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Articles

Methylation and Demethylation in Cobaltabis(dicarbollide) Derivatives

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B(8)−R and B(8′)−R (R = alkyl) disubstituted derivatives of the cobaltabis(dicarbollide) anion $[3,3'\text{-}Co(C_2B_9H_{11})_2]^-$ are reported. The synthesis was achieved by application of a modified Kumada reaction to produce B−C bonds. Molecules containing B(8)−C and B−O bonds are also generated, and interestingly, a high-yield intramolecular oxodemethylation is observed for the first time in boron cluster chemistry. It is also shown that the ^{11}B NMR spectrum of $Cs[3,3'\text{-}Co(C_2B_9H_{11})_2]$ derivatives is the result of the addition of the individual halves.

Introduction

Since its discovery,[1] the chemistry of the cobaltabis(dicarbollide) anion, $[3,3'\text{-}Co(C_2B_9H_{11})_2]^-$ ($[\mathbf{1}]^-$), has been prevalent within the boron cluster literature, and it continues to be a subject of intense study.[2] Halogen-substituted derivatives such as $[8,8',9,9',12,12'\text{-}I_6\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_8)_2]^-$ and $[8,8'\text{-}X_2\text{-}3,3'\text{-}Co(C_2B_9H_{10})_2]$ (X = Cl, Br, I) have been synthesized, but with some exceptions, they have not been considered suitable starting materials[3] to produce derivatives of $[\mathbf{1}]^-$. Recently Hawthorne et al.[4] have reported the synthesis of $[8,8',9,9',12,12'\text{-}(CH_3)_6\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_8)_2]^-$, starting from $[8,8',9,9',12,12'\text{-}I_6\text{-}3,3'\text{-}Co(C_2B_9H_8)_2]^-$, which opens a route to hexasubstituted derivatives of $[\mathbf{1}]^-$. Also, B(8)−O derivatives of $[3,3'\text{-}Co(C_2B_9H_{11})_2]^-$ are available through $[8\text{-}C_4H_8O_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$, which was reported in 1996.[5] This dioxanate compound is susceptible to nucleophilic attack on the positively charged oxygen atom, e.g. by pyrrolyl,[6] imide, cyanide, and amines,[7] phenolate and dialkyl or diaryl phosphite,[8] and *N*-alkylcarbamoyldiphenylphosphine oxides,[9] resulting in one anionic species as a consequence of the opening of the dioxane ring. However, B(8)−R (R = alkyl) mono- or disubstituted derivatives of $[\mathbf{1}]^-$ have not yet been reported. In this work we report on the application of a modified Kumada reaction[10] to produce B−C bonds for the disubstituted cobaltabis(dicarbollide) derivatives. Molecules containing B−C and B−O bonds are also generated, and interestingly, a high-yield oxodemethylation is observed for the first time in cluster boron chemistry.

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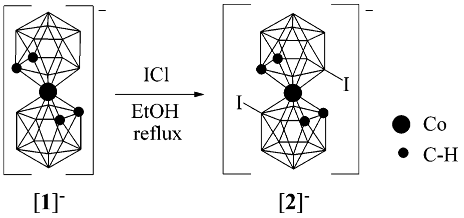
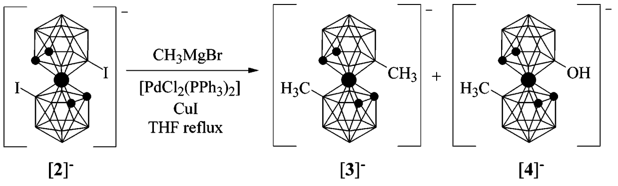
Scheme 1. Preparation of Cesium 8,8′-Diiodocobaltabis(dicarbollide) (Cs[2]).



Scheme 2. 8,8′-Dimethyl Substitution of [1]− by a B−C Cross-Coupling Reaction



Results and Discussion

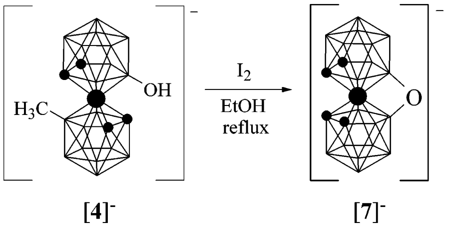
Cesium 8,8′-diiodocobaltabis(dicarbollide), Cs[**2**], was prepared by a modification of the original synthesis by Mátel et al.[3a] employing ICl instead of I_2. The procedure is much more simple and permits the isolation of Cs[**2**] with an easy purification step (Scheme 1). This method provides a rapid and reliable synthesis of multigram quantities of $[\mathbf{2}]^-$ in an overall yield of 98%.

