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REACTIONS BETWEEN ALKALI METALS
AND PENTABORANE-9,
A PRELIMINARY INVESTIGATION

LEWIS BASE REACTIONS OF 1, AND 2-METHYLPENTABORANE

DISSERTATION

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

By

Billy Lee Lockman, B.S., M.Sc.

* * * * * * *

The Ohio State University
1971

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PLEASE NOTE:

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The writer would like to thank Dr. Vincent Brice for his suggestions at crucial times.
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INTRODUCTION

A. Reactions of alkali metals with pentaborane(9)

The chemistry of pentaborane(9) and the alkali metals has not been investigated in great detail to the present time. Alfred Stock, who initiated the research into this field, labored under severe handicaps of inadequate equipment and little knowledge of the behavior of boron hydrides and their compounds, and was thus limited in the appraisals of his experimental results. He reacted pentaborane(9) with potassium amalgam, for example, at room temperature and distilled off the mercury and unreacted potassium at 255° C (1). His analysis of the resulting nonvolatile white residue led him to surmise that it was the salt $K_2B_5H_9$; however, later investigations of x-ray power patterns of this material (2) indicated that it contained sodium borohydride and other materials. The only other investigation of potassium and pentaborane(9) chemistry available in the literature was that described briefly by Lipscomb (3) wherein a reaction between $B_5H_9$ and the metal took place in tetrahydrofuran to produce what was tentatively
believed to be $\text{KB}_{8}\text{H}_{13}$. The sole datum reported concerning this experiment was a boron-11 nmr spectrum, but unfortunately no chemical shifts were included.

The only information available concerning the reaction of pentaborane(9) with lithium was provided by a note in Nuclear Science Abstracts on the work of Schlesinger and Urry (4), but other than mentioning that the reaction was carried out in liquid ammonia, no details were given. However, in a brief survey of the acid-base chemistry of pentaborane(9), it was stated by R. L. Hughes, et. al. (5), that Schlesinger's treatment of lithium solutions in liquid ammonia with pentaborane(9) resulted in a decolorization of the blue solutions without hydrogen evolution. The reaction product was reported to have decomposed upon filtration with no details provided.

B. **Base-catalyzed rearrangements of alkyl-substituted pentaboranes**

In 1961, Onak reported that apically-substituted alkyl pentaboranes could be rearranged to the basal-substituted isomer at room temperature in the presence of excess 2,6-lutidine (6). The reaction was followed by using boron-11 nuclear magnetic resonance techniques,
revealing no detectable intermediate in the rearrangement process. Thus, the mechanism for rearrangement was entirely speculative with slow "symmetrical" cleavage by the base and fast recombination or hydrogen tautomerism suggested as initial possibilities. Subsequent work showed that apically attached substituents rearranging to the basal position may be a common characteristic of substituted pentaboranes, a behavior that was also observed at higher temperatures in the absence of a catalyst (7, 8). The thermal isomerization was attributed to intermolecular hydrogen exchange rather than the intramolecular process postulated for one of the mechanisms of the catalyzed reactions, but was further evidence indicating the great facility with which hydrogen atoms can migrate from one boron to another. Additionally, it is known that hydrogen tautomerism and boron skeletal rearrangement is a common occurrence within boron hydride Lewis base adducts (9, 10). After research following the original discovery (8), Onak attempted to explain the rearrangement process by reasoning that the Lewis base would attack a basal boron to create an intermediate in which all borons, including the alkylated boron, would become equivalent. Disassociation of the base would then allow the substituted boron to be located in the more stable basal position by only a slight amount of rearrange-
ment. He suggested the intermediate may have Structure I, similar to the known 2,4-dimethylenetetraborane.

![Structure 1]

In Onak's rearrangement mechanism, only hydrogen tautomerism occurs and no breaking of a boron-carbon bond takes place. William N. Lipscomb in his extensive treatise on boron hydrides and their chemistry (11) incorporated this concept in a postulated mechanism whereby a donor molecule would bond to an orbital freed by the conversion of a three-center bond to a two-center bond, that is, a basal boron. After shifting of hydrogens and rehybridization of the $B_5$ framework a new boron would become the apex and the formerly alkylated apical boron would assume a basal position. This process is illustrated on the next page. A curved line through a boron atom is an open three-center bond, other curved lines are bridge hydrogen atoms.
In 1965, Burg (12) reported the reversible isomerization of 1-bromopentaborane to 2-bromopentaborane, with hexamethylenetetramine as a catalyst. But, the rearrangement of 1-methylpentaborane with 2,6-lutadine, which produces over 90 percent of the isomerized product, has not been observed to be a reversible process. It has been reported, however, that the apically deuterated pentaborane is isomerized by 2,6-dimethylpyridine after 2 hours to nearly the equilibrium value, the apparent
presence of 1-DB$_5^8$ suggesting a reversibility for this species (8). In a more comprehensive investigation of the problem, Onak and co-workers (13) reported the relative rates of various pyridine and amine bases for apical to basal catalysis of 1-DB$_5^8$, 1-CH$_3^5$B$_5^8$H and some polyalkylated pentaboranes. Since they were unable to duplicate the work of W. V. Hough, et al. (14), the possibility of an ionic intermediate (produced by deprotonation of the borane), (CH$_3$)$_3$NH$^+$/RB$_5^8$H$^-$, as suggested by Hough was not given serious consideration. In his discussion of possible mechanisms, Onak advanced the likelihood of a simple association of the base and the substituted pentaborane, RB$_5^8$H$_L$, as the intermediate in the rearrangement process. This followed from the observation that a catalyst was necessary which possessed "sufficiently" strong Lewis base properties. Another interesting observation was that no correlation could be drawn between the catalytic activity of the base and the Bronsted-Lowry base strength, a weaker but less sterically hindered base being more effective than a stronger but bulky base. For example, 2-chloropyridine (for protonated base, pK$_a=0.72$) (15) isomerized 1-CH$_3$ to 2-CH$_3$B$_3^5$H$_8$ in 30 minutes at 25° C while 2,6-lutidine (pK$_a=6.75$) required 4 hours at the same temperature. He concluded that deprotonation of RB$_5^8$H$_L$ was not a necessary requirement for base-catalyzed rearrangement, nor was
the coordination of two amines, as observed in the bistrimethylamine adduct of \( \text{RB}_5\text{H}_8 \), necessary for the process. However, it has been observed in this laboratory (16) that \( 1-\text{CH}_3\text{B}_5\text{H}_7 \), when deprotonated at \(-78^\circ \text{C}\) by \( \text{KH} \) in \( \text{THF} \) (solvent) produces the ion \( 1-\text{CH}_3\text{B}_5\text{H}_7^- \) which does, in fact, rearrange without a catalyst to the 2-substituted anion at about \( 10^\circ \text{C} \). Since these conditions were not employed in preceding work, this particular behavior had not been reported; thus, preventing the realization of the somewhat more complex nature of the substituted pentaborane systems.

In a recent paper, Onak reports new experimental data, this time including, in some detail, the results of investigating the isomerization of di- and trisubstituted pentaboranes (17). The products obtained and their relative amounts from a given reactant correlated in a way explainable by what the researchers called a "minimum atomic motion (MAM)" scheme. This mechanism, which was regarded as general for the whole series of chloro and methyl substituted pentaboranes, envisioned the migration of the two adjacent bridge hydrogens at a given basal boron to positions between the original apical boron and the 3,5-borons. In this way, a new boron becomes the apex and only minor boron skeletal movement is involved. However, the role played by the
Lewis base catalyst in the rearrangements (hexamethylene-tetramine in most cases) was never subjected to speculation. The minimum atomic motion mechanism was discussed by Lipscomb and co-workers with respect to the isomerization of $1,2-$($\text{CH}_3)_2\text{B}_5\text{H}_8$ to $2,3-$($\text{CH}_3)_2\text{B}_5\text{H}_8$ by utilizing the concept of steric interference between bridge hydrogens and methyl hydrogens as the critical factor controlling the geometry of the product (18, 19). These papers concluded, from the presumed existence of $\text{RB}_5\text{H}_7^-$ (14), that the probable rearranging species is the deprotonated system, ($\text{CH}_3)_2\text{B}_5\text{H}_6^-$. The status of a Lewis base adduct was left unclear. However, in view of the fact that the existence of the $\text{RB}_5\text{H}_7^-$ ion resulting from the conditions cited in reference 14 is disputed, and evidence from this laboratory (16) suggests that alkylated pentaboranes do not deprotonate readily, the advancing of a ($\text{CH}_3)_2\text{B}_5\text{H}_6^-$ ion as the rearranging species for the dialkylated systems is subject to uncertainty.

Recently, investigations were carried out in this laboratory by M. Denniston (20) on isolable Lewis base adducts of pentaborane(9), using, among others, trimethylphosphine and trimethylamine as the coordinating agents. The compounds were characterized as to composition and structure with more recent data from x-ray diffraction studies, generally corroborating the geometry
of the trimethylphosphine complex. The conclusions from these studies indicate that a mole ratio of base to pentaborane was 2:1 in agreement with previous work on the same systems (21, 22, 23) and that the structures, though both apparently having a tetragonal pyramidal geometry, differed, with two trimethylamines basally coordinated in one adduct and one trimethylphosphine attached to the base and one to the apex of the boron framework in the other. Since these compounds are examples of isolable pentaborane systems coordinated permanently to a Lewis base, they may provide theoretical connections between the results reported in this dissertation on similar diadducts of methylated pentaboranes and the results discussed above on the rearranging behavior of substituted pentaboranes with noncoordinating bases.
C. Statement of the Problem

1. In Lipscomb's molecular orbital treatment of pentaborane(9) (3), the calculations resulted in a set of seven molecular orbitals whose energies may be represented as in the following diagram.

<table>
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<td>$H_0 - 2\alpha$</td>
<td>$A_1$</td>
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<tr>
<td>$H_0 - \sqrt{2}\beta$</td>
<td>$E$</td>
</tr>
<tr>
<td>$H_0$</td>
<td>$B_1$</td>
</tr>
<tr>
<td>$H_0 + \sqrt{2}\beta$</td>
<td>$E$</td>
</tr>
<tr>
<td>$H_0 + 2\alpha$</td>
<td>$A_1$</td>
</tr>
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The lowest energy $A_1$ and $E$ levels are bonding in character, the $B_1$ level is nonbonding and the high energy level $A_1$ and $E$ are antibonding. The molecular orbitals were constructed by taking linear combinations of hybridized atomic orbitals of each of the borons in the $B_5$ framework. Those hybridized atomic orbitals used for the four basal borons were $sp^3$ and for the apical boron $sp$. After subtracting two electrons from each boron in the base for terminal and bridge hydrogen bonding, one electron apiece remained, giving a total of four for framework bonding. The apical boron contributes one of its three electrons to the terminal hydrogen bond and donates the other two to the framework. A total of six electrons from all the borons thus reside in the pyramidal $B_5$ framework and are distributed, two each, in the three lowest energy levels as shown in the previous diagram. These levels, $A_1$ and $E$, are filled and an electron in one of the higher levels of the neutral pentaborane(9) molecule would represent an excited state. The presence of an empty nonbonding molecular orbital of moderate energy, as deduced from the calculations, then suggests that it may be possible to insert two electrons into the system were a sufficiently powerful reducing agent available. This could possibly result in the formation of the anion $B_5H_9^-$ which may then undergo further
reactions such as protonation with hydrogen chloride to produce \( B_5H_{10}^- \) or \( B_5H_{11}^- \). The reducing agent chosen initially was potassium metal, but the complexities of the reaction as evidenced by the presence of species containing less or more borons than the pentaborane started with, prompted an expansion to another metal. Some investigations had been carried out with lithium, but the details of these experiments were very sparcely reported in the conventional literature. However, since some success had been attained, further work along similar lines presented itself as a possible fruitful new approach to the problem.

2. The investigations into the reactions of pentaborane(9) with various Lewis bases by M. Denniston (20) led to the isolation of the compound bistrimethylphosphinediboron \(((CH_3)_3PBH_2BH_2P(CH_3)_3\) as a product of decomposition of the adduct.

   It was also observed by F. Yungfleisch (24) that methylated amines appear to attack the B-CH\(_3\) unit of methyldiborane counter to what would be expected from the electronic and steric effects of the methyl group. Assuming then that the Lewis acid-base chemistry of the methylated pentaboranes may be analogous to that of pentaborane(9), the possibility was suggested that
trimethylphosphine adducts of 1- and 2-methylpentaborane could be formed and that if trimethylphosphine behaves in such a system as trimethylamine does with methyldiborane, the methyl analog of the diboron fragment from $\text{B}_5\text{H}_9\text{(P(\text{CH}_3)_3)_2}$ that is $((\text{CH}_3)_3\text{PBH}_2\text{BH}\text{CH}_3\text{P(\text{CH}_3)_3}$, could possibly arise as a decomposition product. This could presumably be formed from the attack of trimethylphosphine at the methylated boron. Studies of such a species would include the optical activity that would be expected because of the asymmetric boron attached to methyl. To fully investigate the chemistry, both methylated isomers of pentaborane were used plus the Lewis base trimethylamine. When the desired diboron compound did not appear, the direction of the problem turned toward detailed considerations of structure, reaction behavior and the mechanistic implications that might be reasonably drawn.
A. Apparatus

1. Vacuum system

A Pyrex high vacuum line was necessary in the preparation and handling of the compounds subject to study. This consisted of a Duo-Seal evacuation pump preceded by a two-stage mercury diffusion pump containing triply distilled mercury and allowing normal working pressures of $10^{-3}$ Torr. Both pumps were protected from corrosive condensable substances by a liquid nitrogen trap and distilling mercury was kept from the Duo-Seal pump by a trap maintained at $-78^\circ$C. The system contained three reaction trains and an interconnected fractionation train all having access to a main manifold. Greaseless Fischer-Porter Teflon stopcocks were utilized extensively. The four-part fractionation train, connected directly to a mercury manometer, was calibrated with SF$_6$ in varying volume combinations according to standard procedures. Included in the reaction trains were ten stations equipped with $14/35$ S inside joints and two horizontal $14/35$ S outside joints, the latter designed for use with the filtration and extraction equipment.
described later. Mercury "blow-out" tubes between the joint and stopcock were available on nine of the ten stations for monitoring pressures in the attached vessels.

Noncondensable gases were transferred by means of a mercury valve Toepler pump of constant static volume into a measuring section, calibrated with varying quantities of carbon dioxide. Measurements of volumes at two temperatures were made to allow temperature corrections when necessary.

2. X-ray measurements

X-ray powder diffraction patterns were obtained on a North American Phillips x-ray generating instrument using a Debye-Sherrer camera 11.46 cm in diameter. A Cu-K target provided the radiation at 12 milliamperes and 32 kilovolts for an exposure time of generally 18 hours. The samples were sealed in 0.5 mm capillary tubes under an inert atmosphere.

3. Infrared spectra

The infrared spectra of the compounds were obtained from a Perkin-Elmer Model 457 grating infrared spectrophotometer calibrated to allow frequencies to be obtained directly from the chart paper. The samples were
mounted between potassium bromide plates either neat or as a Nujol mull. Gas samples were condensed into the side arm of a cylindrical cell 95 mm long and 28 mm in diameter equipped with potassium bromide windows. This cell could be attached to the vacuum line, evacuated and filled with any desirable quantity of condensable sample with usual techniques.

4. Nuclear magnetic resonance spectra

$^{11}$B nuclear magnetic resonance data were obtained at 19.3 MHz on a Varian HA-60 high resolution spectrometer and at 32.1 MHz on a Varian HA-100 instrument employing the side band technique for calibration. Reference compounds used were boron trifluoride etherate (which has been assigned a chemical shift of 0.00 parts per million), trimethylborate (-18.1 ppm with respect to BF$_3$-Et$_2$O) and boron trichloride (-47.0 ppm with respect to BF$_3$-Et$_2$O), all of which were enclosed in small capillaries within the 5 mm nmr sample tube. The latter were joined to the reaction vessel, filled at low temperature by submerging in a Dry Ice-isopropyl alcohol slush and detached with a glass-blowing torch. The chemical shifts of all signals were referenced with respect to boron trifluoride etherate. Low temperature studies were carried out from -80°C to +25°C using a Varian V-4341/V-6057 Variable Temperature Accessory.
Double irradiation experiments were performed with a General Radio Company (Concord, Massachusetts) Coherent Decade Frequency Synthesizer, Model 1164A, equipped with an EIN Model 310L R. F. power amplifier and a Pseudo Random Pulse and Noise Generator Model 270, made by Technical Measurement Corporation (North Haven, Connecticut).

Proton spectra were obtained on the Varian HA-100 instrument using dichloromethane as an internal reference (which served also as the solvent), the chemical shifts then being adjusted to tetramethylsilane in terms of parts per million.

Integration of signal areas was accomplished with a K and E Compensating Planimeter.

