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Metallacarboranes as Building Blocks for Polyanionic Polyarmed Aryl-Ether Materials

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Polyanionic species have been obtained in high yield by a new route in the ring-opening reaction of cyclic oxonium [3,3′-Co(8-$C_4H_8O_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (**2**) by using carboxylic acids, Grignard reagents, and thiocarboranes as nucleophiles. The crystal structures of $Na_3(H_2O)(C_2H_5OH)$[1″,3″,5″-{3,3′-Co(8-O(CH_2CH_2O)$_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)}$_3$-C_6H_3] and $Na(H_2O)$[3,3′-Co(8-O(CH_2CH_2O)$_2$C(O)CH_3-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] show that the chain contributes three or two oxygen atoms for coordination to Na^+, and interestingly, the [3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$]$^-$ moiety provides extra B−H coordination sites. These B−H···Na interactions in the solid state have also been confirmed by dynamic NMR studies in solution. These new polyanionic compounds that contain multiple carborane or metallacarborane clusters at their periphery may prove useful as new classes of boron neutron capture therapy compounds with enhanced water solubility and as a core to make a new class of dendrimers.

Introduction

The derivative chemistry of the most intensively studied anionic borate cluster, the cobaltabisdicarbollide [3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$]$^-$, **1**, remains very much unexplored.[1] The fundamental reason is the synthetic strategy leading to these derivatives. Two basic substitutions may occur on [3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$]$^-$, either on carbon or on boron. With few exceptions,[2] substitutions on carbon have been achieved only at an early stage of the synthetic process, that is, on the starting *o*-carborane,[3] but not by direct reaction at the [3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$]$^-$ cage. Substitution at boron has been achieved under Friedel−Crafts conditions[4] or with strong alkylating agents.[5] Consequently, regioselective substitutions were not possible, and specific derivatives could be obtained only after careful separations of complex mixtures. The high yield synthesis and easy preparation of the zwitterionic 8-dioxanate [3,3′-Co(8-$C_4H_8O_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)], **2**, derivative has been reported.[6,7] Compound **2** has been proven to be susceptible to nucleophilic attack on the positively charged oxygen atom, for example, by pyrrolyl,[8] imide, cyanide or amines,[9] phenolate, dialkyl or diarylphosphite,[10] N-alkylcarbamoyldiphenylphosphine oxides,[3d] alkox-

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ides,[7,11] and nucleosides,[12] resulting in one anionic species formed by the opening of the dioxane ring. A recent review[13] covers the known scope of reactions of different oxonium derivatives of polyhedral boron hydrides. The ring-opening reactions of cyclic oxonium derivatives of polyhedral boron hydrides with sulfur nucleophiles are rare and include the ring-opening reactions of cyclic oxonium derivatives of the *closo*-dodecaborate[14] and *closo*-decaborate anions with dihydrosulfide.[15] The tetramethylene oxonium *closo*-dodecaborate anion reacts with lithium derivatives of carboranes, giving the dianionic $[C_2B_{11}]-[B_{12}]$ double-cage boron compounds.[16]

Cobaltabisdicarbollide **1** has been proposed in a wide range of applications, such as the extraction of radionuclides,[3b−d,17] in conducting organic polymers,[18] or a use in medicine.[19] Recently, the construction of high-boron-content molecules has received considerable interest.[20] At the same time, the introduction of carboranes into different types of dendrimeric structures, at the inner region or at the surface of the molecules, is also being explored.[21] The design of water-soluble boron-rich dendritic or macromolecular systems is of interest for boron neutron capture therapy (BNCT) or for drug delivery systems. The *closo*-carboranes have been tested for boron delivery into tumors; however, their extreme lipophilicity often produces water-insoluble structures with limited bioavailability, precluding thus effective application of such compounds in BNCT. One solution to the problem of the water solubility of BNCT agents could be to replace a neutral carborane with an anionic metallacarborane.

Following our studies on metallacarboranes' direct substitution, we report herein on the high-yield synthesis of polyanionic species as novel high-boron-content molecules with enhanced water solubility. The synthetic ways were based on the use of carboxylic acid, Grignard reagents, and thiocarboranes as nucleophiles in the ring-opening reaction of cyclic oxonium $[3,3'\text{-Co}(8\text{-}C_4H_8O_2\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ (**2**). The crystal structures of $Na_3(H_2O)(C_2H_5OH)[1'',3'',5''\text{-}\{3,3'\text{-Co}(8\text{-O}(CH_2CH_2O)_2\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})\}_3\text{-}C_6H_3]$, $[N(CH_3)_4][3,3'\text{-Co}(8\text{-O}(CH_2CH_2O)_2C(O)C_6H_5\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$, and $Na(H_2O)[3,3'\text{-Co}(8\text{-O}(CH_2CH_2O)_2C(O)CH_3\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ are also reported.

Results and Discussion

Synthesis and Characterization of Monosubstituted Cobaltabisdicarbollide Derivatives Incorporating Three or Four Ether Groups in the *exo*-Cluster Chain. We were interested in exploring the possibility of using both known and new types of nucleophiles to get high-boron-content compounds. Although a large range of nucleophiles has already been investigated in boron clusters, we aimed to use other compounds to compare their nucleophilicity. To learn about the nucleophilic character of carboxylic acids, Grignard reagents, and thiocarboranes in the ring-opening reaction of cyclic oxonium $[3,3'\text{-Co}(8\text{-}C_4H_8O_2\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$, **2**, we have synthesized ligands incorporating both the $(OCH_2CH_2)_2R$ chain and the $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$ moiety. Chart 1 shows the anionic species synthesized from the zwitterionic **2** according to Scheme 1.

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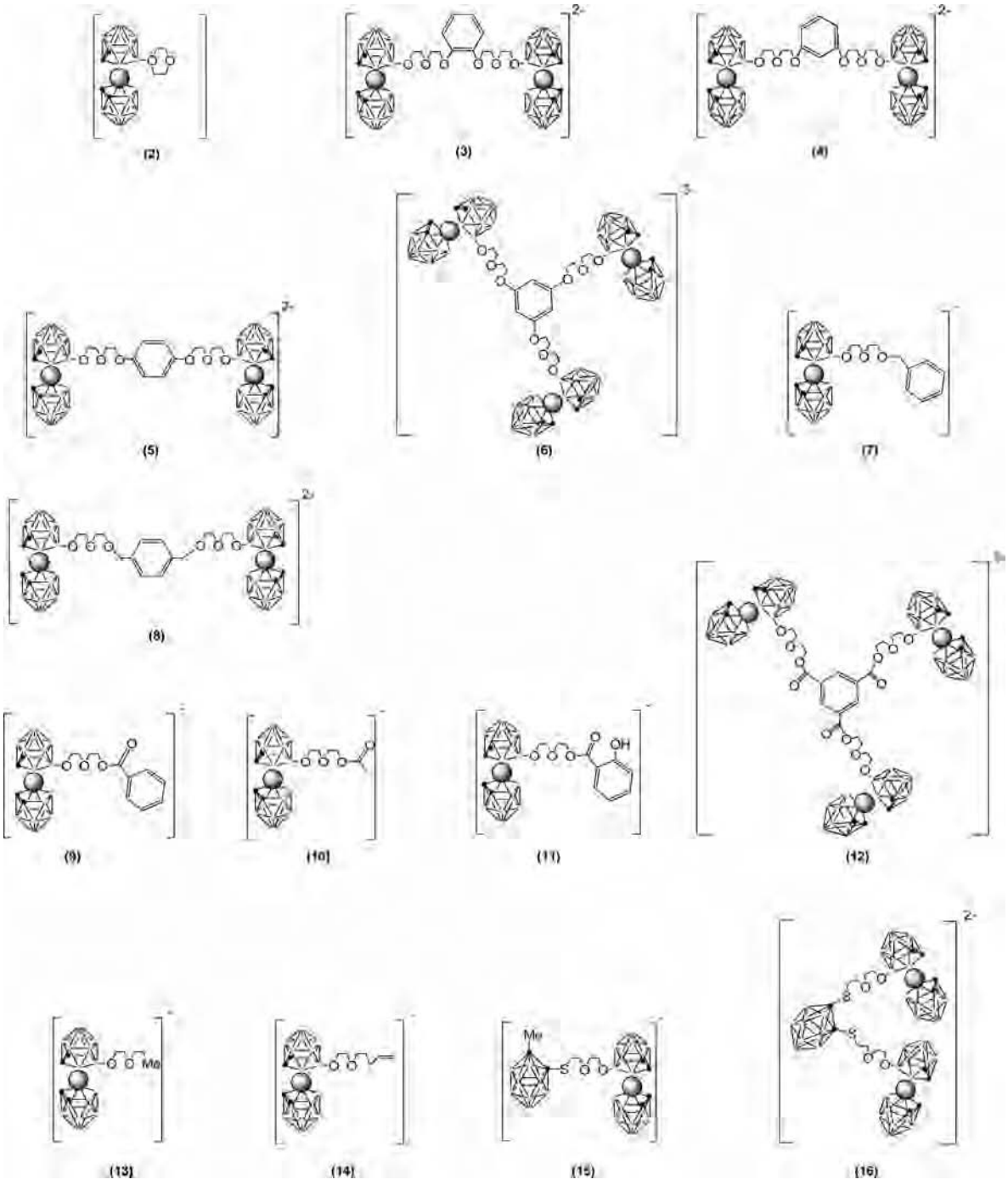
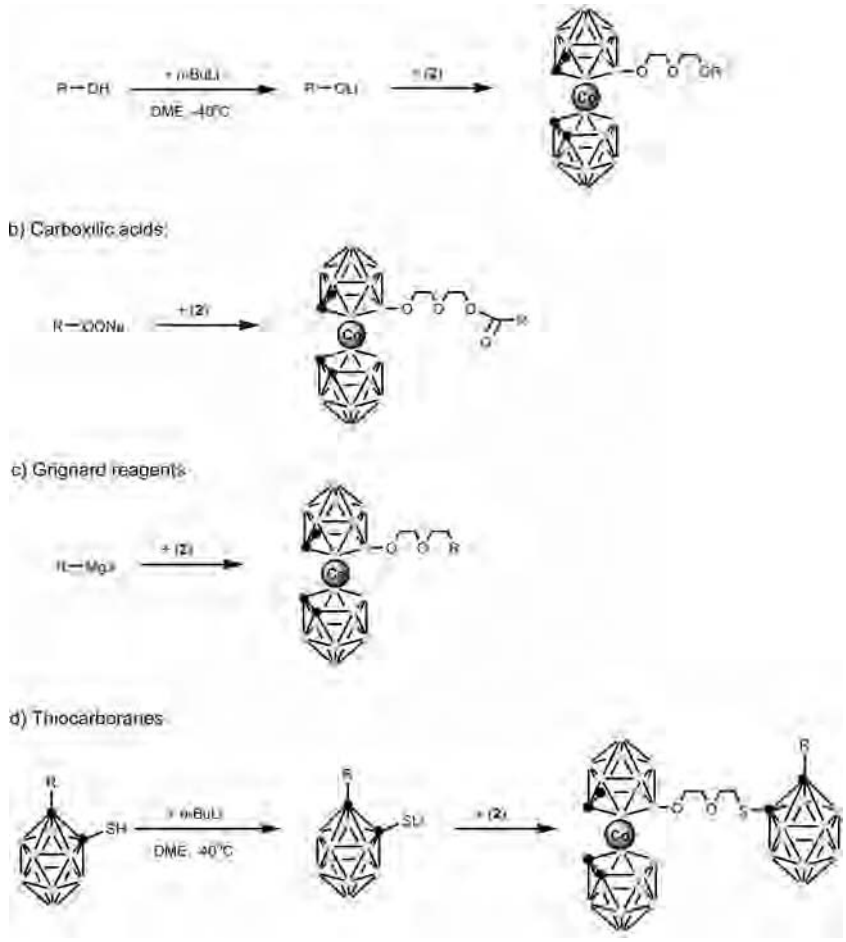
Chart 1. Monosubstituted **2**−**16** Anions



In order to enchance the nucleophilic character of the alcohols and thiocarboranes, we used *n*-BuLi to deprotonate the nucleophile. The addition of the base was done dropwise at low temperatures, and it was left stirring for 1 h. Afterward, the reaction was cooled down again to −40 °C, followed by the addition of **2**. After stirring overnight, the compounds (**3**−**8** and **15** and **16**) were isolated either by evaporation of the solvent or by a cationic metathesis to tetramethylammonium salts, getting in all cases orange solids as the final product. For the organic carboxylic acids, their salts were used as nucleophiles, whereas the Grignard reagents were used as obtained. For these cases, the reagents were mixed together, and after stirring overnight, the compounds (**9**−**14**) were isolated by evaporation of the solvent or by cationic exchange. As the reactivity of Grignard reagents is very high and to prevent the formation of undesired side products, their addition was done dropwise at low temperatures.

