BORON

ANNUAL SURVEY COVERING THE YEAR 1973

PART I: CARBORANES AND HYDROBORATION

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CONTENTS

I. CARBORANES

A. Introduction

A large porportion of carborane chemistry continues to be produced by M. F. Hawthorne's research group in the United States, with most of the effort concentrated on the synthesis of new transition metal complexes of various sizes of carborane cages. L. I. Zakharkin's group in the Soviet Union has continued to be highly productive, with emphasis on derivatives of icosahedral carboranes. W. N. Lipscomb continues as the chief theoretician of carborane chemistry. Many others have become interested in the opportunities offered by carborane chemistry, and the number of workers in the field is continuing to expand.

Nomenclature problems and the general methods for converting closo-carboranes to anions were discussed at the beginning of last year's Annual Survey (J. Organometal. Chem., 58 (1973) 1) and will not be repeated here.

B. Metallocarboranes

1. 13-Atom cages and $B_{10}C_2H_{12}^{2-}$. Recent discoveries that the icosahedral carborane cage can be expanded to 13 atoms by way of reduction of $B_{10}C_2H_{12}$ to $B_{10}C_2H_{12}^{2-}$ and subsequent complexing with cobalt have continued to lead to new carborane chemistry. This is perhaps the least predictable and therefore most interesting frontier region of carborane research.

Reduction of 1,2-diphenyl-o-carborane with sodium in tetrahydrofuran followed by addition of tetramethylammonium chloride in water leads to precipitation of Me_4N^+ $Ph_2C_2B_{10}H_{11}^-$. Tolpin and Lipscomb have determined the structure of this expanded-cage anion by X-ray crystallography (Fig. 1) (1). It should be noted that molecular orbital calculations suggest that the $Ph_2C_2B_{10}H_{10}^{2-}$ anion probably retains the icosahedral structure until it reacts with an acid (contrary to the reviewer's offhand assumption in last year's Annual Survey).

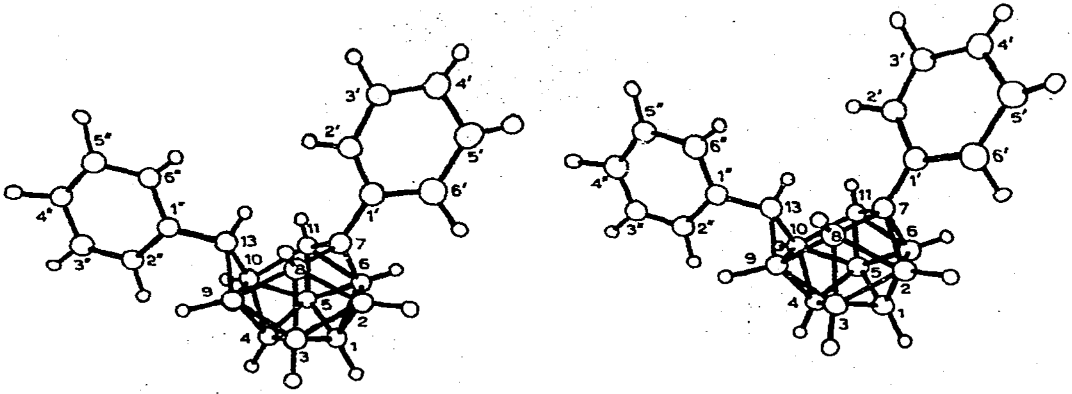


Fig. 1. Stereoview of $PhCHB_{10}H_{10}CPh^-$. (From E. I. Tolpin and W. N. Lipscomb, Inorg. Chem., 12 (1973) 2257).

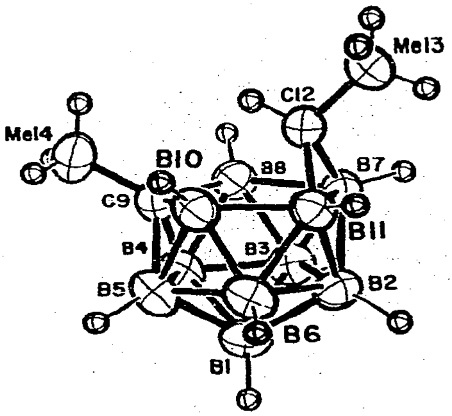


Fig. 2. A general view of the $Me_2B_{10}C_2H_{11}^-$ anion, showing the 50% probability contours of the thermal ellipsoids of nonhydrogen atoms. [Hydrogen atoms are shown as artificial spheres of radius 0.10 Å.] (From M. R. Churchill and B. G. DeBoer, Inorg. Chem., 12 (1973) 2674.)

Churchill and DeBoer have determined the structure of the $B_{10}C_2H_{13}^-$ ion (Fig. 2, 3, and 4) obtained from reduction of *o*-carborane with sodium in THF followed by protonation (2).

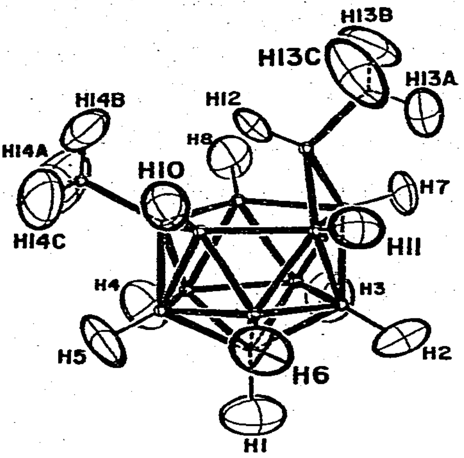


Fig. 3. The same view of the $Me_2B_{10}C_2H_{11}^-$ anion as in Fig. 2, now illustrating the 50% probability contours of the thermal ellipsoids of the hydrogen atoms. [Boron and carbon atoms are shown as spheres of radius 0.07 Å.] (From M. R. Churchill and B. G. DeBoer, Inorg. Chem., 12 (1973) 2674.)

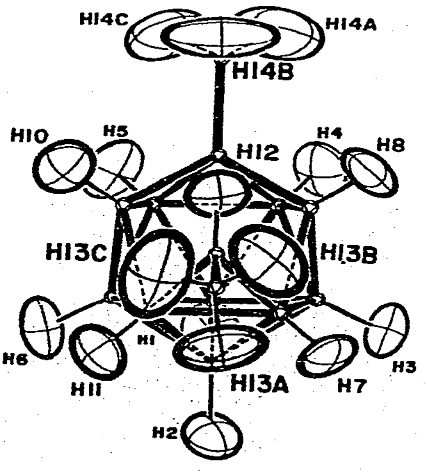


Fig. 4. A view demonstrating the approximate C_s symmetry of the $Me_2B_{10}C_2H_{11}^-$ anion including the orientation of the thermal ellipsoids of hydrogen atoms. Nonhydrogen atoms are shown as spheres of radius 0.07 Å. (From M. R. Churchill and B. G. DeBoer, Inorg. Chem., 12 (1973) 2674.)

Hawthorne and coworkers have converted the $B_{10}C_2H_{12}^{2-}$ ion to iron, cobalt, nickel, molybdenum, and wolfram derivatives. It has been found that the cyclopentadienylcobalt complex contains a rearranged carborane cage in which the carbon atoms are separated by a boron atom, and which exists as two enantiomers which undergo rapid interconversion above -30°, presumably by way of a diamond-square-diamond rearrangement of the cage as illustrated in Fig. 5. Complexes of the general formula $(B_{10}C_2H_{12})_2M^{-1 \text{ or } -2}$ have been obtained with iron, cobalt, and nickel (Fig. 6) and carbonyls of the formula $B_{10}C_2H_{12}M(CO)_3^{-2}$ with molybdenum and tungsten (Fig. 7) (3).

Further studies on the products of reduction of o-, m-, and p-carborane with sodium have been reported by Hawthorne's group (4). Protonation of the $B_{10}C_2H_{12}^{2-}$ ions yielded (13)-9,11-$B_{10}C_2H_{13}^-$ and (13)-7,10-$B_{10}C_2H_{13}^-$, and the 9,11-isomer could be thermally rearranged to the 7,10-isomer. The structures were assigned on the basis of nmr evidence, and are not reproduced here because the X-ray studies by Churchill and DeBoer subsequently showed that significant alteration of the positions of some of the atoms and bonds in the drawings must be made. Pyrolysis of the tetramethylammonium salt of (13)-7,10-$B_{10}C_2H_{13}^-$ yielded the C-substituted o-carborane Me_3N-1-BH_2-1,2-$B_{10}C_2H_{11}$ as well as the Me_4N^+ salt of the protonated dicarbollide ion (12)-7,9-$B_9C_2H_{12}^-$.

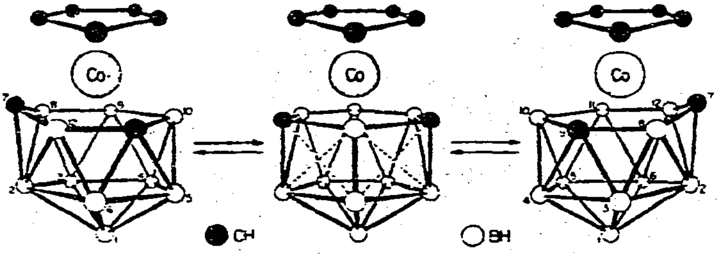


Fig. 5. Proposed mechanism of the rapid interconversion between the $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}7,9\text{-}B_{10}C_2H_{12})$ and $(\pi\text{-}C_5H_5)Co^{III}\text{-}(\pi 7,11\text{-}B_{10}C_2H_{12})$ enantiomers showing an intermediate or transition-state structure containing a plane of symmetry. (From D. F. Dustin, G. B. Dunks, and M. F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 1109.)

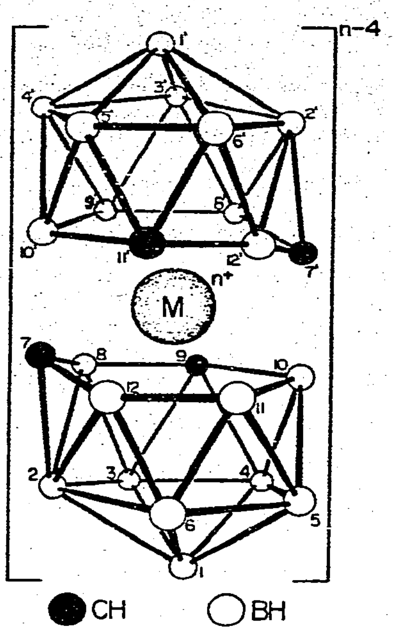


Fig. 6. Proposed structure of the $(\pi\text{-}B_{10}C_2H_{12})_2$ metal complexes. M is Co(III), Fe(II), or Ni(II). (From D. F. Dustin, G. B. Dunks, and M. F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 1109.)

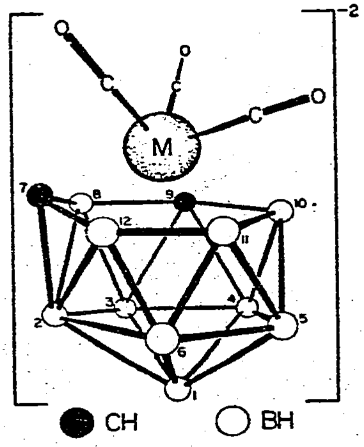


Fig. 7. The proposed structure of the $\pi\text{-}7,9\text{-}B_{10}C_2H_{12}$-molybdenum and -tungsten tricarbonyl dianions. (From D. F. Dustin, G. B. Dunks, and M. F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 1109.)

Treatment of the 13-atom cage compound $(\pi\text{-}C_5H_5)Co(\pi\text{-}6,7\text{-}B_{10}C_2H_{12})$ with hot alcoholic potassium hydroxide results in an unusual cage degradation to form a 9-atom polyhedron containing only one carbon, $(\pi\text{-}C_5H_5)Co(\pi\text{-}2\text{-}B_7CH_8)^-$ (Fig. 8) (5).

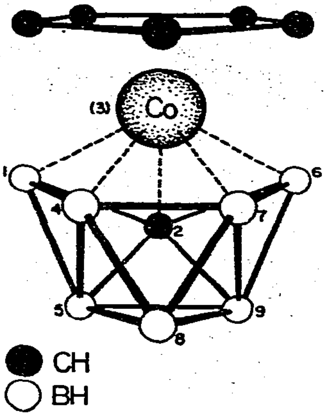


Fig. 8. The proposed structure of π-cyclopentadienyl-π-octahydro-2-carba-nido-octaboratocobaltate(1−), $[(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]^-$. (From D. F. Dustin and M. F. Hawthorne, Inorg. Chem., 12 (1973) 1380.)

p-Carborane has been obtained under mild conditions, in a mixture with o- and m-carborane, by CuCl or $CuCl_2$ oxidation of the 13-atom cage complex formed from $CoCl_2$ and $B_{10}C_2H_{12}{}^{2-}$ prepared by alkali metal reduction of o-carborane (6). The proportion of p-carborane in the product mixtures reached about 7% under the most favorable conditions found, m-carborane being the major product.

2. Transition metal complexes. This section covers all of the carboranes which include a transition metal atom in the cage, with the exception of the 13-atom cages discussed in the preceding section. This is also a rapidly expanding frontier of carborane research, and new and unexpected developments have continued to arise.

