FIFTY YEARS OF THE *closo*-DECABORATE ANION CHEMISTRY

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We have the pleasure to dedicate this paper to Professor Bohumil Štíbr on the occasion of his 70th birthday in recognition of his outstanding contribution to boron cluster chemistry.

The review covers the fifty-year period of chemistry of the *closo*-decaborate anion $[B_{10}H_{10}]^{2-}$ from the first report by Hawthorne and Pitochelli. The main attention is paid to reactions of substitution of various atoms and groups for hydrogen atoms. The general stability of the *closo*-decaborate cage, including its protonation, cage-opening and cage oxidation reactions, is considered as well. A review with 242 references.

Keywords: *closo*-Decaborate; Boranes; Synthesis; Derivatives; Applications.

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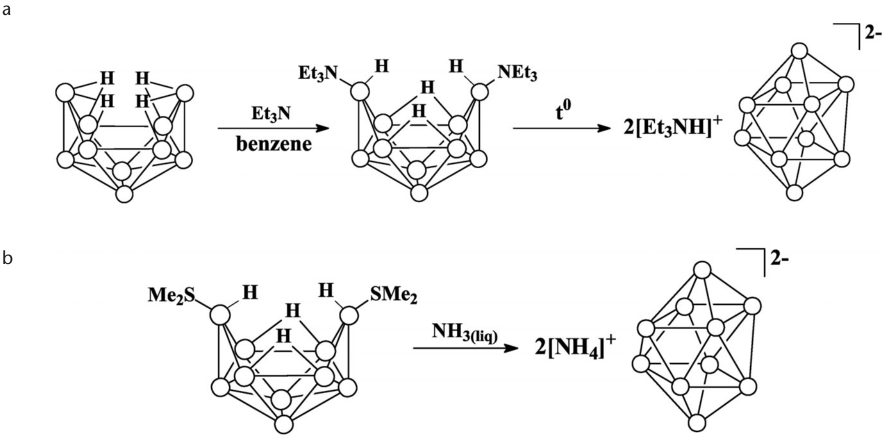
1. INTRODUCTION

Last year it was 50th anniversary of the synthesis of decahydro-*closo*-decaborate anion, the first representative of the *closo*-borane family, which was reported by Hawthorne and Pitochelli[1]. It was the first-born, however, at present it is not the first-string in the boron hydride team starring icosahedral carboranes $C_2B_{10}H_{12}$ [2], *closo*-dodecaborate $[B_{12}H_{12}]^{2-}$ (ref.[3]), carba-*closo*-dodecaborate $[CB_{11}H_{12}]^-$ (ref.[4]) and cobalt bis(dicarbollide) $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ (ref.[5]). Nevertheless, through the last fifty years salts, complexes and derivatives of the *closo*-decaborate anion have been the subject of many investigations. Due to non-icosahedral structure of the $[B_{10}H_{10}]^{2-}$ anion, having structure of bicapped square antiprism with two different types of boron atoms (five-coordinated apical and six-coordinated equatorial), some aspects of its chemistry are unique and have not analogies in the chemistry of icosahedral boron hydrides. Although the chemistry of the $[B_{10}H_{10}]^{2-}$ anion has been studied rather extensively, no reviews on this field have appeared for a long years after the first survey by Hawthorne[6]. Only very recently two reviews taking into consideration different aspects of the $[B_{10}H_{10}]^{2-}$ chemistry have been published[7,8]. However, both these works do not cover all the field of research and are not easily readable due to language problems. Herein we present a review of the current state of the *closo*-decaborate chemistry with a special emphasis on the synthesis and properties of its substituted derivatives.

2. SYNTHESIS OF THE $[B_{10}H_{10}]^{2-}$ ANION

There are two general approaches to the synthesis of the decahydro-*closo*-decaborate anion. The first one is based on a closure of *nido*-decaborane skeleton. The preparative syntheses include reactions of decaborane[1,9] or 6,9-bis(acetonitrile)decaborane[1] with triethylamine in refluxing benzene giving triethylammonium *closo*-decaborate $(Et_3NH)_2[B_{10}H_{10}]$ in 92% yield (Scheme 1a) or the reaction of 6,9-bis(dimethylsulfane)decaborane with liquid ammonia giving ammonium *closo*-decaborate $(NH_4)_2[B_{10}H_{10}]$ in 84% yield[10] (Scheme 1b).

Related reactions are mechanochemical activation of 6,9-bis(ammonia)-decaborane and pyridine hydrochloride[11] and thermal decomposition of europium(II) and ytterbium(II) complexes of *arachno*-decaborate anion $(L)_xLn[B_{10}H_{14}]$ (Ln = Eu, Yb; L = NH_3, MeCN)[12] resulting in $(PyH)_2[B_{10}H_{10}]$ and $Eu[B_{10}H_{10}]$ and $Yb[B_{10}H_{10}]$, respectively. The above described methods allow one to produce the *closo*-decaborate anion in a straightforward and



SCHEME 1

high-yield way, however the absence of a commercial source of decaborane makes them uneconomical.

Alternative approach is based on solid state pyrolysis (185 °C) of easily available tetraethylammonium tetrahydroborate resulting in tetraethylammonium *closo*-decaborate $(Et_4N)_2[B_{10}H_{10}]$ in up to 94% yield[13–17]. $(Et_4N)_2[B_{12}H_{12}]$, $(Et_4N)_2[B_9H_9]$ and $(Et_4N)[B_{11}H_{14}]$ were found to be the by-products of the pyrolysis process. It should be noted that the products ratio and the yield of the goal product of the solid state synthesis depend strongly on such factors as amount of the starting material, size and geometry of the reaction vessel, heating rate and conditions, etc. As a result, the results published by different research groups often could not be reproduced. This problem can be partially solved by using high-boiling hydrocarbons as reaction media. Thus, pyrolysis of $(Et_4N)[BH_4]$ in refluxing decane-dodecane mixture at 185 °C gives up to 50% of $(Et_4N)_2[B_{10}H_{10}]$ [16,17] (Scheme 2).

$$Et_4NBH_4 \xrightarrow[\text{decane-dodecane}]{185\ ^oC} (Et_4N)_2[B_{10}H_{10}]$$

SCHEME 2

The pyrolysis mechanism is not clear, nevertheless the octahydrotriborate anion $[B_3H_8]^-$ is a key intermediate of the process. The study of solid state pyrolysis of tetraethylammonium octahydrotriborate at 185 °C revealed formation of $(Et_4N)_2[B_{10}H_{10}]$ in up to 79% yield[13,16]. Pyrolysis of $(Et_4N)[B_3H_8]$ in hydrocarbons (*trans*-decaline or decane–dodecane mixture) at 185 °C gives 28–47% of $(Et_4N)_2[B_{10}H_{10}]$ [16,18]. As in the solid state pyrolysis, $(Et_4N)_2[B_{12}H_{12}]$, $(Et_4N)_2[B_9H_9]$ and $(Et_4N)[B_{11}H_{14}]$ are the reaction byproducts. It should be noted that the nature of the pyrolysis products is very sensitive to the cation nature. Thus, solid state pyrolysis of tetramethylammonium tetrahydroborate under similar conditions gives mainly trimethylamine borane. On the other hand, the solid state pyrolysis of $(Me_4N)[B_3H_8]$ results in nearly equimolar mixture of $(Me_4N)_2[B_{10}H_{10}]$ and $(Me_4N)_2[B_{12}H_{12}]$ [13]. These results could be explained by participation of $Et_3N{\cdot}BH_3$ formed in the initial step of the $(Et_4N)[BH_4]$ pyrolysis during building up of the octahydrotriborate anion, whereas $Me_3N{\cdot}BH_3$ having lower boiling point leaves the reaction. The addition of triethylamine borane to $(Et_4N)[BH_4]$ or $(Et_4N)[B_3H_8]$ changes ratio of the pyrolysis products but does not increase the yield of the *closo*-decaborate anion[16,17]. Solid state pyrolysis of $K[B_3H_8]$ at 185 °C produces nearly equimolar mixture of the $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ anions as well as some amount of $[B_{11}H_{14}]^-$ (ref.[14]), whereas increasing the temperature to 230 °C leads mainly to $[B_9H_9]^{2-}$ and $[B_{12}H_{12}]^{2-}$ (ref.[19]). Pyrolysis of $Rb[B_3H_8]$ at 230 °C gives a mixture of the $[B_9H_9]^{2-}$, $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ anions[19]. Pyrolysis of $Cs[B_3H_8]$ at 185 °C gives mainly $[B_{10}H_{10}]^{2-}$ and $[B_{11}H_{14}]^-$ (ref.[13]), whereas at 230 °C $[B_9H_9]^{2-}$, $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ are formed[19]. Solid state pyrolysis of $(n\text{-}Pr_4N)[B_3H_8]$ at 185 °C produces solely the $[B_{12}H_{12}]^{2-}$ anion, whereas the pyrolysis in hydrocarbons results in 20% of the *closo*-decaborate anion. In a similar way, solid state pyrolysis of $(n\text{-}Bu_4N)[B_3H_8]$ at 185 °C gives mainly $[B_{12}H_{12}]^{2-}$, whereas the pyrolysis in hydrocarbons results in nearly equimolar mixture of the $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ anions[18]. Closely related syntheses include reactions of sodium tetrahydroborate $Na[BH_4]$ and $R_3N{\cdot}BH_3$ (R = Me, Et) in dodecane in the presence of $AlCl_3$ at 180 °C producing the *closo*-decaborate anion in 32–41% yield[20] and pyrolysis of mixtures of $M[BH_4]$ and $(Et_4N)X$ (M = Na, K; X = Cl, Br) at 185 °C giving up to 76% of $(Et_4N)_2[B_{10}H_{10}]$ [21,22]. In general, the study of pyrolysis of various tetrahydroborates and octahydrotriborates revealed that the direction of the reaction and the yield of *closo*-borate anions depend strongly on nature of the cation, the temperature and the solvent used.

3. SALTS AND COMPLEXES OF THE $[B_{10}H_{10}]^{2-}$ ANION

At present, a number of salts of the *closo*-decaborate anion with various metal cations (lithium[10,23], sodium[10,24], potassium[24], rubidium[24,25], cesium[10], cobalt[10], nickel[10], rare earth metals[12,26]) and ammonium cations (NH_4^+ (refs[10,27,28]), $MeNH_3^+$ (ref.[27]), $Me_2NH_2^+$ (ref.[27]), Me_3NH^+ (ref.[29]), Me_4N^+ (refs[10,27]), $EtNH_3^+$ (ref.[27]), $Et_2NH_2^+$ (ref.[27]), Et_3NH^+ (refs[29,30]), Et_4N^+ (refs[13,27]), *n*-$BuNH_3^+$ (ref.[27]), *n*-$Bu_2NH_2^+$ (ref.[27]), *n*-Bu_3NH^+ (ref.[29]), *n*-Bu_4N^+ (ref.[27]), *t*-$BuNH_3^+$ (ref.[10]), H_2en^{2+} (ref.[31]), $(CH_2)_5N(Me)NH_2^+$ (ref.[32]), $Me_2N(CH_2CH_2)_2NMe_2^{2+}$ (ref.[32]), $NH_2(Me)N(CH_2CH_2)_2N(Me)NH_2^{2+}$ (ref.[32]), H_2dabco^{2+} (ref.[33]), Hpy^+ (ref.[10]), *N*-$Mepy^+$ (ref.[32]), *N*-$C_{12}H_{25}py^+$ (ref.[34]), *N*-NH_2py^+ (ref.[32]), quinolinium$^+$ (ref.[10]), H-2,2′-bipy$^+$ (ref.[10]), $H(2\text{-}py)_2NH^+$ (ref.[35]), pseudocyanine$^+$ (ref.[36]), $NH_2NH_3^+$ (ref.[37]), $NH_2NMe_3^+$ (ref.[32]), $Me_2N(NH_2)_2^+$ (ref.[32]), $[CpFeC_5H_4CH_2NMe_2R]^+$ and $[Fe(C_5H_4CH_2NMe_2R)_2]^{2+}$ (R = Me, Et, Pr, $CH_2CH{=}CH_2$, $CH_2C{\equiv}CH$)[38], $[(CpFeC_5H_4CH_2NMe_2)_2R]^{2+}$ and $[Fe(C_5H_4CH_2NMe_2)_2R]^{2+}$ (R = $\text{-}(CH_2)_4\text{-}$, $\text{-}CH_2C{\equiv}CCH_2\text{-}$)[39]), as well as sulfonium[10], phosphonium[40–43], arsonium[43] and guanidinium[44–46] salts have been described.

The crystal structures of $Na_2[B_{10}H_{10}]$ [24], $K_2[B_{10}H_{10}]$ [24], $Rb_2[B_{10}H_{10}]$ [24], $Rb_2[B_{10}H_{10}]\cdot 1.5H_2O$ [25], $Cs[Na(NH_3)_6][B_{10}H_{10}]\cdot NH_3$ [47], $(NH_4)_2[B_{10}H_{10}]\cdot 1.5H_2O$ [28], $(Me_3NH)_2[B_{10}H_{10}]$ [48], $(Et_3NH)_2[B_{10}H_{10}]$ [30], (*N*-$C_{12}H_{25}py)_2[B_{10}H_{10}]$ [34], (H-2,2′-bipy)$_2[B_{10}H_{10}]$ [49], (H_2-2,2′-bipy)$[B_{10}H_{10}]$ [49], $(H(2\text{-}py)_2NH)_2[B_{10}H_{10}]\cdot 2H_2O$ [35], $[(2,2'\text{-}(1\text{-}Et\text{-}1\text{-}NC_9H_6)_2CH]_2[B_{10}H_{10}]$ [36], $[CpFe(C_5H_4CH_2NMe_3)]_2[B_{10}H_{10}]$ [50], $(Ph_3PEt)_2[B_{10}H_{10}]$ [40] and $(Et_3PNH_2)_2[B_{10}H_{10}]$ [43] have been determined by X-ray diffraction method. In some structures the NH···HB dihydrogen bonds between ammonium cation and the *closo*-decaborate anion were found[28,30,33,43,48,49].

It should be noted that the structure of the *closo*-decaborate anion was determined for the first time by X-ray diffraction study of the cuprous salt $Cu_2[B_{10}H_{10}]$ [51]. However, due to existence of strong interactions between the cations and anions, this compound should be considered as the polymeric complex rather than a simple salt. The characteristic feature of the Cu–H–B interactions is appearance of a broad IR absorption band at 2100–2300 cm^{-1} in addition to the terminal B–H stretching bands at 2510–2570 cm^{-1} (ref.[52]). Later a series of "mixed salts" $M\{Cu[B_{10}H_{10}]\}$ (M = K^+, Cs^+, $R_2NH_2^+$, R_3NH^+, R_4N^+ (R = Me, Et, Bu), Ph_4P^+, $NaphCH_2PPh_3^+$, Ph_4As^+) was prepared by the reaction of copper(II) chloride or sulfate with the corresponding *closo*-decaborates in aqueous solution[41,53–55]. The single crystal X-ray diffraction study of $Cs\{Cu[B_{10}H_{10}]\}$, $(Me_2NH_2)\{Cu[B_{10}H_{10}]\}$ and $(Et_3NH)\{Cu[B_{10}H_{10}]\}$ revealed that the Cu^+ cations and the $[B_{10}H_{10}]^{2-}$ anions form infinite polymeric anionic chains $(\{Cu[B_{10}H_{10}]\}^+)_\infty$ connected by the Cu–H–B bonds[41,55,56]. The monomeric copper(I) complexes $\{(Ph_3P)_2Cu\}_2[B_{10}H_{10}]$ [56,57] and $\{(MeCN)_2Cu\}_2[B_{10}H_{10}]$ [59] were obtained by reactions in

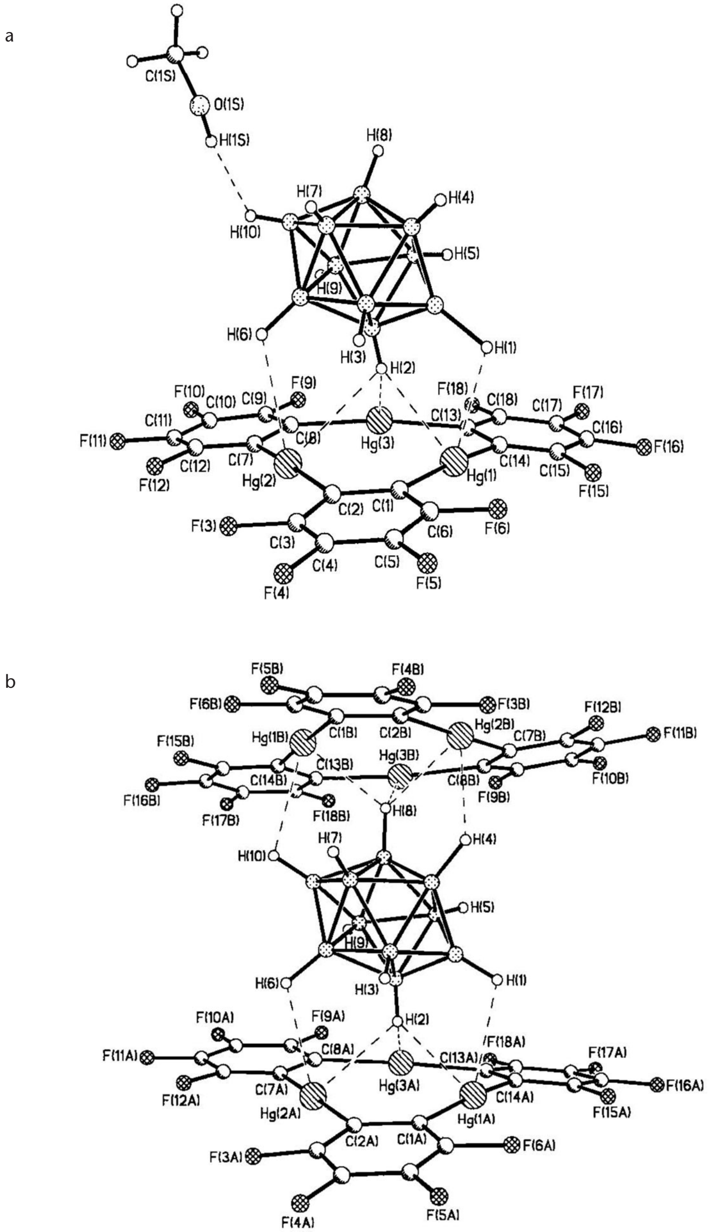


FIG. 1

Molecular structure of $(n\text{-Bu}_4\text{N})_2\{(o\text{-C}_6\text{F}_4\text{Hg})_3\}[\text{B}_{10}\text{H}_{10}]\cdot\text{MeOH}$ (a) and $(\text{PPN})_2\{(o\text{-C}_6\text{F}_4\text{Hg})_3\}_2[\text{B}_{10}\text{H}_{10}]\cdot\text{Et}_2\text{O}$ (b). Reproduced from ref.[66] with permission of Wiley–VCH Verlag GmbH & Co.

non-aqueous media and their structures were determined by single crystal X-ray diffraction method.

