Chameleonic Capacity of $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ in Coordination. Generation of the Highly Uncommon S(thioether)−Na Bond

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The multiple binding modes of $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ allow it to adjust to different coordinating or geometric demands. $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ can behave as a platform on which two types of coordinating moieties exist: the BH's and boron- or carbon-bonded elements with available lone pairs. Until now, no compounds containing Na^+ bonded to thioether ligands were known other than $\text{Na}[7,8\text{-}\mu\text{-}\{\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{S}\}\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]$. The dithioether moiety in the latter compound is preorganized to favor chelation and produces a five-membered ring. This definitely assists in coordination to sodium. To avoid this preorganization and assess the independent strength of the C−S(thioether)−Na bond, the anionic nonpreorganized dithioether $[1,1'\text{-}\mu\text{-}\{\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{S}\}\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$ ligand was synthesized. The two cluster moieties have sufficient accessible rotamers to allow adequate metal coordination, but they do not preorganize. The synthetic procedure leading to $[1,1'\text{-}\mu\text{-}\{\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{S}\}\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$ implied the formation of idealized meso and racemic forms. These forms behave differently toward Na^+. In the meso form coordination to sodium is achieved via the two sulfur (C−S) and three oxygen elements in the exo cluster chain. In the racemic form coordination is achieved via the three oxygen elements in the exo cluster chain, with no thioether participation. The remaining Na^+ coordination sites are filled by oxygen atoms from ancillary ligands. These coordination environments were determined by the crystal structures of $\text{Na}[1,1'\text{-}\mu\text{-}\{\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{S}\}\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]\cdot(\text{CH}_3)_2\text{CO}\cdot\text{CHCl}_3\cdot\text{CH}_2\text{Cl}_2$ (meso form) and $\text{Na}[1,1'\text{-}\mu\text{-}\{\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{S}\}\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]\cdot 2(\text{CH}_3)_2\text{CO}$ (racemic form). Therefore, C−S(thioether)−Na coordination has been demonstrated for the first time with nonpreorganized ligands, although the cluster participation has been found necessary. A situation similar to that obtained with the racemic form of $[1,1'\text{-}\mu\text{-}\{\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{S}\}\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$, having only three coordinating oxygen atoms, is also possible for $[3,3'\text{-Co}(8\text{-}\{\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3\}\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$. This ligand does not have thioethers, and it was interesting to discover how the $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ moiety would behave with a low supply of coordination sites in a more flexible $-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3$ arrangement. The structure of $\text{Na}[3,3'\text{-Co}(8\text{-}\{\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2\text{CH}_3\}\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]$ shows that the chain contributes three oxygen atoms for coordination to Na^+ and, interestingly, the $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ moiety provides three extra B−H coordination sites.

Introduction

In 1990 the molecular structure of $\text{Na}[7,8\text{-}\mu\text{-}\{\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{S}\}\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]$ (**1**) was reported[1] featuring the first S(thioether)−Na bond. The macrocyclic ring external to the cluster is pentacoordinated to Na^+ through two sulfur and three oxygen atoms. Surprisingly, and despite the enormous progress in alkali-metal coordination chemistry,[2] compound **1** has remained the unique example of S(thioether)−Na coordination. This may be attributed to the general assumption that thioethers are poor ligands.[3] Monodentate thioether

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ligands are not efficient metal coordinating agents. At least two thioether moieties performing as a chelating agent are necessary for effective coordination,[4] and even under these circumstances only labile complexes have been produced. However, we have demonstrated that when the sulfur atoms are directly bonded to the anionic 7,8-dicarba-*nido*-undecaborate cluster, then strongly coordinating thioether ligands are produced.[5] The question arises as to why thioether anionic molecules are so strongly coordinating. The *nido*-$[\text{C}_2\text{B}_9]^-$ anionic cluster may largely be responsible for such an effect.

On the other hand, the unit $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ has been the object of many studies[6] since its discovery in 1965.[7] Although *closo*-$[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ and *nido*-$[7,8\text{-C}_2\text{B}_9\text{H}_{12}]^-$ are very different structurally, these two carborane compounds present some remarkable similarities. There is a negative charge delocalized within the cluster, and the cluster carbon atoms are susceptible to being bonded to coordinating elements such as S and P. Thus, it seems reasonable that $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ could be a good probe to show that **1** is not a singular compound featuring a rare example of a S(thioether)−Na bond. In contrast to **1**, the $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ backbone would not be able to take advantage of chelation if the two sulfur atoms were placed on the different $[\text{C}_2\text{B}_9]^-$ moieties. Since there are several possible rotamers of $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$, a preference for a rotamer orientation involving the S(thioether)−Na bond would provide clear evidence for the strength of the latter.

To reach this goal, it was necessary to synthesize the first polydentate macrocycle incorporating $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ as a link. Prior to this work only a few small cyclic compounds using three to five atoms as spacers had been synthesized. These are the polymethylene-bridged, aza-, oxa-, and thiaalkane-1,1′-diyl-bridged carbon-linked cobalt bis(dicarbollides) $[1,1'\text{-}\mu\text{-}\{\text{TsN}(\text{CH}_2\text{CH}_2)_2\}\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$,[8] $[1,1'\text{-}\mu\text{-}(\text{CH}_2\text{OCH}_2)\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$, and $[1,1'\text{-}\mu\text{-}(\text{CH}_2\text{SCH}_2)\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$.[9] In the receptor reported here, the spacer $-(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2-$ is bonded to the cobaltacarborane through two thioether groups, one on each "C_2B_9" moiety, thereby providing five coordinating elements: three oxygen and two sulfur atoms.

For comparative purposes a more relaxed noncyclic (also a three-oxygen binding) $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ ligand and its Na complex have also been synthesized and are reported in this paper. These have been made possible due to the availability of the zwitterionic compound $[3,3'\text{-Co}(8\text{-C}_4\text{H}_8\text{O}_2\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]$ (**2**), which was reported in 1996.[10]

Compound **2** has been shown to be susceptible to nucleophilic attack on the positively charged oxygen atom, e.g. by pyrrolyl,[11] by imide, cyanide, and amines,[12] by phenolate and by dialkyl or diaryl phosphite,[13] and by *N*-alkylcarbamoyldiphenylphosphine oxides,[14] resulting in one anionic species formed by the opening of the dioxane ring. In this paper the opening of the latter ring has been accomplished with $[\text{RO}]^-$ sodium salts.

Results and Discussion

I. Synthesis and Characterization of Functionalized Disubstituted Cobaltabis(dicarbollide) Derivatives Incorporating Five Heteroatoms (Two Thioether and Three Ether Groups) in the Exo-Cluster Chain. To prepare the cobaltabis(dicarbollide) starting material, it was first necessary to prepare the *closo*-carborane/thioether−ether−hydrocarbon backbone $1,1'\text{-}\mu\text{-}\{\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{S}\}(1,2\text{-C}_2\text{B}_{10}\text{H}_{11})_2$ (**3**). This species was produced by reaction of $1\text{-SH-}1,2\text{-C}_2\text{B}_{10}\text{H}_{11}$ with K[EtO] and $\text{ClCH}_2(\text{CH}_2\text{OCH}_2)_3\text{CH}_2\text{Cl}$. Deboronation of **3** with an excess of KOH in ethanol led to the desired nido species $[7,7'\text{-}\mu\text{-}\{\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{S}\}\text{-}(7,8\text{-C}_2\text{B}_9\text{H}_{11})_2]^{2-}$ (**4**). The nonequivalence of the initial substituents on the $[\text{C}_2\text{B}_9]^-$ cluster resulted in the isolation of two geometric isomers.

To synthesize the corresponding cobaltabis(dicarbollide) derivative $[1,1'\text{-}\mu\text{-}\{\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{S}\}\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$ (**5**), we used a method previously developed in our group.[15] After reaction of $[\text{N}(\text{CH}_3)_4]_2[7,7'\text{-}\mu\text{-}\{\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{S}\}(7,8\text{-C}_2\text{B}_9\text{H}_{11})_2]$ with $\text{K}[{}^t\text{BuO}]$ and cobalt(II) chloride in 1,2-dimethoxyethane, the solvent was evaporated and the product was extracted with CH_2Cl_2 and NaCl/water, giving Na[**5**]. The reactions are shown in Scheme 1. A racemic mixture and a meso form are possible (Figure 1), but three major bands named **5a**−**c** were separated by preparative TLC.

