BORON

ANNUAL SURVEY COVERING THE YEAR 1971

PART I: CARBORANES AND HYDROBORATION

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CONTENTS

I. INTRODUCTION

The division of boron chemistry into two sections remains the same as last year. This section contains two parts, carborane chemistry and hydroboration chemistry.

The areas of major activity have continued to develop in the manner established in previous years. M. F. Hawthorne's research group has continued to produce novel types of transition metal derivatives of carboranes, and L. I. Zakharkin and other Russian workers have been synthesizing great numbers of substituted carboranes. H. C. Brown continues to dominate hydroboration chemistry, and many others are beginning to take a serious interest in applying hydroboration to their own ends.

II. CARBORANES

A. Dicarbollyl compounds

1. Transition metals. The largest previously known polyhedron in the carborane series was the icosahedron (12 atoms). Dunks, McKown, and Hawthorne have now announced the synthesis of a 13-atom ($B_{10}C_2Co$) polyhedron. Evidently the alkali metal reduction of carborane (Zakharkin, AS 66; 82) opens a pentagonal face in the icosahedral carborane, which accounts for the tendency of m-carborane

to rearrange to <u>o</u>-carborane on reduction (AS 66; 82) as well as the ability of the reduced species to incorporate a cobalt atom into an enlarged cage. The synthesis was carried out by reducing <u>o</u>-carborane with sodium and naphthalene in tetrahydrofuran to form $B_{10}C_2H_{12}^{2-}$, which was then treated with NaC_5H_5 followed by $CoCl_2$ to yield $(C_5H_5)Co(B_{10}C_2H_{12})$ (Fig. 1) [1].

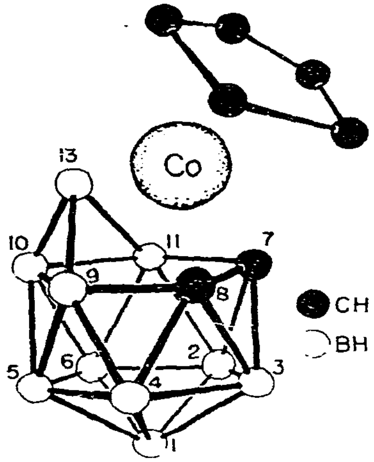


Figure 1. The proposed structure of π-cyclopentadienyl-π-dodecahydro-7,8-dicarba-<u>nido</u>-dodecaboratocobalt, $(C_5H_5)Co(7,8\text{-}B_{10}C_2H_{12})$. (from G. B. Dunks, M. M. McKown, and M. F. Hawthorne, J. Amer. Chem. Soc., 93 (1971) 2542).

The 80.5 MHz boron-11 nmr spectrum (Fig. 2) consists of doublets in the ratio 1:2:1:2:1:2:1, consistent with a molecule containing four unique boron atoms and three unique pairs of boron atoms. The compound initially obtained readily undergoes thermal isomerization in refluxing hexane and a further isomerization in refluxing benzene to form less symmetrical structures (not yet assigned). The anion $(B_{10}C_2H_{12})_2Co^-$ was also apparently formed as a by-product in the preparation of the cyclopentadienyl compound.

In an analogous synthesis involving smaller cages, treatment of $1,6\text{-}B_8C_2H_{10}$ with sodium naphthalide in tetrahydrofuran leads to the dianion $B_8C_2H_{10}^{2-}$, which on treatment with sodium cyclopentadienide and $CoCl_2$ yields the B_8-dicarbollide cobalt cyclopentadienide complex (Fig. 3) [2].

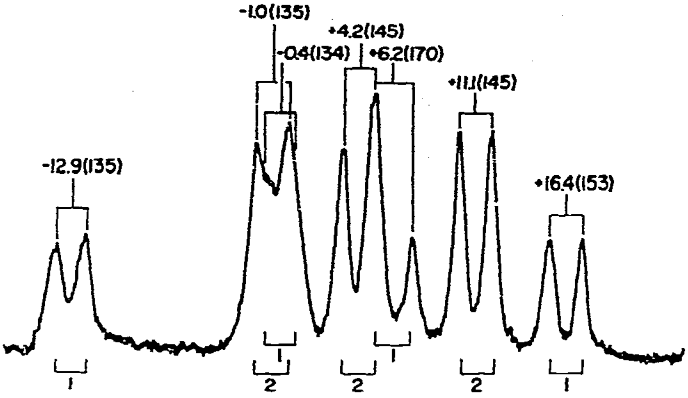


Figure 2. The 80.5-MHz ^{11}B nmr spectrum of $(C_5H_5)Co(7,8\text{-}B_{10}C_2H_{12})$ taken in acetone-$\underline{d}_6$. Chemical shifts (parts per million relative to $BF_3 \cdot O(C_2H_5)_2$ and coupling constants (hertz) are indicated. Relative areas appear beneath the peaks. (from G. B. Dunks, M. M. McKown, and M. F. Hawthorne, J. Amer. Chem. Soc., 93 (1971) 2542).

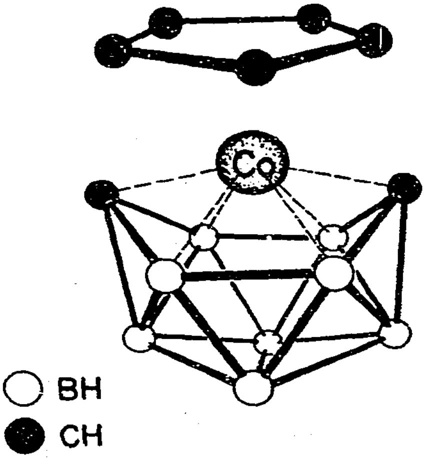


Figure 3. The proposed structure of $B_8C_2H_{10}CoC_5H_5$. (from W. J. Evans and M. F. Hawthorne, J. Amer. Chem. Soc., 93 (1971) 3064).

Thermal rearrangement of π-cyclopentadienyl-(3)-1,2-dicarbollylcobalt (III) and homologs (Fig. 4) at 400-700° in the gas phase has led to a number of isomers

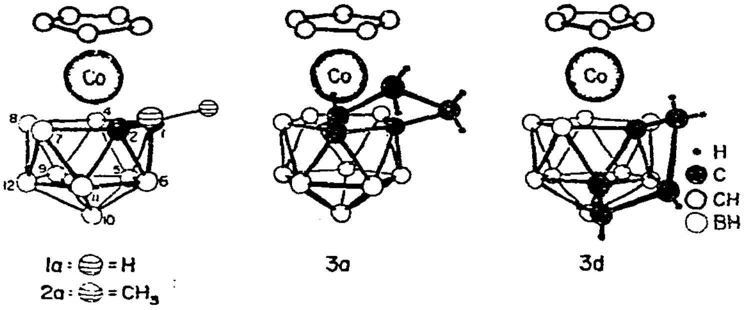


Figure 4. Proposed structures f π-cyclopentadienyl-π-(3)-1,2-dicarbollylcobalt (III) (1a), π-cyclopentadienyl-π-(3)-1,2-dimethyl-1,2-dicarbollylcobalt (III) (2a), π-cyclopentadienyl-π-(3)-μ-1,2-trimethylene-1,2-dicarbollylcobalt (III) (3a), and π-cyclopentadienyl-π-(3)-μ-1,6-trimethylene-1,6-dicarbollylcobalt (III) (3d). (from M. K. Kaloustian, R. J. Wiersema, and M. F. Hawthorne, J. Amer. Chem. Soc., 93 (1971) 4912).

(Fig. 5 and 6), including the first example of a dicarbollyl complex having only boron atoms in the metal-bonding face (Fig. 4, structure 1e) [3].

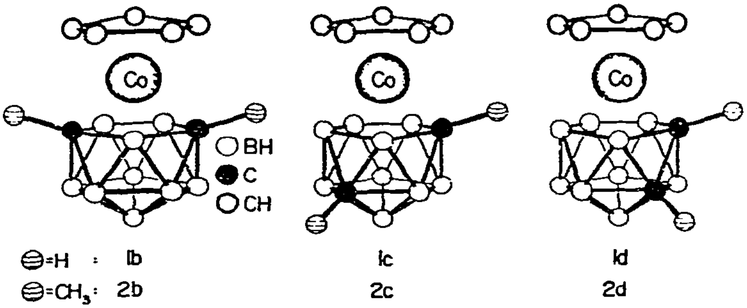


Figure 5. Proposed structures of isomers 1b, 1c, 1d, 2b, 2c, and 2d resulting from the rearrangement of $(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_9R_2)$ (R=H,CH$_3$) at 400-500°. (from M. K. Kaloustian, R. J. Wiersema, and M. F. Hawthorne, J. Amer. Chem. Soc., 93 (1971) 4912).

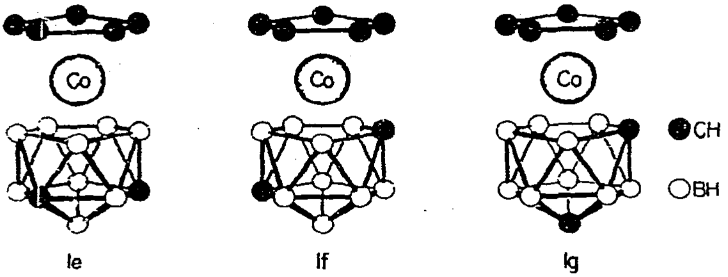


Figure 6. Proposed structures of isomers le, lf, and lg, resulting from the rearrangement of $(\pi-C_5H_5)Co(\pi-1,11-B_9C_2H_{11})$ at 600-700°. (from M. K. Kaloustian, R. J. Wiersema, and M. F. Hawthorne, J. Amer. Chem. Soc., 93 (1971) 4912).

Bisdicarbollyliron(II), $(B_9C_2H_{11})_2Fe^{2-}$, is protonated in strong aqueous acids and the salt $Ph_3PMe^+H(B_9C_2H_{11})_2Fe^-$ has been isolated [4]. Treatment of the protonated species with diethyl sulfide results in replacement of a boron-bound hydrogen by Et_2S to form $(B_9C_2H_{11})Fe(B_9C_2H_{10}SEt_2)^-$ (Fig. 7).

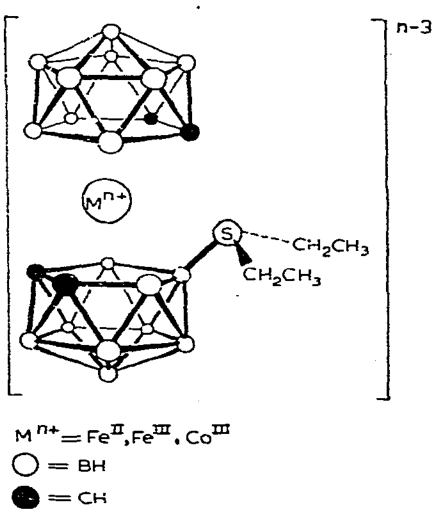


Figure 7. Proposed structures of $([\pi-(3)-1,2-B_9C_2H_{11}][\pi-(3)-1,2-B_9C_2H_{10}S(C_2H_5)_2]M^{n+})^{n-3}$; M = Fe^{II}, Fe^{III}, Co^{III}. (from M. F. Hawthorne, L. F. Warren, Jr., K. P. Callahan, and N. F. Travers, J. Amer. Chem. Soc., 93 (1971) 2407).

Although the protonated dicarbollyl complexes were not isolable, iron(III) and cobalt(III) dicarbollides yielded substitution products with acid and diethyl sulfide.

Francis and Hawthorne have extended their work on the acid catalyzed condensation of carbon disulfide with bis(dicarbollyl)cobalt(III) anion (AS 69; 327) to include reaction of CS_2 with the *m*-dicarbollide isomer to produce a similar cyclic product (Fig. 8), a similar cyclic product from acetic acid and bis(dicarbollyl)cobalt(III) (Fig. 9), and another from CS_2 and bis(dicarbollyl)iron(III) [5].

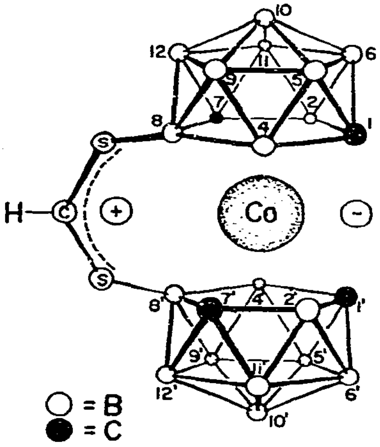


Figure 8. Proposed structure of one enantiomer of *dl*-$(1,7\text{-}B_9C_2H_{10})_2CoS_2CH$ in schematic form with H atoms omitted. (from J. N. Francis and M. F. Hawthorne, Inorg. Chem., 10 (1971) 596).

The X-ray structure of the reaction product from $(B_9C_2H_{11})_2Co^-$ with CS_2, HCl, and $AlCl_3$ has been reported (Fig. 10) [6].

Details of the preparation of two cobalt (3,6)-1,2-dicarbacanastide complexes (AS 68; 12 and 70; 6-8) (Fig. 11 and 12) have been reported [7]. These are based on the hypothetical dicarbacanastide (Spanish "canasta" meaning "basket") anion (Fig. 13), which is not known as an uncomplexed anion. From cyclic

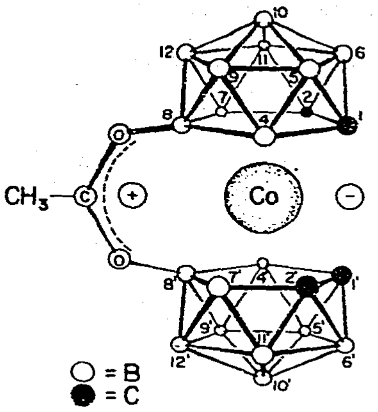


Figure 9. Proposed structure of $(1,2\text{-}B_9C_2H_{10})_2CoO_2C(CH_3)$ in schematic form with H atoms omitted. (from J. N. Francis and M. F. Hawthorne, Inorg. Chem., 10 (1971) 597).

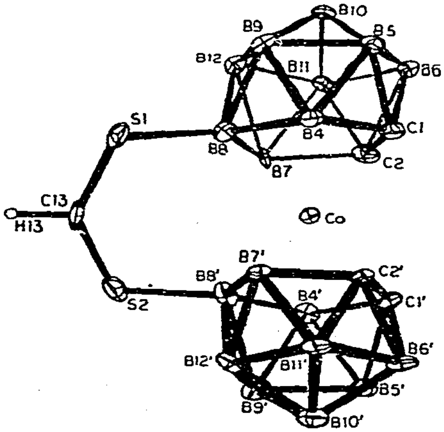


Figure 10. The $[(B_9C_2H_{10})_2S_2CH]Co^{III}$ molecule, projected onto the S(1)-C(13)CS(2) plane (OTLIPS diagram[15]). (from M. R. Churchill and K. Gold, Inorg. Chem., 10 (1971) 1928).

voltammetry studies, it appears that these two- and three-cobalt-atom complexes tend to gain or lose only one electron, as if the electron is delocalized over the entire molecule.

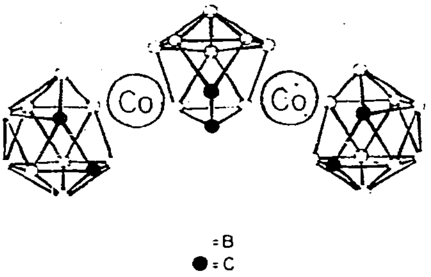


Figure 11. Schematic drawing of $(B_9C_2H_{11})Co(B_8C_2H_{10})Co(B_9C_2H_{11})^{2-}$ ion (I) with H atoms omitted. (from J. N. Francis and M. F. Hawthorne, Inorg. Chem., 10 (1971) 863).

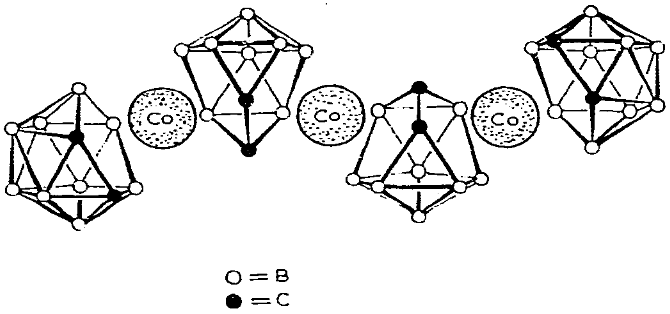


Figure 12. Schematic drawing of $[(B_9C_2H_{11})Co(B_8C_2H_{10})]_2Co^{3-}$ ion (II) with H atoms omitted. (from J. N. Francis and M. F. Hawthorne, Inorg. Chem., 10 (1971) 863).

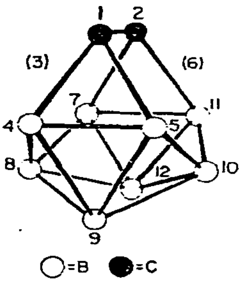


Figure 13. Schematic drawing of the (3,6)-dicarbacanastide ion with H atoms omitted. (from J. N. Francis and M. F. Hawthorne, Inorg. Chem., 10 (1971) 863).

Knoth has reported full details of the synthesis of one-carbon carboranes and carbollide complexes (AS 67; 273-275) from cyanodecaborane [8]. Structures obtained are illustrated in Figs. 14-18.

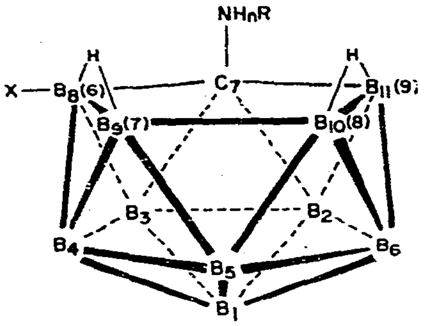


Figure 14. Skeletal structures, where numbers in parentheses refer to original atom positions in decaborane: (A) $B_{10}H_{12}CNH_2R$ (R = H, alkyl, n = 2, X = OH); (B) $B_{10}H_{11}(OH)CNH_3$ (R = H, n = 2, X = OH); (C) $C_6H_5CONHCB_{10}H_{11}S(CH_3)_2$ (R = C_6H_5CO, n = 1, X = $S(CH_3)_2$). (from W. H. Knoth, Inorg. Chem., 10 (1971) 598).

