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Article

Ligand-to-Metal Ratio Controlled Assembly of Cobalt Complexes Containing *ortho*-Carborane Thiolato and Butyl Thiolato Ligands

Yuguang Li,[†] Qibai Jiang,[†] Yizhi Li,[†] Xujie Shen,[†] Hong Yan,*,[†] and Vladimir I. Bregadze*,[‡]

[†] *State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Jiangsu 210093, China , and* [‡] *A. N. Nesmeyanov Institute of Organoelement Compounds (INEOS), Russian Academy of Sciences, Moscow 119991, Russia*

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Treatment of *ortho*-carborane, *n*-butyl lithium, sulfur, and $CpCo(CO)I_2$ with differing ratios led to four new compounds $[(CpCoS_2C_2B_{10}H_{10})(CpCoSC_2B_{10}H_{11})(SC_4H_9)]$ (**3**), $[(CpCo)_2S_2(S_2C_2B_{10}H_{10})(SC_2B_{10}H_{10})(SC_4H_9)]$ (**4**), $[(CpCo)_2Co(SC_4H_9)_6]^+[Co(S_2C_2B_{10}H_{10})_2]^-$ (**5**), and $[(CpCo)_2Co(SC_2B_{10}H_{11})(SC_4H_9)_5]^+[Co(S_2C_2B_{10}H_{10})_2]^-$ (**6**). Compound **3** contains a rhombic $Co_2(\mu_2\text{-}S)_2$ core and can be considered as an adduct of the two 16*e* half-sandwich monomers $CpCo(S_2C_2B_{10}H_{10})$ (**1**) and $CpCo(SC_4H_9)(SC_2B_{10}H_{11})$. Compound **4** is a trinuclear complex containing a cuboidal $[Co_3(\mu_3\text{-}S)_2(\mu\text{-}S)_2]$ core, and one cobalt atom is coordinated by six sulfur atoms in a distorted octahedral geometry. Compound **5** consists of a linear-type trinuclear cobalt(III) monocation bridged by six *n*-butyl thiolato units and a square-planar cobalt(III) monoanion $[Co(S_2C_2B_{10}H_{10})_2]^-$. However, in **6**, one *ortho*-carborane monothiolato ligand $[SC_2B_{10}H_{11}]^-$ has replaced one *n*-butyl thiolato ligand in **5**. This leads to a nonlinear arrangement of the three cobalt atoms in the cation and the nonplanar $[Co(S_2C_2B_{10}H_{10})_2]^-$ anion in **6**. Interestingly, the treatment of the 16*e* half-sandwich $CpCo(S_2C_2B_{10}H_{10})$ (**1**) by $[N(n\text{-}Bu)_4]Br$ afforded the ionic compound **7**, $[N(n\text{-}Bu)_4]^+[Co(S_2C_2B_{10}H_{10})_2]^-$, containing a square-planar anion.

Introduction

The chemistry of sulfur-bridged metal complexes has attracted much interest. This situation has arisen mainly from two reasons. One is vigorous research on transition-metal sulfido clusters,[1−3] for example, iron−sulfur clusters,[3] often considered as synthetic analogues of the active sites of iron−sulfur proteins. The other is extensive efforts on synthesis and investigation of thiolato complexes of transition metals with diversities of structural motifs,[4] for example, linear-type *S*-bridged trinuclear complexes, *fac*-(*S*)-[M(aet)$_3$] (M=Co^{III}, Rh^{III}, Ir^{III}; aet=2-aminoethanethiolate),[5] resulting from coordination of three thiolato sulfur atoms to the transition-metal ions. An important and challenging subject in this chemistry is to develop rational methods to synthesize desirable sulfur cluster complexes of high nuclearity by assembling suitable metal−sulfur fragments.[6] Currently, it has been recognized that thiolato groups, for example, alkyl, aryl thiolato, and silane thiolato ligands,[7] have an affinity with transition-metal ions to form a variety of *S*-bridged polynuclear structures because of their high Lewis

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*Corresponding author. Fax: (+86)-25- 83314502. E-mail: hyan1965@nju.edu.cn.

