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Practical synthesis of 1,4-dioxane derivative of the *closo*-dodecaborate anion and its ring opening with acetylenic alkoxides

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Abstract

Practical method of synthesis of the 1,4-dioxane derivative of the *closo*-dodecaborate anion was developed. The cleavage of the dioxonium ring in $[B_{12}H_{11}O(CH_2CH_2)_2O]^-$ with acetylenic alcohols gave rise to the preparation of *closo*-dodecaborate derivatives with terminal acetylene group. These compounds can be introduced into click reactions with phenylazide leading to the corresponding triazoles. The structures of $(Bu_4N)[B_{12}H_{11}O(CH_2CH_2)_2O]$ and $(Bu_4N)_2[B_{12}H_{11}(OCH_2CH_2)_2OCH_2C{\equiv}CH] \cdot 0.5HOCH_2C{\equiv}CH$ were determined by single-crystal X-ray diffraction.

Keywords: *closo*-Dodecaborate; 1,4-Dioxane derivative; Terminal acetylenes; Triazoles; Synthesis; X-ray structure

1. Introduction

The *closo*-dodecaborate anion $[B_{12}H_{12}]^{2-}$ has been considered for a long time as a promising boron moiety for boron neutron capture therapy (BNCT). BNCT is a binary cancer treatment based on the interaction of two relatively harmless species, a ^{10}B nucleus and a thermal neutron, which results in the formation of the high-energy short-range ^4He and ^7Li particles highly energetic ^4He and ^7Li as products. The selective concentration of the ^{10}B nuclei within the tumor cells, followed by their capturing of thermal neutrons, should result in localized destruction of the malignant cells in the presence of the normal neighboring cells [1–4]. More recently, it was shown that the *closo*-dodecaborate anion could be used also as a linker for introduction of a radiohalogen label into biomolecules for radionuclide diagnostics and therapy [4–7]. Both these modalities require selective delivery of the boron hydride moiety into the tumor cells that can be achieved by its attachment to tumor-specific targeting molecules (antibodies, proteins, carbohydrates, etc.). In order to link the *closo*-dodecaborate anion to a targeting molecule functionalized derivatives of this compound are required. A series of functional derivatives of the *closo*-dodecaborate anion have been prepared and used for its conjugation with various tumor-targeting molecules *via* formation of amide, urea, thiourea, and some other links [3,6–9].

The Cu(I)-catalyzed 1,3-dipolar cycloaddition of alkyne and azide to form a triazole, termed "click chemistry", has been recently established as an important tool for chemical and biological modification of biomolecules. The 1,2,3-triazole functions as rigid linking unit that can mimic the atom placement and electronic properties of a peptide bond without the same susceptibility to hydrolytic cleavage The reactants, alkyne and azide, are convenient to introduce, independently stable, and do not react with common

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organic reagents or functional groups in biomolecules. The triazole formation is irreversible and usually quantitative. In addition, this reaction benefits from an extremely mild and regioselective copper(I) catalyst system that is surprisingly indifferent to solvent and pH. Thus, the potential for this reaction to modify a wide range of functionally complex substances is significant [10–13]. For this reason, alkyne and azide derivatives of the *closo*-dodecaborate anion would be potentially useful for direct conjugation to carrier molecules using "click chemistry" approach. Recently we reported synthesis of azide derivatives of the *closo*-dodecaborate anion [14] and their conjugation with various acetylenes [15] including acetylene-containing sugars [16]. In this contribution we describe practical synthesis of the 1,4-dioxane derivative of *closo*-dodecaborate anion, its ring opening with acetylenic alkoxides as well as cycloaddition of the formed acetylene derivative to aromatic azide.