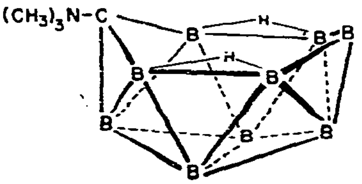


Figure 15. $B_9H_{11}CN(CH_3)_3$ (terminal hydrogen atoms omitted). (from W. H. Knoth, Inorg. Chem., 10 (1971) 599).

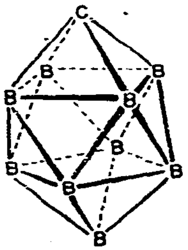


Figure 16. Skeletal structure of 1-$B_9H_9CH^-$. (from W. H. Knoth, Inorg. Chem., 10 (1971) 599).

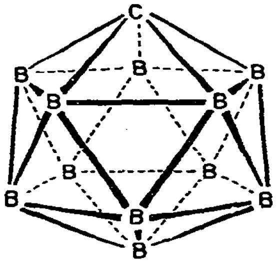


Figure 17. Skeletal structure of $B_{11}H_{11}CH^{-}$. (from W. H. Knoth, Inorg. Chem., 10 (1971) 600).

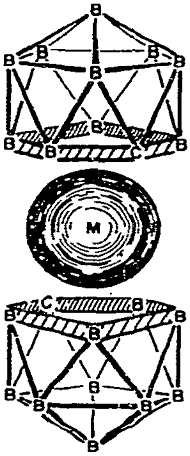


Figure 18. Skeletal structure proposed for metallocarboranes derived from $B_{10}H_{10}CH^{3-}$ and $B_{10}H_{10}CNH_3{}^{2-}$. (from W. H. Knoth, Inorg. Chem., 10 (1971) 601).

The structure of the $(B_9C_2H_9Me_2)_2Cr^{-}$ ion has been determined by X-ray (Fig. 19) [9].

Magnetic susceptibility measurements for $(C_5H_5)Fe(B_9C_2H_{11})$ and $Me_4N^{+}Fe(B_9C_2H_{11})^{-}$ [10] and Mössbauer spectra of bis(dicarbollyl)iron(II) and (III) anions have been reported [11].

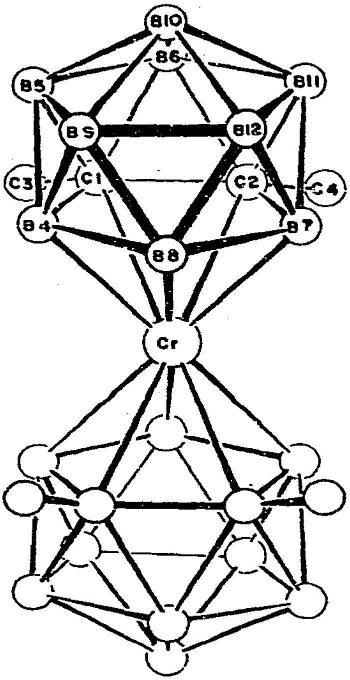


Figure 19. Skeletal drawing of the $Cr[B_9C_2H_9(CH_3)_2]_2^-$ anion (hydrogen atoms not shown) and numbering system. (from D. St. Clair, A. Zalkin, and D. H. Templeton, Inorg. Chem., 10 (1971) 2587).

2. Nontransition elements. Trialkylaluminums and trialkylgalliums react with the nido-carborane (3)-1,2-$B_9C_2H_{13}$ (from protonation of dicarbollide ion) to form 1,2-$B_9C_2H_{12}AlMe_2$ (Fig. 20) and analogous compounds [12]. The X-ray crystal structure of the dimethylaluminum compound has been reported [13]. The dimethylaluminum group is bonded to two boron atoms and appears to have B-H-Al bridges on each side. From nmr studies it appears that the $AlMe_2$ group tautomerizes rapidly between two equivalent positions along the edge of the dicarbollide face (Fig. 21) [12]. Heating the nido compounds $B_9C_2H_{12}MR_2$ in benzene yields the closo derivatives, 1,2-$B_9C_2H_{11}MR$ (Fig. 22). These can be isomerized to the m-carborane analogs, (3)-1,7-$B_9C_2H_{11}MR$, at 410°. Either the

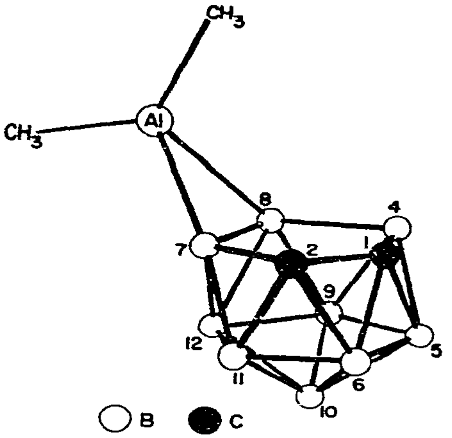


Figure 20. Schematic representation of the reported[9] crystallographic structure of 7,8-μ-dimethylalumino-1,2-dicarba-nido-undecaborane(13), II. (from D. A. T. Young, R. J. Wiersema, and M. F. Hawthorne, J. Amer. Chem. Soc., 93 (1971) 5688).

closo or the nido compounds will react with $TiCl_4$ to produce catalysts which will polymerize ethylene at 25° and 1 atmosphere. The aluminum and gallium carborane derivatives react explosively with water.

The preparation of the dicarbollylberyllium compounds $B_9C_2H_{11}BeOEt_2$ and $B_9C_2H_{11}BeNMe_3$ (AS 68; 19-20) has been reported in detail [14].

Zakharkin and Kysin have reported the rearrangement of o-$B_{10}H_{10}AsCH$ to the m-isomer at 500-550° and to the p-isomer at 600-650° in a flow system [15]. Halogenation of these arsacarboranes was studied under electrophilic and radical conditions, and the rates of halogenation were found to be faster than those of carboranes of phosphacarboranes. m-Phosphacarborane, $B_{10}H_{10}CHP$, has been converted to the lithio derivative, the carboxylic acid, and the acid chloride, $B_{10}H_{10}PC\text{-}COCl$, which acylates benzene in the presence of $AlCl_3$ to form the ketone, $B_{10}H_{10}PC\text{-}COPh$ [16].

3. Dicarbollide anions. Deuterium exchange reactions in conjunction with infrared and ^{11}B nmr studies have provided information about the location of the

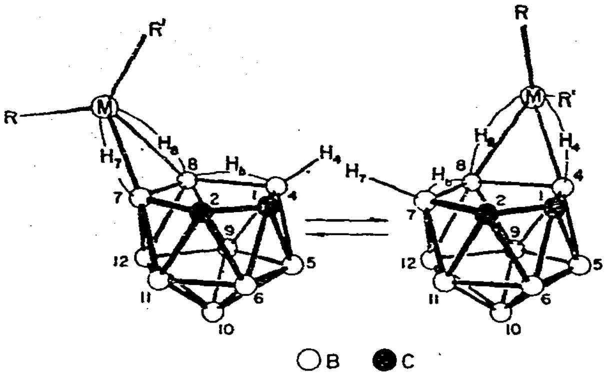


Figure 21. Proposed mechanism for the tautomeric process in the nido-dialkylaluminum and -gallium complexes I, II, and III. (from D. A. T. Young, R. J. Wiersema, and M. F. Hawthorne, J. Amer. Chem. Soc., 93 (1971) 5689).

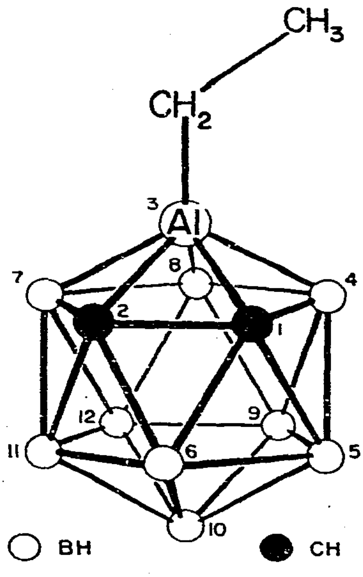


Figure 22. Schematic representation of the reported[8] structure of 3-ethyl-3-alumino-1,2-dicarba-closo-dodecaborane(12), IV. (from D. A. T. Young, R. J. Wiersema, and M. F. Hawthorne, J. Amer. Chem. Soc., 93 (1971) 5691).

open-face-bonded hydrogen atoms in (3)-1,2-$B_9C_2H_{12}^-$, (3)-1,2-$B_9C_2H_{13}$, and (3)-1,7-$B_9C_2H_{12}^-$ [17]. In (3)-1,2-$B_9C_2H_{12}^-$ the extra hydrogen apparently occupies a bridging position between boron atoms 4 and 8 or 7 and 8 (refer to Fig. 23 for numbering but not H location), tautomerizing rapidly between the two on the nmr time scale, or possibly the extra hydrogen forms some sort of bridge involving all three boron atoms at once. If the latter possibility is correct, bonding to the farther borons 4 and 7 appears to be relatively weak, since spin-spin coupling was observed only with boron 8. However, that spin-spin coupling is too small to permit interpretation in terms of a BH_2 unit at position 8. With the protonated structure (3)-1,2-$B_9C_2H_{13}$ it appears that both possible bridging positions, between borons 4 and 8 and between 7 and 8, are occupied. With the m-isomer of the anion, (3)-1,7-$B_9C_2H_{12}^-$, the single possible bridging position between boron atoms 4 and 8 contains the extra hydrogen atom.

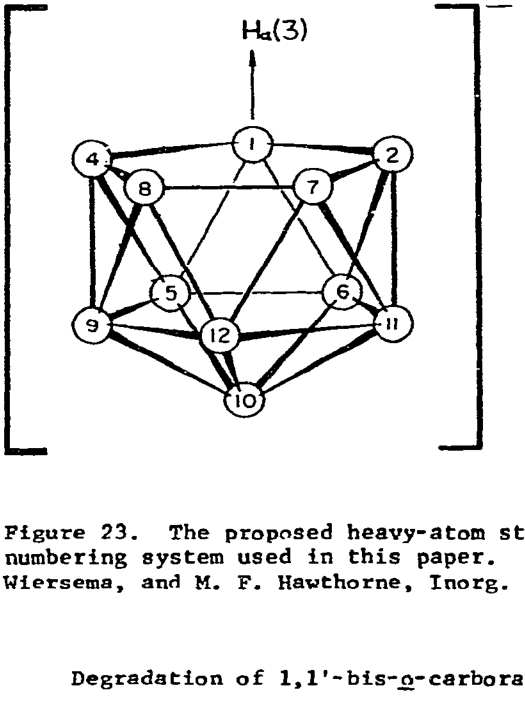


Figure 23. The proposed heavy-atom structure of the $B_9C_2H_{11}$ fragment and the numbering system used in this paper. (from D. V. Howe, C. J. Jones, R. J. Wiersema, and M. F. Hawthorne, Inorg. Chem., 10 (1971) 2517).

Degradation of 1,1'-bis-o-carborane with ethanolic potassium hydroxide at reflux 1.5 h yields the carboranyldicarbollide monoanion (Fig. 24), which on

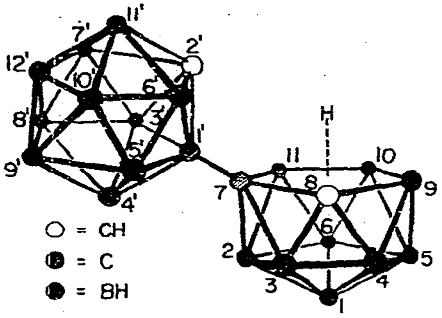


Figure 24. The proposed structure and numbering system for the 7-(1'-1',2'-$B_{10}C_2H_{11}$)-7,8-$B_9C_2H_{11}^-$ ion. (from M. F. Hawthorne, D. A. Owen, and J. W. Wiggins, Inorg. Chem., 10 (1971) 1305).

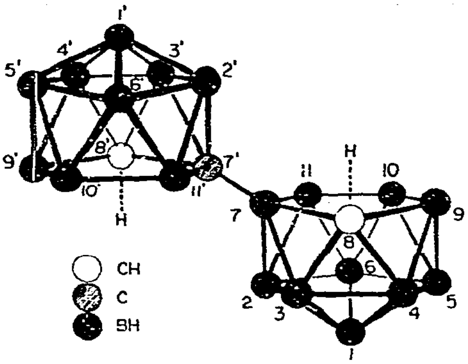


Figure 25. The proposed structure and numbering system for the 7-(7'-7',8-$B_9C_2H_{11}$)-7,8-$B_9C_2H_{11}^{2-}$ ion. (from M. F. Hawthorne, D. A. Owen, and J. W. Wiggins, Inorg. Chem., 10 (1971) 1305).

refluxing 120 h is converted to the bis(dicarbollide) dianion (Fig. 25) [18].

Reaction of phenylmercuric chloride with (3)-1,2-$B_9C_2H_{11}^{2-}$ yields a σ-bonded derivative, $PhHgB_9C_2H_{11}^-$, which was isolated as the tetramethylammonium salt [19].

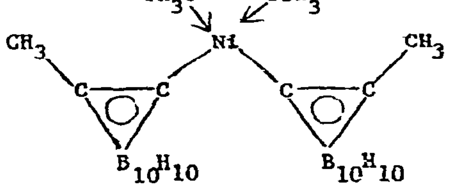
The reaction of B-bromo-1-bromomethyl-2-methyl-o-carborane with trimethylamine to yield 4-$Me_3NB_9H_{10}C_2Me_2$ has been patented in Japan [20].

Stanko and coworkers have reported that reaction of o-carborane-1-carboxamide with alcoholic sodium ethoxide gives mainly the dicarbollide ion, $B_9C_2H_{10}CONH_2^-$, without degradation of the amide [21]. Ethyl *m*-carborane-1-carboxylate is degraded to *m*-carborane, and *m*-carborane-1-carboxamides as well as *p*-carborane-1-carboxamides and carboxylic esters are highly resistant to sodium ethoxide at 140°. Triphenylmethylpotassium in 1,2-dimethoxyethane is said to cause some cleavage of *o*-carborane to dicarbollide ion but leave most of the *o*-carborane unchanged [22]. Since a hydrolysis step was involved before the products were isolated, a critic at this distance could suggest that the actual degradation may have occurred only in the presence of aqueous base, and the experiment has not proved anything.

B. Icosahedral Carboranes

1. Transition metal σ complexes. Owen and Hawthorne have found that biscarborane (Fig. 26) can be converted to a dilithio derivative which reacts with transition metals to form stable chelates (AS 70; 13) [23]. Square planar complexes (Fig. 27) are formed with copper(II), copper(III), nickel(II), nickel(III), cobalt(III), and cobalt(I), according to magnetic susceptibility measurements. Distorted tetrahedral complexes (Fig. 28) are formed with cobalt(II) and zinc(II). These complexes are unusually stable to air and water, apparently as a result of both steric shielding and favorable back bonding between the metal and the carborane cage. As is often the case with carborane-metal complexes, unusual oxidation states of the metal are stabilized. The copper(III) derivative is the product when dilithiobiscarborane reacts with copper(II) chloride, the copper(II) biscarborane complex being oxidized by copper(II) chloride [23].

Reaction of the lithio derivatives of *o*-carborane and $1,10\text{-}B_8C_2H_{10}$ with $(C_5H_5)Fe(CO)_2I$ and $BrMn(CO)_5$ yields σ-bonded derivatives (Fig. 29-32) [24]. Treatment of bis(triphenylphosphine)nickel(II) chloride with carboranyllithiums yields σ-bonded carboranylnickel compounds [25].



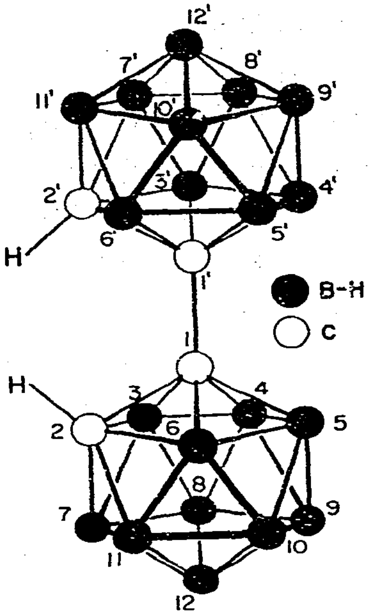
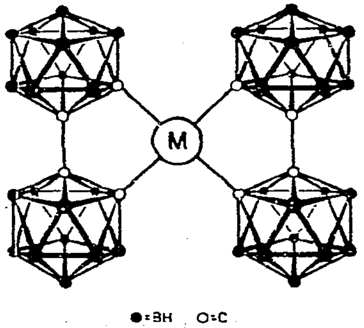


Figure 26. The structure and numbering system for biscarborane [1-(1'-1',2'-$B_{10}C_2H_{11}$)-1,2-$B_{10}C_2H_{11}$]. (from D. A. Owen and M. F. Hawthorne, Amer. Chem. Soc., 93 (1971) 874).



