BORON

ANNUAL SURVEY COVERING THE YEAR 1974

PART I: CARBORANES AND HYDROBORATION

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CONTENTS

Boron. I. Carboranes and hydroboration; Annual Survey covering the year 1973 see J. Organometal. Chem., 75(1974)135-191.

I. CARBORANES

A. Introduction

M. F. Hawthorne and coworkers have been developing the chemistry of boron-carbon-cobalt polyhedral compounds at a dizzy pace, as a glance through the illustrations on the following pages will verify. R. N. Grimes and coworkers have converted small metallocarboranes to what appears to be a unique four-carbon distorted-icosahedral carborane. Rhodacarboranes synthesized by Paxson and Hawthorne have been found to be effective homogeneous hydrogenation catalysts. The "bridge" proton of a substituted protonated dicarbollide monoanion, $R\text{-}C_2B_9H_{11}^-$, undetectable by NMR, has now been found to occupy one vertex of the icosahedron from careful X-ray studies by M. R. Churchill and B. G. DeBoer. The Russian fascination with icosahedral carborane derivatives has continued, with Zakharkin's group producing the greatest number of papers.

Those who must justify their requests for research grant money on the basis that boron compounds may become useful will want to be aware of the important new developments regarding the ^{10}B neutron capture therapy of brain tumors reported during the past year, which are summarized in a separate subsection of this review. In addition to some rather conventional carborane chemistry, this subsection mentions such non-organometallic topics as polyhedral boron hydride anions and brain surgery, which are naturally not covered comprehensively but discussed for their possible interest to carborane chemists, in accord with the tradition of pointing out some of the highlights of polyhedral borane chemistry in these surveys.

Nomenclature of boron cage compounds is inherently difficult, as noted before in these surveys, and new problems continue to arise. The problem of naming $C_2B_9H_{12}^-$ now that the "bridge" hydrogen is known to occupy a vertex of the icosahedron will be discussed, since it seems rather inappropriate to call this a nido structure when it is really a closo structure with hydrogen in place of a metal or boron atom. Otherwise, the reviewer will tend to avoid nomenclature problems by using formulas and referring to drawings. Such handy trivial names as "dicarbollide ion" for $C_2B_9H_{11}^{2-}$ will be used rather than "undecahydrodicarba-nido-undecaborate(2-) ion" and the trivial names o-, m-, and p-carborane will be retained for 1,2-, 1,7-, and 1,12-dicarba-closo-dodecaborane (the icosahedral carboranes).

B. Metallocarboranes

1. Manganese, Iron, Cobalt, and Nickel.

The emphasis in this section will be on cobalt, since that is the element most used by Hawthorne's group for making new types of cage structures. The diversity of structures covered in some individual papers makes this section a bit difficult to organize. The general trend will be to start with larger cage sizes and proceed toward smaller, ignoring the number of heteroatoms, and two examples of nido structures are placed at the end. Most of the chemistry involved is an elaboration of known principles, including (1) thermal rearrangement of polyhedral cages, (2) cage expansion by alkali metal reduction to an anion followed by insertion of an electrophilic atom (such as cobalt), and (3) removal of an atom (usually boron) from the cage by cleavage with base followed by replacement with another atom (often cobalt) by reaction of the carborane anion with a suitable electrophilic species. Polyhedral expansion of some of the smaller carboranes has also been accomplished by direct reaction with transition metal carbonyls. Finally, it should be noted that an unexpected case of intermolecular disproportionation involving cobalt transfer has been encountered.

Hawthorne's group has carried out an extensive investigation of the cage rearrangements of cobaltacarboranes having 9, 10, 11, and 13 atoms in the cage [1]. These all rearrange much more easily than 12-atom (icosahedral) cages, and cobaltacarboranes rearrange more easily than the corresponding non-substituted carboranes. It was found that the cobalt atom always retains the position of highest coordination number, that carbon atoms always migrate further apart, that carbon atoms migrate to vertices of lowest coordination number, and, somewhat surprisingly, that carbon atoms tend to migrate away from cobalt if the other rules permit in a given case. Rearrangements observed are summarized in Figs. 1 through

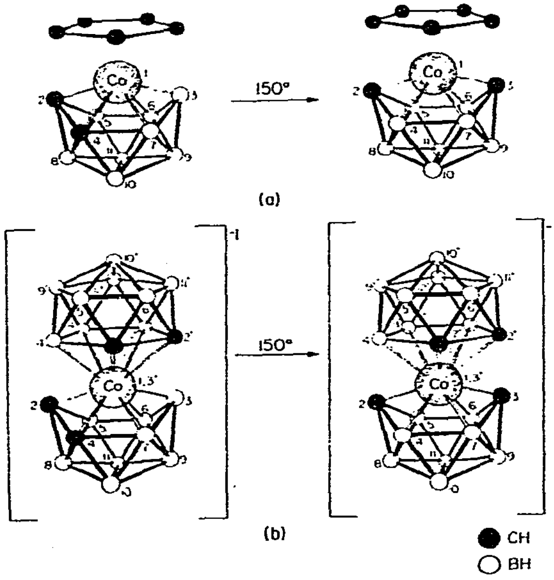


Figure 1. (a) The thermal rearrangement of 1-(η^5-C_5H_5)-1-Co-2,4-$C_2B_8H_{10}$ to 1-(η^5-C_5H_5)-1-Co-2,3-$C_2B_8H_{10}$. (b) The thermal rearrangement of [1,3'-Co(2,4-$C_2B_8H_{10}$)(1',2'-$C_2B_2H_{11}$]$^-$ to [1,3'-Co(2,3-$C_2B_8H_{10}$)(1',2'-$C_2B_9H_{11}$)]$^-$. [From reference 1.]

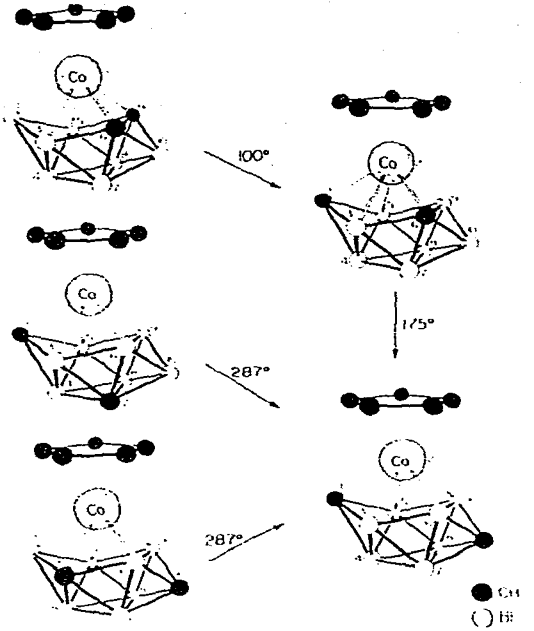


Figure 2. The thermal rearrangements of $(\eta^5\text{-}C_5H_5)CoC_2B_7H_9$. [From reference 1.]

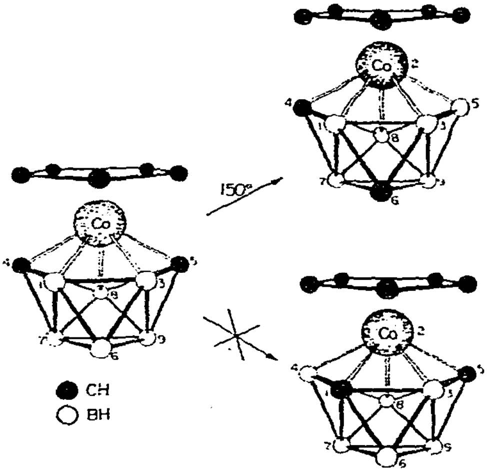


Figure 3. The thermal rearrangement of 2-$(\eta^5\text{-}C_5H_5)$-2-Co-4,5-$C_2B_6H_8$ to 2-$(\eta^5\text{-}C_5H_5)$-2-Co-4,6-$C_2B_6H_8$. [From reference 1.]

5. It may be noted that the π-complexed cyclopentadienyl group is now designated as $\eta^5\text{-}C_5H_5$, though in this review the η^5 will ordinarily be left out as unnecessary. It may also be pointed out that the first four figures show numbering systems used by Hawthorne for all cage sizes 9 through 13, which will be useful for reference where structural formulas

are not reproduced in this review. Hawthorne's system deviates from the IUPAC system so that all isomers of a given type of cage can be numbered with one self-consistent set of numbers.

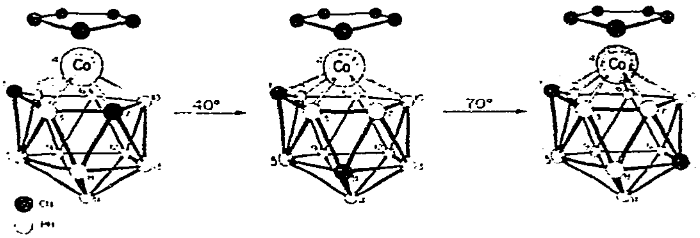


Figure 4. The thermal rearrangements of $(\eta^5\text{-}C_5H_5)CoC_2B_{10}H_{12}$. [From reference 1.]

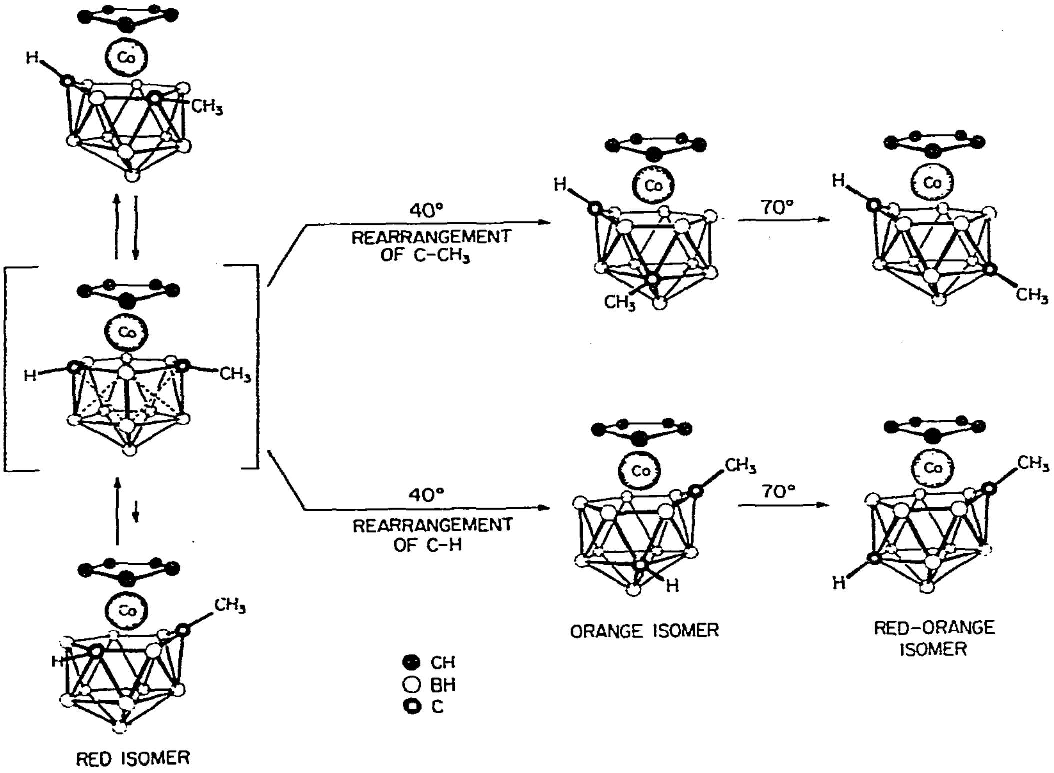


Figure 5. The proposed mechanism of the thermal rearrangements of $(\eta^5\text{-}C_5H_5)\text{-}(CH_3)CoC_2B_{10}H_{11}$. [From reference 1.]

Hawthorne's group has also carried out an extensive investigation of the thermal rearrangements of dicobaltacarboranes having 10, 11, or 12 atoms in the cage [2]. The cobalt atoms, which were capped with the usual η^5-cyclopentadienyl groups, tended to move apart in the cage in the same manner as carbon atoms. Several of the rearrangements observed are illustrated in Figs. 6, 7, and 8.

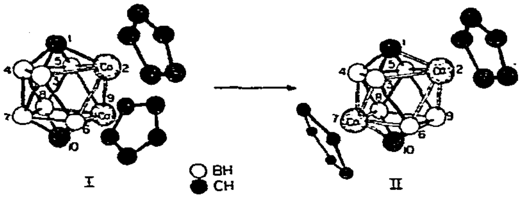


Figure 6. The rearrangement of 2,6,1,10-$(C_5H_5)_2Co_2C_2B_6H_8$ (I) to 2,7,1,10-$(C_5H_5)_2Co_2C_2B_6H_8$ (II). (The enantiomeric 2,9,1,10-structure of I is pictured here.) [From reference 2.]

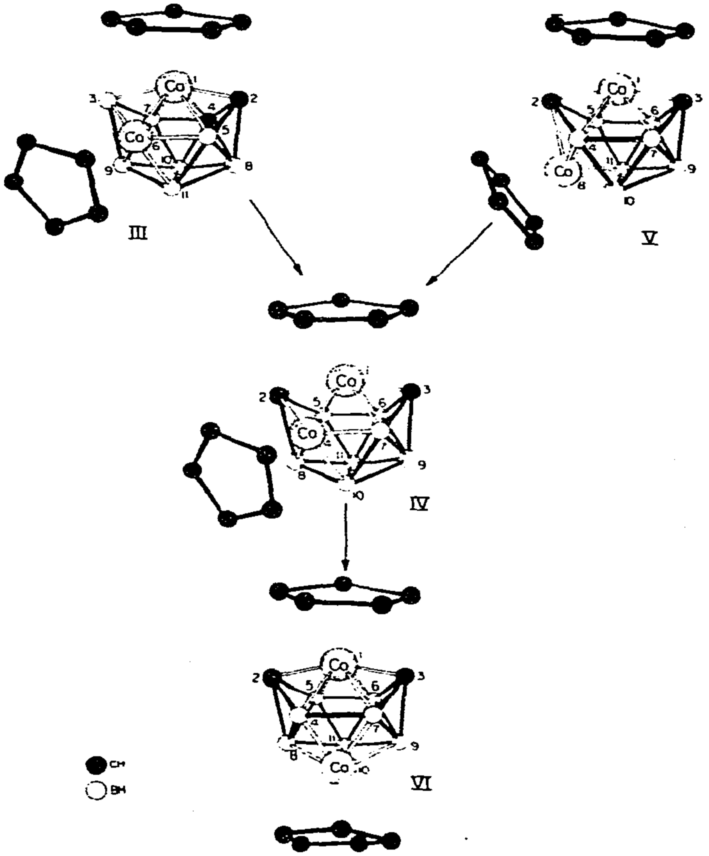


Figure 7. Rearrangements of octadecahedral bimetallocarboranes. The specific enantiomers shown have no mechanistic implications. [From reference 2.]

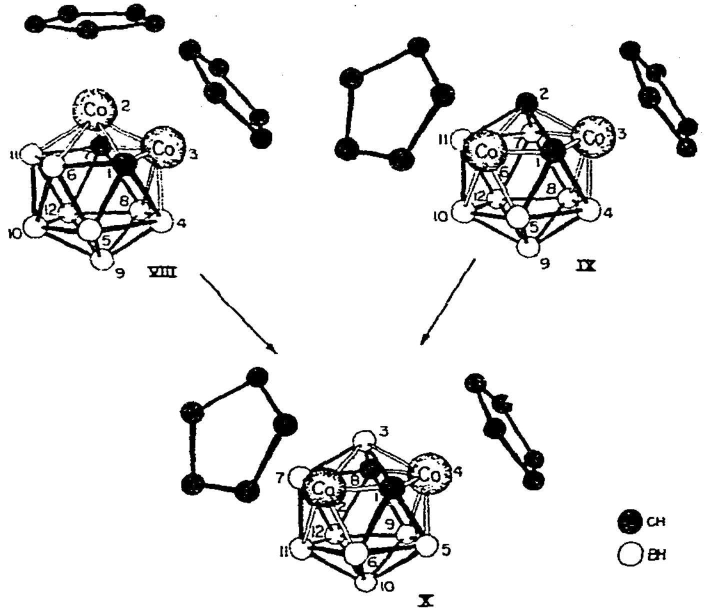


Figure 8. Rearrangement of 2,3,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (VIII) and 3,5,1,2-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (IX) to 2,4,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (X). (The enantiomeric 2,4,1,8-$(C_5H_5)_2Co_2C_2B_8H_{10}$ is pictured here for illustrative purposes.) [From reference 2.]

The structure of 12-(C_5H_5Co)-7,9-$B_{10}C_2H_{12}$ has been determined by X-ray diffraction (Figs. 9 and 10) [3]. This structure requires some rather severe distortions of the normal carborane cage bond angles and

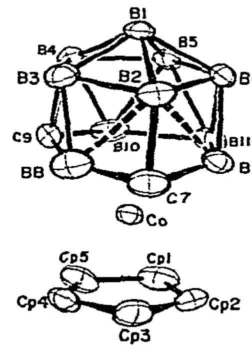


Figure 9. A view of the $(\pi\text{-}C_5H_5)Co(7,9\text{-}B_{10}C_2H_{12})$ molecule, showing the two anomalous four-membered systems B(2)-B(3)-B(8)-C(7) and B(2)-B(6)-B(12)-C(7) (ORTEP diagram, 50% ellipsoids). [From reference 3.]

