Metallacarborane Synthons for Molecular Construction - Functionalization of Cobalt bis(1,2-dicarbollide) with Extendable Ligands

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Posted Date: 17 April 2023

doi: 10.20944/preprints202304.0374.v1

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Article

Metallacarborane Synthons for Molecular Construction—Functionalization of Cobalt bis(1,2-dicarbollide) with Extendable Ligands

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Abstract: The exploitation of the metallacarboranes' potential in various fields of research and practical applications requires the availability of convenient and versatile methods for their functionalization with various functional moieties and/or linkers of different types and lengths. Herein we report a study on cobalt bis(1,2-dicarbollide) functionalization at 8,8'-boron atoms with different hetero-bifunctional moieties containing protected hydroxyl function allowing further modification after deprotection. Moreover, an approach to the synthesis of three and four functionalized metallacarboranes, at boron and carbon atoms simultaneously, *via* additional functionalization at carbon to obtain derivatives carrying three or four rationally oriented and distinct reactive surfaces, is described.

Keywords: metallacarboranes; cobalt bis(1,2-dicarbollide); oligofunctionalization; alkylation; stereochemistry

1. Introduction

Boron clusters, a class of polyhedral caged compounds is playing an increasing role in the development of a broad range of technologies including material science [1,2] and medicinal chemistry [3–5]. They find also applications as labels of nucleic acid fragments [6–8]. Conjugates of DNA-oligonucleotides and functionalized boron clusters have been proposed recently as building blocks for the construction of new nanomaterials for biomedical applications [9,10].

The ability of boron clusters type of dicarbaborate anion (*nido*-7,8-$C_2B_9H_{11}$) to coordinate a wide spectrum of metal ions, such as Fe, Co, Cr, Ta, Mo, W, V, Nb, and form metal complexes, metallacarboranes, additionally extends the range of their prospective applications [11–14]. Among them, the widely used metallocarborane is cobalt bis(1,2-dicarbolide), a sandwich of two $[C_2B_9H_{11}]^{2-}$ (dicarbollide) units with a cobalt ion in the center of the complex structure.

The broad technological potential of metallacarboranes requires access to a diverse array of functionalities (reactive functional groups, alkyl chains, spacers or polymers of various lengths, pharmacologically active species, etc). Furthermore, it could be necessary that more than one of this kind of functionalities will coexist in the same metallacarborane structure to have hetero-functionalized, tailor-made metallacarborane derivatives. The possibility to arrange these functionalities in a specific spatial orientation with respect to the topology of the 3D cluster core makes it possible to achieve the desired covalent modification, following atomic-level precision and allowing control of size and surface composition. Last but not least, highly relevant for molecular design is the opportunity to space the metallacarborane cage from the introduced functional group and the possibility of their further modifications and/or extensions.

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The successful use of functionalized 1,2-dicarbadodecaborane as a core unit in the synthesis of building blocks containing a boron cluster and DNA for the construction of functional nanoparticles carrying therapeutic nucleic acids [9,10] prompted us to extend this technology towards metallacarboranes. Due to the different shape of metallacarboranes, it may be possible to obtain nanoparticles with a different topology than in the case of 1,2-dicarbadodecaborane, which in turn can affect their biological properties. The ability of boron clusters to function as membrane carriers for a broad range of cargo molecules, facilitating the therapeutic nucleic acid cellular uptake, would be an additional advantage of metallacarborane-containing DNA nanoparticles [15–18].

2. Results

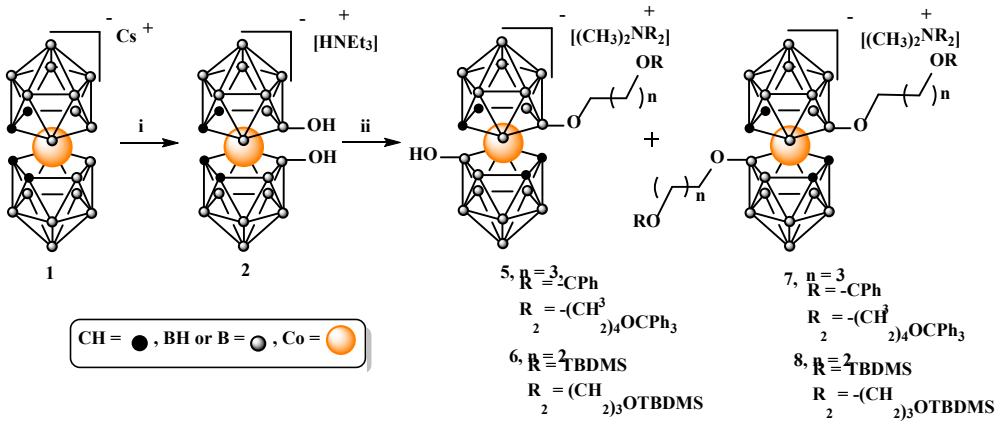
The results of a study on oligofunctionalization of the cobalt bis(1,2-dicarbollide) at boron atoms 8 and 8′ and 1,1′ and/or 2,2′ at carbon atoms with extendable ligands are described. Ligands such as hydroxyalkyls, bearing protected hydroxy function separated from the metallacarborane core by spacers were used. They offer the possibility to maximize the distance of functional moieties from each other and the cluster core, to avoid the influence of the metallacarborane ("metallacarborane effect") [19] on the chemical properties of these moieties. Analogous, but unprotected and substituted at cage carbon atoms alkylhydroxy derivatives of cobalt bis(1,2-dicarbollide) were described by Grüner and colleagues [20,21].

Moreover, the derivatives were designed to test the applicability of two commonly employed in the chemical synthesis of DNA hydroxyl protecting groups, trityl and alkylsilyl protections, to allow the chemo-selection in subsequent chemical manipulation. These results are complemented by studies on further functionalization of the metallocarborane substituted on the 8,8' boron atoms by substitution on the 1,1' and 2,2′ carbon atoms of the carborane ligands.

2.1. Functionalization at 8 and 8′ boron atoms via direct alkylation of hydroxy groups in 8,8′-dihydroxy-bis(1,2-dicarbollide)-3-cobalt(1-)ate (2).

The functionalization procedure starts with converting cobalt bis(1,2-dicarbollide) (**1**) into easily available 8,8′-dihydroxy-bis(1,2-dicarbollido)-3-cobalt(1-)ate (**2**) in the reaction with 80% aqueous sulphuric acid [22]. The substitution reaction proceeds selectively at the 8 and 8′ boron atoms, which are the ones with maximum electron density [23].

As alkylating agents for compound **2**, 4-(trityloxy)butyl-4-methylbenzenesulfonate (**3**) [24] or (3-bromopropoxy)-*tert*-butyldimethylsilane (**4**) differing in leaving groups (tosyl or bromine) and hydroxyl group protection (trityl, -CPh_3 or *tert*-butyldimethylsilyl, TBDMS) were used, NaH was used as a base activating hydroxyl groups in **2** (Scheme 1).



Scheme 1. Alkylation of 8,8′-dihydroxy-bis(1,2-dicarbollide)-3-cobalt(1-)ate (**2**) with $Ts(CH_2)_4OCPh_3$ (**3**) or $Br(CH_2)_3OTBDMS$ (**4**) as electrophiles. i. H_2SO_4 80% 140 °C; ii. NaH, **3** or **4**, 80 °C or 60 °C, DMF; TBDMS = $-Si(CH_3)_2C(CH_3)_3$.

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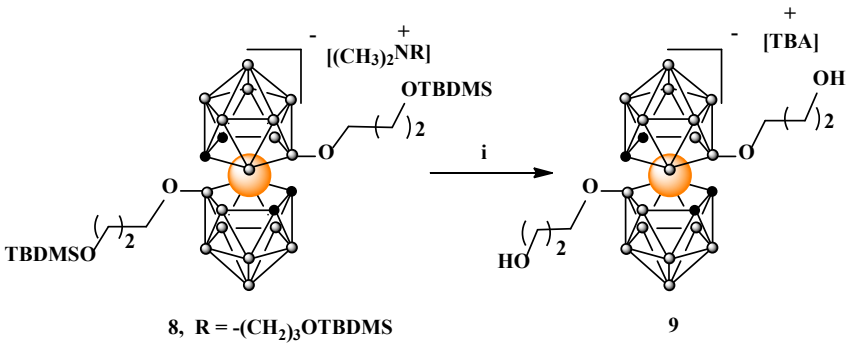
For the reactions involving both the tosylate **3** and the bromide **4**, even if excess of NaH was used, the complete alkylation of both hydroxyl groups was not achieved after 24 h, yielding a mixture of mono-substitution products **5** or **6** (minor products), and bis-substitution products **7** or **8** (major products). Both, mono- and bis alkylated products are easily separable by column chromatography on silica gel using a gradient of methanol or acetonitrile in chloroform as eluting solvent system.

The final yield of trityl protected **7** after purification was found to vary considerably, ranging from 30 to 60 %, although the yield of conversion detected in the crude reaction mixture was high with bis-functionalized derivative as the major product formed. This variability in recovery of the tritylated products **7** and **8** can be ascribed to the relative instability of the trityl protection in **5** and **7**. A reason for this instability could be the known Lewis acidity of the boron cluster cage [25] and the acid lability of trityl protection. Interestingly, it seems that one of the factors influencing this effect may be a distance of the trityl protection from the metallocarborane core, because in compounds **15**, **16,** and **21**, with a longer linker, the instability of the trityl groups do not appear to be a problem.

Compounds **6** and **8** containing silyl protection are reasonably stable anions, which can be purified and separated by column chromatography on silica gel. TBDMS protecting groups can be quantitatively removed from terminal hydroxyls by treatment with 2.5 equivalents of TBAF in THF at room temperature as demonstrated for **8** (Scheme 2). This treatment lead to a counterion exchange in **9** as demonstrated by NMR analysis.



Scheme 2. Deprotection of TBDMS protected **8**. i. 2.5 eq TBAF in THF. TBDMS = -$Si(CH_3)_2C(CH_3)_3$, TBA = $N[(CH_2)_3CH_3]_4$.

As indicated by ^1H NMR (Supplementary Information, Fig. S2, S7, S12) alkylated compounds **5-8** are isolated in the form of tetraalkylammonium $(CH_3)_2NR_2$ salt where R_2 is $-(CH_2)_4OCPh_3$ or $-(CH_2)_3OSi(CH_3)_2C(CH_3)_3$ (Scheme 1). An unexpected structure of tetraalkylammonium counterions is most probably due formation *in situ* sodium dimethylamine as a result of a side reaction involving the reduction of DMF used as a solvent by NaH and its reaction with the alkylating agent [26]. The modest nucleophilicity of the hydroxyls from one side and the erosion of reagents because of this competing reaction with solvent from the other side, account for the use of an excess of reagents to achieve good yields. These undesirable properties of the pair of NaH and DMF are also responsible for the incomplete alkylation of both hydroxyl groups in **2** mentioned above under the condition used, despite other advantages of DMF solvent.

Next, we attempted to functionalize carbon atoms bisubstituted on boron atoms compound **8** (Scheme 3). The reaction was carried out in anhydrous THF at temperature -70 °C to room temperature following a usual procedure. First, to **8** solution in THF nBNuLi in hexane and then ethylene oxide solution in THF were added. After 24 h, the reaction was quenched providing after standard workup, a mono-substitution product **10** formed in the minority and bis-substitution product **11** formed as the major one. Although moderate amounts of the target compounds can be obtained using this approach, synthetic yields are generally not high.

