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NONAHYDROHEXABORATOBIS(CYCLOPENTADIENYL)TITANIUM(III)

DISSERTATION

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

By

Douglas L. Denton, B.S., M.S

The Ohio State University
1973

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(1967).

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Papers, 162nd Meeting Amer. Chem. Soc., Washington,

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Decomposition Products of the Anions, V. T. Brice, H. D.
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FIELDS OF STUDY

Major Field: Inorganic Chemistry

Studies in Non-metal Chemistry. Professors Sheldon
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Studies in Transition Metal Chemistry. Professors
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INTRODUCTION

I. Hexaborane(10)

Hexaborane(10) was among the first boron hydrides isolated and characterized by Alfred Stock and his co-workers forty years ago\(^1\). However, until recently the chemistry of \(\text{B}_6\text{H}_{10}\) has remained virtually unstudied due to the difficulty of its preparation in sufficient quantity for chemical investigations. Since the development of good synthetic procedures the area of hexaborane(10) chemistry has been rapidly expanding.

Stock originally prepared hexaborane(10) in low yields by the acid hydrolysis of magnesium boride\(^1\). This method, which produces a mixture of boron hydrides, was later improved to give 3 to 6 per cent yields\(^2\). Other preparations reported involved the reaction of \((\text{C}_2\text{H}_5)_3\text{NH}^+\text{B}_9\text{H}_{14}^-\) and polyphosphoric acid\(^3\), the decomposition of \(\text{B}_2\text{H}_6\) in a silent discharge\(^4\), and the decomposition of \(\text{B}_5\text{H}_{11}\) in the presence of Lewis bases\(^5,6\). However, in each case only small quantities of hexaborane(10) were obtained.

The first preparation of \(\text{B}_6\text{H}_{10}\) in large quantities

1
was reported by Geanangel and Shore in 1968. Yields up to 22 per cent were obtained from the reaction of LiB$_5$H$_8$ with B$_2$H$_6$ in ether. Johnson improved this method to obtain 33 per cent yields$^8,9$. Recently, a much superior synthesis has been developed by Brice, Johnson and Shore$^{10}$. Using relatively simple vacuum line techniques, 80 per cent yields of hexaborane(10) are produced by the following reaction:

$$K^+[1-\text{BrB}_5\text{H}_7^-] + \frac{3}{2}\text{B}_2\text{H}_6 \xrightarrow{- 350}$\text{B}_6\text{H}_{10} + \text{KBr}$$

Therefore, sufficient quantities of B$_6$H$_{10}$ can now readily be prepared for studies of its chemistry.

Hexaborane(10) is a colorless volatile liquid which freezes at -62.3°C and has a vapor pressure of 7.5 mm Hg at 0°C$^{11}$. It has a strong sickening-sweet odor. In contrast to many other boron hydrides it neither inflames nor explodes on contact with air. Stock reported th B$_6$H$_{10}$ decomposes slowly at room temperature to yield hydrogen and a yellow solid$^1$. In the vapor phase it is considerably more stable being only partially decomposed upon passage through a tube at 300°C. Although it is rapidly decomposed by aqueous acid, decomposition was incomplete after sixteen hours in a 30 per cent aqueous alkali solution at 90°C$^1$.

The X-ray crystal structure of hexaborane(10) was reported by W. N. Lipscomb and co-workers in 1958$^{12,13}$. 
The molecular structure, which is shown in Figure 1a, consists of a pentagonal pyramidal arrangement of boron atoms. One hydrogen atom is terminally bonded to each of the five basal borons and to the apical boron. The remaining four hydrogens form boron-hydrogen-boron bridge bonds below the plane of the basal borons. The unique feature of the structure is the boron-boron bond between the basal borons not joined by a hydrogen bridge. This bond has a length of 1.60 Å which is the shortest B-B distance known in boron hydride chemistry. A valence bond description of $\text{B}_6\text{H}_{10}$ is shown in Figure 1b.

The boron-11 nmr spectrum of hexaborane(10) taken at 12.8 MHz, 32.1 MHz, and 70.6 MHz at ambient temperature consists of two symmetrical doublets in the area ratio of 5:1. The large peak is assigned to the five basal borons and has a chemical shift of -14.1 ppm ($J=158$ Hz) relative to $\text{BF}_3\cdot\text{OEt}_2$. The small resonance at +51.8 ppm ($J=155$ Hz) is attributed to the apical boron. The doublets arise from spin coupling of the boron nuclei with the terminal hydrogens which have a nuclear spin of $\frac{7}{2}$. No coupling with the bridge hydrogens is observed. The apparent equivalence of all five basal borons is not expected on the basis of the solid state structure of Cs symmetry which has three types of basal borons in the ratio of 2:2:1. In addition, unexpected equivalence of the five basal terminal hydrogens and the presence of only one type of bridge hydrogen is observed in the
Figure 1. (a) Molecular structure of hexaborane(10).
(b) A valence bond description of hexaborane(10).
100 MHz and 220 MHz proton nmr spectra. It has been suggested that a rapid exchange process at ambient temperature involving only the bridge hydrogens accounts for this apparent anomaly.

Recently, variable temperature boron-11 and proton nmr studies have conclusively established the tautomerism of the bridge hydrogens in hexaborane(10). Below -70° the doublet in the boron-11 nmr due to the basal borons collapses and shifts downfield as a new peak grows in upfield. At -100° two basal resonances in the area ratio of 4:1 are observed. Equivalence of the basal terminal and of the bridge protons is also removed in the pmr spectrum below -70°. At -130° three basal terminal peaks are resolved in the ratio of 2:2:1 and two bridge hydrogen resonances of equal area are observed. The low temperature nmr spectra are completely consistent with the static structure in the solid state. Chemical shift measurements establish that the basal terminal and bridge hydrogen resonances observed above -70° are the time average of the different resonances which occur at low temperature.

The separate basal terminal and bridge proton resonances in the ratio of 5:4 and the spin coupling of each basal boron with only one hydrogen from -70° to ambient temperature indicates that only the bridge protons are involved in the exchange process. Chemical evidence
also militates against any exchange between the bridge and terminal hydrogens. The exchange reaction between $\text{B}_6\text{H}_{10}$ and $\text{B}_2\text{D}_6$ yields $\text{B}_6\text{H}_5\text{D}_5$ in which deuterium is located exclusively in basal terminal positions$^{21,22}$. Reaction of $\text{B}_6\text{H}_{10}$ with DCI in methyl ether and in the gas phase results in bridge deuteration only$^8,21$. Bridge terminal exchange in bridge deuterated hexaborane(10) occurs very slowly at room temperature in the gas phase$^8$.

A mechanism has been proposed for the intramolecular exchange of the bridge hydrogens$^{17}$. A bridge hydrogen adjacent to the B-B could move to a terminal position forming an intermediate with a BH$_2$ group as shown in Figure 2. The "new terminal hydrogen" could then return to its original bridge position or form a new bridge at the initial site of the B-B bond. Since the bridge hydrogens are located far below the plane of the basal borons and the terminal hydrogens are above this plane only the "new terminal" hydrogen is in a position to reform a bridge$^{21}$. Thus, no exchange of bridge and terminal hydrogens occurs.

Very little is known about the chemistry of hexaborane(10). Reaction of hexaborane(10) with molecular Lewis bases results in formation of an adduct of the composition $\text{B}_6\text{H}_{10}\text{L}_2$ where L$=\text{N(CH}_3)_3$, P(CH$_3$)$_3$, and P(C$_6$H$_5$)$_3$$^{23}$. The substituted hexaborane(10) derivatives prepared include 2,3-(CH$_3$)$_2\text{B}_6\text{H}_8$$^{24}$, 2-CH$_3\text{B}_6\text{H}_9$$^{10}$, and 2-BrB$_6$H$_9$$^{10}$.
Figure 2. A proposed mechanism for the intramolecular exchange of bridge hydrogens in hexaborane(10).
The unique feature of hexaborane(10) chemistry is the amphoteric character which it exhibits. The \( \text{B}_6\text{H}_{10} \) molecule may act as a Brønsted acid by donating an \( \text{H}^+ \) from a bridge site to a strong base to form the conjugate base \( \text{B}_6\text{H}_9^{25} \). However, \( \text{B}_6\text{H}_{10} \) also exhibits Brønsted basicity as protonation of the boron-boron bond results in the formation of \( \text{B}_6\text{H}_{11}^+ \) which has five equivalent \( \text{B}-\text{H}-\text{B} \) bonds \(^{26}\).

Molecular orbital calculations have indicated that the short \( \text{B}-\text{B} \) bond is a center of high electron density which is subject to electrophilic attack\(^{27}\). The basicity of this bond and even the stability of \( \text{B}_6\text{H}_{11}^+ \) was predicted by Lipscomb in 1958\(^{28}\). Recently, the stability of the undecahydrohexaboronium ion was established by the low temperature isolation of \( [\text{B}_6\text{H}_{11}^+][\text{BCl}_4^-] \) and \( [2-\text{MeB}_6\text{H}_{10}^+][\text{BCl}_4^-] \). These salts result from the reaction of the neutral borane with HCl in the presence of \( \text{BCl}_3 \) in methylene chloride at \(-78^\circ\). Protonation of \( \text{B}_6\text{H}_{10} \) and \( 2-\text{CH}_3\text{B}_6\text{H}_9 \) also occur in liquid HBr\(^{19,26}\). Proton nmr unambiguously establishes the presence of five equivalent boron-hydrogen-boron bridges in \( \text{B}_6\text{H}_{11}^+ \). This is the first example of a polyhedral boron cation.

The Brønsted acidity of boron hydrides was first established by the deprotonation of decaborane(14) both in aqueous and nonaqueous solvents\(^{29}\). Evidence that the proton removed was from a bridge position was obtained.
from the reaction of u-D$_4$B$_{10}$H$_{10}$ with NaH which produces only HD$^\circ$. Both n-B$_{18}$H$_{22}$ and i-B$_{18}$H$_{22}$ are strong diprotic acids toward NaH and LiC$_4$H$_9$ as would be expected from its structural relationship to B$_{10}$H$_{14}$. In 1959 Parry and Edwards predicted that the acid character of bridge hydrogens extended to lower boron hydrides and that the relative acid strength increases with increasing size of the polyhedral boron framework. Since their prediction hexaborane(10)$^{25}$, pentaborane(9)$^{33-35}$ and tetra-borane(10)$^{36}$ have been deprotonated. For the boron hydrides of the series B$_n$H$_{n+4}$ the relative acidities established by proton competition reactions agrees with the predicted order$^{25}$.

B$_{10}$H$_{14}$ > B$_6$H$_{10}$ > B$_5$H$_9$

Hexaborane(10) has been deprotonated at low temperature in ether solvents to form the nonahydrohexaborate(1-) ion according to the following reaction$^{8,9,25,37}$:

\[
\text{B}_6\text{H}_{10} + \text{MB} \rightarrow \text{MB}_6\text{H}_9 + \text{HB}
\]

MB = LiCH$_3$, NaH, KH

Hexaborane(10) is sufficiently acidic to react with liquid ammonia to form NH$_4^+ \cdot$B$_6$H$_9$.$^{-19,23}$ Although the solid alkali metal salts of B$_6$H$_9^-$ decompose at room temperature in a week the tetra-n-butylammonium salts exhibit greater thermal stability$^{37}$. Solutions of B$_6$H$_9^-$ completely decompose within two weeks. The primary
decomposition products of $\text{B}_6\text{H}_9^-$ are $\text{B}_{11}\text{H}_{14}^-$ and $\text{BH}_4^-$.  

Chemical and spectral evidence established that the proton removed from hexaborane(10) to form the anion, $\text{B}_6\text{H}_9^-$, is from a bridge site. Reaction of $\text{LiCH}_3$ with hexaborane(10) containing deuterium in basal terminal positions yields only $\text{CH}_4$. Boron-11 nmr indicated the presence of a terminal hydrogen on the apical boron of the anion. The hexaborane(10) generated by the DCl reaction with $\text{B}_6\text{H}_9^-$ contained boron-deuterium-boron bridges as shown by the infrared spectrum. The boron-11 nmr spectrum of $\text{B}_6\text{H}_9^-$ is qualitatively similar to $\text{B}_6\text{H}_{10}$. It consists of two doublets in the area ratio of 5:1 at -9.0 ppm ($J=107$ Hz) and 50.0 ppm ($J=142$ Hz). As in the case of $\text{B}_6\text{H}_{10}$ the equivalence of the five basal borons is attributed to a rapid exchange process or tautomerism of the bridge hydrogens. Some temperature dependence is noted in the boron-11 nmr. Upon cooling from ambient temperature, broadening and loss of resolution of the basal resonance and slight sharpening of the apical peak is observed. Complete loss of resolution of the basal resonance for $\text{KB}_6\text{H}_9$ in THF occurs at about $-40^\circ$. This broadening which is particularly pronounced for $\text{LiB}_6\text{H}_9$ has been attributed to the increased rate of nuclear quadrupolar relaxation which is related to the viscosity of the solution. The sharpening of the apical resonance may be due to the
loss of coupling between the apical and basal borons\textsuperscript{38}.

Brice and Shore have reported the first derivative of the nonahydrohexaborate(1-) ion to be prepared,
\[
[(C_6H_5)_2P]_2CuB_6H_9 \]
This compound will be discussed in the next section on metalloboranes.

II. Metalloboranes

In the past ten years there has been much interest in the synthesis and structure determination of metalloborane compounds. Varied types of bonding are observed depending upon the boron hydride anion involved, the nature of the metal, and the other ligands coordinated to the metal atom. Alkali metal derivatives of boron hydrides are generally ionic salts and of the alkaline earths, only magnesium and beryllium form covalent borane derivatives. Covalent metalloborane compounds of Groups IB, IIB, IIIA, IVA and the transition metals have been prepared. The modes of bonding include boron metal sigma bonds, hydrogen bridges between the metal and a boron atom, boron-metal-boron two electron three center bonds, and bonds analogous to \( \pi \)-cyclopentadienyl-transition metal bonds in the case of large carborane anion ligands.

The extensive metal chemistry of the most simple boron hydride anion, tetrahydroborate, has recently
been reviewed. Tetrahydroborate derivatives exist only for metals with an electronegativity less than that of boron, or when ligands effectively reduce the electronegativity of the metal atom to less than that of boron. It has been suggested that the stability of these derivatives is related to their ionic character. Those compounds of less ionic character than diborane are more unstable.

The calcium, strontium, and barium tetrahydroborates exhibit predominately ionic characteristics, whereas the more polarizing beryllium and magnesium form covalent compounds which are volatile. The controversial vapor phase structure of Be(BH₄)₂ was reported on the basis of electron diffraction data to involve a BeH₂ moiety bridging terminal hydrogens on different borons of the diborane structure. Cook and Morgan, however, claim that a BeH₃ unit bridging through two of the hydrogens replaces a bridge hydrogen of diborane. A recent X-ray study has shown the solid state structure involves a helical polymeric arrangement of BH₄Be and BH₄ units bonded through two hydrogen bridges.

Magnesium bis(tetrahydroborate), which is most easily prepared by the reaction of magnesium hydride with diborane in ether under pressure, exhibits much less ionic character than lithium tetrahydroborate. Although various ether and amine adducts can be formed,
all of the ether can be removed from the compound by heating in vacuo to 180°. No structural or spectroscopic data has been reported for magnesium bis(tetrahydroborate). Becker and Ashby have reported the preparation of \( \text{ClMgBH}_4 \cdot (\text{C}_4\text{H}_8\text{O})_2 \). Wiberg and Henle have reported the preparation of \( \text{Zn(BH}_4)_2 \) and \( \text{Cd(BH}_4)_2 \) from the metathetic reactions of lithium borohydride with the corresponding metal chloride in ether. The zinc tetrahydroborate is stable to 50°, but the cadmium derivative decomposes into the elements at 25°.

Aluminum tetrahydroborate, \( \text{Al(BH}_4)_3 \) which was first prepared by Schlesinger and co-workers, has three borohydride ions bonding through hydrogen bridges to the aluminum. Electron diffraction studies indicate \( \text{D}_{3h} \) (prismatic) symmetry or slightly distorted \( \text{D}_3 \) (antiprismatic) symmetry prevails around the aluminum atom. However, at ambient temperature all twelve of the hydrogens appear equivalent in the proton nmr due to a rapid exchange process.

Wiberg and co-workers have prepared tris(tetrahydroborate) gallium and indium compounds; however, the latter was complexed with three molecules of THF and was unstable above -10°. Thallium(III) is reduced to thallium(I) by the tetrahydroborate ion, but ionic \( \text{TlBH}_4 \) has limited stability at 40°.
The only group IV tetrahydroborates to be prepared, Sn(BH$_4$)$_4$ and (CH$_3$)$_3$PbBH$_4$·NH$_3$ are stable only at low temperature$^{55, 56}$.

Tetrahydroborate derivatives of a large number of transition metals have been prepared; however, only Tl(BH$_4$)$_3$, Zr(BH$_4$)$_4$, and Hf(BH$_4$)$_4$ do not require the stabilization provided by other ligands. The green, volatile compound Tl(BH$_4$)$_3$ decomposes rapidly at 25°C$^{57}$. Noth and Hartwimmer have reported a more stable titanium(III) derivative, (h$_5$-C$_5$H$_5$)$_2$TlBH$_4$ which is a violet crystalline solid that sublimes at 120°C$^{58}$. Infrared evidence suggested that the tetrahydroborate was bonded through two bridge hydrogens. This interpretation was questioned$^{59, 60}$, but Marks and co-workers presented infrared evidence supporting the original assignment$^{61}$. Very recently the presence of two hydrogen bridge bonds was established by Lippard and co-workers using X-ray diffraction$^{62}$.

Reaction of lithium tetrahydroborate with the anhydrous metal chloride yields the zirconium and hafnium derivatives Zr(BH$_4$)$_4$ and Hf(BH$_4$)$_4$.$^{51, 63}$ Both compounds are volatile, colorless, air-sensitive solids that slowly decompose at room temperature. The structure of Zr(BH$_4$)$_4$ at -160°C has been determined by X-ray diffraction. The four borons are arranged tetrahedrally and are bonded to the metal through triple hydrogen
bridge bonds. Infrared data indicates that Hf(BH₄)₄ has the same structure. Both ¹H and ¹¹B nmr evidence establishes that only one kind of hydrogen is present. The apparent equivalence of the terminal and bridge hydrogens is due to a rapid scrambling process. Collapse of the single quartet due to ¹¹B coupling in the ¹H nmr has been recently shown to be due to "thermal decoupling" rather than the slowing of an exchange process in the molecule.

Tetrahydroborate derivatives have been reported for vanadium, niobium, chromium, manganese, iron, cobalt, and nickel but they are generally of limited stability and not well characterized.

Copper(I)tetrahydroborate is only stable below -12°C, but the coordination of ligands to the copper such as triaryl phosphines results in stable derivatives of the formula (R₃P)₂CuBH₄. The structure of (R₃P)₂CuBH₄ as determined from X-ray methods shows the BH₄⁻ bonded to the metal through two hydrogen bridge bonds. However, distortion of the tetrahedral symmetry around the boron and a large P-Cu-P may be indicative of a direct Cu-B bond. In the cation [(R₃P)₂CuBH₄Cu(R₃P)₂]⁺ both copper atoms appear to be bonded to the tetrahydroborate. The silver(I) and gold(III) tetrahydroborates are also stable only at low temperatures but as with copper the triphenyl phosphine derivative...
\((\sigma_3^P)^2\text{AgBH}_4\) is stable\(^{72-74}\).

The actinide derivatives \(\text{U(BH}_4\text{)}_4\), \(\text{Th(BH}_4\text{)}_4\) and \(\text{Np(BH}_4\text{)}_4\) appear to be isostructural with \(\text{Zr(BH}_4\text{)}_4\)\(^{75,76}\). Many stable tetrahydroborate derivatives of lanthanide metals have also been prepared\(^{40}\).

The study of metal derivatives of intermediate boron hydride anions has been much less extensive. The octahydrotriborate\(^{(-1)}\) derivatives \(\text{Mg(B}_3\text{H}_8\text{)}_2\) and \(\text{Mg(B}_3\text{H}_8\text{)(BH}_4\text{)}\) have been isolated as tetrahydrofuran solvates; however, no structural information was obtained for these compounds\(^{77}\). Most of the \(\text{B}_3\text{H}_8^-\) metalloboranes prepared have been transition metal complexes.

Reactions of the metal hexacarbonyls with the triborohydride ion yields a series of complexes \((\text{OC})_4\text{MB}_3\text{H}_8^-\) where \(\text{M} = \text{Cr}, \text{Mo} \text{ and W}\)\(^{59}\). The structure of \((\text{OC})_4\text{CrB}_3\text{H}_8^-\) was determined by single crystal X-ray investigation. Two hydrogens occupy octahedral coordination sites of the metal forming bridges between the chromium atom and the borane\(^{78}\).
The 19.3MHz boron-11 nmr consists of two unresolved peaks in the area ratio of 2:1. Spectral evidence indicates that the molybdenum and tungsten complexes are isostructural with the chromium derivative.

The reduction of \((\pi-C_{5}H_{5})_{2}TiCl_{2}\) with CsB_{3}H_{8} yields the titanium(III) compound \((\pi-C_{5}H_{5})_{2}TiB_{3}H_{8}\). This compound, which exhibits a structureless e.s.r. signal, is also believed to contain metal-hydrogen-boron bridge bonds.

The solid state structure of the copper(I) derivative \([C_{6}H_{5}]_{3}P_{2}CuB_{3}H_{8}\) has been shown by X-ray to involve similar hydrogen bridge bonding to the metal. In contrast to \((OC)_{4}CrB_{3}H_{8}^{-}\), the boron-11 nmr of \([C_{6}H_{5}]_{3}P_{2}CuB_{3}H_{8}\) shows the presence of only one type of boron. All of the hydrogens appear to be equivalent in the proton nmr as in the case of the free B_{3}H_{8}^{-} ion. Low temperature nmr studies reveal that the exchange process which occurs in this molecule is quenched at -100°C. The analogous silver and gold complexes have been made, but both are unstable to reduction.

Each of these B_{3}H_{8}^{-} derivatives may be viewed as having tetraborane(10) structures in which a BH_{2} is replaced by the metal moiety. This analogy is particularly true for \((CH_{3})_{2}AlB_{3}H_{8}\) and \((CH_{3})_{2}GaB_{3}H_{8}\). Although an exchange process occurs in solution at
ambient temperature, the $^{11}\text{B}$ and $^1\text{H}$ nmr evidence is consistent with a static "tetraborane(10) like" structure at low temperature.

Reaction of $\text{B}_2\text{H}_8^-$ salts with bis (trialkyl or triaryl) phosphino platinum dichloride yields compounds of the formula $(\text{R}_3\text{P})_2\text{PtB}_3\text{H}_7$ which were shown by nmr and X-ray structure to be $\pi$-allyl analogues. Similar palladium and nickel complexes were also reported.

The structure of pentaborane(9) is similar to that of hexaborane(10). The five borons are arranged in a square pyramid and a hydrogen is terminally bonded to each boron. There are four B-H-B bridges below the basal plane of the molecule. Removal of one bridge proton by a strong base creates the conjugate base $\text{B}_2\text{H}_8^-$ which has a basal B-B bond. This basic site raises the possibility of metal insertion into the B-B bond to form a three center B-M-B bond.