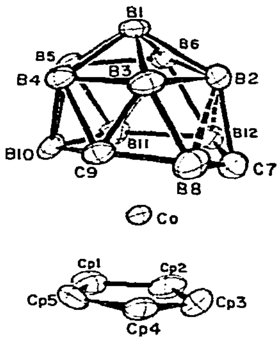


Figure 10. A view of the (π-C_5H_5)Co(7,9-$B_{10}C_2H_{12}$) molecule, showing non-planarity in the hexagonal bonding face of the carborane ligand. [From reference 3.]

distances. In the crystal, the two carbon atoms are nonequivalent and one of them, C(7), is pentacoordinate rather than hexacoordinate. (In solution, the molecule is fluxional and the carbons equilibrate between the two positions.) One of the boron atoms, B(2), is heptacoordinate but with two unusually long bonds.

Stanko and coworkers have reported that oxidation of 13-atom-cage metallocarborane anions of the general formula $(C_2B_{10}H_{12})_2M^-$, where M = Fe, Co, or Ni, by $CuCl_2$ in aqueous acetic acid gives mixtures of o-, m-, and p-carborane [4].

Dustin and Hawthorne have found that treatment of the 13-atom cage cyclopentadienylcobaltacarborane, $(C_5H_5Co)C_2B_{10}H_{12}$, with alcoholic alkali in the presence of cobalt(II) chloride and cyclopentadiene results in removal of one BH unit from the cage and insertion of C_5H_5Co in its place to yield a dicobaltacarborane having a 13-atom cage (Fig. 11) [5]. Thermal isomerization at 150° moves one carbon atom away from the cobalt (Fig. 12). When the degradation of the cobaltacarborane was carried out in the presence of $CoCl_2$ but the absence of cyclopentadiene, a structure having three cobalt atoms resulted (Fig. 13). With $FeCl_2$ and cyclopentadiene, a metallocarborane containing both iron and cobalt was obtained (Fig. 14).

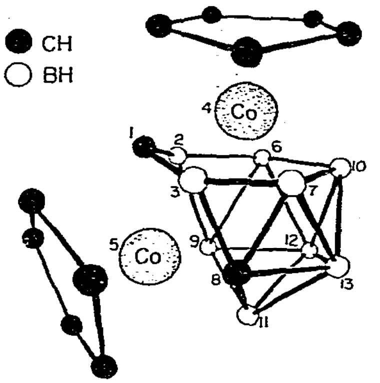


Figure 11. The proposed structure of I, 4,5-(π-C_5H_5)$_2$-4,5-Co_2-1,8-$C_2B_9H_{11}$. [From reference 5.]

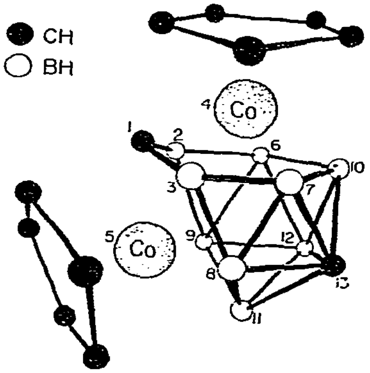


Figure 12. The proposed structure of III, 4,5-(π-C_5H_5)$_2$-4,5-Co_2-1,13-$C_2B_9H_{11}$. [From reference 5.]

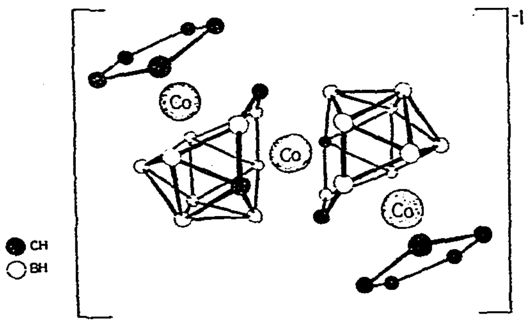


Figure 13. The proposed structure of the trans isomer of V, [(π-C_5H_5)-$CoC_2B_9H_{11}$]$_2Co^-$. [From reference 5.]

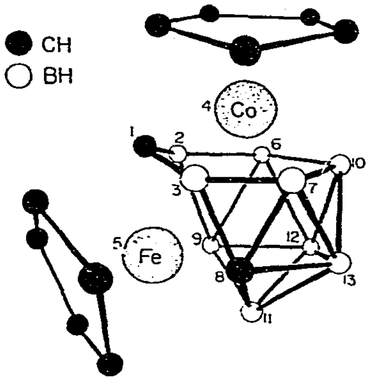


Figure 14. The proposed structure of VI, 4,5-$(C_5H_5)_2$-4-Co-5-Fe-1,8-$C_2B_9H_{11}$. [From reference 5.]

Reduction of the 13-atom cage cobaltacarborane 4,1,12-$(C_5H_5Co)C_2B_{10}H_{12}$ with sodium and naphthalene followed by addition of NaC_5H_5 and $CoCl_2$ and air oxidation has given the 14-atom cage dicobaltacarborane 1,14,2,10-$(C_5H_5Co)_2C_2B_{10}H_{12}$ (Fig. 15) [6]. Similar expansion of the 4,1,8-isomer of the 13-atom cage led to the 1,14,2,9-isomer of the 14-atom cage.

Similar chemistry has been carried out with smaller cages. In a preliminary communication, reduction of 2,1,6-$(C_5H_5Co)C_2B_7H_9$ with sodium

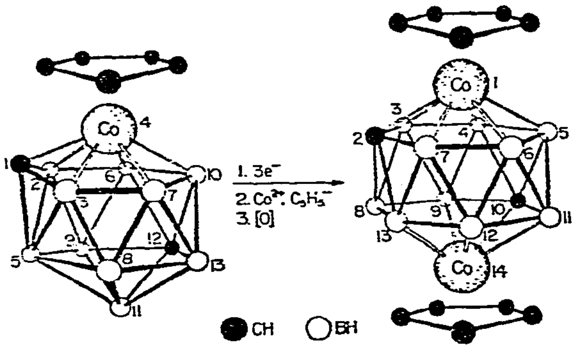


Figure 15. The formation and proposed structure of $(C_5H_5)_2$-$Co_2C_2B_{10}H_{12}$, (I), from the red-orange X[4,1,12-$C_5H_5CoC_2B_{10}H_{12}$]. An idealized view with planar six-membered rings is shown although distortions from this geometry as in $C_5H_5CoC_2B_{10}H_{12}$ are also possible for (I). [From reference 6.]

and naphthalene to a dicobalt complex, 1,8,2,3-$(C_5H_5Co)_2C_2B_7H_9$, and an unexpected icosahedral tricobalt compound, assigned the structure 1,2,8,3,6-$(C_5H_5Co)_3C_2B_7H_9$ on the basis of nmr and other considerations, was described by Evans and Hawthorne [7]. A later paper describes in detail the synthesis of di- and tricobaltacarboranes (Figs. 16-18) by the reduction of the closo-cobaltacarboranes 2,1,6-$(C_5H_5)CoC_2B_7H_9$, 1,2,3-$(C_5H_5)CoC_2B_8H_{10}$, 1,2,4-$(C_5H_5)CoC_2B_8H_{10}$, and 3,1,2-$(C_5H_5)CoC_2B_9H_{11}$ with sodium and naphthalene followed by the addition of cobalt(II) chloride and sodium cyclopentadienide [8].

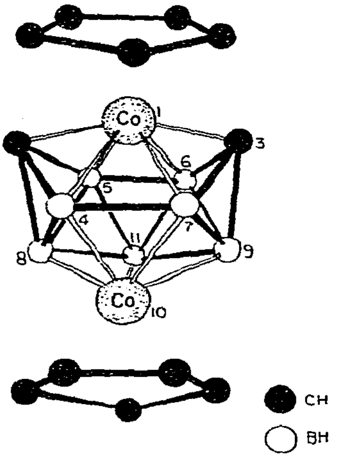


Figure 16. The proposed structure of $(C_5H_5)_2Co_2C_2B_7H_9$, III. [From reference 8.]

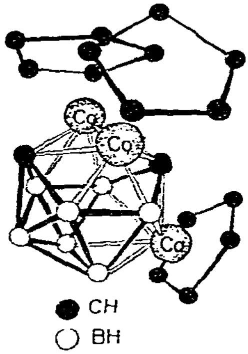


Figure 17. The proposed structure of $(C_5H_5)_3Co_3C_2B_7H_9$, V. [From reference 8.]

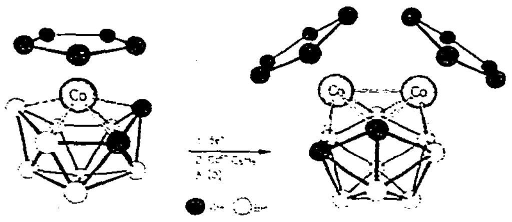


Figure 18. A possible structure of $(C_5H_5)_2Co_2C_2B_8H_{10}$, IX, formed from 1,2,4-$C_5H_5CoC_2B_8H_{10}$. [From reference 8.]

Reduction of 2-(C_5H_5Co)-1,6-$C_2B_7H_9$ with sodium and naphthalene followed by treatment with $FeCl_2$ and NaC_5H_5 has yielded $(C_5H_5Co)C_2B_7H_9(FeC_5H_5)$ [9]. The reaction of $(C_5H_5Co)C_2B_{10}H_{12}$ with alcoholic KOH in the presence of $FeCl_2$ and cyclopentadiene gave $(C_5H_5Co)C_2B_9H_{11}(FeC_5H_5)$.

Pyrolysis of 1-(C_5H_5Co)-2,3-$C_2B_8H_{10}$ in hexadecane at 235° results in an unexpected intermolecular cobalt transfer to form a series of isomeric icosahedral dicobalt complexes, $(C_5H_5Co)_2C_2B_8H_{10}$, one of which has been identified as 2,9-$(C_5H_5Co)_2$-1,12-$C_2B_8H_{10}$ (Fig. 19) [10].

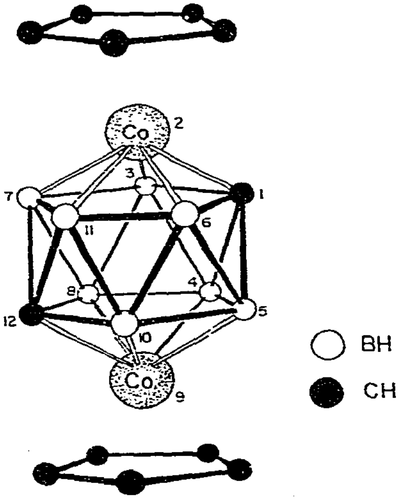


Figure 19. The structure of 2,9-$(\eta$-$C_5H_5)_2$-2,9-Co_2-1,12-$C_2B_8H_{10}$. [From reference 10.]

The structures of $2,6\text{-}(C_5H_5Co)_2\text{-}1,10\text{-}C_2B_6H_8$ (Fig. 20) [11]. $(C_5H_5Co)\text{-}CB_7H_8^-$ (Fig. 21) [12], and $2,3\text{-}(C_5H_5Co)_2\text{-}1,7\text{-}C_2B_8H_{10}$ (Fig. 22) [13] have been determined by X-ray diffraction. The cobalt-cobalt bonds of the two dicobalt compounds were unexpected until X-ray studies revealed them.

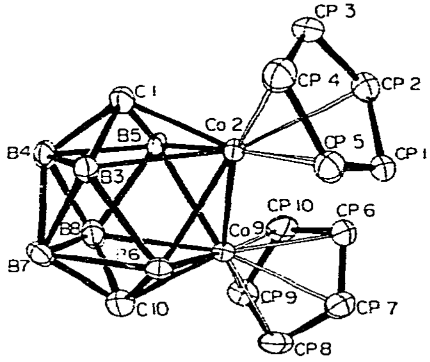


Figure 20. An ORTEP drawing of $2,9\text{-}(\eta C_5H_5)_2\text{-}2,9\text{-}Co_2\text{-}1,10\text{-}C_2B_6H_8$ showing the labeling used in this paper and 50% probability ellipsoids for all nonhydrogen atoms. Each atom except cobalt is also bound to a hydrogen atom which has been omitted for clarity. [From reference 11.]

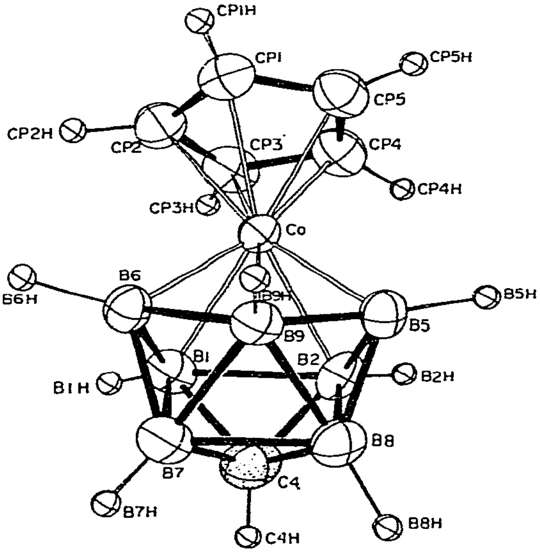


Figure 21. Structure and numbering of the $[C_5H_5CoCB_7H_8]^-$ anion. The hydrogen atoms have been given an arbitrary radius of 0.1 Å. [From reference 12.]

The structure of $(C_5H_5)Co(C_2B_8H_{10})Co(C_2B_8H_{10})^-$ prepared by way of polyhedral expansion of $1,6\text{-}C_2B_8H_{10}$ with sodium at -80^0 has been determined by X-ray (Fig. 23) [14].

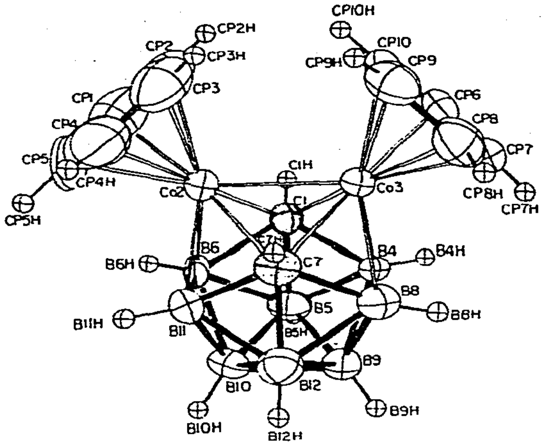


Figure 22. Structure and numbering system of 2,3-($C_5H_5)_2$-2,3-Co_2-1,7-$C_2B_8H_{10}$. The hydrogens have been given arbitrary radii of 0.1 Å. [From reference 13.]

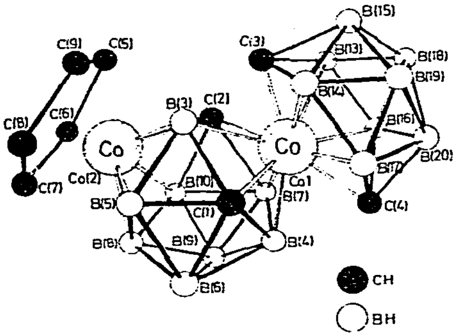


Figure 23. The molecular geometry of the [π-C_5H_5)-Co-$C_2B_8H_{10}$-Co-$C_2B_8H_{10}]^-$ anion. [From reference 14.]

Wiersema and Hawthorne have studied the ^{11}B and ^{13}C nmr spectra of a series of metallocarboranes, $(C_5H_5)M(C_2B_nH_{n+2})$ and $M(C_2B_nH_{n+2})_2$, where n = 6, 7, 8, or 9 amd M = Cr(III), Fe(III), Ni(III), or Co(II) [15]. The isotropic shifts due to the paramagnetism of these complexes reveal that the primary electron delocalization in these complexes involves ligand to metal charge transfer, except in the case of the icosahedral (B_9) cobalt(II) complex, where metal to ligand charge transfer dominates. Only the boron and carbon atoms bonded directly to the transition metal atom show large contact shifts, indicating that the unpaired electron character is not appreciably delocalized into the remainder of the carborane cage. Todd and coworkers have found that the 70.6 MHz ^{11}B nmr spectra of halogenated o- and m-carboranes, phosphacarboranes, and cobaltacarborane anions show shielding of the boron opposite the point of substitution [16].

Reaction of $CB_{10}H_{13}^-$ and cyclopentadiene with $CoCl_2$ in the presence of alcoholic KOH yields the cyclopentadienylcobalt carbollide 12-(C_5H_5Co)-7-$CB_{10}H_{11}$. The analogous nickel(IV) compound (Fig. 24) has also been prepared in low yield, starting from the triple-decker sandwich compound $(C_5H_5)Ni(C_5H_5)Ni(C_5H_5)^+BF_4^-$ and $CB_{10}H_{11}^{3-}$ and oxidizing the nickel(II) intermediate with air. The nickel(IV) compound undergoes the usual sort of ortho to meta to para cage rearrangement at 450° (Fig. 24) [17].

