

Review

Combining Two Types of Boron in One Molecule (To the 60th Anniversary of the First Synthesis of Carborane)

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Abstract: This review is an attempt to bring together the data from the literature on the synthesis and properties of icosahedral carborane derivatives, in which *exo*-polyhedral three- and four-coordinated boron substituents are attached directly to the carborane cage through boron–carbon or boron–boron bonds. Various classes of compounds are considered, including carboranyl aryl boranes, boronic acids and their derivatives, boroles, diazaboroles, etc. Particular attention is paid to carborane-fused heterocycles containing boron atoms.

Keywords: carborane; boronic acid derivatives; trihydridoborate; arylborane; benzodiazaborole; carborane-fused boron-containing heterocycles; 9-borafluorene; 9,10-diboraanthracene; azoborole; borirane

1. Introduction

The synthesis of carboranes in the early 1960s [1–5] revolutionized the chemistry of boron, giving researchers boron compounds with extraordinary stability and, at the same time, practically unlimited possibilities for their modification [6,7]. At the same time, this development led to the split of organic boron chemistry into two practically non-overlapping branches: the chemistry of classical organoboron compounds, which operates with compounds of the BR_3 type and their derivatives; and the chemistry of polyhedral carboranes and boranes. Despite the first attempt to bind organic boron to the carborane cage being undertaken shortly after the synthesis of the carboranes themselves [8], as well as a number of other studies in this area [9–13], this direction did not undergo significant development until relatively recently due to the rather low stability of the C–B bond in such compounds. Moreover, the use of carboranyl boronic acid esters has been proposed as a convenient method for the synthesis of C-hydroxy carboranes and derivatives thereof [14–26]. The use of generated in situ carboranyl boronic acid esters in Pd-catalyzed cross-coupling reactions has also been described [27]. The situation changed only about 10 years ago due to good prospects for the use of some carborane derivatives as luminescent materials [28–30], which in turn stimulated a notable increase in interest in further research in the field of carborane derivatives with the C–B bond. Subsequent research, especially over the last five years, has led to significant progress in this area. At the same time, no serious attempt has yet been made to generalize the results obtained in this area.

Therefore, the purpose of this work was to collect and summarize the fragmented information available in the literature on the preparation and properties of carborane derivatives with *exo*-polyhedral C–B and B–B bonds.

2. Early Work on Carborane Derivatives with *exo*-Polyhedral Carbon-Boron Bonds

Most of the early work on carborane derivatives with *exo*-polyhedral carbon-boron bonds was more of an exploratory foray into this territory than targeted research aimed at its development. Perhaps the exception here is a series of little-known works by Shagova and Mikhailov in the 1970s, who described the preparation of a fairly large number of such



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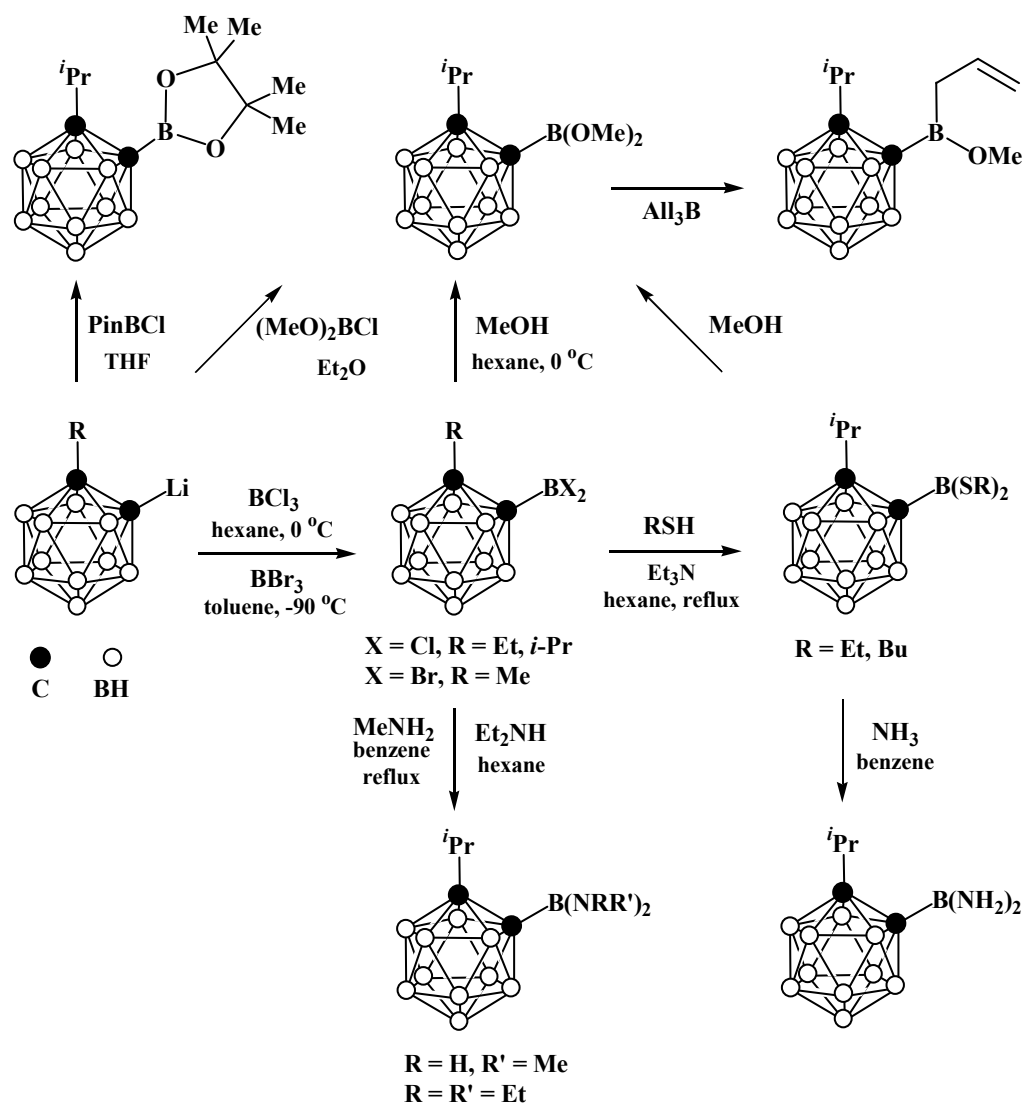
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compounds despite the difficulties with their identification due to imperfections of the instruments of that time.

The reactions of the lithium derivatives of *C*-alkyl-*ortho*-carboranes with BCl_3 or BBr_3 led to the corresponding *ortho*-carboranylboron dihalides $1\text{-X}_2\text{B-2-R-1,2-C}_2\text{B}_{10}\text{H}_{10}$ ($\text{X} = \text{Cl}$, $\text{R} = \text{Et}$, *i*-Pr; $\text{X} = \text{Br}$, $\text{R} = \text{Me}$) (Scheme 1, Figure 1) [9,31–33]. The resulting carboranylboron dichlorides react with two equivalents of alcohols, mercaptans, and amines to form the corresponding esters, thioethers, and amides of *ortho*-carboranylboronic acids, respectively (Scheme 1) [9]. The reaction of the dimethyl ester $1\text{-(MeO)}_2\text{B-2-}i\text{-Pr-1,2-C}_2\text{B}_{10}\text{H}_{10}$ with an excess of methanol leads to the cleavage of the C-B bond to give *C*-isopropyl-*ortho*-carborane [9]. The dimethyl ester $1\text{-(MeO)}_2\text{B-2-}i\text{-Pr-1,2-C}_2\text{B}_{10}\text{H}_{10}$ can also be prepared by the direct reaction of the lithium derivative of *C*-isopropyl-*ortho*-carborane with $(\text{MeO})_2\text{BCl}$ (Scheme 1, Figure 1) [33]. Similarly, the pinacol ester $1\text{-PinB-2-}i\text{-Pr-1,2-C}_2\text{B}_{10}\text{H}_{10}$ was prepared by the reaction of the lithium derivative of *C*-isopropyl-*ortho*-carborane with PinBCl (Scheme 1) [33]. The reaction of $1\text{-(MeO)}_2\text{B-2-}i\text{-Pr-1,2-C}_2\text{B}_{10}\text{H}_{10}$ with an excess of triallylborane results in the corresponding allyl-methoxyboryl derivative $1\text{-All(MeO)B-2-}i\text{-Pr-1,2-C}_2\text{B}_{10}\text{H}_{10}$ (Scheme 1) [33].



Scheme 1. Syntheses of the $\text{X}_2\text{B-ortho}$ -carborane derivatives ($\text{X} = \text{Cl}, \text{Br}, \text{OR}, \text{SR}, \text{NR}_2$).

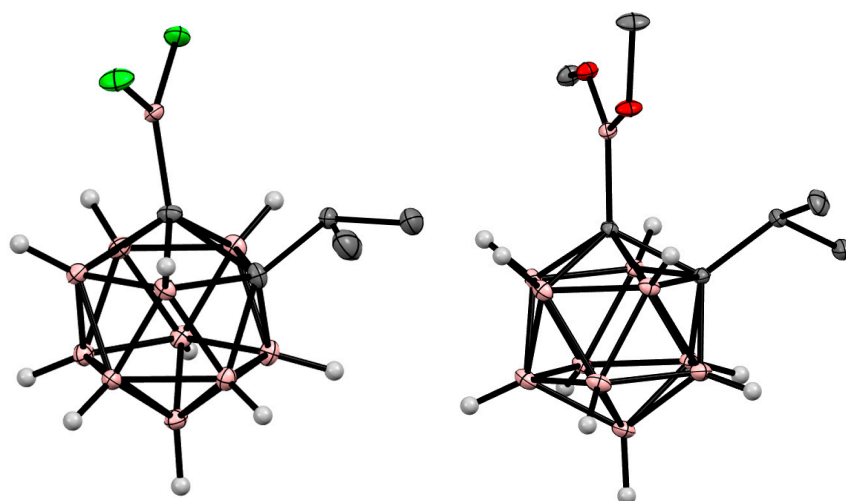


Figure 1. Single crystal structures of 1-Cl₂B-2-*i*-Pr-1,2-C₂B₁₀H₁₀ (**left**) and 1-(MeO)₂B-2-*i*-Pr-1,2-C₂B₁₀H₁₀ (**right**). Hydrogen atoms of organic substituents are omitted for clarity.

The reaction of 1-Cl₂B-2-*i*-Pr-1,2-C₂B₁₀H₁₀ with 2 equiv. of pentafluorophenol in dichloromethane leads to μ -1,1'-O(1-(C₆F₅O)B-2-*i*-Pr-C₂B₁₀H₁₀)₂ (Figure 2) as a product of dehydration of the carboranyl boronic acid pentafluorophenyl monoester [33].

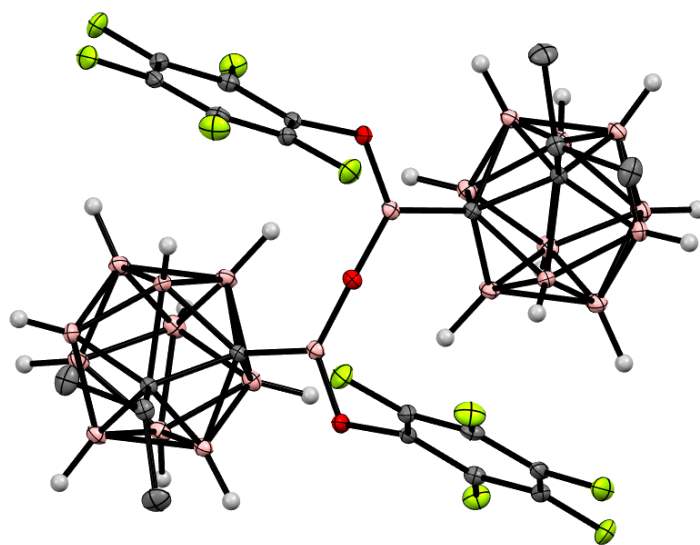
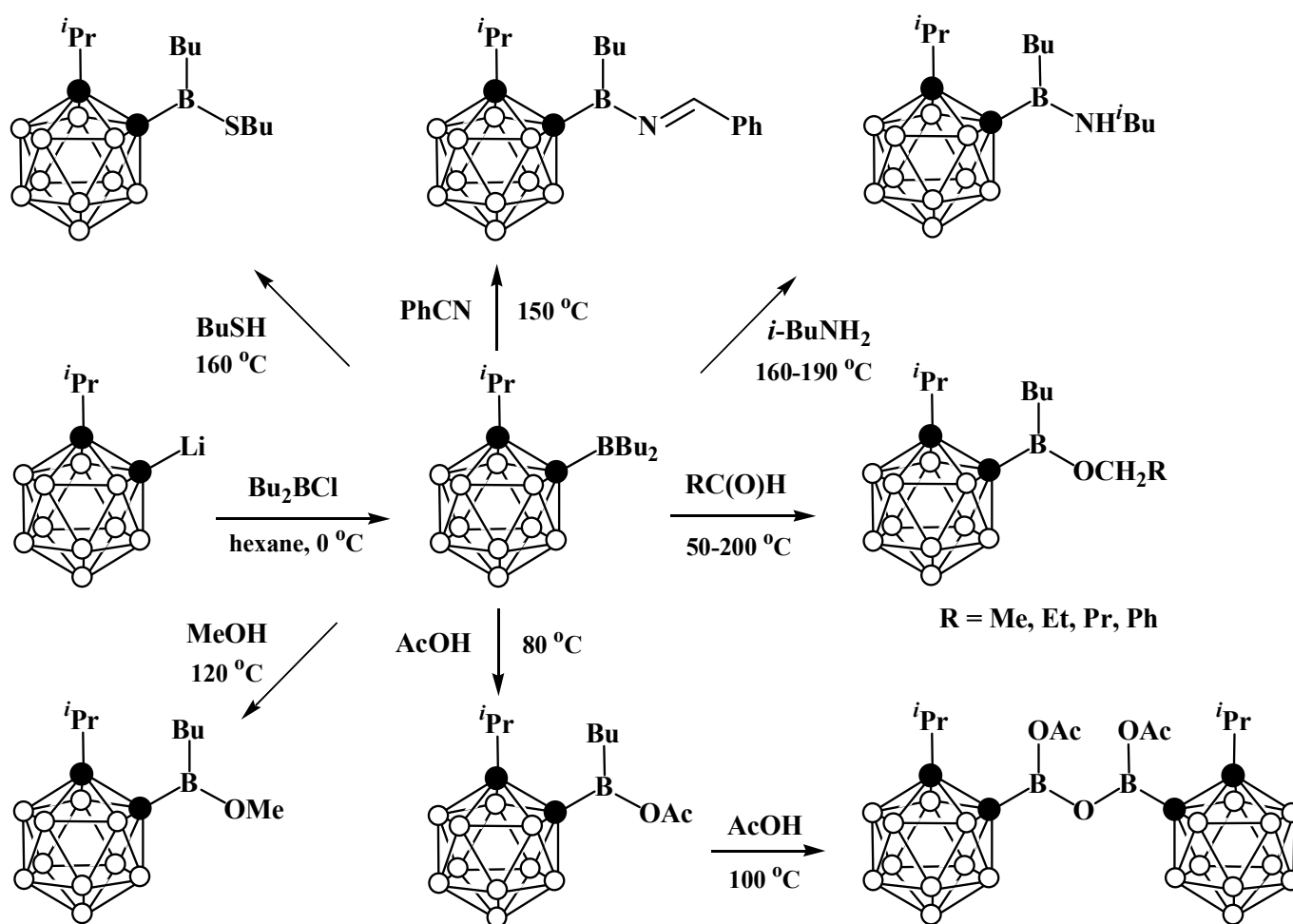


Figure 2. Single crystal structure of μ -1,1'-O(1-(C₆F₅O)B-2-*i*-Pr-C₂B₁₀H₁₀)₂. Hydrogen atoms of organic substituents are omitted for clarity.

The dimethoxyboryl derivative of unsubstituted *ortho*-carborane 1-(MeO)₂B-1,2-C₂B₁₀H₁₁ was prepared by the reaction of 6,9-bis(diethylsulfide)decaborane with ethynyldimethoxyborane HC≡CB(OMe)₂ in refluxing benzene [8]. The 1,2-bis(dimethoxyboryl) derivative 1,2-((MeO)₂B)₂-1,2-C₂B₁₀H₁₀ was prepared by the reaction of the dilithium derivative of *ortho*-carborane with bis(dimethoxy)boron chloride (MeO)₂BCl [34].

The reaction of the lithium derivative of *C*-isopropyl-*ortho*-carborane with Bu₂BCl in hexane produces the corresponding *ortho*-carboranyl dibutylborane 1-Bu₂B-2-*i*-Pr-1,2-C₂B₁₀H₁₀ [35]. Its reactions with aliphatic aldehydes at 50–100 °C lead to the corresponding *ortho*-carboranyl butylborinate esters 1-RO(Bu)B-2-*i*-Pr-1,2-C₂B₁₀H₁₀ (R = Et, Pr, Bu), whereas the reaction with benzaldehyde requires heating at 100–200 °C (Scheme 2) [36]. It should be noted that the reactions with aliphatic aldehydes at 140–150 °C proceed with the cleavage of the C-B bond, with the release of *C*-isopropyl-*ortho*-carborane [36]. The reaction of 1-Bu₂B-2-*i*-Pr-1,2-C₂B₁₀H₁₀ with benzaldehyde in polar donor solvents,

such as pyridine or hexamethylphosphoramide (HMPA), at 100–120 °C proceeds through addition to the C=O double bond with cleavage of the C_{carb}-B bond [36]. Similarly, the reactions of 1-Bu₂B-2-*i*-Pr-1,2-C₂B₁₀H₁₀ with aromatic nitriles in hexamethylphosphoramide at 80–150 °C proceed through addition of the C≡N triple bond with cleavage of the C_{carb}-B bond [37]. At the same time, the reaction with benzonitrile at 150 °C in the absence of HMPA leads to *ortho*-carboranyl phenylaldiminobutylborane 1-PhCH=N(Bu)B-2-*i*-Pr-1,2-C₂B₁₀H₁₀ (Scheme 2) [38]. The reaction of 1-Bu₂B-2-*i*-Pr-1,2-C₂B₁₀H₁₀ with 1 equivalent of glacial acetic acid at 80 °C results in removal of one butyl group with the formation of the *ortho*-carboranyl acetoxybutylborane 1-AcO(Bu)B-2-*i*-Pr-1,2-C₂B₁₀H₁₀, while the reaction with an excess of acetic acid at 100 °C leads to the *ortho*-carboranyl pyroboracetic anhydride μ-1,1'-O(1-(AcO)B-2-*i*-Pr-1,2-C₂B₁₀H₁₀)₂ (Scheme 2) [35,38].

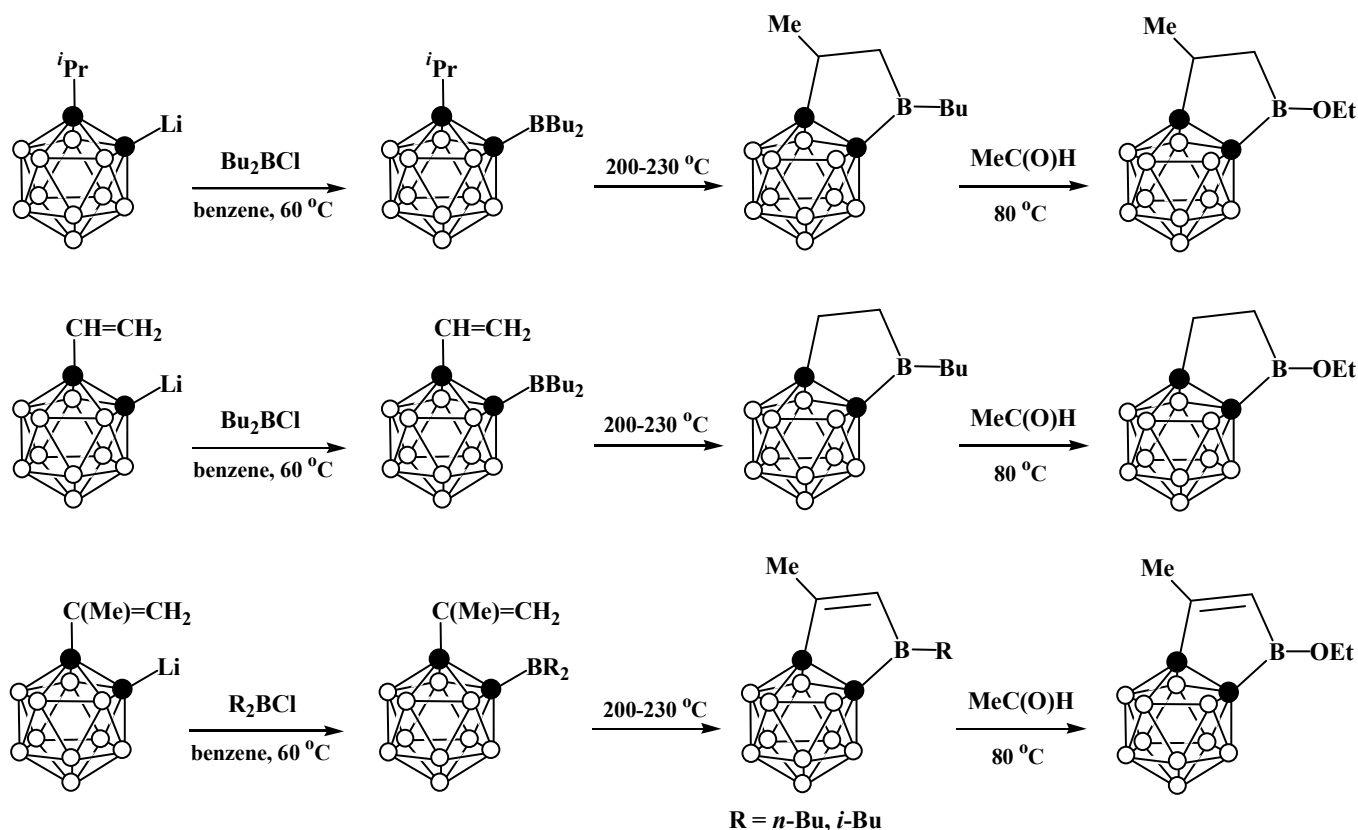


Scheme 2. Synthesis of 1-Bu₂B-2-*i*-Pr-*ortho*-carborane and its transformations.

The reaction of 1-Bu₂B-2-*i*-Pr-1,2-C₂B₁₀H₁₀ with 1 equivalent of butylthiol at 160 °C results in the thioester 1-BuS(Bu)B-2-*i*-Pr-1,2-C₂B₁₀H₁₀, while the reactions with methanol at 120 °C and isobutylamine at 160–190 °C give ester 1-MeO(Bu)B-2-*i*-Pr-1,2-C₂B₁₀H₁₀ and aminoborane 1-*i*-BuNH(Bu)B-2-*i*-Pr-1,2-C₂B₁₀H₁₀, respectively, together with C-isopropyl-*ortho*-carborane as the product of the C-B bond cleavage (Scheme 2) [35,38].

It should be noted that all the carborane derivatives given above, with the exception of the acetoxy derivatives, are vacuum-distillable oils or low-melting solids. However, the dibutylborane derivative 1-Bu₂B-2-*i*-Pr-1,2-C₂B₁₀H₁₀, which is a viscous, colorless liquid, when heated to 200–230 °C, splits off one butyl group with release 1- and 2-butene, and it undergoes cyclization to form 1,2-μ-(1'-butyl-3'-methyl-1'-borapropylene)-*ortho*-carborane with release of dihydrogen (Scheme 3) [39,40]. Similarly, heating 1-Bu₂B-2-

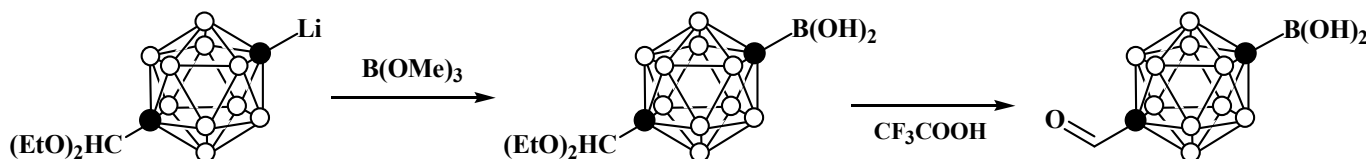
$\text{H}_2\text{C}=\text{CH}-1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$, $1\text{-Bu}_2\text{B}-2\text{-H}_2\text{C}=\text{C}(\text{Me})-1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$, and $1\text{-(i-Bu)}_2\text{B}-2\text{-H}_2\text{C}=\text{C}(\text{Me})-1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ at $200\text{--}230\text{ }^\circ\text{C}$ results in the corresponding five-membered cyclization products $1,2\text{-}\mu\text{-(BuBCH}_2\text{CH}_2\text{)}-1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$, $1,2\text{-}\mu\text{-(BuBCH}=\text{CMe)}-1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$, and $1,2\text{-}\mu\text{-(i-BuBCH}=\text{CMe)}-1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$, respectively (Scheme 3) [40]. As in the case of the acyclic dibutylborane derivative $1\text{-Bu}_2\text{B}-2\text{-i-Pr}-1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$, the resulting cyclic derivatives react with acetaldehyde to form the corresponding ethoxy derivatives $1,2\text{-}\mu\text{-(EtOBCH}_2\text{CHMe)}-1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$, $1,2\text{-}\mu\text{-(EtOBCH}_2\text{CH}_2\text{)}-1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$, and $1,2\text{-}\mu\text{-(EtOBCH}=\text{CH)}-1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ (Scheme 3) [40].



Scheme 3. Thermal cyclization of $1\text{-R}_2\text{B}-2\text{-R}'\text{-ortho-carboranes}$.

Reduction of $1,2\text{-}\mu\text{-(EtOBCH}_2\text{CHMe)}-1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ with LiAlH_4 in diethyl ether yields the corresponding borane isolated as the complex with triethylamine $1,2\text{-}\mu\text{-(Et}_3\text{N}\cdot\text{HBCH}_2\text{CHMe)}-1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ [41].

The *para*-carboranyl boronic acid $1\text{-(HO)}_2\text{B}-12\text{-H(O)C}-1,12\text{-C}_2\text{B}_{10}\text{H}_{10}$ was synthesized by the reaction of the diacetal protected *para*-carboranyl aldehyde with *n*-butyllithium, followed by treatment with trimethylborate B(OMe)_3 and deprotecting the aldehyde function with trifluoroacetic acid (Scheme 4) [13].

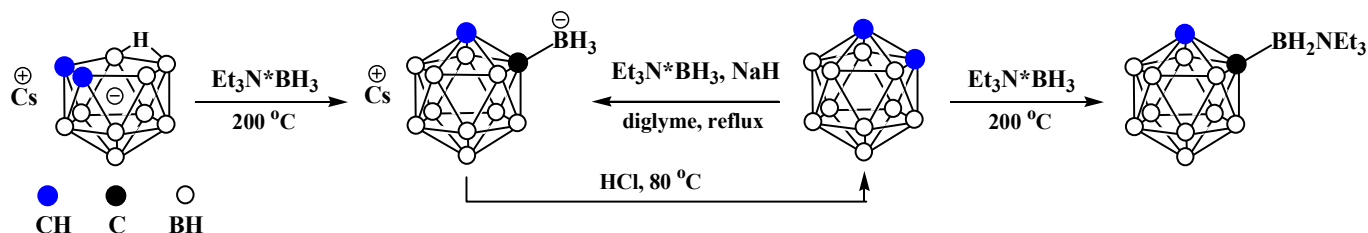


Scheme 4. Synthesis of the *para*-carboranyl boronic acid $1\text{-(HO)}_2\text{B}-12\text{-H(O)C}-1,12\text{-C}_2\text{B}_{10}\text{H}_{10}$.

3. Anionic Carboranes with BX_3 Substituents and Derivatives Thereof

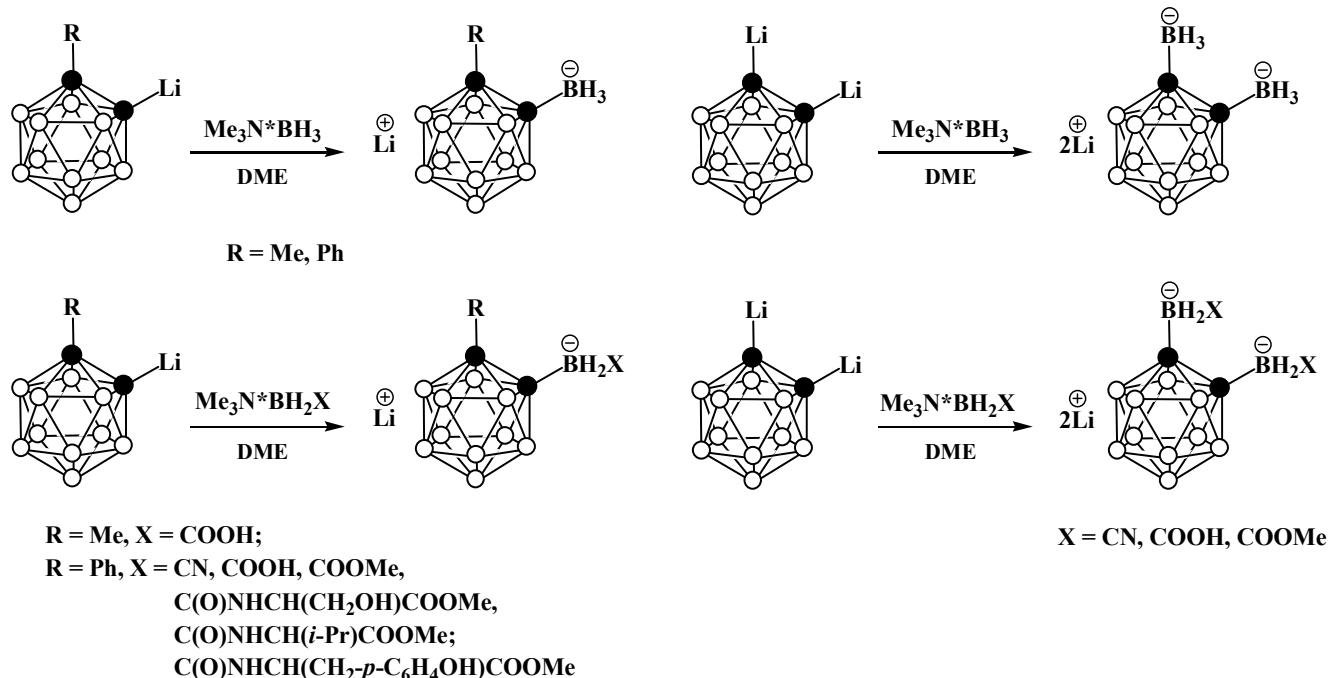
The anionic trihydridoborate derivative of *ortho*-carborane $\text{Cs}[1\text{-H}_3\text{B}-1,2\text{-C}_2\text{B}_{10}\text{H}_{11}]$ was obtained by heating the cesium salt of *nido*-carborane in triethylamine-borane $\text{Et}_3\text{N}\cdot\text{BH}_3$

at 200 °C. It was suggested that the formation of the trihydridoborate derivative occurs upon the interaction of the resulting deprotonated *ortho*-carborane with an excess of triethylamine-borane. Indeed, the reaction of *ortho*-carborane with triethylamine-borane in refluxing diglyme in the presence of NaH, followed by the addition of tetramethylammonium chloride in water, leads to $(\text{Me}_4\text{N})[1\text{-H}_3\text{B-1,2-C}_2\text{B}_{10}\text{H}_{11}]$, while the reaction of *ortho*-carborane with triethylamine-borane at 200 °C gives the triethylammonium-dihydridoborate derivative $1\text{-Et}_3\text{NBH}_2\text{-1,2-C}_2\text{B}_{10}\text{H}_{11}$ (Scheme 5) [11]. Short-term (30 min) heating of $\text{Cs}[1\text{-H}_3\text{B-1,2-C}_2\text{B}_{10}\text{H}_{11}]$ in an acidic aqueous solution leads to its complete hydrolysis to the parent *ortho*-carborane [11].



