Butyllithium Deprotonation *vs* Alkali Metal Reduction of Cobalt Dicarbollide: A New Synthetic Route to C-Substituted Derivatives

Rebecca Miller Chamberlin,*,† Brian L. Scott, Miryam M. Melo, and Kent D. Abney*

Chemical Science and Technology Division, Mail Stop J514, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Reduction of $Cs[Co(1,2-C_2B_9H_{11})_2]$ ($Cs[\mathbf{I}]$) with 1 equiv of Na(Hg) amalgam or Cs metal forms the cobalt(II) dianion, $[Co(1,2-C_2B_9H_{11})_2]^{2-}$ (**II**), which reverts to **I** upon exposure to 0.5 equiv of I_2. The molecular structure of $[Cs_2(DME)_4][Co(1,2-C_2B_9H_{11})_2]$ shows the carbon atoms of dianion **II** occupy *transoid* rotational geometry about the cobalt center, consistent with isoelectronic nickel(III) bis(dicarbollide). Reaction of THF solutions of **I** with 1.0 and 2.0 equiv of *n*-butyllithium forms purple $Cs[Co(LiC_2B_9H_{10})(C_2B_9H_{11})]$ ($Cs[\mathbf{I}\text{-}\mathbf{Li}]$) and blue $Cs\text{-}[Co(LiC_2B_9H_{10})_2]$ ($Cs[\mathbf{I}\text{-}\mathbf{Li}_2]$), respectively. Treating **I-Li** and **I-Li₂** with water causes reversion to **I**; reaction with D_2O forms a dicarbollide C−D bond (IR: $\nu(CD/CH) = 2275/3040$ cm^{-1}). Mono- and dilithio(cobalt dicarbollide) react with alkyl halides (R−X) to form the corresponding alkyl(cobalt dicarbollide) complexes, $[Co(RC_2B_9H_{10})(C_2B_9H_{11})]^-$ and $[Co(RC_2B_9H_{10})_2]^-$ (**I-R** and **I-R₂**; R = CH_3, C_6H_{13}). Alkylation of **I-Li₂** using methyl iodide gives a mixture of *meso* and *rac* isomers of $[Co(1\text{-}Me\text{-}1,2\text{-}C_2B_9H_{10})_2]^-$ (**I-1,1′-Me₂**). In contrast, treating **I-Li,Me** (generated via deprotonation of **I-Me**) with methyl iodide forms $[Co(1,2\text{-}Me_2\text{-}1,2\text{-}C_2B_9H_9)\text{-}(C_2B_9H_{11})]^-$ (**I-1,2-Me₂**; 30%), plus *meso-* and *rac-***I-1,1′-Me₂** (70% total). The stereochemistry of alkylation is kinetically determined by the sites of deprotonation. Reaction of **I-Li₂** with 2 equiv of $CH_3OCH_2CH_2OCH_2Cl$ (MEM-Cl) produces only the structurally characterized *rac* isomer of $Cs[\mathbf{I}\text{-}1,1′\text{-}MEM_2]$. Crystal data for $[Cs_2(DME)_4][Co(C_2B_9H_{11})_2]$: triclinic $P\bar{1}$, $a = 9.7930(10)$ Å, $b = 10.1300(10)$ Å, $c = 12.1010(10)$ Å, $\alpha = 101.13°$, $\beta = 98.16°$, $\gamma = 114.09°$, $V = 1042.1(2)$ Å^3, $Z = 1$. Crystal data for $Cs[Co(1\text{-}MEM\text{-}1,2\text{-}C_2B_9H_{10})_2]$: monoclinic $P2_1/c$, $a = 11.5780(10)$ Å, $b = 14.0880(10)$ Å, $c = 16.998(2)$ Å, $\beta = 96.21°$, $V = 2756.3(4)$ Å^3, $Z = 4$.

Introduction

Three decades after the explosion in metallocarborane chemistry initiated by the synthesis of the first bis(dicarbollide) sandwich complexes,[1] interest in modifying the cobalt(III) anion, $[Co((3)\text{-}1,2\text{-}C_2B_9H_{11})_2]^-$ (**I**), continues unabated. New cobalt dicarbollide derivatives for applications as diverse as nuclear waste remediation[2−5] and medical imaging and radiotherapy[6−8] have been recently described. Methods for introducing substituents onto cobalt dicarbollide fall into two general categories: (i) modifying the dicarbollide ligand or its precursor, *o*-carborane, before incorporating it into the sandwich complex[2,6,7,9] and (ii) modifying anion **I** itself.[3−5,9] In the second approach, the reaction conditions are generally electrophilic, and

the products invariably contain substituents on the boron atoms of the dicarbollide ligands.

Metallation of the C−H bonds in cobalt dicarbollide has not been specifically investigated as a route to new derivatives, despite the fact that deprotonation and nucleophilic substitution reactions at the carbon atoms in *o*-carborane, $C_2B_{10}H_{12}$, have been known since 1963.[10] Similarly, the dicarbollide C−H bonds in $Co(C_5H_5)(C_2B_9H_{11})$, can be metallated using *n*-butyllithium and converted to carboxylates.[11] A significant advantage of lithio(cobalt dicarbollide) substitutions over existing methods would be the ability to introduce substituents which would not survive the harsh alkaline conditions used during the synthesis of cobalt dicarbollide.[9]

In their preliminary communication[1] on the synthesis of cobalt dicarbollide, Hawthorne and Andrews briefly described the reaction of **I** with *n*-butyllithium, producing a purple complex which was inferred to be the cobalt(II) dianion, $[Co(C_2B_9H_{11})_2]^{2-}$. Although characterization was not attempted, the authors noted its reversion to **I** upon exposure to air. Reaction of **I** with *n*-butyllithium was not described again until 1994, when Jorgensen and co-workers reported[12,13] that pretreating **I** with *n*-butyllithium allowed it to be covalently attached to chloromethylated polystyrene. The authors clearly planned a deprotonation and nucleophilic substitution sequence but did not

† Née Rebecca L. Miller.
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Table 1. NMR Spectral Data^a for Cobalt Dicarbollide Derivatives (δ in ppm, (Integral, Multiplicity, *J*, Assignment))

compound	^{11}B{^{1}H} NMR^b	^{1}H NMR^c	^{13}C{^{1}H} NMR
Cs[Co(1,2-C$_2$B$_9$H$_{11}$)$_2$] (Cs[**I**], THF-d_8)	5.69 (2B), 1.23 (2B), −5.81 (8B), −17.25 (4B), −22.78 (2B)		
Cs[Co(1-Li-1,2-C$_2$B$_9$H$_{10}$)(C$_2$B$_9$H$_{11}$)] (Cs[**I**-Li], THF-d_8)	5.36, 2.10, −5.37, −6.82, −18.22		
Cs[Co(1-Li-1,2-C$_2$B$_9$H$_{10}$)$_2$] (Cs[**I**-Li$_2$], THF-d_8)	2.09, −6.35, −11, −19		
NaCs[Co(1,2-C$_2$B$_9$H$_{11}$)$_2$] (NaCs[**II**], THF-d_8)	132.30 (2B), 68.32 (4B), −1.34 (2B), −22.85 (4B), −65.65 (6B)	30.17 (2H), −8.36 (4H), −9.55 (4H), −37.20 (8H), −64.51 (4H)	
Cs[Co(1-CH$_3$-1,2-C$_2$B$_9$H$_{10}$)(C$_2$B$_9$H$_{11}$)] (Cs[**I**-Me])	6.18, 0.84, −3.68, −5.83, −8.16, −12.09, −17.24, −22.51	3.92 (1H, s, C$_{cage}$H), 3.61 (2H, s, C$_{cage}$H), 2.08 (3H, s, CH$_3$)	58.43 (C$_{cage}$H), 52.20 (C$_{cage}$H), 30.19 (CH$_3$)
Cs[Co(1-CH$_3$-1,2-C$_2$B$_9$H$_{10}$)$_2$], mixture of *rac* and *meso* (Cs[**I**-1,1′-Me$_2$])	7.48, 0.72, −4.73, −9.68, −11.64, −16.50	major isomer: 3.49 (1H, s, C$_{cage}$H), 2.23 (3H, s, CH$_3$) minor isomer: 4.11 (1H, s, C$_{cage}$H), 2.38 (3H, s, CH$_3$)	major isomer: 66.98 (C$_{cage}$H), 33.06 (CH$_3$) minor isomer: 59.50 (C$_{cage}$H), 30.98 (CH$_3$)
Cs[Co(1,2-(CH$_3$)$_2$-1,2-C$_2$B$_9$H$_9$)(C$_2$B$_9$H$_{11}$)] (Cs[**I**-1,2-Me$_2$])		3.41 (s, 2H, C$_{cage}$H), 2.11 (s, 6H, CH$_3$)	
Cs[Co(1-C$_6$H$_{13}$-1,2-C$_2$B$_9$H$_{10}$)(C$_2$B$_9$H$_{11}$)] (Cs[**I**-Hx])	6.01, 0.81, −6.21, −14.54, −17.58, −22.81	3.90 (1H, s, C$_{cage}$H), 3.60 (1H, s, C$_{cage}$H), 3.54 (1H, s, C$_{cage}$H), 2.52, 2.14 (2H, mult), 1.47 (2H, mult), 1.23 (6H, br s), 0.85 (3H, t, 6 Hz)	57.99 (C$_{cage}$H), 52.04 (C$_{cage}$H), 40.98, 32.27, 31.43, 29.82, 23.36, 14.39 (hexyl)
Cs[Co(1-C$_6$H$_{13}$-1,2-C$_2$B$_9$H$_{10}$)$_2$] (Cs[**I**-Hx$_2$]), mixture of isomers		3.98 (s, minor C$_{cage}$H), 3.46 (s, major C$_{cage}$H), 2.90, 2.5−2.2 (mult), 1.50, 1.24 (s), 0.86 (t, 7 Hz)	
rac-Cs[Co(1-MEM-1,2-C$_2$B$_9$H$_{10}$)$_2$] (Cs[*rac*-**I**-1,1′-MEM$_2$])	9.86, 3.34, −1.69, −3.55, −5.55, −11.45, −14.50, −16.38	4.70 (2H, s, C$_{cage}$H), 4.50 (2H, d, CHH), 3.80 (2H, d, CHH), 3.4−3.5 (8H, mult, MEM), 3.27 (s, 6H, CH$_3$)	77.46, 72.40, 71.24 (−CH$_2$), 68.33 (C$_{cage}$MEM), 59.10 (−CH$_3$), 52.39 (C$_{cage}$H)