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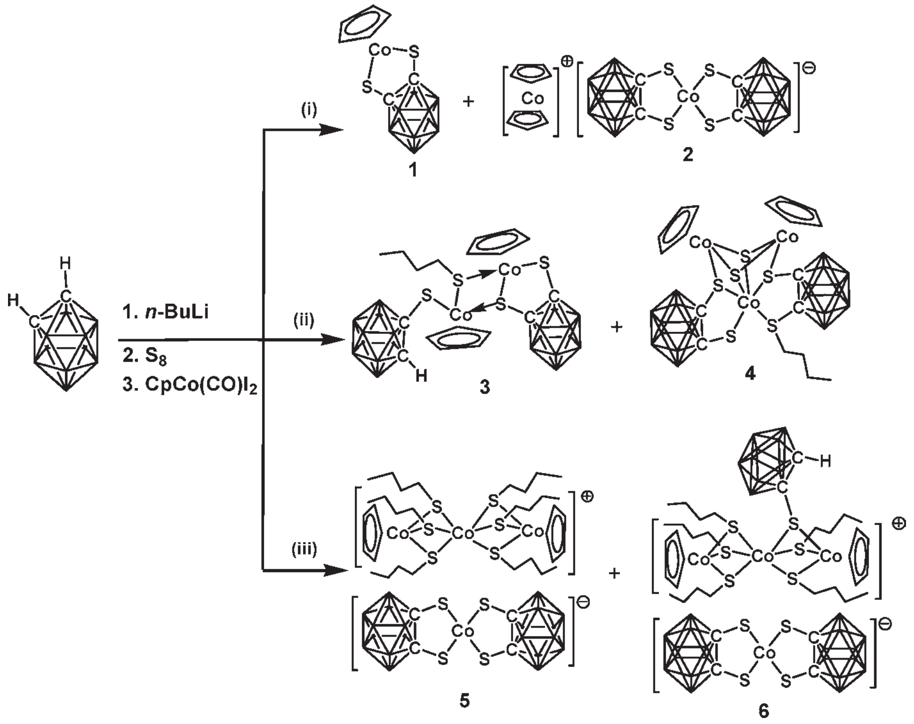
Scheme 1. Synthesis of Compounds **1**−**6**; (i) THF/Et_2O, −10 °C, 1:2:2:1;[15] (ii) THF/Et_2O, −10 °C, 1:2.2:4:2; and (iii) THF/Et_2O, −10 °C, 1:5:5:2



basicity. Relative to other dithiolato ligands,[8,9] *ortho*-carborane dithiolato ligand $(S_2C_2B_{10}H_{10})^{2-}$ also exhibits a rich coordination chemistry.[10−13] In particular, owing to the possession of the bridging or chelating characteristics of sulfur atoms, assembly around metal centers could proceed in diverse arrangements that leads to unprecedented structures.[13]

Recently, a mixed valent diruthenium complex (*p*-cymene)-Ru(μ-S_2)Ru$(S_2C_2B_{10}H_{10})_2$ bearing two $(S_2C_2B_{10}H_{10})^{2-}$ units and one S−S bridging ligand, an unprecedented tetranuclear mixed valent Ru(IV)Ru(II)$_3$S$_{12}$ cluster (*p*-cymene)$_2$Ru$_4$S$_4$-$(S_2C_2B_{10}H_{10})_4$(HC=CFc),[14] and an unusual square-planar tetrathiolate cobalt(III) compound $(Cp_2Co)^+[Co(S_2C_2B_{10}H_{10})_2]^-$,[15] have been described by our group. As a continuation of this interesting chemistry, our research has been focused on the construction of novel transition-metal clusters with chalcogen elements. In this paper, we report on the reaction system of *ortho*-carborane, *n*-butyl lithium, sulfur, and CpCo(CO)I$_2$ and explore the dependence of the product type on the reactant ratio. Four sulfur-bridged cobalt compounds, $[(CpCoS_2C_2B_{10}H_{10})(CpCoSC_2B_{10}H_{11})(SC_4H_9)]$ (**3**), $[(CpCo)_2S_2(S_2C_2B_{10}H_{10})(SC_2B_{10}H_{10})(SC_4H_9)]$ (**4**), $[(CpCo)_2Co(SC_4H_9)_6]^+[Co(S_2C_2B_{10}H_{10})_2]^-$ (**5**), and $[(CpCo)_2Co(SC_2B_{10}H_{11})(SC_4H_9)_5]^+[Co(S_2C_2B_{10}H_{10})_2]^-$ (**6**) were isolated.