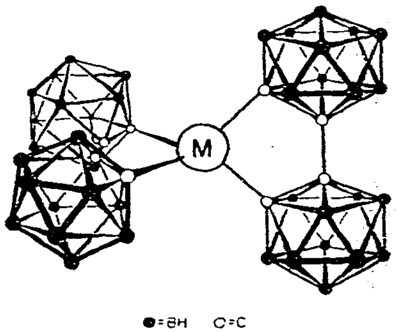
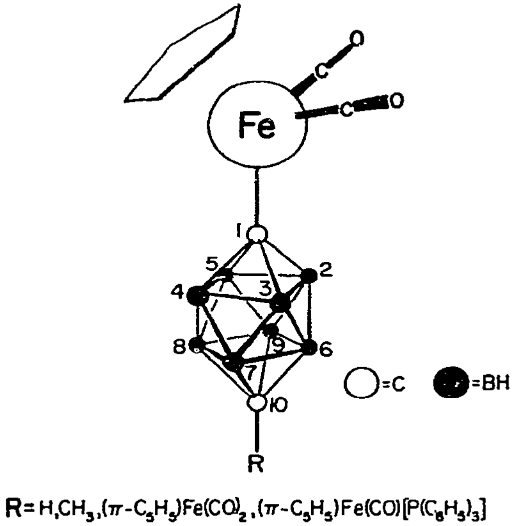


Figure 27. The proposed structure for the planar $M^{(4-\underline{n})+}[(B_{10}C_2H_{10}{-}{-})_2]_2^{\underline{n}-}$ (M = Ni, Cu. *n* = 1,2; M = Co, *n* = 1,3) derivatives. (from D. A. Owen and M. F. Hawthorne, J. Amer. Chem. Soc., 93 (1971) 875).

Figure 28. The proposed structure for the pseudotetrahedral $M^{(4-\underline{n})+}[(B_{10}C_2H_{10}{-}{-})_2]_2^{\underline{n}-}$ (M = Co,Zn; *n* = 2) derivatives. (from D. A. Owen and M. F. Hawthorne, J. Amer. Chem. Soc., 93 (1971) 877).



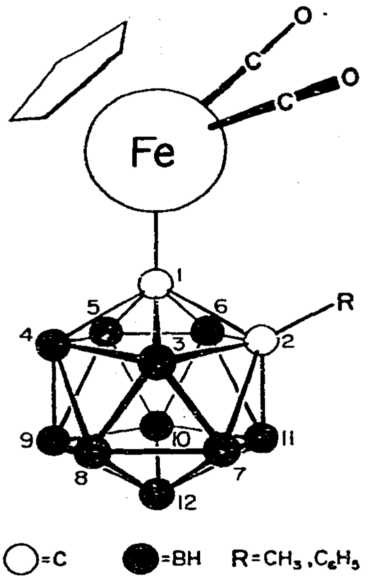


Figure 29. The proposed structure and numbering system for 1-[$(\pi\text{-}C_5H_5)Fe(CO)_2$]-1,10-($\sigma$-$B_8C_2H_9$) and its 10-substituted derivatives. (from D. A. Owen et al, J. Amer. Chem. Soc., 93 (1971) 1363).

Figure 30. The proposed structure and numbering system for 1-[$(\pi\text{-}C_5H_5)Fe(CO)_2$]-2-$CH_3$-1,2-($\sigma$-$B_{10}C_2H_{10}$) and its 2-phenyl derivative. (from D. A. Owen et al., J. Amer. Chem. Soc., 93 (1971) 1366).

The σ-bonded gold complexes $(B_9C_2H_{10}Ph)AuPPH_3$ and $(B_9C_2H_{10}Ph)AuPPh_3Br_2$ have been reported [26].

Zakharkin and Orlova have reported that reaction of carborane-3-carbonyl chloride with $NaFe(CO)_2C_5H_5$ yields the acyliron compound, which loses CO on heating to form the 3-carboranyliron derivative, which has a boron-iron σ-bond [27].

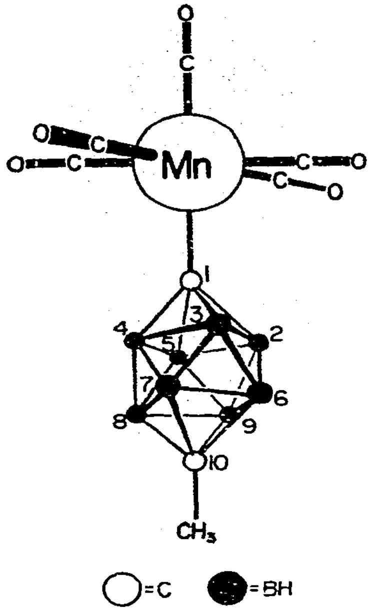
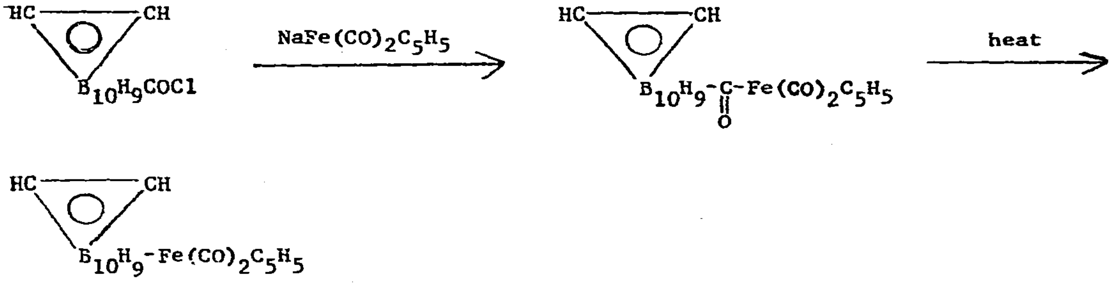


Figure 31. The proposed structure and numbering system for 1-[Mn(CO)$_5$]-10-CH$_3$-1,10-(σ-B$_8$C$_2$H$_8$), (from D. A. Owen *et al.*, J. Amer. Chem. Soc., 93 (1971) 1366).



A boron-rhenium bond has been formed in a similar manner, the reaction of *o*-$B_{10}C_2H_{11}$-3-COCl with NaRe$(CO)_5$ yielding $B_{10}C_2H_{11}$-3-CO-Re$(CO)_5$, which decarbonylates to $B_{10}C_2H_{11}$-3-Re$(CO)_5$ [28].

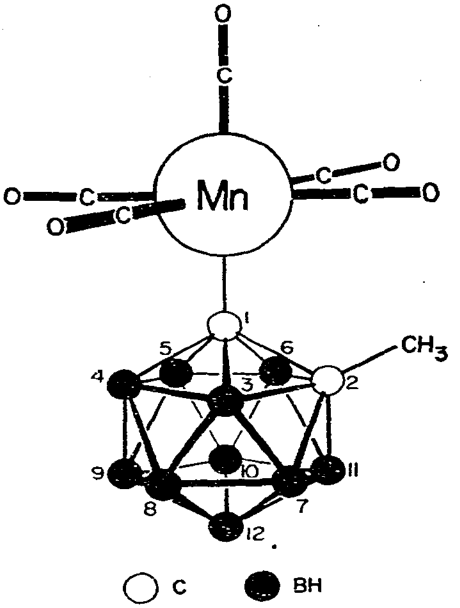
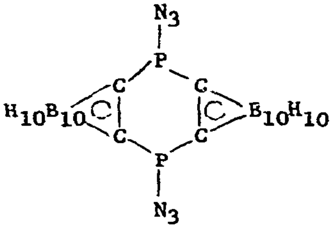


Figure 32. The proposed structure and numbering system for 1-[$Mn(CO)_5$]-2-CH_3-1,2-(σ-$B_{10}C_2H_{10}$). (from D. A. Owen et al., J. Amer. Chem. Soc., 93 (1971) 1366).

2. Nontransition metal and metalloid σ-linkages. Readers seeking real novelty and excitement should skip this subsection. The reaction of 2-isopropyl-1-o-carboranyllithium with boron trichloride has yielded 2-isopropyl-1-o-carboranylboron dichloride, which was converted to boronic ester and thioester derivatives by reactions with alcohols and thiols [29]. B-Decachloro-o-carborane, $B_{10}Cl_{10}C_2H_2$, is mercurated by $Hg(OAc)_2$ to form $(B_{10}Cl_{10}C_2H)_2Hg$, and other decachloro-o-carboranylmercury compounds have also been prepared by mercuration [30]. Tris(o-carboranyl)antimony and bismuth compounds have been prepared from carboranyllithiums and $SbCl_3$ or $BiCl_3$ [31]. A number of C-o-carboranylphosphonic acids and other phosphorus compounds have been prepared from halophosphorus

compounds and C-lithiocarboranes [32]. The reaction of m-$LiCB_{10}H_{10}CLi$ with Me_3SiCl to produce $Me_3SiCB_{10}H_{10}CSiMe_3$ and a number of related preparations of silyl-m-carboranes have been described [33]. Alkoxydialkylsilyl-m-carboranes have been patented in the U. S. S. R. [34]. A Soviet patent has also been issued on silicon-substituted carboranes prepared from m-carboranyllithium and dialkylchlorosilanes [35]. Another cyclic compound containing two carborane cages linked through phosphorus has been patented [36].



3. Boron-bound functional substituents. Boron-bound functional groups on carboranes have become available only recently, with the exception of halogens (part B-5), which are not generally useful for making anything else. Zakharkin and coworkers have made a long series of B-hydroxycarboranes and their derivatives [37]. 3-Hydroxy-o-carboranes were prepared by diazotization of the corresponding amines, which are available by way of reduction of o-carboranes with sodium in liquid ammonia and reoxidation (AS 69; 335). Mixtures of 8- and 9-hydroxycarboranes were obtained by lithium aluminum hydride reductions of chlorosulfonates obtained from o-carboranes and chlorosulfonic acid. This approach failed with m-carborane, which was chlorinated instead by chlorosulfonic acid. The B-hydroxycarboranes were methylated by diazomethane and had acidities comparable to phenol. Phosphite, borate, and trimethylsilyl esters of the B-hydroxycarboranes were prepared.

The synthesis of o-carborane-3-carboxylic acid from 3-o-carboranylamine has been described [38]. The amine was converted to the formamide, the isonitrile, rearranged to the nitrile, hydrolyzed to the amide, and converted to the acid with nitrous acid. Migration of the 3-o-carboranyl group to electron-deficient carbon has been observed with suitable 3-*o*-carboranyl compounds in Wolff, Beckmann, Hofmann, Curtius, Schmidt, and Bayer-Villiger rearrangements [39]. Oxidation of *o*, *m*, or *p*-carborane with $KMnO_4$ in acetic acid gives 25-30% yields of all possible B-monohydroxycarborane products [40].

Boron-bonded iron and rhenium substituents have been mentioned in part B-1 of this review [27, 28].

4. Carbon-bound functional substituents. Metals and metalloids have been covered in parts B-1 and B-2, and other types of carbon-bound substituents follow. It is easy to hang various side chains on the carborane carbon atoms by the use of carboranyllithium or magnesium compounds with electrophilic reagents, or to synthesize substituted carboranes from substituted acetylenes and decaborane. Accordingly, this is the field which continues to show the greatest volume of activity. Occasionally it is even possible to turn up something new and interesting.

Young, Paxson, and Hawthorne have synthesized two new alkenylcarboranes (Fig. 33) [41].

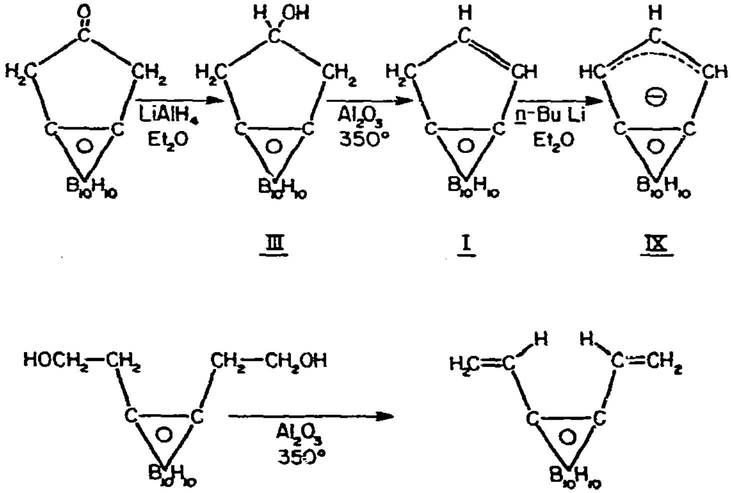
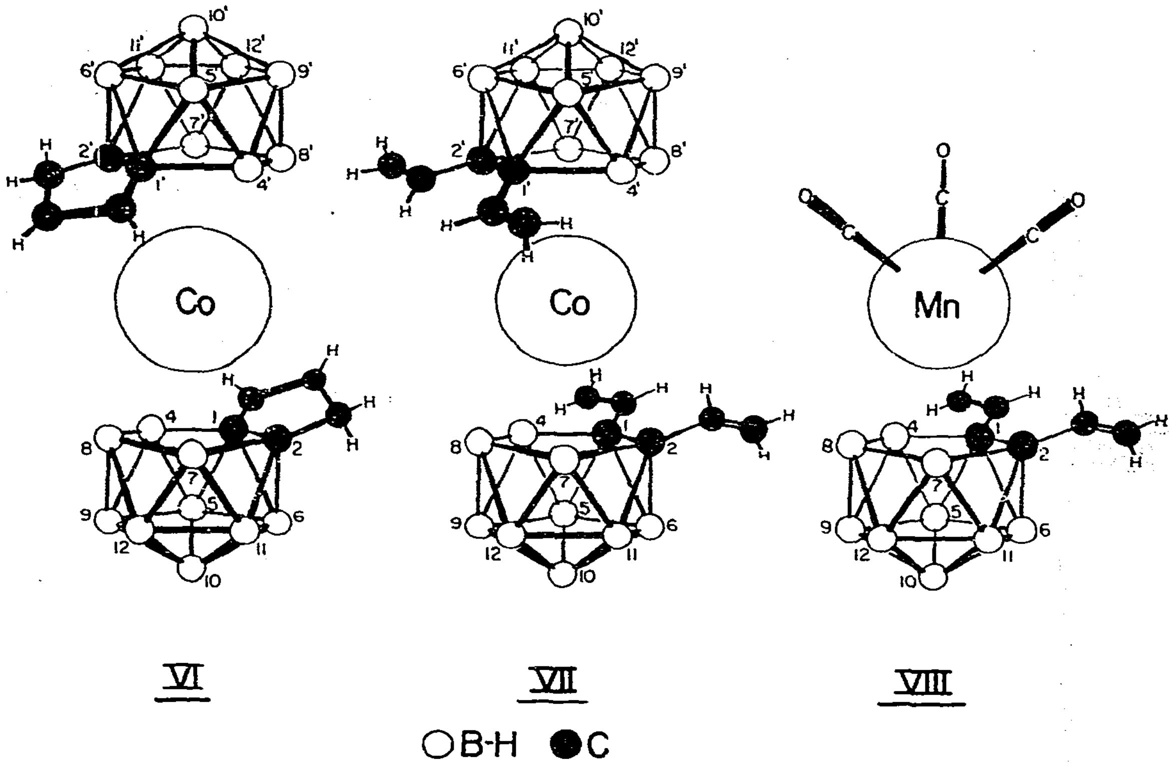


Figure 33. Syntheses of the 1,2-substituted carboranes and formation of the anionic 1,2-π-allyl-substituted carborane IX. (from D. A. T. Young, T. E. Paxson, and M. F. Hawthorne, Inorg. Chem., 10 (1971) 787).

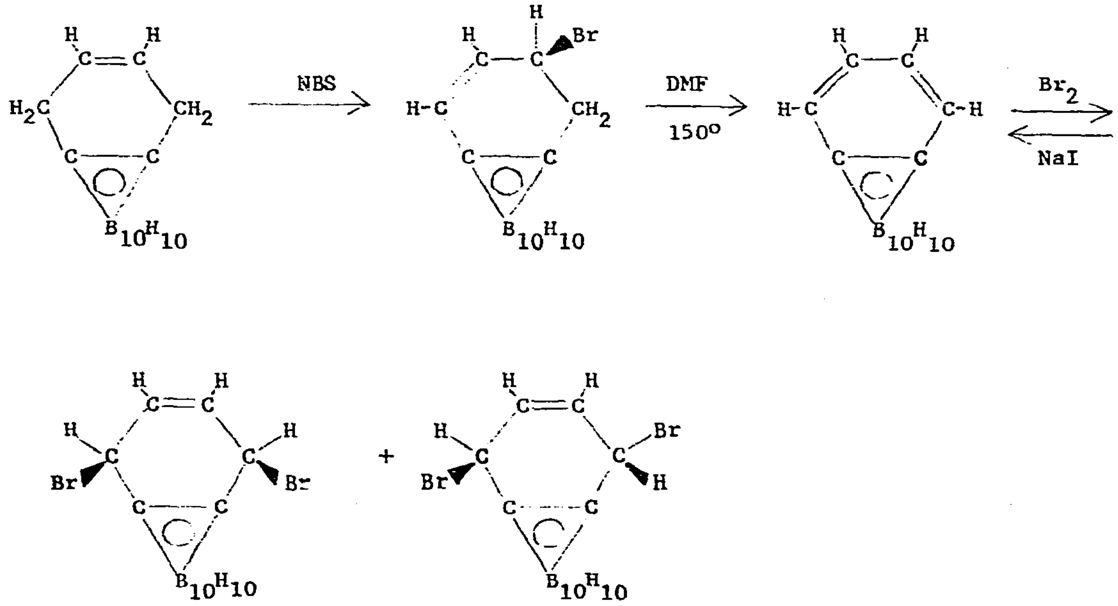
These have been converted to dicarbollide anions and then to dicarbollyl complexes (Fig. 34). Conjugation is unimportant in alkenylcarboranes, but ultraviolet spectra show some evidence of conjugation between dicarbollide anions and alkenyl substituents.



VI VII VIII

Figure 34. The proposed structures of $(B_9C_5H_{13})_2Co^-$, VI, $(B_9C_6H_{15})_2Co^-$, VII, and $(B_9C_6H_{15})Mn(CO)_3^-$, VIII, ions. VI has two possible configurations of the alkenyl groups which may give *dl* and meso stereoisomers. The orientation of the vinyl groups in VII and VIII is unknown. (from D. A. T. Young, T. E. Paxson, and M. F. Hawthorne, Inorg. Chem., 10 (1971) 789).