Sodium naphthalide reduces 1,7-$C_2B_6H_8$, 4,5-$C_2B_7H_9$, 1,6-$C_2H_8B_{10}$, 1,10-$C_2B_8H_{10}$, and 2,3-$C_2B_9H_{11}$ to form anions (7). Treatment of these anions with $CoCl_2$ or $FeCl_2$ in the presence of sodium cyclopentadienide has yielded a variety of new metallocarboranes, illustrated in Fig. 9-15.

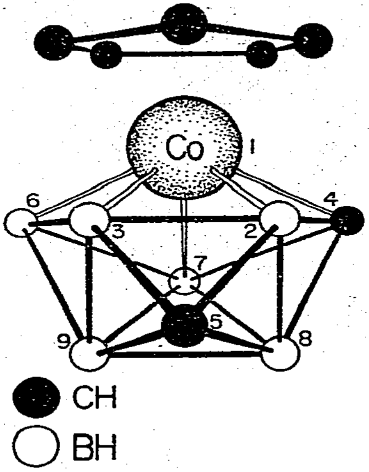


Fig. 9. Proposed structure of $C_5H_5CoC_2B_6H_8$. (From W. J. Evans, G. B. Dunks, and M. F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 4565.)

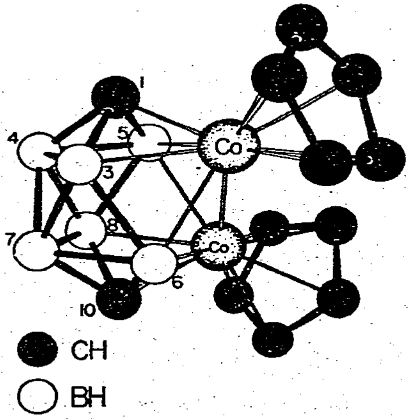


Fig. 10. Structure of $(C_5H_5Co)_2C_2B_6H_8$. (From W. J. Evans, G. B. Dunks, and M. F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 4565.)

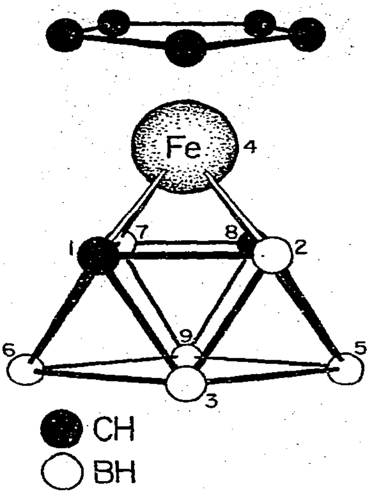


Fig. 11. Proposed structure of $C_5H_5FeC_2B_6H_8$. (From W. J. Evans, G. B. Dunks, and M. F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 4565.)

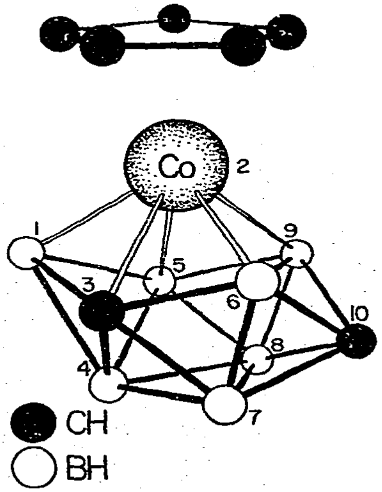


Fig. 12. Possible structure of $C_5H_5CoC_2B_7H_9$. Only one enantiomer shown. (From W. J. Evans, G. B. Dunks, and M. F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 4565.)

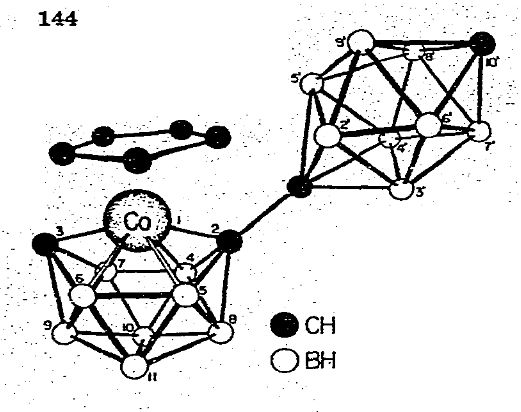


Fig. 13. Proposed structure of $C_5H_5CoC_2B_8H_9(C_2B_8H_9)$. (From W. J. Evans, G. B. Dunks, and M. F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 4565.)

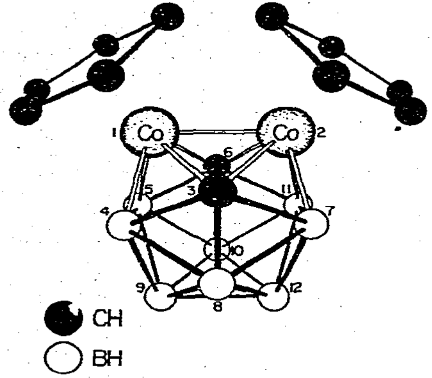


Fig. 14. Possible structure of $(C_5H_5Co)_2C_2B_8H_{10}$. (From W. J. Evans, G. B. Dunks, and M. F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 4565.)

Pyridine opens the cage of $(\pi\text{-}C_5H_5)Co(C_2B_8H_{10})$ to form a nido-cobaltacarborane (Fig. 16) (8). Analogous results were obtained with a dicarbollide ligand in place of the cyclopentadienide ligand on the cobalt. Oxidation of the nido compounds yielded closo derivatives bearing an N-pyridyl substituent on boron (Fig. 17). To obtain unsubstituted *nido* cobaltacarboranes, bis(dicarbollyl)cobalt(III) monoanion, $(B_9C_2H_{11})_2Co^-$, was degraded with sodium hydroxide. Protonation of the degradation product by methanolic HCl yielded the *nido*-cobaltacarborane anion (Fig. 18).

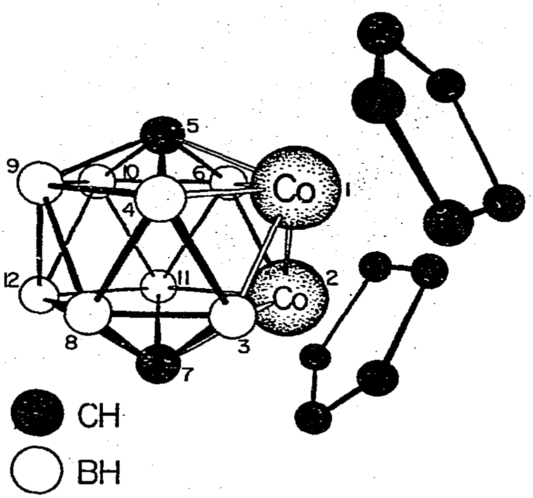


Fig. 15. Possible structure of $(C_5H_5Co)_2C_2B_8H_{10}$. (From W. J. Evans, G. B. Dunks, and M. F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 4565.)

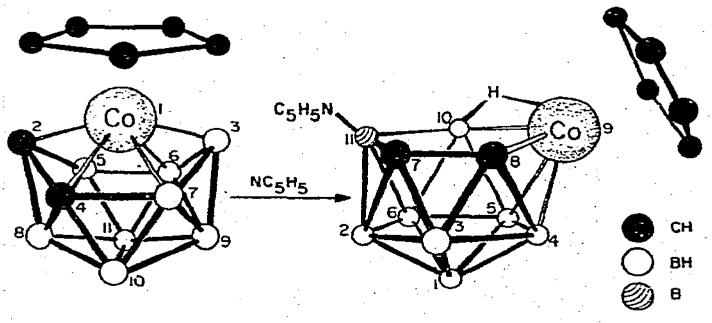


Fig. 16. Formation of a *nido*-cobaltacarborane from [(*n*-C_5H_5)-2,4,1-$C_2CoB_8H_{10}$] and pyridine. (From C. J. Jones, J. N. Francis, and M. F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 7633.)

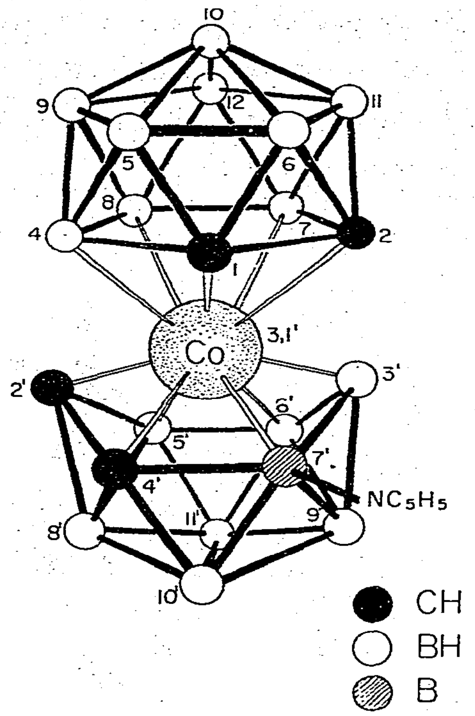


Fig. 17. Proposed structure of IV with $[1,2,3\text{-}C_2CoB_9H_{11}]^+$ in place of $[(\eta\text{-}C_5H_5)Co]^{2+}$, V, and VI with $[1,2,3\text{-}C_2CoB_9H_{11}]^+$ in place of $[(\eta\text{-}C_5H_5)Co]^{2+}$ and C_5H_5N in place of $C_5H_{10}N$. Only one enantiomer is illustrated. (From C. J. Jones, J. N. Francis, and M. F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 7633.)

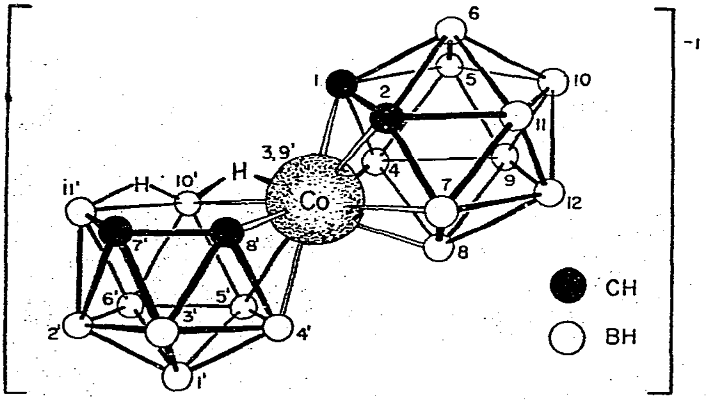


Fig. 18. Proposed structure for VIII or XI with $[1,2,3\text{-}C_2CoB_9H_{11}]^+$ in place of $[(\pi\text{-}C_5H_5)Co]^{2+}$. Only one enantiomer is illustrated. (From C. J. Jones, J. N. Francis, and M. F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 7633.)

The structure of Et_4N^+ $B_9C_2H_{11}CoC_8B_2H_{10}py^-$ has been determined by X-ray diffraction (Fig. 19) (9).

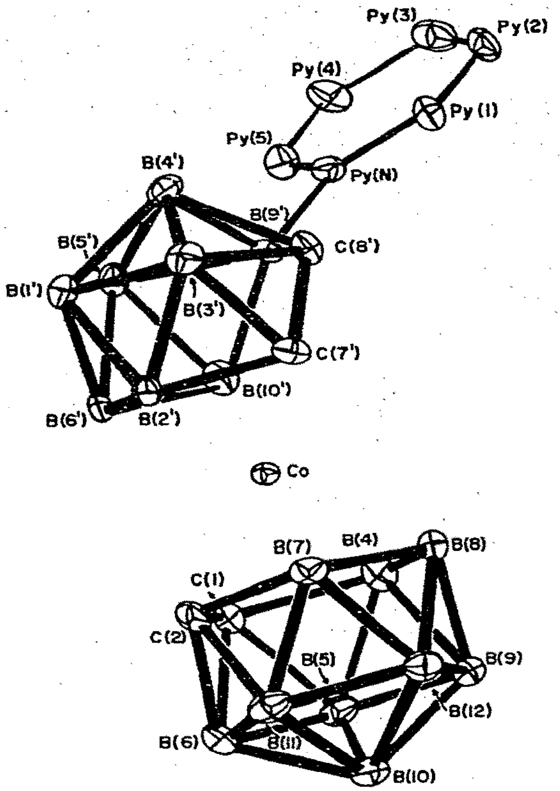


Fig. 19. The $[(B_9C_2H_{11})Co(B_8C_2H_{10}py)^-]$ ion, projected on (001). (From M. R. Churchill and K. Gold, Inorg. Chem., 12 (1973) 1157.)

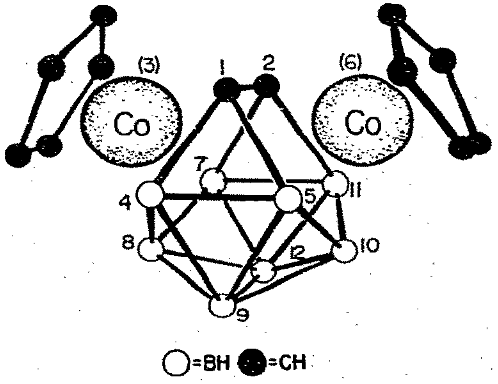


Fig. 20. Proposed structure for I. (From C. J. Jones and M. F. Hawthorne, Inorg. Chem., 12 (1973) 608.)

An improved preparation of $(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})$ has been reported (10). As a by-product, the dicobalt complex $(C_5H_5Co)_2B_8C_2H_{10}$ (Fig. 20) was obtained. The major product, $C_5H_5CoB_9C_2H_{11}$, was degraded with base and the resulting anion reacted with cobaltous chloride to form a monoanion containing three cobalt atoms and two carborane ("canastide") cages (Fig. 21).