Scheme 5. Synthesis of the trihydridoborate derivative of *ortho*-carborane and its complex with triethylamine.

The anionic trihydridoborate derivatives of *ortho*-carborane $\text{Li}[1\text{-H}_3\text{B-2-R-1,2-C}_2\text{B}_{10}\text{H}_{10}]$ ($\text{R} = \text{Me, Ph}$) and $\text{Li}_2[1,2\text{-(H}_3\text{B)}_2\text{-1,2-C}_2\text{B}_{10}\text{H}_{10}]$ were prepared by the reactions of the corresponding lithium derivatives of *ortho*-carborane with trimethylamine-borane $\text{Me}_3\text{N}\cdot\text{BH}_3$ in 1,2-dimethoxyethane. Using the same approach, a series of functionalized dihydridoborate derivatives of *ortho*-carborane were synthesized (Scheme 6) [41].



Scheme 6. Synthesis of the trihydridoborate derivatives of *ortho*-carborane and their analogs containing various functional groups.

The difluorohydridoborate derivative of $(\text{Me}_4\text{N})[1\text{-HF}_2\text{B-1,2-C}_2\text{B}_{10}\text{H}_{11}]$ (Figure 3) was unexpectedly isolated as a side product of the *ortho*-carborane deboronation reaction with anhydrous $(\text{Me}_4\text{N})\text{F}$ in tetrahydrofuran. The formation of the difluorohydridoborate derivative was rationalized by partial deprotonation of *ortho*-carborane with F^- to result in $[\text{closo-1,2-C}_2\text{B}_{10}\text{H}_{11}]^-$, which participates in the deboronation of the second equivalent of

closo-1,2- $C_2B_{10}H_{10}$. $(Me_4N)[1-HF_2B-9,12-I_2-1,2-C_2B_{10}H_9]$ (Figure 3) was obtained similarly, starting from the 9,12-diiodo derivative of *ortho*-carborane [42].

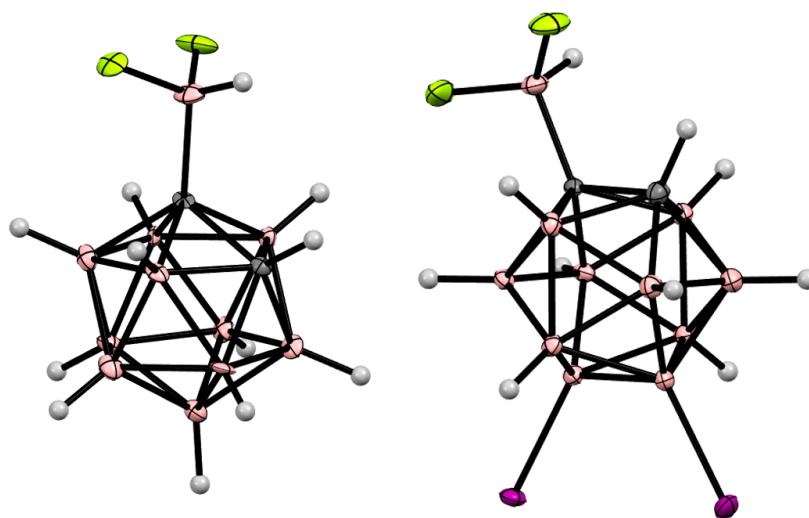
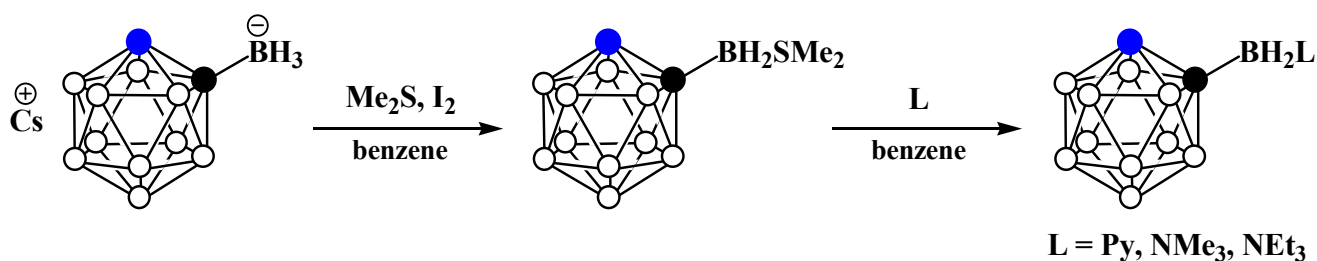


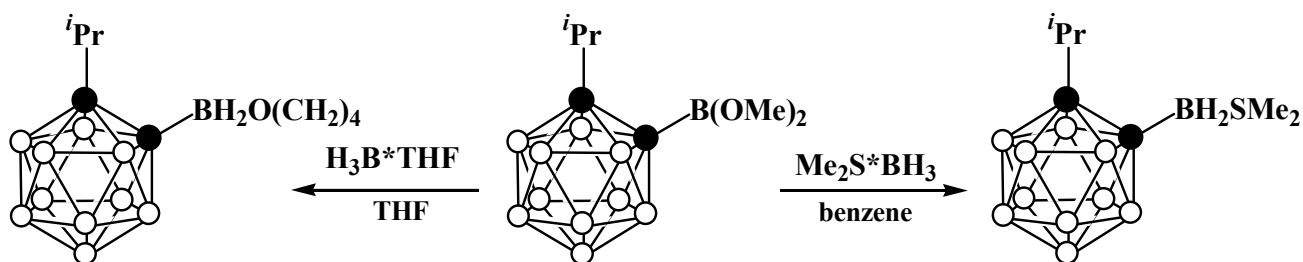
Figure 3. Single crystal structures of $[1-HF_2B-1,2-C_2B_{10}H_{11}]^-$ (left) and $[1-HF_2B-9,12-I_2-1,2-C_2B_{10}H_9]^-$ (right) anions.

The treatment of $Cs[1-H_3B-1,2-C_2B_{10}H_{11}]$ in dimethylsulfide with iodine in benzene results in the dimethylsulfonium-dihydridoborate derivative $1-Me_2SBH_2-1,2-C_2B_{10}H_{11}$, which in turn reacts with amines in benzene to form of the corresponding amine-dihydridoborate derivative $1-LBH_2-1,2-C_2B_{10}H_{11}$ ($L = Py, Me_3N, Et_3N$) (Scheme 7) [11].



Scheme 7. Synthesis of amine complexes with the dihydridoborate derivative of *ortho*-carborane.

The dimethylsulfonium- and pentamethyleneoxonium-dihydridoborate derivatives $1-Me_2SBH_2-2-i-Pr-1,2-C_2B_{10}H_{10}$ and $1-(CH_2)_5OBH_2-2-i-Pr-1,2-C_2B_{10}H_{10}$ were synthesized by reactions of $1-(MeO)_2B-2-i-Pr-1,2-C_2B_{10}H_{10}$ with $Me_2S \cdot BH_3$ in diethyl ether and BH_3 in tetrahydrofuran, correspondingly (Scheme 8) [33]. The tetrahydrofuran molecule in $1-(CH_2)_5OBH_2-2-i-Pr-1,2-C_2B_{10}H_{10}$ can be replaced by 4-dimethylaminopyridine to give $1-p-Me_2NC_5H_4NBH_2-2-i-Pr-1,2-C_2B_{10}H_{10}$ (Figure 4) [33].



Scheme 8. Synthesis of Lewis base complexes with the dihydridoborate derivative of 1-isopropyl-*ortho*-carborane.

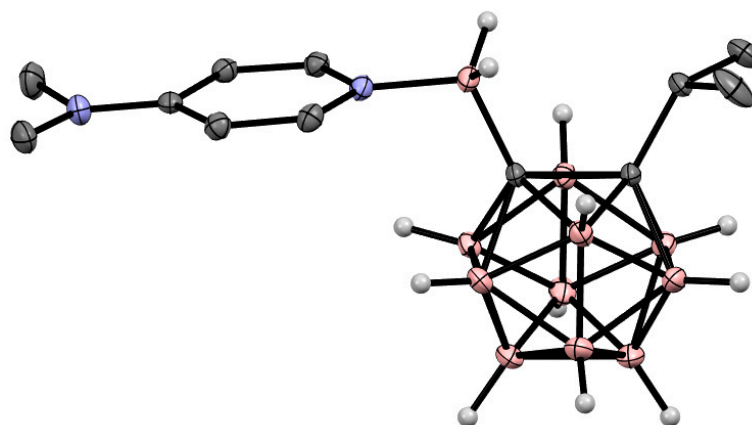
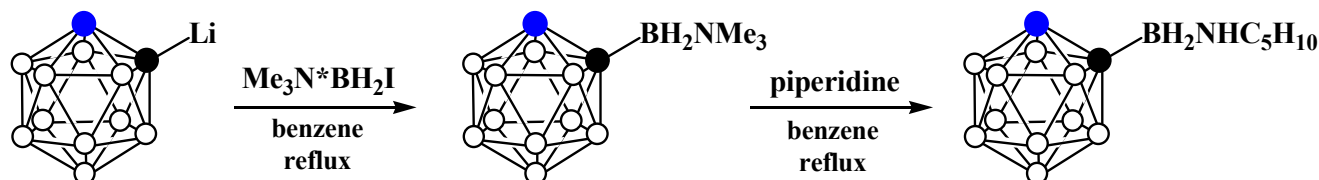


Figure 4. Single crystal structure of 1-*p*-Me₂NC₅H₄NBH₂-2-*i*-Pr-1,2-C₂B₁₀H₁₀. Hydrogen atoms of organic substituents are omitted for clarity.

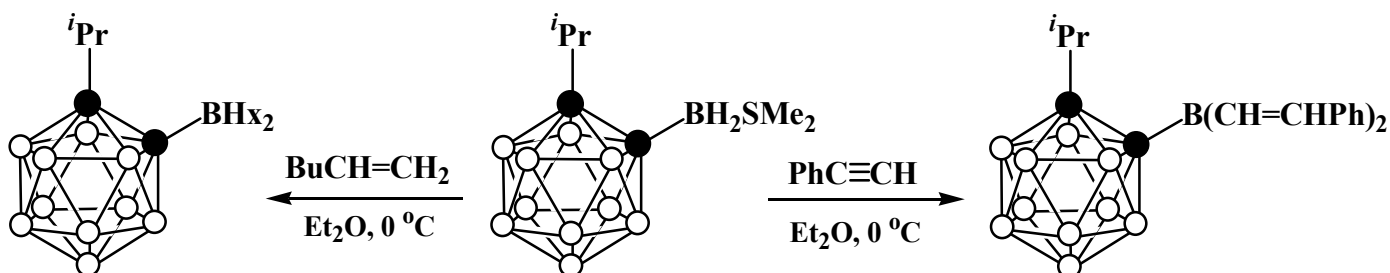
The trimethylammonium-dihydridoborate derivative 1-Me₃NBH₂-1,2-C₂B₁₀H₁₁ can be also prepared by the reaction of the lithium derivative of *ortho*-carborane with Me₃N·BH₂I in benzene (Scheme 9) [10,43]. In contrast to the trihydridoborate derivative [1-H₃B-1,2-C₂B₁₀H₁₁][−], the trimethylammonium-dihydridoborate derivative is resistant to acid and alkaline hydrolysis. At the same time, the CH group in 1-Me₃NBH₂-1,2-C₂B₁₀H₁₁ exhibits properties typical of carboranes. In particular, its treatment with *n*-butyllithium followed by methyl iodide gives 1-Me₃NBH₂-2-Me-1,2-C₂B₁₀H₁₀ [10]. Heating 1-Me₃NBH₂-1,2-C₂B₁₀H₁₁ under reflux in piperidine results in the replacement of trimethylamine with piperidine to form the piperidinium-dihydridoborate derivative 1-C₅H₁₀NBH₂-1,2-C₂B₁₀H₁₁ (Scheme 9) [10].



Scheme 9. Synthesis of amine complexes with the dihydridoborate derivative of *ortho*-carborane.

The trimethylammonium-dihydridoborate derivative 1-Me₃NBH₂-1,2-C₂B₁₀H₁₁ has also been obtained by thermal decomposition of the tetramethylammonium salt of reduced *ortho*-carborane (Me₄N)[C₂B₁₀H₁₃] at 200 °C [10].

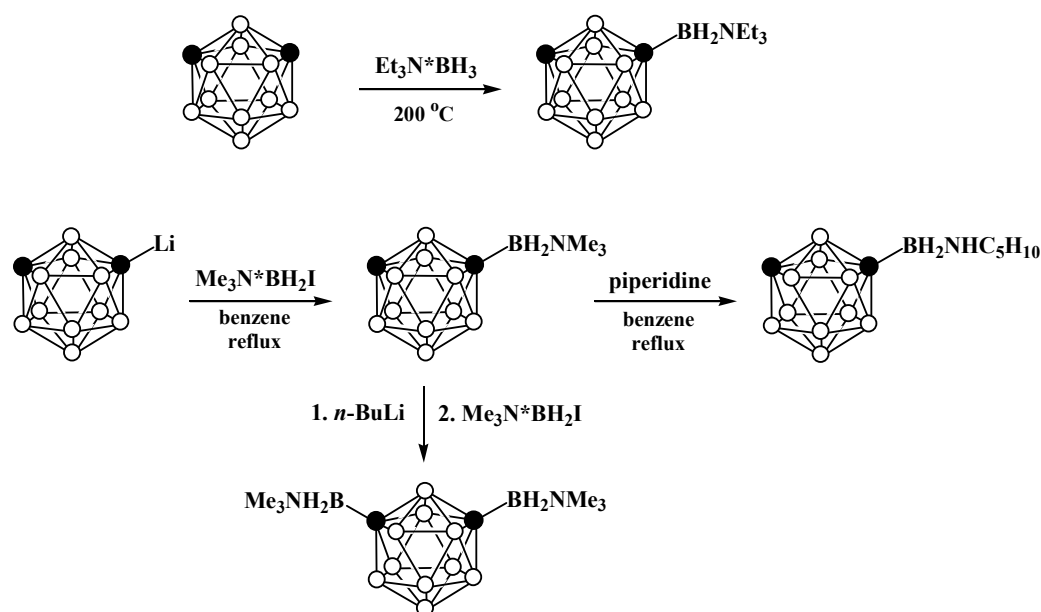
Hydroboration of hex-1-ene and phenylacetylene with 1-Me₂SBH₂-2-*i*-Pr-1,2-C₂B₁₀H₁₀ in diethyl ether results in the corresponding di(*n*-hexyl)boryl- and di(phenylethylenyl) carboranes 1-(*n*-Hx)₂B-2-*i*-Pr-1,2-C₂B₁₀H₁₀ and 1-(PhCH=CH)₂B-2-*i*-Pr-1,2-C₂B₁₀H₁₀, respectively (Scheme 10) [33].



Scheme 10. Hydroboration of double and triple bonds with 1-Me₂SBH₂-2-*i*-Pr-1,2-C₂B₁₀H₁₀.

The triethylammonium-dihydridoborate derivative of *meta*-carborane 1-Et₃NBH₂-1,7-C₂B₁₀H₁₁ in low yield was obtained by heating *meta*-carborane in triethylamine-borane

at 200 °C (Scheme 11) [11]. The trimethylammonium-dihydridoborate derivative of *meta*-carborane 1-Me₃NBH₂-1,7-C₂B₁₀H₁₁ was prepared by the reaction of the lithium derivative of *meta*-carborane with Me₃N·BH₂I in benzene. The treatment of 1-Me₃NBH₂-1,2-C₂B₁₀H₁₁ with *n*-butyllithium in benzene, followed by heating with Me₃N·BH₂I, leads to 1,7-(Me₃NBH₂)₂-1,7-C₂B₁₀H₁₀. Heating 1-Me₃NBH₂-1,7-C₂B₁₀H₁₁ under reflux in piperidine results in the replacement of trimethylamine with piperidine to form the piperidinium-dihydridoborate derivative 1-C₅H₁₀NHBH₂-1,7-C₂B₁₀H₁₁ (Scheme 11) [10].



Scheme 11. Synthesis of amine complexes with the trihydridoborate derivative of *meta*-carborane.

An interesting example of compounds in which the carborane cage is bonded to an *exo*-polyhedral four-coordinated boron atom are *ortho*-carboranyl-capped iron(II) clatrocyclates (Figure 5) [32,34].

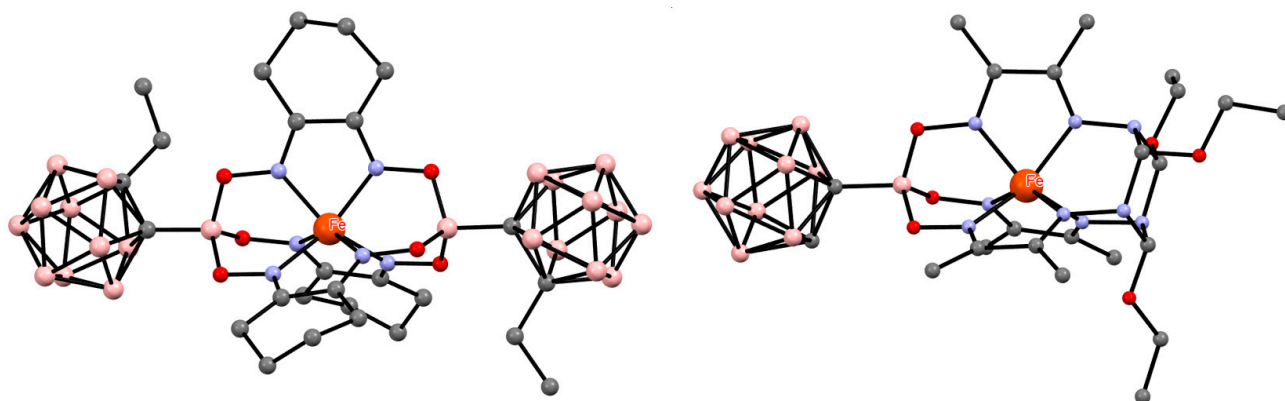
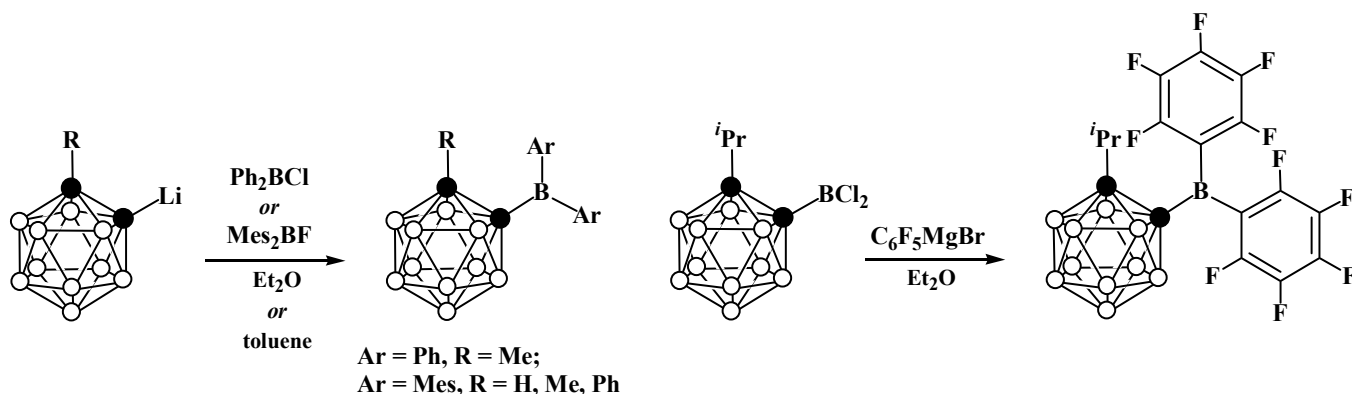


Figure 5. Single crystal structures of *ortho*-carboranyl-capped iron(II) clatrocyclates. Hydrogen atoms are omitted for clarity.

4. Arylboryl Derivatives of Carboranes

A series of *C-ortho*-carboranyl diarylboranes 1-Ar₂B-2-R-1,2-C₂B₁₀H₁₀ (Ar = Ph, R = Me; Ar = Mes, R = H, Me, Ph) was prepared by the reactions of lithium derivatives of carboranes with diphenylboron chloride or dimesitylboron fluoride (Scheme 12, Figure 6) [12,44,45]. 1-Ph₂B-2-Me-1,2-C₂B₁₀H₁₀ was found to undergo complete hydrolysis in boiling water to the corresponding carborane and diphenylborinic acid within 8 h [12]. 1-Mes₂B-2-R-1,2-C₂B₁₀H₁₀ is considered to be rather water stable; however, it slowly hydrolyzes in

the solid state on prolonged exposure to air (within three weeks for R = H and within 18 months for R = Ph) to give mesitylene and the corresponding carboranyl boronic acid 1-(HO)₂B-2-R-1,2-C₂B₁₀H₁₀. However, in the presence of fluoride ions, they easily hydrolyze in acetonitrile solution to the corresponding carboranes and dimesitylboric acid [44]. The bis(pentafluorophenyl)boryl derivative 1-(C₆F₅)₂B-2-Me-1,2-C₂B₁₀H₁₀ was prepared by the reaction of the corresponding dichlorocarboranylborane with C₆F₅MgBr in diethyl ether (Scheme 12, Figure 6) [33].



Scheme 12. Synthesis of diarylboryl derivatives of *ortho*-carborane.

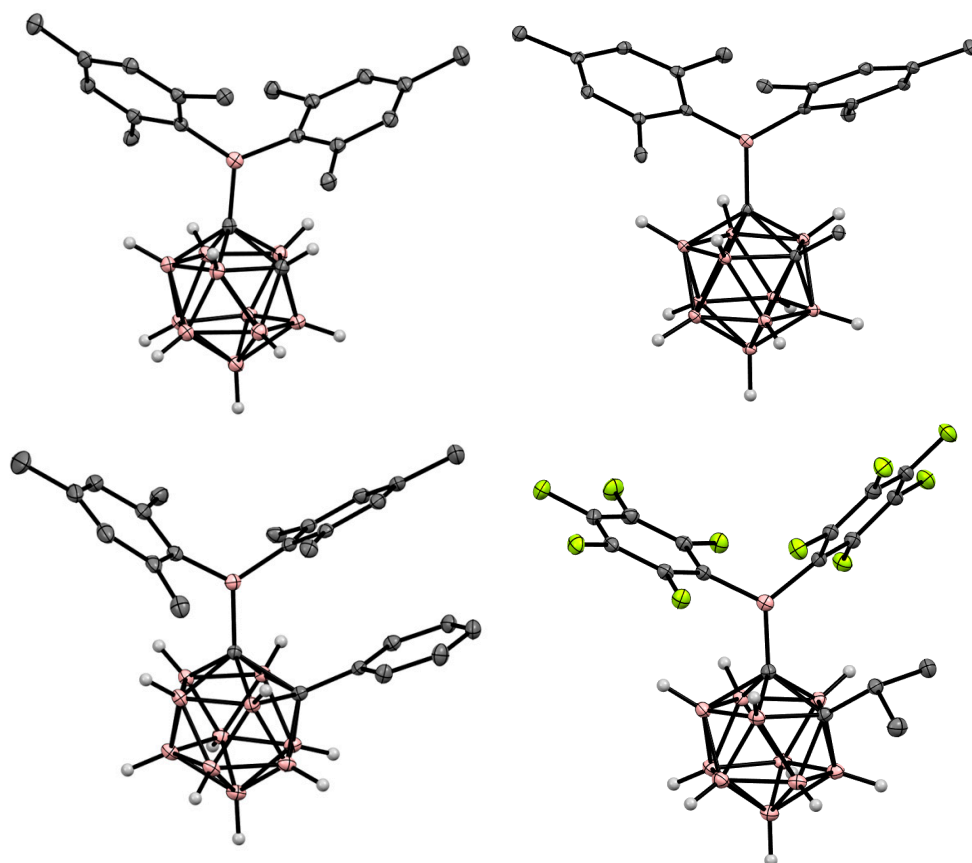
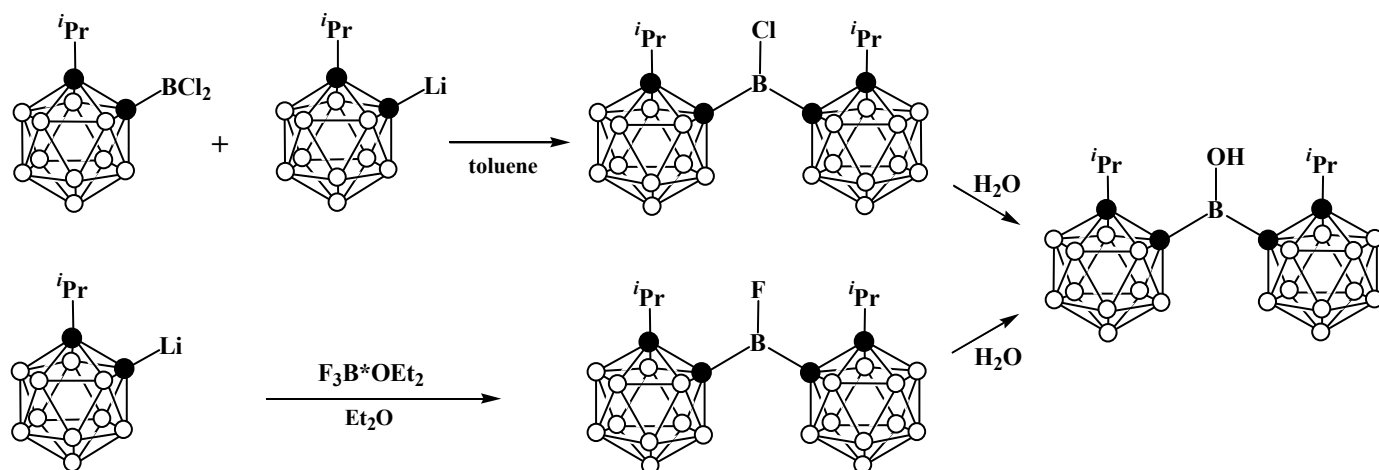


Figure 6. Single crystal structures of 1-Mes₂B-1,2-C₂B₁₀H₁₁ (**top left**), 1-Mes₂B-2-Me-1,2-C₂B₁₀H₁₀ (**top right**), 1-Mes₂B-2-Ph-1,2-C₂B₁₀H₁₀ (**bottom left**), and 1-(C₆F₅)₂B-2-*i*-Pr-1,2-C₂B₁₀H₁₀ (**bottom right**). Hydrogen atoms of organic substituents are omitted for clarity.

Initial attempts to prepare tris(*ortho*-carboranyl)borane from the lithium derivative of *ortho*-carborane and boron trichloride in diethyl ether were unsuccessful [8]. Later, bis(C-isopropyl-*ortho*-carboranyl)boron chloride and bis(C-isopropyl-*ortho*-carboranyl)boron flu-

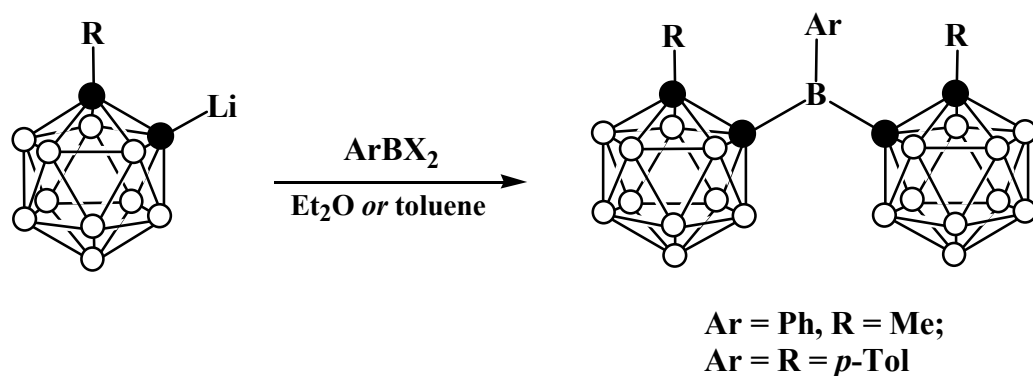
oxide were prepared by the reactions of *C*-isopropyl-*ortho*-carboranylboron dichloride with the lithium derivative of *C*-isopropyl-*ortho*-carborane or the lithium derivative of *C*-isopropyl-*ortho*-carborane with boron trifluoride etherate, respectively. Both are easily hydrolyzed to form (*C*-isopropyl-*ortho*-carboranyl)borinic acid (Scheme 13) [46].



Scheme 13. Synthesis of bis(carboranyl)boron derivatives $1,1'-(2-i\text{-Pr-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})_2\text{BX}$ ($\text{X} = \text{F}, \text{Cl}, \text{OH}$).

Bis(*ortho*-carboranyl)arylboranes $\mu\text{-}1,1'\text{-ArB(}2\text{-R-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})_2$ ($\text{Ar} = \text{Ph}$, $\text{R} = \text{Me}$; $\text{Ar} = \text{R} = p\text{-Tol}$) were prepared by the reactions of the lithium derivatives of the corresponding carboranes with diarylboron dichloride or dibromide (Scheme 14, Figure 7) [12,47]. $\mu\text{-}1,1'\text{-PhB(}2\text{-Me-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})_2$ undergoes hydrolysis by warm (40–50 °C) water over 2 h, giving 1-methyl-*ortho*-carborane and phenylboronic acid [12].

