BORON I. CARBORANES AND HYDROBORATION
ANNUAL SURVEY COVERING THE YEAR 1976

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CONTENTS

Boron I. Carboranes and Hydroboration: Annual Survey Covering the Year 1975, see J. Organomet. Chem., 119 (1976) 1-55.

I. CARBORANES

A. Introduction

The event of the year in boron chemistry was the award of the Nobel Prize in Chemistry to Professor William N. Lipscomb of Harvard University. Those who have followed Professor Lipscomb's work are, of course, well aware of its significance and intellectual breadth. It is hard to think of even a few other chemists in this generation who do an outstanding job of everything: quantum theory, X-ray crystallography, synthesis of new and unusual compounds, reaction mechanisms, and even biochemistry. Professor Lipscomb's contributions to our understanding of chemical bonding are unique. We extend our congratulations, and we look forward to seeing more boron chemistry from Professor Lipscomb's laboratories in the future.

The field of metallocarborane chemistry has continued to expand at a slower rate during the past year. Hawthorne's and Grimes' groups have made the greatest number of contributions. Work on the smaller carboranes has continued, but the number of papers is less than formerly. Icosahedral carborane chemistry is now almost entirely confined to Russia, with Zakharkin's group publishing the greatest number of papers.

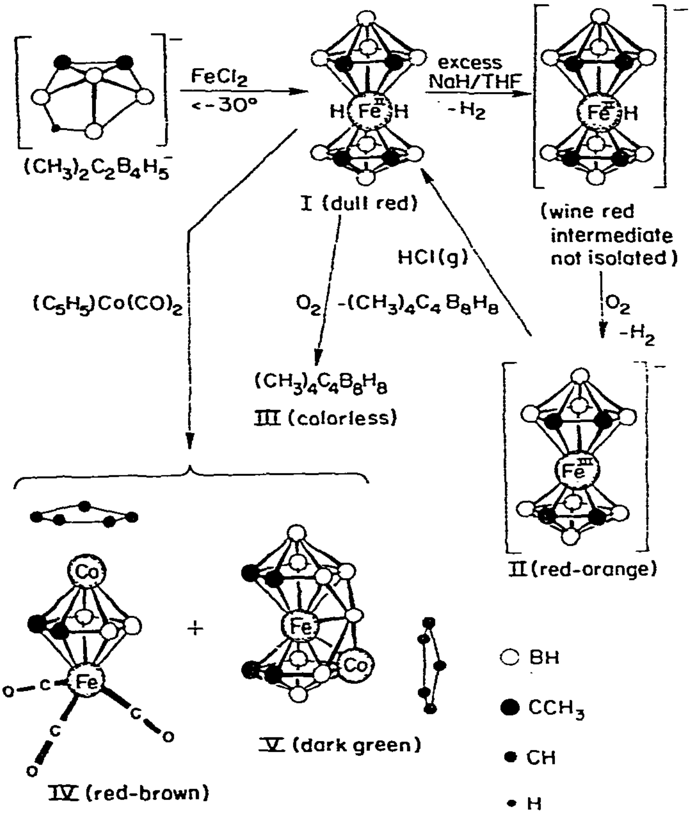
In accord with customs established in previous Surveys, this section will treat carboranes and metallocarboranes in detail, and boranes and metalloboranes which lack carbon-boron bonds but may be of interest to carborane chemists will be mentioned briefly at the end.

B. Metallocarboranes having Transition Metals in the Cage

1. Small and Medium Cages. The trend in this chemistry appears to be toward more metal atoms and a greater diversity of structural types. Odd and unpredicted structures crystallize out of reaction mixtures. Compounds having metal-hydrogen bonds are being found increasingly frequently, and attract attention because of their possible catalytic activity for hydrogenations or related reactions.

Grimes and coworkers have investigated the chemistry of $(Me_2C_2B_4H_4)_2FeH_2$ (I in Fig. 1), which was made from $Na^+ Me_2C_2B_4H_5^-$ and $FeCl_2$ [1]. Several other transformations of $(Me_2C_2B_4H_4)_2FeH_2$ are outlined in Fig. 1. Oxidation leads to the four-carbon carborane $Me_4C_4B_8H_8$, a colorless, sublimable crystalline solid, mp 138°C, which on the basis of ^{11}B NMR spectra is believed to have structure A (middle structure, Fig. 2), but which after a few minutes in solution establishes an equilibrium with isomer B (top structure, Fig. 2), with the B/A ratio being about 0.5 in several different solvents.

The reaction of $(2,3\text{-}Me_2C_2B_4H_4)_2FeH_2$ with $C_5H_5Co(CO)_2$ under ultraviolet irradiation has yielded a new type of carborane-metal cluster consisting of two polyhedra joined along one edge, $Me_4C_4B_8H_8FeCoC_5H_5$ (Fig. 3) [2]. The structure was proved by X-ray crystallography.



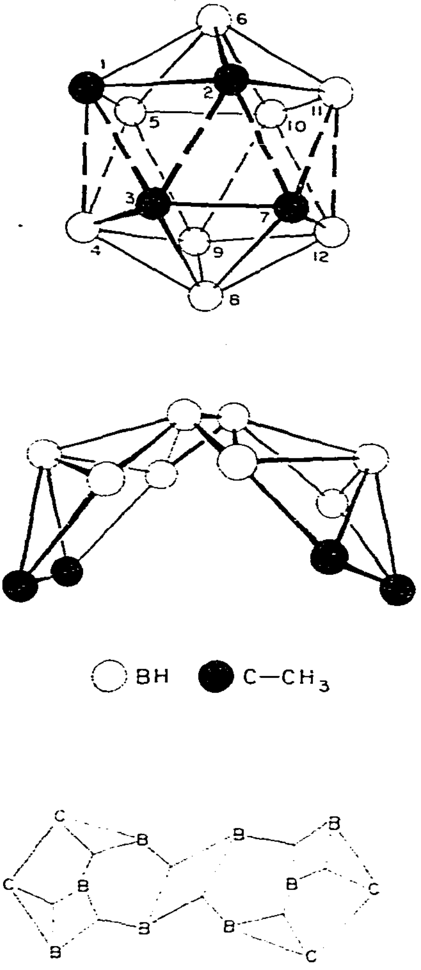


Figure 1. Reactions of $(Me_2C_2B_4H_4)_2FeH_2$ (I). [Reprinted with permission from W. M. Maxwell, V. R. Miller, and R. N. Grimes, Inorg. Chem., 15 (1976) 1343. Copyright by the American Chemical Society.]

Figure 2. Possible structures for $Me_4C_4B_8H_8$ isomers A (middle) and B (top), with one of several possible valence-bond diagrams for A shown at bottom. The terminal H and CH_3 groups are omitted. [Reprinted with permission from W. M. Maxwell, V. R. Miller, and R. N. Grimes, Inorg. Chem., 15 (1976) 1343. Copyright by the American Chemical Society.]

The reaction of Na^+ $Me_2C_2B_4H_5^-$ with $CoCl_2$ yields the sandwich compound (or small bisdicarbollycobalt analog) $(Me_2C_2B_4H_4)_2CoH$, which readily undergoes several types of deboronation, demetallation, or metal insertion reactions as

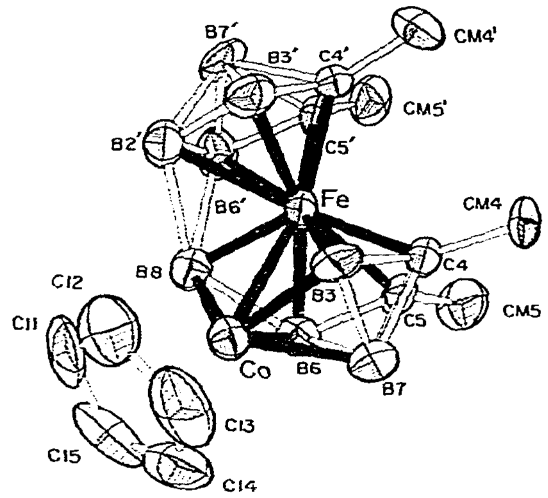


Figure 3. The structure of $Me_4C_4B_8H_8FeCoC_5H_5$, with hydrogen atoms omitted for clarity. [Reprinted with permission from W. M. Maxwell, E. Sinn, and R. N. Grimes, J. Am. Chem. Soc., 98 (1976) 3490. Copyright by the American Chemical Society.]

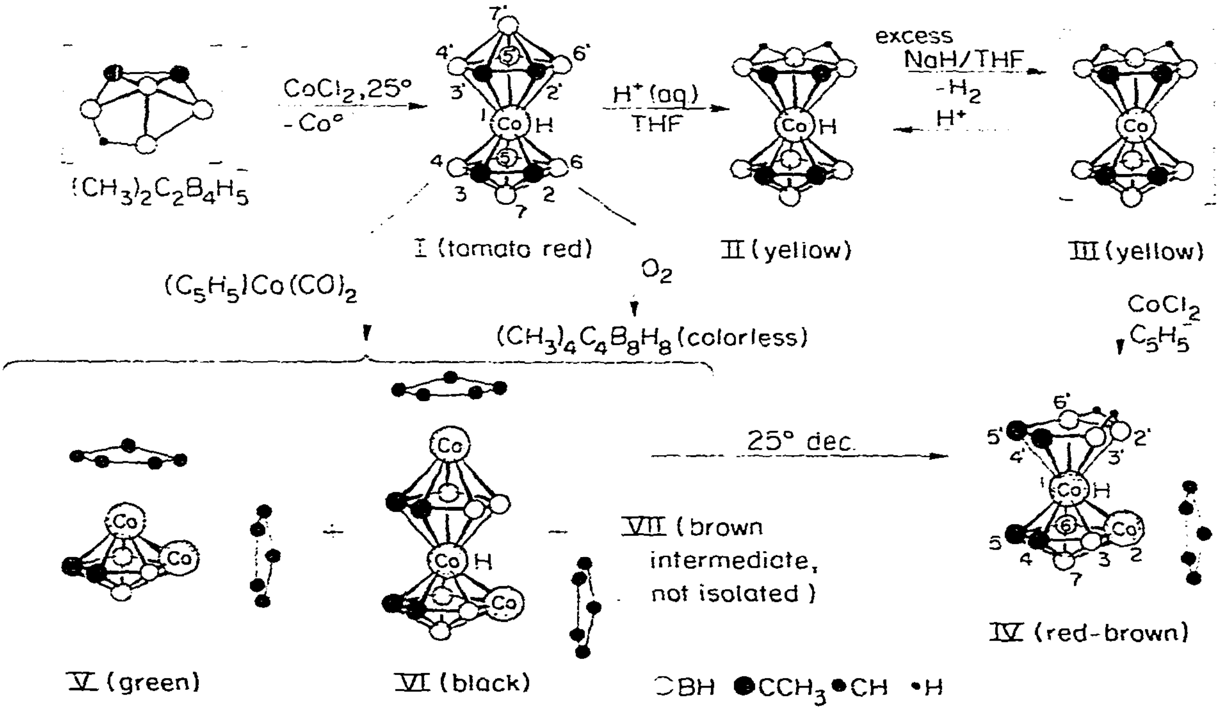
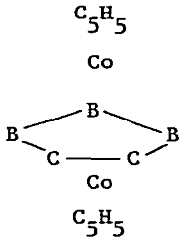


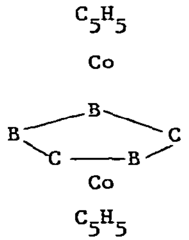
Figure 4. Preparation and reactions of $(Me_2C_2B_4H_4)_2CoH$ (I). [Reprinted with permission from W. M. Maxwell, V. R. Miller, and R. N. Grimes, J. Am. Chem. Soc., 98 (1976) 4818. Copyright by the American Chemical Society.]

summarized in Fig. 4 [3]. The four-carbon carborane $Me_4C_4B_8H_8$ listed in Fig. 4 without its structure is the same compound shown in Fig. 2.

Electronic effects in the triple-decked sandwich compounds 1,7,2,3- and 1,7,2,4-$(C_5H_5Co)_2C_2B_3H_5$ have been studied by ^{11}B and ^1H pulse Fourier transform NMR [4]. The central ring of the 1,7,2,4-complex shows a high degree of electron delocalization, and the other isomer shows more localized bonding character.



(H atoms omitted)



1,7,2,3-isomer (localized bonding)   1,7,2,4-isomer (delocalized bonding)

(For drawings with numbering, see JOM 75 (1974) 151, Fig. 26.)

The structures of 1,8-$(C_5H_5Co)_2$-5,6-$C_2B_5H_7$ (Fig. 5) and 1,7-$(C_5H_5Co)_2$-5,6-$C_2B_5H_7$ (Fig. 6) have been determined by X-ray diffraction [5]

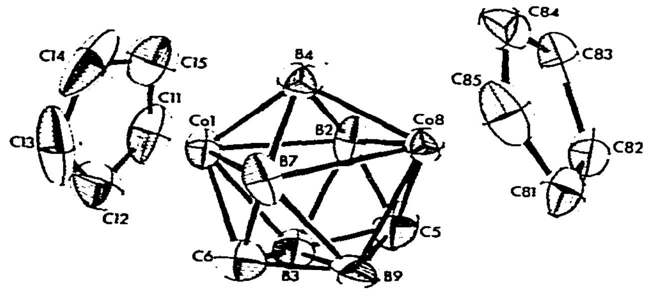


Figure 5. Structure of 1,8-$(C_5H_5Co)_2$-5,6-$C_2B_5H_7$ (H atoms omitted). [Reprinted with permission from R. N. Grimes, A. Zalkin, and W. T. Robinson, Inorg. Chem., 15 (1976) 2274. Copyright by the American Chemical Society.]

Carbon is a convenient accessory rather than a necessity for boron-metal cages. Most metalloboranes are discussed later in a separate section, but one group is too closely related to carboranes and too interesting to leave until then. Several cobalt-boron cluster compounds are formed in the reaction of $Na^+B_5H_8^-$ with $CoCl_2$ and NaC_5H_5 in THF and have been isolated by chromatography by Miller and Grimes [6]. These include $(C_5H_5)_3Co_3B_3H_5$, $(C_5H_5)_3Co_3B_4H_4$, and $(C_5H_5)_4Co_4B_4H_4$ (Fig. 7), all of which are air-stable crystalline solids.

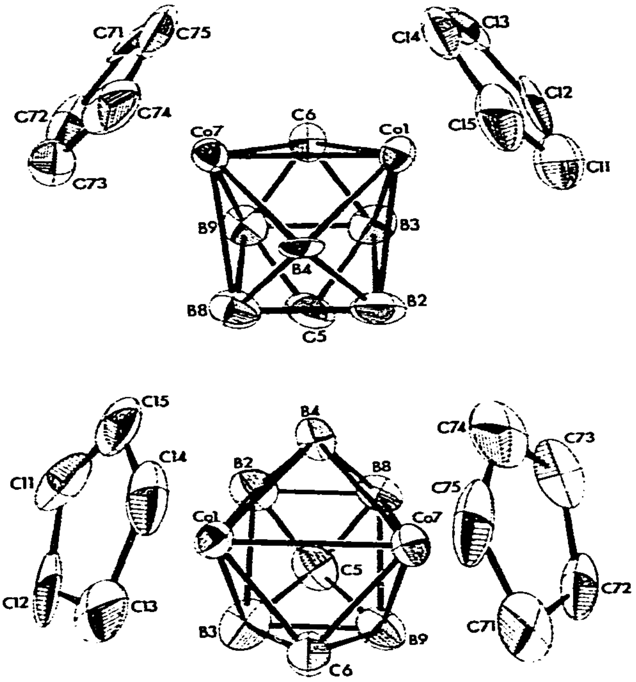


Figure 6. Two views of the structure of 1,7-$(C_5H_5Co)_2$-5,6-$C_2B_5H_7$ (H atoms omitted). [Reprinted with permission from R. N. Grimes, A. Zalkin, and W. T. Robinson, Inorg. Chem., 15 (1976) 2274. Copyright by the American Chemical Society.]