5. Mass spectra

The mass spectra were obtained on an AEI, Ltd. Ms-9 mass spectrometer operating at 70 volts with a trap current of 450 microamps. Solid samples of less than a milligram were enclosed between two perforated alumina plugs in a melting point capillary whose end was partially closed. The tube was inverted in the inlet opening which was heated to volatize the sample.
6. Reaction glassware

Transferral, measurement and separation of most volatile materials was carried out on the vacuum line and in its calibrated trap system; however, extended separation and measurement of less volatile material was performed on a small fractionation train composed of four detachable traps and connected by 9 mm Fisher-Porter Solv-seal joints. The final trap in this train was outfitted with a 5 mm side arm for preparation of nmr samples after the quantity of material had been determined by weight difference. This arrangement allowed relatively low volatility materials to be separated and transferred quantitatively by pumping them directly through a U-trap maintained at -196°C. The filtration and washing of air-sensitive solids was accomplished at reduced temperatures by means of the apparatus shown in Figure 1. The body of the apparatus above the sintered glass frit could be cooled by liquid nitrogen poured carefully over glass wool wrapping or, in one system, by a Dry Ice isopropanol slush poured into a surrounding cup. The filtering operation was performed by rotating the apparatus 180° about the 14/35 S connecting joint.
Figure 1 - Filtration and Extraction Apparatus
7. Glove box

Nonvolatile samples were handled under a helium atmosphere purged of oxygen and water by sodium-potassium alloy in a gas-tight box equipped with rubber gloves.

B. Reactants and Solvents

Pieces of potassium metal were scraped clean in the glove box then placed in the bottom of a tube about 30 mm in diameter equipped with 24/40 S stockpot adapter. Several small weighed tubes (about 5 mm diameter) and fused at one end were also enclosed open end down. The system was evacuated. About 40 Torr of dry nitrogen gas was then allowed into the apparatus and the potassium was melted with a heat blower. While the metal was still liquid, more nitrogen was allowed into the system to force the metal into the small 5 mm tubes. The weighed tubes were removed from the solidified potassium in the glove box, stopped with tared rubber septa and reweighed. The potassium was easily removed from the tubes by melting under a low nitrogen pressure in a reaction tube followed by slow evacuation of the gas. The nitrogen trapped by the potassium in the small tube forced the molten metal out into the bottom of the reaction vessel.
where rotation of the latter allowed deposition of a metal coating 1 to 2 cm in height and about 1 - 2 mm in thickness. The metal surface was shiny and completely free of evidence of corrosion.

Lithium metal was cleaned and cut into small cubes (approximately 1 mm on a side) under mineral oil, placed in an extractor (Figure 1) and washed with dried pentane.

Pentaborane(9) was obtained from the Callery Chemical Company; volatile impurities were removed at -78°C.

1-methylpentaborane was prepared from pentaborane(9) and methyl chloride using the method reported by Ryschkewitsch, et al., (25) modified by limiting the reaction time to 12 hours. 2-methylpentaborane was prepared by isomerizing 1-methylpentaborane in the manner prescribed by Onak and co-workers (13).

Trimethylamine was obtained from the Matheson Company and was dried by stirring over sodium metal under a -78° condensing finger. Trimethylphosphine was prepared according to the method used by Burg (26) and recovered as the silver iodide complex as reported by Mann (27).
Ammonia, purchased from the Matheson Company, was dried over sodium metal.

Dimethyl ether was obtained from the Union Carbide Chemical Company and dried over sodium metal. Ethyl ether, from the J. T. Baker Chemical Company, and THF were purified by stirring over lithium aluminum hydride. Normal pentane bought through the Mallinckrodt Chemical Works was dried in the same manner. Dichloromethane, also purchased from Mallinckrodt was stirred overnight with phosphoric anhydride. Commercial fuel grade propane was purified by fractionation through a -130° trap, the more volatile hydrocarbon being volatile at this temperature while the additive diethyl sulfide was retained. The process was performed a second time on the material passing -130° from the first fractionation. Toluene was dried over lithium aluminum hydride.

C. Exploratory investigations of the reaction of pentaborane(9) with alkali metals

1. The reaction of pentaborane(9) and potassium

The reactivity of potassium with pentaborane(9) and the products obtained varied widely with the solvent.
Because of this difference, the reactions will be discussed according to the particular solvent used.

**Ethyl ether.** In the only reaction attempted in diethyl ether, 2.23 moles of pentaborane(9) were stirred at 0°C over 2.9 moles of metallic potassium in the form of a mirror coating in about 10 ml of the solvent. After several hours, no evidence of reaction was observed, so the metal was stirred with an additional 3.3 moles of B₅H₉ at ambient temperature overnight. No change in the appearance of the system nor residue after removal of volatile materials was seen. Thus, it was concluded that the rate of reaction in diethylether is extremely slow or that reaction does not occur in that solvent.

**Tetrahydrofuran (THF).** Potassium reacts with pentaborane(9) in the more basic solvent tetrahydrofuran, so a range of temperatures from -95°C to 0°C and reaction times from several hours to several days were employed to investigate the nature of this medium as thoroughly as possible. However, regardless of temperature and time conditions, the reactions were always characterized by a decline in their rate to an essential halt with unreacted starting materials still present.
Hydrogen and a dark-purple solid, insoluble in THF, was produced after several hours of reaction time, the composition of which, as indicated by x-ray power pattern, consisted of potassium borohydride and elemental potassium. The only other material observed in the dark solution prior to filtration was the unreacted metal still plated to the wall of the vessel, dulled somewhat by what seemed to be a thin coating of the finely divided purple solid. If all solvent and solvent-soluble components were removed from the metal by filtration, the reaction could be reinitiated by remelting the potassium to expose fresh surfaces and condensing the solvent and unreacted $B_5H_9$ back in. This treatment was of limited value, however, because unreacted potassium and pentaborane were still present after the reaction had again slowed to a stop. Evidently, the coating of $KBH_4$ gradually built up on the metal until it became sufficiently thick to deactivate it.

In tetrahydrofuran, pentaborane(9) reacted with potassium as evidenced by hydrogen formation and the production of a turbid dark purple solution at temperatures as low as $-95^\circ C$. The reaction rate, as indicated by the vigor of hydrogen production, seemed to increase as higher temperatures were employed. However, at temperatures much above $-40^\circ C$ yellow solutions resulted
with the intensity of the color increasing with increasing reaction temperature. When the products were warmed to room temperature, they would become bright yellow and opaque within 1/2 hour, requiring several hours to reach this state when maintained at 0° to -20°.

The amounts of hydrogen evolved were never large, being from 1/2 to 1-1/2 millimoles from an estimated reaction of 5 - 8 mmoles of pentaborane(9). Because of the incompleteness of the reaction and the difficulty of separating unreacted \( \text{B}_5\text{H}_9 \) from the solvent, it was impossible to determine whether the hydrogen that was formed possessed a reproducible stoichiometric relationship to the reactants, and whether this relationship was affected by the temperature. The rate of hydrogen evolution usually declined rather quickly after the start of the reaction - a phenomenon more noticeable at higher temperatures.

In a typical reaction, 15.9 mmoles of potassium metal was removed from its weighing tube in the manner described previously. Following this procedure, 10-15 ml of dry tetrahydrofuran and 14.0 mmoles of pentaborane were condensed into the vessel. The reaction was carried out at -31°C (overnight at -78°C) with measurements of hydrogen made at various intervals. The sharp decrease
In the rate of hydrogen evolution reflected the growing deactivation of the potassium surface up to the point of an effective stoppage of the reaction. Thus, after 57 hours at -31° and about 129 hours at -78° measurable additional amounts of hydrogen were no longer obtainable. The purple coloration and turbidity were first evident within an hour after the reaction began, becoming more intense over longer periods of time.

When no more hydrogen was evolved, the solution was filtered using a cooling jacket to prevent warming of the products. Removal of the solvent at -45° left a viscous, apparently highly solvated THF-soluble material from which a free crystalline solid could not be isolated, either by evacuation or by reprecipitation techniques. The compound was identified by its nmr spectrum as the solvated $KB_{5}H_{14}$ (Figure II.) The example illustrated was obtained from a 19.3 MHz instrument and was identical to the spectrum, also at 19.3 MHz, of the deprotonated $B_{5}H_{9}$, $B_{5}H_{8}^{-}$, after "aging" at room temperature (28). The identity of this converted $B_{5}H_{8}^{-}$ ion as $B_{8}H_{14}^{-}$ was confirmed through the agreement in appearance and chemical shifts of its boron nmr spectrum at 32.1 MHz (29) with that of authentic $B_{8}H_{14}^{-}$ obtained at 28.9 MHz by Greenwood (30). When the viscous residue was treated with aqueous tetramethylammonium chloride, dissolved in
Boron-11 NMR Spectrum of $KB_9H_{14}$ and $B_5H_9$ Resulting from Reaction in Tetrahydrofuran

Figure 2
1,2-dimethoxyethane (glyme) and reprecipitated with ethyl ether, a white solid was isolated whose x-ray powder pattern matched that of \((\text{CH}_3)_4\text{NB}_9\text{H}_{14}\) reported by Geanangel (29), offering conclusive evidence of the identity of the product.

Unreacted pentaborane(9) was observed in the infrared spectra of volatile materials removed from the reaction system, but quantitative separation from the solvent could not be facilitated. However, a rough estimate of the extent of reaction was obtained from analysis of the unreacted potassium. This was accomplished by carefully hydrolyzing all the metal in air, dissolving in water, filtering and diluting to 250.00 ml. Then 25.000 ml aliquots were acidified with an excess of standard acid and quickly back titrated with standard base. Although potassium borohydride is quite stable toward hydrolysis in hot alkaline solutions or cold water, it is hydrolyzed in aqueous acid (31) and its presence would bring about low results in this analysis. Thus, a value of 7.1 mmoles of potassium (hydroxide) obtained from the titration is probably low indicating that out of the initial 15.9 mmoles of potassium, very likely less than 8.8 mmoles reacted.

As has been described, pentaborane(9) reacts with potassium in tetrahydrofuran at temperatures as low as \(-95^\circ\), apparently producing the same products, \(\text{B}_9\text{H}_{14}\).
BH$_4^-$ and H$_2$ in all cases. However, if the reaction takes place for extended periods of time at ambient temperature, products are obtained whose boron-11 nmr does not show the unambiguous presence of B$_9$H$_{14}$-. The nature of the material resulting from the higher temperature reaction of B$_5$H$_9$ and potassium has not been clarified.

**Dimethyl ether.** Pentaborane(9) reacts with potassium in dimethyl ether at what appeared to be a somewhat faster rate than in THF from observation of hydrogen formation. As was the case with tetrahydrofuran, the reaction rate decreased noticeably over a period of several hours, and though a greater tendency to proceed to completion seemed to be characteristic of the dimethyl ether systems, unreacted starting materials were still in evidence after 125 hours of reaction time. The rate of hydrogen evolution appeared to be quite dependent on temperature and declined with time, appearing to fall abruptly after 40-45 hours. Thus when 5.31 mmoles of pentaborane(9) reacted in about 15 ml of dimethyl ether with 11 mmoles of potassium, 0.36 mmole of hydrogen were measured after 20 hours and 45 minutes at -78°C. Following this treatment, reaction for about 4 hours at -63.5° produced 0.20 mmole of hydrogen or more the one half the H$_2$ in one-fifth the time at -78°.
The amount of $B\textsubscript{5}H\textsubscript{9}$ consumed per hydrogen formed was not calculable in this reaction due to lack of recovery of unreacted starting material, but the maximum value (100 percent reaction) would be $5.31/1.93 = 2.75$, where $5.31$ is the entire mmole quantity of pentaborane(9) and $1.93$ is the total number of millimoles of hydrogen "atoms" recovered (Table I). Since complete reaction was unlikely, as suggested by other experiments where unreacted $B\textsubscript{5}H\textsubscript{9}$ was recovered, the ratio is probably somewhat less than $2.75$.

In a carefully controlled reaction, $7.94$ mmoles $B\textsubscript{5}H\textsubscript{9}$ were reacted with $16.4$ mmoles of potassium in about $10$ ml of dimethyl ether at $-31^\circ$C. Immediate hydrogen production occurred and within $15$ minutes, the solution contained a white precipitate. After another $4$ hours, it had just begun to acquire the purple coloration usually observed with the potassium reactions. When $H\textsubscript{2}$ evolution had become quite slow following alternating $-31^\circ$ and $-78^\circ$ reaction temperatures, all volatile materials were removed and fractionated yielding about $2.3$ mmoles of unreacted pentaborane(9). The total amount of hydrogen measured (Table II) was $1.31$ mmoles. The non-volatile residue was stirred at reduced temperature in dimethyl ether and filtered yielding a yellow solid material that was only partially soluble in diethyl
ether at room temperature. The insoluble component was extracted with \(\text{CH}_3\text{O}\) producing a considerable amount of methyl ether-insoluble \(\text{KBH}_4\) and a small quantity of the more soluble \(\text{KB}_3\text{H}_8\) and some unidentified material. That fraction of the initial product which dissolved in diethyl ether, because of its viscosity and yellow color, appeared to be essentially polymeric and contained \(\text{KB}_3\text{H}_8\). The unreacted potassium was remelted and reacted further in dimethyl ether with 2.21 mmoles of \(\text{B}_5\text{H}_9\) at \(-36^\circ\), a somewhat lower temperature than the first treatment. The rather large amount of white precipitate observed at \(-31^\circ\) was not present when the reaction proceeded at \(-36^\circ\), a fact that may indicate significant decomposition side reactions at too high a reaction temperature. Volatile materials were again removed and fractionated, after the hydrogen evolution rate had lessened, with 0.4 mmole of \(\text{B}_5\text{H}_9\) retained in the \(-126^\circ\)C trap. The total amount of hydrogen measured was 0.16 mmole (Table II). A boron-11 nmr spectrum (Figure III) of the methyl ether-soluble product indicated what appeared to be \(\text{B}_{9}\text{H}_{14}\), on the basis of comparison with a reliable spectrum of this material (27), and unreacted pentaborane(9). The total amount of pentaborane(9) that did not react was estimated as 1.4 mmoles, the nmr evidence and quantity of starting materials resulting in the pentaborane(9)-hydrogen ratio of 2.5 (Table II).
TABLE 1

Reaction data of 5.31 mmoles of \( \text{B}_5\text{H}_9 \) reacting with 11 mmoles of potassium metal in dimethyl ether solvent. Reaction temperatures, times at each temperature and the resulting quantity of hydrogen are included.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>20 hr</th>
<th>45 min</th>
<th>4 hr</th>
<th>5 min</th>
<th>1 hr</th>
<th>55 min</th>
<th>20 hr</th>
<th>45 min</th>
<th>2 hr</th>
<th>10 min</th>
<th>16 hr</th>
<th>&lt; 0.01</th>
<th>57 hr</th>
<th>30 min</th>
<th>4 hr</th>
<th>5 min</th>
<th>4 hr</th>
<th>5 min</th>
<th>3 hr</th>
<th>5 min</th>
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</tbody>
</table>

The mole ratio of pentaborane(9) to hydrogen atoms =

\[
\frac{5.31}{1.92} = 2.75
\]

based on the reaction of 100 percent of the pentaborane(9).
TABLE 2

Reaction data of 7.94 mmoles of B₅H₉ reacting with 16.4 mmoles of potassium metal in dimethyl ether solvent. Reaction temperatures, times at each temperature and the resulting quantity of hydrogen are included.

A. First reaction

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Time</th>
<th>H₂ (mmoles)</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td></td>
<td>20 hr</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>40 hr 50 min</td>
<td>1.31</td>
</tr>
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</table>

Mole ratio of pentaborane(9) to hydrogen atoms = \( \frac{7.94 - 2.3}{2.62} = 2.15 \)

B. Second Reaction

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Time</th>
<th>H₂ (mmoles)</th>
</tr>
</thead>
<tbody>
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<tr>
<td></td>
<td>6 hr 25 min</td>
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</tr>
<tr>
<td></td>
<td>9 hr 50 min</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>54 hr</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Mole ratio of pentaborane(9) to hydrogen atoms = \( \frac{2.2 - 1.4}{0.32} = 2.5 \)

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*a* Reaction was continued until hydrogen evolution rate had considerably decreased. Volatile condensable materials were then removed, fractionated and measured.