More recently, tris(*ortho*-carboranyl)borane $1,1',1''\text{-}\mu^3\text{-B(}1,2\text{-C}_2\text{B}_{10}\text{H}_{11})_3$ was prepared by the reaction of the lithium derivative of *ortho*-carborane with BCl_3 or BBr_3 in toluene (Scheme 15, Figure 8) [48].



Scheme 14. Synthesis of bis(*ortho*-carboranyl) aryl boranes.

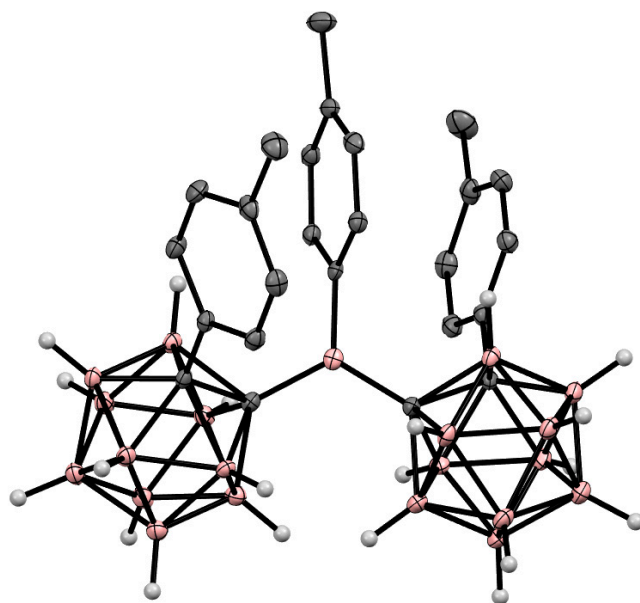
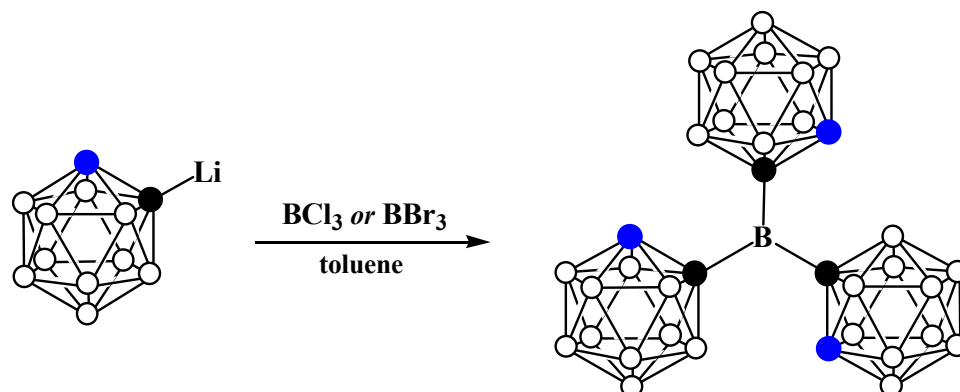


Figure 7. Single crystal structure of μ -1,1'-*p*-TolB(2-*p*-Tol-1,2- $C_2B_{10}H_{10}$)₂. Hydrogen atoms of organic substituents are omitted for clarity.



Scheme 15. Synthesis of tris(*ortho*-carboranyl) borane 1,1',1''- μ^3 -B(1,2- $C_2B_{10}H_{11}$)₃.

Tris(*ortho*-carboranyl)borane forms stable complexes with benzaldehyde, acetonitrile, and triethylphosphine oxide (Figure 8). A single crystal X-ray diffraction study validated stronger binding of the donor molecules to 1,1',1''- μ^3 -B(1,2- $C_2B_{10}H_{11}$)₃ than $B(C_6F_5)_3$. In solution, the Gutmann–Beckett studies indicated that the Lewis acidity of tris(*ortho*-carboranyl)borane exceeds the values in the literature for known fluorinated aryl boranes [48,49].

The reaction of the dilithium derivative of *meta*-carborane with diphenylboron chloride in toluene leads to the disubstituted carborane derivative 1,7-(Ph_2B)₂-1,7- $C_2B_{10}H_{10}$, while the reaction of the lithium derivative with phenylboron dichloride produces μ -1,1'-PhB(1,7- $C_2B_{10}H_{11}$)₂ (Scheme 16). μ -1,1'-PhB(1,7- $C_2B_{10}H_{11}$)₂ undergoes complete hydrolysis in boiling water to the corresponding carborane and diphenylborinic acid within 8 h, whereas the disubstituted derivative 1,7-(Ph_2B)₂-1,7- $C_2B_{10}H_{10}$ was found to resist boiling water for 10 h, and a similar period in contact with 4 M NaOH at 80–90 °C was needed for its complete hydrolysis [12].

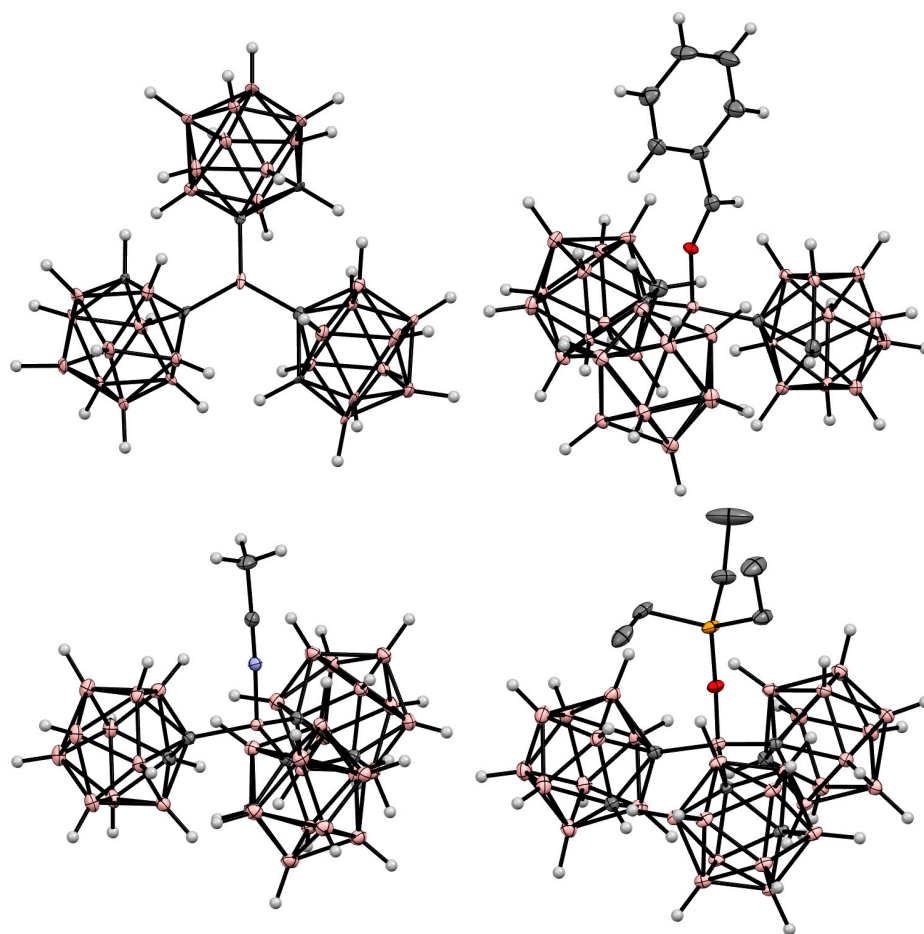
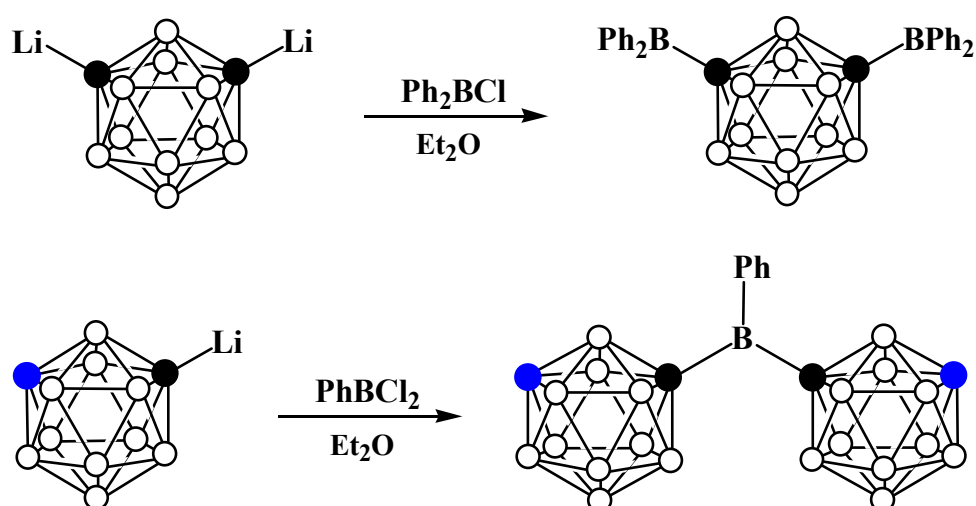


Figure 8. Single crystal structures of tris(*ortho*-carboranyl)borane $1,1',1''\text{-}\mu^3\text{-B(1,2-C}_2\text{B}_{10}\text{H}_{11})_3$ (**top left**) and their complexes $\text{PhC(O)H}\cdot 1,1',1''\text{-}\mu^3\text{-B(1,2-C}_2\text{B}_{10}\text{H}_{11})_3$ (**top right**), $\text{MeCN}\cdot 1,1',1''\text{-}\mu^3\text{-B(1,2-C}_2\text{B}_{10}\text{H}_{11})_3$ (**bottom left**), and $\text{Et}_3\text{PO}\cdot 1,1',1''\text{-}\mu^3\text{-B(1,2-C}_2\text{B}_{10}\text{H}_{11})_3$ (**bottom right**). Hydrogen atoms of the ethyl groups in the Et_3PO molecule are omitted for clarity.

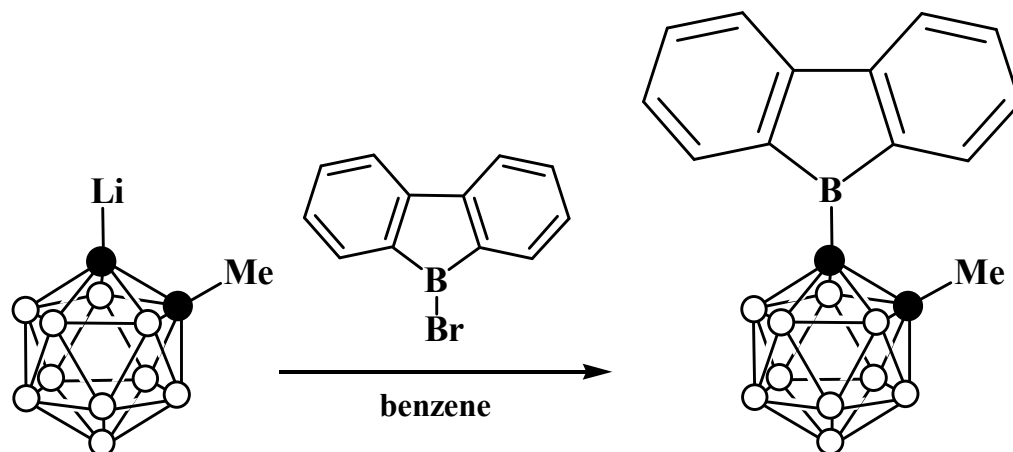


Scheme 16. Synthesis of carboranyl aryl derivatives of *meta*-carborane.

Benzanullated boroles or 9-borafluorenes can be described as biphenyl units linked by a tricoordinate boron center or as an antiaromatic BC_4 ring with two fused arene rings. Lewis bases can coordinate with the boron center across a wide range of Lewis acidities for 9-borafluorenes, dependent on the substitution at boron. As a result of the vacant p

orbital extending π -conjugation through the tricyclic system, this class of compounds has interesting photophysical properties, much like polycyclic aromatic hydrocarbons. Adduct formation results in a disruption of conjugation, as well as altered fluorescence, which can be exploited in molecular sensing [50,51].

The *ortho*-carboranyl derivative of 9-borafluorene 1- $\text{C}_{12}\text{H}_8\text{B}$ -2-Me-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ was prepared by the reaction of the lithium derivative of 1-methyl-*ortho*-carborane with 9-bromo-9-borafluorene (Scheme 17, Figure 9) [52].



Scheme 17. Synthesis of the *ortho*-carboranyl derivative of 9-borafluorene 1- $\text{C}_{12}\text{H}_8\text{B}$ -2-Me-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$.

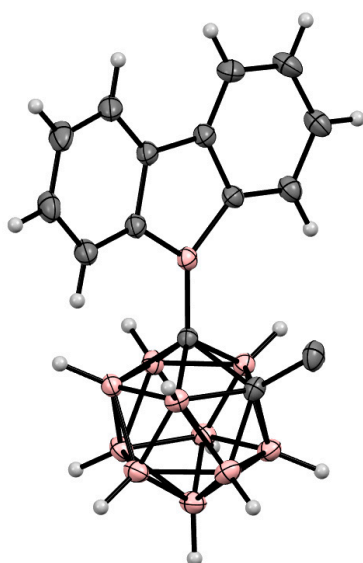


Figure 9. Single crystal structure of the *ortho*-carboranyl derivative of 9-borafluorene 1- $\text{C}_{12}\text{H}_8\text{B}$ -2-Me-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$. Hydrogen atoms of the methyl group are omitted for clarity.

The synthesized *ortho*-carboranyl derivative of 9-borafluorene readily form adducts with various Lewis bases, including 4-dimethylaminopyridine, pyridine, tetrahydrofuran, and acetone (Figure 10). Its Lewis acidity, determined by the Gutmann–Beckett method, is comparable to that of 9-bromo-9-borafluorene [52].

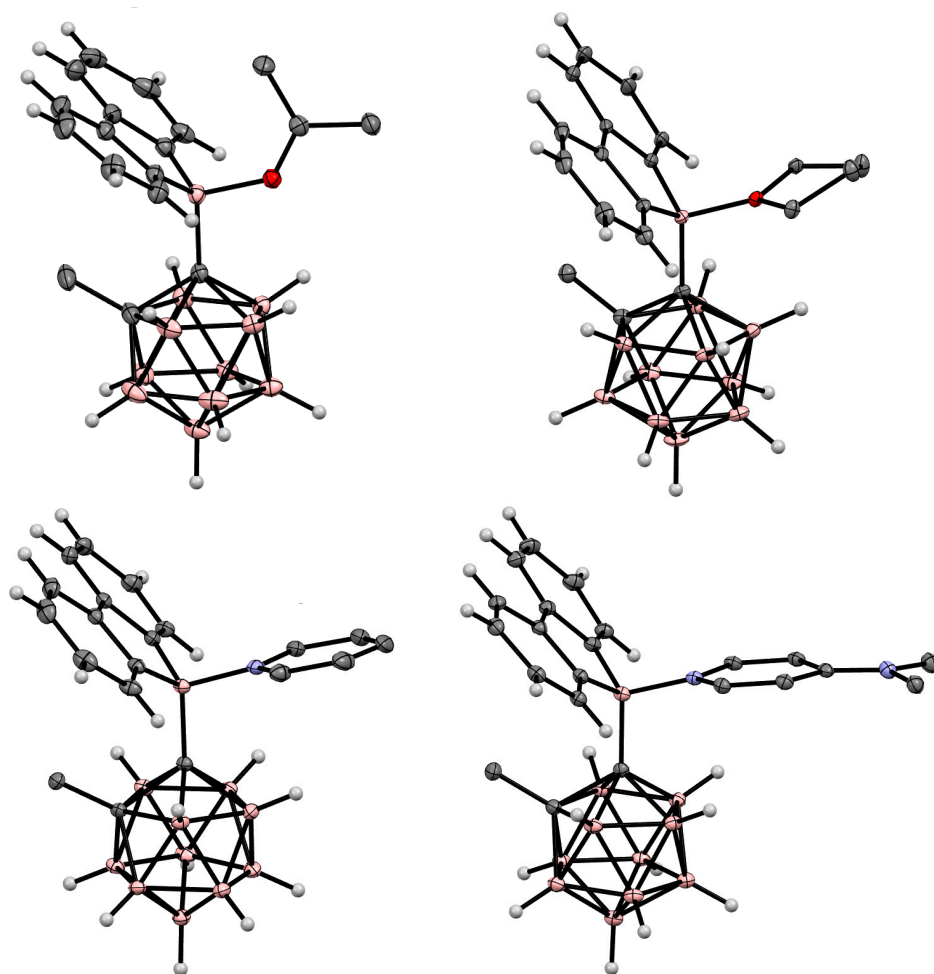
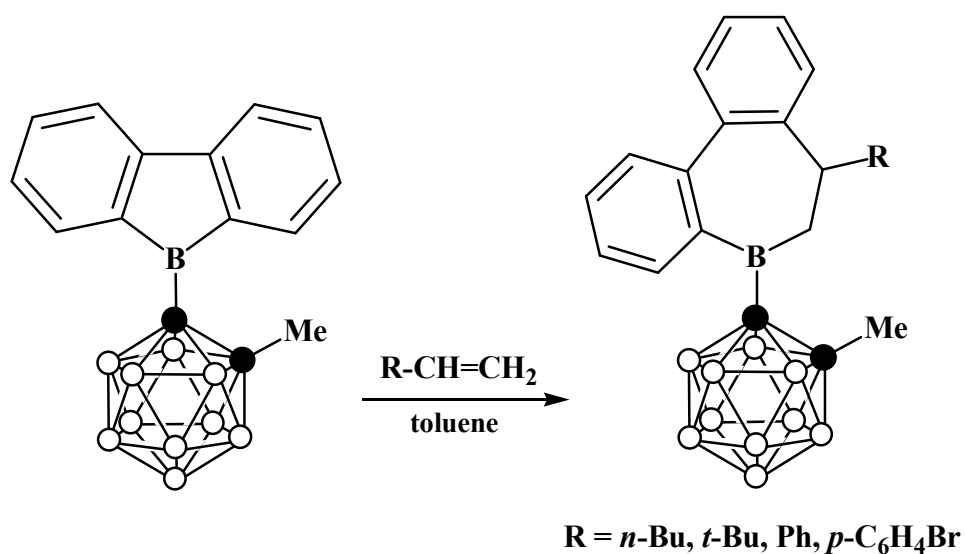


Figure 10. Single crystal structures of *ortho*-carboranyl-9-borafluorene complexes with acetone (**top left**), tetrahydrofuran (**top right**), pyridine (**bottom left**), and *p*-dimethylaminopyridine (**bottom right**). Hydrogen atoms of the methyl group and Lewis bases are omitted for clarity.

The reactions of *ortho*-carboranyl-9-borafluorene with alkenes lead to the alkene insertion to form the corresponding 6,7-dihydroborepines (Scheme 18, Figure 11) [52].



Scheme 18. Alkene insertion into the *ortho*-carboranyl derivative of 9-borafluorene.

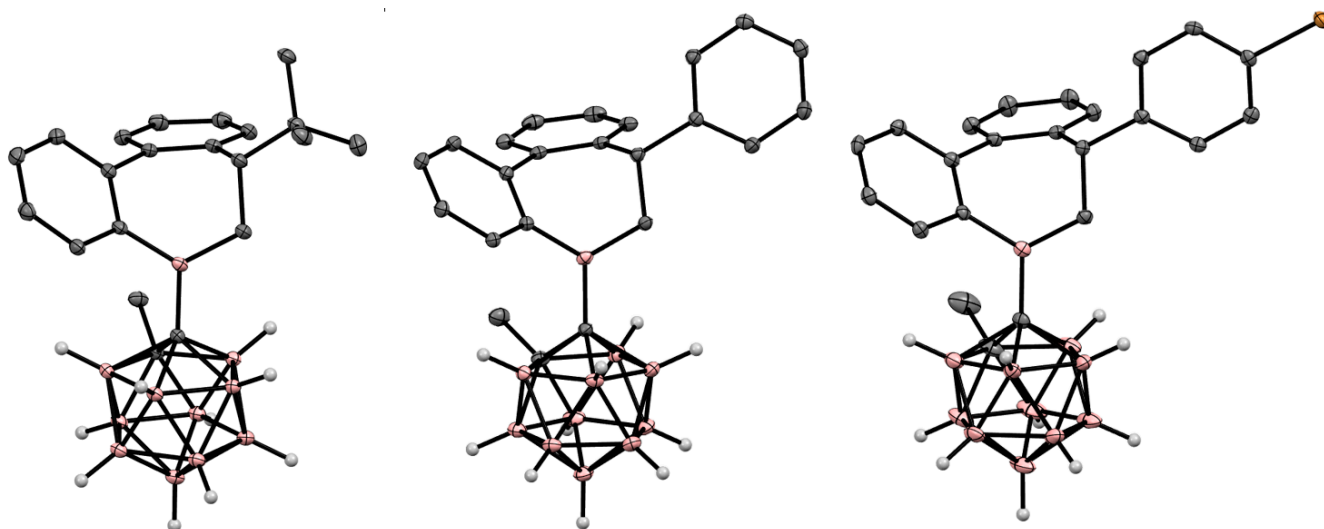
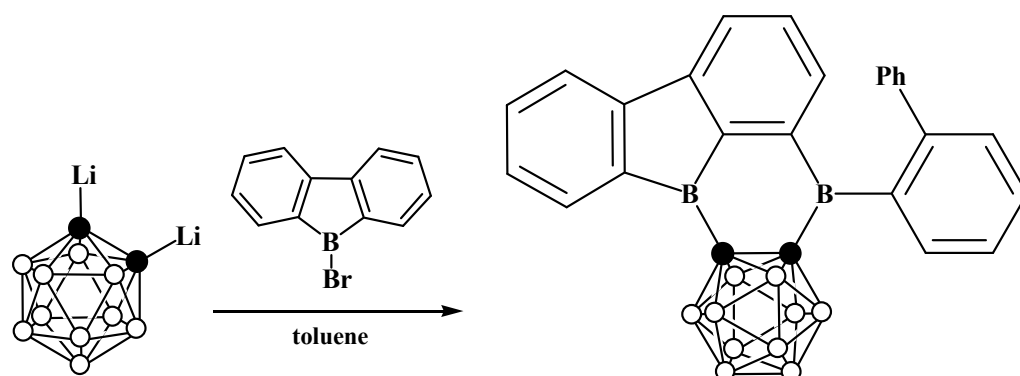


Figure 11. Single crystal structures of 5-*ortho*-carboranyl-7-R-6,7-dihydrodibenzo[*b,d*]borepines (R = *t*-Bu (**left**), R = Ph (**center**), and R = *p*-C₆H₄Br (**right**)). Hydrogen atoms of organic substituents are omitted for clarity.

An attempt to synthesize the disubstituted 9-borafluoren-9-yl derivative of *ortho*-carborane 1,2-(C₁₂H₈B)₂-1,2-C₂B₁₀H₁₀ by the reaction of the dilithium derivative of *ortho*-carborane with 9-bromo-9-boradibenzofluorene in toluene unexpectedly gave a rearrangement product as a result of C-H activation of one 9-boradibenzofluorenyl substituent. The other 9-borafluorene unit undergoes a ring opening process, resulting in an *ortho*-biphenyl substituent (Scheme 19, Figure 12). The crystallization of the product from toluene via hexane diffusion in the presence of a small amount of tetrahydrofuran leads to a complex with one THF molecule, indicating higher Lewis acidity of the five-membered BC₄ ring (Figure 12) [53].



Scheme 19. Reaction of the dilithium derivative of *ortho*-carborane with 9-bromo-9-boradibenzofluorene.

The similar reaction of the dilithium derivative of *ortho*-carborane with 9-bromo-9-boradibenzofluorene in tetrahydrofuran gave an adduct of expected bis(9-borafluorenyl) derivative with two molecules of 5-bromopentanol as a product of the THF ring opening, while the reaction in dimethylsulfide produced the complex of *ortho*-carboranyl-9-borafluorene with dimethylsulfide Me₂S·1-C₁₂H₈B-2-MeS-1,2-C₂B₁₀H₁₀ (Figure 13) [53].

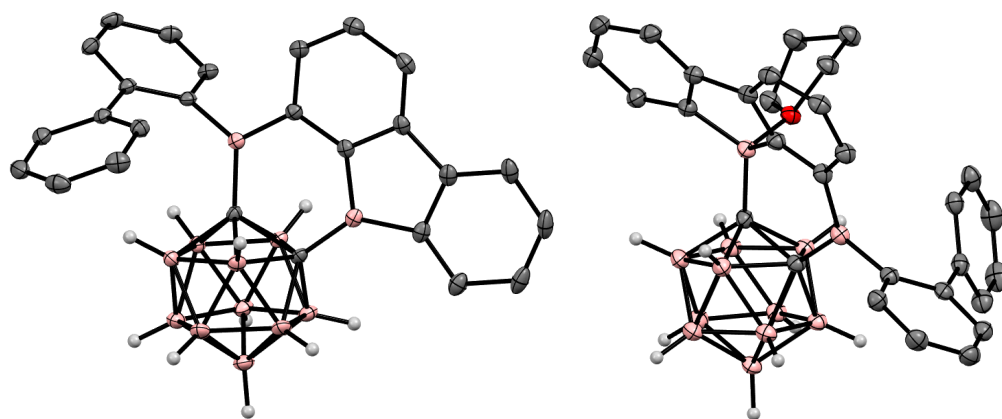


Figure 12. Single crystal structures of the product of the reaction of the dilithium derivative of *ortho*-carborane with 9-bromo-9-borafluorene (**left**) and its complex with THF (**right**). Hydrogen atoms of organic substituents are omitted for clarity.

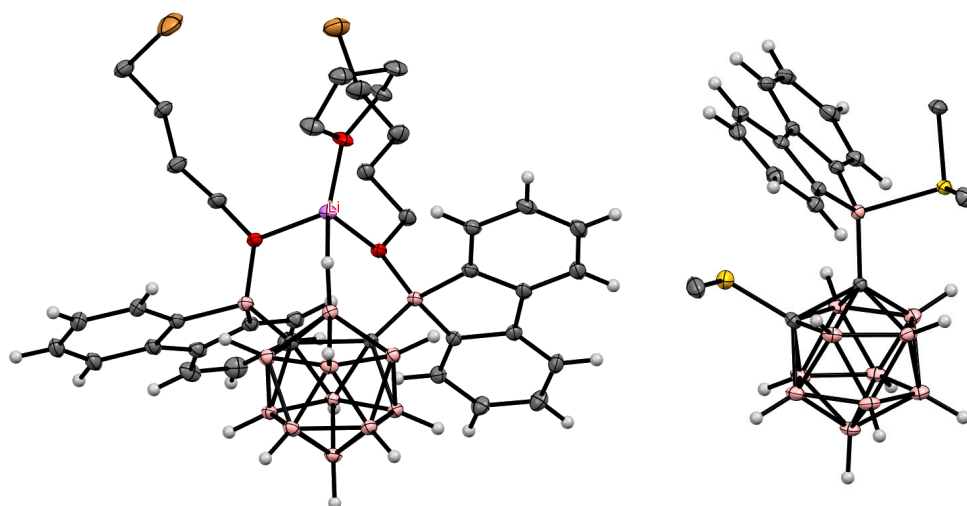
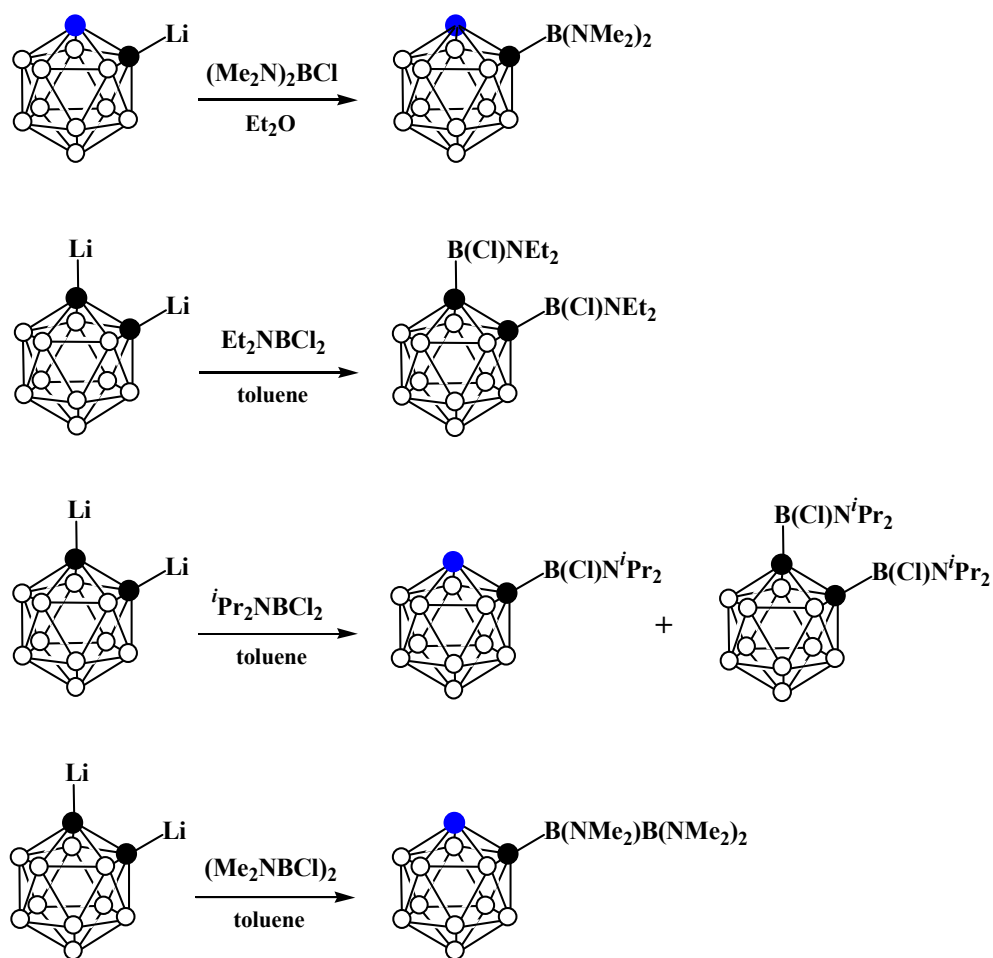


Figure 13. Single crystal structures of the products of the reaction of the dilithium derivative of *ortho*-carborane with 9-bromo-9-borafluorene in tetrahydrofuran (**left**) and in dimethylsulfide (**right**). Hydrogen atoms of alkyl groups are omitted for clarity.