The nature of anions **3**−**16** with cations like $[N(CH_3)_4]^+$, Li^+, and Na^+ has been corroborated by elemental analysis, matrix-assisted laser desorption/ionization−time of flight mass spectrometry (MALDI-TOF-MS); IR; and ^1H, $^1H\{^{11}B\}$, $^{13}C\{^1H\}$, ^{11}B, and $^{11}B\{^1H\}$ NMR spectroscopies. For $Na_3[\mathbf{6}]\cdot H_2O\cdot C_2H_5OH$, $[N(CH_3)_4][\mathbf{9}]$ and $Na_2[\mathbf{10}]_2\cdot 2H_2O$, the solid-state X-ray crystal structures were also determined.

Scheme 1. Opening of the *exo*-Cluster Dioxanate Ring Reaction by Nucleophilic Attack[a]



[a] Atoms in black are CH vertexes, the rest of the vertices in the clusters are BH.

Table 1. $^{11}B\{^1H\}$ NMR Spectra (all in ppm) of B(8) Monosubstituted Derivatives of $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$[a]

1	6.5B(8,8′)		1.4B(10,10′)		−6.0 B(4,4′,7,7′,9,9′,12,12′)			−17.2 B(5,5′,11,11′)		−22.7 B(6,6′)		<δ> −8.1
	24.6	8.4	4.9	−2.7	−4.1	−8.0	−9.3	−15.0	−18.5	−20.8	−26.5	
2	*B(8)*	B(8′)	B(10)	B(10′)	B(4′,7′)	B(4,7)	B(9,9′,12,12′)	B(5′,11′)	B(5,11)	B(6)	B(6′)	−7.8
3	*25.5*	6.4	2.8	−0.2	−2.0	−5.0	−5.9	−15.1	−18.2	−19.5	−26.3	−6.4
4	*25.3*	6.3	2.8	−0.1	−1.8	−5.1	−5.8	−14.9	−18.0	−19.5	−26.0	−6.3
5	*25.2*	6.2	2.8	−0.1	−1.7	−5.1	−5.8	−14.9	−18.0	−19.5	−26.0	−6.3
6	*25.3*	6.3	2.8	−0.1	−1.9	−5.1	−5.8	−14.9	−18.1	−19.6	−26.1	−6.4
7	*25.0*	5.9	2.7	−0.2	−1.9	−5.2	−6.0	−15.0	−18.2	−19.5	−26.2	−6.5
8	*25.2*	6.2	2.7	−0.2	−1.9	−5.1	−5.9	−15.0	−18.2	−19.5	−26.2	−6.8
9	*30.3*	11.3	7.9	5.0	3.3	0.0	−0.8	−9.8	−12.9	−14.4	−21.0	**-1.6**
10	*30.5*	11.5	7.9	5.1	3.3	−0.1	−0.7	−9.7	−12.8	−14.3	−20.9	**-1.2**
11	*25.3*	6.3	2.6	−0.2	−2.1	−5.2	−6.1	−15.1	−18.3	−19.8	−26.5	−6.6
12	*23.6*	4.7	1.1	−1.8	−3.5	−6.7	−7.5	−16.5	−19.7	−21.2	−27.6	**-8.0**
13	*25.2*	6.3	2.7	−0.2	−1.9	−5.1	−5.9	−14.9	−18.0	−19.5	−26.1	−6.4
14	*22.8*	3.7	−0.4	−2.5	−4.1	−7.5	−8.3	−17.3	−20.5	−21.9	−28.4	**-8.8**

[a] In each column, the number of boron atoms is preserved. In italics are represented the resonances due to B−O. <δ> is the mean value of the ^{11}B NMR spectrum for each compound.

NMR Spectral Considerations. The $^{11}B\{^1H\}$ NMR spectra of anions **3**−**16** featured an identical 1:1:1:1:2:2:4:2:2:1:1 pattern ranging from +31 to −28 ppm. The $^{11}B\{^1H\}$ NMR of **2** and monosubstituted **3**−**16** anions, except for the carborane-containing molecules, are shown in Table 1. The resonance at the lowest field remains as a singlet in the ^{11}B NMR spectrum, corresponding to the B(8) substituted boron atom. The mean value <δ> of the ^{11}B NMR spectrum of each compound is also presented in Table 1. This value represents the electronic effect of the B(8) substituent in the cluster. The <δ> of $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$, **1**, is −8.1, and the introduction of the dioxane moiety in the zwiterionic species **2** produces a deshielding of 0.3 ppm due to the withdrawing effect of the B−O bond. When the ring opening has taken place, a <δ> value in the range −6.3 to −6.8 is observed for most of the compounds except for **9**, **10**, **12**, and **14**.

The observed ^{11}B NMR pattern, 1:1:1:1:2:2:4:2:2:1:1, reflects the C_s symmetry of the molecules (12 different signals). The boron resonance with a relative intensity of 4 is due to a coincidental overlap of two resonances with a

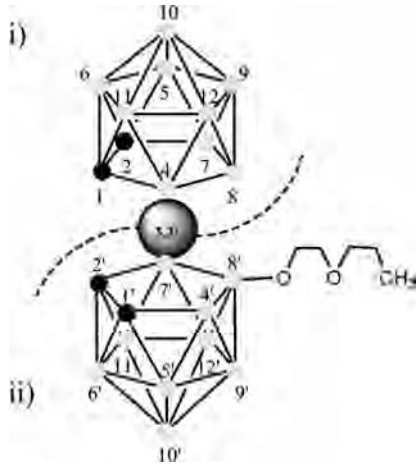


Figure 1. The $^{11}B\{^1H\}$ NMR spectrum of **13** is the result of the addition of the two individual halves: i + ii. Vertexes numbering for **13**.

2:2 relative intensity. The $^{11}B\{^1H\}$ NMR of [3,3′-Co(1,2-$C_2B_9H_{11})_2$]$^-$ displays five resonances in the range +6.5 to −22.7 ppm with a 2:2:8:4:2 pattern, in agreement with an averaged C_{2v} symmetry. The ^{11}B NMR chemical shifts' assignments of [3,3′-Co(1,2-$C_2B_9H_{11})_2$]$^-$ were determined by 2D $^{11}B\{^1H\}-^{11}B\{^1H\}$ COSY spectroscopy and correspond to B(8,8′), B(10,10′), B(4,4′,7,7′,9,9′,12,12′), B(5,5′,11,11′), and B(6,6′) from low to high field.[22] The incorporation of one substituent at position B(8) lowers the symmetry to C_s, maintaining only one symmetry plane and making the two dicarbollide moieties no longer equivalent. A stick representation of the chemical shifts and relative intensities in the $^{11}B\{^1H\}$ NMR spectra of [3,3′-Co(1,2-$C_2B_9H_{11})_2$]$^-$ and **13** are shown in Figure S.1 (Supporting Information).We have reported[7,11] that the ^{11}B NMR spectrum of monosubstituted derivatives of [3,3′-Co(1,2-$C_2B_9H_{11})_2$]$^-$ is the result of the plain addition of the two individual halves, as schematized in Figure 1. As an example, the $^{11}B\{^1H\}$ NMR of Cs[3,3′-Co(8-$(OCH_2CH_2)_2CH_3$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (**13**) is the addition of the $^{11}B\{^1H\}$ NMR of the parent Cs[3,3′-Co(1,2-$C_2B_9H_{11})_2$] plus the spectrum of [3,3′-Co((8,8′-$(OCH_2CH_2)_2CH_3)_2$-1,2-$C_2B_9H_{10})_2$]$^-$. The spectrum of Cs[3,3′-Co(1,2-$C_2B_9H_{11})_2$] displays resonances at 6.5(1), 1.4(1), −6.0(4), −17.2(2), and −22.7(1) ppm, and the spectrum of Cs[3,3′-Co(8-$(OCH_2CH_2)_2CH_3$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (**13**) displays resonances at 25.2(1), 6.3(1), 2.7(1), −0.2(1), −1.9(2), −5.1(2), −5.9(4), −14.9(2), −18.0(2), −19.5(1), and −26.1(1) ppm. If resonances attributable to the unsubstituted ligand, showing only minor shifts in respect to parent Cs[3,3′-Co(1,2-$C_2B_9H_{11})_2$], are removed, the resonances of the unknown disubstituted [3,3′-Co(8,8′-$(OCH_2CH_2)_2CH_3)_2$-1,2-$C_2B_9H_{10})$]$^-$ ligand could be clearly distinguished and assigned at 25.2(1), −0.2(1), −1.9(2), −5.1(2), −14.9(2), and −19.5(1) ppm. The 1:1:2:2:2:1 pattern is consistent with a C_s fragment symmetry, and the high chemical shift value at 25.2 strongly supports assignment to B(8)−O−.

Stuctures of the Salts in the Solid State. Red crystals, suitable for X-ray diffraction structure determination, were obtained from diffusion crystallization using a CH_2Cl_2/C_2H_5OH/*i*-octane system. Interesting features in the structure (Figure 2 and Table S.1, Supporting Information) consist of the coordination of three sodium atoms. This evidence, species **6** exists in solution and in the solid state as the true trivalent anion, points to no possible exchange of sodium for the proton having occurred even after aqueous treatment. This can be assumed to be a result of the relatively tight coordination of each sodium atom by all three oxygens (with the exception of Na2, where the distance Na2−O4 is unbonding) present in ethyleneglycol chains. Another coordination site is formed by B(8′)− and B(4′ or 7′)−H···Na bonding interactions. Along with a few univalent anion structures where B(8′)−H···M$^+$ (M = Na$^+$ or K$^+$) bonds were present,[7,10] this is the most convincing example of high hydrolytic stability of this kind of coordination. The coordination sphere of sodium atom Na1 is completed by a molecule of ethanol. One molecule of water is coordinated to the Na2 sodium atom, replacing coordination by the O4 oxygen from the trihydroxybenzene, which remains at a long unbonded distance (2.757 Å).

Crystallization by slow diffusion of a dichloromethane solution of [$N(CH_3)_4$][**9**] at room temperature afforded air- and moisture-insensitive red single crystals suitable for X-ray analysis, which confirmed the proposed structure of [$N(CH_3)_4$][**9**]. A drawing of the compound is shown in Figure 3, and selected bond lengths and angles are listed in Table S.2 (Supporting Information). The cation and the anion are held together by electrostatic forces. Weak H bonds (C2H2···O4^i and C2′H2′···O4^i, i = 1/2 + x, 1/2 − y, 1/2 + z) can be found. Other weak interactions are BH···C(phenyl) and BH···H and CH···H contacts.

Crystallization by the slow diffusion of a toluene solution of Na[**10**] at room temperature afforded air- and moisture-insensitive yellow needle-shaped single crystals suitable for X-ray analysis, which revealed that the polymeric structure with dinuclear [$Na_2(H_2O)_2$(**10**)$_2$] units had formed (the compound is named as Na_2[**10**]$_2\cdot 2H_2O$ in the text). A drawing of the dinuclear unit with the extra O4 and C17 atoms which are part of the molecules that link the dinuclear units to polymers is shown in Figure 4, and selected bond lengths and angles are listed in Table S.3 (Supporting Information). The ligand [**10**]$^-$ coordinates as a tetradentate ligand in the solid state. Also, two bridging water molecules bond to the sodium cation that has a distorted octahedral coordination sphere. The distortions in bonding are due to a rigid carborane polyether ligand. It is typical for Na$^+$ to use two bridged water molecules to fullfil its coordination sphere (88 hits in the Cambridge Structural Database, CSD, version 5.29, November 2007).

The Na−O1 and Na−O2 bonds are 2.393(3) Å and 2.362(3) Å, respectively. Due to the negative charge of the ligands, the sodium is bonded quite tightly to the ligand's oxygen atoms. For example, the shortest Na−O distances in the dinuclear [Na(L)]I compound are 2.375 and 2.395 Å, whereas there are several longer Na−O bonds (L = cyclic polyether).[23]

(22) Janousek, Z.; Plesek, J.; Hermanek, S.; Base, K; Todd, L. J.; Wright, W. F. *Collect. Czech. Chem. Commun.* **1981**, *46*, 2818.

