SYNTHESIS OF FUNCTIONAL DERIVATIVES OF 7,8-DICARBA-*nido*-UNDECABORATE ANION BY RING-OPENING OF ITS CYCLIC OXONIUM DERIVATIVES+

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A new approach to synthesis of functional derivatives of 7,8-dicarba-*nido*-undecaborate anion based on ring-opening of its cyclic oxonium derivatives [10-$(CH_2)_4$O-7,8-$C_2B_9H_{11}$] and [10-O$(CH_2CH_2)_2$O-7,8-$C_2B_9H_{11}$] with various nucleophiles was developed. Both cyclic oxonium derivatives can be obtained as single isomers by reaction of the parent anion [7,8-$C_2B_9H_{12}]^-$ with mercury(II) chloride in the corresponding solvents. Mechanism of formation of the cyclic oxonium derivatives of 7,8-dicarba-*nido*-undecaborate anion was proposed. A series of 7,8-dicarba-*nido*-undecaborate derivatives with terminal carboxylic and azide functions were prepared by the ring-opening reactions of the cyclic oxonium derivatives with substituted phenolate and azide ions, respectively.

Keywords: Carboranes; Functionalization; Oxonium derivatives; Carboxylic acids; Azides; Boron clusters; Boron hydrides.

Cyclic oxonium derivatives of polyhedral boron hydrides have received increased interest in recent years due to their ability to be easily attached to various substrates, including bio- and macromolecules, via nucleophilic ring-opening reactions[2–6]. The main attention in this field was paid to derivatives of the *closo*-dodecaborate anion $[B_{12}H_{12}]^{2-}$ (ref.[2]) and, especially, to

+ Preliminary results, see ref.[1]

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derivatives of the cobalt bis(1,2-dicarbolide) anion [3,3′-Co(1,2-$C_2B_9H_{11})_2]^-$ (refs[4–6]).

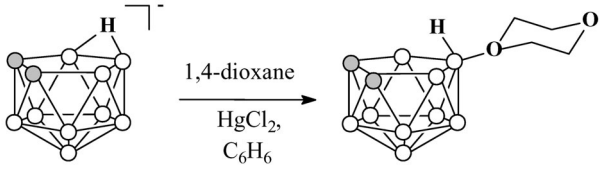
Surprisingly, but to our knowledge, no ring-opening reactions have been reported for cyclic oxonium derivatives of 7,8-dicarba-*nido*-undecaborate anion [7,8-$C_2B_9H_{12}]^-$ despite the fact that their synthesis was first reported about 40 years ago[7]. The single compound, that could be considered as a product of the ring-opening reaction, [10-$Me_2S(CH_2CH_2O)_2$-7,8-$C_2B_9H_{11}$] (ref.[8]), was prepared in direct reaction of the protonated form of 7,8-dicarba-*nido*-undecaborate [7,8-$C_2B_9H_{13}$] with 1,4-dioxane in the presence of SMe_2 (this synthesis was kindly reported us by anonymous referee). Functional derivatives of 7,8-dicarba-*nido*-undecaborate anion were shown to be promising compounds for synthesis of new catalysts based on bifunctional ligands[9,10] and for use in nuclear medicine and diagnostics of cancer[11–13]. That is why synthesis of functional derivatives of 7,8-dicarba-*nido*-undecaborate starting from the parent anion [7,8-$C_2B_9H_{12}]^-$ is of great importance.

In this contribution we try to fill this gap and describe the synthesis of a series of functional derivatives of 7,8-dicarba-*nido*-undecaborate anion containing carboxylate and azide terminal functions via nucleophilic ring opening reactions of its cyclic oxonium derivatives [10-$(CH_2)_4$O-7,8-$C_2B_9H_{11}$] (**1**) and [10-O$(CH_2CH_2)_2$O-7,8-$C_2B_9H_{11}$] (**2**).

RESULTS AND DISCUSSION

Synthesis of tetrahydrofuran oxonium derivatives of 7,8-dicarba-*nido*-undecaborate anion was reported for the first time by Hawthorne et al.[7] by the reaction of the parent anion with anhydrous iron(III) chloride in benzene–tetrahydrofuran solution. The reaction gives a mixture of isomeric tetrahydrofuran oxonium derivatives [9-$(CH_2)_4$O-7,8-$C_2B_9H_{11}$] and [10-$(CH_2)_4$O-7,8-$C_2B_9H_{11}$] which can be separated by column chromatography on silica. Later on, the formation of [10-$(CH_2)_4$O-7,8-$C_2B_9H_{11}$] and small amount of [9-$(CH_2)_4$O-7,8-$C_2B_9H_{11}$] in the reaction of *nido*-carborane dimer $C_4B_{18}H_{22}$ with tetrahydrofuran was reported by Janoušek et al.[14]. Zakharkin et al.[15] found out that the reaction of the parent 7,8-dicarba-*nido*-undecaborate with mercuric chloride in benzene–tetrahydrofuran results in the formation of [10-$(CH_2)_4$O-7,8-$C_2B_9H_{11}$] as the single isomer. Some time later Plešek et al.[16] described the synthesis of [10-$(CH_2)_4$O-7,8-$C_2B_9H_{11}$] and [10-O$(CH_2CH_2)_2$O-7,8-$C_2B_9H_{11}$] by the treatment of the parent anion with acetaldehyde (formaldehyde) in a mixture of toluene, aqueous hydrochloric acid and the corresponding cyclic ether.