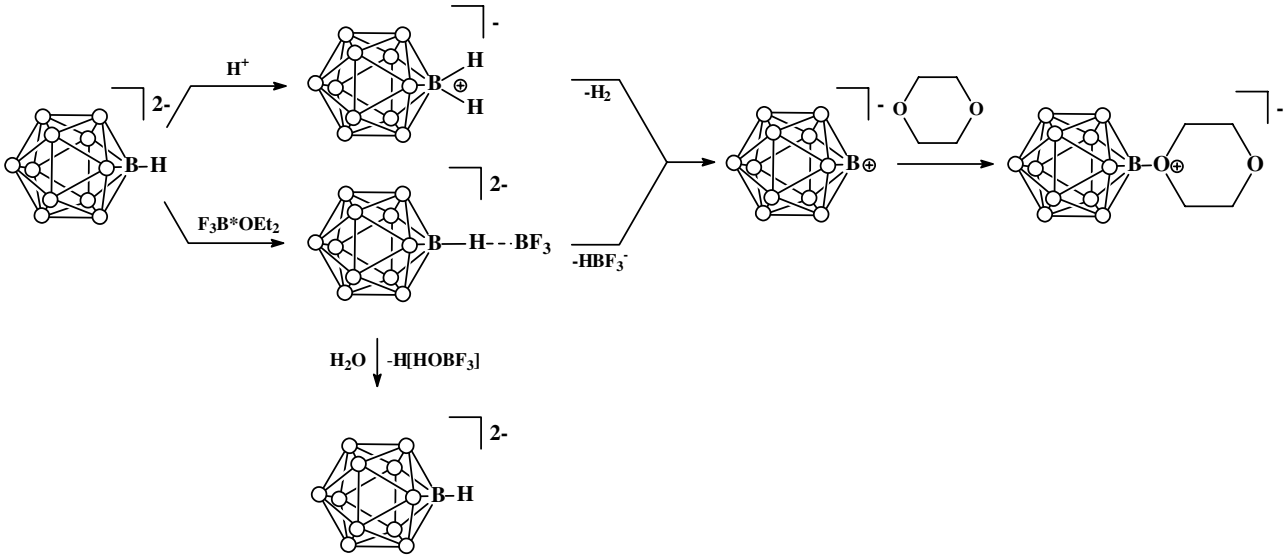
2. Results and discussion

A few years ago we described the preparation of the 1,4-dioxane derivative of *closo*-dodecaborate anion by the treatment of solution of the parent *closo*-dodecaborate in 1,4-dioxane with boron trifluoride etherate [17]. The reaction was supposed to proceed *via* abstraction of the hydride hydrogen atom to form a pseudoelectrophilic centre on boron atom which then is subjected to the attack of 1,4-dioxane, as the most abundant nucleophile (see Scheme). ^{11}B NMR study of the reaction mixture revealed however that the reaction intermediate is rather stable and the formation of the 1,4-dioxane derivative takes place only after addition of water during the workup procedure. Hydrolysis of the reaction intermediate in its turn can result in elimination of $[HBF_3]^-$ with formation of $[B_{12}H_{11}]^-$ as a masked electrophilic particle or $[HOBF_3]^-$ with regeneration of the parent *closo*-dodecaborate depending on the workup conditions. It makes the yield of the goal product is very sensitive to the workup conditions as well as to dryness of hygroscopic sodium *closo*-dodecaborate using as the starting material.

Having in mind high potential synthetic utility of the 1,4-dioxane derivative of *closo*-dodecaborate we developed a new convenient practical method of its synthesis using solution of hydrogen chloride in 1,4-dioxane in the presence of sodium tetrafluoroborate. The first stage of this reaction is protonation of the *closo*-dodecaborate anion with formation of highly unstable intermediate $[B_{12}H_{13}]^-$ [18] that eliminates hydrogen molecule giving the $[B_{12}H_{11}]^-$ electrophile which is subjected to the attack of 1,4-dioxane (see Scheme 1). The probable role of sodium tetrafluoroborate is generation of $H[BF_4]$ as a non-nucleophilic acid and removal of chloride nucleophile as insoluble sodium chloride. This mechanism can be described as the Acid-Assisted Nucleophilic Substitution and is a special case of the Electrophile-Induced Nucleophilic Substitution [19].

The main advantages of this method over the previously published one [17] are high yield of the goal product (83 against 38%), high reproducibility, and use of non-hygroscopic and easy-handling tetrabutylammonium *closo*-dodecaborate as the starting material.

