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NUCLEAR MAGNETIC RESONANCE STUDIES
OF HEPTABORANE SPECIES

DISSERTATION

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

By

James D. Ragaini, B.A.

***

The Ohio State University

1977

Reading Committee:

Dr. D. W. Meek
Dr. S. G. Shore
Dr. A. Wojcicki

Approved By

[Signature]

Department of Chemistry
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February 11, 1947 . . . . Born - Norwalk, Connecticut

1969 . . . . . . . . . . B.A., University of Connecticut, Storrs, Connecticut


1970-1972 . . . . . Correctional Specialist, United States Army

1972-1974 . . . . . Teaching Associate, Department of Chemistry, The Ohio State University, Columbus, Ohio

1974-1977 . . . . . Research Associate, Department of Chemistry, The Ohio State University, Columbus, Ohio

PUBLICATIONS


FIELDS OF STUDY

Major Field: Inorganic Chemistry

Studies in Nonmetal Chemistry. Professor Sheldon G. Shore
Studies in Transition Metal Chemistry. Professors Daryle H. Busch, Andrew Wojcicki, Devon W. Meek, Daniel L. Leussing, and Eugene P. Schram.
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INTRODUCTION

I. Historical

Productive study of the boron hydrides was begun in the early part of this century by A. Stock and his coworkers (1). Their achievements are noteworthy since they developed a completely new era of chemistry while simultaneously developing vacuum techniques to handle these reactive compounds in the absence of air, moisture and grease.

Stock and his coworkers discovered $B_2H_6$, $B_5H_9$, $B_6H_{10}$ and $B_{10}H_{14}$ which they classified as members of the $B_nH_{n+4}$ homologous series and $B_{5}H_{11}$ and $B_6H_{12}$ as members of the $B_nH_{n+6}$ homologous series (1).

In the 1930's, research into the chemistry and preparation of the boron hydrides was begun in the United States by Schlesinger and Burg (2,10). After World War II, extensive research programs were instituted to develop high energy fuels consisting of boron hydride derivatives (3). When the programs ended, interest in the compounds continued due to their intrinsically interesting chemical nature and structural characteristics. Once categorized as chemical oddities, parallels can now be found, between features of the boron hydrides and carbocations and transition metal cluster compounds (4,5,27,28,58).
II. The Chemistry of Hexaborane(10)

A. Preparation of Hexaborane(10)

The first preparation of $B_6H_{10}$ involved acidification of magnesium boride resulting in approximately 0.1% yield (1). Much later the yield was increased to about 6% (6). A number of workers used methods involving silent electric discharge to produce $B_6H_{10}$ from gaseous mixtures containing $B_2H_6$, however the yields were very small (7-9). Reacting basic reagents such as $(C_2H_5)_3N$ (11) or $(CH_3)_2O$ (12) with $B_5H_{11}$ produced small amounts of $B_6H_{10}$ also. However separation from other products was tedious. The reaction of $(C_2H_5)_3NH[B_9H_{14}]^-$ with polyphosphoric acid formed some $B_6H_{10}$ but again the yield was small (13). Hexaborane(10) was also produced from the decomposition of $B_5H_{11}$ but only very slowly (14). This method was used to purify samples mixed with small amounts of $B_5H_{11}$.

By far the most practical method for producing $B_6H_{10}$ is from the reaction of a pentaborate salt and diborane (15, 16). The sequence as shown produces $B_6H_{10}$ in 75% yield (16).

$$Br_2 + B_5H_9 \rightarrow 1-BrB_5H_8 + HBr \quad (17)$$

$$1-BrB_5H_8 + KH \rightarrow K^+[1-BrB_5H_7]^- + H_2$$

$$K^+[1-BrB_5H_7]^- + 1/2 B_2H_6 \rightarrow B_6H_{10} + KBr$$

B. Physical Properties of Hexaborane(10)

Hexaborane(10) is a colorless mobile liquid which decomposes slowly at ambient temperature with evolution of $H_2$ (1). It is not hydrolyzed completely by water on alkali (1). Hexaborane(10) has a
melting point of -62.3° (18), a boiling point of 108° (18), and a vapor pressure of 7.5 mm at 0° (15). In contrast to $B_2H_6$ and $B_5H_9$ for example, $B_6H_{10}$ does not ignite or explode in air (1).

C. Structure and Bonding in Hexaborane(10) and Related Species

The X-ray crystal structure of $B_6H_{10}$ indicates that the molecule possesses $C_{5v}$ symmetry (19,20,30). The boron atoms form a pentagonal pyramid wherein each boron atom is bonded to a terminal hydrogen. In addition there are four bridging hydrogens, each of which is bonded to two boron atoms in the basal plane. A boron-boron bond is also present between two boron atoms in the basal plane (Figure 1a).

Another boron hydride which is also pyramidal is pentaborane(9), $B_5H_9$. The X-ray crystal structure (21,22) reveals it to be a square pyramid ($C_{4v}$ symmetry) of boron atoms with four bridging and five terminal hydrogens (Figure 2a).

Structural characteristics of boron hydrides cannot be described solely in terms of traditional two electron, two center bonds since boron exhibits coordination numbers greater than four when only four atomic orbitals are available for bonding. For example in the case of pentaborane(9), the apical boron atoms uses one orbital in bonding with the terminal hydrogen. The other three hybrid orbitals are available for bonding with the four boron atoms in the basal plane. If two hybrid orbitals of two basal boron atoms overlap in a central fashion with one hybrid orbital of the apical boron atom (Figure 2b), a three center bond results. Hexaborane(10) possesses two of these three center bonds (Figure 1b).
Figure 1. Structure of Hexaborane(10)
(a) Molecular structure
(b) Valence structure
Figure 2. Structure of Pentaborane(9)

(a) Molecular structure
(b) Valence structure
(c) Valence structure utilizing fractional bonds (reference 111)
The bonding of the bridge hydrogens also involves a three center interaction. The hydrogen s orbital overlaps with hybrid orbitals of two adjacent boron atoms in the basal plane. The remaining interactions may be described in terms of two center bonds (Figure 1b, 2b). The fact that $B_9H_9$ possesses $C_{4v}$ symmetry is explained by the existence of resonance structures (23).

A system for bookkeeping electrons in polyhedral borane structures has also been developed. In essence the method involves summing all available electrons and subtracting two for each boron atom to account for boron-hydrogen terminal bonds. Those remaining comprise the polyhedral framework bonding electrons (5,28,58). Thus two electrons are allotted to each three center bond.

The concepts of the three center bond and resonance structures have been developed into a topological theory to describe the unusual structures of boron hydride molecules (23,24) (Figures 1b, 2b). Localized orbital studies have resulted in refinements of these concepts with the development of fractional three center bonds (110,29) (Figure 2c).

Both the boron-11 and proton n.m.r. spectra of $B_9H_9$ are consistent with $C_{4v}$ symmetry (25). In the case of $B_6H_{10}$ however the spectra at ambient temperature indicate $C_{5v}$ symmetry (26). This degree of symmetry cannot be rationalized solely in terms of three center bonds and resonance structures (Figure 1b). It has been shown that a rapid intramolecular migration of the bridging hydrogens produces apparent $C_{5v}$ symmetry on the n.m.r. time scale (26). At low
temperature the migration is quenched and the spectra indicate $C_3$ symmetry (26).

A localized orbital study of $\text{B}_6\text{H}_{10}$ (137) has shown that the bridge hydrogens and basal boron atoms are slightly positively charged while the apical boron atom and the terminal hydrogen atoms are slightly negatively charged.

D. Reactions of Hexaborane(10) and Related Species

Before practical procedures for the preparation of $\text{B}_6\text{H}_{10}$ were discovered, its derivative chemistry was virtually unstudied. Recently however there has been a much greater interest in the chemistry of $\text{B}_6\text{H}_{10}$ since it can be easily prepared and purified (16). Isolation of the alkylated derivatives $2,3-(\text{CH}_3)_2\text{B}_6\text{H}_6$ (31,32) and $2-(\text{CH}_3)\text{B}_6\text{H}_9$ (16) has been reported. A halogenated species $2-\text{BrB}_6\text{H}_9$ (26,32) has been prepared. Adducts with Lewis bases have also been formed. There appeared a report of the preparation of $\text{B}_6\text{H}_{10}\text{P(}C_6\text{H}_5\text{)}_3$ (33), however independent verifications have been unsuccessful (34,35). On the other hand there have been several reports of bis-ligand adducts: $\text{B}_6\text{H}_{10}\text{[N(}C\text{H}_3\text{)}_3\text{]}_2$ (34,35), $\text{B}_6\text{H}_{10}\text{[P(}C_6\text{H}_5\text{)}_3\text{]}_2$ (35), $\text{B}_6\text{H}_{10}\text{[P(}C\text{H}_3\text{)}_3\text{]}_2$ (35). In fact X-ray crystallographic evidence corroborates the existence of bis-ligand adducts (36,37). The boron hydride $\text{B}_{15}\text{H}_{23}$ has been described as a Lewis acid-base adduct between the reactants $\text{B}_9\text{H}_{15}$ and $\text{B}_6\text{H}_{10}$ (38).

An alkali metal hydride (NaH,KH) or lithium alkyl (Li\text{CH}_3) will abstract a proton from $\text{B}_5\text{H}_9$ (39-41). The reaction with KH proceeds as shown.
\[ \text{KH} + \text{B}_5\text{H}_9 \rightarrow \text{K}^+\text{[B}_5\text{H}_{8}]^- + \text{H}_2 \]

Boron-11 and proton n.m.r. studies indicate that \( C_{4v} \) symmetry is maintained. This fact is consistent with removal of a bridging hydrogen in the deprotonation reaction. Rapid intramolecular migration of the remaining three bridge hydrogens among the four available bridging sites in the anion occurs. Consequently \( C_{4v} \) symmetry is observed on the n.m.r. time scale (39-41).

Hexaborane(10) also behaves as a Brønsted acid under the same reaction conditions. At low temperature, a bridge proton is abstracted, and an alkali metal salt of the \([\text{B}_6\text{H}_9]^-\) anion can be isolated (42,45,46). The reaction with \( \text{KH} \) proceeds as shown.

\[ \text{KH} + \text{B}_6\text{H}_{10} \rightarrow \text{K}^+\text{[B}_6\text{H}_{9}]^- + \text{H}_2 \]

Both the boron-11 and proton n.m.r. spectra of the \([\text{B}_6\text{H}_9]^-\) anion are consistent with rapid intramolecular migration of the remaining three bridge hydrogens among the five available sites in the basal plane of the pyramid (45,46). This migration produces apparent \( C_{5v} \) symmetry on the n.m.r. time scale.

The fact that a bridge hydrogen is removed in the deprotonation reaction is also supported by infrared studies of deuterated species. When \( \text{B}_5\text{H}_9 \) or \( \text{B}_6\text{H}_{10} \) are deprotonated and subsequently reacted with DCl, a deuterium isotope shift of the absorption assigned to the bridge hydrogen (B-H-B) stretch is observed. However no deuterium isotope shifts of terminal B-H absorptions are observed (43). A bridge hydrogen can also be removed from \( \text{B}_6\text{H}_{10} \) (35) and \( \text{B}_5\text{H}_9 \) (44) with the Lewis base \( \text{NH}_3 \).
The alkali metal salts $M^+[B_5H_8]^- \text{ and } M^+[B_6H_9]^- (M = \text{Li, Na, K})$ have limited thermal stability (45). If the following metathesis reaction is performed, the resulting salts have greater resistance to decomposition (46).

$$\text{(n-C}_4\text{H}_9\text{)}_4\text{NI} + K^+[B_5H_8]^- \rightarrow \text{(n-C}_4\text{H}_9\text{)}_4N^+[B_5H_8]^- + KI$$

$$\text{(n-C}_4\text{H}_9\text{)}_4\text{NI} + K^+[B_6H_9]^- \rightarrow \text{(n-C}_4\text{H}_9\text{)}_4N^+[B_6H_9]^- + KI$$

Not only does $B_6H_{10}$ perform as Brønsted acid in the presence of a base (35, 39-42, 45, 46), but also as a Brønsted base in the presence of an appropriate acid (47). The reactive site in this instance is the localized boron-boron bond in the base of the pentagonal pyramid. The boron-boron bond can be protonated using liquid HBr or an HCl/BCl$_3$ mixture at low temperature as indicated in the following reactions.

$$B_6H_{10} + HBr \rightarrow [B_6H_{11}]^{+}Br^-$$

$$B_6H_{10} + HCl + BCl_3 \rightarrow [B_6H_{11}]^{+}BCl_4^-$$

As a result, a boron hydride cation of true $C_{5v}$ symmetry is produced (47) (Figure 3).

An interesting aspect of the chemistry of $B_6H_{10}$ is its ability to form compounds with transition metal complexes. The compounds Ni(CO)$_3(B_6H_{10})$, Rh(B$_6H_{10}$)$_2$ (acetylacetonate), [Rh(B$_6H_{10}$)$_2$Cl]$_2$, and [Ir(B$_6H_{10}$)$_2$Cl]$_2$ can be prepared from the corresponding ethylene complexes except in the case of nickel where Ni(CO)$_4$ is used (48). In each compound, the transition metal is thought to bond to two basal boron atoms in a bridging fashion which is similar to the mode of
Figure 3. Proposed Structure of the Cation \([\text{B}_6\text{H}_{11}]^+\)
bonding for a bridging hydrogen. In addition $\text{B}_6\text{H}_{10}$ is able to displace ethylene from Zeise's salt, $\text{K}^+[(\text{C}_2\text{H}_4)\text{PtCl}_3]^-\text{, to form } (\text{B}_6\text{H}_{10})_2\text{PtCl}_2$ (48) whose X-ray crystal structure (49) indicates trans-hexaborane(10) groups. Again a bridging interaction between platinum and the hexaborane polyhedra is indicated.

Hexaborane(10) also reacts with Fe$_2$(CO)$_9$ to produce an adduct formulated as $\mu-(\text{CO})_4\text{Fe-B}_6\text{H}_{10}$ (48,50) (Figure 4). Spectral studies of the volatile yellow compound favor a bridging (CO)$_4$Fe group resulting from a Lewis acid-base interaction with the B-B bond. The fact that the integrity of the $\text{B}_6\text{H}_{10}$ framework has not been disturbed extensively is demonstrated by the retention of its Brönsted acidity. Potassium hydride reacts to form $\text{K}^+[(\mu-(\text{CO})_4\text{Fe-B}_6\text{H}_{9})^- with removal of a bridging hydrogen (51,62). In fact reaction of this salt with one-half equivalent of $\text{B}_2\text{H}_6$ produces $\text{K}^+[(\mu-(\text{CO})_4\text{Fe-B}_7\text{H}_{12})^- whose X-ray crystal structure (52) represents the first definitive characterization of a heptaborane species (Figure 5). The added $\text{BH}_3$ unit bonds in a bridging fashion.

