BORON I. CARBORANES AND HYDROBORATION

ANNUAL SURVEY COVERING THE YEAR 1975

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CONTENTS

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I. CARBORANES

A. Introduction

The rate of production of totally unexpected new findings in this field has slowed, and 1975 publications may be characterized as filling in the gaps and extending the known general principles. Polyhedral cages containing transition metal atoms as well as carbon and boron have received considerable attention and will be surveyed first, followed by carboranes having transition metal substituents outside the polyhedral framework. Hawthorne continues to lead the way, though interest has spread to several other American, European, and Russian research groups. One trend of this work is toward cages containing more transition metal atoms and fewer carbon and boron atoms, with cage rearrangements being of particular interest. Carbon can be dispensed with altogether, and although such compounds are not "organoboron compounds" by the usual definition, they have been included with the others in this survey, without detailed discussion or structures. A second area of interest is the synthesis of various ruthenium, rhodium, palladium, iridium, and platinum derivatives of carboranes, which sometimes show interesting catalytic properties. Progress has also been made in including nonmetallic heteroatoms, especially nitrogen and sulfur, within carborane (and borane) polyhedra.

Theoretical studies of bonding and structure have continued to appear, with Lipscomb being the leading contributor. These have mostly dealt with the smaller carboranes and are included in that section. Theoretical studies on boron hydrides are also mentioned in the same section. There has been some synthetic activity in the field of small carboranes. The synthesis of B-alkylcarboranes by Köster and coworkers is novel.

A mechanistic study of the formation of the icosahedral carborane cage has appeared. Zakharkin, Stanko, and other Russian workers have continued to elaborate the chemistry of the icosahedral carboranes.

The most common carboranes and metallocarboranes contain a 12-atom icosahedral cage or an 11-atom icosahedral fragment. A few figures illustrating such compounds will be reproduced, but for most examples the reader will be referred to the numbering scheme illustrated in Figure 1. Removal of boron atom number 3 from the icosahedron (I) leaves the 11-atom fragment (II), in which all of the atoms are renumbered according to the official system. Thus, 1,2-$C_2B_{10}H_{12}$ (I) is converted (by treatment with base) to 7,9-$C_2B_9H_{11}^{2-}$ (II).

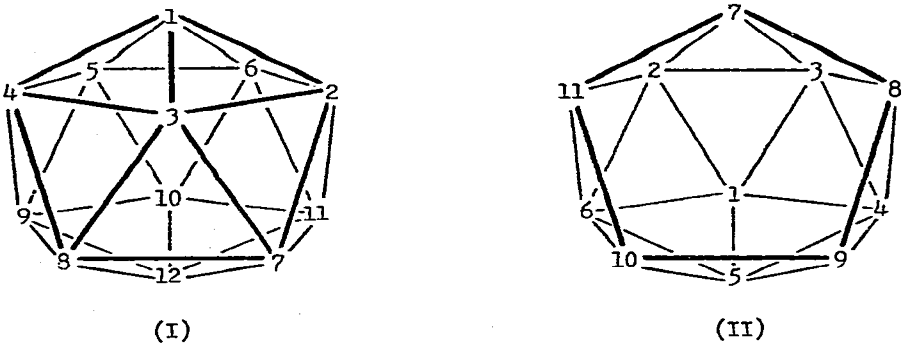


Figure 1. Numbering schemes for the icosahedron (I) and for the 11-atom icosahedral fragment (II) formed by removing atom number 3 from the icosahedron.

The numbering system is even more complex than this simplified illustration suggests. Structure (II) has been numbered in the wrong chiral sense so that the common 1,2-(I) to 7,8-(II) and 1,7-(I) to 7,9-(II) transformations might be readily perceived from one illustration. Another numbering problem related to chirality is that boron atoms 3 and 6 are equivalent in 1,2-$C_2B_{10}H_{12}$ and 2 and 3 are equivalent in the 1,7-isomer. However, until someone reports the optical resolution of a substituted icosahedral carborane and its stereospecific conversion to an 11-atom fragment, these complexities reduce to choosing which chirality of numbering yields the lowest set of substituent numbers for a given structure.

For brevity and convenience, the trivial names *o*-carborane, *m*-carborane, and *p*-carborane will be used for the 1,2-, 1,7-, and 1,12-isomers, respectively, of dicarba-*closo* dodecarborane (12).

B. Transition Metal Metallocarboranes

1. *Cages Containing Metal Atoms*. The diversity of metals included in various combinations makes this section difficult to arrange in logical order. In general, smaller polyhedra will be discussed first, followed by icosahedral structures and then 13-atom cages. All of the compounds included here have *closo* structures.

Rearrangements of polyhedral cages are of considerable current interest. Miller and Grimes have described the vapor phase thermal rearrangements of several cyclopentadienylcobaltacarboranes having 1-3 cobalt atoms and 3-5 boron atoms (Figures 2-6)[1]. Intramolecular rearrangements were observed

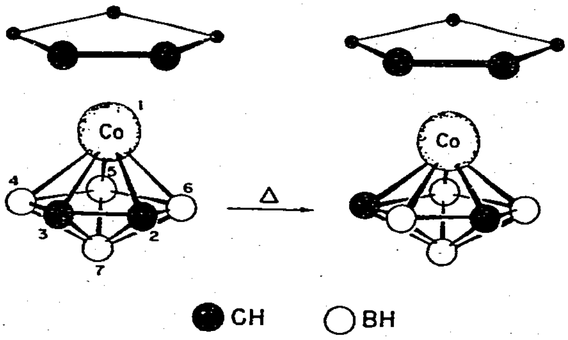


Figure 2. Thermal rearrangement of 1,2,3-$(\eta^5\text{-}C_5H_5)CoC_2B_4H_6$ to 1,2,4-$(\eta^5\text{-}C_5H_5)CoC_2B_4H_6$. [Reprinted with permission from V. R. Miller and R. N. Grimes, J. Amer. Chem. Soc., 97 (1975) 4213. Copyright by the American Chemical Society.]

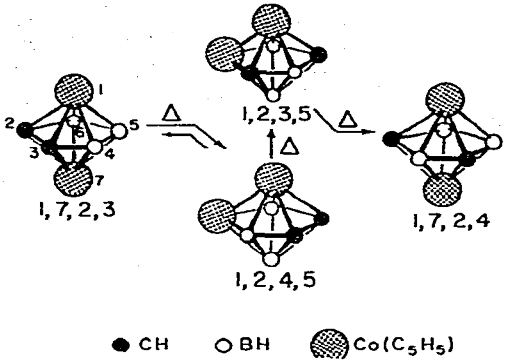
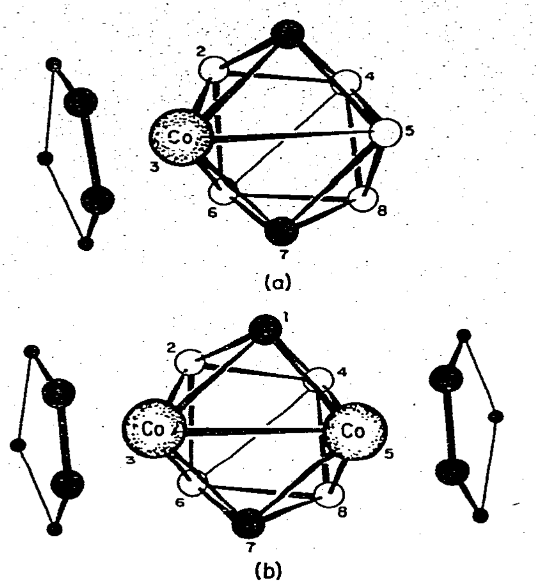


Figure 3. The principal rearrangement sequence for $(\eta^5-C_5H_5)Co_2C_2B_3H_5$-isomers. [Reprinted with permission from V. R. Miller and R. N. Grimes, J. Amer. Chem. Soc., 97 (1975) 4213. Copyright by the American Chemical Society.]

with CoC_2B_4, $Co_2C_2B_3$, $Co_2C_2B_5$, and $Co_3C_2B_5$ cages, but not with the CoC_2B_3, CoC_2B_5, or $Co_2C_2B_4$ cages that were studied. Intermolecular transfer of the cyclopentadienylcobalt group was observed in all cases except the $Co_2C_2B_3$ series, none of the four isomers of which underwent disproportionation. Hawthorne's rules for predicting the relative stabilities of larger-cage dicobaltacarborane isomers [J. Organometal. Chem., 98 (1975) 298] also appear to be applicable to these smaller cages, except that the tendecy of cobalt to migrate away from carbon in the larger cages was not observed with the smaller cages.

Mercer, Tribo and Scholer have studied the thermal rearrangement of the 11-atom cage cobaltacarborane, $1-(C_5H_4Co)-2,4-(CH_3)_2-2,4,-C_2B_8H_8$ (Fig. 7), and found that Hawthorne's rules for predicting the directions of rearrangements in icosahedral metallocarboranes apply to the 11-atom cage as well [2].



(a)

(b)

Figure 4. Proposed structures of eight-vertex cobaltacarboranes: (a) 3,1,7-(η^5-C_5H_5)$CoC_2B_5H_7$, (b) 3,5,1,7-(η^5-C_5H_5)$_2Co_2C_2B_4H_6$. [Reprinted with permission from V. R. Miller and R. N. Grimes, J. Amer. Chem. Soc., 97 (1975) 4213. Copyright by the American Chemical Society.]

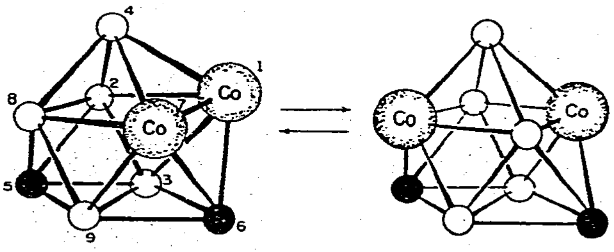


Figure 5. Reversible rearrangement of 1,7,5,6- and 1,8,5,6-(η^5-C_5H_5)$_2Co_2C_2B_5H_7$ (cyclopentadienyl rings omitted for clarity). [Reprinted with permission from V. R. Miller and R. N. Grimes, J. Amer. Chem. Soc., 97 (1975) 4213. Copyright by the American Chemical Society.]

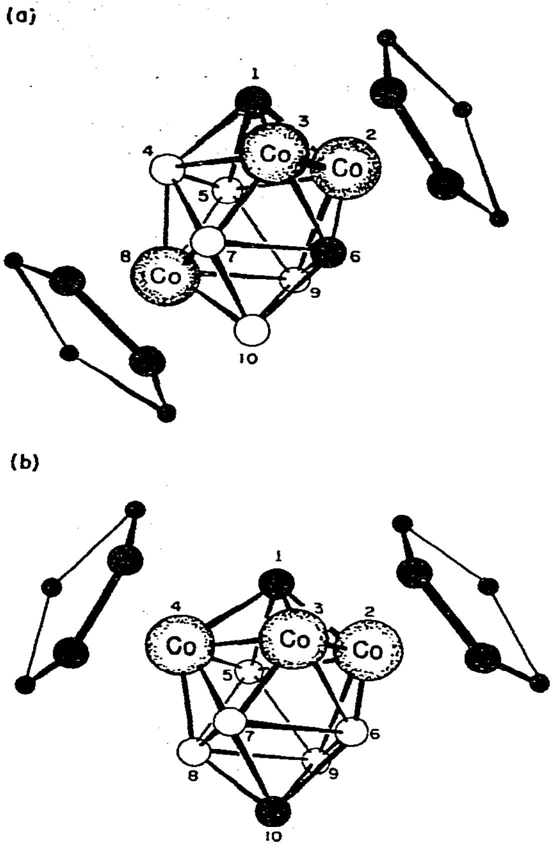


Figure 6. Structures of (a) 2,3,8,1,6- and (b) 2,3,4,1,10-$(\eta^5\text{-}C_5H_5)_3Co_3C_2B_5H_7$ (with one cyclopentadienyl ring omitted from each drawing). [Reprinted with permission from V. R. Miller and R. N. Grimes, J. Amer. Chem. Soc., 97 (1975) 4213. Copyright by the American Chemical Society.]

It has become something of a challenge to replace as many of the carborane cage boron atoms as possible by transition metals, and Maxwell and Grimes have achieved a new high metal/boron ratio with the synthesis of $[Fe(CO)_3]_2$-$(C_2H_5Co)B_4H_4C_2(CH_3)_2$ (Fig. 8)[3].