Very acidic species such as $\text{BH}_3$ and $\text{B(CH}_3\text{)_2}^+$ have been shown to insert into the boron-boron bond of $\text{B}_2\text{H}_8^-$. Group IV metal derivatives of the formula $\mu$-$\text{R}_3\text{MB}_5\text{H}_8$ have also been prepared where $M=\text{Si}$ or Ge, $R=\text{C}_5\text{H}_5, \text{CH}_3, \text{H}$ and where $M=\text{Sn}$ or Pb, $R=\text{CH}_3$. The bridged silicon and germanium compounds have been found to isomerize at room temperature to the 2-substituted product. Other terminally substituted metal derivatives of pentaborane(9) are $2-[\text{Re(CO)}_5]\text{B}_2\text{H}_8$ and $2-[\text{Mn(CO)}_5]\text{B}_2\text{H}_8$. 
Brice and Shore reported the preparation of an air-stable copper(I) metalloborane, \([\text{C}_6\text{H}_5\text{F}]_2\text{CuB}_6\text{H}_8\). The boron-11 nmr spectrum consisted of a doublet due to the apical boron and a broad unresolved basal resonance. Although the boron-11 nmr is consistent with equivalent basal borons, the proton nmr from \(-60^\circ\) to \(+25^\circ\) shows two different basal terminal resonances and two distinct bridge hydrogen signals. This data is consistent with a static structure in which the copper atom is inserted into the boron-boron bond.

Brice and Shore also prepared \([\text{C}_6\text{H}_5\text{F}]_2\text{CuB}_6\text{H}_9\), but it is not known if a static structure prevails in solution. As in the case of the octahydropenta-borate(I-) analogue the boron-11 nmr exhibits one broad basal resonance. Due to this compound's low solubility no pmr spectra have been obtained for it.

During the preparation of this manuscript two hexaborane(10)-metal derivatives were reported. Davidson and co-workers synthesized \(\mu\text{-Fe(CO)}_4\text{B}_6\text{H}_{10}\) and \((\text{B}_6\text{H}_{10})_2\text{PtCl}_2\) was prepared by Brennan and Schaeffer. Preliminary X-ray crystal data for \((\text{B}_6\text{H}_{10})_2\text{PtCl}_2\) has shown that the platinum is inserted into the boron-boron bond of \(\text{B}_6\text{H}_{10}\).

A large number of metalloboranes have been derived from decaborane(14). In 1958, Siegel and co-workers reported that \(\text{B}_{10}\text{H}_{14}\) reacts as a monoprotic or diprotic
acid towards Grignard reagents such as methylmagnesium iodide\textsuperscript{92}.

\[
\text{B}_{10}\text{H}_{14} + \text{CH}_3\text{MgI} \xrightarrow{\text{Et}_2\text{O}} \text{B}_{10}\text{H}_{13}\text{MgI} + \text{CH}_4
\]

\[
\text{B}_{10}\text{H}_{14} + 2 \text{CH}_3\text{MgI} \xrightarrow{\text{Et}_2\text{O}} \text{B}_{10}\text{H}_{12}(\text{MgI})_2 + 2 \text{CH}_4
\]

Both magnesium derivates were isolated as etherates which were oils. It was later shown that a competing reaction, nucleophilic attack by the methyl group resulted in 10 to 20 per cent yields of $6$-$\text{CH}_3\text{B}_{10}\text{H}_{13}$\textsuperscript{91}. Reaction of $\text{B}_{10}\text{H}_{13}\text{MgI}$ with benzyl chloride\textsuperscript{92}, alkylfluorides\textsuperscript{94}, dimethyl and diethyl sulfate, and triethylxonium fluoroborate\textsuperscript{93} yielded substituted decaborane(14) derivatives. Unfortunately, the yields of alkyl decaboranes were not high and often a mixture of products was obtained. It was later shown that the reactivity of $\text{B}_{10}\text{H}_{13}\text{MgI}$ is very similar to that of $\text{NaB}_{10}\text{H}_{13}$\textsuperscript{95}.

Decaborane(14) has also been deprotonated by the dimethyl and diethyl derivatives of magnesium, zinc, and cadmium to form the corresponding $\text{B}_{10}\text{H}_{12}M^2\textsuperscript{2-}(\text{Ether})$ metalloboranes\textsuperscript{96,97}. Although dimethyl mercury does not react with decaborane(14), a mercury complex, $\text{Hg(B}_{10}\text{H}_{12})_2\textsuperscript{2-}$, has been prepared by an alternative synthetic approach\textsuperscript{98,99}. In ionizing solvent, the zinc and cadmium dodecahydrodecaborate compounds disproportionate to form $M^2+\left[M(\text{B}_{10}\text{H}_{12})_2\right]^{2-}$. The corresponding magnesium
derivative decomposes in hydrolytic solvents.

Initially it was thought that the tetrahedrally bonded metal bridged the 6,9- boron positions of the decaborane(14) framework. However, Muetterties and co-workers prepared a series of transition metal complexes of \( \text{B}_{10}^2 \); \( M(\text{B}_{10}^2) \), where \( M = \text{Co, Ni, Pd, Pt} \); \( M(\text{B}_{10}^2)L_2 \) where \( M = \text{Pd, Pt} \); \( L = \text{triorganophosphines} \); and \( M(\text{B}_{10}^2)L_3 \) where \( M = \text{Co, Rh, Ir} \); \( L = \text{CO and P(C}_6\text{H}_5)_3 \) which suggested an alternative. An X-ray diffraction study of \( (\text{CH}_3)_4\text{Ni}^2(\text{B}_{10}^2) \) showed the nickel atom was simultaneously incorporated on the open face of both \( \text{B}_{10}^2 \) ions to yield two \( \text{B}_{10}^2 \) atom icosahedral frameworks. The \( \text{B}_{10}^2 \) ion may be viewed as a bidentate ligand, but the bonding is possibly more delocalized than this model may imply. A recent X-ray crystal study- established that a similar bonding scheme is involved in \( \text{Zn}(\text{B}_{10}^2)_2 \). The borane anions are oriented in a tetrahedral configuration around the zinc as shown in Figure 3a whereas square planar coordination occurs in the nickel complex. It has recently been determined that \( \text{CdB}_{10}^2 \cdot 2\text{Et}_2\text{O} \) is actually dimeric in the solid state. In a related, but unique structure, two cadmium atoms are each simultaneously bonded to the same two \( \text{B}_{10}^2 \) units as shown in Figure 3b.

The compounds \( M(\text{B}_{10}^2)_2 \) (\( M = \text{Co, Ni, Pd, Pt} \))
Figure 3. Heavy atom structures of (a) Zn(B_{10}H_{12})_2^{2-} and (b) Cd(B_{10}H_{12}) \cdot 2Et_20 dimer. The hydrogens and ethyl carbon atoms are not shown.
have also been prepared by a different synthetic procedure\textsuperscript{104}. Muettertties recently described an apparently isostructural series of derivatives (CO)\textsubscript{4}M(B\textsubscript{10}H\textsubscript{12})\textsuperscript{2-} (M = Cr, Mo, W) which are obtained from a novel series of quasi-icosahedral derivatives (CO)\textsubscript{4}M(B\textsubscript{10}H\textsubscript{10}COH)\textsuperscript{2-} or (CO)\textsubscript{3}CCMOCB\textsubscript{10}H\textsubscript{10}\textsuperscript{2-}.\textsuperscript{105} The B\textsubscript{10}H\textsubscript{12}\textsuperscript{2-} ion may be also acting as a bidentate ligand in the anion B\textsubscript{10}H\textsubscript{12}AlH\textsubscript{2}\textsuperscript{-}\textsuperscript{106} and the complex pyCoX\textsubscript{2}B\textsubscript{10}H\textsubscript{11}py, where py = pyridine and X = Cl, Br\textsuperscript{99}.

The moiety [(C\textsubscript{2}H\textsubscript{5})\textsubscript{3}P]\textsubscript{2}Pt\textsuperscript{2+} has not only been inserted into the B\textsubscript{10}H\textsubscript{12}\textsuperscript{2-} framework\textsuperscript{99}, but also into the isostructural B\textsubscript{9}H\textsubscript{10}S\textsuperscript{2-} structure as well as B\textsubscript{9}H\textsubscript{11}\textsuperscript{2-} and B\textsubscript{8}H\textsubscript{12}\textsuperscript{2-}.\textsuperscript{107} Other B\textsubscript{9}H\textsubscript{12}S\textsuperscript{2-} complexes which have been prepared include [(C\textsubscript{6}H\textsubscript{5})\textsubscript{3}P]\textsubscript{3}MB\textsubscript{9}H\textsubscript{12}S where M = Cu, Ag, Au\textsuperscript{59}. An X-ray diffraction study of the gold complex revealed that no interaction occurs between the gold atom and the thiaborane anion\textsuperscript{59}. Numerous other metal compounds of higher boranes have proven to be primarily ionic such as [(C\textsubscript{6}H\textsubscript{5})\textsubscript{3}P]\textsubscript{3}MB\textsubscript{9}H\textsubscript{4} where M = Cu, Ag, Au; [(C\textsubscript{6}H\textsubscript{5})\textsubscript{3}P]\textsubscript{3}MB\textsubscript{10}H\textsubscript{13} where M = Ag, Au; [(C\textsubscript{6}H\textsubscript{5})\textsubscript{3}P]\textsubscript{3}MB\textsubscript{11}H\textsubscript{14}, where M = Cu, Au. Some covalent bonding may be involved in the copper and silver derivatives [(C\textsubscript{6}H\textsubscript{5})\textsubscript{3}P]\textsubscript{2}MB\textsubscript{10}H\textsubscript{13}\textsuperscript{59}. The compound (CH\textsubscript{3})\textsubscript{2}Tl\textsuperscript{+}B\textsubscript{10}H\textsubscript{13}\textsuperscript{-} appears to be ionic, but a covalent interaction may occur in (CH\textsubscript{3})\textsubscript{2}Tl\textsuperscript{+}[(CH\textsubscript{3})\textsubscript{2}Tl\textsuperscript{-}TlB\textsubscript{10}H\textsubscript{12}\textsuperscript{-}]\textsuperscript{108}.

The anion n-B\textsubscript{18}H\textsubscript{20}\textsuperscript{2-} which may be viewed structurally
as two fused $\text{B}_{10}$ frameworks possibly bonds like the $\text{B}_{10}\text{H}_{12}^{2-}$ ligand in the complexes $(\text{CO})_3\text{Co}(n-\text{B}_{18}\text{H}_{20})^{-}$, 

$$[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Ni}(n-\text{B}_{18}\text{H}_{20})$$ and $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2\text{Ni-}
(n-\text{B}_{18}\text{H}_{20})^{109}$.

The extensive chemistry of metalallocarborane compounds has been discussed in numerous reviews$^{110-112}$. Various carborane anions such as $\text{B}_9\text{C}_2\text{H}_{11}^{2-}$ possess an open pentagonal face which contain six delocalized electrons in five nearly equivalent orbitals. Metal ions have been found to bond to the faces of these anions in a manner similar to metal-$\Pi$-cyclopentadienyl compounds. In this way stable compounds such as $[\Pi-\text{C}_6\text{H}_5]\text{Fe}[\Pi-(3)-1,2,-\text{B}_9\text{C}_2\text{H}_{11}]$ have been prepared. In the past five years scores of metalloboranes have been made with this and ten other related carborane anions bonded to numerous transition and representative metals.

This cursory discussion of metalloborane chemistry provides an indication of its breadth and its diversity. At least one metalloborane derivative has been prepared with most of the stable boron hydride anions, but with the possible exception of $\text{BH}_4^-$, none have been studied extensively. Most notably lacking is the metalloborane chemistry of the middle boron hydride anions which are generally very air sensitive and thermally unstable. In addition to the many varied types of metal-borane bonding which have been observed, interest has been
further stimulated by the fluxional character exhibited by many of these metal derivatives. Obviously many years of research remain to be done in this rapidly expanding area of boron hydride chemistry.

III. Statement of the Problem

The Brønsted acidity of the bridge hydrogens of boron hydrides is well known. Johnson and Shore established the relative acidities of the following series: $B_{10}^1 > B_{6}^1 > B_{5}^1$. Decaborane(14) has been deprotonated by Grignard reagents and dialkyl derivatives of magnesium, zinc, and cadmium to form a series of interesting metalloboranes. Therefore, it was of interest to determine if the weaker acids hexaborane(10) and pentaborane(9) would also react with these organo-magnesium, zinc and cadmium reagents to form stable metalloboranes.

Boron-11 and proton nuclear magnetic resonance studies of the resulting compounds were undertaken to elucidate the nature of the metal-borane bonds. Specifically, it was to be determined if metal insertion into the basal boron-boron bond had occurred. The preparation of thermally stable nonahydrohexaborate(1-) derivatives was particularly desirable to provide crystals for X-ray diffraction studies. In addition to providing definitive information on the metal-borane interaction,
it would possibly establish the structure of $\text{B}_6\text{H}_9^-$ in the solid state. The possible synthetic value of the borane magnesium halide derivatives was to be investigated.

NMR evidence indicates that the nonahydrohexaborate(1-) ion, $\text{B}_6\text{H}_9^-$, has two equivalent basal boron-boron bonds. The basicity of both bonds has been established by protonation reactions. Thus, the nonahydrohexaborate(1-) ion has the potential to act as a bidentate ligand. To explore this possibility an appropriate transition metal compound, $(\text{h}^5\text{C}_5\text{H}_5)_2\text{TiCl}$, was chosen for reaction with $\text{KB}_6\text{H}_9$ and the resulting metalloborane was studied by numerous instrumental techniques.
EXPERIMENTAL

I. Apparatus and Procedures

A. Vacuum System

Since the boron hydrides and organometallic compounds utilized were very reactive toward air and moisture, often thermally unstable, and in some cases extremely toxic, standard vacuum line techniques were used. The volatility of most of the compounds and solvents employed made manipulations in the vacuum line very convenient. Non-volatile materials were handled in the glove box and then transferred to the vacuum line.

The vacuum line consisted of a pumping station, a main manifold, two reaction manifolds, and a fractionation train. The pumping station included a mechanical pump and a mercury diffusion pump which were each protected by a \(-196^\circ C\) trap. One reaction manifold used 4 mm greased stopcocks, whereas the second was made of Kontes 4 mm teflon valves which provided a grease-free system. Both manifolds employed 14/35 standard taper ground glass joints and mercury blowouts which were useful to monitor the pressure in reaction vessels.
and prevented the pressure from exceeding one atmosphere. The fractionation train consisted of four U-traps with greased stopcocks, and was used for separation of volatile materials. Since the volume of each trap was determined by calibration with SF$_6$, they were used to measure amounts of condensible gases and liquids with high vapor pressures. The high vacuum stopcocks on the line were greased with Apiazon 100 or a 50/50 mixture of Apiazon N and T.

Mercury manometers were employed for pressure measurements and the ultimate vacuum was determined with a McLeod gauge. A Toepler system calibrated with SF$_6$ was used to measure amounts of non-condensible gases.

B. Glove Box

Three different inert atmosphere glove boxes were used for handling air-sensitive compounds. In each case the port was evacuated and refilled with gas from the box twice before chemicals and apparatus were admitted into the box. A stainless steel box made by Kewanee Scientific Company was continuously purged with nitrogen dried by passage through four columns containing Linde 4 Å molecular sieve, calcium hydride, and phosphorous pentoxide. A small glove box with a static helium atmosphere that was constructed within the chemistry
department, employed stirred sodium/potassium alloy as a dessicant and oxygen scavenger. A large Vacuum/Atmospheres glove box was used for handling all Ti(III) compounds. A recirculating purification system was made using copper tubing. The water and oxygen levels in the nitrogen atmosphere were maintained at 1 p.p.m. by the use of Linde 13X molecular sieve and Dow's Q-1 respectively. For details of this purification system see Appendix A.

C. Reaction Vessels

Pyrex tubes and round bottom flasks with standard taper ground glass joints were used as reaction vessels. Teflon valve or greased stopcock adaptors with the appropriate standard taper joints were used to attach the vessels to the vacuum line. The ground glass surfaces were lubricated with Dow Corning high vacuum silicon grease. Reaction solutions were stirred with teflon covered magnetic stirring bars. The bar could be turned even when the vessel was at low temperature in a dewar flask by a powerful magnet mounted in a motor driven stirring head.

D. Nuclear Magnetic Resonance Spectra (NMR)

Boron-11 nmr spectra were obtained on a Varian HA-100 high resolution spectrometer operating at 32.08 MHz in the HR mode. An external oscillator was used to
vary the sideband frequency from 2500 Hz up to 3400 Hz depending upon the situation. Liquid BCl$_3$ and BF$_3$·OEt$_2$ in sealed capillaries were used as external standards. All chemical shifts reported are relative to BF$_3$·OEt$_2$. The chemical shift of BCl$_3$ was determined experimentally to be -46.8 p.p.m.

Proton nmr spectra were also recorded on the Varian HA-100 spectrometer in the HA mode operating at 100 MHz. Benzene, chloroform, or methylene chloride proton resonances were used as a lock signal.

Heteronuclear boron-11 and proton spin decoupling was achieved by irradiation of the sample with an RF signal generated by a General Radio Company 1164-A coherent decade frequency synthesizer and a Hewett Packard 3722 A noise generator. The decoupler, which was assembled by Mr. John Kelly, also employed a Hewett Packard 461 A amplifier and an Electronic Navigation Industries 320L RF power amplifier.

Air sensitive sample solutions were tipped from reaction vessels through a side arm into 5 mm o.d. nmr tubes and sealed with a torch flame.

E. Infrared Spectra

All infrared spectra were obtained on a Perkin-Elmer model 457 spectrometer and were calibrated using a polystyrene film. Solid samples were finely ground
in the glove box and run as mulls in nujol on hexachloro-
butadiene between KBr plates in an airtight Teflon
holder. Gas samples were held in a 10 cm glass cell
with a Teflon valve and standard taper joint. The
KBr plates were sealed to the cell with Kel-F wax.

F. X-ray Powder Diffraction Patterns

X-ray patterns were obtained with a Debye-Scherrer
type camera of 11.46 cm diameter and a North American
Phillips X-ray generator utilizing a copper target with
a nickel filter. A 12 milliamp current at 32 kilovolts
was maintained and exposure times of eight to twenty
hours were used depending on the compound.

The samples were finely ground in the glove
box and loaded into 0.3 mm capillary tubes. Silicone
grease was used to seal the tubes and they were sealed with
a small flame outside the box.

G. Electron Paramagnetic Resonance Spectra (EPR)

All electron paramagnetic resonance spectra were
run on a Varian V4500-10A EPR employing a Varian V4560
100 KC field modulation unit. The frequency in the X
band region was measured by an echo box manufactured
by Aeromotive Equipment Corporation. The magnetic
field was measured by a Varian Fieldial Mark I which
was calibrated with diphenylpicrylhydrazine (dpph).
The esr cell consisted of a 5 mm quartz tube with a
graded seal to a Pyrex standard taper outer 10/30 joint. The cell was fitted with a Fisher-Porter Teflon stopcock adaptor. The epr spectra were obtained by Mr. Steve Hallack.

II. Starting Materials

A. \( \text{B}_5\text{H}_9 \)

Pentaborane(9) was purchased from the Gallery Chemical Company and was used without purification.

B. \( \text{B}_6\text{H}_{10} \)

Hexaborane(10) was prepared by the reaction of \( \text{LiB}_5\text{H}_8 \) with \( \text{B}_2\text{H}_6 \) in \( (\text{CH}_3)_2\text{O} \) and by the reaction of \( \text{K}[\text{1-BrB}_5\text{H}_7] \) with diborane in \( (\text{CH}_3)_2\text{O} \) according to the reaction of Brice, Johnson, and Shore. The hexaborane(10) was fractionated until the vapor pressure agreed with the accepted value of 7.47 mm at 0°C, and stored under vacuum at -78°C.

C. \( \text{CH}_3\text{MgBr} \)

Methylmagnesium bromide was prepared on the vacuum line by reacting methyl bromide from a cylinder (Matheson) with excess magnesium in diethyl ether. The Grignard concentration was determined by toeplerizing the methane evolved by methyl alcohol hydrolysis. The solution was stored under dry nitrogen in a bulb with a Teflon
D. \((\text{CH}_3)_2\text{Mg}\)

Dimethylmagnesium was prepared by the addition of anhydrous dioxane to a solution of methylmagnesium bromide and subsequent isolation of the ether soluble product\(^{113}\). The active methyl concentration was determined by methanol hydrolysis and magnesium content of the sample was determined by EDTA titration. A potentiometric titration using silver nitrate assured the absence of a measurable quantity of bromide ions.

E. \((\text{CH}_3)_2\text{Zn}\)

Dimethylzinc was formed by disproportionation of methylzinc iodide, which was produced by the reaction of methyl iodide with a zinc-copper couple\(^{114}\). The zinc-copper couple was prepared by heating a 90/10 mixture of the powdered metals to the melting point of zinc. Turnings of the resulting alloy were made using a drill press. The product was fractionated until the infrared spectrum and vapor pressure (123 mm at 0°)\(^{115}\) agreed with reported data, then stored in a vessel with a Teflon stopcock.

F. \((\text{CH}_3)_2\text{Cd}\)

Dimethylcadmium was produced on the vacuum line by the addition of anhydrous cadmium chloride (J.T.}
Baker) to a diethyl ether solution of methyllithium (Foote Chemical Company)\textsuperscript{116}. The volatile products were repeatedly fractionated through a $-50^\circ\text{C}$ trap until the infrared spectrum included only absorptions attributable to dimethylcadmium. It was stored at $-78^\circ\text{C}$ in a vessel with a Teflon stopcock.

G. $\text{(CH}_3\text{)}_2\text{Hg}$

Dimethylmercury was generously supplied by Dr. Thomas Durkin.

H. $\text{(C}_5\text{H}_5\text{)}_2\text{TiCl}$

Bis(cyclopentadienyl)titanium(III)chloride was prepared by the method of Reid and Wailes\textsuperscript{117}. Anhydrous tetrahydrofuran was added to equimolar quantities of titanium(III) chloride (Anderson Chemical Company) and bis(cyclopentadienyl)magnesium which was prepared by the procedure of Barber\textsuperscript{118}. The green-brown product was sublimed at $170^\circ$ and melted at $286^\circ - 287^\circ\text{C}$. All manipulations were performed under high vacuum or under an inert atmosphere with rigorous exclusion of moisture and oxygen.

I. $\text{KH}$

Potassium hydride was purchased as a 50\% mineral oil suspension from ROC/RIC. Repeated washing with pentane in an extractor removed the oil. The activity
of the KH was determined by measurement of the evolved hydrogen upon hydrolysis with methanol. It was 98% active and was stored in the dry box.

J. HCl

Hydrogen chloride was purchased from the Matheson Company and was used directly from the cylinder.

K. Solvents

Diethyl ether, tetrahydrofuran, methylene chloride, chloroform, and dioxane were dried over lithium aluminum hydride and distilled into storage bulbs with Teflon stopcocks. Dimethyl ether was likewise dried, but was stored at -78° using a long vessel with a greased stopcock.

L. Deuterated Solvents

Methylene chloride-d₂ and tetrahydrofuran-d₈ were purchased from Mallinckrodt Nuclear Company. The CD₂Cl₂ was dried over lithium aluminum hydride and the THF-d₈ was dried with 3A molecular sieves. Methyl ether-d₆ was prepared by the reaction of KOCH₃ with CD₃I in tetrahydrofuran. The CD₃I and CD₃OD were purchased from Stohler Isotopes Company. All deuterated solvents were stored in glass vessels with Teflon stopcocks.
III. Analytical Procedures

A. Hydrolyzable Hydrogen

In the dry box a carefully weighed sample (50-100 mg) of the compound to be analyzed was placed in a hydrolysis tube. The tube was fitted to a Fisher-Porter stopcock adaptor with a Penton Coupling and a Solve-seal seal. The vessel was then evacuated on the line and two milliliters of methanol dried with sodium was condensed into the tube. With the stopcock closed tightly the vessel was warmed to room temperature. To avoid a very high pressure in the tube the solution was periodically cooled to -196\(^\circ\) and the hydrogen was measured with the Toepler pump. After the rate of hydrogen evolution had slowed, several millimoles of HCl were added to dissolve any precipitate and to complete the hydrolysis. Generally, complete hydrolysis of \(\text{B}_6\text{H}_9^-\) compounds did not require elevated temperatures.

