The Non-Icosahedral Carboranes: Synthesis and Reactions

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In 1933 Stock set down in his monumental book[1] his collected research which contained the beginnings of polyhedral borane chemistry and a large proportion of the boron hydrides known today. In the 40 years which have elapsed since that time, polyhedral borane chemistry has truly emerged, and the chemistry of these borane derivatives has expanded to include three families of isoelectronic polyhedral borane species: anions of the general formula $B_nH_n^{2-}$, n = 6–12;[2] the one-carbon carborane anions $B_nCH_{n+1}^-$, n = 5, 9–11;[3-5] and the neutral two-carbon carboranes of the general formula $B_nC_2H_{n+2}$, n = 3–10.[6] There now also exists a large group of polyhedral boranes which contain heteroatoms other than carbon. These include the metallocarboranes,[6-9] which alone form an immense vista of new chemistry.

In this Account we discuss the non-icosahedral $B_nC_2H_{n+2}$ carboranes where n = 3–9, with especial emphasis on the interesting methods by which they were obtained and some of the unique reactions which they were found to undergo.

Nomenclature

Discrepancies in the numbering and nomenclature systems used in the literature for carborane and related species abound. Several attempts[10] have been made to standardize these systems, but the older nomenclature still persists. The nomenclature used in this Account conforms to that encountered in the bulk of the current literature dealing with carboranes;[2] consequently, in some instances, the numbering system used here is not in agreement with that in cited references.

Large Carboranes

2,3-Dicarba-*closo*-undecaborane(11), 2,3-$B_9C_2H_{11}$. The well-known icosahedral carboranes, 1,2- and 1,7-$B_{10}C_2H_{12}$,[6] react quite easily with basic reagents such as ethanolic ethoxide ion to produce the (3)-1,2-$B_9C_2H_{12}^-$ and (3)-1,7-$B_9C_2H_{12}^-$ ions, respectively.[11,12] The protonation of the (3)-1,2-$B_9C_2H_{12}^-$ ion produced a water-soluble acid which was characterized as 1,2-$B_9C_2H_{13}$. Similar treatment of (3)-1,7-$B_9C_2H_{12}^-$ produced an analogous 1,7-$B_9C_2H_{13}$ which was not sufficiently stable to allow its characterization.[11] Pyrolysis, in solution, of the 1,2- and 1,7-$B_9C_2H_{13}$ species and their C-substituted derivatives

$$B_9C_2H_{13} \longrightarrow 2,3\text{-}B_9C_2H_{11} + H_2$$

proceeded to yield hydrogen and 2,3-$B_9H_2H_{11}$ or the corresponding C-substituted derivatives.[13] These reactions are summarized in Figure 1.

The isoelectronic eleven-particle systems $B_{11}H_{11}^{2-}$,[14] $B_{10}CH_{11}^-$,[4] and the 2,3-$B_9C_2H_{11}$ carborane present a unique structural problem since the nuclear magnetic resonance spectra of both of the ionic species indicate much higher symmetry[4,15,16] than can be accommodated by the C_{2v} geometry proposed.[2,4] It has recently been proposed that rapid "rotation of belts" of atoms accounts for this apparent symmetry.[15] Fortunately, in the case of 2,3-$B_9C_2H_{11}$ carborane and its derivatives, the nuclear magnetic resonance spectrum[13] and X-ray diffraction[17] data confirm the geometry shown in Figure 2. This structure contains a unique seven-coordinate apex position unprecedented in carborane chemistry.

Few reactions of 2,3-$B_9C_2H_{11}$ have been reported. However, one general type of reaction is known in which the carborane forms Lewis acid–base adducts with a variety of electron donors ranging from ethyl isocyanide and hydroxide ion[11] to the carbanion produced by removal of a proton from 1,2-$B_{10}C_2H_{12}$.[18]

$$B_9C_2H_{12}^- + H_3O^+ \rightleftharpoons B_9C_2H_{13} + H_2O$$

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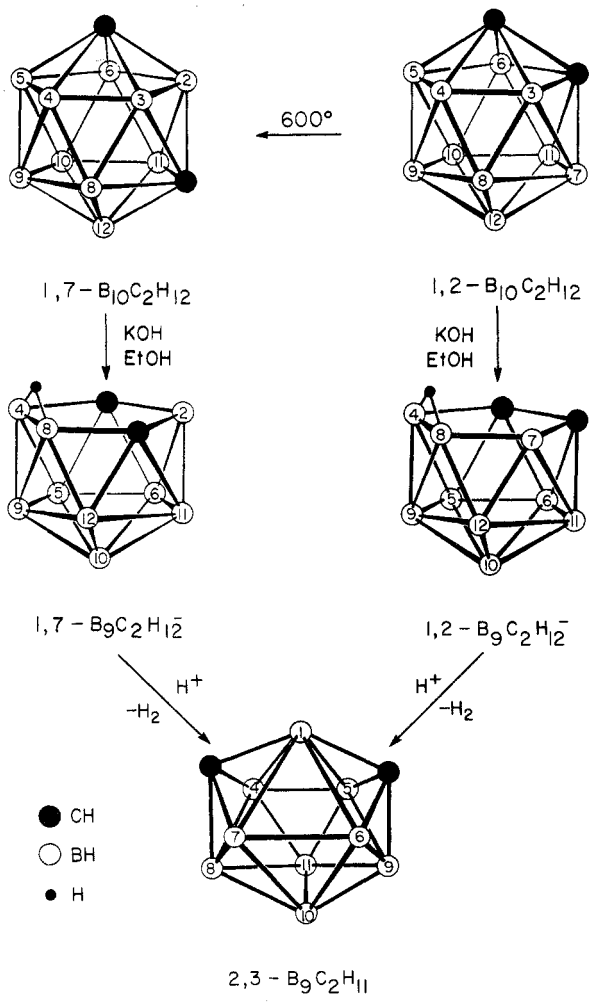

Figure 1. The schematic conversion of 1,2- and 1,7-$B_{10}C_2H_{12}$ carboranes to 2,3-$B_9C_2H_{11}$.

