Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2015, **44**, 9860

Cyanide free contraction of disclosed 1,4-dioxane ring as a route to cobalt bis(dicarbollide) derivatives with short spacer between the boron cage and terminal functional group†‡

Akim V. Shmal'ko,[a,b] Marina Yu. Stogniy,[a] Grigorii S. Kazakov,[a] Sergey A. Anufriev,[a] Igor B. Sivaev,*[a] Leonid V. Kovalenko[b] and Vladimir I. Bregadze[a]

Received 3rd April 2015,
Accepted 7th April 2015

DOI: 10.1039/c5dt01293g

www.rsc.org/dalton

The 1,4-dioxane derivative of cobalt bis(dicarbollide) reacts with dialkylsulfides and triphenylphosphine to give the corresponding sulfonium and phosphonium derivatives $[8\text{-L}(CH_2CH_2O)_2\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})\text{-}(1',2'\text{-}C_2B_9H_{11})]$ (L = SMe_2, $S(CH_2CH_2)_2O$, PPh_3). The treatment of the triphenylphosphonium derivative with sodium hydroxide results in contraction of the side chain with formation of $[8\text{-HOCH}_2CH_2O\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$. The same product was obtained by treatment of the dimethylsulfonium derivative with the poorly nucleophilic base *t*-BuOK, whereas the stronger nucleophiles induce the sulfur demethylation to give $[8\text{-MeS}(CH_2CH_2O)_2\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$. The alcohol was used for the synthesis of a series of other short-spacer functional derivatives $[8\text{-XOCH}_2CH_2O\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ (X = NH_2, SH, N_3). A similar contraction of the disclosed 1,4-dioxane ring *via* the reactions with SMe_2 and PPh_3 can be used for the synthesis of short-spacer functional derivatives of *nido*-carborane, whereas the 1,4-dioxane derivatives of *closo*-decaborate and *closo*-dodecaborate anions, being stronger electron donors, are more stable and do not react with dimethylsulfide and triphenylphosphine.

Introduction

Since its discovery fifty years ago by Hawthorne, cobalt bis(dicarbollide) anion $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$ has occupied a unique position among metallacarboranes due to its availability, high chemical stability, ionic character, low nucleophilicity, as well as diamagnetic character allowing to monitor easily its substitution reactions by NMR spectroscopy.[1,2] The ring-opening of the dioxane derivative $[8\text{-O}(CH_2CH_2)_2\text{O-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ with various nucleophiles was proposed as a synthetically feasible route to derivatives with pendant functional groups connected to the metallacarborane cage through flexible spacers.[3–5] An extensive application of this approach started in 2002 and resulted in the synthesis of many compounds for various purposes, including efficient agents for radionuclide extraction from spent nuclear fuel,[4,6–8] polymer additives,[9] highly boronated dendrimer-like compounds,[10–12] boron-containing biologically active compounds, such as aminoacids,[3,13] nucleosides,[14–16] porphyrins,[17–19] phthalocyanines,[20,21] and HIV protease inhibitors.[18,22]

Due to their nontoxic, nonionic, and hydrophilic character short oligo(ethylene glycol) fragments are widely used as linkers in the design of various biologically active molecules and conjugates. The 1,4-dioxane ring opening produces cobalt bis(dicarbollide) derivatives with the diethylene glycol spacer between the boron cage and the functional moiety. The spacer length can be increased using nucleophiles containing ethylene glycol fragments.[7,23,24] However, in some cases molecular design requires a shorter spacer. Only few examples of synthesis of cobalt bis(dicarbollide) derivatives with a short spacer between the boron cage and the functional group were reported. A series of the *C*-substituted derivatives $[1\text{-X}(CH_2)_n\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ (X = OH, n = 1–3; X = COOH, n = 1,2; X = NH_2, n = 1) were obtained by lithiation of the parent cobalt bis(dicarbollide) with *n*-BuLi followed by alkylation and functional group interconversions.[25–27] Unfortunately, the lithiation does not proceed selectively resulting in a mixtures of mono- and disubstituted derivatives. Another approach including the introduction of a hydroxyl group

---

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Str., 119991 Moscow, Russia. E-mail: sivaev@ineos.ac.ru*

[b] *D. I. Mendeleev Russian Chemical Technological University, 9 Miusskaya Sq., 125047 Moscow, Russia*

† In memory of Professor Kenneth Wade (1932–2014).

‡ Electronic supplementary information (ESI) available. See DOI: 10.1039/c5dt01293g

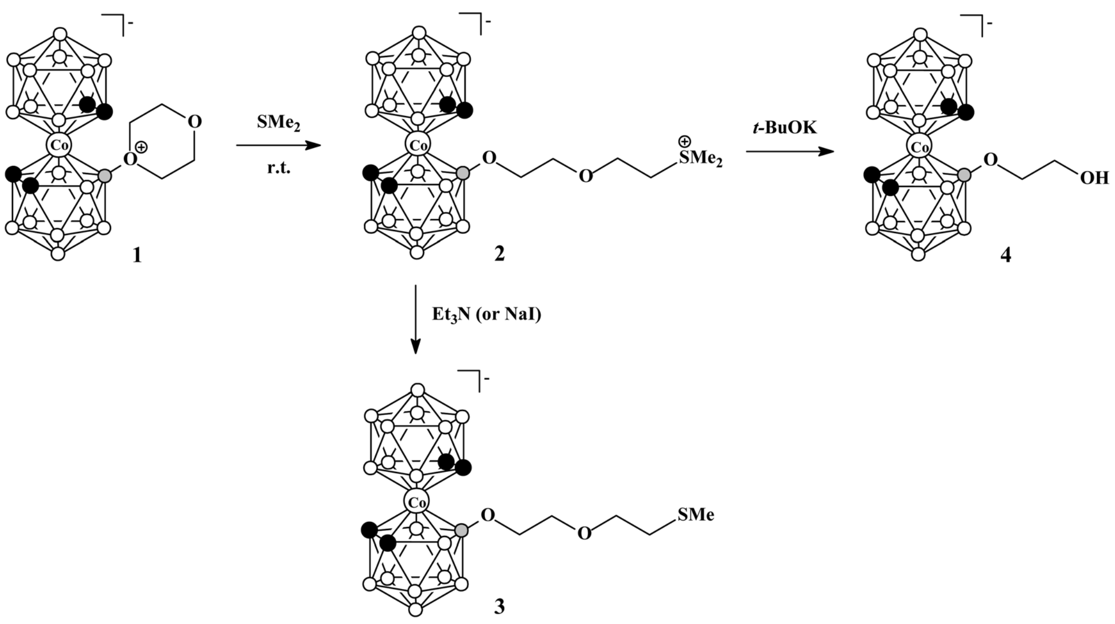
followed by its alkylation was used for the synthesis of [8-HOOCCH$_2$O-3,3′-Co(1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)]$^-$.[26] The drawback of this approach is the formation of a mixture of the mono- and dihydroxy derivatives in the first step. Another more promising approach includes contraction of the diethylene glycol spacer forming on disclosure of the 1,4-dioxane ring. It can be obtained by the reaction of the dioxane derivative with cyanide ions followed by elimination of acrylonitrile under treatment with alkali resulting in [8-HOCH$_2$CH$_2$O-3,3′-Co(1,2-C$_2$B$_9$H$_{10}$)-(1′,2′-C$_2$B$_9$H$_{11}$)]$^-$.[3] This route utilizes the well known synthesis of the 1,4-dioxane derivative[7,28] and reaction of its nucleophilic disclosure resulting in the target product in high yield. The main drawback of this approach is the use of highly toxic cyanide ions. Later the same product was obtained in an attempt to prepare a Grignard reagent from the bromide-disclosed 1,4-dioxane derivative.[29]

In this contribution we describe cyanide free contraction of disclosed 1,4-dioxane ring using dimethylsulfide and triphenylphosphine and some functional group interconversions of [8-HOCH$_2$CH$_2$O-3,3′-Co(1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)]$^-$. The applicability of this approach to the synthesis of short spacer functional derivatives of other polyhedral boron hydrides is also discussed.

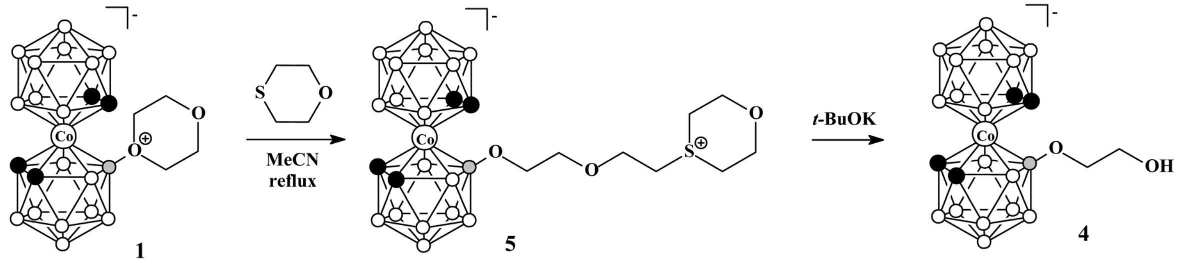
Results and discussion

The ring-opening of the 1,4-dioxane derivative of cobalt bis (dicarbollide) with various nucleophiles was extensively studied.[5] However, it should be noted that the main interest was directed to the reactions with hard nucleophiles, such as alcoholates (phenolates) and amines. In this contribution we describe the reaction of [8-O(CH$_2$CH$_2$)$_2$O-3,3′-Co(1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)] (**1**) with soft nucleophiles such as dialkylsulfides and triphenylphosphine.