^{a} Spectra were obtained in CD$_3$CN unless otherwise noted. ^{b} ^{11}B signal intensities are reported only when peak overlap is minor. ^{c} Broad, indistinct B−H resonances also appear in the δ 0−4 ppm region for all of the Co(III) complexes.

characterize the purple intermediate or the polymer−bound material beyond noting the appearance of a strong B−H stretching band at 2580 cm^{-1} in the infrared spectrum of the product and a concomitant decrease in intensity of the CH$_2$−Cl stretch at 1265 cm^{-1}.

Our objective in this study was to resolve the apparent discrepancy in these two prior reports and to establish whether a stable deprotonated complex of cobalt dicarbollide could be prepared and isolated. In this paper, we describe the synthesis and reactivity of two products of *n*-butyllithium deprotonation, [Co(1-Li-1,2-C$_2$B$_9$H$_{10}$)$_n$(C$_2$B$_9$H$_{11}$)$_{2-n}$]$^-$ (*n* = 1, **I**-Li; *n* = 2, **I**-Li$_2$), and clearly distinguish them from the Co(II) species, [Co(C$_2$B$_9$H$_{11}$)$_2$]$^{2-}$ (**II**), produced by alkali metal reduction.

Experimental Section

General. *o*-Carborane (98%) was purchased from Consumer Health Products, Los Angeles, CA, and used as received. Cs[Co((3)-1,2-C$_2$B$_9$H$_{11}$)$_2$] (Cs[**I**]) was prepared via literature methods^9 and dried at 105 °C in a vacuum oven prior to use. Tetrahydrofuran (THF) for air-sensitive manipulations was freshly distilled from sodium/benzophenone ketyl. Anhydrous dimethoxyethane (DME) was purchased from Aldrich and stored over activated 4-Å sieves. THF-d_8 was dried over sodium metal and distilled prior to use. CH$_3$I, C$_6$H$_{13}$Br, and CH$_3$-OCH$_2$CH$_2$OCH$_2$Cl (MEM-Cl) were dried over activated 4-Å sieves. All other reagents were used as received from Aldrich or Janssen. Air-sensitive manipulations were carried out under nitrogen or helium atmospheres, using standard glove box and Schlenk techniques.

NMR spectra (Table 1) were obtained on a Bruker AF250 spectrometer. ^{11}B NMR spectra were referenced to external BF$_3$·OEt$_2$ in acetonitrile-d_3; ^{1}H and ^{13}C spectra were referenced to TMS. Elemental analyses were performed on a Perkin-Elmer 2400 CHN Analyzer. Infrared spectra were obtained as KBr pellets. All other physical characterization was carried out using standard instrumental methods.

CsNa[Co(1,2-C$_2$B$_9$H$_{11}$)$_2$]·2DME. Synthesis. To a solution of Cs-[**I**] (250 mg, 0.55 mmol) in 30 mL of DME was added an excess of 0.9% Na(Hg) amalgam (2.1 g, 0.82 mmol of Na). The mixture was stirred under inert atmosphere for 4 h; then the solution was filtered through Celite. Pentane (15 mL) was added, and the resulting slurry was cooled to −30 °C for 3 days. The resulting brown crystals were isolated by filtration and dried *in vacuo* to give 337 mg (93% yield) of brown solid. Anal. Calcd for C$_{12}$H$_{42}$B$_{18}$CoCsNaO$_4$: C, 21.84%; H 6.42%. Found: C, 22.11%; H, 6.34%.

NMR Studies. A solution of Cs[**I**] (20 mg, 0.044 mmol) in 0.7 mL of THF-d_8 was transferred into an NMR tube with a septum cap. An excess of 0.9% Na(Hg) amalgam (0.45 g, 0.18 mmol of Na) was injected into the NMR tube via syringe. The tube was shaken briefly to generate a brown color and then inserted into the probe to record the NMR spectrum; this process was repeated until no further change was observed.

Cs$_2$[Co(1,2-C$_2$B$_9$H$_{11}$)$_2$]·0.9DME. In a glovebox, cesium metal (300 mg, 2.26 mmol) was combined with a slight excess of Cs[**I**] (1.05 g, 2.30 mmol) and 25 mL of anhydrous DME in an Erlenmeyer flask equipped with a glass-covered stir bar. The mixture was warmed on a hot plate to melt the Cs and stirred until all of the Cs was consumed and a dark brown solution resulted (about 15 min). The flask was capped and stored at room temperature for 3 days. The brown crystals that formed were filtered and dried *in vacuo*. The product obtained was a brown powder (1.41 g, 91% yield based on Cs[**I**]). Anal. Calcd for C$_{7.6}$H$_{31}$B$_{18}$CoCs$_2$O$_{1.8}$: C, 13.53%; H 4.78%. Found: C, 13.39%; H, 4.65%.

Cs[Co(1-Li-1,2-C$_2$B$_9$H$_{10}$)(C$_2$B$_9$H$_{11}$)]·3THF. Under inert atmosphere, 0.88 mL of *n*-butyllithium (2.5 M in hexanes, 2.2 mmol) was slowly added to a stirred solution of Cs[**I**] (1.00 g, 2.19 mmol) in 30 mL of anhydrous THF. During the addition, the solution color changed from orange to purple. Pentane (15 mL) was added, and the solution was cooled to −30 °C for 18 h. The resulting crystals were collected by filtration and dried *in vacuo* for 12 h. Purple crystals (1.09 g, 73% yield) were isolated. Anal. Calcd for C$_{16}$H$_{45}$B$_{18}$CoCsLiO$_3$: C, 28.31%; H, 6.68%. Found: C, 28.01%; H, 6.76%.

Cs[Co(1-Li-1,2-C$_2$B$_9$H$_{10}$)$_2$]·3THF. Under inert atmosphere, 1.75 mL of *n*-butyllithium (2.5 M in hexanes, 4.4 mmol) was slowly added to a stirred solution of Cs[**I**] (1.00 g, 2.19 mmol) in 30 mL of anhydrous THF. During the addition, the solution color changed from orange, to purple, and finally to blue-green. The solution was cooled to −30 °C for 18 h. The resulting dark crystals were collected by filtration and

Table 2. Details of Crystal Data Collection Parameters for [Cs$_2$(DME)$_4$][Co(C$_2$B$_9$H$_{11}$)$_2$] and Cs[Co(RC$_2$B$_9$H$_{10}$)$_2$] (R = CH$_2$OCH$_2$CH$_2$OCH$_3$)

	[Cs$_2$(DME)$_4$][Co(C$_2$B$_9$H$_{11}$)$_2$]	Cs[Co(1-MEM-1,2-C$_2$B$_9$H$_{10}$)$_2$]
formula	C$_{20}$H$_{62}$B$_{18}$CoCs$_2$O$_8$	C$_{12}$H$_{38}$B$_{18}$CoCsO$_4$
fw	950.03	632.84
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	9.7930(10)	11.5780(10)
b, Å	10.1300(10)	14.0880(10)
c, Å	12.1010(10)	16.998(2)
α, deg	101.13	
β, deg	98.16	96.21
γ, deg	114.09	
V, Å^3	1042.1(2)	2756.3(4)
Z	1	4
ρ(calcd), g/cm^3	1.514	1.525
absorp coeff, mm^{-1}	2.170	1.945
cryst size, mm	0.16 × 0.25 × 0.50	0.04 × 0.21 × 0.33
temp, K	173	183
radiation	Mo Kα (0.710 69 Å)	Mo Kα (0.710 73 Å)
scan technique	ω (1.0°)	ω (1.0°)
absorp correc	semiempirical	none applied
min/max transm	0.735/0.949	
$F(000)$	473	1256
reflcns collec	6872	4637
independent reflcns	5915 (R_{int} = 0.0169)	3598 (R_{int} = 0.0473)
data/restraints/parameters	5915/0/256	3597/0/385
θ range, deg	3.0 to 30.0	2.67 to 22.49
index ranges	$-1 \le h \le +13$, $-13 \le k \le +12$, $-17 \le l \le 16$	$-1 \le h \le +12$, $-1 \le k \le +15$, $-18 \le l \le 18$
R, R_w	0.0256, 0.0628 [5310 $F_o > 4\sigma(F_o)$]	0.0462, 0.0928 [2328 $F_o > 4\sigma(F_o)$]
R, R_w (all data)	0.0312, 0.0654	0.0913, 0.1124
goodness-of-fit on F^2	1.054	0.998

dried *in vacuo* for 12 h. Dull blue crystals (1.43 g, 95% yield) were isolated. Anal. Calcd for C$_{16}$H$_{44}$B$_{18}$CoCsLi$_2$O$_3$: C, 28.07%; H, 6.48%. Found: C, 28.10%; H, 6.61%.

