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The Zwitterion (8,8'-mu-CH₂O(CH₃)-(1,2-C₂B₉H₁₀)₂-3,3'-Co](o) as a Versatile Building Block To Introduce Cobalt Bis(Dicarbollide) Ion into Organic Molecules

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The Zwitterion $[8,8'-\mu\text{-CH}_2\text{O}(\text{CH}_3)\text{-}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2\text{-}3,3'\text{-Co}]^0$ as a Versatile Building Block To Introduce Cobalt Bis(Dicarbollide) Ion into Organic Molecules

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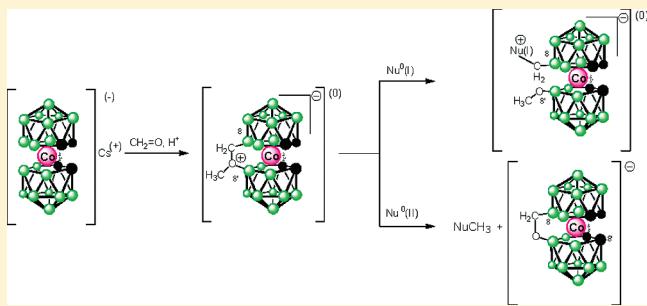
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Supporting Information

ABSTRACT: The synthesis of a new bridged $[8,8'\text{-}\mu\text{-CH}_2\text{O}(\text{CH}_3)\text{-}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2\text{-}3,3'\text{-Co}]^0$ derivative (**2**), arising from the acid-catalyzed reaction of cobalt bis(1,2-dicarbollide) (**1**⁻) ion with formaldehyde, is reported. The proposed reaction path is supported by the isolation of side products including two zwitterionic compounds, the known bridged $[8,8'\text{-}\mu\text{-}(\text{CH}_3\text{O})\text{-}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2\text{-}3,3'\text{-Co}]^0$ derivative (**3**), the new zwitterion $[(8\text{-}(\text{CH}_3)_2\text{O}\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})\text{-}(1',2'\text{-C}_2\text{B}_9\text{H}_{11})\text{-}3,3'\text{-Co}]^0$ (**4**), and two anionic compounds—the known $[(8,8'\text{-Cl}_2\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})_2\text{-}3,3'\text{-Co}]^-$ and the newly characterized dimethoxy derivative $[(8,8'\text{-}(\text{CH}_3\text{O})_2\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})_2\text{-}3,3'\text{-Co}]^-$ of the cobalt bis(dicarbollide) ion. Compound **2** serves as a versatile building block for the construction of zwitterionic derivatives, as exemplified by the synthesis of a series of compounds of general formulation $[(8\text{-X-CH}_2\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})(8'\text{-CH}_3\text{O-}1',2'\text{-C}_2\text{B}_9\text{H}_{10})_2\text{-}3,3'\text{-Co}]^0$ (**6**). Compounds of type **6** bear organic end groups ($\text{X} = \text{NC}_5\text{H}_5$ (**6a**), $\text{C}_6\text{H}_{13}\text{NH}_2$ (**6b**), $2\text{-HOC}_2\text{H}_4\text{NH}_2$ (**6c**), $(\text{C}_6\text{H}_5)_3\text{P}$ (**6d**)) adjacent to the cluster via a methylene spacer. The reactions with alcoholates or phenolates, demonstrated by the isolation of a derivative with $\text{X} = 1\text{-O}(4\text{-}t\text{-Bu-C}_6\text{H}_4)$ (**7**⁻) in low yield, seem less advantageous due to the competing demethylation of the oxonium bridge in **2**, which results in the preferential formation of the anion $[8,8'\text{-}\mu\text{-CH}_3\text{O-}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2\text{-}3,3'\text{-Co}]^-$ (**8**⁻). A similar side reaction was found to occur in the synthesis of a tetrasubstituted *tert*-butyl-calix[4]arene (**9**⁻), where one calixarene OH site was methylated producing the metallacarborane ion **8**⁻ instead of the bridge opening. The molecular structures of **6a,c-e**, **8**⁻, and **9**⁻ were determined by single-crystal X-ray diffraction analyses, and all compounds were characterized by high-resolution NMR (¹H, ¹³C, and ¹¹B) and mass spectrometry.



INTRODUCTION

Since its discovery by Hawthorne¹ four decades ago, the cobalt(I) bis(dicarbollide)(1⁻) anion (**1**⁻) has continued to attract considerable interest,² due to its close similarity to metallocenes, ionic character, high thermal, chemical, and radiolytical stability, and diamagnetic properties. During the past few years, a need for synthetic approaches has intensified, resulting in the modification of its cage by reactive groups that allow for easy introduction of the metallacarborane framework as a building block into larger functional molecules and materials. Although the substitution chemistry of the anion **1**⁻ is associated with the most extensively explored areas of boron cluster chemistry,² the availability of such simple, versatile, and high-yielding synthetic methods is still limited to a considerable extent. Several years ago, we reported on the dioxane-**1** derivative,³ its unique feature being an easy cleavage of the dioxane ring by a variety of nucleophiles.⁴⁻⁹ This compound

served as the most versatile reagent in the chemistry of complex **1**⁻ and opened up synthetically feasible routes to various designed ionic molecules for many particular applications. These applications include efficient extraction agents for lanthanides and actinides,^{4,6,9-15} additives and doping agents for conducting polymers,¹⁶⁻²² use in biomedicine as HIV protease inhibitors,^{23,24} boron labeling of DNA fragments²⁵⁻²⁹ for boron neutron capture therapy (BNCT), UV, IR, and electrochemical markers,²⁹⁻³⁴ etc. The scope of these reactions was reviewed recently.³⁵ We report here synthetic procedures providing a similarly useful derivative of the cobalt bis(dicarbollide) sandwich **1** bearing another easily cleavable ring substituent consisting of a diatomic bridge {—CH₂—O⁺(CH₃)—} interconnecting B(8) and B(8') cage positions (**2**)

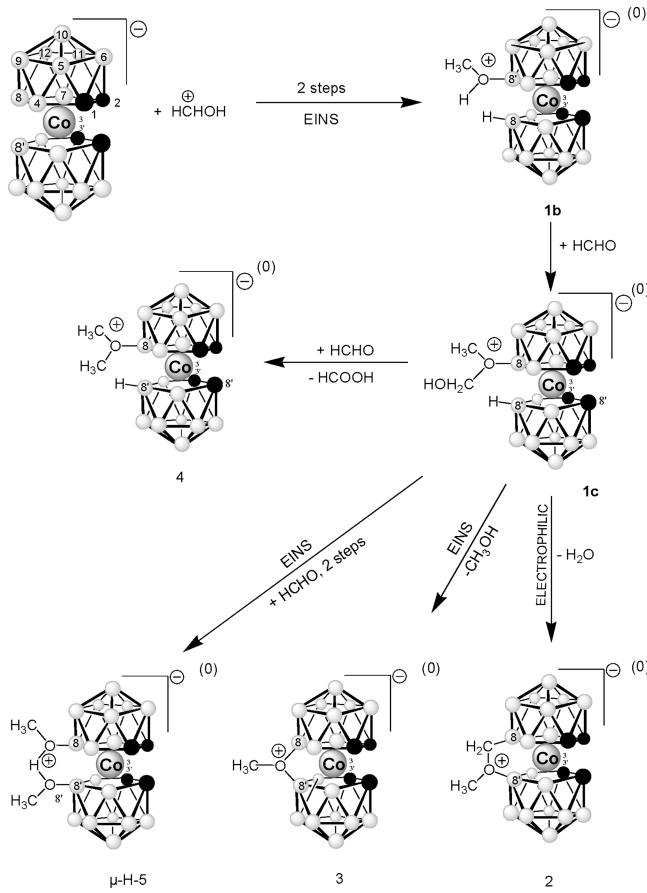
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(see Scheme 1). This paper outlines the scope and limitations of the bridge cleavage reactions of **2**, which proceeded

Scheme 1



smoothly with a large variety of amines as nucleophiles but were carried out with difficulty when the nucleophile was anionic or sterically demanding. Presented as well are crystal

structures of compound **2** and the majority of products isolated from the basic set of ring-opening reactions.

RESULTS AND DISCUSSION

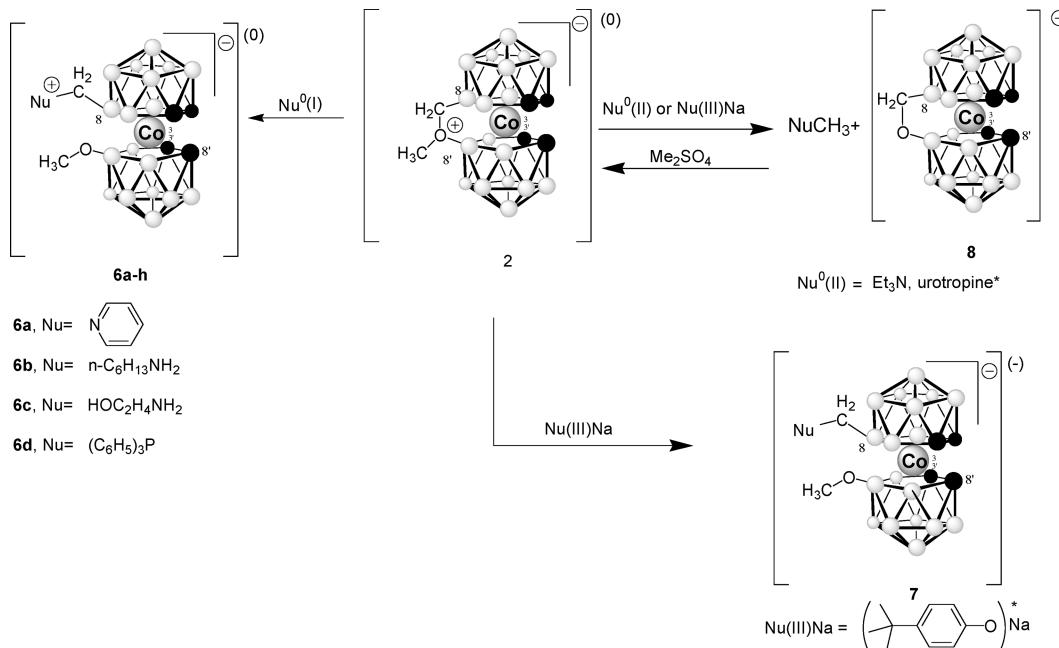
Many years ago, we reported that heating the Cs^+ salt of anion **1**⁻ with formaldehyde in acetic acid anhydride as the auxiliary solvent in the presence of sulfuric acid resulted in a red zwitterionic derivative with a monoatomic oxonium bridge, $[8,8'\text{-}\mu\text{-CH}_3\text{O}\text{-}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2\text{-}3,3'\text{-Co}]^0$ (**3**).³⁶ Only recently, to our surprise, we have found that using slightly different reaction conditions gives the yellow compound $[8,8'\text{-}\mu\text{-(CH}_3\text{OCH}_2\text{)}\text{-}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2\text{-}3,3'\text{-Co}]^0$ (**2**) as the second main neutral product. The reaction conditions were further optimized on the basis of 85 experiments systematically mapping the influence of reaction conditions on product composition. In Table 1, we present only a small portion of these data that we believe illustrates the effect of several main factors governing the formation of **2** and **3**. The main differences favoring the formation of **2** are the different ratio of the reagents, the use of dichloroethane as the solvent, and the use of hydrochloric acid for activation.

