CHEMISTRY OF PENTABORANE(9). A REVIEW

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Received March 3, 1999
Accepted March 18, 1999

Dedicated to Dr Stanislav Heřmánek on the occasion of his 70th birthday.

The chemistry of pentaborane(9) (B_5H_9) is reviewed on work reported since 1981. All aspects of its synthesis, reactivity, NMR spectroscopy as well as most its important derivatives including metallaboranes and linked B_5 cages are presented and discussed. A review with 60 references.

Key words: Boranes; Pentaboranes; Metallaboranes; Boron clusters; NMR spectroscopy.

1. INTRODUCTION

Pentaborane(9) was reported in 1923 by Stock and Kuss[1], and its structure was determined by Dulmage and Lipscomb[2] twenty-nine years later. It is the most stable boron hydride with fewer than ten boron atoms, and, as such, has been the subject of extensive research including an extraordinarily large investigation into its potential as a high energy jet fuel[3]. However, it is not an easy compound to handle being toxic and pyrophoric.

Pentaborane(9) (Fig. 1) has a square-pyramidal boron skeleton and its symmetry is C_{4v}. The molecule has boron atoms in two environments, one apical boron atom, B1, and four equivalent basal boron atoms, B2–B5. Each boron atom bears a terminal hydrogen atom, and so there are two environments for terminal hydrogens. In addition are the four equivalent bridging hydrogen atoms, which connect basal boron atoms by three-center, two-electron, B–H–B bonds.

Previous reviews on the chemistry of pentaborane(9) have appeared in 1973 (ref.[4]) and 1981 (ref.[5]). The structures and ^{11}B NMR spectra of ions derived from B_5H_9 and some rearrangements of bridge substituted B_5H_9 have been reviewed very recently[6]. The use of isotopic labeling to explore intramolecular rearrangements in B_5H_9 has been explored[7] and reviewed[8,9]. Boron hydride reactions involving metals received extensive description in 1982 (ref.[10]). This paper will concentrate on work not covered in these reviews.

2. ^{11}B NMR

Nuclear magnetic resonance (NMR), particularly ^{11}B NMR, shares with X-ray crystallography the position of one of the two paramount techniques for structure determination of boron compounds including pentaborane(9)

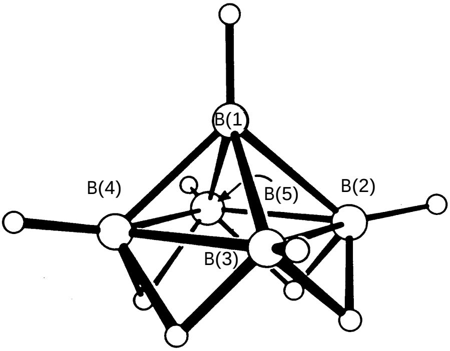

FIG. 1
The structure and numbering system of pentaborane(9), B_5H_9. Reprinted with permission from Fig. 1 of Gaines D. F.: *Acc. Chem. Res.* **1973**, *6*, 416. Copyright 1973 American Chemical Society.

derivatives. Much has been written about this technique including quadrupolar relaxation and fluxional behavior. We will consider two relatively recently reported aspects.

2.1. Two-Dimensional ^{11}B-^{11}B NMR

The most successful rapid analysis tool for structure determination of boranes and their derivatives has historically been ^{11}B NMR spectroscopy. The more recent application of two-dimensional ^{11}B-^{11}B NMR, correlated spectroscopy (COSY), allows unequivocal assignments for many one-dimensional ^{11}B NMR spectra by detecting spin-spin coupling among ^{11}B nuclei and thus the connectivity of these nuclei. Studies have been reported on a number of pentaborane(9) derivatives[11].

The methyl derivative of pentaborane(9) with the methyl group substituted for a hydrogen atom on B2, 2-MeB_5H_8, shows coupling between all basal boron atoms and the apical boron. This is not unexpected since these pairs of boron atoms, which are separated by a distance of 1.69 Å in B_5H_9, are bonded directly to each other. However, coupling is also observed between the pairs of basal boron atoms, which are at a distance of 1.80 Å and presumably connected only by the B–H–B, three-center, bridge bond. Similar results are reported for (μ-Me_2NCH_2)B_5H_8 (Fig. 2), a bridge-substituted derivative, except that coupling does not occur between B2 and B3, which are separated more than in the unsubstituted borane and bridged by the N–C moiety. In another bridge-substituted derivative, (μ-$Me_3CCH=N$)B_5H_8 (Fig. 3), the COSY spectrum shows again that coupling does not occur between the borons that are bridged by the substituent group. Furthermore, it

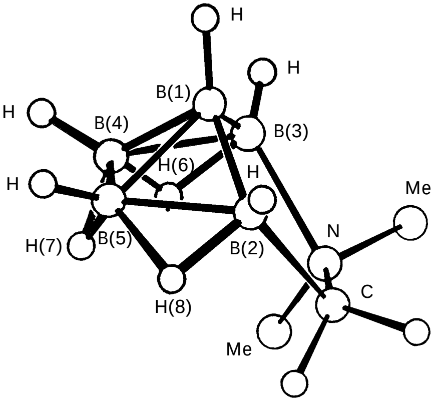

FIG. 2
Structure of the two-atom bridged pentaborane(9) derivative, (μ-Me_2NCH_2)B_5H_8. Reprinted with permission from Fig. 2 of Gaines D. F., Coons D. E.: *Inorg. Chem*. **1986**, *25*, 364. Copyright 1986 American Chemical Society.

shows that B4 and B5 are magnetically nonequivalent, a result that is not discernible from the one-dimensional spectra. Two pentaborane(9) derivatives that do not show coupling between basal boron atoms are $(CO)_3MnB_5H_8$ and $(CO)_3ReB_5H_8$. These MB_5 pentagonal pyramidal molecules are quite rigid on the NMR time scale, and the lack of observable boron atom coupling interactions illustrates our relatively primitive understanding of coupling transmission phenomena between atoms that are linked by bridging hydrogen atoms. Semiempirical theoretical techniques have been employed to understand the factors governing coupling between boron nuclei in pentaborane(9) derivatives[12].