We found that the reaction of **1** with dimethylsulfide in dichloromethane at room temperature results in the corresponding dimethylsulfonium derivative [8-Me$_2$S(CH$_2$CH$_2$O)$_2$-3,3′-Co(1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)] (**2**) in practically quantitative yield. The ^{1}H NMR spectrum of **2** contains the characteristic singlet of sulfonium SMe$_2$ group at 3.22 ppm. Alkyl sulfonium salts generally are more stable and less reactive than the corresponding oxonium salts, nevertheless they are widely used in organic synthesis as powerful alkylating agents.[30,31] Since the sulfonium center has two different types of substituents, one can expect formation of a mixture of two products in reaction of **2** with nucleophiles. However, we found that the reaction proceeds very selectively and the reaction products depend strongly on the nucleophile nature. The reaction of **2** with triethylamine, which is a good nucleophile and a good base, results in selective demethylation of the sulfur atom and methylation of the amine nitrogen atom giving the triethylmethylammonium salt (Et$_3$NMe)-[8-MeS(CH$_2$CH$_2$O)$_2$-3,3′-Co(1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)] (**3a**) (Scheme 1). A similar result was obtained using iodide ion as "non-basic" nucleophile. The reaction of **2** with sodium iodide in DMF at 120 °C produces Na[8-MeS(CH$_2$CH$_2$O)$_2$-3,3′-Co(1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)] (**3b**) (Scheme 1). In the ^{1}H NMR spectra the sulfur demethylation results in the characteristic upper-field shift of the methyl group singlet to 2.13 ppm. On the other hand, the use of *t*-BuOK as "non-nucleophilic" base results in a contraction of the side chain giving K[8-HOCH$_2$CH$_2$O-3,3′-Co(1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)] (**4a**) (Scheme 1). The ^{1}H NMR spectrum of **4** is characterized by the



Scheme 1



Scheme 2

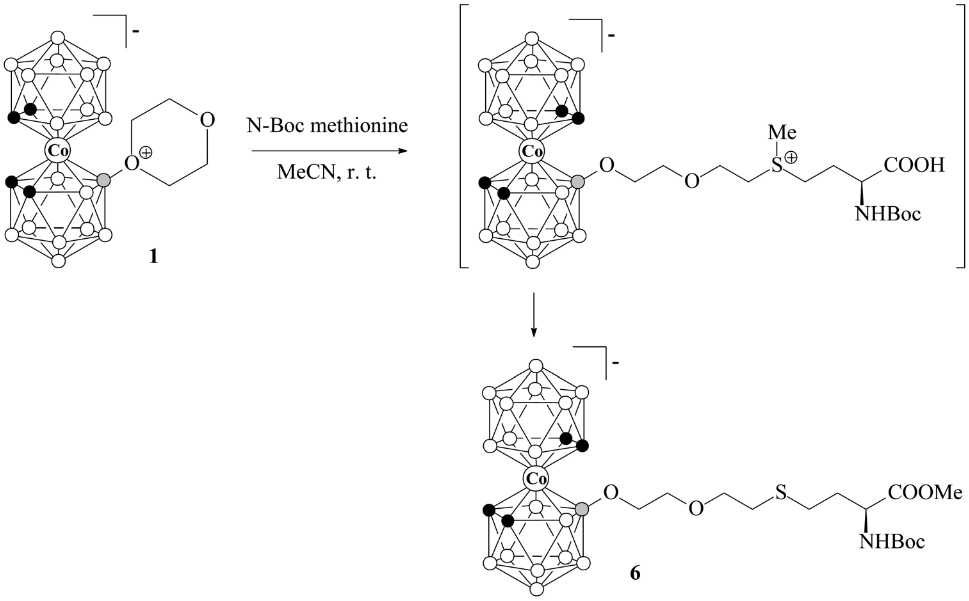
presence of two overlapping broad singlets of the carborane CH groups at 4.19 ppm and apparent singlet corresponding to two OCH_2 groups at 3.56 ppm with the peak integral ratio of 1 : 1. The reaction mechanism probably includes elimination of alkene as dimethylvinyl sulfonium cation. The similar chain shortening with acrylonitrile elimination was reported earlier on alkaline hydrolysis of the nitrile $[8\text{-}NC(CH_2CH_2O)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$,[3] however the dimethylsulfonium group is a much better leaving group for alkene-forming elimination than cyanide.[32] The additional advantages of using dimethylsulfide as a reagent for the side chain contraction are simple work-up procedure and avoidance of highly toxic cyanides. Thus, the reactions of **2** with good nucleophiles lead to partial demethylation of the sulfur atom, whereas the reactions with bases being poor nucleophiles lead to the side chain contraction.

Another subject of our interest was 1,4-thioxane. Its reaction with **1** in refluxing acetonitrile gives the corresponding cyclic sulfonium derivative $[8\text{-}O(CH_2CH_2)_2S(CH_2CH_2O)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ (**5**) (Scheme 2). It could be expected that reaction of **5** with nucleophiles will produce the 1,4-thioxane ring-opening product with elongation of the side chain. However, surprisingly the treatment of **5** with triethylamine in refluxing acetonitrile did not result in the 1,4-thioxane ring opening. On the other hand, the reaction of **5** with *t*-BuOK, as expected, results in the side chain contraction to give **4a** (Scheme 2).

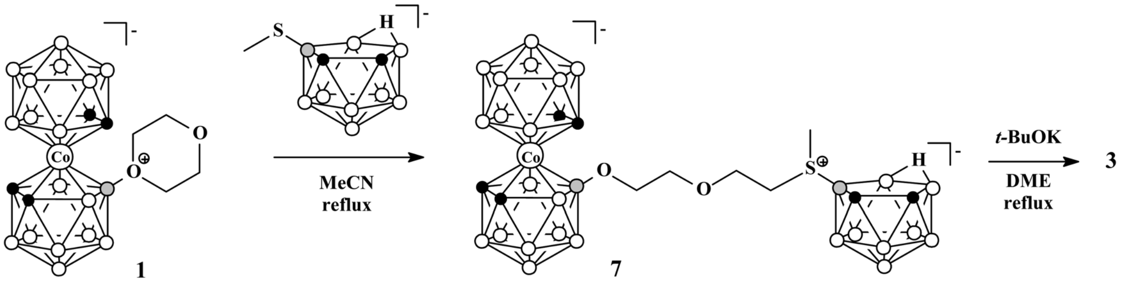
S-Adenosylmethionine (ademetionine) is a ubiquitous metabolite that is present in all cells and biological fluids, and serves as a methyl donor in a multitude of different methylation reactions involving proteins, phospholipids, catecholamines and DNA. It was found to be a promising antidepressant and shows potential in drug treatment for other disorders of the central nervous system including cognitive dysfunction, AIDS-associated myelopathy and brain ischaemia.[33] *S*-Methylmethionine, $Me_2S^+CH_2CH_2CH(NH_2)COO^-$, is known as one of the most important sulphur-containing compounds in plant metabolism, taking part in methylation processes and the regulation of methionine biosynthesis.[34,35] Therefore, it was interesting to synthesize boron-containing analogues of these compounds. Since methionine has several nucleophilic reaction centers, we used *N*-Boc-protected methionine to avoid alkylation at the nitrogen atom. Surprisingly we found that the main reaction product is not the expected sulfonium derivative of methionine, but the isomeric methyl ester of the corresponding sulfide $H[8\text{-}MeOOCCH(NHBoc)CH_2CH_2S(CH_2CH_2O)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ (**6**). This assignment is supported by the appearance of the characteristic methyl ester singlet at 3.72 ppm and the absence of the sulfonium methyl singlet approx. at 3.2 ppm as well as signals of the corresponding methylene groups. We suppose that the initially formed sulfonium derivative acts as methylating agent resulting in intramolecular methylation of the amino acid carboxyl group (Scheme 3).

In another experiment 9-methylthio-*nido*-carborane $[9\text{-}MeS\text{-}7,8\text{-}C_2B_9H_{11}]^-$ was used as a nucleophilic agent. It was reported recently that alkylation of $[9\text{-}MeS\text{-}7,8\text{-}C_2B_9H_{11}]^-$ with various halogen alkanes results in the stable alkylmethyl sulfonium derivatives $[9\text{-}R(Me)S\text{-}7,8\text{-}C_2B_9H_{11}]$.[36] The sulfonium centre in these derivatives is stabilized by a strong electron-donating effect of the *nido*-carborane cage.[37,38] Therefore it was interesting to synthesize such cobalt bis(dicarbollide)-*nido*-carborane hybrid and study its properties. The reaction of **1** with $Cs[9\text{-}MeS\text{-}7,8\text{-}C_2B_9H_{11}]$ in refluxing acetonitrile resulted in the target hybrid **7** as a mixture of diastereomers due to the presence of two chiral centers – asymmetrically substituted *nido*-carborane and sulfonium groups (Scheme 4). The ^1H NMR spectrum of **7** contains the characteristic set of signals of methyl and methylene groups indicating formation of the sulfonium group[36] as well as the signals of the CH_{carb} protons of the cobalt bis(dicarbollide) and *nido*-carborane fragments (Fig. S1‡). The ^{13}C NMR spectrum also contains the characteristic set of signals of methyl and α-methylene groups attached to the sulfur atom as well as the characteristic signals of different carborane fragments (Fig. S2‡). The ^{11}B NMR spectrum of **7** contains two overlapping sets of signals corresponding to the cobalt bis(dicarbollide) and the *nido*-carborane fragments (Fig. S3 and S4‡).

The treatment of **7** with triethylamine in refluxing acetonitrile does not lead to any reaction whereas both **2** and $[9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{11}]$ undergo demethylation under the same conditions. The lack of reactivity probably can be explained by steric reasons. On the other hand the treatment of **7** with *t*-BuOK in refluxing 1,2-dimethoxyethane resulted not in the side chain contraction, but in the cleavage of the boron–sulfur bond with formation of the methylsulfide **3** (Scheme 4).



