

The Non-Icosahedral Carboranes: Synthesis and Reactions

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In 1933 Stock set down in his monumental book¹ 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.

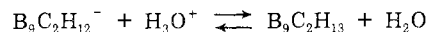
In this Account we discuss the non-icosahedral $B_nC_2H_{n+2}$ carboranes where $n = 3-9$, with especial emphasis on the interesting methods by which they were obtained and some of the unique reactions which they were found to undergo.

Nomenclature

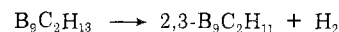
Discrepancies in the numbering and nomenclature systems used in the literature for carborane and related species abound. Several attempts¹⁰ have been made to standardize these systems, but the older nomenclature still persists. The nomenclature used in this Account conforms to that encountered in the 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 charac-



terized 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



proceeded to yield hydrogen and 2,3- $B_9C_2H_{11}$ 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 spectrum¹³ and X-ray diffraction¹⁷ 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 ion¹¹ to the carbanion produced by removal of a proton from 1,2- $B_{10}C_2H_{12}$.¹⁸

(1) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(2) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968.

(3) W. H. Knoth, *J. Amer. Chem. Soc.*, **89**, 1274 (1967); *Inorg. Chem.*, **10**, 598 (1971).

(4) D. E. Hyatt, F. R. Scholer, L. J. Todd, and J. L. Warner, *Inorg. Chem.*, **6**, 2229 (1967).

(5) S. R. Prince and R. Schaeffer, *Chem. Commun.*, 451 (1968).

(6) R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970.

(7) "The Chemistry of Hydrogen and Its Compounds," E. L. Muetterties, Ed., Vol. II, Marcel Dekker, Inc., New York, N. Y., in press.

(8) M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968).

(9) L. J. Todd, *Advan. Organometal. Chem.*, **8**, 87 (1970).

(10) R. Adams, *Inorg. Chem.*, **2**, 1087 (1963); **7**, 1945 (1968).

(11) R. A. Wiesboeck and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **86**, 1642 (1964); M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *ibid.*, **90**, 862 (1968).

(12) The position of the vacant icosahedral vertex is denoted by a prefix numeral in parentheses.

(13) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 869 (1968).

(14) F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, **5**, 1955 (1966).

(15) R. J. Wiersema and M. F. Hawthorne, *Inorg. Chem.*, **12**, 785 (1973).

(16) R. L. Middaugh and R. J. Wiersema, *Inorg. Chem.*, **10**, 423 (1971).

(17) C. D. Tsai and W. E. Streib, *J. Amer. Chem. Soc.*, **88**, 4513 (1966).

(18) D. A. Owen and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 6002 (1969).

M. Frederick Hawthorne obtained his Ph.D. from UCLA in 1953. After a year of postdoctoral research at Iowa State College under George Hammond, he joined the staff of the Rohm and Haas Co., Redstone Arsenal Research Division, and headed a group concerned with boron hydride and carborane chemistry. He became Professor of Chemistry at the University of California, Riverside, in 1962, and in 1969 he shifted to the Los Angeles campus. He is Editor of *Inorganic Chemistry*. His principal interests are exploratory syntheses and reaction mechanism studies of inorganic and metallorganic systems with emphasis upon polyhedral borane species.

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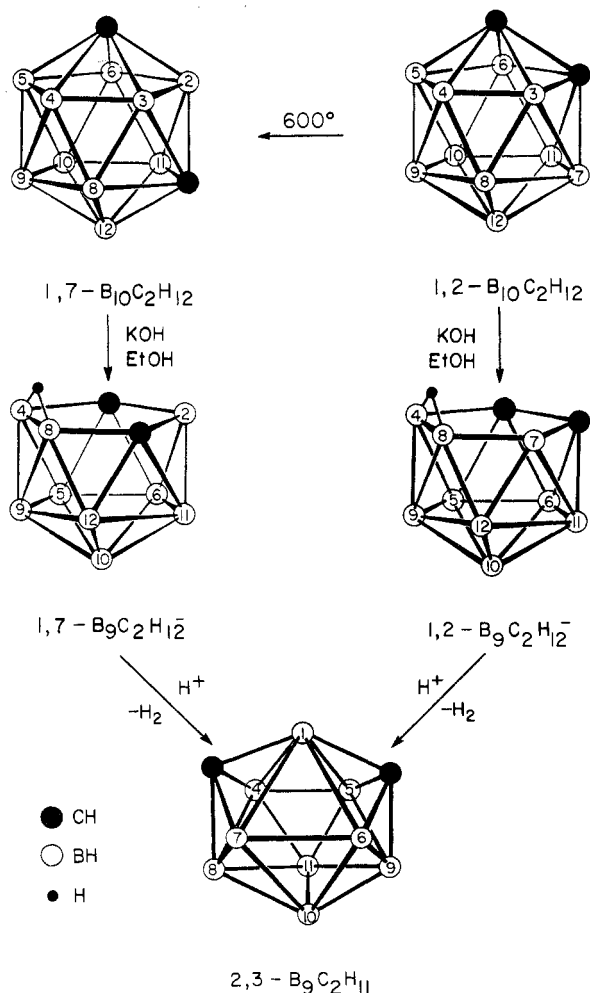


Figure 1. The schematic conversion of 1,2- and 1,7- $B_{10}C_2H_{12}$ carboranes to 2,3- $B_9C_2H_{11}$.

