FOUR DECADES OF ORGANIC CHEMISTRY OF *closo*-BORANES: A SYNTHETIC TOOLBOX FOR CONSTRUCTING LIQUID CRYSTAL MATERIALS. A REVIEW

Piotr KASZYNSKI

Organic Materials Research Group, Chemistry Department, Vanderbilt University, Nashville, TN 37235, U.S.A.; e-mail: piotr@ctrvax.vanderbilt.edu

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Dedicated to Dr Stanislav Heřmánek on the occasion of his 70th birthday in recognition of his outstanding contributions to the areas of borane chemistry and NMR spectroscopy.

Introduction and transformations of organic functional groups to ten- and twelve-vertex *closo*-boranes and heteroboranes is reviewed in the context of preparation of liquid crystalline compounds. The review, containing 198 references, is designed as a synthetic manual for materials chemists and focuses on methods for engineering molecules with elongated shapes and variable dipole moments. Several underdeveloped aspects of *closo*-borane chemistry are identified.

Key words: Boranes; Carboranes; Heteroboranes; Clusters; Liquid crystals.

1. INTRODUCTION

The synthesis of the first organic derivatives of *closo*-dodecaborate (**1**, Fig. 1) and *closo*-decaborate **7** in 1962 (ref.[1]) followed by a number of organic derivatives of *ortho*-carborane **4** (refs[2,3]) and *meta*-carborane **5** (ref.[4]), signaled the beginning of an exciting period for *closo*-borane chemistry and applications of inorganic-organic hybrid materials[5]. High chemical, thermal and electrochemical stability of the ten- and, especially, twelve-vertex *closo*-

boranes[6] (Fig. 1) have been utilized in preparation of thermostable polymers[7]. The low toxicity[8] of *closo*-borates **1** and **7** makes them suitable for biomedical applications such as boron neutron capture therapy[9,10]. More recently, boron clusters have been used as non-nucleophilic anions[11] and for molecular materials such as molecular-scale construction sets[12–14]. Exploration of boron clusters as structural elements for liquid crystals is the most recent chapter in the chemistry and application of *closo*-boranes[15]. So far only several of the ten clusters, decaborate **7** (refs[16,17]), monocarbaborate **2** (ref.[18]), and *para*-carboranes **6** and **10** (refs[17,19–23]), have been used in the synthesis of liquid crystals. The results obtained to date[15] demonstrate the structural versatility of these compounds and their enormous potential in the study of the phenomenon and applications of liquid crystals.

The rich chemistry of the clusters in Fig. 1 and the understanding of their properties has been driven by scientific curiosity and materials demands and described in several reviews[6,24–31]. Here we will concentrate on the transformations of *closo*-boranes that lead to disubstitution in the antipodal position giving electrically neutral molecules with the most extended molecular shapes which are prerequisite for liquid crystalline behavior[15].

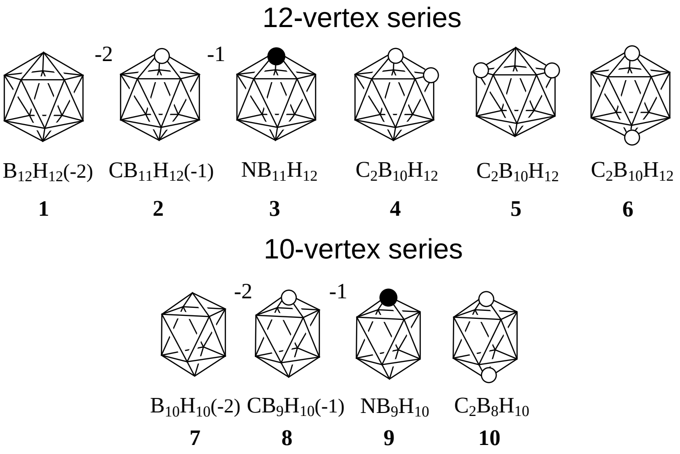
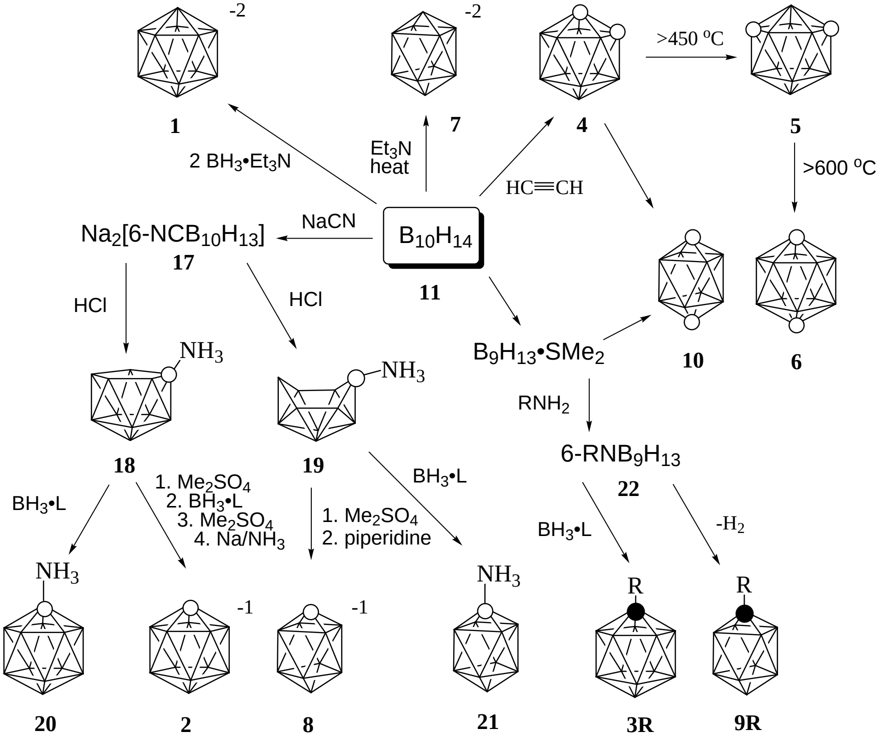


FIG. 1
Skeletal representations of the borates (**1**, **7**), monocarbaborates (**2**, **8**), azaboranes (**3**, **9**), *ortho*-carborane (**4**), *meta*-carborane (**5**), and *para*-carboranes (**6**, **10**) shown with chemical formulas. In the structures each vertex corresponds to a B–H fragment and the CH and NH groups are marked by open and filled circles, respectively

2. PREPARATION OF THE PARENT CLUSTERS

Commercially available decaborane(14) (**11**) is the common precursor to all ten clusters **1**–**10** as shown in Scheme 1. Generally the twelve-vertex *closo*-clusters are more convenient to prepare than the ten-vertex analogs. For the former, insertion reactions are typically used, while the synthesis of the ten-vertex clusters involves selective degradation processes of the eleven- and twelve-vertex species.

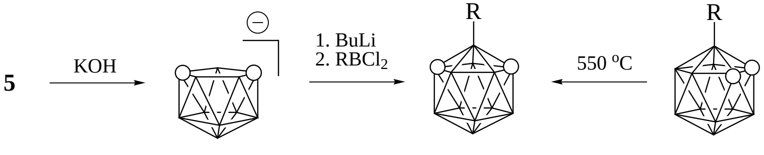
The transformation of $[B_{10}H_{14}]$ (**11**) to the anions **1** (ref.[32]) and **7** (ref.[33]) were the first syntheses of the *closo*-skeleton which involved borane insertion[34] or amine-induced dehydrogenation[35] reactions, respectively.



SCHEME 1

The twelve-vertex *ortho*-carborane **4** (ref.[2]) has been obtained by acetylene insertion to decaborane **11** (refs[36,37]). Reaction of substituted acetylenes provides a convenient route to mono- and disubstituted derivatives of **4** (refs[2,38,39]).

Thermolysis of *ortho*-carborane **4** at 465–500 °C (ref.[4]) or in a flow system at 600 °C (ref.[40]) produces the *meta* isomer **5** in high yield[4], while higher temperatures give an equilibrium mixture of *para*-carborane **6** and its *meta* isomer. The *para* isomer **6** (ref.[41]) can be separated chromatographically[42], taking advantage of the difference in the polarity[43] (2.85 D for **5**) or by selective conversion of the *meta* isomer to the $[C_2B_9H_{12}]^-$ *nido* anion (**12**, Scheme 2)[44]. This latter method is particularly convenient for large-scale preparations of **6**.