These results are interesting in light of the fact that many previous reports of the existence of heptaborane species have been inferred from mass spectral studies of pyrolysis products of boranes (53-57). Proposed structures for $\text{B}_7\text{H}_{11}$, $\text{B}_7\text{H}_{13}$ and $\text{B}_7\text{H}_{15}$ have been formulated by Lipscomb and are based on topological considerations (59,60). Another report of the formation of a heptaborane species results from the tensimetric titration of $\text{B}_2\text{H}_6$ with a $[\text{B}_6\text{H}_{9}]^-$ salt (61). The addition of a $\text{BH}_3$ group to the hexaborane framework was postulated.
Figure 4. Proposed Molecular Structure of $\mu-(\text{CO})_4\text{Fe-B}_6\text{H}_{10}$
Figure 5. Polyhedral Structure of the Anion $[\mu-(\text{CO})_4\text{Fe-B}_7\text{H}_{12}]^-$
The salt $K^+\left[\mu-(CO)\lambda Fe-B^\lambda H^\lambda 12\right]^{-}$ can be reacted with liquid HCl to produce $(CO)\lambda FeB^\lambda H^\lambda 11$ upon loss of $H_2$ (51,62). Mass spectral evidence supports the existence of this heptaborane(62).

There are many examples of the isolation of derivatives of the carborane $2,3-C_2B_4H_8$ (or $2,3-(\text{CH}_3)C_2B_4H_6$) which is the isoelectronic (5) and isostructural analog of $B_6H_{10}$ (C is isoelectronic with BH) (Figure 6). It is useful to consider these compounds since one can imagine similar compounds in the case of $B_6H_{10}$. In all cases, one of the two bridge hydrogens is removed from the carborane cage by reaction with hydride anion. The carborane salt then undergoes bridge substitution via reaction with an electrophile. Species which have been inserted into a bridge position are $(\text{CH}_3)_3Si$ (63,64,67), $(\text{CH}_3)_3Ge$ (63,64,67), $H_3Si$ (64,67), $H_3Ge$ (64,67), $(\text{CH}_3)_3Pb$ (65,67), $(\text{CH}_3)_3Sn$ (65,67), $(C_5H_5)(CO_2)Fe$ (66,67), $(\text{CH}_3)_2B$ (67), $(\text{CH}_3)_2Al$ (67), $(\text{CH}_3)_2Ga$ (67), $[P(C_6H_{15})_3]Rh$ (67), $[P(C_6H_{15})_3]Au$ (67), $(C_6H_{15})Hg$ (67). An interesting compound formulated as $\mu\mu\mu-SiH_2(C_2B_4H_{12})_2$ has been reported wherein the silicon apparently bonds simultaneously to two carborane cages (65) (Figure 7).

It is also instructive to note analogous compounds derived from pentaborane(9). They possess some similar structural characteristics as compared with hexaborane(10) analogs. The derivatives are bridge substituted pentaborane species prepared similarly to the bridge substituted compounds above. They have the general formula $R_3M-B_5H_8$ where $M = Si, Ge, Sn, Pb$ and $R = C_2H_5, \text{CH}_3, H$, halogen (68). The silicon derivative of $1-\text{BrB}_5H_8$ contains a bridging trimethylsilyl group, $1-\text{Br-}\mu-(\text{CH}_3)_3Si-B_5H_7$. The X-ray crystal structure (80) indicates...
Figure 6. Structure of $2,3\text{-}C_2B_4H_8$

(a) Molecular structure
(b) Valence structure
(c) Valence structure utilizing fractional bonds (reference 111)
Figure 7. Proposed Molecular Structure of $\mu^\mu\text{-SiH}_2(C_2B_4H_7)_2$. 

![Molecular structure diagram](image.png)
formation of a three center bond between silicon and two adjacent boron atoms in the basal plane of the pentaborane pyramid (Figure 8). Other groups which have been inserted into a bridging position are BH₃ (41,61,90), (CH₃)₂B (31), and F₃C(CH₃)P (81).

Besides participating in bridge substitution reactions, B₅H₉ and 1- or 2-BrB₅H₈ can also oxidatively add to trans-IrCl(CO)_[P(CH₃)₃]₂ (69). Spectral data are consistent with a two center, two electron sigma bond between a basal boron atom and Ir. The X-ray crystal structure of 2-[IrBr₂(CO)P(CH₃)₂]B₅H₈ unambiguously supports the formation of a sigma (basal boron-Ir) bond (69).

The first air stable derivative of B₅H₉ was reported in 1970 (70,71), and was prepared according to the following equation.

\[ [P(C₆H₅)₃]₂CuCl + K⁺[B₅H₈]^- \rightarrow [P(C₆H₅)₃]₂CuB₅H₈ + KCl + P(C₆H₅)₃ \]

A structure with copper bonded to two basal boron atoms via a three center bond was favored (70,71). Recently infrared and n.m.r. studies (72,73) confirmed the proposed B-Cu-B interaction. In addition an X-ray crystal structure has been performed on [P(C₆H₅)₃]₂CuB₅H₈ and the same conclusion was reached (74). Consequently copper possesses a coordination number of three in this molecule (Figure 9). The fact that treatment with HCl regenerated B₅H₉ suggests that [P(C₆H₅)₃]₂Cu⁺ bonds in a fashion similar to that of a bridging hydrogen (70,74).

A compound formulated as [P(C₆H₅)₃]₂CuB₆H₉ has been prepared in an analogous manner from K⁺[B₆H₉]^- (70). It is not clear if copper bonds to two boron atoms in a three center fashion or if a Cu-H-B interaction exists. An infrared spectroscopic study has indicated the
Figure 8. Molecular Structure of 1-Br-μ-(CH₃)₃Si-B₅H₇
Figure 9. Molecular Structure of \[ (\mathrm{C}_6\mathrm{H}_5)_3\mathrm{P}_2\mathrm{CuB}_5\mathrm{H}_8 \]
possibility of a Cu-H-B interaction (73). There is also n.m.r. evi­
dence that the $[\text{P(C}_6\text{H}_5\text{)}_3\text{]}_2\text{Cu}^+$ group is stereochemically nonrigid with respect to $[\text{B}_6\text{H}_9]^-$ (73).

It appears, therefore, that copper has the ability to bond in various ways to boron hydride groups. In $[\text{P(C}_6\text{H}_5\text{)}_3\text{]}_2\text{CuBH}_4$ (75-77), copper exists with coordination number four and two Cu-H-B bridge interactions are present. This bonding scheme in which copper is four coordinate has been postulated from X-ray crystallographic studies (78). In solution, n.m.r. spectral studies suggest rapid intramolecular hydrogen scrambling (83-85). A phosphino-copper cationic species containing the tetrahydroborate moiety, $[\text{P(C}_6\text{H}_5\text{)}_3\text{]}_2\text{CuH}_2\text{BH}_2\text{Cu}[\text{P(C}_6\text{H}_5\text{)}_3\text{]}_2^+$ (79) also possesses Cu-H-B bonds, but in this case there are four such interactions. The compound containing the arachno-octahydrotriborionate group $[\text{P(C}_6\text{H}_5\text{)}_3\text{]}_2\text{CuB}_3\text{H}_8$ contains Cu-H-B bridge bonds as indicated by the X-ray crystal structure (82) (Figure 10). In solution the molecule is dynamic. The octahydrotriborionate moiety is involved in a scrambling process with respect to copper, resulting in apparently equivalent hydrogens on the n.m.r. time scale (84,86). In addition, for analogous compounds, the phosphino-copper group apparently undergoes intramolecular and intermolecular exchange processes depending on the temperature. Not only are phosphorous environments averaged within the molecule, but phosphine ligands may be exchanged with free ligand in solution under the correct conditions (87,88). Another compound containing a closo-decahydrodecaborate group, $\{[\text{P(C}_6\text{H}_5\text{)}_3\text{]}_2\text{Cu}\}_2\text{B}_{10}\text{H}_{10}\text{CHCl}_3$, also exhibits Cu-H-B interactions (89). Thus subtle differences in characteristics
Figure 10. Molecular Structure of $[(C_6H_5)_3P]_2CuB_3H_8$
of the boron hydride moieties appear to influence greatly the mode of bonding to copper.

Reactions of $\text{B}_6\text{H}_{10}$ have been reported for other transition metal centers as indicated in the following reactions (91,92).

$$2 \text{B}_6\text{H}_{10} + \text{(CH}_3\text{)}_2\text{M} \xrightarrow{\text{THF}} \text{M(B}_6\text{H}_9)\text{.THF} + 2 \text{CH}_4 \quad (91)$$

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

$$2 \text{B}_6\text{H}_{10} + 2 \text{CH}_3\text{MgX} \rightarrow \text{(B}_6\text{H}_9)\text{.Mg} + 2 \text{CH}_4 + \text{MgX}_2 \quad (91)$$

$X = \text{Br, I}$

$$\text{K}^+ [\text{B}_6\text{H}_9]^- + (\eta^5 - \text{C}_5\text{H}_5)_2\text{TiCl} \rightarrow (\eta^5 - \text{C}_5\text{H}_5)_2\text{TiB}_6\text{H}_9 + \text{KCl} \quad (92)$$

The mode of bonding proposed involves a three center bridge interaction between the metal and two boron atoms in the hexaborane framework. The X-ray crystal structure of $\text{Mg(B}_6\text{H}_9)\text{.THF}_2$ supports this type of bond (91). Similarities in n.m.r. spectra indicate a similar mode of metal boron bonding in the other complexes (91,92). It is interesting to note the similarity in the structure of $\text{Mg(B}_6\text{H}_9)\text{.THF}_2$ (91) to $\text{Pt(B}_6\text{H}_{10})\text{.Cl}_2$ (49) and to the proposed structures of $\text{SiH}_2(\text{C}_2\text{B}_4\text{H}_7)_2$ (65), $\text{Rh(B}_6\text{H}_{10})\text{.acetylacetonate}$ (48), $[\text{Rh(B}_6\text{H}_{10})\text{.Cl}_2]$ (48), and $[\text{Ir(B}_6\text{H}_{10})\text{.Cl}_2]_2$ (48). In each case two hexaborane (or its isoelectronic analog) fragments bond to the same central atom via three center bonds of the type B-M-B. A proposed structure for $(\eta^5 - \text{C}_5\text{H}_5)_2\text{TiB}_6\text{H}_9$ as a dimeric species contains two boron-metal-boron bridge interactions for each hexaborane fragment (92).

III. Insertion of Transition Metals into Borane Polyhedra

Under the correct conditions a ligated transition metal can insert into a boron hydride (or carborane) framework to become a new
vertex (93-98). The transition metal center appears to replace an existing vertex or expand the polyhedron by one vertex. The compound \((\eta^5-C_5H_5)Co(C_2B_3H_7)\) is formally isoelectronic with \(2,3-C_2B_4H_8\) (which is isoelectronic with \(B_6H_{10}\)) (94) (Figure 11). The \((\eta^5-C_5H_5)Co\) group is a two electron donor to the polyhedral framework (5) and thus is isoelectronic with BH. Consequently the heavy atom polyhedron (disregarding the \(C_5H_5\) ligand) is isostructural to that of \(2,3-C_2B_4H_8\) (or \(B_6H_{10}\)). The analogy in the framework electron count suggested that \((\eta^5-C_5H_5)Co(C_2B_3H_7)\) would also be a Brønsted acid which is indeed the case (94). The method of counting framework electrons in polyhedral structures has been described in detail by Wade (5).

If Fe(CO)\(_5\) and \(B_5H_9\) are combined in a hot-cold reactor, (CO)\(_3\)FeB\(_4\)H\(_8\) is produced (95). The (CO)\(_3\)Fe group formally replaces the apical BH group in \(B_5H_9\). Since (CO)\(_3\)Fe is a two electron donor (5), (CO)\(_3\)FeB\(_4\)H\(_8\) is isoelectronic and isostructural with \(B_5H_9\) (Figure 12). Under slightly different conditions, the ferraborane \(B_5H_9Fe(CO)_3\) can be isolated (97). In this case, the Fe(CO)\(_3\) group has inserted into the base of the \(B_5H_9\) framework and has expanded the polyhedron to six vertices.

A \((\eta^5-C_5H_5)Co\) group can also insert into a pentaborane cage (93). The reaction of NaB\(_5\)H\(_8\) with CoCl\(_2\) and NaC\(_3\)H\(_5\) produces \((\eta^5-C_5H_5)CoB_4H_8\). The X-ray crystal structure of one isomer (96) indicates the cobalt is situated in the four atom basal plane of the tetragonal pyramid (Figure 13). Interestingly the cobalt atom bonds to neighboring boron atoms through hydrogen bridges. In the second isomer, the cobalt atom is apparently situated at the apex of the square pyramid (93).
Figure 11. Proposed Molecular Structure of \((\eta^5-C_5H_5)CoC_2B_3H_7\)
Figure 12. Proposed Molecular Structure of $(\text{CO})_3\text{FeB}_4\text{H}_8$
Figure 13. Molecular Structure of \((\eta^5-C_5\text{H}_5)\text{CoB}_4\text{H}_8\)
IV. The Chemistry of 2,3-Dicarba-nido-hexaborane(8)

A. Preparation of 2,3-Dicarba-nido-hexaborane(8)

The carborane 2,3-C$_2$B$_4$H$_8$ is systematically named 2,3-dicarba-nido-hexaborane(8) (99,100). The preparation of 2,3-C$_2$B$_4$H$_8$ is most practically (40% yield) carried out by heating a mixture of B$_5$H$_9$ and C$_2$H$_2$ in a large volume at 215° (101). The reaction of C$_2$H$_2$ and B$_5$H$_9$ apparently occurs without rupture of carbon-carbon or carbon-hydrogen bonds (102). There is a nucleophilic attack by C$_2$H$_2$, and substituted acetylenes react with more ease (101,125) but, of course, produce a carbon substituted product. An inferior method (in terms of percent yield) involves a room temperature reaction of C$_2$H$_2$, B$_5$H$_9$ and 2,6-dimethylpyridine (101,107). The isolation of the product from the reactants can be achieved chromatographically (104) or by a combination of physical and chemical methods (105). The reaction of B$_4$H$_{10}$ and C$_2$H$_2$ in the gas phase at 25-50° also produces some 2,3-C$_2$B$_4$H$_8$ (103).

B. Physical Properties of 2,3-Dicarba-nido-hexaborane(8)

The carborane 2,3-C$_2$B$_4$H$_8$ is a colorless, mobile liquid at ambient temperature (106). Its melting point is -88° and its boiling point is 63.8° (106). Its vapor pressure at 0° is 57 mmHg (106). In air 2,3-C$_2$B$_4$H$_8$ decomposes slowly (106).

C. Structure and Bonding in 2,3-Dicarba-nido-hexaborane(8)

The carbon and boron atoms form a pentagonal pyramid, the same type of polyhedral structure possessed by B$_6$H$_{10}$. If two adjacent boron atoms and two bridging hydrogens in B$_6$H$_{10}$ are replaced with carbon atoms (which are isoelectronic with a BH group), 2,3-C$_2$B$_4$H$_8$ is
obtained. There are then two hydrogen bridge bonds in the pentagonal base (Figure 6). An X-ray crystal structure determination has been performed (108,109) to confirm this model. The carbon-carbon distance of 1.42 Å is shorter than an sp² carbon-sp² carbon single bond distance (1.50 Å) but longer than sp²-sp² double bond distance (1.34 Å) (108,109).

Various attempts have been made to describe the bonding in 2,3-C₂B₄H₈ (107,112,109) (Figure 6b). At present, the best single valence structure, which has been formulated from a localized orbital study (111), violates topological rules (110), but appears to correlate well with the actual molecular structure (Figure 6c).

The boron-¹¹ and proton n.m.r. studies (113,114) indicate C₈ symmetry and are consistent with the structure determined by X-ray crystallography (108,109). Boron-¹¹ spin-decoupling methods applied to proton n.m.r. spectroscopy indicate the site of bridge hydrogen attachment, since the bridge proton resonance sharpens at the boron-¹¹ frequency of the basal boron atoms (115). A feature of the boron-¹¹ n.m.r. spectrum of 2,3-C₂B₄H₈ not often observed in boron hydride compounds is resolvable spin-coupling of basal boron atoms with bridge hydrogens (113,114) (J_B-µH = 43 Hz).