2.2. Shift Reagents

The effects of paramagnetic Sm(II) on the ^{11}B NMR spectra of $B_5H_8^-$ and B_5H_9 have been found to be quite different[13]. Reaction of $SmI_2(THF)_x$ with two equivalents of $B_5H_8^-$ in tetrahydrofuran solution results in a green solution but no isolatable Sm-borane derivative. The ^{11}B resonances were shifted substantially upfield, but the FTIR spectrum of $B_5H_8^-$ was essentially unchanged. Thus it appears that the effect was magnetic and not structural. The extent of upfield shift was found to be directly proportional to the $SmI_2(THF)_x$ concentration. However, reaction of neutral B_5H_9 with $SmI_2(THF)_x$ in THF produced only a small shift in the ^{11}B resonances and that was *downfield*. Clearly, the interaction of the Sm(II) and the $B_5H_8^-$ is much stronger than that with B_5H_9. This result also shows that the B_5H_9 is not deprotonated to $B_5H_8^-$ by the I^- ion in $SmI_2(THF)_x$.

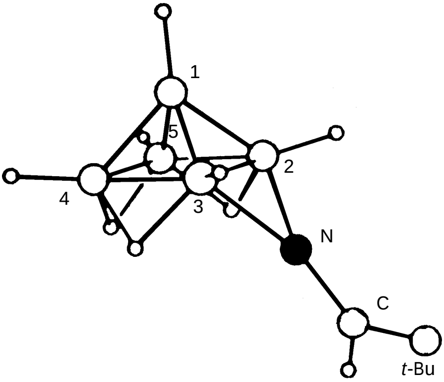

FIG. 3
Proposed structure of $(\mu\text{-}Me_3CCH{=}N)B_5H_8$. Reprinted with permission from Fig. 6 of Gaines D. F., Edverson G. M., Hill T. G., Adams B. R.: *Inorg. Chem.* **1987**, *26*, 1813. Copyright 1987 American Chemical Society.

3. PREPARATION OF PENTABORANE(9)

Pentaborane(9) has been prepared by catalytic pyrolysis of B_2H_6 (ref.[14]). Large stocks of the compound left over from the jet fuels program have precluded the need for continued synthesis of the compound for use as a reagent. Study of other preparative methods has been primarily aimed at elucidating the mechanisms of pentaborane formation and reaction.

One such reaction that produces pentaborane(9) is the slow decomposition of B_4H_{10} in diethyl ether,

$$5\ B_4H_{10} \longrightarrow 2\ B_5H_9 + 5\ B_2H_6 + H_2$$

which was postulated to proceed by way of a Lewis base adduct intermediate[15],

$$B_4H_{10} + (C_2H_5)_2O \longrightarrow B_3H_7{\cdot}O(C_2H_5)_2\ .$$

The existence of a Lewis base adduct as an intermediate in the decomposition of B_4H_{10} in ether gets credence from a preparation of pentaborane(9) employing the reaction of tetraborane(10) with dimethyl sulfide in a two step process[16]. The first step is the symmetrical cleavage of B_4H_{10},

$$B_4H_{10} + 2\ (Me)_2S \longrightarrow B_3H_7{\cdot}S(Me)_2 + BH_3{\cdot}S(Me)_2\ .$$

The two products were then separated and additional dimethyl sulfide was reacted with the $B_3H_7{\cdot}S(Me)_2$,

$$3\ B_3H_7{\cdot}S(Me)_2 + (Me)_2S \longrightarrow B_5H_9 + 4\ BH_3{\cdot}S(Me)_2\ .$$

The isolation of the intermediate and the faster production of B_5H_9 using dimethyl sulfide rather than ether is postulated to be related to the stronger basicity of the sulfide. The authors do point out, however, that the reactions are not strictly mechanistically analogous since one produces H_2 gas and the other produces the Lewis base adduct of borane. However, it is possible that the H_2 is the product of a side-reaction and that these two preparations of B_5H_9 proceed by similar paths.

Pentaborane(9) has been recovered from its halogenated derivatives through reduction with tributyltin hydride[17].

$$1\text{-}ClB_5H_8 \text{ or } 2\text{-}ClB_5H_8 \xrightarrow{Bu_3SnH} B_5H_9$$

4. STABILIZATION OF PENTABORANE(9)

Pentaborane(9) is extremely useful in the preparation of a large number of other boron cluster compounds including a number of carboranes. The unpredictable reactivity of pentaborane(9) with oxygen, however, has often been a deterrent in exploring the full extent of its reaction chemistry. It has been determined that pentaborane(9) dissolved in tetrahydrofuran is greatly stabilized with respect to oxidation while maintaining much of its synthetic utility[18]. Solutions of B_5H_9 in THF stored under an inert atmosphere have been found to be completely unchanged for periods of months. When exposed to a static air environment, a 0.1 M solution of B_5H_9 was found still to contain 59% of the original compound after one month.

Reactions of these THF-stabilized solutions of B_5H_9 with substituted acetylenes have been shown to produce the alkyl- and arylcarboranes, *nido*-2,3-$(CH_3CH_2)_2C_2B_4H_6$, *nido*-2,3-$(C_6H_5)HC_2B_4H_6$ and the difficult to prepare, sterically crowded *nido*-2,3-$(C_6H_5)_2C_2B_4H_6$. Investigation of the THF solutions of B_5H_9 by ^{11}B NMR indicated that, as expected, cleavage of the molecule such as is observed in B_2H_6 and B_4H_{10} does not occur. A very weak, short-lived complex in which a B–H–B is broken and the THF is bonded to basal boron atom seems likely. This is in agreement with earlier ^{11}B investigations of B_5H_9 derivatives showing that the exchange,

$$\mu\text{-}DB_5H_8 \longrightarrow 2\text{-}DB_5H_8$$

occurs in the presence of ethers but not in their absence[19].