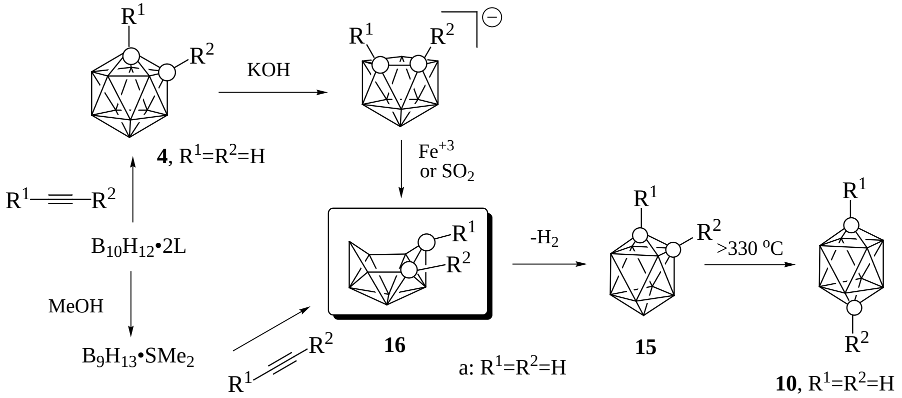
Scheme 2

Some C-substituted *meta*-carboranes, but not *para*-carboranes, have been obtained by thermal rearrangement of the corresponding C-substituted *ortho*-carboranes. This method is limited to methyl[4], ethyl[45], and phenyl[46] derivatives while other alkyls[45] and functional groups[4] show limited thermal stability.

2-Substituted *meta*-carboranes **13** have been efficiently prepared either by $RBCl_2$ (R = Ph (ref.[47]), R = C_6H_4-4-Me (ref.[47]), R = C_6H_4-4-F (ref.[47]), R = vinyl (refs[48,49]), and R = F (ref.[50])) insertion reaction into the *nido* anion **12** or skeletal rearrangement of 3-substituted *ortho*-carboranes **14**. Flash vacuum thermal rearrangement of 3-CN, 3-NH_2, 3-OH, and 3-F (ref.[50]) derivatives of *ortho*-carboranes **14** gives good yields of equimolar mixtures of the 2- and 4-substituted *meta*-carboranes, which can be separated using chromatographic methods[50,51].

Ten-vertex *para*-carborane[52] **10** has been obtained in a similar way to its twelve-vertex analog **6** by thermal rearrangement of the corresponding *ortho*-carborane **15a** *via* the *meta* isomer at the relatively low temperatures of 330–350 °C (Scheme 3)[52]. The *ortho*-carborane **15a** is prepared by thermal[53] or base-induced dehydrogenation[54,55] of *nido*-carborane **16a** obtained either through sequential deboronation[54,56] of twelve-vertex *ortho*-carborane **4** or by acetylene insertion[57] to $B_9H_{13}(SMe_2)$. The overall yield of *para*-carborane **10** is 30–50% based on the starting *ortho*-carborane **4**.

Preparation of C-substituted *para*-carboranes generally follows the preparation of the parent carborane **10** and it takes advantage of the relatively low skeletal rearrangement temperatures tolerated by some organic substituents[58]. Thus, thermal isomerization of C-methyl[52,59], C-pentyl[58], C-hexyl[58], C-phenyl[52], C-(C_6H_4-4-Br) (ref.[58]), and C-(C_6H_4-4-F) (ref.[60]) ten-vertex *closo*-carboranes has been reported to form the corresponding *para* isomers in high yields at 350 °C. The main difference between the preparation of the parent carborane **10** and its derivatives lies in the generally low yield for the second deboronation reaction[56,58] but the lower volatility of the substituted carboranes simplifies the thermolysis step[58].



SCHEME 3

Monocarbaborate anions **2** and **8** were prepared relatively early[61,62] and several reviews on their chemistry and properties have recently appeared[11,28,31]. The carbon atom is introduced as a nitrile ligand to form *arachno* adduct **17** (Scheme 1), which, upon hydrolysis and partial degradation with HCl, yields a mixture of *nido* amines [7-NH_3-$CB_{10}H_{12}$] (**18**) and [6-$NH_3CB_9H_{11}$] (**19**) in proportions dependent upon the reaction conditions[63–65]. N-Methylation followed by dehydrogenation–deamination of the latter using piperidine yields **8** (ref.[66]), while **18** requires borane insertion and sodium metal cleavage of the [1-NMe_3-$CB_{11}H_{11}$] to furnish **2** (ref.[65]).

C-Amino substituted monocarbaboranes **20** and **21** have been obtained in good yields *via* borane insertion to [7-NH_3-$CB_{10}H_{12}$] (**18**) (ref.[67]) and borane-induced dehydrogenation of [6-NH_3-CB_9H_{11}] (**19**) (ref.[68]), respectively. Borane insertion reactions to [7-SMe_2-$CB_{10}H_{12}$] (ref.[67]) or [7-NMe_3-$CB_{10}H_{12}$] (ref.[65]) result in demethylation and products [1-SMe-$CB_{11}H_{11}$]$^-$ and [1-NMe_2-$CB_{11}H_{11}$]$^-$, respectively, have been obtained. The latter is also obtained in 61% yield in the cage expansion reaction of [1-NMe_3-CB_9H_9] with borane[68].

The newest addition to the pool of *closo*-heteraboranes are the azaboranes[69]. Unlike the synthesis of **9** (ref.[70]), the preparation of the parent $[NB_{11}H_{12}]$ (**3**) is rather inefficient and involves the dangerous hydrazoic acid[71]. N-Substituted derivatives are easily prepared using the corresponding amines and $[B_9H_{13}(SMe_2)]$ *via* the *nido* derivative **22** (Scheme 1)[69]. Subsequent thermal dehydrogenation of **22** yields ten-vertex derivatives **9R** (ref.[72]) whereas borane insertion to **22** leads to the corresponding **3R** derivatives[73,74].

3. FUNCTIONALIZATION OF THE TEN- AND TWELVE-VERTEX CLUSTERS

Over the last 35 years the chemistry of all ten boron clusters **1**–**10** has been well advanced and methods for substitution at the boron, carbon, and nitrogen sites have been developed. Among the clusters, the twelve-vertex carboranes **4**–**6** and borates **1** and **7** are the most studied, largely due to their availability. Least investigated are monocarbaborate **8** and the recently prepared azaboranes **3** and **9**, which are less readily available due to more complicated syntheses.

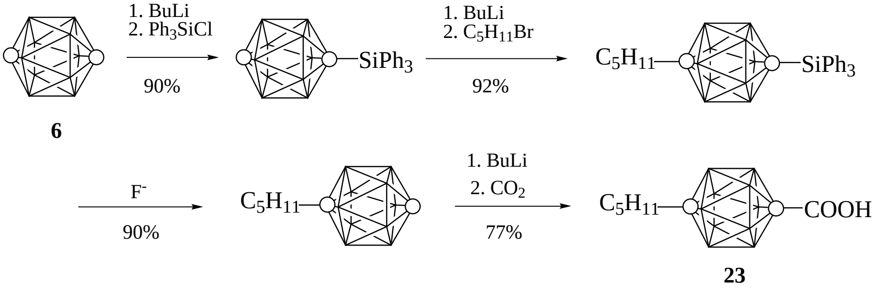
The hydrogen atoms on the endoskeletal carbon and nitrogen atoms in **2**–**6** and **8**–**10** exhibit protic character (*e.g.*, $pK_a = 26.8$ for **6** and 27.3 for **10**)[75]. They can easily be removed using alkyllithiums[25], LDA (ref.[13]), and *t*-BuOK (refs[13,76]) giving rise to highly nucleophilic heteroanions (C-anions or N-anions). The skeletal B–H groups undergo electrophilic substitution reactions with a variety of electrophiles with the preference for the antipodal position to the heteroatom.

In principle, substitution and chemical transformations of the boron, carbon, and nitrogen centers are transferable between the clusters and between the ten- and twelve-vertex series, although differences in reactivity and regiochemistry are occasionally observed. For instance, carbon chemistry developed for *ortho*- and *meta*-carboranes and described in previous reviews[25,27] is applicable to the less available *para*-carboranes **6** and **10** and, to a large extent, to monocarbaborates **2** and **8**. On the other hand, stable dinitrogen derivatives are unique to decaborate **7** although several clusters undergo synthetically useful diazotization-substitution reactions (*vide infra*).

