First Example of a Bis(dicarbollide) Metallacarborane Containing a B,C′-Heteronuclear Bridge

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The first example of B,C′-bridging in the *commo* bis(dicarbollide) series are presented. The sandwich metallacarborane synthesized is neutral due to the formation of a sulfonium group bridging one carbon from one half and one boron from the second half to yield [1′,8-μ-SEt-3,3′-Co(1-Ph-2-SEt-1,2-$C_2B_9H_9$)(9′-Ph-1′,9′-$C_2B_9H_8$)]. A nucleophilic substitution is involved to account for its formation. A rearrangement from 3,1,2-CoC_2B_9 to 3,1,9-CoC_2B_9 has taken place. The molecular structure is proven by an X-ray analysis.

Introduction

Since the preparation of the first metallacarborane[1] [3,3′-Fe-$(C_2B_9H_{11})_2]^{2-}$, metallacarborane chemistry has grown in both scope and diversity. New and useful practical applications for these species have been found, many resulting from their solubility in electron-donating organic solvents and their kinetic stability.[2] The use of bis(dicarbollide)cobaltate(1−), [3,3′-Co-$(C_2B_9H_{11})_2]^-$, and its stable hexachlorinated derivative in the extraction of radionuclides is particularly noteworthy.[2] Other potential uses have been realized, *e.g.*, as a radiometal carrier,[3,4] as a weakly coordinating counterion for polymerization catalysts,[5] and in the case of [3,3′-Ni$(C_2B_9H_{11})_2$], as an electron acceptor molecule.[6]

To optimize the kinetic stability[7] of these metallacarboranes, electrophilic substitution is required at those boron atoms having the greatest ground state electron density.[8] Although the chemistry of boron-substituted carboranes and metallacarboranes is not so well developed as that of their carbon-substituted analogues, the field is currently expanding rapidly and now includes substitution at B not only by halogens[9] but also by a wide variety of other functional groups.[10]

Nevertheless, the tremendous potential of metallacarboranes has led us to study further their boron substitution. One way to enhance the kinetic stability of bis(dicarbollide) complexes is to bridge the participating dicarbollyl moieties. B−B′ bridging[11] and, more recently, C−C′ bridging[7] has been reported for bis(dicarbollide) complexes. However, examples of mixed B−C′ bridging are currently unknown. Herein we report the synthesis and characterization of compounds containing an unprecedented B−C′ bridge between two dicarbollide units.

Results and Discussion

The *nido* species [$HNMe_3$][7-Ph-8-SR-7,8-$C_2B_9H_{10}$], R = Me, was allowed to react with KO^{t}Bu and $CoCl_2$ in refluxing dimethoxyethane (1:10:10 ratio) for 24 h. Following evaporation of the solvent, the products were extracted with water/CH_2Cl_2, the organic layer was separated and evaporated, and the residue was redissolved in EtOH. Addition of excess aqueous [NMe_4]Cl afforded in all cases a red solid. For R = Me, purification by thin layer chromatography [silica G, CH_2Cl_2/MeCN (10:1.5)] yielded a number of isomers, the most abundant of which ($R_f \approx 0.35$) was analytically pure **1** (51%), shown by microanalysis and ^1H, ^{13}C, and ^{11}B NMR spectroscopy to be [NMe_4][3,3′-Co(1-Ph-2-SMe-1,2-$C_2B_9H_9)_2$]. A similar procedure was followed for R = Et and Bu. Purification by thin layer chromatography [silica G, CH_2Cl_2/MeCN (10:1.5)] yielded the most abundant band for both reactions at $R_f \approx 0.25$ to give **2** (56%) and **3** (46%). Their nature was proven by microanalysis and ^1H, ^{13}C, and ^{11}B NMR spectroscopy to be [NMe_4][3,3′-Co(1-Ph-2-SEt-1,2-$C_2B_9H_9)_2$] and [NMe_4][3,3′-Co(1-Ph-2-SBu-1,2-$C_2B_9H_9)_2$], respectively.

