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BORON I. CARBORANES AND HYDROBORATION
ANNUAL SURVEY COVERING THE YEAR 1978

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CONTENTS

Boron I, Carboranes and hydroboration; Annual Survey covering the year 1977 see J. Organometal. Chem., Vol. 163 (1978)17-58.

I. CARBORANES

A. Introduction

Metallacarborane chemistry has continued to provide the most novel developments, with Grimes' and Hawthorne's groups publishing the largest number of new structures in this field. Hawthorne's entry into the chemistry of catalytically active carboranes has been followed to some extent by Zakharkin's group, though the major Russian emphasis continues to be centered on derivatives of the classical icosahedral carboranes. Lipscomb and other theoreticians have continued to report new calculations on carboranes and polyhedral boranes, and Lipscomb and coworkers have suggested the interesting possibility that cages considerably larger than icosahedral may turn out to be stable.

As is customary, a brief section on boron hydride and metallaborane chemistry has been included, since any distinction between carboranes as "organometallic" and boranes as "inorganic" is arbitrary. The reviewer's method of covering the literature, which places considerable reliance on Chemical Abstracts for the large number of journals which contain only an occasional paper on boron chemistry, will not necessarily cover all papers on "carboranes without carbon", though these do appear to be listed under such keywords as "borane" in the organic sections of Chemical Abstracts. Patent coverage is limited to items which struck the reviewer as having some degree of chemical novelty or possible utility. Reviews have proliferated, and those listed in Chemical Abstracts are cited here, except where the number of citations in the review is small and the language has a limited number of readers.

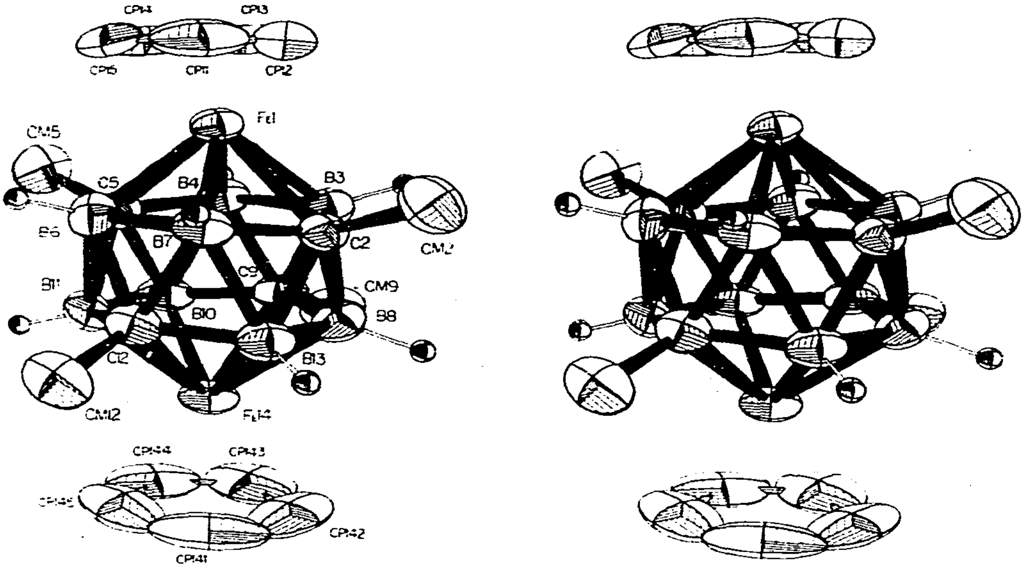


Figure 1. Stereodrawing of the symmetrical closo isomer of $(C_5H_5)_2Fe_2C_4(CH_3)_4B_8H_8$. [Reprinted with permission from J. R. Pipal and R. N. Grimes, Inorg. Chem., 17 (1978) 6. Copyright by the American Chemical Society.]

B. Metallacarboranes

Pipal and Grimes have determined the structure of a closo 14-vertex four-carbon diferracarborane by X-ray diffraction (Fig. 1) [1]. This compound is the product of thermal rearrangment of a nido isomer prepared from $(CH_3)_4C_4B_8H_8^{2-}$, $FeCl_2$, and NaC_5H_5.

The structure of a triple-decked sandwich dicobaltcarborane having a cyclopentadiene ring fused into the central cage has been determined by X-ray crystallography (Fig. 2) [2].

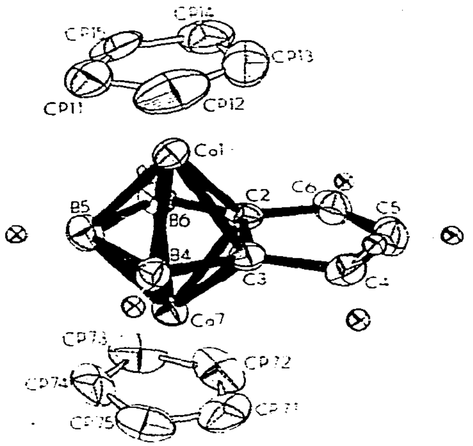


Figure 2. The structure of $(C_5H_5)_2Co_2B_3H_3C_5H_4$. [Reprinted with permission from J. R. Pipal and R. N. Grimes, Inorg. Chem., 17 (1978) 10. Copyright by the American Chemical Society.]

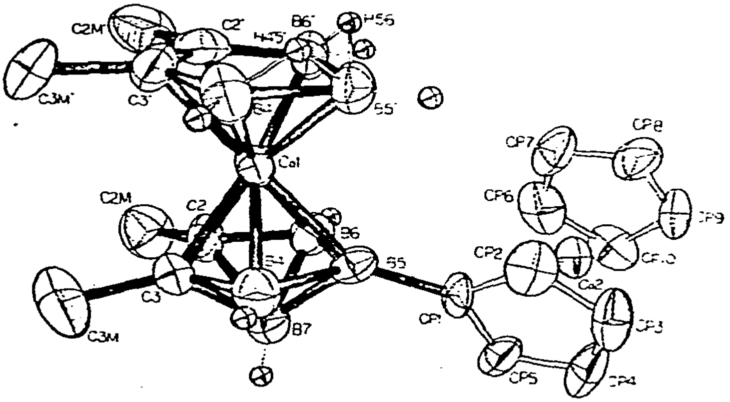


Figure 3. The structure of $(Me_2C_2B_3H_5)Co(Me_2C_3B_4H_3)$-$(C_5H_4)Co(C_5H_5)$. Atoms are shown as 50% probability ellipsoids, except H, which is omitted or shown as a small sphere. [Reprinted with permission from J. R. Pipal, W. M. Maxwell, and R. N. Grimes, Inorg. Chem., 17 (1978) 1447. Copyright by the American Chemical Society.]

The structure of a nido-closo-dicarboranylcobalt compound having a cobaltocenium substituent has been determined by X-ray diffraction (Fig. 3) [3].

Polyhedral expansion of $(C_5H_5)FeC_2B_9H_{11}$ has led to a 13-vertex biferracarborane which is electron deficient, having only 2n framework electrons, but diamagnetic (Fig. 4) [4]. Electron-deficient ferracarboranes do not undergo polyhedral rearrangements. In addition to the compound illustrated, the reaction of $(C_5H_5)FeC_2B_9H_{11}^{3-}$ with $FeCl_2$ and $C_5H_5^-$ yielded $(C_5H_5)FeC_2B_9H_{11}FeC_2B_8H_{11}^-$ (which presumably has a dicarbollyl cage in place of one of the cyclopentadiene rings) and a 12-vertex 2-electron deficient compound, $(C_5H_5)_2Fe_2C_2B_8H_9OH$.

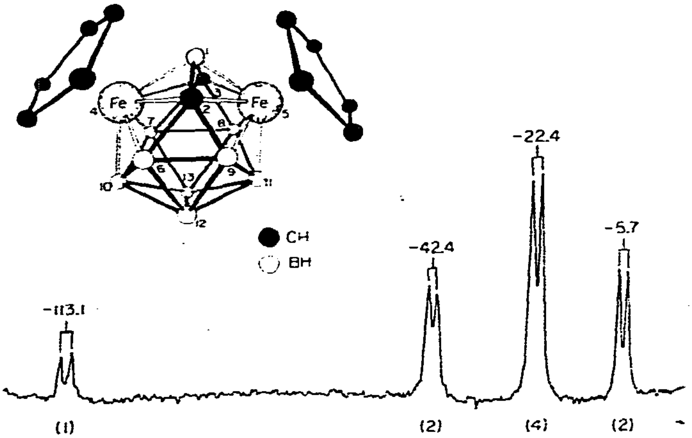


Figure 4. Proposed structure and 80.5-MHz ^{11}B NMR spectrum of $(C_5H_5)_2Fe_2C_2B_9H_{11}$. [Reprinted with permission from C. G. Salentine and M. F. Hawthorne, Inorg. Chem., 17 (1978) 1498. Copyright by the American Chemical Society.]

Structures have been determined by X-ray crystallography for an 11-vertex iron-cobalt carborane (Fig. 5) [5] and a 10-vertex nickel-cobalt carborane (Fig. 6) [6].

2-$(C_5H_5)CoB_4H_8$ is structurally analogous to pentaborane(9) and undergoes similar reactions, including formation of an anion $(C_5H_5)CoB_4H_7^-$ which reacts with $CoCl_2$ and $C_5H_5^-$ to form a dicobaltaborane, $(C_5H_5)_2Co_2B_4H_6$. Reaction of $(C_5H_5)CoB_4H_8$ with acetylene has yielded some of the known cobaltacarborane, $(C_5H_5)CoC_2B_3H_7$ [7].

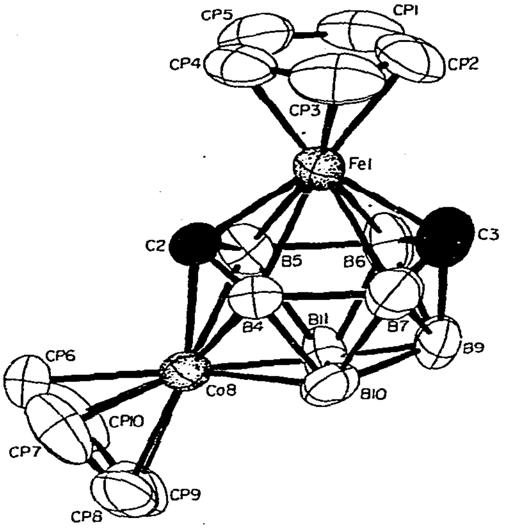


Figure 5. The structure of $(C_5H_5)_2FeCoC_2B_7H_9$, H atoms omitted. [Reprinted with permission from K. P. Callahan, A. L. Sims, C. B. Knobler, F. Y. Lo, and M. F. Hawthorne, Inorg. Chem., 17 (1978) 1658. Copyright by the American Chemical Society.]

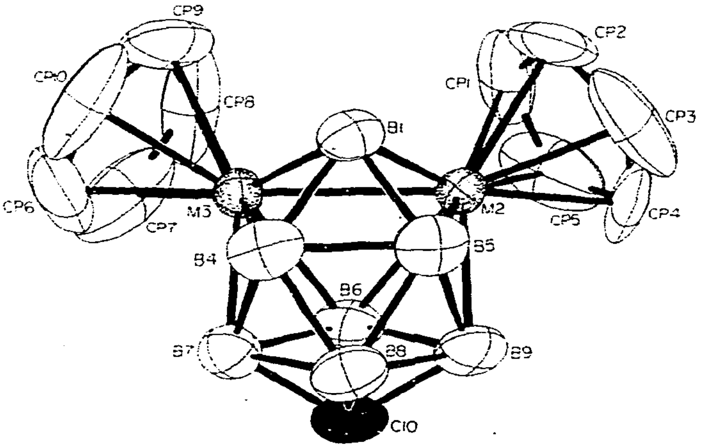
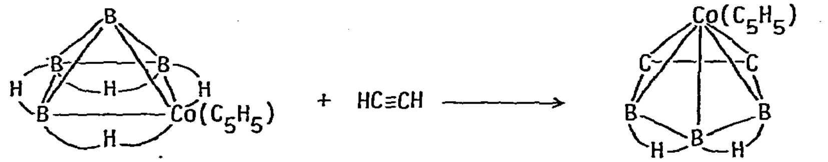


Figure 6. The structure of $(C_5H_5)_2NiCoCB_7H_8$, H atoms omitted. [Reprinted with permission from G. E. Hardy, K. P. Callahan, and M. F. Hawthorne, Inorg. Chem., 17 (1978) 1662. Copyright by the American Chemical Society.]



$2\text{-}(C_5H_5)CoB_4H_8$ $(C_5H_5)CoC_2B_3H_7$ (Terminal H's omitted)

A cage expansion reaction of $(C_5H_5)CoB_4H_8$ with $Fe(CO)_5$ which gave a small yield of $(C_5H_5)_2Co_2B_3H_3Fe(CO)_4$ was also reported.

Wong and Hawthorne have described the synthesis of icosahedral 7,8- and 7,9-dicarbollylruthenium complexes of the composition $(Ph_3P)_2H_2RuC_2B_9H_{11}$. The 2,1,7-isomer (from $7,9\text{-}C_2B_7H_{11}{}^{2-}$, nonadjacent carbons) reversibly eliminates one molecule of hydrogen on heating under vacuum. Its structure has been illustrated previously [JOM 147 (1978) 29]. One hydrogen is readily replaced by CO on treatment with carbon monoxide, and the 3,1,2-isomer showed similar behavior. A pyridinium substituted monohydridoruthenium complex was also synthesized (Fig. 7) [8].

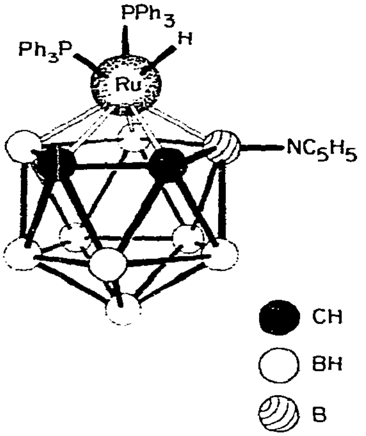


Figure 7. Proposed structure of $(Ph_3P)_2HRu(C_2B_9H_{10})\text{-}NC_5H_5$. [Reprinted with permission from E. H. S. Wong and M. F. Hawthorne, Inorg. Chem., 17 (1978) 2863. Copyright by the American Chemical Society.]

The rhodacarborane $3,3\text{-}(PPh_3)_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11}$ is readily oxidized to a dimeric species, $(Ph_3PRhC_2B_9H_{11})_2$, which is an effective hydrogenation catalyst, and which has Rh-H-B bridge bonds as shown by the X-ray structure (Fig. 8) [9].

Rhodacarborane complexes of the type first synthesized by Hawthorne's group (JOM 98 (1975) 316-317) have been used by Zakharkin and coworkers to catalyze the hydrosilylation of olefins [10]. Resolution of a 1-phenyl-3-rhodacarborane, $1\text{-Ph-}3,3\text{-}(Ph_3P)_2\text{-}3H\text{-}3,1,2\text{-}RhC_2B_9H_{11}$, has been followed by use of the optically active carborane to catalyze the reduction of acetophenone by $PhSiHMe_2$ to form $PhCHOHCH_3$ having 14-42% optical purity [11].

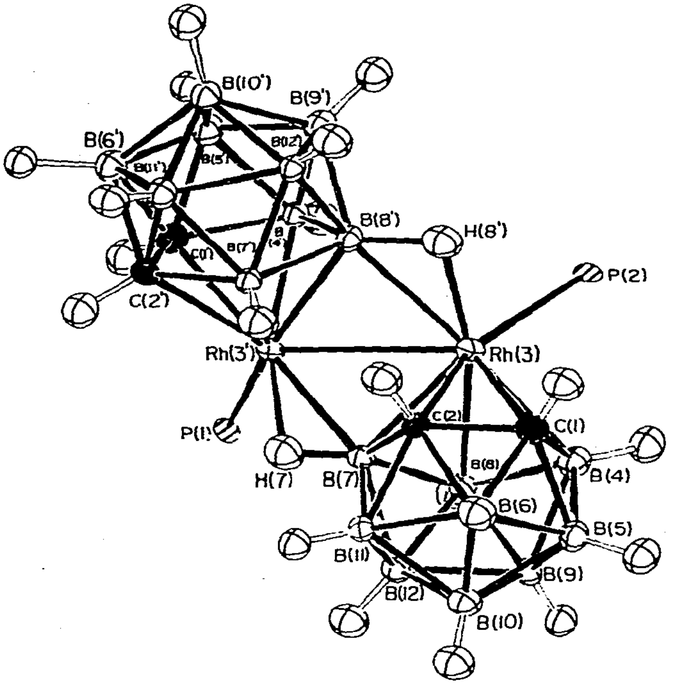
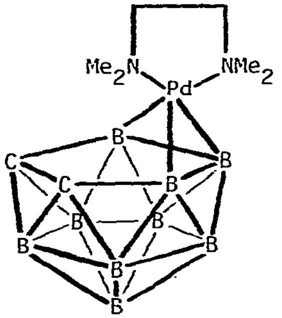


Figure 8. The structure of $(Ph_3PRhC_2B_9H_{11})_2$. (The phenyl groups on phosphorus are omitted for clarity. [Reprinted with permission R. T. Baker, R. E. King III, C. Knobler, C. A. O'Con, and M. F. Hawthorne, J. Am. Chem. Soc., 100 (1978) 8266. Copyright by the American Chemical Society.]

o-Carborane has been attached to a polystyrene resin by the reaction $Li^+C_2B_{10}H_{11}^- + (polymer)\text{-}CH_2Cl \rightarrow (polymer)\text{-}CH_2\text{-}C_2B_{10}H_{11}$, and the resin-bound carborane has been degraded with piperidine to form the dicarbollide, $(polymer)\text{-}CH_2C_2B_9H_{11}^-$, which has been converted to the rhodacarborane, $(polymer)\text{-}CH_2\text{-}C_2B_9H_{10}RhH(PPh_3)_2$. However, the rhodacarborane failed to retain appreciable catalytic activity in the system used [12].

The structures of $(Me_2NCH_2CH_2NMe_2)PhC_2B_9H_{11}$ and the $(Me_3P)_2Pd$ analogue have been determined by X-ray crystallography, and both have been found to have the slipped cage configuration, with the palladium bonded to the three boron atoms of the pentagonal face of the carborane cage [13].



(Cage H's omitted)

Reaction of dicarbollylthallium with $AuBr_2(S_2C\text{-}NEt_2)$ has yielded two dicarbollylgold complexes, $3,3'\text{-}Au(1,2\text{-}C_2B_9H_{11})_2^-$ and $3\text{-}(Et_2N\text{-}CS_2\text{-}Au)\text{-}1,2\text{-}C_2B_9H_{11}$ [14]. The structure of the latter was determined by X-ray crystallography and found to have the slipped structure with the gold bonded primarily to the three boron atoms of the distorted pentagonal face of the carborane cage, similar to the palladium compound illustrated.