The structure of $(Bu_4N)[B_{12}H_{11}O(CH_2CH_2)_2O]$ was determined by single-crystal X-ray diffraction (Fig. 1). The crystal data and structure refinement parameters are presented in Table 1 and selected atomic distances and angles are summarized in Table 2. The 1,4-dioxane ring attached to the boron icosahedron has chair conformation. The interatomic distances B–O_{ox} (1.546 Å), O_{ox}–C (1.463 and 1.478 Å), and O–C (1.423 and 1.428 Å) fall within the range of equivalent distances for known 1,4-dioxane derivatives of other polyhedral boron hydrides [20–23]



Scheme 1.

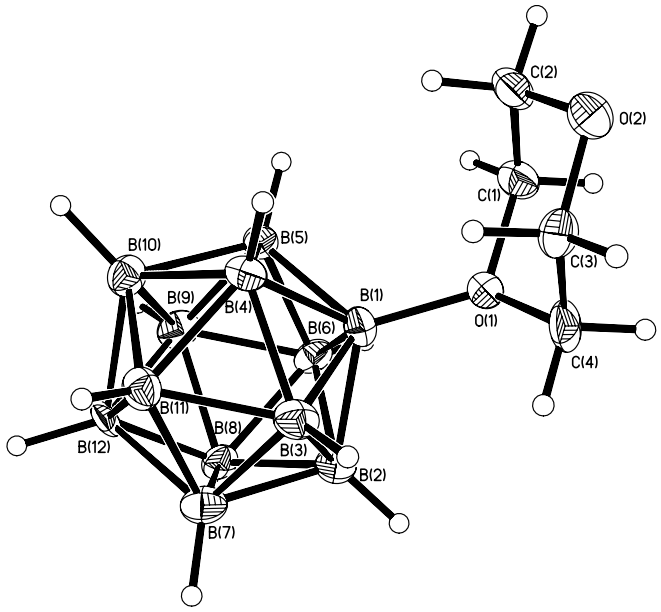


Fig. 1. General view of the $[B_{12}H_{11}O(CH_2CH_2)_2O]^-$ anion in crystal structure of **1** presented by thermal ellipsoids at 50% probability.

Table 1
Crystallographic data for $(Bu_4N)[B_{12}H_{11}O(CH_2CH_2)_2O]$ (**1**) and $(Bu_4N)_2[B_{12}H_{11}(OCH_2CH_2)_2OCH_2C{\equiv}CH] \cdot 0.5HOCH_2C{\equiv}CH$ (**2**)

	1	**2**
Formula	$C_{20}H_{55}B_{12}NO_2$	$C_{40.5}H_{96}B_{12}N_2O_{3.5}$
Formula weight	471.37	796.91
Color	Colorless	Colorless
Temperature (K)	120(2)	110(2)
Crystal system	Orthorhombic	Triclinic
Space group	$Pna2_1$ (No. 33)	$P\bar{1}$ (No. 2)
a (Å)	22.800(5)	11.3334(11)
b (Å)	14.588(3)	13.4299(13)
c (Å)	8.999(2)	17.7232(18)
α (°)		87.240(2)
β (°)		75.554(2)
γ (°)		78.405(2)
U (Å^3)	2993.3(12)	2559.0(4)
Z	4	2
D_{calc} (Mg m^{-3})	1.046	1.034
Crystal size (mm)	0.25 × 0.30 × 0.50	0.41 × 0.30 × 0.25
μ (Mo Kα) (mm^{-1})	0.059	0.059
F(000)	1032	882
θ Range (°)	1.66–29.08	1.55–27.00
Number of reflections measured	32357	24732
Number of unique reflections, R_{int}	7922, 0.1015	10979, 0.0553
Number of reflections with $I > 2\sigma(I)$	2386	6129
Number of parameters	316	623
Goodness-of-fit on F^2	0.976	1.226
Final R_1 ($I > 2\sigma(I)$), wR_2	0.0670, 0.0885	0.0751, 0.1153

Table 2
Selected bond distances (Å) and angles (°) for $[B_{12}H_{11}O(CH_2CH_2)_2O]^-$

