DECABORANE-14 AND ITS DERIVATIVES

M. Frederick Hawthorne

Department of Chemistry, University of California, Riverside, California

I. Introduction

Among the many boron hydrides characterized by Alfred Stock and his co-workers (*76*) was a remarkably versatile material, $B_{10}H_{14}$. Decaborane-14 may be prepared by the pyrolysis of diborane and today this material is commercially available to the chemical investigator. This availability is a relatively new condition since decaborane-14 was virtually unavailable prior to 1950. During the last decade the boron hydrides, as a class, have been extensively investigated as candidate reaction motor fuels. This impetus has extended the frontiers of boron hydride chemistry to such an extent that boron hydride chemistry might someday become a truly major area of chemical technology. It seems unlikely, however, that boron hydride chemistry will ever challenge the chemistry of carbon hydrides in popularity or general usefulness. In any event it is likely that decaborane-14 will play a prominent role in the future as an easily handled starting material for synthetic, structural, and mechanistic studies.

The present article will be devoted to the discussion of decaborane-14 and compounds which may be obtained from this hydride by relatively simple reactions. Any discussion of decaborane-14 chemistry would be incomplete if the newly discovered and characterized (*21, 22*) decaborane-16 were not included. Figure 1 represents the interrelationships of the various derivatives of decaborane. This outline will be followed as closely as possible in the present discussion. It is seen that this organizational outline is formally based upon proton, hydride ion and electron transfer reactions. Particular compounds, where possible, will be treated as derivatives of the parent hydrides shown in Fig. 1.

The reader is referred to an excellent review by Lipscomb (*43*) for a discussion of the principles which support current ideas regarding the

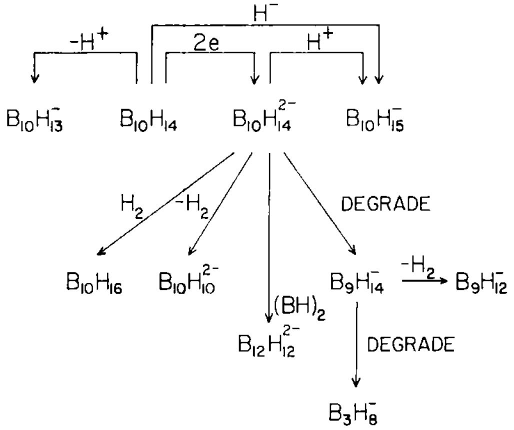


FIG. 1. Interrelationship of $B_{10}H_{14}$ derivatives.

bonding and structure of the boron hydrides. Indeed, the topological method of Lipscomb and co-workers and their treatment of electron-deficient bonding have made boron-hydride chemistry truly comprehensible for the first time. Jumbled facts have fallen into place and accurate chemical predictions based on these principles are now well known to the chemical public.

II. The Preparation and Structure of Decaborane-14

A. PREPARATION OF $B_{10}H_{14}$

The preparation of decaborane-14 is based upon the pyrolysis of diborane-6 at temperatures near 100° (*76*). Under these conditions the crystalline $B_{10}H_{14}$ (m.p. 100°) is accompanied by varying amounts of the lower hydrides (B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, etc.) and chalky $(BH)_x$ polymer of uncertain structure. The hydride products are easily separated from one another by distillation and sublimation or recrystallization from hydrocarbon solvents. The fact that $B_{10}H_{14}$ is commercially available attests to the efficiency of existing preparative methods.

The mechanism of the pyrolysis reaction which leads to the formation of $B_{10}H_{14}$ is presently unclear. A recent review (*43*) indicates the complexity of the over-all reaction sequence which appears to involve the formation of key B_5 intermediates by combination of smaller fragments. It has been suggested (*21*) that $B_{10}H_{14}$ results from the thermal degradation of the newly discovered $B_{10}H_{16}$. The over-all sequence might then be the following in which an unidentified B_5 hydride, B_5H_x, reacts with B_5H_9 to form $B_{10}H_{16}$.

$$B_5H_9 + B_5H_x \rightarrow B_{10}H_{16} + (x - \tfrac{7}{2})H_2$$

$$B_{10}H_{16} \rightarrow B_{10}H_{14} + H_2$$

The chemistry of $B_{10}H_{16}$ and its observed rearrangement to $B_{10}H_{14}$ and $B_{10}H_{14}$ derivatives (*21*) will be discussed below. That two B_5H_9 molecules do not combine to form $B_{10}H_{16}$ and one mole of hydrogen is shown by the work of Hillman *et al.* (*34*) who observed that the reaction of isotopically normal B_5H_9 with $B_2{}^{10}H_6$ produced decaborane-14 which contained five B^{10} labeled atoms per molecule. Thus, for the above scheme to be correct, B_5H_x must arise from the pyrolysis of diborane-6 alone.

B. STRUCTURE OF $B_{10}H_{14}$

The structure of $B_{10}H_{14}$ was first elucidated from the single crystal X-ray diffraction studies of Kasper *et al.* (*38*). Later, least squares refinement of the original data by Moore *et al.* (*52*) has produced the structure and B—B distances to a high degree of certainty. The geometrical arrangement of boron atoms in the $B_{10}H_{14}$ molecule is that of an icosahedron with two nearest neighbor atoms removed. Figure 2 presents the structure of decaborane-14 and the icosahedron from which it is formally derived. The numbering system commonly employed throughout $B_{10}H_{14}$ chemistry is shown in Fig. 2. Accurate B—H distances are not available but the observed B—H distances average about 1.30 Å. That the B—H—B bridge is unsymmetrical with respect to the hydrogen position is seen in the refined data (*52*). The B_6—H bridge distance varies from 1.43 to 1.50 Å while the B_5—H bridge distance varies from 1.25 to 1.39 Å.

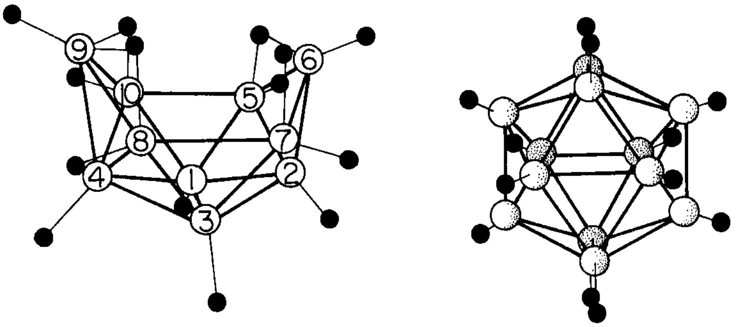


FIG. 2. $B_{10}H_{14}$ and the icosahedral $B_{12}H_{12}{}^{2-}$ ion.

C. BONDING IN $B_{10}H_{14}$

Decaborane-14, in common with all other boron hydrides, is "electron-deficient." Each boron atom contributes four atomic orbitals, $2s$, $2p_x$, $2p_y$, and $2p_z$ which might be hybridized sp, sp^2, and sp^3. Each boron atom contributes three valence electrons which may be used for bonding to hydrogen or other boron atoms. The fourteen hydrogen atoms each contribute a 1*s* orbital and one electron. Thus a total of 54 atomic orbitals and 22 electron pairs are available for bonding in $B_{10}H_{14}$. Assuming that each of the four bridge hydrogen atoms utilizes one orbital from each of its neighbor boron atoms as well as its own 1*s* orbital a total of 18 of the 40 boron orbitals available are employed in bonding to hydrogen. The four 3-center hydrogen bridge bonds consume a total of four electron pairs and the ten B—H two-center bonds consume a total of ten electron pairs. Arithmetic thus shows that 22 boron atomic orbitals remain to hold the eight remaining electron pairs which furnish bonding in all existing boron-boron interactions. These eight electron pairs may be fully utilized only if they occupy six B—B—B 3-center orbitals (one pair each) and two 2-center orbitals. Thus the bonding in decaborane-14 may be described as ten B—H 2-center bonds, four B—H—B 3-center bonds, two B—B 2-center bonds and six B—B—B 3-center bonds. Arguments similar to those presented above have been employed by Eberhardt *et al.* (*12*) to establish a set of topological rules which rationalize the bonding arrangements in the boron hydrides and their derivatives. These topological rules will be referred to throughout this article and the reader is referred to a recent review (*43*) for a critical examination of their basis. Using the topological language of Dickerson and Lipscomb (*6*), the known decaborane-14 is described as 4620 (s,t,y,x).

The parameters s, t, y, and x have been previously defined (*12*) to describe the number and types of bonds in possibly existent boron hydrides and their derivatives. Thus, s refers to the number of B—H—B bridge arrays, t is the number of B—B—B 3-center bonds ("open" or "closed" types), y is the number of B—B 2-center bonds and x is the number of —BH_2 groups present in a given molecule. These four parameters are interrelated by the three equations: $s + x = q$, $s + t = p$, and $p = t + y + q/2$. Code symbols are given in the order s, t, y, and x.

Other, as yet unknown, decaborane-14 molecules may be envisaged (*43*) (3711 and 2802).

The valence bond structure for decaborane preferred by Lipscomb (*43*), on the basis of molecular geometry and interrelationships with other boron hydrides, is that shown in Fig. 3. In this model boron atoms 2 and 4 are trigonally hybridized sp^2 and all other boron atoms are tetrahedrally hybridized sp^3. The two B—B 2-center bonds required in the $B_{10}H_{14}$ topology are between boron atoms 2—6 and 4—9. The $2p_z$ orbital of boron atoms 2 and 4 overlap with sp^3 orbitals from boron atoms 5 and 7 and 8 and 10, respectively.

The localized valence-bond structure of $B_{10}H_{14}$ shown in Fig. 3 is, in common with all such representations, an overly simplified description since some delocalization of the framework electrons probably exists. Therefore, Moore *et al.* (*53*) have undertaken a molecular orbital approach to the $B_{10}H_{14}$ molecule in order to more accurately predict the charge densities present in this molecule. Localized bonds predict *(12)* charges of $-\frac{2}{3}e$ on boron atoms 2 and 4, zero charge on boron atoms 1, 3, 6 and 9 and $+\frac{1}{3}e$ on boron atoms 5, 7, 8, and 10. These charge densities predict a dipole moment of 6.6 Debyes for decaborane-14. The molecular orbital approach, in which a $-0.2e$ charge is assigned to each bridge hydrogen atom, yields the following results *(53)*: $-0.254e$ on boron atoms 2 and 4, $+0.046e$ on boron atoms 1 and 3, $+0.069e$ on boron atoms 5, 7, 8, and 10, and $+0.468e$ on boron atoms 6 and 9. Without correction for the $-0.2e$ charge present on each bridge hydrogen atom, a dipole moment of 3.6 Debyes was calculated *(53)*. This is in agreement with the observed dipole moment of 3.52 Debyes *(42)*. It is seen from these results that the localized valence bond structure for $B_{10}H_{14}$ qualitatively fits the known facts although the molecular orbital treatment gives much closer agreement. It might be concluded that in molecules of low symmetry, such as $B_{10}H_{14}$, the localized bond picture is adequate for purposes of chemical discussion. About the same degree of success could be expected in boron hydride molecules as is obtained in organic molecules when using this simplified approach.

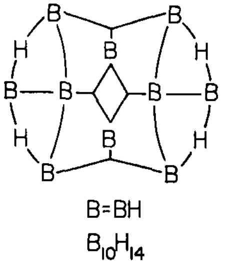


FIG. 3. Topological drawing of $B_{10}H_{14}$.

D. NUCLEAR MAGNETIC RESONANCE ASSIGNMENTS FOR $B_{10}H_{14}$

Perhaps the most economical structural tool available to the boron hydride chemist is the nuclear magnetic resonance spectrometer. B^{11} probes are available (ca. 12.8 Mc at 10,000 gauss) and yield the most useful spectra. During the last decade a considerable number of workers have employed H^1 and B^{11} spectra in the solution of structural problems. Decaborane-14 and its derivatives have been examined in detail and these spectra will be referred to throughout this review.

Figure 4 presents the H^1 NMR spectrum of $B_{10}H_{14}$ obtained at 40 Mc and Fig. 5 is the B^{11} NMR spectrum of isotopically normal $B_{10}H_{14}$ obtained at 12.8 Mc. Figure 4 also presents the H^1 NMR spectrum of bridge deuterated decaborane in which only the terminal protons are observed. The resonance peaks labeled (a) are due to protons at the 2 and 4 positions and

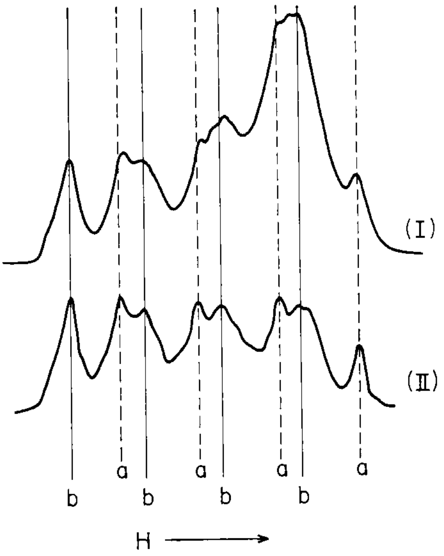


FIG. 4. (I) H^1 nuclear magnetic resonance spectra of $B_{10}H_{14}$; and (II, bridge deuterated) $B_{10}H_{10}D_4$; a = apical sites, b = all other terminal sites. High peak in (I) is due to bridge protons.