Matteson and Hota have improved the synthesis of benzocarborane (Fig. 35) (AS 68; 21) and reported the results in detail [42]. The aromatic character of the formally benzenoid ring is less than was thought at first, the ultraviolet spectrum being more indicative of molecular rigidity than aromaticity. The nmr spectrum indicates some ring current but the shift is smaller than in true benzenoid compounds. In the synthesis, the bromination of dihydrobenzocarborane was found not to give benzocarborane directly but to yield a mixture of bromodihydrobenzocarboranes which must be dehydrobrominated to obtain benzocarborane. Benzocarborane adds bromine and the diastereoisomeric 1,4-adducts can be debrominated (at grossly different rates) by sodium iodide to furnish pure benzocarborane. Attempts to nitrate or sulfonate benzocarborane failed.



Ultraviolet and infrared spectra show that conjugation between a phenyl substituent and a carborane cage is negligible, but some evidence is seen in the C-phenyldicarbollide monoanion [43].

Russian workers have continued the process of applying every reaction an organic chemist could think of to functionally substituted carboranes. 1-Ethynyl-*o*-carborane is more reactive than 1-vinyl-*o*-carborane toward bromine, and several other miscellaneous reactions of the ethynyl group have been reported [44]. A number of reactions involving 2-perfluoroalkenyl side chains

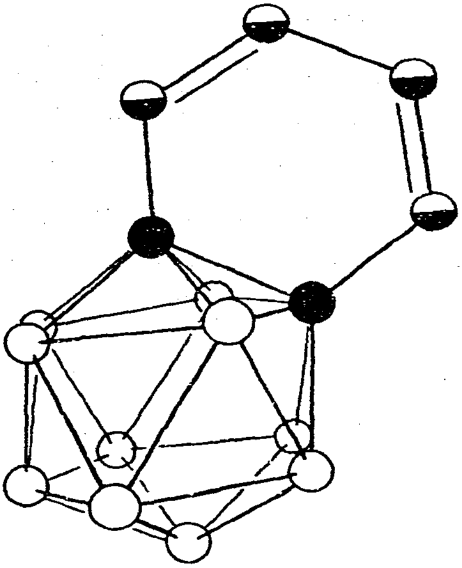
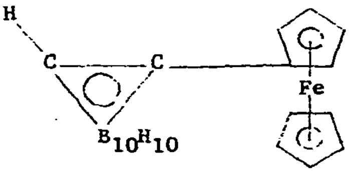
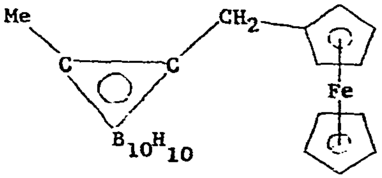


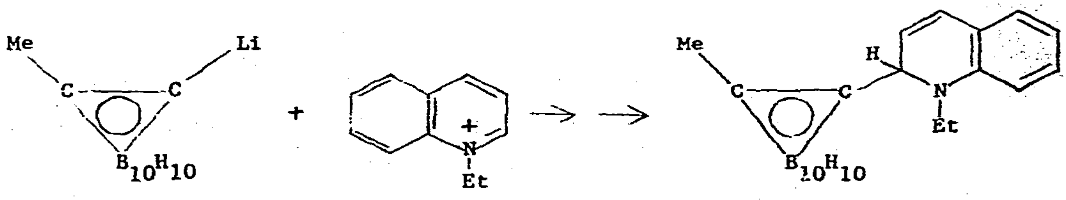
Figure 35. Benzocarborane(1): ○, BH; ◒, CH; ●, C. (from D. S. Matteson and N. K. Hota, J. Amer. Chem. Soc., 93 (1971) 2894).

on 1-methyl-*o*-carborane have been described [45]. 1-Ferrocenyl-*o*-carborane has been prepared from ferrocenylacetylene and decaborane, and several ferrocenylmethylcarboranes have been prepared from chloromethylferrocene and the carboranyllithium [46].

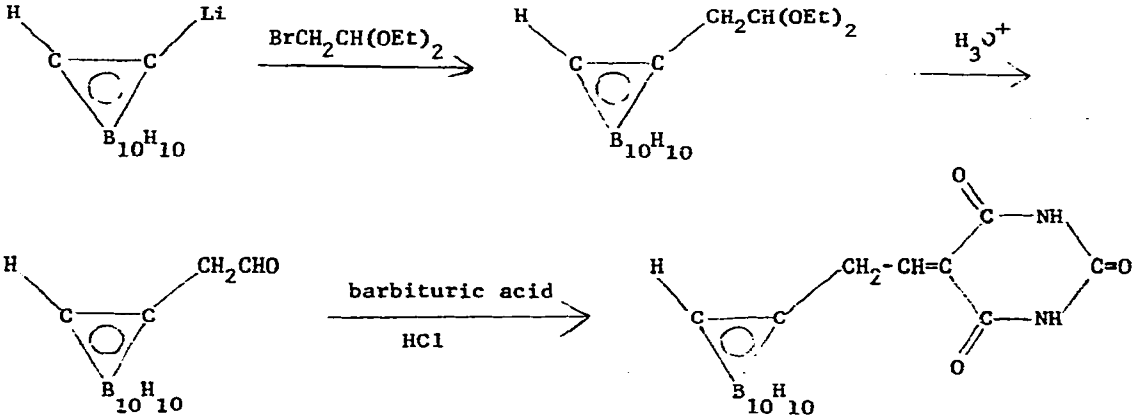




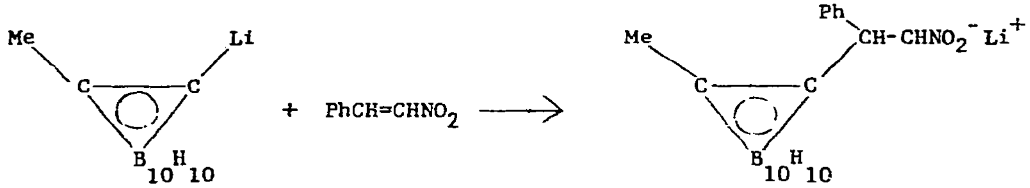
Carboranyllithiums add to N-alkylquinolinium and related cations [47].



Carboranylacetaldehydes have been prepared from lithio or sodio derivatives of *o*- and *m*-carboranes and $BrCH_2CH(OEt)_2$ followed by acid hydrolysis of the acetals [48]. *o*-Carboranylacetaldehyde and related compounds have been condensed with barbituric acid [49].



Lithium and magnesium derivatives of carboranes add to the double bond of nitroalkenes [50].



1-Formyl-*p*-carborane has been prepared by hydrogenation of the acid chloride and some of its chemistry has been studied [51].

Reaction of *o*- or *m*-$B_{10}C_2H_{10}(CH_2OH)_2$ with ClCN and Et_3N has yielded the cyanate esters, $B_{10}C_2H_{10}(CH_2O\text{-}C{\equiv}N)_2$ [52]. Cyanate esters are usually unstable and difficult or impossible to make, and these must owe their stability to steric protection by the bulky carborane cage. A pyrilium salt has been made from the condensation of 2-naphthol with 1-chloro-3-keto-4-(2-methyl-1-*o*-carboranyl)-1-butene [53]. 1-(Aminoalkyl)-*o*-carboranes have been patented as bactericides in Japan [54]. The dihydrazide of 1,2-bis(p-carboxyphenyl)-o-carborane has been prepared from the acid chloride and hydrazine [55]. In the search for stable compounds based on carboranes, $Ti(OBu)_4$ was heated with the cyclic phosphate ester of 1,2-bis(hydroxymethyl)-o-carborane to yield butanol and a pot residue for which Andrianov and coworkers wrote a structural formula [56], but we won't.

The reaction of oxygen with C-lithiocarboranes leads to C-hydroxycarboranes [57]. Several C-hydroxycarboranes have been prepared from the carboranyllithiums and benzoyl peroxide, and the hydroxy compounds have been acylated and converted to other typical derivatives [58]. The pK_a of 1-hydroxy-o-carborane in 50% aqueous ethanol is 5.25 and the pK_a of the m-isomer is 8.24.

Peracid oxidation of C-phenylthio and related derivatives of o-carborane yielded sulfoxides, and similar oxidation of m- or p-carborane analogs gave sulfones [59]. Oxidation of C-amino-m-carboranes with CrO_3 in HOAc yields C-nitroso-m-carboranes, and oxidation of either the amines or the nitroso compounds with CrO_3in HOAc-H_2SO_4 gives C-nitro-m-carboranes [60]. Attempts to oxidize C-amino-o-carboranes in the same manner failed.

Japanese patents have been issued on o-$B_{10}C_2HNMe_3{}^+Br^-$, $B_9H_9CNMe_3$, and related compounds [61, 62]. $R_3NCB_{10}H_{11}OH$ and related structures have been patented [63].

5. Halocarboranes. The halogenation of carboranes was once a fascinating new phenomenon, then grew and threatened to become a cure for insomnia. Russian papers on halocarboranes in the 1970-71 period covered by this review have dwindled to six. 1-Methyl-2-bromo-o-carborane has been prepared in 99% yield by bromination of 1-methyl-2-o-carboranylmagnesium bromide, which was prepared from 1-methylcarborane and ethylmagnesium bromide [64]. Studies of metalation of bromomethyl-o-carborane and related compounds were also reported. B-Iodocarboranes exchange iodide with $Na^{131}I$ in tetrahydrofuran [65]. Further studies of the C-halogenation of o-carboranyllithium and magnesium compounds have been published [66]. C-Halo-p-carboranes have been prepared by halogenation

of C-lithio-p-carboranes [67]. Chlorination of p-carborane with CCl_4 in the presence of ultraviolet light proceeds by a radical mechanism and yields a statistical mixture of products [68]. Stanko and coworkers have reported more studies of the thermal isomerization of halogenated carboranes, and also of the isomerization in the reverse direction which occurs on reduction of carboranes to dianions with alkali metal followed by reoxidation to the carborane. [69]. Various B-chlorocarboranes have been patented in the U. S. [70].

6. Physical measurements. Bond distances in o-, m-, and p-carborane have been determined by electron diffraction [71]. For p-carborane, the bond lengths are B-C = 1.710 Å, B2-B3 = 1.792 Å, B2-B7 = 1.772, accurate to ± 0.01 Å, and B-H = 1.22 ± 0.02 Å, C-H = 1.15 ± 0.09 Å. In o-carborane the C-C bond is 1.65 ± 0.05 Å, the average B-C bond is 1.711 ± 0.014, and the average B-B bond is 1.793 ± 0.010 Å. In m-carborane the average B-C bond is 1.726 Å and the average B-B bond is 1.805 Å.

The pK_a's of o-carborane and various alkylcarboranes have been measured by equilibration with potassium fluorenide in ether or dimethoxyethane and found to fall in the range 22.6-23.3, close to the pK_a of fluorene [72]. Lithium fluorenide yielded values of carborane pK_a's in the range 22-22.8. The kinetics of H-D exchange in NH_3 and NaOEt--EtOH have been measured for o-carborane and 1-methyl-o-carborane [73]. The alkoxide-catalyzed exchange of carbon-bound deuterium or tritium of m-carborane with the protons of NH_3, EtOH, or t-BuOH gave k_D/k_T = 1, not expected on theoretical grounds [74]. The dianion formed by reducing o-carborane with sodium-potassium alloy in tetrahydrofuran reduces benzophenone and related compounds to ketyls and is itself oxidized back to o-carborane [75].

Electronic effects of the carboranyl substituent have been investigated in a series of aromatic compounds bearing 1-m-, 1-o-, or 3-o-carboranyl groups in the m- or p-position of the aromatic ring [76]. The electron-withdrawing effect is purely inductive (as noted a number of times previously) and the electron-withdrawing strength decreases in the order 1-o-, 1-m-, 3-o-carboranyl. The ^{199}Hg-C-H coupling constants in a series of carboranyl-$HgCH_3$ compounds correlate with the polarity of the carboranyl group and the solvating ability of the solvent [77]. A series of 2-substituted 1-carboxyphenyl-o-carboranes have been prepared and their pK_a's measured in aqueous ethanol [78].

C. Smaller Carboranes

1. Synthesis and reactions. The smaller carboranes have been relatively difficult to make and have a considerable variety of possible structures. Accordingly, the novelty per publication in this field is a good deal greater than in the more developed icosahedral carborane chemistry.

Thompson and Grimes have reported the most unusual new carborane of the year, $B_5C_3H_7$, which contains one unprotonated, carbanion-like carbon atom (Fig. 36) [79]. This compound arose unexpectedly in the gas phase pyrolysis of μ-silyl- or 4-silyl-2,3-dicarba-nido-hexaborane (8), $SiH_3C_2B_4H_7$, at 220-250°. The ^{11}B and ^{1}H nmr spectra (Figs. 37 and 38) suggest rapid equilibration between two equivalent structures. Pyrolysis of $C_3B_5H_7$ at 400° yields 2,4-$C_2B_5H_7$.

A different isomer of $B_8C_2H_{12}$ is produced by treatment of the sodio derivative of 1,3-$B_7C_2H_{13}$ with diborane (Fig. 39) [80]. The structure is analogous to that of decaborane but lacks the stabilizing bridge hydrogens for the boron atom introduced between the two carbons. Consequently, the compound is acidic and readily forms a trimethylamine adduct (Fig. 40). Cleavage of the trimethylamine adduct with HCl yields not the parent carborane but hydrogen, trimethylamine hydrochloride, and the B-chloro derivative of the carborane. The reaction B_8H_{12} with acetylene in diethyl ether has yielded two new nido carboranes, $B_7C_2H_{11}$ and $B_8C_2H_{12}$ [81]. With 2-butyne the dimethyl homologs $B_7C_2H_9Me_2$ (Fig. 41) and $B_8C_2H_{10}Me_2$ (Fig. 42) are formed.

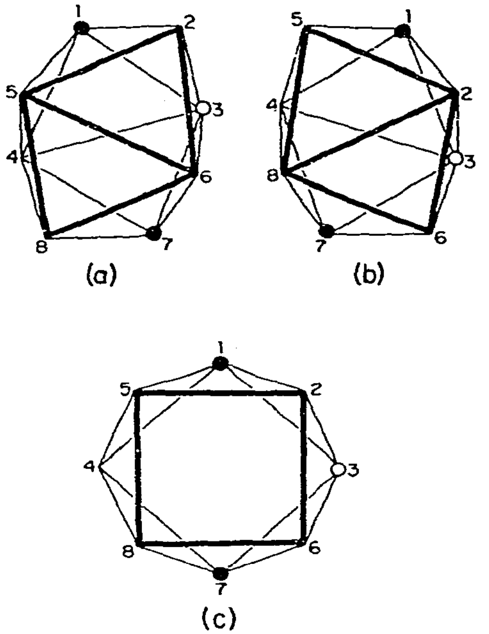


Figure 36. (a and b) Proposed dodecahedral equilibrium structures for $C_3B_5H_7$. (c) Square antiprism time-averaged geometry for $C_3B_5H_7$: ● , CH groups; ○ , unsubstituted carbon atom; the remaining vertices are occupied by BH groups. (from M. L. Thompson and R. N. Grimes, J. Amer. Chem. Soc., 93 (1971) 6678).

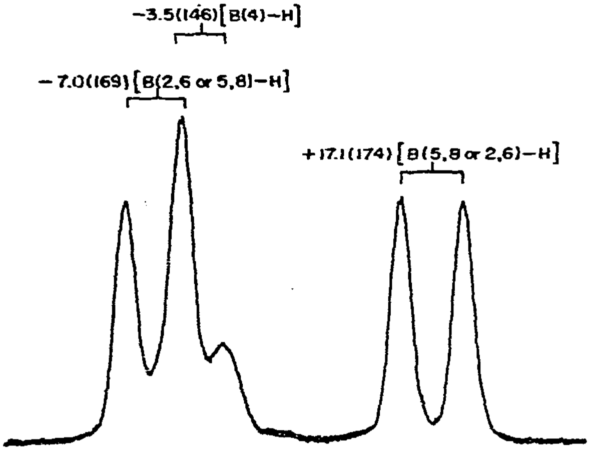


Figure 37. ^{11}B nmr spectrum (32.2 MHz) of $C_3B_5H_7$ (CS_2 solution). Chemical shifts are in parts per million relative to external $BF_3 \cdot O(C_2H_5)_2$ and coupling constants are in parentheses. Coupling constants for the two overlapped low-field doublets are taken from the proton nmr spectrum. (from M. L. Thompson and R. N. Grimes, J. Amer. Chem. Soc., 93 (1971) 6678).

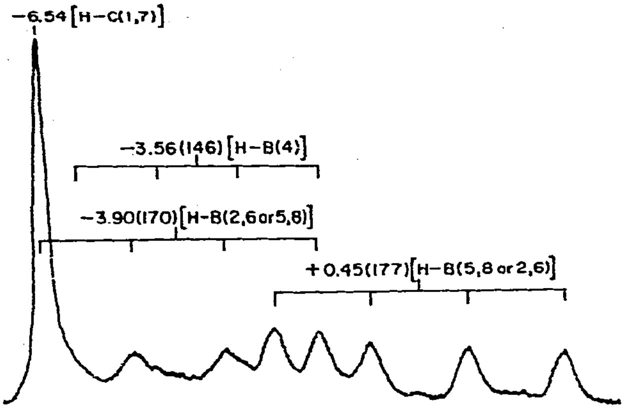
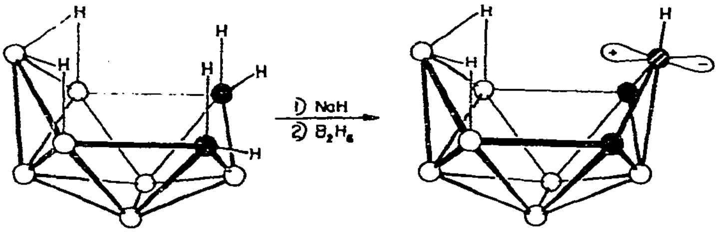


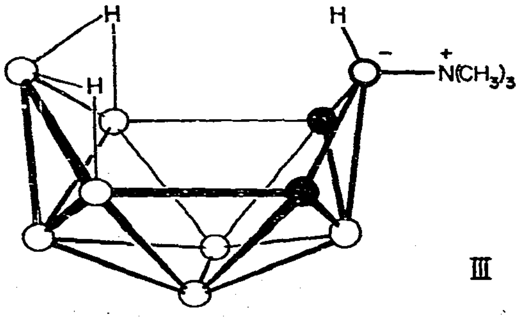
Figure 38. ^1H nmr spectrum (100 MHz) of $C_3B_5H_7$ (CS_2 solution). Chemical shifts are in parts per million relative to external $Si(CH_3)_4$, and coupling constants are in parentheses. The area 2 H-B quartets are clearly apparent, but assignment of the area 1 quartet, expected for the unique boron, is less certain due to masking by the stronger peaks. (from M. L. Thompson and R. N. Grimes, J. Amer. Chem. Soc., 93 (1971) 6678).