The reaction involves refluxing a mixture of Cs[**1**] and ICl in ethanol (10 h) to obtain a solution containing Cs[**2**] and an excess of ICl. After the latter is destroyed with Na_2SO_3, pure Cs[**2**] is obtained by concentrating the solution, from which a crystalline orange solid separates.

Dimethyl substitution of $[\mathbf{1}]^-$ at the 8,8′-positions was achieved by a B−C cross-coupling reaction employing a modified Kumada reaction (Scheme 2). Addition of 5 equiv of methylmagnesium bromide to a cooled (0 °C) solution of Cs[**2**] in THF, followed by a catalytic amount of $[PdCl_2(PPh_3)_2]$ and CuI and reflux for 5 h, gave a mixture of compounds according to ^{11}B NMR. After evaporation of the THF, the residue was extracted with acidic water and diethyl ether. After chromatography on silica with AcOEt, four different bands were separated. Two of these accounted for more than 90% of the collected masses and have been the ones studied. These bands correspond to $Cs[8,8'\text{-}(CH_3)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$ (Cs[**3**]) and to $Cs[8\text{-}CH_3\text{-}8'\text{-}OH\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$ (Cs[**4**]). For the specific conditions utilized in this preparation, the ratio of Cs[**3**] to Cs[**4**] is 2/1. This coupling reaction was repeated for 2, 15, and 30 h of reflux time. Although minor variations in the ratio of Cs[**3**] to Cs[**4**] were observed, these were attributed to differences in the workup method and not to the transformation of $[\mathbf{3}]^-$ into $[\mathbf{4}]^-$. The chemical stability of Cs[**3**] toward Grignard derivatives was further proven by adding methylmagnesium bromide to a cooled (0 °C) solution of Cs[**3**] in THF (ratio 5/1), followed by a catalytic amount of $[PdCl_2(PPh_3)_2]$ and CuI and reflux for 5 h. The ^{11}B NMR spectrum of the crude reaction mixture indicated that $[\mathbf{3}]^-$ remained unaltered.

Similarly, the chemical stability of $[\mathbf{3}]^-$ toward iodine was proven by adding the latter to a solution of Cs[**3**] in EtOH (ratio 2/1) and refluxing for 2 h. Again the ^{11}B NMR spectrum of the crude reaction mixture confirmed that $[\mathbf{3}]^-$ remained unaltered.

Scheme 3. Schematic Representation of the Oxodemethylation Process



The same coupling procedure has been utilized to produce $Cs[8,8'\text{-}(CH_3CH_2)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$ (Cs[**5**]) and $Cs[8\text{-}OH\text{-}8'\text{-}CH_2CH_3\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$ (Cs[**6**]) with ethylmagnesium bromide instead of methylmagnesium bromide. The dependence of the Cs[**5**]/Cs[**6**] ratio is comparable to that of the $[\mathbf{3}]^-$ and $[\mathbf{4}]^-$ analogues.

Reaction of Cs[**4**] with I_2 in refluxing ethanol (2 h) leads through an unprecedented oxodemethylation process to a solution containing $[8,8'\text{-}\mu\text{-}O\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ ($[\mathbf{7}]^-$) (Scheme 3). Pure Cs[**7**] is obtained in 47% yield after concentrating the solution and eluting the residue with AcOEt in a SiO_2 column. The necessity of I_2 was proven by refluxing Cs[**4**] in EtOH for 2 h. Under these experimental conditions unaltered Cs[**4**] was obtained. The relevance of the alkyl group in the oxodealkylation reaction was studied by reacting Cs[**6**] with I_2 under the same experimental conditions as for Cs[**4**]. For R = Et no reaction was observed.

Full structural elucidation of $[\mathbf{3}]^-$ was obtained with an X-ray diffraction study of [PPN][**3**] (PPN = bis(triphenylphosphoranylidene)nitrogen(1+)). [PPN][**3**] was produced by dissolving the orange solid Cs[**3**] in the minimum amount of EtOH and adding a solution of [PPN]Cl in EtOH/water, resulting in the precipitation of [PPN][**3**]. This was filtered off, washed with water and petroleum ether, and dried under vacuum. Crystals suitable for single-crystal data collection were obtained by slow evaporation of an ethanol/acetone solution of the compound.