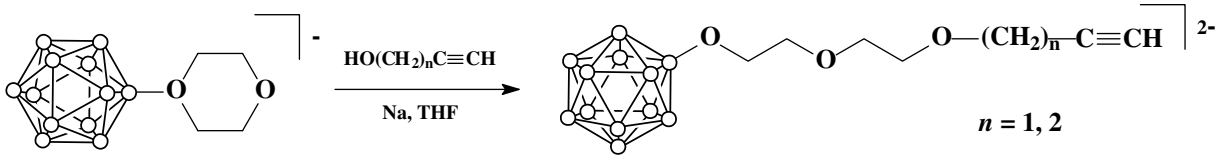
B(1)–O(1)	1.546(4)	B(3)–B(7)	1.773(6)
O(1)–C(1)	1.463(3)	B(3)–B(11)	1.787(6)
O(1)–C(4)	1.478(4)	B(4)–B(10)	1.785(5)
O(2)–C(2)	1.428(3)	B(4)–B(11)	1.769(5)
O(2)–C(3)	1.423(3)	B(5)–B(9)	1.759(5)
C(1)–C(2)	1.505(4)	B(5)–B(10)	1.768(5)
C(3)–C(4)	1.497(4)	B(6)–B(8)	1.776(5)
B(1)–B(2)	1.750(5)	B(6)–B(9)	1.737(5)
B(1)–B(3)	1.738(5)	B(7)–B(8)	1.756(5)
B(1)–B(4)	1.742(5)	B(7)–B(11)	1.771(5)
B(1)–B(5)	1.754(5)	B(8)–B(9)	1.758(5)
B(1)–B(6)	1.759(5)	B(9)–B(10)	1.788(5)
B(2)–B(3)	1.784(5)	B(10)–B(11)	1.790(5)
B(2)–B(6)	1.776(5)	B(7)–B(12)	1.734(6)
B(3)–B(4)	1.766(5)	B(8)–B(12)	1.746(5)
B(4)–B(5)	1.775(5)	B(9)–B(12)	1.779(5)
B(5)–B(6)	1.775(5)	B(10)–B(12)	1.793(5)
B(2)–B(7)	1.750(5)	B(11)–B(12)	1.760(5)
B(2)–B(8)	1.773(5)		
B(1)–O(1)–C(1)	120.7(3)	O(1)–C(1)–C(2)	109.9(3)
B(1)–O(1)–C(4)	120.4(3)	O(1)–C(4)–C(3)	108.4(3)
C(1)–O(1)–C(4)	108.9(2)	O(2)–C(2)–C(1)	111.1(3)
C(2)–O(2)–C(3)	110.4(3)	O(2)–C(3)–C(4)	111.8(3)

and are close to the corresponding bond lengths found in structure of $(PPN)[B_{12}H_{11}O(CH_2CH_2)_2CH_2]$ [24].

It was shown that the related 1,4-dioxane derivative of cobalt bis(dicarbollide) anion [8-$O(CH_2CH_2)_2O$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] is useful synthon for preparation of various functional derivatives for medical application through the ring-opening reactions with various nucleophiles [25–28]. The 1,4-dioxane ring opening gives compounds with the –$(CH_2CH_2O)_2$– chain spacer between the boron cage and bioactive part of molecule. This spacer can be considered as a short poly(ethylene glycol) (PEG) fragment with reasonable number of ethylene glycol units and has the advantages of high degree of freedom, biocompatibility, and simple synthetic procedure of its introduction. PEG is widely used as a covalent modifier of biological macromolecules and particulates as well as a linker for preparing bioconjugates with various biologically relevant molecules, including proteins, peptides, lipids and oligonucleotides [29].