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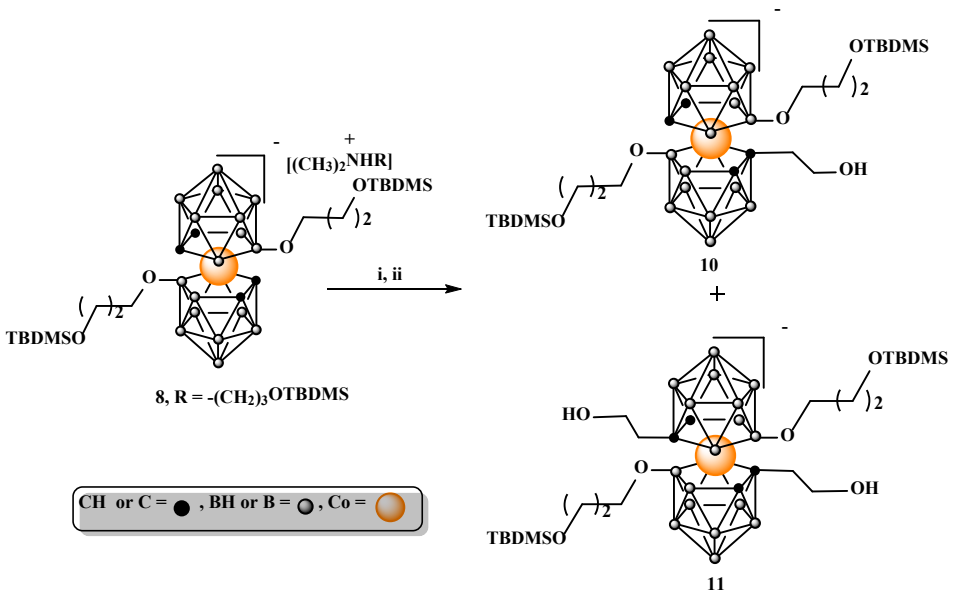

Scheme 3. Substitution on carbon atoms in 8,8′-alkoxy functionalized metallacarborane **8**. i. nBuLi, THF; ii. ethylene oxide. TBDMS = -Si(CH3)2C(CH3)3.

We hypothesize that the reasons for the limited susceptibility of compounds type **8** to functionalization on carbon atoms may include the electron-donating effect of boron cluster ligands, steric hindrance due to the presence of large substituents at the 8 and 8′ positions hampering the electrophile's access to the activated carbon atoms, formation of intramolecular hydrogen bonds between oxygen atoms of substituents at 8,8′ position and acidic carborane C-H groups (Figure 1) analogously to C-H···X-B hydrogen bonds [27,28], and rotations of 1,2-dicarbollide ligands around an axis decreasing susceptibility of C-H groups to activation and alkylation. Consequently, we decided to test a different approach based on derivatives of cobalt bis(1,2-dicarbollide) with arrested rotation containing phosphorothioate bridging moiety, **13**.

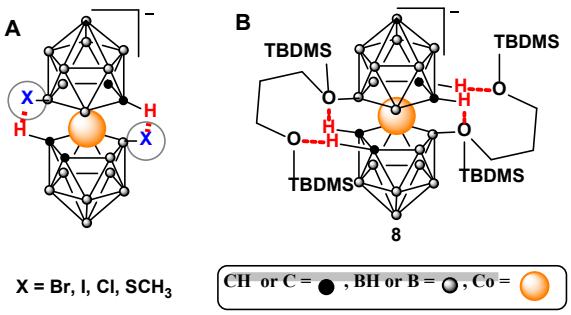

Figure 1. Intramolecular hydrogen bonds in halogenated cobalt bis(1,2-dicarbollide) (**A**) and hypothetical intramolecular interactions in 8,8′-bisalkylated 8 (**B**).

2.2. Functionalization at boron atoms 8 and 8′ via S-alkylation of 8,8′-O,O-[cobalt bis(1,2-dicarbollide)]phosphorothioate (13)

2.2.1. Synthesis of 8,8′-bridged 8,8'-O,O-[cobalt bis(1,2-dicarbollide)]phosphorothioate (13)

The target compound **13** was obtained in a simple, two-step procedure. In the first step the 8,8′-dihydroxy-derivative **2** was converted into 8,8′-bridged 8,8'-O,O-[cobalt bis(1,2-dicarbollide)] H-phosphonate acid ester (**12**) in the reaction with tris(1H-imidazol-1-yl)phosphine [29] and *in situ* hydrolysis of the resultant imidazolide.

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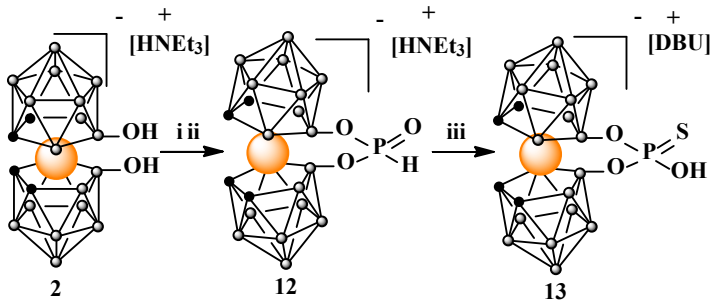


Scheme 4. Synthesis of H-phosphonate (**12**) and thiophosphate (**13**) esters of 8,8′-dihydroxy-bis(1,2-dicarbollido)-3-cobalt(1-)ate (**2**); i. PCl_3, imidazole, Et_3N in THF; ii. H_2O, iii. S_8, DBU in MeOH. DBU = 1,8-diazabicyclo(5.4.0)undec-7-en.

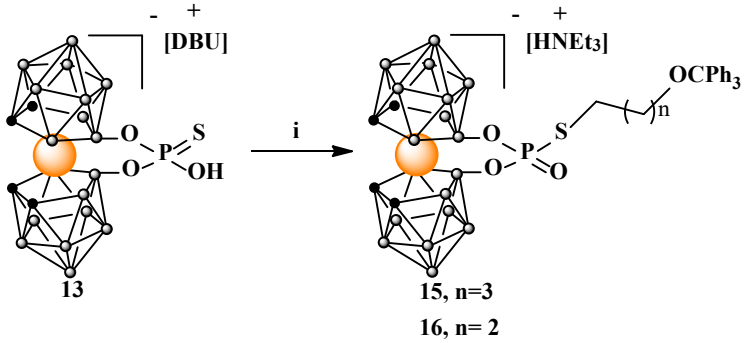
In the second step H-phosphonate acid ester **12** was dissolved in anhydrous methanol then elemental sulfur S_8 was added. To the resultant suspension strong organic base, 1,8-diazabicyclo(5.4.0)undec-7-en (DBU) was added and the reaction was left for 96 hours at room temperature with stirring. After evaporation of the methanol, the residue containing crude product was purified by silica gel column chromatography using a gradient of acetonitrile in chloroform as eluting solvent system.

2.2.2. S-alkylation of 8,8′-bridged 8,8'-O,O-[cobalt bis(1,2-dicarbollide)]phosphorothioate (13) with linear and branched alkylating agents.

Sulfur is a larger atom than oxygen, making its electrons more polarizable and sulfur more nucleophilic. Alkylation of the sulfur atom of phosphorothioates is a viable method for the synthesis of their S-alkylated derivatives. This methodology takes an advantage of the excellent nucleophilic properties of sulfur and is commonly used in organophosphorus chemistry [30].

Using these advantageous properties of phosphorothioates, we attached both linear **13**, **14,** or branched **20** ligands containing hydroxyl functions protected by a trityl group to the metallocarborane derivative **13**. The alkylation reaction proceeds smoothly and yields of isolated alkylated products **15**, **16**, and **21** were high (Scheme 5).

It is worth noting that derivatives of known 8,8′-bridged 8,8'-O,O-[cobalt bis(1,2-dicarbollide)]phosphate [22], a counterpart of **13** containing an 8,8′-O,O-phosphate bridge instead of a phosphorothioate one, have not been described so far. The expected low nucleophilicity of the phosphorus center resulting from the metallocarborane effect [19] and the low nucleophilicity of oxygen atoms can be one of the reasons for this.



Scheme 5. Alkylation of 8,8'-O,O-[cobalt bis(1,2-dicarbollide)]phosphorothioate (**13**) with linear alkylating agent. i. $Ts(CH_2)_4OCPh_3$ (**3**) or $Br(CH_2)_3OCPh_3$ (**14**), acetone, NEt_3, 60 °C, 24 h. DBU = 1,8-diazabicyclo(5.4.0)undec-7-en.

Then study on the functionalization of **13** carbon atoms was undertaken. For this purpose, a method for the synthesis of a branched alkylating agent **20**, in this case, a glycerol derivative, was first developed. In the first step bis(trityloxy)propan-2-ol (**18**) was synthesized according to the

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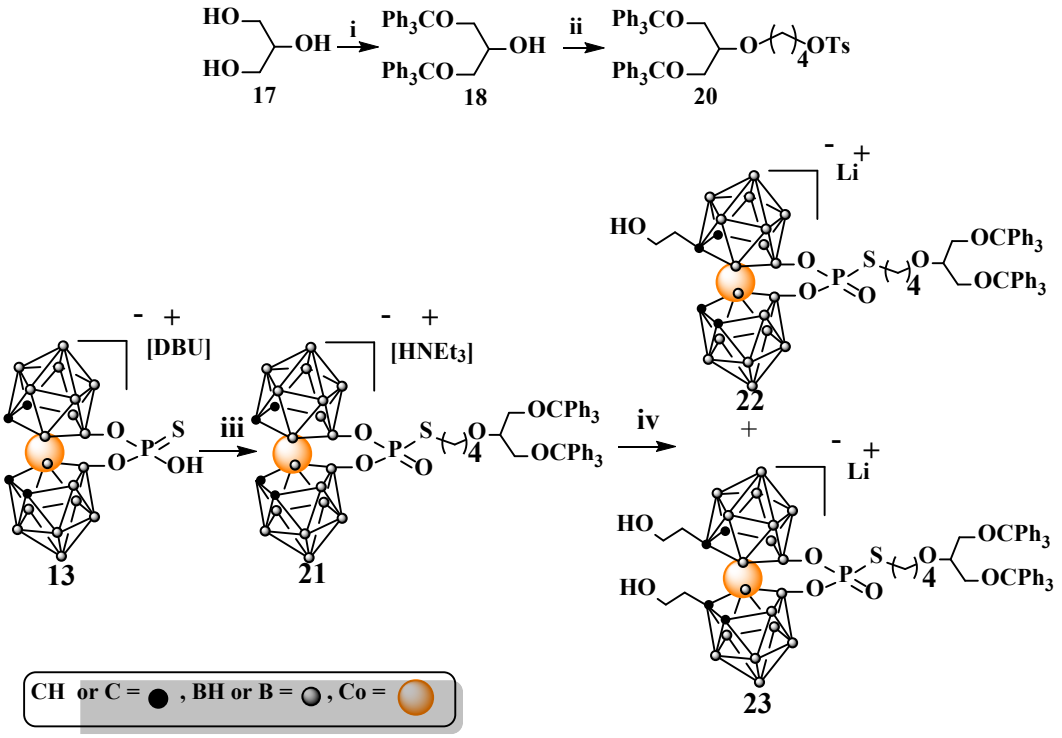
literature method [31]. Next **18** was reacted with 1,4-bis(*p*-toluenesulfonyloxy)butane (**19**) providing a branched alkylating agent with elongated linker **20**.



Scheme 6. Synthesis of branched alkylation agent 4-(1,3-bis(trityloxy)propan-2-yloxy)butyl-4-methylbenzenesulfonate (**20**), its use to alkylate of 8,8'-O,O-[cobalt bis(1,2-dicarbollide)]phosphorothioate (**13**) and functionalization of **21** on carbon atoms: i. $ClCPh_3$ (trityl chloride), pyridine; ii. NaH, DMF, 1,4-bis-(4-methylbenzenesulfonate)butane (**19**); iii. NaH, **20** in DMF; iv. nBuLi, THF; ethylene oxide; DBU = 1,8-diazabicyclo(5.4.0)undec-7-en.

