BORON I. CARBORANES; BORANES IN ORGANIC SYNTHESIS
ANNUAL SURVEY COVERING THE YEAR 1979 [*]

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CONTENTS

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[*] Previous survey see J. Organometal. Chem., 180 (1979) 19-63.

I. CARBORANES

A. Introduction

The award of the Nobel Prize to Herbert C. Brown is the event of the year in boron chemistry, and the reviewer's comments and congratulations will be extended in Section IIA of this survey. It has only been since 1976 that William N. Lipscomb received the Nobel Prize for his theoretically oriented studies of polyhedral borane chemistry. The past two decades have been an exciting period of discovery and growth in diverse types of boron chemistry, and this reviewer has been privileged to watch it all unfold, while indulging in a few small projects of his own. The field shows every promise of continued vigor for years to come.

Development of carborane and polyhedral borane chemistry is continuing at a rapid rate. This survey will follow the pattern established in recent years, with attempted comprehensive coverage of references on carboranes, followed by a brief survey of related polyhedral borane chemistry, which includes references to all of the publications the reviewer was able to find but omits drawings of structures and other details included in the survey of the carbon-containing carboranes.

B. Metallacarboranes

1. Four-Carbon Metallacarboranes. The most novel and unexpected structures reported in the past year belong to metallacarboranes, and the series of four-carbon cobaltacarboranes discovered by Grimes and coworkers are in a class by themselves.

The structure of a 12-vertex arachno carborane, $Me_4C_4B_8H_8^{-}$-$(C_5H_4)Co(C_5H_5)^{+}$, has been determined by X-ray crystallography (Fig. 1) [1]. A structure diagram shows the relationship of the C_4B_8 cage to a 14-vertex polyhedron (Fig. 2).

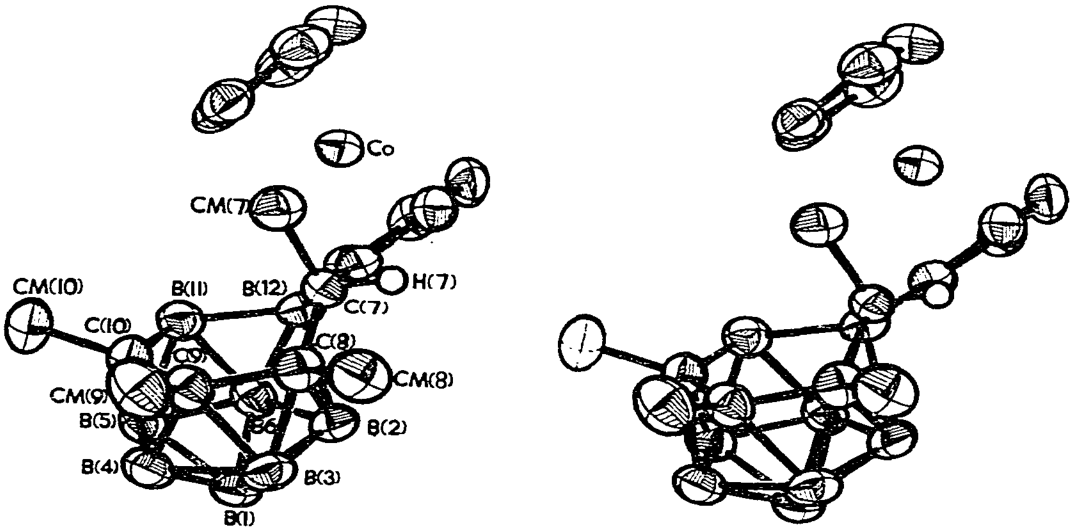

Figure 1. Stereoview of $[Me_4C_4B_8H_8]^-$-$[(C_5H_4)Co(C_5H_5)]^+$, H atoms omitted except for H(7). [Reprinted with permission from R. N. Grimes, J. R. Pipal, and E. Sinn, J. Am. Chem. Soc., 101 (1979) 4175. Copyright by the American Chemical Society.]

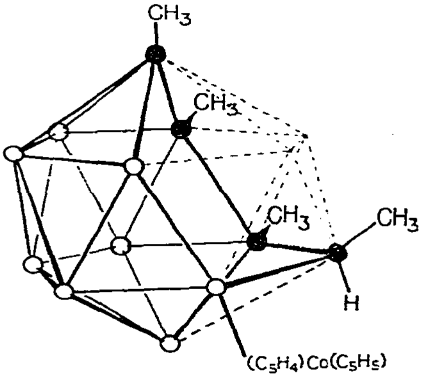

Figure 2. Geometry of the C_4B_8 cage of $[Me_4C_4B_8H_8]^-$-$[(C_5H_4)Co(C_5H_5)]^+$, shown as a fragment of a 14-vertex closo polyhedron (opposite enantiomer to that shown in Fig. 1).

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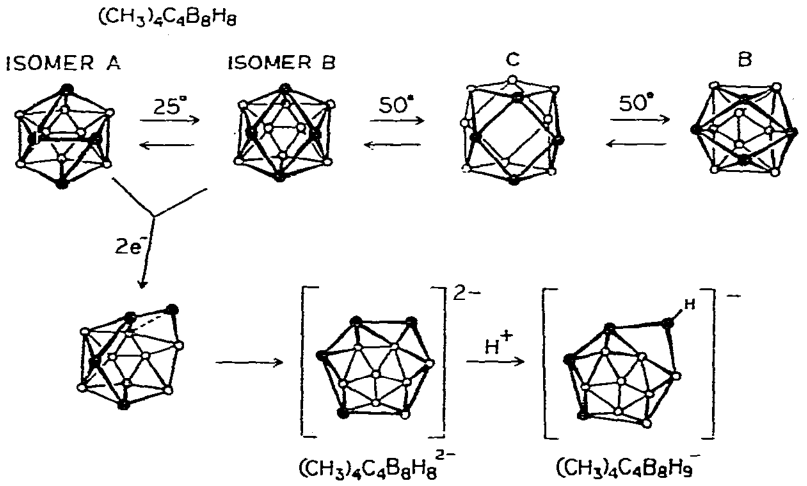

Figure 3. Proposed scheme for the interconversion of neutral $Me_4C_4B_8H_8$ isomers A and B, the fluxional rearrangement of B at 50 °C, and the formation of $Me_4C_4B_8H_8^{2-}$ and $Me_4C_4B_8H_9^-$ ions.

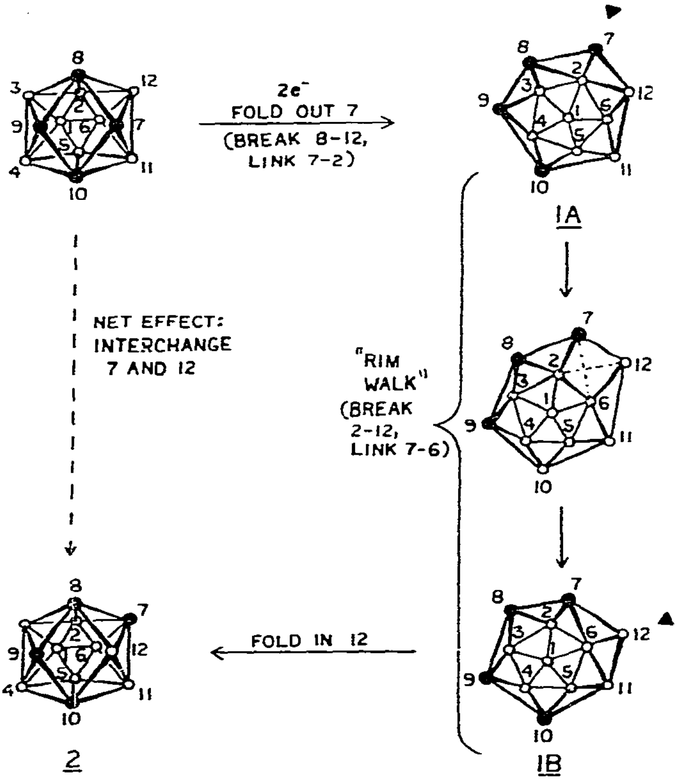

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Figure 4. Proposed mechanisms for the fluxional rearrangement of the $Me_4C_4B_8H_8^{2-}$ framework. Isomer 1a corresponds to the geometry established for $(C_5H_5)Co-(C_5H_4)^+-Me_4C_4B_8H_8^-$; isomer 1b is similar but the unique low-coordinate position (marked by wedges in both structures) is occupied by a BH instead of a CCH_3 unit.

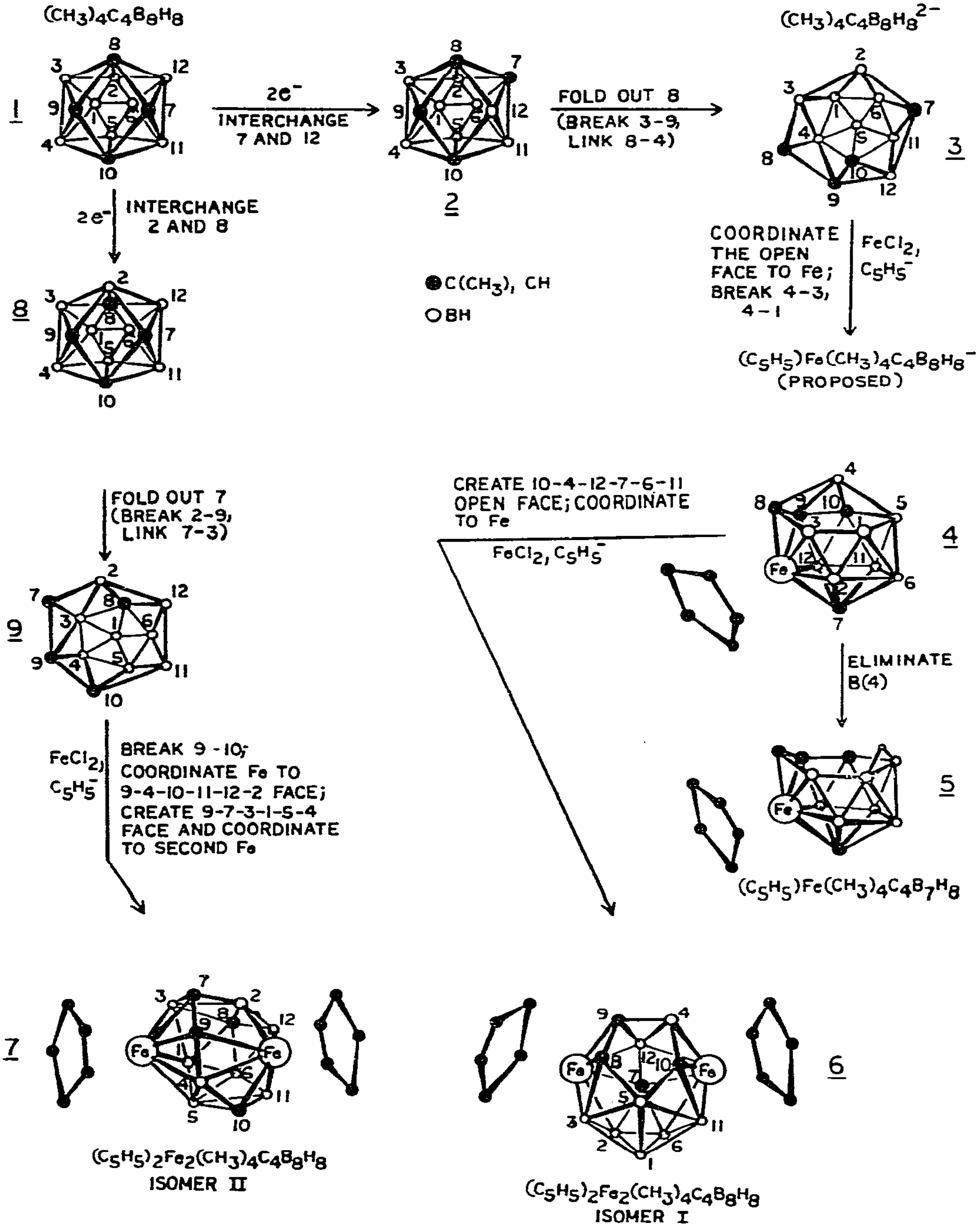

Figure 5. Proposed mechanisms for formation of ferracarboranes from isomers of $Me_4C_4B_8H_8^{2-}$, which can be formed by processes of the kind illustrated in Fig. 4. [Reprinted with permission from R. N. Grimes, J. R. Pipal, and E. Sinn, J. Am. Chem. Soc., 101 (1979) 4179. Copyright by the American Chemical Society.]

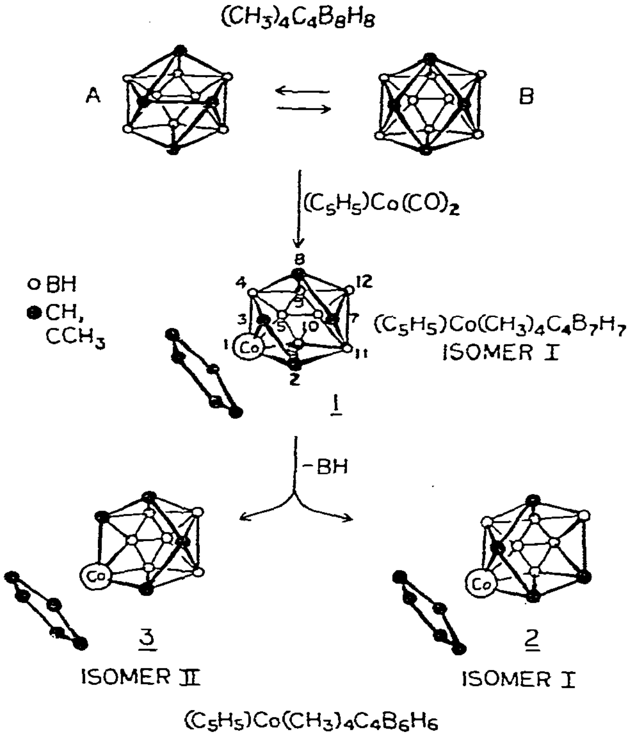

Figure 6. Scheme for preparation of 11- and 12-vertex *nido*-cobaltacarboranes from neutral $Me_4C_4B_8H_8$. [Reprinted with permission from W. M. Maxwell and R. N. Grimes, Inorg. Chem., 18 (1979) 2176. Copyright by the American Chemical Society.]

Reaction schemes were also proposed for the interconversion of isomers of neutral $Me_4C_4B_8H_8$ and their opening to anions (Fig. 3), fluxional rearrangement of the $Me_4C_4B_8H_8^{2-}$ framework (Fig. 4), and conversions of $Me_4C_4B_8H_8$ to ferracarboranes (Fig. 5) [1].

Details of the synthesis of a series of four-carbon cobaltacarboranes have been reported [2]. Reaction of neutral $Me_4C_4B_8H_8$ with $(C_5H_5)Co(CO)_2$ yields $(C_5H_5)Co(Me_4C_4B_7H_7)$ and two isomers evidently derived from this compound by loss of a BH unit (Fig. 6). Reduction of $Me_4C_4B_8H_8$ with sodium naphthalide to form $Me_4C_4B_8H_8^{2-}$ followed by treatment with $CoCl_2$ and $C_5H_5^-$ yields B_8 and B_7 derivatives (Fig. 7). An alternative synthesis of $(C_5H_5)Co(Me_4C_4B_7H_7)$ begins with $(Me_2C_2B_4H_4)CoH(Me_2C_2B_3H_5)$ (Fig. 8).

The structure of "isomer V" of $(C_5H_5)_2Co_2(Me_4C_4B_6H_6)$ has been determined by X-ray crystallography (Fig. 9) [3]. This compound has an unusual open face with no bonding between the two sets of carbon atoms. Proposed pathways to this compound and isomers are illustrated (Fig. 10).

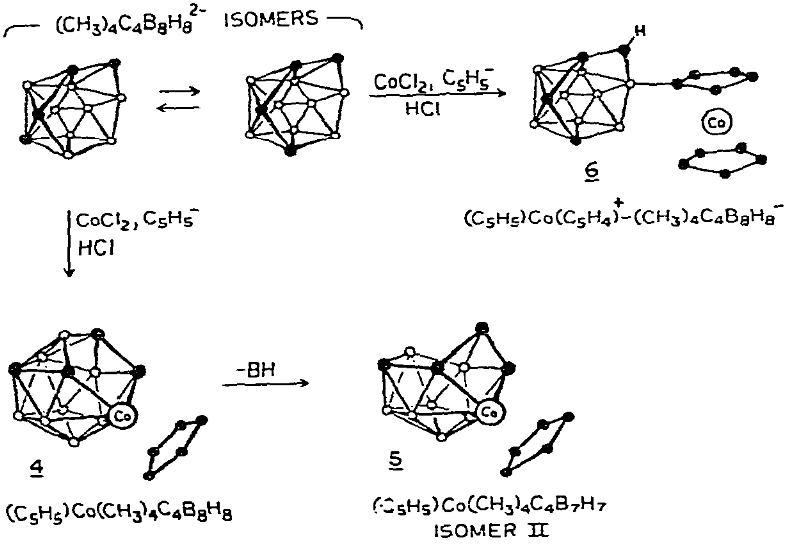

Figure 7. Scheme for the preparation of $(C_5H_5)Co(C_5H_4)^+-(Me_4C_4B_8H_8)^-$, $(C_5H_5)Co(Me_4C_4B_8H_8)$, and $(C_5H_5)Co(Me_4C_4B_7H_7)$ from the dianion $Me_4C_4B_8H_8^{2-}$. [Reprinted with permission from W. M. Maxwell and R. N. Grimes, Inorg. Chem., 18 (1979) 2176. Copyright by the American Chemical Society.]

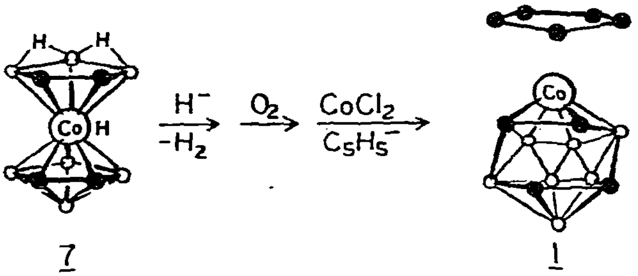

Figure 8. Alternate synthesis of $(C_5H_5)Co(Me_4C_4B_7H_7)$, "Isomer I." [Reprinted with permission from W. M. Maxwell and R. N. Grimes, Inorg. Chem., 18 (1979) 2177. Copyright by the American Chemical Society.]