The asymmetric unit of [PPN][**3**] consists of half of the $[8,8'\text{-}(CH_3)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ or $[\mathbf{3}]^-$ complex unit, with the metal occupying an inversion center, and half of the $[PPN]^+$ ion, with the nitrogen atom at a 2-fold axis. Thus, the methyl groups of the centrosymmetric $[\mathbf{3}]^-$ moiety as well as the cage carbons lie on opposite sides of the complex moiety. Crystallographic parameters for [PPN][**3**] are presented in Table 1. A drawing of $[\mathbf{3}]^-$ with selected bond lengths and angles is shown in Figure 1.

The clusters for [PPN][**3**] have the expected near-icosahedral geometry with the lengths of the differing types of connectivities standing in the expected sequence $C{-}C < C{-}B < B{-}B$, the magnitude of these connectivities being comparable to those determined for $[\mathbf{1}]^-$.[6,8,9] A notable exception is the short B−C bond of the B(8)−CH_3 exo-cluster group, which is 1.488(6) Å. For example, in $[8,8',9,9',12,12'\text{-}(CH_3)_6\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_8)_2]^-$,[4] the shortest B−$CH_3$ bond length in a similar chemical environment is 1.679(12) Å.

Characterization of the remaining synthesized compounds has been done mostly with ^{11}B NMR and MALDI-TOF mass spectra. The ^{11}B NMR spectrum of

Table 1. Crystallographic Parameters for [PPN][3]

empirical formula	$C_{42}H_{56}B_{18}CoNP_2$
fw	890.33
cryst syst	monoclinic
cryst habit, color	block, red
space group	*C*2/*c*
a (Å)	30.9930(7)
b (Å)	8.9763(2)
c (Å)	18.5724(5)
β (deg)	115.9374(11)
V (Å^3)	4646.44(19)
Z	4
T (°C)	−100
λ (Å)	0.710 73
ρ (g cm^{-3})	1.273
μ (cm^{-1})	4.72
goodness of fit^a on F^2	1.039
R^b ($I > 2\sigma(I)$)	0.0478
$R_w{}^c$ ($I > 2\sigma(I)$)	0.1027

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

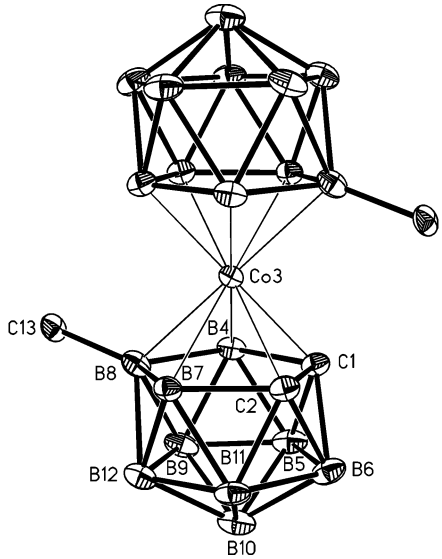


Figure 1. Drawing of $[3]^-$ with 20% thermal displacement ellipsoids. Selected bond lengths (Å) and angles (deg) for [PPN][**3**]: Co(3)−C(1), 2.017(3); Co(3)−C(2), 2.017(3); Co(3)−B(4), 2.087(3); Co(3)−B(7), 2.101(4); Co(3)−B(8), 2.159(4); C(1)−C(2), 1.645(4); B(8)−C(13), 1.488(6); P−N, 1.5787(12); C(13)−B(8)−Co(3), 117.5(3); C(13)−B(8)−B(4). 124.9(3); C(13)−B(8)−B(7), 124.3(3); P−N−P^d, 146.9(2). The superscript *d* indicates the equivalent position $-x$, y, $-z + {}^1/_2$.