Recently, we reported the 1,4-dioxane ring opening in $[B_{12}H_{11}O(CH_2CH_2)_2O]^-$ by treatment with various nucleophiles, including azide [14], phenolate [30], and diethylmalonate [31] anions and amines [32]. Similar approach was used here for synthesis of *closo*-dodecaborate-based acetylenes. We found that the reaction of $[B_{12}H_{11}O(CH_2CH_2)_2O]^-$ with acetylenic sodium alkoxides $HC{\equiv}C(CH_2)_nONa$ ($n = 1, 2$) resulted in the corresponding acetylenic derivatives of the *closo*-dodecaborate anion $[B_{12}H_{11}(OCH_2CH_2)_2O(CH_2)_n$-$C{\equiv}CH]^{2-}$ (Scheme 2). The alkoxide anions were generated *in situ* by addition of sodium metal to solution of $(Bu_4N)[B_{12}$-$H_{11}O(CH_2CH_2)_2O]$ and the corresponding alcohols in anhydrous tetrahydrofuran and the reaction mixture was stirred at ambient temperature for 3–4 days.

In the case of acetylene derivative with longer spacer the product was found to be precipitated from the reaction mixture as the mixed sodium–tetrabutylammonium salt that contains no sodium-coordinated solvent molecules



Scheme 2.

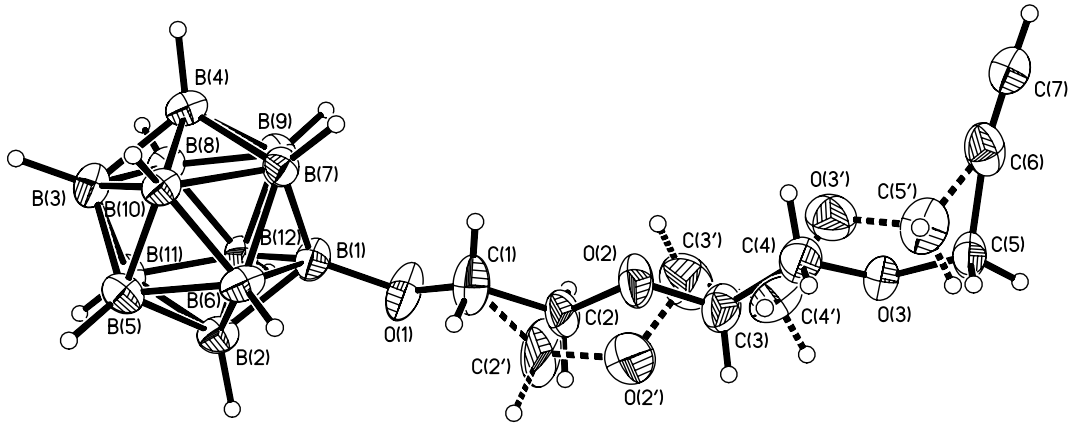
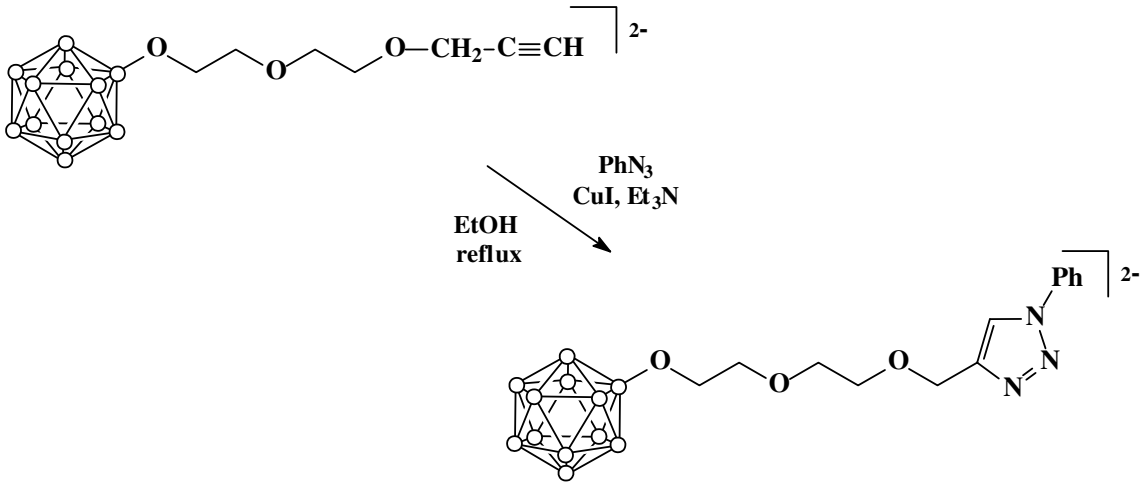


Fig. 2. General view of the $[B_{12}H_{11}OCH_2CH_2OCH_2CH_2OCH_2C{\equiv}CH]^{2-}$ anion in crystal structure of **2** presented by thermal ellipsoids at 50% probability.