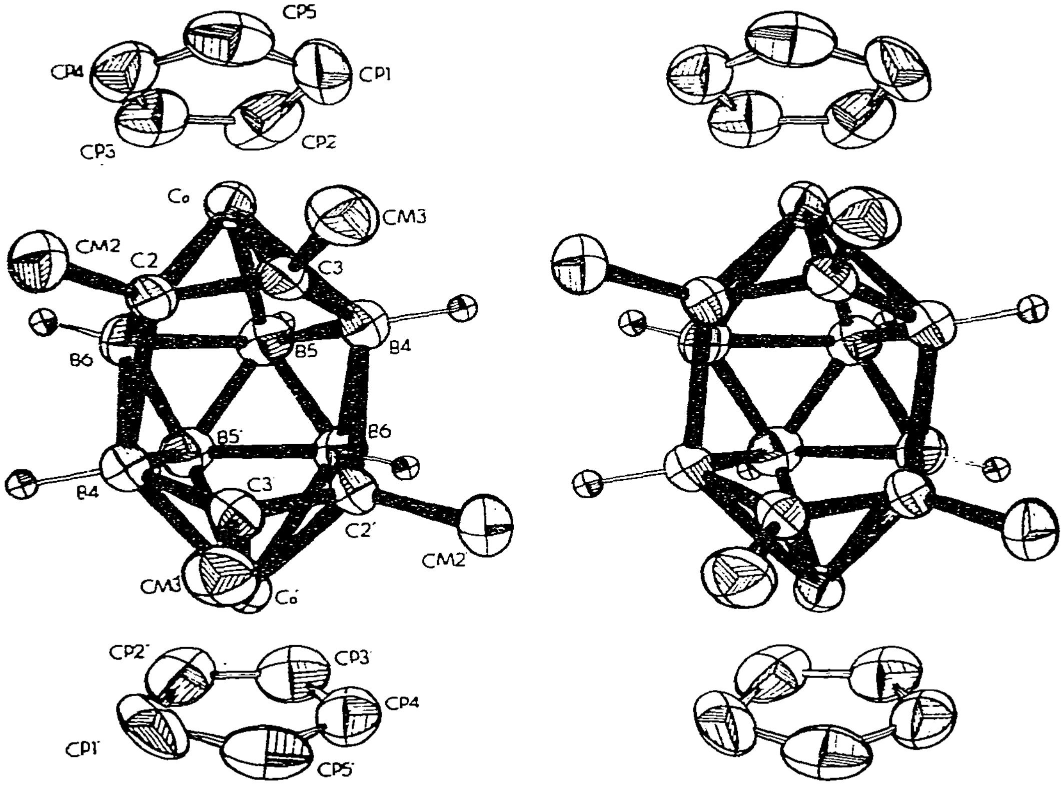

Figure 9. Molecular structure of $(C_5H_5)_2Co_2(Me_4C_4B_6H_6)$, "Isomer V." [Reprinted with permission from J. R. Pipal and R. N. Grimes, Inorg. Chem., 18 (1979) 1938. Copyright by the American Chemical Society.]

2. Non-Icosahedral Metallacarboranes. This section includes a variety of first-row transition metal atoms and diverse polyhedral cage structures.

The structure of $(2,3\text{-}Me_2C_2B_4H_4)_2FeH_2$ has been determined by X-ray crystallography (Fig. 11) [4].

Reaction of $B_5H_8^-$ with nickelocene has yielded $(C_5H_5)_4Ni_4B_4H_4$ and $(C_5H_5)_4Ni_4B_5H_5$, the structures of which have been determined by X-ray crystallography. Analogous reaction of $Me_2C_2B_4H_5^-$ with nickelocene has yielded the nickelacarboranes $(C_5H_5)_2Ni_2Me_2C_2B_4H_4$ and $(C_5H_5)_2Ni_2Me_2C_2B_5H_5$, proposed structures of which are illustrated in Fig. 12 [5].

Plotkin and Sneddon have prepared a series of new metallacarboranes from the coupled carboranes $(2,4\text{-}C_2B_5H_6)_2$ and $(2,3\text{-}Me_2C_2B_4H_5)_2$ [6]. Those from $(2,4\text{-}C_2B_5H_6)_2$ have been characterized by NMR (Figs. 13 and 14). A rearrangement equilibrates two of the isomers at 220 °C, and since the rearrangement process does not move two cobalt atoms into adjacent positions, it was postulated that the mechanism does not involve a triangle rotation within a cage but a migration

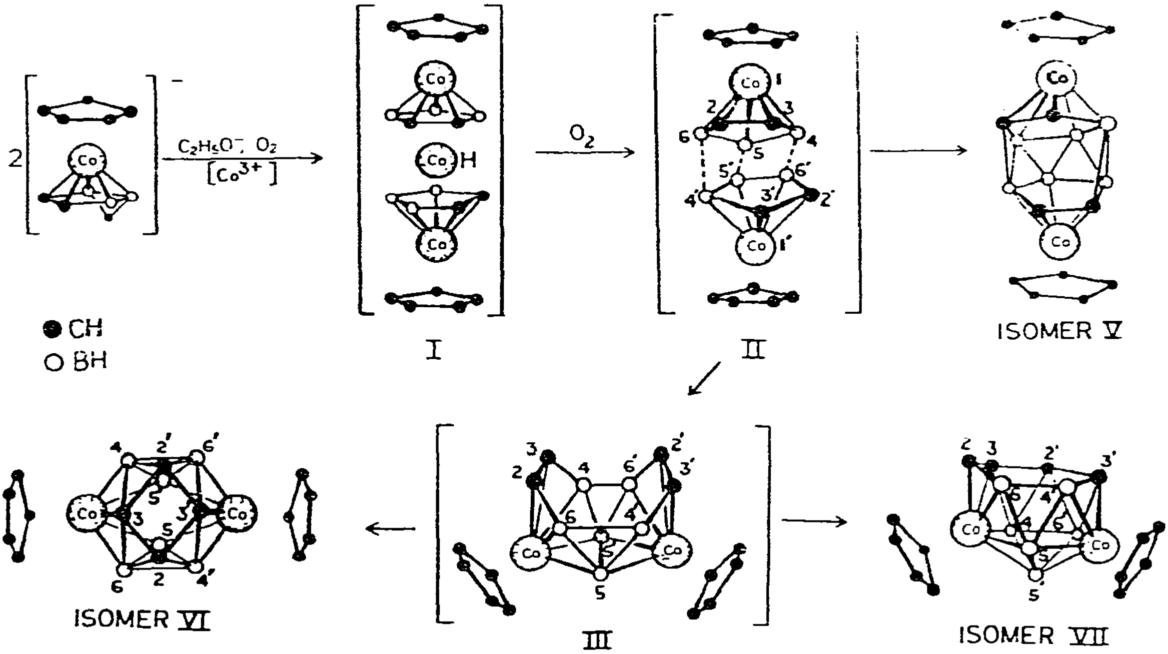

Figure 10. Proposed mechanism of formation of $(C_5H_5)_2Co_2Me_4C_4B_6H_6$ isomers. The structures of V and VII are established and that of VI is proposed from NMR evidence. Species I, II, and III are suggested reaction intermediates. The conversion of II to III can occur via insertion of B(5') between B(5) and B(4) and insertion of B(5) between B(5') and B(4'), with subsequent linkage of B(5') to Co(1) and of B(5) to Co(1'); the other rearrangements depicted are obvious. [Reprinted with permission from J. R. Pipal and R. N. Grimes, Inorg. Chem., 18 (1979) 1939. Copyright by the American Chemical Society.]

of one cage from one boron to another of the second cage by way of a three-center bonded intermediate or transition state (Fig. 15). The structures of the cobalt derivatives of $(2,3\text{-}Me_2C_2B_4H_5)_2$ could not be completely determined but a general reaction scheme was provided (Fig. 16).

Todd and coworkers have reported an improved preparation of $B_9H_{11}C\text{-}NMe_3$ and converted this compound to $(C_5H_5)CoB_9H_9C\text{-}NMe_3$, which undergoes rapid interchange of some of the boron atom positions at 70 °C. Treatment of $B_9H_{11}C\text{-}NMe_3$ with sodium polyselenide in ethanol has produced a low yield of $SeB_9H_9C\text{-}NMe_3$ [7].

The triple-decker sandwich compounds $(C_5H_5)Co(C_2B_3H_5)Co(C_5H_5)$ (two isomers of $C_2B_3H_5$ ring) have been studied electrochemically and found to yield -1, -2, and +1 ions reversibly, and a +2 ion irreversibly [8]. Magnetic susceptibility data have been obtained for salts of $Cr(C_2B_{10}H_{12})_2^{2-}$ and $Cr(C_2B_{10}H_{12})_2^{-}$ in the temperature range 1.4-80 K [9].

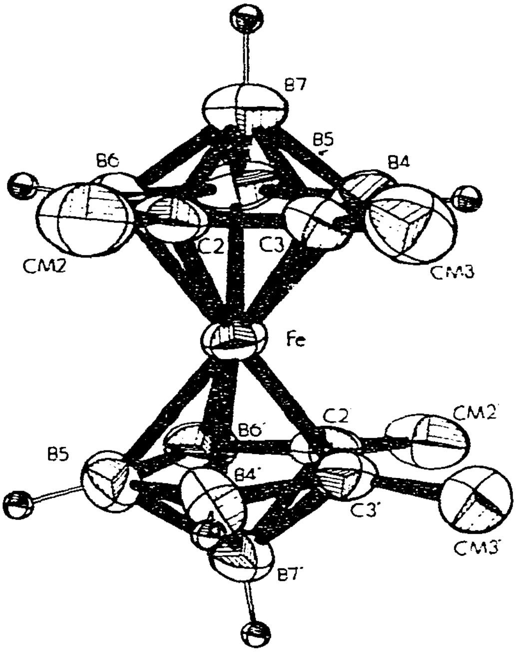

Figure 11. The structure of $(2,3\text{-}Me_2C_2B_4H_4)_2FeH_2$, with nonhydrogen atoms shown as 50% probability ellipsoids and B-H hydrogens as small spheres. There are two hydrogen atoms not located which are believed to be bound to the FeB_2 triangular faces and to tautomerize rapidly between several bridging positions. [Reprinted with permission from J. R. Pipal and R. N. Grimes, Inorg. Chem., 18 (1979) 265. Copyright by the American Chemical Society.]

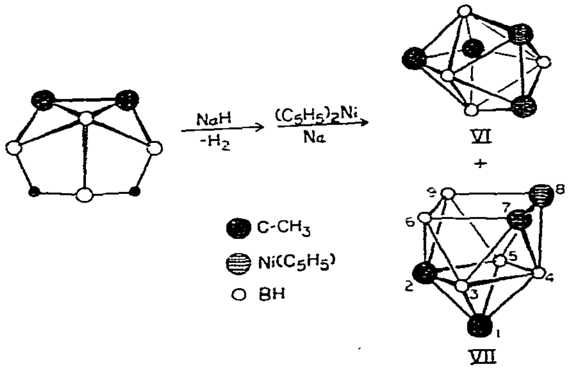

Figure 12. Reaction scheme for the synthesis of $(C_5H_5)_2Ni_2Me_2C_2B_4H_4$ (VI) and $(C_5H_5)_2Ni_2Me_2C_2B_5H_5$ (VII), showing proposed structures. [Reprinted with permission from J. R. Bowser, A. Bonny, J. R. Pipal, and R. N. Grimes, J. Am. Chem. Soc., 101 (1979) 6233. Copyright by the American Chemical Society.]

3. Rhodacarboranes. These are set apart from the other icosahedral metallacarboranes (Section B4) because of their catalytic activity. Hawthorne and coworkers originated this work and continue to be the leading contributors.

Reaction of 3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$ with sulfuric acid results in evolution of hydrogen gas and formation of the bisulfate of the rhodacarborane, 3,3-$(Ph_3P)_2$-3-(HSO_4)-3,1,2-$RhC_2B_9H_{11}$, which was isolated as the crystalline monoetherate and characterized by X-ray crystallography (Fig. 17) [10]. Reaction of this rhodacarborane bisulfate with hydrogen in THF regenerates the original hydridorhodacarborane, and reaction of the rhodacarborane bisulfate with ethanol or propanol yields the hydridorhodacarborane and acetaldehyde or propionaldehyde, respectively.

The rhodacarborane 3,3-$(PPh_3)_2$-4-C_5H_5N-3,1,2-$RhC_2B_9H_{10}$ has been synthesized from the corresponding dicarbollide anion and $RhCl(PPh_3)_2$, and has been found to be a catalyst for the hydroformylation reaction. Treatment of this compound with CO yields 3-PPh_3-3-CO-4-C_5H_5N-3,1,2-$RhC_2B_9H_{10}$, also catalytically active, the structure of which has been determined by X-ray crystallography (Fig. 18) [11].

Nitric acid converts 3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$ to a derivative having two oxygens of a nitrate ion bonded to the rhodium, 3-(PPh_3)-3,3-(NO_3)-3,1,2-$RhC_2B_9H_{11}$, the structure of which has been determined by X-ray crystallography (Fig. 19) [12].

The rhodacarborane 3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$, its 1-Ph derivative, and its m-carborane isomer, known from Hawthorne's work to be active catalysts for hydrogenation and isomerization of alkenes [JOM 98 (1975) 316-317], have been reported by Zakharkin and Agakhanova to catalyze such isomerizations as $R\text{-}CH{=}CH\text{-}CH_2OH$ to $R\text{-}CH_2CH_2CHO$ and $R\text{-}CHOH\text{-}CH{=}CH_2$ to $RCOCH_2CH_3$ [13]. The rhodacarborane 3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$ and its 1-Ph derivative also catalyze the reaction of $PhMe_2SiH$ with ketones to form a mixture of silyl enol ethers and secondary alcohol silyl ethers [14].

Electrochemical reduction of $(C_2B_9H_{11})_2Rh^-$ reversibly yields unstable $(C_2B_9H_{11})_2Rh^{2-}$ [15].

4. Icosahedral Metallacarboranes (Dicarbollides). This series of compounds has been known for many years, and most recent contributions are studies of physical and chemical properties rather than syntheses of new compounds. For the numbering of icosahedral cages, see the rhodacarborane structures illustrated in Section B3 and the icosahedral numbering scheme illustrated in Section D1.

The structure of 3,3-(Et_3P)-3-Pt-1,2-$C_2B_9H_{11}$ has been found by X-ray crystallography to have a highly distorted or "slipped" icosahedral cage, in accord with extended Hückel calculations [16]. The cage geometry resembles that of analogous nickel and copper systems, as well as an $L_2AuC_2B_9H_{11}$ compound [structure shown in JOM 147 (1977) 31].

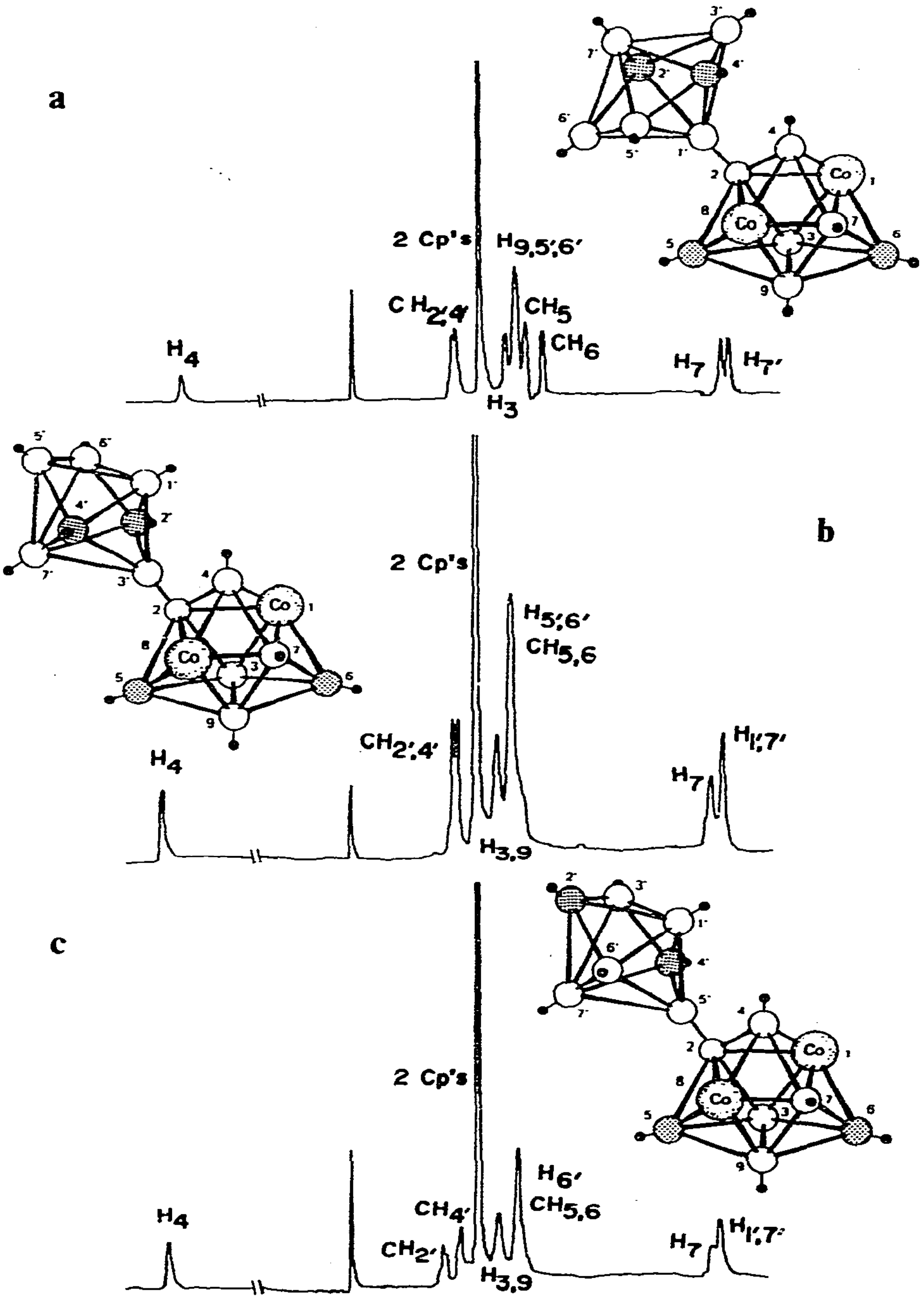

Figure 13.