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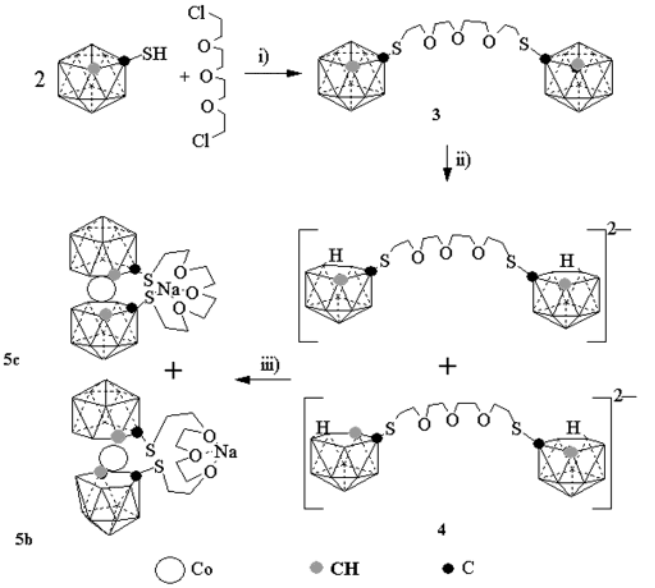
Scheme 1. Synthesis of *closo*-1,1′-μ-{$S(CH_2CH_2O)_3CH_2CH_2S$}$(1,2\text{-}C_2B_{10}H_{11})_2$, *nido*-[7,7′-$\mu$-{$S(CH_2CH_2O)_3CH_2CH_2S$}$(7,8\text{-}C_2B_9H_{11})_2$]$^{2-}$, and [1,1′-$\mu$-{$S(CH_2CH_2O)_3CH_2CH_2S$}-3,3′-Co$(1,2\text{-}C_2B_9H_{10})_2$]$^-$ [a]



[a] Legend: (i) KOH, EtOH, reflux 2 h; (ii) NMe_4OH, EtOH, reflux 4 h; (iii) K[^{t}BuO], $CoCl_2$, 1,2-dimethoxyethane, reflux 24 h, NaCl in the workup.

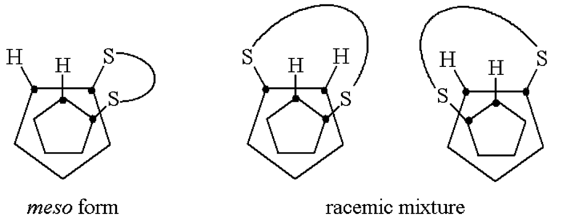
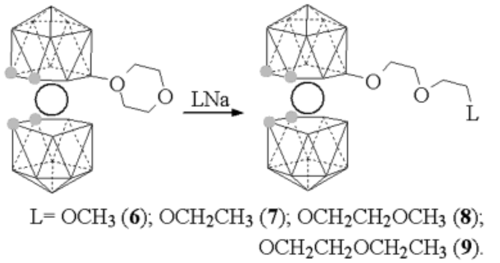


Figure 1. Geometric isomers of the anionic complex **[5]**$^-$ (view from the top of the pentagonal faces).

Scheme 2. Opening of the Exo-Cluster Dioxanate Ring Reaction by Nucleophilic Attack: Synthesis of Complexes 6−10[a]



[a] Atoms in gray are CH vertexes; the rest of the vertices in the clusters are BH.

The ^1H NMR spectra of these compounds are very similar, displaying four resonances between 4.36 and 2.90 ppm: two broad singlets corresponding to the hydrogen atoms bonded to the cluster carbon atoms and two multiplet signals that correspond to the methylene units of the exo-cluster chain. The $^{11}B\{^1H\}$ NMR spectra of compounds **5a**−**c** are similar and appear in the range from +8 to −20 ppm. The $^{13}C\{^1H\}$ NMR resonances were striking in regard to the cluster carbon atom chemical shifts. Compound **5a** displayed these resonances at 63.89 and 67.73 ppm, compound **5b** at 65.30 and 67.39 ppm, and compound **5c** at 58.27 and 60.58 ppm. Those for **5c** are distinctly different from the first two sets. If comparison of these resonances is made with a similar, albeit nonmacrocyclic, compound, [NMe_4][1,1′-$(SCH_2CH_3)_2$-3,3′-Co$(1,2\text{-}C_2B_9H_{10})_2$], with a cation which is not susceptible to coordination,[15] some sense may be made of these chemical shift values. The cluster $^{13}C\{^1H\}$ NMR resonances in [NMe_4][1,1′-$(SCH_2CH_3)_2$-3,3′-Co$(1,2\text{-}C_2B_9H_{10})_2$] are observed at 63.84 and 67.00 ppm, values comparable to these found for **5a**,**b**, suggesting that in **5c** the two thioether groups participate in coordination. This is less probable for **5a**,**b**. The $^{13}C\{^1H\}$ NMR chemical shift difference between **5a**/**5b** and **5c** parallels the electrochemical Fc/Fc$^+$ shift observed in ferrocene (Fc) macrocycles upon coordination to a substrate.[16] In these, the Fc/Fc$^+$ $E_{1/2}$ potential depends on the degree of communication between the receptor and ferrocene sites, communication that could be achieved by directly bonding one of the receptor coordinating sites to the ferrocene fragment.[17] This also takes place in the cobaltacarborane macrocycles described here, where the two coordinating sites in the receptor, the thioether groups, are directly bonded to the cobaltacarborane moiety. As a consequence, the $^{13}C\{^1H\}$ NMR chemical shift difference between **5c** and **5a**/**5b** can arise via coordination of the macrocycle's S and O atoms to either Na or K in a well-communicated receptor/[3,3′-Co$(1,2\text{-}C_2B_9H_{11})_2$]$^-$ system. Na and K ions coexist in the mother liquor but, as will be shown later, only Na is coordinated. Elemental analyses for **5a** are in agreement with the Na[1,1′-μ-{$S(CH_2CH_2O)_3CH_2CH_2S$}-3,3′-Co$(1,2\text{-}C_2B_9H_{10})_2$] formulation but were not decisive for **5b**,**c**. More information about the coordination geometry required a single-crystal X-ray structural information.

II. Synthesis and Characterization of Functionalized Monosubstituted Cobaltabis(dicarbollide) Derivatives Incorporating Three or Four Ether Groups in the Exo-Cluster Chain. To study the cluster influence on coordination, we synthesized a ligand incorporating the $(OCH_2CH_2)_2OR$ chain and the [3,3′-Co$(1,2\text{-}C_2B_9H_{11})_2$]$^-$ moiety. It was expected that a polyether open chain would allow higher cluster participation in bonding than a polyether macrocycle. With this aim, the anionic species [3,3′-Co(8-{$O(CH_2CH_2O)_nR$}-$1,2\text{-}C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ (n = 2, 3; R = $-CH_3$, $-CH_2CH_3$) were synthesized from the zwitterionic [3,3′-Co(8-$C_4H_8O_2$-$1,2\text{-}C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (**2**) compounds[10] according to Scheme 2.

Compound **2** was prepared by the reaction of the cobaltabis(dicarbollide) anion with $Et_2O{\cdot}BF_3$ in 1,4-dioxane analogously to the synthesis of the similar derivative of the *closo*-dodecaborate anion [$B_{12}H_{11}O_2C_4H_8$]$^-$.[18] This synthesis gives a higher yield (94% compared to

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Table 1. Crystallographic Parameters for Na[5b]·2$(CH_3)_2CO$, Na[5c]·$(CH_3)_2CO$·$CHCl_3$·CH_2Cl_2, and Na[7]

	Na[5b]·2$(CH_3)_2CO$	**Na[5c]**·$(CH_3)_2CO$·$CHCl_3$·CH_2Cl_2	Na[7]
empirical formula	$C_{18}H_{48}B_{18}CoNaO_5S_2$	$C_{17}H_{45}B_{18}Cl_5CoNaO_4S_2$	$C_{10}H_{34}B_{18}CoNaO_3$
fw	685.18	831.40	478.87
cryst syst	orthorhombic	monoclinic	monoclinic
space group	$Pna2_1$ (No. 33)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	18.625(2)	15.542(2)	15.0356(4)
b (Å)	10.710(2)	11.393(2)	11.4643(3)
c (Å)	17.715(1)	22.150(2)	14.7322(3)
β (deg)	90	91.266(8)	105.3940(11)
V (Å^3)	3533.7(8)	3921.1(9)	2448.32(10)
Z	4	4	4
T (°C)	21	21	−100
λ (Å)	0.710 69	0.710 69	0.710 73
ρ (g cm^{-3})	1.288	1.408	1.299
μ (cm^{-1})	6.46	9.23	7.32
goodness of fit	1.040	1.104	1.073
R1^a ($I > 2\sigma(I)$)	0.0552	0.0692	0.0461
wR2^b ($I > 2\sigma(I)$)	0.1164	0.1734	0.0923
Flack param x	0.04(4)		

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) for Na[5b]·2$(CH_3)_2CO$

Co3−C1	2.112(9)	S1−C1	1.806(10)
Co3−C2	2.070(8)	S2−C1′	1.792(10)
Co3−B4	2.109(12)	Na−O1	2.344(9)
Co3−B7	2.099(12)	Na−O2	2.366(9)
Co3−B8	2.122(12)	Na−O3	2.403(9)
Co3−C1′	2.129(9)	Na−O4	2.292(12)
Co3−C2′	2.083(10)	Na−O5	2.242(12)
Co3−B4′	2.124(11)	C1−C2	1.629(14)
Co3−B7′	2.121(12)	C1′−C2′	1.631(14)
Co3−B8′	2.133(11)		

45%) and has a better workup procedure than the one reported earlier.[10b]

The highly nucleophilic character of [RO]$^-$ anions has been used to obtain partially degraded *o*-carborane derivatives.[19] Thus, it was expected that they would have sufficient nucleophilic power to open the exo-cluster aliphatic ring of the zwitterionic [3,3′-Co(8-$C_4H_8O_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] derivative of [Co($C_2B_9H_{11}$)$_2$]$^-$ and yield the corresponding salts.