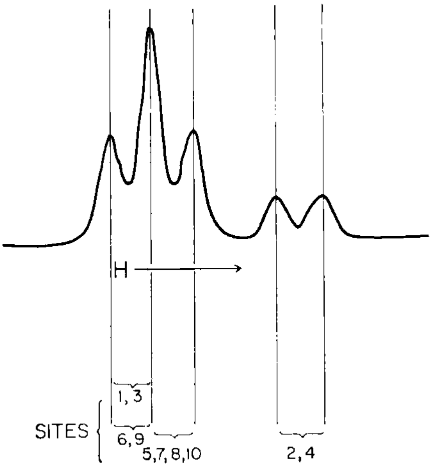


FIG. 5. B^{11} nuclear magnetic resonance spectrum of $B_{10}H_{14}$.

the resonances labeled (b) are comprised of all other terminal proton resonances. These assignments were made by Schaeffer *et al.* (*73*) on the basis of double resonance experiments with B^{11} excited. Due to the coincidental overlap of terminal protons in the H^1 spectrum many workers have found the B^{11} spectrum more informative.

The B^{11} resonances presented in Fig. 5 are assigned as shown on the basis of the B^{11} spectrum of $B_{10}D_{14}$ first reported by Williams and Shapiro (*83*). The unusual feature found in the B^{11} spectrum is the coincidental near-identity of the resonances due to the 1,3 and the 6,9 boron atoms.

Phillips *et al.* (*57*) have shown that B^{11} NMR resonances are quite sensitive to the chemical environment of boron. They report chemical shifts for B^{11} over a range of 130 ppm. In comparison, fluorine chemical shifts extend over 300 ppm while hydrogen is observed over a 20 ppm range.

III. Proton Abstraction from Decaborane-14

A. TITRIMETRIC EVIDENCE FOR $B_{10}H_{13}^-$

The acidic character of $B_{10}H_{14}$ was first recognized by Stock who observed that $B_{10}H_{14}$ dissolved in aqueous caustic. Much later, Guter and Schaeffer (*23*) successfully titrated $B_{10}H_{14}$ potentiometrically as a strong mono-protic acid in 75% ethanol-water. Decaborane-14 was recovered by acidification of the basic solution. Other solvent media have subsequently been employed in the titration of $B_{10}H_{14}$ (*2*, *20*, *29*) and amines have been employed as bases (*29*). A single report of the titration of $B_{10}H_{14}$ as a dibasic acid (*2*) was later shown to be in error (*20*). These results strongly suggested that the yellow (λ_{max} 267 and 335 mμ; ϵ, 2.5 and 1.7 × 10^3, respectively) salt produced upon the neutralization of decaborane was the $B_{10}H_{13}^-$ ion and not the $B_{10}H_{14}OH^-$ ion.

$$B_{10}H_{14} + OH^- \leftrightarrows B_{10}H_{13}^- + H_2O$$

$$B_{10}H_{14} + OH^- \rightleftharpoons B_{10}H_{14}OH^-$$

B. THE PREPARATION OF $B_{10}H_{13}^-$ SALTS

The reaction of $B_{10}H_{14}$ and sodium hydride in diethyl ether proceeded to form an ether soluble, yellow salt (*36*, *51*) in accord with the following equation.

$$B_{10}H_{14} + NaH \xrightarrow[Et_2O]{} H_2 + Na\ B_{10}H_{13}\ \text{(solvated)}$$

Attempts to isolate a crystalline sodium salt were unsuccessful due to formation of strong $B_{10}H_{13}^-$-ether complexes. The first reported crystalline salt of the $B_{10}H_{13}^-$ ion was obtained by the reaction of triphenylmethylene phosphorane with decaborane in diethyl ether (*25*). The

$$B_{10}H_{14} + \varphi_3\overset{+}{P}\overset{-}{C}H_2 \rightarrow \varphi_3\overset{+}{P}CH_3B_{10}H_{13}^-$$

product was characterized and found to display the ultraviolet absorption spectrum of the yellow salt produced by titration of decaborane with other bases. Later work characterized the diethylammonium and the tetramethylammonium salts of the $B_{10}H_{13}^-$ ion (*29*). The former salt was obtained from the reaction of diethylamine with $B_{10}H_{14}$.

C. THE IDENTITY OF THE ACIDIC HYDROGEN ATOM

The demonstration that a proton could be readily removed from decaborane at once raised the question as to the identity of the acidic hydrogen atom. This problem was considered to be solved when infrared (*28*, *51*) and nuclear magnetic resonance spectral studies (*74*) proved that the bridge hydrogen atoms of $B_{10}H_{14}$ were rapidly exchanged for deuterium atoms when $B_{10}H_{14}$ was equilibrated with D_2O-dioxane. Thus, $B_{10}H_{10}D_4$ (bridge —d_4) was made available. Later work (*9*) established that the same exchange reactions could be accomplished under more easily controlled conditions and with higher recovery by employing anhydrous DCl in dioxane solution as the deuterium source.

As a by-product of these base-catalyzed deuterium exchange studies it was established (*28*, *51*, *74*) that bridge deuterons would slowly equilibrate with the 5, 6, 7, 8, 9, and 10 protons of the $B_{10}H_{14}$ molecule in the presence of a basic solvent. Thus, it is a relatively simple process to prepare 5, 6, 7, 8, 9, 10 and bridge —d_{10} decaborane by continued exchange with D_2O-dioxane (*51*, *74*) or DCl-dioxane (*9*). The mechanism of the bridge hydrogen migration reaction is presently unknown but a mechanism has been proposed (*74*).

D. STRUCTURE OF THE $B_{10}H_{13}^-$ ION

The structure of the $B_{10}H_{13}^-$ ion has not been established experimentally. No single crystal X-ray diffraction studies or definitive nuclear magnetic resonance data have been reported.

Lipscomb (*43*) has proposed two possible structures which are related by hydrogen tautomerism. These two structures are represented topologically in Fig. 6. It is assumed that the $B_{10}H_{13}^-$ ion has the approximate geometry of $B_{10}H_{14}$. The tautomer which contains a BH_2 group is suggested by unpublished infrared data (*71*) which indicates the presence of a BH_2

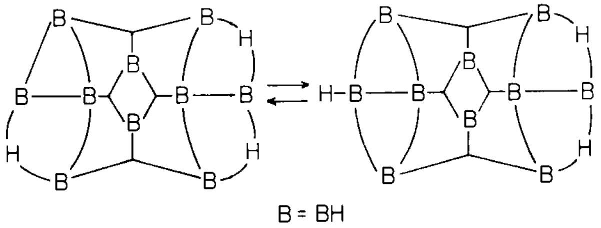


FIG. 6. Topological drawings of possible $B_{10}H_{13}^-$ tautomers.

group. A BH_2 group was suggested by Lipscomb (*43*) as an efficient device for stabilizing negative charge.

E. Decaboran(14)yl Magnesium Iodide

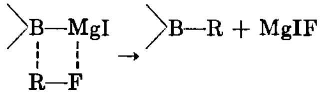
Siegel and co-workers (*75*), and later, Dunstan *et al.* (*8*) have described the preparation of a "decaboranyl Grignard reagent" from the reaction of decaborane-14 and methyl magnesium iodide.

$$B_{10}H_{14} + CH_3MgI \rightarrow CH_4 + B_{10}H_{13}MgI$$

Treatment of decaboran(14)yl magnesium iodide with benzyl chloride (*75*), alkyl fluorides (*75*), dialkyl sulfates (*8*) and trialkyloxonium ions (*8*, *75*) produced a mono-alkylated decaborane.

$$RX + B_{10}H_{13}MgI \rightarrow RB_{10}H_{13} + MgXI$$

These are the first reported examples of alkylation with a derivative of the $B_{10}H_{13}^-$ ion. In these reactions the entering alkyl group is attached to the 6-position as shown by B^{11} NMR spectra (*75*). The question of the amount of covalent character between magnesium and boron in decaboran(14)yl magnesium iodide remains unanswered. If the degree of covalency is high, the magnesium derivative might best be considered as a substituted tautomer of $B_{10}H_{14}$. The fact that sulfate, fluoride and etheral oxygen are the most effective leaving groups suggests a four-center transition state for the displacement reactions.



Palchak, Norman, and Williams have reported that the reaction of $NaB_{10}H_{13}$ with benzyl bromide produces 6- or 1-benzyl decaborane-14 (*56*).

F. Substituted $B_{10}H_{13}^-$ Ions

Aftandilian, Miller, and Muetterties (*1*) have prepared a series of $B_{10}H_{12}Z^-$ ions where Z is a monovalent anion. The cyanide, cyanate, thiocyanate, methoxide, and cyanoformate reactions were conducted in a variety of ethereal solvents and the products were characterized as their sodium or tetramethylammonium salts. The preparative reactions may be described by the following equation where X^- is the anionic reagent.

$$B_{10}H_{14} + X^- \xrightarrow[0\text{-}25^\circ]{R_2O} B_{10}H_{12}X^- + H_2$$

The structures of the products have not been determined although 6-(9-) substitution is preferred by the authors.

IV. Electrophilic Substitution of Hydrogen in Decaborane-14

A. HALOGENATION REACTIONS

Stock (*76*) first reported the preparation of halogen-substituted decaborane-14 derivatives from the uncatalyzed reaction of the halogens with $B_{10}H_{14}$. Stock succeeded in isolating a diiodo- and a dibromodecaborane-14. Single crystal X-ray diffraction studies by Schaeffer (*70*) proved the diiodocompound (m.p. 261°) to be 2,4-diiododecaborane-14. A monoiodo derivative (m.p. 116°) was studied by Schaeffer *et al.* (72) by NMR techniques and shown to be 2-iododecaborane-14. Recently Hillman (*33*) has carried out a detailed study of the Stock iodination reaction. From these studies another $B_{10}H_{13}I$ (m.p. 100°) and another $B_{10}H_{12}I_2$ (m.p. 155°) were obtained. On the basis of deuterium tracer work and other chemical evidence, Hillman denoted these new derivatives as 5-iodo- and 2,5-diiododecaborane-14, respectively. The aluminum chloride-catalyzed-iodination of decaborane was later reported by Hillman (*32*) to produce the same products as the uncatalyzed iodination reaction.

B. ALKYLATION REACTIONS WITH INCIPIENT CARBONIUM IONS

R. L. Williams and co-workers (*5*, *82*) have recently described a study of the ethylation and methylation of decaborane-14. These alkylation reactions were brought about through the use of an aluminum chloride catalyst and the corresponding alkyl bromide in carbon disulfide solution. The similarity of these reactions and the well known Friedel-Crafts reaction is obvious.

$$B_{10}H_{14} + RBr \xrightarrow[CS_2]{AlCl_3} B_{10}H_{13}R + HBr$$

Depending upon the reaction conditions, mono-, di-, and higher alkylated products are obtained. Separation of these products by vapor-liquid chromatography followed by B^{11} nuclear magnetic resonance characterization proved that substitution occurred in the 1, 2, 3, and 4 positions of $B_{10}H_{14}$. The ratio of 2-methyldecaborane to 1-methyldecaborane was about 3:1. No evidence for substitution at the 5-position was obtained. This latter result contrasts strongly with the results of iodination described above (*33*).

C. ELECTROPHILIC PROTON EXCHANGE WITH DEUTERIUM CHLORIDE–ALUMINUM CHLORIDE

Under equilibrium conditions at room temperature, decaborane-14 was reported (*11*) to exchange six protons for deuterons when treated with a large excess of deuterium chloride in the presence of aluminum chloride. The six deuterons were erroneously assigned

$$B_{10}H_{14} + D^+AlCl_4^- \rightleftarrows B_{10}H_{13}D + H^+AlCl_4^-$$

to the 1, 2, 5, 7, 8, and 10 positions of $B_{10}H_{14}$ on the basis of B^{11} nuclear magnetic resonance spectra. More recently, this exchange reaction has been reexamined under kinetic conditions (*9*) and the original interpretation was modified. When $B_{10}H_{14}$ was treated with anhydrous deuterium chloride in carbon disulfide solution in a flow system and in the presence of a small quantity of aluminum chloride, rapid exchange of four protons was observed. These reactions were conducted at 26°. Kinetic analysis of the rate data proved that the exchange reactions were first-order in $B_{10}H_{14}$ at constant deuterium chloride and aluminum chloride activities. The four exchange positions were kinetically indistinguishable. Analysis of the reaction mixture by B^{11} nuclear magnetic resonance spectrum measurements as a function of time proved that the four exchanging protons were located at the 2,4- and either the 1,3- or the 6,9- positions. Since base-catalyzed exchange of the resultant $B_{10}H_{10}D_4$ with hydrogen chloride in dioxane did not occur it was concluded that the 1, 2, 3, and 4- positions were involved in electrophilic exchange. The kinetic characteristics of the reaction and the nature of the observed B^{11} nuclear magnetic resonance spectra proved that the 1,3-protons exchanged at the same rate as the 2,4-protons. This is quite different than the selectivity shown by the methylation reaction (*82*) which produces the 2-methyl three times faster than the 1-methyl compound.

D. MECHANISM OF ELECTROPHILIC SUBSTITUTION

The results described above indicate that $B_{10}H_{14}$ is labile to attack by electrophiles at the 1, 2, 3, and 4- positions. The deuterium exchange studies which were carried out under equilibrium conditions (*11*) are inconclusive since the long exchange times and tedious experimental technique employed may have allowed secondary reactions to enter the picture. No explanation of the 5-substitution observed in the case of iodination (*33*) may be offered at this time. However, the iodonium ion is an unusual electrophile due to its large steric requirement and its high polarizability. It appears likely that the process which leads to 5-iododecaborane-14 is not a typical electrophilic substitution reaction.