Salentine, Strouse, and Hawthorne have reported that reduction of $CB_9H_{10}^-$ in THF with sodium amalgam in the presence of cobaltacene yields the icosahedral dicobaltacarborane anion 2,11-$(C_5H_5Co)_2$-1-$CB_9H_{10}^-$ (Fig. 8) [7]. Analogous reduction of CB_5H_9 in the presence of nickelocene yielded a mixture of products, from which two nido isomers of $(C_5H_5Ni)_3CB_5H_6$ were isolated. One of the isomers was characterized by X-ray crystallography (Figs. 9 and 10) [7,8]. An unusual feature is the four-membered open face of the nido cage.

Stone and coworkers have found that reaction of $Ni(C_8H_8)(PEt_3)_2$ with 5,9-Me_2-5,9-$C_2B_7H_{11}$ results in evolution of H_2 and formation of 6,6-$(Et_3P)_2$-5,9-Me_2-6,5,9-$NiC_2B_7H_9$, the structure of which has been determined by X-ray diffraction [9]. (See JOM 98 (1975) 315, Fig. 32, for structure. The figure legend indicates 11 hydrogens, but should read 9.) The Me_3P analog and three $(R_3P)_2Pt$ analogs have also been prepared.

Welch has reported the structure of 2,7-Me_2-9,9-$(Me_3P)_2$-2,7,9-$C_2PtB_7H_7$ as determined by X-ray crystallography [10]. This compound is the same as that numbered as 10,2,8-$PtC_2B_7H_7$ in a preliminary report (JOM 98 (1975) 318), except

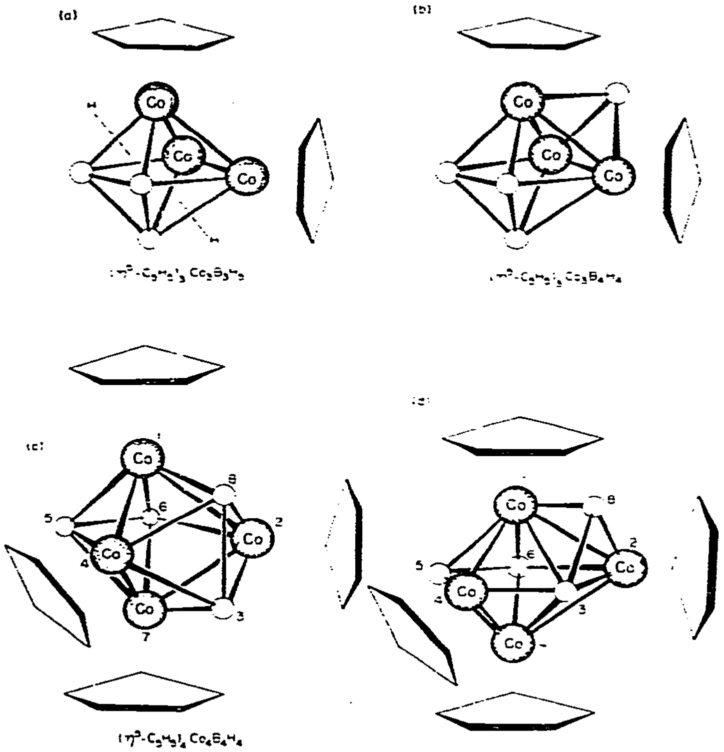


Figure 7. Proposed structures of $(C_5H_5)_3Co_3B_3H_5$ (a), $(C_5H_5)_3Co_3B_4H_4$ (b), and $(C_5H_5)_4Co_4B_4H_4$ (c or d). One cyclopentadienyl group is omitted for clarity in a and in b, and circles represent BH groups. [Reprinted with permission from V. R. Miller and R. N. Grimes, J. Am. Chem. Soc., 98 (1976) 1600. Copyright by the American Chemical Society.]

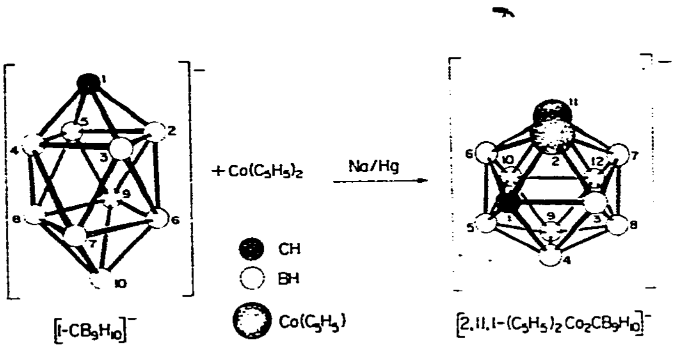


Figure 8. Conversion of $CB_8H_{10}^-$ to $2,11\text{-}(C_5H_5Co)_2CB_9H_{10}^-$. [Reprinted with permission from C. G. Salentine, C. E. Strouse, and M. F. Hawthorne, Inorg. Chem., 15 (1976) 1833. Copyright by the American Chemical Society.]

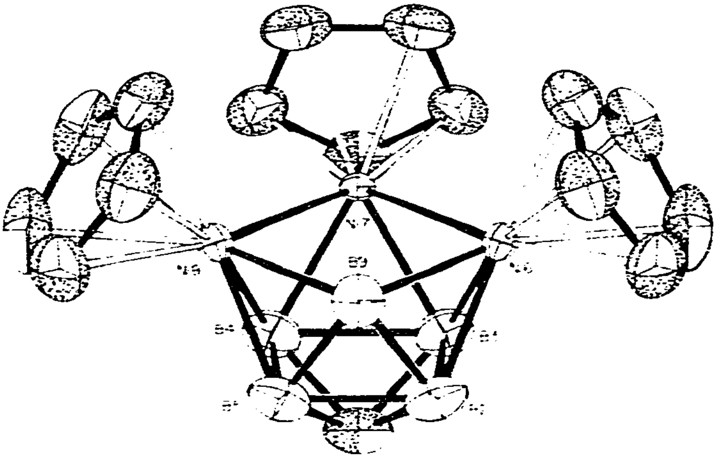


Figure 9. The structure of nido-$(C_5H_5Ni)_3CB_5H_6$ (H atoms omitted). [Reprinted with permission from C. G. Salentine, C. E. Strouse, and M. F. Hawthorne, J. Am. Chem. Soc., 98 (1976) 841. Copyright by the American Chemical Society.]

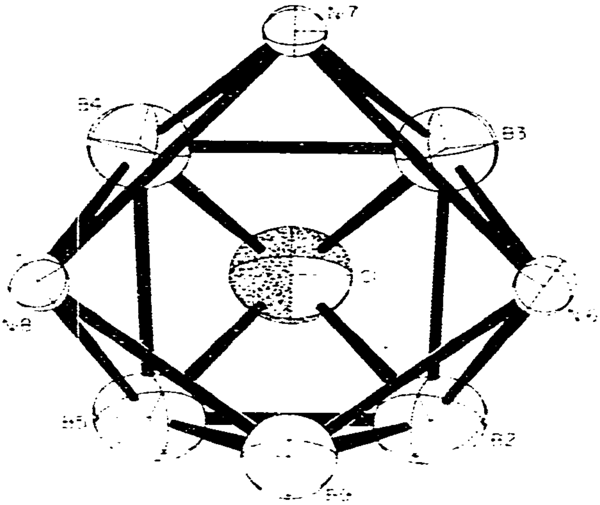
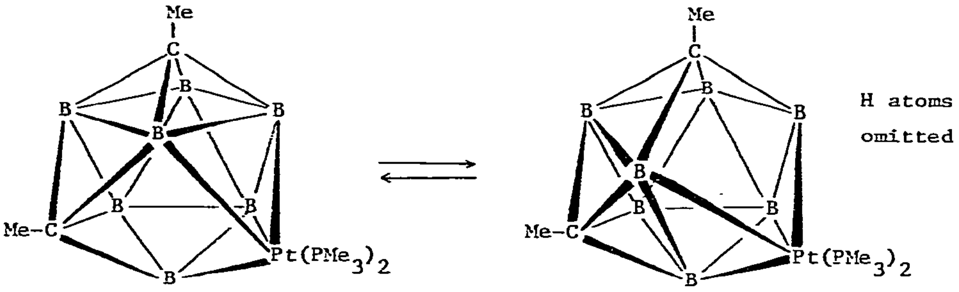


Figure 10. View of the nine-atom polyhedron of nido-$(C_5H_5Ni)_3CB_5H_6$ approximately normal to the nido face. [Reprinted with permission from C. G. Salentine, C. E. Strouse, and M. F. Hawthorne, J. Am. Chem. Soc., 98 (1976) 841. Copyright by the American Chemical Society.]

that it has Me_3P in place of Et_3P. The 2,8,10 numbering appears correct to the reviewer. This compound exhibits fluxional behavior, and since the figure illustrating that behavior somehow got lost from the previous Survey, we will type in the structures at this point in the hope of circumventing Murphy's Law.



The X-ray data show that the Pt–C distance is long and therefore nonbonding, and a 4-atom nido face results. Moving the front center B atom as illustrated shifts the position of the nido face.

Reaction of $NaC_2B_7H_{12}$ with $MCl(PAr_3)_3$, where M = Rh or Ir, has yielded $6,6-(Ar_3O)_2-6-H-6,2,3-MC_2B_7H_9$ (Fig. 11) [11]. Similar reaction of $RuHCl(PPh_3)_3$ gave $6,6-(PPh_3)_3-6,2,3-RuC_2B_7H_9$. From $IrCl(PPh_3)_3$ and $NaC_2B_8H_{11}$, $1,1-(Ph_3P)_2-1-H-1,2,4-IrC_2B_8H_{10}$ (Fig. 11) was obtained.

2. Icosahedral and Larger Cages. Salentine and Hawthorne have synthesized a series of metallocarborane anions of the general formulas $M(C_2B_{10}H_{12})_2^{2-}$ (M = Ti, V, Cr, Mn) and $M(Me_2C_2B_{10}H_{10})_2^{2-}$ (M = Ti, Zr, Hf, V), which have 13-atom cages, metals in the +2 oxidation state, and electron deficient structures lacking 1 to 4 electrons of a closed-shell configuration around the metal atom [12]. (See JOM 119 (1976) 15 for structure drawing.) The general synthesis begins with o-carborane (or its C,C'-dimethyl homolog), which is reduced with Na in THF to $Na_2C_2B_{10}H_{12}$ (or $Na_2Me_2C_2B_{10}H_{10}$) and reacted with MCl_x (x = 2,3 or 4) to form the complex. In spite of the lack of closed shell structure, these anions are stable and moderately to highly resistant to air oxidation. Magnetic susceptibility measurements show 1 unpaired electron in the Mn complex, 2 in the Cr, and 1 in the V anion. The Zr and Hf complexes undergo facile polyhedral rearrangement. Reaction of $(C_8H_8TiCl)_2$ with $Na_2C_2B_{10}H_{12}$ gave the Ti(III) anion, $C_8H_8TiC_2B_{10}H_{12}^-$ which on air oxidation yielded the neutral Ti(IV) complex, $C_8H_8TiC_2B_{10}H_{12}$ (Fig. 12) [12,13]. Thermal decomposition of this complex at 250°C yielded m-carborane. Reaction of $(C_8H_8TiCl)_2$ with 7,8- or $7,9-C_2B_9H_{11}^{2-}$ gave $C_8H_8TiC_2B_9H_{11}^-$, which oxidized readily to $C_8H_8TiC_2B_9H_{11}$ (Fig. 13). $C_5H_5TiC_2B_{10}H_{12}^-$ has also been reported [13].

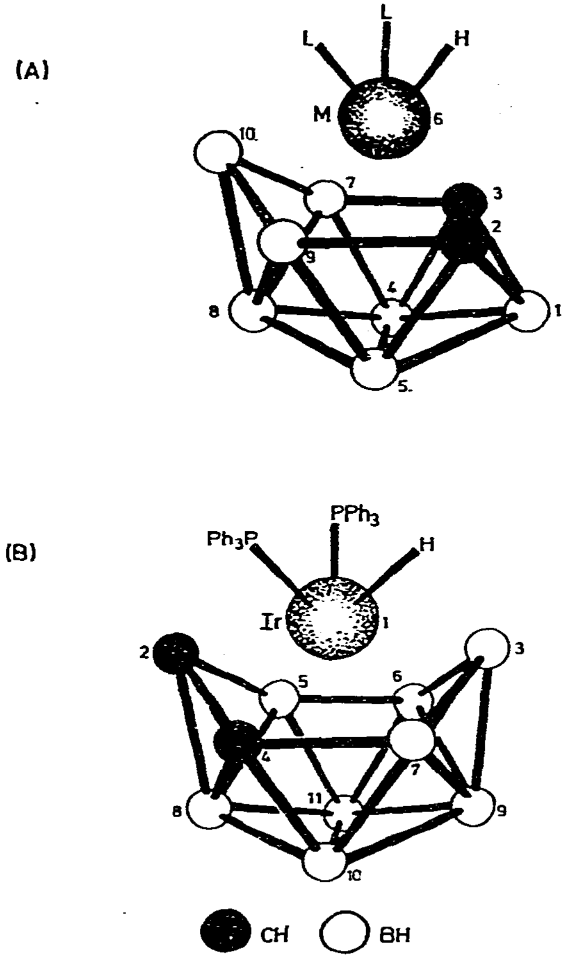


Figure 11. Proposed structures of (A) 6,6-$(Ar_3P)_2$-6-H-6,2,3-$MC_2B_7H_9$ (L = Ar_3P; Ar = C_6H_5 or p-$CH_3C_6H_4$) and (B) 1,1-$(Ph_3P)_2$-1-H-1,2,4-$IrCl_2B_8H_{10}$. [Reprinted with permission from C. W. Jung and M. F. Hawthorne, J. Chem. Soc., Chem. Commun., (1976) 499. Copyright by the Chemical Society.]

Maxwell, Sinn, and Grimes have found that reaction of $Me_4C_4B_8H_8$ (Fig. 2) with sodium naphthalenide, NaC_5H_5, and $FeCl_2$ produces at least four isomers of $(\eta^5\text{-}C_5H_5)_2Fe_2Me_4C_4B_8H_8$. Two of these have been characterized by X-ray crystallography and found to have 14-vertex polyhedra. However, these are not closo structures as predicted by electron counting rules, but one has a 5-membered open face and the other a 4-membered open face (Figs. 14 and 15) [14]. Both isomers undergo thermal rearrangements to other isomers of undetermined structure.

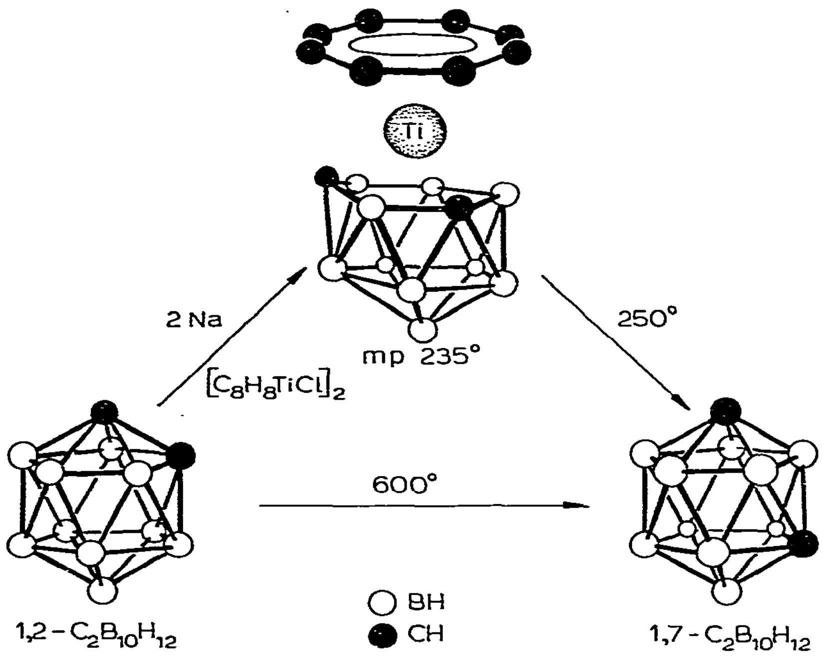


Figure 12. Conversion of o-carborane to $C_8H_8TiC_2B_{10}H_{12}$ and to m-carborane. [Reprinted with permission from C. G. Salentine and M. F. Hawthorne, Inorg. Chem., 15 (1976) 2872. Copyright by the American Chemical Society.]