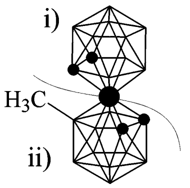


Figure 2. Individual halves (i and ii) of $[8\text{-}CH_3\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$, giving the $^{11}B\{^1H\}$ NMR spectrum.

derivatives of Cs[**1**] is the result of the addition of the individual halves, as shown in Figure 2. As an example, the $^{11}B\{^1H\}$ NMR spectrum of $Cs[8\text{-}CH_3\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ is the addition of the $^{11}B\{^1H\}$ NMR spectrum of Cs[**1**] plus that of Cs[**3**]. The spectrum of Cs[**1**] displays resonances at 6.5 (1), 1.4 (1), −6.0 (4), −17.2 (2), and −22.7 (1) ppm and the spectrum of Cs[**3**] at 14.9 (1), 1.0 (1), −4.0 (4), −17.4 (2), and −24.2 (1) ppm. The spectrum of $Cs[8\text{-}CH_3\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ should then be very close to 14.9 (1), 6.5 (1), 1.4 (1), 1.0 (1), −4.0 (4), −6.0 (4), −17.2 (2), −17.4 (2), −22.7 (1), and −24.2 (1) ppm. The experimental spectrum of $Cs[8\text{-}CH_3\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$[11] consists of bands at 16.6 (1), 7.6 (1), 0.6 (2), −3.5 (2), −4.7 (2), −5.2 (2), −6.2 (2), −17.3 (2), −17.8 (2), −22.4 (1), and −25.3 (1) ppm. We have tested this method with other available examples, and it works extremely well. It is therefore a remarkable tool to assist in the structural elucidation of derivatives of $[\mathbf{1}]^-$, mainly when other techniques such as COSY and GIAO are not applicable. The ^{11}B NMR spectrum of Cs[**4**] displays resonances at 23.7 (1), 13.1 (1), 0.3 (1), −2.5 (1), −4.2 (4), −5.7 (2), −6.9 (2), −17.6 (2), −19.8 (2), −24.1 (1), −28.4 (1) ppm. If resonances attributable to the expected participant component Cs[**3**] are removed, the spectrum is left with the resonances of the unknown fragment at 23.7 (1), −2.5 (1), −5.7 (2), −6.9 (2), −19.8 (2), and −28.4 (1) ppm. The 1:1:2:2:2:1 pattern is consistent with a C_s fragment symmetry, and the high chemical shift value at 23.7 ppm strongly supports assignment to B(8)−OH. The synthesis of $Cs[8,8'\text{-}(OH)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$ had been carried out by the reductive acetoxylation of Cs[**1**].[12] The reported NMR spectrum displays resonances at 25.8 (1), −4.6 (1), −5.6 (2), −8.6 (2), −19.8 (2), and −29.6 (1) ppm. The matching with the non-methyl moiety of Cs[**4**] is excellent, proving the $Cs[8\text{-}OH\text{-}8'\text{-}CH_3\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$ nature of Cs[**4**]. Its atomic composition was elucidated by comparison of the highest mass peak envelope found near *m*/*z* 354 in the MALDI-TOF mass spectrum, with the simulated peak for $B_{18}CoC_5OH_{24}$ corresponding to the formula of $[\mathbf{4}]^-$. A similar reasoning was applied for the structural elucidation of Cs[**5**] and Cs[**6**].

Compound $[\mathbf{7}]^-$ was characterized by MALDI-TOF mass spectrometry and by comparison of the ^{11}B NMR spectrum with reported data.[13] Compound Cs[**7**] had been earlier synthesized by reaction of Cs[**1**] with paraformaldehyde and H_2SO_4 in acetic anhydride (19.7% yield). The structure had been initially[13] reported to correspond to $[8,8'\text{-}\mu\text{-}(OCH_3)\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$, but a later X-ray diffraction[14] analysis confirmed it to be $Cs[8,8'\text{-}\mu\text{-}O\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$.

The synthesis of $[\mathbf{3}]^-$−$[\mathbf{6}]^-$ has shown that the modified Kumada reaction can be applied to produce B−C bonds for disubstituted cobaltabis(dicarbollide) metallacarboranes. For the reaction to proceed and avoid unreacted diiodo starting material, a high ratio (2.5/1) of the Grignard reagent to iodine in $[\mathbf{2}]^-$ has to be used. When the ratio is lowered to 1.25/1, a large proportion of unreacted starting material is recovered. This suggests that other reactions consuming CH_3MgBr or CH_3CH_2MgBr take place in addition to the formation of the $B-CH_3$ or $B-CH_2CH_3$ moieties. The syntheses of $[\mathbf{4}]^-$ and $[\mathbf{6}]^-$ are explained through unknown intermediates, shown as [**"4"**]$^-$ in Figure 3, which upon hydrolysis produce the hydroxy derivative. The [**"4"**]$^-$ intermediate