We found that the reaction of the potassium salt of the 7,8-dicarba-*nido*-undecaborate anion K[7,8-$C_2B_9H_{12}$] with mercuric chloride in a boiling benzene–1,4-dioxane mixture results in formation of [10-O(CH_2CH_2)$_2$O-7,8-$C_2B_9H_{11}$] in virtually quantitative yield (Scheme 1).

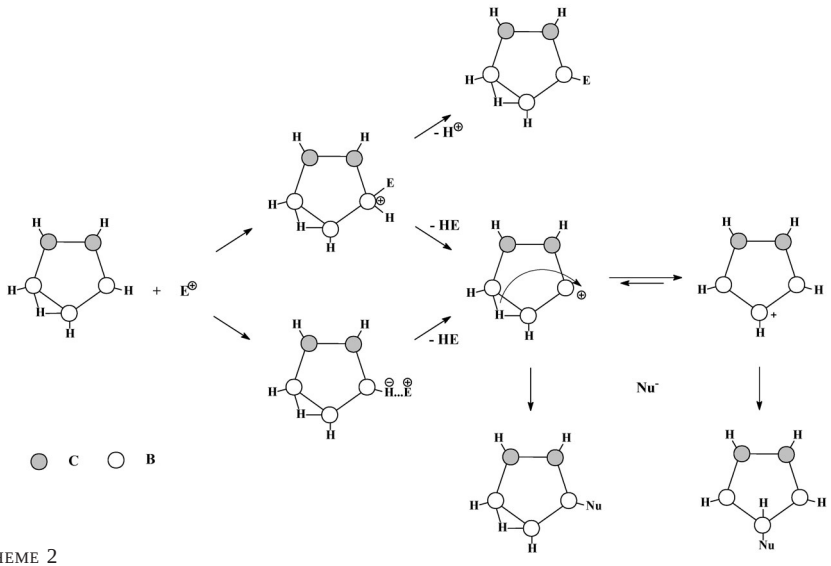


SCHEME 1

It should be noted that at this moment no general mechanism describing substitution at boron atoms in the 7,8-dicarba-*nido*-undecaborate anion has been proposed. Polyhedral boron hydrides are generally accepted as three-dimensional aromatic systems[17] and it is reasonably to assume that the mechanism of electrophilic aromatic substitution should be one of the main mechanisms of substitution in the [7,8-$C_2B_9H_{12}$]$^-$ anion. At the same time, taking into account the hydride character of hydrogen atoms in polyhedral boron hydrides, another possible mechanism may involve the attack of an electrophilic agent resulting in elimination of the hydride hydrogen atom to form a quasi-electrophilic centre on the boron atom, which is then subjected to the attack of a nucleophilic species. This mechanism is called electrophile-induced nucleophilic substitution (EINS)[18]. The nature of the intermediate formed upon the attack of an electrophilic agent is not clear. It could be an arenium ion (Wheland intermediate) or an ion pair formed by electrophilic species and the hydride hydrogen atom. In particular, the EINS mechanism describes well reactions of polyhedral boron hydrides with solvent molecules resulting in formation of charge-compensated derivatives, in which the solvent molecule (e.g., tetrahydrofuran or 1,4-dioxane) serves as a weak nucleophile present in large excess.

As the place of electrophilic attack should be the same for both the mechanisms, substitution should, in general, result in products with electrophilic and nucleophilic substituents at the same position of the boron hydride cage. However, this is not the case of the [7,8-$C_2B_9H_{12}$]$^-$ anion. On the one hand, reactions typically proceeding by on electrophilic aromatic substitution mechanism (e.g., the H–D exchange and halogenation) result in products of substitution at positions 9 and 11 adjacent to the carbon atoms of the 7,8-dicarba-*nido*-undecaborate cage giving [9-X-7,8-$C_2B_9H_{11}$]$^-$ and [9,11-X_2-7,8-$C_2B_9H_{10}$]$^-$ (X = D, Cl, Br, I)[19–22]. On the other hand, as it was

shown above, the EINS mechanism results in products of substitution at positions 9 and/or 10. These results can be explained using Scheme 2.



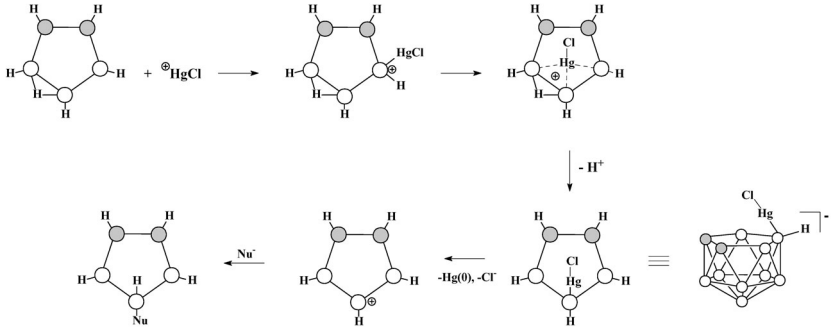
SCHEME 2

The initial electrophilic attack proceeds at position 9 and usually gives "normal" products of electrophilic substitution and only minor amounts of EINS substitution products, as it was found for bromination of 7,8-dicarba-*nido*-undecaborate anion in tetrahydrofuran, when [10-$(CH_2)_4$O-7,8-$C_2B_9H_{11}$] was isolated in <5% yield together with [9-Br-7,8-$C_2B_9H_{11}$]$^-$ as the main product[21a].