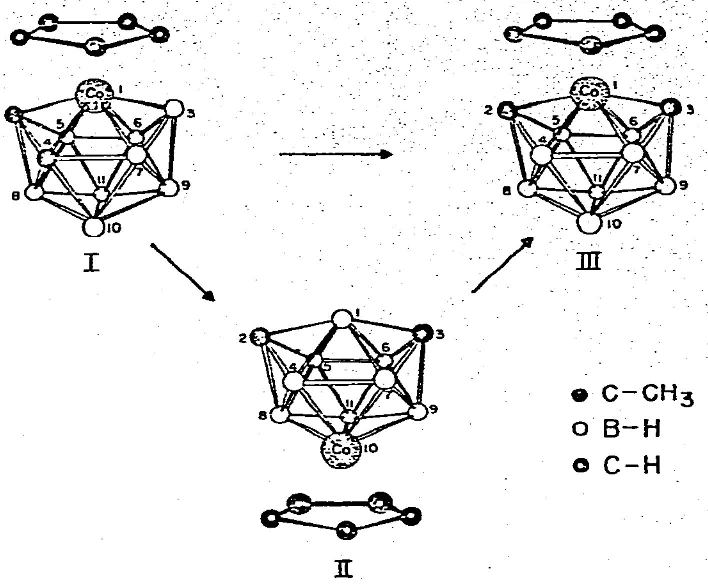


Figure 7. Rearrangement of an 11-atom cage cobaltacarborane, $1-(C_5H_5)-2,4-Me_2-1,2,4-CoC_2B_8H_8$ (I), to the 10,2,3-isomer (II) at 110°C and the 1,2,3-isomer (III) at 125°C. [Reprinted with permission from G. D. Mercer, M. Tribo, and F. R. Scholer, Inorg. Chem., 14 (1975) 764. Copyright by the American Chemical Society.]

The structure of the "triple-decked sandwich" compound $2-Me-1,7-(C_5H_5)_2-1,7,2,4-Co_2C_2B_3H_4$ has been determined by X-ray diffraction (Fig. 9)[4].

Hawthorne and coworkers have reported that the reduction of $4,5-C_2B_7H_9$ with sodium in THF followed by reaction with NaC_5H_5 and $FeCl_2$ has yielded a new diferracarborane, $(C_5H_5)_2Fe_2C_2B_6H_8$, which is paramagnetic but on standing at room temperature for several weeks in the solid state, undergoes rearrangement to a diamagnetic isomer. The structure of the diamagnetic isomer has been determined by X-ray crystallography (Fig. 10)[5].

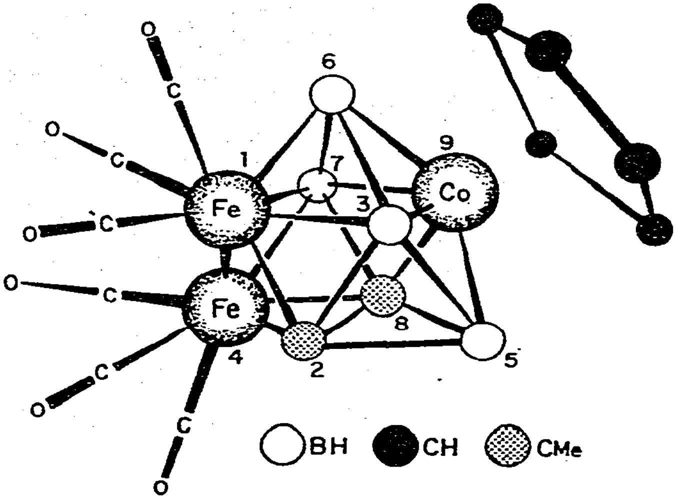


Figure 8. Proposed structure of $[Fe(CO)_3]_2(C_5H_5Co)B_4H_4C_2(CH_3)_2$. [Reprinted with permission from W. M. Maxwell and R. N. Grimes, J. Chem. Soc., Chem. Commun., (1975) 943. Copyright by the Chemical Society (London).]

The reaction of $B_9H_{12}^-$, $Ni(C_5H_5)_2$, and sodium amalgam has yielded $C_5H_5NiB_9H_9$, which isomerizes at 150°C [6]. The cage rearrangement changes the nickel atom from having five boron neighbors to only four boron neighbors (equatorial to apical migration in the 10-atom cage).

Salentine and Hawthorne have reported details of the rearrangement of one isomer of $(C_5H_5)_2CoNiCB_7H_8$ to three other isomers (Fig. 11), and have described the unexpected synthesis of a naphthalene cobaltacarborane, 2-$(\eta^6$-$C_{10}H_8)$-2-Co-1-$CB_{10}H_{11}$ (Fig. 12), which was obtained during an attempt to prepare a Co-Ni carborane from $(C_5H_5)CoCB_{10}H_{11}^-$ by way of reduction with sodium naphthalide followed by treatment with Ni(II)[7].

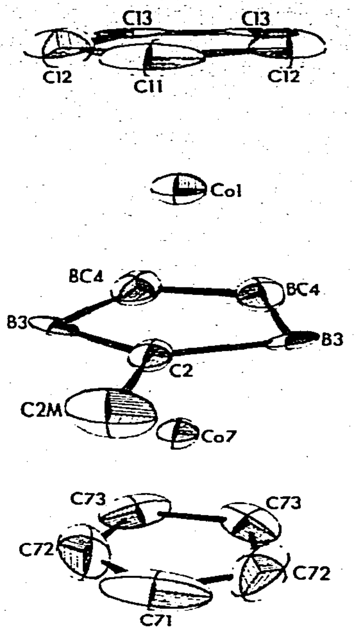


Figure 9. The structure of 2-Me-1,7-(η^5-C_5H_5)$_2$-1,7,2,4-$Co_2C_2B_3H_4$. [Reprinted with permission from W. T. Robinson and R. N. Grimes, Inorg. Chem., 14 (1975) 3056. Copyright by the American Chemical Society.]

The reaction of 3-(η^5-C_5H_5)-3,1,2-$CoC_2B_9H_{11}$ with Na followed by $PhBCl_2$ did not result in expansion of the carborane cage but instead resulted in insertion of the PhB group into the cyclopentadiene ring to from the B-phenylborabenzenecobalt complex (Fig. 13)[8].

A series of icosahedral metallocarboranes of the general formula 2,2-L_2-1,7-Me_2-2,1,7-$MC_2B_9H_9$ has been reported by Stone and coworkers, where M is Pt or Ni and L is R_3P or M is Pd and L is t-BuNC [9]. (See Fig. 1 for numbering of icosahedron.) These were prepared by insertion reactions of

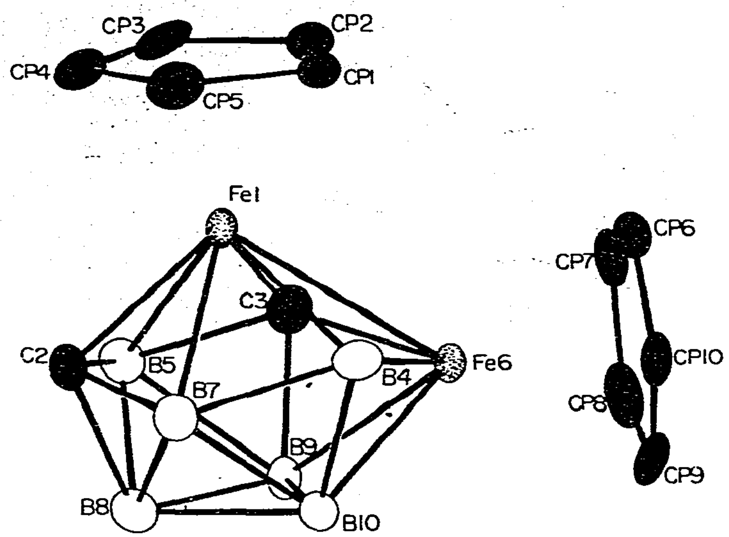


Figure 10. The structure of the diamagnetic diferracarborane, $1,6-(\eta^5-C_5H_5)_2-1,6,2,3-Fe_2C_2B_6H_8$, showing the numbering system used. Atoms are shown as 50% probability ellipsoids and hydrogens are omitted for clarity. [Reprinted with permission from K. P. Callahan, W. J. Evans, F. Y. Lo, C. E. Strouse, and M. F. Hawthorne, J. Amer. Chem. Soc., 97 (1975) 296. Copyright by the American Chemical Society.]

various metal complexes such as $Pt(PEt_3)_3$, $(Et_3P)_2Ni(C_8H_{12})$, etc., with the 11-atom closo-carborane $2,3-Me_2-2,3-C_2B_9H_9$. Similar insertion of $(Et_3P)_2Pt$—trans-stilbene into $1-(C_5H_5)-1,2,4-CoC_2B_8H_{10}$ gave $4,4-(Et_3P)_2-7-(\eta^5-C_5H_5)-4,7,1,2-PtCoC_2B_8H_{10}$ (See Fig. 1)[9].

Siedle has prepared the icosahedral ruthenium complexes $3,3,3-(OC)_3-3,1,2-RuC_2B_9H_{11}$ and $3-(OC)-3,3-(Ph_3P)_2-3,1,2-RuC_2B_9H_{11}$ from $7,8-C_2B_9H_{11}^{2-}$ and $(OC)_3RuCl_2$ or $(Ph_3P)_2(OC)_2RuCl_2$, respectively (see Fig. 1)[10]. The rhodium compound $3-Cl-3,3-(Ph_3P)_2-3,1,2-RhC_2B_9H_{11}$ was similarly prepared

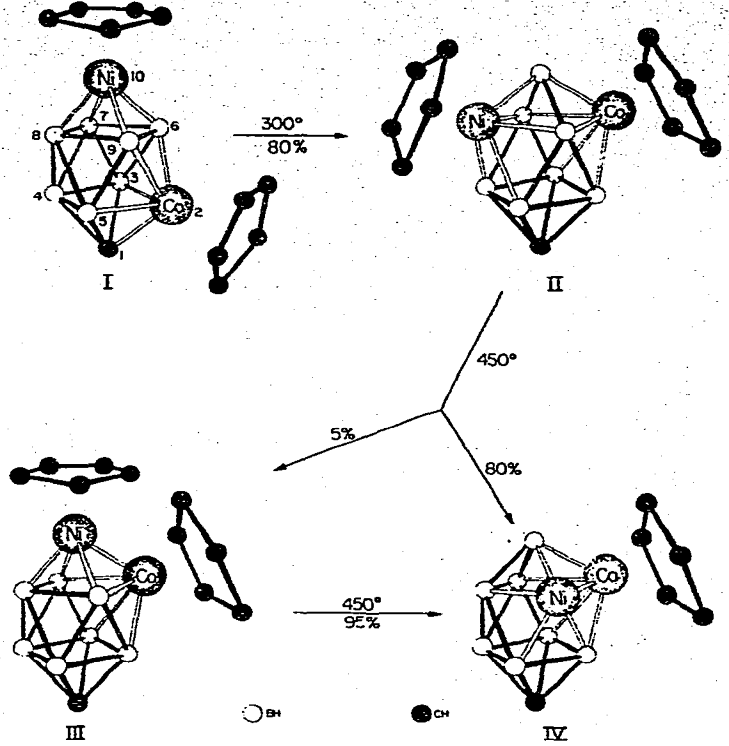


Figure 11. The proposed rearrangement scheme for the $(C_5H_5)_2CoNiCB_7H_8$ isomers. (A C_5H_5 ring has been omitted from IV for clarity.) [Reprinted with permission from C. G. Salentine and M. F. Hawthorne, J. Amer. Chem. Soc., 97 (1975) 6382. Copyright by the American Chemical Society.]

from $7,8\text{-}C_2B_9H_{11}^{2-}$ and $(Ph_3P)_2Rh(CO)Cl$, and analogs with other ligands on rhodium were also prepared [10].

The reaction of cis-$(Ph_3P)_2PtCl_2$ with 1,2-Me_2-*o*-$C_2B_{10}H_{10}$ has yielded the icosahedral platinum compounds 1,2-Me_2-3,3-$(Ph_3P)_2$-3,1,2-$PtC_2B_9H_9$, and two analogous compounds have been prepared from 1-Ph-*o*-carborane and $(R_3P)_2PtCl_2$ (R = Et, Pr)[11].

