Journal of Organometallic Chemistry 904 (2019) 121007

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis of novel carboranyl azides and "click" reactions thereof

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ARTICLE INFO

Article history:
Received 1 October 2019
Received in revised form
27 October 2019
Accepted 28 October 2019
Available online xxx

Keywords:
Carboranes
bis(2-chloroethyl) ether
Azides
Click chemistry
Cycloaddition

ABSTRACT

Novel *nido*-carboranyl azide [7-$N_3CH_2CH_2OCH_2CH_2O$-7,8-$C_2B_9H_{11}$]$^-$ was prepared by the reaction of 1-hydroxy-*ortho*-carborane with bis(2-chloroethyl) ether followed by the conversion to its *nido*-form and reactions with sodium iodide and sodium azide. Previously undescribed carboranyl azides 1-$N_3CH_2CH_2OCH_2CH_2S$-1,2-$C_2B_{10}H_{11}$ and [7-$N_3CH_2CH_2OCH_2CH_2S$-7,8-$C_2B_9H_{11}$]$^-$ were synthesized by alkylation of trimethylammonium salt of 1-mercapto-*ortho*-carborane with bis(2-chloroethyl) ether followed by reactions with sodium iodide and with sodium azide and by the conversion of *closo*-derivative to water soluble *nido*-form. *closo*- and *nido*-Carboranyl azides 1-$N_3CH_2CH_2OCH_2CH_2S$-1,2-$C_2B_{10}H_{11}$ and [7-$N_3CH_2CH_2OCH_2CH_2S$-7,8-$C_2B_9H_{11}$]$^-$ were used for the copper(I)-catalyzed azide-alkyne cycloaddition with phenyacetylene. The compounds prepared can be used for the copper(I)-catalyzed conjugation with biomolecules that act as tumor-targeting vectors for radionuclide diagnostics and boron neutron capture therapy of cancer.

1. Introduction

Boron neutron capture therapy (BNCT) is a binary method for the treatment of cancer, which is based on the nuclear reaction of two essentially nontoxic species, nonradioactive ^{10}B and low-energy thermal neutrons. The neutron-capture reaction by ^{10}B produces α-particle and $^7Li^{3+}$ ion together with 2.4 MeV of kinetic energy and 478 keV photon. These high-linear-energy transfer ions dissipate their energy traveling in biological tissues distance close to a cell diameter, that allows to use BNCT for precise killing tumor cells. Therefore, selective delivery and high accumulation of boron into the tumor tissue (20–35 μg ^{10}B/g) are the most important requirements to achieve efficient neutron capture therapy of cancer [1–6].

The promising trend aiming to achieve the necessary therapeutic concentration of boron in the tumor is the use of carboranes and other polyhedral hydrides containing ten or more boron atoms in the molecule [7–9]. Another promising trend is development of various nanomaterials, such as liposomes, dendrimers, nanoparticles, etc., that could be used as both boron host molecules and delivery agents [10–15]. The attachment of carboranes to various bio- and nanomolecules requires a large library of their functional derivatives. It should be noted that many functional derivatives of carboranes (alcohols, acids, amines, etc.) were synthesized quite soon after their discovery more than 50 years ago [16]. However, the concept of click chemistry, developed in the early 2000s [17], has led to an innovative approach in the field of drug discovery, in which molecules are effectively synthesized using the main group of highly efficient reactions that exhibit several specific features. Such reactions must proceed rapidly under ambient conditions, resulting in a high yield of one desired product. A subclass of click reactions, the components of which are inert with respect to the surrounding biological environment, is called biorthogonal [18–20]. Azide is one the most popular biorthogonal functional group due to its small size coupled with stability to water and inertness towards endogenous biological functionalities [19]. In addition to the Cu(I)-catalyzed azide-alkyne cycloaddition reactions usually termed as click-reactions [21–33], some other transformations, such as the Cu-free strain-promoted azide-alkyne cycloaddition [27,34] and Staudinger ligation [35,36] are also highly effective for biorthogonal labeling. Therefore, synthesis of azide derivatives of carboranes for boronation of nano- and biomolecules is of great importance. Synthesis of several azide derivatives of carboranes with a short (varying from 1 to 3 methylene groups) spacer between the boron cage and the terminal functional group was described [37–42] and some of them were successfully used to prepare boron-containing nucleotides [39,42], dendrimers [43] and

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https://doi.org/10.1016/j.jorganchem.2019.121007
0022-328X/

single-wall carbon nanotubes [41]. Recently, the ability of carboranyl azides to react with strained olefins in click-type cycloaddition reaction has been demonstrated as well [44].

In this contribution we describe synthesis of new carborane-based azides with longer hydrophilic spacers between the carborane cage and the terminal functional group.

2. Results and discussion

Synthesis of azide derivatives of various anionic polyhedral boron hydride via nucleophilic ring-opening of their cyclic oxonium derivatives was described [45]. In a such way the azide derivatives of *closo*-dodecaborate $[B_{12}H_{12}]^{2-}$ [46], *closo*-decaborate $[B_{10}H_{10}]^{2-}$ [47], and 7,8-dicarba-*nido*-undecaborate $[7,8\text{-}C_2B_9H_{12}]^-$ [48] anions as well as cobalt bis(dicarbollide) $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ [48b,49] containing bis(ethylene glycol) spacer between the boron cage and the azide group were prepared. These azides were successfully applied for the synthesis of boron-containing nucleosides [48b,50] and porphyrins [51], as well as for preparation of high-boron-content liposomes [52]. Since it is impossible to obtain similar oxonium derivatives of carboranes due to the weak hydride nature of their BH groups, alkylation of the hydroxy derivative 1-HO-1,2-$C_2B_{10}H_{11}$ [53] was suggested as a route to the carboranyl azide with the bis(ethelene glycol) spacer between the boron cage and the functional group. It was reported that 1-HO-1,2-$C_2B_{10}H_{11}$ can be effectively alkylated with chloromethyl ethyl ether using NaH as the base [54]. The same approach was used recently for alkylation of 8-mono- and 8,8′-dihydroxy derivatives of cobalt bis(dicarbollide) [55].