Scheme 3.

according to the data of element analysis and NMR spectroscopy and is air- and moisture insensitive. We were not able to obtain crystals suitable for X-ray analysis, nevertheless it could be supposed that the Na^+ cation in this compound is coordinated with both polyether oxygen atoms of side chain and BH groups of the *closo*-dodecaborate cluster. Similar coordination was found recently in closely related derivatives of cobalt- [33,34] and ferra-[23] bis(dicarbollide) anions.

The structure of $(Bu_4N)_2[B_{12}H_{11}(OCH_2CH_2)_2OCH_2C{\equiv}CH] \cdot 0.5HOCH_2C{\equiv}CH$ was determined by single-crystal X-ray diffraction (Fig. 2). The crystal data and structure refinement parameters are presented in Table 1.

The acetylene derivatives of the *closo*-dodecaborate anion can be used for conjugation to various azide-modified biomolecules using "click chemistry" approach. To testify this possibility we studied reaction of $(Bu_4N)_2$-$[B_{12}H_{11}(OCH_2CH_2)_2OCH_2C{\equiv}CH]$ with phenyl azide in the presence of copper(I) iodide and triethylamine and found that this reaction gives the corresponding triazole in high yield (Scheme 3).

3. Experimental

2-Propyn-1-ol, 3-butyn-1-ol, and 4 M solution of HCl in 1,4-dioxane were received from Aldrich and used as pur-

chased. 1,4-Dioxane and tetrahydrofuran were distilled from sodium benzophenone before use. ^{1}H and ^{11}B NMR spectra were recorded with Bruker Avance 400 spectrometer operating at 400.13 and 128.38 MHz, respectively, whereas the ^{13}C NMR spectrum was recorded with Bruker AM 360 spectrometer operating at 90.58 MHz. Chemical shift values for ^{11}B NMR spectra were referenced to $Et_2O \cdot BF_3$, and those for ^{1}H and ^{13}C NMR spectra were referenced to $SiMe_4$.

3.1. Synthesis of $(Bu_4N)[B_{12}H_{11}O(CH_2CH_2)_2O]$

To suspension of 1.25 g (2.0 mmol) $(Bu_4N)_2[B_{12}H_{12}]$ and 1.10 g (10.0 mmol) $NaBF_4$ in 70 ml of 1,4-dioxane 1.0 ml of 4 M solution HCl in 1,4-dioxane was added. The reaction mixture was heated at reflux for 2 h, allowed to cool to room temperature, filtered and concentrated near to dryness under reduced pressure. The residue was dissolved in 20 ml of acetone, 30 ml of ethanol and 10 ml of water were added, and the solution obtained was concentrated under reduced pressure. Precipitate was filtered, washed with a small amount of water and ethanol and dried in air to give 0.78 g (83% yield) of the product. ^{1}H NMR (acetone-d_6, ppm): 4.53 (4H, m), 3.93 (4H, m), 3.42 (8H, m, Bu_4N^+), 1.80 (8H, m, Bu_4N^+), 1.44 (8H, m, Bu_4N^+), 0.98 (12H, t, Bu_4N^+). ^{13}C NMR ($CDCl_3$, ppm): 79.7, 65.1, 58.9 (Bu_4N^+), 24.1 (Bu_4N^+), 19.7 (Bu_4N^+), 13.7 (Bu_4N^+). ^{11}B NMR (acetone-d_6, ppm): 9.6 (1B, s), −15.8 (5B, d, $J = 128$ Hz), −16.8 (5B, d, $J = 127$ Hz), −18.8 (1B, d, $J = 129$ Hz).