Previously, the orientation of substituents in electrophilic substitution reactions on decaborane-14 have been discussed in terms of the charge distribution in the unperturbed $B_{10}H_{14}$ molecule (*70*, *82*). The 2 and 4-positions of $B_{10}H_{14}$ have been recognized as the points of highest electron density in $B_{10}H_{14}$ for some time (*12*). Indeed, the results of a detailed calculation of electron densities (Section I,C) confirms this conclusion and points out that the 5, 7, 8, and 10-positions are actually only slightly more positive (+0.069*e*) than the 1 and 3-positions. Consequently, the order with respect to increasing negative charge is 6,9 < 5,7,8,10 < 1,3 < 2,4. These results are in agreement with experiment. The problem is quite similar to that encountered in predicting positions of electrophilic substitution in aromatic hydrocarbons. The fact that 1,3-substitution competes so favorably with 2,4-substitution in alkylation and deuteron exchange suggests that the transition state for 1,3-substitution is stabilized by a unique structural feature which compensates for a less favorable charge density in the reactant $B_{10}H_{14}$. An alternative explanation for the equality of 1,3- and 2,4-deuteron exchange rates has been advanced (*9*) and suggests that both 1,3- and 2,4-proton exchange proceed through a common intermediate which provides rapid distribution of the entering deuteron between the 1, 2, 3, and 4 positions.

V. Electron Transfer to Decaborane-14

A. DECABORANE-14 AS AN ELECTRON ACCEPTOR

Consideration of the valence bond structure of decaborane-14 led Lipscomb to predict (*44*) $B_{10}H_{14}^{2-}$ as a stable ion with a geometry resembling $B_{10}H_{14}$. The most probable topological structure of $B_{10}H_{14}^{2-}$ is shown in Fig. 7. It is to be noted that the negative charges are largely localized at the 6 and 9-positions which have been converted to BH_2 groups. Two bridge hydrogen atoms are placed in a plane of symmetry. As will be seen below, the $B_{10}H_{14}^{2-}$ ion and its substituted derivatives constitute an important series of decaborane derivatives.

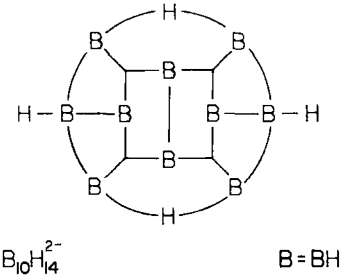


FIG. 7. Topological drawing of $B_{10}H_{14}^{2-}$.

B. PREPARATION AND REACTIONS OF $B_{10}H_{14}^{2-}$

Toeniskoetter (*77*) and Toeniskoetter *et al.* (*78*) have described the reactions of decaborane-14 with sodium in liquid ammonia and ethereal solvent systems. In the former case, $B_{10}H_{14}^{2-}$ is produced in high yield. Disodium tetradecahydrodecaborate is a white crystalline solid soluble in liquid ammonia and tetrahydrofuran. When the reaction of decaborane-14 with sodium is conducted in diethylether or tetrahydrofuran, a red intermediate is observed which either dimerizes (*77*) or reacts further with sodium to produce the colorless $B_{10}H_{14}^{2-}$ ion. On standing, the red intermediate decomposes to produce hydrogen and $NaB_{10}H_{13}$. On the basis of its color, stoichiometry of formation and low stability the red intermediate was formulated as a $B_{10}H_{14}^{-}$ ion-radical. Treatment of the $B_{10}H_{14}^{2-}$ ion with decaborane-14 generates the red species and illustrates the reversibility of the electron-transfer process. These interconversions are summarized in the following equations.

$$\begin{tikzcd}
B_{10}H_{14} + e^- \arrow[r] & B_{10}H_{14}\cdot^- \arrow[r, shift left, "e^-"] \arrow[d] & B_{10}H_{14}^{2-} \arrow[l, shift left] \\
& B_{10}H_{13}^- + \tfrac{1}{2}H_2 &
\end{tikzcd}$$

The reactions of the $B_{10}H_{14}^{2-}$ ion have not been fully investigated. Hydrogen chloride and $Na_2B_{10}H_{14}$ produce decaborane-14 along with some uncharacterized chlorination products (*77*). Iodine and $B_{10}H_{14}^{2-}$ react to produce decaborane-14 and iodide ion (*66*) in high yield.

$$B_{10}H_{14}^{2-} + I_2 \rightarrow B_{10}H_{14} + 2I^-$$

C. THE $B_{10}H_{15}^-$ ION FROM $B_{10}H_{14}^{2-}$

Titration of $Na_2B_{10}H_{14}$ with hydrogen chloride in 50% ethanol results in the reversible uptake of one proton and the formation of the ion $B_{10}H_{15}^-$ (*10*). The addition of methyl triphenyl phosphonium, tetramethylammonium, or triethylammonium ions to acidified solution of the $B_{10}H_{14}^{2-}$ ion resulted in the formation of the corresponding $B_{10}H_{15}^-$ salts. The infrared spectrum of these salts contained terminal B—H stretching bands at 3.95, 4.20, and 4.30 μ. A weak absorption band was observed at 5.10 μ which

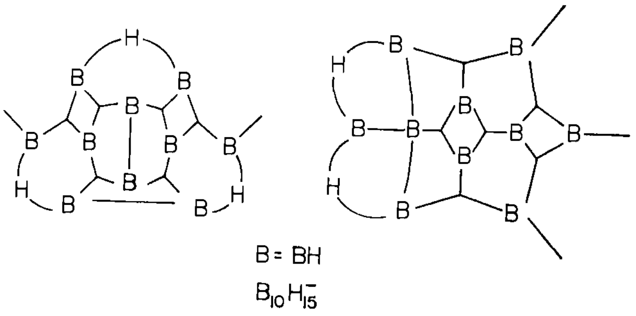


FIG. 8. Topological drawings of possible $B_{10}H_{15}^-$ structures.

indicates the presence of B—H—B bridges. The B^{11} nuclear magnetic resonance spectrum of $B_{10}H_{15}^-$ salts revealed only three resonances at +27.6, 34.9, and 43.2 ppm relative to trimethyl borate. An interpretation of this spectrum has not been carried out.

It is interesting to note that Reddy and Lipscomb (*64*) predicted the possible existence of the $B_{10}H_{15}^-$ ion in 1959. Lipscomb has recently presented (*45*) two plausible topological formulations of this ion which are shown in Fig. 8.

VI. Substituted Tetradecahydrodecaborate Ions. $B_{10}H_{12}X_2$ Compounds

A. EARLY WORK WITH $B_{10}H_{10}X_2$ COMPOUNDS

In 1957 Riley Schaeffer reported (*69*) the preparation of a decaborane-14 derivative which presaged a new area of decaborane-14 chemistry. The reported reaction involved the treatment of decaborane-14 with excess acetonitrile at the reflux temperature. The compound $B_{10}H_{12} \cdot 2CH_3CN$ was formed in essentially quantitative yield along with one mole of hydrogen per mole of derivative.

$$B_{10}H_{12} + 2CH_3CN \rightarrow B_{10}H_{12} \cdot 2CH_3CN + H_2$$

Somewhat later, other derivatives of this general type were reported (*30*) in which diethylcyanamide or triphenylphosphine served as ligands. The observation was also made that the diethylcyanamide and triphenylphosphine derivatives could be prepared by displacement of acetonitrile from $B_{10}H_{12} \cdot 2CH_3CN$ with the desired ligand. Thus, the probable preparation a large series of $B_{10}H_{12}X_2$ derivatives became apparent.

B. STRUCTURE ELUCIDATION AND TOPOLOGY OF $B_{10}H_{12}X_2$ COMPOUNDS

Reddy and Lipscomb (*64, 65*) reported the results of their single crystal X-ray diffraction study of $B_{10}H_{12} \cdot 2CH_3CN$ in 1959. The structure of $B_{10}H_{12} \cdot 2CH_3CN$ obtained from this study was the topological equivalent of the 2632 structure of the $B_{10}H_{14}^{2-}$ ion. Reddy and Lipscomb (*64*) first recognized and established a most useful concept: The formal displacement of a hydride ion by a ligand carrying a nonbonded electron pair will produce a topologically equivalent structure. This rule is illustrated for the case at hand with the following equation.

$$B_{10}H_{14}^{2-} + 2CH_3CN \rightarrow B_{10}H_{12}(CH_3CN)_2 + 2H^-$$

Figure 9 presents a schematic drawing which illustrates the $B_{10}H_{12} \cdot 2CH_3CN$ geometry and its topological representation. Later work by Sands and Zalkin (*67*) confirmed the assumption that $B_{10}H_{12} \cdot 2(CH_3)_2S$ (*16*) was isostructural with $B_{10}H_{12} \cdot 2CH_3CN$. Pace *et al.* (*55*) have obtained B^{11}

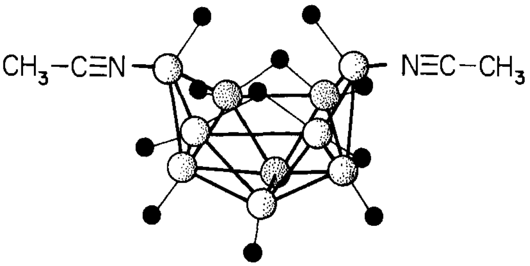


FIG. 9. Geometry of $B_{10}H_{12}\cdot 2CH_3CN$.

nuclear magnetic resonance spectra of $B_{10}H_{12}\cdot 2CH_3CN$ and $B_{10}H_{12}\cdot 2(CH_3)_2S$ which are in agreement with spectra predicted on the basis of the known structures of these compounds.

C. FURTHER EXAMPLES OF $B_{10}H_{12}X_2$ COMPOUNDS

Evidence accumulated over the past several years points out the generality of the reaction of decaborane-14 with two neutral ligand molecules. The types of

$$B_{10}H_{14} + 2X \rightarrow B_{10}H_{12}X_2 + H_2$$

ligands which have been successfully employed include the following: nitriles (*69*), dialkylcyanamides (*30*), alkyl isonitriles (*26*), dialkylsulfides (*16*, *17*), dialkylsulfoxides (*41*), phosphines (*30*), phosphite and phosphinite esters (*63*), phosphine oxides (*41*), amides (*41*), thioamides (*41*), tertiary amines (*31*), alkylated thioureas (*4*), heterocyclic amines (*15*) and tetrazoles (*13*). Other types of neutral ligand molecules will no doubt be found to be effective in this general reaction.

An unusual property of $B_{10}H_{12}X_2$ compounds which contain heterocyclic amines or tetrazoles as ligands is their highly colored nature. Thus $B_{10}H_{12}(\text{pyridine})_2$ is bright yellow. Other members of $B_{10}H_{12}X_2$ family are colorless or nearly so when pure. An explanation of this absorption in the

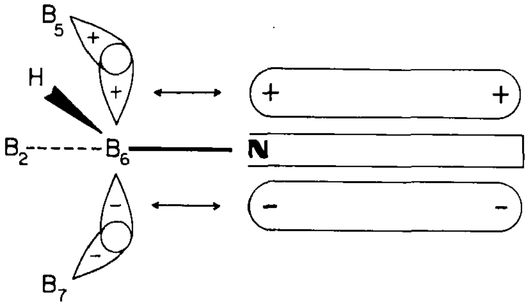


FIG. 10. Extended molecular orbitals in $B_{10}H_{12}Py_2$.

visible region has been proposed (*15*). In Fig. 7 it is seen that the topology of $B_{10}H_{12}X_2$ molecules suggests that the boron atoms which bear the ligand molecules are hybridized sp^2. Each of these boron atoms contributes a $2p$-orbital to an open three-center bond which in turn, must have the symmetry property of a p-orbital. When the attached ligand contains a π-electron system with a low-lying and empty antibonding orbital, back coordination of delocalized electrons in the $B_{10}H_{12}$ unit may occur upon excitation. Figure 10 depicts the geometrical arrangement involved. Figure 11 illustrates a successful correlation of excitation energies of absorption bands in the visible with the Hammett sigma constants of substituents placed on the pyridine nucleus. This concept has been extended by Kaufman (*39*) in a more quantitative fashion.

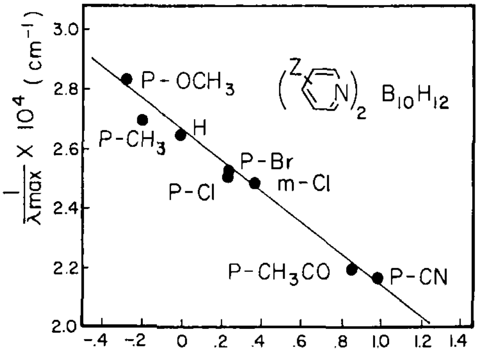


FIG. 11. Correlation of excitation energies with the Hammett sigma constants of substituents in $B_{10}H_{12}$ (Py-Z)$_2$, Z = substituent.