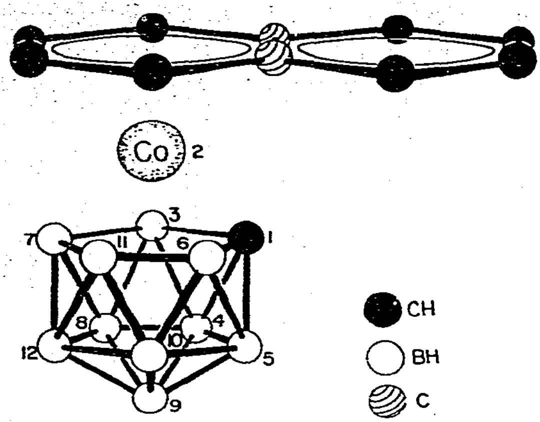


Figure 12. The proposed structure of 2-(η^6-$C_{10}H_8$)-2-Co-1-$CB_{10}H_{11}$. [Reprinted with permission from C. G. Salentine and M. F. Hawthorne, J. Amer. Chem. Soc., 97 (1975) 6382. Copyright by the American Chemical Society.]

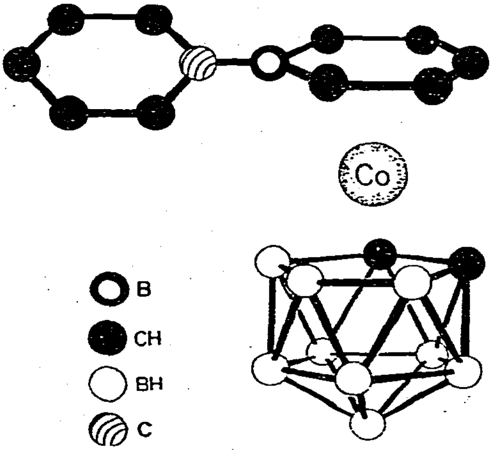


Figure 13. The proposed structure of 3-[1-Ph(η^6-BC_5H_5)]-3,1,2-$CoC_2B_9H_{11}$. [Reprinted with permission from R. N. Leyden and M. F. Hawthorne, Inorg. Chem., 14 (1975) 2018. Copyright by the American Chemical Society.]

Zakharkin and Bikkineev have reported that bromination of 3-(C_5H_5)-3,1,2-$CoC_2B_9H_{11}$ yields B-bromo derivatives having one to three bromine atoms [12]. Several compounds of the class 1-R-3-(C_5H_5)-3,1,2-$CoC_2B_9H_{10}$ have been obtained from C_5H_5Tl, $CoCl_2$, and $Tl_2RC_2B_9H_{10}$ (R = CH_2OH, $CH{=}CH_2$, CH_2CN, CO_2Me, $CF{=}CFCF_3$), and the CH_2OH side chain has been oxidized to the aldehyde and the acid [13]. ArMgBr attacks the cyclopentadienyl ring of 3-(C_5H_5)-3,1,2-$CoC_2B_9H_{11}$ to form 3-(C_5H_4Ar)-3,1,2-$CoC_2B_9H_{11}$ [14].

The icosahedral nickelaborane $(C_5H_5)NiB_{11}H_{11}^-$ has been obtained from the reduction of $Na_2B_{11}H_{13}$ with Na-Hg in the presence of $Ni(C_5H_5)_2$, and the dinickelaborane $(C_5H_5)_2Ni_2B_{10}H_{10}$ has been synthesized from $B_{10}H_{10}^{2-}$ and $(C_5H_5NiCO)_2$[15].

Salentine and Hawthorne have reacted $Na_2C_2B_{10}H_{12}$ with $TiCl_4$ to form the bis-13-atom-cage compound $Ti(C_2B_{10}H_{12})_2^{2-}$, which was crystallized as the tetraethylammonium salt. The compound is red-orange, diamagnetic, and moderately stable to air in the solid state. The C,C-dimethyl homolog is stable to air for several weeks. Zirconium forms a similar but less air-stable compound, and vanadium yields a paramagnetic analog [16]. The structure of $(Me_4N^+)_2Ti(C_2B_{10}H_{10}Me_2)_2^{2-}$ has been determined by X-ray diffraction (Fig. 14) [17].

Oxidation of $(C_2B_{10}H_{12})_2Co^-$ and other 13-atom-cage metallocarboranes with $CuCl_2$ removes the metal atom from the cage to generate 95% o-carborane and 5% m-carborane [18].

2. Cages Having External Metal Substituents. This section begins with some externally metal-substituted icosahedral carboranes and then proceeds to nido-carboranes and boranes, including those having a metal atom along the edge of the open face.

Hoel and Hawthorne have reported the details of the preparation of several B-iridium-substituted carboranes [19]. In the first series of experiments, C-carboranyldimethylphosphine reacted with an iridium(I) complex, $[Ir(C_8H_{14})_2$-

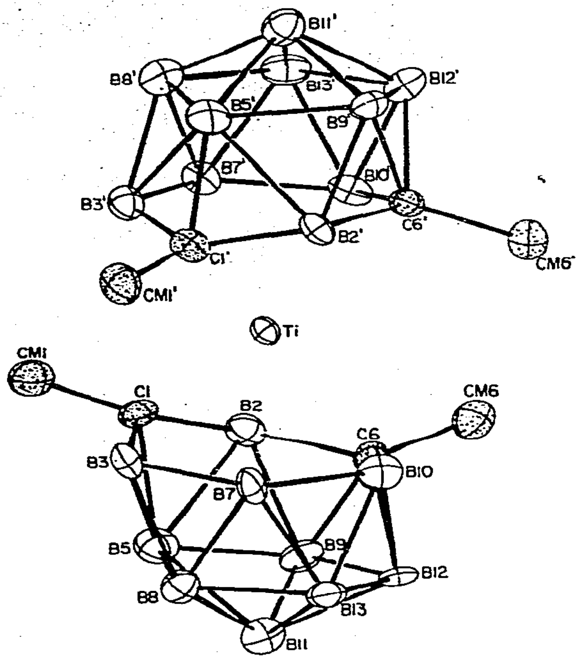


Figure 14. The structure of $4,4'\text{-Ti}(1,6\text{-Me}_2\text{-}1,6\text{-C}_2B_{10}H_{10})_2^{2-}$, a titanacarborane dianion having two 13-atom cages linked at the titanium atom. [Reprinted with permission from F. Y. Lo, C. E. Strouse, K. P. Callahan, C. B. Knobler, and M. F. Hawthorne, J. Amer. Chem. Soc., 97 (1975) 428. Copyright by the American Chemical Society.]

$Cl]_2$, to form a cyclic B-carboranyliridium complex (Fig. 15). To prove that the iridium is bonded to boron and not carbon, C-carboranyldimethylphosphine was prepared with deuterium labeling at all of the possible substitution sites (Fig. 16), and it was found that an Ir–D bond was indeed formed. The particular boron to which the iridium is bonded could not be positively identified, but the 3,6-position seems most likely based on other results. It

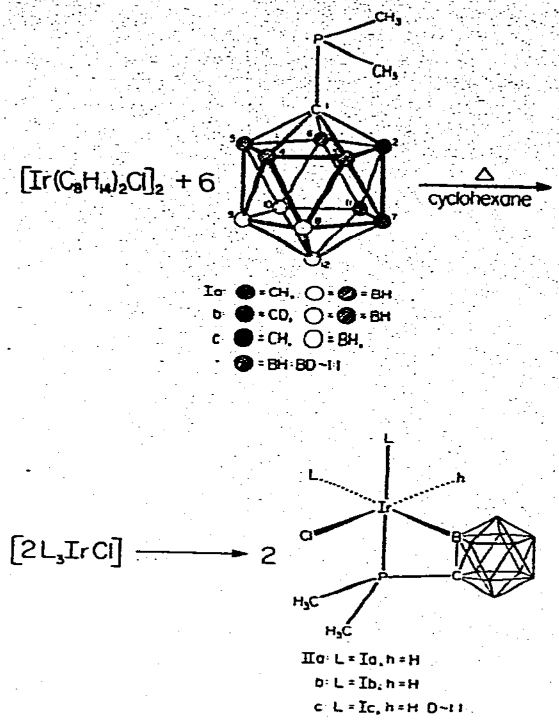


Figure 15. The preparation of B-carboranyliridium complexes by intramolecular oxidative addition. [Reprinted with permission from E. L. Hoel and M. F. Hawthorne, J. Amer. Chem. Soc., 97 (1975) 6388. Copyright by the American Chemical Society.]

was then found possible to react o-carborane with $[Ir(C_8H_{14})_2Cl]_2$ and PPh_3 or $AsPh_3$ to form B-iridium-substituted carboranes (Fig. 17). The position of substitution was proved by the use of $3,6\text{-}D_2\text{-}o\text{-}C_2B_{10}H_{10}$. Similar derivatives of m- and p-carborane were also obtained (Fig. 18), but yields were only moderate and excess carborane was required.

The preparation of a cyclic palladium derivative of 1-phenyl-o-carborane has been described [20]. Several $1\text{-}(Ph_3P)_3Rh$-substituted o-carboranes, 1-

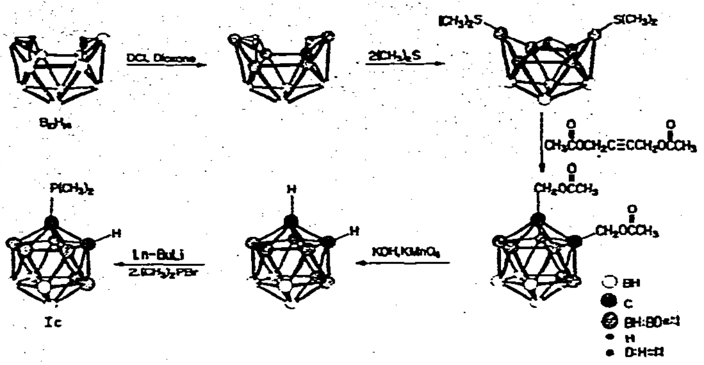
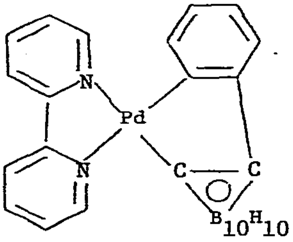


Figure 16. Preparation of $1\text{-}PMe_2\text{-}3,4,5,6,7,11\text{-}D_6\text{-}\underline{o}\text{-}C_2B_{10}H_5$ (50% labeled). [Reprinted with permission from E. L. Hoel and M. F. Hawthorne, J. Amer. Chem. Soc., 97 (1975) 6388. Copyright by the American Chemical Society.]

$(Ph_3P)_3Rh\text{-}2\text{-}R\text{-}1,2\text{-}C_2B_{10}H_{10}$, have been prepared from the lithiocarboranes and



$(Ph_3P)_3RhCl$ [21]. The reaction of $(Ph_3P)_3$ IrCl with $1\text{-}Li\text{-}2\text{-}Me\text{-}\underline{o}\text{-}C_2B_{10}H_{10}$ has been postulated to proceed by way of an unstable iridium-carborane σ-bonded complex, which decomposes to form a cyclic o-phenylene-P-Ir derivative containing no carborane [22].

Reaction of $(C_5H_5)Fe(CO)_2$—cyclohexene cation with $7,8\text{-}C_2B_9H_{12}^-$ has yielded $9\text{-}[(C_5H_5)Fe(CO)_2]\text{-}7,8\text{-}C_2B_9H_{12}$, and a related derivative of $B_{10}H_{13}^-$ has also been described [23].