From the liquid crystal point of view, substituents such as n-alkyl, n-alkoxyl, n-alkylthio, cycloalkyl and aryl and functional groups such as esters, nitriles, Schiff bases and azo groups are particularly useful structural elements[77–79]. Judicious choice of these groups allows for modulation and tuning of thermal, optical and dielectric properties of the materials. Here we will concentrate on synthetic methods that allow for introduction of these substituents onto the boron cluster. The chemistry of azaboranes will be omitted in the following discussion. Although azaboranes **3** and **9** can be N-alkylated[80] and B-halogenated[81] they exhibit rather significant sensitivity to solvents and nucleophiles[69] and their usefulness for materials purposes is questionable[74].

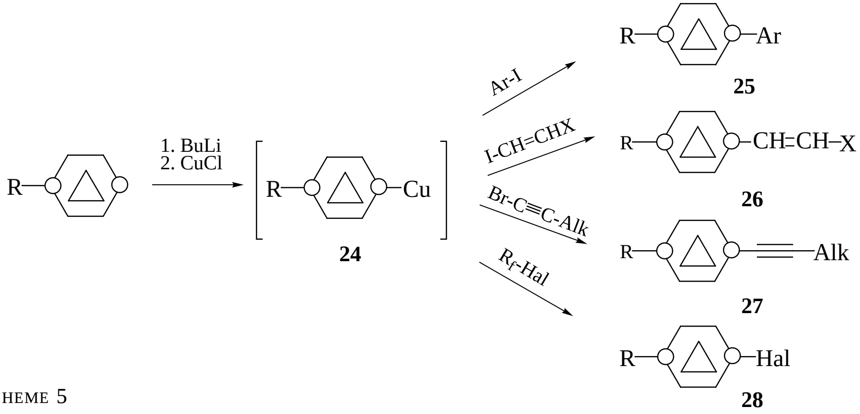
3.1. Carbon Substitution

Carbon–carbon bonds. Carborane and monocarbaborate-derived anions are highly nucleophilic and react with a wide range of C-electrophiles providing a convenient route to C–C bonds. The C-lithium reagents are particularly useful in the alkylation with primary iodides and bromides and carboxylation reactions described for carboranes including *para*-carboranes **6** (refs[20,82,83]) and **10** (refs[58,84,85]), and also for monocarbaborates **2** (refs[67,86]) and **8** (ref.[61]). The preparation of 12-pentyl-*para*-carborane-1-carboxylic acid (**23**, Scheme 4) is an example of both processes[20,82]. It also demonstrates our recently developed strategy for efficient differentiation of the two carbon atoms in **6** using a Ph_3Si substituent, which induces crystallinity and UV activity facilitating isolation, purification and storage of the products and intermediates[82]. Other methods for hetero-disubstitution in **6** (refs[87,88]), **10** (ref.[12]), and **4** (refs[89,90]) are less general.



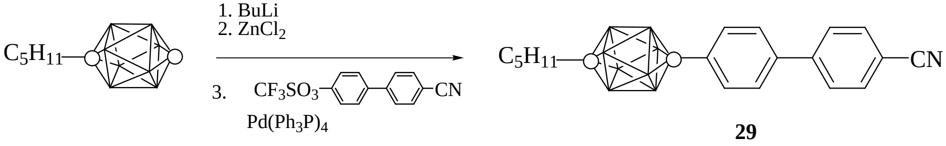
SCHEME 4

Carboranylcopper reagents **24** provide excellent means for the preparation of C-aryl **25**, C-vinyl **26** (ref.[91]), and C-acetylene **27** (refs[23,82,91]) derivatives (Scheme 5). Unlike the carboranyllithiums, the carboranylcopper reagents do not equilibrate with the C–H acid form and high degrees up to 80% of monoarylation of **6** have been obtained[13,82,92]. The original Wade procedure[76] for arylation of the twelve-vertex carboranes[13,82,92,93] has been extended to arylation[58,94] and ethynylation[23] of the ten-vertex *para*-carborane **10**. Attempts to use the procedure for the introduction of perfluoroalkyl derivatives proved unsuccessful, and only carboranyl halides **28** (bromides and iodides) were obtained in the metal–halogen exchange process (Scheme 5)[82]. A similar metal–halogen exchange reaction is also observed with some acetylene iodides and bromides.



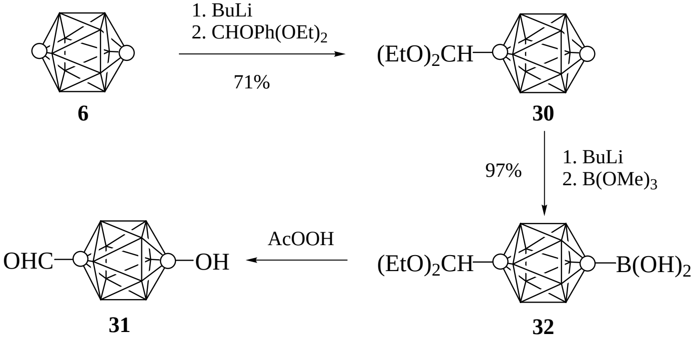
SCHEME 5

It appears that carboranylcoper species are the only effective reagents in arylation reactions. Ten-vertex carboranylzinc is the only exception found so far, and it reacts with 4′-cyano-4-biphenyl triflate under the Negishi reaction conditions, giving a modest yield of the coupling product **29** (ref.[95]). The analogous Pd-catalyzed coupling reactions of twelve-vertex *para*-carboranylzinc[96] or stannane[13] with iodobenzene or with aryl triflates were unsuccessful and no coupling product was observed.



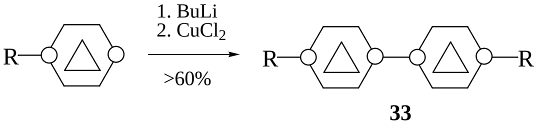
Among other carbon electrophiles that react with carboranyl anions are PhOCN, preferred for preparation of the ten-vertex *para*-carborane nitriles[97], and tosyl cyanide, the reagent of choice for synthesis of twelve-vertex carboranenitriles[98].

The reaction of orthoformates with ten-[97] or twelve-vertex[88,99] carboranyllithium yields carboranyl acetals which are easily converted to the corresponding aldehydes. For instance, *para*-carborane-1,12-dicarbaldehyde was obtained in 23% overall yield based on *para*-carborane **6** (ref.[99]). The reaction of *para*-carborane **6** under controlled conditions gives a non-statistical yield of acetal **30**, which is converted to 12-hydroxy-*para*-carborane-1-carbaldehyde (**31**) *via* boronic acid **32** (Scheme 6)[88].



SCHEME 6

A special case of the C–C bond formation is the dimerization reaction of *para*-carborane. Oxidative coupling of either ten-[12,84] or twelve-vertex[12,100,101] carboranyllithium with anhydrous $CuCl_2$ gives a high yield of the desired dimeric product **33**. If more than one equivalent of BuLi is used then higher oligomers are formed[12,101].

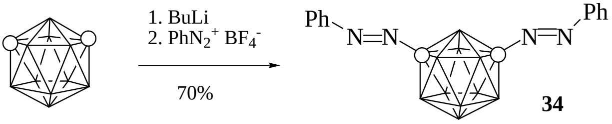


Carbon–nitrogen bonds. There are relatively few examples of C–N bond formation. Direct amination of dilithio-*para*-carborane with MeONHLi has been reported to give a mixture of the 1-amino- and 1,12-diamino-*para*-carboranes[87]. Attempts to extend this procedure to $[12\text{-}(n\text{-}C_7H_{15})\text{-}1\text{-}Li\text{-}CB_{11}H_{10}]$ resulted in only traces of the desired 1-amino product[94].

An alternative approach to the desired C-amino carboranes utilizes the acid-catalyzed cleavage of triazines that can be obtained from carboranyllithium and phenylazide in about 80% yield[102].

C-Nitrosylation of *para*-carboranyllithium with NOCl was reported to proceed in about 30% yield[103]. C-Nitrosylation of monosubstituted *ortho*- and *meta*-carboranyllithium occurs in good yield and *meta*-carboranyllithium can be dinitrosylated in 30% yield[104,105]. Attempted C-nitrosylation of $[12\text{-}(n\text{-}C_7H_{15})\text{-}1\text{-}Li\text{-}CB_{11}H_{10}]$ was unsuccessful[94].