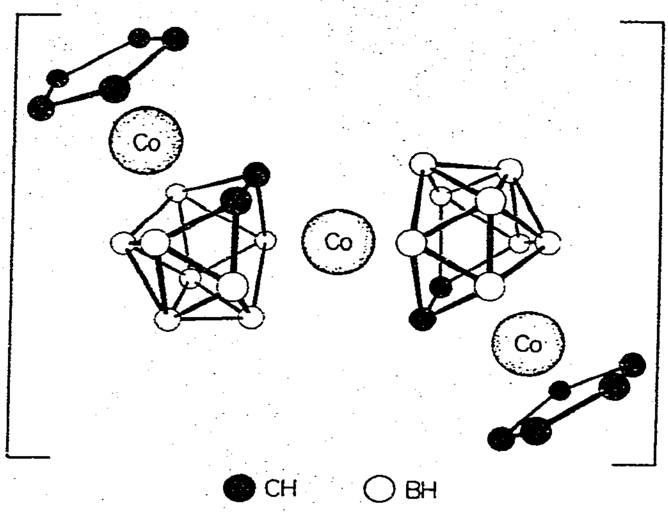


Fig. 21. Proposed structure for II. (From C. J. Jones and M. F. Hawthorne, Inorg. Chem., 12 (1973) 608.)

Thermal isomerization of dicobalt carboranes such as 2,6,1,10-$(C_5H_5Co)_2C_2B_6H_8$ yield products in which the cobalt atoms are nonadjacent in this case 2,7,1,10-$(C_5H_5Co)_2C_2B_6H_8$. The compounds with adjacent cobalt atoms are generally green, those with nonadjacent cobalt atoms are red. Several cage sizes were explored, including 8,9,10,11, and 12-atom polyhedra (11).

Reduction of $C_5H_5CoCB_7H_8$ with sodium naphthalide followed by treatment with nickel bromide and C_5H_5Na has yielded four isomers of the bimetallic mixed metal carborane $C_5H_5Co^{III}CB_7H_8Ni^{IV}C_5H_5$ (12).

Miller and Grimes have obtained a number of new cyclopentadienylcobalt(III) complexes of small carboranes derived from reduction of $C_2B_5H_7$ with sodium naphthalide followed by treatment with $CoCl_2$ and NaC_5H_5 and then air oxidation (Fig. 22) (13).

Details of the synthesis of several small cyclopentadienylferracarboranes such as $(\pi\text{-}C_5H_5)Fe(\pi C_2B_4H_6)$ have been reported by Grimes and coworkers (14). The structures were illustrated in last year's survey (J. Organometal. Chem., 58 (1973) 11). Three new ferracarborane carbonyls have been prepared by the reactions of $C_2B_4H_8$ and $C_2B_5H_7$ with $Fe(CO)_5$ vapor. Their structures are illustrated in Fig. 23-25.

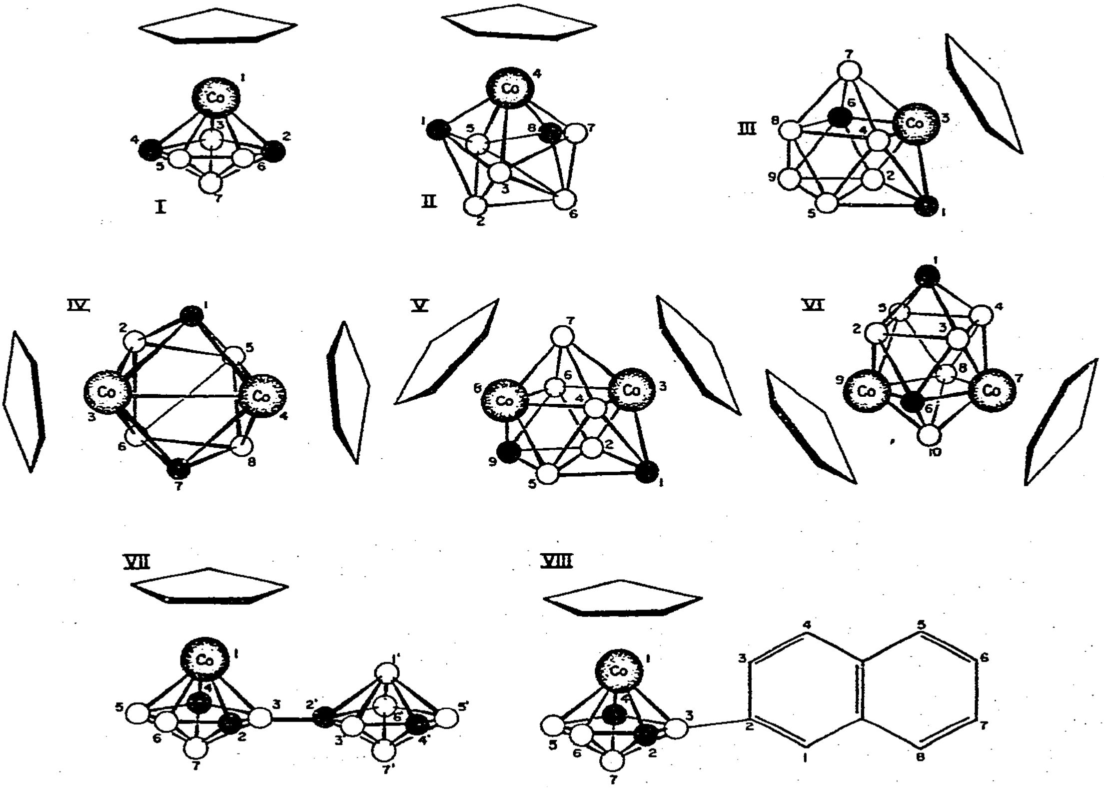


Fig. 22. Proposed structures of metallocarboranes I-VIII. Solid circles represent carbon, open circles boron; hydrogen atoms are omitted for clarity. (From V. R. Miller and R. N. Grimes, J. Amer. Chem. Soc., 95 (1973) 2830.)

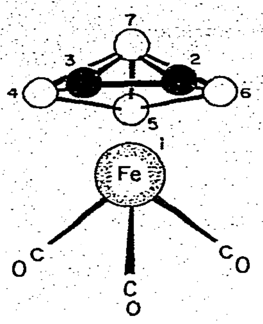


Fig. 23. Proposed structure of (π-2,3-$C_2B_4H_6$)Fe(CO)$_2$. (From L. G. Sneddon, D. C. Beer, and R. N. Grimes, J. Amer. Chem. Soc., 95 (1973) 6623.)

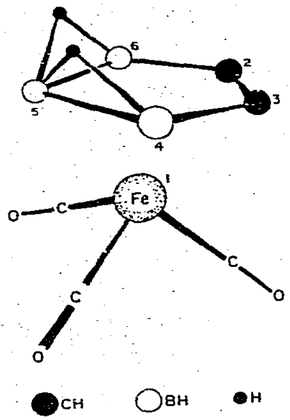


Fig. 24. Established structure of (π-2,3-$C_2B_3H_7$)Fe(CO)$_3$. (From L. G. Sneddon, D. C. Beer, and R. N. Grimes, J. Amer. Chem. Soc., 95 (1973) 6623.)

Triple-decked sandwich compounds having a $C_2B_3H_5$ ring as the middle layer have been obtained from reactions of $CoCl_2$ and NaC_5H_5 with the carborane anion derived from 1,6-$C_2B_4H_6$ by reduction with sodium naphthalide and with the <u>nido</u> anion $C_2B_4H_7^-$ (Fig. 26) (15).

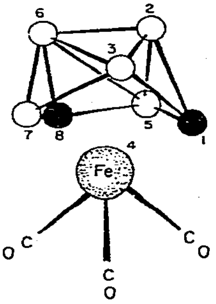


Fig. 25. Proposed structure of [π-(4)-1,8-$C_2B_5H_7$)]Fe(CO)$_3$. (From L. G. Sneddon, D. C. Beer, and R. N. Grimes, J. Amer. Chem. Soc., 95 (1973) 6623.)

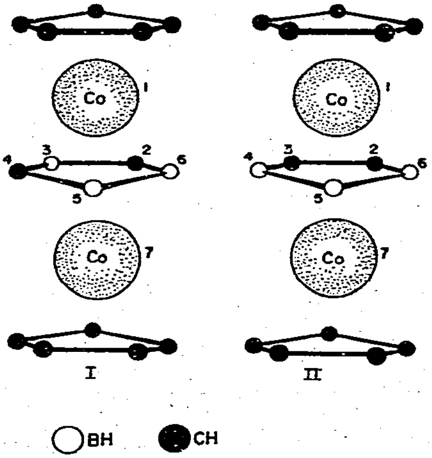


Fig. 26. Schematic side view and numbering system of (π-(1,7)-2,4-$C_2B_3H_5$)Co_2(π-C_5H_5)$_2$, (π-(1,7)-2,3-$C_2B_3H_5$)Co_2(C_5H_5)$_2$, and (π-3-CH_3-(1,7)-2,3-$C_2B_3H_4$)Co_2(C_5H_5)$_2$. The relative ring orientation depicted is arbitrary; in each compound the C_5H_5 protons are nmr equivalent in solution at room temperature, and rapid rotation of the outer rings is assumed. (From D. C. Beer, V. R. Miller, L. G. Sneddon, R. N. Grimes, M. Mathew, G. J. Palenik, J. Amer. Chem. Soc., 95 (1973) 3046.)

Stone and coworkers have found that dithallium salts of dicarbollide ions can be obtained from $B_9C_2H_{12}^-$ in aqueous alkaline solution with TlOAc, and these can be used in the synthesis of iron, cobalt, platinum, and palladium dicarbollyl complexes (16). Polyhedral expansion of closo-1,8-$Me_2C_2B_9H_9$ was also investigated with bis(1,5-cyclooctadienyl)nickel and related Ni, Pd, and Pt complexes to prepare (1,5-C_8H_{12})Ni($B_9H_9C_2Me_2$) and other dicarbollide complexes of the general formula $L_2M(B_9H_9C_2Me_2)$, where L is a phosphine or isonitrile ligand and M is Ni, Pd, or Pt.

Improved yields of (π-C_5H_5)Fe($C_2B_9H_{11}$) have been obtained by the use of methanol as solvent in the reaction of $C_2B_9H_{12}^-$ with KOH, $FeCl_2$, and cyclopentadiene, and by running the reaction at -50° (17). The conversion of $C_5H_5CoC_2B_9H_{11}$ to $(C_5H_5Co)_2C_2B_8H_{10}$ also worked well under similar conditions.

Rates of electron transfer in the oxidation of $(C_5H_5)Fe(B_9C_2H_{11})^-$ and $Fe(B_9C_3H_{11})_2^{2-}$ have been investigated (18).

Stability rules have been derived for metallocarboranes, which require that an n-vertex closo-metallocarborane containing one transition metal atom in the cage have 2n + 14 bonding electrons, and with two metal atoms, 2n + 26 electrons are required (19).

3. Nontransition metal complexes. The reaction of GeI_2 with 7,9-$B_9C_2H_{11}^{2-}$ has yielded 3-Ge-1,7-$B_9C_2H_{11}$ (Fig. 27) (20). The analogous tin compound could not be isolated. Instead, $SnCl_2$ oxidizes the 7,9-dicarbollide ion to the closocarborane 2,3-$B_9C_2H_{11}$ (Fig. 28). The stannacarborane 3-Sn-1,2-$B_9C_2H_{11}$ is stable (Organometal. Chem. Rev. B, 6 (1970) 328-330) but can be pyrolyzed to tin and $B_9C_2H_{11}$. The nucleophile becomes a boron-bound ligand in this process, and nmr evidence indicates that the ligand is bound to a boron away from the open face. This type of cage opening is illustrated in Fig. 29. The figures are all numbered according to the newly recommended convention, which is totally confusing to anyone trying to follow these reactions

without the aid of structural formulas, even though it may make sense from the standpoint of the librarian who merely catalogs compounds. Icosahedral carboranes containing germanium together with phosphorus or arsenic in the cage have been prepared from GeI_2 and 7,8- or 7,9-$HCB_9H_9P^{2-}$ or the arsenic analogs (21) (Fig. 30). A preliminary study of the thermal isomerization of 1,2,7-GeB_9H_9CHP has been carried out.

Photochemical reactions of 7,8-$B_9H_{10}CHP^-$ and the 7,9-isomer with $Fe(CO)_5$ and $Mn_2(CO)_{10}$ yields complexes in which a phosphorus-bonded carboranyl group replaces CO, for example, $[7,8\text{-}B_9H_{10}CHP\text{-}Fe(CO)_4]^-$ (22).

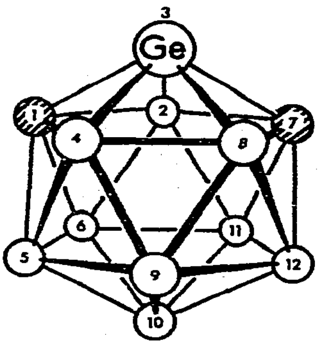


Fig. 27. The proposed structure and numbering convention for 3-Ge-1,7-$B_9C_2H_{11}$. Carbon atoms are shaded; all vertices except Ge actually have exodeltahedral hydrogens attached.. (From V. Chowdhry, W. R. Pretzer, D. N. Rai, and R. W. Rudolph, J. Amer. Chem. Soc., 95 (1973) 4560.)