Metallacarborane cluster compounds have been obtained from reaction of cobalt atoms with cyclopentadiene, pentaborane(9), and 2-butyne, and also from the reaction of $(C_5H_5)Co(CO)_2$ with 2-butyne and pentaborane(9) [15]. Reversed phase thin layer chromatography has been used to separate the cobaltacarboranes from the reaction of $(2,4\text{-}C_2B_5H_6)_2$ with $(C_5H_5)Co(CO)_2$ [16].

The ferracarboranes $C_2B_3H_5Fe(CO)_3$ and $C_2B_3H_7Fe(CO)_3$ as well as the ferraboranes $B_4H_8Fe(CO)_3$, $B_5H_9Fe(CO)_3$, and $B_5H_3Fe(CO)_5$ have been examined by ultraviolet photoelectron spectroscopy and the results interpreted in terms of the bonding orbitals [17]. X-ray photoelectron spectra (ESCA) of some cobaltacarboranes have been reported [18].

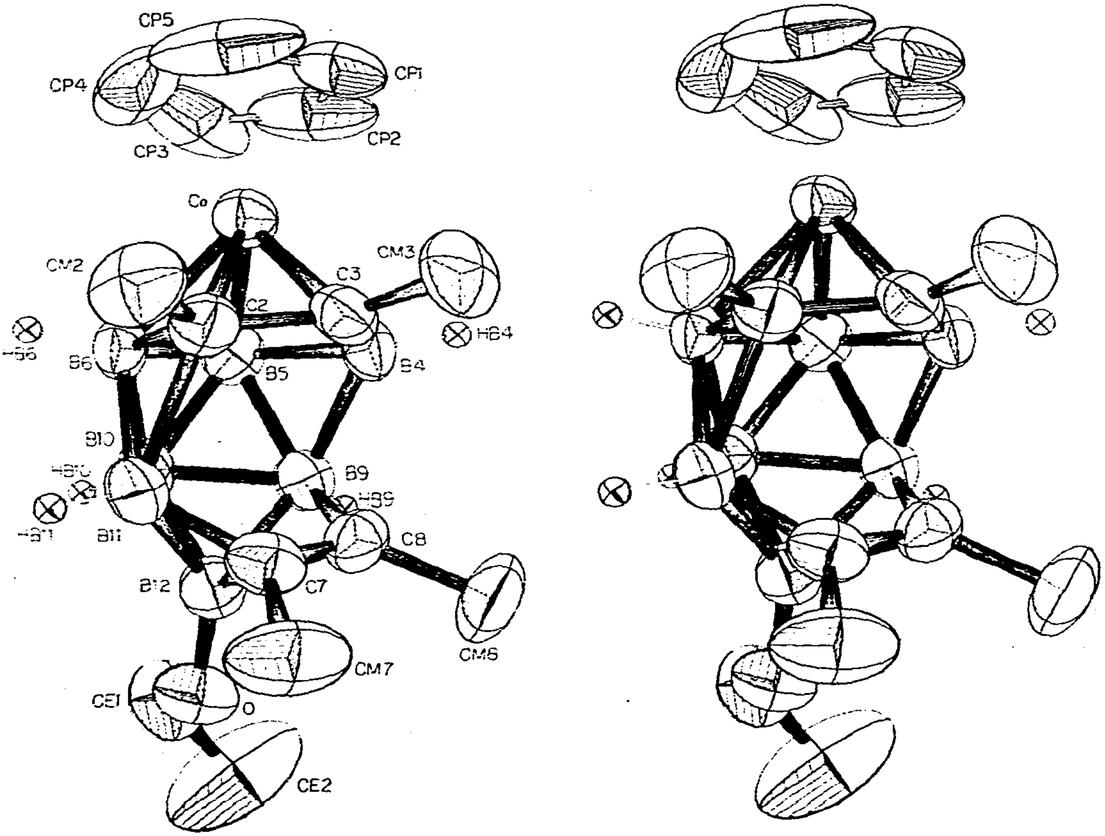


Figure 9. Stereoscopic drawing of $(C_5H_5)CoC_4(CH_3)_4B_7H_6OC_2H_5$, with most H atoms omitted for clarity, 50% probability thermal ellipsoids for nonhydrogen atoms. [Reprinted with permission from R. J. Pipal and R. N. Grimes, J. Am. Chem. Soc., 100 (1978) 3083. Copyright by the American Chemical Society.]

The structure of the four-carbon cobaltacarborane $(C_5H_5)CoC_4(CH_3)_4B_7H_6OC_2H_5$ has been determined by X-ray crystallography (Fig. 9) [19]. For comparison, the structure of all of the 12-vertex 28-electron cages that have been determined crystallographically are illustrated (Fig. 10).

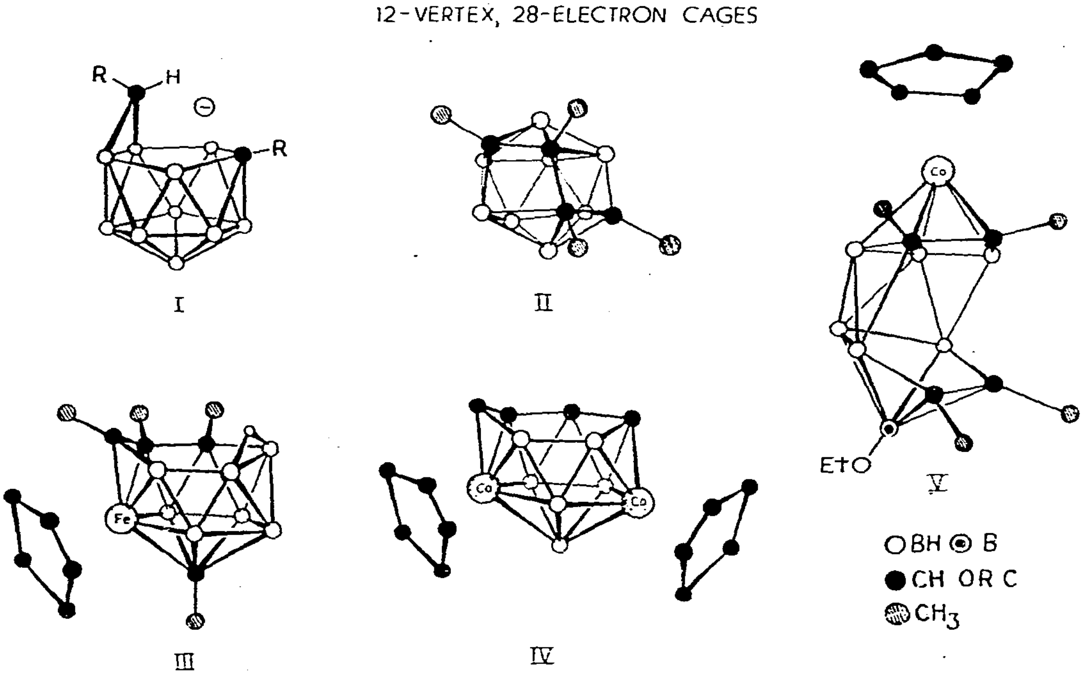
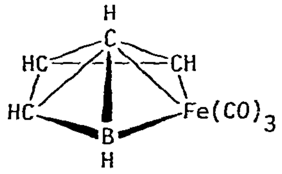


Figure 10. Structures of the five crystallographically studied 12-vertex, 28-electron cage systems: $R_2C_2B_{10}H_{11}^-$, R = Ph or Me (I); $Me_4C_4B_8H_8$ (II); $(C_5H_5)FeC_4Me_4B_7H_8$ (III); $(C_5H_5)_2Co_2C_4B_6H_{10}$ (IV); and $(C_5H_5)CoC_4Me_4B_7H_6OC_2H_5$ (V). [Reprinted with permission from J. R. Pipal and R. N. Grimes, J. Am. Chem. Soc., 100 (1978) 3083. Copyright by the American Chemical Society.]

Grimes and coworkers have synthesized non-methylated four-carbon dicobaltacarboranes by oxidative cage dimerization (Fig. 11) [20].

Ultraviolet irradiation of cyclobutadiene iron tricarbonyl in the presence of pentaborane-9 has yielded a ferracarborane containing four carbons and one boron. The structure tentatively assigned is illustrated [21].



Tentative structure of $BC_4H_5Fe(CO)_3$.

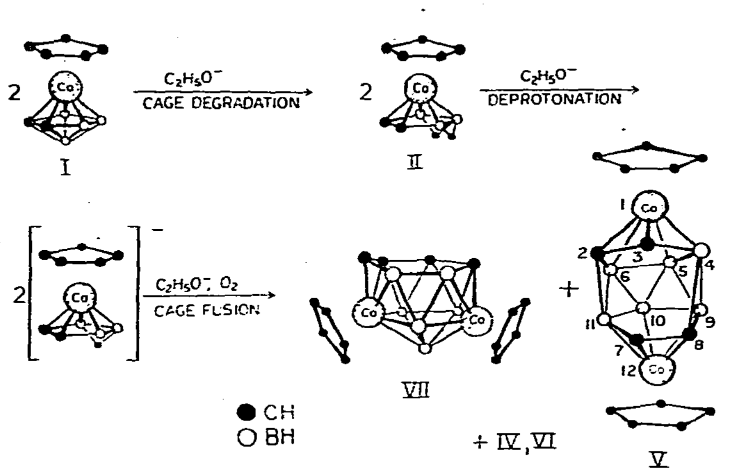
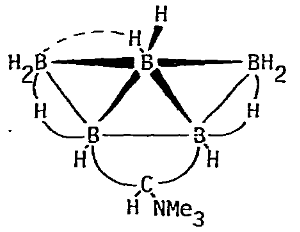


Figure 11. Conversion of dicarbon cobaltacarboranes (I) and (II) to tetracarbon dicobaltacarboranes, $(C_5H_5)_2Co_2C_4B_6H_{10}$, (V) and (VII) as well as an isomer (VI) of unknown structure, and also a monocobaltacarborane, $(C_5H_5)CoC_4B_7H_{11}$ (IV), of unknown structure. The structure of (VII) has been confirmed by X-ray crystallography, that of (V) related by NMR to the known C-tetramethyl derivative. [Reprinted with permission from K.-S. Wong, J. R. Bowser, J. R. Pipal, and R. N. Grimes, J. Am. Chem. Soc., 100 (1978) 5045. Copyright by the American Chemical Society.]

C. Small and Medium Carboranes

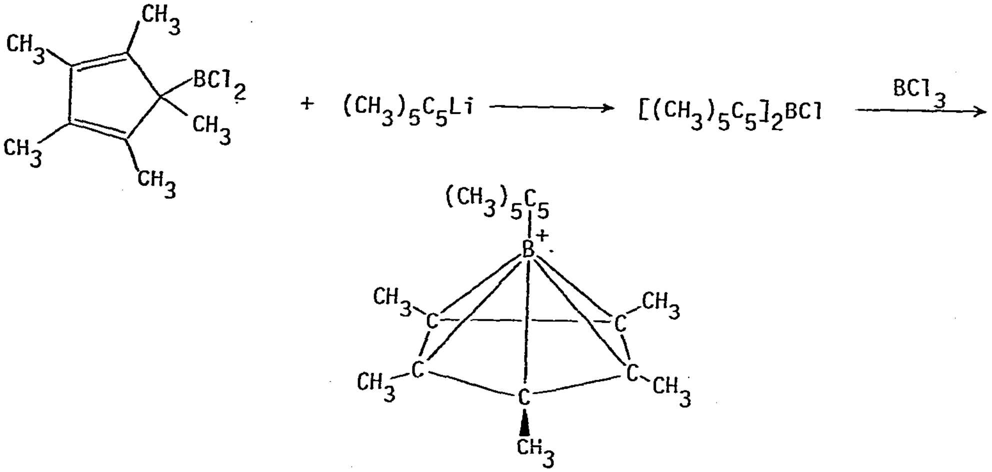
Pyrolysis of $CH_2B_8H_{12}$ at 350°C has given high yields of the nido carborane CB_8H_{12}, which has a plane of symmetry bisecting the carbon atom and a pentagonal open face with two identical and one different bridging hydrogens [22].

Reaction of 6-Me_3N-6-CB_9H_{11} with methanol and base has yielded a carborane analogue of B_5H_{11} in which the 3,4-bridging hydrogen is replaced by the bridging $CHNMe_3$ group [23].



(The binding H connected by the broken line is believed to be fluxional, alternating between the left and right BH_2 groups.)

A carborane cage having only one boron and five carbon atoms has been reported by Jutzi and Seufert [24].



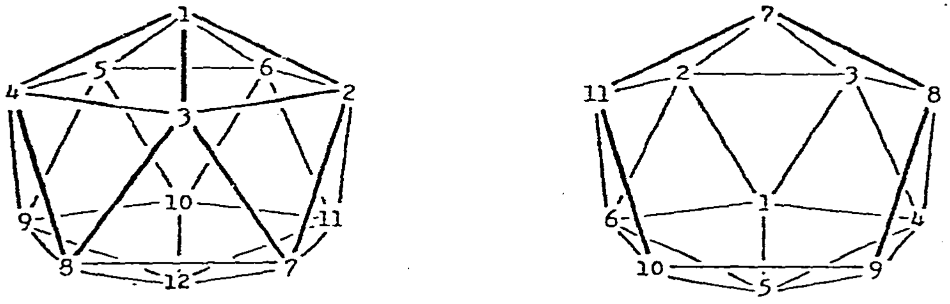
Pyrolysis of $B(CH_3)_3$ yields mixtures of B-permethylated carboranes, including $Me_3B_3C_2H_2$ and $Me_5B_5C_2H_2$, as well as the hexaboraadamantane $Me_6B_6C_4H_4$ [25]. Pyrolysis of trimethylborane in the presence of hydrogen yields mixtures of partially methylated dicarbaheptaboranes, $Me_xH_{(5-x)}B_5C_2H_2$ (x = 2 to 5) in 60-66% total yield.

Methylation of $C_2B_5H_7$ with CH_3Cl and $AlCl_3$ has been patented [26].

Ultraviolet photoelectron spectra of a series of small carboranes ($C_2B_3H_5$, $C_2B_4H_6$, $C_2B_4H_8$, $C_2B_5H_7$, CB_5H_9), as well as pentaborane-9 and -11 and hexaborane-10 and -12, have been reported and interpreted in terms of the cage bonding orbitals involved [27]. The NMR, IR, and mass spectra of a series of silylated derivatives of $C_2B_5H_7$ have been reported [28].

D. Icosahedral Carboranes

1. <u>11-Atom Icosahedral Fragments</u>. These are generally made by basic cleavage of a boron atom from an icosahedral cage, and provide synthetic routes to some of the metallacarboranes described in Part C. The numbering systems used for the icosahedron and the 11-atom icosahedral fragment are illustrated in Fig. 12.

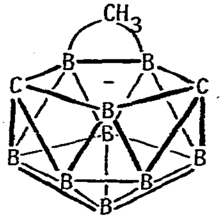


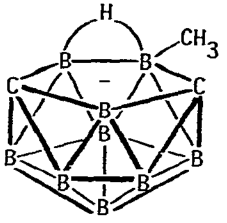
(I)

(II)

Figure 12. Numbering schemes for the icosahedron (I) and the 11-atom icosahedral fragment (II) derived by removing atom number 3 from the icosahedron.

Methylation of 7,9-$C_2B_9H_{11}^{2-}$ with methyl iodide in THF-NH_3 has yielded the μ-methyl monoanion, which rearranges to the 10-methyl isomer at room temperature [29].





(terminal H's omitted for clarity)

Treatment of $B_{10}H_{12}C\text{-}NMe_3$ with triethylamine followed by $RPCl_2$ yields the derivative $RPB_{10}H_{10}C\text{-}NMe_3$ having an RP bridging group between two of the boron atoms in the pentagonal open face, as shown by an X-ray structure of the PhP compound (Fig. 13) [30].

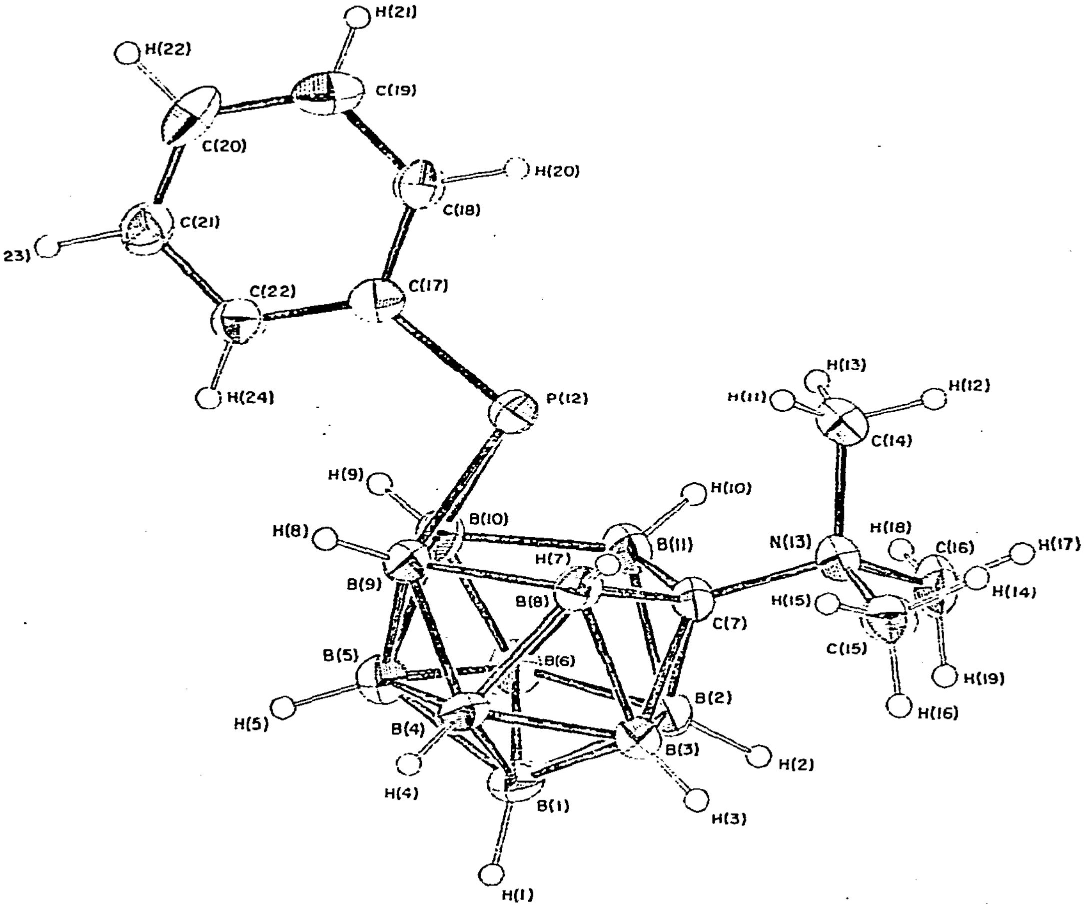


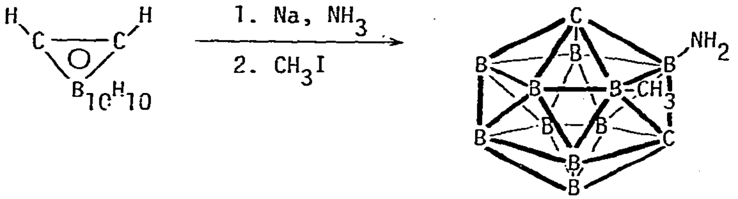
Figure 13. The structure of $Me_3N\text{-}CB_{10}H_{10}PPh$. [From W. F. Wright, J. C. Huffman, and L. J. Todd, J. Organometal. Chem., 148 (1978) 7.]