One molecule of hydrogen is evolved for each hydridic hydrogen present in the compound. In addition, one hydrogen molecule is evolved for each boron-boron bond present in the compound. Each \(\text{B}_6\text{H}_9^-\) has nine hydridic hydrogens and five boron-boron bonds; thus, fourteen moles of hydrogen are expected as predicted by the balanced equation.

\[
\text{B}_6\text{H}_9^- + 18 \text{CH}_3\text{OH} + \text{H}^+ \rightarrow 6 \text{B(OCH}_3\text{)}_3 + 14 \text{H}_2
\]
B. **Boron**

The trimethylborate which was formed in the methanolysis of the compound was distilled on the vacuum line into a 100 ml bulb containing 5 ml of doubly distilled, demineralized water at -196°. The vessel containing the hydrolysis products was heated to assure complete transfer of the B(OCH₃)₃. When the distillation was finished the stopcock on the receiving vessel was closed and the bulb was slowly warmed to room temperature. This results in the total hydrolysis of the trimethylborate to boric acid. The solution was then quantitatively transferred to a volumetric flask and diluted to 100 ml.

The pH of a 10 ml aliquot was then adjusted to 6.8 and mannitol was added in excess above saturation. The solution was then titrated with 0.050 N NaOH to the inflection point. This was accurately identified by plotting $\Delta \mathrm{pH}/\Delta V$ versus $V$. One equivalent of sodium hydroxide is required for each equivalent of boric acid present.

C. **Magnesium, Zinc, and Cadmium**

The non-volatile solid remaining in the hydrolysis tube after the distillation of the trimethylborate was dissolved in distilled water. This solution was quantitatively transferred to a volumetric flask and diluted to 50 ml. A 10 ml aliquot of the sample solution
and 20 ml of a pH 10 buffer solution were placed in an Erlenmeyer flask. A small amount of Eriochrome Black T (G. Frederick Smith Chemical Company) was added to the solution to give it a faint red color. The solution was then titrated with a 0.0100 N EDTA (disodium dihydrogen ethylenediaminetetraacetate dihydrate) solution until the color was a distinct blue. Magnesium, zinc, and cadmium form one to one complexes with EDTA.

IV. Reactions of B₆H₁₀ with Dimethyl Derivatives of Mg, Zn, Cd, and Hg

A. Preparation and Isolation of Mg(B₆H₁₀)₂·2THF

In the dry box 1.00 ml of 0.428 M (CH₃)₂Mg in THF was syringed into a reaction bulb which was fitted to a vacuum line extractor. On the line the solution was frozen, the vessel was evacuated and 0.85 mmole of B₆H₁₀ was condensed into the bulb. The B₆H₁₀ was measured as a liquid at 0° (0.69 g/ml) in a calibrated tube. The reaction mixture was then warmed to -78°. The walls of the vessel were warmed slightly to allow the hexaborane(10) to melt and flow into the solution. Immediately, rapid methane evolution commenced accompanied by the formation of a white solid. The mixture was stirred at -78° until the pressure as monitored on the blow out no longer increased. The vessel was then frozen to -196° and the methane was measured with the Toepler
pump. The non-condensable gas amounted to 0.431 mmole. The reaction mixture was again warmed. At -45° methane evolution proceeded at a slow rate. After 90 minutes 0.419 mmole of gas had been evolved. Thus, the total methane evolution was 0.850 mmole. If a 0° bath is used for the second step of this reaction it is completed in 15 minutes. In a similar experiment the second equivalent of CH₄ was evolved at -78°, but required six hours for complete reaction.

At this point only a "dry" white solid remained in the reaction vessel. About 10 ml of THF were added to form a slurry at 0°. The extractor was then inverted and the white solid was washed several times with the THF at low temperature. After the THF was removed from the extractor the stark white solid was pumped on for several hours at room temperature. In the dry box the product was transferred to a glass tube fitted with a stopcock adaptor. On the line the solid was pumped on as the temperature was slowly raised to 65°. The temperature was maintained at 65° until THF no longer came off the solid. The THF can be removed at room temperature but requires pumping on the solid for 24-36 hours. The product was stored in the vessel under vacuum. Yields of 95% were obtained.

Heating the solid to 80° caused slow decomposition. The solid melted with rapid decomposition at 100°.
Although the compound is stable for weeks at room temperature it was generally stored at \(-78^\circ\) C.

The preparation of Mg(B\(_6\)H\(_9\))\(_2\) may be done in methyl ether at the same temperatures as in THF, but the temperatures must be raised about 60-70\(^\circ\) C for the same reaction in diethyl ether. Removal of the methyl ether from the reaction product results in an intractable gum. No solid could be isolated from the oil produced by the reaction in diethyl ether.

The elemental analysis, proton nmr and infrared spectrum indicated the presence of coordinated solvent in the white solid isolated from THF. The elemental analysis is consistent with two molecules of THF per formula. Calculated for Mg(B\(_6\)H\(_9\))\(_2\)·2THF: B, 39.2; Mg, 7.35; mmole H\(_2\)/mmole formula, 28.0. Found: B, 38.3; Mg, 7.44; mmole H\(_2\)/mmole formula, 27.5.

The proton nmr spectrum of Mg(B\(_6\)H\(_9\))\(_2\)·2THF in CD\(_2\)Cl\(_2\) at ambient temperature obtained at low RF power settings consists of a triplet at 5.907, a multiplet at 7.927 and a broad singlet at 13.247. The area ratios are 1.00: 0.99: 0.78 respectively.

The infrared spectrum of Mg(B\(_6\)H\(_9\))\(_2\)·2THF in a nujol mull is shown in Figure 4. A hexachlorobutadiene mull was used to obtain the regions of the spectrum masked by nujol. Absorptions which may be assigned to coordinated THF are as follows: 2993(m),
Figure 4. Infrared spectrum of Mg(B₆H₉)₂·2THF in nujol.
2930(w), 2905(m), 1472(w), 1457(w), 1448(w), 1300(w),
1250(br,m), 1180(w), 1010(s), 956(m), 915(m) cm⁻¹.
The peaks which may be attributed to the B₆H₉⁻ are
as follows: 2580(s), 2540(s), 2490(s), 1990(w,br),
1890(w,br), 1790(w,br), 770(m), 714(m), 690(w), 623(m),
597(m), 569(w) cm⁻¹. Bands which cannot be unambiguously
assigned to the borane or the solvent are at 1407(m),
1388(m,sh), 1349(m), 1065(m,sh), 1058(m), 1041(m),
872(s), 861(s), 830(m), and 800(m) cm⁻¹. The B-H
terminal region from 2600-2400 cm⁻¹ did not change
when the compound was dissolved in methylene chloride.

The compound is very sensitive to air. A strong
odor of hexaborane(10) was generated upon exposure to
the atmosphere and the infrared spectrum showed very
weak B-H terminal bands after a nujol mull was left
open to the air for five hours.

The solid Mg(B₆H₉)₂·2THF was reacted with HCl(ℓ)
at -111° for ten minutes. The volatile products were
fractionated through a -97° trap. Hexaborane(10) and
THF collected in the -97° trap were identified by their
infrared spectrum. Measurement of the hydrogen produced
by the reaction of the regenerated hexaborane(10) with
excess potassium hydride was used to determine the
yield of B₆H₁₀. A 65% recovery of hexaborane(10) was
obtained.

The X-ray powder diffraction pattern data for
Mg(B₆H₉)₂·2THF is listed in Table 1.

Single crystals of Mg(B₆H₉)₂·2THF were grown from a saturated methylene chloride solution by slow cooling from +20° to -10° using the apparatus discussed in Appendix B. Crystals were mounted in a dry box using sodium potassium alloy as an oxygen scavenger and desiccant. From precession X-ray camera data the cell dimensions were determined to be $a=b=11.29\ \AA$ and $c=16.41\ \AA$.

Interpretation of the zero and first layer photographs primarily by Mr. John Ruble showed the space group to be $P\overline{4}_{1}2_{1}2$ or $P4_{3}2_{1}2$. Diffractometer data was collected and interpreted by Dr. Edward Meyers and Dr. W. R. Clayton, but packing disorder of the crystal prevented the molecular structure from being determined.

B. Reaction of B₆H₁₀ with (CH₃)₂Mg in 1:1 Mole Ratio

In the glove box 2.0 ml of 0.35 M dimethylmagnesium in THF was syringed into a reaction tube which was fitted to a vacuum line extractor. On the line the solution was cooled to -196° and the vessel was evacuated. Then, exactly 0.70 millimoles of B₆H₁₀ was condensed into the vessel. The temperature of the solution was raised to -78° and the walls were allowed to warm further to melt the B₆H₁₀. The methane evolved was measured with the Toepler pump to assure that the reaction was completed. About 10 ml of THF was distilled into the vessel and
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it was cooled to -196°. The extractor was then inverted and the cold jacket was filled with a dry ice-isopropanol slush. The white solid product was repeatedly washed with the THF. During the extraction the temperature was maintained below 0°. The THF was then distilled from the extractor and the product was pumped on for 24 hours at room temperature.

The infrared spectrum in nujol and X-ray powder pattern were identical to those of Mg(B₆H₉)₂·2THF. Stirring a sample of the solid in HCl(l) at -78° did not result in the evolution of a significant amount of methane. An elemental analysis of the solid also indicated the presence of Mg(B₆H₉)₂·2THF. Calculated from Mg(B₆H₉)₂·2THF: B, 39.22; Mg, 7.35; mmole H₂/mmole formula, 28.0. Found: B, 36.49; Mg, 7.59; mmole H₂/mmole formula, 28.5. The slightly high Mg and H₂(CH₄) and low boron may be due to the presence of some CH₃MgB₆H₉·2THF.

Reaction of methanol at -78° with the THF soluble solids washed through the frit during the extraction resulted in the evolution of 0.64 mmoles of CH₄. Acid hydrolysis of the resulting solution evolved only a trace of hydrogen.

C. Reaction of B₆H₁₀ with (CH₃)₂Zn

In a typical reaction 1.0 mmoles of (CH₃)₂Zn
measured by liquid volume (1.39 g/ml)\textsuperscript{120} and about 0.1 milliliter of THF were condensed into a reaction tube which was fitted to a stopcock adaptor. Then 1.0 millimole of hexaborane(10) was condensed in at -196\degree. The vessel was allowed to warm to 0\degree and it was stirred vigorously. After one hour 85\% of the CH\textsubscript{4} expected was evolved. Generally, the reaction rate had significantly decreased at this point and decomposition had begun so the reaction was stopped. Nearly all of the methane was evolved if the reaction was allowed to continue but the solution turned yellow-green and some reduction of the zinc to metal was noted. Upon termination of the reaction excess dimethyl-zinc and hexaborane(10) were distilled from the reaction vessel. A viscous yellow oil remained in the reaction tube.

A solid was isolated from this oil by dissolving it in chloroform followed by the addition of diethyl ether. A white precipitate resulted. All volatiles were then distilled from the vessel leaving a white crystalline solid which was only partially soluble in chloroform. Equal volumes of chloroform and diethyl ether were condensed into the vessel and were frozen at -196\degree. Under dry nitrogen the reaction tube was transferred to a vacuum line extractor for filtration. The white solid was washed several times at low tem-
perature. The solvents were then distilled from the extractor and the product was pumped on for several hours at room temperature.

The elemental analysis indicated a product of the formula \( \text{Zn(B}_6\text{H}_9)_2 \cdot 2\text{THF} \). Calculated: Zn, 17.6; B, 34.8, mmole \( \text{H}_2/\text{mmole formula} \) 28.0. Found: Zn, 17.8; B, 34.6, mmole \( \text{H}_2/\text{mmole formula} \) 28.6.

The yield of \( \text{Zn(B}_6\text{H}_9)_2 \cdot 2\text{THF} \) based on the \( \text{B}_6\text{H}_{10} \) used was 50%.

The infrared spectrum of \( \text{Zn(B}_6\text{H}_9)_2 \cdot 2\text{THF} \) which was recorded as a nujol mull is shown in Figure 5. Absorptions masked by the nujol were obtained using a hexachlorobutadiene mull. Absorptions which may be attributed to coordinated THF are as follows: 2992(m), 2955(w), 2932(w), 2905(m), 2880(w), 1448(s), 1312(w), 1300(w), 1262(w), 1248(w), 1178(w), 1138(w), 1018(s), 973(m), 914(m), 860(s,br) cm\(^{-1}\). Peaks due to B-H terminal stretches are at 2587(vs), 2540(vs) and 2520(sh) cm\(^{-1}\) and B-H-B absorptions are at 1960(vw,br), 1920(w), and 1880(vw,br) cm\(^{-1}\). Other peaks which may be due to \( \text{B}_6\text{H}_9 \) are at 1385(m), 1070(m), 765(m), 710(m), 627(m), 610(m), 585(m), 561(w) cm\(^{-1}\). Bands which may be due to either THF or \( \text{B}_6\text{H}_9 \) are at 1385(m), 1365(w), 1348(m), 1070(m), 1050(m), 1038(m), 795(m,sh) and 787(m) cm\(^{-1}\). The infrared shows no change after several hours at room temperature.
Figure 5. Infrared spectrum of Zn(B₆H₉)₂·2THF in nujol.
The X-ray powder diffraction data for Zn(B₆H₉)₂·2THF is reported in Table 2.

D. Reaction of B₆H₁₀ with (CH₃)₂Cd

In a typical reaction 1.50 millimoles of B₆H₁₀ and 0.15 milliliters of THF were condensed into a reaction tube fitted with a stopcock adaptor. The tube was warmed to allow the liquids to flow to the bottom of the vessel. Then 1.50 millimoles of (CH₃)₂Cd measured by liquid volume (1.99g/ml) was condensed into the tube at -196°. The reaction solution was then vigorously stirred at the temperature of a cyclohexane slush (+6.5°). This temperature provided a reasonable reaction rate with minimum decomposition. The reaction mixture appeared to be light-sensitive. Decomposition that yielded metallic cadmium was reduced by excluding light from the vessel with aluminum foil. In two and one-half hours at 6.5° 1.2 millimoles of methane was evolved. Ninety-five per cent methane evolution could be obtained by further reaction at the expense of increased decomposition.

Generally, after 75% of the expected methane was evolved all volatiles (THF, B₆H₁₀ and (CH₃)₂Cd) were distilled from the resulting yellow oil. Removal of the volatiles results in the formation of a white solid. Five milliliters of chloroform and five milliliters of diethyl ether or pentane were then condensed
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into the reaction tube. This solvent mixture dissolved
the yellow decomposition products, but not the white
solid. The mixture was then frozen to -196\(^{\circ}\), and the
tube was transferred to a vacuum line extractor under
dry nitrogen. The white solid was then filtered, and
washed several times at -78\(^{\circ}\) with the solvent mixture.
The solid produced in this reaction was extremely fine
so careful slow filtration was necessary to prevent
it from passing through the frit. Exposure of the product
to light was minimized during the extraction. The
solvent was distilled from the extractor and the solid
was pumped on for about one hour. The extractor was
then taken into the dry box and the solid was transferred
to a storage tube.

The elemental analysis best fit a formula of
\(\text{Cd}(\text{B}_6\text{H}_9)_2\). Calculated: cadmium, 43.3\%; boron, 49.8\%;
mmole \(\text{H}_2/\text{mmole formula}, 28.0\). Found: cadmium, 41.5\%;
boron, 45.2\%; mmole \(\text{H}_2/\text{mmole formula} 26.7\). The low
analysis may indicate the presence of some THF in the
sample.

The yield of \(\text{Cd}(\text{B}_6\text{H}_9)_2\) based on the \(\text{B}_6\text{H}_{10}\) used
was 35%.

The infrared spectrum of the solid compound
shown in Figure 6 was obtained as a nujol mull. A
hexachlorobutadiene mull was used to record the regions
of the spectrum obscured by nujol. Absorption due
Figure 6. Infrared spectrum of Cd(BgH₉)₂ in nujol.
to \( \text{B}_6\text{H}_9^- \) are as follows\(^9\): 2620 (m), 2610 (s), 2575 (s), 2565 (s), 2545 (s), 1940 (w, br), 1830 (w, br), 790 (m), 755 (w), 718 (m), 680 (w), 623 (m), 602 (m) cm\(^{-1}\). A very weak set of C-H bands were observed at 2960, 2910 and 2880 cm\(^{-1}\) which may be due to the presence of some THF. Noticeably absent are any bands from 1350 to 1050 cm\(^{-1}\), numerous strong bands from 1050 to 1000 cm\(^{-1}\) and a strong broad peak at 865 cm\(^{-1}\) which are observed for coordinated THF\(^9\). Peaks which are unassigned are at 1500 (m), 1440 (w), 1420 (w), 1021 (m), 1003 (s), 898 (w), 858 (w), 818 (w). These may be due to \( \text{B}_6\text{H}_9^- \) and very strong THF peaks.

Although solutions of \( \text{Cd(\text{B}_6\text{H}_9)}_2 \) are unstable at room temperature the pure solid exhibits thermal stability. A sample of the compound heated to 90° for one hour showed no significant changes in its infrared spectrum. Solid \( \text{Cd(\text{B}_6\text{H}_9)}_2 \) also has some stability towards air. A sample of the solid that was exposed to the atmosphere for 25 minutes did not generate a hexaborane(10) odor and showed only minor decomposition in the infrared spectrum. Very broad bands had grown in at 3400, 1600 and 1050 cm\(^{-1}\) which is indicative of boric acid\(^{121}\).

The X-ray powder diffraction pattern data for \( \text{Cd(\text{B}_6\text{H}_9)}_2 \) is reported in Table 3.
### TABLE 3

X-RAY POWDER DIFFRACTION DATA FOR Cd(D6H)2

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E. Reaction of $\text{B}_6\text{H}_{10}$ with $(\text{CH}_3)_2\text{Hg}$

Approximately 0.3 ml of THF, 0.50 millimoles of $\text{B}_6\text{H}_{10}$ and 0.50 millimoles of $(\text{CH}_3)_2\text{Hg}$ measured by volume as a gas, were condensed into a reaction tube cooled to -196°. The reactants were slowly warmed to room temperature but no gas evolution commenced. Stirring at room temperature for eight hours yielded a negligible amount of non-condensible gas.

The boron-11 nmr spectrum of the sample solution ($\delta_b=-14.3$ ppm, $J=156$ Hz, $\delta_a=51.5$ ppm, $J=156$ Hz) did not differ from that of hexaborane(10) in ether.\(^9\)

V. Reactions of $\text{B}_6\text{H}_{10}$ and $\text{B}_5\text{H}_9$ with Grignard Reagents

A. Reaction of $\text{B}_6\text{H}_{10}$ with $\text{CH}_3\text{MgBr}$

The Grignard reagents $\text{CH}_3\text{MgBr}$ and $\text{CH}_3\text{MgI}$ deprotonate hexaborane(10) in ether solvents to generate methane and magnesium borane derivatives.

In a typical reaction 1.0 ml of 1.50 M $\text{CH}_3\text{MgBr}$ in THF was syringed into a reaction tube in the dry box. The reaction vessel which was fitted with a Teflon stopcock adaptor was moved to the vacuum line, cooled to -196° and evacuated. Then 1.50 millimoles of $\text{B}_6\text{H}_{10}$, which was measured volumetrically as a liquid, was condensed into the reaction vessel. The liquid nitrogen bath was then replaced with a dry ice-isopropanol slush.
The sides of the vessel were warmed above -78° to melt the B₆H₁₀ and allow it to run into the solution. At -78° a steady evolution of methane occurred, which was monitored on the mercury blow out. Simultaneously with the gas evolution, a heavy white precipitate formed in the solution. When the methane evolution ceased the mixture was frozen to -196° and the non-condensible gas was measured with a Toepler pump. In each case the methane evolution was 98-100% and its vapor pressure was 10 mm of Hg at -196°. The THF was distilled from the mixture leaving a white chalky solid. If the reaction was done in a vacuum line extractor additional THF was added and the extractor was tipped to wash the product with THF at low temperature. The dried product was transferred to a storage vessel in the dry box.

When diethyl ether was used as the reaction solvent, the rate of methane evolution was considerably slower. In diethyl ether a 0° bath was required to observe the same reaction rate as a THF reaction solution at -78° with the same concentration of reactants. Unlike the THF solutions, the reaction product, B₆H₂MgBr was completely soluble in diethyl ether. Removal of all the diethyl ether at room temperature resulted in a viscous, colorless oil.

There was no evidence that B₆H₂MgBr could be deprotonated by a second mole of Grignard reagent or
by potassium hydride.

Reaction of $B_6H_9$MgBr with HCl(I) at $-111^\circ$ regenerated hexaborane(10) as identified by its infrared spectrum. Eighty-three per cent of the $B_6H_{10}$ was recovered.

Pumping on the $B_6H_9$MgBr at room temperature for 36-48 hours removes the excess THF from the solid and results in a better resolved infrared spectrum in the B-H terminal region from 2600-2500 cm$^{-1}$.

The elemental analysis of the white solid product most accurately fit the empirical formula $Mg(B_6H_9)Br \cdot 1.7THF$. Calculated: B, 21.1; Mg, 7.90; mmole H$_2$/mmole formula, 14.0. Found: B, 20.2; Mg, 7.84; mmole H$_2$/mmole formula, 14.2.

Although the overall formula was $Mg(B_6H_9)Br \cdot 1.7THF$, more than half of the lines in the X-ray powder diffraction pattern were major lines in the diffraction pattern of $Mg(B_6H_9)_2 \cdot 2THF$. The X-ray powder diffraction data is listed in Table 4. The remaining lines are presumably due to a THF solvate of magnesium bromide which comprises 50 mole per cent of the sample.

The infrared spectrum of $Mg(B_6H_9)Br \cdot 1.7THF$ in nujol is identical to that of $Mg(B_6H_9)_2 \cdot 2THF$.

A variety of reactions were attempted with $B_6H_9$-MgBr to determine the synthetic value of the reagent. Most of the reactions were based on reactions of $B_{10}H_{15}$MgI
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*a* Lines present in pattern of \( \text{Mg(B}_{6}\text{H}_{9})_{2}^{2}\text{THF}.  

*b* Lines of less intensity in pattern of \( \text{Mg(B}_{6}\text{H}_{9})_{2}^{2}\text{THF}.  

**TABLE 4**

X-RAY POWDER DIFFRACTION DATA FOR \( \text{Mg(B}_{6}\text{H}_{9})_{2}^{2}\text{THF} \)
which were somewhat successful. Several derivatives
of decaborane(14) were prepared from B_{10}H_{13}MgI, but
generally the yields were not high and the separation
of isomers was difficult^{92-94}. Reactions of benzyl
chloride, dimethyl sulfate, acetone and iodine with
B_{6}H_{9}MgBr in ethyl ether resulted primarily in the decom­
position of the borane, whereas methyl iodide gave no
reaction. A sample of B_{6}H_{9}MgBr·2THF dissolved in methylene
chloride reacted with one-half equivalent of diborane
at -97^\circ. The sample was slowly warmed while being
monitored with the 19.3 MHz boron-11 nmr. At -50^\circ
an asymmetric doublet at 43.8 ppm and a broad unresolved
resonance at 18 ppm were observed. Upon warming to
-20^\circ the spectrum changed to an asymmetric triplet
at 39.3 (J=123) and a hump at lower field with maxima
at -10.5, 0.6, 6.5, 12.0, and 19.0 ppm. Similar spectra
have been obtained by Dr. Howard Johnson for the addition
of one-half equivalent of diborane to the lithium,
potassium, and tetra-n-butyl ammonium salts of B_{6}H_{9}.^{114}
At the present time no interpretation of the spectra
has been made.