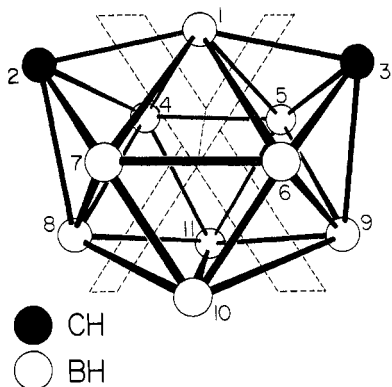
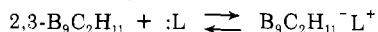


Figure 2. Idealized structure of a "close" eleven-particle polyhedron exhibiting C_{2v} symmetry. The structure of 2,3- $B_9C_2H_{11}$ exhibits C_{2v} symmetry.¹⁷ In the $B_{11}H_{11}^{2-}$ and $B_{10}CH_{11}^{-}$ ions of similar geometry, the planes indicated by dotted lines separate belts of four and 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



proposed for these adducts (Figure 3) probably resembles that of the $B_9C_2H_{11}^{-}L^{+}$ compounds formed by oxidative ligand substitution on the $B_9C_2H_{12}^{-}$ ions¹⁹ and requires the migration of a terminal B-H

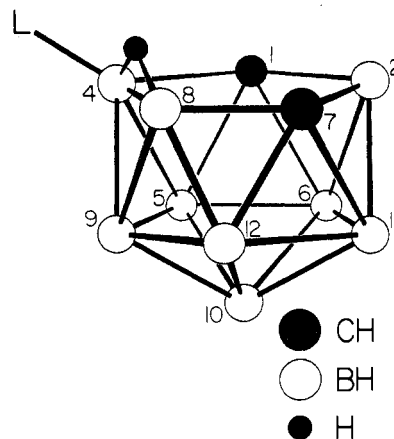


Figure 3. The proposed structure of the adducts formed by the reaction of donor species L to 2,3- $B_9C_2H_{11}$.

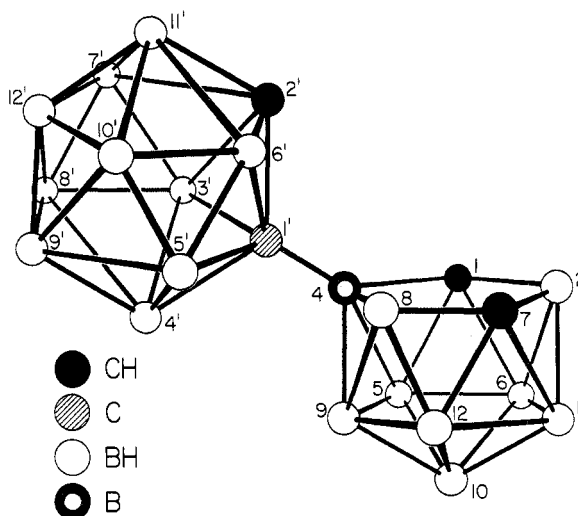
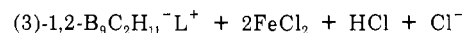
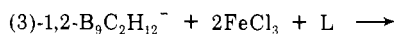
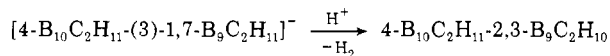
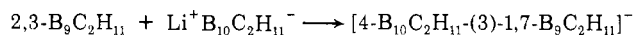


Figure 4. The proposed structure of $[4-(1,2-B_{10}C_2H_{11})][(3)-1,7-B_9C_2H_{10}]^{-}$ formed by reaction of 1,2- $B_{10}C_2H_{11}^{-}Li^{+}$ and 2,3- $B_9C_2H_{11}$. The "bridging" hydrogen atom was omitted for clarity.



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- $B_9C_2H_{12}^{-}$ ions¹⁸ (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



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-

(19) D. C. Young, D. V. Howe, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 91, 859 (1969).

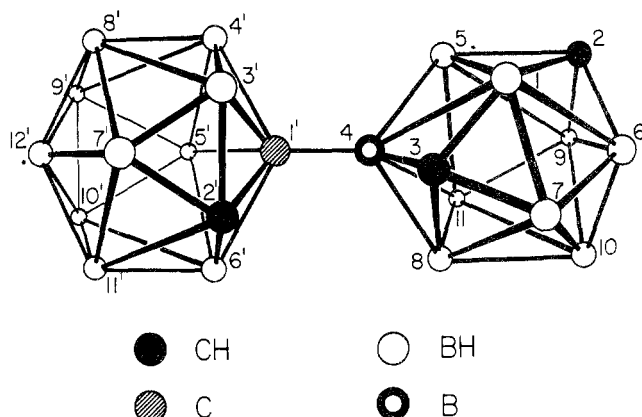


Figure 5. The proposed structure of 4-(1,2-B₁₀C₂H₁₁)-2,3-B₉C₂H₁₀.