Reactions of *ortho*- or *meta*-carboranyllithium with a benzenediazonium salt yield the corresponding azo derivatives such as **34**, which exhibit remarkably high thermal and chemical stability[106,107].



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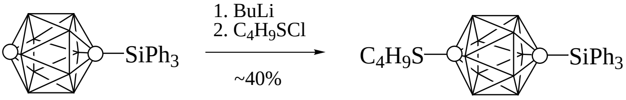
Catalytic reduction of azocarboranes[107] is a recommended method for the preparation of C-amino derivatives and is preferable to the reduction of C-nitroso[104] or C-nitro[85] compounds.

Carbon–sulfur bonds. Formation of the C–S bond can be effected by treatment of the C-lithium or C-sodium derivatives of *ortho*-carborane **4** (refs[89,108–111]), *meta*-carborane **5** (refs[108,109,111]), *para*-carborane **6** (refs[82,103,109,111,112]) and monocarbaborate **2** (ref.[67]) with elemental sulfur[67,89,103,108–112], sulfur dioxide[103,108], dialkyl disulfide[110], or alkylsulfenyl halides[82] as shown for **35**.



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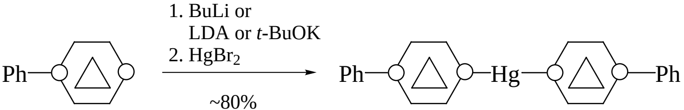
The C–S bond has rather limited stability. Lithium salts of the carboranethiols in benzene and aqueous carboranesulfinic acids undergo thermal desulfurization above 50 °C (ref.[108]). Alkylthio derivatives such as **35** undergo partial decomposition on silica[82] and are susceptible to attack and cleavage by alkyllithiums[110] and fluoride anion[82]. 1-Alkylthio-*ortho*-carboranes, however, have been reacted with BuLi and converted into the corresponding C-anions in high yields[113].

Carbon–oxygen bonds. Direct C-oxygenation has been accomplished by reacting carboranyllithium with oxygen[114] or peroxides[115] among which trimethylsilyl peroxide was found to work best, giving yields of the C-hydroxy-*para*-carborane up to 30% (refs[88,116]). An even more efficient method for introduction of the hydroxy group through the oxidation of the corresponding C-boronic acid was reported recently (Scheme 6)[88]. The sequence of reactions starting from **30** gives 12-hydroxy-*para*-carborane-1-carbaldehyde (**31**), a carborane analog of 4-hydroxybenzaldehyde, in 88% of overall yield.

Carbon–halogen bonds. There are relatively few examples of the formation of C–halogen bonds. The C-halogenation reaction is highly efficient[85,103,117] and occasionally observed as an undesired processes (*vide supra*). The C–I compounds have limited synthetic utility (*vide infra*)[118] while the C–F and C–Cl compounds may be used to increase molecular dipole moments[119] and to introduce axial chirality in 2,9-disubstituted *meta*-carboranes. All C-halogen derivatives are susceptible to base-induced dehalogenation.

Carbon–mercury bonds. Reaction of ten- or twelve-vertex *para*-carboranyl anion with mercury(II) halide leads to the formation of a stable dicarboranylmercury, *e.g.* **36**, with an extended molecular shape[13,103,120]. The anion has been generated using alkyllithiums[120] or LDA (ref.[13]) and reacted with mercury halide or formed *in situ* with potassium *tert*-butoxide in DMF in the presence of $HgBr_2$ (ref.[13]).



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3.2. Boron Substitution

The regiochemistry of electrophilic substitution in boron clusters is frequently complicated by the presence of two or more types of boron atoms in the cage. Although one position in the cage typically has higher electron density and is thermodynamically preferred (B(2) in **6** and **10**, B(9) in **4** and **5**, B(1) and B(10) in **7**, B(10) in **8** and **9**, B(12) in **2** and **3**), the substitution occasionally occurs at kinetic sites (*vide infra*). The regioselectivity of substitution depends on the cluster, type of electrophile, and, occasionally, reaction conditions.

There are two general types of electrophiles which react with a negatively charged cluster to yield either charged or electrically neutral products as shown for a monocarbaborate in Fig. 2.

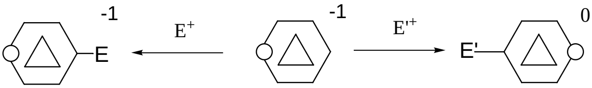
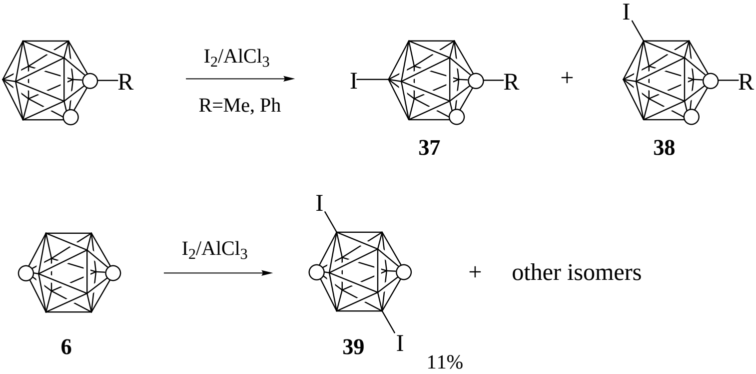


FIG. 2
Substitution with electrophiles E^+ or E'^+ shown using the monocarbaborate as example

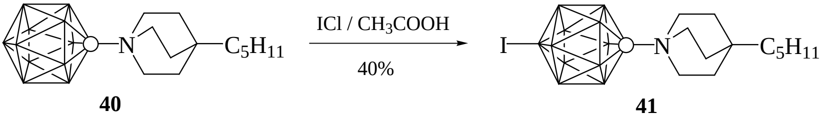
Among the electrophilic reactions, iodination, diazotization, metallation, and sulfurization reactions provide particularly valuable and versatile intermediates in the context of synthesis of liquid crystals. Other reactions are much less selective or preferentially yield the undesired regioisomers.

Boron–iodine bonds. Iodination of the clusters typically proceeds in high yield and with high regioselectivity for the thermodynamic position. The reaction rate and the conditions depend on the type of the cluster; charged clusters undergo iodination under mild conditions while neutral boranes and, in particular *para*-carborane **6**, require Lewis acids as catalysts. Monoiodination[121,122] of 1-methyl- and 1-phenyl-*ortho*-carborane[123–125] yields a mixture of 12- and 9-iodo derivatives, **37** and **38**, respectively, from which the desired 12-iodo isomer **37** can be separated chromatographically[124,125]. Diiodination of *para*-carborane **6** proceeds in high yield but lacks selectivity and the desired 2,9-isomer **39** has been isolated in only 11% yield (Scheme 7)[126].



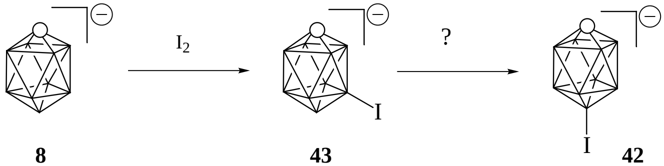
SCHEME 7

Iodination of twelve-vertex monocarbaborate anion **2** proceeds in a high yield and is highly selective for the 12-position[67]. Similarly, iodination of quinuclidine derivative **40** with ICl predominantly yields the 12-iodo derivative **41** in 40 or 73% yield based on recovered starting material[127]. Iodination of the 1-NMe_3 analog with I_2 and $AlCl_3$ as the catalyst was reported to give 81% yield of the corresponding 12-iodo product[128].



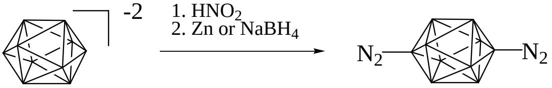
Reaction of I_2 with $[1\text{-}NHMe_2\text{-}CB_{11}H_{11}]$ under basic conditions led to the N-demethylation product[129].

Iodination as well as other halogenation reactions of ten-vertex analog **8** exhibits high regioselectivity for the 6 position and the desired 10-iodo-1-carba-*closo*-decaborate (**42**) is formed in less than 2% yield[130]. It has been proposed that the latter may be obtained by thermal rearrangement of the kinetic 6-isomer **43** isolated in 51% yield[130].