In the present work, sodium salts of [RO]$^-$ (R = $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2OCH_3$, $-CH_2CH_2OCH_2CH_3$) were used as nucleophilic agents. The larger derivatives would provide information about the nucleophilic dependence on the size and on the possibilities to modulate solubility in the resulting ligands. All Na[RO] salts were prepared by dissolving NaOH in the corresponding alcohol. Once the sodium salts had been formed, the addition of the zwitterionic species **2** to the solution of the nucleophilic agent yielded the addition compound in about 45 min. The nucleophilic attack was carried out at room temperature to avoid secondary reactions. Following purification the pure compounds [3,3′-Co(8-{O(CH_2CH_2O)$_2CH_3$}-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ (**6**), [3,3′-Co(8-{O(CH_2CH_2O)$_2CH_2CH_3$}-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ (**7**), [3,3′-Co(8-{O(CH_2CH_2O)$_3$-CH_3)-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ (**8**), and [3,3′-Co(8-{O(CH_2CH_2O)$_3CH_2CH_3$)-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ (**9**) were obtained. The ^{1}H NMR spectra of these compounds are very similar, displaying four resonances between 4.19 and 3.44 ppm: two broad singlets corresponding to the hydrogen atoms bonded to the cluster carbon atoms, a triplet signal that corresponds to the methylene units to B(8)−O, and a multiplet from the other O−CH_2 groups of the exo-cluster chain. At room temperature the proton resonances for the hydrogen atoms on the two cluster carbon atoms for compound **8** overlap at 4.17 ppm but two singlets are observed at 4.19 and 4.13 ppm at −60 °C, providing the nonequivalency of the two cluster fragments. The ^{1}H{^{11}B} NMR spectra display nine additional signals, in the range 2.96−1.44 ppm, assigned to the B−H exo-cluster hydrogen atoms. The ^{11}B{^{1}H} NMR spectra corresponding to compounds **6**−**9** featured an identical 1:1:1:1:2:4:2:2:2:1:1 pattern ranging from +24 to −28 ppm. The resonance at the lowest field remains a singlet in the ^{11}B NMR spectrum and is assigned to the B(8)-substituted boron atom. The observed ^{11}B NMR pattern reflects the C_s symmetry of the molecules (12 different signals). The boron resonance with relative intensity 4 is due to coincidental overlap of two different resonances with a 2:2 ratio. The MALDI-TOF mass spectrum of **7** displays a signal group centered at m/z 456.14 corresponding to the anionic fragment **7**.

III. Coordination Motif to Hard Metal Ions. Ligands **5** and **6**−**9** mostly differ in the additional chelating capacity provided by the −OCH_2CH_2O− units. To learn the effects on coordination, solid-state studies were conducted on the sodium salts of **5b**,**c** and solid and solution studies were conducted on the sodium salt of **7**.

(a) Cluster Participation in Na Coordination in the Presence of the Thioether/Polyether Exo-Cluster Chain. Dissolution of either **Na[5b]** or **Na[5c]** in a CH_2Cl_2/$CHCl_3$/$(CH_3)_2CO$ solvent mixture (initially 2:1:1) yielded blood red single crystals of sufficient quality to allow the crystal structures of **Na[5b]** and **Na[5c]** to be determined from X-ray diffraction data.[20] **Na[5b]** crystallizes out in an enantiomeric space group.

Crystallographic analyses of **Na[5b]**·2$(CH_3)_2CO$ (Tables 1 and 2, Figure 2) and **Na[5c]**·$(CH_3)_2CO$·$CHCl_3$·CH_2Cl_2 (Tables 1 and 3, Figure 3) confirmed that in both compounds the [3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$]$^-$ structural frag-

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(19) (a) Warren, L. F.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1642−1643. (b) Hawthorne, M. F.; Wegner, P. A.; Stafford, R. C. *Inorg. Chem.* **1965**, *4*, 1675. (c) Hawthorne, M. F.; Andrews, T. D.; Garret, P. M.; Olsen, F. P.; Reintjes, M.; Tebbe, F. N.; Warren, L. F.; Wegner, P. A.; Young, D. C. *Inorg. Syn.* **1967**, *10*, 91-.

(20) Sheldrick, G. M. SHELX-97; University of Göttingen, Göttingen, Germany, 1997.

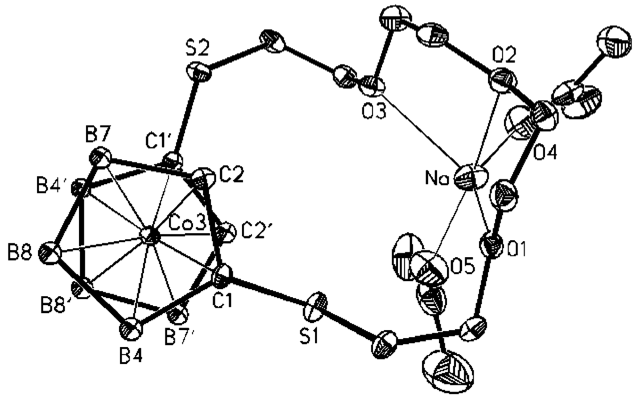

Figure 2. Simplified molecular structure of **Na[5b]·**2$(CH_3)_2CO$. Noncoordinated boron atoms are omitted.

Table 3. Selected Bond Lengths (Å) for Na[5c]·$(CH_3)_2CO·CHCl_3·CH_2Cl_2$

Co3−C1	2.070(6)	S1−Na	2.893(3)
Co3−C2	2.131(6)	S2−Na	2.900(3)
Co3−B4	2.107(8)	S1−C2	1.805(6)
Co3−B7	2.128(7)	S2−C1′	1.804(6)
Co3−B8	2.142(7)	Na−O1	2.353(5)
Co3−C1′	2.131(6)	Na−O2	2.421(5)
Co3−C2′	2.072(6)	Na−O3	2.393(5)
Co3−B4′	2.119(7)	Na−O4	2.249(6)
Co3−B7′	2.098(7)	C1−C2	1.640(8)
Co3−B8′	2.144(7)	C1′−C2′	1.661(8)

ment is a part of the macrocycle, but the fragments are made of different geometric isomers. Connections to the sulfur atoms on the organic fragment take place via one cluster carbon atom on each dicarbollyl moiety. The flexible macrocyclic chain in **Na[5b]** is coordinated by three oxygen atoms to Na^+, and two oxygen atoms from two acetone molecules complete the pentacoordination around Na^+. The coordination geometry of Na^+ is a distorted trigonal bipyramid. The short Na−O(acetone) distances suggest that acetone ligands are quite tightly bonded to the sodium cation.

As expected from the $^{13}C\{^1H\}$ NMR data for **Na[5c],** the structure found for this complex is different from that of **Na[5b]**. The coordination number for the Na^+ cation is 6, and the flexible macrocyclic chain coordinates to Na^+ through all five of its donor atoms, including the two thioether S atoms. The sixth coordination position is occupied by the oxygen atom of one acetone, completing a pentagonal-pyramidal structure. One chlorine atom of the dichloromethane solvate is at a distance of 3.399(4) Å from the sodium. This distance is too long to be considered bonding to the Na^+ ion.

The two structures are markedly different, especially considering the site around Na^+, and the cobaltabis(dicarbollide) rotamers are also different. In both structures, **Na[5b]** and **Na[5c]**, the dicarbollide ligands adopt a staggered conformation with all four cluster carbon atoms in a cisoid disposition. Thus, the projection of one of the two carbon atoms from one dicarbollide into the C_2B_3 plane of the second dicarbollide lies between the two cluster carbon atoms. This can be understood if we assume that the more stable rotamers are those where the more electronegative cluster elements are facing the same side of the dicarbollide moiety. We have also observed this phenomenon in mixed pyrrolyl/dicarbollide Co(III) complexes,[21] where the nitrogen projection on the C_2B_3 face bisects the C_c-C_c bond (C_c is cage carbon). This has also been reported for other molecules incorporating $[3,3'-Co(1,2-C_2B_9H_{11})_2]^-$ structural fragments.[22] There are major differences between the backbone conformations in **Na[5b]** and **Na[5c]** that may be described by the torsion angles through the centers of Co-coordinated C_2B_3 faces (marked c and c′). Thus the C1−c−c′−C1′ torsion angles have values of −97.2(5) and −118.4(3)° for **Na[5b]** and **Na[5c]**, while the values for C2−c−c′−C1′ torsion angles are −27.7(6) and −48.6(3)°. The differences in both cases are ca. 21°. A more pronounced difference between **Na[5b]** and **Na[5c]** is, however, the different conformations of the organic flexible spacer $-S(CH_2CH_2O)_3CH_2CH_2S-$, resulting from its distinct connections to the $[3,3'-Co(1,2-C_2B_9H_{11})_2]^-$ moiety. These correspond to the idealized racemic and meso forms, respectively (Figure 1). The meso **Na[5c]** form exhibits a considerably shorter S···S distance (3.510(2) Å), than for the racemic **Na[5b]** (4.951(4) Å); hence, a type of spatial chelating site "SCCS" with a S···S distance comparable to that found in **1** (3.371 Å) is formed.[1] Consequently in **Na[5c]** both sulfur atoms have structural conditions suitable for chelating the metal, in contrast to **Na[5b]**. Ligand **5** provides five coordinating sites in the meso isomer and only three in the racemic one. The coordinated metal binds the solvent in order to fulfill its coordination requirement.