D. Reactions of 2,3-Dicarba-nido-hexaborane(8)

Pyrolysis at 295° (101), exposure to a silent electric discharge (101) or photolysis (116) of 2,3-C₂B₄H₈ produces various closo-carboranes in low to moderate yields. Isotope tracer studies involving 2,3-C₂B₄H₈ showed that D₂ will exchange with all terminal hydrogens
attached to boron atoms (102). The reaction of $B_2D_6$ in diglyme promotes exchange with terminal hydrogens on the basal borons nearest the carbon atoms (102,114). The pyrolysis of $C_2D_2$ and $B_5H_9$ produces only $D_2C_2B_4H_6$ (101,102) indicating that the carbon-carbon bond in the acetylene molecule does not rupture in the synthesis of $2,3-C_2B_4H_8$. Friedel-Crafts halogenation occurs singly and only at a basal boron neighboring a carbon atom (106-117). A permethyl closo- species, $C_2B_5(CH_3)_7$, has been generated in the pyrolysis of $2,3-C_2B_4H_8$ with $B(CH_3)_3$ (118). Friedel-Crafts methylation destroys the carborane polyhedron (119).

As expected from the similarities in structure with $B_6H_{10}$, $2,3-C_2B_4H_8$ behaves as a Brønsted acid. A single bridge hydrogen can be removed with the production of one equivalent of $H_2$ (114). Two cycles of deprotonation with $H^-$ and protonation with DCI result in sufficient bridge deuteration that boron-11 spin-coupling to the bridge protons cannot be observed in the boron-11 n.m.r. spectrum (114).

Decaborane(14) is a stronger Brønsted acid than $2,3-C_2B_4H_8$ since $B_{10}H_{14}$ will react with $[2,3-C_2B_4H_7]^{-}$ to regenerate the neutral carborane (114). The presence of a boron-boron bond in the anion introduces a potential site of electrophilic reaction. A $(CH_3)_2B$ group will bond to the site in the reaction of $(CH_3)_2BCl$ and $Na^+[2,3-(CH_3)_2C_2B_4H_3]^{-}$ to form a compound stable below 0° (120). Trimethylgallium reacts with $2,3-C_2B_4H_8$ to form a polyhedron formulated as $\text{closo-}(CH_3)GaC_2B_4H_6$ in which Ga occupies the apex (121) of a pentagonal bipyramid. Other reactions of $2,3-C_2B_4H_8$ in which bridging substituents are introduced have been discussed earlier (63-67).
Sneddon, Beer and Grimes (66) have reported several interesting ferracarboranes isolated from reactions of 2,3-C\textsubscript{2}B\textsubscript{4}H\textsubscript{8}. If \(\mu-[(\eta^5-C_5H_5)Fe(CO)_2]2,3-C_2B_4H_7\) is irradiated with ultraviolet light, \((\eta^5-C_5H_5)Fe(\text{II})H(C_2B_4H_6)\) and \((\eta^5-C_5H_5)Fe(\text{III})(C_2B_4H_6)\) are produced. The iron atom may be considered to be "sandwiched" between the two \(\pi\)-ligands \([C_5H_5]^–\) and \([C_2B_4H_6]^2–\) (66). Nuclear magnetic resonance studies indicate the possibility of an Fe-H-B bridge interaction in \((\eta^5-C_5H_5)Fe(\text{II})H(C_2B_4H_6)\). The pyrolysis of 2,3-C\textsubscript{2}B\textsubscript{4}H\textsubscript{8} and Fe(CO)\textsubscript{5} apparently produces \(\text{closo-}(C_2B_4H_6)Fe(CO)_3\) wherein the Fe(CO)\textsubscript{3} group occupies an apical vertex of a pentagonal bipyramid (66) (Figure 14). In addition \(\text{nido-}(C_2B_3H_7)Fe(CO)_3\) is formed in the pyrolysis (Figure 15). An X-ray structural determination confirms the pentagonal pyramidal geometry with the iron atom at the apex (122). Since Fe(CO)\textsubscript{3} is isoelectronic with a B-H group (5), \((C_2B_3H_7)Fe(CO)_3\) is isoelectronic and isostructural with B\textsubscript{6}H\textsubscript{10}.

Several metallo-carboranes in which a \((\eta^5-C_5H_5)Co\) or \((\eta^5-C_5H_5)Ni\) group (isoelectronic with a BH group) (5) bonds to a carborane fragment have been prepared from \(Na^+[C_2B_4H_7]^–\), MCl\textsubscript{2} (M = Co, Ni), and NaC\textsubscript{5}H\textsubscript{5} followed by oxidation (94). In these compounds, polyhedral vertices are occupied by metal atoms.

V. Statement of the Problem

The compound B\textsubscript{5}H\textsubscript{9}Fe(CO)\textsubscript{3} had been synthesized but characterization was limited to a mass spectral analysis. The investigation of the structural and chemical characteristics of this compound was to be undertaken to further elucidate some of the apparently unusual features.
Figure 14. Proposed Molecular Structure of closo-\((\text{C}_2\text{H}_6\text{B}_4)\text{Fe(CO)}_3\)
Figure 15. Molecular Structure of \textit{nido-}(C_2B_3H_7)Fe(CO)_3
Specific reactions known to occur in the case of hexaborane(10) were to be conducted.

It is known that boron hydrides often possess stereochemically nonrigid bridge hydrogens (85). Boron-11 n.m.r. spectra of K⁺[μ-(CO)₄Fe-B₆H₁₀]⁻ were suggestive of transition metal migration (62). It was of interest to carry out a variable temperature n.m.r. study to elucidate the nature of the (CO)₄Fe migration.

There have been several reports of heptaborane species in the literature (53-57,61), however only one has been well characterized (51,52). Carboranes in many cases appear to be more stable under a given set of conditions than their boron hydride analogs. It was thought that a heptaborane analog could be prepared from 2,3-C₂B₄H₈. In addition, a route to other carboranes through polyhedral expansion reactions (16,61,90) might be found.
EXPERIMENTAL

I. Apparatus

A. Vacuum System

Since many materials used during the course of this investigation are highly reactive in the atmosphere, a vacuum system similar to that described by Sanderson (123) was utilized to manipulate volatile materials. The apparatus consisted of a Welch Duo-Seal rotary pump and a two stage mercury diffusion pump. Liquid nitrogen traps were maintained between the vacuum system and the diffusion pump and between the diffusion pump and the rotary pump as protection against reactive vapors and to maintain a low operating pressure. The ultimate pressure in the system was approximately $10^{-6}$ mm Hg as measured by McLeod gauge.

The Pyrex vacuum apparatus consisted of two U-trap fractionation trains and a reaction train. One fractionation train employed grease stopcocks and the other utilized Kontes 4 mm Teflon valves. The greaseless fractionation train was used primarily since many compounds under study had a tendency to dissolve in stopcock grease. This fractionation train also possessed an isolable manometer. This manometer was used in conjunction with the fractionation train, which was calibrated against a known volume, to measure quantities of volatile materials as gases. The reaction train was fitted with Fisher-Porter valves which possessed either standard taper 14/35 inner joints or
9 mm Solv-seal joints to be used when grease was to be excluded. Attached to some of these outlets were mercury blowouts to monitor or relieve excessive pressure in the system.

B. Glove Boxes

A Vacuum Atmospheres glove box was used to manipulate nonvolatile substances which were air sensitive. Entrance was through an antichamber which was alternately evacuated and flushed with prepurified nitrogen. The nitrogen atmosphere in the working area was continually purified by recirculation over Linde-4X molecular sieves and Dow Q-1 scavenger to remove water and oxygen. The operation of this glove box has been discussed in detail (92).

Another glove box manufactured by Kewaunee Scientific Equipment Co. was used solely for mounting crystals at low temperature for X-ray structural determination. The antichamber could be alternately evacuated and refilled with nitrogen, and the atmosphere of the working area was continually purged with prepurified nitrogen. An open dish of \( \text{P}_2\text{O}_5 \) was used to scavenge \( \text{H}_2\text{O} \). When crystals were being mounted, a cake of dry ice was taken into the glove box. An aluminum plate and a petri dish were placed on the dry ice and allowed to cool. In this way, crystals could be manipulated in the petri dish and still remain cold to prevent decomposition. Thin wires were used to insert crystals into thin walled capillaries, which were then flame sealed and stored at \(-78^\circ\) until ready for examination.
C. Glassware

Pyrex vessels used in the synthetic procedures were fitted with standard taper or Solv-seal joints to permit attachment to the vacuum line or to stopcock adapters possessing appropriate joints when isolation from the atmosphere was necessary. Often these vessels contained Teflon covered magnets which could stir solutions through use of an externally spinning magnet. In some cases these vessels possessed sidearms to which an n.m.r. tube could be attached. This design allowed some of the solution to be transferred, at low temperature if required, under vacuum to the n.m.r. tube which was then sealed with a torch. If filtration was required, a small powdered glass frit was fused into the sidearm of the vessel. When large scale filtrations were required, vacuum extractors were used. These were vessels constructed from powdered glass frits to which other vessels could be attached on either side and which could be evacuated. As a result filtrations of nonvolatile materials could be conveniently carried out on the vacuum line.

Dry solvents and starting materials were stored under vacuum or dry nitrogen gas in containers fitted with Kontes, Fisher-Porter or grease stopcocks depending on the particular properties of the substances.

Cleaning of the glassware was accomplished by soaking in a concentrated KOH/C₂H₅OH bath overnight followed by adequate rinsing and drying in an oven maintained at 110°.
D. Nuclear Magnetic Resonance Spectra

Spectra were routinely obtained on a Varian HA-100 high resolution spectrometer operating in the HA mode at 100 MHz to observe proton resonances or in the HA mode at 32.1 MHz to observe boron-11 resonances. The probe was fitted with an apparatus to allow for the flow of cold nitrogen gas in order to carry out low temperature investigations. Measurement of temperature was achieved with a copper-constantan thermocouple inserted into the probe near the sample.

Heteronuclear spin-decoupling experiments (broadband or narrow-band) could be conducted through the use of a General Radio Co. 1164A frequency synthesizer, a Hewlett Packard Co. 3722A noise generator, and an Electronic Navigation Laboratories 3100L Amplifier.

Some n.m.r. spectra were obtained on a Bruker HX-90 spectrometer operating at 90 MHz, 22.62 MHz, 28.87 MHz, 36.43 MHz for observing, respectively, proton, carbon-13, boron-11, and phosphorous-31 resonances. Heteronuclear spin-decoupling (broadband or narrowband) was performed with the B-SV3-B noise decoupler. With this spectrometer computerized Fourier transform methods could be used to examine solutions too dilute for observing resonances by continuous wave techniques.

All boron-11 chemical shifts are reported relative to BF$_3$·O(C$_2$H$_5$)$_2$ at 0.0 ppm. Increasing values correspond to increasing magnetic field. The determination of these values was made through the use of standards sealed in capillaries. Other standards used (with their chemical shifts) were BCl$_3$ at -46.8 ppm and B(OCH$_3$)$_3$ at -18.1 ppm.
Proton chemical shifts are reported in \textit{tau} values and are relative to tetramethylsilane whose resonance is assigned a value of 10 \textit{\tau}. Increasing \textit{tau} values correspond to increasing magnetic field. Other internal standards were usually more convenient to use than tetramethylsilane. The standards and chemical shifts used are CHCl$_3$ at 2.76 \textit{\tau}, CH$_2$Cl$_2$ at 4.68 \textit{\tau}, C$_6$H$_6$ at 2.74 \textit{\tau}, (CH$_3$)$_2$O at 6.76 \textit{\tau}, CHCl$_2$F at 2.54 \textit{\tau} ($J_{\text{H-F}} = 54$ Hz), CHClF$_2$ at 2.75 \textit{\tau} ($J_{\text{H-F}} = 60$ Hz).

Carbon-13 chemical shifts are reported relative to tetramethylsilane whose resonance is assigned a value of 0.0 ppm. Increasing values correspond to decreasing magnetic field. Other standards used were C$_6$H$_6$ at 128.0 ppm, (CH$_3$)$_2$O at 57.9 ppm and CH$_2$Cl$_2$ at 53.8 ppm.

Phosphorous-31 chemical shifts are reported relative to phosphoric acid whose resonance is assigned a value of 0.0 ppm. Increasing values correspond to increasing magnetic field.

Relative areas were measured with a polar planimeter.

E. X-ray Powder Diffraction

Samples for X-ray powder diffraction studies were ground into a fine powder with an agate mortar and pestle. After inserting the sample into a thin walled capillary, it was flame sealed and placed in a Phillips Debye-Scherrer camera of 11.46 cm diameter. Eastman Kodak NS-392F X-ray film was exposed to the diffracted X-rays generated by a North American Phillips X-ray generator. The copper K\textsubscript{\textit{\alpha}} radiation (nickel filter) was produced at 32 Kv and 12 m amp.
F. Infrared Spectra

Infrared spectra were obtained with a Perkin-Elmer 457 spectrometer. Solid samples were analyzed in pressed KBr discs, as Nujol mulls pressed between KBr plates or in solution. Solution spectra were obtained using matched 0.1 mm path length solution infrared cells with KBr windows and manufactured by Perkin-Elmer (model number 186-0072). One cell was filled with the solvent and placed in the reference beam of the infrared spectrometer in order to compensate for solvent absorptions in the recorded spectrum of the sample plus the solvent. Gaseous samples were analyzed in a 10 cm path length cell which could be attached to the vacuum line. The KBr windows were sealed onto the ends of the cell with glyptal paint.

Spectra were calibrated with polystyrene.

II. Reagents

A. Acetylene

Acetylene was obtained from Matheson Gas Products. The \( \text{C}_2\text{H}_2 \) was passed through a \(-126^\circ\) U-trap to remove acetone (124). The purified \( \text{C}_2\text{H}_2 \) was stored at \(-196^\circ\).

B. Bromine

Bromine was obtained from J. T. Baker Chemical Co. and used as received.

C. Cuprous Chloride

Cuprous Chloride was obtained from J. T. Baker Chemical Co. The \( \text{CuCl} \) was washed with dilute acetic acid solution, ethanol and petroleum
ether to remove oxidation and hydration products. The resulting white CuCl was stored under vacuum.

D. Diborane(6)
Diborane(6) was obtained from Callery Chemical Co. and passed through a U-trap at -140°. The B$_2$H$_6$ was stored at -196°.

E. Hydrogen Bromide
Hydrogen bromide was obtained from Matheson Gas Products and passed through a U-trap at -127° before use. The HBr was stored at -196°.

F. Iodomethane-d$_3$
Iodomethane-d$_3$ was purchased from Stohler Isotope Chemicals and stored under vacuum.

G. Iron Pentacarbonyl
Iron Pentacarbonyl was purchased from Alfa Inorganics. It was used as received.

H. Lithium Aluminum Hydride
Lithium aluminum hydride was obtained as a powder from Alfa Inorganics. It was used as received.

I. Methanol-d$_4$
Methanol-d$_4$ was purchased from Stohler Isotope Chemicals and stored under vacuum.
J. Pentaborane(9)

Pentaborane(9) was obtained from Callery Chemical Co. It was used as received and stored under vacuum at -196°.