Obviously, iron(III) chloride can act only as Lewis acid abstracting the hydride hydrogen atom from position 9 via formation of the ion pair. The abstraction of hydride generates a quasi-electrophilic centre at position 9. In the presence of strong nucleophiles (e.g., pyridine), this intermediate reacts with them, forming only one isomer with a substituent at position 9 [9-C_5H_5N-7,8-$C_2B_9H_{11}$] (ref.[7]). In the case of weaker nucleophiles (e.g., tetrahydrofuran), the reaction proceeds more slowly giving possibility of isomerization of the intermediate (probably through migration of bridging or terminal hydrogen atom) to a more stable symmetric species with a quasi-electrophilic centre at position 10. So, in this case the formation of a mixture of 9- and 10-isomers [9- and 10-$(CH_2)_4$O-7,8-$C_2B_9H_{11}$] takes place. The presence of protons in the reaction with acetaldehyde[16] could promote the hydrogen migration in the intermediate resulting in selective formation of 10-isomer [10-$(CH_2)_4$O-7,8-$C_2B_9H_{11}$].

This scheme describes well the known results of electrophilic and electrophile-induced nucleophilic substitution in the 7,8-dicarba-*nido*-undecaborate anion under mild conditions (in absence of strong bases and acids).

The other scheme could be proposed for reactions in the presence of mercuric chloride. On the first step, $HgCl^+$ formed upon dissociation of $HgCl_2$ acts as the electrophilic agent producing on intermediate σ-bonded mercury complex. In the case of *closo*-carboranes and metallacarboranes[23], the σ-bonded mercury complexes are known to be stabilized by proton elimination. The second step includes migration of the mercury atom with formation of a symmetrical π-bonded mercury complex (Scheme 3) or its dimer $[10,10'\text{-}(7,8\text{-}C_2B_9H_{11})_2Hg]^{2-}$ (ref.[24]), which can be considered as mercuracarboranes with η^1-10-$(7,8\text{-}C_2B_9H_{11})$ ligands. Heating this complex results in elimination of mercury and generation of quasi-electrophilic centre at position 10 followed by its attack by nucleophile. The selective substitution at position 10 takes place as a result.



SCHEME 3

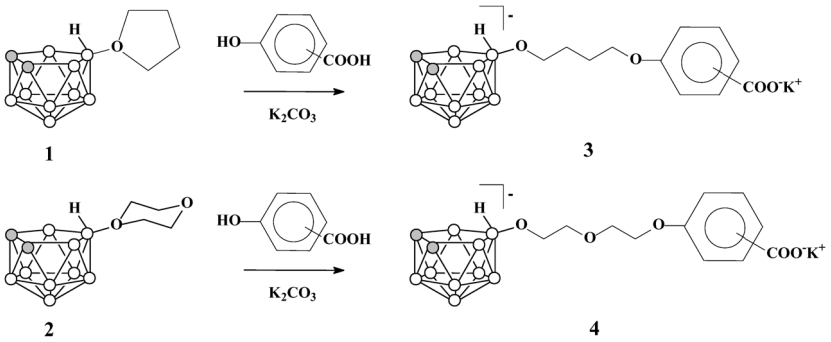
To verify formation of the oxonium derivatives through π-bonded mercury complex we studied thermolysis $Cs_2[10,10'\text{-}(7,8\text{-}C_2B_9H_{11})_2Hg]$ (ref.[24]) in a refluxing benzene–tetrahydrofuran (1,4-dioxane) mixture and revealed the formation of the corresponding cyclic oxonium derivatives as well as of some products of their ring opening.

It should be noted that the mercury-mediated approach can also be used for synthesis of other 10-substituted derivatives of 7,8-dicarba-*nido*-undecaborate anion (e.g., dialkylsulfonium derivatives[25]).

Having a good idea of using 7,8-dicarba-*nido*-undecaborate in synthesis of compounds for nuclear medicine, we decided to synthesize a series of functional derivatives that can be attached to various biomolecules using standard methods of bioorganic chemistry.

Formation of the peptide bond –NHCO– is widely used for attachment of low-molecular-weight compounds including polyhedral boron hydrides to various biomolecules[11,26]. The 1,2,3-triazole function is a rigid linking unit that can mimic the atom placement and electronic properties of a peptide bond without being susceptible to hydrolytic cleavage. The Cu(I)-catalyzed 1,3-dipolar cycloaddition of azide and alkyne to form a triazole, termed "click chemistry", has been recently established as an important tool for chemical and biological modification of biomolecules[27].