Hydrolysis and Titration of I−Li and I−Li$_2$. A sample (50−100 mg) of **I**-Li or **I**-Li$_2$ was loaded into a screw-cap vial under inert atmosphere, for accurate weighing. Water (15 mL) was introduced into the vial, and the mixture was shaken until a yellow-orange solution resulted. The hydroxide liberated by the quench was titrated potentiometrically against standardized 0.16 N H$_2$SO$_4$.

Cs[Co(1-R-1,2-C$_2$B$_9$H$_{10}$)(C$_2$B$_9$H$_{11}$)]. General Procedure. Under inert atmosphere, *n*-butyllithium (2.5 M in hexanes) was added dropwise to a stirred solution of Cs[**I**] (2.00 g, 4.38 mmol) in 50 mL of anhydrous THF, until a persistent slight darkening of the solution was observed. *n*-Butyllithium (1.75 mL, 4.38 mmol) was then added slowly, and the resulting purple solution was stirred for 5 min. Dry CH$_3$I (1.0 g, 7 mmol) was added, causing a rapid color change to orange and precipitation of off-white solids. Under ambient atmosphere, the solution was filtered and evaporated to dryness. The solids were dissolved in 100 mL of 1 M NaCl and precipitated with aqueous CsCl. The orange solid was collected and recrystallized from acetone/water, yielding 1.71 g of orange crystals (83% yield) of Cs[**I**-Me]. Anal. Calcd for C$_5$H$_{24}$B$_{18}$CoCs: C, 12.76%; H, 5.14%. Found: C, 13.21%; H, 5.21%.

A similar workup was used for Cs[**I**-Hx], except that the noncrystalline solid was precipitated from acetone/water and isolated by decantation of the mother liquor. After drying at 50 °C for several days, a glassy orange solid was obtained in 80−90% yield. Anal. Calcd for C$_{10}$H$_{34}$B$_{18}$CoCs: C, 22.21%; H, 6.34%. Found: C, 22.14%; H, 6.18%.

Cs[Co(1-R-1,2-C$_2$B$_9$H$_{11}$)$_2$]. General Procedure. Under inert atmosphere, *n*-butyllithium (2.5 M in hexanes) was added dropwise to a stirred solution of Cs[**I**] (2.00 g, 4.38 mmol) in 50 mL of anhydrous THF, until a persistent slight darkening of the solution was observed. *n*-Butyllithium (3.50 mL, 8.75 mmol) was then added slowly, and the resulting dark blue solution was stirred for 5 min. Dry CH$_3$I (2.0 g, 14 mmol) was added, causing a rapid color change to red-orange. Workup of Cs[**I**-Me$_2$] proceeded as for Cs[**I**-Me], above, yielding 1.81 g of red-orange crystals (85% yield). Anal. Calcd for C$_6$H$_{26}$B$_{18}$CoCs: C, 14.87%; H, 5.41%. Found: C, 15.28%; H, 5.55%.

Crystal Structure Determinations of [Cs$_2$(DME)$_4$][Co(1,2-C$_2$B$_9$H$_{11}$)$_2$] and Cs[Co(1-CH$_2$OCH$_2$CH$_2$OCH$_3$-1,2-C$_2$B$_9$H$_{10}$)$_2$]. Or-

ange plates of [Cs$_2$(DME)$_4$][Co(C$_2$B$_9$H$_{11}$)$_2$] ([Cs$_2$(DME)$_4$][**II**]) were grown from DME solvent and handled at low temperature under inert atmosphere; orange plates of Cs[Co(1-CH$_2$OCH$_2$CH$_2$OCH$_3$-1,2-C$_2$B$_9$H$_{10}$)$_2$]- (Cs[**I**-MEM$_2$]) were grown from acetone/water under ambient atmosphere. X-ray data (Table 2) were collected at low temperature on a Siemens P4/PC diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) and the ω (1.0°) scan technique. Lattice parameters were optimized from a least-squares calculation on 25 accurately centered reflections of high Bragg angle. Three check reflections monitored every 97 reflections showed no systematic variation of intensities. Lattice determination and data collection were carried out using XSCANS Version 2.10b software. Data reduction, including Lorentz and polarization corrections and structure solution and graphics, was performed using SHELXTL PC Version 4.2/360 software. Structure refinements were performed using SHELX 93 software.[14] Data for [Cs$_2$(DME)$_4$][**II**] were corrected for absorption using the laminar option in the XEMP facility of SHELXTL PC.

The structures were solved using Patterson techniques, yielding cesium and cobalt atom positions. Subsequent Fourier synthesis gave all remaining heavy atom positions. Refinement was by full-matrix least-squares on F^2. All dicarbollide ligand atoms were initially assigned as boron; two atoms on each cage were reassigned as carbon when their subsequent least-squares refinement showed very low temperature factors. Dicarbollide ligand hydrogen atoms were located from the next difference map and refined with isotropic temperature factors set to 0.08 Å^2. Aliphatic hydrogen atoms were fixed in positions of ideal geometry, with a C−H distance of 0.97 Å for ethyl hydrogens and 0.96 Å for methyl hydrogens, and refined using the riding model in the HFIX facility in SHELXL 93. These idealized H atoms had their isotropic temperature factors fixed at 1.2 times ($-$CH$_2-$) or 1.5 times ($-$CH$_3$) the equivalent isotropic U of the adjacent carbon atom.

The final refinements included anisotropic thermal parameters on all non-hydrogen atoms and converged to $R = 0.0256$ and $R_w = 0.0628$ for [Cs$_2$(DME)$_4$][**II**] [15] and $R = 0.0462$ and $R_w = 0.0928$ for (Cs[**I**-MEM$_2$]).[16]

(14) XSCANS, SHELXTL PC, PATSEE and SHELXL 93 are products of Siemens Analytical X-ray Instruments, Inc., Madison, WI.

(15) $R = \sigma||F_o| - |F_c||/\sigma|F_o|$ and $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. The parameter $w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 0.3257P]$.

(16) $R = \sigma||F_o| - |F_c||/\sigma|F_o|$ and $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. The parameter $w = 1/[\sigma^2(F_o^2) + (0.0459P)^2]$.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\mathring{A}^2 \times 10^3$) for $[Cs_2(DME)_4][Co(C_2B_9H_{11})_2]$

	x	y	z	$U(eq)^a$
Co	5000	0	5000	15(1)
Cs	6363(1)	6343(1)	6751(1)	24(1)
B(4)	5793(2)	2284(2)	5906(2)	19(1)
B(5)	5842(3)	2786(3)	7422(2)	22(1)
B(6)	5495(3)	1214(3)	7969(2)	22(1)
B(7)	6879(2)	185(2)	6245(2)	19(1)
B(8)	7327(2)	1824(2)	5762(2)	19(1)
B(9)	7593(3)	3300(2)	6977(2)	20(1)
B(10)	7395(3)	2609(3)	8221(2)	22(1)
B(11)	6956(3)	674(3)	7775(2)	22(1)
B(12)	8279(3)	1977(3)	7186(2)	21(1)
O(1)	8017(2)	7356(2)	9383(2)	40(1)
O(2)	9875(2)	8076(2)	7723(2)	43(1)
O(3)	2646(2)	4098(2)	5642(2)	32(1)
O(4)	3671(2)	6637(2)	7619(2)	39(1)
C(1)	4646(2)	1024(2)	6540(2)	20(1)
C(2)	5263(2)	−141(2)	6750(2)	20(1)
C(3)	7220(4)	6482(4)	10080(3)	60(1)
C(4)	9534(3)	7511(4)	9516(2)	45(1)
C(5)	10417(3)	8645(4)	8936(2)	49(1)
C(6)	10620(4)	9144(5)	7136(3)	68(1)
C(7)	2053(3)	2790(3)	6042(2)	34(1)
C(8)	1852(3)	4999(3)	5852(3)	39(1)
C(9)	2074(3)	5714(3)	7110(3)	43(1)
C(10)	3983(4)	7431(4)	8798(3)	55(1)
HC1	3617(48)	733(45)	6449(35)	80
HC2	4518(48)	−1101(45)	6719(35)	80
HB4	5301(47)	2839(45)	5376(37)	80
HB5	5354(48)	3506(45)	7788(35)	80
HB6	4786(48)	946(46)	8546(36)	80
HB7	7209(48)	−715(45)	6002(35)	80
HB8	8000(48)	2061(45)	5123(35)	80
HB9	8344(47)	4529(44)	7088(35)	80
HB10	8045(46)	3338(45)	9157(35)	80
HB11	7216(48)	71(45)	8274(36)	80
HB12	9515(48)	2285(45)	7466(35)	80

^{a} $U(eq)$ is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Results and Discussion

Alkali Metal Reduction of Cobalt Dicarbollide. Hawthorne's assignment of the air-sensitive purple species from the reaction of **I** with *n*-butyllithium as a Co(II) complex was based on the observation of a reversible electrochemical reduction of **I** (-1.42 V vs SCE),[1] and the realization that alkyllithium reagents may act as reducing agents. Since we were specifically interested in developing deprotonation reactions and wished to remove the ambiguity associated with *n*-BuLi, we carried out reductions using sodium amalgam and cesium metal.