I

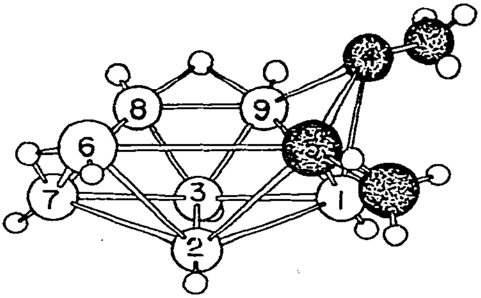
II

Figure 39. The reaction of $B_7C_2H_{13}$(I) with (1) sodium hydride and (2) diborane, which produces $B_8C_2H_{12}$(II), and the proposed structure of II. For I, ○ = BH, ● = carbon; for II, ○ = BH, ● = CH, ▨ = sp-hybridized boron atom with empty p orbital. (from P. M. Garrett, G. S. Ditta, and M. F. Hawthorne, J. Amer. Chem. Soc., 93 (1971) 1266).



III

Figure 40. Proposed structure of $N(CH_3)_3B_8C_2H_{12}$(III): ○ = BH, ○ = boron, ● = CH. (from P. M. Garrett, G. S. Ditta, and M. F. Hawthorne, J. Amer. Chem. Soc., 93 (1971) 1266).



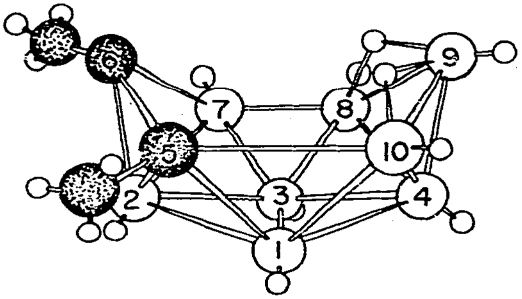


Figure 41. One enanticmorph of the possible structure for $B_7C_2H_9(CH_3)_2$. Note that varying placement of the bridge protons is possible. (R. R. Rietz and R. Schaeffer, J. Amer. Chem. Soc., 93 (1971) 1264).

Figure 42. One enantiomorph of the possible structure for $B_8C_2H_{10}(CH_3)_2$. Single-bridge pmr resonance mitigates against varying the placement of the bridge hydrogens. (from R. R. Rietz and R. Schaeffer, J. Amer. Chem. Soc., 93 (1971) 1264).

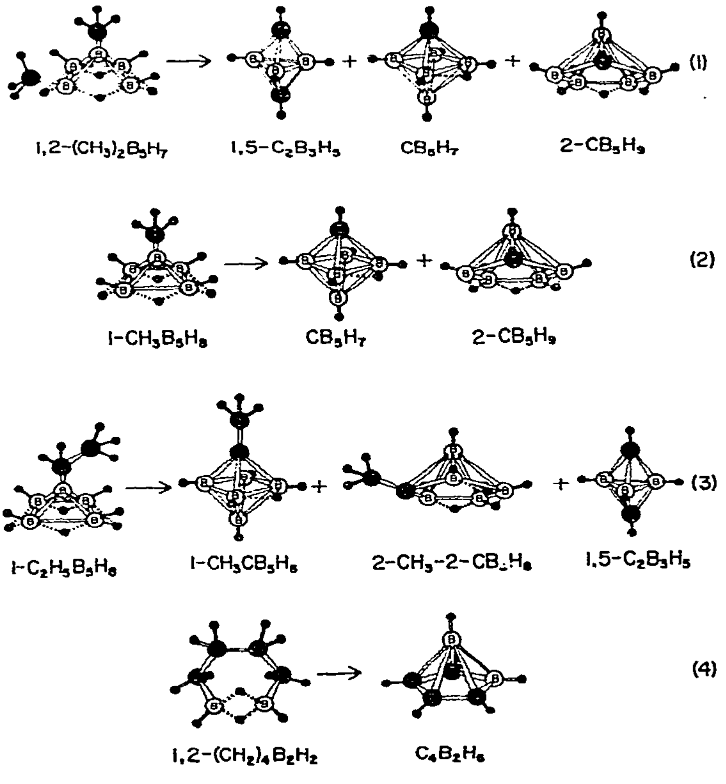
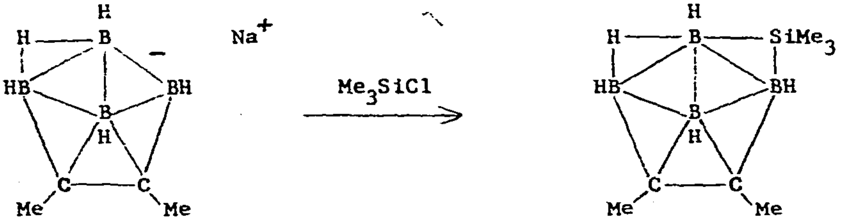


Figure 43. Pyrolysis routes to small carboranes. (from E. Groszek <u>et al.</u>, Inorg. Chem., 10(1971)2772).

Pyrolysis of alkylated pentaboranes or of tetramethylenediborane leads to a variety of small carboranes. (Fig. 43) [82]. The synthesis of 1,5-$B_3C_2H_5$, 1,6-$B_4C_2H_6$, and 2,4-$B_5C_2H_7$ by pyrolysis of the <u>nido</u>-carborane 4,5-$B_4C_2H_8$ at 460° in a flow system has been patented [83].

Reaction of the sodio derivative of 4,5-dimethyl-4,5-dicarbahexaborane(8) with Me_3SiCl and Me_3GeCl has yielded derivatives having a silicon or germanium bridge [84].



Some C-silyl derivatives of 2,3-$C_2B_4H_8$ have been prepared [85]. The preparation and properties of 3-halo derivatives of $B_4C_2H_8$, $B_4C_2H_7Me$, and $B_4C_2H_6Me_2$ have been described [86].

Heating the readily available small carborane $C_2B_4H_8$ with excess $Fe(CO)_5$ at 240° in a Pyrex tube yields (π-$C_2B_4H_6$)$Fe(CO)_3$ (Fig. 44) [87]. (π-$C_2B_3H_7$)$Fe(CO)_3$ (Fig. 45) is also formed in the reaction.

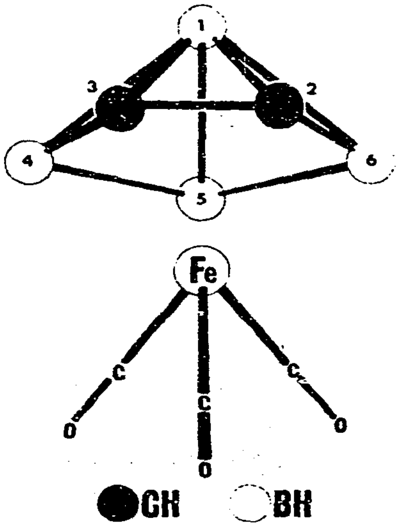


Figure 44. Proposed structure of (π-$C_2B_4H_6$)$Fe(CO)_3$. (from R. N. Grimes, J. Amer. Chem. Soc., 93 (1971) 261).

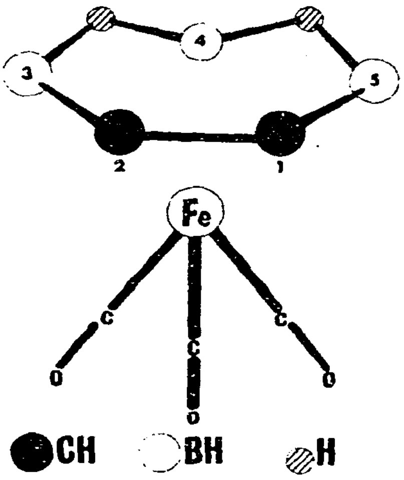
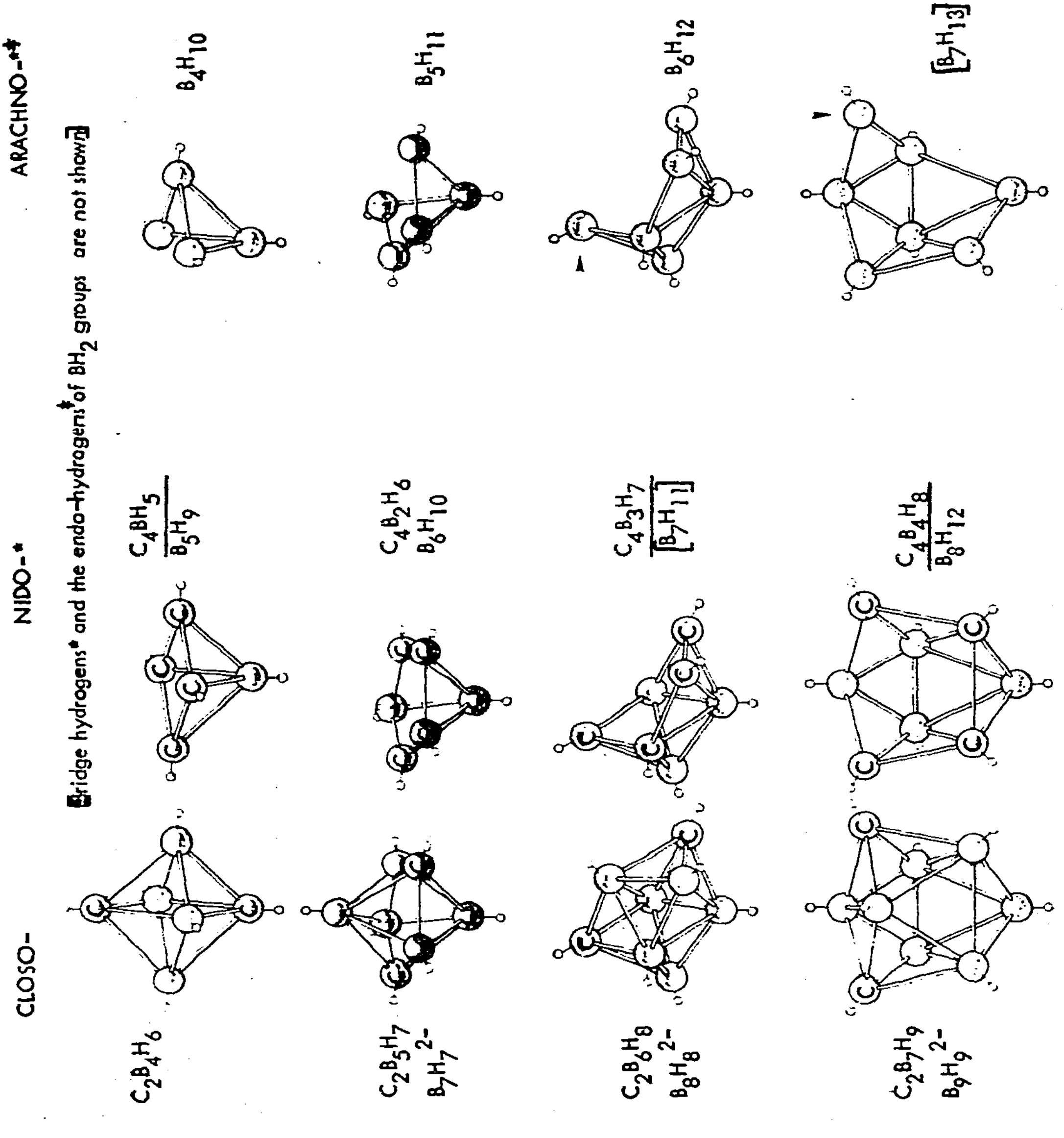


Figure 45. Proposed structure of (π-$C_2B_3H_7$)$Fe(CO)_3$. (from R. N. Grimes, J. Amer. Chem. Soc., 93 (1971) 262).

A closo dicarbollide complex of less than icosahedral size has been covered in part A-1 [2].

Several reactions of 1,6-HCB_4H_4CH have been investigated [88]. Lithiation with butyllithium was unusually slow compared to other carboranes, but the dilithio derivative was obtained in 48 h at 25°, and reaction with methyl iodide led to $CH_3CB_4H_4CCH_3$. Bromination in the presence of $AlBr_3$ yielded only the B-bromocarborane. A C-bromocarborane, $BrCB_4H_4CCH_3$, was obtained by bromination of the corresponding lithio derivative.

The gas phase reaction of B_4H_{10} with acetylene is first-order in B_4H_{10} and zero-order in acetylene for the over-all reaction by initial rate measurements at 40-60° [89]. Formation of the carboranes 2-$CH_3C_3B_3H_6$, 2,3-$(CH_3)_2C_3B_3H_5$, and 2,4-$(CH_3)_2C_3B_3H_5$ is, like the overall reaction, first-order in B_4H_{10}, but shows a negative order in acetylene. The mechanism proposed involves rate-determining formation of B_4H_8 from B_4H_{10}. The B_4H_8 reacts rapidly with acetylene, and the


CLOSO-
NIDO-*
ARACHNO-*‡
Bridge hydrogens* and the endo-hydrogens‡ of BH_2 groups are not shown]
$C_2B_4H_6$
C_4BH_5
B_5H_9
B_4H_{10}
$C_2B_5H_7$
$B_7H_7^{2-}$
$C_4B_2H_6$
B_6H_{10}
B_5H_{11}
$C_2B_6H_8$
$B_8H_8^{2-}$
$C_4B_3H_7$
$[B_7H_{11}]$
B_6H_{12}
$C_2B_7H_9$
$B_9H_9^{2-}$
$C_4B_4H_8$
B_8H_{12}
$[B_7H_{13}]$

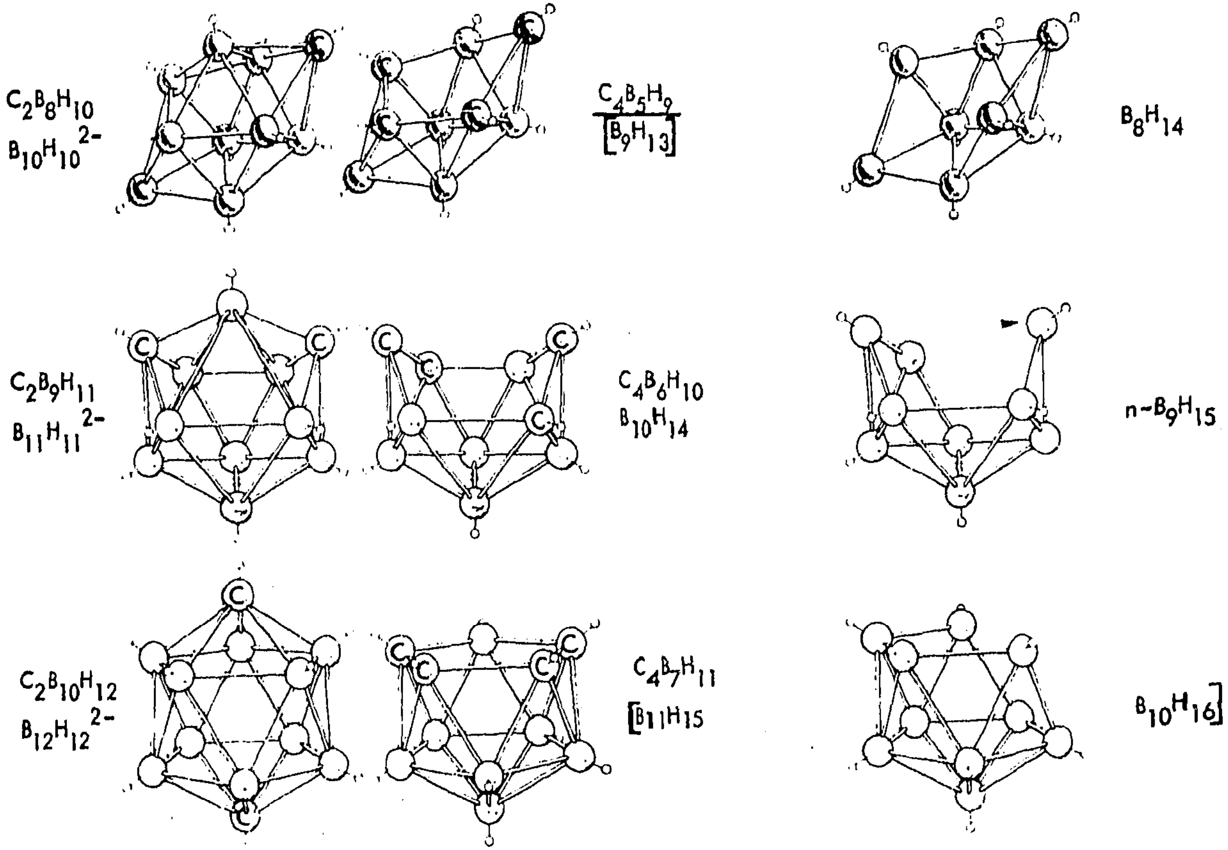


Figure 46. Structures of carboranes and related compounds. Species underlined are predicted; those in brackets are expected to be unstable if they can be isolated. (from R. E. Williams, Inorg. Chem., 10 (1971) 211).

major reaction does not yield small carboranes but a polymer formed from one mole of B_4H_8 and four of C_2H_2 and having the composition $[C_2BH_4]_n$.