Reaction of sodium selenite with decaborane has yielded 7,8-diselena-*nido*-undecaborane, and similar reaction with 7,8-$C_2B_9H_{12}^-$ has yielded 7,8-dicarba-10-selena-*nido*-undecaborane [31]. Reaction of $B_{10}H_{12}CH^-$ with As_2O_3 yields 1,2-$B_{10}H_{10}CHAs$, and $B_{11}H_{11}Se$ and $B_{11}H_{11}Te$ have been prepared from $B_{11}H_{14}^-$ and $NaHSeO_3$ or TeO_2 [32].

2. *B*-Substituted Derivatives. *B*-Substitution of the carborane cage has been achieved by reduction of $C_2B_{10}H_{12}$ to $C_2B_{10}H_{12}^{-2}$ followed by alkylation and oxidation, by reacting an 11-atom icosahedral fragment (dicarbollide ion) with an alkylboron or arylboron halide, or by Friedel-Crafts or other aromatic substitution reactions. Some *B*-substituents are replaceable and serve as sources of a variety of *B*-substituted carboranes. Soviet and Czech groups have led the way in this field, and have continued to discover new and interesting reactions.

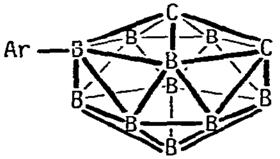
For numbering of the icosahedron, see Fig. 12. The possible dicarbaborane isomers are 1,2- designated *ortho*-, 1,7-, *meta*-, and 1,12-, *para*-.

Reduction of *o*-carborane with sodium in liquid ammonia followed by addition of methyl iodide has yielded 2-amino-6-methyl-*m*-carborane, and several analogous reactions and further transformations of the products have also been reported [33].

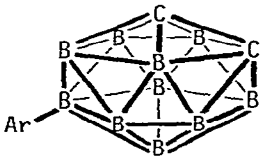


(cage H's omitted for clarity)

Reaction of $C_2B_{10}H_{12}^{2-}$ with ArMgX or ArLi followed by oxidation with $CuCl_2$ yields mixtures of *B*-aryl-*o*-carboranes having the aryl substituent at positions 3, 4, 8, or 9 [34]. X-Ray structures of 1,2-dimethyl-9-aryl-*o*-carboranes and 4-(*p*-tolyl)-*o*-carborane have been determined. On the basis of ionization constants of carboxylic acids in the series and also ^{19}F NMR spectra, the 4-*o*- and 9-*o*-carboranyl substituents are electron releasing toward the benzene ring.



4-aryl-*o*-carborane



9-aryl-*o*-carborane (H's omitted for clarity)

B-Bonded thallium substituted *o*- and *m*-carboranes, 9-$(F_3CCO_2)_2Tl$-*o*- or -*m*-$B_{10}C_2H_{11}$, have been obtained either by displacement of mercury with $Tl(O_2CCF_3)_3$ or by direct thallation of the unsubstituted carboranes with

$Tl(O_2CCF_3)_3$ [35,36]. 9,9'-Bis(*o*- or *m*-carboranyl)mercury has been used for the preparation of 9-carboranyl-$AsCl_2$, -$SbCl_2$, -$SnCl_2$-9-carboranyl, and -S-S-9-carboranyl [37]. Treatment of bis(9-*o*- or -*m*-carboranyl)mercury with $AsCl_3$ or $SbCl_3$ yields 9-carboranyl-$AsCl_2$ or -$SbCl_2$ [38,39]. Acetylation of bis(9-*o*- or -*m*-carboranyl)mercury with acetyl chloride and aluminum chloride yields the corresponding 9-acetylcarborane [40]. Reaction of $(Ph_3P)_3Pt$ with mercurated carboranes have been reported [41]. Platinum replaces *B*-bonded mercury but forms a Pt-Hg bond to *C*-bonded mercury.

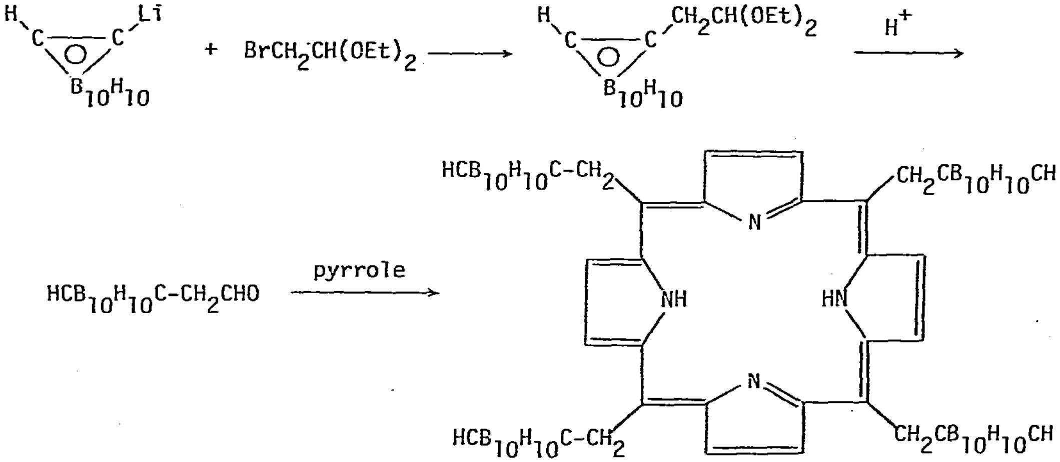
$$9\text{-}(ClHg)\text{-}1,2\text{-}C_2B_{10}H_{11} \longrightarrow 9\text{-}[(Ph_3P)_2ClPt]\text{-}1,2\text{-}C_2B_{10}H_{11}$$

$$1\text{-}(ClHg)\text{-}2\text{-}Ph\text{-}1,2\text{-}C_2B_{10}H_{10} \longrightarrow 1\text{-}[(Ph_3P)_2ClPt\text{-}Hg\text{-}]\text{-}2\text{-}Ph\text{-}1,2\text{-}C_2B_{10}H_{10}$$

Treatment of *m*-carborane with sulfur and aluminum chloride yields 60% of 9-Hs-*m*-$C_2B_{10}H_{11}$ [42]. By-products include the sulfide, disulfide, and trisulfide. Reaction of sulfur with *o*- and *m*-carboranes in the presence of aluminum chloride leads to sulfhydryl substitution in the most electron rich positions. Compounds prepared by this route include 8- and 9-HS-*o*-$C_2B_{10}H_{11}$, 8- and 9-HS-3,1,2-$(C_5H_5Co)C_2B_9H_{10}$, and 8,8'-HS-3,3'-Co$(1,2\text{-}C_2B_9H_{10})_2$. Aluminum chloride in benzene converts $Co(C_2B_9H_{11})_2^-$ to the derivative having a bridging *o*-phenylene group between the 8 and 8' boron atoms [43].

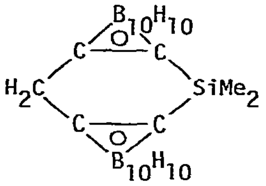
The structure of 4-benzyloxy-*o*-carborane has been determined by X-ray [44].

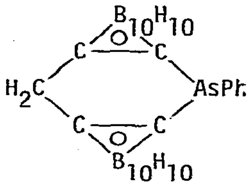
3. *C*-Substituted Derivatives. It has long been known that the CH protons of carboranes are acidic and that the carbanions resulting from deprotonation react with a variety of electrophiles to form *C*-substituted carboranes. The inertness and steric bulk of the carborane cage dominates the chemistry. These properties of the carborane cage may have useful applications in the solution of chemical problems not particularly connected with carborane chemistry, as in the series of (carboranylmethyl)porphyrins prepared by Haushalter and Rudolph [45].



Some evidence was obtained that the carboranylmethyl groups are too bulky to rotate freely across the place of the porphyrin ring.

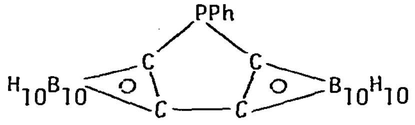
Soviet chemists have continued to produce great numbers of papers on C-substituted icosahedral carboranes. Several syntheses of heterocyclic derivatives have been described. A series of heterocyclic derivativies of methylenebis(o-carborane) have been prepared by Zakharkin and Shemyakin [46].



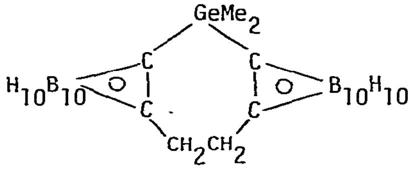


and similar compounds

Heterocycles have been prepared from group IV and V dihalides and the lithio-o-carboranes $LiCB_{10}H_{10}C\text{-}CB_{10}H_{10}CLi$ and $LiCB_{10}H_{10}C\text{-}CH_2CH_2\text{-}CB_{10}H_{10}CLi$ [47].

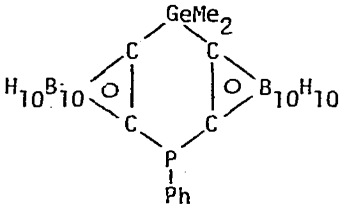


and MeAs analogue

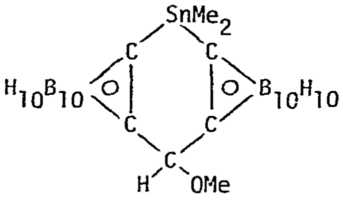


and Me_2Si and MeAs analogues

X-ray data show that a heterocycle formed from two carborane units plus germanium and phosphorus has the phosphorus atom 0.33 Å out of the plane of the C-C-Ge-C-C atoms. A similar heterocycle with tin and carbon as bridging atoms has a planar ring [48].

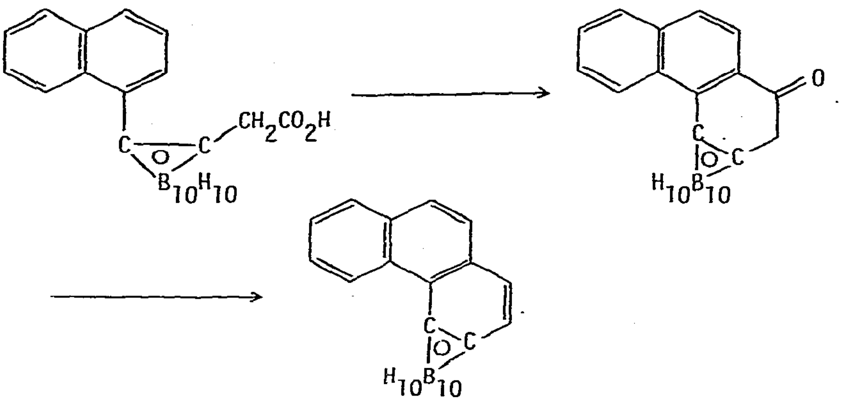


center ring puckered

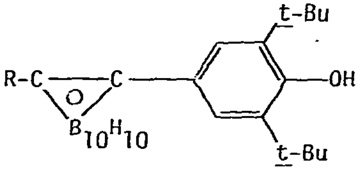


center ring planar

Phenanthreno[3,4]-o-carborane has been synthesized [49].



Addition of carboranylmagnesium bromide to 2,6-di-t-butyl-1,4-benzoquino followed by reduction with zinc has yielded the carboranylphenol, and several further reactions have been reported [50]. On the basis of ESR data, it has been concluded that m-carborane bearing a di-t-butylphenoxy radical substituent isomerizes to the o-carborane [51].



Treating o- or m-R-$CB_{10}H_{10}C$-Li with $TlCl_3$ leads to (R-$CB_{10}H_{10}C$-$)_2TlCl$ [52]. Reaction of C-lithiocarboranes with R_2NCH_2Cl has yielded the R_2NCH_2-substituted carboranes [53]. Coupling of Ar-$N_2^+BF_4^-$ with o-, m-, or p-$HCB_{10}H_{10}C$-Cu yields $HBC_{10}H_{10}C$-Ar [54]. Reaction of m-Li-$CB_{10}H_{10}C$-Li with $EtOSiClMe_2$ yielded $EtOMe_2Si$-$CB_{10}H_{10}C$-$SiMe_2OEt$ containing impurities which included a B-methylated homologue of the major product as well as some material containing an $SiHMe_2$ group [55]. Disproportionation of o- and m-RME_2Si-$CB_{10}H_{10}CH$ in the presence of KOH or potassium perfluorobutyrate has been reported [56]. Reaction of o-Li-$CB_{10}H_{10}C$-Li with $ClP(NMe_2)_2$ has yielded $(Me_2N)_2P$-$CB_{10}H_{10}C$-$P(NMe_2)_2$, and related compounds have also been prepared [57]. The reaction of sodio-o-carborane with R-Cl to form R-$CB_{10}H_{10}CH$ has been extended to R = -CH_2CN [58].

Chelated nickel complexes of 1,2-bis(diphenylphosphino)-o-carborane [59] and nickel, palladium, and platinum complexes of o-carboranyldithiocarboxylates [60] have been reported.

Reactions of o-carboranylallyllithiums, R-$CB_{10}H_{10}C$-CH=CH-$CH_2^-Li^+$, with various electrophiles such as alkyl halides, ethylene oxide, formaldehyde, carbon dioxide, mercuric chloride, and chlorotrimethylsilane have been found to yield mixtures of allylic isomers [61]. Attempted hydroformylation of vinyl, isopropenyl, or allyl o-carborane has yielded only hydrogenation products, even when CO was used without added hydrogen. By deuterium labeling studies, it was shown that the hydroxyl hydrogen of the alcohol solvent is incorporated into the product [62]. The Arbuzov reaction of o-$HCB_{10}H_{10}C-P(OEt)_2$ with methyl sulfate is accompanied by transesterification of the phosphonic ester and yields o-$HCB_{10}H_{10}C-P(O)(OCH_3)CH_3$ [63].

The preparation of a number of peroxy derivatives of the type 1,7-$ROOCOCB_{10}H_{10}CCO_3R$ has been reported [64]. Treatment of various carboranyl carboxylic acid chlorides with hydroperoxy compounds and pyridine has yielded peroxy derivatives [65,66].

Friedel-Crafts acetylation of a series of aryl substituted carboranes has been described [67]. Carboranylpyrans and carboranylpyrilium salts have been prepared [68]. Treatment of 1,2-bis(p-hydroxyphenyl)-o-carborane with cyanogen halide and tertiary amine has yielded the bis(p-cyanotophenyl) derivative [69].

Gamma ray irradiation of 1-phenyl-o-carborane leads to oligomer formation [70]. Metallocarboranes such as $LiC_2B_{10}H_{11}$ abstract a proton from an o-position on the phenyl group of $(Ph_3P)_3IrCl$ to yield cyclic $Ph_2PC_6H_4Ir$ complexes rather than carboranyliridium derivatives [71].

The structure of 1,2,3,6-tetramethyl-o-carborane has been determined by X-ray crystallography [72]. The structure of bis(o-carboranyl)dimethylgermane has been determined by X-ray [73].

4. Physical Measurements. Icosahedral carboranes and related compounds have continued to attract the attention of physical chemists. X-Ray data and all kinds of data pertaining to smaller cages are noted in the sections pertaining to the respective structural types, but spectroscopic, kinetic, and thermodynamic type measurements on icosahedral cage compounds are collected in this section.

The reviewer's belated attention has been called to the work of a French group led by R. Freymann on low temperature infrared studies of o- and m-carboranes [74-77]. The low temperature spectra (15K and 80K) show a wealth of detail not observed at higher temperatures, and would seem essential to any attempt at full interpretation of the molecular vibrations. This group has also reported proton NMR studies on o- and m-carborane and several derivatives [78].

Olah and coworkers have studied the ^{13}C NMR chemical shifts of pentacoordinate and hexacoordinate carbon in aluminum compounds and carboranes and found relationships between the coordination number of carbon and its chemical shift and C-H coupling constant [79]. Substituents in icosahedral carboranes produce an NMR chemical shift at the position opposite (para) to the substituent, and these shifts have been correlated with ^{13}C chemical shifts at the p-position in substituted benzenes [80]. Effects of Me_3Si, Me_3Ge, Me_3Sn, Me_2CH, and MeHg substituents on the ^1H and ^{11}B NMR spectra and IR spectra of substituted carboranes have been correlated with structure [81]. Rotational barriers around the carbon-nitrogen bond of the amide group in some cobaltacarboranes substituted with a $CONMe_2$ group on a cage carbon atom have been reported [82].

Polarographic reduction of a series of *B*-mercurated carboranes has been found to require higher reducing potentials than analogous *C*-mercurated carboranes [83]. The B-Hg bond in *p*-carboranes is more easily reduced than the B-Hg bond in *o*- or *m*-carboranes.

Rates of cleavage of C-formyl, benzoyl, and trimethylstannyl derivatives of *o*, *m*, and *p*-carborane have been reported [84]. The kinetics of cleavage of a series of *m*-$RMe_2Si\text{-}CB_{10}H_{10}CH$ by butanol have been measured and correlated with the Taft substituent constant [85].

Reaction of *o*-$C_2B_{10}H_{12}^{2-}$ with *p*-FC_6H_4MgBr and related reagents has given small yields of *B*-arylcarboranes, and the inductive effect of the *B*-carboranyl groups on the aryl systems was found to be electron donating [86]. The pKa of *p*-(4-*m*-carboranyl)benzoic acid is 6.53, and the pKa of the corresponding *m*-substituted benzoic acid is 6.60 [87].

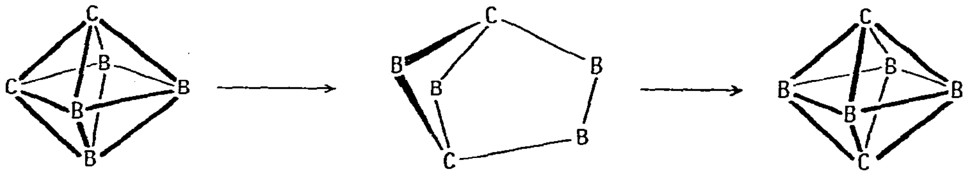
Mass spectra of some silylated *m*-carboranes have been determined [88].

E. Theoretical Studies

This section includes quantum mechanical calculations on polyhedral boranes, carboranes, and metallaboranes of all cage sizes. Lipscomb continues to lead the way in this field.