The proposed reaction mechanism leading to derivative **2** and to other products is depicted in Scheme 1. This is based on HPLC monitoring of the resulting species **2**–**4** after reactions carried out under a large variety of experimental conditions (see also Table 1), giving the product mass balance and full characterization of all the isolatable products **2**–**4**, along with the deprotonated species $[8,8'\text{-(CH}_3\text{O})_2\text{-}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2\text{-}3,3'\text{-Co}]^-$ (**5**⁻). Our study indicates that the reaction pathways leading to **2** start with electrophile induced nucleophilic substitution (EINS), wherein a transient electrophile abstracts the most hydridic hydrogen atom from the cage position B(8'). The vacancy is then occupied by the oxygen end of the $\{\text{CH}_2\text{OH}\}$ moiety, arising from the protonation of formaldehyde to form the intermediate **1b**. The addition of another formaldehyde molecule to the oxygen atom leads to the formation of another presumed intermediate **1c**. This could not be isolated, but its existence can explain the formation of four

Table 1. Overview of the Experimentally Used Reaction Conditions Illustrating the Effect of Main Factors Affecting the Yield of Zwitterionic Products **2 and **3****

run	molar ratio Cs 1 : formaldehyde	acid	solvent	temp (°C)	time (h)	yield of zwitterions ^a (%)	yield of 2 ^{b,c} by HPLC (%)	yield of 3 ^{b,c} by HPLC (%)
1	1:2	HCl(aq) ^d	Cl(CH ₂) ₂ Cl	80	2	60.4	31.4	23.1
2	1:4	HCl(aq) ^d	Cl(CH ₂) ₂ Cl	80	2	62.2	70.5	25.2
3	1:6	HCl(aq) ^d	Cl(CH ₂) ₂ Cl	80	2	71.3	56.7	37.3
4	1:30	HCl(aq) ^d	Cl(CH ₂) ₂ Cl	80	2	39.1	21.0	24.0
5	1:4	SOCl ₂	Cl(CH ₂) ₂ Cl	80	5	61.0	59.3	30.5
6	1:4	HCl(aq) ^d	CH ₂ Cl ₂	20	20	48.0	62.3	30.5
7	1:4	HCl(aq) ^d	CHCl ₃	70	2	55.0	44.8	31.5
8	1:4	HCl _(aq) ^d	benzene	80	5	48.5	61.8	36.9
9	1:4	H ₂ SO ₄	Cl(CH ₂) ₂ Cl	80	2	58.4	36.4	46.6
10	1:4	H ₂ SO ₄	CHCl ₃	80	3	56.0	30.3	62.1
11	1:4	H ₂ SO ₄	CH ₂ Cl ₂	20	20	60.3	39.2	27.2
12	1:4	H ₃ PO ₄	benzene	80	4	39.3	65.6	32.3
13	1:4	HCl(aq) ^d	H ₂ O	80	2	17.7	24.7	60.9
14	1:3	HCOOH(aq)	HCOOH	80	2	28.1	16.6	82.5
15	1:4	HCl(aq) ^d	CH ₃ OH	65	4	0		

^aYields that were isolated. ^bThe percentages of the products **2** and **3** in the zwitterionic fractions from peak areas on HPLC chromatograms; the peaks were detected at wavelength 264 nm. ^cThe difference in the addition of observed areas corresponds to the presence of the neutral compounds **4** and $\mu\text{-H-5}$; these data are not shown. ^d35% aqueous HCl.

Scheme 2. Ring Cleavage Reactions Using Different Types of Nucleophilic Reagents^a

^aNucleophiles that provide two different reaction paths.

main electroneutral products that were observed in the reaction mixtures. Thus, the electrophilic substitution step, where the carbon end of the moiety attached to B(8') in **1c** acts as an electrophile attacking the B(8')–H site, results after elimination of water in an intramolecular cyclization reaction with the formation of the biatomic bridge in **2**. Indirect support for this pathway is observed when reactions carried out in the presence of water significantly reduce the formation of **2** (see Table 1). In contrast, the EINS-type reaction where the oxygen atom in **1c** with a lone pair of electrons is acting as the nucleophile would provide, after subsequent elimination of methanol, the monoatomic bridge present in **3**. Convincing but limited support for this step is seen in the experimental evidence that methanol quenches the whole reaction sequence. An alternate EINS type reaction of the intermediate **1c** would explain the presence of the doubly substituted product (μ -H-**5**). This probably would be formed by repeating the reaction sequence with formaldehyde at the second available skeletal site B(8'). The poorly stable neutral zwitterion $[(8\text{-}(CH_3)_2O\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})\text{-}3,3'\text{-}Co]^0$ (**4**) present in low ratios would probably again originate from the presumed intermediate **1c** via a second addition of the formaldehyde to the oxygen atom, followed by the loss of formic acid. Indeed, our observations indicate that the presence of formic acid in the reaction mixture completely suppresses its formation.

The formation of compound **3** in the product mixture could not be completely eliminated, at least under a variety of tested reaction conditions. Nevertheless, the product composition can be shifted significantly toward **2** (see Table 1). As determined by analytical HPLC, the best ratio (ca. 7:3) between **2** and **3** can be obtained under optimized conditions consisting of heating **Cs1** with 4 equiv of formaldehyde (using *p*-formaldehyde as a more suitably defined alternative) in 1,2-dichloroethane for 2 h under acid catalysis by hydrochloric acid. Lower ratios of formaldehyde slightly decrease the overall

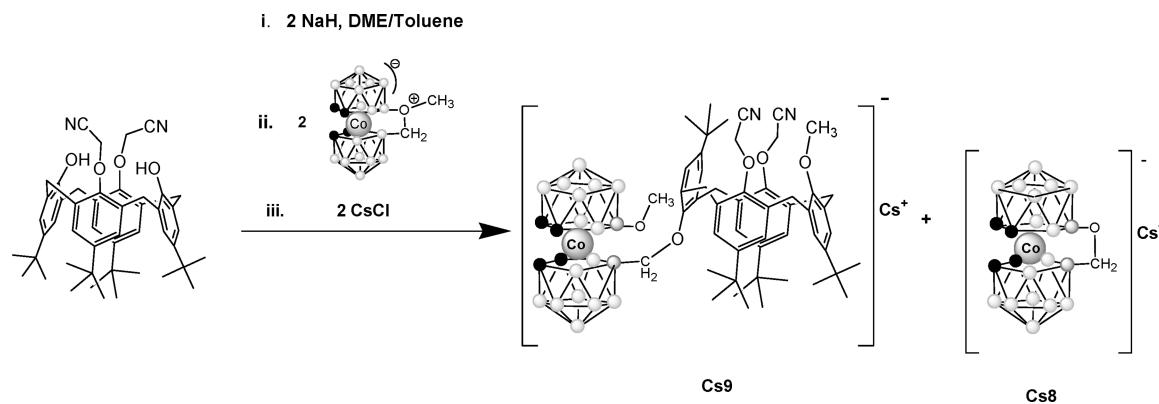
yield, while the use of higher ratios leads to increased amounts of **3**.

The acid used for activation plays an important role in both the product composition and the overall yields. The use of aqueous hydrochloric acid proved advantageous for the formation of **2**. Sulfuric and formic acid and their mixtures promoted a competitive formation of **3**. The following solvents were mainly tested: water, methanol, formic acid, acetic acid, benzene, toluene, dichloromethane, chloroform, dichloroethane, and carbon disulfide. Enhanced formation of **2** was observed only if chlorinated alkanes and benzene were used. Table 1 depicts the best yields of **2** achieved using 1,2-dichloroethane. Other advantages of this solvent are a faster reaction rate than with benzene and easier isolation of the zwitterionic products. Despite the complexity of the reaction, compounds **2** and **3** are formed as almost single neutral products and can be easily isolated by filtration and alkaline washing (see below) in an overall yield of up to 70%. The only compound present in the zwitterionic fraction after this treatment was identified as **4**, isolatable in a low yield of around 4%.

Removal of the main ionic side product (identified as the known $Cs[8,8'\text{-Cl}_2\text{-}(1,2\text{-}C_2B_9H_{10})_2\text{-}3,3'\text{-}Co]$) that is present in the reaction mixture only if the reaction is carried out in chlorinated solvents is easily and quantitatively accomplished by filtration of the reaction mixture. This product also forms in 1,2-dichloroethane, however in an appreciably lower yield (ca. 10–15%) than in other halogenated solvents ($CHCl_3$, CH_2Cl_2). It should be noted that this chloro derivative is obtained in high chemical and isomeric purity by extraction of the solids after filtration by acetone.

The second ionic product, 5^- , is released into the aqueous phase by extraction with aqueous Na_2CO_3 due to easy deprotonation of the resulting neutral compound μ -H-**5**. Compounds **2** and **3** can be separated from the fraction containing the neutral products by flash chromatography using

Scheme 3. Alkylation of **2** with Cyanomethyl Ether *tert*-Butyl-calix[4]arene Resulting in the Products of Alkylation and Demethylation Reactions



a 1:1 ether–hexane mixture as the mobile phase, in which **2** elutes first, but their isolation on a larger scale is tedious due to similar chromatographic properties and limited solubility of both species.

A striking feature of this derivative is the presence of a diatomic $\{-O^+(CH_3)-CH_2-\}$ bridge between the two dicarbollide ligands sandwiching the cobalt atom. As shown in Scheme 1, the oxygen atom is substituted by a methyl group. Thus, its oxonium character enables further ring-opening reactions (see Schemes 2 and 3). Derivative **2** can be used to easily incorporate the very stable cobalt(III) bis(dicarbollide) anion **1** into various organic molecules, thus resembling the previously reported dioxane-**1** derivative^{3,5,6,29} but providing a shorter connection to the cage (see Scheme 2). In our experience, this is the only known method to conveniently and reliably attach a functional group to the cage boron atom for a short distance. As a consequence of splitting the $\{CH_2-O^+(CH_3)\}$ bond, the methoxy group remains at the second dicarbollide ligand. In general, ring-cleavage reactions of **2** with uncharged N or P nucleophiles result after acidification (even on the silica gel column) in the formation of zwitterions with positively charged terminal moieties (see Scheme 2). The base is attached via a methylene linkage, which is a distinct structural difference from the previously reported series of compounds with substituents attached via a diethylene glycol spacer, available by ring opening of the dioxane derivative, where the oxygen atom sitting on a B(8) position can be relatively easily protonated. Thus, the room-temperature reactions of compound **2** with amines or phosphines in toluene–DME solutions gave rise to the corresponding ammonium or phosphonium derivatives (see Scheme 2). For example, we report here structurally characterized compounds with pyridinium (**6a**), 2-hydroxyethylammonium (**6c**), and triphenylphosphonium (**6d**) end groups obtained in high yields of 96, 82, 66, and 90%, respectively. The crystallographically determined molecular structures of compounds **6a,c,d** are depicted in Figures 2–4. We present also NMR, MS, HPLC, and other data necessary for a complete characterization and purity assay of all derivatives.

In reactions of this type, when using less expensive amines and phosphines as nucleophiles, applicable in larger excess, a solution in toluene–DME can be stirred at room temperature with a mixture of both zwitterionic derivatives **2** and **3**, without prior separation. Compound **3**, acting as a strong methylating agent, then loses the methyl, which leads to a dark violet anion, whereas compound **2** undergoes ring cleavage to produce a

neutral yellow species. These products differ significantly and can be smoothly separated in almost quantitative yields by chromatography on a short silica gel column with the use of either toluene or CH_2Cl_2 as the solvent. The observed rate of reaction of **2** is distinctly faster than the demethylation reaction of **3**. This further contributes to the high level of purity of the products as determined by HPLC and MS. Application of this procedure enables real preparative access to ammonium and phosphonium derivatives resulting from the ring cleavage of **2**.