Synthesis of similar silver(I) complexes $\{Ag_2[B_{10}H_{10}]\}$ [10] and $M\{Ag[B_{10}H_{10}]\}$ ($M = Cs^+$, $R_2NH_2^+$, R_3NH^+, R_4N^+ (R = Me, Et, Pr, Bu))[60] was described and the crystal structures of $Cs\{Ag[B_{10}H_{10}]\}$ [60], $(Et_3NH)\{Ag[B_{10}H_{10}]\}$ [60] and $\{Ag_2[B_{10}H_{10}](DMF)\}$ [61] were determined by single crystal X-ray diffraction method. It should be noted that in the presence of both Cu^+ and Ag^+ cations the preferential coordination of the *closo*-decaborate anion to the silver cation takes place resulting in formation of $[Cu(NCMe)_3]\{Ag[B_{10}H_{10}]\}$ [59]. Synthesis and structure of silver(I) complexes with triphenylphosphine ligand $\{((Ph_3P)Ag)_2[B_{10}H_{10}]\}_n$ [62], $\{(Ph_3P)_2Ag\}_2[B_{10}H_{10}]$ [58] were described. Complexation of the *closo*-decaborate anion with cyclic trinuclear copper and silver 3,5-bis(trifluoromethyl)pyrazolates $\{[3,5\text{-}(CF_3)_2pz]Cu\}_3$ and $\{[3,5\text{-}(CF_3)_2pz]Ag\}_3$ was reported[63].

Only few examples of other than copper(I) and silver(I) complexes containing the $[B_{10}H_{10}]^{2-}$ anion in the inner coordination sphere where reported. They are $\{(Pb(2,2'\text{-bipy})[B_{10}H_{10}]\}$, $\{(Pb(1,10\text{-phen})[B_{10}H_{10}]\}$ [64], $\{cis\text{-}((Ph_3P)_2Pt)[B_{10}H_{10}]\}$ [65] and the complexes with cyclic trimeric tetrafluoro-1,2-phenylene mercury and [12]-mercuracarborand-4. Crystal structures of $\{(Pb(2,2'\text{-bipy})[B_{10}H_{10}]\}$ [64], $(n\text{-}Bu_4N)_2\{(o\text{-}C_6F_4Hg)_3\}[B_{10}H_{10}]\cdot MeOH$ (Fig. 1a)[66], $(PPN)_2\{(o\text{-}C_6F_4Hg)_3\}_2[B_{10}H_{10}]\cdot Et_2O$ (Fig. 1b)[66] and $(Ph_3PMe)_4\{(o\text{-}1,2\text{-}C_2B_{10}H_8\text{-}9,12\text{-}Et_2Hg)_4\}[B_{10}H_{10}]_2$ (Fig. 2)[67] were determined.

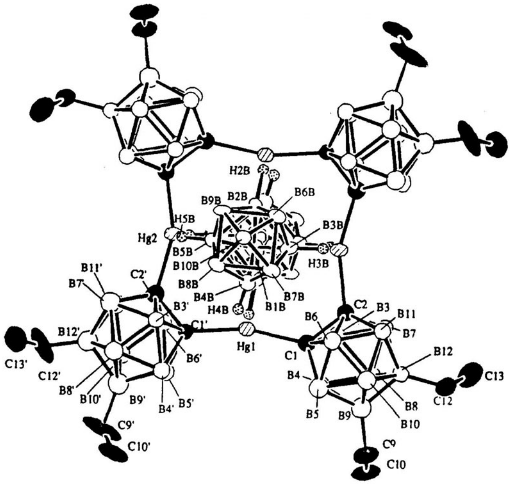
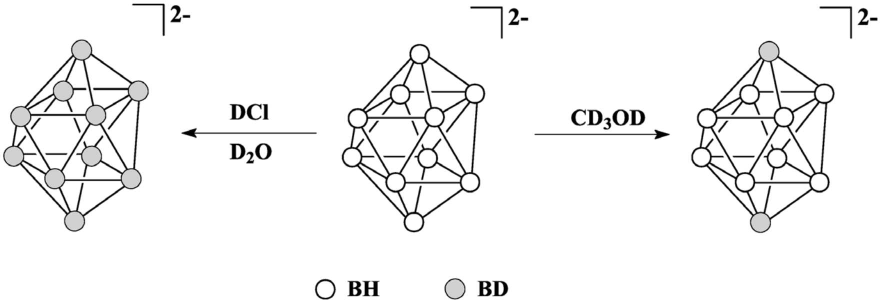


FIG. 2
Molecular structure of $(Ph_3PMe)_4\{(o\text{-}1,2\text{-}C_2B_{10}H_8\text{-}9,12\text{-}Et_2Hg)_4\}[B_{10}H_{10}]_2$. Reproduced from ref.[67] with permission of American Chemical Society

Syntheses of complexes of nickel[10,35,67–73], cobalt[10,67–71,75,76], iron[77,78], chromium[79], lead[80], cadmium[81], rare earth metals[82–86] and uranium[87], where *closo*-decaborate serves as outer-sphere anion, were reported. Crystal structures of $[Cd_2\{1,2\text{-}C_6H_4(NH_2)_2\}_5(DMF)_4][B_{10}H_{10}]_2$ (ref.[81]) and $[UO_2\{OC(NH_2)_2\}_5][B_{10}H_{10}]\cdot 2OC(NH_2)_2$ (ref.[87d]) were determined.

4. THE H–D EXCHANGE AND PROTONATION

In contract to $[B_{12}H_{12}]^{2-}$, the *closo*-decaborate anion was found to be strongly hydrated in aqueous solutions. Water molecules were considered to hydrogen bond mainly at the two apical vertex of the $[B_{10}H_{10}]^{2-}$ anion[88]. There is rapid proton exchange between water and the *closo*-decaborate anion under acidic conditions. This effect is clearly evidenced by rapid changes in the characteristic ^{11}B NMR spectrum of solution of the $[B_{10}H_{10}]^{2-}$ anion in D_2O on addition of catalytic amount of DCl resulting in the perdeuterated product $[B_{10}D_{10}]^{2-}$ (Scheme 3). The H–D exchange at the apical vertex was found to proceeds five times faster than at the equatorial vertex and 330-fold faster than in $[B_{12}H_{12}]^{2-}$ (ref.[10]).



SCHEME 3

The selectively deuterated *closo*-decaborate anion $[1,10\text{-}B_{10}H_8D_2]^{2-}$ was prepared by the reaction of $[B_{10}H_{10}]^{2-}$ with methanol-d_4 at room temperature[89] (Scheme 3). The selective H–D exchange could be explained by preferable solvation at the apical vertex of the *closo*-decaborate anion[90]. Somewhat later the effect of various substituents on the H–D exchange in *closo*-decaborate derivatives was studied[91].

In aqueous solution the acid form of the *closo*-decaborate anion exhibits properties of strong acid comparable to sulfuric acid and can be isolated in the solid state as the tetrahydrate[10]. In non-aqueous solutions *closo*-decaborate reacts with strong acids with formation of the protonated form $[B_{10}H_{11}]^-$. Protonation of the $[B_{10}H_{10}]^{2-}$ anion with formation of $[B_{10}H_{11}]^-$

was first reported at the beginning of the 1970s [92]. Although a series of salts of the $[B_{10}H_{11}]^-$ anion with various cations (R_4N^+ (R = Me, Et, Pr, Bu), Ph_3RP^+ (R = Et, Ph, CH_2Ph), Ph_4As^+) has been prepared[93–95], our the knowledge on the nature of this species until recently was based mainly on the NMR spectroscopy data[92–94] and quantum chemical calculations[93,96]. The early published structural studies of $(Ph_4P)[B_{10}H_{11}]$ and $(Ph_3PEt)[B_{10}H_{11}]$ could not refine the position of the extra proton associated with the B_{10} cluster[97]. More recently the exact structure of the $[B_{10}H_{11}]^-$ anion was determined by single crystal diffraction study of $(Ph_3PCH_2Ph)[B_{10}H_{11}]$ (Fig. 3a)[93] and $(Ph_3PCH_2Naph)[B_{10}H_{11}]$ [40]. The 11th hydrogen atom asymmetrically caps a polar face of the B_{10} cluster (the $B_{ap}–H_{(11)}$ and $B_{eq}–H_{(11)}$ bond lengths for $(Ph_3PCH_2Ph)[B_{10}H_{11}]$ were found to be 1.20 and 1.54 Å at –123 °C, and 1.07 and 1.55 Å at 24 °C, respectively). The significant elongation of bonds lengths between the boron atoms that are capped by the 11th hydrogen was found as well[93]. In solution, migration of the extra hydrogen atom H(*) over the neighbor polar faces complicated by an exchange process between the H(1) and H(*) atoms takes place. The fluxional behavior of H(1) and H(*) can be stopped at low temperatures (–90 °C) (Fig. 3b)[93].

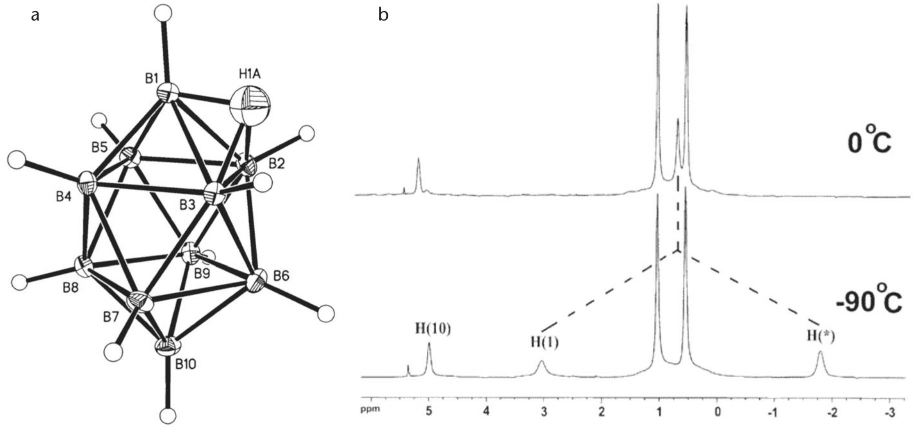


FIG. 3
Structure of the $[B_{10}H_{11}]^-$ at 24 °C (a) and $^1H\{^{11}B\}$ spectra of $[PPh_4][B_{10}H_{11}]$ at –90 and 0 °C (b). Reproduced from ref.[93] with permission of American Chemical Society

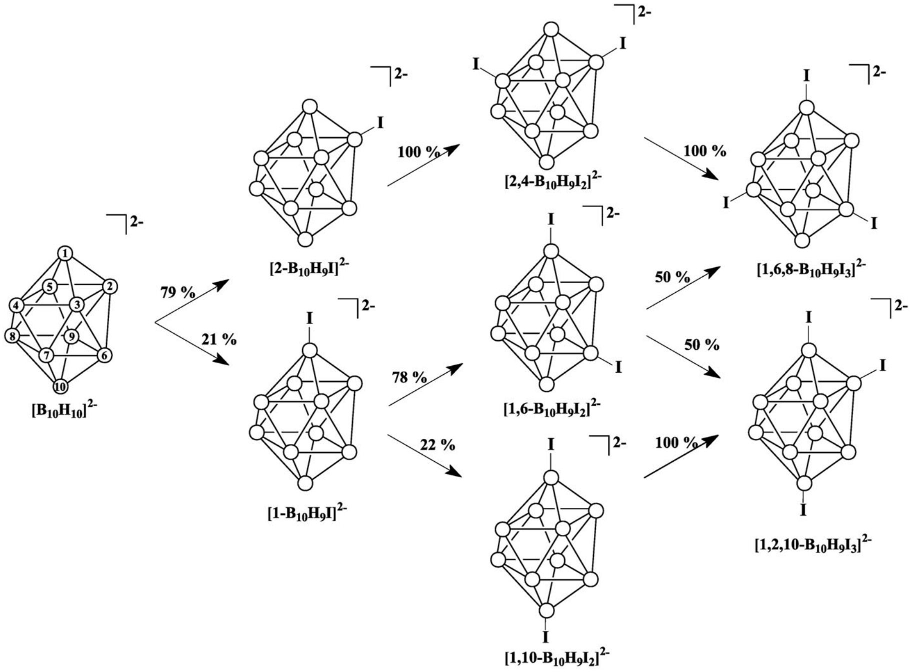
5. DERIVATIVES WITH BORON–HALOGEN BOND

Halogenations of the *closo*-decaborate anion were studied repeatedly by several research groups. In contrast to the $[B_{12}H_{12}]^{2-}$ anion, treatment of *closo*-decaborate with liquid hydrogen fluoride at various temperatures ranging from –70 to +25 °C does not produce any decaborate fluoro derivative, but results in the cage degradation[98,99]. The fluorination with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) gives a mixture of mono-, di- and trifluoro derivatives that were partially separated by column chromatography[99,100]. Synthesis of $[2\text{-}B_{10}H_9F]^{2-}$ by the reaction of $5\text{-F-}6,9\text{-}(Me_2S)_2B_{10}H_{11}$ with liquid ammonia has been described[101]. The crystal structures of $[Ag(MeCN)_3]_2\{Ag_2[2\text{-}B_{10}H_9F]_2\}$ [99] and $(Ph_4P)_2[1,10\text{-}B_{10}H_8F_2]\cdot 3CH_2Cl_2$ (ref.[100]) were determined.

Chlorination of $[B_{10}H_{10}]^{2-}$ with gaseous chlorine in aqueous solution gives a mixture of derivatives with different substitution level $[B_{10}H_{10-x}Cl_x]^{2-}$ (x = 1–10) that can be separated by electrophoresis or ion exchange chromatography[23,102–105]. Formation of a mixture of mono-, di- and trichloro derivatives in the reaction of *closo*-decaborate with hydrogen chloride in 1,2-dichloroethane was reported[106]. The reaction of $[B_{10}H_{10}]^{2-}$ with triphenylmethyl chloride, 1-bromoadamantane or *n*-butylbromide in 1,2-dichloroethane was found to produce selectively $[2\text{-}B_{10}H_9Cl]^{2-}$ (ref.[107]). Minor amounts of mono-, di- and trichloro derivatives were obtained as by-products in the oxidation of $[B_{10}H_{10}]^{2-}$ with $FeCl_3$, whereas the oxidation with $KClO_3$ gave tetrachloro derivative as the reaction by-product[108]. Syntheses of complexes of iron[109], platinum[110], palladium[111], lead[112] and uranium[87b,87c,113] with chloro derivatives of the *closo*-decaborate anion were reported. The crystal structures of $[(C_5H_5N)_2CH_2][2\text{-}B_{10}H_9Cl]$ [114] and $(Me_4N)[1,6,8\text{-}B_{10}H_7Cl_3]$ [115] were determined by single crystal X-ray diffraction. The perchloro derivative *closo*-$[B_{10}Cl_{10}]^{2-}$ was found to undergo reversible oxidation at $E_{1/2}$ = 1.01 V versus Fc/Fc^+ in acetonitrile with formation of violet radical anion *hypercloso*-$[B_{10}Cl_{10}]^{\bullet-}$ (refs[105,116]). The same result can be obtained by the chemical oxidation with Ce^{IV} (ref.[113]) or Tl^{3+} (ref.[105]) in acetonitrile, by the treatment with SO_2Cl_2 in dichloromethane[116] or by the controlled dehydration of $H_2[B_{10}Cl_{10}]\cdot 7.5H_2O$ at 100–160 °C [117].