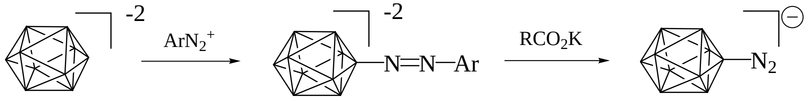
8 **43** **42**

Boron–nitrogen bonds. The formation of stable dinitrogen inner salts is specific to the $[B_{10}H_{10}]^{2-}$ anion (**7**) and no other cluster has been reported to form such derivatives. Thus diazotization of **7** with nitrous acid followed by reductive workup yields about 15–25% of the 1,10-bis(dinitrogen)-*closo*-decaborane (**44**) as the only product[131]. The uniquely high isomeric purity of the isolated **44** and other analogous compounds[132,133] is not necessarily related to the high regioselectivity of the substitution. It is more likely that other isomers are formed but only the 1,10- isomer is stable enough to be isolated. Our *ab initio* calculations support this hypothesis showing that the apical N_2 group is twice as stable to heterolytic cleavage than that in the equatorial position[96].



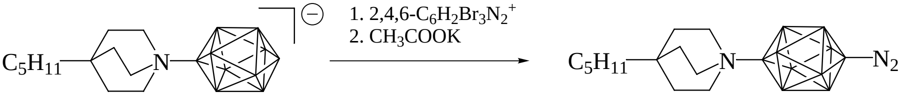
7 **44**

Reaction of the *closo*-decaborate anion (**7**) with one equivalent of arenediazonium salts to form azo compounds **45** is another example of a transformation unique to this cage and highly regiospecific for the apical position[134,135]. The observation that certain aryl groups eliminate under weakly basic conditions yielding the dinitrogen derivatives allowed for selective preparation of 1-dinitrogen-*closo*-decaborate (**46**) and differentiation of the apical position[136,137].



7 **45** **46**

This method also permits the introduction of the dinitrogen to the substituted decaborate monoanions providing an invaluable tool for hetero-disubstitution of **7** (*vide infra*)[136]. For instance, dinitrogen derivative **47** was obtained from the anion **48** in >50% yield using the Hawthorne method[136], while diazotization–reduction sequence of the Knoth method[131,132] is only half as efficient[16].

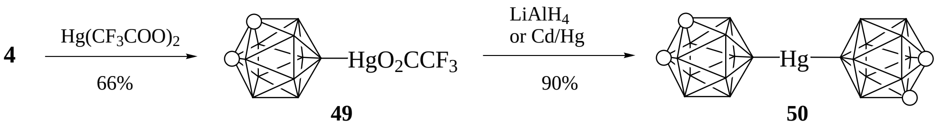


48 **47**

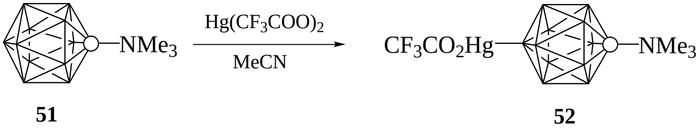
Direct electrophilic amination reactions of charged boranes yield the kinetic *meta* isomers as the major products and only traces of the desired *para* isomers are formed. Reaction of *closo*-dodecaborate anion **1** with hydroxylamine-*O*-sulfonic acid results in the formation of small quantities (<10%) of the desired 1,12-diamine[138,139], while the same reaction for the ten-vertex analog **7** yields equatorial diamines only[138]. Similar results are obtained for hydroxylation reactions with amides and sulfones[140,141].

Amination of monocarbaborate **2** with hydroxylamine-*O*-sulfonic acid gives only traces of the desired 12-amino isomer and the *meta* isomer is the sole product in addition to the recovered starting **2** (ref.[142]).

Boron–metal bonds. Metallation of twelve-vertex boron *closo*-clusters with mercury or thallium trifluoroacetates occurs at the thermodynamic position with high selectivity[143,144]. Parent and substituted carboranes **4** and **5** yield 9-metallo derivatives (*e.g.* **49**) and *para*-carborane **6** gives the 2-metallo derivative in high yields[145]. Reduction of the resulting metallo derivatives leads to dicarboranylmercury (*e.g.* **50**), typically obtained in high yields[143,145]. The regioselectivity of mercuration of C-monosubstituted carboranes has not been investigated[145].



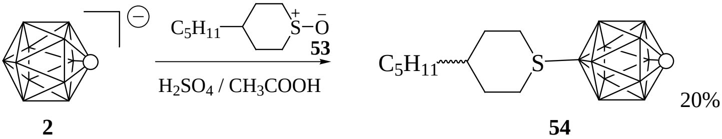
Mercuration of monocarbaborate **2** results in the 12-mercurio derivative obtained in 72% yield[86] and its 1-NMe_3 derivative **51** was mercurated to form **52** in 37% yield[146].



Mercuration of $[B_{12}H_{12}]^{2-}$ gives high yields of dimercurio derivatives, the regiochemistry of which has not been established[147].

Boron–sulfur bonds. 9-Mercaptocarboranes of *ortho*- and *meta*-carboranes have been obtained by direct sulfhydrylation with elemental sulfur in the presence of $AlCl_3$ catalyst in good to excellent yields[109,148,149]. Alternatively, the thiols have been prepared by reaction of carboranes with S_2Cl_2 in the presence of $AlCl_3$, followed by reduction with Zn dust and acid or $NaBH_4$ (ref.[150]).

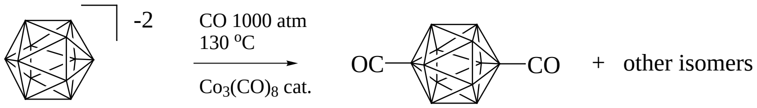
Reaction of monocarbaborate **2** with dimethyl sulfoxide (DMSO) under acidic conditions leads to the neutral 12-dimethylsulfido derivative isolated in 44% yield along with 23% of a byproduct arising from a DMSO self-condensation reaction[67]. Extending this procedure to cyclic sulfoxide **53** gives about 20% yield of the desired product **54** (ref.[151]).



A similar reaction of *closo*-decaborate **7** with DMSO in the presence of HCl yields mixtures of apical and equatorial products[133,152]. Electrophilic sulfurization of *closo*-dodecaborate **1** with DMSO (ref.[153]) or $(SCN)_2$ (ref.[154]) results in the almost exclusive formation of the 1,7-isomers, although a small amount of $[1,12\text{-}(SCN)_2\text{-}B_{12}H_{10}]^{2-}$ has been isolated[154].

Other elements bonded to boron. Although B-chloro and B-fluoro derivatives are too unreactive to be useful intermediates in Pd-catalyzed coupling reactions, they can be used to modify the molecular dipole moments[155,156] and break the symmetry introducing axial chirality.

A high-pressure carbonylation reaction of the dodecaborate anion **1** gives the highest selectivity among the substitution reactions for the desired 1,12- isomer and dicarbonyl compound **55** was obtained in 40% yield[157]. Unfortunately, the difficult reaction conditions needed to form this compound hinder its broader use as the starting material for preparation of other 1,12-disubstituted derivatives of **1**.



1

55 40%

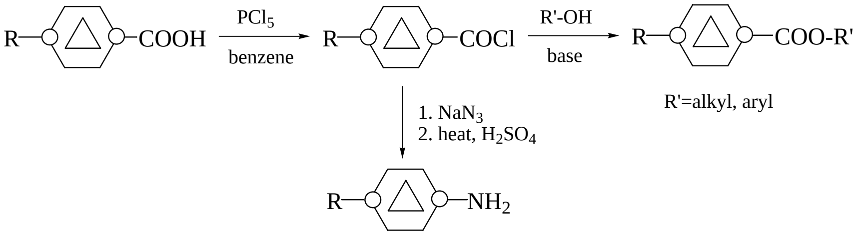
Reactions of $[B_{12}H_{12}]^{2-}$ with other electrophiles proceed with the formation of predominately *meta* (1,7-) isomers and the desired *para* (1,12-) isomers are minor products which are difficult to detect and isolate[132,140,153]. Similarly, other electrophilic substitution reactions of $[B_{10}H_{10}]^{2-}$ yield either mixtures of apical/equatorial or exclusively equatorial[6] products: *e.g.* reaction with halogens[158], carbonyl chlorides[132,140,158,159], protonated MeCN (ref.[160]), and *N*,*N*-dimethylthioformamide[152].