As an exception, a reaction with strongly basic tertiary amines and sterically demanding bases in which compound **2** is preferentially demethylated produces the orange anion $[(8,8'-\mu-OCH_2)-(1,2-C_2B_9H_{10})_{2,3,3'}-Co]^0$ (**8** $^-$). This reaction was observed to be quantitative with triethylamine, and partly with urotropine, giving both possible products in the ratio ca. 2:1, according to NMR and HPLC (details are not shown here). The triethylammonium salt of the demethylated orange, bare-oxygen anion **8** $^-$ was structurally characterized (see Scheme 2 and Figure 5). It should be noted that both anions resulting from the demethylation of **2** and **3** are easily and quantitatively remethylated using dimethyl sulfate in CH_3CN or in suitable alcohols (MeOH, EtOH, PrOH, etc.).

If the ring-opening nucleophile is an anion (alcoholate or phenolate), ionic species are produced. However, the demethylation path leading to the **8** $^-$ ion also enters significantly into play here. Nevertheless, the ring-opening products could still be obtained (see Scheme 2). Thus, the 1-oxy-4-*tert*-butylphenyl derivative (**7** $^-$), as an example of this kind of substitution, could be isolated in only 19% yield from the reaction of **2** with the respective phenolate in toluene–DME. A similar ratio of product to demethylated anion **8** $^-$ was observed (by HPLC and NMR) when **2** was reacted with sodium guaiacolate (details are not given here).

Another convincing example of the ambiguous behavior of compound **2** is its reaction with the deprotonated *tert*-butyl-calix[4]arene substituted by two cyanomethyl ether groups located in distal 1,3-positions of the calixarene platform (see Scheme 3). The only isolatable product (**9** $^-$), obtained in 31% yield from the reaction with **2**, is the calix[4]arene modified by a one-cobalt bis(dicarbollide) cluster cage. Consequently, the second OH group available for the reaction was methylated. It can be assumed that a greater steric crowding by the nitrile substituents and the bulky boron cage play some role in this path. The cesium salt of this calixarene **Cs9** was structurally characterized (see below).

Structural Considerations. All compounds were characterized by NMR spectroscopy and mass spectrometry and for six compounds by X-ray crystallography. The purity of all species was determined by HPLC methods.³⁷ The crystallographically determined molecular structures of derivatives 2, 6a,c,d, 8⁻, and 9⁻ are presented in Figures 1–6, respectively,

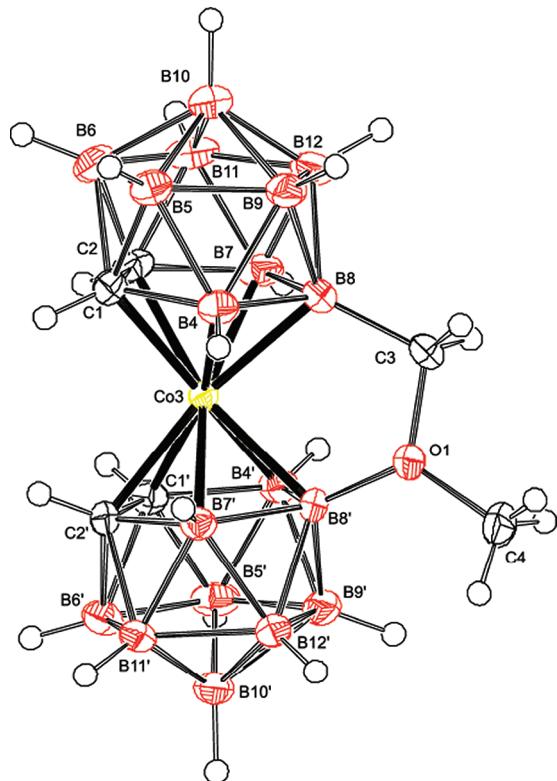


Figure 1. ORTEP presentation of the structure of 2 with atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond distances (\AA) and angles (deg): Co1–C21 = 2.0522(19), Co1–C2 = 2.0535(18), Co1–B8 = 2.072(2), Co1–B8' = 2.046(2), B8–C1 = 1.586(3), B8'-O1 = 1.510(2), B8–B12 = 1.804(3), O1–C2 = 1.465(2), O1–C1 = 1.509(2); O1–B8–B9' = 120.94(15), O1–B8'–B12' = 119.65(15), O1–B18–B14 = 123.28(15), C1–B8–B4 = 118.80(17), C1–B28–B29 = 119.59(17) C1–B8–B9 = 119.59(17), C1–B8–B12 = 124.07(16), C1–B8–B7 = 126.79(18), C1–B8–Co1 = 111.40(13).

along with selected interatomic distances and angles. All the structures confirm the presence of the expected substituent covalently bound at the B(8) site of the cage. Bond distances and angles of all compounds fall within the usual limits. An interesting feature is the presence of intramolecular hydrogen bonds between the OCH_3 oxygen and the hydrogen atoms of the $-\text{NH}_2$ (6c) and $-\text{CH}_2\text{B}-$ (6a,d) groupings, respectively. The O···N and O···C bond lengths of 2.62–2.76 and 3.03–3.08 \AA , respectively, provide evidence for strong interactions, which probably stem from the mutual orientations of the carborane cages.

The crystal structure of Cs9 (see Figure 6) consists of two molecules (I and II) in the asymmetric unit surrounded by a shell of solvating chloroform molecules, only seven of which could be localized with certainty. The symmetrically independent molecules differ mainly in the inclination of one aromatic ring of the *tert*-butyl-calix[4]arene. The dihedral angles between opposite phenyl rings C1A–C6A, C1C–C6C,

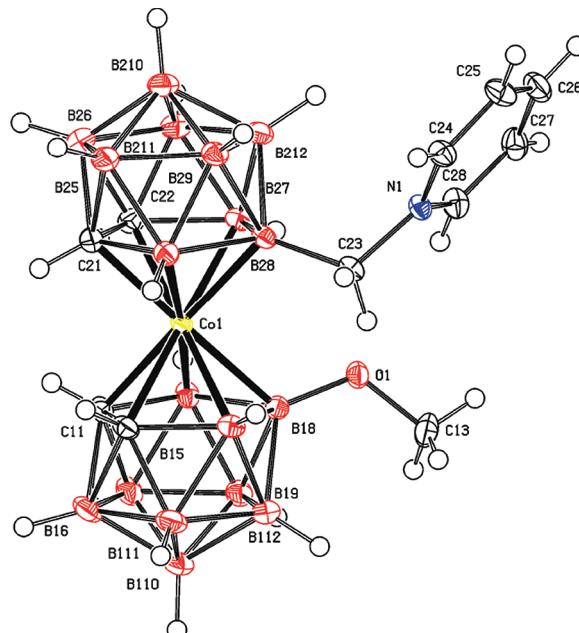


Figure 2. ORTEP presentation of the structure of 6a with atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond distances (\AA) and angles (deg): Co1–B28 = 2.1268(13), Co1–B18 = 2.1422(13), B18–O1 = 1.4150(15), B18–B19 = 1.8138(18), B28–C23 = 1.6211(18), C13–O1 = 1.4293(15), C23–N1 = 1.4883(14), C28–N1 = 1.3465(15); B28–Co1–B18 = 95.94(5), O1–B18–B19 = 118.15(10), O1–B18–B17 = 126.66(10), N1–C23–B28 = 111.85(10).

and C1E–C6E, C1G–C6G correspond to 64.3(3) and 50.3(3) $^\circ$ for molecules I and II, respectively. The most interesting feature of 9⁻ seems to be the coordination of the Cs⁺ cation. To the best of our knowledge, this structure is probably a rather rare example of a calix[4]arene, adopting the partial cone conformation upon hosting the Cs⁺ cation located inside the cavity. Although this conformation was observed in the X-ray structures of several *tert*-butyl-calix[4]arenes bearing small substituents,^{38,39} only one compound, i.e., [2,4-bis[(2-pyridylmethyl)oxy]-(1,3)-*p*-*tert*-butyl-calix[4]arene-(1,3)-crown-6],⁴⁰ incorporating cesium in the partial cone conformation could be found in the Cambridge Structural Database. However, in this case the cesium cation is situated inside the cavity formed by the crown ether ring, which clearly contributes to a complex stability and helps to fix this conformation.⁴⁰

In the structure of compound Cs9, the cesium cation is situated close to the upper rim of the calixarene (see Figure 6), sandwiched between two π -coordinated aromatic rings C1B–C6B, C1D–C6D for molecule I and C1F–C6F, C1H–C6H for molecule II. This coordination is manifested by the distances between Cs and the ring centroid Cs1–cgB = 3.084(3) \AA , Cs1–cgD = 3.109(3) \AA for I and Cs2–cgF = 3.093(3) \AA , Cs2–cgH = 3.059(3) \AA for II, respectively. The Cs⁺ cation is coordinated additionally to two phenoxide oxygen atoms (bond lengths Cs1–O1A = 2.946(5) \AA , Cs1–O1C = 3.109(5) \AA , Cs2–O1E = 2.955(5) \AA , and Cs2–O1G = 3.203(5) \AA) sitting on phenyl rings bearing the cobalt bis(dicarbollide) anion and the methoxy group. Among the rest of the coordination environment, the most exceptional is the interaction with one hydrogen atom of the carborane cage, as follows from the Cs1–H212 and Cs2–H412 distances

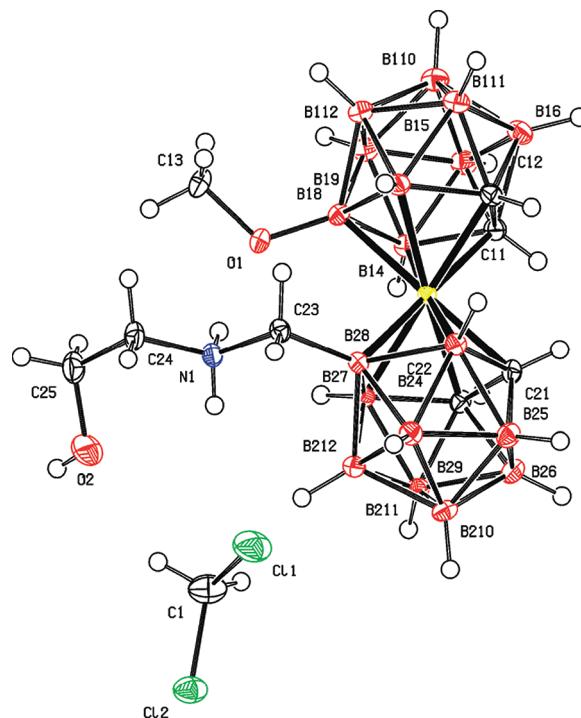


Figure 3. ORTEP presentation of structure of **6c** with atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond distances (\AA) and angles (deg): Co₃–B₂₈ = 2.1457(14), Co₃–B₁₈ = 2.1378(14), B₁₇–B₁₈ = 1.827(2), B₁₈–O₁ = 1.4365(17), B₂₈–C₂₃ = 1.6115(18), C₁₃–O₁ = 1.4351(15), C₂₃–N₁ = 1.5046(16), C₂₄–N₁ = 1.4925(16), C₂₅–O₂ = 1.4167(19); B₂₇–B₂₈–B₂₉ = 106.44(9), N₁–C₂₃–B₂₈ = 109.20(10), O₁–C₁₃–H_{13C} = 109.5, N₁–C₂₄–C₂₅ = 109.03(11), O₂–C₂₅–C₂₄ = 106.06(11).

which, at 2.987 and 3.04 \AA , are far below the sum of van der Waals radii (3.67 \AA). These interactions are enabled by the opposite orientation of one calixarene phenyl ring, bearing the cobalt bis(dicarbollide) substituent, with respect to the three remaining phenyl rings. This kind of bonding, therefore, can be considered to be a supportive force for the preference of the partial cone conformation of Cs₉ in the solid state. Studies of conformational dynamics in solution show that the partial cone conformation may be more thermodynamically stable for the Cs⁺ complex of *tert*-butyl-calix[4]arene bearing small residues (e.g., four methoxy groups at the upper rim),⁴¹ although other conformations seems to be prevailing due to kinetic reasons.^{41,42} The clear preferences of the Cs⁺ cation for the 1,3-alternate or the cone conformation is observed in numerous previous examples of crystal structures.^{9,38,39} Therefore, the presence of the partial cone conformation in the structure of Cs₉ seems rather unusual.

