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Article

Toward the Synthesis of High Boron Content Polyanionic Multicluster Macromolecules

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Reported are further consequences of the dioxane ring opening in [3,3′-Co(8-$(CH_2CH_2O)_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)], [**1**], with 12-vertex carborane mono- and dianions. The removal of one BH vertex from the 1,2-*closo*-$C_2B_9H_{12}$ part of the double-cluster monoanions of type [1″-X-2″-R-*closo*-1″,2″-$C_2B_{10}H_{11}$]$^-$, [**2**]$^-$ (where X = [3,3′-Co(8-$(CH_2CH_2O)_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ and R = H, [**2**]$^-$; CH_3, [**8**]$^-$ and C_6H_5, [**9**]$^-$), via heating with ethanolic KOH or CsF led to the isolation of a series of orange dianions having the general formula [7″-X-8″-R-7″,8″-*nido*-$C_2B_9H_{11}$]$^{2-}$ (R = H, [**11**]$^{2-}$; CH_3, [**12**]$^{2-}$; and C_6H_5, [**13**]$^{2-}$). The same procedure applied to the dianionic triple-cluster compound [1″,2″-X_2-1″,2″-*closo*-$C_2B_{10}H_{10}$]$^{2-}$, [**5**]$^{2-}$, yielded the trianionic species [7″,8″-X_2-7″,8″-*nido*-$C_2B_9H_{10}$]$^{3-}$, [**14**]$^{3-}$. Boron degradation of the related 1,7-carborane anion [1″-X-1″,7″-*closo*-$C_2B_{10}H_{11}$]$^-$, [**3**]$^-$, was achieved upon heating with CsF in ethylene glycol to generate the [7″-X-7″,9″-*nido*-$C_2B_9H_{11}$]$^{2-}$, [**15**]$^{2-}$, dianion. However, the degradation of the corresponding [1″,7″-X_2-1″,7″-*closo*-$C_2B_{10}H_{10}$]$^{2-}$, [**6**]$^{2-}$, dianion under the same conditions led only to the cleavage of the ether chain with no possible isolation of the expected [7″,9″-X_2-7″,9″-*nido*-$C_2B_9H_{10}$]$^{3-}$ trianion. The study has been complemented by experimental procedures leading to the still not fully reported starting monoanionic compounds [**2**]$^-$, [**3**]$^-$, [**8**]$^-$ and [**9**]$^-$ and to the starting dianions [**5**]$^{2-}$ and [**6**]$^{2-}$. The anions containing the eleven-vertex moiety can be isolated as either Cs^+ or $[N(CH_3)_4]^+$ salts and can be converted into other salts via metathesis with suitable countercations. The structures of all compounds isolated in this study have been suggested on the basis of NMR and mass spectrometry methods. The disarticulation of complex ^{11}B NMR spectra has been successfully achieved in this work and has been proven to be a powerful tool for the characterization of multicluster boron-containing molecules.

Introduction

The synthetic strategy based on the attack of oxonium derivatives of borane[1] and metallacarborane[2] anions in the presence of nucleophilic agents was first reported in 1976.[3] The discovery of the nucleophilic ring-opening reaction in boranes[4] and metallacarboranes[5] has been one of the most important features in boron chemistry over the past several years. A review on this field has been published recently, summarizing some of the nucleophiles that have been used so far.[6]

The derivatization of boranes and metallacarboranes may open the way for new possible applications of these anions.

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The use of a variaty of ring-opening nucleophiles on [3,3′-Co(8-$(CH_2CH_2O)_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)], [**1**], has led to the synthesis of compounds of promising practical uses in various fields, including the treatment of nuclear wastes,[7] conducting polymers in materials science,[8] solid electrolytes, strong nonoxidizing acids,[9] weakly coordinating anions,[10] ionic crystals[11] and enzyme inhibitors.[12] Applications associated with the properties of boron as element within deltahedral species primarily exploit the ^{10}B isotope for neutron capture, which led to the development of the boron neutron capture therapy (BNCT)[13] of cancer tumors.

Compound [**1**] has been shown to be susceptible to nucleophilic attack at the dioxane carbon adjacent to the positively charged oxygen atom by a variety of nucleophile agents containing oxygen,[14,15] nitrogen,[5a,8b,12,16,17] phosphorus[5c,18] and carbon.[5e,15d,19]

Sivaev et al.[19] demonstrated that the tetrahydrofuran (THF) ring in the $[B_{12}H_{11}\cdot THF]^-$ anion can be opened by all three isomers (1,2-, 1,7- and 1,12-) of $Li[C_2B_{10}H_{11}]$. Additionally, in a preliminary communication,[20] we have briefly outlined the synthesis and isolation of mono- and dianion species combining the [3,3′-Co(1,2-$C_2B_9H_{11})_2]^-$ and $[C_2B_{10}H_{12}]$ structural motifs.

In this paper, we extend this viable concept of multicage boron chemistry by giving full experimental details and complete structural data. Moreover, the deboronation of the *closo*-carborane moieties allowed the preparation of a novel type of polyanionic water-soluble high boron content macromolecules that could be good candidates for increasing BNCT techniques' efficiency.

Results and Discussion

Synthesis and Characterization of *closo*-C_2B_{10} or *nido*-$[C_2B_9]^-$ Frameworks Incorporating Monosubstituted Cobaltabisdicarbollide Derivatives. Following our studies on cobaltabisdicarbollides' direct substitution[15d] to obtain novel high boron content polyanionic species with enhanced water solubility, we have recently explored the possibility of using lithiated boron clusters as nucleophiles to produce a new family of high boron content polyanionic macromolecules.[15d,20] This has been, in part, stimulated by the high water solubility of the cobaltabisdicarbollide salts of potassium, sodium, or lithium.[21] With these two points in mind, we studied the nucleophilic behavior of 1,2-*closo*-, 1,7-*closo*-, and Li[1,12-*closo*-$C_2B_{10}H_{11}$] isomers and their nucleophilic behavior toward [3,3′-Co(8-$(CH_2CH_2O)_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)], [**1**]. Scheme 1 shows that treatment of $Li[C_2B_{10}H_{11}]$ (1,2-, 1,7-, and 1,12- isomers) with [**1**] (molar ratio 1:1) produces Li[1″-X-1″,2″-*closo*-$C_2B_{10}H_{11}]^-$, Li[**2**], Li[1″-X-1″,7″-*closo*-$C_2B_{10}H_{11}]^-$, Li[**3**] and Li_2[1″-X-1″,12″-*closo*-$C_2B_{10}H_{11}$], Li_2[**4**] (where X = [3,3′-Co(8-$(CH_2CH_2O)_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$), results already published in a previous communication.[20] In order to establish substituent effects in this series, we have applied the same synthetic procedure to the C anions Li[1-R-1,2-$C_2B_{10}H_{10}]^-$ (where R = CH_3 and C_6H_5), which led as expected to the isolation of the C-methylated and phenylated analogues, the structures of which were in agreement with the constitution of the monoanionic salts Li[1″-X-2″-CH_3-1″,2″-*closo*-$C_2B_{10}H_{10}$], Li[**8**], and Li[1″-X-2″-C_6H_5-1″,2″-*closo*-$C_2B_{10}H_{10}$], Li[**9**]. The anions were isolated for their full characterization either as Cs^+ or $[N(CH_3)_4]^+$ salts and can be converted into other salts via metathesis with suitable countercations. As anticipated and shown in Scheme 1, an analogous treatment of the corresponding dilithium carboranes $Li_2[C_2B_{10}H_{10}]$ (1,2-, 1,7-, and 1,12- isomers) with [**1**] (molar ratio 1:2) at room temperature in THF leads generally to the formation of a series of orange triple-cluster dianionic salts formulated as Li_2[1″,2″-X_2-1″,2″-*closo*-$C_2B_{10}H_{10}$], Li_2[**5**], Li_2[1″,7″-X_2-1″,7″-*closo*-$C_2B_{10}H_{10}$], Li_2[**6**]$^{2-}$ and Li_2[1″,12″-X_2-1″,12″-*closo*-$C_2B_{10}H_{10}$], Li_2[**7**]. The Li_2[**7**] compound was also isolated as a side product in the preparation of the monoanionic salt Li[**4**].

Even if the *closo* carborane clusters are structures showing high stability with respect to strong acids, they do however react with Lewis bases, yielding more opened structures, known as *nido*, by a partial deboronation process that implies the loss of a cluster's vertex. Several

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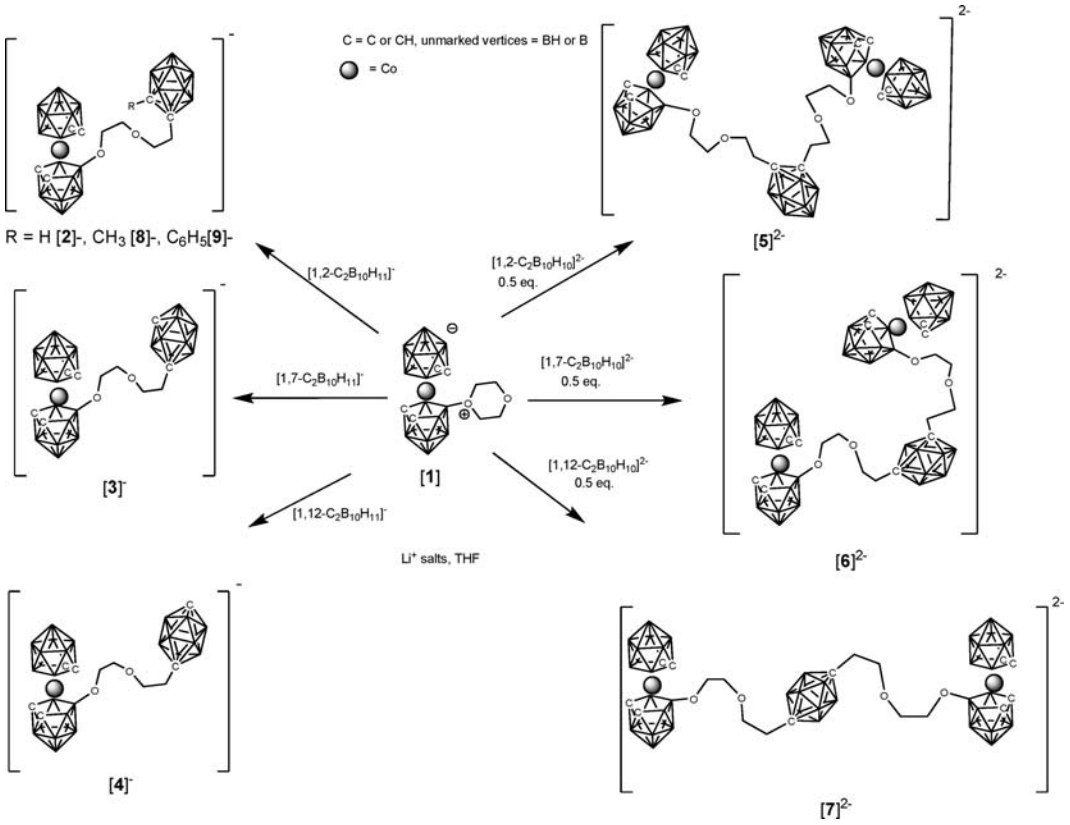
Scheme 1. Simplified Structures and Formation of the Monoanionic and Dianionic Twelve-Vertex Dicarboranes Modified by the Eight-Substituted $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ Function via a 1,4-Dioxahexane Interconnection Chain