3.2. Synthesis of $(Ph_4P)_2[B_{12}H_{11}(OCH_2CH_2)_2OCH_2C{\equiv}CH]$

To solution of 0.47 g (1.0 mmol) $(Bu_4N)[B_{12}H_{11}O(CH_2CH_2)_2O]$ and 1.5 ml (1.44 g, 25.0 mmol) 2-propyn-1-ol in 10 ml of anhydrous tetrahydrofuran 0.05 g (2.2 mmol) sodium metal was added. The reaction mixture was stirred for 4 days, filtered and concentrated near to dryness under reduced pressure. The residue was dissolved in 30 ml of aqueous ethanol (1:1) and treated with solution of 0.82 g (2.2 mmol) Ph_4PCl in 25 ml of hot water. The solution was concentrated under reduced pressure to remove ethanol. The precipitate formed was filtered, washed with small amount of cold water and dried over P_2O_5 to give 0.71 g (74% yield) of the product as a white solid. ^{1}H NMR (acetone-d_6, ppm): 7.78 (8H, m, Ph_4P^+), 7.72 (16H, m, Ph_4P^+), 7.56 (16H, m, Ph_4P^+), 3.65 (2H, m), 3.58 (2H, m), 3.52 (4H, m), 3.03 (2H, d, $J = 2.4$ Hz), 2.27 (1H, t, $J = 2.4$ Hz). ^{11}B NMR (acetone-d_6, ppm): 7.7 (1B, s), −15.5 (5B, d, $J = 128$ Hz), −17.2 (5B, d, $J = 128$ Hz), −22.1 (1B, d, $J = 126$ Hz). Anal. Calc. for $C_{55}H_{62}B_{12}O_3P_2$: C, 68.62; H, 6.49; A, 13.47. Found: C, 68.35; H, 6.37; A, 13.45%. In one experiment the filtrate was left to stand in air for 3 months to give a few colorless crystals of $(Bu_4N)_2[B_{12}H_{11}(OCH_2CH_2)_2OCH_2C{\equiv}CH]$, that were suitable for X-ray diffraction study.

3.3. Synthesis of $Na(Bu_4N)[B_{12}H_{11}(OCH_2CH_2)_2OCH_2CH_2C{\equiv}CH]$ and $(Ph_4P)_2[B_{12}H_{11}(OCH_2CH_2)_2OCH_2CH_2C{\equiv}CH]$

To solution of 0.47 g (1.0 mmol) $(Bu_4N)[B_{12}H_{11}O(CH_2CH_2)_2O]$ and 1.5 ml (1.39 g, 19.8 mmol) 3-butyn-1-ol in 40 ml of anhydrous tetrahydrofuran 0.04 g (1.7 mmol) sodium metal was added and the reaction mixture was stirred for 3 days. The precipitate formed was filtered, rinsed with cold diethyl ether and dried to give 0.35 g (62% yield) of $Na(Bu_4N)[B_{12}H_{11}(OCH_2CH_2)_2OCH_2CH_2C{\equiv}CH]$. ^{1}H NMR (acetone-d_6, ppm): 3.70 (2H, m), 3.65 (4H, m), 3.55 (2H, m), 3.43 (8H, m, Bu_4N^+), 2.51 (2H, dt, $J = 6.8$ Hz, $J = 2.5$ Hz), 2.45 (1H, t, $J = 2.5$ Hz), 1.84 (8H, m, Bu_4N^+), 1.45 (8H, m, Bu_4N^+), 0.99 (12H, t, Bu_4N^+). ^{13}C NMR (dmso-d_6, ppm): 81.8, 72.0, 71.8, 69.4, 68.5, 67.0, 57.6 (Bu_4N^+), 23.1 (Bu_4N^+), 19.2 (Bu_4N^+), 19.1, 13.4 (Bu_4N^+). ^{11}B NMR (acetone-d_6, ppm): 7.5 (1B, s), −15.7 (5B, d, $J = 137$ Hz), −17.2 (5B, d, $J = 138$ Hz), −21.8 (1B, d, $J = 127$ Hz). Anal. Calc. for $C_{24}H_{60}B_{12}NNaO_3$: C, 51.16; H, 10.73; N, 2.49; A, 23.02. Found: C, 51.00; H, 10.81; N, 2.36; A, 23.16%. The filtrate was evaporated near to dryness under reduced pressure. The residue was dissolved in 30 ml of aqueous ethanol (1:1) and treated with solution of 0.37 g (1.0 mmol) Ph_4PCl in 15 ml of hot water. The solution was concentrated under reduced pressure to remove ethanol. The precipitate formed was filtered, washed with small amount of cold water and dried over P_2O_5 to give 0.22 g (22% yield) of additional product as $(Ph_4P)_2[B_{12}H_{11}(OCH_2CH_2)_2OCH_2CH_2C{\equiv}CH]$. Anal. Calc. for $C_{56}H_{64}B_{12}O_3P_2$: C, 68.86; H, 6.60; A, 13.28. Found: C, 68.63; H, 6.48; A, 13.32%.

