Nucleophilic substitution in *closo*-decaborate $[B_{10}H_{10}]^{2-}$ in the presence of carbocations

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Nucleophilic substitution at the *exo*-polyhedral boron atoms of *closo*-decaborate $[B_{10}H_{10}]^{2-}$ in the presence of carbocations, which were generated *in situ* from various halocarbons (triphenylmethyl chloride, 1-bromoadamantan, *n*-butyl bromide), was studied. The reactions carried out in nucleophilic solvents (cyclic ethers and thioethers, *N*,*N*-disubstituted amides, and carboxylic acids) and in the presence of halocarbons afforded mono- and disubstituted compounds with the *exo*-polyhedral B—O and B—S bonds, which contained a molecule of the solvent as substituent. The structures of the compounds synthesized were confirmed by the IR, mass, and ^{1}H, ^{11}B, and ^{13}C NMR spectra.

Key words: boron hydrides, carbocations, electrophilic-induced nucleophilic substitution.

Derivatives of *closo*-borates are widely used for the synthesis of the substances promising for the boron neutron capture therapy (BNCT)[1,2] of tumors, for the design of composite materials by the powder metallurgy,[3] and for selective extraction of rare earth elements.[4,5]

Electrophilic-induced nucleophilic substitution is the common method for functionalization of the boron clusters.[6] This method involved the reaction of the *closo*-borates with protic acids[7—9] or the Lewis acids[10—12] in the presence of nucleophiles.

Carbocations, being the Lewis acids, could also induced the similar reactions of borates, for example in the $[B_{12}H_{12}]^{2-}$ anion.[13,14] However, no examples of such reactions have been documented for the $[B_{10}H_{10}]^{2-}$ anion. The aim of the present work was to develop novel synthetic methods for the functionalizaion of *closo*-decaborates by the electrophilic-induced nucleophilic substitution.

Results and discussion

To achieve this goal, we studied the reactions of the *closo*-decaborates with nucleophiles in the presence of trityl chloride (thriphenylmethyl chloride, TrCl), 1-bromoadamantan (1-AdBr) or *n*-butyl bromide (Bu^nBr) as the initiators of the reaction. It was shown that the reactions under consideration gave mono- and disubstituted compounds depending on the halocarbons, the nature of the nucleophile, and the reaction conditions (Scheme 1).

With the aim to determine the role of TrCl, 1-AdBr, and Bu^nBr in the initiation of the nucleophilic substitution, we studied the reactions of *closo*-decaborate (in the form of tetrabutylammonium $(Bu^n{}_4N)_2[B_{10}H_{10}]$ (**1**) and potassium $K_2[B_{10}H_{10}]$ salts) with carbocations in the non-nucleophilic solvents, such as dichloromethane and benzene (see Scheme 1 and Experimental). Addition of the halocarbon (1 equiv.) to the salt of the $[B_{10}H_{10}]^{2-}$ anion led to the changes in the ^{11}B NMR and IR spectra, which were similar to that observed upon protonation of *closo*-decaborate.[15] Thus in the IR spectra, the absorption band of the stretching vibration attributed to the B—H bonds shifted toward the higher wavenumbers by 60—70 cm^{-1} with respect to that of the $[B_{10}H_{10}]^{2-}$ anion. The ^{11}B NMR spectra exhibited three signals at δ 25.6 (B(10)), −22.4 (B(1), B(2), B(3), B(4), and B(5)), and −24.8 (B(6), B(7), B(8), and B(9)) with integral intensity ratio of 1 : 5 : 4, respectively. Without the broad band spin decoupling, these signals appeared as doublets. If the reaction was initiated by trityl chloride, the increase in the concentration of the carbocation in the solution of the $\{[B_{10}H_{10}]^{2-}...E^+\}^-$ complex ($E^+ = Tr^+$) resulted in the decrease of the intensity of the low field signal, which is corresponded to the opposite apical boron atom. This signal disappeared completely, when the two-fold excess of TrCl was attained. Therefore, the ^{11}B NMR spectra exhibited only one broadened signal at δ −21.3 (upon this conditions all boron atoms are equivalent). These