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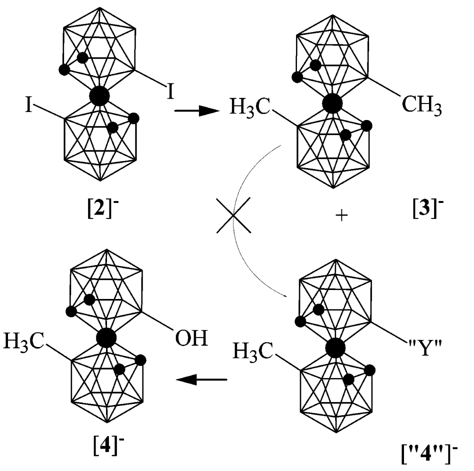

Figure 3. From diiodine to hydroxymethyl, showing the intermediate precursor of the latter. The crossed arrow indicates that [**"4"**]$^{-}$ does not have its origin in [**3**]$^{-}$.

is not derived from [**3**]$^{-}$, as was proven earlier when discussing the stability of [**3**]$^{-}$ toward Grignard reagents. It must be formed in parallel to [**3**]$^{-}$. It is remarkable that an unprecedented demethylation process was found for [**4**]$^{-}$ to yield [**7**]$^{-}$ and that a deethylation did not occur with [**6**]$^{-}$.

Experimental Section

General Considerations. Elemental analyses were performed using a Carlo Erba EA1108 microanalyzer. IR spectra were recorded from KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. ^{1}H and ^{1}H{^{11}B} NMR (300.13 MHz), ^{13}C{^{1}H} NMR (75.47 MHz), and ^{11}B NMR (96.29 MHz) spectra were recorded with a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. All NMR spectra were recorded from CD_3COCD_3 solutions at 25 °C. Chemical shift values for ^{11}B NMR spectra were referenced to external $BF_3 \cdot OEt_2$, and those for ^{1}H, ^{1}H{^{11}B}, and ^{13}C{^{1}H} NMR spectra were referenced to $Si(CH_3)_4$. Chemical shifts are reported in units of parts per million downfield from the reference, and all coupling constants are reported in hertz.

All reactions were performed under an atmosphere of dinitrogen by employing standard Schlenk techniques. Column chromatography was performed on Matrix silica 60 (0.040−0.063 mm). Methylmagnesium bromide and ethylmagnesium bromide were obtained from Aldrich as 3.0 M solutions in diethyl ether. THF was distilled from sodium benzophenone prior to use. EtOH was dried over molecular sieves and deoxygenated prior to use. The cesium salt of compound [**1**]$^{-}$ was supplied by Katchem Ltd. (Prague, Czech Republic) and used as received. All other reagents were obtained from commercial sources and used as purchased. Bis(triphenylphosphine)palladium dichloride[15] was synthesized according to the literature. The mass spectra were recorded in the negative ion mode using a Bruker Biflex matrix-assisted laser desorption/ionization instrument (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)).

Synthesis of Cs[8,8′-I_2-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (Cs[2]). Iodine monochloride (3.0 g, 18.48 mmol) was added to a solution of Cs[3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$] (3.92 g, 8.58 mmol) in 80 mL of EtOH. The reaction mixture was refluxed for 10 h. The excess iodine monochloride was descomposed by addition of 1.68 g (13.34 mmol) of Na_2SO_3 in 40 mL of water, and the whole solution was boiled for 5 min. The solvent was concentrated until the precipitation of an orange solid. This was filtered off and washed with water and petroleum ether. The solid was dried in vacuo. Yield: 5.99 g (98%). Anal. Calcd for $C_4H_{20}B_{18}CoCsI_2$: C: 6.78, H: 2.85. Found: C: 7.00, H: 2.83. IR (ν (cm^{-1})): 3039 (C_c−H), 2592, 2563, 2530 (B−H), 978, 772. ^{1}H NMR (δ): 4.40 (br s, 4H, C_c−*H*), 3.22−1.82 (br m, 16H, B−*H*). ^{1}H{^{11}B} NMR (δ): 4.40 (br s, 4H, C_c−*H*), 3.22 (br s, 4H, B−*H*), 3.06 (br s, 2H, B−*H*), 2.59 (br s, 4H, B−*H*), 2.12 (br s, 2H, B−*H*), 1.82 (br s, 4H, B−*H*).^{13}C{^{1}H} NMR (δ): 60.07 (s, *C_c*-H). ^{11}B NMR (δ): 3.6 (d, ^{1}J(B,H) = 144, 2B), −2.5 (d, ^{1}J(B,H) = 144, 8B), −4.4 (s, 2B, B(8,8′)), −16.2 (d, ^{1}J(B,H) = 159, 4B), −21.7 (d, ^{1}J(B,H) = 171, 2B). MALDI-TOF-MS (*m*/*z*): 575.4 (M), 449.5 (M − I), 322.5 (M − 2I).