nucleophiles such as alkoxides,[22] amines,[23] fluorides[24] and phosphanes[25] have been used. The nucleophilic attack takes place at the boron atoms directly bound to both carbon atoms, the B(3) or its equivalent B(6), since they both present electronic deficiency. Scheme 2 shows that regioselective removal of one BH vertex from the 1,2-*closo*-$C_2B_{10}H_{12}$ cluster of the double-cluster monoanion of type $[1''\text{-X-}2''\text{-R-}1'',2''\text{-}closo\text{-}C_2B_{10}H_{10}]^-$, $[\mathbf{2}]^-$, species (R = H, $[\mathbf{2}]^-$; CH_3, $[\mathbf{8}]^-$; and C_6H_5, $[\mathbf{9}]^-$) takes place via heating with ethanolic KOH or CsF. This reaction led to a good yield isolation (68, 55 and 70%, respectively) of a series of orange dianions with the general formula $[7''\text{-X-}8''\text{-R}-7'',8''\text{-}nido\text{-}C_2B_9H_{10}]^{2-}$ (R = H, $[\mathbf{11}]^{2-}$; CH_3, $[\mathbf{12}]^{2-}$ and C_6H_5, $[\mathbf{13}]^{2-}$). The fragmentation of $[\mathbf{8}]^-$ and $[\mathbf{12}]^{2-}$ is illustrated in Figure 1.

As expected, the same degradation procedure applied to the dianionic triple-cluster compound $[1'',2''\text{-}X_2\text{-}1'',2''\text{-}closo\text{-}C_2B_{10}H_{10}]^{2-}$, $[\mathbf{5}]^{2-}$, gave rise to the trianionic species $[7'',8''\text{-}X_2\text{-}\ 7'',8''\text{-}nido\text{-}C_2B_9H_{10}]^{3-}$, $[\mathbf{14}]^{3-}$, which is substituted at both carbon atoms of the eleven-vertex dicarborane cluster. For their full characterization, these anionic species can be isolated as either Cs^+ or $[N(CH_3)_4]^+$ salts and converted into other salts via metathesis with suitable countercations.

Boron degradation of the cage isomeric 1,7-carborane anion $[1''\text{-X-}closo\text{-}1'',7''\text{-}C_2B_{10}H_{11}]^-$, $[\mathbf{3}]^-$, requires more severe reaction conditions—the loss of one boron vertex was achieved upon heating with CsF in ethylene glycol to generate the $[7''\text{-X}\ -7'',9''\text{-}nido\text{-}C_2B_9H_{11}]^{2-}$, $[\mathbf{15}]^{2-}$ dianion. Nevertheless, application of a similar procedure to the disubstituted dianion $[1'',7''\text{-}X_2\text{-}1'',7''\text{-}closo\text{-}C_2B_{10}H_{10}]^{2-}$, $[\mathbf{6}]^{2-}$, did not lead to the expected $[7'',9''\text{-}X_2\text{-}7'',9''\text{-}nido\text{-}C_2B_9H_{10}]^{3-}$ trianion. Moreover, the prolonged treatment (2 days) with a large excess of CsF (10 molar) led to a cleavage of ether chains. It should also be noted that no degradation of the 1,12-carborane cluster of anions $[\mathbf{4}]^-$ and $[\mathbf{7}]^{2-}$ was observed with CsF under comparable conditions.

NMR Studies. In the absence of suitable crystals for X-ray diffraction studies, the structures of all compounds isolated have been solved by multinuclear NMR spectroscopy and mass spectrometry.

a. *Closo* Species. One of our groups reported[15d] that the ^{11}B NMR spectrum of monosubstituted derivatives of $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ is the result of plain addition of the spectra of the two individual halves. In a similar manner, Figure 2 shows how the ^{11}B NMR spectrum of $[\mathbf{8}]^-$ can be analyzed as two fragments. The spectrum of fragment I is approximated by that of the anion $[3,3'\text{-}Co(8\text{-}(CH_2CH_2O)_2\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ and

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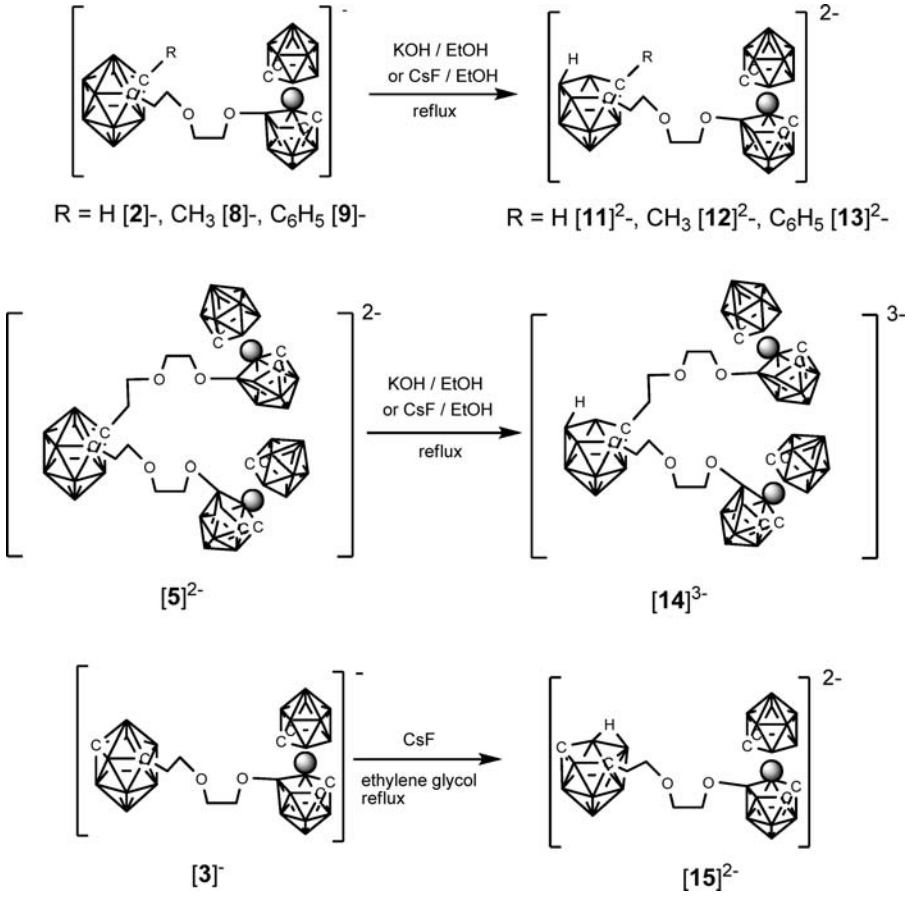
Scheme 2. Partial Deboronation Reaction of Closo Compounds Yielding the Corresponding Di- and Tri-Anionic Species



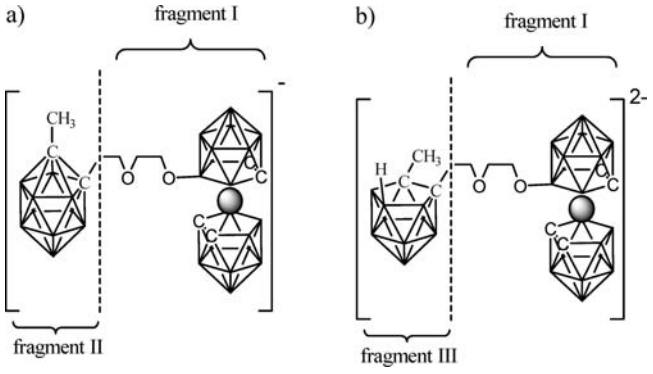


Figure 1. (a) Notional fragmentation of the monoanionic methyl derivative $[\mathbf{8}]^-$. (b) Fragmentation of the dianionic methyl derivative $[\mathbf{12}]^{2-}$.

the one of fragment II by the spectrum of 1-CH_3-1,2-*closo*-$C_2B_{10}H_{11}$ or more precisely by the one of the model compound 1-CH_3-2-$CH_3OCH_2CH_2$-1,2-*closo*-$C_2B_{10}H_{10}$, [**10**]. Compound **10** has been synthesized only for this purpose.

In order to understand the spectrum and assign the peaks corresponding to each fragment, we have used the DM2008 program.[26] The latter has been used almost exclusively for modeling solid-state NMR spectra of noncluster compounds, and in this paper we report for the first time on the computational disarticulation of the ^{11}B NMR spectra in solution to analyze the multicluster compounds isolated. These species contain either 28 or 46 boron atoms of different degrees of symmetry. Table 1 and Figure 2a exemplify the disarticulation of the ^{11}B NMR spectrum of the methylated anion $[\mathbf{8}]^-$, for which it is possible to find 14 different Gaussian-type curves fitting experimental spectra.

