone will be designated in this text as R_3NBNB). A more convenient and general preparation of this and other related compounds was the reaction of μ -dimethylaminodiborane with amines. Hahn and Schaeffer investigated trimethyl-, dimethyl-, and monomethylamine, and ammonia derivatives of NBNB. The compounds were characterized by their infrared spectra (table 3), boron-11 (table 5) and proton nmr spectra which unequivocally showed the existence of both BH_2 and BH_3 groups. Furthermore the pyrolysis of $(\text{CH}_3)_2\text{NHBNB}$ (eq 3-3) at 280° yielded dimethylaminoborane and hydrogen. All data collected were consistent with the proposed structure, namely an analog of n-butane.



Recently the preparation of sodium bis(borane)-dimethylamide(1-) by Keller³⁹ has afforded a convenient

preparation of these NBNB compounds. $\text{Na}(\text{CH}_3)_2\text{N}(\text{BH}_3)_2$ reacts with various amine hydrochlorides at 50-60° to produce the corresponding NBNB compounds in good yields.



These compounds were identified by comparing their infrared spectra to those published by Hahn and Schaeffer.³⁸

This synthesis of NBNB compounds has led us to react lithium bis(borane)dimethylphosphide(1-)²⁶ with amine hydrochlorides to produce the new series of compounds, $\text{R}_3\text{NBH}_2\text{P}(\text{CH}_3)_2\text{BH}_3$, which are formally amine complexes of μ -dimethylphosphinodiborane. These compounds all have a N-B-P-B backbone and will be designated as R_3NBPB throughout the text.

Experimental Section

General Data

Reactions were carried out with the aid of a standard high vacuum system as described in the appendix. Air-sensitive materials were manipulated in nitrogen-filled drybags or in the vacuum line. Monoglyme (1,2-dimethoxyethane), toluene, dioxane and benzene were stored in evacuated bulbs over lithium aluminum hydride and when needed, were condensed directly into the reaction vessel. Boron-11 and proton nmr spectra were obtained

using a Varian HA-100 spectrometer operating at 32.1 MHz and 100 MHz, respectively. Boron and proton chemical shifts were in ppm relative to diethyl ether - boron trifluoride and TMS, respectively. Infrared spectra were obtained using Perkin Elmer 137 and 337 spectrophotometers. Mass spectra were obtained with a Hitachi Perkin Elmer RMU-6E double-focusing spectrometer.

Reagents

The amine hydrochlorides, $(\text{CH}_3)_3\text{NHCl}$, $(\text{CH}_3)_2\text{NH}\cdot\text{HCl}$, $(\text{CH}_3)\text{NH}_2\cdot\text{HCl}$ and NH_4Cl , and boron trifluoride were obtained from commercial sources; all were used without further purification. Lithium bis(borane)dimethylphosphide(1-)²⁶ was prepared as indicated in chapter 2. Trimethylamine was prepared from its hydrochloride by reaction with concentrated aqueous sodium hydroxide and purified by fractionating through a -78° slush bath on the vacuum line. Purity was checked by comparing its gas phase infrared spectrum⁴⁰ and vapor pressure² with the literature.

The Reaction of $\text{Li}(\text{CH}_3)_2\text{P}(\text{BH}_3)_2$ with $(\text{CH}_3)_3\text{NHCl}$

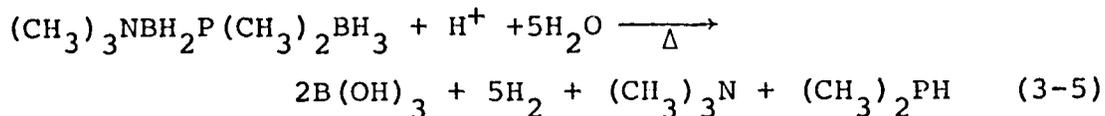
In a typical reaction, a 100 ml reaction vessel, equipped with a magnetic stirrer, was charged with 0.245 g (1.33 mmol) of $\text{Li}(\text{CH}_3)_2\text{P}(\text{BH}_3)_2\cdot\text{C}_4\text{H}_8\text{O}_2$ and 0.155 g (1.63 mmol) of trimethylamine hydrochloride in a drybag. The vessel was transferred to the vacuum

line and evacuated. About 5 ml of dry monoglyme was condensed into the vessel, heated with an oil bath to 60-65° and stirred for 17 hours. Cooling the vessel to -196° and removing the noncondensable gas with a Toepler pump, yielded 1.39 mmol of hydrogen, 104% based on lithium bis(borane)dimethylphosphide(1-). The other volatiles were removed by warming the vessel to 0° and pumping. Only monoglyme, dioxane and a small trace of trimethylamine-borane were recovered. The latter compound was due to a small impurity of lithium borohydride in lithium bis(borane)dimethylphosphide(1-) (see chapter 2).

Purification. In a drybag a sublimator was attached to the vessel and the entire apparatus returned to the vacuum line, evacuated, and heated with an oil bath to about 40°. The sublimable product was collected on the cold finger maintained at 0°. Following sublimation an infrared spectrum taken of the solid residue indicated absorptions due only to the solvent coordinated to lithium chloride, and to trimethylamine hydrochloride. The sublimed colorless solid was weighed, 0.133 g, (0.910 mmol) implying about a 70% recovery of $(\text{CH}_3)_3\text{NBH}_2\text{P}(\text{CH}_3)_2\text{BH}_3$ based on $\text{Li}(\text{CH}_3)_2\text{P}(\text{BH}_3)_2 \cdot \text{C}_4\text{H}_8\text{O}_2$.

Analysis. A portion of the product was weighed (0.0375 g, 0.255 mmol) and placed in a 100 ml flask, evacuated and dissolved in 1 ml of dioxane. Analysis

was accomplished by acid hydrolysis according to eq 3.5.



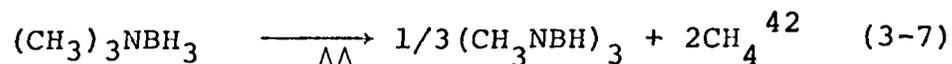
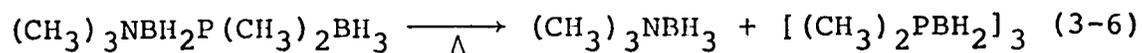
Sulfuric acid, about 6 M, was carefully added to the vessel through the stopcock. Hydrolysis was slow as indicated by sluggish effervescence, so the vessel was heated at 70° for 50 hours and then cooled to -196°; the hydrogen evolved was measured with a Toepler pump. The acidity of the solution was reduced to pH 6 by the addition of concentrated base, and the dimethylphosphine recovered by fractionation on the vacuum line. The remaining solution once made decidedly basic, was distilled into a flask containing a known amount of standard hydrochloric acid, and analyzed for nitrogen according to the Kjeldahl procedure,⁴¹ by back-titrating with standard base to a bromcresol green endpoint. The solid residue containing boric acid was adjusted to pH 7.35, complexed with a large excess of D-mannitol, reducing the pH to 4.3, and back-titrated with standard base until pH 7.35 was reattained. Anal. Calculated for $(\text{CH}_3)_3\text{NBH}_2\text{P}(\text{CH}_3)_2\text{BH}_3$: N, 9.51; P, 21.1; B, 14.7; hydridic h, 3.40. Found: N, 9.39; P, 20.7; B, 14.9; hydridic H, 3.60. The N:B:P:H ratio was calculated as 1.0:2.0:1.0:5.0 and found to be 0.99:2.0:1.0:5.1.

Characterization. $(\text{CH}_3)_3\text{NBPB}$ dissolves without reaction in benzene, monoglyme, acetone, dioxane, trichloroethylene, and ethanol; it is insoluble in water. Addition of aqueous acid to a solution of $(\text{CH}_3)_3\text{NBPB}$ results in slow hydrolysis at room temperature (eq 3-5). The compound is stable in air for at least 2 weeks as evidenced by its unchanged infrared spectrum.

The proton nmr spectrum of $(\text{CH}_3)_3\text{NBPB}$ in benzene is indicated in table 6 and figure 5; the boron-11 nmr spectrum is shown in figure 6 and the parameters are listed in table 4. Table 2 lists the infrared spectrum of $(\text{CH}_3)_3\text{NBPB}$ (KBr matrix) while table 7 tabulates the monoisotopic mass spectrum (the mass spectrum with the boron-10 isotope removed). The product melted over the range of 48-49° without decomposition.

Pyrolysis. A 0.041 g (0.28 mmol) sample of $(\text{CH}_3)_3\text{NBPB}$ was placed in a tube equipped with a break-seal, sealed off with a torch, and heated in an oven at 240° for 15 hours. The vessel was then cooled to -196°, opened to the vacuum line, and 0.985 mmol of noncondensable gas, presumably methane, was collected. The other products were identified by their infrared spectra as trimethylamine-borane, 0.106 g (0.18 mmol); N-trimethylborazine, 0.01 mmol; and 0.02 g (0.09 mmol) of dimethylphosphino-borane trimer. Based on the reaction products, reasonable

equations representing the pyrolysis are



Preparation of Other NBPB Compounds

$(\text{CH}_3)_2\text{NHBPB}$, $\text{CH}_3\text{NH}_2\text{BPB}$ and NH_2BPB were prepared similarly to the trimethylamine derivative at temperatures of 60-80°. The preparations of the monomethylamine and ammonia derivatives were often contaminated with an unidentified oil which could be removed by repeated washing with cold, dry heptane. The infrared spectra of the solid residues gave no indication that they contained anymore than the corresponding amine hydrochloride, lithium chloride and coordinated monoglyme.

Characterization of $(\text{CH}_3)_2\text{NHBPB}$. The compound is a colorless air-stable solid, sublimable at 50° with a mp in the range of 76-77°. Although it is soluble without decomposition in benzene, monoglyme, toluene, cyclohexane, dioxane, and trichloroethylene, it is insoluble in neutral water. Addition of aqueous acid to a solution of the compound results in hydrolysis.

The proton nmr spectrum of $(\text{CH}_3)_2\text{NHBPB}$ in benzene is shown in figure 7; a weak, broad singlet at -5.12 ppm is not shown; the parameters are indicated in table 6. The boron-11 nmr spectrum resembles figure 6; the parameters are listed in table 4.

Table 2 indicates the infrared spectrum (KBr matrix) while table 8 presents the monoisotopic mass spectrum.

Analysis of $(\text{CH}_3)_2\text{NHBPB}$. Analysis of the compound was conducted analogously to $(\text{CH}_3)_3\text{NBPB}$ except that dimethylamine was not recovered. Anal. Calculated for $(\text{CH}_3)_2\text{NHBH}_2\text{P}(\text{CH}_3)_2\text{BH}_3$: P, 23.4; B, 16.2; and hydridic H, 3.76. Found: P, 23.8; B, 16.1; and hydridic H, 3.57. The B:H:P ratio was calculated as 2.0:5.0:1.0 and found to be 1.98:4.7:1.0.

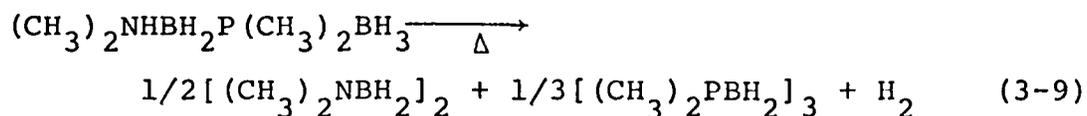
Molecular Weight Determination of $(\text{CH}_3)_2\text{NHBPB}$. In order to determine the state of aggregation of the dimethylamine derivative of NBPB, a freezing point depression experiment was undertaken. The procedure is aptly described in Shoemaker and Garland.⁴³ Benzene was used as the solvent and the freezing point lowering of 0.555° for 0.0994 g of $(\text{CH}_3)_2\text{NHBPB}$ in 7.0180 g benzene, yielded a molecular weight of 131, according to eq 3-8.

$$\text{MW} = \frac{[\text{g}((\text{CH}_3)_2\text{NHBPB})](1000)K_f}{[\text{G}(\text{benzene})](\Delta T_f)} \quad (3-8)$$

This compared favorably with that calculated for $(\text{CH}_3)_2\text{NHBH}_2\text{P}(\text{CH}_3)_2\text{BH}_3$ (133).

Pyrolysis of $(\text{CH}_3)_2\text{NHBPB}$. Moderate pyrolysis of the compound was attempted by placing a 0.043 g (0.32 mmol) sample into a tube equipped with a break-seal, and heating in an oven at 150° . After 1 hour, the

vessel was frozen and opened to the vacuum line; only 0.07 mmol of gas, presumably hydrogen was collected. The boron-11 nmr of the solid indicated that most (about 80%) of the starting material was unchanged, although some dimethylphosphinoborane trimer and dimethylaminoborane dimer were also present. The products support the proposed pyrolysis (eq 3-9).



Reaction of $(\text{CH}_3)_2\text{NHBPB}$ with BF_3 . Boron trifluoride and $(\text{CH}_3)_2\text{NHBPB}$ were reacted in an attempt to displace dimethylamine. A reaction of a 0.100 g (0.75 mmol) sample of $(\text{CH}_3)_2\text{NHBPB}$ and 0.85 mmol of BF_3 in dry toluene in an evacuated 100 ml flask for 1 hour was attempted. Separation of the products resulted only in recovery of the starting materials, indicating no reaction had occurred.

Characterization of $\text{CH}_3\text{NH}_2\text{BPB}$. The compound is a colorless solid, sublimable at 55° . Although less air-stable than the trimethyl- and dimethylamine derivatives, it can be handled in air briefly without decomposition. Considerable difficulty was encountered in obtaining a sharp mp. The most reproducible results were in the range of $60-65^\circ$. The compound appears to be considerably less soluble in non-polar solvents such as heptane, benzene, and carbon tetrachloride than the trimethyl- and

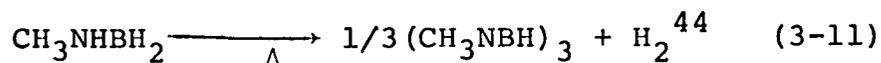
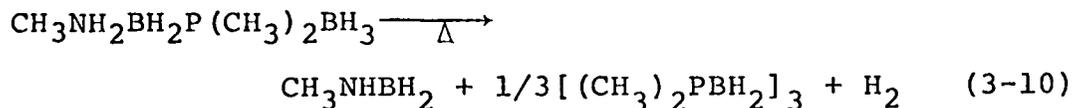
dimethylamine derivatives previously discussed, although it is at least slightly soluble in all of them. Its solubility is much greater in monoglyme, acetone, and trichloroethylene. Although soluble in ethanol, effervescence indicates decomposition may be taking place; it is insoluble in water. Rapid hydrolysis results from adding aqueous acid to a solution of the compound.

The proton nmr spectrum of $\text{CH}_3\text{NH}_2\text{BPB}$ in benzene is shown in figure 8, and the parameters in table 6. The boron-11 nmr spectrum resembles figure 6, and the parameters are listed in table 4. Table 2 indicates the infrared spectrum (KBr matrix) of $\text{CH}_3\text{NH}_2\text{BPB}$, while table 9 shows the monoisotopic mass spectrum.

Analysis of $\text{CH}_3\text{NH}_2\text{BPB}$. Analysis for boron, nitrogen, and hydridic hydrogen was conducted as previously described. Anal. Calculated for $\text{CH}_3\text{NH}_2\text{BH}_2\text{P}(\text{CH}_3)_2\text{BH}_3$: B, 18.5; hydridic H, 4.21; and N, 11.8. Found: B, 18.1; hydridic H, 4.03; and N, 11.2. The B:H:N ratio was calculated as 2.0:5.0:1.0 and found to be 2.1:5.1:1.0.

Pyrolysis of $\text{CH}_3\text{NH}_2\text{BPB}$. A 0.018 g (0.15 mmol) sample of the compound was pyrolyzed as described for the trimethylamine derivative, at 240° . The products were hydrogen, N-trimethylborazine, and dimethylphosphinoborane trimer. Reasonable equations to explain

the products are indicated in eq 3-10 and 3-11.

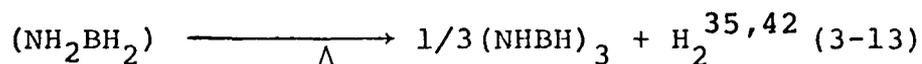
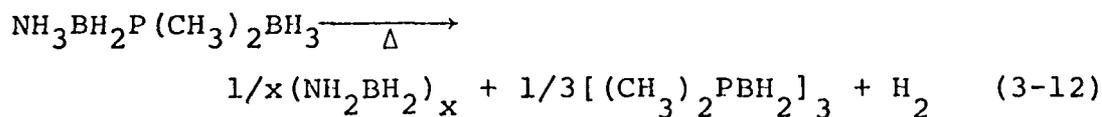


Characterization of NH_3BPB . The compound is a colorless solid, sublimable at 55° . It shows the same poor air stability already noted for the monomethylamine derivative. The compound begins to decompose at 72° . NH_3BPB is soluble in polar solvents like monoglyme, acetone, and to a small extent dioxane. Although soluble in methanol, ethanol, and water, slow decomposition is evident by effervescence. Aqueous acidification of a solution of this derivative results in rapid hydrolysis. Its solubility in benzene, n-heptane, toluene and trichloroethylene is very slight.

The proton nmr spectrum of NH_3BPB in benzene is weak because of its low solubility. Nevertheless the spectrum is shown in figure 9 and the parameters indicated in table 6. The boron-11 nmr spectrum in benzene resembles figure 6 and exhibits the parameters listed in table 4. The infrared spectrum (KBr matrix) is tabulated in table 2 while the monoisotopic mass spectrum is presented in table 10.