The crystallographically determined structures are also consistent with spectroscopic data. The ¹¹B NMR spectrum of **2** consists of a superposition of resonances of the two differently substituted dicarbollide subclusters L–CH₂–B₈ and CH₃O⁺–B(8'). The NMR shifts of the oxygen-substituted dicarbollide part are consistent with previously published data for hydroxy, oxoalkyl, or bridged derivatives^{15,36,43} and can be distinguished on that basis. The ¹¹B NMR spectrum of the new zwitterionic dicarbollide derivative **2** consists of 12 symmetrically nonequivalent signals of intensities 1:1:1:1:2:2:2:2:2:1:1, the first two resonances of which are singlets. After demethylation of the bridge, the singlet of the methylene-

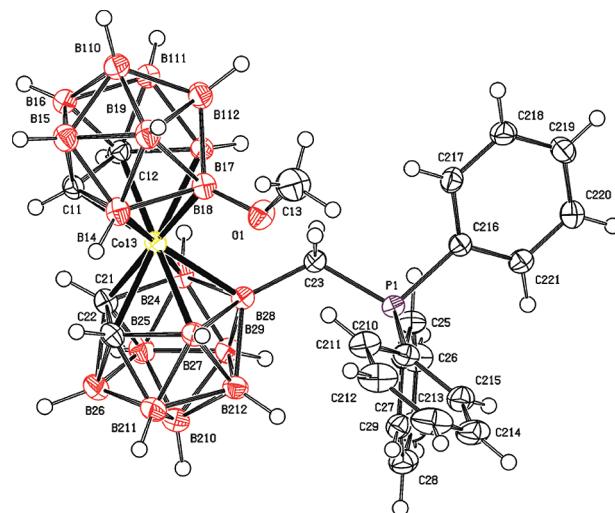


Figure 4. ORTEP presentation of the structure of **6d** with atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond distances (\AA) and angles (deg): Co₁₃–C₂₁ = 2.0491(17), Co₁₃–B₁₈ = 2.137(2), Co₁₃–B₂₈ = 2.1642(19), B₁₇–B₁₈ = 1.837(3), B₁₈–O₁ = 1.411(2), C₁₃–O₁ = 1.396(2), B₂₈–C₂₃ = 1.617(2), C₂₃–P₁ = 1.7960(16), P₁–C₂₁₀ = 1.7919(17), P₁–C₂₁₆ = 1.8112(16); C₁₁–Co₁₃–B₁₈ = 83.93(7), C₂₁–Co₁₃–B₁₈ = 175.43(7), C₁₁–Co₁₃–B₂₈ = 175.99(7), O₁–B₁₈–B₁₉ = 119.32(15), C₂₃–B₂₈–B₂₇ = 127.79(14), B₂₉–B₂₈–B₂₇ = 105.87(13), C₂₃–B₂₈–Co₁₃ = 117.60(11), P₁–C₂₃–H_{23A} = 106.6, C₁₃–O₁–B₁₈ = 121.96(16), C₂₄–P₁–C₂₃ = 113.02(8), C₂₄–P₁–C₂₁₆ = 105.22(8).

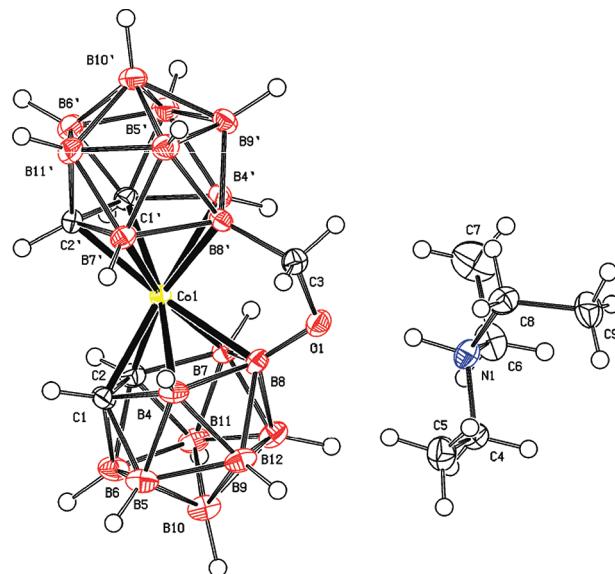


Figure 5. View of the X-ray structure of Et₃NH·**8** with atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond distances (\AA) and angles (deg) Co₁–B_{8'} = 2.075(2), Co₁–B₈ = 2.097(2), B_{8'}–O₁ = 1.424(3), B_{8'}–B₉' = 1.811(4), B_{8'}–B₁₂ = 1.814(4), B₈–C₃ = 1.599(3), B₈–B₉ = 1.805(3), B₈–B₁₂ = 1.810(3), O₁–C₃ = 1.466(3); B_{8'}–Co₁–B_{7'} = 52.88(11), O₁–B_{8'}–B_{9'} = 119.06(18), O₁–B_{8'}–B_{12'} = 121.36(19), O₁–B_{8'}–B_{4'} = 121.89(19), O₁–B_{8'}–Co₁ = 114.99(16), B_{4'}–B_{8'}–Co₁ = 64.76(11), C₃–B₈–B₄ = 118.46(18), C₃–B₈–B₁₂ = 125.78(18), C₃–B₈–B₇ = 126.73(19), C₃–B₈–Co₁ = 110.09(15), B_{8'}–O₁–C₃ = 113.72(18), O₁–C₃–B₈ = 109.82(17).

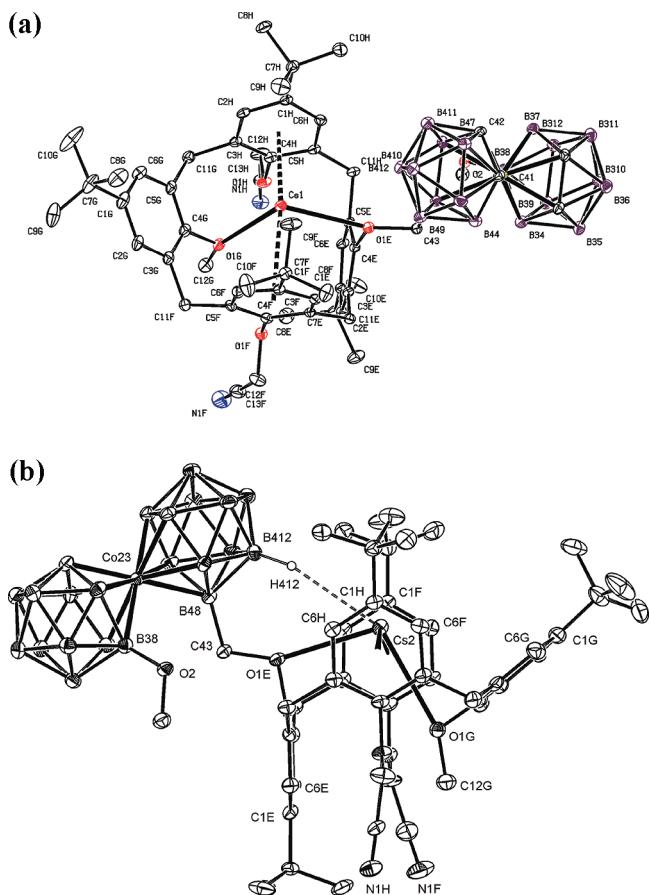


Figure 6. (a) View of molecule II in the solid-state structure of Cs9 with atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level; hydrogen atoms are omitted for clarity. Selected bond distances (\AA) and angles (deg): Cs2–C1F = 3.340(7), Cs2–C2F = 3.306(7), Cs2–C6F = 3.350(7), Cs2–C1H = 3.401(7), Cs2–C2H = 3.349(7), Cs2–C6H = 3.333(7), Cs2–O1E = 2.955(5), Cs2–O1G = 3.203(5); O1E–Cs2–O1G = 102.20(13), C1F–Cs2–C1H = 156.68(18). (b) View of the coordination sphere of Cs⁺ in the structure of Cs9⁻. Irrelevant hydrogen atoms and atom labels are omitted. Selected bond lengths (\AA), angles (deg), and dihedral angles (ring planes are defined as CpE = C1E–C6E, CpF = C1F–C6F, CpG = C1G–C6G, and CpH = C1H–C6H): Cs2–H412 = 3.040, B412–H412···Cs2 = 148, H412···Cs2–O1E = 54.2, H412···Cs2–O1G = 150.6, CpE–CpF = 89.2(2), CpF–CpG = 83.1(3), CpG–CpH = 77.4(3), CpH–CpE = 89.9(2), CpE–CpG = 50.3(3), CpF–CpH = 24.8(4).

substituted boron B8 vertex in 8' is shifted downfield by approximately 12 ppm, whereas the signal of the CH₃OB8' boron is shifted only by 2 ppm and remains close to the former position in zwitterion 2. On the other hand, the cleavage of the bridge causes higher field shifts of about 3 ppm for both B8 and B8' signals with respect to the starting zwitterion 2. This helps to easily distinguish one of the two possible reaction paths. All the signals of both dicarbollide ligands present in this complex could be assigned from ¹¹B-¹¹B COSY NMR spectroscopy in combination with ¹H{¹¹B_{selective}} spectra. All B-H signals could be found by ¹H{¹¹B_{selective}} experiments. These techniques were also particularly useful for assigning the B(4,7), B(4',7') and B(9,12), B(9',12') resonances that often overlap in the ¹¹B spectrum. Nevertheless, proton resonances of the BH positions adjacent to the cobalt center, H(4,7,4',7'), are found at the lower field of the ¹H{¹¹B} spectra in a region close to 3.0 ppm,

whereas the H(9,12) and H(9',12') signals are shifted upfield by approximately 1 ppm. Noteworthy as well is the significant downfield shift of B(8') for anion **7**⁻ compared to the neutral alkylammonium species, e.g., **6b**, in the same solvent.