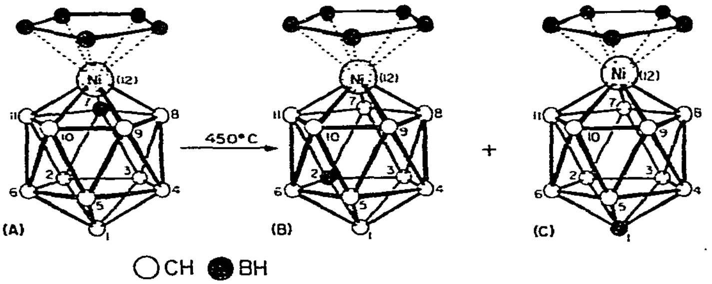


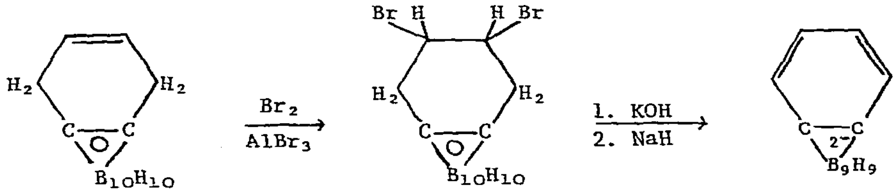
Figure 24. Proposed structures and numbering for $(\pi\text{-}C_5H_5)Ni^{II}(\pi\text{-}B_{10}CH_{11})$ isomers. [From reference 17.]

Zakharkin and coworkers have synthesized the hydroxymethyl "dicarbacanastide" complex 3,6-$(C_5H_5Co)_2$-1,2-HCB_8H_8C-CH_2OH in the usual manner for such complexes (see Organometal. Chem. Rev. B, 5 (1969) 12) modified by the inclusion of cyclopentadiene in the reaction mixture, starting from the appropriate hydroxymethyldicarbollide monoanion [18]. The hydroxymethyl group was then oxidized to the aldehyde with CrO_3.

By a bit of sloppy lab technique, Matteson had the necessary $AlBr_3$

catalyst for bromination of the double bond of dihydrobenzocarborane fall into his flask, and with Grunzinger expanded this lucky accident into a more convenient synthesis of the benzodicarbollide anion [19]. Benzocarborane (J. Organometal. Chem., 41 (1972) 37-38) could not be made by this approach because opening of the cage by base proved faster than dehydrobromination. The benzodicarbollide anion was converted to tricarbonylmanganese(I) (Fig. 25) and cobalt(III) (Fig. 26) derivatives, as well as to a diamagnetic nickel complex of uncertain structure.

A bis(dicarbollyl)cobalt complex having a sulfur bridge between boron atoms of the two icosahedra, $8,8'\text{-}S(C_2B_9H_{10})_2Co^-$, has been prepared from $H^+(C_2B_9H_{11})_2Co^-\cdot(Me_2SO)_2$ and S_2Cl_2 in CH_2Cl_2 [20]. Methylation with di-



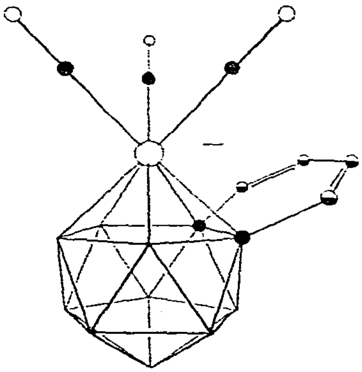


Figure 25. Structure diagram of the benzodicarbollylmanganese(I) tricarbonyl ion (14). The large open circle represents Mn; small open circles represent O, darkened circles C, half-filled circles CH, and unmarked line junctions BH. [From reference 19.]

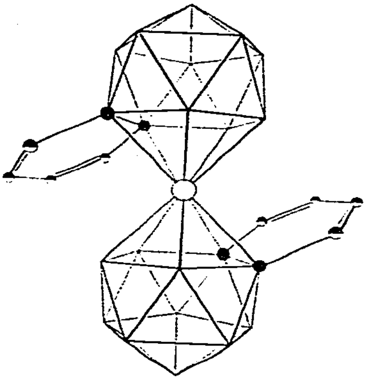


Figure 26. Structure diagram of the bis(benzodicarbollyl)cobaltate(III) ion (16). The large open circle represents Co; darkened circles represent C, half-filled circles CH, and unmarked line junctions BH. The relative rotational orientations of the two cages were chosen to show both rings clearly and do not necessarily represent a preferred conformation. [From reference 19.]

methyl sulfate gave the zwitterionic $MeS^+(C_2B_9H_{10})Co^-$.

Small amounts of 10-(C_5H_5Ni)-1-CB_8H_9, a nickel(IV) complex having the nickel bonded to four boron atoms, have been isolated from the reaction of $Na_3CB_{10}H_{11}$ and NaC_5H_5 with nickel(II) bromide (Fig. 27) [21].

Grimes and coworkers have synthesized a number of small and medium metallocarboranes by polyhedral expansion of small carboranes [22]. The small carboranes react directly with suitable metal carbonyls or related compounds to form the cage-expanded products. Reaction schemes are illus-

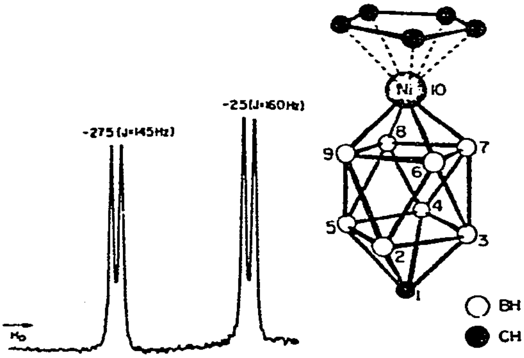


Figure 27. Proposed structure and 80.5-MHz ^{11}B nmr spectrum (CH_2Cl_2 solution) of 10-(C_5H_5Ni)-1-CB_8H_9. [From reference 21.]

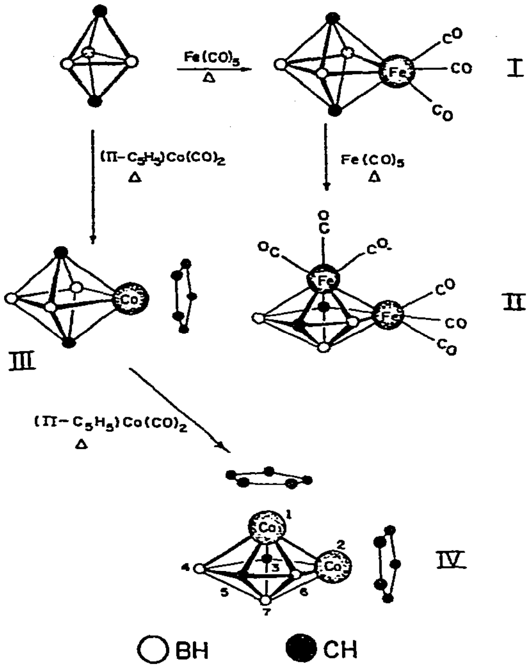


Figure 28. Reaction scheme for the gas-phase polyhedral expansion of 1,5-$C_2B_3H_5$. Structures shown for metallocarborane products are proposed from spectroscopic data. An additional product of the cobalt reaction sequence is 1,7,2,4-$(\pi\text{-}C_5H_5)_2Co_2C_2B_3H_5$. [From reference 22.]

trated in Figs. 28 and 29, a dicobaltacarborane in Fig. 30, and two isomers of tricobaltacarboranes in Fig. 31.

Grimes and coworkers have also published a detailed report of the synthesis of a triple-decked sandwich compound, $(C_5H_5)Co(C_2B_3H_5)Co(C_5H_5)$, and other small cobaltacarboranes from $NaC_2B_4H_7$ [23]. Structures of the types of compounds synthesized were illustrated from a preliminary communication in last year's survey (J. Organometal. Chem., 75 (1974) 149-151). Two nickel derivatives, $(2,3\text{-}C_2B_4H_6)Ni(Ph_2PCH_2CH_2PPh_2)$ and $(C_5H_5)_2Ni_2C_2B_5H_7$, were also prepared.

The reaction of $Ni(PEt_3)_4$ with 1,3-$(CH_3\text{-}C)_2B_7H_{11}$ leads to $(Et_3P)_2NiB_7H_{11}(C\text{-}CH_3)_2$, the structure of which has been determined by

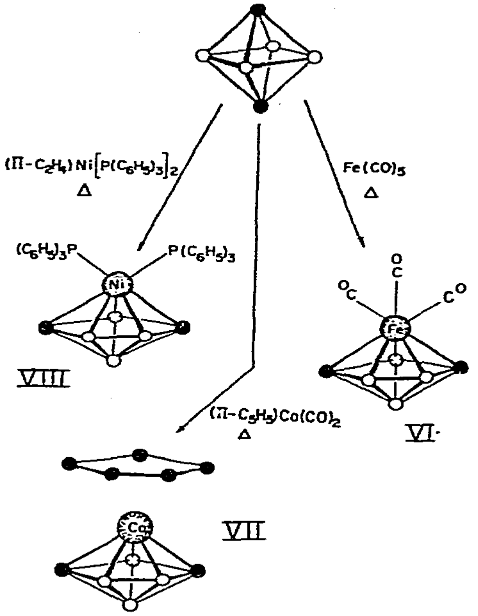


Figure 29. Reaction scheme for the gas-phase and solution polyhedral expansion of 1,6-$C_2B_4H_6$, showing proposed metallocarborane structures. [From reference 22.]

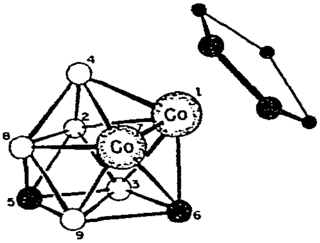


Figure 30. Schematic drawing of the proposed structure of 1,7,5,6-$(\pi\text{-}C_5H_5)_2Co_2C_2B_5H_7$. One of the $\pi\text{-}C_5H_5$ ligands has been omitted for clarity. [From reference 22.]

X-ray diffraction and found to be analogous to that of decaborane (Fig. 32) [24].

The structure of 8-(C_5H_5Co)-6,7-$C_2B_7H_{11}$ has been determined (Fig. 33 and 34) [25].

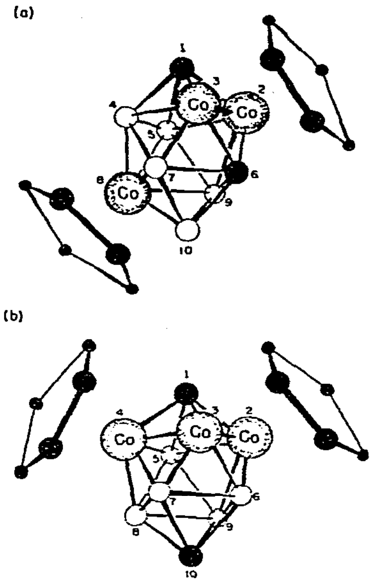


Figure 31. Schematic drawings of the proposed structures of (a) 2,3,8,1,6-$(\pi\text{-}C_5H_5)_3Co_3C_2B_5H_7$ (XIII) and (b) 2,3,4,1,10-$(\pi\text{-}C_5H_5)_3Co_3C_2B_5H_7$ (XIV). In both structures the $\pi\text{-}C_5H_5$ ligand on Co(3) is omitted for clarity. [From reference 22.]

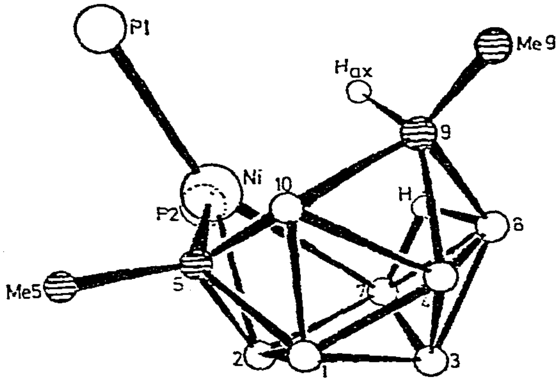


Figure 32. The structure of $(Et_3P)_2NiB_7H_{11}(C\text{-}CH_3)_2$. [From reference 24.]

2. A Four-Carbon Carborane from Metallocarboranes. Grimes and coworkers have isolated what appears to be an icosahedral 4-carbon carborane, $Me_4C_4B_8H_8$, from the decomposition of cobalt or iron derivatives of

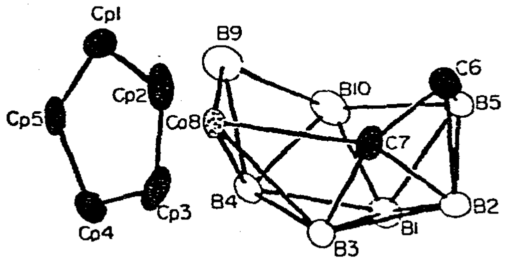


Figure 33. Structure and numbering of 8-η^5-C_5H_5-8-Co-6,7-$C_2B_7H_{11}$. The terminal and bridge hydrogen atoms are omitted for clarity. Atoms shown as 50% probability ellipsoids. [From reference 25.]

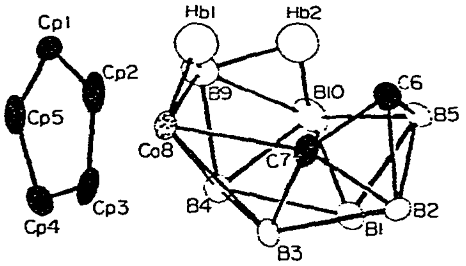


Figure 34. Alternate view of 8-η^5-C_5H_5-8-Co-6,7-$C_2B_7H_{11}$ showing positions of bridging hydrogen atoms. [From reference 25.]

$Me_2C_2B_4H_5^-$ (Fig. 35) [26]. This cage has two electrons too many for optimum bonding and is isoelectronic with $C_2B_{10}H_{12}^{2-}$. Reaction of $Me_4C_4B_8H_8$ with $Mo(CO)_6$ has yielded a 13-atom cage molybdenum complex, $Me_4C_4B_8H_8Mo(CO)_3$.

3. Rhodium and Platinum. Paxson and Hawthorne have prepared icosahedral rhodacarboranes by the reaction of $(Ph_3P)_3Rh^+$ with 7,8-$C_2B_9H_{12}^-$ or 7,9-$C_2B_9H_{12}^-$ (protonated *o*- and *m*-dicarbollide ions, respectively). These rhodacarboranes have the empirical formula $(Ph_3P)_2RhHC_2B_9H_{11}$, with a rhodium-hydrogen bond, and they catalyze the hydrogenation of 1-hexene to hexane in benzene solution at 1 atmosphere of H_2 [27]. They also catalyze isomerization of alkenes and the hydrosilylation of ketones. The isomer illustrated (Fig. 36) is 2-$(Ph_3P)_2RhH$-1,7-$C_2B_9H_{11}$, derived

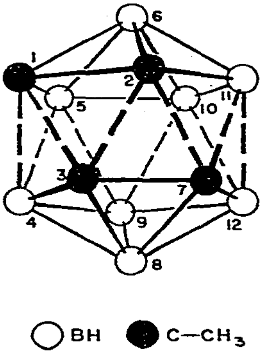


Figure 35. Possible structure for isomer B, formed by face-to-face fusion of two $(CH_3)C_2B_4H_4$ units. Distortion from regular icosahedral symmetry is suggested by broken lines. [From reference 26.]

from $7,9-C_2B_9H_{12}^-$. It was also found that these rhodacarboranes are efficient catalysts for hydrogen-deuterium exchange of the boron-bound hydrogen, but not C-H, of a variety of closo-carboranes and boranes [28]. The same type of H-D exchange is also catalyzed by $(Ph_3P)_2RuHCl$, but not as effectively as by the rhodacarborane catalyst. For more material on the mechanism of H-D exchange, see part B-6.

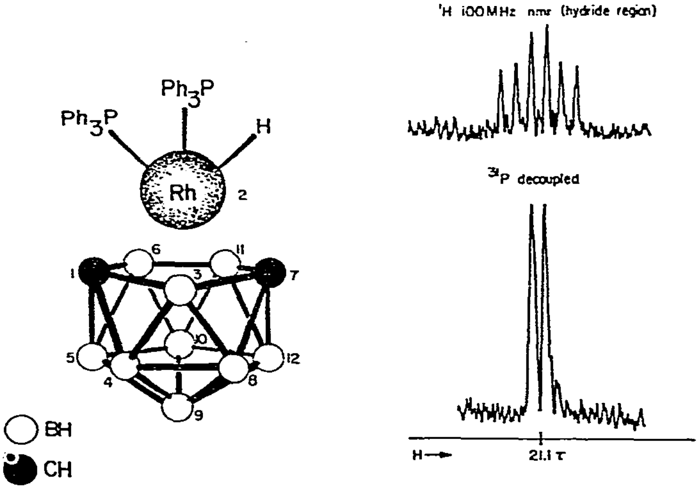


Figure 36. The proposed structure of 2,2-bis(triphenylphosphine)-2-hydridoundecahydro-1,7-dicarba-2-rhoda-closo-dodecaborane (II) and the 100-MHz ^1H nmr spectrum of the hydride region. [From reference 27.]

Stone and coworkers have shown by X-ray crystallography that 7,9-Me_2-7,9-$C_2B_9H_9$-12-Pt($PPhMe_2$)$_2$ has the expected distorted icosahedral structure, and they have also isolated and characterized a new stereochemically nonrigid platinacarborane, <u>nido</u>-10,10-(Et_3P)$_2$-2,8-Me_2-10,2,8-$PtC_2B_7H_7$ (Fig. 37 and 38), from the reaction of <u>closo</u>-1,6-Me_2-1,6-$C_2B_7H_7$ with Pt(PEt_3)$_3$ [29].