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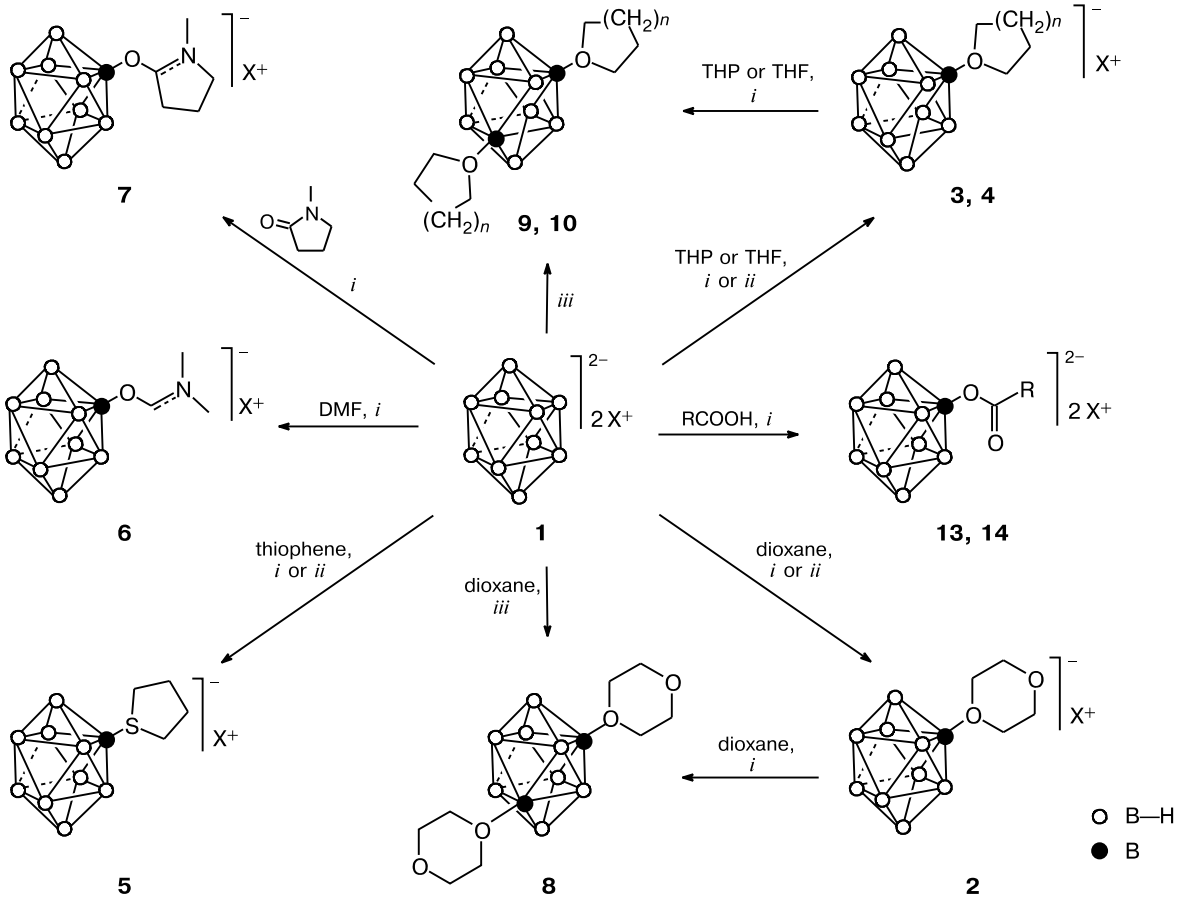
Scheme 1



n = 1 (**3**, **9**), 2 (**4**, **10**); X = $[Bu^n_4N]^+$, R = H (**13**), Me (**14**)

Reagents and condition: *i*. TrCl (1 equiv.), 20 °C; *ii*. 1-AdBr (1 equiv.) or Bu^nBr (1 eqviv.), reflux; *iii*. TrCl (2 equiv.), 20 °C.

changes could be attributed to the formation of the $\{[B_{10}H_{10}]^{2-}...2E^+\}$ complex ($E^+ = Tr^+$). Similar to the above described, the IR spectra showed the shift of the absorption band of the B—H stretching vibrations to the higher wavenumbers by 60—70 cm^{-1}. No such phenomenon was observed with the use of other initiators (1-AdBr and Bu^nBr).

Aside from the $[B_{10}H_{11}]^-$ anion, the addition of the nucleophiles to the resulting complexes according to the spectroscopic data furnished the corresponding substituted derivatives even at room temperature. The structures and compositions of the compounds synthesized were established based on the data from the ^1H, ^{11}B, and ^{13}C NMR and IR spectroscopy and confirmed by elemental analysis. The spectral data are consistent with that documented.[8,16—18]

Apparently, the carbocation abstracted the hydride ion from the boron framework giving the $[B_{10}H_9]^-$ ion, which reacted immediately with the nucleophilic center of the reagent yielding the substituted derivatives of the $[2\text{-}B_{10}H_9Nu]^-$ ion (compounds **2—7**). In the presence of the two-fold excess of trityl chloride, second hydride ion was also removed from the boron atom of the neighboring equatorial belt of the cluster giving neutral compounds [*eq*-$B_{10}H_8Nu_2$] **8—10**.