^{11}B-Decoupled 100-MHz ^{1}H NMR spectra of cobaltacarboranes derived from $(2,4\text{-}C_2B_5H_6)_2$ and $(C_5H_5)Co(CO)_2$. The Co atoms bear C_5H_5 ligands, omitted for clarity. Open circles represent boron, shaded circles carbon, and black dots hydrogen atoms. The unassigned peak to the right of the break marks is resid-

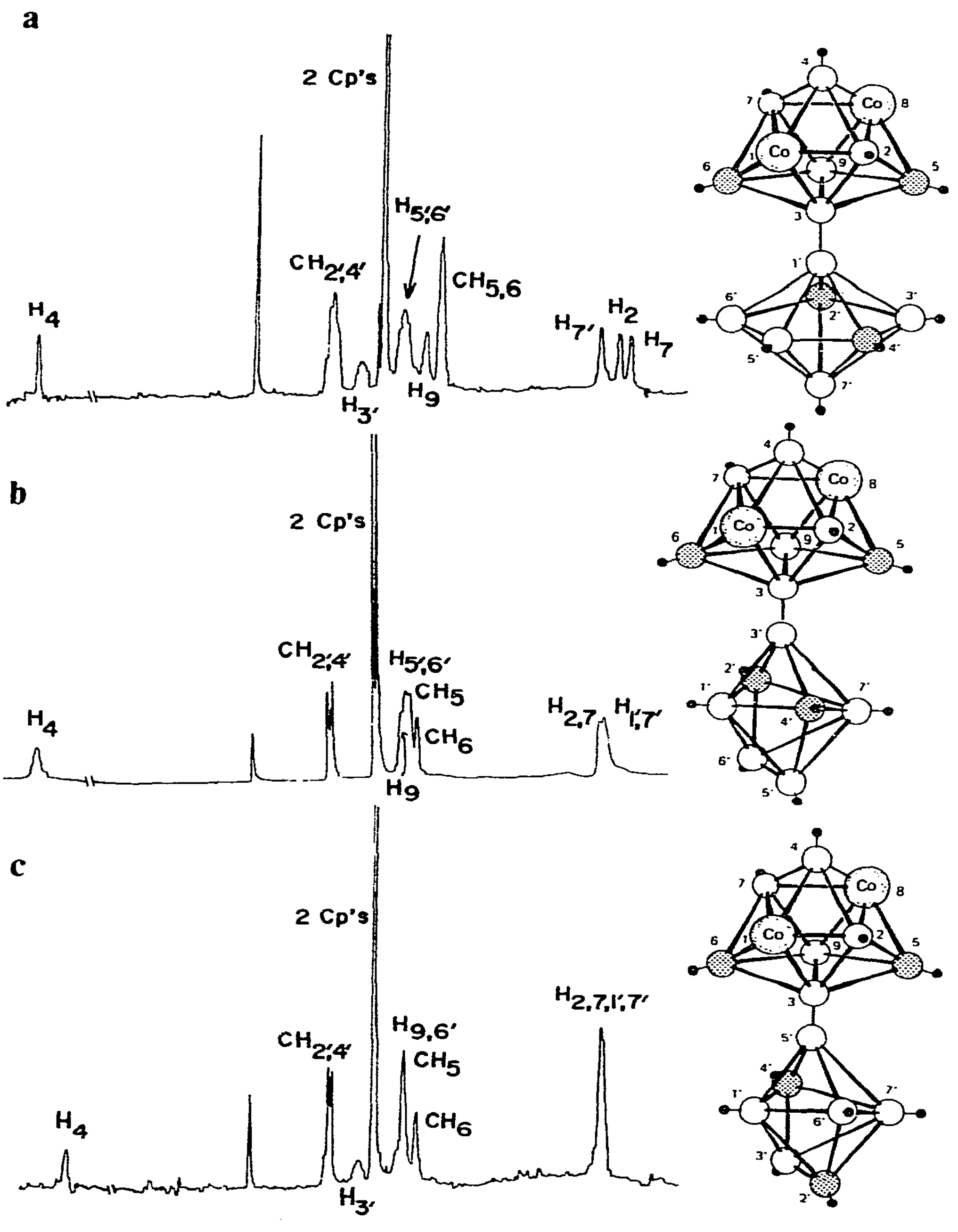

Figure 14.

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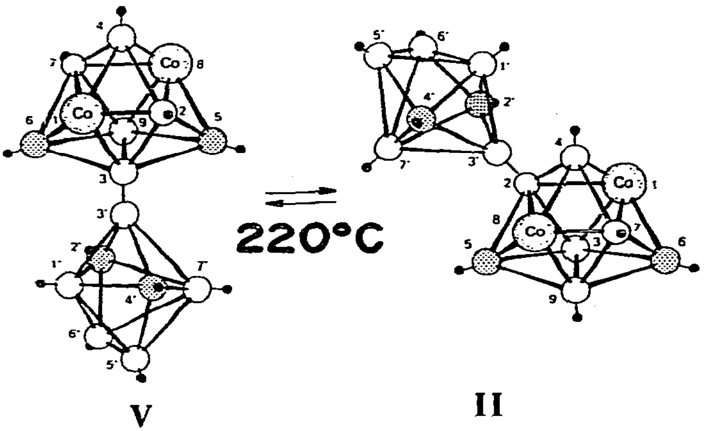


Figure 15. Isomerization of carboranyldicobaltacarboranes at 220 °C. [Reprinted with permission from J. S. Plotkin and L. G. Sneddon, Inorg. Chem., 18 (1979) 2171. Copyright by the American Chemical Society.]

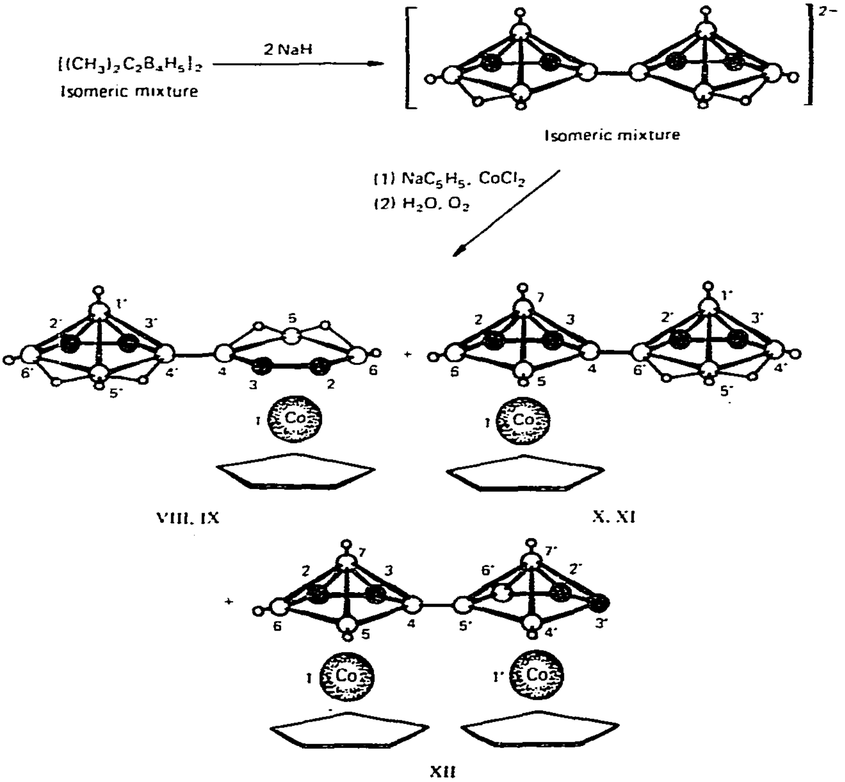


Figure 16. Reaction scheme for the synthesis of sandwich complexes from $(2,3\text{-}Me_2C_2B_4H_5)_2$. The structures labelled VIII, IX and X, XI represent only one possibility for each of the observed isomer pairs, the specific structures of which could not be determined. Open circles represent B, large solid circles $C\text{-}CH_3$, and small open circles H. [Reprinted with permission from J. S. Plotkin and L. G. Sneddon, Inorg. Chem., 18 (1979) 2172. © American Chemical Society.]

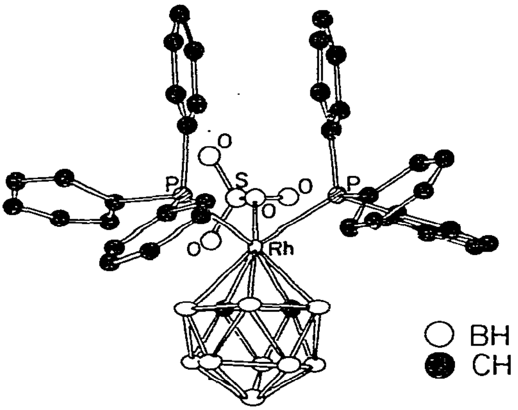


Figure 17. The molecular geometry of $3,3\text{-}(Ph_3P)_2\text{-}3\text{-}(HSO_4)\text{-}3,1,2\text{-}RhC_2B_9H_{11}$. The ether molecule and hydrogen atoms have been omitted for clarity. Bond distances include Rh-B (av) = 2.243 (18), Rh-C (av) = 2.182 (14), Rh-P (av) = 2.387 (4), Rh-O = 2.243 (8), B-B (av) = 1.806 (8), C-B (av) = 1.723, carborane C-C = 1.682 (17) Å. The P-Rh-P bond angle is 98.7 (1)°. [Reprinted with permission from W. C. Kalb, R. G. Teller, and M. F. Hawthorne, J. Am. Chem. Soc., 101 (1979) 5418. Copyright by the American Chemical Society.]

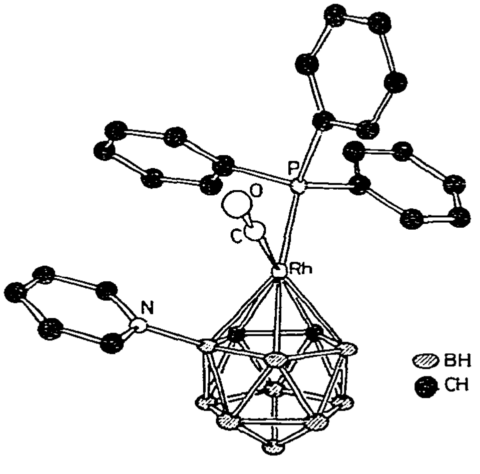


Figure 18. The structure of $3\text{-}PPh_3\text{-}3\text{-}CO\text{-}4\text{-}C_5H_5N\text{-}3,1,2\text{-}RhC_2B_9H_{10}$. [Reprinted with permission from R. G. Teller, J. J. Wilczynski, and M. F. Hawthorne, J. Chem. Soc., Chem. Commun., (1979) 472. Copyright by the Chemical Society (London).]

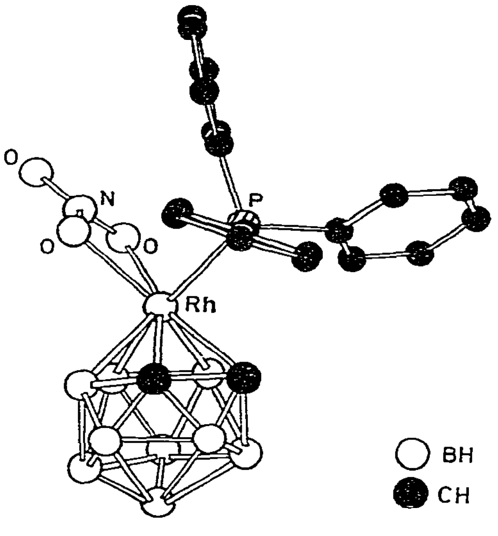
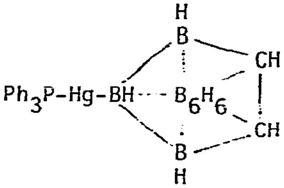


Figure 19. The structure of $3\text{-}PPh_3\text{-}3,3\text{-}(NO_3)\text{-}3,1,2\text{-}RhC_2B_9H_{11}$. [Reprinted with permission from Z. Demidowicz, R. G. Teller, and M. F. Hawthorne, J. Chem. Soc., Chem. Commun., (1979) 832. Copyright by the Chemical Society (London).]

A series of copper(I), gold(I), and mercury(II) derivatives of o-$C_2B_9H_{11}{}^{2-}$ have been prepared, and the structure of the mercury compound $Ph_3PHgC_2B_9H_{11}$ has been determined by X-ray crystallography and found to have the mercury bonded to the boron atom at the 10-position, with a bond distance of 2.20 Å [17].



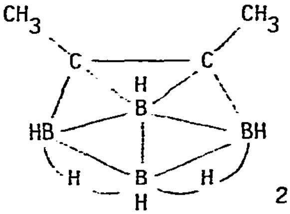
Cyclic voltammetry studies of $(C_5H_5)Co(C_2B_9H_{11})$, $(C_5H_5)Co(C_2B_9H_8Br_3)$, and $Co(C_2B_9H_{11})_2^-$ in the presence of phenol have been reported, and it was concluded that in the cyclopentadienyl compounds the cyclopentadiene ring was protonated directly without formation of any Co-H bonded intermediate [18].

Thallium(III) trifluoroacetate introduces a trifluoroacetoxy group at the 8-position of 3-(C_5H_5)-3,1,2-$FeC_2B_9H_{11}$ [19]. Bromination of (o-$C_2B_9H_{11})_2Co^-$ in methanol has yielded the 8,8'-dibromo derivative, which is the same as the product obtained by radiolysis of $(C_2B_9H_{11})_2Co^-$ in $CHBr_3/PhNO_2$ [20]. 3-(C_5H_5)-3-Co-1,2-$C_2B_9H_{11}$ exchanges carbon-bound protons from the carborane cage 100 times faster than the cyclopentadienyl protons [21]. ^{59}Co NQR data have been reported for 3-(C_5H_5)-3,1,2-$CoC_2B_9H_{11}$ and a series of derivatives [22]. High pressure liquid chromatography has been investigated as a tool for separating metallocarboranes such as 3-(C_5H_5)-3-Co-1,2-$C_2B_9H_{11}$ and related compounds [23]. The thermal decomposition of (o- and m-$C_2B_9H_{11})_2Ni^{IV}$ to B_7 and B_9 carboranes has been reported [24].

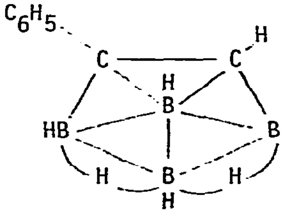
C. Small and Medium Cages

Synthetic and physical studies have been reported for a variety of compounds in this category, which includes all cage sizes up to and including C_2B_9, 11 atoms. Preparations which involved metallacarboranes have been included in Sections B1 and B2.

Hosmane and Grimes have reported bench scale preparation of 2,3-$Me_2C_2B_4H_6$ and 2-$PhC_2B_4H_7$ in quantities of a gram or two, starting from B_5H_9 or $B_3H_8^-$, the appropriate acetylene, and triethylamine [25]. However, this liquid phase type of reaction failed to yield the parent $C_2B_4H_8$ because acetylene/pentaborane mixtures polymerize in the presence of a Lewis base.



2,3-Me_2-2,3-$C_2B_4H_6$



2-Ph-2,3-$C_2B_4H_7$

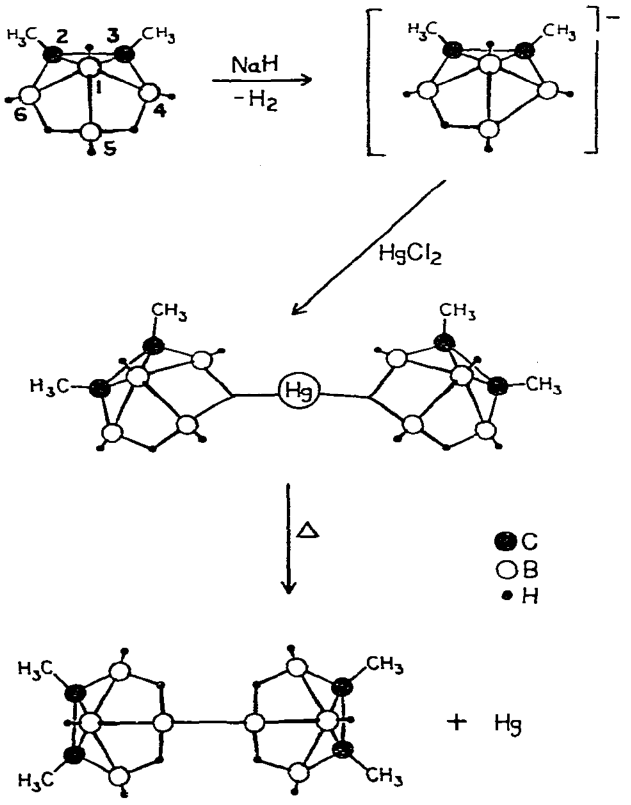


Figure 20. Scheme for conversion of 2,3-$Me_2C_2B_4H_6$ to μ,μ'-$(Me_2C_2B_4H_5)_2Hg$ and then 5,5'-$(Me_2C_2B_4H_5)_2$. The mercury compound is shown as the isomer having $\underline{C}_s$ symmetry, but presumably exists as a mixture of $\underline{C}_s$ and $\underline{C}_2$ isomers, with free rotation about the B_2-Hg bond axes. [Reprinted with permission from N. S. Hosmane and R. N. Grimes, Inorg. Chem., 18 (1979) 2887. Copyright by the American Chemical Society.]

Reaction of 2,3-$Me_2C_2B_4H_5^-$ with $HgCl_2$ has yielded μ,μ'-$(Me_2C_2B_4H_5)_2Hg$, which is linked by three-center B_2Hg bridge bonds [26]. At 180 °C this compound decomposes to metallic mercury and a single carborane product, 5,5'-$(Me_2C_2B_4H_5)_2$ (Fig. 20). The $(Me_2C_2B_4H_5)_2$ is air sensitive, and in benzene solution in the presence of oxygen undergoes an unusual oxidative addition to form 4-Ph-2,3-$Me_2C_2B_4H_5$ (Fig. 21).

Onak and coworkers have studied the thermal isomerization of a series of B-methylated 2,4-*closo*-dicarbaheptaboranes at 300 °C and found that statistically corrected equilibrium values favor methyl substitution at position 3 followed by 1 and 7 with 5 and 6 least favored [27]. The mechanism is believed to involve diamond-square-diamond rearrangement (Fig. 22) or perhaps cage triangle rotation.

