BORON

ANNUAL SURVEY COVERING THE YEAR 1972

PART I: CARBORANES AND HYDROBORATION

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CONTENTS

I. Carboranes

A. *nido*-Anions (dicarbollides) and their complexes

1. *Introduction*. New discoveries regarding opening, closing, expanding, and contracting carborane cages continue to be reported, and together with work on smaller carboranes (Part B) provide the most novel and interesting developments in carborane chemistry.

Fundamentally, *closo*-carborane cages can be opened in two ways. Cleavage with base removes a boron (or other) atom from the cage, leaving a pentagonal open face, as in Hawthorne's synthesis of the dicarbollide monoanion $C_2B_9H_{12}^-$ from $C_2B_{10}H_{12}$. Addition of an electron pair by reduction with alkali metal can also open a pentagonal face in a *closo*-carborane, without removing any atoms from it. The reverse of these processes will close the open-faced anions to *closo*-carboranes. Thus, reaction of a dicarbollide dianion $C_2B_9H_{11}^{2-}$ with a Lewis acid such as $RBCl_2$ yields the *closo*-carborane $C_2B_{10}H_{11}R$, or with a transition metal cation forms the dicarbollide-transition metal complex having one vertex of the icosahedron occupied by the metal atom. Oxidation of $C_2B_9H_{11}^{2-}$ can yield the *closo*-carborane $C_2B_9H_{11}$.

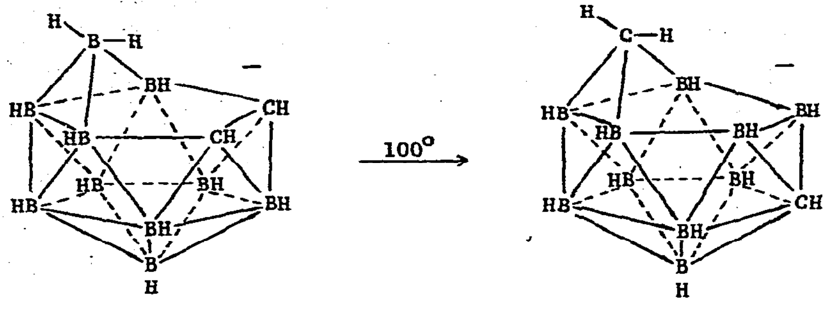
2. *Nomenclature*. The reader who is somewhat inexperienced with carborane chemistry can find information on nomenclature in earlier Annual Surveys, especially Organometal. Chem. Rev. B, 5 (1969) 1. The new borane nomenclature rules for numbering of *nido*-carboranes proposed by the American Chemical Society are being gradually adopted even by Hawthorne, whose own numbering system for dicarbollide anions makes more sense from the practicing

chemist's (as opposed to the abstractor and indexer's) point of view. However, readers must be cautioned that two very different numbering systems are in current use, and a structural formula or some familiarity with the chemistry is necessary in order to decipher what is meant by a name in any given instance.

Within this Annual Survey, the reader can find properly numbered icosahedral carboranes in Figs. 6 and 18, a dicarbollyl complex numbered according to Hawthorne's system in Fig. 2, a smaller dicarbollyl-type complex numbered according to the official system in Fig. 10, and a third approach to the numbering, assigning the metal atom number "1", in Fig. 13.

As has been the custom in these Surveys, the icosahedral carboranes will be referred to by the trivial names "*o*-carborane" for 1,2-dicarba-*closo*-dodecaborane(12), "*m*-carborane" for the 1,7-isomer, and "*p*-carborane" for the 1,12-isomer.

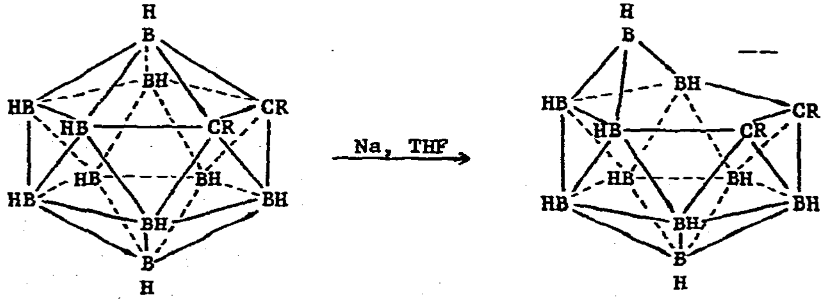
3. $C_2B_{10}H_{12}^{2-}$ anions and 13-atom cages. Zakharkin was the first to discover that alkali metals can add two electrons to the icosahedral carborane cage without removing any atoms, thus converting $C_2B_{10}H_{12}$ to $C_2B_{10}H_{12}^{2-}$. Hawthorne and coworkers in 1971 showed that this reduction opens a pentagonal face in the cage and thus amounts to a cage expansion, and they made a cobalt complex, $(C_5H_5)Co(C_2B_{10}H_{12})$, having a 13-atom polyhedral cage structure (see J. Organometal. Chem., 41 (1972) 14). Hawthorne's group has now reported the isolation of the tetramethylammonium salt of the derived monoanion, $C_2B_{10}H_{13}^-$. Reduction of *o*-$C_2B_{10}H_{12}$ with sodium in tetrahydrofuran gave the dianion (12)-7,8-$C_2B_{10}H_{12}^{2-}$, which on treatment with $BF_3 \cdot OEt_2$ and then H_2O yields (12)-7,8-$C_2B_{10}H_{13}^-$ (numbered according to the new American Chemical Society rules). The tetramethylammonium salt undergoes anion rearrangement at 100° to form (12)-3,13-$C_2B_{10}H_{13}^-$, structure assigned on the basis of nmr spectra, and further pyrolysis at 200° yields the icosahedral carborane $Me_3NBH_2C_2B_{10}H_{11}$ and dicarbollide monoanion $C_2B_9H_{12}^-$ (1).

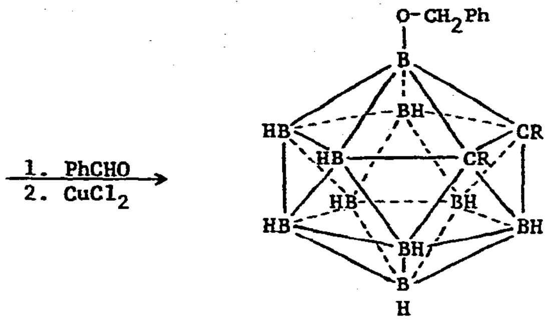


$(12)\text{-}7,8\text{-}C_2B_{10}H_{13}^{-}$ $(12)\text{-}3,13\text{-}C_2B_{10}H_{13}^{-}$

Zakharkin and Kalinin have prepared the $(12)\text{-}7,8\text{-}C_2B_{10}H_{12}^{2-}$ dianion, reacted it with cobalt chloride to produce a cobalt complex similar to that previously reported by Hawthorne and coworkers, and then isomerized the cobalt complex by refluxing it in tetrahydrofuran (2). Oxidation with cupric chloride was found to remove the cobalt from the rearranged cage to generate m-carborane. It was noted that this isomerization proceeds under much milder conditions of temperature than the usual ortho- to meta-carborane rearrangement, which requires 400-500°.

Kalinin and Zakharkin have also found that the anions $R_2C_2B_{10}H_{10}^{2-}$ will reduce aldehydes in a manner analogous to that of BH_4^-, except that the most exposed boron atom of the opened cage bonds firmly to the carbonyl oxygen. The initially formed anionic product is oxidized with cupric chloride to again form the closo-o-carborane, which then has the alkoxy group bonded to boron at the 3-position of the icosahedron (3).





4. Transition metal dicarbollide and related complexes. The most interesting new developments in this area involve various cage expansions and contractions studied by Hawthorne and coworkers. Both the base-acid and reduction-oxidation approaches to cage opening and closing, already described in subsection 1, have been used for this work.

Degradation of $(C_5H_5)Co(C_2B_9H_{11})$ with aqueous base followed by oxidation with hydrogen peroxide has yielded the cage-contracted product $(C_5H_5)Co(C_2B_8H_{10})$ (Structure II in Fig. 1) (4). Further transformations of this product included opening the cage and removing a boron atom with $FeCl_3$ in refluxing ethanol to produce a nido-dicarbollylcobalt complex, pyrolysis to a closo-B_7-dicarbollylcobalt complex, and pyrolytic rearrangements of the closo-B_7-dicarbollylcobalt complex (Fig. 1). Similar B_7 compounds have been prepared previously by other methods (Organometal. Chem. Rev. B, 6 (1970) 331-332). Analogous degradation of $Co(C_2B_9H_{11})_2^-$ to $(C_2B_9H_{11})Co(C_2B_8H_{10})$ was also carried out (4).

The contracted cage compound $(C_5H_5)Co(C_2B_8H_{10})$opens to a nido-derivative $(C_5H_5)Co(C_2B_8H_{10}-NC_5H_5)$ on treatment with pyridine (5). The analogous $(C_2B_9H_{11})Co(C_2B_8H_{10})$ behaves similarly (5), and Churchill and Gold have reported the crystal structure of the pyridine derivative (Fig. 2) (6).

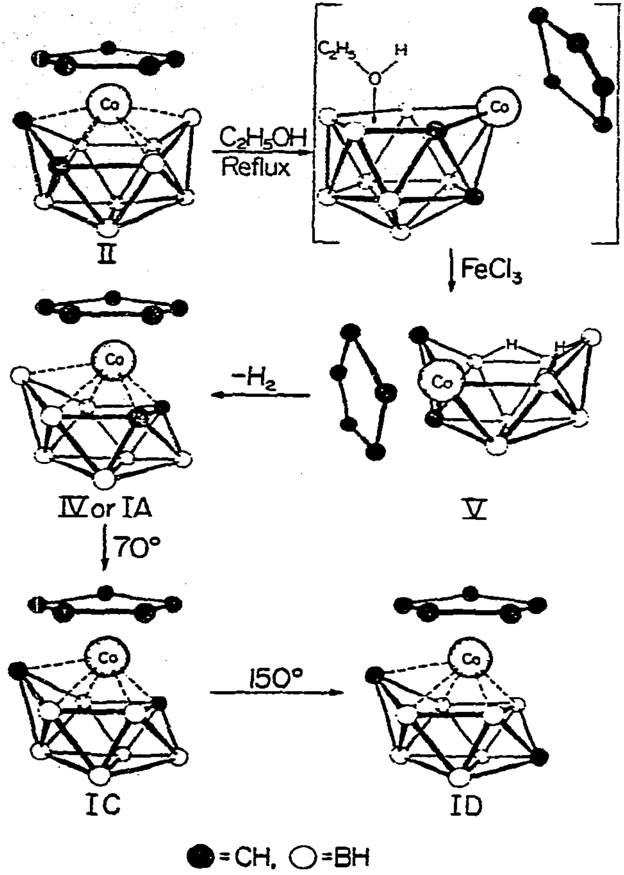


Fig. 1. Reaction scheme for the degradation of II by $FeCl_3$ to give V, followed by elimination of H_2 from V to give $[(\pi\text{-}C_5H_5)\text{-}Co(\pi\text{-}(2)\text{-}6,7\text{-}B_7C_2H_9)]$. [From C. J. Jones, J. N. Francis, and M. F. Hawthorne, J. Amer. Chem. Soc., 94 (1972) 8395.]

Reductive opening of a CoC_2B_8 cage has been observed by Evans and Hawthorne, who have treated $(C_5H_5)Co(C_2B_8H_{10})$ (an isomer of II in Fig. 1; for structure, See J. Organometal. Chem., 41 (1972) 16) with sodium naphthalide, and on reaction with NaC_5H_5 and $CoCl_2$ obtained the biscobalt dicarbacanastide complex $(C_5H_5)Co(C_2B_8H_{10})Co(C_5H_5)$ (Fig. 3) (7).

Substitution reactions of dicarbollide complexes have also provided some novel chemistry. Thermal decomposition of the benzenediazonium salt of bis-

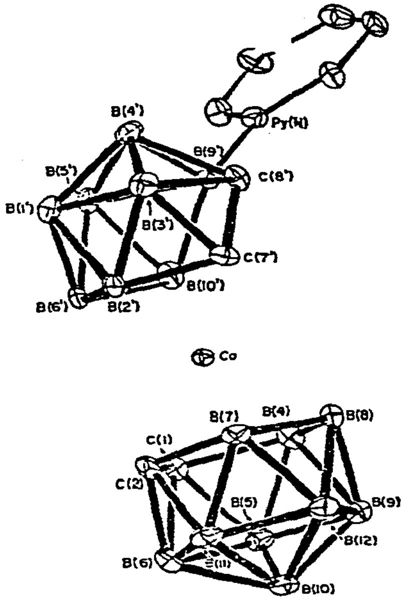


Fig. 2. Geometry of a [$(B_9C_2H_{11})Co(B_8C_2H_{10}\cdot C_5H_5N)^{2-}$] anion, with hydrogen atoms omitted. (The conventional nomenclature leads to the depicted B_8C_2 ion having a rather different numbering scheme to its enantiomer <u>viz.</u>, [π-(11)-7,8-$B_8C_2H_{10}$-9-$C_5H_5N^{2-}$] <u>vs.</u> [π-(9)-7,8-$B_8C_2H_{10}$-11-$C_5H_5N^{2-}$]). [From M. R. Churchill and K. Gold, J. Chem. Soc., Chem. Commun., (1972) 902.]

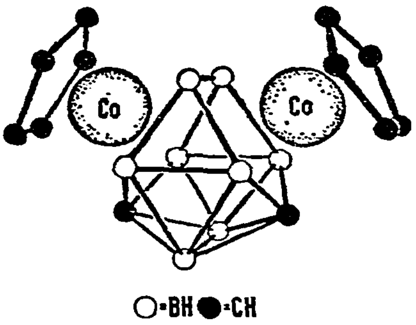


Fig. 3. A possible structure for $C_5H_5CoB_8C_2H_{10}CoC_5H_5$. [From W. J. Evans and M. F. Hawthorne, J. Chem. Soc., Chem. Commun., (1972) 611.]

(dicarbollyl)cobalt(III) in benzene at 60° has yielded a bis(dicarbollyl)-cobalt(III) anion having the two carborane cages linked by an *o*-phenylene group (Fig. 4) (8). By running the reaction with a toluenediazonium salt in benzene, Hawthorne and coworkers showed that the *o*-phenylene group is derived

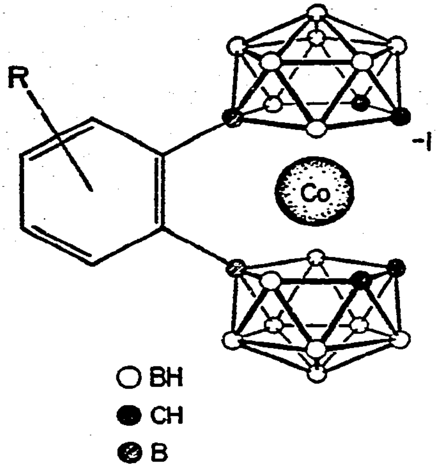


Fig. 4. The proposed structure of the anion $[(\pi\text{-}7,8\text{-}B_9C_2H_{10})_2\text{-}C_6H_3RCo]^-$ (R = H or CH_3). [From J. N. Francis, C. J. Jones, and M. F. Hawthorne, J. Amer. Chem. Soc., 94 (1972) 4879.]

from the solvent, and the evidence suggests that a free radical mechanism is involved.