Bicerano, Marynick, and Lipscomb have used the PRDDO (partial retention of diatomic differential overlap) method to calculate energies for large $(BH)_n^{2-}$ polyhedra where n is 9 to 24. Although icosahedral $(BH)_{12}^{2-}$ is the most stable member of the series, significant stability was predicted for larger cages up to n = 22. Larger cages with n = 23 and 24 were calculated to be significantly less stable, and the cage sizes n = 14 and n = 17 were predicted to be more stable than others. Unexpectedly, the neutral species $(BH)_{16}$ with T_d symmetry, $(BH)_{19}$ with C_{3v} symmetry, and $(BH)_{22}$ with T_d symmetry were predicted to be stable, and the corresponding $(BH)_n^{2-}$ anions were found to have degenerate orbitals which would lead to Jahn-Teller distortions [89,90].

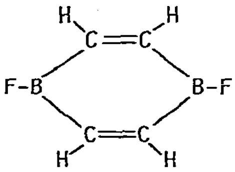
Lipscomb and coworkers have carried out PRDDO calculations on isomers of $C_2B_3H_5$, $C_2B_4H_6$, and $C_4B_2H_6$ [91]. In the $C_2B_4H_6$ system, the cage-opened bicyclic isomer illustrated proved unexpectedly stable and is now believed to be the intermediate in the cage isomerization instead of the distorted trigonal prism postulated on the basis of previous calculations [JOM 119 (1976) 24].



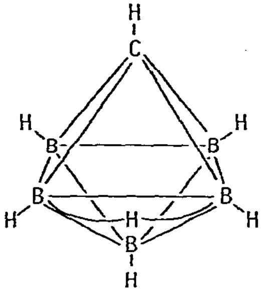
bicyclic intermediate

(H atoms omitted)

In the B-fluorinated series, the non-cage "classical" structures are relatively stabilized, and in the C_4B_2 series the known six-membered ring compound illustrated is calculated to be more stable than a cage isomer.



From PRDDO calculations, Lipscomb and coworkers have found that the bridge hydrogen in CB_5H_7 is essentially a normal bridge hydrogen between two of the equitorial boron atoms [92], rather than a cap of a three-center face as suggested previously on the basis of electron diffraction and other studies [JOM 98 (1975) 324; JOM 119 (1976) 25]. This bridge hydrogen tautomerizes by way of an equatorial--apical BHB bridge to the other equatorial--equitorial positions.



Revised structure for CB_5H_7.

Lipscomb and coworkers have carried out a comparison of various molecular orbital calculation programs for speed and accuracy, and have included a number of boranes and carboranes as test structures [93]. The CNDO/2 and INDO programs are fastest but least accurate, and STO-3G is slow but highly accurate. The PRDDC method eliminates 93% of the error of the CNDO/2 method at 6% of the additional cost of going to STO-3G.

Calculations using the PRDDO method have been carried out for the fluxional behavior of $B_{11}H_{11}^{2-}$, for which C_{2v} (closo) and C_s (one four-membered face) structures are calculated to have nearly equal energies [94].

Extended Hückel calculations on $Cu(B_{11}H_{11})_2^{n-}$ and related species account for the observed slip distortion in the dicarbollylcopper series [95]. Molecular orbital calculations by the SCCC method have been reported for $(C_5H_5)FeC_2B_9H_{11}^-$ and the iron-cage bonding has been found to be similar to that in ferrocene, except that the cage orbitals involved are σ rather than π [96]. The u.v. photoelectron spectrum of $B_4H_8Fe(CO)_3$ correlates well with SCF-Xα-SW molecular orbital calculations, a first-principle one-electron treatment [97]. Extended

Hückel calculations for icosahedral platinacarboranes and related compounds have been reported [98].

Dewar and McKee have reported MNDO calculations for a series of boron hydrides B_3H_7 and $B_{10}H_{16}$ and boron hydride anions up to $B_{12}H_{12}^{2-}$ [99]. The MNDO calculations have proved satisfactory for boron where MINDO/3 did not.

PRDDO calculations indicate that $B_3H_8^-$ should be fluxional and that B_5H_{11} should be nonfluxional with C_s symmetry [100].

Hückel-type calculations using 3-center B-B-B localized orbitals as basis functions have been carried out by Aihara on the series of polyhedral boranes, $B_nH_n^{2-}$ [101]. The calculation method is analogous to the original Hückel method used for conjugated hydrocarbons, except that in place of the single atomic orbitals treated as points in the hydrocarbon calculations, the triangular faces of the borane are used as the basis set. For N triangular faces of a borane, an N X N matrix is required, with the nth row and nth column in a 1:1 correspondence with the nth triangular face, the diagonal matrix elements assigned the value α, and the off-diagonal elements assigned the value β if the faces have an edge in common, and 0 if they do not. Aromatic delocalization energies were obtained by comparing the delocalized system with a hypothetical system having only localized three-center bonds.

A theoretical discussion of bonding in metallocarboranes having fewer than (n + 1) electron pairs in an n atom cage has been presented [102]. In such cases, the metal is expected to donate electrons from filled d orbitals to the cage. The diferracarborane $(C_5H_5Fe)_2C_2B_6H_8$ was discussed.

Advanced quantum mechanical calculations on BH have been reported by Lipscomb and coworkers [103].

F. Metallaboranes and Polyhedral Boranes

The compounds included here are technically not organoboron compounds, since they lack a carbon-boron bond, except for an occasional alkyl substituent on a cage. Treatment is therefore brief, and is not necessarily as complete as the survey of the true carboranes. However, metallaboranes and metallacarboranes have many properties in common, as do polyhedral boranes and carboranes, and it seems appropriate to provide as much coverage as the reviewer can conveniently find by way of the most commonly used journals and Chemical Abstracts.

Reaction of $Fe(CO)_4^{2-}$ with $BH_3 \cdot THF$ has yielded the anion $B_2H_5Fe(CO)_4^-$, which has the iron carbonyl group in place of one of the bridge hydrogens of diborane [104]. The structure of $B_3H_8Mn(CO)_3$ has been determined by X-ray crystallography [105], and the preparations of $B_3H_8Mn(CO)_4$ and several related compounds of Mn, Re, Fe, Mo, and W have been reported [106]. Two new tetranickelaboranes, $(C_5H_5)_4Ni_4B_4H_4$ and $(C_5H_5)_4Ni_4B_5H_5$, have been obtained from the reaction of NaB_5H_8 with $(C_5H_5)_2Ni$ and sodium amalgam in THF [107]. The cuprapentaborane $(Ph_3P)_2CuB_4H_9$ has been prepared [108]. Pentaborane-9 undergoes oxidative addition to $IrCl(CO)(PMe_3)_2$ at a basal B-H to form the 2-iridiopentaborane. 1-Halopentaboranes react similarly, and the adducts on warming rearrange from XB_5H_7-$IrX(CO)(PMe_3)_2H$ to B_5H_8-$IrX_2(CO)(PMe_3)_2$ [109]. The preparation of iron substituted pentaboranes 2-$B_5H_8Fe(CO)_2(C_5H_5)$ and 2,4-$B_5H_7[Fe(CO)_2(C_5H_5)]_2$ has been reported [110]. Reaction of B_5H_9 with $Fe(CO)_5$ and $LiAlH_4$ yields $B_4H_8Fe(CO)_3$ and a new ferraborane containing B-H-Fe bridge bonds, $B_2H_6Fe_2(CO)_6$ [111].

Syntheses of $Co(B_{10}H_{10}As)_2^{3-}$, $Ni(B_{10}H_{10}As)_2^{2-}$, $(C_5H_5)Co(B_{10}H_{10}As)^-$, $Co(B_9H_9As_2)_2^-$, and $(C_5H_5)Co(B_9H_9As_2)$ have been reported [112].

Reaction of $(C_5H_5)_2Ni$ with $B_{11}H_{13}^{2-}$ in the presence of a catalytic amount of sodium amalgam in glyme yields the icosahedral nickelaborane anion $C_5H_5NiB_{11}H_{11}^-$ [113]. Analogous reactions have been used to prepare nido-$(C_5H_5)NiB_{10}H_{12}^-$ and closo 1- and 2-$(C_5H_5)NiB_9H_9^-$ ions. Other nickelaboranes prepared include $(C_5H_5)NiB_{10}H_{13}$, $(C_5H_5)NiB_{10}H_{12}^-$, $(C_5H_5)_2Ni_2B_{10}H_{10}$, and the cobalt derivative $C_5H_5)_2CoNiB_{10}H_{10}^-$. Chlorination of 2-$(C_5H_5)NiB_9H_9^-$ to 2-$(C_5H_5)NiB_9Cl_9^-$ and thermal rearrangement to 1-$(C_5H_5)NiB_9Cl_9^-$ was also reported.

Reaction of $Na_2B_{10}H_{12}$ with Me_2SiCl_2 has yielded $Me_2SiB_{10}H_{12}$ [114]. Halogenation of $(CH_3)_2SnB_{10}H_{12}$ has yielded 5,10-$X_2B_{10}H_{12}$ [115].

The reaction of 1-ClB_5H_8 with $Be(BH_4)_2$ yields $B_5H_{10}BeBH_4$, which has been converted to $B_5H_{10}BeBr$, which in turn serves as a source of $B_5H_{10}BeB_5H_{10}$, $B_5H_{10}BeCH_3$, and $B_5H_{10}BeC_5H_5$ [116]. The structures of $B_5H_{10}BeBH_4$ and $B_5H_{10}BeB_5H_{10}$ have been determined by low-temperature X-ray diffraction studies, and show that the beryllium atom is inserted into a basal position of the B_5H_9 pyramid, making a $B(B_4Be)$ pyramid having Be-H-B bridge hydrogens [117]. NMR studies of $Be(BH_4)_2$, $Be(B_3H_8)_2$, $(C_5H_5)Be(B_3H_8)$, and $(CH_3BeB_3H_8)_2$ have been reported [118].

A convenient laboratory synthesis of decaborane from sodium borohydride by way of $B_{11}H_{14}^-$ has been reported by Dunks and Ordonez [119,120]. Pyrolysis of tetramethylammonium borohydride to $B_{10}H_{10}^{2-}$ has been patented in France [121].

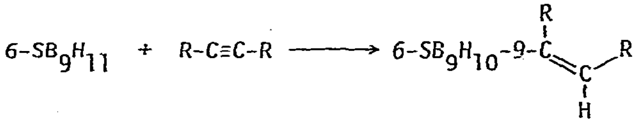
The kinetics of the isomerization of 1-ClB_5H_8 to 2-ClB_5H_8 in ether have been measured and suggest a cage rearrangement rather than a B-Cl bond cleavage [122].

Analysis of the ^{11}B NMR spectra of B_4H_{10} and B_5H_9 indicates that the broadness of the ^{11}B absorptions depends upon B-B spin-spin coupling, scalar relaxation, and partially collapsed spin-spin multiplets in addition to the small amount of broadening (less than 10 Hz) resulting from quadrupolar ^{11}B relaxation [123].

Irradiation of diborane with a CO_2 laser leads to formation of pentaborane-9 and -11, decaborane, and a polymer of approximate composition $(BH)_n$ [124,125]. The reaction of $B_5H_9^+$ with CH_3CN to produce B_5H_8 radical and CH_3CNH^+ has been observed mass spectrometrically [126].

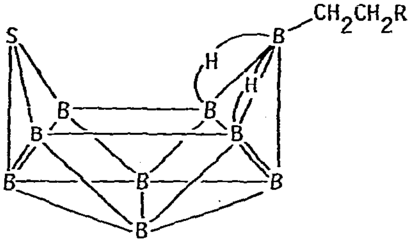
Hydroboration of alkenes and alkynes by 6-SB_9H_{11} procede efficiently to yield 9-alkyl- or 9-alkenyl-6-SB_9H_{10} [127].

$$6\text{-}SB_9H_{11} + R\text{-}CH{=}CH_2 \longrightarrow 6\text{-}SB_9H_{10}\text{-}9\text{-}CH_2CH_2R$$



$$6\text{-}SB_9H_{11} + R\text{-}C{\equiv}C\text{-}R \longrightarrow 6\text{-}SB_9H_{10}\text{-}9\text{-}C(R){=}C(H)R$$

6-SB_9H_{10}-9-CH_2CH_2R structure:
(terminal H's omitted)



The clusters B_9Cl_9 and $B_9Cl_9^{2-}$ have been reported [128].

G. Biological Studies

Included here are reports on toxicity studies of carboranes and publications regarding the ^{10}B neutron capture therapy of brain tumors.

Because $B_{12}H_{11}SH^{2-}$ has desirable properties for the boron neutron capture theory of brain tumors, efficient routes to this compound from $B_{12}H_{12}^{2-}$ have been worked out [129,130]. Hydrogen sulfide treatment leads to by-products and purification difficulties, but N-methylbenzothiazole-2-thione reacts to form an easily hydrolyzed intermediate [129]. Two papers on the biological effectiveness of ^{10}B in increasing the effective radiation does when cells are irradiated with neutrons have appeared [131,132]. An epithermal neutron technique for ^{10}B neutron capture therapy of brain tumors has been described [133]. A system for monitoring neutron flux for ^{10}B neutron capture tumor therapy has been described [134].

Carboranylmethyl propionate has been found to be moderately toxic on ingestion, slightly toxic when applied dermally, in several test animals [135]. Toxicity studies on n-hexylcarborane, carboranylmethyl ethyl sulfide, and carboranylmethyl propyl sulfide have been published [136]. Of these, only carboranylmethyl ethyl sulfide was mutagenic in the Ames test.

H. Reviews

Grimes has reviewed structure and stereochemistry in metalloboron cage compounds [137], carborane compounds of group IV elements [138], and reactions of metallocarboranes [139]. Stibr and coworkers have reviewed their work on monocarbaboranes and related compounds [140]. The Gmelin Handbook has been updated with two new volumes on carboranes [141]. An updated bibliography of carborane chemistry is available from National Technical Information Service [142]. Organoboron chemistry [143] and carborane chemistry [144] have been reviewed. Carboranes have been reviewed in German [145]. Greenwood has reviewed his work on metallotetra-, -penta-, -hexa-, and -decaboranes [146].

II. HYDROBORATION

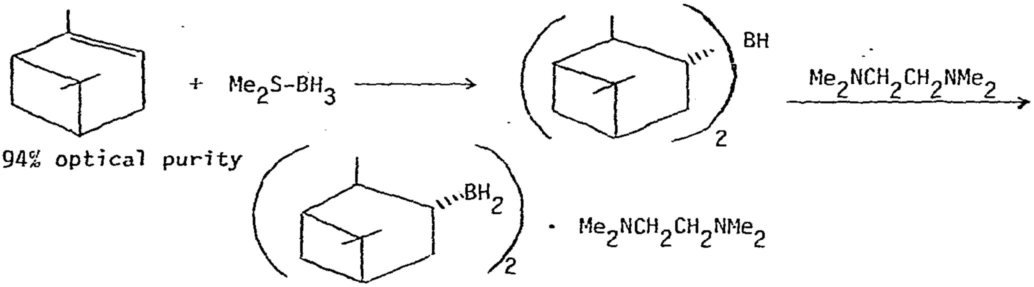
A. Introduction

"Alkylboranes in Organic Synthesis" might be a more appropriate title for this section, since many of the items covered involve hydroboration only as a source of starting materials, or may not involve hydroboration at all but are related to the synthetic applications of alkylborane chemistry.

H. C. Brown continues to lead the way in hydroboration chemistry, though he officially retired last year. The Journal of Organometallic Chemistry has published an issue in honor of Professor Brown, part 1 of volume 156 (1978). This is a thick issue filled with a variety of papers contributed by many of Professor Brown's students and admirers, and provides a fitting tribute to Brown's work as well as a very interesting collection of articles for anyone interested in any aspect of organoborane chemistry. We wish Professor Brown many more years of fruitful boron chemistry.

B. Borane Reagents

Brown, Schwier, and Singaram have described a synthesis of optically pure isopinocampheylborane as the air stable $Me_2NCH_2CH_2NMe_2$ complex, as well as the reaction of this complex with $BF_3 \cdot Et_2O$ to form solutions of the optically pure isopinocampheylborane [147]. Reaction of $Me_2NCH_2CH_2NMe_2$ with RBH_2 generally yields air stable complexes, $RBH_2Me_2NCH_2CH_2NMe_2$ or $RBH_2Me_2NCH_2CH_2NMe_2H_2BR$, from which the free monoalkylboranes can be generated easily by treatment with $BF_3 \cdot OEt_2$ [148].

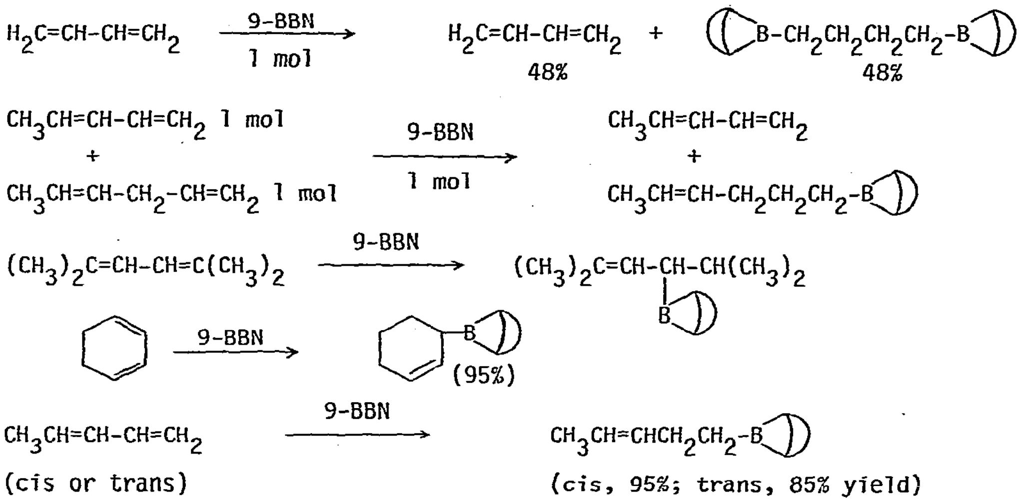


air stable, can be crystallized to high optical purity

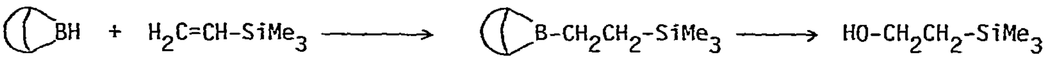
Hydroboration of cis-2-butene and cis-3-hexene with diisopinylcampheylborane followed by oxidation yields alcohols of 94-99% optical purity, but hydroboration with monoisopinocampheylborane yields alcohols of opposite configuration and only 20-24% optical purity [149].

Brown and Ravindran have reported the hydroboration of olefins with $BrBH_2 \cdot SMe_2$ to form dialkylbromoboranes in excellent yields [150].

Brown, Liotta, and Kramer have carried out a study of hydroboration of dienes with 9-BBN [151]. Some of the more noteworthy results are summarized below.



