CHEMISTRY OF *closo*-DODECABORATE ANION $[B_{12}H_{12}]^{2-}$: A REVIEW

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We have the pleasure to dedicate this paper to Jaromír Plešek on the occasion of his 75th birthday in recognition of his outstanding contribution to cage-boron chemistry.

Synthesis and chemical properties of the *closo*-dodecaborate anion $[B_{12}H_{12}]^{2-}$ and its derivatives are reviewed. Attention is also paid to potential applications of the *closo*-dodecaborate derivatives with emphasis on medical applications. A review with 325 references.
Keywords: *closo*-Dodecaborate; Synthesis; Derivatives; Applications.

1. INTRODUCTION

After the discovery of the first boranes by Alfred Stock in 1912, these compounds were considered for several decades as very exotic and to be of only academic interest[1]. The boom in borane chemistry started at the end of 1940's when some of them, namely pentaborane B_5H_9 and decaborane $B_{10}H_{14}$, were believed to be most powerful rocket fuels superior to the avail-

able hydrocarbon fuels. More than 100 million dollars in the United States (Project ZIP), along with a similar number of millions of rubles in the Soviet Union, were invested in the research and development of these materials. Although this idea was abandoned later, the synthesis of these boranes on sizable scale was worked on and great efforts of many groups of chemists created a firm basis and gave a mighty impulse for the future development of borane chemistry. The real brain break in understanding borane chemistry was the concept of three-center two-electron bonding proposed by Lipscomb[2,3] followed by the classification of the main types of deltahedra, which are the key structure units in polyhedral boron structures, by Williams[4,5]. As a result, fifty years of intensive investigations of boranes and their derivatives have shown that this class of compounds is extremely rich and the capacity of boron to form self-bonded complex molecular networks is as extensive as of any element in the nature except for carbon.

2. SYNTHESIS AND PROPERTIES OF THE $[B_{12}H_{12}]^{2-}$ ANION

Among many thousands of known boron hydride compounds, one of central places belongs to the dodecahydro-*closo*-dodecaborate anion $[B_{12}H_{12}]^{2-}$. It has a structure of a regular icosahedron and looks as incarnation of the highest simplicity and the highest symmetry (Fig. 1). Its chemistry is not such amazing as the chemistry of metallaboranes and metallacarboranes, but it is impossible to imagine borane chemistry without this species. The history of the dodecahydro-*closo*-dodecaborate anion started in 1955 when Longuet-Higgins and Roberts[6] on the basis of MO-LCAO calculations predicted that icosahedral borane would be stable only as dianion $[B_{12}H_{12}]^{2-}$.

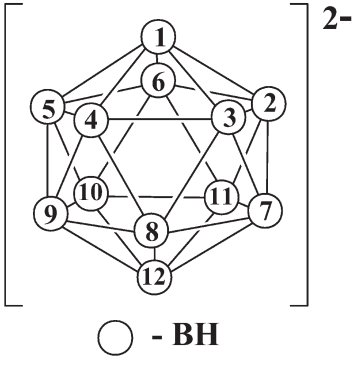


FIG. 1
Structure and numbering of atoms in the $[B_{12}H_{12}]^{2-}$ anion

This prediction was verified experimentally by Hawthorne and Pitochelli in 1960 when the *closo*-dodecaborate anion was prepared for the first time as a side-product of the reaction of 2-iododecaborane and triethylamine in refluxing benzene[7]. The isolated yield of $[B_{12}H_{12}]^{2-}$ in this reaction was less than 4%. However a few years later several high-yield methods of synthesis of the $[B_{12}H_{12}]^{2-}$ anion were proposed by different research groups[8–12].

At present there are numerous preparative methods for the synthesis of the $[B_{12}H_{12}]^{2-}$ anion. The first group of the methods includes reactions of various boranes with $H_3B{\cdot}L$ complexes (L is Lewis base, usually NEt_3). Triethylammonium *closo*-dodecaborate is the reaction product. The reactions of triethylamine-borane with diborane at 180 °C [8,9] and that of triethylamine-borane with pentaborane B_5H_9 at 125 °C [9] both produce the $[B_{12}H_{12}]^{2-}$ anion in 90% yield. The reaction of the coupled pentaborane dimer 1:2′-$[B_5H_8]_2$ with triethylamine-borane in decane at 100 °C produces the $[B_{12}H_{12}]^{2-}$ anion in 59% yield[13]. Availability of pentaborane makes these reaction sequencies attractive routes.

However, reactions employing decaborane(14) seems to be more convenient, especially in laboratory practice. One of the most convenient methods of synthesis of the *closo*-dodecaborate anion is pyrolysis of triethylamine-borane with decaborane(14) in ultrasene at 190 °C giving the desired product in 92% yield[9,10,14] (Scheme 1).

$$B_{10}H_{14} + 2\,Et_3N{\cdot}BH_3 \xrightarrow{190\ ^oC} (Et_3NH)_2[B_{12}H_{12}] + 3\,H$$

SCHEME 1

The second group of the methods consists in interaction of alkali metal tetrahydroborates with boranes or $H_3B{\cdot}L$ complexes. The reaction of $NaBH_4$ with diborane at 180 °C in the presence of triethylamine gives the *closo*-dodecaborate anion in 80% yield[8,9]. Another convenient and widely used in laboratory practice method of synthesis the $[B_{12}H_{12}]^{2-}$ anion is the reaction of sodium tetrahydroborate with decaborane in refluxing diglyme giving the target product in 91% yield[11,15,16] (Scheme 2).

$$B_{10}H_{14} + 2\,NaBH_4 \xrightarrow[\text{diglyme}]{160\ ^oC} Na_2[B_{12}H_{12}] + 5\,H_2$$

SCHEME 2

The reactions of $NaBH_4$ or KBH_4 with trimethyl- and triethylamine-borane in high-boiling alkanes (dodecane, hexadecane) at 200–250 °C result in the *closo*-dodecaborate anion in up to 95% yield and give the possibility to avoid highly toxic decaborane as starting material[17–19]. Note

however that this approach was described very briefly and did not find wide application.

Another group of methods of the $[B_{12}H_{12}]^{2-}$ anion synthesis includes pyrolytic transformations of various boron hydrides. Pyrolysis of $(Et_4N)BH_4$ gives a mixture of $(Et_4N)_2[B_{10}H_{10}]$ and $(Et_4N)_2[B_{12}H_{12}]$ as well as some $(Et_4N)_2[B_9H_9]$ and $(Et_4N)[B_{11}H_{14}]$. The product ratio depends strongly on the pyrolysis temperature. The formation of $(Et_4N)_2[B_{10}H_{10}]$ was predominant at 185 °C [20,21]. However, when the pyrolysis was performed in the presence of triethylamine-borane, the *closo*-dodecaborate anion was the main product[22]. Pure $(Et_4N)_2[B_{12}H_{12}]$ can be obtained by chromatographic separation of a $(Et_4N)_2[B_{10}H_{10}]$–$(Et_4N)_2[B_{12}H_{12}]$ mixture[23] or by reacting this mixture with triethylamine-borane[22].

The study of pyrolysis of various octahydrotriborates revealed that the direction of the reaction and the yield of *closo*-borate anions depend strongly on the nature of the cation, the temperature, and the solvent used. The synthesis of the *closo*-dodecaborate anion by pyrolysis of $Na[B_3H_8]$ was proposed for the first time in early of 1960's [12], and improved later giving the desired product in the yield up to 90% [24,25]. Pyrolysis of $K[B_3H_8]$ at 185 °C gave a mixture of the $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ anions as well as some $[B_{11}H_{14}]^-$ [20], whereas increasing the temperature above 200 °C leads mainly to $[B_9H_9]^{2-}$ and $[B_{12}H_{12}]^{2-}$ [26]. Pyrolysis of $Rb[B_3H_8]$ above 200 °C gave a mixture of the $[B_9H_9]^{2-}$, $[B_{10}H_{10}]^{2-}$, and $[B_{12}H_{12}]^{2-}$ anions[26]. Pyrolysis of $Cs[B_3H_8]$ at 185 °C gave mainly $[B_{10}H_{10}]^{2-}$ and $[B_{11}H_{14}]^-$ [20], whereas at 230 °C $[B_9H_9]^{2-}$, $[B_{10}H_{10}]^{2-}$, and $[B_{12}H_{12}]^{2-}$ formed[26]. Thermal decomposition of magnesium, calcium, and strontium octahydrotriborates produce the $[B_{12}H_{12}]^{2-}$ anion in reasonable yields[27]. Pyrolysis of tetraalkylammonium octahydroborates $(R_4N)[B_3H_8]$ (R = Me_4N, Et_4N, Pr_4N, Bu_4N) gives $[B_{12}H_{12}]^{2-}$ as the sole product only in the case of R = Pr, whereas with R = Et, two major components are $[B_9H_9]^{2-}$ and $[B_{10}H_{10}]^{2-}$ [20,28]. Recently reported[29] an unprecedented formation of the $[B_{12}H_{12}]^{2-}$ anion in the treatment of the octahydrotriborate complex $(Bu_4N)[W(B_3H_8)Br(\equiv CC_6H_3Me_2)_2(CO)_2]$ with butyllithium at –78 °C also should be mentioned here despite it is not pyrolytic process. It should be noted that this group of the methods requare pre-synthesis of the octahydrotriborate anion, and the yield of the goal product, especially in the solid state pyrolytic processes, depends strongly on design of the apparatus used.

Thermal decomposition of the 1,4-diazabicyclo[2.2.2]octane–$2BH_3$ complex in inert atmosphere at 350–450 °C was shown to result in the formation of the corresponding *closo*-dodecaborate salt[30], however this process can not be considered as preparative method.

A few attempts to realize synthesis of the $[B_{12}H_{12}]^{2-}$ anion starting from other than boron hydride reagents were described. The reaction of solid NaH with a BCl_3–H_2 mixture at 250–350 °C was found to give $NaBH_4$ and $Na_2[B_{12}H_{12}]$; however, the reaction produced also considerable amounts of undesirable chloro derivatives $Na_2[B_{12}H_{12-n}Cl_n]$ (n = 1–6) as side products. Using $NaBH_4$ instead of NaH, the *closo*-borate yield can be increased up to 80%, but the chloro derivatives are always present in the product[31].

Another approach consists in the use of widely available boron raw materials, such as boric acid and sodium borates in combination with various reducing agents[32]. More recently a solid-state synthesis of the *closo*-dodecaborate anion from potassium tetrafluoroborate and calcium hydride was proposed[33]. Further development of this approach can give the *closo*-dodecaborate anion in large amount at reasonable price and open the door for its practical application.

It should be noted that the formation of the *closo*-dodecaborate anion, which is the most stable among the polyhedral boron hydrides, always takes place in the course of synthesis of other anions of the $[B_nH_n]^{2-}$ series, such as the *closo*-hexaborate $[B_6H_6]^{2-}$ [34–36] and the *closo*-nonaborate $[B_9H_9]^{2-}$ [26] anions. In the case of the $[B_6H_6]^{2-}$ anion, $[B_{12}H_{12}]^{2-}$ is present in amounts exceeding the amount of the desired product and can be easily recovered[35,36]. Similarly, the *closo*-dodecaborate anion can be prepared by the cage-expansion reactions of other *closo*-borates such as $[B_{10}H_{10}]^{2-}$ [22] and $[B_{11}H_{11}]^{2-}$ [37] with triethylamine-borane.

At present, a number of salts of the *closo*-dodecaborate anion with various metal cations (lithium[15,16], sodium[15,16,38,39], potassium[15,16,38], rubidium[15,16], cesium[15,16,38–40], beryllium[41], magnesium[41,42], calcium[41–43], strontium[41–43], barium[38,41–43], cadmium[41], zinc[41], aluminum[38], scandium[44], yttrium[44], rare earth metals[38,44], zirconium[45], hafnium[45], uranium[46], copper(I)[38,47], silver(I)[48], thallium(I)[38,49]) and ammonium cations (NH_4^+ [50], $Me_2NH_2^+$ [50], Me_3NH^+ [51], Me_4N^+ [38,50], $Et_2NH_2^+$ [50], Et_3NH^+ [38,51], Et_4N^+ [50], $Bu_2NH_2^+$ [50], Bu_3NH^+ [51], Bu_4N^+ [50], $hexyl_4N^+$ [38], $(2\text{-}Py)_2NH_2^+$ [52], $H_2NNH_3^+$ [53], H_2en^{2+} [54], $HN(C_2H_4)_3NH^{2+}$ [30], $Hbipy^+$ [55]), as well as the trimethylsulfonium[38], tetraphenylphosphonium[56], and guanidinium[47] salts have been described.

The solubility in the $M_2[B_{12}H_{12}]$–MCl–H_2O (M = K, Cs, Rb)[57], $K_2[B_{12}H_{12}]$–KBr–H_2O [58], $Cs_2[B_{12}H_{12}]$–CsI–H_2O [59], $Cs_2[B_{12}H_{12}]$–$CsNO_3$–H_2O [60], and $Cs_2[B_{12}H_{12}]$–Cs_2SO_4–H_2O [61] systems at 25 °C have been investigated. It was found that alkali metal *closo*-dodecaborates form mixed salts with the corresponding halides, $M_2[B_{12}H_{12}]\cdot MX$ (M = K, X = Br, I; M = Rb, X = Cl, Br, I; M = Cs, X = Cl, Br, I)[38,62–64]. It was shown that the formation of the mixed salts is determined by the sum of the ionic diameters of the metal

and halogen, which should be more than 6.46 Å [64]. In addition to the mixed salts of *closo*-dodecaborates of alkali metals and thallium with the corresponding nitrates $M_2[B_{12}H_{12}]\cdot MNO_3$ (M = Rb, Cs, Tl) and tetrahydroborates $M_2[B_{12}H_{12}]\cdot MBH_4$ (M = K, Rb, Cs, Tl), were prepared[49,65,66]. Synthesis of the 1 : 2 complexes of $(R_4N)_2[B_{12}H_{12}]$ (R = Me, Et, Bu) with $Al(BH_4)_3$ was also described[67].