5. Aminoboryl Derivatives of Carboranes and Their Analogs

The first C-aminoboryl-*ortho*-carborane 1-(Me₂N)₂B-1,2-C₂B₁₀H₁₁ was prepared by the reaction of the lithium derivative of *ortho*-carborane with bis(dimethylamino)boron chloride (Me₂N)₂BCl in diethyl ether (Scheme 20) [8]. The reaction of the dilithium derivative of *ortho*-carborane with diethylaminoboron dichloride Et₂NBCL₂ in toluene leads to 1,2-(Et₂N(Cl)B)₂-1,2-C₂B₁₀H₁₀, while the reaction with diisopropylaminoboron dichloride *i*-Pr₂NBCL₂ results in a mixture of the corresponding mono- and disubstituted aminoboryl-*ortho*-carboranes 1-*i*-Pr₂N(Cl)B-1,2-C₂B₁₀H₁₁ and 1,2-(*i*-Pr₂N(Cl)B)₂-1,2-C₂B₁₀H₁₀ (Scheme 20, Figure 14) [54]. The reaction of the dilithium derivative of *ortho*-carborane with 1,2-dichloro-1,2-bis(dimethylamino)-diborane(4) (Me₂NBCL)₂ in toluene results in 1-(Me₂N)₂B(Me₂N)B-1,2-C₂B₁₀H₁₁ (Scheme 20, Figure 14) [55].



Scheme 20. Preparation of aminoboryl derivatives of *ortho*-carborane.

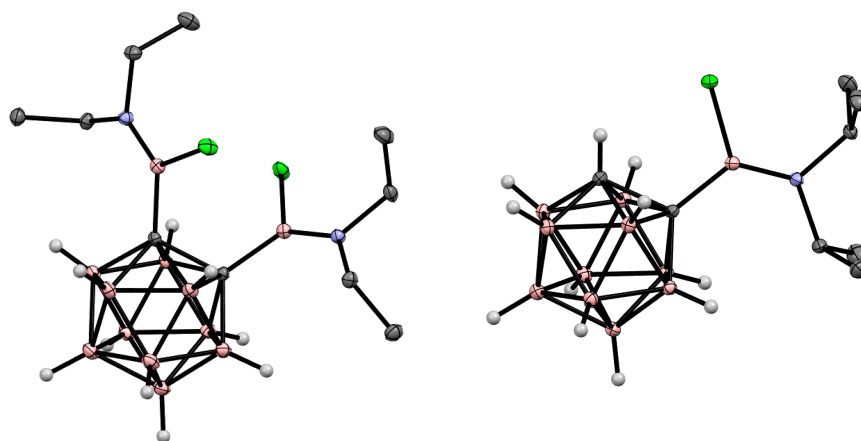


Figure 14. Cont.

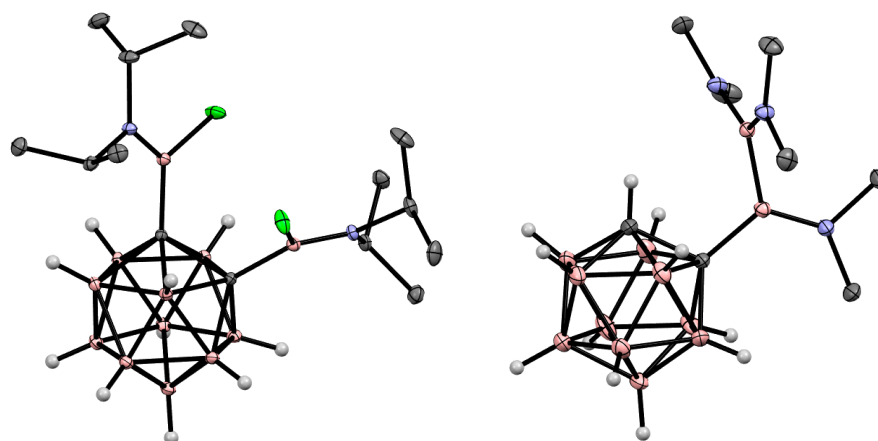
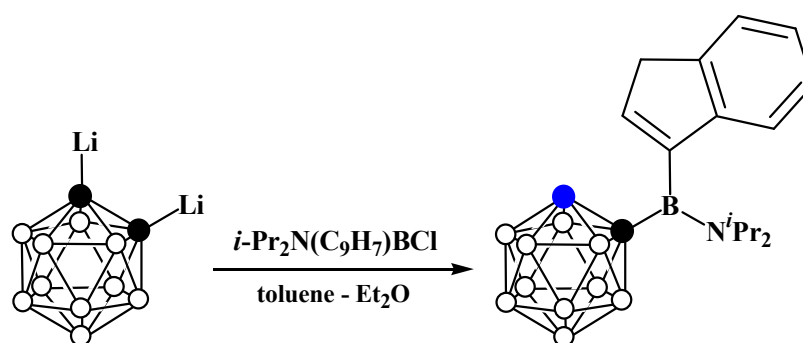


Figure 14. Single crystal structures of 1,2-(Et₂N(Cl)B)₂-1,2-C₂B₁₀H₁₀ (**top left**), 1-*i*-Pr₂N(Cl)B-1,2-C₂B₁₀H₁₁ (**top right**), 1,2-(*i*-Pr₂N(Cl)B)₂-1,2-C₂B₁₀H₁₀ (**bottom left**), and 1-(Me₂N)₂B(Me₂N)B-1,2-C₂B₁₀H₁₁ (**bottom right**). Hydrogen atoms of alkyl groups are omitted for clarity.

The dilithium derivative of *ortho*-carborane with diisopropylamino(inden-3-yl)boryl chloride gave the indenyl derivative 1-(*i*-Pr₂N)(C₉H₇)B-1,2-C₂B₁₀H₁₁ (Scheme 21, Figure 15) [56], which was used to synthesize a series of indenyl-carborane complexes with lanthanides and the group 4 metals [56,57].



Scheme 21. Synthesis of the indenyl derivative of *ortho*-carborane 1-(*i*-Pr₂N)(C₉H₇)B-1,2-C₂B₁₀H₁₁.

The 1,3-diethyl-1,3,2-benzodiazaborolyl group is known as a good π -donor comparable with the methoxy and dimethylamino groups [58], which has led to the synthesis of numerous “push-pull” type organoboron compounds as promising emitting materials for potential application in electro-optical devices [59]. On the other hand, the *C-ortho*-carboranyl fragment has strong electron-withdrawing properties [6]. Therefore, *ortho*-carborane derivatives have been tested as electron-withdrawing substituents in systems in which benzodiazaboroles act as donors. It was expected that the obtained 1,3,2-benzodiazaborolyl-*ortho*-carboranes could form a new family of donor-acceptor systems. The simplest compound of this type, 1-(1',3'-H₂-1',3',2'-N₂BC₆H₄-2'-)-2-Me-1,2-C₂B₁₀H₁₀ (Figure 15), was synthesized by the cyclocondensation of *C*-carboranylboron dibromide 1-Br₂B-2-Me-1,2-C₂B₁₀H₁₀ with 1,2-phenylene diamine (Scheme 22) [32]. A series of *N,N'*-dialkyl and *N,N'*-diaryl substituted 1,3,2-benzodiazaborolyl-*ortho*-carboranes 1-(1',3'-R'-2'-1',3',2'-N₂BC₆H₄-2'-)-2-R-1,2-C₂B₁₀H₁₀ (R = H, R' = Et, *i*-Pr, Ph; R = Me, R' = Et, Ph; R = *t*-Bu; R' = Et, Ph; R' = SiMe₃, R' = Et, *i*-Pr, Ph; R = Ph, R' = Et) and 1-(1',3'-Ph₂-1',3',2'-N₂BC₆H₂Me₂-2'-)-2-R-1,2-C₂B₁₀H₁₀ (R = H, *t*-Bu, SiMe₃) were prepared by the reactions of lithium derivatives of *ortho*-carboranes with the corresponding bromo-1,3,2-benzodiazaboroles (Scheme 22) [32,60,61]. The solid-state structures of the synthesized 1,3,2-benzodiazaborolyl-*ortho*-carboranes were determined by single crystal X-ray diffraction (Figures 16–18), and their photophysical and electrochemical properties were studied [32,60,61].

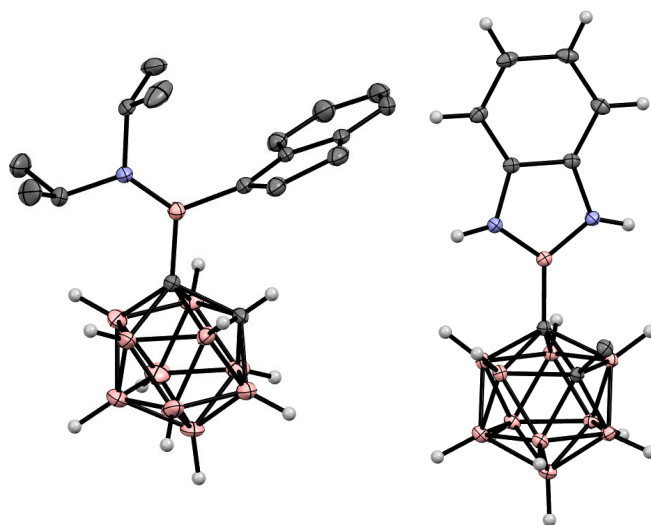
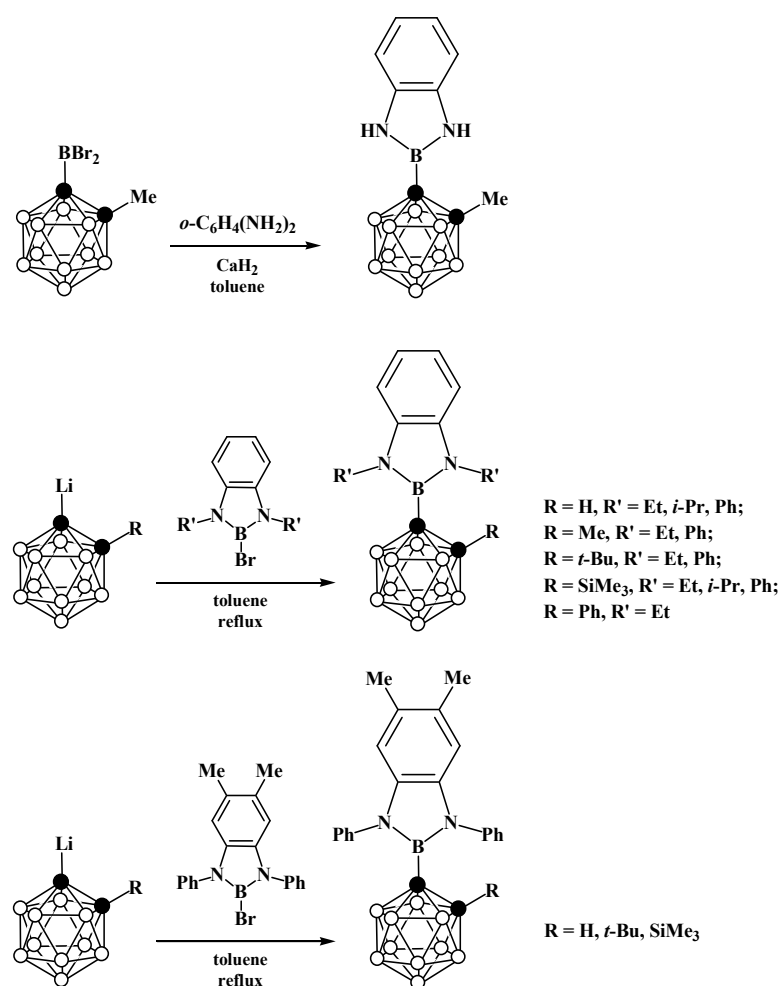


Figure 15. Single crystal structures of 1-(*i*-Pr₂N)(inden-3-yl)B-1,2-C₂B₁₀H₁₁ (**left**) and 1-(1',3'-H₂-1',3',2'-N₂BC₆H₄-2'-)-2-Me-1,2-C₂B₁₀H₁₀ (**right**). Hydrogen atoms of isopropyl and indenyl groups are omitted for clarity.



Scheme 22. Synthesis of *N,N'*-dialkyl and *N,N'*-diaryl substituted 1,3,2-benzodiazaborolyl-*ortho*-carboranes.

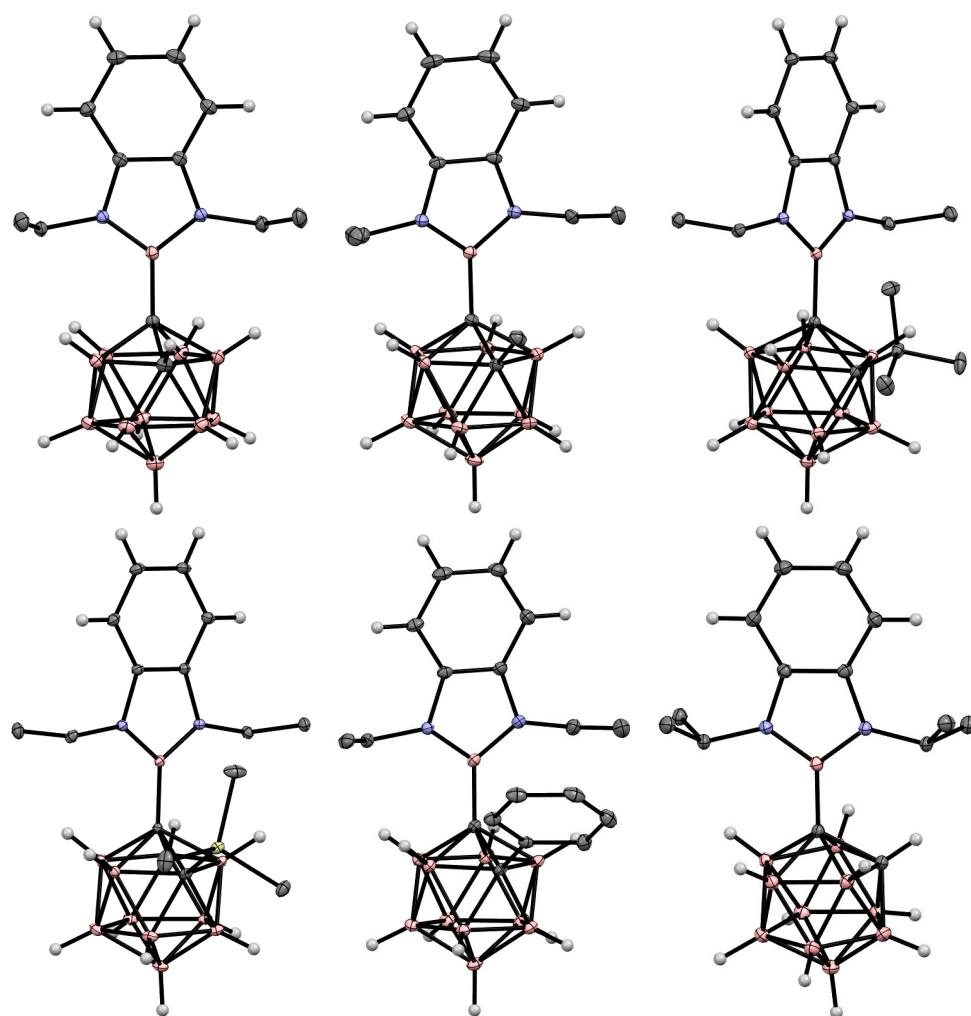


Figure 16. Single crystal structures of 1-(1',3'-Et₂-1',3',2'-N₂BC₆H₄-2'-)-1,2-C₂B₁₀H₁₁ (**top left**), 1-(1',3'-Et₂-1',3',2'-N₂BC₆H₄-2'-)-2-Me-1,2-C₂B₁₀H₁₀ (**top middle**), 1-(1',3'-Et₂-1',3',2'-N₂BC₆H₄-2'-)-2-*t*-Bu-1,2-C₂B₁₀H₁₀ (**top right**), 1-(1',3'-Et₂-1',3',2'-N₂BC₆H₄-2'-)-2-Me₃Si-1,2-C₂B₁₀H₁₀ (**bottom left**), 1-(1',3'-Et₂-1',3',2'-N₂BC₆H₄-2'-)-2-Ph-1,2-C₂B₁₀H₁₀ (**bottom middle**), and 1-(1',3'-*i*-Pr)₂-1',3',2'-N₂BC₆H₄-2'-)-1,2-C₂B₁₀H₁₁ (**bottom right**). Hydrogen atoms of alkyl groups are omitted for clarity.

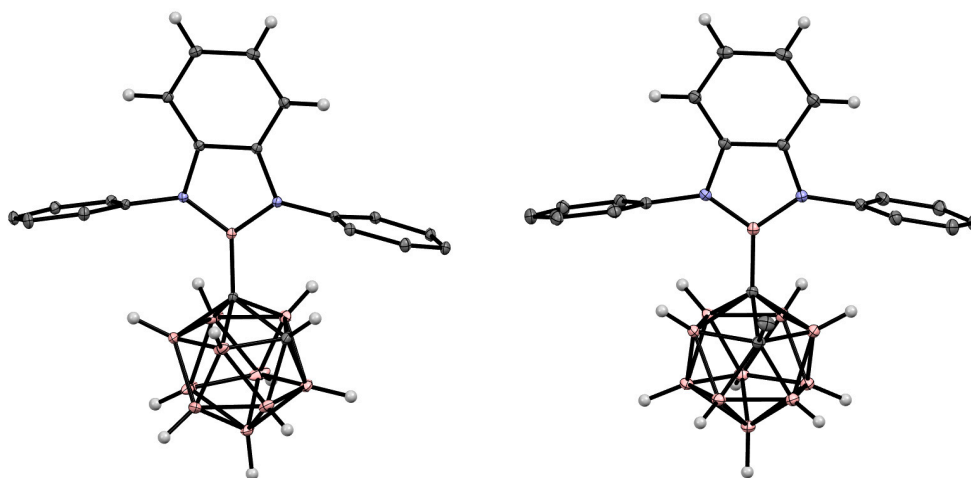


Figure 17. *Cont.*

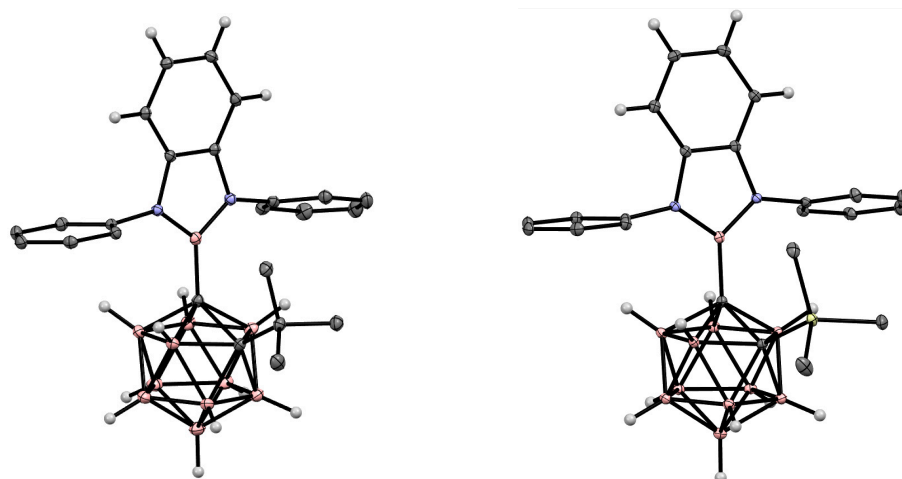


Figure 17. Single crystal structures of 1-(1',3'-Ph₂-1',3',2'-N₂BC₆H₄-2'-)-1,2-C₂B₁₀H₁₁ (**top left**), 1-(1',3'-Ph₂-1',3',2'-N₂BC₆H₄-2'-)-2-Me-1,2-C₂B₁₀H₁₀ (**top right**), 1-(1',3'-Ph₂-1',3',2'-N₂BC₆H₄-2'-)-2-*t*-Bu-1,2-C₂B₁₀H₁₀ (**bottom left**), and 1-(1',3'-Ph₂-1',3',2'-N₂BC₆H₄-2'-)-2-Me₃Si-1,2-C₂B₁₀H₁₀ (**bottom right**). Hydrogen atoms of alkyl and phenyl groups are omitted for clarity.

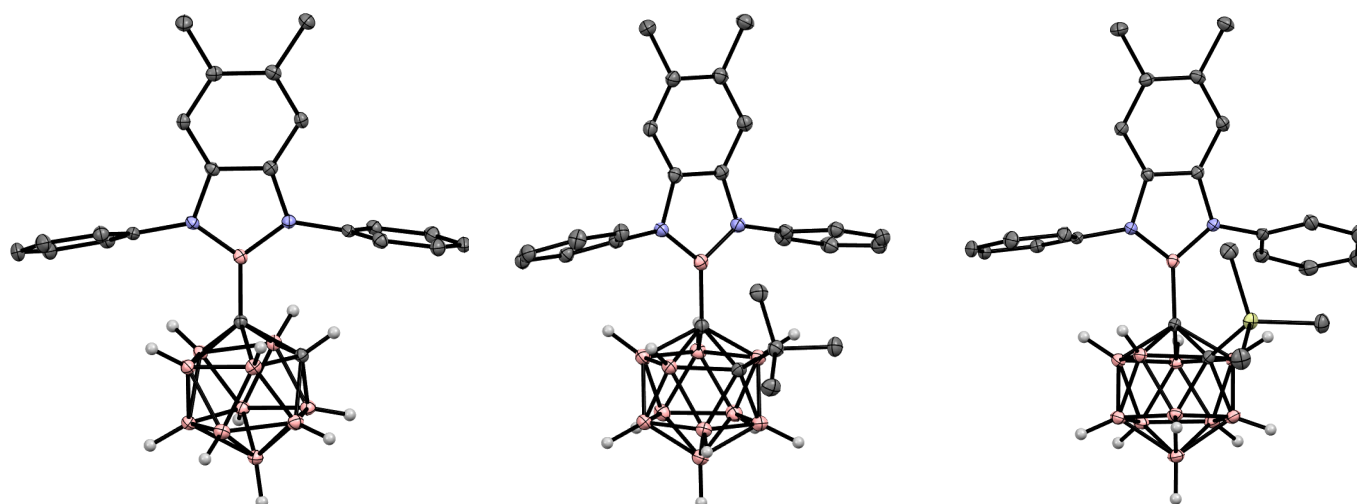
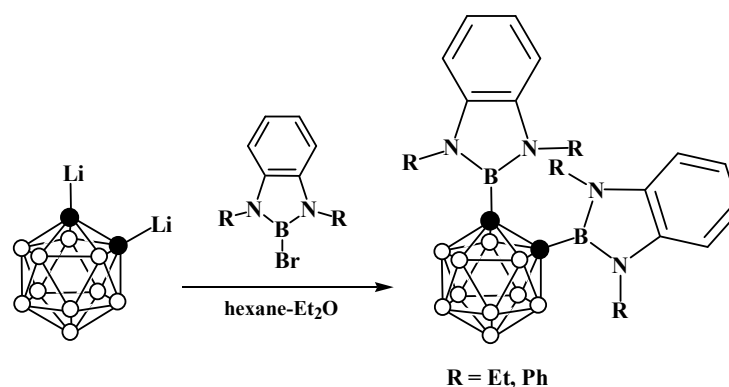


Figure 18. Single crystal structures of 1-(1',3'-Ph₂-1',3',2'-N₂BC₆H₂Me₂-2'-)-1,2-C₂B₁₀H₁₁ (**left**), 1-(1',3'-Ph₂-1',3',2'-N₂BC₆H₂Me₂-2'-)-2-*t*-Bu-1,2-C₂B₁₀H₁₀ (**middle**), and 1-(1',3'-Ph₂-1',3',2'-N₂BC₆H₂Me₂-2'-)-2-Me₃Si-1,2-C₂B₁₀H₁₀ (**right**). Hydrogen atoms of alkyl and phenyl groups are omitted for clarity.

In most synthesized compounds, the plane of the 1,3,2-benzodiazaborolyl group was found to be nearly perpendicular to the carborane C-C bonds ($\psi \approx 90^\circ$), and these compounds demonstrate remarkable low-energy fluorescence emissions with large Stokes shifts of 15,100–20,260 cm^{−1} and quantum yields of up to 70% on excitation in the solid state. In contrast, the compounds with a different orientation of the 1,3,2-benzodiazaborolyl group ($\psi \approx 0^\circ$), namely 1-(1',3'-R₂-1',3',2'-N₂BC₆H₄-2'-)-1,2-C₂B₁₀H₁₁ (R = *i*-Pr, Ph) and 1-(1',3'-Ph₂-1',3',2'-N₂BC₆H₂Me₂-2'-)-1,2-C₂B₁₀H₁₁, do not emit low-energy radiation upon excitation in the solid state [32,60,61].

The *ortho*-carborane derivative containing two 1,3,2-benzodiazaborolyl groups 1,2-(1',3'-R₂-1',3',2'-N₂BC₆H₄-2'-)₂-1,2-C₂B₁₀H₁₀ (R = Et, Ph) was prepared by the reaction of the dilithium derivative of *ortho*-carborane with the corresponding 2-bromo-1,3,2-benzodiazaboroles (Scheme 23, Figure 19) [61].



Scheme 23. Synthesis of 1,2-bis(*N,N'*-diethyl- and *N,N'*-phenyl-1,3,2-benzodiazaborolyl) derivatives of *ortho*-carborane.

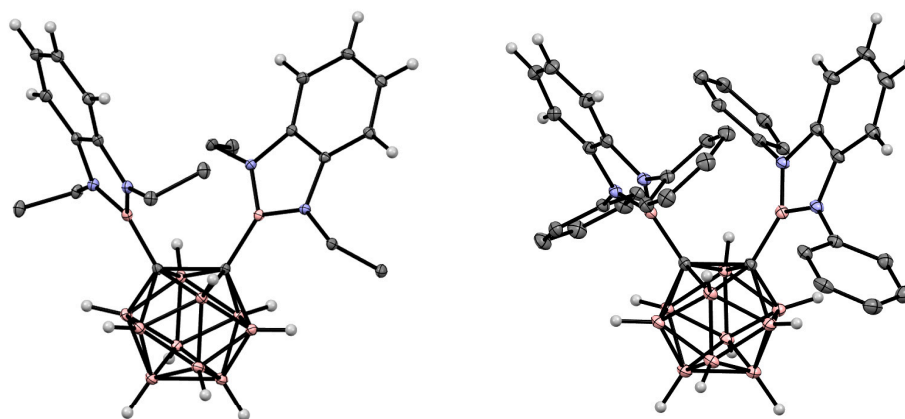
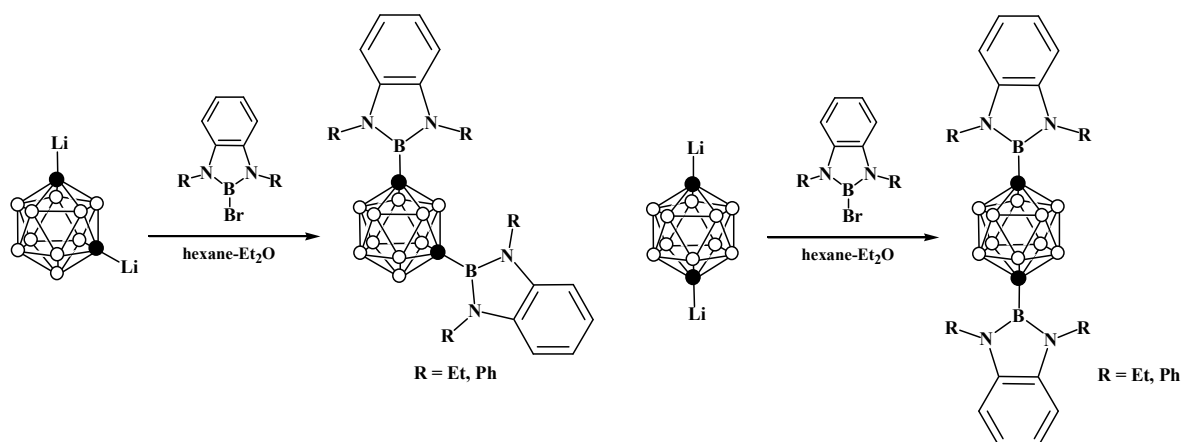


Figure 19. Single crystal structures of 1,2-(1',3'-Et₂-1',3',2'-N₂BC₆H₄-2'-)₂-1,2-C₂B₁₀H₁₀ (**left**) and 1,2-(1',3'-Ph₂-1',3',2'-N₂BC₆H₄-2'-)₂-1,2-C₂B₁₀H₁₀ (**right**). Hydrogen atoms of alkyl and phenyl groups are omitted for clarity.

The disubstituted derivatives demonstrate the low-energy fluorescence typical for the 1,3,2-benzodiazaborolyl derivatives of *ortho*-carborane Stokes shifts between 17,330 and 21,290 cm^{−1}; however, the quantum yields are very low both in solution and in the solid state [61].

The *meta*- and *para*-carborane derivatives with the same substituents 1,7-(1',3'-R₂-1',3',2'-N₂BC₆H₄-2'-)₂-1,7-C₂B₁₀H₁₀ and 1,12-(1',3'-R₂-1',3',2'-N₂BC₆H₄-2'-)₂-1,12-C₂B₁₀H₁₀ (R = Et, Ph) were prepared similarly (Scheme 24, Figure 20) [61].



Scheme 24. Synthesis of 1,2-bis(1,3,2-benzodiazaborolyl) derivatives of *meta*- and *para*-carboranes.