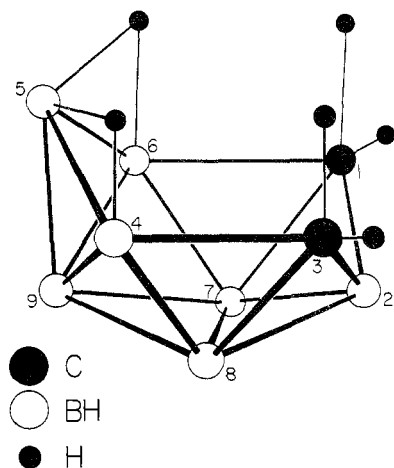
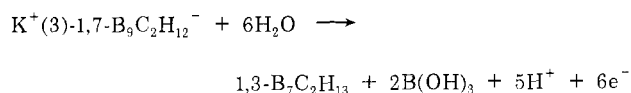


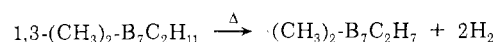
Figure 6. The structure of 1,3-B₇C₂H₁₃.

substituted derivatives (Figure 6).^{13,20} The structure of these species, shown in Figure 6, was predicted from nuclear magnetic resonance data²⁰ and confirmed by X-ray diffraction studies.²¹ Subsequently, an improved synthesis of 1,3-B₇C₂H₁₃ was developed²² in which the (3)-1,7-B₉C₂H₁₂⁻ ion was oxidized directly to 1,3-B₇C₂H₁₃, thus entirely eliminating the preparation and isolation of the 2,3-B₉C₂H₁₁ intermediate.



The 1,3-B₇C₂H₁₃ carborane is of particular interest because it is the precursor of the B_{*n*}C₂H_{*n*+2} carboranes where *n* = 6–8.

Preparation of *closo*-Carboranes by the Pyrolysis of 1,3-B₇C₂H₁₃. Thermal decomposition of 1,3-(CH₃)₂-B₇C₂H₁₁ in diphenyl ether was investigated in an attempt to produce the then unknown carborane (CH₃)₂B₇C₂H₇. Instead of a single reaction



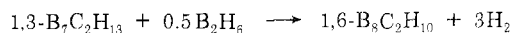
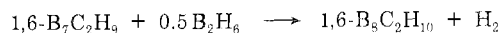
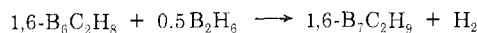
(20) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **88**, 607 (1966).

(21) D. Voet and W. N. Lipscomb, *Inorg. Chem.*, **6**, 113 (1967).

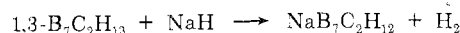
(22) P. M. Garrett, T. A. George, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **8**, 2008 (1969).

product, three new materials were obtained and characterized as the C,C'-dimethyl derivatives of 1,6-B₈C₂H₁₀, 1,6-B₇C₂H₉, and 1,6-B₆C₂H₈.^{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 B₇C₂H₁₃ starting material.²⁴

The addition of diborane during these pyrolyses shifted the product distribution toward more of the 1,6-B₈C₂H₁₀ component at the expense of 1,6-B₆C₂H₈ and 1,6-B₇C₂H₉.¹³ The slow, low-pressure pyrolysis of 1,3-B₇C₂H₁₃ and its C-methyl derivatives formed as major products 2,4-B₅C₂H₇, 1,6-B₆C₂H₈, 1,6-B₇C₂H₉, and 1,6-B₈C₂H₁₀, and their corresponding C-methyl derivatives together with diborane and hydrogen.²⁵ In another experiment, 1,6-B₆C₂H₈ 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-B₇C₂H₉, and 1,6-B₈C₂H₁₀. These results, plus the fact that the addition of diborane during the pyrolysis of 1,3-B₇C₂H₁₃ in diphenyl ether gave enhanced yields of 1,6-B₈C₂H₁₀ and very little 1,6-B₆C₂H₈, suggested that the thermal decomposition of 1,3-B₇C₂H₁₃ yields primarily 1,6-B₆C₂H₈, diborane, and hydrogen. This step may be followed by progressive recombination of 1,6-B₆C₂H₈ and diborane to yield 1,6-B₇C₂H₉, 1,6-B₈C₂H₁₀, and hydrogen. The direct reaction of 1,3-B₇C₂H₁₃ and diborane to produce 1,6-B₈C₂H₁₀ may also occur.²⁵



Dicarbido-*closo*-decaborane(10), B₈C₂H₁₀. In addition to the pyrolytic methods in which 1,6-B₈C₂H₁₀ was produced in conjunction with the B₇, B₆, and B₅ carboranes, an improved method for its preparation is known. In this synthesis the monoanion, B₇C₂H₁₂⁻, was treated with specific amounts of



1,3-B₇C₂H₁₃ and diborane to yield 1,6-B₈C₂H₁₀.²⁶ This method not only provides 1,6-B₈C₂H₁₀ in high yield, but there are no difficult separation problems in its purification.

Like the other known isoelectronic ten-particle polyhedra, B₁₀H₁₀²⁻,^{27,28} and B₉CH₁₀⁻,²⁹ 1,6-

(23) F. N. Tebbe, P. M. Garrett, D. C. Young, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **88**, 609 (1966).

(24) P. M. Garrett, J. C. Smart, G. S. Ditta, and M. F. Hawthorne, *Inorg. Chem.*, **8**, 1907 (1969).