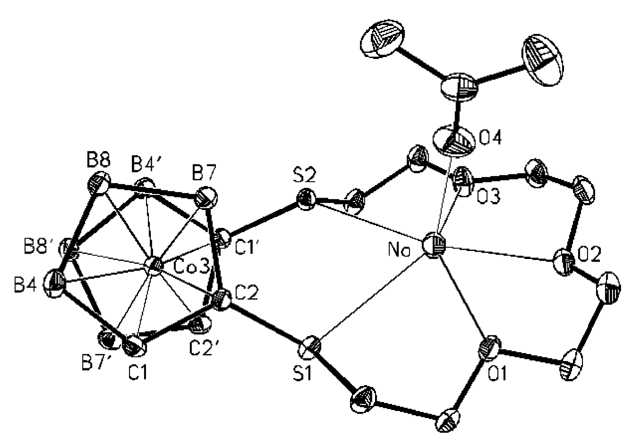

Figure 3. Simplified molecular structure of **Na[5c]·**$(CH_3)_2CO·CHCl_3·CH_2Cl_2$. Noncoordinated boron atoms and chloroform and dichloromethane molecules are omitted.

With the structure **Na[5c]** we have shown that other examples of S(thioether)−Na coordination are possible and that it is not necessary to have a preorganized S···S disposition, as was the case in Na[7,8-*μ*-$\{S(CH_2CH_2O)_3CH_2CH_2S\}$-7,8-$C_2B_9H_{10}$], in order to get S(thioether)−Na coordination. The only reported ex-

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[21] (a) Lamrani, M.; Gómez, S.; Viñas, C.; Teixidor, F.; Sillanpää, R.; Kivekäs, R. *New J. Chem.* **1996**, *20*, 909−912. (b) Teixidor, F.; Gómez, S.; Lamrani, M.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *Organomatallics* **1997**, *16*, 1278−1283. (c) Gómez, S.; Viñas, C.; Lamrani, M.; Teixidor, F.; Kivekäs, R.; Sillanpää, R. *Inorg. Chem.* **1997**, *36*, 3565−3567. (d) Llop, J.; Viñas, C.; Teixidor, F.; Victori, L.; Kivekäs, R.; Sillanpää, R. *Organometallics* **2001**, *19*, 4024−4030. (e) Llop, J.; Viñas, C.; Teixidor, F.; Victori, L.; Kivekäs, R.; Sillanpää, R. *Organometallics* **2002**, *21*, 355−361. (f) Llop, J.; Viñas, C.; Teixidor, F.; Victori, L.; Kivekäs, R.; Sillanpää, R. *Inorg. Chem.* **2002**, *41*, 3347−3352. (g) Sillanpää, R.; Llop, J.; Viñas, C.; Teixidor, F.; Kivekäs, R. *Acta Crystallogr.* **2001**, *C57*, 900−901.

[22] (a) Petrina, A.; Malý, K.; Petrícek, V.; Subrtová, V.; Línek, A.; Hummel, L. *Z. Kristallogr.* **1981**, *154*, 217−226. (b) Chamberlin, R. M.; Scott, B. L.; Melo, M. M.; Abney, K. D. *Inorg. Chem.* **1997**, *36*, 809−817.

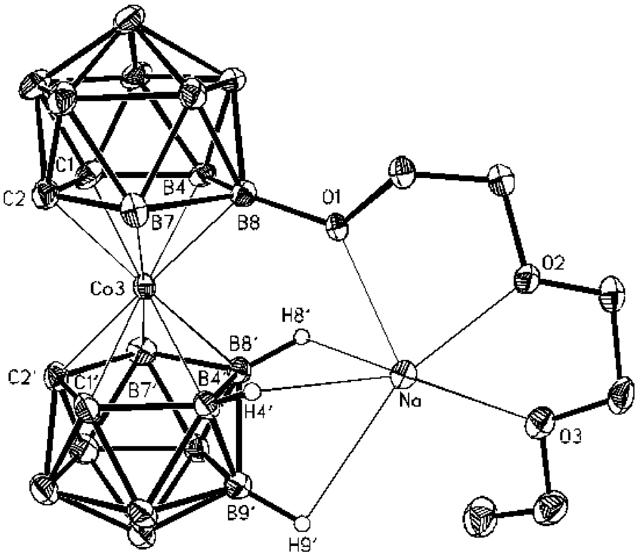

Figure 4. Molecular structure of **Na[7]**.

Table 4. Selected Bond Lengths (Å) for Na[7]

Co3−C1	2.037(3)	Na−O1	2.357(2)
Co3−C2	2.044(3)	Na−O2	2.287(3)
Co3−B4	2.080(3)	Na−O3	2.407(2)
Co3−B7	2.098(3)	Na−H4′	2.368
Co3−B8	2.132(4)	Na−H8′	2.448
Co3−C1′	2.041(3)	Na−H9′	2.867
Co3−C2′	2.049(3)	O1−B8	1.433(4)
Co3−B4′	2.080(3)	C1−C2	1.622(4)
Co3−B7′	2.104(3)	C1′−C2′	1.603(4)
Co3−B8′	2.114(3)		

amples of S(thioether)−Na bonds are restricted to thioether sulfur bonded to negatively charged carboranes via the cluster carbon atoms. The cluster seems to play a role in facilitating the bonding. Also, S(thioether)−Na bonding has been possible with the assistance of coordinating entities associated with the $ROCH_2CH_2OCH_2CH_2OR$ group, as present in **1** and **5**. In this regard we were interested in investigating how the [3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$]$^-$ cluster incorporating the $ROCH_2CH_2OCH_2CH_2OR$ group, but with an absence of −S−, would behave toward Na coordination.

(b) Cluster Participation in Na Coordination in the Presence of the Polyether Exo-Cluster Chain. 1. Coordination in the Solid State. Crystallization by slow diffusion of hexane into a saturated dichloromethane solution of **Na[7]** at controlled temperature (4 °C) afforded air- and moisture-insensitive orange plate-shaped monocrystals suitable for X-ray analysis. An X-ray diffraction study of **Na[7]** confirmed the proposed structure. A drawing of the compound is shown in Figure 4, and selected bond lengths and angles are listed in Table 4.

In the absence of the two S(thioether) moieties present as in **Na[5b]** and **Na[5c]**, the Na^+ coordinates three B−H groups: B4−H4, B8−H8, and B9−H9. It is of note that the B4···Na, B8···Na, and B9···Na contacts are short with distances of 2.857(4), 2.895(4), and 3.141(4) Å. Overall, the number of sodium short contacts is 6 in **Na[7],** one contact less than in **Na[5c]**. The coordination geometry is not typical for 6-coordination. This is due to a rigid ligand and the fact that coordinative saturation and bond directionality for Na^+ are far less significant factors than in many transition-element complexes. A short cluster B−H···Na interaction was reported recently in a [3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$]$^-$ derivative. The X-ray crystal structure of Na[8-(OCH_2CH_2)$_2$$OC_6H_4$-2-$OCH_3$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)][13] shows that the Na presents six short contacts: four Na−O contacts derived from the four oxygen atoms of the ligand, one Na−O contact derived from an ancillary water molecule, and a B8′−H contact with a Na−H distance of 2.23(3) Å. This H···Na distance is clearly shorter than the ones reported in this paper for B4H4···Na, B8H8···Na, and B9H9···Na bonds (2.368, 2.448, and 2.867 Å). The above description supports our earlier statement that boron clusters, if required, involve themselves in coordination to satisfy the metal's requirements.

2. 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 **7**, 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.

Variable-temperature $^1H\{^{11}B\}$ NMR spectra recorded in the range 22 to −80 °C using dichloromethane as a solvent are shown in Figure 5. There is a high dependence of the chemical shift of one B−H signal on temperature. This B−H resonance becomes broader and shifts to lower fields as the temperature decreases. At room temperature the signal is a well-defined singlet. With a decrease in temperature, the signal becomes a very broad singlet. These spectroscopic data are in agreement with intramolecular B−H···Na^+ 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.

IV. Role of the Electron-Rich Atom (O) Directly Bonded to a Cluster Boron Atom. It has been proven that anionic clusters containing electron-rich exo-cluster substituents (S or P) dissipate electron density into the electron-rich element. [5,23] This element becomes a strong Lewis base and a very good coordinating ligand.[5,24] Most probably the oxygen atom in the B(8)−O bond in **6**−**9** can play the same role as S and P atoms, dissipating the negative charge and becoming a strong Lewis base. Thus, the anionic species can coordinate to a Lewis acid through the oxygen atom at the B(8) position. This coordination, shown in Chart 1, could easily be formed in an almost irreversible reaction upon contact with protons from an acidic medium. A high pK_a acid is generated due to the strong basicity of the B−O group and the existence of a second oxygen atom that can also

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(23) (a) Teixidor, F.; Núñez, R.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *Inorg. Chem.* **2001**, *40*, 2587−2594.