The anions of salts **1**, **2**, and **3** represent the first examples of η^5 coordination by a carborane ligand bearing an *exo*-thioether

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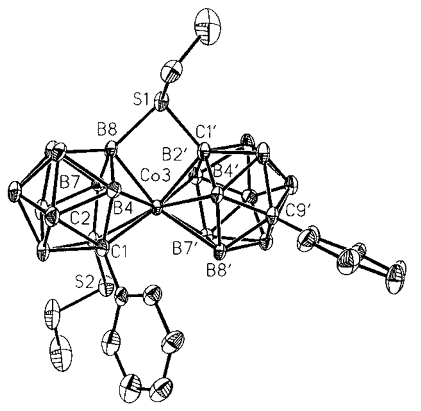
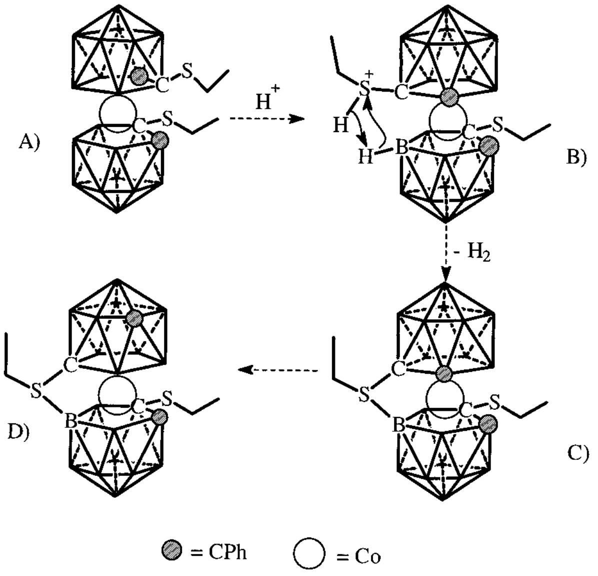


Figure 1. Molecular structure of **5** with atom labeling and hydrogen atoms omitted for clarity.

Scheme 1. Possible Mechanism for the Formation and Isomerization of the B−C′ Bridged Species **5** following Protonation of the Anion of **2**



group directly bound to carbon. The anions are expected to exist in both *meso* and *dd/ll* forms (the latter a racemic mixture), and the broadness of the ^{11}B resonances would not be inconsistent with both forms being present in **1**, **2**, and **3**. Scheme 1 includes a representation of the one enantiomer of the anion **2** as motif A.

On some occasions the organic phase in the initial stages of workup of the anions of salts **1**, **2**, and **3** is an emulsion. In order to prevent this, extraction into *acidic* water/Et_2O was attempted. The organic layer was separated and dried and the residue obtained after removal of solvent purified by thin layer chromatography [silica G, hexane/ethyl acetate (10:1.5) for R = Me and Et; silica G, hexane/ethyl acetate (10:1) for R = Bu]. For R = Me, Et, Bu, the most abundant band, $R_f \approx 0.27$, 0.31, and 0.30, respectively, yielded analytically pure compounds **4** (10%), **5** (10%), and **6** (10%) and was studied by microanalysis and ^1H, ^{13}C, and ^{11}B NMR spectroscopy. Compound **5** was studied by a single-crystal X-ray diffraction study and shown to be the neutral species [1,8-μ-SEt-3,3′-Co-(1-Ph-2-SEt-1,2-$C_2B_9H_9$)(9′-Ph-1′,9′-$C_2B_9H_8$)]. A perspective view of a single molecule of **5** is shown in Figure 1.

Compound **5** represents the unprecedented example of a bis(dicarbollide) metallacarborane containing a B−C′ bridge, in this particular case a {SEt} unit, thus allowing the molecule to be viewed as the zwitterionic (metallacarborane)$^-$(μ-SEt)$^+$. B−S bond formation under acidic conditions has been previously noted in bis(dicarbollide) metallaborane chemistry[12] but has never before led to bridge formation.

Although the individual icosahedral components of **5** have undistorted structures, the whole molecule is somewhat jackknifed about the metal atom (B(10)−Co(3)−B(10′) angle = 160.0(1)°) as the result of the monoatomic bridge. Moreover, the two metal-bonded pentagonal carborane faces are held in a mutually eclipsed conformation. Unexpectedly, the upper carborane cage has undergone polyhedral isomerization, with the {C(9)−Ph} unit now located in the second pentagonal belt. We believe that this low-temperature isomerization is a direct consequence of the B−C′ bridge formation, as illustrated in Scheme 1 for the one of the enantiomers of the *dd/ll* racemate of the anion of **2** (motif A).