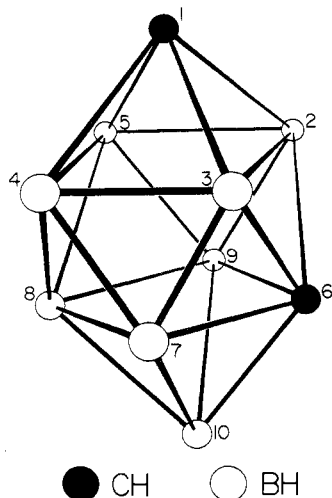
(25) G. B. Dunks and M. F. Hawthorne, *Inorg. Chem.*, **7**, 1038 (1968).

(26) P. M. Garrett, G. S. Ditta, and M. F. Hawthorne, *Inorg. Chem.*, **9**, 1947 (1970).

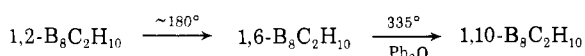
(27) M. F. Hawthorne and A. R. Pitochelli, *J. Amer. Chem. Soc.*, **81**, 5519 (1959).

(28) R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 1779 (1962).

(29) W. H. Knoth, *J. Amer. Chem. Soc.*, **89**, 1274 (1967); *Inorg. Chem.*, **10**, 598 (1971).

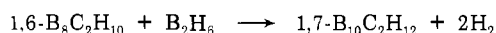
Figure 7. The structure of 1,6-B₈C₂H₁₀.

B₈C₂H₁₀ has the bicapped Archimedean antiprism structure illustrated in Figure 7. Three carbon atom positional isomers, 1,2-, 1,6-, and 1,10-B₈C₂H₁₀, are known. The 1,2-B₈C₂H₁₀ isomer^{30,31} undergoes facile thermal rearrangement to 1,6-B₈C₂H₁₀. The

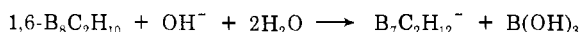


subsequent thermal rearrangement of 1,6-B₈C₂H₁₀ to 1,10-B₈C₂H₁₀ has been studied in detail.^{13,23,32} First-order kinetics were observed during the rearrangement with $\Delta S^\ddagger = +4.6$ cal/(mol deg) and $\Delta H^\ddagger = +48.8$ kcal/mol.³²

Three general types of reactions involving the polyhedral structure are known for the B₈C₂H₁₀ carboranes. One is the thermal polyhedral rearrangement discussed above. Secondly, hydroboration of 1,6-B₈C₂H₁₀ to 1,7-B₁₀C₂H₁₂ has been observed.¹³ The

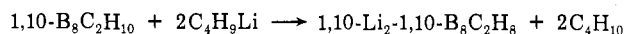
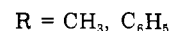
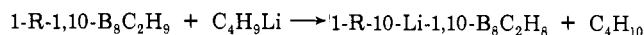
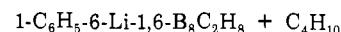
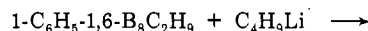


third example of cage chemistry of the B₈C₂H₁₀ system is hydrolytic degradation.¹³ Hydrolysis of 1,6-

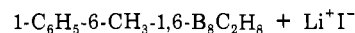
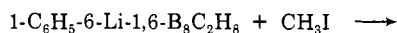


B₈C₂H₁₀ in basic, aqueous ethanol produced the B₇C₂H₁₂⁻ ion in high yield.¹³ In acid medium, 1,6-B₈C₂H₁₀ was completely decomposed to yield boric acid. Under similar conditions 1,10-B₈C₂H₁₀ was much less reactive, possibly due to the fact that, in the 1,10 isomer, all boron atoms are equivalent; thus 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.

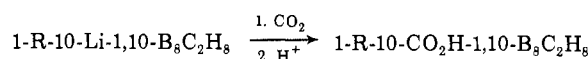
A rather extensive substitution chemistry of the two exo polyhedral carbon-hydrogen bonds is known for the 1,6- and 1,10-B₈C₂H₁₀ carboranes. Treatment of substituted 1,6- and 1,10-B₈C₂H₁₀ carboranes with *n*-butyllithium gave mono- and dilithio salts³³



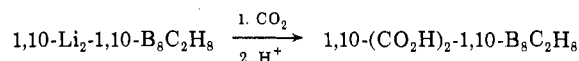
which react with a variety of electrophiles. Reaction with methyl iodide produced *C*-methyl derivatives.³³



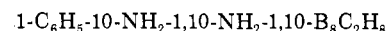
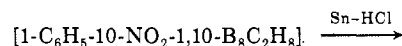
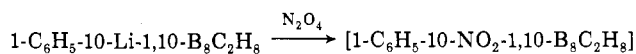
Carbon dioxide reacted with 1-R-10-Li-1,10-B₈C₂H₈ (R = CH₃, C₆H₅) followed by acidification



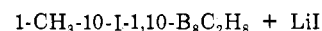
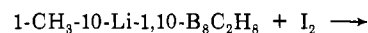
to produce 10-monocarboxylic acids. Similarly, the 1,10-dilithio derivative reacted with carbon dioxide followed by acidification to yield the 1,10-dicarboxy-