Functionalization of **21** at carbon atoms was achieved *via* activation of cage C-H groups with nBuLi and then treatment with ethylene oxide. As expected carrying out the synthesis of **22** and **23** required overcoming the low susceptibility of the intermediate **21** towards the substitution on carbon atoms. However, mono- and disubstituted derivatives **22** and **23** were obtained with yields enabling their full characterization and use for further chemical manipulations. Easy availability and high yields of synthesis of intermediates **13** and **21** allow for easy scale-up of the **22** and **23** synthesis if needed.

3. Discussion

Description in the literature of metallacarborane building blocks with hydroxyl or other functional groups separated from the cluster cage by an alkyl spacer seems limited. In this contribution, we report on the development of the methods for functionalization of cobalt bis(1,2-dicarbollide) (**1**) with hetero bifunctional derivatives of silyl- or trityl-protected alcohols attached directly to boron atoms, and trityl protected branched alcohols attached to the metallacarborane through a phosphorothioate bridge. An approach to the synthesis of oligofunctionalized metallacarboranes *via* carbon deprotonation through nBuLi to obtain derivatives carrying substituents at both, boron and carbon atoms is also described.

After a long period of discussion, the aromatic, three-dimensional (3D) nature of boron clusters is now widely accepted [32,33]. As in the case of aromatic organic molecules, the attachment of a substituent to one of the atoms of a 3D aromatic boron cluster system changes the distribution of electron density of the entire molecule and affects the properties of other reactive centers. This makes the oligofunctionalization of metallacarboranes, especially simultaneously on boron and carbon atoms, a particular challenge. On this, an complicated stereochemistry of substituted

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metallacarboranes having a source in the presence of various types of chirality in the same molecule is superimposed.

One of the practical manifestations of an effect of synchronized changes in electron density within the whole metallacarborane molecule on properties of reactive centers is the preference for the formation of disubstituted derivatives on boron atoms 8 and 8' and carbon atoms 1,2 and 1',2'. This is illustrated by the preferential formation of disubstituted derivatives compared to monosubstituted ones in the case of **7** vs. **5**, **8** vs. **6**, **11** vs. **10,** or **23** vs. **22**. This is clearly due to activation of a second nucleophilic center such as B-OH or C-H groups activated by a strong base, after a previous substitution at the first center. However, it does not change the fact that the overall alkylation efficiency of C-H groups in derivatives of **1** already substituted on 8 and 8'' boron atoms is low.

For example, monoalkylation derivatives of 8,8'-dihydroxy-bis(1,2-dicarbollide)-3-cobalt(1-)ate (**2**) and bisalkylation derivatives are isolated in the ratio 1:12 for **5** and **7** and 1:4 for **6** and **7**. Mono-substituted and bis-substituted at carbon atoms derivatives of bis-substituted at boron atoms compound **8** are isolated in the ratio 1:3 for **10** and **11**. The same trend, though less pronounced is observed for boron and carbon functionalized derivatives **22** and **23** with arrested rotation where the ratio of mono-substitution on carbon bis-substitution is 1:1.2.

Another property significantly influencing the chemistry of oligofunctionalized metallacarboranes is their stereochemistry. The phenomenon of boron cluster chirality was recognized early [34–36], however, this did not initially arouse much interest. The increasing use of boron clusters in the field of new materials, nanotechnology, and medical chemistry makes the stereochemistry of boron clusters increasingly important.

Perversely, though the most symmetric species in nature is the $B_{12}H_{12}^{-}$ ion, relatively minor changes in the boron cluster structure might render the basic framework dissymmetric enough to provoke chirality [37,38]. This is particularly evident in the case of oligofunctionalized metallacarboranes. The derivatives type **22** and **23** are an extreme examples containing various sources of chirality such as chiral center at phosphorus atom, axial and planar chirality due to bending of the metallacarborane molecule and the existence of a number of isomers due to substitution at carbon atoms in addition to boron substitution.

Comparison of ^{11}B-NMR spectra for compounds **13**, **15**, **16**, **21**, **22,** and **23** with arrested rotation as well as their ^{31}P-NMR spectra clearly shows changes in the number of isomers of individual products depending on substitution. Compounds **13**, **15**, **16,** and **21** show a singlet at δ about 23 ppm attributed to 2B(8,8′) in the ^{11}B-NMR spectrum and a singlet at 48.62 ppm for **13** and at about 16 ppm for compounds **15**, **16**, **21** in the ^{31}P-NMR spectrum which is consistent with the relative symmetry of the complexes.

On the contrary, ^{11}B- and ^{31}P-NMR spectra of mono- and bisalkylated at carbon atoms derivatives **22** and **23** show dramatic change in symmetry due to many possible combinations of substitution on carbon atoms as well as due to the formation of a center of chirality on the phosphorus atom in monosubstituted **22** and in some isomers of bissubstituted **23**. In consequence, four signals at 25.37, 24.65, 23.69, 22.93 ppm in integral intensity ratio 2:2:1:1 corresponding to B8,8′ for **22** and five signals at 25.35, 24.40, 23.64, 22.80, 22.23 ppm in approximate integral intensity ratio 1:2:1.5:1:1 for **23** are observed. A similar effect in ^{31}P-NMR spectra with seven signals at 15.10, 14.94, 14.57, 14.42, 14.11, 13.74, 13.49 ppm for **22** and five signals at 14.99, 14.39, 14.16, 14.01, 13.38 ppm for **23** reflecting asymmetry of these compounds and formations of isomers is seen.

The sensitivity of standard chromatographic techniques is insufficient to distinguish these isomers and allows only the separation of mono- and disubstituted derivatives on carbon atoms, already substituted on boron atoms as in case **10**, **11,** and **22**, **23**. A complete or partial separation of the isomers is probably possible by HPLC, however, for further practical applications of these derivatives, it is not necessary at the present stage.

4. Materials and Methods

4.1. Materials

All solvents were purchased in the highest available quality required for the specific application. The reactions requiring anhydrous conditions were carried under argon using anhydrous solvents treated with activated molecular sieves for at least 24 h. Molecular sieves (4Å and 3Å) were purchased by Alfa Aesar and heat activated under vacuum before use. Triethylamine, trityl chloride, toluene-sulfonyl chloride, $NaHCO_3$, Na_2SO_4, 1,4-butanediol, P_2O_5, sodium hydride, n-butyllithium (1.6 M solution in hexane), (3-bromopropoxy)-*tert*-butyldimethylsilane (**4**) and ethylene oxide (2.9-3.1 M solution in THF) were purchased from Sigma Aldrich. Cobalt bis(1,2-dicarbollide) was purchased from Katchem Ltd., Czech Republic.

4.2. Methods

Chromatography. A DIONEX Ultramate 3000 HPLC system equipped with a photodiode array detector (fixed wavelength 210, 270, 310, 330 nm) was used to check purity of products. The method consisted in a gradient elution from 20% to 90% aqueous acetonitrile trough a Thermo Scientific Hypersil Gold (5µm particle size) reverse phase column at 25°C. HPLC data were acquired and processed by Chromaleon 6.8 software. Chromatography for purification of products was performed on a 230–400 mesh silica gel (Sigma Aldrich) filled glass column. Analytical TLC was performed on F254 silica gel plates purchased by Sigma Aldrich. Compounds were visualized using UV light (254 nm) and or by staining with 0.05 %w/v palladium chloride solution in MeOH/HCl.

NMR spectroscopy. ^{1}H, ^{11}B, $^{11}B\{^{1}H\}$, $^{13}C\{^{1}H\}$, ^{31}P, $^{31}P\{^{1}H\}$ NMR spectras were recorded with a Bruker Advance III 600 MHz spectrometer.

UV-Vis spectrophotometry and line fitting analysis. Measurements were performed with a Jasco V-750 UV-spectrophotometer at room temperature in acetonitrile.

MS and FT-IR MALDI-TOF MS spectras were recorded with a Voyager–Elite mass spectrometer (PerSeptive Biosystems) with 3-hydroxypicolinic acid (HPA) as the matrix. ESI MS mass spectra were recorded using Agilent 6546 LC/Q-TOF (Santa Clara, Kalifornia, United States). Negative ions were detected. Infrared absorption spectra were recorded using a Nicolet 6700 FT-IR spectrometer (Thermo Scientific) equipped with a Smart orbit diamond Attenuated Total Reflectance (ATR) accessory. Samples to be analyzed were placed on a diamond ATR element in the solid form or by casting from CH_2Cl_2 solution. Data were acquired and processed by Omnic 8.1 software.

*8,8′-dihydroxy-bis(1,2-dicarbollido)-3-cobalt(1-)ate HNEt$_3$ (**2**) was synthesized according to the procedure reported by Plešek et al. [22].*

*4-Trityloxybutyl 4-methylbenzenesulfonate (**3**) was obtained as described [39].*

*3-Bromo-1-trityloxypropane (**14**) was synthesized as described previously [10].*

*1,3-Bis(trityloxy)propan-2-ol (**18**) was synthesized according to the literature procedure [31].*

*1,4-bis-(4-methylbenzenesulfonate)butane (**19**) was synthesized according to the modified literature procedure [40].*

*Synthesis of 3,3′-Co{[(8-O(CH$_2$)$_4$OCPh$_3$]-1,2-C$_2$B$_9$H$_{10}$}(8′-OH-1,2-C$_2$B$_9$H$_{10}$) (CH$_3$)$_2$N[(CH$_2$)$_4$OPh$_3$]$_2$ (**5**) and 3,3′-Co[(8-O(CH2)$_4$OCPh$_3$-1,2-C$_2$B$_9$H$_{10}$)]$_2$ (CH$_3$)$_2$N[(CH$_2$)$_4$OPh$_3$]$_2$ (**7**).* Compound **2** (50 mg, 0.10 mmol) was dissolved in 0.5 mL of anhydrous dimethoxyethane (DME) and added to 60% NaH in mineral oil dispersion (4.4 mg, 0.10 mmol NaH) under argon atmosphere. The reaction mixture was stirred for 2 h at room temperature. After this time the solvent was evaporated under reduced pressure and the resultant solid residue was dissolved in 0.5 mL of anhydrous dimethylformamide (DMF) and added to a second aliquot of 60% NaH in mineral oil dispersion (26.2 mg, 0.65 mmol NaH). After 2 h at room temperature the mixture was dropped into a solution of **3** (318.8 mg, 0.65 mmol) in 0.5 mL of anhydrous DMF and then the reaction mixture was heated at 80 °C (oil bath temperature) for 24 h. The post-reaction mixture was concentrated then 3 mL of H_2O was added. The resulting precipitate was washed with several aliquots of H_2O. Then the solid was dissolved in 5 mL of CH_2Cl_2, and the solution was dried with anhydrous Na_2SO_4, filtered and concentrated. The repeated column chromatography on silica gel using a gradient of CH_3OH in CH_3Cl (0 to 20%) as eluting solvent system gave **5** and **7** as the first and second band respectively. Fractions containing compound **7** were collected, evaporated to dryness then crystallized from hexane, providing 96% pure product as determined by HPLC. Monosubstituted compound **5** was obtained as a red oil.

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(5): **Yield**: ca 5 %; **TLC** ($CHCl_3$: MeOH 4:1); **R_f**: 0.53; **MALDI-MS** (m/z): 670.5 (calc. for $C_{27}B_{18}H_{44}O_3Co_1$: 670.17). Due to obtaining too small quantities of this product, it was not further analyzed by NMR.