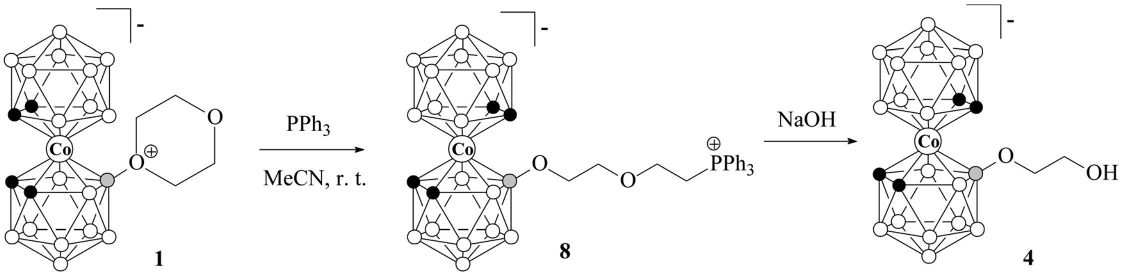
Scheme 3



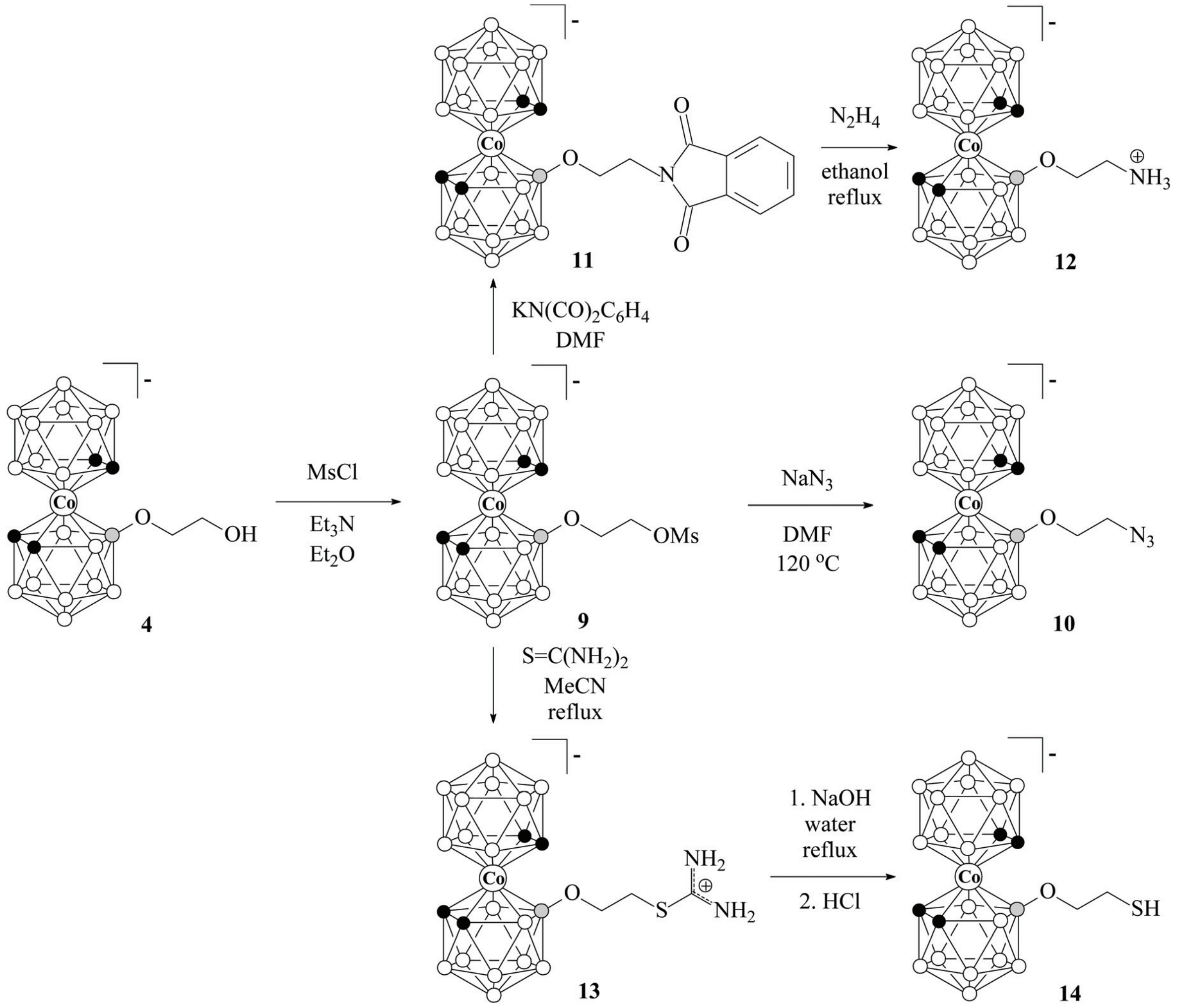
Scheme 4

The triphenylphosphonium group is an even better leaving group for alkene-forming elimination than the dimethylsulfonium one.[32] The reaction of **1** with triphenylphosphine in acetonitrile at room temperature results in the corresponding triphenylphosphonium derivative [8-$Ph_3P(CH_2CH_2O)_2$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (**8**) in high yield (Scheme 4). A similar reaction was described earlier for the 1,4-dioxane derivative of iron bis(dicarbollide).[39] The treatment of **8** with sodium hydroxide in refluxing ethanol results in the side chain contraction to give Na[8-$HOCH_2CH_2O$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (**4b**) (Scheme 5).

The alcohol **4** was converted to the corresponding mesylate K[8-$MesOCH_2CH_2O$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (**9**) by the treatment with mesyl chloride in diethyl ether (Scheme 6).



Scheme 5



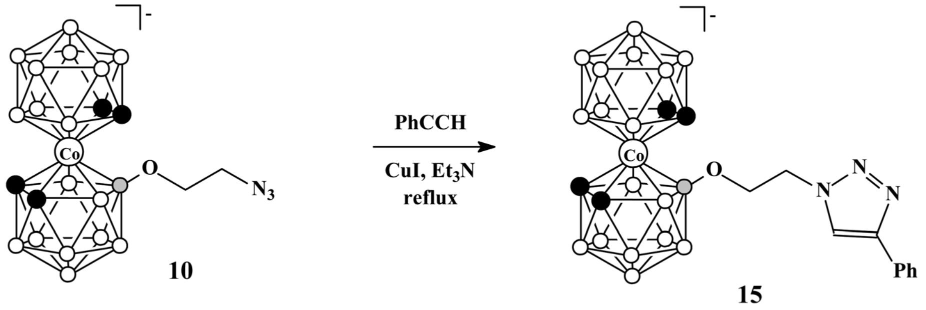
Scheme 6

The latter compound was used for the synthesis of a series of cobalt bis(dicarbollide) derivatives with a shortened spacer between the boron cage and the terminal functional group. The reaction of **9** with sodium azide in DMF at 120 °C gave the corresponding azide K[8-$N_3CH_2CH_2O$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (**10**). The reaction with potassium phthalimide under similar conditions produced the phthalimide **11**, that was converted to amine [8-$H_3NCH_2CH_2O$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (**12**) by the treatment with hydrazine hydrate. The earlier described 8-hydroxy derivative of cobalt bis (dicarbollide) [8-HO-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ (ref. 40) was identified as the main reaction by-product. The reaction of **9** with thiourea in refluxing acetonitrile gave the thiouronium derivative **13** which was hydrolyzed to the corresponding thiol [8-$HSCH_2CH_2O$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ (**14**) (Scheme 6).

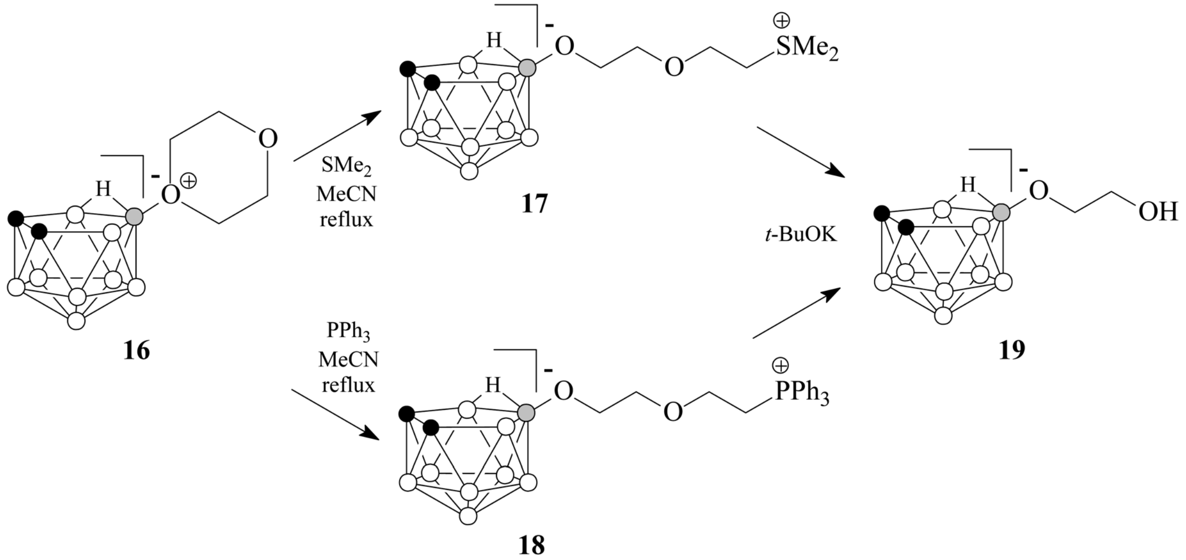
The reaction of azido derivative **10** with phenyl acetylene in the presence of copper(I) iodide and triethylamine gave the corresponding triazole **15** in good yield (Scheme 7).

Having an effective method of synthesis of cobalt bis(dicarbollide) derivatives with a shortened spacer between the boron cage and the terminal functional group, we decided to use this approach for the synthesis of similar derivatives of other polyhedral boron hydrides. We found that the reactions of the 1,4-dioxane derivative of *nido*-carborane 10-O(CH_2CH_2)$_2$O-7,8-$C_2B_9H_{11}$ (**16**) with dimethylsulfide and triphenylphosphine in refluxing acetonitrile produce the corresponding sulfonium 10-$Me_2S(CH_2CH_2O)_2$-7,8-$C_2B_9H_{11}$ (**17**) and phosphonium 10-$Ph_3P(CH_2CH_2O)_2$-7,8-$C_2B_9H_{11}$ (**18**) derivatives in high yields (Scheme 8). The sulfonium derivative **17** was obtained earlier in the reaction of the protonated form of *nido*-carborane with 1,4-dioxane in the presence of dimethylsulfide at 100 °C.[41] The treatment of **17** and **18** with *t*-BuOK produces the corresponding alcohol with a shortened side chain K[10-$HOCH_2CH_2O$-7,8-$C_2B_9H_{11}$] (**19**) (Scheme 8).