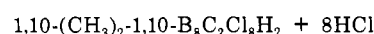
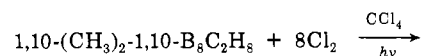
lic acid. The *C*-methyl and *C*-phenyl acids titrated as strong monoprotic acids with apparent $\text{p}K_a$'s of 4.2 and 4.1, respectively. The 1,10-dicarboxylic acid titrated as a strong diprotic acid with only one potentiometric inflection with an apparent $\text{p}K_a$ of 3.8.³³ Reaction of 1-C₆H₅-10-Li-1,10-B₈C₂H₈ with nitrogen dioxide followed by reduction with tin and



hydrochloric acid produced the 1-phenyl-10-amino derivative of 1,10-B₈C₂H₁₀.³³ The monolithio derivative of 1-CH₃-1,10-B₈C₂H₉ reacted with iodine to



give the 1-methyl-10-iodo derivative of 1,10-B₈C₂H₁₀.³³ The 1,10-dimethyl-*B*-octachloro derivative of 1,10-B₈C₂H₁₀ was prepared by passage of chlorine gas through a solution of 1,10-(CH₃)₂-1,10-



B₈C₂H₈.³³ Finally, 1,10-Li₂-1,10-B₈C₂H₈ reacted with (π-C₅H₅)Fe(CO)₂I to produce the novel σ-

(30) S. Hermánek, private communication.

(31) R. Rietz, private communication.

(32) T.-C. Yu, M.S. Thesis, University of California, Riverside, Calif., 1968.

(33) P. M. Garrett, J. C. Smart, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 91, 4707 (1969).

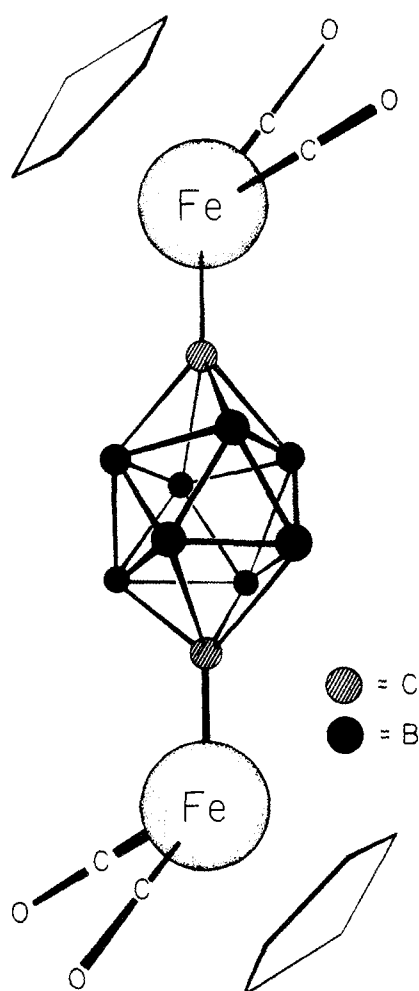


Figure 8. The proposed structure of $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{-1,10-(}\sigma\text{-B}_8\text{C}_2\text{H}_8\text{)}$.

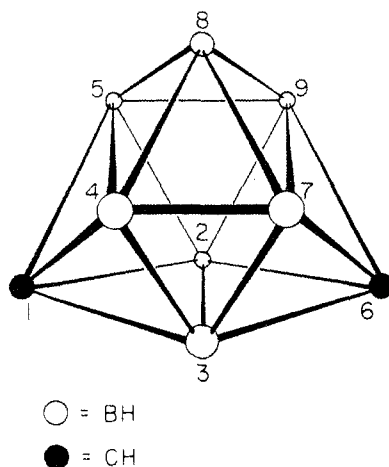
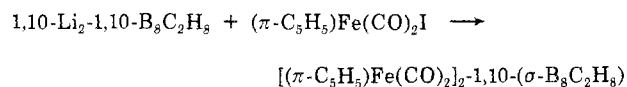


Figure 9. The structure of $1,6\text{-B}_7\text{C}_2\text{H}_9$.

bonded complex $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{-1,10-(}\sigma\text{-B}_8\text{C}_2\text{H}_8\text{)}$ ³⁴ (Figure 8).



1,6-Dicarba-closo-nonaborane(9), $1,6\text{-B}_7\text{C}_2\text{H}_9$. The known isoelectronic nine-particle polyhedra

(34) J. C. Smart, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 1031 (1969).

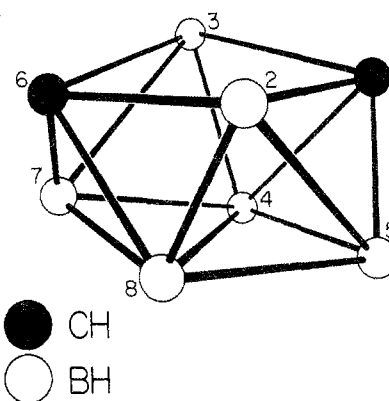
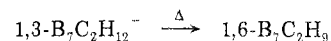
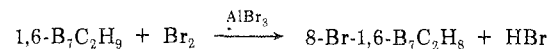
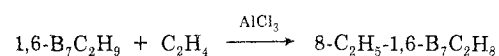
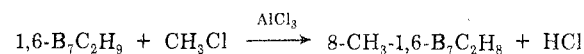


Figure 10. The structure of $1,6\text{-B}_6\text{C}_2\text{H}_8$.