K. Potassium Hydride

Potassium hydride was received as a mineral oil suspension from Research Organic/Inorganic Chemical Corp. The mineral oil was removed by repeated washings with anhydrous pentane. The activity of the resulting white powder was 94 percent in reactions with methanol.

L. Tetra(n-butyl)ammonium bromide

Tetra(n-butyl)ammonium bromide was obtained from Matheson, Coleman and Bell. It was heated to 110° under vacuum to drive off adsorbed water and stored in the dry box.

M. Trimethylamine

Trimethylamine was obtained from Matheson Gas Products. The \((\text{CH}_3)_3\text{N}\) was stirred over \(\text{LiAlH}_4\) and stored under vacuum.

N. Triphenylphosphine

Triphenylphosphine was purchased from Matheson, Coleman and Bell. The \((\text{C}_6\text{H}_5)_3\text{P}\) was recrystallized from ethanol before use.

III. Solvents

The deuterated solvents dichloromethane-d\(_2\) and trichloromethane-d were obtained from Stohler Isotope Chemicals and dried over \(\text{LiAlH}_4\) before use.
Dimethyl ether-d$_6$ was prepared according to the following reactions.

$$\text{CD}_3\text{OD} + \text{KH} \rightarrow \text{CD}_3\text{O}^-\text{K}^+ + \text{HD}$$

$$\text{CD}_3\text{O}^-\text{K}^+ + \text{CD}_3\text{I} \rightarrow (\text{CD}_3)_2\text{O} + \text{KI}$$

The procedure has been previously described in detail (32). The (CD$_3$)$_2$O was stored at -78°.

Dimethyl ether was obtained from Matheson Gas Products. It was stirred over KH for several days at -78°, then stored at -78°.

Dichlorofluoromethane and chlorodifluoromethane were obtained in cylinders from Matheson Gas Products and used as received.

Other solvents were reagent grade. When used with air sensitive materials, they were dried over LiAlH$_4$ or KH before use. The solvents were stored under vacuum.

IV. Preparation of Starting Materials

A. 2,3-Dicarba-nido-hexaborane(8)

The carborane 2,3-C$_2$B$_4$H$_8$ was obtained from Chemical Systems, Inc. and used as received or prepared (101) and purified (105) according to published methods.

In a typical synthesis, a one liter vessel equipped with a Kontes valve (Figure 16) was charged with 80 mmole C$_2$H$_2$ and 10 mmole B$_5$H$_9$. The vessel was placed in an oven and heated to 215° for 3 days. At the end of this period, the contents were frozen and the noncondensibles were removed. The contents were then passed through U-traps maintained at -126° and -196° leaving behind dark solids. The excess
Figure 16. One Liter Reaction Vessel
C$_2$H$_2$ was collected in the -196° trap. The 2,3-C$_2$B$_4$H$_8$ and unreacted B$_5$H$_9$ in the -126° trap were combined in another vessel with excess (CH$_3$)$_3$N to react with B$_5$H$_9$. Warming slowly to room temperature with stirring allowed the formation of the amine-pentaborane adduct as the solution turned yellow. When the reaction was complete (after a few minutes), the noncondensible gases were removed at -196°. The volatile products (2,3-C$_2$B$_4$H$_8$ and (CH$_3$)$_3$N) were transferred to another vessel and reacted with excess B$_2$H$_6$. Upon slowly warming to room temperature (CH$_3$)$_3$HBH$_3$ formed. At this point the mixture was fractionally distilled through traps at -80° to separate (CH$_3$)$_3$NBH$_3$, -140° to separate 2,3-C$_2$B$_4$H$_8$, and -196° to collect excess B$_2$H$_6$. The typical yield relative to B$_5$H$_9$ was 20 percent. The 2,3-C$_2$B$_4$H$_8$ was stored at -78° under vacuum.

The product had a vapor pressure of 57 mm Hg at 0° (106) and its boron-11 n.m.r. agreed well with published spectra (113,114). The boron-11 n.m.r. resonance for the two basal boron atoms nearest the carbon atoms is 3.3 ppm ($J_{B-H_{\text{terminal}}} = 155$ Hz; $J_{B-H_{\text{bridge}}} = 43$ Hz). The other basal boron atom resonates at 0.6 ppm. The apical boron atom exhibits a resonance at 53.0 ppm ($J_{B-H} = 186$ Hz).

The proton n.m.r. spectrum (114) exhibits resonances at 3.68 τ assigned to hydrogens bonded to carbon, 6.56 τ ($J_{H-B} = 158$ Hz) assigned to hydrogens bonded to the basal borons, 11.3 τ ($J_{H-B} = 181$ Hz) assigned to the apically bonded hydrogen and 12.4 τ assigned to bridging hydrogens.
B. Deprotonation of \( \text{C}_2 \text{B}_4 \text{H}_8 \)

The previously published method (114) for deprotonation of \( \text{C}_2 \text{B}_4 \text{H}_8 \) was followed with slight modification. The procedure used is similar to that published for deprotonation of hexaborane(10) (42,46).

In a typical reaction \( \text{KH} \) was weighed into a reaction tube in the glove box. After evacuation an equimolar quantity of \( \text{C}_2 \text{B}_4 \text{H}_8 \) was condensed onto the \( \text{KH} \). Enough solvent (tetrahydrofuran, diethyl ether or dimethyl ether) was added to make the final concentration of carborane salt approximately 1 molar. The mixture was allowed to warm to \(-78^\circ\) with stirring. After quantitative \( \text{H}_2 \) was evolved, the solution became clear and the solvent could be removed to isolate the white \( \text{K}^+ \text{[C}_2 \text{B}_4 \text{H}_7]^- \) salt as a powder.

The boron-11 n.m.r. spectrum (proton decoupled) (Figure 17) exhibits three resonances at -5.5 ppm, 6.8 ppm and 56.0 ppm with relative area ratios of 2:1:1 respectively. The resonances are assigned to \( \text{B}_{4,6}, \text{B}_5, \text{B}_1 \) respectively. The proton n.m.r. spectrum (boron-11 decoupled) (Figure 18) exhibits four resonances at 4.87 \( \tau \), 6.42 \( \tau \), 7.57 \( \tau \), 14.86 \( \tau \). Their assignments and relative areas are respectively: the terminal hydrogens bonded to \( \text{C}_{2,3} \) (area 2), the terminal hydrogens bonded to \( \text{B}_{4,6} \) (area 2), the terminal hydrogen bonded to \( \text{B}_5 \) (area 1), and coincidentally overlapping resonances assigned to the bridging hydrogen and the terminal hydrogen bonded to \( \text{B}_1 \) (area 2). The resonance at 6.76 \( \tau \) is due to the proton impurity in the solvent.
Figure 17. 32.1 MHz Boron-11 NMR Spectrum of K$^+$\((2,3-C_2B_4H_7)^-\) in \((CH_3)_2O\) at -30° (Proton Decoupled)
Figure 18. 100 MHz Proton NMR Spectrum of $K^+[2,3-C_2B_4H_7]^- in (CD_3)_2O at -55^\circ$ (Boron-11 Decoupled)
C. Hexaborane(10)

The preparation of $\text{B}_6\text{H}_{10}$ from $1\text{-BrB}_5\text{H}_8$ as published in the literature was followed (16).

Into a 1 liter bulb (Figure 16) was syringed 4.4 ml (80 mmole) $\text{Br}_2$. After evacuation, 75 mmole $\text{B}_5\text{H}_9$ was added. The mixture was allowed to remain at room temperature for one day. The volatile products were then removed. The $1\text{-BrB}_5\text{H}_8$ was separated in a $-45^\circ$ U-trap. An 80 percent yield of $1\text{-BrB}_5\text{H}_8$ was obtained (8.9 g; 62 mmole). The bromopentaborane was transferred to a reaction tube having a rotatable sidearm which had been previously charged with 3.5 g KH (78 mmole).

About 40 ml (CH$_2$)$_2$O were condensed onto the $1\text{-BrB}_5\text{H}_8$ and the mixture was stirred at $-78^\circ$ until a clear solution resulted. The KH was slowly tipped into the solution resulting in the generation of $\text{H}_2$. The $\text{H}_2$ was pumped away while the solution was frozen and then KH was again added slowly to the stirred solution at $-78^\circ$. This process was repeated until completion of the reaction. To this solution of $\text{K}^+\text{[1-BrB}_5\text{H}_7]^-$ at $-78^\circ$, 40 mmole $\text{B}_2\text{H}_6$ was slowly added. Warming to $-35^\circ$ for one-half hour resulted in the precipitation of KBr and the formation of $\text{B}_6\text{H}_{10}$. The vessel was then cooled to $-78^\circ$ and the volatile materials allowed to distill through U-traps at room temperature, $-78^\circ$ and $-196^\circ$. When the fractionation became slow, the vessel was warmed to $-35^\circ$. After a few hours the $-35^\circ$ bath was placed around the room temperature trap and the vessel was allowed to warm to room temperature. The $-78^\circ$ trap contained mostly $\text{B}_6\text{H}_{10}$. After a second fractionation of the impure $\text{B}_6\text{H}_{10}$ through $-35^\circ$, $-78^\circ$, and $-196^\circ$ traps, the contents of the $-78^\circ$ trap exhibited a vapor pressure of 7.5 mm Hg at
0° which agreed with the literature value of 7.5 mm Hg at 0° (15). The yields of $\text{B}_6\text{H}_{10}$ were typically in excess of 70 percent based on 1-Br$\text{B}_5\text{H}_8$. The $\text{B}_6\text{H}_{10}$ was stored under vacuum at -196°.

The boron-$^{11}$ chemical shifts at ambient temperature agreed with published values for $\text{B}_6\text{H}_{10}$ (26). In $\text{CH}_2\text{Cl}_2$, basal boron atoms resonate at -14.1 ppm ($J_{\text{B-H}} = 155$ Hz) and the apical boron atom resonates at 51.8 ppm ($J_{\text{B-H}} = 155$ Hz).

D. Diironenneacarbonyl

Diironenneacarbonyl was generously supplied by Dr. O. Hollander and K. Inkrott.

The synthesis of $\text{Fe}_2(\text{CO})_9$ involved photolysis of $\text{Fe}(\text{CO})_5$ in acetic acid. The precipitated $\text{Fe}_2(\text{CO})_9$ was filtered and washed with ethanol and ether (126,127).

E. \(\mu\)-Tetracarbonyliron(0)-hexaborane(10)

The preparation of \(\mu\)-(CO)$_4\text{Fe-B}_6\text{H}_{10}$ has been published previously (48).

The reaction was carried out in a vessel equipped with a sublimation probe (Figure 19). Typically 0.8 g (2.2 mmole) $\text{Fe}_2(\text{CO})_9$ was placed in the vessel. After evacuation 5 mmole $\text{B}_6\text{H}_{10}$ and 5 ml $\text{C}_5\text{H}_{12}$ were condensed onto the solid. The mixture was allowed to stir at room temperature overnight (12 hours). When all the solids dissolved, the solution was cooled to -35° and $\text{C}_5\text{H}_{12}$ was distilled out of the vessel. Upon warming to 0°, excess $\text{B}_6\text{H}_{10}$ and the byproduct $\text{Fe}(\text{CO})_5$ could be distilled away. The sublimation probe was cooled to -78° and
Figure 19. Sublimation Apparatus
μ-(CO)$_4$Fe-B$_6$H$_{10}$ was allowed to sublime at room temperature. A yield of 85 percent was obtained as 0.45 g μ-(CO)$_4$Fe-B$_6$H$_{10}$ (1.9 mmole) sublimed.

The boron n.m.r. spectrum was the same as that reported in the literature (48). Boron-11 resonances (proton decoupled) in CH$_2$Cl$_2$ appear at -11.0 ppm, -5.0 ppm, 0.0 ppm and 54.1 ppm with relative area ratios of 1:2:2:1 respectively.

F. Preparation of K$^+[$μ-(CO)$_4$Fe-B$_6$H$_9]$$^-$

The synthesis of K$^+[$μ-(CO)$_4$Fe-B$_6$H$_9]$$^-$ was previously reported (51,62). The procedure is similar to that used for the deprotonation of B$_6$H$_{10}$ (42,46).

A 0.143 g sample of μ-(CO)$_4$Fe-B$_6$H$_9$ (0.59 mmole) and excess KH were placed in a reaction vessel. After evacuation, 0.5 ml dimethyl ether was added and the mixture was stirred at -78°. After quantitative H$_2$ was measured the reaction vessel was tipped and filtered into the attached n.m.r. tube at -78°. The tube was sealed and stored at -196°.

G. Preparation of K$^+[$μ-(CO)$_4$Fe-B$_7$H$_{12}$]$^-$

The synthesis of K$^+[$μ-(CO)$_4$Fe-B$_7$H$_{12}$]$^-$ has been reported (51,62). The procedure used is essentially the same.

A filtered solution of 0.66 mmole K$^+[$μ-(CO)$_4$Fe-B$_6$H$_9]$ in 1 ml (CH$_3$)$_2$O was reacted with 0.39 mmole B$_2$H$_6$ at -78° for 6 hours. After removal of volatile materials, an oil remained (probably ether solvated product). If 1 ml CHClF$_2$ was added, a tan solid precipitated. When the freon was distilled away some solvate was still present. The process was repeated until a tan powder resulted. The powder was
dissolved in 0.4 ml (CD$_3$)$_2$O at -78° and the solution was tipped into the attached n.m.r. tube which was then sealed.

H. Chlorotris(triphenylphosphine)copper(I)

The method published by Lippard and Ucko (75) was followed in the preparation of $[\{(C_6H_5)_3P\}]_3CuCl$.

Triphenylphosphine, 6.6 g (25 mmole), was dissolved in 50 ml CHCl$_3$. To this solution was added 0.62 g (6.5 mmole) CuCl. The reaction produced a clear solution with the liberation of heat. After stirring for one hour 200 ml C$_2$H$_5$OH was added. The solution was cooled for 3 days. The crystals were filtered and washed with ethyl ether and petroleum ether. After drying under vacuum 5.4 g $[\{(C_6H_5)_3P\}]_3CuCl$ (95%) was obtained.

I. Bromobis(triphenylphosphine)copper(I) hemibenzenate

The compound $[\{(C_6H_5)_3P\}]_2CuBr\cdot1/2C_6H_6$ was generously supplied by Dr. R. Goetze.

The synthesis involved combination of ethanolic solutions of CuBr$_2$ and $(C_6H_5)_3P$. The crystalline product was recrystallized from benzene/cyclohexane (128).

J. Methyl-d$_3$-triphenylphosphonium iodide

Methyl-d$_3$-triphenylphosphonium iodide was generously supplied by Dr. G. Outterson.

The preparation involved addition of CD$_3$I to a diethyl ether solution of $(C_6H_5)_3P$. The precipitate was washed with diethyl ether and dried under vacuum (129).
V. Reactions

A. Preparation of $B_5H_9Fe(CO)_3$

The reaction conditions have been published previously (97) and are similar to those for the preparation of $(CO)_3FeB_4H_8$ (95).

The preparation of $B_5H_9Fe(CO)_3$ was carried out in a glass vessel 100 mm x 300 mm. Cross sectionally concentric to this tube was another whose dimensions were 60 mm x 280 mm. The U-shaped space between these tubes could be evacuated through a Kontes 4 mm valve (Figure 20). Another vessel with a 10 mm annular space proved to be less efficient for the production of $B_5H_9Fe(CO)_3$.