D. Ligand Displacement Reactions with $B_{10}H_{12}X_2$ Compounds

Treatment of $B_{10}H_{12}\cdot 2CH_3CN$ with triphenylphosphine or diethylcyanamide produced $B_{10}H_{12}\cdot 2P(C_6H_5)_3$ and $B_{10}H_{12}\cdot 2(C_2H_5)_2NCN$ which were identical to those obtained from decaborane-14 and these ligands (*30*). These reactions were found to be irreversible under ordinary conditions. Similarly, treatment of $B_{10}H_{12}\cdot 2(C_2H_5)_2NCN$with triphenylphosphine produced $B_{10}H_{12}\cdot 2P(C_6H_5)_3$. The retroreaction could not be brought about. Later work by Pace *et al.* (*55*) included other examples of ligand displacement reactions which employed dimethylacetamide, triethylamine, and pyridine. With this additional data in hand it was possible to formulate a displacement reactivity series in which a ligand on the right would displace all ligands to its left.

$$(CH_3)_2S < CH_3CN < (C_2H_5)_2NCN < HCON(CH_3)_2 = CH_3CON(CH_3)_2$$
$$< (C_2H_5)_3N = C_5H_5N = P(C_6H_5)_3$$

Triphenylphosphine and pyridine are probably the most tightly bound ligands since triphenylphosphine will displace triethylamine (*31*). The possibility of back coordination of delocalized electrons in the $B_{10}H_{12}$ fragment with the unfilled π-orbitals of pyridine and an unfilled *d*-orbital of phosphorous in triphenylphosphine may account for this strong bonding.

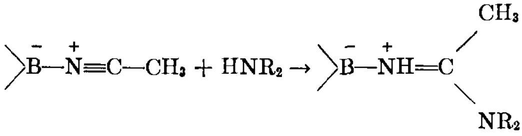
The mechanism of these displacement reactions has not been reported. It is interesting to note that these reactions are totally stereospecific.

It is important to note that dialkyl sulfides are the most readily replaced ligands known. This fact coupled with the ease of preparation of $B_{10}H_{12}{\cdot}2SR_2$ derivatives (*15, 16*) makes these materials especially valuable intermediates for synthetic work.

E. Nucleophilic Addition Reactions with Unsaturated Ligands as Substrates

While the displacement of ligands from $B_{10}H_{12}X_2$ compounds by other ligands is a general reaction, an interesting side reaction often occurs when the ligand attached to boron is unsaturated and the attacking nucleophile is an extremely weak acid (*31*).

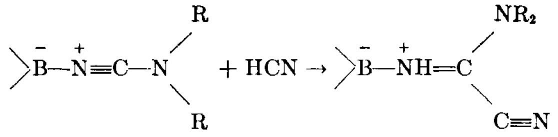
The compound $B_{10}H_{12}{\cdot}2CH_3CN$ reacts with primary and secondary alkylamines to produce $B_{10}H_{12}X_2$ derivatives in which the attached ligand contains both the original ligand and the attacking nucleophile. The following equation presents this reaction in general terms.



$$>\overset{-}{B}\text{—}\overset{+}{N}\equiv C\text{—}CH_3 + HNR_2 \rightarrow\ >\overset{-}{B}\text{—}\overset{+}{N}H{=}C\begin{matrix} \diagup CH_3 \\ \diagdown NR_2 \end{matrix}$$

Thus, nitrile ligands may be converted to substituted amidine ligands in high yield (*31*). The resulting $B_{10}H_{12}{\cdot}2$ Amidine derivatives will not react with triphenylphosphine.

Liquid hydrogen cyanide and the compound $B_{10}H_{12}{\cdot}2(C_2H_5)_2NCN$ react slowly at room temperature (*30*) and in the absence of solvent to produce a brilliant red derivative of composition $B_{10}H_{12}{\cdot}2(C_2H_5)_2NCN{\cdot}2HCN$. The product has an absorption maximum at 450 mμ ($\epsilon = 9.5 \times 10^3$). The original formulation of the complex ligand in this derivative (*30*) is probably in error. In view of the now recognized spectral properties of $B_{10}H_{12}X_2$ compounds which contain conjugated, electron-withdrawing ligands (Section VI,C), it appears likely that the ligand is actually a C-cyanoformamidine. This view is strengthened by the observations of Pace *et al.* (*55*) that dialkylcyanamides are bonded to the $B_{10}H_{12}$ fragment through nitrile nitrogen. The over-all reaction may be written as follows:



These reactions are novel in that unusual organic reactions may be carried out while the unsaturated substrate is firmly bonded to the $B_{10}H_{12}$ fragment. The role of such reactions in synthetic organic chemistry has not, as yet, been exploited.

F. $B_{10}H_{12}S(CH_3)_2$ FROM $B_{10}H_{12}{\cdot}2S(CH_3)_2$

Knoth and Muetterties (*41*) have recently described the preparation of $B_{10}H_{12}S(CH_3)_2$ by the slow pyrolysis of $B_{10}H_{12}{\cdot}2S(CH_3)_2$ in mesitylene solution. The product is a stable white solid which does not react with acetonitrile or dimethyl sulfide at room temperature. Treatment of $B_{10}H_{12}S(CH_3)_2$ with triphenylphosphine or dimethylsulfide at higher temperatures produces $B_{10}H_{12}{\cdot}2P(C_6H_5)_3$ and $B_{10}H_{12}{\cdot}2(CH_3)_2S$, respectively.

The ultraviolet spectrum of $B_{10}H_{12}S(CH_3)_2$ is similar to that of $B_{10}H_{13}^-$ ion and the B^{11} nuclear magnetic resonance spectrum of these two substances are identical in shape but not superimposable. Thus, $B_{10}H_{12}S(CH_3)_2$ was formulated as a substituted $B_{10}H_{13}^-$ ion (*41*). In this case an H^- of $B_{10}H_{13}^-$ is replaced by dimethylsulfide.

G. THE PREPARATION AND PROBABLE STRUCTURE OF $B_{10}H_{13}X^-$ IONS

The reaction of decaborane-14 with excess diethylamine in cyclohexane solution was reported (*29*) to give a product of composition $B_{10}H_{14}{\cdot}2(C_2H_5)_2NH$. Later work (*15, 18*) proved this material to be a diethylammonium salt with the anion $B_{10}H_{13}{\cdot}(C_2H_5)_2NH^-$. The anion is undoubtedly produced by the coordination of the amine with the $B_{10}H_{13}^-$ ion.

Potentiometric titration of this salt with hydrogen chloride in nonaqueous media consumed one equivalent of acid and precipitated diethylammonium chloride. Hydrogen was not evolved. The neutralization of the anion undoubtedly produced $B_{10}H_{14}(C_2H_5)_2NH$, a monosubstituted $B_{10}H_{15}^-$ ion (*18* and Section V,B).

$$B_{10}H_{13}NH(C_2H_5)_2 + H^+ \rightarrow B_{10}H_{14}NH(C_2H_5)_2$$

An improved and general method for the preparation of $B_{10}H_{13}X^-$ ions was developed (*18*). This method made use of the following reaction sequence where X = ligand.

$$B_{10}H_{14} + NaH \xrightarrow{Et_2O} H_2 + NaB_{10}H_{13}$$

$$NaB_{10}H_{13} + X \xrightarrow{Et_2O} NaB_{10}H_{13}X$$

The resulting anions were isolated and characterized as their tetramethylammonium salts. Diethylamine, ethylamine, triethylamine, piperidine, pyridine, and triphenylphosphine were employed as ligands. Knoth and Muetterties (*41*) employed a similar method to prepare the anion $B_{10}H_{13}S(CH_3)_2^-$.

The structure of the $B_{10}H_{13}X^-$ anions is most likely identical to that of $B_{10}H_{12}X_2$ compounds (Fig. 9) in which one of the ligand molecules is replaced by a hydride ion (*18*, *41*). This formulation is supported by the similarity of the B^{11} nuclear magnetic resonance spectra (*41*) of $B_{10}H_{12}\cdot 2(CH_3)_2S$ and $B_{10}H_{13}S(CH_3)_2^-$ and by chemical evidence cited below (*18*).

H. CONVERSION OF $B_{10}H_{13}X^-$ IONS TO $B_{10}H_{12}X_2$ DERIVATIVES

Since $B_{10}H_{13}X^-$ ions most likely contain a negatively charged BH_2 group at the 6-(9-) position it was reasonable to expect these ions to react with the conjugate acids of ligands in accord with the following equation where X = ligand.

$$B_{10}H_{13}X^- + \overset{+}{HX} \rightarrow H_2 + B_{10}H_{12}X_2$$

This reaction proved to be general (*18*) and was employed in the preparation of a variety of $B_{10}H_{12}X_2$ derivatives. By employing the conjugate acid of a ligand which differed from the ligand present in $B_{10}H_{13}X^-$, it was possible to prepare unsymmetrical $B_{10}H_{12}XX'$ derivatives (*18*). Amine hydrochlorides were most commonly employed as HX^+, however, $B_{10}H_{13}(C_2H_5)_2NH^-$ and anhydrous hydrogen chloride reacted in acetonitrile or diethyl sulfide solvent to produce hydrogen and $B_{10}H_{12}\cdot CH_3CN\cdot(C_2H_5)_2NH$ and $B_{10}H_{12}\cdot(C_2H_5)_2S\cdot(C_2H_5)_2NH$, respectively. These reactions are to be contrasted with the titration of $B_{10}H_{13}(C_2H_5)_2NH^-$ with hydrogen chloride in dioxane (Section VI,G), a poorly nucleophilic solvent.

The mechanism of these protolysis reactions is presently obscure. However, it is likely that the attacking, protonated ligand enters into a three or four-center transition state with the BH_2 group of the anion to produce hydrogen and product (*18*). In the former case a discrete $B_{10}H_{12}X$ intermediate would be involved. In the latter case, the process would be concerted and lead directly to products.

I. OXIDATION OF A $B_{10}H_{13}X^-$ ION TO $B_{10}H_{13}X$. ALKOXYLATION OF DECABORANE-14

The attempted iodination of the $B_{10}H_{13}^-$ ion in diethyl ether led to the formation of an ethoxydecaborane-14, $B_{10}H_{13}OC_2H_5$. This reaction proved to be general and several alkoxyl and aryloxyl decaborane-14 derivatives were prepared (*27*). The position of substitution was not rigorously established although 6-(9-) substitution is compatible with the B^{11} nuclear magnetic resonance spectra obtained.

In view of the ability of weakly nucleophilic ligands to coordinate with the $B_{10}H_{13}^-$ ion (Section VI,G) it appears likely that solutions of $B_{10}H_{13}^-$ prepared in ethereal solvents contain small quantities of the $B_{10}H_{13}X^-$ ion in which the ligand is identical to the solvent. The ether ligand would bear a positive

$$B_{10}H_{14} + NaH \xrightarrow{R_2O} H_2 + B_{10}H_{13}OR_2^-Na^+$$

charge on oxygen. The reaction of $B_{10}H_{14}^{2-}$ with iodine produces $B_{10}H_{14}$ and iodide ion in high yield (Section V,B). Due to the topological identity of $B_{10}H_{14}^{2-}$ and $B_{10}H_{13}OR_2^-$ the oxidation of $B_{10}H_{13}OR_2^-$ to $B_{10}H_{13}OR_2^+$ might well occur upon the addition of iodine. Attack of the produced iodide ion upon the $-\overset{+}{O}R_2$ group would produce alkyl iodide. The $-\overset{+}{O}R_2$ group might also eliminate a proton and an olefin molecule.

$$B_{10}H_{13}OR_2^- + I_2 \rightarrow 2I^- + B_{10}H_{13}\overset{+}{O}R_2$$

$$B_{10}H_{13}\overset{+}{O}R_2 + I^- \rightarrow RI + B_{10}H_{13}OR$$

$$B_{10}H_{13}\overset{+}{O}R_2 \rightarrow B_{10}H_{13}OR + H^+ + \text{Olefin}$$

Palchak *et al.* (*56*) have reinvestigated the iodination of $B_{10}H_{13}^-$ in diethyl ether and have obtained evidence for the formation of ethyl iodide as well as ethoxy decaborane-14 and iodinated decaborane-14's.

Further work with simple oxidation reactions might allow the preparation of $B_{10}H_{13}X^+$ cations which

$$B_{10}H_{13}X^- + I_2 \rightarrow 2I^- + B_{10}H_{13}X^+$$

are substituted decaborane-14's.

J. $B_{10}H_{13}Z^{2-}$ Ions from $B_{10}H_{13}^-$ and Nucleophilic Anions, Z^-

Knoth and Muetterties (*41*) have prepared the $B_{10}H_{13}CN^{2-}$ anion by the reaction of two equivalents of sodium cyanide with $B_{10}H_{14}$ in aqueous solution.

$$2NaCN + B_{10}H_{14} \xrightarrow{H_2O} Na_2B_{10}H_{13}CN + HCN$$

In the same publication these authors reported the preparation of the $B_{10}H_{12}{\cdot}CN{\cdot}S(CH_3)_2^-$ anion from the reaction of $B_{10}H_{14}$ with sodium cyanide in dimethyl sulfide solution.

$$NaCN + (CH_3)_2S + B_{10}H_{14} \rightarrow H_2 + NaB_{10}H_{12}{\cdot}CN{\cdot}S(CH_3)_2$$

Both the $B_{10}H_{13}CN^{2-}$ and the $B_{10}H_{12}\cdot CN\cdot S(CH_3)_2^-$ ions exhibited B^{11} nuclear magnetic resonance spectra which were similar in shape to that of the $B_{10}H_{13}S(CH_3)_2^-$ ion. The ultraviolet absorption spectra of these three ions were also similar. It therefore appears correct to assign the $B_{10}H_{13}CN^{2-}$ and the $B_{10}H_{12}\cdot CN\cdot S(CH_3)_2^-$ ions the structures of 6- and 9- substituted $B_{10}H_{14}^{2-}$ ions.