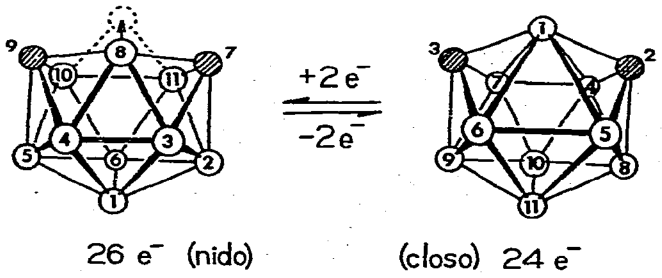


Fig. 28. The interconversion of nido and closo 11-atom frameworks and the numbering conventions for each. (From V. Chowdhry, W. R. Pretzer, D. N. Rai, and R. W. Rudolph, J. Amer. Chem. Soc., 95 (1973) 4560.)

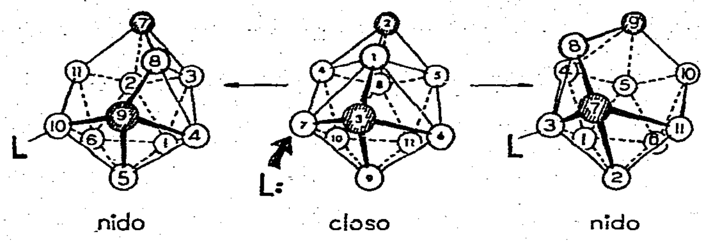


Fig. 29. Possible manners for the opening of the 2,3-$B_9C_2H_{11}$ deltahedron subsequent to nucleophilic attack. Note that the numbering conventions are not intended to indicate atom rearrangement but merely represent the accepted numbering scheme for each polyhedron. (From V. Chowdhry, W. R. Pretzer, D. N. Rai, and R. W. Rudolph, J. Amer. Chem. Soc., 95 (1973) 4560.)

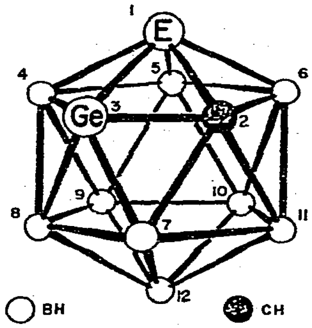


Fig. 30. Proposed structure for 1,2,3-GeB_9H_9CHE (E = P or As). The germanium atom in this compound may be "slipped" toward boron atoms 4, 7 and 8. (From D. C. Beer and L. J. Todd, J. Organometal. Chem., 50 (1973) 93.)

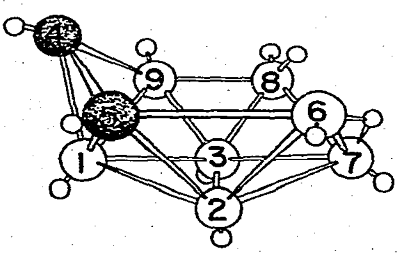


Fig. 31. Possible structure for $B_7C_2H_{11}$. As drawn, this molecule represents one enantiomorph of a d,l pair. Note that varying placement of the bridge and/or -BH_2 protons is possible. (From R. R. Rietz and R. Schaeffer, J. Amer. Chem. Soc., 95 (1973) 6254.)

Infrared and Raman spectra of *o*-, *m*-, and *p*-$HCB_{10}H_{10}P$ and -$HCB_{10}H_{10}As$ show evidence that the CH bond can hydrogen bond to polar molecules such as dimethyl sulfoxide (23).

C. Small and medium sized carboranes

1. *nido-Carboranes and anions*. Rietz and Schaeffer have obtained the *nido*-carboranes $B_7C_2H_{11}$ (Fig. 31) and $B_8C_2H_{12}$ (Fig. 32) from the reaction of acetylene with B_8H_{12} in diethyl ether (24). From ^{11}B nmr spectra, it appears that $B_7C_2H_{11}$ differs significantly in structure from $B_7C_2H_9(CH_3)_2$ (Fig. 33). The structure of the latter was obtained by X-ray crystallography (25). There appears to be no such difference between $B_8C_2H_{12}$ and $B_8C_2H_{10}(CH_3)_2$ (Fig. 32). The dimethyl compounds were obtained by using dimethylacetylene in place of acetylene in the synthesis.

A new *nido*-carborane, $B_6C_2H_{10}$ (Fig. 34), has been obtained by Williams and coworkers from the reaction of B_2H_6 and $C_2B_3H_5$ in a flow system (26).

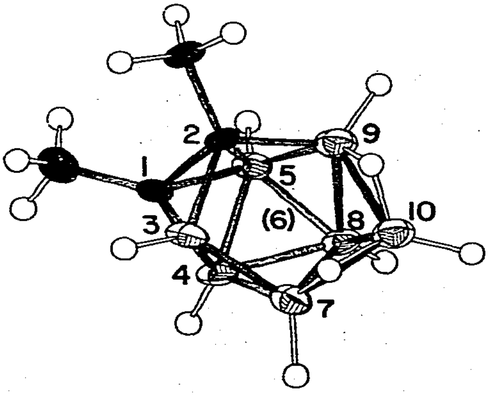


Fig. 32. Crystal structure of *nido*-1,2-$B_7C_2H_9(CH_3)_2$. The molecule is numbered to be consistent with other known bicapped Archimedian antiprismatic structures. Here the molecule is missing position 6. The enantiomorph shown is paired with the other *d,l* form in the crystalline state. R. R. Rietz and R. Schaeffer, *J. Amer. Chem. Soc.*, 95 (1973) 6254.)

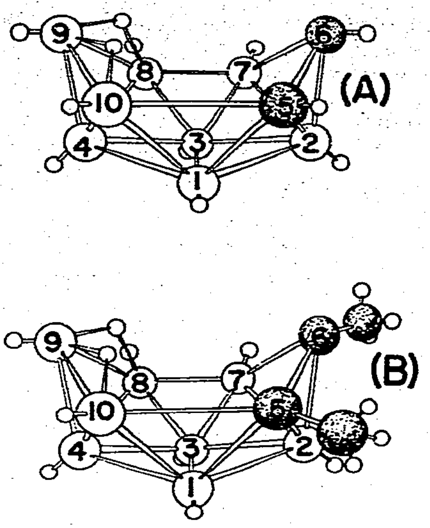


Fig. 33. Proposed structures for $B_8C_2H_{12}$ (A) and $B_8C_2H_{10}(CH_3)_2$ (B). With such molecules, another d,l enanticmorph would exist with cage carbons in the 6,7 positions. The single bridge pmr resonance mitigates against varying the placement of the bridge hydrogens. (From R. R. Rietz and R. Schaeffer, J. Amer. Chem. Soc., 95 (1973) 6254.)

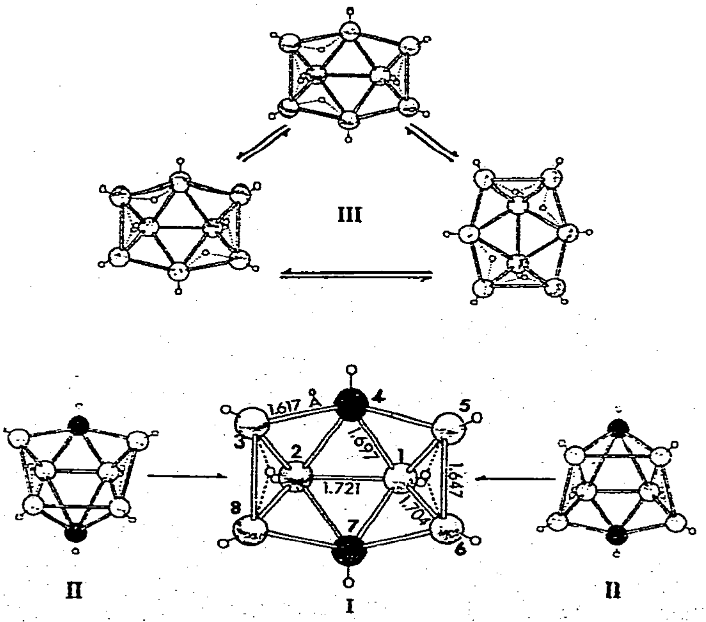


Fig. 34. Eight-vertex nido-carboranes of the $C_2B_6H_{10}$-B_8H_{12} family: III, nido-B_8H_{12} tautomers, arachno structures dominant; II, nido structure; I, nido-$C_2B_6H_{10}$ (bond distances estimated from ADD theory), arachno structure; II', nido structure. (From A. J. Gotcher, J. F. Ditter, and R. E. Williams, J. Amer. Chem. Soc., 95 (1973) 7514.)

Iodination of the nido carborane $C_2B_4H_8$ in the presence of Al_2I_6 yields only $3\text{-}IC_2B_4H_7$ and its enantiomer. Iodination of the closo carborane $C_2B_4H_6$ is relatively slow and yields the B-iodocarborane $2\text{-}IC_2B_4H_5$ (only one isomer possible) (27).

Tabereaux and Grimes have reported the synthesis of $\mu\text{-}Me_3SnC_2B_4H_7$ and the analogous lead compound (XXXX) (Fig. 35) (28). Unlike the silicon analogs reported previously (J. Organometal. Chem., 58 (1973) 19), these tin and lead compounds do not undergo thermal isomerization to the terminally substituted isomers. Details of the work on the silicon compounds were also presented in this paper.

Cyclohexyl isocyanide and $i\text{-}B_{18}H_{22}$ react to form a one-carbon nido carborane (Fig. 36) (29). Sneath and Todd also prepared several metal complexes from $B_{18}H_{20}{}^{2-}$.

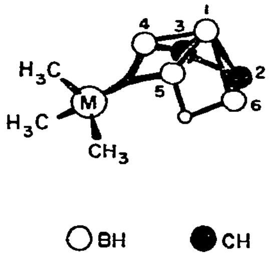


Fig. 35. Proposed structure of $\mu\text{-}(CH_3)_3MC_2B_4H_7$ carboranes, with M = Si, Ge, Sn, or Pb. (From A. Tabereaux and R. N.Grimes, Inorg. Chem., 12 (1973) 792.)

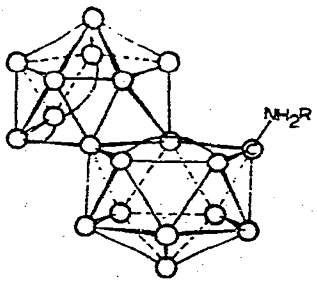
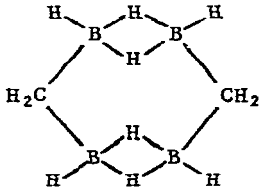


Fig. 36. Proposed structure of $i\text{-}B_{18}H_{20}CNH_2C_6H_{11}$ (R = C_6H_{11}). (From R. L. Sneath and L. J. Todd, Inorg. Chem., 12 (1973) 44.)

Oxidation of $B_9C_2H_{12}^-$ with chromic acid has yielded the dimeric oxidation products $B_{18}C_4H_{22}$ and $B_{18}C_4H_{23}^-$, which are *nido*-carboranes (30). Degradation of *p*-carborane with potassium hydroxide in propanediol at 170° has yielded 2,9-$C_2B_9H_{12}^-$, which on acidification gave 2,9-$C_2B_9H_{13}$ (31). Thermal decomposition of 5,6-dicarba-*nido*-decaborane(12) yields a mixture of the *closo* carboranes 1,6- and 1,10-$B_8C_2H_{10}$ (32). Heating $NaB_8C_2H_{11}$ to 200° yields 1,2-$B_8C_2H_{10}$ and $Na_2B_8C_2H_{10}$.

It might be expected that the reduction of $C[B(OMe)_2]_4$ and related compounds would lead to carboranes, but this turned out to be exceedingly difficult. A sequence beginning with $HC[B(OMe)_2]_3$, which was converted to $HC(BCl_2)_3$ by repeated treatment with BCl_3 and then reduced with lithium borohydride, led to small amounts of unstable *nido* carboranes. A more promising result was obtained by converting $CH_2[B(OMe)_2]_2$ to $CH_2(BCl_2)_2$ and reducing it to the dimer of $CH_2(BH_2)_2$, which is stable (33).



2. *closo*-Carboranes. Wiersema and Hawthorne have studied the electrochemistry and 80.5 MHz ^{11}B nmr spectra of the monocarbon carborane anions $B_{11}CH_{12}^-$, $B_{10}CH_{11}^-$, $B_{10}CH_{13}^-$, and $B_9CH_{10}^-$ (34). From the nmr spectrum, it appears that the $B_{10}CH_{11}^-$ ion undergoes rapid rearrangement which renders positions 1, 4, 7, and 8 equivalent, 3, 5, 6, 9, and 11 equivalent, and position 10 unique, yielding the 4:5:1 integral ratio of the ^{11}B nmr spectrum (Fig. 37). The carbon atom, position 2, is also unique, and its coordination number never exceeds five. Oxidation of $B_9CH_{10}^-$ yields a coupled product, $B_{18}C_2H_{18}^{2-}$ (Fig. 38).