The vessel was charged with 10 mmole $B_5H_9$ and 30 mmole $Fe(CO)_5$. The inner tube was filled with sand, which could be warmed by a resistance heater. The outer tube was immersed in a water bath (25°) and the inner tube was heated to 220°. Every 24 hours the reactants were cooled to -196° and noncondensible gas was removed. After 1 week, the condensible components were removed. The bulk consisted of unreacted $Fe(CO)_5$ and $B_5H_9$. The ferraborane $B_5H_9Fe(CO)_3$ is a deep red material which is therefore visually distinguishable from yellow $Fe(CO)_5$ and clear $B_5H_9$. Most $Fe(CO)_5$ and $B_5H_9$ was separated from $B_5H_9Fe(CO)_3$ by rapid volatilization to a U-trap maintained at -196°. When the condensate began to take on a red color, the volatile material was passed through a -35° trap. At this temperature $B_5H_9Fe(CO)_3$ distills at a slower rate compared to $Fe(CO)_5$ and $B_5H_9$. A relatively pure product (by n.m.r. analysis) can be obtained in a fairly short time. Usually $B_{10}H_{14}$ is also a byproduct in the pyrolysis but it can be
Figure 20. Hot-Cold Reactor for the Preparation of $\text{B}_5\text{H}_9\text{Fe(CO)}_3$
separated from the ferraborane by distillation through a U-trap main­
tained at 0°.

The yield of $\text{B}_5\text{H}_9\text{Fe(CO)}_3$ by this procedure is extremely small
(approximately 1%). The compound is a deep red mobile liquid at room
temperature with a vapor pressure of less than 1 mm Hg. The
$\text{B}_5\text{H}_9\text{Fe(CO)}_3$ was stored under vacuum of −196°. The ferraborane decom­
poses to a nonvolatile brown residue at temperatures slightly above
ambient.

Caution: The Pyrex hot-cold reactor exhibited signs of struc­
tural weakness after several syntheses. Apparently the boron hydrides
involved in the synthesis react with glass to cause etching at the tem­
peratures used. Consequently frequent inspection and replacement of
the reactor is suggested. The maximum time between replacement should
be no more than four months, if the reactor is used continually.

B. Protonation of $\text{B}_5\text{H}_9\text{Fe(CO)}_3$

The reaction was carried out in a fashion analogous to the proce­
dure for the protonation of $\text{B}_6\text{H}_{10}$ (47).

A U-tube was attached to the vacuum line (Figure 21). A dynamic
vacuum could be applied while condensing reactants in one arm. A 14/35
inner joint at the bottom of the tube permitted attachment of an n.m.r.
tube. Into the U-tube was condensed 0.07 ml (at 0°) $\text{B}_5\text{H}_9\text{Fe(CO)}_3$ (0.4
mmole). The ferraborane was allowed to drip into the n.m.r. tube and
then was cooled to −196°. Approximately 0.2 ml liquid HBr was con­
densed onto the solid. The n.m.r. tube was sealed. When the reac­
tants were warmed to −78°, the color of the solution changed from red
to brown. The sample was stored at −196°.
Figure 21. U-tube Adapter
C. Deprotonation of $\text{B}_5\text{H}_9\text{Fe(CO)}_3$

The general procedure used was similar to a previously published method (42,46) for the deprotonation of hexaborane(10).

In a typical preparation, approximately 2 mmole KH (0.09 g) was placed in a vessel in the glove box. The vessel was then closed. On the vacuum line was a U-tube which possessed a 14/35 inner joint at the bottom (Figure 21). The vessel containing the KH was quickly transferred under a $\text{N}_2$ gas stream to the U-tube. After evacuation, 0.075 ml $\text{B}_5\text{H}_9\text{Fe(CO)}_3$ (at 0°) was condensed in one arm of the U-tube. This design permitted distillation of $\text{B}_5\text{H}_9\text{Fe(CO)}_3$ under dynamic vacuum to minimize decomposition. The U-tube was isolated from the vacuum and the $\text{B}_5\text{H}_9\text{Fe(CO)}_3$ was allowed to liquify and drip into the reaction vessel which was maintained at -196°. The vessel was then transferred under $\text{N}_2$ gas to a stopcock adapter. Dimethyl ether (0.6 ml) was condensed into the vessel which was then allowed to warm to -78°. After 2 hours 0.38 mmole $\text{H}_2$ was measured. The yellow solution was then tipped and filtered into an n.m.r. tube. The tube was sealed and stored at -196°.

An approximate density of $\text{B}_5\text{H}_9\text{Fe(CO)}_3$ was obtained from this reaction, since it has been shown that only one bridge hydrogen has been removed from the framework during deprotonation (97). If 0.38 mmole $\text{H}_2$ was liberated then 0.38 mmole (0.075 ml) $\text{B}_5\text{H}_9\text{Fe(CO)}_3$ reacted. From the molecular weight the calculated density at 0° is about 1.0 g/ml or 5.1 mmole/ml.
D. Relative Acidity of $\text{B}_5\text{H}_9\text{Fe(CO)}_3$ versus $\text{B}_6\text{H}_{10}$

Two parallel reactions were performed to determine which conjugate base ([B$_5$H$_9$Fe(CO)$_3$]$^-$ or [B$_6$H$_9$]$^-$) had the greatest affinity for a proton.

A reaction vessel was charged with 0.050 g K$^+\text{[B}_5\text{H}_9\text{Fe(CO)}_3\text{]}^-$ (0.21 mmole). The vessel was evacuated and 0.21 mmole $\text{B}_6\text{H}_{10}$ and 0.5 ml (CH$_3$)$_2$O were condensed onto the solid. The mixture was warmed to $-78^\circ$ and stirred for 0.5 hour. The mixture was then tipped into the attached n.m.r. tube at $-78^\circ$. The tube was sealed and stored at $-196^\circ$.

A vessel attached to a powdered glass frit was charged with 0.045 g KH (1 mmole). After evacuating the vessel, 0.5 mmole $\text{B}_6\text{H}_{10}$ and 0.7 ml (CH$_3$)$_2$O were condensed onto the KH. The evolved H$_2$ was collected and measured (0.48 mmole). The excess KH was filtered from the solution at $-78^\circ$. The receiver ($-196^\circ$) was then transferred under N$_2$ gas to the bottom of a U-tube into which 0.094 ml $\text{B}_5\text{H}_9\text{Fe(CO)}_3$ (0.48 mmole) was condensed. The $\text{B}_5\text{H}_9\text{Fe(CO)}_3$ was allowed to drip onto the frozen solution of K$^+\text{[B}_6\text{H}_9\text{]}^-$. The mixture was then stirred at $-78^\circ$ for 0.5 hour. The solution was tipped into the attached n.m.r. tube at $-78^\circ$ and the tube was sealed and stored at $-196^\circ$.

E. Preparation of (n-C$_4$H$_9$)$_4\text{N}^+\text{[B}_5\text{H}_9\text{Fe(CO)}_3\text{]}^-$

The metathesis reaction to produce (n-C$_4$H$_9$)$_4\text{N}^+\text{[B}_5\text{H}_9\text{Fe(CO)}_3\text{]}^-$ is similar to a published procedure for the preparation of analogous boron hydride salts (46). The metathesis was undertaken to produce an easily crystallizable salt for an X-ray structural analysis of $\text{[B}_5\text{H}_9\text{Fe(CO)}_3\text{]}^-$. 
A reaction vessel with a rotatable sidearm was charged with 0.050 g KH (1.2 mmole). The sidearm was filled with 0.210 g \((n-C_{4}H_{9})_{4}NBr\) (0.65 mmole). After 0.13 ml \(B_{5}H_{9}Fe(CO)_{3}\) (at 0°; 0.65 mmole) was transferred into the vessel through use of the U-tube, the vessel was transferred under \(N_{2}\) gas to an extractor. When 1 ml \((CH_{3})_{2}O\) was condensed into the vessel it was allowed to warm to -78° as deprotonation occurred. The evolved H\(_{2}\) measured 0.69 mmole. At this time \((n-C_{4}H_{9})_{4}NBr\) was tipped into the solution and it was stirred at -23° for 45 minutes. The solvent was then distilled out of the vessel and 3 ml \(CH_{2}Cl_{2}\) was condensed onto the remaining orange solid. The solution was stirred at -23° to dissolve the \((n-C_{4}H_{9})_{4}N^{+}[B_{5}H_{8}Fe(CO)_{3}]^{-}\). The solution was filtered at -23° to remove excess KH and the metathesis product KBr (later identified by X-ray powder diffraction). The \(CH_{2}Cl_{2}\) was then distilled away leaving behind an orange solid. The \((n-C_{4}H_{9})_{4}N^{+}[B_{5}H_{8}Fe(CO)_{3}]^{-}\) was stored at -78°.

F. Preparation of Crystals of \((n-C_{4}H_{9})_{4}N^{+}[B_{5}H_{8}Fe(CO)_{3}]^{-}\)

The apparatus used for growing crystals consisted of two chambers separated by a Kontes stopcock. One chamber fitted with 14/35 joints could be detached and filled with the sample. The other chamber was isolated from the atmosphere by another Kontes stopcock. The whole apparatus (except for the stopcocks) could be immersed in a low temperature bath (Figure 22).

About 20 mg \((n-C_{4}H_{9})_{4}N^{+}[B_{5}H_{8}Fe(CO)_{3}]^{-}\) was placed in the demountable chamber in the glove box. After evacuation 1 ml \(CH_{2}Cl_{2}\) was added
Figure 22. Apparatus for Growing Crystals
to dissolve the salt. The stopcock to this chamber was then closed and several milliliters of diethyl ether were condensed into the other chamber. The apparatus was then placed in a -78° bath and the stopcock between the chambers was opened. Overnight crystals formed as diethyl ether slowly diffused into the chamber containing the sample. To isolate the crystals, the apparatus was tipped to remove most of the solvent into the chamber which did not contain the crystals. The last traces of solvents were removed from the crystals by distillation at -78°. The apparatus was then quickly taken into the glove box used for mounting crystals. The crystals were sealed into the thin walled capillaries as described previously and stored at -78° until needed.

G. Preparation of \([\text{C}_6\text{H}_5\text{P}]^3\text{CuB}_5\text{H}_8\text{Fe(CO)}\)\(^3\)

The preparation of \([\text{C}_6\text{H}_5\text{P}]^3\text{CuB}_5\text{H}_8\text{Fe(CO)}\)\(^3\) was done analogously to the published method for the preparation of \([\text{C}_6\text{H}_5\text{P}]^3\text{CuB}_6\text{H}_9\) (70).

A reaction vessel with a rotatable sidearm was charged with 0.018 g KH (0.40 mmole). The sidearm was filled with 0.354 g \([\text{C}_6\text{H}_5\text{P}]\)\(^3\)\text{CuCl} (0.40 mmole). The vessel was attached to a U-tube and 0.08 ml (at 0°) \(\text{B}_5\text{H}_9\text{Fe(CO)}\)\(^3\) (0.4 mmole) was condensed in the U-tube and allowed to drip into the reaction vessel. The vessel (at -196°) was transferred under \(\text{N}_2\) gas to an extractor. After condensing 1 ml \((\text{CH}_3)_2\text{O}\) into the vessel, the contents were warmed to -78° with stirring to allow for deprotonation. Measurement of the \(\text{H}_2\) indicated 0.40 mmole had been evolved. The \([\text{C}_6\text{H}_5\text{P}]^3\text{CuCl} \) was tipped into the solution and 2.5 ml \(\text{CH}_2\text{Cl}_2\) were added. The mixture was stirred at -78° for 2 hours and all solvents were removed at low temperature. The resulting yellow solid was stirred with 10 ml \(\text{CH}_2\text{Cl}_2\) at -45°, to dissolve most of
the solid. The solution was quickly filtered to remove KCl (later identified by its X-ray powder diffraction pattern). After reducing the volume of the filtrate (at -45°) to about 2 ml, 5 ml \((\text{C}_2\text{H}_5)_2\text{O}\) were added and the solution was cooled to -78° to cause precipitation of the product and to dissolve uncoordinated \((\text{C}_6\text{H}_5)_3\text{P}\). The yellow precipitate was quickly filtered and washed with \((\text{C}_2\text{H}_5)_2\text{O}\). Approximately 0.2 g \([\text{(C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_5\text{H}_8\text{Fe(CO)}_3\) (0.25 mmole; 65\%) was recovered.

An alternate method of preparation utilized \([\text{(C}_6\text{H}_5)_3\text{P}]_2\text{CuBr} \cdot 1/2\text{C}_6\text{H}_6\). The synthetic procedure remained the same, however this reagent is superior as no free \((\text{C}_6\text{H}_5)_3\text{P}\) is in the reaction mixture. Thus the product is more easily purified.

H. Preparation of Crystals of \([\text{(C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_5\text{H}_8\text{Fe(CO)}_3\)

Single crystals for X-ray diffraction studies were grown in the apparatus described for \((\text{n-C}_4\text{H}_9)_4^+\text{N}^+\text{[B}_5\text{H}_8\text{Fe(CO)}_3\text{]}^-\). In this case the copper compound was dissolved in toluene and equilibrated with \text{n-pentane at 0°}. The procedure for mounting the crystals was the same as previously described.

An experimental density determination was performed on crystals from the reaction involving \([\text{(C}_6\text{H}_5)_3\text{P}]_3\text{CuCl}\). By flotation in a carbon tetrachloride/hexane mixture, the density was 1.32 g/ml.

I. Preparation of \([\text{(C}_6\text{H}_5)_3\text{PCD}_3]^+\text{[µ-(CO)}_3\text{Fe-B}_6\text{H}_9\text{]}^-\)

The metathesis reaction for the preparation of the phosphonium salt is completely analogous to that for \((\text{n-C}_4\text{H}_9)_4^+\text{N}^+\text{[B}_5\text{H}_8\text{Fe(CO)}_3\text{]}^-\) as described earlier.
The salt (0.305 g; 0.76 mmole) \((C_6H_5)_3PCl_3I\) was added to a solution of \(K^+\mu-(CO)_4Fe-B_6H_6\) (0.21 g; 0.86 mmole) in 1 ml \((CH_3)_2O\) and 3 ml \(CH_2Cl_2\). After reaction at -23°, all volatiles were removed. The resulting phosphonium salt was dissolved in 3 ml \(CH_2Cl_2\) and the KI (later identified by X-ray powder diffraction) was filtered at -23° from the solution. The \(CH_2Cl_2\) was then distilled from the solution and replaced with 0.5 ml \(CHCl_2F\). The solution was tipped into an n.m.r. tube and it was sealed.

J. Preparation of \(K^+[2,3-C_2B_5H_{10}]^-\)

The salt \(K^+[2,3-C_2B_4H_8]^-\) was prepared in a manner similar to a previously reported procedure (114).

In a typical synthesis, a reaction tube was charged with 0.32 g KH (0.72 mmole). The tube was evacuated, and 0.9 mmole 2,3-\(C_2B_4H_8\) and 1 ml \((CH_3)_2O\) were condensed onto the KH. Deprotonation of the carborane occurred at -78°. The \(H_2\) evolved was measured (0.74 mmole). All volatiles were then removed. The vessel was warmed to room temperature to ensure complete removal of excess 2,3-\(C_2B_4H_8\). The dimethyl ether solvent was replaced and 0.45 mmole \(B_2H_6\) was condensed into the vessel. The solution was stirred at -78° overnight. All volatiles were then removed at -78° in order to separate excess \(B_2H_6\). The dimethyl ether solvent was replaced and the solution was tipped (at -78°) into the attached n.m.r. tube which was then sealed.