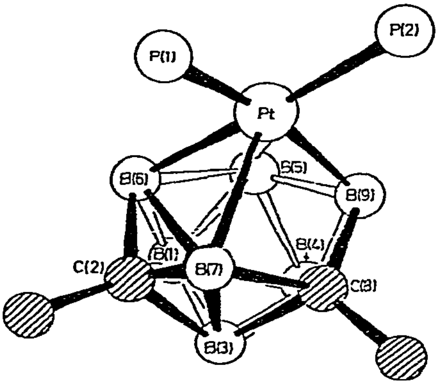


Figure 37. Structure of [$Me_2C_2B_7H_7$]Pt[PEt_3]$_2$. Phosphino ethyl groups are omitted for clarity. [From reference 29.]

Figure 38. Interconversion of valence tantomers of [$Me_2C_2B_7H_7$]Pt[PEt_3]$_2$. [From reference 29.]

The reaction of the trans-stilbene--$Pt(PMe_3)_2$ complex with 1,6-Me_2-1,6-$C_2B_6H_6$ has yielded two new platinacarboranes, one a closo structure (Fig. 39) and the other a nido structure (Fig. 40) [30].

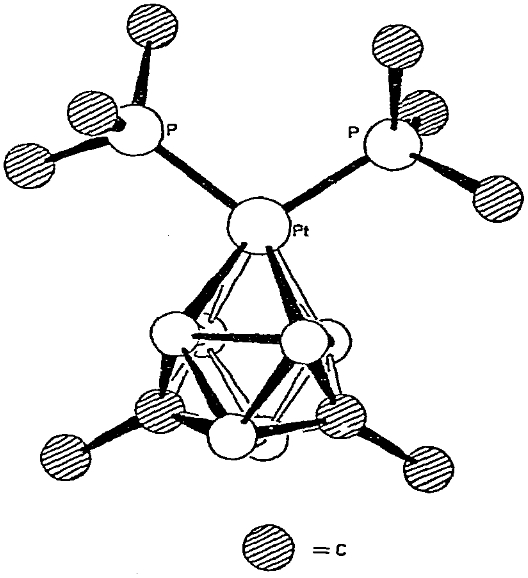


Figure 39. closo-1,1-$(Me_3P)_2$-1-Pt-6,8-Me_2-6,8-$C_2B_6H_6$. [From reference 30.]

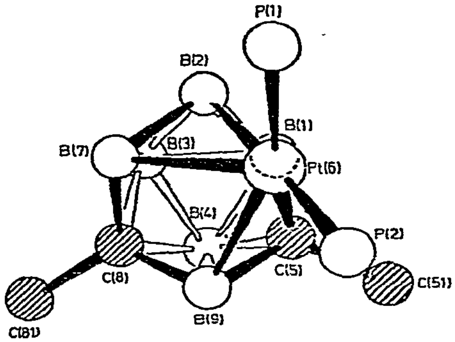


Figure 40. nido-6,6-$(Et_3P)_2$-5,8-Me_2-6,5,8-$PtC_2B_6H_6$. [From reference 30.]

4. Group IV and V Metallocarboranes. Smith and Hawthorne have prepared arsacarboranes (Fig. 41) by the reaction of Tl_2-7,8-$C_2B_9H_{11}$ with CH_3AsBr_2, $PhAsCl_2$, or $BuAsCl_2$ [31]. The usual sodium dicarbollide failed to work in this synthesis, and for this reason the thallium compound was used in its place. The reaction of Li-7,8-$C_2B_9H_{12}$ with Me_2AsCl led to $(Me_2As)_2C_2B_9H_{11}$, the structure of which is not yet known but which must be a nido-carborane having the arsenic atoms somewhere along the edge of the open face.

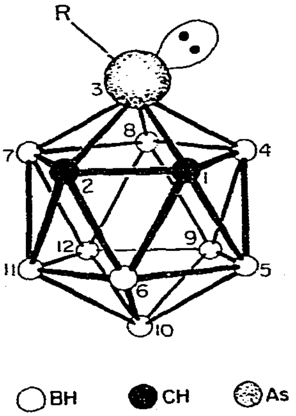


Figure 41. Proposed structure of 3-R-3-As-1,2-$C_2B_9H_{11}$. [From reference 31.]

Shortly before Smith and Hawthorne's report that it wouldn't work appeared, Siedle and Todd succeeded in making $C_2B_9H_{11}AsPh$ "in low yield" from Na_2-7,8-$C_2B_9H_{11}$ (disodium dicarbollide) and $PhAsCl_2$ [32]. This leaves the thallium salt as the better approach, but should perhaps remind us not to have too much faith in anyone's negative results.

The synthesis of several icosahedral germacarboranes, including 1-CH_3-1,2-$GeCB_{10}H_{11}$, 1,2-$CB_{10}H_{11}Ge^-$, 1,2-$CB_{10}H_{11}GeCr(CO)_5$ (Fig. 42), and related compounds has been reported in detail by Wikholm and Todd [33].

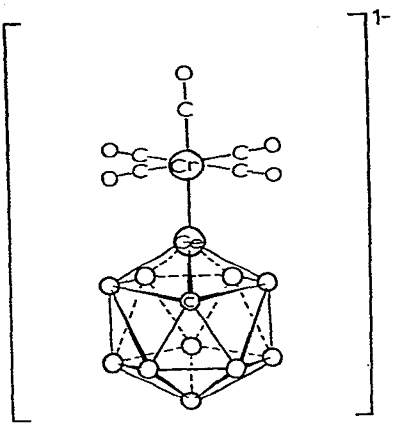


Figure 42. Proposed Structure of the 1,2-$B_{10}H_{10}CHGeCr(CO)_5^-$ ion. [From reference 33.]

A series of σ-bonded metalloheteroboranes have been prepared from reactions of cyclohexene-$Fe(CO)_2(C_5H_5)^+$ or $(C_7H_7)Mo(CO)_3^+$ with 1,2-$GeCB_{10}H_{11}^-$, 7,8-$PCB_9H_{10}^-$, 7,8-$As_2B_9H_{10}^-$, $B_{10}H_{12}P^-$, or $B_{10}H_{12}As^-$. Typical products include $(C_5H_5)Fe(CO)_2GeCB_{10}H_{11}$, which has an Fe-Ge σ-bond, and $(C_7H_7)Mo(CO)_2GeCB_{10}H_{11}$, which has an Mo-Ge σ-bond [34].

The ^{119}Sn Mossbauer spectrum of 3-Sn-1,2-$C_2B_9H_{11}$ indicates that tin(II) is the oxidation state [35].

5. Hydrogen as a Heteroatom in Polyhedra. Churchill and DeBoer have carried out a thorough X-ray structure determination on a substituted protonated dicarbollide ion, $[(C_5H_5)Co^+(C_5H_4)]$-$C_2B_9H_{11}^-$, which is an unexpected by-product of the reaction of $C_2B_{10}H_{12}^{2-}$ with NaC_5H_5 and $CoCl_2$ [36]. The hydrogen atoms were located accurately, with the surprising result that the "bridge" proton on the protonated dicarbollide ion was found to occupy one of the vertices of the icosahedron and be bonded simultaneously to the three boron and two carbon atoms of the open face of the ion. The bonding of the facial hydrogen is strongest to B(8) and weakest to the two carbon atoms, but all five neighbors must parti-

cipate to some extent in bonding to this hydrogen atom. This result accounts for previous failures to locate this proton by means of nmr spectra. The structure of the compound is illustrated in Fig. 43 and the environment of the facial hydrogen in Figs. 44 and 45.

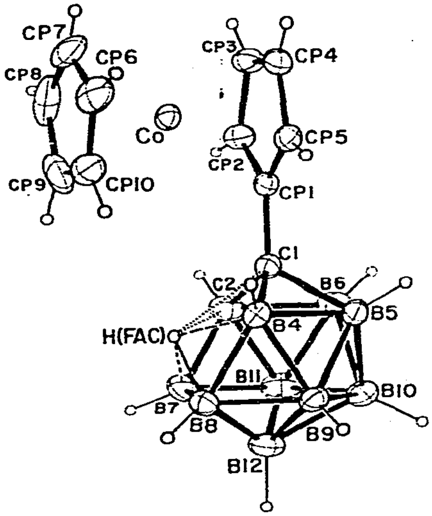


Figure 43. A general view of the (π-C_5H_5)Co(π-$C_5H_4\cdot B_9C_2H_{11}$) molecule, showing the scheme used for labeling atoms. (ORTEP diagram, 30% ellipsoids; hydrogen atoms are artificially reduced to spheres of radius 0.07Å). [From reference 36.]

As pointed out in the introduction, these results leave the systematic name "dodecahydro-7,8-dicarba-nido-undecaborate(1-) ion" for 7,8-$C_2B_9H_{12}^-$ a bit inconsistent with the facts. A more descriptive name would be "dodecahydro-1,2-dicarba-3-hydra-closo-dodecaborate(1-) ion" if H is regarded as replacing BH of dodecahydrododecaborate, or "undecahydro. . . ." if H is considered to replace B. (The reviewer favors the former, since it preserves "dodecahydro-closo-dodecaborate" as fundamental structure on which the name is based, though it might be noted that specifying the number of hydrogens in a closo structure is redundant in any case, since there must be one hydrogen for each vertex in any unsubstituted closo borane or carborane.) The multicoordinate hydrogen atom appears

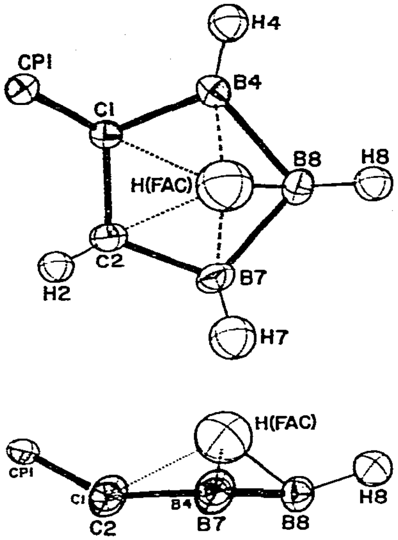


Figure 44. The environment of the "facial" hydrogen atom. (a) Projection on to the least-squares plane of the open pentagonal face (ORTEP diagram; 30% ellipsoids for all atoms; carbon and boron atoms shaded). (b) "Side-on" view of the facial hydrogen over the B_3C_2 face; only substituents C(1), HB(8), and H(FAC) are shown (ORTEP diagram; 30% ellipsoids). [From reference 36.]

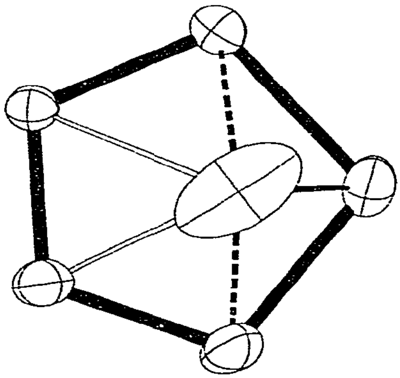
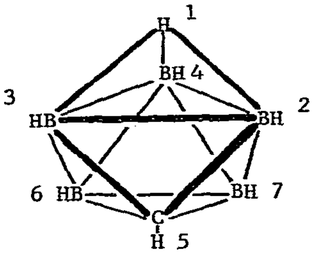


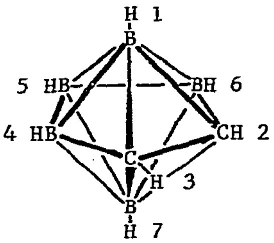
Figure 45. The C(1)-C(2)-B(7)-B(8)-B(4) face, showing the orientation of the vibration ellipsoid associated with atom H(FAC). (This diagram has the same perspective as Figure 3.) Details of the thermal parameters of H(FAC) are as follows: B_{11} = 7.3 (10), B_{22} = 5.3 (8), B_{33} = 10.6 (11), B_{12} = -0.4 (8), B_{13} = -4.6 (9), B_{23} = -6.0 (7) Å^2. The rms amplitudes of vibration along the principal axes of the ellipsoid are 0.03, 0.29, and 0.48 Å, the thin direction being perpendicular to the plane of projection of this figure. [From reference 36.]

to be a monster never before faced by a nomenclature committee, and the "hydra" terminology would seem to have the right flavor here. However, the potential arguments over the fine points that may be raised ("hydra" versus "hydrogena", "dodecahydro" versus "undecahydro") leave this reviewer yearning for the good old days when Hawthorne got unequivocal trivial names at La Paloma Restaurant, which undoubtedly would have christened $C_2B_9H_{12}^-$ as "dicarbollatapadide ion" (*olla tapada* = "jar with lid" -- *gracias a la profesora* Marianna Matteson).

A somewhat similar vertex hydrogen is apparently present in the one-carbon carborane CB_5H_7. Beaudet and coworkers have found by microwave spectroscopy that the carbon-boron framework is a distorted octahedron. The "bridge" hydrogen must occupy the triangular B-B-B face having long B-B distances (1.88 Å) rather than the normal B-B cage distances (1.7 Å) [37]. This result agrees with Onak's conclusion based on NMR studies (part C [44]).



CB_5H_7 numbered as 7-atom polyhedron (C_3 symmetry)



2,3-$C_2B_5H_7$, the more common type 7-atom polyhedron (D_{5h} symmetry)

The conventional *closo*--*nido* distinction again seems inappropriate. However, the "hydra" nomenclature works perfectly, and CB_5H_7 becomes 1-hydra-5-carba-*closo*-heptaborane(7, C_3). The "C_3" refers to the symmetry of the hypothetical parent borane on which the name is based and distinguishes this structure from the more common 7-atom polyhedron of

D_{5h} symmetry as found in $C_2B_5H_7$. This addition of the symmetry symbol is a standard though little-used feature of borane nomenclature, and is not absolutely necessary even in the present situation. The allowed isomers of $C_2B_5H_7$ are 1,2-, 1,7-, 2,3-, and 2,4- (with the latter two being known compounds), in order to assign the lowest possible numbers to the heteroatoms, and 1-hydra-5-carba-... must belong to a different cage symmetry.

6. σ-Bonded Transition Metal-Substituted Carboranes. The mechanism for hydrogen-deuterium exchange of carborane B-H bonds catalyzed by rhodacarborane and other transition metal hydride catalysts (part B-3) [27, 28] apparently involves a reversible oxidative addition of the B-H bond to the transition metal catalyst. Support for this idea is provided by the isolation of the product of oxidative addition of o-carborane to $(Ph_3P)_3IrCl$ with loss of one PPh_3 to yield $3\text{-}[(Ph_3P)_2IrHCl]\text{-}1,2\text{-}C_2B_{10}H_{11}$ (Fig. 46) [38]. Treatment of this addition product with CO regenerates o-carborane and $(Ph_3P)_2Ir(CO)Cl$. The latter is thermodynamically favored and will not regenerate the addition product with o-carborane even on prolonged refluxing in toluene, but it does catalyze the deuteration of o-carborane, suggesting that it forms an addition product present in small concentration at equilibrium with o-carborane.

The reaction of trans-bis(trialkylphosphine)platinum dichlorides with 1-lithio-o-carboranes was reported last year to yield σ-bonded carboranylplatinum compounds, but with an odd sort of loss of hydrogen and apparent ring-closure of one of the alkyl groups of one of the phosphine ligands to the platinum atom (J. Organometal. Chem., 75 (1974) 163). The structure of one of these complexes has now been determined by X-ray crystallography and has been found to contain a three-membered Pt-P-C ring [39].

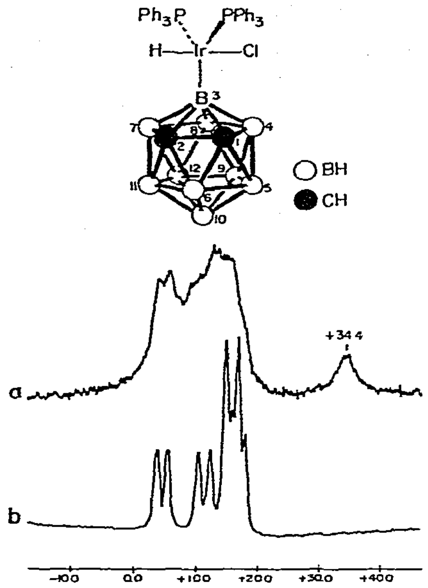
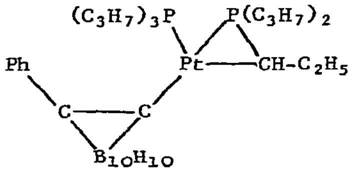


Figure 46. The proposed structure of I, 3-[(PPh$_3$)$_2$IrHCl]-1,2-C$_2$B$_{10}$H$_{11}$, and the 80.53-MHz ^{11}B nmr spectra of I (a) and 1,2-C$_2$B$_{10}$H$_{12}$ (b). [From reference 38.]



Several 1-lithiocarboranes have been reacted with *trans*-(Et$_3$P)$_2$PtHCl to form the *cis*- or *trans*-1-(Et$_3$P)$_2$PtH-carborane [40].

Several rhodium(I) derivatives of *o*- and *m*-carboranes have been isolated, including 1-[(Ph$_3$P)$_2$Rh]-2-CH$_3$-*o*-C$_2$B$_{10}$H$_{10}$ and related compounds [41].

o-, *m*-, and *p*-HCB$_{10}$H$_{10}$CCu have been prepared from the corresponding lithiocarboranes and CuCl. Reaction of the copper derivatives with iodobenzene yields 30-35% of the corresponding 1-phenylcarboranes [42].