Beer and Todd have found that the photochemical reaction of chromium, molybdenum, or tungsten carbonyl with $Fe(1,7\text{-}CB_9H_{10}P)_2^-$ or $Fe(1,7\text{-}CB_9H_{10}As)_2^-$ leads to phosphorus- or arsenic-linked complexes of the metal carbonyl (Fig. 5) (9).

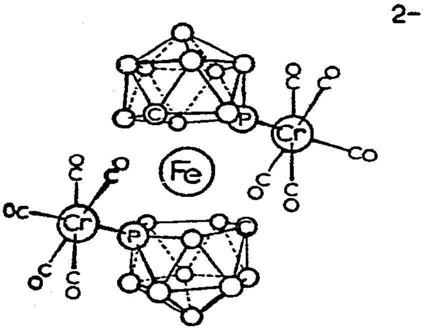


Fig. 5. Proposed structure of the $([1,7\text{-}B_9H_9CHP\cdot Cr(CO)_5]_2Fe)^{2-}$ ion and related complexes. [From D. C. Beer and L. J. Todd, J. Organometal. Chem., 36 (1972) 83.]

More examples of thermal rearrangement of dicarbollide complexes have been reported. μ-1,2-Trimethylene-o-carborane (Fig. 6) has been prepared from dilithio-o-carborane and 1,3-dibromopropane and has been converted to the corresponding dicarbollide ion and its cobalt and nickel complexes (10). The nickel(II) and nickel(III) complexes are interconvertible, but rearrangements occur on oxidation to nickel(IV) (Fig. 7).

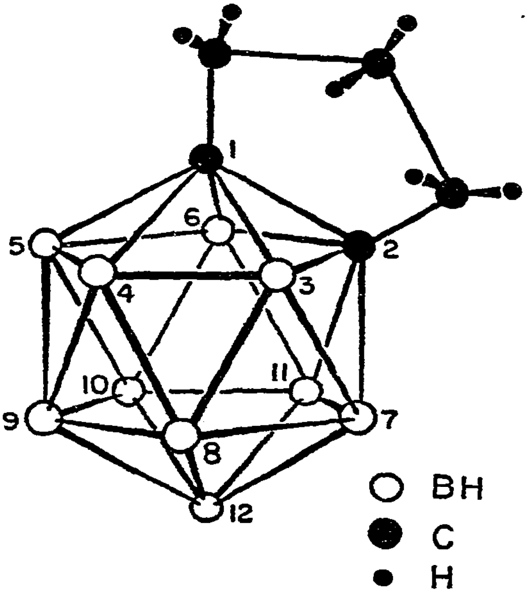


Fig. 6. Proposed structure of μ-1,2-trimethylene-1,2-dicarba-closo-dodecaborane(12). [From T. E. Paxson, M. K. Kaloustian, G. M. Tom, R. J. Wiersema, and M. F. Hawthorne, J. Amer. Chem. Soc., 94 (1972) 4882.]

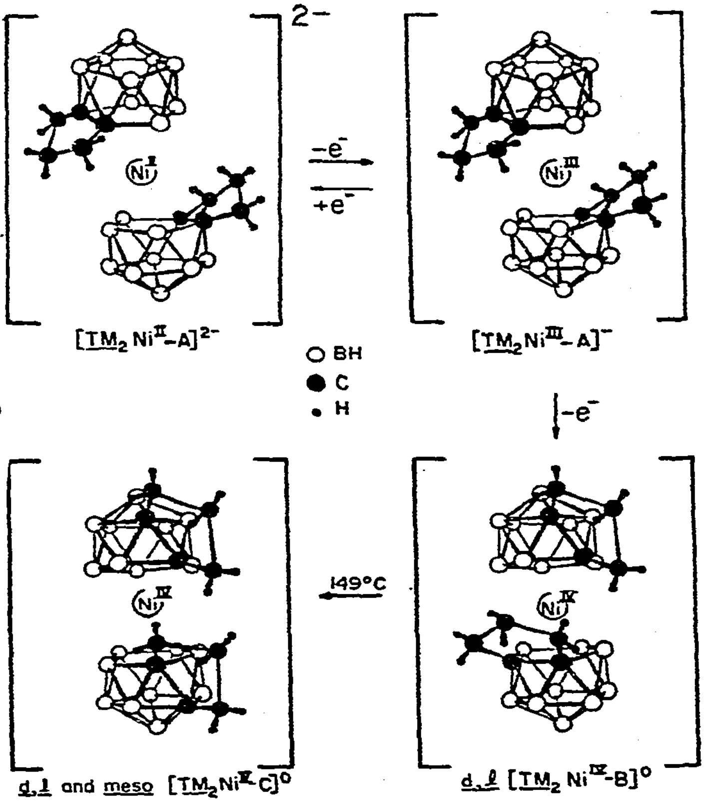


Fig. 7. Reaction sequence and stereochemistry of the bis(π-μ-1,2-trimethylene-1,2-dicarbollyl)nickel system. [From T. E. Paxson, M. K. Kaloustian, G. M. Tom, R. J. Wiersema, and M. F. Hawthorne, J. Amer. Chem. Soc., 94 (1972) 4884.]

Like *o*-carborane itself, dicarbollylcobalt(III) complexes of the type $(C_5H_5)Co(C_2B_9H_9R_2)$ rearrange at 400° and above. Structures of some of the compounds isolated were shown in last year's annual survey (JOM 41 (1972) 17), based on the preliminary communication, and the full paper on this work has now appeared (11).

The crystal structure of one of the isomers of $NEt_4^+\ Co(C_2B_7H_9)_2^-$ (Hawthorne's "bisdicarbazapylcobalt" ion, Organometal. Chem. Rev. B, 6 (1970) 331) has been determined (Fig. 8) (12).

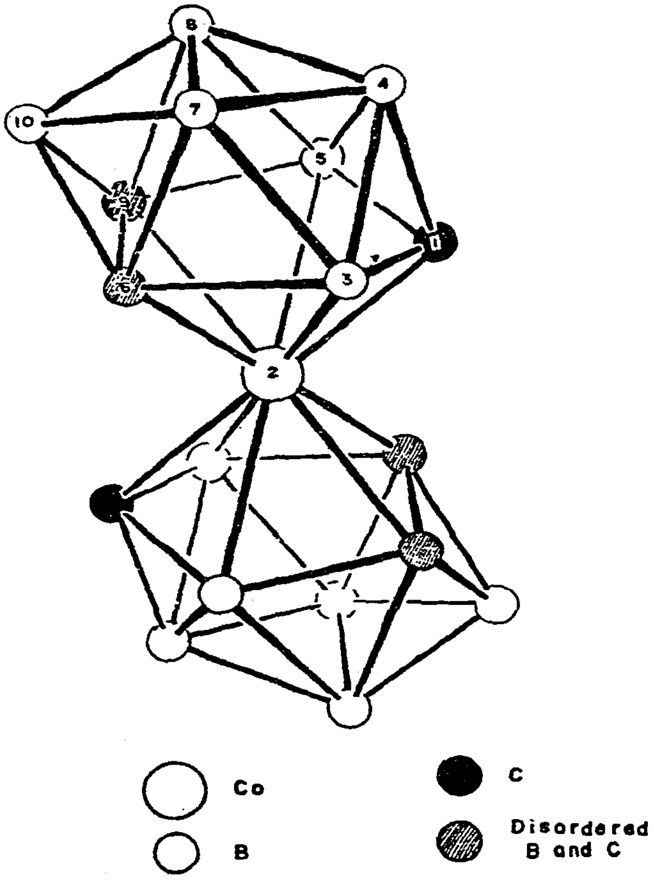


Fig. 8. Skeletal drawing of the $Co(B_7C_2H_9)_2^-$ anion. [From D. St. Clair, A. Zalkin, and D. H. Templeton, Inorg. Chem., 11 (1972) 378.]

Dicarbollide anion analogs in the smaller size range can be made by abstracting a proton from a nido-carborane and have been investigated by Grimes and coworkers. Reaction of $Na^+C_2B_4H_7^-$ with $(C_5H_5)Fe(CO)_2I$ yields μ-$[(C_5H_5)Fe(CO)_2]C_2B_4H_7$, which apparently contains a B-Fe-B bridge bond, and this compound on ultraviolet irradiation loses carbon monoxide to form a mixture of $(C_5H_5)Fe(C_2B_4H_7)$ and $(C_5H_5)Fe(C_2B_4H_6)$ (Fig. 9) (13).

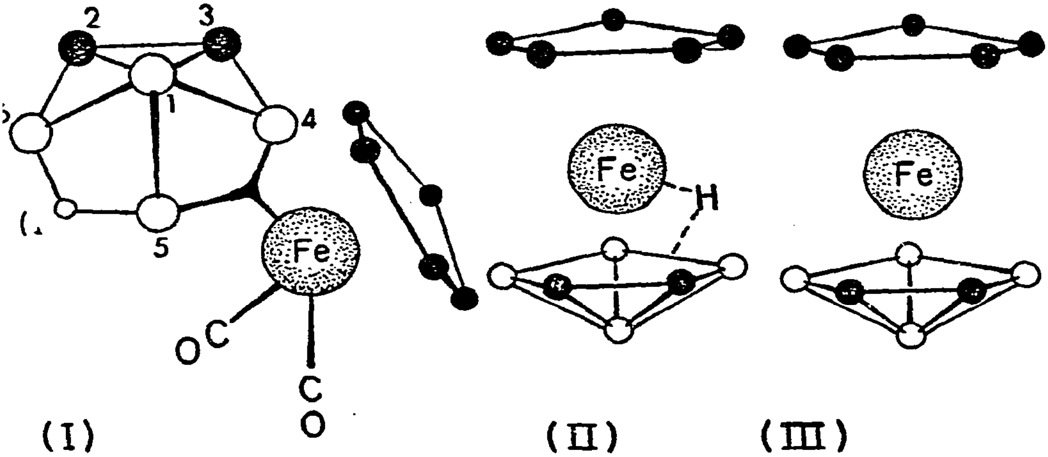


Fig. 9. Proposed structures of μ-$[(\pi\text{-}C_5H_5)Fe(CO)_2]C_2B_4H_7$ (I), $(\pi\text{-}C_5H_5)$-$Fe^{II}(\pi\text{-}C_2B_4H_7)$ (II), and $(\pi\text{-}C_5H_5)Fe^{III}(\pi\text{-}C_2B_4H_6)$ (III). The solid circles represent CH groups and the open circles BH groups. A possible location for anomalous hydrogen atom in II, involving partial bonding to iron and to the carborane cage, is indicated schematically. If an Fe-H bonding interaction exists in II, the C_5H_5 and carborane rings are likely to be skewed relative to each other. [From L. G. Sneddon and R. N. Grimes, J. Amer. Chem. Soc., 94 (1972) 7162.]

Methyl-substituted derivatives of the three-carbon nido-carborane $C_3B_3H_7$ (Fig. 10) have been studied by Howard and Grimes (14). 2-CH_3-2,3,4-$C_3B_3H_6$ reacts with sodium hydride in tetrahydrofuran to form Na^+ $CH_3C_3B_3H_5^-$. Either reaction of this sodium salt with $BrMn(CO)_5$ or reaction of $CH_3C_3B_3H_6$ with $Mn_2(CO)_{10}$ in the gas phase at 175-200° yielded the manganese complex $(CH_3C_3B_3H_5)Mn(CO)_3$ (Fig. 11).

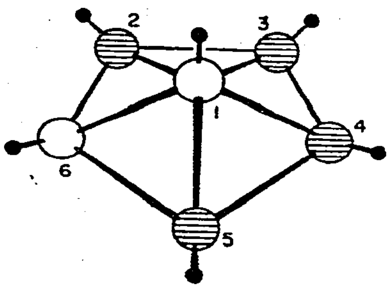


Fig. 10. Structure of the $C_3B_3H_7$ cage system. Shaded circles represent carbon atoms, and open circles, boron.

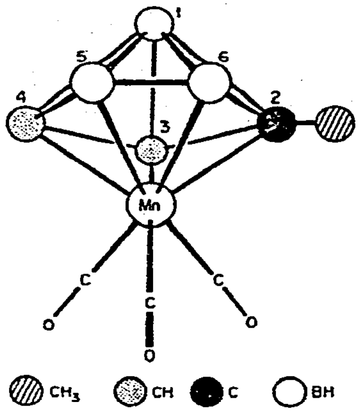


Fig. 11. Proposed structure of (π-2-$CH_3C_3B_3H_5$)$Mn(CO)_3$.

[Figs. 10 and 11 from J. W. Howard and R. N. Grimes, Inorg. Chem., 11 (1972) 264.]

5. Dicarbollide and related chemistry of nontransition elements.

Some of this chemistry has already been covered in the process of discussing the transition metal complexes and will not be repeated here. What remains includes cage openings by bases, compounds formed by combination of a group III element with a dicarbollide-type anion, and a removal of phosphorus from a phosphacarborane. Other phosphacarborane and arsacarborane chemistry is included in Part C on icosahedral carboranes.

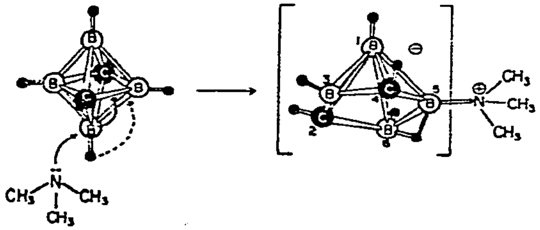
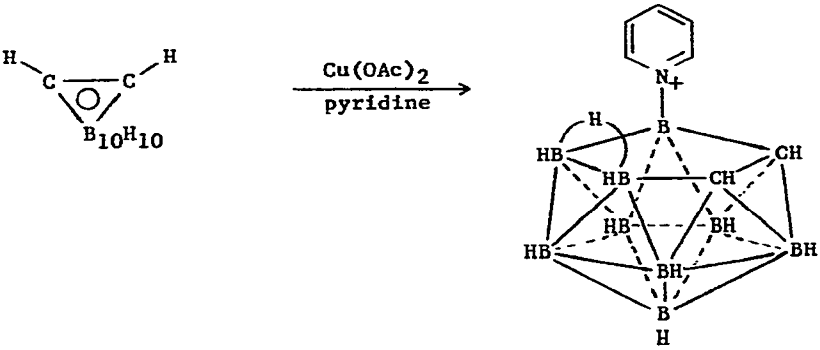


Fig. 12. Reaction of 1,6-$C_2B_4H_6$ with trimethylamine to give 5-$(CH_3)_3N^+$-[2,4-$C_2B_4H_6^-$] (proposed overall mechanism). [From B. Lockman and T. Onak, J. Amer. Chem. Soc., 94 (1972) 7923.]