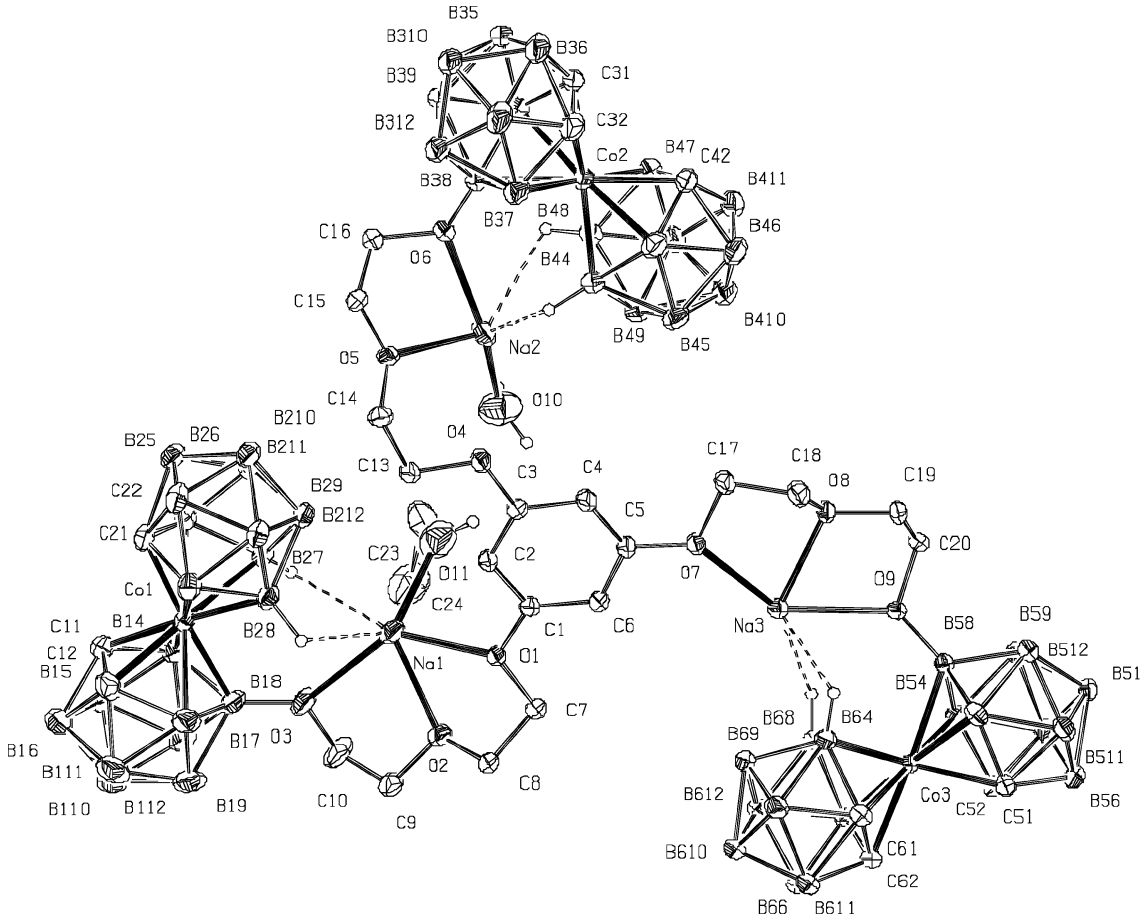


Figure 2. Overall view on the Na_3[**6**]·H_2O·C_2H_5OH salt. The displacement ellipsoids are drawn on the 30% probability level (PLATON).

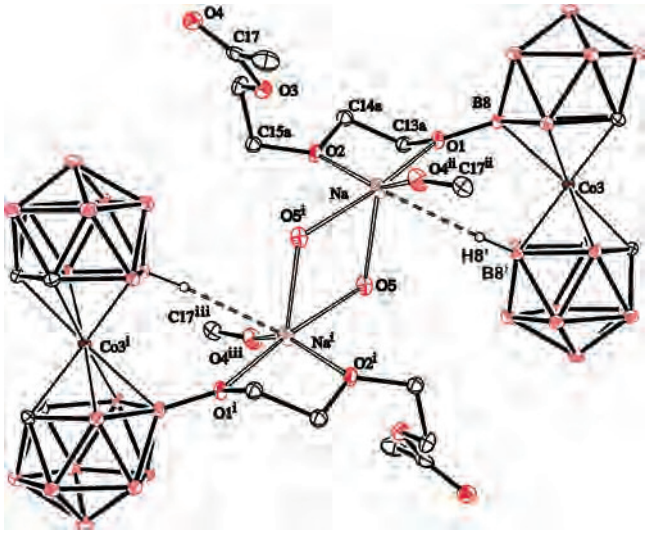


Figure 3. Solid-state structure of $[N(CH_3)_4]$[**9**]. From the disordered alkyl chain, only the main conformer (74%) is depicted.

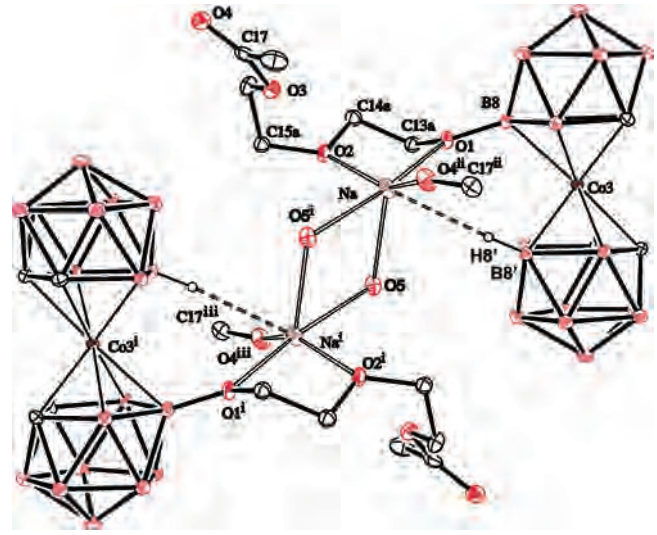


Figure 4. Dinuclear structural motif of Na_2[**10**]$_2$·$2H_2O$. Hydrogens are omitted for clarity (except H8′). From the disordered alkyl chain, only the main conformer (75%) is depicted. Half of the molecule has been generated by inversion ($i = -x, 1 - y, -z$). Also, a part of the coordinating ester group (O4 and C17) with symmetry operations $ii = -1/2 - x, -1/2 + y, z$ and $iii = 1/2 + x, 11/2 + y, -z$ is presented.

The packing in Na_2[**10**]$_2$·$2H_2O$ is dominated by the shortest Na−O4(ester carbonyl) bond, 2.327 Å (that causes polymerization), from the neighbor molecule and weak van der Waal's interactions.

Coordination in Solution. Although definitive evidence for B−H···Na^+ interactions in the solid state is given by the X-ray analysis of the sodium salt of **10**, no proof of its existence in solution has been found in the $^1H\{^{11}B\}$ NMR spectrum at room temperature. We have run low-temperature experiments with the aim of freezing out the more stable rotamers and fixing specific B−H···Na^+ interactions. How-

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ever, we have noticed that even at room temperature the compound is extremely dependent upon the solvent. Figure S.2 (Supporting Information) shows a comparison between $^1H\{^{11}B\}$ NMR spectra recorded in acetone and those in dichloromethane. Although peaks corresponding to B−H bonds do not change much, it can be observed that the broad signal corresponding to C_c−H in acetone has moved upfield, splitting into two singlets in dichloromethane. The shape of the ^1H NMR spectrum in dichloromethane resembles the corresponding spectrum of any B(8)−O monosubstituted ligand where the four C_c−H's should appear as a 2:2 pattern.

Variable-temperature $^1H\{^{11}B\}$ NMR spectra recorded in the range 295−204 K using dichloromethane as a solvent are shown in Figure S.3 (Supporting Information). As it can be seen, there is a high dependence of the chemical shift of one B−H signal on the temperature. This B−H resonance becomes broader and shifts to lower field as the temperature decreases. These spectroscopic data are in agreement with intramolecular B−H···Na^+ or Na^+···O interactions, most probably corresponding to those observed in the solid state (Figure 4). The NMR data above −70 °C could be explained either by the rapid exchange between the available geometric rotamers providing different B−H···Na^+ interactions or by a progressive increase in the number of molecules whose B−H···Na^+ interactions have been replaced by coordinating solvent molecules. There is also a significant change in the shift of the CH_2 at 4.34 ppm as the temperature decreases, due to the C−H···Na^+ interactions also observed in the X-ray analysis.

The Role of the Electron-Rich Atom (O) Directly Bonded to a Cluster Boron Atom. It has been proven that anionic monothioether- and monophosphine-*nido*-carborane clusters containing electron-rich *exo*-cluster substituents (S or P) dissipate electron density into the electron-rich element.[24] This element becomes a strong Lewis base and a very good coordinating ligand.[25] Most probably the oxygen atom in the B(8)−O bond in **3**−**16** can play the same role as S and P atoms, dissipating the negative charge and becoming a strong Lewis base. Thus, the anionic **3**−**16** species can coordinate to a Lewis acid through the oxygen atom at the B(8) position. The existence of a second oxygen atom that can also interact with the Lewis acid like sodium or lithium cations (M) forming a O···M···O interaction facilitates the coordination.

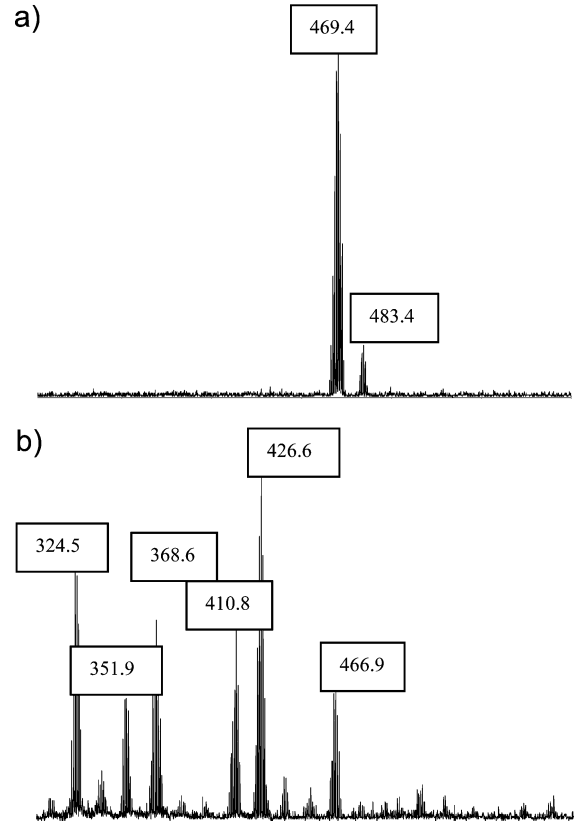

Figure 5. MALDI-TOF-MS spectra of compounds **3** (a) and **5** (b). See the Experimental Section for the fragmentation.

MALDI[26] supports, although does not confirm, the special nucleophilic character of the B−O unit. Compounds **3**−**16** were studied by the MALDI-MS technique at the negative ion mode without the use of matrices. The lack of matrices aids the interpretation of the primary and secondary mechanisms. We understand as a "primary" mechanism the separation of the anionic cobaltabisdicarbollide derivatives from the bonded cation. The "secondary" mechanism can give some clues about the nucleophilic character of the electron-rich oxygen atom directly bonded to the cluster B(8) boron atom. Figure 5 shows the MALDI-TOF-MS spectra of compounds **3** and **5** as a representative example. A peak with an ion mass higher than the molecular ion peak at 469.4 ((M + Li)/2) is observed at 483.4, although with less intensity, corresponding to (M + CH_2). This had been noted previously[7] and can be interpreted as an electrophilic reaction between like anions. Of more importance is the different behavior between isomers on the interaction between the polyether chain and the cation, O−M−O, and their own stability against the laser pulse. For compound **3**, the strong interaction with O−Li−O allows that the cation is ionized along with the molecule, and the peak corresponding to (M + Li) appears in the spectra. However, in compound **5**, this is not observed, probably due to the longer distance between the two polyether chains. Moreover, compound **3** stays almost intact upon applying the laser pulse with only two

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peaks in its MALDI-TOF spectrum. This can be explained again for the strong O−Li−O interaction present in the molecule. The decomposition in **5** is explained by breaking the molecule into smaller parts, and all the peaks in their MALDI-TOF spectra can be assigned thereby.

Conclusions

The present study has opened a new route in the ring-opening reaction of cyclic oxonium [3,3′-Co(8-$C_4H_8O_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (**2**) by using carboxylic acids, Grignard reagents, and thiocarboranes as nucleophiles. The crystal structures of $Na_3(H_2O)(C_2H_5OH)$[1″,3″,5″-{3,3′-Co-(8-O(CH_2CH_2O)$_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)}$_3$-C_6H_3] and Na(H_2O)[3,3′-Co(8-O(CH_2CH_2O)$_2$C(O)CH_3-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] show that the polyether chain contributes three oxygen atoms for coordination to Na^+, and interestingly, the [3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$]$^-$ moiety provides extra B−H coordination sites. The availability of B−H groups and their geometrical distribution offers an extraordinary possibility to satisfy metal's demand. These B−H−Na interactions in the solid state have also been confirmed by dynamic NMR studies in solution. We have shown that polyanionic species, as novel high-boron-content molecules, can be obtained in high-yield synthesis. Furthermore, compounds **13**−**16** can be used as cores to make a new class of dendrimers that contain multiple carborane or metallacarborane clusters at their periphery. Further work to synthesize potential new classes of BNCT water-soluble compounds is now underway.