Analysis of NH₃BPB. Analysis was conducted as previously described. Anal. Calculated for NH₃BH₂P(CH₃)₂BH₃: N, 13.3; P, 29.5; B, 20.5; and hydridic H, 4.80. Found: N, 11.4; P, 29.8; B, 20.8; and hydridic H, 4.96. The B:H:N:P ratio was calculated as 2.0:5.0:1.0:1.0 and found to be 2.0:4.96:0.85:1.0.

Pyrolysis of NH₃BPB. The compound was pyrolyzed as previously described for the trimethylamine derivative at 170° for 24 hours. The products were identified as hydrogen, borazine, aminoborane polymer,⁴⁵ and dimethylphosphinoborane trimer. Reasonable pyrolysis equations, consistent with the products are shown in eq 3-12 and 3-13.



Reaction of NH₃BPB with Trimethylamine. In an attempt to displace ammonia with trimethylamine, a somewhat stronger base, 0.0177 g (0.168 mmol) of NH₃BPB was placed in a 100 ml flask and evacuated. Dry monoglyme was condensed in followed by 0.54 mmol of trimethylamine. The reaction was allowed to run for 40 minutes at room temperature. Careful examination of the infrared spectrum of the amine recovered indicated no evidence for ammonia.⁴⁰ Furthermore, the KBr matrix infrared spectrum of the solid was unchanged, indicating no reaction had occurred.

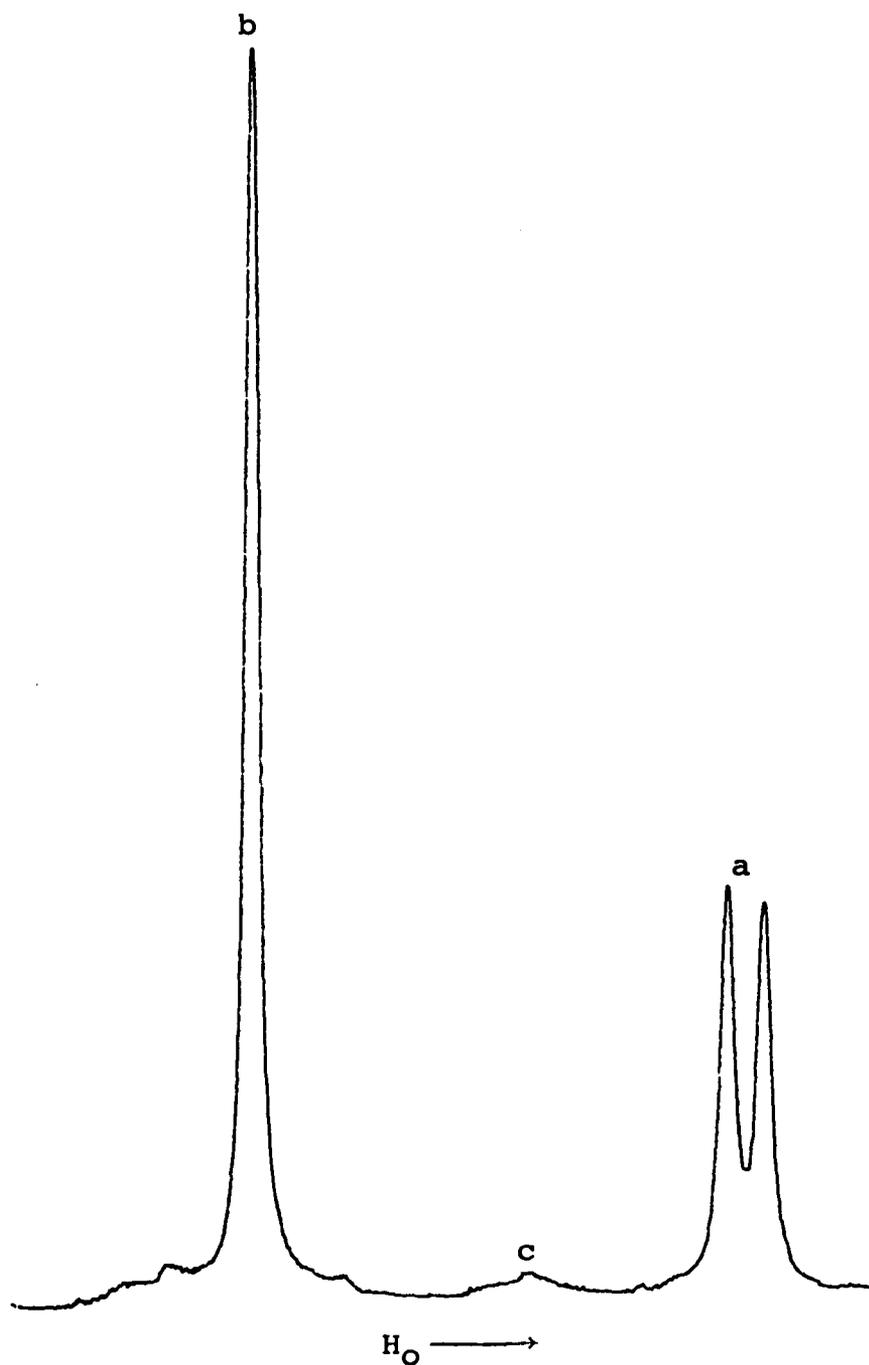


Figure 5. ^1H NMR of $(\text{CH}_3)_3\text{NBPB}$ in Benzene

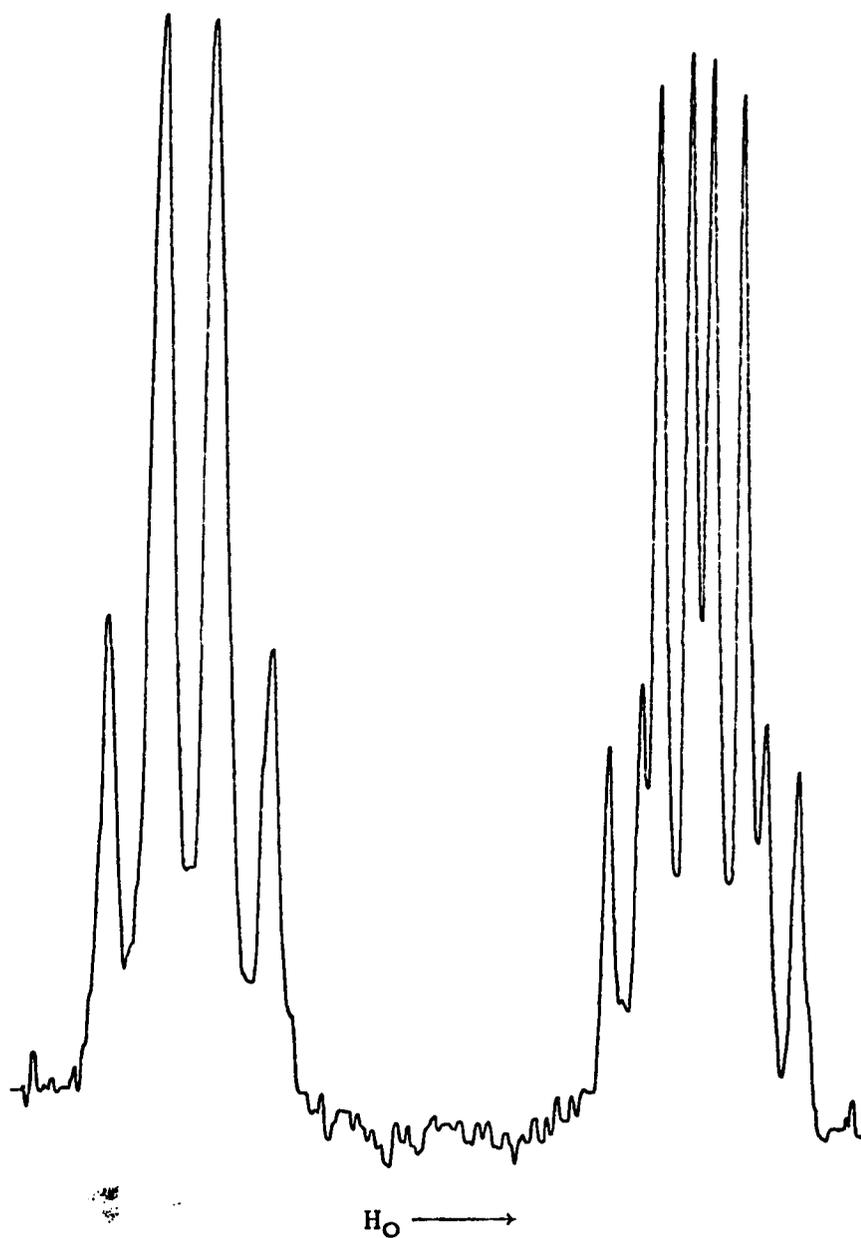


Figure 6. ^{11}B NMR of $(\text{CH}_3)_3\text{NBPB}$ in Benzene

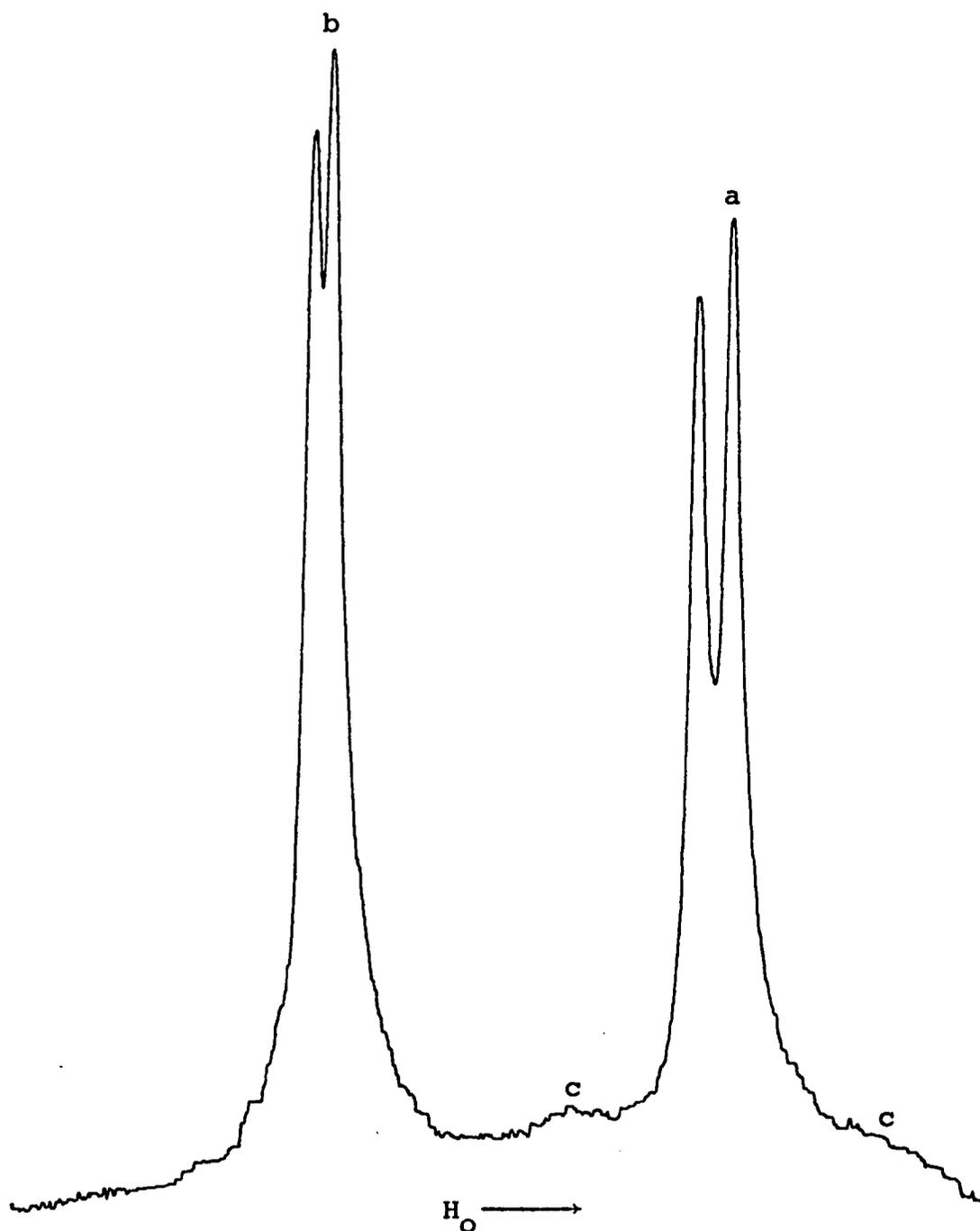


Figure 7. ^1H NMR of $(\text{CH}_3)_2\text{NHBPB}$ in Benzene
(downfield singlet at -5.12 ppm is not shown)

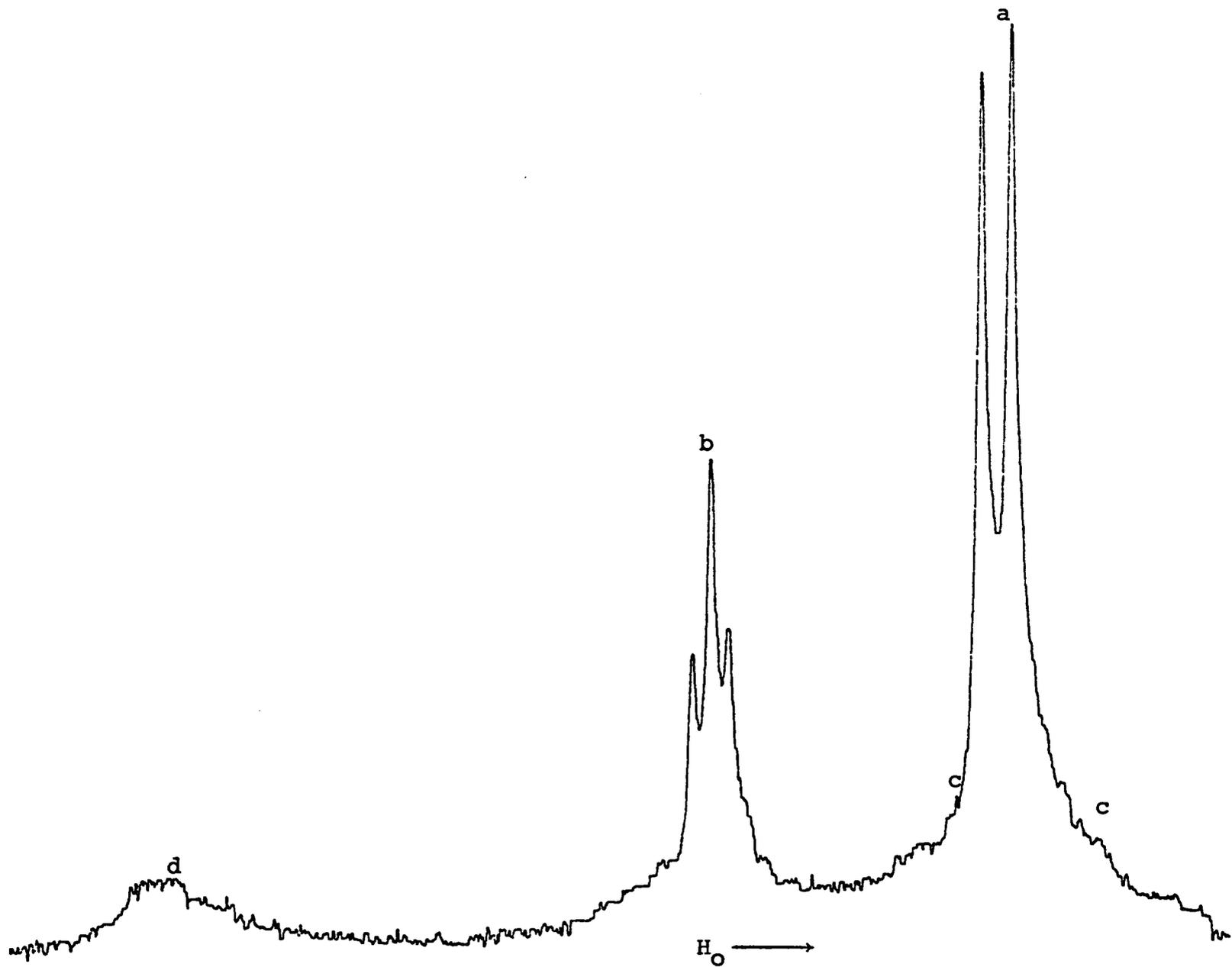


Figure 8. ^1H NMR of $\text{CH}_3\text{NH}_2\text{BPB}$ in Benzene

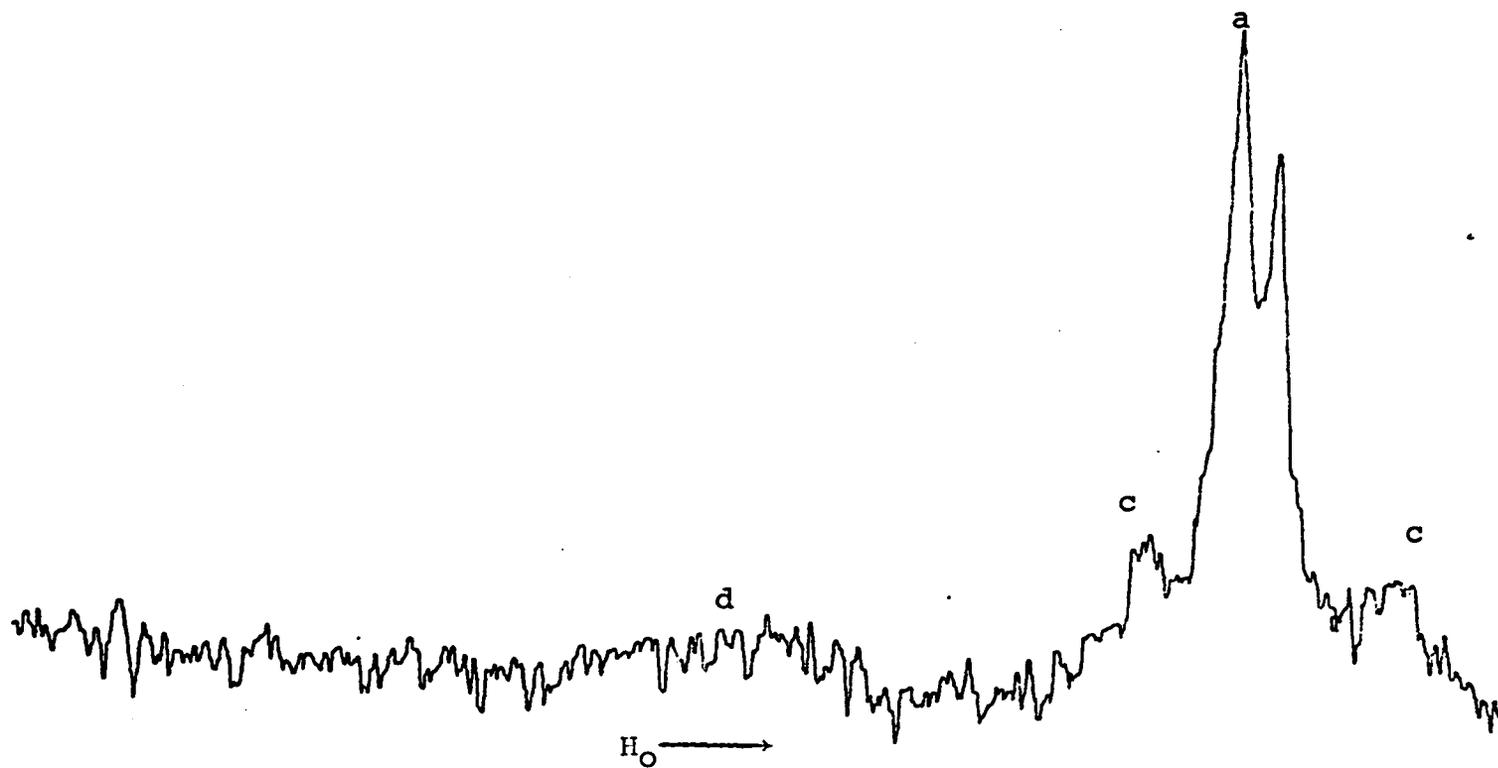


Figure 9. ^1H NMR of NH_3BPB in Benzene

Table 2. Infrared Frequencies for NBPB Derivatives (cm^{-1})