Bromination of $[B_{10}H_{10}]^{2-}$ with bromine in water at 0 °C gives a mixture of derivatives with different substitution level $[B_{10}H_{10-x}Br_x]^{2-}$ (x = 1–6) that can be separated by chromatography methods[102–104]. The reaction of $[B_{10}H_{10}]^{2-}$ with 1,2-dibromoethane in the presence of triphenylmethyl chloride, 1-bromoadamantane or *n*-butylbromide as activators was found to produce selectively $[2\text{-}B_{10}H_9Br]^{2-}$ (ref.[107]). Preparations of $[2\text{-}B_{10}H_9Br]^{2-}$ by reaction of $5\text{-Br-}6,9\text{-}(Me_2S)_2B_{10}H_{11}$ with liquid ammonia[101] and reaction of $2\text{-Br-}6,9\text{-}(Et_2S)_2B_{10}H_{11}$ with triethylamine in benzene or toluene[42] have been described as well. The perbromo derivative $[B_{10}Br_{10}]^{2-}$ was prepared by the reaction of $[B_{10}H_{10}]^{2-}$ with excess of bromine in refluxing ethanol[102,105]. Syntheses of complexes of nickel[68], iron[109], platinum[68,110] and palladium[68,111,118] with bromo derivatives of the *closo*-decaborate anion were reported. Crystal structures of $[(C_5H_5N)_2CH_2][2\text{-}B_{10}H_9Br]$ [114], $Cs_2[B_{10}Br_{10}]\cdot 2H_2O$ [105] and $[(\eta^3\text{-}C_3H_5)Pd(MeCN)_2]_2[B_{10}Br_{10}]\cdot C_6H_6$ [118b] were determined. The perbromo derivative *closo*-$[B_{10}Br_{10}]^{2-}$ was found to undergo reversible oxidation at $E_{1/2}$ = 1.14 V versus Fc/Fc^+ in acetonitrile with formation of black radical anion *hypercloso*-$[B_{10}Br_{10}]^{\bullet-}$ (ref.[105]).

Iodination of $[B_{10}H_{10}]^{2-}$ with iodine at 0–25 °C gives a mixture of iodo derivatives $[B_{10}H_{10-x}I_x]^{2-}$ (x = 1–4) that can be effectively separated by electrophoresis or ion exchange chromatography[102–104,119]. The reaction pathway was determined based on the analysis of the products distribution (Scheme 4)[119]. The equatorially substituted iodo derivative $[2\text{-}B_{10}H_9I]^{2-}$ can be prepared by the reaction of $[B_{10}H_{10}]^{2-}$ with iodine at –70 °C in ethanol[120] or by reaction of 5-I-6,9-$(Me_2S)_2B_{10}H_{11}$ with liquid ammonia[101].

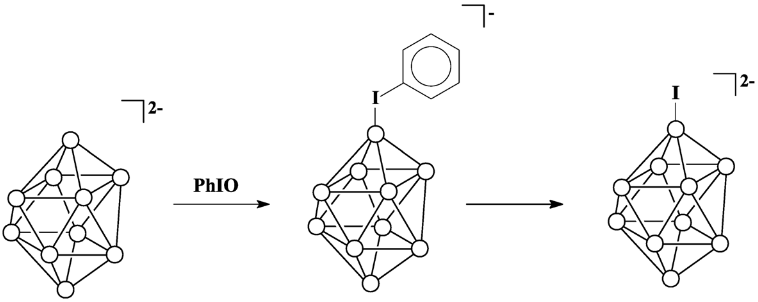


SCHEME 4

The apically substituted iodo derivative $[1\text{-}B_{10}H_9I]^{2-}$ was prepared by photolytic or electrolytic reduction of the 1-phenyliodonium derivative (Scheme 5)[121].

The hexaiodo derivative $[B_{10}H_4I_6]^{2-}$ was prepared by the reaction of $[B_{10}H_{10}]^{2-}$ with iodine in refluxing ethanol and the periodo derivative

$[B_{10}I_{10}]^{2-}$ was synthesized by the treatment of the hexaiodo derivative with iodine monochloride[102]. Crystal structures of $[(C_5H_5N)_2CH_2][1\text{-}B_{10}H_9I]$ [122] and $[(C_5H_5N)_2CH_2][2\text{-}B_{10}H_9I]$ [114] were determined.



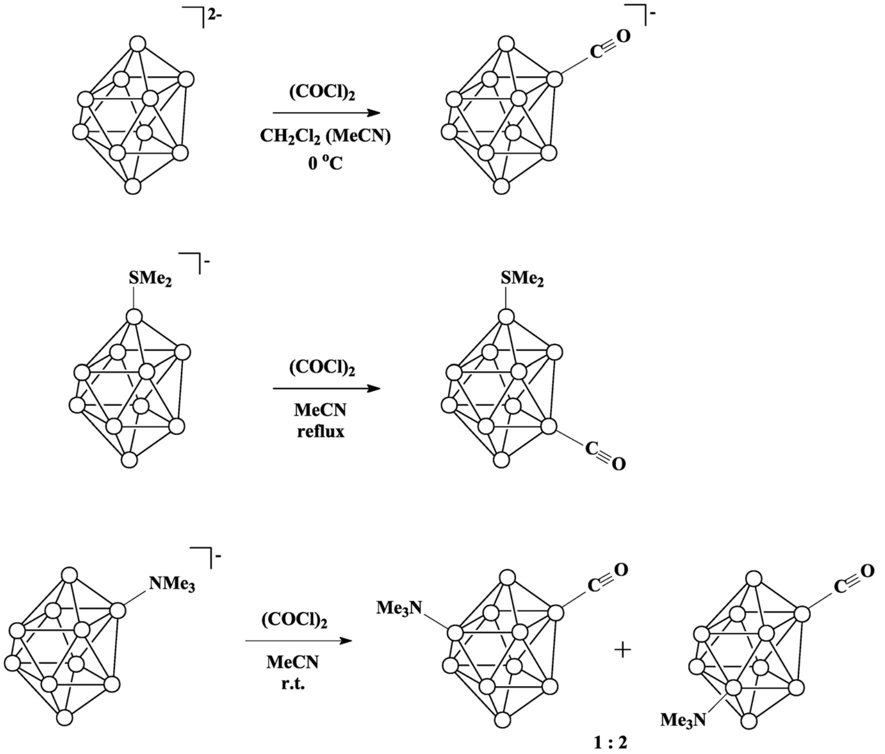
SCHEME 5

6. DERIVATIVES WITH BORON–CARBON BOND

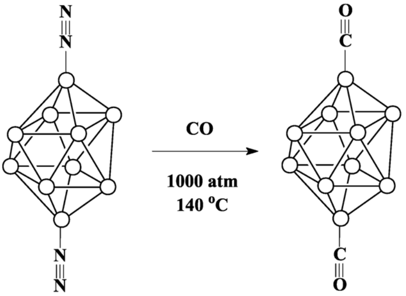
At present a large number of derivatives of the *closo*-decaborate anion with boron–carbon bond were described. The most interesting of them are carbonyl derivatives. The reaction of $[B_{10}H_{10}]^{2-}$ with oxalyl chloride in dichloromethane or acetonitrile at 0 °C results into the carbonyl derivative $[2\text{-}B_{10}H_9CO]^-$ in high yield (Scheme 6)[123]. The reactions with $[1\text{-}B_{10}H_9SMe_2]^-$ and $[2\text{-}B_{10}H_9NMe_3]^-$ proceed in a similar way giving $[1,6\text{-}Me_2SB_{10}H_8CO]$ and the 1:2 mixture of $[2,4\text{-}Me_3NB_{10}H_8CO]$ and $[2,7(8)\text{-}Me_3NB_{10}H_8CO]$, respectively (Scheme 6)[124]. Crystal structure of $(Ph_3PMe)[2\text{-}B_{10}H_9CO]$ was determined by single crystal X-ray diffraction method[123].

1,10-Dicarbonyl derivative $[1,10\text{-}B_{10}H_8(CO)_2]$ was prepared by high pressure reaction of 1,10-diazo derivative $[1,10\text{-}B_{10}H_8(N_2)_2]$ (see below) with carbon monoxide (100 MPa, 140 °C) (Scheme 7)[125]. The reaction in cyclohexane results in the solvent C–H activation with formation of $[C_6H_{11}B_{10}H_7(CO)_2]$ and $[(C_6H_{11})_2B_{10}H_6(CO)_2]$ [125]. The products of C–H activation of methane ($[CH_3B_{10}H_7(CO)_2]$ and $[(CH_3)_2B_{10}H_6(CO)_2]$) and benzene ($[C_6H_5B_{10}H_7(CO)_2]$) were reported as well[126]. The location of alkyl and aryl substituents was not established.

The dicarbonyl derivative $[1,10\text{-}B_{10}H_8(CO)_2]$ is colorless sublimable solid with good solubility in a variety of polar and nonpolar solvents. The dissolution in protic solvents is accompanied by solvolysis. On dissolution in water the carbonyl groups react with water to form the dicarboxylic acid (pK_a ~ 9.1 in water). The reaction is reversible and the dicarbonyl derivative can be regenerated by evaporation of aqueous solution of the acid form.



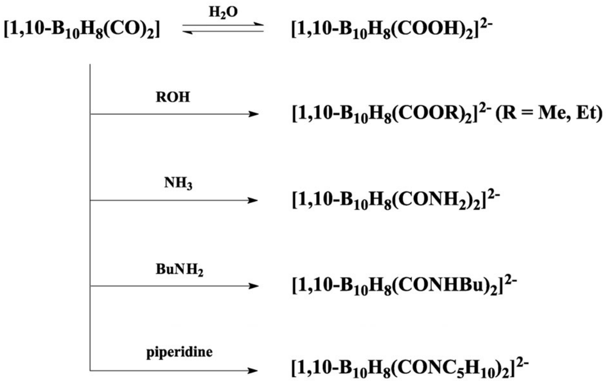
SCHEME 6



SCHEME 7

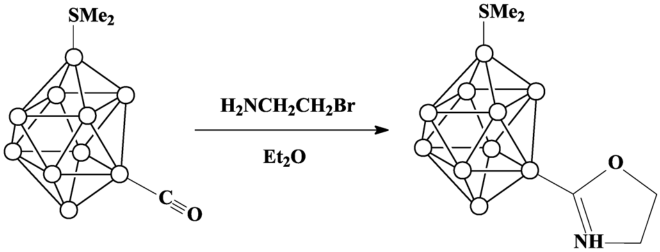
The reactions with alcohols and amines result in the corresponding esters and amides (Scheme 8)[127].

The monocarbonyl derivative $[2\text{-}B_{10}H_9CO]^-$ demonstrates a similar reactivity and its reactions with alcohols and amines were used for the synthesis of various derivatives including boron containing lipids[128], biotin and streptavidin[129] derivatives and some other compounds[130].



SCHEME 8

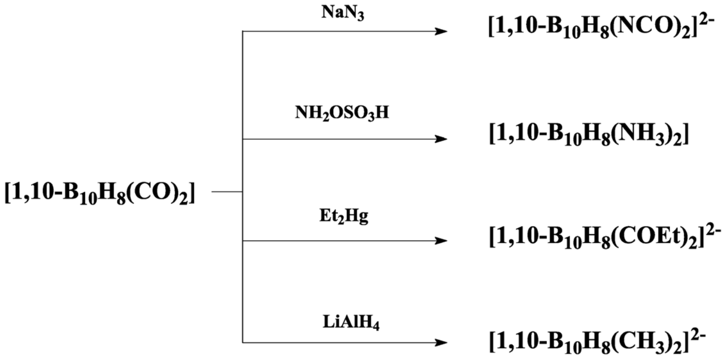
Formation of stable dihydrooxazole derivative in the reaction of $[1,6\text{-}Me_2SB_{10}H_8CO]$ with 2-bromoethylamine was reported (Scheme 9)[131].



SCHEME 9

Other examples of high reactivity of carbonyl groups in *closo*-decaborate derivatives include reactions with sodium azide resulting in the corresponding isocyanate derivatives as products of a spontaneous Curtius rearrangement of the acyl azides formed[123,124,127,132], reactions with hydroxylamine-*O*-sulfonic acid giving the corresponding amino derivatives[124,127,133], reaction with diethylmercury producing the corresponding ketone[127]. The reduction of $[1,10\text{-}B_{10}H_8(CO)_2]$ with $LiAlH_4$ gives the corresponding dimethyl derivative (Scheme 10)[127], whereas the reduction of $[2\text{-}B_{10}H_9CO]^-$ under the same conditions results in the corresponding alcohol[130].

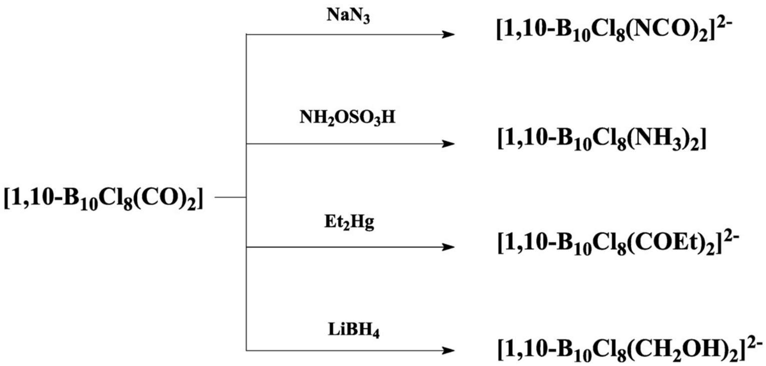
The carbonyl derivatives of the *closo*-decaborate anion can act as acylating agents in reactions with activated aromatics. Thus, the reaction of $[1,10\text{-}B_{10}H_8(CO)_2]$ with *N,N*-dimethylaniline in refluxing acetonitrile produces aromatic diketone $[1,10\text{-}B_{10}H_8(COC_6H_4\text{-}4\text{-}NMe_2)_2]^{2-}$ (ref.[134]). In a similar way, various carbonyl derivatives of the $[B_{10}H_{10}]^{2-}$ anion react with the parent *closo*-decaborate or some its derivatives with formation of a series of bis(boranyl) ketones, exemplified by $[Me_2SB_{10}H_8COB_{10}H_9]^{3-}$. The carbonyl groups in these ketones are exceedingly basic, and they are isolated in the *O*-protonated form, e.g., $[Me_2SB_{10}H_8COHB_{10}H_9]^{2-}$. The $B_{10}C(OH)B_{10}$ moiety in this compounds can be alternatively described as containing a stabilized carbonium ion[134].



SCHEME 10

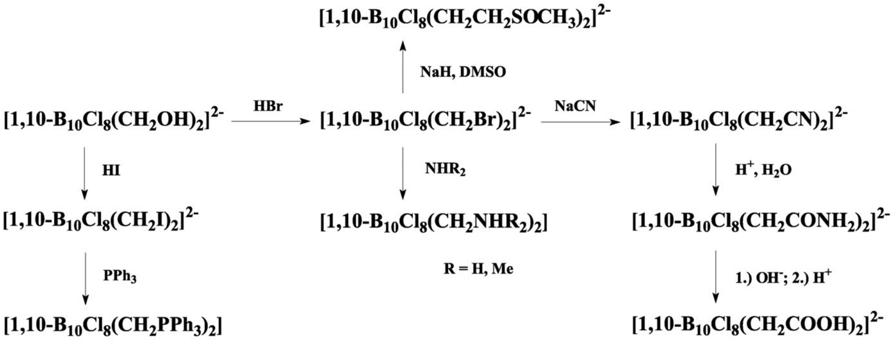
The dicyanide $Cs_2[1,10\text{-}B_{10}H_8(CN)_2]$ was obtained by the dehydratation of the amide $Cs_2[1,10\text{-}B_{10}H_8(CONH_2)_2]$ at 300–375 °C [125a,135]. Treatment of the dicyano derivative with chlorine or bromine results in the corresponding perhalogenated derivatives $[1,10\text{-}B_{10}X_8(CN)_2]^{2-}$ (X = Cl, Br)[136]. The mixed cyano carbonyl derivative $[1,10\text{-}B_{10}H_8(CN)CO]^-$ was prepared by the treatment of $Cs_2[1,10\text{-}B_{10}H_8(CONH_2)_2]$ with oxalyl chloride[127].