C. Small- and Medium-Sized Carboranes

Pyrolysis of nido-2-CB_5H_9 has yielded m-carborane (Fig. 47) [43].

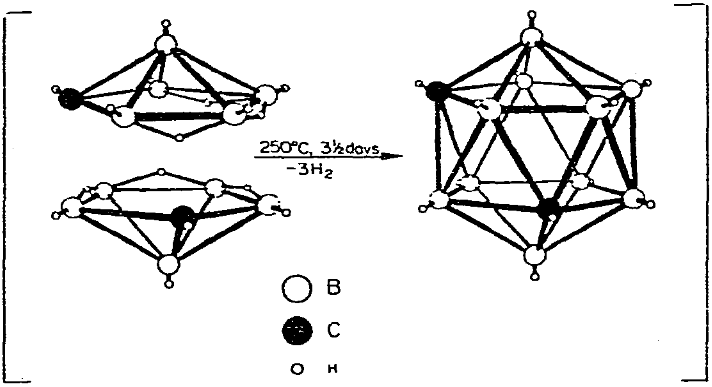
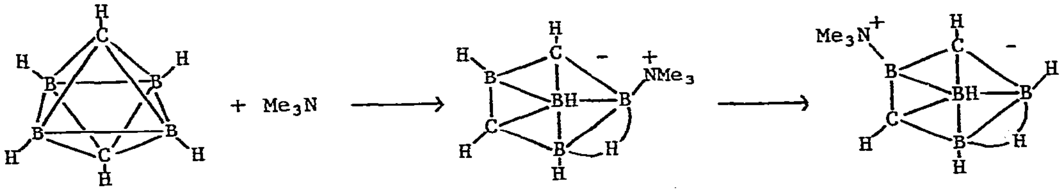


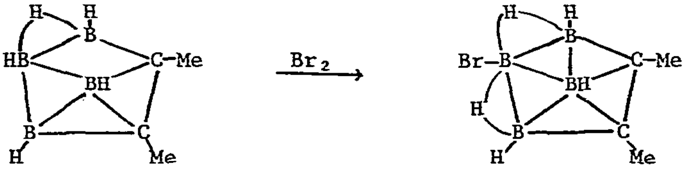
Figure 47. Schematic representation of the fusion of two B_5C skeletons to produce the 1,7-$B_{10}C_2$ skeleton. [From reference 43.]

^{11}B-decoupled proton NMR spectra of the small closo-carboranes 1,5-$C_2B_3H_5$, CB_5H_7, 1,2-$C_2B_4H_6$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$ have been measured by Onak and Wan. Long-range proton-proton spin couplings of 10-12 Hz were found between opposite positions in the first three compounds. From $^{11}B^{13}C$, $^{1}H^{13}C$, and $^{1}H^{11}B$ coupling constants it was concluded that most of the cage-orbital s-character appears in the C-B bonds and the B-B bonds are essentially derived from p-orbitals [44].

The closo-carborane cage of 1,6-$C_2B_4H_6$ is opened by trimethylamine to form 5-Me_3N^+-nido-2,4-$C_2B_4H_6^-$, which rearranges thermally to the 3-Me_3N^+-isomer [45]. Sodium hydride converts either of the trimethylamino isomers to the 2,4-$C_2B_4H_7^-$ ion.



The nido-carborane anion 4,5-Me_2-4,5-$C_2B_4H_5^-$ has been prepared by treatment of $Me_2C_2B_4H_6$ with BuLi or H^- and reacted with Br_2 to form 3-$BrMe_2C_2B_4H_5$ or with ICl to give a mixture of 2- and 3-$ClMe_2C_2B_4H_5$ [46].



Onak and coworkers have reported that the reaction of B_2H_6 with CO in a reactor having a hot zone and a cold finger yields B_4H_8CO, which reacts with ethylene to form $(CH_2)_2B_4H_8$ or higher alkenes to form alkyl derivatives of $(CH_2)_2B_4H_8$ [47]. Reilly and Burg have obtained $C_2B_6H_{10}$ in 36% yield from the reaction of $C_2B_3H_5$ with B_2H_6 in a specially designed reactor [48]. Maya and Burg have prepared the bis(phosphino)carborane $[(CF_3)_2P\text{-}C]_2B_5H_5$ from $Li_2C_2B_5H_5$ and $(CF_3)_2PCl$ [49].

Periodic acid oxidation of 1,8-$(CH_3C)_2B_9H_9$ (cage structure shown in Fig. 48) has yielded the 3-hydroxy derivative or the 3,7-dihydroxy derivative, depending on the reaction conditions [50]. Several reactions of these compounds were investigated.

The dicarbollide monoanion 6,7-$C_2B_9H_{12}^-$ has been oxidized with aqueous ferric chloride to the nido-carborane 5,6-$C_2B_8H_{12}$, which has been dehydrogenated at 245° to the closo-carborane 1,6-$C_2B_8H_{10}$ [51]. p-$PhCB_8H_8CLi$ reacts with PhCOCl to form $PhCB_8H_8CCOPh$, Ac_2O to form $PhCB_8H_8CCOCH_3$, $PhOCH(OEt)_2$ to form $PhCB_8H_8CCHO$, PhCHO to form $PhCB_8H_8CCH(OH)Ph$, CH_2O to form $PhCB_8H_8CCH_2OH$, PhOCN to form $PhCB_8H_8CCN$, and $PhCB_8H_8CCOCl$ to form $(PhCB_8H_8C)_2CO$ [52].

Dipole moments of 1,6-$C_2B_7H_9$, 1,6-$C_2B_8H_{10}$, 1,10-$C_2B_8H_{10}$, and 1,8-$C_2B_9H_{11}$ have been measured [53].

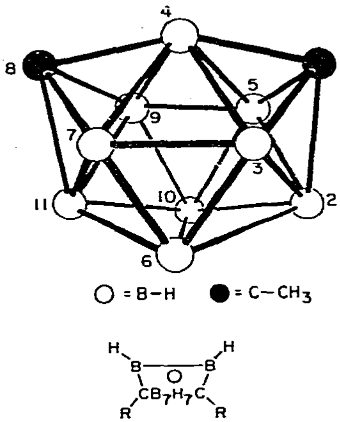


Figure 48. The cage structure of 1,8-$(CH_3C)_2B_9H_9$. (Professor Scholer has pointed out that the latest nomenclature would renumber the 1 and 8 positions as 2 and 3, the 3 and 7 positions as 4 and 7.) [From reference 50.]

D. Icosahedral Carboranes

1. Cage Syntheses and Rearrangements. The synthesis of m-carborane from CB_5H_9 has already been noted in part C [43]. The oxidation of 13-atom-cage metallocarborane anions to icosahedral carboranes has been noted in part B-1 [4].

Gregor and Stuchlik have reported that the reaction of 2-bromodecaborane or its diethyl sulfide derivative with acetylene yields a mixture of 3-, 4-, 8-, and 9-Br-o-$C_2B_{10}H_{11}$ and not the single product reported previously by Kalinin and Zakharkin [54].

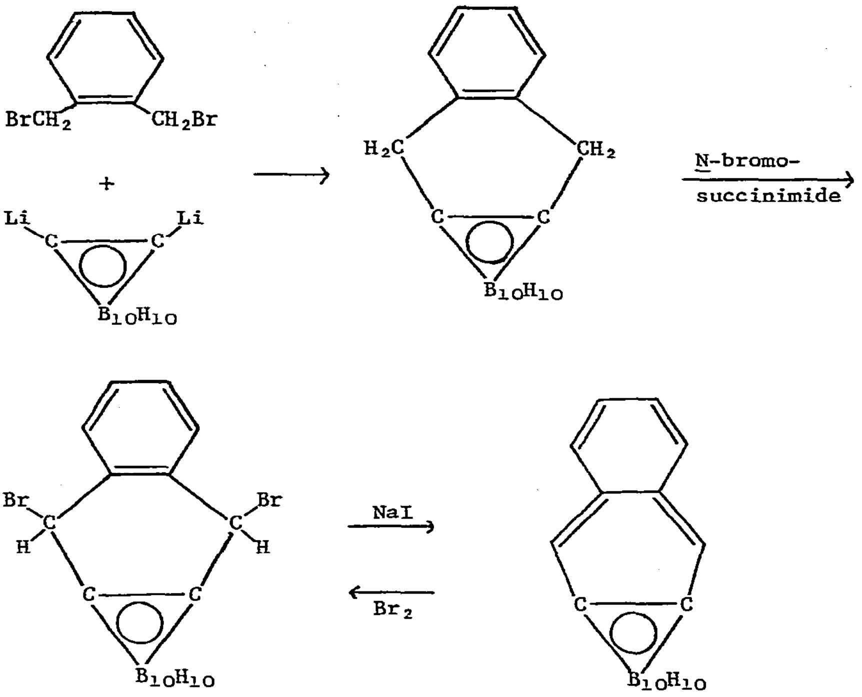
Stanko and coworkers have found that the anion $C_2B_{10}H_{12}{}^{2-}$ from the reduction of p-carborane with sodium in liquid ammonia is stable in tetrahydrofuran for as long as a month and yields exclusively m-carborane on oxidation with benzoquinone. The B nmr spectrum of the anion consists of three lines in the intensity ratio 4:5:1. Similar treatment of 1-methyl-p-carborane leads to 95% 1-methyl-o-carborane and 5% 1-methyl-m-carborane. When o-carborane was reduced to the dianion and oxidized with $KMnO_4$ in liquid ammonia the major product was 3-amino-o-carborane [55].

Zakharkin, Kalinin, and Gedymin have reported that the reaction of m-$C_2B_9H_{11}{}^{2-}$ with CH_2=CH-BCl_2 at -50° yielded 2-vinyl-m-carborane, which was oxidized with CrO_3 to 2-carboxy-m-carborane, and several standard transformations of the carboxyl group were carried out [56]. Reaction of the carboxylic acid with HN_3 yielded 2-amino-m-carborane, which was diazotized and converted to 2-fluoro-m-carborane.

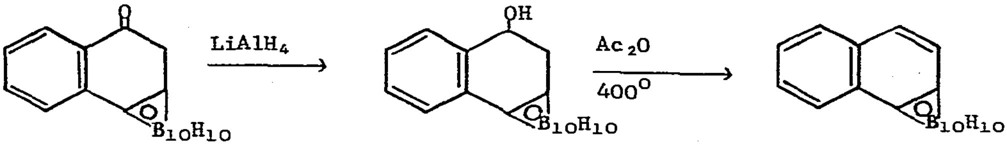
Zakharkin and coworkers have studied the decomposition of o-, m-, and p-carboranes at high temperatures (300-700°) [57]. Decomposition products are hydrogen, methane, and a polymeric insoluble residue having the approximate composition $C_{1.9}B_{10}H_{8.9}$. Phenyl groups were lost from 1-phenyl- or 1,7-diphenyl-m-carborane at 500°.

2. Rings Fused to Carborane Cages. The chemistry reported here is not essentially different from other organic chemistry of substituted carboranes, but the steric constraints put on a ring fused to a carborane cage sometimes lead to unusual results. The conversion of benzocarborane to benzodicarbollylmetal complexes has been noted in part B-1 [19].

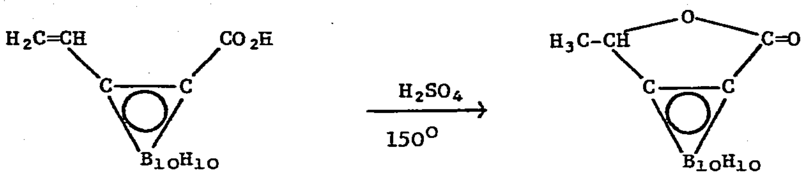
Matteson and Davis have synthesized 1,2-(2,3-naphtho)-o-carborane by a route that is straightforward in principle and has an amusing little twist in practice, namely, that the dihydro intermediate with NBS yields only dibromo compound [58]. The carbocyclic rings show no positive evidence of π-bonding with the carborane cage, though a small degree of such π-bonding is not precluded by the available evidence, and the compound has the properties of a sterically hindered o-xylylene. (For positive evidence of π-bonding involving a carborane cage, see part D-4.) Bromine and oxygen attack the inner ring, dienophiles add to the outer ring, and tetracyanoethylene is sterically hindered from reacting at all.

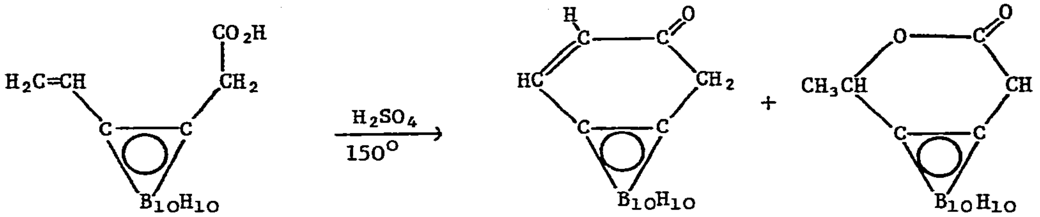


The stable isomer, 1,2-(1,2-naphtho)-o-carborane, offers no special difficulties or unusual properties, the aromaticity of the benzene ring being unconstrained, and Zakharkin and coworkers have made it by a straightforward route [59].

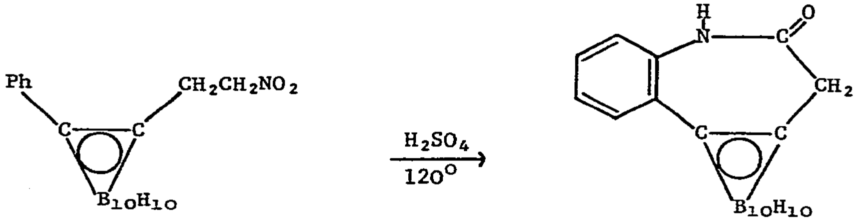


Zakharkin and coworkers have reported ring closures involving vinyl and carboxyl substituents on o-carborane [60].

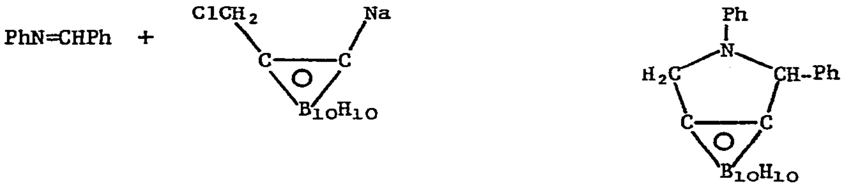




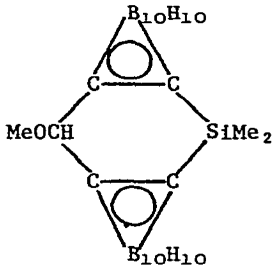
Treatment of a nitroalkylcarborane with sulfuric acid at 120° converted the $-CH_2NO_2$ group to $-CO_2H$. When an adjacent phenyl group was present, cyclization accompanied the internal oxidation-reduction [61].



Shiff bases give cyclic adducts with *o*-$ClCH_2$-$CB_{10}H_{10}CNa$ [62].



Zakharkin and Shemyakin have made a series of heterocyclic *o*-carborane derivatives containing Si, As, Ge, Sn, or P, of which a typical example is illustrated, by reacting the appropriate dilithiobiscarboranylmethane with the methyl- or dimethylheteroatom dihalide [63].



An analogous series of compounds having an Me_2Si or Me_2Ge group in place of the MeOCH group has also been prepared [64].

Bis(diphenylphosphino)carborane, "dpc", has been found to form tetrahedral cobalt(II) complexes, $Co(dpc)X_2$, and cobalt(II) and nickel(II) complexes of the general formula $[M(dpc)_2X]X$, where X is halide [65].

3. Side Chain Chemistry of Carboranes. It is easy to attach organic side chains or silicon or phosphorus to the carbon of an icosahedral carborane by use of the alkali metal derivative and a suitable electrophile, or to synthesize substituted carboranes by the use of an appropriately substituted acetylene, and further transformations can be carried out as if the material were an ordinary organic compound, except where the steric bulk or electronegative character of the carborane cage interferes. As usual, the majority of this work has been done in the U.S.S.R., but the flood of papers seems to be (mercifully) slowing somewhat.

Several types of carboranyltropylium ions ("carbaousenium" ions) have been prepared by Harmon and coworkers (Fig. 49) [66]. The carborane cage tends to destabilize the tropylium ion and there is little π-bonding between the ring and the cage.

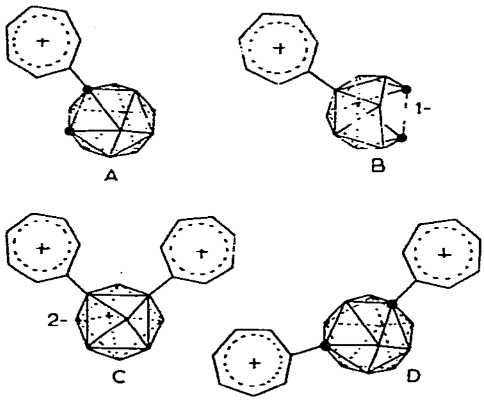


Figure 49. Ousene-type compounds: (A) [7.12^1]-1,2-dicarbahemiousenium ion, (B) [7.11^x]-nido-(3)-1,2-dicarbahemiousene, (C) [7.7.10^{2,x}] ousene, and (D) [7.7.12^{1,7}]-1,7-dicarbaousenium ion. The positions of the ring in B and of the second ring in C are not known and are drawn as shown for convenience. [From reference 66.]