(24) (a) Teixidor, F.; Flores, M. A.; Viñas, C.; Kivekäs, R.; Sillanpää, R. *J. Am. Chem. Soc.* **2000**, *122*, 1963−1973. (b) Teixidor, F.; Romerosa, A.; Viñas, C.; Rius, J.; Miravitlles, C.; Casabó, J. *J. Chem. Soc., Chem. Commun.* **1991**, 192−193. (c) Teixidor, F.; Ayllón, J. A.; Viñas, C.; Rius, J.; Miravitlles, C.; Casabó, J. *J. Chem. Soc., Chem. Commun.* **1992**, 1279−1280. (d) Teixidor, F.; Casabó, J.; Romerosa, A. M.; Viñas, C.; Rius, J.; Miravitlles, C. *J. Am. Chem. Soc.* **1991**, *113*, 9895−9896.

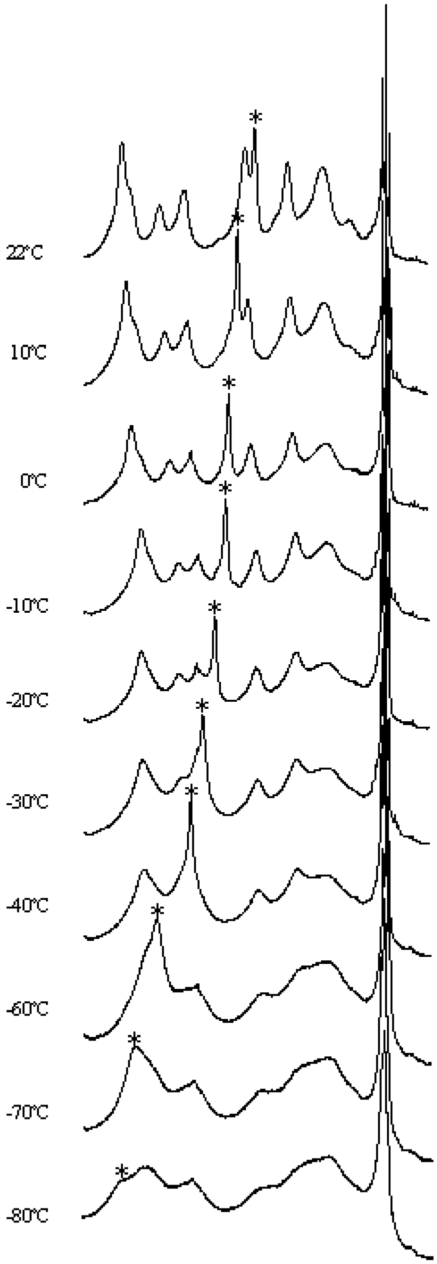
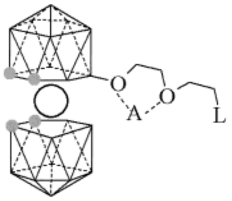


Figure 5. $^{1}H\{^{11}B\}$ NMR spectra of **7** in dichloromethane for **Na[7]** as a function of temperature. The asterisks denote signals corresponding to H atoms from intramolecular B−H···Na^{+} interactions.

Chart 1. Suggested Species Formed by Coordination of the Oxygen Atom in Addition Compounds with Lewis Acids (A)



interact with a Lewis acid (A), forming a O···A···O interaction.

Matrix-assisted laser desorption/ionization (MALDI)[25] supports, although does not confirm, the special nucleophilic character of the B−O unit. MALDI is widely used for mass spectrometric analysis of large, nonvolatile

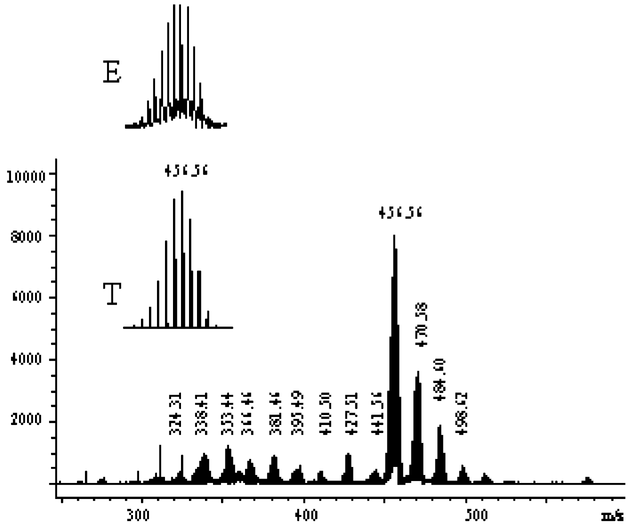


Figure 6. MALDI-TOF mass spectrum obtained for the anionic compound **7** (T = calculated, E = experimental).

biomolecules; e.g., peptides, proteins, oligonucleotides, and oligosaccharides.[26] Synthetic polymers of high molecular weight, fullerene derivatives, and synthetically prepared dendrimers have also been studied by MALDI-MS. The possible ion formation mechanisms in MALDI spectrometry are primary and secondary. “Primary” ionization refers to generation of the first ions from neutral molecules in the sample. “Secondary” mechanisms are those which lead to ions that are not directly generated by primary processes. In the mass spectrum, the products of primary and secondary processes are both usually observed. One attractive mechanism different from the former ones is that the ions observed in MALDI mass spectra are already present in the solid sample and are merely liberated by the laser pulse. This mechanism is potentially most relevant for molecules that form strong metal ion complexes such as crown ethers, ionophores, and metal-binding proteins.[27] Under these circumstances, the larger the ions, the easier the separation. Compounds **6**−**9** fulfill these requirements and were studied by the MALDI-MS technique at the negative ion mode without the use of matrixes. The lack of matrixes aids the interpretation of the primary and secondary mechanisms. We understand as a “primary” mechanism the separation of the anionic cobaltabis(dicarbollide) derivatives from the bonded sodium 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 6 shows the MALDI-TOF-MS spectrum of compound **7** as a representative example. Peaks with

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(25) (a) Karas, M.; Hillenkamp, F. *Anal. Chem.* **1988**, *60*, 2299. (b) Karas, M.; Bachmann, D.; Hillenkamp, F. *Anal. Chem.* **1985**, *57*, 2935. (c) Tanaka, K.; Waki, H.; Ido, Y.; Akita, S.; Yoshida, Y.; Yoshida, T. *Rapid Commun. Mass Spectrom.* **1988**, *2*, 151.

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ion masses higher than the molecular ion peak at *m*/*z* 456.56 (M) are observed at *m*/*z* 470.58, 484.60, and 498.62, with intensities decreasing in this order. These peaks correspond to $(M + CH_2)$, $(M + CH_2CH_2)$, and $(M + CH_2CH_2CH_2)$, respectively. Peaks with ion masses lower than the molecular peak are observed at *m*/*z* 441.56 $(M - CH_3)$ and 427.51 $(M - CH_2CH_3)$. It appears that part of the polyether chain in some molecules is transferring methylene groups to like molecules, thereby increasing their molecular weight by 14 or 15. These peaks can be interpreted as an electrophilic reaction between like anions. This is also observed in compounds **6**−**9** and has been noted previously[28] for R = $-OCH_2CH_2OCH_2CH_2$-pyr (pyr = pyrrolyl, indolyl, carbazolyl). This indicates that the CH_2 supplier is the initial $-OCH_2CH_2OCH_2CH_2-$ fragment and not the ring-opening nucleophile. Our interpretation is that the nucleophilic B−O group enhances the CH_2 trapping. There are several structures that can accommodate this CH_2 increment. Work is underway to see if this could be a synthetic procedure for cobaltabis(dicarbollide) methyl derivatives.

Conclusion

This work demonstrates the extraordinary chameleonic capacity of $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ toward coordination of a metal ion, Na^+. No other examples of S(thioether)−Na coordination besides $Na[7,8\text{-}\mu\text{-}\{S(CH_2CH_2O)_3CH_2CH_2S\}\text{-}7,8\text{-}C_2B_9H_{10}]$ are known. Extra coordination sites are filled with the oxygen atoms of the macrocycle or from solvent molecules. Given that there are fewer oxygen coordinating sites accessible, the $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ fragment supplies B−H moieties to fulfill the metal's coordination demands. The $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ enhances the coordinating capacity of X in B−X moieties (X = O, S, P), converting a weakly coordinating element, thioether, into a good nucleophile or an ether oxygen into a strong nucleophile. The availability of B−H groups and their geometrical distribution offers an unusual way of satisfying the metal's demand.

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 ^1H NMR, $^1H\{^{11}B\}$ NMR (300.13 MHz), ^{11}B NMR (96.29 MHz), and $^{13}C\{^1H\}$ NMR (75.47 MHz) spectra were recorded with a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. Chemical shift values for ^{11}B NMR spectra were referenced to external $BF_3 \cdot OEt_2$, and those for ^1H, $^1H\{^{11}B\}$, and $^{13}C\{^1H\}$ 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)).