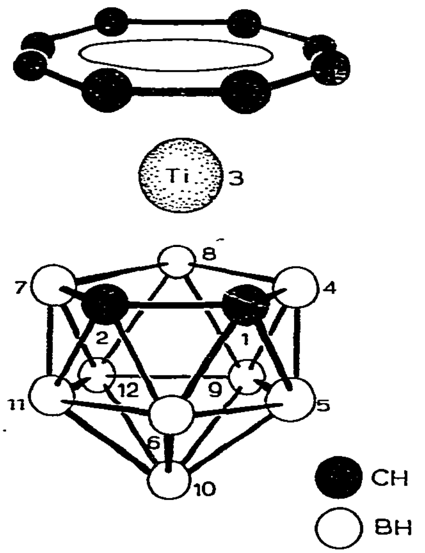
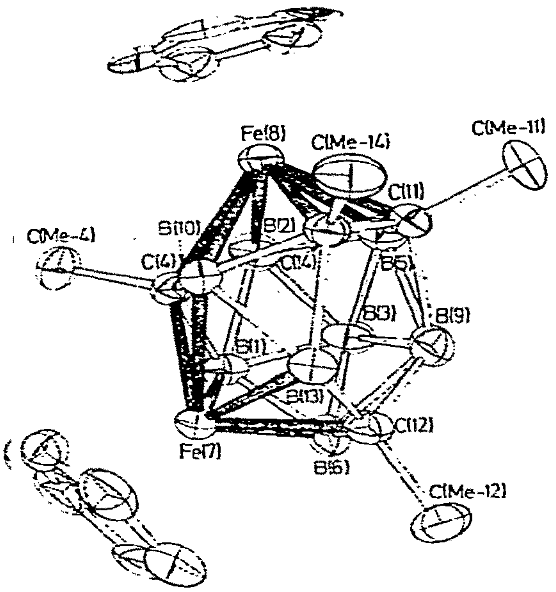


Figure 13. Proposed structure of 3-(C_8H_8Ti)-1,2-$C_2B_9H_{11}$. [Reprinted with permission from C. G. Salentine and M. F. Hawthorne, Inorg. Chem., 15 (1976) 2872. Copyright by the American Chemical Society.]



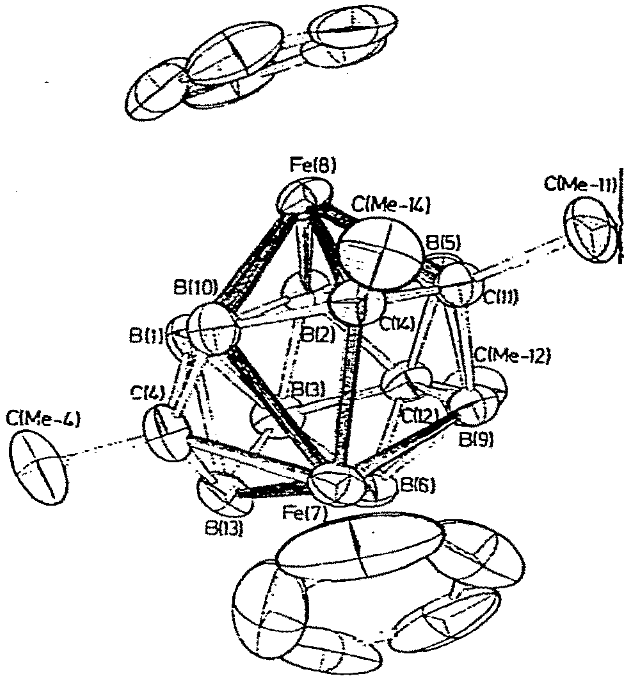


Figure 14. Structure of one of the isomers of $(C_5H_5)_2Fe_2Me_4C_4B_8H_8$. The carbons projecting out from the cage belong to CH_3 groups. Hydrogen atoms are omitted for clarity. [Reprinted with permission from W. M. Maxwell, E. Sinn, and R. N. Grimes, J. Chem. Soc., Chem. Commun., (1976) 389. Copyright by the Chemical Society.]

Figure 15. Structure of the second isomer of $(C_5H_5)_2Fe_2Me_4C_4B_8H_8$. [Reprinted with permission from W. M. Maxwell, E. Sinn, and R. N. Grimes, J. Chem. Soc., Chem. Commun., (1976) 389. Copyright by the Chemical Society.]

Wong and Hawthorne have reported the reaction of 7,8- and 7,9-$C_2B_9H_{12}$ with $(Ph_3P)_3$RuHCl to yield 3,1,2- and 2,1,7-$[(Ph_3P)_2RuH_2]C_2B_9H_{11}$, and have established the structure of the latter by X-ray crystallography (Fig. 16) [15]. The 3,1,2-isomer loses H_2 reversibly, the 2,1,7-isomer irreversibly, or heating, and both isomers are homogeneous catalysts hydrogenation of olefins.

Reaction of 7,8-$C_2B_9H_{11}{}^{2-}$ with $(Ph_3P)_2NiCl_2$ in THF yields icosahedral closo-3,3-$(Ph_3P)_2$-2,1,2-$NiC_2B_9H_{11}$, which on refluxing in benzene undergoes an unusual exchange of Ph_3P and H between nickel and boron, with formation of an Ni-H bond (Fig. 17) [16].

Hawthorne and Paxson have patented the catalytically active rhodacarboranes (see JOM 98 (1975) 316-317) and analogous iridium compounds [17].

Reaction of UCl_4 with 7,8-$C_2B_9H_{11}{}^{2-}$ in THF has yielded $Cl_2U(C_2B_9H_{11})_2{}^{2-}$,

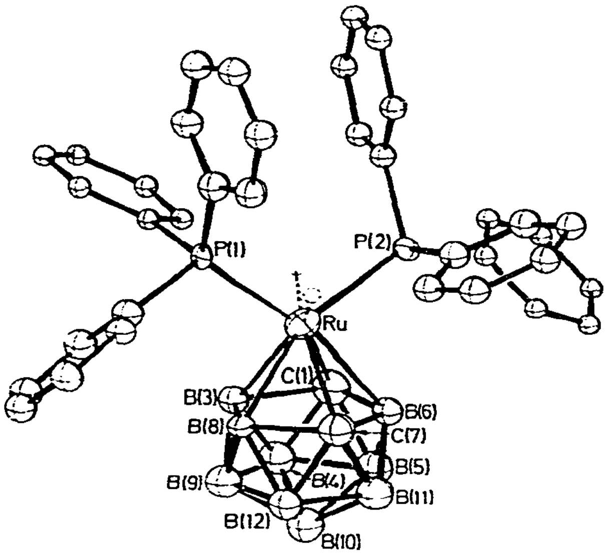
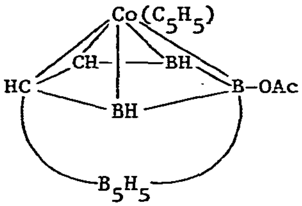


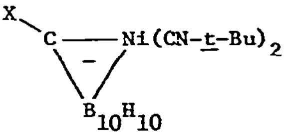
Figure 16. The structure of 2,1,7-[$(Ph_3P)_2RuH_2$]$C_2B_9H_{11}$. [Reprinted with permission from E. H. S. Wong and M. F. Hawthorne, J. Chem. Soc., Chem. Commun., (1976) 257. Copyright by the Chemical Society.]

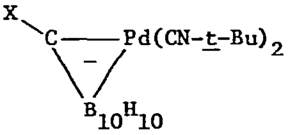
which has been isolated as the $Li(THF)_4^+$ salt and characterized by X-ray diffraction (Fig. 18) [18].

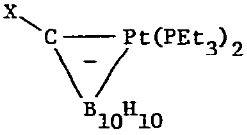
Friedel-Crafts acetylation of 3-(C_5H_5Co)-1,2-$C_2B_9H_{11}$ has yielded a series of substitution products 3-(C_5H_5Co)-1,2-$C_2B_9H_{10}$-9-X, where X = Cl, OAc, OH, and Ac, and the structure of the X = OAc compound was proved by X-ray diffraction [19].



Stone and coworkers have made a series of icosahedral metallocarboranes from $HCB_{10}H_{10}^-$ or Me_3N-$CB_{10}H_{10}$ and (t-Bu-NC)$_2$Ni(C_8H_8), (t-Bu-NC)$_2$Pd, or $(Et_3P)_2Pt(PhCH{=}CHPh)$ [20].







X = H or Me_3N^+

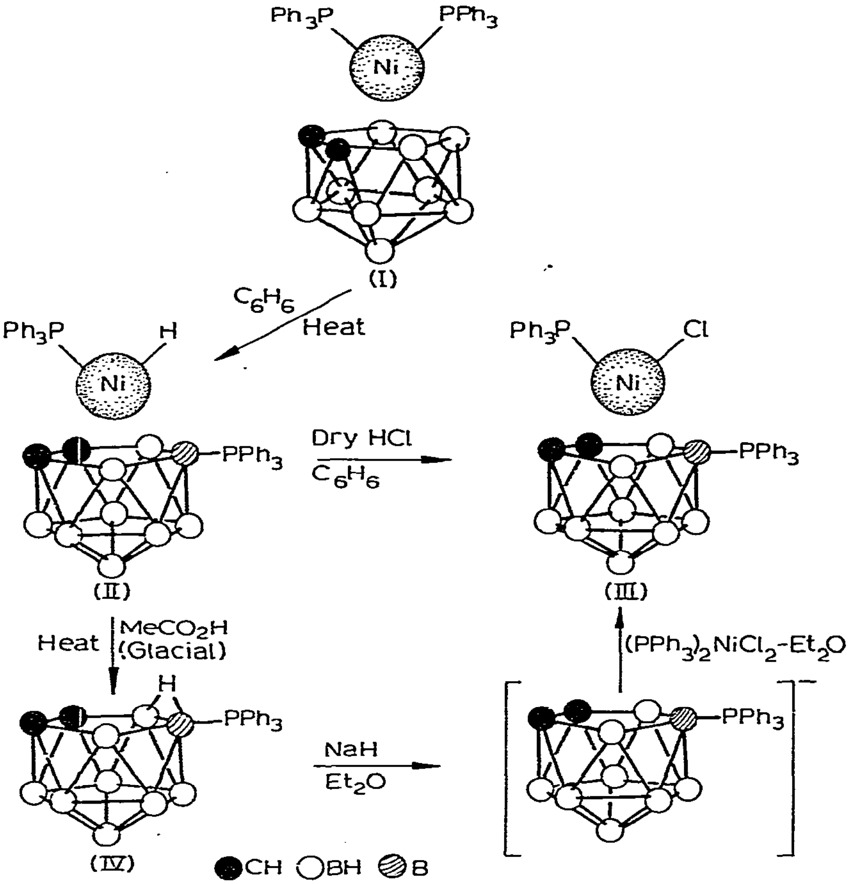


Figure 17. Reactions of 3,3-$(Ph_3P)_2$-3,1,2-$NiC_2B_9H_{11}$. [Reprinted with permission from S. B. Miller and M. F. Hawthorne, J. Chem. Soc., Chem. Commun., (1976) 786. Copyright by the Chemical Society.]

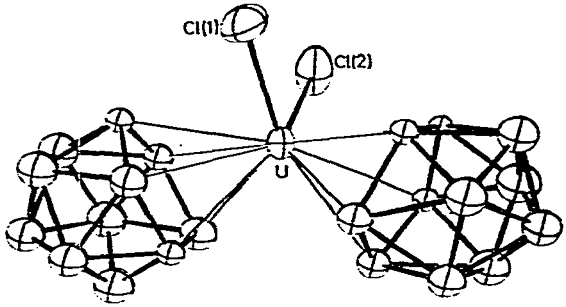


Figure 18. The structure of $Cl_2U(C_2B_9H_{11})_2^{2-}$. Thermalellipsoids are drawn at the 20% probability level, and H atoms are omitted. [Reprinted with permission from F. R. Fronczek, G. W. Halstead, and K. N. Raymond, J. Chem. Soc., Chem. Commun., (1976) 279. Copyright by the Chemical Society.]

The X-ray structure of (t-Bu-NC)$_2$Pd(B$_{10}$H$_{10}$)C-NMe$_3$ showed a distorted icosahedral cage having a relatively long Pd-C bond distance.

Zakharkin and coworkers have found that BuLi and PhLi attack 3,6-(C$_5$H$_5$)$_2$-3,6,1,2-Co$_2$C$_2$B$_8$H$_{10}$ at a cyclopentadienyl ring to yield derivatives having BuC$_5$H$_4$ or PhC$_5$H$_4$ in place of one C$_5$H$_5$ group [21]. Nitration of 1-Ph-3-C$_5$H$_5$-3,1,2-CoC$_2$B$_9$H$_{10}$ has yielded 16% of the p-nitrophenyl derivative and 9% of a B-nitrato-p-nitrophenyl derivative. Similarly, 3-(Ph-C$_5$H$_4$)-3,1,2-CoC$_2$B$_9$H$_{11}$ nitrates somewhat faster on the phenyl group than it undergoes -ONO$_2$ substitution on the boron cage. Nitration of 3-(C$_5$H$_5$)-3,1,2-CoC$_2$B$_9$H$_{11}$ gave 24% 3-(C$_5$H$_5$)-3,1,2-CoC$_2$B$_9$H$_{10}$ONO$_2$, which was reduced to the B-hydroxy derivative [22].

Reaction of Tl$_2$ (7,8-C$_2$B$_9$H$_{11}$) with Et$_2$NCS$_2$AuBr$_2$ yields the known (1,2-C$_2$B$_9$H$_{11}$)$_2$Au$^-$ and also a new 18-electron species (1,2-C$_2$B$_9$H$_{11}$)Au(S$_2$CNEt$_2$) which was shown by X-ray crystallography to have the "slipped" structure previously found only in 20- or 21-electron systems (Fig. 19) [23].

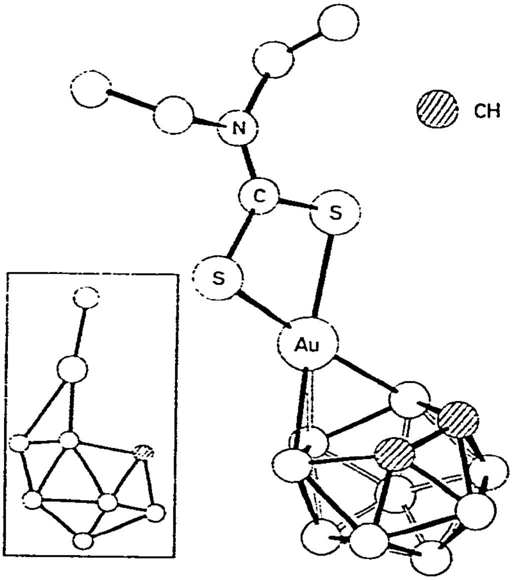


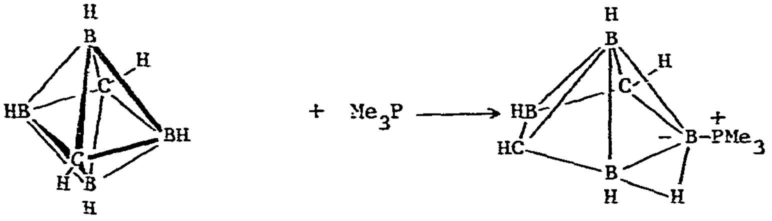
Figure 19. Molecular structure of 3-(Et$_2$NCS$_2$)-3,1,2-AuC$_2$B$_9$H$_{11}$. Hydrogen atoms are omitted for clarity. Inset shows a portion of the structure projected parallel to the cage C-C bond. [Reprinted with permission from H. M. Colquhoun, T. J. Greenhough, and M. G. H. Wallbridge, J. Chem. Soc., Chem. Commun., (1976) 1019. Copyright by the Chemical Society.]