K. MECHANISM OF $B_{10}H_{12}X_2$ FORMATION

Only two studies which deal with the mechanism of $B_{10}H_{12}X_2$ formation have been reported in the literature. Beachell and Dietrich (*3*) have examined the kinetics of the reactions of a series of substituted anilines with decaborane-14 in benzene solution at 25.0°. In a later study Beachell and Hoffman (*4*) examined the kinetics of the reaction of *sym*-diethyl thiourea with decaborane-14 in benzene solution at 25.0°.

The reactions of substituted anilines with decaborane-14 were first-order in the aniline and first-order in a 1:1 aniline:$B_{10}H_{14}$ complex. All reactions were followed by measurement of evolved hydrogen. $d[H_2]/dt = k_2[B_{10}H_{14}\cdot\text{Aniline}][\text{Aniline}]$. Application of a Hammett treatment (*24*) to the data obtained indicated a *rho* value of −2.75. Small primary kinetic isotope effects were observed with partially deuterated reactants (B—D or N—D) and provided evidence for B—H bond-breaking in the rate-determining step. The product from N-deuterated *p*-toluidine contained B—D stretching bands in the infrared spectrum. Thus, equilibration of the protons attached to nitrogen with certain protons present in decaborane-14 readily occurs during the reaction. This exchange process most likely proceeds through the B—H—B bridge exchange described in Section III,C.

The kinetic study of the reaction of *sym*-diethyl thiourea with decaborane-14 was only briefly reported (*4*). The authors claim that the observed second-order reaction was consistent with the rate expression:

$$d[H_2]/dt = k_2\,[\text{thiourea}\cdot B_{10}H_{14}]\,[\text{thiourea}]$$

An attempt to arrive at a generalized mechanism for $B_{10}H_{12}X_2$ formation is complicated by the relatively basic character of the anilines employed in the initial study and the known acid-base reactions of $B_{10}H_{14}$ with amines (Sections III,A and III,B). The study with *sym*-diethylthiourea as the nucleophile is perhaps more informative since the pK_B of this species is approximately 5 units greater than that of aniline. However, both studies point to a rate-determining transition state which has the composition of a ($B_{10}H_{14}\cdot$nucleophile) complex and a free nucleophile molecule. The data presently available are consistent with several possible ionic mechanisms. Before definite conclusions are drawn a great deal more experimental work must be carried out.

VII. Enneaborane-15 Derivatives from Substituted $B_{10}H_{14}^{2-}$ Ions

A. EARLY WORK ON ENNEABORANE-15 DERIVATIVES

In the first report of the preparation of a $B_{10}H_{12}X_2$ derivative, Schaeffer (*69*) referred to the solvolytic degradation of $B_{10}H_{12}\cdot 2CH_3CN$ with methanol at the reflux temperature. The product obtained from this reaction showed a C=N stretching band in its infrared spectrum. It was suggested by Schaeffer (*68*) that this product might be a B_9 derivative.

Fitch and Laubengayer (*14*) reported that the acidolysis of a product formed from $B_{10}H_{14}$ and dimethylamine produced a volatile solid derivative. It was suggested by these authors that the acidolysis product was a B_9 derivative. Later work, to be described below, proved that the compounds of Schaeffer and Fitch and Laubengayer were B_9H_{15} derivatives. These derivatives and many others constitute a series of substituted B_9H_{15} species which are analogous to the $B_{10}H_{12}X_2$ derivatives. Their general composition may be expressed as $B_9H_{13}X$ where X is a ligand molecule.

B. STRUCTURE AND TOPOLOGY OF $B_9H_{13}X$ COMPOUNDS

Wang *et al.* (*79*) first reported the results of a single crystal X-ray diffraction study of $B_9H_{13}\cdot CH_3CN$ (*16*) in 1961. A later publication by these authors (*80*) expanded their initial views and presented a review of the evolution of $B_9H_{13}X$ structural studies with respect to the present topological theory of boron hydrides and derivatives.

The determined geometry of $B_9H_{13}\cdot CH_3CN$ is shown in Fig. 12 along with the corresponding topological representation of this type of derivative. It is important to note that $B_9H_{13}X$ derivatives are topologically equivalent to the unknown $B_9H_{14}^-$ ion, which in turn, is related by proton transfer to the unknown B_9H_{15} with 6330 topology shown in Fig. 12. As previously pointed out (*79, 80*), this 6330 topology violates one of the original topological rules (*6, 43*). This rule states that it is impossible to bond two bridge hydrogen atoms to a boron atom which is connected to four other nearest boron atoms. Therefore, it was predicted that this particular B_9H_{15} would probably be unstable (*80*). The conceptual transformation of the hypothetical 6330 B_9H_{15} to $B_9H_{13}X$ derivatives involves a newly described tautomerization reaction which involves bridge hydrogen atoms and uniquely predicts the known $B_9H_{13}X$ structure without violation of any topological rule (*80*). The reader is referred to the original paper for details of this transformation.

The bonding of ligands to boron in $B_9H_{13}X$ derivatives is seen to be virtually identical to that found in $B_{10}H_{12}X_2$ derivatives (Section VI,B).

The hybridization of the boron atom which carries the ligand is seen in Fig. 12 to be *sp*^{2}. It was interesting to find spectroscopic evidence (*19*) for this hybridization in the ultraviolet absorption spectra of a series of $B_9H_{13}Py$ derivatives where Py represents a substituted pyridine ligand. These compounds exhibited absorption maxima between 284 mμ (4-methoxypyridine) and 358 mμ (4-cyano-pyridine). The excitation energies of these maxima were successfully correlated with the Hammett sigma constant (*24*) of the various substituents. The rationale of these results is identical to that presented for the case of $B_{10}H_{12}Py_2$ derivatives (Section VI,C).

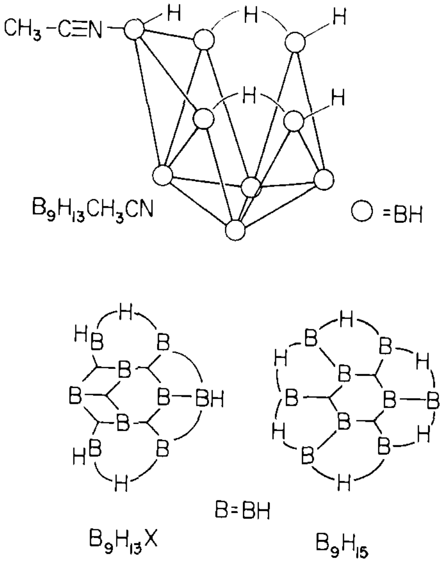


FIG. 12. Approximate geometry of $B_9H_{13}CH_3CN$; topological drawings of $B_9H_{13}X$, $B_9H_{14}^-$ ($X = H^-$), and B_9H_{15}.

C. PREPARATION OF $B_9H_{13}X$ DERIVATIVES FROM $B_{10}H_{13}X^-$ IONS

The compound $(C_2H_5)_2\overset{+}{N}H_2B_{10}H_{13}^-\cdot(C_2H_5)_2NH$, described in Section VI,G, was found to react quantitatively with aqueous acids as shown in the following equation.

$$B_{10}H_{13}\cdot(C_2H_5)_2\overset{-}{N}H + H_3^+O + 2H_2O \rightarrow 2H_2 + B(OH)_3 + B_9H_{13}(C_2H_5)_2NH$$

The composition of the hydride product was deduced (*16*, *19*) from these quantitative results to be $B_9H_{13}\cdot(C_2H_5)_2NH$. Comparison of this reaction with that described by Fitch and Laubengayer (Section VII,A) leaves no doubt that these authors obtained the compound $B_9H_{13}\cdot(CH_3)_2NH$. That a negatively charged 6-(9-) BH_2 group and its bonded hydrogen had been removed in this acidolysis reaction was deduced from this chemical evidence (*16, 19*) and further evidence presented below. On the basis of a preliminary B^{11} nuclear magnetic resonance spectrum Lipscomb predicted (*46*) the correct boron arrangement in $B_9H_{13}X$ derivatives.

The acidolysis of $B_{10}H_{13}X^-$ ions to produce $B_9H_{13}X$ derivatives was extended to systems which contained other ligands and a general preparative method was developed (*19*). Thus, $B_9H_{13}X$ derivatives were prepared by this method which contained diethylamine, ethylamine, triethylamine, triphenylphosphine and pyridine as ligands.

D. Preparation of $B_9H_{13}X$ Derivatives by Alcoholysis of $B_{10}H_{12}X_2$ Compounds and Their Interconversion

The early work of Schaeffer (Section VII,A) suggested that the alcoholysis of $B_{10}H_{12}X_2$ derivatives produced B_9 derivatives. Accordingly, the compound $B_{10}H_{12}\cdot 2(C_2H_5)_2S$ was solvolytically degraded in methanol at the reflux temperature (*16, 19*). The product of this reaction was obtained in 70% yield. Characterization by elemental analysis and its B^{11} nuclear magnetic resonance spectrum allowed this material to be formulated as $B_9H_{13}\cdot(C_2H_5)_2S$. Further characterization was afforded by the conversion of the diethyl sulfide derivative to the known $B_9H_{13}\cdot(C_2H_5)_2NH$ by a ligand displacement reaction (Section VI,D). Thus, the over-all degradation reaction may be written

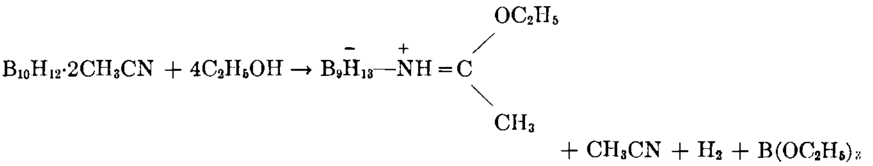
$$B_{10}H_{12}\cdot 2(C_2H_5)_2S + 3ROH \rightarrow B_9H_{13}\cdot(C_2H_5)_2S + H_2 + B(OR)_3 + (C_2H_5)_2S$$

By employing ligand displacement reactions

$$B_9H_{13}\cdot(C_2H_5)_2S + X \rightarrow B_9H_{13}X + (C_2H_5)_2S$$

it was possible to prepare derivatives (*16, 19*) which contained diethylamine, triphenylphosphine, acetonitrile, and a series of substituted pyridines. In every case in which comparison was possible, the products were identical to those produced by acidolysis of the $B_{10}H_{13}X^-$ ion (Section VII,C).

Reinvestigation (*16, 19*) of the alcoholysis of $B_{10}H_{12}\cdot 2CH_3CN$ (*69*) but with ethanol rather than methanol resulted in a product which was formulated as $B_9H_{13}\cdot NH=C(OC_2H_5)CH_3$.



$$B_{10}H_{12}\cdot 2CH_3CN + 4C_2H_5OH \rightarrow \overset{-}{B_9H_{13}}-\overset{+}{N}H=C\begin{matrix} OC_2H_5 \\ CH_3 \end{matrix} + CH_3CN + H_2 + B(OC_2H_5)_3$$

The over-all transformation thus involved a solvolytic degradation reaction coupled with a ligand addition reaction (Section VI,E).

E. MECHANISM OF $B_9H_{13}X$ FORMATION

The fact that $B_{10}H_{12}X_2$ derivatives which contain a strongly bonded ligand (X = triphenylphosphine, triethylamine, etc.) are not solvolytically degraded to $B_9H_{13}X$ derivatives (*19*) suggests that these degradation reactions involve the initial displacement of a ligand molecule by solvent. In the case of acidolysis of $B_{10}H_{13}X^-$ ions this process may be accomplished by protonation of the "hydride ion ligand." Thus, the intermediate $B_{10}H_{12} \cdot X \cdot ROH$ is most likely involved in both types of reaction. Subsequent degradation of this intermediate could lead to the observed products by a variety of feasible paths. Further speculation is not worthwhile at the present time. It seems reasonable, however, to expect solvolytic degradation reactions to play a useful role in future synthetic work.

F. THE $B_9H_{12}X^-$ AND $B_9H_{12}^-$ IONS

Treatment of $B_9H_{13} \cdot C_2H_5NH_2$ with one equivalent of ethylamine produced a salt $C_2H_5NH_3^+B_9H_{12} \cdot C_2H_5NH_2$ in quantitative yield (*16*, *19*). Similar reactions were attempted with other amine derivatives and were unsuccessful. Thus, anions of the general composition $B_9H_{12}X^-$ were shown to be capable of existence. Formally, such anions are topological equivalents of a $B_9H_{13}^{2-}$ ion.

The pyridine derivative, $B_9H_{13}Py$ was found to react with sodium hydride in tetrahydrofuran solution to produce an air-sensitive, blood-red anion and one mole of hydrogen. Neutralization of this anion with anhydrous hydrogen chloride regenerated the $B_9H_{13}Py$ (*19*). This represents the second reported preparation of a $B_9H_{12}X^-$ ion.

Wang *et al.* (*79, 80*) have formulated two possible structures for ions of this type. These structures are represented in topological form in Fig. 13. These authors have also proposed a novel tautomerization process for the interconversion of these isomers and suggest that $B_9H_{12}X^-$ ions are important candidates for structure determination.