The ^1H and ^{13}C NMR spectra of **2**, **4**, **5**⁻, **6a-d**, **7**⁻, and **8**⁻ are in complete agreement with the expected structures and product compositions. The ^1H spectrum of **Cs9** reflects the C_s symmetry of a tetrasubstituted calix[4]arene bearing two identical substituents in opposite positions and two different substituents at the remaining sites. The ratios of the cage CH signals vs the respective calix[4]arene signals in the ^1H NMR spectra are in accord with the presence of two $-\text{CH}_2\text{CN}$ residues, one cobalt bis(dicarbollide) ion attached by a methylene spacer, and one methyl group. For the calixarene platform three singlets for aromatic protons (intensities 2:1:1) were observed in the spectrum measured at room temperature, along with two sets of doublets with geminal coupling for the methylene bridges and three singlets for the *tert*-butyl groups (again of intensities 2:1:1). The two sets of doublets of the methylene bridges show separation corresponding to an AX system ($\Delta\delta = 1.6$ and 1.4 ppm, respectively). The spectral pattern thus indicates C_s symmetry and the presence of either the partial-cone or the cone conformation in the solution.⁴² The C_s symmetry of the spectrum can even result from a fast exchange of the conformations on the NMR time scale. It should be noted that the methoxy group (as well as both acetonitrile residues) are still small enough to flip through the annulus and the molecule can thus adopt any of the two possible conformations⁴² as verified previously also for other cyanomethoxy calix[4]arenes.⁴⁴ Temperature-dependent measurements in the interval -35 to $+50$ °C showed no symmetry transformation within the whole range, only the two doublets corresponding to the equatorial $-\text{CH}_2-$ protons of the calixarene at approximately 3.2 ppm broadened and collapsed to one multiplet at the highest temperatures 40 and 50 °C, in agreement with typically observed temperature effects.

Almost all compounds exhibit the respective molecular m/z base peaks $[M]$ for ionic and $[M-H]$ for zwitterionic compounds in their ESI⁻ mass spectra, with the exception of **6a**, which was more accurately measured in the positive (ESI⁺) mode, showing the corresponding $[M+H]^+$ ion. The compound **2** is labile under ESI conditions, but using the APCI ionization provides a clean molecular peak. For each particular boron cluster compound, the experimental and calculated isotopic patterns were in agreement with those calculated (using Mass Spectrometric's software, EXcalibur).

■ CONCLUSIONS

We can conclude that synthetic strategies based on ring-opening reactions of **2** may become a multipurpose tool in the hands of a synthetic chemist. As has been proven earlier, ammonium derivatives of the ion **1**⁻ with different structures can serve as particularly useful building blocks for the synthesis of functional molecules.^{15,33-35,45} The clean reaction with amines and phosphines, which proceeds even more efficiently than that of the widely used dioxane-**1** derivative, provides options for a variety of more sophisticated products than the compounds **6a-d** presented here. It can serve to generate a wide range of novel cobaltacarborane-containing compounds, where the boron cage is attached by a short methylene spacer to other groups comprising, for instance, ammonium, amide, and phosphonium functions. Experiments leading to the design and synthesis of such target compounds for applications in

Table 2. X-ray Crystallographic Data

	2	6a	6c	6d	8⁻	9⁻
formula	C ₆ H ₂₃ B ₁₈ CoO	C ₁₁ H ₃₀ B ₁₈ CoNO	C ₈ H ₃₂ B ₁₈ CoNO ₂ CH ₂ Cl ₂	C ₂₄ H ₄₀ B ₁₈ CoOP·0.5CHCl ₃	C ₁₃ H ₃₄ B ₁₈ CoNO·C ₂ H ₃ N	C ₅₅ H ₈₄ B ₁₈ CoS ₂ N ₂ O ₅ ·3.5CHCl ₃
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group (No.)	P ₂ ₁ /n (14)	P ₂ ₁ /c (14)	P ₂ ₁ /c (14)	C2/c (15)	P ₂ ₁ /c (14)	P ₁ (2)
<i>a</i> (Å)	15.01830(10)	13.33333(2)	10.62960(10)	38.2599(3)	13.70190(10)	14.5021(2)
<i>b</i> (Å)	10.42780(10)	12.9059(2)	9.91130(10)	12.90460(10)	12.62520(10)	18.3083(3)
<i>c</i> (Å)	35.8282(3)	13.5899(2)	23.2108(3)	34.2320(3)	34.1481(3)	31.5734(5)
α (deg)					94.4656(11)	
β (deg)					99.3420(10)	
γ (deg)					107.1882(7)	
<i>Z</i>	12	4	4	16	8	4
no. of measd reflns	71 567	37 488	50 837	145 843	98 559	70 041
no. of indep diffractions ($R_{\text{int}}^{\text{a}}$)	1254 (0.027)	5154 (0.029)	5597 (0.031)	16 131 (0.045)	12 684 (0.080)	26 398 (0.065)
no. of obsd diffractions ($I > 2\sigma(I)$)	10 256	4689	5076	12 691	9222	19 151
no. of params	946	370	391	973	689	1721
R_f^b , R_w for observed diffractions	0.035, 0.0807	0.0251, 0.0629	0.0247, 0.0636	0.0361, 0.0989	0.0327, 0.0736	0.0822, 0.2236
R_f , wR for all data	0.0493, 0.0861	0.0288, 0.0647	0.0288, 0.0659	0.0490, 0.1048	0.0398, 0.0780	0.1093, 0.2400
GOF ^c	1.05	1.047	1.041	1.069	1.046	1.049
resid electron density (e/Å ³)	0.63, -0.42	0.24, -0.37	0.60, -0.55	0.40, -0.42	0.42, -0.38	2.11, -1.19

^a $R_{\text{int}} = \sum |F_o|^2 / \sum F_o^{\text{mean}} 2 / |\sum F_o|^2$. ^b $R(F) = \sum |F_o| / |\sum F_o|$; $R_w(F) = [\sum (w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2))^2]^{1/2}$. ^c GOF = $[\sum (w(F_o^2 - F_c^2)^2) / (N_{\text{diffs}} - N_{\text{params}})]^{1/2}$.

biomedicine are currently being examined in our laboratories. These compounds are otherwise unavailable by other conventional methods. An ambiguous action of **2** was observed when phenolates were used as nucleophiles, although the compounds arising from ring-opening reactions can be still obtained, as shown here by isolation of Na⁷ and Cs⁹. The solid-state crystal structure of Cs⁹ reveals the quite unusual partial cone conformation of the calix[4]arene substituted by one cobalt bis(dicarbollide) anion.

EXPERIMENTAL SECTION

The cesium salt of cobalt bis(dicarbollide) (**1**) was purchased from Katchem Ltd., Czech Republic. Solvents, i.e. tetrahydrofuran (THF), ethylene glycol dimethyl ether (DME), and toluene, were dried with sodium diphenyl ketyl and distilled prior to use. Other chemicals and solvents were purchased from Aldrich and from Lachema a.s. and Penta Ltd., Czech Republic, respectively, and used without purification. Analytical TLC was carried out on TLC plates, Silufol (silica gel layer on aluminum foil with starch as the binder) from Lachema, Czech Republic, or RP-8-F₂₅₄ S, Merck (0.25 mm layer of octyl silica on glass formers 20 × 5 cm), in the reverse phase mode. Unless otherwise specified, column chromatography was performed on a high-purity silica gel (Merck grade, Type 7754, 70–230 mesh, 60 Å).

All reactions were performed using standard vacuum or inert-atmosphere techniques as described by Shriver,⁴⁶ although some operations, such as flash chromatography and crystallization, were carried out in air.

Melting points were determined in sealed capillaries on a Büchi melting point B-545 apparatus and are not corrected. As previously verified, the data of elemental analyses of metal bis(dicarbollide) ions and particularly these arising from combinations with organic calixarenes are often misleading, due to inclusion of solvent molecules or formation of boron carbide during burning, and cannot be thus considered as a reliable criterion of purity.^{11,47,48} Nevertheless, the identity of all the reported compounds has been unambiguously proven by combination of the ¹¹B, ¹³C, and ¹H NMR spectral data (complete assignment of the resonances) with mass spectrometry (two decimal digits resolution), IR, melting points, TLC, and other methods. The purity was assessed by an analytical HPLC with DAD detection, being better than 98% for all compounds reported in this article.

Instrumental Techniques. ¹H, ¹³C, and ¹¹B NMR Spectra. These spectra were measured on a Varian Mercury 400^{plus} Instrument. The spectra of all compounds were measured immediately after dissolution. ¹¹B NMR (128 MHz) chemical shifts are given in ppm to high frequency (low field) to F₃B-OEt₂ as the external reference. Residual solvent ¹H resonances were used as internal secondary standards. Coupling constants J(¹¹B-¹H) are taken from resolution-enhanced ¹¹B spectra with a digital resolution of 2 Hz. The NMR data are presented in the text as follows. ¹¹B NMR: ¹¹B chemical shifts δ(¹¹B) (ppm), multiplicity, coupling J(¹¹B-¹H) constants in Hz. Signal assignments are based on [¹¹B-¹¹B] COSY NMR spectroscopy. ¹H NMR (400 MHz) and ¹³C (100 MHz): chemical shifts δ(¹H) in ppm relative to Me₄Si (0 ppm) as the external standard, coupling constants J(H,H) in Hz; δ(¹H){¹¹B} data also presented, and assignments based on selectively decoupled δ(¹H){¹¹B selective} NMR experiments.

Mass Spectrometry Measurements. These measurements were performed on a Thermo-Finnigan LCQ-Fleet Ion Trap instrument using electrospray (ESI) ionization with detection of negative ions. Samples dissolved in acetonitrile (concentrations approximately 100 ng mL⁻¹) were introduced to the ion source by infusion of 5 μL min⁻¹, source voltage -5.57 kV, tube lens voltage -49.8 V, capillary voltage -80.0 V, drying temperature 188 °C, drying gas flow 8 L min⁻¹, auxiliary gas pressure 6 bar. In most cases the negative ions corresponding to the molecular ion were observed with 100% abundance for the highest peak in the isotopic distribution plot.

Molecular ions [M]⁻ were detected for all univalent anions and [M-H]⁻ for zwitterionic compounds as the base peaks in the spectra. The compound **6a** was measured in a positive mode exhibiting correct [M + H]⁺. Full agreement of the experimental and calculated isotopic distribution pattern was observed for all these compounds. The isotopic distribution in the boron plot of all peaks is in perfect agreement with the calculated spectral pattern. The data are presented for the most abundant mass in the boron distribution plot (100%) and for the peak corresponding to the m/z value.

Analytical HPLC. This method was used to check the purity, and the Merck-Hitachi HPLC system LaChrom 7000 series equipped with DAD 7450 detector and an Intelligent Injector L7250 was used. Chromatographic procedures: an analytical normal phase separation was used for determining the ratios of zwitterionic products **2** and **3** isolated from the reaction mixtures. Chromatographic conditions: column, steel (250 × 4 mm i.d.) packed with Merck Lichrosorb 10 μm; solvent, hexane-CH₂Cl₂ 4:1 v:v; flow rate, 1.0 mL/min; detection, DAD (235–600 nm); fixed wavelength, 264 nm; sample concentration, approximately 0.5 mg mL⁻¹ injected in the solvent. A RP chromatographic method with an isocratic elution was used for a purity check: i.e., column, RP Separon SGX C8, 7 μm (silica with chemically bonded octyl groups) Tessek Prague, Czech Republic.

Chromatographic Conditions. The solvent for zwitterionic compounds was 70% aqueous acetonitrile, DAD detection (220–600 nm), fixed wavelengths 264, 285, 290, and 312 nm, with a sensitivity range of 0.2 AUFS samples of concentration approximately 0.5 mg mL⁻¹ in the mobile phase or CH₃CN were injected (1–5 μL), which resolved most of the anionic and neutral compounds from the real reaction mixtures for purity assay and control. For anionic species, the chromatographic IP-RP procedure based on the methods previously reported³¹ for the separation of hydrophobic borate anions was applied by using a buffer containing 4.5 mmol/L hexylamine acetate in 58% aqueous CH₃CN, pH 6.5, as the solvent; for the anion **9**⁻ a previously developed gradient method¹² was used. Capacity factors $k' = (t_R - t_0)/t_0$ (where t_R is the retention time and t_0 is the void retention time of an non-retained peak) are given for individual compounds; $k' = 3.3$ was observed for the parent ion **1**⁻ under the chromatographic conditions used for analysis. The purity assay was based on the peak area on the chromatograms of the individual compounds.