In addition, the syntheses of a number of compounds of the *closo*-dodecaborate anion with complex nickel[38,53,68–77], cobalt[38,69–74,78], iron[69,79–88], chromium[38], manganese[70], platinum[69], palladium[69,89], ruthenium[90], lead[53,91–93], copper[70,94–95], mercury[70], cadmium[70], zinc[70], rare earth metals[96–104], and uranium[105–109] cations have been described. The $[B_{12}H_{12}]^{2-}$ anion ranks among weakly coordinating anions[110,111] and serves as an outer-sphere anion in the absolute majority of these complexes. The rare examples where the *closo*-dodecaborate anion acts as inner-sphere ligand are $Me_4N[CuB_{12}H_{12}]$ [94,95] and $[(PhMe_2P)_3RuB_{12}H_{12}]$ [90]. Another example of coordination of $[B_{12}H_{12}]^{2-}$ to the metal atoms is its complex with cyclic trimeric tetrafluoro-1,2-phenylenemercury $(Bu_4N)_2\{[(1,2\text{-}C_6F_4Hg)_3]_2[B_{12}H_{12}]\}$, where the *closo*-dodecaborate anion is coordinated to all six mercury atoms of two molecules of the Lewis acid[112] (Fig. 2). It was shown that the weakly

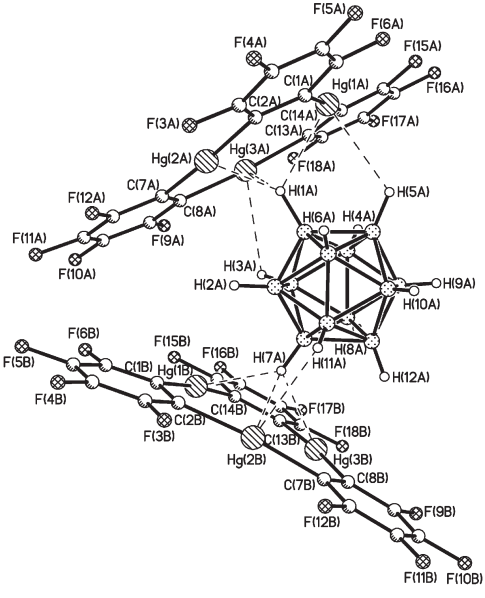


FIG. 2
Crystal structure of $(Bu_4N)_2\{[B_{12}H_{12}][(C_6F_4Hg)_3]_2\}$

coordinating ability of the *closo*-dodecaborate anion can be used to prepare salts with labile double-charged cations[113].

The crystal structures of $Na_2[B_{12}H_{12}]\cdot 4H_2O$ [114,115], $K_2[B_{12}H_{12}]$ [116], $Rb_2[B_{12}H_{12}]$ [117], $Cs_2[B_{12}H_{12}]$ [118], $[Ca(H_2O)_7][B_{12}H_{12}]$ [119,120], $[Sr(H_2O)_7][B_{12}H_{12}]$ [121], $[Sr(H_2O)_8][B_{12}H_{12}]$ [120], $[Ba(H_2O)_6][B_{12}H_{12}]$ [120,122], $[UO_2(H_2O)_5][B_{12}H_{12}]\cdot 6H_2O$ [123], $(Me_3NH)_2[B_{12}H_{12}]\cdot 2DMF$ [124], $(Me_4N)_2[B_{12}H_{12}]$ [125], $(Me_4N)_2[B_{12}H_{12}]\cdot MeCN$ [125], $(Et_3NH)_2[B_{12}H_{12}]$ [126], $(Bu_4N)_2[B_{12}H_{12}]$ [29], $K_2[B_{12}H_{12}]\cdot KBr$ [64], $[Ni(en)_3][B_{12}H_{12}]$ [127], $(\eta^5\text{-}C_5H_4CH_2NHMe_2)]_2[B_{12}H_{12}]$ [129], $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_4\text{-}1,2\text{-}(CH_2)_4)]_2[B_{12}H_{12}]$ [130], $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_5CH(CH_3)_2]_2[B_{12}H_{12}]$ [131], $[Pb(bipy)_2][B_{12}H_{12}]$ [91], $[Pb(bipy)(DMF)][B_{12}H_{12}]$ [92], $[(DIME)Yb(CH_3CN)_5][B_{12}H_{12}]$ [96], and $(Bu_4N)_2\{[(1,2\text{-}C_6F_4Hg)_3]_2[B_{12}H_{12}]\}$ [112] have been determined by the single-crystal X-ray diffraction method.

The $[B_{12}H_{12}]^{2-}$ anion is stable to heating in strong aqueous sodium hydroxide and 3 M hydrochloric acid at 95 °C. The acid form $(H_3O)_2[B_{12}H_{12}]\cdot xH_2O$ displays properties of a strong acid which is comparable in strength with sulfuric acid. The *closo*-dodecaborate salts with thermally stable cations have also high thermal stability. For example, $Cs_2[B_{12}H_{12}]$ does not change under heating at 810 °C [38]. The electrochemical study of $(Et_4N)_2[B_{12}H_{12}]$ in acetonitrile revealed that the *closo*-dodecaborate anion undergoes one-electron oxidation at $E_{1/2}$ = + 1.50 V (*vs* SCE) giving anion $[B_{24}H_{23}]^{3-}$ as the product[132]. The high stability of the *closo*-dodecaborate anion can be explained by the three-dimensional aromatic character of the bonding in the B_{12} cage[133,134].

3. DERIVATIVES WITH BORON–HALOGEN BOND

In accordance with its aromatic character, the chemistry of the $[B_{12}H_{12}]^{2-}$ anion features mainly aromatic substitution reactions. Halogenations of the *closo*-dodecaborate anion were studied repeatedly by several research groups. Fluorination of the *closo*-dodecaborate anion with hydrogen fluoride gives derivatives with different substitution degrees $[B_{12}H_{12-x}F_x]^{2-}$, x = 1–12 [135–142]. The substitution degree depends on the molar ratio of the reagents and the reaction temperature. The structures of the fluoro derivatives prepared were determined by NMR spectrocopy and X-ray diffraction analysis and the substitution sequence was established. It was shown that a fluorine atom acts as deactivating *meta*-directing substituent. A nucleophilic aromatic substitution mechanism was proposed for the fluorination in liquid hydrogen fluoride[139], however more probably that this reaction proceeds *via* electrophile-induced nucleophilic substitution mechanism. The experimental data were found to be in good agreement with the results

of the semiempirical MNDO calculations of the different isomers of $[B_{12}H_{12-x}F_x]^{2-}$ [139]. The monofluoro derivative $[B_{12}H_{11}F]^{2-}$ was also prepared by heating $K_2[B_{12}H_{12}]$ in KHF_2 melt at 290 °C [141] and by reaction of $Cs_2[B_{12}H_{12}]$ with 1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) at room temperature in aqueous dimethylformamide[143a]. The perfluoro derivative can be prepared easily by treatment of solution of $[1,2,8,10\text{-}B_{12}H_8F_4]^{2-}$ in liquid hydrogen fluoride with fluorine gas at room temperature[143b]. The crystal structures of $K_2[1,7\text{-}B_{12}H_{10}F_2]\cdot H_2O$, $Cs_2[1,2,4,5,8,9,11\text{-}B_{12}H_5F_7]\cdot H_2O$, $Cs_2[1,2,4,5,7,8,9,11\text{-}B_{12}H_4F_8]\cdot 2H_2O$, $0.4K_2[B_{12}H_4F_8]\cdot 0.6K_2[B_{12}H_3F_9]\cdot 2H_2O$, and $Cs_2[B_{12}F_{12}]\cdot H_2O$ were determined[139,141,144].

The monochloro derivative $[B_{12}H_{11}Cl]^{2-}$ can be prepared by the reaction of $(H_3O)_2[B_{12}H_{12}]\cdot nH_2O$ with anhydrous hydrogen chloride at 85 °C [135] as well as by the reaction of the tetrabutylammonium salt with dichloromethane in the presence of trifluoroacetic acid[145], or by the treatment of the sodium salt in water with $H[AuCl_4]$ [135]. Chlorination of $[B_{12}H_{12}]^{2-}$ with chlorine in water gives a mixture of $[B_{12}H_{11}Cl]^{2-}$, $[1,2\text{-}B_{12}H_{10}Cl_2]^{2-}$, $[1,7\text{-}B_{12}H_{10}Cl_2]^{2-}$, $[1,2,3\text{-}B_{12}H_9Cl_3]^{2-}$, and $[1,7,9\text{-}B_{12}H_9Cl_3]^{2-}$ derivatives[146,147], which can be separated by chromatography on 2-hydroxyethyl methacrylate gels[148]. The reaction of $(H_3O)_2[B_{12}H_{12}]\cdot nH_2O$ with chlorine in water at 0 °C gives $[B_{12}H_6Cl_6]^{2-}$ [135]. The perchloro derivative $[B_{12}Cl_{12}]^{2-}$ has been prepared by the treatment of $[B_{12}H_{12}]^{2-}$ with chlorine at 85 °C in acidic aqueous solution[149,150] or at 150 °C in water[135,151]. The crystal structure of $[1,1'\text{-}CH_2(C_5H_5N)_2][B_{12}H_{11}Cl]\cdot 2(CH_3)_2SO$ was determined[145].

The monobromo derivative $[B_{12}H_{11}Br]^{2-}$ was prepared by the reaction of $[B_{12}H_{12}]^{2-}$ with dibromomethane in the presence of trifluoroacetic acid[145]. Treatment of $[B_{12}H_{12}]^{2-}$ with bromine in a water–tetrachloromethane mixture gave a mixture of $[B_{12}H_{11}Br]^{2-}$, $[1,2\text{-}B_{12}H_{10}Br_2]^{2-}$, and $[1,7\text{-}B_{12}H_{10}Br_2]^{2-}$ derivatives[146,147], which can be separated by chromatography on 2-hydroxyethyl methacrylate gels[148]. The reaction of $[B_{12}H_{12}]^{2-}$ with bromine in aqueous methanol at –10 °C was shown to give a mixture of tetra- and pentabromo derivatives[152], whereas the same reaction at 5 °C gives the hexabromo derivative $[B_{12}H_6Br_6]^{2-}$ [135]. Heating $(H_3O)_2[B_{12}H_{12}]\cdot nH_2O$ with bromine in water at 80–90 °C results in the decabromo derivative $[B_{12}H_2Br_{10}]^{2-}$ [135]. The perbromo derivative $[B_{12}Br_{12}]^{2-}$ was prepared by the treatment of $[B_{12}H_6Br_6]^{2-}$ with bromine in the presence of chlorine in 50% aqueous methanol[135,151]. The crystal structure of $[1,1'\text{-}CH_2(C_5H_5N)_2]$-$[B_{12}H_{11}Br]$ was determined[145].

The monoiodo derivative $[B_{12}H_{11}I]^{2-}$ was prepared by the reaction of $[B_{12}H_{12}]^{2-}$ with 1 equivalent of iodine in aqueous methanol at 0 °C [135] and by the reaction with diiodomethane in the presence of trifluoroacetic acid[145]. The use of 2 equivalents of iodine results in the disubstituted product which is mainly 1,7-isomer[135]. The periodo derivative $[B_{12}I_{12}]^{2-}$ was prepared by refluxing $Na_2[B_{12}H_{12}]$ with iodine monochloride in 1,1,2,2-tetrachloroethane or nonyl alcohol[135,151]. The crystal structures of $[1,1'\text{-}CH_2(C_5H_5N)_2][B_{12}H_{11}I]$ [145] and $Cs_2[B_{12}I_{12}]\cdot 2MeCN$ [153] were determined.

Acid properties of the perhalogenated *closo*-dodecaborate acids $(H_3O)_2[B_{12}X_{12}]\cdot nH_2O$ (X = Cl, Br, I) were investigated and was shown that like $(H_3O)_2[B_{12}H_{12}]\cdot nH_2O$ they are strong acids[151,154–156].

A series of mixed halogen derivatives of the *closo*-dodecaborate anion have been prepared by straightforward combinations of the halogenation reactions[135] and photoinduced nucleophilic substitution in perhalogenated *closo*-dodecaborates[152].

A number of complexes of halogenated *closo*-dodecaborates with various metals have been synthesized[68,105,106,113,157–161]. In all the cases halogenated *closo*-dodecaborates serve as outer-sphere anions.

4. DERIVATIVES WITH BORON–CARBON BOND

At present a large number of derivatives of the $[B_{12}H_{12}]^{2-}$ anion with boron–carbon bond were described. Probably, the most interesting of the *closo*-dodecaborate derivatives with boron–carbon bond are carbonyl derivatives. The reaction of the $[B_{12}H_{12}]^{2-}$ acid with carbon monoxide at 1 000 atm and 130 °C in the presence of $[Co_2(CO)_8]$ as a catalyst gives almost a quantitative conversion to a mixture of mono- and disubstituted carbonyl derivatives, $[B_{12}H_{11}CO]^-$ (50%), $[1,12\text{-}B_{12}H_{10}(CO)_2]$ (40%), and $[1,7\text{-}B_{12}H_{10}(CO)_2]$ [162,163]. The 1,7- and 1,12-isomers can be separated by fractional crystallization from water as cesium salts of the corresponding carboxylic acid derivatives[163] (Scheme 3).

$$[B_{12}H_{12}]^{2-} + CO \xrightarrow[1\,000\ atm,\ 130\ ^oC]{[Co_2(CO)_8]} [B_{12}H_{11}CO]^- + [1,7\text{-}B_{12}H_{10}(CO)_2] + [1,12\text{-}B_{12}H_{10}(CO)_2]$$

SCHEME 3

The neutral carbonyl derivatives are colorless, easily subliming hygroscopic compounds, which are highly soluble in both polar and non-polar solvents[163]. In aqueous solutions, an equlibrium between the carbonyl and carboxylic forms was proposed[162] (Scheme 4).

$$[B_{12}H_{10}(CO)_2] \underset{}{\overset{H_2O}{\rightleftharpoons}} (H_3O)^+[B_{12}H_{10}(CO)(COOH)]^- \overset{H_2O}{\rightleftharpoons} (H_3O)_2^+[B_{12}H_{10}(COOH)_2]^{2-} \xrightarrow{OH^-} [B_{12}H_{10}(COO)_2]^{4-}$$

SCHEME 4

It should be noted that the predominant formation of [1,12-$B_{12}H_{10}(CO)_2$] is very rare example of *para*-substitution in the $[B_{12}H_{12}]^{2-}$ anion. It can be explained by significant redistribution of electron density in the boron cage after introduction of the first carbonyl group resulting in the most positive charge on the antipodal boron atom. This conclusion is supported by the ^{11}B NMR spectrum of $[B_{12}H_{11}CO]^-$ demonstrating uniquely large high- and low-field shifts for signals corresponding to the substituted and antipodal boron atoms, respectively[175].

The structure of [1,12-$B_{12}H_{10}(CO)_2$] (Fig. 3) was determined by the method of X-ray diffraction[164]. The molecule has D_{5d} symmetry with average B–B distances: apical–equatorial 1.768 Å, equatorial–equatorial 1.824 Å, and equatorial–equatorial′ 1.779 Å. The B–CO fragment is nearly linear (B–C–O 179.18°; B–C 1.543 Å, C–O 1.119 Å). It should be noted that the experimentally determined bond lengths significantly differ from those based on the MNDO calculations[165]. The presence of the carbonyl groups considerably disturbs the charge distribution in the boron hydride system. The BH groups in [1,12-$B_{12}H_{10}(CO)_2$] have a charge equal to –0.04 (in comparison with –0.17 for $[B_{12}H_{12}]^{2-}$ [166]), and the charge of the BCO fragment is distributed in the following manner: B, –0.32; C, +0.58; O, –0.06 [165]. This results correlate well with another calculation giving an overall charge for the CO group +0.4 [164].