5. HYDROGEN ISOTOPE EXCHANGE

The first regiospecific deuteration of B_5H_9 was accomplished using DCl in the presence of $AlCl_3$ to produce 1-DB_5H_8. The deuterium source may also be perdeutero benzene or another aromatic compound having a perdeuterated ring[20]. In the presence of $AlCl_3$ catalyst, exchange occurs at the apical boron atom, the most negative boron atom according to calculated charge distributions[21]. Uncatalyzed hydrogen–deuterium exchange occurs at elevated temperatures, but it occurs in the terminal positions of all boron atoms and at sufficiently high temperatures is also observed for the bridges. A Lewis acid-base mechanism for the uncatalyzed exchange is ruled out since such an exchange would be specific to the apical boron atom of the cage. In the reverse reaction, when deuterated B_5H_9 is reacted with toluene and *p*-xylene, deuterium substitution occurs only on the aromatic ring indicating that the reaction is specific to the aromatic system. A reversible hydroboration of the aromatic ring has been postulated as a likely mechanism that can explain these observations.

6. LINKED B_5 CAGES

Pentaborane cages can be linked directly or by another atom. An example of each is given here.

6.1. Linkage by σ-Bonds

In the first isolated example of the direct linking of two pentaborane(9) cages, the two-center σ-bond connected the two apical boron atoms giving $1,1'$-$(B_5H_8)_2$ (ref.[22]). This was prepared by an electric discharge in gaseous B_5H_9. The other $(B_5H_8)_2$ isomers were first discovered as low-volatility residues in commercially prepared pentaborane(9)[23]. Rational syntheses of these compounds and some of their chemical properties were reported subsequently.

The $1,2'$-$(B_5H_9)_2$ isomer was prepared by a Friedel–Crafts reaction using B_5H_9 and a 2-halo pentaborane(9). For example,

$$2\text{-}BrB_5H_8 + B_5H_9 \longrightarrow 1,2'\text{-}(B_5H_9)_2$$

and the 2,2′ isomer was made by a nucleophilic displacement reaction[24],

$$KB_5H_8 + 2\text{-}BrB_5H_8 \longrightarrow 2,2'\text{-}(B_5H_9)_2\ .$$

A number of reactions of the two isomers have been explored[25]. The 2,2′ isomer in benzene was found to rearrange partly to the 1,2′ isomer at 100 °C after several weeks in the presence of Ph_3As. Steric considerations most likely promote this, which would make isomerization to the 1,1′ appear particularly attractive. However, juxtaposition of ^{11}B resonances prevented determining if any of the 1,1′ isomer was produced.

The boron–boron σ-bond in the 1,2′ isomer can be cleaved by HBr at 65 °C, and this can be compared with the cleavage of the previously reported 1,1′

isomer by HI at room temperature. The presence of $AlBr_3$ is necessary to cleave the boron–boron σ-bond in the 1,2′ isomer. The conversion of the 1,1′ isomer to $B_{10}H_{14}$ in the presence of either HBr or $AlBr_3$ (ref.[22]) is not observed for the 1,2′ and 2,2′ isomers.

6.2. Linkage by Sn Atoms

Two B_5H_9 cages can be linked by a $SnPh_2$ group using the reaction of $K[B_5H_8]$ with $SnCl_2Ph_2$ in a 2 : 1 molar ratio at –35 °C in CH_2Cl_2 solvent[26]. The immediate product is μ,μ′-$SnPh_2(B_5H_8)_2$. If this product is dissolved in $CDCl_3$ and stands for about a month at 25 °C, the isomer, μ-2'-$SnPh_2(B_5H_8)_2$ (Fig. 4), is detected in the ^{119}Sn NMR spectrum. This isomer can also be prepared by reaction of $K[B_5H_8]$ and $SnCl_2Ph_2$ in diethyl ether. If the μ,μ′ isomer, dissolved in $CDCl_3$, stands for about four months, the isomer μ-1′-$SnPh_2(B_5H_8)_2$ can be detected in the NMR spectrum. This isomer can also be prepared by reacting $K[B_5H_8]$ with 1-$(SnClPh_2)B_5H_8$ in CH_2Cl_2 at –35 °C. In the presence of a Lewis base, ready isomerization of μ,μ′-$SnPh_2(B_5H_8)_2$ to μ-2′-$SnPh_2(B_5H_8)_2$ would be consistent with the observation that μ-substituted pentaboranes isomerize to terminally substituted isomers in the presence of Lewis bases[27]. The isolation of μ,μ‘-$SnPh_2(B_5H_8)_2$ in CH_2Cl_2 can be attributed to the low basicity of the solvent.

7. DERIVATIVES OF PENTABORANE(9)

Pentaborane(9) forms a wide range of derivatives, some of which are mentioned below. Most of the mono-substituted derivatives involve substitu-

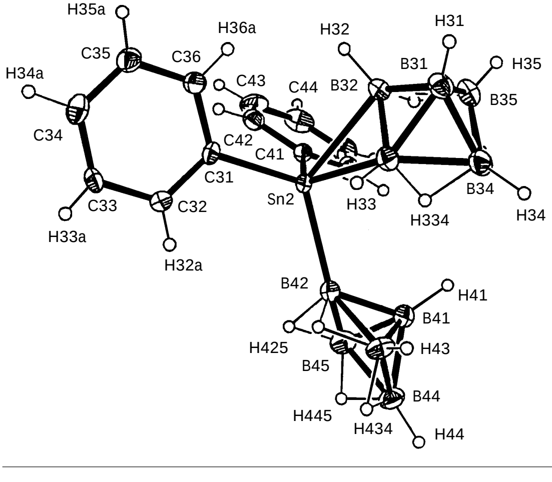

FIG. 4
Structure of μ-2'-$SnPh_2(B_5H_8)_2$. Reprinted with permission from Fig. 1 in Fang H., Zhao D., Brammer L., Barton L.: *J. Chem. Soc., Chem. Commun.* **1994**, 1531.

tion of one of the three types of hydrogen atoms in the molecule, (1) the terminal hydrogen on B1, (2) a terminal hydrogen on one of the four equivalent basal boron atoms, B2-B5, and (3) one of the bridge hydrogen atoms between two basal boron atoms.