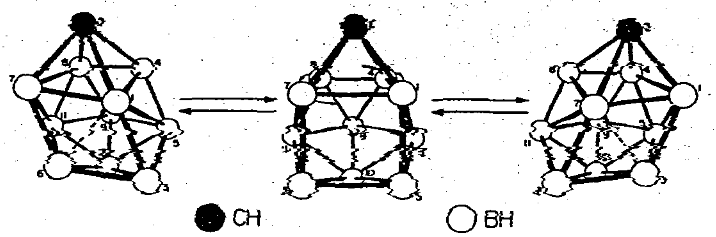


Fig. 37. Sequence of "dsd" type rearrangements resulting in rotation of belts in an 11-particle polyhedron. (From R. J. Wiersema and M. F. Hawthorne, Inorg. Chem., 12 (1973) 785.)

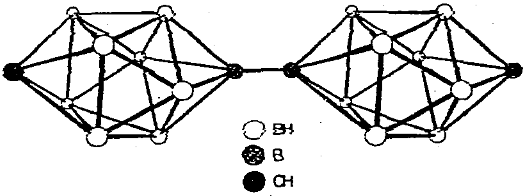
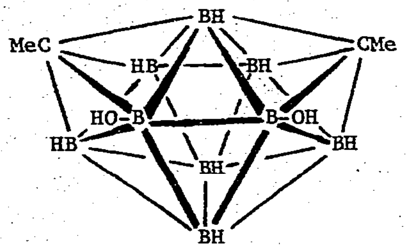


Fig. 38. Proposed structure of the $B_{18}C_2H_{18}{}^{2-}$ ion. (From R. J. Wiersema and M. F. Hawthorne, Inorg. Chem., 12 (1973) 785.)

From gas-phase electron diffraction measurements, the bond distances in 1,5-$B_3C_2H_5$ are B-C = 1.556 Å, B-B = 1.853 Å, C-H = 1.071 Å, and B-H = 1.183 Å. For 1,6-$B_4C_2H_6$, the distances are B-C = 1.633 Å, B-B = 1.720 Å, C-H = 1.103 Å, and B-H = 1.244 Å (35). The long B-B and short B-C distances in $B_3C_2H_5$ are consistent with an essentially classical structure, it being possible to write an acceptable structure for this compound having tetravalent carbon and trivalent boron, and the bond lengths in $B_4C_2H_6$ are consistent with the delocalized bonding required for that structure. The structure of $C_4B_2Me_6$ has also been determined by electron diffraction (36).

Oxidation of 1,8-Me_2-1,8-$C_2B_9H_9$ with chromic acid yields a dihydroxy derivative having the hydroxyl groups on adjacent boron atoms, 1,8-Me_2-3,7-$(HO)_2$-1,8-$C_2B_9H_7$ (37).



Several mercury, tin, and phosphorus derivatives of 1-Ph-1,6- and -1,10-$C_2B_8H_9$ have been prepared (38).

Localized molecular orbitals from self-consistent field calculations on $C_2B_4H_6$ indicate open three-center B-C-B bonds in the 1,2-isomer and fractional cyclic three-center bonds in the 1,6-isomer (39).

Epstein has described a topological approach to the prediction of reaction pathways in electrophilic and nucleophilic substitutions on boron hydrides (40). Good correlation with experimental findings was noted. No numerical calculations are necessary, and the method is essentially an extension of the resonance structure approach familiar to organic chemists, except that the three-center bonds of the boron compounds add considerable complexity.

The electronic structures of $C_2B_3H_5$, $C_2B_4H_6$, and $C_2B_5H_7$ based on ab initio calculations and of larger carboranes based on semiempirical INDO calculations and the role of delocalized bonding in these structures have been discussed from a theoretical point of view (41).

D. Icosahedral carboranes

1. Cage rearrangement. Hart and Lipscomb have published further studies regarding the mechanism of cage isomerization of icosahedral boranes (Organometal. Chem. Rev. B, 6 (1970) 333-334) (42). The numbering convention for the icosahedron is shown in Fig. 39. The most favored pathway for the isomerization of o-carborane to m-carborane involves opening to a cuboctahedral intermediate, as illustrated in Fig. 40. This mechanism keeps atoms which were opposite (1,12) to each

other in the starting material still opposite in the product. Thus, when 9,12-dichloro-1,2-dimethyl-*o*-carborane rearranges, the chlorine substituents are opposite the carbon atoms in both the starting material and in the major product, 5,12-dichloro-1,7-dimethyl-*m*-carborane, the structure of which has been determined by X-ray and is illustrated in Fig. 41. To isomerize *m*- and *p*-carborane requires a triangle rotation in the cuboctahedral intermediate and a considerably higher activation energy.

The isomerization of *o*- to *m*- and *p*-carborane under mild conditions by way of the 13-atom cobalt complex has already been noted in part B-1.

2. *Transition metal σ-complexes*. Reaction of 1,2-dilithio-*o*-carborane with bis(triphenylphosphine)nickel(II) chloride yields an

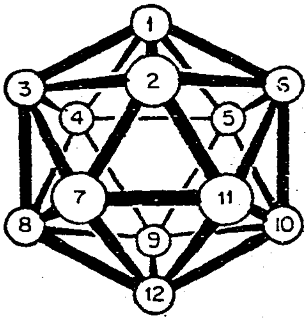


Fig. 39. Numbering convention for icosahedral structures. (From H. V. Hart and W. N. Lipscomb, Inorg. Chem., 12 (1973) 2644.)

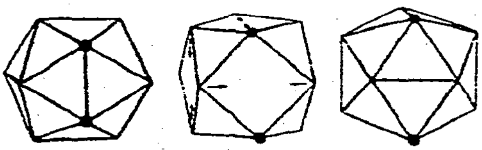


Fig. 40. Transformation of *o*- to *m*-carborane through the cuboctahedral intermediate. (From H. V. Hart and W. N. Lipscomb, Inorg. Chem., 12 (1973) 2644.)

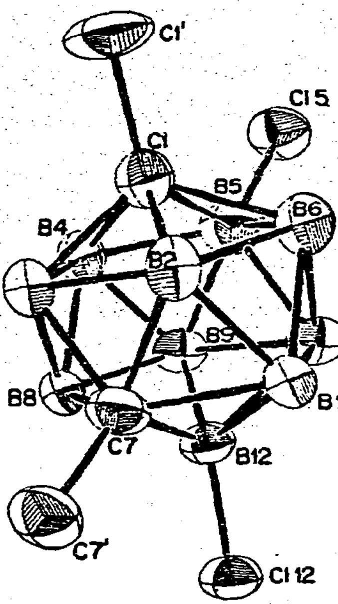


Fig. 41. Molecular structure of $5,12\text{-}Cl_2\text{-}\underline{m}\text{-}B_{10}H_8C_2(CH_3)_2$ with 50% probability thermal ellipsoids. Conventional atom numbers (ref 13) are preceded by the symbol of the element, B, C, or Cl. Hydrogen atoms have been eliminated for clarity. (From H. V. Hart and W. N. Lipscomb, Inorg. Chem., 12 (1973) 2644.)

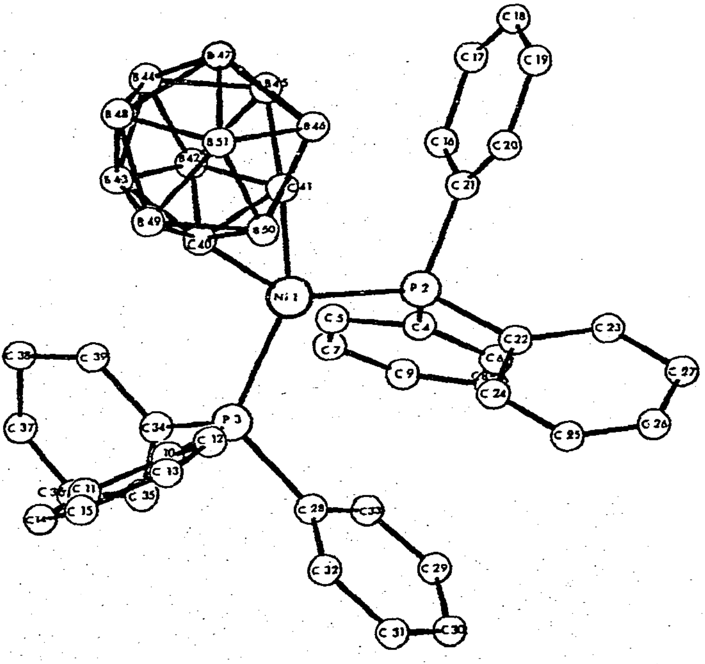
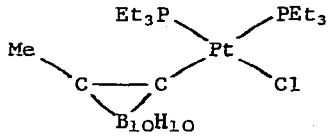


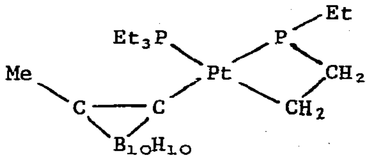
Fig. 42. Molecular structure of $[(C_6H_5)_3P]_2NiC_2B_{10}H_{10}$. (From A. A. Sayler, H. Beall, and J. F. Sieckhaus, J. Amer. Chem. Soc., 95 (1973) 5790.)

unusual σ-bonded nickel complex in which the nickel bridges the 1,2-positions of the carborane (Fig. 42) (43).

Bis(trialkylphosphine)platinum dichlorides react with lithiocarboranes to form σ-bonded carboranylplatinum compounds (44). The <u>cis</u>-platinum chlorides form carboranylplatinum chlorides, but the <u>trans</u> isomers lose HCl, apparently binding an alkyl group to the phosphine in a ring to the platinum, and shifting the phosphorus atoms to a <u>cis</u> relationship in the product.



from <u>cis</u> dichloride



from <u>trans</u> dichloride

Reaction of an iridium complex with 1-dimethylphosphinocarborane has yielded iridium substitution on boron in a cyclic complex of incompletely determined structure (Fig. 43) (45).

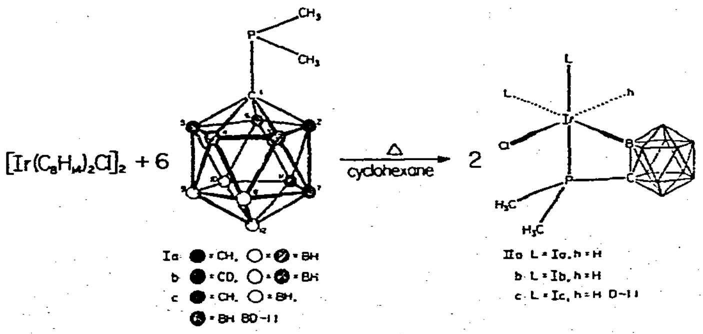


Fig. 43. (From E. L. Hoel and M. F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 2712.)

Zakharkin and coworkers have reported a fairly extensive study of the chemistry of σ-bonded carboranyliron compounds, o- and m-$RCB_{10}H_{10}C\text{-}Fe(CO)_2(C_5H_5)$ (46). The carbon-iron bond survives under conditions sufficiently vigorous to brominate the carborane cage. However, mercuric chloride cleaves the carbon-iron bond and yields carboranylmercury compounds. The carboranyliron compounds are made from $RCB_{10}H_{10}C\text{-}COCl$ and $NaFe(CO)_2(C_5H_5)$. Polarographic studies on these carboranyliron compounds were also reported.

3. Organocarborane chemistry. Icosahedral carboranes can be attached to a great variety of typical organic functional groups and side chains. The effects of the carborane substituent as a very bulky, highly stable, electron-withdrawing group are by now fairly well explored and the properties of new compounds fairly predictable. Russian workers continue to publish the majority of the papers in this area.

Paxson, Callahan, and Hawthorne have described an improved preparation of 1,1'-biscarborane. The starting materials are diacetylene and $B_{10}H_{12}(SEt_2)_2$ (47). Zakharkin and Kovredov have prepared biscarboranes in 55-75% yields by the coupling of o-, m-, or p-C-lithiocarborane with CuCl or $CuCl_2$ (48).

The chemistry of ethynylcarborane has been studied in detail by Callahan and Hawthorne (49). Trimerization in the presence of bis-(acrylonitrile)nickel(0) yields 1,2,4-tri-o-carboranylbenzene (Fig. 44). Reaction of the ethynyl group with dicobalt octacarbonyl leads to the expected adduct (Fig. 45). Addition of the ethynyl group to Vaska's complex, trans-$IrCl(CO)(PPh_3)_2$, results in formation of a compound containing one carboranylvinyl and one carboranylethynyl group (Fig. 46). Coupling by oxygen in the presence of copper(I) tetramethylethylenediamine led to the dicarboranylbutadiyne, $B_{10}H_{11}C_2\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}C_2B_{10}H_{11}$.

Zakharkin and coworkers have obtained a Russian patent on the preparation of acetylene-substituted carboranes from diacetylenes and

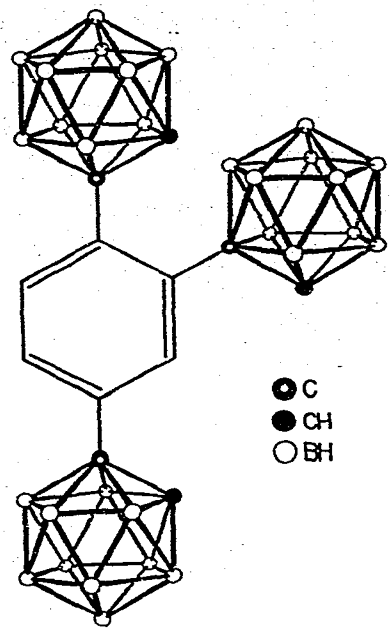


Fig. 44. Proposed structure of II. (From K. P. Callahan and M. F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 4574.)