Addition of TrCl (1 equiv.) to a solution of salt **3** in dichloromethane led to the changes in the ^{11}B NMR spectra, which could be explained by complexation with carbocation. Thus the signal for the B(4) atom shifted to the weaker field and was observed at δ 23.9, the signals for the B(7) and B(8) atoms broadened. No noticeable changes in the positions of other signals were observed as compared with the spectra of the starting $[2\text{-}B_{10}H_9OC_4H_8]^-$ anion (compound **3**). As in the case of the unsubstituted *closo*-borate, the addition of the nucleophile to this mixture resulted in disubstitutes compound **9**.

It should be noted that even very weak nucleophiles, such as alkyl dihalides, can react at elevated temperature

with *closo*-decaborate in the presence of the carbocations. This reaction gave the corresponding halogen-substituted derivatives **11** and **12** (see Experimental).

In summary, novel method for the synthesis of mono- and disubstituted *closo*-decaborate derivatives under mild conditions was developed. The use of trityl cation for the initiation of the reaction resulted in the mono- and disubstituted derivatives, while *n*-butyl and adamantyl cations, being the weaker Lewis acids, furnished only monosubstituted derivatives. The use of cyclic ethers as nucleophiles resulted in the corresponding mono- and disubstituted products, while in the case of thioethers, amides and carboxylic acids only monosubstituted derivatives were formed. It should be emphasized that all studied reactions, which were carried out in the presence of TrCl as the initiator of the reaction, proceeded at room temperature. This feature makes the developed method especially promising for the direct synthesis of the biologically active derivatives of *closo*-borates.

Experimental

Tetrabutylammonium decahydro-*closo*-decaborates(2−) $(Bu^n_4N)_2[B_{10}H_{10}]$ (**1**) and potassium decahydro-*closo*-decaborates $K_2[B_{10}H_{10}]$ were synthesized by the known methods.[19,20] 1,4-Dioxane, tetrahydrofuran, and diethyl ether were purified by the known procedures.[21] Acetic and formic acids, tetrahydropyran, tetrahydrothiophene, 1-bromoadamantan, trityl chloride, 1-bromobutane, DMF, 1,2-dichloroethane, and 1,2-dibromoethane (assay ≥99%) were used as purchased. Elemental analysis on boron was performed by the atom absorption spectroscopy (AAS) on Perkin—Elmer 2100 (HGA-700) and Perkin—Elmer 403 (HGA-72) instruments applying electrothermal ionization. The samples were prepared in accordance with published procedure.[22] The IR spectra were recorded on an Infralum FT-02 Fourier-transform IR spectrometer in the range of 7000—300 cm^{-1} with the resolution of 1 cm^{-1} in a KBr cell. The samples were prepared as suspensions in Nujol (Aldrich) or fluorinated oil (Fluorolube, Merck). The ^{11}B NMR spectra were recorded on a Bruker AC-200 instrument operating at 64.2 MHz, the deuterium resonance of the solvent was used as the lock signal. The chemical shifts are given relative to boron trifluoride etherate. The mass spectra (ESI) were run on a Bruker Esquire 3000 plus mass spectrometer (Electrospray Voltage +(−)4500 V). The samples were dissolved in acetonitrile or a mixture acetonitrile—water (1 : 1), average analytical concentration of the sample was 1.00±0.20 mg mL^{-1}.

All substituted derivatives of *closo*-decaborate were synthesized analogously, the synthetic procedures differed only in the reaction time.

Tetrabutylammoium 2-[1-(1,4-dioxanium)]nonahydro-*closo*-decaborate(−), $(Bu^n_4N)[2\text{-}B_{10}H_9O_2C_4H_8]$ (2). ***A.*** To a suspension of **1** (1.0 g, 1.6 mmol) in 1,4-dioxane (20 mL), a solution of TrCl (0.50 g, 1.8 mmol) in 1,4-dioxane (10 mL) was added with stirring. Gradual dissolution of salt **1** and formation of blue solution were observed. After stirring for 48 h, the solvent was removed in oil pump *vacuo*. Treatment of the resulting deep blue waxy residue with diethyl ether (50 mL) gave the white precipitate and blue-colored solution. The precipitate that formed was filtered off, washed with diethyl ether (3×25 mL), and recrystalized from ethanol to give salt **2** in a yield of 0.63 g (88%). Found (%): B, 24.10. $C_{20}H_{53}B_{10}NO_2$. Calculated (%): 24.14. IR, ν/cm^{-1}: 2452 (ν(B—H)); 1104 (δ(B—B—H)); 697 (δ(B—B—B)); 971 (ν(C—O), C—O(B)—C); 1086 (ν(C—O), C—O—C). ^{11}B NMR (CD_3CN), δ: 9.0 (s, B(2)); 2.0 (d, B(10)); −5.4 (d, B(1)), −20.4 (d, B(3), B(5), B(6), B(9)); −22.3 (d, B(4), B(7), B(8)). MS (ESI), *m/z*: $[2\text{-}B_{10}H_9O_2C_4H_8]^-$, found 205.30, calculated 205.29, $C_4H_{17}{}^{10}B_2{}^{11}B_8O_2$.