B. Reaction of B_{6}H_{9} with CH_{3}MgBr

In the dry box 1.00 ml of 1.5 M CH_{3}MgBr in diethyl
ether was syringed into a reaction vessel. On the
vacuum line the diethyl ether was removed at room tem­
perature and replaced by an equal volume of tetrahydro-
furan. Then, 1.50 millimoles of pentaborane(9) were
condensed into the vessel at -196°. The temperature
of the reaction mixture was slowly raised by use of
different slush baths. Methane evolution commenced at
-35°, but at a very slow rate. A more rapid gas evolution
occurred at -23°. Initially the solution remained clear,
but after several minutes a heavy white solid began to
precipitate. The gas evolution ceased after two to three
hours. The rate of the reaction was increased for the
last 30 to 60 minutes by raising the temperature to
0°. The total methane production was about 60% of the
amount expected for a complete reaction.

The THF was removed from the reaction mixture
and the resulting white solid was dissolved in methylene
chloride. A portion of this solution was then tipped
into an nmr sidearm and sealed off. The 32.1 MHz boron-
11 nmr of this solution exhibited a doublet at +7.9 ppm
(J=136 Hz), an asymmetric triplet at +21.5 ppm (J=125 Hz)
and a small doublet at +51.1 ppm (J=158 Hz) as shown
in Figure 7. Upon proton spin decoupling both doublets
collapsed to singlets and the triplet changed to two
singlets at 20.6 ppm and 23.3 ppm. At ambient tempera-
ture the collapse of the triplet reveals the presence
of a broad resonance at +15.7 ppm. The three resonances
at 7.9, 20.6, and 23.3 ppm, which are in a 1:1:1 area
Figure 7. Undecoupled 32.1 MHz boron-11 nmr spectrum of B$_2$H$_9$ + CH$_3$MgBr reaction products dissolved in CH$_2$Cl$_2$ at ambient temperature. Peaks labeled A are due to B$_9$H$_{14}^-$ and peaks marked B are attributed to a B$_5$H$_8^-$ derivative.
ratio, are attributed to $B_9H_{14^-}$, which is the major decomposition product of $B_5H_8^-$. The smaller broad resonance at +15.7 ppm and the doublet at +51.1 ppm are apparently due to $B_5H_8^-$ or its magnesium derivative.

A higher yield of $B_9H_{14^-}$ is obtained if the ratio of the reactants is adjusted to two equivalents of pentaborane(9) for each equivalent of CH$_3$MgBr used. In such a reaction 80% of methane expected from the CH$_3$MgBr used was actually evolved. The volatiles were vacuum distilled from the reaction product and it was dissolved in methylene chloride. The boron-11 nmr of this solution showed only peaks attributable to $B_9H_{14^-}$.

In a separate experiment 4.0 ml of 0.90 M CH$_3$MgBr in THF was reacted with 5.64 mmoles of B$_5$H$_9$ (1.0/1.6 mole ratio) at -23° for 3 hours, at 0° for 1 hour and finally for an hour at room temperature. A total of 2.35 mmoles of methane was evolved. This represents a 65% reaction based on the Grignard used. An infrared spectrum of the volatiles distilled from the reaction mixture indicated the presence of pentaborane(9) and THF only. Reaction of the pentaborane(9) with an excess of KH yielded 1.38 mmoles of hydrogen. This indicates that the ratio of CH$_3$MgBr/B$_5$H$_9$ consumed in the reaction is 1.0/1.8. Addition of an aqueous alkaline solution of excess tetramethylammonium chloride to the reaction
mixture yields the methysis product \((\text{CH}_3)_4\text{NB}_9\text{H}_{14}\)^{37}. The infrared spectrum in nujol and the X-ray powder pattern agreed with those of an authentic sample of \((\text{CH}_3)_4\text{NB}_9\text{H}_{14}\) prepared according to the literature by Dr. Vincent Brice^{124}. An 80\% yield of \((\text{CH}_3)_4\text{NB}_9\text{H}_{14}\) was obtained based upon the pentaborane(9) consumed by the reaction.

VI. NMR Studies of Magnesium Derivatives of \(\text{B}_6\text{H}_{10}\)

A. Boron-11 NMR of \(\text{B}_6\text{H}_9\text{MgBr}\)

The 32.1 MHz boron-11 nmr spectrum of \(\text{B}_6\text{H}_9\text{MgBr}\) in diethyl ether at ambient temperature consists of two resonances as shown in Figure 8. A very broad peak is centered at \(-9.8\) ppm and a small doublet occurs at \(+50.1\) ppm (\(J=147\) Hz) relative to \(\text{BF}_3\cdot\text{OEt}_2\). The large unresolved peak becomes considerably broader upon cooling the sample. The area of the broad peak discernible above the base line decreases with decreasing temperatures. At ambient temperature the area ratio of the two peaks is 4.2:1.

The boron-11 nmr of \(\text{B}_6\text{H}_9\text{MgI}\) in diethyl ether is essentially identical to that of the bromide compound. A methylene chloride solution of \(\text{B}_6\text{H}_9\text{MgBr}\) prepared in diethyl ether exhibits a similar boron-11 spectrum with a broad resonance at \(-9.7\) ppm and a doublet at \(+49.8\) ppm (\(J=143\) Hz).
Figure 8. 32.1 MHz boron-11 nmr of $\text{B}_6\text{H}_9\text{MgBr}$ in ethyl ether at ambient temperature.
B. Boron-11 NMR of CH₃MgB₆H₆

The solid product of the 1:1 reaction of hexaborane(10) and dimethyl magnesium in THF was dissolved in methylene chloride. The boron-11 nmr of the methylene chloride solution consisted of two resonances, a large, poorly-resolved doublet at -9.9 ppm (J=116 Hz) and a small doublet at +49.9 ppm (J=142).

C. Boron-11 NMR of Mg(B₆H₆)₂·2THF

The 32.1 MHz boron-11 nmr of a saturated solution of Mg(B₆H₆)₂·2THF in methylene chloride (ca. 0.2 M) also displays two resonances. At ambient temperature a broad unresolved basal boron signal is centered at -9.6 ppm and an apical doublet peak occurs at 49.3 ppm (J=146 Hz). As the temperature is lowered the basal resonance rapidly collapses and broadens. Below -60° the basal peak is barely discernable from the baseline. In contrast, the apical resonance shows no signs of collapse until -20° and displays doublet character down to -60°. Upon warming the sample from -60° the area ratio of the basal to apical peak increases. At ambient temperature the area ratio of the two signals is 5.0:1.0. Irradiation of the sample at the appropriate proton decoupling frequency collapses the apical doublet to a singlet. Spin decoupling of the basal terminal hydrogens sharpens the broad resonance slightly to give a peak
width at half-height of 240 Hz. The width of the undecoupled resonance is 300 Hz at ambient temperature.

D. PMR of Mg(B₆H₉)_2·2THF

A sample of Mg(B₆H₉)_2·2THF was prepared using THF-d₈ as the solvent. The sample was dissolved in CD₂Cl₂ and benzene (6% by volume) was added to provide a lock signal.

At ambient temperature the pmr of Mg(B₆H₉)_2·2THF-d₈ consists of a broad doublet centered at 6.14T, which is attributed to the basal terminal hydrogens, an apical quartet at 11.65T (J=148 Hz), and a sharp bridge proton peak at 13.22T. The doublet and the quartet collapsed to sharp singlets upon spin decoupling of the respective boron nuclei. The area ratio of the decoupled resonances was 4.9:1.0:3.0.

Upon cooling the sample to -40° the basal terminal resonance collapsed further from a doublet to a broad singlet. Simultaneously, the bridge resonance became sharper. At -60° both the basal terminal and the bridge proton peaks began to broaden asymmetrically. On cooling to -70° the basal terminal peak split into two peaks at 5.41T and 6.80T with an area ratio of 2.0:3.2 respectively. At the same temperature the bridge resonance split into two peaks of area ratio 1:2 at 12.80T and 13.42T. The resonance at 6.80T was broad and displayed
some asymmetry. By using the appropriate boron decoupling frequency and cooling to \(-90^\circ\) a shoulder was resolved on the upfield side of the peak. The peaks appeared to be centered at 6.77 and 6.97. At \(-80^\circ\) where "thermal decoupling" is very effective the area ratio of the basal terminal peaks to the bridge peaks recorded at a relatively low RF power setting was 4.92:3.00.

E. NMR Studies of Mg(B_6H_9)_2 \cdot \text{XCH}_3\text{CN}

A 0.5 mmole sample of Mg(B_6H_9)_2 \cdot 2\text{THF} was transferred in the dry box into a reaction tube with an nmr sidearm. After evacuation of the vessel on the vacuum line one ml of dry acetonitrile was condensed onto the solid at \(-78^\circ\). The mixture was stirred until all of the solid had dissolved. The volatiles were then distilled out of the tube. The resulting solid was then pumped on for ten minutes at room temperature. The solid was then dissolved in 0.5 ml of CD_2Cl_2 and 0.05 ml of benzene. The solution was tipped onto the nmr tube and sealed off.

The pmr spectrum of the sample was recorded at very low power settings at \(-20^\circ\). It consisted of a sharp singlet at 7.657 due to coordinated \text{CH}_3\text{CN}, multiplets at 6.017 and 7.917 due to coordinated \text{THF} and a very broad peak at 13.57 attributed to the bridge protons of the B_6H_9\text{⁻}. The approximate area ratio of the peaks
was 8:2:2:3 respectively.

The chemical shifts of uncoordinated CH$_3$CN in CH$_2$Cl$_2$ was determined to be 8.077. The multiplets in a 10% THF solution in CH$_2$Cl$_2$ occurred at 6.377 and 8.227.

At ambient temperature the boron-11 nmr of a CH$_2$Cl$_2$ solution of Mg(B$_6$H$_9$)$_2$·XCH$_3$CN prepared in the same manner as above included two well-resolved doublets in an area ratio of 5:1. The large doublet was at -10.2 ppm (J=130 Hz) and the small doublet was at 49.5 ppm (J=137 Hz). A similar spectrum was obtained for Mg(B$_6$H$_9$)$_2$·2THF dissolved in CH$_3$CN. Upon cooling the acetonitrile solution to 0° the large basal resonance remained unchanged but the apical doublet became more clearly resolved. At -20° the small doublet was very sharp but the basal doublet was less well-defined. At -40° the basal peak was collapsed to a broad singlet, but the apical resonance remained well-resolved. At -60° the basal peak was very broad and the upfield doublet had partially collapsed.

F. PMR of LiB$_6$H$_9$

As in the case of Mg(B$_6$H$_9$)$_2$·2THF, the basal boron resonance of the boron-11 nmr spectrum of LiB$_6$H$_9$ in ether solvents is not well-resolved$^8,9$. Johnson found that cooling the LiB$_6$H$_9$ solution below 0° collapses
all doublet character and the peak broadens considerably with further cooling. These observations are in contrast to the solutions of NaB₆H₉ and KB₆H₉ which do not show such temperature dependence. The temperature dependence of the LiB₆H₉ boron-11 nmr was attributed to the viscosity of the solution. Lithium-7 nmr indicated that no covalent interaction occurred between the Li⁺ and the B₆H₉⁻. In order to observe the behavior of the bridge hydrogens in this salt at low temperature the pmr spectrum was obtained.

A sample of LiB₆H₉ was prepared in methyl ether-d₆ according to the procedure of Johnson. Chloroform was used to provide a lock signal. The concentration of LiB₆H₉ was 0.85 M. The pmr spectrum over the temperature range of -40° to -130° displayed one basal terminal and one bridge resonance. The chemical shifts were measured to be 6.377 for the basal terminal hydrogens, 11.987 for the apical hydrogen and 13.757 for the bridge protons. At -40° the undecoupled spectrum shows a broad doublet due to the basal hydrogens, but a very well-resolved quartet is observed for the apical hydrogen.

VII. NMR Studies of Zinc Derivatives of B₆H₁₀

A. Boron-11 NMR of CH₃ZnB₆H₉

Hexaborane(10) and dimethylzinc were reacted in THF to yield one equivalent of methane and a product
formulated as $\text{CH}_3\text{ZnB}_6\text{H}_9$. The THF soluble sample was tipped into an nmr tube sidearm containing a capillary of BCl$_3$ and it was sealed off.

At $40^\circ$ the 32.1 MHz boron-11 nmr of a 1.5 M THF solution of $\text{CH}_3\text{ZnB}_6\text{H}_9$ consisted of two doublets in the area ratio of 5:1. The large doublet was very poorly resolved. It was centered at -11.9 ppm ($J=115$ Hz) relative to BF$_3$OEt$_2$. The small doublet was very sharp and was located at +50.6 ppm ($J=147$ Hz).

As the temperature of the sample was lowered from $40^\circ$ to $-20^\circ$ the large doublet collapsed and the peak broadened symmetrically from a width of 290 Hz to a width of 500 Hz as is shown in Figure 9. Over the same temperature range only a slight broadening of the small doublet was detected.

B. PMR of $\text{CH}_3\text{ZnB}_6\text{H}_9$

A sample of $\text{CH}_3\text{ZnB}_6\text{H}_9$ was prepared in THF-d$_8$. After the reaction was completed the volume of the sample was doubled by the addition of Me$_2$O-d$_6$. Benzene, which comprised 5% of the sample volume, was used for a look signal.

The pmr spectrum of the sample at $-20^\circ$ at low RF power settings displayed two signals. A very sharp methyl peak occurred at 10.807 and a broad resonance due to the three bridging protons of B$_6$H$_9^-$ was at 12.87.
Figure 9. 32.1 MHz boron-11 nmr of CH$_3$ZnB$_6$H$_9$ in THF.
The area ratio of the two peaks was 1.2:1.

The pmr spectrum recorded at a higher RF power and with spin decoupling of the appropriate boron atoms reveals a basal terminal resonance at 5.8\(\text{T}\), an apical terminal resonance at 11.4\(\text{T}\), and a bridge proton peak at 12.78\(\text{T}\). The area ratios of the peaks was 5:1:3.

In the absence of spin decoupling the basal hydrogen resonance appears as a broad doublet, the apical terminal peaks are not distinguishable from the baseline and the bridge peak is somewhat broadened.

At -60\(^\circ\) the undecoupled basal terminal resonance is a broad symmetric singlet and the bridge peak is very symmetric. However, at -80\(^\circ\) the basal terminal peak is very asymmetric and appears to be separating into two separate resonances. The spectrum at -100\(^\circ\) clearly shows two different basal terminal peaks at 5.23\(\text{T}\) and 6.24\(\text{T}\), but only a single asymmetric bridge peak is observed. The area ratio of these peaks is 1.9:3.0:3.0.

At this temperature spin decoupling has very little effect on the peak shapes. The only effect of cooling the sample further to -120\(^\circ\) is to make the shoulder on the downfield side of the bridge peak slightly more pronounced.

C. PMR of Zn(B\(_6\)H\(_9\))\(_2\)·2THF

A 0.3 millimole sample of Zn(B\(_6\)H\(_9\))\(_2\)·2THF which was prepared in THF-d\(_8\) was dissolved in 0.25 ml of
THF-d₈. To this solution was added 0.25 ml of methyl ether-d₆ and 0.05 ml of benzene. The sample was tipped into an nmr sidearm at -78° and the tube was sealed off.

At 0° the pmr spectrum of Zn(B₆H₉)₂·2THF consists of a single basal terminal hydrogen resonance at 5.877° and only one bridge hydrogen peak at 12.757°. The apical hydrogen resonance is located at 11.507°. The area ratio of the basal terminal to bridge hydrogen peak is 5:3. Upon cooling the sample, the bridge proton peak broadens and splits into two peaks of area 1:2 at -30°. The two peaks are positioned at 12.457° and 13.047°. Further cooling causes the basal terminal peak to broaden and then split into two peaks of unequal area at -50°. The peaks are centered at 5.337° and 6.337°. The area of the high field peak was not determinable as it overlapped with a resonance due to the protonated THF impurity in the THF-d₈. The area ratio of the downfield basal terminal peak to the bridge peak was 1.95:3.0. In cooling from -30° to -70° a slight change was noted in the lower field bridge proton resonance from 12.457° to 12.60°.

D. Boron-11 NMR of Zn(B₆H₉)₂·2THF

The sample of Zn(B₆H₉)₂·2THF prepared in 1:1 tetrahydrofuran-d₈/methyl ether-d₆ was used for boron-11 nmr. Chemical shifts were measured using a trimethylboron reference signal provided by tube interchange.
The chemical shift of trimethylboron was measured to be -86.0 ppm relative to BF$_3$OEt$_2$. All chemical shifts are reported relative to BF$_3$OEt$_2$.

At +20° the boron-11 nmr spectrum of Zn(B$_6$H$_9$)$_2$ consists of a large poorly resolved doublet at -13.2 ppm and a small sharp doublet at +48.9 ppm (J=138 Hz). Upon cooling to 0° all doublet character is lost in the basal resonance and the peak is broadened. At -30° the large peak is broadened further and is asymmetric due to its splitting into two peaks. At -50° to -60° two separate resonances are present. A peak is centered at approximately -6.5 ppm and has a broad downfield shoulder which appears to be at about -17 ppm. Proton spin decoupling only sharpens the resonance slightly. Both peaks broaden considerably upon cooling below -60°.

The apical doublet remains well-resolved down to -60°.

VIII. NMR Studies of Cadmium Derivatives of B$_6$H$_{10}$

A. Boron-11 NMR of CH$_3$CdB$_6$H$_9$

The 32.1 MHz boron-11 nmr of the hexaborane(10) and dimethylcadmium reaction product was obtained using THF as a solvent. At +20° the spectrum exhibited a broad resonance at -12.4 ppm which had some doublet character. A small well-resolved doublet was located at +51.4 ppm (J=146 Hz). On cooling the sample the basal resonance
collapsed in a symmetric manner and became very broad while the small doublet remained well-resolved. The area ratio of the peaks decreased with decreasing temperature. At +20° the ratio of the peak areas was 4.5:1.

B. PMR of CH$_3$CdB$_6$H$_9$

A pmr sample of CH$_3$CdB$_6$H$_9$ was prepared in THF-$d_8$ according to the procedure outlined above. Any excess B$_6$H$_{10}$ on Cd(CH$_3$)$_2$ was removed by briefly pumping on the product to remove the volatiles. Sufficient THF-$d_8$ and methyl ether-$d_6$ was added for a 1:1 solution which was about 1 M. Benzene was added to provide a lock signal.

The pmr spectrum of CH$_3$CdB$_6$H$_9$ at -20° using low RF power settings showed a sharp methyl resonance at 10.467 and a broad peak at 12.657 due to the three B-H-B bridge hydrogens of the B$_6$H$_9^-$. The ratio of the areas of these two peaks was 1:1.

At higher RF power settings the pmr spectrum of CH$_3$CdB$_6$H$_9$ over the temperature range of +20° to -100° includes a single basal terminal resonance at 5.777, an apical peak at 11.367, and a symmetric bridge hydrogen peak. At -60° the bridge resonance shifted slightly from 12.657 to 12.757 and at -70° two small resonances grew in on either side of the methyl peak. These peaks, which were separated by 73 Hz, may be attributable to
The area ratio of the spin decoupled spectrum at \(-60^\circ\) for the basal terminal, apical, and bridge hydrogens was 4.9:1.0:3.0. The spectrum recorded at \(-100^\circ\) is shown in Figure 10.

On further cooling to \(-125^\circ\) a slight shoulder was detected on the downfield side of the bridge proton resonance and the basal terminal peak broadened noticeably in an asymmetric manner. However, separate basal terminal peaks could not be observed. Further cooling broadened all the resonances in the spectrum due to increased viscosity.

C. PMR of \(\text{Cd}(\text{B}_6\text{H}_9)_2\)

In the dry box a 0.5 mmole sample of solid \(\text{Cd}(\text{B}_6\text{H}_9)_2\) was transferred to a vessel with an nmr sidearm. The sample was dissolved in 0.25 ml THF-d\(_8\) at low temperature. Then, 0.25 ml of methyl ether-d\(_6\) and 0.05 ml of benzene were condensed into the tube. At \(-78^\circ\) the sample solution was tipped into the sidearm and the nmr tube was sealed off.

At \(-30^\circ\) the spin-decoupled spectrum of \(\text{Cd}(\text{B}_6\text{H}_9)_2\) includes a single basal terminal hydrogen resonance at 5.887, an apical peak at 11.447, and a bridge proton singlet at 12.677. The approximate area ratio of the peaks was 5:1:3. At \(-50^\circ\) the basal terminal resonance became noticeably broader and was skewed towards the
Figure 10. 100 MHz pmr spectrum of CH$_3$CdB$_9$H$_9$ in THF-d$_8$/Me$_2$O-d$_6$ at -100°.

The apical boron nuclei are spin decoupled.
downfield side. On cooling to $-60^\circ$ the basal terminal peak split into two distinctly different peaks and a shoulder grew in on the downfield side of the bridge resonance. At $-100^\circ$ the lowfield set of peaks which were in the approximate area ratio of 2:3 were centered at $5.15\tau$ and $6.21\tau$. An exact area ratio could not be measured as the larger peak overlapped a peak due to the protonated THF impurity in the THF-d$_8$. The bridge peak which had a relative area of 3 had a maximum at $12.82\tau$ and a distinct shoulder at $12.67\tau$.

D. Boron-11 NMR of Cd(B$_6$H$_9$)$_2$

The sample prepared for the pmr was also used for boron-11 nmr. The chemical shifts were determined from a trimethyl boron sample ($\delta=-86.0$ ppm) using tube interchange. Chemical shifts are reported relative to BF$_3$·OEt$_2$ ($\delta=0.0$ ppm).

At $0^\circ$ the boron-11 nmr of Cd(B$_6$H$_9$)$_2$ consists of a symmetric poorly-resolved doublet at -12.8 ppm ($J=118$) and a well-resolved doublet at +51.3 ppm ($J=148$ Hz). The area ratio of the two peaks was 4.7:1. At $-40^\circ$ the basal resonance is a broad hump. Cooling to $-50^\circ$ resulted in the loss of symmetry of the broad peak. Further reduction of the temperature increases the asymmetry. At $-70^\circ$ two broad basal boron resonances are visible at -17 ppm and at -5 ppm. The higher field peak appears to be the larger of the two, but the overlap
of these broad peaks did not allow area ratios to be measured. Further cooling of the sample resulted only in broadening of the basal and apical resonances.

IX. Preparation and Characterization of Nonahydrohexaboratobis(cyclopentadienyl)titanium(III)

A. Reaction of \( (h^5-C_5H_5)_2TiCl \) with \( KB_6H_9 \)

In a typical reaction 0.85 g (4.0 mmoles) of \( (h^5-C_5H_5)_2TiCl \) was weighed out in a dry box which contained an atmosphere rigorously free of oxygen. The \( (h^5-C_5H_5)_2TiCl \) was placed in a small tube which was sealed by a Kontes 4 mm Teflon valve. The tube was fitted to the reaction vessel with a 14/35 standard taper joint. The reaction tube which contained a stirring bar was charged in the dry box with 4.0 mmoles of KH measured by packing a calibrated glass pig. The reaction vessel was fitted to a vacuum line extractor and transferred to the line by evacuation.

After evacuation of the extractor about 4 ml of methyl ether was condensed onto the KH at -196°. Then, 0.434 ml (4.0 mmoles) of \( B_6H_{10} \) was condensed into the vessel and it was allowed to react according to the procedure of Johnson and Shore."
THF was condensed into the reaction tube and it was stirred to dissolve all of the KB₆H₉.

The Teflon valve to the sidearm was opened and the \((h^5-C_5H_5)_2TiCl\) was tapped into the solution. This produced a green solution, but most of the \((h^5-C_5H_5)_2TiCl\) did not dissolve. The temperature of the solution was then raised to 0°. As the starting material dissolved at 0° the solution became blue-green in color and a blue solid began to form. After stirring the mixture at 0° for 6-8 hours, it was cooled to -78° and an additional 5 ml of THF was condensed into the reaction tube. The solution was frozen at -196° and the extractor was inverted. Immediately the cold jacket of the extractor was filled with a dry ice-isopropanol slush. Upon melting the reaction mixture, it fell to the frit and very high purity Matheson nitrogen (5 ppm O₂) was used to force the green solution through to the lower bulb which was cooled to -78°. The nitrogen was pumped from the extractor so that the THF could be distilled up to the blue solid on the frit. The solid was washed and filtered once at -78°. All of the volatiles were then removed from the extractor.