(Intensities: v = very, s = strong, m = medium, w = weak, and sh = shoulder)

$(\text{CH}_3)_3\text{N}^-$	$(\text{CH}_3)_2\text{NH}^-$	CH_3NH_2^-	NH_3^-
2950 m	3270 s	3220 vs	3200 s
2900 sh m		3150 m	
	2995 sh w		2960 vw
2370 vs	2950 m	3010 w	2910 vw
2320 vs	2920 sh w	2950 w	
2220 sh s	2760 w	2900 w	2330 vs
2110 sh w			2290 vs
	2340 sh s	2380 sh vs	
1490 sh m	2315 vs	2350 sh vs	1575 m
1470 s	2270 sh s	2330 vs	
1430 sh m	2125 vw	2280 vs	1480 s
1410 m		2100 w	
	1450 s		1290 sh w
1293 w	1420 s	1595 m	1280 w
1275 w			
1253 sh m	1310	1460 m	1158 s
1243 m		1420 m	1110 s
	1280 vw		
1150 m	1260 m	1320 m	1060 s
1120 s			1020 w
	1160 sh m	1290 vw	
1080 s	1140 m	1275 vw	942 s
1055 s			922 s
1008 m	1080 s	1150 m	
	1060 s	1126 s	863 m
975 m	1015 w		
945 m		1080 sh w	758 m
917 m	955 sh m	1070 w	742 w
	945 m	1048 m	712 m
860 s	925 m	1002 w	
	910 sh m		678 w
775 w		963 w	628 m
750 m	855 w	941 sh w	
705 m		922 s	541 w
	755 w		
696 sh	735 vw	860 w	
660 sh	715 m		
650 m		784 vw	
	660 w	752 w	
555 m	640 vw	730 vw	
		672 vw	
481 m	570 w	640 vw	
		562 w	

Table 3. Infrared Frequencies for NBNB Derivatives (cm^{-1})
 (Intensities: s = strong, m = medium, w = weak)³⁸

$(\text{CH}_3)_3\text{N}^-$	$(\text{CH}_3)_2\text{NH}^-$	CH_3NH_2^-	NH_3^-
2970 s	3190 m	3250 s	3300 s
2820 s		3150 m	
2780 s	2950 s		2960 s
		2995 s	2945 m
2550 s	2385 s	2945 m	2845 w
2485 m	2275 s	2820 m	
2380 m			2440 s
	1465 s	2630 w	2385 s
1640 s	1440 s		2300 s
	1415 m	2420 s	2260 s
1480 m		2380 s	
1460 m	1395 m	2300 s	1830 w
1443 m	1380 w	2255 s	
	1305 m	2105 w	1660 w
1398 m			1600 s
	1225 m	1585 s	
1275 m	1205 s		1470 s
		1480 s	
1195 m	1180 s	1435 m	1390 s
1180 s	1150 s	1400 m	
1120 w			1240 s
	1045 w	1320 s	1205 s
1065 s	1023 m		
		1235 s	1190 s
947 s	973 m		1175 s
	915 m	1198 s	1155 s
850 w		1158 s	1115 m
830 m	899 m	1115 m	
	878 w		1085 m
	820 m	1035 m	1040 s
		1025 s	1020 s
		1010 s	
			953 s
		975 s	925 s
		928 s	910 m
		900 m	905 m
		833 s	819 m
		815 s	
			777 w
		720 w	
		694 w	

Table 4. The ^{11}B NMR of NBPB Derivatives

-BPB	$\delta(\text{BH}_3)$ (ppm)	J_{BH} (Hz)	J_{BP} (Hz)	$\delta(\text{BH}_2)$ (ppm)	J (Hz)
$(\text{CH}_3)_3\text{N}$	+35.2	93.4	56.8	+6.2	85.6
$(\text{CH}_3)_2\text{NH}$	+36.2	91.5	64.5	+9.2	89.5
CH_3NH_2	+37.6	90.5	63.6	+11.1	108
NH_3	+36.8	88.5	63.5	+9.3	100

Table 5. The ^{11}B NMR of NBNB Derivatives

-BNB	$\delta(\text{BH}_3)$ (ppm)	J_{BH} (Hz)	$\delta(\text{BH}_2)$ (ppm)	J_{BH} (Hz)
$(\text{CH}_3)_3\text{N}$	+11.65	95	-3.45	108
$(\text{CH}_3)_2\text{NH}$	+12.4	95	-3.0	110
CH_3NH_2	+12.1	95	+3.18	106
NH_3	+10.2	94.5	+2.9	104

Table 6. The ^1H NMR of NBPB Derivatives in ppm

-BPB	δ (PCH)	J_{PCH} (Hz)	δ (NCH)	J_{NHCH} (Hz)	δ (NH)
$(\text{CH}_3)_3\text{N}$	-0.98	4.8	-2.26	---	-----
$(\text{CH}_3)_2\text{NH}$	-1.06	5.0	-2.91	2.5	-5.12
CH_3NH_2	-1.05	5.0	-2.02	3.0	-3.88
NH_3	-1.06	5.0	-----	---	-2.84

Table 7. The Monoisotopic Mass Spectrum of $(\text{CH}_3)_3\text{NBPB}$

m/e	I/I ₀	Ion (+)
147	2.6	$(\text{CH}_3)_3\text{NBHP}$ $(\text{CH}_3)_2\text{BH}_3$ $(\text{C}_5\text{H}_{20}\text{B}_2\text{NP})$
146	12.6	" $-\text{H}$
145	8.6	" -2H
144	6.2	" -3H
141	5.6	" -6H
134	8.8	" $-\text{BH}_2$ or $-\text{CH}$
133	85.1	" $-\text{BH}_3$ or $-\text{CH}_2$
132	19.0	" $-\text{BH}_4$ or $-\text{CH}_3$
118	2.6	" $-\text{BH}_3$ and CH_3 , or $-\text{C}_2\text{H}_5$
117	6.3	" $-\text{BH}_3$ and CH_4 , or -2CH_3
116	1.3	" -2CH_3 and H
98	3.2	$(\text{C}_2\text{H}_7\text{NB}_2\text{P})$
97	1.3	$(\text{C}_2\text{H}_6\text{NB}_2\text{P})$
89	5.6	$(\text{C}_2\text{H}_9\text{NBP})$, $(\text{C}_2\text{H}_{12}\text{B}_2\text{P})$
88	4.1	$(\text{C}_2\text{H}_8\text{NBP})$, $(\text{C}_2\text{H}_{11}\text{B}_2\text{P})$
86	5.6	$(\text{C}_2\text{H}_6\text{NBP})$, $(\text{C}_2\text{H}_9\text{B}_2\text{P})$
75	5.0	$(\text{C}_2\text{H}_9\text{PB})$, (CH_7NBP)
74	3.2	$(\text{CH}_3)_2\text{PBH}_2$, (CH_6NBP)
73	10.0	$(\text{C}_2\text{H}_7\text{PB})$, (CH_5NBP) , $(\text{CH}_3)_3\text{NBH}_3$
72	100.0	$(\text{C}_2\text{H}_6\text{PB})$, (CH_4NBP) , $(\text{C}_3\text{H}_{11}\text{NB})$
71	11.2	$(\text{C}_2\text{H}_5\text{PB})$, (CH_3NBP) , $(\text{C}_3\text{H}_{10}\text{NB})$
70	42.0	$(\text{C}_2\text{H}_4\text{PB})$, (CH_2NBP) , $(\text{C}_3\text{H}_9\text{NB})$
69	10.4	$(\text{C}_2\text{H}_3\text{PB})$, (CHNBP) , $(\text{C}_3\text{H}_8\text{NB})$
68	3.9	$(\text{C}_2\text{H}_2\text{PB})$, (CNBP) , $(\text{C}_3\text{H}_7\text{NB})$
67	3.1	(C_2HPB) , $(\text{C}_3\text{H}_6\text{NB})$
62	5.8	$(\text{CH}_3)_2\text{PH}$
61	2.6	$(\text{CH}_3)_2\text{P}$
60	1.9	$(\text{C}_2\text{H}_5\text{P})$, $(\text{CH}_3)_3\text{NH}$
59	18.5	$(\text{C}_2\text{H}_4\text{P})$, $(\text{CH}_3)_3\text{N}$, $(\text{C}_2\text{H}_9\text{NB})$
58	37.3	$(\text{C}_2\text{H}_3\text{P})$, $(\text{C}_3\text{H}_8\text{N})$, $(\text{C}_2\text{H}_8\text{NB})$, C_4H_{10}
57	8.4	$(\text{C}_2\text{H}_2\text{P})$, $(\text{C}_3\text{H}_7\text{N})$, $(\text{C}_2\text{H}_7\text{NB})$, C_4H_9
56	19.7	(C_2HP) , $(\text{C}_3\text{H}_6\text{N})$, $(\text{C}_2\text{H}_6\text{NB})$, C_4H_8
55	6.8	(C_2P) , $(\text{C}_3\text{H}_6\text{N})$, $(\text{C}_2\text{H}_6\text{NB})$, C_4H_7
54	5.2	$(\text{C}_3\text{H}_5\text{N})$, $(\text{C}_2\text{H}_5\text{NB})$, C_4H_6
46	6.5	CH_3P , $(\text{CH}_3)_2\text{NH}_2$, BH_4P
45	5.2	CH_2P , $(\text{CH}_3)_2\text{NH}$, BH_3P
44	4.8	CHP , $(\text{CH}_3)_2\text{N}$, BH_2P , C_3H_8
43	4.2	CP , $(\text{C}_2\text{H}_5\text{N})$, BHP , C_3H_7

Table 7. Continued

42	11.8	(C ₂ H ₄ N), BP, C ₃ H ₆
41	16.1	(C ₂ H ₃ N), C ₃ H ₅
40	7.8	(C ₂ H ₂ N), C ₃ H ₄
39	3.9	(C ₂ HN), C ₃ H ₃
30	10.3	C ₂ H ₆ , CH ₄ N
29	6.2	C ₂ H ₅ , CH ₃ N
28	12.0	C ₂ H ₄ , CH ₂ N, N ₂ , CH ₅ B, BH ₃ N
27	15.6	C ₂ H ₃ , CHN, CH ₄ B, BH ₂ N
26	6.5	C ₂ H ₂ , CN, CH ₃ B, BHN

Table 8. The Monoisotopic Mass Spectrum of $(\text{CH}_3)_2\text{NHBPB}$

m/e	I/I ₀	Ion (+)
133	4.5	$(\text{CH}_3)_2\text{NHBH}_2\text{P}(\text{CH}_3)_2\text{BH}_3$ ($\text{C}_4\text{H}_{18}\text{B}_2\text{BP}$)
132	23.8	" -H
131	13.1	" -2H
130	4.9	" -3H
129	1.7	" -4H
128	5.0	" -5H
127	3.9	" -6H
121	1.3	" -BH or -C
120	14.7	" -BH ₂ or -CH
119	62.6	" -BH ₃ or -CH ₂
118	100.0	" -BH ₄ or -CH ₃
117	8.9	" -BH ₅ or -CH ₄
116	9.0	" -BH ₆ or -CH ₅
115	2.7	" -BH ₇ or -CH ₆
114	8.4	" -BH ₈ or -CH ₇
113	2.8	" -BH ₉ or -CH ₈
104	6.8	$(\text{C}_3\text{H}_{12}\text{BNP})$, $(\text{C}_2\text{H}_{13}\text{B}_2\text{NP})$
103	10.0	$(\text{C}_3\text{H}_{11}\text{BNP})$, $(\text{C}_2\text{H}_{12}\text{B}_2\text{NP})$
102	3.4	$(\text{C}_3\text{H}_{10}\text{BNP})$, $(\text{C}_2\text{H}_{11}\text{B}_2\text{NP})$
89	5.0	$(\text{C}_2\text{H}_9\text{BNP})$, $(\text{C}_2\text{H}_{12}\text{B}_2\text{P})$
88	2.3	$(\text{C}_2\text{H}_8\text{BNP})$, $(\text{C}_2\text{H}_{11}\text{B}_2\text{P})$
87	2.6	$(\text{C}_2\text{H}_7\text{BNP})$, $(\text{C}_2\text{H}_{10}\text{B}_2\text{P})$
86	2.4	$(\text{C}_2\text{H}_6\text{BNP})$, $(\text{C}_2\text{H}_9\text{B}_2\text{P})$
85	2.0	$(\text{C}_2\text{H}_5\text{BNP})$, $(\text{C}_2\text{H}_8\text{B}_2\text{P})$
84	6.2	$(\text{C}_2\text{H}_4\text{BNP})$, $(\text{C}_2\text{H}_7\text{B}_2\text{P})$
83	5.0	$(\text{C}_2\text{H}_3\text{BNP})$, $(\text{C}_2\text{H}_6\text{B}_2\text{P})$
82	3.0	$(\text{C}_2\text{H}_2\text{BNP})$, $(\text{C}_2\text{H}_5\text{B}_2\text{P})$
75	25.2	$(\text{C}_2\text{H}_9\text{BP})$, (CH_7BNP)
74	14.1	$(\text{CH}_3)_2\text{PBH}$, (CH_6BNP)
73	9.4	$(\text{C}_2\text{H}_7\text{BP})$, (CH_5BNP) , $(\text{CH}_3)_3\text{NBH}_3$
72	13.2	$(\text{C}_2\text{H}_6\text{BP})$, (CH_4BNP) , $(\text{C}_3\text{H}_{11}\text{NB})$
71	3.6	$(\text{C}_2\text{H}_5\text{BP})$, (CH_3BNP) , $(\text{C}_3\text{H}_{10}\text{NB})$
70	10.8	$(\text{C}_2\text{H}_4\text{BP})$, (CH_3BNP) , $(\text{C}_3\text{H}_9\text{NB})$
69	8.6	$(\text{C}_2\text{H}_3\text{BP})$, (CH_2BNP) , $(\text{C}_3\text{H}_8\text{NB})$
68	5.6	$(\text{C}_2\text{H}_2\text{BP})$, (CHBNP) , $(\text{C}_3\text{H}_7\text{NB})$
67	1.3	(C_2HBP) , (CBNP) , $(\text{C}_3\text{H}_6\text{NB})$
66	4.9	(C_2BP) , $(\text{C}_3\text{H}_5\text{NB})$
63	15.1	$(\text{CH}_3)_2\text{PH}$
62	73.1	$(\text{CH}_3)_2\text{P}$
61	9.2	$(\text{C}_2\text{H}_5\text{P})$