B. To a suspension of **1** (1.0 g, 1.6 mmol) in 1,4-dioxane (20 mL), a solution of 1-AdBr (0.39 g, 1.8 mmol) in 1,4-dioxane (5 mL) was added. The mixture was rapidly heated and refluxed for 30 min. Gradual dissolution of salt **1** was observed. The solvent was removed *in vacuo*. The resulted white waxy residue was treated with diethyl ether (50 mL), the precipitate that formed was filtered off and washed with diethyl ether (3×25 mL). Salt **2** was obtained in a yield of 0.57 g (79%).

C. Bu^nBr (0.20 mL, 1.8 mmol) was added to a suspension of **1** (1.0 g, 1.6 mmol) in 1,4-dioxane (25 mL), the mixture was rapidly heated and refluxed for 30 min. Gradual dissolution of salt **1** was observed. The solvent was removed *in vacuo*, the yellowish oily residue was treated with diethyl ether (50 mL), the precipitate that formed was filtered off and washed with diethyl ether (3×25 mL) to give salt **2** in a yield of 0.60 g (84%).

Tetrabutylammonium 2-[1-tetrahydrofuranium]nonahydro-*closo*-decaborate(1−), $(Bu^n_4N)[2\text{-}B_{10}H_9OC_4H_8]$ (3) was obtained as described for **2**. The reaction between a suspension of salt **1** (1.0 g, 1.6 mmol) in tetrahydrofuran (20 mL) and a solution of TrCl (0.50 g, 1.8 mmol) in tetrahydrofuran (5 mL), which was carried out by protocol ***A*** for 60 h, afforded salt **3** in a yield of 0.61 g (89%). Found (%): B, 24.98. $C_{20}H_{53}B_{10}NO$. Calculated (%): B, 25.04. ^{11}B NMR (CD_3CN), δ: 5.9 (s, B(2)); 1.9 (d, B(10)); −4.6 (d, B(1)); −22.4 (d, B(3), B(5), B(6), B(9)); −30.0 (d, B(4), B(7), B(8)). IR, ν/cm^{-1}: 2454 (δ(B—H)); 1104 (δ(B—B—H)); 697 (δ(B—B—B)); 968 (ν(C—O), C—O(B)—C). MS (ESI), *m/z*: $[2\text{-}B_{10}H_9OC_4H_8]^-$, found 189.28, calculated 189.28, $C_4H_{17}{}^{10}B_2{}^{11}B_8O$.

The reaction between a suspension of **1** (1.0 g, 1.6 mmol) in tetrahydrofuran (20 mL) and a solution of 1-AdBr (0.39 g, 1.8 mmol) in tetrahydrofuran (5 mL), which was carried out by protocol ***B*** for 1 h, afforded salt **3** in a yield of 0.44 g (61%)

The reaction of a suspension of **1** (1.0 g, 1.6 mmol) with Bu^nBr (0.20 mL, 1.8 mmol) in tetrahydrofuran (25 mL), which was carried out by protocol ***C*** for 30 min, afforded salt **3** in a yield of 0.52 g (73%).

Tetrabutylammonium 2-[1-tetrahydropyranium]nonahydro-*closo*-decaborate(1−), $(Bu^n_4N)[2\text{-}B_{10}H_9OC_5H_{10}]$ (4) was obtained as described for **2**. The reaction between a suspension of salt **1** (1.0 g, 1.6 mmol) in tetrahydropyran (20 mL) and a solution of TrCl (0.50 g, 1.8 mmol) in tetrahydropyran (5 mL), which was carried out by protocol ***A*** for 72 h, afforded salt **4** in a yield of 0.59 g (83%). Found (%): B, 24.25. $C_{21}H_{55}B_{10}NO$. Calculated (%): B, 24.25. IR, ν/cm^{-1}: 2450 (ν(B—H)); 1104 (δ(B—B—H)); 697 (δ(B—B—B)); 944 (ν(C—O), C—O(B)—C). ^{11}B NMR (CD_3CN), δ: 4.8 (s, B(2)); −1.1 (d, B(10)); −7.9 (d, B(1)); −23.4 (d, B(6), B(9)); −25.3 (d, B(3), B(5)); −31.6 (d, B(4), B(7), B(8)). MS (ESI), *m/z*: $[2\text{-}B_{10}H_9OC_5H_{10}]^-$, found 203.32, calculated 203.33, $C_5H_{19}{}^{10}B_2{}^{11}B_8O$.