After thorough drying the extractor was moved from the vacuum line into the dry box. The lower bulb which contained a viscous green oil was replaced with a clean bulb and the extractor was returned to the vacuum
line. After evacuation, 10-15 ml of THF was condensed onto the blue solid on the frit. Numerous washings at about 0° were required to wash all of the blue material through the frit. A small quantity of fine white solid remained on the frit which was identified as potassium chloride by its X-ray powder diffraction pattern. Again, all of the solvent was removed from the extractor and after drying it was moved into the dry box. In the dry box the blue solid was transferred into a test tube vessel with a sidearm vessel of equal volume. The tube was fitted with a stopcock adaptor and was transported to the vacuum line for further purification of the product.

About 8 ml of THF was distilled onto the blue solid at -78°. Brief warming to room temperature allowed all of the solid to dissolve. The solution was then slowly cooled back to -78° by periodic submersion of the vessel in a dry ice-isopropanol slush. Slow cooling resulted in the formation of large light blue particles. After most of the precipitate had formed and the solution was no longer deep blue the mixture was allowed to stand for 30-45 minutes at -78° to allow the solid to settle. The solution which then had a green cast was decanted into the sidearm vessel. The THF was then distilled back onto the blue solid. Repeated decantations were carried out until the decantate was no longer colored.
The THF was then removed from the vessel and in the dry box the blue product was transferred to a storage vessel. The yield of \((h^5-C_5H_5)_2TiB_6H_9\) was 60%.

B. Characterization of \((h^5-C_5H_5)_2TiB_6H_9\)

1. Thermal Stability and Air Sensitivity

The blue microcrystalline solid, \((h^5-C_5H_5)_2TiB_6H_9\), was found to be extremely oxygen sensitive. A controlled slow exposure to oxygen in solution or as a solid resulted in a color change to yellow-orange. Rapid exposure of the solid to air resulted in a violent flash. Manipulations of the compound were carried out in nitrogen with an oxygen level less than 1 ppm. At 10-15 ppm \(O_2\) the solid showed a noticeable color change in 20 seconds.

A sample of \((h^5-C_5H_5)_2TiB_6H_9\) exposed to oxygen displayed an absorption in the infrared spectrum at 720 cm\(^{-1}\) which is characteristic of a Ti-O-Ti structure\(^{125}\).

The compound appeared to be very stable as a solid at room temperature. No color or infrared spectrum changes occurred after three weeks at room temperature.

A sample of \((h^5-C_5H_5)_2TiB_6H_9\) sealed under nitrogen melted with decomposition at 123°. Noticeable color changes occur in solutions of the compound at room temperature after several days. This decomposition is much more rapid if impurities are present in the solution.

In addition to methyl ether, ethyl ether and THF, \((h^5-C_5H_5)_2TiB_6H_9\) is also soluble in the non-polar solvents.
toluene and benzene. Solutions in chlorinated solvents such as methylene chloride and chloroform turned green within minutes at room temperature which may be indicative of a reaction.

The compound exhibits volatility at elevated temperature. Fine dark blue crystals slowly formed on the cold finger of a sublimator heated to 100°. Below 90° the sublimation was extremely slow. The infrared spectrum of the sublimated solid was very similar to that of the \((h^5-C_5H_5)_2TiB_6H_9\) obtained from solution. The terminal B-H absorptions from 2600 to 2500 cm\(^{-1}\) were not resolved in the sublimated material and a new broad peak was centered at 2320 cm\(^{-1}\). All of the lower energy bands due to \(B_6H_9^-\) remained unchanged. Some thermal decomposition of the unsublimed compound occurred. If the sublimation was carried out at 120-125° a series of new peaks grew in at 2420, 2380, 2280, 2080, 2040, and 1940 cm\(^{-1}\) which are all attributed to \((h^5-C_5H_5)_2TiBH_4^+\).

2. Reaction with HCl

Reaction of a 0.14 g sample of \((h^5-C_5H_5)_2TiB_6H_9\) with an excess of HCl in methyl ether at -97° resulted in a rapid color change from blue to green. Fractionation of the volatiles yielded a white solid that stopped at -78° which was identified by its gas phase infrared spectrum to be hexaborane(10). The amount of hexaborane(10)
was determined by measurement of the hydrogen evolved from its reaction with potassium hydride in methyl ether. The B$_6$H$_{10}$ recovered from the (h$^5$C$_5$H$_5$)$_2$TiB$_6$H$_9$ represented 86% of the theoretical amount expected.

3. Elemental Analysis

The results of an analysis by Swarzkopf Microanalytical Laboratory gave the following Ti/B/C/H ratio: 1.000/1.356/2.495/0.413. The ratio calculated for (C$_5$H$_5$)$_2$TiB$_6$H$_9$ is 1.000/1.354/2.507/0.400. A halide analysis showed 1.44% chloride in the sample which is probably due to a trace of potassium chloride impurity. However, the mass balance only accounts for 93% of the sample which probably arises from the reaction of the compound with one equivalent of oxygen in the process of analysis.

4. Infrared Spectrum

The infrared spectrum of (h$^5$C$_5$H$_5$)$_2$TiB$_6$H$_9$ was recorded as a mull in nujol. Regions of the spectrum obscured by nujol were obtained with a fluorolube mull. Absorptions which are attributed to the pentahaptocyclo-pentadienyl rings based on the i.r. of (h$^5$C$_5$H$_5$)$_2$TiCl are at 3100(m), 2290(w), 1840(vw,br), 1745(w,br), 1650(w,br), 1435(m), 1010(s), 812(vs), 417(m) and 378(m) cm$^{-1}$. Five B-H terminal absorptions are at 2585(m), 2565(m), 2530(s), 2515(s), and 2400(w) cm$^{-1}$. Other bands that may be assigned to B$_6$H$_{12}^-$ are at 1890(vw,br), 1324(m),
1060(w), 738(m) and 715(m) cm\(^{-1}\). Unassigned bands are at 955(w), 913(w), 675(w), 630(m), 608(m) and 588(m) cm\(^{-1}\).

5. X-ray Powder Diffraction

The X-ray powder diffraction data for \((h^5-C_5H_5)_2TiB_6H_9\) are listed in Table 5.

6. Mass Spectrum of \((h^5-C_5H_5)_2TiB_6H_9\)

The mass spectrum of \((h^5-C_5H_5)_2TiB_6H_9\) was obtained by Mr. Richard Weisenburger using an AEI MS-9. Due to the low volatility of the compound direct insertion techniques were employed with a source temperature of 150\(^\circ\). All spectra were run at an emission level of 70 e.V. with a pressure of \(1 \times 10^{-6}\) torr. The mass spectral data for \((h^5-C_5H_5)_2TiB_6H_9\) is listed in Table 6. The relative intensity for each m/e peak is expressed as per cent of the most intense peak.

7. Molecular Weight

The molecular weight was determined using an air-tight cryoscopic cell fitted with a glass spiral stirrer that was driven magnetically. The temperature change was measured with a platinum resistance thermometer using a potentiometer bridge.

Samples were prepared in a small bulb fitted with a Teflon valve using about 100 mg of freshly purified \((h^5-C_5H_5)_2TiB_6H_9\). Approximately 15 ml of benzene was condensed into the vessel at -78\(^\circ\) and the exact weight
### TABLE 5

**X-RAY POWDER DIFFRACTION DATA FOR (h\(^5\)-C\(_5\)H\(_5\))\(_2\)TIB\(_6\)H\(_9\)**

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TABLE 6

MASS SPECTRAL DATA FOR \((\text{h}^5-\text{C}_5\text{H}_5)_2\text{TiB}_6\text{H}_9\)

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*aMost intense peak of envelope.

bLower m/e value of two peaks at approximately the same m/e value.
of the solvent was determined by difference. Sample concentrations of 0.01 to 0.02 molal were used. In the dry box the sample solution was syringed into the cryoscopic cell. Repeated freezing point measurements were made. A previously determined cryoscopic constant for the benzene of 4.9°/mole was used. The frozen solvent appeared as colorless crystals indicating that no solid solution had formed which would cause anomalous results. The molecular weight of the compound in benzene was determined to be 535 g/mole ± 25 g/mole. The molecular weight calculated for the dimer of Cp₂TiB₆H₉ is 504 g/mole.

8. Visible Spectrum of (h⁵-C₅H₅)₂TiB₆H₉

The visible spectrum of the compound in THF was recorded on a Cary 14 Spectrophotometer. It displayed a very broad asymmetric peak at 16,840 cm⁻¹. The peak was skewed to the low energy side. A second sharper peak appeared as a shoulder at 24,850 cm⁻¹ of a very intense peak which extended into the UV region.

9. EPR Spectrum of (h⁵-C₅H₅)₂TiB₆H₉

The electron paramagnetic resonance spectrum of (h⁵-C₅H₅)₂TiB₆H₉ in benzene solution showed a single peak with a g value of 1.9786. This spectrum was almost identical to the spectrum of the compound dissolved in THF for which g=1.9780. Freezing the THF solution to -196° broadened the spectrum considerably, but no
asymmetry was detected. However, the epr spectrum of the solid at room temperature displays an asymmetry characteristic of three overlapping signals due to an anisotropic electronic environment surrounding the metal atom. The signals give the following g values: \( g_1 = 1.9864 \), \( g_2 = 1.9797 \), and \( g_3 = 1.9685 \). The average of these three values is 1.9782 which is within experimental error of the g obtained for the compound in solution.

10. Boron-11 NMR of \( (h^5-C_5H_5)_2TiB_6H_9 \)

The 32.1 MHz boron-11 nmr of \( (h^5-C_5H_5)_2TiB_6H_9 \) in a saturated toluene solution at 35° consisted of two very broad symmetric peaks of unequal area. The peaks had a width at half height of approximately 500 Hz. The smaller upfield resonance was power sensitive and was easily saturated. The area ratio of the two peaks at low RF power settings was 2.0:1.0. No other resonances were observed in the 32.1 MHz spectrum.

The 80.2 MHz boron-11 nmr spectrum of \( (h^5-C_5H_5)_2TiB_6H_9 \) in toluene at 26° was recorded by Dr. J. C. Carter at the University of Pittsburgh. Spectra were obtained by frequency sweep operation with a constant field strength without a lock. The construction and stability of this instrument have been previously described. The chemical shifts were measured relative to a capillary of trimethyl borate, but are reported relative to boron trifluoride etherate. A value of -19.0 ppm was used.
for the chemical shift of trimethyl borate\textsuperscript{127}. In addition to the two resonances observed in the 32.1 MHz nmr spectrum a very broad peak (3000 Hz at half height) was observed at -93 ppm. The other two peaks were located at -37 ppm and at +19 ppm. The approximate area ratios were 2:2:1 respectively. Unfortunately the nmr insert used was constructed Pyrex glass so that a boron nmr spectrum was observed for the empty probe at the sweep widths and RF power settings required for this sample. This precluded very accurate peak area measurements and may have obscured the presence of an additional very broad resonance. The frequency, which was modulated at 20 KHz, was swept from -1000 ppm to +1000 ppm but no other resonances were observed.

Paramagnetic broadening due to the Ti(III) in addition to the nuclear quadrapolar broadening of the boron nuclei prevented observation of the proton nmr spectrum.

\textbf{X. Preparation of }
\textit{Octahydopentaboratobis(cyclopentadienyl)titanium(III)}

\textbf{A. Reaction of }KB_5H_8\textit{ with }\textit{(h}^5\textit{-C}_5\textit{H}_5\textit{)}_2\textit{TiCl}\textit{ }

For the purpose of comparison with \textit{(h}^5\textit{-C}_5\textit{H}_5\textit{)}_2\textit{TiB}_6\textit{H}_9 the analogous pentaborane(9) derivative was prepared. Using identical equipment and similar procedures to the \textit{(h}^5\textit{-C}_5\textit{H}_5\textit{)}_2\textit{TiB}_6\textit{H}_9 synthesis described
above, \((h^5-C_5H_5)_2TiCl\) was reacted with \(KB_5H_8\) in methyl ether at \(-78^\circ\). Mixing 4.0 millimoles of the green titanium(III) starting material with 4.0 ml of a 1.0 M \(KB_5H_8\) solution resulted in an immediate color change to an intense purple. The solution was allowed to stir overnight at \(-78^\circ\). Much of the product was present as a purple solid. The addition of an equal volume of pentane caused further precipitation of purple solid. After freezing the reaction mixture at \(-196^\circ\), the vacuum line extractor was inverted and the outer jacket was rapidly filled with a dry ice-isopropanol slush. The solid was then filtered and washed at \(-78^\circ\). Some green material and a brown solid were washed through the frit.

All the volatiles were then distilled from the extractor. The dry extractor was quickly moved to the dry box where it was fitted with a clean bulb. On the line THF was condensed into the apparatus at \(-78^\circ\) which dissolved the purple solid. All of the colored material was washed into the lower bulb, leaving a white solid on the frit which was later identified by its X-ray powder diffraction pattern as \(KCl\). The THF was then removed from the extractor and in the dry box the purple solid was transferred to a tube with a large sidearm vessel.

On the vacuum line equal volumes of ethyl ether and pentane were condensed into the tube. At about \(0^\circ\)
most of the solid was dissolved by the solvent mixture, but the product was reprecipitated upon slow cooling of the solution to -78°. After the purple solid had sufficiently settled the brown solution was carefully decanted into the sidearm. The solvents were then distilled back into the main tube to repeat the precipitation and decantation. The process was repeated until the decantate was no longer brown. The solvent was then removed and the product was transferred to a storage vessel in the dry box. The product was stored under vacuum at -78°.

The product, \((h^5-C_5H_{15})_2TiB_5H_8\), appeared to be less thermally stable than \((h^5-C_5H_{15})_2TiB_6H_9\) as it noticeably discolored and the infrared spectrum changed in hours at room temperature. The crystalline solid was found to melt under nitrogen at 88-89°. The compound was extremely oxygen sensitive and turned yellow-orange upon exposure to air.

Reaction of the purple solid with HCl at -97° in methyl ether caused a rapid color change to green. The volatiles were fractionated and \(B_5H_9\) as identified by its infrared spectrum was recovered in a 60% yield. The pentaborane(9) was determined by measurement of \(H_2\) generated by its reaction with excess KH in methyl ether.
B. **Infrared Spectrum**

The infrared spectrum of the solid compound in nujol included bands characteristic of an $h^5$-cyclopentadienyl ring as well as boron hydride peaks. A strong B-H terminal peak was observed at 2558 cm$^{-1}$ with a shoulder at 2540 cm$^{-1}$ of medium intensity. The B-H-B bridge region was obscured by $C_5H_5^-$ absorptions. Other peaks attributable to $B_5H_8^{-8}$ were at 1300(w), 992(w), 878(w), 642(m), 615(m), 602(m) and 557(m) cm$^{-1}$. Absorptions which are probably due to cyclopentadienyl moieties are at 3095(m), 2295(m), 1825(w,br), 1735(w,br), 1620(w,br), 1022(s), 1017(s), 1007(s), 810(vs), 415(m) and 375(a) cm$^{-1}$. Other bands in the spectrum were at 1260(m), 970(m), 917(m) and 461(m) cm$^{-1}$.

C. **Mass Spectrum**

The mass spectrum of $(h^5-C_5H_5)_2TiB_5H_8$ was obtained using direct insertion techniques on an AEI MS 9 with a source temperature of 150° at an emission level of 70 eV. The most prominent feature of the spectrum was the characteristic fragmentation pattern of polyisotopic $B_5H_9$ with a maximum at m/e=59$^{128}$. Other intense peaks occurred at m/e=65, 66(Cp$^+$, CpH$^+$), 113(Cp$^+$Tl$^+$) and 178 (Cp$^+$Tl$^+$). A broad weak envelope was observed with a cut-off at m/e=241 which corresponds to $(^{12}_C_5^{1}H_5)_2$ $^{48}_{Ti}^{11}B_5^{1}H_8$. A relatively intense envelope with a cut-off at 193 and a maximum at 191 may be attributed
to a Cp₂TiBH₄⁺ species and its loss of hydrogens. The presence of some Cp₂TiCl impurity in this particular sample was noted as peaks occurred at m/e=148(CpTi³⁵Cl⁺), 150(CpTi³⁷Cl⁺), 213(Cp₂Ti³⁵Cl⁺) and 215(Cp₂Ti³⁷Cl⁺).

D. ESR Spectrum

The esr spectrum of (h⁻c⁻CH⁻)₂TiBH₄ in benzene at ambient temperature displayed a single symmetric signal at g=1.9719. The finely ground solid compound also showed only one symmetric peak at g=1.9714 with no h.f.s.

E. Boron-11 NMR Spectrum

The boron-11 nmr of (h⁻c⁻CH⁻)₂TiBH₄ in toluene at -10° consisted of two broad resonances of unequal area. The peaks were very power sensitive and the upfield resonance was saturated at high power levels. At low RF power settings the area ratio of the peaks was 2:1. The chemical shifts were +38 ppm and +111 ppm respectively measured relative to an external BF₃·OEt₂ reference in the sample solution. However, it should be noted that Cp₂TiB₂H₉ solutions caused a 5 ppm downfield shift in the position of the BF₃·OEt₂ reference resonance.
CONCLUSIONS AND DISCUSSION

I. Preparation and Isolation of Magnesium, Zinc, and Cadmium Derivatives of B$_6$H$_{10}$

A. Deprotonation Reactions

Hexaborane(10) is sufficiently acidic to be deprotonated by dimethyl derivatives of magnesium, zinc, and cadmium in ether solvents according to the following reactions:

$$\text{CH}_3\text{MgX} + \text{B}_6\text{H}_{10} \rightarrow \text{B}_6\text{H}_{9}\text{MgX} + \text{CH}_4$$

$$X = \text{Br, I}$$

$$\text{(CH}_3\text{)}_2\text{M} + \text{B}_6\text{H}_{10} \rightarrow \text{CH}_3\text{MB}_6\text{H}_9 + \text{CH}_4$$

$$\text{M} = \text{Mg, Zn, Cd, } \neq \text{Hg}$$

$$\text{(CH}_3\text{)}_2\text{Mg} + 2\text{B}_6\text{H}_{10} \rightarrow \text{Mg(B}_6\text{H}_9)_2 + 2\text{CH}_4$$

Methylmagnesium halides and dimethylmagnesium are considerably more reactive towards B$_6$H$_{10}$ than the dimethyl derivatives of zinc and cadmium. Dimethylmercury does not react with hexaborane(10) at 40$^\circ$ within eight hours.

Although methylmagnesium bromide also deprotonates pentaborane(9) in THF the reaction occurs at a higher temperature and at a slower rate than the corresponding hexaborane(10) reaction, which is consistent with the
weaker acidity of pentaborane(9)\textsuperscript{25}. Under the reaction conditions the product is unstable and rapidly decomposes to give a high yield of the \( \text{B}_6\text{H}_{14}^- \) anion. This reaction is discussed in Section G.

General observations of these reactions are consistent with those previously reported for deprotonation reactions\textsuperscript{8,9}. The rate of these reactions was found to be extremely dependent upon concentration, solvent, and in some cases, rate of stirring. The rate of deprotonation of boron hydrides has been found to increase with increasing basicity of the solvent but no reaction occurs in non-ether solvents\textsuperscript{9,130}. In agreement with this, these reactions were found to proceed more rapidly in THF and methyl ether than in ethyl ether. It has been well-established that deprotonation of \( \text{B}_6\text{H}_{10} \) occurs by the loss of one bridge proton\textsuperscript{9,25}.

Solutions of methyl magnesium bromide (1 M) and dimethylmagnesium (0.4 M) in THF react with \( \text{B}_6\text{H}_{10} \) at \(-78^\circ\) to yield one equivalent of methane within five to ten minutes. Although the second equivalent of methane is evolved more slowly for the reaction of \((\text{CH}_3)_2\text{Mg}\) with two equivalents of \( \text{B}_6\text{H}_{10} \) at \(-78^\circ\), the second half of the reaction is completed in minutes at \(0^\circ\). The reaction of a 1 M dimethylzinc solution with hexaborane(10) requires 90-120 minutes at \(0^\circ\) for completion. The corresponding reaction with dimethylcadmium is best run at
6.5° for 3-4 hours but shows significant decomposition in this time.

The order of reactivity of the dimethyl metal compounds toward hexaborane(10), Mg > Zn > Cd > Hg, is consistent with the increasing electronegativity of the metal going from magnesium to mercury. As the electronegativity of the metal increases the ionic character of the metal-carbon bond decreases making it less reactive. Thus, the most electropositive member of the series, magnesium, is expected to form the most reactive alkyl derivatives. The same order of reactivity was observed for the deprotonation of decaborane(14) with dialkyls of magnesium, zinc, and cadmium. Dimethylmercury does not deprotonate decaborane(14) in refluxing diethyl ether.

Essentially quantitative evolution of methane occurred for the reactions of dimethylmagnesium and methylmagnesium halides with $B_6H_{10}$. Although the reactions of dimethylzinc and dimethylcadmium with $B_6H_{10}$ were generally not allowed to go to completion due to increased decomposition in the later stages of the reaction, one equivalent of methane could be obtained in each case if the reaction was allowed to continue. No evidence for nucleophilic attack on the boron framework by the methide ion was detected in the nmr spectra of the reaction solutions. Decaborane(14) was alkylated in a side reaction
to its deprotonation by Grignard reagents.

**B. Mg(B₆H₉)₂·2THF**

Dimethylmagnesium deprotonates two equivalents of hexaborane(10) in ether solvents in a two-step reaction.

\[(\text{CH}_3)_2\text{Mg + 2B}_6\text{H}_{10} \rightarrow \text{Mg(B}_6\text{H}_9)_2 + 2\text{CH}_4\]

In THF the first equivalent of methane is rapidly evolved at -78°. The second equivalent is produced in six hours at -78° or in minutes at 0°. Although similar rates are observed for the reaction in methyl ether, the reaction requires higher temperatures in ethyl ether. The nature of the product is dependent on the solvent used for the reaction. The Mg(B₆H₉)₂ prepared in diethyl ether is very soluble in that solvent. Removal of the excess ether yields a colorless, clear oil. Preparation of Mg(B₆H₉)₂ in methyl ether yields a white solid, but it changes to an intractable gum when pumped on at room temperature. The product of the reaction in THF immediately precipitates upon formation. Excess THF is removed by several hours of heating at 65° in vacuo to yield an air-sensitive, chalky white solid of the formula Mg(B₆H₉)₂·2THF.

The presence of two molecules of THF per formula is indicated by the pmr spectrum of the compound in CD₂Cl₂. At very low power settings multiplets are
present at 5.907 and 7.927 which are attributed to coordinated THF. These values represent a downfield shift of 0.46 ppm for the α hydrogens and 0.29 ppm for the β hydrogens compared to uncoordinated THF. A very broad peak due to the three bridge hydrogens of the B₆H₉⁻ is centered at 13.27. The area ratio of these three peaks is 4:4:3, which is expected if THF and B₆H₉⁻ are present in equimolar quantities. The elemental analysis for magnesium, boron and hydrogen suggests the presence of 2.2THF molecules/formula by weight difference.

The infrared spectrum also indicated the presence of coordinated THF in the compound. Although most bands could be assigned to B₆H₉⁻ or to coordinated solvent some absorptions between 1400 and 800 cm⁻¹ were unassigned. Three strong well-resolved peaks were observed in the B-H terminal stretching region. They were at 2580, 2540 and 2490 cm⁻¹. This is in contrast to the B-H terminal region of nujol mulls of KB₆H₉ and n-Bu₄NB₆H₉ which display a broad absorption at 2490 cm⁻¹ and a shoulder at 2540 cm⁻¹. The splitting of the B-H terminal peaks in Mg(B₆H₉)₂·2THF cannot be attributed to lattice effects as a similar spectrum is obtained for a methylene chloride solution of the compound. The presence of well-resolved sharp B-H terminal stretches may be indicative of slight structural changes as were observed by Erice for (σ₃P)₂CuB₆H₉.⁹³,⁸⁸
Chemical evidence that the hexaborane(10) framework remains essentially unchanged in Mg(B₆H₉)₂·2THF is provided by the rapid low temperature reaction with HCl which regenerates B₆H₁₀.