Hydroboration of $CH_2=CH-CH_2-R$, where R is CH_2OH, CH_2OAc, CH_2Cl, CH_2OCH_3, CO_2Et, or CN, with 9-BBN proceeds with better than 98% regioselectivity and in high yields [152]. Although diborane is relatively unselective, dialkylboranes hydroborate vinyltrimethylsilane with high preference for addition of boron at the β-carbon [153]. This reaction provides convenient access to β-hydroxyethylsilanes.



Kabalka, Newton, and Jacobus have shown that the reactions of (E)- and (Z)-1-hexene-1,2-d_2 with dicyclohexylborane and with 9-BBN produce the threo- and erythro-1,2-dideuteriohexylboranes, respectively, on the basis of examination of the proton NMR spectra of the boranes [154]. Hydroboration-oxidation is, of course, well known to be *cis*, and the oxidation mechanism requires retention and not inversion, but the present study provides direct evidence that the hydroboration step itself is a *cis* addition.

Potassium trialkylborohydrides are conveniently synthesized from potassium hydride and trialkylboranes in tetrahydrofuran [155]. Potassium triethylboro-

$$R_3B + KH \longrightarrow K^+ R_3BH^- \qquad R = \text{primary or secondary alkyl, cycloalkyl}$$

hydride forms a stable 1:1 adduct with triethylborane, $Et_3B-H-BEt_3^-$, in THF at 25°C [156]. Rates of reaction of a series of trialkylboranes, R_3B, with lithium or sodium hydride in THF to form the trialkylborohydrides, R_3BH^-, have been reported [157]. Lithium triethylborohydride in THF reduces primary and secondary tosylates to hydrocarbons in excellent yields [158]. Triethylborohydrides have been used to reduce Se to Li_2Se [159] and $Fe(CO)_5$ to $K_2Fe(CO)_4$ [160]. The reaction of dialkylboranes with alkyllithium or phenyllithium does not yield trialkylborohydrides but a mixture of tetraalkylborate and dialkylborohydride [161].

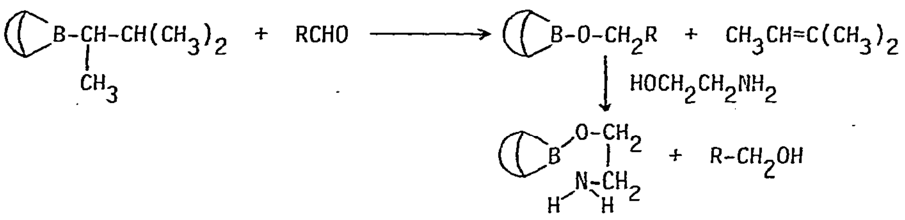
$$R_2BH + R'Li \longrightarrow R_2\bar{B}R'_2\ Li^+ + R_2BH_2^-\ Li^+$$

R = cyclohexyl, siamyl; or R_2BH = 9-BBN
R' = CH_3, n-C_4H_9, Ph

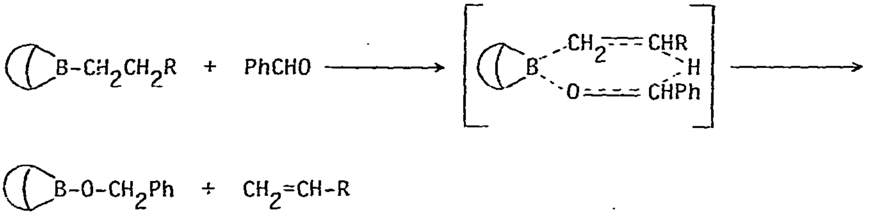
Borane methyl sulfide reduces aldehydes and ketones in the presence of carbon-carbon double bonds [162].

The hydroboration of alkenes and alkynes by 6-SB_9H_{11} has been noted in the carbonate section. Oxidation of some of the alkylboranes with hydrogen peroxide has yielded alcohols, and the alkenylboranes have yielded ketones [127].

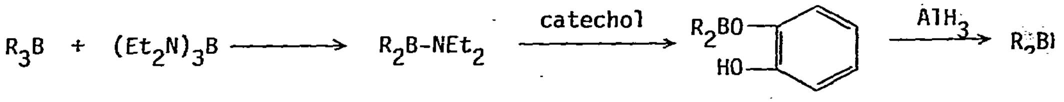
B-Siamyl-9-BBN readily reduces aldehydes, and is selective for aldehydes in the presence of ketones [163].



B-Alkyl-9-borabicyclononanes reduce benzaldehyde with elimination of olefins [164]. Alkyl substitution on the carbon bearing the eliminated β-hydrogen increases the rate. The kinetics are first-order in each reactant, and the data are consistent with a cyclic transition state.



9-Bromo-9-BBN is a useful and selective reagent for ether cleavage [165]. Hydroboration of 2-substituted methylenecyclohexanes and cyclopentanes has been found to occur mainly from the side of the double bond opposite the substituent, with increasing steric bulk of the substituent leading to a greater proportion of the resulting cis-1,2-product [166]. Hydroboration of $ArSO_2CH_2CH{=}CHCH_3$ with diborane followed by oxidation yields almost exclusively $ArSO_2CH_2CHOHCH_2CH_3$, but with 9-BBN the major product is $ArSO_2CH_2CH_2CHOHCH_3$ [167]. An efficient synthesis of dialkylboranes and dialkylborinic acid derivatives from trialkylboranes utilizes a disproportionation of trialkylborane with tris(diethylamino)-borane [168].

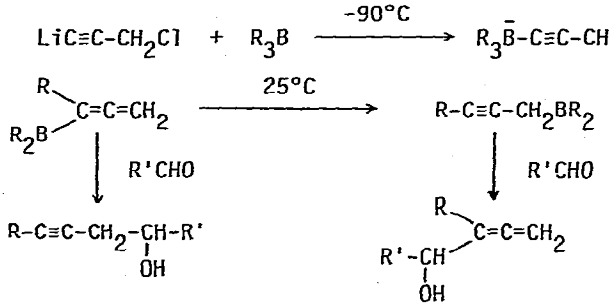


R = Et, 1-Bu, 2-Bu, i-Bu

Hydralumination of 1,4-hexadiene with $LiAlH_4$-$TiCl_4$ followed by $BF_3 \cdot OEt_2$ yields $B(CH_2CH_2CH_2CH{=}CHCH_3)_3$ [169].

C. Replacement of Boron

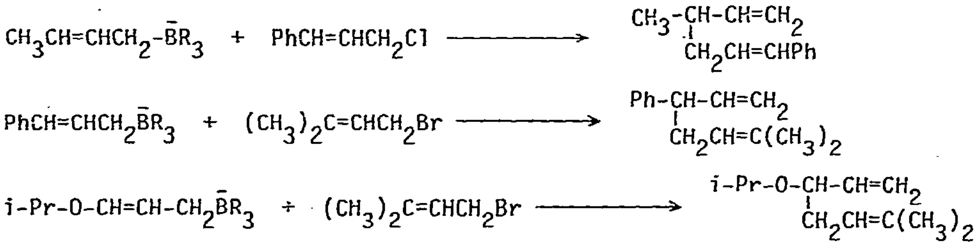
1. Ate Complex Rearrangements. Zweifel and coworkers have found that the product obtained from $LiC{\equiv}C$-CH_2Cl, R_3B, and an aldehyde depends on the reaction temperature prior to addition of the aldehyde, the initially formed allenylborane undergoing rearrangement at 25°C [170].



Yields 73-89% isolated

R = cyclopentyl, cyclohexyl, n-hexyl; R' = n-, s-, or t-alkyl, cycloalkyl, aryl vinyl

Controlled regioselective coupling of two allylic groups has been achieved by Yamamoto and Maruyama, using allylic boron ate complexes and allylic halides [171].



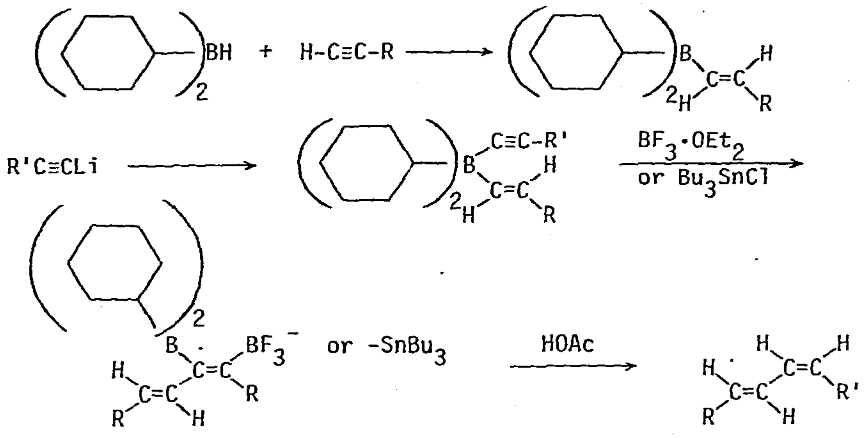
$$CH_3CH{=}CHCH_2\text{-}\bar{B}R_3 + PhCH{=}CHCH_2Cl \longrightarrow CH_3\text{-}\underset{CH_2CH=CHPh}{CH}\text{-}CH{=}CH_2$$

$$PhCH{=}CHCH_2\bar{B}R_3 + (CH_3)_2C{=}CHCH_2Br \longrightarrow Ph\text{-}\underset{CH_2CH=C(CH_3)_2}{CH}\text{-}CH{=}CH_2$$

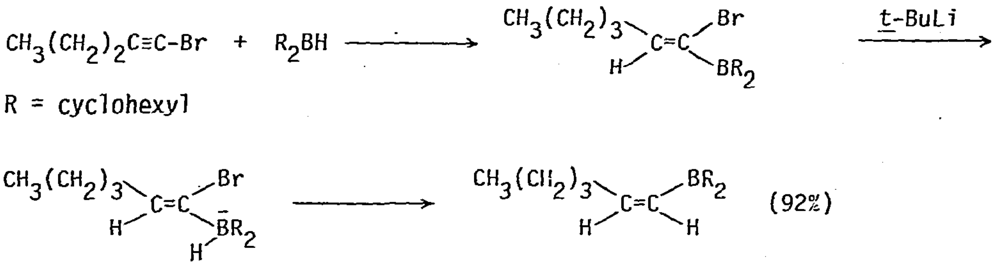
$$i\text{-}Pr\text{-}O\text{-}CH{=}CH\text{-}CH_2\bar{B}R_3 + (CH_3)_2C{=}CHCH_2Br \longrightarrow i\text{-}Pr\text{-}O\text{-}\underset{CH_2CH=C(CH_3)_2}{CH}\text{-}CH{=}CH_2$$

(BR_3 is tributylborane or 9-butyl-9-BBN)

Zweifel and Backlund have described an efficient synthesis of (E, Z)-1,3-dienes from lithium dicyclohexyl(trans-1-alkenyl)(1-alkynyl)borates [172].



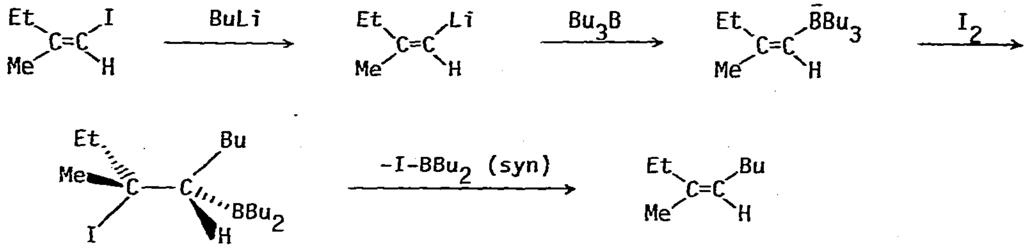
An improved synthesis of cis-alkenylboranes utilizes the hydroboration of 1-halo-1-alkynes followed by treatment with t-butyllithium at -78°C [173].



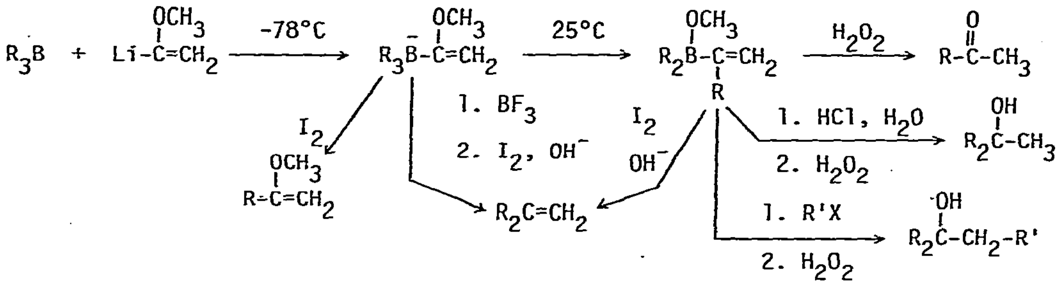
R = cyclohexyl

The reaction is somewhat faster if 1-iodo-1-alkynes are used, and yields are somewhat reduced if disiamylborane is used in place of dicyclohexylborane. 9-BBN failed to give useful results because of competing carbon migration accompanied by expansion of the 9-BBN ring, which proved faster than hydride migration in this system.

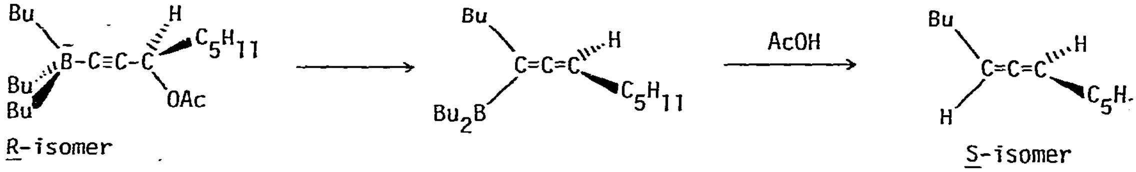
Lithium trialkylvinylborates prepared from trialkylboranes and vinyllithiums rearrange on treatment with iodine to yield trisubstituted olefins [174]. This process differs from previously reported related olefin syntheses (see JOM 147 (1978) 50-51) in that the alkenyl group is derived from the acetylenic precursor not by hydroboration but by an organocopper route to 1-iodo-2,2-dialkylethenes, and it also differs in that the final boron-iodide elimination is syn and intramolecular, the strongly electrophilic BR_2 group requiring no external base to effect elimination. ^{13}C NMR evidence indicated that this synthesis is stereospecific within the limit of sensitivity of the analysis, which would have detected 5% of the opposite isomer.



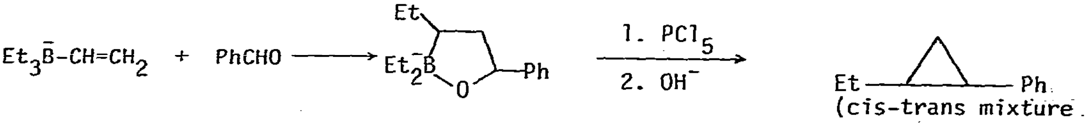
Trialkylboranes and α-methoxyvinyllithium react at -78°C to form an ate complex, which on iodination at -78° rearranges and eliminates to yield enol ethers, or on warming to room temperature rearranges to a synthetically useful alkenyldialkylmethoxyborate [175].



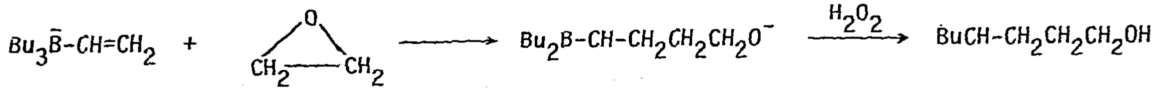
Treatment of R-(+)-1-octyn-3-ol acetate with butyllithium followed by tributylborane and protodeboronation with acetic acid yields predominantly the S-(+)-allene, 5,6-dodecadiene, indicating that the migration of the butyl group from boron to carbon occurs preferentially anti to the leaving acetate group [176].



Utimoto and coworkers have reported reactions of $R_3\bar{B}\text{-CH=CH}_2$ with aldehydes [177].

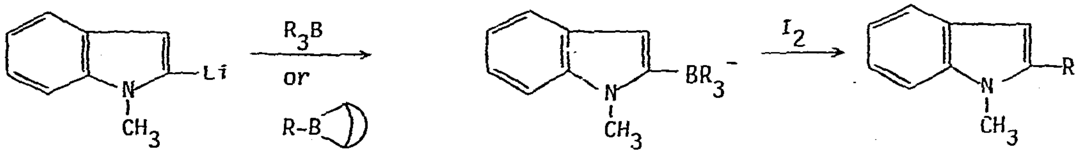


Trialkylvinylborates react efficiently with epoxides or with iodine [178].

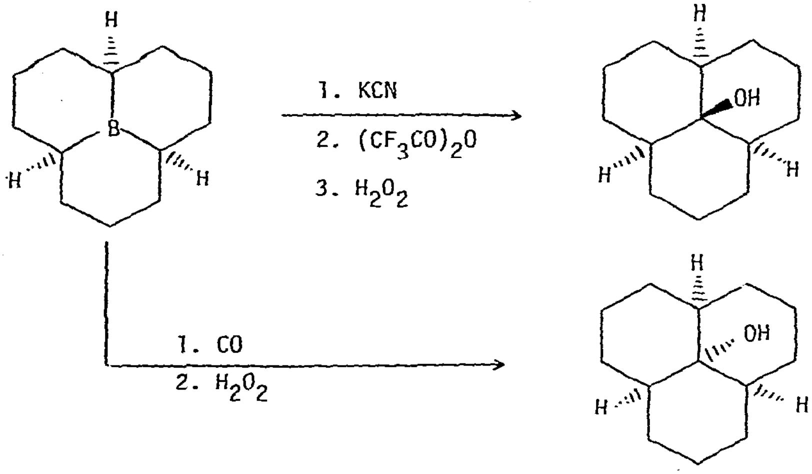


$$R_3\bar{B}\text{-CH=CH}_2 + I_2 \xrightarrow{OH^-} \text{R-CH=CH}_2$$

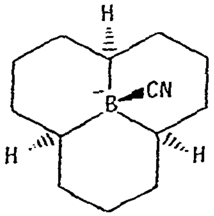
Reaction of N-methyl-2-lithioindole with trialkylboranes followed by iodination yields 2-alkyl-N-methylindoles [179].

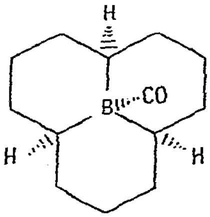


The cyanoborate process applied to cis,cis-perhydro-9b-boraphenylene gives trans,trans,trans-perhydrophenalenol, in contrast to carbonylation, which gives the cis,cis,cis-isomer [180].