Figure 2b represents the typical 1:1:1:1:2:2:(2+2):2:2:1:1 ^{11}B NMR spectrum of a fragment I [3,3′-Co-(8-$(CH_2CH_2O)_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ anion with a C_s symmetry (12 different signals, two overlapped). This leaves only two signals corresponding to fragment II (heterosubstituted methyl-carborane), although there should be others overlapped with the peaks of fragment I. To get the spectrum of fragment II, it is possible to subtract the already known spectrum of fragment I from the full spectrum of $[\mathbf{8}]^-$.

The result is shown in Figure 2c where five different signals can be seen. Moreover, it is possible to get the pattern of this fragment II by subtracting the integrals of fragment I from the full spectrum. As it is shown in Table 1, it is possible to get a 1:1:2:2:4 pattern for fragment II. To compare this theoretical spectrum, we have also synthesized [1-$CH_3OCH_2CH_2$-2-CH_3-1,2-*closo*-$C_2B_{10}H_{10}$], [**10**], which is very similar to fragment II. As seen in Figure 2c, the theoretical spectrum of [**10**] is in excellent agreement with experimental data obtained for [**10**] with 1:1:2:2:4 resonances at −4.28, −5.82, −9.25, −9.90 and −10.54 (see Figure 2d).

(26) Massiot, D.; Fayon, F.; Capron, M.; King, I.; Le Calvé, S.; Alonso, B.; Durand, J.-O.; Bujoli, B.; Gan, Z.; Hoatson, G. *Magn. Reson. Chem.* **2002**, *40*, 70.

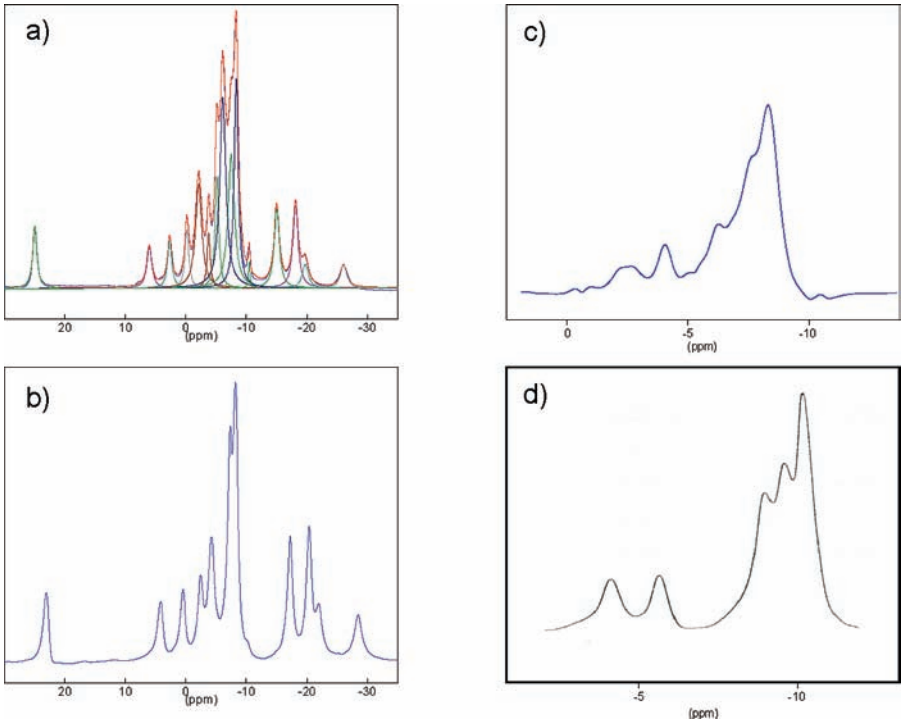


Figure 2. (a) Disarticulation of the experimental ^{11}B NMR spectrum of [**8**]$^-$. Each Gaussian-type fitting curve is represented by a different color. (b) ^{11}B NMR spectrum of [3,3′-Co-8-$(CH_2CH_2O)_2$-(1,2-$C_2B_9H_{10}$)-(1′,2′-$C_2B_9H_{11}$)]$^-$. (c) Theoretical spectrum of fragment II. (d) Experimental ^{11}B NMR spectrum of [**10**].

Table 1. Summary of Disarticulation of the ^{11}B NMR Signals for Compound [**8**]$^-$ Together with Peak Assignments

Gaussian no.	δ (ppm)	% integral	overall integration	fragm. I	fragm. II
1	24.95	4.19	1	1	
2	6.04	3.37	1	1	
3	2.67	3.28	1	1	
4	−0.16	3.61	1	1	
5	−2.11	10.68	3	2	1
6	−3.77	2.80	1		1
7	−5.11	6.47	2	2	
8	−6.1	19.15	6	4	2
9	−7.49	13.86	2		2
10	−8.31	13.96	4		4
11	−15.01	6.48	2	2	
12	−18.12	6.96	2	2	
13	−19.73	2.29	1	1	
14	−26.05	2.26	1	1	

The most diagnostic feature of the ^{1}H NMR spectra of monoanions [**2**]$^-$, [**3**]$^-$ and [**4**]$^-$ is the presence of C_c−H signals corresponding to the [3,3′-Co(8-$(CH_2CH_2O)_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ unit (integral intensity 2 + 2 or 4) along with one carborane CH resonance of relative area 1, corresponding to 1,2-*closo*-$C_2B_9H_{11}$, which is missing in the spectra of [**8**]$^-$ and [**9**]$^-$ and dianionic compounds [**5**]$^{2-}$, [**6**]$^{2-}$ and [**7**]$^{2-}$. The signals of the $BOCH_2$−, $-CH_2OCH_2-$, and $-CH_2-$carborane units of the interconnecting 1,4-dioxahexane chain usually occur within the range $\delta \approx 3.7-1.9$ ppm.

b. *Nido* Species. Similar considerations were used for analyzing the spectra of the corresponding *nido*-$[C_2B_9]^-$ counterparts. The typical differences between the spectra of *closo* compounds and their eleven-vertex *nido* counterparts are exemplified for the methylated species [**8**]$^-$ and [**12**]$^{2-}$ in Figure 3.

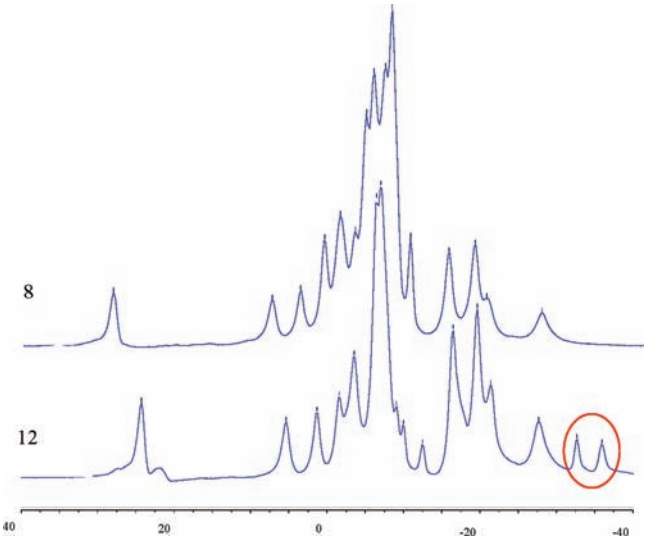


Figure 3. Comparison between ^{11}B{^{1}H} NMR spectra of the *closo* compound [**8**]$^-$ and its corresponding *nido* species [**12**]$^{2-}$.

The NMR analysis used for the characterization of all of the above presented compounds gives valuable information regarding the differences between the *closo* and the nido species. As presented in Figure 3, additional peaks for the *nido* compounds with respect to the corresponding *closo* species appear in the experimental ^{11}B{^{1}H} NMR spectra in the range $\delta \approx -34/-36$ ppm, which clearly confirms the deboronation of the neutral *closo* $[C_2B_{10}]$ cluster to the anionic *nido* $[C_2B_9]^-$ one. As shown in Figure 1b, the methylated *nido* dianion [**12**]$^{2-}$ could be considered as the sum of fragment I and fragment III. As exemplified in Figure 4, the schematic representation of the ^{11}B{^{1}H} NMR spectrum of the

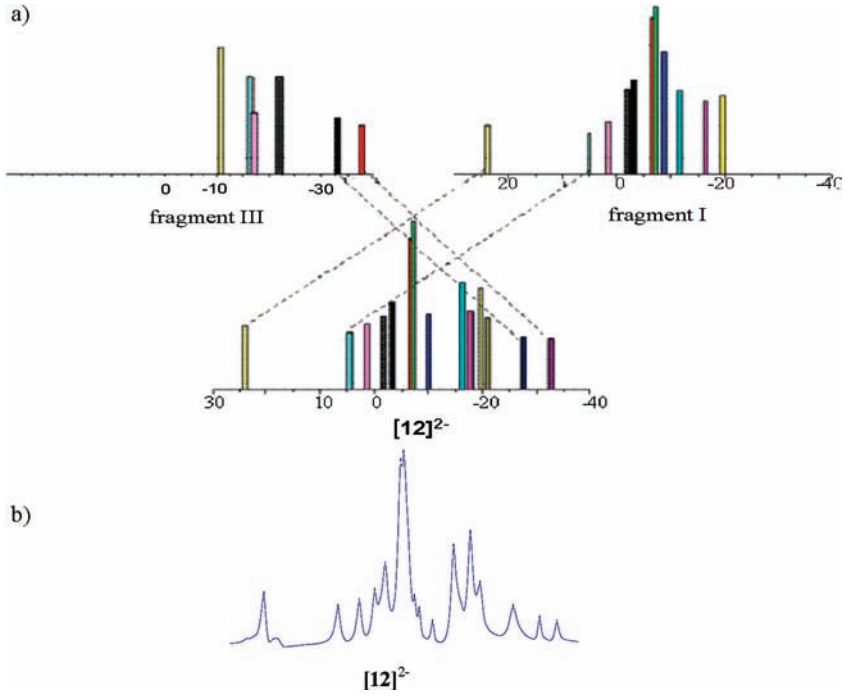


Figure 4. (a) Schematic representation of the $^{11}B\{^1H\}$ NMR spectrum of compound $[\mathbf{12}]^{2-}$ as a sum of fragments I and III and (b) its experimental one.