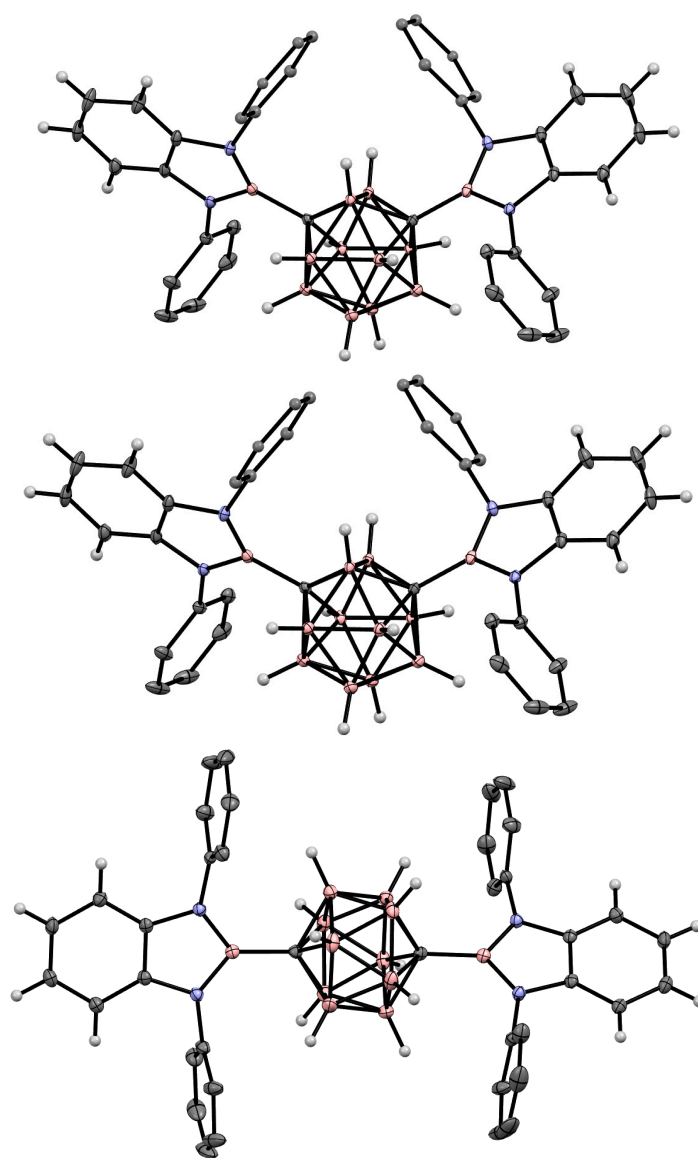
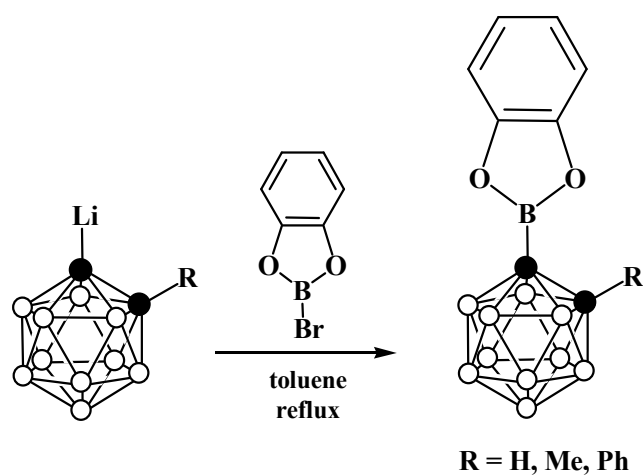


Figure 20. Single crystal structures of 1,7-(1',3'-Et₂-1',3',2'-N₂BC₆H₄-2'-)₂-1,7-C₂B₁₀H₁₀ (**top**), 1,7-(1',3'-Ph₂-1',3',2'-N₂BC₆H₄-2'-)₂-1,7-C₂B₁₀H₁₀ (**middle**), and 1,12-(1',3'-Ph₂-1',3',2'-N₂BC₆H₄-2'-)₂-1,12-C₂B₁₀H₁₀ (**bottom**). Hydrogen atoms of ethyl and phenyl groups are omitted for clarity.

The bis(1,3,2-benzodiazaborolyl) derivatives of *meta*- and *para*-carboranes were found to demonstrate low-energy emissions with Stokes shifts between 8320 and 15,170 cm^{−1}. The fluorescence quantum yields for bis(1,3,2-benzodiazaborolyl)-*meta*- and -*para*-carboranes depend on the substituents at the nitrogen atoms of the heterocycle. Thus, the *para*-carborane derivative with *N*-ethyl substituents has a quantum yield value of 41% in cyclohexane solution and only 9% in the solid state, whereas the analogous derivative with *N*-phenyl substituents demonstrates quantum yields of 3% in cyclohexane solution and 72% in the solid state [61].

A series of 1,3,2-benzodioxaborolyl-*ortho*-carboranes 1-(1',3',2'-O₂BC₆H₄-2'-)-2-R-1,2-C₂B₁₀H₁₀ (R = H, Me, Ph) were prepared by the reactions of lithium derivatives of the corresponding *ortho*-carboranes with 2-bromo-1,3,2-benzodioxaborole (Scheme 25, Figure 21) [45,62].



Scheme 25. Synthesis of 1,3,2-benzodioxaborolyl derivatives of *ortho*-carborane.

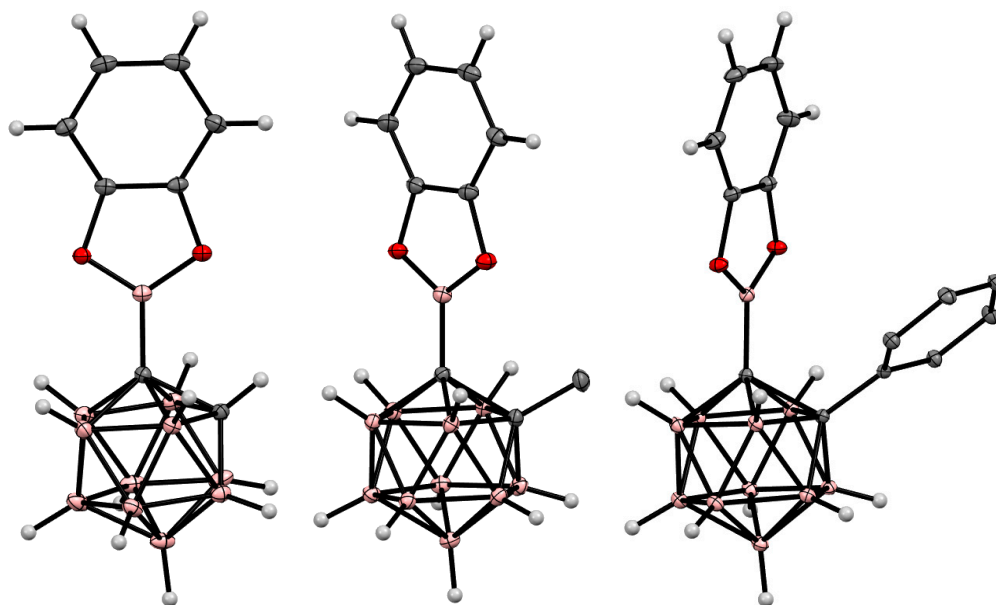


Figure 21. Single crystal structures of 1-(1',3',2'-O₂BC₆H₄-2'-)-1,2-C₂B₁₀H₁₁ (**left**), 1-(1',3',2'-O₂BC₆H₄-2'-)-2-Me-1,2-C₂B₁₀H₁₀ (**middle**), and 1-(1',3',2'-O₂BC₆H₄-2'-)-2-Ph-1,2-C₂B₁₀H₁₀ (**bottom**). Hydrogen atoms of methyl and phenyl groups are omitted for clarity.

Similarly, 1-(1',3',2'-benzodioxaborolyl)-7-diphenylphosphino-*meta*-carborane 1-(1',3',2'-O₂BC₆H₄-2'-)-2-Ph₂P-1,7-C₂B₁₀H₁₀ (Figure 22) was prepared by the reaction of the lithium derivatives of the 1-diphenylphosphino-*meta*-carborane with 2-bromo-1,3,2-benzodioxaborole [45].

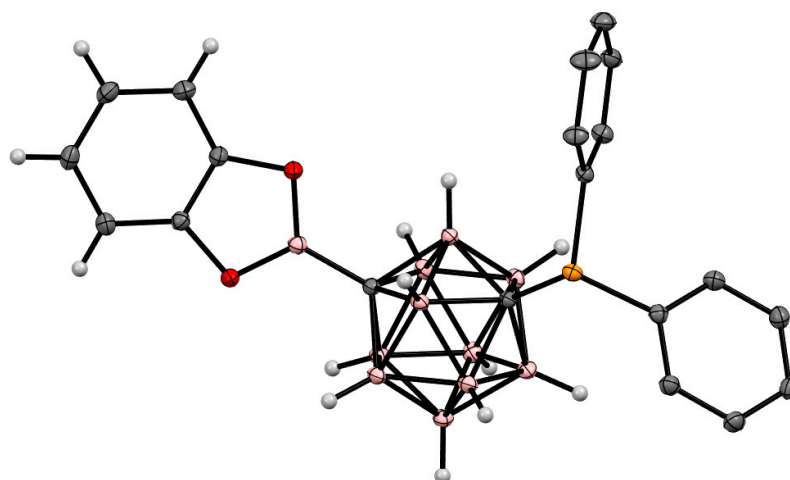
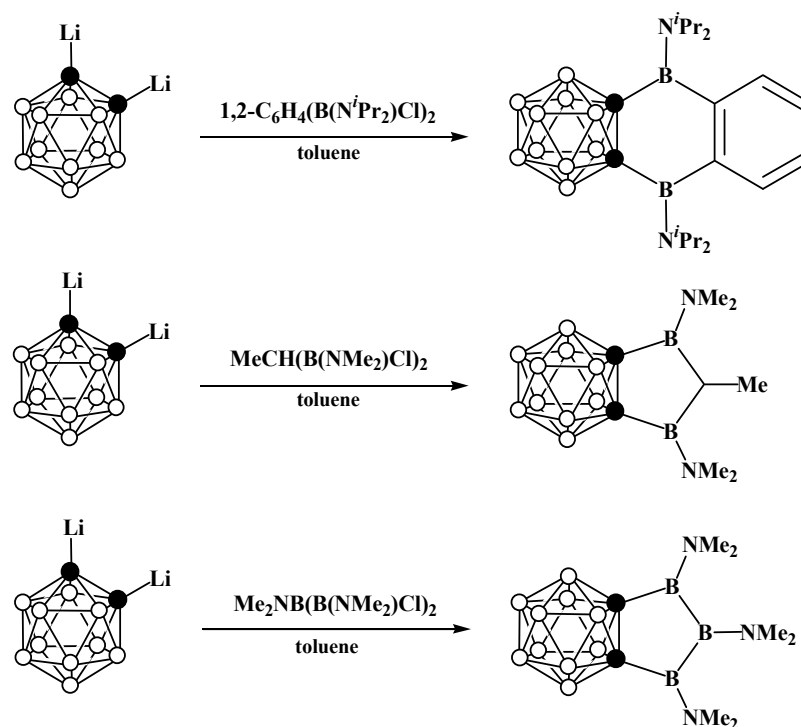


Figure 22. Single crystal structure of 1-(1',3',2'-O₂BC₆H₄-2'-)-7-Ph₂P-1,7-C₂B₁₀H₁₀. Hydrogen atoms of phenyl groups are omitted for clarity.

6. Carboranyl-Fused Boron-Containing Heterocycles

The carborane derivative with the fused *exo*-polyhedral C₂B₂C₂ heterocycle 1,2-μ-(1',2'-C₆H₄(BN^{*i*}Pr₂)₂)-1,2-C₂B₁₀H₁₀ was synthesized by the reaction of the dilithium derivative of *ortho*-carborane with the 1,2-diborylbenzene derivative 1,2-C₆H₄(B(N^{*i*}Pr₂)Cl)₂ in toluene (Scheme 26) [55]. The NBC₂ fragments in the structure of 1,2-μ-(1',2'-C₆H₄(BN^{*i*}Pr₂)₂)-1,2-C₂B₁₀H₁₀ are planar, indicating the double character of the B=N bonds; however, the C₂B₂C₂ ring is bent along the B-B axis by ~55° with CBC angles of ~109° (Figure 23). The analogous reactions with 1,1-bis(dimethylaminochloroboryl)ethane MeCH(B(NMe₂)Cl)₂ and with 1,3-dichloro-1,2,3-tris(dimethylamino)triborane(5) afforded the corresponding carborane derivative with the fused *exo*-polyhedral five-membered C₂B₂C and C₂B₃ rings (Scheme 26) [55]. The C₂B₃ ring in the structure of 1,2-μ-(Me₂NB)₃-1,2-C₂B₁₀H₁₀ is puckered by ~35° with CBB and BBB angles of ~104° (Figure 23).



Scheme 26. Synthesis of carborane-fused six- and five-membered heterocycles.

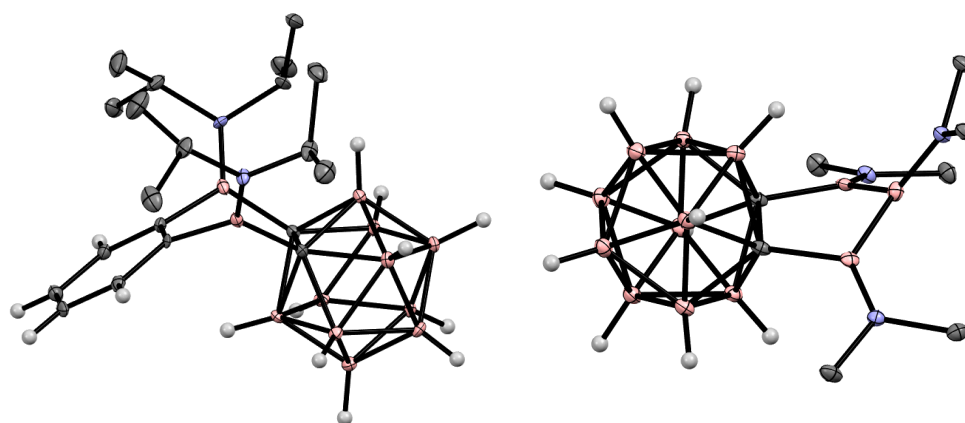
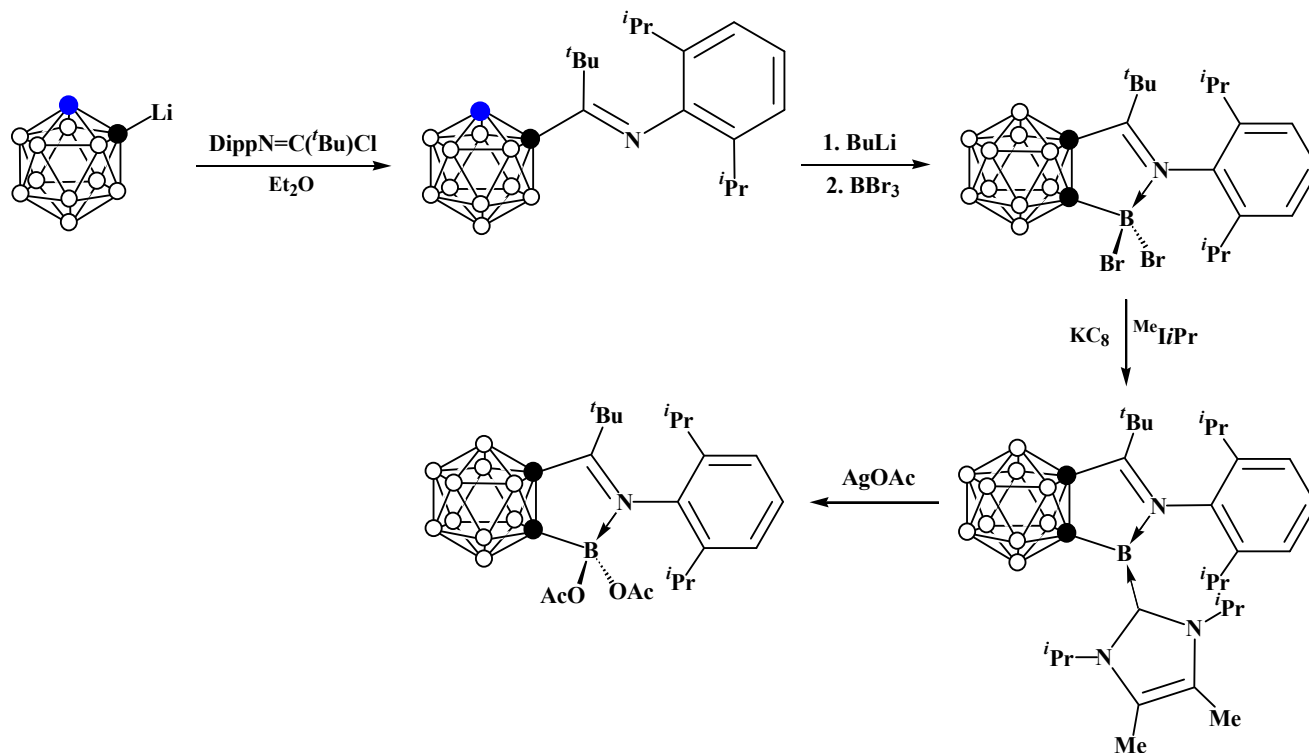


Figure 23. Single crystal structures of 1,2-μ-(1',2'-C₆H₄(BN^{*i*Pr})₂)-1,2-C₂B₁₀H₁₀ (left) and 1,2-μ-(Me₂NB)₃-1,2-C₂B₁₀H₁₀ (right). Hydrogen atoms of alkyl groups are omitted for clarity.

The reaction of iminocarborane 1-DippN=C(^{*t*}Bu)C-1,2-C₂B₁₀H₁₁ (Dipp = 2',6'-C₆H₃^{*i*}Pr₂) with *n*-BuLi in toluene, followed by the addition of boron tribromide, leads to the closure of the five-membered ring with the formation of iminocarboranyldibromoborane 1,2-μ-Br₂BN(Dipp)=C^{*t*}Bu-1,2-C₂B₁₀H₁₀. Its reduction of dibromoborane with KC₈ in the presence of 1,3-diisopropyl-4,5-dimethylimidazole-2-ylidene (^{Me}IiPr) in toluene results in the *N*-heterocyclic carbene-stabilized carborane-fused azaborole 1,2-μ-(^{Me}IiPr)BN(Dipp)C^{*t*}Bu-1,2-C₂B₁₀H₁₀, which in turn can be reoxidized with silver acetate in tetrahydrofuran to give iminocarboranyldiacetoxyborane 1,2-μ-(AcO)₂BN(Dipp)=C^{*t*}Bu-1,2-C₂B₁₀H₁₀ (Scheme 27, Figure 24) [63].



Scheme 27. Synthesis of the *N*-heterocyclic carbene-stabilized carborane-fused azaborole 1,2-μ-(^{Me}IiPr)BN(Dipp)C^{*t*}Bu-1,2-C₂B₁₀H₁₀.

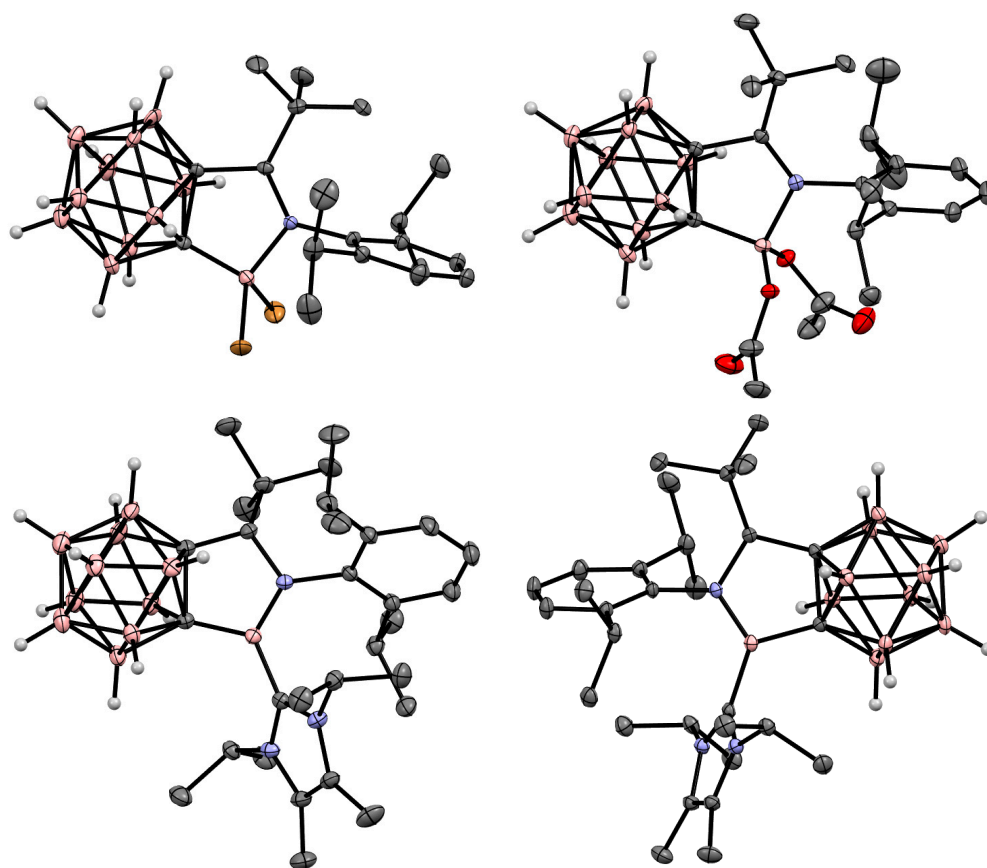
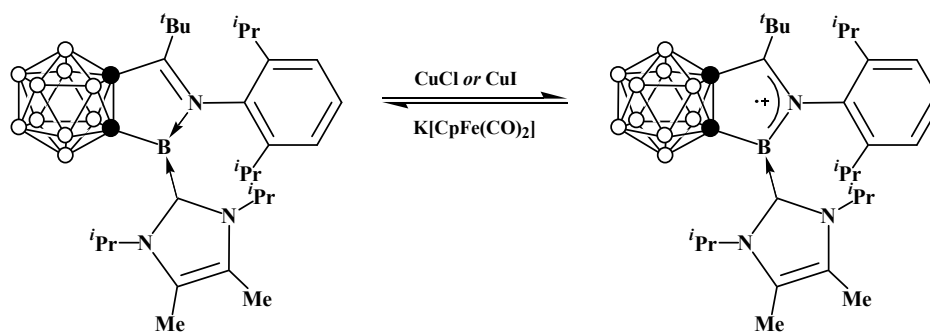


Figure 24. Single crystal structures of 1,2- μ -Br₂BN(Dipp)=C^tBu-1,2-C₂B₁₀H₁₀ (**top left**), 1,2- μ -(AcO)₂BN(Dipp)=C^tBu-1,2-C₂B₁₀H₁₀ (**top right**), 1,2- μ -(^{Me}IiPr)BN(Dipp)C^tBu-1,2-C₂B₁₀H₁₀ (**bottom left**), and the [1,2- μ -(^{Me}IiPr)BN(Dipp)C^tBu-1,2-C₂B₁₀H₁₀]^{•+} radical (**bottom right**). Hydrogen atoms of organic substituents are omitted for clarity.

The one-electron oxidation of the carborane-fused azaborole 1,2- μ -(^{Me}IiPr)BN(Dipp)C^tBu-1,2-C₂B₁₀H₁₀ with CuCl or CuI in tetrahydrofuran results in a carbene-stabilized carborane-fused azaborolyl radical cation isolated as the corresponding salts [1,2- μ -(^{Me}IiPr)BN(Dipp)C^tBu-1,2-C₂B₁₀H₁₀][CuCl₂][−] and [1,2- μ -(^{Me}IiPr)BN(Dipp)C^tBu-1,2-C₂B₁₀H₁₀]₂[Cu₂I₄]^{2−} (Scheme 28). The geometry of the resulting radical cation is close to that of the starting compound, except for some redistribution of bond lengths in the carborane-fused five-membered heterocycle. The dihedral angles of the azaborole and N-heterocyclic carbene planes are 67.9° and 67.4° for the [CuCl₂][−] and [Cu₂I₄]^{2−} salts, respectively, which are very close to that of 65.3° observed in the starting compound (Figure 24). These data strongly suggest that the carbene acts solely as a σ donor, not as a π acceptor [64].



Scheme 28. Synthesis of carborane-fused azaborolyl radical cation [1,2- μ -(^{Me}IiPr)BN(Dipp)C^tBu-1,2-C₂B₁₀H₁₀]^{•+}.

The reaction of 1,2- μ -(^{Me}IiPr)BN(Dipp)C^tBu-1,2-C₂B₁₀H₁₀ with elemental sulfur in tetrahydrofuran at room temperature unexpectedly leads to the deboration of the *ortho*-carborane cage with the formation of the dicarbollide-fused azaborole 7,8- μ -(^{Me}IiPr)BN(Dipp)C^tBu-7,8-C₂B₉H₉. The open pentagonal C₂B₃ face is fused with another C₃BN five membered ring with a dihedral angle of 122.2° (Figure 25). The quantum chemical calculations demonstrate the π conjugation between two fused five-membered rings formally bearing charges of +2 (C₃BN) and −2 (C₂B₃) [64].

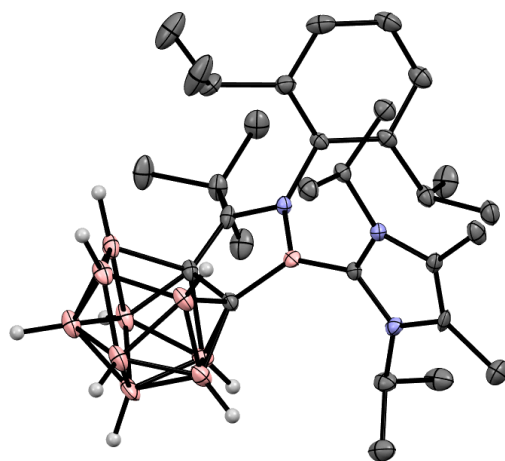
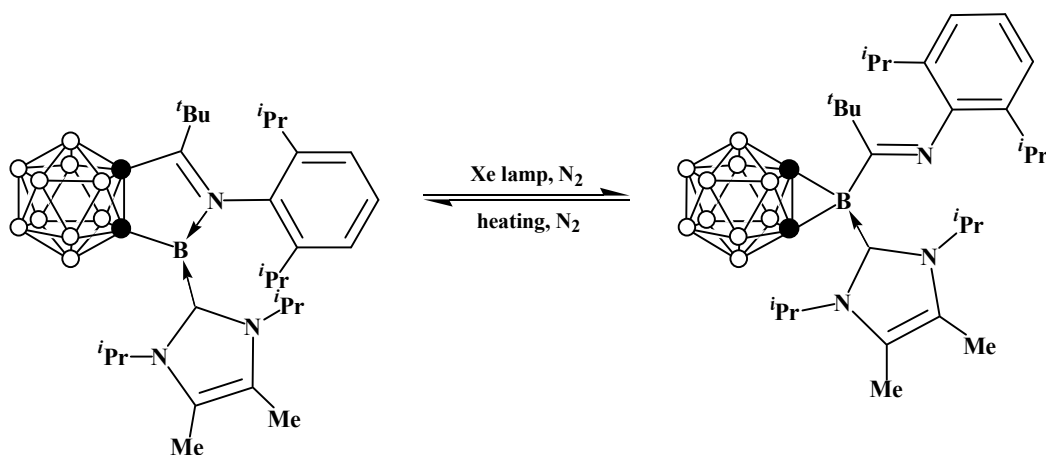


Figure 25. Single crystal structure 7,8- μ -(^{Me}IiPr)BN(Dipp)C^tBu-7,8-C₂B₉H₉. Hydrogen atoms of organic substituents are omitted for clarity.

Irradiation of solution of the carborane-fused azaborole 1,2- μ -(^{Me}IiPr)BN(Dipp)C^tBu-1,2-C₂B₁₀H₁₀ in tetrahydrofuran with a Xe light lamp (400–1500 nm, 300 W) at ambient temperature under N₂ atmosphere results in its photoisomerization to the carbene-stabilized carborane-fused borirane 1,2- μ -DippN=(^tBu)C(^{Me}IiPr)B-1,2-C₂B₁₀H₁₀. This transformation is completely reversible under an inert atmosphere and is accelerated by heating (Scheme 29, Figure 26) [65].



Scheme 29. Synthesis of the carbene-stabilized carborane-fused borirane 1,2- μ -DippN=(^tBu)C(^{Me}IiPr)B-1,2-C₂B₁₀H₁₀.

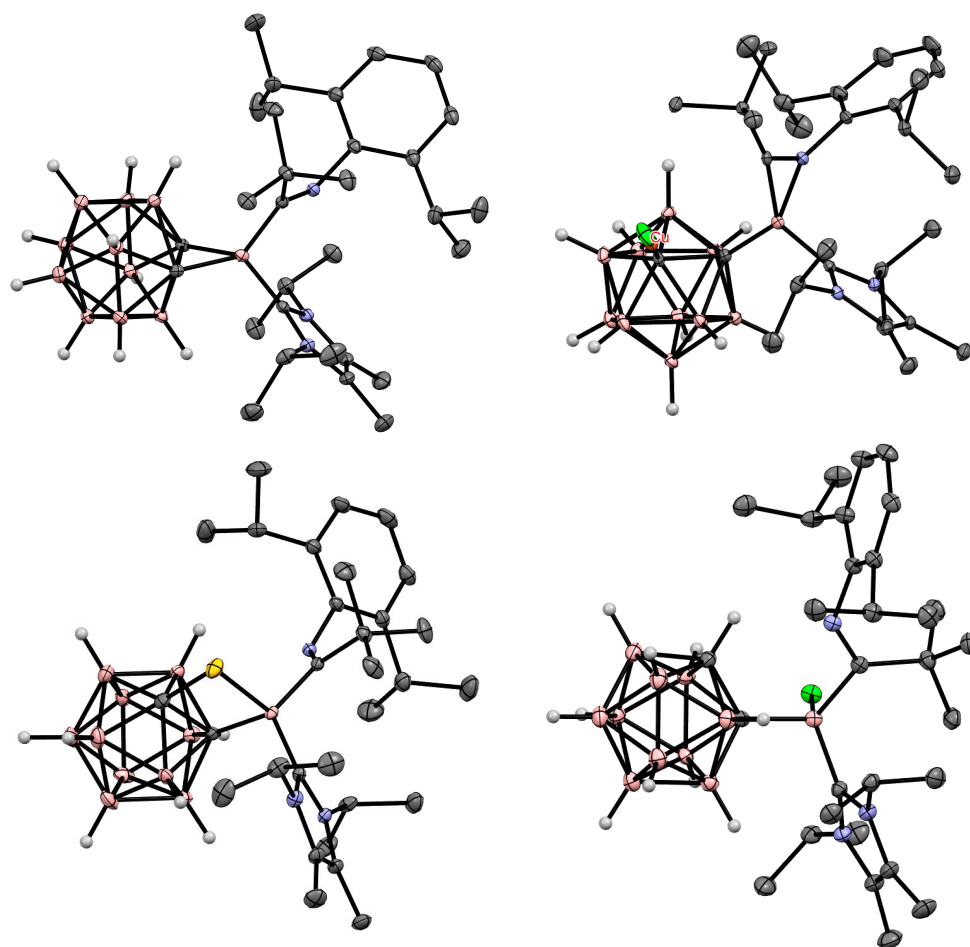
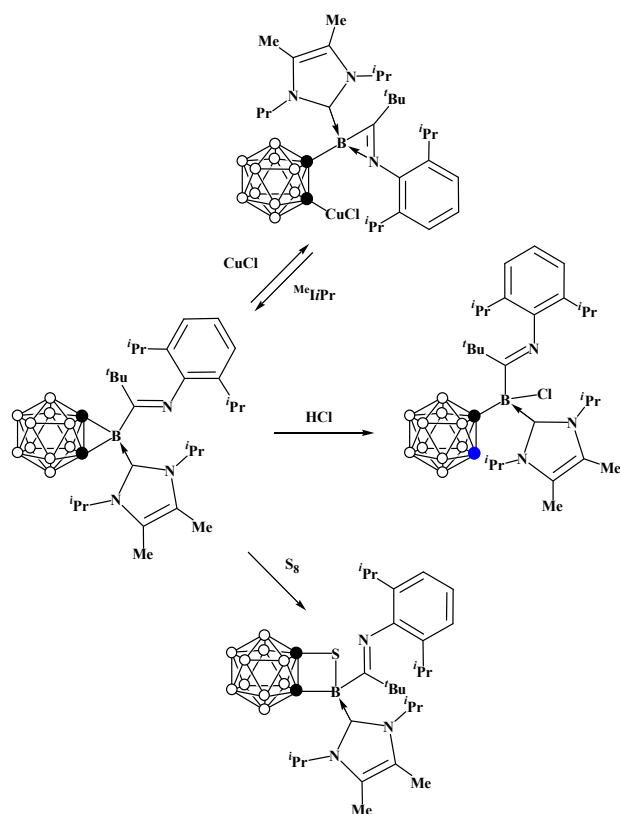


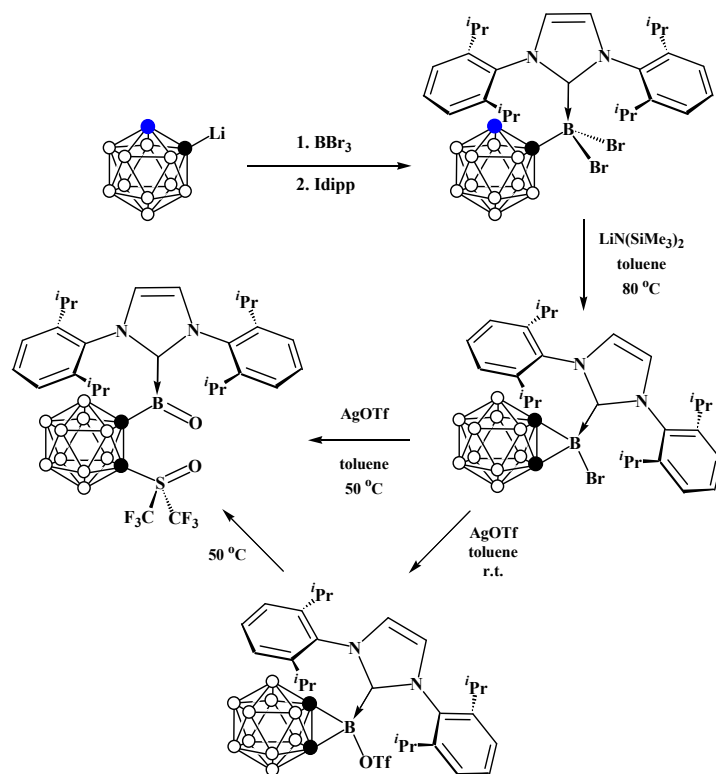
Figure 26. Single crystal structures of 1,2- μ -DippN=(*t*Bu)C(^{Me}IiPr)B-1,2-C₂B₁₀H₁₀ (**top left**), 1-cyclo-(Dipp)N=(*t*Bu)C(^{Me}IiPr)B-2-ClCu-1,2-C₂B₁₀H₁₀ (**top right**), 1,2- μ -DippN=(*t*Bu)C(^{Me}IiPr)BS-1,2-C₂B₁₀H₁₀ (**bottom left**), and 1-DippN=(*t*Bu)C(^{Me}IiPr)ClB-1,2-C₂B₁₀H₁₁ (**bottom right**). Hydrogen atoms of organic substituents are omitted for clarity.