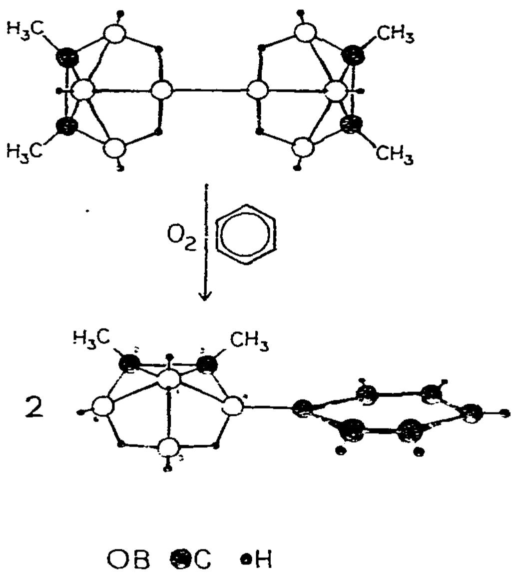


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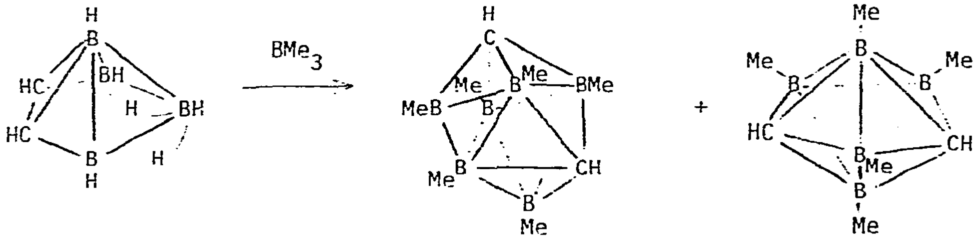
Figure 21. Scheme for reaction of 5,5'-$(Me_2C_2B_4H_5)_2$ with oxygen and benzene to form 4-Ph-2,3-$Me_2C_2B_4H_5$.

Reaction of 2,3-$C_2B_4H_8$ with trimethylborane at 220-240 °C yields a mixture of the cage-expanded products B-Me_5-closo-2,4-$C_2B_5H_2$, B-Me_6-closo-$C_2B_6H_2$, and analogues having fewer B-methyl groups [28].



Cage expansion of closo-1,6-$C_2B_4H_6$ with trimethylborane occurs at 550-600 °C to yield B-Me_2-closo-2,4-$C_2B_5H_5$ [28].

Mercury atoms excited by 2537-Å ultraviolet light have sufficient energy to break B-H bonds, yielding a boron radical, a hydrogen atom, and ground state mercury. Mercury-sensitized photolysis of small carboranes, including 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, 2,3-$C_2B_4H_8$, and 2,3-Me_2-2,3-$C_2B_4H_6$, as well as pentaborane and related compounds, has been reported by Plotkin, Astheimer, and Sneddon [29]. The most successful results were obtained with 2,4-$C_2B_5H_7$, which under proper conditions gave high yields of a mixture of isomers of $(2,4\text{-}C_2B_5H_6)_2$.

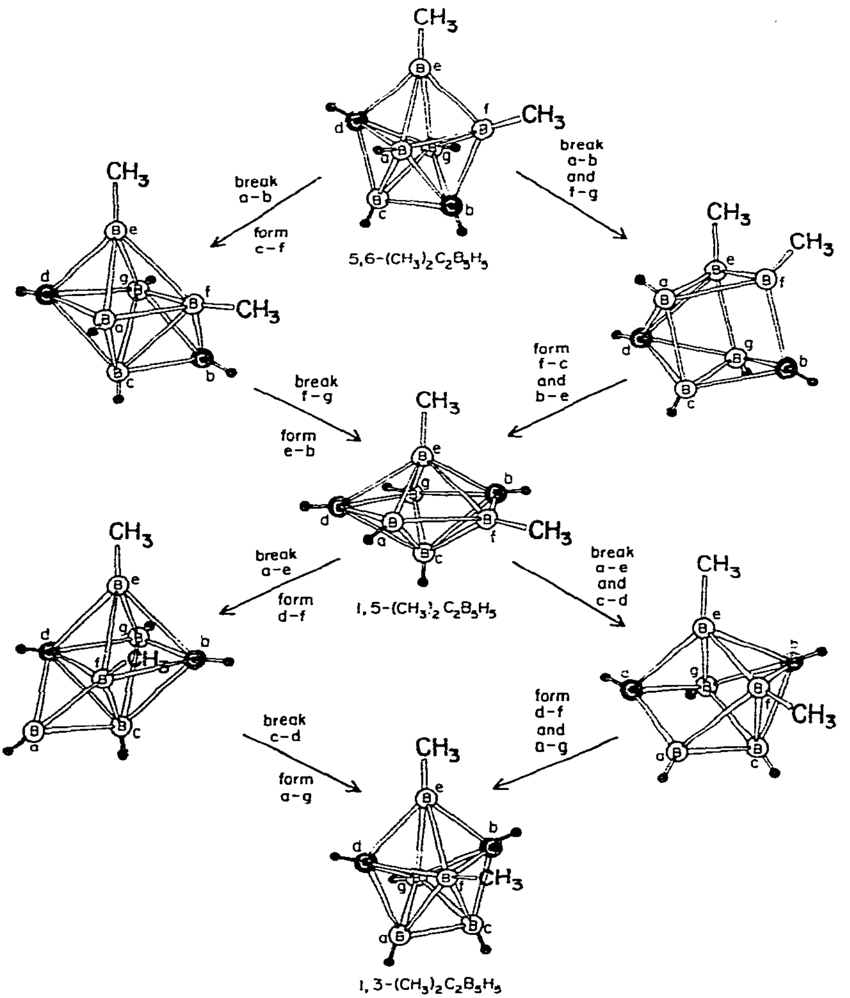
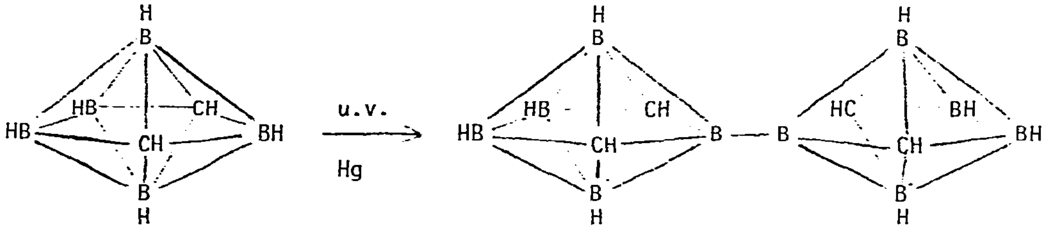


Figure 22. Partial mechanistic scheme for the diamond-square-diamond rearrangement of 5,6-Me_2-2,4-$C_2B_5H_5$. [Reprinted with permission from T. Onak, A. P. Fung, G. Siwapinyoyos, and J. B. Leach, Inorg. Chem., 18 (1979) 2881. Copyright by the American Chemical Society.]

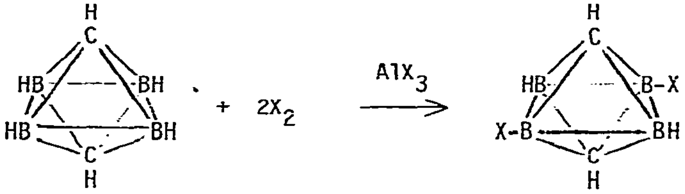


and other B-B bonded isomers

The proton-decoupled ^{11}B NMR spectra of 1,2'-$(B_5H_8)_2$ and 1,5'-(2,4-$C_2B_5H_6)_2$

show B-B coupling constants of 106 and 109 Hz, respectively, between the boron atoms linking the cages [30].

The photoelectron spectra of 2-halo- and 2,4-dihalo-1,6-dicarba-closo-hexaboranes and the synthesis of the latter have been reported [31]. The surface orbitals of the cluster play an important role in determining the effect of substitution on the cluster properties.



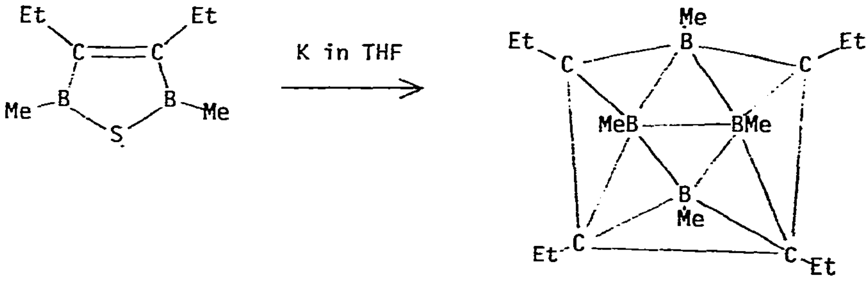
(X = Cl, Br, I)

Oxidation of K^+ 7,8-$C_2B_9H_{12}^-$ with $FeCl_3$ has yielded 10-Cl-5,6-$C_2B_8H_{11}$, 5,6-$C_2B_8H_{11}OH$ (position of OH uncertain), 4,5-$C_2B_7H_{11}$, and the previously reported 5,6-$C_2B_8H_{12}$ [32].

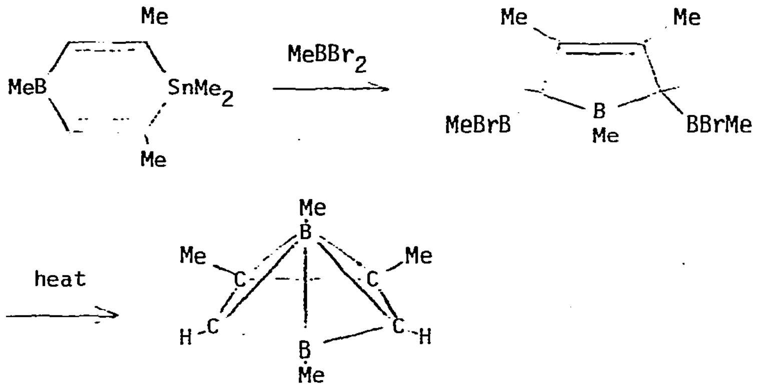
The pK_a's of H_2-7,8-$C_2B_9H_{11}$ in aqueous solution have been measured potentiometrically and spectrophotometrically and found to be 2.98 and 14.25 [33]. The 70.6-MHz ^{11}B NMR spectra of a series of derivatives of 4,7-$(HO)_2$-2,3-Me_2-2,3-$C_2B_9H_7$ have been reported and the specific boron resonances assigned [34].

Several isomers of Me_2S^+-$C_2B_9H_{11}^-$ have been prepared, including 7-(Me_2S)-7,8-$C_2B_9H_{11}$ from degradation of 1-MeS-1,2-$C_2B_{10}H_{11}$ followed by methylation, 5-(Me_2S)-7,8-$C_2B_9H_{11}$ from similar treatment of 9-MeS-1,2-$C_2B_{10}H_{11}$, 9-(Me_2S)-7,8-$C_2B_9H_{11}$ from Me_2SO and 7,8-$C_2B_9H_{12}^-$, 8-(Me_2S)-7,9-$C_2B_9H_{11}$ from Me_2SO and 7,9-$C_2B_9H_{12}^-$, and 10-(Me_2S)-7,9-$C_2B_9H_{11}$ from 2,3-$C_2B_9H_{11}$ and Me_2S [35]. Treatment of $(1,2\text{-}C_2B_9H_{11})_2Co^-$ with Me_2SO yielded 8-(Me_2S)-1,2-$C_2B_9H_{10}$Co-1,2-$C_2B_9H_{11}$.

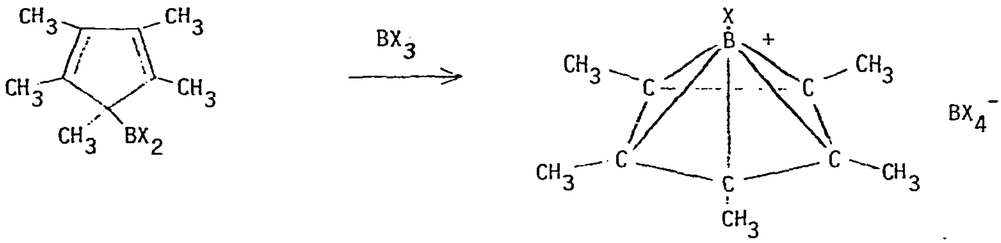
A C_4B_4-carborane has been obtained by treatment of a peralkyl 1,2,5-thiadiborolene with potassium in tetrahydrofuran [36]. The structure is supported by NMR evidence and similarity to a previously reported C_4B_4 cage [JOM 163 (1978) 26].



Alkylated two-boron carboranes have been synthesized [37].

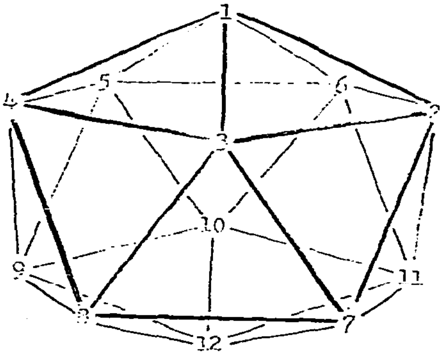


Halide abstraction from permethylcyclopentadienylboron dihalides leads to one-boron carborane cations [38].

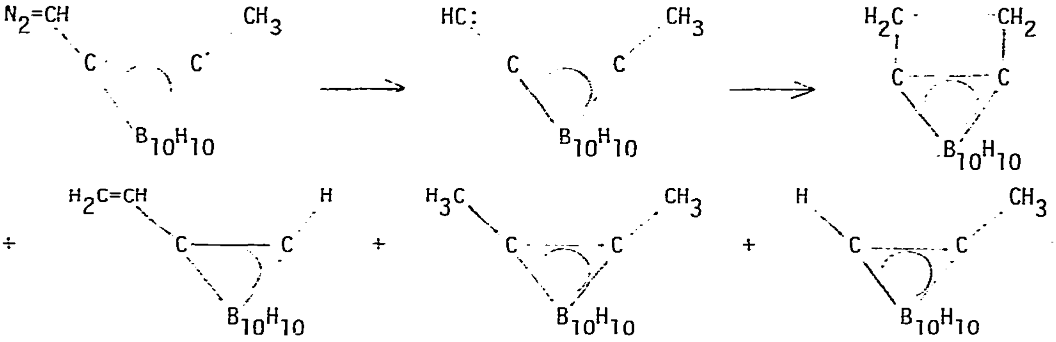


D. Icosahedral Cages

1. *Syntheses*. The stable icosahedral carboranes are a well known class of compounds, and most of the recent synthetic efforts have been directed toward introducing an even wider variety of substituents. Those which seem to have some degree of mechanistic or biochemical interest are covered first. The nonsystematic but convenient designations *o*-, *m*-, and *p*-carborane are often used for the 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaborane isomers, respectively. The numbering system for the icosahedron is illustrated below.



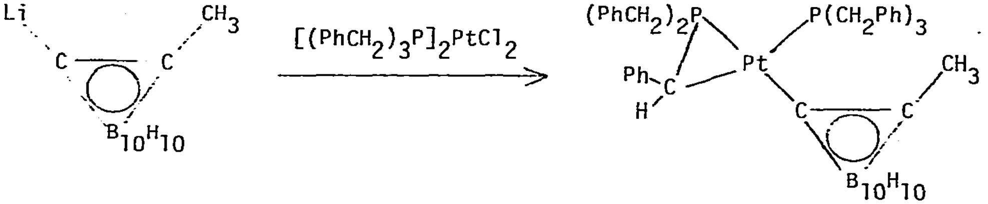
Passage of 1-diazomethyl-2-methyl-o-carborane through a hot tube (400-500 °C) at low pressure (10^{-3} Torr) results in formation of a carboranylcarbene, which rearranges mainly to cyclobutanocarborane and lesser amounts of vinylcarborane, methylcarborane, and dimethylcarborane [39]. It was shown by ^{13}C labeling that the terminal carbon of the vinyl group of the vinylcarborane is derived from the methyl group of the starting material.



Several polypeptides containing a carboranylalanine residue have been prepared, including analogues of bradykinin, enkephalin, and angiotensin [40]. An improved preparation of carboranylalanine and its incorporation into an enkephalin analogue have been described [41]. The carborane analogue had a higher affinity for rat brain opiate receptors than the natural enkephalin.

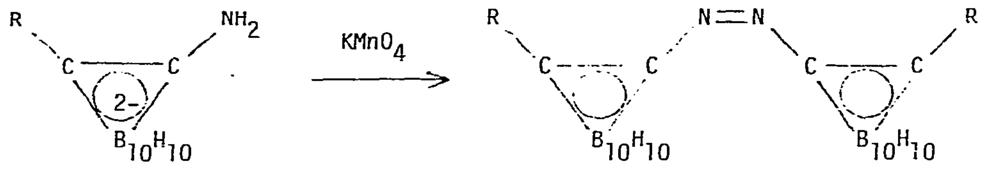
Carboranyl-substituted porphyrins [see JOM 180 (1979) 32 for a representative structure] form cobalt complexes which bind reversibly with O_2 [42].

Reaction of cis-$[(PhCH_2)_3P]_2PtCl_2$ with 1-lithio-2-methyl-o-carborane yields a carboranylplatinum compound containing a three-membered Pt-P-C ring derived from one of the benzylphosphine ligands. The structure has been established by X-ray crystallography [43].



Reaction of m-Ph-$CB_{10}H_{10}C$-Ir(CO)$(PPh_3)_2$ with RCN yields Ph-$CB_{10}H_{10}C$-Ir(CO)(RCN)(PPh_3), which readily adds molecular hydrogen to form an octahedral complex, which can undergo further substitution reactions [44].

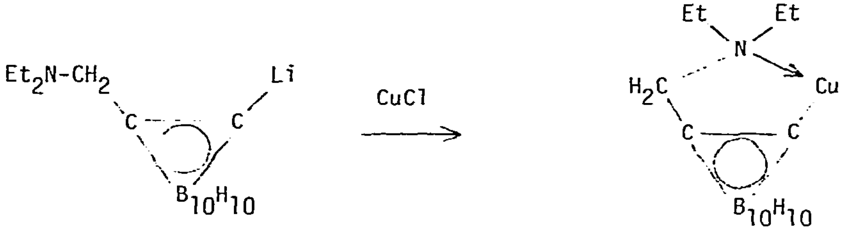
Oxidation of anions from reduction of o-$RCB_{10}H_{10}CNH_2$ with Na in liquid NH_3 has yielded azo compounds [45].



(R = H, CH_3, Ph)

Reaction of *o*-Me_2CH-$CB_{10}H_{10}C$-BBu_2 with acetic acid results in cleavage of a B-Bu bond to form Me_2CH-$CB_{10}H_{10}C$-B(Bu)OAc, and reaction with MeOH or BuSH in the presence of tertiary amines or THF results in cleavage of the carboranyl group to form Me_2CH-$CB_{10}H_{10}CH$ and $MeOBBu_2$ or $BuSBBu_2$ [46]. With aldehydes, RCHO, Me_2CH-$CB_{10}H_{10}C$-BBu_2 is cleaved at 50-100 °C to give mainly Me_2CH-$CB_{10}H_{10}C$-B(Bu)OCH_2R, but at 140-150 °C to give mostly Me_2CH-$CB_{10}H_{10}C$-H [47]. Me_2CH-$CB_{10}H_{10}C$-BBu_2 with PhCN in $(Me_2N)_3PO$ followed by methanolysis yielded Me_2CH-$CB_{10}H_{10}C$-C(=NH)Ph [48].