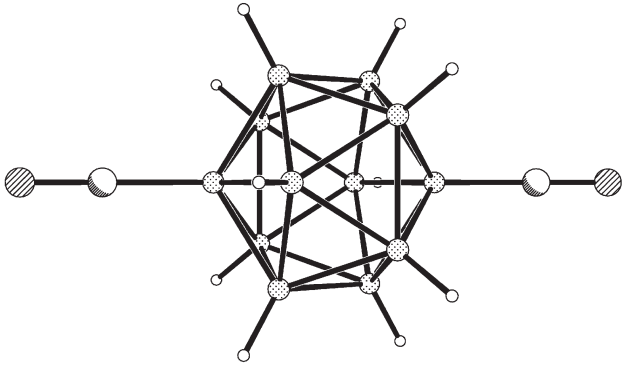


FIG. 3
Molecular structure of [1,12-$B_{12}H_{10}(CO)_2$]

The X-ray structure study of the hydrated acidic form $[1,12\text{-}B_{12}H_{10}(CO_2H_2)_2]\cdot 4H_2O$ revealed unexpectedly that, at least in the solid state, it exists in the carbene diol form (Fig. 4) (B–C 1.589 Å, C–O 1.288 Å, O–H 0.85 Å)[164]. The data on the acidic properties of the hydrated form are some contradictory. The pK_1 and pK_2 values reported are 4.2 and 9.0 (preliminary data)[164] as well as 9.07 and 10.24 [167]. It seems, however, that this contradiction is imaginary: more probably that the 4.2 value corresponds to loss of the first two protons from the carbene diols giving $[1,12\text{-}B_{12}H_{10}(COOH)_2]^{2-}$, whereas the 9.0 value coresponds to loss of the two carboxylic protons giving $[1,12\text{-}B_{12}H_{10}(COO)_2]^{4-}$; the 9.07 and 10.24 values were from the beginning determined for dissociation of the first and the second protons from $[1,12\text{-}B_{12}H_{10}(COOH)_2]^{2-}$ giving $[1,12\text{-}B_{12}H_{10}(COOH)(COO)]^{3-}$ and $[1,12\text{-}B_{12}H_{10}(COO)_2]^{4-}$, respectively. It should be noted however, that actual form of the existence of the dicarboxylic derivative (dihydroxycarbene or hydroxonium salt) in solutions and especially in diluted solutions is unknown.

The decrease in the effective negative charge on the BH groups apparently explains the extremely slow rate of halogenation of the carbonyl derivatives in anhydrous media. However, halogenation of the carboxylic species readily takes place in water with the formation of the completely substituted derivatives $[B_{12}Br_{11}COOH]^{2-}$, $[1,12\text{-}B_{12}Br_{10}(COOH)_2]^{2-}$, and $[1,12\text{-}B_{12}I_{10}(COOH)_2]^{2-}$ [163].

Carbonyl derivatives of the *closo*-dodecaborate anion have a high reactivity with respect to nucleophiles and can serve as starting compounds for synthesis of various derivatives of the $[B_{12}H_{12}]^{2-}$ anion. Their reactions with

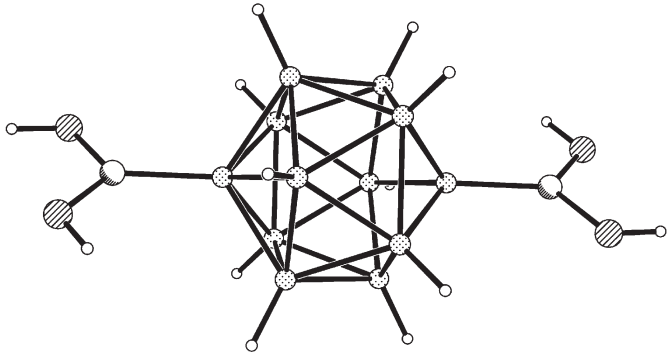
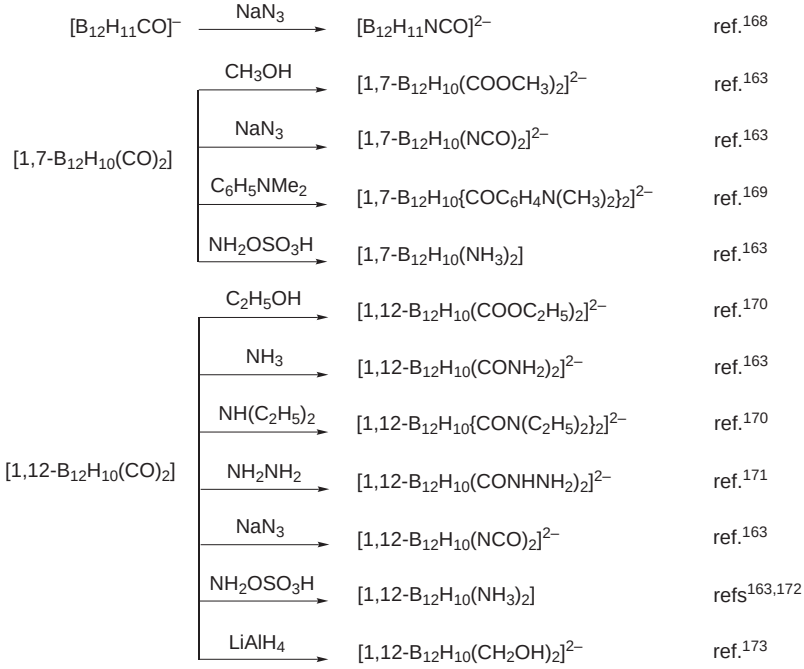


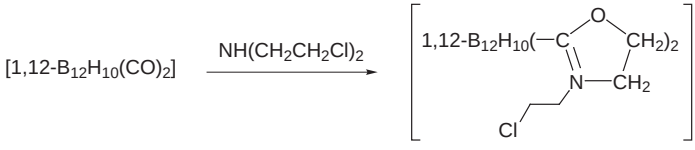
FIG. 4
Molecular structure of $[1,12\text{-}B_{12}H_{10}(C(OH)_2)_2]$

alcohols and amines give the corresponding esters and amides, the reaction with sodium azide results in isocyanate derivatives, *etc.* (Scheme 5).



SCHEME 5

The amide linkage in $[1,12\text{-}B_{12}H_{10}(CONEt_2)_2]$ was found to be very labile; it hydrolyzes smoothly with cold aqueous sodium hydroxide to the corresponding carboxylate and gives in refluxing ethanol the corresponding ester[170]. In contrast, the product obtained by the reaction of $[1,12\text{-}B_{12}H_{10}(CO)_2]$ with bis(2-chloroethyl)amine is very stable presumably due to the oxazoline formation[170] (Scheme 6).



SCHEME 6

Dehydration of $Cs_2[1,12\text{-}B_{12}H_{10}(CONH_2)_2]$ at 300–375 °C gives the cyano derivative $Cs_2[1,12\text{-}B_{12}H_{10}(CN)_2]$ [163,174].

The carbonyl function can be introduced also by the treatment with oxalyl chloride. The reaction of $[B_{12}H_{12}]^{2-}$ with oxalyl chloride in dichloromethane or acetonitrile at room temperature results in its quantitative conversion into the monocarbonyl derivative $[B_{12}H_{11}CO]^-$ [175,176]. This method gives possibility to easy prepare $[B_{12}H_{11}CO]^-$ in ordinary chemical laboratory and makes it a very promising synthon for preparation of various monosubstituted derivatives of the *closo*-dodecaborate anion. The reaction of $[B_{12}H_{11}NMe_3]^-$ with oxalyl chloride in refluxing acetonitrile gives a mixture of [1,7- and 1,12-$Me_3NB_{12}H_{10}CO$] in low yield[177].

The reduction of [1,12-$B_{12}H_{10}(CO)_2$] with lithium aluminium hydride in 1,2-dimethoxyethane gave the hydroxymethyl derivative [1,12-$B_{12}H_{10}(CH_2OH)_2]^{2-}$. The latter was converted to the iodomethyl derivative [1,12-$B_{12}H_{10}(CH_2I)_2]^{2-}$ by heating in 57% hydroiodic acid at 40–50 °C. A number of anionic and neutral nucleophiles were used in turn to displace iodide from the iodomethyl derivative to make [1,12-$B_{12}H_{10}(CH_2X)_2]^{2-}$ (X = N_3, SCN) and [1,12-$B_{12}H_{10}(CH_2L)_2$] (L = NMe_3, $NHMe_2$, PMe_3). The second-generation derivatives were obtained by proton abstraction from [1,12-$B_{12}H_{10}(CH_2NHMe_2)_2$] with butyllithium, followed by the reaction with organic halides, to make [1,12-$B_{12}H_{10}(CH_2NMe_2Y)_2$] (Y = Me, CH_2COOEt, CHMeCOOEt, COOEt)[173].

Chlorination of the hydroxymethyl derivative in acetonitrile results in its chlorination and oxidation to the chlorinated carboxylic derivative [1,12-$B_{12}Cl_{10}(COOH)_2]^{2-}$ [173]. The carboxyl groups can be cleaved from the B_{12} cage by halogen under free-radical conditions with the formation of perhalogenated derivatives[163].

The ketone derivatives $[B_{12}H_{11}COR]^{2-}$ (R = $CH_2C_6H_5$, $CH_2CH_2C_6H_5$, C_6H_5, 1-$C_{10}H_7$, 4-$O_2NC_6H_4$, 4-ClC_6H_4, 4-BrC_6H_4) were prepared by the reaction of $Na_2[B_{12}H_{12}]$ with the corresponding acyl chlorides in acetone. $[B_{12}H_{11}OH]^{2-}$ was the reaction by-product. The ratio of the products obtained depended on the nature of R [178].

The reactions of $(Bu_4N)_2[B_{12}H_{12}]$ with iodo-, bromo-, 1,3-dibromo-, 1,3-dichloro-, 1,2-dichloro-, and 1,2,3-trichlorobenzenes at 160–180 °C resulted in the coresponding aryl derivatives $[B_{12}H_{12-n}Ar_n]^{2-}$ (n = 1–3)[179–181]. The phenyl derivative $[B_{12}H_{11}C_6H_5]^{2-}$ was obtained by the reaction of $(Bu_4N)_2[B_{12}H_{12}]$ with triphenyltin chloride Ph_3SnCl at 170 °C [182].

The phenyl derivative was also prepared by the palladium-catalyzed coupling of $(Bu_4N)_2[B_{12}H_{11}I]$ with PhMgBr in 1,4-dioxane[183] or with PhZnCl in tetrahydrofuran[184]. The reaction of $[B_{12}H_{10}INH(CH_2Ph)_2]^-$ with 1-naphthylmagnesium bromide in refluxing tetrahydrofuran in the presence of

$[PdCl_2(PPh_3)_2]$ and CuI gives $[(PhCH_2)_2HNB_{12}H_{10}$-1-$C_{10}H_7]^-$ [185]. Similar reactions of with $(Bu_4N)_2[B_{12}H_{11}I]$ with methylmagnesium bromide in 1,4-dioxane, or methylzinc chloride or octadecylmagnesium chloride in tetrahydrofuran result in the corresponding alkyl derivatives $[B_{12}H_{11}R]^{2-}$ (R = CH_3, $C_{18}H_{37}$)[183,184]. The monomethyl derivative was obtained also by the reaction of $[B_{12}H_{11}I]^{2-}$ with refluxing trimethylaluminium[186].

The permethylated derivative $[B_{12}Me_{12}]^{2-}$ was prepared by heating $(Bu_4N)_2[B_{12}H_{12}]$ with trimethylaluminium and methyl iodide[186]. The permethylated dianion $[B_{12}Me_{12}]^{2-}$ can be easily oxidized with cerium(IV) ammonium nitrate to give the air-stable blue anion-radical $\{[B_{12}Me_{12}]^{\bullet}\}^-$, which can be reversibly reduced with sodium borohydride[187].

The structures of $(Ph_4As)_2[B_{12}H_{11}Ph]$ [182], $((Ph_3P)_2N)_2[B_{12}H_{11}Ph]\cdot 2Me_2SO\cdot$toluene[183], $Cs_2[B_{12}H_{11}Me]$ [183], $[(C_5H_5N)_2CH_2][B_{12}Me_{12}]\cdot$MeCN [186], and $((Ph_3P)_2N)[B_{12}Me_{12}]$ [187] were determined by X-ray diffraction.

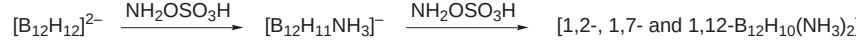
It was reported that the $[B_{12}H_{12}]^{2-}$ anion reacts with olefins in acid medium to form alkyl and polyalkyl derivatives[188,189]. However, these reactions are difficult to control, and result in mixtures of derivatives with varying degree of substitution.

The reaction of $(H_3O)_2[B_{12}H_{12}]\cdot nH_2O$ with tropylium bromide results in the tropylium derivative $[B_{12}H_{11}C_7H_6]^-$, which belongs to the class of so-called "ousenes", compounds, which offer an opportunity for charge transfer from the negatively charged boron cage to the positively charged aromatic ring[190–192]. The recent molecular orbital study[192b] revealed hat the tropilium derivative has additional low lying π-orbital in which a pair of the cage electrons are completely delocalized throughout the cage and the ring that results in the extraordinary stability of this tropilium derivative.

It was reported[152,193] that the dodecabromo-*closo*-dodecaborate anion $[B_{12}Br_{12}]^{2-}$ undergoes nucleophilic substitution with the cyanide ion under UV irradiation in aqueous solution to give successively $[B_{12}Br_3(CN)_9]^{2-}$, $[B_{12}HBr_2(CN)_9]^{2-}$, and $[B_{12}H_2Br(CN)_9]^{2-}$. Under similar conditions, $[B_{12}H_2Br_{10}]^{2-}$ gives $[B_{12}H_2Br_2(CN)_8]^{2-}$ and $[B_{12}H_2Br(CN)_9]^{2-}$. The less substituted halogen derivatives do not undergo a photoinduced nucleophilic substitution. The heating of $[B_{12}H_2Br(CN)_9]^{2-}$ and $[B_{12}H_2Br_2(CN)_8]^{2-}$ at 200 °C in concentrated sulfuric acid results in the corresponding carboxylic derivatives. The dodecachloro-*closo*-dodecaborate anion $[B_{12}Cl_{12}]^{2-}$ reacts with cyanide ion under UV irradiation to give $[B_{12}Cl_5(CN)_7]^{2-}$. In principle, these derivatives could serve as precursors for synthesis of supramolecular structures, however, on our knowledge this study was never revised and stereochemistry of the polycyano derivatives are unknown.