The treatment of the carborane-fused borirane 1,2- μ -DippN=(*t*Bu)C(^{Me}IiPr)B-1,2-C₂B₁₀H₁₀ with CuCl in tetrahydrofuran leads to the disclosure of carborane-fused three-membered ring with the formation of a new BNC three-membered ring, giving 1-cyclo-(Dipp)N=(*t*Bu)C(^{Me}IiPr)B-2-ClCu-1,2-C₂B₁₀H₁₀. The reaction of the carborane-fused borirane with HCl in 1,4-dioxane also proceeds with the ring disclosure, resulting in 1-DippN=(*t*Bu)C(^{Me}IiPr)ClB-1,2-C₂B₁₀H₁₁. Unexpectedly, the reaction of the carborane-fused borirane with elemental sulfur in tetrahydrofuran at room temperature leads to the ring expansion with the formation of 1,2- μ -DippN=(*t*Bu)C(^{Me}IiPr)BS-1,2-C₂B₁₀H₁₀ (Scheme 30, Figure 26) [65].

Another carborane-fused borirane was prepared in a more straightforward manner. The reaction of the lithium derivative of *ortho*-carborane with boron tribromide BBr₃ in the presence of 1,3-bis(2',6'-diisopropyl)imidazol-2-ylidene (Idipp) gives the *N*-heterocyclic carbene-coordinated carboranyl boron dibromide 1-(Idipp)Br₂B-1,2-C₂B₁₀H₁₁, which on the treatment with lithium bis(trimethylsilyl)amide (LiN(TMS)₂) in toluene at 80 °C produces the carborane-fused borirane 1,2- μ -(Idipp)BrB-1,2-C₂B₁₀H₁₀. Subsequent treatment of 1,2- μ -(Idipp)BrB-1,2-C₂B₁₀H₁₀ with AgOTf in toluene at ambient temperatures results in the replacement of bromide with triflate, giving 1,2- μ -(Idipp)(TfO)B-1,2-C₂B₁₀H₁₀. The last one on heating to 50 °C isomerizes with the three-membered cycle disclosure to give oxoborane 1-(Idipp)(O)B-2-CF₃O₂S-1,2-C₂B₁₀H₁₀ (Scheme 31, Figure 27) [66].



Scheme 30. Reactions of the carborane-fused borirane $1,2\text{-}\mu\text{-DippN}=(^t\text{Bu})\text{C}(\text{MeI}/i\text{Pr})\text{B-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$.



Scheme 31. Synthesis and reactions of the carborane-fused borirane $1,2\text{-}\mu\text{-(Idipp)BrB-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$.

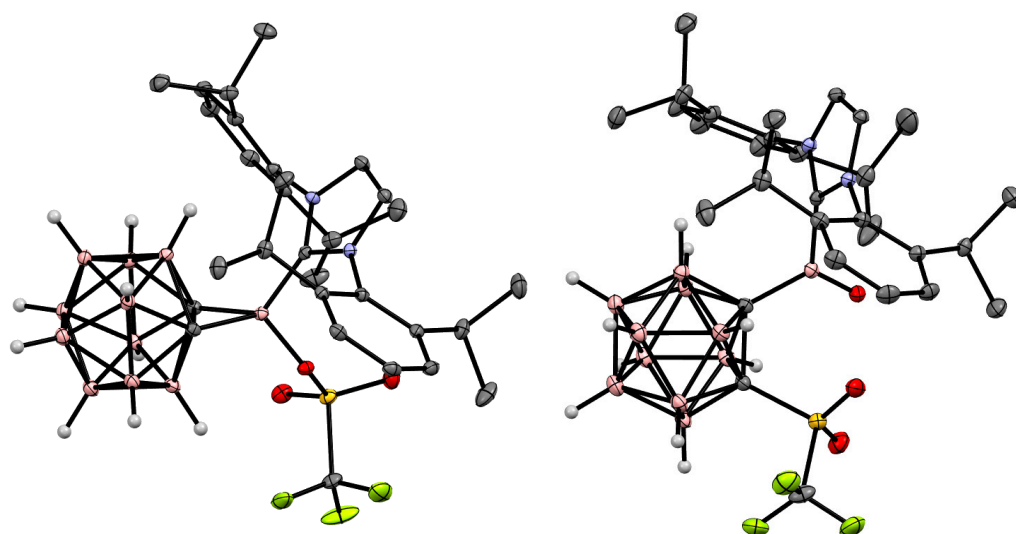
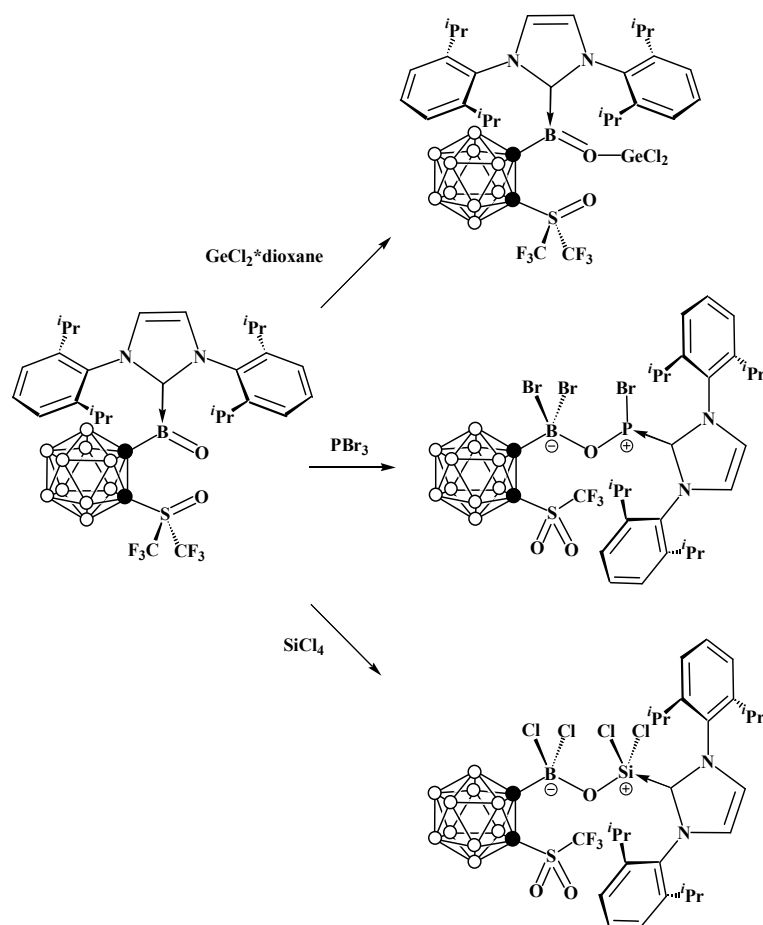


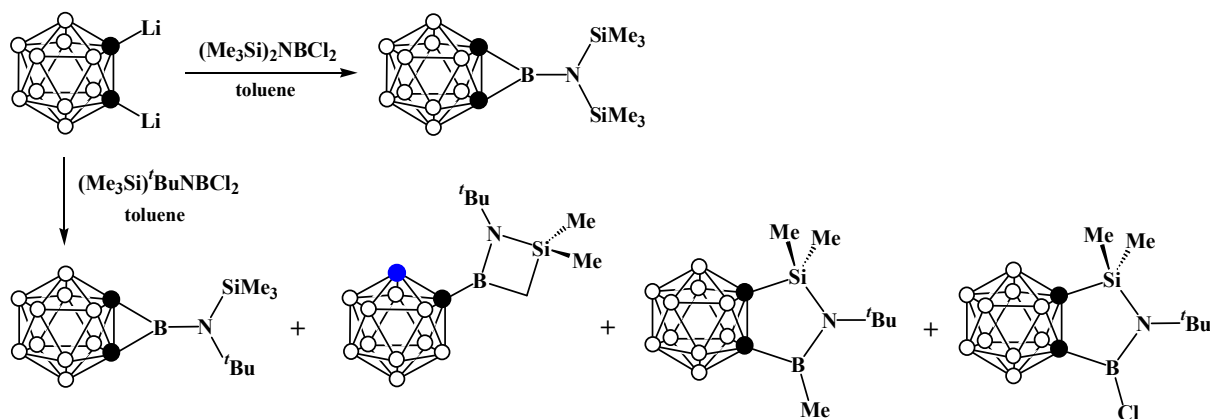
Figure 27. Single crystal structures of 1,2- μ -(Idipp)(TfO)B-1,2-C₂B₁₀H₁₀ (**left**) and 1-(Idipp)(O)B-2-CF₃O₂S-1,2-C₂B₁₀H₁₀ (**right**). Hydrogen atoms of organic substituents are omitted for clarity.

The carboranyl oxoborane 1-O=(Idipp)B-2-CF₃O₂S-1,2-C₂B₁₀H₁₀ reacts with GeCl₂·1,4-dioxane to give the corresponding Lewis acid-base adduct 1-Cl₂Ge·O=(Idipp)B-2-CF₃O₂S-1,2-C₂B₁₀H₁₀. On the other hand, the reactions with PBr₃ and SiCl₄ result in 1-(Idipp)BrPOBr₂B-2-CF₃O₂S-1,2-C₂B₁₀H₁₀ and 1-(Idipp)Cl₂SiOCl₂B-2-CF₃O₂S-1,2-C₂B₁₀H₁₀ (Scheme 32) [66].



Scheme 32. Reactions of carboranyl oxoborane 1-O=(Idipp)B-2-CF₃O₂S-1,2-C₂B₁₀H₁₀.

The reaction of the dilithium derivative of *ortho*-carborane with bis(trimethylsilyl)amino dichloroborane $(\text{Me}_3\text{Si})_2\text{NBCl}_2$ in toluene results directly in the corresponding symmetrical carborane-fused borirane 1,2- μ -($\text{Me}_3\text{Si})_2\text{NB}$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (Scheme 33, Figure 28) [67]. A similar reaction with trimethylsilyl-*t*-butylamino dichloroborane, along with 1,2- μ -($\text{Me}_3\text{Si})^t\text{BuNB}$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$, gives 1-(*cyclo*- $\text{H}_2\text{CMe}_2\text{Si}^t\text{BuN}=\text{B}$)-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$, 1,2- μ - $\text{Me}_2\text{Si}^t\text{BuNClB}$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$, and 1,2- μ - $\text{Me}_2\text{Si}^t\text{BuNMeB}$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (Scheme 33, Figure 28) [68].



Scheme 33. Synthesis of carborane-fused boriranes 1,2- μ -RR'NB-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$.

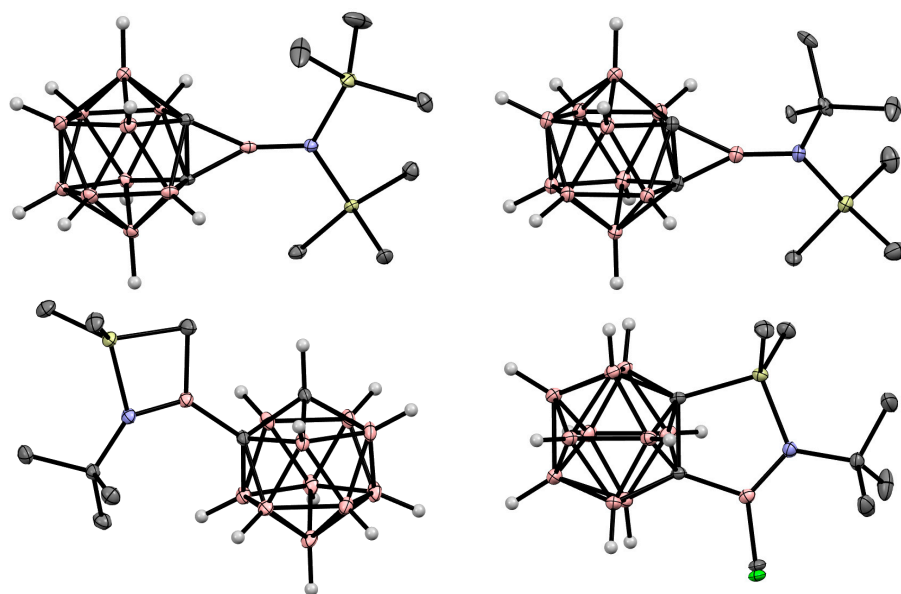
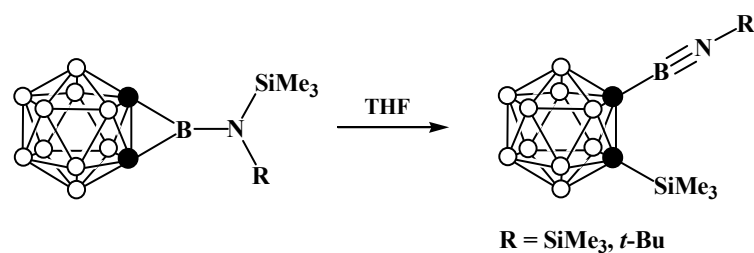


Figure 28. Single crystal structures of 1- $\text{Me}_3\text{SiN} \equiv \text{B}$ -2- Me_3Si - $\text{C}_2\text{B}_{10}\text{H}_{10}$ (**top left**), 1,2- μ -($\text{Me}_3\text{Si})^t\text{BuNB}$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (**top right**), 1-(*cyclo*- $\text{H}_2\text{CMe}_2\text{Si}^t\text{BuN}=\text{B}$)-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ (**bottom left**), and 1,2- μ - $\text{Me}_2\text{Si}^t\text{BuN}(\text{Me}/\text{Cl})\text{B}$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (**bottom right**).

The treatment of the carborane-fused borirane 1,2- μ -RR'NB-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ ($\text{R} = \text{R}' = \text{SiMe}_3$; $\text{R} = \text{SiMe}_3$, $\text{R}' = t\text{-Bu}$) in hexane with THF as a Lewis base leads to ring disclosure with the formation of the corresponding iminoboryl carborane 1- $\text{RN} \equiv \text{B}$ -2- Me_3Si - $\text{C}_2\text{B}_{10}\text{H}_{10}$ ($\text{R} = \text{SiMe}_3$, $t\text{-Bu}$) (Scheme 34, Figure 29) [69].



Scheme 34. THF-promoted rearrangement of the carborane-fused borirane 1,2- $\mu\text{-RR'NB-1,2-C}_2\text{B}_{10}\text{H}_{10}$.

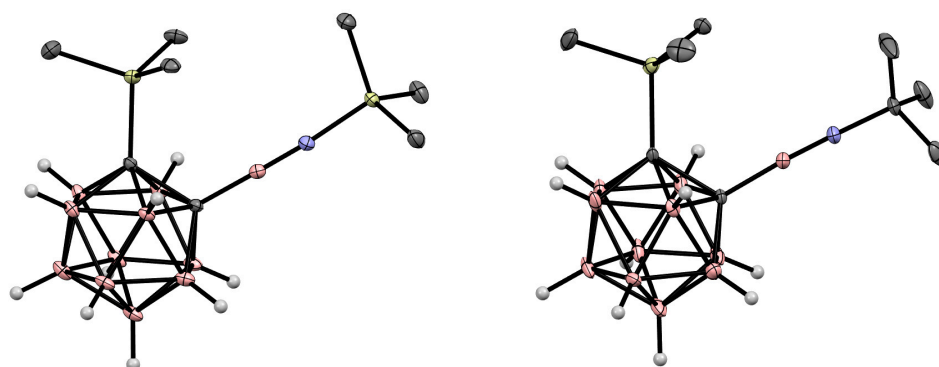


Figure 29. Single crystal structures of 1- $\text{Me}_3\text{SiN}\equiv\text{B-2-Me}_3\text{Si-C}_2\text{B}_{10}\text{H}_{10}$ (left) and 1- $t\text{-BuN}\equiv\text{B-2-Me}_3\text{Si-C}_2\text{B}_{10}\text{H}_{10}$ (right). Hydrogen atoms of alkyl groups are omitted for clarity.

In the presence of catalytic amounts of *tert*-butylisocyanide *t*-BuNC in benzene, 1- $\text{Me}_3\text{SiN}\equiv\text{B-2-Me}_3\text{Si-C}_2\text{B}_{10}\text{H}_{10}$ undergoes dimerization with the formation of the central B_2N_2 ring of a butterfly geometry (interplanar angle of 156.0°). In the presence of an excess of *tert*-butylisocyanide, one molecule of *t*-BuNC is coordinated to the central B_2N_2 ring, changing its geometry to planar (Figure 30) [69].

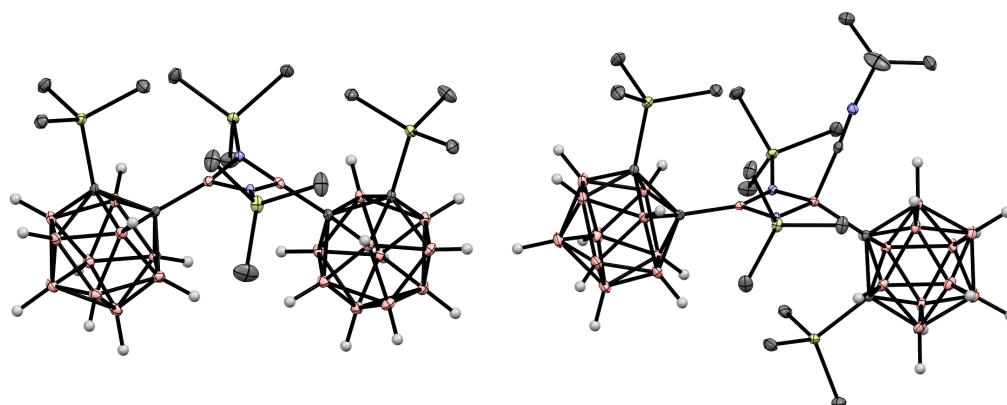
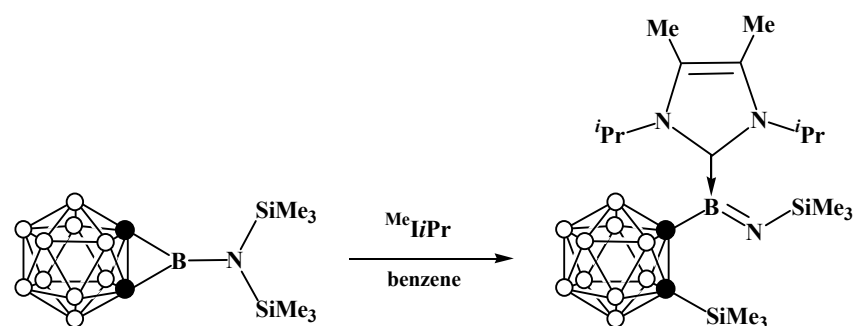


Figure 30. Single crystal structures of the products of dimerization of 1- $\text{Me}_3\text{SiN}\equiv\text{B-2-Me}_3\text{Si-C}_2\text{B}_{10}\text{H}_{10}$ in the presence of *t*-BuCN. Hydrogen atoms of alkyl groups are omitted for clarity.

The reaction of the carborane-fused borirane 1,2- $\mu\text{-(Me}_3\text{Si)}_2\text{NB-1,2-C}_2\text{B}_{10}\text{H}_{10}$ with 1,3-diisopropyl-4,5-dimethylimidazole-2-ylidene ($^{\text{Me}}\text{IiPr}$) in benzene results in the disclosure of the borinane ring with the formation of the *N*-heterocyclic carbene iminoborane adduct 1- $\text{Me}_3\text{SiN}=(^{\text{Me}}\text{IiPr})\text{B-2-Me}_3\text{Si-1,2-C}_2\text{B}_{10}\text{H}_{10}$ (Scheme 35, Figure 31) [68].



Scheme 35. Reaction of 1,2-μ-(Me₃Si)₂NB-1,2-C₂B₁₀H₁₀ with *N*-heterocyclic carbene MeIiPr.

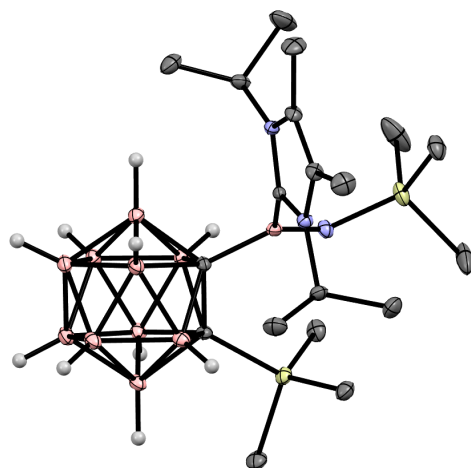
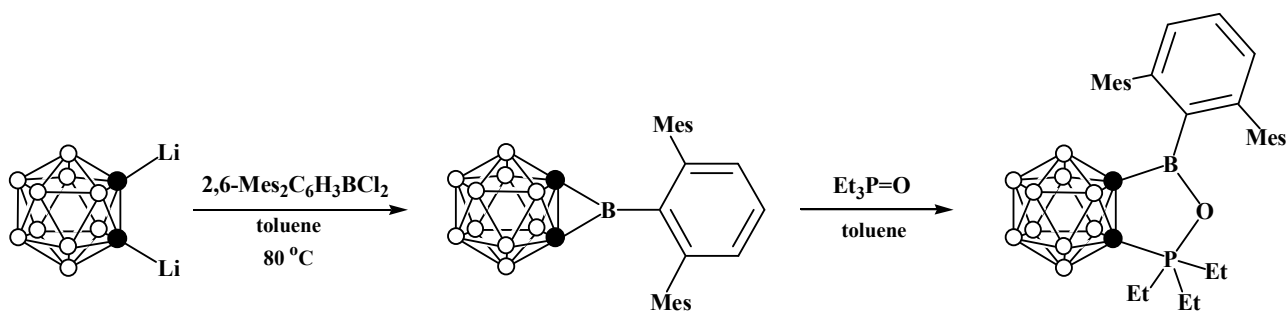


Figure 31. Single crystal structure of the products of dimerization of 1-Me₃SiN=(^{Me}IiPr)B-2-Me₃Si-1,2-C₂B₁₀H₁₀. Hydrogen atoms of alkyl groups are omitted for clarity.

Another symmetrical carborane-fused borirane 1,2-μ-(2',6'-Mes₂C₆H₃B)-1,2-C₂B₁₀H₁₀ was prepared by the reaction of the dilithium salt of *ortho*-carborane with 2,6-dimesitylphenyl boron dichloride in toluene at 80 °C. An attempt to determine its Lewis acidity by the Gutmann–Beckett method resulted in the formation of the carborane derivative with fused C₂BOP five-membered heterocycle 1,2-μ-(Et₃PO(2',6'-Mes₂C₆H₃B))-1,2-C₂B₁₀H₁₀ (Scheme 36, Figure 32) [70].



Scheme 36. Synthesis of the carborane-fused borirane 1,2-μ-(2',6'-Mes₂C₆H₃B)-1,2-C₂B₁₀H₁₀.

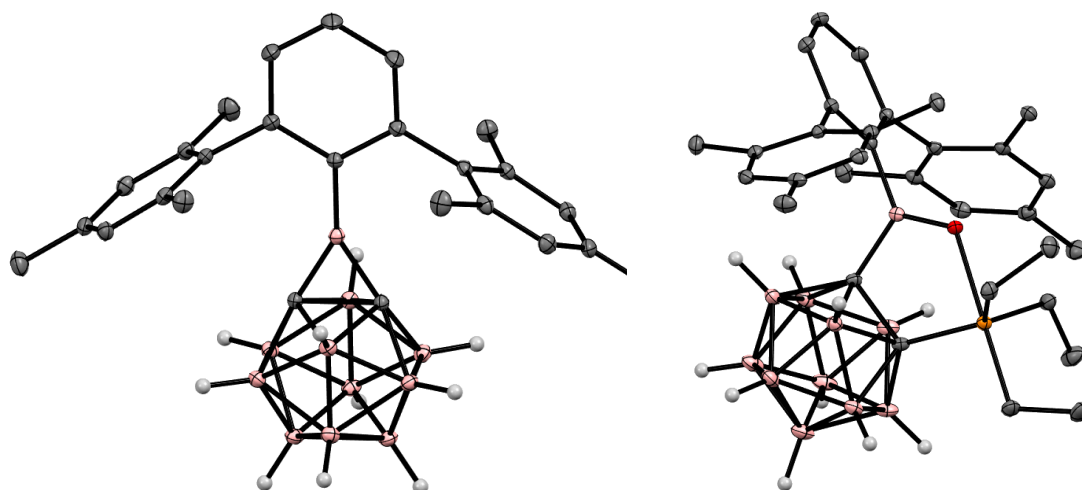
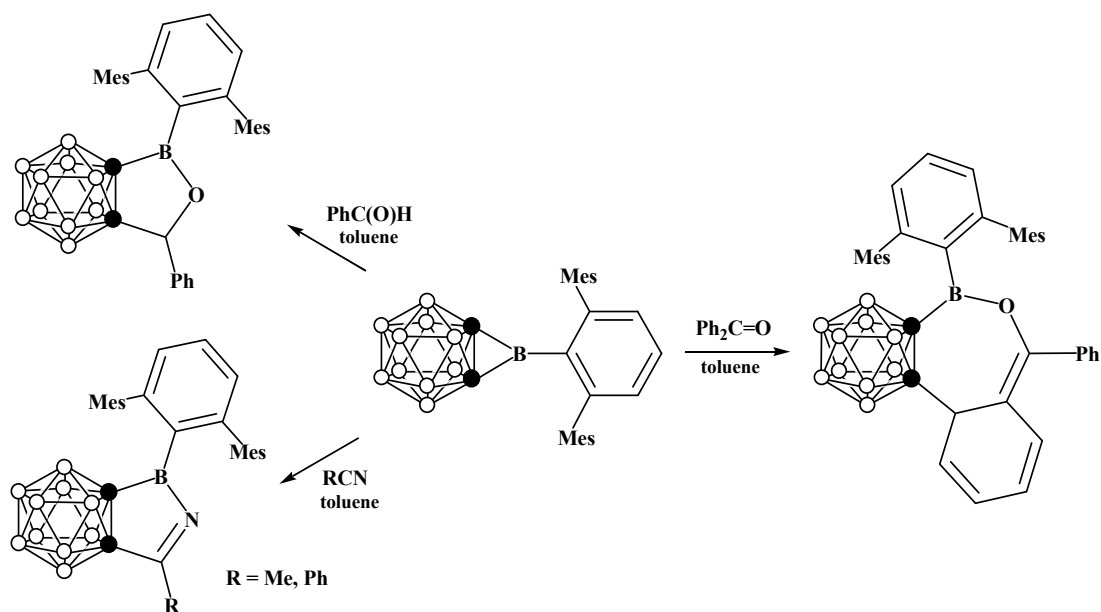


Figure 32. Single crystal structures of 1,2- μ -(2',6'-Mes₂C₆H₃B)-1,2-C₂B₁₀H₁₀ (**left**) and 1,2- μ -(Et₃PO(2',6'-Mes₂C₆H₃)B)-1,2-C₂B₁₀H₁₀ (**right**). Hydrogen atoms of organic substituents are omitted for clarity.

The reactions of 1,2- μ -(2',6'-Mes₂C₆H₃B)-1,2-C₂B₁₀H₁₀ with benzaldehyde and benzophenone in toluene produce the five- and seven-membered carborane-fused heterocycles 1,2- μ -(PhHCO(2',6'-Mes₂C₆H₃)B)-1,2-C₂B₁₀H₁₀ and 1,2- μ -(*o*-C₆H₅=(Ph)CO(2',6'-Mes₂C₆H₃)B)-1,2-C₂B₁₀H₁₀, respectively (Scheme 37, Figure 33) [70].