Experimental Section

Instrumentation. Elemental analyses were performed using a Carlo Erba EA1108 microanalyzer. IR spectra were recorded from KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. The ^{1}H NMR, ^{1}H{^{11}B} NMR (300.13 M), ^{11}B NMR (96.29 M), and ^{13}C{^{1}H} NMR (75.47 M) spectra were recorded with a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories using deuterated acetone as the solvent. Chemical shift values for ^{11}B NMR spectra were referenced to external BF_3·OEt_2, and those for ^{1}H, ^{1}H{^{11}B}, and ^{13}C{^{1}H} NMR spectra were referenced to Si(CH_3)$_4$. Chemical shifts are reported in units of parts per million downfield from the reference, and all coupling constants are reported in hertz. The mass spectra were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF-MS (N_2 laser; λ_{exc} 337 nm, 0.5 ns pulses; voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)) or in the negative ion mode using a Bruker Daltonics esquire3000 (N_2 laser; λ_{exc} 337 nm, 0.5 ns pulses; Skim1 voltage 37.5 V).

Materials. Experiments were carried out, except when noted, under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques, with some subsequent manipulation in the open laboratory. 1,2-Dimethoxyethane (DME) and tetrahydrofuran (THF) were distilled from sodium benzophenone before use. Other solvents were reagent grade. All organic and inorganic salts were Fluka or Aldrich analytical reagent grade and were used as received. [8-{3,3′-Co(8-$C_4H_8O_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (**2**), 1-SH-2-CH_3-*closo*-1,2-$C_2B_{10}H_{10}$, and 1,2-SH-*closo*-1,2-$C_2B_{10}H_{10}$ were prepared according to the literature.[27]

Synthesis of [Li$_2$(DME)][1″,2″-{3,3′-Co(8-O(CH_2CH_2O)$_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)}$_2$-C_6H_4] (3). Under an inert atmosphere, *n*-butyllithium (0.305 mL, 0.488 mmol; 1.6 M in hexanes) was added dropwise to a stirred solution of catechol (25.6 mg, 0.232 mmol) in 15 mL of anhydrous DME at −40 °C. The resulting solution was stirred for 1 h at a low temperature. Then, a solution of **2** (200 mg, 0.488 mmol) in 15 mL of anhydrous DME was added dropwise at a low temperature. After stirring overnight, a white precipitate appeared and was discarded. The solvent was removed, and acidic water (20 mL; 1 M HCl) was added to the orange residue. This was extracted with diethyl ether (3 × 20 mL). The solvent was removed; the product was redissolved in the minimum volume of ethanol, and an aqueous solution containing an excess of [N(CH_3)$_4$]Cl was added, resulting in the formation of an orange precipitate. This was filtered off, washed with water and petroleum ether, and dried in vacuo. Yield: 0.333 g (74%). Anal. calcd for $C_{26}H_{72}B_{36}Co_2Li_2O_8$: C, 30.21; H, 7.02. Found: C, 29.40; H, 6.62. IR: ν (cm^{-1}) 3043 (C_c−H), 2947, 2877, 2752 (C−H)$_{alkyl}$, 2607, 2597, 2561, 2478, 2357 (B−H), 1505, 1475 δ(CH_2), 1253 δ(CH), 1160 (C−O−C). ^{1}H NMR: δ 7.04−6.92 (m, 4H, C_6H_4), 4.24 (br s, 8H, C_c−H), 4.19 (t, ^3J(H,H) = 5, 4H, OCH_2CH_2), 3.85 (t, ^3J(H,H) = 5, 4H, OCH_2CH_2), 3.64 (t, ^3J(H,H) = 2, 8H, OCH_2CH_2), 3.45 (s, 4H, DME), 3.27 (s, 6H, DME), 2.92−1.47 (m, 34H, B−H). ^{1}H{^{11}B} NMR: δ 7.04−6.92 (m, 4H, C_6H_4), 4.24 (br s, 8H, C_c−H), 4.19 (t, ^3J(H,H) = 5, 4H, OCH_2CH_2), 3.85 (t, ^3J(H,H) = 5, 4H, OCH_2CH_2), 3.64 (t, ^3J(H,H) = 2, 8H, OCH_2CH_2), 3.45 (s, 4H, DME), 3.27 (s, 6H, DME), 2.92 (s, 8H, B−H), 2.75 (s, 4H, B−H), 2.71 (s, 2H, B−H), 2.52 (s, 2H, B−H), 2.01 (s, 4H, B−H), 1.79 (s, 4H, B−H), 1.66 (s, 4H, B−H), 1.56 (s, 4H, B−H), 1.47 (s, 2H, B−H). ^{13}C{^{1}H} NMR: δ 121.63 (s, C_6H_4), 114.86 (s, C_6H_4), 71.87 (s, OCH_2), 71.54 (s, OCH_2), 69.23 (s, OCH_2), 68.38 (s, OCH_2), 54.15 (s, C_c−H), 46.41 (s, C_c−H). ^{11}B NMR: δ 25.5 (s, 2B, B(8)), 6.4 (d, ^1J(B,H) = 135, 2B), 2.8 (d, ^1J(B,H) = 148, 2B), −0.2 (d, ^1J(B,H) = 158, 2B), −2.0 (d, ^1J(B,H) = 165, 4B), −5.0 (d, ^1J(B,H) = 84, 4B), −5.9 (d, ^1J(B,H) = 114, 8B), −15.1 (d, ^1J(B,H) = 150, 4B), −18.2 (d, ^1J(B,H) = 151, 4B), −19.5 (d, 2B), −26.3 (d, ^1J(B,H) = 132, 2B). MALDI-TOF-MS: (*m*/*z*) 469.38 ((M + Li)/2, 100%); 483.39 ((M + Li)2 + CH_2; 15%).

Synthesis of [N(CH_3)$_4$]$_2$[1″,3″-{3,3′-Co(8-O(CH_2CH_2O)$_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)}$_2$-C_6H_4] (4). This compound was prepared using the same procedure as for **3**, but using resorcinol (25.6 mg, 0.232 mmol) instead of catechol. Yield: 0.374 g (83%). Anal. calcd for $C_{30}H_{86}B_{36}Co_2N_2O_6$: C, 33.42; H, 8.04; N, 2.60. Found: C, 33.70; H, 7.95; N, 2.65. IR: ν(cm^{-1}) 3041 (C_c−H), 2918, 2864, 2825 (C−H)$_{alkyl}$, 2584, 2482, 2364, 2228 (B−H), 1483, 1462 δ(CH_2), 1286, 1255 δ(CH), 1184, 1124 (C−O−C), 941 (C−N). ^{1}H NMR: δ 7.15 (t, ^3J(H,H) = 8, 1H, C_6H_4), 6.54 (s, 1H, C_6H_4), 6.52 (d, ^3J(H,H) = 2, 2H, C_6H_4), 4.28 (br s, 8H, C_c−H), 4.10 (t, ^3J(H,H) = 5, 4H, OCH_2CH_2), 3.80 (t, ^3J(H,H) = 5, 4H, OCH_2CH_2), 3.59 (t, ^3J(H,H) = 3, 8H, OCH_2CH_2), 3.43 (s, 24H, N(CH_3)$_4$), 2.99−1.47 (m, 34H, B−H). ^{1}H{^{11}B} NMR: δ 7.15 (t, ^3J(H,H) = 8, 1H, C_6H_4), 6.54 (s, 1H, C_6H_4), 6.54 (d, ^3J(H,H) = 2, 2H, C_6H_4), 4.28 (br s, 8H, C_c−H), 4.10 (t, ^3J(H,H) = 5, 4H, OCH_2CH_2), 3.80 (t, ^3J(H,H) = 5, 4H, OCH_2CH_2), 3.59 (t, ^3J(H,H) = 3, 8H, OCH_2CH_2), 3.43 (s, 24H, N(CH_3)$_4$), 2.99 (s, 8H, B−H), 2.77 (s, 4H, B−H), 2.69 (s, 2H, B−H), 2.44 (s, 2H, B−H), 1.99 (s, 4H, B−H), 1.78 (s, 4H, B−H), 1.67 (s, 4H, B−H), 1.57 (s, 4H, B−H), 1.47 (s, 2H, B−H).

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$^{13}C\{^1H\}$ NMR: δ 160.34 (s, C_6H_4), 129.73 (s, C_6H_4), 106.83 (s, C_6H_4), 101.26 (s, C_6H_4), 71.96 (s, OCH_2), 69.37 (s, OCH_2), 68.34 (s, OCH_2), 67.44 (s, OCH_2), 55.16 (s, $N(CH_3)_4$), 54.56 (s, C_c−H), 46.36 (s, C_c−H). ^{11}B NMR: δ 25.3 (s, 2B, B(8)), 6.3 (d, ^1J(B,H) = 134, 2B), 2.8 (d, ^1J(B,H) = 152, 2B), −0.1 (d, ^1J(B,H) = 148, 2B), −1.8 (d, ^1J(B,H) = 160, 4B), −5.1 (d, ^1J(B,H) = 80, 4B), −5.8 (d, ^1J(B,H) = 121, 8B), −14.9 (d, ^1J(B,H) = 156, 4B), −18.0 (d, ^1J(B,H) = 150, 4B), −19.5 (d, 2B), −26.0 (d, ^1J(B,H) = 150, 2B). MALDI-TOF-MS: (*m*/*z*) 1003.8 (M + $N(CH_3)_4$).

Synthesis of $[N(CH_3)_4]_2[1'',4''$-{3,3′-Co(8-O$(CH_2CH_2O)_2$-1,2-$C_2B_9H_{10})(1',2'$-$C_2B_9H_{11})\}_2$-$C_6H_4]$ (5). This compound was prepared using the same procedure as for **3**, but using hydroquinone (25.6 mg, 0.2324 mmol) instead of cathecol. Work-up and purification ends without the cation exchange. Yield: 0.386 g (85%). Anal. calcd for $C_{30}H_{86}B_{36}Co_2N_2O_6$: C, 33.42; H, 8.04; N, 2.60. Found: C, 33.64; H, 8.00; N, 2.42. IR: ν(cm^{-1}) 3039 (C_c−H), 2920, 2864, 2831 $(C-H)_{alkyl}$, 2610, 2482, 2545, 2434, 2363, 2339 (B−H), 1504, 1481, 1454 $\delta(CH_2)$, 1284 δ(CH), 1232, 1178, 1126 (C−O−C), 943 (C−N). ^1H NMR: δ 6.88 (s, 4H, C_6H_4), 4.28 (br s, 8H, C_c−H), 4.06 (t, ^3J(H,H) = 5, 4H, OCH_2CH_2), 3.77 (t, ^3J(H,H) = 5, 4H, OCH_2CH_2), 3.57 (t, ^3J(H,H) = 3, 8H, OCH_2CH_2), 3.44 (s, 24H, $N(CH_3)_4$), 2.92−1.45 (m, 34H, B−H). $^1H\{^{11}B\}$ NMR: δ 6.88 (s, 4H, C_6H_4), 4.28 (br s, 8H, C_c−H), 4.06 (t, ^3J(H,H) = 5, 4H, OCH_2CH_2), 3.77 (t, ^3J(H,H) = 5, 4H, OCH_2CH_2), 3.57 (t, ^3J(H,H) = 3, 8H, OCH_2CH_2), 3.44 (s, 24H, $N(CH_3)_4$), 2.92 (s, 8H, B−H), 2.77 (s, 4H, B−H), 2.69 (s, 4H, B−H), 2.42 (s, 2H, B−H), 1.99 (s, 4H, B−H), 1.78 (s, 4H, B−H), 1.67 (s, 4H, B−H), 1.57 (s, 2H, B−H), 1.45 (s, 2H, B−H). $^{13}C\{^1H\}$ NMR: δ 115.39 (s, C_6H_4), 71.94 (s, OCH_2), 69.50 (s, OCH_2), 68.38 (s, OCH_2), 67.99 (s, OCH_2), 55.18 (s, $N(CH_3)_4$), 54.68 (s, C_c−H), 46.91 (s, C_c−H). ^{11}B NMR: δ 25.2 (s, 2B, B(8)), 6.2 (d, ^1J(B,H) = 141, 2B), 2.8 (d, ^1J(B,H) = 151, 2B), −0.1 (d, ^1J(B,H) = 141, 2B), −1.7 (d, ^1J(B,H) = 162, 4B), −5.1 (d, ^1J(B,H) = 90, 4B), −5.8 (d, ^1J(B,H) = 110, 8B), −14.9 (d, ^1J(B,H) = 153, 4B), −18.0 (d, ^1J(B,H) = 150, 4B), −19.5 (d, 2B), −26.0 (d, ^1J(B,H) = 140, 2B). MALDI-TOF-MS: (*m*/*z*) 466.91 (M/2, 38%), 426.5 (M − $C_{14}H_{33}B_{18}CoO_3$, 100%), 410.7 (M − $C_{14}H_{33}B_{18}CoO_4$, 55%), 368.5 (M − $C_{16}H_{37}B_{18}CoO_5$, 58%), 351.8 (M − $C_{17}H_{41}B_{18}CoO_5$, 35%), 324.3 (M − $C_{18}H_{41}B_{18}CoO_6$, 73%).