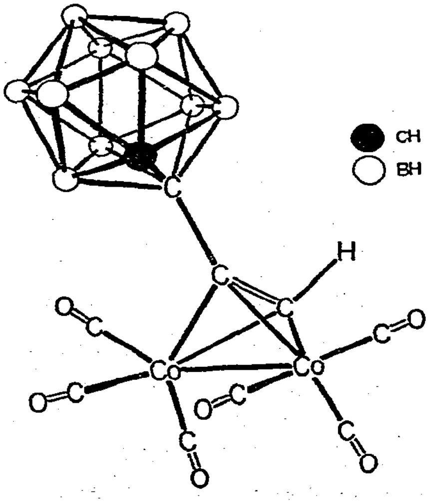


Fig. 45. Proposed structure of III. (From K. P. Callahan and M. F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 4574.)

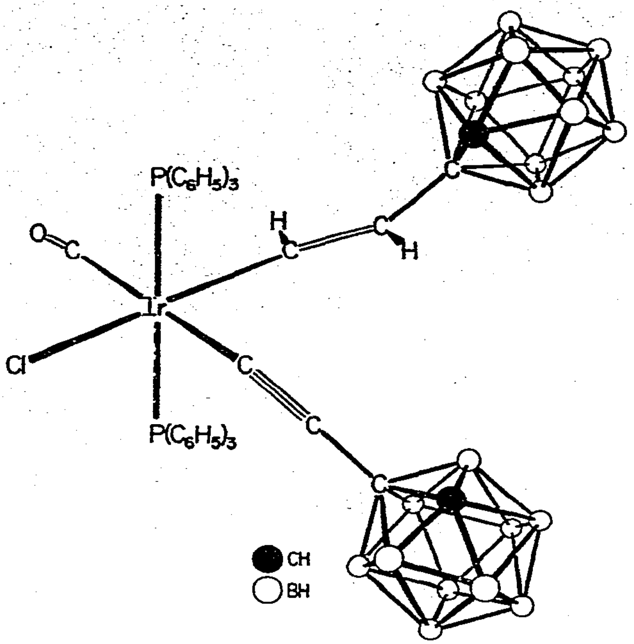


Fig. 46. Structure of IV. (From K. P. Callahan and M. F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 4574.)

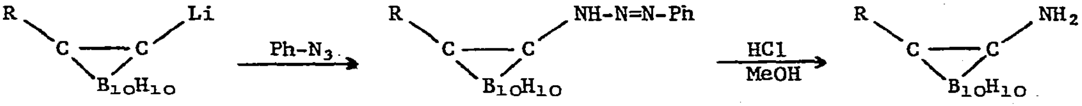
decaborane--Lewis base complexes (50). Decaborane and pentafluorophenylacetylene react to form the expected carborane (51).

Zakharkin and coworkers have reported that the reaction of the 7,9-dicarbollide ion (made from *m*-carborane) with CH_2=CH-BCl_2 yields 2-vinyl-*m*-carborane, *m*-$HCB_{10}H_9(CH{=}CH_2)CH$ (52). The vinyl group provides a route to a variety of other *B*-substituted *m*-carboranes by way of chromic acid oxidation to 2-carboxy-*m*-carborane, which can be converted to 2-CO_2Me, 2-$HOCH_2$, 2-CH_3CO, and 2-NH_2 by standard organic methods, and the NH_2 group has been converted to OH by diazotization and hydrolysis.

Vinylsilicon compounds alkylate *o*- *m*-, and *p*-carboranes on boron in the presence of aluminum trichloride at 80-120° (53,54). For example, $HCB_{10}H_{10}CH$ and $CH_2{=}CHSiCl_3$ yield $HCB_{10}H_{10-n}(CH_2CH_2SiCl_3)_nCH$, where n = 1 to 3.

Pyridine attacks the cage of o-$CH_3CB_{10}H_{10}CCH_2Br$ to form pyridinium-substituted B_9 compound (see J. Organometal. Chem., 58 (1973) 13). With $HCB_{10}H_{10}CCH_2Br$ the major product is that of simple displacement of the bromine (55). In spite of the steric hindrance present in o-$HCB_{10}H_{10}C$-CH_2Br, diethylamine easily displaces the bromide to form o-$HCB_{10}H_{10}C$-CH_2NEt_2, apparently by way of coordination of the amine with a boron atom in the cage prior to the displacement step (56). Brominated o-carboranes form adducts with two molecules of pyridine (57). It was suggested that the pyridine adds to the boron atoms at positions 3 and 6 without opening the icosahedral cage, forming a structure analogous to $C_2B_{10}H_{12}^{2-}$. However, the presence of an additional ligand on boron (both H and C_5H_5N) makes this doubtful, since $C_2B_{10}H_{12}^{2-}$ loses its presumed icosahedral geometry on complexing with Lewis acid.

Carboranyltriazenes are easily synthesized and provide a good route to aminocarboranes (58).



R = Me or Ph

Perfluoro-m-carborane has been obtained from the direct fluorination of m-carborane (59).

A mixture of 1,9- and 1,12-dibromo-o-carborane has been obtained either by brominating 1-bromo-o-carborane or by brominating 9(12)-bromo-o-carboranyl-1-magnesium bromide (60).

Reaction of Me_3NBH_2I with o- and m-carboranyllithium has yielded the corresponding $Me_3NBH_2CB_{10}H_{10}CH$ (61). Degradation of these compounds by piperidine to form the protonated dicarbollide derivatives was also reported

Reduction of 1-halomethyl-*o*-carboranes with sodium in liquid ammonia followed by oxidation of the anions with $KMnO_4$ has yielded mixtures of 1-methyl-*o*-carborane, 1-methyl-3-amino-*o*-carborane, unchanged halomethylcarborane, 1-methyl-*m*-carborane, and unsubstituted *o*-carborane (62).

Hexafluorobenzene reacts with *o*- or *m*-$MeCB_{10}H_{10}CLi$ to form 1,4-$(MeCB_{10}H_{10}C)_2C_6F_4$ (63). Chloropentafluorobenzene yields 1-Cl-4-$(MeCB_{10}H_{10}C)C_6F_4$. The reaction of *o*-$MeCB_{10}H_{10}CLi$ with MeI or EtI has been reported to give $MeCB_{10}H_{10}C$-Me or -Et in 98% yield (64).

Because of the electron-withdrawing inductive effect of the carboranyl group, it is possible to add R_2NLi to the vinyl group of 1-vinyl-2-alkyl-*o*-carboranes. The products after hydrolysis are R'-$CB_{10}H_{10}C$-$CH_2CH_2NR_2$ (65).

Lithiocarboranes have been added to the double bond of α-nitroolefins (66). Reaction of *o*-$PhCB_{10}H_{10}CLi$ with $Cl_2C{=}CHCHO$ followed by treatment with sulfuric acid has yielded $PhCB_{10}H_{10}C$-$CH{=}CH$-CO_2H, and several derivatives were made from the carboxylic acid group (67).

Reaction of $Hg(GeEt_3)_2$ with *o*-1-$ClHgCB_{10}H_{10}CH$ and related compounds (68). Reduction of *o*-$PhCB_{10}H_{10}CHgCl$ with lithium naphthalide yields $(PhCB_{10}H_{10}C)_2Hg$, which is cleaved by mercuric chloride back to the carboranylmercuric chloride only in hot nitrobenzene (69).

Carboranyl-*C*,*C*'-bis(phthalic anhydride)s have been prepared by chromic acid oxidation of dixylylcarboranes (70). Some reactions of $PhCB_{10}H_{10}C$-SO_2Br with unsaturated compounds to form carboranylsulfones have been reported (71).

Soviet patents have been issued on the radical-initiated addition of organotin hydrides to the double bond of alkenylcarboranes (72), hydrolysis of *m*-$ROSiMe_2CB_{10}H_{10}CSiMe_2OR$ to $HOSiMe_2CB_{10}H_{10}CSiMe_2OH$ (73), the hydrolysis of 1,7-bis(dimethylsilyl)-*m*-carborane to the corresponding -$Si(OH)Me_2$ compound (74), the condensation of 1,7-bis(hydroxydimethylsilyl)-m-carborane with diorganodiacetoxysilanes (75), and the preparation of 1,7-bis(hydroxytetraorganosiloxanyl)-m-carboranes (76).

4. Physical measurements. The electronic effects of the 2-m-carboranyl group (note that the point of attachment is boron in this case) have been investigated for a series of 2-aryl-m-carboranes by measuring the acidities of the m- and p-carboxyphenyl compounds and the ^{19}F-nmr chemical shifts of the fluorophenyl compounds and estimating the appropriate Hammett and related substituent constants (77). The 1-m-carboranyl group has been found to increase the acidity of a $-SiMe_2OH$ substituent (78). Equilibrium acidities have been determined for several substituted carboranes in equilibrium with aromatic radical anions in glyme (79).

Dipole moments of monobromo-o-carboranes have been found to increase in the order 1-Br<3-Br<4-Br<8-Br<9-Br, that is, with increasing distance between the carbon atoms and the bromine atom (80).

From NQR measurements on a series of o-X-$CB_{10}H_{10}CCH_2Cl$, it has been concluded that steric effects tend to dominate in the transmission of substituent effects from X to Cl in this system (81). The relationship between structure and ^{199}Hg-H coupling constants in the nmr spectra of several $Me_2C{=}CH$-Hg-substituted o- and m-carboranes has been investigated (82). Proton nmr chemical shifts have been determined for a number of B-halo-C-methylcarboranes (83).

Mass spectral cracking patterns of carboranes substituted at the 1- and 3-positions with a $-CH_2CH_2SiCl_3$ group have been examined, and it was found that the substituent was cleaved more easily from boron than from carbon (84). Mass spectra of C-hydroxy- and C-acetoxy-carboranes have been reported (85).

The kinetics of alkaline cleavage of o, m, and p isomers of 1-Me_3Sn-$CB_{10}H_{10}CH$ have been investigated (86). The rates are first-order in substrate and first-order in OH^-, and show no significant deuterium isotope effect. Coordination of OH^- with the tin atom must be involved in the transition state.

The polarographic reduction of a number of organomercurials, including $(\underline{o}\text{-}RCB_{10}H_{10}C\text{-})_2Hg$ and $\underline{o}\text{-}RCB_{10}H_{10}CHgR'$, where R' is halide or methyl, has been studied (87).

Kinetics of reaction of m- and p-carboranedicarbonyl chloride with aniline have been measured (88). Rates of hydrogenation of carboranyl-substituted unsaturated alcohols over a nickel-chromium catalyst have been studied (89). Thin-layer chromatography of icosahedral carboranes works well on silica with starch as a binder, which improves the detectability with iodine vapor (90).

E. Polyhedral boranes

These compounds are "organometallic" if they bear alkyl substituents, but in general this field is "inorganic." Coverage is therefore incomplete, and examples are selected for their possible interest to carborane chemists.

The $B_8H_8{}^{2-}$ anion can exist in two forms in solution, a bicapped trigonal prism having C_{2v} symmetry and a square antiprism having D_{4d} symmetry, and these do not interconvert rapidly on the nmr time scale at room temperature (91).

Reaction of $B_9H_{14}{}^-$ with $BrMn(CO)_5$ in tetrahydrofuran has yielded $(OC)_3Mn(B_9H_{13})^-$ and $(OC)_3Mn(B_9H_{12}THF)$ (92). Several cyclopentadienylcobalt derivatives of B_4 and B_9 boron hydrides have been prepared (93).

An exponential line-narrowing technique applied to Fourier transform ^{11}B nmr spectra has resolved previously unobservable splitting in B_4 through B_{10} boron hydrides (94,95). ^{11}B-^{11}B coupling has been observed in the double resonance nmr spectrum of 6-methyldecaborane(14) (96).

The kinetics of benzoylation of $B_{10}H_{10}^{2-}$ have been investigated by Wegner and coworkers (97).

B_6H_{10} and its derivatives 2-BrB_6H_9 and 2-$CH_3B_6H_9$ exhibit stereochemical nonrigidity, the basal hydrogens migrating around the base of the pyramidal molecule, and the kinetics have been determined by nmr measurements (98). Potassium hydride deprotonates pentaboranes such as 1-MeB_5H_8 and 2-MeB_5H_8 to the corresponding $MeB_5H_7^-$ anions (apical substituent) to 2-$MeB_5H_7^-$ (basal substituent) occurs in a few minutes at 10° (99).

The preparation of 2-methylhexaborane(10) and an improved preparation of B_6H_{10} have been described (100).

The decomposition of _i_-B_9H_{15} at -30° under 25 atmospheres of carbon monoxide yields the carbonyl $B_9H_{13}CO$ (101). The structure of triborane carbonyl, B_3H_7CO, has been determined by X-ray crystallography (102).

A sulfur analog of a closo carborane, 1-B_9H_9S, has been obtained by pyrolysis of $B_9H_{11}S$ (103). Reaction of _i_-B_9H_{15} with B_6H_{10} has yielded the new boron hydride $B_{15}H_{23}$ (104). The diazonium ion 1-$B_{10}H_9N_2^-$, which is potentially very useful for making derivatives of $B_{10}H_{10}^{2-}$, has been made by coupling $B_{10}H_{10}^{2-}$ with ArN_2^+ and pyrolyzing the product (105).