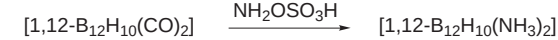
5. DERIVATIVES WITH BORON–NITROGEN BOND

The *closo*-dodecaborate derivatives with boron-nitrogen bond attract attention of boron chemists from the 1960's when simple and effective methods for substitution of nitrogen functions for hydrogen atom were developed. One of the most important is the reaction of the *closo*-dodecaborate anion with hydroxylamine-*O*-sulfonic acid in aqueous solution giving mono- and disubstituted amino derivatives which, because of their high basicity, are readily isolated in the *N*-protonated forms. The diamino derivative was obtained as a mixture of the 1,7-, 1,12-, and a small amount of 1,2-isomers, which can be separated by fractional crystallization from water[172,185,194] (Scheme 7).



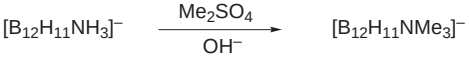
SCHEME 7

The 1,12-isomer can also be obtained by the reaction of hydroxylamine-*O*-sulfonic acid with the dicarbonyl derivative [1,12-$B_{12}H_{10}(CO)_2$] [163,172] (Scheme 8).



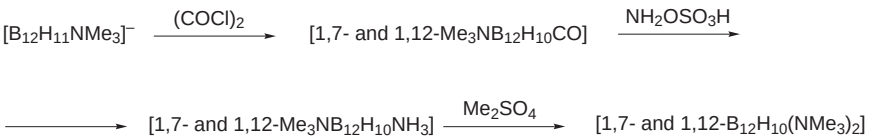
SCHEME 8

Treatment of the amino derivatives with dimethyl sulfate in alkaline solution results in the corresponding trimethylamine derivatives[172] (Scheme 9).



SCHEME 9

The disubstituted trimethylamine derivatives were obtained also by the reaction of $[B_{12}H_{11}NMe_3]^-$ with oxalyl chloride in refluxing acetonitrile followed by the treatment with hydroxylamine-*O*-sulfonic acid and dimethyl sulfate[176] (Scheme 10).



SCHEME 10

Thermal stability of the $[B_{12}H_{10}(NMe_3)_2]$ isomers was found to decrease in the order 1,12- > 1,7- > 1,2-isomer. The 1,12-isomer does not melt up to 530 °C

and fails to undergo polyhedral isomerization up to this temperature. The 1,7-isomer undergoes slight isomerization to the 1,2-isomer at 400 °C. The 1,2-isomer undergoes rapid decomposition at the melting point[174] (375 °C).

A series of alkylamine derivatives were prepared by deprotonation of $[B_{12}H_{11}NH_3]^-$ with strong bases (sodium hydride or potassium hydroxide) followed by the reaction with alkyl halides[185,195,196] (Scheme 11).

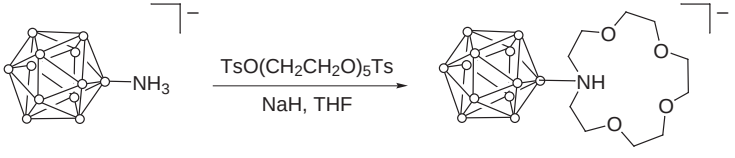
$$[B_{12}H_{11}NH_3]^- \xrightarrow{B} [B_{12}H_{11}NH_2]^{2-} \xrightarrow{RX} [B_{12}H_{11}NH_2R]^- + [B_{12}H_{11}NHR_2]^- + [B_{12}H_{11}NR_3]^-$$

R = C_2H_5, $(CH_3)_2CH$, *n*-$C_{12}H_{25}$, *n*-$C_{16}H_{33}$, $C_6H_5CH_2$, 2-$C_{10}H_7CH_2$, 3-(2-chlorophenothiazin-10-yl)propyl, (18-crown-6)methyl

SCHEME 11

The alkylation reaction gives, as a rule, a mixture of derivatives with varying substitution degrees. Using an excess of the alkylating agent results in derivatives with the maximum possible degree of substitution, which is dependent on the steric restrictions offered by the alkyl groups. This can be demonstrated by the reaction of $[B_{12}H_{11}NH_3]^-$ with ethyl iodide which gives $[B_{12}H_{11}NEt_3]^-$, whereas the reaction with benzyl chloride gives $[B_{12}H_{11}NH(CH_2Ph)_2]^-$. The use of equimolar amounts of alkylating agent usually gives mixtures of mono- and dialkylamine derivatives. The dialkylamine derivatives $[B_{12}H_{11}NHR_2]^-$ can be methylated with dimethyl sulfate or methyl iodide to give $[B_{12}H_{11}NR_2Me]^-$. The monoalkylamine derivatives could be obtained in reasonable yields only in the case of strongly sterically hindered alkylating agents, such as phthalocyanine derivatives[197,198].

The $[(15\text{-azacrown-5})B_{12}H_{11}]^-$ anion was prepared by the reaction of $[B_{12}H_{11}NH_3]^-$ with pentaethylene glycol ditosylate in the presence of sodium hydride in tetrahydrofuran[185] (Scheme 12).



SCHEME 12

A number of trialkylamine derivatives $[B_{12}H_{11}NR_3]^-$ were prepared by high-temperature reactions of diborane or adducts of borane with Lewis bases BH_3·L (L is trimethylamine, ethyl(dimethyl)amine, diethyl(methyl)amine, *N*-methylpiperidine, cyclohexyl(dimethyl)amine)[8,9]. The triethylamine derivative $[B_{12}H_{11}NEt_3]^-$ was obtained also in the reaction of

decaborane $B_{10}H_{14}$ with triethylamine-borane[8,10]. The unsubstituted *closo*-dodecaborate anion is the main product in all of these reactions; however, the $[B_{12}H_{11}NEt_3]^-$ yield can be increased by up to 60% in the presence of an excess of triethylamine[199].

The triethylamine derivative was found to form unexpectedly in the reaction of $(Et_3NH)_2[B_{12}H_{12}]$ with $[RuCl_2(PPh_3)_3]$ in refluxing ethanol and was isolated as the $[(PPh_3)_2ClRuB_{12}H_{11}NEt_3]$ complex[90].

The crystal molecular structures of $Cs[B_{12}H_{11}NH_3]\cdot 2MeOH$ [200], $K[B_{12}H_{11}NEt_3]$ [199], $(Me_4N)[B_{12}H_{11}NEt_3]$ [201], $(Bu_4N)[B_{12}H_{11}NEt_3]$ [196], $[(PPh_3)_2ClRuB_{12}H_{11}NEt_3]$ [90], $((Ph_3P)_2N)[B_{12}H_{11}NH_2\text{-i-Pr}]$ [196], $((Ph_3P)_2N)[B_{12}H_{11}NH(i\text{-Pr})_2]$ [196], $((Ph_3P)_2N)[B_{12}H_{11}NH(CH_2Ph)_2]$ [196], and $[1,7\text{-}B_{12}H_{10}(NH_3)_2]\cdot 0.5H_2O$ [194] were determined by X-ray diffraction.

Halogenation of amine- and alkylamine derivatives of the *closo*-dodecaborate anion under variuous conditions was studied[185,202,203]. The crystal structures of $(Ph_3C)[B_{12}F_{11}NMe_3]$ and $(Bu_4N)[B_{12}F_{11}NH(CH_2C_6H_5)_2]$ were determined by X-ray diffraction[203].

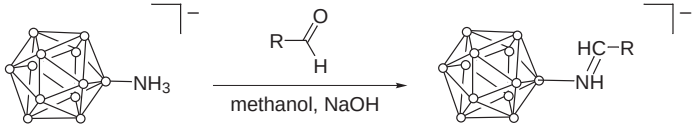
The (chloromethyl)dimethylamine derivatives were obtained by the reaction of the *closo*-dodecaborate anion with the Vilsmeier reagent[204] (Scheme 13).

$$[B_{12}H_{12}]^{2-} \xrightarrow[DMF]{POCl_3} [B_{12}H_{11}N(CH_3)_2CH_2Cl]^- \xrightarrow[DMF]{POCl_3} [B_{12}H_{10}\{N(CH_3)_2CH_2Cl\}_2]^-$$

SCHEME 13

This reaction was re-examined recently and $[1,7\text{-}B_{12}H_{10}(NMe_2CH_2Cl)_2]$ was shown to be the main product isolated in 51% yield, whereas the monosubstituted derivative $[B_{12}H_{11}NMe_2CH_2Cl]^-$ and $[B_{12}H_{11}OH]^{2-}$ formed in lower amounts. The crystal molecular structure of $[1,7\text{-}B_{12}H_{10}(NMe_2CH_2Cl)_2]$ was determined[205].

The reaction of $[B_{12}H_{11}NH_3]^-$ with aldehydes in methanol in the presence of catalytic amounts of alkali gives the corresponding Schiff bases $[B_{12}H_{11}NH{=}CHR]^-$ [206–208] (Scheme 14).

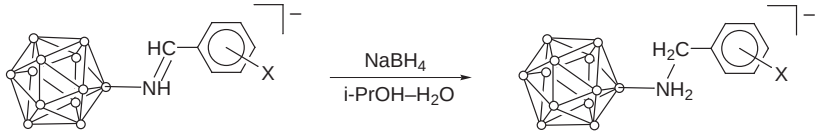


R = C_6H_5, 2-$MeOC_6H_4$, 4-$MeOC_6H_4$, 4-$MeSC_6H_4$, 4-$Me_2NC_6H_4$, 4-$AcNHC_6H_4$, 4-NCC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 3,4-$CH_2O_2C_6H_3$, 1-$C_{10}H_7$, 2-$C_{10}H_7$, Me-CH=CH, Ph-CH=CH

SCHEME 14

The crystal molecular crystal structures of $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}4\text{-}NMe_2]\cdot CHCl_3$ and $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}2\text{-}OMe]$ have been determined by single-crystal X-ray analysis. Both anions were found to have *trans*-configuration[206].

The reduction of the Schiff bases with sodium borohydride in aqueous propan-2-ol gives the corresponding amines[206–208] (Scheme 15).



SCHEME 15

This approach was used for the synthesis of a series of derivatives of the *closo*-dodecaborate anion with various functional groups connected to the aromatic ring $[B_{12}H_{11}NH_2CH_2C_6H_4\text{-}4\text{-}X]^-$ (X = NH_2, COOH, NCS)[206–208].

The reactions of $(Bu_4N)_2[B_{12}H_{12}]$ with 4-aminopyridine and 2,2′-bipyridine at 190 °C gave $[(4\text{-pyridyl}NH_2)B_{12}H_{11}]^-$ and $[1\text{-}(2,2'\text{-bipyridyl})B_{12}H_{11}]^-$, respectively. The crystal molecular structures of $(Ph_4As)[(4\text{-pyridyl}NH_2)\text{-}B_{12}H_{11}]\cdot 2MeCN$ [209] and $(Ph_4As)[1\text{-}(2,2'\text{-bipyridyl})B_{12}H_{11}]\cdot MeCN$ [210] were determined by X-ray diffraction.

The alkylamide derivatives can be prepared by reaction of the amino derivative with acyl chlorides[185] (Scheme 16).

$$[B_{12}H_{11}NH_3]^- \xrightarrow[\text{NaH, THF}]{C_{15}H_{31}COCl} [B_{12}H_{11}NH_2COC_{15}H_{31}]^-$$

SCHEME 16

The acetamide, acrylamide, and cyanoacetamide derivatives were prepared by the reaction of the *closo*-dodecaborate anion with the corresponding nitriles in the presence of 4-methylbenzene-1-sulfonic acid. The nitrilium intermediate was hydrolyzed with traces of water to give the corresponding amides[132,211–213] (Scheme 17).

$$[B_{12}H_{12}]^{2-} \xrightarrow[H^+]{RCN} [B_{12}H_{11}NCR]^- \xrightarrow{H_2O} [B_{12}H_{11}NH_2COR]^-$$

R = CH_3, $CH{=}CH_2$, CH_2CN

SCHEME 17

The lanthanide complexes with the acetamide and acrylamide ligands $Ln[B_{12}H_{11}NH_2COR]_3\cdot 5H_2O$ (Ln = La, Pr, Nd, Sm, Eu, Gd, Ho, Er, Tm, Yb, Ln) were synthesized[211–213].

Small amounts of $[B_{12}H_{11}NH_2COCH_3]^-$, $[B_{12}H_{11}NH_2COCH_2COOEt]^-$, $[B_{12}H_{11}NH_2COCH_2OSO_2Ph]^-$, and $[B_{12}H_{10}(NH_2COCH_2CONH_2)_2]$ were isolated from the reaction of the $[B_{12}H_{12}]^{2-}$ anion with the appropriate nitriles (acetonitrile, ethyl cyanoacetate, cyanomethyl benzenesulfonate, malononitrile) in the presence of $FeCl_3$ [214].

The isocyanate derivatives $[B_{12}H_{11}NCO]^{2-}$, [1,7- and 1,12-$B_{12}H_{10}(NCO)_2]^{2-}$ were prepared by the reaction of the corresponding carbonyl derivatives with sodium azide[163,168]. Hydrolysis of [1,12-$B_{12}H_{10}(NCO)_2]^{2-}$ in acidic solution gives the diamino derivative [1,12-$B_{12}H_{10}(NH_3)_2$], whereas the reaction with alcohol in the presence of acid results in urethane[163] (Scheme 18).

$$[1,12\text{-}B_{12}H_{10}(NCO)_2]^{2-} \xrightarrow[HCl]{EtOH} [1,12\text{-}B_{12}H_{10}(NHCOOEt)_2]^{2-}$$

SCHEME 18

The nitroso derivative $[B_{12}H_{11}NO]^{2-}$ derivative was prepared by the treatment of the *closo*-dodecaborate with nitrous acid in aqueous solution or with isopentyl nitrite and nitrosyl chloride in noaqueous solutions[215].

Short irradiation (1.5–2 h) of the dodecabromo-*closo*-dodecaborate anion $[B_{12}Br_{12}]^{2-}$ in the presence of excess of azide ion produces $[B_{12}Br_{11}N_3]^{2-}$ and $[B_{12}Br_{10}(N_3)_2]^{2-}$ anions which could be separated by fractional crystallization[152].

6. DERIVATIVES WITH BORON–PHOSPHORUS AND BORON–ARSENIC BONDS

The trimethylphosphonium derivatives of the dodecaborate anion were obtained by pyrolysis of the trimethylphosphine–borane complex, where the $[B_{12}H_{11}PMe_3]^-$ yield reaches 60% [8,9] (Scheme 19).

$$Me_3P{\cdot}BH_3 \longrightarrow [B_{12}H_{11}PMe_3]^- + [B_{12}H_{10}(PMe_3)_2]$$

SCHEME 19

The [1,7-$B_{12}H_{10}(PMe_2Ph)_2$] complex was obtained by the reaction of the *closo*-dodecaborate anion with $[PdCl_2(Me_2PhP)_2]$ in tetrahydrofuran[216] (Scheme 20).

$$[B_{12}H_{12}]^{2-} \xrightarrow{[PdCl_2(Me_2PhP)_2]} [1,7\text{-}B_{12}H_{10}(PMe_2Ph)_2]$$

SCHEME 20

The trimethylarsonium derivatives $[B_{12}H_{11}AsMe_3]^-$ and $[B_{12}H_{10}(AsMe_3)_2]$ were obtained by pyrolysis of the trimethylarsine–borane complex[8,9].