Results and Discussion

In the related chemistry, the half-sandwich cobalt(III) complex $CpCo(S_2C_2B_{10}H_{10})$ (**1**) and the square-planar cobalt(III) compound $[Cp_2Co]^+[Co(S_2C_2B_{10}H_{10})_2]^-$ (**2**) were previously reported by Kang's[16] and our group,[15] respectively, which were prepared from the reaction of *ortho*-carborane, *n*-butyl lithium, sulfur, and CpCo(CO)I$_2$, as outlined in Scheme 1. In our recent work, four novel cobalt compounds **3**−**6** have been isolated from the above reaction system through control of the ratio of the starting materials, as summarized in Scheme 1, Table 1, and Figures 1−4.

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Table 1. Crystallographic Data and Structural Refinement Details of Compounds **3**−**7**

	3	**4**	**5**	**6**	**7**
chemical formula	$C_{18}H_{40}B_{20}Co_2S_4$	$C_{19}H_{40}B_{20}Cl_3Co_3S_6$	$C_{38}H_{84}B_{20}Co_4S_{10}\cdot H_2O$	$C_{72}H_{172}B_{60}Co_8S_{20}\cdot H_2O$	$C_{20}H_{56}B_{20}CoNS_4$
crystal size (mm)	0.40 × 0.20 × 0.20	0.3 × 0.20 × 0.20	0.30 × 0.26 × 0.24	0.30 × 0.25 × 0.23	0.38 × 0.22 × 0.16
formula weight	718.80	960.21	1331.59	2817.35	714.03
temperature (K)	293(2)	291(2)	273(2)	291(2)	291(2)
radiation	Mo−Kα (0.71073 Å)	Mo−Kα (0.71073 Å)	Mo−Kα (0.71073 Å)	Mo−Kα (0.71073 Å)	Mo−Kα (0.71073 Å)
crystal system	triclinic	monoclinic	orthorhombic	monoclinic	Orthorhombic
space group	*P*-1	*P*2(1)/*n*	*Pbca*	*P*2(1)/*n*	*Pbca*
a (Å)	9.937(5)	14.5475(7)	16.152(4)	12.4526(19)	16.616(5)
b (Å)	10.918(6)	16.0408(8)	20.159(5)	28.730(4)	21.607(6)
c (Å)	15.988(8)	17.3320(8)	20.159(4)	20.179(3)	22.366(7)
α (°)	80.302(7)	90.00	90.00	90.00	90.00
β (°)	85.016(7)	94.8230(10)	90.00	102.228(3)	90.00
γ (°)	88.648(7)	90.00	90.00	90.00	90.00
V ($Å^3$)	1703.3(15)	4030.2(3)	6564(3)	7055.3(18)	8030(4)
Z	2	4	4	2	8
ρ_{calc} ($g\cdot cm^{-3}$)	1.402	1.583	1.347	1.326	1.181
absorp. coeff. (mm^{-1})	1.234	1.750	1.342	1.250	0.653
F(000)	732	1928	2760	2900	2992
θ range (°)	2.06−26.00	1.73−26.00	1.91−26.00	1.75−26.00	1.79−26.00
reflns collected	9260 (R_{int} = 0.0973)	21 611 (R_{int} = 0.0459)	33 904 (R_{int} = 0.0940)	38 384 (R_{int} = 0.0538)	41 087 (R_{int} = 0.0965)
indep. reflns	6534	7904	6438	13755	7868
refns obs.[$I > 2\sigma(I)$]	3286	5961	3839	9684	4744
data/restr./paras	6534/0/398	7904/0/461	6438/0/340	13 755/0/734	7868/0/419
GOF	1.029	1.020	1.040	1.075	1.013
$R_1/wR_2 I > 2\sigma(I)$]	0.0702/0.1499	0.0527/0.1148	0.0616/0.1059	0.0594/0.1103	0.0558/0.1011
R_1/wR_2 (all data)	0.1312/0.1881	0.0724/0.1195	0.1163/0.1160	0.0907/0.1174	0.0994/0.1099
larg. peak/hole ($e\cdot Å^{-3}$)	1.179/−0.771	0.381/−0.448	0.329/−0.321	0.653/−0.535	0.361/−0.268