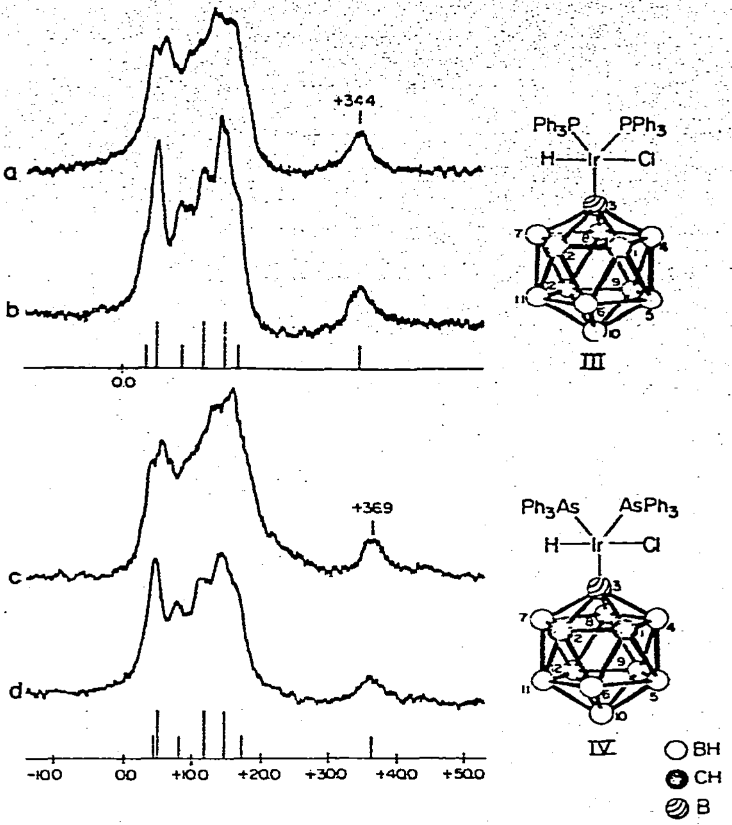
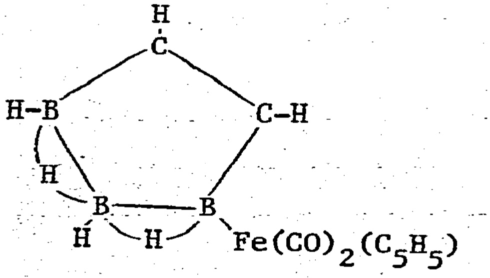
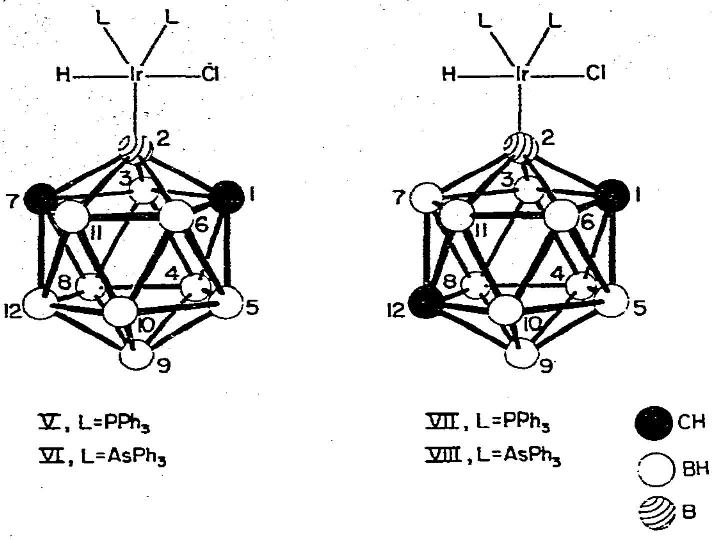


Figure 17. The proposed structures and 80.5 MHz ^{11}B NMR spectra of 3-[(PPh$_3$)$_2$IrHCl]-o-$C_2B_{10}H_{11}$ (III) and the As analog (IV). Spectra b and d are proton decoupled. [Reprinted with permission from E. L. Hoel and M. F. Hawthorne, J. Amer. Chem. Soc., 97 (1975) 6388. Copyright by the American Chemical Society.]



Top view of 9-[(C_5H_5)Fe(CO)$_2$]-7,8-$C_2B_9H_{12}$ with lower B_6H_6 omitted for clarity. (See Fig. 1 for complete 11-atom icosahedral fragment.)

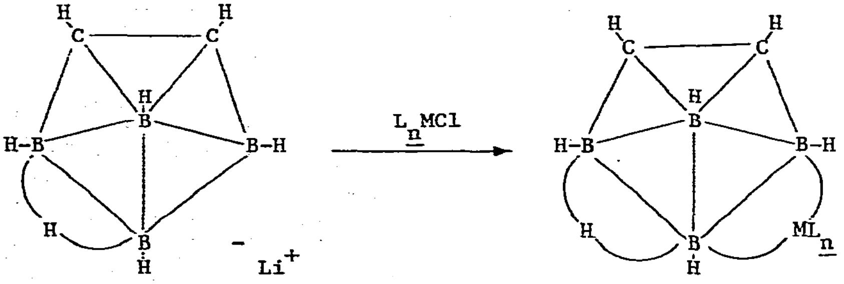


V, L=PPh$_3$
VI, L=AsPh$_3$

VII, L=PPh$_3$
VIII, L=AsPh$_3$

Figure 18. Proposed structures of *B*-(L$_2$IrHCl)-*m*- and -*p*-$C_2B_{10}H_{11}$. [Reprinted with permission from E. L. Hoel and M. F. Hawthorne, J. Amer. Chem. Soc., 97 (1975) 6388. Copyright by the American Chemical Society.]

Reaction of 2,3-$C_2B_4H_7^-$ with organometallic chlorides L_nMCl results in insertion of the metal into an edge of the carborane structure [24].



(where ML_n = $AlMe_2$, $GaMe_2$, $Rh(PPh_3)_3$, $AuPPh_3$, HgPh)

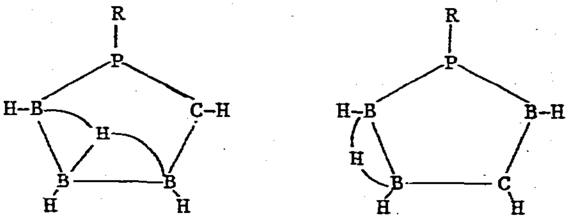
The aluminum derivative (ML_n = $AlMe_2$) is unstable in condensed phases, but was pyrolyzed at 100°C in the gas phase to form the closo carborane $CH_3AlC_2B_4H_6$.

Nido-metalloboranes having 11-atom cages have been prepared from $B_{10}H_{10}^{2-}$ and $LLPtCl_2$, where L is an arylphosphine ligand [25]. The iridium-borane anion $B_{10}H_{12}Ir(CO)(PPh_3)_2^-$ exchanges boron-bound hydrogen atoms with molecular D_2 [26]. An iridium-substituted pentaborane has been reported [27]. The structure of $[(Ph_3P)_2Cu]_2B_{10}H_{10}$ involves Cu-H-B bridge bonds [28].

C. Nonmetal Heterocarboranes

Wong and Lipscomb have investigated the thermal rearrangement of several B-chlorophosphacarboranes, $CHPB_{10}H_9Cl$, and concluded that the data are inconsistent with the usual cuboctahedral intermediate characteristic of $C_2B_{10}H_{12}$ derivatives or the alternative triangle rotation mechanism, but favor a mechanism involving the mutual rotation of two opposite pentagonal pyramids in the icosahedron (Fig. 19) [29].

The phosphacarbollide monoanions $7,8PCB_9H_{11}^-$ and $7,9\text{-}PCB_9H_{11}^-$ have been alkylated on phosphorus with benzyl, allyl, and cinnamyl bromides and with ethyl iodide [30]. The resulting $R\text{-}PCB_9H_{11}$ are notably malodorous.



Top views of 7-R-7,8- and -7,9-PCB_9H_{12} with B_6H_6 below omitted. (See Fig. 1 for complete 11-atom icosahedral fragment.)

Czech [31] and Russian [32] groups have reacted $7,8\text{-}C_2B_9H_{12}^-$ with nitrous acid and obtained mixtures of $10,7,8\text{-}NC_2B_8H_{11}$ and $NC_2B_8H_{13}$. The former has been N-benzylated and the structure of the derivative proved by X-ray diffraction

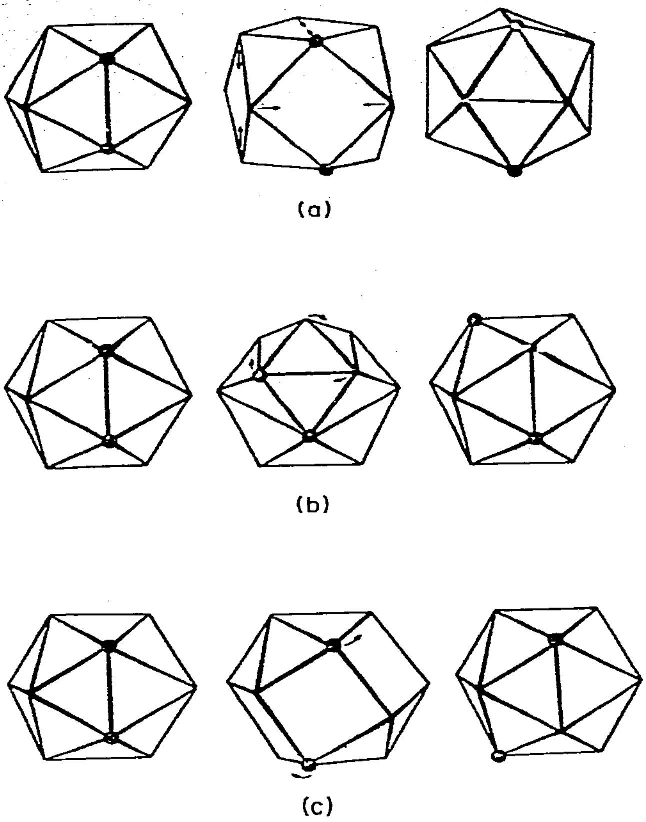
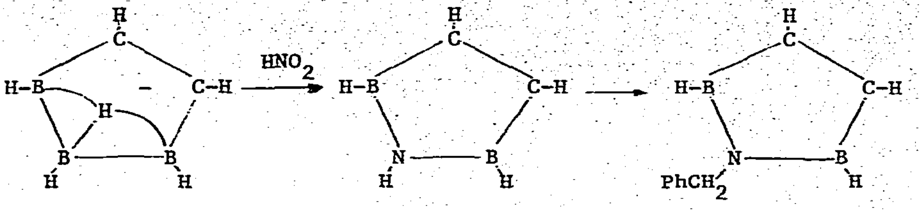


Figure 19. (a) Icosahedral rearrangement through the cuboctahedral intermediate; (b) Triangle rotation; (c) Mutual rotation of two opposite pentagonal pyramids in the icosahedron. [Reprinted with permission from H. S. Wong and W. N. Lipscomb, Inorg. Chem., 14 (1975) 1350. Copyright by the American Chemical Society.]

[33]. Differing structures were assigned to $NC_2B_8H_{13}$ [31,32]. Sodium bisulfite converts 7,8-$C_2B_9H_{12}^-$ to 10,7,8-$SC_2B_8H_{10}$ [32].



Preparation of 10-(PhCH$_2$)-10,7,8-NC$_2$B$_8$H$_{10}$, top views with B$_6$H$_6$ below omitted. (See Fig. 1 for complete 11-atom icosahedral fragment.)

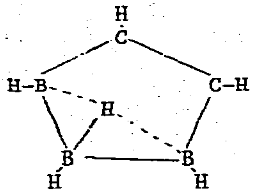
Nitrous acid converts decaborane to 4-NB$_8$H$_{13}$, the structure of which has been determined by X-ray diffraction [34].

Icosahedral SB$_{11}$H$_{11}$ has been synthesized [35]. The structure of 2,2'-(1-B$_9$H$_8$S)$_2$ has been determined by X-ray diffraction [36].

D. Small and Medium Carboranes

1. Theory and Structure. A number of theoretical calculations and structure determinations have been reported on a variety of small and medium closo- and nido-carboranes and boron hydrides. Boron hydrides often serve as simpler models for theoretical predictions regarding carboranes.

Lipscomb and coworkers have reported molecular orbital calculations on open boron hydrides and carboranes, including $C_2B_7H_{13}$, $C_2B_8H_{12}^-$, and $C_2B_{10}H_{13}^-$ using the partial retention of differential overlap approximation [37]. The 7,8-$C_2B_9H_{12}^-$ is of particular interest because of the question of the location of the twelfth hydrogen atom, which was found last year by X-ray crystallography to occupy a position near the missing vertex of the icoshedron [J. Organometal. Chem., 98 (1975) 321–324], though it was located closest to the boron atom in the pentagonal face farthest from the two adjacent carbon atoms (boron atom number 10 in the official system). The calculations predict the hydrogen to be 1.33 Å from this boron atom, with only weak bonding to the two adjacent boron atoms. Bonding to the carbon atoms was not mentioned (but is evidently negligible).



Top view of the bridge-bond hydrogen in 7,8-$C_2B_9H_{12}^-$, with six BH groups below omitted for clarity. (See Figure 1 for structure of 11-atom icosahedral fragment.)

It has previously been reported that a calculation of the energy of prism-shaped ($\underline{D_{3h}}$ symmetry) $C_2B_4H_6$ yielded such an unfavorable value that it appeared unlikely that this geometry was on the reaction pathway for isomerizing 1,2-$C_2B_4H_6$ to 1,6-$C_2B_4H_6$ [Organomet. Chem. Rev. B, 8 (1971) 20]. Lipscomb's group has now developed a new approach to computing reaction pathways and found that a distorted trigonal prism, "like the sagging of an improperly braced sawhorse," has a much more favorable energy than the trigonal prism itself. The structures involved are illustrated in Fig. 20 [38].