Table 8. Continued

60	2.1	C ₂ H ₄ P	, (CH ₃) ₃ NH		
59	17.0	C ₂ H ₃ P	, (CH ₃) ₃ N	, (C ₂ H ₁₀ NB)	
58	61.0	C ₂ H ₂ P	, C ₃ H ₈ N	, (C ₂ H ₉ NB)	, C ₄ H ₁₀
57	62.1	C ₂ HP	, C ₃ H ₇ N	, (C ₂ H ₈ NB)	, C ₄ H ₉
56	18.1	C ₂ P	, C ₃ H ₆ N	, (C ₂ H ₇ NB)	, C ₄ H ₈
55	31.2		C ₃ H ₅ N	, (C ₂ H ₆ NB)	, C ₄ H ₇
54	9.4		C ₃ H ₄ N	, (C ₂ H ₅ NB)	, C ₄ H ₆
53	3.8		C ₃ H ₃ N	, (C ₂ H ₄ NB)	, C ₄ H ₅
52	5.8		C ₃ H ₂ N	, (C ₂ H ₃ NB)	, C ₄ H ₄
48	4.3	CH ₅ P			
47	5.6	CH ₄ P	, BH ₅ P		
46	37.1	CH ₃ P	, BH ₄ P	, (CH ₃) ₂ NH ₂	
45	42.0	CH ₂ P	, BH ₃ P	, (CH ₃) ₂ NH	
44	59.5	CHP	, BH ₂ P	, (CH ₃) ₂ N	, C ₃ H ₈
43	5.6	CP	, BHP	, C ₂ H ₅ N	, C ₃ H ₇
42	35.0		BP	, C ₂ H ₄ N	, C ₃ H ₆
41	32.1			C ₂ H ₃ N	C ₃ H ₅
40	17.4			C ₂ H ₂ N	C ₃ H ₄
39	8.1			C ₂ HN	C ₃ H ₃
30	19.2	C ₂ H ₆	, CH ₄ N		
29	10.2	C ₂ H ₅	, CH ₃ N		
28	21.8	C ₂ H ₄	, CH ₂ N	, N ₂	, CH ₅ B
27	26.2	C ₂ H ₃	, CHN		, CH ₄ B
26	14.2	C ₂ H ₂	, CN		, CH ₃ B
18	15.8	NH ₄	, H ₂ O	(impurity)	
17	5.1	NH ₃	, HO	"	
16	2.9	NH ₂	, O	"	, CH ₄
15	10.2	NH			, CH ₃ , BH ₄
13	5.9				, CH, BH ₂

Table 9. The Monoisotopic Mass Spectrum
of $\text{CH}_3\text{NH}_2\text{BPB}$

m/e	I/I ₀	Ion (+)
119	1.8	$\text{CH}_3\text{NH}_2\text{BH}_2\text{P}(\text{CH}_3)_2\text{BH}_3$ ($\text{C}_3\text{H}_{16}\text{B}_2\text{NP}$)
118	10.8	" -H
117	6.8	" -2H
116	3.4	" -3H
106	4.7	" -BH ₂ or -CH
105	100.0	" -BH ₃ or -CH ₂
104	15.2	" -BH ₄ or -CH ₃
103	5.0	" -BH ₅ or -CH ₄
102	5.9	" -BH ₆ or -CH ₅
90	2.0	" -C ₂ H ₅ or -BH ₃ and CH ₃
89	5.0	" -2CH ₃ or -BH ₃ and CH ₃
88	2.3	" -C ₂ H ₇ or CH ₅ N or BCH ₈
75	13.5	CH ₇ NBP , C ₂ H ₉ PB
74	9.3	CH ₆ NBP , C ₂ H ₈ PB
73	6.7	CH ₅ NBP , C ₂ H ₇ PB
72	3.6	CH ₄ NBP , C ₂ H ₆ PB
71	2.4	CH ₃ NBP , C ₂ H ₅ PB
70	2.5	CH ₂ NBP , C ₂ H ₄ PB
69	4.1	CHNBP , C ₂ H ₃ PB
68	2.3	CNBP , C ₂ H ₂ PB
67	2.4	C ₂ HPB
66	2.0	C ₂ PB
63	5.9	(CH ₃) ₂ PH
62	51.0	(CH ₃) ₂ P
61	4.1	C ₂ H ₅ P
60	2.1	C ₂ H ₄ P , CH ₆ PB
59	5.9	C ₂ H ₃ P , CH ₅ PB , C ₂ H ₉ NB
58	5.8	C ₂ H ₂ P , CH ₄ PB , C ₂ H ₈ NB
57	7.0	C ₂ HP , CH ₃ PB , C ₂ H ₇ NB
56	8.2	C ₂ P , CH ₂ PB , C ₂ H ₆ NB
55	6.9	CHPB , C ₂ H ₅ NB
54	2.9	CPB , C ₂ H ₄ NB
47	2.3	CH ₄ P , BH ₅ P
46	8.8	CH ₃ P , BH ₄ P
45	7.5	CH ₂ P , BH ₃ P , CH ₃ NH ₂ BH ₃
44	35.8	CHP , BH ₂ P , CH ₇ NB , C ₃ H ₈
43	15.3	CP , BHP , CH ₆ NB , C ₃ H ₇
42	28.1	BP , CH ₅ NB , C ₃ H ₆
41	18.5	CH ₄ NB , C ₃ H ₅

Table 9. Continued

40	8.8			CH ₃ NB	, C ₃ H ₄
39	4.5			CH ₂ NB	, C ₃ H ₃
32	4.5	CH ₃ NH ₃	, PH	, O ₂	(impurity)
31	2.7	CH ₃ NH ₂	, P		
30	7.0	CH ₄ N	, C ₂ H ₆		
29	2.3	CH ₃ N	, C ₂ H ₅		
28	12.3	CH ₂ N	, C ₂ H ₄	, N ₂	, CH ₅ B
27	14.0	CHN	, C ₂ H ₃	,	CH ₄ B
26	8.8	CN	, C ₂ H ₂	,	CH ₃ B

Table 10. The Monoisotopic Mass Spectrum
of NH_3BPB

m/e	I/I ₀	Ion (+)
105	1.0	$\text{NH}_3\text{BH}_2\text{P}(\text{CH}_3)_2\text{BH}_3$ ($\text{C}_2\text{H}_{14}\text{B}_2\text{NP}$)
104	7.7	" -H
103	4.5	" -2H
102	3.0	" -3H
101	2.8	" -4H
100	2.5	" -5H
92	3.3	" -BH ₂ or -CH
91	100.0	" -BH ₃ or -CH ₂ or -N
90	10.0	" -BH ₄ or -CH ₃ or -NH
89	3.1	" -BH ₅ or -CH ₄ or -NH ₂
88	2.6	" -BH ₆ or -CH ₅ or -NH ₃
87	2.5	" -BH ₇ or -CH ₆ or -NH ₄
86	4.9	$\text{CH}_7\text{B}_2\text{NP}$, $\text{C}_2\text{H}_6\text{BNP}$, $\text{C}_2\text{H}_9\text{B}_2\text{P}$
85	4.0	$\text{CH}_6\text{B}_2\text{NP}$, $\text{C}_2\text{H}_5\text{BNP}$, $\text{C}_2\text{H}_8\text{B}_2\text{P}$
84	2.0	$\text{CH}_5\text{B}_2\text{NP}$, $\text{C}_2\text{H}_4\text{BNP}$, $\text{C}_2\text{H}_7\text{B}_2\text{P}$
83	2.7	$\text{CH}_4\text{B}_2\text{NP}$, $\text{C}_2\text{H}_3\text{BNP}$, $\text{C}_2\text{H}_6\text{B}_2\text{P}$
82	3.9	$\text{CH}_3\text{B}_2\text{NP}$, $\text{C}_2\text{H}_2\text{BNP}$, $\text{C}_2\text{H}_5\text{BP}$
75	14.9	$\text{C}_2\text{H}_9\text{BP}$, CH_7NBP , $\text{B}_2\text{H}_7\text{PN}$
74	21.5	$\text{C}_2\text{H}_8\text{BP}$, CH_6NBP , $\text{B}_2\text{H}_6\text{PN}$
73	15.0	$\text{C}_2\text{H}_7\text{BP}$, CH_5NBP , $\text{B}_2\text{H}_5\text{PN}$
72	9.8	$\text{C}_2\text{H}_6\text{BP}$, CH_4NBP , $\text{B}_2\text{H}_4\text{PN}$
70	3.3	$\text{C}_2\text{H}_4\text{BP}$, CH_2NBP , $\text{B}_2\text{H}_2\text{PN}$
69	3.0	$\text{C}_2\text{H}_3\text{BP}$, CHNBP , B_2HPN
68	3.1	$\text{C}_2\text{H}_2\text{BP}$, CNBP , B_2PN
63	5.9	$(\text{CH}_3)_2\text{PH}$
62	94.0	$(\text{CH}_3)_2\text{P}$
61	7.3	$\text{C}_2\text{H}_5\text{P}$, BH_6NP
60	1.8	$\text{C}_2\text{H}_4\text{P}$, BH_5NP
59	11.0	$\text{C}_2\text{H}_3\text{P}$, BH_4NP , $\text{C}_2\text{H}_9\text{NB}$, CH_5PB
58	4.9	$\text{C}_2\text{H}_2\text{P}$, BH_3NP , $\text{C}_2\text{H}_8\text{NB}$, CH_4PB
57	7.5	C_2HP , BH_2NP , $\text{C}_2\text{H}_7\text{NB}$, CH_3PB
56	7.4	C_2P , BNP , $\text{C}_2\text{H}_6\text{NB}$, CH_2PB
55	9.8	$\text{C}_2\text{H}_5\text{NB}$, CHPB
54	3.1	$\text{C}_2\text{H}_4\text{NB}$, CPB
48	7.5	CH_5P , BH_6P
47	3.8	CH_4P , BH_5P
46	2.1	CH_3P , BH_4P
45	12.1	CH_2P , BH_3P , CH_8NB
44	10.2	CHP , BH_2P , CH_7NB

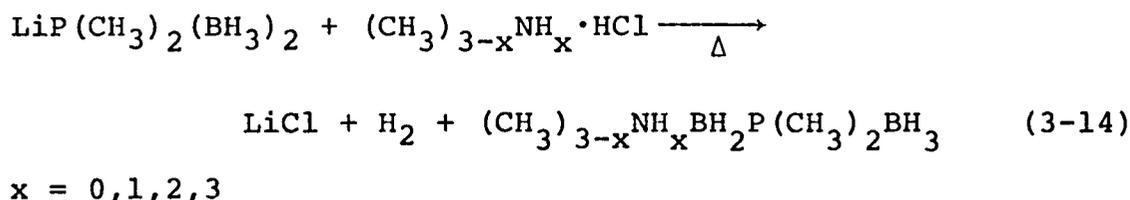
Table 10. Continued

43	3.2	CP	BHP	CH ₆ NB	
42	17.5		BP	CH ₅ NB	
41	28.1	CH ₄ NB			
40	12.8	CH ₃ NB			
39	4.2	CH ₂ NB			
38	2.6	CHNB			
37	4.4	CNB			
30	32.2	C ₂ H ₆	BH ₅ N	CH ₄ N	
29	11.8	C ₂ H ₅	BH ₄ N	CH ₃ N	
28	40.5	C ₂ H ₄	BH ₃ N	CH ₂ N	N ₂
27	12.0	C ₂ H ₃	BH ₂ N	CHN	
26	10.8	C ₂ H ₂	BHN	CN	
18	6.9	NH ₄	H ₂ O	(impurity)	
17	7.8	NH ₃	HO		
16	2.4	NH ₂	O		CH ₄

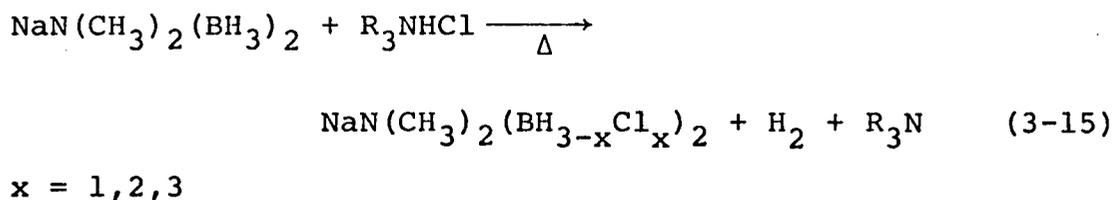
Results and Discussion

Formation of NBPB Compounds

The reaction of lithium bis(borane)dimethylphosphide(1-) with amine hydrochlorides in monoglyme yields the corresponding NBPB compounds in good yields (eq 3-14).



The reactions show no indication of chlorination reactions noted by Keller³⁹ for the nitrogen analog, as evidenced by the absence of any free amine among the volatile



products or any boron-containing species in the solid residue. Occasionally a small amount of amine-borane was detected in the products, but its presence was attributed to the reaction of lithium borohydride, and impurity in $\text{Li}(\text{CH}_3)_2\text{P}(\text{BH}_3)_2$ (see chapter 2), with the amine hydrochlorides.

Properties of NBPB Compounds

The boron-11 and proton nmr spectra and the pyrolysis products are consistent with the assigned structure, a linear N-B-P-B chain, and also compare favorably with Hahn and Schaeffer's NBNB compounds.³⁸ The infrared spectra and boron-11 nmr parameters of these two series of compounds are compared in tables 2 and 3, and 4 and 5, respectively.

In the proton nmr spectrum of $(\text{CH}_3)_3\text{NBPB}$ (fig 5), (a) is due to the six methyl protons associated with phosphorus and split by ^{31}P into a doublet of relative intensity one, (b), intensity two, is due to the nine equivalent methyl protons associated with nitrogen. The weaker, unresolved signals, (c) are created by the protons associated with boron. These signals are rather obscure because of the quadrupole moment of boron. Figure 7 illustrates the ^1H nmr of $(\text{CH}_3)_2\text{NHBPB}$. (a), intensity one, is again due to the methyl protons associated with phosphorus, split by ^{31}P ; (b), intensity one, is created by the six methyl protons associated with nitrogen and split into a doublet by the lone proton attached to nitrogen. A weak signal (not shown in fig 7) at -5.12 ppm associated with the protons attached to nitrogen, broadened by the quadrupole moment of nitrogen,⁴⁶ while (c) is due to the proton attached to boron. The methylamine derivative (figure 8) shows the

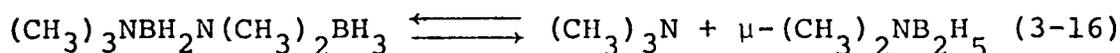
familiar upfield doublet (a), with intensity two, and a downfield triplet (b) created by the methyl protons associated with nitrogen and split by the two protons attached to nitrogen; the triplet has intensity one. The resonance (c), the protons attached to boron, is nearly unintelligible while (d), due to the protons attached to nitrogen, is broad and unresolved. The ammonia (fig 9) derivative shows the familiar doublet (a) due to the methyl protons associated with phosphorus; (c) is created by the protons on boron and (d) is due to the protons on nitrogen.

The boron-11 nmr spectra of these compounds are all similar (figure 6, table 4). The upfield signal consists of two overlapping quartets, created by a similarity in the B-P and B-H coupling constants. The downfield quartet consists of two overlapping triplets resulting from nearly identical B-P and B-H coupling constants.

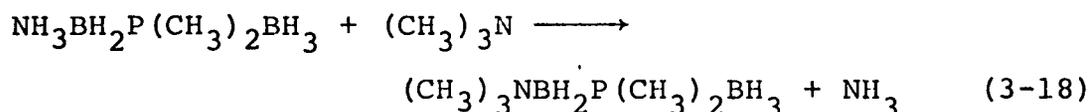
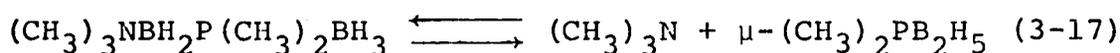
The infrared spectra (table 2) of these NBPB compounds compare favorably with the corresponding NBNB derivatives (table 3).³⁸

The thermal and hydrolytic stabilities of the NBPB compounds are at least as great as those reported for the related NBNB compounds.^{36,37,38}

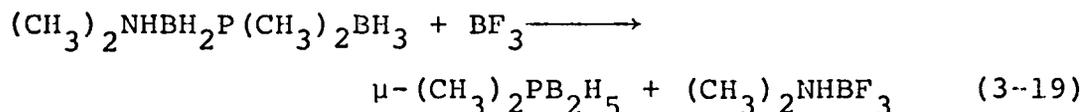
In their investigation of Lewis base adducts of μ -dimethylaminodiborane, Burg and Sandhu³⁷ found that these adducts are at least partially dissociated in the gas phase at room temperature (eq 3-16). Such a process



(eq 3-17) seems unlikely for the NBPB derivatives as evidenced by the inability of trimethylamine to displace or exchange with ammonia from NH_3BPB (eq 3-18).



Furthermore there is no tendency to form the parent μ -dimethylphosphinodiborane by trapping the complexed amine with boron trifluoride (eq 3-19), a strong Lewis acid. The stability of the NBPB unit suggests that it may be appropriate for further chemical investigations.



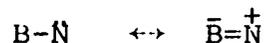
CHAPTER 4

THE REACTION OF N-SUBSTITUTED LITHIUM AMIDES WITH DIBORANE

Boron-nitrogen compounds are probably the most investigated area of synthetic boron chemistry.^{42,43,47} A special feature of these substances is that the boron-nitrogen bond is isoelectronic with the carbon-carbon bond.

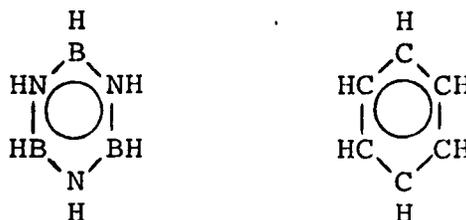
Despite the vast number of boron-nitrogen compounds, many can be classified into a small number of subgroups. These include: coordination compounds, aminoboranes, borazines, diborylamines, heterocyclic compounds, and μ -aminodiboranes. Boron-nitrogen coordination compounds consist of the amine-borane complexes (R_3NBH_3) and the salts containing the bis(amine)boronium cation $[(R_3N)_2BH_2]^+$, the symmetrical and unsymmetrical cleavage products (chapter 1), respectively. These contain four-coordinate boron and have a boron-nitrogen dative bond, where the electron pair associated with nitrogen is "donated" to the empty orbital of boron.