To synthesize 7,8-dicarba-*nido*-undecaborate derivatives with terminal carboxylic function we used the ring-opening reactions of their oxonium derivatives with phenolates generated by the treatment of hydroxybenzoic acids with K_2CO_3 in acetonitrile (Scheme 4). As a result, a complete set of the corresponding isomeric benzoic acids **3** and **4** was prepared and isolated as water soluble potassium salts. Previously, the oxonium ring opening with phenolate ions was used for synthesis of various derivatives of *closo*-dodecaborate $[B_{12}H_{12}]^{2-}$ (ref.[2b]) and cobalt bis(dicarbollide) $[3,3'\text{-}Co(C_2B_9H_{11})_2]^-$ (refs[4b,4e,5]) anions.

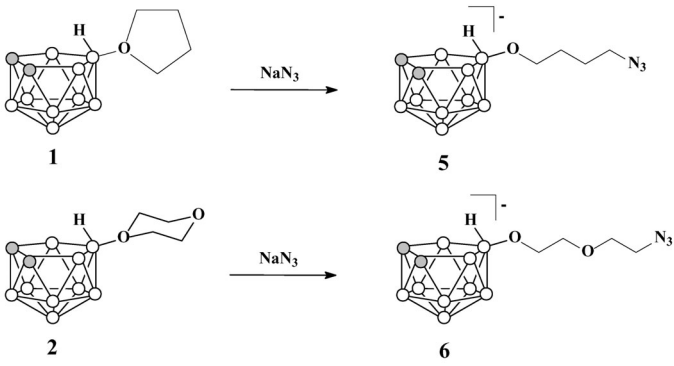


SCHEME 4

7,8-Dicarba-*nido*-undecaborate derivatives with terminal azido group **5** and **6** were prepared by the ring-opening reactions of the corresponding cyclic oxonium derivatives with sodium azide in ethanol (Scheme 5) and isolated as the tetramethylammonium salts. Synthesis of the corresponding azide derivatives of the *closo*-dodecaborate anion has been described recently[2c]. The azide derivatives of 7,8-dicarba-*nido*-undecaborate are not stable in air that did not give possibility to obtain correct elemental analysis of these compounds.

The compounds prepared were characterized by ^1H, ^{13}C, ^{11}B NMR and IR spectroscopy. The ^{11}B NMR spectra of the ring-opening products do not differ significantly from the spectra of the parent oxonium derivatives indicat-

ing retention of the carborane cage symmetry. The most notable difference found is a high-field shift of the signal of the antipodal B(3) vertex by some 3 ppm. The ^{1}H and ^{13}C NMR spectra demonstrate characteristic patterns of the disclosed tetrahydrofuran and 1,4-dioxane rings as well as signals of the corresponding aromatics (in the case of benzoic acids). The IR spectra of the ring-opening products contain absorption bands of the B–H stretching of the carborane cage as well as bands of the corresponding functional groups (carboxylate or azide group).



SCHEME 5

It should be noted that the shapes of signals of the disclosed dioxane fragment in ^{1}H NMR spectra are different for the potassium and tetramethylammonium salts, being more complicated in the former case. This can be explained by complexation of the potassium cation with the polyether oxygen donor atoms. Such type of coordination was found earlier in the solid state structures[4b,4c] and in solutions[4c] of ring-opening products of the dioxonium derivative of cobalt bis(dicarbollide). More drastic changes were found in the ^{1}H NMR spectrum of K[10-(3-$KOOCC_6H_4OCH_2CH_2$-OCH_2CH_2O)-7,8-$C_2B_9H_{11}$] after 45-day standing in solution in methanol-d_4 (Fig. 1). These changes include splitting of signals of aromatic protons as well as strong splitting of signal corresponding to the methylene group bonded to the aromatic ring through the oxygen atom. We assume that these changes can be caused by the formation of supramolecular structure including π-complexation of the potassium cation with electron-rich phenolic ring. Such type of interactions is well documented[28], especially for complexes of arene-side armed macrocyclic polyethers[29]. The importance of these and other cation–π-interactions has been recognized for some time in biological processes, including bimolecular recognition, protein–ligand binding, and the selectivity of K^+ within the K^+ channels in cell[29h,30,31].

X-ray and spectroscopic evidence for cation–π-interactions in the solid state has been widely reported in the literature over the past several decades[28,29]. However, spectroscopic evidence for cation–π-interactions in solution has been extremely limited[32]. The study aimed of determining a structure and stability of the complex formed in aged solution is in progress and will be published elsewhere.