7. DERIVATIVES WITH BORON–OXYGEN BOND

At present, many methods for the synthesis of the hydroxy derivative of the *closo*-dodecaborate anion $[B_{12}H_{11}OH]^{2-}$ are described in the literature. One approach includes the interaction of the $[B_{12}H_{12}]^{2-}$ anion with amides in acid media followed by alkaline hydrolysis of the formed intermediates. For example, heating the $[B_{12}H_{12}]^{2-}$ anion with 1-methylpyrrolidin-2-one at 180 °C in the presence of hydrochloric acid gives the corresponding 1-methyl-1-pyrrolinio-2-yloxy derivative which can be easily hydrolyzed with alkali to $[B_{12}H_{11}OH]^{2-}$ [189,217]. The reaction of the $[B_{12}H_{12}]^{2-}$ anion with tetramethylurea at 165 °C in the presence of concentrated sulfuric acid gives $[B_{12}H_{11}OC(NMe_2)_2]^-$ in high yield; however, its hydrolysis has not been reported[202]. The other method consists in the reaction of the $[B_{12}H_{12}]^{2-}$ anion with sulfones under acid conditions. The reactions with tetrahydrothiophene 1,1-dioxide or dipropyl sulfone gave the corresponding derivatives, $[B_{12}H_{11}OS(O)C_4H_8]^-$ or $[B_{12}H_{11}OS(O)Pr_2]^-$. Alkaline hydrolysis of the first one was reported to result in the hydroxy derivative[202].

The hydroxy derivative was also prepared by refluxing the $[B_{12}H_{12}]^{2-}$ anion in acidic propan-2-ol followed by hydrolysis of the formed isopropoxy derivative with concentrated hydrobromic acid[189]. The hydroxy derivative can be prepared also by the reaction of the $[B_{12}H_{12}]^{2-}$ anion with acetyl chloride in acetone[218], by the reaction of the $[B_{12}H_{12}]^{2-}$ acid with sulfur dioxide at 60 °C under pressure[189], or by mild oxidation of the *closo*-dodecaborate anion with oxalic acid[189,219]. The syntheses of the hydroxy derivative $[B_{12}H_{11}OH]^{2-}$ by the reaction of the *closo*-dodecaborate with aqueous sulfuric acid at 90 °C [220,221] or with refluxing acetic acid followed by alkaline hydrolysis of the acetoxy intermediate[222] have been described quite recently. It should be mentioned that only the methods based on the alkaline hydrolysis of the pyrrolidinium intermediate[217] or the acetoxy[222] derivative, and the hydroxylation of the *closo*-dodecaborate with sulfuric acid[220] give high yields (to 75–80%) and can be used as preparative methods.

The perchloro derivative $[B_{12}Cl_{11}OH]^{2-}$ was prepared by chlorination of the $[B_{12}H_{12}]^{2-}$ anion with gaseous chlorine in aqueous solution at 90 °C [189]. The perbromo analogue $[B_{12}Br_{11}OH]^{2-}$ was prepared by bromination of $[B_{12}H_{11}O\text{-i-Pr}]^{2-}$ with bromine in water[189].

The dihydroxy derivative $[B_{12}H_{10}(OH)_2]^{2-}$ was obtained as a mixture of the 1,2- and 1,7-isomers by heating $[B_{12}H_{12}]^{2-}$ in a mixture of acetone and concentrated hydrochloric acid at 80 °C [215]. The pure $[1,2\text{-}B_{12}H_{10}(OH)_2]^{2-}$ isomer was obtained by alkaline hydrolysis of $[1,2\text{-}C_6H_5CH_2C(O)OB_{12}H_{10}OH]$ [223]. The pure $[1,7\text{-}B_{12}H_{10}(OH)_2]^{2-}$ isomer was prepared by the

reaction of the $[B_{12}H_{12}]^{2-}$ anion with 1-methylpyrrolidin-2-one at 205–250 °C in the presence of hydrochloric acid followed by alkaline hydrolysis of the intermediate formed[171,189,220] or by the reaction of $(H_3O)_2[B_{12}H_{12}]\cdot nH_2O$ with ethylene glycol at 160 °C [224] and by the reaction of the $[B_{12}H_{12}]^{2-}$ anion with aqueous sulfuric acid at 90 °C [221]. The bromination of $[1,7\text{-}B_{12}H_{10}(OH)_2]^{2-}$ with bromine in aqueous solution gives the corresponding perbromo derivative $[1,7\text{-}B_{12}Br_{10}(OH)_2]^{2-}$ [189].

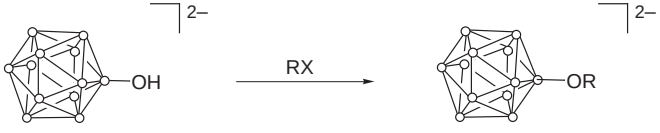
The trisubstituted hydroxy derivative $[1,2,3\text{-}B_{12}H_9(OH)_3]^{2-}$ was obtained by heating of the $[B_{12}H_{12}]^{2-}$ anion in a mixture of acetone and concentrated hydrochloric acid at 100 °C [218], whereas the 1,7,9-isomer was shown to form in the reaction of the $[B_{12}H_{12}]^{2-}$ anion with aqueous sulfuric acid at 110 °C [220,221].

The tetrasubstituted hydroxy derivative $[1,2,8,10\text{-}B_{12}H_8(OH)_4]^{2-}$ was obtained by the reaction of the $[B_{12}H_{12}]^{2-}$ anion with aqueous sulfuric acid at 175 °C [220,221].

The perhydroxy derivative $[B_{12}(OH)_{12}]^{2-}$ was prepared by heating the $[B_{12}H_{12}]^{2-}$ anion with 30% hydrogen peroxide under reflux[225,226]. The same product was also obtained from the reaction of the monocarboxylato derivative $[B_{12}H_{11}COO]^{2-}$ and hydrogen peroxide, whereas $[B_{12}H_{11}C_6H_5]^{2-}$ and $[B_{12}H_{11}I]^{2-}$ were degraded to boric acid when heated with 30% hydrogen peroxide at the reflux[226].

The crystal structures of $Cs_2[B_{12}H_{11}OH]\cdot AcOH$ [222], $(Ph_3PMe)_2[B_{12}H_{11}OH]$ [220], $(Ph_4P)_2[B_{12}H_{11}OH]\cdot 0.74AcOH\cdot 0.52H_2O$ [222], $(Ph_3PMe)_2[1,7\text{-}B_{12}H_{10}(OH)_2]$ [220], $Na_2[B_{12}(OH)_{12}]\cdot 4H_2O$ [226], $K_2[B_{12}(OH)_{12}]$ [226], $Rb_2[B_{12}(OH)_{12}]\cdot 2H_2O$ [226], and $Cs_2[B_{12}(OH)_{12}]\cdot 2H_2O$ [225,226] have been established by the X-ray diffraction method.

Alkylation of $[B_{12}H_{11}OH]^{2-}$ with alkyl halides in dimethyl sulfoxide in the presence of potassium hydroxide[227] or in acetone in the presence of potassium carbonate[228] gives the alkoxy derivatives $[B_{12}H_{11}OR]^{2-}$ (Scheme 21).



R = C_2H_5, $(CH_3)_2CH$, $CH_3(CH_2)_{15}$, $CH_2{=}CHCH_2$, $C_6H_5CH_2$, 4-$NCC_6H_4CH_2$, 4-$O_2NC_6H_4CH_2$, 4-$O_2NC_6H_4CH_2CH_2$, $C_6H_4(CO)_2NCH_2CH_2$

SCHEME 21

The synthesis of a boron-containing glucoside based on the $[B_{12}H_{11}OH]^{2-}$ anion was reported[229].

The alkoxy derivatives were obtained also by the reaction of the *closo*-dodecaborate anion with alcohols and ethers in acidic media. Formation of a number of such derivatives has been described in the early 1960's [189]. Recently the ethoxy derivative $[B_{12}H_{11}OEt]^{2-}$ was shown to be formed by the treatment of the $[B_{12}H_{12}]^{2-}$ anion with hydrogen fluoride in ethanol[230].

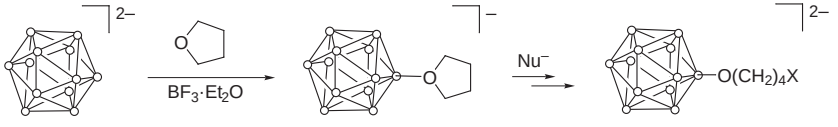
The phenoxy derivative $[B_{12}H_{11}OPh]^{2-}$ was prepared by refluxing $(Bu_4N)_2[B_{12}H_{12}]$ in anisole[179]. Its perbromo analogue $[B_{12}Br_{11}OPh]^{2-}$ was obtained by UV irradiation of the $[B_{12}Br_{12}]^{2-}$ anion in aqueous solution of potassium phenolate[152].

The 1,7-dialkoxy derivatives $[1,7\text{-}B_{12}H_{10}(OR)_2]^{2-}$ (R = Me, Et) were obtained by the reaction of $Na_2[B_{12}H_{12}]$ with dichloromethyl methyl ether in acetone followed by alcoholysis of the formed intermediate with the corresponding alcohols[231].

The reaction of $[B_{12}(OH)_{12}]^{2-}$ with benzyl bromide in acetonitrile in the presence of ethyl(diisopropyl)amine at the reflux temperature produces the per-*O*-benzylated derivative $[B_{12}(OCH_2C_6H_5)_{12}]^{2-}$. Salts of the $[B_{12}(OCH_2C_6H_5)_{12}]^{2-}$ anion slowly air-oxidize to give purple paramagnetic anion-radical $[B_{12}(OCH_2C_6H_5)_{12}]^{\bullet-}$. The latter can be easily obtained by one-electron oxidation of $[B_{12}(OCH_2C_6H_5)_{12}]^{2-}$ with 1 equivalent of iron(III) chloride. The sequential two-electron oxidation of $[B_{12}(OCH_2C_6H_5)_{12}]^{2-}$ with excess of $FeCl_3$ in ethanol gives dark orange *hypercloso*-$[B_{12}(OCH_2C_6H_5)_{12}]$ [232].

The crystal structures of $Cs[(Ph_3P)_2N][B_{12}(OCH_2C_6H_5)_{12}]$, $[(Ph_3P)_2N]$-$[B_{12}(OCH_2C_6H_5)_{12}]$, and $[B_{12}(OCH_2C_6H_5)_{12}]$ have been established by the single-crystal X-ray diffraction[232].

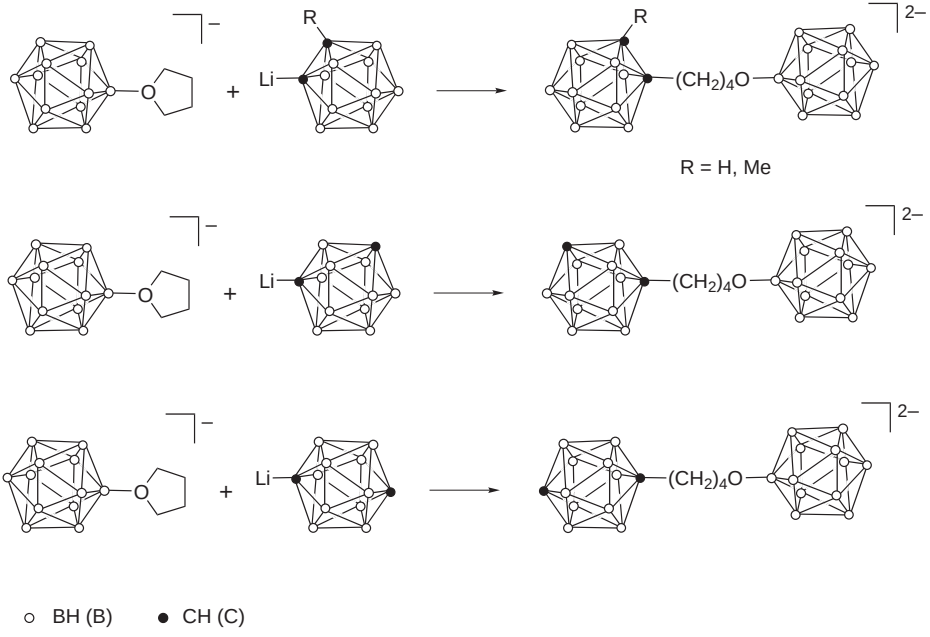
The oxonium derivatives $[B_{12}H_{11}O(CH_2)_4]^-$ or $[B_{12}H_{11}O(CH_2CH_2)_2O]^-$ were prepared by the treatment of the parent *closo*-dodecaborate anion with $BF_3{\cdot}Et_2O$ in tetrahydrofuran or 1,4-dioxane, respectively. The diethyloxonium derivative $[B_{12}H_{11}OEt_2]^-$ was obtained by the reaction of $[B_{12}H_{12}]^{2-}$ with 4-nitrobenzoyl chloride in an acetone–diethyl ether mixture[233]. The tetramethylene oxonium derivative $[B_{12}H_{11}O(CH_2)_4]^-$ undergoes the ring opening under nucleophilic attack with various nucleophiles giving a useful method for the synthesis of a series of functional derivatives of the *closo*-dodecaborate anion $[B_{12}H_{11}O(CH_2)_4X]^{2-}$ (X = OH, NH_2, COOH, $CH(NH_2)COOH$)[233,234] (Scheme 22).



X = OH, NH_2, COOH, $CH(NH_2)COOH$

SCHEME 22

Using lithium derivatives of *o*-, *m*-, and *p*-carboranes as nucleophiles, the compounds containing both the *closo*-dodecaborate and the coresponding carborane cages were synthesized[234] (Scheme 23).

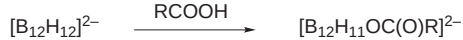


SCHEME 23

A similar approach was used for the synthesis of neutral oxonium derivatives on the basis of dibenzylamino-*closo*-dodecaborate – $[(C_6H_5CH_2)_2HNB_{12}H_{10}O(CH_2)_4]$ and $[(C_6H_5CH_2)_2HNB_{12}H_{10}O(CH_2CH_2)_2O]$. The ring-opening reaction in these derivatives was used for preparation of extractants for purification of nuclear wastes[235].

The pentamethylene oxonium derivative $[B_{12}H_{11}O(CH_2)_5]^-$ was prepared by the reaction of $[B_{12}H_{11}OH]^{2-}$ with 1,5-dibromopentane in the presence of potassium hydroxide in dimethyl sulfoxide[227]. This compound also undergoes the ring-opening reaction, under nucleophilic attack with fluoride or hydroxide ions, giving the corresponding alkoxy derivatives $[B_{12}H_{11}O(CH_2)_5X]^{2-}$ (X = F, OH)[236].