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. EtOH was dried over molecular sieves and deoxygenated prior to use. 1,2-Dimethoxyethane and 1,4-dioxane 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. $1\text{-}SH\text{-}1,2\text{-}C_2B_{10}H_{11}$ was prepared according to the literature.[29]

Synthesis of $[3,3'\text{-}Co(8\text{-}C_4H_8O_2\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ (2). To 0.90 g (2.0 mmol) of $Cs[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]$ in 100 mL of 1,4-dioxane was added 2.0 mL (16.0 mmol) of $Et_2O \cdot BF_3$ and the reaction mixture heated at reflux under an N_2 atmosphere for 5 h. The solution was cooled to room temperature, filtered, and evaporated to dryness. The residue was taken up in dichloromethane and passed through a layer of silica using dichloromethane as the eluent. The eluate was evaporated in vacuo, giving 0.76 g (94%) of orange solid, for which the ^1H and ^{11}B NMR spectra were identical with those of an authentic sample prepared according to the literature.[10b]

Synthesis and Isolation of $1,1'\text{-}\mu\text{-}\{S(CH_2CH_2O)_3CH_2CH_2S\}\text{-}(1,2\text{-}C_2B_{10}H_{11})_2$ (3). To a stirred solution of KOH (0.48 g, 8.51 mmol) in EtOH was added 1.50 g (8.51 mmol) of $1\text{-}SH\text{-}1,2\text{-}C_2B_{10}H_{11}$. The mixture was stirred at room temperature for 30 min, and then bis[2-(2-chloroethoxy)ethyl] ether (0.98 g, 4.26 mmol) was added. The solution was refluxed for 2 h. After removal of the solvent, the residue was extracted with water and diethyl ether. The organic phase was washed with a KOH solution and dried over anhydrous magnesium sulfate. The solvent was removed, and the yellow residue was purified by column chromatography using ethyl acetate as the mobile phase ($R_f = 0.875$). Yield: 1.7 g (78%). ^1H NMR ($(CD_3)_2CO$): δ 3.93 (s, 2H, C_c-*H*), 3.69−3.62 (m, 12H, CH_2O), 3.10 (t, $^3J(H,H) = 7$, 4H, CH_2O). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ 74.66 (C_c−H), 71.27 (C_c−H), 70.34 (CH_2O), 69.22 (CH_2O), 68.16 (CH_2O), 37.00 (SCH_2). ^{11}B NMR ($(CD_3)_2CO$): δ −1.3 (d, $^1J(B,H) = 156$, 1B, B(9)), −4.7 (d, $^1J(B,H) = 148$, 1B, B(12)), −8.6 (d, $^1J(B,H) = 143$, 4B), −12.2 (d, $^1J(B,H) = 163$, 4B). IR (cm^{-1}): ν 3067, 3041 (C_c−H), 2942, 2869 (C−H), 2599 (B−H), 1119 (C−O). Anal. Calcd for $C_{12}H_{38}B_{20}O_3S_2$: C, 28.22; H, 7.50; S, 12.55. Found: C, 28.61; H, 7.42; S, 12.17.

Synthesis and Isolation of $[N(CH_3)_4]_2[7,7'\text{-}\mu\text{-}\{S(CH_2CH_2O)_3CH_2CH_2S\}(7,8\text{-}C_2B_9H_{11})_2]$ (4). To a stirred solution of **3** (0.40 g, 0.78 mmol) in 15 mL of EtOH was added 1.08 g (11.86 mmol) of NMe_4OH (in MeOH at 25%). The solution was refluxed for 4 h. A white precipitate appeared after cooling with ice. The solid was collected by filtration and washed with water and petroleum ether. Yield: 0.37 g (91%). ^1H NMR ($CDCl_3$): δ 3.66−3.57 (m, 12H, CH_2O), 3.44 (s, 24H, $N(CH_3)_4$), 3.13−2.99 (m, 2H, SCH_2), 2.71−2.62 (m, 2H, SCH_2), −2.81 (br s, 2H, B−*H*−B). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 71.17 (CH_2O), 70.19 (CH_2O), 70.01 (CH_2O), 55.25 ($N(CH_3)_4$), 35.67 (SCH_2). ^{11}B NMR ($CDCl_3$): δ −9.5 (d, $^1J(B,H) = 77$, 1B), −10.2 (d, $^1J(B,H) = 72$, 1B), −14.5 (d, $^1J(B,H) = 251$, 1B), −17.0 (d, $^1J(B,H) = 134$, 3B), −21.8 (d, $^1J(B,H) = 152$, 1B), −32.6 (d, $^1J(B,H) = 131$, 1B), −36.2 (d, $^1J(B,H) = 143$, 1B). IR (cm^{-1}): ν 3045 (C_c−H), 2916, 2867 (C−H), 2531 (B−H), 1480 ($\delta(C-H)_{alkyl}$), 1116, 1083 (C−O). Anal. Calcd for $C_{20}H_{62}B_{18}N_2O_3S_2$: C, 37.68; H, 9.80; N, 4.39; S, 10.06. Found: C, 37.48; H, 9.44; N, 4.18; S, 9.16.

Synthesis and Isolation of $[1,1'\text{-}\mu\text{-}\{S(CH_2CH_2O)_3CH_2CH_2S\}\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ ($[5]^-$). To 30 mL of dimethoxyethane containing 0.27 g (0.42 mmol) of **4** were added 1.12 g (8.64 mmol) of $CoCl_2$ and 0.96 g (8.64 mmol) of K[^{t}BuO]. The mixture was refluxed for 24 h. The solvent was evaporated, and a CH_2Cl_2/H_2O mixture was added, along with an excess of NaCl and a few drops of 1 M HCl. A red organic layer was obtained along with a brown solid in the CH_2Cl_2/H_2O interlayer. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed, and the residue was purified by successive preparative TLC in silica gel/gypsum using CH_2Cl_2/CH_3CN (10:1) as eluent. Three bands were separated: **5a** ($R_f = 0.05$), **5b** ($R_f = 0.08$),

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and **5c** ($R_f = 0.24$). The brown solid from the interlayer was treated with an acidic aqueous solution and CH_2Cl_2, to produce a red-orange organic layer. After drying, separation was performed as above to produce the same set of bands. The combined yield were as follows: **5a**, 51%, 0.125 g; **5b**, 20%, 0.057 g; **5c**, 11%, 0.038 g. **Na[5]** (**5a**): ^1H NMR ($(CD_3)_2CO$): δ 4.36 (s, 1H, C_c-H), 4.28 (s, 1H, C_c-H), 4.03−3.63 (m, 12H, CH_2O), 3.18−3.13 (m, 4H, SCH_2). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ 69.68 (CH_2O), 67.73 (C_c-H), 63.89 (C_c-H), 37.59 (SCH_2). ^{11}B NMR ($(CD_3)_2CO$): δ 8.1 (d, $^1J(B,H) = 50$), 1.0, −2.1, −6.1, −7.4, −15.1 (d, $^1J(B,H) = 88$). IR (cm^{-1}): ν 3029 (C_c-H), 2824, 2868 (C−H), 2553 (B−H), 1082 (C−O). Anal. Calcd for $C_{12}H_{36}B_{18}CoNaO_3S_2$: C, 25.35; H, 6.32; S, 11.27. Found: C, 25.73; H, 6.11; S, 11.18. **Na[5]**·2$(CH_3)_2CO$ (**5b**): ^1H NMR ($(CD_3)_2CO$): δ 4.15 (s, 2H, C_c-H), 3.78−3.56 (m, 12H, CH_2O), 3.29−2.90 (m, 4H, SCH_2), 2.90 (s, 12H, $(CH_3)_2CO$). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ 70.46 (CH_2O), 70.27 (CH_2O), 69.65 (CH_2O), 67.39 (C_c-H), 65.30 (C_c-H), 37.59 (SCH_2). ^{11}B NMR ($(CD_3)_2CO$): δ 7.9 (d, $^1J(B,H) = 141$, 2B), 0.6 (d, $^1J(B,H) = 141$, 2B), −3.1 (d, $^1J(B,H) = 129$, 2B), −4.1 (d, $^1J(B,H) = 111$, 4B), −7.2 (d, $^1J(B,H) = 143$, 2B), −11.7 (d, $^1J(B,H) = 154$, 2B). −15.7 (d, $^1J(B,H) = 153$, 2B), −20.4 (d, $^1J(B,H) = 154$, 2B). IR (cm^{-1}): ν 3030 (C_c-H), 2931, 2900 (C−H), 2554 (B−H), 1108, 1082 (C−O). Anal. Calcd for $C_{18}H_{48}B_{18}CoNaO_5S_2$: C, 31.55; H, 7.06; S, 9.36. Found: C, 31.08; H, 6.86; S, 8.85. **Na[5]**·$(CH_3)_2CO$·$CHCl_3$·CH_2Cl_2 (**5c**): ^1H NMR ($(CD_3)_2CO$): δ 4.16 (s, 1H, C_c-H), 3.93 (s, 1H, C_c-H), 3.89−3.46 (m, 12H, CH_2O), 3.31−2.97 (m, 4H, SCH_2), 2.91 (s, 6H, $(CH_3)_2CO$). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ 70.51 (CH_2O), 69.94 (CH_2O), 69.67 (CH_2O), 60.58 (C_c-H), 58.27 (C_c-H), 38.31 (SCH_2), 37.54 (SCH_2). ^{11}B NMR ($(CD_3)_2CO$): δ 6.3 (d, $^1J(B,H) = 122$, 2B), 0.9 (d, $^1J(B,H) = 145$, 2B), −2.9 (d, $^1J(B,H) = 139$, 3B), −4.4 (d, $^1J(B,H) = 144$, 1B), −6.8 (d, $^1J(B,H) = 104$, 6B), −12.6 (d, $^1J(B,H) = 177$, 2B), −15.8 (d, $^1J(B,H) = 119$, 1B), −17.3 (d, $^1J(B,H) = 126$, 1B). IR (cm^{-1}): ν 2970, 2931, 2868 (C−H), 2561 (B−H), 1110, 1082 (C−O). Anal. Calcd for $C_{17}H_{45}B_{18}Cl_5CoNaO_4S_2$: C: 24.56; H, 5.45; S, 7.71. Found: C, 24.28; H, 5.66; S, 8.05.