Halogenation of $[1,10\text{-}B_{10}H_8(CO)_2]$ in non-aqueous media was found to be extremely slow. However, the halogenation with chlorine or bromine in aqueous solution easily gives the perhalogenated acids $[1,10\text{-}B_{10}Cl_8(COOH)_2]^{2-}$ and $[1,10\text{-}B_{10}Br_8(COOH)_2]^{2-}$. The periodo derivative $[1,10\text{-}B_{10}I_8(COOH)_2]^{2-}$ was prepared by the treatment of $[1,10\text{-}B_{10}H_8(COOH)_2]^{2-}$ with iodine monochloride in refluxing tetrachloroethane. The boron cage halogenation results in higher acidity of the halogenated derivatives ($pK_a \sim 7.5$ in water for $[1,10\text{-}B_{10}Cl_8(COOH)_2]^{2-}$). The dehydration of the halogenated diacids produces the corresponding dicarbonyl derivatives $[1,10\text{-}B_{10}X_8(CO)_2]$ (X = Cl, Br, I)[127]. Reactivity of the halogenated dicarbonyl derivatives in general resembles that of the parent dicarbonyl compounds including reactions with sodium nitrite, hydroxylamine-*O*-sulfonic acid, organomercury compounds, etc. (Scheme 11)[127].



SCHEME 11

The reduction of $[1,10\text{-}B_{10}Cl_8(CO)_2]$ with $LiBH_4$ in glyme results in the corresponding alcohol $[1,10\text{-}B_{10}Cl_8(CH_2OH)_2]^{2-}$ (ref.[137]). The hydroxy groups in the last compound are readily acylated by acetic anhydride and are easily replaced by bromine or iodine upon reaction with the corresponding hydrohalic acid. Similarly to benzyl halides, the halogen atoms in $[1,10\text{-}B_{10}Cl_8(CH_2X)_2]^{2-}$ (X = Br, I) are readily replaced by various nucleophiles. The reaction with aqueous sodium cyanide produces the corresponding nitrile, which can be hydrolyzed to the corresponding amide and carboxylic acid $[1,10\text{-}B_{10}Cl_8(CH_2COOH)_2]^{2-}$. The reactions with amines and phosphines result in the corresponding ammonium and phosphonium derivatives (Scheme 12)[137].



SCHEME 12

It should be noted here that synthetic utility of the carbonyl derivatives of the *closo*-decaborate anion is limited mainly to the easily accessible monocarbonyl compound $[2\text{-}B_{10}H_9CO]^-$.

The reaction of the *closo*-decaborate anion with benzoyl chloride results in the corresponding ketone $[2\text{-}B_{10}H_9COPh]^{2-}$ (refs[130,138,139]). Kinetics of the reaction of $[B_{10}H_{10}]^{2-}$ with benzoyl chloride and benzoyl bromide in acetonitrile was studied[92]. In the presence of strong acids the formation of dark red protonated form takes place. The nature of the protonated form is not fully understood but probably involves the carbonyl group and not the boron cage. Reactions of the *closo*-decaborate anion with 4-methoxy-[130], 4-carboxy-[130] and 4-[bis(2-chloroethyl)amino]-[131] benzoyl chlorides proceed in a similar way[131]. The ketonic character of the carbonyl group in $[2\text{-}B_{10}H_9COAr]^{2-}$ was demonstrated by their conversion to hydrazones[130] and semicarbazones[138,139] using standard techniques and by Bayer–Villiger oxidation to $[2\text{-}B_{10}H_9OC(O)Ph]^{2-}$ by hydrogen peroxide[138,139]. Chlorination and bromination of $[2\text{-}B_{10}H_9COPh]^{2-}$ with elemental halogens result in the corresponding halogenated ketones $[2\text{-}B_{10}X_9OC(O)Ph]^{2-}$ (X = Cl, Br)[138,139].

The reaction of the *closo*-decaborate acid with tropylium bromide results in highly colored stable tropylium derivative $[2\text{-}B_{10}H_9C_7H_6]^{2-}$. The strong hypsochromic shift of the long-wavelength absorption band of the tropenylium derivative with increasing solvent polarity (from 439 nm in water (orange) to 536 nm in acetone (deep purple)) or decreasing cation radius in the solid state (the cesium salt is orange and the tetrabutylammonium salt is purple) suggests anion-to-cation charge transfer[140]. Ab initio molecular orbital study of $[2\text{-}B_{10}H_9C_7H_6]^{2-}$ revealed the presence of an additional low lying bonding orbital, arising from complete delocalization of one pair of the cage electrons throughout the cage–ring system[141].

Few alkyl derivatives of the *closo*-decaborate anion wee obtained from the corresponding decaborane derivatives: the ethyl derivative $[2\text{-}B_{10}H_9C_2H_5]^{2-}$ was prepared by the reaction of a mixture of 1- and $2\text{-}B_{10}H_{13}C_2H_5$ with triethylamine in refluxing benzene[42]; the cyclohexyl derivative $[2\text{-}B_{10}H_9C_6H_{11}]^{2-}$ was prepared by the reaction of $6\text{-}C_6H_{11}\text{-}5\text{-}(CH_3)_2SB_{10}H_{11}$ with sodium hydride in refluxing tetrahydrofuran[142]. Unexpected formation of another alkyl derivative in the reaction of $[2\text{-}B_{10}H_9NH_3]^-$ with ethylene oxide producing $[H_3NB_{10}H_7(CH_2CH_2OH)_2]^-$ as well as some transformations of this compound were reported, however the alkylation positions were not established[143].

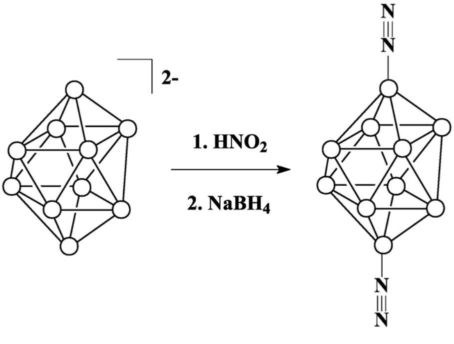
The product of C–H activation of the pyridine ring was obtained in the reaction of $(Bu_4N)_2[B_{10}H_{10}]$ with di(2-pyridyl)amine. The structure of

$(Ph_4P)_2[2\text{-}\{2\text{-}(2\text{-}(C_5H_4N)NH)(C_5H_3N)\text{-}5\}B_{10}H_9]$ was determined by single crystal X-ray diffraction study[144].

UV irradiation of aqueous solution of decachloro-*closo*-decaborate $[B_{10}Cl_{10}]^{2-}$ in the presence of excess of potassium cyanide results in nucleophilic substitution of chlorine with formation of a mixture of cyano derivatives $[B_{10}Cl_{10-n}(CN)_n]^{2-}$ ($n = 1–3$). The stereochemistry of the reaction products is unknown[136].

7. DERIVATIVES WITH BORON–NITROGEN BOND

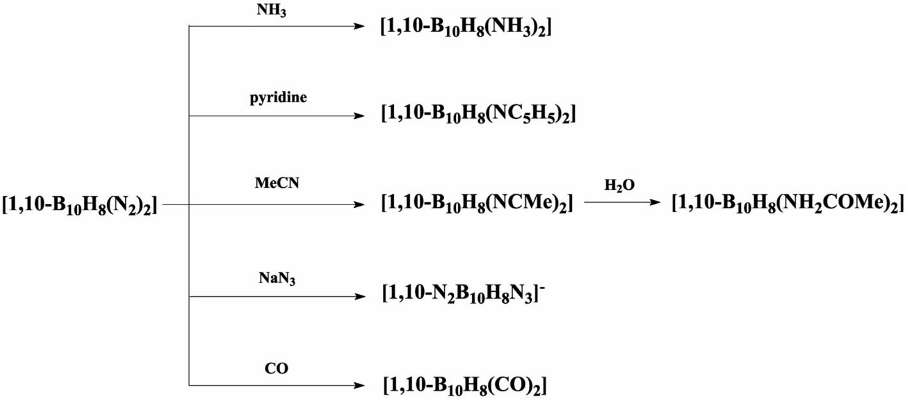
The *closo*-decaborate compounds with boron-nitrogen bond form the most numerous group of its derivatives and are, as a rule, easily accessible. The most interesting of them are diazonium derivatives that are isoelectronic with the above described carbonyl derivatives. The reaction of aqueous solution of $(NH_4)_2[B_{10}H_{10}]$ with excess of nitrous acid followed by reduction of a precipitated intermediate with $NaBH_4$ in methanol or with Zn in HCl gives 1,10-bis(diazonium) derivative $[1,10\text{-}B_{10}H_8(N_2)_2]$ in a low (15–25%) yield (Scheme 13)[125]. The reactions with $[1\text{-}B_{10}H_9SMe_2]^-$, $[2\text{-}B_{10}H_9NMe_3]^-$ and $[1,6\text{-}Me_2SB_{10}H_8CO]$ proceed in a similar way giving $[1,10\text{-}N_2B_{10}H_8SMe_2]$ [145], $[1,6\text{-}N_2B_{10}H_8NMe_3]$ [135] and $[1\text{-}Me_2SB_{10}H_7\text{-}6\text{-}COOH\text{-}10\text{-}N_2]$ [124], respectively, in moderate yields.



SCHEME 13

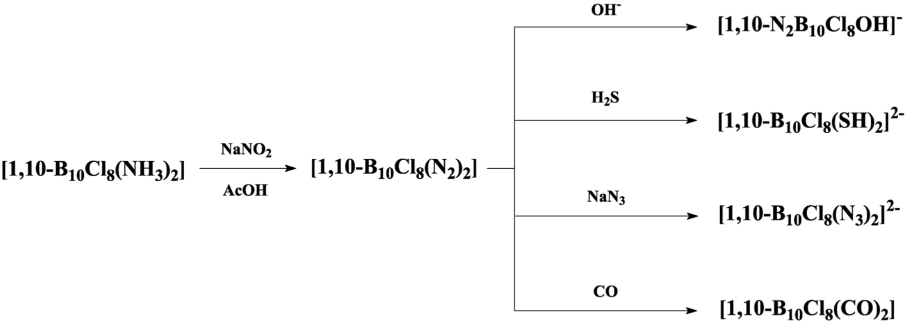
$[1,10\text{-}B_{10}H_8(N_2)_2]$ is a colorless, crystalline solid, stable toward air, water, diluted acids or bases. It is soluble in common organic solvents including benzene and insoluble in water. It sublimes readily in vacuo and begins to decompose at about 125 °C [125]. Structure of $[1,10\text{-}B_{10}H_8(N_2)_2]$ was determined by single crystal X-ray diffraction[146].

Despite the remarkably high stability of the bis(diazonium) *closo*-decaborate derivative that contrasts with the reactivity of aromatic diazonium salts, this group is very valuable in the $[B_{10}H_{10}]^{2-}$ chemistry because it is the only substituent found that is readily displaceable by a variety of nucleophiles. The examples include reactions with ammonia, pyridine, acetonitrile, carbon oxide, hydrazine, and sodium azide (Scheme 14)[125].



SCHEME 14

The halogenated derivatives $[1,10\text{-}B_{10}Cl_8(N_2)_2]$ and $[1,10\text{-}B_{10}I_8(N_2)_2]$ were prepared by diazotization of the corresponding amines. The reactivity of the chlorinated diazonium derivative resembles that of the non-halogenated analogue (Scheme 15)[125].



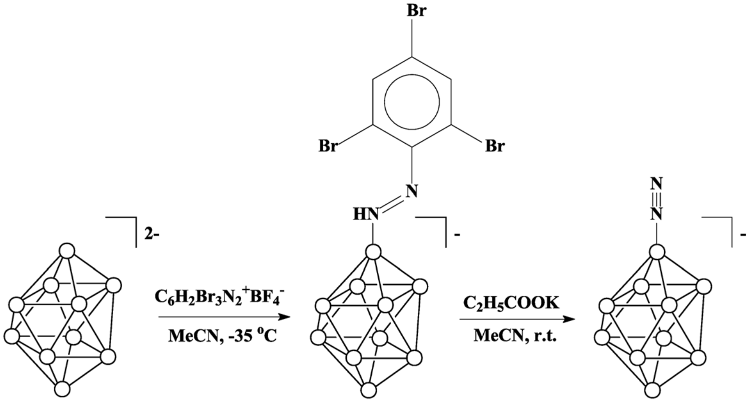
SCHEME 15

It should be noted that synthetic utility of the 1,10-bis(diazonium) derivatives is limited by a low yield of $[1,10\text{-}B_{10}H_8(N_2)_2]$. Consequently, the monosubstituted derivative $[1\text{-}B_{10}H_9N_2]^-$ attracts more interest. It can be obtained by the reaction of phenylazo derivatives of the *closo*-decaborate anion with weak bases (see below).

The reaction of $[B_{10}H_{10}]^{2-}$ with phenyldiazonium salts in acetonitrile results in highly colored phenylazo derivatives isolated in the *N*-protonated form $[1\text{-}B_{10}H_9NH{=}NC_6H_4X]^-$ (X = H, 3-F, 4-F, 3-Br, 4-Br, 2,4,6-Br_3, 3-CH_3, 3-OCH_3, 4-OCH_3, 4-$NHCOCH_3$, 4-$NHCOCF_3$, 3-CF_3, 4-CF_3, 3-NO_2, 4-NO_2, 4-CN)[147–149]. The acidity of the protonated form depends on donor/acceptor properties of the substituent in the aromatic ring with pK_a varying from 6.98 for X = 4-CH_3 to 4.74 for X = 4-NO_3 [147]. The reactions with polycyclic aryldiazonium salts (1- and 2-naphthyl, 4-acenaphthyl diazonium, 4,4′-diphenylene bis(diazonium)) proceed in a similar way[150].

Reduction of the arylazo derivatives with zinc dust, basic hydrosulfite or tin in acidic methanol results in the corresponding amino derivative $[1\text{-}B_{10}H_9NH_3]^-$ (ref.[147]). The same product was obtained by hydrogenation of $[1\text{-}B_{10}H_9NH{=}NC_6H_5]^-$ at 15–18 MPa on Pd/$BaSO_4$, Pd/C or Ni/Re catalyst[151]. The hydrogenation at atmospheric pressure gives the phenylhydrazine derivative $[1\text{-}B_{10}H_9NH_2NHC_6H_5]^-$. The last one is very air-sensitive and is easily oxidized to the phenylazo derivative[151].

The diazonium derivative $[1\text{-}B_{10}H_9N_2]^-$ was prepared by the treatment of $[1\text{-}B_{10}H_9NH{=}NC_6H_2\text{-}2,4,6\text{-}Br_3]^-$ with sodium propionate in acetonitrile (Scheme)[152,153]. Similarly to the bis(diazonium) derivative, $[1\text{-}B_{10}H_9N_2]^-$ is thermally stable and its tetramethylammonium salt decomposes at 140–160 °C with formation of $[B_{20}H_{18}]^{2-}$ (Scheme 16)[154]. Crystal structures of $(Et_3NH)[1\text{-}B_{10}H_9N_2]$ and $(Et_3NH)[Cu(1\text{-}B_{10}H_9N_2)_2]$ (Fig. 4) were determined by single crystal X-ray diffraction (Fig. 4)[153]. $[1,10\text{-}N_2B_{10}H_8NMe_3]$, $[1,6\text{-}N_2B_{10}H_8NMe_3]$, $[1,10\text{-}N_2B_{10}H_8NC_5H_5]$ and $[1,10\text{-}N_2B_{10}H_8SMe_2]$ were prepared in a similar way starting from $[1\text{-}B_{10}H_9NMe_3]^-$, $[2\text{-}B_{10}H_9NMe_3]^-$, $[1\text{-}B_{10}H_9NC_5H_5]^-$ and $[1\text{-}B_{10}H_9SMe_2]^-$, respectively[152].