Stirring a DME solution of $Cs[Co(1,2\text{-}C_2B_9H_{11})_2]$ (Cs[**I**]) with 1.0 equiv of Na(Hg) amalgam resulted in a rapid darkening of the cobalt dicarbollide solution from orange to brown, forming the cobalt(II) dianion, $[Co(1,2\text{-}C_2B_9H_{11})_2]^{2-}$ (**II**, eq 1). Isolation

$$Cs[Co^{III}(C_2B_9H_{11})_2] + \underset{(M = Na\ or\ Cs)}{M^0} \rightarrow$$
$$Cs[\mathbf{I}]$$
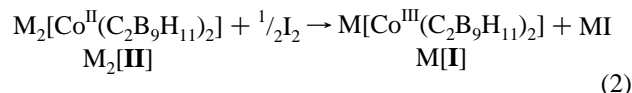$$\underset{MCs[\mathbf{II}]}{MCs[Co^{II}(C_2B_9H_{11})_2]}\ (1)$$
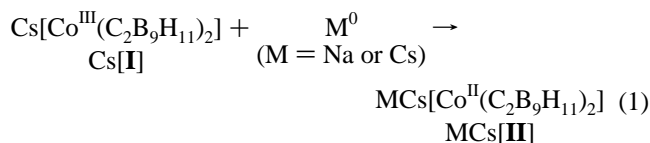
of the sodium reduction product by adding pentane, cooling to $-30\ ^\circ$C and drying the resulting brown crystals *in vacuo*, gave a 93% yield of $NaCs[Co(C_2B_9H_{11})_2]\cdot 2DME$ (NaCs[**II**]). Reduction with more than 1 equiv of Na(Hg) proceeded more rapidly but gave the same final product, even after prolonged contact. The corresponding product from reduction with 1 equiv of cesium metal precipitated slowly as brown crystals from DME
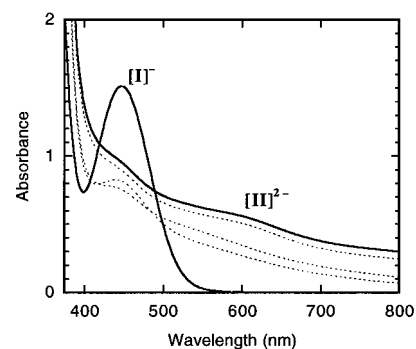
Figure 1. Absorption spectra for the formation of CsNa[**II**] from the reaction of Cs[**I**] with Na(Hg) in THF solution (3.5 mM). Dashed lines represent spectra at intermediate stages in the reaction.

at ambient temperature. Elemental analysis showed less than one DME solvent molecule remaining in the lattice after drying *in vacuo*, implying a 91% yield of $Cs_2[Co(C_2B_9H_{11})_2]\cdot 0.9DME$ (Cs_2[**II**]).

Re-oxidation of NaCs[**II**] and Cs_2[**II**] with 0.5 equiv of I_2 in THF yielded anion **I**, along with insoluble salts (eq 2). The

$$M_2[Co^{II}(C_2B_9H_{11})_2] + {}^1/_2I_2 \rightarrow M[Co^{III}(C_2B_9H_{11})_2] + MI$$
$$M_2[\mathbf{II}] \qquad\qquad M[\mathbf{I}]$$
$$(2)$$

Co(II) salts also reverted slowly to yellow-orange cobalt(III) dicarbollide (**I**) in the solid state upon exposure to dry air. Both reactions were confirmed by ^{11}B and ^{1}H NMR spectroscopy.

Observation of the Na(Hg) reduction process by ^{11}B and ^{1}H NMR spectroscopy (Table 1) revealed the formation of a paramagnetic 19-electron complex. The ^{11}B NMR spectrum of $Co[(C_2B_9H_{11})_2]^{2-}$ is dispersed over a chemical shift range of δ +132 to −66 ppm, in contrast to diamagnetic **I** which has peaks in the region δ +6 to −23 ppm. The ^{1}H NMR spectrum of **II** also shows cage B−H and C−H resonances in the chemical shift range δ +30 to −65 ppm. Wiersema and Hawthorne[17] previously reported a grossly similar ^{11}B NMR spectrum for **II** and interpreted the data in terms of a complex with an unpaired electron localized on the metal center, as opposed to a cage-centered radical.[17,18] The integrated signal intensities in the ^{11}B and ^{1}H NMR spectra indicate a mirror plane of symmetry through the dicarbollide ligands and overall C_{2h} symmetry for the anion. However, the NMR data alone do not distinguish whether this symmetry reflects the ground state preference or time-averaged rotational disorder.

Spectra were also recorded at early conversion times in the reaction of **I** with Na(Hg). The ^{11}B NMR spectrum shows a distinct intermediate species with broad resonances at δ +16 ppm ($\Delta\nu_{1/2}$ = 1630 Hz) and δ −26 ppm ($\Delta\nu_{1/2}$ = 1200 Hz) and sharp resonances at δ −1.00 and −20.48 ppm. Changes in the visible-range absorption spectrum during the reduction are shown in Figure 1. The conversion from **I** to **II** is indicated by the disappearance of the absorption band at 444 nm (ϵ_{max} = 433 M^{-1} cm^{-1}) for the d^6 complex, and ingrowth of weaker maxima at 440 nm (ϵ_{max} = 290 M^{-1} cm^{-1}) and 560 nm (ϵ_{max} = 170 M^{-1} cm^{-1}), corresponding to the d^7 complex. The absence of an isosbestic point during the conversion is further indication that an intermediate species is present in the conversion. The nature of this intermediate is unknown, but we

(17) Wiersema, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1974**, *96*, 761−770. The NMR solvent was not identified in this paper, which may account for minor differences reported herein.
(18) *Chemical Applications of NMR in Paramagnetic Molecules*; LaMar, G. N., Horrocks, W. D., Jr., Holm, R. H., Eds.; Academic Press: New York, 1973.
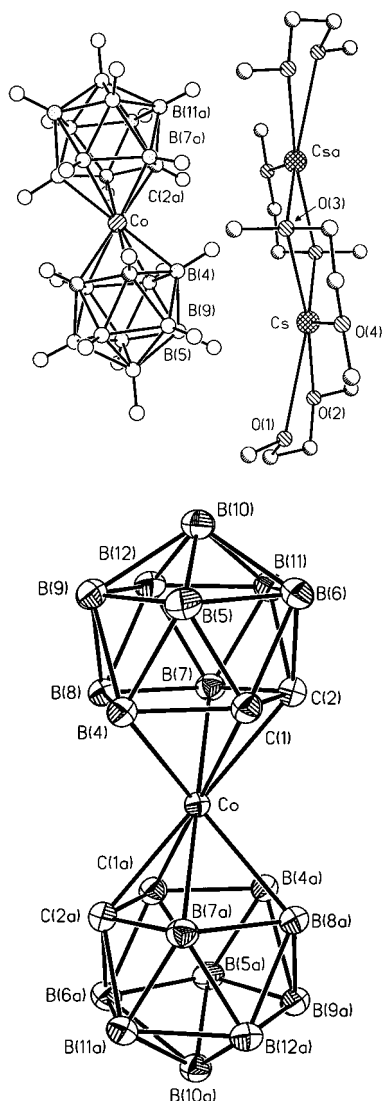
Figure 2. Molecular structure of $[Cs_2(DME)_4][Co(1,2-C_2B_9H_{11})_2]$, drawn with 50% thermal ellipsoids. (a, top) Molecular unit, showing near-neighbor interactions of $[Cs_2(DME)_4]^{2+}$ with hydrides on B(7a), B(4), B(5), and B(9). (b, bottom) Detail of anion $[Co(1,2-C_2B_9H_{11})_2]^{2-}$ (**II**), with hydrogen atoms omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[Cs_2(DME)_4][Co(C_2B_9H_{11})_2]$