In contrast to the results reported above, treatment of $B_9H_{13}(C_2H_5)_2S$ with very strong bases such as tetramethylammonium hydroxide or triphenylmethylene phosphorane results in the near quantitative formation of the ion $B_9H_{12}^-$ (*16, 17, 19*). This ion is probably similar in structure to the $B_9H_{13}X$ compounds since it may be converted to authentic $B_9H_{13}Py$ by treatment with pyridinium chloride in tetrahydrofuran (*19*).

$$B_9H_{13} \cdot (C_2H_5)_2S + OH^- \rightarrow B_9H_{12}^- + (C_2H_5)_2S + H_2O$$

$$B_9H_{12}^- + PyH^+ \rightarrow B_9H_{13}Py$$

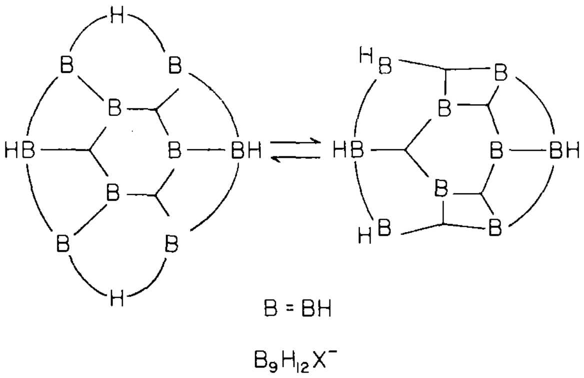


FIG. 13. Topological drawing of possible $B_9H_{12}X^-$ structures.

Further reactions of the $B_9H_{12}^-$ ion have been observed. Methanolysis of the tetramethyl ammonium salt yields tetramethylammonium octahydrotriborate (*17*). This reaction is of preparative importance since the $B_3H_8^-$ ion is difficult to obtain by other means.

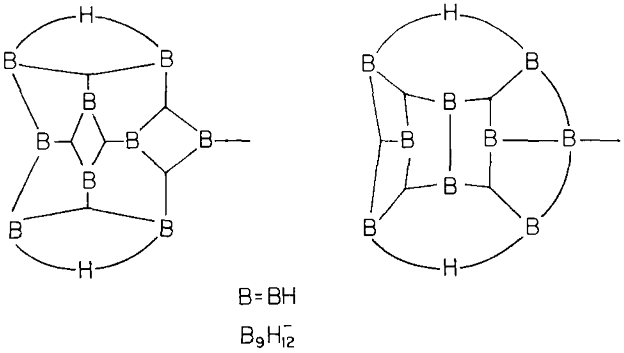


FIG. 14. Topological drawing of possible $B_9H_{12}^-$ structure.

Recent studies by Lipscomb have led to two proposed structures for the $B_9H_{12}^-$ ion (*47*). These structures are shown in Fig. 14.

VIII. The $B_{10}H_{10}^{2-}$ Ion and Its Reactions

A. PREPARATION AND STRUCTURE OF $B_{10}H_{10}^{2-}$

During a study of the ligand displacement reactions of amines with the compound $B_{10}H_{12}\cdot 2CH_3CN$ (*31*), it was observed that triethylamine produced the expected $B_{10}H_{12}\cdot 2(C_2H_5)_3N$ and a second isomer which appeared to be ionic in nature. Conversion of this salt to a *bis*-tetramethylammonium salt required that the accompanying anion be formulated as $B_{10}H_{10}^{2-}$ (*31*). Molecular weight determinations confirmed this formulation (*59*).

$$B_{10}H_{12}\cdot 2CH_3CN + 2(C_2H_5)_3N \rightarrow B_{10}H_{12}\cdot 2(C_2H_5)_3N + 2CH_3CN$$

$$B_{10}H_{12}\cdot 2CH_3CN + 2(C_2H_5)_3N \rightarrow 2(C_2H_5)_3N^{+}H + B_{10}H_{10}^{-2} + 2CH_3CN$$

Later work proved that $B_{10}H_{10}^{2-}$ could be formed in essentially quantitative yield by simply treating $B_{10}H_{12}\cdot 2CH_3CN$ with excess triethylamine in benzene solution at the reflux temperature for several hours. The observation was also made (*31*) that covalent $B_{10}H_{12}\cdot 2(C_2H_5)_3N$ could be converted to the *bis*-triethylammonium salt of $B_{10}H_{10}^{2-}$ by heating with triethylamine in benzene. Thus, $B_{10}H_{12}X_2$ derivatives were tentatively identified as intermediates.

Examination of the reaction of $B_{10}H_{12}\cdot 2(C_2H_5)_2S$ with triethylamine, triphenylmethylene phosphorane and tetramethylammonium hydroxide led to the rapid formation of $B_{10}H_{10}^{2-}$ ion at low temperatures. The rate of conversion of $B_{10}H_{12}X_2$ derivatives to the $B_{10}H_{10}^{2-}$ ion therefore appears to involve the nature of ligand bonding in the $B_{10}H_{12}X_2$ derivative employed. The $B_{10}H_{12}X_2$ derivatives which contain the more weakly bound ligands react most rapidly with bases.

The B^{11} nuclear magnetic resonance spectrum of the $B_{10}H_{10}^{2-}$ ion is shown in Fig. 15. The striking simplicity of this spectrum suggested that the $B_{10}H_{10}^{2-}$ ion had a high order of symmetry. On the basis of this spectrum it was proposed (*49*) that the $B_{10}H_{10}^{2-}$ ion was a polyhedron of D_{4d} symmetry. This geometry is presented in Fig. 16. A simplified molecular orbital treatment, based upon the accepted bonding modes in B_5H_9 and other simplifying assumptions, indicated that the D_{4d} structure was consistent with a 2− ionic charge (*49*). This structure was very recently confirmed by Dobrott and Lipscomb (*7*) by a single crystal X-ray diffraction study of $Cu_2B_{10}H_{10}$. This same study revealed evidence for a novel covalent inter-

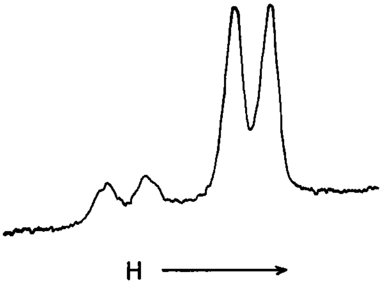


FIG. 15. B^{11} nuclear magnetic resonance spectrum of $B_{10}H_{10}^{2-}$.

action of Cu^I with the $B_{10}H_{10}^{2-}$ polyhedron; the first reported example of three-center interactions of metal ions with boron hydride derivatives.

The discovery and structure elucidation of the polyhedral $B_{10}H_{10}^{2-}$ ion has opened a new door along the corridor of chemistry. The icosahedral $B_{12}H_{12}^{2-}$ ion discussed in Section IX is a second example of a polyhedral ion. Lipscomb has presented attractive arguments for the possible existence of polyhedral $B_5H_5^{2-}(D_{3h})$, $B_6H_6^{2-}(O_h)$ and $B_7H_7^{2-}(D_{5h})$ ions (*47*).

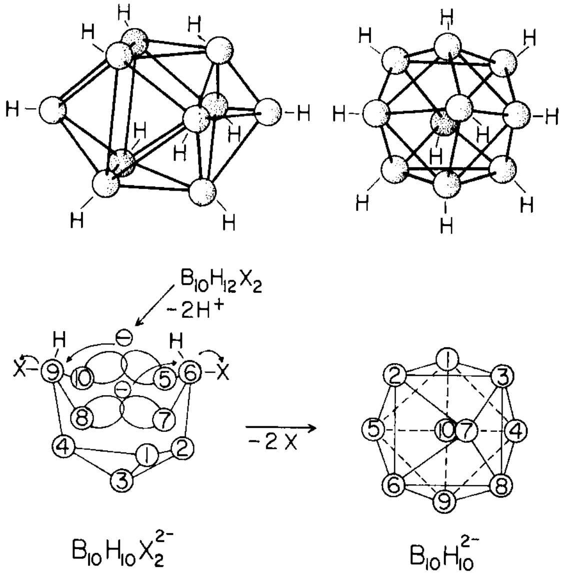


FIG. 16. Geometry of $B_{10}H_{10}^{2-}$ and probable mechanism of formation from $B_{10}H_{12}X_2$.

It is most important to emphasize the fact that polyhedral ions are stabilized by electron delocalization and they may be considered as the inorganic counterparts of aromatic organic compounds. For this reason the topological treatment is uninformative when applied to these polyhedral species. However, molecular orbital methods are most effective even in their most simplified form. The reader is referred to the recent work of Moore *et al.* (*53*) and Hoffmann and Lipscomb (*35*) for dramatic demonstrations of this procedure.

B. MECHANISM OF $B_{10}H_{10}^{2-}$ FORMATION

Evidence cited above strongly suggests that the $B_{10}H_{10}^{2-}$ ion is formed from $B_{10}H_{12}X_2$ derivatives (Section VI) in a base-promoted process. The geometrical arrangement of the

$$B_{10}H_{12}X_2 + 2\ \text{Base} \rightarrow B_{10}H_{10}^{2-} + 2\ \text{Base}\ H^+ + 2X$$

boron atoms in $B_{10}H_{12}X_2$ and $B_{10}H_{10}^{2-}$ are quite different and any proposed mechanism must take this factor into account. Consideration of this problem led to the conclusion that attachment of the 8-(10-) boron atom to the 6-position and similar attachment of 5-(7-) boron atom to the 9-position would uniquely produce the $B_{10}H_{10}^{2-}$ boron atom array (*47*, *58*). The role of base has been attributed to the removal of the bridge hydrogens from the $B_{10}H_{12}X_2$ reactant. The resulting anionic species could collapse to form $B_{10}H_{10}^{2-}$ with the expulsion of the ligand molecules (*58*). The nature of the rate-determining step is not clear at the present time nor is it possible to state that the rearrangement process is concerted or involves discrete intermediates.

The suggested geometrical change has been confirmed (*58*) by determining the location of deuterium atoms in the $B_{10}H_{10}^{2-}$ produced from 1,2,3,4-tetradeuteriodecaborane-14 (*9*). In agreement with prediction, the resulting $B_{10}H_{10}^{2-}$ ion exhibited a "half-collapsed" high field doublet in its B^{11} nuclear magnetic resonance spectrum. This could only come about if the 1, 2, 3, and 4-boron atoms were converted to equatorial positions in the $B_{10}H_{10}^{2-}$ ion. Figure 16 illustrates this point and the proposed mechanism.

C. SUBSTITUTED $B_{10}H_{10}^{2-}$ IONS

Knoth *et al.* (*40*) recently reported the preparation of a series of substituted $B_{10}H_{10}^{2-}$ ions. These materials were, in essence, prepared by electrophilic substitution reactions. Details of this work are not available at the present time.

The $B_{10}H_{10}^{2-}$ ion was totally or partially halogenated by reaction with the halogens in aqueous or ethanolic solution. $B_{10}Cl_{10}^{2-}$, $B_{10}H_3Br_7^{2-}$, $B_{10}H_6I_4^{2-}$ and $B_{10}I_{10}^{2-}$ are examples of halogenated ions of this type (*40*). It was reported that $Cs_2B_{10}Cl_{10}$ was thermally stable to at least 400°C and inert to strong nucleophiles such as hydroxide and methoxide ions.

The hydronium ion salt of $B_{10}H_{10}^{2-}$, $(H_3O)_2B_{10}H_{10}\cdot XH_2O$, proved to be an important reagent in a wide variety of substitution reactions (*40*). As examples, $B_{10}H_9COC_6H_5^{2-}$ and $B_{10}H_9CH(CH_3)C_6H_5^{2-}$ were prepared from this reagent and benzoyl chloride and styrene, respectively. Chlorination of $B_{10}H_9COC_6H_5^{2-}$ produced $B_{10}Cl_9COC_6H_5^{2-}$. Oxidation of $B_{10}H_9COC_6H_5^{2-}$ with hydrogen peroxide produced $B_{10}H_9OCOC_6H_5^{2-}$. Amides, thioethers, ethers, alcohols, and other similar reagents react with the hydronium ion salt to produce substituted derivatives. Examples of these products are $B_{10}H_9N(CH_3)_2H^-$, $B_{10}H_9(CH_3)_2S^-$, $B_{10}H_8\cdot 2(CH_3)_2S$ and $B_{10}H_9OCHO^{2-}$. Preliminary work (*40*) indicates that the $B_{10}H_{10}^{2-}$ ion is most sensitive to electrophilic attack at the apical positions since $B_{10}H_8\cdot 2(CH_3)_2S$ is substituted in both apical positions. Similarly acid-catalyzed deuterium exchange initially occurs in the apical positions.

Hoffmann and Lipscomb (*35*) have carried out a series of molecular orbital calculations for the $B_{10}H_{10}^{2-}$ and substituted $B_{10}H_{10}^{2-}$ ions. From the results of these calculations these authors were able to predict the observed preference for electrophilic attack at the apical positions. By consideration of the resonance and inductive effects present in substituted $B_{10}H_{10}^{2-}$ ions the sequence of further electrophilic substitution was obtained. It is exceedingly clear that the first and second substituents which enter the $B_{10}H_{10}^{2-}$ ion must become attached to the two apical positions.

The preparation of $B_{10}H_9OH^{2-}$ by Kaczmarczyk *et al.* (*37* and Section VIII,D) led to a product with the substituent initially located at an apical position. The large high field doublet, initially like that in $B_{10}H_{10}^{2-}$, of the B^{11} nuclear magnetic resonance spectrum became unsymmetrical after a few hours. This change suggested that the —OH substituent had migrated to an equatorial position. A novel, and thus far substantiated, rearrangement was postulated (*37*). In this process the original B—OH bond does not break, but rather, the polyhedron rearranges in such a fashion as to interconvert apical and equatorial positions with a surprisingly small movement of boron atoms. A further apparent example of this rearrangement is described in the following section (VIII,D). The generality of this type of rearrangement has not been fully examined, but it must be considered in treating the chemistry of all polyhedral ions and derivatives.