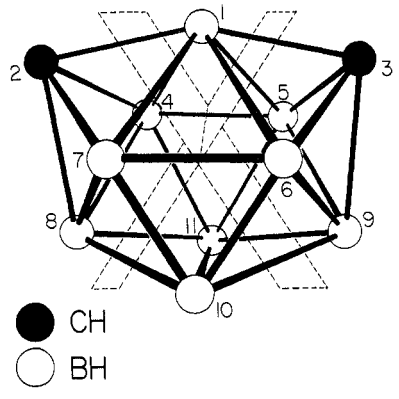

Figure 2. Idealized structure of a "closo" eleven-particle polyhedron exhibiting C_{2v} symmetry. The structure of 2,3-$B_9C_2H_{11}$ exhibits C_{2v} symmetry.[17] In the $B_{11}H_{11}^{2-}$ and $B_{10}CH_{11}^-$ ions of similar geometry, the planes indicated by dotted lines separate belts of four and five atoms which may rapidly rotate relative to one another. This rotation apparently imparts higher symmetry to the ions.[4,14,15]

With simple uncharged ligands such as triethylamine, a zwitterionic adduct is formed. The geometry

$$2,3\text{-}B_9C_2H_{11} + :L \rightleftarrows B_9C_2H_{11}{}^-L^+$$

proposed for these adducts (Figure 3) probably resembles that of the $B_9C_2H_{11}{}^-L^+$ compounds formed by oxidative ligand substitution on the $B_9C_2H_{12}^-$ ions[19] and requires the migration of a terminal B–H

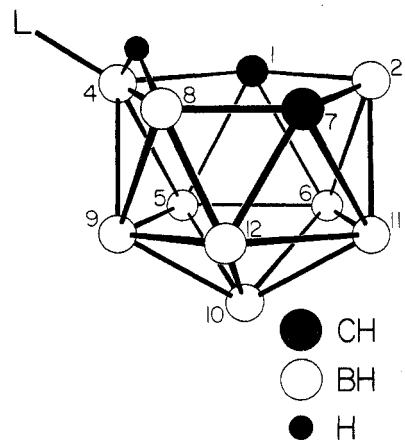

Figure 3. The proposed structure of the adducts formed by the reaction of donor species L to 2,3-$B_9C_2H_{11}$.

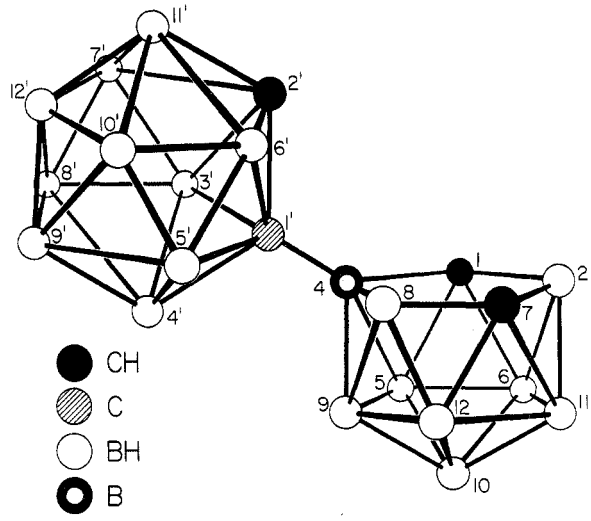

Figure 4. The proposed structure of $\{4\text{-}(1,2\text{-}B_{10}C_2H_{11})[(3)\text{-}1,7\text{-}B_9C_2H_{10}\}^-$ formed by reaction of 1,2-$B_{10}C_2H_{11}{}^-Li^+$ and 2,3-$B_9C_2H_{11}$. The "bridging" hydrogen atom was omitted for clarity.

$$(3)\text{-}1,2\text{-}B_9C_2H_{12}{}^- + 2FeCl_3 + L \longrightarrow$$

$$(3)\text{-}1,2\text{-}B_9C_2H_{11}{}^-L^+ + 2FeCl_2 + HCl + Cl^-$$

hydrogen atom to a B–H–B bridge position during the reaction. Treatment of 2,3-$B_9C_2H_{11}$ or its *C,C'*-dimethyl derivative with various carbanions and carborane anions produced 4-substituted (3)-1,7-$B_9C_2H_{12}^-$ ions[18] (Figure 4). Certain of these ions were converted to 4-substituted 2,3-$B_9C_2H_{11}$ derivatives (Figure 5) by protonation followed by thermal

$$2,3\text{-}B_9C_2H_{11} + Li^+B_{10}C_2H_{11}{}^- \longrightarrow [4\text{-}B_{10}C_2H_{11}\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11}]^-$$

$$[4\text{-}B_{10}C_2H_{11}\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11}]^- \xrightarrow[-H_2]{H^+} 4\text{-}B_{10}C_2H_{11}\text{-}2,3\text{-}B_9C_2H_{10}$$

H_2 evolution. These compounds represent the first examples of molecules which contain carborane polyhedra joined through a B–C σ bond.

The oxidation of 2,3-$B_9C_2H_{11}$ and its carbon-substituted derivatives provided the new *arachno* carborane, 1,3-$B_7C_2H_{13}$, and its corresponding carbon-

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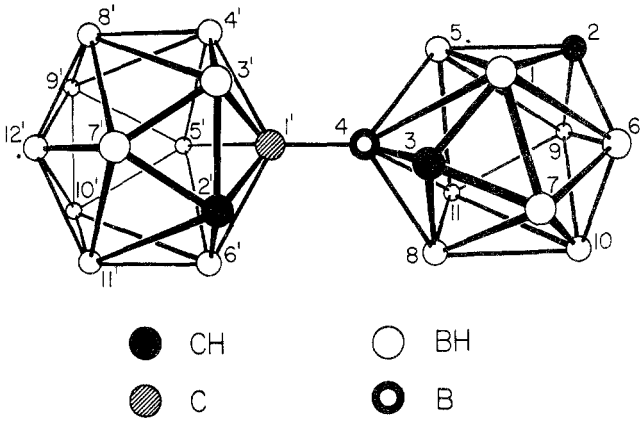

Figure 5. The proposed structure of 4-(1,2-$B_{10}C_2H_{11}$)-2,3-$B_9C_2H_{10}$.