7.1. Stability of Derivatives

Experimental and *ab initio* calculational methods have been used to determine the relative stabilities of B_5H_9 derivatives[28]. For some 28 derivatives, they yield the following results:

1) Me- and Cl- substituents are most stable in basal, terminal positions.

2) SiH_3- is more stable in the apical, terminal position.

3) Two basal substituents are most stable in adjacent, terminal positions.

4) If a Me- and a Cl- are both substituted onto a B_5 cage and one is in an apical position, then the more stable isomer has the Cl- at the apex.

Comparisons of experimental and calculated ^{11}B and ^{1}H chemical shifts were also included in this study.

7.2. Beryllium Derivatives

The reaction of KB_5H_8 with excess C_5H_5BeCl in a pentane slurry at –40 °C yields μ-[η^5-(C_5H_5)Be]B_5H_8 (Fig. 5)[29]. In this structure the Be atom occupies the position of a bridging hydrogen atom between two adjacent basal boron atoms. This is in contrast to the previously reported 2-[η^5-(C_5H_5)]-2-BeB_5H_{10} in which the Be atom assumes the position of a bo-

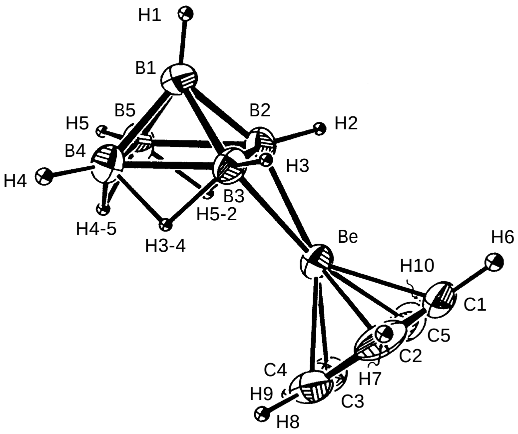

FIG. 5
Crystal structure of μ-[η^5-(C_5H_5)Be]B_5H_8. Reprinted with permission from Fig. 1 in Gaines D. F., Coleson K. M., Calabrese J. C.: *Inorg. Chem.* **1981**, *44*, 84. Copyright 1981 American Chemical Society.

ron atom in the cage giving a structure that is very similar to the pentagonal pyramidal B_6H_{10} molecule[30]. Broensted acids will substitute a proton for the bridging $Be(C_5H_5)$ group in μ-[η^5-$(C_5H_5)Be]B_5H_8$ producing B_5H_9. Reaction of μ-[η^5-$(C_5H_5)Be]B_5H_8$ with B_2H_6 results in the formation of $B_{10}H_{14}$ as well as other boron hydrides in a complex reaction sequence.

7.3. Boryl Derivatives

Compounds of the formula 1-$(X_2B)B_5H_8$ (X = Cl, Br, F) have received considerable experimental and theoretical attention over the years. The preparation of 1-$(Cl_2B)B_5H_8$ (Fig. 6) by the Friedel–Crafts reaction of B_5H_9 with BCl_3 in the presence of an $AlCl_3/PCl_3$ catalyst system was reported in 1982 (ref.[31]). Characterization was by ^1H and ^{11}B NMR spectroscopy and mass spectrometry. No reaction was observed in the absence of the specified catalysts. The compound reacts with diethyl ether at 50 °C to produce the complex 1-$[Cl_2B{\cdot}OEt_2]B_5H_8$, which decomposes at 70 °C to produce B_5H_9.

Convenient preparations of 1-$(Cl_2B)B_5H_8$ and 1-$(Br_2B)B_5H_8$ with almost quantitative yields were reported in a later study[32]. In these reactions B_2Cl_4 or B_2Br_4 was reacted with B_5H_9 for 12 to 20 min at ambient temperature in a sealed tube. The 1-$(Cl_2B)B_5H_8$ was reacted with $(CF_3)_2Hg$, MeOH and *t*-BuLi to yield 1-$(BF_2)B_3H_8$, 1-$(ClBOMe)B_5H_8$, and 1-*t*-$BuBCl)B_5H_8$ and 1-*t*-$Bu_2B)B_5H_8$. Reduction with $LiBH_4$ yielded a mixture of unidentified boron hydrides.

Extensive gas phase electron diffraction and theoretical calculations have been performed on 1-$(BCl_2)B_5H_8$ and 1-$(BF_2)B_5H_8$ (refs[33,34]). Besides confirming the structure proposed previously from spectroscopic evidence and providing precise structural parameters, it was shown that the BF_2 unit is free to rotate about the B–B σ-bond.

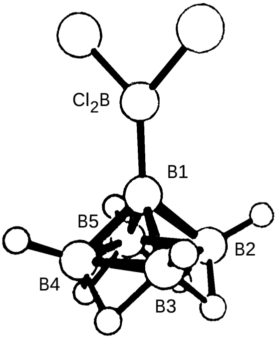

FIG. 6

Structure of 1-$(Cl_2B)B_5H_8$. Reprinted with permission from Fig. 1 (lower) in Gaines D. F., Heppert J. A., Coons D. F., Jorgenson M. W.: *Inorg. Chem*. **1981**, *21*, 3663. Copyright 1981 American Chemical Society.

Reaction of the $B_5H_8^-$ anion with *B*-chloro-9-borabicyclo[3.3.1]nonane (*B*-Cl-9-BBN) yields the bridge-substituted *nido*-pentaborane, (μ-9-BBN)B_5H_8 (Fig. 7)[35], which has a boron atom in a bridging position. In solution, the 9-BBN fragment rotates relative to the pentaborane framework. In diethyl ether solution, the compound slowly converts to a *nido*-hexaborane cluster, 4,5-(cyclooctane-1,5-diyl)B_6H_8 (Fig. 8), in which the bridging boron atom is incorporated into the boron cluster. The bicyclic hydrocarbon group is bonded to two adjacent basal boron atoms.