Solid Mg(B₆H₉)₂·2THF decomposes slowly over months at room temperature. Solutions, however, begin to show decomposition after a day or two.

C. 1:1 Reaction of B₆H₁₀ with (CH₃)₂Mg

Dimethylmagnesium reacts rapidly at -78° in THF with hexaborane(10) to yield a white THF insoluble solid and one equivalent of methane.

\[
(CH₃)₂Mg + B₆H₁₀ \xrightarrow{THF,-78°} CH₃MgB₆H₉ + CH₄
\]

The solid was then filtered and washed thoroughly with THF at about 0° in a vacuum line extractor. After removal of all the excess solvent at room temperature the white solid was identified by elemental analysis, X-ray powder pattern and infrared spectrum to be Mg(B₆H₉)₂·2THF. Methanol hydrolysis of the THF soluble material washed through the frit evolved 0.93 equivalent of methane. Acid hydrolysis of the resulting solution generated a small quantity of hydrogen indicating the presence of only a trace of boranes.

Apparently under the conditions used for this reaction the product CH₃MgB₆H₉ disproportionates according
to the following reaction:

$$2\text{CH}_3\text{MgB}_6\text{H}_9 \longrightarrow \text{Mg(B}_6\text{H}_9)_2 + (\text{CH}_3)_2\text{Mg}$$

This may actually be an equilibrium reaction which is forced to the right by the insolubility of the Mg(B$_6$H$_9$)$_2$ and the removal of the THF soluble Mg(CH$_3$)$_2$. The existence of CH$_3$MgB$_6$H$_9$ in THF at -78° is implied by the distinct decrease in the rate of reaction after the evolution of one equivalent of methane in the 2:1 reaction of B$_6$H$_{10}$ with (CH$_3$)$_2$Mg. Since CH$_3$MgB$_6$H$_9$ does disproportionate, two reaction paths are possible for the second half of the 2:1 reaction. It may simply proceed by the reaction of CH$_3$MgB$_6$H$_9$ with B$_6$H$_{10}$.

$$\text{CH}_3\text{MgB}_6\text{H}_9 + \text{B}_6\text{H}_{10} \longrightarrow \text{Mg(B}_6\text{H}_9)_2 + \text{CH}_4$$

On the other hand, the final product may be formed by the disproportionation of CH$_3$MgB$_6$H$_9$ which generates (CH$_3$)$_2$Mg that reacts with the B$_6$H$_{10}$.

$$2\text{CH}_3\text{MgB}_6\text{H}_9 \longrightarrow \text{Mg(B}_6\text{H}_9)_2 + (\text{CH}_3)_2\text{Mg}$$

$$(\text{CH}_3)_2\text{Mg} + \text{B}_6\text{H}_{10} \longrightarrow \text{CH}_3\text{MgB}_6\text{H}_9 + \text{CH}_4$$

It is not readily determinable whether both of these paths or only one are involved in the reaction.

D. Preparation of B$_6$H$_{10}$MgX

Methylmagnesium bromide reacts with B$_6$H$_{10}$ in THF to form a white solid product and evolves one equiv-
alent of methane. However, when the reaction of CH$_3$MgBr or CH$_3$Mgl is carried out in diethyl ether it proceeds at a slower rate and an ether soluble product results. Evaporation of the excess ether results in the formation of colorless, viscous oils. On standing, ether solutions of B$_6$H$_9$MgX were found to separate into two phases. This phenomena is observed for Grignard solutions and the second phase has been found to be rich in magnesium halide$^{132}$. Addition of THF to ether solutions of B$_6$H$_9$MgX results in the immediate formation of a heavy white precipitate. Hexaborane(10) is regenerated by the low temperature reaction of HCl with B$_6$H$_9$MgX prepared in ethyl ether or THF.

The magnesium, boron and hydrogen analysis of the solid Grignard derivative prepared in THF is consistent with the formulation of B$_6$H$_9$MgBr$\cdot$1.7THF. However, the X-ray powder diffraction pattern contains all of the major lines found in the pattern of Mg(B$_6$H$_9$)$_2$$\cdot$2THF. Additional lines observed in the pattern may be due to a THF solvate of magnesium bromide although they were not specifically identified. The infrared spectrum of B$_6$H$_9$MgBr$\cdot$1.7THF was identical to that of Mg(B$_6$H$_9$)$_2$$\cdot$2THF. The X-ray powder pattern of the solid resulting from the addition of THF to an ethyl ether solution of B$_6$H$_9$MgI also included the major lines of Mg(B$_6$H$_9$)$_2$$\cdot$2THF.

In THF B$_6$H$_9$MgX apparently disproportionates in
a manner similar to \( \text{CH}_3\text{MgB}_6\text{H}_9 \) to yield the "symmetric" products according to the following reaction:

\[
2\text{B}_6\text{H}_9\text{MgX} \xrightarrow{\text{THF}} \text{Mg(B}_6\text{H}_9)_2 + \text{MgX}_2
\]

\( X = \text{Br}, \text{I} \)

It is known that the addition of dioxane to Grignard solutions precipitates \( \text{MgX}_2 \cdot 2(\text{dioxane}) \) leaving \( \text{R}_2\text{Mg} \) in solution\textsuperscript{133}, although it is dependent on experimental conditions and time\textsuperscript{134,135}. This phenomena has been attributed to the shifting of the Schlenk equilibrium by the precipitation of the magnesium halide\textsuperscript{133}.

\[
\text{RMgX} \rightleftharpoons \text{R}_2\text{Mg} + \text{MgX}_2
\]

It has also been established that \( \text{CH}_3\text{MgI} \) does not exist in THF solution, but is disproportionated to \( \text{MgI}_2 \) and \( (\text{CH}_3)_2\text{Mg} \textsuperscript{136}. \) The similarity of the characteristics of \( \text{B}_6\text{H}_9\text{MgX} \) and \( \text{RMgX} \) may indicate that the actual nature of \( \text{B}_6\text{H}_9\text{MgX} \) in solution is as complicated as Grignard solutions\textsuperscript{137}.

Various possible reactions of \( \text{B}_6\text{H}_9\text{MgBr} \) were investigated to determine its usefulness as a reagent to prepare substituted hexaborane(10) derivatives. Unfortunately, none of the desired products could be readily prepared from the attempted reactions. The reactions attempted are discussed in the Experimental Section.
E. Isolation of Zn(B₆H₉)₂·2THF

Dimethylzinc reacts with hexaborane(10) in a 1:1 reaction in THF to generate methane according to the reaction

\[(\text{CH}_3)_2\text{Zn} + \text{B}_6\text{H}_{10} \rightarrow \text{CH}_3\text{ZnB}_6\text{H}_9 + \text{CH}_4\]

Removal of all of the volatiles at the end of the reaction yields a light yellow oil. However, if the oil is dissolved in chloroform the addition of diethyl ether precipitates a white crystalline solid of the formula Zn(B₆H₉)₂·2THF. The insolubility of the product in the solvent mixture evidently provides the driving force for the disproportionation reaction.

\[2\text{CH}_3\text{ZnB}_6\text{H}_9 \rightarrow \text{Zn}(\text{B}_6\text{H}_9)_2 + (\text{CH}_3)_2\text{Zn}\]

A similar disproportionation is observed for CH₃ZnI at elevated temperatures.\(^{114}\)

\[2\text{CH}_3\text{ZnI} \rightarrow \text{ZnI}_2 + (\text{CH}_3)_2\text{Zn}\]

Although the pure solid Zn(B₆H₉)₂·2THF was stable for days an impure sample showed color and infrared spectral changes within hours at room temperature. A THF solution became yellow after an hour at room temperature but no change was noted in the nmr spectrum after several hours. The compound was air-sensitive but did not react with moisture as rapidly as the corresponding magnesium derivative.
In addition to bands due to coordinated THF absorption, characteristics of $B_6\text{H}_9\cdot$ were observed in the infrared spectrum of the solid. The B-H terminal stretching region showed three peaks at slightly higher energy and with less splitting than in the case of $\text{Mg}(B_6\text{H}_9)\cdot 2\text{THF}$. The peaks were at 2587, 2540 and 2520 (sh) cm$^{-1}$ and very weak bridge absorptions were at 1960, 1920 and 1880 cm$^{-1}$.

F. Isolation of Cd($B_6\text{H}_9$)$_2$

Dimethylcadmium was found to slowly deprotonate hexaborane(10) at 6.5° according to the reaction

$$\text{(CH}_3\text{)}_2\text{Cd} + \text{B}_6\text{H}_{10} \rightarrow \text{CH}_3\text{CdB}_6\text{H}_9 + \text{CH}_4$$

In addition to being thermally unstable the reaction solution was also light sensitive. A more pure product was obtained by vacuum distilling the solvent and the excess reactants from the reaction vessel when the methane evolution became very slow. An oily residue remained after removal of the volatiles, but further pumping resulted in some solid formation. The precipitation was enhanced by the addition of chloroform followed by pentane or ethyl ether. The solid isolated from the mixture was analyzed to be Cd($B_6\text{H}_9$)$_2$. As in the case of the analogous zinc compound disproportionation of the initial product evidently occurs.
The formation of the solid \( \text{Cd}(\text{B}_6\text{H}_9)_2 \) upon distillation of the volatiles may be attributed to the removal of the dimethylcadmium from the system which would enhance the disproportionation.

Pure solid \( \text{Cd}(\text{B}_6\text{H}_9)_2 \) is thermally stable and is the least air-sensitive compound of the series. Heating the solid to 90° for an hour had no effect on the infrared spectrum, and a thirty minute exposure to the atmosphere caused only minor decomposition. Solutions of the compound, however, have very limited stability.

The infrared spectrum shows five very sharp terminal B-H stretches at relatively high energy. They occur at 2620, 2610, 2575, 2565 and 2545 cm\(^{-1}\). The B-H terminal stretch for \( \text{B}_6\text{H}_{10}(\text{g}) \) is at 2600 cm\(^{-1}\) \(^{138}\). Two very weak bridge stretches are at 1940 and 1830 cm\(^{-1}\). Some very weak C-H absorptions and a low elemental analysis indicate that a small amount of coordinated THF may be present in the compound, but it is considerably less than one molecule of THF/Cd.

**G. Reaction of \( \text{B}_5\text{H}_9 \) with \( \text{CH}_3\text{MgBr} \)**

Pentaborane(9) is deprotonated by methylmagnesium bromide in THF at -23° according to the reaction

\[
\text{B}_5\text{H}_9 + \text{CH}_3\text{MgBr} \rightarrow \text{B}_5\text{H}_8\text{MgBr} + \text{CH}_4
\]
However, the reaction proceeds much slower than the corresponding reaction with B$_6$H$_{10}$ at -78° and does not go to completion even at room temperature. The fact that methylmagnesium bromide is less reactive towards pentaborane(9) than hexaborane(10) is consistent with their relative acidities$^{8,25}$. The reaction product, B$_5$H$_8$MgBr, is apparently unstable in the presence of unreacted B$_5$H$_9$ at the reaction temperature and decomposition to the B$_9$H$_{14}^-$ anion occurs.

After the methane evolution had ceased at -23° the THF and excess B$_5$H$_9$ were vacuum distilled from the reaction vessel. Methylene chloride was condensed onto the solid product and an nmr sample was tipped at low temperature. Although the sample contained some solid, it was warmed in the probe and everything was dissolved at room temperature.

The most predominant features of the 32.1 MHz boron-11 nmr spectrum at ambient temperature were a doublet at 7.9 ppm (J=136 Hz) and an apparent triplet due to two overlapping doublets at 20.6 and 23.3 ppm which were all attributed to B$_9$H$_{14}^-$. Evidence for the presence of B$_5$H$_8^-$ was provided by a small doublet at 51.2 ppm (J=158 Hz) and a broad peak at 15.7 ppm which was revealed by the collapse of the B$_9$H$_{14}^-$ doublets by spin decoupling. These values are close to the chemical shifts for the two doublets in the spectrum of
n-Bu₄NB₃H₈ in methylene chloride at 16.3 ppm (J=135 Hz) and 52.6 ppm (J=152 Hz)⁷⁷. The broadness of the low field resonance at this temperature may be due to interaction of the magnesium with the basal B-B bond of the B₃H₈⁴⁻. Similar broadening has been observed in the ¹¹B nmr of Mg(B₆H₉)₂ which is discussed in Section II and in the spectrum of (Φ₂P)₂CuB₅H₈⁵⁸. Since no apparent broadening or shift of any of the resonances of B₉H₁₄⁻ was observed it is believed that there is no significant interaction between this anion and magnesium. Based on the stoichiometry one would formulate the cation as MgBr⁺, however, Mg²⁺ may be present via a disproportionation reaction.

No changes were noted in the boron-11 nmr spectrum after several hours at room temperature, which is indicative of the stability of the B₅H₈⁻ derivative in methylene chloride in the absence of B₅H₉. It has been found that B₉H₁₄⁻, B₇H₈⁻ and BH₄⁻ are the primary decomposition products of KB₅H₈ and that the rate of decomposition is accelerated by the presence of impurities such as pentaborane(9)⁴⁷,⁹⁹. This phenomena appears to be very general. Muetterties has reported that neutral boron hydrides can be reacted with any boron hydride anion to build up the framework to large polyhedral anions¹⁴⁰.

Recently, it has been shown that BH₄⁻ reacts with pentaborane(9) below room temperature to produce B₉H₁₄⁻.
B$_3$H$_8^-$ and one other unidentified product, but no yield was reported$^{141}$. The first reported preparation of B$_9$H$_{14}^-$ was by aqueous base attack on decaborane(14) which gave a 60% yield$^{142}$. Although no experimental details have been published the nmr spectrum of B$_9$H$_{14}^-$ produced by the reaction of excess potassium with pentaborane(9) has been reported$^{143}$.

By adjustment of the reaction stoichiometry to two moles of pentaborane(9) per mole of methylmagnesium bromide the only reaction product observed in the nmr spectrum was B$_9$H$_{14}^-$ although it is likely that some BH$_4^-$ and/or B$_2$H$_8^-$ are produced. Measurement of the excess B$_5$H$_9$ recovered from the reaction mixture indicated that the stoichiometry of the reaction was 1.8/1.

A metathesis reaction of the product yielded (CH$_3$)$_4$NB$_9$H$_{14}$ as identified by infrared spectrum and X-ray powder pattern. The yield of B$_9$H$_{14}^-$ based on the B$_5$H$_9$ consumed by the reaction was 80%. The high yield of this reaction and the ease of the preparation may qualify this reaction as a useful synthetic method of preparing B$_9$H$_{14}^-$ from B$_5$H$_9$. 
II. NMR Studies of Magnesium, Zinc and Cadmium Derivatives of Hexaborane(10)

A. Boron-11 NMR

1. General Features of Spectra

The 32.1 MHz boron-11 nmr spectra of all magnesium, zinc and cadmium derivatives of hexaborane(10) prepared in this investigation are related to the spectra for \( \text{B}_6\text{H}_{10} \) and \( \text{B}_6\text{H}_9^- \). In each case the spectrum of the compound above 0° consists of two resonances in the area ratio of approximately 5:1. The smaller of the two peaks was invariably a well-resolved doublet at a relatively high field position (+49 to +51 ppm). This peak indicates the presence of an apical boron atom bonded to one terminal hydrogen. The magnetic environment of the apical boron of these metalloboranes is similar to apical borons of \( \text{B}_6\text{H}_{10} \) and \( \text{B}_6\text{H}_9^- \). For each of these metal derivatives a single broad basal boron resonance was observed which occurred at a field position intermediate between that of hexaborane(10) and its anion nonahydro-hexaborate(1-) as is shown in Table 7. The overall similarity of the \( ^{11}\text{B} \) nmr spectra of these metal derivatives with that of hexaborane(10) provides spectral evidence that the hexaborane framework is not significantly altered in these compounds. This is consistent with the chemical evidence provided by the rapid low
TABLE 7

BORON-11 NMR DATA FOR HEXABORANE(10) AND ITS DERIVATIVES

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta^{a}$ (J_{B-H})^{b}(base)</th>
<th>$\delta^{a}$ (J_{B-H})^{b}(apex)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiB$_6$H$_9$^{c, d}</td>
<td>-9.0 (107)</td>
<td>50.0 (142)</td>
</tr>
<tr>
<td>B$_6$H$_9$MgBr$^e$</td>
<td>-9.8</td>
<td>50.1 (147)</td>
</tr>
<tr>
<td>Mg(B$_6$H$_9$)$_2$·2THF$^f$</td>
<td>-9.6</td>
<td>49.3 (146)</td>
</tr>
<tr>
<td>Zn(B$_6$H$_9$)$_2$ at 0°</td>
<td>-13.2</td>
<td>48.9 (138)</td>
</tr>
<tr>
<td>Zn(B$_6$H$_9$)$_2$ at -70°</td>
<td>-17, -6.5</td>
<td>48.9 (138)</td>
</tr>
<tr>
<td>CH$_3$ZnB$_6$H$_9$</td>
<td>-11.9 (115)</td>
<td>50.6 (147)</td>
</tr>
<tr>
<td>Cd(B$_6$H$_9$)$_2$ at 0°</td>
<td>-13.3 (118)</td>
<td>50.8 (148)</td>
</tr>
<tr>
<td>Cd(B$_6$H$_9$)$_2$ at -70°</td>
<td>-17, -5</td>
<td>50.8 (148)</td>
</tr>
<tr>
<td>CH$_3$CdB$_6$H$_9$</td>
<td>-12.4</td>
<td>51.4 (146)</td>
</tr>
<tr>
<td>B$_6$H$<em>9$$</em>{10}$^{d, e}</td>
<td>-13.9 (150)</td>
<td>52.6 (153)</td>
</tr>
</tbody>
</table>

$^a$ chemical shift in ppm relative to BF$_3$·OEt$_2$

$^b$ coupling constant in Hz

$^c$ in tetrahydrofuran

$^d$ reference 8, 9

$^e$ in diethyl ether

$^f$ in methylene chloride

$^g$ in tetrahydrofuran/methyl ether solution
temperature regeneration of $B_6H_{10}$ upon addition of HCl to these compounds.

2. Boron-11 NMR of Magnesium Derivatives of $B_6H_{10}$

The 32.1 MHz boron-11 nmr of Mg($B_6H_9$)$_2\cdot2$THF in CH$_2$Cl$_2$ at 40° consists of a basal boron resonance with slight doublet character and a well-resolved apical doublet in the area ratio of 5:1. Upon cooling the sample the basal resonance broadens rapidly in a totally symmetric manner as is seen in Figure 11. At -60° the peak is so broad that virtually no resonance is observed. This is in contrast to the basal resonances of $B_6H_9$ and KB$_6H_9$ which display distinct doublet character down to -70° and to below -30° respectively. Over the temperature range of +40° to -20° only minor changes in the apical resonance is noted, but below -20° the doublet slowly broadens. The fact that only one basal resonance is observed at +40° indicates that on the nmr time scale all five basal borons appear to be in equivalent environments. The time averaged equivalence of the basal borons appears to be maintained down to at least -40° as the broad resonance shows no asymmetry.

Since the collapse of the basal resonance upon cooling is symmetric and no "new" resonances appear from -40° to -100° the broadening of this peak is not attributable to the slowing of the exchange process which causes the basal borons to appear equivalent.
Figure 11. 32.1 MHz boron-11 nmr of Mg(B₆H₉)₂·2THF in methylene chloride.
This is confirmed by the equivalence of the basal terminal hydrogens down to -60° in the pmr spectrum (vide infra). Rather, the extreme broadening is attributed to the rapid quadrupolar relaxation of the basal boron nuclei.

In addition to the spin-lattice relaxation arising from fluctuating local magnetic fields, nuclei such as boron which have a nuclear spin I=1 may also undergo relaxation by the interaction of the nuclear-quadrupole moment with the fluctuating electric field gradient at the nucleus. The rate of nuclear quadrupole relaxation depends on the magnitude of the quadrupole constant for the particular nucleus in the molecule, the local symmetry around the nucleus, and the rotational correlation time which characterizes the rate of re-orientation of the molecule in solution. The latter is generally found to be directly proportional to the molecular size and the macroscopic viscosity of the solution, but inversely proportional to the temperature. For a given compound, temperature dependent spectral changes are generally due almost entirely to changes in the correlation time.

In this case the methylene chloride solutions were not noticeably viscous at low temperature. However, the molecular size difference between Mg(B₆H₉)₂·2THF and B₆H₉⁻ is sufficient to expect slower rotation in solution for the former which would give rise to a
longer correlation time and thus, more rapid quadrupole relaxation. The fact that the basal boron resonance is broadened much more than the apical peak may be attributed to the presence of the magnesium near the base of the framework which could increase the electric field gradient by decreasing the local symmetry. However, it has been shown that in $B_6H_{10}$ the basal boron nuclei relax faster than the apical boron. Some of the broadening is due to spin coupling of the basal terminal hydrogens with the basal borons as irradiation of the sample at ambient temperature with the appropriate decoupling frequency narrows the peak from $f = 300$ Hz to 240 Hz.

Evidence that the broadening of the basal boron resonance is attributable to the bonding of the magnesium to the borane framework is provided by the nmr spectrum of $Mg(B_6H_9)_2 \cdot XCH_3CN$. A sample of $Mg(B_6H_9)_2 \cdot 2$THF was dissolved at low temperature in the more basic solvent acetonitrile. After removal of the solvent, the solid was dissolved in $CD_2Cl_2$. The area ratios of the peaks in the low power pmr spectrum indicated the presence of about one molecule of coordinated THF and approximately five molecules of coordinated $CH_3CN$ per magnesium. These amounts are based on the presence of six bridge hydrogens from the two $B_6H_9^-$ per magnesium. The chemical shift of the bridge hydrogen resonance was $13.57$ which is 0.3 ppm upfield from the bridge protons of
Mg(B₆H₉)_2·2THF and is consistent with more anionic character of the borane. Thus, apparently the acetonitrile essentially fills the coordination sphere of the magnesium ion as the B₆H₉⁻ does not effectively compete for coordination sites. The boron-11 nmr of this solution, unlike that of Mg(B₆H₉)_2·2THF exhibits a well-resolved doublet from ambient temperature to -30° and the apical resonance sharpened noticeably upon cooling. This temperature dependence, the chemical shifts, and coupling constants of the peaks agree very well with those reported for CH₂Cl₂ solutions of n-Bu₄NB₆H₉ in which the free anion is present.

The boron-11 nmr spectra of B₆H₉MgI and B₆H₉MgBr in diethyl ether are very similar to that of Mg(B₆H₉)_2·2THF and exhibit the same temperature dependence. The basal boron resonance of the magnesium halide derivatives are somewhat broader, but this is very possibly due to solvent and viscosity effects. A similar, but less well-resolved spectrum was obtained for a methylene chloride solution of "CH₃MgB₆H₉", which was most likely a mixture of CH₃MgB₆H₉, Mg(B₆H₉)_2 and (CH₃)₂Mg.

3. Boron-11 NMR of Zinc and Cadmium Derivatives of B₆H₁₀

At +20° slight doublet character was evident in the basal boron resonance for the compounds of the apparent formulations CH₃ZnB₆H₉ and CH₃CdB₆H₉. The peaks did broaden markedly upon cooling the THF solutions.
to -20°, although the apical doublets sharpened slightly. It has been suggested that the sharpening of apical peaks for pyramidal frameworks is due to a loss of coupling with the basal borons due to their more rapid nuclear quadrupolar relaxation\(^14\). The chemical shifts of the basal boron resonances, which are listed in Table 7, are found to be considerably closer to the basal resonance of \(\text{B}_6\text{H}_{10}\) than those of the magnesium derivatives.