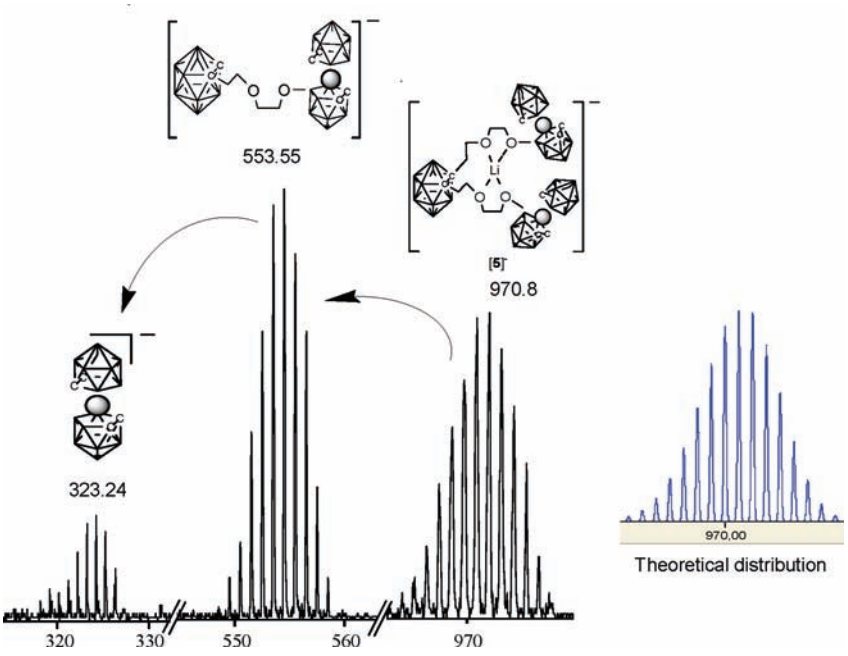


Figure 5. The experimental MALDI-TOF-MS spectrum of $[NMe_4]Li[\mathbf{5}]$ with its theoretical molecular peak MS spectrum.

methylated *nido* dianion $[\mathbf{12}]^{2-}$ consists of 12 resonances from fragment I plus nine resonances of fragment III. Its experimental $^{11}B\{^1H\}$ NMR spectrum (Figure 4b) confirms it.

MALDI-TOF-MS Characterization. Another method used for the characterization of these newly synthesized high boron content anionic compounds was matrix-assisted laser desorption/ionization (MALDI)[27] spectroscopy. The MALDI-TOF-MS (TOF = time of flight) spectrum of compound $[\mathbf{5}]^{2-}$ is taken as a representative example of the divalent *closo* family of ions, with the properly isotopic distribution showing a peak at 970.80, which corresponds to $[M + Li^+]^-$ and the fragmentation peaks at 553.55 and 323.24, respectively (Figure 5). The capability of electrospray ionization (ESI) mass spectrometry for studying weak, noncovalent interactions between metal cations and organic ligands was recognized

(27) (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.

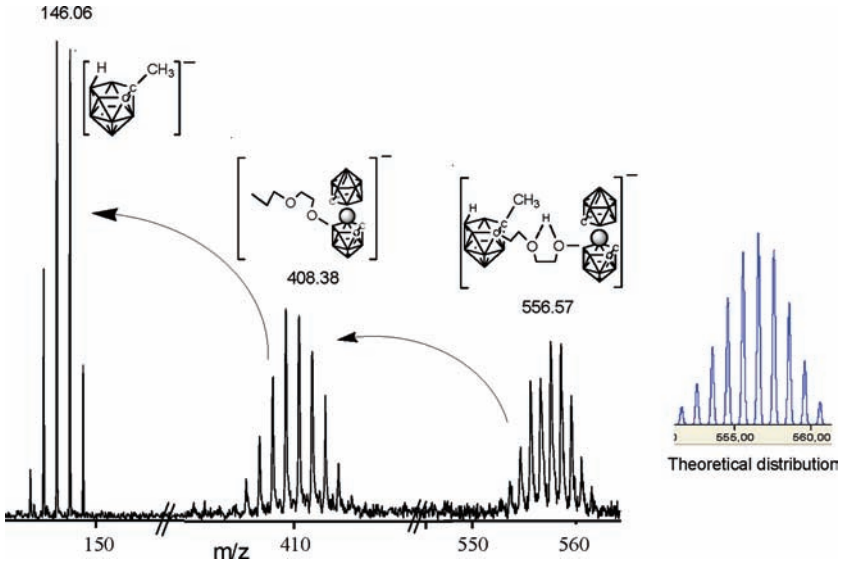


Figure 6. The MALDI-TOF-MS spectroscopy of compound $[NMe_4]_2$[**12**].

almost immediately after the introduction of this technique,[28] but there is no reported example by using MALDI-TOF-MS. The MALDI-TOF-MS spectrum of compound $[\mathbf{12}]^{2-}$, taken as a representative example of the divalent *nido* family of ions, displays a signal group centered at *m*/*z* 556.57 corresponding to the molecular peak $[M + H^+]^-$ and peaks at 408.38 and 146.06, similar with fragments I and III, respectively. As shown in Figures 5 and 6, the experimental isotopic pattern was in good agreement with the calculated isotopic plot (Molecular Weight Calculator for Windows 9x/NT/00/ME/XP, version 6.83). In agreement with MALDI-TOF-MS spectra, we have encountered that the polyanionic species appear as monovalent compounds, by adding either sodium, lithium, potassium or hydrogen cations.

Conclusions

It should be concluded that the reactions shown in Schemes 1 and 2 lead to monoanionic, dianionic, and trianionic compounds containing both metal cobaltabisdicarbollide and carborane structural motifs within the same molecule. The presence of carborane subclusters may add new properties to boron clusters and, in fact, give rise to new species which can be used potentially in various fields of chemistry, biology, and medicine. Moreover, the deboronation of the *closo*-carborane moieties allowed the obtaining of a novel type of high boron content (almost 50%) polyanionic macromolecules. Likewise, the fact that these compounds are polyanionic makes them more soluble in water, which therefore increases their potential for biological uses. Furthermore, the carborane subunits can be easily modified by attaching variable substituents onto the carbon and boron vertex, making out of these structurally flexible compounds potential candidates for BNCT[13] of cancer and HIV-protease inhibition. In this last respect, these compounds were primarily designed to help elucidate the effect of steric and hydrophobic interactions on the efficiency of the HIV-protease inhibition in the region of enzyme flaps as well as the effect of overall charge on the mechanism of inhibition. Corresponding HIV-protease inhibition tests on compounds studied in this research are in progress in our laboratories. The disarticulation of complex ^{11}B NMR spectra has been successfully achieved in this work and has been proven to be a powerful tool for the characterization of multicluster boron-containing molecules.

4. Experimental Section

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 Advanced II instrument equipped with the appropriate decoupling accessories and on a Varian Mercury Plus 400 MHz spectrometer at 295 K in acetone-d_6 (frequencies 399.893 MHz for ^1H, 128.329 MHz for ^{11}B and 100.55 MHz for ^{13}C). 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, δ, are reported in parts per million and coupling constants in hertz. The mass spectra were recorded either 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)], in the negative ion mode using a Bruker Daltonics esquire 3000 [N_2 laser; λ_{exc} 337 nm, 0.5 ns pulses; Skim1 voltage 37.5 V], or a LCQ-Fleet Ion Trap (Thermo-Finnigan) spectrometer using ESI. Negative ions were detected in all cases. Full scans and zoom scans in the range of 100 Da around the molecular ions were measured with a resolution of two decimal digits. Samples dissolved in acetonitrile (concentrations 1 mg μL^{-1}) were introduced to the ion source with a syringe pump, at a flow rate of 5 μL min^{-1}, a drying temperature of 180 °C and a nebula gas flow of 12 L min^{-1}. Analytical high-performance liquid chromatography (HPLC) was used to check the purity.

(28) (a) Bienkowski, T.; Brodzik-Bienkowska, A.; Danikiewicz, W. *J. Mass Spectrom.* **2002**, *37*, 617. (b) Gatlin, C. L.; Tureček, F. In *Electrospray Ionization Mass Spectrometry: Fundamentals, Instrumentation and Applications*; Cole, R. B., Ed.; Wiley: New York, 1997; chapter 15. (c) Henderson, W.; Scott McIndoe, J. S. In *Mass Spectroscopy of Inorganic, Coordination and Organometallic Chemistry*; Wiley: New York, 2005. (d) Gatlin, C. L.; Tureček, F. In *Electrospray Ionization Mass Spectrometry: Fundamentals, Instrumentation and Applications*; Cole, R. B., Ed.; Wiley: New York, 1997.

A Merck-Hitachi HPLC LaChrom 7000 series system equipped with a DAD 7450 detector and an L7250 intelligent injector was used. The chromatographic procedure was as follows: An ion-pair RP chromatographic method with an isocratic elution was based on the methods reported previously for the separation of hydrophobic borate anions. The column was an RP Separon SGX C8, 7 μm (silica with chemically bonded octyl groups), Tessek Prague, Czech Repupblic. The chromatographic conditions were as follows: solvent, 3 mmol L^{-1} hexylamine acetate in 65% aqueous acetonitrile; detection, DAD; fixed wavelengths, 254, 225, 290 and 312 nm; sensitivity range, 0.2 A.U.F.S. Samples of a concentration of approximately 0.5 mg mL^{-1} in the mobile phase or CH_3CN were injected (3 μL); the method allowed the resolution of most of the compounds from the real reaction mixtures and for the purity assay. The purity of all of the compounds was more than 97%. Capacity factors $k' = (t_R - t_0)/t_0$ (where t_R is retention time and t_0 is the void retention time of a nonretained peak) are given for individual compounds.