Ab initio molecular orbital calculations (STO-3G and 6-31G* levels) have been reported for 17 simple boron compounds, including BH_3, HB=BH, H_2B-BH_2, BCH, $HB=CH_2$, and H_2B-CH_3 [39]. Ab initio calculations have been reported for BH_5 and $B_2H_7^-$ [40]. Without electron correlation SCF calculations predict BH_5 to be unstable with respect to BH_3 and H_2, but with correlation it has a binding energy of −2 kcal/mol in a $\underline{C}_s$ geometry. Ab initio molecular orbital calculations on $C_2B_3H_5$ and $C_2B_4H_6$ have been reported [41].

Extended Hückel calculations suggest that the isomers of $C_2B_3H_5^{2-}$, which are square pyramidal structures analogous to pentaborane, can be interconverted by relatively open transition states, and that $C_2B_4H_6^{2-}$ isomers likewise have an open face and are interconvertible through open transition states, in all cases avoiding the <u>closo</u> polyhedral forms characteristic of the neut-

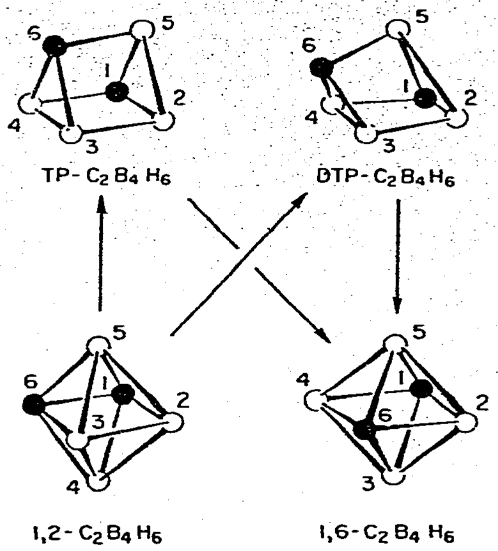


Figure 20. Possible pathways for rearrangement of 1,2-$C_2B_4H_6$ to 1,6-$C_2B_4H_6$. The atoms are identified throughout by the numbers of the positions to which they move in the 1,6-isomer. The intermediate labeled DTP-$C_2B_4H_6$ is the one calculated to have low enough energy to lie on the reaction pathway. [Reprinted with permission from T. A. Halgren, I. M. Pepperberg, and W. N. Lipscomb, J. Amer. Chem. Soc., 97 (1975) 1248. Copyright by the American Chemical Society.]

ral molecules $C_2B_3H_5$ and $C_2B_4H_6$ [42]. Extended Hückel calculations suggest that a dodecahedron of 18 carbon and 2 boron atoms may be capable of existence [43].

Muetterties, Hawthorne, and coworkers have noted that $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$ as well as the isoelectronic carboranes, undergo cage rearrangements much more easily than do other cage sizes, and have provided a theoretical discussion of the known experimental data [44]. Wegner has pointed out the similarity in electronic structure of the distorted icosahedral cages of d^8 and d^9 bis(dicarbollyl)metal complexes to the anions $C_2B_{10}H_{12}^-$ and $C_2B_{10}H_{12}^{2-}$ and explained the "slipped" cage geometry on the basis of filling of antibonding molecular orbitals [45].

The structures of 1,2-$C_2B_4H_6$ and CB_5H_7 have been determined by gas-phase electron diffraction [46]. The structure of CB_5H_7 is unusual in having a triply-bridging hydrogen atom which essentially occupies one apex of a 7-atom cage (Fig. 21). These results are in agreement with the conclusions based on microwave and NMR spectra which were reported last year [J. Organometal. Chem., 98 (1975) 324]. The structures of 2,4-$C_2B_5H_7$ and 1,6-$C_2B_4H_6$ have been determined by electron diffraction [48]. Electron diffraction studies have yield-

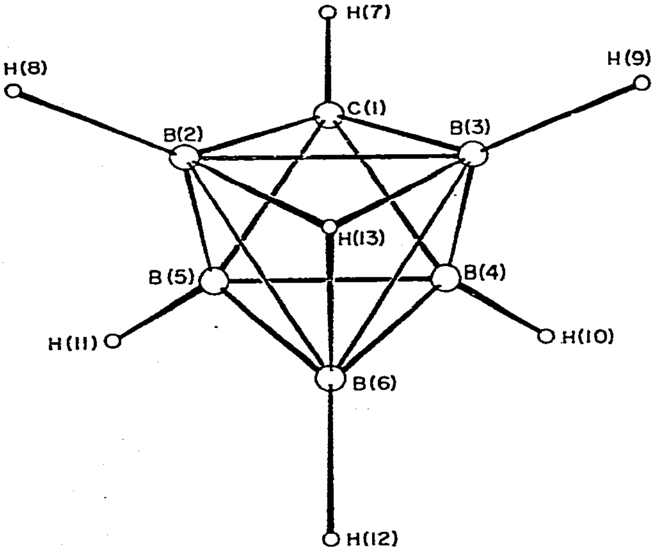


Figure 21. Projection of CB_5H_7 down the pseudo threefold axis defined by atoms B(2)B(3)B(6). [Reprinted with permission from E. A. McNeill and F. R. Scholer, Inorg. Chem., 14 (1975) 1081. Copyright by the American Chemical Society.]

ed the boron-carbon bond distances 1.595 (± 0.005) Å for 1-methylpentaborane and 1.592 (± 0.005) Å for 2-methylpentaborane.

Fehlner has concluded that the He(I) photoelectron spectra of 1,5-$C_2B_3H_5$, 1,6-$C_2B_3H_6$, 2,4-$C_2B_5H_7$, and 1,7-$C_2B_{10}H_{12}$ are consistent with loss of electrons from exo-polyhedral orbitals [50]. Compton scattering of ν-rays by decaborane agrees with localized molecular orbital theory [51].

The 70.6-MHz ^{11}B NMR spectra of 7,9-$C_2B_9H_{12}^-$ and a series of its derivatives have been measured and the chemical shifts of the various boron atoms elucidated [52]. Boron-carbon NMR coupling constants have been determined for a series of trialkylboranes, alkyldiboranes, and alkylpentaboranes, as well as BH_3CO and BH_3CN^- [53]. The ^{11}B NMR spectrum of B_4H_8CO at -20°C reveals the presence of two stereoisomers, probably <u>endo</u> and <u>exo</u> [54]. The stereochemically nonrigid anions $B_4H_9^-$, $B_5H_{12}^-$, $B_6H_{11}^-$, and $B_7H_{12}^-$ have been studied by proton and boron-11 NMR spectroscopy [55].

2. <u>Synthesis and Reactions</u>. Scholer and coworkers have observed that the electrochemical reduction of a cyclic 4,7-dioxy-2,3-dicarba-<u>closo</u>-undecaborane(11) (Fig. 22) is electrochemically reversible in the first step and gives a stable radical anion, which is detectable by ESR. The second electron added evidently results in rearrangement, perhaps to a <u>nido</u> anion, and is electrochemically irreversible, but the original <u>closo</u> carborane can be regenerated by chemical oxidation [56]. The compound studied and several analogs were made by reacting glycols with 4,7-$(HO)_2$-2,3-Me_2-2,3-$C_2B_6H_7$, and by the use of oxygen-18 labeled ethylene glycol it was shown that the <u>B</u>-hydroxyl groups of the borane are replaced [57].

Koster and coworkers have synthesized alkylated C_2B_3 carboranes from the reaction of $R_2B\text{-}C{\equiv}C\text{-}R'$ with $(R_2BH)_2$, and also from the conversion of $HC[B(OMe)_2]_3$ to $HC(BEt_2)_3$ with BEt_3 followed by treatment with $AlEt_3$ [58]. The latter reaction also yielded hexaethylhexaboraadamantane.

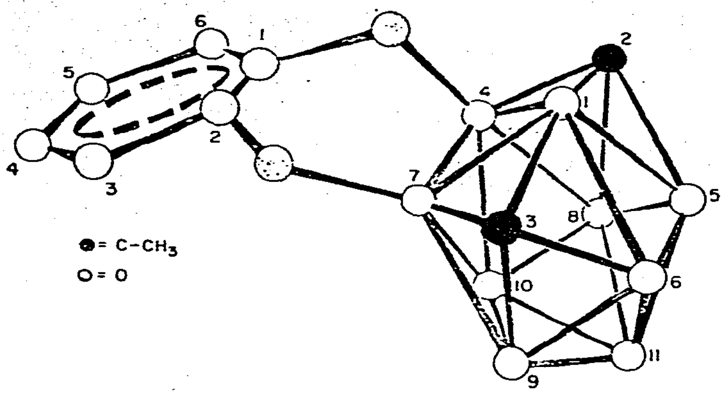
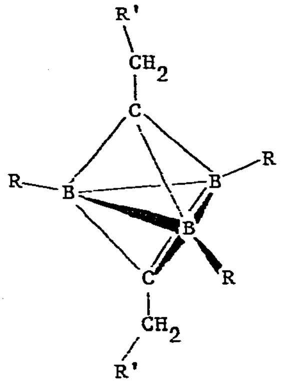
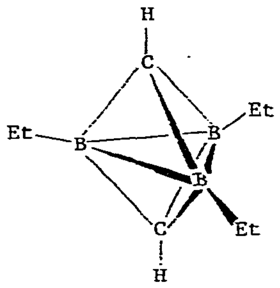
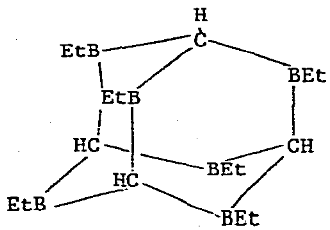


Figure 22. The structure of 4,7-[1,2-phenyldiylbis(oxy)]-2,3-dimethyl-2,3-dicarba-closo-undecaborane(11). [Reprinted with permission from G. D. Mercer, J. Lang, R. Reed, and F. R. Scholer, Inorg. Chem., 14 (1975) 761. Copyright by the American Chemical Society.]







Flash thermolysis of $1,2\text{-}(Me_3Si)_2B_5H_7$ yields several silylated small closo carboranes, including $1\text{-}SiH_3\text{-}1,5\text{-}C_2B_3H_4$, $1\text{-}SiMeH_2\text{-}1,5\text{-}C_2B_3H_4$, $1\text{-}SiH_3\text{-}2\text{-}Me\text{-}1,5\text{-}C_2B_3H_3$, and also 2- and $4\text{-}Me\text{-}CB_5H_6$, which equilibrate [59]. Fluorination of $2,4\text{-}C_2B_5H_7$ with elemental fluorine at low temperature has yielded a series of monofluorinated and difluorinated derivatives as well as the cage cleavage product $F_2BCH_2BF_2$ [60].

Coupling of $1\text{-}Li\text{-}1,10\text{-}C_2B_8H_9$ with CuCl has yielded $HCB_8H_8C\text{-}CB_8H_8CH$ [61]. A useful preparation of the diazonium compound $1\text{-}B_{10}H_9N_2^-$ from $B_{10}H_{10}^{2-}$ and ArN_2^+ has been described [62].

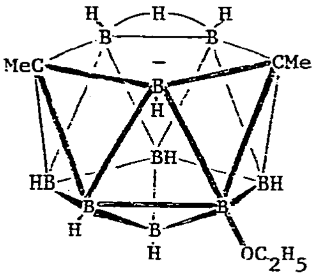
The synthesis of the nido carborane $6,9\text{-}C_2B_8H_{14}$ has been reported [63]. Reaction of 1- and $2\text{-}(Me_3Si)B_5H_8$ with butyllithium followed by Me_2BCl yields boranes having a basal Me_2B bridging group in place of a bridge hydrogen [64]. The germanium analogs behave similarly. A new synthesis of pentaborane(9) from $Bu_2N^+B_3H_8^-$ and HBr followed by pyrolysis of the resulting $Bu_4N^+B_3H_7Br^-$ at 100° has been reported [65].

Oxidation of $7,8\text{-}C_2B_9H_{12}^-$ with chromic acid has yielded an anion, $C_4B_{18}H_{23}^-$, believed to consist of two dicarbollide cages linked by a single hydrogen bridge between boron atoms 9 and 9', and a neutral product $C_4B_{18}H_{22}$, having two B-H-B linkages between dicarbollide units. Reaction of $C_4B_{18}H_{22}$ with diborane gave a mixture of o-carborane and 4,4'-bis-o-carborane, and reduction of the cesium salt of $C_4B_{18}H_{22}$ with sodium in ammonia gave $9,9'\text{-}(7,8\text{-}C_2B_9H_{11})_2$ (See Fig. 1 for the structure and numbering of the 11-atom icosahedral fragment.) The synthesis of $B_{14}H_{18}$, in which the decaborane and hexaborane frameworks share a common edge, has been reported [67]. Small amounts of a new boron hydride, $B_{14}H_{20}$, have been prepared and the structure has been determined by X-ray diffraction [68].