4. FUNCTIONAL GROUP TRANSFORMATIONS

Several classes of *closo*-borane derivatives are particularly important intermediates in synthesis of liquid crystalline materials. Among them are carboxylic acids, which are precursors to esters, amines, and nitriles. B-Iodo derivatives are key intermediates to introduce alkyl, aryl, and acetylene groups. Amines and dinitrogen derivatives of borates **1** and **7** are particularly useful for introduction of onium substituents such as pyridinium and sulfonium. Alkylation and alkylation–cyclization of hydroxy, mercapto, and amino derivatives of boranes are convenient ways to introduce a flexible chain or to build a ring into the molecular rigid core.

Derivatives of closo-boranecarboxylic acids. Formation of esters from carboranecarboxylic acids is typically accomplished in high yield by using carboxylic acid chlorides and an alcohol or phenol in the presence of pyridine or Et_3N (Scheme 8)[17,19,20]. The chlorides of either C- or

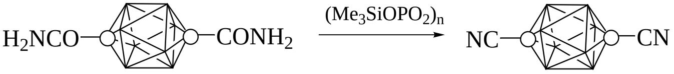
B-carboxylic acids[48,49] are prepared by using PCl_5, which is superior to other reagents.



SCHEME 8

Carboxylic acids and their anhydride forms (*e.g.* **55**) have been used for the synthesis of amines. For instance, C- and B-carboranecarboxylic acids[48,49] and also carbonyl derivatives of **1** and **7** undergo a Schmidt-type reaction with H_2NOSO_3H in aqueous solution to yield the corresponding amines[132,157]. A Curtius-type reaction of acid chlorides or anhydrides with NaN_3 leads to the corresponding amines[87,103,157,161,162] *via* intermediate isocyanates (Scheme 8)[157,162].

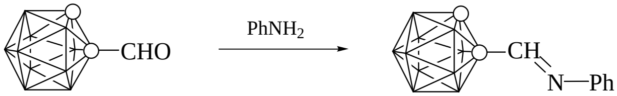
Dehydration of carboxamides, conveniently prepared by ammonolysis of carbonyl chlorides[25], with trimethylsilyl polyphosphate[163] provides a high yield route to carboranylnitriles (*e.g.* **56**)[96].



56

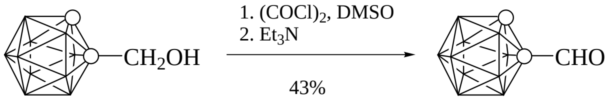
Acid hydrolysis of B-cyanocarboranes furnishes the corresponding carboxylic acids and provides an alternative route to this class of compounds[51].

C-Carboranecarbaldehydes such as **57** are susceptible to amine-induced cleavage of the C–C bond as well as cage deboronation (*e.g.* butylamine). Only the less basic aromatic amines (*e.g.* aniline) were successfully reacted to form the corresponding Schiff base **58** in good yields[164].



57 **58**

Aldehydes, *e.g.* **57** are most reliably prepared from the corresponding hydroxymethyl derivatives using the Swern oxidation reaction[165]. The hydroxymethyls are typically obtained from reaction of carboranyllithiums and formaldehyde[166].

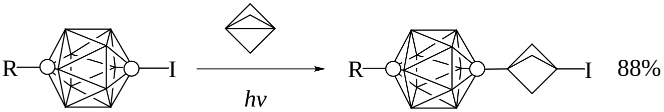


57

Baeyer–Villiger oxidation of *closo*-borane ketones has not been investigated in detail except in the case of derivatives of $[B_{12}H_{12}]^{2-}$ and $[B_{10}H_{10}]^{-}$, which provide access to the corresponding B-hydroxy derivatives[132,140]. Other routes to the B-hydroxy compounds include hydrolysis of amide and sulfone adducts to **1** and **7** (ref.[141]).

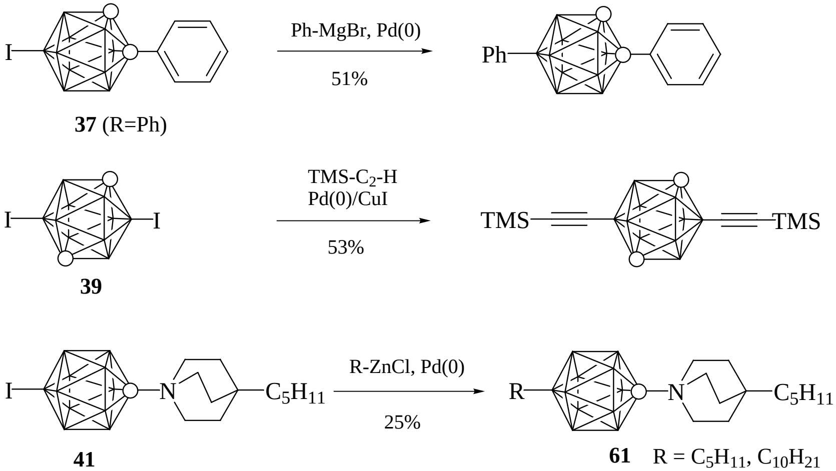
All carborane C-carbonyl compounds including esters[166,167], aldehydes[99,168], and ketones[169] are susceptible to nucleophile-induced cleavage but are stable under acidic conditions. For the carboranes, the rate of alkaline deformylation follows the order *ortho* > *meta* > *para*[168]. It was demonstrated, however, that basic hydrolysis of ethyl *ortho*-carborane-1-carboxylate gives excellent yield of the corresponding acid[170].

Iodo-closo-boranes. A photochemical insertion of [1.1.1]propellane to the C–I bond of 1-iodo-*para*-carborane (**59**) to form **60** is a very elegant, and so far the only synthetic application of carborane C–I derivatives[118]. The resulting iodobicyclo[1.1.1]pentane derivative **60** was dimerized to form the corresponding [2]staffane derivative in 75% yield[118].



59 **60**

B-Iodo compounds undergo Pd-catalyzed cross-coupling reactions with alkyl[171–176], aryl[123,126,139,173–178] (*e.g.* **37**)[123] hetaryl[177], and acetylenyl[126,174,179] (*e.g.* **39**)[126] organometallic reagents. First demonstrated for iodocarboranes[175], the reaction has also been applied to charged species derived from $[B_{12}H_{11}]^{2-}$ (**1**) (refs[139,176]), $[CB_{11}H_{11}]^{-}$ (**2**) (ref.[180]), and neutral compounds such as *ortho*-carborane **4** (refs[123,171,173–175,177,178]), *meta*-carborane **5** (refs[173–175,177,178]), and *para*-carborane **6** (refs[126,175,179]). More recently we have used it to transform **41** to **61** (Scheme 9)[18].



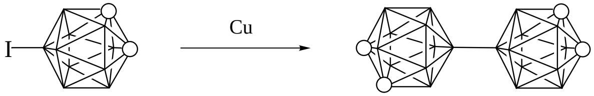
SCHEME 9

Several types of organometallic compounds, including organic derivatives of Mg (refs[123,126,171–173,175–178]), Zn (refs[18,174,181]), and B (ref.[182]) have been used and the choice of the metal depends on the iodide structure and the type of organic residue. It was found that in coupling reactions 9-iodo-*ortho*-carborane is more reactive than the *meta* isomer[177], organozinc reagents are most reactive in the cross-coupling reactions[18,174], and the reactivity of Grignard reagents can be improved using benzene as the co-solvent[177]. Cross-coupling reactions of boronic acids with B-iodocarboranes under Suzuki conditions are inefficient giving a large fraction of byproducts[182]. Pd(0) catalysts have been found to be more effective than Ni(0) complexes, and the use of CuI as co-catalyst has a beneficial effect on the reaction[126,173,180].

Iodide **41** was found to react slowly with alkylzinc reagents in the presence of $(PPh_3)_4Pd$ and it proved resistant to all coupling reactions performed under other conditions[94]. Palladium-catalyzed coupling with either arylboronic esters, alkynes or CuCN failed[94].