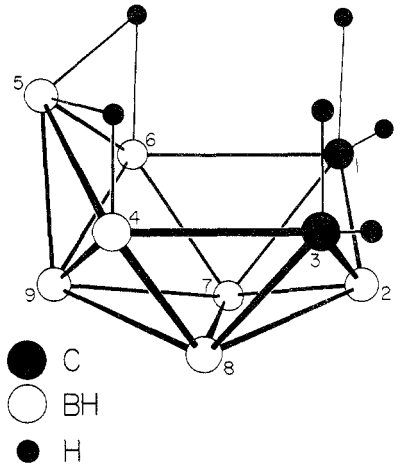

Figure 6. The structure of 1,3-$B_7C_2H_{13}$.

substituted derivatives (Figure 6).[13,20] The structure of these species, shown in Figure 6, was predicted from nuclear magnetic resonance data[20] and confirmed by X-ray diffraction studies.[21] Subsequently, an improved synthesis of 1,3-$B_7C_2H_{13}$ was developed[22] in which the (3)-1,7-$B_9C_2H_{12}^-$ ion was oxidized directly to 1,3-$B_7C_2H_{13}$, thus entirely eliminating the preparation and isolation of the 2,3-$B_9C_2H_{11}$ intermediate.

$$K^+(3)\text{-}1,7\text{-}B_9C_2H_{12}^- + 6H_2O \longrightarrow 1,3\text{-}B_7C_2H_{13} + 2B(OH)_3 + 5H^+ + 6e^-$$

The 1,3-$B_7C_2H_{13}$ carborane is of particular interest because it is the precursor of the $B_nC_2H_{n+2}$ carboranes where n = 6–8.

Preparation of *closo*-Carboranes by the Pyrolysis of 1,3-$B_7C_2H_{13}$. Thermal decomposition of 1,3-$(CH_3)_2$-$B_7C_2H_{11}$ in diphenyl ether was investigated in an attempt to produce the then unknown carborane $(CH_3)_2B_7C_2H_7$. Instead of a single reaction

$$1,3\text{-}(CH_3)_2\text{-}B_7C_2H_{11} \xrightarrow{\Delta} (CH_3)_2\text{-}B_7C_2H_7 + 2H_2$$

product, three new materials were obtained and characterized as the *C,C'*-dimethyl derivatives of 1,6-$B_8C_2H_{10}$, 1,6-$B_7C_2H_9$, and 1,6-$B_6C_2H_8$.[13,23] Subsequently, the unsubstituted, *C*-methyl and *C*-phenyl derivatives of each of the new carboranes were prepared by similar pyrolysis in diphenyl ether of the appropriate $B_7C_2H_{13}$ starting material.[24]

The addition of diborane during these pyrolyses shifted the product distribution toward more of the 1,6-$B_8C_2H_{10}$ component at the expense of 1,6-$B_6C_2H_8$ and 1,6-$B_7C_2H_9$.[13] The slow, low-pressure pyrolysis of 1,3-$B_7C_2H_{13}$ and its *C*-methyl derivatives formed as major products 2,4-$B_5C_2H_7$, 1,6-$B_6C_2H_8$, 1,6-$B_7C_2H_9$, and 1,6-$B_8C_2H_{10}$, and their corresponding *C*-methyl derivatives together with diborane and hydrogen.[25] In another experiment, 1,6-$B_6C_2H_8$ was allowed to stand in the presence of excess diborane for 1 month at ambient temperature. The recovered compounds included the starting material, 1,6-$B_7C_2H_9$, and 1,6-$B_8C_2H_{10}$. These results, plus the fact that the addition of diborane during the pyrolysis of 1,3-$B_7C_2H_{13}$ in diphenyl ether gave enhanced yields of 1,6-$B_8C_2H_{10}$ and very little 1,6-$B_6C_2H_8$, suggested that the thermal decomposition of 1,3-$B_7C_2H_{13}$ yields primarily 1,6-$B_6C_2H_8$, diborane, and hydrogen. This step may be followed by progressive recombination of 1,6-$B_6C_2H_8$ and diborane to yield 1,6-$B_7C_2H_9$, 1,6-$B_8C_2H_{10}$, and hydrogen. The direct reaction of 1,3-$B_7C_2H_{13}$ and diborane to produce 1,6-$B_8C_2H_{10}$ may also occur.[25]

$$1,3\text{-}B_7C_2H_{13} \longrightarrow 0.5B_2H_6 + 1,6\text{-}B_6C_2H_8 + H_2$$

$$1,6\text{-}B_6C_2H_8 + 0.5B_2H_6 \longrightarrow 1,6\text{-}B_7C_2H_9 + H_2$$

$$1,6\text{-}B_7C_2H_9 + 0.5B_2H_6 \longrightarrow 1,6\text{-}B_8C_2H_{10} + H_2$$

$$1,3\text{-}B_7C_2H_{13} + 0.5B_2H_6 \longrightarrow 1,6\text{-}B_8C_2H_{10} + 3H_2$$

Dicarba-*closo*-decaborane(10), $B_8C_2H_{10}$. In addition to the pyrolytic methods in which 1,6-$B_8C_2H_{10}$ was produced in conjunction with the B_7, B_6, and B_5 carboranes, an improved method for its preparation is known. In this synthesis the monoanion, $B_7C_2H_{12}^-$, was treated with specific amounts of

$$1,3\text{-}B_7C_2H_{13} + NaH \longrightarrow NaB_7C_2H_{12} + H_2$$

1,3-$B_7C_2H_{13}$ and diborane to yield 1,6-$B_8C_2H_{10}$.[26] This method not only provides 1,6-$B_8C_2H_{10}$ in high yield, but there are no difficult separation problems in its purification.

Like the other known isoelectronic ten-particle polyhedra, $B_{10}H_{10}^{2-}$ [27,28] and $B_9CH_{10}^-$,[29] 1,6-

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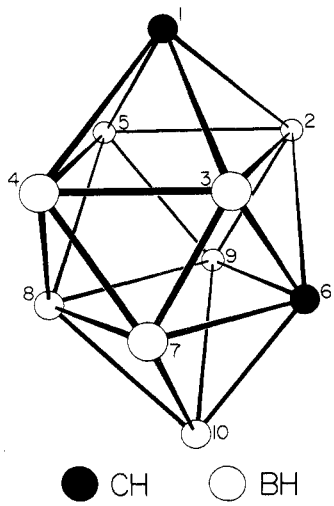

Figure 7. The structure of 1,6-$B_8C_2H_{10}$.