Scheme 37. Ring-expansion reactions of 1,2- μ -(2',6'-Mes₂C₆H₃B)-1,2-C₂B₁₀H₁₀.

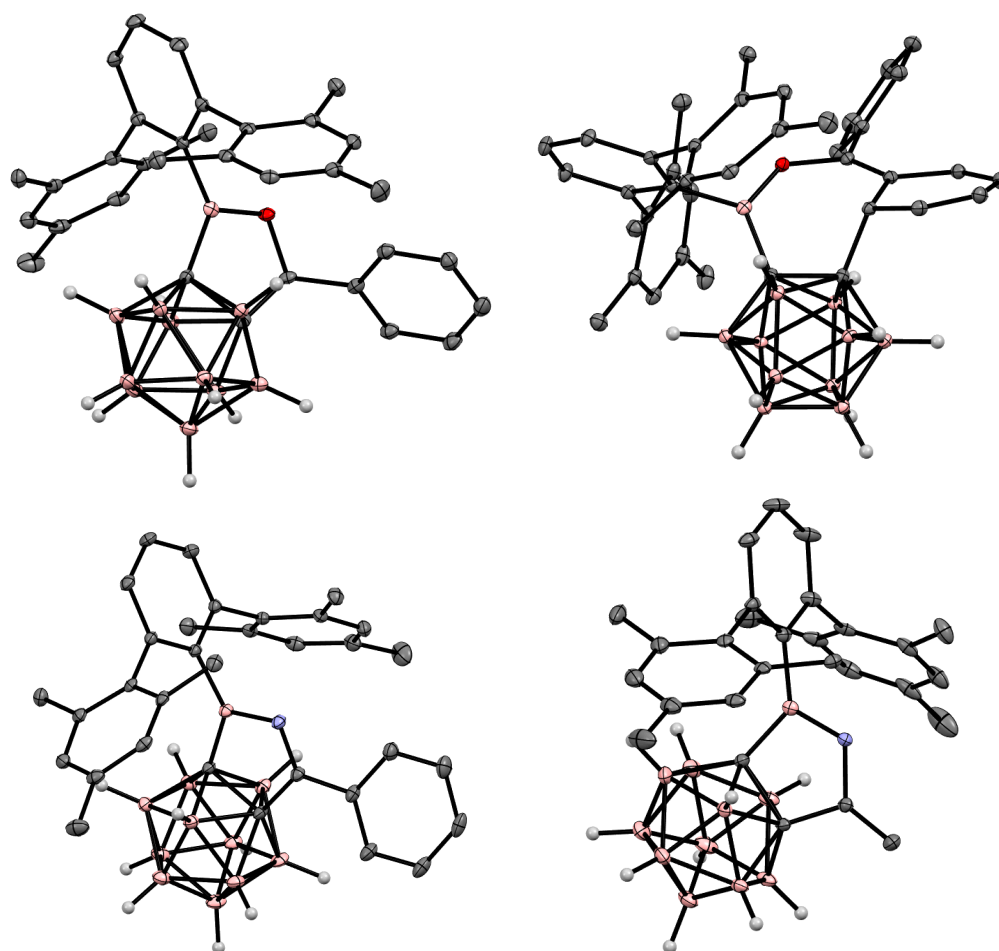


Figure 33. Single crystal structures of 1,2- μ -(PhHCO(2',6'-Mes₂C₆H₃)B)-1,2-C₂B₁₀H₁₀ (**top left**), 1,2- μ -(*o*-C₆H₅=(Ph)CO(2',6'-Mes₂C₆H₃)B)-1,2-C₂B₁₀H₁₀, (**top right**), 1,2- μ -(PhC=N(2',6'-Mes₂C₆H₃)B)-1,2-C₂B₁₀H₁₀ 1,2- μ -(2',6'-Mes₂C₆H₃)B)-1,2-C₂B₁₀H₁₀ (**bottom left**), and 1,2- μ -(MeC=N(2',6'-Mes₂C₆H₃)B)-1,2-C₂B₁₀H₁₀ 1,2- μ -(Et₃PO(2',6'-Mes₂C₆H₃)B)-1,2-C₂B₁₀H₁₀ (**bottom right**). Hydrogen atoms of organic substituents are omitted for clarity.

The reactions with nitriles in toluene also lead to the five-membered carborane-fused heterocycle 1,2- μ -(RC=N(2',6'-Mes₂C₆H₃)B)-1,2-C₂B₁₀H₁₀ (R = Me, Ph) (Scheme 37, Figure 33) [70].

7. Bis(Carboranyl)-Fused Boron-Containing Heterocycles

The three-dimensional inorganic analogs of 9-borafluorene 2,2'- μ -XB-1,1'-bis(*ortho*-carborane) (X = Cl, Br) (Figure 34) were synthesized by the reaction of the dilithium derivative of 1,1'-bis(*ortho*-carborane) with BX₃ in hexane (Scheme 38) [71], while the reaction of the dilithium derivative of 1,1'-bis(*ortho*-carborane) with BBr₃ in toluene unexpectedly resulted in the anionic dibromoborate derivative Li⁺[2,2'- μ -Br₂B-1,1'-bis(*ortho*-carborane)][−] (Figure 34) [71].

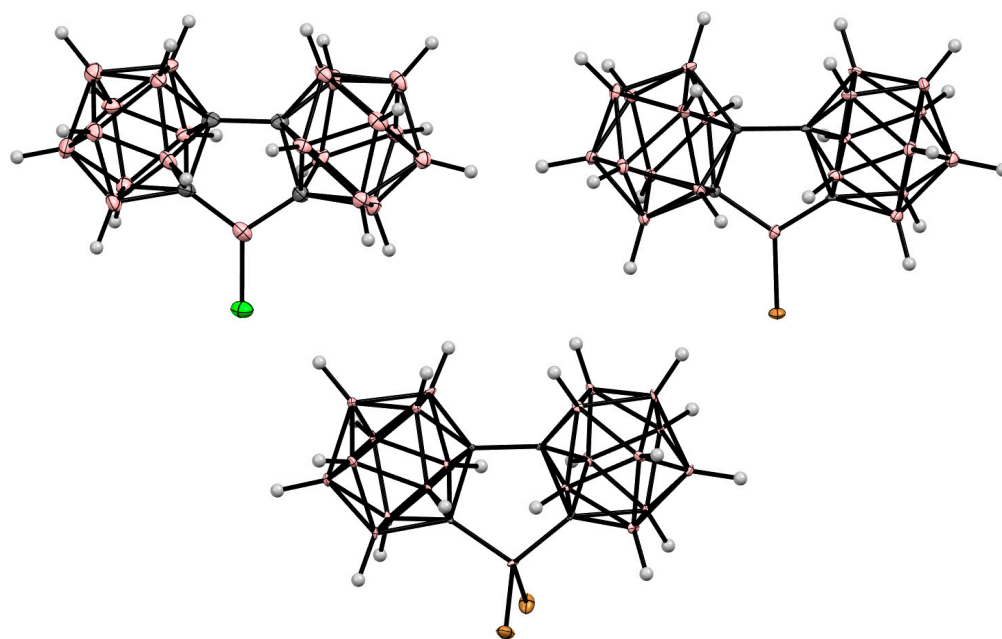
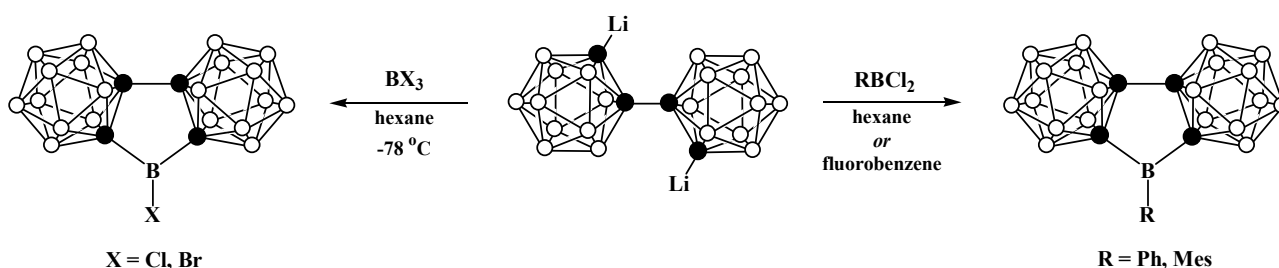


Figure 34. Single crystal structures of μ -2,2'-ClB-1,1'-bis(*ortho*-carborane) (**top left**), μ -2,2'-BrB-1,1'-bis(*ortho*-carborane) (**top right**), and the $[\mu$ -2,2'-Br₂B-1,1'-bis(*ortho*-carborane)][−] anion (**bottom**).



Scheme 38. Synthesis of bis(carboranyl) analogs of 9-borafluorene 2,2'- μ -XB-1,1'-bis(*ortho*-carborane) (X = Cl, Br, Ph, Mes).

Due to their high Lewis acidity, the synthesized bis(carboranyl) 9-borafluorene analogs form stable complexes with diethyl ether 2,2'- μ -Et₂O·(X)B-1,1'-bis(*ortho*-carborane) (X = Cl, Br), the structure of which in the solid state was determined by a single crystal X-ray diffraction study (Figure 35), and the existence in solution was established by ¹H and ¹¹B NMR spectroscopy [71].

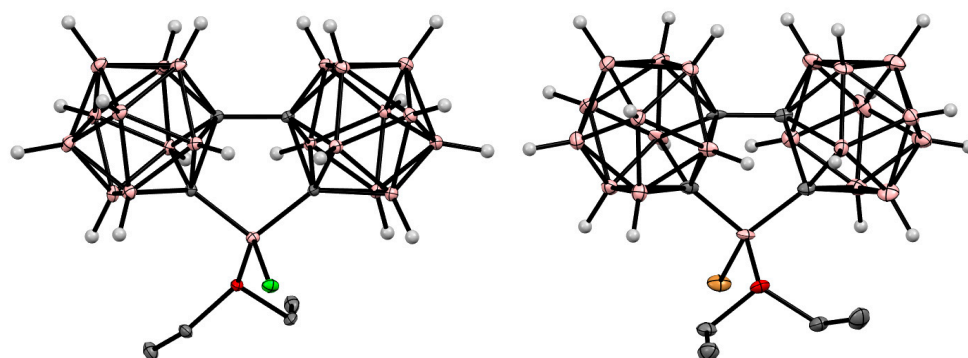


Figure 35. Single crystal structures of μ -2,2'-Et₂O(Cl)B-1,1'-bis(*ortho*-carborane) (**left**) and μ -2,2'-Et₂O(Br)B-1,1'-bis(*ortho*-carborane) (**right**). The hydrogen atoms of Et₂O are omitted for clarity.

The reaction of 2,2'- μ -BrB-1,1'-bis(*ortho*-carborane) with Et_3SiH leads to the anionic dihydride derivative $(\text{Et}_3\text{Si})^+ [2,2'-\mu\text{-H}_2\text{B-1,1'-bis}(\textit{ortho}\text{-carborane})]^-$. An attempt to obtain the neutral hydride derivative by removing the silane in a high vacuum was unsuccessful; however, its complex with diethyl ether 2,2'- μ -Et₂O(H)B-1,1'-bis(*ortho*-carborane) was synthesized by the reaction of the complex of the bromo derivative with diethyl ether 2,2'- μ -Et₂O(H)B-1,1'-bis(*ortho*-carborane) 2,2'- μ -Et₂O(Br)B-1,1'-bis(*ortho*-carborane) with Et_3SiH . The ^1H NMR spectrum of the hydride complex displays an upfield shift of the signal of the α -proton of the coordinated diethyl ether (3.31 ppm) with respect to that of the chloro and bromo complexes (3.55 and 3.58 ppm), indicating its relatively weaker Lewis acidity [71].

The aryl derivatives of the bis(carboranyl) analog of 9-borafluorene 2,2'- μ -RB-1,1'-bis(*ortho*-carborane) (R = Ph, Mes) were prepared by the reaction of the dilithium derivative of 1,1'-bis(*ortho*-carborane) with the corresponding aryldichloroborane RBCl_2 in hexane or fluorobenzene (Scheme 38) [71,72]. A single crystal X-ray diffraction study of the aryl derivatives revealed that they have notable structural differences. In the phenyl derivative, the aryl group and the C₄B ring are nearly coplanar, as indicated by the small dihedral angle (10.7°), while in the mesityl derivative, the aryl group displays a significantly enlarged dihedral angle of 65.47° (Figure 36), which can be explained by steric repulsion between the *ortho*-methyl groups of the mesityl substituent and the BH groups of the carborane units, which presumed a hindered rotation of the mesityl group around the B-C bond [71]. As a result, the phenyl derivative was found to form a complex with diethyl ether 2,2'- μ -Et₂O·(Ph)B-1,1'-bis(*ortho*-carborane) (Figure 37), while the mesityl derivative is unable to do so [71].

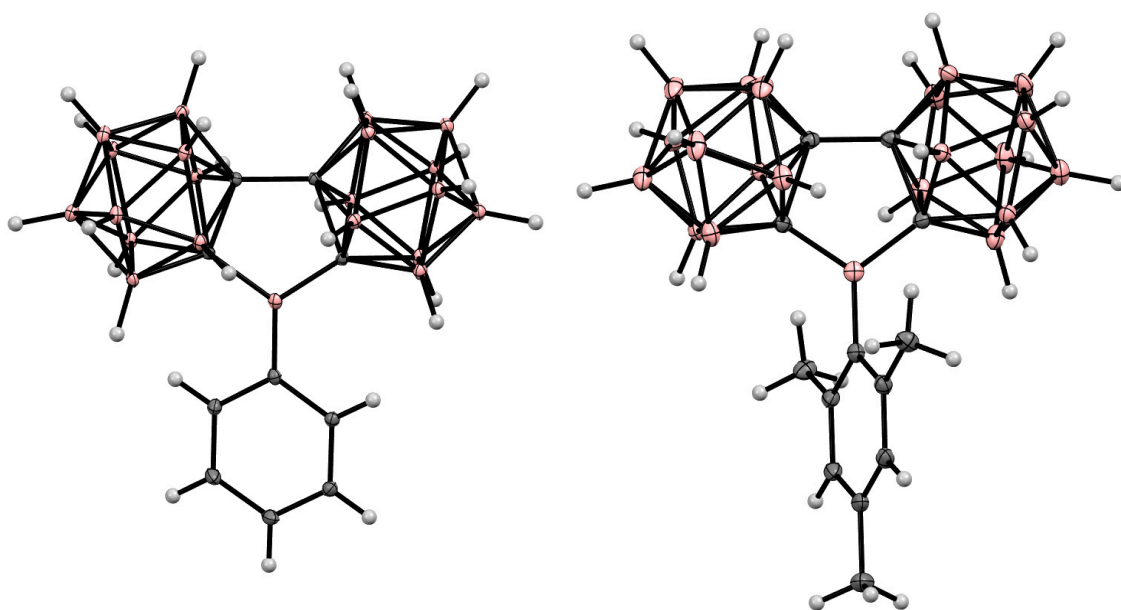


Figure 36. Single crystal structures of μ -2,2'-PhB-1,1'-bis(*ortho*-carborane) (**left**) and μ -2,2'-MesB-1,1'-bis(*ortho*-carborane) (**right**).

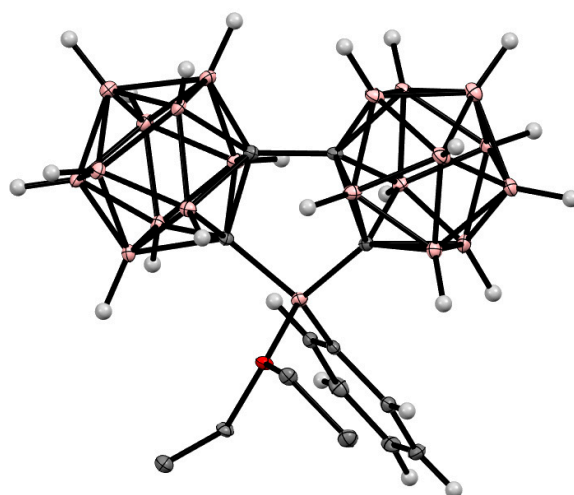


Figure 37. Single crystal structure of μ -2,2'-Et₂O·(Ph)B-1,1'-bis(*ortho*-carborane). The hydrogen atoms of Et₂O are omitted for clarity.

Most notably, the significant difference in the rotation of the aryl group on boron in the phenyl and mesityl derivatives led to their different photophysical properties. In particular, the absorption maximum in the UV-visible spectrum of the mesityl derivative (334 nm) is red-shifted by ~55 nm compared to that of the phenyl derivative (279 nm). Moreover, while the mesityl derivative demonstrates bluish-violet fluorescence, the phenyl derivative displayed no distinct fluorescent properties. This outcome is presumably caused by the nonradiative relaxation of the excited states, associated with rotation of the exocyclic phenyl group, which is largely hindered for the mesityl group. The emission maximum of for the mesityl derivative is strongly bathochromically shifted in polar solvents, thus indicating that the emission should arise from an intramolecular charge-transfer (ICT) transition [71].

The reaction of the phenyl derivative with Ph₃CBr in pentane proceeds with bromide ion transfer from carbon to boron, producing the anionic phenyl bromide derivative (Ph₃C)⁺[2,2'-μ-Ph(Br)B-1,1'-bis(*ortho*-carborane)][−] (Figure 38), which can be regarded as a weakly coordinating anion [71].

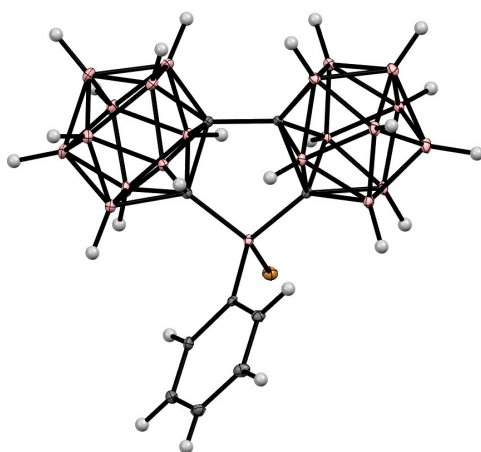


Figure 38. Single crystal structure of the [μ-2,2'-Ph(Br)B-1,1'-bis(*ortho*-carborane)][−] anion.

Due to the unique spatial environment of the trigonal planar boron in the phenyl derivative of the bis(carboranyl) analog of 9-borafluorene, it has good potential for use in frustrated Lewis pair chemistry. Indeed, in contrast to purely organic 9-borafluorenes and B(C₆F₅)₃, which form stable complexes with triphenylphosphine, the phenyl derivative of the bis(carboranyl) analog of 9-borafluorene is not capable of doing so. However, the exposure of a 1:1 mixture of phenyl derivative and triphenylphosphine to 1 atm. H₂ at

room temperature leads to the activation of the latter with the formation of the triphenylphosphonium salt of the anionic phenyl hydride derivative $(\text{Ph}_3\text{PH})^+ [2,2'\text{-}\mu\text{-Ph(H)B-1,1'-bis(ortho-carborane)}]^-$. Likewise, the treatment of a 1:1 mixture of the phenyl derivative and triphenylphosphine with excess Et_3SiH results in the similar triethsilyltriphenylphosphonium salt $(\text{Ph}_3\text{PSiEt}_3)^+ [2,2'\text{-}\mu\text{-Ph(H)B-1,1'-bis(ortho-carborane)}]^-$, the structure of which was determined by single crystal X-ray diffraction (Figure 39) [71].

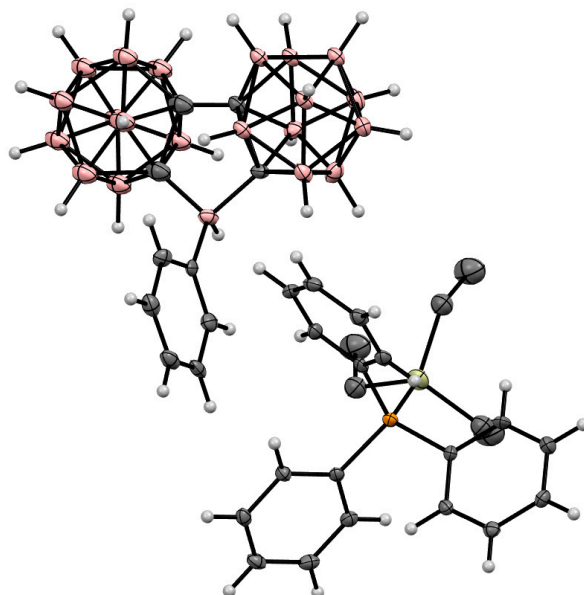
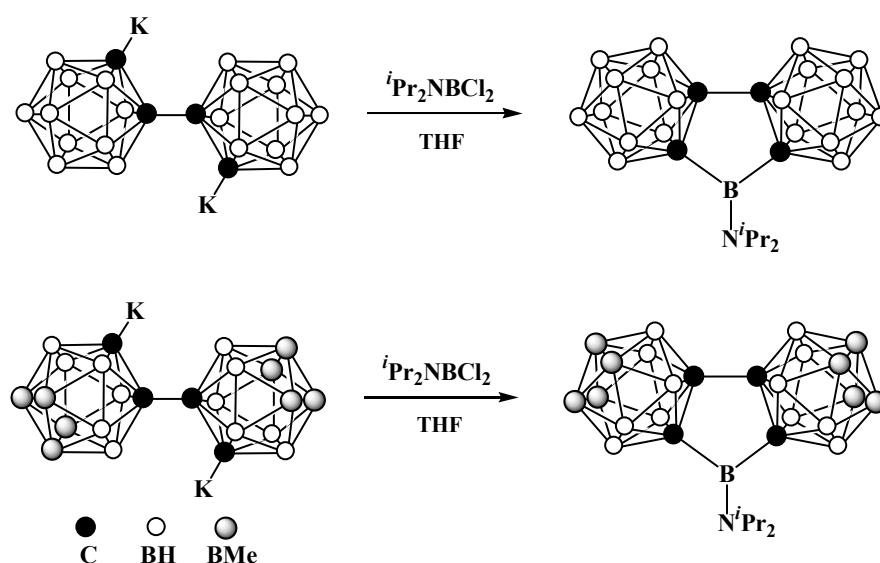


Figure 39. Single crystal structure of $(\text{Ph}_3\text{PSiEt}_3)^+ [2,2'\text{-}\mu\text{-Ph(H)B-1,1'-bis(ortho-carborane)}]^-$. The hydrogen atoms of the ethyl groups are omitted for clarity.

Other carboranyl analogs of 9-borafluorene 1,1'-bis(ortho-carborane) 2,2'- μ -(*i*-Pr) $_2$ NB-1,10-bis(ortho-carborane) and 2,2'- μ -(*i*-Pr) $_2$ NB-1,1'-bis(ortho-carborane-8,9,10,12-Me $_4$) were synthesized by the reaction of the dipotassium derivatives of 1,1'-bis(ortho-carborane) and its methylated analog with (*i*-Pr) $_2$ NBCl $_2$ in tetrahydrofuran (Scheme 39, Figure 40) [72].



Scheme 39. Synthesis of 2,2'- μ -(*i*-Pr) $_2$ NB-1,1'-bis(ortho-carborane) and 2,2'- μ -(*i*-Pr) $_2$ NB-1,1'-bis(ortho-carborane-8,9,10,12-Me $_4$).

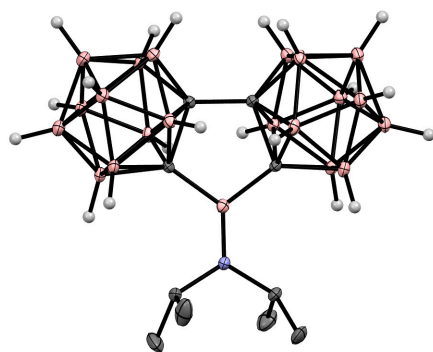


Figure 40. Single crystal structure of 2,2'-μ-(*i*-Pr)₂NB-1,1'-bis(*ortho*-carborane). The hydrogen atoms of the isopropyl groups are omitted for clarity.

The Lewis acidity of the synthesized bis(carboranyl) analogs of 9-borafluorene 2,2'-μ-XB-1,1'-bis(*ortho*-carborane) was determined by the Gutmann–Beckett method, and it was found that it decreases in the series Br > Cl > Ph > N^{*i*}Pr₂ [45,71,72].

The three-dimensional inorganic analogs of 9,10-diboraanthracene 1,1',2,2'-μ-(XB)₂-(*ortho*-carborane)₂ (X = Cl, Br) (Figure 41) were synthesized by the reaction of the dilithium derivative of *ortho*-carborane with BX₃ in dichloromethane (Scheme 40) [73].

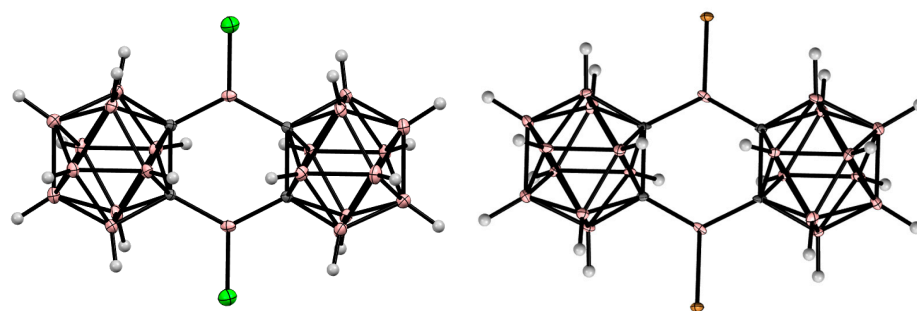
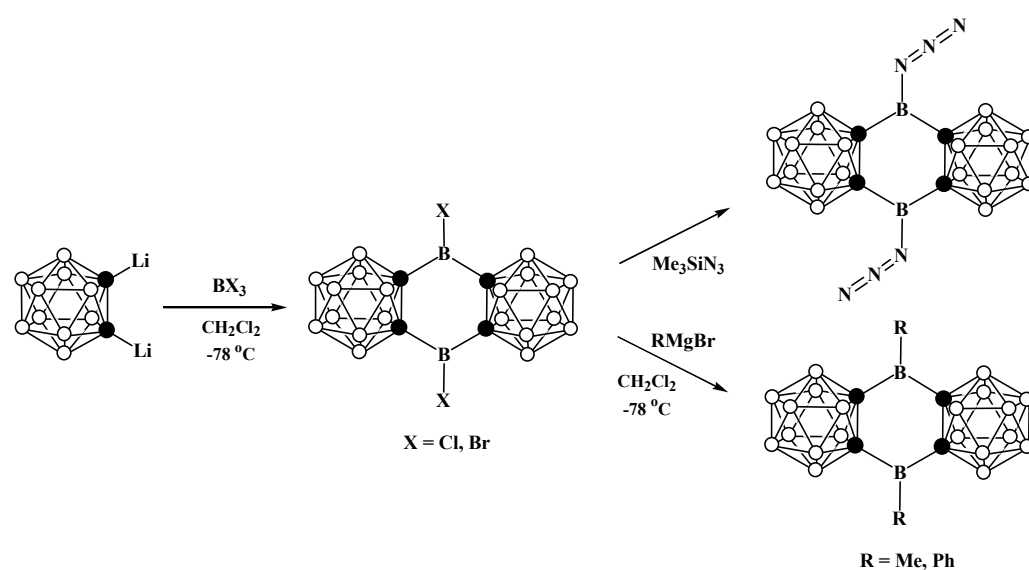


Figure 41. Single crystal structures of 1,1',2,2'-μ-(ClB)₂-(*ortho*-carborane)₂ (left) and 1,1',2,2'-μ-(BrB)₂-(*ortho*-carborane)₂ (right).



Scheme 40. Synthesis of the bis(carboranyl) analog 9,10-diboraanthracene 1,1',2,2'-μ-(XB)₂-(*ortho*-carborane)₂ (X = Cl, Br, N₃, Me, Ph).

Further reactions of the synthesized halogen derivatives of the carboranyl analog of 9,10-diboraanthracene with trimethylsilylazide in toluene result in the azido derivative $1,1',2,2'\text{-}\mu\text{-(N}_3\text{B)}_2\text{-(ortho-carborane)}_2$ (Scheme 40, Figure 42) [74], while the reactions with the Grignard reagent RMgBr lead to the corresponding methyl and phenyl derivatives $1,1',2,2'\text{-}\mu\text{-(RB)}_2\text{-(ortho-carborane)}_2$ ($\text{R} = \text{Me, Ph}$) (Scheme 40, Figure 43) [73]. The Lewis acidity of the synthesized carboranyl analogs of 9,10-diboraanthracene $1,1',2,2'\text{-}\mu\text{-(XB)}_2\text{-(ortho-carborane)}_2$ decreases in the series $\text{Br} > \text{Cl} > \text{Ph} > \text{N}_3 > \text{Me}$ [73,74]. Their Lewis acidities are somewhat less than that of the corresponding derivatives of the bis(carboranyl) analog of 9-borfluorene but much greater than that of $\text{B(C}_6\text{F}_5)_3$ [49]. The azido derivative was found to form a stable complex with acetonitrile $1,1',2,2'\text{-}\mu\text{-(MeCN(N}_3\text{)B)}_2\text{-(ortho-carborane)}_2$ (Figure 42) [74].

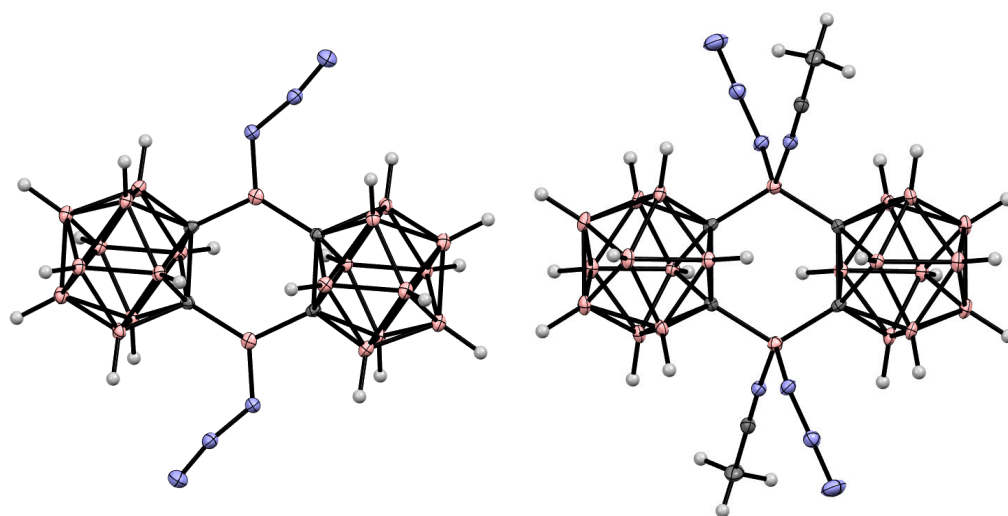


Figure 42. Single crystal structures of $1,1',2,2'\text{-}\mu\text{-(N}_3\text{B)}_2\text{-(ortho-carborane)}_2$ (left) and $1,1',2,2'\text{-}\mu\text{-(MeCN(N}_3\text{)B)}_2\text{-(ortho-carborane)}_2$ (right).