In Scheme 1, motif B is merely an S-protonated rotamer of A, oriented so that the {$^+$SH(Et)} unit is able to interact with the {B(8)−H} unit of the nonprotonated cage, affording motif C. C has {CPh} groups in close proximity, and sterically-induced low-temperature isomerization, as has been noted recently in metallacarboranes made deliberately overcrowded,[13] would relieve this congestion and yield compound **5**, shown in schematic form as motif D.

Conclusion

A natural conclusion of Scheme 1 is that similar acid-promoted B−C′ bridge formation starting with the *meso* isomer of the anion of **2** would give rise to a relatively uncrowded isomer of **5** that probably need not isomerize. We are currently directing studies toward the possible isolation of this species and toward a fuller understanding of the precise mechanism of formation of such bridged species.

Experimental Section

Instrumentation. Elemental analyses were performed in our analytical laboratory using a Carlo Erba EA1108 microanalyzer. IR spectra were obtained with KBr pellets on a Nicolet 710-FT spectrophotometer. The ^1H NMR, ^{11}B NMR, and ^{13}C NMR spectra were obtained by using a Bruker ARX 300 instrument.

Materials. Before use, commercial *o*-carborane and decaborane were sublimed under high vacuum; phenyl-*o*-carborane and 1-mercapto-2-phenyl-*o*-carborane were prepared according to the literature.[14,15] The 1-SR-2-Ph-1,2-$C_2B_{10}H_{10}$ and [7-SR-8-Ph-7,8−$C_2B_9H_{10}$]$^-$ (R = Me, Et, Bu) were prepared according to the literature.[16] All organic and inorganic salts were Fluka or Aldrich analytical reagent grade and were used as received. The solvents were reagent grade. All solvents were deoxygenated before use. All reactions were carried out under a dinitrogen atmosphere employing Schlenk techniques.

Synthesis of [NMe_4][3,3′-Co(1-Ph-2-SMe-1,2-$C_2B_9H_9$)$_2$] (1). To 50 mL of deoxygenated dimethoxyethane containing 0.30 g (0.91 mmol) of [NMe_4][7-Ph-8-SMe-7,8-$C_2B_9H_{10}$] was added 1.06 g (8.18 mmol) of $CoCl_2$. The solution was stirred during 30 min, and then 0.92 g (8.18 mmol) of *t*-BuOK was added. The mixture was refluxed for 27 h. When the mixture was at room temperature, it was filtrated and the solvent was evaporated. A water/dichloromethane (1:1) mixture was added. Stirring was continued for 10 min before the two layers were

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separated. The organic layer was separated, and the solvent was evaporated. The residue was dissolved in 5 mL of ethanol, and an aqueous solution of tetramethylammonium chloride was slowly added, resulting in the formation of a red precipitate. This was filtered off, washed with water and hexane, and dried in vacuum. Purification by thin layer chromatography (silica G, dichloromethane) yielded a number of isomers, the most abundant of which ($R_f = 0.35$) was analytically pure **1**. Yield: 0.18 mg (51%). Anal. Calcd for $C_{22}H_{46}B_{18}CoNS_2$: C, 41.14; H, 7.22; N, 2.18; S, 9.98. Found: C, 40.56; H, 6.62; N, 2.17; S, 9.38. FTIR (KBr): $\upsilon_{\max}$ (C_{aryl}−H) = 3051, 3030 cm^{-1}, $\upsilon_{\max}$ (C−H) = 2917 cm^{-1}, $\upsilon_{\max}$ (B−H) = 2573 cm^{-1}. ^{1}H NMR (300 MHz, d_6-acetone, 25 °C, TMS) δ (ppm): 3.14 (s, 6H, CH_3), 3.43 (s, 12H, N(CH_3)$_4$), 7.02−7.48 (m, 10H, C_6H_5). ^{11}B{^{1}H} NMR (96 MHz in d_6-acetone , 25 °C, BF_3·Et_2O) δ (ppm): 8.59 (d, ^1J(BH) = 124 Hz), −1.45 (d, ^1J(BH) = 91 Hz), −4.82 (d, ^1J(BH) = 127 Hz), −7.09 (d, ^1J(BH) = 91 Hz), −10.32 (d, ^1J(BH) = 131 Hz), −12.21 (d, ^1J(BH) = 104 Hz), −15.2 (d, ^1J(BH) = 104 Hz), −16.6 (d, ^1J(BH) = 152 Hz). ^{13}C{^{1}H} NMR (75 MHz, d_6-acetone, 25 °C, TMS) δ (ppm): 17.98 (CH$_3$), 21.16 (CH$_3$), 55.18 (N(CH$_3$)$_4$), between 125.05 and 128.02 (C_6H$_5$).