Zakharkin and coworkers have investigated the lithiation of *o*-RCB$_{10}$H$_{10}$CCH$_2$CH=CHR', where R = Me or Ph and R' = H, Me, or Ph, with butyllithium. Treatment of the lithio derivatives with H$_2$O, CO$_2$, CH$_2$O, Br$_2$, or HgCl$_2$ yielded allylic mixtures of RCB$_{10}$H$_{10}$CCH=CH-CHXR' and RCB$_{10}$H$_{10}$CCHX-CH=CHR', where X = H, CO$_2$H, CH$_2$OH, Br, or HgCl, respectively. Coupling of the allyl groups by CuCl was observed [67]. The metallation of the allylcarborane 1-Me-2-CH$_2$=CH-CH$_2$-*o*-C$_2$B$_{10}$H$_{10}$ with sodium in liquid ammonia removes the allylic proton, and the allyl anion can then be protonated by water to form mainly the starting material or by *t*-butyl alcohol to yield 1-Me-2-CH$_3$CH=CH-*o*-C$_2$B$_{10}$H$_{10}$ [68]. Reaction of *o*-RCB$_{10}$H$_{10}$CNa with epichlorohydrin leads to a mixture of RCB$_{10}$H$_{10}$CR', where R' is 2,3-epoxypropyl, and RCB$_{10}$H$_{10}$C-CH=CH-CH$_2$OH [69]. Oxidation of the latter with MnO$_2$ yields carboranylacroleins, RCB$_{10}$H$_{10}$C-CH=CH-CHO [70]. The reaction of *o*-RCB$_{10}$H$_{10}$CLi with α,β-unsaturated aldehydes has been used to prepare RCB$_{10}$H$_{10}$CCHOHCH=CHR', which on treatment with SOCl$_2$ yield RCB$_{10}$H$_{10}$CCH=CHCHClR' [71]. The reaction of perfluoroalkenyl-substituted carboranes with sodium borohydride results in partial replacement of the fluorine by hydrogen [72].

Heating 3-amino-o-carborane at 220-250° in the presence of toluenesulfonic acid in benzene has yielded bis(3-o-carboranyl)amine, and heating 3-amino-o-carborane with aniline has given 3-anilino-o-carborane [73].

Nitration of isopropenylcarborane with N_2O_4 followed by chromatography of the resulting mixture of dinitro and nitrosonitro compounds on silica gel has yielded $HCB_{10}H_{10}C\text{-}C(CH_3){=}CHNO_2$, which has been patented as a burning rate catalyst for double-base propellants for use by the world's most affluent army [74].

From the inscrutable (to Americans) world of Soviet patents come recipes for oxidative purification of o-carboranes made from acetylenes and decaborane [75] and the conversion of carboranyl-CH_2OCOR to $-CH_2OP(O)(OH)_2$ [76]. Soviet patents have been issued for improved yield syntheses of carborane-substituted acetophenones [77] and alkoxysilylcarboranes [78], esterification of carboranylchlorosilanes with mixtures of C_6 and larger alcohols [79], the preparation of silicon-substituted carboranes from carboranes, chloromethylsilanes, and $AlCl_3$ [80], the preparation of silicon-containing carboranes by the reaction of unsaturated silicon compounds with o-, m-, or p-carboranes in the presence of $AlCl_3$ [81], and the conversion of $1,7\text{-}(R_2SiH)_2\text{-}m\text{-}C_2B_{10}H_{10}$ to $1,7\text{-}(R'CO_2SiR_2)_2\text{-}m\text{-}C_2B_{10}H_{10}$ with $R'CO_2H$ and a catalyst such as H_2PtCl_6 [82].

The silylation of $1,7\text{-}(HOMe_2Si)_2\text{-}m\text{-}C_2B_{10}H_{12}$ with a variety of chlorosilanes to form terminal $Si\text{-}O\text{-}SiR_2X$ groups hydrolyzable to $Si\text{-}O\text{-}SiR_2OH$ groups suitable for making carborane--siloxane polymers has been described [83]. Reaction of $(EtO)_2PCl$ with o-$MeCB_{10}H_{10}CLi$ yields $MeCB_{10}H_{10}C\text{-}P(OEt)_2$, which reacts with BuSCl to form $MeCB_{10}H_{10}C\text{-}P(O)(OEt)SBu$ [84].

4. Physical Measurements. Bushweller and coworkers have proposed conjugation between the carborane cage and a carbonyl substituent as the explanation of the unusually low rotation barrier found by proton NMR

measurements for the carbonyl carbon-nitrogen bond in $1,2\text{-}(Me_2N\text{-}CO)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ [85]. The normal electron delocalization pattern of the amide group would be disrupted by π-bonding to the carborane cage and the carbon-nitrogen bond order would be lowered. However, π-bonding to the cage should not restrict the rotation about the cage--substituent linkage, since π-bonding to a cage atom is not an appreciable function of rotational angle. Restricted rotation of the substituents was observed, but was attributed to steric factors. For other approaches to the π-bonding question, which yielded essentially negative results, see parts B-1 [19], D-2 [58], and D-3 [66].

A detailed proton NMR study of several closo carboranes has been reported [86]. A tendency toward decoupling of the ^1H and ^{11}B spins at lower temperatures due to quadrupole relaxation was observed.

The 80.2-MHz ^{11}B NMR spectrum of 8-iodo-o-carborane has been observed and interpreted in detail [87]. NMR studies of icosahedral carboranes, phosphacarboranes, and cobaltacarborane anions [16] and of paramagnetic metallocarboranes [15] have been noted in part B-1, and a proton NMR study of several smaller carboranes in part C [44]. ^{11}B nmr spectra have been measured and interpreted for a number of halogenated o-, m-, and p-carboranes [88].

Kinetics of hydrolysis of o-, m-, and p-carboranyl phenyl ketones and trimethylstannyl o-, m-, and p-carboranes by potassium hydroxide have been measured, and the relative rates in both series have been found to be o-> m-> P- [89].

Vapor pressure as a function of temperature has been measured for $1\text{-}(Me_3SiCH_2CH_2)\text{-}1,7\text{-}C_2B_{10}H_{11}$ and $1,7\text{-}(Me_3SiCH_2CH_2)_2\text{-}1,7\text{-}C_2B_{10}H_{10}$ [90]. Heats of combustion, formation, and sublimation have been measured for o-, m-, and p-carborane and their $1\text{-}CH_2OH$ derivatives [91].

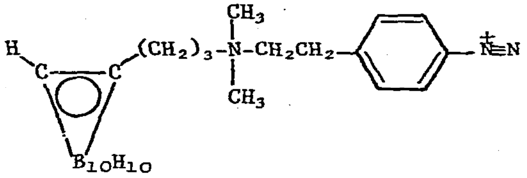
From the integral intensities of the CH bands of about 50 substituted o-carboranes it has been concluded that substituent effects are transmitted from one carbon to the other in the carborane cage by an inductive effect, but the transmission mechanism is more complex if the substituent is at B-3 [92]. Infrared spectra of 43 halogenated carboranes have been correlated with structure [93]. Mass spectra of several B-($X_3SiCH_2CH_2$)-substituted o-, m-, and p-carboranes, where X = CH_3 or Cl, have been reported [94].

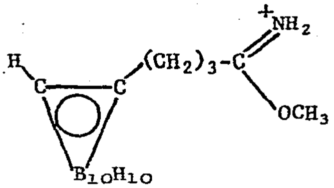
Tertiary amines catalyze the acylation of aniline by m-$HCB_{10}H_{10}C$-COCl [95].

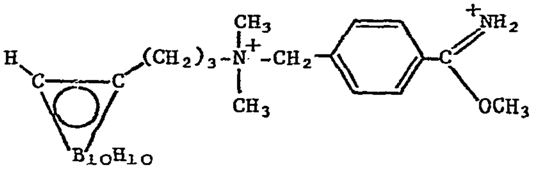
E. New Approaches to ^{10}B-Neutron Capture Therapy of Brain Tumors

Two recent developments in this field, which involve both carboranes and polyhedral borane anion chemistry, are of considerable potential importance. First, after a suggestion by Soloway that binding of boron to antibodies might provide a way to incorporate boron selectively into tumors, Hawthorne and coworkers reported in 1972 that the carborane 1-o-$C_2B_{10}H_{11}$-p-$C_6H_4N{\equiv}N^+$ does bind to an antibody to bovine serum albumin, though the amount of boron carried by the antibody without causing precipitation and denaturation was only sufficient to demonstrate possible biological effects *in vitro* and would not be enough for eradicating tumor cells in living systems [96]. Soloway and coworkers have synthesized a series of Me_2S-$B_{10}H_8$-SMeR and Me_2S-$B_{12}H_{10}$-SMeR in which the group R contains such substituents as carboxyl, nitroaryl, aminoaryl, isothiocyanate, or unsaturation and have found that these will bind to proteins but that more polar compounds will be required in order to achieve sufficient boron incorporation without precipitation of the protein [97].

Lipscomb and coworkers have synthesized several substituted o-carboranes containing ionic centers in the hope of finding compounds that will bind considerable amounts of boron to antibodies without precipitating the protein [98]. Representative examples are illustrated.







These and several related compounds were found to bind to γ-globulin with up to about 0.6% boron incorporation when 50% of the protein was precipitated, and boron concentrations up to 1.77% were achieved with the polyhedral anion $(Me_2S\text{-}B_{10}H_8\text{-}N{=}C{=}O)^-$ [99].

The second major development in the ^{10}B-neutron capture treatment of brain tumors is the clinical success reported by Hatanaka and coworkers in treating terminally ill glioblastoma patients with the aid of $B_{12}H_{11}SH^{2-}$ prepared by the Shionogi Pharmaceutical Company [100, 101]. At first, only patients who had previously received ^{60}Co treatment were treated, and the ^{10}B neturon capture therapy prolonged life but could not restore functions lost due to radiation damage of the brain. More recently, initial treatment of four patients with the boron method has resulted in three cases of reversal of brain impairment by the tumor and return of the patients to regular work. At the time the second article was written, one patient had been alive and well for 19 months [101]. These results are very hopeful, but a number of problems remain unresolved. Questions have been raised by American workers as to whether the active compound really is $B_{12}H_{11}SH^{2-}$, but the reviewer has not found any published data, and the outcome of further experiments is unpredictable.

F. Boron Hydrides

The reaction of pentaborane(9) with $Fe(CO)_5$ has yielded $B_4H_8Fe(CO)_3$, in which the $Fe(CO)_3$ group replaces the apex BH of the pentaborane [102]. The ferraboranes $B_7H_{12}Fe(CO)_4^-$ and $B_7H_{11}Fe(CO)_4$ have been prepared [103]. $B_6H_{10}Fe(CO)_4$ and several related transition metal complexes of hexaborane have been synthesized [104].

The crystal structure of $B_8H_{13}Mn(CO)_3$ has been determined by X-ray and the Mn found to be linked to the borane cage by three Mn-H-B bridge bonds [105]. $Mn(CO)_5Br$ and KB_9H_{14} in tetrahydrofuran form a compound having a cage analogous to decaborane in which the $Mn(CO)_3$ group is located at one of the two projecting positions along the open face of the cage and one of the cage boron atoms is substituted by THF [106]. Rhenium forms a similar derivative. Triethylamine attacks the tetrahydrofuran ring and opens it to form a derivative which has been characterized by X-ray diffraction [107].

Arsaboranes such as $7\text{-}B_{10}H_{12}As^-$ have been obtained from decaborane [108]. Synthetic chemistry based on $B_9H_{13}^{2-}$, $B_9H_{11}S^{2-}$, and $B_9H_9S^{2-}$ has led to the new compounds $6\text{-}PhB_{10}H_{13}$, $(B_9H_{11}S)M^{2-}$ (M = Ni or Pd), and $(B_9H_9S)PdL_2$ where the Pd is part of a closo cage and L_2 is $(PPh_3)_2$, phenanthroline, or $C_2S_2(CN)_2$ [109]. $2\text{-}CH_3B_6H_9$ has been synthesized from $B(CH_3)_3$ and B_5H_9, and $1\text{-}Me_3SiB_6H_9$ from H_2BCl etherate and $Me_3SiB_5H_7^-$ [110]. Several reactions of $B_{10}H_{14}$ have been studied, including that with acetone to form $B_{10}H_{13}CH_3$ [111]. $(B_5H_8)_2SiHCH_3$ and related compounds have been prepared [112]. ^{11}B nmr spectra of several monohalogenated decaboranes have been measured and the chemical shifts assigned [113].

Ab initio self-consistent-field calculations have been reported for B_4F_4 and B_4Cl_4 [114] and for B_8H_{12}, B_9H_{15}, $B_6H_6^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{10}H_{14}^{2-}$ [115]. Ab initio molecular orbital calculations have been reported for

BH_3CO [116]. A revised topological approach has been used to determine allowed transition states for nucleophilic and electrophilic reactions of polyhedral boranes [117].

Decomposition of B_3H_7CO leads to bis(carbonyl)diborane(4), $OCBH_2$-BH_2CO, evidently by way of the intermediate B_2H_4 [118].

The ion $B_{10}H_9IC_6H_5^-$ has been prepared and found to be analogous to diphenyliodonium ion [119]. Electrochemical oxidations of $B_{10}H_9L^-$ ions to B_{20} ions have been studied [120].

G. Reviews

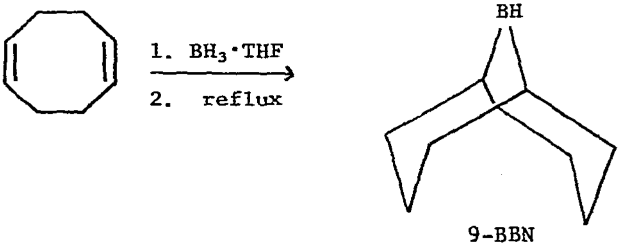
Carborane and metallocarborane chemistry has been reviewed by Onak [121]. Zakharkin and Kalinin have reviewed metal carborane chemistry in Russian [122]. A brief review of carboranes has appeared [123]. Mass spectra of boron compounds, including carboranes and trialkylboranes, have been reviewed [124]. A lecture on carborane structures and the limitations of conventional bonding theory has been published [125].

II. HYDROBORATION

A. Hydroborating Agents

Enough reagents useful for various types of hydroborations are now known that the rate of discovery of new types has slowed considerably. However, detailed experimental procedures for preparing and utilizing some of the more recently discovered hydroborating agents have appeared during the past year.

Brown and coworkers have published a detailed account of the synthesis of 9-borabicyclo[3.3.1]nonane, better known as "9-BBN", from 1,5-cyclooctadiene and borane in THF [126]. The initial hydroboration product contains about 28% of the [4.2.1]-isomer, but refluxing in THF for an hour isomerizes this to 9-BBN. As Brown has reported in previous communications (Organometal. Chem. Rev. B, 5 (1969) 38; 6 (1970) 349-352), 9-BBN is a particularly useful hydroborating agent because of its extremely high stereoselectivity and regioselectivity [127], and because of the finding that several of the borane reactions that can only utilize one of the alkyl groups on boron proceed preferentially with the target alkyl group and not with the 9-BBN moiety. Like most dialkylboranes, 9-BBN exists as the H-bridged dimer, but unlike the usual dialkylboranes, 9-BBN is stable enough toward oxygen to permit weighing in air if it is done quickly, though the best technique is to use an inert atmosphere at all times.



9-BBN

Köster and Binger have published a detailed description of the synthesis of 9-BBN from 1,5-cyclooctadiene and tetraethyldiborane [128].

Potential users of 9-BBN may note that this compound is now commercially available (from Aldrich Chemical Company).

Borane-methyl sulfide, Me_2SBH_3, is a convenient, commercially available hydroborating agent. Lane has published a useful description of its use for carrying out a variety of standard hydroboration--oxidation reactions [129].

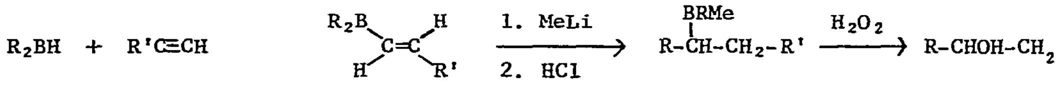
Hydroboration of alkenes can be carried out very conveniently by the use of sodium borohydride and acetic acid in tetrahydrofuran [130]. The yields were good, though perhaps somewhat inferior to those obtained with Me_2SBH_3.

The hydroboration of ethylene with $MaHBEt_3$ to form $NaBEt_4$ has been described in detail [131].

B. Boranes in Carbon-Carbon Bond Formation

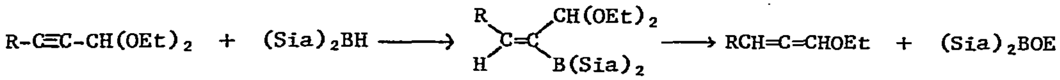
1. Polar Rearrangements. It has been known for some time that tetracoordinate boron compounds having an electrophilic center adjacent to boron can undergo rearrangement with carbon-carbon bond formation. (For the earliest examples see Matteson and Mah, J. Amer. Chem. Soc., 85 (1963) 2599; Jäger and Hesse, Chem. Ber., 95 (1962) 345; Hillman, J. Amer. Chem. Soc., 84 (1962) 4715.) With the development of hydroboration as a source of boron compounds, this type of rearrangement has become a useful synthetic tool, and exploration of the wide variety of possibilities has provided the bulk of the more interesting papers related to hydroboration during the past year.