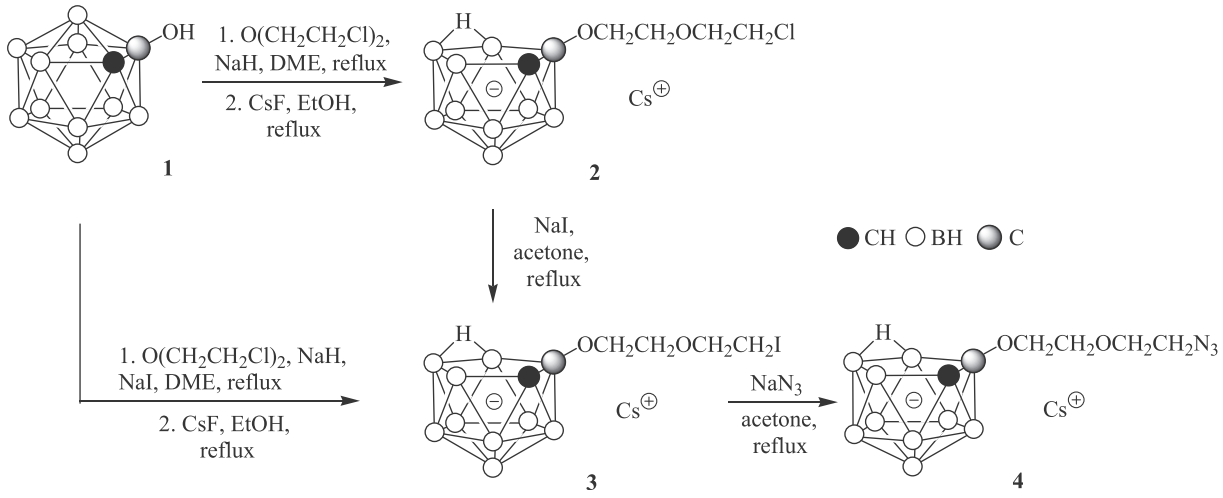
However, we found that alkylation of 1-HO-1,2-$C_2B_{10}H_{11}$ (**1**) with bis(2-chloroethyl) ether proceeds very slowly and leads to 1-$ClCH_2CH_2OCH_2CH_2O$-1,2-$C_2B_{10}H_{11}$ in low yield. It can be explained by rather high acidity of 1-HO-1,2-$C_2B_{10}H_{11}$ (pK_a 5.25 [56]) from the one hand, and much weaker neighboring-group participation effect of bis(2-chloroethyl) ether in comparison with its sulfur analogue [57] from the another hand, whereas *O,O*-acetals are known to demonstrate rather good neighboring-group participation effect [58]. The addition of an excess of sodium iodide increases the alkylation rate and leads to the corresponding iodo derivative 1-$ICH_2CH_2OCH_2CH_2O$-1,2-$C_2B_{10}H_{11}$. Unfortunately, neither in the case of the chloro derivative nor in the case of the iodo derivative, all attempts to purify the final products by column chromatography were unsuccessful. In this regard, the both *closo*-carborane derivatives by the treatment with CsF in refluxing ethanol [59] were converted to *nido*-carborane chloride $Cs[7\text{-}ClCH_2CH_2OCH_2CH_2O\text{-}7,8\text{-}C_2B_9H_{11}]$ (**2**) and iodide $Cs[7\text{-}ICH_2CH_2OCH_2CH_2O\text{-}7,8\text{-}C_2B_9H_{11}]$ (**3**), correspondently, that allowed purification of these compounds by column chromatography. The iodide **3** was also obtained by the exchanged reaction of chloride **2** with sodium iodide in refluxing acetone. The corresponding azide $Cs[7\text{-}N_3CH_2CH_2OCH_2CH_2O\text{-}7,8\text{-}C_2B_9H_{11}]$ (**4**) was prepared in moderate yield from iodide **3** by the treatment with sodium azide in refluxing acetone (Scheme 1).

The ^{11}B NMR spectra of all *nido*-carborane derivatives **2**–**4** contain nine signals of equal integral intensity approx. at −13.3, −14.1, −14.7, −17.3, −21.0, −23.4, −25.0, −34.2 and −37.9 ppm. In the ^{1}H NMR spectra of compounds **2**–**4** the signals of the OCH_2-groups appear in the range of 3.48–3.69 ppm, the signal of the CH_2Cl group is observed at 3.54 ppm, whereas the triplets of the CH_2I and CH_2N_3 groups appear at 3.26 and 3.35 ppm, respectively. In addition, the signals of the CH_{carb} groups and the B*H*B bridging hydrogen are observed approx. at 2.0 and −2.8 ppm, correspondingly. In the ^{13}C NMR spectra the signals of the OCH_2-groups appear in the range of 69.6–71.5 ppm, but the most characteristic are signals of CH_2X (X = Cl, I, N_3) groups. For example, the signal of the CH_2Cl appears at 43.0 ppm, whereas the substitution of chlorine for iodine shifts this signal to the high field by 4.3 ppm and the substitution for azide results in the low-field shift to 50.5 ppm. The signals of the C_{carb} cage atoms are observed in the ^{13}C NMR spectra of *nido*-carborane derivatives **2**–**4** at ~44.5 ppm. The B–H stretching bands in the IR spectra of *nido*-carborane derivatives **2**–**4** demonstrate the low-frequency shift in comparison with the parent *closo*-carborane and appear at 2527-2578 cm^{-1}. The azide stretching band in the IR spectrum of **4** is located at 2128 cm^{-1}.

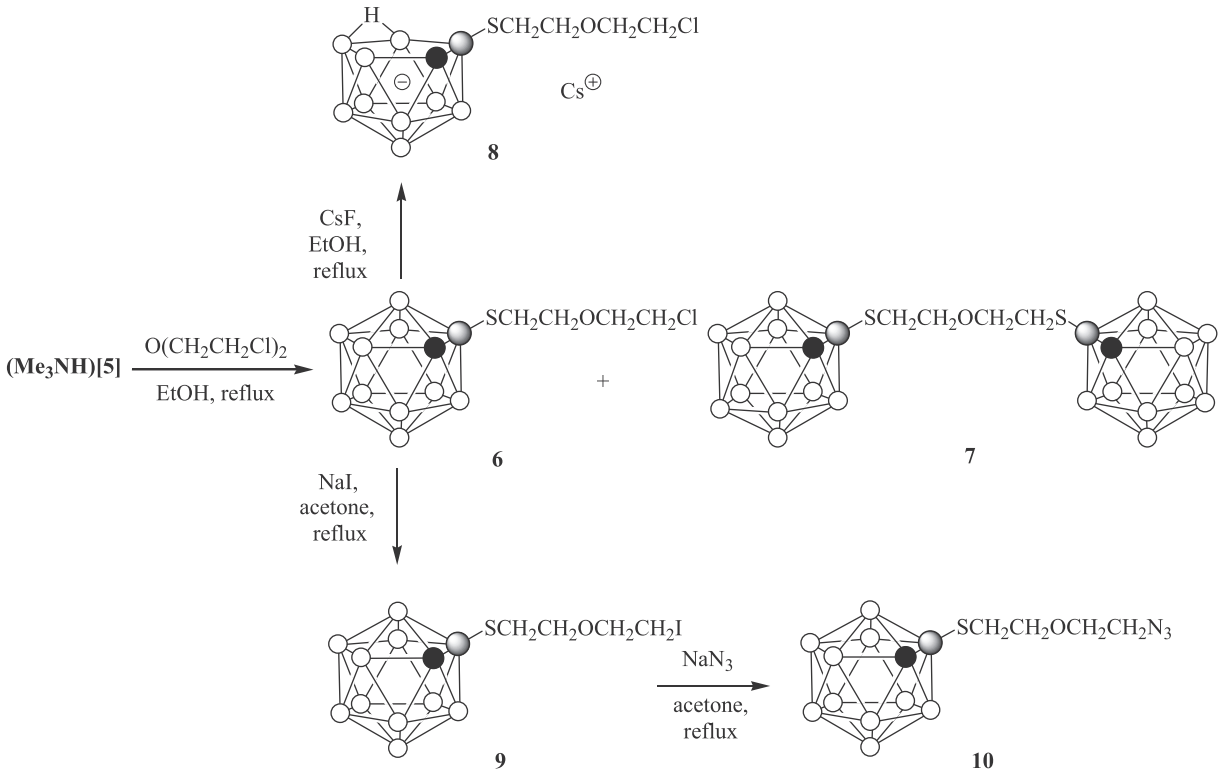
Earlier we developed the practical method for synthesis of monosubstituted *closo*- and *nido*-carborane functional derivatives based on alkylation of 1-mercapto-*ortho*-carborane 1-HS-1,2-$C_2B_{10}H_{11}$ (**5**) [60–63]. The mercapto derivative is rather strong acid (pK_a 3.3 [64]) that allows to isolate it as salts with various organic cations. This prompted us to synthesize a similar azide based on 1-mercapto-*ortho*-carborane. The trimethylammonium salt of mercapto-carborane $(Me_3NH)[1\text{-}S\text{-}1,2\text{-}C_2B_{10}H_{11}]$ ((Me_3NH)[**5**]) was prepared in one-pot reaction of the parent *ortho*-carborane with sodium hydride and sulfur [64] followed by the precipitation with $(Me_3NH)Cl$ from water (See Experimental). The reaction of (Me_3NH)[**5**] with bis(2-chloroethyl) ether in refluxing ethanol produced a mixture of 1-$ClCH_2CH_2OCH_2CH_2S$-1,2-$C_2B_{10}H_{11}$ (**6**) and $(1,2\text{-}C_2B_{10}H_{11}\text{-}1\text{-}SCH_2CH_2)_2O$ (**7**) which was separated by column chromatography. The chloro derivative **6** can be converted to the corresponding *nido*-carborane $Cs[7\text{-}ClCH_2CH_2OCH_2CH_2S\text{-}7,8\text{-}C_2B_9H_{11}]$ (**8**) by the treatment with CsF in refluxing ethanol (Scheme 2). Compound **6** was transformed to the corresponding iodo derivative 1-$ICH_2CH_2OCH_2CH_2S$-1,2-$C_2B_{10}H_{11}$ (**9**) using Finkelstein reaction conditions and then it was converted to the azide 1-$N_3CH_2CH_2OCH_2CH_2S$-1,2-$C_2B_{10}H_{11}$ (**10**) by the treatment with sodium azide in refluxing acetone (Scheme 2).