The acyloxy derivatives $[B_{12}H_{11}OC(O)R]^{2-}$ were shown to be formed by the reaction of $(Bu_4N)_2[B_{12}H_{12}]$ with formic, acetic, cyanoacetic, phenylacetic, propionic, butyric, palmitic, and stearic acids at 90–150 °C [223,237] (Scheme 24).

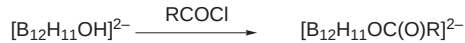


R = H, CH_3, C_2H_5, *n*-C_3H_7, *n*-$C_{15}H_{31}$, *n*-$C_{17}H_{35}$, $CH_2C_6H_5$, CH_2CN

SCHEME 24

The disubstituted [1,2- and 1,7-$B_{12}H_{10}(OC(O)R)_2]^{2-}$ derivatives were by-products in the case of acetic, propionic, and butyric acids and the main products in the case of palmitic and stearic acids at 120–150 °C, whereas in the case of phenylacetic acid [1,2-$C_6H_5CH_2C(O)OB_{12}H_{10}OH]^{2-}$ forms. A high yield (70%) was obtained only for the acetoxy derivative $[B_{12}H_{11}OAc]^{2-}$ [223,237].

The acyloxy derivatives were also prepared by acylation of the $[B_{12}H_{11}OH]^{2-}$ anion with acyl chlorides in acetonitrile in the presence of a base[217,227] (Scheme 25).



R = CH_3, C_6H_5, 4-ClC_6H_4, 4-$MeOC_6H_4$

SCHEME 25

In the case of acyl chlorides of dicarboxylic acids (oxalyl chloride, terephthaloyl and isophtaloyl chlorides), the corresponding bridged dicluster compounds $[B_{12}H_{11}OC(O)RC(O)OB_{12}H_{11}]^{4-}$ were obtained in good yields[224].

Slow addition of iodine in propan-2-ol to aqueous solution of $[B_{12}H_{11}OC(O)CH_3]^{2-}$ results in formation of [1-$CH_3C(O)O$-12-I-$B_{12}H_{10}]^{2-}$ [238].

Acylation of [1,2-$B_{12}H_{10}(OH)_2]^{2-}$ with oxalyl chloride gives the cyclic oxalato derivative [1,2-μ-$OC(O)C(O)O$-$B_{12}H_{10}]^{2-}$. Similarly, the reaction of [1,7-$B_{12}H_{10}(OH)_2]^{2-}$ with sebacoyl chloride produces [1,7-μ-$OC(O)(CH_2)_8C(O)O$-$B_{12}H_{10}]^{2-}$ [224].

Acylation of $[B_{12}(OH)_{12}]^{2-}$ with acetic anhydride or with benzoyl chloride in acetonitrile in the presence of triethylamine at reflux temperature gives the corresponding per-*O*-acylated derivatives $[B_{12}(OC(O)CH_3)_{12}]^{2-}$ and $[B_{12}(OC(O)C_6H_5)_{12}]^{2-}$ [239]. This approach was used for synthesis of the dodeca-(carboranyl)-substituted anion, $[B_{12}(OC(O)(CH_2)_6$-1-(2-CH_3-1,2-$C_2B_{10}H_{10})_{12}]^{2-}$ [240].

Heating the acyloxy derivatives in 1 M NaOH at 60 °C results in complete hydrolysis to the parent hydroxy derivatives[223,237].

The reactions of $[B_{12}H_{11}OH]^{2-}$ with thionyl or sulfonyl chlorides in acetonitrile in the presence of pyridine give $[B_{12}H_{11}OS(O)OB_{12}H_{11}]^{4-}$ and $[B_{12}H_{11}OSO_2OB_{12}H_{11}]^{4-}$, respectively[224]. The phosphorylation of $[B_{12}H_{11}OH]^{2-}$ with phosphorus oxychloride in pyridine gives

$[B_{12}H_{11}OPO_3H]^{3-}$ and $[B_{12}H_{11}OPO_3H_2]^{2-}$ depending on the medium acidity. A similar reaction with $(PhO)_2POCl$ results in $[B_{12}H_{11}OP(O)(OPh)_2]^{2-}$ and $[B_{12}H_{11}OP(O)(OPh)OH]^{2-}$ as products[241].

The reaction of $[1,2\text{-}B_{12}H_{10}(OH)_2]^{2-}$ with sulfuryl chloride results in the formation of the cyclic sulfato $[1,2\text{-}\mu\text{-}OSO_2O\text{-}B_{12}H_{10}]^{2-}$ derivative[224]. The reaction of $[1,7\text{-}B_{12}H_{10}(OH)_2]^{2-}$ with methanesulfonyl chloride in refluxing pyridine gives $[1,7\text{-}B_{12}H_{10}(OSO_2Me)_2]^{2-}$ [220]. Phosphorylation of $[1,7\text{-}B_{12}H_{10}(OH)_2]^{2-}$ with phosphorus oxychloride gives $[1,7\text{-}B_{12}H_{10}(OPO_3H)_2]^{4-}$, $[1,7\text{-}B_{12}H_{10}(OPO_3H)(OPO_3H_2)]^{3-}$, and $[1,7\text{-}B_{12}H_{10}(OPO_3H_2)_2]^{2-}$ depending on the medium acidity[241]. The bromination of the phosphate derivatives with bromine in aqueous solution produces $[1,7\text{-}B_{12}Br_{10}(OPO_3H)_2]^{4-}$. The reaction of $[1,7\text{-}B_{12}H_{10}(OH)_2]^{2-}$ with $(PhO)_2POCl$ results in $[1,7\text{-}B_{12}H_{10}(OP(O)(OPh)_2)_2]^{2-}$ [241].

The crystal molecular structures of $[1,1'\text{-}CH_2(C_5H_5N)_2][B_{12}H_{11}OEt]$ [231], $(Bu_4N)_2[B_{12}H_{11}OEt]$ [227], $Cs[(Ph_3P)_2N][B_{12}(OCH_2C_6H_5)_{12}]$ [232], $[(Ph_3P)_2N][B_{12}H_{11}O(CH_2)_5]$ [227], $(Bu_4N)_2[B_{12}H_{11}OC(O)Me]$ [227], $(Bu_4N)_2[B_{12}H_{11}OC(O)Ph]$ [227], $Cs_2[1,2\text{-}\mu\text{-}OC(O)C(O)O\text{-}B_{12}H_{10}]\cdot MeOH$ [224], $Cs_2[B_{12}(OC(O)CH_3)_{12}]\cdot 2SC(NH_2)_2$ [239], $(Ph_4P)_2[B_{12}(OC(O)C_6H_5)_{12}]$ [239], and $(pyH)_2[1,7\text{-}B_{12}H_{10}(OSO_2Me)_2]$ [220] were determined by X-ray diffraction.

The reactions of $[B_{12}H_{11}OH]^{2-}$, $[1,7\text{-}B_{12}H_{10}(OH)_2]^{2-}$, and $[1,7,9\text{-}B_{12}H_{10}(OH)_2]^{2-}$ with titanocene dichloride Cp_2TiCl_2 in refluxing acetonitrile gave the corresponding dichloro(cyclopentadienyl)titaniumoxy derivatives $[B_{12}H_{11}OTiCpCl_2]^{2-}$, $[1,7\text{-}B_{12}H_{10}(OTiCpCl_2)_2]^{2-}$, and $[1,7,9\text{-}B_{12}H_9(OTiCpCl_2)_3]^{2-}$. The crystal structure of $(Ph_3PMe)_2[B_{12}H_{11}OTiCpCl_2]$ was determined by X-ray diffraction[220].

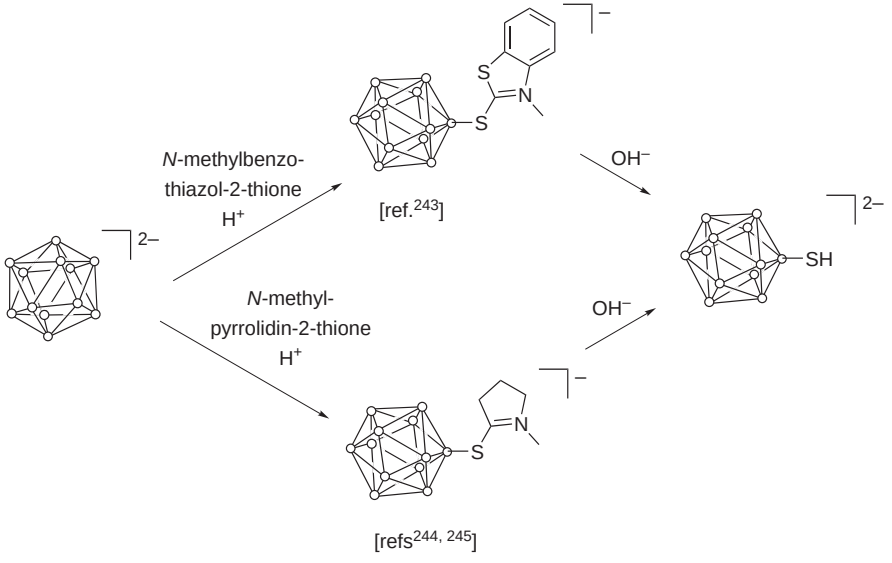
The reaction of $[B_{12}H_{11}OH]^{2-}$ with phenyl isocyanate in pyridine gives the corresponding carbamate $[B_{12}H_{11}OC(O)NHPh]^{2-}$ [220]. In a similar way, the reactions $[B_{12}(OH)_{12}]^{2-}$ with isocyanates give the corresponding carbamates[242]. UV irradiation of the dodecabromo-*closo*-dodecaborate anion $[B_{12}Br_{12}]^{2-}$ in aqueous solution in the presence of excess of the cyanate ion gives the cyanato derivatives, $[B_{12}Br_{11}OCN]^{2-}$ and $[B_{12}Br_{10}(OCN)_2]^{2-}$, which can be easily hydrolyzed to the corresponding hydroxy derivatives[152].

8. DERIVATIVES WITH BORON–SULFUR BOND

At present the chemistry of the *closo*-dodecaborate derivatives with boron–sulfur bond is the most actively studied field in the $[B_{12}H_{12}]^{2-}$ chemistry. The great interest to these compounds is caused by the use of sodium mercapto-*closo*-dodecaborate $Na_2[B_{12}H_{11}SH]$ as an agent for boron neutron capture therapy for cancer.

The mercapto derivative was obtained for the first time by the reaction of $(H_3O)_2[B_{12}H_{12}]\cdot nH_2O$ with hydrogen sulfide in the early 1960's [189]. It was shown later that the reaction gives a mixture of the mono- and dimercapto derivatives as well as the hydroxy derivatives[243]. However, the yield of the monomercapto derivative $[B_{12}H_{11}SH]^{2-}$ after work-up does not exceed 25%.

More convenient methods of synthesis of the mercapto derivative which are used in its routine preparation include the interaction of the $[B_{12}H_{12}]^{2-}$ anion with thiocarbonyl compounds in acid media followed by alkaline hydrolysis of the formed intermediates (Scheme 26).



SCHEME 26

An alternative method consists in the reaction of the $[B_{12}H_{12}]^{2-}$ anion with thiourea under conditions of electrochemical oxidation[246] (Scheme 27).

$$[B_{12}H_{12}]^{2-} \xrightarrow[-2\,e]{\text{thiourea}} [B_{12}H_{11}SC(NH_2)_2]^{-} \xrightarrow{OH^-} [B_{12}H_{11}SH]^{2-}$$

SCHEME 27

The crystal structure of $Cs_2[B_{12}H_{11}SH]\cdot H_2O$ was determined by single-crystal X-ray diffraction[247].

The acidic properties of the $[B_{12}H_{11}SH]^{2-}$ anion were studied and it was found that the mercapto group has an unusually high pK_a value of 13.4 [248].

A few examples of formation of complexes with participation of the $[B_{12}H_{11}SH]^{2-}$ anion were described. The reaction of $Cs_2[B_{12}H_{11}SH]$ with

$[RuCl(NH_3)_5]Cl_2$ in aqueous solution results in a dark blue complex, $[(B_{12}H_{11}S)Ru(NH_3)_5]\cdot 2H_2O$, the structure of which was determined by X-ray diffraction. The $[B_{12}H_{11}S]^{3-}$ ligand is strongly nucleophilic and demonstrates a strong *trans* effect[249].

Formation of self-assembled monolayers by spontaneous adsorption of the $[B_{12}H_{11}SH]^{2-}$ anions on gold surface from aqueous solutions of $Cs_2[B_{12}H_{11}SH]$ was shown[250]. The exchange of PPh_3 in $Au_{55}(PPh_3)_{12}Cl_6$ for $Na_2[B_{12}H_{11}SH]$ using a phase-transfer reaction from dichloromethane to water results in the very stable $Na_{24}[Au_{55}(B_{12}H_{11}SH)_{12}Cl_6]$ complex[251] (Fig. 5) .

Mild oxidation of $[B_{12}H_{11}SH]^{2-}$ with sodium iodosobenzoate[243,252] or nickel peroxide[253,254] gives the disulfide $[B_{12}H_{11}SSB_{12}H_{11}]^{4-}$ (Scheme 28).

$$[B_{12}H_{11}SH]^{2-} \xrightarrow[\text{or nickel peroxide}]{OIC_6H_4COONa} [B_{12}H_{11}SSB_{12}H_{11}]^{4-}$$

SCHEME 28

The disulfide formation was found also as a result of the autooxidation of $[B_{12}H_{11}SH]^{2-}$ with molecular oxygen in aqueous solution[243,254–256].

Treatment of $[B_{12}H_{11}SSB_{12}H_{11}]^{4-}$ with iodine monochloride in tetrachloroethane results in the periodinated disulfide derivative $[B_{12}I_{11}SSB_{12}I_{11}]^{4-}$ [257].

Acidification of solutions of the disulfide $[B_{12}H_{11}SSB_{12}H_{11}]^{4-}$ in some organic solvents (acetone, ethanol, acetonitrile, dimethylformamide, dimethyl sulfoxide) results in formation of a deep blue stable radical. The

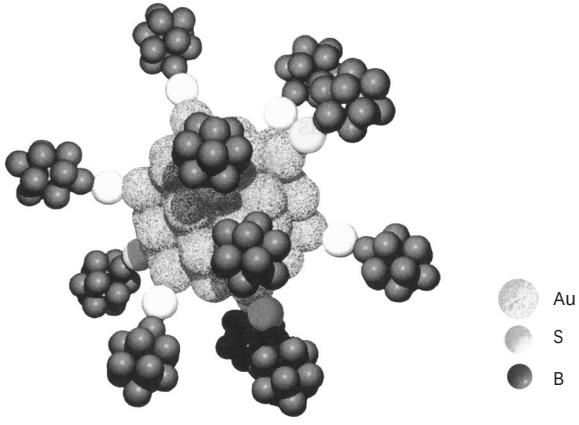
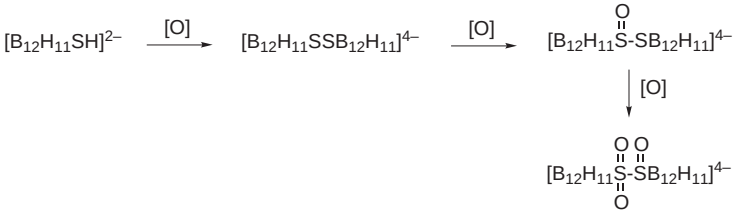


FIG. 5
Model of the cluster part $[Au_{55}(B_{12}H_{11}SH)_{12}]^{24-}$

reaction rate is strongly dependent on the oxygen concentration as well as on the concentration of H^+ and the disulfide[252]. The formation of the radical was used for determination of the $[B_{12}H_{11}SSB_{12}H_{11}]^{4-}$ anion[258]. Reversible formation of the radical was also found in acid aqueous solutions at 90 °C [252].