Bond Lengths			
Co−C(1)	2.097(2)	B(6)−B(11)	1.756(3)
Co−C(2)	2.136(2)	B(11)−C(2)	1.695(3)
Co−B(4)	2.114(2)	B(11)−B(10)	1.777(3)
Co−B(7)	2.125(2)	B(11)−B(12)	1.777(3)
Co−B(8)	2.183(2)	B(12)−B(9)	1.769(3)
C(1)−C(2)	1.573(3)	B(12)−B(10)	1.783(3)
B(7)−C(2)	1.707(3)	B(9)−B(10)	1.782(3)
B(4)−C(1)	1.712(3)	C(1)−HC(1)	0.91(4)
B(7)−B(8)	1.774(3)	C(2)−HC(2)	0.94(4)
B(7)−B(12)	1.789(3)	B(4)−HB(4)	1.11(4)
B(7)−B(11)	1.805(3)	B(5)−HB(5)	1.08(4)
B(8)−B(9)	1.785(3)	B(6)−HB(6)	1.05(4)
B(8)−B(12)	1.786(3)	B(7)−HB(7)	1.09(4)
B(4)−B(9)	1.789(3)	B(8)−HB(8)	1.09(4)
B(4)−B(5)	1.795(3)	B(9)−HB(9)	1.13(4)
B(5)−C(1)	1.703(3)	B(10)−HB(10)	1.15(4)
B(5)−B(6)	1.765(3)	B(11)−HB(11)	1.01(4)
B(5)−B(9)	1.774(3)	B(12)−HB(12)	1.10(4)
B(5)−B(10)	1.775(3)	Cs−HB(4)	3.27(4)
B(6)−C(2)	1.726(3)	Cs−HB(5)	3.20(4)
B(6)−C(1)	1.747(3)	Cs−HB(8)	3.21(4)
B(6)−B(10)	1.755(3)	Cs−HB(7a)	3.10(4)

Bond Angles			
C(2)−B(7)−B(8)	106.7(2)	C(2)−B(7)−Co	66.74(10)
B(4)−B(8)−B(7)	104.9(2)	B(8)−B(7)−Co	67.42(10)
C(1)−B(4)−B(8)	105.8(2)	B(4)−B(8)−Co	63.72(10)
C(2)−C(1)−B(4)	112.0(2)	B(7)−B(8)−Co	63.97(10)
C(1)−C(2)−B(7)	110.3(2)	C(1)−B(4)−Co	65.50(9)
C(1)−Co−B(4)	47.96(8)	B(8)−B(4)−Co	67.80(10)
C(1)−Co−C(2)	43.62(7)	C(2)−C(1)−Co	69.51(10)
B(7)−Co−C(2)	47.25(8)	B(4)−C(1)−Co	66.54(10)
B(4)−Co−B(8)	48.48(9)	C(1)−C(2)−Co	66.87(10)
B(7)−Co−B(8)	48.61(8)	B(7)−C(2)−Co	66.01(9)

tentatively suggest that it may be a high-energy rotamer of the final product (*vide infra*).

Structure of $[Cs_2(DME)_4][Co(C_2B_9H_{II})_2]$. While a large number of transition metal bis(dicarbollide) complexes have been structurally characterized,[19,20] the d^7 complex $[Co(C_2B_9-H_{11})_2]^{2-}$ was notably missing from the series. Attempts to grow X-ray quality crystals of NaCs[**II**] from THF or DME were complicated by loss of solvent and crystal degradation when removed from the mother liquor. The dicesium salt, Cs_2[**II**], is minimally soluble in these inert solvents, but a dilute solution of the dianion in DME slowly deposited single crystals, which were maintained at low temperature for X-ray analysis.

The molecular structure of $[Cs_2(DME)_4][Co(1,2-C_2B_9H_{11})_2]$ is shown in Figure 2, with important distances and angles given in Table 4. The compound crystallizes in the triclinic space group $P\bar{1}$, with the cobalt atom occupying a special position in the lattice. The remaining atoms are related by inversion symmetry about the cobalt center, and only one dicarbollide

ligand is uniquely determined. The compound crystallizes in a chain-like structure (Figure 2a), wherein several of the electron-rich hydrogen atoms of the dicarbollide cages appear to occupy coordination sites on the Cs^+ ions. The shortest $Cs \cdots H$ distances (3.1−3.3 Å), for hydrides on B(7a), B(4), B(5), and B(9), are comparable to the sum of the ionic radii of Cs^+ and H^- (3.19 Å). Thus, there may be a significant bonding component to the interaction, assuming that the hydrogen atoms on the boron cages are hydridic in character. The nearly planar coordination geometry of the $[Cs_2(DME)_4]^{2+}$ moiety further suggests that the boron hydrides play a role in donating electron density into the Cs^+ ions.

The cobalt(II) dianion, **II**, shown in detail in Figure 2b, has approximate C_{2h} molecular symmetry. The carbon atoms occupy *transoid* rotational geometry about the cobalt center; thus, the structure is consistent with the isoelectronic nickel-(III) complex, $[Ni(C_2B_9H_{11})_2]^-$.[21] Compared to the Co(III) starting material (**I**),[20] reduction to Co(II) (**II**) results in three structural perturbations. Most significant, the orientation of the carbon atoms in the cages is rotated from the *cisoid* geometry preferred for the d^6 complexes (Figure 3), to the *transoid* geometry previously observed for the Ni(III) complex. This change in the rotational geometry may hint at the nature of the intermediate observed during the reduction of **I**. If we assume that electron transfer into the LUMO of **I** occurs while the anion is in its ground-state *cisoid* rotational configuration and that there is a small barrier to ligand rotation in d^7 product **II**, then the d^7 *cisoid* rotamer might be observable by NMR and UV−vis spectroscopy during its finite lifetime.

Additional structural perturbations are apparent in the bond distance comparision (Table 7) between complexes **I** and **II**.

(19) Callahan, K. P.; Hawthorne, M. F. *Adv. Organometal. Chem.* **1976**, *14*, 145−186.

(20) Borodinsky, L.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1982**, *21*, 1686−1689.

(21) Hansen, F. V.; Hazell, R. G.; Hyatt, C.; Stucky, G. D. *Acta Chem. Scand.* **1973**, *27*, 1210−1218.

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for $Cs[Co(1\text{-}MEM\text{-}1,2\text{-}C_2B_9H_{10})_2]$

	x	y	z	$U(eq)^a$
Cs	1761(1)	6345(1)	718(1)	38(1)
Co	133(1)	3718(1)	2121(1)	28(1)
C(1)	766(8)	2349(6)	1950(5)	37(2)
C(2)	1745(7)	3081(6)	2326(5)	33(2)
B(4)	21(9)	2845(7)	1119(6)	36(3)
B(5)	1105(10)	1952(8)	1055(6)	43(3)
B(6)	2216(9)	2109(7)	1841(6)	40(3)
B(7)	1768(8)	4104(8)	1804(6)	34(2)
B(8)	666(9)	3964(7)	990(6)	32(2)
B(9)	1071(10)	2958(7)	450(6)	41(3)
B(10)	2428(10)	2508(8)	894(6)	45(3)
B(11)	2837(9)	3209(8)	1731(6)	38(3)
B(12)	2152(8)	3757(8)	864(5)	37(2)
C(11)	71(7)	4556(6)	3132(4)	36(2)
C(12)	−594(7)	3571(7)	3168(5)	40(2)
B(14)	−344(9)	5133(7)	2242(6)	41(3)
B(15)	−861(10)	5480(8)	3174(7)	51(3)
B(16)	−1006(10)	4470(9)	3743(7)	54(3)
B(17)	−1560(9)	3377(8)	2361(7)	47(3)
B(18)	−1468(8)	4395(7)	1737(6)	38(3)
B(19)	−1840(10)	5408(9)	2292(7)	50(3)
B(20)	−2241(10)	5000(9)	3210(7)	55(3)
B(21)	−2045(10)	3743(10)	3251(7)	56(3)
B(22)	−2603(10)	4302(8)	2371(7)	49(3)
C(3)	270(8)	1550(6)	2419(5)	45(2)
C(4)	101(8)	906(7)	3683(6)	54(3)
C(5)	−114(8)	1292(7)	4460(5)	53(3)
C(6)	758(11)	2005(10)	5600(6)	87(4)
C(13)	1256(8)	4687(6)	3630(5)	44(2)
C(14)	2463(9)	3959(8)	4674(5)	68(4)
C(15)	3601(9)	4155(7)	4390(7)	73(4)
C(16)	4997(8)	3515(9)	3631(7)	97(5)
O(1)	636(5)	1622(4)	3240(3)	44(2)
O(2)	932(5)	1496(5)	4923(3)	55(2)
O(3)	1549(5)	3844(4)	4044(3)	42(2)
O(4)	3928(5)	3368(5)	3950(4)	55(2)

^{a} $U(eq)$ is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The distances around the C_2B_3 bonding face of the dicarbollide ligand are slightly distorted in the d^7 complex, such that the C—C and B—B distances are shorter and the C—B distances are slightly longer. Because of the large estimated standard deviations (esd's) for some atoms in the Co(III) structure, only the C—C shortening is statistically significant. These changes may indicate a slight distortion toward a π-allyl bonding mode containing localized C=C and B⸫B⸫B bonds. This distortion is fully manifested in the "slipped" d^8 bis(dicarbollide) complexes such as copper(III) dicarbollide.[22] Finally, all of the cobalt—cage distances are lengthened by population of a metal—ligand antibonding orbital in this 19-electron complex.