Synthesis of [NMe$_4$][3,3′-Co(1-Ph-2-SEt-1,2-C$_2$B$_9$H$_9$)$_2$] (2). The complex **2** was obtained by the same method using 0.33 g (0.95 mmol) of [NMe$_4$][7-Ph-8-SEt-7,8-C$_2$B$_9$H$_{10}$], 1.10 g (8.46 mmol) of CoCl$_2$, and 0.95 g (8.46 mmol) of *t*-BuOK. Purification by thin layer chromatography [silica G, dichloromethane/acetonitrile (10:1.5)] yielded at R_f = 0.25 compound **2**. Yield: 0.18 g (56%). Anal. Calcd for $C_{24}H_{50}B_{18}CoNS_2$: C, 43.13; H, 7.24; N, 2.10; S, 9.60. Found: C, 43.71; H, 7.60; N, 2.46; S, 8.12. FTIR (KBr): $\upsilon_{\max}$ (C_{aryl}−H) = 3050, 3029 cm^{-1}, $\upsilon_{\max}$ (C−H) = 2959, 2931, 2854 cm^{-1}, $\upsilon_{\max}$ (B−H) = 2572 cm^{-1}. ^{1}H NMR (300 MHz, d_6-acetone, 25 °C, TMS) δ (ppm): 1.26−1.29 (m, 6H, CH_3), 3.05−3.20 (m, 4H, −CH_2−), 3.45 (s, 12H, N(CH_3)$_4$), 7.12−7.57 (m, 10H, C_6H_5). ^{11}B{^{1}H} NMR (96 MHz in d_6-acetone, 25 °C, BF_3·Et_2O) δ (ppm): 10.76 (d, ^1J(BH) = 148 Hz), 8.96 (d, ^1J(BH) = 163 Hz), 1.87 (d, ^1J(BH) = 115 Hz), −4.77 (d, ^1J(BH) = 122 Hz), −6.67 (d, ^1J(BH) = 122 Hz), −10.98 (d, ^1J(BH) = 129 Hz), −11.92 (d, ^1J(BH) = 72 Hz), −14.92 (d, ^1J(BH) = 110 Hz), −16.46 (d, ^1J(BH) = 197 Hz). ^{13}C{^{1}H} NMR (75 MHz, d_6-acetone, 25 °C, TMS) δ (ppm): 11.82 (CH$_3$), 32.68 (−CH$_2$−), 55.09 (N(CH$_3$)$_4$), between 125.48 and 128.04 (C_6H$_5$).