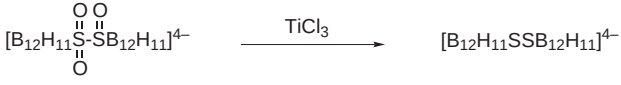
Further oxidation of the disulfide derivative with molecular oxygen gives the sulfide-sulfoxide $[B_{12}H_{11}SS(O)B_{12}H_{11}]^{4-}$ and subsequently the sulfoxide-sulfone $[B_{12}H_{11}S(O)SO_2B_{12}H_{11}]^{4-}$ [254,255] (Scheme 29).



SCHEME 29

The process of autooxidation of the mercapto derivative with molecular oxygen has been studied by ESR spectroscopy and the formation of the superoxide anion-radicals in the presence of the $[B_{12}H_{11}SH]^{2-}$ anion was revealed[259,260].

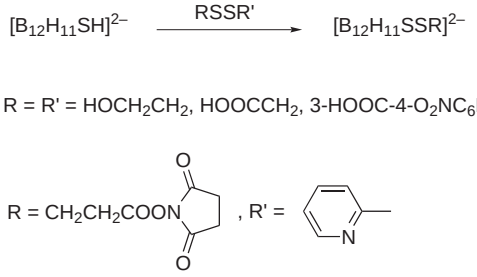
The sulfide-sulfoxide can be also obtained by oxidation of the disulfide derivative with an equivalent amount of 3-chloroperbenzoic acid[254] or hydrogen peroxide[243]. Further oxidation of the sulfide-sulfoxide with an excess of 3-chloroperbenzoic acid results in the sulfoxide-sulfone[254]. The latter can be converted back to the disulfide derivative by the treatment with $TiCl_3$ in water[254] (Scheme 30).



SCHEME 30

The reduction of the sulfide-sulfoxide $[B_{12}H_{11}SS(O)B_{12}H_{11}]^{4-}$ with Zn or Sn in hydrochloric or acetic acid results in the parent mercapto derivative[261]. The oxidation-reduction procedure based on this reaction was proposed for purification of the $[B_{12}H_{11}SH]^{2-}$ anion[261].

The reaction of $[B_{12}H_{11}SH]^{2-}$ with various organic disulfides gives the corresponding unsymmetric disulfides[243,256,262] (Scheme 31).

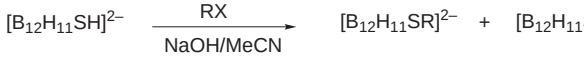


SCHEME 31

Acidification of a solution of $[B_{12}H_{11}SSCH_2CH_2COON(CO)_2(CH_2)_2]^{2-}$ in dimethyl sulfoxide with formic acid resulted in the formation of stable deep blue radical, providing evidence of a disulfide group linked to the boron cage[262].

The reactions of $[B_{12}H_{11}SH]^{2-}$ with 4-methylbenzenesulfinyl chloride and 4-methylbenzenesulfonyl chloride in water gave the same product, $[B_{12}H_{11}SSO_2C_6H_4CH_3]^{2-}$. No evidence of the sulfide-sulfoxide was observed[243].

Alkylation of the mercapto derivative with alkyl halides results, as a rule, in mixtures of the corresponding sulfide and sulfonium derivatives[248,263,264] (Scheme 32).

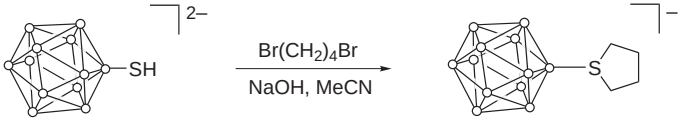


R = $(CH_3)_2CH$, $CH_2{=}CHCH_2$, $NCCH_2$, $NCCH_2CH_2$, $NC(CH_2)_3$, $CH_2{=}CHOCH_2CH_2$, $(CH_2)_2O_2CH(CH_2)_3$, $(C_2H_5O)_2CH(CH_2)_3$, $4\text{-}NCC_6H_4CH_2$

SCHEME 32

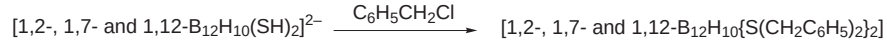
The monoalkylated compounds are formed with secondary halides, such as 2-iodopropane, whereas primary halides give mixtures of mono- and dialkyl products. This approach was successfully used in synthesis of boron-containing porphyrins[264,265] and glycosides[229,265,266].

The cyclic sulfonium derivative was obtained in the case of 1,4-dibromobutane[248] (Scheme 33).



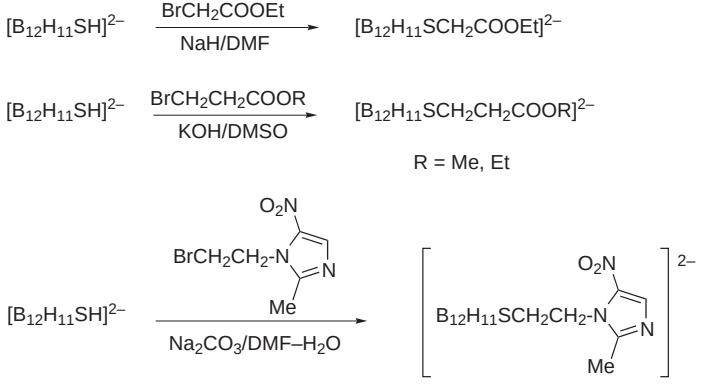
SCHEME 33

Alkylation of the dimercapto derivatives [1,2-, 1,7-, and 1,12-$B_{12}H_{10}(SH)_2]^{2-}$ gives the corresponding bis(sulfonium) derivatives[263] (Scheme 34).



SCHEME 34

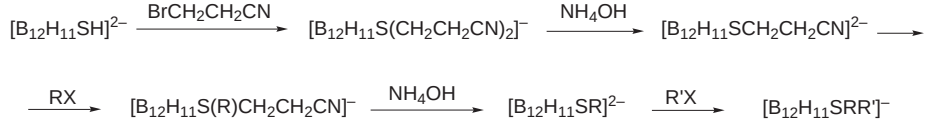
It should be noted that other authors report successful preparation of the monoalkylated derivatives containing various functional groups[267,268] (Scheme 35).



SCHEME 35

Alkylation of the $[B_{12}H_{11}SH]^{2-}$ anion was used to produce the artificial host molecule for various oxoanions (sulfate, 4-nitrophenyl phosphate, squarate, croconate, rhodizonate)[269–271] (Fig. 6).

It was found that the cyanoethyl group can be easily removed from the sulfonium sulfur atom by treatment with alkali and therefore it could be used as a convenient protective group for synthesis of monoalkyl and unsymmetrical dialkyl derivatives of the $[B_{12}H_{11}SH]^{2-}$ anion[248] (Scheme 36).



SCHEME 36

The structure of the $[B_{12}H_{11}SCH_2CH_2CN]^{2-}$ anion was determined by X-ray diffraction[272].

This approach has been successfully used in the synthesis of boron-rich building blocks for phosphodiester oligomers[272,273].

The dimethylsulfonium derivative $[B_{12}H_{11}SMe_2]^-$ was prepared by the treatment of the mercapto derivative with trimethylsulfonium iodide[189] (Scheme 37).

$$[B_{12}H_{11}SH]^{2-} \xrightarrow{Me_3SI} [B_{12}H_{11}SMe_2]^-$$

SCHEME 37

An other approach to the synthesis of the dimethylsulfonium derivatives consists in heating the *closo*-dodecaborate anion in dimethyl sulfoxide in the presence of acetic anhydride[274,275] (Scheme 38).

$$[B_{12}H_{12}]^{2-} \xrightarrow[Ac_2O]{Me_2SO} [B_{12}H_{11}SMe_2]^- \xrightarrow[Ac_2O]{Me_2SO} [B_{12}H_{10}(SMe_2)_2]$$

SCHEME 38

By a suitable choice of temperatures and concentrations, yields as high as 90% of the desired products can be obtained. The dipropylsulfonium derivative $[B_{12}H_{11}SPr_2]^-$ was prepared in a similar way[274].

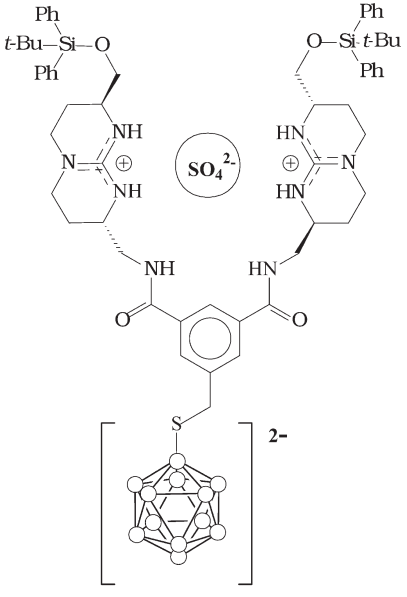
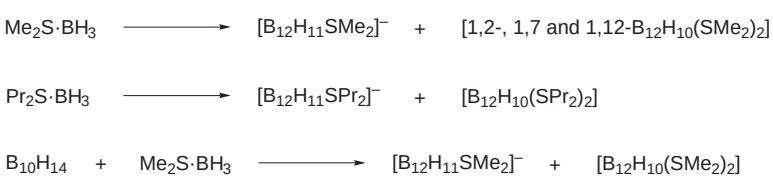


FIG. 6
Artificial host molecule based on the mercapto-*closo*-dodecaborate anion

An alternative route to synthesis of the dialkylsulfonium derivatives is the pyrolysis of dialkyl sulfide–borane complexes[8,9,276,277] or the reaction of the dimethyl sulfide–borane complex with decaborane[8] (Scheme 39).

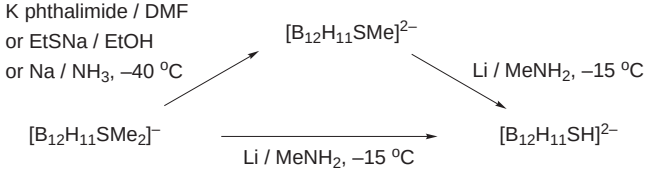


SCHEME 39

In all cases, the 1,7-isomer is the major component and only a small amount of the 1,2-isomer was isolated[277].

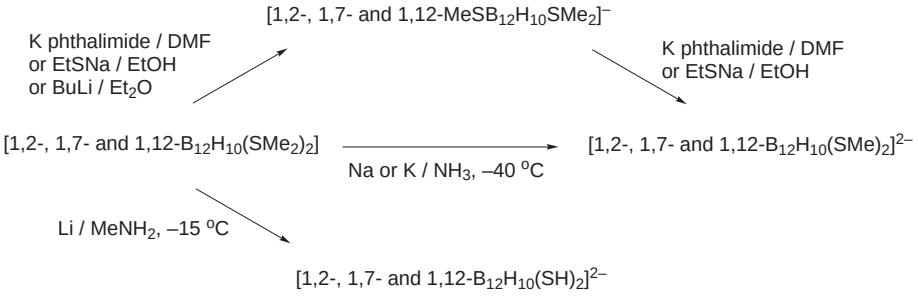
Formation of the dimethyl sulfide derivatives [1,7- and 1,12-$B_{12}H_{10}(SMe_2)_2$] was also found in the reaction of the $[B_{12}H_{12}]^{2-}$ anion with $[PdCl_2(SMe_2)_2]$ [218].

The dimethylsulfonium derivative $[B_{12}H_{11}SMe_2]^-$ can be partially demethylated by the treatment with potassium phthalimide in dimethylformamide, sodium ethylthiolate in ethanol, or alkali metal in liquid ammonia[278]. The second methyl group can be removed by the treatment with lithium metal in methylamine at –15 °C [263]. After some optimization of the $[B_{12}H_{11}SMe_2]^-$ synthesis, this method can be in principle used for preparation of the mercapto derivative of the *closo*-dodecaborate anion (Scheme 40).



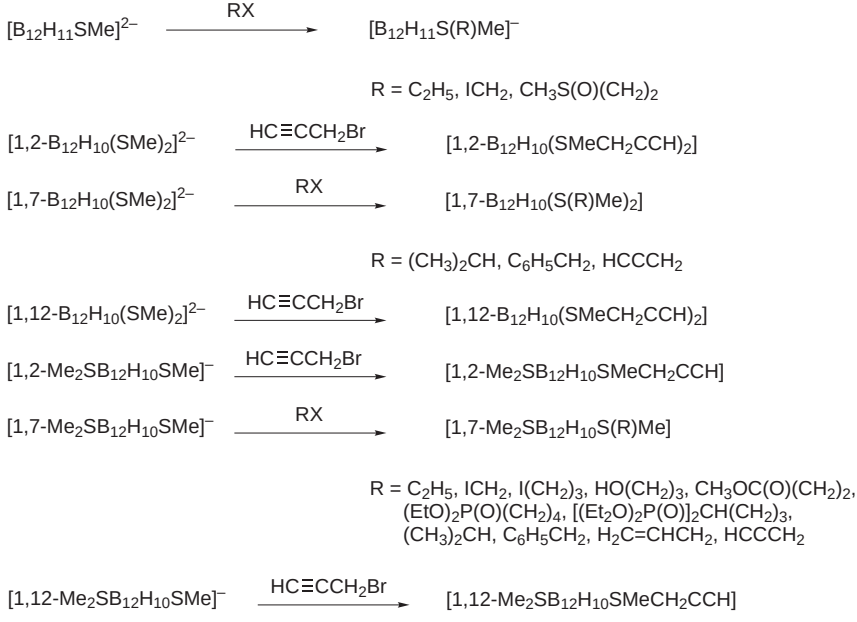
SCHEME 40

In a similar way, [1,2-, 1,7-, and 1,12-$B_{12}H_{10}(SMe_2)_2$] can be demethylated to the corresponding monoanions with potassium phthalimide in dimethylformamide, with butyllithium in ether, or with sodium ethylthiolate in ethanol. Using excess of potassium phthalimide or sodium ethylthiolate, the corresponding bis(methyl sulfide) derivative [1,2-, 1,7-, and 1,12-$B_{12}H_{10}(SMe)_2]^{2-}$ were prepared. The same results can be obtained with an excess of alkali metal in liquid ammonia[278]. Reduction of the bis(dimethylsulfonium) derivatives with lithium metal in methylamine at –15 °C results in the corresponding dimercapto derivatives [1,2-, 1,7-, and 1,12-$B_{12}H_{10}(SH)_2]^{2-}$ [263] (Scheme 41).