However, our attempts to extend this approach to other polyhedral boron hydrides, such as *closo*-decaborate [$B_{10}H_{10}$]$^{2-}$ and *closo*-dodecaborate [$B_{12}H_{12}$]$^{2-}$ anions, were unsuccessful and only starting materials, 1,4-dioxane derivatives (Bu_4N)[2-$B_{10}H_9O$-(CH_2CH_2)$_2$O][42] and (Bu_4N)[$B_{12}H_{11}O(CH_2CH_2)_2O$],[43] were recovered after refluxing with dimethylsulfide and triphenyl-



Scheme 7



Scheme 8

phosphine in acetonitrile. The increased stability of cyclic oxonium derivatives of *closo*-decaborate and *closo*-dodecaborate anions is in good agreement with their electron donating properties which increase in the series $[8\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^- < [10\text{-}nido\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]^- < [\text{B}_{12}\text{H}_{11}]^{2-} < [2\text{-B}_{10}\text{H}_9]^{2-}$.[37]

Conclusion

The reactions of the 1,4-dioxane derivative of cobalt bis(dicarbollide) with dialkylsulfides and triphenylphosphine produce the corresponding sulfonium and phosphonium derivatives $[8\text{-L}(\text{CH}_2\text{CH}_2\text{O})_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]$ (L = SMe_2, $\text{S}(\text{CH}_2\text{CH}_2)_2\text{O}$, PPh_3). The treatment of the triphenylphosphonium derivative with sodium hydroxide results in contraction of the side chain with formation of $[8\text{-HOCH}_2\text{CH}_2\text{O-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$. The same product was obtained by treatment of the dimethylsulfonium derivative with "non-nucleophilic" bases such as *t*-BuOK, whereas the stronger nucleophiles induce the sulfur demethylation to give $[8\text{-MeS}(\text{CH}_2\text{CH}_2\text{O})_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$. The alcohol derivative was used for the synthesis of a series of other short-spacer functional derivatives $[8\text{-XOCH}_2\text{CH}_2\text{O-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (X = NH_2, SH, N_3). It was demonstrated that similar contraction of the disclosed 1,4-dioxane ring *via* the reactions with SMe_2 and PPh_3 can be used for the synthesis of short-spacer functional derivatives of *nido*-carborane, whereas the 1,4-dioxane derivatives of *closo*-decaborate $[2\text{-B}_{10}\text{H}_9\text{O}(\text{CH}_2\text{CH}_2)_2\text{O}]^-$ and *closo*-dodecaborate $[\text{B}_{12}\text{H}_{11}\text{O}(\text{CH}_2\text{CH}_2)_2\text{O}]^-$ anions, being stronger electron donors, are more stable and do not react with dimethylsulfide and triphenylphosphine.

Experimental

$[8\text{-O}(\text{CH}_2\text{CH}_2)_2\text{O-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]$ (**1**),[7] $[10\text{-O}(\text{CH}_2\text{CH}_2)_2\text{O-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]$ (**16**)[44] and $\text{Cs}[9\text{-MeS-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]$[38] were synthesized as described in the literature. All other chemicals were of reagent grade and received from standard commercial vendors. The ^{1}H, ^{11}B, ^{11}B{^{1}H}, and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer. ^{1}H chemical shifts were referenced to residual protons in the lock solvents. ^{11}B chemical shifts were referenced externally to $BF_3{\cdot}OEt_2$. The infrared spectra were recorded on Specord IR 75 and Infralum FT-801 spectrophotometers. The EI and ESI mass-spectra were obtained using KratosMS890 and Thermo Finnigan LCQ Advantage mass spectrometers, respectively. The reaction's progress was monitored by TLC (Merck F254 silica gel on aluminum plates). Acros Organics silica gel (0.060–0.200 mm) was used for column chromatography.

[8-$Me_2S(CH_2CH_2O)_2$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (2)

Dimethylsulfide (0.45 ml, 0.38 g, 6.13 mmol) was added to a solution of **1** (0.50 g, 1.22 mmol) in dichloromethane (50 ml) and the reaction mixture was stirred at ambient temperature for 10 h. The solvent was removed under reduced pressure to obtain 0.55 g (96%) of the light brown product. ^{1}H NMR (acetone-d_6, ppm): 4.14 (4H, m, $-CH_2-$ + CH_{carb}), 4.04 (2H, s, CH_{carb}), 3.79 (2H, t, $-CH_2-$), 3.64 (4H, m, $-CH_2-$), 3.22 (6H, s, $-S(CH_3)_2$). ^{13}C NMR (acetone-d_6, ppm): 72.4 (OCH_2), 68.8 (OCH_2), 65.0 (OCH_2), 46.3 (C_{carb}), 44.2 (SCH_2), 39.7 (C_{carb}), 25.3 ($S(CH_3)_2$). ^{11}B NMR (acetone-d_6, ppm): 24.2 (1B, s), 5.9 (1B, d, J = 135 Hz), 0.3 (1B, d, J = 136 Hz), −2.8 (1B, d, J = 147 Hz), −4.8 (2B, d, J = 153 Hz), −7.0 (2B, d, J = 135 Hz), −7.6 (2B, d, J = 132 Hz), −8.8 (2B, d, J = 128 Hz), −17.4 (2B, d, J = 156 Hz), −20.2 (2B, d, J = 154 Hz), −22.4 (1B, d, J = 160 Hz), −28.8 (1B, d, J = 146 Hz). ESI-MS m/z for $C_{10}H_{35}B_{18}O_2SCo$: calcd 473.3487, obsd 458.3706 $[M - CH_3]^-$. Anal. Calcd for $C_{10}H_{35}B_{18}O_2SCo$: C, 25.40; H, 7.46; B, 41.14. Found: C, 25.14; H, 7.62; B, 41.08.

(Et_3NMe)[8-$MeS(CH_2CH_2O)_2$-3,3′-Co(1,2-$C_2B_9H_{10}$)-(1′,2′-$C_2B_9H_{11}$)] (3a)

Triethylamine (44 µl, 32 mg, 0.317 mmol) was added to a solution of **2** (50 mg, 0.106 mmol) in acetonitrile (25 ml) and the reaction mixture was heated under reflux for 6 h. After cooling to room temperature the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica using a mixture of dichloromethane and acetone (3 : 2) as the eluent to give 51 mg (83%) of the brown product. ^{1}H NMR (acetone-d_6, ppm): 4.31 (4H, d, CH_{carb}), 3.64–3.47 (12H, m, $-OCH_2CH_2OCH_2CH_2SCH_3$ + $NCH_3(CH_2CH_3)_3$), 3.19 (3H, s, $NCH_3(CH_2CH_3)_3$), 2.64 (2H, t, $-OCH_2CH_2SCH_3$), 2.13 (3H, s, $-OCH_2CH_2SCH_3$), 1.45 (9H, m, $NCH_3(CH_2CH_3)_3$). ^{13}C NMR (acetone-d_6, ppm): 71.6 (OCH_2), 70.6 (OCH_2), 68.3 (OCH_2), 55.9 ($NCH_3(CH_2CH_3)_3$), 54.7 (C_{carb}), 46.4 ($NCH_3(CH_2CH_3)_3$), 46.3 (C_{carb}), 33.1 (SCH_2), 15.1(SCH_3), 7.2 ($NCH_3(CH_2CH_3)_3$). ^{11}B NMR (acetone-d_6, ppm): 27.9 (1B, s), 8.7 (1B, d, J = 142 Hz), 5.6 (1B, d, J = 141 Hz), 2.8 (1B, J = 140 Hz), 1.0 (2B, d, J = 150 Hz), −2.3 (2B, d, J = 130 Hz), −3.2 (4B, m), −12.1 (2B, d, J = 156 Hz), −15.3 (2B, d, J = 154 Hz), −16.7 (1B, d, J = 129 Hz), −23.3 (1B, d, J = 167 Hz). ESI-MS m/z for $C_9H_{32}B_{18}O_2SCo$: calcd 458.3252, obsd 458.3245 $[M]^-$. ESI-MS m/z for $C_7H_{18}N$: calcd 116.1434, obsd 116.1445 $[M]^+$.

Na[8-$MeS(CH_2CH_2O)_2$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (3b)

Sodium iodide (159 mg, 1.06 mmol) was added to a solution of **2** (50 mg, 0.106 mmol) in DMF (25 ml) and heated at 120 °C for 6 h. After cooling to room temperature the solvent was removed under reduced pressure. The crude product was dissolved in dichloromethane, filtered and evaporated *in vacuo* to obtain 46 mg (91%) of the brown product. ^{1}H NMR (acetone-d_6, ppm): 4.30 (4H, d, CH_{carb}), 3.64–3.58 (4H, m, $-OCH_2CH_2O-$), 3.50 (2H, t, $-OCH_2CH_2SCH_3$), 2.65 (2H, t, $-OCH_2CH_2SCH_3$), 2.13 (3H, s, $-OCH_2CH_2SCH_3$). ^{11}B NMR (acetone-d_6, ppm): 23.0 (1B, s), 4.1 (1B, d, J = 144 Hz), 0.4 (1B, d, J = 143 Hz), −2.4 (1B, d, J = 144 Hz), −4.3 (2B, d, J = 152 Hz), −7.3 (2B, d, J = 131 Hz), −8.2 (4B, m), −17.3 (2B, d, J = 154 Hz), −20.5 (2B, d, J = 155 Hz), −21.9 (1B, d, J = 132 Hz), −28.4 (1B, d, J = 168 Hz).

K[8-$HOCH_2CH_2O$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (4a)

A. Potassium *tert*-butylate (71 mg, 0.63 mmol) was added to a solution of **2** (100 mg, 0.21 mmol) in 1,2-dimethoxyethane (50 ml). The reaction mixture was stirred at ambient temperature for 12 h, filtered and evaporated *in vacuo* to give 81 mg (90%) of the light brown product. B. Potassium *tert*-butylate (71 mg, 0.63 mmol) was added to a solution of **5** (108 mg, 0.21 mmol) in 1,2-dimethoxyethane (50 ml). The reaction mixture was stirred at ambient temperature for 12 h, filtered and evaporated *in vacuo* to give 70 mg (78%) of the light brown product. ^{1}H NMR (acetone-d_6, ppm): 4.18 (2H, s, CH_{carb}), 4.20 (2H, s, CH_{carb}), 3.56 (4H, s, $-OCH_2CH_2O-$). ^{13}C NMR (acetone-d_6, ppm): 70.4 (OCH_2), 62.8 (OCH_2), 53.5 (C_{carb}), 46.4 (C_{carb}). ^{11}B NMR (acetone-d_6, ppm): 23.4 (1B, s), 4.4 (1B, d, J = 148 Hz), 0.1 (1B, d, J = 142 Hz), −2.5 (1B, d, J = 142 Hz), −4.6 (2B, d, J = 153 Hz), −7.4 (2B, d, J = 132 Hz), −8.1 (4B, m), −17.4 (2B, d, J = 156 Hz), −20.3 (2B, d, J = 154 Hz), −22.3 (1B, d, J = 130 Hz), −28.7 (1B, d, J = 166 Hz). Anal. Calcd for $C_6H_{26}B_{18}O_2CoK$: C, 17.04; H, 6.20; B, 46.01. Found: C, 16.92; H, 6.32; B, 45.98.