Synthesis of [NMe$_4$][3,3′-Co(1-Ph-2-SBu-1,2-C$_2$B$_9$H$_9$)$_2$] (3). The complex **3** was obtained by the same method as that used for **1** using 0.20 g (0.53 mmol) of [NMe$_4$][7-Ph-8-SBu-7,8-C$_2$B$_9$H$_{10}$)], 0.63 g (4.84 mmol) of CoCl$_2$, and 0.54 g (4.84 mmol) of *t*-BuOK. Purification by thin layer chromatography [silica G, dichloromethane/acetonitrile (10:1.5)] yielded at R_f = 0.25 compound **3**. Yield: 0.08 g (46%). Anal. Calcd for $C_{28}H_{58}B_{18}CoNS_2$: C, 46.30; H, 8.05; N, 1.93; S, 8.83. Found: C, 45.96; H, 7.66; N, 2.04; S, 6.73. FTIR (KBr): $\upsilon_{\max}$ (C_{aryl}−H) = 3040 cm^{-1}, $\upsilon_{\max}$ (C−H) = 2961, 2929, 2860 cm^{-1}, $\upsilon_{\max}$ (B−H) = 2570 cm^{-1}. ^{1}H NMR (300 MHz, d_6-acetone, 25 °C, TMS) δ (ppm): 0.72−0.96 (m, 6H, CH_3), 1.54−1.62 (m, 8H, −CH_2−), 3.08 (t, ^1J(HH) = 6.87 Hz, 4H, S−CH_2−), 3.44 (s, 12H, N(CH_3)$_4$), 7.11−7.53 (m, 10H, C_6H_5). ^{11}B{^{1}H} NMR (96 MHz in d_6-acetone, 25 °C, BF_3·Et_2O) δ (ppm): 10.62 (d, ^1J(BH) = 127 Hz), 1.92 (d, ^1J(BH) = 118 Hz), −4.88 (d, ^1J(BH) = 117 Hz), −6.84 (d, ^1J(BH) = 172 Hz), −11.05, −16.76. ^{13}C{^{1}H} NMR (75 MHz, d_6-acetone, 25 °C, TMS) δ (ppm): 13.23 (CH$_3$), 22.08, 37.35, 38.60 (−CH$_2$−), 55.16 (N(CH$_3$)$_4$), between 125.48 and 129.69 (C_6H$_5$).

Synthesis of [1′,8-μ-SMe-3,3′-Co(1-Ph-2-SMe-1,2-C$_2$B$_9$H$_9$)(9′-Ph-1′,9′-C$_2$B$_9$H$_8$)] (4). To 50 mL of deoxygenated dimethoxyethane containing 0.30 g (0.91 mmol) of [NMe$_4$][7-Ph-8-SMe-7,8-C$_2$B$_9$H$_{10}$] was added 1.06 g (8.18 mmol) of CoCl$_2$. The solution was stirred for 30 min, and then 0.92 g (8.18 mmol) of *t*-BuOK was added. The mixture was heated to reflux for 27 h. After cooling to room temperature, the mixture was filtrated and the solvent was evaporated. An acidic water/diethyl ether (1:1) mixture was added. Stirring was continued for 10 min before the two layers were separated. The organic layer was dried with MgSO$_4$ and filtrated, and the solvent was evaporated. The residue was heated at 45 °C for 1 h. The resulting solid was purified by column chromatography [silica G, hexane/ethyl acetate (10:1.5)], yielding several isomers, the most abundant of which (analytical R_f = 0.27) was analytically pure **4**. Yield: 0.402 g (10%). Anal. Calcd for $C_{18}H_{34}B_{18}CoS_2$: C, 38.12; H, 5.86; S, 11.31. Found: C, 38.15; H, 5.46; S, 10.18. FTIR (KBr): $\upsilon_{\max}$ (C_{aryl}−H) = 3057 cm^{-1}, $\upsilon_{\max}$ (C−H) = 2954, 2922, 2856 cm^{-1}, $\upsilon_{\max}$ (B−H) = 2619−2580 cm^{-1}. ^{1}H NMR (300 MHz, d_6-acetone, 25 °C, TMS) δ (ppm): 3.11 (s, 3H, CH_3), 3.28 (s, 3H, CH_3), 7.19−7.57 (m, 10H, C_6H_5). ^{11}B{^{1}H} NMR (96 MHz in d_6-acetone, 25 °C, BF_3·Et_2O) δ (ppm): 7.16, 5.72, 3.98, 1.76 (d, ^1J(BH) = 146 Hz), −1.07, −7.96, −11.09, −11.84, −13.77, −17.94. ^{13}C{^{1}H} NMR (75 MHz, d_6-acetone, 25 °C, TMS) δ (ppm): 31.72 (CH$_3$), between 126.7 and 128.2 (C_6H$_5$).