In conclusion, a new approach to synthesis of functional derivatives of 7,8-dicarba-*nido*-undecaborate anion, based on ring-opening reactions of its cyclic oxonium derivatives [10-$(CH_2)_4$O-7,8-$C_2B_9H_{11}$] and [10-O$(CH_2CH_2)_2$O-7,8-$C_2B_9H_{11}$] with various nucleophilic agents, was developed and a series of 7,8-dicarba-*nido*-undecaborate derivatives with terminal carboxylic and azide functions were prepared. The proposed approach has important advantages over the generally used functionalization of *closo*-carborane *o*-$C_2B_{10}H_{12}$ through the carbon atom followed by its degradation to the corresponding *nido*-carborane derivative: (i) simple and straightforward synthetic scheme based on easily available parent *nido*-carborane [7,8-$C_2B_9H_{12}$]$^-$, which excludes using protective groups and precludes formation of disubstituted products; (ii) substitution at position 10 of the *nido*-carborane

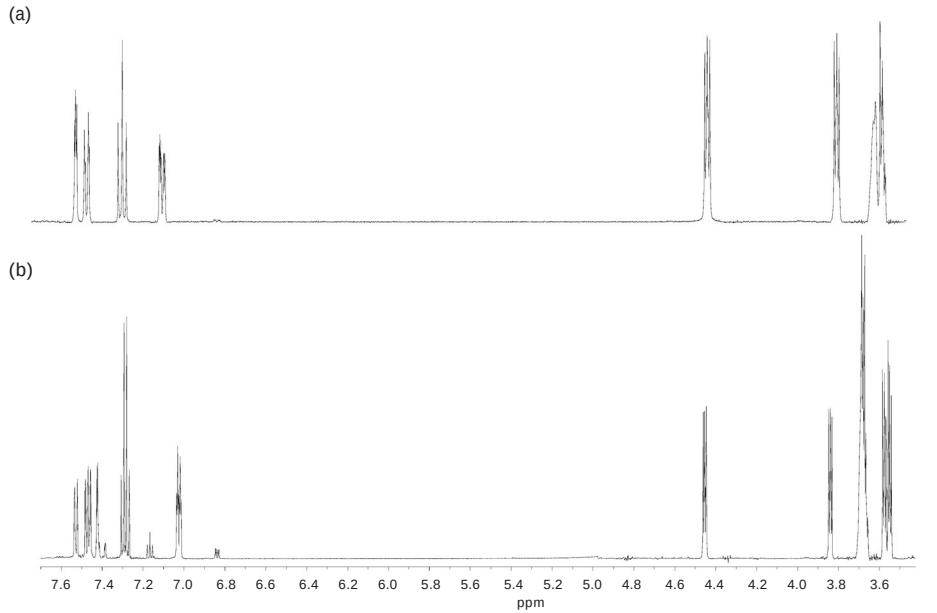


FIG. 1
^{1}H NMR spectra of solution of K[10-(3-KOOCC$_6$H$_4$OCH$_2$CH$_2$OCH$_2$CH$_2$O)-7,8-$C_2B_9H_{11}$] in methanol-d_4 after 4 h (a) and after 45 days (b)

cage excludes formation of racemic or diastereomeric mixtures of products, which is the case in functionalization through the carbon atom. The last advantage could be of great importance for medical applications of carboranes.

EXPERIMENTAL

^{1}H, ^{13}C and ^{11}B NMR spectra (δ, ppm; *J*, Hz) were collected using Bruker AM360, Bruker Avance-400 and Bruker Avance-600 spectrometers. IR spectra were obtained on a Specord M-82 (Carl Zeiss Jena) FTIR spectrometer. Elemental analyses were performed in the Laboratory of Microanalysis of the Institute of Organoelement Compounds (Moscow).

Synthesis of [10-$(CH_2)_4$O-7,8-$C_2B_9H_{11}$] (**1**)

[10-$(CH_2)_4$O-7,8-$C_2B_9H_{11}$] was prepared as described in the literature[14]. ^{1}H NMR (400 MHz, $CDCl_3$): 4.49 m, 2 H (-OC**H**$_2$CH$_2$-); 2.24 m, 2 H (-OCH$_2$C**H**$_2$-); 2.00 s, 2 H (CH_{carb}); 2.5 to –0.5 br s, 9 H (BH). ^{13}C NMR (90 MHz, $CDCl_3$): 82.6, 42.8, 25.4. ^{11}B NMR (128 MHz, $CDCl_3$): –11.4 s, 1 B; –12.5 d, 2 B, *J* = 144; –16.9 d, 2 B, *J* = 137; –21.8 d, 3 B, *J* = 153; –39.4 d, 1 B, *J* = 144.

Synthesis of [10-O$(CH_2CH_2)_2$O-7,8-$C_2B_9H_{11}$] (**2**)

K[7,8-$C_2B_9H_{12}$] (2.00 g, 11.5 mmol) and mercury chloride (3.12 g, 11.5 mmol) in a mixture of benzene (30 ml) and 1,4-dioxane (30 ml) were heated under reflux for 4 h. After cooling to room temperature, the solution was decanted, and the residue was washed with benzene. The washings were combined with the solution and evaporated under reduced pressure to give 2.48 g (97%) of a white product. ^{1}H NMR (400 MHz, $CDCl_3$): 4.50 m, 4 H (B-O(C**H**$_2$CH$_2$)$_2$O); 3.95 m, 4 H (B-O(CH$_2$C**H**$_2$)$_2$O); 2.01 s, 2 H (CH_{carb}); 2.9 to –0.5 br s, 9 H (BH). ^{13}C NMR (100 MHz, $CDCl_3$): 81.6, 64.8, 42.9. ^{11}B NMR (128 MHz, $CDCl_3$): –9.2 s, 1 B; –12.5 d, 2 B, *J* = 142; –16.9 d, 2 B, *J* = 137; –21.6 d, 3 B, *J* = 155; –39.4 d, 1 B, *J* = 144.