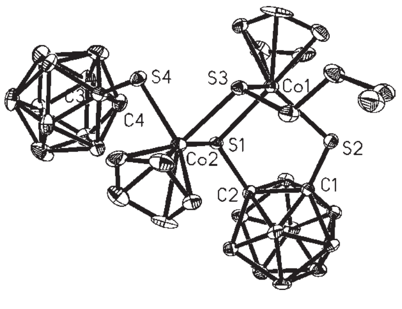

Figure 1. Molecular structure of **3** with 30% probability ellipsoids. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Co1−S1 2.260(2), Co1−S2 2.244(2), Co1−S3 2.259(2), Co2−S1 2.285(2), Co2−S3 2.248(2), Co2−S4 2.274(2), C1−C2 1.682(9), C3−C4 1.633(11), Co1−S1−Co2 95.71(8), Co2−S3−Co1 96.79(8), S2−Co1−S1 92.52(8), S3−Co1−S1 83.85(8), and S3−Co2−S1 83.51(7).

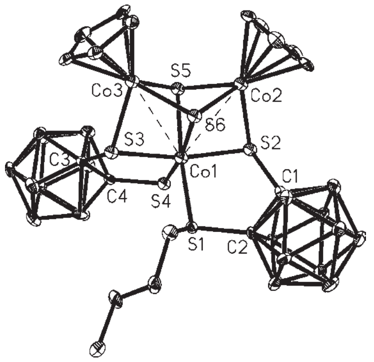

Figure 2. Molecular structure of **4** with 30% probability ellipsoids. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Co1−Co3 2.9267(9), Co2−Co1 2.9185(8), Co1−S6 2.2771(12), Co2−S6 2.2248(12), Co3−S6 2.2415(12), S5−Co3 2.2247(13), S5−Co2 2.2311(11), S5−Co1 2.2499(11), C1−C2 1.688(5), C3−C4 1.657(5), Co2−Co1−Co3 69.13(2), Co3−S5−Co2 96.19(4), Co2−S6−Co3 95.89(4), S5−Co3−S6 75.38(4), S6−Co2−S5 75.59(4), and S5−Co1−S6 74.20(4).

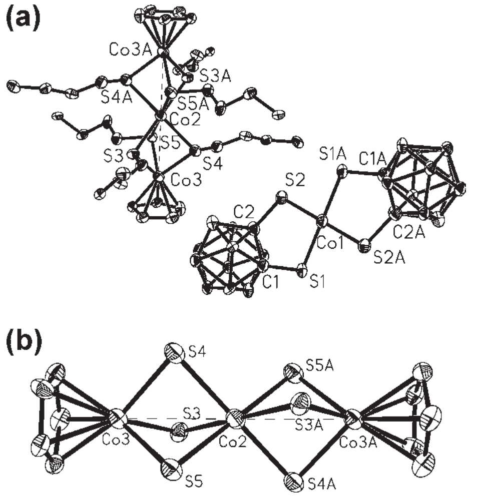

Figure 3. (a) Molecular structure of **5** with 30% probability ellipsoids. Hydrogen atoms were omitted for clarity. (b) View of the CpCo(μ_2-S)$_3$Co(μ_2-S)$_3$CoCp core in **5**.