$B_8C_2H_{10}$ has the bicapped Archimedean antiprism structure illustrated in Figure 7. Three carbon atom positional isomers, 1,2-, 1,6-, and 1,10-$B_8C_2H_{10}$, are known. The 1,2-$B_8C_2H_{10}$ isomer[30,31] undergoes facile thermal rearrangement to 1,6-$B_8C_2H_{10}$. The

$$1,2\text{-}B_8C_2H_{10} \xrightarrow{\sim 180^\circ} 1,6\text{-}B_8C_2H_{10} \xrightarrow[Ph_2O]{335^\circ} 1,10\text{-}B_8C_2H_{10}$$

subsequent thermal rearrangement of 1,6-$B_8C_2H_{10}$ to 1,10-$B_8C_2H_{10}$ has been studied in detail.[13,23,32] First-order kinetics were observed during the rearrangement with $\Delta S^* = +4.6$ cal/(mol deg) and $\Delta H^* = +48.8$ kcal/mol.[32]

Three general types of reactions involving the polyhedral structure are known for the $B_8C_2H_{10}$ carboranes. One is the thermal polyhedral rearrangement discussed above. Secondly, hydroboration of 1,6-$B_8C_2H_{10}$ to 1,7-$B_{10}C_2H_{12}$ has been observed.[13] The

$$1,6\text{-}B_8C_2H_{10} + B_2H_6 \longrightarrow 1,7\text{-}B_{10}C_2H_{12} + 2H_2$$

third example of cage chemistry of the $B_8C_2H_{10}$ system is hydrolytic degradation.[13] Hydrolysis of 1,6-

$$1,6\text{-}B_8C_2H_{10} + OH^- + 2H_2O \longrightarrow B_7C_2H_{12}^- + B(OH)_3$$

$B_8C_2H_{10}$ in basic, aqueous ethanol produced the $B_7C_2H_{12}^-$ ion in high yield.[13] In acid medium, 1,6-$B_8C_2H_{10}$ was completely decomposed to yield boric acid. Under similar conditions 1,10-$B_8C_2H_{10}$ was much less reactive, possibly due to the fact that, in the 1,10 isomer, all boron atoms are equivalent; thus no one boron site is more prone to basic attack than any other and the ground-state charge distribution does not favor facile nucleophilic attack.

A rather extensive substitution chemistry of the two exo polyhedral carbon–hydrogen bonds is known for the 1,6- and 1,10-$B_8C_2H_{10}$ carboranes. Treatment of substituted 1,6- and 1,10-$B_8C_2H_{10}$ carboranes with *n*-butyllithium gave mono- and dilithio salts[33]

$$1\text{-}C_6H_5\text{-}1,6\text{-}B_8C_2H_9 + C_4H_9Li \longrightarrow 1\text{-}C_6H_5\text{-}6\text{-}Li\text{-}1,6\text{-}B_8C_2H_8 + C_4H_{10}$$

$$1\text{-R-}1,10\text{-}B_8C_2H_9 + C_4H_9Li \longrightarrow 1\text{-R-}10\text{-}Li\text{-}1,10\text{-}B_8C_2H_8 + C_4H_{10}$$

$$R = CH_3,\ C_6H_5$$

$$1,10\text{-}B_8C_2H_{10} + 2C_4H_9Li \longrightarrow 1,10\text{-}Li_2\text{-}1,10\text{-}B_8C_2H_8 + 2C_4H_{10}$$

which react with a variety of electrophiles. Reaction with methyl iodide produced *C*-methyl derivatives.[33]

$$1\text{-}C_6H_5\text{-}6\text{-}Li\text{-}1,6\text{-}B_8C_2H_8 + CH_3I \longrightarrow 1\text{-}C_6H_5\text{-}6\text{-}CH_3\text{-}1,6\text{-}B_8C_2H_8 + Li^+I^-$$

Carbon dioxide reacted with 1-R-10-Li-1,10-$B_8C_2H_8$ (R = CH_3, C_6H_5) followed by acidification

$$1\text{-R-}10\text{-}Li\text{-}1,10\text{-}B_8C_2H_8 \xrightarrow[2.\ H^+]{1.\ CO_2} 1\text{-R-}10\text{-}CO_2H\text{-}1,10\text{-}B_8C_2H_8$$

$$R = CH_3,\ C_6H_5$$

to produce 10-monocarboxylic acids. Similarly, the 1,10-dilithio derivative reacted with carbon dioxide followed by acidification to yield the 1,10-dicarboxylic acid. The *C*-methyl and *C*-phenyl acids titrated as strong monoprotic acids with apparent pK_a's of 4.2 and 4.1, respectively. The 1,10-dicarboxylic acid titrated as a strong diprotic acid with only one potentiometric inflection with an apparent pK_a of 3.8.[33] Reaction of 1-C_6H_5-10-Li-1,10-$B_8C_2H_8$ with nitrogen dioxide followed by reduction with tin and

$$1,10\text{-}Li_2\text{-}1,10\text{-}B_8C_2H_8 \xrightarrow[2.\ H^+]{1.\ CO_2} 1,10\text{-}(CO_2H)_2\text{-}1,10\text{-}B_8C_2H_8$$

$$1\text{-}C_6H_5\text{-}10\text{-}Li\text{-}1,10\text{-}B_8C_2H_8 \xrightarrow{N_2O_4} [1\text{-}C_6H_5\text{-}10\text{-}NO_2\text{-}1,10\text{-}B_8C_2H_8]$$

$$[1\text{-}C_6H_5\text{-}10\text{-}NO_2\text{-}1,10\text{-}B_8C_2H_8] \xrightarrow{Sn\text{-}HCl} 1\text{-}C_6H_5\text{-}10\text{-}NH_2\text{-}1,10\text{-}NH_2\text{-}1,10\text{-}B_8C_2H_8$$