Copper, palladium, and platinum derivatives of 2-dialkylaminomethyl-*o*-carboranes have chelate structures [49].



Treatment of *o*-, *m*-, or *p*-$RCB_{10}H_{10}CLi$ with EtO-PClMe has yielded the corresponding phosphinites, $RCB_{10}H_{10}C$-P(OEt)Me, and the reactions of these with *p*-nitrophenyl azide, chlorine, methyl iodide, methyl sulfate, and chloral have been investigated [50]. Reactions of lithiocarboranes with $ClP(NEt_2)_2$ and $ClP(O)(OEt)_2$ to give the corresponding phosphorus derivatives have been reported [51]. Several *B*-sulfur substituted *o*- and *m*-carboranes have been prepared, including disulfides, methylthio, sulfinic acid, sulfonic acid, and sulfone derivatives [52].

Lithiocarboranes react with $ClCH_2SiMe_2OMe$ to form carboranyl-CH_2SiMe_2OMe [53]. Protodesilylation of silylated *m*-carboranes with KF in methanol has been patented [54]. Reduction of *o*- or *m*-$RCB_{10}H_{10}CCOCl$ with Et_3SiH over a 5% Pd/C catalyst yields $RCB_{10}H_{10}CCHO$ [55].

Decarboxylation of various mercury(II) carboranylcarboxylates has yielded the corresponding *B*- or *C*-bonded carboranylmercury compounds [56].

Treatment of *o*- or *m*-$CuCB_{10}H_{10}CH$ with ICH=CHX (X = H, Cl, I) has yielded $HCB_{10}H_{10}C$-CH=CHX, and *m*-$CuCB_{10}H_{10}CCu$ has been converted to $ICH=CHCB_{10}H_{10}CCH=CHI$ [57]. Allenyl *o*- and *m*-carboranes have been prepared from $CuCB_{10}H_{10}CH$ and propargyl bromide [58].

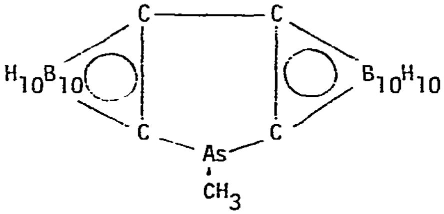
o-$CH_3CB_{10}H_{10}CLi$ opens butadiene epoxide to form both isomeric alcohols, which have been converted to the acetates and pyrolyzed to 1- and 2-(carboranyl)-butadiene [59]. Oxidative and acid openings of the three-membered thiirane ring have been reported for carboranylmethylthiiranes [60]. $RCB_{10}H_{10}C\text{-}CH{=}CH\text{-}CH_2Li$ reacts as would be expected at the terminal carbon with Me_3SiCl and other electrophiles [61].

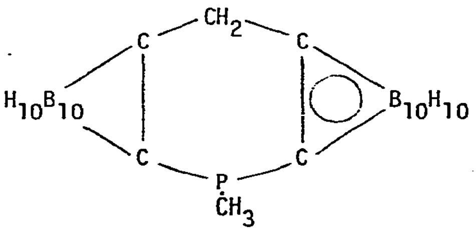
Gas phase isomerization of 3-aryl-o-carboranes at 550-600 °C in a flow system yields equal amounts of 2- and 4-aryl-m-carboranes, which are easily separable by column chromatography [62]. The standard carborane synthesis from acetylenes and decaborane has been used to prepare 1,2-bis(p-halophenyl)-o-carboranes [63]. Oxidation of 4-(o- or m-1-carboranyl)-2,6-di-t-butylphenols leads to free radicals having the unpaired electron in the carboranyl group, and a rearrangement of a m-carboranyl- to an o-carboranyl group was observed [64].

Reaction of perfluoroacyl hydrazides with 1,7-$ClCOCB_{10}H_{10}CCOCl$ has yielded 1,7-$R_FCONHNHCOCB_{10}H_{10}CCONHNHCOR_F$ [65]. Several o-carborane derivatives, R-$CB_{10}H_{10}CH$ (R = H, Me, Ph, isopropenyl, cyanoethyl) have been cyanoethylated with acrylonitrile in the presence of trimethylbenzylammonium hydroxide to form R-$CB_{10}H_{10}C\text{-}CH_2CH_2CN$ [66]. m-$HCB_{10}H_9CH$-10-COCl has been converted to the 10-CO-O-O-t-Bu and 10-CO_2CH_2-O-O-t-Bu derivatives [67], and several t-Bu-O-O-$SiMe_2$-carboranes have been prepared from t-Bu-O-O-$SiMe_2Cl$ and carboranyllithiums [68]. Unsymmetrical diacyl peroxides of the general formula m-$HCB_{10}H_{10}C$-CO-OO-COAr have been prepared [69]. Cyclization of some aryl- and alkenyl-carborane alcohols by polyphosphoric acid has been described [70]. o-Carborane catalyzes the thermal trimerization and oligomerization of isophthalonitrile [71].

2. Physical Measurements. Raman spectra of a series of bis(carboranyl)-mercury isomers, carboranylmercury halides and alkyls, and bis(carboranyl)-thallium chlorides all show strong polarized lines in the region 130-180 cm^{-1}, which appear to result from a metal-cage stretching vibration, in which the entire carborane cage behaves as a rigid body pseudoatom [72].

The structures of two bis(carboranyl) heterocycles have been determined by X-ray crystallography [73].





Electron diffraction indicates a C-I bond length of 2.08 Å in m-$ICB_{10}H_{10}CI$ [74].

A study of pK_a's of a series of carboranylthioacetic acids and their correlation with the pK_a's of mercaptocarboranes has been published [75]. ^{13}C NMR spectra of a long series of 1-substituted carboranes have been determined and correlated with structure [76]. NMR data indicate C-C rotational barriers of 13.6 and 14.5 kcal/mol in 2-PhCH$_2$- and 2-PhCHCl-1-(*o*-*i*-PrC$_6$H$_4$-)-1,2-C$_2$B$_{10}$H$_{10}$ [77]. The relationship between dipole moments and conformations of diarylcarboranes has been studied [78]. Gas chromatography of carboranes has been reported [79].

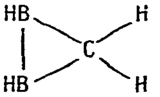
E. Calculations and Theory

Lipscomb has discussed the bonding in distorted 12-vertex, 28-electron cages such as $(C_5H_5)_2Co_2Me_4C_4B_6H_6$, which show considerable separation between the adjacent pairs of carbon atoms and a tendency to localize the bonding as if the cage consisted of two $C_2B_4H_6$ groups (or equivalent $C_2B_3H_5Co(C_5H_5)$ groups, with cobalt in place of boron) fused at the boron atoms along one edge [80].

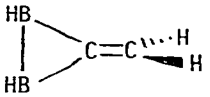
Lipscomb has pointed out that his *styx* valence rules for boron hydrides B_pH_{p+q}, which are based on the electron count in the inner polyhedral surface, are equivalent to Wade's rules for formulation of closo, nido, arachno, and hypho boron hydrides [81].

Kleier and Lipscomb have reported PRDDO calculations for various geometries of $B_8H_8^{2-}$ in a theoretical study of its fluxional behavior [82]. Molecular orbital calculations of the PRDDO type have been carried out on a series of beryllaboranes of the general formula $B_5H_{10}BeX$, where X = BH_4, B_5H_{10}, CH_3, or C_5H_5 [83]. PRDDO calculations on polymeric solid-state beryllium borohydride have been reported [84]. Calculations on B_2H_6, BH_3CO, and BH_3NH_3 using many body perturbation theory have been reported [85].

Calculations of the STO-3G and related types have suggested that planar carbon would be the favored geometry in diboracyclopropane and related systems [86].



Calculated to be planar



Calculated to be perpendicular

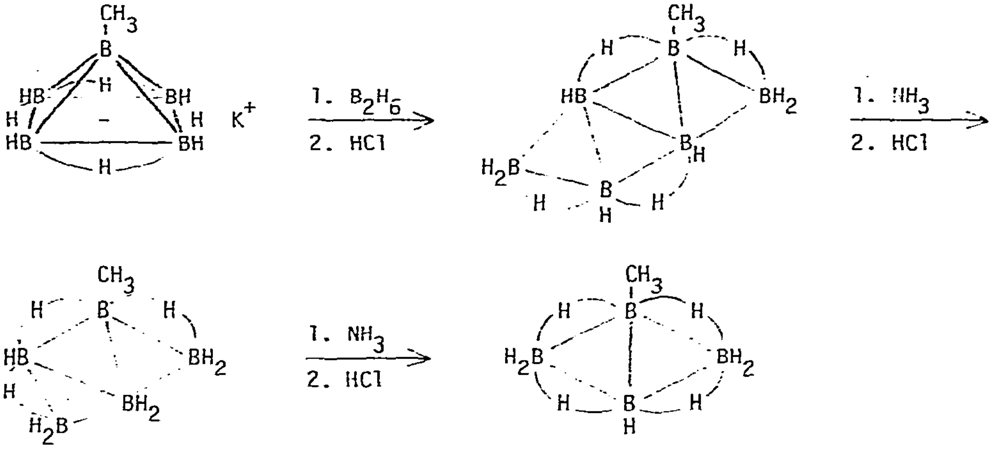
Capturing these species in a bottle or microwave waveguide does not seem too likely, and transition metal analogues of this type of bonding were suggested as perhaps more feasible experimental goals [86].

A theoretical interpretation based on the structures of *hypho* borane clusters and carboranes can be extended to account for the puckered structure of cyclobutane [87].

CNDO/2 calculations on *p*-carborane have been reported [88].

F. Boron Cages Without Carbon

1. Polyhedral Boranes. Regiospecific syntheses of 3-$CH_3B_6H_{11}$, 3-$CH_3B_5H_{10}$, and 1-$CH_3B_4H_9$ have been reported by Shore and coworkers [89].



The bis(pentaboranyls) 1,2'-$(B_5H_8)_2$ and 2,2'-$(B_5H_8)_2$ have been synthesized [90].

Passing BCl_3 through a radio frequency discharge has yielded 3 to 5 mg of B_4Cl_4 per hour [91].

Hexamethylenetetramine reacts with B_5H_{11} in chloroform to form $(CH_2)_6N_4B_4H_8$, with B_4H_{10} to form $(CH_2)_6N_4{\cdot}2B_3H_7{\cdot}2BH_3$, and with $THF{\cdot}B_3H_7$ to form $(CH_2)_6N_4{\cdot}2B_3H_7$ [92]. Reaction of $R_2SB_4H_8$ or B_5H_{11} with trimethylamine yields $Me_3NB_4H_8$ [93]. The preparation of $B_4H_8(PMe_3)_2$ and related compounds has been reported [94]. ^1H, ^{11}B, ^{19}F, and ^{31}P NMR studies have indicated the existence of two geometric isomers of $B_4H_8PF_2NMe_2$ in solution [95].

1,8-Bis(dimethylamino)naphthalene, which is highly basic but weakly nucleophilic, deprotonates $B_{10}H_{14}$ to $B_{10}H_{13}^-$ and converts B_5H_9 to $B_9H_{14}^-$ [96]. NMR studies have indicated a transition between anisotropic and isotropic molecular tumbling of $B_{10}H_{14}$ in $C_6D_5CD_3$ solution between -35 and +25 °C [97]. The structure of a $B_{20}H_{26}$ isomer, 1,5'-bidecaboran(14)yl, has been determined by X-ray crystallography [98]. The structure of a $B_{20}H_{26}$ isomer obtained from thermolysis of decaborane in the presence of tetrahydrothiophene has been identified as 6,6'-bis(nido-decaboranyl) by ^{11}B NMR [99]. Another $B_{20}H_{26}$ isomer from photolysis of $B_{10}H_{14}$ has been shown to be 2,2'-bis(nido-decaboranyl) by X-ray crystallography [100].

Partial hydrolysis of $B_3H_8^-$ at -78 °C has yielded $B_3H_7OH_2$, which is converted by base to $B_3H_7OH^-$ [101]. $B_3H_7OH_2$ solutions decompose at -45 °C to yield boric acid and hydrogen, and $B_3H_7OH^-$ decomposes above -65 °C to borohydride and borate.

Diborane and methyllithium yield methyldiborane, $CH_3BH(H_2)BH_2$ [102].

A Soviet patent has been issued for an improved preparation of $B_{12}H_{12}^{2-}$ [103].

The anion $B_{11}H_9Se_3^{2-}$ arises from reaction of $NaB_{11}H_{14}$ with ammonium polyselenide and has been found to consist of a B_{11} cage fused with a ring containing the three Se atoms [104]. The structure of 9-Et_3N-6-SB_9H_{11} has been determined by X-ray crystallography [105].

2. *Metallaboranes*. Reaction of KB_5H_8 with $(C_5H_5)BeCl$ has yielded μ-[η^5-$(C_5H_8)Be]B_5H_8$, which has the cyclopentadienyl-capped beryllium atom in place of one of the basal bridge hydrogens of pentaborane [106].

The structure of a six-vertex cluster compound, 1,2-$(C_5H_5)_2Co_2B_4H_6$, has been determined by X-ray crystallography, and it was found by refinement of the structure that there are bridging hydrogen atoms approximately centered over the Co_2B triangular faces [107]. The eight-vertex cluster $(C_5H_5)_4Co_4B_4H_4$ has been characterized by X-ray crystallography and found to have nearly D_{2d} symmetry [108]. Two new cobaltaborane complexes, $(C_5H_5)CoB_5H_9$ and $(C_5H_5)CoB_9H_{13}$, have been obtained from reaction of B_5H_9 with $(C_5H_5)Co(CO)_2$ in a hot-cold reactor [109].

The ferraboranes $(C_5H_5)FeB_5H_{10}$ and $(C_5H_5)FeB_{10}H_{15}$ have been obtained from $B_5H_8^-$, Fe^{2+}, and $C_5H_5^-$ [110]. The preparation of $B_5H_9Fe(CO)_3$ from B_5H_9 and $Fe(CO)_5$ in a hot-cold reactor has been described [111]. The structure of $B_3H_7Fe_2(CO)_6$ has been determined by X-ray and found to resemble pentaborane-9 in which the apical and one basal BH have each been replaced by $Fe(CO)_3$ [112]. The crystal structure of the copper(I) ferraborane $(Ph_3P)_2CuB_5H_8Fe(CO)_3$ has been determined [113]. An iron-bridged diborane has been obtained from B_2H_6 and K^+ $(C_5H_5)Fe(CO)_2^-$ [114].

Preparation and reactions of 2-$(OC)_3MnB_5H_{10}$ have been described [115]. The platinathiadecaborane 9,9-$(Ph_3P)_2$-6,9-$SPtB_8H_{10}$ and its 8-ethoxy derivative have been synthesized and characterized by X-ray crystallography [116]. Preparations of the icosahedral stiba- and arsastiba-boranes 1,2-$B_{10}H_{10}AsSb$, 1,2-$B_{10}H_{10}Sb_2$, $(C_5H_5)Co(7,8\text{-}B_9H_9AsSb)$, and $(C_5H_5)Co(7,8\text{-}B_9H_9Sb_2)$ have been described [117]. Syntheses of CuB_3H_8 and $Cu_2B_{10}H_{10}$ have been reported [118].

G. Reviews

Grimes has reviewed metal sandwich complexes of carboranes [119]. Leach has reviewed carborane chemistry [120]. The relation of structure and reactivity in rearrangements of dicarba-*nido*-undecaborates [121] and carborane rearrangements [122] have been reviewed in Russian. Odom has reviewed organoboron chemistry [123].

II. BORANES IN ORGANIC SYNTHESIS

A. Introduction

The award of the 1979 Nobel Prize to Professor Herbert C. Brown is the ultimate recognition of a long and fruitful career, and he has our congratulations and best wishes for many more interesting discoveries. Professor Brown's infectious enthusiasm for chemistry has been an inspiration for his many successful students, as it has been for some of us who have not had the privilege of working with him but have learned something about the power of optimistic thinking as well as the unique synthetic potential of organoboron compounds from his numerous publications and lectures. This section of Annual Surveys owes its existence to Professor Brown's innovations, and the replacement of the title "Hydroboration" with "Boranes in Organic Synthesis" is meant to reflect the broader implications and significance of the subject matter, as well as to indicate the content more accurately.

This section covers such topics as new reagents for hydroboration, reactions of trialkylboranes, reductions with trialkylborohydrides (but not sodium borohydride and related long-established reagents), and synthetic uses of boronic esters (alkyldialkoxyboranes). In general, reactions which do not involve a carbon-boron bond in some way are excluded, though recent synthetic developments utilizing enol borinate intermediates, in which the carbon-boron bonds are not directly involved, are included. Synthetic studies directed toward borazines, boron chelates, or other alkylboron compounds prepared for their own sake rather than their further synthetic organic potential are not covered here but in Part II by K. Niedenzu. Boronic ester derivatives of carbohydrates, used as blocking groups for chromatographic or other purposes, are also not included here.

B. Borane Reagents

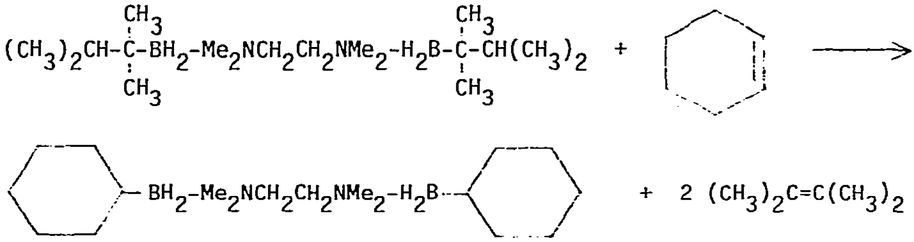
1. *Hydroborating Agents*. Brown and coworkers have continued to develop new reagents for hydroboration. Tetramethylethylenediamine (TMEDA) forms crystalline, air-stable complexes with one or two moles of monoalkylboranes, from which the monoalkylborane is easily regenerated by displacement with BF_3 [124].

$$Me_2NCH_2CH_2NMe_2 \xrightarrow{RBH_2} Me_2NCH_2CH_2NMe_2\text{-}BH_2R \xrightarrow{RBH_2} RBH_2\text{-}Me_2NCH_2CH_2NMe_2\text{-}BH_2R$$

$$\xrightarrow{BF_3\text{-}OEt_2} F_3B\text{-}Me_2NCH_2CH_2NMe_2\text{-}BF_3 \text{ (insoluble)} + RBH_2$$

Dialkylboranes form soluble complexes with ethylenediamine having the formula $R_2BH\text{-}H_2NCH_2CH_2NH_2\text{-}HBR_2$, from which the dialkylboranes are readily regenerated by treatment with BF_3 [125]. These amine complexes provide a good way to store the boranes for extended periods.