SCHEME 16

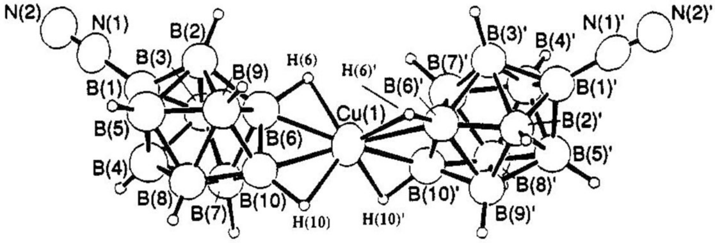
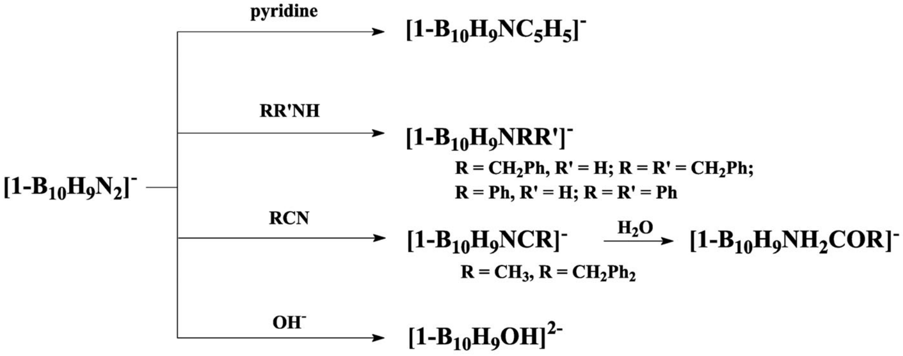


FIG. 4
Molecular structure of $(Et_3NH)[Cu(1-B_{10}H_9N_2)_2]$. Reproduced from ref.[153] with permission of American Chemical Society

Similarly to the bis(diazonium) derivatives, $[1-B_{10}H_9N_2]^-$ reacts with amines, nitriles and hydroxide ion with the formation of the corresponding derivatives (Scheme 17)[152,155,156].



SCHEME 17

The diazo group in the *closo*-decaborate derivatives can act as a two-electron donor in transition metal complexes and a series of ruthenium(II) complexes with $[1,10-N_2B_{10}H_8SMe_2]$ and $[1,10-B_{10}H_8(N_2)_2]$ as ligands was described. The Ru–N≡N–B moiety is very stable as shown by its inertness to hydrogen chloride, sodium tetrahydroborate, platinum-catalyzed hydrogenolysis, atmospheric oxidation, etc. (Scheme 18)[157]. The crystal structure of $\{(Ph_3P)_3RuH_2[1,10-N_2B_{10}H_8SMe_2]\}\cdot 3C_6H_6$ was determined by single crystal X-ray diffraction (Fig. 5)[158].

The reaction of $[B_{10}H_{10}]^{2-}$ with hydroxylamine-*O*-sulfonic acid in aqueous solutiuon results in mono- and diamino derivatives which are readily isolated in the *N*-protonated form due to their high basicity (Scheme 19)[159].

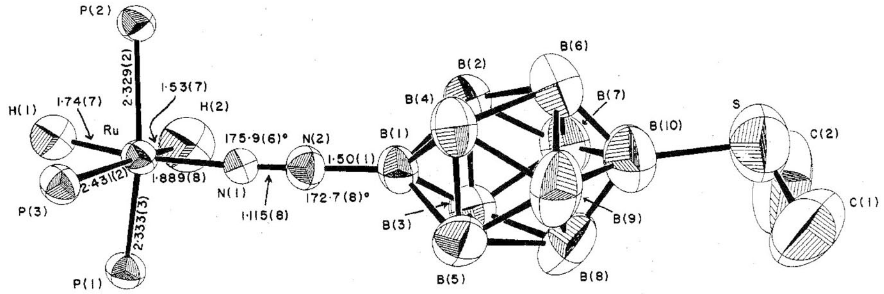
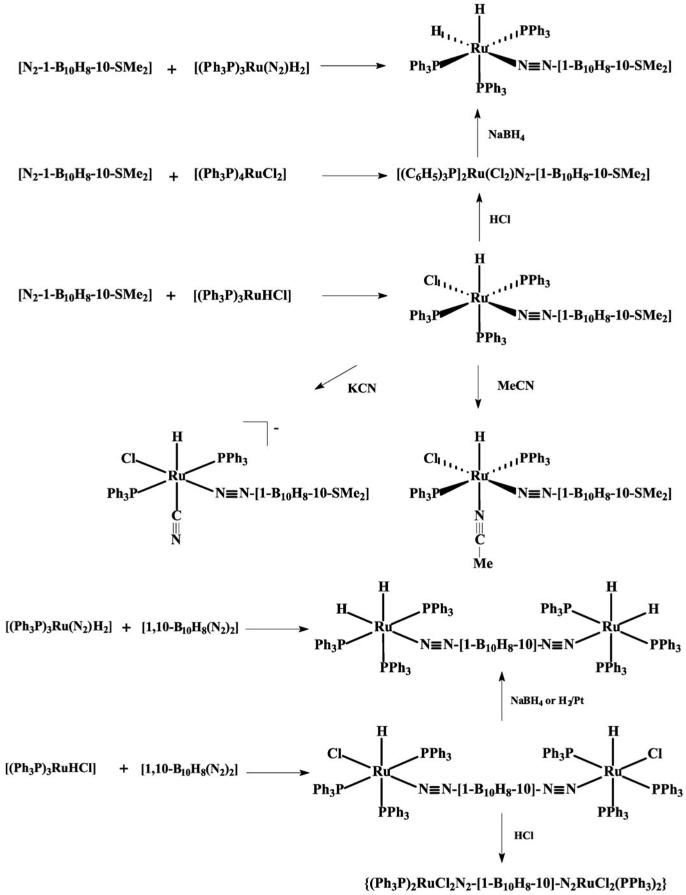


FIG. 5
Molecular structure of $\{(Ph_3P)_3RuH_2[1,10\text{-}N_2B_{10}H_8SMe_2]\}\cdot 3C_6H_6$. The phenyl groups of the triphenylphosphine ligands were omitted for clarity. Reproduced from ref.[158] with permission of American Chemical Society

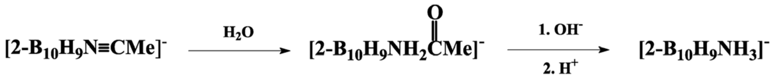


SCHEME 18

$$[B_{10}H_{10}]^{2-} \xrightarrow{NH_2OSO_3H} [2\text{-}B_{10}H_9NH_3]^- \xrightarrow{NH_2OSO_3H}$$
$$[2,3\text{-}B_{10}H_8(NH_3)_2] + [2,4\text{-}B_{10}H_8(NH_3)_2] + [2,7(8)\text{-}B_{10}H_8(NH_3)_2]$$

SCHEME 19

More convenient method of synthesis of monosubstituted amino derivative $[2\text{-}B_{10}H_9NH_3]^-$ consist in hydrolysis of acetonitrilium derivative of the *closo*-decaborate anion (see below) (Scheme 20)[160].



$$[2\text{-}B_{10}H_9N{\equiv}CMe]^- \xrightarrow{H_2O} [2\text{-}B_{10}H_9NH_2\overset{O}{\overset{\|}{C}}Me]^- \xrightarrow[2.\ H^+]{1.\ OH^-} [2\text{-}B_{10}H_9NH_3]^-$$

SCHEME 20

Methylation of $[2\text{-}B_{10}H_9NH_3]^-$ with dimethyl sulfate gives $[2\text{-}B_{10}H_9NHMe_2]^-$ or $[2\text{-}B_{10}H_9NMe_3]^-$ depending on the reaction conditions, whereas methylation of a mixture of disubstituted derivatives produces the corresponding mixture of $[2,3\text{-}B_{10}H_8(NMe_3)_2]$, $[2,4\text{-}B_{10}H_8(NMe_3)_2]$ and $[2,7(8)\text{-}B_{10}H_8(NMe_3)_2]$ that can be separated by crystallization and chromatography on alumina[159].

The apically substituted derivatives $[1\text{-}B_{10}H_9NH_3]^-$ and $[1\text{-}B_{10}H_9NMe_3]^-$ were obtained by reduction of arylazo derivatives (Scheme 21)[147,151].

$$[1\text{-}B_{10}H_9NHNAr]^- \xrightarrow{[H]} [1\text{-}B_{10}H_9NH_3]^- \xrightarrow[OH^-]{Me_2SO_4} [1\text{-}B_{10}H_9NMe_3]^-$$

SCHEME 21

The preparation of $[1\text{-}B_{10}H_9NH_3]^-$ by reduction of the corresponding nitro derivative (see below) with aluminum in alkaline solution was reported as well[161].

Six of seven possible isomers of disubstituted trimethylamino derivative $[B_{10}H_8(NMe_3)_2]$ were prepared using different synthetic approaches. The 1,6-isomer was prepared from $[1,6\text{-}N_2B_{10}H_8NMe_3]$ (see above) (Scheme 22)[135].

$$[1,6\text{-}N_2B_{10}H_8NMe_3] \xrightarrow{NH_3} [1,6\text{-}H_3NB_{10}H_9NMe_3] \xrightarrow[OH^-]{Me_2SO_4} [1,6\text{-}B_{10}H_8(NMe_3)_2]$$

SCHEME 22

The 1,10-isomer can be prepared by the reaction of $[1,10\text{-}B_{10}H_8(CO)_2]$ with hydroxylamine-*O*-sulfonic acid[125a,127], by the reaction of $[1,10\text{-}B_{10}H_8(N)_2]$ with ammonia[125], or by the step-by-step approach via the 1-arylazo- and 1-diazonium derivatives[147]. Similar halogenated derivatives $[1,10\text{-}B_{10}Cl_8\text{-}$

$(NH_3)_2$] and [1,10-$B_{10}I_8(NH_3)_2$] were prepared by the reaction of the corresponding carbonyl derivatives with hydroxylamine-*O*-sulfonic acid[125]. The electron-withdrawing character of halogen substituents increases acidity of the protonated amine (pK_a^{MeCN} = 12.2 and 10.9 for [1,10-$B_{10}H_8(NH_3)_2$] and [1,10-$B_{10}Cl_8(NH_3)_2$], respectively[125b]. The reaction of [1,10-$B_{10}H_8(NH_3)_2$] with dimethyl sulfate under basic conditions gives [1,10-$B_{10}H_8(NMe_3)_2$][159].

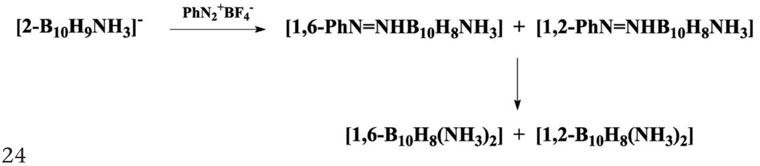
The 2,7(8)-isomer was prepared by reduction of the corresponding chlorodimethylamino derivative obtained by the reaction of *closo*-decaborate with the Vilsmeier reagent [ClCH=NMe_2]Cl (Scheme 23)[162].

SCHEME 23

The reaction is rather selective and produces only small amount of the 2,6(9)-isomer[163]. The reactions with the *N*-methylformanilide- and *N*-formylmorpholine-based Vilsmeier reagents proceed in a similar way giving [2,7(8)-$B_{10}H_8(NMePh(CH_2Cl))_2$] and [2,7(8)-$B_{10}H_8(N(CH_2Cl)(CH_2CH_2)_2O)_2$] as the main products[163].

Synthesis of optically active [2,7-$B_{10}H_8(NMe_3)_2$] and [2,8-$B_{10}H_8(NMe_3)_2$] was achieved in the following way. The reaction of [2-$B_{10}H_9NMe_3$]$^-$ with oxalyl chloride in acetonitrile gave a 1:2 mixture of [2,4-$Me_3NB_{10}H_8CO$] and [2,7(8)-$Me_3NB_{10}H_8CO$]. Treatment of this mixture with aqueous brucine hydrochloride gave a mixture of [brucine-H][$Me_3NB_{10}H_8COOH$], from which the highly soluble 2,4-isomer was removed by warm ethanol. Fractional crystallization of the remaining mixture of diastereomeric salts from ethanol–acetonitrile followed by reconversion of carboxyl group to the carbonyl one gave the 2,7- and 2,8-enantiomers of [$Me_3NB_{10}H_8CO$]. The carbonyl derivatives were transformed to the corresponding trimethylamine derivatives by the reaction with hydroxylamine-*O*-sulfonic acid followed by methylation with dimethylsulfate[127,133].

The 1,2-diamino derivative [1,2-$B_{10}H_8(NH_3)_2$] was obtained as a minor product in the reaction of [2-$B_{10}H_9NH_3$]$^-$ with phenyldiazonium tetrafluoroborate followed by reduction of a mixture of the phenylazo derivatives (Scheme 24)[160].



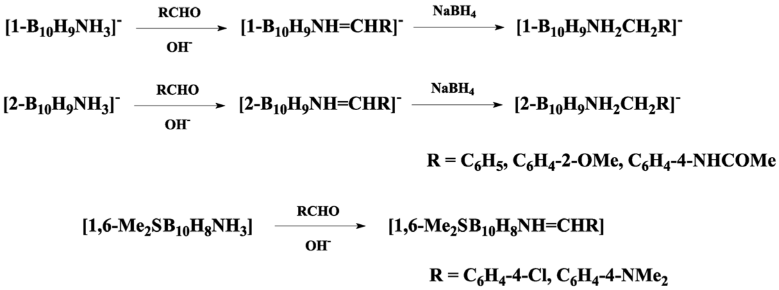
SCHEME 24

Individual isomers of the bis(trimethylamino) derivative undergoes isomerization at 300 °C to give an equilibrium mixture of isomers with dominating 2,7(8)- and 1,6-isomers. The least stable 2,3-isomer undergoes to isomerization at a lower temperature and at 230 °C rearranges exclusively to the 1,6-isomer[135].

The crystal structures of $(Ph_4P)[1\text{-}B_{10}H_9NH_3]$ [151], $[2,7(8)\text{-}B_{10}H_8(NMe_2CH_2Cl)_2]$ [163] and $[3(5)\text{-}Me\text{-}7(8)\text{-}Cl\text{-}2,8(7)\text{-}B_{10}H_6(NMe_2CH_2Cl)_2]$ [163] were determined by single crystal X-ray diffraction.

A series of alkylamino derivatives $[1\text{-}B_{10}H_9NR_2R']^-$ and $[2\text{-}B_{10}H_9NR_2R']^-$ were prepared by removal of the extra *N*-proton with strong bases (sodium hydride or potassium hydroxide) followed by the reaction with various alkyl halides[143,155,164].

The reactions of the amino derivatives with aromatic aldehydes in the presence of catalytic amounts of alkali give the corresponding Schiff bases. The last ones can be reduced with sodium tetrahydroborate to the corresponding benzylamino derivatives (Scheme 25)[145,151,160,165].



$$[1\text{-}B_{10}H_9NH_3]^- \xrightarrow[OH^-]{RCHO} [1\text{-}B_{10}H_9NH{=}CHR]^- \xrightarrow{NaBH_4} [1\text{-}B_{10}H_9NH_2CH_2R]^-$$

$$[2\text{-}B_{10}H_9NH_3]^- \xrightarrow[OH^-]{RCHO} [2\text{-}B_{10}H_9NH{=}CHR]^- \xrightarrow{NaBH_4} [2\text{-}B_{10}H_9NH_2CH_2R]^-$$

$R = C_6H_5,\ C_6H_4\text{-}2\text{-}OMe,\ C_6H_4\text{-}4\text{-}NHCOMe$

$$[1,6\text{-}Me_2SB_{10}H_8NH_3] \xrightarrow[OH^-]{RCHO} [1,6\text{-}Me_2SB_{10}H_8NH{=}CHR]$$

$R = C_6H_4\text{-}4\text{-}Cl,\ C_6H_4\text{-}4\text{-}NMe_2$

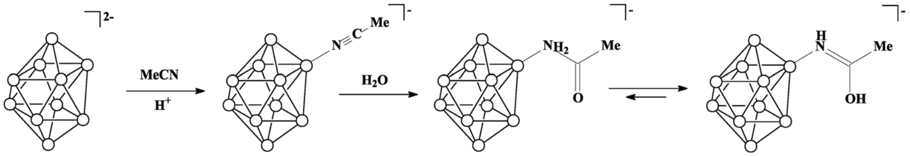
SCHEME 25

The reaction of the *closo*-decaborate anion $[B_{10}H_{10}]^{2-}$ with acetonitrile in the presence of strong acids results in the nitrilium derivative $[2\text{-}B_{10}H_9N{\equiv}CMe]^-$ (refs[160,166–168]). The nitrilium derivative is easily hydrolyzed with water to give the corresponding amide which was isolated in the *O*-protonated tautomeric form (Scheme 26)[160].

In a similar way, the reactions of $[2\text{-}B_{10}H_9N{\equiv}CMe]^-$ with aliphatic alcohols ROH result in the corresponding imidates $[2\text{-}B_{10}H_9NH{=}C(Me)OR]^-$ (R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, *t*-Bu, *n*-amyl, *i*-amyl, *n*-hexyl, CH_2CH_2OEt)[169].

The reactions with butyronitrile[86], acrylonitrile[170] and benzonitrile[166,171] proceed in a similar way. A series of rare earth metal complexes with the butyramido[86] and acrylamido[170a] derivatives was prepared.

The benzoylamido derivative $[2\text{-}B_{10}H_9NH{=}C(OH)Ph]^-$ was prepared also by the reaction of $[2\text{-}B_{10}H_9NH_3]^-$ with benzoyl chloride (Scheme 27)[143].