7.4. Alkyl and Aryl Derivatives

It was shown in the 1960s that reaction of olefins with B_5H_9 yielded 2-substituted alkyl derivatives[36], and Friedel–Crafts catalyzed attack of B_5H_9 by alkenes and alkyl halides led to 1-substituted derivatives[37]. Aryl pentabo-

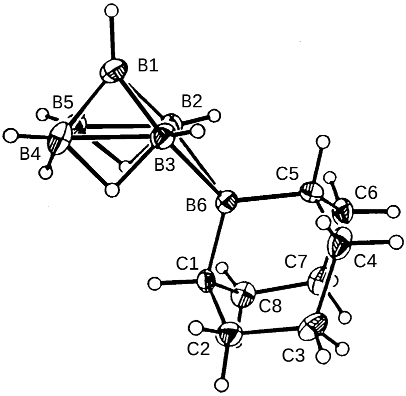

FIG. 7
Structure of the bridge-substituted *nido*-pentaborane, (μ-9-BBN)B_5H_8. Reprinted with permission from Fig. 1 in Edvenson G. M., Gaines D. F., Harris H. A., Campana C. F.: *Organometallics* **1990**, *9*, 401. Copyright 1990 American Chemical Society.

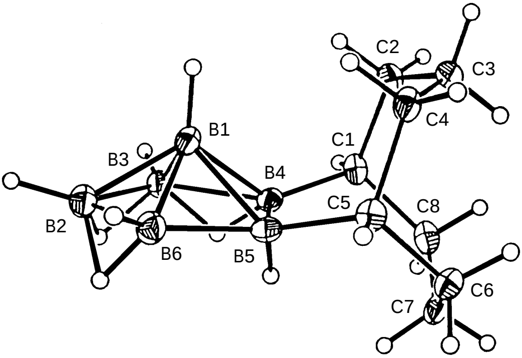

FIG. 8
Structure of the bicylic B_6H_{10} derivative, 4,5-(cyclooctane-1,5-diyl)B_6H_8. Reprinted with permission from Fig. 2 in Edvenson G. M., Gaines D. F., Harris H. A., Campana C. F.: *Organometallics* **1990**, *9*, 401. Copyright 1990 American Chemical Society.

rane derivatives were apparently unobtainable by the latter route because of the low Friedel–Crafts reactivity of the aryl halides.

In 1982 2-substituted aryl pentaboranes were synthesized by the reaction of 2-ClB_5H_8 with a number of aromatic hydrocarbons[38]. Success was obtained with benzene, toluene and *m*-xylene but not with mesitylene, presumably, because of steric constraints imposed by the two α-methyl groups. Attempts to prepare 1-substituted arylpentaboranes by isomerization of the 2-substituted compounds were unsuccessful.

The extremely strong nucleophile lithium triethylhydridoborate, $LiEt_3BH$, alkylates pentaborane(9) in a spectacular fashion yielding the trialkyl compound, 2,3,4-$Et_3B_5H_6$ (ref.[39]). A B_6, *hypho* intermediate has been proposed for this unusual reaction.

Aluminum chloride is the most used catalyst for alkylating B_5H_9 and other boron hydrides. However, the use of this catalyst results not only in relatively low yields but has also been long known to yield a number of side-products. A range of metal chlorides has been examined for optimizing the Friedel–Crafts alkylation of B_5H_9 (ref.[40]). The borane and isopropyl chloride were reacted in a 1 : 1 ratio with 10 mole % of catalyst. Products observed included the expected 1-$iPrB_5H_8$ as well as 1-PrB_5H_8, 2-$iPrB_5H_8$, 1-EtB_5H_8 and unreacted B_5H_9. Catalysts tested included $AlCl_3$, $FeCl_2$, $NbCl_5$, $TaCl_5$, $ZrCl_4$ and $HfCl_4$. Aluminum chloride gave the lowest yield of 1-$iPrB_5H_8$ (12.2%), the highest yield of 1-PrB_5H_8 (16.8%) and 4.3% of 2-$iPrB_5H_8$. Yields of between 40 and 60% were observed for $FeCl_2$, $NbCl_5$ and $TaCl_5$ with 5% or less of 1-PrB_5H_8 and only traces of 2-$iPrB_5H_8$. A yield of 80.9% was achieved with $HfCl_4$, but the side-products, 1-PrB_5H_8 and 2-$iPrB_5H_8$, were produced in yields of 11.5 and 7.7%, respectively. The most effective catalyst was $ZrCl_4$ with a yield of the desired 1-$iPrB_5H_8$ of 89.5% and only 2.3% of 1-PrB_5H_8 as the only significant side-product. In these studies, raising the proportion of catalyst raised yields only marginally, and using an excess of isopropyl chloride lowered selectivity. In general, lower temperatures resulted in higher selectivity and lower yields.

7.5. Tin Derivatives

There are three possible isomers of (triphenylstannyl)-*nido*-pentaborane(9). Two of these have been prepared by the reaction of $K[B_5H_8]$ and $SnClPh_3$ (refs[41,42]). The isomer 1-$(Ph_3Sn)B_5H_8$ is produced if the reaction is run in tetrahydrofuran whereas 2,3-μ-$(Ph_3Sn)B_5H_8$ is the product if the reaction is run in CH_2Cl_2. Attempts to prepare the 2-$(Ph_3Sn)B_5H_8$ isomer using the reaction of $K[B_5H_8]$ and $SnClPh_3$ were made under a variety of conditions, but one or both of the other two isomers were always observed as impurities. Contrary to other derivatives of B_5H_9, thermal isomerization of 2,3-μ-$(Ph_3Sn)B_5H_8$ to a terminally substituted derivative is not observed. The compound 1-$(ClPh_2Sn)B_5H_8$ was prepared in a reaction analogous to the preparation of 1-$(Ph_3Sn)B_5H_8$.