Na[8-$HOCH_2CH_2O$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (4b)

Sodium hydroxide (25 mg, 0.63 mmol) was added to a solution of **8** (143 mg, 0.21 mmol) in ethanol (50 ml). The reaction mixture was heated under reflux for 12 h, filtered and evaporated under reduced pressure. The residue was treated with dichloromethane (20 ml), filtered and evaporated to dryness. The crude product was dissolved in water (50 ml) and washed with dichloromethane (2 × 50 ml). The aqueous solution was evaporated *in vacuo* and the residue obtained was subjected to column chromatography on silica with a mixture of dichloromethane and acetone (2 : 3) as the eluent to give 80 mg (89%) of the brown product. ^{1}H NMR (acetone-d_6, ppm): 4.19 (4H, s, CH_{carb}), 3.56 (4H, s, $-OCH_2CH_2O-$). ^{11}B NMR (acetone-d_6, ppm): 23.6 (1B, s), 4.7 (1B, d, J = 149 Hz), 0.3 (1B, d, J = 142 Hz), −2.6 (1B, d, J = 142 Hz), −4.5 (2B, d, J = 154 Hz), −7.2 (2B, d, J = 135 Hz), −7.9 (4B, m), −17.3 (2B, d, J = 159 Hz), −20.3 (2B, d, J = 152 Hz), −22.2 (1B, d, J = 128 Hz), −28.7 (1B, d, J = 170 Hz).

[8-$O(CH_2CH_2)_2S(CH_2CH_2O)_2$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (5)

1,4-Thioxane (45 μl, 50 mg, 0.48 mmol) was added to a solution of **1** (100 mg, 0.24 mmol) in acetonitrile (50 ml) and the reaction mixture was heated under reflux for 6 h. After cooling to room temperature the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica using dichloromethane followed by a mixture of dichloromethane and acetone (3 : 2) as the eluent to give 140 mg (87%) of the brown product. ^1H NMR (acetone-d_6, ppm): 4.44–4.40 (2H, m, –CH_2–), 4.15–4.11 (6H, m, –CH_2– + CH_{carb}), 4.02 (4H, m, –CH_2– + CH_{carb}), 3.92–3.87 (2H, m, –CH_2–), 3.67–3.64 (6H, m, –CH_2–). ^{13}C NMR (acetone-d_6, ppm): 72.5 (OCH_2), 68.8 (OCH_2), 65.2 (OCH_2), 62.7 ($O(CH_2)_2$), 52.2 (C_{carb}), 46.5 (C_{carb}), 41.7 (SCH_2), 35.0 ($S(CH_2)_2$). ^{11}B NMR (acetone-d_6, ppm): 24.2 (1B, s), 5.9 (1B, d, *J* = 151 Hz), 0.2 (1B, d, *J* = 145 Hz), −2.8 (1B, d, *J* = 149 Hz), −4.8 (2B, d, *J* = 147 Hz), −7.63 (6B, m), −17.4 (2B, d, *J* = 151 Hz), −20.3 (2B, d, *J* = 159 Hz), −22.5 (1B, d, *J* = 144 Hz), −28.9 (1B, d, *J* = 158 Hz). Anal. Calcd for $C_{12}H_{37}B_{18}O_3SCo$: C, 27.99; H, 7.24; B, 37.78. Found: C, 27.92; H, 7.26; B, 37.84.

H[8-MeOOCCH(NHBoc)$CH_2CH_2S(CH_2CH_2O)_2$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (6)

A solution of *N*-Boc-methionine (61 mg, 0.24 mmol) and **1** (100 mg, 0.24 mmol) in acetonitrile (30 ml) was stirred for 30 h. The solvent was removed *in vacuo* and the crude product was purified by column chromatography on silica using dichloromethane followed by a mixture of dichloromethane and acetone (3 : 2) as the eluent to give 134 mg (83%) of the product. ^1H NMR (acetone-d_6, ppm): 6.30 (1H, s, N*H*), 4.40 (1H, m, C*H*), 4.30 (4H, s, CH_{carb}), 3.72 (3H, s, $COOCH_3$), 3.64 (2H, t, OCH_2), 3.58 (2H, t, OCH_2), 3.52 (2H, t, OCH_2), 2.98 (2H, m, OCH_2CH_2S), 2.74 (2H, m, SCH_2CH_2CH), 2.26–2.10 (2H, m, SCH_2CH_2CH), 1.43 (9H, s, $C(CH_3)_3$). ^{13}C NMR (acetone-d_6, ppm): 171.5 ($C{=}O_{BOC}$), 155.3 (*C*OOMe), 78.6 (O*C*Me$_3$), 71.6 (OCH_2), 70.9 (OCH_2), 67.0 (OCH_2), 54.6 (C_{carb}), 54.0 (*C*HCOOMe), 51.6 ($COOCH_3$), 46.4 (C_{carb}), 34.0 (SCH_2), 31.8 (SCH_2), 29.7(SCH_2CH_2), 27.7($C(CH_3)_3$). Anal. Calcd for $C_{18}H_{48}B_{18}NO_6SCo\cdot 5H_2O$: C, 28.82; H, 7.79; N, 1.87; B, 25.94. Found: C, 28.92; H, 7.76; N, 1.96; B, 25.78.

Cs[8-(7″,8″-$C_2B_9H_{11}$-9″-)S(Me)$CH_2CH_2OCH_2CH_2O$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (7)

A solution of **1** (50 mg, 0.122 mmol) and Cs[9-MeS-7,8-$C_2B_9H_{11}$] (60 mg, 0.192 mmol) in acetonitrile (50 ml) was heated under reflux for 10 h. The solvent was removed *in vacuo* and the crude product was purified by column chromatography on silica using a mixture of dichloromethane and acetone (3 : 2) as the eluent to give 62 mg (86%) of the product. ^1H NMR (acetone-d_6, ppm): 4.22 (2H, s, CH_{carb}), 4.20 (2H, s, CH_{carb}), 4.03 (2H, m, OCH_2CH_2S), 3.62 (4H, m, OCH_2), 3.51 (1.2H, m, OCH_2CH_2S), 3.38 (0.8H, m, OCH_2CH_2S), 2.92 (1.2H, s, SCH_3), 2.82 (1H, s, CH_{carb}), 2.75 (1.8H, s, SCH_3), 2.18 (1H, s, CH_{carb}), −3.23 (1H, br s, B*H*B). ^{13}C NMR (acetone-d_6, ppm): 72.2 (CH_2O), 68.5 (OCH_2), 66.5 (OCH_2CH_2S), 66.4 (OCH_2CH_2S) 53.9 (CH_{carb}), 51.6 (CH_{carb}), 46.5 (CH_{carb}), 45.9 (CH_2S), 42.9 (CH_2S), 37.8 (CH_{carb}), 25.6 (SCH_3) 23.2(SCH_3). ^{11}B NMR (acetone-d_6, ppm): 23.2 (1B, s), 4,6 (1B, d, *J* = 137 Hz), 0.4 (1B, d, *J* = 146 Hz), −2.6 (1B, d, *J* = 159 Hz), −4.5 (3B, m), −6.6 (1B, s), −7,3 (2B, d, *J* = 132 Hz), −8.2 (4B, d, *J* = 123 Hz), 12.5 (1B, d, *J* = 152 Hz), 16.7 (1B, d, Hz), −17.3 (2B, d), 18.3 (1B, d), −20.3 (2B, d, *J* = 156 Hz), 22.2 (1B, d), 23.3 (1B, d, *J* = 151 Hz), −26.4 (1B, d, *J* = 142 Hz), −28.6 (1B, d), −30.1 (1B, d, *J* = 139 Hz), −36.9 (1B, d, *J* = 139 Hz). ESI-MS *m*/*z* for $C_{11}H_{43}B_{27}O_2SCo$: calcd 590.5023, obsd 590.5016 $[M]^-$.

[8-$Ph_3P(CH_2CH_2O)_2$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (8)

Triphenylphosphine (0.19 g, 0.72 mmol) was added to a solution of **1** (0.10 g, 0.24 mmol) in acetonitrile (50 ml) and the reaction mixture was stirred at ambient temperature for 12 h. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica using dichloromethane as the eluent to give 0.14 g (87%) of the brown product. ^1H NMR (acetone-d_6, ppm): 7.93 (9H, m, Ar–*H*), 7.80 (6H, m, Ar–*H*), 4.20 (2H, s, CH_{carb}), 4.09 (2H, s, CH_{carb}), 4.01–3.84 (4H, m, CH_2), 3.42 (2H, t, CH_2), 3.28 (2H, t, CH_2). ^{11}B NMR (acetone-d_6, ppm): 23.7 (1B, s), 5.2 (1B, d, *J* = 137 Hz), 0.2 (1B, d, *J* = 137 Hz), −2.6 (1B, d, *J* = 148 Hz), −4.6 (2B, d, *J* = 154 Hz), −7.1 (2B, d, *J* = 138 Hz), −7.8 (2B, d, *J* = 136 Hz), 8.6 (2B, d, *J* = 130 Hz), −17.3 (2B, d, *J* = 156 Hz), −20.3 (2B, d, *J* = 155 Hz), −22.3 (1B, d, *J* = 158 Hz), −28.5 (1B, d, *J* = 148 Hz). Anal. Calcd for $C_{26}H_{44}B_{18}O_2PCo$: C, 46.39; H, 6.59; B, 28.91. Found: C, 46.43; H, 6.64; B, 28.88.

K[8-$MeSO_3CH_2CH_2O$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (9)

To a solution of **4a** (81 mg, 0.19 mmol) and triethylamine (78 μl, 57 mg, 0.57 mmol) in diethyl ether (30 ml), a solution of methanesulfonyl chloride (44 μl, 65 mg, 0.57 mmol) in diethyl ether was added at 0 °C, allowed to warm to room temperature and stirred for 5 h. The supernatant was decanted and the solid residue was dried *in vacuo* to give 72 mg (81%) of the product. ^1H NMR (acetone-d_6, ppm): 4.24 (2H, t, –OCH_2CH_2O–), 4.17 (2H, s, CH_{carb}), 4.14 (2H, s, CH_{carb}), 3.71 (2H, t, –OCH_2CH_2O–), 3.07 (3H, s, –SO_2CH_3). ^{13}C NMR (acetone-d_6, ppm): 71.5 (OCH_2), 66.8 (OCH_2), 53.6 (C_{carb}), 46.5 (C_{carb}), 36.7 (OSO_2CH_3). ^{11}B NMR (acetone-d_6, ppm): 23.3 (1B, s), 5.2 (1B, d, *J* = 148 Hz), 0.6 (1B, d, *J* = 143 Hz), −2.5 (1B, d, *J* = 143 Hz), −4.4 (2B, d, *J* = 152 Hz), −7.1 (2B, d, *J* = 136 Hz), −8.1 (4B, m), −17.2 (2B, d, *J* = 158 Hz), −20.2 (2B, d, *J* = 153 Hz), −22.1 (1B, d, *J* = 130 Hz), −28.5 (1B, d, *J* = 168 Hz). Anal. Calcd for $C_7H_{28}B_{18}O_4SCoK$: C, 16.78; H, 5.63; B, 38.84. Found: C, 16.84; H, 5.72; B, 38.70.