3.4. Synthesis of $Cs_2[B_{12}H_{11}(OCH_2CH_2)_2OCH_2$-4-(1-Ph-1,2,3-triazole)]

The mixture of 0.193 g (0.20 mmol) of $(Ph_4P)_2[B_{12}H_{11}(OCH_2CH_2)_2OCH_2C{\equiv}CH]$, 0.025 g (0.20 mmol) of phenylazide, 0.002 g (0.02 mmol) of triethylamine and 0.002 g (0.01 mmol) of copper(I) iodide in 5 ml of ethanol was refluxed for 48 h. The solvent was evaporated and the residue was dissolved in 5 ml of methanol and the resulting solution was treated with 0.060 g (0.40 mmol) of cesium fluoride in 5 ml of methanol. The precipitate was filtered off, washed with CH_2Cl_2 (3 ml) and dried in air to afford 0.13 g (94%) of the product. ^{1}H NMR (dmso-d_6, ppm): 8.81 (1H, s, C*H*-triazole), 7.51(2H, m, Ph), 7.45 (3H, m, Ph), 5.39 (2H, s, CH_2-O-triazole), 3.60 (8H, m, CH_2O), 1.9–0.1 (11H, broad m, B*H*). ^{13}C NMR (dmso-d_6, ppm): 145.4 (*C*-triazole), 137.1 (*C*H-triazole), 130.3 (Ph), 129.1 (Ph), 122.8 (Ph), 120.5 (Ph), 72.7 (*C*H_2O), 69.6 (*C*H_2O), 67.6 (*C*H_2O), 68.7 (*C*H_2O), 55.4 (*C*H_2O). ^{11}B NMR (dmso-d_6, ppm): 5.5 (1B, s), −16.9 (5B, d), −17.8 (5B, d), −22.3 (1B, d). IR (Nujol, cm^{-1}): 2473 (νBH), 1698 (triazole). Anal. Calc. for $C_{13}H_{27}B_{12}N_3O_3Cs_2$: C, 23.34; H, 4.07; N, 6.28; B, 19.39. Found: C, 23.01; H, 4.15; N, 6.22; B, 19.08%.

3.5. X-ray diffraction study

Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD area detector at 120 K and a Bruker APEX2 CCD area detector at 110 K, for **1** and **2**, respectively. In both experiments graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) was used. The low temperature of the crystals was maintained with a Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat. Reflection intensities were integrated using SAINT [35] and APEX2 [36] software for **1** and **2**, respectively. Absorption correction for **1** was applied semi-empirically using SADABS program [37]. The structures were solved by direct method and refined by the full-matrix least squares method against F^2 in anisotropic (for non-hydrogen atoms) and isotropic (for H atoms) approximation. All hydrogen atoms were located from the difference Fourier syntheses. In the structure of **2** the substituent chain is disordered between two positions with relative occupancy 72% and 28% and the solvent molecule is disordered between two positions with relative occupancy 60% and 40%. All calculations were performed using the SHELXTL software [38].

Acknowledgement

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Appendix A. Supplementary material

CCDC 605907 and 662247 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.11.027.

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