The synthesized carborane derivatives were characterized by ^{1}H, ^{13}C and ^{11}B NMR, IR spectroscopy and mass-spectrometry. The ^{11}B NMR spectra of compounds **6**, **7**, **9** and **10** demonstrate the characteristic pattern 1 : 1: 3 : 1: 4 with chemical shifts at approx. −1.6, −5.1, −8.8, −9.7 and −12.5 ppm, respectively, that agree well with the planar symmetry of a *C*-monosubstituted *ortho*-carborane cage. The ^{1}H and ^{13}C NMR spectra of **6**, **7**, **9** and **10** contain characteristic signals of the OCH_2 groups at 3.61–3.71 ppm and 68.6–71.7 ppm, correspondingly and the SCH_2 groups at ~3.13 ppm and 37.0 ppm, correspondingly. The signals of the CH_2Cl group in the ^{1}H and ^{13}C NMR spectra of **6** appear at 3.61 ppm and at 42.7 ppm, respectively. The substitution chlorine for iodine causes the high-field shift of the CH_2I group signal in **9** to 3.21 and 2.3 ppm in the ^{1}H and ^{13}C NMR spectra, respectively, whereas the signals of CH_2N_3 group in **10** are observed in the low-field at 3.36 and 50.6 ppm in the ^{1}H and ^{13}C NMR spectra, respectively. The signals of the CH_{carb} groups in the ^{1}H NMR spectra of **6**, **7**, **9** and **10** appear as broad singlets at ~3.80 ppm; in the ^{13}C NMR spectra the signals of CH_{carb} and CS_{carb} groups appear at ~68.3 and ~74.5 ppm, respectively. The IR spectra of compounds **6**, **7**, **9** and **10** contain the characteristic bands of C–H and B–H stretching of the carborane cage at ~3050 cm^{-1} and 2600 cm^{-1}, respectively. The IR spectrum of **10** also contains stretching band of the azido-group at 2109 cm^{-1}.

The treatment of **10** with cesium fluoride in refluxing ethanol results in conversion of the *closo*-carborane cage to the *nido*-form with formation of $Cs[7\text{-}N_3CH_2CH_2OCH_2CH_2S\text{-}7,8\text{-}C_2B_9H_{11}]$ (**11**) (Scheme 3). It should be noted that the conversion to the *nido*-form produces significant splitting the signal of the SCH_2 group in the ^{1}H NMR spectrum. In contrast to *nido*-carborane compounds **2**–**4**, where signals of the C_{carb}-OCH_2 group are observed as poorly resolved multiplets, in the case of *nido*-carboranes **8** and **11** both enantiotopic protons of prochiral SCH_2-group appears as well-separated multiplets at ~3.04 and ~2.65 ppm. The ^{11}B NMR spectra of compounds **8** and **11** demonstrate the 1 : 1: 1 : 3: 1 : 1: 1 pattern.



Scheme 1. The synthesis of carborane-containing azide derived from 1-HO-1,2-$C_2B_{10}H_{11}$.

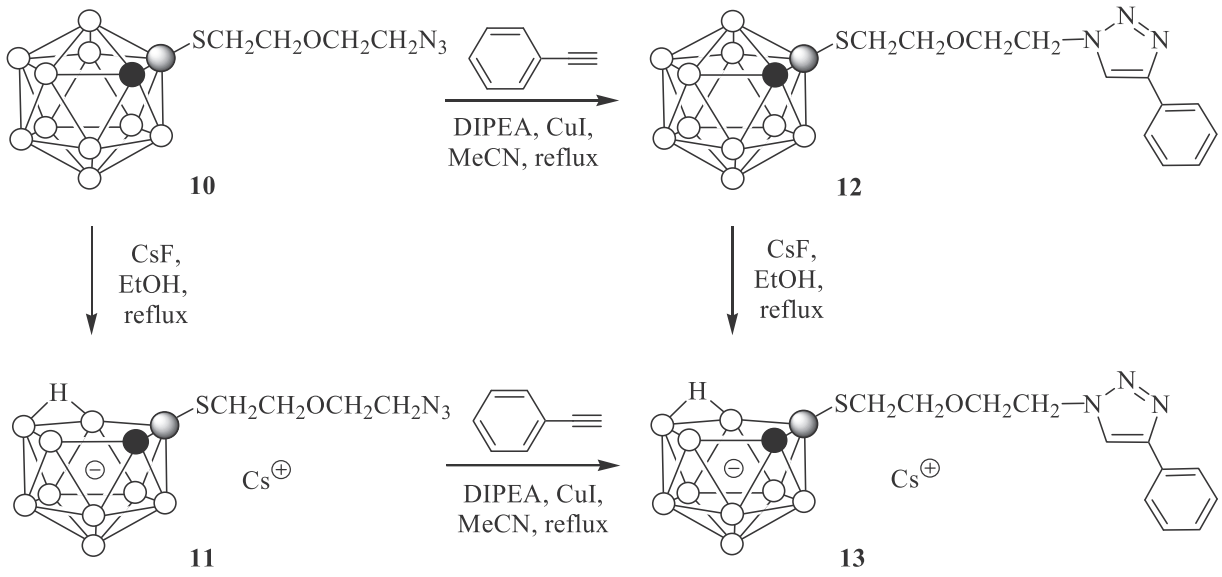


Scheme 2. The synthesis of carborane containing azide derived from 1-HS-1,2-$C_2B_{10}H_{11}$.