All reactions were performed with the use of standard vacuum or inert-atmosphere techniques as described by Shriver and Drezdon,[29] although some operations, such as flash chromatography and crystallization, were carried out in air.

Materials. Cs[3,3′-Co(1,2-$C_2B_9H_{11})_2$], 1-R-1,2-*closo*-$C_2B_{10}H_{11}$ (R = H, CH_3, C_6H_5), 1,7-*closo*-$C_2B_{10}H_{12}$, and 1,12-*closo*-$C_2B_{10}H_{12}$ carboranes were purchased from Katchem Ltd., Czech Republic. [3,3′-Co(8-$(CH_2CH_2O)_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)], [**1**], was prepared according to a described procedure[14] and was dried in vacuum for 8−12 h over P_2O_5, at 60 °C, prior to use. Cs[1″-X-1″,2″-*closo*-$C_2B_{10}H_{11}$], Cs[**2**]; Cs[1″-X-1″,7″-*closo*-$C_2B_{10}H_{11}$], Cs[**3**]; Cs[1″-X-1″,12″-*closo*-$C_2B_{10}H_{11}$], Cs[**4**]; and Cs_2[1″,12″-X_2-1″,12″-*closo*-$C_2B_{10}H_{10}$], Cs_2[**7**] (where X = [3,3′-Co(8-$(CH_2CH_2O)_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$) were prepared according to the literature.[20]

1,2-dimethoxyethane (DME), diethyl ether, and THF were dried with sodium/benzophenone. N-butyllithium (1.6 M in hexane) and other chemicals were purchased from Aldrich; the solvents were acquired from Aldrich and Penta Ltd. Czech Republic, respectively, and used without purification. Analytical thin-layer chromatography was carried out on Silufol (silica gel on aluminum foil, starch as the binder, Kavalier, Czech Republic). Unless otherwise specified, column chromatography was performed on a high-purity silica gel (Merck grade, type 7754, 70−230 mesh, 60 Å), using 1:3 acetonitrile/dichloromethane as the mobile phase.

Monoanions. Synthesis of [$N(CH_3)_4$][1″-{3,3′-Co(8-$(CH_2CH_2O)_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)}-2″-CH_3-*closo*-1″,2″-$C_2B_{10}H_{10}$], [$N(CH_3)_4$][8]. Under an inert atmosphere, *n*-butyllithium (0.305 mL, 0.488 mmol; 1.6 M in hexane) was added dropwise to a stirred solution of 1″-CH_3-1″,2″-*closo*-$C_2B_{10}H_{11}$ (76.92 mg, 0.488 mmol) in anhydrous DME (15 mL) at 0 °C. The resulting solution was stirred for 1 h at a low temperature. Then, a solution of [**1**] (200 mg, 0.488 mmol) in 15 mL of anhydrous DME was added dropwise at a low temperature. After stirring overnight, a white precipitate appeared, which was discarded. The solvent was removed and 1 M HCl (20 mL) was added to the orange residue. The organic phase was extracted with diethyl ether (3 × 20 mL). The solvent was evaporated, the solid dissolved in the minimum volume of ethanol and an aqueous solution containing an excess of $[N(CH_3)_4]Cl$ was added, resulting in the formation of an orange precipitate. This was filtered off, washed with water and petroleum ether and dried in vacuum. Yield: 280 mg (89%). Anal. Calcd for $C_{15}H_{54}B_{28}CoNO_2$: C, 28.05; H, 8.47; N, 2.18. Found: C, 28.02; H, 8.56; N, 2.23. IR: ν(cm^{-1}) 3051, 3037 (C_c−H), 2943, 2916, 2894, 2864 ($C-H)_{alkyl}$, 2598, 2561, 2511 (B−H), 1481, 1448, 1415 $\delta(CH_2)$, 1359, 1284, 1247 δ(CH), 1174, 1120, 1110 (C−O−C), 945 (C−N). ^{11}B NMR: δ 25.0 (s, 1B, B(8)), 5.9 (d, ^1J(B,H) = 132, 1B), 2.7 (d, ^1J(B,H) = 140, 1B), −0.1 (d, ^1J(B,H) = 150, 1B), −2.0 (d, ^1J(B,H) = 185, 2B), −3.7 (d, ^1J(B,H) = 151, 1B), −5.2 (d, ^1J(B,H) = 108, 2B), −6.1 (d, ^1J(B,H) = 111, 4B), −7.6 (d, ^1J(B,H) = 167, 4B), −8.2 (d, ^1J(B,H) = 157, 4B), −10.4 (d, 1B), −15.0 (d, ^1J(B,H) = 147, 2B), −18.1 (d, ^1J(B,H) = 157, 2B), −19.6 (d, ^1J(B,H) = 165, 1B), −26.2 (d, ^1J(B,H) = 135, 1B). ^{1}H {^{11}B} NMR: δ 4.28 (br s, 4H, C_c−H), 3.62 (t, ^3J(H,H) = 6, 2H, OCH_2CH_2), 3.53 (t, ^3J(H,H) = 6, 2H, OCH_2CH_2), 3.47 (t, ^3J(H,H) = 6, 2H, OCH_2CH_2), 3.45 (s, 12H, $N(CH_3)_4$), 2.61 (t, ^3J(H,H) = 6, 2H, CH_2), 2.94 (br s, 1H, BH), 2.90 (br s, 2H, BH), 2.81 (br s, 2H, BH), 2.78 (br s, 2H, BH), 2.70 (br s, 1H, BH), 2.40 (br s, 2H, BH), 2.28 (br s, 6H, BH), 2.18 (s, 3H, CH_3), 2.08 (br s, 2H, BH), 1.97 (br s, 2H, BH), 1.79 (br s, 2H, BH), 1.68 (br s, 2H, BH), 1.57 (br s, 2H, BH), 1.48 (br s, 1H, BH). ^{13}C{^{1}H} NMR: δ 72.3 (s, C_c), 71.8 (s, OCH_2), 68.8 (s, OCH_2), 68.2 (s, OCH_2), 55.2 (s, $N(CH_3)_4$), 54.6 (s, C_c−H), 46.4 (s, C_c−H), 35.2 (s, CH_2), 22.8 (s, CH_3). MALDI-TOF-MS: *m*/*z* 567.41 (M, 100%).

Synthesis of [$N(CH_3)_4$][1″-{3,3′-Co(8-$(CH_2CH_2O)_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)}-2″-C_6H_5-*closo*-1″,2″-$C_2B_{10}H_{10}$], [$N(CH_3)_4$][9]. The compound was prepared following the same procedure as for [$N(CH_3)_4$][**8**] but using 1-C_6H_5-1,2-*closo*-$C_2B_{10}H_{11}$. Yield: 290 mg (85%); Anal. Calcd for $C_{20}H_{56}B_{28}CoNO_2$: C, 34.11; H, 8.01; N, 1.99. Found: C, 34.45; H, 8.25; N, 2.01. IR: ν(cm^{-1}) 3053, 3041 (C_c−H), 2953, 2914, 2894, 2862 ($C-H)_{alkyl}$, 2604, 2565 (B−H), 1481, 1446, 1415 $\delta(CH_2)$, 1359, 1284, 1249 δ(CH), 1174, 1121, 1097 (C−O−C), 945 (C−N). ^{11}B NMR: δ 24.9 (s, 1B, B(8)), 5.9 (d, *J* = 137, 1B), 2.6 (d, ^1J(B,H) = 144, 1B), −0.4 (d, ^1J(B,H) = 125, 1B), −1.7 (d, ^1J(B,H) = 137, 3B), −5.2 (d, 2B), −6.1 (d, ^1J(B,H) = 140, 4B), −8.3 (d, ^1J(B,H) = 146, 8B), −10.5 (d, 1B), −15.1 (d, ^1J(B,H) = 152, 2B), −18.2 (d, ^1J(B,H) = 156, 2B), −19.7 (d, ^1J(B,H) = 146, 1B), −26.3 (d, ^1J(B,H) = 159, 1B). ^{1}H{^{11}B} NMR: δ 7.78−7.50 (m, 5H, C_6H_5), 4.26 (br s, 2H, C_c−H), 4.22 (br s, 2H, C_c−H), 3.46 (t, ^3J(H,H) = 5, 2H, OCH_2CH_2), 3.45 (s, 12H, $N(CH_3)_4$), 3.44 (t, ^3J(H,H) = 5, 2H, OCH_2CH_2), 3.33 (t, ^3J(H,H) = 5, 2H, OCH_2CH_2), 2.94 (br s, 1H, BH), 2.87 (br s, 2H, BH), 2.79 (br s, 1H, BH), 2.74 (br s, 2H, BH), 2.69 (br s, 2H, BH), 2.55 (br s, 1H, BH), 2.50 (br s, 1H, BH), 2.39 (br s, 3H, BH), 2.35 (br s, 3H, BH), 2.22 (br s, 2H, BH), 2.12 (t, ^3J(H,H) = 6, 2H, CH_2), 1.95 (br s, 2H, BH), 1.78 (br s, 2H, BH), 1.62 (br s, 2H, BH), 1.56 (br s, 2H, BH), 1.48 (br s, 1H, BH). ^{13}C{^{1}H} NMR: δ 131.3 (s, C_6H_5), 131.0 (s, C_6H_5), 129.2 (s, C_6H_5), 127.4 (s, C_6H_5), 84.0 (s, C_c), 80.6 (s, C_c), 71.6 (s, OCH_2), 68.5 (s, OCH_2), 68.2 (s, OCH_2), 55.1 (s, $N(CH_3)_4$), 54.6 (s, C_c−H), 46.3 (s, C_c−H), 34.6 (s, CH_2). MALDI-TOF-MS: *m*/*z* 644.48 (M + CH_2, 15%), 630.49 (M, 100%), 384.19 (M − $C_{10}B_{10}H_{29}$, 10%)