*b* The unreacted B₅H₉ plus solvent was returned to the reaction vessel after remelting the potassium metal still present.
Boron-11 NMR Spectrum of $KB_9H_{14}$ and Unreacted $B_5H_9$ from Reaction in Dimethyl Ether

Figure 3
The insoluble purple solid obtained from the reaction, which was shown to contain only \( \text{KBH}_4 \) and elemental potassium in its x-ray powder pattern, was slowly hydrolyzed in air and digested for several days in hot aqueous acid solution. The solution was then diluted to 250.00 ml and 25.00 ml aliquots used for boron and potassium analysis. Boron was determined with the usual mannitol procedure by titrating with standard base to a pH of 6.8. The total amount of potassium was weighed as \( \text{KB(C}_6\text{H}_5\text{)}_4 \), an insoluble salt precipitated by an aqueous solution of \( \text{NaB(C}_6\text{H}_5\text{)}_4 \). The result for potassium yielded 11.2 mmoles which included the unreacted metal as well as the potassium ions present in \( \text{KBH}_4 \). Thus, 6.1 mmoles of boron were present as \( \text{BH}_4^- \) leaving 5.1 mmoles of potassium unreacted. Since 16.4 mmoles of potassium were used initially, 16.4 - 5.1 = 11.3 mmoles of the metal had apparently reacted with \( \text{B}_5\text{H}_9 \). If the amount of unreacted \( \text{B}_5\text{H}_9 \) of 1.4 mmoles is considered approximately correct, \( 7.94 - 1.4 = 6.5 \) mmoles as the quantity of pentaborane(9) that may be calculated to have reacted with 11.3 mmoles of potassium. This gives a potassium to pentaborane(9) ratio of 1.7, a relationship that carries the implication that, under the particular conditions of this reaction at least, potassium does not simply donate two electrons to \( \text{B}_5\text{H}_9 \). Rather, the possibility may be considered that after receiving
one electron, the pentaborane(9) framework is in a highly active state and, at the higher reaction temperature of -31°, attacks neighboring molecules. Further electron donation may be made on a non-stoichiometric basis to intermediates of this reaction.

The ratio of pentaborane to hydrogen has in every calculable case been more than two but less than three (Tables I, II). The origin of the hydrogen is unclear since such small amounts are evolved relative to what may be potentially available in B₅H₉, but the observation can be made that at higher reaction temperatures a greater quantity of hydrogen is produced than at lower temperatures, suggesting perhaps that hydrogen formation may be the product of competing decomposition reactions occurring during the formation of B₉H₁₄⁻ from the reduced species.

**Liquid ammonia.** When pentaborane(9) reacted with potassium dissolved in liquid ammonia, an extremely vigorous reaction ensued, even at -78°, which was concluded within half an hour. The reaction went to completion as evidenced by the loss of blue color in the presence of excess pentaborane(9). This behavior seems explainable by the increased basicity of the solvent, and the solubility of the metal which prevents its deactivation as observed in the ether solvents.
Thus 13.4 millimoles of potassium dissolved in 25 ml of liquid ammonia reacted quickly with 9.19 millimoles of penta­borane(9) when the system was warmed from -196° to -78°C. Hydrogen was evolved extremely rapidly, and decoloration of the ammonia solution was immediate in the region where reactants were combining. Hydrogen evolu­tion ceased in less than 30 minutes, but the reaction medium was still deep blue from unreacted potassium. Treatment of the unreacted potassium with an additional 2.24 millimoles of B₅H₉ resulted in a decolorized solution containing a white precipitate. Then 1.0 millimole more of H₂ was liberated by reaction with the second quantity of B₅H₉, but since the volatiles present were not fraction­ated the amount of unreacted pentaborane(9), if any, was unknown. However, the ratio of B₅H₉ to H would have had a maximum value of 2.24/2 = 1.12, if the boron hydride had been completely consumed. The actual value is probably less than this, but in any case, an increased relative yield of hydrogen is obtained in the more basic ammonia solvent. Filtration of this solution produced 0.660 g of white solid which evolved no hydrogen and did not become gummy at room temperature. This behavior seemed to be evidence that little or no pentaborane(9) reacted with the ammonia, since such a reaction product vigorously produces hydrogen and viscous polymeric compounds upon ambient temperature decomposition. The
insoluble material that was filtered off dissolved readily in ammonia, suggesting that a saturated solution of this substance had been present initially rather than another less soluble component. The identifiable components of the reaction product from x-ray powder pattern evidence were shown to be KBH₄ and KB₃H₈. The 32.1 MHz boron-11 nmr spectrum of the products in liquid ammonia at -40°C verified the presence of these materials and an additional compound which, on the basis of evidence to be described below, was apparently KB₉H₁₄. Extraction of the white residue mixture with dimethyl ether dissolved all the components except KBH₄ whose identity and purity were ascertained by x-ray powder pattern. The weight of the potassium borohydride was found to be 0.34 g, indicating that the material soluble in dimethyl ether weighed 0.66 - 0.34 = 0.32 g. The boron-11 nmr spectrum at 19.3 MHz of the (CH₃)₂O solution of the soluble residue obtained at -32°C revealed the presence of a considerable amount of KB₃H₈ (δ = 29.6 ppm). Resonances at 6.2, 11.4 and 19.0 ppm indicate the presence of KB₉H₁₄, thus substantiating it as the species observed in the 32.1 MHz spectrum of the ammonia solution.

Boron analysis of the KB₃H₈ - KB₉H₁₄ mixture by the acid hydrolysis mannitol process gave a value of 50.3 percent boron, consistent with a mole fraction for
the two component system of 0.26 for $\text{KB}_9\text{H}_{14}$ and 0.74 for $\text{KB}_3\text{H}_8$. Using these mole fractions, the amount of $\text{KB}_9\text{H}_{14}$ and $\text{KB}_3\text{H}_8$ in the 0.32 g isolated of the mixture may be calculated as 0.87 mmole and 2.5 mmoles respectively. Since this mixture of salts is assumed to represent at least 90 percent of the $\text{KB}_9\text{H}_{14}$ and $\text{KB}_3\text{H}_8$ produced in the reaction, the approximate yield of $\text{KB}_9\text{H}_{14}$ may be obtained, based on the following equation:

$$2\text{B}_5\text{H}_9 + 2\text{K} \rightarrow \text{KB}_9\text{H}_{14} + \text{KBH}_4$$

The yield lies in the range of 15 percent to 19 percent, the former based on 11.4 mmoles of $\text{B}_5\text{H}_9$ reactant, the latter on 9.19 mmoles. The salt $\text{KB}_3\text{H}_8$ is regarded as a product of a competing side reaction, whose relative quantity appears to increase as the basicity of the solvent and reaction temperature increases.

2. The reaction of pentaborane(9) and lithium

**Liquid ammonia.** In a reaction tube attached to an extractor, 0.179 g (25.9 mmoles) of lithium metal were dissolved in about 25 ml of liquid ammonia. With careful stirring at $-78^\circ$, pentaborane(9) was allowed into the reaction system in small increments from a side arm through a Teflon stopcock. The additions were made until the dark blue of the metal-ammonia solution changed suddenly to yellow-green. A small increment of excess
was added with no change in appearance of the system. No gas was observed as a reaction product. The not inconsiderable amount of greenish-yellow precipitate was filtered cold yielding a clear slightly yellow filtrate having substantially less volume than the amount of solvent ammonia used initially. The reaction tube with the side arm, still containing unreacted pentaborane(9), was removed from the extractor under positive nitrogen pressure, and carefully washed, then dried under vacuum. The pentaborane(9) was weighed and the quantity, 1.57 g (24.8 mmoles) subtracted from the 39.1 mmoles used initially indicating that 14.3 mmoles of $B_5H_9$ had been admitted into the Li-ammonia solution. The ratio of lithium to pentaborane(9), $25.9/14.3 = 1.8$, suggested that two lithiums donate electrons to each pentaborane(9). Indeed, if the amount of $B_5H_9$ added "in excess" beyond the observed end point were subtracted from the amount reacted, the ratio would be yet closer to 2:1.

The solid isolated from the reaction exhibited reversible color changes which depended upon the temperature, being yellow-green at $-78^\circ$ and becoming bluer as the temperature was lowered. At $-196^\circ$ the product possessed a beautiful blue-green color. When warmed slightly above $-78^\circ$, the green quality of the color vanished leaving the solid bright yellow. However, if
further increases in the temperature took place, estimated at above -60°, the material irreversibly became white. Further warming produced a paste at about -45° then, at higher temperatures, a clear nonvolatile oil appeared accompanied by the liberation of hydrogen. Ammonia, as discussed below, was apparently evolved at -45°.

The yellow filtrate became colorless after standing several hours at -78°, and after removal of the solvent at that temperature, a white solid remained which decomposed in the above manner on warming. When extraction of the yellow-green solid with tetrahydrofuran appeared to produce no THF-soluble component, the tetrahydrofuran was removed with warming to -45°. The material turned white, then became pasty and dissolved in fresh THF to produce a brown but nearly transparent solution. No hydrogen was produced. All volatile materials removed were fractionated through a -126° trap yielding 35.4 mmoles of ammonia as the only component other than solvent. The ratio of ammonia recovered to the amount of pentaborane(9) necessary to have reacted with 25.9 mmoles of lithium in a 1:2 ratio is 35.4/12.9 = 2.74, or rather near 3. It may be speculated, then, that were the ammonia lost during the manipulation and investigation of other parts of this reaction product to be combined with that recovered, the
ratio of ammonia to the $2\text{Li}_3 - B_5\text{H}_9$ product would in fact tend toward 3:1. Since no ammonia was released at -78°, it is possible that the change in nature of the white solid at -45° is connected with the disassociation of complexed ammonia. It is also possible, of course, that more than three ammonias were associated with the $2\text{Li} - B_5\text{H}_9$ substrate with only three being labile, but clarification of this point would require nitrogen analysis of the material.

The boron-11 nmr spectrum of the deammoniated product was obtained at 32.1 MHz using tetrahydrofuran at the solvent (Figure IV).

**Dimethyl ether.** In about 15 ml of dimethyl ether, 0.0829 g (11.9 mmole) of lithium metal, cut into small blocks under mineral oil and washed with pentane, were stirred with 6.10 mmoles of pentaborane(9) at alternating -78° and -36° reaction temperatures. The total times at each temperature were 116 hours at -78° and 46 hours at -36°. The solution soon became ink-black and eventually contained small silvery bits of metallic lithium. Hydrogen was not evolved at any time throughout the reaction. The volatile components were removed at -45° and fractionated through a -126° trap, but only about 0.06 mmole of some unidentified material was stopped at that temperature. Through its infra red
Boron-11 NMR Spectrum of the Product of Lithium and $B_5H_9\text{in}$ Ammonia after Standing at $-45^\circ$ (Solvent in Tetrahydrofuran)

Figure 4
spectrum, it was shown not to have been \((\text{CH}_3)_2\text{O}, \text{B}_2\text{H}_6, \text{B}_4\text{H}_{10}, \text{B}_5\text{H}_9, \text{or B}_5\text{H}_{11}\), a result that indicated that the reaction had consumed all the pentaborane(9). The appearance of the reaction system prior to the fractionation, however, indicated that a substantial amount of unreacted lithium was still present in the form of the massive metal. Filtration of the system in fresh dimethyl ether yielded a solution that was somewhat yellow and contained a small amount of the insoluble black precipitate that had so intensely colored the unfiltered medium. Removal of the solvent at \(-78^\circ\) produced a white crystalline-appearing solid that decomposed to a cloudy yellow oil after several hours at room temperature.

The boron-11 nmr spectrum of the dimethyl ether solution maintained at reduced temperatures (Figure V) consisted of two doublets with chemical shifts of 17.2 and 53.3 ppm and coupling constants of 137 and 167 cps respectively. Overlapping the doublets were resonances of considerably lesser intensity having estimated chemical shifts of about 24 and 60 ppm. The spectrum was obtained at \(-40^\circ\)C on the 32.1 MHz instrument. Several observations may be immediately made from this data. Given the chemical shifts and coupling constants for the compound \(\text{LiB}_5\text{H}_8\) as 17.0 ppm \((J = 127 \text{ cps})\) and 52.7 ppm \((J = 156 \text{ cps})\) for two doublets of 4:1 relative intensity (32),
Boron-11 NMR Spectrum from Reaction in Dimethyl Ether

Figure 5

-40°C
The agreement with the spectrum of the lithium-penta-
boranide(9) product established its identity with little
doubt as LiB$_5$H$_8$. It is also apparent, considering the
intensities of the various resonances, that the major
dimethyl ether-soluble component is this compound. Also
LiBH$_4$, which is soluble in (CH$_3$)$_2$O, was not present in
the nmr spectrum, nor in the black solid which was
filtered from the solution as evidenced by a comparison
of its x-ray powder pattern with that of a known sample
of LiBH$_4$. However, a component other than lithium was
present in the solid. The d values from the powder
pattern are listed in Table III with those not belonging
to lithium metal marked with an asterisk. An additional
observation concerning the insoluble black material was
its density compared to that of lithium. The metal,
being less dense, floated in the solvent; the black
solid sank. Some of the pentaborane(9), then, evidently
formed some species other than LiBH$_4$ and combined in
some way with metallic lithium.

The black residue and unreacted lithium metal
were exposed to moist air for a few days to hydrolyze
and were dissolved in 250.00 ml of boiled distilled
water. Then 10.00 ml aliquots were titrated with
standard acid resulting in the determination of 2.76
mmoles of unreacted lithium as lithium hydroxide. This
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* d values for lithium metal are marked with an asterisk.

Intensities: W = weak, M = Medium, S = Strong, V = Very.
value is assumed to be low because of the probable hydrolysis of the unidentified boron hydride that is evidently present to form boric acid. However, if viewed as a point of departure for making a rough estimate, one may calculate that $11.9 - 2.8 = 9.1$ mmolles or less of lithium had reacted with $6.1$ mmolles of $B_5H_9$. The nonstoichiometric relationship between lithium and pentaborane(9) from this analysis may indicate that the metal reduced other species than $B_5H_9$ in the reaction, or that a 1-electron process was involved with only the reduction of $B_5H_9$ taking place, but obscured by the interference of boric acid in the analytical procedure. What seems to be clear, however, is that a 2:1 metal to pentaborane(9) relationship was not involved as was apparently the case in liquid ammonia.

D. 1- and 2-Methylpentaborane Reactions with Lewis Base

1. Reactions with trimethylphosphine

Since previous reactions of pentaborananes with Lewis bases often resulted in varying stoichiometries and cleavage products (16, 17, 18, 33, 34, 35, 36), due apparently to the attack by excess base on the soluble adduct, M. Denniston (20) developed a means to avoid
these difficulties which complicate the investigation of the adducts themselves. When the methylpentaboranes (or pentaborane) were reacted at various reduced temperatures with a given Lewis base in a hydrocarbon solvent, the insoluble adduct precipitated from the solution effectively preventing its undergoing further attack by the base. At the completion of the reaction, all volatile materials were withdrawn, measured and identified to establish the stoichiometry.

a. Trimethylphosphine and 1-methylpentaborane

Reaction at -45°. In a small amount of liquid propane, 0.931 mmole of 1-methylpentaborane and 2.53 mmoles of trimethylphosphine were stirred at -45°C for 52 hours. The reaction was stopped by cooling to -196°, for convenience, in order to maintain a single reaction temperature. Volatile material was removed at -78° and -45° and fractionated through a train of traps cooled at -111°, -140° and -196°. No noncondensable gas was formed; \( P(\text{CH}_3)_3 \) was retained at -140°C and propane at -196° allowing satisfactory separation and quantitative measurement of the components. Following this operation, 0.63 mmole of trimethylphosphine was recovered and no 1-methylpentaborane, giving a stoichiometry of 2:04:1.00 (\( P(\text{CH}_3)_3 \) to \( 1\text{-CH}_3\text{B}_5\text{H}_8 \)) in the residue. The evolution of volatile material was essentially complete.
at \(-45^\circ\) and interpretation of the $B^{11}$ and $H^1$ nmr spectra of the residue indicated a reaction free of competing side reactions. The diadduct, $\text{CH}_3\text{B}_5\text{H}_8[\text{P(CH}_3)_3]^2$, is a white solid which is soluble in methylene chloride and toluene, but insoluble in hydrocarbons and ethyl ether. However, unless the compound is pumped extensively to remove the last vestiges of reactants, it tends to decompose rather rapidly at room temperature to trimethylphosphineborane, $(\text{CH}_3)_3\text{P}\text{BH}_2\text{CH}_3$ and a glassy polymeric liquid which yellows on standing.

The boron nmr spectrum (Figure VI) shows a complex set of resonances fairly typical of medium size open framework boranes such as $B_{6}H_{10}$, $B_5H_9$ and the substituted pentaboranes. Thus, a lower field grouping of signals at 10, 26 and 28.5 ppm and a high field signal appearing at 53 ppm were observed with a peak area ratio of about 4:1 respectively. A doublet arising from coupling with either a hydrogen or phosphorus atom ($J = 90\text{Hz}$) was present at the lowest field resonance while the peak at 53 ppm underwent no discernable coupling. The doublet at 10 ppm was visible in the temperature range $+20^\circ\text{C}$ to $-15^\circ\text{C}$ but, below the latter temperature was no longer present, presumably because of increased nuclear quadrupole interactions by the boron involved (9). Theoretical considerations concerning structure and mechanism plus mass spectral data within
Boron-11 NMR Spectrum of $\text{2-CH}_3\text{B}_5\text{H}_8(\text{P(CH}_3)_3)_2$
the conclusion section, attempt to distinguish whether phosphorous or hydrogen is responsible for the coupling.