(7): **Yield**: 62% (68.2 mg); **TLC** ($CHCl_3$: MeOH 4:1); **R_f** 0.64; **^{1}H NMR** (500 MHz, CD_3CN) δ: 7.43 (m, 24H, *H*$_{arom}$), 7.32 (m, 24H, *H*$_{arom}$), 7.25 (m, 12H, *H*$_{arom}$), 4.18 (s, 4H, *CH*$_{carborane}$), 3.31 (t, J = 6.2 Hz, 4H, BO*CH*$_2$CH$_2$CH$_2$CH$_2$OTr), 3.07 (m, 8H, *CH*$_2$OTr), 2.99 (t, J = 6.4 Hz, 4H, N*CH*$_2$CH$_2$CH$_2$CH$_2$OTr), 2.86 (s, 6H, N(*CH*$_3$)$_2$), 1.68 (m, 4H, NCH$_2$*CH*$_2$CH$_2$CH$_2$OTr), 1.60 (m, 8H, *CH*$_2$CH$_2$OTr), 1.48 (m, 4H, BOCH$_2$*CH*$_2$CH$_2$CH$_2$OTr); **^{13}C{^{1}H} NMR** (126 MHz, CD_3CN) δ: 145.53, 145.18 (12C, *aromatic*$_{trityl}$); 129.44, 129.41 (24C, *aromatic*$_{trityl}$); 129.37, 128.83 (24C, *aromatic*$_{trityl}$); 128.21 (12C, *aromatic*$_{trityl}$); 87.43, 87.06 (4C, *C(Ph)*$_3$), 69.43 (2C, BO*CH*$_2$CH$_2$CH$_2$CH$_2$OTr), 64,30 (2C, BOCH$_2$CH$_2$CH$_2$*CH*$_2$OTr), 63,30 (2C, NCH$_2$CH$_2$CH$_2$*CH*$_2$OTr), 62.33 (2C, N*CH*$_2$CH$_2$CH$_2$CH$_2$OTr), 51.56 (4C, *CH*$_{carb}$), 30.39, 29.68 (4C, *CH*$_2$CH$_2$OTr), 27.51, 27.13 (2C, BOCH$_2$*CH*$_2$CH$_2$CH$_2$OTr), 20.29 (NCH$_2$*CH*$_2$CH$_2$CH$_2$OTr); **^{11}B{^{1}H} NMR** (160 MHz, CD_3CN) δ: 20.63 (s, 2B, B$^{8,8'}$), -3.56 (s, 2B, B$^{10,10'}$), -7.52 (s, 4B, B$^{4,4',7,7'}$), -9.03 (s, 4B, B$^{9,9',12,12'}$), -20.53 (s 4B, B$^{5,5',11,11'}$), -28.38 (s, 2B, B$^{6,6'}$) **^{11}B NMR** (160 MHz, CD_3CN) δ: 20.66 (s, 2B, B$^{8,8'}$), -3.59 (d, 2B, B$^{10,10'}$), -8.22 (m, 8B, B$^{9,9',12,12',4,4',7,7'}$), -20.48 (d, 2B, B$^{5,5',11,11'}$), -28.09 (d, 2B, B$^{6,6'}$); **FT-IR** (cm^{-1}): 3083.53, 3055.16, 3029.62 (ν C-H aromatic, (C-H$_{carb}$); 2927.18 (ν C-H$_{asym}$, CH_2); 2867.43 (ν C-H, CH_2O, ν C-H$_{sym}$, CH_2); 2543.23 (ν B-H); 1596.06, 1488.72, 1447.49 (ν C=C); 1152.23; 745.10, 693.37 (δ C-H aromatic); 703.89 (ν B-B); **MALDI-MS** (m/z): found 984.2 (calc. for $C_{50}B_{18}H_{66}O_4Co_1$: 984.59).

*Synthesis of 3,3′-Co[8-O(CH$_2$)$_3$OTBDMS]-1,2-C$_2$B$_9$H$_{10}$)(8′-OH-1,2-C$_2$B$_9$H$_{10}$) (CH$_3$)$_2$N[(CH$_2$)$_3$OTBDMS)]$_2$ (**6**) and 3,3′-Co[8-O(CH$_2$)$_3$OTBDMS-1,2-C$_2$B$_9$H$_{10}$)]$_2$ (CH$_3$)$_2$N[(CH$_2$)$_3$OTBDMS)]$_2$ (**8**).* Compound **2** (300 mg, 0.65 mmoles) was dissolved in 3 mL of anhydrous DME under argon atmosphere and added to 60% NaH in mineral oil dispersion (26.2 mg, 0.65 mmol NaH). The reaction mixture was stirred for 2h at room temperature. After this time the solvent was evaporated and the solid residue was dissolved in 3 mL of anhydrous DMF and added to a second portion of 60% NaH in mineral oil dispersion (157 mg, 3.93 mmol NaH). After 2 h at room temperature the mixture was heated at 60 ˚C (oil bath temperature) and 911 μL of (3-bromopropoxy)(*tert*-butyl)dimethylsilane (**4**) (3.93 mmol) was added dropwise. After 22 h, additional quantity of **4** (600 μL, 2.59 mmol) was added and the mixture was stirred for next 24 h at 60 ˚C. A white solid was formed. The post-reaction mixture was then filtered through syringe filter (5 μm, PTFE, Carl Roth) and DMF was evaporated under reduced pressure. The solid residue was treated with 2 mL of $CHCl_3$, filtered, the filtrate was concentrated and loaded on a silica gel column for separation of products. 100% $CHCl_3$ first and then 5% and 10% CH_3CN in $CHCl_3$ were used as eluting solvent system. Compound **8** was isolated as first fraction and was obtained in the form of orange crystals after solvent evaporation, its purity was above 95% as determined by HPLC. The second fraction containing **6** was obtained as red oil after solvent evaporation. Both products, **6** and **8** were isolated as N,N-bis[(3-(*tert*-butyldimethylsilyloxypropyl)]-N,N-dimethyl ammonium salts [26].

6: Yield: 10%; **TLC** ($CHCl_3$: CH_3CN 3:1) R_f 0.53; **^{1}H NMR** (600 MHz, CD_3CN) δ: 6.05 (s, 1H, *OH*), 3.73 (t, J = 6.5 Hz, 2H, BOCH$_2$CH$_2$*CH*$_2$OSi), 3.69 (m, 4H, N*CH*$_2$CH$_2$CH$_2$OSi), 3.65 (m, 2H, BO*CH*$_2$CH$_2$CH$_2$OSi), 3.56 (s, 2H, *CH*$_{carb}$), 3.45 (s, 2H, *CH*$_{carb}$), 3.27 (m, 4H, NCH$_2$CH$_2$*CH*$_2$OSi), 2.97 (s, 6H, N(*CH*$_3$)$_2$), 1.88 (m, 4H, NCH$_2$*CH*$_2$CH$_2$OSi), 1.74 (m, J = 6.4 Hz, 2H, BOCH$_2$*CH*$_2$CH$_2$OSi), 0.90 (s, 9H, BOCH$_2$CH$_2$CH$_2$OSi(CH$_3$)$_2$C(*CH*$_3$)$_3$), 0.89 (s, 18H, NCH$_2$CH$_2$CH$_2$OSi(CH$_3$)$_2$C(*CH*$_3$)$_3$), 0.07 (s, 6H, BOCH$_2$CH$_2$CH$_2$OSi(*CH*$_3$)$_2$C(CH$_3$)$_3$), 0.05 (s, 12H, NCH$_2$CH$_2$CH$_2$OSi(*CH*$_3$)$_2$C(CH$_3$)$_3$); **^{13}C{^{1}H} NMR** (126 MHz, CD_3CN) δ: 67.05 (1C, BO*CH*$_2$CH$_2$CH$_2$OSi), 62.56 (2C, NCH$_2$CH$_2$*CH*$_2$OSi), 61.23 (1C, BOCH$_2$CH$_2$*CH*$_2$OSi), 60.17 (2C, N*CH*$_2$CH$_2$CH$_2$OSi), 52.03 (2C, N(CH$_3$)$_2$), 46.23 (2C, CH$_{carb}$), 45.51 (2C, CH$_{carb}$), 35.92 (1C, BOCH$_2$*CH*$_2$CH$_2$OSi), 26.45 (2C, NCH$_2$*CH*$_2$CH$_2$OSi), 26.27 (6C, OSi(CH$_3$)$_2$C(*CH*$_3$)$_3$), 26.11 (3C, OSi(CH$_3$)$_2$C(*CH*$_3$)$_3$), 18.81 (1C, OSi(CH$_3$)$_2$*C*(CH$_3$)$_3$), 18.72 (2C, OSi(CH$_3$)$_2$*C*(*CH*$_3$)$_3$), -5.10 (2C, OSi(*CH*$_3$)$_2$C(CH$_3$)$_3$), -5.40 (4C, OSi(*CH*$_3$)$_2$C(CH$_3$)$_3$) **^{11}B{^{1}H} NMR** (193 MHz, CD_3CN) δ: 27.16 (s, 1B, B$^{8'}$), 25.10 (s, 1B, B^8), -5.02 to -9.09 (10B, overlapped B$^{9,9',10,10'12,12',4,4',7,7'}$), -20.10 to -20.69 (4B, B$^{5,5',11,11'}$), -29.18 to -30.16 (2B, B$^{6,6'}$); **^{11}B NMR** (160 MHz, CD_3CN) δ: 27.16 (s, 1B, B$^{8'}$), 25.09 (s, 1B, B^8), -3.22 to -9.40 (10B, overlapped B$^{9,9',10,10'12,12',4,4',7,7}$) -19.72 to -21.11 (4B, B$^{5,5',11,11'}$), -28.81 to -30.49 (2B, B$^{6,6'}$), **FT-IR** (cm^{-1}): 3278.64, 2952.00, 2927.58, 2855.64, 2539.99, 1470.65, 1387.53, 1360.69, 1252.66, 1156.76, 1093.25, 1005.54,

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972.16, 938.48, 880.24, 832.61, 774.98, 718.29, 661.26; **ESI- MS** (m/z): found 530.39, 472.35 [M-*t*Butyl]$^-$ (calc. for $C_{13}B_{18}H_{43}Si_1O_3Co_1$: 529.09)