Trimethylamine opens the *closo*-carborane 1,6-$C_2B_4H_6$ to a zwitterionic *nido*-carborane (Fig. 12) (15).

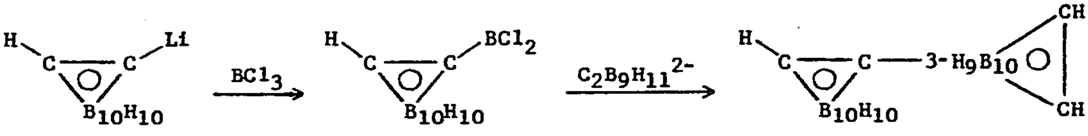
Heating *o*-carborane with copper(II) acetate and aqueous pyridine followed by acidification has yielded 9-pyridinium-7,8-dicarba-*nido*-undecaborate(12), and various substituted analogs have been similarly prepared (16).



Oxidation of the protonated *o*-dicarbollide anion, $C_2B_9H_{12}^-$, with $FeCl_3$ in aqueous acid has yielded 5,6-dicarba-*nido*-decaborane, which eliminates hydrogen on treatment with N-ethylpiperidine-borane at 120° to form the *closo*-carborane 1,2-$C_2B_8H_{10}$ (17).

The crystal structure of $C_2B_9H_{12}AlMe_2$ has been determined at -100° and the full details have been published (18). The Me_2Al group bridges between two boron atoms in the open face of the dicarbollide group. (For a drawing of the structure, see J. Organometal. Chem., 41 (1972) 25.) Full details of the crystal structure of 3-ethyl-3-alumina-*o*-carborane have been published (19). (For a drawing of the structure, see J. Organometal. Chem., 41 (1972) 26.)

Zakharkin and Kozlova have synthesized C-B linked bis-*o*-carboranes (20).



Trimethylgallium reacts with the <u>nido</u>-carborane 2,3-$C_2B_4H_8$ to form $CH_3GaC_2B_4H_6$ (Fig. 13), which has been characterized by nmr, mass, and infrared spectra and also by X-ray diffraction. The unexpected geometry of the Ga-CH_3 group was interpreted by Grimes and coworkers as being the result of back bonding from a filled d orbital of the gallium to an antibonding molecular orbital of the carborane ligand. A similar indium compound was prepared (21).

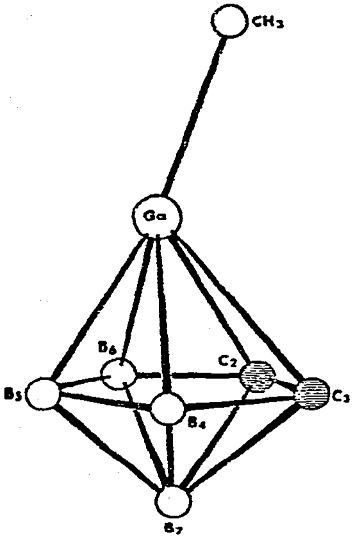
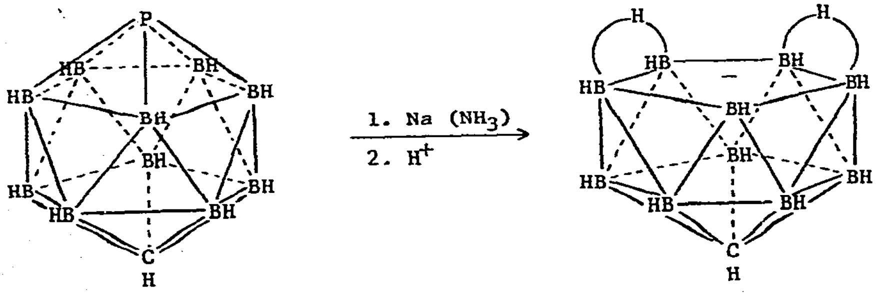


Fig. 13. Structure of 1-$CH_3GaC_2B_4H_6$. [From R. N. Grimes, W. J. Rademaker, M. L. Denniston, R. F. Bryan, and P. T. Greene, J. Amer. Chem. Soc., 94 (1972) 1867.]

Todd and coworkers have found that phosphorus or arsenic is removed from 1,2-$CB_{10}H_{11}P$ or 1,12-$CB_{10}H_{11}As$ on treatment with sodium in liquid ammonia, yielding the anion 1-$CB_{10}H_{13}^-$ (22).



B. Smaller carboranes

1. closo-Carboranes. The smaller $C_2B_nH_{n+2}$ carboranes are all known and only a few details have been added to their chemistry during the past year. The cage opening described in Part A-5 (Fig. 12) (15) should be noted.

Ditter, Klusmann, and Williams have patented the preparation of $C_2B_6H_8$, $C_2B_8H_{10}$, and $C_2B_{10}H_{12}$ by pyrolysis of $C_2B_5H_7$ in the presence of B_2H_6 (23). Small amounts of B-methyl closo-carboranes are formed as by-products in the pyrolysis of acetylene and pentaborane to produce the smaller closo-carboranes (24).

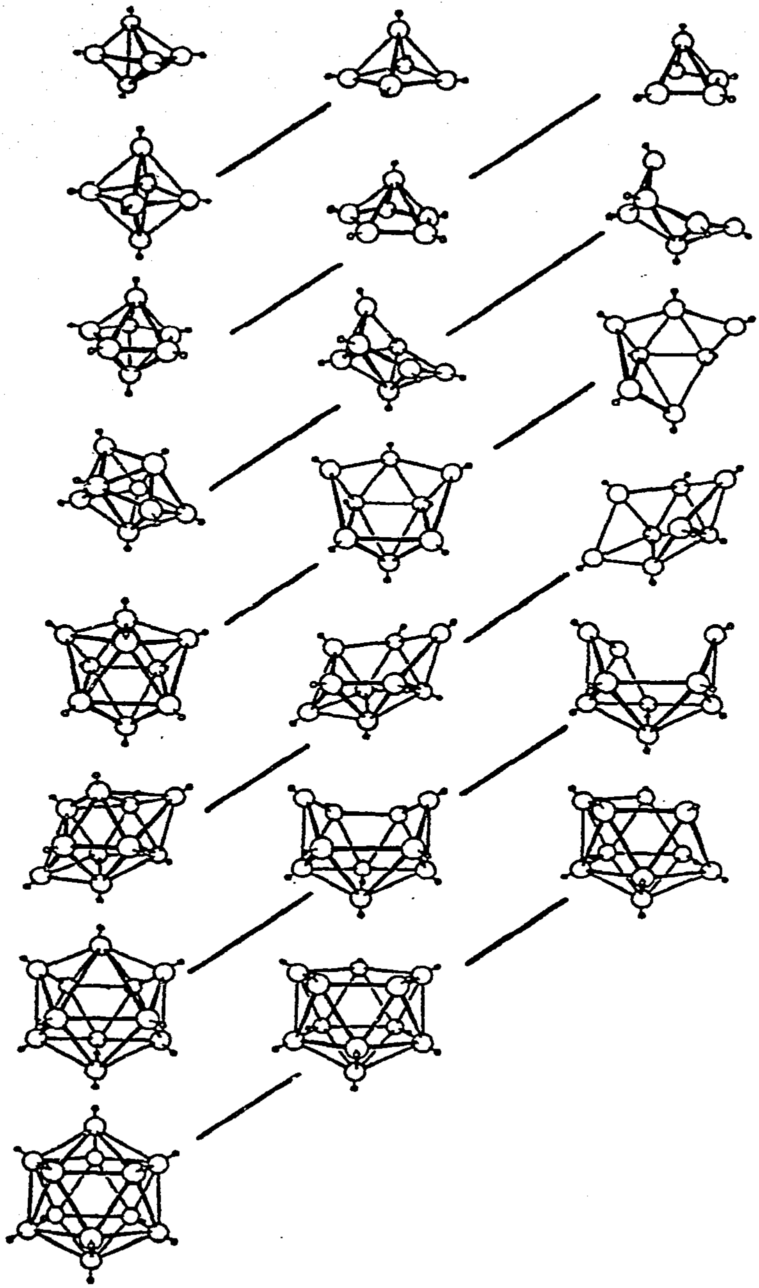
Burg and Reilly have studied some of the chemistry of 1,5-$C_2B_3H_5$ (25). The trimethylamine adduct is stable at -78° but polymerizes rapidly on melting. $C_2B_3H_5$ itself polymerizes after several weeks at 25°. Chlorination yielded polymeric product. $C_2B_3H_5$ hydroborates methylacetylene to form the B-propenylcarborane.

Pyrolysis of trimethylborane at 500° has yielded a mixture of $Me_2BCH_2BMe_2$ and the carboranes $C_2H_3(BMe)_3$ and $C_4H_4(BMe)_6$ (26).

Marynick and Lipscomb have presented an interpretation of quantum mechanical calculations on 1,6-$C_2B_4H_6$ and other small carboranes in terms of fractional three-center bonds (27). They have also published detailed results of self-consistent field calculations on the closo-carborane 2,4-$C_2B_5H_7$ (28) and the nido-carborane 4,5-$C_2B_4H_8$ (29), complete with a number of electron density maps and localized orbital descriptions.

2. nido-Carboranes. The nido-carboranes are generally more reactive and less thoroughly studied than the closo-carboranes, and the volume of new literature in this area is much greater.

New theoretical work on carborane structures has continued to appear. (Note also Lipscomb's calculations mentioned in the preceding subsection.) Rudolph and Pretzer have presented a theoretical analysis of bonding rules for closo-, nido-, and arachno-carboranes (Fig. 14) (30). For stability,



the magic numbers of framework electron in the closo series are 2n + 2, in the nido series 2n + 4, and in the arachno series 2n + 6, where n is the number of cage boron or carbon atoms.

Onak and coworkers have found that the negative ion mass spectra of the nido-carboranes 2,3-$C_2B_4H_8$, 2-CH_3-2,3-$C_2B_4H_7$, and 2,3-$(CH_3)_2$-2,3-$C_2B_4H_6$ yield the P - 1 anion by loss of hydrogen as well as further fragmentation by loss of BH_3 (31). The negative ion mass spectrum of 2,3-$C_2B_4H_8$ shows strong peaks corresponding to the closo-anions $C_2B_4H_5^-$ and $C_2B_3H_4^-$ (32).

The nido-carborane 6,9-$C_2B_8H_{14}$, which is isoelectronic with $B_{10}H_{14}^{2-}$ (part D) and the decaborane-ligand complexes $B_{10}H_{12}L_2$ (where L is CH_3CN, R_2S, etc.), has been assigned the structure analogous to these boranes on the basis of its boron-11 nmr, mass, and infrared spectra (33).

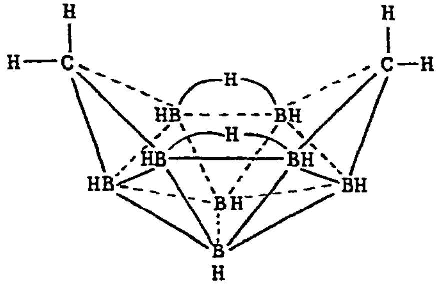


Fig. 14. Idealized structures for closo, nido, and arachno boranes and heteroboranes. From left to right, the vertical columns give the basic closo, nido, and arachno frameworks; bridge hydrogens and BH_2 groups are not shown, but when appropriate, they are placed around the open face of the framework in a manner which preserves the symmetry of the basic nido or arachno framework. Any nido or arachno structure can be derived from the appropriate deltahedron by ascending a diagonal from left to right; this progression generates the nido structure by removing the most highly connected vertex of the deltahedron; the arachno structure is generated by removing the most highly connected atom in the open face of the nido structure. Each horizontal row indicates the basic structural changes which occur as the number of framework electrons is varied from 2n + 2 to 2n + 4 to 2n + 6. It appears that these correlations can be extended to include a 12-atom nido framework: G. B. Dunks, M. M. McKown, and M. F. Hawthorne, J. Amer. Chem. Soc., 93, 2541 (1971). [From R. W. Rudolph and W. R. Pretzer, Inorg. Chem., 11 (1972) 1975.]

Grimes and coworkers have synthesized several new nido-carboranes. In the direction of replacing almost all of the boron of a carborane with carbon, the reaction of 1,2-$C_2B_3H_7$ with acetylene yields $C_4B_2H_6$, which has a pentagonal pyramid structure (Fig. 15). By studies with isotopically labeled and methyl substituted acetylenes the reaction was shown to involve direct alkyne insertion into the carborane cage, primarily with C-B but also with some C-C bond breaking (34).

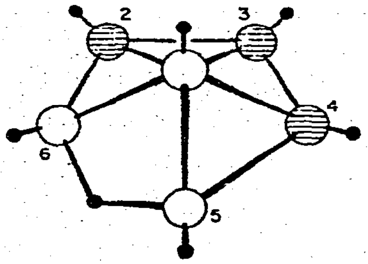
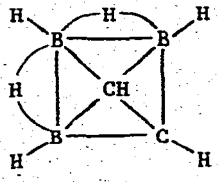


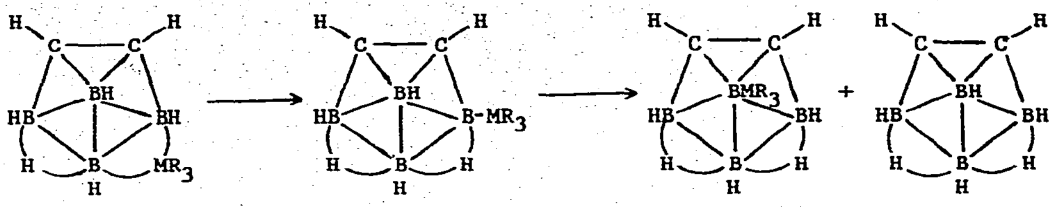
Fig. 15. Structure and numbering system for $C_4B_2H_6$. Boron atoms are open and carbon atoms are shaded. [From V. R. Miller and R. N. Grimes, Inorg. Chem., 11 (1972) 863.]

The nido-carborane 1,2-$C_2B_3H_7$ has been obtained from the reaction of tetraborane(10) with acetylene and several of its reactions reported, including its rapid polymerization in the liquid state (35).