X-ray Structure Determinations. Single crystals suitable for X-ray diffraction studies were grown as follows: derivative **2** by slow evaporation of the acetonitrile solution; **6a,c,d**, Et₃NH-**8**, and Cs⁹ by slow diffusion of hexane into CHCl₃ or CH₂Cl₂ solutions of the salts (a few drops of MeOH were added to accomplish dissolution of the salts of **8**⁻ and **9**⁻ in the solvent). Crystallographic data for all structures determined are given in Table 2. Crystals were mounted on a glass capillary and measured on a Nonius Kappa CCD diffractometer by monochromated Mo Kα radiation ($\lambda = 0.710\text{73}\text{\AA}$) at 150(2) K. Absorption was neglected ($\mu = 0.64\text{--}1.08\text{ mm}^{-1}$). The structures were solved by direct methods (SIR92, Altomare, 1994)⁴⁹ and refined by full-matrix least squares based on F^2 (SHELXL97).⁵⁰ A PLATON/SQUEEZE⁵¹ procedure was used to correct the data of **6d** and Cs⁹ for the presence of the disordered solvents. The poor quality of the crystal of **9**, caused by the irresolvable disorder of *tert*-butyl moieties of calix[4]arene as well as the disorder of solvating trichloromethane, prevents reaching a standard level of structure determination. However, this structure illustrates the scope of reactions of **2** and therefore was included in the series of structures. The hydrogen atom on carbons (except those of carborane cages) were placed in idealized positions and fixed during refinement (riding model) with assigned temperature factors $U_{\text{iso}}(\text{H}) = 1.2[U_{\text{eq}}(\text{pivot atom})]$ or 1.5U_{eq} for the methyl moiety. Other hydrogen atoms of structures **2**, **6a,c**, were refined isotropically; those in structures **6d** and **8**⁻ were positioned geometrically and only hydrogen atoms bonded to nitrogen were refined, whereas all hydrogen atoms were fixed into idealized positions for the structure of Cs⁹.

Synthetic Procedures. *Synthesis of the Zwitterionic Compound [8,8'-μ-(CH₂O(CH₃))₂(1,2-C₂B₉H₁₀)₂-3-Co]²⁻ (2): Optimized Procedure.* To a stirred slurry of Cs¹ (2.29 g, 5 mmol) in 1,2-

dichloroethane (10 mL) was added paraformaldehyde (0.6 g, 20 mmol), followed by HCl (35%, 5 cm³, 60 mmol), and the flask was heated to 80 °C (bath temperature) for 2 h. After cooling and standing for 2 h, the formed precipitate was filtered and washed with 1,2-dichloroethane (2 × 10 mL). The resulting solid is a mixture of [8,8'-Cl₂-(1,2-C₂B₉H₁₁)₂]Cs and CsS, as identified by NMR, MS, and HPLC. The chloro derivative was isolated by extraction of the solids with acetone (3 × 20 mL) and evaporation of the combined extracts in a yield of 0.31 g (12%). The supernatant after filtration was washed with water (20 mL), 5% aqueous Na₂CO₃ (3 × 10 mL) (to remove the rest of 5⁻), and water (3 × 10 mL) and evaporated to dryness to give 1.28 g (ca. 70%) of a mixture of zwitterionic products 2 and 3, together with minor amounts of compound 4. The ratio of 2, 3, and 4 (determined by HPLC) was 57:37:6, respectively. Compound 4 can be removed by chromatography on silica gel in hexane-CH₂Cl₂ (2:1); compounds 2 and 3 can be then isolated by chromatography (from repeated injections of 5 mL of ether solution) on a Merck Lobar column (Size C, 440 × 37, silica gel Lichroprep Si 60, 40–63 μm) in hexane (or CCl₄)-diethyl ether solvent mixture (6:4 v:v) to give the following isolatable yields of pure products: 2 (0.39 g, 21%), 3 (0.30 g, 17%), and 4 (75 mg, 4%). Single crystals for X-ray diffraction were grown by slow evaporation of an acetonitrile solution of 2. Anion 5⁻ can be recovered from sodium carbonate extracts by extraction into diethyl ether (3 × 20 mL), washing with HCl (3 M, 3 × 20 mL), evaporation of the ether extracts with water (20 mL), and precipitation with aqueous Me₄NCl.

Data for [8,8'-μ-(CH₃OCH₂)-(1,2-C₂B₉H₁₀)₂-3,3'-Co]⁰ (2) are as follows. HPLC: *k'* = 7.46, purity assay 98.4%, *R_f* (CH₂Cl₂-hexane 3:1) = 0.71. Mp: 195 °C. IR: ν (cm⁻¹) 2608, 2548 (B-H), 1457, 1442 δ(CH), 1094, 1014 (C-O-C). δ_B (128 MHz, CD₃COCD₃, Et₂O-BF₃): 30.70 (s, 1 B, B8'), 13.01 (s, 1B, B8), 0.67 (d, 1B, *J* = 143, B10), -3.64 (d, 1B, overlap, B10'), -5.44 (d, 4B, *J* = 144, B4,7,9,12), -8.82 (d, 4B, *J* = 143, B4',7',9',12'), -14.43 (d, 2B, *J* = 159, B5,11), -16.77 (d, 2B, *J* = 158, B5',11'), -23.78 (d, 1B, *J* = 171, B6), -28.53 (d, 1B, *J* = 174, B6'). δ_H (400 MHz, CD₃COCD₃, Me₄Si): 4.967 (br s, 2H, CH₂), 4.244 (br s, 2H, CH_{carb}), 4.208 (s, 3H, CH₃O), 3.975 (s, 2H, CH_{carb}). B-H signals from ¹H{¹¹B-selective} NMR: δ (ppm) 2.97 (H10), 2.76 (H10'), 3.34, 2.04 (H4,7,9,12), 3.52, 2.22 (H4',7',9',12'), 1.84 (H5,11), 1.76, 1.56 (H5',11'), 1.74 (H6), 1.53 (H6'). δ_C {¹H} (100 MHz, CD₃CN, Me₄Si): 98.77 (br q, CH₂) 72.90 (CH₃O), 51.74, 46.99 (CH_{carb}). MS *m/z* (APCI⁺): 366.78 (100), 370.29 (4) (calcd 370.29) [M]⁺.

Data for [8-(CH₃)₂O-1,2-C₂B₉H₁₀](1',2'-C₂B₉H₁₁)-3,3'-Co]⁰ (4) are as follows. HPLC: *k'* = 5.46, purity assay 98.8%, *R_f* (CH₂Cl₂-hexane 3:1) = 0.53. Mp: >410 °C dec. IR: ν (cm⁻¹) 3041, 2965 (CH), 2573, 2547, 2504 (B-H), 1464, 1447, 1425 δ(CH), 1099, 995, 983, 896, 753 (C-O). δ_B (128 MHz, CD₃COCD₃, Et₂O-BF₃): 24.55 (s, 1 B, B8'), 8.05 (d, 1B, *J* = 146, B8), 4.39 (d, 1B, *J* = 143, B10), -3.31 (d, 1B, *J* = 137, B10'), -4.31 (d, 4B, *J* = 147, B4,7,9,12), -8.03 (d, 2B, *J* = 153, B4',7'), -9.45 (d, 2B, *J* = 180, B9',12'), -15.28 (d, 2B, *J* = 158, B5,11), -18.77 (d, 2B, *J* = 159, B5',11'), -21.23 (d, 1B, *J* = 168, B6), -26.98 (1 B, d, *J* = 177, B6'). δ_H (400 MHz, CD₃COCD₃, Me₄Si): 4.409 (br. s, 2H, CH_{carb}), 4.387 (s, 6H, CH₃O), 4.036 (br. s, 2H, CH_{carb}). B-H signals from ¹H{¹¹B-selective} NMR δ (ppm): 3.48 (H8'), 3.19 (H10), 2.73 (H10'), 2.92, 2.12 (H4,7,9,12), 3.12, 2.33 (H4',7',9',12'), 1.75 (H5,11), 1.68 (H5',11'), 1.77 (H6), 1.52 (H6'). δ_C (100 MHz, CD₃CN, Me₄Si): 69.32 (CH₃O), 53.96 (br s, CH₂), 51.47, 47.70 (CH_{carb}). MS *m/z* (APCI⁺): 369.32 (100), 372.31 (4) (calcd 372.31) [M]⁺.

Data for [8,8'-(CH₃O)₂-(1,2-C₂B₉H₁₀)₂-3,3'-Co]Me₄N (5Me₄N) are as follows. Yield: 14.0%. HPLC: *k'* = 1.86 (58% CH₃CN, 4.5 mM HAA), purity assay 98.7%, *R_f* (CH₂Cl₂-CH₃CN 3:1) 0.41. Mp: 281–283 °C. IR: ν (cm⁻¹) 3432, 3038, 2934, 2823 (C-H), 2605, 2556 (B-H), 1486 δ(CH), 1141, 1114, 943, 894 (C-O). δ_B (128 MHz, CD₃COCD₃, Et₂O-BF₃): 21.08 (s, 2B, B8,8'), -3.34 (d, 2B, *J* = 143, B10,10'), -7.35 (d, 4B, overlap, B4,7,4',7'), -9.14 (d, 4B, *J* = 140, B9,12,9',12'), -20.51 (d, 4B, *J* = 153, B5,11,5',11'), -28.38 (d, 2B, *J* =

168, B6,6'). δ_H (400 MHz, CD₃COCD₃, Me₄Si): 4.154 (br s, 4H, CH_{carb}), 3.465 (s, 12H, Me₄N⁺), 3.222, 3.213 (2s, 6H, CH₃O). B-H signals from ¹H{¹¹B-selective} NMR: δ (ppm) 2.63 (H10,10'), 2.88 (H4,7,4',7'), 1.92 (H9,12,9',12'), 1.57 (H5,11,5',11'), 1.43 (H6,6'). δ_C {¹H} (100 MHz, CD₃COCD₃, Me₄Si): 57.22 (CH_{carb}), 54.18, 53.67 (2s, CH₃O), 51.29 (Me₄N⁺). MS *m/z* (ESI⁻): 384.42 (100), 387.45 (2) (calcd 387.29) [M]⁻.

General Method for the Synthesis of 8-N-alkylammonium- or Trialkylphosphonium-8'-methoxy-3,3-cobalt Bis(1,2-dicarbollide) (6a–d). **Method 1.** The starting zwitterionic derivative 2 (0.2 g, 0.55 mmol) was dried under vacuum and then dissolved in toluene–ethylene glycol dimethyl ether (DME) (9:1, 10 mL), and a solution of the respective amine (1.10 mmol) in the same solvent (10 mL) was added. The reaction mixture was stirred for 12 h at ambient temperature, and the solvents were evaporated under reduced pressure. The residue was dissolved in CH₂Cl₂–hexane (1:1, 3 mL), the solution was injected atop a silica gel column (2.5 × 25 cm), and the orange band was eluted using the same solvent mixture as the mobile phase. Crystals for X-ray diffraction were grown by a slow diffusion of hexane into dichloromethane or CHCl₃ solution (6a,d) or by a slow evaporation of the acetonitrile solution (6c). The yields of particular compounds below are based on this procedure: i.e., by using pure compound 2 as the starting material.