The reaction between a suspension of **1** (1.0 g, 1.6 mmol) in tetrahydropyran (20 mL) and a solution of 1-AdBr (0.39 g,

1.8 mmol) in tetrahydropyran (5 mL), which was carried out by protocol ***B*** for 1 h, afforded salt **4** in a yield of 0.44 g (61%).

The reaction of salt **1** (1.0 g, 1.6 mmol) with Bu^nBr (0.20 mL, 1.8 mmol) in tetrahydropyran (25 mL), which was carried out by protocol ***C*** for 40 min, afforded salt **4** in a yield of 0.52 g (73%).

Tetrabutylammonium 2-[1-tetrahydrothiophenium]nonahydro-*closo*-decaborate(1–), $(Bu^n_4N)[2\text{-}B_{10}H_9SC_4H_8]$ (5) was obtained as described for **2**. The reaction between a suspension of salt **1** (1.0 g, 1.6 mmol) in tetrahydrothiophene (20 mL) and a solution of TrCl (0.50 g, 1.8 mmol) in tetrahydrothiophene (5 mL), which was carried out by protocol ***A*** for 96 h, afforded salt **5** in a yield of 0.59 g (82%). Found (%): B, 24.05. $C_{20}H_{53}B_{10}NS$. Calculated (%): B, 24.14. ^{11}B NMR (CD_3CN), δ: 1.1 (d, B(10)); –5.2 (d, B(1)); –17.0 (s, B(2)); –27.5 (d, B(3), B(5), B(6), B(9)); –31.2 (d, B(4), B(7), B(8)). IR, ν/cm^{-1}: 2458 (ν(B—H)); 1102 (δ(B—B—H)); 698 (δ(B—B—B)); 680 (ν(C—S), C—S—C); 2686 (ν(C—H), S—CH_2); 1420 (δ(C—H), S—CH_2). MS (ESI), *m/z*: $[2\text{-}B_{10}H_9SC_4H_8]^-$, found 205.36, calculated 205.35, $C_4H_{17}{}^{10}B_2{}^{11}B_8S$.

The reaction between a suspension of salt **1** (1.0 g, 1.6 mmol) in tetrahydrothiophene (20 mL) and a solution of 1-AdBr (0.39 g, 1.8 mmol) in tetrahydrothiophene (5 mL), which was carried out by protocol ***B*** for 1 h, afforded salt **5** in a yield of 0.42 g (60%).

The reaction of a suspension of **1** (1.0 g, 1.6 mmol) with Bu^nBr (0.20 mL, 1.8 mmol) in tetrahydrothiophene (5 mL), which was carried out by protocol ***C*** for 30 min, afforded salt **5** in a yield of 0.49 g (68%).

Tetrabutylammonium 2-[*N,N*-dimethylaminomethylenoxonium]nonahydro-*closo*-decaborate(1–), $(Bu^n_4N)[2\text{-}B_{10}H_9OC(H)N(CH_3)_2]$ (6). To a suspension of **1** (1.0 g, 1.6 mmol) in DMF (20 mL), a solution of TrCl (0.50 g, 1.8 mmol) in DMF (5 mL) was added. The color of the solution quickly changed to deep blue. The mixture was stirred at room temperature for 48 h. Salt **6** was isolated as above in a yield of 0.64 g (93%). Found (%): B, 24.62. $C_{19}H_{52}B_{10}N_2O$. Calculated (%): B, 24.98. IR, ν/cm^{-1}: 2463 (ν(B—H)); 1112 (δ(B—B—H)); 699 (δ(B—B—B)); 1676 (ν(C=O)). ^{11}B NMR (CD_3CN), δ: –0.5 (s, B(2)); –1.9 (d, B(10)); –6.3 (d B(1)); –23.5 (d, B(3), B(5)); –25.4 (d, B(6), B(9)); –30.5 (d, B(7), B(8)); –32.9 (d, B(4)). MS (ESI), *m/z*: $[2\text{-}B_{10}H_9OC(H)N(CH_3)_2]^-$, found 190.29, calculated 190.27, $C_3H_{16}N^{10}B_2{}^{11}B_8O$.