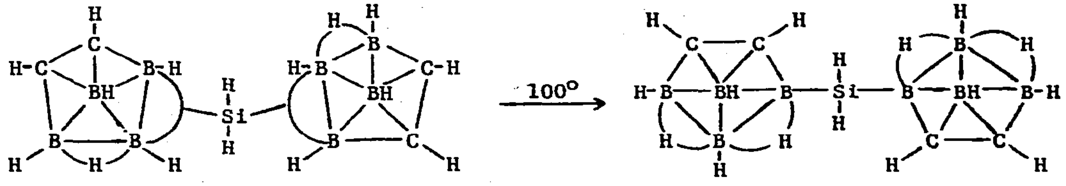
1,2-$C_2B_3H_7$

The μ-silyl and μ-germyl derivatives of $C_2B_4H_8$ have been obtained from reactions of the anion $C_2B_4H_7^-$ with H_3SiCl, Me_2SiCl, H_3GeCl, and Me_3GeCl (36). On heating these rearrange to σ-bonded silylcarboranes and eventually to closo-carboranes.

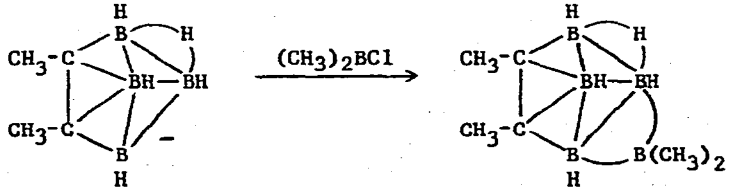


M = Si or Ge, R = H or Me

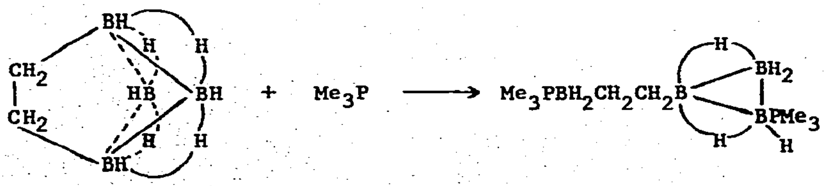
Reaction of H_2SiCl_2 with two moles of $Na^+C_2B_4H_7^-$ in tetrahydrofuran at 0° has yielded the B-Si-B bridged compound μ,μ'-$SiH_2(C_2B_4H_7)_2$, which rearranges to 4,4'-$SiH_2(C_2B_4H_7)_2$ at 100° (37).



Savory and Wallbridge have obtained μ-substituted derivatives of $Me_2C_2B_4H_5^-$ by reaction with Me_3SiCl, Me_3GeBr, Me_2BCl, and Me_2SiCl_2 (38).



Bowen and Phillips have reported that trimethylphosphine opens 2,4-dimethylenetetraborane at 0° (39).



C. Icosahedral carboranes and related topics

1. Introduction. Two new developments in σ-bonded transition metal complexes are described in subsection 2, and a possibly handy laboratory preparation of o-carborane at the beginning of subsection 3. The remaining coverage is not strictly restricted to icosahedral carboranes but also includes a few references to C_2B_8 carboranes, phosphacarboranes, and a phosphacarbollide--transition metal complex. What the items in subsections 3 (synthesis) and 4 (physical organic) really have in common is that they are all straightforward extensions of well-known carborane chemistry. If a chemist had a five-year plan with a numerical quota of publications to fulfill, he would be shrewd to pick the carborane system with its high stability and good chemical predictability, yet not too much prior literature, for his research. It turns out that 89% of the references in these two subsections are Russian.

2. Transition metal σ-complexes. The crystal structure of NEt_4^+ $Co[(C_2B_{10}H_{10})_2]_2^-$, which was prepared from 2,2'-dilithiobiscarborane and

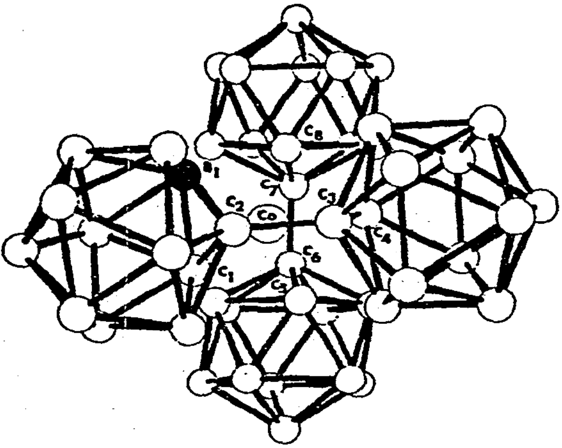


Fig. 16. The structure of the $Co[(B_{10}C_2H_{10})_2]_2^-$ anion.

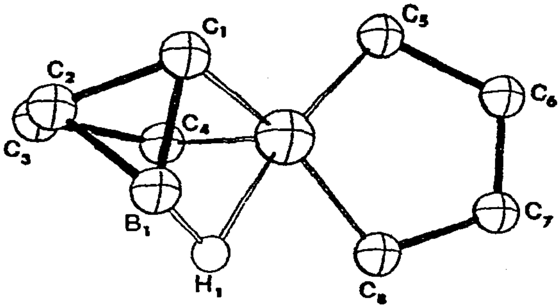
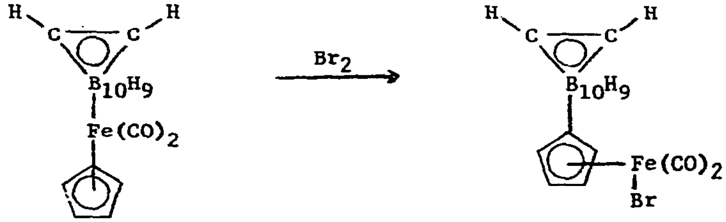


Fig. 17. The coordination about the cobalt atom, simplified to show only the atoms in the immediate vicinity of the cobalt atom.

[Figs. 16 and 17 from R. A. Love and R. Bau, J. Amer. Chem. Soc., 94 (1972) 8275.]

cobalt chloride, has been determined (Fig. 16). The bonding around the cobalt atom is unusual in that it includes a B-H-Co bond as well as the four C-Co bonds (Fig. 17) (40).

Zakharkin and coworkers have found that halogenation of 3-*o*-$C_2B_{10}H_{11}$-$Fe(C_5H_5)(CO)_2$ (Fig. 18) results in rearrangement to a B-carboranyl-substituted cyclopentadiene-iron complex (41,42).



(See Fig. 18 for
detailed structure)

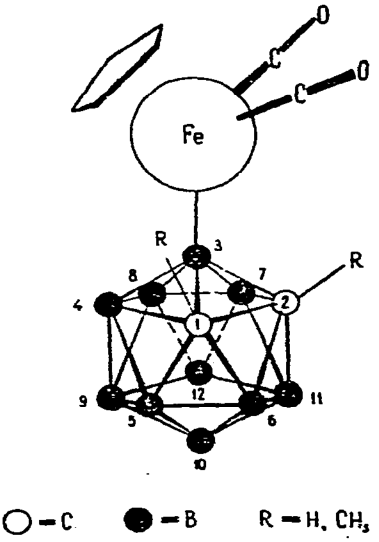
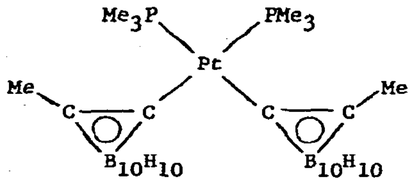
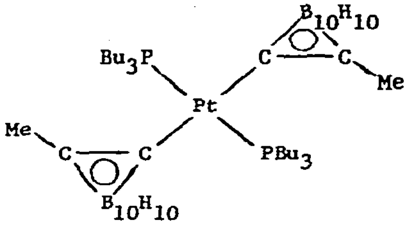


Fig. 18. The proposed structure and numbering system for 3-[π-$C_5H_5Fe(CO)_2$]-σ-$B_{10}C_2H_{11}$ dimethyl derivative. [From L. I. Zakharkin, L. V. Orlova, B. V. Lokshin, and L. A. Federov, J. Organometal. Chem., 40 (1972) 15.]

Several σ-bonded platinum complexes of C-methyl-o-carborane have been prepared (43).



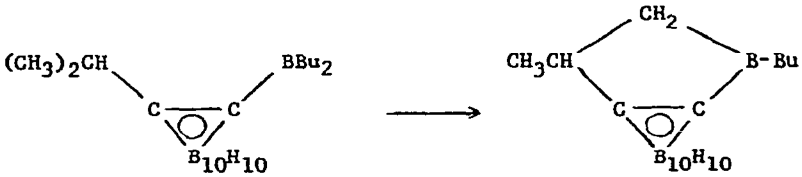


3. Synthetic chemistry of carboranes. Beall has described a simplified one-step preparation of o-carborane from solid decaborane-ligand complexes and gaseous acetylene, in which the o-carborane sublimes directly from the reaction mixture (44).

In the field of lithiocarborane chemistry, Zakharkin and coworkers have converted 1-Ph-1,6- and -1,10-CB_8H_8CH to their C-lithio derivatives, $PhCB_8H_8CLi$, and converted these to such typical C-substituted compounds as $(PhCB_8H_8C)_2Hg$, $PhCB_8H_8CSiMe_3$, and $(PhCB_8H_8C)_3P$ (45). Reaction of various lithiocarboranes $LiCB_{10}H_{10}CR$ with $PhOCH(OEt)_2$ yields $(EtO)_2CH\text{-}CB_{10}H_{10}CR$, which can be hydrolyzed to the formylcarboranes $OHC\text{-}CB_{10}H_{10}CR$ (46). 1-Methyl-2-phenylazo-o-carborane, $MeCB_{10}H_{10}C\text{-}N{=}N\text{-}Ph$, and related compounds have been prepared by two routes, the reaction of $MeCB_{10}H_{10}CLi$ with $PhN_2{}^+BF_4{}^-$ and the reaction of $MeCB_{10}H_{10}C\text{-}N{=}O$ with $PhNH_2$ (47). m-Carboranyllithium and $(Et_2N)_2PCl$ have yielded $HCB_{10}H_{10}C\text{-}P(NEt_2)_2$, which was converted to $HCB_{10}H_{10}C\text{-}PCl_2$ by HCl. Hydrolysis of the dichloride gave $HCB_{10}H_{10}C\text{-}P(OH)_2$, and chlorination of the dichloride followed by hydrolysis yielded $HCB_{10}H_{10}C\text{-}PO_3H_2$ (48). A number of 1-alkenyl-2-phosphino-o-carboranes have been prepared by the reaction of $CH_2{=}CH\text{-}CB_{10}H_{10}CLi$ or various analogs with Ph_2PCl or $(Et_2N)_2PCl$ (49). More synthesis of carboranyl phosphorus compounds such as PhPCl-o-$(CH_3)C_2B_{10}H_{10}$ and various biscarboranylphosphorus and cyclic bis(carboranylphosphorus) compounds have been reported (50). Treatment of 1-$HOCH_2$-o-

$C_2B_{10}H_{11}$ with SF_4 has yielded 1-FCH_2-o-$C_2B_{10}H_{11}$, which has been converted to the 2-lithio derivative and from there to the 2-methyl, 2-carboxyl, 2-chloromercuri, and 2-trifluorovinyl derivatives (51).

Mikhailov and Shagova have investigated carboranylborane chemistry. Reaction of o-$Me_2CHCB_{10}H_{10}CBCl_2$ with o-$Me_2CHCB_{10}H_{10}CLi$ has yielded $(Me_2CHCB_{10}H_{10}C)_2$-BOH (52). Reaction of o-Me_2CH-$CB_{10}H_{10}CLi$ with $ClBBu_2$ has yielded Me_2CH-$CB_{10}H_{10}C$-BBu_2, from which the butyl groups are cleaved on treatment with acetic acid to form $(Me_2CHCB_{10}H_{10}C$-$BOAc$-$)_2O$ (53). Heating 1-(dibutylboryl)-2-isopropyl-o-carborane at 200° closes a five-membered boron heterocyclic ring (54).



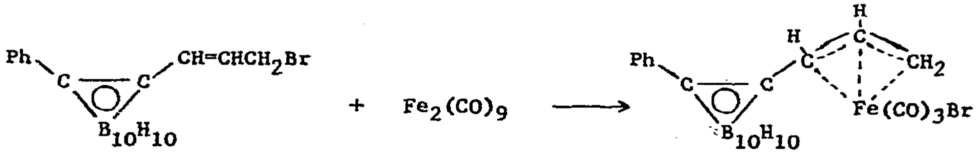
Stanko and Gol'tyapin have reported a study of metalation of p-carborane with sodamide and butyllithium and reactions of the metalated carborane with various electrophiles such as methyl iodide, ethylene oxide, sulfur, allyl bromide, and formaldehyde (55).

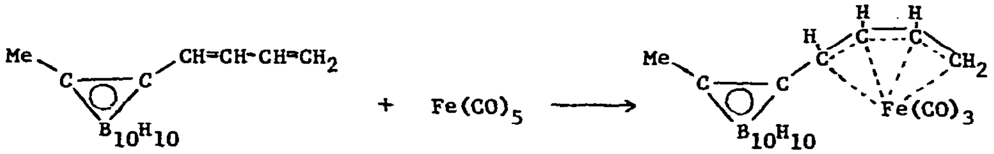
In more work by Zakharkin's group, reaction of $MeCB_{10}H_{10}CCH_2CH{=}CH_2$ with BuLi followed by CO_2 has yielded $MeCB_{10}H_{10}CCH_2CH{=}CHCO_2H$ and $MeCB_{10}H_{10}CCH$-$(CO_2H)CH{=}CH_2$ (56). Reactions of m-$CH_3CB_{10}H_{10}C$-$CF{=}CFCl$ and related fluoroalkenylcarboranes with nucleophiles such as RLi, RONa, or RONa result in substitution on the alkenyl group to form $CH_3CB_{10}H_{10}CCF{=}CRF$, etc., but secondary amines attack the carborane cage in preference to the fluoroalkenyl group (57). Both o- and m-$MeCB_{10}H_{10}C$-$CF{=}CFCl$ have been treated with BuLi to form $MeCB_{10}H_{10}C$-$CF{=}CFLi$, and the lithio compounds have been treated with water to form $MeCB_{10}H_{10}C$-$CF{=}CFH$, with CO_2 to form trans-$MeCB_{10}H_{10}C$-$CF{=}CFCO_2H$, and with $FClO_3$ to form $MeCB_{10}H_{10}$-C-$CF{=}CF_2$ (58). Butyllithium adds to the vinyl group of o-$MeCB_{10}H_{10}C$-$CH{=}CH_2$

to form $MeCB_{10}H_{10}C\text{-}CHLiCH_2C_4H_9$, which on treatment with CO_2 leads to $MeCB_{10}H_{10}\text{-}C\text{-}CH(CO_2H)CH_2C_4H_9$ (59).