2. Bonding theory. Problems of accounting for the bonding in carboranes have continued to interest theoreticians and experimentalists. Williams has pointed out that all the known boranes and carboranes are either closed polyhedra or fragments of the polyhedra corresponding to the *closo*-carborane structures [90]. The boranes and carboranes may be classified into three groups: (1) *closo*, having the formula $C_{0-2}B_nH_{(n+2)}$; (2) *nido*, having the formula $C_{0-4}B_nH_{(n+4)}$; and (3) *arachno*, having the formula $C_{0-6}B_nH_{(n+6)}$. It has been customary to regard boranes as icosahedral fragments, even though ordinary pentaborane, B_5H_9, is not an icosahedral fragment. Williams predicts that many more carboranes will be found which are polyhedral fragments but not necessarily icosahedral fragments. Some of the expected structural relationships are illustrated in Fig. 46 and 47.

Wade has noted that in carboranes and other cage structures, species with *n*-skeletal atoms adopt *closo* structures if there are *n* + 1 bonding electron pairs, *nido* structures if there are *n* + 2 bonding electron pairs, and *arachno* structures if there are *n* + 3 bonding electron pairs in the cage structure [91]. (An example may be seen in the expansion of the icosahedral carborane, part A-1 [1]).

Epstein and Lipscomb have described a new refinement of valence structure representations of boron hydrides [92]. Three-center B-B-B bonds are considered to be all of one type, which is closed triangular and not in a topological sense open or linear. Their topological analysis was programmed for a computer to predict possible new stable boron hydrides or reaction intermediates. This bonding scheme can also be adapted to carboranes. Self-consistent field molecular orbital calculations have been carried out for B_6H_{10} [93].

The microwave spectrum of CB_5H_9 (fig. 48) has been studied [94]. The dipole moment is 1.53 ± 0.03 D. Boron-boron bond distances are B(3)-B(4) = 1.759 Å, B(4)-B(5) = 1.830 Å, B(1)-B(3) = 1.782 Å, and B(1)-B(4) = 1.781 Å.

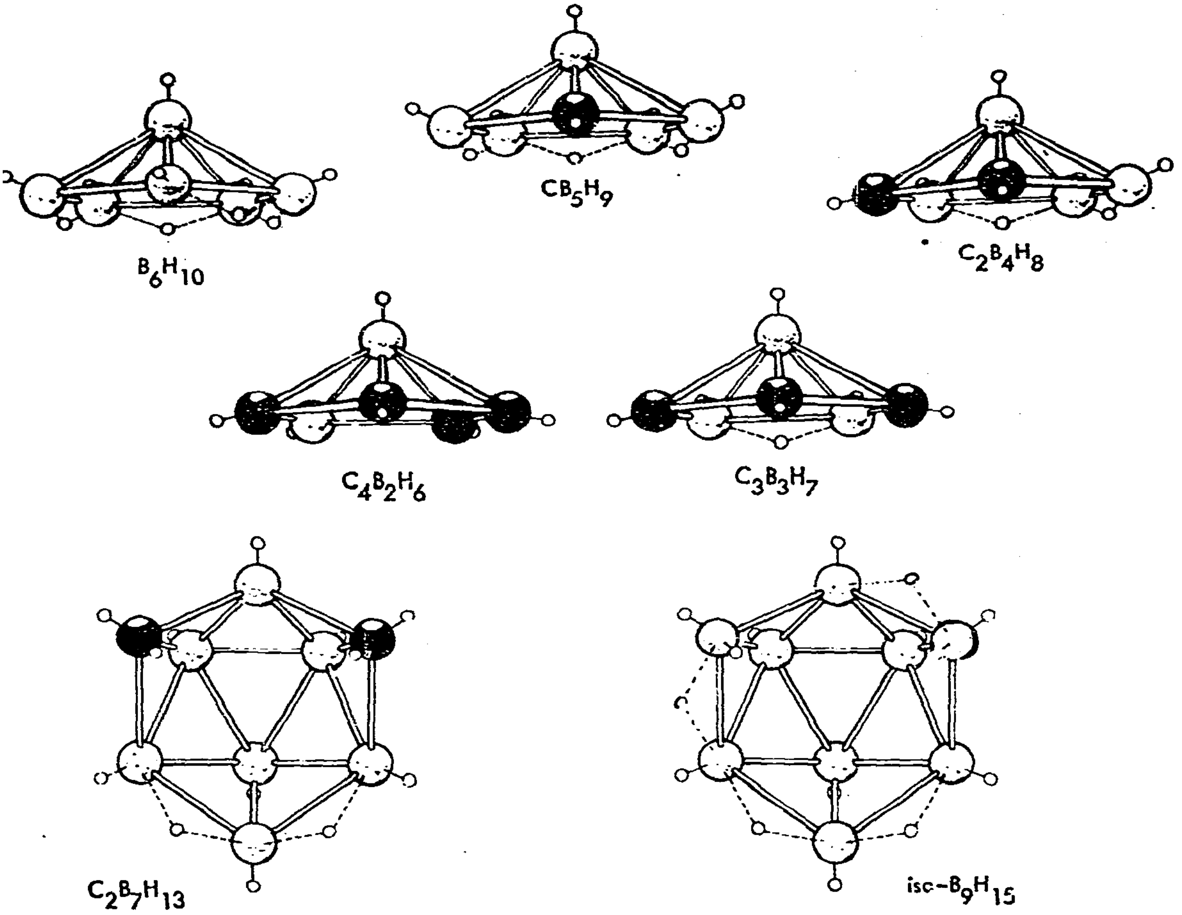


Figure 47. A series of nido-carboranes (top) and related arachno-carboranes (below). (from R. E. Williams, Inorg. Chem., 10 (1971) 212).

The microwave spectrum of 2-chloro-1,6-dicarbahexaborane(8) (Fig. 49) has been reported [95].

D. Boron Hydrides

This section lists papers on non-organometallic boron hydrides which the reviewer thinks may be of interest to carborane chemists. It is not comprehensive.

The ^{13}C nmr spectrum of 1-methylpentaborane show a ^{11}B-^{13}C coupling constant

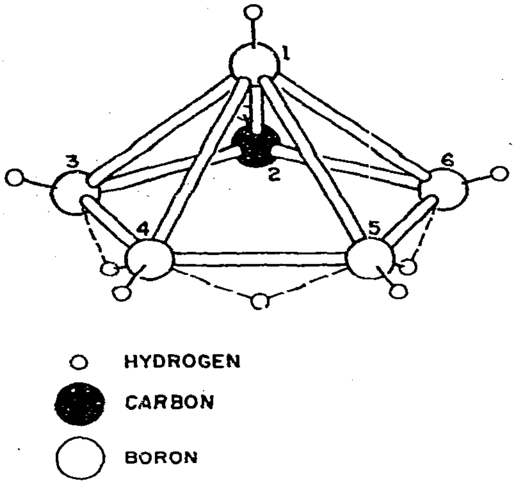


Figure 48. Geometry of CB_5H_9. (from C.-C. S. Cheung and R. A. Beaudet, Inorg. Chem., 10 (1971) 1145).

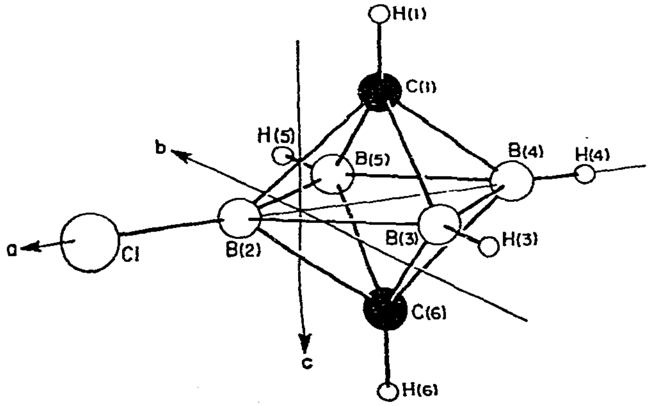


Figure 49. Structure of 2-chloro-dicarbahexaborane(6). (from G. L. McKown and R. A. Beaudet, Inorg. Chem., 10 (1971) 1352).

of 72.6 Hz [96]. The high resolution ^{11}B nmr spectrum of pentaborane reveals a boron-boron coupling constant of 19.4 Hz [97]. 1-Trimethylsilylpentaborane has been prepared by thermal isomerization of the 2-isomer [98]. The structure of

1-bromo-μ-trimethylsilylpentaborane, which contains three-center B-Si-B bridge bond, has been determined by X-ray crystallography [99].

Reaction of the sodio derivative of decaborane, $NaB_{10}H_{13}$, with trimethyltin chloride, Me_3SnCl, yields the stannaundecaborane $B_{10}H_{12}SnMe_2$ [100]. The germanium analog was also reported. The sodio derivative of decaborane reacts with $PhPCl_2$ in ether to produce a <u>nido</u>-phosphaborane, $B_{10}H_{12}PPh$ [101]

X-ray structures have been reported for $B_{20}H_{18}^{2-}$ [102] and $B_{10}H_9(NO)B_{10}H_9$ [103]. A procedure for obtaining 6,9-dideuteriodecaborane has been found [104]. Ion cyclotron resonance studies of B_4H_{10}, B_5H_9, B_5H_{11}, and B_6H_{10} indicate that B_nH_{n+4} hydrides lose H^+ to form negative ions and B_nH_{n+6} hydrides lose BH_3^+ [105]. Radical cations are favored over even-electron cations.

The X-ray crystal structure of lithium tetramethylboron, $LiB(CH_3)_4$, shows it to be a polymer linked by unusual single linear (177.6° and 179.6°) boron-methyl-lithium bridges [106].

Hawthorne and coworkers have found both S_N1 and S_N2 mechanisms at boron in nucleophilic displacements of amines from amine boranes [107-109].

E. Reviews

The syntheses of a wide variety of carboranes and related compounds have been reviewed by Scholer and Todd [110]. Grimes has published a comprehensive and very useful book on carborane chemistry [111].

III. HYDROBORATION

A. Radical Reactions of Trialkylboranes

Many of the more novel developments in the chemistry of hydroboration products during the past year have involved radical reactions. The most general reaction is displacement of an alkyl radical R• from boron by an oxidizing radical X• (where the unpaired electron is on oxygen, halogen, sulfur, or nitrogen).

$$R_3B + X^{\bullet} \longrightarrow R_2BX + R^{\bullet}$$

The exception to this type of reaction is the bromine atom, which abstracts an α-hydrogen from an alkyl group on boron in preference to displacing the alkyl group (AS 70; 29). The bulk of this work has been reported by H. C. Brown and coworkers, with the exception of some mechanistic studies led by Davies and by Lissi.

Reaction of trialkylboranes in tetrahydrofuran with oxygen at 0° gives high yields of alcohols [112]. The air oxidation of trialkylboranes can be controlled to yield $R\text{-}B(\text{-}O\text{-}O\text{-}R)_2$ at -78° to 0°, depending on the alkyl group used [113]. Oxidation with hydrogen peroxide then yields the alkyl hydroperoxide R-O-OH in a 2:1 mixture with the alcohol ROH. Iodine has been found to be a particularly effective inhibitor of the autoxidation of trialkylboranes, which is evidently a radical reaction having very long chains [114]. From studies using iodine as an inhibitor, it has been shown that the autoxidation of trialkylboranes is initiated more slowly when the borane is more hindered sterically [115]. The kinetics of the free-radical chain reactions of oxygen with Bu_3B, *sec*-Bu_3B, and *t*-Bu_3B have been studied [116]. A plausible mechanism for these autoxidations can be written.

$R_3B + O_2 \longrightarrow R_2B\text{-}O\text{-}O\cdot + R\cdot$ (initiation)

$R\cdot + O_2 \longrightarrow R\text{-}O\text{-}O\cdot$ (propagation)

$R\text{-}O\text{-}O\cdot + R_3B \longrightarrow R_2B\text{-}O\text{-}O\text{-}R + R\cdot$ (propagation)

The reaction of trialkylboranes with oxygen in the presence of allyl or benzyl iodide yields alkyl iodide and the coupling products of allyl or benzyl radicals [117]. A radical chain mechanism was proposed.

$R_3B + O_2 \longrightarrow R_2BO_2\cdot + R\cdot$ (initiation)

$R\cdot + PhCH_2I \longrightarrow RI + PhCH_2\cdot$ (chain transfer)

$2\ PhCH_2\cdot \longrightarrow PhCH_2CH_2Ph$ (termination)

$PhCH_2\cdot + O_2 \longrightarrow PhCH_2O_2\cdot$ (propagation)

$PhCH_2O_2^{\bullet} + R_3B \longrightarrow PhCH_2O_2BR_2 + R^{\bullet}$ (propagation)

$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet} \xrightarrow{R_3B} RO_2BR_2 + R^{\bullet}$ (propagation)

By adjusting the proportions of reactants the reaction can be made efficient for the production of either alkyl halide or bibenzyl.

Dialkyl disulfides react with trialkylboranes by a free radical mechanism [118].

$R_3B + O_2 \longrightarrow RBO_2^{\bullet} + R^{\bullet}$ (initiation)

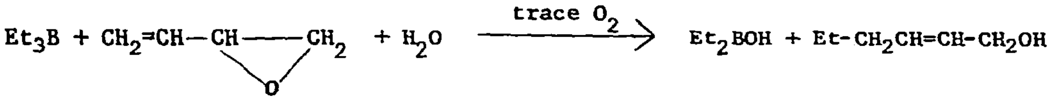
$R^{\bullet} + MeSSMe \longrightarrow RSMe + MeS^{\bullet}$ (propagation)

$MeS^{\bullet} + R_3B \longrightarrow MeSBR_2 + R^{\bullet}$ (propagation)

$MeSBR_2 + MeS^{\bullet} \longrightarrow (MeS)_2BR + R^{\bullet}$ (propagation)

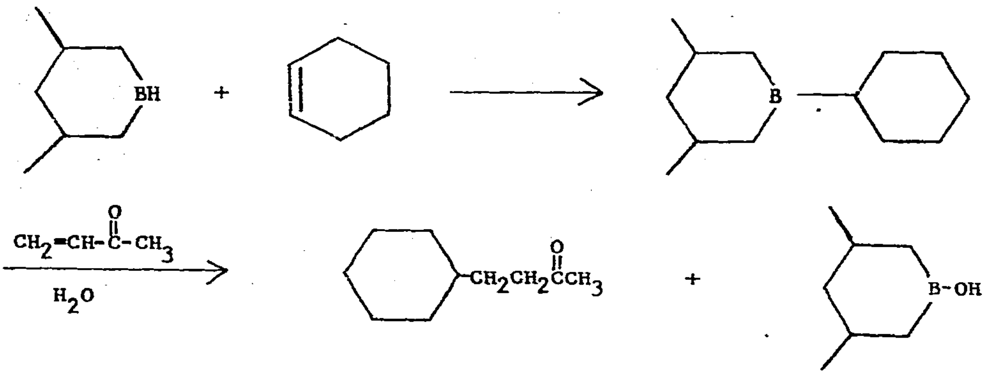
$(MeS)2BR + MeS^{\bullet} \longrightarrow (MeS)_3B + R^{\bullet}$ (propagation)

Under the influence of oxygen or other free radical initiators, butadiene monoxide reacts with trialkylboranes to give a four-carbon chain homologation [119].



$$Et_3B + CH_2{=}CH{-}\overset{}{CH{-}CH_2}\,(O) + H_2O \xrightarrow{\text{trace } O_2} Et_2BOH + Et{-}CH_2CH{=}CH{-}CH_2OH$$

Though very useful for many syntheses involving polar bond cleavages at boron, B-alkyl-9-borabicyclo[3.3.1]nonanes (AS 69; 350) fail in radical reactions because the secondary radical formed by ring opening is relatively stable, and the desired cleavage of the B-alkyl group does not occur selectively [120]. This problem has now been solved for secondary alkyl groups by the use of substituted borinanes, which can be used to hydroborate olefins to form B-alkylborinanes. The B-sec-alkyl group is selectively cleaved in radical reactions such as that with methyl vinyl ketone.



Trialkylboranes react with $CuBr_2$ in the presence of water to yield alkyl bromides [121]. Two moles of cupric bromide are required, and a radical mechanism was postulated.

$$H_2O + Bu_3B + CuBr_2 \longrightarrow Bu^{\bullet} + Bu_2BOH + H^+ + Br^- + CuBr$$
$$Bu^{\bullet} + CuBr_2 \longrightarrow BuBr + CuBr$$

The thermal iodination of triethylborane in cyclohexane solution follows the equation $-d[I_2]/dt = k[I_2]^{(1/2)}[Et_3B]$ at 100-140° [122]. The evidence indicates a free radical mechanism.

$$I_2 \rightleftarrows 2\,I^{\bullet}$$
$$I^{\bullet} + Et_3B \longrightarrow IBEt_2 + Et^{\bullet}$$
$$Et^{\bullet} + I_2 \longrightarrow EtI + I^{\bullet}$$

The initial rate of the ultraviolet initiated reaction of iodine with Et_3B at 20° is 3/2-order in iodine and first-order in Et_3B, indicating that the rate-determining step involves $I_2 + I^{\bullet} + Et_3B$ [123].