Monoalkylboranes are ordinarily difficult to synthesize because of the tendency of hydroboration to involve a second molecule of olefin indiscriminately unless the olefin is highly hindered. This problem has been overcome by using the complex of thexylborane with tetramethylethylenediamine as the hydroborating agent, which results in replacement of tetramethylethylene from the borane by the less hindered olefinic reactant, with formation of a stable complex of the new monoalkylborane with tetramethylethylenediamine [126].



The amine-borane complexes are generally air-stable crystalline solids, and can be isolated and stored easily. Regeneration of the free monoalkylborane in solution is accomplished by treatment of the complex with BF_3-OEt_2.

Monoisopinocampheylborane, from hydroboration of alpha-pinene with 1 mol of BH_3-THF, is a useful chiral hydroborating agent but suffers loss of chiral selectivity if BH_3 is present, and BH_3 is formed by disproportionation of the reagent. This problem has been solved by adding enough TMEDA to precipitate all of the BH_3 as the amine borane, leaving a mixture of mono- and di-isopinocampheylborane in solution. The monoisopinocampheylborane is the much more reactive component, and stereoselectively hydroborates trisubstituted alkenes. An alternative procedure involves precipitating and removing the BH_3-TMEDA complex, followed by precipitating the monoisopinocampheylborane-TMEDA complex, from which the chiral borane is easily regenerated by treatment with BF_3-OEt_2 [127].

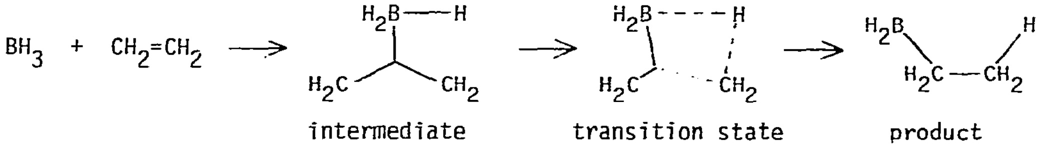
Brown, Ravindran, and Kulkarni have reported a detailed study of the use of H_2BX-SMe_2 (X = Cl, Br, I) as difunctional hydroborating agents [128]. These are particularly useful for making dialkylboron halides, which have a variety of synthetic applications.

$$CH_3CH_2CH{=}CH_2 \xrightarrow{H_2BCl\text{-}SMe_2} (CH_3CH_2CH_2CH_2)_2BCl \xrightarrow{CH_3OH} (CH_3CH_2CH_2CH_2)_2BOCH_3$$

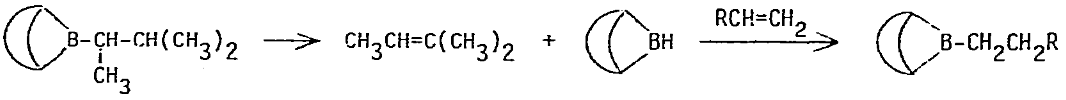
Deuterated 9-BBN has been prepared from B_2D_6 and cyclooctadiene [129]. Dissociation of 9-BBN amine complexes has been measured by an infrared technique [130]. Thexylborane-N,N-diethylaniline has been found to be a useful hydroborating and reducing agent [131]. Decaborane has been reported to be effective but much less reactive than diborane for the hydroboration-oxidation of natural products, including camphene, Δ^2-cholestene, and Δ^5-cholestene [132]. A process for gas-phase hydroboration of olefins over Pd/C has been patented in Japan [133].

2. Mechanism of Hydroboration. Previous mechanistic studies of hydroboration have tended to yield somewhat ambiguous results, in part because the exact hydroborating agent present in solution is often difficult to define, or may be a mixture of diastereoisomers as in the case of disiamylborane. However, these difficulties have been overcome by the use of 9-BBN, which is present in carbon tetrachloride solution as a single dimeric species. The observed kinetics are first-order in $(9\text{-BBN})_2$ and independent of the olefin concentration with reactive olefins, and half-order in $(9\text{-BBN})_2$ and first-order in olefin with less reactive olefins. These results clearly indicate that the first step in hydroboration is dissociation of the borane dimer, which is followed by a more or less rapid reaction of the borane monomer with the olefin [134].

Lipscomb and coworkers have reported PRDDO and some 4-31G calculations on the reaction pathway for hydroboration of ethylene with BH_3 [135]. These calculations indicate that hydroboration passes through an intermediate having the character of a $C_2H_4\text{-}BH_3$ pi-complex, followed by a transition state of only slightly higher energy. In the transition state, electron density is transferred from the BH_3 hydrogens to the boron, especially from the H atom being transferred to carbon, and there is some increase in the electron density of both carbon atoms, with the greatest increase being on the carbon attacked by boron. This electron density distribution is consistent with the observed electronic effects in hydroboration reactions.



Midland and coworkers have studied the facile exchange reaction between 9-alkyl-9-BBN's and olefins in refluxing THF [136]. The kinetics indicate that the mechanism involves dehydroboration followed by hydroboration.



[For a complete illustration of a 9-BBN group see Section D-2 at ref. 184.]

3. Trialkylborohydrides. Highly hindered trialkylboranes such as trisiamylborane fail to react with LiH, NaH, or KH, but the hindered trialkylborohydrides can be formed by reaction of the trialkylborane with lithium aluminum hydride in the presence of triethylenediamine, $N(CH_2CH_2)_3N$, which precipitates AlH_3 as a complex from diethyl ether and leaves pure $LiHBR_3$ in solution [137].

Hindered trialkylborohydrides, $K^+\ HBR_3^-$ (R = siamyl, 2-methyl-1-cyclopentyl; or BR_3 = thexyl-9-BBN), that cannot be prepared directly from KH and BR_3 have been prepared by reaction of $K^+\ HB(O\text{-}\underline{i}\text{-}Pr)_3^-$ with BR_3 in THF at 25 °C [138].

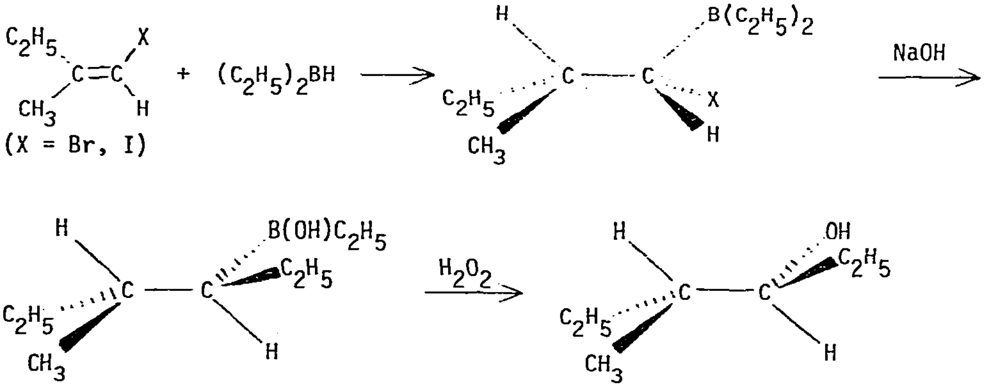
Addition of R_3B to $LiAlH(OMe)_3$ in THF yields a gel of $Al(OMe)_3$ polymer (which dissolves on addition of LiOMe) and a solution of $LiHBR_3$. It is not necessary to remove the $Al(OMe)_3$ (or $LiAl(OMe)_4$) in order to use the trialkylborohydride [139]. Contrasting results were obtained with LiAlH(O-t-Bu)$_3$, which in the presence of a catalytic amount of R_3B rapidly cleaves THF to 1-butanol. Tetrahydropyran is cleaved only slowly under similar conditions [140]. A combination of LiHAl(O-t-Bu)$_3$ with BEt_3 is a powerful reducing agent which readily cleaves a variety of ethers [141]. For example, tetrahydrofuran is cleaved to 1-butanol, 7-oxabicyclo[2.2.1]heptane to cyclohexanol, and dimethyl ether to methanol and methane. However, tetrahydropyran and oxepane are attacked only very slowly by this reagent at room temperature, and tetrahydropyran is a useful solvent for cleavages of other ethers.

Lithium triethylborohydride selectively reduces a MEM ester, $RCO_2CH_2OCH_2CH_2OCH_3$, in the presence of other ester groups such as a 2,2,2-trichloroethyl ester [142]. Reduction of rigid cyclic α,β-unsaturated ketones with trialkylborohydrides tends to give the pseudoequatorial allylic alcohol predominantly, but the stereochemistry can be altered by ether substituents [143]. Trialkylborohydrides efficiently convert metal carbonyl dimers to anions such as $Co(CO)_4^-$ and $Mn(CO)_5^-$ [144].

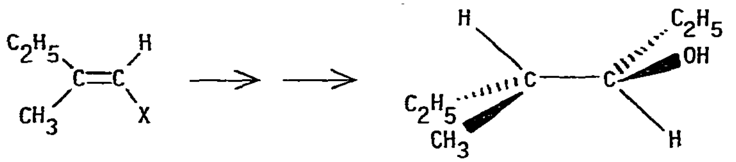
C. Carbon-Carbon Bond Formation

1. Boranate Complex Rearrangements. Rearrangements of $R_3\bar{B}$—CXR'_2 to R_2B-CRR'_2 + X^-, or $R_3\bar{B}$—CR'=CR'_2 + E^+ to R_2B-CRR'-CR'_2-E, and mechanistically related transformations provide a useful approach to carbon-carbon bond formation with control of stereochemistry, and research in this area has continued to be active and productive.

Displacement of an α-halide by base-induced rearrangement of a stereochemically defined α-haloalkyldialkylborane has been shown to proceed with inversion of the α-carbon [145]. The α-haloalkylboranes are epimerized very readily by THF or Me_2S, and it was necessary to carry out the hydroboration reaction with purified borane and vinylic halide in the absence of solvent in order to demonstrate the stereospecificity, which was greater than 99%.

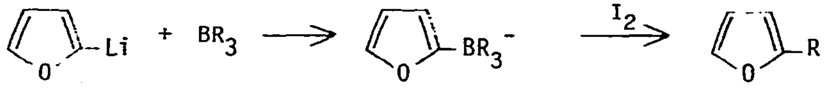


(RS,SR enantiomeric pair)

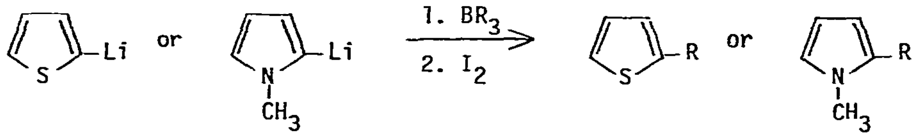


(*RR*,*SS* enantiomeric pair)

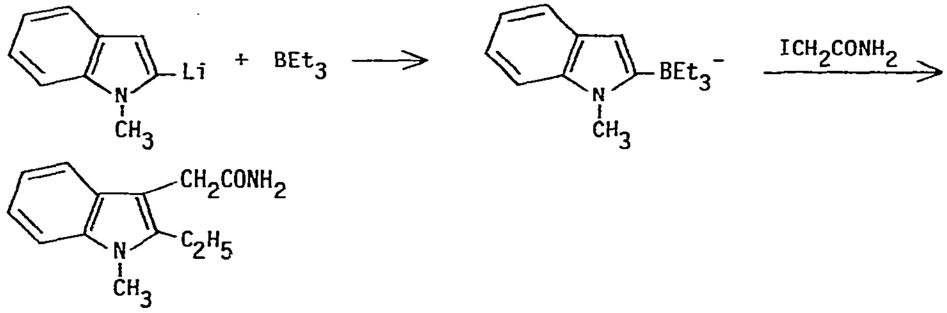
Alkylfurans have been prepared by lithiation of furan, treatment with a trialkylborane, and rearrangement of the borate complex with iodine [146].



Alkylation of thiophenes and pyrroles has been accomplished by lithiation, treatment with trialkylborane, and finally treatment with iodine [147].

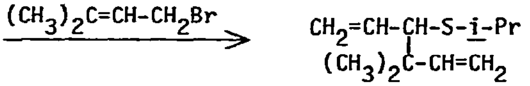


Reaction of 1-methyl-2-lithioindole with trialkylboranes followed by treatment of the intermediate borates with carbon electrophiles yields regiospecifically substituted 2,3-dialkyl-1-methylindoles [148].



Reaction of *i*-PrS-CH=CH-CH_2Li with Et_3B yields the intermediate borate complex *i*-Pr-S-CH=CH-CH_2-BEt_3^- Li^+, which reacts with carbonyl compounds RR'C=O at the position *alpha* to the sulfur to form RR'C(OH)CH(S-*i*-Pr)CH=CH_2 [149]. Reaction of trialkylboranes with *i*-Pr-S-CH=CH-CH_2Li followed by allylic halides gives head-to-tail 1,5-dienes in good yields [150].

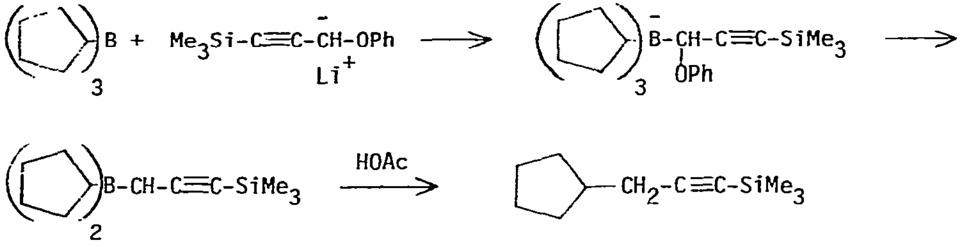
$$Bu_3B + LiCH_2\text{-}CH{=}CH\text{-}S\text{-}\textit{i}\text{-}Pr \longrightarrow Bu_3\bar{B}\text{—}CH_2\text{-}CH{=}CH\text{-}S\text{-}\textit{i}\text{-}Pr\ \ Li^+$$



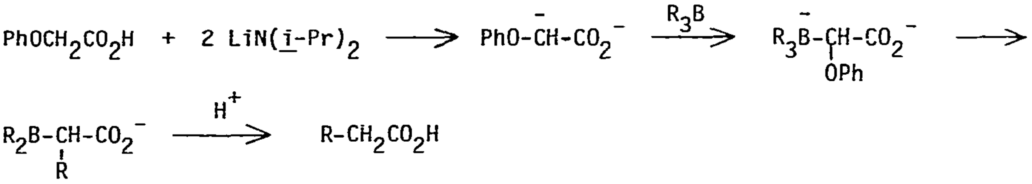
$$\xrightarrow{(CH_3)_2C=CH\text{-}CH_2Br} \begin{array}{l} CH_2{=}CH\text{-}CH\text{-}S\text{-}\textit{i}\text{-}Pr \\ \quad (CH_3)_2C\text{-}CH{=}CH_2 \end{array}$$

96% of product, 78% yield

1-Trimethylsilylacetylenes have been prepared from trialkylboranes and trimethylsilylpropargyl phenyl ether in yields of 36-51% and isomeric purities of 92-100% [151].



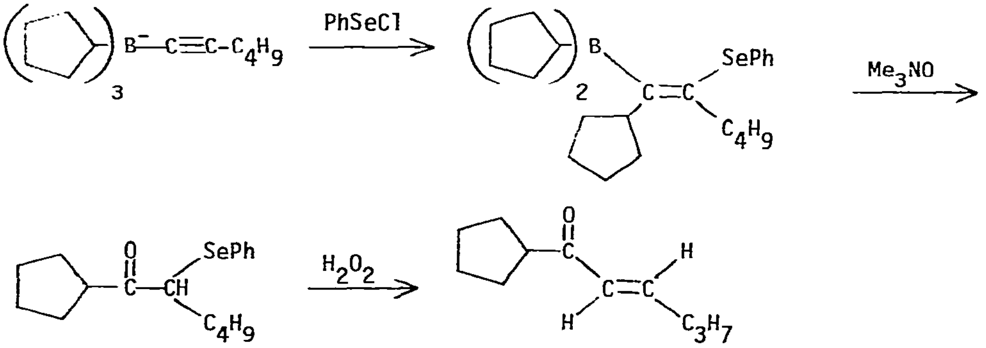
The dianion of phenoxyacetic acid reacts with trialkylboranes and 9-alkyl-9-BBN derivatives to form alkylacetic acids [152].



$$PhOCH_2CO_2H + 2\ LiN(\underline{i}\text{-}Pr)_2 \longrightarrow PhO\text{-}\overset{-}{C}H\text{-}CO_2^- \xrightarrow{R_3B} R_3\overset{-}{B}\text{-}\underset{OPh}{CH}\text{-}CO_2^- \longrightarrow$$

$$R_2B\text{-}\underset{R}{CH}\text{-}CO_2^- \xrightarrow{H^+} R\text{-}CH_2CO_2H$$

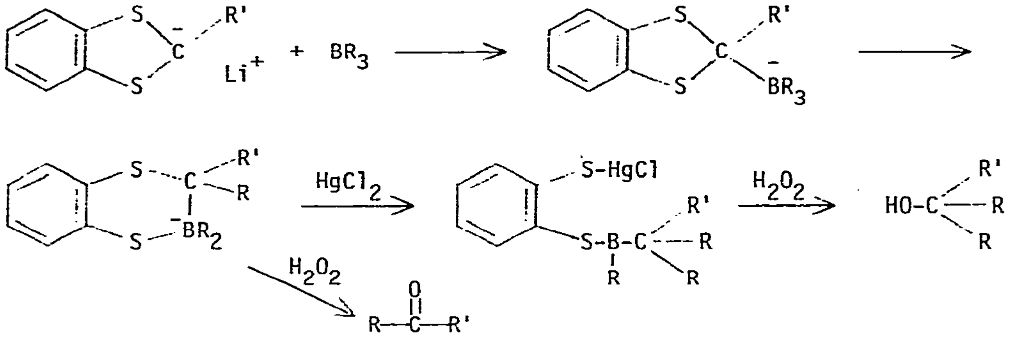
Reaction of trialkylalkynylborate salts with PhSeCl followed by stepwise oxidation leads to α,β-unsaturated ketones [153].



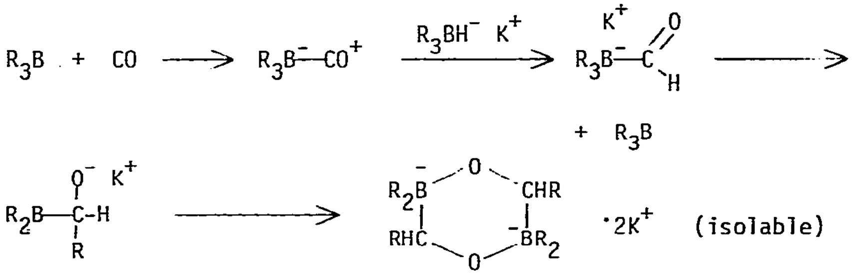
Charge-delocalized organolithium reagents having a pK_a less than about 20, such as cyclopentadienyllithium or lithioacetophenone, fail to form borate salts $R'BR_3^-$ in the presence of organoboranes R_3B [154].