Aminoboranes are derivatives with boron-nitrogen sigma bonds, enhanced by a π -bond created by the back donation of the electron pair of nitrogen into the empty orbital of boron. These compounds include

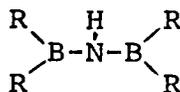


tri(amino)boranes, $(R_2N)_3B$, di(amino)boranes, $(R_2N)_2BH$, and monoaminoboranes, R_2NBH_2 . The latter compounds are generally not found in the monomeric state at room temperature.⁴⁸ The parent, $(NH_2BH_2)_x$ is usually^{45,49} a high polymer while R_2NBH_2 ($R = \text{alkyl}$) are generally dimers, and $RHNBH_2$ are primarily trimers. The association of these derivatives is discussed more fully elsewhere.^{42,47,48,49}

Borazines are analogs of benzene. Both compounds are planar and have similar physical constants, although chemically, they are quite different with borazines being more reactive.⁵⁰

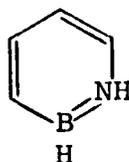


Diborylamines are compounds in which two boron atoms are bound to a central nitrogen. These derivatives are quite rare.^{42,50}

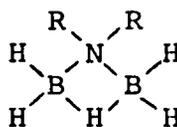


Another rare group of boron-nitrogen compounds are the heterocyclic⁵⁰ or heteroaromatic⁴² derivatives.

This classification refers to conjugated rings containing both boron and nitrogen in place of two carbons.

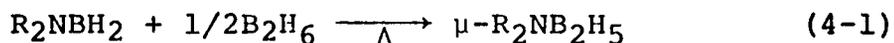


The last category of B-N compounds to be discussed are the μ -aminodiboranes, diborane with a bridge hydrogen replaced by a NR_2 group.

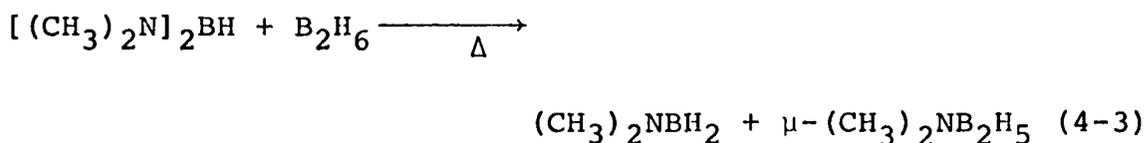
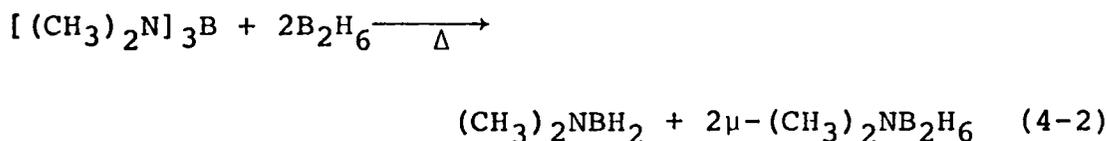


Schlesinger, Ritter and Burg³⁵ first reported the characterization of μ -aminodiborane in 1938 as a by-product from the preparation of borazine. Although the bridge structure of diborane was still unknown, these workers postulated the B-N-B structure based on the reactions of ammonia and trimethylamine with μ -aminodiborane (see chapter 3).

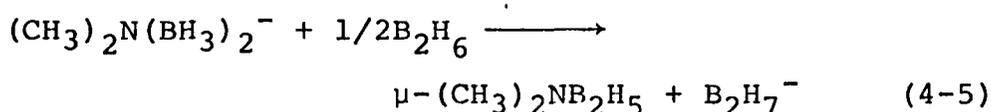
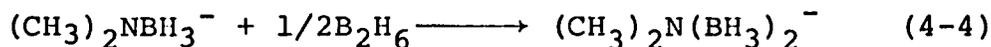
In 1949 Burg and Randolph³⁶ devised a general method of preparation for μ -aminodiboranes by passing diborane over a heated sample of an aminoborane (eq 4-1).



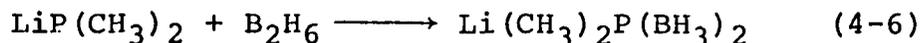
In related work, it was found that tris(dimethylamino)borane and bis(dimethylamino)borane yielded μ -dimethylaminodiborane when heated with diborane.^{37,51}



Recently P.C. Keller^{13,14,16} has found that the salt sodium dimethylamidotrihydroborate yields μ -dimethylaminodiborane in good yields when reacted with diborane in monoglyme. The reaction sequence is summarized in eq 4-4 and 4-5.

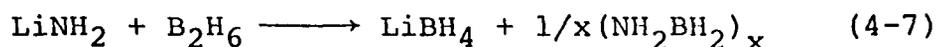


The recent investigation of the reaction between lithium dimethylphosphide(1-) and diborane²⁶ (eq 4-6; see also chapter 2) has led to the study of the



reactions of N-alkyl substituted lithium amide (LiNHR , $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, i\text{-C}_3\text{H}_7, n\text{-C}_4\text{H}_9, s\text{-C}_4\text{H}_9, t\text{-C}_4\text{H}_9, n\text{-C}_5\text{H}_{11}, \text{and } \text{C}_6\text{H}_5\text{CH}_2$; LiNR'_2 , $\text{R}' = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, \text{and } i\text{-C}_3\text{H}_7$) with diborane under similar conditions. The examination of this system has been discouraged by the report of Schaeffer and Basile¹⁰ that lithium amide and diborane react in diethyl ether to form only lithium

borohydride and polymeric aminoborane (eq 4-7). We have



found reaction 4-7 to be unique; N-alkyl substituents alter the course of the process. The description of the investigation, the discussion of the results, and the characterization of some new μ -aminodiboranes are the subjects of this chapter.

Experimental Section

General Data

Standard high vacuum and inert atmosphere techniques discussed in chapter 2 and in the appendix were used throughout this investigation. Diethyl ether, benzene, toluene, and monoglyme (1,2-dimethoxyethane) were stored over lithium aluminium hydride in evacuated bulbs and, when needed, were condensed directly into the reaction vessel. Boron-11 nmr (see appendix) spectra were obtained using a Varian HA-100 spectrometer operating at 32.1 MHz; chemical shifts are in ppm relative to diethyl ether - boron trifluoride. Reactions monitored by boron-11 nmr were performed in specially constructed vessels equipped with a Kontes high vacuum stopcock (see appendix). Infrared spectra were obtained using Perkin Elmer 137 and 337 spectrophotometers; gas samples were contained in 5 or 10 cm path length cells with

sodium chloride windows. Mass spectra were obtained using a Hatchi Perkin Elmer RMU-6E spectrometer (see appendix).

Vapor pressure readings were made with an immersible tensimeter and a cathetometer. The compounds were condensed into the evacuated tensimeter and the entire vessel placed in a constant temperature bath maintained by a thermostat. Readings were taken for 5 different temperatures, except when decomposition became evident, as evidenced by evolution of hydrogen. The temperatures ($^{\circ}\text{K}$) were plotted versus log pressure (Clausius-Clapeyron eq 4-8) and extrapolated to 760 mm,

$$\ln \frac{P_2}{P_1} = - \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (4-8)$$

yielding the boiling point (T_{bp}). The heat of vaporization and Trouton constant were calculated from eq 4-9 and 4-10, respectively.

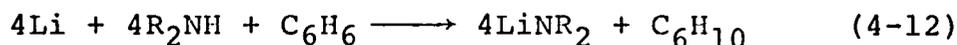
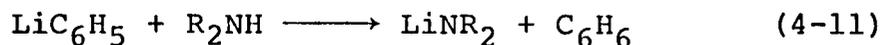
$$\Delta H = \frac{-R \ln \frac{P_2}{P_1}}{\frac{1}{T_2} - \frac{1}{T_1}} \quad (4-9)$$

$$\Delta S = \frac{\Delta H}{T_{\text{bp}}} \quad (4-10)$$

Reagents

Diborane was prepared by treating sodium borohydride with warm polyphosphoric acid as described in chapter 2. Mono- and dimethylamine were purified on

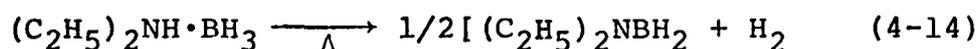
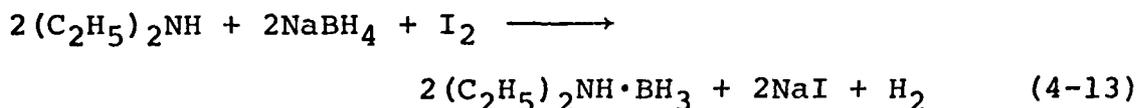
the vacuum line after preparation from the reaction of their hydrochlorides with concentrated sodium hydroxide. Reagent grade ethyl-, n-propyl-, i-propyl-, n-butyl-, s-butyl-, t-butyl-, n-pentyl-, benzyl-, diethyl-, di-i-propyl, and di-i-propylamine were obtained from commercial sources; before use, samples were dried with calcium hydride and purified on the vacuum line. Lithium wire containing 1% sodium (Alpha Inorganics, Inc.) was used with bromobenzene in diethyl ether to prepare phenyllithium.²⁷ Lithium n-propylamide, di-n-propylamide, and di-i-propylamide were prepared by the reaction of phenyllithium with the appropriate amine in diethyl ether.^{52,53} Lithium methylamide, ethylamide, i-propylamide, n-butylamide, s-butylamide, t-butylamide, n-pentylamide, benzylamide, dimethylamide, and diethylamide were prepared by the direct sealed tube reaction between lithium wire and the respective amine in benzene.^{52,53,54}



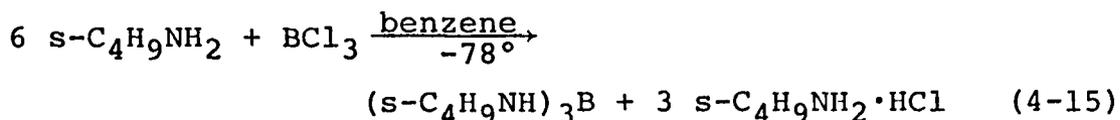
Lithium wire was cut into tiny pieces and placed in a vessel which was then evacuated. Dry benzene and the appropriate amine were then condensed into the vessel which was then sealed off with a torch. The reaction rates

varied from a few hours for methylamine to about a week for diethylamine. The resulting amides were grey to yellow-white in color, with the exception of benzyl amide which was crimson, when vacuum dried for a few hours.

Diethylamine-borane was prepared by the method of Nainan and Ryschkewitsch (eq 4-13).⁵⁵ Diethylamino-borane dimer was prepared by the sealed tube pyrolysis of diethylamine-borane (eq 4-14).⁵⁶ Tri(*s*-butylamino)-borane was prepared from the reaction between boron



trichloride and excess *s*-butylamine at -78° in benzene (eq 4-15).⁵⁷ Boron trichloride, *s*-butylamine and benzene



were condensed into an evacuated 500 ml vessel and maintained at -78° overnight. The volatiles were removed by pumping and the product washed with dry benzene in a Schlenk² tube. The benzene was removed by vacuum pumping.

The Reaction of Lithium Diethylamide with Diborane

With the exception of lithium methyl-, ethyl-, and benzylamide, all systems investigated behaved in

a similar fashion. The detailed study of lithium diethylamide - diborane system described here is typical. Two essentially parallel experiments are outlined. In the first, the progress of the reaction was monitored by boron-11 nmr as diborane was added to lithium diethylamide solution. In the second, the conditions of the nmr study were duplicated, and the products were separated on the vacuum line and identified by infrared and mass spectroscopy.

A 1.12 mmole sample of diborane was added to a solution of 2.14 mmol of lithium diethylamide in 1 ml of diethyl ether in a nmr reaction vessel. The nmr spectrum of this solution is shown in figure 10; isolation and identification of the products confirmed the assignment of the observed resonances to tris(diethylamino)-borane (only the high field sideband of the broad singlet at -28.7 ppm is shown in figure 10), μ -diethylamino-diborane (triplet, 19.0 ppm), and lithium borohydride (quintet, 38.0 ppm). Occasionally at this point a trace of diethylamine-borane was isolated. Since this facet of the experiment was not reproducible, the origin of the compound is believed to stem from the reaction of diborane with a small amount of diethylamine retained by the lithium diethylamide after its preparation. Addition of another 1.12 mmol of diborane to the nmr reaction vessel produced the solution giving the nmr

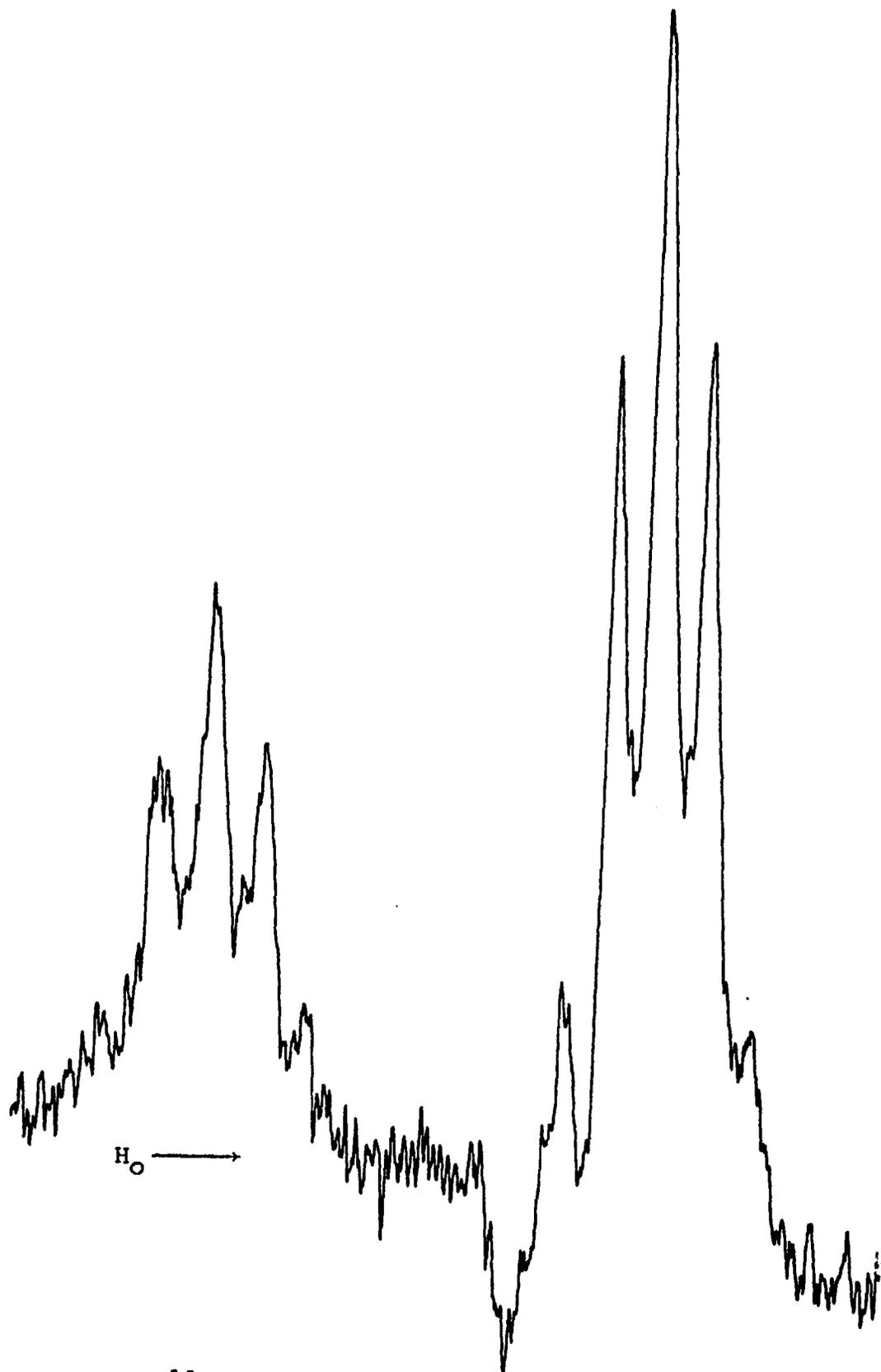


Figure 10. ^{11}B NMR of the Reaction Between 2.14 Mmol Lithium Diethylamide and 1.12 Mmol of Diborane

spectrum shown in figure 11. Isolation and characterization of these products in the separate parallel experiment confirmed the assignment of the resonances to tris(diethylamino)borane and bis(diethylamino)borane (only the high field sidebands of overlapping broad signals centered at -32 ppm are shown in figure 11), diethylaminoborane dimer (triplet, -1.6 ppm), μ -diethylaminodiborane (triplet of doublets, 18.7 ppm), and lithium borohydride (quintet, 38.2 ppm). The spectrum shown in figure 12 resulted after addition of a final 1.12 mmol of diborane to the nmr vessel. Separation of these products from the nmr reaction confirmed the assignment of the spectrum, and produced the following: diethylaminoborane dimer, 0.825 g (0.15 mmol); μ -diethylaminodiborane, 1.81 mmol (85% yield based on lithium diethylamide); lithium borohydride, 2.10 mmol (by hydrolytic hydrogen); and diborane, 0.26 mmol, implying a net consumption of 3.10 mmol. The presence of excess diborane caused the collapse of the borohydride quintet owing to rapid exchange.

Characterization of New μ -Aminodiboranes

The boron-11 nmr parameters, the infrared absorptions, and the vapor pressure data of the new μ -aminodiboranes produced in this work are listed in tables 11, 12 and 13, respectively.