K[8-$N_3CH_2CH_2O$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (10)

Sodium azide (72 mg, 1.08 mmol) was added to a solution of **9** (50 mg, 0.11 mmol) in DMF (25 ml) and the reaction mixture was heated at 120 °C for 10 h. After cooling to room temperature the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica using the mixture of dichloromethane and acetone (3 : 1) as the eluent to give 40 mg (85%) of the brown product. ^{1}H NMR (acetone-d_6, ppm): 4.27 (4H, s, CH_{carb}), 3.64 (2H, t, $\mathrm{–OC}H_2\mathrm{CH_2N_3}$), 3.29 (2H, t, $\mathrm{–OCH_2C}H_2\mathrm{N_3}$). ^{13}C NMR (acetone-$d_6$, ppm): 68.8 ($\mathrm{O}C\mathrm{H_2}$), 55.3 ($C_{\mathrm{carb}}$), 53.5 ($C\mathrm{H_2N_3}$), 47.3 ($C_{\mathrm{carb}}$). ^{11}B NMR (acetone-$d_6$, ppm): 22.8 (1B, s), 4.2 (1B, d, J = 146 Hz), 0.5 (1B, d, J = 144 Hz), −2.6 (1B, d, J = 143 Hz), −4.3 (2B, d, J = 152 Hz), −7.4 (2B, d, J = 135 Hz), −8.4 (4B, m), −17.3 (2B, d, J = 156 Hz), −20.4 (2B, d, J = 154 Hz), −22.0 (1B, d, J = 130 Hz), −28.5 (1B, d, J = 166 Hz). IR (Nujol, ν/cm^{-1}): 2121 (N$_3$); 2567 (BH). Anal. Calcd for $\mathrm{C_6H_{25}B_{18}ON_3CoK}$: C, 16.09; H, 5.63; N, 9.36; B, 43.84. Found: C, 15.97; H, 5.78; N, 9.43; B, 43.69.

$\mathrm{K[8\text{-}C_6H_4(CO)_2NCH_2CH_2O\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]}$ (11)

Potassium phthalimide (104 mg, 0.54 mmol) was added to a solution of **9** (50 mg, 0.11 mmol) in DMF (25 ml). The reaction mixture was heated at 120 °C for 10 h, allowed to cool to room temperature and evaporated under reduced pressure. The crude product was purified by column chromatography on silica using a mixture of dichloromethane and acetone (3 : 2) as the eluent to give 41 mg (69%) of the brown product. ^{1}H NMR (acetone-d_6, ppm): 7.86 (2H, m, $\mathrm{C_6}H_4\mathrm{(CO)_2N}$–), 7.80 (2H, m, $\mathrm{C_6}H_4\mathrm{(CO)_2N}$–), 4.10 (2H, s, C$H_{\mathrm{carb}}$), 4.04 (2H, s, C$H_{carb}$), 3.78 (2H, t, $\mathrm{–OC}H_2\mathrm{CH_2}$–), 3.72 (2H, t, $\mathrm{–OCH_2C}H_2$–). ^{11}B NMR (acetone-d_6, ppm): 22.7 (1B, s), 4.4 (1B, d, J = 144 Hz), 0.6 (1B, d, J = 144 Hz), −2.5 (1B, d, J = 143 Hz), −4.5 (2B, d, J = 151 Hz), −7.4 (2B, d, J = 133 Hz), −8.4 (4B, m), −17.2 (2B, d, J = 155 Hz), −20.4 (2B, d, J = 153 Hz), −22.2 (1B, d, J = 132 Hz), −28.6 (1B, d, J = 164 Hz). Anal. Calcd for $\mathrm{C_{14}H_{29}B_{18}O_3NCoK}$: C, 30.46; H, 5.30; N, 2.54; B, 35.25. Found: C, 30.36; H, 5.44; N, 2.59; B, 35.27.

$\mathrm{[8\text{-}H_3NCH_2CH_2O\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]}$ (12)

Hydrazine monohydrate (86 μl, 83 mg, 1.66 mmol) was added to a solution of **11** (50 mg, 0.09 mmol) in ethanol (20 ml) and the reaction mixture was heated under reflux for 12 h. After cooling the solvent was removed under reduced pressure. The residue was dissolved in diethyl ether (50 ml), washed with water (2 × 50 ml) and acidified with 2 drops of hydrochloric acid. The solution was filtered and evaporated. The crude product was purified by column chromatography on silica using a mixture of dichloromethane and acetone (3 : 1) as the eluent to give 21 mg (61%) of the brown product. ^{1}H NMR (acetone-d_6, ppm): 4.02 (4H, t + s, $\mathrm{–C}H_2$– + CH_{carb}), 3.93 (2H, s, CH_{carb}), 3.84 (2H, t, $\mathrm{–C}H_2$–). ^{11}B NMR (acetone-d_6, ppm): 22.7 (1B, s), 4.4 (1B, d, J = 142 Hz), 0.6 (1B, d, J = 136 Hz), −2.5 (1B, d, J = 142 Hz), −4.4 (2B, d, J = 152 Hz), −7.4 (2B, d), −8.3 (4B, m), −17.2 (2B, d, J = 154 Hz), −20.3 (2B, d, J = 147 Hz), −22.2 (1B, d, J = 159 Hz), −28.6 (1B, d, J = 142 Hz). ESI-MS, m/z for $\mathrm{C_6H_{28}B_{18}ONCo}$: calcd 383.3219 [M]$^-$, found 383.3161 [M]$^-$.

$\mathrm{[8\text{-}(H_2N)_2CSCH_2CH_2O\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]}$ (13)

Thiourea (26 mg, 0.33 mmol) was added to a solution of **9** (50 mg, 0.11 mmol) in acetonitrile and the reaction mixture was heated under reflux for 24 h. After cooling the reaction mixture was filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica using a mixture of dichloromethane and acetone (3 : 2) as the eluent to give 39 mg (81%) of the brown product. ^{1}H NMR (acetone-d_6, ppm): 9.38 (2H, s, $\mathrm{–N}H_2$), 8.43 (2H, s, $\mathrm{–N}H_2$), 4.05 (2H, t, $\mathrm{–OCH_2C}H_2\mathrm{S}$–), 3.99 (2H, s, C$H_{\mathrm{carb}}$), 3.93 (2H, s, C$H_{\mathrm{carb}}$), 3.43 (2H, t, $\mathrm{–OC}H_2\mathrm{CH_2S}$–). ^{13}C NMR (acetone-$d_6$, ppm): 173.5 ($\mathrm{(NH_2)_2}C\mathrm{S}$), 70.1 ($\mathrm{O}C\mathrm{H_2}$), 51.1 ($C_{\mathrm{carb}}$), 46.9 ($C_{\mathrm{carb}}$), 34.9($\mathrm{S}C\mathrm{H_2}$). ^{11}B NMR (acetone-$d_6$, ppm): 24.5 (1B, s), 7.6 (1B, d, J = 135 Hz), 0.8 (1B, d, J = 140 Hz), −2.7 (1B, d, J = 137 Hz), −6.1 (6B, m), −9.1 (2B, d, J = 137 Hz), −17.1 (2B, d, J = 156 Hz), −19.9 (2B, d, J = 149 Hz), −22.4 (1B, d, J = 142 Hz), −28.5 (1B, d, J = 149 Hz). EI-MS m/z for $\mathrm{C_7H_{28}B_{18}OSN_2Co}$: calcd 442 [M]$^-$, found 442 [M]$^-$. Anal. Calcd for $\mathrm{C_7H_{29}B_{18}OSN_2Co}$: C, 18.98; H, 6.60; N, 6.33; B, 43.93. Found: C, 19.02; H, 6.68; N, 6.45; B, 43.89.

$\mathrm{Na[8\text{-}HSCH_2CH_2O\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]}$ (14)

A solution of **13** (40 mg, 0.09 mmol) and sodium hydroxide (36 mg, 0.90 mmol) in water (25 ml) was heated under reflux for 12 h. After cooling to room temperature the solvent was removed under reduced pressure. The crude product was dissolved in dichloromethane, filtered and evaporated *in vacuo*. The residue was dissolved in water (15 ml), the solution was adjusted to pH 7 with diluted hydrochloric acid, filtered and evaporated *in vacuo*. The crude product was purified by column chromatography on silica using a mixture of dichloromethane and acetone (3 : 2) as the eluent to give 29 mg (79%) of the brown product. ^{1}H NMR (acetone-d_6, ppm): 4.31 (2H, s, CH_{carb}), 4.28 (2H, s, CH_{carb}), 3.71 (2H, t, $\mathrm{–OC}H_2\mathrm{CH_2}$–), 2.85 (2H, t, $\mathrm{–OCH_2C}H_2\mathrm{S}$–). ^{11}B NMR (acetone-$d_6$, ppm): 22.5 (1B, s), 3.6 (1B, d, J = 140 Hz), 0.5 (1B, d, J = 142 Hz), −2.5 (1B, d, J = 146 Hz), −4.2 (2B, d, J = 152 Hz), −7.5 (4B, d), −8.4 (2B, d), −17.2 (2B, d, J = 152 Hz), −20.4 (2B, d, J = 161 Hz), −21.8 (1B, d, J = 158 Hz), −28.7 (1B, d, J = 140 Hz). ESI-MS m/z for $\mathrm{C_9H_{32}B_{18}O_2SCo}$: calcd 400.2826, obsd 399.3118 [2M − 2H]$^{2-}$.