The boron-11 nmr spectra of \(\text{Zn(B}_6\text{H}_9\text{)}_2\cdot2\text{THF}\) and \(\text{Cd(B}_6\text{H}_9\text{)}_2\) dissolved in a 1:1 THF/methyl ether mixtures are very similar. Doublet character in the basal resonance is barely discernable at 20° for \(\text{Zn(B}_6\text{H}_9\text{)}_2\) whereas it is lost at 0° for \(\text{Cd(B}_6\text{H}_9\text{)}_2\). In both cases sharp apical doublets were observed down to -60°. Upon cooling from 20° to -30° the basal peak of \(\text{Zn(B}_6\text{H}_9\text{)}_2\) rapidly broadened in a symmetric manner. However, at -30° and below, the signal became increasingly asymmetric. At -60° two broad overlapping peaks of unequal area were observed at approximately -17 ppm and -6.5 ppm. The same phenomena occurred for the \(\text{Cd(B}_6\text{H}_9\text{)}_2\) solution although a slightly lower temperature, -70°, was required to observe the same degree of separation. The two broad basal peaks which were at about -17 ppm and -5 ppm are shown in Figure 12. In both cases the upfield peak appeared larger, but the overlap of the resonances prevented
Figure 12. 32.1 MHz boron-11 nmr spectrum of Cd(B₆H₉)₂ in THF/Me₂O at -70°.
area ratio measurements. Thus, at least two different types of basal borons are present in Zn(B$_6$H$_9$)$_2$ and Cd(B$_6$H$_9$)$_2$ and they are time averaged at higher temperature through an exchange process.

Although the boron-11 nmr studies of these compounds provide evidence that some covalent interaction occurs between the metal and the B$_6$H$_9^-$ anion, little insight as to the mode of bonding is provided. In this respect the pmr studies proved to be much more informative.

B. PMR Studies

1. PMR of Mg(B$_6$H$_9$)$_2$·2THF

The pmr spectrum of Mg(B$_6$H$_9$)$_2$·2THF·d$_8$ in CD$_2$Cl$_2$ at +20° exhibited only three resonances as is shown in Figure 13. A broad doublet of area 5 was observed in the basal terminal region of the spectrum at 6.147. Boron-11 spin decoupling collapsed the peak to a very sharp singlet establishing that all of the basal terminal hydrogens are equivalent on the nmr time scale. The equivalence of the bridge protons is indicated by the presence of a single peak of area 3 at 13.227. The narrow width of the bridge peak results from the absence of strong coupling with the basal borons. A single quartet (one arm appears as a shoulder on the upfield side of the bridge resonance) is seen for the apical terminal hydrogen which is spin coupling with the apical
Figure 13. 100 MHz pmr spectra of Mg(B₆H₉)₂·2THF-d₈ in CD₂Cl₂.
boron nucleus \((I=3/2)\). Spin decoupling of the apical boron collapses the quartet to a singlet at 11.657. As seen in Table 8 the chemical shift of each of these resonances is between the respective resonances of \(\text{B}_6\text{H}_{10}\) and \(\text{LiB}_6\text{H}_9\).

Upon cooling the sample to \(-20^\circ\) the basal terminal doublet collapses to a broad singlet which becomes progressively sharper as the temperature is lowered to \(-50^\circ\). Since these hydrogens are directly bonded to the basal borons the resonance is expected to be a quartet as is observed for the apical terminal hydrogen. This lack of strong coupling is a result of the rapid nuclear quadrupolar relaxation of the basal boron nuclei as was discussed in Section II,A. This phenomena, which has been termed "thermal decoupling", has been observed for several other boron hydride compounds\(^{80}\). Most notably, \(\text{B}_3\text{H}_8^-\) is effectively decoupled at \(-100^\circ\) and below, exhibiting a very broad boron-11 resonance and a single sharp proton resonance\(^{80,148}\). The presence of a metal bonded to the anion appears to raise the temperature at which thermal decoupling is effective. The pmr spectrum of \(\phi_2\text{P}_2\text{CuB}_3\text{H}_8\) is as sharp at \(20^\circ\) as the free anion is at \(-100^\circ\)\(^{80}\). In a thorough treatment Marks and Shimp recently showed that the temperature dependence of the pmr spectra of \(\text{Zr(BH}_4)_4\) and \(\text{Hf(BH}_4)_4\) may be attributed to the quadrupole relaxation of the
TABLE 8

PMR DATA FOR HEXABORANE(10) AND ITS DERIVATIVES

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\tau^a$(basal)</th>
<th>$\tau^a$(bridge)</th>
<th>$\tau^a$(apical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{LiB}_6\text{H}_9$ at $-40^\circ$</td>
<td>6.37</td>
<td>13.75</td>
<td>11.98</td>
</tr>
<tr>
<td>$\text{Mg(B}_6\text{H}_9)\text{}_2\cdot 2\text{THF}^c$</td>
<td>6.14</td>
<td>(6.22)$^d$</td>
<td>(13.21)</td>
</tr>
<tr>
<td></td>
<td>$-100^\circ$5.41</td>
<td>6.70 6.9</td>
<td>12.80 13.42</td>
</tr>
<tr>
<td>$\text{Zn(B}_6\text{H}_9)\text{}_2^e$</td>
<td>5.87</td>
<td>12.75</td>
<td>11.75</td>
</tr>
<tr>
<td>$-50^\circ$ to $-100^\circ$</td>
<td>5.33 6.33</td>
<td>12.45 13.04</td>
<td>&quot;</td>
</tr>
<tr>
<td>$\text{Cd(B}_6\text{H}_9)\text{}_2^e$</td>
<td>5.88</td>
<td>(5.79)</td>
<td>(12.74)</td>
</tr>
<tr>
<td>$-60^\circ$ to $-100^\circ$</td>
<td>5.15 6.21</td>
<td>12.6 12.82</td>
<td>&quot;</td>
</tr>
<tr>
<td>$\text{CH}_3\text{ZnB}_6\text{H}_9^f$</td>
<td>5.81</td>
<td>(5.84)</td>
<td>11.43</td>
</tr>
<tr>
<td>$-100^\circ$</td>
<td>5.23 6.24</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CdB}_6\text{H}_9^f$ from $30^\circ$ to $-130^\circ$</td>
<td>5.77</td>
<td>12.65</td>
<td>11.36</td>
</tr>
<tr>
<td>$\text{B}<em>6\text{H}</em>{10}^g$</td>
<td>5.82</td>
<td>(5.84)</td>
<td>(11.00)</td>
</tr>
<tr>
<td>$-150^\circ$5.42 5.76 6.85</td>
<td>9.86 12.14</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

$^a$chemical shifts in ppm relative to tetramethylsilane=10.00

$^b$in methyl ether-d$_6$

$^c$in methylene chloride-d$_2$

$^d$appropriately weighted averages in parentheses

$^e$in 1:1 tetrahydrofuran-d$_6$/methyl ether-d$_6$

$^f$in tetrahydrofuran-d$_8$

$^g$reference 150
boron nuclei.

At -60° the basal terminal resonance displays some asymmetry, and at -70° a split into two peaks is evident. Simultaneously with this change the bridge hydrogen peak also becomes asymmetric and divides into two separate signals. The spectrum at -100° shows two basal terminal peaks in the area ratio of 2:3 and two bridge peaks of areas 1:2. The apical hydrogen resonance is partially collapsed and requires boron spin decoupling to be observed. A distinct shoulder is evident on the upfield side of the large basal terminal peak which is indicative of a third type of basal terminal hydrogen. Accurate areas were measured on spectra recorded at low RF power settings. Since "thermal decoupling" was very effective at -100° and boron-10 (19%) undergoes nuclear quadrupole relaxation at approximately the same rate as boron-11 (81%) the area under the peaks represents all of the protons in the compound.

At -100° the chemical shifts of the basal resonances are 5.417, 6.707 and 6.977 (shoulder) and the bridge proton peaks are at 12.807 and 13.427. The weighted average of these shifts, 6.227 and 13.217, are within experimental error of the shifts of the single peaks at higher temperature, 6.147 and 13.227. Clearly, the pmr spectrum of Mg(B6H9)2·2THF above -60° represents the time average of the low temperature spectrum.
2. PMR of Zn(B₆H₉)₂ and Cd(B₆H₉)₂

As in the case of the boron-11 nmr the pmr spectra of Zn(B₆H₉)₂ and Cd(B₆H₉)₂ in THF/methyl ether resembled one another. At 0° the spectrum of each compound includes a single basal terminal peak, one bridge resonance and an apical hydrogen signal. Chemical shifts are listed in Table 8. The peaks are all shifted downfield from the corresponding peaks of Mg(B₆H₉)₂·2THF and are closer to the positions for B₆H₁₀ and less like the B₆H₉⁻ spectrum. The area ratio of the basal terminal to bridge proton resonances was approximately 5:3. Cooling the sample solutions again caused dramatic spectral changes as the basal terminal and bridge hydrogen peaks split. For Zn(B₆H₉)₂ the bridge resonance divided at -20° and two basal terminal peaks were observed at -50°. A slightly lower temperature, -60°, was required to detect the same basal terminal split in the Cd(B₆H₉)₂ spectrum. Although two bridge resonances were evident at this temperature, they were not sufficiently separated to be resolved (See Figure 14). Area ratios could not be accurately measured for the basal terminal peaks of these spectra due to overlap of the upfield peak with a THF resonance, but they approximated 2:3. The bridge peaks of Zn(B₆H₉)₂ were clearly 2:1. Data listed in Table 8 shows that the weighted average of the separated peaks in each case is within experimental error of the
Figure 14. Spin decoupled 100 MHz pmr spectrum of Cd(B₆H₉)₂ in THF-d₈/Me₂O-d₆ at -80°.
chemical shifts observed in the higher temperature spectra.

The qualitative similarities of the spectra suggest the existence of similar low temperature solution structures for the magnesium, zinc and cadmium derivatives. It is interesting to note that the chemical shift differences between the basal terminal peaks and between the bridge peaks are larger for the magnesium compound than for the zinc and cadmium derivatives (Table 8).

The observation of non-equivalent basal terminal and bridging hydrogens is unquestionably due to the interaction of the metal with the \( \text{B}_6\text{H}_9^- \) anion. The pmr spectrum of \( \text{LiB}_6\text{H}_9 \) establishes the equivalence of the basal terminal and of the bridge hydrogens down to at least \(-130^\circ\) as only one resonance is observed for each type of proton. This supports the conclusion of Johnson, Geanangel and Shore that the low temperature broadening of the basal resonance in the boron-11 nmr spectrum of \( \text{LiB}_6\text{H}_9 \) is due to increased nuclear quadrupole relaxation induced by solution viscosity rather than chemical interaction of the lithium ion with \( \text{B}_6\text{H}_9^- \). The exchange of bridge protons in \( \text{B}_6\text{H}_9^- \) has also been found to be rapid on the pmr time scale in methyl ether solutions of \( \text{KB}_6\text{H}_9 \) at \(-140^\circ\). In contrast to the behavior of \( \text{B}_6\text{H}_9^- \), the bridge hydrogen exchange in hexaborane(10) begins to slow at \(-95^\circ\). At \(-150^\circ\) a spectrum consistent
with the static solid state structure of $C_8$ symmetry as observed in solution$^{20,148}$.

3. Possible Structures and Exchange Processes

As stated above, chemical and nmr evidence indicate that the B$_6$H$_{10}$ framework is not significantly modified in the formation of the magnésium, zinc and cadmium derivatives. The presence of five basal terminal and one apical terminal hydrogens is established by the pmr spectra which precludes substitution of a terminal hydrogen by the metal. If, in the static structure the metal were bonded to the borane through two of the basal terminal hydrogens as in the case of ($\mathcal{O}_3$)$_2$CuB$_3$H$_8$$^{79}$ or (OC)$_4$CrB$_3$H$_8$$^{-78}$, the M-H-B bridge protons would be expected to resonate at much higher field position than the terminal hydrogens$^{151}$. However, no such shift was observed in any of the pmr spectra. The metal could possibly occupy a basal terminal site below the plane of the basal borons analogous to a BH$_2$ groups, but this would very likely give rise to a magnetically unique basal boron and basal terminal hydrogen which are not observed.

The mode of bonding is actually believed to involve insertion of the metal into the boron-boron bond. This would form a three center boron-metal-boron bond. The basal B-B bond of hexaborane(10) represents a center of high electron density according to molecular orbital
calculations and as evidenced by the isolation of the $B_6H_{11}^+$ ion$^{26,27}$. Removal of a bridge hydrogen from $B_6H_{10}$ produces a very basic ion with a second basal boron-boron bond which could coordinate to a metal. The insertion of zinc and cadmium into such a bond has recently been established for $\text{Zn}(B_{10}H_{12})_2^{2-}$ and $[\text{Cd}(B_{10}H_{12})_2E_2]_2$ (See Introduction)$^{102,103}$. The insertion of silicon, germanium, tin and lead in the basic B-B bond of the anion $B_5H_8^-$ has also been definitively established$^{86}$. Recently obtained pmr evidence confirms that copper is inserted into the base of $B_5H_8^-$ in $(\phi_3P)_2\text{CuB}_5H_8$ and metal insertion may occur in $(\phi_2P)_2\text{CuB}_6H_9$.$^{39}$

Except for the possible fortuitous overlap of peaks which are unrelated by symmetry the low temperature pmr spectrum is consistent with a structure of $C_s$ symmetry. A mirror plane is indicated by the area ratios for the basal terminal hydrogens, 2:3 (2:2:1 for $\text{Mg}(B_6H_9)_2\cdot2\text{THF}$), and for the bridge protons, 1:2. This symmetry can arise through various static and dynamic structures for the metal-borane moiety. In each of the $M(B_6H_9)_2$ compounds, both anions appear to be in identical magnetic environments.

The possibility exists that the metal could be bonded to both boron-boron bonds of the framework simultaneously. The bonds may be adjacent or opposite to one another. A model of $B_6H_9^-$ in which the B-B bonds
are opposite reveals that the three bridge hydrogens would impose considerable steric crowding on the metal below the basal boron plane. In addition, ligand repulsions would be great, particularly around the small magnesium atom which must accommodate two $\text{B}_6\text{H}_9^{-}$'s and two molecules of THF. If the B-B bonds were adjacent, the steric crowding would be reduced, but still a factor. Such a configuration around magnesium would represent a donation of six electron pairs from eight bonding atoms. This structure is not favored as magnesium usually is four coordinate with a tetrahedral arrangement of the ligands. The metals were found to be four coordinate in both $\text{Zn}(\text{B}_{10}\text{H}_{12})_2^{2-}$ and $[\text{Cd}(\text{B}_{10}\text{H}_{12})_2^{2-}]_2\text{Et}_2\text{O}]_2^{102,103}$. Therefore, a structure in which only one of the B-B bonds is coordinated to the metal is favored.

Neither of the two possible static structures for the $\text{M-B}_6\text{H}_9$ moiety is consistent with the pmr spectrum. No matter whether the metal is adjacent to the boron-boron bond (I or IV) or opposite to it (II or III) there is no mirror plane of symmetry (See Figure 15). However, time averaging of either of these two structures with its respective mirror image or averaging all four of the structures by an exchange process does give rise to $C_s$ symmetry.

Averaging structures I and IV represents the
Figure 15. Possible representations of the bonding for magnesium, zinc and cadmium derivatives of hexaborane(10).
metal exchanging between two sites with the bridge hydrogens remaining static. Since the basal terminal hydrogens become non-equivalent at higher temperatures in these metal derivatives than in hexaborane(10) the barrier to intramolecular exchange is apparently raised by the substitution of a proton with the metal. This fact militates against the possibility of a metal exchange process which is more rapid than the proton exchange.

Exchange between structures II and III represents a model in which only one bridge proton tautomerizes between two equivalent sites while the metal bridge and the two hydrogen bridges adjacent to it are fixed. A similar limited exchange of bridge protons has been observed at low temperature for 2-CH$_3$B$_6$H$_9$ and 2-BrB$_6$H$_9$. In the temperature range of -25° to -50° the pmr spectrum of 2-CH$_3$B$_6$H$_9$ is consistent with two static bridge protons adjacent to the methyl boron while the other two bridge protons are exchanging between the remaining three bridge sites. At -115° a spectrum is observed which is consistent with an unsymmetric static structure. A similar two step process is observed at slightly lower temperatures for 2-BrB$_6$H$_9$. However, in this case the B-B bond is found to be adjacent to the substituted boron.

The possibility exists that the low temperature pmr spectrum may represent the average of all the structures
I-IV. In this case only the inserted metal would remain static while the bridge hydrogens exchange. Based on the intramolecular exchange mechanism proposed for $\text{B}_6\text{H}_{10}$\textsuperscript{17}, which would not permute the bridge protons (See Introduction), the bridge proton opposite the metal bridge would experience an average magnetic environment which would be different than the average environment of the two adjacent bridge protons.

The lack of solubility of these compounds at low temperature in solvents suitable for very low temperature pmr studies prevented such investigations.

The low temperature solution structures of $\text{Mg}(\text{B}_6\text{H}_9)_2\cdot2\text{THF}$ and $\text{Zn}(\text{B}_6\text{H}_9)_2\cdot2\text{THF}$ may be closely related to their solid state structures. A reasonable structure based on chemical and spectral data would involve a quasi-tetrahedral coordination of the two THF molecules and the two B-B bonds around the metal. The two oxygen atoms and the four borons would thus be in a pseudo-octahedral configuration. Since $\text{Cd}(\text{B}_6\text{H}_9)_2$ is not solvated by two THF molecules the solid state structures may be considerably different, although its solution structure appears to be quite similar to the zinc and magnesium derivatives.

As stated above when the solution temperature of these derivatives is raised the pmr spectra show the equivalence of the five basal terminal and of the
three bridge protons. Examination of the four structures shown in Figure 15 shows that participation of the metal in a rapid intramolecular exchange process in which the metal moves to an adjacent site (I to IV or vice versa) as in the mechanism proposed for $B_6H_{10}$ will account for the equivalence of the basal terminal hydrogens, but the bridge protons will remain non-equivalent. Only a shift of the metal to an opposite B-B bond (II to III) with bridge proton exchange between "jumps" would mix the bridge hydrogens. However, this mechanism requires a $3 \AA$ displacement of the metal and the pathway would be sterically crowded due to the bridge hydrogens. Thus, the equivalence of the bridge protons may be best accounted for by the dissociation of the metal from the $B_6H_9^-$. This process could involve the formation of an ion pair or possibly an intermolecular exchange of $B_6H_9^-$ which would allow the rapid intramolecular exchange of the bridge hydrogens. The fact that the higher temperature spectra represent the weighted average of the low temperature spectra for these compounds and the peaks of the boron and proton chemical shifts are significantly different from those of nonahydrohexaborate salts militates against the presence of only unassociated $B_6H_9^-$ in solution at higher temperatures. Significant interaction between the metal and the borane anion appears to occur up to ambient temperature for each of these
compounds.

In one case evidence was obtained which suggested that intramolecular migration of the metal to an adjacent site occurred. In the temperature range of \(-20^\circ\) to \(-40^\circ\) the pmr spectrum of \(\text{Zn}(\text{B}_6\text{H}_9)_2\cdot2\text{THF}\) dissolved in THF/Me\(_2\)\(\text{O}\) exhibits two well-resolved bridge resonances but only one symmetric basal terminal peak as shown in Figure 16. Upon further cooling the basal terminal peak splits and the low field bridge resonance of area \(1.0\) shifts upfield by \(0.15\) ppm which is indicative of a slightly different environment at the lower temperature.

With the exception of the presence of a large methyl resonance, the pmr spectrum of \(\text{CH}_3\text{ZnB}_6\text{H}_9\) and \(\text{CH}_3\text{CdB}_6\text{H}_9\) at \(0^\circ\) are almost identical to those of \(\text{Zn}(\text{B}_6\text{H}_9)_2\) and \(\text{Cd}(\text{B}_6\text{H}_9)_2\), respectively. They exhibit similar line shapes, relative areas and chemical shifts (See Table 8). However, in the case of both methyl derivatives much lower temperatures are required to quench the exchange process occurring in these systems through which the basal terminal and bridge hydrogens appear equivalent. This difference may be attributable to the apparent intermolecular exchange of methyl groups in these solutions.

For a 1 M solution of \(\text{CH}_3\text{CdB}_6\text{H}_9\) rapid intramolecular exchange of the methyl groups down to \(-70^\circ\) is indicated by the presence of only one methyl proton peak. However, below \(-70^\circ\) the exchange is slowed so that two small peaks
Figure 16. 100 MHz pmr spectrum of Zn(B₆H₉)₂ in THF-d₈/Me₂O-d₆ at -30°.

The basal boron nuclei are spin decoupled.
attributed to methyls bonded to $^{111}\text{Cd}(I=\frac{1}{2})$ and $^{113}\text{Cd}(I=\frac{3}{2})$ are observed on either side of the large $^{112}\text{Cd}-\text{CH}_3$ peak (Figure 10). The couplings constants, $J_{111}\text{Cd}-\text{C}-\text{H}$ and $J_{113}\text{Cd}-\text{C}-\text{H}$ both equaled 73 Hz and were not resolved. These coupling constants, which are very sensitive to other substituents on the metal, are considerably large than the $J's$ of 52 Hz observed for dimethyl-cadmium in THF$^{153}$. This indicates that $\text{CH}_3\text{CdB}_6\text{H}_9$ is the species actually present in solution rather than a mixture of $(\text{CH}_3)_2\text{Cd}$ and $\text{Cd}(\text{B}_6\text{H}_9)_2$. Although the chemical shift of the basal terminal resonance and the bridge hydrogen peak of $\text{CH}_3\text{CdB}_6\text{H}_9$ are very close to those of $\text{Cd}(\text{B}_6\text{H}_9)_2$ (See Table 8), splitting of these peaks occurs at $-60^\circ$ in the latter, but only a slight asymmetry of the peaks is noted at $-125^\circ$ in the former. Although no direct detection of methyl exchange in $\text{CH}_3\text{ZnB}_6\text{H}_9$ could be observed, the same effect was noted for the borane proton resonances. Whereas non-equivalence of the basal terminal and bridge hydrogen is detected by the pmr at $-50^\circ$ for $\text{Zn}(\text{B}_6\text{H}_9)_2$, 1 M solutions of $\text{CH}_3\text{ZnB}_6\text{H}_9$ had to be cooled to $-100^\circ$ to see the same effect. Evidence supporting the rapid exchange of methyl groups of dimethylzinc has been reported$^{154}$. Exchange of both methyls and $\text{B}_6\text{H}_9^-'$s is consistent with the disproportionation of the $\text{CH}_3\text{MB}_6\text{H}_9$ species.

In summary, the low temperature pmr spectra
establishes the covalent nature of the bonding in this series of metalloboranes of magnesium, zinc and cadmium formed by the deprotonation of hexaborane(10). In solution at low temperature the metal appears to be inserted into a single boron-boron bond while intramolecular bridge proton exchange maintains $C_3$ symmetry of the $M-B_6H_9$ moiety. At higher temperature equivalence of all the basal sites is observed as a result of an exchange process which probably involves metal-borane dissociation.

III. Nonahydrohexaboratobis(cyclopentadienyl)titanium(III)

A. Preparation and Characterization

Bis(cyclopentadienyl)titanium(III) chloride reacts with potassium nonahydrohexaborate in tetrahydrofuran at $0^\circ$ according to the following reaction:

$$(\text{h}_5^5\text{C}_5\text{H}_5)_2\text{TiCl} + \text{KB}_6\text{H}_9 \rightarrow (\text{h}_5^5\text{C}_5\text{H}_5)_2\text{TiB}_6\text{H}_9 + \text{KCl}$$

Generally a 60% yield of the blue solid products was obtained. The KCl formed was identified by its X-ray powder diffraction pattern.