Synthesis and Isolation of the Sodium Salt of $[3,3'\text{-}Co(8\text{-}\{O(CH_2CH_2O)_2CH_3\}\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ (6). A 60 mL portion of deoxygenated CH_3OH containing 68.4 mg (1.22 mmol) of NaOH was stirred for 45 min. Then 500 mg (1.22 mmol) of $[8\text{-}(OCH_2CH_2)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ (**2**) was added. The mixture was stirred for 15 min, and then this was evaporated to dryness in vacuo. Purification by thin-layer chromatography (silica gel, dichloromethane/ethanol (9:1)) yielded analytically pure **6**. Yield: 555 mg (98%). ^1H NMR ($(CD_3)_2CO$): δ 4.10 (br s, 2H, C_c-H), 4.04 (br s, 2H, C_c-H), 3.99 (br s, 2H, OCH_2), 3.68 (t, $^3J(H,H) = 4$, 6H, OCH_2), 3.45 (s, 3H, CH_3), 3.20−1.44 (br m, 17H, B−H). $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$): δ 4.10 (br s, 2H, C_c-H), 4.04 (br s, 2H, C_c-H), 3.99 (t, $^3J(H,H) = 4$, 2H, OCH_2), 3.68 (t, $^3J(H,H) = 4$, 6H, OCH_2), 3.45 (s, 3H, CH_3), 3.20 (br s, 1H, B−H), 2.99 (br s, 3H, B−H), 2.74 (br s, 3H, B−H), 2.13 (br s, 2H, B−H), 1.96 (br s, 2H, B−H), 1.70 (br s, 1H, B−H), 1.64 (br s, 2H, B−H), 1.54 (br s, 2H, B−H), 1.44 (br s, 1H, B−H). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ 71.69 (OCH_2), 70.62 (OCH_2), 69.87 (OCH_2), 69.00 (OCH_2), 57.87 (CH_3), 52.55 (C_c-H), 47.17 (C_c-H). ^{11}B NMR ($(CD_3)_2CO$): δ 23.8 (s, 1B, B(8)), 8.0 (d, $^1J(B,H) = 137$, 1B), 2.5 (d, $^1J(B,H) = 139$, 1B), −1.5 (d, $^1J(B,H) = 146$, 1B), −3.9 (d, $^1J(B,H) = 130$, 2B), −5.1 (d, $^1J(B,H) = 123$, 2B), −5.8 (d, $^1J(B,H) = 143$, 2B), −8.2 (d, $^1J(B,H) = 142$, 2B), −15.9 (d, $^1J(B,H) = 152$, 2B), −19.2 (d, $^1J(B,H) = 159$, 2B), −21.2 (d, $^1J(B,H) = 158$, 1B), −27.2 (d, $^1J(B,H) = 157$, 1B). IR (cm^{-1}): ν 3034 (C_c-H), 2932, 2883, 2839 ($C_{alkyl}-H$), 2573, 2544, 2534 (B−H), 1099, 1049 (C−O and ν_{as}(C−O−C)), 1454, 1365 (δ($C_{alkyl}-H$)), 1296, 750 (γ($C_{alkyl}-H$)). Anal. Calcd for $C_9H_{32}B_{18}CoNaO_3$: C, 23.25; H, 6.94. Found: C, 23.52; H, 7.33. MALDI-TOF (*m/z*): 442.54 (M; 100%), 456.54 (M + CH_2; 76%), 470.54 (M + CH_2CH_2; 47%), 427.50 (M − CH_3; 18%), 411.51 (M − OCH_3; 35%), 397.48 (M − CH_2OCH_3; 47%), 382.47 (M − $CH_2CH_2OCH_3$; 49%), 367.46 (M − $OCH_2CH_2OCH_3$; 58%), 353.46 (M −$CH_2OCH_2CH_2OCH_3$; 60%), 339.44 (M − $CH_2CH_2OCH_2CH_2OCH_3$; 61%), 324.43 (M − $OCH_2CH_2OCH_2CH_2OCH_3$; 60%).

Synthesis and Isolation of the Sodium Salt of $[3,3'\text{-}Co(8\text{-}\{O(CH_2CH_2O)_2CH_2CH_3\}\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ (7). This compound was prepared by utilizing the same procedure as for **6**, but in deoxygenated CH_3CH_2OH. Yield: 572 mg (98%). ^1H NMR (CD_2Cl_2): δ 3.81 (br s, 2H, OCH_2), 3.71−3.61 (m, 10H: 8H, OCH_2; 2H, C_c-H), 3.49 (br s, 2H, C_c-H), 2.96−1.47 (br m, 17H, B−H), 1.23 (t, $^3J(H,H) = 7$, 3H, CH_3). $^1H\{^{11}B\}$ NMR (CD_2Cl_2): δ 3.81 (t, $^3J(H,H) = 4$, 2H, OCH_2), 3.71−3.61 (m, 10H: 8H, OCH_2; 2H, C_c-H), 3.49 (br s, 2H, C_c-H), 2.96, 2.90 (br s, 4H, B−H), 2.71 (br s, 1H, B−H), 2.54 (br s, 2H, B−H), 2.15 (br s, 2H, B−H), 2.09 (br s, 2H, B−H), 1.87 (br s, 2H, B−H), 1.64 (br s, 3H, B−H), 1.47 (br s, 1H, B−H), 1.23 (t, $^3J(H,H) = 7$, 3H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 71.71 (OCH_2), 69.17 (OCH_2), 68.95 (OCH_2), 68.32 (OCH_2), 67.39 (OCH_2), 51.08 (C_c-H), 47.50 (C_c-H), 14.67 (CH_3). ^{11}B NMR (CD_2Cl_2): δ 26.9 (s, 1B, B(8)), 6.4 (d, $^1J(B,H) = 133$, 1B), 1.9 (d, $^1J(B,H) = 141$, 1B), −1.1 (d, $^1J(B,H) = 150$, 1B), −5.7 (d, $^1J(B,H) = 134$, 6B), −7.5 (d, $^1J(B,H) = 174$, 2B), −16.1 (d, $^1J(B,H) = 161$, 2B), −17.9 (d, $^1J(B,H) = 164$, 2B), −20.9 (d, $^1J(B,H) = 162$, 1B), −28.0 (d, $^1J(B,H) = 144$, 1B). IR (cm^{-1}): ν 3038 (C_c-H), 2980, 2912, 2874 ($C_{alkyl}-H$), 2554, 2534 (B−H), 1121, 1105, 1082, 1075 (C−O and ν_{as}(C−O−C)), 1454, 1348 (δ($C_{alkyl}-H$)), 1248, 748 (γ($C_{alkyl}-H$)). Anal. Calcd for $C_{10}H_{34}B_{18}CoNaO_3$: C, 25.08; H, 7.16. Found: C, 25.01; H, 7.27. MALDI-TOF (*m/z*): 456.56 (M; 100%), 470.58 (M + CH_2; 46%), 484.60 (M + CH_2CH_2; 23%), 498.62 (M + $CH_2CH_2CH_2$; 7%), 441.56 (M − CH_3; 7%), 427.51 (M − CH_2CH_3; 17%), 410.50 (M − OCH_2CH_3; 5%), 395.49 (M − $CH_2OCH_2CH_3$; 7%), 381.46 (M − $CH_2CH_2OCH_2CH_3$; 11%), 366.46 (M − $OCH_2CH_2OCH_2CH_3$; 10%), 353.44 (M − $CH_2OCH_2CH_2OCH_2CH_3$; 15%), 338.41 (M − $CH_2CH_2OCH_2CH_2OCH_2CH_3$; 11%), 324.31 (M − $OCH_2CH_2OCH_2CH_2OCH_2CH_3$; 5%).