Onak has reviewed the synthesis and structure of carboranes and metallocarboranes (106). Hawthorne and Dunks have reviewed metallocarboranes (107) and non-icosahedral carboranes (108). Lipscomb has reviewed three-center bonds in electron-deficient compounds (109). Gaines has reviewed the chemistry of pentaborane (110).

II. HYDROBORATION

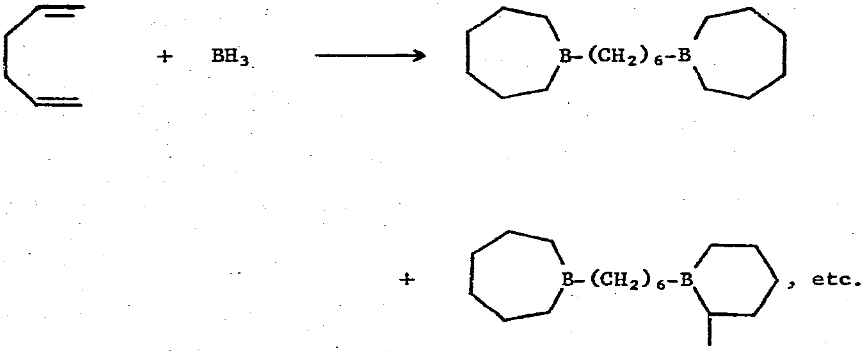
A. The hydroboration reaction

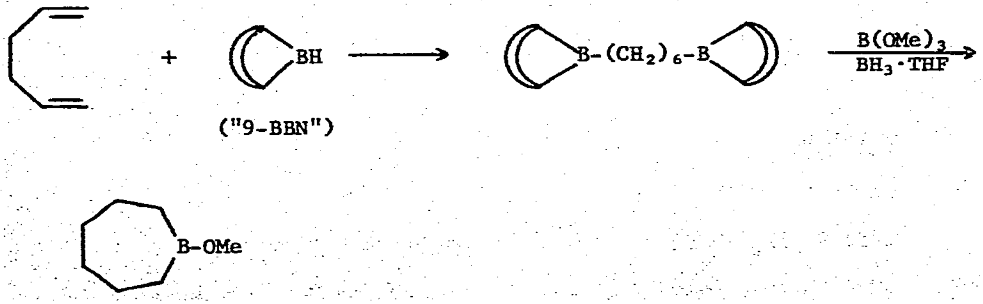
1. Hydroborating agents. The development of hydroboration as a synthetic tool has continued at a rapid pace, led by H. C. Brown and

coworkers. New hydroborating agents offer special properties advantageous for certain types of syntheses. Chloroborane etherate is much more selective than diborane in hydroboration of olefins (111). With unsymmetrically substituted olefins, the boron goes at least 99.5% to the less substituted carbon. It was concluded that the directive effect is largely electronic rather than steric. Chloroborane etherate readily hydroborates alkynes (112).

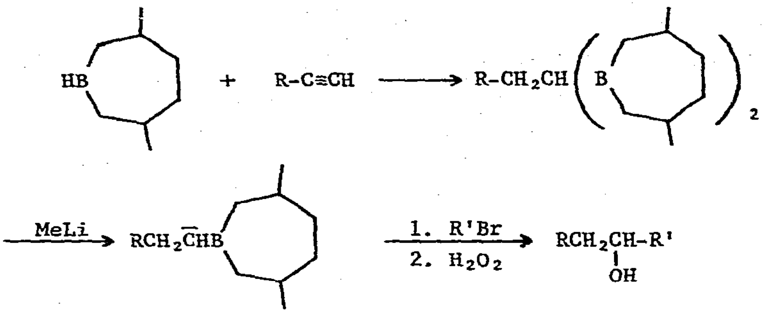
Alkyldichloroboranes are easily prepared by hydroborating alkenes with $HBCl_2 \cdot OEt_2$ in the presence of BCl_3, which displaces free $HBCl_2$ from the etherate (113). The hydroboration of alkynes with $HBCl_2 \cdot OEt_2$ in the presence of BCl_3 in pentane yields alkenyldichloroboranes, $RCH{=}CHBCl_2$ (114).

Hydroboration of 1,5-hexadiene leads to 7-membered ring boron compounds (borepanes) (115).

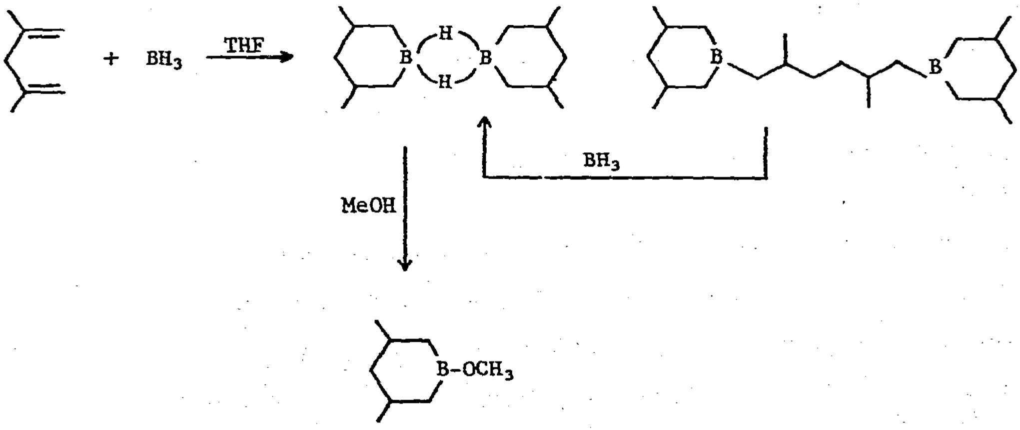


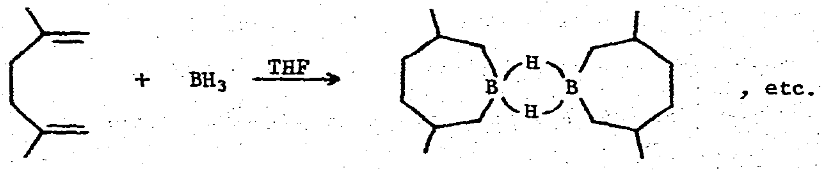


The 7-membered borane obtained from 2,5-dimethyl-1,5-hexadiene has been used for the dihydroboration of acetylenes, and the resulting 1,1-diborylalkanes have been converted to α-boryl carbanions and alkylated with reactive alkyl halides (116).



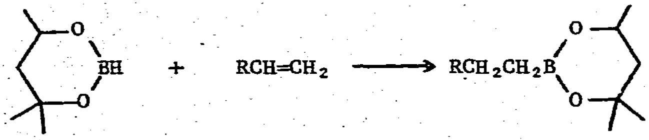
The presence of methyl substituents at the 2 and 4 positions of 1,4-pentadiene or the 2 and 5 positions of 1,5-hexadiene makes it easier to obtain well-defined cyclic derivatives on hydroboration (117).





, etc.

Relative rates of hydroboration of several olefins with 4,4,6-trimethyl-1,3,2-dioxaborinane have been studied (118). This reagent reacts more slowly than disiamylborane or catechol borane.



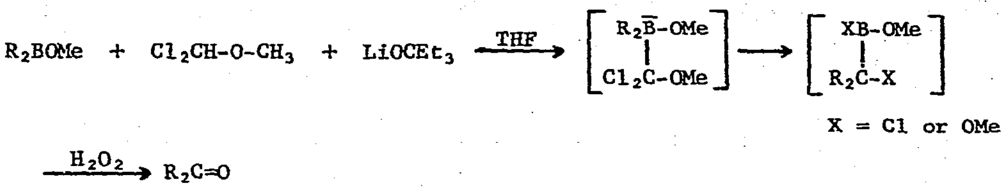
2. Mechanistic studies. From a detailed study of the hydroboration of allenes with (+)-tetra-3-pinanyldiborane, also known as diisopinocampheylborane, Moore and coworkers have proposed some significant modification of the transition state previously suggested for the asymmetric hydroboration of olefins (Organometal. Chem. Rev. B, 6 (1970) 358-360) (119).

The hydroboration of trans- and cis-2-butene with BD_3 led to pure threo- and erythro-2-butan-3-d-ol, respectively, showing that hydroboration is stereospecifically cis with simple acyclic alkenes (120).

Brown and coworkers have published a detailed study of steric effects in addition to norbornene and 7,7-dimethylnorbornene (121). Hydroboration of the former with 9-BBN yields 99.5% exo attack, and the latter yields only 3% exo and 97% endo attack. Hydroboration has been used as a probe for steric bulk of substituents in syn-7-substituted norbornenes (122). Studies on the hydroboration of 2-alkyl-1-propenes with disiamylborane have led to the proposal of a new steric substituent constant scale for the correlation of hydroboration and other reactions having similar steric requirements (123).

B. Alkylboranes in synthesis

1. Carbon-carbon bond formation. Borinic esters react with Cl_2CHOCH_3 and $LiOCEt_3$ to form intermediates which are easily oxidized to ketones (124).



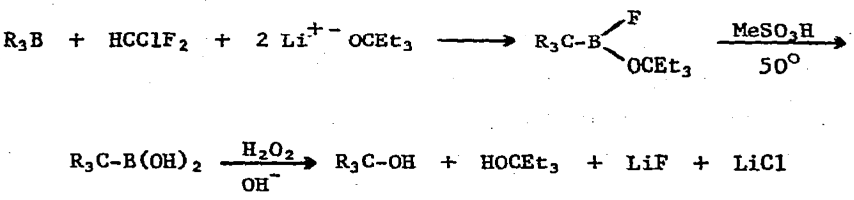
$$R_2BOMe + Cl_2CH\text{-}O\text{-}CH_3 + LiOCEt_3 \xrightarrow{THF} \left[\begin{array}{c} R_2\bar{B}\text{-}OMe \\ | \\ Cl_2C\text{-}OMe \end{array}\right] \longrightarrow \left[\begin{array}{c} XB\text{-}OMe \\ | \\ R_2C\text{-}X \end{array}\right] \xrightarrow{H_2O_2} R_2C{=}O$$

X = Cl or OMe

Tertiary carbinols are easily prepared by way of the reaction of $Cl_2CH\text{-}OCH_3$ and Et_3COLi with organoboranes (125).

$$R_3B + Cl_2CH\text{-}OCH_3 + Et_3COLi \longrightarrow R_3C\text{-}BX_2 \longrightarrow R_3C\text{-}OH$$

The reaction of trialkylboranes with $HCClF_2$ and $LiOCEt_3$ leads to an unusually stable sterically hindered alkylalkoxyfluoroborane intermediate, which resists alkaline hydrogen peroxide and must be cleaved by methanesulfonic or sulfuric acid (126).

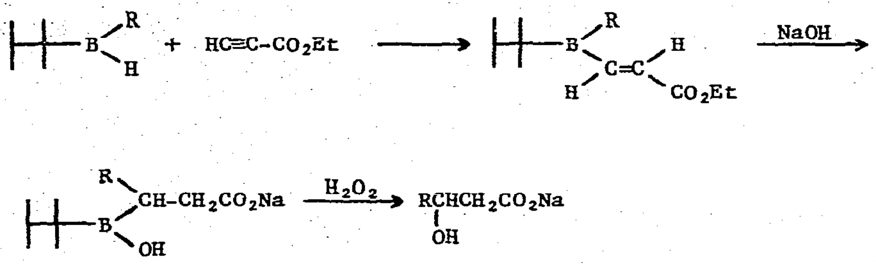


$$R_3B + HCClF_2 + 2\ Li^{+-}OCEt_3 \longrightarrow R_3C\text{-}B\begin{array}{l} \diagup F \\ \diagdown OCEt_3 \end{array} \xrightarrow[50^{\circ}]{MeSO_3H}$$

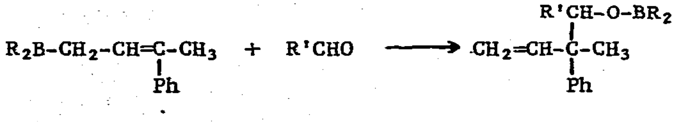
$$R_3C\text{-}B(OH)_2 \xrightarrow[OH^-]{H_2O_2} R_3C\text{-}OH + HOCEt_3 + LiF + LiCl$$

Reaction of tricyclohexylborane with carbon monoxide in the presence of sodium followed by the usual oxidative work-up has yielded $(C_6H_{11})_2CHOH$ (127). Brown has patented the carbonylation of organoboranes in the presence of $LiBH_4$ and $LiHAl(OMe)_3$ (128).

The addition of thexylmonoalkylboranes to propiolic esters yields β-borylacrylic esters which rearrange on treatment with base to yield a product that can be oxidized and hydrolyzed to the β-hydroxy carboxylic acid (129).

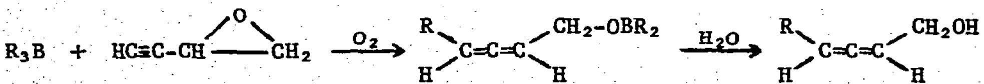


Disiamylborane hydroborates 1-methyl-1-phenylallene to form an allylic borane which transfers the allylic group with rearrangement to the carbonyl carbon of aldehydes or ketones (130).



$$R_2B\text{-}CH_2\text{-}CH{=}\underset{\displaystyle Ph}{\underset{|}{C}}\text{-}CH_3 + R'CHO \longrightarrow CH_2{=}CH\text{-}\overset{\displaystyle R'CH\text{-}O\text{-}BR_2}{\overset{|}{\underset{\displaystyle Ph}{\underset{|}{C}}}}\text{-}CH_3$$

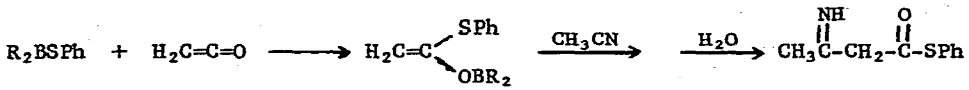
Oxygen-initiated addition of trialkylboranes to 3,4-epoxy-1-butynes leads to allenic alcohols (131).