Both azides **10** and **11** easily react with phenylacetylene in acetonitrile in the presence of diisopropylethylamine (DIPEA) and catalytic amount of CuI to give the corresponding 1,2,3-triazoles **12** and **13** in almost quantitative yields. The 1,2,3-triazole **13** was also obtained by the deboronation of 1,2,3-triazole **12** with cesium fluoride in refluxing ethanol (Scheme 3). The ^{1}H and ^{13}C NMR spectra of compounds **12** and **13** along with the signals of the heteroaliphatic chain and the phenyl group contain the characteristic signals of the triazole cycle. In the ^{1}H NMR spectra signals of the $CH_{triazole}$ hydrogens appear at 7.91 and 8.43 ppm for **12** and **13**, respectively. In the ^{13}C NMR spectra the broad signals of the $CH_{triazole}$ carbons for **12** and **13** are observed at 130.5 and 132.4 ppm correspondingly, whereas the signals of the $C_{triazole}$ carbons appear at 147.7 and 144.8 ppm, respectively. The signals of methylene group next to the triazole cycle are observed at 4.56 and 4.66 ppm for **12** and **13**, respectively. The ^{1}H NMR spectrum of compound **13** similarly to the spectra of **8** and **11** demonstrates the splitting of the SCH_2 signal into two multiplets at 3.03 and 2.69 ppm. The IR spectra of **12** and **13** demonstrate an absence of the azide band stretching and the appearance of the band of the triazole cycle at 2247 and 2255 cm^{-1} for **12** and **13**, respectively.

3. Conclusions

In this work we prepared and characterized a series of carborane based azides 1-$N_3CH_2CH_2OCH_2CH_2S$-1,2-$C_2B_{10}H_{11}$ and [7-



Scheme 3. The copper(I)-catalyzed azide-alkyne cycloaddition of carborane based azides with phenylacetylene.

$N_3CH_2CH_2OCH_2CH_2X$-7,8-$C_2B_9H_{11}]^-$ (X = S, O), derived from the reaction of bis(2-chloroethyl) ether with trimethylammonium salt of 1-mercapto-*ortho*-carborane or with 1-hydroxy-*ortho*-carborane, followed by the sequential exchanged reactions with sodium iodide and sodium azide. The compounds prepared can be used for the conjugation via the copper(I)-catalyzed azide-alkyne cycloaddition with biomolecules that act as tumor-targeting vectors and used for boron neutron capture therapy and radionuclide diagnostics. The possibility of using "click" chemistry in regard to the obtained compounds was demonstrated on the reaction of *closo*- and *nido*-carboranyl azides 1-$N_3CH_2CH_2OCH_2CH_2S$-1,2-$C_2B_{10}H_{11}$ and [7-$N_3CH_2CH_2OCH_2CH_2S$-7,8-$C_2B_9H_{11}]^-$ with phenyacetylene.

4. Experimental

The 1-hydroxy-*ortho*-carborane 1-HO-1,2-$C_2B_{10}H_{11}$ (**1**) was prepared according to the literature procedure [53]. 1,2-Dimethoxyethane (Abcr GmbH), bis(2-chloroethyl) ether, sodium hydride 60% dispersion in mineral oil (Sigma-Aldrich Chemie GmbH), cesium fluoride (Sigma-Aldrich Chemie GmbH), sodium iodide (Sigma-Aldrich Chemie GmbH), diisopropylethylamine (Carl Roth GmbH), CuI (PANREAC QUIMICA SA) were used without further purification. Acetonitrile, ethanol, diethyl ether, $CHCl_3$, CH_2Cl_2, acetone, phenylacetylene and NaN_3 were commercially analytical grade reagents. The reaction progress was monitored by thin-layer chromatography (Merck F254 silica gel on aluminum plates) and visualized using 0.5% $PdCl_2$ in 1% HCl in aq. MeOH (1:10). Acros Organics silica gel (0.060–0.200 mm) was used for column chromatography. The NMR spectra at 400.1 MHz (^{1}H), 128.4 MHz (^{11}B) and 100.0 MHz (^{13}C) were recorded with a Bruker Avance-400 and Varian Inova-400 spectrometers. The residual signal of the NMR solvent relative to Me_4Silane was taken as the internal reference for ^{1}H and ^{13}C NMR spectra. ^{11}B NMR spectra were referenced using $BF_3 \cdot Et_2O$ as external standard. Infrared spectra were recorded on an IR Prestige-21 (SHIMADZU) instrument. High resolution mass spectra (HR MS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The measurements were done in a negative ion mode (3200 V); mass range from *m*/*z* 50 to *m*/*z* 3000; external or internal calibration was done with ESI Tuning Mix, Agilent. A syringe injection was used for solutions in acetonitrile (flow rate 3 ml/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C. The electron ionization mass spectra were obtained with a Kratos MS 890 instrument operating in a mass range of *m*/*z* 50–800.