Dianions. Synthesis of [NMe_4]Li[1″,2″-{3,3′-Co(8-$(CH_2CH_2O)_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)}-1″,2″-*closo*-$C_2B_{10}H_{10}$], [NMe_4]Li[5]. A solution of 1,2-*closo*-$C_2B_{10}H_{12}$ (35 mg, 0.24 mmol) in DME (10 mL) was treated with 1.6 M *n*-butyllithium in hexane (0.31 mL, 0.49 mmol) at 0 °C for 30 min and left under stirring at room temperature for an additional 30 min. A solution of [**1**] (200 mg, 0.49 mmol) in DME (30 mL) was added to the dilithium salt $Li_2[C_2B_{10}H_{11}]$ and refluxed for 30 min. The solvent was vacuum evaporated and the orange solid dissolved in water. Treatment of the solution containing [**5**]$^{2-}$ with an aqueous solution of $[N(CH_3)_4]Cl$ gave the [NMe_4]Li[**5**] salt. Yield: 221 mg (87%). R_f (CH_2Cl_2/CH_3CN 3:1) 0.10. HPLC k' = 3.31. Anal. Calcd for $C_{22}H_{80}B_{46}Co_2LiNO_4$: C, 25.29; H, 7.72; N, 1.34. Found: C, 25.16; H, 7.58; N, 1.38. IR: ν(cm^{-1}) 3051, 3037 (C_c−H), 2920, 2901, 2866 ($C-H)_{alkyl}$, 2597, 2576, 2561, 2528 (B−H), 1481, 1446, 1418 $\delta(CH_2)$, 1359, 1284, 1249 δ(CH), 1174, 1120, 1107, 1099 (C−O−C), 947 (C−N). ^{11}B NMR: δ 23.8 (s, 2B, B8), 3.8 (d, ^1J(B,H) = 137, 2B), 0.5 (d, ^1J(B,H) = 140, 2B), −2.4 (d, ^1J(B,H) = 161, 2B), −4.2 (d, ^1J(B,H) = 130, 4B), −4.9 (d, ^1J(B,H) = 120, 2B), −7.4 (d, ^1J(B,H) = 130, 6B), −8.3 (d, ^1J(B,H) = 130, 8B), −10.5 (d,

(29) Shriver, D. F.; Drezdon, M. A. *Manipulation of Air Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

^1J(B,H) = 149, 2 B), −17.2 (d, ^1J(B,H) = 155, 4B), −20.4 (d, ^1J(B,H) = 156, 4B), −22.0 (d, ^1J(B,H) = 175, 2B), −28.4 (d, ^1J(B,H) = 175, 2B). ^{1}H {^{11}B} NMR: δ 4.29 (br s, 8H, C_c−H), 3.65−3.47 (m, 12H, OCH_2CH_2), 3.45 (s, 12H, $N(CH_3)_4$), 2.66−2.58 (m, 4H, CH_2), 2.94−1.48 (m, 44H, B−H). ^{13}C{^{1}H} NMR: δ 78.8 (s, C_c), 71.7 (s, O−CH_2), 68.9 (s, O−CH_2), 68.2 (s, O−CH_2), 55.2 (s, $N(CH_3)_4$), 54.7 (s, C_c), 54.1 (s, C_c), 46.4 (s, C_c), 34.9 (s, CH_2). MALDI-TOF-MS: *m*/*z* 970.8 (M + Li, 71%), 553.55 ($CoC_{10}B_{28}H_{40}O_2$, 100%), 323.24 (3,3′-Co($C_2B_9H_{11}$)$_2$, 26%).

Synthesis of Na_2[1″,2″-{3,3′-Co(8-(CH_2CH_2O)$_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)}$_2$-1″,2″-*closo*-$C_2B_{10}H_{10}$], Na_2[5]. A solution of 1,2-*closo*-$C_2B_{10}H_{12}$ (200 mg, 1.39 mmol) in THF (5 mL) was treated with 2.5 M *n*-butyllithium in THF (1.2 mL, 3.0 mmol) at ca. −33 °C for 1 h and left under stirring for 2−3 h at ambient temperature. The solution of the corresponding dilithium salts $Li_2[C_2B_{10}H_{11}]$ was then treated with a solution of [**1**] (1200 mg, 2.92 mmol) in THF (30 mL) and stirred for an additional 4 h. The mixture was then decomposed by adding CH_3OH (1 mL) and 3 M HCl (0.25 mL) and the organic volatiles were removed by vacuum evaporation. The acidic aqueous solution was extracted with diethyl ether (3 × 10 mL), 3 M HCl (10 mL) and 10% Na_2CO_3 (3 × 10 mL). The organic layer was dried over $MgSO_4$, filtered, evaporated in vacuum and dried at room temperature. The residue (crude Na^+_2 salts) was dissolved in a minimum amount of CH_2Cl_2 and purified by LC chromatography on silica gel to collect the main orange bands of the dianions. IR and ^{11}B and ^{1}H{^{11}B} NMR spectra are the same as above. ^{13}C{^{1}H} NMR: δ 79.7 (s, C_c), 72.6 (s, O−CH_2), 69.8 (s, O−CH_2), 69.1 (s, O−CH_2), 55.5 (s, C_c), 47.3 (s, C_c), 35.7 (s, CH_2). MS (ESI): *m*/*z* 482.25 (M/2; 100%), 986.83 (M + Na; 10%).

Synthesis of Cs_2[1″,7″-{3,3′-Co-(8-(CH_2CH_2O)$_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)}$_2$-1″,7″-*closo*-$C_2B_{10}H_{10}$], Cs_2[6]. The same procedure as for $[N(CH_3)_4]$Li[**5**] was followed but using 1,7-*closo*-$C_2B_{10}H_{12}$. The treatment of the solution containing $[\mathbf{6}]^{2-}$ with an aqueous solution of CsCl gives the corresponding dicesium salt, which can be recrystallized from hot aqueous ethanol and additional crystallization of the solid from CH_2Cl_2-hexane. Yield: 585 mg (40%): R_f (CH_2Cl_2/CH_3CN, 3:1) 0.07. HPLC k' = 3.31. Anal. Calcd for $C_{18}H_{68}B_{46}Co_2Cs_2O_4$: C, 17.58; H, 5.57. Found: C, 17.40; H, 5.62. IR: ν(cm^{-1}) 3041 (C_c−H), 2926, 2871, 2867 (C−H)$_{alkyl}$, 2565, 2538 (B−H), 1455 δ(CH_2), 1365, 1247, 1249 δ(CH), 1150, 1134, 1097 (C−O−C). ^{11}B NMR (in CD_2Cl_2): δ 24.5 (s, 2B, B8), 5.2 (d, ^1J(B,H) = 141, 2B), 0.1 (d, ^1J(B,H) = 144, 2B), −3.1 (d, ^1J(B,H) = 118, 2B), −6.6 (d, ^1J(B,H) = 140, 4B), −7.5 (d, z^1J(B,H) = 137, 10B), −10.0 (d, 4B), −11.9 (d, ^1J(B,H) = 156, 4B), −14.5 (d, ^1J(B,H) = 160, 2B), −16.2 (d, ^1J(B,H) = 190, 2B), −18.1 (d, ^1J(B,H) = 165, 4B), −20.3 (d, ^1J(B,H) = 165, 4B), −21.5 (d, ^1J(B,H) = 175, 2B), −29.5 (d, ^1J(B,H) = 175, 2B). ^{1}H{^{11}B} NMR (CD_2Cl_2): δ 3.83 (br s, 8H, C_c−H), 3.66−3.51 (m, 12H, OCH_2), 2.27−2.35 (m, 4H, CH_2), 3.85−1.58 (m, 44H, B−H). ^{13}C{^{1}H} NMR: δ 74.5 (s, C_c), 72.4 (s, O−CH_2), 70.0 (s, O−CH_2), 69.1 (s, O−CH_2), 55.6 (s, C_c), 47.2 (s, C_c), 37.3 (s, CH_2)). MS (ESI): *m*/*z* 987.92 (M + Na; 100%).

Synthesis of 1-$CH_3OCH_2CH_2$-2-CH_3-1,2-*closo*-$C_2B_{10}H_{10}$, 10. 1-CH_3-1,2-*closo*-$C_2B_{10}H_{11}$ (1 g, 6.32 mmol) was dissolved in 70 mL of diethyl ether under nitrogen. Then, it was cooled down to 0 °C for 30 min and *n*-butyllithium (5 mL, 6.32 mmol) was added dropwise. The reaction was left for 30 min at 0 °C and 30 min at room temperature. It was then cooled again at 0 °C and ethyl methyl ether chloride (0.7 mL, 3.88 mmol) was added slowly. After 30 min at a low temperature, the solution was stirred for 5 h at 25 °C. Finally, it was treated with water; the organic layer was washed several times. The organic phase was dried over $MgSO_4$, filtered and evaporated to dryness. The final residue was treated with hot hexane to obtain a transparent oil. Yield: 1.21 g (88.6%). Anal. Calcd for $C_6H_{20}B_{10}O$: C, 33.31; H, 9.32. Found: C, 33.35; H, 9.08. IR: ν(cm^{-1}) 2987, 2938, 2903, 2838, 2804 (C−H), 2587 (B−H), 1482, 1462, 1426, 1391 δ(C−H), 1201, 1124 (C−O). ^{11}B NMR: δ −4.3 (d, ^1J(B,H) = 178, 1B), −5.8 (d, ^1J(B,H) = 167, 1B), −9.2 (d, 2B), −9.9 (d, 2B), −10.5 (d, ^1J(B,H) = 155, 4B). ^{1}H NMR: δ 3.50 (t, ^3J(H,H) = 6, 2H, OCH_2), 3.31 (s, 3H, OCH_3), 2.46 (t, ^3J(H,H) = 6, 2H, CH_2−C_c), 2.03 (s, 3H, CH_3−C_c). ^{13}C{^{1}H} NMR: δ 75.9 (s, C_c), 74.8 (s, C_c), 70.5 (s, OCH_2), 58.6 (s, OCH_3), 35.1 (s, CH_2−C_c), 23.3 (s, CH_3−C_c).