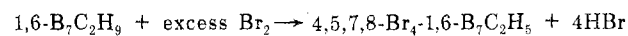
$\text{B}_9\text{H}_9^{2-14}$ and $\text{B}_7\text{C}_2\text{H}_9$ ³⁵ possess a tricapped trigonal prismatic geometry (Figure 9). In addition to the pyrolytic methods described above for the preparation of $1,6\text{-B}_7\text{C}_2\text{H}_9$, there is a newer method²⁴ which gives a rather pure product, thus eliminating the separation problems which were previously encountered. The pyrolysis of the $\text{B}_7\text{C}_2\text{H}_{12}^-$ ion¹³ in diphenyl ether produced $1,6\text{-B}_7\text{C}_2\text{H}_9$ (38%) with no hydrogen evolution.²⁴



Calculations show that in the ground state³⁵ the boron atom in the 8 (apex) position of $1,6\text{-B}_7\text{C}_2\text{H}_9$ 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 $1,6\text{-B}_7\text{C}_2\text{H}_9$ and its *C*-methyl and *C,C'*-dimethyl derivatives were shown to undergo such reactions³⁶ when treated with methyl chloride, ethylene, and bromine in the presence of a Lewis acid. In all cases,



the substituent was attached to the boron atom present in the 8 position. When $1,6\text{-B}_7\text{C}_2\text{H}_9$ was allowed to react with excess bromine, a tetrabromo derivative was produced.³⁶



1,6-Dicarba-closo-octaborane(8), $1,6\text{-B}_6\text{C}_2\text{H}_8$. The isoelectronic eight-particle systems, $\text{B}_8\text{H}_8^{2-}$ ³⁷ and $1,6\text{-B}_6\text{C}_2\text{H}_8$,³⁸ have slightly distorted dodecahedral geometry, as depicted in Figure 10.

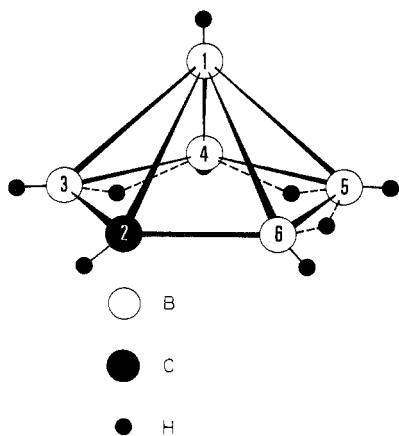
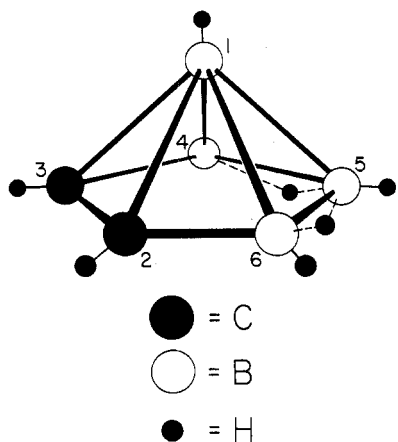
The $1,6\text{-B}_6\text{C}_2\text{H}_8$ carborane and its *C*-methyl and *C,C'*-dimethyl derivatives are obtained in highest

(35) T. F. Koetzle, F. E. Scarbrough, and W. N. Lipscomb, *Inorg. Chem.*, **7**, 1076 (1968).

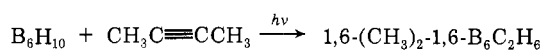
(36) G. B. Dunks and M. F. Hawthorne, *Inorg. Chem.*, **9**, 893 (1970).

(37) F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1271 (1967).

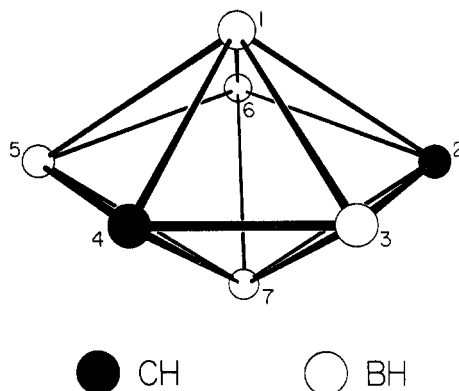
(38) H. Hart and W. N. Lipscomb, *Inorg. Chem.*, **7**, 1070 (1968).

Figure 11. The structure of 2-B₅CH₉.Figure 12. The structure of 2,3-B₄C₂H₈.

yield by the pyrolytic method described above,²⁵ although other syntheses have been reported.^{13,23} The first reported preparation of 1,6-(CH₃)₂-1,6-B₆C₂H₆, however, involved the ultraviolet irradiation of mixtures of hexaborane and dimethylacetylene.³⁹



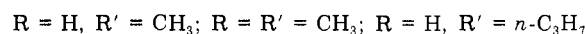
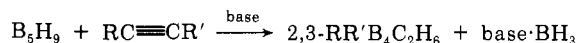
The chemistry of 1,6-B₆C₂H₈ and its C-alkyl derivatives is largely unexplored. One reaction that has been studied is the treatment of 1,6-B₆C₂H₈ with borohydride ion followed by treatment with hydrogen chloride, which produced 2-carba-nido-hexaborane, B₅CH₉⁴⁰ (Figure 11), and several of its methyl derivatives.⁴¹ A similar reaction using 1-CH₃-1,6-B₆C₂H₇ as the starting material produced analogous products in which the polyhedral carbon atom in the B₅CH₉ 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-(CH₃)₂-1,6-B₆C₂H₆ was used as the starting material, all of the substituted B₅CH₉ 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

Figure 13. The structure of 2,4-B₅C₂H₇.