$\mathrm{K[8\text{-}(1''\text{-}Ph\text{-}1'',2'',3''\text{-}triazol\text{-}4''\text{-}yl)\text{-}CH_2CH_2O\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})\text{-}(1',2'\text{-}C_2B_9H_{11})]}$ (15)

To a solution of **10** (50 mg, 0.12 mmol) in acetonitrile (25 ml) phenylacetylene (51 μl, 47 mg, 0.48 mmol), copper(I) iodide (2 mg, 0.01 mmol) and 3 drops of triethylamine were added. The reaction mixture was heated under reflux for 6 h. After cooling the reaction mixture was filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica using a mixture of dichloromethane and acetone (3 : 2) as the eluent to give 51 mg (83%) of the brown product. ^{1}H NMR (acetone-d_6, ppm): 8.41 (1H, s, –CH_{triazole}), 7.91 (2H, d, –*Ph*), 7.42 (2H, t, –*Ph*), 7.30 (1H, t, –*Ph*), 4.54 (2H, t, $\mathrm{–OCH_2C}H_2\mathrm{N}$–), 4.14 (2H, s, C$H_{\mathrm{carb}}$), 4.08 (2H, s, C$H_{\mathrm{carb}}$), 3.91 (2H, t, $\mathrm{–OC}H_2\mathrm{CH_2N}$–). ^{13}C NMR (acetone-$d_6$, ppm): 146.7($C_{\mathrm{triazole}}$), 131.8($C_{ipso}$–Ph), 128.6($C_{ortho}$–Ph), 127.4($C_{para}$–Ph), 125.5($C_{meta}$–Ph), 121.6($C\mathrm{H_{triazole}}$), 67.5 ($\mathrm{O}C\mathrm{H_2}$), 53.0($C_{\mathrm{carb}}$), 52.1($C\mathrm{H_2}$), 46.5($C_{\mathrm{carb}}$). ^{11}B NMR (acetone-$d_6$, ppm): 23.8 (1B, s), 5.8 (1B, d, J = 135 Hz), 0.4 (1B, d, J = 128 Hz), −3.0 (1B, d, J = 151 Hz), −4.6 (2B, d, J = 160 Hz), −6.9 (2B, d, J = 152 Hz), −8.3 (4B, d, J = 122 Hz), −17.3 (2B, d, J = 156 Hz), −20.1 (2B, d, J = 151 Hz), −22.3 (1B, d, J = 156 Hz),

−28.9 (1B, d, *J* = 154 Hz). Anal. Calcd for $C_{14}H_{35}B_{18}ON_3CoK$: C, 30.35; H, 6.37; N, 7.58; B, 35.12. Found: C, 30.19; H, 6.44; N, 7.64; B, 35.19.

[10-$Me_2SCH_2CH_2OCH_2CH_2O$-7,8-$C_2B_9H_{11}$] (17)

Dimethylsulfide (1.0 ml, 0.86 g, 13.8 mmol) was added to a solution of **16** (0.50 g, 2.3 mmol) in acetonitrile (30 ml) and the reaction mixture was heated under reflux for 10 h. After cooling the solvent was removed under reduced pressure to obtain 0.58 g (91%) of the white product. ^{1}H NMR (acetone-d_6, ppm): 3.85 (2H, m), 3.53 (2H, m), 3.51 (4H, m), 2.90 (6H, s), 1.51 (2H, s, CH_{carb}), 2.8 ÷ −0.1 (8H, m, B*H*), −0.7 (1H, s, B*H*B). ^{13}C NMR (acetone-d_6, ppm): 71.8 (OCH_2), 69.3 (OCH_2), 64.7 (OCH_2), 43.3(SCH_2), 38.5 (C_{carb}), 25.3 (S(CH_3)$_2$). ^{11}B NMR (acetone-d_6, ppm): −9.3 (1B, s), −12.4 (2B, d, *J* = 141 Hz), −17.5 (2B, d, *J* = 132 Hz), −24.0 (2B, d, *J* = 150 Hz), −25.3 (1B, d, *J* = 163 Hz), −40.4 (1B, d, *J* = 137 Hz). ESI-MS, *m*/*z* for $C_8H_{25}B_9O_2S$: calcd 284.2529 [M]$^-$, obsd 284.2529 [M]$^-$.

[10-$Ph_3PCH_2CH_2OCH_2CH_2O$-7,8-$C_2B_9H_{11}$] (18)

Triphenylphosphine (0.72 g, 3.3 mmol) was added to a solution of **16** (0.85 g, 3.3 mmol) in acetonitrile (25 ml) and the reaction mixture was heated under reflux for 10 h. After cooling the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica using chloroform as the eluent to give 1.23 g (78%) of the product. ^{1}H NMR (dmso-d_6, ppm): 7.77 (15H, m, C_6H_5), 3.90 (2H, m, CH_2P), 3.68 (2H, m, OCH_2), 3.18 (4H, m, OCH_2), 1.49 (2H, s, CH_{carb}), 3.0 ÷ −0.4 (8H, m, B*H*), −0.7 (1H, s, B*H*B). ^{13}C NMR (dmso-d_6, ppm): 135.1 (d, *J* = 2.9 Hz, PC_{para}), 134.3 (d, *J* = 10.3 Hz, PC_{meta}), 130.4 (d, *J* = 12.5 Hz, PC_{ortho}), 119.5 (d, *J* = 86.6 Hz, PC_{ipso}), 72.1 (OCH_2), 68.8 (OCH_2), 63.7 (d, *J* = 5.9 Hz, OCH_2CH_2P), 38.4 (C_{carb}), 23.6 (d, *J* = 52.1 Hz, PCH_2). ^{11}B NMR (dmso-d_6, ppm): −9.3 (1B, s), −12.4 (2B, d, *J* = 138 Hz), −17.6 (2B, d, *J* = 130 Hz), −24.0 (3B, d, *J* = 149 Hz), −40.4 (1B, d, *J* = 142 Hz). MALDI-MS, *m*/*z* for $C_{24}H_{34}B_9O_2P$ 482.80 [M], obsd 481.30 [M − H]$^-$.

K[10-$HOCH_2CH_2O$-7,8-$C_2B_9H_{11}$] (19)

A. Potassium *tert*-butylate (0.44 g, 3.9 mmol) was added to a solution of **17** (0.55 g, 1.9 mmol) in 1,2-dimethoxyethane (30 ml) and heated under reflux for 5 h. After cooling the solvent was removed under reduced pressure, the residue was treated with diethyl ether (50 ml) and water (30 ml). The aqueous layer was separated and evaporated to dryness *in vacuo*. The residue was dissolved in acetone (30 ml), filtered and evaporated under reduced pressure. The crude product was purified by column chromatography on silica with ethyl acetate as the eluent to give 0.29 g (66%) of the oily product. B. Potassium *tert*-butylate (0.21 g, 1.9 mmol) was added to a solution of **18** (0.62 g, 1.2 mmol) in ethanol (30 ml) and heated under reflux for 4 h. After cooling the solvent was removed under reduced pressure, the residue was treated with diethyl ether (50 ml) and water (30 ml). The aqueous layer was separated and evaporated to dryness *in vacuo*. The residue was dissolved in acetone (10 ml), filtered and evaporated under reduced pressure. The crude product was purified by column chromatography on silica with dichloromethane followed by acetone as the eluent to give 0.15 g (57%) of the oily product. ^{1}H NMR (acetone-d_6, ppm): 3.57 (4H, m, OCH_2CH_2O), 1.51 (2H, s, CH_{carb}), 2.5 ÷ −0.1 (8H, m, B*H*), −0.6 (1H, s, B*H*B). ^{13}C NMR (acetone-d_6, ppm): 70.9 (OCH_2), 62.4 (OCH_2), 38.5 (C_{carb}). ^{11}B NMR (acetone-d_6, ppm): −9.3 (1B, s), −12.3 (2B, d, *J* = 137 Hz), −17.2 (2B, d, *J* = 127 Hz), −23.9 (2B, d, *J* = 151 Hz), −25.3 (1B, d, *J* = 168 Hz), −40.5 (1B, d, *J* = 144 Hz). IR (neat, cm^{-1}): 3559 (ν_{OH}), 2531 (ν_{BH}). ESI-MS, *m*/*z* for $C_4H_{16}B_9O_2$: calcd 194.2033 [M − K]$^-$, obsd 194.2027 [M − K]$^-$.

Acknowledgements

The authors are grateful to the Russian Foundation for Basic Research (12-03-00772 and 13-03-00581) and the Russian Academy of Sciences (Program "Development of methods of synthesis of chemical compounds and design of new materials") for financial support.

References

1 (*a*) M. F. Hawthorne and T. D. Andrews, *Chem. Commun.*, 1964, 443–444; (*b*) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Hove, R. L. Pilling, A. D. Pitts, M. Reinjes, L. F. Warren and P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 879–896.

2 I. B. Sivaev and V. I. Bregadze, *Collect. Czech. Chem. Commun.*, 1999, **64**, 783.

3 I. B. Sivaev, Z. A. Starikova, S. Sjöberg and V. I. Bregadze, *J. Organomet. Chem.*, 2002, **649**, 1–8.

4 J. Plešek, B. Grüner, S. Heřmanek, J. Bača, V. Mareček, J. Jänchenova, A. Lhotsky, K. Holub, P. Selucky, J. Rais, I. Cisařova and J. Časlavsky, *Polyhedron*, 2002, **21**, 975–986.

5 (*a*) A. A. Semioshkin, I. B. Sivaev and V. I. Bregadze, *Dalton Trans.*, 2008, 977–992; (*b*) I. B. Sivaev and V. I. Bregadze, *Boron Science: New Technologies and Applications*, ed. N. S. Hosmane, CRC Press, Boca Raton, 2012, p. 623.

6 B. Grüner, J. Plešek, J. Bača, J. F. Dozol, V. Lamare, I. Cisařova, M. Belohradsky and J. Časlavsky, *New J. Chem.*, 2002, **26**, 867–875.

7 F. Teixidor, J. Pedrajas, I. Rojo, C. Viñas, R. Kivekäs, R. Sillanpää, I. Sivaev, V. Bregadze and S. Sjöberg, *Organometallics*, 2003, **22**, 3414–3423.

8 (*a*) B. Grüner, L. Mikulašek, J. Bača, I. Cisařova, V. Böhmer, C. Danila, M. M. Reinoso-Garcia, W. Verboom, D. N. Reinhoudt, A. Casnati and R. Ungaro, *Eur. J. Org. Chem.*, 2005, 2022–2039; (*b*) L. Mikulašek, B. Grüner, C. Danila, V. Bőhmer, J. Časlavsky and P. Selucky, *Chem. Commun.*, 2006, 4001–4003; (*c*) L. Mikulašek, B. Grüner, C. Dordea, V. Rudzevich, V. Böhmer, J. Haddaoui, V. Hubscher-Bruder, F. Arnaud-Neu, J. Čáslavský and P. Selucký, *Eur. J. Org. Chem.*, 2007, 4772–4783;

(*d*) B. Grüner, V. Böehmer, C. Dordea, P. Selucký and M. Bubeníková, *J. Organomet. Chem.*, 2013, **747**, 155–166.

9 (*a*) J. Llop, C. Masalles, C. Viñas, F. Teixidor, R. Sillanpää and R. Kivekäs, *Dalton Trans.*, 2003, 556–561; (*b*) E. Crespo, S. Gentil, C. Viñas and F. Teixidor, *J. Phys. Chem. C*, 2007, **111**, 18381–18386.