The slipped cage structure of Ni(C$_2$B$_9$H$_{11}$)$_2^{2-}$ and related complexes having too many electrons for a closo icosahedral structure has been interpreted on the basis of the Jahn-Teller effect [24]. The visible-ultraviolet spectrum of Ni(C$_2$B$_9$H$_{11}$)$_2^{2-}$ has been interpreted [25].

C. Small and Medium Carboranes

Details of the microwave spectrum of CB_5H_7 have been published by Beaudet and coworkers [26]. These results provide additional confirmation of the unusual structure, which has a triply bridging hydrogen occupying one apex of a 7-atom cage, as described in the preceding two Annual Surveys [JOM, 98 (1975) 324; 119 (1976) 25].

Onak and coworkers have found that degradation of 1,5-$C_2B_3H_5$ with methanol yields $(MeO)_2BCH_2B(OCH_3)CH_2B(OCH_3)_2$ or with water yields $(HO)_2BCH_2B(OH)CH_2B(OH)_2$. 2,4-$C_2B_5H_7$ and 1,6-$C_2B_4H_6$ react more slowly, the former yielding $(MeO)_2BCH_2B(OMe)_2$, $CH_3B(OMe)_2$, and $B(OMe)_3$ with methanol, the latter $CH_3B(OMe)_2$ and $B(OMe)_3$ [27]. A study of the reactivity of the small carboranes 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$ with Me_3N and Me_3P has shown that the smallest cage is the most reactive, and the largest is not attacked. $C_2B_4H_6$ forms a stable nido adduct with Me_3P, as illustrated. Me_2NH cleaves all three carboranes to small fragments [28].



Chlorination of 1,5-$C_2B_3H_5$ in CF_2Cl_2 starting at -70° yielded 2-Cl-1,5-$C_2B_3H_4$ [29]. Reaction of 1,5-$C_2B_3H_5$ with BMe_3 in hot/cold reactor gave a mixture of mono, di, and trimethyl derivatives in $C_2B_3H_5$, and also 2,2'-$(C_2B_3H_4)_2$ and a series of methyl derivatives up to tetramethyl. Photolysis of 4-Cl-2,3-$C_2B_4H_7$ yields 2-Cl-1,6-$C_2B_4H_5$, which has also been obtained from photochlorination of 1,6-$C_2B_4H_6$ [30].

Methylation of 2,4-$C_2B_5H_7$ (see Fig. 20 for structure and numbering) with CH_3Cl in the presence of aluminum chloride has been found to proceed with relative rates 5,6>1,7>3 to give a series of methylated derivatives having 1 to 5 methyl groups [31]. The results are in accord with theoretical expectation for an electrophilic substitution mechanism.

Irradiation of 2,4-$C_2B_5H_7$ at 2537 Å results in H_2 elimination and B-B bond formation to yield 3,3'-(2,4-$C_2B_5H_6)_2$ (Fig. 21) [32]. Similar irradiation of B_5H_9 yields 2,2'-$(B_5H_8)_2$.

Reduction of 6-Me_3N-6-CB_9H_{11} (I in Fig. 22) with Na in liquid NH_3 followed by treatment with methanol has yielded a new carborane anion, $CB_9H_{12}^-$ (II in Fig. 22), which has been hydrolyzed with aqueous acid to form the monocarbon arachno

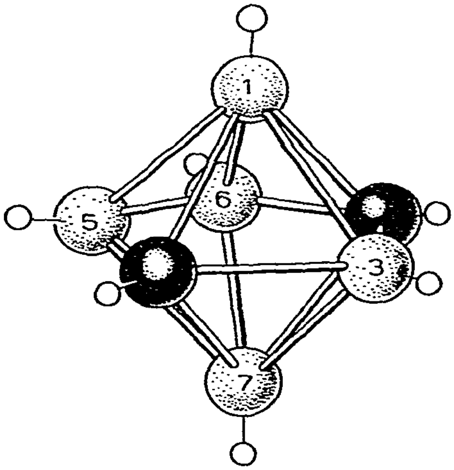


Figure 20. The structure and numbering of 2,4-$C_2B_5H_7$. Reprinted with permission from J. F. Ditter, E. B. Klusmann, R. E. Williams, and T. Onak, Inorg. Chem., 15 (1976) 1063. Copyright by the American Chemical Society.]

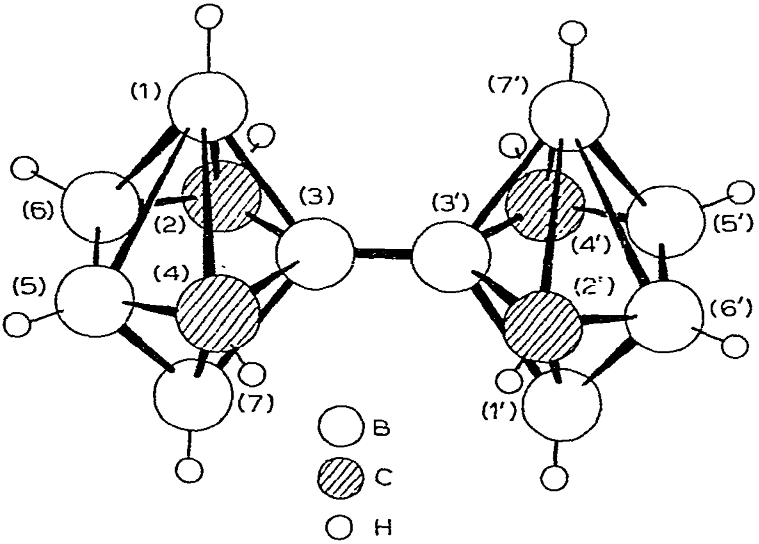


Figure 21. The proposed structure of 3,3'-(2,4-$C_2B_5H_6)_2$. [Reprinted with permission from J. S. Plotkin and L. G. Sneddon, J. Chem. Soc., Chem. Commun., (1976) 95. Copyright by the Chemical Society.]

carborane CB_8H_{14} (III) in Fig. 22) [33]. A new stable monocarborane, 4-CB_8H_{12}, has been reported [34], but since only the title is available to the reviewer, the relationship of this compound to CB_8H_{14} is unclear.

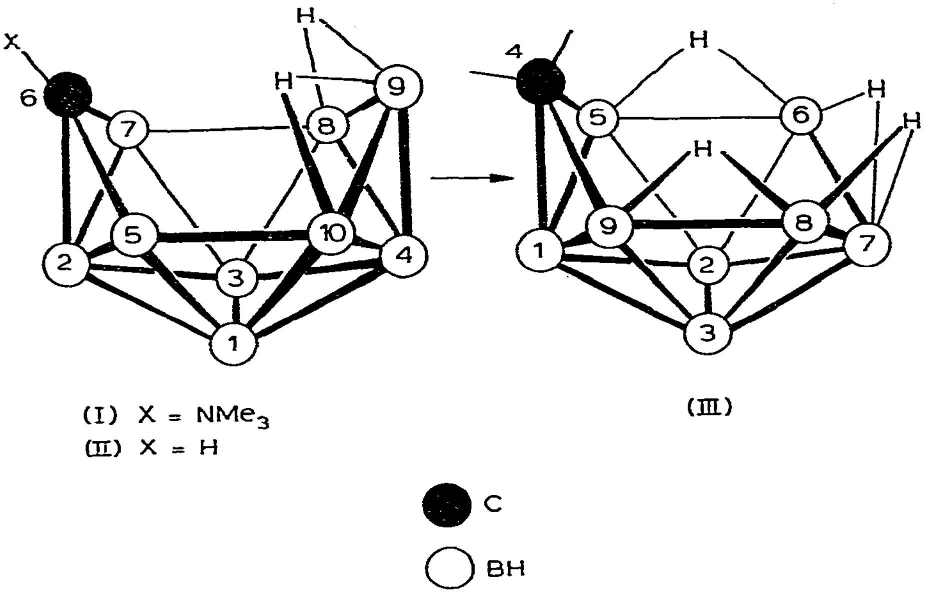


Figure 22. The proposed structures of $6\text{-}CB_9H_{12}^-$ and $4\text{-}CB_8H_{14}$. [Reprinted with permission from B. Stibr, K. Base, S. Hermánek, and J. Plesek, J. Chem. Soc., Chem. Commun., (1976) 150. Copyright by the Chemical Society.]

Copyrolysis of $6\text{-}SB_9H_{11}$ with m-carborane or with $7,9\text{-}C_2B_9H_{13}$ has yielded carboranylthiaboranes $1\text{-}SB_9H_8\text{-}m\text{-}C_2B_{10}H_{11}$ or $1\text{-}SB_9H_8\text{-}2,3\text{-}C_2B_9H_{10}$, respectively, of as yet undetermined structures, except that more than one isomer is present in each case and the cages appear to be linked through B-B bonds [35]. Pyrolysis of $6\text{-}SB_9H_{11}$ gives $1\text{-}SB_9H_9$, together with 2,2'-, 2,6'-, and $6,6'\text{-}(1\text{-}SB_9H_8)_2$. Pyrolysis of $7\text{-}SB_{10}H_{12}$ gives $1\text{-}SB_{11}H_{11}$ and a mixture of $1\text{-}SB_9H_8\text{-}1\text{-}SB_{11}H_{10}$ isomers of undetermined structure.

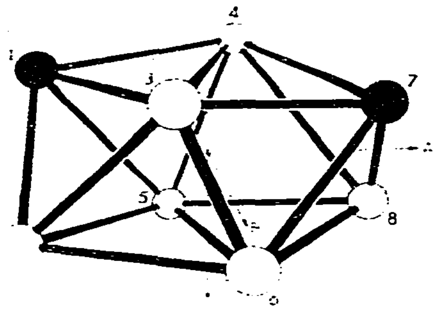
Beaudet and coworkers have determined the structure of $1,7\text{-}C_2B_6H_8$ by microwave spectroscopy, and the slightly distorted D_{2d} geometry earlier found by X-ray measurements has been confirmed to exist in the gas phase (Fig. 23) [36]. Bond distances are $B_2\text{-}B_3$ = 1.813 Å, $B_2\text{-}B_5$ = 1.843 Å, $B_2\text{-}B_6$ = 1.685 Å, $B_3\text{-}B_4$ = 1.886 Å, $B_2\text{-}B_6$ = 1.880 Å, and $B_5\text{-}B_6$ = 1.949 Å. The dipole moment is 1.40 ± 0.01 D.

The structure of $1,6\text{-}C_2B_7H_9$ has been determined by microwave spectroscopy (Fig. 24) [37]. From the Stark effect, the dipole moment was determined to be 2.14 ± 0.17 D.

An electon diffraction study of $1,10\text{-}C_2B_8H_{10}$ has yielded the bond distances B-C = 1.60, basal B-B - 1.87, equatorial B-B = 1.80, and B-H = 1.17 Å [38].

D. Icosahedral Carboranes

1. Introduction. Icosahedral carborane chemistry is getting to the point where it reminds this reviewer of the music of Vivaldi: straightforward to



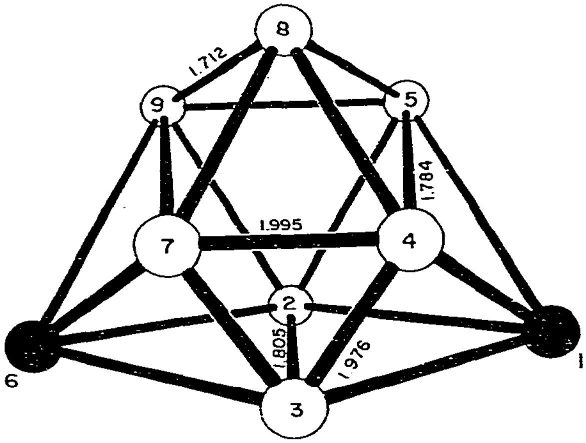
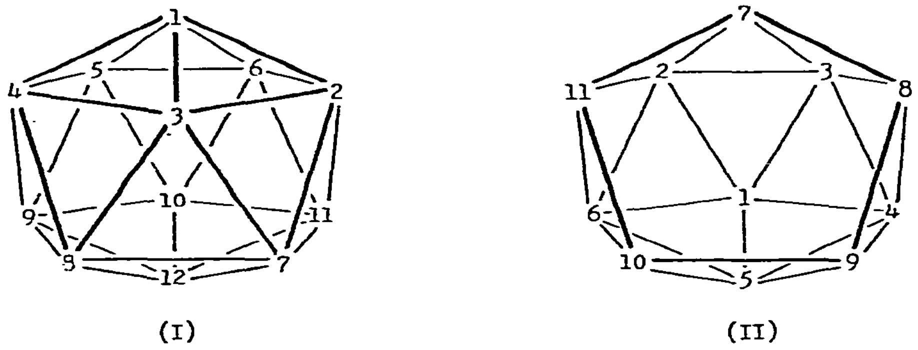


Figure 23. The structure of $C_2B_6H_8$ (hydrogens omitted). [Reprinted with permission from H. N. Rogers, K. K. Lau, and R. A. Beaudet, Inorg. Chem., 15 (1976) 1775. Copyright by the American Chemical Society.]

Figure 24. The structure of 1,6-$C_2B_7H_9$. [Reprinted with permission from K.K. Lau and R. A. Beaudet, Inorg. Chem., 41 (1976) 1060. Copyright by the American Chemical Society.]

perform, an endless supply of variations on a theme, pleasant enough, but more interesting to the performers than the spectators. The reviewer is more a fan of Prokofiev, who seems to have nothing in common with most current icosahedral carborane chemistry other than Russian origin. Accordingly, most of the reviews will be very brief, with only a few highlights mentioned in any detail.

The numbering of the icosahedron and of the 11-atom icosahedral fragment formed by removing one boron atom from the cage are illustrated in Fig. 25. For more detailed comment, see last year's Survey (JOM 119 (1976) 3).



(I)

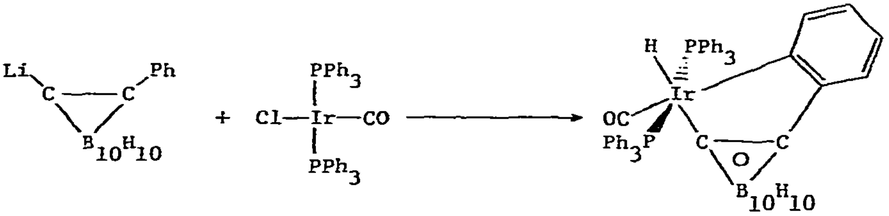
(II)

Figure 25. Numbering schemes for the icosahedron (I) and for the 11-atom icosahedral fragment (II) formed by removing atom number 3 from the icosahedron.

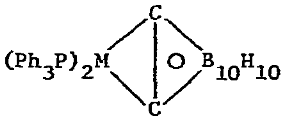
As is customary, the trivial names o-carborane, m-carborane, and p-carborane will be used for 1,2-, 1,7-, and 1,12-$C_2B_{10}H_{12}$, respectively. Most of the derivatives to be discussed are substituted only on carbon, but where B-substitution is indicated by such numbers as 3-, 4-, or 8-, the structure may be visualized by referring to Fig. 25.