Synthesis and Isolation of the Sodium Salt of $[3,3'\text{-}Co(8\text{-}\{O(CH_2CH_2O)_3CH_3\}\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ (8). This compound was prepared using the same procedure as for **6**, but in deoxygenated $CH_3OCH_2CH_2OH$. Yield: 595 mg (96%). ^1H NMR ($(CD_3)_2CO$): δ 4.17 (br s, 4H, C_c-H), 3.75 (br s, 2H, OCH_2), 3.65−3.54 (m, 10H, OCH_2), 3.35 (s, 3H, CH_3), 2.94−1.46 (br m, 17H, B−H). ^1H NMR ($(CD_3)_2CO$, −60 °C)): δ 4.19 (br s, 2H, C_c-H), 4.13 (br s, 2H, C_c-H), 3.75 (br s, 2H, OCH_2), 3.65−3.54 (m, 10H, OCH_2), 3.35 (s, 3H, CH_3), 2.94−1.46 (br m, 17H, B−H). $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$): δ 4.17 (br s, 4H, C_c-H), 3.75 (t, $^3J(H,H) = 4$, 2H, OCH_2), 3.65−3.54 (m, 10H, OCH_2), 3.35 (s, 3H, CH_3), 2.94 (br s, 3H, B−H), 2.84 (br s, 1H, B−H), 2.71 (br s, 3H, B−H), 2.05 (br s, 2H, B−H), 1.87 (br s, 2H, B−H), 1.64 (br s, 3H, B−H), 1.55 (br s, 2H, B−H), 1.46 (br s, 1H, B−H). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ 71.27 (OCH_2), 69.68 (OCH_2), 69.46 (OCH_2), 68.60 (OCH_2), 58.12 (CH_3), 52.88 (C_c-H), 46.76 (C_c-H). ^{11}B NMR ($(CD_3)_2CO$): δ 24.4 (s, 1B, B(8)), 6.5 (d, $^1J(B,H) = 137$, 1B), 1.6 (d, $^1J(B,H) = 141$, 1B), −1.6 (d, $^1J(B,H) = 153$, 1B), −3.9 (d, $^1J(B,H) = 158$, 2B), −6.0 (d, $^1J(B,H) = 150$, 2B), −6.4 (d, $^1J(B,H) = 132$, 2B), −7.9 (d, $^1J(B,H) = 139$, 2B), −16.3 (d, $^1J(B,H) = 153$, 2B), −19.5 (d, $^1J(B,H) = 158$, 2B), −21.3 (d, $^1J(B,H) = 167$, 1B), −27.6 (d, $^1J(B,H) = 160$, 1B). IR (cm^{-1}): ν 3042 (C_c-H), 2932, 2903, 2874 ($C_{alkyl}-H$), 2573, 2538 (B−H), 1161, 1094, 1057 (C−O and ν_{as}(C−O−C)), 1470, 1350 (δ($C_{alkyl}-H$)), 1252, 748 (γ($C_{alkyl}-H$)). Anal. Calcd for $C_{11}H_{36}B_{18}CoNaO_4$: C, 25.96; H, 7.13. Found: C, 25.83; H, 7.24. MALDI-TOF (*m/z*): 499.58 (M; 100%), 514.60 (M + CH_3; 49%), 528.61 (M + CH_2CH_3; 13%), 456.53 (M − OCH_2CH_2; 5%), 442.52 (M − $CH_2OCH_2CH_2$; 4%), 428.50 (M − $CH_2CH_2OCH_2CH_2$; 3%), 383.46 (M − $CH_2CH_2OCH_2CH_2OCH_2CH_2$; 4%), 354.44 (M − $CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2$; 4%), 340.42 (M − $CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2$ CH_2; 20%), 324.41 (M − $OCH_2CH_2OCH_2CH_2OCH_2CH_2$ OCH_2CH_2; 17%).

Synthesis and Isolation of the Sodium Salt of $[3,3'\text{-}Co(8\text{-}\{O(CH_2CH_2O)_3CH_2CH_3\}\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ (9). This compound was prepared using the same procedure as for **6** but in deoxygenated $CH_3CH_2OCH_2CH_2OH$. Yield: 611 mg (96%). ^1H NMR ($(CD_3)_2CO$): δ 4.19 (br s, 2H, C_c-H), 4.16 (br s, 2H, C_c-H), 3.69−3.44 (m, 14H, OCH_2), 2.91−1.37 (br m, 17H, $B-H$), 1.15 (t, $^3J(H,H) = 6$, 3H, CH_3). $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$): δ 4.19 (br s, 2H, C_c-H), 4.16 (br s, 2H, C_c-H), 3.69−3.44 (m, 14H, OCH_2), 2.91 (br s, 3H, $B-H$), 2.72 (br s, 1H, $B-H$), 2.68 (br s, 3H, $B-H$), 2.02 (br s, 2H, $B-H$), 1.81 (br s, 2H, $B-H$), 1.63 (br s, 1H, $B-H$), 1.54 (br s, 2H, $B-H$), 1.46 (br s, 2H, $B-H$), 1.37 (br s, 1H, $B-H$). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ 71.80 (OCH_2), 70.22 (OCH_2), 70.02 (OCH_2), 69.96 (OCH_2), 69.41 (OCH_2), 68.47 (OCH_2), 66.05 (OCH_2), 53.38 (C_c-H), 46.56 (C_c-H), 14.62 (CH_3). ^{11}B NMR ($(CD_3)_2CO$): δ 24.4 (s, 1B, B(8)), 5.9 (d, $^1J(B,H) = 128$, 1B), 1.3 (d, $^1J(B,H) = 140$, 1B), −1.6 (d, $^1J(B,H) = 186$, 1B), −3.7 (d, $^1J(B,H) = 166$, 2B), −6.3 (d, $^1J(B,H) = 139$, 6B), −16.4 (d, $^1J(B,H) = 145$, 2B), −19.5 (d, $^1J(B,H) = 152$, 2B), −21.2 (d, $^1J(B,H) = 115$, 1B), −27.5 (d, $^1J(B,H) = 135$, 1B). IR (cm^{-1}): ν 3038 (C_c-H), 2922, 2870 ($C_{alkyl}-H$), 2557 ($B-H$), 1097 ($C-O$ and $\nu_{as}(C-O-C)$), 1454, 1348 ($\delta(C_{alkyl}-H)$), 1248, 748 ($\gamma(C_{alkyl}-H)$). Anal. Calcd for $C_{12}H_{38}B_{18}CoNaO_4$: C, 27.56; H, 7.32. Found: C, 27.55; H, 7.26. MALDI-TOF (m/z): 500.56 (M; 100%), 514.58 (M + CH_2; 62%), 528.60 (M + CH_2CH_2; 16%), 383.45 (M − $CH_2CH_2OCH_2CH_2OCH_2CH_3$; 5%), 367.45 (M − $OCH_2CH_2OCH_2CH_2OCH_2CH_3$; 4%), 353.43 (M − $CH_2OCH_2CH_2OCH_2CH_2OCH_2\ CH_3$; 4%), 339.41 (M − $CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_3$; 14%), 323.41(M − $OCH_2\ CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_3$; 11%).

X-ray Diffraction Studies. X-ray Structure Determinations of Na[5b]·$2(CH_3)_2CO$, Na[5c]·$(CH_3)_2CO\cdot CHCl_3\cdot CH_2Cl_2$, and Na[7]. Single-crystal data collections for **Na[5b]**·$2(CH_3)_2CO$ and **Na[5c]**·$(CH_3)_2CO\cdot CHCl_3\cdot CH_2Cl_2$ were performed at room temperature on a Rigaku AFC5S diffractometer using graphite-monochromated Mo Kα radiation, while a crystal of **Na[7]** was measured on a Nonius KappaCCD diffractometer at −100 °C. Totals of 3213, 6912, and 4774 unique reflections were collected for **Na[5b]**·$2(CH_3)_2CO$, **Na[5c]**·$(CH_3)_2CO\cdot CHCl_3\cdot CH_2Cl_2$, and **Na[7]**, respectively.

The structures were solved by direct methods and refined on F^2 by the SHELXL97 program.[20] For **Na[5b]**·$2(CH_3)_2CO$, boron atoms were refined with isotropic displacement parameters, but other non-hydrogen atoms were refined with anisotropic displacement parameters. **Na[5b]**·$2(CH_3)_2CO$ crystallizes in a noncentrosymmetric space group, and the absolute configuration of **Na[5b]**·$2(CH_3)_2CO$ was determined by refinement of the Flack x parameter. For **Na[5c]**·$(CH_3)_2CO\cdot CHCl_3\cdot CH_2Cl_2$ and **Na[7]**, all non-hydrogen atoms were refined with anisotropic displacement parameters. For all structures, the hydrogen atoms were treated as riding atoms using the SHELX97 default parameters.

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Supporting Information Available: Tables giving detailed crystallographic data, atomic positional and thermal displacement parameters, and bond distances and angles for $Na[1,1'\text{-}\mu\text{-}\{S(CH_2CH_2O)_3CH_2CH_2S\}\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]\cdot 2(CH_3)_2CO$ (**Na[5b]**·$2(CH_3)_2CO$), $Na[1,1'\text{-}\mu\text{-}\{S(CH_2CH_2O)_3CH_2CH_2S\}\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]\cdot(CH_3)_2CO\cdot CHCl_3\cdot CH_2Cl_2$ (**Na[5c]**·$(CH_3)_2CO\cdot CHCl_3\cdot CH_2Cl_2$), and $Na[3,3'\text{-}Co(8\text{-}\{O(CH_2CH_2O)_2CH_2CH_3\}\text{-}1,2\text{-}(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ (**Na[7]**). This material is available free of charge via the Internet at http://pubs.acs.org.

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