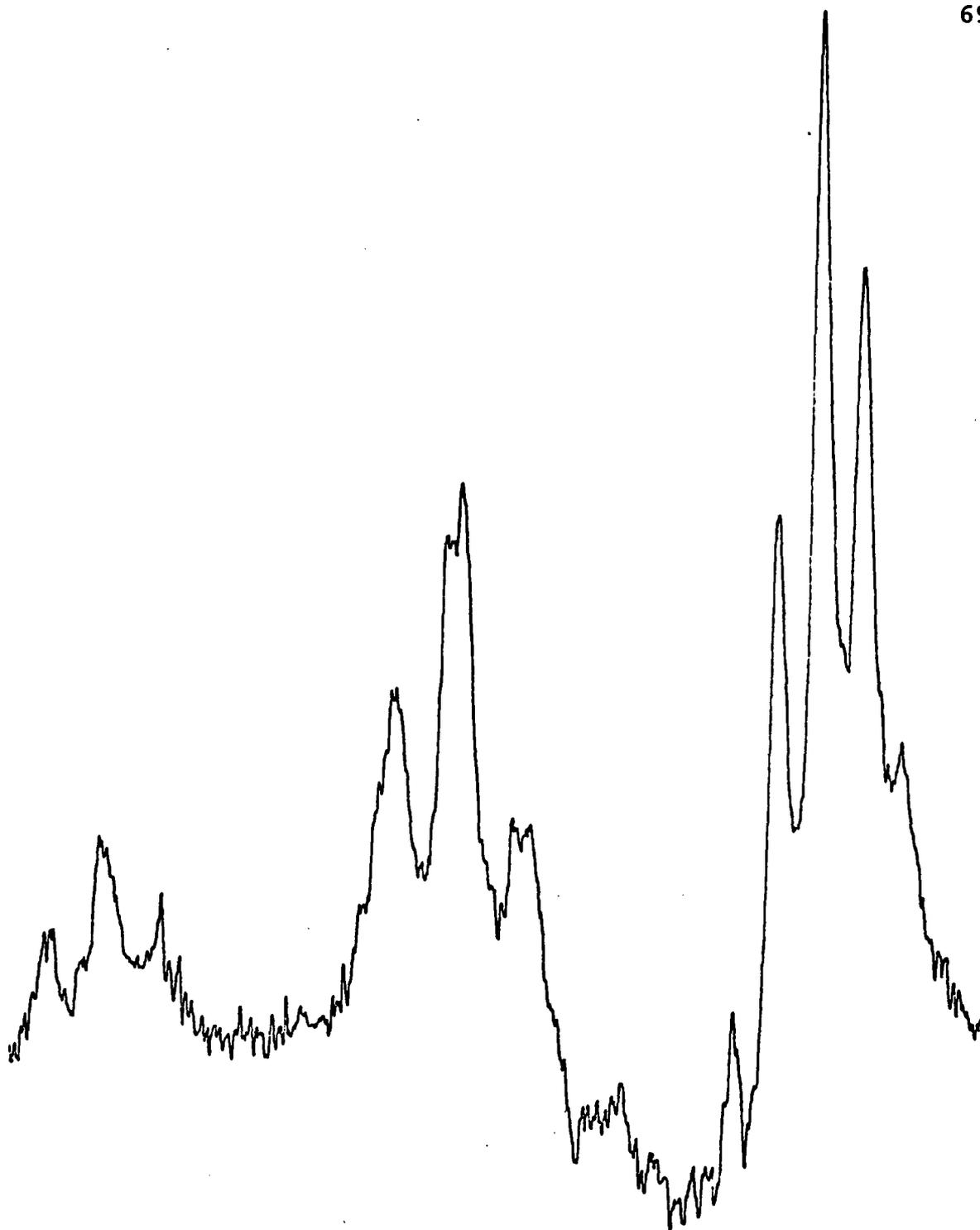


Figure 11. ^{11}B NMR of the Reaction Between 2.14 Mmol Lithium Diethylamide and 2.24 Mmol Diborane

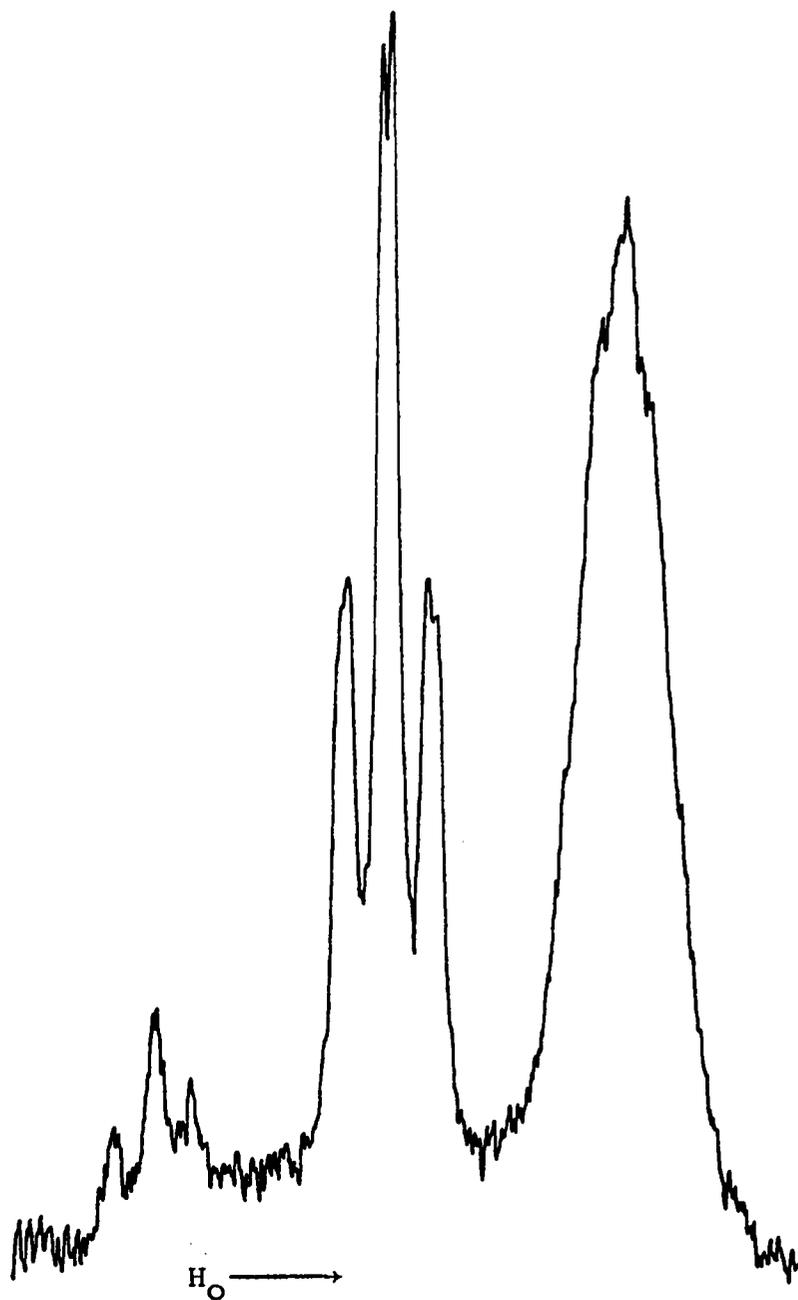


Figure 12. ^{11}B NMR of the Reaction Between 2.14 Mmol Lithium Diethylamide and 3.36 Mmol Diborane

Table 11. ^{11}B NMR Parameters for μ -Aminodiboranes

Coupling Constants, $J_{\text{BH}} = 130 \pm 3$ Hz, and
 $J_{\text{BHB}} = 30 \pm 3$ Hz; Chemical Shifts Compared
 to Diethyl Ether - Boron Trifluoride

$-\text{B}_2\text{H}_5$	δ (ppm)	solvent
CH_3NH	+22.7	neat
$\text{C}_2\text{H}_5\text{NH}$	23.4	toluene
$n\text{-C}_3\text{H}_7\text{NH}$	23.2	neat
$i\text{-C}_3\text{H}_7\text{NH}$	24.5	neat
$n\text{-C}_4\text{H}_9\text{NH}$	22.5	diethyl ether
$s\text{-C}_4\text{H}_9\text{NH}$	23.4	diethyl ether
$t\text{-C}_4\text{H}_9\text{NH}$	23.6	diethyl ether
$n\text{-C}_5\text{H}_{11}\text{NH}$	22.2	diethyl ether
$(\text{CH}_3)_2\text{N}$	17.6	diethyl ether
$(\text{C}_2\text{H}_5)_2\text{N}$	19.0	neat
$(n\text{-C}_3\text{H}_7)_2\text{N}$	18.6	neat
$(i\text{-C}_3\text{H}_7)\text{N}$	21.0	neat

Table 12. Infrared Absorption of
 μ -Aminodiboranes

(v = very, s = strong, m = medium,
w = weak, and sh = shoulder)

μ -n-C ₃ H ₇ NHB ₂ H ₅ :	3400 m, 2990 vs, 2950 sh s, 2880 sh m, 2540 vs, 1890 m, 1625 s, 1575 w, 1450 m, 1420 m, 1380 m, 1350 m, 1290 m, 1170 vs, 1140 m, 1050 s, 950 s, 830 w, 700 m.
μ -i-C ₃ H ₇ NHB ₂ H ₅ :	3390 m, 2980 vs, 2900 sh s, 2870 sh m, 2545 vs, 2470 vs, 2460 w, 1890 w, 1635 s, 1580 sh, 1470 m, 1380 m, 1320 w, 1290 w, 1170 vs, 1080 s, 1040 m, 945 s, 730 w.
μ -n-C ₄ H ₉ NHB ₂ H ₅ :	3400 w, 2960 s, 2880 m, 2800 sh w, 2530 vs, 2460 s, 2280 vw, 1970 vw, 1890 w, 1625 s, 1575 sh w, 1420 m, 1340 sh w, 1250 m, 1180 m, 1100m, 1050 m, 950 m, 920 w, 870 sh, 840 m, 800 m, 760 w, 690 w.
μ -s-C ₄ H ₉ NHB ₂ H ₅ :	3390 w, 2970 vs, 2940 sh m, 2890 m, 2530 vs, 2460 s, 2330 vw, 1910 vw, 1880 w, 1630 s, 1580 w, 1450 m, 1380 m, 1290 vw, 1250 vw, 1155 vs, 1080 vs, 1045 s, 950 s, 840 vw, 725 m.
μ -t-C ₄ H ₉ NHB ₂ H ₅ :	3380 w, 2960 s, 2900 sh m, 2860 sh w, 2530 vs, 2470 s, 2360 sh w, 1870 w, 1640 sh w, 1625 m, 1450 w, 1370 m, 1230 m, 1185 s, 1130 w, 1068 s, 950 m, 800 w, 725 w.
μ -n-C ₅ H ₁₁ NHB ₂ H ₅ :	3420 vw, 2970 sh m, 2940 m, 2849 m, 2870 sh w, 2540 s, 2470 m, 1890 vw, 1625 m, 1465 sh w, 1420 w, 1380 sh, 1170 w, 1105 w, 1045 m, 935 m, 800 w.
μ -(n-C ₃ H ₇) ₂ NB ₂ H ₅ :	2977 s, 2945 sh m, 2880 m, 2540 vs, 2475 s, 1880 vw, 1640 s, 1580 w, 1470 m, 1420 m, 1380 m, 1350 m, 1190 m, 1070 s, 960 s, 870 vw.
μ -(i-C ₃ H ₇) ₂ NB ₂ H ₅ :	2985 vs, 2945 sh vs, 2885 sh s, 2545 vs, 2465 s, 2400 sh w, 1880 vw, 1640 m, 1470 sh s, 1450 s, 1325 s, 1200 vs, 1175 sh, 1140 m, 1105 w, 1070 m, 1040 w, 985 sh w, 945 sh w, 910 vw, 745 w, 700 w.

Table 13. Vapor Pressure Measurements For
New μ -Aminodiboranes

μ -i-C₃H₇NHB₂H₅:

t (°C)	0.0	11.0	15.0	19.0	24.0
P _{mm} (obsd)	15.0	25.0	33.1	37.2	52.0
P _{mm} (calcd)	13.8	25.7	33.2	37.9	52.5

$$\log_{10} P_{\text{mm}} = 8.62 - 2065/T$$

extrapolated bp = 99°C

μ -n-C₄H₉NHB₂H₅:

t (°C)	20.5	25.0	30.0	35.5	42.7
P _{mm} (obsd)	12.0	14.6	19.0	26.6	38.4
P _{mm} (calcd)	11.8	14.7	19.0	26.2	28.1

$$\log_{10} P_{\text{mm}} = 8.08 - 2085/T$$

extrapolated bp = 123°C

μ -s-C₄H₉NHB₂H₅:

t (°C)	0.0	18.0	22.8	29.0
P _{mm} (obsd)	4.7	11.5	15.0	20.0
P _{mm} (calcd)	4.4	11.9	15.1	20.1

$$\log_{10} P_{\text{mm}} = 8.07 - 2038/T$$

extrapolated bp = 119°C

μ -t-C₄H₉NHB₂H₅:

t (°C)	0.0	23.0	29.9	35.0
P _{mm} (obsd)	12.3	41.3	55.0	67.2
P _{mm} (calcd)	12.0	40.8	54.9	67.5

$$\log_{10} P_{\text{mm}} = 7.69 - 1804/T$$

extrapolated bp = 102°C

μ -n-C₅H₁₁NHB₂H₅:

t (°C)	24.1	30.3	36.0	41.0	47.0
P _{mm} (obsd)	8.2	11.4	15.0	19.0	24.0
P _{mm} (calcd)	7.5	11.5	14.9	18.6	24.0

$$\log_{10} P_{\text{mm}} = 7.715 - 2025/T$$

extrapolated bp = 145°C

Table 13, Continued

 μ -(n-C₃H₇)₂NB₂H₅:

t (°C)	23.9	30.7	33.8	42.0	50.0
P _{mm} (obsd)	8.2	12.2	14.3	24.0	31.0
P _{mm} (calcd)	8.6	12.3	14.5	24.0	31.3

$$\log_{10} P_{\text{mm}} = 7.71 - 2004/T$$

extrapolated bp = 143°C

 μ -(i-C₃H₇)₂NB₂H₅:

t (°C)	24.0	29.0	31.0	38.0	49.0
P _{mm} (obsd)	13.6	16.8	18.2	25.6	41.0
P _{mm} (calcd)	13.2	16.6	18.2	25.5	40.8

$$\log_{10} P_{\text{mm}} = 7.73 - 1972/T$$

extrapolated bp = 133°C

The Reaction of Lithium
Methylamide with Diborane

At ambient temperatures the reaction of lithium methyl- or ethylamide with diborane differs from the process outlined above. Near 0° however, these compounds give products similar to the other substituted amides. The lithium methylamide - diborane reaction is representative.

A stirred diethyl ether suspension of 0.0585 g (1.58 mmol) of sparingly soluble lithium methylamide was treated with 1.80 mmol of diborane at room temperature for 3 hours. Vacuum line separation of the volatile products gave 0.20 mmol diborane, 0.26 mmol of N-trimethylborazine and a trace of μ -methylaminodiborane contaminated with diethyl ether (about 1% yield). The solid residue was washed with benzene and filtered; the benzene soluble material was identified as methylamineborane, 0.80 mmol, while the insoluble residue contained 1.51 mmol of lithium borohydride (by hydrolytic hydrogen). The lithium ethylamide experiment yielded essentially the same results, except slightly more μ -ethylaminodiborane (about 10% based on lithium ethylamide) was recovered.

In an experiment in which the temperature was maintained between 0 and 5°, a 0.044 g (1.20 mmol) sample of lithium methylamide reacting with 2.85 mmol of diborane in diethyl ether for 15 minutes gave the

following products: 1.26 mmol diborane (1.49 mmol consumed), 0.10 N-trimethylborazine, 0.30 mmol methylamineborane, 0.10 mmol methylaminoborane trimer, 1.21 mmol lithium borohydride (by hydrolytic hydrogen), and 0.47 mmol μ -methylaminodiborane (26% yield). Methylamineborane and methylaminoborane trimer were isolated and weighed as a mixture; the proportions of the two were estimated from peak areas in the boron-11 nmr spectrum (benzene solution). Since the μ -methylaminodiborane was very difficult to separate from diethyl ether, the quantity produced was determined from the hydrogen evolved upon acid hydrolysis of the ether - μ -methylaminodiborane fraction.

Further Details on the Lithium Substituted Amide Reaction

Although the amides essentially parallel the studies discussed above, a few differences are noted below along with the yields of μ -aminodiboranes, based on the lithium amide as the limiting reagent.

Lithium Dimethylamide. The boron-11 nmr study reveals that the intermediate reactions appear more complicated than with most of the other amides. When the lithium dimethylamide - diborane ratio is 1:1, two downfield triplets at 1.8 and -4.7 ppm are evident. Upon standing, the upfield triplet disappears. The

yield of μ -dimethylaminodiborane, determined by acid hydrolysis of the diethyl ether fraction, was about 50%.

Lithium Di-n-propylamide. The stepwise addition of diborane was not examined with ^{11}B nmr. The μ -di-n-propylaminodiborane produced (50% yield) is a viscous liquid and is completely pyrolyzed in the mass spectrometer at 150° . Monoglyme was also found to be a useful solvent for the reaction.

Lithium Di-i-propylamide. The stepwise addition of diborane was not examined with boron-11 nmr. The μ -di-i-propylaminodiborane, whose yield is about 70%, is more volatile than the di-n-propyl isomer.

Lithium n-Propylamide. The reaction sequence was not followed by ^{11}B nmr. The yield of μ -n-propylaminodiborane was about 50%. The compound has been previously characterized by Burg and Good.⁵⁸

Lithium i-Propylamide. The reaction was attempted in both diethyl ether and toluene with yields of μ -i-propylaminodiborane of 80% and 50%, respectively. The lower toluene yield may have been due to solubility problems. μ -i-Propylaminodiborane is more volatile than the n-propyl derivative.⁵⁸

Lithium n-Butylamide. The yield of μ -n-butylaminodiborane was about 60%.