A U. S. patent has been issued on the treatment of various dilithiocarboranes with sulfur followed by acid, which yields the dithiols, and with dialkyl disulfides, which yields the bis(alkylthio)carboranes (60). 1,12-$HSCB_{10}H_{10}CSH$ has been chlorinated to $ClSCB_{10}H_{10}CSCl$ and oxidized with sodium hypochlorite to $ClSOCB_{10}H_{10}CSOCl$ and the compounds have been patented (economists and environmentalists to the contrary notwithstanding) as high energy rocket fuels (61). Peracetic acid oxidizes *C*-MeS-*o*- or *m*-$C_2B_{10}H_{11}$ to $MeSOC_2B_{10}H_{11}$ and $MeSO_2C_2B_{10}H_{11}$ (62). The *o*-compounds are easily degraded with base to $MeSOC_2B_9H_{11}^-$ or $MeSO_2C_2B_9H_{11}^-$.

Returning to Zakharkin's work, ultraviolet irradiation of $(1,7\text{-}CB_9H_{10}PCH_3)\text{-}Mn(CO)_3$ in the presence of Ph_3P leads to replacement of one carbonyl group to form $(1,7\text{-}CB_9H_{10}PCH_3)Mn(CO)_2PPh_3$ (63). Preparations of carboranylallyl and carboranylbutadienyl iron complexes have been described (64).





Treatment of 9-iodocarborane with NaSPh in tetrahydrofuran followed by water yields the iododicarbollide monanion (65). In the same paper, removal of iodine from 2-iodo-*p*-carborane with sodium in liquid ammonia is described, and several unsuccessful attempts to couple iodocarboranes to form biscarboranes are recorded.

In other Russian work, several more carboranyl-substituted alcohols have been oxidized to ketones, aldehydes, or carboxylic acids (66). Reaction of o-carborane with Et_2N-SnR_3 at 120-140° results in tin substitution on the carborane carbon to form $R_3SnC_2B_{10}H_{11}$ (67). Heating Et_3SNNEt_2 with o-carborane at 120° has yielded $Et_3SnC_2B_{10}H_{11}$, and several other carboranes having a tin substituent on carbon have been similarly prepared (68).

Zakharkin and Kyskin have studied the preparation and alkaline cleavage of acyl-m-arsacarboranes, RCO-$CB_{10}H_{11}As$, where R is m-carboranyl, m-phosphacarboranyl, or phenyl (69), and yet another study of the halogenation of carboranylmagnesium halides with carbon tetrachloride has been reported (70).

4. Physical measurements. From ^{19}F nmr spectra of C-m- and -p-FC_6H_4-1,6- and -1,10-$C_2B_8H_9$, it has been concluded that both isomeric $C_2B_8H_9$ groups have weak electron withdrawing ability (71). Nitration of 1-Ph-1,10-$C_2B_8H_9$ was also reported. From the ^{19}F nmr chemical shifts in 1-(p-FC_6H_4)-1,7-$C_2B_6H_7$, 1-(p-FC_6H_4)-1,6-$C_2B_7H_8$, and their m-FC_6H_4 isomers it was concluded that both of these carborane cages have a weak inductive electron-withdrawing effect (72).

As might be expected, B-decachlorocarboranyl groups are more electron attracting than unsubstituted carboranyl groups, and C-phenyl-B-decachloro-o-carborane resists nitration under conditions considerably more vigorous than those required for nitration of C-phenyl-o-carborane. From the ^{19}F nmr chemical shifts of p- and m-fluorophenyl-B-decachlorocarboranes, it was found that σ_I = 0.87 and $\sigma_R{}^o$ = 0.10 for the 1-B-decachloro-o-carboranyl group and σ_I = 0.71 and $\sigma_R{}^o$ = 0.09 for the m-isomer (75).

From proton nmr spectra of p-$MeHgCB_{10}H_{10}CH$, p-$MeHgCB_{10}H_{10}As$, and p-$MeHgCB_{10}H_{10}P$ it has been concluded that the electron accepting power of the carboranyl groups increases in the order listed, and a similar order was found for the corresponding series of m-isomers (74). From rates of proton-deuteron exchange, the acidity of the C-H bond increases in the order m-$HCB_{10}H_{10}CH$, m-$HCB_{10}H_{10}As$, and m-$HCB_{10}H_{10}P$, in agreement with the relative electron attracting powers of these cage systems determined by other methods (75).

Metalation of 1-methyl-*o*-carborane with fluorenyllithium has been followed kinetically in diethyl ether at 25° but was too fast to measure in other ethers such as tetrahydrofuran (76). Equilibrium constants in various ether solvents were also measured. Rate constants for the reaction of *o*-carborane-1,2-dicarbonyl chloride, $C_2B_{10}H_{10}(COCl)_2$, with aniline to form the mono and dianilides have been reported (77). Infrared spectra of carboranyl substituted acetoacetic esters have been reported (78). Several liquid methylsilyl-substituted *m*-carboranes have been prepared and the molar refraction of the *m*-carborane nucleus has been found to be 44.61 cm^3 (79). Mössbauer spectra of 16 triethyltin derivatives of *o*-, *m*- and *p*-carborane have been measured, and the results are in accord with the *o*-carborane cage being the strongest electron acceptor and the *p*-isomer the weakest (80).

D. Polyhedral boranes

Alkylated polyhedral boranes are included here because by strict definition they are organometallic, though the reviewer's method of literature searching probably leaves out some references to these essentially inorganic compounds. A few references to nonalkylated polyhedral boranes are also included where the reviewer considered them to be of possible theoretical interest to carborane chemists.

The boron-11 nmr spectrum of $B_{10}H_{14}^{2-}$ (81) indicates that this anion has a structure analogous to $C_2B_8H_{14}$ (33)(part B-2), with which it is isoelectronic.

An analysis of boron-11 chemical shift data on 1- and 2-X-B_5H_8, where X is CH_3, C_2H_5, or halogen indicates that the chemical shifts can be accounted for semiquantitatively on the basis of resonance and inductive effects (82). Protonation of B_6H_{10} and 2-$CH_3B_6H_9$ has been shown to occur at the unbridged basal boron-boron bond (83). Tetra-*n*-butylammonium salts of $B_5H_8^-$ and $B_6H_9^-$ are stable and soluble in methylene chloride and other organic solvents (84). Both 1- and 2-methylpentaborane(9) form the same trimethylamine adduct, the structure of which is not yet certain (85).

The reaction of pentaborane(9) with liquid ammonia yields the $B_4H_7^-$ ion, which has a trigonal pyramid structure with a hydrogen bridge along each base of the pyramid (86).

King has presented a theoretical discussion of the possible borane-type polyhedra having up to twelve boron atoms (87). Self-consistent field calculations have been carried out on decaborane(14) by Lipscomb and coworkers (88).

E. Reviews

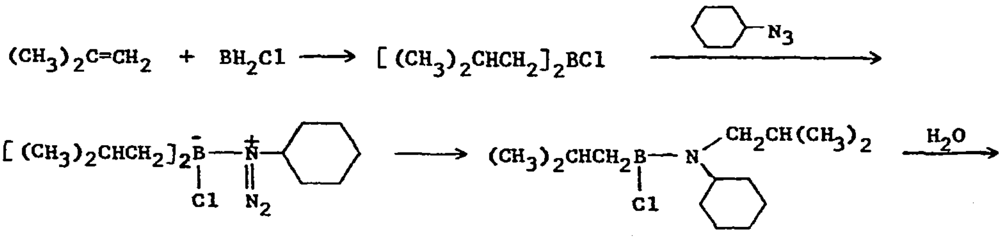
Hawthorne has reviewed recent developments in the chemistry of carborane-metal compounds (89), Todd has reviewed recent work in carborane chemistry (90), and Zakharkin has reviewed several aspects of carborane chemistry related to his work, including rearrangements of carboranes and B-halocarboranes, the anions formed on reduction of carboranes with alkali metals, and 3-amino-o-carborane (91). Other reviews of carborane chemistry have appeared (92,93).

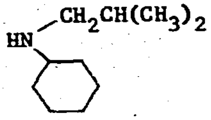
II. HYDROBORATION

A. Borane rearrangements and alkylations

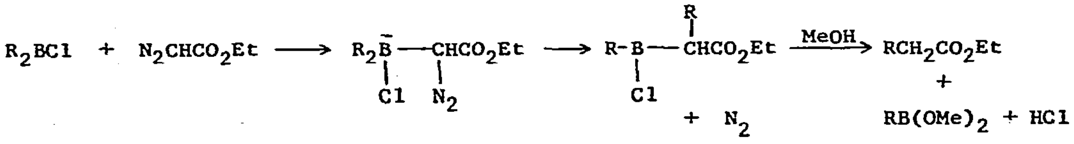
Hydroboration is becoming a relatively mature field, and emphasis is shifting toward applications rather than fundamental new discoveries in organoborane chemistry. However, several new discoveries have been made in the area of alkylation and rearrangement reactions of trialkylboranes, and as usual H. C. Brown and coworkers are major contributors in this field.

Monochloroborane, BH_2Cl, in diethyl ether readily hydroborates olefins to form dialkylchloroboranes (94). These react much more readily with organic azides than do trialkylboranes to form secondary amines (95).





Dialkylchloroboranes also undergo a facile and useful reaction with ethyl diazoacetate, extending an alkyl chain by two carbon atoms (96).

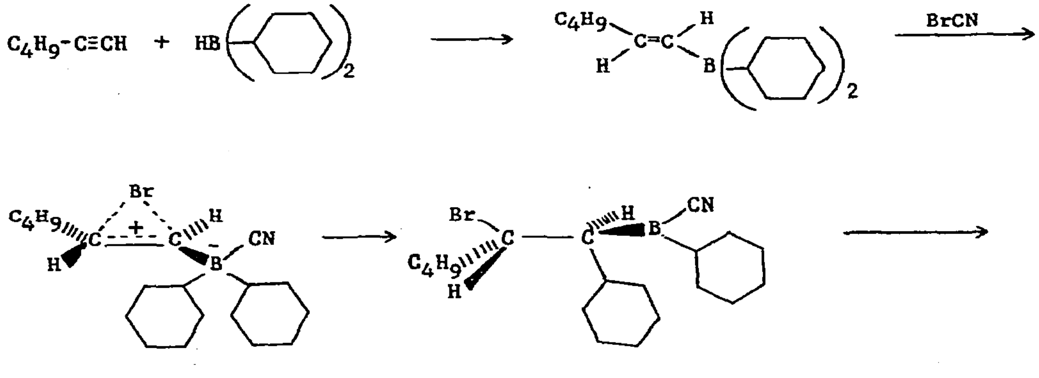


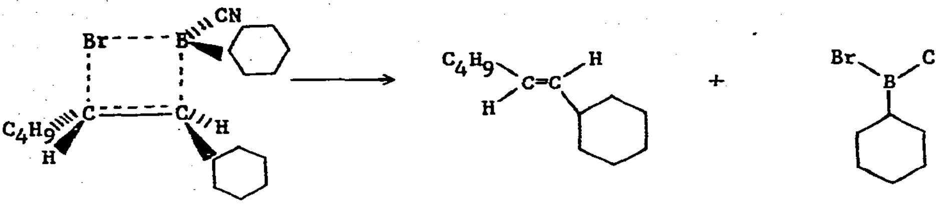
$$R_2BCl + N_2CHCO_2Et \longrightarrow R_2\underset{Cl}{\underset{|}{\bar{B}}}-\underset{N_2}{\underset{|}{C}}HCO_2Et \longrightarrow R-\underset{Cl}{\underset{|}{B}}-\overset{R}{\overset{|}{C}}HCO_2Et + N_2 \xrightarrow{MeOH} RCH_2CO_2Et + RB(OMe)_2 + HCl$$

Trialkylboranes having primary or cyclic alkyl groups react with BCl_3 in the presence of a catalytic amount of alkylboron hydride at 110° to form alkyldichloroboranes (97). If the alkyl groups are secondary, the reaction is sluggish and the boron in part migrates from its original position.

$$(RCH_2CH_2)_3B + 2\ BCl_3 \longrightarrow 3\ RCH_2CH_2BCl_2$$

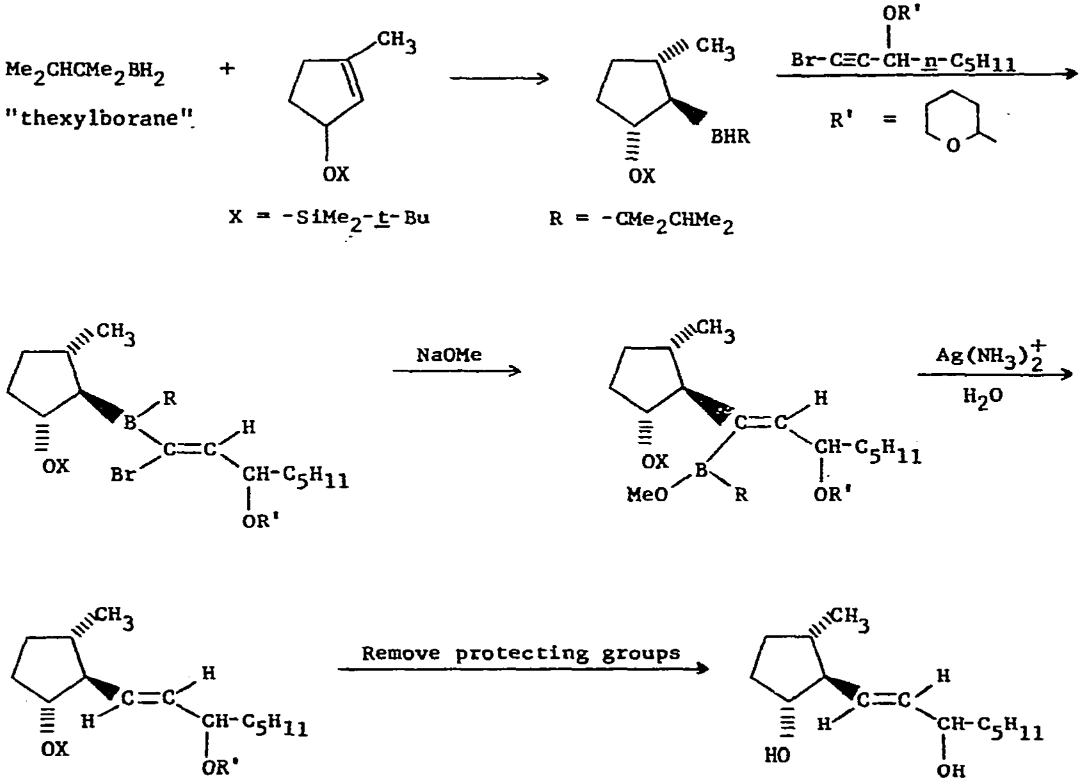
Zweifel and coworkers have reported a synthesis of <u>trans</u> olefins from alkynes by way of hydroboration and reaction of the alkenylborane with cyanogen bromide or iodide (98).