2. 11-Atom Icosahedral Fragments. A series of substituted o-carboranes have been degraded by known methods to the nido $R_2C_2B_9H_{10}^-$ anions [39]. (See also section D-5, ref. 57.) Acylation of 7,8-$C_2B_9H_{12}^-$ with RCOCl or $(RCO)_2O$ yields 10-RCO-7,8-$C_2B_9H_{12}$, and 7,9-$C_2B_9H_{12}^-$ similarly yields a B-benzoyl derivative with PhCOCl [40].

3. Metal Substituents (Excluding Li). A series of iridium-substituted o- and m-carboranes have been prepared by treating a benzene suspension of trans-$(Ph_3P)_2Ir(CO)Cl$ with 1-Li-2-R-1,2-$C_2B_{10}H_{10}$ (R = H, CH_3) or 1-Li-7-R-1,7-$C_2B_{10}H_{10}$ (R = H, CH_3, Ph) in ether [41]. When 1-Li-2-Ph-1,2-$C_2B_{10}H_{10}$ was used, the iridium inserted into the ortho C-H bond of the benzene ring to form a cyclic derivative. A series of new platinum carborane complexes of the general formula cis- and trans-$L_2PtH(C_2B_{10}H_{10}R)$ have been prepared, where L is trialkyl- or triarylphosphine, R is H, CH_3, or Ph, and both the Pt and R are bonded to the carbons of o- or m-carborane [42].



Reaction of $(Ph_3P)_2MCl_2$, where M = Pd or Pt, with dilithio o-carborane gives the cyclic products analogous to the known nickel derivative (JOM 75 (1974) 162, Fig. 42) [43].



Although o- and m-carboranes are unaffected by mercuric acetate, both can be mercurated with mercuric trifluoroacetate, both at position 9. o-Carborane reacts faster than the m-isomer. The structures were proved by replacement of the mercury by Br_2 [44].

A series of alkynylcarboranes have been prepared from $RCB_{10}H_{10}CCu$ and BrC≡CR' [45].

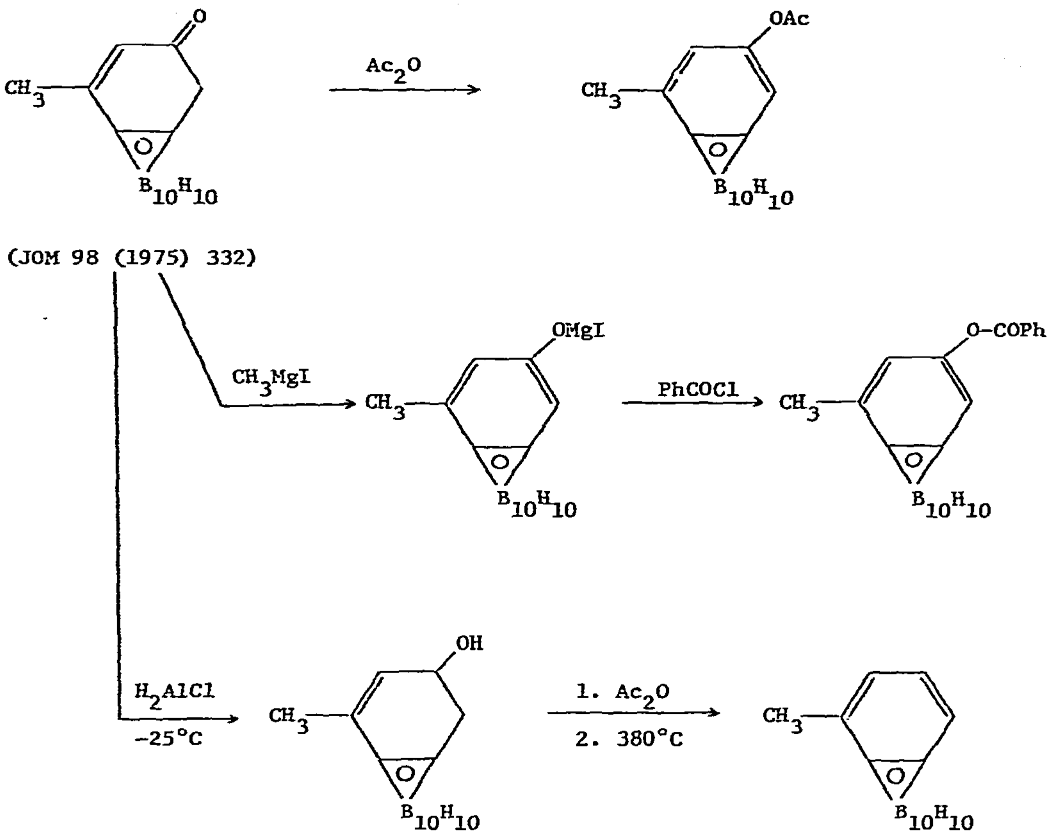
4. Nonmetal Substituents on B; $C_2B_{10}H_{12}^{2-}$ Chemistry. Reduction of o-$HCB_{10}H_{10}C-CH_2CH_2$-o-$CB_{10}H_{10}CH$ with Na in liquid ammonia followed by oxidation with $KMnO_4$ or $CuCl_2$ yielded o-$HC(B_{10}H_9NH_2)C-CH_2CH_2$-o-$C(B_{10}H_9NH_2)CH$, and similar treatment of the analog having p-C_6H_4 in place of $-CH_2CH_2-$ gave similar results [46]. The preparation of 1,2-bis(B-aminocarboranyl)ethane has been patented in the U.S.S.R. [47]. Reduction of o-$C_2B_{10}H_{12}$ with Na naphthalenide to form $C_2B_{10}H_{12}^{2-}$ followed by reaction with benzaldehyde and then $CuCl_2$ yields 3- and 4-$(PhCH_2-O-)C_2B_{10}H_{11}$, which yield the corresponding B-hydroxycarboranes on cleavage with $AlBr_3$ [48]. The ^{13}C NMR spectra of 1,2-Ph_2-o-, 1,7-Ph_2-m-, and 1,12-Ph_2-p-carborane and the mono- and dianions from reduction of these compounds were examined. The monoanions all gave the same ^{13}C NMR, and the dianions from the o- and m-carborane gave the same spectrum but that from the p-isomer was different [49].

Stanko and coworkers have studied the reduction of o-, m-, and p-$CH_3CB_{10}H_{10}CCl$ with Na in liquid ammonia, which leads to $CH_3CB_{10}H_{10}CH$ on reoxidation, with o-isomer yielding only o-product, m-isomer both m- and o-product, and p-isomer all three isomers of product [50]. Reduction of 1-methyl-o-carborane with Na in liquid NH_3 followed by addition of methyl iodide yields a 1,B-dimethyl-B'-amino-o-carborane [51].

Isomerization of 3-amino-o-carborane at 550-600°C leads to 2- and 4-amino-m-carborane, which can be isomerized back to 3-amino-o-carborane by way of reduction with Na in NH_3 [52]. Gas phase isomerization of 3-substituted o-carboranes at 550-600°C gives equal amounts of 2- and 4-substituted m-carboranes, where the substituent is $-OH$, $-OCH_3$, or $-CN$ [53].

Oxidation of o- and m-carboranes having one or two $-CH_2CH_2SiMe_3$ substituents on boron has yielded B-carboxycarboranes, o- and m-$HC(B_{10}H_9CO_2H)CH$ and $HC[B_{10}H_8(CO_2H)_2]CH$ [54].

5. Nonmetal Substituents on C. Zakharkin and Ermaganbetov have synthesized 1-methylbenzocarborane and related compounds by a simple route [55]. The previous synthesis of benzocarborane by Matteson and Hota (JOM 41 (1972) 37-38) was simple in principle but tedious in the laboratory, and it is hoped that this new approach will make benzocarboranes more readily accessible.



(JOM 98 (1975) 332)

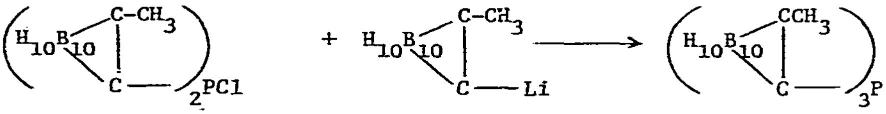
Zakharkin and coworkers have reported the reaction of PhOCN with *m*-$RCB_{10}H_{10}CLi$ to yield *m*-$RCB_{10}H_{10}C{-}CN$ and with *o*-$HCB_{10}H_{10}CCH_2MgBr$ to yield *o*-$HCB_{10}H_{10}CCH_2CN$ [56]. A series of substituted *o*-carboranes prepared from $RCB_{10}H_{10}CLi$ and various electrophiles, for example, $ClCH_2CH_2NMe_2$, as well as the $RR'C_2B_9H_{10}^-$ anions derived from them by degradation with base, have been tested for biological activity and some have been found to have neurotropic properties [57]. Another example of carboranyl side chain chemistry is the synthesis of 2,3-bis(*o*-carboranyl)butadiene by coupling $H_2C{=}CBr{-}C_2B_{10}H_{11}$ with Cu [58].

As for side chain chemistry of substituted carboranes, the Russians have done it again. Monosilyl-*m*-carboranes disproportionate in the presence of alkali to disilyl and unsubstituted carboranes [59] (JOM 119 (1976) 31). Alkyltin hydrides add to the double bond of vinylcarboranes and will form a cyclic derivative if suitable bifunctionality is provided [60]. Lithiocarboranes can be silylated and will form cyclic disilyl derivatives (JOM 98 (1975) 333) if the operation is done twice [61]. A nitroalkyl side chain will ring close to a phenyl group in acid to form a 7-membered amide-containing ring fused to *o*-

carborane (JOM 98 (1975) 332) [62]. Carborane anions add Michael fashion to $RCH{=}C(CO_2Et)_2$ [63]. ArCHO with $CH_3COCB_{10}H_{10}CPh$ in the presence of boric acid yields $ArCH{=}CHCOCB_{10}H_{10}CPh$ [64]. The epoxypropyl group substituted onto *o*-carborane undergoes the usual sort of epoxide ring opening reactions with various reagents [65]. Epoxypropylcarboranes have been prepared from the reaction of *o*-$R{-}CB_{10}H_{10}CLi$ with epichlorohydrin [66]. U.S.S.R. Patents have been issued for syntheses of 1,2-bis(4-cyanatobenzyl)-*o*-carboranes [67], mono- and bis(4-hydroxybenzyl)carboranes [68], cyanomethyl derivatives of *o*-carborane [69], 1,7-*m*-carboranylene diisocyanate [70], and 2,3-bis(*o*-carboranyl)butadiene [71]. Alkylation of pyridine with carboranylethyl and carboranylpropyl bromides to form carboranylalkylpyridinium salts and related reactions have been reported [72]. Treatment of *o*-, *m*-, and *p*-$Li_2C_2B_{10}H_{10}$ or $Na_2C_2B_{10}H_{10}$ with *p*-$MeOC_6H_4CH_2Cl$ followed by acid hydrolysis has yielded $(HOC_6H_4CH_2)_2C_2B_{10}H_{10}$ [73]. The conversion of $Li_2C_2B_{10}H_{10}$ and *p*-$CH_3C_6H_4CH_2Br$ to $(CH_3C_6H_4CH_2)_2C_2B_{10}H_{10}$ followed by oxidation to $(HO_2CC_6H_4CH_2)_2C_2B_{10}H_{10}$ has been patented in the U.S.S.R. [74]. The preparation and some reactions of 1,7-$(PhCOCO)_2$-*m*-$C_2B_{10}H_{10}$ have been reported [75]. The PhCOCO groups are readily cleaved from the carborane cage by bases.

The reaction of *p*-$CH_3OC_6H_4{-}C{\equiv}C{-}C_6H_4OCH_3$ with decarborane to form the *o*-carborane and hydrolysis to the carboranylbisphenol has been described [76]. The conversion of bis(3,4-dimethylphenyl)acetylene to the *o*-carborane, rearrangement to the *m*-carborane, and oxidation of both isomers to bis(3,4-dicarboxyphenyl)carboranes has been reported [77].

Tris(2-methyl-1-*o*-carboranyl)phosphine has been prepared from $CH_3C_2B_{10}H_{10}{-}Li$ and $(CH_3C_2B_{10}H_{10})_2PCl$ [78]. A series of *o*-carboranylphosphonites, $(EtO)_2PCB_{10}H_{10}CR$,



have been prepared from $(EtO)_2PCl$ and $LiCB_{10}H_{10}CR$ and their reactions with a variety of electrophilic reagents have been investigated [79]. Reaction of *o*-$RCB_{10}H_{10}C{-}P(OEt)_2$ with Cl_3CCHO has yielded *o*-$RCB_{10}H_{10}C{-}PO(OEt)OCH{=}CCl_2$, and similar results were obtained with p-$HCB_{10}H_{10}C{-}P(OEt)_2$ [80]. Mercaptocarboranyl derivatives of cyclotriphosphazene have been patented in the U.S.S.R. [81].

Treatment of *m*-$LiCB_{10}H_{10}CLi$ with $(Me_2SiO)_3$ yields $LiCB_{10}H_{10}C{-}SiMe_2OLi$, which on treatment with RR'MeSiCl (R' = H or alkoxy, R = Me, Ph, $CF_3CH_2CH_2$) yields $RR'MeSiCB_{10}H_{10}CSiMe_2OSiMeRR'$ [82]. Similar series based on $(PhMeSiO)_3$ and $[(CF_3CH_2CH_2)MeSiO]_3$ were also reported. A U.S.S.R. patent has been issued on bifunctional 1-silyl-7-disiloxanyl-*m*-carboranes [83]. Chlorination of *o*- and *m*-$Me_2HSiCB_{10}H_{10}CSiMe_2H$ has yielded $Me_2ClSiCB_{10}H_{10}CSiMe_2Cl$ [84].

Aminomethylcarborane displaces chloride from 7-chlorotetracycline or 7-chloroanhydrotetracycline to form the carboranylmethylamino-substituted antibiotics, which have been patented in the U.S. for use as food preservatives and for sterilization of milk [85]. *m*-HO_3S-$CB_{10}H_{10}CSO_3H$ has been patented [86]. Carboranyl substituted esters of dipeptides have been used as a stationary phase in the separation of enantiomers of amino acid derivatives by gas chromatography [87].

6. Physical Measurements. Molecular reorientation in crystalline *o*-carborane has been studied by ^{1}H, ^{10}B, and ^{11}B NMR and the activation energies determined for reorientation above and below the phase transition at 274°K [88].

Protonation of *o*-MeC($B_{10}H_{10}$)C-CH=CH-CH_2Li and related carboranyllithium or magnesium compounds with a variety of protonating agents and solvents gives varying ratios of carboranyl-CH=CH-CH_3 and -CH_2-CH=CH_2 [89]. For a series of *o*-R-C($B_{10}H_{10}$)C-CH_2-CH=CH_2, it was shown that treatment with *t*-BuOK in *t*-BuOH led to complete isomerization to *o*-R-C($B_{10}H_{10}$)C-CH=CH-CH_3 (R = CH_3, iPr, Ph, CH_2 = C(CH_3)$^-$) [90]. Under similar conditions, *o*-CH_3C($B_{10}H_{10}$)CCH_2CH=CHCH_3 predominated in an equilibrium mixture with *o*-CH_3C($B_{10}H_{10}$)CCH=CH-CH_2CH_3, 75.5 to 24.5. Rate constants for the rearrangement of iPrC($B_{10}H_{10}$)C-CH_2CH=CH_2 with t-BuOK in t-BuOH at 26.5 and 36.5° were measured, $\Delta H^{\ddagger}$ = 15.8 kcal/mol, $\Delta S^{\ddagger}$ = 13.2 e.u. The carborane cage is not attacked under these conditions.