Lithium s-Butylamide. The yield of μ -s-butylaminodiborane was about 65%; it decomposed completely

upon standing in an evacuated bulb at room temperature for 2 months. The boron-11 nmr spectrum of s-butylamino-borane trimer was not well resolved in either the amide or the tri(s-butylamino)borane reaction.

Lithium t-Butylamide. μ -t-Butylaminodiborane, the most volatile of the butylaminodiboranes, was produced in about 70% yields. The compound was quite unstable over 40°.

Lithium n-Pentylamide. μ -n-Pentylaminodiborane, a liquid of low volatility, was obtained in about 50% yields. The boron-11 spectrum of n-pentylaminoborane, like that of the s-butyl derivative, was not well resolved.

Lithium Benzylamide. The amide was crimson in color. Additionally the compound appeared to be more highly solvated with amine than the other amides investigated. The boron-11 nmr spectrum of the reaction products of benzylamide and diborane was similar to the other amides investigated with a triplet at 22 ppm, presumably due to μ -benzylaminodiborane (μ -C₆H₅CH₂NHB₂H₅). However although a liquid of low volatility (<1 mm pressure at 25°) was obtained from the reaction mixture, no positive identification could be made due to decomposition (hydrogen evolution).

The Reaction of Diethylaminoborane with Diborane in Diethyl Ether

To determine whether diborane reacted with diethylaminoborane under the conditions of the above reactions, equal quantities of diborane and diethylaminoborane dimer were allowed to react in diethyl ether at room temperature for 30 minutes. Separation of the products resulted in recovery of the starting materials, indicating no reaction had occurred.

The Reaction of Tri(s-butylamino)borane with Diborane

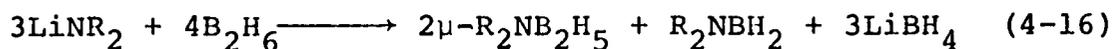
A solution of 1.0 mmol of tri(s-butylamino)borane in 1 ml of diethyl ether in an nmr reaction vessel was treated with 1.0 mmol of diborane. The boron-11 nmr spectrum generally resembled that shown in figure 11 with the single exception of the absence of the borohydride quintet. Separation of the products confirmed the assignment of the spectrum by producing μ -s-butylamino-diborane, tri(s-butylamino)borane, di(s-butylamino)borane, and trimeric s-butylaminoborane.

Results and Discussion

The Course of the Reaction

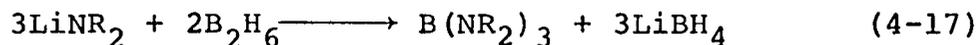
Mono- and di-N-alkyl substituted lithium amides react with excess diborane in diethyl ether according to eq 4-16, although the ratio of μ -aminodiborane to

aminoborane is often significantly greater than 2:1.



With the exception of lithium methyl- and ethylamide, discussed below, and lithium benzylamide, previously discussed, all reactions are complete within 30 minutes at room temperature with μ -aminodiborane yields from 50 to 85% based on lithium amide as the limiting reagent.

When diborane is added to the solution of lithium N-alkylamide, so that the latter is in excess, the first products that can be nmr detected and isolated are a tri(amino)borane and lithium borohydride (eq 4-17). The product distribution (eq 4-17) is generally supported by relative peak intensities in the nmr. No aminoboranes

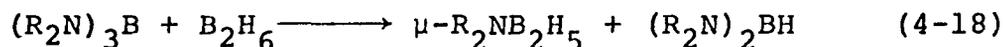


are found at this point. The next stages of the reaction involve the interaction of diborane with the tri(amino)-borane.

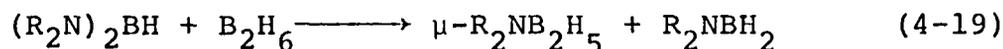
Burg and Randolph studied the solvent-free behavior of tris(dimethylamino)borane and bis(dimethylamino)-borane in the presence of diborane.⁵¹ Both compounds reacted readily below ambient temperatures to produce a small quantity of μ -dimethylaminodiborane (compare figure 10) and a mixture of more complex intermediate species. Warming the latter with diborane resulted

in quantitative conversion to μ -dimethylaminodiborane, and some dimethylaminoborane.

In this work only reactions conducted at room temperature in homogeneous solutions were studied and the supply of diborane was controlled in order to observe intermediate species. Under these conditions in many cases it was possible to detect, isolate, and identify a di(amino)borane formed through reaction 4-18. The



action of more diborane upon the di(amino)borane is the final stage of the reaction, although often less aminoborane was found than predicted by eq 4-19. The



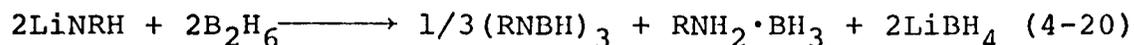
aminoboranes are dimeric when formed from di-N-alkylamides, and trimeric from mono-N-alkylamides. As a check on our proposed sequence of reactions, we have demonstrated, using independently prepared tri(s-butylamino)borane, that reactions 4-18 and 4-19 occur smoothly and quickly in diethyl ether at room temperature.

Burg and Randolph found similar low aminoborane yields in their gas phase studies,⁵¹ but such results can easily be explained by their μ -dimethylaminodiborane synthesis (eq 4-1).³⁶ This process occurs too slowly in diethyl ether at room temperature to explain the

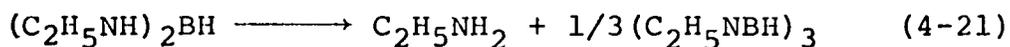
aminoborane shortage in our experiments. The low reaction rate at room temperature probably results from the dimeric or trimeric nature of the aminoboranes; in the gas phase a significant concentration of the more reactive monomer exists. If a monomeric aminoborane is produced by reaction 4-19, this species may have the opportunity to react with diborane before di- or trimerization occurs.

The Case of Lithium Methyl- and Ethylamide.

Near 0° lithium methyl- and ethylamide react normally with diborane; at room temperature however, reaction 4-20 predominates. Assuming initial sequential



formation of a tri- and di(amino)borane as outlined above, the deviation can be explained by the thermal instability of the latter intermediates. Di(ethylamino)borane is known to decompose at room temperature in a manner approximating eq 4-21.⁵⁹ Di(methylamino)borane

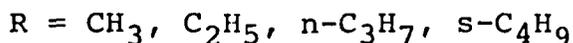


might be expected to be less stable and, indeed, information on the compound is not available. Since no intermediates were positively identified, it is impossible to say whether the tri(amino)borane is a precursor

to the di(amino)borane. A process like reaction 4-22 could occur, followed by the decomposition of the



di(amino)borane (eq 4-21) and subsequently by the reaction of the amine with diborane to form the amineborane. A related reaction involving several tri(alkylamino)boranes and boron trihalides has been reported by Greenwood, Hooton, and Walker⁶⁰ (eq 4-23). Intermediate



formation of a di(alkylamino)boron halide was suggested.

Reactions of Diborane with Lithium

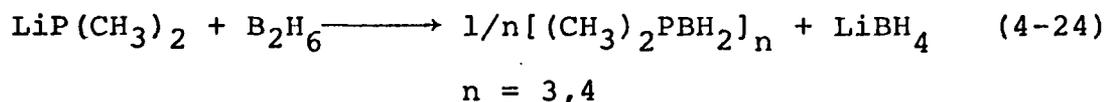
Amide and Lithium Dimethylphosphide(1-)

The reaction between diborane and lithium amide in diethyl ether (eq 4-7)¹⁰ is unique; the formation of polymeric, ether-insoluble aminoborane probably causes the cessation of the reaction. In the N-alkyl amide systems all intermediates are ether-soluble and labile, thus allowing the ultimate formation of μ -aminodiboranes via reactions 4-17, 4-18 and 4-19.

Unlike the amides described above, lithium dimethylphosphide reacts quantitatively with diborane in diethyl ether without the formation of detectable intermediates to produce lithium bis(borane)dimethylphosphide(1-) (eq 4-6).²⁶ The crucial difference

between nitrogen and phosphorus systems is that all nitrogen intermediates are compounds of three coordinate boron stabilized by B-N π -bonding, while in the latter case only a four-coordinate σ -bonded B-P compound is found. Boron-phosphorus π -bonding is either very weak or absent in most BP compounds;²³ monomeric phosphinoboranes R_2PBH_2 , di(phosphino)boranes $(R_2P)_2BH$, and tri(phosphino)boranes $(R_2P)_3B$ are unknown.²² Since these phosphorus analogs of the intermediates and products of reactions 4-17, 4-18 and 4-19 are not stabilized by B-P π -bonding, boron is forced to remain four coordinate and form the σ -bonded bis(borane)adduct.

In view of the low reactivity of polymeric dimethylphosphinoboranes,²¹ it is at first surprising that no evidence for reaction 4-24 has been found. If

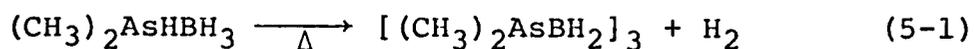


this process requires the intermediate formation of monomeric dimethylphosphinoborane, it would be much less favorable under mild conditions than simple adduct formation. The great resistance to ring opening and dissociation of dialkylphosphinoboranes may, in large part, result from the instability of the monomer.

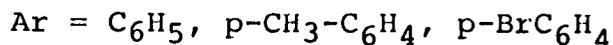
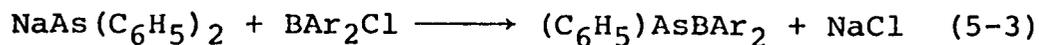
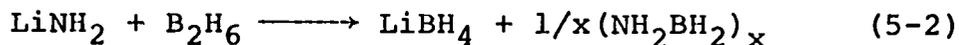
CHAPTER 5

THE PREPARATION OF LITHIUM BIS(BORANE)DIMETHYLARSENIDE (1-)

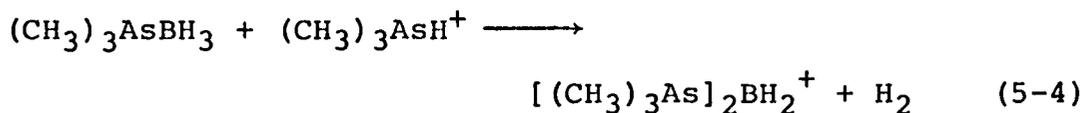
Although arsenic-boron derivatives have been known since 1901, few workers have pursued the field since.⁶¹ Presently there have been less than 25 boron-arsenic compounds reported. Over 50 years elapsed since Stock's original report of $\text{AsH}_3 \cdot \text{BBr}_3$ before the next arsenic-boron compounds, $(\text{CH}_3)_3\text{AsBH}_3$ and $(\text{C}_2\text{H}_5)_3\text{AsBH}_3$, were mentioned in the literature.⁶² The following year, 1954, Stone and Burg reported the first extensive investigation into arsenic-boron chemistry. They characterized $(\text{CH}_3)_3\text{AsBH}_3$, $(\text{CH}_3)_2\text{AsHBH}_3$ and $\text{CH}_3\text{AsH}_2\text{BH}_3$. Furthermore they found that the gentle pyrolysis of $(\text{CH}_3)_2\text{AsHBH}_3$ formed primarily dimethylarsinoborane trimer, paralleling the reaction of dimethylphosphine-borane (eq 5-1).⁶³ More recently Coates and



Livingstone²³ have characterized three other arsinoboranes utilizing the Schaeffer-Basile¹⁰ (eq 5-2 and 5-3) reaction.

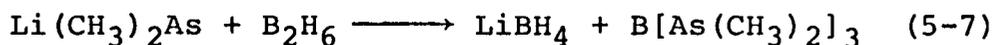
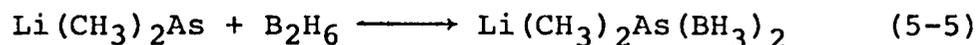


In 1961 Miller and Muetterties reported the synthesis of an arsenic-boron cation, $[(\text{CH}_3)_3\text{As}]_2\text{BH}_2^+$.



The cation was fairly resistant to hydrolysis by neutral water, but was rapidly hydrolyzed in aqueous base.⁶⁴

Our investigations of the reactions of lithium dimethylphosphide²⁶ (chapter 2) and lithium N-alkylamides (chapter 4) with diborane have led us to react lithium dimethylarsenide with diborane. Although this work is still incomplete, it is important enough to warrant inclusion in this text. Past results (chapter 2 and chapter 4) have indicated that eq 5-5 through 5-7 were possible reactions for lithium dimethylarsenide and diborane.



Our preliminary studies have shown that eq 5-5 occurs exclusively. This chapter will discuss the preparation and a few properties of lithium bis(borane)dimethylarsenide(1-).

Experimental Section

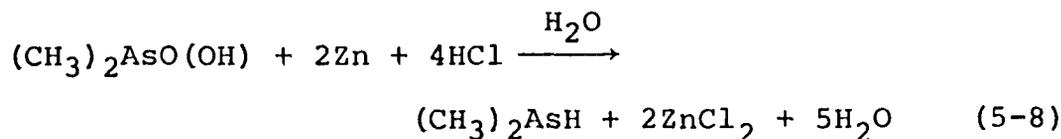
General Data

Reactions were carried out with the aid of a standard high vacuum system as described in the appendix. Air sensitive materials were manipulated in nitrogen-filled drybags or in the vacuum line. Diethyl ether, monoglyme (1,2-dimethoxyethane), and dioxane were stored in evacuated bulbs over lithium aluminium hydride and, when needed, were condensed directly into the reaction vessel. Boron-11 and proton nmr spectra were obtained using a Varian HA-100 spectrometer operating at 32.1 MHz and 100 MHz, respectively. Boron and proton chemical shifts are in ppm relative to diethyl ether - boron trifluoride and TMS, respectively. Infrared spectra were obtained using Perkin-Elmer 137 and 337 spectrophotometers.

Reagents

Diborane was prepared by the reaction of warm polyphosphoric acid with sodium borohydride. Details of this reaction are fully described in chapter 2. N-butyllithium in hexane, approximately 1.6 M (Foote Chemical Co.) was used without purification. All samples were contaminated with lithium bromide and lithium butoxide. N-butyllithium was always handled in the dry-bag and stored in a refrigerator to retard decomposition.

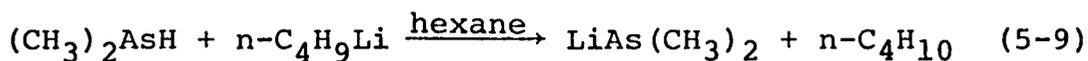
The Preparation of Dimethylarsine. A modification of the Feltham and Silverthorn procedure⁶⁵ was used to prepare dimethylarsine (eq 5-8). Typically



15 mmol of cacodylic acid and 40 mmol of zinc dust were placed in a 200 ml 3-necked flask, equipped with an addition funnel and stopcock connection to the vacuum line and a magnetic stirrer. The flask was evacuated and about 25 ml of water added through the stopcock; slow reaction was evident. Concentrated hydrochloric acid was placed in the addition funnel and slowly added to the flask's contents, while stirring, over a 30 minute period. The vessel was opened to the vacuum line manometer in order to monitor the course of the reaction. When about 400 mm of pressure developed, the volatile products were pumped through a -196° trap; a quantity of hydrogen passed. After 30 minutes the flask was removed from the vacuum line and residual amounts of dimethylarsine were destroyed with sodium hypochlorite. The volatile products were fractionated through -63° and -112° traps to remove water and hydrogen chloride. The purity of the dimethylarsine was determined by comparison of its 0° vapor pressure (183 mm) with the literature value of 179 mm.²

The Preparation of Lithium Dimethylarsenide(1-).

Lithium dimethylarsenide was prepared from dimethylarsine and n-butyllithium in hexane (eq 5-9). In a drybag a known amount of n-butyllithium was injected into a flask. The flask was quickly transferred to the vacuum line where it was frozen to -196° and evacuated. A slight excess of dimethylarsine was condensed into the vessel



which was then warmed to room temperature and stirred magnetically. After 15 minutes the colorless solution turned cloudy and a white precipitate of lithium dimethylarsenide settled out when stirring was discontinued. After 30 minutes the precipitate began turning yellow; further standing resulted in a dark yellow and finally, a dark orange precipitate and a considerable quantity of non-condensable gas. If the reaction of dimethylarsine and n-butyllithium was halted after 30 minutes, by removing all volatiles, and immediately using the prepared lithium dimethylarsenide product, little decomposition occurred. The quantity of lithium dimethylarsenide was estimated from the dimethylarsine consumption and the n-butane evolved. The product, lithium dimethylarsenide, was used without purification.

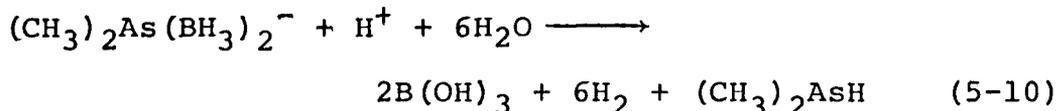
The Reaction of Lithium Dimethylarsenide with Diborane

In a typical reaction, a 200 ml reaction vessel was charged with 1.6 mmol (determined from dimethylarsine

consumption) of lithium dimethylarsenide; the vessel was evacuated, followed by condensing in 5 ml of diethyl ether, the resulting solution was yellow. A 2.7 mmol sample of diborane was condensed in the evacuated vessel which was then warmed to room temperature and stirred magnetically for one hour. During the course of the reaction the solution turned from dark-yellow to colorless. Separation of the volatile products on the vacuum line produced diethyl ether and 0.9 mmol of diborane, implying a 1.8 mmol consumption of diborane. The involatile residue consisted of a viscous oil which, after treatment with 5 ml of anhydrous dioxane and evaporation of the solution under vacuum, yielded a colorless crystalline solid. The product was contaminated with an appreciable (about 10%) quantity of lithium borohydride, introduced from the lithium butoxide impurity,^{9,34} in the n-butyllithium. Although an analysis was not conducted on the product, the diborane consumption and the spectral properties imply the formation of lithium bis(borane)dimethylarsenide, $\text{Li}(\text{CH}_3)_2\text{As}(\text{BH}_3)_2$, coordinated to dioxane.