4.1. Synthesis of Cs[7-$ClCH_2CH_2OCH_2CH_2O$-7,8-$C_2B_9H_{11}$] (2)

To a solution of 1-HO-1,2-$C_2B_{10}H_{11}$ (**1**) (0.99 g, 6.18 mmol) in anhydrous 1,2-dimethoxyethane (30 ml) under argon atmosphere 60% sodium hydride dispersion in mineral oil (0.49 g, 12.40 mmol) was added. The mixture was stirred for 15 min and bis(2-chloroethyl) ether (3.63 ml, 30.90 mmol) was added. The reaction mixture was heated under reflux conditions for 30 h. After cooling the solvent was evaporated *in vacuo*. The residue was treated with diethyl ether (30 ml) and water (30 ml). The organic layer was separated, washed with water (2 × 30 ml), dried over Na_2SO_4 and evaporated under reduced pressure. Due to the column chromatography didn't allow to separate the product completely from bis(2-chloroethyl) ether, the residue was dissolved in ethanol (10 ml) and CsF (1.88 g, 12.36 mmol) was added. The reaction mixture was heated under reflux conditions for 30 h. The precipitate formed was filtered off and the filtrate was evaporated under reduced pressure. The residue was dissolved in acetone (20 ml) and unreacted CsF was filtered off. The filtrate was evaporated *in vacuo*. The product was purified by column chromatography: the unreacted bis(2-chloroethyl) ether was removed with CH_2Cl_2 as eluent and the product was washed out from silica gel by acetone to give white solid of **2** (0.10 g, 5% yield). ^{1}H NMR (acetone-d_6, ppm): δ 3.69 (m, 6H, 3 x OCH_2), 3.54 (m, 2H, CH_2Cl), 2.03 (s, 1H, CH_{carb}), 2.6 ÷ (−0.5) (br s, 9H, B*H*), −2.8 (br s, 1H, B*H*B). ^{13}C NMR (acetone-d_6, ppm): δ 71.4 (OCH_2), 71.0 (OCH_2), 70.2 (OCH_2), 44.6 ($C_{carb}H$), 43.0 (CH_2Cl). ^{11}B NMR (acetone-d_6, ppm): δ −13.2 (d, J = 126 Hz, 1B), −14.1 (d, J = 112 Hz, 1B), −14.7 (d, J = 177 Hz, 1B), −17.2 (d, J = 135 Hz, 1B), −20.9 (d, J = 148 Hz, 1B), −23.4 (d, J = 176 Hz, 1B), −25.0 (d, J = 162 Hz, 1B), −34.1 (dd, J = 139, 45 Hz, 1B), −37.9 (d, J = 140 Hz, 1B). IR (KBr, cm^{-1}): 3058 (br, ν_{C-H}), 2931 (br, ν_{C-H}), 2867 (br, ν_{C-H}), 2578 (br, ν_{B-H}), 1638, 1427, 1359, 1291. ESI HRMS for $C_6H_{19}B_9ClO_2$: calcd. *m*/*z* 256.1964 $[M]^-$, obsd. *m*/*z* 256.1970 $[M]^-$.

4.2. Synthesis of Cs[7-$ICH_2CH_2OCH_2CH_2O$-7,8-$C_2B_9H_{11}$] (3)

Method 1. To a solution of 1-HO-1,2-$C_2B_{10}H_{11}$ (**1**) (1.00 g,

6.24 mmol) in anhydrous 1,2-dimethoxyethane (50 ml) under argon atmosphere 60% sodium hydride dispertion in mineral oil (0.50 g, 12.48 mmol) was added. The mixture was stirred for 15 min and bis(2-chloroethyl) ether (3.66 ml, 31.20 mmol) and anhydrous NaI (9.35 g, 62.40 mmol) was added. The reaction mixture was heated under reflux conditions for 40 h. After cooling the mixture was filtered and the solvent was evaporated *in vacuo*. The residue was treated with diethyl ether (50 ml) and water (50 ml). The organic layer was separated, washed with water (2 × 50 ml), dried over Na_2SO_4 and evaporated under reduced pressure. Similarly to the synthesis of **2**, the column chromatography was not useful to separate the product from bis(2-chloroethyl) ether and its iodinated derivatives. In this way, the residue was dissolved in ethanol (20 ml) and CsF (1.90 g, 12.48 mmol) was added. The reaction mixture was heated under reflux conditions for 30 h. The precipitate formed was filtered off and the filtrate was evaporated under reduced pressure. The residue was dissolved in acetone (20 ml) and unreacted CsF was filtered off. The filtrate was evaporated *in vacuo*. The product was purified by column chromatography: the unreacted organic ethers were removed with CH_2Cl_2 as eluent and the product was washed out from silica gel by acetone to give white solid of **3** (0.33 g, 11% yield).

Method 2. Compound **2** (0.08 g, 0.24 mmol) was dissolved in acetone (10 ml) and anhydrous NaI (0.71 g, 4.72 mmol) was added. The reaction mixture was stirred under reflux conditions for 40 h. The formed precipitate was filtered off and the filtrate was evaporated under reduced pressure to give white solid of **3** (0.11 g, 95% yield).

^{1}H NMR (acetone-d_6, ppm): δ 3.64 (m, 2H, OCH_2), 3.57 (m, 2H, OCH_2), 3.48 (m, 2H, OCH_2), 3.26 (t, 2H, J = 6.7 Hz, CH_2I), 1.98 (s, 1H, CH_{carb}), 2.6 ÷ (−0.5) (br s, 9H, B*H*), −2.9 (br s, 1H, B*H*B). ^{13}C NMR (acetone-d_6, ppm): δ 71.5 (OCH_2), 71.4 (OCH_2), 69.7 (OCH_2), 44.7 (C_{carb}H), 4.3 (CH_2I). ^{11}B NMR (acetone-d_6, ppm): δ −13.3 (d, J = 126 Hz, 1B), −14.2 (d, J = 109 Hz, 1B), −14.8 (d, J = 163 Hz, 1B), −17.4 (d, J = 140 Hz, 1B), −21.1 (d, J = 150 Hz, 1B), −23.5 (d, J = 187 Hz, 1B), −25.1 (d, J = 150 Hz, 1B), −34.2 (dd, J = 131, 41 Hz, 1B), −38.0 (d, J = 142 Hz, 1B). IR (KBr, cm^{-1}): 2952 (br, $\nu_{C\text{-}H}$), 2924 (br, $\nu_{C\text{-}H}$), 2873 (br, $\nu_{C\text{-}H}$), 2584 (br, $\nu_{B\text{-}H}$), 2557 (br, $\nu_{B\text{-}H}$), 2528 (br, $\nu_{B\text{-}H}$), 2502 (br, $\nu_{B\text{-}H}$), 1618, 1606, 1466, 1431, 1418, 1369, 1248. ESI HRMS for $C_6H_{19}B_9IO_2$: calcd. *m/z* 348.1314 [M]$^-$, obsd. *m/z* 348.1311 [M]$^-$.

4.3. Synthesis of Cs[7-$N_3CH_2CH_2OCH_2CH_2O$-7,8-$C_2B_9H_{11}$] (4)

Compound **3** (0.30 g, 0.62 mmol) was dissolved in acetone (20 ml) and NaN_3 (0.81 g, 12.47 mmol) was added. The heterogeneous reaction mixture was stirred under reflux conditions for 60 h. The precipitate was filtered off and the filtrate was evaporated under reduced pressure. The product was separated using column chromatography on silica in the mixture of CH_2Cl_2 and acetone (1:1) as eluent to give white solid of **4** (0.08 g, 33% yield). ^{1}H NMR (acetone-d_6, ppm): δ 3.65 (m, 2H, OCH_2), 3.60 (m, 2H, OCH_2), 3.49 (m, 2H, OCH_2), 3.35 (t, 2H, J = 5.1 Hz, CH_2N_3), 1.98 (s, 1H, CH_{carb}), 2.5 ÷ (−0.5) (br s, 9H, B*H*), −2.9 (br s, 1H, B*H*B). ^{13}C NMR (acetone-d_6, ppm): δ 70.1 (OCH_2), 69.8 (OCH_2), 69.6 (OCH_2), 50.5 (CH_2N_3), 44.3 (C_{carb}H). ^{11}B NMR (acetone-d_6, ppm): δ −13.3 (d, J = 128 Hz, 1B), −14.1 (d, J = 180 Hz, 1B), −14.7 (d, J = 101 Hz, 1B), −17.3 (d, J = 137 Hz, 1B), −21.0 (d, J = 151 Hz, 1B), −23.4 (d, J = 180 Hz, 1B), −25.0 (d, J = 166 Hz, 1B), −34.2 (dd, J = 135, 54 Hz, 1B), −37.9 (d, J = 140 Hz, 1B). IR (KBr, cm^{-1}): 3034 (br, $\nu_{C\text{-}H}$), 2932 (br, $\nu_{C\text{-}H}$), 2878 (br, $\nu_{C\text{-}H}$), 2547 (br, $\nu_{B\text{-}H}$), 2527 (br, $\nu_{B\text{-}H}$), 2128 (br, ν_{N3}), 1615, 1458, 1366, 1259, 1240. ESI HRMS for $C_6H_{19}B_9N_3O_2$: calcd. *m/z* 263.2361 [M]$^-$, obsd. *m/z* 263.2359 [M]$^-$.