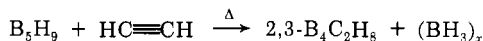
ethyl substituent. Grimes recently reported⁴² the thermal extrusion of a polyhedral carbon atom.

Small Carboranes

Preparation and Pyrolysis of 2,3-B₄C₂H₈. Synthesis of Small *closo*-Carboranes. As observed in the case of 1,3-B₇C₂H₁₃, which is the precursor of the B_nC₂H_{n+2} carboranes where n = 6-8, 2,3-B₄C₂H₈,⁴³ 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-B₄C₂H₈ is the base-catalyzed reaction of pentaborane(9) with the appropriate acetylene.⁴⁴ The synthesis of the



parent compound, 2,3-B₄C₂H₈, was achieved by the reaction of pentaborane(9) and acetylene in the gas



phase.⁴⁵ The pyrolysis of 2,3-B₄C₂H₈ and its C-alkyl derivatives produced mixtures which contained 2,4-B₅C₂H₇, 1,2- and 1,6-B₄C₂H₆, and 1,5-B₃C₂H₅,⁴⁵⁻⁴⁷ and some of their C-alkyl derivatives. Photolysis of 2,3-B₄C₂H₈ at ambient temperature has been shown to produce mixtures of 1,5-B₃C₂H₅, 1,2-B₄C₂H₆, and 1,6-B₄C₂H₆.⁴⁸

Dicarbapentaborane(7), B₅C₂H₇. The isoelectronic B₇H₇²⁻ ion³⁷ and the 2,4-B₅C₂H₇ carborane⁴⁹ possess pentagonal-bipyramidal geometry (Figure 13). The 2,3- and 2,4-B₅C₂H₇ carbon atom positional isomers are known.

The 2,4-B₅C₂H₇ and its C-methyl derivatives were among the products obtained from the pyrolysis of

(39) R. E. Williams and F. J. Gerhart, *J. Amer. Chem. Soc.*, **87**, 3513 (1965).

(40) C. S. Cheung and R. A. Beudet, *Inorg. Chem.*, **10**, 1144 (1971).

(41) G. B. Dunks and M. F. Hawthorne, *Inorg. Chem.*, **8**, 2667 (1969).

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(45) T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964).

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(47) J. F. Ditter, *Inorg. Chem.*, **7**, 1748 (1968).

(48) J. R. Spielman and J. E. Scott, Jr., *J. Amer. Chem. Soc.*, **87**, 3512 (1965).

(49) R. A. Beudet and R. L. Poynter, *J. Amer. Chem. Soc.*, **86**, 1258 (1964).

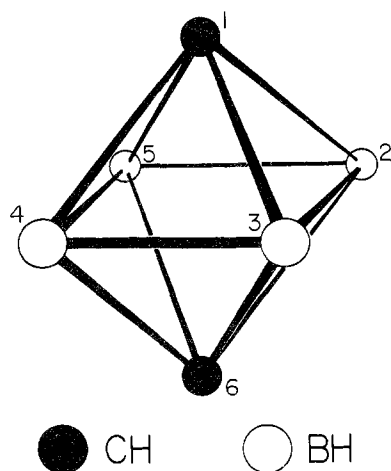
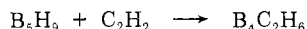


Figure 14. The structure of 1,6- $B_4C_2H_6$.

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

Dicarbapentaborane(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

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



Possibly due to its thermal instability, no chemis-

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 (51) R. R. Rietz, Ph.D. Thesis, Indiana University, Bloomington, Ind., 1971.
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 (53) R. Warren, D. Paquin, T. Onak, G. Dunks, and J. R. Spielman, *Inorg. Chem.*, **9**, 2285 (1970).
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 (55) T. Onak, G. B. Dunks, R. A. Beaudet, and R. L. Poynter, *J. Amer. Chem. Soc.*, **88**, 4622 (1966).
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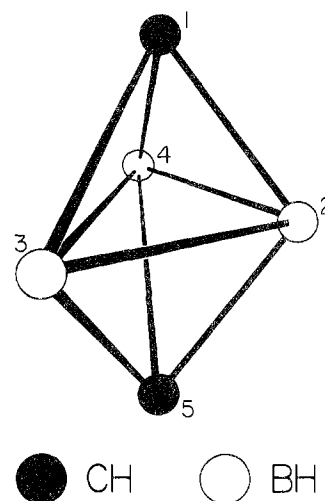


Figure 15. The structure of 1,5- $B_3C_2H_5$.

try has been reported for the 1,2- $B_4C_2H_6$ carborane. 2-Chloro⁵⁸ and 2-bromo⁵⁹ 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

Dicarbapentaborane(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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 (59) R. R. Olsen and R. N. Grimes, *Inorg. Chem.*, **10**, 1103 (1971).
 (60) J. R. Spielman, G. B. Dunks, and R. Warren, *Inorg. Chem.*, **8**, 2172 (1969).
 (61) A. B. Burg and T. J. Reilly, *Inorg. Chem.*, **11**, 1962 (1972).
 (62) W. J. Evans and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **93**, 3063 (1971).
 (63) M. F. Hawthorne, presented before the XIVth Meeting, International Conference on Coordination Chemistry, Toronto, Canada, 1972.
 (64) W. J. Evans, G. B. Dunks, and M. F. Hawthorne, in preparation.