In another preparation of \(K^+[2,3-C_2B_5H_{10}]^-\) the addition of \(B_2H_6\) to \(K^+[2,3-C_2B_4H_8]^-\) in diethyl ether solution at -78° was measured tensimetrically. Small increments of \(B_2H_6\) were added to the stirred
solution and the residual pressure after equilibration was monitored. A sharp break at 0.5 mole fraction $B_2H_6/K^+[2,3-C_2B_4H_7]^-$ was noted (Figure 23).

The reaction of $K^+[2,3-C_2B_{4}H_{8}]^-$ with liquid HCl yielded some $2,3-C_2B_4H_8$ but no isolable heptaborane analog.
Figure 23. Tensimetric Titration Plot of $B_2H_6$ versus $K^+[2,3-C_2B_4H_7]$
RESULTS AND DISCUSSION

I. Nuclear Magnetic Resonance Spectra of B\textsubscript{5}H\textsubscript{9}Fe(CO)\textsubscript{3}

The boron-11 n.m.r. spectrum of B\textsubscript{5}H\textsubscript{9}Fe(CO)\textsubscript{3} in dimethyl ether at 25° is shown in Figure 24. Since the molecular formula has been determined from mass spectrometric studies (97), the appearance of only three resonances indicates apparent C\textsubscript{5} symmetry on the boron-11 time scale. The molecular structure which best fits the analytical data is illustrated in Figure 25. This structure is the result of an Fe(CO)\textsubscript{3} group inserting itself into the basal boron plane of a pentaborane(9) square pyramid and thus expanding the polyhedral framework to an approximate pentagonal pyramid. When this insertion occurs, note that there remain four bridging hydrogen atoms to bond among five possible sites in the basal plane of the pentagonal pyramid. If the hydrogen bonded to the iron atom migrates between the two available positions (Figure 26), the molecule will possess C\textsubscript{5} symmetry and give rise to three boron-11 resonances in the relative area ratio 2:2:1. The resonance at -46.6 ppm ($J_{\text{B-H}} = 150$ Hz) is assigned to $B_{3,6}$, -8.6 ppm ($J_{\text{B-H}} = 150$ Hz) to $B_{4,5}$ and 47.1 ppm ($J_{\text{B-H}} = 140$ Hz) to $B_1$. The method for assignment involves narrowband spin-decoupling experiments described below.

When the temperature of the sample is lowered to -80°, the migration of the hydrogen bonded to the iron atom is quenched since five
Figure 24. 32.1 MHz Boron-11 NMR Spectra of $B_5H_9Fe(CO)_3$ in $CH_2Cl_2$ at 25°
Figure 25. Proposed Molecular Structure of $B_5H_9Fe(CO)_3$
Figure 26. Proposed Hydrogen Migration in $B_5H_9Fe(CO)_3$
resonances appear in the boron-11 n.m.r. spectrum (Figure 27). The quenched structure is asymmetric ($C_1$ symmetry). Boron-11 n.m.r. resonances are assigned as follows: -59.4 ppm ($B_3$), -41.5 ppm ($B_6$), -19.1 ppm ($B_4$ or $B_5$), -7.0 ppm ($B_5$ or $B_4$) and 42.3 ppm ($J_{B-H} = 140$ Hz) ($B_1$).

Variable temperature boron-11 spin-decoupled proton n.m.r. spectra of $B_2H_9Fe(CO)_3$ in dimethyl ether support the theory involving a migration of the hydrogen bonded to the iron atom (Figure 28). At 25° there are two sets of resonances (3.60 $\tau$ and 5.81 $\tau$) which are assigned to the basal terminally bonded hydrogens. The bridge hydrogens resonate at 9.90 $\tau$, and the apically bonded hydrogen resonates at 11.19 $\tau$. The resonance of the hydrogen bonded to the iron atom appears at 26.79 $\tau$. This chemical shift is similar to the 24.40 $\tau$ resonance assigned to Fe-H in ($\eta^5-C_3H_5$)Fe(II)H($C_2B_4H_6$) (66). At -80°, when the hydrogen migration is quenched all nine nonequivalent hydrogens exhibit nine distinct resonances. An important feature of these spectra is the invariance of the chemical shift of the hydrogen bonded to the iron atom. The hydrogen appears to be always bonded to the iron atom during migration. Consequently the hydrogens bridging the boron atoms are not involved in any fluxional process. At 25°, the pseudo-$C_s$ symmetry produced by the single migrating hydrogen effectively causes averaging of the bridge hydrogens between $B_3$ and 4 and $B_5$ and 6 which resonate at 9.18 $\tau$ and 10.72 $\tau$. The averaged resonance coincidentally overlaps the resonance of the bridge hydrogen between $B_4$ and $B_5$ (9.92 $\tau$), and all three resonances appear as a single peak.
Figure 27. 32.1 MHz Boron-11 NMR Spectra of $B_5H_9Fe(CO)_3$ in $(CD_3)_2O$ at $-80^\circ$
Figure 28. Composite Variable Temperature 100 MHz Proton NMR Spectra of $\text{B}_3\text{H}_9\text{Fe(CO)}_3$ in Dimethyl Ether (Boron-11 Decoupled)
Other assignments have been made from the results of narrowband decoupling experiments. When the absolute boron-11 frequency associated with the -41.5 ppm resonance is used as the boron-11 spin-decoupling frequency while observing the proton spectrum, the resonances at 4.03 $\tau$ and 26.79 $\tau$ sharpen noticeably. This phenomenon, which has been previously used as an aid in assignment of resonances (115), indicates that the atoms producing these resonances are bonded to one another. Therefore the hydrogen bonded to iron is also bonded to $B_6$, and the resonance at 4.03 $\tau$ is produced by the terminal hydrogen on $B_6$. The resonance at 3.16 $\tau$ must then be assigned to the terminal hydrogen on $B_3$. These resonances (4.03 $\tau$ and 3.16 $\tau$) average to 3.60 $\tau$ when pseudo-$C_5$ symmetry exists. Although narrowband decoupling experiments have been helpful in assigning the low field resonances in both the proton and boron-11 spectra, the proton resonances at 5.47 $\tau$ and 6.14 $\tau$ (whose average is 5.81 $\tau$) cannot be assigned exactly. They are due to the terminal protons on $B_4$ and $B_5$. The apically bonded proton resonance at 11.19 $\tau$ as expected remains essentially invariant with temperature.

The carbon-13 n.m.r. spectrum of $B_7H_9Fe(CO)_3$ in diethyl ether was recorded at various temperatures. The spectral results are consistent with a rotation or pseudo-rotation about the iron atom such that the hydrogen atom can migrate to the other available position. While migration occurs the carbonyl groups effectively average to a single peak (206.3 ppm) (Figure 29). When the migration is quenched (at -120°), three nonequivalent carbon-13 resonances are observed (210.5 ppm, 207.7 ppm and 206.6 ppm).
Figure 29. Variable Temperature 22.62 MHz Carbon-13 NMR Spectra of $B_5H_9Fe(CO)_3$ in Dimethyl Ether
II. Protonation of $\text{B}_5\text{H}_9\text{Fe(CO)}_3$

The reaction of $\text{B}_6\text{H}_{10}$ with liquid HBr or HCl/BCl$_3$ has resulted in protonation of the boron-boron bond (47). The protonation of the boron-iron bond (the analog of the boron-boron bond in $\text{B}_5\text{H}_9\text{Fe(CO)}_3$) has occurred in B$_5$H$_9$Fe(CO)$_3$. The boron-11 n.m.r. spectrum of a mixture of B$_5$H$_9$Fe(CO)$_3$ and liquid HBr at -80° (Figure 30) indicates $C_s$ symmetry as expected when five bridging hydrogens are present. It should be noted for comparison that the boron-11 n.m.r. spectrum of B$_5$H$_9$Fe(CO)$_3$ at -80° exhibits five resonances. The assignment of the resonances at -37.1 ppm and -20.5 ppm is uncertain, however they appear to be due to the two symmetry equivalent sets of basal boron atoms (B$_{3,6}$ or B$_{4,5}$). The resonance at 43.5 ppm ($J_{\text{B-H}} = 140 \text{ Hz}$) can be assigned to the apical boron atom.

The proton n.m.r. spectrum also indicates $C_s$ symmetry (Figure 31). The resonances at 4.14 $\tau$ and 5.25 $\tau$ can be assigned to the pairs of symmetry equivalent basal terminal hydrogens. The 9.05 $\tau$ resonance is assigned to the three hydrogens bridging the boron atoms. The resonance at 10.29 $\tau$ is assigned to the apically bonded hydrogen. The two hydrogens bridging between iron and boron resonate at 23.60 $\tau$. The resonance at 4.67 $\tau$ and the multiplet at 12.36 $\tau$ are due to the protium impurity in CD$_2$Cl$_2$ and HBr respectively.

The carbon-13 n.m.r. spectrum at -80° in liquid HBr exhibits a single resonance at 193.0 ppm. Rapid exchange of the hydrogen atoms bonded to the iron atom with H$^+$ in the solvent could be occurring. As a result the allowed rotation or pseudo-rotation about the iron atom would result in indistinguishable carbonyl groups.
Figure 30. 32.1 MHz Boron-11 NMR Spectrum of \([\text{B}_5\text{H}_{10}\text{Fe(CO)}_3]^+\text{Br}^-\) in Liquid HBr at -80°.
Figure 31. Composite 90 MHz Proton NMR Spectra of $\left[\text{B}_5\text{H}_{10}\text{Fe(CO)}_3\right]^+\text{Br}^-$ in Liquid HBr at $-80^\circ$ (Boron-11 Decoupled)

(a) and (b) low field resonances sharpen with variations in boron-11 decoupling frequency.
The stoichiometry of the reaction has been established by a tensimetric titration of HCl with a CHCl₃ solution containing equimolar amounts of B₅H₉Fe(CO)₃ and BCl₃ at -78° to produce a yellow solid. A break in the curve of pressure versus mole ratio HCl/B₅H₉Fe(CO)₃ indicated that one mole HCl reacted with one mole B₅H₉Fe(CO)₃.

The instability of the yellow solid was evident as decomposition to the starting materials occurred above -45°. Below -45°, the solid was insoluble in chlorinated hydrocarbons.

III. Nuclear Magnetic Resonance Spectra of K⁺[B₅H₉Fe(CO)₃]⁻

The boron-11 n.m.r. spectrum of K⁺[B₅H₉Fe(CO)₃]⁻ is illustrated in Figure 32. Outwardly there is similarity to the boron-11 spectrum of B₅H₉Fe(CO)₃. The chemical shifts have of course changed. Such a similarity suggests that deprotonation has not caused major alteration of the boron framework. Boron-11 spectra for the neutral and the bridge deprotonated species in the cases of B₅H₁⁰ and B₅H₉ also show similarities (42,45). Therefore, it appears that a bridging hydrogen has been removed from B₅H₉Fe(CO)₃ in the reaction with KH. Narrowband decoupling experiments were not as helpful in making assignment of the resonances as they were in the case of B₅H₉Fe(CO)₃. Nevertheless, from comparison with the B₅H₉Fe(CO)₃ boron-11 spectrum, the resonance at -42.2 ppm (J₉⁻H = 130 Hz) can be assigned to B₃,6, -19.8 ppm to B₄,5, and 32.2 ppm (J₉⁻H = 100 Hz) to B₁. There exists the possibility however that the assignments for B₃,6 and B₄,5 are reversed. Low temperature boron-11 n.m.r. studies were not informative as severe broadening of the resonances occurred.
Figure 32. 32.1 MHz Boron-11 NMR Spectra of K^+[B_5H_8Fe(CO)_3]^− in (CD_3)_2O at -25°
The problem that arises is to determine which proton is removed. The proton n.m.r. spectra (Figure 33) indicate the continued presence of the hydrogen bonded to the iron atom from the resonance at 26.24 \( \tau \). The constancy of its chemical shift over the temperature range studied (25° to -140°) indicates that this particular hydrogen does not participate in any migratory process connected with the hydrogens bridging boron atoms. Consequently, the proton removed in the deprotonation reaction must be one bridging the boron atoms. This assertion is corroborated by the appearance of the bridge hydrogen region of the proton n.m.r. spectra (Figure 34). The apically bonded hydrogen resonance at 11.33 \( \tau \) as expected is invariant with change in temperature. However the single bridge hydrogen resonance (13.43 \( \tau \)) at -100° is consistent with rapid migration among the three available positions. At -113° two nonequivalent bridge hydrogens (12.93 \( \tau \) and 13.91 \( \tau \)) are indicated. The question of whether the appearance of nonequivalent bridge resonances is due to a quenching of the rotation or pseudorotation about the iron or to a quenching of the bridge hydrogen tautomerism between boron atoms can be answered with some certainty. With a loss of symmetry indicated by a quenching of the migration of the hydrogen bonded to the iron atom, one would expect the resonances assigned to the basal terminal hydrogen (3.83 \( \tau \) and 5.53 \( \tau \)) to become nonequivalent. Although slight broadening of the resonance at 3.83 \( \tau \) is noticed at -113°, it does not split into two resonances until the temperature is lowered to -140°. The resonance at 5.53 \( \tau \) is invariant over the temperature range studied (25° to -140°) and coincidental overlap of the resonances of terminally bonded protons on \( B_4 \) and \( B_5 \).
Figure 33. Composite Variable Temperature 90 MHz Proton NMR Spectra of K⁺[B₅H₈Fe(CO)₃]⁻ in (CD₃)₂O (Boron-11 Decoupled)
Figure 34. Variable Temperature 100 MHz Proton NMR Spectra of the Bridge Hydrogen Region of K⁺[B₅H₆Fe(CO)₃]⁻ in (CD₃)₂O (Boron-11 Decoupled)
appears to be the explanation. As a result, the hydrogen bonded to the iron atom migrates at -113° but the bridge hydrogen migration between boron atoms appears to be quenched. If only two possible arrangements of static structures with bridging hydrogens between B_3 and 4 and B_4 and 5 as opposed to one with bridge hydrogens between B_4 and 5 and B_5 and 6 are possible, these arrangements will give rise to only two bridge hydrogen resonances at -113°. At lower temperatures (-140°) when the migration of the hydrogen bonded to the iron atom is quenched, nonequivalent terminally bonded protons on B_3 and B_6 are observed as well. Although two isomers can be envisioned, the X-ray crystal structure (described later) indicates only one in the solid state. Solution spectra (at -140°) are consistent with the existence of one isomer also.

The carbon-13 n.m.r. spectrum at -120° does not indicate distinct resonances for the three carbonyl groups. Apparently rotation about the iron atom still occurs at -120° since the resonance at 214.3 ppm is also present at -50°. Thus these spectral results are consistent with a quenching of the rotation or pseudo-rotation about iron below -120°.