4.4. Synthesis of (Me_3NH)[1-S-1,2-$C_2B_{10}H_{11}$] ((Me_3NH)[5])

To a solution of 1,2-dicarba-*closo*-dodecaborane (3.00 g, 20.80 mmol) in 1,2-dimethoxyethane under argon atmosphere 60% sodium hydride dispertion in mineral oil (1.66 g, 41.60 mmol) was added. The mixture was stirred for approx. 10 min and sulfur (1.33 g, 41.60 mmol) were added. The mixture that quickly became dark orange was refluxed for 4 h. After cooling the mixture was filtered and the filtrate was evaporated under reduced pressure. To the residue distilled water (30 ml) and petroleum ether (30 ml) was added. The water fraction was separated and washed one more time with petroleum ether (30 ml). To the water fraction the water solution of trimethylammonium chloride (2.00 g, 20.90 mmol in 10 ml of water) was added. The formed precipitate was filtered and dried over P_2O_5 to give 3.40 g (79% yield) of white product. ^{1}H NMR (acetone-d_6, ppm): δ 4.17 (s, 1H, CH_{carb}), 2.92 (s, 9H, NCH_3), 3.5 ÷ 0.8 (br s, 10H, B*H*). ^{13}C NMR (acetone-d_6, ppm): δ 72.7 (C_{carb}S), 72.5 (C_{carb}H), 44.0 (NCH_3). ^{11}B NMR (acetone-d_6, ppm): δ −3.3 (d, J = 144 Hz, 1B), −7.5 (d, J = 166 Hz, 4B), −10.4 (d, J = 149 Hz, 2B), −12.8 (d, J = 158 Hz, 3B). ESI HRMS for $C_2H_{11}B_{10}S$: calcd. *m/z* 175.1585 [M]$^-$, obsd. *m/z* 175.1581 [M]$^-$.

4.5. Synthesis of 1-$ClCH_2CH_2OCH_2CH_2S$-1,2-$C_2B_{10}H_{11}$ (6) and (1,2-$C_2B_{10}H_{11}$-1-$SCH_2CH_2)_2O$ (7)

To a solution of **(Me_3NH)[5]** (0.70 g, 3.00 mmol) in ethanol (20 ml) bis(2-chloroethyl) ether (0.35 ml, 3.00 mmol) was added and the reaction mixture was heated under reflux for 8 h. After cooling the mixture was evaporated under reduced pressure and the residue was treated with diethyl ether (30 ml) and water (30 ml). The organic layer was separated, washed with water (2 × 30 ml) dried over Na_2SO_4 and evaporated *in vacuo*. The crude products were separated using column chromatography on silica in $CHCl_3$ as eluent to give yellow oil of **6** (0.45 g, 53% yield) and **7** (0.11 g, 9% yield).

Compound **6**. ^{1}H NMR ($CDCl_3$, ppm): δ 3.83 (s, 1H, CH_{carb}), 3.71 (m, 4H, 2 x OCH_2), 3.61 (t, 2H, J = 5.8 Hz, CH_2Cl), 3.14 (t, 2H, J = 6.0 Hz, SCH_2), 3.0 ÷ 1.4 (br s, 10H, B*H*). ^{13}C NMR ($CDCl_3$, ppm): δ 74.6 (C_{carb}S), 71.3 (OCH_2), 69.3 (OCH_2), 68.3 (C_{carb}H), 42.7 (CH_2Cl), 37.0 (SCH_2). ^{11}B NMR ($CDCl_3$, ppm): δ −1.6 (d, J = 149 Hz, 1B), −5.1 (d, J = 147 Hz, 1B), −8.8 (d, J = 141 Hz, 3B), −9.7 (d, J = 130 Hz, 1B), −12.5 (d, J = 164 Hz, 4B). IR (film, cm^{-1}): 3064 (br, $\nu_{C\text{-}H}$), 2923 (br, $\nu_{C\text{-}H}$), 2864 (br, $\nu_{C\text{-}H}$), 2599 (br, $\nu_{B\text{-}H}$), 1653, 1429, 1363, 1299. MS (EI): *m/z* for $C_6H_{19}B_{10}ClOS$: calcd. *m/z* 282.8 [M]$^+$, obsd. *m/z* 282.8 [M]$^+$.

Compound **7**. ^{1}H NMR ($CDCl_3$, ppm): δ 3.81 (s, 2H, CH_{carb}), 3.65 (t, 4H, J = 5.5 Hz, 2 x OCH_2), 3.13 (t, 4H, J = 5.5 Hz, 2 x SCH_2), 3.1 ÷ 1.1 (br s, 20H, B*H*). ^{13}C NMR ($CDCl_3$, ppm): δ 74.4 (C_{carb}S), 69.2 (OCH_2), 68.4 (C_{carb}H), 36.9 (SCH_2). ^{11}B NMR ($CDCl_3$, ppm): δ −1.6 (d, J = 150 Hz, 1B), −5.0 (d, J = 152 Hz, 1B), −8.8 (d, J = 142 Hz, 3B), −9.7 (d, J = 136 Hz, 1B), −12.5 (d, J = 166 Hz, 4B). IR (film, cm^{-1}): 3065 (br, $\nu_{C\text{-}H}$), 2923 (br, $\nu_{C\text{-}H}$), 2869 (br, $\nu_{C\text{-}H}$), 2590 (br, $\nu_{B\text{-}H}$), 1684, 1653, 1559, 1457, 1363. MS (EI): *m/z* for $C_8H_{30}B_{20}OS_2$: calcd. *m/z* 422.6 [M]$^+$, obsd. *m/z* 422.5 [M]$^+$.