Cleavage of *o*-RC($B_{10}H_{10}$)CH, R = H, CH_3, Ph, i-Pr, with BuNH_2, piperdine, and Et_2NH in 95% EtOH have been measured and compared [91]. The reaction is first-order in each reactant, and the reaction is accelerated by electron-withdrawing groups on the carborane.

Acidities of a series of carboranyl carboxylic acids have been correlated with reduction potentials and nuclear gamma resonance spectra of their trimethyltin salts [92]. Solvent effects on the relative acidities of *p*-carborane versus Ph_3CH [93] and on the rate of aniline acylation by *m*-carboranecarbonyl chloride [94] have been studied. Enthalpies of formation of 1-methyl-*o*-, -*m*-, and -*p*-carborane have been found to be −253.0 ± 16.3, −311.6 ± 13.8, and −276.5 ± 15.1 kJ/mol, respectively [95].

The effects of C-methyl substitution in *o*-, *m*-, and *p*-carboranes on the ^{11}B and ^{13}C NMR spectra and on the heats of formation have been interpreted in terms of a molecular orbital description [96]. Infrared and ^{1}H and ^{11}B NMR spectra of a series of halocarboranes reveal strong substituent effects on the atom directly attached to the substituent and also the atom directly opposite in the icosahedron [97, 98]. Dipole moments of halocarboranes have been compared and bond moments for B-X and C-X bonds estimated [99].

Carboranylmercury and tin compounds are more easily oxidized electrochemically when complexed with pyridine or bipyridyl [100]. Rates of benzoylation of 1,7-diamino-*m*-carborane with benzoyl chloride catalyzed by pyridine N-oxide in ethyl acetate do not, according to the abstract, depend on temperature [101]. This result is clearly in accord with Murphy's Law. Last and probably least, an infrared sample holder designed for use at 80-300°K has been used to observe the spectra of a series of *o*-carborane derivatives [102].

E. Boron Cages without Carbon

1. Metalloboranes. First, the boron-cobalt cluster compounds reported by Miller and Grimes and described in section B-1 should be noted.

Since the compounds covered in this section are not organoboron compounds by definition, treatment will be brief.

The structure of $C_5H_5CoB_4H_8$ has been determined by X-ray crystallography and found to contain a square pyramidal metalloborane unit with cobalt occupying a basal position, essentially B_5H_9 with one basal BH replaced by $Co(C_5H_5)$ [103].

The *closo*-ferraborane $B_5H_5Fe(CO)_3$ has been obtained from the reaction of $Fe(CO)_5$ with B_5H_9 in a hot-cold reactor [104]. $B_5H_9Fe(CO)_3$ has been isolated from the reaction of B_5H_9 with $Fe(CO)_5$ in a hot-cold reactor [105].

Several new $B_{10}H_{12}PdL_2$ compounds as well as derivatives of $B_{10}H_{12}IrCO(PPh_3)_2^-$ have been reported [106]. A series of icosahedral cage complexes $(C_5H_5)CoB_{10}H_{10}P$-R have been prepared from 7-$B_{10}H_{12}P$-R, $CoCl_2$, cyclopentadiene, and KOH in ethanol [107]. Reaction of 7-$SB_{10}H_{11}^-$ with $(Ph_3P)_3RhCl$ has yielded $(Ph_3P)_2RhH(SB_{10}H_{10})$ where Rh is incorporated into an icosahedral cage [108]. $(Ph_3P)_2IrCl$ with 1-SB_9H_9 yields 2-$(Ph_3PIrHCl)$-1-SB_9H_9, and similar derivatives have been obtained from 1-$SB_{11}H_{11}$ and also with $(Ph_3As)_2IrCl$, where the metal is a cage substituent.

Reaction of $Be(CH_4)_2$ with 1-Cl-B_5H_8 results in insertion of a Be atom into the base of the cage to give $B_5H_{10}BeBH_4$ [109].

Reaction of $Na_2B_{10}H_{12}$ with Ph_2SnCl_2 yields $Ph_2SnB_{10}H_{12}$, which decomposes under vacuum at 95°C to give a low yield of 6-$PhB_{10}H_{13}$ [110]. Reaction of $Na_2B_{10}H_{12}$ or $NaB_{10}H_{13}$ with Me_3SiCl in ether has resulted in oxygen abstraction from the ether to form 6-$(Me_3SiO)B_{10}H_{13}$, and with $SnCl_4$ in ether has yielded 6-$(EtO)B_{10}H_{13}$. The structure of $Me_2TlB_{10}H_{12}^-$ has been determined by X-ray crystallography [111]. The infrared and ^1H NMR spectra of $[(Ph_3P)_2Cu]_2B_{10}H_{10}$ and 2,3-μ-$(Ph_3P)_2CuB_5H_8$ have been measured and compared [112]. A series of metallo derivatives of hexaborane(10) including $(THF)_2Mg(B_6H_9)_2$, $(THF)_2Zn(B_6H_9)_2$, and $Cd(B_6H_9)_2$ have been isolated as crystalline solids and shown to be stereochemically nonrigid by ^1H NMR. The structure of $(THF)_2Mg(B_6H_9)_2$ has been determined by X-ray crystallography [113].

Reaction of $(Me_2N)_2B$-$B(NMe_2)_2$ with Al_2Me_6 yields a compound believed to have an octahedral core of six boron atoms, $B_6(NMe_2)_{12}(AlMe_2)_6$ [114].

2. Nonmetal Heteroboranes. Several thiaboranes, including 6-SB_9H_{11}, 1-SB_9H_9, 1-$SB_{11}H_{11}$, 4-$SB_8H_9^-$, $SB_{10}H_{11}^-$, and 4-SB_8H_{10}, have been synthesized

[115]. Halogenation of 1-SB_9H_9 is most rapid at the 6-position, even though the 10-position is calculated to have the highest electron density, and the halogenated products readily undergo cage rearrangement [116]. Oxidation of $SB_{10}H_{10}^{2-}$ with Ag^+ in benzene or toluene yields several products, including $SB_{10}H_{12}$ and $ArSB_{10}H_{11}$ [117]. Carboranylthiaboranes have been covered in section C [35].

Trimethylphosphine adds to B_6H_{10} to form $B_6H_{10}(PMe_3)_2$, which has two rows of three boron atoms arranged as a portion of the equatorial belt of an icosahedron, and which shows stereochemically nonrigid behavior by NMR analysis [118].

3. *Boron Hydrides*. Reaction of *m*- or *p*-$FC_6H_4BH_2$ with $B_9H_{14}^-$ yields 6-FC_6H_4-$B_{10}H_{13}$, and alkylation of $B_{10}H_{13}^-$ with *m*-$FC_6H_4CH_2Cl$ gives a mixture of 5- and 6-$(FC_6H_4CH_2)B_{10}H_{13}$ [119]. $Me_2S(B_{10}H_8)S(Me)CH_2CH_2CH(NH_3^+)CO_2^-$ has been synthesized [120]. The structure of $B_{13}H_{19}$ has been determined by X-ray crystallography [121], and the structures of B_8H_{14} and *i*-B_9H_{15} have been studied by ^1H and ^{11}B NMR [122]. NMR relaxation time measurements have been used to estimate boron-boron coupling constants in several boron hydrides [123]. Molecular orbital calculations have been reported for $B_{13}H_{19}$, $B_{14}H_{20}$, $B_{16}H_{20}$, both isomers of $B_{18}H_{22}$, $B_{20}H_{16}$, and two isomers of $B_{20}H_{18}^{2-}$ [124]. Photoelectron spectra of methyl-, halo-, and silyl-pentaboranes have been recorded and interpreted in terms of molecular orbital theory [125].

Ab initio molecular orbital calculations have been reported for a series of XCH_2Y systems where X and Y are BH_2 or Li, BeH, CH_3, NH_2, OH, or F [126]. One of the interesting conclusions is that $LiCH_2BH_2$ is stabilized to the extent of 18 kcal/mol as a result of electron donation from the Li-C σ bond to the B-C π bonding orbital. Similar electronic interactions in $CH_2(BH_2)_2$ provide 4 kcal/mol stabilization, which may be regarded as the beginning of carborane-like electronic interaction.

Independent calculations on BH_5 agree that the most favorable geometry is C_s, with the BH_3 bonded to the side of the H_2, and that the dissociation energy to BH_3 and H_2 is very small [127, 128]. Kinetic experimental evidence indicates greater stability for BH_5 than do the calculations.

Hartree-Fock calculations have been reported for BH_3CO [129]; see also [197].

F. Reviews

Metallocarborane and metalloborane derivatives have been reviewed by Todd and by Gaines and coworkers [130, 131]. Onak has reviewed carborane chemistry [132]. Williams has reviewed carborane structures [133]. Hawthorne and coworkers have reviewed metallocarborane chemistry in a lecture which has been published [134].

II. HYDROBORATION

A. Introduction

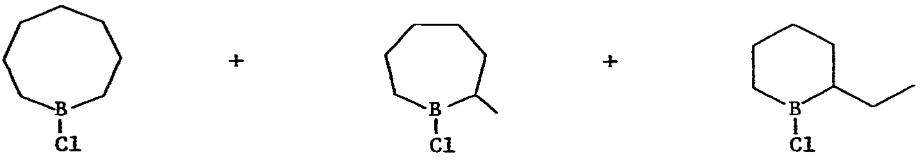
The development of hydroboration chemistry has continued, with H. C. Brown, his students, and his former students still making most of the significant contributions. Work on the addition of boranes to alkenes has been directed toward understanding and improving the specificity of the process. The use of various types of boranes in carbon-carbon bond formation continues to be of interest, with considerable recent emphasis on the behavior of alkenylboranes. Various applications of hydroboration to other synthetic problems are scattered throughout the literature, and the reviewer has to depend on their being indexed under "hydroboration" in Chemical Abstracts in order to find them. As hydroboration continues to develop, more synthetic applications by organic chemists are to be anticipated.

B. Boron Hydride Additions

1. Studies of Hydroboration. Brown, Liotta, and Scouten have reported the details of the relative reactivities of 37 selected olefins toward hydroboration with 9-BBN [135]. Although 9-BBN is a highly hindered hydroborating agent and is generally comparable to disiamylborane in its steric requirements there are some significant differences in behavior between the two reagents. 9-BBN is far more sensitive to electronic influence than is disiamylborane. Disiamylborane hydroborates cis alkenes faster than trans, but the reverse is true with 9-BBN. A methyl substituent on the β carbon (to which the hydrogen becomes attached) retards hydroboration with disiamylborane but often accelerates the reaction of 9-BBN.

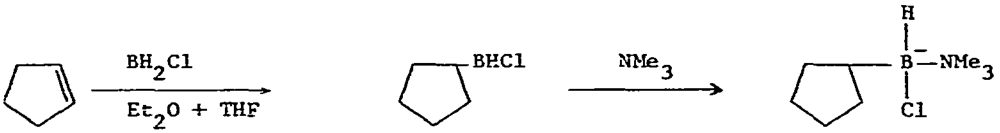
Hydroboration of α,ω-diolefins with chloroborane leads to mixtures of polymeric and cyclic compounds [136]. Heating the polymeric fraction generally leads to depolymerization to cyclic monomers. Ring sizes up to 8 or, using high dilution conditions, 15 or greater, were obtained.

$$H_2C{=}CH(CH_2)_3CH{=}CH_2 \; + \; BH_2Cl \xrightarrow{Et_2O} [-(CH_2)_7BCl-]_{\underline{n}} \xrightarrow{250°}$$

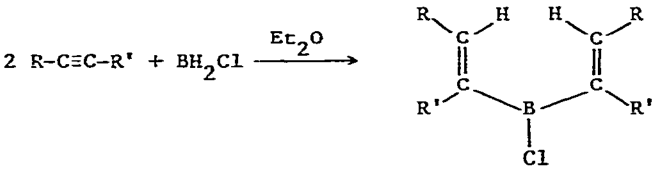


75% 10% 15% (overall yield 91%)

Brown and Ravindran have published detailed descriptions of hydroboration of alkenes and alkynes with monochloroborane etherates [137]. Hydroborations with $BH_2Cl{\cdot}THF$ are slow and incomplete, but $BH_2Cl{\cdot}Et_2O$ reacts rapidly and quantitatively with alkenes at 0°C to form R_2BCl. The selectivity of this reaction to produce the less sterically hindered product is considerably greater than that of $BH_3{\cdot}THF$. Use of a 1:1 ratio of alkene to hydroborating agent gives mixtures of RBHCl and R_2BCl, but the reaction can be stopped cleanly at the RBHCl stage by the addition of 1.2-2.0 moles of THF to the reagent. The RBHCl could be converted to $RBCl_2$ by treatment with HCl or isolated as the trimethylamine complex.



Alkynes can be converted cleanly to dialkenylchloroboranes, which are isolable.



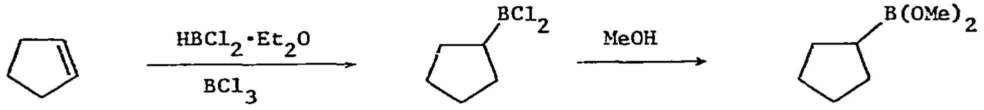
R is alkyl

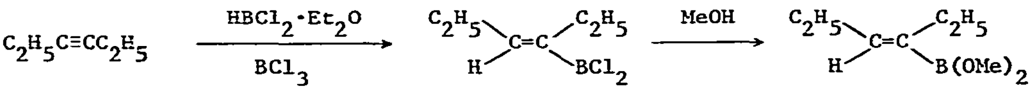
R' is alkyl or H

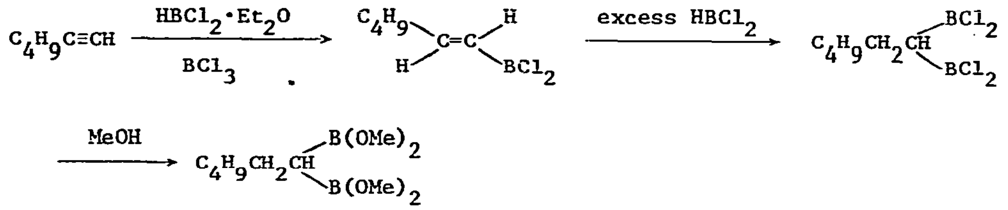
Terminal alkynes (R' = H) tend to undergo dihydroboration to complex products, but this can be avoided by the use of a moderate excess of alkyne.

Dichloroborane etherate is relatively unreactive and generally gives incomplete hydroborations, but by using pentane as solvent and a mole of BCl_3 to catalyze the reaction and complex the ether liberated from conversion of $HBCl_2{\cdot}Et_2O$ to $RBCl_2$, efficient hydroborations of alkenes and alkynes can be carried out [138]. The $RBCl_2$ can easily be isolated or converted to a derivative such as $RB(OMe)_2$.

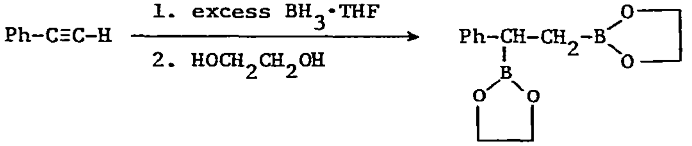
$$CH_3CH_2CH{=}CH_2 \xrightarrow[BCl_3]{HBCl_2\cdot Et_2O} CH_3(CH_2)_3BCl_2 \xrightarrow{MeOH} CH_3(CH_2)_3B(OMe)_2$$







Dihydroboration of phenylacetylene followed by reaction of the borane with ethylene glycol gave not the expected 1,1-bis(ethylenedioxyboryl)-2-phenylethane but the 1,2-isomer instead in 55% yield. This disappointment was labeled a "supervenient synthesis," which merely means that it went the wrong way but somehow sounds much better than that [139].