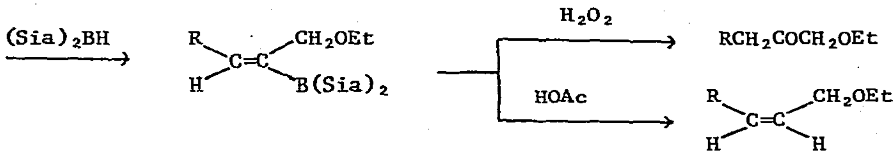
Zweifel and Fisher have found that secondary alkyl groups migrate more rapidly than methyl from boron to carbon. This permits the use of methyllithium as the base for rearrangement of alkenyldicyclohexylboranes [132].



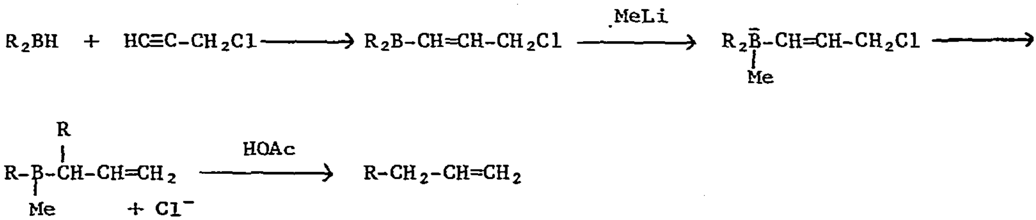
R = 2-methylcyclohexyl, R' = n-Bu

Hydroboration of an acetylenic acetal with disiamylborane results in an addition--elimination--addition sequence to provide a borane which can be oxidized with hydrogen peroxide to an α-alkoxyketone or protonated to a cis-alkoxymethylalkene [133].





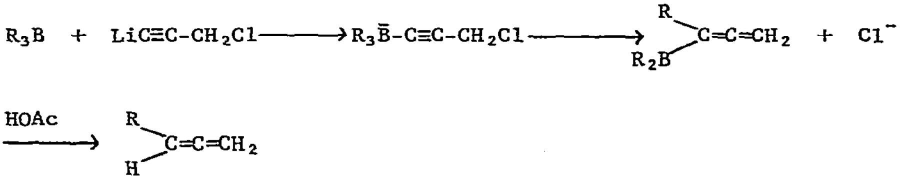
Hydroboration of propargyl chloride with di-*sec*-alkylboranes followed by treatment with methyllithium leads to rearrangement, in which one *sec*-alkyl group becomes bonded to an allyl group [134].



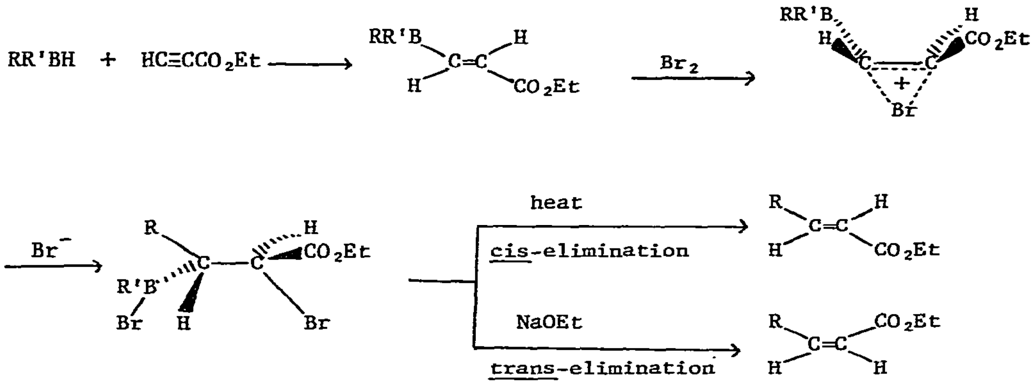
$$R_2BH + HC{\equiv}C\text{-}CH_2Cl \longrightarrow R_2B\text{-}CH{=}CH\text{-}CH_2Cl \xrightarrow{MeLi} R_2\underset{Me}{\overset{-}{B}}\text{-}CH{=}CH\text{-}CH_2Cl \longrightarrow R\text{-}\underset{Me}{B}\text{-}\overset{R}{C}H\text{-}CH{=}CH_2 + Cl^- \xrightarrow{HOAc} R\text{-}CH_2\text{-}CH{=}CH_2$$

R = cyclohexyl, methylcyclohexyl, methylcyclopentyl, pinanyl, or 3-methyl-2-butyl

Leung and Zweifel have found that the lithium salt of propargyl chloride reacts with trialkylboranes with rearrangement to form allenylboranes, which are readily cleaved to the corresponding allene with acetic acid [135].



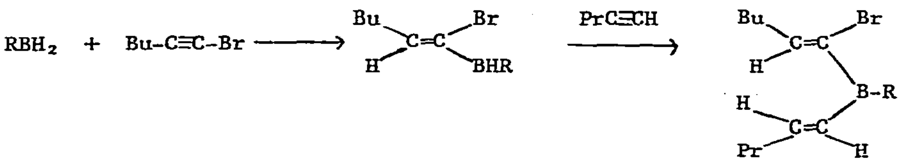
Negishi and coworkers have reported the synthesis of *cis*- or *trans*-alkylpropenoic esters by bromination of the product of hydroboration of ethyl propiolate with a dialkylborane, the stereochemical outcome depending on whether the final elimination is carried out with or without a basic catalyst [136]. It should be noted that the carbethoxy group changes the result of the bromination, ordinary alkenylboranes giving a mixture of cis- and trans-1-bromoalkene on bromination (unless the boron has first been alkylated to the tetracoordinate boron anion).

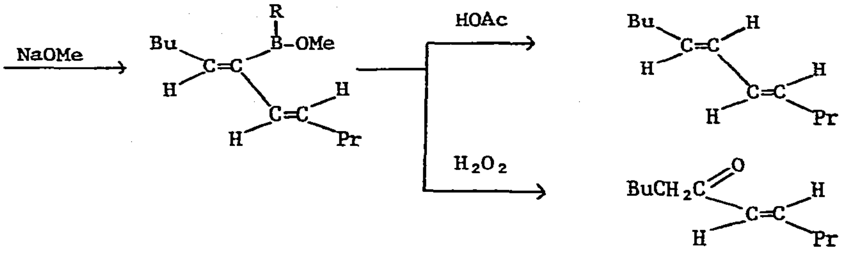


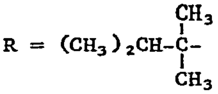
R = cyclohexyl, norbornyl, (E)-2-methylcyclopentyl, 1,2-dimethylpropyl

R' = thexyl (1,1,2-trimethylpropyl)

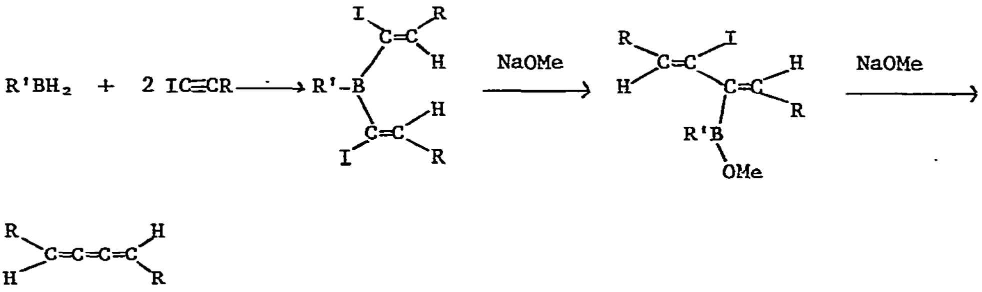
Thexylborane hydroborates 1-haloacetylenes in a 1:1 mole ratio, and the resulting borane hydroborates terminal acetylenes. Rearrangement of the product with sodium methoxide yields a borinic acid which can be cleaved to the trans,trans-diene with acetic acid or oxidized to the α,β-unsaturated ketone with hydrogen peroxide [137].





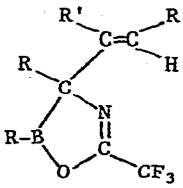

$R = (CH_3)_2CH\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}$

The rather elusive trans-1,2,3-butatriene series can be made stereoselectively by rearrangement and elimination reactions of a suitable bis(iodoalkenyl)borane [138].



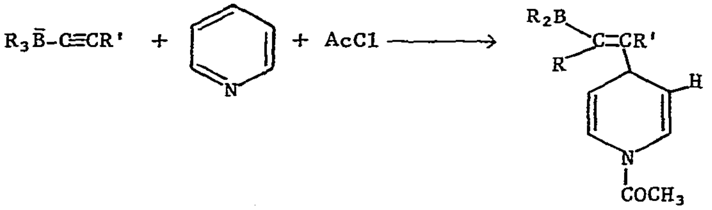
R = n-Bu or cyclohexyl, R' = thexyl

Pelter and coworkers have applied the cyanide--trifluoroacetic anhydride rearrangement reaction to vinyldialkylboranes [139].



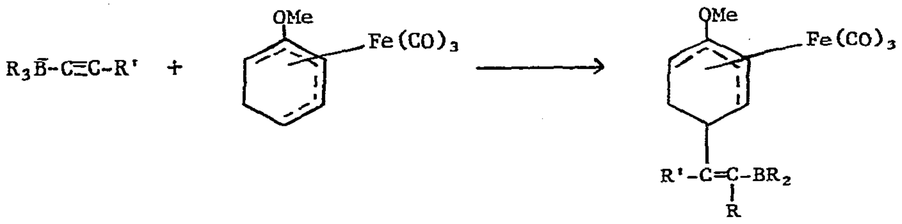
R = cyclohexyl and others; R' = H, C_2H_5, C_4H_9

Pelter and Gould have found that the acetylpyridinium ion will act as the electrophile in the addition--rearrangement type of reaction with alkynyltrialkylborate salts [140]. Yields are high and attack is exclusively at the 4-position of the pyridine ring.

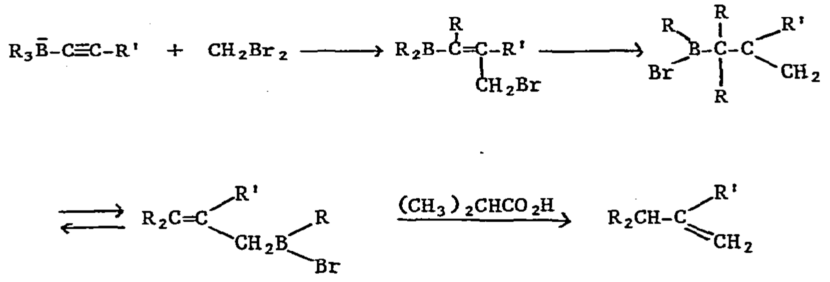


(cis-trans mixture)

The protonated anisole-iron tricarbonyl complex has been used as the electrophile in the rearrangement of alkynyltrialkylborate salts [141].

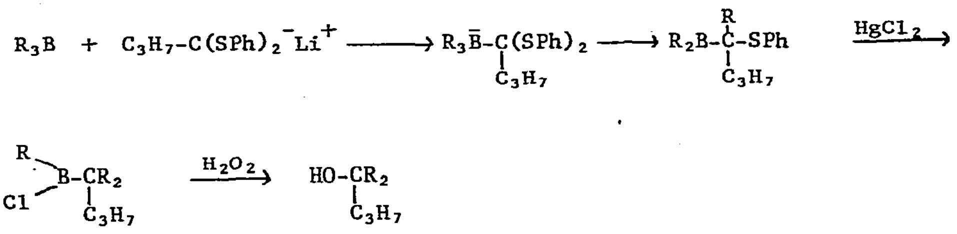


Alkynyltrialkylborate anions also undergo typical electrophilic addition accompanied by rearrangement when methylene bromide or methylene iodide is used as the electrophile [142].

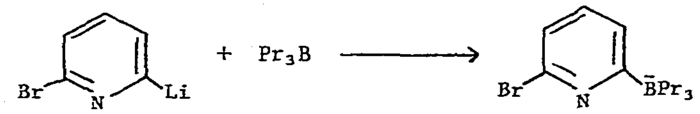


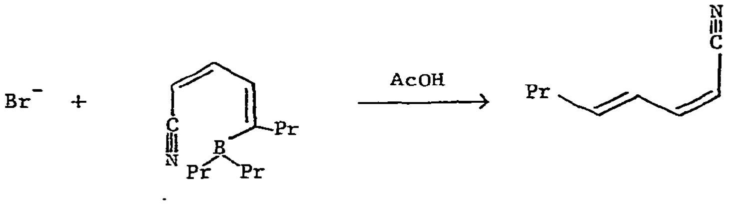
Binger and Köster have reported that $EtC{\equiv}C\text{-}BEt_3^-$ reacts with $ClCH_2OMe$ to form $Et_2B\text{-}C(Et){=}C(Et)CH_2OMe$, and that the same product with 97% E stereochemistry results from the reaction of $Et_3\bar{B}\text{-}C{\equiv}C\text{-}CH_2OMe$ with $Et_3O^+\ BF_4^-$ [143]. This is not "hydroboration chemistry" in the usual sense, but the relationship should be readily apparent.

Trialkylmethanols have been obtained in high yields from the reaction of trialkylboranes with 1-lithio-1,1-bis(phenylthio)alkanes followed by rearrangement with mercuric chloride and oxidation with hydrogen peroxide [144].

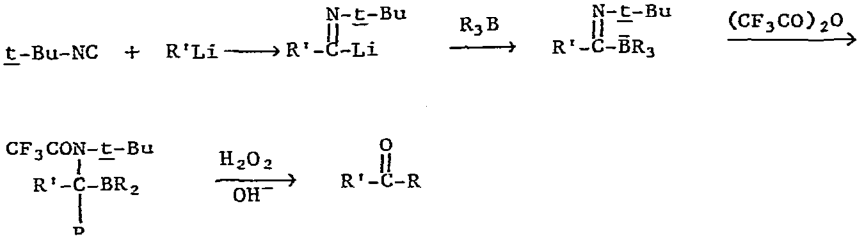


Utimoto and coworkers have discovered a useful five-carbon chain extension in the rearrangement reaction of trialkylboranes with 2-bromo-6-lithiopyridine, which undergoes alkylation and ring opening to form the 5-alkyl-2(Z),4(E)-pentadienenitrile [145].

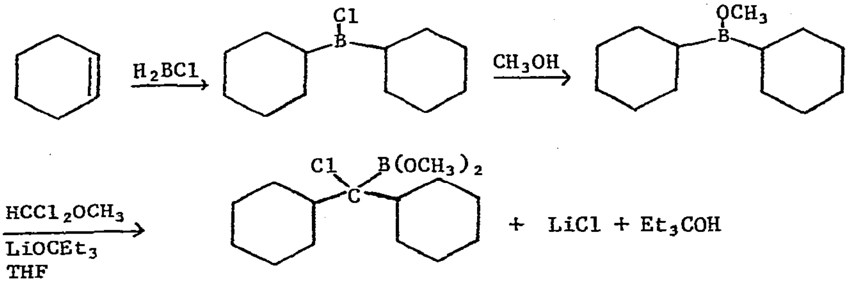




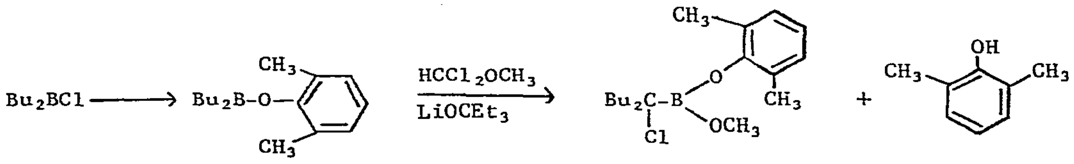
Ketones have been prepared by reaction of trialkylboranes with α-lithioaldimines prepared from t-butyl isocyanide and RLi [146].



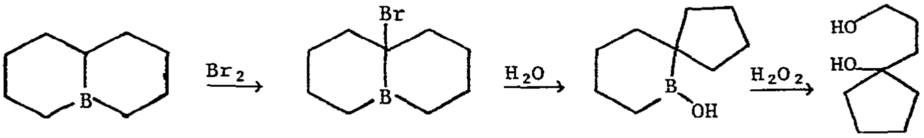
Brown and coworkers have found that treatment of hindered borinic esters with α,α′-dichloromethyl methyl ether and a tertiary alkoxide base gives excellent yields of α-chloroboronic esters [147].

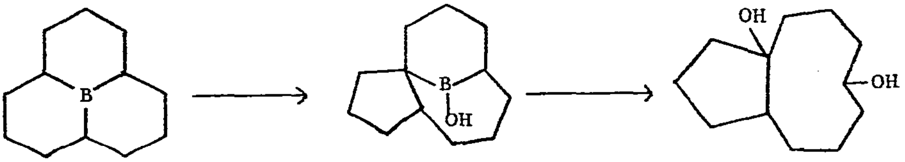


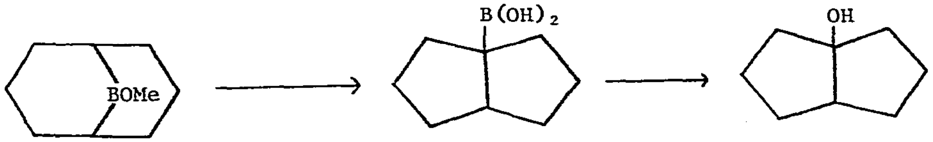
Groups less bulky than cyclohexyl permit displacement of chloride by migration of a methoxide from boron to carbon. In these cases, the α-chloroboronic esters were obtained by the use of 2,6-dimethylphenyl borinic esters.