Reaction of R_3B with LiC≡C-OEt and behavior of the resulting $R_3\overset{-}{B}$—C≡COEt toward electrophiles has been explored [155].

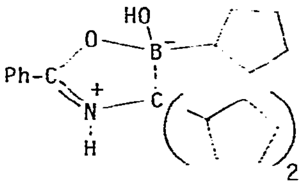
Trialkylboranes react with 2-lithio-2-alkylbenzodithioles to form intermediates which can be oxidized to ketones [156] or further rearranged with $HgCl_2$ and oxidized to tertiary alcohols [157].

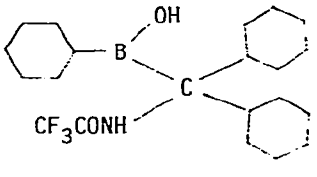


Alkali metal trialkylborohydrides do not react with carbon monoxide unless a small amount of free trialkylborane is present as a catalyst [158]. Lithium trialkylborohydrides contain a small equilibrium amount of trialkylborane, as shown by lack of splitting of the ^{11}B NMR signal by H due to exchange, and are reactive toward carbon monoxide. Potassium trialkylborohydrides show BH coupling in the ^{11}B NMR and are unreactive unless trialkylborane is added, which also collapses the ^{11}B NMR doublet. The mechanism of carbonylation must involve a trialkylborane-carbonyl intermediate.



Crystal structures of two intermediates in cyanoborate rearrangements have been characterized by X-ray crystallography [159].

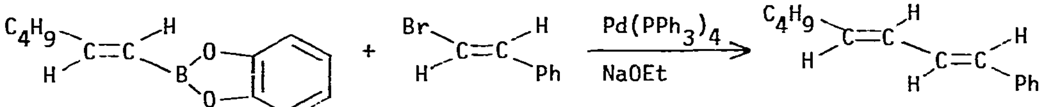




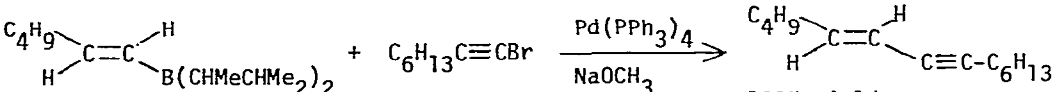
Known carbonylations of trialkylboranes have been used to introduce ^{14}C labels into an aldehyde, a ketone, and an alcohol [160].

2. Transition Metal-Catalyzed Couplings. These are probably mechanistically related to the boranate rearrangements described in the preceding section, with the transition metal catalyst aiding in the formation of the boranate complex and its oxidative rearrangement.

E-1-alkeneboronic esters or alkenylboranes readily couple with 1-alkenyl or 1-alkynyl halides in the presence of a catalytic amount of $(Ph_3P)_4Pd$ and base [161]. The E-dienes or E-enynes are formed with high regio- and stereoselectivity and good yields.

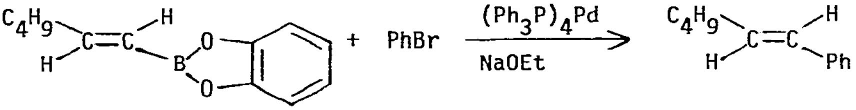


80% yield
>96% isomeric purity

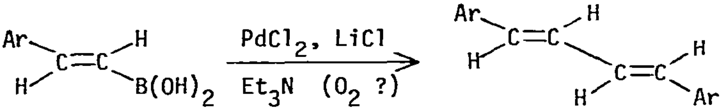


100% yield
>99% isomeric purity

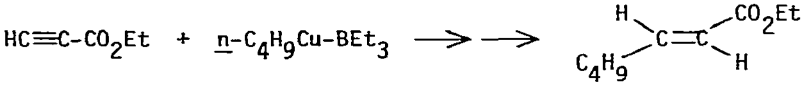
Alkeneboronic esters react with aryl bromides or iodides in a similar manner in the presence of $(Ph_3P)_4Pd$ and NaOEt [162].



Palladium chloride catalyzes the coupling of β-styreneboronic acids to diarylbutadienes in high yields [163]. The nature of the necessary oxidizing agent was not specified, but since the experimental directions do not call for an inert atmosphere, the reviewer surmises that oxygen may be involved.

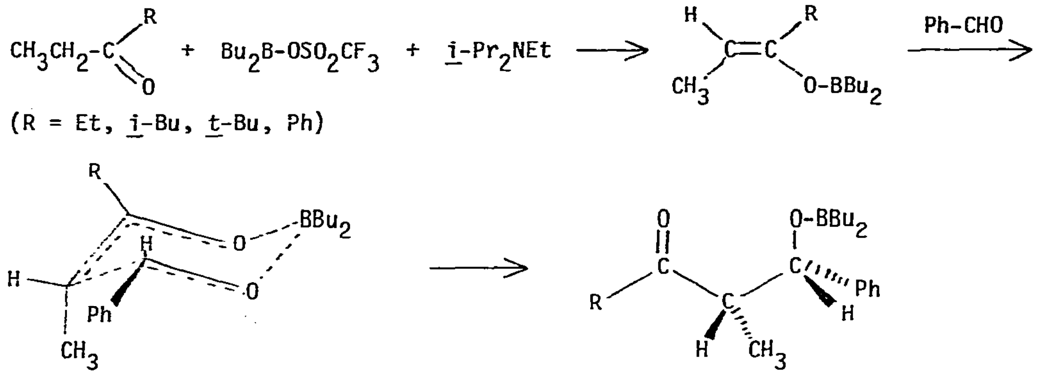


Copper-borane reagents $BuCuBR_3$ add the butyl group and, on methanolysis, a hydrogen stereoselectively cis to the triple bond of α,β-acetylenic esters or ketones [164]. The R groups of the trialkylborane do not add.



98% trans

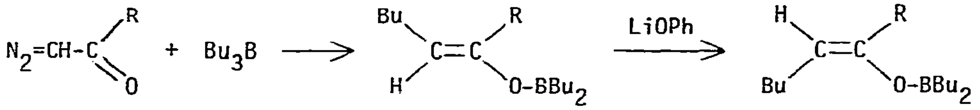
3. Enol Borinates and Others. Evans and coworkers have reported the use of dialkylboron enolates in stereoselective aldol condensations [165]. Reaction of a series of alkyl ethyl ketones with dibutylboron triflate and diisopropylethylamine in ether at -78 °C yielded the Z-enolate exclusively (>99%) in most cases, and these condense with aldehydes by way of cyclic transition states in which steric factors analogous to those in substituted cyclohexanes determine the favored pathway, which leads to predominantly "erythro" products.



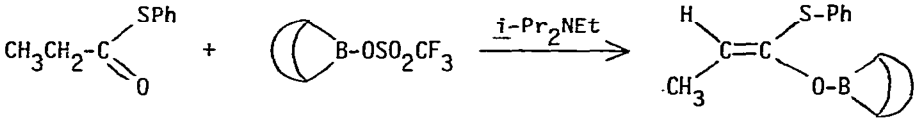
(R = Et, i-Bu, t-Bu, Ph)

When a thiol ester (R = S-t-Bu) was used in place of the ketone and the enolate was initially generated with LDA, the enolate was 95% Z-isomer (opposite from the geometry of the ketone enolate, the relative priority of R being reversed in the nomenclature scheme) and the products were 90-95% "threo."

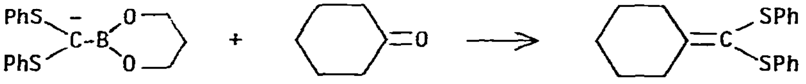
Masamune and coworkers have prepared E-enolates by reaction of tributylborane with α-diazoketones [166]. Treatment with lithium phenoxide or pyridine isomerizes the E-enolates to Z-enolates.



Aldol condensations of these E- and Z-enolates with aldehydes gave "threo" and "erythro" products, respectively, analogous to those described above. Phenyl thiolpropionate has been converted to its E-enolate by 9-BBN triflate, and the utility of this enolate in similar stereoselective enolate condensations has been demonstrated [167].



Carbanions derived from $(PhS)_2CH\text{-}BO_2C_3H_6$ and related boronic esters by deprotonation with LDA react with aldehydes or ketones to form ketene thioacetals [168].



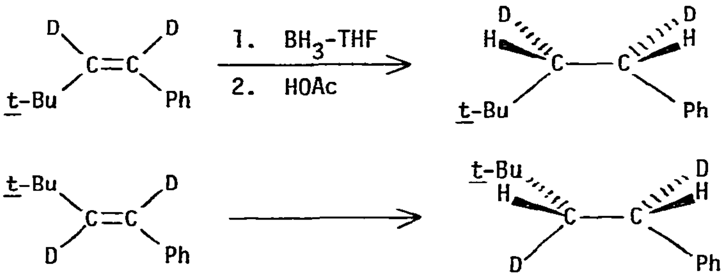
Isocyanates displace boron from the alkynyl group of B-(1-alkynyl)-9-BBN's [169].

Triphenylborane undergoes many of the same reactions that have proved useful with trialkylboranes, including conversion by H_2NOSO_3H to $PhNH_2$ and $HOBPh_2$, iodination to PhI and Ph_2BOH, the sodium cyanide-trifluoroacetic anhydride-peroxide sequence to form Ph_3CH, and carbonylation in the presence of $LiAlH(OMe)_3$ to PhCHO [170].

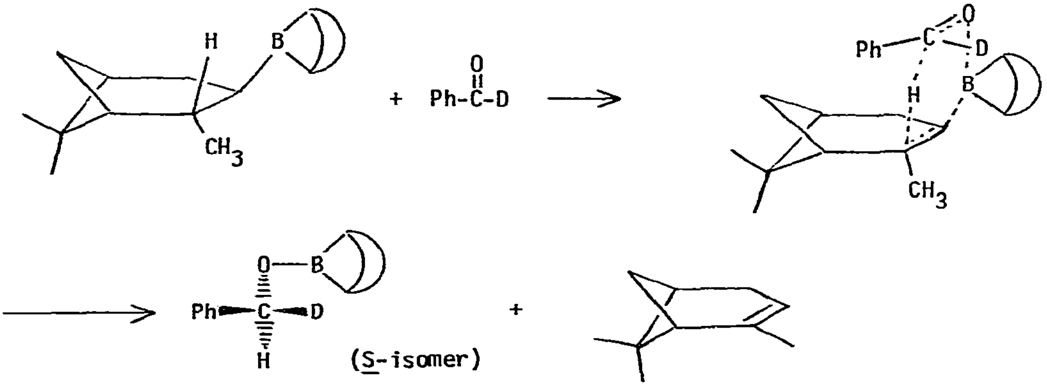
D. Hydroboration in Synthesis

1. Replacements of Boron. Included in this section are a variety of replacements of boron by elements other than carbon.

Kabalka, Newton, and Jacobus have shown that protonolysis of an organoborane proceeds with retention of configuration at carbon [171]. While this has generally been believed to be the case, previous examples were not truly definitive.



3-Pinanyl-9-BBN gives stereoselectivities approaching 100% in the reduction of deuteroaldehydes, R-CDO, to optically active α-deuteroalcohols [172]. The reaction eliminates α-pinene, and the transition state geometry favors having the R group of the aldehyde next to the methylene bridge rather than the methyl group of the pinene. If 9-BBN-9-*d* is used to prepare the 3-pinanyl-9-BBN, the reagent transfers deuterium to the aldehyde during the reduction.

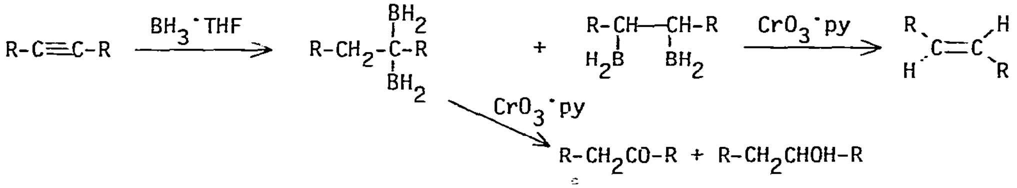


The first conclusive evidence of stepwise attack of a radical at boron has been obtained from a study of the reaction of *t*-butoxy radical with triphenylborane, which yields the $Ph_3\dot{B}$—O-*t*-Bu radical, which has a lifetime of 15 microseconds at 22 °C before it decays to Ph• and Ph_2B-O-t-Bu [173]. Kinetic studies have shown that the thermal decomposition of Bu-O-O-BBu_2 and related peroxides occurs mainly by a nonradical mechanism [174].

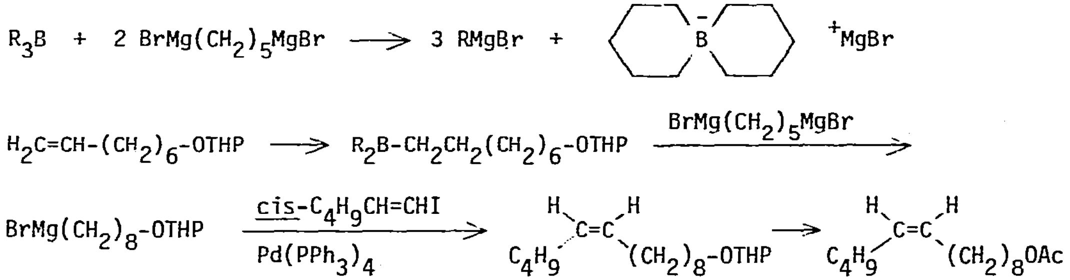
Pyridinium chlorochromate oxidation of primary trialkylboranes gives good yields of aldehydes [175].

$$(RCH_2CH_2)_3B \xrightarrow{C_5H_5N\cdot HCl\cdot CrO_3} RCH_2CHO$$

Chromium trioxide oxidation of 1,1-diboryl compounds derived from dihydroboration of acetylenes gives ketones as major products and alcohols as by-products. Similar oxidation of the 1,2-diboryl compounds in the hydroboration product mixture yields olefins. The 1,2-diboryl compounds appear to predominate somewhat in the products of hydroboration of R-C≡C-R, and the 1,2-derivative is the only observed product from hydroboration of Ph-C≡C-Ph with BH_3-THF [176].



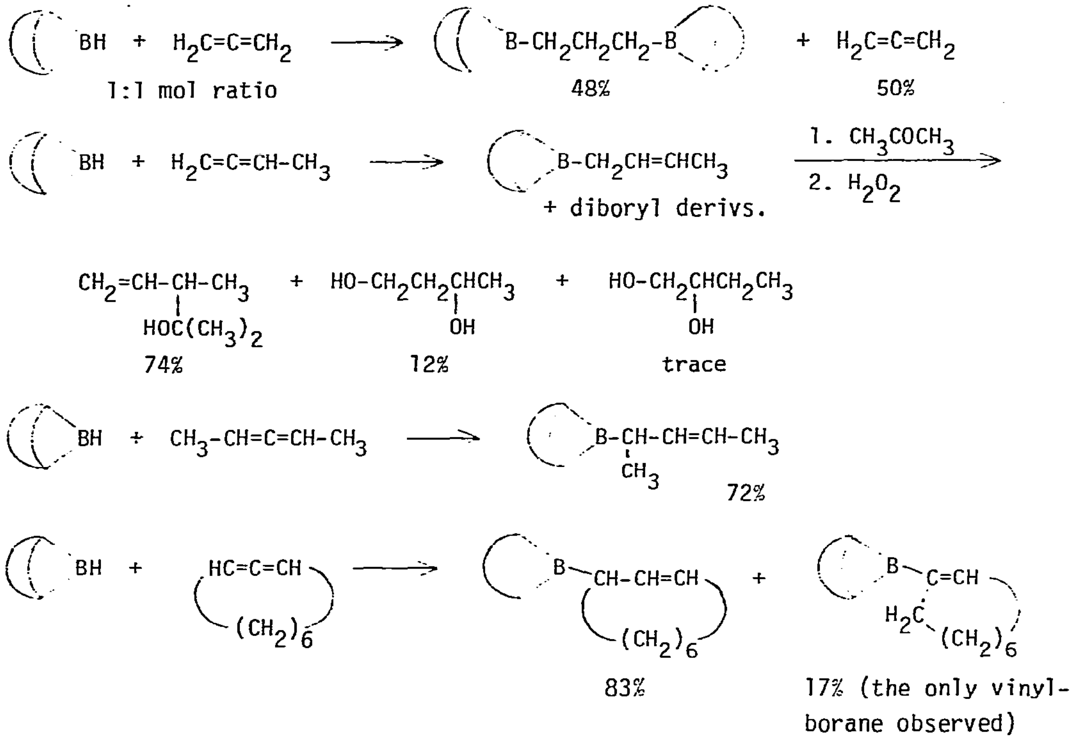
Trialkylboranes can be converted to Grignard reagents by treatment with pentane-1,5-di(magnesium bromide) in benzene [177]. The equilibrium is shifted toward formation of the stable spiro bis(pentamethylene)borate anion. The reaction also works with B-alkyl-9-BBN. Grignard reagents prepared in this manner were shown to be useful in syntheses of insect pheromones.



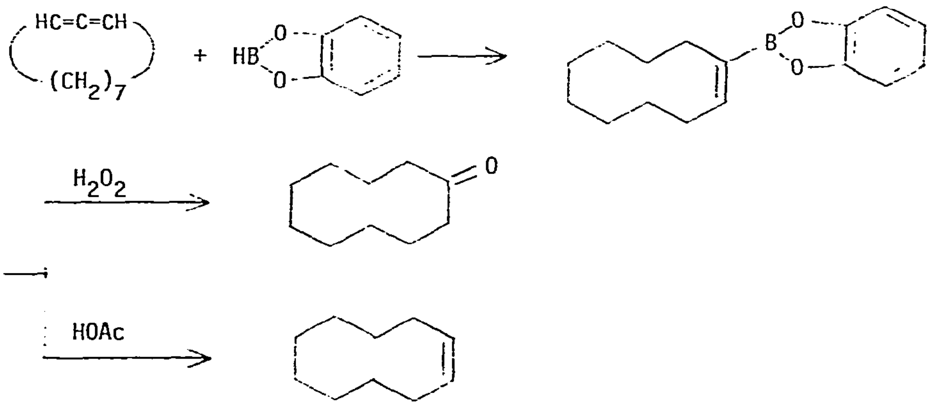
Southern army worm moth pheromone

2. Synthetic Procedures. This section includes a variety of studies directed toward elucidating the specificity of hydroboration processes for synthetic purposes.