10 (*a*) P. Farràs, F. Teixidor, R. Kivekäs, R. Sillanpää, C. Viñas, G. Bohumir and I. Cisařova, *Inorg. Chem.*, 2008, **47**, 9497–9508; (*b*) R. Núñez, E. J. Juárez-Pérez, F. Teixidor, R. Santillan, N. Farfán, A. Abreu, R. Yépez and C. Viñas, *Inorg. Chem.*, 2010, **49**, 9993–10000.

11 B. P. Dash, R. Satapathy, J. A. Maguire and N. S. Hosmane, *Organometallics*, 2010, **29**, 5230–5235.

12 A. Ursu and F. P. Schmidtchen, *Angew. Chem., Int. Ed.*, 2012, **51**, 242–246.

13 I. A. Lobanova, M. Y. Berzina, I. B. Sivaev, P. V. Petrovskii and V. I. Bregadze, *Russ. Chem. Bull.*, 2010, **59**, 2302–2308.

14 (*a*) A. B. Olejniczak, J. Plešek, O. Křiž and Z. J. Lesnikowski, *Angew. Chem., Int. Ed.*, 2003, **42**, 5740–5743; (*b*) A. B. Olejniczak, J. Plešek and Z. J. Leśnikowski, *Chem. – Eur. J.*, 2007, **13**, 311–318.

15 B. A. Wojtczak, A. Andrysiak, B. Grüner and Z. J. Lesnikowski, *Chem. – Eur. J.*, 2008, **14**, 10675–10682.

16 (*a*) A. Semioshkin, V. Bregadze, I. Godovikov, A. Ilinova, Z. J. Lesnikowski and I. Lobanova, *J. Organomet. Chem.*, 2011, **696**, 3750–3755; (*b*) A. Semioshkin, A. Ilinova, I. Lobanova, V. Bregadze, E. Paradowska, M. Studzinska, A. Jabłonska and Z. J. Lesnikowski, *Tetrahedron*, 2013, **69**, 8034–8041; (*c*) A. Ilinova, A. Semioshkin, I. Lobanova, V. I. Bregadze, A. F. Mironov, E. Paradowska, M. Studzinska, A. Jabłonska, M. Białek-Pietras and Z. J. Lesnikowski, *Tetrahedron*, 2014, **70**, 5704–5710.

17 (*a*) E. Hao and M. G. H. Vicente, *Chem. Commun.*, 2005, 1306–1308; (*b*) E. Hao, T. J. Jensen, B. H. Courtney and M. G. H. Vicente, *Bioconjugate Chem.*, 2005, **16**, 1495–1502; (*c*) M. Sibrian-Vazquez, E. Hao, T. J. Jensen and M. G. H. Vicente, *Bioconjugate Chem.*, 2006, **17**, 928–934; (*d*) E. Hao, M. Sibrian-Vazquez, W. Serem, J. C. Garno, F. R. Fronczek and M. G. H. Vicente, *Chem. – Eur. J.*, 2007, **13**, 9035–9047; (*e*) E. Hao, M. Zhang, E. Wenbo, K. M. Kadish, F. R. Fronczek, B. H. Courtney and M. G. H. Vicente, *Bioconjugate Chem.*, 2008, **19**, 2171–2181.

18 P. Kubat, K. Lang, P. Cigler, M. Kožíšek, P. Matějíček, P. Janda, Z. Zelinger, K. Procházka and V. Král, *J. Phys. Chem. B*, 2007, **111**, 4539–4546.

19 (*a*) M. A. Grin, R. A. Titeev, O. M. Bakieva, D. I. Britall, I. A. Lobanova, I. B. Sivaev, V. I. Bregadze and A. F. Mironov, *Russ. Chem. Bull.*, 2008, **57**, 2230–2232; (*b*) V. I. Bregadze, A. A. Semioshkin, J. N. Las'kova, M. Y. Berzina, I. A. Lobanova, I. B. Sivaev, M. A. Grin, R. A. Titeev, D. I. Brittal, O. B. Ulybina, A. V. Chestnova, A. A. Ignatova, A. V. Feofanov and A. F. Mironov, *Appl. Organomet. Chem.*, 2009, **23**, 370–374; (*c*) M. A. Grin, R. A. Titeev, D. I. Brittal, O. V. Ulybina, A. G. Tsiprovskiy, M. Y. Berzina, I. A. Lobanova, I. B. Sivaev, V. I. Bregadze and A. F. Mironov, *Mendeleev Commun.*, 2011, **21**, 84–86; (*d*) A. V. Efremenko, A. A. Ignatova, M. A. Grin, I. B. Sivaev, A. F. Mironov, V. I. Bregadze and A. V. Feofanov, *Photochem. Photobiol. Sci.*, 2014, **13**, 92–102.

20 (*a*) H. Li, F. R. Fronczek and M. G. H. Vicente, *Tetrahedron Lett.*, 2008, **49**, 4828–4830; (*b*) H. Li, F. R. Fronczek and M. G. H. Vicente, *J. Organomet. Chem.*, 2009, **694**, 1607–1611.

21 A. V. Shmal'ko, A. V. Efremenko, A. A. Ignatova, I. B. Sivaev, A. V. Feofanov, E. Hamuryudan, A. Gül, L. V. Kovalenko, S. Qi and V. I. Bregadze, *J. Porphyrins Phthalocyanines*, 2014, **18**, 960–966.

22 (*a*) P. Cígler, M. Kožíšek, P. Řezáčová, J. Brynda, Z. Otwinowski, J. Pokorna, J. Plešek, B. Grüner, L. Dolečkova-Marešova, M. Masa, J. Sedlaček, J. Bodem, H.-G. Kräusslich, V. Král and J. Konvalinka, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 15394–15399; (*b*) P. Řezáčová, J. Pokorná, J. Brynda, M. Kožíšek, P. Cígler, M. Lepšík, J. Fanfrlík, J. Řezáč, K. G. Šašková, I. Sieglová, J. Plešek, V. Šícha, B. Grüner, H. Oberwinkler, J. Sedláček, H.-G. Kräusslich, P. Hobza, V. Král and J. Konvalinka, *J. Med. Chem.*, 2009, **52**, 7132–7141; (*c*) P. Řezáčová, P. Cígler, P. Matějček, M. Lepšík, J. Pokorná, B. Grüner and J. Konvalinka, *Boron Science: New Technologies and Applications*, ed. N. S. Hosmane, CRC Press, Boca Raton, 2012, p. 41.

23 J. Rak, R. Kaplanek and V. Kral, *Bioorg. Med. Chem. Lett.*, 2010, **20**, 1045–1048.

24 M. Tarres, C. Viñas, P. Gonzalez-Cardoso, M. M. Hänninen, R. Sillanpää, V. Ďorďovič, M. Uchman, F. Teixidor and P. Matejiček, *Chem. – Eur. J.*, 2014, **20**, 6786–6794.

25 B. Grüner, P. Švec, V. Šícha and Z. Padělková, *Dalton Trans.*, 2012, **41**, 7498–7512.

26 J. Nekvinda, V. Šícha, D. Hnyk and B. Grüner, *Dalton Trans.*, 2014, **43**, 5106–5120.

27 B. Grüner, V. Šícha, D. Hnyk, M. G. S. Londesborough and I. Císařova, *Inorg. Chem.*, 2015, **54**, 3148–3158.

28 J. Plešek, S. Heřmanek, A. Franken, I. Cisařova and C. Nachtigal, *Collect. Czech. Chem. Commun.*, 1997, **62**, 47–56.

29 P. Farras, F. Teixidor, R. Sillanpää and C. Viñas, *Dalton Trans.*, 2010, **39**, 1716–1718.

30 The Chemistry of the Sulphonium Group, in *The Chemistry of Functional Groups*, ed. C. J. M. Stirling, S. Patai Series, John Wiley & Sons, New York, 1981.

31 *Onium Ions*, ed. G. A. Olah, K. K. Laali, Q. Wang and G. K. Surya Prakash, John Wiley & Sons, New York, 1998.

32 C. J. M. Stirling, *Acc. Chem. Res.*, 1979, **12**, 198–203.

33 T. Bottiglieri, *Expert Opin. Invest. Drugs*, 1997, **6**, 417–426 and references therein.

34 A. D. Patel and N. K. Prajapati, *J. Chem. Pharm. Res.*, 2012, **4**, 209–215.

35 E. Ludmerszki, K. Paldi, I. Racz, Z. Szigeti and S. Rudnoy, *Appl. Ecol. Environ. Res.*, 2014, **12**, 777–785.

36 M. V. Zakharova, I. B. Sivaev, S. A. Anufriev, S. V. Timofeev, K. Y. Suponitsky, I. A. Godovikov and V. I. Bregadze, *Dalton Trans.*, 2014, **43**, 5044–5053.

37 I. B. Sivaev, A. V. Prikaznov and S. A. Anufriev, *J. Organomet. Chem.*, 2013, **747**, 254–256.

38 S. V. Timofeev, M. V. Zakharova, E. M. Mosolova, I. A. Godovikov, I. V. Ananyev, I. B. Sivaev and V. I. Bregadze, *J. Organomet. Chem.*, 2012, **721–722**, 92–96.

39 J. Plešek, B. Grüner, J. Machaček, I. Cisařova and J. Časlavsky, *J. Organomet. Chem.*, 2007, **692**, 4801–4804.

40 J. Plešek, B. Grüner, J. Báča, J. Fusek and I. Císařová, *J. Organomet. Chem.*, 2002, **649**, 181–190.

41 V. Subrtová, V. Petrícek and L. Hummel, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1989, **45**, 1964–1966.

42 K. Y. Zhizhin, V. N. Mustyatsa, E. A. Malinina, N. A. Votinova, E. Y. Matveev, L. V. Goeva, I. N. Polyakova and N. T. Kuznetsov, *Russ. J. Inorg. Chem.*, 2004, **49**, 180–189.

43 I. B. Sivaev, N. Y. Kulikova, E. A. Nizhnik, M. V. Vichuzhanin, Z. A. Starikova, A. A. Semioshkin and V. I. Bregadze, *J. Organomet. Chem.*, 2008, **693**, 519–525.

44 M. Y. Stogniy, E.N. Abramova, I. A. Lobanova, I. B. Sivaev, V. I. Bragin, P. V. Petrovskii, V. N. Tsupreva, O. V. Sorokina and V. I. Bregadze, *Collect. Czech. Chem. Commun.*, 2007, **72**, 1676–1688.