Synthesis of $[Li(DME)]_3[1'',3'',5''$-{3,3′-Co(8-O$(CH_2CH_2O)_2$-1,2-$C_2B_9H_{10})(1',2'$-$C_2B_9H_{11})\}_3$-$C_6H_3]$ $[Li(DME)]_3$[6]. This compound was prepared using the same procedure as for **3**, but using 1,3,5-trihydroxybenzene (26.4 mg, 0.163 mmol) instead of catechol. Work-up and purification were carried out without the cation exchange. Yield: 0.25 g (93%). Anal. calcd for $C_{42}H_{120}B_{54}Co_3Li_3O_{15}$: C, 30.63; H, 7.34. Found: C, 31.15; H, 6.85. IR: ν(cm^{-1}) 3041 (C_c−H), 2935, 2879 $(C-H)_{alkyl}$, 2608, 2570, 2524, 2492, 2358 (B−H), 1514, 1452 $\delta(CH_2)$, 1276, 1249 δ(CH), 1149, 1130, 1097 (C−O−C). ^1H NMR: δ 6.12 (s, 3H, C_6H_3), 4.25 (br s, 12H, C_c−H), 4.14 (t, ^3J(H,H) = 6, 6H, OCH_2CH_2), 3.81 (t, ^3J(H,H) = 5, 6H, OCH_2CH_2), 3.62 (t, ^3J(H,H) = 6, 12H, OCH_2CH_2), 3.45 (s, 12H, DME), 3.28 (s, 18H, DME), 2.94−1.47 (m, 51H, B−H). $^1H\{^{11}B\}$ NMR: δ 6.12 (s, 3H, C_6H_3), 4.25 (br s, 12H, C_c−H), 4.14 (t, ^3J(H,H) = 6, 6H, OCH_2CH_2), 3.81 (t, ^3J(H,H) = 5, 6H, OCH_2CH_2), 3.62 (t, ^3J(H,H) = 6, 12H, OCH_2CH_2), 3.45 (s, 12H, DME), 3.28 (s, 18H, DME), 2.94 (s, 12H, B−H), 2.76 (s, 6H, B−H), 2.70 (s, 3H, B−H), 2.47 (s, 3H, B−H), 2.00 (s, 6H, B−H), 1.79 (s, 6H, B−H), 1.67 (s, 6H, B−H), 1.57 (s, 6H, B−H), 1.47 (s, 3H, B−H). $^{13}C\{^1H\}$ NMR: δ 158.42 (s, C_6H_3), 92.55 (s, C_6H_3), 72.35−67.20 (m, OCH_2), 54.48 (s, C_c−H), 46.41 (s, C_c−H). ^{11}B NMR: δ 25.3 (s, 3B, B(8)), 6.3 (d, ^1J(B,H) = 130, 3B), 2.8 (d, ^1J(B,H) = 145, 3B), −0.1 (d, ^1J(B,H) = 147, 3B), −1.9 (d, ^1J(B,H) = 172, 6B), −5.1 (d, ^1J(B,H) = 85, 6B), −5.8 (d, ^1J(B,H) = 99, 12B), −14.9 (d, ^1J(B,H) = 150, 6B), −18.1 (d, ^1J(B,H) = 152, 6B), −19.6 (d, ^1J(B,H) = 144, 3B), −26.1 (d, ^1J(B,H) = 153, 3B). ESI-MS: (*m*/*z*) 1363.1 (M + Li, 10%), 951.7 (M − C_8 $H_{29}B_{18}CoO_2$ + Na, 100%).

Trisodium Salt Na_3[6]. 1,3,5-Trihydroxybenzene (125 mg, 0.99 mmol) was reacted in toluene−DME (2:1, 25 mL) with NaH (solid 96%, 82 mg, 3.4 mmol), and then **2** (1.24 g, 3.02 mmol) was added in the same solvent (25 mL). The reaction mixture was stirred at 60 °C for 14 h. After cooling down, the reaction was quenched by the addition of CH_3OH (2 mL), water (10 mL), and a few drops of acetic acid (1 M). The organic solvents were vacuum-removed, water (15 mL) was added, and the crude product was extracted into toluene (3 × 15 mL). Combined toluene fractions were evaporated, dissolved in CH_2Cl_2−CH_3CN (1:4), injected on top of a silica gel column (2 × 25 cm), and chromatographed in the same solvent mixture, increasing the CH_3CN content to 1:3. Yield: 805 mg, 57%. The product was characterized with NMR and MS, showing only minor deviations given by the different cation. Compound Na_3[**6**] was dissolved for crystals grown in methylene chloride upon the addition of a drop of ethanol. This solution was layred by *i*-octane and left to crystallize for several days. Red barlike crystals were obtained. ^1H NMR: δ 6.16 (s, 3H, C_6H_3), 4.25 (br s, 12H, C_c−H), 4.11 (t, ^3J(H,H) = 4.8, 6H, OCH_2CH_2), 3.82 (t, ^3J(H,H) = 4.8, 6H, OCH_2CH_2), 3.66 (t, ^3J(H,H) = 4.8, 12H, OCH_2CH_2), 3.61 (t, ^3J(H,H) = 4.8, 12H, OCH_2CH_2), 2.94−1.47 (m, 51H, B−H). $^1H\{^{11}B_{selective}\}$ NMR: δ 2.93 (H10′), 2.75 (H4′,7′), 2.69 (H10), 2.58 (H8′), 2.91, 1.98, 1.80 (H 4, 7, 9, 12, 9′,12′), 1.66 (H5′, 11′), 1.66 (H6′), 1.56 (H5, 11), 1.45 (H6). $^{13}C\{^1H$ } NMR: δ 158.5 (s, C_6O_3), 92.7 (s, C_6H_3), 72.6 (CH_2−O), 70.3 (CH_2−O), 68.2 (CH_2−O), 67.7 (CH_2−O), 54.6 (s, C_c−H), 47.4 (s, C_c−H). ^{11}B NMR: δ 23.2 (s, 3B, B8), 4.3 (d, ^1J(B,H) = 132, 3B, B8′), 0.45 (d, ^1J(B,H) = 138, 3B, B10′), −2.4 (d, ^1J(B,H) = 147, 3B, B10), −4.4 (d, ^1J(B,H) = 149, 6B, B4′, 7′), −7.3 (d), −8.0 (2d, overlap 12B, B9, 12, 9′, 12′), −17.2 (d, ^1J(B,H) = 146, 6B, B5′, 11′), −20.4 (d, ^1J(B,H) = 149, 6B, B5, 11), −22.3 (d, ^1J(B,H) = 158, 3B, B6′), −28.5 (d, ^1J(B,H) = 140, 3B, B6). ESI^- MS: (*m*/*z*) = 451.9 (30%), 455.3 (2%) $(M)^{3-}$ (4%); 689.9 (100%), 694.6 (M + $Na)^{2-}$ (4%), 1400.9 (20%), 1411.8 (2%) $(M + Na)^-$.

Synthesis of $[N(CH_3)_4][3,3'$-Co(8-O$(CH_2CH_2O)_2CH_2C_6H_5$-1,2-$C_2B_9H_{10})(1',2'$-$C_2B_9H_{11})]$ (7). This compound was prepared using the same procedure as for **3**, but using benzyl alcohol (0.046 mL, 0.444 mmol) instead of catechol. Yield: 0.25 g (87%). Anal. calcd for $C_{19}H_{48}B_{18}CoNO_3$: C, 38.54; H, 8.17; N, 2.37. Found: C, 38.23; H, 7.98; N, 2.18. ^1H NMR: δ 7.35 (s, 5H, C_6H_5), 4.55 (s, 2H, CH_2), 4.29 (br s, 4H, C_c−H), 3.62 (m, 4H, OCH_2CH_2), 3.58 (t, ^3J(H,H) = 5, 2H, OCH_2CH_2), 3.51 (t, ^3J(H,H) = 5, 2H, OCH_2CH_2), 3.43 (s, 12H, $N(CH_3)_4$), 2.93−1.48 (m, 17H, B−H). $^1H\{^{11}B\}$ NMR: δ 7.35 (s, 4H, C_6H_4), 4.55 (s, 2H, CH_2), 4.29 (br s, 4H, C_c−H), 3.62 (m, 4H, OCH_2CH_2), 3.58 (t, ^3J(H,H) = 5, 2H, OCH_2CH_2), 3.51 (t, ^3J(H,H) = 5, 2H, OCH_2CH_2), 3.43 (s, 12H, $N(CH_3)_4$), 2.93 (s, 4H, B−H), 2.77 (s, 2H, B−H), 2.70 (s, 1H, B−H), 2.39 (s, 1H, B−H), 1.99 (s, 2H, B−H), 1.78 (s, 2H, B−H), 1.67 (s, 2H, B−H), 1.56 (s, 2H, B−H), 1.48 (s, 1H, B−H). $^{13}C\{^1H\}$ NMR: δ 139.04 (s, C_6H_4), 128.12 (s, C_6H_4), 127.49 (s, C_6H_4), 127.18 (s, C_6H_4), 72.57 (s, OCH_2), 71.87 (s, OCH_2), 70.29 (s, OCH_2), 69.63 (s, OCH_2), 68.39 (s, CH_2), 55.15 (s, $N(CH_3)_4$), 54.59 (s, C_c−H), 46.39 (s, C_c−H). ^{11}B NMR: δ 25.0 (s, 1B, B(8)), 5.9 (d, ^1J(B,H) = 135, 1B), 2.7 (d, ^1J(B,H) = 141, 1B), −0.2 (d, ^1J(B,H) = 155, 1B), −1.9 (d, ^1J(B,H) = 158, 2B), −5.2 (d, ^1J(B,H) = 80, 2B), −6.0 (d, ^1J(B,H) = 131, 4B), −15.0 (d, ^1J(B,H) = 154, 2B), −18.2 (d, ^1J(B,H) = 152, 2B), −19.5 (d, ^1J(B,H) = 141, 1B), −26.2 (d, ^1J(B,H) = 165, 1B). MALDI-TOF-MS: (*m*/*z*) 518.52 (M, 100%); 532.43 (M + CH_2, 15%).

Synthesis of [Li(DME)]$_2$[1″,4″-{3,3′-Co(8-O(CH$_2$CH$_2$O)$_2$CH$_2$-1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)}$_2$-C$_6$H$_4$] (8). This compound was prepared using the same procedure as for **3**, but using 1,4-benzene dimethanol (32.11 mg, 0.244 mmol) instead of catechol. Work-up and purification ends without the cation exchange. Yield: 0.40 g (86%). Anal. calcd for $C_{32}H_{86}B_{36}Co_2Li_2O_{10}$: C, 33.36; H, 7.52. Found: C, 33.08; H, 7.26. IR: ν(cm^{-1}) 3039 (C$_c$−H), 2931, 2877 (C−H)$_{alkyl}$, 2607, 2572, 2505, 2362 (B−H), 1454, 1426 δ(CH$_2$), 1245, 848 δ(CH), 1151, 1122 (C−O−C). ^{1}H NMR: δ 7.33 (s, 4H, C$_6$H$_4$), 4.54 (s, 4H, CH$_2$), 4.26 (br s, 8H, C$_c$−H), 3.63 (m, 8H, OCH$_2$CH$_2$), 3.59 (t, ^3J(H,H) = 5, 4H, OCH$_2$CH$_2$), 3.53 (t, ^3J(H,H) = 5, 4H, OCH$_2$CH$_2$), 3.45 (s, 8H, DME), 3.27 (s, 12H, DME), 2.92−1.47 (m, 34H, B−H). ^{1}H{^{11}B} NMR: δ 7.33 (s, 4H, C$_6$H$_4$), 4.54 (s, 4H, CH$_2$), 4.26 (br s, 8H, C$_c$−H), 3.63 (m, 8H, OCH$_2$CH$_2$), 3.59 (t, ^3J(H,H) = 5, 4H, OCH$_2$CH$_2$), 3.53 (t, ^3J(H,H) = 5, 4H, OCH$_2$CH$_2$), 3.45 (s, 8H, DME), 3.28 (s, 12H, DME), 2.92 (s, 8H, B−H), 2.76 (s, 4H, B−H), 2.69 (s, 2H, B−H), 2.45 (s, 2H, B−H), 1.99 (s, 4H, B−H), 1.79 (s, 4H, B−H), 1.66 (s, 4H, B−H), 1.56 (s, 4H, B−H), 1.47 (s, 2H, B−H). ^{13}C{^{1}H} NMR: δ 137.99 (s, C$_6$H$_4$), 127.49 (s, C$_6$H$_4$), 72.46 (s, OCH$_2$), 71.82 (s, OCH$_2$), 70.25 (s, OCH$_2$), 69.45 (s, OCH$_2$), 68.40 (s, CH$_2$), 54.48 (s, C$_c$−H), 46.43 (s, C$_c$−H). ^{11}B NMR: δ 25.2 (s, 2B, B(8)), 6.2 (d, ^1J(B,H) = 132, 2B), 2.7 (d, ^1J(B,H) = 141, 2B), −0.2 (d, ^1J(B,H) = 159, 2B), −1.9 (d, ^1J(B,H) = 161, 4B), −5.1 (d, ^1J(B,H) = 80, 4B), −5.9 (d, ^1J(B,H) = 124, 8B), −15.0 (d, ^1J(B,H) = 156, 4B), −18.2 (d, ^1J(B,H) = 152, 4B), −19.5 (d, ^1J(B,H) = 153, 2B), −26.2 (d, ^1J(B,H) = 151, 2B). MALDI-TOF-MS: (*m*/*z*) 964.91 (M + Li, 100%); 978.91 (M + Li + CH2, 18%), 547.47 (M − C$_8$H$_{29}$B$_{18}$CoO$_2$, 47%).