8: Yield: 80%; **TLC** ($CHCl_3$: CH_3CN 3:1) R_f 0.70; **^{1}H NMR** (500 MHz, CD_3CN) δ: 4.18 (s, 4H, $\underline{CH_{carb}}$), 3.69 (m, 4H, $BOCH_2CH_2\underline{CH_2}OSi$), 3.64 (t, J = 6.4 Hz, 4H, $N\underline{CH_2}CH_2CH_2OSi$), 3.38 (t, J = 6.0 Hz, 4H, $BO\underline{CH_2}CH_2CH_2OSi$), 3.27 (m, 4H, $NCH_2CH_2\underline{CH_2}OSi$), 2.97 (s, 6H, $N(\underline{CH_3})_2$), 1.88 (m, 4H, $NCH_2\underline{CH_2}CH_2OSi$), 1.58 (m, J = 6.2 Hz, 4H, $BOCH_2\underline{CH_2}CH_2OSi$), 0.90 (s, 18H, $OSi(CH_3)_2C(\underline{CH_3})_3$), 0.88 (s, 18H, $OSi(CH_3)_2C(\underline{CH_3})_3$), 0.07 (s, 12H, $OSi(\underline{CH_3})_2C(CH_3)_3$), 0.04 (s, 12H, $OSi(\underline{CH_3})_2C(CH_3)_3$); **^{13}C NMR** (126 MHz, CD_3CN) δ: 66.18 (2C, $BOCH_2CH_2\underline{CH_2}OSi$), 62.54 (2C, $NCH_2CH_2\underline{CH_2}OSi$), 60.95 (2C, $BO\underline{CH_2}CH_2CH_2OSi$), 60.17 (2C, $N\underline{CH_2}CH_2CH_2OSi$), 52.06 (2C, $N(\underline{CH_3})_2$), 51.60 (4C, $\underline{CH_{carb}}$), 35.97 (2C, $BOCH_2\underline{CH_2}CH_2OSi$), 26.46 (2C, $NCH_2\underline{CH_2}CH_2OSi$), 26.28 (6C, $OSi(CH_3)_2C(\underline{CH_3})_3$), 26.12 (6C, $OSi(CH_3)_2C(\underline{CH_3})_3$ 18.83 (2C, $OSi(CH_3)_2\underline{C}(CH_3)_3$), 18.72 (2C, $OSi(CH_3)_2\underline{C}(CH_3)_3$), -5.09 (4C, $OSi(\underline{CH_3})_2C(CH_3)_3$), -5.39 (4C, $OSi(\underline{CH_3})_2C(CH_3)_3$) **^{11}B{^{1}H} NMR** (160 MHz, CD_3CN) δ: 20.61 (s, 2B, $B^{8,8'}$), -3.61 (s, 2B, $B^{10,10'}$), -7.45 (s, 4B, $B^{4,4',7,7'}$), -9.03 (s, 4B, $B^{9,9',12,12'}$), -20.51 (s, 4B, $B^{5,5',11,11'}$), -28.38 (s, 2B, $B^{6,6'}$) **^{11}B NMR** (160 MHz, CD_3CN) δ: 20.76 (s, 2B, $B^{8,8'}$), -3.59 (d, 2B, $B^{10,10'}$), -7.18 to -9.37 (m, 8B, overlapped $B^{4,4',7,7',9,9',12,12'}$), -20.48 (d, 4B, $B^{5,5',11,11'}$), -28.02 (d, 2B, $B^{6,6'}$); **FT-IR** (cm^{-1}): 3048.6 (C-H_{carb}); 2949.4 (ν C-H_{asym}, CH_3); 2927.4 (ν C-H_{asym}, CH_2), 2891.6, 2884.2 (ν C-H_{sym} CH_3); 2856.2 (ν C-H, CH_2O, ν C-H_{sym}, CH_2); 2605.2, 2550.6 (ν B-H); 1470.8 (δ C-H_{sym}, CH_2), 1436.0; 1386.2; 1359.5; 1251.2 (Si-CH_3), 1161.9 (Si-O-C); 1093.1 (ν Si-O); 1019.3; 1006.3; 975.2; 955.3; 942.7; 881.; 831.8, 772.4 (ν Si-C); 710.9; 661.0; **MALDI-MS** (m/z): found 700.5 (calc. for $C_{22}B_{18}H_{62}CoO_4Si_2$ 700.43).

*Deprotection of compound **8** to obtain [3,3′-Co(8-O(CH_2)$_3$OH-1,2-$C_2B_9H_{10}$)$_2$] TBA (**9**).* Compound **8** (20 mg, 0.027 mmol) was dissolved in 0.2 mL of tetrahydrofuran (THF). To the obtained solution 69 µL of terabutylammonium fluoride (TBAF) (1M solution in THF, 0.069 mmol) was added and the reaction mixture was stirred at room temperature overnight. Next, solvent was evaporated under reduced pressure and the resulting oil was dissolved in $CHCl_3$ and applied to the silica gel column prepared in the same solvent. Elution in a gradient 1 to 20% CH_3CN in $CHCl_3$ provided 96 % pure **9** (determined by HPLC) as TBA salt. **Yield**: 95%; **TLC** ($CHCl_3$: CH_3CN 3:1) R_f 0.47; **^{1}H NMR** (500 MHz, CD_3CN) δ: 4.17 (s, 4H, $\underline{CH_{carb}}$), 3.52 (t, , J = 6.3 Hz, 4H, $BOCH_2CH_2\underline{CH_2}OH$), 3.43 (t, J = 6.0 Hz, 4H, $BO\underline{CH_2}CH_2CH_2OH$), 3.10 – 3.03 (m, 8H, $N\underline{CH_2}CH_2CH_2CH_3$), 2.58 (s, 2H, $\underline{OH}$), 1.59 (m, J = 8.2, 3.7 Hz, 12H, $BOCH_2\underline{CH_2}CH_2OH$, $NCH_2\underline{CH_2}CH_2CH_3$), 1.41 – 1.28 (m, 8H, $NCH_2CH_2\underline{CH_2}CH_3$), 0.96 (t, J = 7.4, 12H, $NCH_2CH_2CH_2\underline{CH_3}$); **^{13}C NMR** (126 MHz, CD_3CN) δ: 67.47 (2C, $BOCH_2CH_2\underline{CH_2}OH$), 60.63 (2C, $BO\underline{CH_2}CH_2CH_2OH$), 59.23 (4C, $N\underline{CH_2}CH_2CH_2CH_3$), 51.39 (4C, $\underline{CH_{carb}}$orane), 35.54 (2C, $BOCH_2\underline{CH_2}CH_2OH$), 24.21 (4C, $NCH_2\underline{CH_2}CH_2CH_3$), 20.25 (4C, $NCH_2CH_2\underline{CH_2}CH_3$), 13.72 (4C, $NCH_2CH_2CH_2\underline{CH_3}$); **^{11}B{^{1}H} NMR** (160 MHz, CD_3CN) δ: 20.95 (s, 2B, $B^{8,8'}$), -3.49 (s, 2B, $B^{10,10'}$), -7.71 (s, 4B $B^{4,4',7,7'}$), -8.85 (s, 4B, $B^{9,9',12,12'}$), -20.44 (s, 4B, $B^{5,5',11,11'}$), -28.14 (s, 2B, $B^{6,6'}$); **^{11}B NMR** (160 MHz, CD_3CN) δ: 20.97 (s, 2B, $B^{8,8'}$), -3.48 (d, 2B, $B^{10,10'}$), -7.18 to -9.26 (m, 8B, $B^{4,4'7,7'9,9',12,12'}$), -20.42 (d, 4B, $B^{5,5',11,11'}$), -28.19 (d, 2B, $B^{6,6'}$); **FT- IR** (cm^{-1}): 3588.76 (ν O-H); 3450.79 (ν N^+-R); 3052.83 (C-H_{carb}); 2962.10 (ν C-H_{asym}, CH_2); 3932.36, 2873.70 (ν C-H, CH_2O, ν C-H_{sym}, CH_2); 2529.19 (ν B-H); 1467.75 (ν N^+-R), 1380.63; 1161.25 (HO-C); 1105.54; 1062.05; 1007.15; 969.00; 945.10; 920.29; 876.90; 789.11; 735.69; 696.07; 664.83; **MALDI-MS** (m/z): found 472.8 (calc. for $C_{10}B_{18}H_{34}O_4Co_1$ 471.90).

*Synthesis of 3,3′-Co{[8-O(CH_2)$_3$OTBDMS-1-(CH_2)$_2$OH]-1,2-$C_2B_9H_9$)}[8′-O(CH_2)$_3$OTBDMS-1′,2′-$C_2B_9H_{10}$)]$^-$ (**10**) and 3,3′-Co[(8-O(CH_2)$_3$OTBDMS-1-(CH_2)$_2$OH-1,2-$C_2B_9H_9$)]$_2^-$ (**11**).* Compound **8** (50 mg, 0.04 mmol) was dried by co-evaporation with anhydrous benzene and then kept under vacuum over P_2O_5 overnight. Next it was dissolved in anhydrous DME (1 mL) and the solution was cooled in CO_2/isopropanol cooling bath. After 15 min. n-BuLi (43 µL, 1.6 M solution in hexane, 1.5 eq) was added and the reaction mixture was stirred for 10 min. After that time, cooling bath was removed and the mixture was stirred for next 10 min. Then the reaction mixture was cooled again in cooling bath and another portion of n-BuLi (43 µL) was added. After 15 min, ethylene oxide (60 µL, 2.9-3.1 M solution in THF, 4.5 eq) was added and the reaction was left overnight in cooling bath. Next CH_2Cl_2 (3 mL) was added to the reaction mixture, the reaction was quenched by addition of water and the organic solution was washed three times with 5 mL portions of water. Organic layer was separated and dried over $MgSO_4$ then solvents were evaporated. Crude product was purified and mono- and

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bis-substituted products separated by silica gel column chromatography using a gradient of MeOH in CH_2Cl_2 from 0 to 3% of MeOH.

10 Yield: 4,7 mg (9%) **TLC** (silica gel on Al, 8% MeOH/CH_2Cl_2): **R_f:** 0.28, **ESI-MS** (m/z): found 744.55, (calc. for $C_{24}B_{18}H_{66}O_5Si_2Co_1$ 744.48). Due to obtaining too small quantities of this product, it was not further analyzed by NMR.

11 Yield: 15 mg (27%) **TLC** (silica gel on Al, 8% MeOH/CH_2Cl_2): **R_f**: 0.16 **^{1}H NMR** (500 MHz, CD_3CN) δ: 4.32-4.08 (s, 2H, diastereoizomeric $\underline{CH_{carborane}}$), 3.77 to 3.52 (m, 16H, overlapped $N\underline{CH_2}CH_2CH_2O$, $NCH_2CH_2\underline{CH_2}O$, $BO\underline{CH_2}CH_2CH_2O$, $BOCH_2CH_2\underline{CH_2}O$), 3.52 to 3.39 (m, 4H, $HO\underline{CH_2}CH_2C_{carb}$), 3.39 to 3.31 (m, 4H, $HOCH_2\underline{CH_2}C_{carb}$), 3.03 (s, 6H, $N(\underline{CH_3})_2$), 1.74 (m, 4H, $NCH_2\underline{CH_2}CH_2O$), 1.65 (m, 4H, $BOCH_2\underline{CH_2}CH_2O$) 0.90 (s, 18H, $NCH_2CH_2CH_2OSi(CH_3)_2C(\underline{CH_3})_3$), 0.88 (s, 18H, $BOCH_2CH_2CH_2OSi(CH_3)_2C(\underline{CH_3})_3$), 0.07 (s, 12H, $BOCH_2CH_2CH_2OSi(\underline{CH_3})_2C(CH_3)_3$), 0.05 (s, 12H, $NCH_2CH_2CH_2OSi(\underline{CH_3})_2C(CH_3)_3$, **^{13}C{^{1}H} NMR** (126 MHz, CD_3CN) δ: 67.39 (2C, $BO\underline{CH_2}CH_2CH_2O$), 66.93 (1C, $\underline{CH_{carborane}}$), 64.82 (1C, $\underline{CH_{carborane}}$), 64.10 (2C, $NCH_2CH_2\underline{CH_2}OSi$), 62.28 (2C, $BOCH_2CH_2\underline{CH_2}O$), 61.00 (2C, $HO\underline{CH_2}CH_2C_{carb}$), 57.17 (2C, $N\underline{CH_2}CH_2CH_2O$), 56.24 (2C, $N(\underline{CH_3})_2$), 53.22 (2C, $C_{carborane}$), 45.17 (2C, $HOCH_2\underline{CH_2}C_{carb}$) 36.89 (2C, $NCH_2\underline{CH_2}CH_2O$), 27.28 (2C, $BOCH_2\underline{CH_2}CH_2O$), 26.98 (6C, $OSi(CH_3)_2C(\underline{CH_3})_3$) 26.77 (6C, $OSi(CH_3)_2C(\underline{CH_3})_3$), 19.53 (2C, $OSi(CH_3)_2\underline{C}(CH_3)_3$), 19.39 (2C, $OSi(CH_3)_2\underline{C}(CH_3)_3$), -4.38 (4C, $OSi(\underline{CH_3})_2C(CH_3)_3$), -4.73 (4C, $OSi(\underline{CH_3})_2C(CH_3)_3$). **^{11}B{^{1}H} NMR** (120 MHz, CD_3CN) δ: 29.65, 25.25, 24.28, 23.33, 21.98 (in ratio: 3:1.5:1:1:10), 31.27 to 19.66 (m, overlapped diastereoizomeric $B^{8,8'}$), -2.63 to -13.75 (m, overlapped diastereoizomeric, $B^{10,10',9,9',12,12',4,4',7,7'}$), -14.09 to -21.65 (m, overlapped diastereoizomeric $B^{5,5',11,11'}$), -22.11 to -29.38 (m, overlapped diastereoizomeric $B^{6,6'}$) **^{11}B NMR** (120 MHz, CD_3CN) δ: 30.85-20.54 (m, overlapped diastereoizomeric $B^{8,8'}$), -2.16 to -13.03 (m, overlapped diastereoizomeric, $B^{10,10',9,9',12,12',4,4',7,7'}$), -13.91 to -21.45 (m, overlapped diastereoizomeric, $B^{5,5',11,11'}$), -21.52 to -27.10 (m, overlapped diastereoizomeric, $B^{6,6'}$), **ESI-MS** (m/z): found 788.58 (calc. for $C_{26}B_{18}H_{70}O_6Si_2Co_1$ 788.53)