Deprotonation of Cobalt Dicarbollide. Reaction of THF solutions of **I** with *n*-butyllithium (Scheme 1) provides a striking contrast with the alkali metal reduction described above. Addition of 1.0 equiv of *n*-BuLi to a sample of Cs[**I**] in THF-d_8 showed formation of a diamagnetic product in the ^{11}B NMR spectrum, with a chemical shift range comparable to the starting material. The color of the resulting solution is purple, arising from an electronic transition at $\lambda_{max} = 562$ nm ($\epsilon_{max} = 415$ M^{-1} cm^{-1}). The intensity of this red-shifted absorption band is similar to that of the starting material **I** (444 nm; 433 M^{-1} cm^{-1}) and alkyl derivatives of cobalt(III) dicarbollide,[9] thus, no reduction of the metal center is indicated.

The purple material was isolated as a crystalline solid by adding pentane to the THF solution and cooling to −30 °C.

(22) Wing, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 4828−4834.
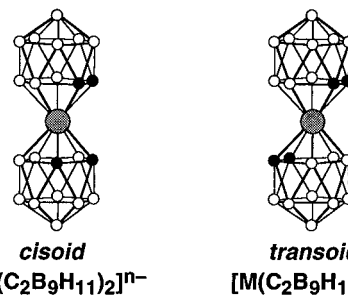
Figure 3. Rotational isomers of symmetrically bonded bis(dicarbollide) sandwich complexes. The *cisoid* geometry is preferred for the d^6 Co-(III) and Ni(IV) complexes; *transoid* geometry is preferred for the d^7 Co(II) and Ni(III) complexes.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $Cs[Co(1\text{-}MEM\text{-}1,2\text{-}C_2B_9H_{10})_2]$

Bond Lengths			
Co−C(1)	2.094(8)	C(3)−O(1)	1.416(10)
Co−C(2)	2.067(8)	O(1)−C(4)	1.438(10)
Co−B(4)	2.093(10)	C(4)−C(5)	1.474(13)
Co−B(7)	2.095(10)	C(5)−O(2)	1.401(10)
Co−B(8)	2.109(10)	C(6)−O(2)	1.389(11)
Co−C(11)	2.092(8)	C(12)−C(11)	1.591(12)
Co−C(12)	2.060(8)	C(12)−B(17)	1.694(14)
Co−B(14)	2.084(10)	C(11)−B(14)	1.739(13)
Co−B(17)	2.100(11)	B(17)−B(18)	1.79(2)
Co−B(18)	2.123(10)	B(18)−B(14)	1.81(2)
C(1)−C(2)	1.612(11)	C(11)−C(13)	1.543(11)
C(1)−B(4)	1.722(12)	C(13)−O(3)	1.404(10)
C(2)−B(7)	1.694(13)	O(3)−C(14)	1.430(10)
B(7)−B(8)	1.788(13)	C(14)−C(15)	1.48(2)
B(8)−B(4)	1.769(14)	C(15)−O(4)	1.411(12)
C(1)−C(3)	1.527(11)	C(16)−O(4)	1.419(11)

Bond Angles			
C(1)−Co−C(2)	45.6(3)	C(11)−C(12)−B(17)	112.9(7)
B(4)−Co−C(1)	48.6(3)	C(12)−B(17)−B(18)	105.8(8)
B(4)−Co−B(8)	49.8(4)	B(17)−B(18)−B(14)	105.4(7)
B(7)−Co−B(8)	50.3(4)	C(11)−B(14)−B(18)	105.1(7)
C(2)−Co−B(7)	48.0(4)	C(12)−B(17)−B(14)	110.6(7)
C(12)−Co−C(11)	45.1(3)	C(2)−C(1)−C(3)	123.6(7)
B(14)−Co−C(11)	49.2(4)	B(4)−C(1)−C(3)	122.9(7)
C(12)−Co−B(17)	48.1(4)	C(12)−C(11)−C(13)	119.2(7)
B(14)−Co−B(18)	50.9(4)	B(14)−C(11)−C(13)	124.5(7)
B(17)−Co−B(18)	50.3(4)	C(1)−C(3)−O(1)	111.8(7)
C(1)−Co−C(11)	132.6(3)	C(3)−O(1)−C(4)	111.5(6)
C(1)−Co−C(12)	102.0(4)	O(1)−C(4)−C(5)	109.6(8)
C(2)−Co−C(11)	102.5(3)	C(4)−C(5)−O(2)	111.0(8)
C(2)−Co−C(12)	104.9(3)	C(5)−O(2)−C(6)	112.1(8)
C(1)−C(2)−B(7)	112.8(6)	C(11)−C(13)−O(3)	109.1(7)
C(2)−B(7)−B(8)	105.1(7)	C(13)−O(3)−C(14)	113.5(7)
B(4)−B(8)−B(7)	106.1(7)	O(3)−C(14)−C(15)	113.0(8)
C(1)−B(4)−B(8)	106.4(7)	C(14)−C(15)−O(4)	109.0(8)
C(2)−C(1)−B(4)	109.5(6)	C(15)−O(4)−C(16)	112.6(9)

Elemental analysis of the product indicated formation of a THF solvate of lithio(cobalt dicarbollide) with the composition Cs-$[Co(LiC_2B_9H_{10})(C_2B_9H_{11})]\cdot 3THF$ (Cs[**I**-Li]). Adding water to the deprotonated material caused reversion to **I**, and titration of the resulting aqueous solution revealed the release of 1.3 mequiv of OH$^-$/(g of Cs[**I**-Li]), consistent with 0.9 deprotonated sites per molecule. Deuteration of the compound, by treating **I**-Li with D$_2$O, proved that deprotonation occurred at a carbon atom, as evidenced by the appearance of a C—D stretching band in the infrared spectrum of the product (**I**-*d*; ν(CD/CH) = 2275/3040 cm^{-1}).

It was also possible to prepare and isolate the doubly deprotonated species, $[Co(LiC_2B_9H_{10})_2]^-$ (**I**-Li$_2$) by reaction with 2.0 equiv of *n*-BuLi. Dilithio(cobalt dicarbollide), **I**-Li$_2$, is blue in color and much less soluble in THF than **I**-Li. This product can be isolated in a fashion similar to that described above, but the crystals isolated from THF rapidly lose solvent at 25 °C.

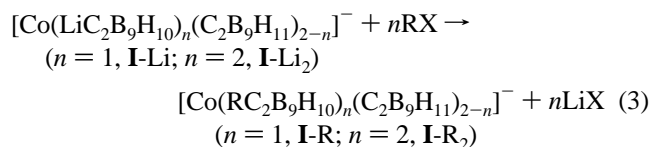**Table 7.** Comparison of Average Bond Lengths in Cobalt(III)[20] and Cobalt(II) Bis(dicarbollide) Sandwich Complexes

	C(1)−C(2)	C(1,2)−B(4,7)	B(8)−B(4,7)	Co−C(1,2)	Co−B(4,7)	Co−B(8)
Co(III)	1.624 (05)	1.699 (10)	1.798 (27)	2.046 (08)	2.093 (10)	2.104 (07)
Co(II)	1.573 (03)	1.710 (04)	1.770 (06)	2.117 (28)	2.120 (08)	2.183 (02)

Scheme 1

Figure 4. Isomers of di-C-substituted cobalt dicarbollide.
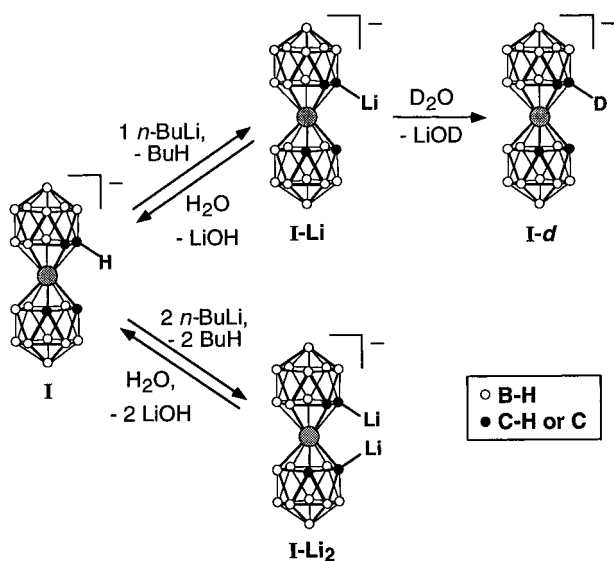
The product finally obtained is a dull blue powder, which analyzes as Cs[Co(LiC₂B₉H₁₀)₂]·3THF. Water quenching and titration of this product yielded 2.66 mequiv of OH⁻/(g of **I**-Li₂), or 1.8 deprotonated sites per molecule.

If more than 2.0 equiv of *n*-BuLi are added to **I**, the solution turns brown and eventually precipitates an insoluble brown-black material. Adding water to the solution fails to regenerate **I**; thus, the complex is irreversibly destroyed. Although the solid product was not sufficiently crystalline to be identified by powder X-ray diffraction, the ferromagnetic behavior of the material suggests that cobalt metal may be one product. In light of this undesirable side reaction, slow addition of a precisely stoichiometric amount of *n*-BuLi is recommended.