Method 2. Alternatively, the mixture of 2 and 3 from which only compound 4 was removed (as the last eluting band) by chromatography in hexane-CH₂Cl₂ (1:1) was treated with a 5 M excess of the corresponding amine or phosphine at room temperature and isolated by liquid chromatography, as above. The dark violet anion resulting from demethylation of 3 is retained atop the column under these conditions.

Data for [(8-C₅H₅N-CH₂-1,2-C₂B₉H₁₀)(8'-CH₃O-1',2'-C₂B₉H₁₀)-3,3'-Co]⁰ (6a) are as follows. Yield: 97%. HPLC: *k'* = 5.37, purity assay 99.5%; TLC *R_f* = 0.12 (TLC plate Silufol, silica gel, CH₂Cl₂–hexane 3:1). Mp: 293 °C. IR: ν (cm⁻¹) 3447 (N-H), 2931, 2835 (C-H), 2594, 2559, 2534 (B-H), 1632 δ(NH), 1485 δ(CH), 1189, 1131, 961, 685 (C-O). δ_B (128 MHz, CD₃COCD₃, Et₂O-BF₃): 27.19 (s, 1B, B8'), 12.46 (s, 1B, B8), -2.09 (d, 2B, overlap, B10,10'), -6.43, -6.81 (d, 6B, overlap, B4,7,9,12,9',12'), -8.86 (d, 2B, *J* = 147, B4',7'), -17.61 (d, 2B, *J* = 159, B5,11), -18.85 (d, 2B, *J* = 159, 147, B5',11'), -24.01 (d, *J* = 171, B6), -28.52 (d, 1B, *J* = 171, B6'). δ_H (400 MHz, CD₃COCD₃, Me₄Si): 8.778 (d, *J* = 5.8, 2H, C₆H₅N), 8.490 (t, *J* = 7.6, 1H, C₆H₅N), 8.111 (m, *J* = 6.4, 2H, C₆H₅N), 4.961 (s, 2H, B-CH₂NH₂), 4.119 (s, 2H, CH_{carb}), 3.919 (s, 2H, CH_{carb}), 3.544 (s, 3H, CH₃O). ¹H{¹¹B-selective} NMR (CD₃COCD₃): δ_{B-H} (ppm) 2.71, 2.58 (H10,10'), 2.86, 2.29, 1.17 (H4,7,9,12,9',12'), 2.89 (H4',7'), 1.57 (H5,11), 1.62 (H5',11'), 1.56 (H6), 1.45 (H6'). δ_C {¹H} (100 MHz, CD₃CN, Me₄Si): 145.21 (2C, ArC), 143.61 (1C, ArC), 128.36 (2C, ArC), (62.75 br s, B-CH₂-N), 57.73 (CH₃O), 50.81 (2C, CH_{carb}), 48.75 (2C, CH_{carb}). MS *m/z* (ESI⁺): 477.40 (100), 451.36 (2) (calcd 451.34) [M + H]⁺.

Data for [(8-n-C₆H₁₃NH₂-CH₂-1,2-C₂B₉H₁₀)(8'-CH₃O-1',2'-C₂B₉H₁₀)-3,3'-Co]⁰ (6b) are as follows. Yield: 82%. HPLC: *k'* = 13.3, purity assay 99.8%. TLC: *R_f* = 0.63 (TLC plate Silufol, silica gel, CH₂Cl₂–hexane 3:1). Mp: 220 °C. IR: ν (cm⁻¹) 3239, 3038 (N-H), 2956, 2926, 2857, 2830 (C-H), 2572, 2542 (B-H), 1464, 1378 δ(CH), 1202, 1125, 1106, 1015, 970 (C-O), 748 (C-C), δ_B (128 MHz, CD₃CN, Et₂O-BF₃): 26.55 (s, 1B, B8'), 10.02 (s, 1B, B8), -0.13 (d, 1B, *J* = 143, B10), -2.53 (d, 1B, *J* = 143, B10'), -5.15 (d, 2B, *J* = 149, B9,12), -6.46 (d, 4B, *J* = 168, B4,7,9',12'), -8.21 (d, 2B, 128, B4',7'), -18.32 (d, 2B, *J* = 141, 156, B5,11), -19.23 (2d, *J* = 140, B5',11'), -23.17 (d, *J* = 134, B6), -28.31 (d, 1B, *J* = 147, B6'). δ_H (400 MHz, CD₃CN, Me₄Si): 7.064 (br s, 2H, NH), 3.882 (br s, 2H, CH_{carb}), 4.852 (br. s, 2H, CH_{carb}), 3.406 (s, 3H, CH₃O-B), 2.936 (m, 4H, CH₂NH, B-CH₂N), 2.157 (s, 3H, CH₃O-B), 1.627 (m, 2H, CH₂), 1.454 (m, 6H, CH₂), 0.870 (t, 2H, *J* = 7.2 Hz, CH₃). B-H signals from ¹H{¹¹B-selective} NMR (CD₃COCD₃): δ_{B-H} (ppm) 2.84 (H10), 2.60 (H10'), 1.86 (H9,12), 2.71 (H4,7), 2.19 (H9',12'), 2.82 (H4',7'), 1.52 (H5,11), 1.58 (H5',11'), 1.53 (H6), 1.42 (H6'). δ_C (100 MHz, CD₃CN, Me₄Si): 57.74 (d, CH₃CH₂NH), 51.44 (d, CH_{carb}),

50.88 (s, CH_3O), 48.32 (d, CH_{carb}), ca. 47.0 (br s, $\text{HN}-\text{CH}_2-\text{B}$), 31.71 (CH_2), 26.57 (CH_2), 26.19 (CH_2), 22.89 (CH_2), 14.04 (CH_3). MS m/z (ESI $^-$): 467.50 (100), 471.42 (2) (calcd 471.41) [$\text{M} - \text{H}]^-$.

Data for [(8-(2-HO-C₂H₄-1-NH₂)-CH₂-1,2-C₂B₉H₁₀)(8'-CH₃O-1',2'-C₂B₉H₁₀)-3,3'-Co]⁰ (**6c**) are as follows. Yield: 66%. HPLC: k' = 1.23, purity assay 99.8%. TLC: R_f = 0.66 (TLC plate Silufol, silica gel, $\text{CH}_2\text{Cl}_2-\text{CH}_3\text{CN}$ 3:1). Mp: 253–255 °C. IR: ν (cm⁻¹) 3602, 3569 (O-H), 3213, 3054 (N-H), 2960, 2939, 2834 (C-H), 2566 (B-H), 1579 δ (NH), 1441, 1376, 1201, δ (CH)_{alkyl}, 1129, 1107 (C-O), 965, 746 (C-C)_{alkyl}. δ_B (128 MHz, CD₃CN, Et₂O-BF₃): 26.81 (s, 1B, B8'), 10.12 (s, 1B, B8), -0.32 (d, 1B, J = 143, B10), -2.51 (d, 1B, J = 143, B10'), -5.30 (d, 2B, J = 150, B9,12), -6.55 (d, 4B, J = 164, B4,7,9,12'), -8.17 (d, 2B, overlap, B4',7'), -18.20, (d, 2B, J = 143, 147, B5,11), -19.11 (d, 2B, J = 143, B5',11'), -23.32 (d, J = 174, B6), -28.36 (1B, d, J = 174, B6'). δ_H (400 MHz, CD₃CN, Me₄Si): 7.75 (br s, 2H, NH), 3.88 (br s, 4H, CH_{carb}), 3.83 (br s, 4H, CH_{carb}), 4.721 (t, 2H, J = 4.9 Hz, CH_2O), 3.421 (s, 3H, CH_3O), 3.068 (br t, 2H, $\text{CH}_2\text{CH}_2\text{N}$), 2.971 (br s, 2H, B-CH₂N). B-H signals from ¹H{¹¹B-selective} NMR (CD₃CN): $\delta_{\text{B}-\text{H}}$ (ppm) 2.82 (H10), 2.60 (H10'), 1.87 (H9,12), 2.72 (H4,7), 2.12 (H9',12'), 2.97 (H4',7'), 1.53 (H5,11), 1.53 (H5',11'), 1.41 (H6), 1.25 (H6'). δ_C (100 MHz, CD₃CN, Me₄Si): 58.07 (d, CH_2O), 56.89 (d, CH_3O), 51.42 (d, CH_{carb}), 52.32 (CH_3N), 48.40 (d, CH_{carb}), ca. 47.5 (br.s, $\text{HN}-\text{CH}_2-\text{B}$). MS m/z (ESI $^-$): 427.50 (100), 430.40 (8) (calcd 430.34) [$\text{M} - \text{H}]^-$.

Data for [(8-(C₆H₅)₃P-CH₂-1,2-C₂B₉H₁₀)(8'-CH₃O-1',2'-C₂B₉H₁₀)-3,3'-Co]⁰ (**6d**) are as follows. Yield: 90%. HPLC: k' = 15.8, purity assay 99.5%. TLC: R_f 0.42 (TLC plate Silufol, silica gel, CH_2Cl_2 -hexane 3:1). Mp: 254 °C. IR: ν (cm⁻¹) 3442, 3048, 2933, 2829 (C-H) 2604, 2555, 2522 (B-H), 1900–1700 (C-C)_{phenyl}, 1590 (C-H)_{aryl}, 1436 (CH), 1200, 1135, 1097, 965, 756, 686, 505 (C-O, P-C). δ_B (128 MHz, CD₃C(O)CD₃, Et₂O-BF₃): 27.06 (s, 1B, B8'), 10.15 (s, 1B, B8), -1.20 (d, 1B, J = 161, B10), -2.55 (d, 2B, J = 180, B10'), -5.24 (d, 2B, J = 174, B9,12), -6.47 (d, 4B, J = 147, B4,7,9,12'), -7.90 (d, 2B, J = 135, B4',7'), -17.87 (d, 2B, J = 152, B5,11), -18.82 (d, 2B, 153, B5',11'), -23.72 (d, 1B, J = 170, B6), -28.26 (d, 1B, J = 180, B6'). δ_H (400 MHz, CD₃CN, Me₄Si): 8.011 (2d, 6H, ArH), 7.770 (m, 3H, ArH), 7.685 (m, 6H, ArH), 4.080 (s, 2H, CH_{carb}), 3.885 (s, 2H, CH_{carb}), 3.780 (br. d, $J_{\text{P}-\text{H}} = 8.5$, 2H, B-CH₂P), 3.478 (s, 3H, CH_3O). ¹H{¹¹B-selective} NMR (CD₃CN): $\delta_{\text{B}-\text{H}}$ (ppm) 2.33 (H10), 2.57 (H10'), 2.82, 2.19, 1.04 (H4,7,9,12,9',12'), 2.85 (H4',7'), 1.30 (H5,11), 1.48 (H5',11'), 1.36 (H6), 1.31 (H6'). δ_C {¹H} (100 MHz, CD₃CN, Me₄Si): 134.55 (ArC), 130.27 (ArC), 124.23 (d, 3C, $J_{\text{C}-\text{P}} = 85$ Hz), 57.55 (CH_3O), 50.54, 48.48 (CH_{carb}), ca. 27.5 (br d, P-CH₂-B). MS m/z (ESI $^-$): 630.52 (100), 433.40 (4) (calcd 433.40) [$\text{M} - \text{H}]^-$.