Characterization of these compounds was made by mass spectrometry, X-ray crystallography and ^{1}H, ^{11}B and ^{119}Sn NMR. Coupling with ^{11}B and ^{10}B was observed in the ^{119}Sn NMR spectra of two of the 1-substituted compounds. The observed $J(^{119}Sn-^{11}B)$ values were 1 117 Hz for 1-$(Ph_3Sn)B_5H_8$ and 1 272 Hz for 1-$(ClPh_2Sn)B_5H_8$, both somewhat higher than previously observed coupling constants for these nuclei.

7.6. Nitrogen Derivatives

Derivatives of pentaborane(9) in which a bridging hydrogen atom has been replaced by a C–N two-atom bridge have been prepared by reacting lithium or potassium salts of $B_5H_8^-$ with the iminium salt, $[Me_2NCH_2]I$ (see Fig. 2)[43]:

$$[Me_2NCH_2]I + MB_5H_8 \longrightarrow \mu\text{–}Me_2NCH_2B_5H_8 + MI\ .$$

Structure determination was made by ^{11}B NMR. The nitrogen atom delivers two electrons to the borane cage rendering the new compound a derivative of B_5H_{11} and an *arachno* species according to electron counting procedures[44]. There is no evidence of direct bonding between the boron atoms connected by the C–N bridge. Reaction of the iminium salt with 1-substituted pentaborane(9) compounds (C_2H_5- and Br-) gave the analogous two-atom bridged products.

Terminal substitution of B_5H_9 by a nitrogen atom has been achieved by reacting X-B_5H_8 (X = Cl or Br) with secondary or tertiary amines. For example, hexamethyldisilazane reacts with 2-BrB_5H_8 in CH_2Cl_2 solution at –78 °C to produce 2-(bis(trimethylsilyl)amino)pentaborane(9), 2-$[(Me_3Si)_2N]B_5H_8$ (ref.[45]).

$$2\text{-}BrB_5H_8 + (Me_3Si)_2NH \longrightarrow [(Me_3Si)_2N]B_5H_8 + HBr$$

Several side-products are reported in this reaction including a μ-aminodiborane[46], B_5H_9, an amine derivative of B_3H_7 (ref.[47]), and two or more borazines. Analogous 2-aminopentaboranes were produced by reacting 2-BrB_5H_8 with $(Me_2SiH)_2NH$, $(iBuMe_2Si)_2NH$ and $(Me_3Si)_2NMe$ (ref.[48]).

Reaction of 2-BrB_5H_8 with *t*-Bu(Me_3Si)NH in the presence of excess B_5H_9 in CH_2Cl_2 solution yields the expected 2-aminopentaborane, 2-[*t*-Bu(Me_3Si)N]B_5H_8, as well as *hypho*-2,3-μ-(*t*-BuNH)B_5H_{10} (Fig. 9), which is unusually stable to H_2O and MeOH. In this *hypho* compound the nitrogen atom is occupying a position in the cage rather than the position of a bridging hydrogen atom as in μ-$Me_2NCH_2B_5H_8$.

7.7. Phosphorus Derivatives

Pentaborane(9) derivatives in which a phosphorus atom occupies a position equivalent to a bridging hydrogen atom can result in two geometric isomers if the phosphorus atom is bonded to two different groups in addition to the B_5 cage[49] (Fig. 10). For example, reaction of $(Me_3Si)_2CHPCl_2$ with the

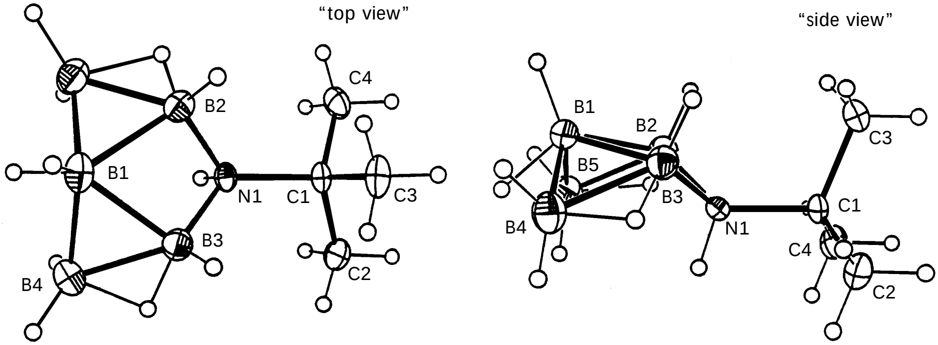

FIG. 9
Crystal structure *hypho*-2,3-μ-(*t*-BuNH)B_5H_{10}. Reprinted with permission from figure in McGaff R. W., Gaines D. F., Powell D. R.: *Inorg. Chem*. **1993**, *32*, 2612. Copyright 1993 American Chemical Society.

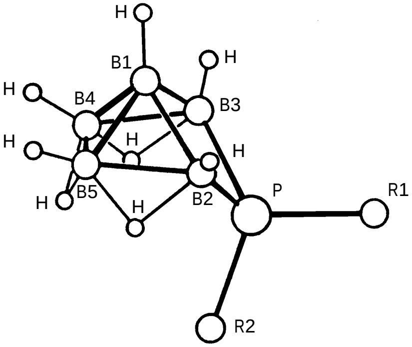

FIG. 10
Proposed structure of (μ-phosphino)pentaborane(9) derivatives. Geometric isomers can occur if R(1) and R(2) are not the same. Reprinted with permission from Fig. 1 in Coons D. E., Gaines D. F.: *Inorg. Chem*. **1987**, *26*, 1885. Copyright 1987 American Chemical Society.