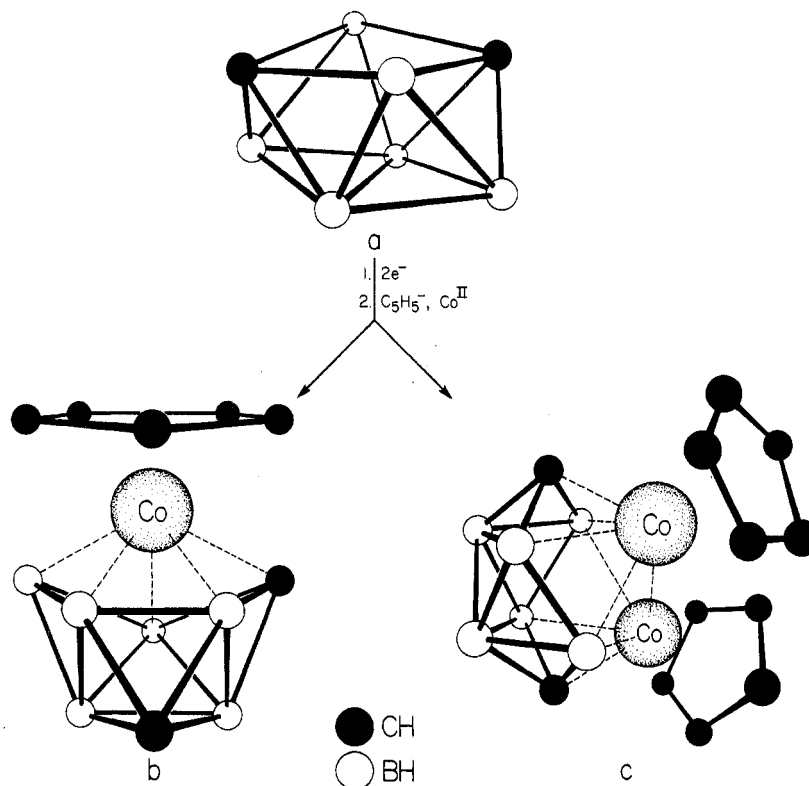


Figure 16. A schematic representation of the polyhedral expansion reaction applied to a $B_n C_2 H_{n+2}$ carborane. Treatment of 1,6- $B_6 C_2 H_8$ (a) with sodium followed by NaC_5H_5 and $CoCl_2$ produced the metallocarboranes $(C_5H_5)Co(B_6C_2H_8)$ (b) and $(C_5H_5Co)_2B_6C_2H_8$ (c).

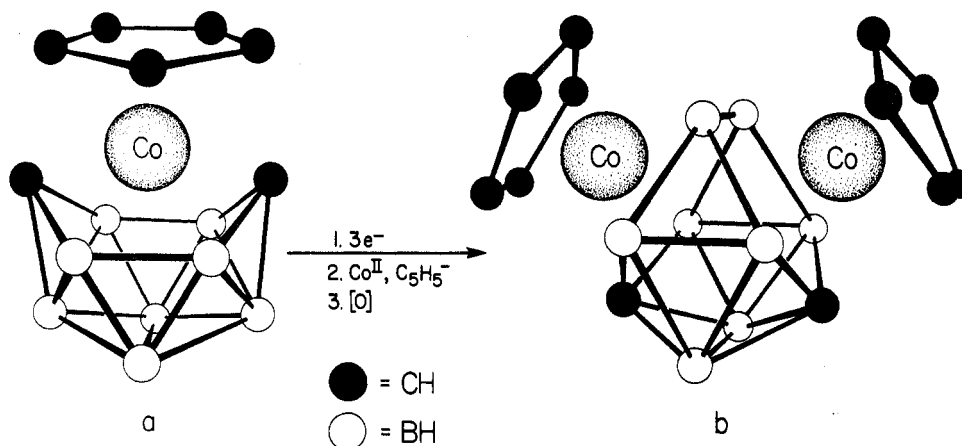
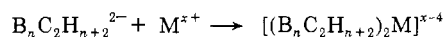
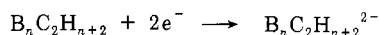


Figure 17. A schematic representation of the polyhedral expansion reaction as applied to a metallocarborane. The reaction of $(B_8C_2H_{10})(C_5H_5)Co^{III}$ (a) with sodium followed by NaC_5H_5 and $CoCl_2$ produced $(C_6H_5Co)_2B_8C_2H_{10}$ (b).



expansion reaction has been demonstrated on the $B_n C_2 H_{n+2}$ 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 un-

known, 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.