Synthesis of Na[8-(4-tert-Bu-C₆H₄-1-O)-CH₂-1,2-C₂B₉H₁₀)(8'-CH₃O-1',2'-C₂B₉H₁₀)-3,3'-Co] (Na7). A solution of **2** (0.40 g, 0.11 mmol) in toluene-DME (3:1, 15 mL) was added to a solution of 4-tert-butylphenol (0.150 g, 1.05 mmol) deprotonated using NaH (95%, 25 mg, 1.1 mmol) in the same solvent (15 mL). The reaction mixture was stirred at room temperature for 16 h. Water and a few drops of 3 M HCl were then added, organic solvents were removed under vacuum, and the crude product was extracted into ether (3 × 15 mL). The combined extracts were washed with water and then dried. The product was purified by repeated chromatography on silica gel using $\text{CH}_2\text{Cl}_2-\text{CH}_3\text{CN}$ (3:1) for elution and then crystallized from CH_2Cl_2 -hexane. The main product was identified by NMR and MS as the anion **8** (for its characterization see the data presented below).

Data for Na7 are as follows. HPLC: k' = 15.2 (58% CH₃CN, 4.5 mM HAA). Isolatable yield: 110 mg, 19%. HPLC: k' = 15.92, purity assay 98.4%. TLC: R_f = 0.28 (TLC plate Silufol, $\text{CH}_2\text{Cl}_2-\text{CH}_3\text{CN}$ 3:1). Mp: 98 °C. IR: ν (cm⁻¹) 3447 (C-H)_{aryl}, 3057, 2965, 2932 (C-H), 2603, 2577, 2540 (B-H), 1606, 1513 δ (CH)_{aryl}, 1228 δ (CH), 1124, 956, 836 (C-O). δ_B (128 MHz, CD₃CN, Et₂O-BF₃): 23.29 (s, 1B, B8'), 8.46 (s, 1B, B8), -0.25 (d, 1B, J = 143, B10), -2.63 (d, 2B, J = 145, B10'), -5.33 (d, 2B, J = 195, B9,12), -6.79 (d, 4B, J = 146, B4,7,9,12'), -8.69 (d, 2B, J = 137, B4',7'), -18.82 (d, 2B, J = 180, B5,11), -20.39 (d, 2B, J = 184, B5',11'), -23.63 (d, J = 159, B6), -28.10 (d, 1B, J = 168, B6'). δ_H (400 MHz, CD₃CN, Me₄Si): 7.376 (d, J = 8.8, 2H, ArH), 6.783 (d, J = 8.4, ArH), 4.735 (s, 2H, CH_{carb}), 4.229 (s, 2H, CH_{carb}), 3.634 (s, 2H, B-CH₂O), 3.270 (s, 3H, CH_3O), 1.251

(s, 9H, *tert*-C₄H₉). ¹H{¹¹B-selective} NMR (CD₃CN): $\delta_{\text{B}-\text{H}}$ (ppm) 2.85 (H10), 2.56 (H10'), 2.77, 1.88, 1.68 (H4,7,9,12,9',12'), 2.75 (H4',7'), 1.54 (H5,11), 1.43 (H5',11'), 1.29 (H6), 1.26 (H6'). δ_C {¹H} (100 MHz, CD₃CN, Me₄Si): 127.75 (ArC), 118.16 (ArC), 57.46 (CH₃O), 54.38 (CH_{carb}), 47.65 (CH_{carb}), 34.37 (B-CH₂O), 31.62 (*tert*-C₄H₉). MS m/z (ESI $^-$): 517.50 (100), 519.40 (8) (calcd 519.40) [$\text{M}]^-$.

Synthesis of [8,8'-μ-(CH₂O)-(1,2-C₂B₉H₁₀)₂,3-Co](Et₃NH) (8) by Demethylation of 2 by Triethylamine. The starting zwitterionic derivative **2** (0.5 g, 1.37 mmol) was dried under vacuum and then dissolved in toluene-DME (9:1, 10 mL); excess triethylamine (5 mmol) diluted by the same solvent (10 mL) was added. The reaction mixture was stirred for 12 h, and then the solvents were evaporated under reduced pressure; the residue was dissolved in $\text{CH}_2\text{Cl}_2-\text{CH}_3\text{CN}$ (1:3, 3 mL) and injected atop a silica gel column (2.5 × 25 cm), and the orange band was eluted using the same solvent mixture as the mobile phase.

Data for (NH(CH₂CH₃)₃)[·]8 are as follows. Yield: 84%. HPLC: k' = 1.94 (58% CH₃CN, 4.5 mM HAA), purity assay 99.5%. TLC: R_f = 0.39 (TLC plate Silufol, silica gel, $\text{CH}_2\text{Cl}_2-\text{CH}_3\text{CN}$ 3:1). Mp: 289 °C. IR: ν (cm⁻¹) 3437 (N-H), 2944, 2840 (C-H), 2604, 2566, 2539, 2494 (B-H), 1480, 1441 δ (CH), 1129, 1097 (C-O). δ_B (128 MHz, CD₃CN, Et₂O-BF₃): 32.74 (s, 1B, B8'), 25.34 (s, 1B, B8), -4.22 (d, 1B, J = 140, B10), -6.62 (d, 5B, J = 174, B9,12,9',10',9,12'), -8.82 (d, 2B, J = 177, B4,7), -11.88 (d, 2B, J = 149, B 4',7'), -16.68 (d, 2B, J = 156, B5,11), -17.92 (d, 2B, J = 156, B5',11'), -27.14 (d, 1B, J = 162, B6), -31.78 (1B, d, J = 168, B6'). δ_H (400 MHz, CD₃CN, Me₄Si): 7.6 (br s, 1H, NH), 3.911 (br s, 2H, CH_2O), 3.504 (br s, 2H, CH_{carb}), 3.358 (s, 2H, CH_{carb}), 3.911 (m, 6H, CH₂NH, Et₃NH⁺), 3.911 (t, 9H, CH₂CH₃, Et₃NH⁺). B-H signals from ¹H{¹¹B-selective} NMR: δ (ppm) 3.02, 2.89 (H4,7,4',7'), 2.54 (H10), 2.34 (H10'), 1.94, 1.83 (H9,12,9',12'), 1.54 (H5,11), 1.53 (H5',11'), 1.45 (H6), 1.27 (H6'). 3Na⁺ δ_C (100 MHz, CD₃CN, Me₄Si): 77.10 (br s, CH_2O), 44.49, 42.79 (CH_{carb}). MS m/z (ESI $^-$): 352.46 (100), 355.34 (9) (calcd 355.27) [$\text{M}]^-$.

Synthesis of 1,3-Dicyanomethyl-2-(8-methylene-8'-methoxycobalt bis(dicarbollide))-4-methyl-tert-butyl-calix[4]arene (Cs9). The starting 1,3-dicyanomethyl-calix[4]arene (see Scheme 3) (495 mg, 0.67 mmol) was stirred in DME (5 mL) until dissolution, and toluene (15 mL) was then injected. After that, solid NaH (95%, 35 mg, 1.46 mmol) was added and stirring was continued for 2 h. A solution of **2** (500 mg, 1.35 mmol) in toluene-DME (1:1, 10 mL) was then added, and the reaction mixture was stirred at room temperature until the spot of **2** on the TLC disappeared (42 h). The resulting solution was neutralized with a small amount of 1 M aqueous acetic acid and evaporated. The crude product was dissolved in Et₂O (25 mL) and washed twice with water. The organic layer was filtered to remove traces of the starting calixarene and evaporated to dryness after adding water (5 mL), and the solids were then dried under vacuum. The semisolid material was dissolved in $\text{CH}_2\text{Cl}_2-\text{CH}_3\text{CN}$ (4:1) and chromatographed on a silica gel column in the same solvent mixture as the mobile phase, increasing the acetonitrile content to 3:1. The first intense orange band contained the sodium salt of the crude product (305 mg), while the last chromatographic fraction contained the demethylated anion **8**⁻. The crude product was dissolved in 70% aqueous ethanol, after which excess aqueous CsCl was added. The precipitate was removed by filtration, washed with 30% aq. ethanol and crystallized twice from hot 70% aqueous ethanol. The solid product was dried under vacuum and dissolved in CHCl₃ by adding a few drops of MeOH, and this solution was then layered with hexane and left to crystallize for 2 days. The crystals were collected, inclusive of those used for X-ray diffraction.

Data for Cs9 are as follows. Yield: 260 mg (31%, calculated on the starting calixarene). HPLC (gradient elution): purity assay 97.8%, R_f = 0.35 ($\text{CH}_2\text{Cl}_2-\text{CH}_3\text{CN}$ 3:1). Mp: 232–234 °C. IR: ν (cm⁻¹) 3449, 2962 (C-H)_{aryl}, 2561 (B-H), 1601, 1480, 1366 (C-H), 1256 δ (CH), 1201, 1107, 1020, 872, 795 (CO). δ_B (128 MHz, CD₃COCD₃, 25 °C, Et₂O-BF₃): 24.13 (s, 1B, B8'), 9.50 (s, 1B, B8), 0.04 (d, 1J = 144, 1B, B10'), -2.27 (d, J = 143, 1B, B10), -5.03 (d, overlap, 2B, B9,12), -6.47 to -7.95 (2d, J = 163 and 168 Hz, 6B; B4,7,4',7',9',12'), -17.68

(d, $J = 177$ Hz, 2B; B5',11'), -20.06 (d, $J = 152$ Hz, 2B; B5,11), -21.6 (d, overlap, 1B; B6'), -28.36 ppm (d, $^1J = 139$, 1B; B6). ^1H NMR (400 MHz, acetone- d_6 , 25 °C, TMS): δ_{H} 7.31 (2s, 4H; ArH), 6.66 (s, 2H; ArH), 6.33 (s, 2H; ArH), 5.484 (d, 2H; $^2J(\text{H},\text{H}) = 16.4$ Hz, OCH₂CN), 4.974 (s, 2H; $J = 16.8$ Hz, OCH₂CN), 4.659 (d, $J = 12.8$ Hz, 2H; ArCH₂Ar, H_{ax}), 4.383 (d, $J = 13.2$ Hz, 2H; ArCH₂Ar, H_{ax}), 4.366 (2s, 4H; CH_{carb}), 3.807 (s, 3H; CH₃O), 3.633 (s, 2H; CH₂), 3.34 (s, 3H; CH₃O), 3.273 (d, $^2J(\text{H},\text{H}) = 13.2$ Hz, 2H; ArCH₂Ar, H_{eq}), 3.257 (d, $^2J(\text{H},\text{H}) = 12.8$ Hz, 2H; ArCH₂Ar, H_{eq}), 1.39 (s, 18H; t-Bu), 0.943 (s, 9H; t-Bu), 0.733 (s, 9H; t-Bu). B-H signals from $^1\text{H}\{\text{B}-\text{selective}\}$ NMR: δ (ppm) 3.03 (H10), 2.907 (H9,12), 2.70 (H10'), 2.877, 2.207, 2.021 (H4,7,4',7',9',12'), 1.773 (HS,11), 1.56 (HS',11'), 1.43 (H6), 1.35 (H6'). MS (ESI⁻) m/z (%): 1106.70 (100), 1110.20 (14) [M]⁻ (calcd 1109.74).

■ ASSOCIATED CONTENT

Supporting Information

CIF files giving crystallographic data for **6a,c,d**, [8](Et₃NH⁺), and Cs**9** and ^1H , $^1\text{H}\{\text{B}\}$, ^{13}C , and $^{11}\text{B}\{\text{H}\}$ NMR spectra of all new compounds that are described in this paper (**2**, **4**, **5**, **6a-d**, **7-**, **8-**, and **9-**). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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