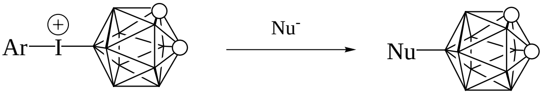
B-Iodocarboranes are largely unreactive towards copper-mediated coupling reactions and substitution with thiolate anions[183]. 9-Iodo-*ortho*-carborane was converted, however, to the corresponding 9-cyano derivative using CuCN under forcing conditions[184] and it dimerized with copper powder to form **62** (ref.[185]).

Carboranyl iodides and other B-halides can be activated towards nucleophilic displacement by converting them into the corresponding



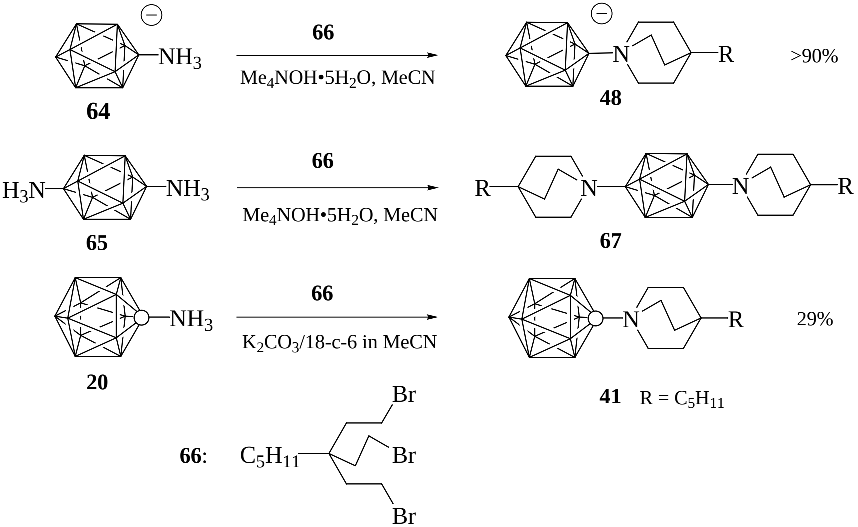
62

arylcarboranylhalonium salts *e.g.* **63** (refs[186,187]). The reaction has been demonstrated for *ortho*-, *meta*-, and *para*-carboranes and a variety of nucleophiles, and constitutes one the best ways to functionalize the B(9) position in these clusters. The yields are in the range of 11–100% depending on the cluster, halide, aryl substituent, nucleophile and the reaction conditions[186].



63 Nu = F^-, CN^-, SCN^-, N_3^-, OH^-, RCO_2^-

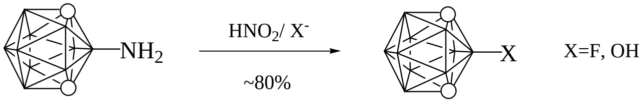
Amino-closo-boranes. Boranamines are rather weak nucleophiles and their trialkylation requires either a strong electrophile or dipolar aprotic reaction conditions. Generally, alkylation–cyclization of ten-vertex boranamines is easier than that of their twelve-vertex analogs. For instance, amine **64** and diamine **65** were alkylated with tribromide **66** in MeCN and in the presence of $Me_4NOH \cdot 5\,H_2O$ as the base to yield the corresponding 4-pentylquinuclidines **48** and **67**, respectively (Scheme 10)[16]. Similar alkylation of **20**



SCHEME 10

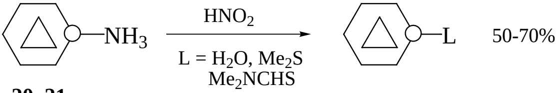
with **66** under the same conditions gave largely HBr elimination products, while using K_2CO_3/18-crown-6 in MeCN allowed isolation of 29% of the quinuclidine **41** (ref.[127]).

C-Amino and B-amino groups provide a convenient route to C–S, C–O, and B–F derivatives by diazotization in the presence of the appropriate Lewis base. For instance, the diazotization reaction of 2-amino-*meta*-carborane **68** in water yields 2-hydroxy-*meta*-carborane while the same reaction in liquid HF furnishes 83% of 2-fluoro-*meta*-carborane[48,49].



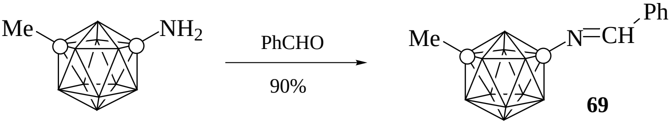
68

Diazotization of [1-NH_3-$CB_{11}H_{11}$] (**20**) (ref.[67]) or 1-amino-*ortho*-carborane[104] in the presence of water or acetic acid yields the corresponding C-hydroxy derivatives in 36% and 60% yield, respectively. Similarly, reaction of **20** (ref.[67]) or [1-NH_3-CB_9H_9] (**21**) (ref.[68]) in the presence of dimethyl sulfide furnishes the 1-dimethylsulfido derivatives in about 60% yield. Diazotization of [1-NH_3-$CB_{11}H_{11}$] (2**0**) in the presence of dimethylthioformamide as the nucleophile allowed for isolation of the corresponding sulfur derivative [1-($SCHNMe_2$)-$CB_{11}H_{11}$] (ref.[151]).



20, **21**

Reaction of carboranylamines[104] and 1-amino-*closo*-decaborate (**64**)[133,188] with benzaldehyde has been reported to produce the corresponding Schiff bases (*e.g.* **69**) in high yields.



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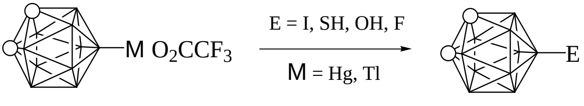
B-Metallated derivatives. B-Metallo derivatives of *closo*-boranes such as **70** react with a range of electrophiles under mild conditions, providing access to many important functional groups. Among them are iodides[86,143] (from I_2), mercaptans[189] (from S_8), hydroxyls[190] (from CrO_3), and fluorides[191] (from $BF_3·Et_2O$) obtained either from the mercurio or thallio derivatives.



70

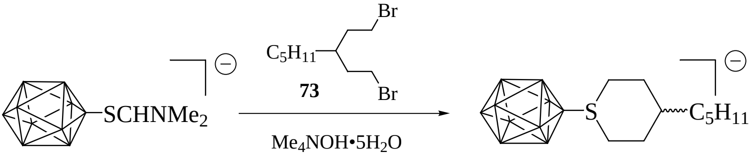
The B-mercurio derivatives photodissociate upon irradiation with UV light, and the resulting radicals react with arenes and olefins giving the corresponding B-substitution products in modest to good yields[144].

Hydroxy-closo-boranes. The O-anions derived from highly acidic carboranyl OH groups[115,116] are rather poor nucleophiles and they react well with strong alkylation reagents such as diazomethane[115], dimethylsulfate ($[1\text{-}(OH)_2\text{-}CB_{11}H_{11}]$) (ref.[67]), and allyl iodide[116]. Acid chlorides[115] and anhydrides[48,51,192] convert the C-hydroxy[115] and B-hydroxy[48,51,192] compounds into corresponding esters in good yields.

An alkylation–cyclization and the formation of the pyran **71** in good yield has been demonstrated for the $[HO\text{-}B_{12}H_{11}]^{2-}$ (ref.[192]).

71

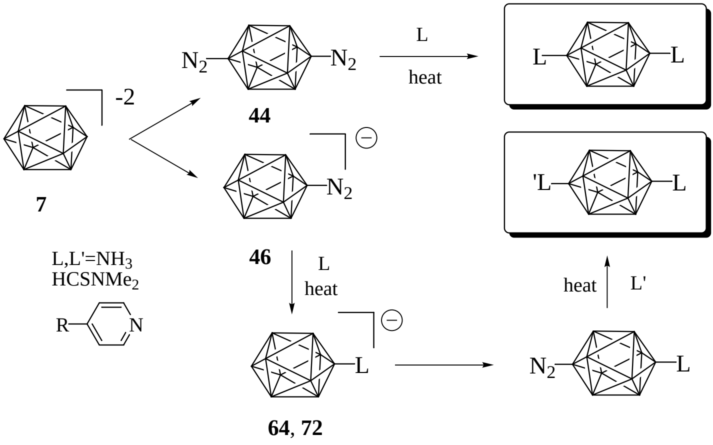
Mercapto-closo-boranes. S-Alkylation of either C-thiols[108,113] or B-thiols[149,150,193,194] is readily accomplished using moderately reactive electrophiles such as MeI (refs[108,111,149,150,194]) dimethyl sulfate ($[1\text{-}(SH_2)\text{-}CB_{11}H_{11}]$ (ref.[67]) and alkyl bromides[113,193]. Alkylation–cyclization of thiolates generated *in situ* by hydrolysis of thioformamide **72** with dibromide **73** gives the corresponding thiacyclohexane derivative **74** (ref.[16]).