The yellow powder K^[B_5H_8Fe(CO)_3]^- can be isolated from solution by removal of the solvent at low temperature. The salt can be handled at ambient temperature in the glove box for at least an hour with no apparent decomposition. Solutions of K^[B_5H_8Fe(CO)_3]^- in (CH_3)_2O are stable even at ambient temperature. The n.m.r. spectra indicate little if any decomposition for at least an hour.
IV. Relative Acidity Study of $\text{B}_5\text{H}_9\text{Fe(CO)}_3$ versus $\text{B}_6\text{H}_{10}$

From the following proton competition reactions in dimethyl ether, $\text{B}_5\text{H}_9\text{Fe(CO)}_3$ was shown to be a stronger Brønsted acid than $\text{B}_6\text{H}_{10}$:

$$\text{B}_5\text{H}_9\text{Fe(CO)}_3 + K^+[\text{B}_6\text{H}_{10}]^- \rightarrow K^+[\text{B}_5\text{H}_8\text{Fe(CO)}_3]^- + \text{B}_6\text{H}_{10}$$

$$\text{B}_6\text{H}_{10} + K^+[\text{B}_5\text{H}_8\text{Fe(CO)}_3]^- \rightarrow \text{No Reaction}$$

The $\text{Fe(CO)}_3$ moiety is an electron withdrawing group with respect to the borane cage. This result parallels the greater Brønsted acidity of $\mu-(\text{CO})_4\text{Fe}-\text{B}_6\text{H}_{10}$ with respect to $\text{B}_6\text{H}_{10}$ (62). In this case, the anion is stabilized by $(\text{CO})_4\text{Fe}$ which is an electron withdrawing group. This property is expected since the compound is the result of a Lewis acid-base interaction between the $(\text{CO})_4\text{Fe}$ group and the two center, two electron boron-boron bond in hexaborane(10) (48,50,51,62).

V. Properties and Structure of $(\text{n-C}_4\text{H}_9)_4\text{N}^+[\text{B}_5\text{H}_8\text{Fe(CO)}_3]^-$

Although some crystals were briefly exposed to air, $(\text{n-C}_4\text{H}_9)_4\text{N}^+[\text{B}_5\text{H}_8\text{Fe(CO)}_3]^- \text{ dissolved in CH}_2\text{Cl}_2 \text{ exhibited the same boron-11 n.m.r. spectrum as that of K}^+[\text{B}_5\text{H}_8\text{Fe(CO)}_3]^- \text{ in dimethyl ether solution. The yellow ammonium salt apparently is stabilized by the cation. This result is not unexpected since the tetra-n-butylammonium salts of other borane anions are known to possess greater stability that the corresponding potassium salts (46).}$

Unlike $K^+[\text{B}_5\text{H}_8\text{Fe(CO)}_3]^-$ which is insoluble in chlorinated hydrocarbons, $(\text{n-C}_4\text{H}_9)_4\text{N}^+[\text{B}_5\text{H}_8\text{Fe(CO)}_3]^- \text{ is soluble in CH}_2\text{Cl}_2 \text{ and CHCl}_3 \text{ but insoluble in ethyl ether and hydrocarbons.}$
The crystal and molecular structure of \((\text{n-}C_{4}H_{9})_{4}N^+[B_{5}H_{8}\text{Fe(CO)}_{3}]^-\) was determined from X-ray data by Dr. M. M. Mangion (97) of this laboratory (Figure 35).

Crystals of \((\text{n-}C_{4}H_{9})_{4}N^+[B_{5}H_{8}\text{Fe(CO)}_{3}]^-\) are monoclinic with space group \(P2_1/\overline{b}\). The unit cell dimensions are: \(a = 11.108(6) \text{ Å}, b = 15.462(12) \text{ Å}, c = 15.443(9) \text{ Å}\) and \(\gamma = 95.87(5)^\circ\). The calculated density is 1.10 g/cm\(^3\). \(Z = 4\). The data were refined to \(R\) (conventional) = 0.080 and \(R\) (weighted) = 0.092 (97). Selected bond distances and angles are given in Table 1.

Since there are similarities in the n.m.r. spectra of \(B_{3}H_{9}\text{Fe(CO)}_{3}\) and \([B_{5}H_{8}\text{Fe(CO)}_{3}]^-\), their solid state structures are believed to be similar.

The iron atom has inserted into the basal plane of the boron polyhedron (97). The square pyramid of the pentaborane framework has been expanded to a pentagonal pyramid since the maximum standard deviation of any atom from the \(\text{Fe}, B_{3}, B_{4}, B_{5}, B_{6}\) plane in \([B_{5}H_{8}\text{Fe(CO)}_{3}]^-\) is 0.04 \(\text{Å}\). The apical boron lies 0.97 \(\text{Å}\) above this plane.

An interesting feature of the solid state structure of \([B_{5}H_{8}\text{Fe(CO)}_{3}]^-\) is the position of the boron-boron bond. It is situated between \(B_{3}\) and \(B_{4}\). This result is consistent with low temperature proton n.m.r. spectra which indicate an asymmetric structure (Figures 33, 34). This position of the boron-boron bond is reasonable in view of the electron withdrawing effect of the tricarbonyl iron group on this localized two electron, two center bond.

The \(\text{Fe-H}\) distance is 1.52 \(\text{Å}\) and is similar to previously reported distances for terminally bonded hydrogen atoms (130, 131).
Figure 35. Structure of the Anion $[\text{B}_5\text{H}_8\text{Fe(CO)}_3]^{-}$
TABLE 1

Selected Bond Distances and Angles for $[B_5H_8Fe(CO)]^-$ \(^a\)

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Distance (Å)</th>
<th>Angle (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe - B(_1)</td>
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</tr>
<tr>
<td>Fe - B(_3)</td>
<td>2.08(2)</td>
<td></td>
</tr>
<tr>
<td>Fe - B(_6)</td>
<td>2.13(1)</td>
<td></td>
</tr>
<tr>
<td>B(_1) - B(_6)</td>
<td>1.76(2)</td>
<td></td>
</tr>
<tr>
<td>B(_1) - B(_3)</td>
<td>1.73(2)</td>
<td></td>
</tr>
<tr>
<td>B(_1) - B(_4)</td>
<td>1.80(2)</td>
<td></td>
</tr>
<tr>
<td>B(_1) - B(_5)</td>
<td>1.83(2)</td>
<td></td>
</tr>
<tr>
<td>B(_3) - B(_4)</td>
<td>1.67(2)</td>
<td></td>
</tr>
<tr>
<td>B(_4) - B(_5)</td>
<td>1.71(2)</td>
<td></td>
</tr>
<tr>
<td>B(_5) - B(_6)</td>
<td>1.78(2)</td>
<td></td>
</tr>
<tr>
<td>Fe - H</td>
<td>1.52</td>
<td></td>
</tr>
<tr>
<td>B(<em>6) - H(</em>{Fe})</td>
<td>1.12</td>
<td></td>
</tr>
<tr>
<td>B(_3) - Fe - B(_6)</td>
<td>83.5(6)</td>
<td></td>
</tr>
<tr>
<td>B(_1) - Fe - B(_3)</td>
<td>48.1(6)</td>
<td></td>
</tr>
<tr>
<td>Fe - B(_1) - B(_3)</td>
<td>63.7(6)</td>
<td></td>
</tr>
<tr>
<td>B(_3) - B(_1) - B(_4)</td>
<td>56.6(8)</td>
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</tr>
<tr>
<td>Fe - B(_3) - B(_1)</td>
<td>68.3(7)</td>
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<tr>
<td>Fe - B(_6) - B(_5)</td>
<td>119.1(9)</td>
<td></td>
</tr>
<tr>
<td>B(_1) - Fe - B(_6)</td>
<td>48.6(5)</td>
<td></td>
</tr>
<tr>
<td>Fe - B(_1) - B(_6)</td>
<td>65.0(6)</td>
<td></td>
</tr>
<tr>
<td>B(_4) - B(_1) - B(_5)</td>
<td>56.2(8)</td>
<td></td>
</tr>
<tr>
<td>B(_5) - B(_1) - B(_6)</td>
<td>59.3(8)</td>
<td></td>
</tr>
<tr>
<td>Fe - B(_3) - B(_4)</td>
<td>120.2(10)</td>
<td></td>
</tr>
<tr>
<td>Fe - B(_6) - B(_1)</td>
<td>66.4(6)</td>
<td></td>
</tr>
<tr>
<td>B(_3) - B(_4) - B(_5)</td>
<td>112.2(11)</td>
<td></td>
</tr>
<tr>
<td>B(_4) - B(_5) - B(_6)</td>
<td>104.7(10)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Reference 138.
Nevertheless, as discussed earlier, solution n.m.r. studies are consistent with interaction between the hydrogen atom bonded to the iron atom and the adjacent basal boron atom.

VI. Properties and Nuclear Magnetic Resonance Spectra of \([\left((C_6H_5)_3P\right)\]_2CuB_5H_8Fe(CO)_3

The yellow solid \([\left((C_6H_5)_3P\right)\]_2CuB_5H_8Fe(CO)_3 is soluble in CHCl_3, CHCl_3 and toluene. It is insoluble in ethyl ether and hydrocarbons. It appears stable in air as a solid since no noticeable decomposition was detected for a period of several hours.

The boron-11 n.m.r. spectrum exhibits three broad resonances suggestive of C_3 symmetry (Figure 36). The resonance at -39.9 ppm and -11.6 ppm are assigned to the symmetry equivalent sets of boron atoms in the basal plane. The resonance at 33.6 ppm is assigned to the apical boron atom. Interestingly the phosphino-copper group appears to bond in the B_4,5 position rather than the B_3,4 position as one might have expected after studying the X-ray crystal structure of \([B_5H_8Fe(CO)_3]\) (97). Possibly the copper group prefers to bond opposite iron as a result of unfavorable steric interactions.

The proton n.m.r. spectrum also indicates C_3 symmetry (Figure 37). The resonances at 3.92 \(\tau\) and 4.64 \(\tau\) are assigned to the equivalent sets of basal terminal hydrogen atoms. The apically bonded hydrogen, the two bridge hydrogens between boron atoms and the hydrogen bonded to the iron atom are assigned respectively to the resonances at 10.85 \(\tau\), 12.97 \(\tau\), and 27.00 \(\tau\). The resonance at 2.7 \(\tau\) is due to the hydrogens of \((C_6H_5)_3P\). Over the temperature range studied (25° to -80°), no quenching of the expected migration of the hydrogen bonded to the
Figure 36. 32.1 MHz Boron-11 NMR Spectrum of \([((C_6H_5)_3P)_2CuB_5H_8Fe(CO)_3] in CDCl_3 at 25^\circ\)
Figure 37. Composite 90 MHz Proton NMR Spectrum of \([\text{Cp}_3]_2\text{CuB}_5\text{H}_8\text{Fe(CO)}_3\) in CDCl₃ (Boron-11 Decoupled)
iron was noticed. Lower temperatures caused precipitation of the sample.

From studies of other phosphino-copper-boranes as described in the introduction, it appears that copper bonds in various ways with borane anions. A boron-copper-boron three center interaction is present in \([\text{C}_6\text{H}_5\text{P}]_2\text{CuB}_3\text{H}_8\) (Figure 9) and its methyl derivatives (70-74). On the other hand, copper-hydrogen-boron bridge interactions are indicated for \(\text{Cu}_2\text{B}_{10}\text{H}_{10}\) (136), \([\text{C}_6\text{H}_5\text{P}]_2\text{CuB}_3\text{H}_8\) (Figure 10) (82), \([\text{C}_6\text{H}_5\text{P}]_2\text{CuBH}_4\) (78) and \([\text{C}_6\text{H}_5\text{P}]_2\text{Cu}_2\text{B}_{10}\text{H}_{10}\cdot\text{CHCl}_3\) (89). The bonding interaction of the Cu moiety in \([\text{C}_6\text{H}_5\text{P}]_2\text{CuB}_3\text{H}_8\text{Fe(CO)}_3\) in solution appears to be similar to that of a bridge hydrogen, and involves a three center boron-copper-boron. The proton n.m.r. spectrum does not indicate the presence of copper-hydrogen-boron bridge interactions. The phosphorous-31 n.m.r. spectrum appears to support this contention also, since a single resonance at \(-0.54\) ppm is observed at ambient temperature. Unless coincidental overlap of phosphorous resonances occurs, a freely rotating copper would allow averaging of the two phosphorous resonances. The solid state structure, however, indicates another mode of interaction.

VII. Structure of \([\text{C}_6\text{H}_5\text{P}]_2\text{CuB}_3\text{H}_8\text{Fe(CO)}_3\)

The crystal and molecular structure of \([\text{C}_6\text{H}_5\text{P}]_2\text{CuB}_3\text{H}_8\text{Fe(CO)}_3\) was determined from X-ray data by Dr. M. M. Mangion of this laboratory (135) (Figures 38, 39).

The crystals are triclinic with space group P1. The unit cell dimensions are: \(a = 11.113(5)\) Å, \(b = 14.670(8)\) Å, \(c = 15.034(7)\) Å, and \(\alpha = 95.60(4)°\), \(\beta = 121.01(3)°\), \(\gamma = 106.29(4)°\). The calculated
Figure 38. Structure of $[(C_6H_5)_3P]_2CuB_8H_8Fe(CO)_3$
Figure 39. Structure of the Metalloborane Cage in $[(C_6H_5)_3P]_2CuB_5H_8Fe(CO)_3$.
density is 1.36 g/cm$^3$ which agrees with the experimental density of 1.34 g/cm$^3$. $Z$ is 2. The data were refined to $R$ (conventional) = 0.058 and $R$ (weighted) = 0.067 (135). Selected bond distances and angles are given in Table 2. All hydrogen atoms were located.

The X-ray crystallographic data support the fact that the $[(C_6H_5)_3P]_2Cu^+$ group has effectively replaced a bridge hydrogen between $B_4$ and $B_5$. The remainder of the molecule has structural characteristics which are similar to $[B_5H_8Fe(CO)_3]^-$ except for the placement of the bridging hydrogen between $B_3$ and $B_4$ (97). Two slightly different molecules in terms of bond angles and distances crystallize in the triclinic unit cell, however the overall structural features of the two are very similar. The maximum distance of any atom from the plane of Fe, $B_3$, $B_4$, $B_5$, $B_6$ is 0.03 Å. The copper atom lies about 0.4 Å below this plane, and the apical boron lies 0.98 Å above this plane (135).