*Synthesis of 8,8'-bridged [8,8'-$O_2P(O)H$-3,3'-Co(1,2-$C_2B_9H_{10})_2$] $HNEt_3$ H-phosphonate (**12**).* Imidazole (0.51 g, 7.5 mmol) was dissolved in minimum ammount of anhydrous acetonitrile. The solvent was evaporated under reduced pressure and the procedure was repeated twice. After drying under vacuum for 1.5 h imidazole was redissolved in 16 mL of anhydrous THF and the solution was cooled down at -70 °C in a dry ice/isopropanol bath under argon atmosphere. PCl_3 (210 μL, 2.40 mmol) was added dropwise followed by Et_3N (1 mL, 7.17 mmol) mixed with 1 mL of anhydrous THF. The whole was stirred at -70 °C for 15 min. and then solution of 8,8'-dihydroxy-bis(1,2-dicarbollido)-3-cobalt(1-)ate $HNEt_3$ (**2**) (320 mg, 0,69 mmoles) in 13 mL of THF was added dropwisely. After further 30 min., the reaction mixture was removed from cooling bath and allowed to warm up to room temperature. After another 1 h the reaction was quenched with 30 mL of water and extracted four times with 40 mL of diethyl ether (Et_2O). The combined ether extracts were dried with $MgSO_4$ and the solvent was evaporated. The resultant solid crude product was dryed under vacuum then was purified by silica gel (230-400 mesh) column chromatography using CH_3CN : $CHCl_3$ 1:4 as eluting solvent system. **Yeld**: 91%; **TLC** (CH_3CN : $CHCl_3$ 1:2): **R_f** 0.35; **^{1}H NMR** (500 MHz, CD_3CN) δ: 7.47,6.07 (1H, *P-H*), 3.70 (s, 4H, $CH_{carborane}$), 3.10 (m, 6H, $N\underline{CH_2}CH_3$), 1.24 (t, 9H, $NCH_2\underline{CH_3}$); **^{13}C{^{1}H} NMR** (125 MHz, CD_3CN) δ: 47.96 (4C, C_{carb}), 47.74 (3C, $N\underline{CH_2}CH_3$), 9.24 (3C, $NCH_2\underline{CH_3}$); **^{11}B{^{1}H} NMR** (120 MHz, CD_3CN) δ: 23.02 (s, 2B, $B^{8,8'}$), -2.83 (s, 2B, $B^{10,10'}$), -5.70 (s, 4B, $B^{9,9',12,12'}$), -7.94 (s, 2B, $B^{4,4'}$), -8.74 (s, 2B, $B^{7,7'}$), -18.89 (s, 4B, $B^{5,5',11,11'}$), -27.85 (s, 2B, $B^{6,6'}$); **^{11}B NMR** (125 MHz, CD_3CN) δ: 23.02 (s, 2B, $B^{8,8'}$), -2.83 (d, 2B, $B^{10,10'}$), -5.70 (d, 4B, $B^{9,9',12,12'}$), -8,36 (t, 4B, $B^{4,4',7,7'}$), -18,91 (d, 4B, $B^{5,5',11,11'}$), -27.84 (d, 2B, $B^{6,6'}$); **^{31}P{^{1}H} NMR** (202 MHz, CD_3CN) δ: -3.01 (s, P-H); **^{31}P NMR** (202 MHz, CD_3CN) δ: -3,00 (d, P-H); **ATR-IR (cm^{-1}):** 3621, 3029, 2993, 2544, 1609, 1474, 1446, 1393, 1218, 1152, 1137, 1094, 1025, 993, 981, 920, 903, 871, 849, 787, 743, 691, 666. **UV-Vis** λ_{max} (nm): 297, 445. **ESI-MS** (m/z)**:** found 402,24 (calc. for $C_4H_{21}O_3B_{18}P_1Co_1$: 401,71).

*Synthesis of 8,8'-bridged [8,8'-$O_2P(O)SH$-3,3'-Co(1,2-$C_2B_9H_{10})_2$] HDBU phosphorothioate (**13**).* H-phosphonate acid ester **12** (130 mg, 0,26 mmol) was dissolved in anhydrous MeOH (6,5 mL). The solution was added under argon atmosphere to S_8 (85 mg, 2.6 mmol). 1,8-Diazabicyclo(5.4.0)undec-7-en (DBU) (160 μL, 1.05 mmoles) was then added and the mixture was stirred for 96 h at room temperature. After this time solvent was evaporated under reduced pressure. The crude product was dissolved in CH_3CN then purified by silica gel column chromatography using a gradient of CH_3CN

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: $CHCl_3$ from 1:4 to 1:1 as eluting solvent system. Finally, the product **13** was eluted from the column using 100% MeOH as eluent. **Yield:** 70%; **TLC** (CH_3CN : $CHCl_3$ 2:1) **Rf:** 0.5; **^{1}H NMR** (500 MHz, CD_3CN) δ: 9.14 (s, 1H, *NH*), 3.58 (s, 4H, *CH$_{carborane}$*), 3.50 (m, 2H, NH*CH$_2$*CH_2), 3.44 (t, J = 5.9 Hz, 2H, CH_2N*CH$_2$*CH_2CH_2NH), 3.31 (s, 2H, *CH$_2$*$NCH_2CH_2CH_2$NH), 2.69 (dd, J = 6.6, 3.5 Hz, 2H, NHC*CH$_2$*), 1.97 (dd, J = 6.6, 2H, CH_2NCH_2*CH$_2$*CH_2NH), 1.72 (m, 4H, NHCCH_2*CH$_2$CH$_2$*), 1.65 (dt, J = 14.9, 5.2 Hz, 2H, NHC$CH_2CH_2CH_2$*CH$_2$*); **^{13}C{^{1}H} NMR** (125 MHz, CD_3CN) δ: 166.94 (NH*C*CH_2), 54.98 (*CH$_2$*$NCH_2CH_2CH_2$NH), 49.26 (CH_2N*CH$_2$*CH_2CH_2NH), 46.76 (C_{carb}), 46.63 (C_{carb}), 39.04 (NH*CH$_2$*), 33.42 (NHC*CH$_2$*), 29.47 (NHCCH_2*CH$_2$*CH_2), 27.05 (NHC$CH_2CH_2CH_2$*CH$_2$*), 24.52 (NHCCH_2CH_2*CH$_2$*), 19.96 (CH_2NCH_2*CH$_2$*CH_2NH); **^{11}B{^{1}H} NMR** (120 MHz, CD_3CN) δ: 23.46 (s, 2B, B$^{8,8'}$), -3.54 (s, 2B, B$^{10,10'}$), -5.72 (s, 4B, B$^{9,9',12,12'}$), -8.73 (s, 4B, B$^{4,4',7,7'}$), -19.49 (s, 4B, B$^{5,5',11,11'}$), -28.25 (s, 2B, B$^{6,6'}$); **^{11}B NMR** (120 MHz, CD_3CN) δ: 23.46 (s, 2B, B$^{8,8'}$), -3.50 (d, 2B, B$^{10,10'}$), -5.74 (d, 4B, B$^{9,9',12,12'}$), -8.71 (d, 4B, B$^{4,4',7,7'}$), -19.53 (d, 4B, B$^{5,5',11,11'}$), -28.34 (d, 2B, B$^{6,6'}$), **^{31}P{^{1}H}NMR** (202 MHz, CD_3CN) δ: 48.63 (s); **^{31}P NMR** (202 MHz, CD_3CN) δ: 48.62 (s); **ATR-IR (cm^{-1}):** 3383 (ν OH), 3223 (ν NH), 3091 (ν NH), 3026, 2926 (ν CH), 2856(ν CH), 2799 (ν CH), 2545 (ν BH), 1725, 1640, 1607, 1465, 1444, 1363, 1321, 1292, 1205, 1157, 1103, 1076, 978, 936, 910, 887, 836, 747, 690. UV-Vis λ_{max} (nm) 215, 296, 450. **ESI- MS** (m/z): found: 434.20 (calc. for $C_4H_{21}O_3B_{18}P_1S_1Co_1$ 433.78).

*Synthesis of 8,8'-bridged [8,8'-$O_2P(O)S(CH_2)_nOCPh_3$-3,3'-Co(1,2-$C_2B_9H_{10})_2$] $HNEt_3$ S-alkylated phosphorothioates **15** and **16**.* [8,8'-$O_2P(O)SH$-3,3'-Co(1,2-$C_2B_9H_{10})_2$] HDBU (**13**) (13 mg, 0.02 mmol) was dissolved in acetone (0.520 mL) then Et_3N (65 µL, 0.46 mmol) was added under stirring at room temperature. The mixture was heated to 60 °C in an oil bath and then the alkylating agent **3** or **14** (0.04 mmol, dissolved in 130 µL of CH_2Cl_2) was added. The reaction mixture was kept overnight at 60 °C with stirring, then was cooled down to room temperature and solvents were evaporated under reduced pressure. The residue was dispersed in CH_2Cl_2, filtered and the solution was loaded on silica gel column prepared in CH_2Cl_2. The chromatography was performed using a gradient of MeOH in CH_2Cl_2 from 0 to 3% MeOH. **15, Yield:** 90%; **TLC** (silica gel on Al, CH_3CN : $CHCl_3$ 1:2): **Rf:** 0.71; **^{1}H NMR** (500 MHz, CD_3CN): δ 7.41 (d, J = 7.5 Hz, 6H, *H$_{arom}$*), 7.31 (t, J = 7.6 Hz, 6H, *H$_{arom}$*), 7.23 (t, J = 7.2 Hz, 3H, *H$_{arom}$*), 3.67 (s, 4H, *CH$_{carborane}$*), 3.07 (q, J = 7.3 Hz, 6H, N*CH$_2$*CH_3), 3.00 (t, J = 6.0 Hz, 2H $SCH_2CH_2CH_2$*CH$_2$*OTr), 2.78 (dt, 2H, S*CH$_2$*$CH_2CH_2CH_2$OTr), 1.72 (m, J = 7.1 Hz, 2H SCH_2CH_2*CH$_2$*CH_2OTr), 1.64 (m, *J = 6.9* Hz, 2H SCH_2*CH$_2$*CH_2CH_2Otr), 1.21 (t, *J* = 7.3 Hz, 9H, NCH_2*CH$_3$*); **^{13}C{^{1}H} NMR** (126 MHz, CD_3CN): δ 145.55 (3C, *aromatic$_{trityl}$*), 129.54 (6C, *aromatic$_{trityl}$*), 128.87 (6C, *aromatic$_{trityl}$*), 128.01 (3C, *aromatic$_{trityl}$*), 87.30 (1C, O*C(Ph)$_3$*), 63.90 (1C, $SCH_2CH_2CH_2$*CH$_2$*OTr), 47.76 (overlapped 3C, HN*CH$_2$*CH_3, 4C, $CH_{carborane}$), 31.20 (1C, S*CH$_2$*$CH_2CH_2CH_2$OTr), 29.75 (1C, SCH_2CH_2*CH$_2$*CH_2OTr), 28.84 (1C, SCH_2*CH$_2$*CH_2CH_2OTr), 9.29 (1C, NCH_2*CH$_3$*) **^{11}B{^{1}H} NMR** (160 MHz, CD_3CN): δ 23.08 (s, 2B, B$^{8,8'}$), -2.86 (s, 2B, B$^{10,10'}$), -5.54 (s, 4B, B$^{9,9',12,12'}$), -8.36 (s, 4B, B$^{4,4',7,7'}$), -18.87 (s, 4B, B$^{5,5',11,11'}$), -27.70 (s, 2B, B$^{6,6'}$); **^{11}B NMR** (160 MHz, CD_3CN): δ 23.06 (s, 2B, B$^{8,8'}$), -2.87 (d, 2B, B$^{10,10'}$), -5.57 (d, 4B, B$^{9,9',12,12'}$), -8.16 (d, 4B, B$^{4,4',7,7'}$), -18.92 (d, 4B, B$^{5,5',11,11'}$), -27.63 (d, 2B, B$^{6,6'}$); **^{31}P NMR{^{1}H}** (202 MHz, CD_3CN): δ 16.72 (s), 11.37 (s); **^{31}P NMR** (202 MHz, CD_3CN): δ 16.72 (t), 11.37 (t); **ATR-IR (cm^{-1})** 3032 (ν CH aromatic), 2987 (ν CH aliphatic), 2925 (ν CH aliphatic), 2851 (ν CH aliphatic), 2681, 2566 (ν BH), 1727, 1595, 1474, 1447, 1392, 1264, 1200, 1134, 1103, 1068, 1032, 1016, 980, 941, 917, 901, 849, 735 (aromatic CH bending), 705(aromatic CH bending). **UV-Vis** λ_{max} (nm) 196, 299, 440. **ESI-MS** (m/z): found: 748.37 (calc. for $C_{27}B_{18}H_{43}O_4P_1S_1Co_1$: 748.24).