The reaction of 1,7-dimethyl-m-carborane with KOH in ethanol under pressure at 160° yields $3\text{-}EtO\text{-}7,9\text{-}Me_2\text{-}7,9\text{-}C_2B_9H_9^-$ [69]. Alkylation of dicarbollide ion, $7,8\text{-}C_2B_9H_{11}^{2-}$, with RX (R = Me, Et, Bu, allyl; X = Cl, Br,

I) initially occurs at boron number 9, but leads to cage rearrangement resulting in formation of 3-R-7,8-$C_2B_9H_{11}^-$ [70]. (See Fig. 1 for numbering of the 11-atom icosahedral fragment, or note the considerable similarity between this structure and the one immediately preceding.) Alkylation of 7,9-$C_2B_9H_{11}^{2-}$ occurs at an edge boron and is not accompanied by rearrangement.

1,7-Me_2-1,7-$C_2B_{10}H_{10}$



Alkylated beryllium-boron hydride mixtures from Me_2Be and B_4H_{10} and related ingredients have been patented as liquid fuels [71]. The fate of those who breathe the exhaust fumes was not mentioned.

E. Icosahedral Carboranes

1. Mechanism of Cage Formation. The mechanism of carborane formation from $(Me_2S)_2B_{10}H_{12}$ and a series of substituted acetylenes has been studied by Hill, Johnson, and Novak [72]. It was found that $(Me_2S)_2B_{10}H_{12}$ dissociates reversibly to $Me_2SB_{10}H_{12}$ + Me_2S, and the rate-determining step is the combination of $Me_2SB_{10}H_{12}$ with R-C≡CH. The rate was found to be first-order in $(Me_2S)_2B_{10}H_{12}$ and first-order in acetylene and to be suppressed by excess Me_2S. Good correlation of ΔH* and ΔS* with Taft polar substituent constants was noted. Electron-donating substituents on the acetylene lower ΔH* but the isokinetic temperature is 12°C, and accordingly the ΔS* term dominates

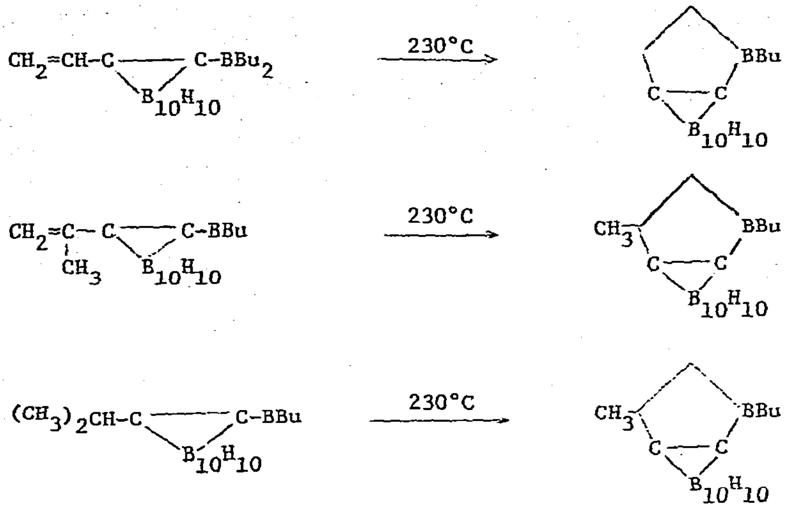
the relative rates in the temperature range studied, 37-60°C, so that the rate increases slightly with increasing electron-withdrawing character of the substituent.

2. Derivative Chemistry. Reactions which convert icosahedral carboranes to cages of other sizes or vice versa have been noted in preceding sections [16, 18, 69]. What follows consists of one U.S. patent and 18 Russian publications, most of them by Zakharkin's group.

Stanko and Anorova have reported more studies on the rearrangement of the dianion from sodium reduction of p-carboranes to o- and m-carboranes [73].

Sulfur reacts with m-$RCB_{10}H_{10}CNa$ to form m-$RCB_{10}H_{10}CSNa$, and several typical thiol reactions have been carried out with these compounds, including oxidation to the sulfonic acids [74]. The oxidation of dilithio m- and p-carboranes to C,C'-dihydroxycarboranes has been patented [75]. C-Lithio-o-carboranes have been employed in Michael additions to ethylidenemalonic and benzylidenemalonic esters [76]. Epoxypropylcarboranes have been prepared from lithiocarboranes and epichlorohydrin [77]. Reaction of an epoxypropylcarborane with dilithio-o-carborane has led to a compound having three carborane cages linked through aliphatic chains. $MeCB_{10}H_{10}C\text{-}CH_2CHOHCH_2\text{-}CB_{10}H_{10}C\text{-}CH_2CHOHCH_2\text{-}CB_{10}H_{10}CMe$ [78]. Epoxide opening reactions of 1-epoxyisopropyl-o-carborane have been described [79]. 1-Cyclopropyl-o-carborane has been made from cyclopropylacetylene and decaborane [80].

Mikhailov and Shagova have reported the synthesis of some boracyclopentano-o-carboranes and boracyclopenteno-o-carboranes [81].



C-Aminocarboranes have been prepared by reduction of the nitroso compounds and have been formylated and acetylated and converted to Schiff bases [82]. Reaction of *o*-RCB$_{10}$H$_{10}$C-CH$_2$X (R = H or Me, X = Cl, Br, or I) with Et$_2$NH in benzene gave good yields of *o*-RCB$_{10}$H$_{10}$C-CH$_2$NEt$_2$, but with piperidine the major reactions involved the usual removal of a boron atom from the cage. With ethanolic Me$_2$NH, *o*-HCB$_{10}$H$_{10}$C-CH$_2$Br gave mostly the substituted dicarbollide derivative, [7,8-HCB$_9$H$_{10}$C-CH$_2$NMe$_2$]$^-$, which was *N*-methylated and then reacted with sodium cyanide to form [7,8-HCB$_9$H$_{10}$C-CH$_2$CN]$^-$ [83]. The acid-catalyzed cyclotrimerization of *p*-acteylphenyl-*o*- and -*m*-carboranes forms the tris(carboranylphenyl)benzenes [84]. Mixtures of *B*-acetoxycarboranes have been obtained from the oxidation of *o*- or *m*-carborane with KMnO$_4$ or CrO$_3$ in acetylating media [85].

The preparation of disilylated *m*-carboranes from dilithio-*m*-carborane and MeOSiMe$_2$Cl or related chlorosilanes has been reported [86]. Refluxing 1-RMe$_2$Si-*m*-CB$_{10}$H$_{10}$CH in ether with a catalytic amount of alkali causes disproportionation to *m*-carborane and RMe$_2$Si-CB$_{10}$H$_{10}$C-SiMe$_2$R [87]. Russian patents have been issued for the reaction of lithiocarboranes with aryl cyanates to form C-cyanocarboranes [88], the preparation of carboranyl-substituted aromatic nitriles [89], the synthesis of difunctional silicon derivatives of m-carborane [90], and o-carboranyl organosilicon peroxides related to intermediates for polymerization [91].

3. Physical Organic Studies. Radical intermediates in the gamma-ray induced polymerization of alkenylcarboranes have been examined by ESR spectroscopy [92]. Russian workers have published ten more papers on various physical measurements of carborane properties. Chlorine-35 NQR data have been obtained on 1-Cl-o-carborane, the meta and para isomers, and their C-chloro-C'-methyl homologs [93]. Hydrogen bonding in a series of carboranyl-substituted alcohols has been examined by infrared spectroscopy [94]. Mass spectra of 1-vinyl- and 1-(1-methylvinyl)-1,2-$C_2B_4H_5$, -$C_2B_5H_6$, and -$C_2B_{10}H_{11}$ have been described in detail and interpreted [95]. NMR spectra of C-trimethylstannyl- and C-trimethylplumbyl-carboranes have been measured and interpreted [96]. Electrophilic displacements of mercury from 1,1-bis(2-phenyl-o-carboranyl)-mercury have been studied [97]. Proton and carbon-13 NMR spectra of 1-isopropyl-o-carborane and its protonated dicarbollide derivative have been observed and interpreted [98]. Hydrogen bonding of o-$HCB_{10}Cl_{10}CCH_3$ with various solvents has been observed by infrared spectroscopy [99]. Kinetics of the reactions of m-carborane-1,7-dicarbonyl and p-carborane-1,12-dicarbonyl dichloride with aniline in various solvents have been reported [100]. Kinetics of the reaction of m-carboranecarbonyl chloride with aniline have been measured in several solvents [101]. More evidence for the electron-withdrawing character of the 1-p-carboranyl substituent has been gathered and its Taft σ constant determined [102].

F. Reviews

Muetterties has edited a book on boron hydride chemistry with chapters by active workers in the field on various aspects of carborane, metallocarborane, and hydroboration chemistry [103].

Several reviews of carborane and metallocarborane chemistry have appeared [104-112]. Aspects of icosahedral carborane chemistry have been reviewed in Russian [113, 114] and English [115].

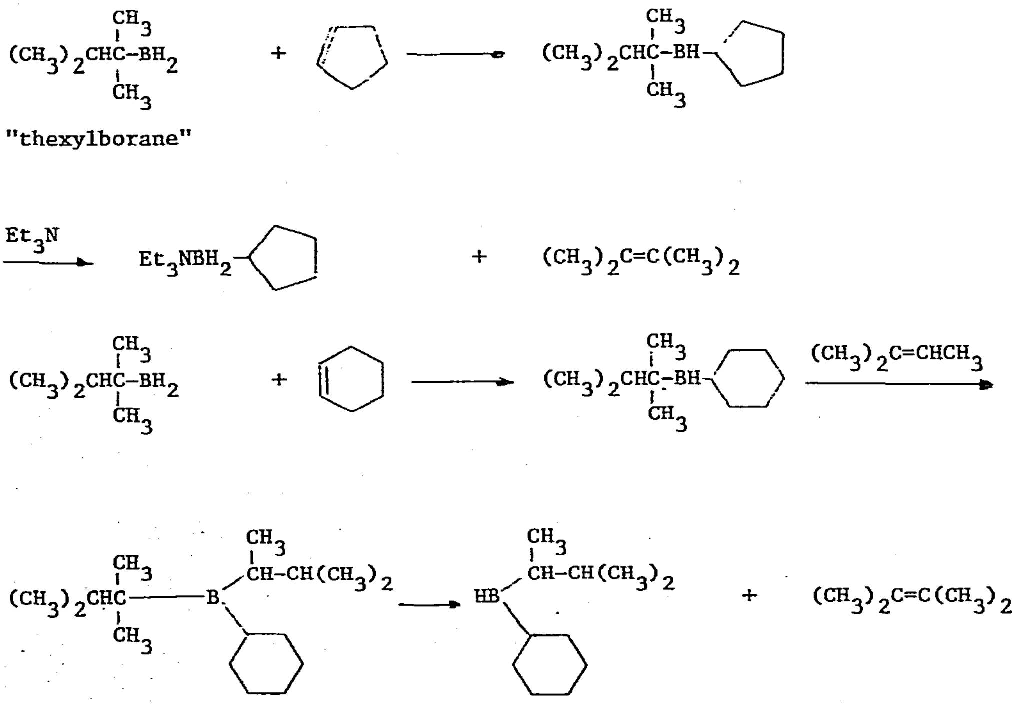
II. HYDROBORATION

A. Boron Hydride Reactions

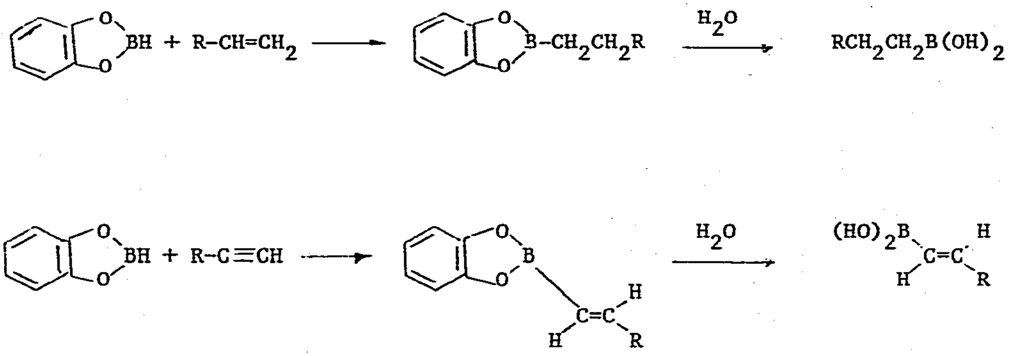
This section deals mainly with the hydroboration reaction itself and various reagents and techniques used to control its outcome. Further applications of hydroboration products in synthesis are covered in parts B and C.