hydrochloric acid produced the 1-phenyl-10-amino derivative of 1,10-$B_8C_2H_{10}$.[33] The monolithio derivative of 1-CH_3-1,10-$B_8C_2H_9$ reacted with iodine to

$$1\text{-}CH_3\text{-}10\text{-}Li\text{-}1,10\text{-}B_8C_2H_8 + I_2 \longrightarrow 1\text{-}CH_3\text{-}10\text{-}I\text{-}1,10\text{-}B_8C_2H_8 + LiI$$

give the 1-methyl-10-iodo derivative of 1,10-$B_8C_2H_{10}$.[33] The 1,10-dimethyl-*B*-octachloro derivative of 1,10-$B_8C_2H_{10}$ was prepared by passage of chlorine gas through a solution of 1,10-$(CH_3)_2$-1,10-

$$1,10\text{-}(CH_3)_2\text{-}1,10\text{-}B_8C_2H_8 + 8Cl_2 \xrightarrow[h\nu]{CCl_4} 1,10\text{-}(CH_3)_2\text{-}1,10\text{-}B_8C_2Cl_8H_2 + 8HCl$$

$B_8C_2H_8$.[33] Finally, 1,10-Li_2-1,10-$B_8C_2H_8$ reacted with (π-C_5H_5)Fe(CO)$_2$I to produce the novel σ-

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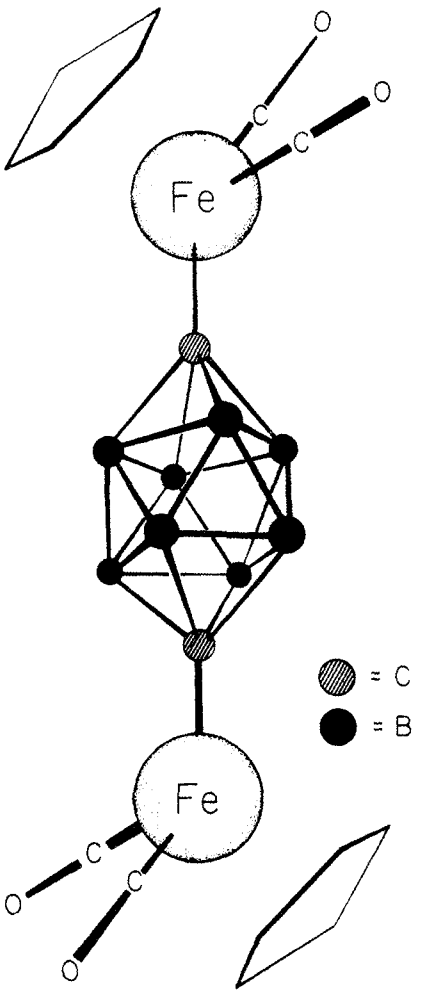

Figure 8. The proposed structure of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\text{-}1,10\text{-}(\sigma\text{-}B_8C_2H_8)$.

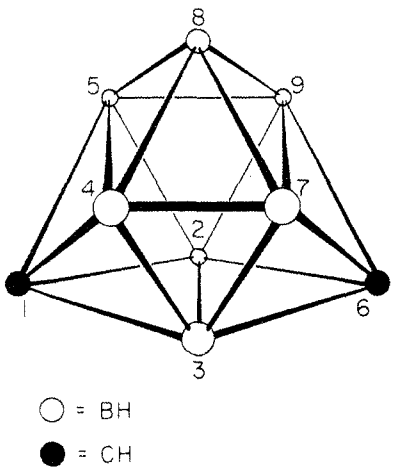

Figure 9. The structure of $1,6\text{-}B_7C_2H_9$.

bonded complex $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\text{-}1,10\text{-}(\sigma\text{-}B_8C_2H_8)$[34] (Figure 8).

$$1,10\text{-}Li_2\text{-}1,10\text{-}B_8C_2H_8 + (\pi\text{-}C_5H_5)Fe(CO)_2I \longrightarrow [(\pi\text{-}C_5H_5)Fe(CO)_2]_2\text{-}1,10\text{-}(\sigma\text{-}B_8C_2H_8)$$

1,6-Dicarba-*closo*-nonaborane(9), $1,6\text{-}B_7C_2H_9$. The known isoelectronic nine-particle polyhedra $B_9H_9^{2-}$[14] and $B_7C_2H_9$[35] possess a tricapped trigonal prismatic geometry (Figure 9). In addition to the pyrolytic methods described above for the preparation of $1,6\text{-}B_7C_2H_9$, there is a newer method[24] which gives a rather pure product, thus eliminating the separation problems which were previously encountered. The pyrolysis of the $B_7C_2H_{12}^-$ ion[13] in diphenyl ether produced $1,6\text{-}B_7C_2H_9$ (38%) with no hydrogen evolution.[24]

$$1,3\text{-}B_7C_2H_{12}^- \xrightarrow{\Delta} 1,6\text{-}B_7C_2H_9$$

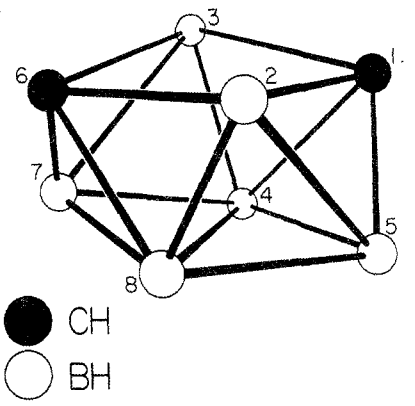

Figure 10. The structure of $1,6\text{-}B_6C_2H_8$.