An unusual aspect of the structure is the presence of a copper-hydrogen-boron bridge interaction. One of the two Cu-H distances in each molecule within the unit cell is slightly shorter than the corresponding Cu-B distance (135) (Figure 39). However, a copper-hydrogen interaction is not apparent from the n.m.r. spectral studies. The Cu-H and Cu-B distances where a Cu-H-B interaction is present are reasonable compared to those in $[(C_6H_5)_3P]_2CuB_3H_8$, $[(C_6H_5)_3P]_2CuBH_4$ and $[(C_6H_5)_3P]_2CuB_10H_{10}·CHCl_3$ where Cu-H-B interactions are also indicated. In addition the Cu-H and Cu-B distances where no Cu-H-B interaction is indicated are similar to those of $[(C_6H_5)_3P]_2CuB_2H_8$ where no Cu-H-B interactions are postulated (Table 3). The range of
### TABLE 2

Selected Bond Distances and Angles for \([(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_5\text{H}_8\text{Fe(CO)}_3\)^a

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Distance (Å)</th>
<th>Angle (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu - B₄</td>
<td>2.256(15)</td>
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</tr>
<tr>
<td>Cu - B₅</td>
<td>2.193(21)</td>
<td></td>
</tr>
<tr>
<td>Fe - B₁</td>
<td>2.182(19)</td>
<td></td>
</tr>
<tr>
<td>Fe - B₃</td>
<td>2.126(20)</td>
<td></td>
</tr>
<tr>
<td>Fe - B₆</td>
<td>2.091(15)</td>
<td></td>
</tr>
<tr>
<td>B₁ - B₃</td>
<td>1.79(3)</td>
<td></td>
</tr>
<tr>
<td>B₁ - B₄</td>
<td>1.76(3)</td>
<td></td>
</tr>
<tr>
<td>B₁ - B₅</td>
<td>1.79(2)</td>
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<tr>
<td>B₁ - B₆</td>
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<td>B₄ - B₅</td>
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<td>Cu - H₅</td>
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<td>Cu - H₄</td>
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<td>Fe - H</td>
<td>1.51(13)</td>
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<tr>
<td>B₃ - H\text{Fe}</td>
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<td>B₄ - Cu - B₅</td>
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<td>43.6(6)</td>
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<td>49.1(8)</td>
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<td>B₁ - Fe - B₆</td>
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<td>49.7(6)</td>
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<td>Fe - B₁ - B₆</td>
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<td>62.5(7)</td>
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<td>61.4(9)</td>
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<td>B₄ - B₁ - B₅</td>
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<td>55.6(11)</td>
</tr>
<tr>
<td>B₅ - B₁ - B₆</td>
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<td>56.1(9)</td>
</tr>
</tbody>
</table>

^aReference 138.
### TABLE 3

Comparative Bond Distances for Copper-Boranes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cu-H</th>
<th>Cu-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecule A</td>
<td>1.90 Å</td>
<td>2.19 Å</td>
</tr>
<tr>
<td>Molecule B</td>
<td>2.06</td>
<td>2.16</td>
</tr>
</tbody>
</table>

- \([(C_6H_5)_3P]_2CuB_3H_8\)
- \([(C_6H_5)_3P]_2CuBH_4\)
- \([(C_6H_5)_3P]_2CuB_5H_8\)
- \{\[(C_6H_5)_3P\]_2Cu\}_2B_{10}H_{10}CHCl_3\)

\[Cu_2B_{10}H_{10}\]

- Reference 82 and Figure 9.
- Reference 78.
- Reference 74 and Figure 10.
- Reference 89.
- Reference 136.
Cu-B distances found also compares well with those in Cu$_2$B$_{10}$H$_{10}$ (Table 3) where a mixture of Cu-H-B and Cu-B interactions has been postulated (136).

The presence of a Cu-H-B interactions in the solid state structure of $[(C_6H_5)_3P]_2CuB_5H_8Fe(CO)_3$ suggests that the copper atom occupies a vertex position in the polyhedral structure. If this copper vertex $[(C_6H_5)_3P]_2Cu^+$ is replaced with BH$_2^+$ and the Fe(CO)$_3$ group is replaced with its isoelectronic analog (BH), a heptaborane species formulated as B$_7$H$_{11}$ results.

VIII. Infrared Spectra of B$_5$H$_9$Fe(CO)$_3$ and Its Derivatives

The carbonyl stretching frequencies decrease when a bridge hydrogen is removed from B$_5$H$_9$Fe(CO)$_3$ (Table 4). The direction of the shift is as expected if the tricarbonyl iron group withdraws electron density from the polyhedron in order to stabilize the negative charge of the anion. When the bisphosphino-copper group is introduced, the carbonyl stretching frequencies then increase relative to $[B_5H_8Fe(CO)_3]^-$ which is consistent with the behavior of a $[(C_6H_5)_3Cu^+]$ group withdrawing electron density from the polyhedron and reducing the electron density at the iron atom.

An infrared investigation was carried out to seek other evidence for the presence of a copper-hydrogen-boron bridge interaction in $[(C_6H_5)_3P]_2CuB_5H_8Fe(CO)_3$. In Nujol two weak bands occur at 2414 cm$^{-1}$ and 2292 cm$^{-1}$ (Figure 40). Copper-hydrogen-boron bridge vibrational modes have been reported to exhibit broad weak infrared absorptions in the region 2000-2400 cm$^{-1}$ (72,75,76,89,136). Consequently Cu-H-B
**TABLE 4**

Infrared Absorbances of Ferraboranes

<table>
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<tr>
<th>Compound</th>
<th>Medium</th>
<th>$\nu_{\text{CO}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{B}_5\text{H}_9\text{Fe(CO)}_3$</td>
<td>$\text{C}<em>5\text{H}</em>{12}$</td>
<td>2072(vs) 2023(vs) 2022(vs)</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>2062(vs) 2011(sh) 2003</td>
</tr>
<tr>
<td>$(\text{n-C}_4\text{H}_9)_4\text{N}^+\text{[B}_5\text{H}_9\text{Fe(CO)}_3]^-$</td>
<td>THF</td>
<td>2012(vs) 1937(br)</td>
</tr>
<tr>
<td>$\text{[(C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_2\text{H}_8\text{Fe(CO)}_3$</td>
<td>$\text{Nujol}$</td>
<td>2032(vs) 1971(sh) 1960</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>2030(vs) 1961(br)</td>
</tr>
<tr>
<td></td>
<td>Nujol 2513</td>
<td>2513 2414(w) 2292(w)</td>
</tr>
</tbody>
</table>

(vs) very sharp, (br) broad, (w) weak, (sh) shoulder.
Figure 40. Infrared Spectra of $[(C_6H_5)_3P]_2CuB_5H_9Fe(CO)_3$ and $[(C_6H_5)_3P]_2CuB_5H_9$

(a) Nujol mull of $[(C_6H_5)_3P]_2CuB_5H_9Fe(CO)_3$

(b) Tetrahydrofuran solution of $[(C_6H_5)_3P]_2CuB_5H_9Fe(CO)_3$

(c) Nujol mull of $[(C_6H_5)_3P]_2CuB_5H_9$
interactions appear to be operative in the solid state. However when 
the spectrum of \[\text{[(C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_5\text{H}_{11}\text{Fe(CO)}_3\] in tetrahydrofuran solution 
is observed, the absorptions present in the mull disappear. Only a weak broad band centered at about 2330 cm\(^{-1}\) is seen. The fact that the bands which suggest copper-hydrogen-boron bridge bonds are severely attenuated in solution suggests the solid state structure of \[\text{[(C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_5\text{H}_{11}\text{Fe(CO)}_3\] may be different from its structure in solution. This phenomenon may explain the different structural characteristics indicated by X-ray crystallography and n.m.r. spectroscopy.

Perhaps the true explanation is similar to that in the case of the unique hydrogen in \(\text{B}_5\text{H}_{11}\) (23,143-134). The X-ray crystal structure (23) has indicated two terminal hydrogens bonded to the apical boron while n.m.r. studies (132) have indicated one terminal hydrogen and one hydrogen bridging to a basal boron. Theoretical studies have reinforced the idea that this unique hydrogen in \(\text{B}_5\text{H}_{11}\) has properties intermediate to a bridging type or a terminal type (133,134).

The infrared spectrum of \[\text{[(C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_5\text{H}_{11}\text{Fe(CO)}_3\] in Nujol (Figure 40c) suggests the possibility of a Cu-H-B interaction also (73). The position of a weak absorption at about 2360 cm\(^{-1}\) is indicative of a bridged Cu-H-B bond in the solid state, however, such an interaction has not been observed in solution n.m.r. studies (73).

IX. Nuclear Magnetic Resonance Spectra of the Anion \([\mu-(\text{CO})_4\text{Fe-B}_6\text{H}_9]^-\)

At 30°, the boron-11 n.m.r. spectrum exhibits two resonances at -3.2 ppm and 52.9 ppm in approximately 5:1 area ratio (62). They have been assigned respectively to the basal and apical boron atoms. Consequently \(C_{5v}\) symmetry is suggested in the absence of coincidental
overlap of all basal boron resonances. If this degree of symmetry is present, the bridging hydrogens and the \((\text{CO})_4\text{Fe}\) group must be migrating about the basal plane of the boron pyramid. If one considers the smaller mass of the borane fragment, then the migration should be described in terms of movement of the boron cage with respect to the \((\text{CO})_4\text{Fe}\) group. With respect to the boron cage, however, there are two processes occurring which involve migration of the bridging hydrogens and migration of the \((\text{CO})_4\text{Fe}\) group about the basal plane of the boron pyramid. At \(-40^\circ\) the basal boron resonance splits into three resonances at \(-15.1\) ppm, \(-2.9\) ppm and \(2.4\) ppm whose weighted average (respective areas of 1:2:2) is \(-3.2\) ppm which is in agreement with the chemical shift at \(30^\circ\) (62). The upfield resonance (52.9 ppm) remains essentially unchanged (62). This spectrum is interpreted in terms of quenching of the migration of the \((\text{CO})_4\text{Fe}\) group but not the bridging hydrogens and therefore indicates \(C_s\) symmetry at \(-40^\circ\).

At \(10^\circ\), the proton n.m.r. spectrum of the \([\text{C}_6\text{H}_5\text{PCD}_3]^+\) salt in \(\text{CHCl}_2\text{F}\) exhibits three resonances at 6.60 \(\tau\), 11.09 \(\tau\) and 12.23 \(\tau\) which are assigned respectively to basal terminal, bridge and apically bonded protons (Figure 41). The spectrum is indicative of \(C_{5v}\) symmetry and is consistent with both the \((\text{CO})_4\text{Fe}\) group and the bridging hydrogens as fluxional species. Lowering the temperature to \(-67^\circ\) causes the downfield resonance to split into three resonances (6.09 \(\tau\), 6.52 \(\tau\), and 7.10 \(\tau\)) whose weighted average (respective areas of 1:2:2) is 6.67 \(\tau\), in good agreement with the single resonance (6.60 \(\tau\)) observed at \(10^\circ\). Apparently the migration of the \((\text{CO})_4\text{Fe}\) group has been quenched to the extent that \(C_s\) symmetry exists. Quenching of the
Figure 41. Variable Temperature 100 MHz Proton NMR Spectra of the Anion \([\mu-(CO)_4Fe-B_6H_9]^-\)

(a) and (b) \((C_6H_5)_3PCD_3^+\) salt in CHCl$_2$F

(c) Potassium salt in (CD$_3$)$_2$O
fluxional bridge hydrogens has not occurred, although the bridge hydrogen resonance (11.09 \tau) has broadened slightly. The resonance assigned to apically bonded hydrogen has not changed. The migration of bridging hydrogens can be quenched at -100° as seen in the spectrum of \textit{K}^+[\textit{\mu}-(\textit{CO})_4\textit{Fe-B_6H_9}]^- in (CD_3)_20 (Figure 41c). The resonance assigned to the bridge hydrogens apparently splits into three resonances at 10.15 \tau, 11.11 \tau and 12.07 \tau (calculated). Unfortunately the apically bonded hydrogen resonance (12.20 \tau) obscures one of the nonequivalent bridge proton resonances.

The carbon-13 n.m.r. spectrum at -100° exhibits a single resonance at 218.8 ppm. Apparently a mechanism is occurring which causes the carbonyl groups to appear equivalent on the carbon-13 n.m.r. time scale.

X. Nuclear Magnetic Resonance Spectra of \textit{K}^+[\textit{\mu}-(\textit{CO})_4\textit{Fe-B_7H_12}]^-

The X-ray crystal structure determination (51,52) indicates that the added BH$_3$ group has been inserted into a basal boron-boron bond and resides below the basal plane of the boron pyramid. The boron-11 n.m.r. spectrum exhibits no change in chemical shift values to -80° (Figure 42). The added BH$_3$ group produces a quartet (40.1 ppm, \textit{J}_{B-H} = 85 \text{ Hz}) suggesting that there is little bridging interaction between the hydrogens of the added BH$_3$ and adjacent basal boron atoms. Although one arm of the quartet is obscured by the apical boron resonance (48.5 ppm), proton spin-decoupling causes a reduction in multiplicity but no change in the chemical shift. The assignments of the other resonances are not obvious.
Figure 42. 32.1 MHz Boron-11 NMR Spectra of $K^+[(\mu-(CO)_4Fe-B_7H_{12})^-]$ in (CD$_3$)$_2$O at -35°

(a) Undecoupled
(b) Proton decoupled
(c) Valence structure of the anion
(d) Polyhedral structure of the anion
Similarly in the proton n.m.r. spectrum, confident assignments cannot be made except for the resonance at 9.68 \( \tau \) (Figure 43). It is apparent that the 3 equivalent hydrogens on the added BH\(_3\) can be assigned to this resonance. The resonance at 6.76 \( \tau \) is due to the protium impurity in the (CD\(_3\))\(_2\)O solvent.

XI. Nuclear Magnetic Resonance Spectra of K\(^+[2,3-C_2B_5H_{10}]^-\)

Study of the structure of the [2,3-C\(_2\)B\(_5\)H\(_{10}\)]\(^-\) anion by n.m.r. spectroscopy has revealed similarities with the [\(\mu-(CO)\)]\(_4\)Fe-B\(_7\)H\(_{12}\)]\(^-\) anion. The added BH\(_3\) group in [2,3-C\(_2\)B\(_5\)H\(_{10}\)]\(^-\) exhibits a quartet at ambient temperature in tetrahydrofuran at 46.2 ppm (\(J_{B-H} = 97\) Hz) (Figure 44). Proton decoupling collapses this resonance to a singlet with no change in chemical shift. The overlapping doublets at -0.6 ppm and 5.5 ppm are assigned to B\(_5\) and B\(_3,6\) respectively. The apical boron resonance occurs at 57.3 ppm (\(J_{B-H} = 169\) Hz). The added BH\(_3\) group apparently forms a Lewis acid-base adduct with the carborane fragment. Consequently no hydrogen bridge interaction with the carborane fragment is observed.

The proton n.m.r. spectrum exhibits no change to -117° (Figure 45). Corresponding resonances can be found in the proton n.m.r. spectrum of K\(^+[2,3-C_2B_4H_7]\)\(^-\) (Figure 18), except for the resonance at 9.87 \( \tau \) which is assigned to the hydrogen atoms of the added BH\(_3\) group. The 4.59 \( \tau \) and 4.93 \( \tau \) resonances are assigned to the hydrogens attached to carbon, the 6.73 \( \tau \), 7.17 \( \tau \), and 7.50 \( \tau \) resonances are assigned to the three boron atoms in the plane with the carbon atoms, and the 11.39 \( \tau \) resonance is assigned to apparently overlapping bridge
Figure 43. 100 MHz Proton NMR Spectrum of K\(^+\)\([\mu-\text{(CO)}\text{,Fe-B}_7\text{H}_{12}]^-\)
in (CD\(_3\))\(_2\)O at -57° (Boron-11 Decoupled)
Figure 44. 32.1 MHz Boron-11 NMR Spectrum of K$^+$[2,3-C$_2$B$_5$H$_{10}$]$^-$ in Tetrahydrofuran at 25°
Figure 45. 100 MHz Proton NMR Spectrum of $K^+[2,3-C_2B_3H_{10}]^-$ in $(CD_3)_2O$ at $-100^\circ$
hydrogen and apically bonded hydrogen resonances. The resonance at about 6.8 T is due to the proton impurity in the solvent.

Since the n.m.r. spectra exhibit such similarities and the X-ray crystal structure of $K^+[(\mu-(CO)_4Fe-B_7H_{12})^-]$ has shown that the added BH$_3$ group resides below the basal plane of the pentagonal pyramidal borane fragment, the structure of $K^+[2,3-C_2B_5H_{10}]^-$ appears to be analogous to that of $K^+[(\mu-(CO)_4Fe-B_7H_{12})^-]$ (Figures 5, 46).
Figure 46. Proposed Structure of the Anion $[2,3-C_{2}B_{5}H_{10}]^{-}$
LIST OF REFERENCES


138. M. M. Mangion, private communication.