Decoupling of the spectrum at -20° brought about few changes, but did partially resolve another peak at 18 ppm which seemed to have an approximate intensity of one. The combination of resonances whose total intensity is 4 were then sufficiently resolved to support an intensity of 1 each for the 10 and 18 ppm signals and 2 for the two peaks at 26 and 28.5 ppm (Figure VII).

The adduct as prepared was sufficiently stable to persist for a short time at room temperature, but shows significant decomposition when allowed to stand several hours without cooling.

The proton nmr spectrum of the diadduct was dominated by two doublets, at -1.33 and -0.99 ppm with respect to tetramethylsilane (Figure VIII). The coupling constants were 11 cps and 10 cps respectively. These resonances were attributed to the methyl hydrogens on the trimethylphosphine ligands, the phosphorus with a nuclear spin of 1/2 being responsible for the splitting. Another somewhat broad resonance was observed at about 0.34 ppm at higher field than tetramethylsilane with a relative intensity of 2 compared to 9 for one set of the doublets. The intensity of this higher field peak
Boron-11 NMR Spectrum of 
2-CH₃B₅H₈(P(CH₃)₃)₂ with 
Simultaneous Irradiation at 60 MHz - Figure 7
Figure 8

Proton NMR Spectrum of 2-CH$_3$B$_5$H$_8$(P(CH$_3$)$_3$)$_2$
and the general vicinity of its chemical shift allowed reasonable assignment to the two bridging hydrogens contained in the structure to be discussed in the conclusion.

The infrared spectrum in Nujol yielded the following product peaks: 2980(sh), 2930(vs), 2860(sh), 2480(sh), 2400(ms), 2310(m), 1930(m), 1420(m), 1380(m), 1310(m), 1290(ms), 1160(ms), 1110(ms), 1060(w), 1030(w), 955(ms), 875(m), 850(m), 762(m), 742(m), 725(m), 708(m), 659(m), 620(m), 595(m), 543(w), 520(w), 482(mw).

(absorbancies attributed to Nujol have been disregarded.)

When the reaction product was reprecipitated from CH₂Cl₂ solution by adding diethyl ether, in which it is insoluble, it exhibited a somewhat greater stability, however, it appeared to be destroyed in an x-ray beam, and did not survive solution in methylene chloride over a 2 - 3 hour period at ambient temperature. Heating to approximately 45° brought about immediate decomposition to the (pyrolysis) products described. The boron nmr spectrum of the adduct purified in the above manner did not appear to differ from the spectrum of the nonreprecipitated product (Figure X). The mass spectrum of the purified adduct (Figure XI, Table IV) gave mass numbers
which were assignable to various fragments of the species $\text{CH}_3\text{B}_5\text{H}_8(\text{P} (\text{CH}_3)_3)_2$ such as $\text{P}(\text{CH}_3)_3^+$ (64 percent), $\text{CH}_3\text{B}_5\text{H}_8^+$ (40 percent) and smaller borane and methylated phosphorus units. Of structural interest was the appearance, at low intensity (0.04 percent), of a mass number consistent with the ion $(\text{CH}_3)_3\text{PBH}_2\text{BHP}(\text{CH}_3)_3^+$, indicating that the trimethylphosphine may be on neighboring borons. A mass number for the ion $(\text{CH}_3)_3\text{PBHBC} \text{CH}_3\text{P}(\text{CH}_3)_3^+$ was not observed, suggesting that neither trimethylphosphine is attached to the boron containing the methyl group. Supporting this contention was the presence of $m/e = 89$ (1.4 percent), from the ion $(\text{CH}_3)_3\text{PBH}_2^+$, while no fragment was observed related to a $(\text{CH}_3)_3\text{PBH}_2\text{CH}_3$ parent.

**Reaction at -78°.** When trimethylphosphine was reacted in hydrocarbon solvents from 4 to 8 days at -78°, a white insoluble residue, nonvolatile at that temperature, was isolated which dissolved readily in toluene or methylene chloride. The $\text{B}^{11}$ nmr spectrum at low temperature (-65°), however, revealed the presence of unreacted 1-methylpentaborane as the only observable component. In the toluene solution, a reaction was observed as the temperature rose above -50° which produced a product exhibiting signals identical to those
Figure 9
Infrared Spectrum of $2\text{-CH}_3\text{B}_5\text{H}_9\text{(P(CH}_3)_3}_2$
-20° C
Reprecipitated from CH₂Cl₂
Mass Spectrum of $2\text{-CH}_3\text{B}_5\text{H}_8\{(\text{CH}_3)_3\text{C}\}_2$.
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obtained from the product of the reaction carried out initially at -45°, i.e., the diadduct. In methylene chloride, however, this reaction never occurred extensively, even when both starting materials were present. Data, such as nonvolatility, solubility of 1-methylpentaborane in hydracarbons at -78° or nonmelting of the residue at -50° (m.p. = -55° for 1-CH₃B₅H₈), indicated that the material is, in fact, an adduct incorporating trimethylphosphine and was not unreacted 1-methylpentaborane. Unreacted starting materials were usually recovered from the reaction medium, even after a month at -78°, but the mole ratio of P(CH₃)₃ to 1-CH₃B₅H₈ was never near a whole number, being between 1:1 and 2:1. However, if the temperature was gradually increased with continual volatile removal, the final product at the termination of this process indicated a stoichiometry of 2:1. Thus, when 1.93 mmoles of 1-methylpentaborane were reacted in propane at -78° for 32 days with 4.76 mmoles of trimethylphosphine, careful removal at -78° of unreacted materials left a residue having a mole ratio of 1.69:1.00, base to borane. When the product was subjected to a gradual increase in temperature to -23° over a period of several days, an additional 0.20 mmoles 1-CH₃B₅H₈ and 0.03 mmoles P(CH₃)₃ were obtained. The stoichiometric relationship of the product was then 1.91:1.00. The boron nmr spectrum of this compound, how-
ever, revealed it to be essentially the diadduct produced at \(-45^\circ\) with a small amount of unreacted 1-methylpentaborane still present. Another sample treated in a manner similar to that described above except for volatile removal at room temperature, yielded a white powdery solid which persisted unchanged for about 4 days and exhibited the infrared spectrum of the \(-45^\circ\) diadduct. No absorban-
cies attributable to unreacted 1-CH\(_3\)B\(_5\)H\(_8\) or P(CH\(_3\))\(_3\) could be discerned. The eventual ambient temperature decomposition proceeded as previously described.

**Reaction at \(-45^\circ\) and \(-78^\circ\).** Consistent data were obtained when a combination of the temperatures \(-45^\circ\) and \(-78^\circ\) was employed. When 1.27 mmoles of 1-methylpentaborane were allowed to interact with 2.58 mmoles of trimethylphosphine alternately at \(-45^\circ\) during the day and \(-78^\circ\) overnight, 0.10 mmole 1-CH\(_3\)B\(_5\)H\(_8\) and 0.21 mmole (P(CH\(_3\))\(_3\)) were recovered after a total reaction time of 20 hours at the higher temperature and 58 hours at the lower temperature. The mole ratio was 2.02:1.00, base to borane. The \(^{11}\)B nmr spectra revealed the presence of the higher temperature diadduct and unreacted 1-methylpentaborane in an approximate ratio of 10:1 (from relative peak areas of signals attributed to single borons).
This data, plus that obtained from the experiments previously discussed, then, provided a consistent pattern which indicated that a nondissociable diadduct was formed between trimethylphosphine and 1-methylpentaborane when they were reacted at -45°, and that the B₅ framework was probably still intact. Further, if the reaction was carried out at -78°, an adduct was formed that also apparently has a 2:1 stoichiometry, but dissociated in solution into the original reactants. This behavior suggests that the latter compound does not differ significantly in structure from 1-methylpentaborane itself, whereas the structure of the former product may possess important differences. Also, a distinct mechanistic relationship evidently exists between the two forms of the diadduct, since the low temperature product has been observed to convert to the high temperature product on warming under carefully controlled conditions. When P(CH₃)₃ was allowed to react with 1-CH₃B₅H₈ at -45° and -78° the experimental result was a mixture of the two adducts, the relative amounts of each suggesting that the low temperature adduct (dissociating) was formed at both temperatures, but rearranged only at -45°, and that the time of 20 hours was insufficient for completion of the rearrangement process. Therefore, to substantiate this and rule out the possibility that an unrelated compound was formed at -78°,
0.647 mmole of $\text{1-CH}_3\text{B}_5\text{H}_8$ was reacted in propane with 2.12 mmoles of $\text{P(CH}_3\text{)}_3$ at $-45^\circ$ for just 20 hours. This was the length of time the previously described reaction, which utilized two temperatures, was maintained at $-45^\circ$. After the removal of unreacted trimethylphosphine (0.74 mmole) a mole ratio of $\text{P(CH}_3\text{)}_3$ to $\text{1-CH}_3\text{B}_5\text{H}_8$ in the residue was 2.13:1.00. The $\text{B}^{11}$ nmr spectrum at $-20^\circ$ revealed the presence of the nondissociating adduct plus unreacted $\text{1-CH}_3\text{B}_5\text{H}_8$, the latter indicating that the loosely coordinated adduct was one of the reaction components. From comparison of single boron peak intensities, the amount of $\text{1-methylpentaborane}$ relative to the nondissociating adduct was found to be practically identical to that observed in the aforementioned reaction which was maintained part of the time at $-78^\circ$. Since essentially all $\text{1-CH}_3\text{B}_5\text{H}_8$ had reacted in each case (none in fact was recovered in the presently described reaction), it seems apparent that at $-45^\circ$, 20 hours was sufficient time for complete coordination by the base, but, postulating a rearrangement of this initial adduct, not quite long enough to allow total rearrangement to the nondissociating product.

b. Trimethylphosphine and 2-methylpentaborane

Reaction at $-45^\circ$. For a total of 57-1/2 hours at $-45^\circ$ 1.41 mmoles of 2-methylpentaborane were
reacted with 3.22 mmoles of trimethylphosphine using propane as the solvent. Overnight the system was cooled to -196° rather than -78° to insure that only those products formed at -45° would be present. Removal of all volatiles left a white solid which displayed the identical boron-11 and proton nmr spectra observed from the product of the trimethylphosphine reaction with 1-methylpentaborane (Figure XII). The boron chemical shifts for the series of resolved peaks in the undecoupled spectrum at 20°C were 10.1, 26.3, 28.3 and 53 ppm with respect to BF$_3$Et$_2$O. When decoupled at the same temperature, the resonance at 18.4 ppm became visible. The proton nmr spectrum at -30° exhibited doublets at -1.31 and -0.98 ppm downfield from tetramethysilane with coupling constants of 11.4 and 10.5 Hz respectively. A peak was also present at +0.32 ppm (TMS) with about the same intensity as the resonance observed at 0.36 ppm in the 1-CH$_3$B$_5$H$_8$-P(CH$_3$)$_3$ adduct spectrum. From a comparison of the nmr data of the trimethylphosphine adducts of 1- and 2-methylpentaborane, then, (Table V), it is apparent that the same product was formed in each case.

Reaction at -78°. When 0.53 mmole of 2-methylpentaborane was reacted with 1.06 mmoles of trimethylphosphine at -78° in pentane for 10 days, a white nonvolatile residue was formed that yielded only unreacted
Figure 12
Boron-11 NMR Spectrum of \(2\text{-CH}_3\text{B}_5\text{H}_8\text{(P(CH}_3\text{)}_3\text{)}_2\)
Derived from \(2\text{-CH}_3\text{B}_5\text{H}_8\)
### TABLE 5
BORON-11 AND PROTON CHEMICAL SHIFTS COUPLING CONSTANTS AND ASSIGNMENTS FOR 2-CH$_3$B$_5$H$_8$(P(CH$_3$)$_3$)$_2$

<table>
<thead>
<tr>
<th>Boron</th>
<th>Chemical Shift (referenced to BF$_3$·Et$_2$O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(1)</td>
<td>53.0 ppm</td>
</tr>
<tr>
<td>B(2)</td>
<td>10.1 (J = 90Hz)</td>
</tr>
<tr>
<td>B(3), B(5)</td>
<td>26.3, 28.3</td>
</tr>
<tr>
<td>B(4)</td>
<td>18.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Proton</th>
<th>Chemical Shift (referenced to tetramethylsilane)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apex (trimethylphosphine hydrogens)</td>
<td>-0.97 ppm J = 10Hz</td>
</tr>
<tr>
<td>Base (trimethylphosphine hydrogens)</td>
<td>-1.31 ppm J = 11Hz</td>
</tr>
<tr>
<td>Bridge</td>
<td>+0.36 ppm</td>
</tr>
</tbody>
</table>

![Molecular Structure Diagram]
2-CH₃B₅H₁₁ when dissolved in methylene chloride. The nmr spectra which disclosed this showed the lack of reaction from -60° to +25°, a phenomenon attributed to the reaction inhibiting effect of the methylene chloride as was observed with 1-methylpentaborane. No attempt was made to recover the volatiles because of the difficulty in separating the reactants from the solvent pentane.

In another experiment, 0.55 mmole of 2-CH₃B₅H₁₁ was allowed to react with 1.77 mmoles of P(CH₃)₃ in 5 ml of propane for 7 days at -78°. The gradual day by day increase in the quantity of white solid product was sufficiently slower than the reaction of P(CH₃)₃ with 1-CH₃B₅H₁₁ at the same temperature that a qualitative comparison of the relative reaction rates at -78° could be made, to the effect that the latter borane reacted more rapidly. When volatile material was removed at -78° and fractionated through -107° and -140°, about 0.01 mmole of unreacted 2-CH₃B₅H₁₁ and 1.33 mmoles of P(CH₃)₃ were recovered, yielding a mole ratio of base to borane in the residue of 0.81. It should be indicated that volatile components were still being collected after an extensive pumping through a -196°C trap, though at a much slower rate than has been observed for either of the free starting materials, when the process
was terminated to prepare an nmr sample. Such behavior is consistent with either dissociation of the adduct under vacuum conditions or, which is much more likely, no dissociation occurred except in a solvent, and the presence of unreacted starting materials was explained by an incompleteness of the reaction. That the latter is probably true was demonstrated by the fact that volatile material removed from the dissociable adduct, including up to $-45^\circ$, primarily consisted of 2-methylpentaborane with little or no trimethylphosphine being observed. Dissociation should produce twice the molar amount of trimethylphosphine as 2-methylpentaborane if a 2:1 adduct was formed at $-78^\circ$ by the experiment, a result that is in fact shown to be the case discussed in the following section.

The boron-11 nmr spectrum of the white residue having a mole ratio of 0.81:1.00 in CH$_2$Cl$_2$ obtained at $-30^\circ$ exhibited only 2-methylpentaborane, with resonances attributable to the rearranged diadduct being just barely perceptable. That an adduct was initially formed was demonstrated by the presence of nonvolatile trimethylphosphine in the reaction system, plus the fact that the white solid, which did not melt at $-50^\circ$ was not insoluble precipitated 2-methylpentaborane, whose melting point is $-55^\circ$. 
Reaction at -45° and -78°. Alternately

1.00 mmole of \(2-\text{CH}_3\text{B}_5\text{H}_8\) was reacted with 1.79 mmoles of \(\text{P(CH}_3)_3\) at -45° and -78° in the manner described for \(1-\text{CH}_3\text{B}_5\text{H}_8\). The reaction system was at -45° for 24 hours and -78° for 73 hours. After this time, 0.10 mmole of \(\text{P(CH}_3)_3\) and 0.12 mmole of \(2-\text{CH}_3\text{B}_5\text{H}_8\) were recovered unreacted, the materials being removed from the non-volatile residue at temperatures no higher than -45° and separated from the propane solvent and each other by fractionation through -107°, -140° and -196°C. The white product, which at -45° evolved no volatiles in addition to what has been described, exhibited a mole ratio of 1.92:1.00. It dissolved readily in toluene and produced a \(\text{B}^{11}\) nmr spectrum at -55° indicative of a mixture of the nondissociating diadduct and unreacted 2-methylpentaborane. The high field doublet of \(2-\text{CH}_3\text{B}_5\text{H}_8\) was well resolved and did not lose its symmetry until the temperature was increased to -45°, indicating the low relative intensity at -55° of the high field signal of the rearranged diadduct (and thus its relatively low amounts), and the advent of a reaction at -45°. The presence of the nondissociating adduct was verified by the resonances at about 28 ppm which were visible at -55° and which grew steadily in prominence as the sample was warmed (Figure XIII). Since the dissociating adduct had produced the initial starting materials in an apparently 2:1 ratio upon dissolving, it was
Figure 13

$P(CH_3)_3 + 2-CH_3B_5H_8$ in Toluene
interesting to observe that unreacted 2-methylpentaborane was always visible, even to the point of decomposition at room temperature. This is explainable on the basis that the trimethylphosphine which was coordinating the 2-methylpentaborane was also attacking this same diadduct at a greater rate as the temperature increased. At ambient temperature, the P(CH₃)₃ would have been depleted before all the 2-CH₃B₅H₈ could be coordinated, because of this competing reaction.