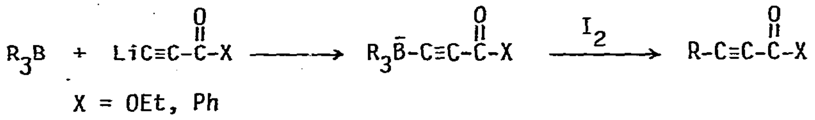
The intermediates are postulated to be the kinetically favored all cis isomer in the case of the CO reaction, and the thermodynamically favored trans intermediate in the case of the CN^- reaction. Carbonylation of R_3B with





$LiAlH(OMe)_3$ and CO followed by treatment with acid and oxidation yields R_2CHOH [181].

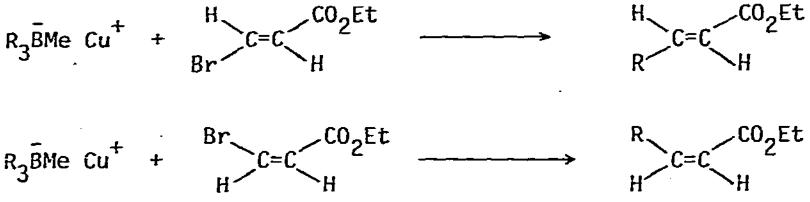
Alkylation of acetylenic carbonyl compounds has been accomplished by way of boron ate complexes [182].

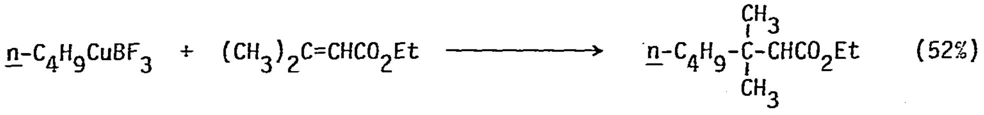


$$R_3B + LiC\equiv C-\overset{O}{\overset{\|}{C}}-X \longrightarrow R_3\bar{B}-C\equiv C-\overset{O}{\overset{\|}{C}}-X \xrightarrow{I_2} R-C\equiv C-\overset{O}{\overset{\|}{C}}-X$$

X = OEt, Ph

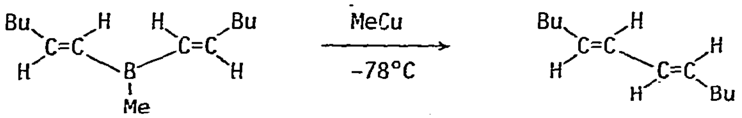
Copper(I) methyltrialkylborates stereospecifically alkylate ethyl β-bromoacrylates [183]. Reaction of α,β-unsaturated esters with $RCuBF_3$ gives good yields of conjugate addition products, even when the ester is β,β-disubstituted [184]. It is not known whether $RCuBF_3$, made from RCu and BF_3, is an organocopper or an organoboron reagent, $RBF_3^-\ Cu^+$.

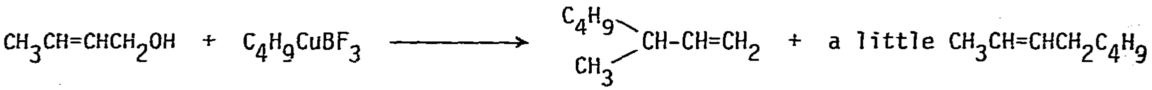




$$n\text{-}C_4H_9CuBF_3 + (CH_3)_2C=CHCO_2Et \longrightarrow n\text{-}C_4H_9-\underset{CH_3}{\overset{CH_3}{C}}-CHCO_2Et \quad (52\%)$$

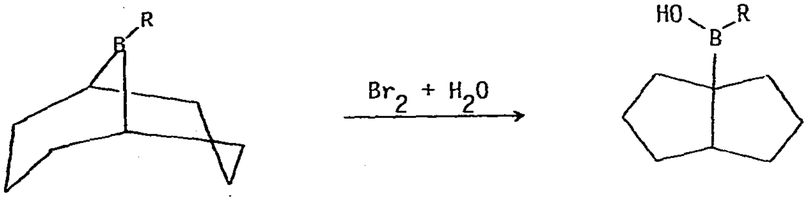
Dialkenylmethylboranes rearrange to dienes on treatment with methylcopper [185]. Allylic alcohols react with $R\text{-}CuBF_3$, the structure of which is uncertain and may be the borane $R\text{-}BF_3Cu$, to form alkenes with allylic rearrangement as the predominant path [186].



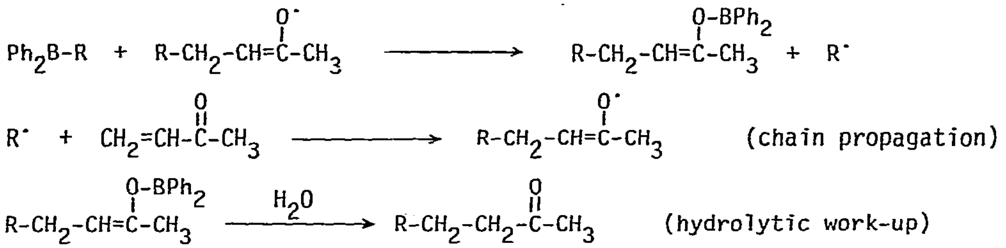


$$CH_3CH=CHCH_2OH + C_4H_9CuBF_3 \longrightarrow \begin{matrix} C_4H_9 \\ CH_3 \end{matrix}\!\!>CH-CH=CH_2 + \text{a little } CH_3CH=CHCH_2C_4H_9$$

B-Alkyl-9-BBN reacts with bromine and water in the dark, with initial loss of a bridgehead hydrogen followed by rearrangement [187].



2. Other Alkylation Reactions. Diphenylborane, Ph_2BH, has been generated by the reaction of Ph_2BOCH_3 with $LiAlH_4$ or treatment of the Ph_2BH-pyridine complex with BF_3 etherate and used to hydroborate olefins. The resulting alkyldiphenylboranes, Ph_2B-R, are particularly useful in the radical catalyzed alkylation of α,β-unsaturated carbonyl compounds such as methyl vinyl ketone, since only the alkyl group is transferred by the radical mechanism [188].



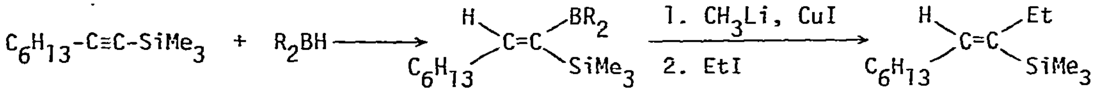
$$Ph_2B\text{-}R + R\text{-}CH_2\text{-}CH{=}\overset{O^{\bullet}}{\overset{|}{C}}\text{-}CH_3 \longrightarrow R\text{-}CH_2\text{-}CH{=}\overset{O\text{-}BPh_2}{\overset{|}{C}}\text{-}CH_3 + R^{\bullet}$$

$$R^{\bullet} + CH_2{=}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \longrightarrow R\text{-}CH_2\text{-}CH{=}\overset{O^{\bullet}}{\overset{|}{C}}\text{-}CH_3 \qquad \text{(chain propagation)}$$

$$R\text{-}CH_2\text{-}CH{=}\overset{O\text{-}BPh_2}{\overset{|}{C}}\text{-}CH_3 \xrightarrow{H_2O} R\text{-}CH_2\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \qquad \text{(hydrolytic work-up)}$$

B-Methylation of $PhCH{=}C(BO_2C_3H_6)_2$ with MeLi followed by oxidation with sodium perborate gives good yields of $PhCH_2COCH_3$, the product of methyl migration from boron to carbon. Examination of the reaction intermediates indicated that the methyl migration is not brought about by water or acid and does not occur until during the oxidation step. Some caution in assigning the structures of organoborane intermediates solely on the basis of their oxidation products, especially when there are reactive neighboring groups present, is advisable on the basis of these results [189].

Hydroboration-alkylation of alkynylsilanes has been reported [190].

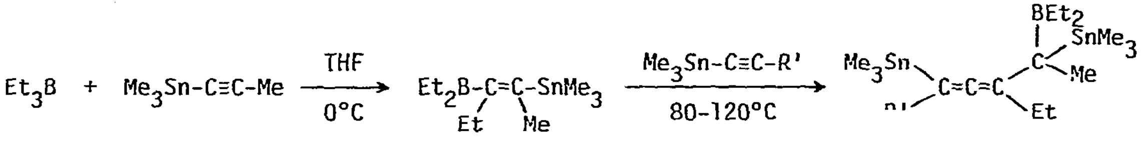


Mikhailov and coworkers have published a convenient procedure for synthesizing homoallylic alcohols $RR'CHOHCH_2CH{=}CH_2$ from allylboranes and carbonyl compounds $RR'C{=}O$ (R, R' = H, alkyl, aryl) [191]. The allylation reaction is accompanied by allylic rearrangement, and $-CH_2CH{=}CHCH_3$ or $-CH_2CH{=}C(CH_3)_2$ rearranges to

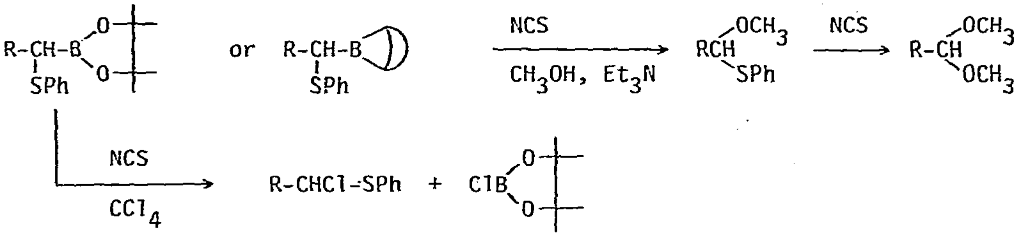
$-CH(CH_3)CH=CH_2$ or $-C(CH_3)_2CH=CH_2$, respectively. Reactive but stable allyldialkylboranes, $R_2B-CH_2CH=CH_2$, have been prepared by allylation of R_2B-OR' and related compounds with allylaluminum, boron, or magnesium compounds [192,193]. The crotyl and dimethylallyl analogues have been similarly prepared. Allylic rearrangement, scrambling the position of attachment of boron, occurs rapidly in these compounds. Reaction of $Et_2BCH_2CH=CH_2$ with EtCHO yields $Et_2B-O-CH(Et)-CH_2CH=CH_2$, and other allylations with allylic boranes have also been reported [194]. Triallylborane adds R_2B and allyl across the double bond of 1,3,3-trimethylcyclopropene [195].

The ate complexes $R_3\bar{B}-C{\equiv}C-OEt$ react with R_3B to replace the ethoxy group and form $R_3\bar{B}-C{\equiv}C-R$ and R_2B-OEt [196]. Treatment of the product with iodine yielded $R-C{\equiv}C-R$.

Wrackmeyer and Zentgraf have reported addition of trialkylboranes to alkynylstannanes [197]. Trialkylboranes add to $R_2Sn(C{\equiv}CCH_3)_2$ to form boroalkylated tin heterocycles and tin-boron heterocycles [198]. This and related chemistry is considered to be outside the scope of organoborane chemistry in organic synthesis and the interested reader is referred to the Boron II survey.



3. Oxidation. N-Chlorosuccinimide deboronates α-(phenylthio)alkylboranes or boronic esters to form monothioacetals or acetals in mildly basic methanol, or α-(phenylthio)alkyl chlorides under free radical conditions [199,200].

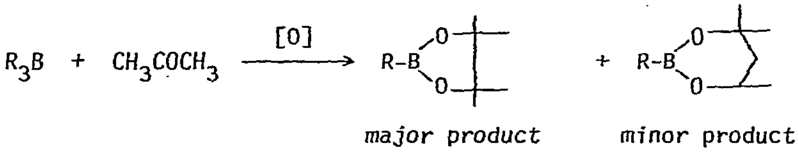


Oxidation of R_3B with $Pb(OAc)_4$ or $PhI(OAc)_2$ yields R-OAc [201]. $PhI(OAc)_2$ reacts only with primary alkylboranes, but $Pb(OAc)_4$ preferentially attacks secondary alkylboranes. Reaction of 1-bromo-1-alkenyldialkylboranes with $Pb(OAc)_4$ or $PhI(OAc)_2$ yields 1-bromo-1,2-dialkylethylenes, with production of E or Z isomer dependent on reaction conditions [202].

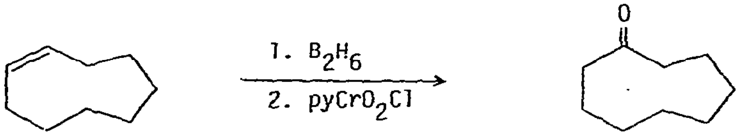
Oxidation of R_3B with the peroxomolybdenum complex $MoO_5{\cdot}OP(NMe_2)_3$ followed by hydrolysis yields ROH [203].

Electrolytic oxidation of R_3B in the presence of $CH_2=CR'-CO_2Et$ (R' = H or CH_3) in acetonitrile has given good yields of $RCH_2CHR'-CO_2Et$ [204].

Electrolytic oxidation of R_3B in acetone yields boronic esters [205]. Electrolysis of R_3B in the presence of PhC≡CH or BuC≡CH has yielded PhC≡C-R or BuC≡C-R [206].

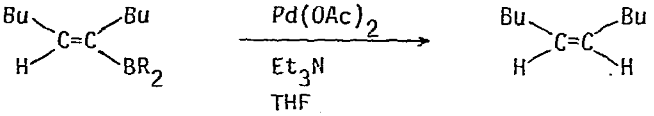


Oxidation of organoboranes derived from C_6-C_{12} cycloalkenes with pyridinium chlorochromate gives high yields of the corresponding cycloalkanones [207].

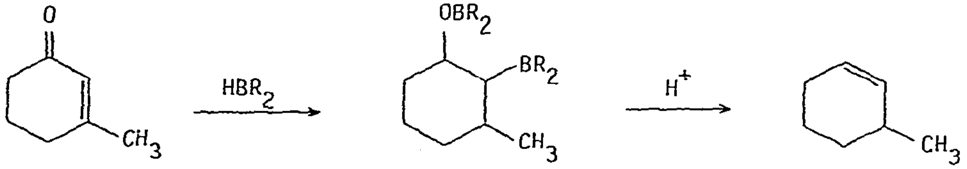


Hydroboration-oxidation has been used in a preparation of bicyclo[2.2.1]-heptane-2,5-dione from bicycloheptadiene, but addition of formic acid to this reactive olefin proved to be a more efficient route [208].

Alkenyldialkylboranes from internal alkynes are easily protodeboronated stereospecifically by treatment with catalytic amounts of palladium acetate [209].



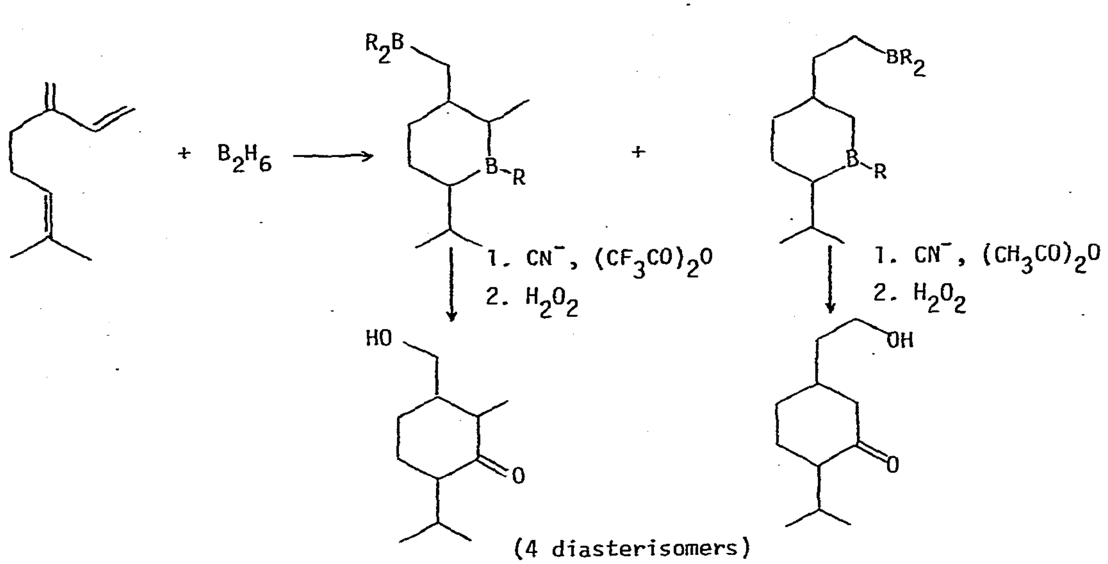
Hydroboration-protolysis of cyclohexenones leads to cyclohexenes [210].



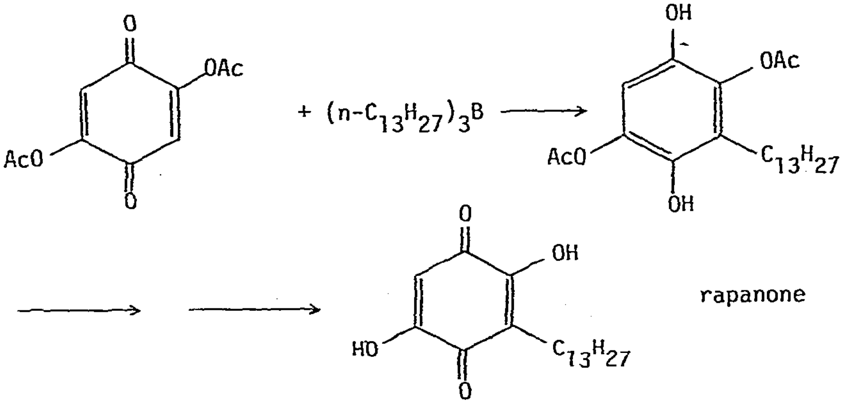
D. *Natural Products*

Monohydroboration of limonene with disiamylborane, which attacks the isopropenyl group selectively, has been used as an initial step in the synthesis of two insect defensive terpenoids, chrysomelidial and plagiolactone [211].

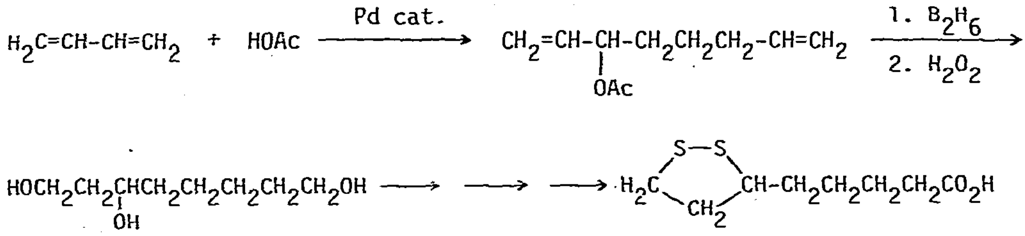
Hydroboration of myrcene with thexylborane and with diborane has been examined and found to yield mixtures of boranes. Treatment with cyanide and trifluoroacetic anhydride led to cyclic ketones [212].