Synthesis of Cs[8,8′-(CH_3)$_2$-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (Cs[3]) and Cs[8-OH-8′-CH_3-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (Cs[4]). A solution of Cs[8,8′-I_2-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (200 mg, 0.28 mmol) in THF (12 mL) was treated with methylmagnesium bromide (0.47 mL, 1.4 mmol; 3.0 M in diethyl ether) at 0 °C, forming a brown precipitate. The mixture was left at room temperature for 30 min, and then [$PdCl_2(PPh_3)_2$] (7.9 mg, 0.01 mmol) and CuI (2.2 mg, 0.01 mmol) were added in a single portion. The brown solution was refluxed for 5 h. The gray solid was discarded by filtration. After removal of the solvent, 20 mL of diethyl ether was added. This solution was extracted three times with 20 mL of dilute HCl (60 mL of water containing 0.15 mL of concentrated HCl). The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed, and the residue was flash-chromatographed over silica gel using ethyl acetate as eluent. Two main bands were separated: [**3**]$^{-}$ (R_f = 0.15) and [**4**]$^{-}$ (R_f = 0.26). The yield were 60% for Cs[**3**] (81.0 mg) and 33% for Cs[**4**] (45.3 mg).

Data for Cs[**3**] are as follows. Anal. Calcd for $C_6H_{26}B_{18}CoCs$: C: 14.87, H: 5.41. Found: C: 14.80, H: 5.38. IR (ν (cm^{-1})): 3048 (C_c−H), 2922, 2831 (C_{alkyl}−H), 2535 (B−H), 747 (B−C), 1373, 1307, 1101, 976. ^{1}H NMR (δ): 4.17 (br s, 4H, C_c−*H*), 2.56−1.60 (br m, 16H, B−*H*), 0.31 (br s, 6H, C*H*$_3$). ^{1}H{^{11}B} NMR (δ): 4.17 (br s, 4H, C_c−*H*), 2.56 (br s, 4H, B−*H*), 1.85 (br s, 4H, B−*H*), 1.60 (br s, 8H, B−*H*), 0.31 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (δ): 51.23 (s, *C_c*−H), 8.02 (br q, ^{1}J(C,B) = 58, B−*C*H$_3$). ^{11}B NMR (δ): 14.9 (s, 2B, B(8,8′)), 1.0 (d, ^{1}J(B,H) = 141, 2B, B(10,10′)), −4.0 (d, ^{1}J(B,H) = 141, 8B, B(4,4′,7,7′,9,9′,12,12′)), −17.4 (d, ^{1}J(B,H) = 153, 4B, B(5,5′,11,11′)), −24.2 (d, ^{1}J(B,H) = 167, 2B, B(6,6′)). MALDI-TOF-MS (*m*/*z*): 352.7 (M).