SCHEME 26

$$[2\text{-}B_{10}H_9NH_3]^- \xrightarrow{\text{PhCOCl}} [2\text{-}B_{10}H_9NH{=}C(OH)Ph]^-$$

SCHEME 27

Crystal structures of $(Et_3NH)[2\text{-}B_{10}H_9N{\equiv}CCH_3]$ [166], $(Ph_4P)[2\text{-}B_{10}H_9N{\equiv}CCH_3]$ [168], $(Bu_4N)[2\text{-}B_{10}H_9NH{=}C(OH)CH_3]$ [160], $(Et_4N)[2\text{-}B_{10}H_9NH{=}C(OH)CH{=}CH_2]$ [170b], $(Ph_4P)[2\text{-}B_{10}H_9NH{=}C(OH)C_6H_5]$ [171], and $(Bu_4N)[2\text{-}B_{10}H_9NH{=}C(OC_4H_9)CH_3]$ [169] were determined.

The apically substituted nitrilium and amido derivatives were obtained by the reaction of the diazonium derivatives with acetonitrile followed by hydrolysis (Scheme 28)[125,155].

$$[1\text{-}B_{10}H_9N_2]^- \xrightarrow{\text{MeCN}} [1\text{-}B_{10}H_9N{\equiv}CMe]^- \xrightarrow{H_2O} [1\text{-}B_{10}H_9NH_2COMe]^-$$

$$[1{,}10\text{-}B_{10}H_8(N_2)_2] \xrightarrow{\text{MeCN}} [1{,}10\text{-}B_{10}H_8(N{\equiv}CMe)_2] \xrightarrow{H_2O} [1{,}10\text{-}B_{10}H_8(NH_2COMe)_2]$$

SCHEME 28

Formation of trace amounts of diamide $[B_{10}H_8(NH_2COMe)_2]$ in the reaction of oxidation *closo*-decaborate with $FeCl_3$ in acetonitrile was reported[172].

The isocyanate derivatives of the *closo*-decaborate anion can be prepared by the reaction of the corresponding carbonyl derivatives (see above) with sodium azide[123–125,132,149]. The reaction of the isocyanates with alcohols produces urethanes[149] whereas acid hydrolysis results in the corresponding amines[124,125].

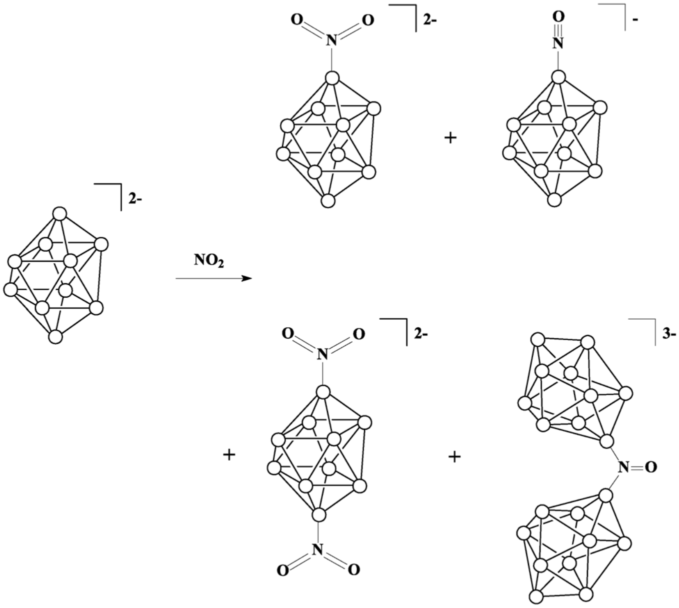
The isothiocyanate derivatives were obtained by the treatment of *closo*-decaborate with $(NCS)_2$ in acetonitrile (Scheme 29)[173].

$$[B_{10}H_{10}]^{2-} \xrightarrow[\text{MeCN}]{(NCS)_2} [2\text{-}B_{10}H_9NCS]^{2-} + [1{,}2\text{-}B_{10}H_8(NCS)_2]^{2-} + [1{,}6\text{-}B_{10}H_8(NCS)_2]^{2-}$$

SCHEME 29

The reaction of the *closo*-decaborate anion with nitrogen dioxide in aqueous acetonitrile produces a mixture of nitro $[1\text{-}B_{10}H_9NO_2]^{2-}$ and $[1{,}10\text{-}B_{10}H_8(NO_2)_2]^{2-}$, nitroso $[1\text{-}B_{10}H_9NO]^-$ and bridged nitroso $[1{,}1'\text{-}\mu\text{-}NO\text{-}$

$(B_{10}H_9)_2]^{3-}$ derivatives that can be separated by ion-exchange chromatography on diethylaminoethyl cellulose[174,175]. The last compound can be obtained also by reaction of *closo*-decaborate with nitric oxide and ferric chloride[174] or with ferric nitrate (Scheme 30)[108].



SCHEME 30

The structures of $[(C_5H_5N)_2CH_2][1\text{-}B_{10}H_9NO_2]$ [175a], $(Ph_4P)_2[1,10\text{-}B_{10}H_8(NO_2)_2]$ [175b], $(Ph_4P)[1\text{-}B_{10}H_9NO]$ [175c] and $(Et_3NH)_3[1,1'\text{-}\mu\text{-}NO(B_{10}H_9)_2]$ [176] were determined by single crystal X-ray diffraction method.

The bridged nitroso derivative can be halogenated using elemental fluorine, chlorine, bromine and iodine to give $[B_{20}H_{10}F_8NO]^{3-}$, $[B_{20}H_2Cl_{16}NO]^{3-}$, $[B_{20}H_4Cl_{14}NO]^{3-}$ and $[B_{20}H_{11}I_7NO]^{3-}$, respectively[174]. The nitroso group can be reduced by hydrazine, hydroxylamine, sodium dithionite or Raney Ni-catalyzed hydrogenation resulting in $[1,1'\text{-}\mu\text{-}NH_2(B_{10}H_9)_2]^{3-}$[174]. The amino group in this compound was of low basicity and rather unreactive. Acylation could be achieved only under forced conditions (heating in a mixture of acetic acid and acetic anhydride at 80 °C for 48 h)[174].

$[2,9\text{-}\{N,N'\text{-}(2\text{-}NHC_5H_4N)\}B_{10}H_8]^-$ was obtained in the reaction of *closo*-decaborate with 2-aminopyridine at 160 °C. The structure of $(Ph_4P)\text{-}[2,9\text{-}\{N,N'\text{-}(2\text{-}NHC_5H_4N)\}B_{10}H_8]$ was determined by single crystal X-ray diffraction[177].

8. DERIVATIVES WITH BORON–PHOSPHORUS BOND

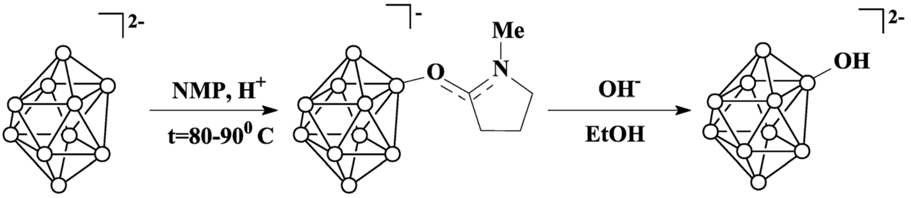
At present, only a few derivatives of the *closo*-decaborate anion with boron–phosphorus bond were reported and all these compounds were obtained in Pd-mediated substitution reactions. The reaction of $Li_2[B_{10}H_{10}]$ with $[(PhMe_2P)_2PdCl_2]$ in dichloromethane at room temperature produced a mixture of $[1,10\text{-}B_{10}H_8(PMe_2Ph)_2]$, $[2,7(8)\text{-}B_{10}H_8(PMe_2Ph)_2]$ and $[1,6\text{-}B_{10}H_8(PMe_2Ph)_2]$ that can be separated by column chromatography on silica[178]. $[1,6\text{-}B_{10}H_8(PPh_3)_2]$ and $[2,4\text{-}B_{10}H_8(PPh_3)_2]$ were isolated from the reaction of $(Et_4N)_2[B_{10}H_{10}]$ with $[(Ph_3P)_2PdCl_2]$ in refluxing ethanol[179].

Formation of small amounts of $[1\text{-}B_{10}H_9PHPh_2]^-$ and $[1\text{-}B_{10}H_9P(OH)Ph_2]^-$ in the reaction of $(Me_4N)[1\text{-}B_{10}H_9N_2]$ with diphenylphosphine at 120 °C was reported. The similar reaction in the presence of $[(Ph_3P)_2PdCl_2]$ and CuI at 150 °C gives mainly $[1\text{-}B_{10}H_9PHPh_2]^-$ and $[1\text{-}B_{10}H_9P(OH)Ph_2]^-$ as well as some amounts of $[1,6\text{-}B_{10}H_8(PHPh_2)_2]$ and $[1,10\text{-}B_{10}H_8(PHPh_2)_2]$ [180].

The crystal molecular structures of $[2,8\text{-}B_{10}H_8(PMe_2Ph)_2]$ [178], $[1,6\text{-}B_{10}H_8(PPh_3)_2]$ [179a] and $[2,4\text{-}B_{10}H_8(PPh_3)_2]\cdot CH_2Cl_2$ [179b] were determined.

9. DERIVATIVES WITH BORON–OXYGEN BOND

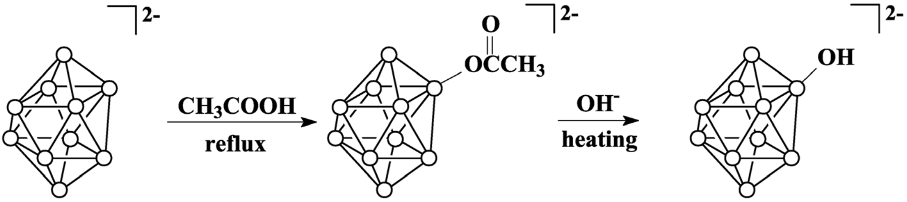
At present, several methods of synthesis of 2-hydroxy derivative of the *closo*-decaborate anion $[2\text{-}B_{10}H_9OH]^{2-}$ were proposed. One approach consists in the reaction of $[B_{10}H_{10}]^{2-}$ with amides in acidic media followed by alkaline hydrolysis of the formed intermediates. For example, heating the $[B_{10}H_{10}]^{2-}$ anion with 1-methylpyrrolidin-2-one (NMP) at 180 °C in the presence of hydrochloric or trifluoroacetic acid gives the 2-(1-methyl-1-pyrrolinio-2-yloxy) derivative $[2\text{-}B_{10}H_9NMP]^-$ (refs[139,181,182]) that can be easily hydrolyzed to $[2\text{-}B_{10}H_9OH]^{2-}$ (ref.[182]) (Scheme 31).



SCHEME 31

The reaction with *N,N*-dimethylformamide proceeds in a similar way[139,181]. The $[2\text{-}B_{10}H_9NMP]^-$ and $[2\text{-}B_{10}H_9DMF]^-$ derivatives can be obtained also by the reaction of $[B_{10}H_{10}]^{2-}$ with the corresponding amides in the presence of triphenylmethyl chloride[107]. A similar method includes the reaction of *closo*-decaborate with tetramethylene sulfone at 85 °C in the presence of *p*-toluenesulfonic acid followed by alkaline hydrolysis of the formed $[2\text{-}B_{10}H_9OS(O)(CH_2)_4]^-$ (ref.[166]). These methods allow one to prepare pure $[2\text{-}B_{10}H_9OH]^{2-}$ without admixtures of di- and trisubstituted derivatives.

Another approach to the synthesis of the 2-hydroxy derivative includes preparation of the ester derivatives followed by their alkaline hydrolysis. The first such example reported already at the at the beginning of the 1960s included oxidation of the ketone $[2\text{-}B_{10}H_9C(O)Ph]^{2-}$ by hydrogen peroxide to give the respective ester $[2\text{-}B_{10}H_9OC(O)Ph]^{2-}$, which upon alkaline hydrolysis gave the equatorially substituted hydroxy derivative[138,139]. More recently, synthesis of the *closo*-decaborate esters $[2\text{-}B_{10}H_9OC(O)R]^{2-}$ (R = H, Me, Et, *i*-Pr, *n*-Bu) by the reaction of the parent anion with the corresponding acids as well as their alkaline hydrolysis were described (Scheme 32)[183,184].



SCHEME 32

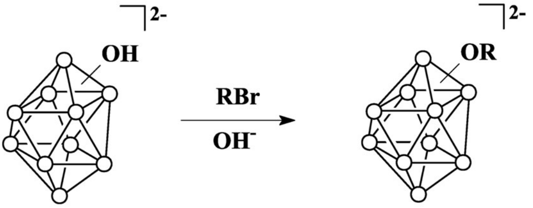
It should be noted that the substitution degree and purity of the goal product are very sensitive to the reaction temperature. At higher temperatures (80–140 °C) mixtures of mono-, di-, tri- and tetrasubstituted derivatives form[183,184]. More effective synthesis includes the reaction of *closo*-decaborate with formic or acetic acids in the presence of triphenylmethyl chloride at room temperature resulting in the corresponding ester $[2\text{-}B_{10}H_9OC(O)R]^{2-}$ (R = H, Me)[107].

The 1-hydroxy derivative $[1\text{-}B_{10}H_9OH]^{2-}$ was prepared by heating the diazonium derivative $[1\text{-}B_{10}H_9N_2]^-$ in aqueous alkaline solution[156].

Alkylation of the 1- and 2-hydroxy derivatives with alkyl bromides in dimethylsulfoxide in the presence of potassium hydroxide results in the corresponding alkoxy derivatives $[1\text{-}B_{10}H_9OR]^{2-}$ and $[2\text{-}B_{10}H_9OR]^{2-}$ (Scheme 33)[182].

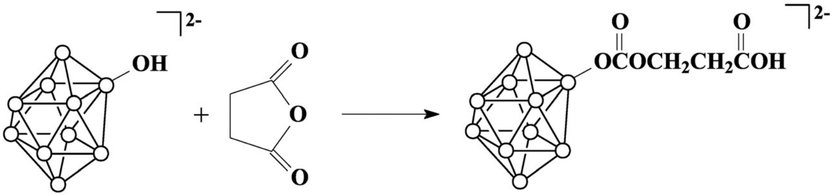
Acylation of $[2\text{-}B_{10}H_9OH]^{2-}$ with succinic anhydride was reported (Scheme 34)[185].

The cyclic oxonium derivatives $[2\text{-}B_{10}H_9O(CH_2)_4]^-$, $[2\text{-}B_{10}H_9O(CH_2)_5]^-$ and $[2\text{-}B_{10}H_9O(CH_2CH_2)_2O]^-$ were prepared by the reaction the parent



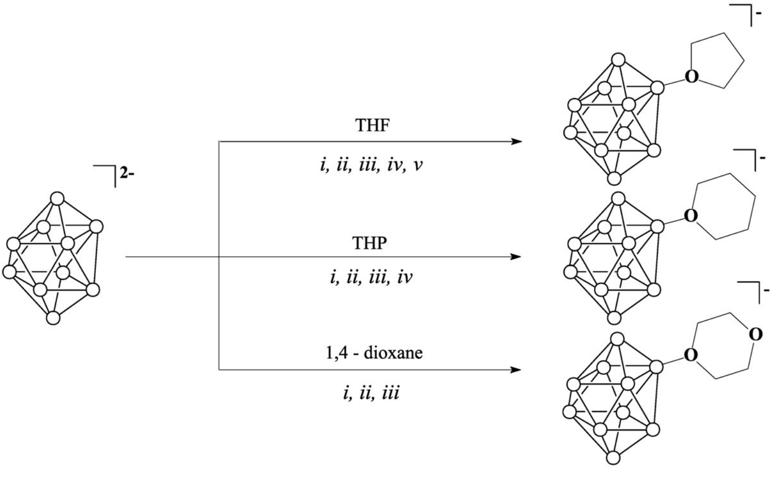
R=C_2H_5, $CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH(CH_3)_2$