Since the stoichiometry of the product mixture was 2:1, with the minor component of the mixture being the nondissociating diadduct, it seems apparent that the dissociating adduct also has a 2:1 ratio of base to borane. As has been mentioned, the B¹¹ nmr spectra of the mixture showed a greater amount of 2-CH₃B₅H₈ (that is, dissociable adduct) than of the nondissociating adduct after the reactants were stirred a day at -45° and 3 days at -78°. In another experiment where P(CH₃)₃ and 2-CH₃B₅H₈ were reacted on an approximately equimolar basis for twice the above time at each temperature (44 hours at -45° and 120 hours at -78°), a mixture was again observed in the nmr spectra, but the relative quantity of the components was reversed, the nondissociated diadduct predominating over 2-methylpentaborane by almost 4 to 1. Presumably the increased length of time at the higher
temperature allowed a greater rate of formation and rearrangement of the dissociable adduct as well as rearrangement of some of this product that had been formed at -78°. The resulting mixture was thus composed of a greater relative quantity of rearranged -- that is, nondissociating--diadduct than was observed in the system which reacted for half the time.

Two interesting comparisons may be made between the mixed temperature reactions of 1- and 2-methylpentaborane which reflect the difference in the chemistry of the two isomers that has been reported in past investigations. Thus, it may first be observed that the reaction times at mixed temperatures of the two systems, though not identical, were similar, 2-CH$_3$B$_5$H$_8$ reacting 4 hours longer at -45° and 5 hours longer at -78° than 1-CH$_3$B$_5$H$_8$ out of a total reaction time of 4 days. Also, the extent of reaction was similar based upon the percent of methylpentaborane reacted to that initially used, calculated to be 92 percent for the 1-CH$_3$B$_5$H$_8$ system and 88 percent for 2-CH$_3$B$_5$H$_8$. Therefore, if the reaction of the isomers occurred to approximately the same extent and in about the same length of time, the reaction rates are probably not too dissimilar, though 1-CH$_3$B$_5$H$_8$ did appear to react somewhat faster. The second observation arises from the comparison of the amount of nondissociating diadduct to unreacted methylpentaborane from the
B^{11} nmr spectra of each reaction medium. The quantity of unreacted 2-CH$_3$B$_5$H$_8$ (and therefore, the nonrearranged dissociable diadduct) was seen to be in some excess to the rearranged nondissociable diadduct, while the reverse situation was true for 1-CH$_3$B$_5$H$_8$, the amount of nondissociable diadduct appearing in approximately a 10:1 ratio to unreacted borane. The implications of these observations will be discussed in the conclusion.

c. Trimethylphosphine and pentaborane(9) at 78°

Pentaborane(9) reacts at room temperature in hydrocarbon solvents with trimethylphosphine to form a stable 2:1 adduct of base to borane (20). Since 1- and 2-methylpentaborane appear to form loosely coordinated adducts at low temperatures, the possibility was considered that pentaborane(9) may behave in a similar manner. To test this hypothesis, 1.38 mmoles of B$_5$H$_9$ were reacted at -78° in propane solvent with 3.39 mmoles of P(CH$_3$)$_3$ for about 8 days. Removal of volatiles at the termination of the reaction produced a residue which was partly white and partly glassy in appearance. After pumping the residue, always maintained at -78°, through a U-trap cooled to -196° for about 2 days (an operation which yielded an insignificant amount of material), it was dissolves in CH$_2$Cl$_2$. The boron-11 nmr spectrum revealed a considerable
amount of unreacted $B_5H_9$ in addition to the diadduct which was the major component (Figure XIV) confirming that pentaborane(9) also forms a disassociable adduct at low temperature. Unreacted $B_5H_9$ was separated from the volatile materials removed from the reaction medium in a -112° trap while the unreacted $P(CH_3)_3$ was measured as $(CH_3)_3PBCl_3$ by weight. The quantity of pentaborane(9) recovered was 0.07 mmole and of trimethylphosphine 0.58 mmole leaving a mole ratio of 2.15:1.00, base to borane, in the residue. The dissociating adduct, therefore, apparently also has a 2:1 stoichiometry.

An interesting aspect of the results of this experiment is that any nondissociating adduct was formed at all. In -78° reactions of one week duration for both 1- and 2-methylpentaborane, the amount of rearranged product was negligible, indicating that if rearrangement of the initial dissociating adduct was responsible for the formation of the higher temperature one, such a rearrangement could occur at -78° in the pentaborane(9) case but not with 1- or 2-methylpentaborane.

d. Decomposition products of $CH_3B_5H_8(P(CH_3)_3)_2$

When the rearranged nondissociating diadduct obtained from the reaction of trimethylphosphine with 1- or 2-methylpentaborane was allowed to warm to room
Figure 14

Boron-11 NMR Spectrum of Residue Obtained from Reaction of P(CH₃) with B₅H₉ at -78°
temperature in solution or as an impure solid it decomposed within an hour or two to yield trimethylphosphineborane \((\text{CH}_3)_3\text{PBH}_3\), trimethylphosphinemethylborane \((\text{CH}_3)_3\text{PBH}_2\text{CH}_3\) and nonvolatile polymeric material of unknown composition. \((\text{CH}_3)_3\text{PBH}_3\) was identified by B nmr (37) and x-ray powder pattern. The new compound, \((\text{CH}_3)_3\text{PBH}_2\text{CH}_3\), was characterized by B\(^{11}\) nmr spectra (Figure XV), hydrogen analysis, and infrared spectra. Boron nmr spectra showed the triplet of doublets expected for a boron coupled to two hydrogen atoms and a phosphorus atom experiencing spin-spin interactions from each. The relative peak areas were calculated to be 1.00:1.97:1.00 also in keeping with the structure presented as a derivative of \((\text{CH}_3)_3\text{PBH}_3\).

Hydrochloric acid hydrolysis of the compound yielded 2.05 moles of hydrogen per mole of sample compared to 2.00 moles as the calculated value. The boron-carbon bond was not broken during this treatment. The infrared spectrum (Figure XVI) obtained neat between potassium bromide plates exhibited the following peaks:
2980(w), 2920(m), 2880(w), 2840(w), 2375(sh), 2310(s), 2260(m), 1425(m), 1385(w), 1315(w), 1295(s), 1145(m), 1085(m), 1075(sh), 1035(w), 955(vs), 890(w), 850(w), 790(w), 760(m), 710(w), 695(w), 570(w), 535(w).
\(s=\text{strong}, \ m=\text{medium}, w=\text{weak}, \ sh=\text{shoulder}, \ v=\text{very}\)
Figure 15

Boron-11 NMR Spectrum of \((\text{CH}_3)_3\text{PBH}_2\text{CH}_3\)
Figure 16

Infrared Spectrum of \((\text{CH}_3)_3\text{PBH}_2\text{CH}_3\)
Trimethylphosphinemethylborane is a colorless, mobile, air sensitive liquid which transfers satisfactorily under vacuum line conditions. It may be roughly separated from trimethylphosphineborane by fractionation through a U-trap maintained at -50°, the more volatile methylated phosphineborane slowly passing this temperature, while \((CH_3)_3PBH_3\) is essentially retained. Several more rapid fractionations through -23° then purify the material. The ratio of \((CH_3)_3PBH_3\) to \((CH_3)_3PBH_2CH_3\) most commonly observed from the decomposition of the trimethylphosphine addition compound was 1.14 for a degradation at room temperature and 1.18 from decomposition carried out at 115°C. The relative quantity of these compounds was obtained by allowing the pyrolysis reaction to reach completion (a process which was allowed several hours), then a quantitative collection of the materials was accomplished by condensing them into a U-trap cooled to -196° and open to the pump. A small amount of methylene chloride, in which both components are extremely soluble, was condensed into the trap and the solution, after mixing well, was poured into an attached 5 mm nmr tube side arm. From the boron nmr spectrum, the relative amounts of each compound were obtained by integrating the outside nonoverlapping signals and calculating the total area of the resonance attributed to each component. Since it was observed
that \((\text{CH}_3)_3\text{PBH}_3\) was more susceptible to saturation effects at high power than was \((\text{CH}_3)_3\text{PBH}_2\text{CH}_3\) (a factor consistent with the higher symmetry of the \(\text{BH}_3\) unit compared to \(\text{BH}_2\text{CH}_3\) (9)), the ratio may in fact be somewhat greater than the values found.

2. Reactions with trimethylamine

a. Trimethylamine and 1-methylpentaborane

In 5-6 ml of dry pentane, 3.17 mmoles of 1-methylpentaborane were reacted several days at -78° with 7.24 mmoles of trimethylamine. When the volatiles were removed at -78°, the excess \(N(\text{CH}_3)_3\) was separated from the solvent by fractionation through a -130° U-trap, a temperature allowing only \(N(\text{CH}_3)_3\) to pass. From this process, 0.40 mmole was obtained and no \(1-\text{CH}_3\text{B}_5\text{H}_8\). The mole ratio was 2.16:1.00. The boron nmr spectra obtained at -40° or lower showed a broad resonance with three peaks slightly resolved having chemical shift values of -0.2, 8.6 and 19.3 ppm with respect to \(\text{BF}_3\cdot\text{Et}_2\text{O}\) as a reference (Figure XVII). A high field doublet with \(\delta = 5.4\) ppm \(J_{\text{BH}} = 85\) cps was the only other signal present in the spectrum. The relative intensities of low to high field resonances was near 4 to 1 indicating that the \(\text{B}_5\) framework was still present. The extreme instability of the compound in solution and the low
Boron-11 NMR Spectrum of the Diadduct of Trimethylamine and 1-Methylpentaborane

Figure 17
temperature broadening effects on the signals made obtaining good spectra difficult and may account for the small deviations of the peak area ratios from the 4 to 1 expected for the simple diadduct. The coupling of the 54 ppm resonance was not visible below -40° and when the sample was warmed to this temperature, the initial stages of decomposition were observed. Further warming brought about radical changes in the appearance of the lower field signals, with the doublet at 54 ppm diminishing in intensity. Between 0° and room temperature, the 54 ppm resonance vanishes and new signals appear, a singlet at -28 ppm, a doublet at 41 ppm (J = 140 cps) and the quartet due to trimethylamine-borane at 8.1 ppm (Figure XVIII). Prior to the appearance of these resonances, another set is observed at -3.9, 10.2 and 20.1 ppm which evidently result from the formation of an unstable intermediate preceding the pyrolysis products formed at higher temperatures. The advent and disappearance of the intermediate species occurs between -45° and 0° C accompanied by the gradual decrease of the initial diadduct and formation of (CH₃)₃NBH₃. Warming beyond 0° brings about a final reaction which produces a measurable but small amount (about 5 - 10 percent in terms of original reactants) of 2-CH₃B₅H₈. Most of the boron and about half of the
Boron-11 NMR Spectrum of the Decomposition Products of the Trimethylamine/1-Methylpentaborane Diadduct

Figure 18
trimethylamine is then evidently tied up in the viscous, nonvolatile, polymeric liquid of unknown composition which usually accompanies the decomposition of base-pentaborane adducts.

The proton spectrum of the diadduct obtained at -70° on the HA-100 instrument (Figure XIX) displayed a group of overlapping peaks dominated by a sharp intense resonance at -2.47 ppm (with respect to TMS). Because of its sharpness, this signal is thought to be caused by equivalent methyl protons on the ligands. Consistent with this view that the trimethylamine molecules are probably in magnetically equivalent environments is the strong indication from the "B nmr spectrum that one donor is not in the substantially different environment of the apical or unique boron as is apparently the case with the trimethylphosphine analog. The doublet coupling and high field signal observed in the boron-11 spectrum is evidence of this. The less intense sharp signal at -2.52 ppm may be the protons on the methyl group attached to a boron atom. The high field resonance at -0.51 ppm is attributed to bridging hydrogens.

In an attempt to isolate and identify the components responsible for the nmr signals at 41 and -28 ppm, a sample of the diadduct was prepared and allowed to
Figure 19
Proton NMR Spectrum of the Diadduct of Trimethylamine and 1-methylpentaborane
warm to -15° with continuous pumping through a -196° trap. The extremely slow collection of volatile material prompted further warming to 0°. At this temperature, the volatile evolution rate increased significantly. The residue at 0° was unchanged from its low temperature (-78°) appearance - a dry white solid. The material collected at -196°, which was liquid somewhat below room temperature when allowed to warm, reacted vigorously to produce a white solid that soon became pasty and after about an hour, converted to a yellow oil. Removal of more volatile material from the original white residue at 0° and finally, at room temperature eventually left only a small amount of yellow resinous solid in the initial reaction tube. The volatiles collected were fractionated through -126° and identified by their infrared spectra as trimethylamine and 2-methylpentaborane. The yield of the latter compound was estimated in excess of 90 percent on the basis of the 1-methylpentaborane starting material. No other components were observed.

b. Trimethylamine and 2-methylpentaborane

For 5 days, 1.22 mmoles of trimethylamine and 0.61 mmole of 2-methylpentaborane were stirred at -78° in pentane. Fractionation of volatile material at the end of that time produced 0.01 mmole 2-methylpentaborane
and no trimethylamine yielding a mole ratio of 2.03:1.00 base to borane. The solution of the resulting white residue in methylene chloride gave a boron nmr (Figure XX) spectrum similar to those described having a lower field group of signals of intensity 4 and a higher field resonance of intensity 1. Temperature studies of the spectra were carried out between -75° C and room temperature and yielded a considerable amount of interesting information. At -75° the lower field peak grouping was drastically broadened while the higher field signal was sharpened and of accentuated intensity. The sharpening of the high field resonance may indicate decoupling between the unique boron and the other borons (9, 38). When the temperature is raised to -65°, the broad downfield resonance was somewhat resolved with chemical shift values calculated at 1.5 and 12.9 ppm. The upfield signal is located at 46.7 ppm appearing as a singlet at temperatures below -50°, but becoming a doublet ($J = 75$ cps) at higher temperatures. Other important changes in the spectra were observed above -50° indicating an alteration of the species initially present as the temperature increased (Figure XXI). The most dramatic of these changes is the decrease in the 46.7 ppm resonance as the 54 ppm doublet of the 1-methylpentaborane adduct and the signals at -28 and 40.5 ppm, due to the
Boron-11 NMR Spectrum of the Diadduct of Trimethylamine and 1-MethyIpentaborane
Figure 21
Decomposition of $N(CH_3)_2-CH_3B_5H_8$ Diadduct
decomposition products previously observed in the 1-CH$_3$B$_5$H$_8$ system, grow in. The doublet at 54 ppm is first observed at about -50° while the doublet at 40.5 ppm appears at -30°, a temperature at which all three overlapping high field resonances may be observed simultaneously. The signal at -28 ppm was unambiguously present at -40° and became more intense as the temperature rose. At -10° C the spectrum of the 2-CH$_3$B$_5$H$_8$ diadduct is very similar to that of the 1-CH$_3$B$_5$H$_8$ diadduct at comparable temperatures, with the signals of the same "triplet-like" structure of the latter observed at -2, +8.5 ((CH$_3$)$_3$NBH$_3$) and 19.4 ppm. Further warming to room temperature leads to the final pyrolysis product, (CH$_3$)$_3$NBH$_3$ and the recovery of about 5 percent 2-CH$_3$B$_5$H$_8$. Thus, given the pronounced instability of the initial diadduct, detailed investigation is limited to nmr spectra obtained at carefully controlled temperatures. This experimentation has indicated that, unlike the results with P(CH$_3$)$_3$, unique compounds were obtained when 1- and 2-CH$_3$B$_5$H$_8$ were reacted with trimethylamine. Also the 2-methylpentaborane diadduct displayed the unexpected property of rearranging to the diadduct of 1-methylpentaborane at approximately -50° C. However, this rearrangement was apparently accompanied by the decomposition of the 1-CH$_3$B$_5$H$_8$ adduct as it was formed,
with further heating producing the same pyrolytic inter-
mediate material and final decomposition products
observed for the latter species, \((\text{CH}_3)_3\text{NBH}_3\) and
2-\(\text{CH}_3\text{B}_5\text{H}_8\). It is important to note that during the
decomposition of the 1- or 2-methylpentaborane systems
no 2-methylpentaborane was actually present. However,
when it did appear in the nmr spectra, the resonances
at -28 and +40.5 ppm disappeared, strongly suggesting
that the compound or compounds producing these signals
were precursors to the 2-\(\text{CH}_3\text{B}_5\text{H}_8\) eventually recovered.
This supposition is supported by the fact that though
sufficient \(\text{N(CH}_3)_3\) was present to complex any of the
initial 1- or 2-\(\text{CH}_3\text{B}_5\text{H}_8\), none was found after the pyrolysis
proceed was completed. Since the adducts are not known to
dissociate at low temperatures, the presence of uncomplexed
2-\(\text{CH}_3\text{B}_5\text{H}_8\) may be explained by assuming it to be formed.
after all trimethylamine had been chemically combined
and thus removed from the reaction system. Such an
occurrence would require the 2-methylpentaborane
observed at room temperature to arise from the interaction
of the noncoordinated boron hydride and methylated boron
hydride fragments resulting from the breakup of the
1- or 2-\(\text{CH}_3\text{B}_5\text{H}_8\) diadduct. These would be the species
evidently responsible for the B\(^{11}\) nmr signals appearing
at -28 and +40.5 ppm. Additional evidence that the
2-\(\text{CH}_3\text{B}_5\text{H}_8\) obtained after pyrolysis was not due to recovery
of the initial reactant was provided by Onak (39) from experiments involving B\textsuperscript{10} enriched diborane addition to the 2:1 adduct of trimethylamine and 1-methylpentaborane. 2-methylpentaborane was liberated exhibiting B\textsuperscript{10} enrichment in all positions except B(2) (methylated boron), with the B(3) (5) and B (1) positions containing more B\textsuperscript{10} than the B(4) position diagonally across from the methyl containing boron. If one may suppose that no appreciable exchange occurs between methylated pentaboranes and diborane, as is the case with pentaborane itself (40), the appearance of B\textsuperscript{10} enriched 2-methylpentaborane necessitates a building up of this compound from B\textsuperscript{10} \textsubscript{2}H\textsubscript{6} and an uncomplexed methylated species produced from the trimethylamine diadduct. However, since diborane was not added to the systems investigated in this thesis, the identity of the intermediates involved must remain an open question. As stated in the previous section, the attempt to isolate these components led only to the dissociation of the adduct.