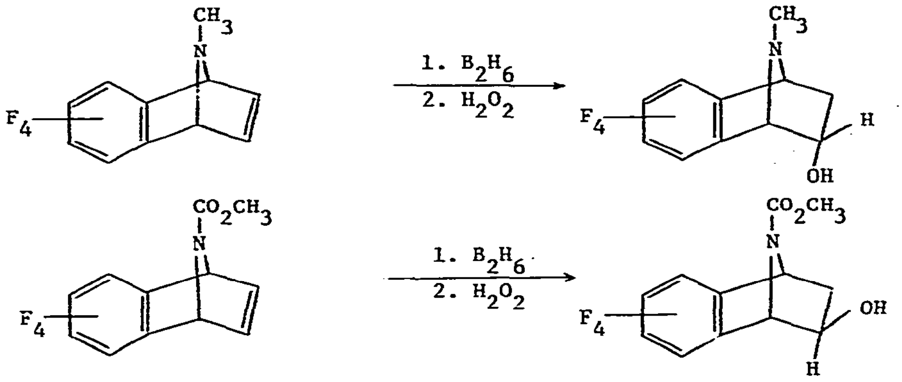
Hydroboration of 1-methylcyclooctene with 9-BBN followed by oxidation yields pure trans-2-methylcyclooctanol, in contrast to the results with other hydroborating agents, which led to mixtures [140]. The reason for the superior result with 9-BBN in this case is that the rearrangement of secondary alkyl 9-BBN derivatives is much slower than rearrangement of most other secondary alkylboranes, and the cyclooctyl system is particularly prone to rearrangement with respect to the position of the attachment of the boron to the ring.

Rates of reduction of a variety of organic functional groups to 9-BBN in THF at 25° have been measured approximately in order to establish which types of functional groups will survive hydroboration conditions [141]. For example, it was found that reduction of cyclohexanone is faster than hydroboration of cyclopentane, which is in turn faster than reduction of ethyl hexanoate or hexanoic acid (after the rapid initial reaction to form $R\text{-}CO_2\text{-}9\text{-}BBN$). In general, aldehydes and ketones tend to be attacked faster than olefins, which react at about the same as quinones, tertiary amides, acid chlorides and anhydrides, and lactones, and which react faster than esters, epoxides, oximes, $R\text{-}CO_2\text{-}BR_2$, sulfoxides, azoxy compounds, nitro compounds, azo compounds, sulfides, disulfides, sulfones, sulfonic acids, tosylates, aromatic halides, and alkyl halides. In the faster reactions of 9-BBN, including hydroboration, dissociation of the 9-BBN dimer is the rate determining step, and relative reactivities were determined by competition experiments.

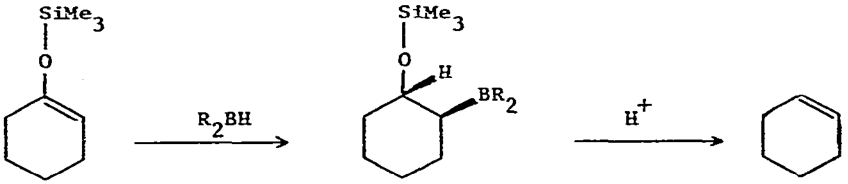
A study of the gas phase hydroboration of ethylene with diborane over catalysts such as Na/Al_2O_3, SiO_2, and Pd/C has been reported [142]. The rate of gas phase hydroboration of ethylene or 1-butene over a Pd/C catalyst is proportional to the half-power of the B_2H_6 pressure and is first-order in olefin [143].

The reaction of Et_3B or $(i\text{-}Pr)_3B$ with BH_3 in THF has been studied by NMR [144]. The first step is formation of $R_2BH_2BH_2$, and subsequent steps depend on R and the ratio of reactants.

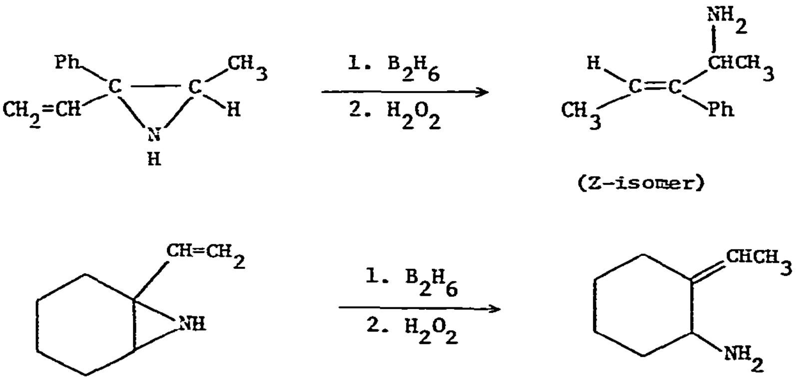
Hydroboration of a benzocycloazaheptadiene system gives endo addition if the nitrogen atom is basic and coordinates with BH_3, but exo addition if the amine function is converted to an amide which does not complex with BH_3 [145].



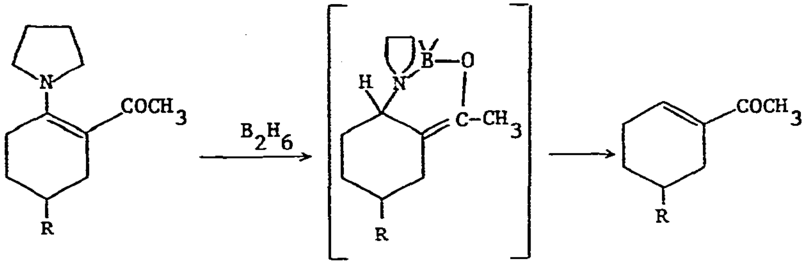
Hydroboration of silyl enol ethers of C_5–C_7 cycloalkanones followed by treatment with HCl yields cycloalkenes [146].



Hydroboration of vinylic aziridines proceeds with a high degree of regio- and stereoselectivity and leads to allylic amines as a result of β-elimination of B and N [147].



Hydroboration of acetylated cyclohexanone enamines followed by boron-nitrogen elimination has been reported [148]. Hydroboration-oxidation of



2-cyclohexenone N-cyclohexylimines yields trans-1-(cyclohexylamino)-2-hydroxycyclohexanes [149].

The stereochemistry of hydroboration of 1,3,5-trisubstituted cyclohexenes and related compounds has been investigated and the steric factors affecting the outcome have been interpreted [150].

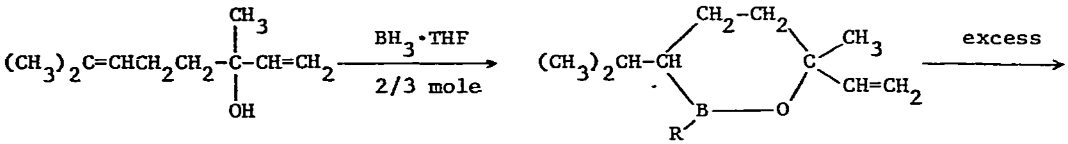
Reaction of $HC{\equiv}C{-}CH{=}CR_2$ ($CR_2 = CMe_2$ or $CHEt$) with $Na^+Et_3BH^-$ yields $Na^+\ Et_3\bar{B}{-}CH{=}CH{-}CH{=}CR_2$, or with $HBEt_2$ yields mixtures of $Et_2B{-}CH{=}CH{-}CH{=}CR_2$ and $CH_2{=}C(BEt_2){-}CH{=}CR_2$ [151].

Hydroboration of vinylsilanes followed by heating with sodium methoxide results in mixtures of protodeboronation, protodesilylation, and B-H elimination products [152].

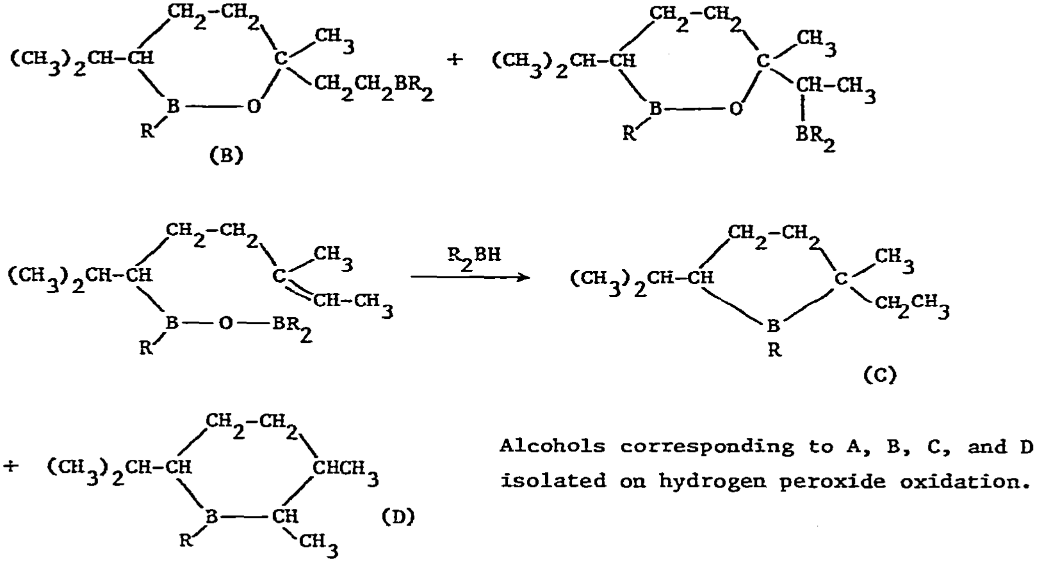
The hydroboration of 1,9-cyclohexadecadiene followed by oxidation of 8-cyclohexadecen-1-one, 1,9-cyclohexadecanedione, 1,8-cyclohexadecanedione, and cyclohexadecanone has been patented [153].

Hydroboration of $ROCH_2C{\equiv}CCH_3$ with Bu_2BH gives a mixture of $ROCH_2C(BBu_2){=}CHCH_3$ and $ROCH_2CH{=}C(CH_3)BBu_2$ [154]. Hydroboration-oxidation of $ArCH{=}CCl_2$ yields $ArCH_2CH_2OH$ [155].

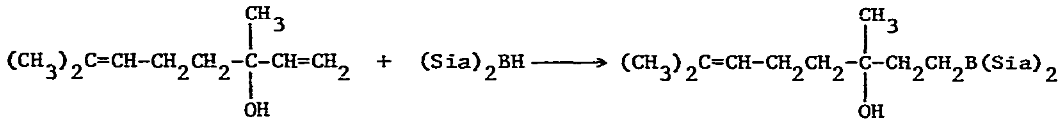
2. Hydroboration of Natural Products. Hydroboration of linalool with borane in tetrahydrofuran yields a complex mixture of products, but the more sterically hindered disiamylborane adds exclusively to the terminal vinyl group in the expected manner [156]. Hydroboration of geraniol or citral with borane in tetrahydrofuran leads to analogous complexities.



(A)



Alcohols corresponding to A, B, C, and D isolated on hydrogen peroxide oxidation.



$$(CH_3)_2C{=}CH{-}CH_2CH_2{-}\underset{OH}{\overset{CH_3}{C}}{-}CH{=}CH_2 + (Sia)_2BH \longrightarrow (CH_3)_2C{=}CH{-}CH_2CH_2{-}\underset{OH}{\overset{CH_3}{C}}{-}CH_2CH_2B(Sia)_2$$

Hydroboration of geraniol followed by reaction with CO, rearrangement of the CN^- adduct, coupling with Ag^+, or photochemical bromination and rearrangement has yielded alicyclic products [157].

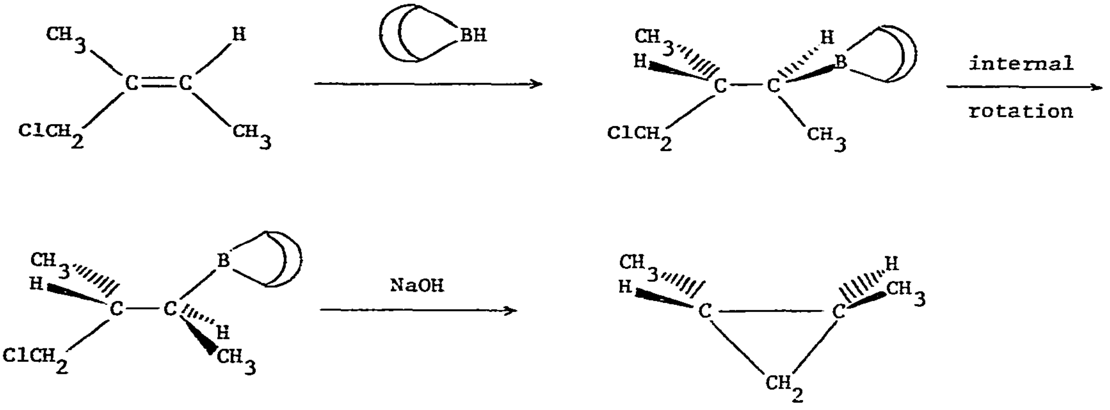
Hydroboration of an 8(14)-ene sterol followed by rearrangement to a mixture of 15α and 15β boranes has been used in the synthesis of 14β-cholest-5-en-3β-ol, which differs from the natural steroid series in having a cis C/D ring junction [158]. Other hydroborations involving the C/D ring junction of steroids have also been reported [159]. Stereochemical studies of hydroboration of cholesta-5,25-dien-3β-ol-THP have been reported [160].

Hydroboration-oxidation of α- and β-pinene and 3-carene with $NaBH_4$--HOAc or $LiBH_4$--HOAc in THF, ether, diglyme, and cyclohexane has been reported [161]. Hydroboration of 3-benzyl-4-hydroxycoumarin to homoisoflavanols has been reported [162]. Hydroboration-oxidation has been used in a synthesis of trimethylbrazilin [163].

For the use of hydroboration in a prostaglandin synthesis, see section C, refs. 172 and 173.

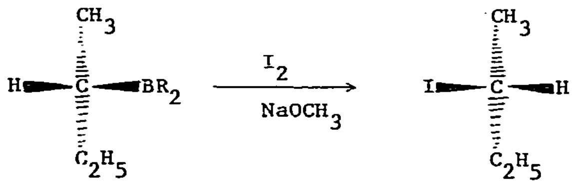
C. Boron Replacement and Borane Rearrangements

In the hydroboration of allylic halides followed by base catalyzed ring closure to cyclopropanes, the ring closure occurs stereospecifically with inverstion of the carbon from which the boron is displaced [164].

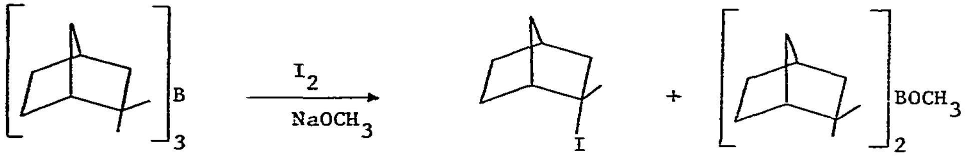


(Similar results were obtained with the Z-isomer).

Brown, Kabalka, and coworkers have found that iodination of trialkylboranes in the presence of sodium methoxide inverts the carbon from which the boron is displaced, opposite the usual stereochemistry of electrophilic displacements of boron [165].