Synthesis of [N(CH$_3$)$_4$][3,3′-Co(8-O(CH$_2$CH$_2$O)$_2$C(O)C$_6$H$_5$-1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)] (9). Under an inert atmosphere, dried sodium benzoate (77.4 mg, 0.488 mmol) and **2** (200 mg, 0.488 mmol) were dissolved in 20 mL of anhydrous DME. After stirring overnight, the solvent was removed. The product was redissolved in the minimum volume of ethanol, and an aqueous solution containing an excess of [N(CH$_3$)$_4$]Cl was added, resulting in the formation of an orange precipitate. This was filtered off, washed with water and petroleum ether, and dried in vacuo. Yield: 0.237 g (88%). Anal. calcd for $C_{19}H_{46}B_{18}CoNO_4$: C, 37.65; H, 7.65; N, 2.31. Found: C, 36.83; H, 7.61; N, 2.31. IR: ν(cm^{-1}) 3033 (C$_c$−H), 2959, 2918, 2866 (C−H)$_{alkyl}$, 2602, 2584, 2543, 2496, 2362 (B−H), 1708 (C═O), 1483, 1450 δ(CH$_2$), 1280 δ(CH), 1178, 1116 (C−O−C), 945 (C−N). ^{1}H NMR: δ 8.04 (d, ^3J(H,H) = 8, 2H, C$_6$H$_5$), 7.62 (t, ^3J(H,H) = 8, 1H, C$_6$H$_5$), 7.51 (dd, ^3J(H,H) = 7, 2H, C$_6$H$_5$), 4.43 (t, ^3J(H,H) = 5, 2H, OCH$_2$CH$_2$), 4.29 (br s, 4H, C$_c$−H), 3.82 (t, ^3J(H,H) = 5, 2H, OCH$_2$CH$_2$), 3.59 (m, 4H, OCH$_2$CH$_2$), 3.46 (s, 12H, N(CH$_3$)$_4$), 2.93−1.49 (m, 17H, B−H). ^{1}H{^{11}B} NMR: δ 8.04 (d, ^3J(H,H) = 8, 2H, C$_6$H$_5$), 7.62 (t, ^3J(H,H) = 8, 1H, C$_6$H$_5$), 7.51 (dd, ^3J(H,H) = 7, 2H, C$_6$H$_5$), 4.43 (t, ^3J(H,H) = 5, 2H, OCH$_2$CH$_2$), 4.29 (br s, 4H, C$_c$−H), 3.82 (t, ^3J(H,H) = 5, 2H, OCH$_2$CH$_2$), 3.59 (m, 4H, OCH$_2$CH$_2$), 3.46 (s, 12H, N(CH$_3$)$_4$), 2.93 (s, 4H, B−H), 2.7 (s, 2H, B−H), 2.71 (s, 1H, B−H), 2.44 (s, 1H, B−H), 2.00 (s, 2H, B−H), 1.79 (s, 2H, B−H), 1.67 (s, 2H, B−H), 1.58 (s, 2H, B−H), 1.49 (s, 1H, B−H). ^{13}C{^{1}H} NMR: δ 165.87 (s, COO), 132.88 (s, C$_6$H$_5$), 129.39 (s, C$_6$H$_5$), 128.45 (s, C$_6$H$_5$), 71.89 (s, OCH$_2$), 68.78 (s, OCH$_2$), 68.49 (s, OCH$_2$), 64.30 (s, OCH$_2$), 54.48 (s, C$_c$−H), 46.38 (s, C$_c$−H). ^{11}B NMR: δ 30.3 (s, 1B, B(8)), 11.3 (d, ^1J(B,H) = 132, 1B), 7.9 (d, ^1J(B,H) = 138, 1B), 5.0 (d, ^1J(B,H) = 152, 1B), 3.3 (d, ^1J(B,H) = 158, 2B), 0.0 (d, ^1J(B,H) = 93, 2B), −0.8 (d, ^1J(B,H) = 128, 4B), −9.8 (d, ^1J(B,H) = 153, 2B), −12.9 (d, ^1J(B,H) = 151, 2B), −14.4 (d, ^1J(B,H) = 165, 1B), −21.0 (d, ^1J(B,H) = 177, 1B). MALDI-TOF-MS: (*m*/*z*) 532.44 (M, 100%); 546.45 (M + CH$_2$, 13%).

Synthesis of Na(H$_2$O)[3,3′-Co(8-O(CH$_2$CH$_2$O)$_2$C(O)CH$_3$-1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)]Na$_2$[10]$_2$·2H$_2$O. This compound was prepared using the same procedure as for **9**, but using sodium acetate (73.1 mg, 0.488 mmol) instead of sodium benzoate. Work-up and purification ends without the cation exchange. Yield: 0.233 g (96.8%). Anal. calcd for $C_{10}H_{32}B_{18}CoNaO_4$: C, 24.37; H, 6.54. Found: C, 24.54; H, 6.36. IR: ν(cm^{-1}) 3035 (C$_c$−H), 2937, 2875 (C−H)$_{alkyl}$, 2576, 2551, 2520, 2447 (B−H), 1716 (C═O), 1448, 1375 δ(CH$_2$), 1267, 1244 δ(CH$_3$), 1139, 1097 (C−O−C). ^{1}H NMR: δ 4.26 (br s, 4H, C$_c$−H), 4.14 (t, ^3J(H,H) = 5, 2H, OCH$_2$CH$_2$), 3.65 (t, ^3J(H,H) = 5, 2H, OCH$_2$CH$_2$), 3.58 (t, ^3J(H,H) = 5, 2H, OCH$_2$CH$_2$), 3.52 (t, ^3J(H,H) = 5, 2H, OCH$_2$CH$_2$), 2.91−1.48 (m, 17H, B−H), 2.00 (s, 3H, CH$_3$). ^{1}H{^{11}B} NMR: δ 4.26 (br s, 4H, C$_c$−H), 4.14 (t, ^3J(H,H) = 5, 2H, OCH$_2$CH$_2$), 3.65 (t, ^3J(H,H) = 5, 2H, OCH$_2$CH$_2$), 3.58 (t, ^3J(H,H) = 5, 2H, OCH$_2$CH$_2$), 3.52 (t, ^3J(H,H) = 5, 2H, OCH$_2$CH$_2$), 2.91 (s, 4H, B−H), 2.76 (s, 2H, B−H), 2.69 (s, 1H, B−H), 2.45 (s, 1H, B−H), 2.00 (s, 3H, CH$_3$), 1.99 (s, 2H, B−H), 1.78 (s, 2H, B−H), 1.65 (s, 2H, B−H), 1.56 (s, 2H, B−H), 1.48 (s, 1H, B−H). ^{13}C{^{1}H} NMR: δ 170.21 (s, COO), 71.52 (s, OCH$_2$), 68.75 (s, OCH$_2$), 68.36 (s, OCH$_2$), 63.45 (s, OCH$_2$), 54.37 (s, C$_c$−H), 46.41 (s, C$_c$−H), 19.85 (s, CH$_3$). ^{11}B NMR: δ 30.5 (s, 1B, B(8)), 11.5 (d, ^1J(B,H) = 136, 1B), 7.9 (d, ^1J(B,H) = 141, 1B), 5.1 (d, ^1J(B,H) = 158, 1B), 3.3 (d, ^1J(B,H) = 160, 2B), −0.1 (d, ^1J(B,H) = 108, 2B), −0.7 (d, ^1J(B,H) = 115, 4B), −9.7 (d, ^1J(B,H) = 153, 2B), −12.8 (d, ^1J(B,H) = 151, 2B), −14.3 (d, ^1J(B,H) = 149, 1B), −20.9 (d, ^1J(B,H) = 180, 1B). MALDI-TOF-MS: (*m*/*z*) 935.69 (M, 100%); 483.43 ((M + Na)/2, 90%).

Synthesis of Na[1″-{3,3′-Co(8-O(CH$_2$CH$_2$O)$_2$C(O)-1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)}-2″-OH-C$_6$H$_4$]] (11). This compound was prepared using the same procedure as for **9**, but using sodium salicylate (85.9 mg, 0.488 mmol) instead of sodium benzoate. Work-up and purification ends without the cation exchange. Yield: 0.248 g (89.3%.). Anal. calcd for $C_{15}H_{32}B_{18}CoNaO_4$: C, 31.55; H, 6.06. Found: C, 32.90; H, 5.66. IR: ν(cm^{-1}) 3629, 3558 (O−H), 3174 (C−H)$_{aryl}$, 3062 (C$_c$−H), 2908, 2873 (C−H)$_{alkyl}$, 2603, 2563, 2520, 2364 (B−H), 1664 (C═O), 1485, 1463 δ(CH$_2$), 1238, 1222 δ(CH), 1115, 1097 (C−O−C). ^{1}H NMR: δ 7.92 (m, 1H, C$_6$H$_4$), 7.52 (m, 1H, C$_6$H$_4$), 6.96 (m, 1H, C$_6$H$_4$), 6.73 (m, 1H, C$_6$H$_4$), 4.50 (t, ^3J(H,H) = 5, 2H, OCH$_2$CH$_2$), 4.26 (br s, 4H, C$_c$-H), 3.87 (t, ^3J(H,H) = 5, 2H, OCH$_2$CH$_2$), 3.61 (m, 4H, OCH$_2$CH$_2$), 2.93−1.48 (m, 17H, B−H). ^{1}H{^{11}B} NMR: δ 7.92 (m, 1H, C$_6$H$_4$), 7.52 (m, 1H, C$_6$H$_4$), 6.96 (m, 1H, C$_6$H$_4$), 6.73 (m, 1H, C$_6$H$_4$), 4.50 (t, ^3J(H,H) = 5, 2H, OCH$_2$CH$_2$), 4.26 (br s, 4H, C$_c$−H), 3.87 (t, ^3J(H,H) = 5, 2H, OCH$_2$CH$_2$), 3.61 (m, 4H, OCH$_2$CH$_2$), 2.93 (s, 4H, B−H), 2.77 (s, 2H, B−H), 2.70 (s, 1H, B−H), 2.48 (s, 1H, B−H), 2.00 (s, 2H, B−H), 1.79 (s, 2H, B−H), 1.66 (s, 2H, B−H), 1.57 (s, 2H, B−H), 1.48 (s, 1H, B−H). ^{13}C{^{1}H} NMR: δ 169.99 (s, COO), 135.78 (s, C$_6$H$_4$), 130.19 (s, C$_6$H$_4$), 119.31 (s, C$_6$H$_4$), 117.18 (s, C$_6$H$_4$), 71.91 (s, OCH$_2$), 71.50 (s, OCH$_2$), 68.51 (s, OCH$_2$), 64.91 (s, OCH$_2$), 54.32 (s, C$_c$−H), 46.40 (s, C$_c$−H). ^{11}B NMR: δ 25.3 (s, 1B, B(8)), 6.3 (d, ^1J(B,H) = 135, 1B), 2.6 (d, ^1J(B,H) = 140, 1B), −0.2 (d, ^1J(B,H) = 164, 1B), −2.1 (d, ^1J(B,H) = 159, 2B), −5.2 (d, ^1J(B,H) = 122, 2B), −6.1 (d, ^1J(B,H) = 102, 4B), −15.1 (d, ^1J(B,H) = 153, 2B), −18.3 (d, ^1J(B,H) = 159, 2B), −19.8 (d, ^1J(B,H) = 157, 1B), −26.5 (d, ^1J(B,H) = 164, 1B). MALDI-TOF-MS: (*m*/*z*) 548.43 (M, 43%); 450.63 (M − C$_6$H$_5$O, 38%); 428.38 (M − C$_7$H$_5$O$_2$, 100%).