Bromination of borapolycyclanes in the presence of water followed by oxidation with alkaline hydrogen peroxide results in carbocyclic ring formation and ultimately leads to cyclic alcohols or diols [148].

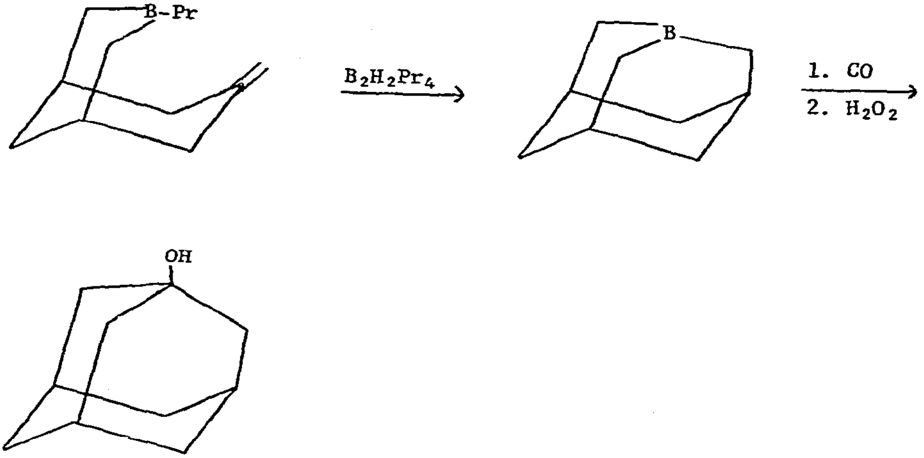






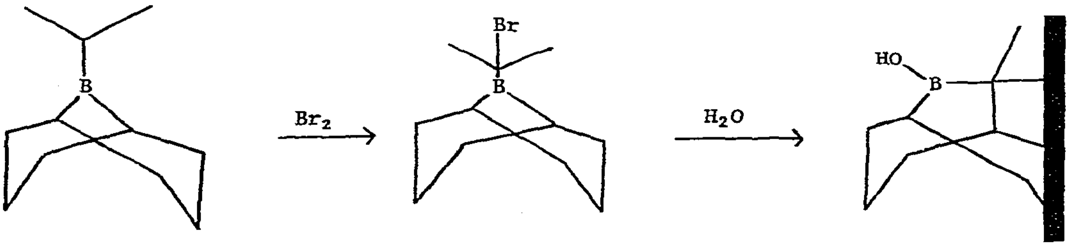
The bromination--rearrangement sequence has been used to convert 6-membered boron heterocycles to 5-membered carbocyclic rings [149]. Mikhailov and

Smirnov have described the synthesis of 1-boraadamantane and its conversion to 1-hydroxyadamantane by carbonylation--oxidation [150].



Russian workers have reinvestigated the carbonylation of trialkylboranes with carbon monoxide in the presence of ethylene glycol [151].

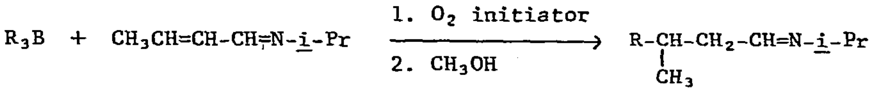
Much hydroboration chemistry is also useful with trialkylboranes that cannot be made by hydroboration. The reaction of methoxy-9-BBN with organolithium reagents RLi in pentane at -78° precipitates an adduct, $C_8H_{14}B(OCH_3)R$ which decomposes on warming to a precipitate of $LiOCH_3$ and a solution of $C_8H_{14}BR$ [152]. B-Isopropyl-9-BBN brominates very rapidly at the α-position of the isopropyl group, 5.5 times faster than cumene and 660 times faster than isobutane [153]. The resulting bromo compound reacts in ways typical of α-bromoalkylboranes, for example rearranging on treatment with water.



An Organic Syntheses article on the hydroboration of alkenes and the reactions of the resulting trialkylboranes with hydrogen peroxide and with diazo ketones has appeared [154].

2. Free Radical Alkylations by Boranes. Since the discovery by Brown and coworkers that the 1,4-addition of $R\text{-}BR_2$ to acrolein and other α,β-unsaturated carbonyl compounds involves a free radical mechanism (Organometal. Chem. Rev. B, 8 (1971) 29), the development of this type of chemistry has proceeded rapidly, and several new examples have been reported during the past year.

Trialkylboranes have been found to react with *N*-isopropylcrotonaldimine in the same manner as with crotonaldehyde [155].

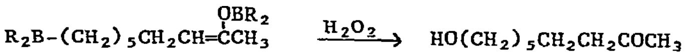


$$R_3B + CH_3CH{=}CH\text{-}CH{=}N\text{-}\underline{i}\text{-}Pr \xrightarrow[2.\ CH_3OH]{1.\ O_2\ \text{initiator}} R\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_2\text{-}CH{=}N\text{-}\underline{i}\text{-}Pr$$

The reaction of R_3B with $PhCH{=}CHSO_2Me$ or $PhCH{=}CHSOMe$ gives good yields of $PhCH{=}CHR$. The products are *trans* even if the starting sulfoxide or sulfone is *cis*, and a radical mechanism was postulated [156].

The free-radical addition of organoboranes to α,β-unsaturated ketones followed by bromination of the resulting vinyloxyboranes and methanolysis yields α-bromoketones [157]. A Japanese patent has been issued for application of the borane--vinyl methyl ketone reaction to the synthesis of long-chain ω-hydroxyketones [158].

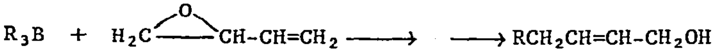
$$H_2C{=}CH\text{-}CH_2\text{-}CH{=}CH_2 + B_2H_6 \longrightarrow R_2B\text{-}(CH_2)_5\text{-}BR_2 \xrightarrow{H_2C{=}CHCOCH_3}$$



$$R_2B\text{-}(CH_2)_5CH_2CH{=}\overset{\displaystyle OBR_2}{\overset{|}{C}}CH_3 \xrightarrow{H_2O_2} HO(CH_2)_5CH_2CH_2COCH_3$$

Suzuki has described several addition reactions of trialkylboranes related to known types [159].

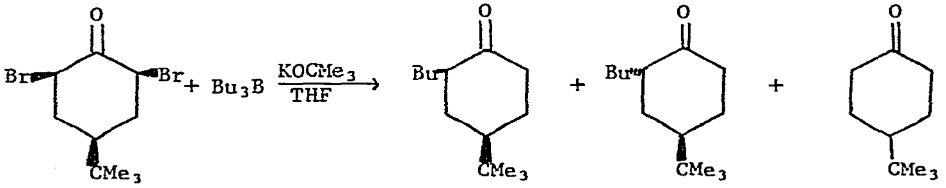
$R_3B \ + \ HC{\equiv}C\text{-}COCH_3 \longrightarrow \quad \longrightarrow RCH{=}CH\text{-}COCH_3$



$R_3B \ + \ H_2C\overset{O}{\text{———}}CH\text{-}CH{=}CH_2 \longrightarrow \quad \longrightarrow RCH_2CH{=}CH\text{-}CH_2OH$

The radical catalyzed addition of R_3B to α,β-unsaturated ketones has been used on a steroidal acetylcyclopentene and given low yields of the β-alkylation products [160].

Prager and Tippett have reported that cis-2,6-dibromocyclohexanones but not their cyclopentanone or cycloheptanone analogs are converted to monoalkylcyclohexanones by trialkylboranes in the presence of tertiary alkoxides in tetrahydrofuran [161]. The reaction "doesn't balance" at first glance, inasmuch as something like t-butyl hypobromite must be written as one of the products, but labeling studies have shown that the THF solvent is the source of hydrogen in the products [162]. With all cis-4-t-butyl-2,6-dibromocyclohexanone and tributylborane, the products include cis- and trans-2-butyl-4-t-butylcyclohexanone as well as unsubstituted 4-t-butylcyclohexanone, which suggests a free radical mechanism.



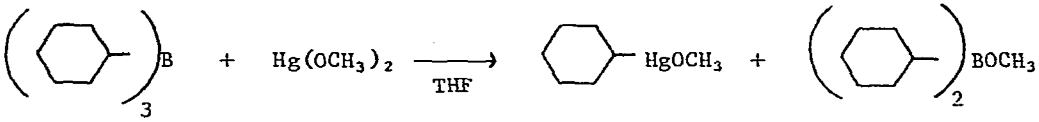
C. Hydroboration--Metallation

Larock has expanded the utility and scope of the replacement of boron by mercury. An efficient anti-Markovnikov conversion of alkenes to esters is based on a hydroboration--mercuration--iodination sequence in which the carboxylate associated with the mercury cation becomes part of the ester [163].

$$RCH{=}CH_2 \xrightarrow{B_2H_6} (RCH_2CH_2)_3B \xrightarrow{Hg(OCOR')_2} RCH_2CH_2HgOCOR' \xrightarrow{I_2}$$

$$[RCH_2CH_2I] \xrightarrow{R'CO_2^-} RCH_2CH_2OCOR'$$

Mercuric methoxide readily attacks tri-sec-alkylboranes by a free radical mechanism to replace boron by mercury [164]. Only one sec-alkyl group normally reacts. Mercuric acetate, which reacts readily with primary alkylboranes, is inert to secondary alkylboron compounds.

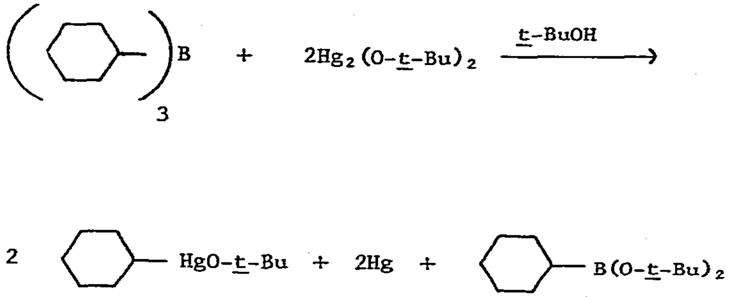


Chain propagation steps (postulated):

$$R\cdot + Hg(OCH_3)_2 \longrightarrow RHgOCH_3 + \cdot OCH_3$$

$$R_3B + \cdot OCH_3 \longrightarrow R_2BOCH_3 + R\cdot$$

The conversion of two secondary alkyl groups of tri-sec-alkylboranes to sec-alkylmercury compounds has been accomplished with mercury(I) alkoxides [165].



Chain propagation steps (postulated):

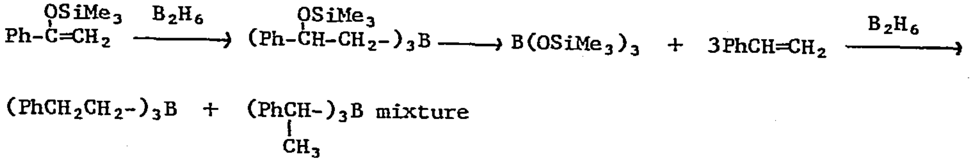
$$R\cdot + Hg_2(OR')_2 \longrightarrow RHgOR' + \cdot OR' + Hg$$

$$R_3B + \cdot OR' \longrightarrow R_2BOR' + R\cdot$$

D. Hydroboration--Oxidation and Miscellaneous

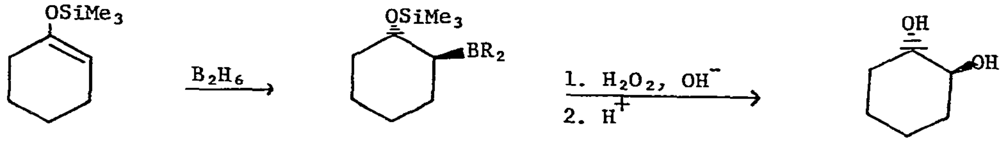
The hydroboration--oxidation reaction sequence is by now well established as a route to alcohols, and with a few exceptions most of the reactions reported here are straightforward applications of known principles. Some rearrangement reactions of trialkylboranes are also included in this section, and some investigations of steric and electronic effects on the hydroboration reaction itself, again for the most part fairly predictable. Finally, hydroboration--amination and a single example of hydroboration--fragmentation are included.

Two independent reports on the hydroboration of silyl enol ethers have appeared [166,167]. The boron attacks β to the silyloxy group, and in acyclic systems the resulting β-silyloxy borane is unstable toward elimination [166]. However, in cyclic systems elimination is prohibited or greatly slowed by steric restraints, and this hydroboration provides a useful route to <u>trans</u>-1,2-diols [166,167].



$$\mathrm{Ph\text{-}\overset{OSiMe_3}{C}{=}CH_2} \xrightarrow{B_2H_6} (\mathrm{Ph\text{-}\overset{OSiMe_3}{C}H\text{-}CH_2\text{-}})_3\mathrm{B} \longrightarrow \mathrm{B(OSiMe_3)_3} + 3\mathrm{PhCH{=}CH_2} \xrightarrow{B_2H_6}$$

$$(\mathrm{PhCH_2CH_2\text{-}})_3\mathrm{B} + (\mathrm{Ph\underset{CH_3}{C}H\text{-}})_3\mathrm{B}\ \text{mixture}$$



The hydroboration--oxidation of two 1-unsaturated 3β-hydroxy steroids to form 1α,3β-dihydroxysteroids has been reported [168]. The hydroboration of an internal double bond and rearrangement of the resulting borane to place the boron on the end of a carbon chain has been applied to a steroid, ergostene [169]. Another hydroboration--rearrangement sequence has been noted in the steroid series [170]. The use of hydroboration--oxidation for transformations of several steroids related to sex hormones has been patented [171].

Tetramethylhematoxylin has been synthesized by hydroboration--oxidation of a substituted indene precursor [172]. Hydroborations of coumarins and related compounds have been reported [173]. Hydroboration--oxidation of some substituted N-methyl-3-piperideines has been found to give mixtures of 3- and 4-piperidinols [174]. Hydroboration of epoxycyclohexenes gives complex results involving both epoxide ring opening and hydroboration of the carbon-carbon double bond [175].

Anodic oxidation of trialkylboranes, R_3B, in methanol containing sodium methoxide and sodium perchlorate yields a mixture of ROMe and RH, and electrolysis in acetic acid with sodium acetate yields ROAc [176].

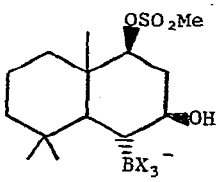
The monohydroboration of cyclopentadiene dimer has been studied in detail [177]. The hydroboration of some substituted pinenes has been investigated and the usual sort of stereochemical trend with increasing bulk of the substituent near the hydroboration site was noted [178]. Hydroboration--oxidation of 1-chloronobornene gives predominantly (63%) 1-chloro-2-exo-norbornanol, not the 3-isomer as previously thought [179]. Although the reaction of 9-BBN with 2-chloronorbornene gives predominantly the expected product having the boron on the same carbon as the chlorine, 2-bromonorbornene yields mainly the unexpected isomer with the boron β to the bromine [180].

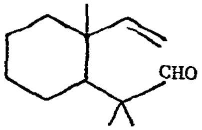
In the hydroboration of 1-cyclohexenyl acetate both α and β addition of the boron have been observed [181]. Hydroboration of (diphenylmethylene)cyclopropane places the boron mainly β to the phenyl groups [182].

A Japanese patent has been issued for the hydroboration of ethylene, propylene, and 1-butene with diborane in the gas phase above 100° in the presence of group VIII metal catalysts (such as Pd/C or Raney Ni) to form trialkylboranes [183].

The hydroboration--amination sequence has been used to convert several $ArCH{=}CH_2$ to $ArCH_2CH_2NH_2$ [184]. Hydroboration followed by treatment of the organoborane with $2,4,6\text{-}Me_3C_6H_2SO_2NH_2$ has given moderate yields of primary amines [185].

Some years ago, Marshall and Bundy described the fragmentation of a 1-boryl-4-methanesulfonyloxydecalin to form the 10-membered ring, a trans-trans-1,5-cyclodecadiene (Organometal. Chem. Rev. B, 4 (1968) 291). This type of chemistry has been reinvestigated by Miyashita and coworkers, who have found that a 2-hydroxy substituent on the decalin leads to peripheral cleavage to form the disubstituted cyclohexane [186].





E. Reviews

Two issues of Intra-Science Chemistry Reports have been devoted to reviews of hydroboration and related chemistry written by specialists in each area in honor of Professor H. C. Brown. Topics reviewed include Brown's own explorations in the chemistry of organoboranes [187], 1,4-addition reactions of organoboranes [188], free radical reactions of organoboranes [189], organic synthesis based on borane chemistry [190], carbonylation of boranes [191], electrophilic metal cations with organoboranes [192], reactions of organoboranes with cyanides and isocyanides [193], chloroboration and related reactions [194], bromination of organoboranes [195], α-haloalkaneboronic esters [196], reactions of α-halocarbanions with organoboranes [197], coupling reactions of organoboranes [198], use of hydroboration to convert alkynes to olefins, allenes, dienes, and enynes [199], and allylboranes [200].

Brown has reviewed the use of boranes in organic chemistry [201]. A review of the use of thexylborane (1,1,2-trimethylpropylborane) as a hydroborating agent has appeared [202].

Rearrangements in organoborane chemistry have been reviewed [203].

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