D. Hydrogen-Bridge Linked Polyhedral Ions

In 1961 Lipscomb (*47*) presented arguments for the possible existence of ions which were derived from the known $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ (Section IX) ions by linking these simple polyhedra through hydrogen bridges. In the $B_{10}H_{10}^{2-}$ series these predicted species were $B_{20}H_{19}^{3-}$ and $B_{20}H_{18}^{2-}$. Figure 17 presents one possible structure for $B_{20}H_{19}^{3-}$ and two possible structures for $B_{20}H_{18}^{2-}$. Other isomers may be devised, but their existence is considered unlikely for steric reasons. The electronic structure within each B_{10} polyhedron is assumed to be the same as in the parent $B_{10}H_{10}^{2-}$ ion. The process of bridge-hydrogen linking may be looked upon as the replacement of two B—H bonds, one from each $B_{10}H_{10}^{2-}$ ion, by a B—H—B bridge. An infinite chain of doubly linked B_{10} polyhedra would approach the composition $(B_{10}H_8)_n^{2-}$. The resulting polymer would retain a net 2− charge, however (*47*).

Oxidation of the $B_{10}H_{10}^{2-}$ ion with aqueous acidified ferric ion (*59*) has been reported to produce one $B_{20}H_{18}^{2-}$ ion isomer. Similar oxidation reactions which employed ceric ion at low temperatures produced a second

$B_{20}H_{18}^{2-}$ ion isomer (*62*). The product of the ferric ion oxidation was tentatively assigned the asymmetrical structure and the ceric ion oxidation product was assigned the symmetrical structure (*62*). It was shown (*62*) that the presumed symmetrical isomer could be converted to the asymmetrical isomer by treatment with aqueous acids. It is likely that the symmetrical ion is a precursor to the asymmetrical ion. At the present time this novel acid-catalyzed rearrangement is looked upon as another example of B_{10} polyhedron inversion cited above (Section VIII,C) and presumably occurs without breaking bridge-hydrogen linkages.

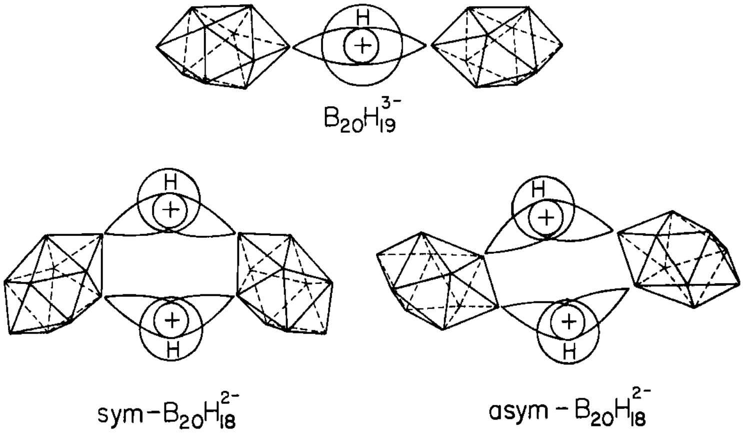


FIG. 17. Approximate geometries of $B_{20}H_{19}^{3-}$ and two $B_{20}H_{18}^{2-}$ isomers.

Treatment of the asymmetrical isomer of $B_{20}H_{18}^{2-}$ with aqueous hydroxide ion leads to the production of apically substituted $B_{10}H_9OH^{2-}$ in quantitative yield (*37*). On aging, the —OH substituent appears, in part, in an equatorial position on the B_{10} polyhedron (Section VIII,C).

The heterogeneous reaction of $CuCl_2(s)$ with $K_2B_{20}H_{10}(s)$ in diethyl ether and other organic solvents produces a novel free radical which is soluble in diethyl ether and purple in color (*37*). The absorption band found at 550 mμ is similar to that of known Cu^{II} complexes. Electron spin measurements yield a *g* value of 2.018 which is small for Cu^{II} but large for free radicals derived from first-row elements (excluding NO). The B^{11} nuclear magnetic resonance spectrum is smeared but resembles the characteristic $B_{10}H_{10}^{2-}$ spectrum (Fig. 15). It was suggested by the discoverers of this reaction that this unusual species is a Cu^{II} complex with a monomeric or polymeric H-bridged B_{10} polyhedron containing species in which the free electron resides most often, but not always, in the B_{10} framework.

Treatment of the presumed asymmetrical $B_{20}H_{18}^{2-}$ ion with an acid ion-exchange resin in ethanol solvent leads to the formation of the salt

$(C_2H_5OH_2)_2B_{20}H_{18}$ which was not isolated. Concentration of this acidic solution followed by the addition of water produced a new boron hydride in 70% yield (*60*). This hydride has been formulated as $B_{18}H_{22}$ and is of unknown structure. Titration of this B_{18} hydride with base proved it to be a strong monoprotic acid. The $B_{18}H_{21}^-$ ion is bright yellow in color with maxima at 216 and 352 mμ.

The reaction of nitrogen dioxide alone or nitric oxide in the presence of ferric ion with the $B_{10}H_{10}^{2-}$ ion produces a variety of highly colored nitrogen containing products (*81*). One of these materials has been characterized (*48*) as a substituted $B_{20}H_{19}^{3-}$ ion, $B_{20}H_{18}NO^{3-}$. The substituted $B_{20}H_{18}^{2-}$ ions $B_{20}H_{14}(NO)_4^{2-}$ and $B_{20}H_{12}(NO)_6^{2-}$ are formed in significant amounts by the same method.The original report of these compounds (*81*) was incorrect in that molecular weight and precise analytical data were not available. The formulas above are based upon the deductions of Lipscomb (*47*, *48*). Hydrogenation of these nitrososubstituted ions with a Raney nickel catalyst produced the corresponding amino derivatives (*81*).

IX. The Icosahedral $B_{12}H_{12}^{2-}$ Ion

A. PREPARATION AND STRUCTURE

The obscure reaction of 2-iododecaborane-14 with triethylamine at the reflux temperature in benzene solution produced the triethyl ammonium salts of the $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ ions (*61*). The latter ion was isolated in little more than trace quantities and this method does not constitute a practical synthesis. Later work reported (*40*) by investigators at the du Pont Company suggests that a practical synthesis of $B_{12}H_{12}^{2-}$ must have been achieved. No other information has been made available on this point.

The $B_{12}H_{12}^{2-}$ ion exhibited a simple doublet in its B^{11} nuclear magnetic resonance spectrum (*61*) and the icosahedral geometry of this ion shown in Fig. 2 was observed by Wunderlich and Lipscomb (*84*) from single crystal X-ray diffraction studies with $K_2B_{12}H_{12}$. Longuet-Higgens (*50*) reported simplified molecular orbital calculations for this ion which were consistent with a 2− net charge. Later calculations by Moore *et al.* (*53*) employed another and more general technique and produced results for related B_{11} hydrides and ions, as well.

B. SUBSTITUTED $B_{12}H_{12}^{2-}$ IONS

Knoth *et al.* (*40*) have reported the preparation of a series of substituted $B_{12}H_{12}^{2-}$ ions. The experimental methods employed were identical to those reported for the preparation of substituted $B_{10}H_{10}^{2-}$ ions (Section VIII,C). Direct halogenation produced $B_{12}F_{12}^{2-}$, $B_{12}Br_{12}^{2-}$, $B_{12}Cl_{10}H_2^{2-}$, $B_{12}H_{11}I^{2-}$, $B_{12}I_{12}^{2-}$ and $B_{12}H_3Br_6Cl_3^{2-}$. Nitration with nitric acid produced the novel ion, $B_{12}H_{11}NO_2^{2-}$. Reaction of the hydronium ion salt $(H_3O)_2B_{12}H_{12}{\cdot}XH_2O$

with oxygen and sulfur containing donor molecules produced derivatives such as $B_{12}H_{11}OCH_3^{2-}$, $B_{12}H_{11}OH^{2-}$ and $B_{12}H_{11}OCOCH_3^{2-}$. Olefins produced alkylated ions such as $B_{12}H_{11}CH(CH_3)C_6H_5^{2-}$.

As in the case of the similar $B_{10}H_{10}^{2-}$ reactions, the mechanism of these reactions is obscure. The problem of sequential electrophilic substitution in the $B_{12}H_{12}^{2-}$ series has been attacked theoretically by Hoffmann and Lipscomb (*35*). Experimental evidence bearing on this point has not been presented.

Lipscomb (*47*) has presented arguments for the possible existence of hydrogen-bridge linked dimers and polymers derived from B_{12} icosahedra. Icosahedra linked by a single B—B bond was also suggested as a possible mode of polymerization. Although hydrogen-bridge linked molecules exist in the B_{10} polyhedra series, no compounds of this type have been reported with B_{12} derivatives.

X. Decaborane-16

A. PREPARATION AND STRUCTURE

A preparation and structure of a new "decaborane," decaborane-16, was recently reported by Grimes *et al.* (*22*). The new hydride was prepared by passing pentaborane-9 through a silent electrical discharge at low pressures and immediately trapping the effluent vapor with cold traps.

The determined structure of $B_{10}H_{16}$ (*22*) is that of two B_5H_9 molecules fused at the apices by a B—B bond with the loss of the apical hydrogen atoms originally present on the B_5H_9 molecules. Figure 18 indicates this geometry. The internal bonding in each B_5H_8 fragment was regarded as identical to that present in B_5H_9 (*43*).

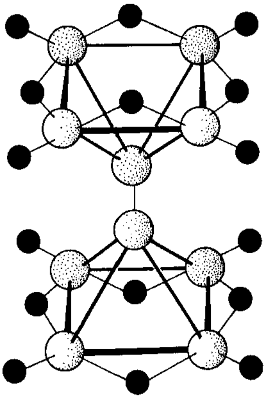


FIG. 18. Approximate geometry of $B_{10}H_{16}$.

B. REACTIONS OF $B_{10}H_{16}$

Grimes and Lipscomb (*21*) have examined a variety of reactions of $B_{10}H_{16}$. In every case, attempted reactions led to the formation of the known $B_{10}H_{14}$ or its derivatives. Thus, iodination of $B_{10}H_{16}$ at 150°C produced $B_{10}H_{14}$ and HI.

$$B_{10}H_{16} + I_2 \rightarrow B_{10}H_{14} + 2HI$$

Aluminum chloride in carbon disulfide converts $B_{10}H_{16}$ to $B_{10}H_{14}$ without hydrogen or hydrogen chloride evolution.

Pyridine and $B_{10}H_{16}$ produced the same materials as were obtained from $B_{10}H_{14}$ and pyridine (Section VI).

The mechanism of these interconversion reactions has not been established. However, a plausible mechanism has been proposed (*21*) which is based upon topological arguments and the known rearrangement (*54*) of apical substituted alkylpentaborane-9 to the basal substituted isomer. The suggestion has also been made that the pyrolytic reaction of B_2H_6 to produce $B_{10}H_{14}$ proceeds via $B_{10}H_{16}$ (*21*, Section II,A).

Hydrogen iodide at room temperature cleaves the apex-apex bond with the formation of pentaborane-9 and iodopentaborane-9. At 100° this reaction produces a quantitative yield of pentaborane-9 while the iodopentaborane-9 is converted to polymeric products. Similar reactions were observed with hydrogen bromide at elevated temperatures.

Decaborane-16 is inert toward iodine and bromine in an anhydrous medium.

XI. Conclusion

As indicated by this brief review, the chemistry of the higher hydrides of boron has barely been touched. It is hoped that research workers and teachers will find this review useful. Its timeliness cannot be guaranteed.

Notes Added in Proof

1. A DERIVATIVE OF AN OCTABORANE

The compound referred to in Section VII,F(*16, 19*) as a $B_9H_{12}X^-$ anion ($X = C_2H_5NH_2$) has recently been shown [R. Lewin, P. G. Simpson, and W. N. Lipscomb, *J. Am. Chem. Soc.* (in press)] to actually be an octaborane derivative. Treatment of $B_9H_{13}X$ ($X = C_2H_5NH_2$) with ethylamine does not result in proton abstraction but rather produces a cleavage reaction with loss of a BH_3 group. The structure of the resulting compound, $C_2H_5NH_2B_8H_{11}NHC_2H_5$, is novel in that it contains a nitrogen atom in a bridge position. The determined structure shows this new octaborane derivative to be a icosahedral fragment and Figure 19 presents its structure in

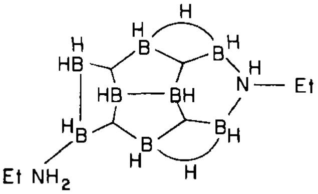


FIG. 19. Topological drawing of $C_2H_5NH_2B_8H_{11}NHC_2H_5$.

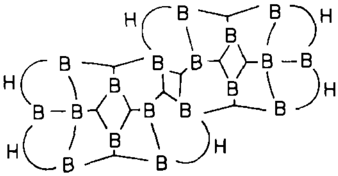


FIG. 20. Topological drawing of $B_{18}H_{22}$.

topological form. This new result does not exclude the probable existence of a $B_9H_{12}X^-$ anion with pyridine as the ligand, X.