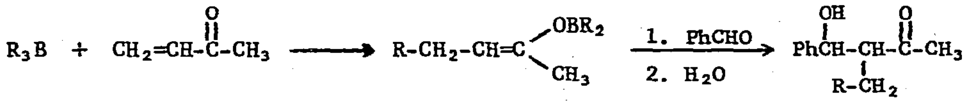
R = cyclopentyl

Tricycloalkylboranes have been added to crotonaldehyde in the presence of pyridine to yield 3-cyclohexylalkylbutanals (132).

Vinyloxyboranes, also known as enol borinates, can be prepared by several routes and are useful synthetic intermediates. For example, they condense with carbonyl compounds or nitriles (133).

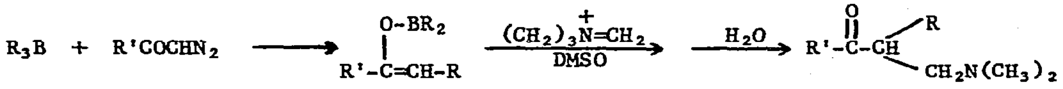


$$R_2BSPh + H_2C{=}C{=}O \longrightarrow H_2C{=}C\begin{matrix}SPh\\OBR_2\end{matrix} \xrightarrow{CH_3CN} \xrightarrow{H_2O} CH_3\overset{NH}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-SPh$$



$$R_3B + CH_2{=}CH-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow R-CH_2-CH{=}C\begin{matrix}OBR_2\\CH_3\end{matrix} \xrightarrow[2.\ H_2O]{1.\ PhCHO} Ph\overset{OH}{\overset{|}{C}}H-\underset{R-CH_2}{\underset{|}{C}H}-\overset{O}{\overset{\|}{C}}-CH_3$$

Enol borinates prepared from trialkylboranes and diazo ketones undergo Mannich condensations with $(CH_3)_2\overset{+}{N}{=}CH_2\ I^-$ (134).



$$R_3B + R'COCHN_2 \longrightarrow \begin{matrix}O-BR_2\\|\\R'-C{=}CH-R\end{matrix} \xrightarrow[DMSO]{(CH_2)_3\overset{+}{N}{=}CH_2} \xrightarrow{H_2O} R'-\overset{O}{\overset{\|}{C}}-CH\begin{matrix}R\\CH_2N(CH_3)_2\end{matrix}$$

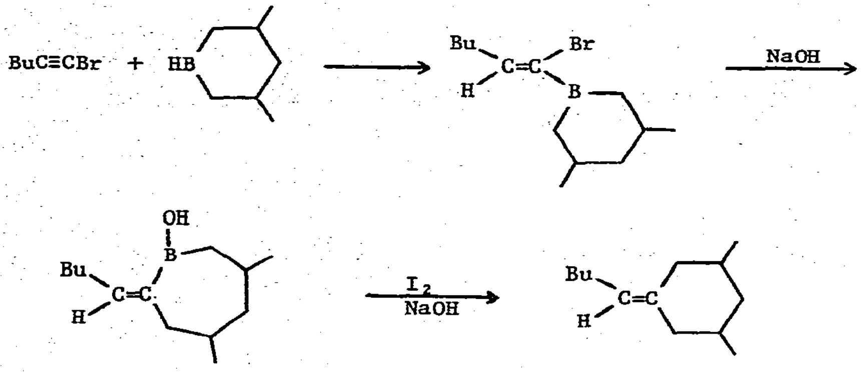
Brown and Yamamoto have reported that N-bromosuccinimide is better than bromine for the α-bromination and rearrangement of trialkylboranes and dialkylborinic acids (135). For example, Et_3B was converted to $Et_2C(OH)Me$ in up to 98% yield.

Electrolysis of R_3B in methanolic potassium hydroxide has yielded R-R, where R is n-octyl or other alkyl (136).

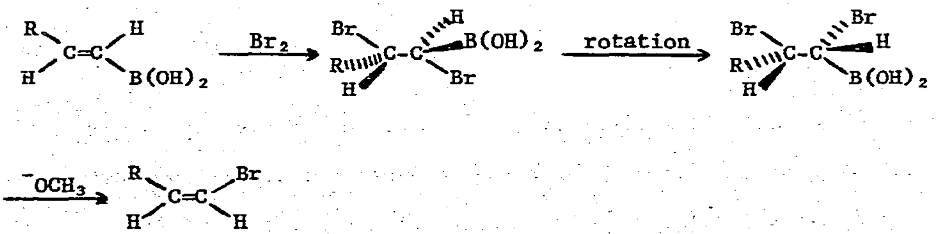
Dialkylacetylenes are obtained when trialkylborane--lithium acetylide adducts are treated with iodine (137).

$$R_3\bar{B}\text{-}C{\equiv}C\text{-}R' + I_2 \xrightarrow{-78^\circ} R\text{-}C{\equiv}C\text{-}R' + R_2BI + I^-$$

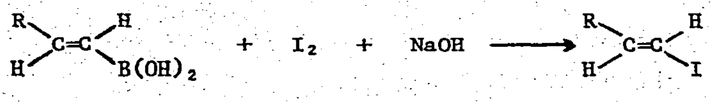
Hydroboration of a bromoacetylene with a boracyclene followed by rearrangement with sodium hydroxide and iodine leads to alkylidenecycloalkanes (138).



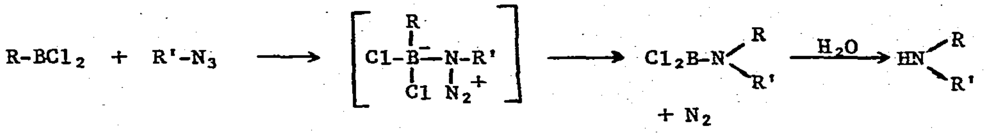
2. Carbon-heteroatom bond formation. Bromination of trans alkeneboronic acids leads to cis-1-bromoalkenes, presumably by an addition-elimination mechanism (139).



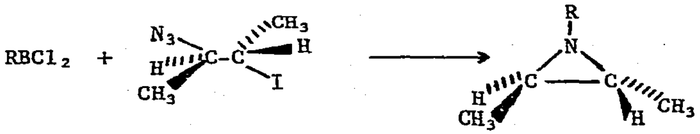
Iodine and sodium hydroxide convert trans alkenylboronic acids to trans-iodoalkenes (140). The boronic acids are readily available from hydroboration of alkynes with catecholborane.



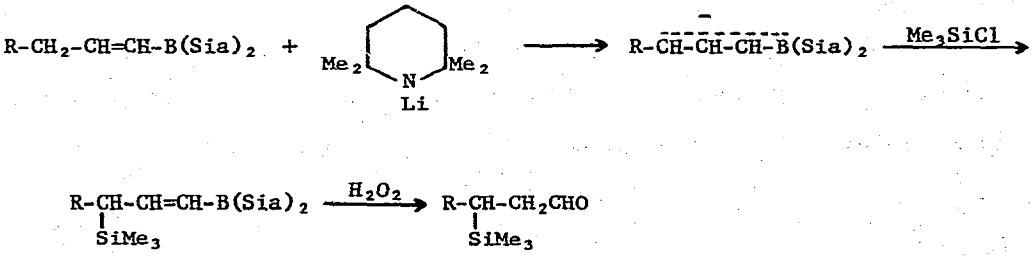
Alkylboron dichlorides react with organic azides to form secondary amines (141).



Alkyldichloroboranes react stereospecifically with 2-iodoalkyl azides to form aziridines (142).

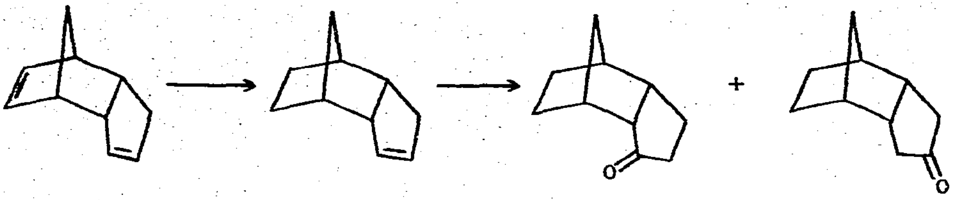


Alkenylboranes formed from acetylenes and disiamylborane lose an allylic proton on treatment with lithium 2,2,6,6-tetramethylpiperidide. The resulting anions have been silylated with trimethylchlorosilane (143).



Dihydroboration of terminal alkynes followed by treatment with methanol, mercuric chloride, and then sodium hydroxide leads to good yields of the alkane-1,1-dimercuric chlorides, RCH$_2$CH(HgCl)$_2$ (144).

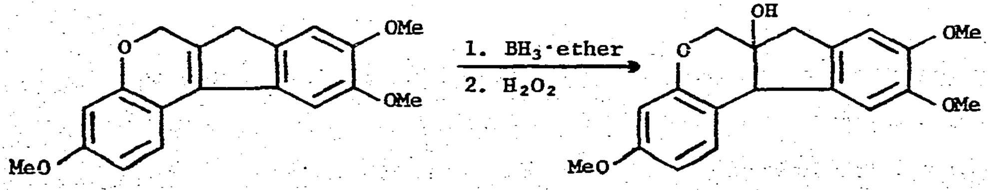
3. Hydroboration-oxidation. Selective hydrogenation of dicyclopentadiene over nickel boride followed by hydroboration and chromic acid oxidation provides a convenient route to endo-5,6-trimethylenenorbornan-8- and -9-one (145).



A detailed procedure for the hydroboration-oxidation of α-pinene has been published in Organic Syntheses (146). Diisopinocampheylborane has been used for the optical resolution of 2-phenyl-1-isobutenylidenecyclopropane (147). Hydroboration of diphenylmethylenecyclopropane leads to the substituted cyclopropanol, but with benzylidenecyclopropane the boron attacks the carbon next to the benzene ring, in accord with the usual rules of steric control of hydroboration (148).

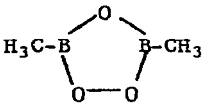
The reaction of trioctylborane with a suitably substituted cyclopentenone has been used in a synthetic approach to the prostaglandin skeleton (149).

A study of the hydroboration of 3-flavenes and the effects of electron-releasing substituents on the reaction has been reported (150). O-Trimethylbrazilin has been prepared by a hydroboration route (151).



Hydroboration of a substituted benzopyranone has been studied as a model system for the synthesis of brazilin and hematoxylin (152). Hydroboration of chromenes, flavenes, and related compounds to produce hydroxy derivatives has been reported (153). The hydroboration of 4-hydroxy-3-methylcoumarin has been reported (154). The hydroboration of cis,cis-1,3-cyclodecadiene and cis,trans-1,5-cyclodecadiene followed by oxidation to cyclodecanediols, cyclodecanone, and cyclodecanol has been studied (155). The hydroboration of trans-2-benzylidenecyclohexanone and related compounds and the stereochemistry leading to 1,3-diols has been investigated (156). Hydroboration of ethynyl derivatives of sugars has been used for synthetic purposes (157). A Japanese patent has been issued on the preparation of a fragrant alcohol by way of hydroboration of isoprene dimer (158).

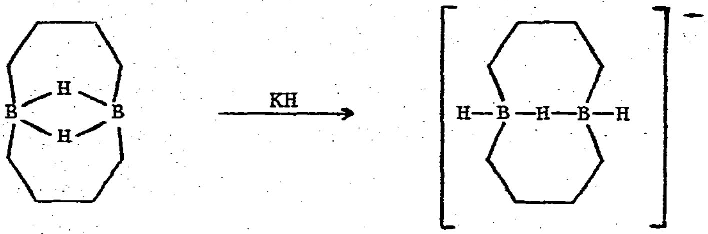
Reaction of $RBCl_2$ in ether with oxygen leads to rapid formation of the peroxy compound $R\text{-}O\text{-}O\text{-}BCl_2$, presumably as the etherate, which can be hydrolyzed to form R-O-OH in high yields (159). Autoxidation of 1,1-dimethyldiborane under special controlled conditions has led to a cyclic peroxy derivative, $Me_2B_2O_3$. The mechanism has been studied and found to involve $Me_2B\text{-}O\text{-}OH$ as an intermediate (160).



Evidence has been obtained for the formation of EtO• and Et• radicals in the autoxidation of Et_3B (161).

4. Borohydride anions. Potassium hydride adds to a variety of hindered boranes to form $R_3BH^-K^+$, useful as stereoselective reducing agents (162). Lithium triethylborohydride, $LiHBEt_3$, is an exceptionally

good nucleophile and is better than $LiAlH_4$ for carrying out the conversion of RBr to RH (163). The butadiene hydroboration product has been converted to a singly bridged anionic species (164).



The use of boron compounds as selective reagents for organic synthesis has been reviewed (165). Hydroboration and organoborane chemistry have been reviewed (166). A book on organoboranes in organic synthesis has appeared (167).

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