Synthesis of Cs_2[7″-{3,3′-Co-(8-(OCH_2CH_2)$_2$-1,2-$C_2B_9H_{10}$)-(1′,2′-$C_2B_9H_{11}$)}-7″,8″-*nido*-$C_2B_9H_{11}$)], Cs_2[11]. Cs[**2**] (100 mg, 1.45 mmol) was dissolved in 96% ethanol (5 mL) and solid CsF (67 mg, 4.35 mmol) was added. The resulting solution was refluxed for 20 h. After cooling down, the solvents were vacuum evaporated and the dried solid residue, dissolved in a mixture of methylene chloride/acetonitrile (3:1), was injected at the top of a silica gel column (1 cm × 15 cm). The product was eluted using the same solvent mixture as the mobile phase, R_f (3:1 CH_2Cl_2/CH_3CN) = 0.15. Yield: 81 mg (68%). For characterization, this salt was dissolved in aqueous ethanol (60%) and precipitated by an excess of aqueous $[HN(CH_3)_3]$Cl; the precipitate was filtered and dried in a vacuum at 60 °C. Anal. Calcd for $C_{10}H_{40}B_{27}CoCs_2O_2$: C, 14.84; H, 4.98. Found: C, 14.51; H, 5.04; IR: ν(cm^{-1}) 3040 (C_c−H), 2924, 2871, 2867 (C−H)$_{alkyl}$, 2563, 2531 (B−H), 1455 δ(CH_2), 1385, 1362, 1247, (CH), 1152, 1132, 1097 (C−O−C). ^{11}B NMR (CD_3CN): δ 23.1 (s, 1B), 3.8 (d, ^1J(B,H) = 117), −0.1 (d, ^1J(B,H) = 140, 1B), −2.7 (d, ^1J(B,H) = 133, 1B), −4.8 (d, ^1J(B,H) = ca. 146, 1B), −8.2 (d, ^1J(B,H) = ca. 130, 6B), −8.6 (d, 2B), −11.33 (d, 2B), −14.5 (d, 1B), −17.6 (d, ^1J(B,H) = 155, 4B), −18.7 (d, ^1J(B,H) = 155, 1B), −20.6 (d, ^1J(B,H) = 156, 2B), −22.4 (d, ^1J(B,H) = ca. 149, 2B), −28.5 (d, ^1J(B,H) = 175, 1B), −33.8 (d, ^1J(B,H) = 107, 1B), −37.8 (d, ^1J(B,H) = 135, 1B). ^{1}H{^{11}B} NMR: 7.05 (br. s, 1H, NH), 4.23 (s, 2H, C_c−H), 4.18 (s, 2H, C_c−H), 3.5 (br t, 2H, CH_2O), 3.4 (m, 2H, CH_2O), 3.36 (t, 2H, ^3J(H,H) = 6.0, CH_2O), 2.78 (s, 9H, $HN(CH_3)_3$), 2.15 (s, 1H, CH), 1.75 (m, 2H, C−CH_2), 2.64 (br s, 4B), 2.63 (br s, 1B), 2.44 (br s, 1B), 2.89, 1.94, 1.88 (br s, 5B), 1.65 (br s, 2B), 1.63, 1.12 (br s, 2B), 1.60 (br s, 1B), 1.57, 1.13 (br s, 4B), 1.47 (br s, 2B), 1.41 (br s, 1B), 1.02 (br s, 1B), 0.36 (br s, 1B), −0.55 (br s, 1B), −2.78 (br s, 1B, BHB). ^{13}C{^{1}H} NMR (CD_3CN): 72.7 (s, CH_2O), 69.2 (s, CH_2O), 55.0 (s, C_c−H), 45.8 (s, $HN(CH_3)_3$), 39.7 (s, CH_2). MS (ESI): *m*/*z* 271.92 (M/2, 100%), 544.50 (M + 2H, 10%).

Synthesis of $[N(CH_3)_4]_2$[7″-{3,3′-Co-(8-(OCH_2CH_2)$_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)}-8″-Me-7″,8″-*nido*-$C_2B_9H_{10}$)], $[N(CH_3)_4]_2$[12]. Under a nitrogen atmosphere, KOH (461 mg, 8.22 mmol) was dissolved completely in ethanol (20 mL), followed by the addition of Li[**8**] (150 mg, 0.26 mmol). The reaction mixture was refluxed on an oil bath for 5 h at 100 °C. The solvent was then evaporated and to the product obtained was added a saturated solution of $[N(CH_3)_4]$Cl, leading to the formation of a yellow compound, $[N(CH_3)_4]_2$[**12**]. Yield: 100 mg (55%); Anal. Calcd for $C_{19}H_{66}B_{27}CoO_2N_2$: C, 32.36; H, 9.37; N, 3.97. Found: C, 32.29; H, 9.59; N, 3.95. IR (cm^{-1}): υ 3035 (C_c−H), 2923 (C_{alkyl}−H), 2866 (N−H), 2527 (B−H), 1481 (N−C). ^{11}B NMR: δ 22.3 (s, 1B), 3.1 (d, ^1J(B,H) = 132, 1B), 0.2 (d, ^1J(B,H) = 147, 1B), −2.7 (d, ^1J(B,H) = 149, 1B), −4.3 (d, ^1J(B,H) = 157, 2B), −7.9, −8.58, −10.9 (d, 12B), −13.6 (d, ^1J(B,H) = 155, 1B), −18.4 (d, ^1J(B,H) = 90, 2B), −20.8 (d, ^1J(B,H) = 154, 2B), −22.5 (d, ^1J(B,H) = 157, 2B), −28.7 (d, ^1J(B,H) = 152, 1B), −34.8 (d, ^1J(B,H) = 200, 1B), −37.2 (d, ^1J(B,H) = 143, 1B). ^{1}H{^{11}B} NMR: δ 4.31 (s, 4H, C_c−H), 3.54 (m, 2H, OCH_2CH_2), 3.51 (m, 2H, OCH_2CH_2), 3.43 (s, 12H, $N(CH_3)_4$), 2.08, 1.96, 1.74, 1.66, 1.54, 1.44, 1.33, 1.18 (br s, B−H), 2.83 (s, 3H, C_c-CH_3), −2.65 (s, 1H, BHB). ^{13}C{^{1}H} NMR (300 MHz, acetone-d_6, 293K): δ 71.9 (s, O−CH_2), 71.4 (s, O−CH_2), 68.3 (s, O−CH_2), 55.2 (s, N-$(CH_3)_4$), 54.7(s, C_c), 46.3 (s, C_c), 35.1 (s, CH_2), 21.5 (s, CH_3). MALDI-TOF-MS: *m*/*z* 556.57 (M, 43%), 408.38 (fragment I, 45%), 146.06 (fragment III, 100%).

Synthesis of $[N(CH_3)_4]_2$[7″-{3,3′-Co-(8-(OCH_2CH_2)$_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)}-8″-C_6H_5-7″,8″-*nido*-$C_2B_9H_{10}$)], $[N(CH_3)_4]_2$[13]. Under a nitrogen atmosphere, KOH (461 mg, 8.22 mmol) was dissolved completely in ethanol (20 mL), followed by the addition

of Li[**9**] (150 mg, 0.23 mmol). The reaction mixture was refluxed on an oil bath for 5 h at 100 °C. The solvent was then evaporated and to the product obtained was added a saturated solution of $[N(CH_3)_4]$-Cl, leading to the obtainment of an orange solid, $[N(CH_3)_4]_2$[**13**]. Yield: 126 mg (70%). Anal. Calcd for $C_{24}H_{68}B_{27}CoN_2O_2$: C, 37.55; H, 8.93, N 3.65. Found: C, 37.17; H, 9.02; N, 3.82. IR (cm^{-1}): υ 3039 (C_c−H), 2534 (B−H), 2924 (C_{alkyl}−H), 2739 (N−H), 1477 (N−C). ^{11}B NMR: δ 23.7 (s, 1B), 4.6 (d, ^1J(B,H) = 134, 1B), 1.4 (d, ^1J(B,H) = 142, 1B), −1.6 (d, ^1J(B,H) = 141, 1B), −3.0 (d, ^1J(B,H) = 145, 2B), −6.6, −7.4, −9.4 (d, 12B), −12.6 (d, ^1J(B,H) = 139, 1B), −16.4 (d, ^1J(B,H) = 161, 2B), −19.5 (d, ^1J(B,H) = 150, 2B), −21.1 (d, ^1J(B,H) = 205, 1B), −27.5 (d, ^1J(B,H) = 152, 1B), −31.7 (d, ^1J(B,H) = 103, 1B), −34.8 (d, ^1J(B,H) = 147, 1B). ^{1}H NMR: δ 7.75−7.05 (m, 5H, C_6H_5), 4.21 (br s, 2H, C_c−H), 4.16 (br s, 2H, C_c−H), 3.44 (s, 12 H, $N(CH_3)_4$), 3.36 (m, 4H, OCH_2CH_2), 2.91−1.74 (br s, B−H), 2.12 (t, 2H, CH_2), −2.2 (s, 1H, BHB). ^{13}C{^{1}H} NMR (300 MHz, acetone-d_6, 293K): δ 131.8−124.2 ($C_{C_6H_5}$), 71.38 (s, O−CH_2), 71.0 (s, O−CH_2), 68.3 (s, O−CH_2), 55.2 (s, $N(CH_3)_4$), 54.4(s, C_c), 46.4 (s, C_c), 35.2 (s, CH_2).