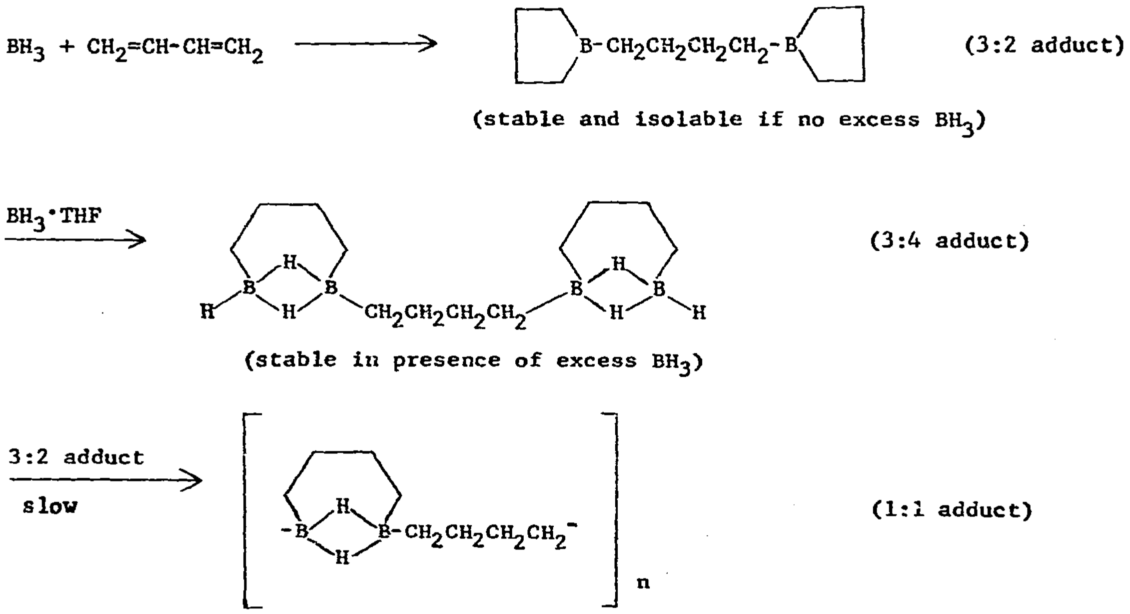
t-Butoxy radicals displace butyl radicals from tributylborane, and the butyl radicals have been observed by esr [124]. The displacement of alkyl radicals from R_3B by $RS^{\bullet}$ radicals has been studied with the aid of esr, and several trialkylboranes have been found to react faster than 1-octene with $RS^{\bullet}$ [125].

The kinetics of reaction of Et_3B with methyl radicals have been measured [126]. Trihexylborane gives radical reactions with neutral aqueous hydrogen peroxide, leading to hydrocarbons as well as hexanol [127]. A report on the radical-catalyzed reaction of methyl vinyl ketone with trialkylboranes (AS 67; 286 and 70; 29) has appeared in the Japanese literature [128].

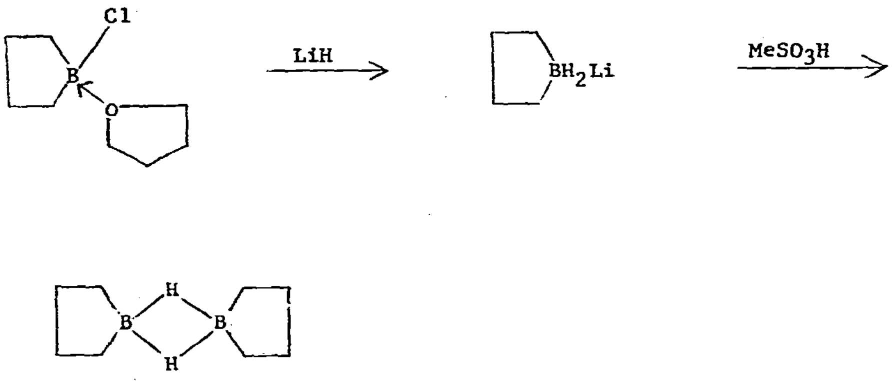
A paper dealing with radical bromination in the presence of water, which leads to a rearrangement with carbon-carbon bond formation, is covered in part C.

B. Preparation of Alkylboron Hydrides

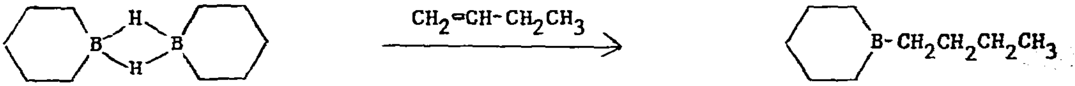
Further study of the reaction of borane in tetrahydrofuran with butadiene (AS 70; 32) indicates that the product from a 1:1 ratio of reactants is polymeric [129]. Excess BH_3 leads to a borane having 4 moles of BH_3 to 3 of butadiene. The results can be accounted for by assuming that butadiene and borane form a 5-membered borolane ring which is expanded rapidly by excess borane.



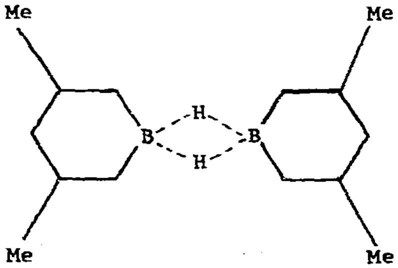
The elusive character of borolane dimer challenged Brown and Negishi to put out enough effort and make the compound in solution [130]. The successful preparation involved treatment of the corresponding borohydride with one equivalent of methanesulfonic acid in an ethereal solvent at -25°.

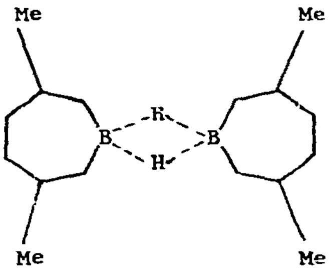


Bisborinane has been prepared by hydroboration of 1,4-pentadiene, and can be used in turn to hydroborate olefins [131]. There is of course no tendency for the six-membered ring to expand, in contrast to the five-membered ring just discussed, and bisborinane is a stable compound.

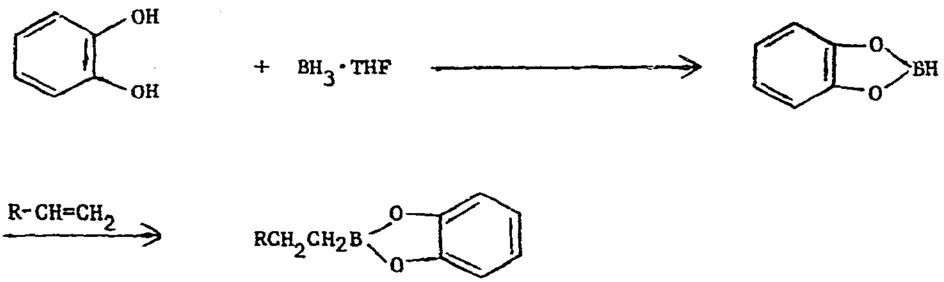


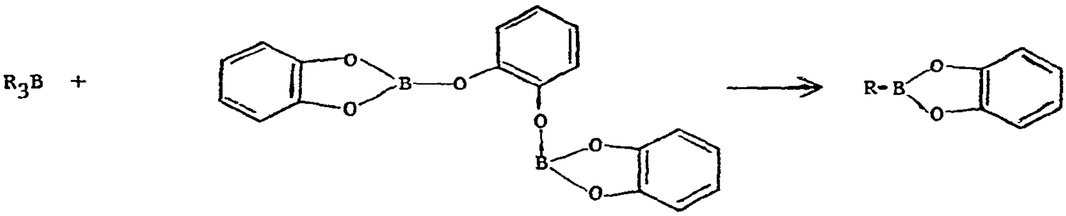
Hydroboration of 2,4-dimethyl-1,4-pentadiene and 1,5-dimethyl-1,5-hexadiene has yielded bis(3,5-dimethylborinane) and bis(3,6-dimethylborepane), which are useful stereoselective hydroborating agents [132].



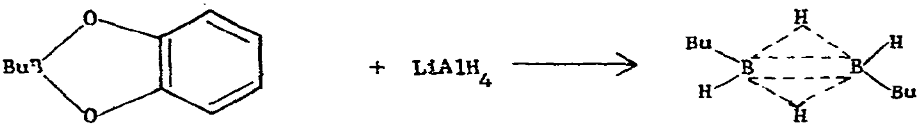


1,3,2-Benzodioxaborole is a useful monofunctional hydroborating agent for preparing boronic esters from olefins at 100° [133]. With lower-boiling olefins, redistribution between catechol borate and the trialkylborane is more convenient.





Monoalkylboranes or, more properly, their dimers, 1,2-dialkyldiboranes, are not very stable and are difficult to synthesize. Brown and Gupta have reported success by treating catechol boronic esters with lithium aluminum hydride or aluminum hydride [134]. The alkylborane-pyridine complexes can be isolated if desired.

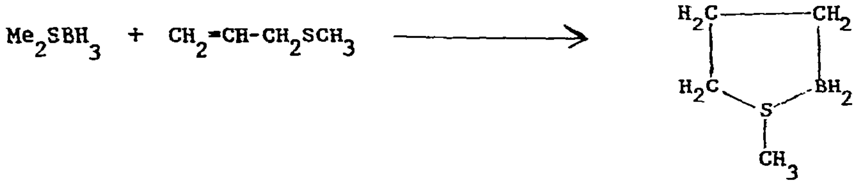


Reduction of B-dialkyl-B-aryloxyboranes with lithium aluminum hydride provides a useful route to solutions of dialkylboranes [135].

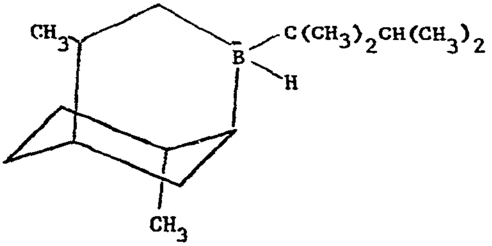
$$Bu_2B\text{-}OPh + LiAlH_4 \longrightarrow Bu_2BH + LiAlH(OPh)_3$$

Aluminum hydride reduces dialkylmethoxyboranes and at the same time forms stable complexes with the resulting dialkylborane [136]. These complexes are useful hydroborating agents, or they can be converted to the stable pyridine-dialkylborane complexes.

Reaction of dimethyl sulfide borane with 3-methylthiopropene yields a monoalkylborane stabilized by chelation with the sulfur [137]. This monoalkylborane can be used to hydroborate olefins.



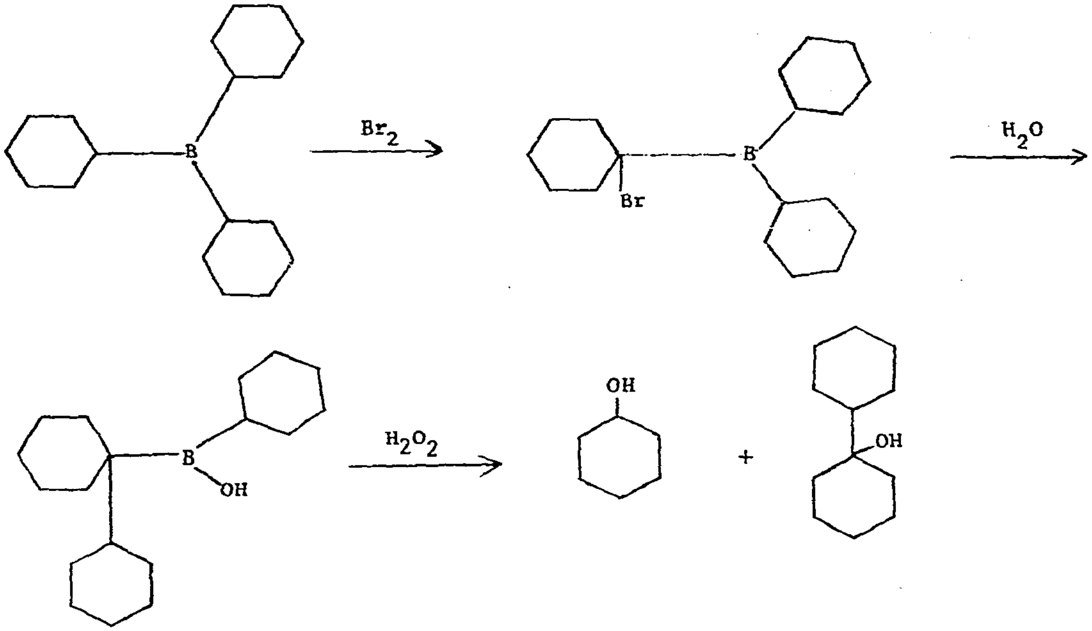
A highly stereoselective borohydride reducing agent for carbonyl groups, useful in the synthesis of prostaglandins, has been prepared by Corey and coworkers from thexylborane and limonene followed by treatment of the resulting borane with _t_-butyllithium, which undergoes a β-elimination and transfers hydride to boron [138].



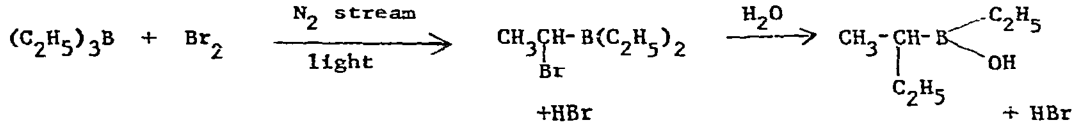
C. Syntheses Involving Rearrangements

The reactions in this section all involve migration of an alkyl group from boron to an electron-deficient carbon or, in one case, nitrogen.

Radical initiated bromination of trialkylboranes in the presence of water yields the products of alkyl migration from boron to carbon [139].



Bromination of triethylborane under conditions of removal of the HBr as fast as it is formed leads to α-bromoethyldiethylborane [140]. The compound is stable in the absence of oxygen or water, but reacts very rapidly with water. An ethyl group migrates from carbon to boron, yielding an unsymmetrical borinic acid.

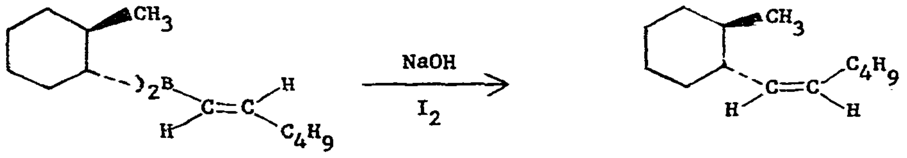


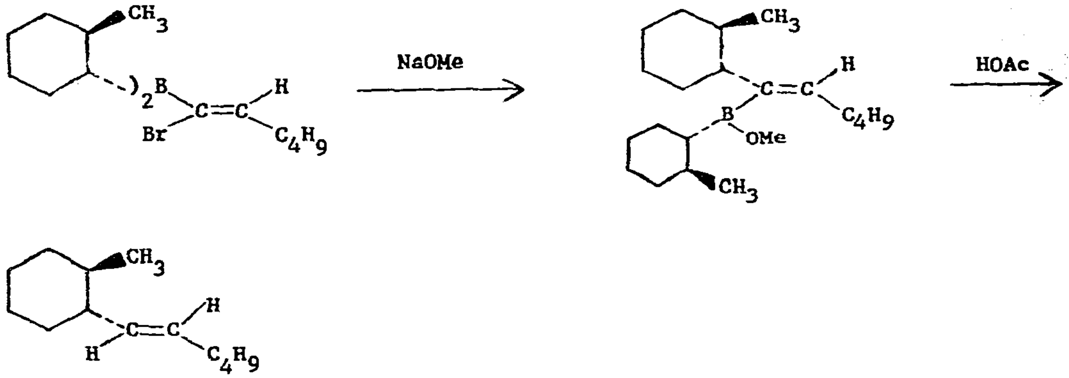
$$(C_2H_5)_3B + Br_2 \xrightarrow[\text{light}]{N_2\ \text{stream}} \underset{+HBr}{CH_3\underset{Br}{CH}-B(C_2H_5)_2} \xrightarrow{H_2O} CH_3-\underset{C_2H_5}{CH}-B\begin{matrix}C_2H_5\\OH\end{matrix} + HBr$$

The lithium triethylcarboxide catalyzed reaction of chlorodifluoromethane with tributylborane followed by the usual hydrogen peroxide oxidation yields 98% of tributylcarbinol [141]. This reaction provides a useful alternative to the reaction of carbon monoxide with trialkylboranes.

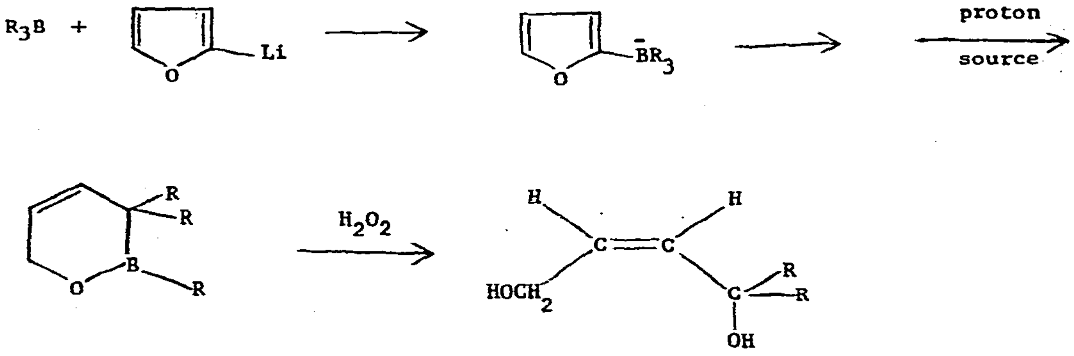
$$Bu_3B + CHF_2Cl + LiOCEt_3 \longrightarrow \underset{\text{(not isolated)}}{Bu_3CBF_2} \xrightarrow{H_2O_2} Bu_3COH$$

Migration of a 2-methylcyclohexyl group from boron to carbon in the iodination of bis(2-methylcyclohexyl)-1-hexenylborane proceeds with retention at the migrating carbon [142]. Sodium methoxide causes rearrangement of the analogous 1-bromo-1-hexenylborane with retention in the migrating 2-methylcyclohexyl group and inversion of the vinylic carbon to which migration occurs. These reactions provide routes to _cis_ and _trans_ alkenes.