4.6. Synthesis of Cs[7-$ClCH_2CH_2OCH_2CH_2S$-7,8-$C_2B_9H_{11}$] (8)

Reaction mixture containing **6** (0.22 g, 0.78 mmol) and CsF (0.24 g, 1.55 mmol) in ethanol (20 ml) was stirred under reflux conditions for 10 h. The precipitate formed was filtered off and the filtrate was evaporated under reduced pressure. The residue was dissolved in acetone (20 ml) and unreacted CsF was filtered off. The filtrate was evaporated *in vacuo*. The product was purified by using column chromatography in the mixture of CH_2Cl_2 and CH_3CN (3:1) as eluent to give a white solid of **8** (0.20 g, 63% yield). ^{1}H NMR (acetone-d_6, ppm): δ 3.72 (m, 4H, 2 x OCH_2), 3.65 (m, 2H, CH_2Cl), 3.04 (m, 1H, SCH_2), 2.65 (m, 1H, SCH_2), 1.96 (s, 1H, CH_{carb}), 2.8 ÷ (−0.6) (br s, 9H, B*H*), −2.8 (br s, 1H, B*H*B). ^{13}C NMR (acetone-

d_6, ppm): δ 71.1 (OCH_2), 70.7 (OCH_2), 55.8 ($C_{carb}S$), 53.4 ($C_{carb}H$), 43.2 (CH_2Cl), 35.6 (SCH_2). ^{11}B NMR (acetone-d_6, ppm): δ −9.8 (d, J = 117 Hz, 1B), −10.6 (d, J = 118 Hz, 1B), −14.8 (d, J = 158 Hz, 1B), −17.3 (d, J = 135 Hz, 3B), −22.1 (d, J = 150 Hz, 1B), −32.9 (dd, J = 134, 53 Hz, 1B), −36.5 (d, J = 140 Hz, 1B). IR (film, cm^{-1}): 3061 (br, ν_{C-H}), 2919 (br, ν_{C-H}), 2862 (br, ν_{C-H}), 2595 (br, ν_{B-H}), 1649, 1431, 1358, 1289. ESI HRMS for $C_6H_{19}B_9ClOS$: calcd. *m/z* 272.1735 $[M]^-$, obsd. *m/z* 272.1732 $[M]^-$.

4.7. Synthesis of 1-$ICH_2CH_2OCH_2CH_2S$-1,2-$C_2B_{10}H_{11}$ (9)

The procedure was analogues to that described for synthesis of **3** using **6** (0.30 g, 1.06 mmol) in acetone (30 ml) and anhydrous NaI (3.18 g, 21.21 mmol) to give a yellow oil of **9** (0.37 g, 93% yield). ^1H NMR ($CDCl_3$, ppm): δ 3.81 (s, 1H, CH_{carb}), 3.69 (t, 2H, J = 6.2 Hz, OCH_2), 3.66 (t, 2H, J = 6.2 Hz, OCH_2), 3.21 (t, 2H, J = 6.2 Hz, CH_2I), 3.12 (t, 2H, J = 6.1 Hz, SCH_2), 3.0 ÷ 1.5 (br s, 10H, B*H*). ^{13}C NMR ($CDCl_3$, ppm): δ 74.6 ($C_{carb}S$), 71.7 (OCH_2), 68.6 (OCH_2), 68.3 ($C_{carb}H$), 37.0 (SCH_2), 2.3 (CH_2I). ^{11}B NMR ($CDCl_3$, ppm): δ −1.7 (d, J = 150 Hz, 1B), −5.1 (d, J = 159 Hz, 1B), −8.8 (d, J = 137 Hz, 3B), −9.8 (d, J = 135 Hz, 1B), −12.5 (d, J = 163 Hz, 4B). IR (film, cm^{-1}): 3064 (br, ν_{C-H}), 2939 (br, ν_{C-H}), 2864 (br, ν_{C-H}), 2601 (br, ν_{B-H}), 2576 (br, ν_{B-H}), 1649, 1470, 1357, 1289. MS (EI): *m/z* for $C_6H_{19}B_{10}IOS$: calcd. *m/z* 374.3 $[M]^+$, obsd. *m/z* 374.3 $[M]^+$.

4.8. Synthesis of 1-$N_3CH_2CH_2OCH_2CH_2S$-1,2-$C_2B_{10}H_{11}$ (10)

The procedure was analogues to that described for synthesis of **4** using **9** (0.30 g, 0.80 mmol) in acetone (30 ml) and NaN_3 (2.08 g, 32.06 mmol). The product was separated using column chromatography on silica in CH_2Cl_2 as eluent to give yellow oil of **10** (0.19 g, 82% yield). ^1H NMR ($CDCl_3$, ppm): δ 3.79 (s, 1H, CH_{carb}), 3.66 (t, 2H, J = 6.1 Hz, OCH_2), 3.61 (t, 2H, J = 4.9 Hz, OCH_2), 3.36 (t, 2H, J = 4.9 Hz, CH_2N_3), 3.12 (t, 2H, J = 6.1 Hz, SCH_2), 3.1 ÷ 1.6 (br s, 10H, B*H*). ^{13}C NMR ($CDCl_3$, ppm): δ 74.6 ($C_{carb}S$), 70.0 (OCH_2), 69.1 (OCH_2), 68.4 ($C_{carb}H$), 50.6 (CH_2N_3), 37.0 (SCH_2). ^{11}B NMR ($CDCl_3$, ppm): δ −1.7 (d, J = 149 Hz, 1B), −5.1 (d, J = 146 Hz, 1B), −8.8 (d, J = 139 Hz, 3B), −9.8 (d, J = 144 Hz, 1B), −12.5 (d, J = 164 Hz, 4B). IR (film, cm^{-1}): 3065 (br, ν_{C-H}), 2925 (br, ν_{C-H}), 2867 (br, ν_{C-H}), 2598 (br, ν_{B-H}), 2109 (br, ν_{N3}), 1473, 1437, 1362, 1288. ESI HRMS for $C_6H_{19}B_{10}N_3OS$: calcd. *m/z* 312.2148 $[M+Na]^+$, obsd. *m/z* 312.2151 $[M+Na]^+$.

4.9. Synthesis of Cs[7-$N_3CH_2CH_2OCH_2CH_2S$-7,8-$C_2B_9H_{11}$] (11)

Reaction mixture containing **10** (0.09 g, 0.31 mmol) and CsF (0.09 g, 0.62 mmol) in ethanol (5 ml) was stirred under reflux conditions for 10 h. The precipitate formed was filtered off and the filtrate was evaporated under reduced pressure. The residue was dissolved in acetone (20 ml) and unreacted CsF was filtered off. The filtrate was evaporated *in vacuo* to give a white solid of **11** (0.12 g, 98% yield). ^1H NMR (acetone-d_6, ppm): δ 3.67 (t, 2H, J = 4.8 Hz, OCH_2), 3.62 (m, 2H, OCH_2), 3.41 (t, 2H, J = 4.8 Hz, CH_2N_3), 3.04 (m, 1H, SCH_2), 2.64 (m, 1H, SCH_2), 1.95 (s, 1H, CH_{carb}), 2.7 ÷ (−0.7) (br s, 9H, B*H*), −2.7 (br s, 1H, B*H*B). ^{13}C NMR (acetone-d_6, ppm): δ 71.2 (OCH_2), 69.4 (OCH_2), 56.6 ($C_{carb}S$), 53.1 ($C_{carb}H$), 50.4 (CH_2N_3), 35.6 (SCH_2). ^{11}B NMR (acetone-d_6, ppm): δ −9.8 (d, J = 118 Hz, 1B), −10.6 (d, J = 118 Hz, 1B), −14.8 (d, J = 161 Hz, 1B), −17.2 (d, J = 128 Hz, 3B), −22.1 (d, J = 148 Hz, 1B), −32.9 (dd, J = 129, 40 Hz, 1B), 36.5 (d, J = 140 Hz, 1B). IR (KBr, cm^{-1}): 3041 (br, ν_{C-H}), 2922 (br, ν_{C-H}), 2868 (br, ν_{C-H}), 2551 (br, ν_{B-H}), 2528 (br, ν_{B-H}), 2505 (br, ν_{B-H}), 2118 (br, ν_{N3}), 1695, 1441, 1346, 1287. ESI HRMS for $C_6H_{19}B_9N_3OS$: calcd. *m/z* 279.2134 $[M]^-$, obsd. *m/z* 279.2134 $[M]^-$.