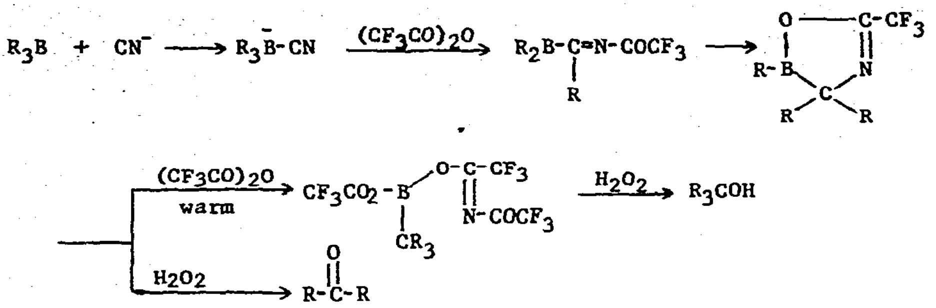


(*cis* elimination)

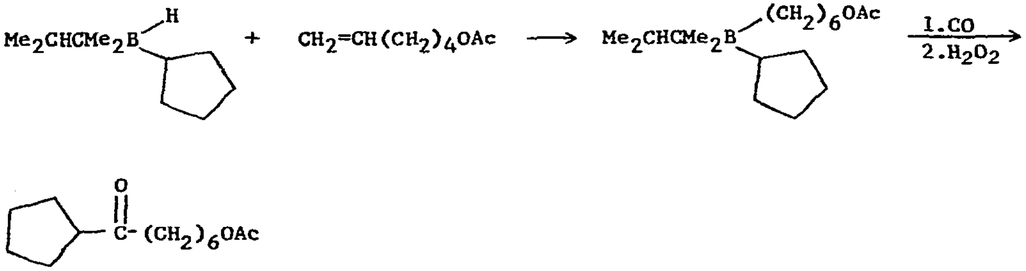
Corey and Ravindranathan have modified some of the alkenylborane chemistry developed by Zweifel and coworkers to that it is useful in the stereocontrolled synthesis of prostaglandins (99).



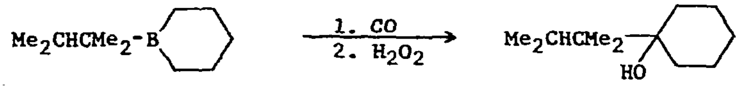
Pelter, Hutchings, and Smith have reported that a combination of sodium cyanide and trifluoroacetic anhydride can be substituted for carbon monoxide in reactions with trialkylboranes, sometimes giving more convenient procedures for laboratory work (100).



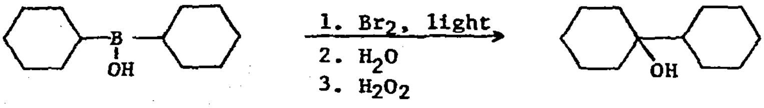
In extensions of previous work by Brown's group, the reaction of carbon monoxide with thexyldialkylboranes has been used to prepare acetoxy-substituted ketones (101).



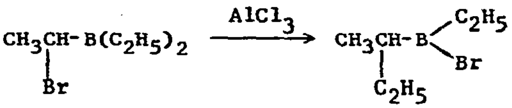
Carbinols substituted with a teriary alkyl group have been made by carbonylation of appropriate trialkylboranes (102).



Brown and Lane have used the bromination of borinic acids followed by rearrangement with water (see J. Organometal. Chem., 41 (1972) 61) and oxidation with hydrogen peroxide to prepare several complex tertiary alcohols (103).

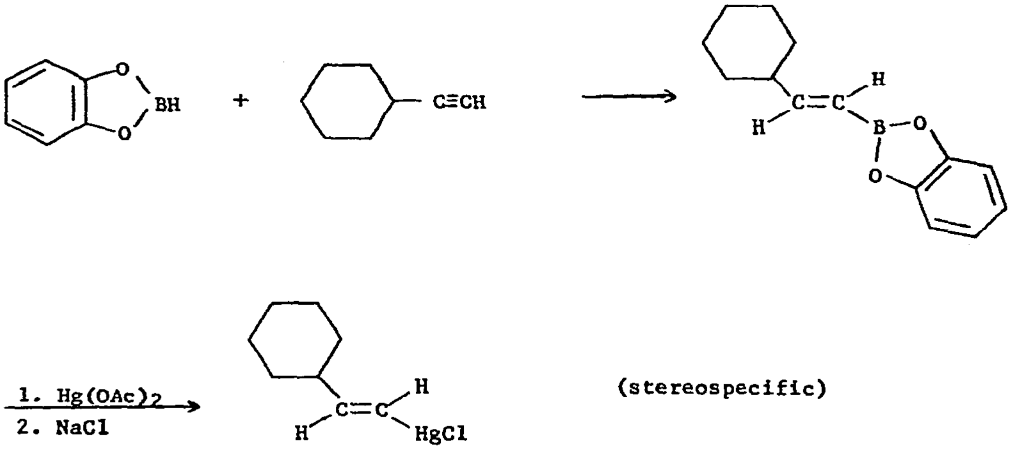


Electrophilic catalysts such as aluminum chloride catalyze the rearrangement of α-bromoalkylboron compounds (104).



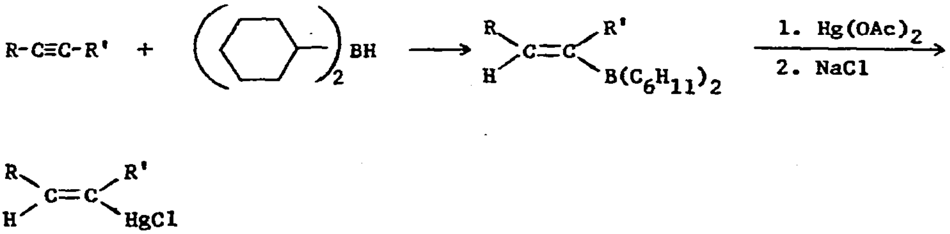
$$CH_3CH(Br)-B(C_2H_5)_2 \xrightarrow{AlCl_3} CH_3CH(C_2H_5)-B(C_2H_5)Br$$

Catecholborane has been found to be particularly useful for the monohydroboration of alkynes (105). The resulting alkeneboronic esters are readily converted into alkenylmercuric salts (106).

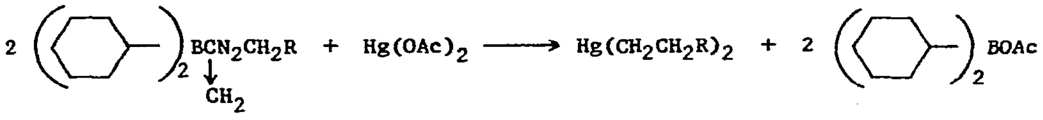


(stereospecific)

A detailed report on the conversion of acetylenes to vinylmercury compounds has appeared (107).



The cleavage of trialkylboranes by mercuric acetate has been studied in detail (108). Two primary alkyl groups of the borane are cleaved rapidly in tetrahydrofuran, the third more slowly. Secondary alkyl groups are unreactive, and dicycloalkylboranes can be converted to dialkylmercury compounds.



The oxygen-initiated reaction of trialkylboranes with formaldehyde leads to homologation of the alkyl group by a free radical mechanism (109).

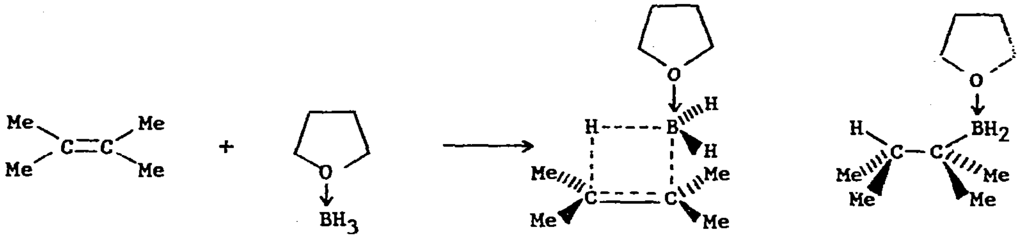
$R_3B + O_2 \longrightarrow R_2B\text{-}O\text{-}O\cdot + R\cdot$ (initiation)

$R\cdot + CH_2O \longrightarrow R\text{-}CH_2\text{-}O\cdot$ (propagation)

$R\text{-}CH_2\text{-}O\cdot + R_3B \longrightarrow \underset{\text{(product)}}{R_2B\text{-}O\text{-}CH_2\text{-}R} + R\cdot$ (propagation

B. Mechanistic studies

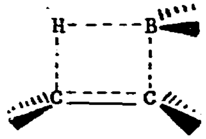
The major features of the mechanism of hydroboration are well known, but new refinements have been added. Pasto and coworkers have reported that the kinetics of the reaction of borane in tetrahydrofuran with tetramethylethylene are first-order in each reactant (110). (Because of complexing with tetrahydrofuran, BH_3 is monomeric in that solvent.) The energy of activation is 9.2 kcal/mol and the entropy of activation is -27 eu. Both boron and hydrogen isotope effects were found. The relative rates of hydroborations by BH_3 and various RBH_2 have also been studied (111). The results are all consistent with a four-center transition state for hydroboration.



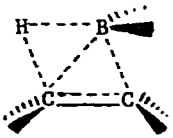
(transition state)

Unimolecular elimination of isobutylene from triisobutylborane occurs in the gas phase and the kinetics have been studied (112).

Jones has pointed out that the orbital symmetry involved in a 4-center transition state for hydroboration is forbidden, but correcting the structure to a π-complex having three-center bonding solves the orbital symmetry problem (113). This refinement implies only a slight modification of the positions of the atoms from that of a simple four-center transition state, and in the reviewer's opinion is consistent with all the available data on hydroboration.



symmetry forbidden



symmetry allowed

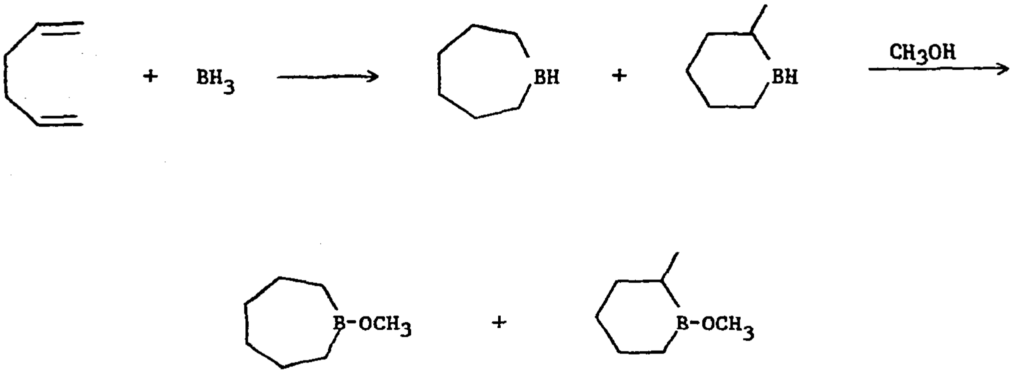
A discussion of correlation of steric effects in hydroboration with those in ester hydrolysis has appeared (114).

C. Hydroborations of miscellaneous compounds

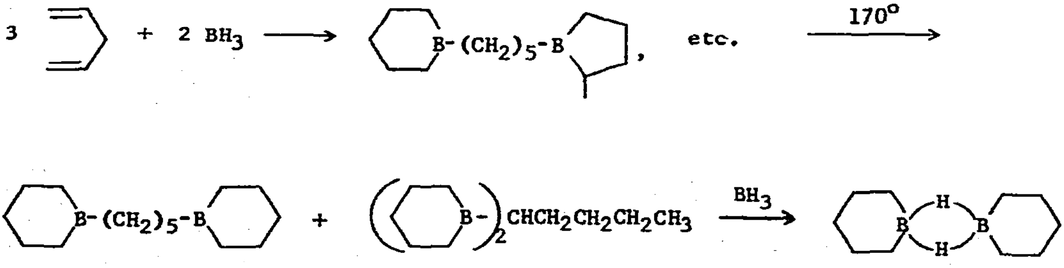
1. Alkenes. Hydroboration has been carried out on a wide variety of unsaturated compounds. First are listed some examples where the course of the hydroboration reaction itself is under investigation, and straightforward synthetic applications follow. The latter are of marginal organometallic

interest and are for the most part summarized very briefly. These references were gathered by using the keyword "hydroboration" in Chemical Abstracts.

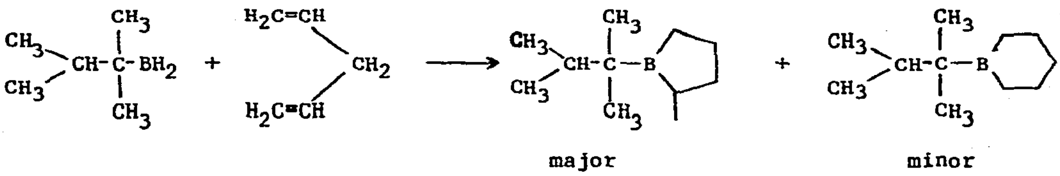
Brown, Negishi, and Burke have found that the hydroboration of 1,4- and 1,5-dienes in a 1:1 molar ratio with borane in tetrahydrofuran yields six- and seven-membered boracyclanes (115). These were characterized by hydrogen peroxide oxidation and by methanolysis to the B-methoxy derivatives.



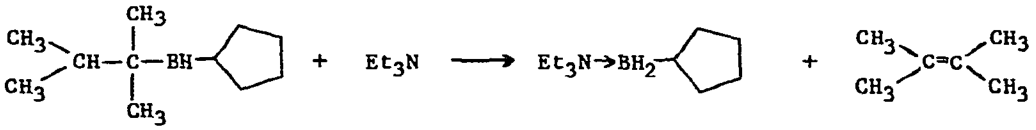
The hydroboration of 1,4-pentadiene in tetrahydrofuran shows considerable complexity. If the ratio of diene to borane is 3:2, the product mixture contains at least six alkylboranes and on oxidation yields 42% 1,5-pentanediol and 58% 1,4-pentanediol. Thermal rearrangement at 170° increases the proportion of 1,5-pentanediol to 80%, with 10% 1,4-pentanediol and 10% 1-pentanol, the last being derived from cleavage of a 1,1-diboryl compound. Treatment of the thermally rearranged product with borane in tetrahydrofuran yields bisborinane, a useful hydroborating agent (116).



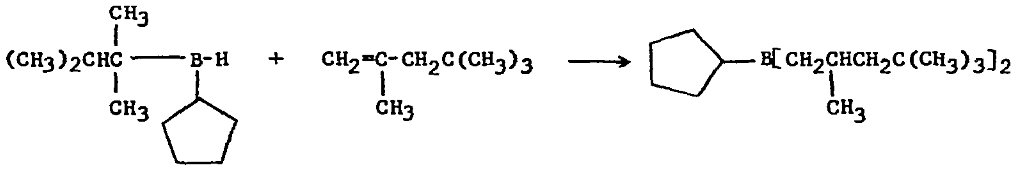
Although boracyclopentanes are easily attacked by borane and the BH compounds are very difficult to prepare (J. Organometal. Chem., 41 (1972) 58), hydroboration with thexylborane favors five-membered over six-membered ring formation (117).