72 **74**

Oxidation of alkylthio-[149] and arylthiocarboranes[150] with H_2O_2–AcOH gives the corresponding sulfoxides and sulfones in excellent yields.

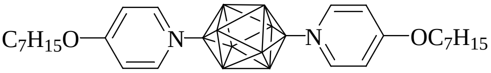
Dinitrogen derivatives of decaborane. Dinitrogen derivatives **44** (ref.[131]) and **46** (ref.[136]) provide unique access to a variety of electrically neutral diapical homo- and heterodisubstituted [$1\text{-LB}_{10}H_8\text{-10-L}'$] (Scheme 11). Thermal decomposition of the dinitrogen derivatives at temperatures above 100 °C in neat Lewis bases such as substituted pyridine[16,17], ammonia[16,131], and *N,N*-dimethylthioformamide[16,152], among others[131–133] yields the substitution product. The reaction presumably proceeds through heterolytic cleavage of the B–N bond and the resulting highly energetic intermediate reacts with the available nucleophile, even with benzene and cyclohexane[131]. Therefore the substitution reactions give good and very good yields only for small nucleophiles, but as the hydrocarbon substituents become dominant in the nucleophile molecule (*e.g.* 4-heptyloxypyridine)[16,17], the yield diminishes.



SCHEME 11

Examples of such syntheses are liquid crystals **75**–**77**, obtained either in a one step process[17] (**75**) or through sequential substitution[16] (**76**, **77**).

Other functional group transformations. Carboranes are relatively resistant to acids and some strong oxidizing reagents and many standard chemical transformations of the side chains and aromatic rings can be accomplished without affecting the carborane ring. It has been found that B-alkyl, -allyl, and -vinyl groups undergo oxidative degradation to form B-COOH acids in high yields[48,49,172,195]. Functionalization of aromatic rings of arylcarboranes have been accomplished by acylation[196], halogenation[196], nitration[47,60,123,170,196–198],



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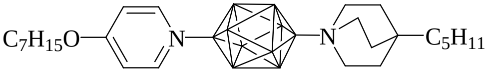

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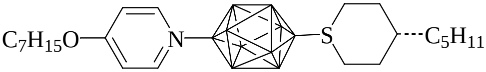

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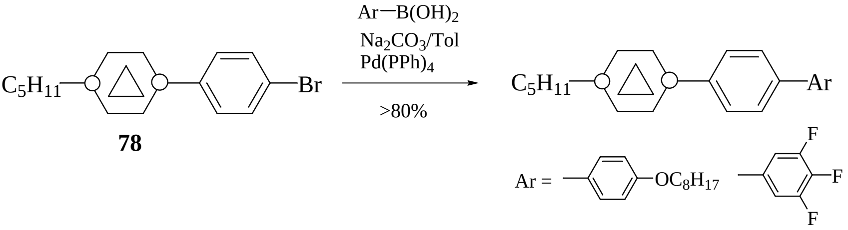
diazotization[198], and oxidation reactions[47]. Phenol-substituted twelve-vertex carboranes have been obtained in good yields by pyridinium salt or HI cleavage of methyl aryl ethers[92]. Electrophilic substitution of the benzene ring preferentially occurs at the 4 position but typically mixtures of the *para* and *meta* isomers are obtained[25].

We have demonstrated the Pd-catalyzed Suzuki coupling reaction of bromide **78** (refs[21,96,151]).



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5. DISCUSSION AND CONCLUSIONS

At first glance, the geometry of *closo*-boranes resembles that of bicyclo[2.2.2]octane (BCO): both antipodally disubstituted derivatives have cylindrical rotational symmetry[17]. The BCO ring is considered an important structural element in synthesis of liquid crystal compounds from both fundamental and practical points of view. Most theories of liquid crystal phases assume molecules as cylindrical objects but in reality there are only very few such compounds except for some BCO derivatives. The use of BCO as structural element has also important practical benefits; incorporation of BCO into the molecular structure significantly enhances thermal stability of liquid crystal phases and promotes their nematogenic behavior.

The cylindrical symmetry of the BCO ring is rather rare among the organic rings. Of three such carbocycles (BCO, cubane, and bicyclo-

[1.1.1]pentane) used as structural elements for liquid crystals, BCO is most synthetically available and, based on empirical data, most beneficial for properties. Unfortunately, the chemistry of the BCO ring is rather limited and the substituents must be "built in" during the ring construction (Fig. 3)[77].

Ten- and twelve-vertex *closo*-boranes provide an alternative set of "cylindrical" structural elements with different stereochemical and electronic properties[15]. Study of a number and variety of such structurally similar liquid crystalline compounds is an important step towards better understanding the origin of liquid crystallinity. This, however, requires facile functionalization methodology for the rings and access to a variety of chemical structures. In contrast to BCO, parent boron clusters undergo straightforward electrophilic or nucleophilic substitution reactions with typically high regioselectivity ensured by their unusual electronic structures. This also allows for introduction of an off-axis substituent Z which will modify stereochemical and dipolar properties of the material. Very few substituents can be "built in" and NH_2 in **20** and **21** is such an example (*vide supra*).

During the four decades of development of chemistry of *closo*-boranes and heteraboranes, an impressive number of organic functional groups have been introduced as substituents. Studies of their chemistry revealed that they undergo typical organic transformations and the clusters generally display reactivity typical of organic compounds rather than of boron hydrides. Further expansion of the "synthetic toolbox" for boron clusters and the availability of a large variety of disubstituted "cylinders" seems straightforward following standard organic-type transformations.

Boron clusters offer much more than an appriopriate shape for liquid crystals. Their conformational properties and electronic structures are unique among the ring structures and studies of their effects on liquid crystal behavior have only begun[22,23]. Full exploration of these effects will require, however, development of more synthetic and structural chemistry of

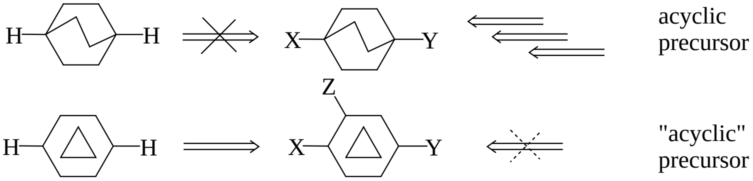

FIG. 3
Functionalization of bicyclo[2.2.2]octane (upper line) and *closo*-boranes (lower line)

the clusters. For instance, methodology for regioselective B(12) substitution of C-monosubstituted *ortho*-carboranes is almost nonexistent (*vide supra*) and B(9) substitution of B(2) derivatives of *meta*-carborane has never been reported. Such compounds would provide access to new liquid crystal structures with variable dipole moments. They could also be used to prepare axially dissymmetric derivatives, which are virtually unknown among the *closo*-boranes[132]. A combination of symmetry (or its lack) with the dipole moment is one of the most important issues in basic and applied science of liquid crystals.

Another unexplored area of *closo*-borane chemistry is the preparation and functionalization of the B(10) position in monocarbadecaborate (**8**). In addition, the methods for the preparation of 12-substituted monocarbaborate (**2**) and 1,12-disubstituted dodecaborate (**1**) derivatives are still unsatisfactory, and compound **55**, currently the best precursor for the latter, is not readily available. All three types of derivatives would give structures with maximally elongated molecular shapes.

Although alkyl and alkylthio substituents have been introduced into boron clusters and their chemistry and stability studied, other groups such as alkoxy, alkylsulfinyl, and alkylsulfonyl are rare. Similarly, the properties of carborane-based azo compounds and Schiff bases is still awaiting more research. Extension of the cylindrical structure of the boranes with quinuclidine and bicyclo[1.1.1]pentane has been reported (*vide supra*) but coupling with a bridgehead iodide such as 1-iodobicyclo[2.2.2]octane has never been reported.

With time, these and other aspects of chemistry of *closo*-boranes will be addressed, bringing more synthetic tools for chemists to engineer new molecular and bulk materials.

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Piotr Kaszynski