B_5H_8 ion produces two isomers of [μ-$(Me_3Si)_2CHPCl]B_5H_8$. Reaction of either of these isomers with 2,6-lutidine results in a dehydrohalogenation yielding $(Me_3Si)_2CPB_5H_8$ (Fig. 11)[50]. In these compounds the phosphorus atom has taken the position of a boron atom in the cluster, which now has the geometry of B_6H_{10}. The same compound, $(Me_3Si)_2CPB_5H_8$, was also produced by the direct reaction of $(Me_3Si)_2C{=}PCl$ and KB_5H_8 in diethyl ether,

$$(Me_3Si)_2C{=}PCl + KB_5H_8 \longrightarrow (Me_3Si)_2CPB_5H_8 + KCl\ .$$

Another reaction that produces phosphorus-bridged derivatives of B_5H_9 involves the high-yield reaction of $(Me_3Si)P{=}C(OSiMe_3)t$-Bu with neutral B_5H_9. The product is μ-[*t*-Bu$(Me_3SiO)CHP(SiMe_3)]B_5H_8$ (ref.[51]). Mechanisms for this reaction are explored with the help of MNDO semiempirical theoretical calculations. This compound is relatively stable thermally and in air although the $(SiMe_3)$ group is replaced by H or D in reactions with H_2O or D_2O.

Reaction of NaB_5H_8 with Ph_2PCl yields the phosphorus-bridged compound (μ-$Ph_2P)B_5H_8$ (ref.[52]). MNDO calculations for this compound suggest that the interaction between the phosphorus atom and the boron cage is best described by two two-electron, two-center bonds. There is some evidence that the lone electron pair on the phosphorus atom is involved in cage bonding. Reaction of (μ-$Ph_2P)B_5H_8$ with NaH results in bridge-deprotonation and yields the corresponding anion, (μ-$Ph_2P)B_5H_7^-$. This anion reacts with Fe(η^5-$C_5H_5)(CO)_2I$ to produce an iron complex described below.

Yet another phosphorus-bridged B_5 compound, μ-(*t*-Bu)(Me_3SiO)-$C{=}P(SiMe_3)$ results from the reaction of *t*-Bu$(Me_3SiO)CHPSiMe_3$ with B_5H_9 (ref.[53]).

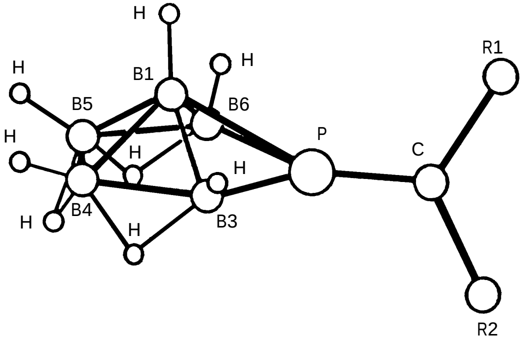

FIG. 11
Proposed structure of compounds of the type $R_2CPB_5H_8$, for example, $(Me_3Si)_2CPB_5H_8$. Reprinted with permission from Fig. 3 in Coons D. E., Gaines D. F.: *Inorg. Chem.* **1987**, *26*, 1885. Copyright 1987 American Chemical Society.

When 1-trimethylphosphine-pentaborane(9)[54] is reacted with KH or NaH, the result is a transfer of hydride ion to the pentaborane yielding the anion, $B_5H_{10}{\cdot}P(Me)_3^-$ (ref.[55]). The ^{11}B NMR spectrum of this ion is consistent with fluxional behavior (Fig. 12). Reaction of the anion with BCl_3 abstracts the hydride and regenerates the original monophosphine derivative of pentaborane(9).

7.8. Transition Metal Derivatives

Investigation of transition metal complexes involving B_5H_9 has followed many paths. Metal carbonyl derivatives of pentaborane(9) include 2-$[Co(CO)_4]B_5H_8$ and 2-$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]B_5H_8$ (ref.[56]). The former is prepared either by the photolysis of $Co_2(CO)_8$ in liquid B_5H_9 or the reaction of $NaCo(CO)_4$ and 2-ClB_5H_8. The iron complex (Fig. 13) is prepared by the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ with LiB_5H_8.

The synthesis of 2,2,2-tricarbonyl-2-manganahexaborane, 2,2,2-$(CO)_3$-2-MnB_5H_{10} (Fig. 14) from B_5H_9, $Mn_2(CO)_{10}$ and H_2 (ref.[57]) has been improved by employing a heterogeneous catalyst, ruthenium on a carbon support[58]. This method is also effective for preparation of the analogous rhenium

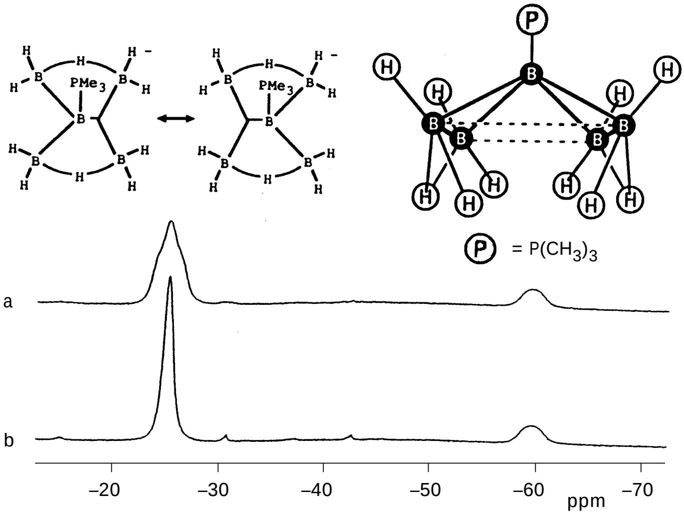

FIG. 12
Fluxional behavior in $B_5H_{10}{\cdot}P(Me)_3^-$ ion: coupled and ^1H decoupled ^{11}B NMR spectra and proposed valence bond and geometrical structures. Reprinted with permission from Fig. 1 of Grundt P., Kodama G.: *Inorg. Chem.* **1994**, *33*, 2056. Copyright 1994 American Chemical Society.

complex. A further, refined preparation of these B_6 derivatives from B_5H_9 has been described[59].