Triethylamine cleaves tetramethylethylene from thexylalkylboranes to form the monoalkylborane-triethylamine complex (118).

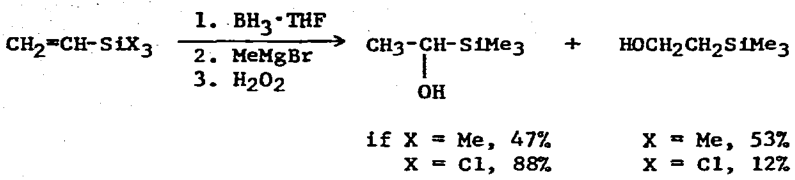


Bulky olefins can displace the thexyl group from thexylcycloalkylboranes (119).



Dithexylborane, (Me$_2$CHCMe$_2$)$_2$BH, exists as the free monomer and fails to complex with tetrahydrofuran as a consequence of the steric bulk of the thexyl groups (120). Thexylborane, Me$_2$CHCMe$_2$BH$_2$, has been studied as a selective reducing agent for organic functional groups (121).

The hydroboration of vinylsilicon and allylsilicon compounds has been studied (122).

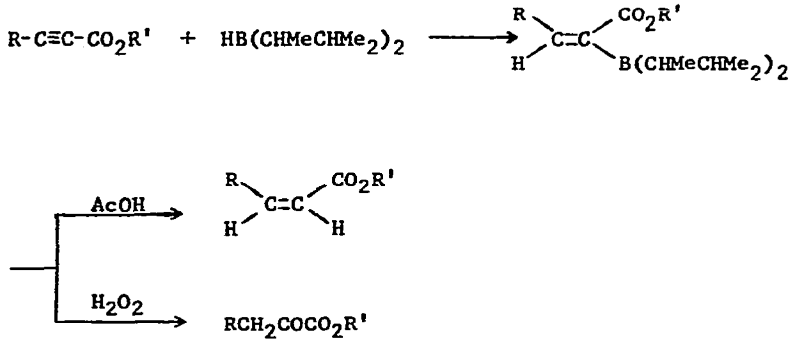


$$CH_2{=}CH{-}SiX_3 \xrightarrow[\substack{2.\ MeMgBr\\ 3.\ H_2O_2}]{1.\ BH_3{\cdot}THF} CH_3{-}\underset{OH}{\underset{|}{C}}H{-}SiMe_3 + HOCH_2CH_2SiMe_3$$

if X = Me, 47% X = Me, 53%
X = Cl, 88% X = Cl, 12%

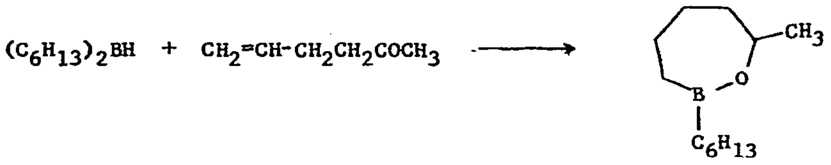
$$CH_2{=}CH{-}CH_2{-}SiX_3 \xrightarrow[\substack{2.\ MeMgBr\\ 3.\ H_2O_2}]{1.\ BH_3{\cdot}THF} HOCH_2CH_2CH_2SiMe_3$$

The hydroboration of 2-alkynoates with disiamylborane introduces the boron at the 2-position, and the boranes can be converted to cis-α,β-unsaturated or α-ketoesters (123).



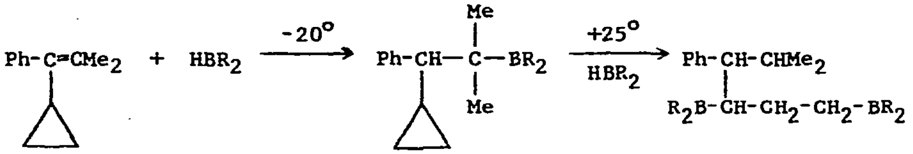
The hydroboration of sodium enolates derived from cyclohexanones has led to trans-1,2-cyclohexanediols (124). The hydroboration of cyclohexen-3-ones and cyclohexen-3-ols followed by peroxide oxidation yields mainly diequatorial trans-1,2-diols (125). The hydroboration of enamines from substituted cyclohexanones has been studied (125). Hydroboration of several substituted cyclohexanone imines has led to 2-aminocyclohexanols, indicating that there is some enamine tautomer present in equilibrium with the ketimine tautomer (127).

Dihexylborane and allylacetone have yielded a 7-membered B-O heterocycle (128).



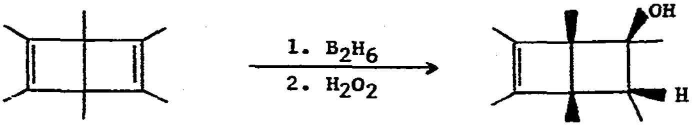
Hydroboration of $BrCH_2CH(OEt)CH_2CH{=}CH_2$ with Bu_2BH has yielded $BrCH_2CH(OEt)$-$CH_2CH_2CH_2BBu_2$, which was converted to the $RB(OMe)_2$ derivative by reaction with trimethyl borate and then allowed to react with primary amines, which displaced the bromide and yielded 7-membered B-N heterocycles (129). Hydroboration of $(CH_3)_2C{=}C{=}CH_2$ with $(HBEt_2)_2$ yields mainly $(CH_3)_2C{=}CHCH_2BEt_2$ (130). Hydroboration of ethoxyacetylene has been used to prepare several trans-ethoxyvinylboranes, $EtOCH{=}CHBX_2$, where X is alkyl, MeO, or ethoxyvinyl (131).

The hydroboration of α-cyclopropyl-β,β-dimethylstyrene at -20° proceeds to yield mainly the expected product, but at room temperature rearrangement of the borane with opening of the cyclopropane ring results (132).



The reaction of diphenylcyclopropenone with excess diborane appears to proceed by way of a cyclopropenyl cation which is then reduced to 1,2-diphenylcyclopropene (133).

Hydroboration-oxidation of one double bond of hexamethyl(Dewar benzene) has been carried out without rearrangement (134).



Hydroboration of vinylferrocene followed by hydrogen peroxide oxidation has given 2-ferrocenyl ethanol, and other analogous hydroborations have been carried out (135).

Reaction of $RNH(CH_2)_2CH=CH_2$ with $H_2BR'\cdot NMe_3$ to form the borazacyclohexanes has been studied (136). Hydroboration of 1,3-dimethyl-3-piperideine under various conditions leads to different mixtures of cis- and trans-1,3-dimethyl-4-piperidinols, with trans predominating (137). Hydroboration of several substituted 3-piperideines has lead to 3- and 4-piperidinols (138). Hydroboration has been used in the synthesis of a series of dibenzazepines patented as tranquilizers (139). Hydroboration of several unsaturated aliphatic alcohols and thermal isomerization of the products has been studied (140). The hydroboration-oxidation of several 3-methylenebicyclo[3.1.1]heptanes has been reported (141).

Heating trialkylboranes above 120° in dimethyl sulfoxide, acetophenone, or dimethylformamide results in elimination of one alkyl group as olefin, and in benzaldehyde or furfural two alkyl groups are eliminated (142). The displacement of propylene from tripropylborane by 1-dodecene yields 78% of tri-1-dodecylborane in 5 minutes at 280° (143). Radical-initiated reaction of $BrCCl_3$ with Et_3B gives a good yield of $CH_3CHBrBEt_2$ and $CHCl_3$ (144).

2. Natural products. The application of hydroboration chemistry to the synthesis of prostaglandins (99) has already been noted in Part A.

Diisopinocampheylborane has been used in a synthesis of optically active amino acids by way of reduction of nitriles to N-diisopinocampheylborylketimines and addition of HCN to the asymmetric ketimines (145).

A number of miscellaneous hydroborations of natural products can be found from the keyword "hydroboration" in Chemical Abstracts and are listed here for completeness, though their organometallic relevance is doubtful. Hydroboration and oxidation has been used to convert desoxytrimethylbrazilone to trimethylbrazilin (146). Hydroborations of dihydrothujopsene (147) and of myrtenyl chloride and bromide (148) have been reported. Autoxidation of the hydroboration product from longifolene gives transannular radical transfer products (149).

The hydroboration of an isopropenyl group on a steroid has been reported (150). Thermal isomerization of boranes to move the boron to the end of a ring D side chain has been employed in the steroid series (151,152). The enamines from 3-oxosteroids are reduced to 3-aminosteroids instead of yielding normal hydroboration products with borane (153). If there is no 19-methyl group or if the amino and borane groups are trans diequatorial, the hydroboration products from the enamines of 3-oxosteroids are stable and can be oxidized to 3-amino-2-oxysteroids (154). Disiamylborane hydroborates an isopropenyl side chain in preference to a double bond in the B ring of a steroid (155). Hydroboration has been used for synthetic transformations in the flavene series (156).

D. Reviews

Brown has written a useful and interesting book covering his recent work on hydroboration and alkylborane chemistry (157).

The chemistry of organoboranes as alkylating and arylating agents has been reviewed by Brown and Rogic (158). Brown and Negishi have reviewed the cyclic hydroboration of dienes to form bisborocyclanes and B-thexylboracyclanes (159). Readers of Japanese may be interested in Suzuki's review of radical reactions of organoboranes (160). Hydroboration has been reviewed in Polish (161,162,163). A review of 1,5,9-cyclododecatriene chemistry, including its hydroboration, has appeared in German (164).

References p. 40

REFERENCES

1 G. B. Dunks, R. J. Wiersema, and M. F. Hawthorne, J. Chem. Soc., Chem. Commun., (1972) 899

2 L. I. Zakharkin and V. N. Kalinin, Zh. Obshch, Khim., 42 (1972) 714

3 V. N. Kalinin and L. I. Zakharkin, Izv. Akad. Nauk SSSR, Ser. Khim., (1971) 2353

4 C. J. Jones, J. N. Francis, and M. F. Hawthorne, J. Amer. Chem. Soc., 94 (1972) 8391

5 C. J. Jones, J. N. Francis, and M. F. Hawthorne, J. Chem. Soc., Chem. Commun., (1972) 900

6 M. R. Churchill and K. Gold, J. Chem. Soc., Chem. Commun., (1972) 901

7 W. J. Evans and M. F. Hawthorne, J. Chem. Soc., Chem. Commun., (1972) 611

8 J. N. Francis, C. J. Jones, and M. F. Hawthorne, J. Amer. Chem. Soc., 94 (1972) 4878

9 D. C. Beer and L. J. Todd, J. Organometal. Chem., 36 (1972) 77

10 T. E. Paxson, M. K. Kaloustian, G. M. Tom, R. J. Wiersema, and M. F. Hawthorne, J. Amer. Chem. Soc., 94 (1972) 4882

11 M. K. Kaloustian, R. J. Wiersema, and M. J. Hawthorne, J. Amer. Chem. Soc., 94 (1972) 6679

12 D. St. Clair, A. Zalkin, and D. H. Templeton, Inorg. Chem., 11 (1972) 377

13 L. G. Sneddon and R. N. Grimes, J. Amer. Chem. Soc., 94 (1972) 7161

14 J. W. Howard and R. N. Grimes, Inorg. Chem., 11 (1972) 263

15 B. Lockman and T. Onak, J. Amer. Chem. Soc., 94 (1972) 7923

16 V. A. Brattsev, G. N. Danilova, and V. I. Stanko, Zh. Obshch. Khim., 42 (1972) 1333

17 J. Plesek and S. Hermanek, Chem. Ind. (London), (1971) 1267

18 M. R. Churchill and A. H. Reis, Jr., J. Chem. Soc., Dalton Trans., (1972) 1314

19 M. R. Churchill and A. H. Reis, Jr., J. Chem. Soc., Dalton Trans., (1972) 1317

20 L. I. Zakharkin and V. S. Kozlova, Zh. Obshch. Khim., 42 (1972) 476

21 R. N. Grimes, W. J. Rademaker, M. L. Denniston, R. F. Bryan, and P. T. Greene, J. Amer. Chem. Soc., 94 (1972) 1865

22 D. C. Beer, A. R. Burke, T. R. Engelmann, B. N. Storhoff, and L. J. Todd, J. Chem. Soc. D, (1971) 1611

23 J. F. Ditter, E. B. Klusmann, and R. E. Williams, U. S. Patent 3,660,494, May 2, 1972, Chem. Abstr., 77 (1972) 48617y

24 J. F. Ditter and R. E. Williams, U. S. Nat. Tech. Inform. Serv., AD Rep. 1971, No. 729692, Chem. Abstr., 76 (1972) 72587p