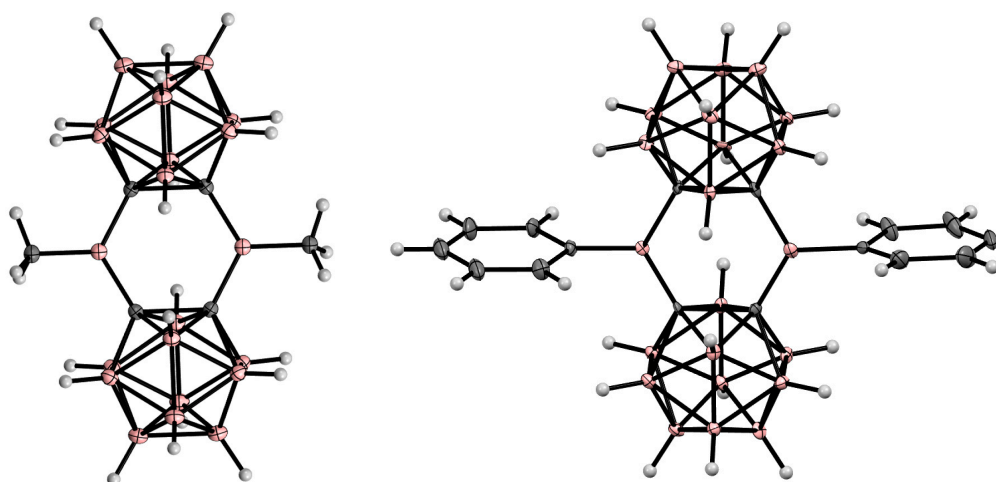


Figure 43. Single crystal structures of $1,1',2,2'\text{-}\mu\text{-(MeB)}_2\text{-(ortho-carborane)}_2$ (left) and $1,1',2,2'\text{-}\mu\text{-(PhB)}_2\text{-(ortho-carborane)}_2$ (right).

The reactions of $1,1',2,2'\text{-}\mu\text{-(XB)}_2\text{-(ortho-carborane)}_2$ with Et_3SiH in benzene result in the borane-silane adduct $(\text{Et}_3\text{Si})_2[1,1',2,2'\text{-}\mu\text{-(H}_2\text{B)}_2\text{-(ortho-carborane)}_2]$ (Figure 44) [73]. The bridging B-H bonds (1.33 Å) are notably longer than the terminal B-H bonds (1.09 Å) but are comparable to the bridging three-center two-electron B-H-B bonds in diborane derivatives, including species such as $[\text{HBMe}_2]_2$ (1.288 Å) [75].

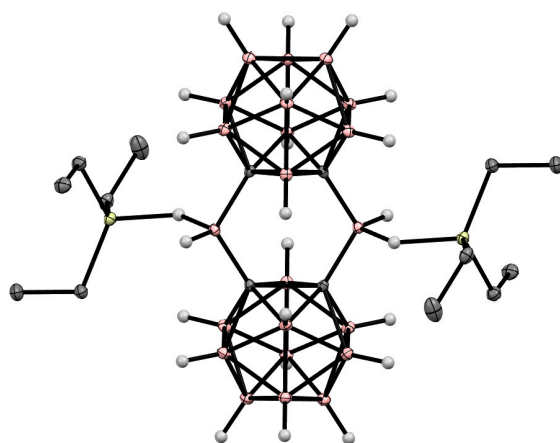
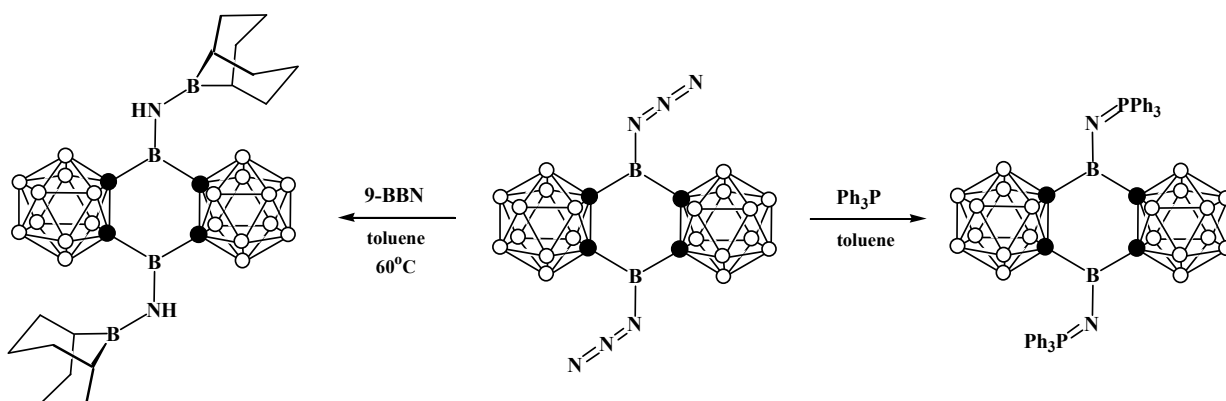


Figure 44. Single crystal structure of $(\text{Et}_3\text{Si})_2[1,1',2,2'\text{-}\mu\text{-(H}_2\text{B)}_2\text{-(ortho-carborane)}_2]$. The hydrogen atoms of the ethyl groups are omitted for clarity.

A number of addition reactions to the azido derivative $1,1',2,2'\text{-}\mu\text{-(N}_3\text{B)}_2\text{-(ortho-carborane)}_2$ have been studied. The reaction with triphenylphosphine in toluene results in the corresponding iminophosphorane $1,1',2,2'\text{-}\mu\text{-(Ph}_3\text{P=N=B)}_2\text{-(ortho-carborane)}_2$ as the Staudinger reaction product (Scheme 41, Figure 45) [74]. The Staudinger reaction is known to proceed via the nucleophilic addition of triarylphosphine to the terminal nitrogen atom of the organic azide, followed by the elimination of dinitrogen. The reaction with 9-borabicyclo [3.3.1]nonane (9-BBN) in toluene at 60°C produces the corresponding aminoborane $1,1',2,2'\text{-}\mu\text{-(9'''-BBN)-NHB)}_2\text{-(ortho-carborane)}_2$ (Scheme 41) [74].



Scheme 41. Reactions of $1,1',2,2'\text{-}\mu\text{-(N}_3\text{B)}_2\text{-(ortho-carborane)}_2$.

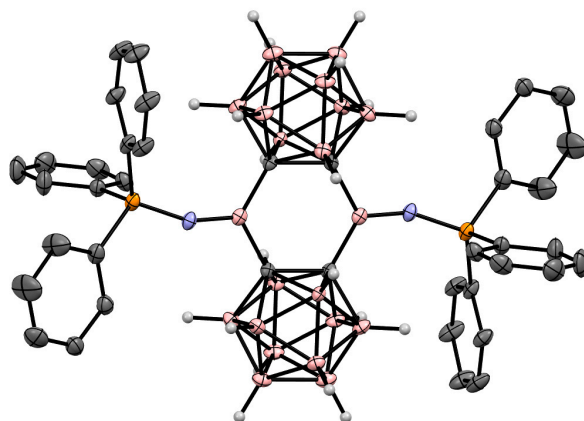


Figure 45. Single crystal structure of $1,1',2,2'\text{-}\mu\text{-(Ph}_3\text{P=N=B)}_2\text{-(ortho-carborane)}_2$. The hydrogen atoms of the phenyl groups are omitted for clarity.

Similarly, the reactions of the azido derivative with tertiary silanes R_3SiH in toluene at $60\text{ }^\circ\text{C}$ result in the corresponding silyl aminoborane $1,1',2,2'-\mu-(R_3SiNHB)_2-(ortho\text{-carborane})_2$ ($SiR_3 = SiEt_3, SiMe_2Ph$); however, if the same reactions are conducted at $-30\text{ }^\circ\text{C}$, it is possible to isolate the initial products of 1,2-addition of the silane $1,1',2,2'-\mu-(R_3Si(N_2)NHB)_2-(ortho\text{-carborane})_2$ as the reaction intermediate (Figure 46, Scheme 42). The complete solid-state conversion of $1,1',2,2'-\mu-(Et_3Si(N_2)NHB)_2-(ortho\text{-carborane})_2$ to $1,1',2,2'-\mu-(Et_3SiNHB)_2-(ortho\text{-carborane})_2$ with N_2 elaboration was observed within three days at $38\text{ }^\circ\text{C}$ (Figure 47, Scheme 42) [74].

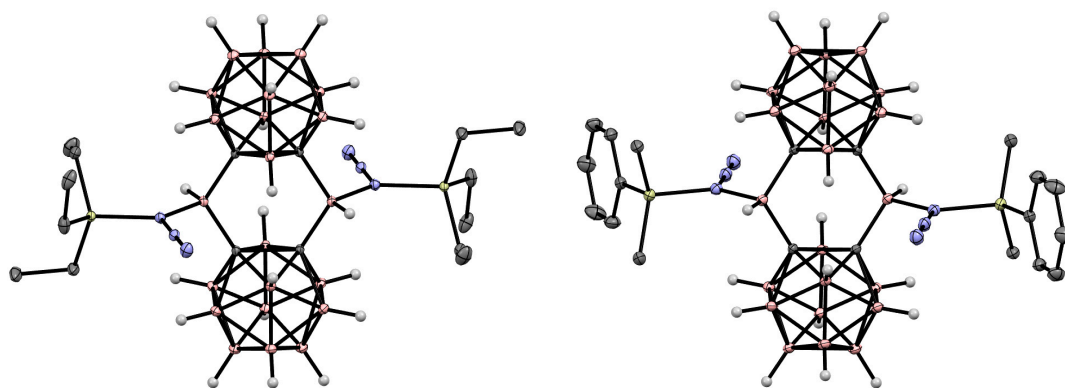
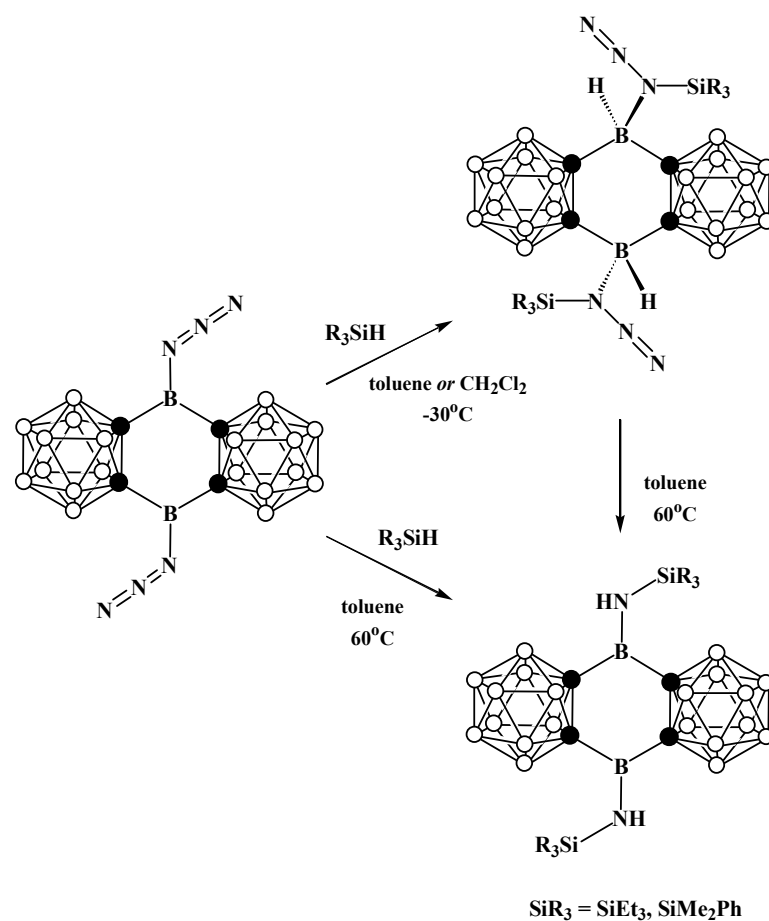


Figure 46. Single crystal structures of $1,1',2,2'-\mu-(Et_3Si(N_2)NHB)_2-(ortho\text{-carborane})_2$ (left) and $1,1',2,2'-\mu-(PhMe_2Si(N_2)NHB)_2-(ortho\text{-carborane})_2$ (right). Hydrogen atoms of alkyl and aryl groups are omitted for clarity.



Scheme 42. Reactions of $1,1',2,2'-\mu-(N_3B)_2-(ortho\text{-carborane})_2$.

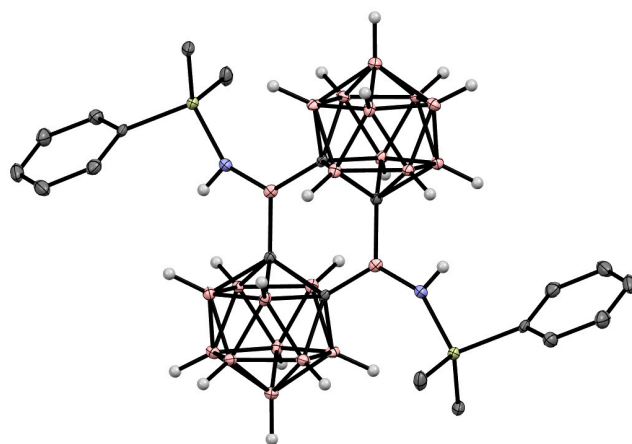
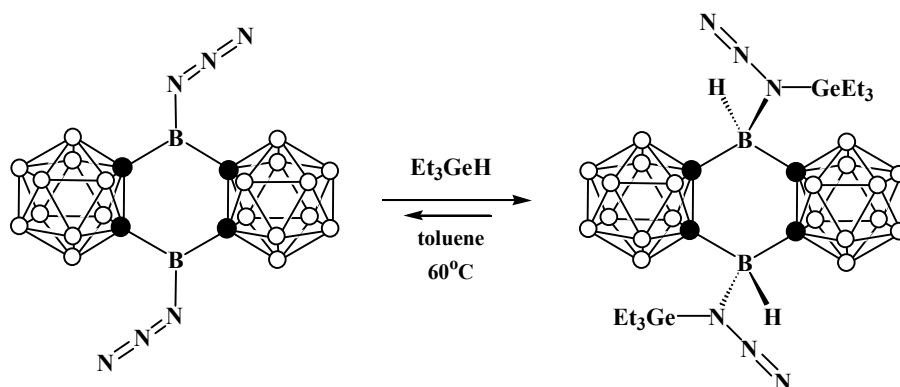


Figure 47. Single crystal structure of 1,1',2,2'-μ-(PhMe₂SiNHB)₂-(*ortho*-carborane)₂. The hydrogen atoms of the phenyl groups are omitted for clarity.

In contrast with the tertiary silane R₃SiH, the reaction of the azido derivative with Et₃GeH in toluene at 60 °C stops at the first stage with the formation of 1,1',2,2'-μ-(Et₃Ge(N₂)NHB)₂-(*ortho*-carborane)₂ (Scheme 43, Figure 48). Moreover, the reaction is reversible, and an increase in temperature promotes the dissociation of the addition product [74].



Scheme 43. Reaction of 1,1',2,2'-μ-(N₃B)₂-(*ortho*-carborane)₂ with Et₃GeH.

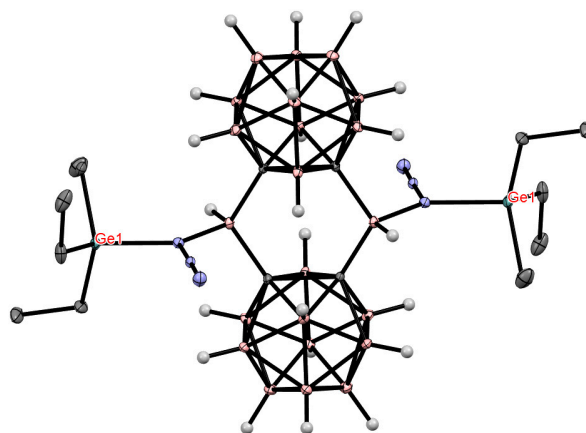
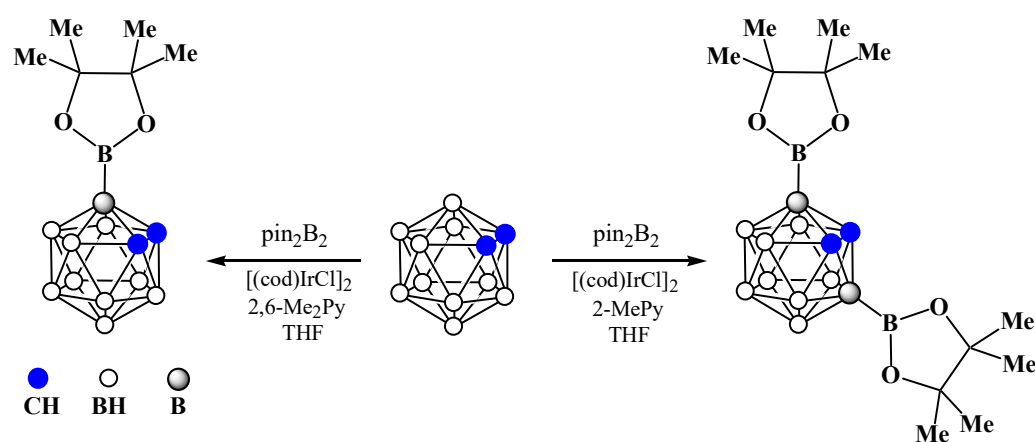


Figure 48. Single crystal structure of 1,1',2,2'-μ-(Et₃Ge(N₂)NHB)₂-(*ortho*-carborane)₂. Hydrogen atoms of the ethyl groups are omitted for clarity.

8. Carborane Derivatives with *exo*-Polyhedral Boron-Boron Bond

Carborane derivatives in which a tri- or four-coordinated boron atom is bonded to the carborane cage by an *exo*-polyhedral boron–boron bond have received much less attention than derivatives with a carbon–boron bond. Interest in such derivatives arose relatively recently and was caused by the development of new methods for the functionalization of carboranes through substitution at boron atoms.

The 3-pinacolborate derivative of *ortho*-carborane 3-pinB-1,2- $C_2B_{10}H_{11}$ was prepared by reacting the parent carborane with dipinacolborane B_2pin_2 in tetrahydrofuran in the presence of 3.5 mol.% [(cod)IrCl] $_2$ and 20 mol.% 2,6-lutidine. When using an excess of B_2pin_2 and 20 mol.% 2-picoline, the main reaction product is the 3,6-di(pinacolborate) derivative 3,6-(pinB) $_2$ -1,2- $C_2B_{10}H_{10}$ (Scheme 44, Figure 49). The same approach can be used for the synthesis of pinacolborate derivatives of *ortho*-carborane containing various substituents at the boron and carbon atoms of the carborane cage [75,76].



Scheme 44. Synthesis of 3-pinB-1,2- $C_2B_{10}H_{11}$ and 3,6-(pinB) $_2$ -1,2- $C_2B_{10}H_{10}$.

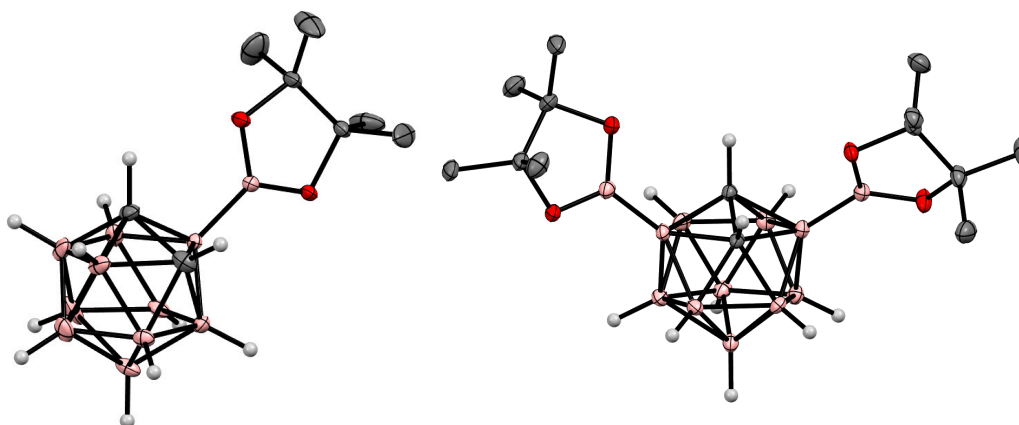
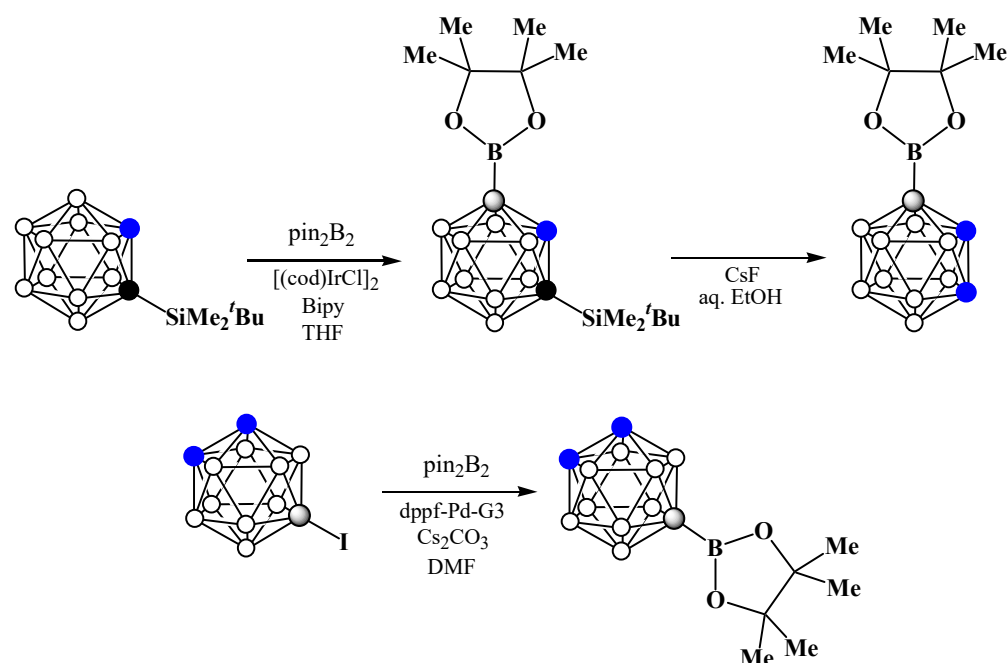


Figure 49. Single crystal structures of 3-pinB-1,2- $C_2B_{10}H_{11}$ (left) and 3,6-(pinB) $_2$ -1,2- $C_2B_{10}H_{10}$ (right). Hydrogen atoms of the methyl groups are omitted for clarity.

The 4-pinacolborate derivative of *ortho*-carborane 4-pinB-1,2- $C_2B_{10}H_{11}$ was prepared by the iridium-catalyzed borylation of 1-*t*-BuMe $_2$ Si-*ortho*-carborane with B_2pin_2 in tetrahydrofuran in the presence of 2,2'-bipyridine, followed by removal of the silyl group with CsF (Scheme 45, Figure 50) [75]. The 9-pinacolborate derivative of *ortho*-carborane 9-pinB-1,2- $C_2B_{10}H_{11}$ was prepared by the reaction of 9-iodo-*ortho*-carborane with B_2pin_2 in *N,N*-dimethylformamide in the presence of 5 mol.% dppf-Pd-G3 pre-catalyst (Scheme 45, Figure 50) [77].



Scheme 45. Synthesis of 4-pinB-1,2-C₂B₁₀H₁₁ and 9-pinB-1,2-C₂B₁₀H₁₁.

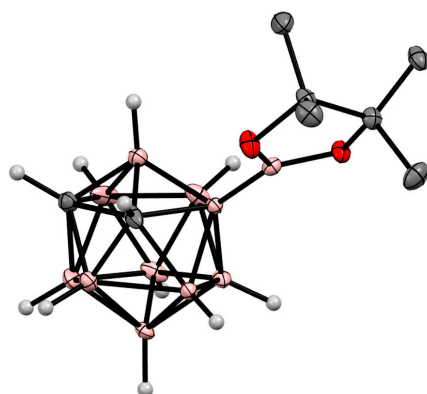
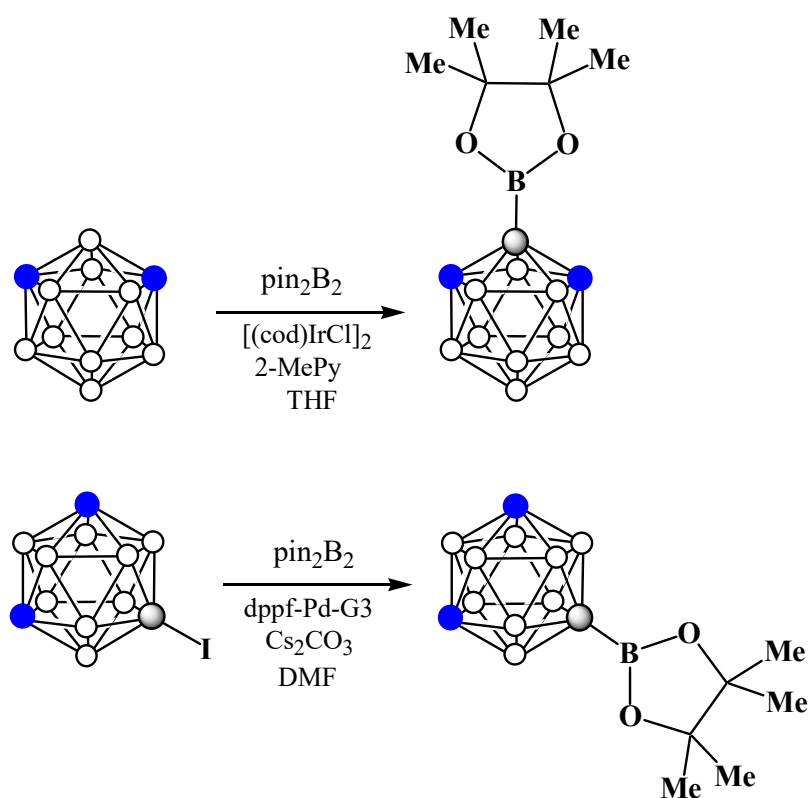


Figure 50. Single crystal structure of 4-pinB-1,2-C₂B₁₀H₁₁. Hydrogen atoms of the methyl groups are omitted for clarity.

The picoline protection in 3-pinB-1,2-C₂B₁₀H₁₁, 9-pinB-1,2-C₂B₁₀H₁₁, and 3,6-(pinB)₂-1,2-C₂B₁₀H₁₀ can be easily removed by treatment with HCl in ethanol or diethanolamine to give the corresponding boronic acids 3-(HO)₂B-1,2-C₂B₁₀H₁₁, 9-(HO)₂B-1,2-C₂B₁₀H₁₁, and 3,6-((OH)₂B)₂-1,2-C₂B₁₀H₁₀ [75,77].

The picolinate groups in 3-pinB-1,2-C₂B₁₀H₁₁ and 3,6-(pinB)₂-1,2-C₂B₁₀H₁₀ can be replaced by a wide variety of functional groups, including amine [75], acetate [75,76], azide [75], halogens [76], allyl [75], and aryl [75] groups.

The 2-pinacolborate derivative of *meta*-carborane 2-pinB-1,7-C₂B₁₀H₁₁ was prepared by the reaction of *meta*-carborane with dipinacolborane B₂pin₂ in tetrahydrofuran in the presence of 3.5 mol.% [(cod)IrCl]₂ and 20 mol.% 2-picoline (Scheme 46, Figure 51) [75]. The 9-pinacolborate derivative of *meta*-carborane 9-pinB-1,7-C₂B₁₀H₁₁ was prepared by the reaction of 9-iodo-*ortho*-carborane with B₂pin₂ in *N,N*-dimethylformamide in the presence of 5 mol.% dppe-Pd-G3 pre-catalyst (Scheme 46, Figure 51) [77].



Scheme 46. Synthesis of 2-pinB-1,7-C₂B₁₀H₁₁ and 9-pinB-1,7-C₂B₁₀H₁₁.

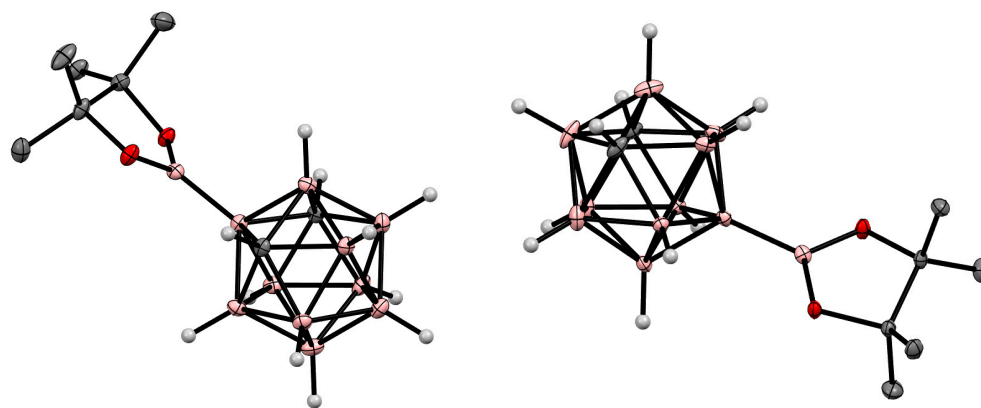


Figure 51. Single crystal structures of 2-pinB-1,7-C₂B₁₀H₁₀ (**left**) and 9-pinB-1,7-C₂B₁₀H₁₀ (**right**). Hydrogen atoms of the methyl groups are omitted for clarity.

The picoline protection in 9-pinB-1,7-C₂B₁₀H₁₁ can be removed by treatment with HCl in ethanol of the corresponding boronic acid 9-(HO)₂B-1,7-C₂B₁₀H₁₁. The reaction of 9-pinB-1,7-C₂B₁₀H₁₁ with potassium fluoride (KF) in a mixture of acetonitrile and methanol results in K[9-F₃B-1,7-C₂B₁₀H₁₁]. Some reactions of the synthesized carboranyl boronic acid and tetrafluoroborate were described [77].

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