Trianions. Synthesis of K_2Li[7″,8″-{3,3′-Co-(8-(OCH_2CH_2)$_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)}$_2$-7″,8″-*nido*-$C_2B_9H_{10}$], K_2Li-[14]. KOH method: In a typical experiment, to a 25 mL round-bottomed flask containing 12 mL of deoxygenated ethanol KOH (620 mg, 11.05 mmol) was added, which was stirred until complete dissolution. Li_2[**5**] (300 mg, 0.307 mmol) was added and the reaction mixture was refluxed for 21 h at ∼100 °C. The reaction mixture was then neutralized with gaseous CO_2; the resulting white precipitate was filtered and the liquid obtained evaporated, yielding an orange compound, K_2Li[**14**]. Yield: 272 mg (86%). Anal. Calcd for $C_{18}H_{68}B_{45}Co_2O_4K_2Li$: C, 20.82; H, 6.60. Found: C, 21.03; H, 6.65. IR (cm^{-1}): υ 3036 (C_c−H), 2922 (C_{alkyl}−H), 2865 (N−H), 2526 (B−H), 1481 (N−C). ^{11}B NMR: δ 23.8 (s, 2B), 4.6 (d, ^1J(B,H) = 128.7, 2B), 1.4 (d, ^1J(B,H) = 143, 2B), −1.5 (d, ^1J(B,H) = 155, 2B), −3.3 (d, ^1J(B,H) = 161, 4B), −6.5, −7.2 (d, 14B), −10.1 (d, ^1J(B,H) = 128, 2B), −13.3 (d, ^1J(B,H) = 119, 1B), −16.3 (d, ^1J(B,H) = 146, 4B), −17.8 (d, ^1J(B,H) = 161.5, 2B), −19.6 (d, ^1J(B,H) = 157, 4B), −21.0 (d, ^1J(B,H) = 126, 2B), −27.5 (d, ^1J(B,H) = 125, 2B), −32.6 (d, ^1J(B,H) = 86, 1B), −36.5 (d, ^1J(B,H) = 160, 1B). ^{1}H{^{11}B} NMR: δ 4.26 (br s, 8H, C_c−H), 3.61−3.48 (m, 8H, CH_2CH_2), 2.92−1.56 (br s, B−H), −2.68 (s, 1H, BHB). ^{13}C{^{1}H} NMR: δ 71.8 (s, O−CH_2), 71.3 (s, O−CH_2), 68.1 (s, O−CH_2), 54.1 (s, C_c), 46.3 (s, C_c), 33.9 (s, CH_2).

Synthesis of Cs_3[7″,8″-{3,3′-Co-(8-(OCH_2CH_2)$_2$-1,2-$C_2B_9H_{10}$)-(1′,2′-$C_2B_9H_{11}$)}$_2$-7″,8″-*nido*-$C_2B_9H_{10}$], Cs_3[14]. CsF method: Cs_2-[**5**] (400 mg, 0.32 mmol) was dissolved in deoxygenated ethanol (15 mL) and CsF (500 mg, 3.27 mmol) was added. The reaction mixture was refluxed for 24 h. Then, the ethanol was evaporated and water (20 mL) was added. The orange aqueous solution was extracted with diethyl ether (2 × 10 mL) and then with ethylacetate (2 × 20 mL) to remove unreacted anion $[\mathbf{5}]^{2-}$ and other impurities. The aqueous solution was evaporated to dryness and dried in vacuum and the resulting solids were extracted with acetone (2× 5 mL). The solution was concentrated to ca. 1 mL, yielding an orange compound. The product Cs_3[**14**] was recrystallized from hot water. Yield: 343 mg (78%). HPLC k' = 3.03 (Separon SGX C8, 250 × 4 mm i.d., 4.5 mM hexylamine acetate in 58% aqueous CH_3CN, pH 5.6), HPLC purity, 98.5%; R_f (CH_2Cl_2/CH_3CN, 3:1) = 0.02. Anal. Calcd for $C_{18}H_{68}B_{45}Co_2Cs_3O_4$: C, 15.99; H, 5.07. Found: C, 15.83; H, 5.12. IR: ν(cm^{-1}) 3042 (C_c−H), 2925, 2871, 2867 (C−H)$_{alkyl}$, 2560, 2531 (B−H), 1608, 1455 δ(CH_2), 1383, 1360, 1249 δ(CH), 1163, 1134, 1107, 1099 (C−O−C). ^{11}B NMR: δ 23.6 (s, 2B, B8), 5.2 (d, ^1J(B,H) = 117, 2B), 0.5 (d, ^1J(B,H) = 140, 2B), −2.4 (d, ^1J(B,H) = 133, 2B), −4.6 (d, ^1J(B,H) = ca. 146, 2B), −7.1 (d, ^1J(B,H) = ca. 130, 8B), −8.6 (d, 2B), −10.1 (d, 2B), −12.1 (d, 1B), −17.1 (d, ^1J(B,H) = 155, 4B), −17.8 (d, ^1J(B,H) = 155, 2B), −19.1 (d, ^1J(B,H) = 155, 2B), −20.3 (d, ^1J(B,H) = 156, 4B), −22.0 (d, ^1J(B,H) = ca. 149, 2B), −28.3 (d, ^1J(B,H) = 175, 2B), −34.0 (d, ^1J(B,H) = 107, 1B), −37.0 (d, ^1J(B,H) = 135, 1B). ^{1}H{^{11}B} NMR: 4.18 (s, 4H, CH), 4.14 (s, 4H, CH), 3.65 (t, 4H, J(H,H) = 4.8, CH_2O), 3.65 (m, 8H, CH_2O), 2.93 (br s, 1BH), 2.900 (s, 2H, H_2O), 2.83 (br s, 1BH), 2.72 (br s, 1BH), −2.71 (br s, 2BH), 2.68 (br s, 1BH), 2.03, 1.97 (br s, 2BH), 1.915 (m, 4H, C−CH_2), 1.82 (br s, 6BH), 1.69 (br s, 4BH), 1.63 (br s, 2BH), 1.45 (br s, 3BH), 1.29 (br s, 1BH), 0.52 (br s, 1BH), 0.05 (br s, 1BH), −1.53 (br s, 1BH), −2.70 (br s, 1BH, BHB). ^{13}C{^{1}H} NMR: 72.8 (s, CH_2O), 72.6 (s, CH_2O), 69.3 (s, CH_2O), 58.5 (s, C_c−H), 53.9 (s, C_c−H), 47.4 (s, C_c−H), 34.9 (s, CH_2). MS (ESI): m/z 318.40 (M/3 + H, 100%), 319.68 (M/3 + 2H, 4%).

Synthesis of Cs_2[7″-{3,3′-Co-(8-(OCH_2CH_2)$_2$-1,2-$C_2B_9H_{10}$)-(1′,2′-$C_2B_9H_{11}$)}-7″,9″-*nido*-$C_2B_9H_{11}$)], Cs_2[15]. Cs[**3**] (100 mg, 1.45 mmol) was dissolved in 1,2-ethanediol (5 mL) and solid CsF (67 mg, 4.35 mmol) was added. The resulting solution was refluxed for 16 h. After cooling down, water (2 mL) was added. The solvents were evaporated in a vacuum and the solid residue dried under reduced pressure. Afterward, it was dissolved in a mixture of 9:1 methylene chloride/ acetonitrile, injected at the top of a silica gel column (1 × 15 cm) and the product eluted using the same solvent mixture as the mobile phase. Yield: 29 mg (24%). Anal. Calcd for $C_{10}H_{40}B_{27}CoCs_2O_2$: C, 14.84; H, 4.98. Found: C, 15.01; H, 5.03. IR: ν(cm^{-1}) 3043, 2958 (C_c−H), 2925, 2874, 2854 (C−H)$_{alkyl}$, 2565, 2537, (B−H), 1616, 1458, δ(CH_2), 1383, 1360, 1262 δ(CH), 1154, 1133, 1098 (C−O−C). ^{11}B NMR: δ 23.9 (s, 1B, B8), 3.7 (d, ^1J(B,H) = 134, 1B), 0.5 (d, ^1J(B,H) = 140, 1B), −1.2 (d, ^1J(B,H) = 153, 1B), −2.4 (d, ^1J(B,H) = 149, 1B), −4.2 (d, ^1J(B,H) = ca. 177, 2B), −4.9 (d, ^1J(B,H) = 128, 1B), ca. 6.2 (d, 1B), −7.4 (d, ^1J(B,H) = ca. 123, 2B), −8.1 (d, ^1J(B,H) = 129, 4B), −17.2 (d, ^1J(B,H) = 143, 2B), −20.5 (d, ^1J(B,H) = 156, 2B), −21.6, (d, ^1J(B,H) = ca. 150, 2B), −22.6 (d, ^1J(B,H) = ca. 150, 2B), ca. −22.9 (d, 1B) −28.4 (d, ^1J(B,H) = 172, 1B), −34.5 (d, ^1J(B,H) = 134, 1B), −35.4 (d, ^1J(B,H) = 135 1B). ^{1}H{^{11}B} NMR: 4.29 (s, 4H, C_c−H), 3.61 (m, 4H, CH_2O), 3.48 (t, 2H, J(H,H) = 4.8, CH_2O), 2.94 (br s, 1H), 2.88 (s, H_2O), 2.76 (br s, 1H), 2.75 (br s, 1H), 2.69 (br s, 1H), 2.40 (br s, 1H), 2.39 (br s, 1H), 2.095 (s, 1H, CH), 1.78 (br s, 2H), 1.65 (br s, 2H), 1.29 (m, 2H, C−CH_2), 3.08, 2.92, 1.97 (br s, 5H), 1.67, (br s, 2H), 1.63, 1.19 (br s, 3H), 1.55 (br s, 2H), 1.46 (br s, 1H), 0.72 (br s, 1H), 0.24 (br s, 1H), −2.18 (br s, 1H, BHB). ^{13}C{^{1}H} NMR ($[HN(CH_3)_3]^+$): 56.2 (s, CH_2O), 51.3 (s, CH), 47.28 (s, CH), 39.5 (s, CH_2C), 21.2 (s, CH). MS (ESI): m/z 271.92 (M/2, 100%), 566.58 (M + Na, 28%).

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