SCHEME 41

The methyl sulfide derivatives can be easily alkylated to give asymmetric sulfonium derivatives[275,279,280] (Scheme 42).



SCHEME 42

The bromination of [1,7-$B_{12}H_{10}(SMe_2)_2$] results in the formation of [1,7-$(Me_2S)_2$-9,10-Br_2-$B_{12}H_8$] which resembles bromination of *m*-carborane. The monobromo derivative [1,7-$(Me_2S)_2$-9-Br-$B_{12}H_9$] can be isolated as a major product from the reaction with one equivalent of brominating agent. The reaction of [1,12-$B_{12}H_{10}(SMe_2)_2$] with excess of Me_2SBr_2 at room temperature results in the monobromo derivative [1,12-$(Me_2S)_2$-2-Br-$B_{12}H_9$] [279].

The crystal and molecular structures of $(Ph_3PMe)_2[B_{12}H_{11}SMe]$ [278], (Me_3S)-$[B_{12}H_{11}SMe_2]\cdot MeCN$ [276], $(Ph_3PMe)[1,7\text{-}Me_2SB_{12}H_{10}SMe]$ [278], $[1,2\text{-}B_{12}H_{10}(SMe_2)_2]$ [277], $[1,7\text{-}B_{12}H_{10}(SMe_2)_2]$ [276], $[1,12\text{-}B_{12}H_{10}(SMe_2)_2]$ [276], and $[1,2\text{-}B_{12}H_{10}(SCH_2Ph)_2]\cdot CD_3CN$ [263] were determined by single-crystal X-ray diffraction.

Under basic conditions, the $[B_{12}H_{11}SH]^{2-}$ anion was shown to add to double bonds of Michael-type substrates giving the corresponding alkylsulfido derivatives[280–282].

The aryl sulfide derivative $[B_{12}H_{11}SC_6H_3\text{-}2,4\text{-}(NO_2)_2]^{2-}$ was obtained by the reaction of the dodecaborate anion with the 2,4-dinitrobenzenesulfenyl chloride[243].

Acylation of the mercapto derivative with acyl halides in acetonitrile in the presence of pyridine gave the corresponding thioesters in high yields[248,263] (Scheme 43).

$$[B_{12}H_{11}SH]^{2-} \xrightarrow{RCOCl} [B_{12}H_{11}SC(O)R]^{2-}$$

R = Me, Ph

SCHEME 43

The acetyl thioester $[B_{12}H_{11}SC(O)Me]^{2-}$ has been prepared also by heating of the $[B_{12}H_{12}]^{2-}$ anion in thioacetic acid[221] and by the reaction of the *closo*-dodecaborate anion with acetylsulfenyl chloride[243].

Oxidation of the methyl sulfide derivative $[B_{12}H_{11}SMe]^{2-}$ with hydrogen peroxide gives the corresponding methyl sulfone $[B_{12}H_{11}SO_2Me]^{2-}$, which can be reduced to the mercapto derivative with lithium in methylamine at –15 °C [263] (Scheme 44).

$$[B_{12}H_{11}SMe]^{2-} \xrightarrow[MeCN]{H_2O_2} [B_{12}H_{11}SO_2Me]^{2-} \xrightarrow[-15\ ^oC]{Li\ /MeNH_2} [B_{12}H_{11}SH]^{2-}$$

SCHEME 44

Reactions of the methyl sulfide derivatives $[B_{12}H_{11}SMe]^{2-}$, $[1,7(12)\text{-}Me_2SB_{12}H_{10}SMe]^{-}$, and $[1,7(12)\text{-}B_{12}H_{10}(SMe)_2]^{2-}$ with hydroxylamine-*O*-sulfonic acid gave unexpectedly the corresponding aminosulfonium salts $[B_{12}H_{11}SMeNH_2]^{-}$, $[1,7(12)\text{-}Me_2SB_{12}H_{10}SMeNH_2]$, and $[1,7(12)\text{-}B_{12}H_{10}(SMeNH_2)_2]$ [280].

The thiocyanate derivative $[B_{12}H_{11}SCN]^{2-}$ was first prepared by the reaction of the parent *closo*-dodecaborate anion with $(SCN)_2$ in dichloromethane[283,284] (Scheme 45).

$$[B_{12}H_{12}]^{2-} \xrightarrow[CH_2Cl_2]{(SCN)_2} [B_{12}H_{11}SCN]^{2-}$$

SCHEME 45

The alternative methods include the reaction of the $[B_{12}H_{12}]^{2-}$ anion with the thiocyanate ion under electrochemical and chemical oxidation conditions[285]. The thiocyanate group in $[B_{12}H_{11}SCN]^{2-}$ is very labile and cleaves easily in alkaline solution, by heating or UV irradiation[284]. The disubstituted derivatives [1,7- and 1,12-$B_{12}H_{10}(SCN)_2]^{2-}$ were obtained by the reaction of the $[B_{12}H_{12}]^{2-}$ anion with the thiocyanate ion under chemical oxidation conditions[285].

Slow addition of ethanolic solution of iodine to aqueous solution of $[B_{12}H_{11}SCN]^{2-}$ results in formation of [1-I-12-NCS-$B_{12}H_{10}]^{2-}$ [238].

The crystal structures of $Cs_2[B_{12}H_{11}SCN]$ [279], $[(Ph_3P)_2N]_2[1,7\text{-}B_{12}H_{10}(SCN)_2]$ [285], $(Et_4N)_2[1,12\text{-}B_{12}H_{10}(SCN)_2]$ [285], and $(Ph_4P)_2[1,12\text{-}B_{12}H_{10}(I,SCN)_2]$ [286] were determined by X-ray diffraction.

9. DERIVATIVES WITH BORON–SELENIUM BOND

The selenocyanato derivative $[B_{12}H_{11}SeCN]^{2-}$ was prepared by the reaction of the *closo*-dodecaborate anion with $(SeCN)_2$ in dichloromethane at –100 °C [287] and the reaction of the $[B_{12}H_{12}]^{2-}$ anion with selenocyanate anion under electrochemical oxidation conditions[285]. Crystal structure of $(Ph_4P)_2[B_{12}H_{11}SeCN]$ was determined by X-ray diffraction[287] (Scheme 46).

$$[B_{12}H_{12}]^{2-} \xrightarrow{(SeCN)_2} [B_{12}H_{11}SeCN]^{2-}$$

$$[B_{12}H_{12}]^{2-} \xrightarrow[-2\ e]{SeCN^-} [B_{12}H_{11}SeCN]^{2-}$$

SCHEME 46

A series of metal salts of the unusual hexaselenoborato-*closo*-dodecaborate anion $[B_{12}(BSe_3)_6]^{8-}$ has been prepared by direct high-temperature solid-state synthesis from the corresponding metal selenides, boron, and selenium. The trigonal-planar BSe_3 selenoborate entities functioning as bidentate ligands complete the B_{12} icosahedron to form a persubstituted *closo*-dodecaborate anion (Fig. 7). The crystal structures of $Cs_8[B_{12}(BSe_3)_6]$, $Rb_8[B_{12}(BSe_3)_6]$, $Cs_4Hg_2[B_{12}(BSe_3)_6]$, and $Rb_4Hg_2[B_{12}(BSe_3)_6]$ were determined by single crystal diffraction[288,289]. The other structure type was found in the sodium salt $Na_6[B_{18}Se_{17}]$: the neighbouring icosahedral B_{12} cluster entities saturated with trigonal-planar BSe_3 units are connected in

one direction *via* exocyclic selenium atoms forming the infinite chain anion $([B_{18}Se_{16}Se_{2/2}]^{6-})_Y$ [290].

10. METALLO DERIVATIVES

The reactions of the *closo*-dodecaborate anion with mercury acetate and trifluoroacetate gave metallated derivatives $[B_{12}H_{12-n}(HgOC(O)CX_3)_n]^{2-}$ (X = H, F; n = 1–12)[291,292]. However, in contrast to the mercurated carborane derivatives[293], the metallated dodecaborate derivatives are unstable and easily decompose in solution and in the solid state.

11. POTENTIAL APPLICATIONS OF *closo*-DODECABORATE DERIVATIVES

If we try to survey possible directions of application of the *closo*-dodecaborate anion and its derivatives, the military direction should be mentioned as the first one. The interest in high boron hydrides as high energy density materials, which arose at the time of Project ZIP, still persists. In this field the *closo*-dodecaborate anion takes advantage of high stability under usual conditions that allows to use its salts as components of high burning composite propellants[294–296]. An important field is using lithium *closo*-dodecaborates $Li_2[B_{12}H_{12}]$ and $Li_2[B_{12}Cl_{12}]$ as nonaqueous electrolytes for advanced rechargable lithium batteries[149,297–300]. Among the other fields of potential application of the *closo*-dodecaborate derivatives, we could mention thermally stable polymers[172], non-linear optics materials[301],

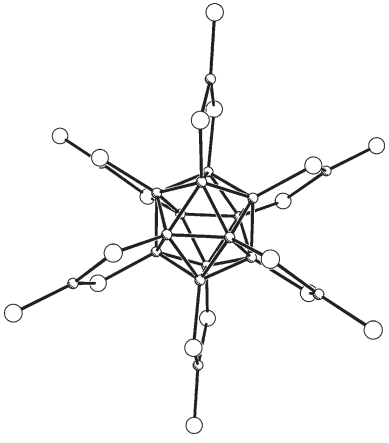


FIG. 7
Structure of the $[B_{12}(BSe_3)_6]^{2-}$ anion

extractants for purification of nuclear wastes[185,235], ion-selective electrodes[302], manufacture of boron carbide[303], catalysts for organic synthesis[304], *etc.* However, the main direction of application of the *closo*-dodecaborate derivatives nowadays is medicine[305].

The possibility of the application of the *closo*-dodecaborate anion in medicine is based on its remarkable chemical and hydrolytical stability and low toxicity. The sodium salt $Na_2[B_{12}H_{12}]$ administered orally to rats was found to have a low order of acute toxicity, with the approximate lethal dose for rats >7.5 g/kg of body weight which is roughly comparable to that of sodium chloride[38].

The leading position in application of polyhedral boron hydrides in medicine belongs to Boron Neutron Capture Therapy (BNCT) – a binary cancer treatment based upon the interaction of two relatively harmless species, a ^{10}B nucleus and a thermal neutron. Capture of the thermal neutron by the ^{10}B nucleus results in the formation of an excited ^{10}B nucleus which decays to yield highly energetic ^{4}He and ^{7}Li as products. Each of these fission products has an effective range of ≈10 μm in tissue, thus effectively limiting the extent of cell damage to approximately one cell diameter. Therefore, the selective concentration of the ^{10}B nuclei within tumor cells, followed by their capture of thermal neutrons, should result in localized destruction of the malignant cells in the presence of the neighboring normal cells[306–309].

The main advantages of the *closo*-dodecaborate anion and its derivatives, in comparison with the extensively explored carborane derivatives, are their high water solubility as sodium salts and simple methods of the parent anion synthesis from ^{10}B-enriched raw material. It should be noted that sodium borocaptate $Na_2[B_{12}H_{11}SH]$ is one of two clinically used BNCT agents.

Although most BNCT research has been focused mainly on malignant tumor cells, this general approach is applicable to any diseased tissue of localized nature. Rheumatoid arthritis (RA) afflicts more than 1% of the adult population and is the most common cause of chronic inflammatory synovitis. The application of BNCT in the treatment of arthritis (boron neutron capture synovectomy) has been proposed[310].

The *closo*-dodecaborate cage could be used also as a linker for the introduction of a radiohalogen label into biomolecules for radioimmunodiagnostics and radioimmunotherapy. Radioactive halogen isotopes play an important role in nuclear medicine. ^{123}I is widely used for gamma-scintigraphy and single-photon emission computerized tomography, and ^{131}I is currently the main radionuclide for radioisotope therapy. There is an increasing interest in application of positron emission tomography in stud-

ies of large biomolecules such as monoclonal antibodies, their fragments and shorter peptides, which necessitates the use of positron-emitting halogens like ^{76}Br and ^{124}I. The α-emitting halogen ^{211}At is considered to be one of the most promising therapeutical nuclides in the near future. However, there is a serious problem in the medical application of radiohalogens, "dehalogenation", *i.e.*, the relatively rapid release of radioactivity from the cells after intracellular processing of the labelled compound.

The feasibility of labelling the parent *closo*-dodecaborate anion with different radiohalogen isotopes has been shown recently and the high stability of the radiohalogen label *in vivo* has been demonstrated[311–317]. Recently the isothiocyanate derivative $[B_{12}H_{11}NH_2CH_2C_6H_4\text{-}4\text{-}NCS]^-$ was proposed as linker for indirect radioiodination and radiobromination of proteins[318,319].

Another possibility of medical application of the *closo*-dodecaborate anion is X-ray contrasting imaging. Highly iodinated molecules have been used in medicine as X-ray contrast agents due to the opacity of iodine atoms to low-energy X-rays[320]. Even with the recent phenomenal growth of Magnetic Resonance Imaging and ultrasound procedures, X-ray imaging studies remain the workhorse of modern radiology (currently 75–80% of all diagnostic imaging procedures are X-ray related). Today, iodinated X-ray contrast agents are used in about 20 million procedures annually in the U.S.A., mainly in computing tomography and angiographic applications. Sales of these agents in the U.S.A. exceeded $550 million in 1997 [321].

Current X-ray contrast agents are composed of substituted iodinated benzene compounds and their dimers. Most of the iodinated benzene derivatives have three iodine atoms substituted in an alternating fashion with other substituents which are designed to increase water solubility and decrease *in vivo* toxicity. Although the current radiographic contrast media have been optimized over many years of development, improvements are still being sought. A method of improving contrast agents is to increase the iodine content in the molecules. It is known that an increase in the percentage of iodine in a contrast agent from 28.7 to 37.5% doubles the contrast of the radiographic image at selected X-ray energies. This fact suggests that chemical moieties other than benzene rings, which can be more highly iodinated, might present new alternatives for contrast agents. The *closo*-dodecaborate cage can be easily halogenated and have the potential of incorporation of a large number of iodine atoms per molecule (compounds containing 65–85 wt.% of iodine can be obtained)[322,323].

Besides the above-mentioned general applications of the *closo*-dodecaborate derivatives, some of them have specific physiological activity. It has

been found that alkylammonium dodecaborates are potent hypolipidemic[324] and antineoplastic[325] agents.

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