Two explosions of bottles of tetrahydrofuran borane have been reported [116, 117]. The cause is believed to be gradual buildup of hydrogen pressure during storage.

A convenient technique for hydroboration of gaseous alkenes using automatic gasimetry has been described [118].

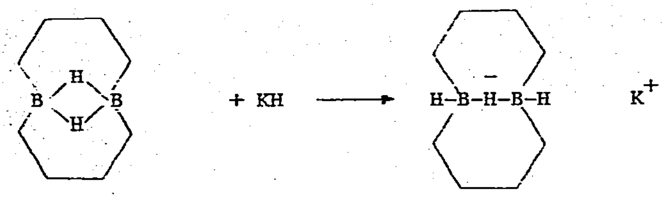


Brown and coworkers have published detailed accounts of the conversion of thexylborane to thexylmonoalkylboranes and their reaction with triethylamine to form the amine complexes of monoalkylboranes [119] or their reaction with a second olefin to form trialkylboranes containing three different alkyl groups and the dethexylation of these to form dialkylboranes containing two different alkyl groups [120]. Brown and Gupta have reported full details of the use of catecholborane as a hydroborating agent, which provides a highly useful route to alkaneboronic and alkeneboronic acids and their derivatives [121].

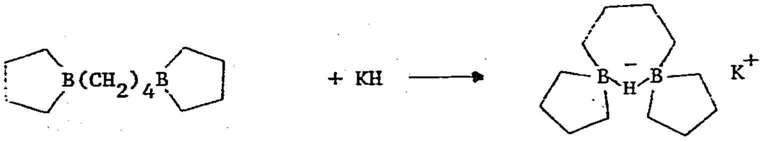


Pelter and coworkers have found that R_2BSR', readily available from radical reaction of R_3B with R'SH (1959 work by Mikhailov and coworkers), reacts with bromine to form R_2BBr [122]. R_2BBr and NaH in the presence of alkenes yield mixed trialkylboranes, R_2BR'', with negligible redistribution of R and R'' [123].

Potassium hydride adds to various hydroboration products from butadiene to form anionic compounds having a single hydrogen bridge between two boron atoms, and the X-ray structure of one of these has been determined [124].



(X-ray structure of Bu_4N^+ salt)



Cyclohexenone, cyclopentenone, crotonaldehyde, and cinnamaldehyde are reduced at the carbonyl group and not hydroborated by 9-BBN [125].

Reaction of ArHgX, where X is Cl, OAc, or Ar, with diborane followed by aqueous work-up gives good to excellent yields of $ArB(OH)_2$ [126]. Reaction of $ArTl(O_2CCF_3)_2$ with diborane followed by hydrolysis also yields $ArB(OH)_2$ [127].

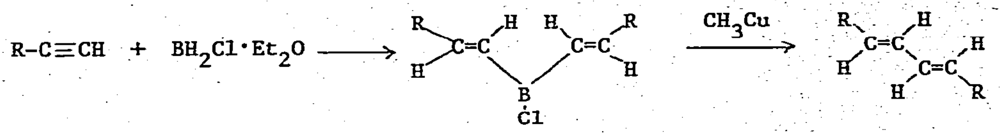
B. Borane Rearrangements

Most of the trialkylboranes used in these rearrangements are prepared by hydroboration and this area is usually considered to be a part of hydroboration chemistry, even though the hydroboration process is not truly essential. The synthetic utility of these reactions is in a period of rapid expansion, and hydroboration of alkenes or alkynes followed by various rearrangements to form carbon-carbon bonds promises to become a very important tool in synthetic organic chemistry. H. C. Brown is still a major contributor, and many of his former students are also developing this field.

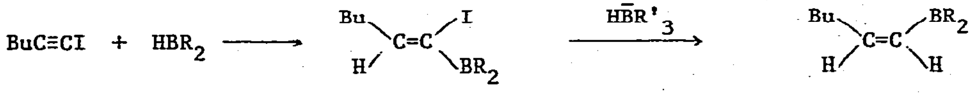
The reaction of $MeSCH_2Li$ with R_3B followed by methylation of the sulfur with methyl iodide results in rearrangement leading to homologation [128].

$$MeSCH_2Li + BBu_3 \longrightarrow MeSCH_2\bar{B}Bu_3 \xrightarrow{MeI} Me_2\overset{+}{S}CH_2\bar{B}Bu_3 \longrightarrow BuCH_2BBu_2 + Me_2S$$

Acetylenic compounds are particularly valuable in hydroboration--rearrangement sequences and have been used in a wide variety of ways. Iodine converts $R'_2B(C\equiv C-R)_2^-$ to $R-C\equiv C-C\equiv C-R$ [129]. Hydroboration of acetylenes with chloroborane followed by treatment of the resulting dialkenylboron chlorides with methylcopper yields (*E*,*E*)-1,3-dienes [130]. The reaction of

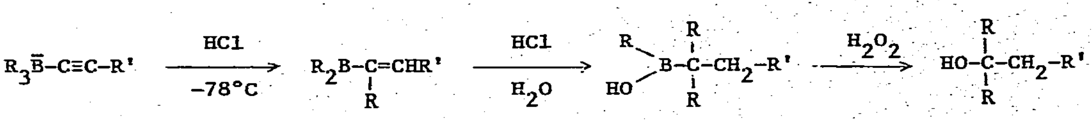


1-halo-1-alkynes with dialkylboranes followed by treatment with $LiBHEt_3$ or $KBH(s\text{-}Bu)_3$ produces *cis*-alkenylboranes stereoselectively and in high yields [131].

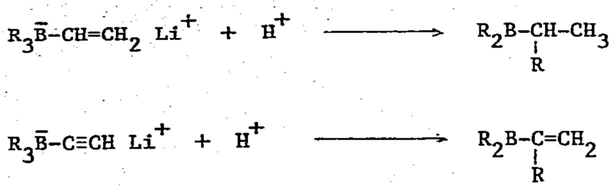


R = cyclohexyl, $-CH(CH_3)CH(CH_3)_2$

The rearrangement of lithium alkynyltrialkylborates in the presence of acid occurs in two stages, the first alkyl migration occurring at -78°C and the second at higher temperatures [132]. Rearrangement of $R_2B-CR=CHR$ in acid is general, except that $R_2B-CH=CHR$ cleaves to $H_2C=CHR$ instead. Boranes having



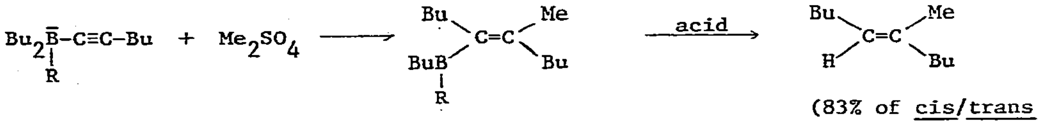
structures not attainable by hydroboration reactions have been obtained from the protonation-rearrangement of vinyltrialkylborates and alkynyltrialkylborates [133]. $PhC{\equiv}C\text{-}BBu_3^-$ treated with propionic acid rearranges and protode-



$$R_3\bar{B}\text{-}CH{=}CH_2\ Li^+ + H^+ \longrightarrow R_2B\text{-}\underset{\substack{|\\ R}}{CH}\text{-}CH_3$$

$$R_3\bar{B}\text{-}C{\equiv}CH\ Li^+ + H^+ \longrightarrow R_2B\text{-}\underset{\substack{|\\ R}}{C}{=}CH_2$$

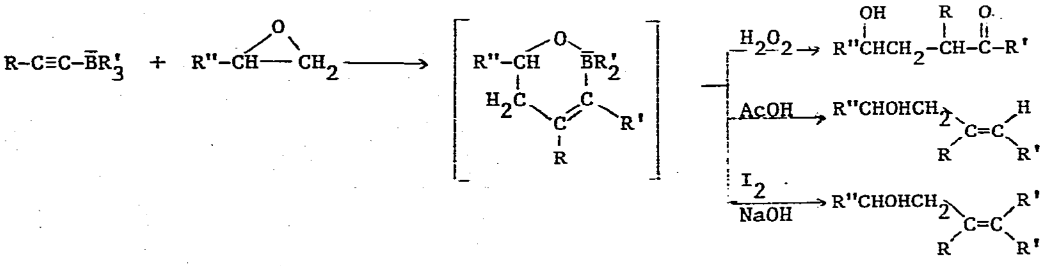
boronates to form $PhCH{=}CHBu$ that is 74% <u>cis</u> and 26% <u>trans</u>. The <u>cis</u> content is increased to 98% if a thexyl group, $-CMe_2CHMe_2$, is used in place of one of the butyl groups, the butyl group migrating preferentially [134]. Thexyldialkylalkynylborates can be alkylated with methyl sulfate to provide a stereoselective route to trisubstituted olefins [135].



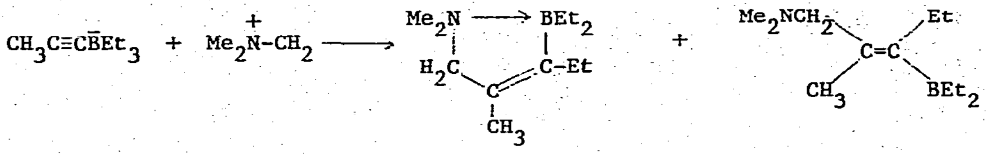
(83% of cis/trans mixture)

(R = thexyl)

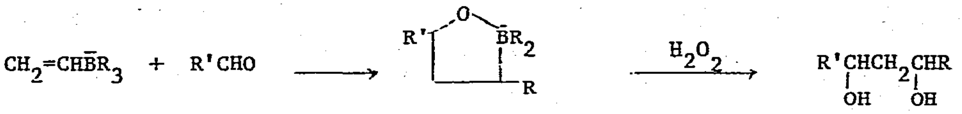
Reactions of $R\text{-}C{\equiv}C\text{-}BR'^-_3$ with epoxides have been reported [136]. Reaction



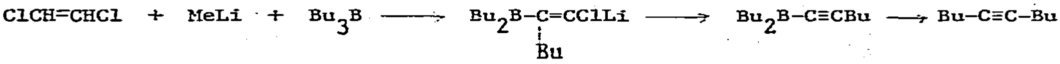
of $R\text{-}C{\equiv}C\text{-}BR_3'^{-}$ with CH_3SOCl yields $R\text{-}C{\equiv}C\text{-}R'$ [137]. Addition of $Me_2\overset{+}{N}{=}CH_2$ to $CH_3C{\equiv}CBR_3^{-}$ gives a mixture of stereoisomers [138].



A rearrangement results when aldehydes react with $CH_2{=}CHBR_3^{-}$ [139].

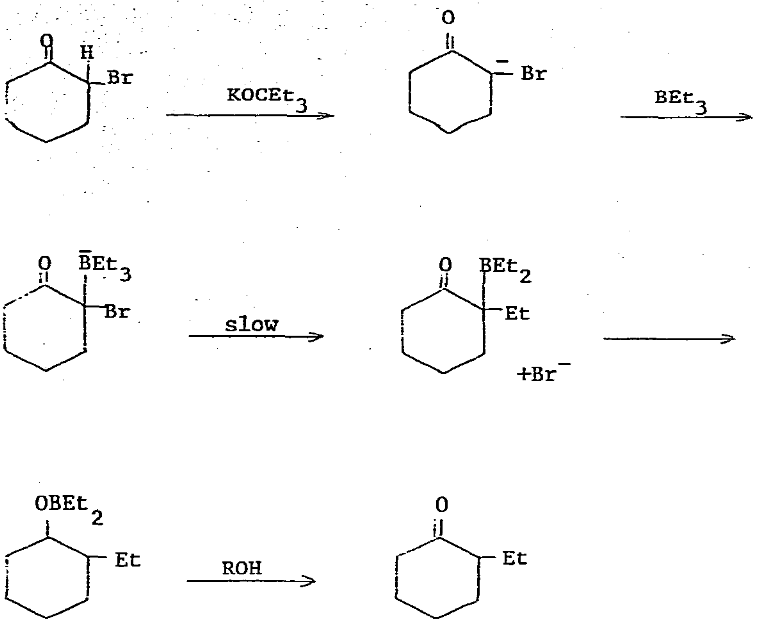


Lithiation of trans-1,2-dichloroethene followed by reaction with tributylborane, rearrangement with iodine, and workup with hydrogen peroxide has yielded 5-decyne [140].



$$ClCH{=}CHCl + MeLi + Bu_3B \longrightarrow Bu_2B\text{-}\underset{Bu}{C}{=}CClLi \longrightarrow Bu_2B\text{-}C{\equiv}CBu \longrightarrow Bu\text{-}C{\equiv}C\text{-}Bu$$

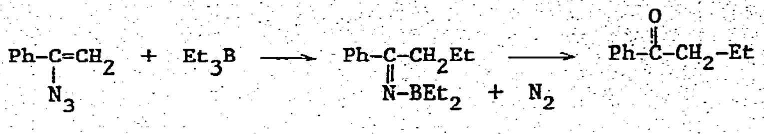
The mechanism of alkylation of 2-bromocycloalkanones by trialkylboranes in the presence of a hindered base has been studied in considerable detail, and the migration of an alkyl group from boron to carbon has been found to be the rate-determining step [141].