SCHEME 33



SCHEME 34

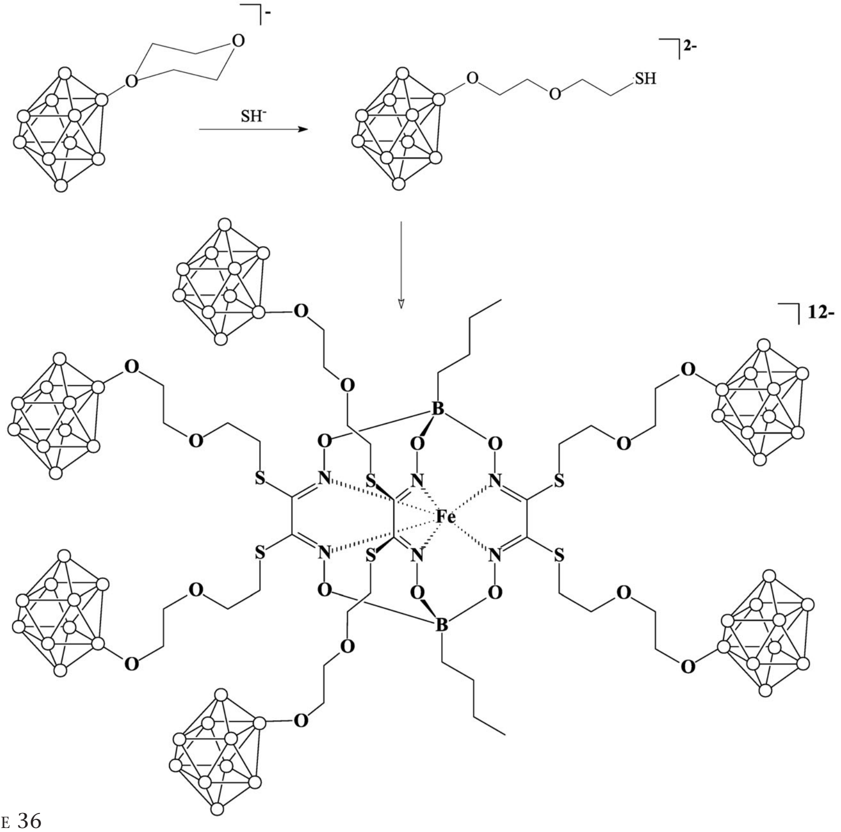
closo-decaborate with the corresponding cyclic ethers in the presence of trifluoroacetic or hydrochloric acid[168b,186,187]. The similar results can be obtained using Lewis acids ($BF_3 \cdot OEt_2$ [188] or Ph_3CCl [107]) (Scheme 35). Synthesis of disubstituted oxonium derivatives [*eq*-$B_{10}H_8L_2$] (L = $O(CH_2)_4$, $O(CH_2)_5$ and $O(CH_2CH_2)_2O$) was reported[107].



i. CF_3COOH *ii.* TrCl (eq) *iii.* 1-AdBr *or* Bu^nBr *iv.* HCl *v.* $Et_2O \cdot BF_3$

SCHEME 35

Cyclic oxonium derivatives of polyhedral boron hydrides were shown to have great potential for modification of various types of organic and bioorganic molecules[189]. At present, several examples of ring-opening reactions of the cyclic oxonium derivatives of the *closo*-decaborate anion were reported. They include reactions with *O*-nucleophiles (OH^- (refs[188,190]), OEt^- (ref.[190]) and functionalized phenolates – derivatives of hydroxy benzoic acids and tyrosine[191]) and *S*-nucleophiles (SH^-, SCN^-, $S_2O_3^{2-}$)[192]. The sulfanyl derivative was used for synthesis of heavily boronated clathrochelates (Scheme 36)[193].

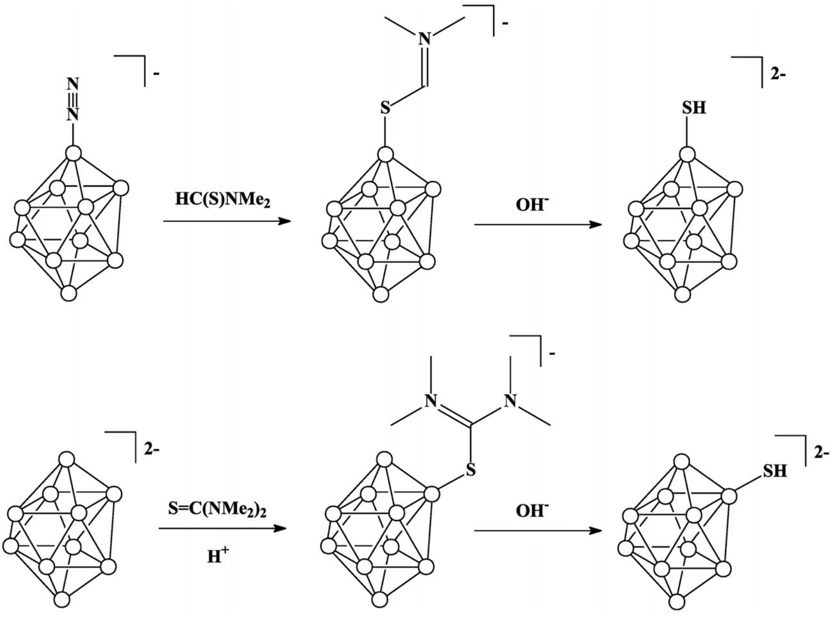


SCHEME 36

Crystal molecular structures of $(Ph_4P)[2\text{-}B_{10}H_9NMP]$[181], $(Ph_4P)[2\text{-}B_{10}H_9O(CH_2)_4]$[188], $(Ph_4P)[2\text{-}B_{10}H_9O(CH_2)_4]$[186], $(Ph_3PCH_2Naph)[2\text{-}B_{10}H_9O(CH_2CH_2)_2O]$[186] $\{Pb(2,2'\text{-bipy})[2\text{-}B_{10}H_9OH](DMF)\}\cdot DMF$[183], $(Ph_4P)\{Pb(2,2'\text{-bipy})[2\text{-}B_{10}H_9OC(O)Me]_2\}$[184], $\{Pb(2,2'\text{-bipy})_2[2,7(8)\text{-}B_{10}H_8(OC(O)Me)_2]\}$[184] and $\{Pb(2,2'\text{-bipy})[2\text{-}B_{10}H_9(OCH_2CH_2)_2\text{-}OEt]\}\cdot 0.5DMF$[190] were determined.

10. DERIVATIVES WITH BORON–SULFUR BOND

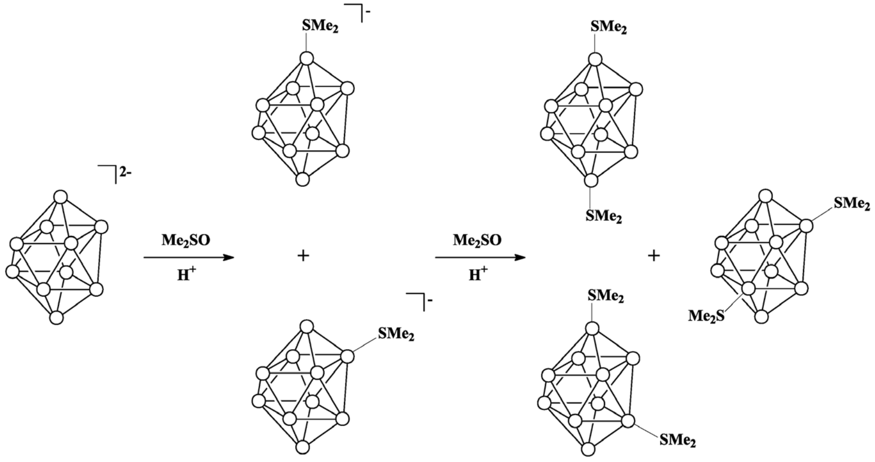
The 1-sulfanyl derivative of the *closo*-decaborate anion $[1\text{-}B_{10}H_9SH]^{2-}$ was prepared by the reaction of the diazonium derivative $[1\text{-}B_{10}H_9N_2]^-$ with *N,N′*-dimethylthioformamide followed by alkaline hydrolysis of the *S*-thioamide intermediate[194]. The 2-sulfanyl derivative $[2\text{-}B_{10}H_9SH]^{2-}$ was prepared by the reaction of the parent *closo*-decaborate with *N,N,N′N′*-tetramethylthiourea in the presence of acid followed by alkaline hydrolysis of the corresponding *S*-thioamide[194]. Crystal molecular structure of $(Me_3NH)_2$-$[2\text{-}B_{10}H_9SH]$ was determined[195]. The 1,10-disulfanylperchloro derivative $[1,10\text{-}B_{10}Cl_8(SH)_2]^{2-}$ was obtained by the reaction of the corresponding diazonium derivative with sulfane (Scheme 37)[125].



SCHEME 37

The treatment of $[1\text{-}B_{10}H_9SH]^{2-}$ and $[2\text{-}B_{10}H_9SH]^{2-}$ with trimethylsulfonium iodide gives the corresponding dimethylsulfane derivative $[1\text{-}B_{10}H_9SMe_2]^-$ and $[2\text{-}B_{10}H_9SMe_2]^-$ (ref.[194]). The dimethylsulfane derivatives can be also prepared by the direct reaction of *closo*-decaborate with dimethyl sulfoxide at 50–60 °C under acidic conditions (Scheme 38)[145,196].

The substitution proceeds preferentially at apical vertices resulting in $[1\text{-}B_{10}H_9SMe_2]^-$ and $[1,10\text{-}B_{10}H_8(SMe_2)_2]$ as the main isomers. Only trace amount of $[2,7(8)\text{-}B_{10}H_8(SMe_2)_2]$ was revealed[196]. Heating $[1,10\text{-}B_{10}H_8\text{-}$



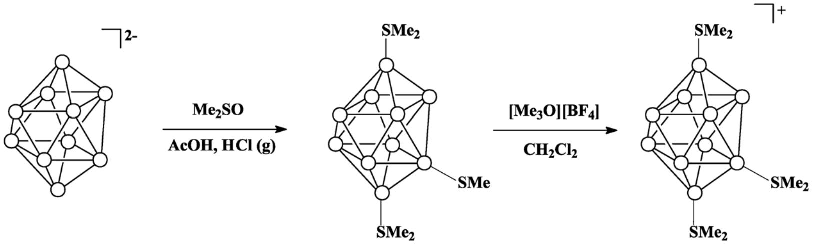
SCHEME 38

$(SMe_2)_2]$ at 220–230 °C for 40 min in Dowtherm (the eutectic mixture of biphenyl and diphenyl ether) results in partial rearrangement to $[2,7(8)\text{-}B_{10}H_8(SMe_2)_2]$. The 2,3-isomer $[2,3\text{-}B_{10}H_8(SMe_2)_2]$ was obtained in a low yield by thermal rearrangement of $[1,6\text{-}B_{10}H_8(SMe_2)_2]$ at 250–260 °C [196]. A similar way was used for an introduction of dimethylsulfonium substituent to other derivatives of the *closo*-decaborate anion[145].

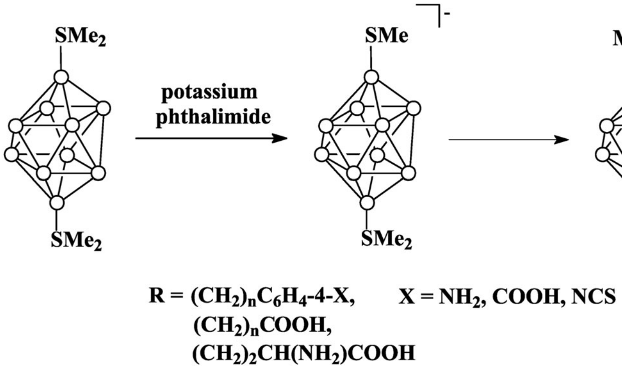
Synthesis of the tetramethylenesulfonium derivative $[2\text{-}B_{10}H_9S(CH_2)_4]^-$ by the reaction of *closo*-decaborate with tetrahydrothiophene in the presence of triphenylmethyl chloride (1-bromoadamantane or *n*-BuBr) was reported[107].

Neutral trisubstituted derivative $[1,10\text{-}B_{10}H_7(SMe_2)_2\text{-}2\text{-}SMe]$ was prepared by the reaction of *closo*-decaborate with dimethyl sulfoxide at 150 °C [196,197]. NMR analysis suggests that the reaction proceeds via a cationic intermediate $[1,2,10\text{-}B_{10}H_7(SMe_2)_3]^+$. This intermediate cannot be isolated directly, it was however prepared by the treatment of $[1,10\text{-}B_{10}H_7(SMe_2)_2\text{-}2\text{-}SMe]$ with $[Me_3O][BF_4]$ (Scheme 39)[197].

Partial demethylation of the dimethylsulfonium substituent in $[1\text{-}B_{10}H_9SMe_2]^-$, $[1,6\text{-}B_{10}H_8(SMe_2)_2]$ and $[1,10\text{-}B_{10}H_8(SMe_2)_2]$ can be achieved by the treatment with potassium phthalimide[145], sodium ethanthiolate[196] or sodium in liquid ammonia[196]. The anions formed are readily alkylated to re-form dialkylsulfane derivatives. This approach was used in the synthesis of various functional derivatives including isothiacyanates, amines, acids and aminoacids (Scheme 40)[198–200].



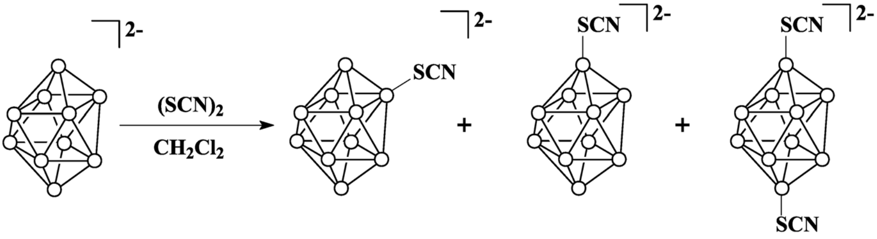
SCHEME 39



SCHEME 40

Molecular structures of $\{Pb(2,2'\text{-bipy})_2[1\text{-}B_{10}H_9SMe_2]_2\}$ [201], $[1,10\text{-}B_{10}H_8(SMe_2)_2]$ [196], $[1,6\text{-}B_{10}H_8(SMe_2)_2]$ [196], $[2,8\text{-}B_{10}H_8(SMe_2)_2]$ [196], $[2,3\text{-}B_{10}H_8(SMe_2)_2]$ [196], $(Me_4N)[1\text{-MeS-}10\text{-}B_{10}H_8SMe_2]$ [196], $(Me_4N)_2[1,6\text{-}B_{10}H_8(SMe)_2]$ [196], $[1,10\text{-}B_{10}H_7(SMe_2)_2\text{-}2\text{-SMe}]$ [196], $[1,2,10\text{-}B_{10}H_7(SMe_2)_3][BF_4]$ [197] were determined by single crystal X-ray diffraction.

The reaction of the *closo*-decaborate anion with $(SCN)_2$ in CH_2Cl_2 gives a mixture of thiocyanato derivatives $[1\text{-}B_{10}H_9SCN]^{2-}$, $[2\text{-}B_{10}H_9SCN]^{2-}$ and $[1,10\text{-}B_{10}H_8(SCN)_2]^{2-}$ that can be separated by ion-exchange chromatography on diethylaminoethyl cellulose (Scheme 41)[202].



SCHEME 41

Crystal molecular structures of $(Ph_4P)_2[1\text{-}B_{10}H_9SCN]$ [203a], $(Ph_4P)_2$-$[2\text{-}B_{10}H_9SCN]\cdot MeCN$ [203b] and $(As_4P)_2[1,10\text{-}B_{10}H_8(SCN)_2]$ [203a] were determined.

11. DERIVATIVES WITH BORON–SELENIUM BOND

The reaction of the *closo*-decaborate anion with $(SeCN)_2$ in CH_2Cl_2 produces the selenocyanato derivative $[1\text{-}B_{10}H_9SeCN]^{2-}$. Structure of $(Ph_4P)_2$-$[1\text{-}B_{10}H_9SeCN]$ was determined by single crystal X-ray diffraction[204].

12. DERIVATIVES WITH BORON–METAL BOND

A few examples of derivatives with boron metal were reported. The reactions of the *closo*-decaborate anion with Ph_3SnCl and Ph_2SnCl_2 give $[2\text{-}B_{10}H_9SnClPh_2]^{2-}$ (ref.[205]) and $[2\text{-}B_{10}H_9SnCl_2Ph]^{2-}$ (ref.[206]), respectively. Structures of $(Ph_4P)_2[2\text{-}B_{10}H_9SnClPh_2]$ and $(Ph_4P)_2[2\text{-}B_{10}H_9SnCl_2Ph]$ were determined by single crystal X-ray diffraction.

The reaction of $\{Ag_2[B_{10}H_{10}]\}$ with $[(Ph_3P)AuCl]$ in an acetonitrile–benzene mixture results in triangular gold complex $\{(Ph_3P)_3Au_3[\mu_3\text{-}1\text{-}B_{10}H_9]\}$ with the *closo*-decaborate cluster playing role of μ_3-bridging ligand. The structure of $\{(Ph_3P)_3Au_3[\mu_3\text{-}1\text{-}B_{10}H_9]\}\cdot C_6H_6\cdot SC_4H_4$ was determined by single crystal X-ray diffraction (Fig. 6)[207].