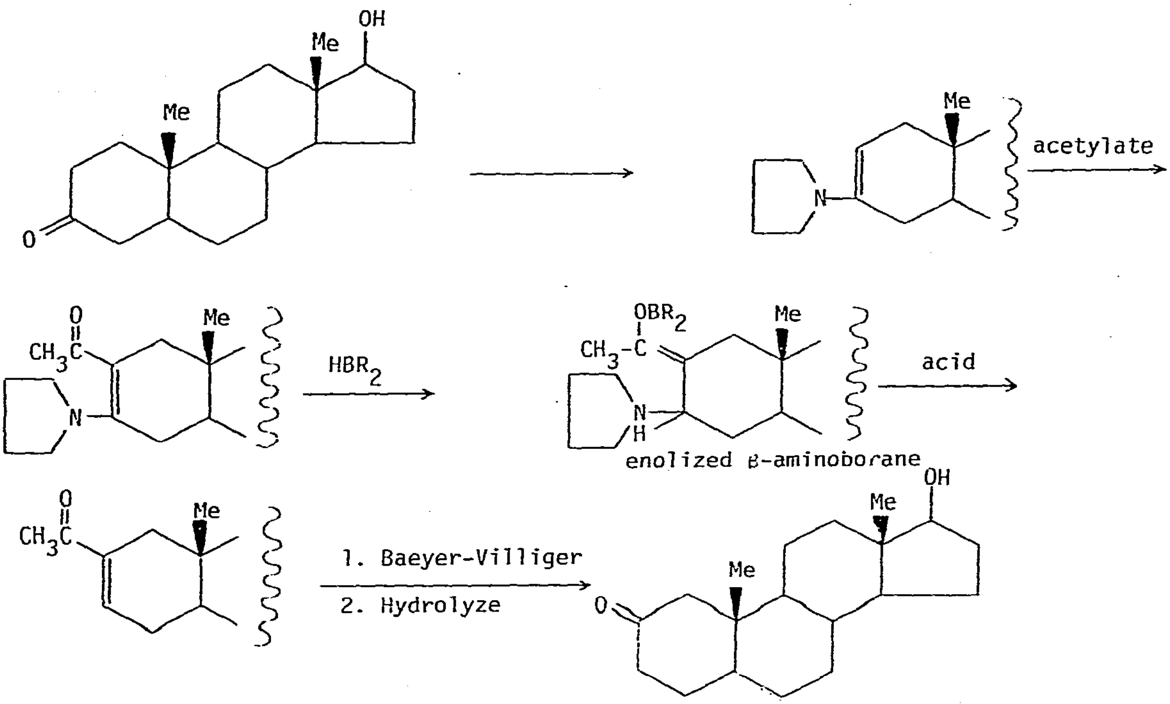
Alkylation of 2,5-dihydroxyquinone with trialkylboranes yields mainly dialkylation and cleavage products, but alkylation of 2,5-diacetoxy-1,4-benzoquinone provides a useful route to monoalkylated derivatives, some of which are natural products and antihelmintics [213].



Hydroboration-oxidation has been used in a synthesis of lipoic acid [214].



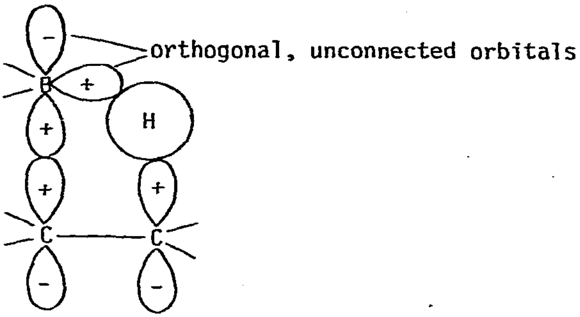
Hydroboration-elimination has been used in a sequence which results in isomerization of a ketone function to an adjacent position [215]. Carbon-boron bond formation is not necessarily involved, but the synthetic equivalent of a β-aminoborane is formed and boron and nitrogen are eliminated. Hydroboration



of 5α-ergost-8-en-3β-ol, thermal rearrangement, and oxidation has yielded 5α,9β-ergostane-3β,7β-diol [216]. Hydroboration, rearrangement, and oxidation of some octahydronaphthalenes has also been studied [217]. Hydroboration-oxidation of $\Delta^{8(14)}$-steroids in 14β-hydroxy steroids has been patented [218]

E. Theoretical Studies

Dewar and McKee have reported MNDO calculations on the hydroboration of olefins by BH_3 [219]. According to the calculations, the rate-determining step is formation of a loose π-complex of BH_3 with the olefin, which rearranges almost without activation energy to form the product. With alkenes, steric effects govern the direction of addition. Hydroboration of $CH_2=CHCl$ is predicted to yield $CH_3CHClBH_2$ (in accord with experimental data on $CH_3CH=CClCH_3$), but $CH_2=CHF$ is predicted to yield $H_2BCH_2CH_2F$ as the initial adduct. It should be noted that hydroborations with BH_3 are not forbidden by orbital symmetry, as might seem to be implied by a simplistic application of the Woodward-Hoffmann rules, but are allowed because the boron atom contributes two bonding orbitals which make the reaction topologically equivalent to an acyclic process

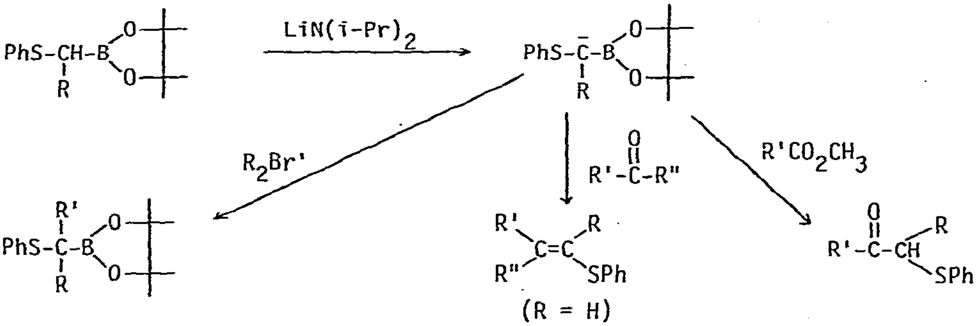


[220]. Borohydride reductions, on the other hand, are symmetry forbidden from having a cyclic transition state and proceed by stepwise acyclic mechanisms.

Clark and Schleyer have carried out ab initio molecular orbital calculations on the reaction of BH_3 with ethylene and found no overall activation barrier, and a very slight activation energy for rearrangement of the π-complex to ethylborane [221]. The transition state is a π-complex held together by a three-center two-electron bond. CNDO/2 calculations similarly suggest that the transition state for addition of borane to ethylene contains a C-B-C three-center bond [222].

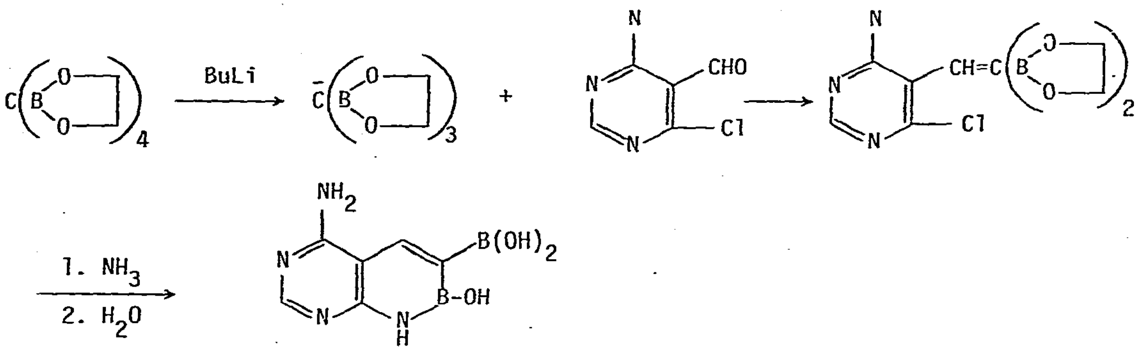
F. Boron Substituted Carbanions

The deprotonation of α-(phenylthio)alkaneboronic esters leads to carbanions which can undergo a variety of useful synthetic transformations [223]. The



efficient acylation by esters to produce α-(phenylthio)ketones after hydrolysis was postulated to involve an enol borate intermediate.

Tetrakis(ethylenedioxyboryl)methane has been utilized as a carbanion sourçe in the synthesis of a borazaroquinazoline [224].



Efficient conversions of $R_2C=O$ and $\bar{C}(BO_2C_3H_6)_3$ to $R_2C=C(BO_2C_3H_6)_2$ and then to $R_2C=C(HgCl)_2$ have been reported [225].

G. Reviews

Reviews by Brown and coworkers of cyclic hydroboration to produce boraheterocycles [226], 9-borabicyclononane [227], and dialkyl-9-borabicyclononane ate complexes [228] have appeared. Kabalka has reviewed the use of catecholborane in organic synthesis [229]. Eisch has reviewed rearrangements of unsaturated organoboron and aluminum compounds [230]. Organoboron and aluminum compounds have been reviewed in Japanese [231]. Alkylborane chemistry has been reviewed in Chinese [232]. Koester has reviewed organoborane chemistry [233]. The use of alkenyl-, alkynyl-, and cyano-borates as synthetic intermediates has been reviewed [234].

References

1. J. R. Pipal and R. N. Grimes, Inorg. Chem., 17 (1978) 6
2. J. R. Pipal and R. N. Grimes, Inorg. Chem., 17 (1978) 10
3. J. R. Pipal, W. M. Maxwell, and R. N. Grimes, Inorg. Chem., 17 (1978) 1447
4. C. G. Salentine and M. F. Hawthorne, Inorg. Chem., 17 (1978) 1498
5. K. P. Callahan, A. L. Sims, C. B. Knobler, F. Y. Lo, and M. F. Hawthorne, Inorg. Chem., 17 (1978) 1658
6. G. E. Hardy, K. P. Callahan, and M. F. Hawthorne, Inorg. Chem., 17 (1978) 1662
7. R. Weiss, J. R. Bowser, and R. N. Grimes, Inorg. Chem., 17 (1978) 1522
8. E. H. S. Wong and M. F. Hawthorne, Inorg. Chem., 17 (1978) 2863
9. R. T. Baker, R. E. King III, C. Knoebler, C. A. O'Con, and M. F. Hawthorne, J. Am. Chem. Soc., 100 (1978) 8266
10. L. I. Zakharkin, I. V. Pisareva, and T. B. Agakhanova, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 2389
11. L. I. Zakharkin and T. B. Agakhanova, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 2632

12. E. S. Chandrasekaran, D. A. Thompson, and R. W. Rudolph, Inorg. Chem., 17 (1978) 760
13. H. M. Colquhoun, T. J. Greenhough, and M. G. H. Wallbridge, J. Chem. Soc., Chem. Commun., (1978) 322
14. H. M. Colquhoun, T. J. Greenhough, and M. G. H. Wallbridge, J. Chem. Soc., Dalton Trans., (1978) 303
15. G. J. Zimmerman, R. Wilczynski, and L. G. Sneddon, J. Organometal. Chem., 154 (1978) C29
16. J. S. Plotkin and L. G. Sneddon, J. Chromatogr., 153 (1978) 289
17. J. A. Ulman, E. L. Andersen, and T. P. Fehlner, J. Am. Chem. Soc., 100 (1978) 456
18. H. Binder, E. Fluck, S. Hermanek, and J. Plesek, Z. Anorg. Allg. Chem., 433 (1977) 26
19. R. J. Pipal and R. N. Grimes, J. Am. Chem. Soc., 100 (1978) 3083
20. K.-S. King, J. R. Bowser, J. R. Pipal, and R. N. Grimes, J. Am. Chem. Soc., 100 (1978) 5045
21. T. P. Fehlner, J. Am. Chem. Soc., 100 (1978) 3250
22. K. Base, S. Hermanek, and B. Stibr, Chem. Ind. (London), (1977) 951
23. J. Duben, S. Hermanek, and B. Stibr, J. Chem. Soc., Chem. Commun., (1978) 287
24. P. Jutzi and A. Seufert, J. Organometal. Chem., 161 (1978) C5
25. M. P. Brown, A. K. Holliday, G. M. Way, R. B. Whittle, and C. M. Woodard, J. Chem. Soc., Dalton Trans., (1977) 1862
26. J. F. Ditter and E. B. Klusmann, U. S. Patent 4,065,509, Dec. 27, 1977, Chem. Abstr., 88 (1978) 121371x
27. J. A. Ulman and T. P. Fehlner, J. Am. Chem. Soc., 100 (1978) 449
28. A. F. Zhigach, A. B. Petrunin, D. B. Bekker, and A. V. Kisin, Zh. Obshch. Khim., 48 (1978) 588
29. S. P. Knyazev, V. A. Brattsev, and V. I. Stanko, Zh. Obshch. Khim., 47 (1977) 2627
30. W. F. Wright, J. C. Huffman, and L. J. Todd, J. Organometal. Chem., 148 (1978) 7
31. K. Base and B. Stibr, Chem. Ind. (London), (1977) 919
32. G. D. Friesen and L. J. Todd, J. Chem. Soc., Chem. Commun., (1978) 349
33. V. I. Stanko, Yu. V. Gol'tyapin, T. P. Klimova, N. I. Kirillova, and Yu. T. Struchkov, Zh. Obshch. Khim., 47 (1977) 2248
34. V. N. Kalinin, N. I. Kobel'kova, A. V. Astakhin, and A. I. Gusev, J. Organometal. Chem., 149 (1978) 9
35. V. I. Bregadze, V. Ts. Kampel, A. Ya. Usyatinskii, and N. N. Godovikov, J. Organometal. Chem., 154 (1978) C1
36. V. I. Bregadze, V. Ts. Kampel, A. Ya. Usyatinskii, and N. N. Godovikov, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1467

37. V. I. Bregadze, V. Ts. Kampel, and N. N. Godovikov, J. Organometal. Chem., 157 (1978) C1
38. V. I. Bregadze, V. Ts. Kampel, and N. N. Godovikov, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1951
39. L. I. Zakharkin and I. V. Pisareva, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1226
40. L. I. Zakharkin and I. V. Pisareva, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1950
41. L. I. Zakharkin and I. V. Pisareva, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 252
42. J. Plesek, Z. Janousek, and S. Hermanek, Collect. Czech. Chem. Commun., 43 (1978) 1332
43. J. Plesek and S. Hermanek, Collect. Czech. Chem. Commun., 43 (1978) 1325
44. A. V. Astakhin, V. N. Kalinin, V. V. Romanov, A. I. Gusev, N. I. Kobel'kova, and L. I. Zakharkin, Zh. Strukt. Khim., (1978) 555
45. R. C. Haushalter and R. W. Rudolph, J. Am. Chem. Soc., 100 (1978) 4628
46. L. I. Zakharkin and N. F. Shemyakin, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 2350
47. L. I. Zakharkin and N. F. Shemyakin, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1450
48. N. G. Bokii, A. I. Yanovskii, Yu. T. Struchkov, N. F. Shemyakin, and L. I. Zakharkin, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 380
49. A. V. Kazantsev, B. T. Ermaganbetov, and E. Sh. Sakpanov, Zh. Obshch. Khim., 48 (1978) 470
50. E. P. Ivakhnenko, V. B. Panov, E. P. Onokolova, and O. Yu. Okhlobystin, Zh. Obshch. Khim., 47 (1977) 2530
51. V. B. Panov, E. P. Ivakhnenko, and O. Yu. Oklobystin, Zh. Obshch. Khim., 47 (1977) 2624
52. V. I. Bregadze, A. Ya. Usyatinskii, and N. N. Godovikov, Dokl. Akad. Nauk SSSR, 241 (1978) 364
53. L. I. Zakharkin and I. S. Savel'ava, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 2622
54. L. I. Zakharkin and A. I. Kovredov, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1693
55. V. V. Korol'ko, V. P. Mileshkevich, A. V. Passet, N. B. Zaitsev, E. B. Dmokhovskaya, E. G. Kagan, A. B. Petrunin, A. F. Zhigach, and L. N. Karmanova, Zh. Obshch. Khim., 48 (1978) 1095
56. V. V. Korol'ko, V. I. Vecherskaya, V. P. Mileshkevich, and T. I. Saratovkina, Zh. Obshch. Khim., 48 (1978) 578
57. W. E. Hill and L. M. Silva-Trivino, Inorg. Chem., 17 (1978) 2495
58. L. I. Zakharkin, V. N. Kalinin, and V. A. Pankratov, Zh. Vses. Khim. O-va., 23 (1978) 227
59. G. Allender and H. D. Smith, Jr., Inorg. Chim. Acta, 26 (1978) L38

60. B. Longato, F. Morandini, and S. Bresadola, Inorg. Chim. Acta, 26 (1978) 157
61. A. V. Kazantsev, N. N. Ivanova, A. I. L'vov, and L. I. Zakharkin, Zh. Obshch. Khim., 48 (1978) 814
62. G. K. I. Magomdevo, L. V. Morozova, V. N. Kalinin, and L. I. Zakharkin, J. Organometal. Chem., 149 (1978) 23
63. A. N. Degtyarev, N. N. Godovikov, V. I. Bregadze, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1442
64. Yu. A. Ol'dekop, L. A. Churkina, T. D. Zvereva, I. A. Shingel, and T. V. Konysheva, Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk, (1977) 78
65. Yu. A. Ol'dekop, L. A. Churkina, T. D. Zvereva, and I. A. Shingel, Zh. Obshch. Khim., 48 (1978) 574
66. Yu. A. Ok'dekop, L. A. Churkina, T. D. Zvereva, and I. A. Shingel, Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk, (1978) 106
67. V. N. Kalinin, M. M. Teolyakov, Ts. L. Gelashvili, A. M. Savitskii, V. M. Dmitriev, and L. I. Zakharkin, Dokl. Akad. Nauk SSSR, 236 (1977) 367
68. O. V. Drigina, G. N. Dorofeenko, and O. Yu. Okhlobystin, Khim. Geterotsikl. Soedin., (1977) 1172
69. S. V. Vinogradova, V. A. Pankratov, A. G. Puchin, E. K. Lyamenkova, P. M. Valetskii, V. V. Korshak, and V. I. Stanko, U. S. S. R. Patent 377,020, Aug. 5, 1977, Chem. Abstr. 88 (1978) 7045u
70. T. J. Klingen and M. A. Mathur, J. Inorg. Nucl. Chem., 39 (1977) 1477
71. S. Bresadola, B. Longato, and F. Morandini, Inorg. Chim. Acta, 25 (1977) L135
72. N. I. Kirillova, M. Yu. Antipin, Yu. V. Gol'tyapin, Yu. T. Struchkov, and V. I. Stanko, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 859
73. M. Yu. Antipin, N. G. Furmanova, A. I. Yanovskii, and Yu. T. Struchkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1447
74. R. Freymann, A. Bullier, G. Capderroque, and M. Selim, Analusis, 4 (1976) 258
75. M. Selim, G. Capderroque, and R. Freymann, C. R. Acad. Sci. Paris, Ser. B, 281 (1975) 33
76. A. Bullier, G. Capderroque, R. Freymann, and M. Selim, C. R. Acad. Sci. Paris, Ser. C, 281 (1975) 963
77. B. Bartet, R. Freymann, D. Gandolfo, F. Mathey, G. Rabilloud, J. Rossarie, and B. Sillion, C. R. Acad. Sci., Paris, Ser. B, 279 (1974) 283
78. M. Selim, B. Bartet, R. Freymann, F. Mathey, G. Rabilloud, and B. Sillion, C. R. Acad. Sci., Paris, Ser. B, 279 (1974) 593
79. G. A. Olah, G. K. S. Prakash, G. Liang, K. L. Henold, and G. B. Haigh, Proc. Natl. Acad. Sci., U. S. A., 74 (1977) 5217
80. S. Hermanek, J. Plesek, V. Gregor, and B. Stibr, J. Chem. Soc., Chem. Commun., (1977) 561