Synthesis of K[10-(X-KOC(O)C_6H_4O$CH_2CH_2CH_2CH_2$O)-7,8-$C_2B_9H_{11}$] (**3**)

To [10-C_4H_8O-7,8-$C_2B_9H_{11}$] (0.11 g, 1.0 mmol) in acetonitrile (30 ml), hydroxybenzoic acid (0.14 g, 1.0 mmol) and potassium carbonate (1.38 g, 10 mmol) were added and the reaction mixture was heated under reflux for 3.5–4 h. The reaction mixture was cooled to room temperature, filtered and evaporated to dryness in vacuo to obtain a white crystalline product.

K[10-(2-KOC(O)C_6H_4O$CH_2CH_2CH_2CH_2$O)-7,8-$C_2B_9H_{11}$] (**3a**). Yield 0.34 g (99%). ^{1}H NMR (600 MHz, methanol-d_4): 7.91 dd, 1 H, *J* = 7.9, 1.7 (CH_{ar}); 7.48 dt, 1 H, *J* = 7.9, 1.7 (CH_{ar}); 6.95 d, 1 H, *J* = 7.6 (CH_{ar}); 6.92 t, 1 H, *J* = 7.6 (CH_{ar}); 4.39 t, 2 H, *J* = 6.5 (-OCH_2); 3.63 m, 2 H (-OCH_2); 1.84 m, 2 H (-OCH$_2$C**H**$_2$C**H**$_2$CH$_2$O-); 1.74 m, 2 H (-OCH$_2$C**H**$_2$C**H**$_2$CH$_2$O-); 1.54 s, 2 H (CH_{carb}); 2.0–0.0, 8 H (BH); –0.50, 1 H (BH). $^{13}C\{^{1}H\}$ NMR (125 MHz, methanol-d_4): 170.1, 161.3, 135.5, 129.8, 119.0, 116.8, 112.5, 69.4, 65.3, 38.6, 27.2, 25.0. ^{11}B NMR (128 MHz, methanol-d_4): –10.1 s, 1 B; –12.5 d, 2 B, J_{BH} = 136; –17.3 d, 2 B, J_{BH} = 134; –23.8 d, 2 B, J_{BH} = 148; –25.0 d, 1 B, J_{BH} = 155; –40.8 d, 1 B, J_{BH} = 140. IR (Nujol, cm^{-1}): 2581 (ν_{BH}), 2523 (ν_{BH}), 2500 (ν_{BH}), 1671 ($\nu_{C=O}$), 1660 ($\nu_{C=O}$). For $C_{13}H_{23}B_9K_2O_4$ (420.2) calculated: 37.28% C, 5.54% H, 23.23% B; found: 37.46% C, 5.82% H, 23.28% B.

K[10-(3-KOC(O)$C_6H_4OCH_2CH_2CH_2CH_2O$)-7,8-$C_2B_9H_{11}$] (**3b**). Yield 0.33 g (97%). ^{1}H NMR (600 MHz, methanol-d_4): 7.51 m, 1 H (CH_{ar}); 7.44 m, 1 H (CH_{ar}); 7.28 t, 1 H, J = 7.8 (CH_{ar}); 7.01 m, 1 H, J = 8.1, 2.7, 1.1 (CH_{ar}); 4.32 t, 2 H, J = 6.5 (-OCH_2); 3.62 m, 2 H (-OCH_2); 1.80 m, 2 H (-$OCH_2C\mathbf{H}_2C\mathbf{H}_2CH_2O$-); 1.72 m, 2 H (-$OCH_2C\mathbf{H}_2C\mathbf{H}_2CH_2O$-); 1.54 s, 2 H ($CH_{carb}$); 2.5–0.0, 8 H (BH); –0.50, 1 H (BH). ^{13}C{^{1}H} NMR (125 MHz, methanol-d_4): 167.0, 157.3, 131.4, 129.2, 120.3, 119.8, 115.6, 69.5, 64.9, 38.0, 27.3, 25.1. ^{11}B NMR (128 MHz, methanol-d_4): –10.1 s, 1 B; –12.5 d, 2 B, J_{BH} = 135; –17.3 d, 2 B, J_{BH} = 134; –23.8 d, 2 B, J_{BH} = 149; –25.0 d, 1 B, J_{BH} = 155; –40.8 d, 1 B, J_{BH} = 140. IR (Nujol, cm^{-1}): 2510 (ν_{BH}), 1700 ($\nu_{C=O}$). For $C_{13}H_{23}B_9K_2O_4$ (420.2) calculated: 37.28% C, 5.54% H, 23.23% B; found: 37.39% C, 5.67% H, 23.24% B.