Data for Cs[**4**] are as follows.Anal. Calcd for $C_5H_{24}B_{18}CoCsO$: C: 12.34, H: 4.97. Found: C: 12.31, H: 4.95. IR (ν (cm^{-1})): 3047 (BO−H), 3039 (C_c−H), 2922, 2834 (C_{alkyl}−H), 2573, 2528 (B−H), 747, 725 (B-C), 1077, 973. ^{1}H NMR (δ): 4.27 (br s, 2H, C_c−*H*), 4.00 (br s, 2H, C_c−*H*), 2.83−1.41 (br m, 16H, B−*H*), 0.26 (br s, 3H, C*H*$_3$).^{1}H{^{11}B} NMR (δ): 4.27 (br s, 2H, C_c−*H*), 4.00 (br s, 2H, C_c−*H*), 2.83 (br s, 1H, B−*H*), 2.75 (br s, 2H, B−*H*), 2.59 (br s, 4H, B−*H*), 1.95 (br s, 2H, B−*H*), 1.79 (br s, 2H, B−*H*), 1.57, 1.53 (br s, 4H, B−*H*), 1.41 (br s, 1H, B−*H*), 0.26 (br s, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (δ): 53.01 (s, *C_c*−H), 48.27 (s, *C_c*−H), 8.49, 7.87, 6.82, 6.16 (br q, B−*C*H$_3$). ^{11}B NMR (δ): 23.7 (s, 1B, B(8)), 13.1 (s, 1B, B(8′)), 0.3 (d, ^{1}J(B,H) = 146, 1B, B(10′)), −2.5 (d, ^{1}J(B,H) = 157, 1B, B(10)), −4.2 (d, ^{1}J(B,H) = 144, 4B, B(4′,7′,9′,12′)), −5.7 (d, ^{1}J(B,H) = 135, 2B, B(9,12)), −6.9 (d, ^{1}J(B,H) = 121, 2B, B(4,7)), −17.6 (d, ^{1}J(B,H) = 163, 2B, B(5′,11′)), −19.8 (d, ^{1}J(B,H) = 167, 2B, B(5,11)), −24.1 (d, ^{1}J(B,H) = 167, 1B, B(6′)), −28.4 (d, ^{1}J(B,H) = 171, 1B, B(6)). MALDI-TOF-MS (*m*/*z*): 354.5 (M).

Synthesis of Cs[8,8′-(CH_3CH_2)$_2$-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (Cs[5]) and Cs[8-OH-8′-CH_2CH_3-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (Cs[6]). A solution of Cs[8,8′-I_2-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$)] (200 mg, 0.28 mmol) in THF (12 mL) was treated with ethylmagnesium bromide (0.47 mL, 1.4 mmol; 3.0 M in diethyl ether) at 0 °C, forming a brown precipitate. The mixture was left at room temperature for 30 min, and then [$PdCl_2(PPh_3)_2$] (7.9 mg, 0.01 mmol) and CuI (2.2 mg, 0.01 mmol) were added in a single portion. The brown solution was refluxed for 6 h. The gray solid was discarded by filtration. After removal of the solvent,

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[15] Blackburn, J. R.; Nordberg, R.; Stevie, F.; Albrigde, R. G.; Jones, M. M. *Inorg. Chem.* **1970**, *9*, 2374.

20 mL of diethyl ether was added. This solution was extracted three times with 20 mL of dilute HCl (60 mL of water containing 0.15 mL of concentrated HCl). The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed, and the residue was flash-chromatographed over silica gel using ethyl acetate as eluent. Two main bands were separated: $[\mathbf{5}]^-$ ($R_f = 0.11$) and $[\mathbf{6}]^-$($R_f = 0.22$). The yield were 62% for Cs[**5**](90 mg) and 32% for Cs[**6**] (45 mg).

Data for Cs[**5**] are as follows. Anal. Calcd for $C_8H_{30}B_{18}$-CoCs: C: 18.74, H: 5.90. Found: C: 18.52, H: 5.80. IR (ν (cm^{-1})): 3039 (C_c-H), 2961, 2922, 2854 ($C_{alkyl}-H$), 2562 (B−H), 747 (B−C), 1378, 1299, 1139, 980. ^{1}H NMR (δ): 4.23 (br s, 4H, C_c-H), 2.60−1.61 (br m, 16H, B−*H*), 1.31 (br m, 4H, C*H*$_2$), 0.85 (br m, 6H, C*H*$_3$). ^{1}H{^{11}B} NMR (δ): 4.23 (br s, 4H, C_c-H), 2.78 (br s, 2H, B−*H*), 2.62 (br s, 4H, B−*H*), 1.95 (br s, 2H, B−*H*), 1.80 (br s, 2H, B−*H*), 1.61 (br s, 4H, B−*H*), 1.51 (br s, 2H, B−*H*), 1.31 (br m, 4H, C*H*$_2$), 0.85 (br m, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (δ): 51.14 (s, C_c−H), 18.90 (s, CH_2CH_3). ^{11}B NMR (δ): 16.8 (s, 2B, B(8,8′)), 1.0 (d, ^1J(B,H) = 133, 2B), −4.4 (d, ^1J(B,H) = 111, 4B), −5.5 (d, ^1J(B,H) = 118, 4B), −17.2 (d, ^1J(B,H) = 148, 4B), −24.0 (d, ^1J(B,H) = 177, 2B). MALDI-TOF-MS (*m*/*z*): 380.7 (M).