81. V. I. Stanko, V. V. Khrapov, T. B. Klimova, T. A. Babushkina, and T. P. Klimova, Zh. Obshch. Khim., 48 (1978) 368
82. L. I. Zakharkin, R. Kh. Bikkineev, and V. A. Antonovich, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 2119
83. V. Ts. Kampel, K. P. Butin, V. I. Bregadze, and N. N. Godovikov, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1508
84. V. I. Stanko and T. V. Klimova, Zh. Obshch. Khim., 47 (1977) 2017
85. V. V. Korol'ko, V. I. Vecherskaya, V. P. Mileshkevich, and N. D. Il'ina, Zh. Obshch. Khim., 48 (1978) 596
86. V. N. Kalinin, N. I. Kobel'kova, A. V. Astakhin, and L. I. Zakharkin, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 2376
87. V. N. Kalinin, N. I. Kobel'kova, and L. I. Zakharkin, Zh. Obshch. Khim., 48 (1978) 938
88. V. V. Korol'ko, A. B. Petrunin, A. V. Kisin, V. P. Mileshkevich, and A. G. Zhigach, Zh. Obshch. Khim., 48 (1978) 538
89. J. Bicerano, D. S. Marynick, and W. N. Lipscomb, Inorg. Chem., 17 (1978) 2041
90. J. Bicerano, D. S. Marynick, and W. N. Lipscomb, Inorg. Chem., 17 (1978) 3443
91. R. N. Camp, D. S. Marynick, G. D. Graham, and W. N. Lipscomb, J. Am. Chem. Soc., 100 (1978) 6781
92. S. K. Lambiris, D. S. Marynick, and W. N. Lipscomb, Inorg. Chem., 17 (1978) 3706
93. T. A. Halgren, D. A. Kleier, J. H. Hall, Jr., L. D. Brown, and W. N. Lipscomb, J. Am. Chem. Soc., 100 (1978) 6595
94. D. A. Kleier, D. A. Dixon, and W. N. Lipscomb, Inorg. Chem., 17 (1978) 166
95. D. M. P. Mingos and M. I. Forsyth, J. Organometal. Chem., 146 (1978) C37
96. D. A. Brown, M. O. Fanning, and N. J. Fitzpatrick, Inorg. Chem., 17 (1978) 1620
97. D. R. Salahub, J. Chem. Soc., Chem. Commun., (1978) 385
98. D. M. P. Mingos, J. Chem. Soc., Dalton Trans., (1977) 602
99. M. J. S. Dewar and M. L. McKee, Inorg. Chem., 17 (1978) 1569
100. I. M. Pepperberg, D. A. Dixon, W. N. Lipscomb, and T. A. Halgren, Inorg. Chem., 17 (1978) 587
101. J. Aihara, J. Am. Chem. Soc., 100 (1978) 3339
102. E. K. Nishimura, J. Chem. Soc., Chem. Commun., (1978) 858
103. J. Bicerano, D. S. Marynick, and W. N. Lipscomb, J. Am. Chem. Soc., 100 (1978) 732
104. G. Medford and S. G. Shore, J. Am. Chem. Soc., 100 (1978) 3953
105 S. J. Hildebrandt, D. F. Gaines, and J. C. Calabrese, Inorg. Chem., 17 (1978) 790
106. D. F. Gaines and S. J. Hildebrandt, Inorg. Chem., 17 (1978) 794
107. J. R. Bowser and R. N. Grimes, J. Am. Chem. Soc., 100 (1978) 4623
108. K. E. Inkrott and S. G. Shore, J. Chem. Soc., Chem. Commun., (1978) 866

109. R. W. Marks, S. S. Wreford, and D. D. Traficante, Inorg. Chem., 17 (1978) 756

110. N. N. Greenwood, J. D. Kennedy, C. G. Savory, J. Staves, and K. R. Trigwell, J. Chem. Soc., Dalton Trans., (1978) 237

111. E. L. Andersen and T. P. Fehlner, J. Am. Chem. Soc., 100 (1978) 4607

112. J. L. Little and S. S. Pao, Inorg. Chem., 17 (1978) 584

113. R. N. Leyden, B. P. Sullivan, R. T. Baker, and M. F. Hawthorne, J. Am. Chem. Soc., 100 (1978) 3758

114. R. E. Loffredo and A. D. Norman, Inorg. Nucl. Chem. Lett., 13 (1977) 599

115. T. J. Dupont, R. E. Loffredo, R. C. Haltiwanger, C. A. Turner, and A. D. Norman, Inorg. Chem., 17 (1978) 2062

116. D. F. Gaines and J. L. Walsh, Inorg. Chem., 17 (1978) 1238

117. D. F. Gaines, J. L. Walsh, and J. C. Calabrese, Inorg. Chem., 17 (1978) 1242

118. D. F. Gaines, J. L. Walsh, J. H. Morris, and D. F. Hillenbrand, Inorg. Chem., 17 (1978) 1516

119. G. B. Dunks and K. P. Ordonez, J. Am. Chem. Soc., 100 (1978) 2555

120. G. B. Dunks and K. P. Ordonez, Inorg. Chem., 17 (1978) 1514

121. J. Cueilleron, G. Guillevic, H. Nongeot, and J. Dazord, French Patent 2,314,921, Jan. 14, 1977, Chem. Abstr., 88 (1978) 89085u

122. D. F. Gaines and J. L. Walsh, Inorg. Chem., 17 (1978) 806

123. R. Weiss and R. N. Grimes, J. Am. Chem. Soc., 100 (1978) 1401

124. S. Shatas, D. Gregory, R. Shatas, and C. Riley, Inorg. Chem., 17 (1978) 163

125. C. Riley, S. Shatas, and V. Arkle, J. Am. Chem. Soc., 100 (1978) 658

126. J.-S. Wang, A. J. DeStefano, and R. F. Porter, Inorg. Chem., 17 (1978) 1374

127. B. J. Meneghelli and R. W. Rudolph, J. Am. Chem. Soc., 100 (1978) 4626

128. R. M. Kabbani and E. H. Wong, J. Chem. Soc., Chem. Commun., (1978) 462

129. E. I. Tolpin, G. R. Wellum, and S. A. Berley, Inorg. Chem., 17 (1978) 2867

130. G. Nakagawa and T. Nagai, Chem. Pharm. Bull., 24 (1976) 2934

131. F. M. Waterman, F. T. Kuchnir, L. S. Skaggs, D. K. Bewly, B. C. Page, and F. H. Attix, Phys. Med. Biol., 23 (1978) 592

132. T. Saigusa and Y. Veno, Phys. Med. Biol., 23 (1978) 738

133. S. An, A. Furuhashi, M. Akiyama, Y. Oka, H. Kugi, et al., J. Fac. Eng., Unive. Tokyo, Ser-A., 15 (1977) 50; Chem. Abstr., 88 (1978) 166162w

134. Y. Hayakawa, S. Harasawa, A. Nakamoto, K. Amano, H. Hatanaka, and J. Egawa, Radiat. Res., 75 (1978) 243

135. J. A. Macko, Jr., J. G. Harvey, Jr., and C. R. Pope, U.S. NTIS, AD Rep., (1977) AD-A041846; Chem. Abstr., 88 (1978) 45803x

136. A. H. McCreesh, Aerosp. Med. Res. Lab., [Tech. Rep.] AMRL-TR (U.S.), (1977) Chem. Abstr., 89 (1978) 158278u

137. R. N. Grimes, Accounts Chem. Res., 11 (1978) 420

138. R. N. Grimes, Rev. Silicon, Germanium, Tin, Lead Cpd., 2 (1977) 223

139. R. N. Grimes in "Organometallic Reactions and Syntheses," E. I. Becker and M. Tsutsui, Eds., Plenum, Vol. 6, 1977

140. B. Stibr, K. Base, J. Plesek, S. Hermanek, J. Dolanski, and Z. Janousek, Pure Appl. Chem., 49 (1977) 803

141. Gmelin Institut, Gmelin Handbook of Inorganic Chemistry, Supplementary Work, Vol. 42 and 43: Boron Compounds, Parts 11 and 12: Carboranes 3 and 4. 8th Ed., (1977)

142. D. M. Cavagnaro, Report (1977), NTIS/PS-77/0825, 227 pp., from Gov. Rep. Announce Index (U.S.), 77 (1977) 91, Chem. Abstr., 89 (1978) 6345a

143. J. D. Odom, Organomet. Chem., 6 (1976) 37

144. T. Onak, Organomet. Chem., 6 (1976) 65

145. W. Stumpf, Themen Chem. Bors., (1976) 85

146. N. N. Greenwood, Pure Appl. Chem., 49 (1977) 791

147. H. C. Brown, J. R. Schwier, and B. Singaram, J. Org. Chem., 43 (1978) 4395

148. B. Singaram and J. R. Schwier, J. Organometal. Chem., 156 (1978) C1

149. A. K. Mandal and N. M. Yoon, J. Organometal. Chem., 156 (1978) 183

150. H. C. Brown and N. Ravindran, Synthesis (1977) 695

151. H. C. Brown, R. Liotta, and G. W. Kramer, J. Org. Chem., 43 (1978) 1058

152. J. C. S. Chen, J. Organometal. Chem., 156 (1978) 213

153. J. A. Soderquist and A. Hassner, J. Organometal. Chem., 156 (1978) C12

154. G. W. Kabalka, R. J. Newton, Jr., and J. Jacobus, J. Org. Chem., 43 (1978) 1567

155. C. A. Brown and S. Krishnamurthy, J. Organometal. Chem., 156 (1978) 111

156. C. A. Brown, J. Organometal. Chem., 156 (1978) C17

157. H. C. Brown, S. Krishnamurthy, and J. L. Hubbard, J. Am. Chem. Soc., 100 (1978) 3343

158. S. Krishnamurthy, J. Organometal. Chem., 156 (1978) 171

159. J. A. Gladysz, J. L. Hornby, and J. E. Garbe, J. Org. Chem., 43 (1978) 1204

160. J. A. Gladysz and W. Tam, J. Org. Chem., 43 (1978) 2279

161. J. L. Hubbard and G. W. Kramer, J. Organometal. Chem., 156 (1978) 81

162. E. Mincione, J. Org. Chem., 43 (1978) 1829

163. M. M. Midland and A. Tramontano, J. Org. Chem., 43 (1978) 1470

164. M. M. Midland, A. Tramontano, and S. A. Zderic, J. Organometal. Chem., 156 (1978) 203

165. M. V. Bhatt, J. Organometal. Chem., 156 (1978) 221

166. Y. Senda, S. Kamiyama, and S. Imaizumi, Tetrahedron, 33 (1977) 2933

167. R. Moreau, Y. Adam, and P. Loiseau, C. R. Hebd. Seances Acad. Sci., Ser. C, 287 (1978) 287

168. S. K. Gupta, J. Organometal. Chem., 156 (1978) 95

169. F. Sato, S. Haga, and M. Sato, Chem. Lett., (1978) 999

170. G. Zweifel, S. J. Backlund, and T. Leung, J. Am. Chem. Soc., 100 (1978) 5561

171. Y. Yamamoto and K. Maruyama, J. Am. Chem. Soc., 100 (1978) 6282

172. G. Zweifel and S. J. Backlund, J. Organometal. Chem., 156 (1978) 159

173. J. B. Campbell and G. A. Molander, J. Organometal. Chem., 156 (1978) 71
174. N. J. LaLima, Jr. and A. B. Levy, J. Org. Chem., 43 (1978) 1279
175. A. B. Levy, S. J. Schwartz, N. Wilson, and B. Christie, J. Organometal. Chem., 156 (1978) 123
176. M. M. Midland and D. C. McDowell, J. Organometal. Chem., 156 (1978) C5
177. K. Utimoto, K. Uchida, and H. Nozaki, Tetrahedron, 33 (1977) 1949
178. K. Utimoto, K. Uchida, M. Yamaya, and H. Nozaki, Tetrahedron, 33 (1977) 1945
179. A. B. Levy, J. Org. Chem., 43 (1978) 4684
180. A. J. Pelter, P. J. Maddocks, and K. Smith, J. Chem. Soc., Chem. Commun., (1978) 805
181. J. L. Hubbard and H. C. Brown, Synthesis, (1978) 676
182. K. Yamada, N. Miyaura, M. Itoh, and A. Suzuki, Synthesis (1977) 679
183. N. Miyaura, N. Sasaki, M. Itoh, and A. Suzuki, Tetrahedron Lett., (1977) 3369
184. Y. Yamamoto and K. Maruyama, J. Am. Chem. Soc., 100 (1978) 3240
185. Y. Yamamoto, H. Yatagai, K. Maruyama, A. Sonoda, and S. Murahashi, Bull. Chem. Soc. Jpn., 50 (1977) 3427
186. Y. Yamamoto and K. Maruyama, J. Organometal. Chem., 146 (1978) C9
187. H. C. Brown and N. R. De Lue, Tetrahedron Lett., (1977) 3007
188. P. Jacob III, J. Organometal. Chem., 156 (1978) 101
189. R. J. Moody and D. S. Matteson, J. Organometal. Chem., 152 (1978) 265
190. K. Uchida, K. Utimoto, and H. Nozaki, Tetrahedron, 33 (1977) 2987
191. B. M. Mikhailov, Yu. N. Bubnov, A. V. Tsyban, and M. Sh. Grigoryan, J. Organometal. Chem., 154 (1978) 131
192. B. M. Mikhailov, Yu. N. Bubnov, and A. V. Tsyban, J. Organometal. Chem., 154 (1978) 113
193. B. M. Mikhailov, Yu. N. Bubnov, A. V. Tsyban, and K. Base. Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1586
194. B. M. Mikhailov, Yu. N. Bubnov, and A. V. Tsyban, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1892
195. Yu. N. Bubnov, B. A. Kazanskii, O. A. Nesmeyanova, T. Yu. Rudashevskaya, and B. M. Mikhailov, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 2545
196. B. M. Mikhailov, M. E. Gurskii, V. G. Kiselev, and M. G. Gvertsiteli, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 2633
197. B. Wrackmeyer and R. Zentgraf, J. Chem. Soc., Chem. Commun., (1978) 402
198. L. Killian and B. Wrackmeyer, J. Organometal. Chem., 153 (1978) 153
199. A. Mendoza and D. S. Matteson, J. Organometal. Chem., 156 (1978) 149
200. A. Mendoza and D. S. Matteson, J. Chem. Soc., Chem. Commun., (1978) 357
201. Y. Masuda and A. Arase, Bull. Chem. Soc. Jpn., 51 (1978) 901
202. Y. Masuda, A. Arase, and A. Suzuki, Chem. Lett., (1978) 665
203. G. Schmitt and B. Olbertz, J. Organometal. Chem., 152 (1978) 271
204. Y. Takahashi, K. Yuasa, M. Tokuda, M. Itoh, and A. Suzuki, Bull. Chem. Soc. Jpn., 51 (1978) 339

205. Y. Takahashi, M. Tokuda, M. Itoh, and A. Suzuki, Chem. Lett., (1978) 669
206. Y. Takahashi, M. Tokuda, M. Itoh, and A. Suzuki, Chem. Lett., (1977) 999
207. V. V. Ramana Rao, D. Devaprabhakara, and S. Chandrasekaran, J. Organometal. Chem., 162 (1978) C9
208. R. T. Hawkins, R. S. Hsu, and S. G. Wood, J. Org. Chem., 43 (1978) 4648
209. H. Yatagai, Y. Yamamoto, and K. Maruyamam, J. Chem. Soc., Chem. Commun., (1978) 702
210. A. Uzarewicz, E. Segeit-Kujawa, and I. Uzarewicz, Rocz. Chem., 51 (1977) 1537
211. J. Meinwald and T. H. Jones, J. Am. Chem. Soc., 100 (1978) 1883
212. R. Murphy and R. H. Prager, J. Organometal. Chem., 156 (1978) 133
213. K. Maruyama, K. Saimoto, and Y. Yamamoto, J. Org. Chem., 43 (1978) 4895
214. J. Tsuji, H. Yasuda, and T. Mandai, J. Org. Chem., 43 (1978) 3606
215. M. Montury and J. Gore, Tetrahedron, 33 (1977) 2819
216. E. Mincione, Ann. Chim. (Rome), 67 (1977) 119
217. E. Mincione and A. Sirna, Ann. Chim. (Rome), 67 (1977) 105
218. G. Langbein, H. J. Siemann, E. Menzer, H. S. Seeger, and I. Gruner, East German Patent 128,564, Nov. 23, 1977, Chem. Abstr., 88 (1978) 191241d
219. M. J. S. Dewar and M. L. McKee, Inorg. Chem., 17 (1978) 1075
220. M. J. S. Dewar and M. L. McKee, J. Am. Chem. Soc., 100 (1978) 7499
221. T. Clark and P. v. R. Schleyer, J. Organometal. Chem., 156 (1978) 191
222. S. DasGupta, M. K. Datta, and R. Datta, Tetrahedron Lett., (1978) 1309
223. D. S. Matteson and K. Arne, J. Am. Chem. Soc., 100 (1978) 1325
224. D. S. Matteson, M. S. Biernbaum, R. A. Bechtold, J. D. Campbell, and R. J. Wilcsek, J. Org. Chem., 43 (1978) 950
225. A. Mendoza and D. S. Matteson, J. Organometal. Chem., 152 (1978) 1
226. H. C. Brown and E. Negishi, Tetrahedron, 33 (1977) 2331
227. H. C. Brown and C. F. Lane, Heterocycles, 7 (1977) 453
228. G. W. Kramer and H. C. Brown, Heterocycles, 7 (1977) 487
229. G. W. Kabalka, Org. Prep. Proced. Int., 9 (1977) 131
230. J. J. Eisch, Adv. Organomet. Chem., 16 (1977) 67
231. K. Utimoto, W. Nagata, and M. Yoshioka, Kagaku no Ryoiki, Zokan, 117 (1977) 75
232. H. Huang, Hua Hsueh Tung Pao, (1977) 220
233. R. Koester, Pure Appl. Chem., 49 (1977) 765
234. G. M. L. Cragg and K. R. Koch, Chem. Soc. Rev., 6 (1977) 393