16, Yield: 86%; **TLC** (silica gel on Al, CH_3CN : $CHCl_3$ 1:2) **Rf**: 0.69; **^{1}H NMR** (500 MHz, CD_3CN) δ: 7.43 (m, 6H, *H$_{arom}$*), 7.33 (m, 6H, *H$_{arom}$*), 7.25 (m, 3H, *H$_{arom}$*), 3.67 (s, 4H, *CH$_{carborane}$*), 3.10 (t, J = 6.0 Hz, 2H SCH_2CH_2*CH$_2$*OTr), 3.08 (q, J = 7.3 Hz, 6H, N*CH$_2$*CH_3), 2.97 (dt, J = *14.9*, 7.3 Hz, 2H, PS*CH$_2$*CH_2CH_2OTr), 2.58 (s, 1H, *CH$_3$OH*), 1.27 (t, J = 5.4 Hz, 2H $PSCH_2$*CH$_2$*CH_2OTr), 1.22 (t, J = 7.3 Hz, 9H, NCH_2*CH$_3$*), 1.18 (s, 3H, CH_3OH); **^{13}C{^{1}H} NMR** (126 MHz, CD_3CN) δ: 145.27 (3C, *aromatic$_{trityl}$*), 129.45 (6C, *aromatic$_{trityl}$*), 128.78 (6C, *aromatic$_{trityl}$*), 127.94 (3C, *aromatic$_{trityl}$*), 87.25 (O*C(Ph)$_3$*), 62.71 ($PSCH_2CH_2$*CH$_2$*OTr), 55.13 (4C, *CH$_{carb}$*), 47.64 (HN*CH$_2$*CH_3), 47.59, 32.14, 31.98 (d, J = 6.1), 30.29, 29.66, 28.41 (d, J = 3.8), 9.17 ($HNCH_2$*CH$_3$*); **^{11}B{^{1}H} NMR** (160 MHz, CD_3CN): δ (ppm) 23.08 (s, 2B, B$^{8,8'}$), -2.86 (s, 2B, B$^{10,10'}$), -5.53 (s, 4B, B$^{9,9',12,12'}$), -8.36 (s, 4B, B$^{4,4',7,7'}$), -18.87 (s, 4B, B$^{5,5',11,11'}$), -27.70 (s, 2B, B$^{6,6'}$); **^{11}B NMR** (160 MHz, CD_3CN): δ 23.07 (s, 2B, B$^{8,8'}$), -2.92 (d, 2B, B$^{10,10'}$), -5.60 (d, 4B, B$^{9,9',12,12'}$), -8.38 (d, 4B, B$^{4,4',7,7'}$), -18.98 (d, 4B, B$^{5,5',7,7'}$), -27.88 (d, 2B, B$^{6,6'}$); **^{31}P{^{1}H} NMR** (202 MHz, CD_3CN) δ: 16.54 (s); **^{31}P NMR**

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(202 MHz, CD_3CN) δ: 16.54 (t); **ATR-IR (cm^{-1})** 3032 (ν CH aromatic), 2987(ν CH aliphatic), 2925 (ν CH aliphatic), 2851 (ν CH aliphatic), 2684, 2567 (ν BH), 1699, 1596, 1474, 1447, 1392, 1265, 1200, 1135, 1104, 1066, 1032, 1016, 980, 941, 917, 902, 849, 735 (aromatic CH bending), 705(aromatic CH bending). **UV-Vis** λ_{max} (nm) 194, 299, 436. **ESI-MS** (m/z): 734.35 (calc. for $C_{26}B_{18}H_{41}O_4P_1S_1Co_1$ 734.17).

*Synthesis of 4-[1,3-bis(trityloxy)propan-2-yl-oxy]butyl-4-methylbenzenesulfonate (**20**).* The reaction was performed under argon atmosphere under anhydrous conditions. 1,3-Bis(trityloxy)propan-2-ol (**18**) (2.35 g, 4.07 mmol) was dissolved in 18 mL of anhydrous DMF then $NaH_{60\%}$ (195 mg, 4.87 mmol) was added. After stirring for 15 min 1,4-bis(*p*-toluenesulfonyloxy)butane [40] (4.23 g, 10.63 mmol), dissolved in 18 mL of DMF was added. The reaction mixture was stirred for another 2 h at room temperature then was cooled in ice bath then an excess of NaH was centrifuged. The supernatant was poured into cooled 40 mL of phosphate buffer. The mixture was extracted with AcOEt (4x 100 mL). Organic extracts were combined, washed with H_2O and dried over $MgSO_4$. Solvents were evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using a gradient of AcOEt in hexane from 0% to 10% as eluting solvent system. **Yield:** 27%, **^{1}H NMR** (600 MHz, $CDCl_3$) δ: 7.78 (d, 2H, H_{arom}), 7.41 (d, 12H, H_{arom}), 7.27 (m, 20H, H_{arom}), 4.04 (t, 2H, $OCH_2CH_2CH_2\underline{CH_2}OSO_2$), 3.55 (p, 1H, $TrOCH_2\underline{CHO}CH_2OTr$), 3.48 (t, 2H, $O\underline{CH_2}CH_2CH_2CH_2OSO_2$), 3.23 (ddd, 4H, $TrO\underline{CH_2}CH$), 2.43 (s, 3H, $\underline{CH_3}_{tosyl}$), 1.75 (m, 2H, $OCH_2CH_2\underline{CH_2}CH_2OSO_2$), 1,58 (m, 2H, $OCH_2\underline{CH_2}CH_2CH_2OSO_2$). **^{13}C{^{1}H} NMR** (125 MHz, CD_3CN) δ: 144.62 (1C, $aromatic_{tosyl}$), 144.05 (6C, $aromatic_{trityl}$), 133.19 (1C, $aromatic_{tosyl}$), 129.81 (2C, $aromatic_{tosyl}$,), 128.73 (12C, $aromatic_{trityl}$,), 127.88 (2C, $aromatic_{tosyl}$), 127.76 (12C, $aromatic_{trityl}$), 126.91 (6C, $aromatic_{trityl}$), 86.52 (2C, $O\underline{C(Ph)_3}$), 78.59 (1C, $TrOCH_2\underline{CHO}CH_2OTr$), 70.51 (1C, $OCH_2CH_2CH_2\underline{CH_2}OSO_2$-), 69.47 (1C, $O\underline{CH_2}CH_2CH_2CH_2OSO_2$-), 63.39 (2C, $TrO\underline{CH_2}CH$), 26.10 (1C, $OCH_2CH_2\underline{CH_2}CH_2OSO_2$), 25.86 (1C, $OCH_2\underline{CH_2}CH_2CH_2OSO_2$), 21.64 (1C, CH_3^{tosyl}); **ATR-IR (cm^{-1}):** 3054, 3018, 2946, 2929, 2869, 1978, 1732, 1596, 1488, 1447, 1352, 1304, 1218, 1187, 1172, 1122, 1094, 1065, 1029, 992, 950, 922, 841, 811, 768, 745, 699**; UV-Vis** λ_{max} (nm): 198, 229, 260; **ESI-MS** (m/z**):** found 825.32 $[M+Na]^-$, 841.29 $[M+K]^-$, (calc. for $C_{52}H_{50}O_6S_1$ 803.01).