Brown and coworkers have published a detailed description of hydroboration of allenes with 9-BBN [178]. Because hydrolysis of allylboranes is rapid and often competes with alkaline hydrogen peroxide oxidation, the reaction of the products with acetone was used in order to detect allylboranes. It was found that 9-BBN shows a high degree of selectivity for the least hindered terminal position of the allene.



Hydroboration of cyclic allenes with catecholborane results in attack of the boron at the center carbon to form the *Z*-cycloalkeneboronic ester [179].



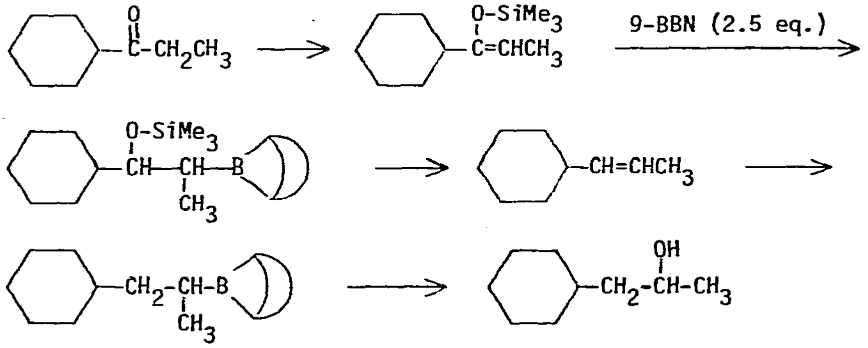
Partial hydroboration of t-Bu(Ph)C=C=C=C=C(t-Bu)Ph with bis(pinanyl)borane resulted in about 5% enrichment of one enantiomer [180].

Details of the reactions of 9-BBN with several acetylenic compounds have been published [181]. Monohydroboration of terminal acetylenes, R-C≡CH, was achieved only by using an excess of the acetylene, 1 mol of 9-BBN to 2 of R-C≡CH yielding 0.90-0.96 mol of 1:1 adduct and 0.02-0.05 mol of 2:1 adduct. Oxidation of the vinylboranes thus produced yielded only aldehyde and no detectable methyl ketones, indicating that 100% of the boron was on the terminal carbon. With internal acetylenes, R-C≡C-R', a 1:1 ratio of 9-BBN to acetylene produced 90% or more of the monohydroboration product. Regioselectivity for $R\text{-}C{\equiv}C\text{-}CH_3$ in favor of $R\text{-}CH{=}C(CH_3)\text{-}9\text{-}BBN$ was 78% for R = n-propyl, 96% for R = isopropyl or cyclohexyl, and 100% for R = t-butyl. Where R = phenyl, electronic effects dominate and 65% of the boron adds next to the phenyl group instead of the methyl. Protonolysis of the vinylic boranes yields exclusively cis-olefins.

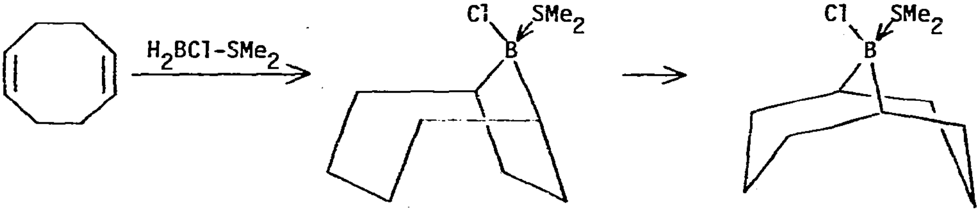
Hydroboration of acetylenes with 9-BBN has been found to be slow compared to hydroboration of structurally similar olefins, permitting selective conversion of certain enynes to acetylenic alcohols [182].

$$CH_3CH_2CH_2C{\equiv}CCH_2CH{=}CH_2 \xrightarrow[2.\ H_2O_2]{1.\ 9\text{-BBN}} CH_3CH_2CH_2C{\equiv}CCH_2CH_2CH_2OH$$

Hydroboration of silyl enol ethers has been used in a reductive 1,2-transposition of ketone groups [183].



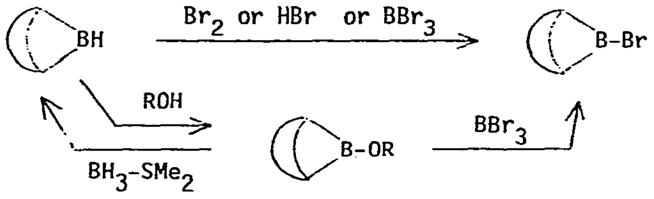
Hydroboration of 1,5-cyclooctadiene with $H_2BX\text{-}SMe_2$ initially yields mostly B-halo-9-borabicyclo[4.2.1]nonane in a mixture with the more stable [3.3.1] isomer, which becomes the only major product when the mixture is heated [184]. These halo-9-BBN compounds are easily isolated as their complexes with dimethyl sulfide.



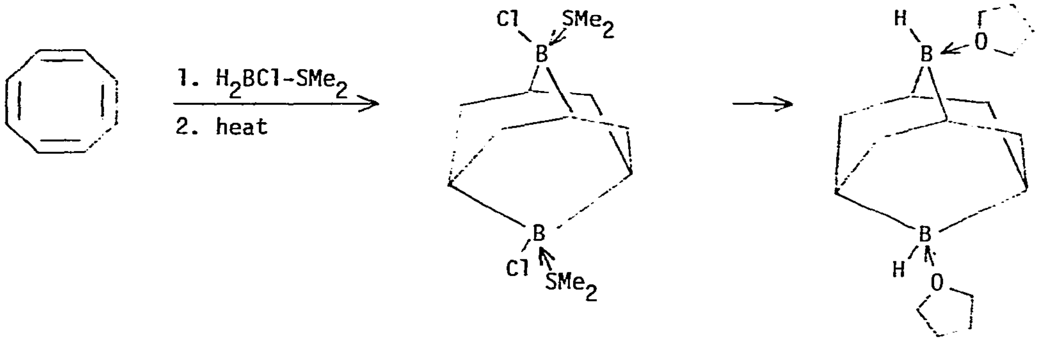
[4.2.1] isomer

[3.3.1] isomer
($9\text{-}Cl\text{-}9\text{-}Me_2S\text{-}9\text{-}BBN$)

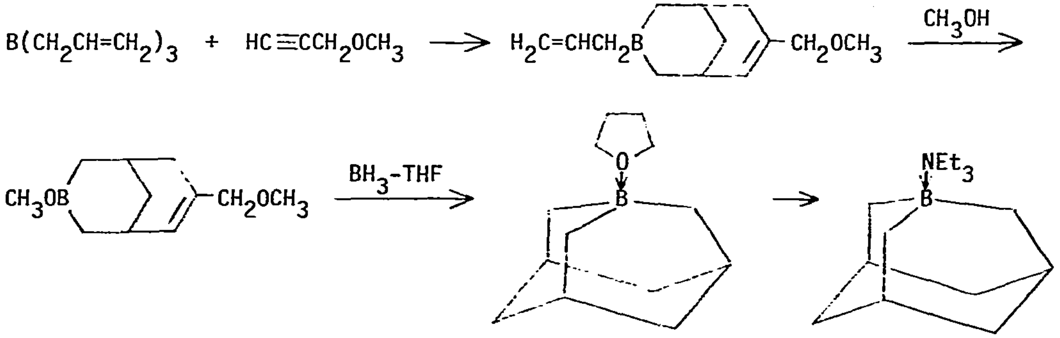
The conversion of 9-BBN to several useful derivatives has been studied [185].



Hydroboration of cyclooctatetraene with H_2BCl-SMe_2 initially yields a polymer which on pyrolysis at reduced pressure is converted to a 2,6-diboraadamantane [186]. Methanolysis of the chloro compound followed by reduction with H_3B-SMe_2 in tetrahydrofuran yields the hydride as a bis(THF) adduct.

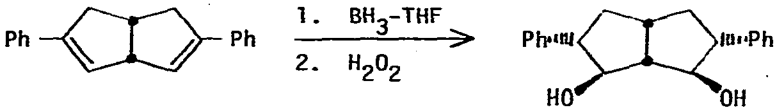


The reaction of propargyl methyl ether with triallylborane followed by further transformations including cyclization with BH_3-THF leads to 1-boraadamantanes [187].

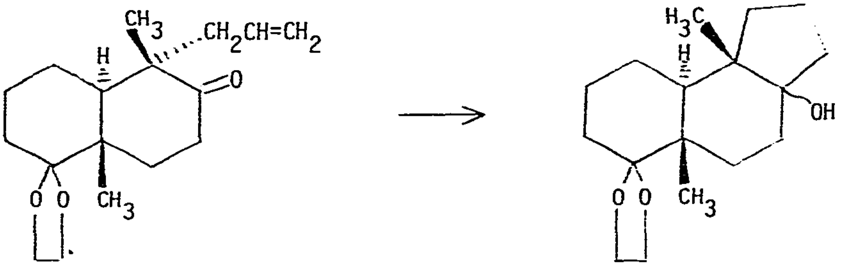


Boraadamantane-amine complexes have been tested as antiviral agents, and the 1-adamantylamine complex showed the most activity against type A flu virus [188].

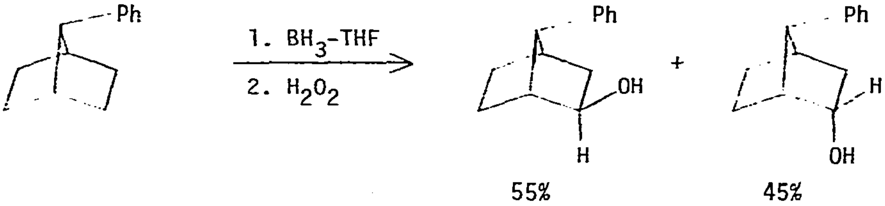
Hydroboration-oxidation has been used to convert 3,7-diphenylbicyclo-[3.3.0]octadienes to 3,7-endo-diphenylbicyclo[3.3.0]octane derivatives [189].



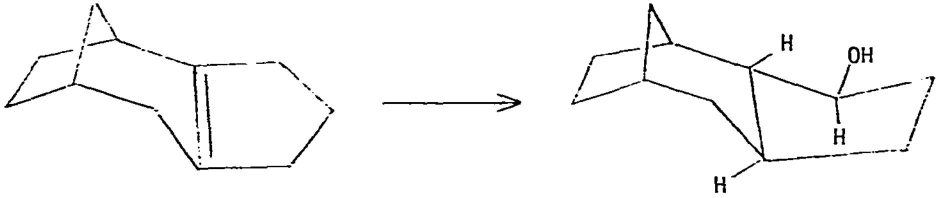
Hydroboration of an allyldecalone has resulted in ring closure [190].



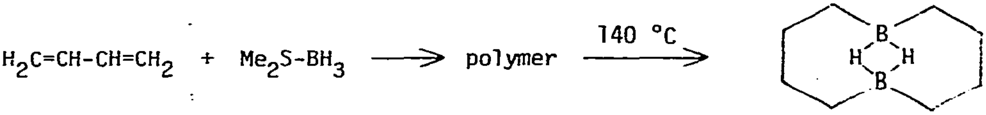
Hydroboration of a series of syn-7-arylnorbornenes with BH_3-THF has yielded mixtures of exo and endo products, with isomer ratios ranging from 42:58 to 60:40 with different aryl groups [191]. A possible explanation suggested was complexing of BH_3 with the aryl group in the transition state.



Hydroboration-oxidation of a tricyclic olefin has yielded an unexpected rearrangement product [192].



Hydroboration of butadiene with Me_2S-BH_3 to form 1,2:1,2-bis(tetramethylene)diborane(6) has been reported in detail [193].

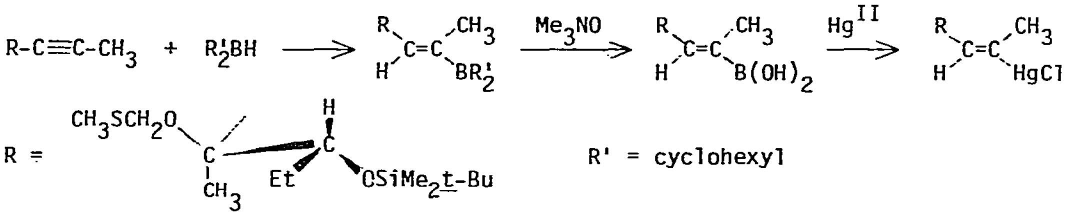


Deprotonation of 1,2:1,2-bis(tetramethylene)diborane(6) with KH results in loss of one B-H-B bridge [194].

Removal of secondary alkyl groups from primary trialkylboranes derived from hydroboration of terminal olefins has been accomplished by successive treatments with anisole and dimethyl sulfoxide, which leaves the purified trialkylboranes for use as synthetic intermediates [195].

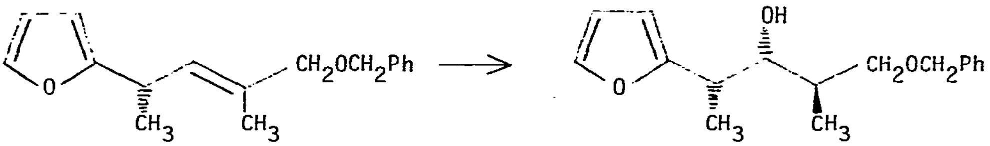
3. Natural Products. This section includes application of known hydroboration chemistry to the synthesis of natural products, as well as various transformations of natural products by hydroboration.

Hydroboration, alkyl group cleavage, and mercurideboronation has been used in the synthesis of an intermediate in the total synthesis of erythronolide A [196].

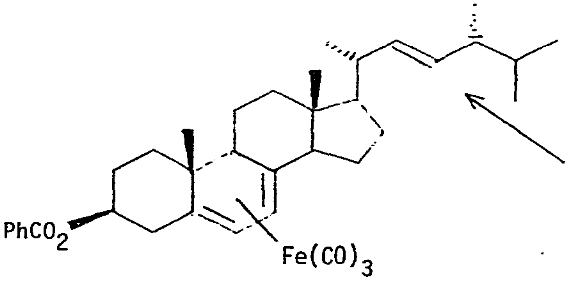


R' = cyclohexyl

Hydroboration-oxidation has been used in a stereocontrolled synthesis of a portion of the antibiotic monensin [197].



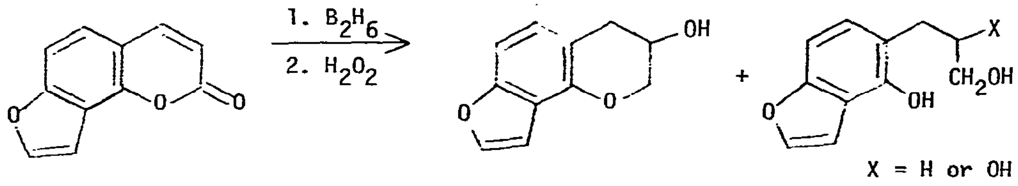
Tricarbonylironergosteryl benzoate is hydroborated only at the double bond in the side chain and not at the diene protected by the tricarbonyliron complex [198]. After the hydroboration-oxidation is completed, the iron carbonyl complex is easily decomposed to diene by $FeCl_3$.



BH_3 attacks this double bond.
(3 isomeric alcohols isolated)

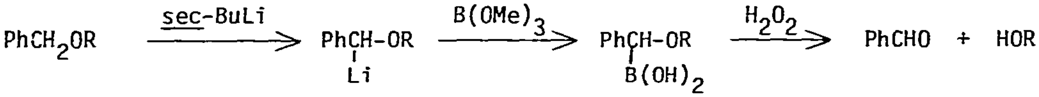
Hydroboration has been used in the lupene series of triterpenes to convert an exo-ethylidene group on a cyclopentane ring to various derivatives [199]. Hydroboration of caryophyllene with dicyclohexylborane in THF occurs preferentially at the trans double bond in the nine-membered ring rather than the exocyclic double bond [200]. Hydroboration of 2-amino- or 2-azido-cis-3-pinene has been reported to yield α-pinene, 4-azido-trans-2-pinene yielded isopinocampheol, and 4-amino-trans-2-pinene failed to react [201]. Hydroboration-oxidation of a homoandrostene derivative has been reported [202]. Hydroboration-oxidation has been used to convert an intermediate containing a terminal vinyl and a ketone function into a diol in a synthesis of gymnomitrol [203].

Hydroboration-oxidation of coumarins gives mixtures of products [204].



E. Miscellaneous

Use of a boronic ester intermediate in a debenzylation method has been reported [205].



$$PhCH_2OR \xrightarrow{sec\text{-}BuLi} \underset{Li}{PhCH}\text{-}OR \xrightarrow{B(OMe)_3} \underset{B(OH)_2}{PhCH}\text{-}OR \xrightarrow{H_2O_2} PhCHO + HOR$$

Reaction of anilines with BCl_3 and then isonitriles leads by way of boron heterocyclic intermediates to anthranilaldehydes [206].

An improved preparation of iodomethaneboronic esters and their reactions with secondary and tertiary amines have been reported [207].

$$PhSCH_2B(OR)_2 + CH_3I \xrightarrow[CH_3CN]{NaI} ICH_2B(OR)_2 \xrightarrow{R_2NH} R_2N\text{-}CH_2B(OR)_2$$

The boronic esters trans-CH_2=CH-CCl=CH-B(OMe)$_2$ and CH_2=CH-C$\equiv$C-B(OEt)$_2$ have been prepared [208]. Addition of B_2X_4 (X = F, Cl) to butadiene yields X_2BCH_2CH=$CHCH_2BX_2$ [209]. Alkenylboranes such as trans-C_4H_9CH=CH-BR_2 where R is siamyl or 2-methylcyclohexyl show two different α and two β proton signals in the NMR spectra because of the presence of diastereoisomers resulting from the chiral centers of the R groups [210]. Where R lacks a chiral center, no such doubling of signals occurs.

Conversion of RCO_2H to RCHO has been accomplished by reduction with BH_3-SMe_2 to $(RCH_2O)_3B$ followed by oxidation with pyridinium chlorochromate [211].

F. Reviews

Pelter and Smith have reviewed a series of topics in organoborane chemistry, including a general introduction, boron-hydrogen compounds, triorganylboranes, organoborate salts, and boron-halogen, -oxygen, -nitrogen, and -sulfur compounds [212]. Zweifel has reviewed alkenylborane chemistry [213]. Midland has reviewed asymmetric synthesis via boranes [214]. The use of trialkylborohydrides in organometallic synthesis has been reviewed [215]. Non-catalytic hydrogenation via organoboranes has been reviewed by Avasthi, Devaprabhakara, and Suzuki [216]. Synthesis using boron and other organometallic intermediates has been reviewed [217]. Yamamoto and Maruyama have reviewed organic synthesis using borate complexes in Japanese [218]. Suzuki has reviewed carbon-carbon bond forming reactions of tetraorganoborates in Japanese [219].

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