Calculations show that in the ground state[35] the boron atom in the 8 (apex) position of $1,6\text{-}B_7C_2H_9$ is the most negative, and, by analogy to other polyhedral borane systems, this suggests that electrophilic substitution reactions may most readily occur at that position. This assumption was confirmed when $1,6\text{-}B_7C_2H_9$ and its *C*-methyl and *C,C'*-dimethyl derivatives were shown to undergo such reactions[36] when treated with methyl chloride, ethylene, and bromine in the presence of a Lewis acid. In all cases,

$$1,6\text{-}B_7C_2H_9 + CH_3Cl \xrightarrow{AlCl_3} 8\text{-}CH_3\text{-}1,6\text{-}B_7C_2H_8 + HCl$$

$$1,6\text{-}B_7C_2H_9 + C_2H_4 \xrightarrow{AlCl_3} 8\text{-}C_2H_5\text{-}1,6\text{-}B_7C_2H_8$$

$$1,6\text{-}B_7C_2H_9 + Br_2 \xrightarrow{AlBr_3} 8\text{-}Br\text{-}1,6\text{-}B_7C_2H_8 + HBr$$

the substituent was attached to the boron atom present in the 8 position. When $1,6\text{-}B_7C_2H_9$ was allowed to react with excess bromine, a tetrabromo derivative was produced.[36]

$$1,6\text{-}B_7C_2H_9 + \text{excess } Br_2 \longrightarrow 4,5,7,8\text{-}Br_4\text{-}1,6\text{-}B_7C_2H_5 + 4HBr$$

1,6-Dicarba-*closo*-octaborane(8), $1,6\text{-}B_6C_2H_8$. The isoelectronic eight-particle systems, $B_8H_8^{2-}$[37] and $1,6\text{-}B_6C_2H_8$,[38] have slightly distorted dodecahedral geometry, as depicted in Figure 10.

The $1,6\text{-}B_6C_2H_8$ carborane and its *C*-methyl and *C,C'*-dimethyl derivatives are obtained in highest

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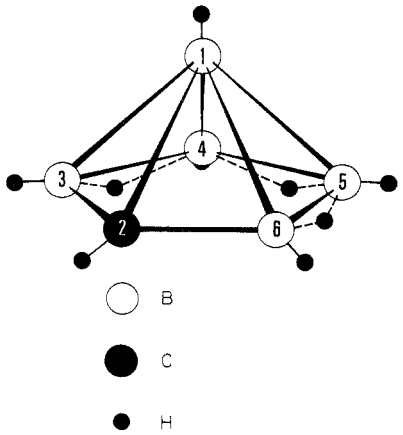

Figure 11. The structure of 2-B_5CH_9.

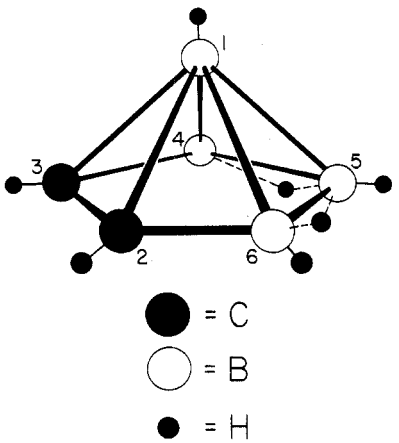

Figure 12. The structure of 2,3-$B_4C_2H_8$.

yield by the pyrolytic method described above,[25] although other syntheses have been reported.[13,23] The first reported preparation of 1,6(CH_3)$_2$-1,6-$B_6C_2H_6$, however, involved the ultraviolet irradiation of mixtures of hexaborane and dimethylacetylene.[39]

$$B_6H_{10} + CH_3C{\equiv}CCH_3 \xrightarrow{h\nu} 1,6\text{-}(CH_3)_2\text{-}1,6\text{-}B_6C_2H_6$$

The chemistry of 1,6-$B_6C_2H_8$ and its *C*-alkyl derivatives is largely unexplored. One reaction that has been studied is the treatment of 1,6-$B_6C_2H_8$ with borohydride ion followed by treatment with hydrogen chloride, which produced 2-carba-*nido*-hexaborane, B_5CH_9[40] (Figure 11), and several of its methyl derivatives.[41] A similar reaction using 1-CH_3-1,6-$B_6C_2H_7$ as the starting material produced analogous products in which the polyhedral carbon atom in the B_5CH_9 was methylated while the unsubstituted carbon atom (in the 6 position) of the starting material was removed from the polyhedron to become a methyl substituent on boron. When 1,6-(CH_3)$_2$-1,6-$B_6C_2H_6$ was used as the starting material, all of the substituted B_5CH_9 products contained a methyl substituent on the cage carbon atom. In addition, *B*-ethyl derivatives were isolated; this indicated that a methylated cage carbon atom in the starting material had been removed and converted to an exo polyhedral ethyl substituent. Grimes recently reported[42] the thermal extrusion of a polyhedral carbon atom.

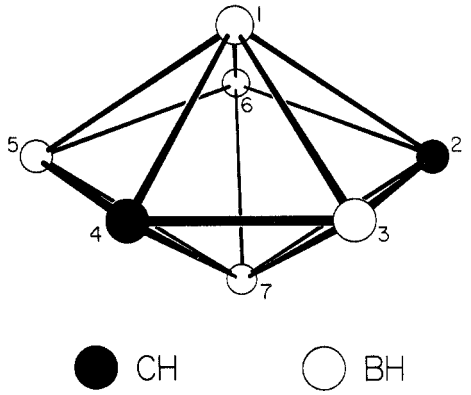

Figure 13. The structure of 2,4-$B_5C_2H_7$.

Small Carboranes

Preparation and Pyrolysis of 2,3-$B_4C_2H_8$. Synthesis of Small *closo*-Carboranes. As observed in the case of 1,3-$B_7C_2H_{13}$, which is the precursor of the $B_nC_2H_{n+2}$ carboranes where n = 6–8, 2,3-$B_4C_2H_8$,[43] depicted in Figure 12, is the precursor to the carboranes where n = 3–5. One of the methods used to prepare *C*-alkyl derivatives of 2,3-$B_4C_2H_8$ is the base-catalyzed reaction of pentaborane(9) with the appropriate acetylene.[44] The synthesis of the

$$B_5H_9 + RC{\equiv}CR' \xrightarrow{\text{base}} 2,3\text{-}RR'B_4C_2H_6 + \text{base}{\cdot}BH_3$$