Synthesis of Na$_3$[C$_{12}$H$_{24}$O$_6$][1″,3″,5″-{3,3′-Co(8-O(CH$_2$CH$_2$O)$_2$CO-1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)}$_3$-C$_6$H$_3$] (12). This compound was prepared using the same procedure as for **3**, but using sodium 1,3,5-benzenetricarboxylate (45 mg, 0.163 mmol) with 18-crown-6 ether (129 mg, 0.488 mmol) instead of hydroquinone and diethyl ether

instead of DME. Work-up and purification ends without the cation exchange. Yield: 0.168 g (61.2%). Anal. calcd for $C_{45}H_{114}B_{54}Co_3Na_3O_{12}$: C, 32.23; H, 6.85. Found: C, 33.21; H, 7.13. IR: ν(cm^{-1}) 3047 (C_c−H), 2951, 2912, 2873 (C−H)$_{alkyl}$, 2598, 2559, 2533 (B−H), 1722 (C═O), 1471, 1454 δ(CH_2), 1353, 1249 δ(CH), 1165, 1134, 1103 (C−O−C). ^{1}H NMR: δ 8.84 (s, 3H, C_6H_3), 4.53 (t, ^3J(H,H) = 5, 6H, OCH_2CH_2), 4.25 (br s, 12H, C_c−H), 3.88 (t, ^3J(H,H) = 6, 5H, OCH_2CH_2), 3.65 (s, 24H, crown ether), 3.61 (m, 12H, OCH_2CH_2), 2.90−1.47 (m, 51H, B−H). ^{1}H{^{11}B} NMR: δ 8.84 (s, 3H, C_6H_3), 4.53 (t, ^3J(H,H) = 5, 6H, OCH_2CH_2), 4.25 (br s, 12H, C_c−H), 3.88 (t, ^3J(H,H) = 6, 5H, OCH_2CH_2), 3.65 (s, 24H, crown ether), 3.61 (m, 12H, OCH_2CH_2), 2.90 (s, 9H, B−H), 2.74 (s, 6H, B−H), 2.68 (s, 3H, B−H), 2.44 (s, 3H, B−H), 1.99 (s, 6H, B−H), 1.80 (s, 3H, B−H), 1.78 (s, 6H, B−H), 1.63 (s, 6H, B−H), 1.55 (s, 6H, B−H), 1.47 (s, 3H, B−H). ^{13}C{^{1}H} NMR: δ 164.53 (s, COO), 135.09 (s, C_6H_3), 131.54 (s, C_6H_3), 71.87 (s, OCH_2CH_2), 69.44 (s, crown ether), 68.60 (s, OCH_2CH_2), 68.47 (s, OCH_2CH_2), 64.91 (s, OCH_2CH_2), 54.39 (s, C_c−H), 46.38 (s, C_c−H). ^{11}B NMR: δ 23.6 (s, 3B, B(8)), 4.7 (d, ^1J(B,H) = 129, 3B), 1.1 (d, ^1J(B,H) = 140, 3B), −1.8 (d, ^1J(B,H) = 152, 3B), −3.5 (d, ^1J(B,H) = 166, 6B), −6.7 (d, ^1J(B,H) = 94, 6B), −7.5 (d, ^1J(B,H) = 104, 12B), −16.5 (d, ^1J(B,H) = 150, 6B), −19.7 (d, ^1J(B,H) = 152, 6B), −21.2 (d, ^1J(B,H) = 125, 3B), −27.6 (d, ^1J(B,H) = 108, 3B). ESI-MS: (*m*/*z*) 480.71 (M/3, 100%); 484.9 ((M + CH_2)/3, 10%).

Synthesis of Cs[3,3′-Co(8-(OCH$_2$CH$_2$)$_2$CH$_3$-1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)] (13). Under an inert atmosphere, a diluted solution of methylmagnesium bromide (0.16 mL, 0.49 mmol) was added slowly to a solution of **2** (200 mg, 0.488 mmol) in 10 mL of anhydrous DME at 0 °C. After stirring overnight, the solvent was removed, the product was redissolved in the minimum volume of ethanol, and an aqueous solution containing an exces of CsCl was added, resulting in the formation of an orange precipitate. This was filtered off, washed with water and petroleum ether, and dried in vacuo. Yield: 0.232 g (85%). Anal. calcd for $C_9H_{32}B_{18}CoCsO_2$: C, 19.34; H, 5.77. Found: C, 20.68; H, 5.12. IR: ν(cm^{-1}) 3043 (C_c−H), 2926, 2922, 2868 (C−H)$_{alkyl}$, 2557, 2551, 2544, 2530 (B−H), 1456, 1423, 1358 δ(CH_2), 1229 δ(CH_3), 1161, 1134, 1097 (C−O−C). ^{1}H NMR: δ 4.26 (br s, 4H, C_c−H), 3.78 (t, ^3J(H,H) = 6, 2H, OCH_2CH_2), 3.55 (t, ^3J(H,H) = 5, 2H, OCH_2CH_2), 3.51 (t, ^3J(H,H) = 6, 2H, OCH_2CH_2), 1.59 (m, 2H, CH_2CH_3), 2.92−1.48 (m, 17H, B−H), 1.22 (s, 3H, CH_3). ^{1}H{^{11}B} NMR: δ 4.26 (br s, 4H, C_c−H), 3.78 (t, ^3J(H,H) = 6, 2H, OCH_2CH_2), 3.55 (t, ^3J(H,H) = 5, 2H, OCH_2CH_2), 3.51 (t, ^3J(H,H) = 6, 2H, OCH_2CH_2), 2.92 (s, 3H, B−H), 2.76 (s, 2H, B−H), 2.69 (s, 1H, B−H), 2.45 (s, 1H, B−H), 1.98 (s, 2H, B−H), 1.79 (s, 2H, B−H), 1.66 (s, 3H, B−H), 1.59 (m, 2H, CH_2CH_3), 1.57 (s, 2H, B−H), 1.48 (s, 1H, B−H), 1.22 (s, 3H, CH_3). ^{13}C{^{1}H} NMR: δ 71.69 (s, OCH_2), 70.88 (s, OCH_2), 68.42 (s, OCH_2), 54.39 (s, C_c−H), 46.40 (s, C_c−H), 31.03 (s, CH_2), 21.93 (s, CH_3). ^{11}B NMR: δ 25.2 (s, 1B, B(8)), 6.3 (d, ^1J(B,H) = 145, 1B), 2.7 (d, ^1J(B,H) = 141, 1B), −0.2 (d, ^1J(B,H) = 149, 1B), −1.9 (d, ^1J(B,H) = 169, 2B), −5.1 (d, ^1J(B,H) = 82, 2B), −5.9 (d, ^1J(B,H) = 117, 4B), −14.9 (d, ^1J(B,H) = 151, 2B), −18.0 (d, ^1J(B,H) = 153, 2B), −19.5 (d, ^1J(B,H) = 145, 1B), −26.1 (d, ^1J(B,H) = 146, 1B). MALDI-TOF-MS: (*m*/*z*) 461.25 (M + ClCs, 26%); 446.23 (M + ClCs − CH_3, 100%).

Synthesis of [NEt$_3$H$^+$] [3,3′-Co(8-(OCH$_2$CH$_2$)$_2$C$_3$H$_5$-1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)] (14). This compound was prepared using the same procedure as for **13** but using allylmagnesium chloride (0.18 mL, 0.24 mmol) instead of methylmagnesium bromide. Work-up and purification ends with the precipitation of the NEt_3H^+ salt. Yield: 0.16 g (79%). Anal. calcd for $C_{17}H_{50}B_{18}Co_1N_1O_2$: C, 36.85; H, 9.10; N, 2.53. Found: C, 37.05; H, 9.51; N, 2.38. IR: ν(cm^{-1}) 3041 (C_c−H), 2954, 2925, 2870 (C−H)$_{alkyl}$, 2600, 2565, 2539 (B−H), 1709 (C═C), 1454, 1433, 1421, 1359 δ(CH_2), 1298, 1230 δ(CH_3), 1151, 1134, 1122, 1097 (C−O−C). ^{1}H NMR: δ 5.83 (ddt, $^3J(H_c,H_a)$ = 17, $^3J(H_c,H_b)$ = 10, $^3J(H_c,H_d)$ = 7, 1H, $CH_{2d}CH_c$═CH_aH_b), 5.00 (dd, $^3J(H_a,H_c)$ = 17, $^3J(H_a,H_b)$ = 2, 1H, $CH_{2d}CH_c$═C**H$_a$**H$_b$), 4.91 (dd, $^3J(H_b,H_a)$ = 2, $^3J(H_b,H_c)$ = 10, 1H, $CH_{2d}CH_c$═CH_a**H$_b$**), 4.29 (br s, 2H, C_c−H), 4.25 (br s, 2H, C_c−H), 3.65 (m, 2H, C**H$_{2d}$**CH_c═CH_aH_b), 3.55 (t, ^3J(H,H) = 4, 2H, OCH_2CH_2), 3.49 (q, ^3J(H,H) = 7, 6H, NEt_3H^+), 3.41 (t, ^3J(H,H) = 6, 2H, OCH_2CH_2), 2.10 (t, ^3J(H,H) = 7, 2H, OCH_2CH_2), 1.63 (q, ^3J(H,H) = 8, 2H, C**H$_2$**CH_{2d}), 2.90−1.46 (m, 17H, B−H), 1.42 (t, ^3J(H,H) = 7, 9H, NEt_3H^+). ^{1}H{^{11}B} NMR: δ 5.83 (ddt, $^3J(H_c,H_a)$ = 17, $^3J(H_c,H_b)$ = 10, $^3J(H_c,H_d)$ = 7, 1H, CH_{2d}C**H$_c$**═CH_aH_b), 5.00 (dd, $^3J(H_a,H_c)$ = 17, $^3J(H_a,H_b)$ = 2, 1H, $CH_{2d}CH_c$═C**H$_a$**H$_b$), 4.91 (dd, $^3J(H_b,H_a)$ = 2, $^3J(H_b,H_c)$ = 10, 1H, $CH_{2d}CH_c$═CH_a**H$_b$**), 4.29 (br s, 2H, C_c−H), 4.25 (br s, 2H, C_c−H), 3.65 (m, 2H, C**H$_{2d}$**CH_c═CH_aH_b), 3.55 (t, ^3J(H,H) = 4, 2H, OCH_2CH_2), 3.49 (q, ^3J(H,H) = 7, 6H, NEt_3H^+), 3.41 (t, ^3J(H,H) = 6, 2H, OCH_2CH_2), 2.90 (s, 2H, B−H), 2.75 (s, 2H, B−H), 2.68 (s, 1H, B−H), 2.42 (s, 1H, B−H), 2.33 (s, 1H, B−H), 2.10 (t, ^3J(H,H) = 7, 2H, OCH_2CH_2), 1.96 (s, 2H, B−H), 1.76 (s, 2H, B−H), 1.69 (s, 1H, B−H), 1.63 (q, ^3J(H,H) = 8, 2H, C**H$_2$**CH_{2d}), 1.63 (s, 2H, B−H), 1.54 (s, 2H, B−H), 1.46 (s, 1H, B−H), 1.42 (t, ^3J(H,H) = 7, 9H, NEt_3H^+). ^{13}C{^{1}H} NMR: δ 138.96 (s, **C**HCH_aH_b), 113.74 (s, CH**C**H_aH_b), 71.78 (s, OCH_2), 70.19 (s, OCH_2), 68.70 (s, OCH_2), 54.44 (s, C_c−H), 46.34 (s, C_c−H), 44.87 (s, NEt_3H^+), 33.12 (s, CH_2**C**H_{2d}), 26.18 (s, **C**H_2CH_{2d}), 13.41 (s, NEt_3H^+). ^{11}B NMR: δ 22.8 (s, 1B, B(8)), 3.7 (d, ^1J(B,H) = 128, 1B), −0.4 (d, ^1J(B,H) = 141, 1B), −2.5 (d, ^1J(B,H) = 151, 1B), −4.1 (d, ^1J(B,H) = 161, 2B), −7.5 (d, ^1J(B,H) = 82, 2B), −8.3 (d, ^1J(B,H) = 124, 4B), −17.3 (d, ^1J(B,H) = 154, 2B), −20.5 (d, ^1J(B,H) = 152, 2B), −21.9 (d, ^1J(B,H) = 147, 1B), −28.4 (d, ^1J(B,H) = 162, 1B). MALDI-TOF-MS: (*m*/*z*) 466.32 (M + CH3, 7%); 452.29 (M, 100%); 426.24 (M, 10%); 411.25 (M, 37%).