Characterization. Lithium bis(borane)dimethylarsenide(1-) coordinated to dioxane, dissolves without reaction in glyme ethers, neutral water, and aqueous base, but is insoluble in diethyl ether, benzene, heptane, and chloroform. After 4 months, a solution of $\text{Li}(\text{CH}_3)_2\text{As}(\text{BH}_3)_2$ in D_2O had undergone only moderate

decomposition as indicated by its boron-11 (fig 13) and proton nmr spectrum. Acidification of an aqueous solution of the compound resulted in rapid hydrolysis, possibly according to eq 5-10.



Although the compound is reasonably air stable, it is quite hygroscopic. The proton and boron-11 nmr spectra are shown in figures 14 and 15, respectively; the infrared spectrum (KBr matrix) is indicated in table 14.

Reactions. The reaction of $\text{Li}(\text{CH}_3)_2\text{As}(\text{BH}_3)_2$ with hydrogen chloride yields only hydrogen and diborane as volatile products; the latter compound may be a result of the lithium borohydride impurity.

The reaction of lithium bis(borane)dimethylarsenide(1-) with diborane in diethyl ether results only in the recovery of the starting materials. Examination of the reaction in the nmr vessel, described in the appendix, indicates only broadening of the quartet associated with $\text{Li}(\text{CH}_3)_2\text{As}(\text{BH}_3)_2$ (fig 13).

Results and Discussion

Formation of $\text{Li}(\text{CH}_3)_2\text{As}(\text{BH}_3)_2$

The reaction of lithium dimethylarsenide with diborane in diethyl ether yields lithium bis(borane)-dimethylarsenide(1-) in good yields (eq 5-5). No

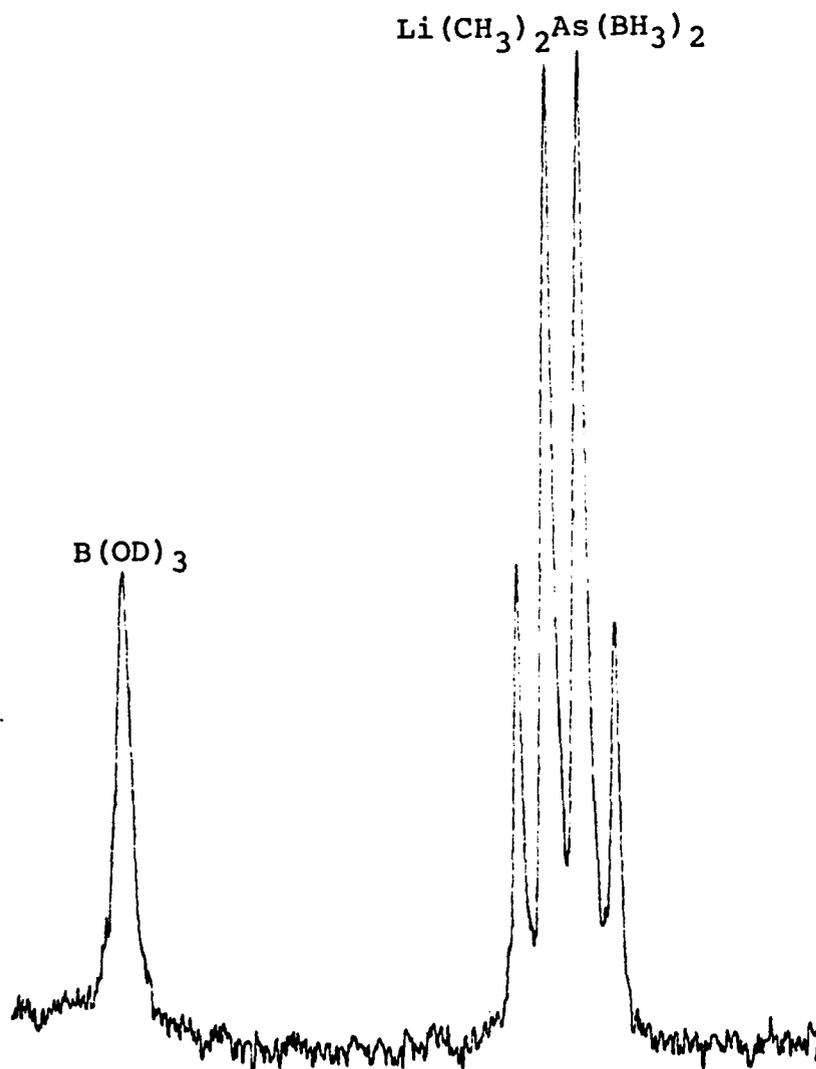


Figure 13. ^{11}B NMR of $\text{Li}(\text{CH}_3)_2\text{As}(\text{BH}_3)_2$ in D_2O

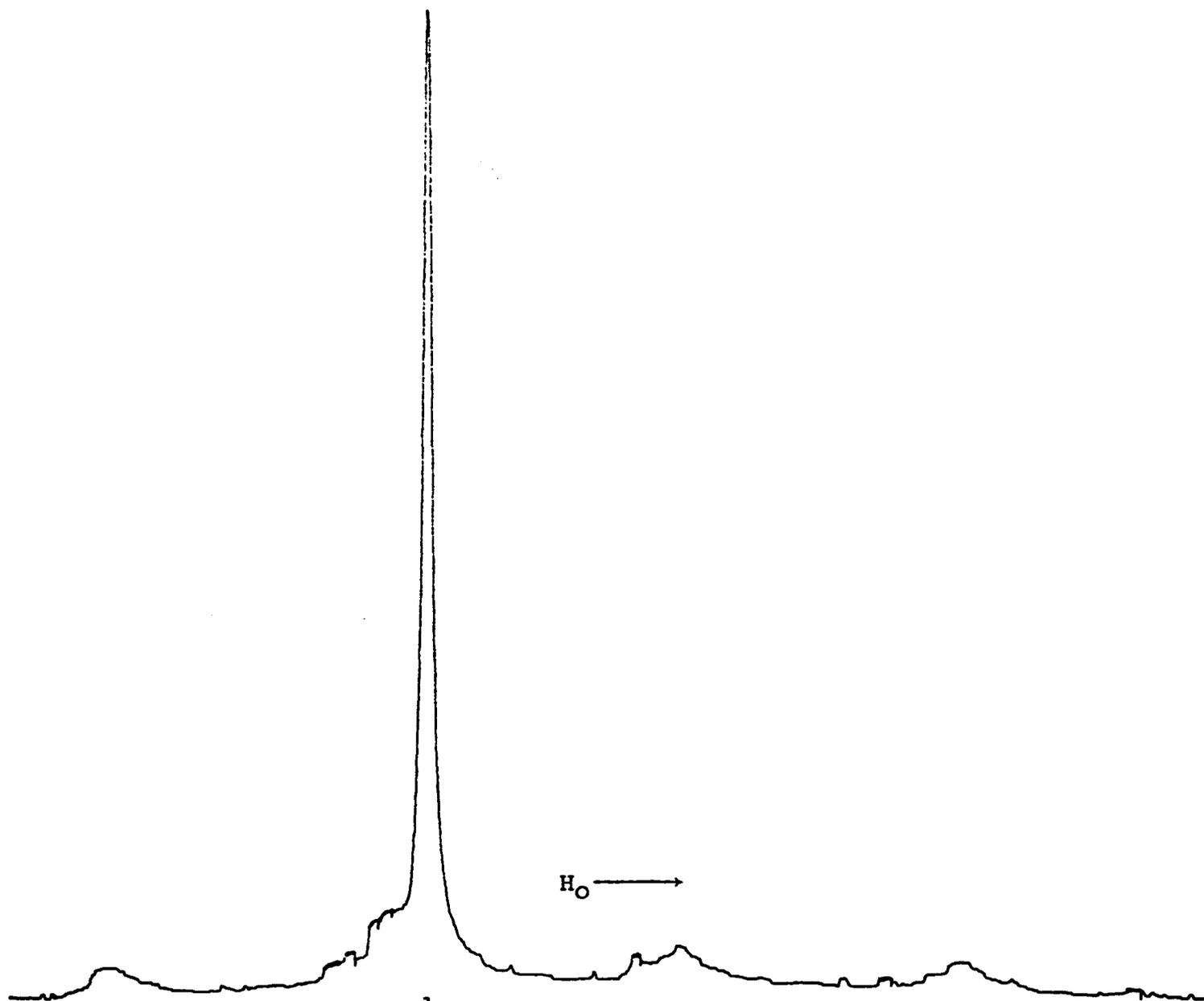


Figure 14. ^1H NMR of $\text{Li}(\text{CH}_3)_2\text{As}(\text{BH}_3)_2$ in D_2O

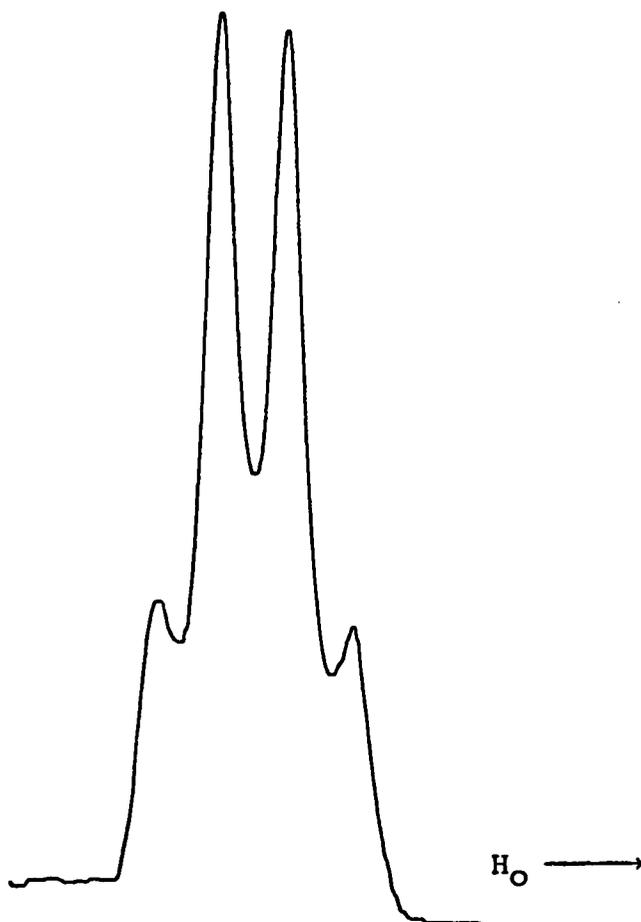


Figure 15. ^{11}B NMR of $\text{Li}(\text{CH}_3)_2\text{As}(\text{BH}_3)_2$ in Diethyl Ether

TABLE 14

INFRARED FREQUENCIES FOR LITHIUM BIS(BORANE) -
DIMETHYLARSENIDE (1-) COORDINATED TO DIOXANE

Frequency (cm ⁻¹)	Intensity
2970	medium
2930	medium
2910	shoulder, weak
2870	medium
2370	very strong
2330	very strong
2290	very strong
1450	medium
1440	shoulder, medium
1420	very weak
1380	very weak
1290	medium
1250	strong
1075	strong
1055	shoulder, weak
1045	shoulder, medium
1040	strong
1015	shoulder, weak
905	shoulder, weak
890	strong
870	very strong
800	weak (broad)
618	strong
605	weak
560	weak

evidence for the presence of dimethylarsinoborane (eq 5-6) or any other arsenic-boron compound could be found.

Properties of Lithium

Bis(borane)dimethylarsenide(1-)

The boron-11 nmr spectrum, shown in figure 15, displays a quartet with chemical shift of +32.6 ppm and with a coupling constant to $J_{B-H} = 93$ Hz, in diethyl ether. The coupling constants and line widths are solvent dependent as indicated by the boron-11 nmr of the compound in D_2O (fig 13). This phenomenon was also noted for $Li(CH_3)_2P(BH_3)_2$ (chapter 2). The proton nmr of $Li(CH_3)_2As(BH_3)_2$ in D_2O (fig 14) shows a chemical shift of $\delta(CH) = -0.71$ ppm due to the 6 methyl protons, and a 1:1:1:1 quartet centered at $\delta(BH) = -0.36$ ppm, with coupling constant of $J_{BH} = 92$ Hz due to the protons on boron. Integration showed the relative peak intensities of CH_3 to BH_3 protons to be 1:1. The broadness of the BH_3 protons is due to the quadrupole moments of boron ($I = 3/2$) and arsenic ($I = 5/2$). The infrared spectrum (table 14) compares favorably to the structurally related compounds $Na(CH_3)_2N(BH_3)_2$ ³⁹ and $Li(CH_3)_2P(BH_3)_2$.²⁶

The air and hydrolytic stabilities of lithium bis(borane)dimethylarsenide(1-) are similar to those reported for the nitrogen³⁹ and phosphorus²⁶ analogs. Attempts to prepare μ -dimethylarsinodiborane from $Li(CH_3)_2As(BH_3)_2$ and hydrogen chloride or diborane failed.

Our preliminary results indicate that lithium bis(borane)dimethylarsenide(1-) behaves similarly to the phosphorus analog. Further investigations are in process.

APPENDIX

VACUUM AND INERT ATMOSPHERE TECHNIQUES

One method of handling air sensitive compounds involves manipulations in vacuum systems. Developed by Stock¹ and his co-workers, the vacuum line is well suited for handling reasonably volatile compounds. Although vacuum techniques are fully discussed elsewhere,^{2,66} a brief explanation will be given here. The vacuum is produced by a mechanical pump and further enhanced by the use of a mercury diffusion pump which helps attain a vacuum of 10^{-5} to 10^{-6} torr. The vacuum system is constructed of pyrex glass; mercury float valves, instead of greased stopcocks which are susceptible to attack by organic compounds, aid in manipulation and separation procedures. Distillation or sublimation of volatile substances within the apparatus is accomplished by cooling the desired part with a dewar filled with liquid nitrogen. Mixtures of different volatility are separated by fractional distillation through traps maintained at low temperatures by baths; a bath is a mixture of a frozen compound in equilibrium with its liquid. Table 15 lists common low temperature baths used in this work.² A mixture of solid carbon dioxide

(dry-ice) and trichloroethylene, although not an equilibrium mixture, served as a cold temperature bath with the approximate temperature of -78° to -80° .

Non-condensable gases like hydrogen and methane were transferred with the aid of a Toepler pump, a recycling pump which uses mercury to displace the gas being handled.² Quantities of gases were measured with monometers on the vacuum line and employing the ideal gas equation (A-1), reliable results were obtained.

$$n = \frac{PV}{RT} \quad (\text{A-1})$$

Unless specifically identified in the text, reaction vessels were standard taper, pyrex round-bottom flasks; the vessel capacity was directly related to the size of the reaction. The nmr reactions discussed in chapters 2, 4, and 5 employed a specially constructed vessel (shown in figure 16), equipped with a Kontes high-vacuum stopcock.

Although vacuum lines are the best way of handling volatile materials, they are not effective with compounds of low volatility. In such cases a polyethylene glove bag flushed with dry nitrogen was employed; filtering and transferring air sensitive materials were thus easily accomplished.

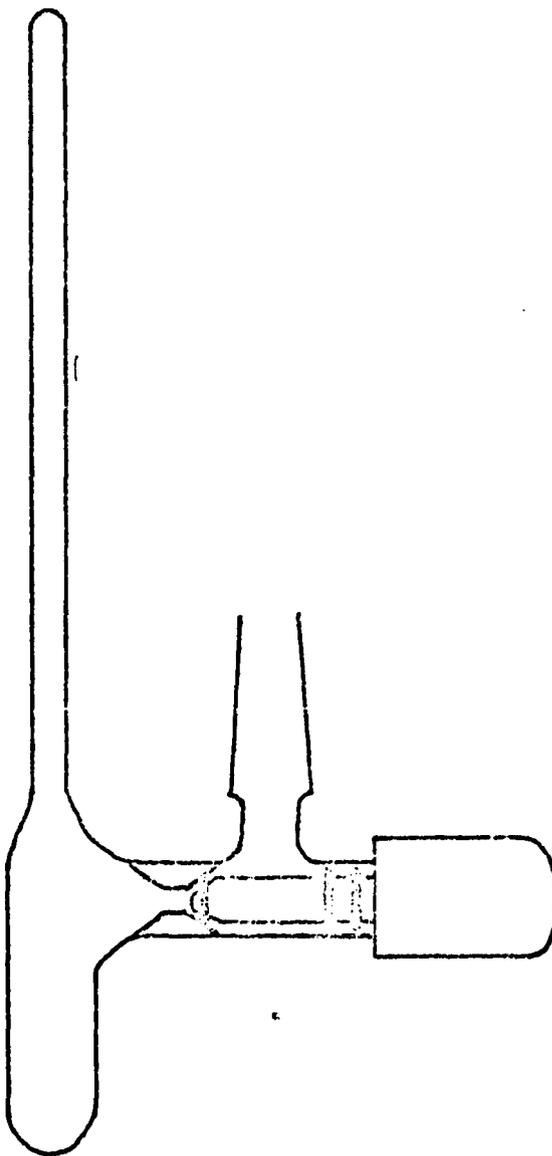


Figure 16. NMR Reaction Vessel

TABLE 15

COMPOUNDS EMPLOYED FOR COLD TEMPERATURE BATHS

T (°C)	Compound
0.0	water
-15.2	benzyl alcohol
-22.95	carbon tetrachloride
-30.82	bromobenzene
-45.2	chlorobenzene
-63.5	chloroform
-95.0	toluene
-111.95	carbon disulfide
-126.59	methylcyclohexane

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