K[10-(4-KOC(O)$C_6H_4OCH_2CH_2CH_2CH_2O$)-7,8-$C_2B_9H_{11}$] (**3c**). Yield 0.34 g (99%). ^{1}H NMR (600 MHz, methanol-d_4): 7.88 d, 2 H, J = 8.9 (CH_{ar}); 6.80 d, 2 H, J = 8.9 (CH_{ar}); 4.28 t, 2 H, J = 6.3 (-OCH_2); 3.61 m, 2 H (-OCH_2); 1.78 m, 2 H (-$OCH_2C\mathbf{H}_2C\mathbf{H}_2CH_2O$-); 1.72 m, 2 H (-$OCH_2C\mathbf{H}_2C\mathbf{H}_2CH_2O$-); 1.54 s, 2 H ($CH_{carb}$); 2.5–0.0, 8 H (BH); –0.50, 1 H (BH). ^{13}C{^{1}H} NMR (125 MHz, methanol-d_4): 167.3, 163.4, 131.4, 120.3, 115.2, 69.6, 64.5, 38.6, 27.3, 25.1. ^{11}B NMR (128 MHz, methanol-d_4): –10.1 s, 1 B; –12.5 d, 2 B, J_{BH} = 136; –17.3 d, 2 B, J_{BH} = 134; –23.8 d, 2 B, J_{BH} = 149; –25.0 d, 1 B, J_{BH} = 154; –40.8 d, 1 B, J_{BH} = 140. IR (Nujol, cm^{-1}): 2520 (ν_{BH}), 1710 ($\nu_{C=O}$). For $C_{13}H_{23}B_9K_2O_4$ (420.2) calculated: 37.28% C, 5.54% H, 23.23% B; found: 37.54% C, 5.81% H, 23.21% B.

Synthesis of K[10-(X-KOC(O)$C_6H_4OCH_2CH_2OCH_2CH_2O$)-7,8-$C_2B_9H_{11}$] (**4**)

To [10-O(CH_2CH_2)$_2$O-7,8-$C_2B_9H_{11}$] (0.67 g, 3.0 mmol) in acetonitrile (60 ml), hydroxybenzoic acid (0.41 g, 3.0 mmol) and potassium carbonate (4.14 g, 30 mmol) were added and the reaction mixture was heated under reflux for 5–6 h. The reaction mixture was cooled to room temperature and filtered and evaporated to dryness in vacuo, the residue was crystallized from aqueous ethanol at 0 °C and dried over P_2O_5 to obtain a white crystalline product.

K[10-(2-KOC(O)$C_6H_4OCH_2CH_2OCH_2CH_2O$)-7,8-$C_2B_9H_{11}$] (**4a**). Yield 1.12 g (94%). ^{1}H NMR (400 MHz, methanol-d_4): 7.91 dd, 1 H, J = 8.1, 1.8 (CH_{ar}); 7.51 dt, 1 H, J = 7.8, 1.8 (CH_{ar}); 6.93 m, 2 H (CH_{ar}); 4.52 m, 2 H (-OCH_2); 3.85 m, 2 H (-OCH_2); 3.50 m, 4 H (-OCH_2); 1.47 s, 2 H (CH_{carb}); 2.7 to –0.7 br s, 9 H (BH). ^{11}B NMR (128 MHz, methanol-d_4): –9.6 s, 1 B; –12.5 d, 2 B, J_{BH} = 142; –17.3 d, 2 B, J_{BH} = 136; –23.8 d, 2 B, J_{BH} = 154; –25.2 d, 1 B, J_{BH} = 176; –40.5 d, 1 B, J_{BH} = 147. IR (Nujol, cm^{-1}): 2575 (ν_{BH}), 2519 (ν_{BH}), 2489 (ν_{BH}), 1710 ($\nu_{C=O}$). For $C_{13}H_{23}B_9K_2O_5$ (436.2) calculated: 35.91% C, 5.33% H, 22.38% B; found: 36.23% C, 5.92% H, 22.39% B.

K[10-(3-KOC(O)$C_6H_4OCH_2CH_2OCH_2CH_2O$)-7,8-$C_2B_9H_{11}$] (**4b**). Yield 1.16 g (97%). ^{1}H NMR (400 MHz, methanol-d_4): 7.49 m, 1 H, J = 1.8, 0.6 (CH_{ar}); 7.44 m, 1 H, J = 7.7 (CH_{ar}); 7.26 t, 1 H, J = 7.9 (CH_{ar}); 7.07 m, 1 H, J = 8.0, 2.6, 1.0 (CH_{ar}); 4.43 m, 2 H (-OCH_2); 3.81 m, 2 H (-OCH_2); 3.61 m, 4 H (-OCH_2); 1.51 s, 2 H (CH_{carb}); 2.7 to –0.2 br s, 9 H (BH). ^{11}B NMR (128 MHz, methanol-d_4): –9.4 s, 1 B; –12.8 d, 2 B, J_{BH} = 135; –17.3 d, 2 B, J_{BH} = 134; –23.7 d, 2 B, J_{BH} = 154; –25.2 d, 1 B, J_{BH} = 172; –40.5 d, 1 B, J_{BH} = 141. IR (Nujol, cm^{-1}): 2584 (ν_{BH}), 2582 (ν_{BH}), 2487 (ν_{BH}), 1716 ($\nu_{C=O}$). For $C_{13}H_{23}B_9K_2O_5$ (436.2) calculated: 35.91% C, 5.33% H, 22.38% B; found: 35.90% C, 5.52% H, 22.38% B.