Tetrabutylammonium 2-[(1-methylpyrrolidin-2-yliden)oxonium]nonahydro-*closo*-decaborate(1–), $(Bu^n_4N)[2\text{-}B_{10}H_9OC(CH_2)_3NCH_3]$ (7). To a suspension of **1** (1.0 g, 1.6 mmol) in *N*-methylpyrrolidone (20 mL), a solution of TrCl (0.50 g, 1.8 mmol) in *N*-methylpyrrolidone (5 mL) was added. The color of the solution changed to deep blue. The mixture was stirred at room temperature for 50 h. Salt **7** was isolated as above in a yield of 0.58 g (79%). Found (%): B, 23.22. $C_{21}H_{54}B_{10}N_2O$. Calculated (%): B, 23.56. IR, ν/cm^{-1}: 2461 (ν(B—H)); 1109 (δ(B—B—H)); 698 (δ(B—B—B)); 1681 (ν(C=O)). ^{11}B NMR (CD_3CN), δ: –0.9 (s, B(2)); –2.7 (d, B(10)); –7.6 (d, B(1)); –25.3 (d, B(3), B(5)); –31.2 (d, B(6), B(9)); –33.5 (d, B(4), B(7), B(8)); –32.9 (d, B(4)). MS (ESI), *m/z*: $[2\text{-}B_{10}H_9OC(CH_2)_3NCH_3]^-$, found 216.31, calculated 216.28, $C_5H_{18}N^{10}B_2{}^{11}B_8O$.

Tetrabutylammonium 2-[formyloxy]nonahydro-*closo*-decaborate(2–), $(Bu^n_4N)_2[2\text{-}B_{10}H_9OC(H)O]$ (13). ***A.*** To a solution of **1** (1.0 g, 1.6 mmol) in formic acid (20 mL), a suspension of TrCl (0.50 g, 1.8 mmol) in formic acid (5 mL) was added at room temperature. After stirring for 96 h, the salt **13** was isolated as above in a yield of 1.01 g (97%). Found (%): B, 16.59. $C_{17}H_{46}B_{10}N_2O_2$. Calculated (%): B, 16.71. IR, ν/cm^{-1}: 2459 (ν(B—H)); 1109 (δ(B—B—H)); 691 (δ(B—B—B)); 1687 (ν(C=O)); 1210 (ν(C—O)). ^{11}B NMR (CD_3CN), δ: –0.46 (d, B(10)); –4.01 (d, B(1)); –4.56 (s, B(2)); –20.34 (d, B(3), B(5), B(6), B(9)); –27.97 (d, B(7), B(8)); –31.60 (d, B(4)). MS (ESI), *m/z*: $\{[2\text{-}B_{10}H_9OC(H)O]^{2-} + (Bu^n_4N)^+\}^-$, found 404.66, calculated 404.67, $C_{17}H_{47}N^{10}B_2{}^{11}B_8O_2$.

B. To a suspension of anhydrous salt $K_2[B_{10}H_{10}]$ (0.32 g, 1.6 mmol) in formic acid (10 mL), a suspension of TrCl (0.50 g, 1.8 mmol) in formic acid (5 mL) was added at room temperature. Gradual dissolution of salt **1** and formation of blue-greenish solution were observed. The suspension was stirred at room temperature for 60 h. After addition of water (50 mL), the clear solution with drops of blue oil on the surface was formed, the oily drops were carefully separated. The water layer was treated with aqueous solution of Bu^n_4NCl (1.05 g, 3.2 mmol), the precipitate that formed was filtered off, washed with water (3×25 mL), and dried *in vacuo* at 50 °C. Salt **13** was obtined in a yield of 0.93 g (93%).

Tetrabutylammonium 2-[acetyloxy]nonahydro-*closo*-decaborate(2–), $(Bu^n_4N)_2[2\text{-}B_{10}H_9O(CO)CH_3]$ (14) was obtained as described for **13**. The reaction between a suspension of salt **1** (1.0 g, 1.6 mmol) in AcOH (20 mL) and a suspension of TrCl (0.50 g, 1.8 mmol) in AcOH (5 mL), which was carried out by protocol ***A*** for 120 h, afforded salt **14** in a yield of 1.01 g (95%). Found (%): B, 16.24. $C_{18}H_{48}B_{10}N_2O_2$. Calculated (%): B, 16.35. IR, ν/cm^{-1}: 2461 (ν(B—H)); 1108 (δ(B—B—H)); 692 (δ(B—B—B)); 1684 (ν(C=O)); 1213 (ν(C—O)). ^{11}B NMR (CD_3CN), δ: –1.36 (d, B(10)); –4.91 (d, B(1)); –5.90 (s, B(2)); –23.38 (d, B(3), B(5), B(6), B(9)); –28.88 (d, B(7), B(8)); –31.16 (d, B(4)). MS (ESI), *m/z*: $\{[2\text{-}B_{10}H_9O(CO)CH_3]^{2-} + (Bu^n_4N)^+\}^-$, found 418.69, calculated 418.71, $C_{18}H_{48}N^{10}B_2{}^{11}B_8O_2$.