Finally, it may be mentioned that when all the trimethylamineborane resulting from decomposition of a 2-methylpentaborane adduct is separated and weighed, somewhat less than 1 mole was observed to be formed per mole of adduct. Equations representing the reactants, diadduct and final decomposition products may be written:
The ratio of trimethylamineborane to the 2-methylpentaborane reactant is 0.78, indicating that at least half the N(CH₃)₃ and about three-fourths of the 2-CH₃B₅H₈ went into the formation of the polymer. Such a reaction might not be expected to be stoichiometric in detail, but may grossly indicate that only one of the trimethylamine units can escape as the borane adduct under the conditions of decomposition at room temperature. However, on the basis of work reported by Burg (41) where two (CH₃)₃NBH₃ per B₅H₉ were produced when B₅H₉(N(CH₃)₃)₂ was heated to 100° with excess N(CH₃)₃, further degradation of the polymer could be expected with similar treatment.

All boron-11 and proton nmr data are listed in Table VI.
<table>
<thead>
<tr>
<th>Adducts of 1-methylpentaborane</th>
<th>Boron chemical shift (ppm with respect to BF₃·Et₂O)</th>
<th>J(Hz)</th>
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<th>Proton chemical shift (ppm with respect to tetramethylsilane)</th>
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<table>
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<tr>
<th>Adduct of 2-methylpentaborane</th>
<th>Boron chemical shift (ppm with respect to BF₃·Et₂O)</th>
<th>J(Hz)</th>
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CONCLUSION

A. Pentaborane(9) reactions with alkali metals

The study of the reactions of pentaborane(9) with the alkali metals potassium and lithium have provided interesting results, however, the hopes of placing two electrons into the system to form the $B_5H_9^-$ ion, as outlined in the statement of the problem were not realized. The reactions instead proved to be more complex, with a $B_9$ framework being formed and, in the case of one lithium reaction, a deprotonation of pentaborane(9) taking place. All reactions were performed in ether solvents or the more basic liquid ammonia at various reduced temperatures.

The discussion of the chemistry of pentaborane(9) and potassium may be started by noting that the major product in tetrahydrofuran and dimethyl ether was the ion $B_9H_{14}^-$. This ion was identified as a reaction product in liquid ammonia also, but was accompanied by a significant amount of fragmentation of the $B_5$ framework
to produce large quantities of $\text{B}_3\text{H}_8^-$. Diethyl ether was apparently insufficiently basic to support a reaction. Since the borohydride ion, $\text{BH}_4^-$, was also present in all the reaction residues, the overall reaction may be described by the following equation:

$$2\text{B}_5\text{H}_9 + 2\text{K} \rightarrow \text{KB}_9\text{H}_{14} + \text{KBH}_4$$

Hydrogen was evolved in every case, but because approximately 5 pentaborane molecules were required to produce about one molecule of hydrogen (a ratio that was never observed to be reproducible), and the quantity of hydrogen evolved seemed to parallel the extent of decomposition in the ammonia reaction (exhibiting a ratio close to 2 to 1), it is thought to not be a necessary part of the process that led to the formation of $\text{B}_9\text{H}_{14}^-$. A trend was observed that appeared to be related to the temperature and basicity of the solvent. This was quantitatively measurable only when dimethyl ether was the solvent because of the practicality of recovering unreacted pentaborane(9) by fractionation. The ratio of pentaborane(9) to hydrogen decreased as the temperature increased, being 2.5 for a reaction carried out at $-36^\circ$ and 2.2 when the reaction temperature was $-31^\circ$. This increase in the relative amount of hydrogen produced per pentaborane(9) reactant with temperature is consistent with the view that hydrogen results from chemical
changes not associated with the formation of \( \text{B}_9\text{H}_{14}^- \). Additionally, one measurement of hydrogen observed from reaction in ammonia solvent at -78° resulted in the ratio \( \text{B}_5\text{H}_9/\text{H}_2 \) of about 2 or less. Thus, the relative amount of hydrogen produced appeared to increase with temperature and solvent basicity. In connection with these findings, it may also be pointed out that from inspection, the solvents may be placed in the following order with respect to the rate of hydrogen evolution:

\[ \text{THF} < (\text{CH}_3)_2\text{O} < < \text{NH}_3. \]

A parallel trend seemed to exist in the production of other components not simply related to the formation of \( \text{B}_9\text{H}_{14}^- \). Thus, in tetrahydrofuran, yellow solutions were observed when the reaction occurred above -40°, the color becoming more intense at higher temperatures. A similar coloration of the dimethyl ether solutions was observed in about the same temperature range. Small amounts of \( \text{KB}_3\text{H}_8 \) were identified from x-ray powder pattern in the residue resulting from reaction in dimethyl ether, but, because of its small quantity, the presence of this compound was not unambiguously ascertained in the boron-11 nmr spectrum. Since solvation of the products in the tetrahydrofuran systems precluded x-ray investigation and the boron-11 nmr spectrum was not sufficiently sensitive to demonstrate its existence in small amounts,
it can only be stated that $\text{KB}_3\text{H}_8$ formation occurred to no greater extent and possibly less in this solvent than in dimethyl ether. In ammonia however, boron-11 nmr and analyses indicated that $\text{KB}_3\text{H}_8$ was the major product even when the reaction was carried out at $-78^\circ$. These data suggest, then, that solvent basicity may be a factor in promoting reactions leading to fragmentation of frameworks of higher boron content with the amount of the ion $\text{B}_3\text{H}_8^-$ increasing with basicity.

As observed in the experimental section reactions in the ethers declined in rate noticeably over several hours and eventually came to an effective halt. Because metallic potassium and $\text{KBH}_4$ were the only components observed in the x-ray patterns of an insoluble purple solid produced in all reactions not taking place in ammonia and a thin coating of this solid seemed to be present on the surface of the unreacted potassium, the explanation for the slowing of the reaction appears to be the covering of the metal by a thin film of $\text{KBH}_4$. This seems plausible in view of the fact that a heterogeneous reaction occurring on the potassium surface which generated $\text{KBH}_4$ as a reaction product could allow some of this salt to remain in intimate contact with the metal and gradually form a layer of adsorbed material. Since
KBH$_4$ is essentially insoluble in THF and (CH$_3$)$_2$O, it could not be removed by solution into the solvent. On the basis of observation and analysis of unreacted potassium, this effect seemed to inhibit the reaction to a greater extent in tetrahydrofuran than in dimethyl ether. In the case of ammonia, however, the substantial solubility of all the components contributed to the swift reaction observed accompanied by no inhibiting effects.

Calculations were made from the analytical results of a reaction product in dimethyl ether which indicated that the ratio of potassium to pentaborane(9) consumed was 1.7. If the data were dependable, this would suggest that a simple one or two electron donation to the B$_5$H$_9$ system may not occur and that other intermediate species were undergoing reduction also. In view of the fundamental importance of the potassium-pentaborane(9) ratio in understanding the chemistry involved, this stoichiometry should be established beyond doubt by further experimentation. However, some conjecture is possible concerning the mechanism that might be in effect if the initial reduction is a two-electron process, but the overall stoichiometry of potassium to pentaborane(9) is 1:1. In this case, the high ratio of 1.7 would be attributed to the reduction of intermediates as well as
pentaborane(9) itself. Thus, 2 electrons may be donated to the $\text{B}_5\text{H}_9$ system forming a highly reactive species which immediately attacks an unreduced pentaborane(9) molecule.

If $\text{BH}_4^-$ were expelled, a complex between the unstable $\text{B}_5\text{H}_9^-$ and $\text{B}_4\text{H}_5^+$ could conceivably be formed which would undergo rearrangement to the more stable $\text{B}_9\text{H}_{14}^-$. The reactions below describe the processes:

$$2\text{K} + \text{B}_5\text{H}_9 \rightarrow 2\text{K}^+ + [\text{B}_5\text{H}_9^-]$$

$$[\text{B}_5\text{H}_9^-] + \text{B}_5\text{H}_9 \rightarrow [\text{H}_9\text{B}_5 \cdot \text{B}_4\text{H}_5^-] + \text{BH}_4^-$$

$$[\text{H}_9\text{B}_5 \cdot \text{B}_4\text{H}_5^-] \rightarrow \text{B}_9\text{H}_{14}^-$$

Since highly reactive species may be present, it would not be unexpected to have decomposition of some intermediate during the reaction. It is, therefore, possible that were the initial reduced product, $\text{B}_5\text{H}_9^-$, in fact formed, its stability would be considerably lessened in more basic solvents and it could fragment into $\text{B}_3\text{H}_8^-$ and perhaps polymeric material.

From the preliminary investigation of the reactions of pentaborane(9) with lithium metal, only the outlines of the chemistry of the systems involved have emerged. More detailed work is necessary before a complete understanding is realized.
The exact nature of the species formed when pentaborane(9) reacts with lithium at -78° in liquid ammonia is not clear. Stoichiometrically, it appears to be an ammonia complex of a reduction product with two lithiums for each pentaborane(9). The initial data suggests that at least three ammonias are coordinated to this system and are removed during a transformation that occurs at about -45° C. Because most boron hydride derivatives are colorless, the adduct is remarkable for its yellow-green appearance, and even more remarkable for its ability to undergo reversible color changes with temperature, becoming bluer as the temperature is lowered. Since the transformation of yellow to white at approximately -60° is irreversible, it is possible that a fundamental chemical change has occurred at that temperature. Another change seems to take place at -45°, as mentioned earlier, with the release of ammonia, but the boron-11 nmr spectrum of that material (Figure IV) suggests it may be a mixture of components. The doublet observed at 51.7 ppm (J = 98 cps), however, cannot be attributed to the species LiB₅H₈ because the coupling constant is too small (also the chemical shift is at a somewhat low field for LiB₅H₈) and the more intense low field doublet is missing. Because of the apparent insolubility of the yellow-green adduct in ammonia or tetrahydrofuran nmr data was unfortunately not available for this compound. Char-
acterization of the ammonia adduct will be difficult because of this fact and its pronounced instability.

The reaction of lithium and pentaborane(9) in dimethyl ether was much clearer than in ammonia. The major product identified was the salt LiB$_5$H$_8$, and though some ambiguity was present in the stoichiometry of metal and pentaborane(9), it did not appear to be a 2 to 1 relationship. No hydrogen was formed, the reaction seemed to go to completion, and, possibly related to this latter factor, no LiBH$_4$ was observed. However, an unidentified component was associated with elemental lithium in the black insoluble residue resulting from the reaction in a manner analogous to the association of KBH$_4$ and potassium.

The analysis of unreacted lithium was probably inaccurate because of interference from the above mentioned unidentified species. Hydrolysis of the boron-containing compound would have produced boric acid and the determination of unreacted lithium would have given low results, indicating that more unreacted lithium was present than was found in the analysis. The implication of these results are that the 9 mmoles calculated for the lithium that reacted would be high and that the ratio of lithium
to pentaborane(9) \((9/16 = 1.5)\) would approach 1:1 if the true amount were substituted in the calculation.

Since no hydrogen was evolved during the reaction, but a deprotonation was observed to take place, the strong implication follows that the reduced species behaved as a Bronsted base toward another species, which was evidently not reduced. The reacting materials which fit these specifications and are also consistent with an overall 1 to 1 relationship between lithium and pentaborane(9) are the ion, \(B_5H_9^-\) and neutral \(B_5H_9\). The reaction processes possibly involved are described in the following equations:

\[
2\text{Li} + B_5H_9 \rightarrow [B_5H_9^-] = 2\text{Li}^+ \\
[B_5H_9^-] + B_5H_9 \rightarrow B_5H_{10}^- + B_5H_8^- 
\]

The reduction process as symbolized by these reactions is analogous to the potassium case, but since a more highly reactive species appears to be present with potassium (as evidenced by the formation of a \(B_9\) framework from \(B_5\) frameworks), it may be that the lithium ion helps stabilize the \(B_5H_9^-\) ion to the extent that it only deprotonates pentaborane(9) rather than attacking its framework. That is, with \(\text{Li}^+\), \(B_5H_9^-\) behaves as
a Bronsted base by accepting a proton rather than displaying the behavior of a Lewis base by acting as an electron pair donor as is apparently the case in the presence of K⁺.

The ion \( \text{B}_5\text{H}_{10}^- \) has been hypothesized by Lipscomb (3) to have the following geometry as possibly the most stable of the various geometries that are predicted according to his topological theory (next section).

![](image)

Structure 3

It is possible then that this ion has been formed and adsorbed on the unreacted finely divided lithium metal to produce the observed black solid in a manner analogous to the KBH₄ associated with unreacted potassium. Consistent with the possibility of \( \text{B}_5\text{H}_{10}^- \) being formed in the reaction is the presence in the boron-11 nmr spectrum of small resonances at somewhat higher field than those
of B$_5$H$_8^-$ (Figure V), specifically at ca. 24 ppm and 60 ppm. The relative intensities are not measurable because of overlap, but if they have a 4:1 relationship this would be consistent with that expected for a species such as B$_5$H$_{10}^-$. The small amount of material observed in the boron-11 nmr spectrum would be in accordance with either a low solubility or an association with metallic lithium forming an insoluble solid. If the latter is the case, a small quantity of the salt could have possessed a kind of secondary association which allowed its solution in the dimethyl ether solvent.

B. Lewis base reactions with 1- and 2-methylpentaborane

1. Trimethylphosphine reactions

The experimental results from reacting the Lewis base trimethylphosphine with 1- and 2-methylpentaborane may be summarized briefly to provide a basis for a detailed discussion of the chemistry involved. Thus, it was found that both methyl-substituted pentaboranes reacted slowly at low temperature (-78°), the basally methylated isomer somewhat slower than the apically substituted isomer, to produce loosely coordinated adducts composed of two trimethylphosphines per methylpentaborane with no destruction of the B$_5$ framework.
If a higher reaction temperature was employed (-45°C) or the weakly coordinated adduct was maintained at a higher temperature, the 1- and 2-methylpentaborane systems produced an identical compound which did not dissociate in dichloromethane, and which displayed a boron-11 nmr spectrum indicative of a B₅ species containing a unique boron. Additionally, the proton nmr spectrum revealed the presence of what appeared to be two bridge hydrogens. This product seemed to be a rearranged isomer of the adduct produced at low temperature, and its formation through the rearrangement of an initial species appeared to take place at a much greater rate in the case of 1-methylpentaborane than 2-methylpentaborane. This behavior has experimental support in the difference of the relative amounts of rearranged adduct to unreacted methylpentaborane observed in the boron-11 nmr spectra. As may be recalled from the experimental section, more unreacted 2-methylpentaborane was present than rearranged adduct in the reaction residue while the opposite was the case for 1-methylpentaborane after about the same length of reaction times at -45° and -78° for both systems; that is, the quantity of rearranged isomer was in significant excess of unreacted 1-methylpentaborane. An additional observation was that the extent of total reaction, i.e., the extent to which the rearranged and non-rearranged alike were formed, was similar for the two systems on the basis of recovered starting materials,
1-methylpentaborane apparently having reacted to a somewhat greater degree than 2-methylpentaborane. These data appeared to reflect a slightly faster rate of initial coordination by the ligand for 1-methylpentaborane than 2-methylpentaborane, and a significantly greater rate of rearrangement for the 1-methyl isomer adduct. The slower coordination of 2-methylpentaborane would not be surprising if steric and possibly electronic opposition was offered by a basally bonded methyl group compared to the same site occupied by hydrogen. The rearrangement rate may also be expected to be more rapid for the dicoordinated 1-methyl adduct because of the apparently greater stability of the basally-substituted species compared to the apically substituted molecule. This relative stability has been described previously for substituted pentaboranes, but it is interesting to find that it may also be true for the diadducts, which are $\text{B}_{5}\text{H}_{11}$ analogs.