Table 1. Atomic Coordinates and Equivalent Displacement Parameters for **5**

	x/a	*y/b*	*z/c*	$U_{eq}{}^a$ (Å^2)
Co(3)	0.61492(4)	0.26380(3)	0.27697(4)	0.0232(1)
S(1)	0.71976(8)	0.43182(6)	0.18188(8)	0.0322(3)
S(2)	0.44365(9)	0.08739(7)	0.1768(1)	0.0441(3)
C(1)	0.4301(3)	0.2851(2)	0.3396(3)	0.030(1)
C(2)	0.4392(3)	0.2181(2)	0.1908(3)	0.031(1)
B(4)	0.4986(4)	0.3900(3)	0.3360(4)	0.029(1)
B(7)	0.5149(4)	0.2792(3)	0.0905(4)	0.031(1)
B(8)	0.5527(3)	0.3894(3)	0.1823(4)	0.028(1)
C(1′)	0.7800(3)	0.3259(2)	0.2744(3)	0.028(1)
B(2′)	0.7739(4)	0.2226(3)	0.1753(4)	0.033(1)
B(4′)	0.7421(3)	0.3093(3)	0.4270(4)	0.026(1)
B(7′)	0.7379(4)	0.1291(3)	0.2731(4)	0.031(1)
B(8′)	0.7184(3)	0.1801(3)	0.4279(4)	0.027(1)
C(9′)	0.8648(3)	0.2290(2)	0.4842(3)	0.031(1)

[a] $U_{eq} = (1/3)\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

Table 2. Selected Bond Lenghts (Å) and Angles (deg) for **5**

Co(3)−C(1)	2.139(3)	Co(3)−B(4′)	2.047(3)
Co(3)−C(2)	2.104(3)	Co(3)−B(7′)	2.169(4)
Co(3)−B(4)	2.144(4)	Co(3)−B(8′)	2.139(4)
Co(3)−B(7)	2.114(4)	S(1)−B(8)	1.921(4)
Co(3)−B(8)	2.056(4)	S(1)−C(1′)	1.819(3)
Co(3)−C(1′)	2.024(3)	S(2)−C(2)	1.790(3)
Co(3)−B(2′)	2.126(4)	C(1)−C(2)	1.771(5)
C(1)−Co(3)−B(8′)	101.5(1)	S(1)−B(8)−B(4)	115.5(2)
C(2)−Co(3)−B(7′)	102.2(1)	S(1)−B(8)−B(7)	117.9(2)
B(8)−Co(3)−C(1′)	78.5(1)	Co(3)−C(1′)−S(1)	99.2(1)
B(8)−S(1)−C(1′)	87.3(2)	S(1)−C(1′)−B(2′)	109.4(2)
Co(3)−C(2)−S(2)	111.0(1)	S(1)−C(1′)−B(4′)	123.4(2)
Co(3)−B(8)−S(1)	94.9(2)		

Table 3. Crystallographic Data for **5**

empirical formula	$C_{20}H_{37}B_{18}CoS_2$
fw	595.2
a, Å	10.637(1)
b, Å	13.747(5)
c, Å	10.464(14)
α, deg	93.36(2)
β, deg	109.55(2)
γ, deg	84.77(2)
V, Å^3	1510.0(6)
Z	2
d_{calc}, g cm^{-3}	1.309
space group	$P\bar{1}$ (No. 2)
T, °C	21
λ, Å	0.710 69
μ, cm^{-1}	7.1
transm coeff	0.956−1.000
F(000)	612
R^a	0.040
$R_w{}^b$	0.045

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Synthesis of [1′,8-μ-SEt-3,3′-Co(1-Ph-2-SEt-1,2-C$_2$B$_9$H$_9$)(9′-Ph-1′,9′-C$_2$B$_9$H$_8$)] (5). The compound **5** was obtained by the same method as that used for compound **4** using 0.33 g (0.95 mmol) of [NMe$_4$][7-Ph-8-SEt-7,8-C$_2$B$_9$H$_{10}$], 1.16 g (8.46 mmol) of CoCl$_2$, and 0.95 g (8.46 mmol) of *t*-BuOK. Purification by thin layer chromatography [silica G, hexane/ethyl acetate, (10:1.5)] yielded at R_f = 0.31 compound **5**. Yield: 0.060 g (21%). Anal. Calcd for $C_{20}H_{37}B_{18}CoS_2$: C, 40.36; H, 6.27; S, 10.77. Found: C, 40.39; H, 5.85; S, 9.14. FTIR (KBr): $\upsilon_{\max}$ (C_{aryl}−H) = 3065 cm^{-1}, $\upsilon_{\max}$ (C−H) = 2973, 2925, 2850 cm^{-1}, $\upsilon_{\max}$ (B−H) = 2592, 2565, 2538 cm^{-1} . ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 25