Data for Cs[**6**] are as follows. Anal. Calcd for $C_6H_{26}B_{18}$-CoCsO: C: 14.39, H: 5.23. Found: C: 14.30, H: 5.19. IR (ν (cm^{-1})): 3039 (C_c-H), 2961, 2922, 2867 ($C_{alkyl}-H$), 2560 (B−H), 743, 724 (B−C), 1099, 979. ^{1}H NMR (δ): 4.35 (br s, 2H, C_c-H), 4.04 (br s, 2H, C_c-H), 2.78−1.51 (br m, 16H, B−*H*), 1.34 (br m, 2H, C*H*$_2$), 0.93 (br m, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR δ: 53.36 (s, C_c−H), 47.90 (s, C_c−H). ^{11}B NMR (δ): 23.4 (s, 1B), 14.3 (s, 1B), 0.3 (d, ^1J(B,H) = 141, 1B), −2.3 (d, ^1J(B,H) = 157, 1B), −4.1 (d, ^1J(B,H) = 179, 2B), −5.8 (d, ^1J(B,H) = 137, 4B), −6.7 (d, ^1J(B,H) = 100, 2B), −17.5 (d, ^1J(B,H) = 155, 2B), −20.0 (d, ^1J(B,H) = 157, 2B), −23.7 (d, ^1J(B,H) = 166, 1B), −28.3 (d, ^1J(B,H) = 166, 1B). MALDI-TOF-MS (*m*/*z*): 367.6 (M).

Synthesis of Cs[8,8′-μ-O-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (Cs[7]). To a solution of Cs[8-OH-8′-CH_3-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (76 mg, 0.16 mmol) in EtOH (5 mL) was added 80 mg (0.31 mmol) of iodine. The orange solution was refluxed for 2 h. The solvent was removed and the residue was purified over silica gel using ethyl acetate as eluent. A red band corresponding to Cs[**7**] was obtained ($R_f = 0.71$). Yield: 47%, 34.5 mg. Anal. Calcd for $C_4H_{20}B_{18}$CoCsO: C: 10.21, H: 4.28. Found: C: 10.01, H: 4.12. IR (ν (cm^{-1})): 3039 (C_c-H), 2573, 2540 (B−H), 1378, 1261, 1037. ^{1}H NMR δ: 3.76 (br s, 4H, C_c-H), 3.99−1.29 (br m, 16H, B−*H*). ^{1}H{^{11}B} NMR (δ): 3.99 (br s, 4H, B−*H*), 3.76 (br s, 4H, C_c-H), 2.13 (br s, 2H, B−*H*), 1.88 (br s, 4H, B−*H*), 1.58 (br s, 4H, B−*H*), 1.29 (br s, 2H, B−*H*). ^{13}C{^{1}H} NMR (δ): 45.24 (s, C_c−H). ^{11}B NMR (δ): 17.5 (s, 2B, B(8,8′)), −1.5 (d, ^1J(B,H) = 149, 2B, B(10,10′)), −8.0 (s, ^1J(B,H) = 143, 4B, B(4,4′,7,7′)), −9.4 (d, ^1J(B,H) = 137, 4B, B(9,9′,12,12′)), −14.2 (d, ^1J(B,H) = 160, 4B, B(5,5′,11,11′)), −25.9 (d, ^1J(B,H) = 163, 2B, B(6,6′)). MALDI-TOF-MS (*m*/*z*): 338.6 (M).

X-ray Diffraction Studies. Single-crystal data collection for [PPN][8,8′-$(CH_3)_2$-3,3′-Co(1,2-$C_2B_9H_{10})_2$] ([PPN][**3**]) was performed at −100 °C on an Enraf-Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα radiation. A total of 7161 reflections were collected, giving 4091 unique reflections ($R_{int} = 0.0521$). The structure was solved by direct methods and refined on F^2 by the SHELXL97 program.[16] Nonhydrogen atoms were refined with anisotropic thermal displacement parameters, but hydrogen atoms were treated as riding atoms using the SHELX97 default parameters.

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Supporting Information Available: Tables giving detailed crystallographic data, atomic positional and thermal displacement parameters, and bond lengths and angles for [PPN][8,8′-$(CH_3)_2$-3,3′-Co(1,2-$C_2B_9H_{10})_2$] ([PPN][**3**]); these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] Sheldrick, G. M. SHELX97; University of Göttingen, Göttingen, Germany, 1997.