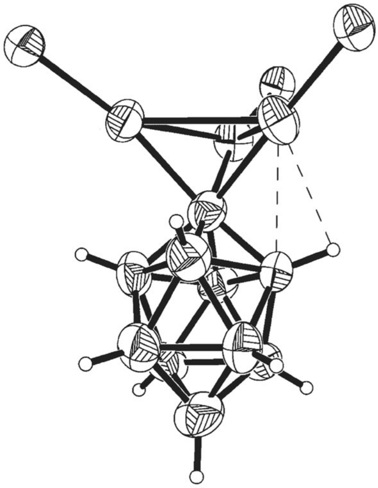
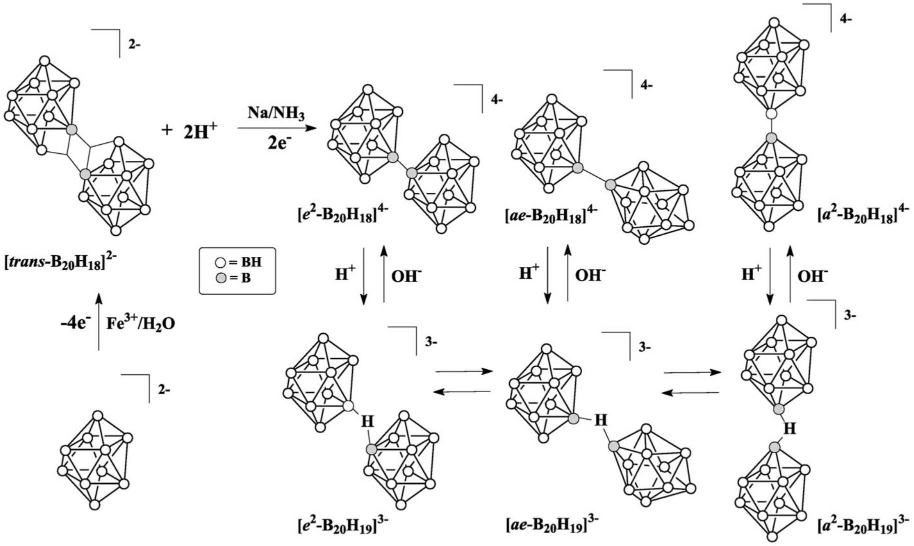


FIG. 6

Molecular structure of $\{(Ph_3P)_3Au_3[\mu_3\text{-}1\text{-}B_{10}H_9]\}\cdot C_6H_6\cdot SC_4H_4$. The phenyl groups of the triphenylphosphine ligands were omitted for clarity. Reproduced from ref.[207] with permission of Springer

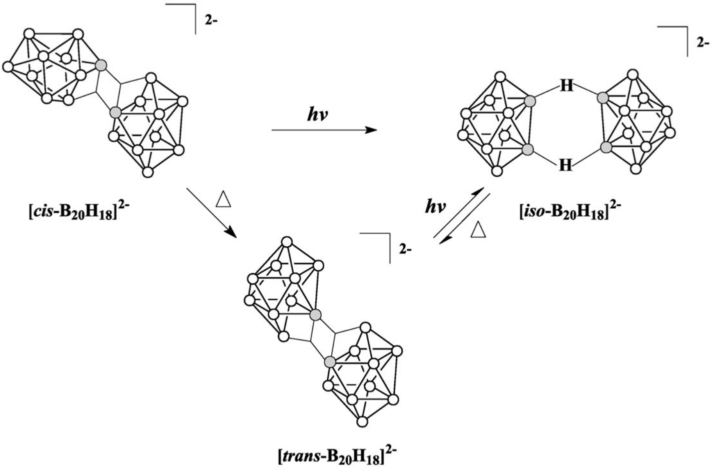
13. OXIDATION: $[B_{20}H_{18}]^{2-}$ AND RELATED SPECIES

The *closo*-decaborate anion was found to be less stable to oxidation than $[B_{12}H_{12}]^{2-}$ and undergoes smooth oxidative conversion to [*trans*-$B_{20}H_{18}]^{2-}$ under treatment with Ce^{4+} or Fe^{3+} in aqueous solution (Scheme 42)[208–210]. The oxidative coupling of $[B_{10}H_{10}]^{2-}$ to [*trans*-$B_{20}H_{18}]^{2-}$ can be achieved in organic solution with 2,3,5,6-tetrachloro-1,4-benzoquinone[211]. The same product was obtained by the exhaustive electrolysis of $(Me_3NH)_2[B_{10}H_{10}]$ in acetonitrile at 0.9 V vs SCE[212]. The oxidation of [*closo*-$B_{10}H_9L]^-$ derivatives (L = NMe_3, SMe_2) proceeds in a similar way resulting in neutral species [*trans*-$B_{20}H_{16}L_2$][121a].



SCHEME 42

The [*trans*-$B_{20}H_{18}]^{2-}$ ion is readily reduced with sodium in liquid ammonia solution to produce the e^2-isomer of $[B_{20}H_{18}]^{4-}$ (ref.[213]). In protic solvents, and more rapidly with acid catalysis, the e^2-isomer rearranges to the *ae*-isomer and subsequently to the a^2-isomer. The proton-assisted rearrangement of the isomeric $[B_{20}H_{18}]^{4-}$ ions suggests the existence of a set of isomeric $[B_{20}H_{19}]^{3-}$ ions resulting from the reversible protonation of the corresponding $[B_{20}H_{18}]^{4-}$ isomers. Due to the fluxionality of the bridging proton and rapid isomer equilibration the only [a^2-$B_{20}H_{19}]^{3-}$ isomer was reliably characterized by the single crystal X-ray diffraction[214]. The reduction of $[B_{20}H_{18}]^{2-}$ to $[B_{20}H_{18}]^{4-}$ is reversible with a variety of oxidizing agents. The particular isomer of $[B_{20}H_{18}]^{2-}$ resulting from the oxidation depends on the isomer of the $[B_{20}H_{18}]^{4-}$ precursor and the reaction conditions. As an example, all three isomers of $[B_{20}H_{18}]^{4-}$ produce thermodynamically preferred [*trans*-$B_{20}H_{18}]^{2-}$ when oxidized with hot aqueous Fe^{3+}, but the [*cis*-$B_{20}H_{18}]^{2-}$ isomer can be obtained as a kinetically controlled product when the oxidation of *ae*-$[B_{20}H_{18}]^{4-}$ is performed at 0 °C in the presence of a precipitating counterion that removes the product from solution before further rearrangement occurs[215]. The third isomer [*iso*-$B_{20}H_{18}]^{2-}$ can be obtained by irradiation of [*trans*-$B_{20}H_{18}]^{2-}$ or [*cis*-$B_{20}H_{18}]^{2-}$ with ultraviolet light in acetonitrile solution[215,216]. Heating [*iso*-$B_{20}H_{18}]^{2-}$ in acetonitrile regenerates the original of [*trans*-$B_{20}H_{18}]^{2-}$ (Scheme 43). More detail discussion of the chemistry of the $[B_{20}H_{18}]^{2-}$ ions including substitution reactions can be found in Hawthorne's review[217].

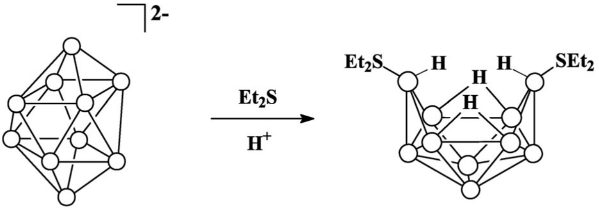


SCHEME 43

14. THE B_{10} CAGE OPENING

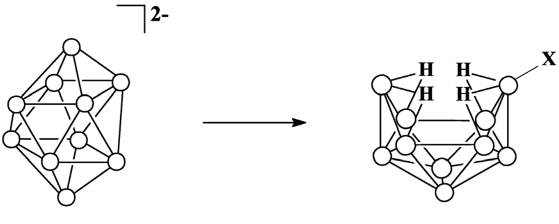
Another example of lower stability of the *closo*-decaborate anion in the comparison with *closo*-dodecaborate is its cage opening. The reaction of $(NH_4)_2[B_{10}H_{10}]$ with anhydrous hydrogen chloride in diethylsulfane was found to result in the cage opening with formation of 6,9-bis(diethylsulfane)decaborane 6,9-$B_{10}H_{12}(SEt_2)_2$ [218]. Later this reaction was extended to other strong acids and other salts of the *closo*-decaborate anion (Scheme 44)[14,219].

The *closo*-decaborate cage-opening studies were stimulated by synthetic utility of decaborane derivatives as potentially important synthons in synthesis of carboranes, polyboranes and organopolyboranes and possibility to prepare them in two step from $(Et_4N)[BH_4]$ avoiding a hazardous diborane pyrolysis reaction.



SCHEME 44

The chloro derivative 6-$B_{10}H_{13}Cl$ was prepared by the reaction of $(Et_4N)_2[B_{10}H_{10}]$ with $AlCl_3$ in hexane in the presence of very small amount of water[220]. The reaction proceeds through the formation of an intermediate complex between $[B_{10}H_{10}]^{2-}$ and $AlCl_3$ [221]. The reactions with $AlBr_3$ and AlI_3 give the corresponding halo derivatives[221]. The reactions of $(NH_4)_2[B_{10}H_{10}]$ with HX in a mixture of [*Bmim*]X and AlX_3 (X = Cl, Br, I; *Bmim* = 1-butyl-3-methylimidazolium) were found to result in the corresponding halo derivatives 6-$B_{10}H_{13}X$ in nearly quantitative yields (Scheme 45)[222]. The reaction of $(NH_4)_2[B_{10}H_{10}]$ with trifluoromethanesulfonic acid in CH_2Cl_2 also gives an excellent yield of the chloro derivative[222]. The corresponding fluoro derivative 6-$B_{10}H_{13}F$ was prepared by the reaction of $(NH_4)_2[B_{10}H_{10}]$ with 1-fluoropentane and trifluoromethanesulfonic acid in pentane[222].



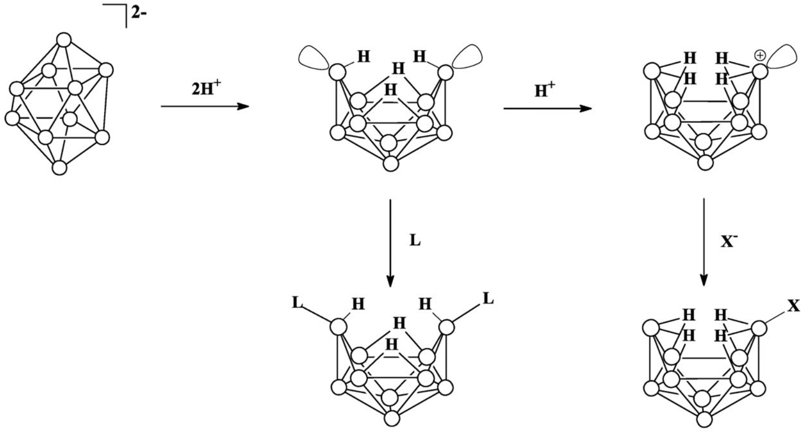
X = F, Cl, Br, I

SCHEME 45

The reaction of $Cs_2[B_{10}H_{10}]$ with trifluoromethanesulfonic acid in benzene gives the phenyl derivative 6-$B_{10}H_{13}Ph$ in a high yield, whereas the similar reaction in cyclohexane produces 6-$B_{10}H_{13}$-*cyclo*-C_6H_{11} and 6-$B_{10}H_{13}OTf$ [223].

The hydroxy derivative 6-$B_{10}H_{13}OH$ was found as a by-product in all the cage-opening reactions whenever H_2O may interfere in the formation process of the product. The preparative synthesis of 6-$B_{10}H_{13}OH$ by the reaction of $(NH_4)_2[B_{10}H_{10}]$ with sulfuric acid in hexane was reported as well[224]. The hydroxy derivative was found to be the intermediate in the dehydration of the acidic form $(H_3O)_2[B_{10}H_{10}]$ resulting in 6,6′-$(B_{10}H_{13})_2O$ [225].

The mechanism of the cage opening is not yet completely clear. Nevertheless the first step definitely includes double protonation of the boron polyhedron resulting in the cage opening to give $B_{10}H_{12}$ being a strong Lewis acid. The subsequent reaction route depends strongly on the presence of nucleophiles in the reaction media. In the presence of classical Lewis bases such as diethylsulfane, the reaction results in *arachno*-6,9-$B_{10}H_{12}L_2$. In the case of weaker nucleophiles, such as halogen anions, the next step probably is protonation of $B_{10}H_{12}$ to strongly electrophilic $B_{10}H_{13}^+$ followed by nucleophilic attack resulting in *nido*-6-$B_{10}H_{13}X$, and at the last, if no or very weak nucleophiles are present, the C–H activation of a solvent takes place. The probable reaction mechanism is presented in Scheme 46.



SCHEME 46

In summary, the B_{10} cage opening presents a very attractive route to decaborane derivatives and decaborane itself. It was shown that 6-$B_{10}H_{13}Br$ can be converted in 70% isolated yield to the parent $B_{10}H_{14}$ upon reaction with Bu_3SnH [222].

The reaction of $(NH_4)_2[B_{10}H_{10}]$ with trifluoromethanesulfonic or sulfuric acid in benzene in the presence of acetonitrile or $(C_6H_5)_2CHCN$ results in 4-$B_9H_{13}L$ (L = $N{\equiv}CCH_3$, $N{\equiv}CCH(C_6H_5)_2$) together with some amounts of 6-$B_{10}H_{13}Ph$ and $B_{10}H_{14}$ [226]. The degradation of the B_{10} cage could be explained by acidolysis of the *arachno*-6,9-$B_{10}H_{12}L_2$ intermediate.

Another type of reactions that in general is out of scope of this review but should be mentioned here is the B_{10} cage opening with an insertion of metal atom(s) resulting in formation of metallaboranes (so-called "reactions of polyhedral expansion"). The first example of such reactions was reported by Paxson and Hawthorne in 1975 who received isomeric platinaboranes $[(Ph_3P)_2PtB_{10}H_{11}OEt]$ by the reaction of $K_2[B_{10}H_{10}]$ with [*cis*-$(Ph_3P)_2PtCl_2$] in hot ethanolic chloroform[227]. The mechanism of this reaction is not very clear. Probably, the first step includes coordination of low valent metal (platinum(II)) to the boron cage followed by a 2-electron cage reduction with insertion of the metal to give the $Pt(IV)B_{10}$ species. The reliability of such mechanism is supported by the conversion of {*cis*-$((Ph_3P)_2Pt)[B_{10}H_{10}]$} into $[(Ph_3P)_2PtB_{10}H_{11}OEt]$ in ethanolic dichloromethane[65]. The reactions of polyhedral expansion of the *closo*-decaborate anion with complexes of platinum[227,228], ruthenium[229,230], osmium[231], rhodium[232], and nickel[233,234] were reported.

15. POTENTIAL APPLICATIONS OF THE *closo*-DECABORATE ANION

Despite the era of boron chemistry aimed at advanced jet and rocket propulsion systems ended in the early 1960s, the interest in the polyhedral boron hydrides as high energy density materials still persists and some salts of the *closo*-decaborate anion were proposed as components of high burning composite propellants[235]. However, the main directions of potential application of the *closo*-decaborate anion lie in other fields, especially in medicine.

The possibility of the application of the *closo*-decaborate anion in medicine is based on its remarkable chemical and hydrolytical stability and low toxicity. The sodium salt $Na_2[B_{10}H_{10}]$ administered orally to rats was found to have a low order of acute toxicity, with the approximate lethal dose for rats higher than 7.5 g/kg of body weight which is roughly comparable to that of sodium chloride[236].

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 ca. 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[237]. It should be noted that the sodium salt of the *closo*-decaborate, $Na_2[B_{10}H_{10}]$ (GB-10), is approved for human use by the US Food and Drug Administration.

Another direction of medical application of the *closo*-decaborate anion is radioimmuno-diagnostics and therapy. 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 studies 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. Polyhedral borane anions were found to be reasonable linkers for the attachment of radiohalogens to tumor-targeting proteins and peptides due to the absence of enzymatic systems for cleavage of the boron–halogen bond, caused by very exogenous nature of such compounds, as well as the negative charges of polyhedral borane anions, which may improve intracellular retention of bound radiohalogens. In comparison with $[B_{12}H_{12}]^{2-}$, the $[B_{10}H_{10}]^{2-}$ anion has an advantage of much faster iodination reaction, which allows one to use it for selective direct labelling of antibodies in the presence of excess of thyrosine residues. The feasibility of radiolabelling antibodies with the derivatives of the *closo*-dodecaborate anion with different radiohalogen isotopes has been shown recently[129,130].

Development of new molecular materials is other promising direction of the use of the *closo*-decaborate anion. The structural and electronic features of this anion, especially strong interactions between the apical boron vertices, provide an attractive alternative to organic aromatics for control the type and degree of electron interactions in molecular materials[238]. Thus, the use of *closo*-decaborate derivatives for design of NLO chromofores was reported recently[239]. Other directions of potential application of the *closo*-decaborate anion is extraction of radionuclides from nuclear waste[240], electrolytes in lithium-ion batteries[241] and components of ionic liquids[242].

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