The results obtained from the two reactions of trimethylphosphine with 1-methylpentaborane, one at $-45^\circ$ for 20 hours and $-78^\circ$ for 68 hours and the other at only $-45^\circ$ for 20 hours may be compared to obtain further insight into the chemistry of this particular system. As has been observed earlier, coordination at $-78^\circ$ occurs slowly, but rearrangement takes place much
more slowly if at all at this temperature. This data plus unrearranged adduct observed at the conclusion of the two-temperature reaction indicated it was likely that the rearrangement process was the slower process in the formation of the nondissociable adduct. The appearance of unreacted 1-methylpentaborane after 20 hours at -45° in approximately the same relative amounts to the rearranged product as observed in the two-temperature reaction indicated that the initial coordination compound formed at high and low temperatures is probably the same in each case and that different species being formed at different temperatures may be ruled out.

Prior to beginning the discussion of possible structures and mechanisms that may be postulated to explain the chemistry of the trimethylphosphine adducts of 1- and 2-methylpentaborane, it is of interest and importance to present reasoning in support of the 2:1 stoichiometry of the low temperature adduct as previously suggested by the two-temperature reactions. The following section will deal with this question in the light of the data obtained from the -78° reaction of 1-methylpentaborane and in addition will discuss some general aspects of the nature and behavior of both methylated systems.
The results from the reaction of 1-methylpentaborane with trimethylphosphine for one month at -78° as described in the experimental section implied that the dissociating adduct formed at that temperature did not dissociate under a vacuum. This was indicated by the observation that no P(CH₃)₃ was collected after an extensive evacuation and recovery process. Only 1-methylpentaborane was removed from the system in any significant quantities even up to -23° as described in the experimental section. The most reasonable explanation for these data seems to be that unreacted 1-methylpentaborane adsorbed on the microcrystalline surfaces of the product and required a high vacuum and moderately high temperature to be removed. The increase in stability of the nondissociating product following the vigorous removal of all volatile material is consistent with this view. A second implication contained in the preceding findings seems to be that the dissociating adduct (capable of dissociating in a solvent, but not under vacuum conditions at any observable temperature) produced at -78° has a 2:1 stoichiometry of trimethylphosphine to 1-methylpentaborane. The reasoning follows from the fact that after volatile removal at -78° in one experiment, a mole ratio of 1.69 to 1.00 was obtained after more than 97 percent of the trimethylphosphine that was to be recovered had been collected. But when
the same system was slowly raised to -23° with pumping through a -196° trap, more 1-methylpentaborane was recovered and a stoichiometric relationship of 1.91 to 1.00 was calculated for the residue. The latter ratio could have resulted from the 1.69:1.00 stoichiometry if either trimethylphosphine had been added to the system or, as was observed, 1-methylpentaborane had been removed. This data suggested that all adducts present had a mole ratio of 2:1 base to borane, the 1.69:1.00 ratio being observed because of the adsorbed 1-methylpentaborane that had not then been removed. The large relative amount of rearranged product observed in the boron-11 nmr spectrum indicated that the majority of the initial adduct had undergone rearrangement. Since no discernable rearrangement had been observed after 8 days at -78° in another experiment, most of the rearranging process was thought to have occurred during warming.

In the case of 2-methylpentaborane, the stoichiometry of the residue formed after several days at -78° was also considerably less than 2:1. It is thought that this could reflect the association of noncoordinated 2-methylpentaborane with the low temperature adduct (the only species observed in the boron-11 nmr spectrum), and thus explain its slow removal, as was evidently occurring.
with 1-methylpentaborane. The experimental data, then, indicated that 0.44 mmole of trimethylphosphine and 0.54 mmole of 2-methylpentaborane remained in the reaction system at the time of termination of volatile removal. If the trimethylphosphine was coordinated in a 2:1 ratio with 2-methylpentaborane, as has been indicated by the two-temperature reactions, 0.54 - 0.22 = 0.33 mmole of unreacted 2-methylpentaborane was present and evidently associated in some way with the nonrearranged diadduct. This "associated" 2-methylpentaborane was evidently the source of that compound that was observed being slowly removed from the reaction medium.

The discussion of the nature of the species formed and their behavior might begin with the consideration of the structure of the low temperature diadducts. Since dissociation readily occurs, the geometry of the species, formed from both 1- and 2-methylpentaborane, probably does not deviate in a major way from the non-coordinated molecules. The question then arises as to which borons are attacked by the trimethylphosphine. One may expect coordination at the apical boron in either case to be unlikely for the following reasons: (1) calculations and experimental results imply the apical boron to be the most negative, therefore, the least likely to
undergo nucleophilic attack; (2) statistically, attack at a basal boron is more likely to occur than at the single apex; (3) coordination of a basal boron requires only the breaking of a bridge hydrogen thus freeing a boron orbital to receive the lone pair of the phosphine; coordination at the apex would appear to require an extensive rehybridization and atom shifting to accommodate the ligand, presumably a process of much higher energy; and (4) for \(1-\text{CH}_3\text{B}_8\text{H}_8\), the apical boron with its methyl group would be expected to be more sterically hindered than the basal borons. Attack by \(P(\text{CH}_3)_3\), then, would appear to take place on basal boron atoms forming a system isoelectronic with \(\text{B}_5\text{H}_{11}^-\). From mechanistic reasoning and \(\text{B}^{11}\text{nmr}\) interpretation to be considered shortly, two points of coordination may be tentatively assigned for each isomer in the equilibrium reactions on the following page.

As may be observed, the square pyramidal geometry of the original methylated pentaborane is essentially maintained after coordination by the trimethylphosphines with the only structural alteration being the conversion of two bridge hydrogens to terminal hydrogens, a process requiring minimal movement of atoms. Presumably, the capacity for reversibility depends only upon the reestablishment of the terminal hydrogens to their bridge positions as the trimethylphosphines disassociated.
Equation 1
Before discussing the possible structure of the nondissociating adduct (higher temperature product), it is necessary to consider the possibilities that are presumed to be available on the basis of the bonding and structure theory developed by William Lipscomb (3). The compounds formed by the coordination of two Lewis base molecules on the methylated pentaboranes may be viewed as species isoelectronic with the hypothetical anion \( B_5H_{11}^- \). The topological theory of Lipscomb then predicts four possible structures for this anion that could have reasonable stability. In the order of decreasing number of bridge hydrogens and increasing number of terminal hydrogens, the structures for the \( B_5H_{11}^- \) anion are on the following page. The numbers under the structures indicate, in order, the number of hydrogen bridges, the number of 3-center boron-boron bonds (central or open), the number of 2-center boron-boron bonds and the number of additional terminal hydrogens on borons already containing one terminal hydrogen. The diadduct, \( CH_3B_5H_8(P(CH_3)_3)_2 \), may be derived from any of these examples by substituting a methyl group and two trimethylphosphine molecules for the hydrogens in terminal (two center) positions. The step of choosing the most reasonable structure and eliminating the others would appear to hinge primarily on the presence and number of
Structure 4
bridge hydrogens as evidenced in the infrared and proton nmr spectra. Since the relative peak intensity of the resonance attributed to bridging hydrogens in the proton nmr spectrum was approximately 2, all structures except 2124, which has two hydrogen bridges, would therefore be rejected. Also, this structure is intuitively more pleasing since it deviates the least from the geometry of the original methylatedpentaboranes, and in fact, is the same type of structure postulated for the low temperature dissociating adduct.

If the structure with 2124 designation is chosen as the most likely candidate for bistrimethylphosphinemethylpentaborane, the problem then becomes one of finding the location of the methyl group and the trimethylphosphine ligands.

The methyl group is thought to be bonded to a basal boron for two reasons. First, apical to basal rearrangement of the alkyl group in apically substitutedpentaboranes in the presence of Lewis bases is a characteristic process. Since the same product is obtained when trimethylphosphine reacts with 1- or 2-methylpentaborane at -45°, basal to apical rearrangement must take place with 2-methylpentaborane if the methyl group is postulated to be on the apical boron in the diadduct. Examples of this reverse rearrangement for
alkyl groups have not been reported. The second reason for assigning the methyl group to a basal position is the presence in the boron-11 nmr spectrum of the rearranged diadduct of a resonance at 10 ppm, an unusually low field signal for a basal boron compared to the chemical shifts of 19.4 and 24.6 ppm observed for unsubstituted basal borons in the analogous $B_5H_9(P(CH_3)_3)_2$ (41). In the noncoordinated pentaborane systems, $CH_3$ invariably lowers the chemical shift of the basal borons to which it is attached by approximately 14 ppm (17). A lowering of the chemical shifts in the trimethylphosphine diadduct need not necessarily be by the same amount, but some field-lowering effect would be expected from a basally attached methyl. This lowering is in fact observed in the nmr spectrum of the adduct.

One trimethylphosphine ligand is probably located on the apical boron of the pyramid-shaped molecule and the other on the base. Evidence supporting this assignment comes primarily from the proton nmr spectrum of the adduct, clearly showing two strong doublets at -1.32 and -0.97 ppm (from TMS) attributable to the phosphorus-coupled methyl protons on the two nonequivalent ligands. The magnitude of the difference in these chemical shifts reflects a difference in the environments of the trimethylphosphines comparable to the difference observed
in the adduct, $B_5H_9(P(CH_3)_3)_2$ (20), where the doublets in the proton spectrum of this latter compound are -1.26 and -1.01 ppm (TMS). The position of one trimethylphosphine in $B_5H_9(P(CH_3)_3)_2$ as determined from proton nmr spectra, mass spectra (20) and preliminary x-ray structure data (41), appears to be the apical boron, the second trimethylphosphine being coordinated to a basal boron. Given the similarity of the proton nmr spectra, the methylated and nonmethylated species, then, it appears reasonable to locate one trimethylphosphine on the apical boron of $CH_3B_5H_8(P(CH_3)_3)_2$. It should be pointed out that the great similarity of the infrared spectra of $B_5H_9(P(CH_3)_3)_2$ and $CH_3B_5H_8(P(CH_3)_3)_2$ puts on a more concrete footing the comparison of various data having structural inferences.

Mass spectral evidence is also available which helps substantiate the apical assignment. A low intensity (0.04 percent) mass number was observed which may be associated with the ion, $(CH_3)_3PBH_2BHP(CH_3)_3^+$, a fragment not likely to be produced unless the borons containing the trimethylphosphines have neighboring positions. However, the proton nmr spectrum indicated that since the trimethylphosphines were in dissimilar environments, their location on two adjacent basal borons would not appear to subject them to sufficiently different surroundings.
to account for this. The other alternative then, would be to position one trimethylphosphine on the apex boron and the second on a basal boron, positions consistent with both proton nmr and mass spectral data.

The location of the basally substituted trimethylphosphine provides a problem that is a bit more ambiguous. Two considerations, however, may be entertained which argue against its attachment to the boron bonded to the methyl group. First, the intensity for mass numbers in the mass spectrum related to simple methylated fragments such as \((\text{CH}_3)_3\text{PBH}_2\text{BHCH}_3\text{P(\text{CH}_3)}_3^+\) or, more importantly, \((\text{CH}_3)_3\text{PBH}_2\text{CH}_3^+\) were zero. Second, assuming that the postulates offered earlier concerning the unlikelihood of apical attack are sound, the two trimethylphosphines initially coordinated at basal positions of 1-methylpentaborane do not lead to a product with a ligand attached to the methylated boron unless one envisages an exchange of the trimethylphosphine from the nonmethylated to the methylated boron upon rearrangement. Though such behavior is not beyond possibility, it does not appear likely, and invoking it as a rationale for allowing the trimethylphosphine to be positioned on the boron containing the methyl group seems like a serious weakness in the argument for this particular configuration.
If the trimethylphosphine attached to a basal boron is not bonded to the boron containing the methyl group, three other possibilities remain: coordination to a neighboring (to methylated boron) boron; coordination to a trans-boron; and a bridging position. These are illustrated below:

Structure 5
Since no precedent has been set for bridging trimethylphosphine groups, (d) is considered the least likely possibility at this time. In making a choice between (a) and (b), a comparison may be made between the boron-11 nmr spectra of $\text{B}_5\text{H}_9\text{P(CH}_3\text{)}_3\text{)}_2$ obtained at 70.6 MHz (41) and $\text{CH}_3\text{B}_5\text{H}_8\text{P(CH}_3\text{)}_3\text{)}_2$ (32.1 MHz). The former spectrum consisted of a group of peaks at lower field with individual resonances well resolved and having apparent relative intensities 1:2:1. The respective chemical shifts were 19.4, 24.6 and 31.2 ppm with respect to $\text{BF}_3\cdot\text{Et}_2\text{O}$. A higher field signal with intensity 1 was observed at 55.0 ppm. This spectrum is consistent with the following structure:

![Structure 6](image-url)
The assignment of peaks places B(1) at 55.0 ppm and, because of the field raising ability of phosphines (42), the coordinated B(2) at 31.2 ppm. Since B(4) is not geometrically equivalent to B(3) or B(5) with respect to B(2), it is assigned the resonance at 19.4 ppm. B(3, 5) would then be responsible for the signals at 24.6 ppm having intensity of 2. The boron-11 spectrum of CH₃B₅H₈(P(CH₃)₃)₂, it may be recalled, consisted also of a lower field grouping of resonances with partial resolution visible of peaks at 10.0 and 18.0 ppm and two overlapping signals at 26 and 28 ppm with respect to BF₃·E₂O. The relative intensities were apparently 1:1:1:1 (the peaks at 26 and 28 ppm were overlapping to the degree that together they appeared to have an intensity near 2). A higher field signal with intensity 1 was observed at 53.0 ppm. One may then consider the effect on the nmr spectrum were the following hypothetical substitution to take place.

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{B} & \quad \text{H} & \quad 
\text{P(CH₃)₃} \\
\text{H} & \quad \text{H} & \quad \text{B} & \quad \text{H} & \quad 
\text{B} & \quad \text{H} & \quad \text{B} & \quad \text{H} & \quad 
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad 
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \\
+ \text{CH₃} & \quad \rightarrow & \quad \text{H} & \quad \text{B} & \quad \text{H} & \quad \text{H} & \quad \text{B} & \quad \text{H} & \quad \text{P(CH₃)₃} \\
\text{H} & \quad \text{H} & \quad \text{B} & \quad \text{H} & \quad \text{B} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \\
\text{H₃C} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \\
\end{align*}
\]

Equation 2
One must assume that the distance effects of substituents (such as the effect of methyl increasing the chemical shift of the boron trans to it by more than 5 ppm in 2-CH$_3$B$_5$H$_8$) in the diadduct may not be analogous to those in the noncoordinated pentaborane derivations because of the alteration in structure. Local effects, that is on the boron attached directly to the substituent, however, may be expected, qualitatively at least, to retain their character. Thus, substituting CH$_3$ trans to P(CH$_3$)$_3$ may not result in its exerting a trans effect, but might be expected to cause a lowering of the chemical shift of the boron to which it is attached. Additionally, it would be reasonable to expect the two borons cis to methyl to each be effected in a similar manner because of their approximate geometric equivalence. The major change envisaged then, in the boron-11 nmr spectrum of B$_5$H$_9$(P(CH$_3$)$_3$)$_2$ upon substituting CH$_3$ for H trans to P(CH$_3$)$_3$, if the preceding considerations are sound, would probably be a lowering of the chemical shift of the methylated boron. And, unless unexpected effects were enacted upon the other borons, a retention in the order of relative intensities of the basal boron resonances of 1:2:1 would be anticipated. That is, the qualitative appearance of the spectrum would not be expected to change. However, since the boron-11 spectrum of CH$_3$B$_5$H$_8$P(CH$_3$)$_3$$_2$
exhibits a peak intensity order of 1:1:2 (read in order of increasing field) and not 1:2:1 in the lower field groups, it is evident that either the considerations on which this reasoning is based are invalid, or the methyl group is not trans to the basally-coordinated trimethylphosphine. For the reasoning to be invalid would apparently require the effect of substituting a methyl group on $B(4)$ (equation II) to raise the chemical shift of $B(3)$ or $B(5)$ by 1-3 ppm and lower the shift of $B(5)$ or $B(3)$ by more than 6 ppm to produce the boron-11 nmr spectrum of $\text{CH}_3B_5H_8^-(P(CH_3)_3)_2$. Though $B(3)$ and $B(5)$ do not have exact geometric equivalence with respect to $B(4)$ (bridging hydrogen separation in one case; gap separation in the other), it may be pointed out that a similar geometric nonequivalence exists for $B(3)$ and $B(5)$ with respect to $B(2)$ in $B_5H_9^-(P(CH_3)_3)_2$; however, if the interpretation of the spectrum is correct, $B(3)$ and $B(5)$ share similar magnetic environments, the bridge hydrogen-gap structural difference notwithstanding. Thus, such a large difference in effects on $B(3)$ and $B(5)$ from substitution of $\text{CH}_3$ on $B(4)$ does not seem likely. It is on this basis that the methyl group is thought to not be trans to the trimethylphosphine.