°C, TMS) δ (ppm): 1.28−1.39 (m, 6H, CH_3), 3.07−3.82 (m, 4H, S−CH_2−), 7.26−7.40 (m, 10H, C_6H_5). $^{11}B\{^1H\}$ NMR (96 MHz, d_6-acetone, 25 °C, $BF_3{\cdot}Et_2O$) δ (ppm): 6.1, 1.9 (d, ^1J(BH) = 144 Hz), −1.9, −7.6, −9.11, −10.7, −14.0, −17.8. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 25 °C, TMS) δ (ppm): 9.39, 12.04 (CH_3), 33.97, 37.04 (−CH_2−), between 127.2 and 127.9 (C_6H_5).

Brown prism (0.16 × 0.22 × 0.38 mm) crystals, suitable to be solved by X-ray difraction, were obtained by slow evaporation of acetone solution.

Synthesis of [1′,8-μ-SBu-3,3′-Co(1-Ph-2-SBu-1,2-$C_2B_9H_9$)(9′-Ph-1′,9′-$C_2B_9H_8$)] (6). The compound **6** was obtained by the same method as that used for compound **4** using 0.20 g (0.53 mmol) of [NMe_4][7-Ph-8-SBu-7,8-$C_2B_9H_{10}$], 0.63 g (4.84 mmol) of $CoCl_2$, and 0.54 g (4.84 mmol) of *t*-BuOK. Purification by thin layer chromatography [silica G, hexane/ethyl acetate, (10:1)] yielded at $R_f = 0.30$ compound **6**. Yield: 0.018 g (11%). Anal. Calcd for $C_{24}H_{45}B_{18}CoS_2$: C, 43.28; H, 6.95; S, 10.05. Found: C, 42.45; H, 6.33; S, 9.88. FTIR (KBr): υ_{max} (C_{aryl}−H) = 3068 cm^{-1}, υ_{max} (C−H) = 2966, 2924, 2861 cm^{-1}, υ_{max} (B−H) = 2587 cm^{-1}. ^1H NMR (300 MHz, d_6-acetone, 25 °C, TMS) δ (ppm): 0.89−1.42 (m, 6H, CH_3), 1.47−1.67 (m, 8H, −CH_2−), 3.12−3.42 (m, 4H, S−CH_2−), 7.32−7.35 (m, 10H, C_6H_5). $^{11}B\{^1H\}$ NMR (96 MHz, d_6-acetone, 25 °C, $BF_3{\cdot}Et_2O$) δ (ppm): 6.24, 1.96 (d, ^1J(BH) = 144 Hz), −2.07, −7.51, −13.86, −17.90. $^{13}C\{^1H\}$ NMR (75 MHz, d_6-acetone, 25 °C, TMS) δ (ppm): 12.7, 13.1 (−CH_3), 21.39, 21.91, 27.00, 26.47, 39.24, 42.04 (−CH_2−), between 127.29 and 128.24 (C_6H_5).

X-ray Studies. X-ray measurements for [1′,8-μ-SEt-3,3′-Co(1-Ph-2-SEt-1,2-$C_2B_9H_9$)(9′-Ph-1′,9′-$C_2B_9H_8$)] (5) were made on a Rigaku AFC5S diffractometer using Mo Kα radiation (λ = 0.710 69 Å), $2\theta_{max}$ = 50°. Data were collected at 21 °C [4017 reflections with $|F| \geq 4\sigma(F)$]. The structure was solved by direct methods using MITHRIL[17] and refined to $R(F) = 0.040$ and $R_w(F) = 0.045$ using the XTAL3.2 program system.[18] Atomic coordinates are presented in Table 1, selected bond lengths and angles in Table 2, and crystallographic data in Table 3.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional and thermal displacement parameters, bond distances and angles, and least-squares planes for [1′,8-μ-SEt-3,3′-Co(1-Ph-2-SEt-1,2-$C_2B_9H_9$)(9′-Ph-1′,9′-$C_2B_9H_8$)] (17 pages). Ordering information is given on any current masthead page.

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