25 A. B. Burg and T. J. Reilly, Inorg. Chem., 11 (1972) 1962

26 M. P. Brown, A. K. Holliday, and G. M. Way, J. Chem. Soc., Chem. Commun., (1972) 850

27 D. S. Marynick and W. N. Lipscomb, J. Amer. Chem. Soc., 94 (1972) 1748

28 D. S. Marynick and W. N. Lipscomb, J. Amer. Chem. Soc., 94 (1972) 8692

29 D. S. Marynick and W. N. Lipscomb, J. Amer. Chem. Soc., 94 (1972) 8699

30 R. W. Rudolph and W. R. Pretzer, Inorg. Chem., 11 (1972) 1974

31 C. L. Brown, K. P. Gross, and T. Onak, J. Amer. Chem. Soc., 94 (1972) 8055

32 C. L. Brown, K. P. Gross, and T. P. Onak, J. Chem. Soc., Chem. Commun., (1972) 68

33 B. Stibr, J. Plesek, and S. Hermanek, Chem. Ind. (London), (1972) 649

34 V. R. Miller and R. N. Grimes, Inorg. Chem., 11 (1972) 862

35 D. A. Franz, V. R. Miller, and R. N. Grimes, J. Amer. Chem. Soc., 94 (1972) 412

36 M. L. Thompson and R. N. Grimes, Inorg. Chem., 11 (1972) 1925

37 A. Tabereaux and R. N. Grimes, J. Amer. Chem. Soc., 94 (1972) 4768

38 C. G. Savory and M. G. H. Wallbridge, J. Chem. Soc., Dalton Trans., (1972) 918

39 R. E. Bowen and C. R. Phillips, J. Inorg. Nucl. Chem., 34 (1972) 382

40 R. A. Love and R. Bau, J. Amer. Chem. Soc., 94 (1972) 8274

41 L. I. Zakharkin, L. V. Orlova, B. V. Lokshin, and L. A. Federov, J. Organometal. Chem., 40 (1972) 15

42 L. I. Zakharkin and L. V. Orlova, Izv. Akad. Nauk SSSR, Ser. Khim., (1972) 209

43 R. Rogowski and K. Cohn, Inorg. Chem., 11 (1972) 1429

44 H. Beall, Inorg. Chem., 11 (1972) 637

45 L. I. Zakharkin, V. N. Kalinin, and E. G. Rys, Zh. Obshch. Khim., 42 (1972) 477

46 L. I. Zakharkin and V. N. Kalinin, Syn. Inorg. Metal-Org. Chem., 2 (1972) 113

47 V. N. Kalinin, G. G. Zhigareva, and L. I. Zakharkin, Syn. Inorg. Metal-Org. Chem., 2 (1972) 105

48 A. V. Kazantsev, M. N. Zhubekova, and L. I. Zakharkin, Zh. Obshch. Khim., 42 (1972) 1570

49 L. I. Zakharkin, M. N. Zhubekova, and A. V. Kazantsev, Zh. Obshch. Khim., 42 (1972) 1024

50 A. V. Kazantsev, M. N. Zhubekova, and L. I. Zakharkin, Zh. Obshch. Khim., 41 (1971) 2027

51 L. I. Zakharkin, B. A. Kvasov, and V. N. Lebedev, ZH. Obshch. Khim., 41 (1971) 2694

52 B. M. Mikhailov and E. A. Shagova, Izv. Akad. Nauk SSSR, Ser. Khim., (1972) 1221

53 B. M. Mikhailov and E. A. Shagova, Izv. Akad. Nauk SSSR, Ser. Khim., (1972) 1222

54 B. M. Mikhailov and E. A. Shagova, Izv. Akad. Nauk SSSR, Ser. Khim., (1972) 1450

55 V. I. Stanko and Yu. V. Gol'tyapin, Zh. Obshch. Khim., 41 (1971) 2033

56 L. I. Zakharkin and L. E. Litovchenko, Zh. Obshch. Khim., 42 (1972) 476

57 L. I. Zakharkin and V. N. Lebedev, Zh. Obshch. Khim., 42 (1972) 558

58 L. I. Zakharkin and V. N. Lebedev, Izv. Akad. Nauk SSSR, Ser. Khim., (1972) 734

59 L. I. Zakharkin, L. E. Litovchenko, and L. S. Podvisotskaya, Zh. Obshch. Khim., 42 (1972) 1170

60 C. O. Obenland, S. Papetti, and H. D. Smith, Jr., U. S. Patent 3,674,853, July 4, 1972, Chem. Abstr., 77 (1972) 88647q

61 H. A. Schroeder and N. S. Semenuk, U. S. Patent 3,634,505, Jan. 11, 1972, Chem. Abstr., 76 (1972) 141011k

62 A. R. Siedle, J. Inorg. Nucl. Chem., 33 (1971) 3677

63 L. I. Zakharkin and A. I. L'vov, Zh. Obshch. Khim., 41 (1971) 1180

64 L. I. Zakharkin, A. V. Kazantsev, and L. E. Litovchenko, Izv. Akad. Nauk SSSR, Ser. Khim., (1971) 2050

65 L. I. Zakharkin and V. N. Kalinin, Izv. Akad. Nauk SSSR, Ser. Khim., (1971) 2310

66 A. V. Kazantsev, M. I. Ibraev, and A. N. Deev, Izv. Akad. Nauk Kaz. SSSR, Ser. Khim., 22 (1972) 79

67 V. I. Grigos, A. F. Zhigach, and V. F. Mironov, Khim. Geterotsikl. Soedin., 7 (1971) 998

68 V. F. Mironov, S. Ya. Pechurina, V. I. Grigos, A. F. Zhigach, and V. I. Siryatskaya, Dokl. Akad. Nauk SSSR, 202 (1972) 1345

69 L. I. Zakharkin and V. I. Kyskin, Izv. Akad. Nauk SSSR, Ser. Khim., (1971) 2053

70 L. I. Zakharkin, G. G. Zhigareva, and L. S. Podvisotskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1971) 2312

71 L. I. Zakharkin, V. N. Kalinin, E. G. Rys, and B. A. Kvasov, Izv. Akad. Nauk SSSR, Ser. Khim., (1972) 507

72 L. I. Zakharkin, V. N. Kalinin, E. G. Rys, and B. A. Kvasov, Izv. Akad. Nauk SSSR, Ser. Khim., (1972) 574

73 L. I. Zakharkin, V. N. Kalinin, and B. A. Kvasov, Zh. Obshch. Khim., 42 (1972) 838

74 L. A. Fedorov, V. I. Kyskin, and L. I. Zakharkin, Izv. Akad. Nauk SSSR, Ser. Khim., (1972) 536

75 E. A. Yakovleva, G. G. Isaeva, V. I. Kyskin, L. I. Zakharkin, and A. I. Shatenshtein, Izv. Akad. Nauk SSSR, Ser. Khim., (1971) 2797

76 E. S. Petrov, L. I. Kruglyak, and A. I. Shatenshtein, Zh. Obshch. Khim., 42 (1972) 554

77 N. K. Vorob'ev, L. I. Smirnova, and E. A. Chizhova, Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol., 14 (1971) 955

78 E. I. Matrosov, Izv. Akad. Nauk SSSR, Ser. Khim., (1972) 521

79 L. P. Dorofeenko, Yu. A. Yuzhelevskii, and A. L. Klebanskii, Zh. Obshch. Khim., 41 (1971) 2025

80 V. V. Khrapov, T. V. Klimova, V. I. Stanko, and O. Yu. Okhlobystin, Zh. Strukt. Khim., 12 (1971) 805

81 W. N. Lipscomb, R. J. Wiersema, and M. F. Hawthorne, Inorg. Chem., 11 (1972) 651

82 A. R. Siedle and G. M. Bodner, Inorg. Chem., 11 (1972) 3108

83 H. D. Johnson, II, V. T. Brice, G. L. Brubaker, and S. G. Shore, J. Amer. Chem. Soc., 94 (1972) 6711

84 V. T. Brice, H. D. Johnson, II, D. L. Denton, and S. G. Shore, Inorg. Chem., 11 (1972) 1135

85 G. Kodama, J. Amer. Chem. Soc., 94 (1972) 5907

86 G. Kodama, U. Engelhardt, C. Lafrenz, and R. W. Parry, J. Amer. Chem. Soc., 94 (1972) 407

87 R. B. King, J. Amer. Chem. Soc., 94 (1972) 95

88 E. A. Laws, R. M. Stevens, and W. N. Lipscomb, J. Amer. Chem. Soc., 94 (1972) 4467

89 M. F. Hawthorne, Pure Appl. Chem., 29 (1972) 547

90 L. J. Todd, Pure Appl. Chem., 30 (1972) 587

91 L. I. Zakharkin, Pure Appl. Chem., 29 (1972) 513

92 R. Snaith and K. Wade, MTP Int. Rev. Sci.: Inorg. Chem., Ser. One, 1 (1972) 139

93 D. T. Haworth, Endeavour, 31 (1972) 16

94 H. C. Brown and N. Ravindran, J. Amer. Chem. Soc., 94 (1972) 2112

95 H. C. Brown, M. M. Midland, and A. B. Levy, J. Amer. Chem. Soc., 94 (1972) 2114

96 H. C. Brown, M. M. Midland, and A. B. Levy, J. Amer. Chem. Soc., 94 (1972) 3662

97 H. C. Brown and A. B. Levy, J. Organometal. Chem., 44 (1972) 233

98 G. Zweifel, R. P. Fisher, J. T. Snow, and C. C. Whitney, J. Amer. Chem. Soc., 94 (1972) 6560

99 E. J. Corey and T. Ravindranathan, J. Amer. Chem. Soc., 94 (1972) 4013

100 A. Pelter, M. G. Hutchings, and K. Smith, J. Chem. Soc. D, (1971) 1048 (two communications on same page)

101 E. Negishi and H. C. Brown, Synthesis, (1972) 196

102 E. Negishi and H. C. Brown, Synthesis, (1972) 197

103 H. C. Brown and C. F. Lane, Synthesis, (1972) 303

104 H. C. Brown and Y. Yamamoto, J. Chem. Soc., Chem. Commun., (1972) 71

105 H. C. Brown and S. K. Gupta, J. Amer. Chem. Soc., 94 (1972) 4370

106 R. C. Larock, S. K. Gupta, and H. C. Brown, J. Amer. Chem. Soc., 94 (1972) 4371

107 R. C. Larock and H. C. Brown, J. Organometal. Chem., 36 (1972) 1

108 J. D. Buhler and H. C. Brown, J. Organometal. Chem., 40 (1972) 265

109 N. Miyaura, M. Itoh, A. Suzuki, H. C. Brown, M. M. Midland, and P. Jacob, III, J. Amer. Chem. Soc., 94 (1972) 6459

110 D. J. Pasto, B. Lepeska, and T.-C. Cheng, J. Amer. Chem. Soc., 94 (1972) 6083

111 D. J. Pasto, B. Lepeska, and V. Balasubramaniyan, J. Amer. Chem. Soc., 94 (1972) 6090

112 K. W. Egger and A. T. Cocks, J. Chem. Soc. A, (1971) 3606

113 P. R. Jones, J. Org. Chem., 37 (1972) 1886

114 R. Fellous, R. Luft, and A. Puill, Tetrahedron Lett., (1972) 245

115 H. C. Brown, E. Negishi, and P. L. Burke, J. Amer. Chem. Soc., 94 (1972) 3561

116 E. Negishi, P. L. Burke, and H. C. Brown, J. Amer. Chem. Soc., 94 (1972) 7431

117 H. C. Brown and E. Negishi, J. Amer. Chem. Soc., 94 (1972) 3567

118 H. C. Brown, E. Negishi, and J.-J. Katz, J. Amer. Chem. Soc., 94 (1972) 5893

119 C. F. Lane and H. C. Brown, J. Organometal. Chem., 34 (1972) C29

120 E. Negishi, J.-J. Katz, and H. C. Brown, J. Amer. Chem. Soc., 94 (1972) 4025

121 H. C. Brown, P. Heim, and N. M. Yoon, J. Org. Chem., 37 (1972) 2942

122 P. R. Jones and J. K. Myers, J. Organometal. Chem., 34 (1972) C9

123 J. Plamondon, J. T. Snow, and G. Zweifel, Organometal. Chem. Syn., 1 (1971) 249

124 J. Klein, R. Levene, and E. Dunkelblum, Tetrahedron Lett., (1972) 2845

125 E. Dunkelblum, R. Levene, and J. Klein, Tetrahedron, 28 (1972) 1009

126 J. J. Barieux and J. Gore, Bull. Soc. Chim. France, (1971) 3978

127 J. Gore and M. Montury, C. R. Acad. Sci., Ser. C, 274 (1972) 2202

128 L. S. Vasil'ev, M. M. Vartanyan, V. S. Bogdanov, V. G. Kiselev, and B. M. Mikhailov, Zh. Obshch. Khim., 42 (1972) 1540

129 L. S. Vasil'ev, M. M. Vartabyan, and B. M. Mikhailov, Izv. Akad. Nauk SSSR, Ser. Khim., (1972) 1678

130 B. M. Mikhailov, V. N. Smirnov, and O. D. Ryazanova, Dokl. Akad. Nauk SSSR, 204 (1972) 612

131 Yu. N. Bubnov, V. S. Bogdanov, I. P. Yakovlev, and B. M. Mikhailov, Zh. Obshch. Khim., 42 (1972) 1313

132 E. Breuer, E. Segall, Y. Stein, and S. Sarel, J. Org. Chem., 37 (1972) 2242

133 E. Dunkelblum, Tetrahedron, 28 (1972) 3879

134 L. A. Paquette, S. A. Lang, Jr., M. R. Short, B. Parkinson, and J. Clardy, Tetrahedron Lett., (1972) 3141

135 C. H. Mauldin, E. R. Biehl, and P. C. Reeves, Tetrahedron Lett., (1972) 2955

136 H. Wille and J. Goubeau, Chem. Ber., 105 (1972) 2156

137 M. Ferles, J. Hauer, and Z. Polivka, Collect. Czech. Chem. Commun., 36 (1971) 4099

138 M. Ferles, J. Hauer, J. Kolar, Z. Polivka, and P. Stern, Collect. Czech. Chem. Commun., 37 (1972) 2464

139 H. Linares, German Patent 2,159,678, June 22, 1972, Chem. Abstr., 77 (1972) 88351p

140 K. Sisido, M. Naruse, A. Saito, and K. Utimoto, J. Org. Chem., 37 (1972) 733

141 Y. Bessiere-Chretien and B. Meklati, Bull. Soc. Chim. France, (1972) 2933

142 A. Arase, Y. Masuda, M. Itoh, M. Itoh, and A. Suzuki, Nippon Kagaku Kaishi, (1972) 395

143 T. Ohtaki, F. Kuniaki, M. Itoh, and A. Suzuki, Kogyo Kagaku Zasshi, 74 (1971) 2129

144 H. C. Brown and Y. Yamamoto, J. Chem. Soc. D, (1971) 1535

145 U. E. Diner, M. Worsley, J. W. Lown, and J. Forsythe, Tetrahedron Lett., (1972) 3145

146 B. S. Kirkiacharian, C. R. Acad. Sci., Ser. C., 274 (1972) 2096

147 A. R. Hochstetler, J. Org. Chem., 37 (1972) 1883

148 I. Uzarewicz, E. Zientek, and A. Uzarewicz, Rocz. Chem., 46 (1972) 1069

149 Y. Tanahashi, J. Lhomme, and G. Ourisson, Tetrahedron, 28 (1972) 2655

150 E. Mincione and O. Rossi, Ann. Chim. (Rome), 61 (1971) 788

151 E. Mincione and C. Iavarone, Gazz. Chim. Ital., 101 (1971) 956

152 E. Mincione and D. Iocco, Ann. Chim. (Rome), 62 (1972) 285

153 J. J. Barieux and J. Gore, Tetrahedron, 28 (1972) 1537

154 J. J. Barieux and J. Gore, Tetrahedron, 28 (1972) 1555

155 J. Bottin and M. Fetizon, Bull. Soc. Chim. France, (1972) 2344

156 J. W. Clark-Lewis and M. I. Baig, Aust. J. Chem., 24 (1971) 2581

157 H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972

158 H. C. Brown and M. M. Rogic, Organometal. Chem. Syn., 1 (1972) 305

159 H. C. Brown, Pure Appl. Chem., 29 (1972) 527

160 A. Suzuki, Yuki Gosei Kagaku Kyokai Shi, 29 (1971) 995

161 M. Zaidlewicz, I. Uzarewicz, and A. Uzarewicz, Wiad. Chem., 25 (1971) 699

162 M. Zaidlewicz, I. Uzarewicz, and A. Uzarewicz, Wiad. Chem., 26 (1972) 33

163 I. Uzarewicz, M. Zaidlewicz, and A. Uzarewicz, Wiad. Chem., 26 (1972) 193

164 K. Kosswig, Chem. Ztg., 96 (1972) 373