R = H, R′ = CH_3; R = R′ = CH_3; R = H, R′ = *n*-C_3H_7

parent compound, 2,3-$B_4C_2H_8$, was achieved by the reaction of pentaborane(9) and acetylene in the gas

$$B_5H_9 + HC{\equiv}CH \xrightarrow{\Delta} 2,3\text{-}B_4C_2H_8 + (BH_3)_x$$

phase.[45] The pyrolysis of 2,3-$B_4C_2H_8$ and its *C*-alkyl derivatives produced mixtures which contained 2,4-$B_5C_2H_7$, 1,2- and 1,6-$B_4C_2H_6$, and 1,5-$B_3C_2H_5$,[45-47] and some of their *C*-alkyl derivatives. Photolysis of 2,3-$B_4C_2H_8$ at ambient temperature has been shown to produce mixtures of 1,5-$B_3C_2H_5$, 1,2-$B_4C_2H_6$, and 1,6-$B_4C_2H_6$.[48]

Dicarba-*closo*-heptaborane(7), $B_5C_2H_7$. The isoelectronic $B_7H_7^{2-}$ ion[37] and the 2,4-$B_5C_2H_7$ carborane[49] possess pentagonal-bipyramidal geometry (Figure 13). The 2,3- and 2,4-$B_5C_2H_7$ carbon atom positional isomers are known.

The 2,4-$B_5C_2H_7$ and its *C*-methyl derivatives were among the products obtained from the pyrolysis of

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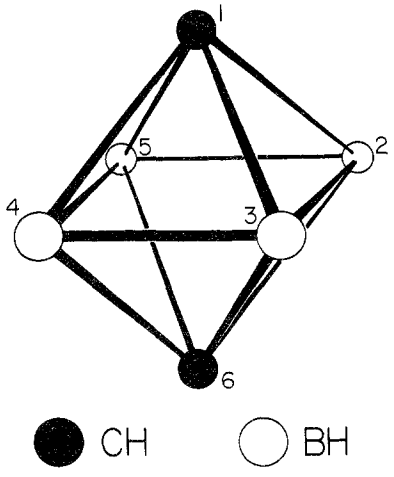

Figure 14. The structure of 1,6-$B_4C_2H_6$.

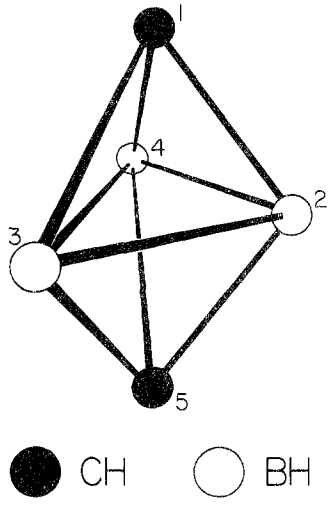

Figure 15. The structure of 1,5-$B_3C_2H_5$.

1,3-$B_7C_2H_{13}$ and its *C*-methyl derivatives. However, the most efficient method for the synthesis of the $B_5C_2H_7$ system is the pyrolysis of 2,3-$B_4C_2H_8$, discussed above. The 2,3-$B_5C_2H_7$ carborane and its *C,C'*-dimethyl derivative were isolated as minor components from the reaction of octaborane(12) with the appropriate acetylene.[50,51] Even though the chemistry of the 2,3-$B_5C_2H_7$ system has not been extensively explored, several derivatives of the 2,4-$B_5C_2H_7$ system are known.[6] Electrophilic substitution occurs preferentially at one of the equivalent 5 or 6 positions (Figure 13)[52,53] which have been assigned, on the basis of molecular orbital calculations, the highest ground-state electron density.[54] Photolytically induced chlorination in the absence of a Lewis acid catalyst occurred at the 1 and 3 positions.[53] Deuterium exchange with B_2D_6 at ambient temperature produced 3,5,6-D_3-2,4-$B_5C_2H_4$. At elevated temperature, 1,3,5,6,7-D_5-$B_5C_2H_2$ was formed.[55] Lithiation of 2,4-$B_5C_2H_7$ was much slower than was observed for the $B_8C_2H_{10}$ system,[34,52] but *C*-methyl, *C*-trimethylsilyl, and *C*-bromo derivatives have been prepared from the lithio salts of 2,4-$B_5C_2H_7$.[52]

Dicarba-*closo*-hexaborane(6), $B_4C_2H_6$. The 1,2- and 1,6-$B_4C_2H_6$ carboranes[56] and the $B_6H_6^{2-}$ ion[57] possess octahedral geometry, as shown in Figure 14. The 1,2 isomer was shown to rearrange to the 1,6 isomer at 250°.[45]

Both of the isomers of $B_4C_2H_6$ are isolated from the pyrolytic and photolytic reactions of 2,3-$B_4C_2H_8$ as discussed above. They were first prepared by silent electric discharge through mixtures of pentaborane(9) and acetylene.[56]

$$B_5H_9 + C_2H_2 \longrightarrow B_4C_2H_6$$

Possibly due to its thermal instability, no chemistry has been reported for the 1,2-$B_4C_2H_6$ carborane. 2-Chloro[58] and 2-bromo[59] derivatives of 1,6-$B_4C_2H_6$ were prepared by direct halogenation of the parent compound. The 2-chloro derivative was also prepared by the photolytic decomposition of 4-Cl-2,3-$B_4C_2H_7$.[58a,60] Deuterium exchange with B_2D_6 produced the 2,3,4,5-D_4-1,6-$B_4C_2H_2$ species.[56]

Dicarba-*closo*-pentaborane(5), $B_3C_2H_5$. Trigonal-bipyramidal geometry is assumed by the $B_3C_2H_5$ carboranes, as shown in Figure 15.[2,6] The 1,5-$B_3C_2H_5$ isomer can be isolated from pyrolysis and photolysis reactions of 2,3-$B_4C_2H_8$.[45-47] This isomer was first prepared by passing a mixture of pentaborane(9) and acetylene through a silent electric discharge.[56] The parent 1,2-$B_3C_2H_5$ isomer has not been reported, although several methyl derivatives are known.[6] With the exception of deuterium exchange in which 2,3,4-D_3-1,5-$B_3C_2H_2$ was formed by equilibration with B_2D_6,[56] the chemistry of the $B_3C_2H_5$ system is limited to a thermal coupling reaction in which two cages are bound together through a B–B bond,[61] and a *B*-propenyl derivative.[61]