The reaction between a suspension of anhydrous salt $K_2[B_{10}H_{10}]$ (0.32 g, 1.6 mmol) in AcOH (10 mL) and a suspension of TrCl (0.50 g, 1.8 mmol) in AcOH (5 mL), which was carried out by protocol ***B*** for 60 h, afforded salt **14** in a yield of 1.01 g (95%).

eq*-Bis[1-(1,4-dioxanium)]octahydro-*closo*-decaborane $[eq\text{-}B_{10}H_8(O_2C_4H_8)_2]$ (8).** ***A. To a suspension of salt **1** (1.0 g, 1.6 mmol) in 1,4-dioxane (20 mL), a solution of TrCl (1.0 g, 3.2 mmol) in 1,4-dioxane (10 mL) was added with stirring at room temperature. Gradual dissolution of salt **1** and formation of blue solution were observed. After stirring for 96 h, a solvent was removed in the oil pump *vacuo*, the resulting residue was purified by the column chromatography (silica gel (40 mesh), column 2×30 cm, elution with dichloromethane). Compound **8** was obtained in a yield of 0.24 g (51%). Found (%): B, 36.8. $C_8H_{24}B_{10}O_4$. Calculated (%): B, 36.97. IR, ν/cm^{-1}: 2462 (ν(B—H)); 1101 (δ(B—B—H)); 695 (δ(B—B—B)); 944 (ν(C—O), C—O(B)—C). ^{11}B NMR (CD_3CN), δ: 2.2 (s, B(2), B(6), B(7)); –11.6 (d, B(1), B(10)); –22.4 (d, B_{eq}); –31.4 (d, B_{eq}); –38.5 (d, B_{eq}).

B. To a suspension of $(Bu^n_4N)[B_{10}H_9O_2C_4H_8]$ (**2**) (0.72 g, 1.6 mmol) in 1,4-dioxane (20 mL), a solution of TrCl (1.0 g, 3.2 mmol) in 1,4-dioxane (10 mL) was added with stirring at room temperature. Dissolution of $(Bu^n_4N)[B_{10}H_9O_2C_4H_8]$ and formation of blue solution were observed. After stirring for 56 h, a solvent was removed in oil pump *vacuo*, the resulting residue was purified by the column chromatography (silica gel (40 mesh), column 2×30 cm, eluent — dichloromethane). Compound **8** was obtained in a yield of 0.27 g (58%).

eq*-Bis[1-tetrahydrofuranium]octahydro-*closo*-decaborane, [*eq*-$B_{10}H_8(OC_4H_8)_2$] (9)** was obtained as described for **8**. The reaction between a suspension of salt **1** (1.0 g, 1.6 mmol) in tetrahydrofuran (20 mL) and a solution of TrCl (1.0 g, 3.2 mmol) in tetrahydrofuran (10 mL), which was carried out by protocol ***A for 80 h, afforded compound **9** in a yield of 0.20 g (48%). Found (%): B, 41.19. $C_{10}H_{24}B_{10}O$. Calculated (%): B, 41.52. IR, ν/cm^{-1}: 2461 (ν(B—H)); 1103 (δ(B—B—H)); 697 (δ(B—B—B)); 968 (ν(C—O), C—O(B)—C). ^{11}B NMR (CD_3CN), δ: 5.1 (s, B(2), B(6), B(7)); −8.0 (d, B(1), B(10)); −18.7 (d, B_{eq}); −25.5 (d, B_{eq}); −33.9 (d, B_{eq}).

The reaction between a suspension of (Bu^n_4N)[$B_{10}H_9OC_5H_{10}$] (**3**) (0.69 g, 1.6 mmol) in tetrahydrofuran (20 mL) and a solution of TrCl (0.50 g, 1.8 mmol) in tetrahydrofuran (10 mL), which was carried out by protocol ***B*** for 60 h, afforded compound **9** in a yield of 0.18 g (43%).

eq*-Bis[1-tetrahydropyranium]]octahydro-*closo*-decaborane, [*eq*-$B_{10}H_8(OC_5H_{10})_2$] (10)** was obtained as described for **8**. The reaction between a suspension of salt **1** (1.0 g, 1.6 mmol) in tetrahydropyran (20 mL) and a solution of TrCl (1.0 g, 3.2 mmol) in tetrahydropyran (10 mL), which was carried out by protocol ***A for 120 h, afforded compound **10** in a yield of 0.26 g (57%). Found (%): B, 37.2. $C_{10}H_{28}B_{10}O_2$. Calculated (%): B, 37.48. IR, ν/cm^{-1}: 2461 (ν(B—H)); 1102 (δ(B—B—H)); 695 (δ(B—B—B)); 954 (ν(C—O), C—O(B)—C). ^{11}B NMR (CD_3CN), δ: −4.34 (s, B(2), B(7), B(8)); −9.76 (d, B(1), B(10)); −20.5 (d, B_{eq}); −29.6 (d, B_{eq}); −36.7 (d, B_{eq}).