K[10-(4-KOC(O)$C_6H_4OCH_2CH_2OCH_2CH_2O$)-7,8-$C_2B_9H_{11}$] (**4c**). Yield 1.01 g (84%). ^{1}H NMR (400 MHz, methanol-d_4): 7.90 m, 2 H, J = 8.9 (CH_{ar}); 6.80 d, 2 H, J = 8.9 (CH_{ar}); 4.41 m, 2 H (-OCH_2); 3.83 m, 2 H (-OCH_2); 3.58 m, 4 H (-OCH_2); 1.50 s, 2 H (CH_{carb}); 2.9 to –0.5 br s,

9 H (BH). ^{11}B NMR (128 MHz, methanol-d_4): –9.5 s, 1 B; –12.4 d, 2 B, J_{BH} = 136; –17.3 d, 2 B, J_{BH} = 132; –23.8 d, 2 B, J_{BH} = 153; –25.2 d, 1 B, J_{BH} = 175; –40.5 d, 1 B, J_{BH} = 140. For $C_{13}H_{23}B_9K_2O_5$ (436.2) calculated: 35.91% C, 5.33% H, 22.38% B; found: 36.10% C, 5.67% H, 22.37% B.

Synthesis of (Me_4N)[10-$N_3CH_2CH_2CH_2CH_2O$-7,8-$C_2B_9H_{11}$] (**5**)

A mixture of [10-C_4H_8O-7,8-$C_2B_9H_{11}$] (0.58 g, 2.82 mmol) and sodium azide (0.45 g, 6.15 mmol) in ethanol (40 ml) was heated under reflux for 7 h. The reaction mixture was cooled to room temperature and filtered, and the filtrate was treated with tetramethylammonium bromide (0.50 g, 3.20 mmol). The white precipitate was filtered, purified by reprecipitation from acetone–water mixture and dried in vacuo to give 0.79 g (87%) of the product. ^{1}H NMR (400 MHz, acetone-d_6): 3.42 s + m, 14 H (-OCH_2 + Me_4N^+); 3.29 t, 2 H (-OCH_2); 1.58 m, 2 H (-$OCH_2C\mathbf{H}_2$-); 1.48 m, 2 H (-$OCH_2C\mathbf{H}_2$-); 1.43 s, 2 H (CH_{carb}); 2.6 to –0.1, 8 H (BH); –0.54, 1 H (BH). ^{11}B NMR (115 MHz, acetone-d_6): –8.3 s, 1 B; –11.6 d, 2 B, J_{BH} = 134; –16.6 d, 2 B, J_{BH} = 131; –23.3 d, 2 B, J_{BH} = 147; –24.7 d, 1 B, J_{BH} = 161; –39.8 d, 1 B, J_{BH} = 141. IR (Nujol, cm^{-1}): 2583 (ν_{BH}), 2544 (ν_{BH}), 2484 (ν_{BH}), 2136 ($\nu_{N=N=N}$), 2116 ($\nu_{N=N=N}$), 2086 ($\nu_{N=N=N}$).

Synthesis of (Me_4N)[10-$N_3CH_2CH_2OCH_2CH_2O$-7,8-$C_2B_9H_{11}$] (**6**)

A mixture of [10-$O(CH_2CH_2)_2O$-7,8-$C_2B_9H_{11}$] (0.31 g, 0.92 mmol) and sodium azide (0.24 g, 3.70 mmol) in ethanol (30 ml) was heated under reflux for 13 h. The reaction mixture was cooled to room temperature, filtered, treated with tetramethylammonium bromide (0.25 g, 1.6 mmol), and evaporated to dryness under reduced pressure. The residue was purified by reprecipitation from a dichloromethane–hexane mixture and dried in vacuo to give 0.12 g (26%) of the product. ^{1}H NMR (400 MHz, acetone-d_6): 3.65 t, 2 H (-OCH_2); 3.59 m, 2 H (-OCH_2); 3.52 t, 2 H (-OCH_2); 3.41 s, 12 H (Me_4N^+); 3.37 t, 2 H (-OCH_2); 1.49 s, 2 H (CH_{carb}); 2.6 to –0.1, 8 H (BH); –0.51, 1 H (BH). ^{13}C NMR (100 MHz, acetone-d_6): 71.6 t, J_{CH} = 142; 70.0 t, J_{CH} = 139; 69.7 t, J_{CH} = 139; 55.3 qt, J_{CH} = 143, J_{CN} = 3.9 (Me_4N^+); 51.0 t, J_{CH} = 141; 39.3 d, J_{CH} = 136. ^{11}B NMR (115 MHz, acetone-d_6): –8.4 s, 1 B; –11.6 d, 2 B, J_{BH} = 129; –16.6 d, 2 B, J_{BH} = 134; –23.3 d, 2 B, J_{BH} = 149; –24.8 d, 1 B, J_{BH} = 155; –39.8 d, 1 B, J_{BH} = 140. IR (Nujol, cm^{-1}): 2583 (ν_{BH}), 2523 (ν_{BH}), 2499 (ν_{BH}), 2108 ($\nu_{N=N=N}$), 2095 ($\nu_{N=N=N}$), 2070 ($\nu_{N=N=N}$).

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