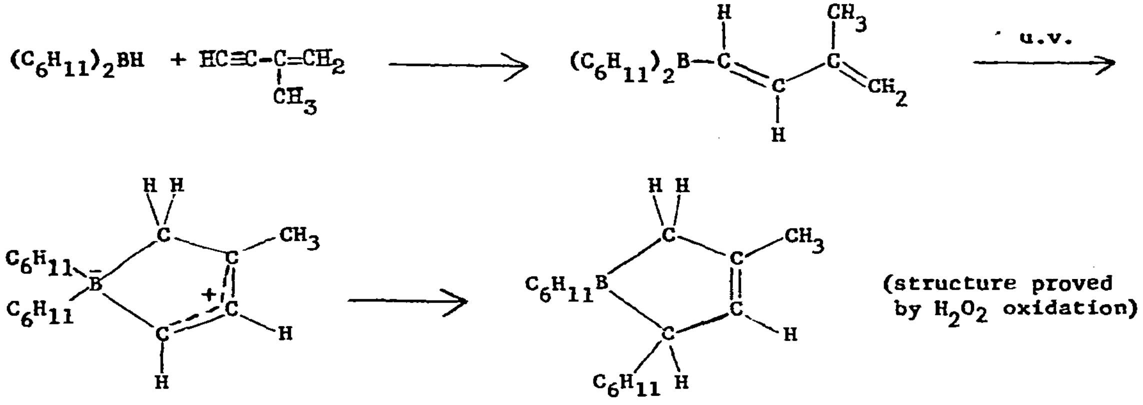




A synthesis of _cis_-2-butene-1,4-diols is provided by the reaction of trialkylboranes with α-lithiofuran [143].



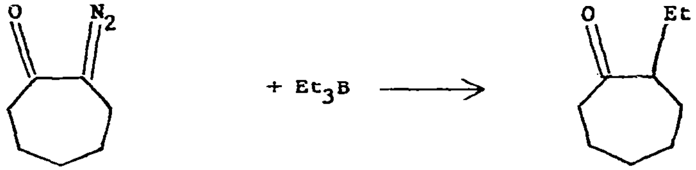
The reaction of dicyclohexylborane with isopropenylacetylene yields dicyclohexyl(3-methyl-trans-1,3-butadienylborane, which on photolysis in tetrahydrofuran undergoes trans to cis isomerization, cyclization, and alkyl migration from boron to carbon [144].



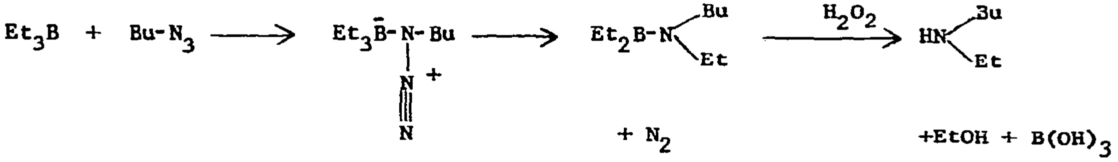
(hypothetical)

(structure proved by H_2O_2 oxidation)

Trialkylboranes and cyclic α-diazoketones yield alkylated cycloalkanones [145].



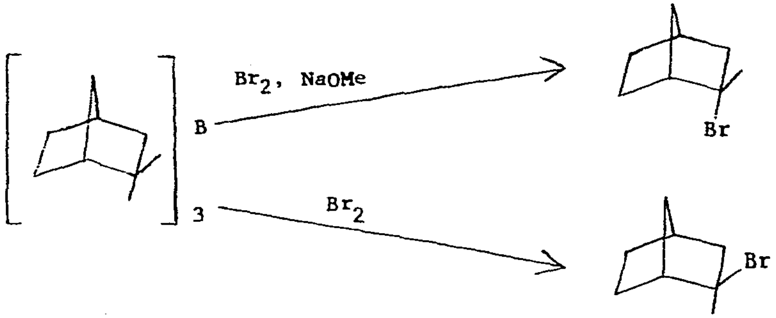
The reaction of trialkylboranes with alkyl azides provides a new route to secondary amines [146].



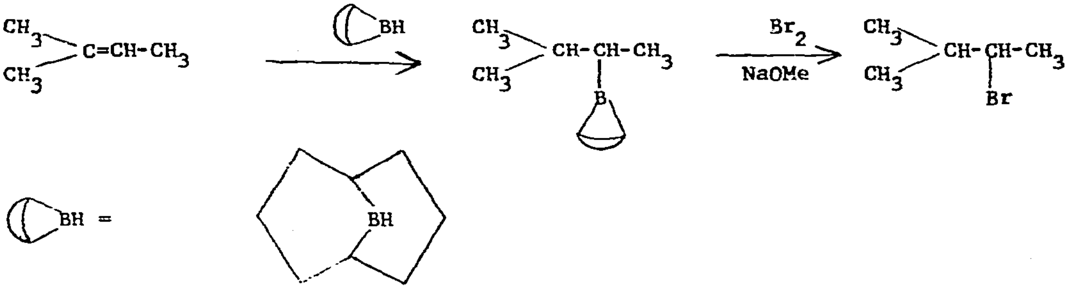
$$Et_3B + Bu\text{-}N_3 \longrightarrow Et_3\bar{B}\text{-}\underset{\underset{\displaystyle N}{|||}}{\overset{}{N^{+}}}\text{-}Bu \longrightarrow Et_2B\text{-}N\begin{matrix}Bu\\Et\end{matrix} + N_2 \xrightarrow{H_2O_2} HN\begin{matrix}Bu\\Et\end{matrix} + EtOH + B(OH)_3$$

D. Displacements and Eliminations

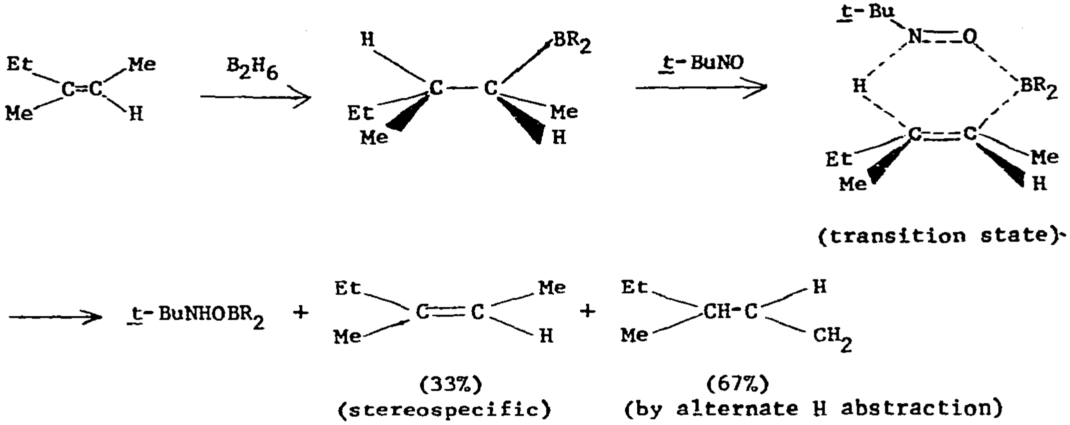
Bromination of tri-exo-norbornylborane in the presence of sodium methoxide proceeds predominantly with inversion to yield endo-bromonorbornane [147]. In the absence of base retention results and the product is exo-bromonorbornane.



The cleavage of trialkylboranes by bromine (AS 70; 30) has been extended to 9-borabicyclononane derivatives, providing a route from internal olefins to the halides corresponding to anti-Markovnikov addition of HBr to the double bond [148].



Mercury(II) salts react sluggishly with trialkylboranes containing secondary alkyl groups, and only two of the three alkyl groups are cleaved [149]. Retention of configuration predominates in the reaction of tri-exo-norbornylborane. Either *t*-BuNO or *cis*-PhN=N-Ph (but not *trans*) will eliminate boron hydride rapidly and stereospecifically from trialkylboranes, apparently by a concerted cyclic mechanism [150, 151].



The redistribution reaction of trialkylboranes with triaryl borates is considerably faster than that with trialkyl borates [152]. The products are aryl dialkylborinates (B-aryloxy-B-dialkylboranes).

$$2\ Bu_3B + (\underline{o}\text{-}MeC_6H_4O)_3B \xrightarrow{100^{\circ}} 3\ Bu_2B\text{-}OC_6H_4Me$$

Isomerization of the boranes derived from hydroboration of mixed isomers of n-hexadiene leads to terminal borane, which can be cleaved by ethylene to form 1,4-hexadiene [153].

Mikhailov and Kuimova have found that the ratio of terminal to internal boranes in the reaction of $ArCH=CH_2$ with Bu_3B to form $C_2H_5CH=CH_2$ and $(ArCH_2CH_2)_3B$ or $(ArCHMe)_3B$ is different from the results of direct hydroboration of $ArCH=CH_2$, and have concluded that the mechanism involves a concerted displacement of one olefin by the other, not elimination of a dialkylborane which then might hydroborate the other olefin [154].

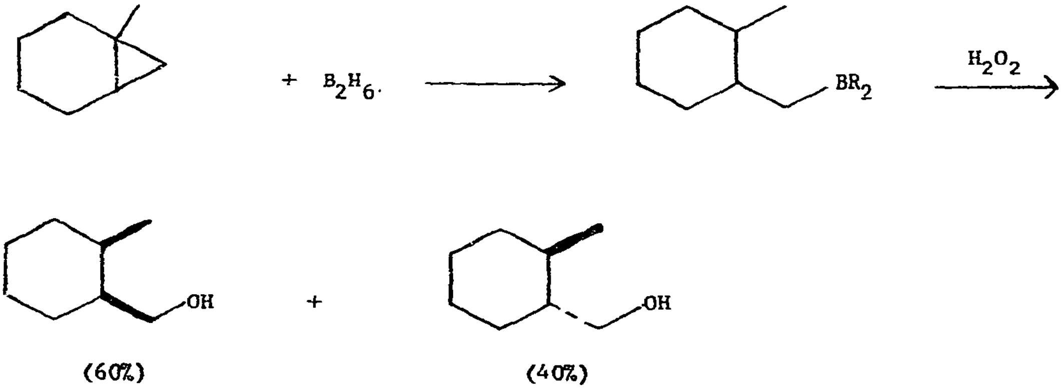
E. Hydroboration of Olefins

1. Mechanism. Fehlner has measured the rate of reaction of free BH_3 (from pyrolysis of F_3PBH_3) with ethylene in the gas phase [155]. The rate constant rises from 0.9×10^9 to 1.6×10^9 l./mol-sec in the temperature range

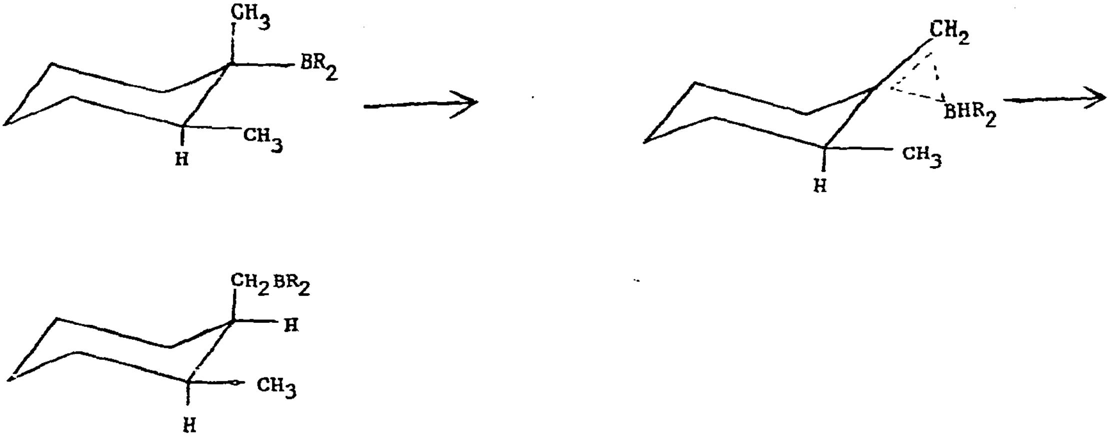
445-590°K, indicating an activation energy of about 2 kcal/mol. From these studies, it may be concluded that if hydroboration in solution proceeds by way of free BH_3 (not very likely) then the formation of BH_3 is rate-determining and and the reaction of BH_3 with olefins is very fast.

$$F_3PBH_3 \xrightarrow{\text{heat}} PF_3 + BH_3 \xrightarrow{C_2H_4} CH_3CH_2BH_2 \longrightarrow \text{dimer}$$

2. <u>Cyclopropanes</u>. In accord with the ability of cyclopropanes to behave like unreactive olefins under some conditions, Rickborn and Wood have found that diborane cleaves cyclopropanes at about 100°, placing the boron atom on the least substituted carbon and the hydrogen on the most substituted carbon [156]. Unlike the olefin addition reaction, the cyclopropane cleavage is inhibited by ethereal solvents. The reaction is not stereospecific. B_4H_{10} also cleaves cyclopropanes, but B_5H_9 does not.

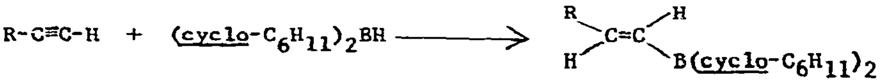


It was also observed that the rearrangement of the hydroboration product of 1,2-dimethylcyclohexene exchanges hydrogen and boron with retention of configuration, as if the rearrangement proceeds through a π-complex without dissociation to BH_3 and olefin.



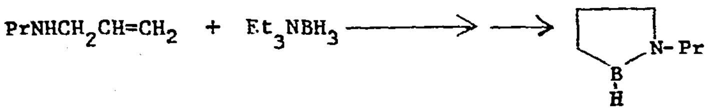
3. Miscellaneous examples. The qualitative results to be expected of hydroboration and reactions of the resulting boranes are by this time well known. It is inevitable that many people should begin to apply hydroboration to the solution of other problems in organic chemistry, and most of the examples which follow are of this type. Much of this literature adds little to knowledge of organoboron chemistry from an organometallic chemist's point of view, and details are therefore omitted from this survey.

Zweifel and coworkers have studied the regiospecificity of monohydroborations of alkynes [157]. Specificities observed range from high selectivity for placing the boron on the terminal carbon in the reactions of dicyclohexylborane or thexylborane with 1-alkynes to essentially random results in the reaction of borane with unsymmetrical disubstituted alkynes.

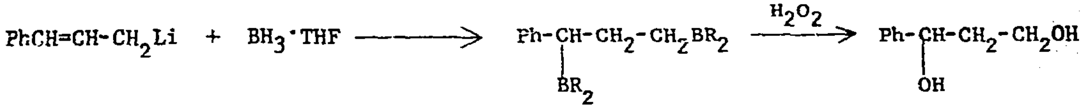


$$\text{R-C}\equiv\text{C-H} + (\underline{\text{cyclo}}\text{-C}_6\text{H}_{11})_2\text{BH} \longrightarrow (\text{R})(\text{H})\text{C=C}(\text{H})\text{B}(\underline{\text{cyclo}}\text{-C}_6\text{H}_{11})_2$$

Hydroboration of ethoxyacetylene has yielded trans-$(\text{EtOCH=CH})_3\text{B}$, which has been converted to $(\text{EtOCH-CH})_2\text{BOMe}$ and EtOCH-CHB(OMe)_2 [158]. Hydroboration of propylallylamine with triethylamine borane leads to 1-propyl-1,2-azaborolidine [159].

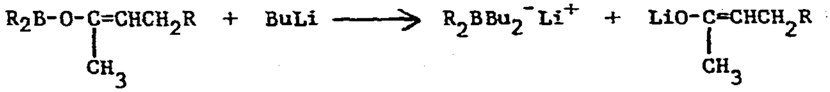


Hydroboration of phenylallyllithium followed by oxidation with alkaline hydrogen peroxide yields 1-phenyl-1,3-propanediol [160].



$$\mathrm{PhCH{=}CH{-}CH_2Li} + \mathrm{BH_3{\cdot}THF} \longrightarrow \mathrm{Ph{-}\underset{\displaystyle BR_2}{\underset{|}{C}H}{-}CH_2{-}CH_2BR_2} \xrightarrow{H_2O_2} \mathrm{Ph{-}\underset{\displaystyle OH}{\underset{|}{C}H}{-}CH_2{-}CH_2OH}$$

Hydroboration studies have been carried out on some cyclic sesquiterpenes [161], an α,β-unsaturated ketone [162], thujopsene [163], α-phellandrene [164], various phytol derivatives [165], and substituted cyclohexanone enamines [166]. The preparation of cis-cyclotridecene by way of hydroboration of cyclotridecyne has been described [167]. Hydroboration has been used in the synthesis of a branched-chain sugar from an unsaturated sugar derivative [168]. Hydroboration of 5,6,7,7a-tetrahydro-7a-methyl-1-indanone [169]and several bicyclo [3.1.1]-heptenols has been studied [170]. Disiamylborane has been used in the selective hydroboration of a cholestadiene [171]. The hydroboration stereochemistry of 7,7-dimethylnorbornene and 1,4,7,7-tetramethylnorbornene has been investigated in a study of torsional effects [172]. Hydroboration has been used as part of a study of the direction of reagent attack on highly chlorinated norbornene derivatives [173]. Asymmetric hydroboration of cholest-2-ene with (-)- and (+)-di-3α-pinanylborane has yielded results opposite to those predicted on the basis of Brown and Zweifel's model [174]. Propionic acid cleaves primary and secondary alkyl groups rather unselectively from trialkylboranes, but tertiary alkyl groups are cleaved more slowly [175]. Vinyloxyboranes from trialkylboranes and either diazo ketones or methyl vinyl ketone have been cleaved by alkyllithium to serve as sources of lithium enolates [176].



$$R_2B{-}O{-}\underset{\substack{|\\ CH_3}}{C}{=}CHCH_2R \;+\; BuLi \longrightarrow R_2BBu_2^{-}Li^{+} \;+\; LiO{-}\underset{\substack{|\\ CH_3}}{C}{=}CHCH_2R$$

Hydroboration has been used to selectively remove $\Delta^{1(9)}$-octalin in a preparation of Δ^{9}-octalin [177].

F. Reviews

H. C. Brown has published a review of some of the more important synthetic applications of hydroboration and borane chemistry [178]. A review of hydroboration has also appeared in India [179].

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