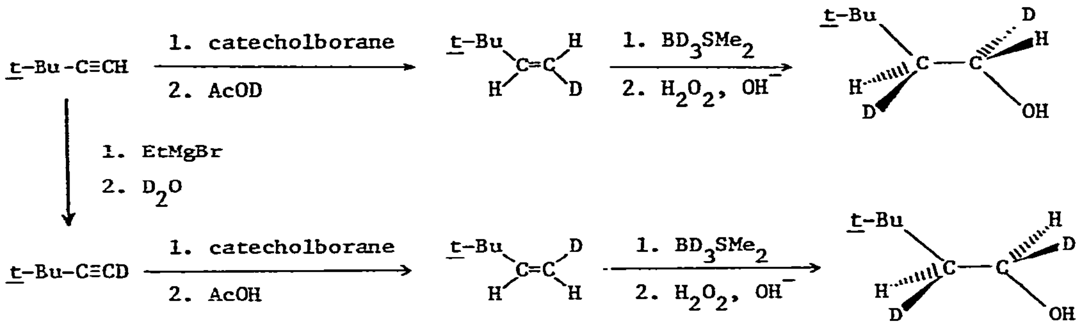
S, 86% optical purity R, 84% optical purity, 49% yield
R = isopinocampheyl from (−)-α-pinene



These results are mechanistically significant, since only a few examples of electrophilic displacement which proceed with inversion are known, and knowledge of the factors favoring retention in most cases has been limited by the restricted variety of counter examples. A similar bromination of organoboranes also gives inversion [JOM 41 (1972) 64], but the tendency of bromine to give radical reactions and complex mechanisms with organoboranes left the mechanistic significance somewhat uncertain.

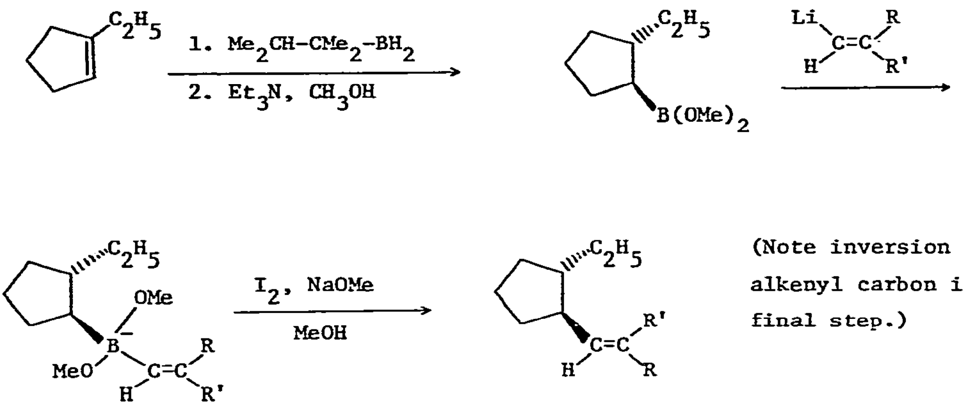
The yield of alkyl iodide from the reaction of R_3B with I_2 is improved by the use of $NaOCH_3$ instead of NaOH [166]. Electrolysis of R_3B in CH_3NO_2 containing tetraalkylammonium bromide or iodide yields RCH_2NO_2 by way of RBr or RI and $^-CH_2NO_2$ [167]. Trialkylboranes with $Fe(SeCN)_3$ yield alkyl selenocyanates [168].

Hydroboration has been used for the stereospecific conversion of t-butylacetylene to erythro- and threo-1,2-dideutero-3,3-dimethyl-1-butanol [169].



Bergbreiter and Rainville have used standard hydroboration procedures starting from t-BuC≡CH to prepare stereospecifically D-labeled isomers of $(t\text{-BuCHDCHD})_3B$, and have shown that inversion of configuration occurs both in the cleavage with Br_2 and CH_3O^- to form t-BuCHDCHDBr (>95% inversion) and with $Hg(OAc)_2$ (90% inversion) to form t-BuCHDCHDHgOAc, the erythro and threo isomers being readily distinguishable by proton NMR [170]. Gielen and Fosty have previously reported similar results with cleavage of the erythro $(t\text{-BuCHDCHD})_3B$ with $HgCl_2$ [171].

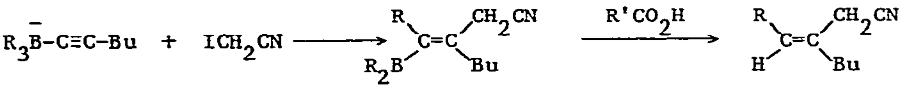
As part of a search for new routes to prostaglandins, Evans and coworkers have worked on the improvement of Zweifel's rearrangement of alkenylborates to alkenes in the presence of iodine and alkali (see JOM 41 (1972) 62; JOM 58 (1973) 28, 29) [172, 173]. After exploration of a variety of reagents and conditions, the best route found involved sythesis of trans-2-ethylcyclopentyl(dimethoxy)borane by hydroboration, followed by treatment with the appropriate lithioalkene to form the ate-complex. Rearrangement with iodine and sodium methoxide in methanol was found to provide considerable improvement over the previous conditions used, with less iododeboronation and improved yields of alkene. The use of alkoxy groups in place of alkyl groups as the nonmigrating ligands on boron leads to specificity in the rearrangement, resulting in full utilization of the desired alkyl and alkenyl groups.



(Note inversion of alkenyl carbon in final step.)

R = $-CH(OSiMe_2$t-Bu$)-C_5H_{11}$, R' = H, or vice-versa.

Lithium trialkylalkynylborates undergo stereospecific rearrangement on treatment with $BrCH_2C\equiv CH$ or ICH_2CN [174].

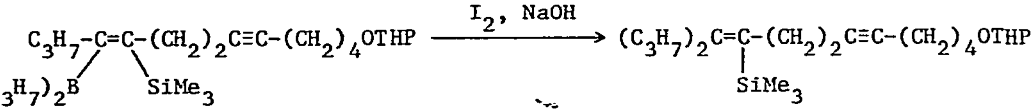


R = n-hexyl, n-octyl, cyclopentyl

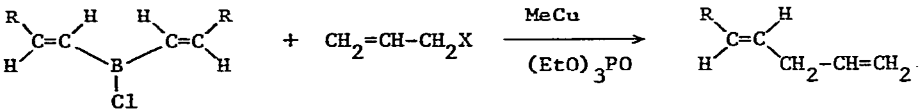
(Z-isomer)

The rearrangements of alkynylborates and alkenylboranes have been used in a synthesis of propylure [175].

$(C_3H_7)_3\bar{B}-C\equiv C-SiMe_3 + TsOCH_2CH_2C\equiv C-(CH_2)_4OTHP \longrightarrow$

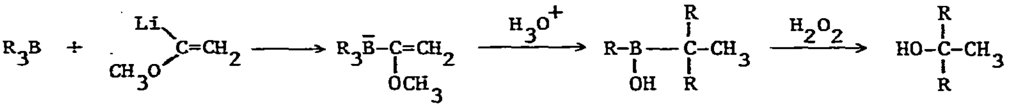


Reaction of Na^+ $Me_3Si-C\equiv C-\bar{B}Et_3$ with alkylating agents yields borylsilylalkenes that are 88-95% E-isomer [176].

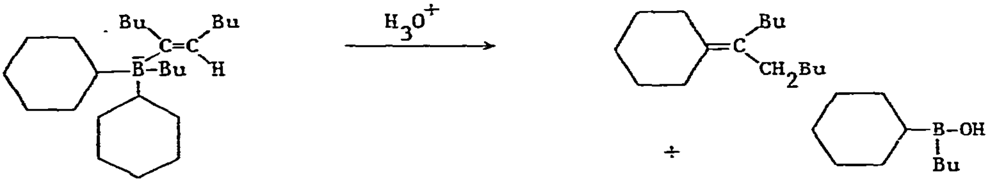


The 1,4-addition of an extended series of R_3B to $H_2C=C(CH_3)CHO$ to form $R-CH_2-C(CH_3)=CH-O-BR_2$ in good to excellent yields has been described [181]. When R was 2-methallyl or phenyl, 1,2-addition to the carbonyl group was observed. Reaction of $CH_3COCH=CH_2$ with BEt_3 leads to the enol borate $Et_2B-O-C(CH_3)=CHCH_2Et$, which reacts with benzaldehyde to form $CH_3COCH(CH_2Et)-CH(OBEt_2)Ph$ [182]. Several related reactions were also reported.

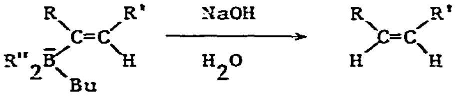
α-Methoxyvinyllithium reacts with trialkylboranes to form intermediates which rearrange on treatment with acid to form tert-alkylborinic acids which yield dialkylmethylcarbinols on oxidation [183].



Acid hydrolysis of alkenyltrialkylboranes results in rearrangement and borane elimination [184].

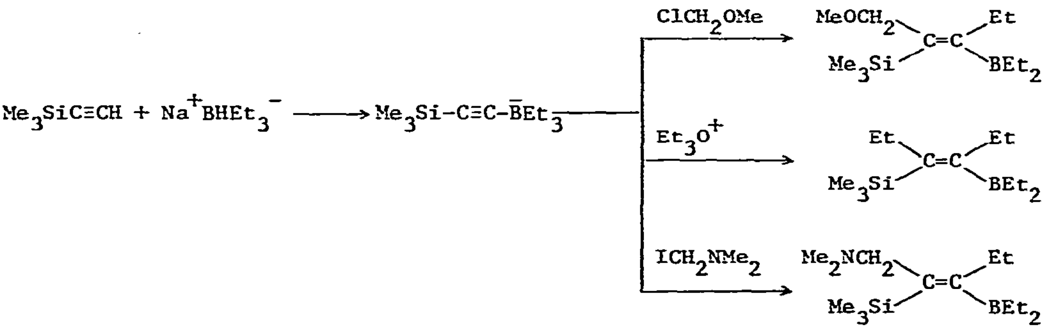


Aqueous sodium hydroxide cleaves alkenyltrialkylborates stereospecifically to alkenes [185].

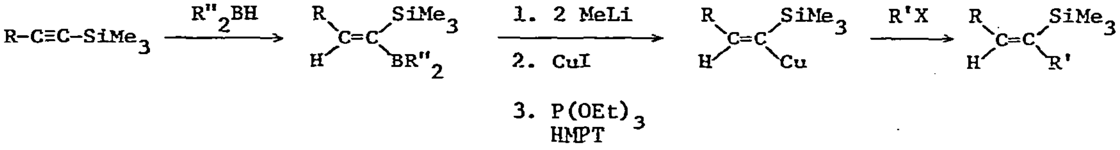


R" = cyclohexyl, siamyl

The oxidative rearrangement of B,B-dialkyl-9-BBN "ate" complexes has been studied by Kramer and Brown [186] and by Yamamoto and coworkers [187]. If the reaction of interest is the rearrangement of the 9-BBN group to bicyclo[3.3.0]octyl, acetyl chloride is an efficient oxidizing agent [186].

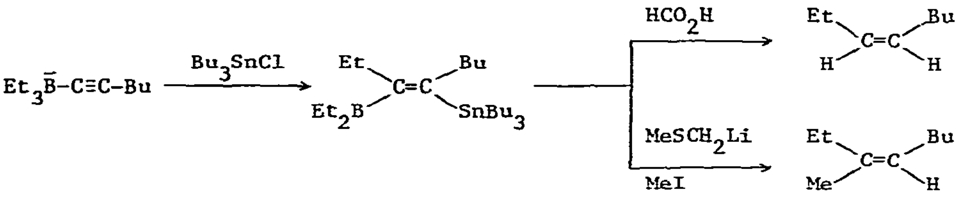


Hydroboration of alkynyltrimethylsilanes has been used in a stereoselective synthesis of alkenyltrimethylsilanes [177].

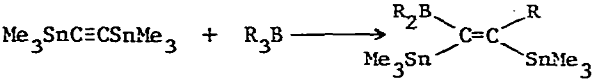


R" = cyclohexyl

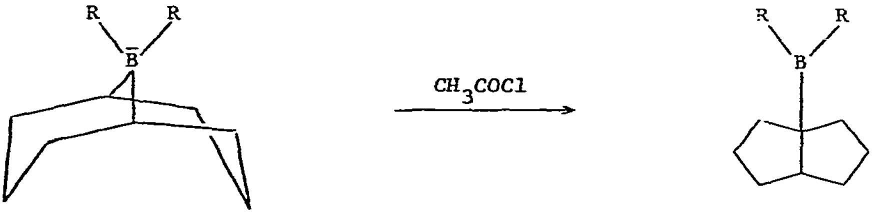
Reaction of $Et_3\bar{B}$-C≡C-Bu with Bu_3SnCl gives the E-borylstannylalkene (borylstannyl-cis-alkene), which on treatment with electrophiles yields alkenes [178].



Trialkylboranes add cis- to bis(trimethylstannyl)acetylene [179].



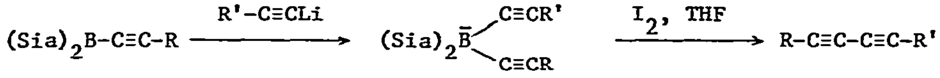
Cross coupling of dialkenylchloroboranes with reactive alkyl halides in the presence of methylcopper yields alkenes stereospecifically [180].



Conversely, the hydride donor properties of the "ate" complex (R = butyl) permit stereoselective reduction of cyclic ketones or the selective reduction of an aldehyde or less hindered ketone in the presence of a more hindered ketone [187]. Lithium trisiamylborohydride is another sterically hindered reducing agent, which provides unusual stereoselectivity in the reduction of cyclic ketones [188].

Reaction of $LiC{\equiv}CLi$ with R_3B forms $R_3\bar{B}-C{\equiv}C-\bar{B}R_3$, which on treatment with BrCN rearranges to form trans-$R-CH=CH-R$, $RCH=CR_2$, and $R_2C=CR_2$, with the proportions of products dependent on the reaction conditions [189].

Oxidation of bis(alkynyl)borate complexes derived from disiamylborane provides an efficient preparation of diacetylenes [190].



$$(Sia)_2B-C{\equiv}C-R \xrightarrow{R'-C{\equiv}CLi} (Sia)_2\bar{B}\begin{matrix}C{\equiv}CR' \\ C{\equiv}CR\end{matrix} \xrightarrow{I_2,\ THF} R-C{\equiv}C-C{\equiv}C-R'$$

Cuprous halides react with $Li^+\ R_3BCH_3^-$ to form $Cu(R_3BCH_3)$, which react with Michael acceptors, for example, $CH_2=CHCN$, which yields $R-CH_2CH_2CN$ after hydrolysis [191]. $(R_3BCH_3)Cu$ couples with $ArCH_2Br$ to form $ArCH_2R$ [192].

Reaction of $(RCH_2)_3B$ with ArCHO yields $ArCH=CH-R$ (R = n-pentyl), or tricyclohexylborane yields $ArCH=C(CH_2)_5$, and under free radical conditions $(RCH_2)_3B$ with $ArCO_2H$, $(ArCO)_2O$, or ArCOCl has yielded $ArCO_2CH_2R$ and tricyclohexylborane has given similar results [193].

Reaction of CEt_3 with PhMgBr and AcCl has yielded o-EtC_6H_4Ac, and several analogous reactions have also been reported [194].

D. Miscellaneous

The ^1H and ^{13}C NMR spectra of BuLi adducts of B-alkyl-9-BBN show greater shielding of the α-protons and α-carbons than in the free B-alkyl-9-BBN [195].

UV and proton NMR spectra of alkenylboranes show evidence of appreciable C-B π bonding [196]. Ab initio molecular orbital calculations have been reported for BH_3CO [197] [see also 129].

Reduction of Bu_2BCl with Na-K alloy does not yield Bu_2BK but a boron hydride species of uncertain composition [198]. Previous evidence for the existence of monomeric $PhCOBBu_2$ is incorrect.

E. Reviews

Lane and Kabalka have reviewed hydroboration with catecholborane [199]. Negishi has reviewed the chemistry of organoborates, R_4B^-, with emphasis on synthetically useful rearrangements which form carbon-carbon bonds [200]. The use of organoboranes for C-C bond formation has been reviewed [201]. Organoboron chemistry has been reviewed [202]. Hydroboration and organoborane chemistry has been reviewed in Japanese by three leading workers in the field, Suzuki, Utimoto, and Yamamoto [203, 204, 205].

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