Nucleophilic Substitution Reactions on Cobalt Dicarbollide. The deprotonated species [Co(LiC₂B₉H₁₀)(C₂B₉H₁₁)]⁻ (**I**-Li) and [Co(LiC₂B₉H₁₀)₂]⁻ (**I**-Li₂), show typical nucleophilic reactivity, summarized in eq 3. Reaction of **I**-Li in THF with

$$[Co(LiC_2B_9H_{10})_n(C_2B_9H_{11})_{2-n}]^- + nRX \rightarrow$$
$$(n = 1, \textbf{I}\text{-Li}; n = 2, \textbf{I}\text{-Li}_2)$$

$$[Co(RC_2B_9H_{10})_n(C_2B_9H_{11})_{2-n}]^- + nLiX \quad (3)$$
$$(n = 1, \textbf{I}\text{-R}; n = 2, \textbf{I}\text{-R}_2)$$

excess methyl iodide causes a rapid color change from purple to orange. After workup, including addition of aqueous cesium chloride and recrystallization, Cs[Co(1-CH₃-1,2-C₂B₉H₁₀)-(C₂B₉H₁₁)] (Cs[**I**-Me]) is isolated. This product is characterized by a methyl resonance at δ 2.08 ppm (integral 3 H) and inequivalent cage C−H peaks at δ 3.61 (2 H) and 3.92 ppm (1 H) in its ¹H NMR spectrum. The failure to observe three distinct cage C−H resonances for **I**-Me can be explained by an accidental degeneracy, since the corresponding *n*-hexyl derivative, Cs[Co(1-C₆H₁₃-1,2-C₂B₉H₁₀)(C₂B₉H₁₁)] (Cs[**I**-Hx]) has 1:1:1 resonances (δ 3.54, 3.60, and 3.90 ppm). Since the symmetry of **I** is destroyed by alkylation, the ¹¹B{¹H} NMR spectra are of little use in characterizing these complexes. Several characteristic peaks are listed in Table 1, but their overlap prevents any meaningful interpretation. Significantly,
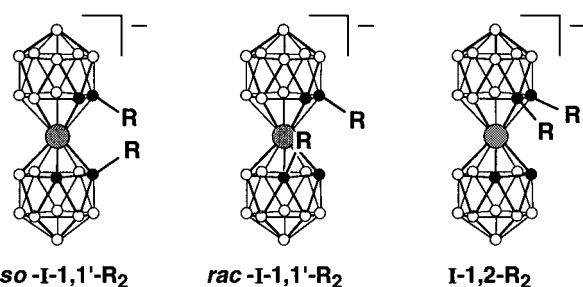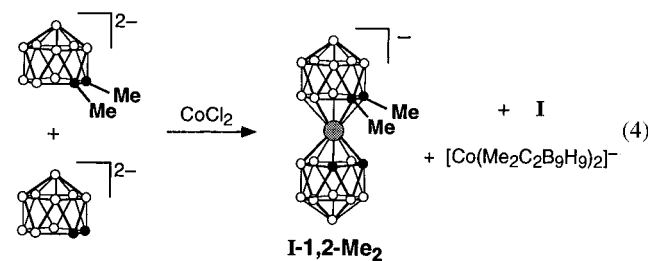
the reactivity of **I**-Li indicates that it exists as a discrete species, not as an equilibrium mixture with multiply lithiated anions.

Similar reactions of dilithio(cobalt dicarbollide), **I**-Li₂, in THF with CH₃I and C₆H₁₃Br yielded the expected dialkylated products, [Co(1-CH₃-1,2-C₂B₉H₁₀)₂]⁻ (**I**-Me₂) and [Co(1-C₆H₁₃-1,2-C₂B₉H₁₀)₂]⁻ (**I**-Hx₂), respectively. While the dimethyl compound Cs[**I**-Me₂] is a red-orange crystalline salt, the corresponding hexyl compound is isolated as an amorphous solid. Unlike the salts of **I** and its methyl derivatives, Cs[**I**-Hx₂] is very soluble in nonpolar aromatic solvents such as toluene and may have applications as an extractant as previously described for its tetra-*C*-hexyl analog.[4]
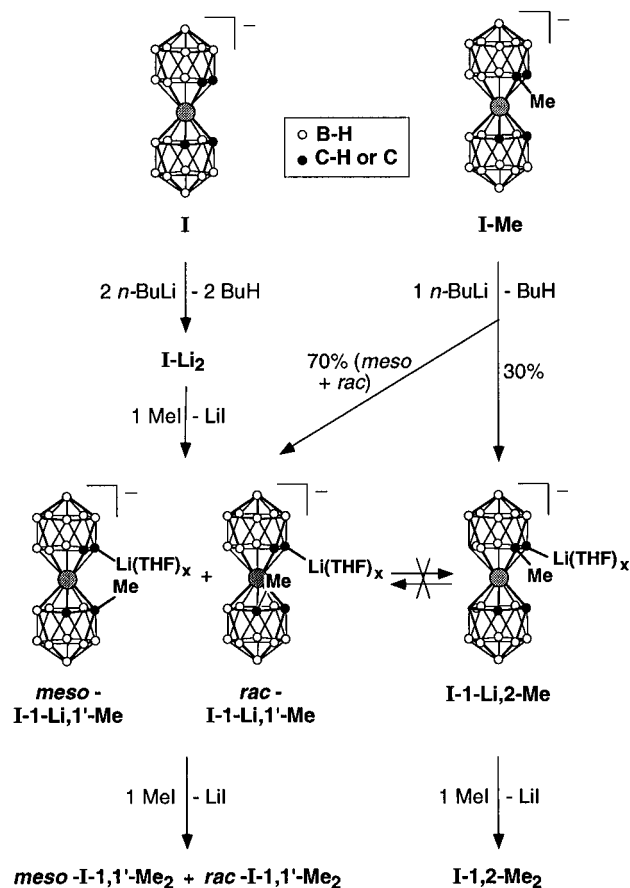
The alkylation reactions of **I**-Li₂ with methyl iodide and hexyl bromide both produce two different product isomers, in an approximate 2.5:1 ratio. In the case of methyl iodide, for example, the residual dicarbollide C−H protons resonate at δ 3.49 ppm (major isomer) and δ 4.10 ppm (minor isomer). Inequivalent methyl resonances also appear in approximately 2.5:1 ratios in the methyl regions of the ¹H and ¹³C NMR spectra. Since two of the dicarbollide C−H bonds are methylated, three isomers of dimethyl(cobalt dicarbollide) are theoretically possible (Figure 4): *meso*-[Co(1-Me-1,2-C₂B₉H₁₀)₂]⁻, (*meso*-**I**-1,1′-Me₂), *rac*-[Co(1-Me-1,2-C₂B₉H₁₀)₂]⁻, (*rac*-**I**-1,1′-Me₂), and the mixed ligand complex, [Co(1,2-Me₂-1,2-C₂B₉H₉)-(C₂B₉H₁₁)] (**I**-1,2-Me₂). Each of these isomers is predicted to show one dicarbollide C−H resonance and one methyl resonance. Since it is known that the dicarbollide ligand in CpCo-(C₂B₉H₁₁) can be singly or doubly deprotonated,[11] none of the possible isomers can be ruled out *a priori*.

In order to determine which two of the three possible isomers are actually formed, we prepared the mixed ligand complex [Co-(1,2-Me₂-1,2-C₂B₉H₉)(C₂B₉H₁₁)] (**I**-1,2-Me₂) by an independent route. A mixture of dimethyl dicarbollide (1,2-Me₂-1,2-C₂B₉H₉)²⁻ and unsubstituted dicarbollide (C₂B₉H₁₁)²⁻ ligands was treated with anhydrous CoCl₂ in THF (eq 4). The resulting

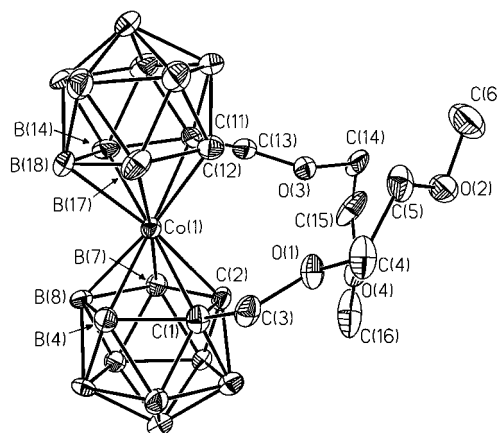product mixture contained Cs[**I**-1,2-Me₂] along with the known

Scheme 2

Figure 5. Molecular structure of the *rac*-[Co(1-MEM-1,2-$C_2B_9H_{10}$)$_2$]$^-$ anion, drawn with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

compounds Cs[**I**] and Cs[Co(1,2-Me$_2$-1,2-$C_2B_9H_9$)$_2$].[9,23] The cage C—H protons of Cs[**I**-1,2-Me$_2$] resonated at δ 3.41 ppm, indicating that the mixed-ligand complex is not formed during alkylation of **I**-Li$_2$.