4.10. Synthesis of 1-$PhCCHN_3CH_2CH_2OCH_2CH_2S$-1,2-$C_2B_{10}H_{11}$ (12)

To the compound **10** (0.10 g, 0.35 mmol) in MeCN (20 ml) under argon atmosphere phenylacetylene (0.06 ml, 0.52 mmol), diisopropylethylamine (0.18 ml, 1.00 mmol) and CuI (6.60 mg, 0.035 mmol) were added. The mixture quickly turned yellow and was heated under refluxed conditions for 5 h. After cooling the solvent was evaporated under reduced pressure. The residue was extracted by diethyl ether (50 ml) from acidified water (50 ml + 5 ml of HCl). The organic layer was separated, dried over Na_2SO_4 and evaporated *in vacuo* to give yellow oil of **12** (0.13 g, 96% yield). ^1H NMR ($CDCl_3$, ppm): δ 7.91 (s, 1H, $CH_{triazole}$), 7.85 (d, 2H, J = 7.6 Hz, $CH_{o\text{-}Ar}$), 7.46 (t, 2H, J = 7.4 Hz, $CH_{m\text{-}Ar}$), 7.37 (t, 1H, J = 7.4 Hz, $CH_{m\text{-}Ar}$), 4.56 (t, 2H, J = 4.9 Hz, NCH_2), 3.85 (t, 2H, J = 4.9 Hz, OCH_2), 3.72 (s, 1H, CH_{carb}), 3.64 (t, 2H, J = 5.8 Hz, OCH_2), 3.10 (t, 2H, J = 5.8 Hz, SCH_2), 3.0 ÷ 1.5 (br s, 10H, B*H*). ^{13}C NMR ($CDCl_3$, ppm): δ 147.7 ($C_{triazole}$), 130.5 ($CH_{triazole}$), 128.9 (C_{Ar}), 128.3 (C_{Ar}), 125.7 (C_{Ar}), 121.2 (C_{Ar}), 74.4 ($C_{carb}S$), 69.3 (OCH_2), 68.8 (OCH_2), 68.5 ($C_{carb}H$), 50.2 (NCH_2), 37.1 (SCH_2). ^{11}B NMR ($CDCl_3$, ppm): δ −1.7 (d, J = 150 Hz, 1B), −5.0 (d, J = 145 Hz, 1B), −8.7 (d, J = 145 Hz, 3B), −9.8 (d, J = 150 Hz, 1B), −12.5 (d, J = 164 Hz, 4B). IR (film, cm^{-1}): 3144, 3058 (br, ν_{C-H}), 2955 (br, ν_{C-H}), 2924 (br, ν_{C-H}), 2869 (br, ν_{C-H}), 2593 (br, ν_{B-H}), 2247 (br, ν_{N3}), 1609, 1466, 1442, 1361, 1288. ESI HRMS for $C_{14}H_{25}B_{10}N_3OS$: calcd. *m/z* 414.2621 $[M+Na]^+$, obsd. *m/z* 414.2615 $[M+Na]^+$.

4.11. Synthesis of Cs[7-$PhCCHN_3CH_2CH_2OCH_2CH_2S$-7,8-$C_2B_9H_{11}$] (13)

Method 1. The procedure was analogues to that described for synthesis of **12** using **11** (37.00 mg, 0.09 mmol) in MeCN (10 ml), phenylacetylene (0.02 ml, 0.14 mmol), diisopropylethylamine (0.05 ml, 0.27 mmol) and CuI (2.00 mg, 0.009 mmol) to give yellow solid of **13** (45.30 mg, 96% yield).

Method 2. The procedure was analogues to that described for synthesis of **11** using **12** (0.10 g, 0.26 mmol) and CsF (0.08 g, 0.51 mmol) in ethanol (8 ml) to give 0.13 g of yellow solid of **13** (98% yield).

^1H NMR (acetone-d_6, ppm): δ 8.43 (s, 1H, $CH_{triazole}$), 7.90 (d, 2H, J = 8.3 Hz, $CH_{o\text{-}Ar}$), 7.41 (t, 2H, J = 7.5 Hz, $CH_{m\text{-}Ar}$), 7.37 (t, 1H, J = 7.5 Hz, $CH_{m\text{-}Ar}$), 4.66 (t, 2H, J = 5.6 Hz, NCH_2), 3.94 (m, 2H, OCH_2), 3.67 (m, 2H, OCH_2), 3.03 (m, 1H, SCH_2), 2.69 (m, 1H, SCH_2), 1.97 (s, 1H, CH_{carb}), 2.7 ÷ (−0.4) (br s, 9H, B*H*), −2.7 (br s, 1H, B*H*B). ^{13}C NMR (acetone-d_6, ppm): δ 144.8 ($C_{triazole}$), 132.4 ($CH_{triazole}$), 129.9 (C_{Ar}), 129.3 (C_{Ar}), 126.4 (C_{Ar}), 124.4 (C_{Ar}), 70.7 (OCH_2), 68.0 (OCH_2), 55.8 (C_{carb}), 53.4 ($C_{carb}H$), 52.2 (NCH_2), 35.9 (SCH_2). ^{11}B NMR (acetone-d_6, ppm): δ −9.8 (d, J = 114 Hz, 1B), −10.5 (d, J = 101 Hz, 1B), −14.7 (d, J = 185 Hz, 1B), −17.2 (d, J = 122 Hz, 3B), −22.0 (d, J = 146 Hz, 1B), −32.8 (dd, J = 127, 48 Hz, 1B), 36.5 (d, J = 143 Hz, 1B). IR (KBr, cm^{-1}): 3139, 3103, 3063, 3034, 2956 (br, ν_{C-H}), 2922 (br, ν_{C-H}), 2866 (br, ν_{C-H}), 2555 (br, ν_{B-H}), 2527 (br, ν_{B-H}), 2500 (br, ν_{B-H}), 2255 (br, ν_{N3}), 1691, 1610, 1556, 1484, 1466, 1345. ESI HRMS for $C_{14}H_{25}B_9N_3OS$: calcd. *m/z* 381.2608 $[M]^-$, obsd. *m/z* 381.2599 $[M]^-$.

Acknowledgment

This work was supported by the Russian Science Foundation (19-72-30005). The NMR spectroscopy data were obtained using equipment of the Center for Molecular Structure Studies at A.N. Nesmeyanov Institute of Organoelement Compounds operating with financial support of Ministry of Science and Higher Education of the Russian Federation. The authors thank Laboratory of Metal Hydrides (A.N. Nesmeyanov Institute of Organoelement Compounds) for the possibility to collect IR spectra.

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