A $(\mu\text{-H})_3(CO)_9Os_3(\mu\text{-C})$ group can be substituted onto the apical boron atom of B_5H_9 by the following reaction[60],

$$[(\mu\text{-H})_3(CO)_9Os_3(\mu\text{-C})]_3(O_3B_3O_3) + B_5H_9 \xrightarrow{BF_3} (\mu\text{-H})_3(CO)_9Os_3(\mu\text{-C})(B_5H_8)\ .$$

The presence of BF_3 is necessary to promote formation of this product (Fig. 15).

The phosphorus-bridged B_5 anion, $(\mu\text{-Ph}_2P)B_5H_7^-$ reacts with $Fe(\eta^5\text{-}C_5H_5)(CO)_2I$ to produce the complex $(\mu\text{-Ph}_2P)B_5H_7Fe(\eta^5\text{-}C_5H_5)(CO)_2$ (Fig. 16)[53]. Note that phosphorus atom maintains its bridge position between B_2 and

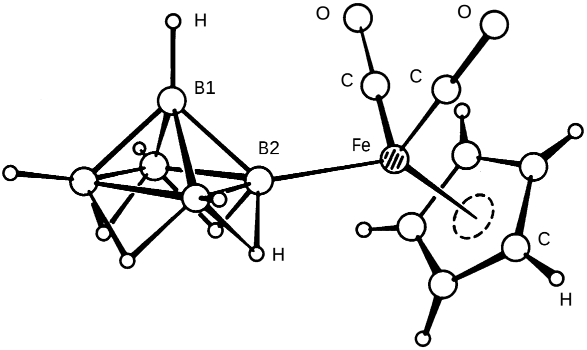

FIG. 13
The proposed structure of 2-$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]B_5H_8$. Reprinted from Fig. 3 of Fischer M. F., Gaines D. F., Ulman J. A.: *J. Organomet. Chem.* **1982**, *231*, 55. Copyright 1982, with permission from Elsevier Science.

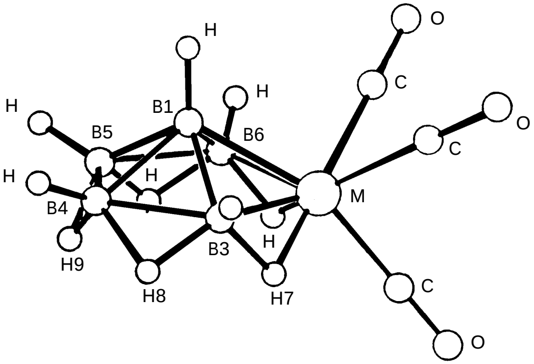

FIG. 14
The structure of 2,2,2-$(CO)_3$-2-MnB_5H_{10}. Reprinted with permission from Fig. 1 of Coons D. E., Gaines D. F.: *Inorg. Chem.* **1985**, *24*, 3774. Copyright 1985 American Chemical Society.

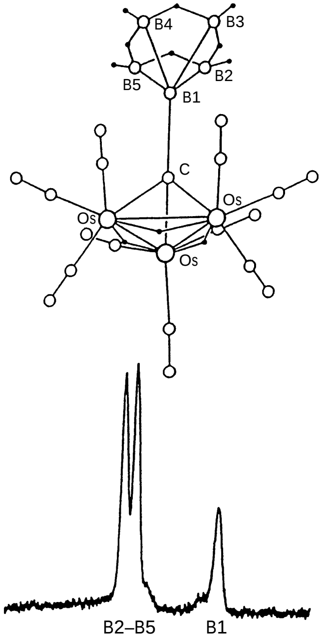

FIG. 15
Proposed structure and ^{11}B NMR spectrum of $(\mu\text{-H})_3(CO)_9Os_3(\mu\text{-C})(B_5H_8)$. Reprinted with permission from Fig. 2 of Wermer J. R., Jan D-Y., Getman T. D., Moher E., Shore S. G.: *Inorg. Chem.* **1988**, *27*, 4274. Copyright 1988 American Chemical Society.

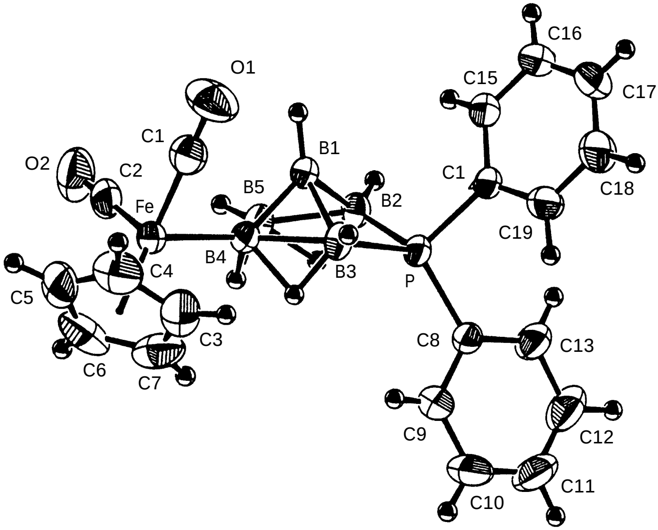

FIG. 16
Crystal structure of $(\mu\text{-Ph}_2P)B_5H_7Fe(\eta^5\text{-}C_5H_5)(CO)_2$. Reprinted with permission from Fig. 3 of Goodreau B. H., Ostrander R. L., Spencer J. T.: *Inorg. Chem.* **1991**, *30*, 2066. Copyright 1991 American Chemical Society.

B_3, and the Fe(η^5-C_5H_5)$(CO)_2$ group is substituted for a terminal hydrogen atom on B_4.

8. CONCLUSIONS

The chemistry of pentaborane(9) continues to be a rewarding area of research. A steady stream of interesting new derivatives of this compound with widely varying properties continues to appear. Although not successful as a jet fuel as was formerly hoped, it has become one of the pillars of boron hydride chemistry research.

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