The only position remaining is methyl cis to basally coordinated trimethylphosphine as represented in structures $V(a)$ and $V(b)$, which differ only in the position
of the bridging hydrogen. This is the structure proposed for the rearranged diadduct, the exact bridge hydrogen configuration being left ambiguous because of inadequate means of distinguishing the isomers.

One final point concerning nmr data may be noted. As has been mentioned (17), CH$_3$ causes a lowering in the chemical shift of the attached boron by 14 ppm for all pentaborane derivatives observed. If one assumes that a basal boron in B$_5$H$_9$(P(CH$_3$)$_3$)$_2$ cis to the trimethylphosphine-coordinated boron resonates at 24.6 ppm, then substitution of a methyl group on this boron to produce the proposed structure for CH$_3$(B$_5$H$_8$(P(CH$_3$)$_3$)$_2$ would be expected to result in a noticeable lowering of its chemical shift. If the signal observed at 10.0 ppm in the spectrum of CH$_3$B$_5$H$_8$(P(CH$_3$)$_3$)$_2$ were assigned to B-CH$_3$, the decrease in the field for that boron from its value in the nonmethylated species would be 24.6-10.0 = 14.6 ppm. This change may be fortuitous, of course, but is close enough to what has been observed in the pentaborane systems to offer further encouragement for the structure proposed.

In considering the problem of a mechanism consistent with the structures postulated for the diadduct, various points seem worthy of discussion. First, it may be noted that the coordination of 1- or 2-methyl-
pentaborane was limited to two moles of trimethylphosphine. The tricoordinated system, \( \text{CH}_3\text{B}_5\text{H}_8(\text{P(\text{CH}_3)}_3)_0 \), would be isoelectronic with \( \text{B}_5\text{H}_{12}^{3-} \) and of unknown stability, but it may also be observed that base attack in the diadduct is likely to have occurred at a boron flanked by two bridging hydrogens. Such a structural unit is no longer available after the coordination of two ligands. Perhaps, also, the addition of a third mole of trimethylphosphine would result in a species too weakened structurally and sterically to survive.

The other aspects of the mechanism problem are concerned with the position of the substituents in the diadduct and how they were placed there. A simple mechanism of rearrangement may be proposed which utilizes the concept of a minimum motion of atoms and bonds (minimum in terms of number and distance involved), and the 3033 structure of the hypothetical \( \text{B}_5\text{H}_{12}^{3-} \) ion as an intermediate. Thus, it may be considered that the initial diadduct, that is the dissociable adduct, of 1-methylpentaborane rearranges to the 3033 intermediate in the following way:
Equation 3
A further relocation of atoms and bonds could then produce the product with the $2124$ structure.

\[
\text{Equation 3 - continued}
\]

A similar mechanism could be envisaged for the $2$-methylpentaborane adduct.

\[
\text{Equation 4}
\]
Were the trimethylphosphine and methyl substituents replaced by hydrogen atoms the same mechanism would also apply in the case of B₅H₉(P(CH₃)₃)₂.

Given the dicoordinated nature of the nonrearranged adduct, the proposed structure for the rearranged isomer and the mechanisms postulated that connect the two species, a necessary consequence has been the initial coordination of the ligands cis to each other on the basal borons. Another mechanism suggested without detail by Onak (17) appears to have the same requirement. The fact that a position trans to each other is also structurally feasible (and perhaps sterically preferred) would seem to indicate that some other effect is operative which directs the position of attack for the second trimethylphosphine. Other than speculating that the first donor coordinated to a basal boron may exert such a directing influence over the point of attack by the second donor, this question must remain unanswered.

As has been previously mentioned, the dissociation of the unrearranged diadduct in a solvent could be easily facilitated by the removal of the ligands and the reestablishment of the hydrogen bridges with no large energy requirements expected. However, once the rearrangement has taken place, the apically attached trimethylphosphine
cannot be removed without making significant structural changes. Such alterations would presumably have greater energy demands than can be met in the dissociation process. The lack of disassociation of the remaining ligand may be caused by an increase in the acidity of the basal portion of the molecule brought about by the transferral of one of the donors to the apical position away from the base.

One last consideration concerns the relatively large amount of \((\text{CH}_3)_3\text{PBH}_2\text{CH}_3\) obtained upon decomposition of the diadduct. If the trimethylphosphine is not coordinated to the methylated boron, then some sort of exchange is necessary at some point to enable it to attack a B-CH\(_3\) unit. Since the basally coordinated boron in the proposed structure has more hydrogens attached than the apical boron and is thus closer in composition to \((\text{CH}_3)_3\text{PBH}_3\), it is possible that most of the latter compound originates from this source. This would presumably require the majority of \((\text{CH}_3)_3\text{PBH}_2\text{CH}_3\) to result from a detachment of the apically coordinated \(\text{P(CH}_3\text{)}_3\) during the decomposition process followed by attack on a B-CH\(_3\) unit. Since a rather large amount of \((\text{CH}_3)_3\text{PBH}_2\text{CH}_3\) is recovered, it would appear necessary to attribute unique acid properties to the B-CH\(_3\) system to render it a favorable reaction site in view of its statistical and possibly steric disadvantages. Some
precedents for such behavior, however, has been observed in the case of the reaction of trimethylamine with methyldiborane, where the amine appears to attack only the methylated boron (24). If the decomposition of CH₃B₅H₈(P(CH₃)₃)₂ produced CH₃B₂H₅ or some other methyl-containing species with similar acid-base properties, it may be possible that trimethylphosphine could react in a manner similar to trimethylamine, and facilitate an exchange from a nonmethylated boron to the methylated one to produce (CH₃)₃PBH₂CH₃.

2. Trimethylamine reactions.

Trimethylamine forms a 2:1 adduct with 1-methylpentaborane whose boron-11 nmr spectrum shows that rearrangement had taken place at the reaction temperature of -78°C. The significant feature of the spectrum was a doublet of intensity 1 at 54 ppm indicating a structure with a unique B-H bond unit. The structural information immediately ascertainable is that neither the methyl group nor the trimethylamine ligands are likely to be attached to this high field boron because of their field lowering effects (42,43), and if the geometry is the 2124 type of the hypothetical B₅H₁₁⁻ ion which has an apical B-H unit, then the methyl group and the two trimethylamines must be attached to basal borons.
That the geometry of the trimethylamine diadduct of 1-methylpentaborane(9) is of the 2124 designation is suggested by a process of elimination. The structures of the 3033 and 1215 types (preceding section) may be excluded because of the unique BH$_2$ group each have that would give rise to a spin coupled triplet at high field instead of the observed doublet. The 0306 structure has no bridge hydrogens, a fact that is in conflict with the proton nmr spectrum of the adduct which displayed a resonance at a higher field position in a region where bridge hydrogens may be observed. Since it is possible to dissociate the adduct by pumping with careful warming, the assumption of a 2124 structure leads to the conclusion that no further rearrangement occurs at higher temperatures. The rationale resides in the recognition that the 2124 structure with methyl on a basal boron is quite similar to the structure of 2-methylpentaborane. The recovery of this compound in high yields would seem to indicate that the structure of the adduct which dissociated also resembled closely that of 2-methylpentaborane and that rearrangement of the initial complex from warming would only result in a geometry further differing from and thus less likely to produce the 2-methylpentaborane observed.
Determining the exact structure of the diadduct is obscured by the broad nature of most resonances in the boron-11 nmr spectra which was caused apparently by quadrupole interactions with the trimethylamine nitrogens and the broadening effects of the low temperatures at which the spectra were necessarily obtained. Decoupling attempts conducted over a range of frequencies were unsuccessful in making meaningful or reproducible changes in the appearance of the resonances, so details of the structure must be inferred from other data. Both trimethylamines are evidently on basal borons as described earlier, but the failure to find even the smallest amount of trimethylaminemethylborane ((CH₃)₃NBH₂CH₃) suggested that coordination had not occurred on the methylated boron. Indeed, if the four considerations proposed in the discussion of the trimethylphosphine adducts concerning the anticipated primacy of basal attack over apical attack by a Lewis base are valid for trimethylamine, attachment of the trimethylamine ligand to the methylated boron resulting from initial coordination of the 1-methylpentaborane substrate would not be expected. If coordination by one trimethylamine to the B-CH₃ unit is not considered probable, only two possibilities remain; the ligands cis to each other or in a position trans to each other according to the following diagram:
The proton nmr spectrum of this compound exhibits an intense sharp peak which has been attributed to the trimethylamine hydrogens and thus suggests that the ligands are in essentially magnetically equivalent environments. However, the environments of the two possible isomers may not differ sufficiently for the proton spectrum to be strongly enough effected to be a helpful measurement. The boron-11 spectrum is poorly resolved, but exhibits sufficient resolution to identify a broad resonance at
about 8.6 ppm whose outline suggests an intensity of two. But even from the boron-11 spectrum, it is not clear that measurable differences would be observed between the two isomers. In fact, from the available physical data, it may not be possible to unambiguously choose the correct isomer. However, certain tentative conclusions may be drawn from the boron-11 nmr spectra of the diadducts of both methylated pentaboranes that are consistent with available experimental observations. These conclusions are only intended to be suggestive of the processes that may be occurring and are chosen because they do not conflict with the interpretation of the nmr data and reasonable assumption concerning the chemistry observed. The observations of the nature of both adducts may be summarized in the following way. As described previously, trimethylamine forms a diadduct with 1-methylpentaborane that appears to have the 2124 structure with the methyl group and the two ligands probably located on basal borons. Although 2-methylpentaborane already has a basally positioned methyl group, surprisingly it does not simply add two trimethylamine molecules to produce a system identical to that derived from 1-methylpentaborane.

Two ligands do apparently coordinate 2-methylpentaborane, but a rearrangement takes place which yields
a unique compound. Therefore, it would seem that for some reason, possibly associated with the relative energy of the adduct obtained from 1-methylpentaborane and the species formed from the coordination of the first trimethylamine on 2-methylpentaborane, that the ligands do not attack 2-methylpentaborane in the same places they are located on the rearranged 1-methylpentaborane adduct. When the compound derived from 2-methylpentaborane is warmed to approximately -50° C it rearranges to the 1-methylpentaborane diadduct with the accompaniment of decomposition of the $B_5$ framework. The boron-11 nmr spectrum of the 2-methylpentaborane adduct may be interpreted in the following way: The low shift of 46.7 ppm observed for the doublet of the unique boron seems to suggest that a substituent in addition to hydrogen is attached to this boron, a factor rendering impossible the 2124 structure for the adduct. This peak is relatively sharp, however, which reduces the possibility that trimethylamine is bonded to the unique boron because of the broadening effect the quadrupole moment of nitrogen exerts on boron resonances. If the methyl group is responsible for the lowering of the chemical shift to 46.7 ppm, apparently a hydrogen atom is also present on the same boron because of the doublet splitting that seems to be evident about -50°. Such a structural unit for a unique boron, two sigma bonds not associated with the
framework, are not available in the 2124 or 0306 geometries of the hypothetical $B_5H_{11}^-$. The 1215 structure appears to be tetragonal pyramidal and though possessing 4 framework bonding electrons instead of 6 as in pentaborane(9) derivatives, the basally attached methyl group may still be the more stable configuration. Consistent with the 3033 structure as the remaining possibility, has been its employment as an intermediate in previous rearrangement mechanisms. Since the diadduct formed from 2-methylpentaborane was observed to convert to the adduct derived from 1-methylpentaborane when the former compound was warmed above $-50^\circ$, it is possible that the species resulting from the $-78^\circ$ reaction of trimethylamine and 2-methylpentaborane was an intermediate for which insufficient energy was available below $-50^\circ$ for the completion of the rearrangement process. The conclusion of the rearrangement, however, must necessarily involve a somewhat different mechanism than proposed for the trimethylphosphine reactions to avoid placing the unique boron containing a ligand (or the methyl group) in the less stable apical position. Migration of the methyl could occur, perhaps, but probably less readily than the hydrogen attached to the same boron. The alternative mechanism suggested promotes another boron to the apical position utilizing the minimum atomic motion employed in previous rearrangements. The follow-
ing reactions describe the processes involved for the trimethylamine groups arbitrarily coordinated in positions trans to each other:

Equation 5
Tentative assignments of the boron-11 nmr spectrum may be made according to the previous criteria of the field lowering effect of the trimethylamine group. However, since the downfield hump on the main peak group appears to have a greater intensity than the shoulder at slightly higher field, it is possible that the three borons, B(3), B(4) and B(5) of the 3033 structure in Reaction VIb are resonating in this region \( (\alpha = 1.5) \) with the shoulder \( (\alpha = 12.9) \) caused by the signal from B(1). A similar overlapping of peaks for a proposed 3033 structure has been reported \( (43) \), and a higher field resonance at 12.0 ppm assigned to a non-coordinated boron of the same type as B(1). The signal at 46.7 ppm is, of course, attributed to the methylated boron, B(2) with the single terminal hydrogen responsible for the observed doublet splitting. Symmetrical orientation of the trimethylamines in this adduct on B(3) and B(4), B(1) and B(5) or B(1) and B(3) would be expected to result in a boron-11 spectrum having greater symmetry than was observed, e.g., a poorly resolved set of signals with intensity of 2:2. Thus, asymmetrical attachment of the ligands is not postulated.

From the preceding discussion, then, the following suppositions have some experimental support. The diadduct obtained from 1-methylpentaborane is probably of the 2124 geometry with the three substituents on basal
borons, the relative positions of the two trimethylamines being ambiguous. The trimethylamine derivative of 2-methylpentaborane possibly has the $3033$ structure with the ligands located asymmetrically on two of the four borons which lie in a plane and the methyl group attached to the unique boron. The latter adduct rearranges to that obtained from 1-methylpentaborane when warmed to $-50^\circ$ C. Finally, the initial points of coordination on 2-methylpentaborane are evidently different from the positions of the ligands on the rearranged 1-methylpentaborane derivative. Further speculation beyond this is not warranted because of the lack of understanding of the phenomena governing the geometry of both methylated species before and after rearrangement. If coordination by the donors render the borons equivalent as suggested by Onak (8), initial attack by the ligands on 1- or 2-methylpentaborane could yield a cis or trans configuration in either case which could then rearrange to a new product with the original cis or trans relationship maintained or reversed. This conclusion justifies the arbitrary assumption of assigning the trimethylamines trans to each other in Reaction VI merely for the purpose of providing an example of coordination and rearrangement. Any other combination of cis or trans rearrangement or coordination could presumably also be employed.
Although the geometry of the diadduct derived from 1-methylpentaborane cannot be predicted precisely, some reasonable assignments of the boron-11 nmr spectrum can be attempted. The assignments may be made on the basis that both trimethylamine and the methyl group lower the chemical shifts of the borons to which they are attached, the methyl by a somewhat greater amount (17, 20). Thus, the signal at 54 ppm (Figure XV) is immediately assigned to the apical boron, and the shoulder observed at -0.2 ppm is attributed to the methylated basal boron. The rather broad resonance centered around 8.6 ppm is attributed to the two borons coordinated by the trimethylamines in either a cis or trans configuration. The slightly resolved peak at 19.3 ppm is near the chemical shift of 22.0 ppm assigned to the noncoordinated basal borons in $B_5H_9(N(CH_3)_3)_2$ (20), so this signal (19.3 ppm) is attributed to the remaining unsubstituted basal boron.

Finally, the possibility of both trimethylamine ligands being on the same boron is discounted because of the lack of an excessively low field chemical shift such as that reported for $B_5H_9(TMED)$ (TMED = N, N$_1$, N', N'-Tetramethylethylanediamine) (43). The value of -18.1 ppm was attributed in this adduct to the boron coordinated to both nitrogens of the ligand. This chemical shift
was far below all resonances observed for the trimethyldamine adducts.

The trimethylamine diadduct derived from 1-methylpentaborane differs significantly in structure from its trimethylphosphine analog. The latter compound presumably has one ligand bonded to the apical boron while the trimethylamine system contains both donors in the base. Yet because the methyl group is evidently also on a basal boron in the amine system, a rearrangement must have occurred. Because no unrearranged adduct was observed as was the case with trimethylphosphine, it is not possible to determine if the rearranging species is a mono- or diadduct. Simple rearrangement routes are available for monoadducts using the hypothetical $\text{B}_5\text{H}_{10}^-$ and its various structures in a manner analogous to that employed for the diadducts. However, since no precedent has been yet established for the rearrangement of a monoadduct the rearranging species will be assumed to be dicoordinated. The following processes may then be proposed with the ligands coordinating cis, again an arbitrary configuration for the purpose of demonstrating possible mechanisms of rearrangement.
Equation 6
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