It has been shown that a compound once supposed to be Bu_2BCOPh is in fact Bu_2BOCH_2Ph, and the existence of acylboranes as stable monomers has been questioned [142]. (Acylboranes have been postulated to be intermediates in the rearrangement of carbonylated trialkylboranes.)

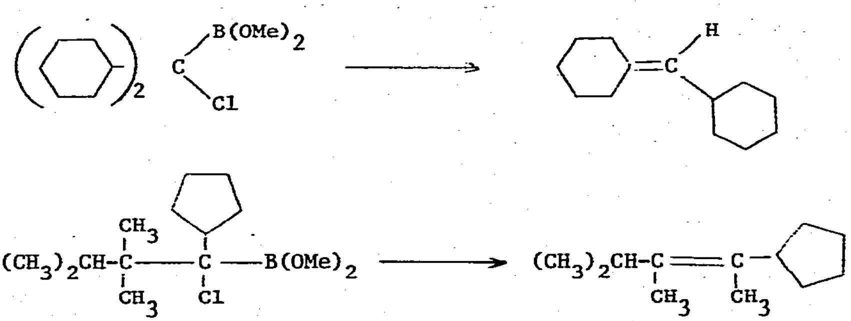
Protonation of R_3BCN^- results in migration of two alkyl groups and formation of a cyclic dimer of H_2N-CR_2-BRCN, which on oxidation yields R_2CO [143]. R_2BCl and t-Bu-N=CR'Li (from t-BuNC and R'Li) give an intermediate t-Bu-N=CR'BR_2 which rearranges on treatment with mercaptoacetic acid to form a borane which can be oxidized to RCOR'. Heating the intermediate borane with sodium hydroxide results in migration of the second B-alkyl group to form $R_2R'CB(OH)_2$. which with hydrogen peroxide yields the tertiary alcohol $R_2R'COH$ [144 145].

The reaction of R_3B with $R'N_3$ to give R_2B-NRR' has been patented in Japan [146]. Reaction of α-azidostyrene with R_3B followed by hydrolysis yields $PhCOCH_2R$ [147].



$$Ph-\underset{N_3}{\underset{|}{C}}=CH_2 + Et_3B \longrightarrow Ph-\underset{N-BEt_2}{\underset{\|}{C}}-CH_2Et + N_2 \longrightarrow Ph-\overset{O}{\overset{\|}{C}}-CH_2-Et$$

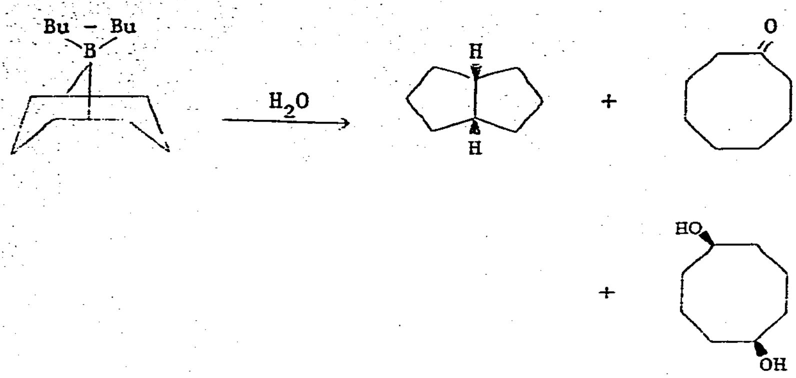
Reaction of Cl_2CHOCH_3 with R_2BOCH_3 is catalyzed by suitable bases to form $R_2CClB(OMe)_2$, which on solvolysis in aqueous ethanol and $AgNO_3$ gives olefins [148].

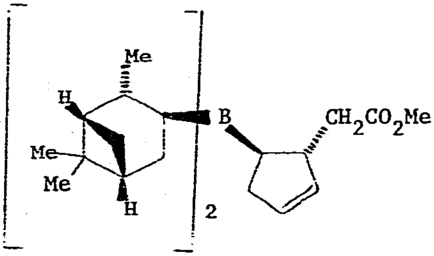


(Rearrangements via $R_2\overset{+}{C}B(OMe)_2$)

Aqueous silver nitrate converts 9-BBN to cyclooctanone and a small amount of cyclooctene [149]. Chromic acid converts 9-BBN to cyclooctanone, 10-bora-bicyclo[4.30]decane to cyclononanone, and 11-borabicyclo[5.30]undecane to cyclodecanone [150]. Hydrogen peroxide oxidation of a 9-BBN "ate" complex produces substantial amounts of bicyclooctanol, an alkyl migration product [151].

Hydroboration of 2,4-cyclopentadiene-1-acetic ester with optically active dipinanylborane yields a useful optically active intermediate for prostaglandin synthesis, which has been patented [152]. Optically active





and mirror image derived from opposite enantiomer of pinene

$(EtCHMeCH_2)_2BH$ has been prepared and used to hydroborate butylacetylene. On rearrangement with iodine and alkali, the product $EtCHMeCH_2CH{=}CHBu$ retained the configuration of the original asymmetric center and had the expected cis double bond. Hydroboration of 1-bromohexyne followed by rearrangement with sodium methoxide and deboronation with propionic acid gave the trans alkene having otherwise the same structure [153].

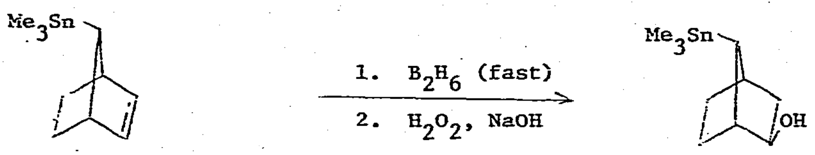
C. Hydroboration in Synthesis

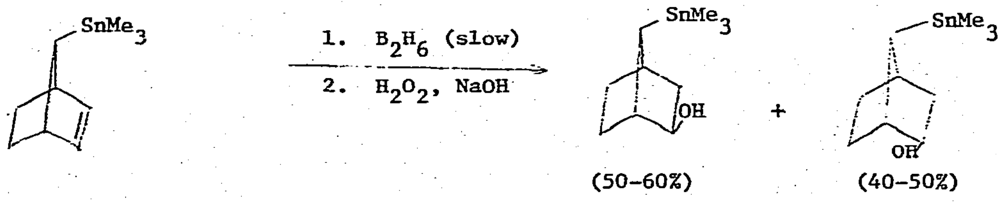
Most of the chemistry covered here involves hydroboration followed by oxidative replacement of the boron, with a few exceptions. Since hydroboration—oxidation sequences have become routine procedure, many of these papers are treated very briefly.

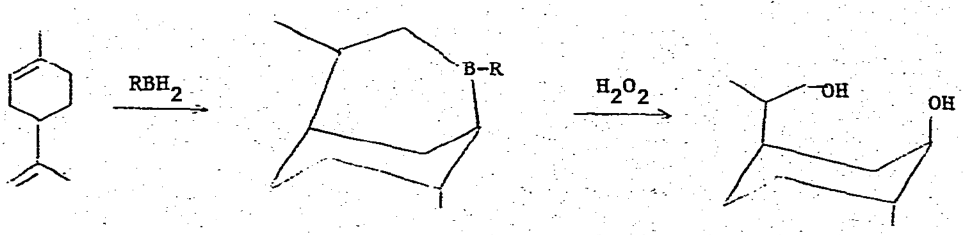
New methods of replacement of boron have been discovered. Trialkylboranes react with ferric chloride in aqueous THF to yield alkyl chlorides and with ferric thiocyanate to yield alkyl thiocyanates [154]. Selenium dioxide converts trialkylboranes to dialkyl selenides [155].

Trimethylamine oxide dihydrate in refluxing diglyme is a mild reagent for converting alkylboranes to alcohols [156].

Hydroboration of _anti_-7-trimethyltin-2-norbornene is much faster than hydroboration of the _syn_ isomer, permitting exclusive hydroboration--oxidation of the former in the presence of the latter. However, the slower hydroboration of the _syn_ isomer does proceed efficiently and surprisingly produces a little more _exo_ than _endo_ product [157]. Details of the hydroboration of limonene have been published [158]. The borane formed is cyclic and

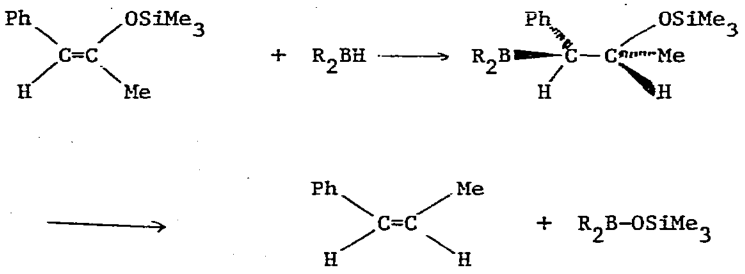






leads stereospecifically to a single diol product. Use of an asymmetric hydroborating agent has established the absolute configuration of some benzonorboranenes synthesized for use in mechanistic studies [159].

Hydroboration-elimination of a silyl enol ether has been shown to proceed with predominant but not exclusive cis elimination of boron and oxygen [160]. The hydroboration--oxidation of cyclohexanone silyl enol ethers has been patented in Japan [161].



Hydroboration has been investigated as a tool in sesquiterpene synthesis [162, 163]. Hydroboration has been used for the selective functionalization of a terminal olefinic group in polyenes related to terpenoids [164].

The stereochemistry of hydroboration of some t-butyl, trimethylsilyl-, and trimethylgermyl-cyclohexenes [165] and of several substituted methylenecyclohexanes has been reported [166].

Directive effects in the hydroboration of substituted vinylferrocenes have been studied [167]. The hydroboration of some allylic ethers with dibutylborane has been reported [168]. More studies of the hydroboration of substitued piperideines have been reported [169, 170]. Hydroboration of $Me_2N(CH_2)_2$-$CHMeCH=CH_2$ has been reported [171].

Hydroboration of a series of methoxy-2-hexynes has been studied and the regioselectivity interpreted on the basis of steric and inductive effects of the methoxyl group [172]. 9-BBN gives the dihydroboration product with allene, $R_2BCH_2CH_2CH_2BR_2$, and the monohydroboration product with 1,1-dimethylallene, $(CH_3)_2C=CHCH_2BR_2$ (where R_2 is 1,5-cyclooctadiyl) [173]. Hydroboration of a highly hindered methylated octalin has been described [174]. Hydroboration--oxidation of the Diels-Alder adduct of cyclohexadiene with cyclopentadiene has been reported [175]. The hydroboration of $FCClH-CF_2-CH=CH_2$ has been reported [176]. Hydroboration--oxidation of some steroids has been patented in Japan [177]. Hydroboration has been used in the preparation of isoflavones [178, 179].

Tricyclohexylborane and nitrobenzene yield a mixture of N-cyclohexylaniline and nitrosobenzene [180]. Hydroboration of diphenylacetylene to $PhCH(BH_2)CH(BH_2)Ph$ followed by oxidation with CrO_3 yields trans-stilbene [181]. Hydroboration of enamines as a method of reduction has been examined [182].

Hydroboration of bicyclo[3.3.1]nona-2,6-diene with tetraethyldiborane followed by heating with triethylborane has yielded B-alkylboraadamantanes [183]. Hydroboration leading to small carboranes and a hexaboryladamantane has been noted in Section I, Part D-2 [58].

D. Reviews

Brown has written a book on the use of boranes in organic synthesis [184]. Onak has written a book which covers the general field of organoborane chemistry [185]. Muetterties' book contains chapters on mechanistic aspects of hydroboration [103].

Brown has reviewed some of the history of the development of hydroboration chemistry [186]. The preparation of organoboranes has been reviewed by Smith [187]. Suzuki [188] and Yamamoto [189] have reviewed organoborane chemistry in Japanese.

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