*Synthesis of 8,8′-bridged {8,8′-$O_2P(O)S[(CH_2)_4OCH(CH_2OCPh_3)_2]$-3,3′-Co(1,2-$C_2B_9H_{10})_2$} $HNEt_3$ (**21**).* [8,8'-$O_2P(O)SH$-3,3'-Co(1,2-$C_2B_9H_{10})_2$] HDBU (**13**) (440 mg, 0.75 mmol) was dissolved in 20 mL of anhydrous acetone then to the resultant solution anhydrous Et_3N (2.15 mL, 15.42 mmol) was added under stirring at room temperature. The mixture was heated to 60 °C then 4-[1,3-bis(trityloxy)propan-2-yl-oxy]butyl-4-methylbenzenesulfonate (**20**) (901 mg, 1.12 mmol) dissolved in 20 mL of anhydrous AcOEt was added dropwise. After stirring overnight at 60 °C the mixture was cooled down and solvents evaporated under reduced pressure. The residue was dispersed in CH_2Cl_2, filtered and the filtrate was loaded to the silica gel column prepared in CH_2Cl_2. The chromatography was performed using a gradient of CH_3OH in CH_2Cl_2 from 0 to 3% of CH_3OH. **Yield:** 560 mg 64% **TLC** (silica gel on Al, CH_3CN:$CHCl_3$ 1:2), **R_f** = 0.60, **^{1}H NMR** (600 MHz, CD_3CN) δ: 7.41 (d, 12H, $H_{aromatic}$), 7.31 (m, 18H, $H_{aromatic}$), 3.70 (s, 4H, $\underline{CH}_{carborane}$), 3.60 (p, 1H, $TrOCH_2\underline{CHO}CH_2OTr$), 3.45 (t, 2H, $PSCH_2CH_2CH_2\underline{CH_2}O$), 3.19 (ddd, 4H, $CHO\underline{CH_2}OTr$), 3,10 (q, 6H, $HN\underline{CH_2}CH_3$), 2.85 (dt, 2H, $PS\underline{CH_2}CH_2CH_2CH_2O$), 1.71 (m, 2H, $PSCH_2CH_2\underline{CH_2}CH_2O$), 1.61 (m, 2H, $PSCH_2\underline{CH_2}CH_2CH_2O$), 1.24 (t, 9H, $NCH_2\underline{CH_3}$) **^{13}C{^{1}H} NMR** (125 MHz, CD_3CN) δ: 144.73 (6C, $aromatic_{trityl}$), 129.10 (12C, $aromatic_{trityl}$), 128.41 (12C, $aromatic_{trityl}$), 127.60 (6C, $aromatic_{trityl}$), 86.89 (2C, $O\underline{C(Ph)_3}$), 78.47 (1C, $TrOCH_2\underline{CHO}CH_2OTr$), 69.92 (1C, $PSCH_2CH_2CH_2\underline{CH_2}O$), 63.66 (2C, $CHO\underline{CH_2}OTr$), 47.28 (3C, $HN\underline{CH_2}CH_3$), 47.18 (4C, $\underline{CH}_{carborane}$), 31.89 (1C, $PS\underline{CH_2}CH_2CH_2CH_2O$), 22.93 (1C, $PSCH_2CH_2\underline{CH_2}CH_2O$), 13.96 (1C, $PSCH_2\underline{CH_2}CH_2CH_2O$), 8.80 (3C, $HNCH_2\underline{CH_3}$) **^{11}B{^{1}H} NMR** (120 MHz, CD_3CN) δ: 23.02 (s, 2B, $B^{8,8'}$), -3.04 (s, 2B, $B^{10,10'}$), -5.67 (s, 4B, $B^{9,9',12,12'}$), -8.55 (s, 4B, $B^{4,4',7,7'}$), -19.07 (s, 4B, $B^{5,5',11,11'}$), -27.99 (s, 2B, $B^{6,6'}$). **^{11}B NMR** (120 MHz, CD_3CN) δ: 23.02 (s, 2B, $B^{8,8'}$), -2.98 (d, 2B, $B^{10,10'}$), -5.64 (d, 4B, $B^{9,9',12,12'}$), -8.19 (d, 4B, $B^{4,4',7,7'}$), -19.05 (d, 4B, $B^{5,5',11,11'}$), -27.99 (d, 2B, $B^{6,6'}$). $^{31}P\{^1H\}$NMR (202 MHz, CD_3CN) δ (ppm) 16.49 (s); **^{31}P NMR** (202 MHz, CD_3CN) δ: 16.48(t); **ATR-IR (cm^{-1}):** 3031, 2929, 2870, 2564, 2564, 2161, 1978, 1644, 1595, 1489, 1447, 1322, 1202, 1134, 1096, 1031, 940, 899, 848, 763, 747, 697; **UV-Vis** λ_{max} (nm): 196, 233, 299, 453; **MS (ESI)** (m/z): found 1064.52 (calc. for $C_{49}B_{18}H_{63}O_6P_1S_1Co_1$ 1064.59)

*Synthesis of 8,8′-bridged {8,8′-$O_2P(O)S[(CH_2)_4OCH(CH_2OCPh_3)_2]$-3,3′-Co[1-$(CH_2)_2$OH-1,2-$C_2B_9H_{10})$](1′,2′-$C_2B_9H_{10})$} $HNEt_3$ (**22**) and {8,8′-$O_2P(O)S[(CH_2)_4OCH(CH_2OCPh_3)_2]$-3,3′-Co[1-$(CH_2)_2$OH-1,2-$C_2B_9H_{10})$] [1′-$(CH_2)_2$OH-1′,2′-$C_2B_9H_{10})$]} $HNEt_3$ (**23**).*Compound **21** (175 mg, 0.15 mmol) was dried

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by co-evaporation with anhydrous benzene and then kept under vacuum over P_2O_5 overnight. Next it was dissolved in anhydrous DME (3 mL) and the solution was cooled in CO_2/isopropanol cooling bath. After 15 min. n-BuLi (140 μL, 1.6 M solution in hexane, 1.5 eq) was added and the reaction mixture was stirred for 10 min. After that time, cooling bath was removed and the mixture was stirred for next 10 min. Then the reaction mixture was cooled again in cooling bath and another portion of n-BuLi (140 μL) was added. After 15 min, ethylene oxide (200 μL, 2.9-3.1 M solution in THF)) was added and the reaction was left overnight in cooling bath. Next CH_2Cl_2 (5 mL) was added to the reaction mixture, the reaction was quenched by addition of water and then the organic solution was washed three times with 5 mL portions of water. Organic layer was separated and dried over $MgSO_4$ then solvents were evaporated. Crude product was purified and mono- and bis-substituted products separated by silica gel column chromatography using a gradient of MeOH in CH_2Cl_2 from 0 to 3% of MeOH. **22**, **Yield**: 17 mg (10 %); **TLC** (silica gel on Al, 8% MeOH/CH_2Cl_2): **R_f**: 0.13; **^{1}H NMR** (500 MHz, CD_3CN): δ (ppm) 7.41 (d, 12H, $H_{aromatic}$), 7.31 (m, 18H, $H_{aromatic}$), 3.90 (s, $CH_{carborane}$), 3.78 to 3.54 (m, overlapped, $CH_{carborane}$, HO$CH_2$$CH_2C_{carb}$, TrO$CH_2$$CHOCH_2$OTr), 3.44 (t, 2H, PS$CH_2$$CH_2CH_2CH_2$$CH_2$O-), 3.19 (ddd, 4H, CHO$CH_2$OTr), 3.02 to 2.64 (m, overlapped, PS$CH_2$$CH_2CH_2CH_2$O-, HO$CH_2$$CH_2C_{carb}$), 1.65 (m, 4H, overlapped, PS$CH_2$$CH_2CH_2$$CH_2$O); **^{11}B{^{1}H} NMR** (120 MHz, CD_3CN) δ (ppm) 25.37, 24.65, 23.69, 22.93 (in ratio 2:2:1:1) 26.6 to 21.37 (m, overlapped diastereoizomeric $B^{8,8'}$), 0.52 to -11.61 (m, overlapped diastereoizomeric, $B^{10,10',9,9',12,12',4,4',7,7'}$), -12.05 to -11.61 (d, overlapped diastereoizomeric $B^{5,5',11,11'}$), -21.45 to -28.25 (s, overlapped diastereoizomeric $B^{6,6'}$); **^{11}B NMR** (120 MHz, CD_3CN) δ (ppm) 27.17 to 21.57 (m, overlapped diastereoizomeric $B^{8,8'}$), 2.85 to -11.77 (m, overlapped diastereoizomeric, $B^{10,10',9,9',12,12',4,4',7,7'}$), -11.82 to -21.00 (d, overlapped diastereoizomeric $B^{5,5',11,11'}$), -21.10 to -29.92 (s, overlapped diastereoizomeric $B^{6,6'}$); **^{31}P{^{1}H}NMR** (202 MHz, CD_3CN) δ: 14.94, 14.58, 14.43, 14.12, 13.49 (in ratio: 4:1:2:1.5:15); **^{31}P NMR** (202 MHz, CD_3CN) δ: 14.94(t), 14.42 (t), 14.12 (t), 13.49 (t**); ATR-IR (cm^{-1}):** 3630, 3370, 3057, 3031, 2925, 2869, 2565, 2161, 1979, 1596, 1489, 1448, 1255, 1202, 1128, 1077, 1032, 985, 898, 871, 763, 746, 699; **ESI-MS** (m/z): found: 1108.54 m/z (calc. for $C_{51}B_{18}H_{67}O_7P_1S_1Co_1$ 1108.64).

23, **Yield:** 21 mg (12%); **TLC** (silica gel on Al, 8% MeOH/CH_2Cl_2): **R_f:** 0.27; **^{1}H NMR** (500 MHz, CD_3CN) δ: 7.40 (d, 12H, $H_{aromatic}$), 7.31 (m, 18H, $H_{aromatic}$), 3.84 to 3.51 (m, overlapped, $CH_{carborane}$, HO$CH_2$$CH_2$-, TrO$CH_2$$CHO$$CH_2$OTr,), 3.44 (t, 2H, PS$CH_2$$CH_2CH_2$$CH_2$O-), 3.18 (ddd, 4H, CHO$CH_2$OTr), 3.12 to 2.66 (m, overlapped, PS$CH_2$$CH_2CH_2CH_2O, HOCH_2$$CH_2C_{carborane}$,), 1.65 to 1.55 (m, 4H, overllaped, PS$CH_2$$CH_2CH_2$$CH_2$O); **^{11}B{^{1}H} NMR** (120 MHz, CD_3CN) δ: 25.36, 24.41, 23.65, 22.80, 22.23 (in ratio 1:2:1.5:1:1) 26.59 to 20.45 (m, overlapped diastereoizomeric $B^{8,8'}$), 2.75 to -12.40 (m, overlapped diastereoizomeric, $B^{10,10',9,9',12,12',4,4',7,7'}$), -12.34 to -24.64 (m overlapped diastereoizomeric $B^{5,5',11,11'6,6'}$); **^{11}B NMR** (120 MHz, CD_3CN) δ: 26.65 to 20.21 (m, overlapped diastereoizomeric $B^{8,8'}$), 2.32 to -12.88 (m, overlapped diastereoizomeric, $B^{10,10',9,9',12,12',4,4',7,7'}$), -12.84 to -25.84 (m overlapped diastereoizomeric $B^{5,5',11,11'6,6';}$); **^{31}P{^{1}H}NMR** (202 MHz, CD_3CN) δ: 15.00, 14.16, 14.02, 13.38 (in ratio 5:1:3:1); **^{31}P NMR** (202 MHz, CD_3CN) δ: 15.99(t), 14.40 (s), 14.01 (t), 13.38 (t); **ATR-IR (cm^{-1}):** 3566, 3357, 3056, 3027, 2920, 2889, 2857, 2565, 2166, 1596, 1489, 1448, 1291, 1255, 1201, 1120, 1078, 1032, 1001, 889, 871, 764, 746, 699 **ESI-MS** (m/z): found: 1152.57 (calc. for $C_{53}B_{18}H_{71}O_8P_1S_1Co$ 1152.69).

5. Conclusions

Although derivatives of metallocarboranes containing various, simple substituents attached to the boron or carbon atoms of the complex carboranyl ligands are abundant, they usually do not allow further chemical transformations. One of the notable exceptions are the adducts of some metallacarboranes and cyclic ethers. In this work, we propose methods that attempt to, at least partially, fill this gap by using extendable ligands

The exploitation of the icosahedral metallacarborane's immense potential in various fields of chemistry and technology requires the availability of convenient and versatile methods for their modification with various functional moieties and/or linkers of various type and length. Herein we report a convenient approach to introduce extendible arms on 8,8'-dihydroxy cobalt bis(1,2-dicarbollide). The approach can be used to introduce different hetero-bifunctional electrophiles containing protected hydroxyl function allowing further modification.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org, MS, ^{1}H-, ^{13}C-, ^{11}B-NMR spectra of compounds **6**-**13**, **15**,**16**, **20**-**23**; ^{31}P-NMR spectra of compounds **12**, **13**, **15**, **16**, **21**-**23**, FT-IR spectra of compounds **12**, **13**, **15**, **16**, **22**, **23**.

Author Contributions: Conceptualization, investigation, data curation, writing—original draft preparation, KS; conceptualization, investigation, data curation, writing—original draft preparation, CS; conceptualization, validation, formal analysis, investigation, data curation, writing—review and editing, supervision, project administration, funding acquisition, ZL.

Funding: This work was supported in part by the National Science Center, Poland, grant 2015/16/W/ST5/00413.

Acknowledgments: The electrospray ionization (ESI) mass spectra for **10**-**13**, **15**, **16**, **21**-**23**, were recorded on Agilent 6546 LC/Q-TOF at the National Library of Chemical Compounds (NLCC) established within the project POL-OPENSCREEN financed by the Ministry of Science and Higher Education (decision no. DIR/WK/2018/06 of October 24, 2018). The authors thank Ms. Dorota Borowiecka and Ms. Agata Kraj of NLCC for recording the mass spectra.

Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: Samples of the new compounds synthesized in this work are available from the authors.

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