Synthesis of [Li(THF)$_2$][1″-{3,3′-Co(8-(OCH$_2$CH$_2$)$_2$S-1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)}−2″-CH$_3$-1″,2″-C$_2$B$_{10}$H$_{10}$)] (15). This compound was prepared using the same procedure as for **3**, but using 1-SH-2-CH_3-1,2-*closo*-$C_2B_{10}H_{10}$ (92.7 mg, 0.488 mmol) instead of catechol and THF instead of DME. Work-up and purification ends without the cation exchange. Yield: 0.315 g (86%). Anal. calcd for $C_{19}H_{58}B_{28}CoLiO_4S$: C, 30.37; H, 7.78; S, 4.27. Found: C, 29.84; H, 7.92; S, 4.03. IR: ν(cm^{-1}) 3049, 3039 (C_c−H), 2981, 2937, 2879 (C−H)$_{alkyl}$, 2593, 2565, 2531, 2490, 2360, 2343 (B−H), 1473, 1458 δ(CH_2), 1380, 1352, 1280 δ(CH), 1143, 1132, 1087, 1041 (C−O−C), 748, 723 (C−S). ^{1}H NMR: δ 4.26 (br s, 4H, C_c−H), 3.73 (t, ^3J(H,H) = 6, 2H, OCH_2CH_2), 3.63 (m, 8H, THF), 3.56 (t, ^3J(H,H) = 6, 2H, OCH_2CH_2), 3.51 (t, ^3J(H,H) = 6, 2H, OCH_2CH_2), 3.19 (t, ^3J(H,H) = 6, 2H, CH_2), 2.19 (s, 3H, CH_3), 1.79 (m, 8H, THF), 2.94−1.46 (m, 27H, B−H). ^{1}H{^{11}B} NMR: δ 4.26 (br s, 4H, C_c−H), 3.73 (t, ^3J(H,H) = 6, 2H, OCH_2CH_2), 3.63 (m, 8H, THF), 3.56 (t, ^3J(H,H) = 6, 2H, OCH_2CH_2), 3.51 (t, ^3J(H,H) = 6, 2H, OCH_2CH_2), 3.19 (t, ^3J(H,H) = 6, 2H, CH_2), 2.94 (s, 1H, B−H), 2.90 (s, 2H, B−H), 2.76 (s, 2H, B−H), 2.69 (s, 1H, B−H), 2.47 (s, 4H, B−H), 2.30 (s, 3H, B−H), 2.21 (s, 4H, B−H), 2.19 (s, 3H, CH_3), 2.09 (s, 2H, B−H), 1.98 (s, 2H, B−H), 1.79 (m, 8H, THF), 1.66 (s, 2H, B−H), 1.58 (s, 3H, B−H), 1.46 (s, 1H, B−H). ^{13}C{^{1}H} NMR: δ 85.86 (s, C_c−S), 81.82 (s, C_c−CH_3), 72.72 (s, OCH_2), 71.09 (s, OCH_2), 69.39 (s, OCH_2), 68.06 (s, THF), 55.31 (s, C_c−H), 47.28 (s, C_c−H), 38.47 (s, CH_2S), 26.15 (s, THF), 23.47 (s, CH_3). ^{11}B NMR: δ 25.1 (s, 1B, B(8)), 6.3 (d, ^1J(B,H) = 139, 1B), 2.7 (d, ^1J(B,H) = 137, 1B), −0.2 (d, ^1J(B,H) = 140, 1B), −1.9 (d, ^1J(B,H) = 157, 2B), −2.9 (d, ^1J(B,H) = 135, 2B), −5.1 (d, ^1J(B,H) = 93, 2B), −6.1 (d, ^1J(B,H) = 125, 6B), −7.6 (d, ^1J(B,H) = 162, 6B), −14.9 (d, ^1J(B,H) = 141, 2B), −18.1 (d,

^1J(B,H) = 156, 2B), −19.6 (d, ^1J(B,H) = 141, 1B), −26.1 (d, ^1J(B,H) = 177, 1B). MALDI-TOF-MS: (*m*/*z*) 601.42 (M, 100%) 615.41 (M + CH_2, 18%).

Synthesis of [N(CH$_3$)$_4$]$_2$[1″,2″-{3,3′-Co(8-(OCH$_2$CH$_2$)$_2$S-1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)}$_2$-1″,2″-C$_2$B$_{10}$H$_{10}$)] (16). This compound was prepared using the same procedure as for **3**, but using 1,2-$(SH)_2$-1,2-*closo*-$C_2B_{10}H_{10}$ (50.7 mg, 0.244 mmol) instead of catechol and THF instead of DME. Work-up and purification ends with the precipitation of the $N(CH_3)_4$ salt. Yield: 0.288 g (57%). Anal. calcd for $C_{26}H_{92}B_{46}Co_2N_2O_4S_2$: C, 26.55; H, 7.88; S, 5.45. Found: C, 26.78; H, 7.09; S, 5.25. IR: ν(cm^{-1}) 3037, 3020 (C_c−H), 2920, 2860 (C−H)$_{alkyl}$, 2597, 2555, 2516, 2360, 2343 (B−H), 1481 δ(CH_2), 1284 δ(CH), 1170, 1119, 1097 (C−O−C), 748, 723 (C−S). ^{1}H NMR: δ 4.27 (br s, 8H, C_c−H), 3.76 (t, ^3J(H,H) = 6, 4H, OCH_2CH_2), 3.58 (t, ^3J(H,H) = 6, 4H, OCH_2CH_2), 3.55 (t, ^3J(H,H) = 6, 4H, OCH_2CH_2), 3.45 (s, 24H, $N(CH_3)_4$), 3.18 (t, ^3J(H,H) = 6, 4H, CH_2), 2.91−1.48 (m, 44H, B−H). ^{1}H{^{11}B} NMR: δ 4.27 (br s, 8H, C_c−H), 3.76 (t, ^3J(H,H) = 6, 4H, OCH_2CH_2), 3.58 (t, ^3J(H,H) = 6, 4H, OCH_2CH_2), 3.55 (t, ^3J(H,H) = 6, 4H, OCH_2CH_2), 3.45 (s, 24H, $N(CH_3)_4$), 3.18 (t, ^3J(H,H) = 6, 4H, CH_2), 2.91 (s, 2H, B−H), 2.77 (s, 4H, B−H), 2.69 (s, 4H, B−H), 2.53 (s, 4H, B−H), 2.42 (s, 4H, B−H), 2.34 (s, 4H, B−H), 2.25 (s, 2H, B−H), 2.10 (s, 2H, B−H), 1.98 (s, 4H, B−H), 1.78 (s, 4H, B−H), 1.68 (s, 4H, B−H), 1.56 (s, 4H, B−H), 1.48 (s, 2H, B−H). ^{13}C{^{1}H} NMR: δ 94.50 (s, C_c−S), 71.76 (s, OCH_2), 68.56 (s, OCH_2), 67.22 (s, OCH_2), 55.13 (s, $N(CH_3)_4$), 54.50 (s, C_c−H), 48.56 (s, C_c−H), 37.61 (s, CH_2S). ^{11}B NMR: δ 25.0 (s, 2B, B(8)), 6.1 (d, ^1J(B,H) = 138, 2B), 2.7 (d, ^1J(B,H) = 144, 2B), −0.2 (d, ^1J(B,H) = 148, 2B), −1.8 (d, ^1J(B,H) = 152, 4B), −5.2 (d, ^1J(B,H) = 99, 8B), −6.0 (d, ^1J(B,H) = 116, 8B), −7.8 (d, ^1J(B,H) = 183, 4B), −10.9 (d, ^1J(B,H) = 155, 2B), −14.9 (d, ^1J(B,H) = 148, 4B), −18.1 (d, ^1J(B,H) = 152, 4B), −19.5 (d, ^1J(B,H) = 130, 2B), −26.2 (d, ^1J(B,H) = 144, 2B). MALDI-TOF-MS: (*m*/*z*) 1049.5 (M + Li + CH_2, 15%); 1035.5 (M + Li, 100%); 586.35 (M − $C_8H_{29}B_{18}CoO_2S$, 67%).

X-Ray Structure Determinations of Na$_3$[6]·H$_2$O·C$_2$H$_5$OH, [N(CH$_3$)$_4$][9], and Na$_2$[10]$_2$·2H$_2$O. A red crystal of dimensions 0.4 × 0.2 × 0.18 mm of Na_3[**6**]·H_2O·C_2H_5OH was mounted into a Lindemann capillary and measured on a Nonius KappaCCD diffractometer by monochromatized Mo Kα radiation (λ = 0.71073 Å) at 150(2) K. An absorption was neglected (μ = 0.73 mm^{-1}); a total of 137 134 reflections were measured in the ranges h = −17 to +17, k = −26 to +26, and l = −35 to +35 (θ_{max}= 27.5°), from which 16 892 were unique (R_{int} = 0.050) and 12 266 were observed according to the $I > 2\sigma(I)$ criterion. Cell parameters were from 17 287 reflections (θ = 1−27.5°). The structure was solved by direct methods (SIR92)[28] and refined by full-matrix least-squares based on F^2 (SHELXL97).[30] The hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors of either H_{iso}(H) = 1.2U_{eq} (pivot atom) or H_{iso}(H) = 1.5U_{eq} (pivot atom) for the methyl moiety. The refinement converged (Δ/σ_{max} = 0.001) to R = 0.050 for observed reflections and $wR(F^2)$ = 0.145 and GOF = 1.02 for 929 parameters and all 16892 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{max}$ = 0.81, $\Delta\rho_{min}$ −0.64 e Å^{-3}). The results are presented in a condensed form in Figure 2 and Table 2.

Table 2. Crystallographic Data and Refinement Parameters of Na$_3$[**6**]·H$_2$O·C$_2$H$_5$OH, [NMe$_4$][**9**], and Na$_2$[**10**]$_2$·2H$_2$O

	Na$_3$[**6**]·H$_2$O·C$_2$H$_5$OH	[NMe$_4$][**9**]	Na$_2$[**10**]$_2$·2H$_2$O
empirical formula	$C_{32}H_{98}B_{54}Co_3Na_3O_{11}$	$C_{19}H_{46}B_{18}CoNO_4$	$C_{20}H_{68}B_{36}Co_2Na_2O_{10}$
fw	1488.60	606.08	1021.74
cryst syst	monoclinic	monoclinic	orthorhombic
cryst habit, color	bar, red	plate, red	needle, yellow
space group	$P2_1/n$	$P2_1/n$ (no. 14)	$Pbca$ (no. 61)
a (Å)	13.38900 (10)	16.9749(5)	14.6132(4)
b (Å)	20.1590 (2)	12.0269(3)	11.4205(2)
c (Å)	27.5480 (2)	17.0544(4)	29.7296(8)
β (deg)	97.5690 (5)	113.182(2)	90
V (V^3)	7370.66 (11)	3200.63(14)	4961.6(2)
Z	4	4	4
T (°C)	−123	−100	−100
λ (Å)	0.71073	0.71073	0.71073
ρ (g cm^{-3})	1.341	1.258	1.368
μ (mm^{-1})	0.73	0.566	0.733
data/restraints/params	6892/-/929	7755/4/389	6095/13/321
goodness-of-fit[a] on F^2	1.020	1.026	1.048
$R1$[b] [$I > 2\sigma(I)$]	0.050	0.0681	0.0530
$wR2$[c] [$I > 2\sigma(I)$]	0.145	0.1225	0.1213

[a] $S = [\sum(w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

Single-crystal data collections for [N(CH$_3$)$_4$][**9**] and Na$_2$[**10**]$_2$·2H$_2$O were performed at −100° with an Enraf Nonius KappaCCD diffractometer using graphite monochromatized Mo Kα radiation. The structures were solved by direct methods and refined on F^2 by the SHELXL97 program.[29] The structure of [N(CH$_3$)$_4$][**9**] is partially disordered with the atoms O2, C14, C15, and C16 each occupying two positions. An asymmetric unit of the structure of Na$_2$[**10**]$_2$·2H$_2$O consists of half of the dimeric unit, and in the asymmetric unit, the atoms C13, C14, and C15 are disordered, each occupying two positions. DFIX restraints were utilized to obtain reasonable bond parameters for the atoms at the disordered parts of the molecules. For both compounds, the disordered non-hydrogen atoms were refined with isotropic thermal displacement parameters and the rest of the non-hydrogen atoms with anisotropic displacement parameters. The hydrogen atoms were treated as riding atoms using the SHELX97 default parameters, except positional parameters of the hydrogen atoms connected to the water molecule in Na$_2$[**10**]$_2$·2H$_2$O, which were refined. Crystallographic parameters for [NMe$_4$][**9**] and Na$_2$[**10**]$_2$·2H$_2$O are gathered in Table 2.

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Supporting Information Available: Crystallographic data (CIF) for Na$_3$[**6**]·H$_2$O·C$_2$H$_5$OH, [NMe$_4$][**9**], and Na$_2$[**10**]$_2$·2H$_2$O; Figures S.1, S.2, and S.3 and Tables S.1, S.2, and S.3. This material is available free of charge via the Internet at http://pubs.acs.org.

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