The solid $(\text{h}_5^5\text{C}_5\text{H}_5)_2\text{TiB}_6\text{H}_9$ was found to be relatively stable, decomposing very slowly over months at room temperature. However, the compound is extremely oxygen-sensitive as expected for a Ti(III) compound, and could only be manipulated under high vacuum or in
an atmosphere containing no more than 1 ppm of oxygen.

The molecular nature of the compound is suggested by its solubility in non-polar solvents such as benzene and toluene and by its volatility. The compound was found to sublime slowly at 90-100° although it was accompanied by thermal decomposition. Sublimation at temperatures approaching the melting point, 123°, yielded considerable decomposition to the volatile compound \((h^5-C_5H_5)_2TiBH_4\)^58.

The rapid low temperature regeneration of \(B_6H_{10}\) upon reacting the compound with HCl is evidence that the hexaborane(10) framework remains intact in the compound. This also militates against the possibility that the titanium is terminally bonded to the borane. In the case of the terminally substituted \(\text{2-}[\text{Mn(CO)}_5]-B_5H_8\) reaction with HCl, it does not regenerate pentaborane(9)^87 whereas bridge-substituted metalloboranes such as \((\phi_3P)_2CuB_5H_8\) and HCl react to produce the parent borane^39,^88.

The infrared spectrum of the compound establishes that the cyclopentadienyl rings are pentahapto and displays absorption for the borane. Pentahaptocyclopentadienyl ring systems have a relatively simple i.r. spectrum with three main bands at 3050-3100(m), 1000(s) and 800(vs) cm\(^{-1}\) and variable bands at 1100 and 1400 cm\(^{-1}\) in contrast to monohaptocyclopentadienes which
have very complex spectra. The spectrum of \((\text{C}_5\text{H}_5)_2\text{TiB}_6\text{H}_9\) as shown in Figure 17 included a single peak at 3100 cm\(^{-1}\), a sharp peak at 1010 cm\(^{-1}\) and a very strong broad peak at 812 cm\(^{-1}\). A medium band at 1435 cm\(^{-1}\) could be due to either the \(\text{C}_5\text{H}_5^−\) or \(\text{B}_6\text{H}_9^−\). No other strong bands were observed for the cyclopentadienyl rings. One of the three medium intensity bands at 630, 608 and 588 cm\(^{-1}\) may also be due to \(\text{C}_5\text{H}_5\). The B-H terminal region exhibited four sharp, strong absorptions and a weak broad peak at 2400 cm\(^{-1}\). The weak band at 2290 cm\(^{-1}\) was present in the spectrum of \((\text{h}^5-\text{C}_5\text{H}_5)_2\text{TiCl}\).

B. Mass Spectrum

The mass spectrum of the compound, which was consistent with the formulation of \((\text{h}^5-\text{C}_5\text{H}_5)_2\text{TiB}_6\text{H}_9\), included several very prominent features. The most intense peak in the entire spectrum is at \(m/e=178\) which corresponds to a \(\text{Cp}_2\text{Ti}^+\) fragment (\(\text{Cp}=\text{h}^5-\text{C}_5\text{H}_5\)). An envelope with a maximum at \(m/e=89\) is attributed to \(\text{CpTi}^+\). A notable envelope with its strongest peak at \(m/e=71\) fits the characteristic polyisotopic fragmentation pattern of \(\text{B}_6\text{H}_{10}\). A relatively intense peak is present at 76 which is the parent mass of \(\text{B}_6\text{H}_{10}\) indicating that the anion readily picks up a proton in the spectrometer. Hexaborane(10) fragments containing four and five borons were also observed. The intense peak
Figure 17. Infrared spectrum of \((h^5-C_5H_5)_2TiB_6H_9\) in nujol.
at m/e=191 may represent the single boron fragment \( \text{Cp}_2\text{TiBH}_2^+ \).

A moderately intense envelope appears for the molecular species \( \text{Cp}_2\text{TiB}_6\text{H}_9 \). The largest peak is at m/e=252 and corresponds to the mass of the molecule which is expected to be statistically most abundant, \( (^{12}\text{C}_5\text{H}_5)^2^{48}\text{Ti}^{10}\text{B}^{11}\text{B}_5\text{H}_9^+ \). The peak at 253 would be due primarily to \( (^{12}\text{C}_5\text{H}_5)^2^{48}\text{Ti}^{11}\text{B}_6\text{H}_9^+ \). In addition to species containing carbon-13 or deuterium some contribution to the small peak at m/e=254 may be attributed to \( (\text{C}_5\text{H}_5)^2\text{TiB}_6\text{H}_{10}^+ \).

With the exception of two small peaks at 257 and 259 no masses are observed above 254. Some weak peaks due to the fragmentation of the hexaborane(10) framework bonded to a \( \text{Cp}_2\text{Ti} \) moiety were observed, but particularly intense envelopes at m/e=203 and 213 from \( \text{Cp}_2\text{TiB}_2^+ \) and \( \text{Cp}_2\text{TiB}_3^+ \) with varying numbers of hydrogens were detected. The presence of a strong set of peaks from a single boron species bonded to \( \text{Cp}_2\text{Ti}^+ \) was noted above. Broad sets of masses which may be attributed to \( \text{CpTi}^+ \) bonded to one, two, three, and four boron fragments show maxima at m/e=124, 137, 152 and 161 respectively. A peak at m/e=48 appears for Ti\(^+\) and peaks at 65 and 66 are probably due primarily to \( \text{C}_5\text{H}_5^+ \) and \( \text{C}_5\text{H}_6^+ \). Brintzinger and Bercaw have attributed the presence of an m/e=66 peak as an empirical indication...
of the σ-bonded C₅H₄. However, in this case, i.r. establishes that the rings are pentahapto C₅H₅ and the C₅H₆⁺ is believed to arise from the availability of protons in the spectrometer from the borane fragmentation. No fragmentation of the cyclopentadienyl rings is detected which is consistent with observations for similar compounds.

C. Boron-11 NMR

The 80.2 MHz boron-11 nmr spectrum, which is shown in Figure 18 shows two relatively sharp singlets at -37 ppm and +19 ppm of relative area 2:1 respectively. These peaks are shifted approximately 30 ppm downfield from the normal position of the basal and apical resonances of B₆H₉⁻. It has been found that the presence of paramagnetic ions such as Fe(III), Mn(II), or Cr(III) in solutions of boron hydrides shifts the entire nmr spectrum and decouples the hydrogens from the borons. This phenomena was found to be particularly effective for boron hydride anions such as B₁₀H₁₀⁻ and B₃H₈⁻. The 80.2 MHz nmr also reveals an extremely broad resonance at -93 ppm. Measurement of the peak was very difficult but it appears to represent two borons. This accounts for four of the basal borons. No other resonances could be observed. However, portions of the spectrum were obscured by resonances from the pyrex insert. The broadness of the lowfield peak and its large shift of
Figure 18. 80.2 MHz boron-11 nmr spectrum of \((h^5-c_{5}H_5)_{2-}TiB_6H_9\) in toluene at 26°.
82 ppm downfield from the position of a basal boron resonance of $\text{B}_6\text{H}_9^-$ suggests that these borons are directly bonded to the paramagnetic metal. This is consistent with the observation of contact and pseudo-contact shifts by Hawthorne in metallocarboranes containing paramagnetic metals\textsuperscript{159}. For (3)-1,2-dicarbollyliron(III) derivatives, borons not bonded directly to the metal appeared as broadened singlets. Two borons bonded directly to the Fe(III) were shifted to very high field and were extremely broad. The resonance for the third boron bonded to the metal was so broad that it could not be definitively located.

In this case it appears that the apical boron and two basal borons are not interacting directly with the titanium and are therefore not greatly affected by the unpaired electron. The three other basal borons, however, appear to be greatly affected by the metal and may be bonded directly to it. In light of the rapid reaction with HCl and results presented in the discussion of Group II metal derivatives (Section II) the titanium is believed to be inserted into a boron-boron bond rather than terminally substituted. Insertion of the metal into one B-B bond would leave three borons unaffected, whereas insertion into two opposite B-B bonds would broaden all but one basal resonance. Therefore, metal insertion appears to occur at two adjacent boron-boron
bonds. One titanium may be able to simultaneously bond to the two B-B bonds of $B_6H_9^-$. However, molecular weight measurements in benzene established that the species in solution is dimeric. Therefore, it is believed that each titanium is simultaneously bonded to two $B_6H_9^-\cdot$s, and each $B_6H_9^-$ is bonded to two titanium atoms as shown in Figure 19. The two titanium(III) atoms would like in a plane bisecting all four cyclopentadienyls while the two nonahydrohexaborates which bridge the metals would be related by a center of inversion. The boron which is bonded to both titaniuums may be the unique boron not observed in the nmr spectrum.

This structure fulfills the electronic, charge and steric requirements of the titanium. While the $-1$ charge of the $B_6H_9$ anion provides neutrality for the complex, the donation of two electron pairs brings the total number of outer electrons around titanium to 17, which is one short of attaining an effective atomic number of 36. The ligand configuration is often found to be quasi-tetrahedral around titanium(III) in bis-cyclopentadienyl derivatives. This criterion is met if each boron-boron bond is considered to occupy one coordination site. Often it is found that polymerization occurs through bridging ligands to meet these electronic and steric conditions such as in $(Cp_2TiCl)_2$, $(Cp_2TiCN)_3$ and $(Cp_2TiSCN)_3$. Numerous examples
Figure 19. Proposed structure of $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiB}_6\text{H}_9$ dimer.
have also been found where a single ligand acts as a
bidentate towards titanium as in Cp₂TiO₂CR (R=H, CH₃,
C₆H₅, CH₃(CH₂)₈, CH₃(CH₂)₁₆₁⁶₃, Cp₂TiBH₄⁵₈,⁶₂ and n-
allyl derivatives Cp₂TiC₃H₄R¹⁶₄. Thus, one may expect
that the titanium(III) to utilize both of the basic
boron-boron bonds of B₆H₉⁻.

D. EPR Spectrum

The epr spectrum in benzene solution at ambient
temperature shows no indication of interaction between
the two titaniuims. Only a single symmetric signal was
observed and no signal was found near g=4 which would
correspond to a M=2 transition arising from a triplet
state¹⁶⁵ (See Figure 2Q). The g_avg value of 1.979 is
consistent with observations of numerous Ti(III) com-
plexes¹⁶₆. A similar spectrum was observed in THF.
No hyperfine splitting was observed for this compound.
Splitting was also absent from the spectra for Cp₂TiBH₄
and Cp₂TiB₃H₈.

The e.p.r. spectrum of the finely-ground solid
(Figure 20) exhibits a line shape characteristic of
anisotropy which yields three different g values¹⁶⁷.
The average of the three values is within experimental
error of the value observed for the solution spectrum.

E. Octahydropentaboratobis(cyclopentadienyl)titanium(III)

The reaction of potassium octahydropentaborate
Figure 20. EPR spectrum of \((h^5-C_5H_5)2TiB_6H_9\) at ambient temperature: a) as a solid, b) in benzene solution.
with bis(cyclopentadienyl)titanium(III) chloride proceeds according to the reaction

\[ \text{KB}_5\text{H}_8 + (\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiCl} \xrightarrow{\text{Me}_2\text{O}, -78^\circ\text{C}} (\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiB}_5\text{H}_8 + \text{KCl} \]

The oxygen sensitive purple product obtained from this reaction appeared to be considerably less stable than the corresponding hexaborane(10) derivative and was not as well characterized. The infrared spectrum established the presence of B-H terminal groups and the penta-hapto bonding of the cyclopentadienyl rings. The paramagnetic nature of the compound was confirmed by the observation of a single unstructured epr signal.

As in the case of the hexaborane(10) derivative the rapid low temperature regeneration of the original neutral boron hydride with HCl indicates that the framework is not significantly altered in the derivative and suggests that the metal is not terminally bonded. The 32.1 MHz boron-11 nmr displays only two resonances in the area ratio of 2:1. Again, it is possible that two basal borons are bonded directly to the titanium and are so broadened that they were not observed.
APPENDIX

A. Glove Box

1. Description of Glove Box

The purpose of the glove box is to provide a dry, oxygen free inert atmosphere in which non-volatile, water and oxygen-sensitive compounds can be manipulated. Derivatives of hexaborane(10) and pentaborane(9) are generally air and moisture-sensitive and titanium(III) compounds are extremely reactive towards oxygen. Therefore, a glove box with an atmosphere containing no more than several parts per million (ppm) of oxygen and water was required to successfully study the chemistry of these compounds.

A model HE-43-2 Dri-Lab glove box was purchased from the Vacuum/Atmospheres Corporation of Los Angeles, California. It was equipped with a mineral oil bubbler to prevent an excess positive pressure build-up in the box. Both ante chamber (port) doors were sealed with a rubber o-ring. Charco Buta-Sol gloves that were 30/1000 of an inch thick were purchased from the Charleston Rubber Company, Charleston, South Carolina.
gloves were worn by the user to reduce the diffusion of water through the gloves.

A model 1402 Welch Duo-Seal vacuum pump with a free air displacement of 140 liters/minute was employed for the evacuation of the ante chamber. To filter the oil from the exhaust air and to muffle the operational noise of the pump a filter was devised. A piece of wire screen was soldered to the threaded end of a twenty inch long, one inch copper pipe. The pipe which screwed into the exhaust chambers of the pump was half filled with #1 steel wool. An eight inch layer of #0 and two inches of #00 steel wool were packed above the first layer. The box was equipped with ball valves to regulate the flow of air from the port to the pump, and to open the evacuated port to the main chamber of the box. The ante chamber pressure was monitored by a vacuum pressure gauge.

2. Purification System

The purification tower consisted of a brass drum which was divided into two sections by a piece of stainless steel screen. The bottom section contained five pounds of Linde 13X molecular sieve for water and solvent removal. The sieve has a capacity of 0.031 lb. H₂O/lb. sieve. The upper section held four pounds of Dow's Q-1 catalyzed copper which was purchased from Aertronic
Associates, Inc., Dayton, Ohio. One pound of 13X molecular sieve was placed on top of the Q-1 to prevent dusting. The Q-1, which consists of finely-divided copper on an aluminum matrix, readily reacts with oxygen at room temperature to form cuprous or cupric oxide. The Q-1 removes 2.3 ml of O_2/g Q-1 at a rate as high as 6000 volumes of gas/volume of Q-1/hour.

The purification tower was wrapped in two heating jackets which were custom made by the Briscoe Manufacturing Company, Columbus, Ohio. The 788 and 672 watt jackets were each regulated with individual 115 volt Briskeat percentage controllers that were also made by the Briscoe Mfg. Co. The jackets contained iron-constantan thermocouple leads for temperature measurement.

The Q-1 and 13X molecular sieve are regenerated in the same process. The copper oxide is reduced by passing a stream of 5% hydrogen in nitrogen countercurrent to the normal flow through the tower at a temperature of 150-300°. The regeneration product is water. The sieve is regenerated at 200-600° by purging with dry gas followed by evacuation. Although repeated regeneration does not reduce the efficiency of the Q-1, it is deactivated by exposure to H_2S and other compounds containing reduced sulfur. Inorganic acids poison the molecular sieve.

The atmosphere was continuously recirculated
through the purification tower by a light-duty M-D blower, model number 11*02.5-395, which was manufactured by MGD Pneumatics, Inc., Racine, Wisconsin. The blower was driven by a Dayton one-third horsepower (1725 RPM) electric motor. To prevent the transfer of vibrations of the blower to the dry box one inch stainless steel bellows were employed for connection to the system.

One inch hard copper tubing was used for the primary recirculation line. One-half inch tubing was used for the secondary gas lines. Copper fittings were all silver soldered. Connections were also made with ball and socket joints or Swagelok connections and unions depending on the situation. Electrical valve control was achieved by using Asco 9/32 inch solenoid valves. Lunkenheimer 711XL-T stainless steel ball valves with Teflon seats were manually operated.

3. Normal Operation

A schematic drawing of the dry box and purification system is shown in Figure 21. Nitrogen from the main chamber is continuously pulled through the filter into the blower. The gas is then forced through the purification tower and is filtered again as it re-enters the box. Additional nitrogen is supplied to the system when necessary from a cylinder of Matheson Prepurified nitrogen or nitrogen may be removed from the system by the vacuum pump. If the differential between the dry
Figure 21. Schematic of recirculation and purification system the atmosphere of glove box.
box pressure and the atmospheric pressure approaches zero, solenoid valve 1 is activated by a Dwyer no. 1822-1 pressure switch. This allows nitrogen to flow into the system until the pressure differential is increased to the point that the pressure switch no longer activates solenoid valve 1. Solenoid 1 may also be activated manually by depression of the right side of the dual foot switch (Linemaster "Executive"). Solenoid valve 2 which opens the system to the vacuum pump to remove nitrogen may be activated by depression of the left side of the dual foot switch. Utility valves with nozzles in the dry box are connected directly to the nitrogen cylinder and to the evacuated portion of the system. A large mineral oil bubbler prevents an excessive pressure build-up from occurring in the dry box.

A user of the box checks that valve D is closed; then opens the outer ante chamber door. After placing the equipment in the port the outer door is closed and valve C is opened to evacuate the ante chamber. After ten minutes valve C is closed and valve D is opened. This allows purified nitrogen from the box to flow into the port. As the pressure decreases in the box the pressure switch activates solenoid valve 1 and cylinder nitrogen rushes into the box to maintain a positive pressure differential with the atmosphere. When the pressure in the ante chamber exceeds one atmosphere the pressure
switch deactivates solenoid valve 1. Valve D is then closed; valve C is opened to evacuate the port a second time. After ten minutes the port is again filled with nitrogen. As the port is being filled the user pushes his hands into the glove box. Once the port pressure equals the main chamber pressure the inner door may be opened. To leave the glove box the inner door is securely closed, valve D is closed and the outer door is opened. After usage the port is again evacuated and refilled with nitrogen.

4. **Regeneration of Purification Tower**

Under normal circumstances the purification tower will require regeneration every thirty to ninety days depending upon its usage. The procedure begins by turning off the blower, closing ball valves A and B, and opening valve F. The percentage controllers for both heating blankets are turned on and adjusted to a setting of forty-five. Approximately one hour is required to heat the tower to 300°. The temperature is monitored by the iron-constantan thermocouples in the heating mantles using a potentiometer and a 0° reference bath. Once the temperature has reached 300° the percentage controllers are adjusted to 35-40 and valve E is opened to allow 5% hydrogen in nitrogen (Burdett) to flow through the tower at a rate of one cubic foot per minute. The
flow rate is monitored by a gas flow meter. After the hot moist air exits the tower it passes through a cooling coil and escapes from a mineral oil bubbler. The exit gas from the tower should not exceed 350°. This temperature is measured by a thermocouple which is placed in a small well at the base of the tower. Similar wells are placed near ball valves A, B, and F to monitor their temperature. To avoid damage to the Teflon seats of these valves the temperature must be kept below 180°. After one hour (60 c. ft. of 5% H₂) the cold trap is filled with liquid nitrogen, valve E is closed, valve F is closed and solenoid valve 2 is activated by the manual switch. After one to two hours both heating blankets are turned off and the tower is allowed to cool overnight under vacuum.

To resume normal operation solenoid valve 2 is deactivated with the manual switch and valve B is slowly opened to refill the tower with nitrogen. Valve A is then opened and the blower is turned on. The stopcocks associated with the cold trap are closed and the water-filled trap is replaced by a clean dry trap.

5. Methods of Testing Atmosphere

Several different methods were used to determine the relative oxygen and water content of the glove box atmosphere. A light bulb provided a good test for atmos-
phere purity. The glass was carefully removed from a 25 watt light bulb; then it was plugged in inside the glove box. At 1 to 5 ppm oxygen and water the bulb will burn for days or weeks. However, the filament will last only hours or minutes at higher impurity levels. The primary disadvantage of this method is the time required to make a determination and the non-uniformity of light bulbs.

Various chemical methods are available to check for excessive oxygen and water in a dry box. Titanium-(III) compounds which undergo color changes upon oxidation were found to provide an excellent test for the presence of oxygen.

A method for measuring the oxygen level of the dry box was developed which involved mass spectral analysis. An evacuated bulb with a stopcock and a 14/35 standard taper joint was taken into the dry box and a sample of the atmosphere was collected. After recording several background spectra at different settings, the mass spectrum of the dry box gas sample was recorded in the region from m/e=29 to 33 on an AEI MS-10. Generally, best results were obtained with the highest sensitivity setting, a trap current of 150 uA and the slowest scan rate. All spectra were obtained at an electron beam control setting of 70 e.v. with an analyzer pressure of 5.4 X 10^{-6} torr.
Since the natural relative abundance of $^{15}\text{N}$ is 0.36%, the fraction of $^{15}\text{N}_2$ in a nitrogen sample is $(0.0036)^2$ or $13 \times 10^{-6}$. Therefore, the concentration of $\text{N}_2$ with a mass of 30 a.m.u. is 13 ppm. Using this standard the concentration of $^{16}\text{O}_2$ can be determined approximately by comparison of the area of the m/e 30 peak to the area of the m/e 32 in the mass spectrum. The areas of these two peaks were determined using a plane polarimeter. Correcting for the background present in the instrument the following equation is used to determine the oxygen concentration:

$$\frac{\text{Area}(\text{m/e}=32) - \text{Area(}\text{m/e}=32, \text{background})}{\text{Area(}\text{m/e}=30) - \text{Area(}\text{m/e}=30, \text{background})} \times 13 \text{ ppm} = \text{O}_2 \text{ in ppm}$$

This method has proven to give at least a semi-quantitative measure of the oxygen content in the glove box in a relatively small amount of time.
B. Crystal Growing Apparatus

1. Description of Apparatus

To grow crystals of \((B_6H_9)_2Mg\cdot2THF\), which are air-sensitive and have limited thermal stability in solution, the apparatus shown in Figure 22 was constructed. This system allows a concentrated solution to be cooled at a steady controllable rate to the temperature where the solubility of the solute is exceeded and crystal formation begins.

The apparatus consists of a two liter glass dewar that is filled with an appropriate liquid such as isopropyl alcohol. Cold nitrogen is passed through a copper heat exchanger in the bottom of the dewar. The liquid is rapidly stirred to keep the temperature equilibrated throughout the system. The temperature is monitored with a low temperature thermometer. The cold nitrogen is supplied by passing current through a nichrome wire heater which is suspended near the bottom of a 50 l. dewar of liquid nitrogen. The rate of nitrogen boil-off is controlled by adjusting the current supplied to the heating coil with a Variac variable resistor.

The vessel used for growing the crystals consisted of a glass tube with a disecarm that was fitted to a
Figure 22. Apparatus for growing crystals from a saturated solution at low temperature.
30 ml. Kjeldahl flask with a 14/35 standard taper joint. The tube was also fitted with a Teflon stopcock adaptor. The overall dimensions must allow for the entire side-arm to be below the liquid surface with adequate space for the stirrer to turn without striking the lower bulb.

2. Operation of the Apparatus

A nearly saturated solution of the solute to be crystallized was prepared in the Pyrex tube. If a stirring bar was required it was then moved to the lower bulb by manipulation with a large magnet. The vessel was then suspended in the cold bath which was previously adjusted to the starting temperature. By regulating the current to the heater in the liquid nitrogen dewar, the temperature decrease of the bath was adjusted to 3° to 5° per hour. As crystal formation commenced the rate of cooling was decreased to less than 1° per hour. The growth of the crystals was followed, without disturbing the solution, by use of a dental mirror.

When a large number of crystals had attained an appropriate size for mounting in X-ray capillaries (0.3-0.5 mm) the vessel was raised out of the bath and the mother liquor was rapidly but carefully tipped into the sidearm bulb. The lower bulb was then maintained at a lower temperature than the remainder of the apparatus.
to prevent condensation of the solvent which could dissolve the crystals. On the vacuum line the solvent was distilled from the lower bulb.
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