2. THE STRUCTURE OF $B_{18}H_{22}$

The new boron hydride $B_{18}H_{22}$ described in Section VII,D(*60*) has been shown by single crystal X-ray studies [P. G. Simpson and W. N. Lipscomb, *Proc. Nat'l. Acad. Sci. U.S.* (in press)] to be closely related to $B_{10}H_{14}$. The determined structure of $B_{18}H_{22}$ is that of two decaborane molecules sharing boron atoms 6 and 9 in common. The topological structure of $B_{18}H_{22}$ is shown in Fig. 20. The unusual boron atoms which are shared in common by the two icosahedral fragments are each co-ordinated to six other boron atoms. In addition, a hydrogen bridge serves to connect each shared boron atom to one of its 6 neighboring boron atoms.

3. THE PREPARATION OF ICOSAHEDRAL 11,12-DICARBADODECABORANE

Very recently workers at the Olin Mathieson Chemical Corporation, [H. Schroeder, T. L. Heying, J. R. Reiner, *J. Inorg. Chem.* (in press)] have described the preparation of a carborane isoelectronic with the $B_{12}H_{12}^{2-}$ ion. This carborane, $B_{10}C_2H_{12}$, was readily formed from acetylene, decaborane and diethylsulfide in *n*-propyl ether at elevated temperatures. [C. C. Clark, U.S. Patent 3,062,756 (November 6, 1962).]

Chlorination of this new carborane results in successive replacements of hydrogen by chlorine at boron. In this manner $B_{10}Cl_{10}C_2H_2$ and $B_{10}Cl_{10}C_2HCl$ were prepared. Examination of the B^{11} nuclear magnetic resonance spectra of $B_{10}C_2H_{12}$ and its chlorinated derivatives indicates that the two carbon atoms were nearest neighbors in the icosahedral framework.

4. CORRECTION REGARDING $B_{20}H_{18}^{2-}$ ISOMERS

The oxidation of triethylammonium $B_{10}H_{10}^{2-}$ with ceric ion does not produce the second (symmetrical) isomer of $B_{20}H_{18}^{2-}$ (*62*) (M. F. Hawthorne and R. L. Pilling, unpublished results) as discussed in Section VIII,D. The product obtained is a double salt,

$$(Et_3\overset{+}{N}H)_5\, B_{20}H_{18}^{2-}\ (\text{asymmetrical})\ B_{20}H_{19}^{3-},$$

which has been separated into its component ions.

The hydroxide ion cleavage of asymmetrical $B_{20}H_{18}^{2-}$ yields $B_{20}H_{17}OH^{4-}$ rather than the previously reported apically substituted $B_{10}H_9OH^{2-}$ (*37*). These and other related results will be reported elsewhere in the near future.

References

1. Aftandilian, V. D., Miller, H. C., and Muetterties, E. L., *J. Am. Chem. Soc.* **83,** 2471 (1961).
2. Atteberry, R. W., *J. Phys. Chem.* **62,** 1458 (1958).
3. Beachell, H. C., and Dietrich, B. F., *J. Am. Chem. Soc.* **83,** 1347 (1961).
4. Beachell, H. C., and Hoffman, D. E., *J. Am. Chem. Soc.* **84,** 180 (1962).
5. Blay, N. J., Dunstan, I., and Williams, R. L., *J. Chem. Soc.* 430 (1960).
6. Dickerson, R. E., and Lipscomb, W. N., *J. Chem. Phys.* **27,** p. 212 (1957).
7. Dobrott, R. D., and Lipscomb, W. N., *J. Chem. Phys.* **37,** 1779 (1962).
8. Dunstan, I., Blay, N. J., and Williams, R. L., *J. Chem. Soc.* p. 5016 (1960).
9. Dupont, J. A., and Hawthorne, M. F., *J. Am. Chem. Soc.* **84,** 1804 (1962).
10. Dupont, J. A., and Hawthorne, M. F., *Chem. & Ind.* (*London*) p. 405 (1962).
11. Dupont, J. A., and Hawthorne, M. F., *J. Am. Chem. Soc.* **81,** 4998 (1959).
12. Eberhardt, W. H., Crawford, B. L., and Lipscomb, W. N., *J. Chem. Phys.* **22,** 989 (1954).
13. Fetter, N. R., *Chem. & Ind.* (*London*) p. 1548 (1959).
14. Fitch, S. J., and Laubengayer, A. W., *J. Am. Chem. Soc.* **80,** 5911 (1958).
15. Graybill, B. M., and Hawthorne, M. F., *J. Am. Chem. Soc.* **83,** 2573 (1961).
16. Graybill, B. M., Pitochelli, A. R., and Hawthorne, M. F., *Abstrs. Papers 138th Meeting Am. Chem. Soc., New York, Sept., 1960,* p. 45N.
17. Graybill, B. M., Ruff, J. K., and Hawthorne, M. F., *J. Am. Chem. Soc.* **83,** 2669 (1961).
18. Graybill, B. M., Pitochelli, A. R., and Hawthorne, M. F., *J. Inorg. Chem.* **1,** 622 (1962).
19. Graybill, B. M., Pitochelli, A. R., and Hawthorne, M. F., *J. Inorg. Chem.* **1,** 626 (1962).
20. Griffiths, J. V., and Williams, R. L., *Chem. & Ind.* (*London*) p. 655 (1958).
21. Grimes, R. N., and Lipscomb, W. N., *Proc. Natl. Acad. Sci. U. S.* **48,** 496 (1962).
22. Grimes, R., Wang, F. E., Lewin, R., and Lipscomb, W. N., *Proc. Natl. Acad. Sci. U. S.* **47,** 996 (1961).
23. Guter, G. A., and Schaeffer, G. W., *J. Am. Chem. Soc.* **78,** 3546 (1956).
24. Hammett, L. P., "Physical Organic Chemistry." McGraw-Hill, New York, 1940.
25. Hawthorne, M. F., *J. Am. Chem. Soc.* **80,** 3480 (1958).
26. Hawthorne, M. F., *Abstrs. Papers 135th Meeting Am. Chem. Soc., Boston, Massachusetts, April, 1959,* p. 40-O.
27. Hawthorne, M. F., and Miller, J. J., *J. Am. Chem. Soc.* **82,** 500 (1960).
28. Hawthorne, M. F., and Miller, J. J., *J. Am. Chem. Soc.* **80,** 754 (1958).
29. Hawthorne, M. F., Pitochelli, A. R., Strahm, R. D., and Miller, J. J., *J. Am. Chem. Soc.* **82,** 1825 (1960).
30. Hawthorne, M. F., and Pitochelli, A. R., *J. Am. Chem. Soc.* **80,** 6685 (1958).
31. Hawthorne, M. F., and Pitochelli, A. R., *J. Am. Chem. Soc.* **81,** 5519 (1959).
32. Hillman, M., *J. Inorg. & Nucl. Chem.* **12,** 383 (1960).
33. Hillman, M., *J. Am. Chem. Soc.* **82,** 1096 (1960).
34. Hillman, M., Mangold, D. J., and Norman, J. H., *Abstrs. Papers 133rd Meeting Am. Chem. Soc., San Francisco, California, April, 1958,* p. 18L.

35. Hoffmann, R., and Lipscomb, W. N., *J. Chem. Phys.* **37**, 2872 (1962).
36. Hough, W. V., and Edwards, L. J., *Abstrs. Papers 133rd Meeting Am. Chem. Soc., San Francisco, California, 1958*, p. 28L.
37. Kaczmarczyk, A., Dobrott, R. D., and Lipscomb, W. N., *Proc. Natl. Acad. Sci. U. S.* **48**, 729 (1962).
38. Kasper, J. S., Lucht, C. M., and Harker, D., *Acta Cyst.* **3**, 436 (1950).
39. Kaufman, J. J., *Abstrs. Papers 141st Meeting Am. Chem. Soc., Washington, D. C., March, 1962*, p. 3R.
40. Knoth, W. H., Miller, H. C., England, D. C., Parshall, G. W., and Muetterties, E. L., *J. Am. Chem. Soc.* **84**, 1056 (1962).
41. Knoth, W. H., and Muetterties, E. L., *J. Inorg. & Nucl. Chem.* **20**, 66 (1961).
42. Laubengayer, A. W., and Bottei, R., *J. Am. Chem. Soc.* **74**, 1618 (1952).
43. Lipscomb, W. N., *Advances in Inorg. Chem. Radiochem.* **1**, 117 (1959).
44. Lipscomb, W. N., *J. Phys. Chem.* **62**, 381 (1958).
45. Lipscomb, W. N., *Proc. Natl. Acad. Sci. U. S.* **47**, 1791 (1961).
46. Lipscomb, W. N., Private Communication (1960).
47. Lipscomb, W. N., *Proc. Natl. Acad. Sci. U. S.* **47**, 1791 (1961).
48. Lipscomb, W. N., Private Communication (1962).
49. Lipscomb, W. N., Pitochelli, A. R., and Hawthorne, M. F., *J. Am. Chem. Soc.* **80**, 6685 (1958).
50. Longuet-Higgins, H. C., and Roberts, M., *Proc. Roy. Soc.* **A230**, 110 (1955).
51. Miller, J. J., and Hawthorne, M. F., *J. Am. Chem. Soc.* **81**, 4501 (1959).
52. Moore, E. B., Dickerson, R. E., and Lipscomb, W. N., *J. Chem. Phys.* **27**, 209 (1957).
53. Moore, E. B., Lohr, L. L., and Lipscomb, W. N., *J. Chem. Phys.* **34**, 1329 (1961).
54. Onak, T. P., *J. Am. Chem. Soc.* **83**, 2584 (1961).
55. Pace, R. J., Williams, J., and Williams, R. L., *J. Chem. Soc.* p. 2196 (1961).
56. Palchak, R. J. F., Norman, J. H., and Williams, R. E., *J. Am. Chem. Soc.* **83**, 3380 (1961).
57. Phillips, W. D., Miller, H. C., and Mueterties, E. L., *J. Am. Chem. Soc.* **81**, 4496 (1959).
58. Pitochelli, A. R., Ettinger, R., Dupont, J. A., and Hawthorne, M. F., *J. Am. Chem. Soc.* **84**, 1057 (1962).
59. Pitochelli, A. R., and Hawthorne, M. F., Unpublished Results (1959).
60. Pitochelli, A. R., and Hawthorne, M. F., *J. Am. Chem. Soc.* **84**, 3218 (1962).
61. Pitochelli, A. R., and Hawthorne, M. F., *J. Am. Chem. Soc.* **82**, 3228 (1960).
62. Pitochelli, A. R., Lipscomb, W. N., and Hawthorne, M. F., *J. Am. Chem. Soc.* **84**, 3026 (1962).
63. Polak, R. J., and Heying, T. L., *J. Org. Chem.* **27**, 1483 (1962).
64. Reddy, J., and Lipscomb, W. N., *J. Chem. Phys.* **31**, 610 (1959).
65. Reddy, J., and Lipscomb, W. N., *J. Am. Chem. Soc.* **81**, 754 (1959).
66. Ruff, J. K., and Hawthorne, M. F., Unpublished Results (1958).
67. Sands, D. E., and Zalkin, A., *Acta Cyst.* **13**, 1030 (1960).
68. Schaeffer, R., Private communication (1956).
69. Schaeffer, R., *J. Am. Chem. Soc.* **79**, 1006 (1957).
70. Schaeffer, R., *J. Am. Chem. Soc.* **79**, 2726 (1957).
71. Schaeffer, G. W., and Burns, J. J., *Abstrs. Papers 135th Meeting Am. Chem. Soc., Boston, Massachusetts, April, 1959*, p. 44M.
72. Schaeffer, R., Shoolery, J. N., and Jones, R., *J. Am. Chem. Soc.* **80**, 2670 (1958).
73. Schaeffer, R., Shoolery, J. N., and Jones, R., *J. Am. Chem. Soc.* **79**, 4606 (1957).
74. Shapiro, I., Lustig, M., and Williams, R. E., *J. Am. Chem. Soc.* **81**, 4998 (1959)

75. Siegel, B., Mack, J. L., Lowe, J. V., and Gallaghan, J., *J. Am. Chem. Soc.* **80,** 4523 (1958).

76. Stock, A., "Hydrides of Boron and Silicon." Cornell Univ. Press, Ithaca, New York, 1935.

77. Toeniskoetter, R. H., Thesis, St. Louis University, St. Louis, Missouri, (1956).

78. Toeniskoetter, R. H., Schaeffer, G. W., Evers, E. C., Hughes, R. E., and Bagley, G. E., *Abstrs. Papers 134th Meeting Am. Chem. Soc., Chicago, Illinois, Sept., 1958,* p. 23N.

79. Wang, F. E., Simpson, P. G., and Lipscomb, W. N., *J. Am. Chem. Soc.* **83,** 491 (1961).

80. Wang, F. E., Simpson, P. G., and Lipscomb, W. N., *J. Chem. Phys.* **35,** 1335 (1961).

81. Wiesboeck, R. A., Pitochelli, A. R., and Hawthorne, M. F., *J. Am. Chem. Soc.* **83,** 4109 (1961).

82. Williams, R. L., Dunstan, I., and Blay, W. J., *J. Chem. Soc.* p. 5006 (1960).

83. Williams, R. E., and Shapiro, I., *J. Chem. Phys.* **29,** 677 (1958).

84. Wunderlich, J. A., and Lipscomb, W. N., *J. Am. Chem. Soc.* **82,** 4427 (1960).