The reaction between a suspension of (Bu^n_4N)[$B_{10}H_9OC_5H_{10}$] (**4**) (0.71 g, 1.6 mmol) in tetrahydropyran (20 mL) and a solution of TrCl (0.50 g, 1.8 mmol) in tetrahydropyran (10 mL), which was carried out by protocol ***B*** for 80 h, afforded compound **10** in a yield of 0.27 g (59%).

Tetrabutylammonium 2-[chloro]nonahydro-*closo*-decaborate(2−), ($(Bu^n_4N)_2$[$B_{10}H_9Cl$] (11). ***A.*** To a solution of salt **1** (1.0 g, 1.6 mmol) in 1,2-dichloroethane (20 mL), a solution of TrCl (0.50 g, 1.8 mmol) in 1,2-dichloroethane (10 mL) was added with stirring. The formation of deep blue solution was observed. The reaction mixture was rapidly heated and refluxed for 15 min. The mixture was cooled to room temperature and the solvent was removed *in vacuo*. The resulting deep blue waxy residue was treated with diethyl ether, which gave white precipitate and the blue solution. The precipitate that formed was filtered off, washed with diethyl ether (3×50 mL), and recrystallized from ethanol to give salt **11** in a yield of 0.90 g (88%). Found (%): B, 16.92. $C_{32}H_{81}B_{10}N_2Cl$. Calculated (%): B, 16.96. IR, ν/cm^{-1}: 2446 (ν(B—H)); 1104 (δ(B—B—H)); 964 (δ(B—B—Cl)); 697 (δ(B—B—B)). ^{11}B NMR (CD_3CN), δ: −2.3 (d, B(1), B(10)); −7.2 (s, B(2)); −20.7 (d, B(3), B(5), B(6), B(9)); −24.5 (d, B(7), B(8)); −28.8 (d, B(4)). MS (ESI), *m/z*: {[2-$B_{10}H_9Cl]^{2-}$ + ($Bu^n_4N)^+$}$^-$, found 395.10, calculated 395.42, $C_{16}H_{45}{}^{10}B_2{}^{11}B_8{}^{35}Cl$.

B. A solution of **1** (1.0 g, 1.6 mmol) and 1-AdBr (0.39 g, 1.8 mmol) in 1,2-dichloroethane was refluxed for 20 min. The solvent was removed *in vacuo*, the precipitate that formed was filtered off, washed on filter with diethyl ether (3×25 mL) to give salt **11** in a yield of 0.84 g (82%).

C. A solution of **1** (1.0 g, 1.6 mmol) and Bu^nBr (0.2 mL, 1.8 mmol) in 1,2-dichloroethane was refluxed for 20 min. The solvent was removed *in vacuo*, the the resulting yellowish oily residue was treated with diethyl ether (50 mL), the precipitate that formed was filtered off, washed with diethyl ether (3×25 mL) to give salt **11** in a yield of 0.87 g (85%).

Tetrabutylammonium 2-[bromo]nonahydro-*closo*-decaborate(2−), ($(Bu^n_4N)_2$[$B_{10}H_9Br$] (12) was obtained as described for **11**. The reaction of salt **1** (1.0 g, 1.6 mmol) and TrCl (0.50 g, 1.8 mmol) in 1,2-dibromoethane, which was carried out by protocol ***A***, afforded salt **12** in a yield of 0.89 g (82%). Found (%): B, 15.79. $C_{32}H_{81}B_{10}N_2Br$. Calculated (%): B, 15.85. IR, ν/cm^{-1}: 2448 (ν(B—H)); 1104 (δ(B—B—H)); 833 (δ(B—B—Br)); 697 (δ(B—B—B)). ^{11}B NMR (CD_3CN), δ: −2.7 (d, B(1), B(10)); −8.9 (s, B(2)); −25.1 (d, B(3), B(5), B(6), B(9)); −27.5 (d, B(7), B(8)); −29.8 (d, B(4)). MS (ESI), *m/z*: {[2-$B_{10}H_9Br]^{2-}$ + ($Bu^n_4N)^+$}$^-$, found 439.55, calculated 439.37, $C_{16}H_{45}{}^{10}B_2{}^{11}B_8{}^{79}Br$.

The reaction of salt **1** (1.0 g, 1.6 mmol) and 1-AdBr (0.39 g, 1.8 mmol) in 1,2-dibromoethane, which was carried out by protocol ***B***, afforded salt **12** in a yield of 0.93 g (85%).

The reaction of salt **1** (1.0 g, 1.6 mmol) and Bu^nBr (0.20 mL, 1.8 mmol) in 1,2-dibromoethane, which was carried out by protocol ***C***, afforded salt **12** in a yield of 0.87 g (80%).

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