From this information, it may be deduced that the products of alkylation of dilithio(cobalt dicarbollide) by methyl iodide or hexyl bromide are *meso* and *rac* isomers of [Co(1-Me-1,2-$C_2B_9H_{10}$)$_2$]$^-$ (*meso*- and *rac*-**I**-1,1′-Me$_2$, Scheme 2). Preliminary attempts to separate the isomers by fractional crystallization were unsuccessful; thus, it is not currently known which isomer is the predominant product in the reaction. The absence of the mixed-ligand complex Cs[**I**-1,2-Me$_2$] as a product may indicate either of two mechanistic conclusions. First, deprotonation of both carbon atoms on a single ligand may be disfavored, by either reduced acidity or steric crowding of the site. Alternatively, the stereochemistry may be determined by the thermodynamic instability of a monomethylated intermediate, [Co(1-Li-2-Me-1,2-$C_2B_9H_9$)($C_2B_9H_{11}$)]$^-$ (**I**-1-Li,2-Me). This intermediate could undergo rapid inter- or intramolecular proton transfers to form the preferred *meso* and *rac* isomers of **I**-1-Li,1′-Me (eq 5).

$$[\text{Co}(\text{LiMeC}_2\text{B}_9\text{H}_9)(\text{C}_2\text{B}_9\text{H}_{11})]^- \rightleftharpoons$$
$$\textbf{I}\text{-1-Li,2-Me}$$

$$[\text{Co}(\text{LiC}_2\text{B}_9\text{H}_{10})(\text{MeC}_2\text{B}_9\text{H}_{10})]^- \quad (5)$$
$$\textbf{I}\text{-1-Li,1'-Me}$$
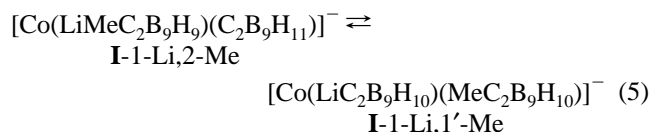
(23) The 60-MHz ^{1}H NMR spectrum reported for [Co(Me$_2$C$_2$B$_9$H$_9$)$_2$]$^-$ in ref 9 contains one methyl signal at δ 2.60 ppm. Spectra obtained at 250 MHz show two rotamers (δ 2.57, *transoid*; δ 2.55, 2.37, *cisoid*) in the slow-exchange regime below 30 °C. Miller R. L.; Pinkerton A. B.; Hurlburt P. K.; Abney K. D. *Abstr. Am. Chem. Soc.* **1995**, *209*, 97.

The nature of the intermediate species was probed indirectly, by deprotonation of **I**-Me with *n*-butyllithium. If the stereochemistry of the dialkyl products is determined by fast isomerization of the intermediate **I**-1-Li,2-Me according to eq 5, then the isomer ratio in the products should be independent of the method of preparing the intermediate. Conversely, if different isomer ratios are formed in the alkylation of **I**-Li$_2$ vs **I**-Li,Me, then the kinetic sites of deprotonation of **I** to form **I**-Li$_2$ must determine the stereochemistry of the dialkyl products.

The result of treating **I**-Li,Me with methyl iodide was the formation of *all three* isomers of dimethyl(cobalt dicarbollide) (Scheme 2). The mixed ligand complex **I**-1,2-Me$_2$ was formed in 30% yield by ^{1}H NMR, while the *meso* and *rac* isomers of **I**-1,1′-Me$_2$ made up the remaining 70% of the product (a 2.5:1 ratio was again observed). This result indicates that deprotonation of **I**-Li is directed onto the second dicarbollide ligand of the complex, while all three sites on **I**-Me can be deprotonated. As a corollary to this conclusion, any isomerization of the presumed lithiomethyl(cobalt dicarbollide) intermediate **I**-Li,Me must be slow compared to the rate of alkylation. Apparently, the steric bulk of the solvated C—Li(THF)$_x$ moiety is sufficient to block deprotonation of the adjacent C—H site, but the smaller methyl group allows approach of the butyllithium reagent.

The only stereospecific substitution discovered to date is in the reaction of **I**-Li$_2$ with 2 equiv of CH$_3$OCH$_2$CH$_2$OCH$_2$Cl (MEM-Cl). A single isomer of the disubstituted anion [Co(1-MEM-1,2-$C_2B_9H_{10}$)$_2$]$^-$ (**I**-MEM$_2$) is formed, as evidenced by the appearance of one type of residual cage C—H proton (δ 4.70 ppm) and one pair of doublets for the diastereotopic methylene groups adjacent to the cage (δ 4.50 and 3.80, $J = 10$ Hz) in the ^{1}H NMR spectrum of the crude product. Single crystal X-ray diffraction on Cs[**I**-MEM$_2$] (Figure 5, Table 6) showed that the *rac* isomer is formed selectively in the reaction.

Several features of the **I**-1,1′-MEM$_2$ anion are notable. First, the *cisoid* rotamer of the ligands is preferred in the solid state, despite the presence of substituents on the carbon atoms. Any potential steric crowding from the MEM substituents is avoided by orienting the substituted carbon atoms (C(1) and C(11)) as far apart as possible in the *cisoid* orientation. Also, the dicarbollide bonding faces are canted so that the (*centroid*)—Co—(*centroid*) angle is 175.2° and the carbon atoms are further apart than the boron atoms. This feature cannot necessarily be interpreted as a steric perturbation arising from the MEM substitution, because a similar distortion is apparent in the *cisoid* rotamer of unsubstituted cobalt dicarbollide (**I**).[20] Thus, it appears that the MEM ligands exert minimal steric influence on the overall structural details of **I**-1,1′-MEM$_2$, and

that the major structural features of **I** and **I**-1,1′-MEM$_2$ are primarily electronic in origin.

The unique stereospecificity of the MEM-Cl reaction suggests that the chelating −CH$_2$OCH$_2$CH$_2$OCH$_3$ group engenders the *rac* geometry found in the product. Instead of the isomeric mixture normally formed in the reactions with simple alkyl halides, the MEM group apparently promotes an isomerization reaction which converts all of the *meso* isomer to *rac*, presumably in the intermediate species **I**-Li,MEM. This surprising result suggests that, with appropriate choice of Li$^+$-coordinating solvents (e.g., TMEDA or crown ethers), it may be possible to control the stereochemistry in *all* of the nucleophilic substitution reactions on dilithio(cobalt dicarbollide).

Similar alkylation reactions were attempted with dichloro- and dibromo(cobalt dicarbollide), Co(8-X-1,2-C$_2$B$_9$H$_{10}$)$_2$ (X = Cl, Br; eq 6).[2] The ability to alkylate these anions would

$$X = Cl, Br$$
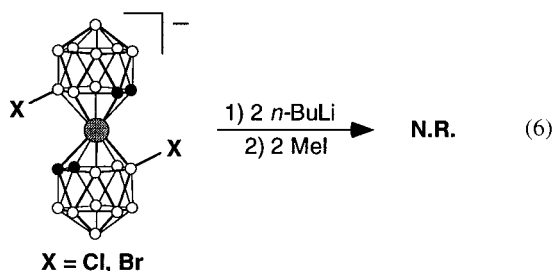
provide a convenient route to cation extraction agents with modified solubility properties[4] and the high nitric acid stability that is frequently required for nuclear waste processing.[3] However, no reaction occurred when THF solutions of Cs[Co-(8-Cl-1,2-C$_2$B$_9$H$_{10}$)$_2$] or Cs[Co(8-Br-1,2-C$_2$B$_9$H$_{10}$)$_2$] were treated with *n*-BuLi followed by methyl iodide. The chlorinated derivative is known to prefer the *transoid* rotational geometry,[2] placing the B−X group in the staggered position between the two C−H sites on the opposite cage. It is not surprising that the large size and electron-rich character of the halogens blocks approach of the *n*-butyllithium to the acidic carbon sites in these compounds.

(24) Fino, S. A.; Balaich, G. J.; Chamberlin, R. M.; Abney, K. D. Submitted for publication in *Inorg. Chem.*

Conclusions

This work demonstrates that reaction of cobalt dicarbollide with *n*-butyllithium produces isolable mono- or dilithio(cobalt dicarbollide), depending on the stoichiometry. These species are diamagnetic d^6 complexes which are metallated at the carbon atoms of the dicarbollide ligands and which display subsequent reactivity typical of carbon-centered nucleophiles. Although we have described the isolation of mono- and dilithio(cobalt dicarbollide), it is also convenient to carry out the deprotonation and substitution reactions sequentially in one pot. In contrast to the deprotonation reactions, the d^7 cobalt(II) complex, [Co-(1,2-C$_2$B$_9$H$_{11}$)$_2$]$^{2-}$ (**II**), is produced by alkali metal reduction.

These reactions provide an important complement to exisiting methods for preparing cobalt dicarbollide derivatives. Deprotonation and nucleophilic substitution is the only practical method for preparing mono-C-substituted cobalt dicarbollide and is also suited to heterogeneous grafting reactions, as described by Jorgensen *et al.*[11] It should now be possible to prepare a variety of previously unknown mono- and disubstituted cobalt dicarbollide species. As an example, we have synthesized a dicarboxylic acid derivative of cobalt dicarbollide, which reacts with organic diamides to form polyamides with cobalt dicarbollide in the polymer main chain.[24] In our continued efforts, we will explore the versatility of these synthetic procedures and attempt to improve the stereocontrol of the substitution reactions.

Supporting Information Available: Figures of additional ORTEP views and complete listings of fractional coordinated, bond distances and angles, and thermal parameters for [Cs$_2$(DME)$_4$][**II**] and Cs[**1**-1,1′-MEM$_2$] (22 pages). Ordering information is given on any current masthead page.

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