Polyhedral Expansion of the $B_nC_2H_{n+2}$ Carboranes. One reaction, which appears to have general applicability to the $B_nC_2H_{n+2}$ carboranes, has been termed "polyhedral expansion."[62] This method allows the incorporation of new polyhedral vertices by the sequential addition of transition metal atoms to carborane and metallocarborane polyhedra.[62-64] The essence of the method rests upon the fact that carboranes and metallocarboranes have accessible unfilled molecular orbitals which will accept one or more electrons from an alkali metal. The anions thus produced can then complex transition metal ions to form closo polyhedral transition metal complexes which contain one or more additional vertices than the starting material.[62-69] At present the polyhedral

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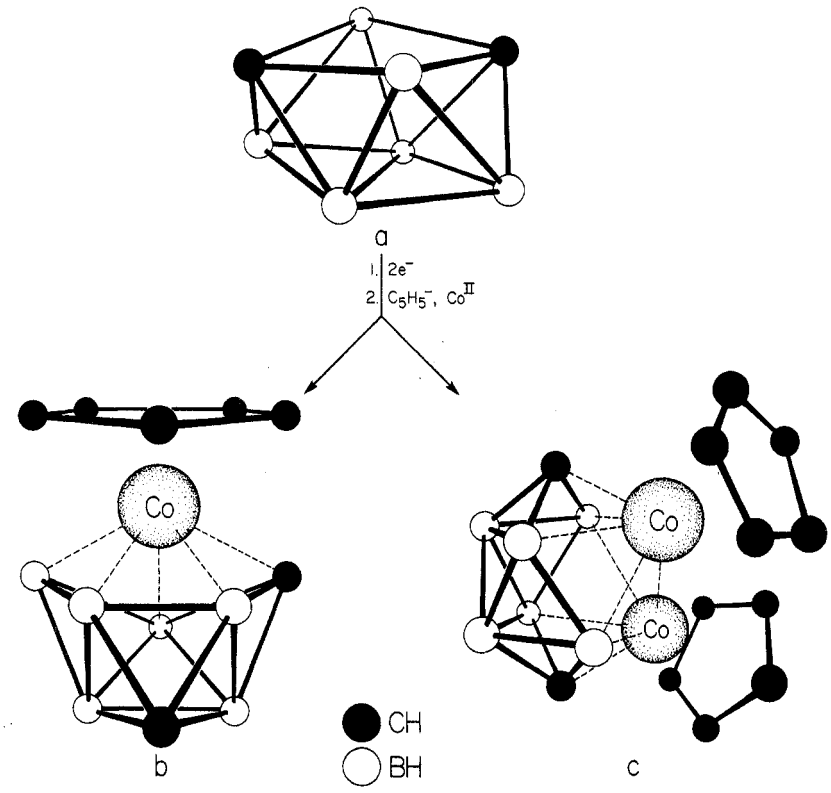

Figure 16. A schematic representation of the polyhedral expansion reaction applied to a $B_nC_2H_{n+2}$ carborane. Treatment of 1,6-$B_6C_2H_8$ (a) with sodium followed by NaC_5H_5 and $CoCl_2$ produced the metallocarboranes $(C_5H_5)Co(B_6C_2H_8)$ (b) and $(C_5H_5Co)_2B_6C_2H_8$ (c).

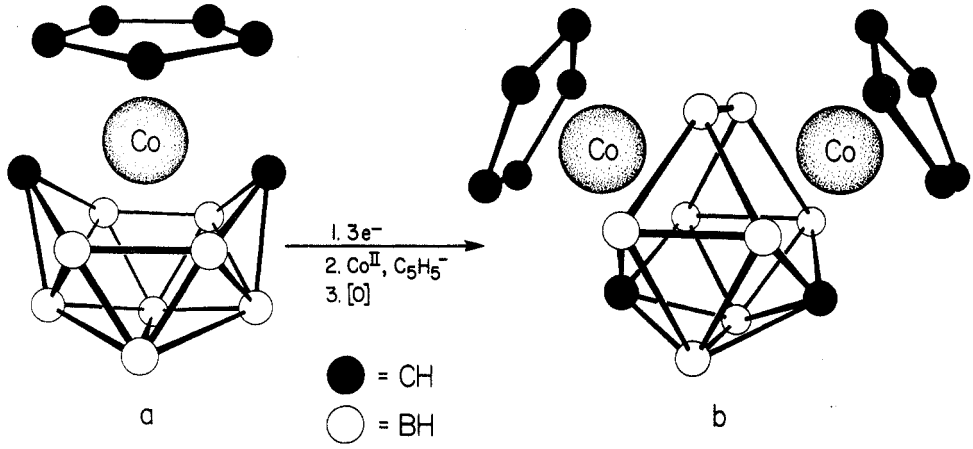

Figure 17. A schematic representation of the polyhedral expansion reaction as applied to a metallocarborane. The reaction of $(B_8C_2H_{10})(C_5H_5)Co^{III}$ (a) with sodium followed by NaC_5H_5 and $CoCl_2$ produced $(C_5H_5Co)_2B_8C_2H_{10}$ (b).

$$B_nC_2H_{n+2} + 2e^- \longrightarrow B_nC_2H_{n+2}{}^{2-}$$

$$B_nC_2H_{n+2}{}^{2-} + M^{x+} \longrightarrow [(B_nC_2H_{n+2})_2M]^{x-4}$$

expansion reaction has been demonstrated on the $B_nC_2H_{n+2}$ carboranes where n = 6–10,[62-68] Figure 16, and on the $(B_8C_2H_{10})(C_5H_5)Co^{III}$ metallocarborane,[69] Figure 17. The limit to which polyhedral expansion reactions may be utilized in sequence is unknown, although 13-vertex metallocarboranes have been prepared.[67,68] The 13-vertex and larger polyhedra are unprecedented in carborane chemistry. This method potentially allows different transition metal atoms to be included in a stepwise manner in the same molecule such that mixed metal complexes could be prepared. The implications of this synthesis route are varied and need not be strictly limited to carboranes and metallocarboranes. Polyhedral transition metal clusters might be found to undergo similar reduction and expansion reactions.

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The authors are indebted to their coworkers whose names appear in the literature cited. This research was supported in part by the National Science Foundation, the U. S. Army Research Office—Durham, and the Office of Naval Research.