Compounds 3 and 4. In contrast to the generation of compounds **1** and **2** (see Scheme 1), if excess sulfur and CpCo(CO)I_2 are used, for instance, the reaction of *ortho*-carborane, *n*-butyl lithium, sulfur, and CpCo(CO)I_2 in a ratio of 1:2.2:4:2 leads to products **1** (28%), **3** (8%), and **4** (17%) (Scheme 1). The molecular structure of **3** was solved by single-crystal X-ray analysis as given in Figure 1. It shows a sulfur-bridged dinuclear cobalt(III) structure consisting of one chelating $(S_2C_2B_{10}H_{10})^{2-}$, one $(SC_2B_{10}H_{11})^{-}$, and one $(n\text{-BuS})^{-}$ ligands. In solution, its ^{1}H NMR spectrum indicates a butyl group in the range of 0.94−2.79 ppm and a broad singlet at 4.15 ppm, assigned to the C−H unit of the *ortho*-carborane monothiolato ligand. Compound **3** can be considered as an adduct of the two 16*e* half-sandwich monomers CpCo($S_2C_2B_{10}H_{10}$)

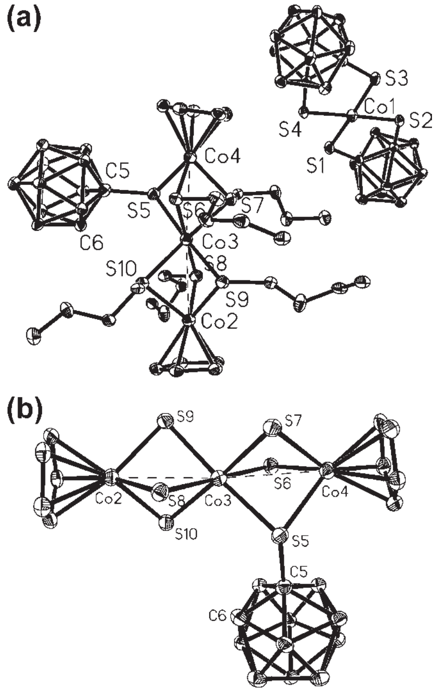

Figure 4. (a) Molecular structure of **6** with 30% probability ellipsoids. Hydrogen atoms were omitted for clarity. (b) View of the $CpCo(\mu_2\text{-}S)_3Co(\mu_2\text{-}S)_3CoCp$ core in **6**.

(**1**) and $CpCo(SC_4H_9)(SC_2B_{10}H_{11})$. The former is thermally stable, however, the latter is not, but the addition of both makes each cobalt center meet the 18-electron rule. This manner of dimerization is identical to those of cobalt–dithiolene complexes previously described,[17−19] presenting either planar or nonplanar $Co_2(\mu\text{-}S)_2$ cores. The analogous chemistry also has been described for Mn(III), Fe(III), and Ni(II).[8,20] Note that the solid-state structure of **3** possesses a rhombic $Co_2(\mu\text{-}S)_2$ core with a Co···Co distance of 3.370 Å, which is in the range of 3.289−3.506 Å observed in the previously reported analogues, $[CpCo(Q_2C_6H_4)]_2$ (Q = S, Se)[17] and $\{[(\eta^5\text{-}C_5H_4)(CH_2)_2OCH_3]Co(Q_2C_2B_{10}H_{10})\}_2$ (Q = Se).[18]

Suitable crystals of **4** were obtained from $CHCl_3$/petroleum ether at ambient temperature. Its solid-state structure displays a sulfur-bridged trinuclear cobalt(III) cluster, as shown in Figure 2, having a cuboidal $Co_3(\mu_3\text{-}S)_2(\mu\text{-}S)_2$ core. In **4** two of the three cobalt atoms present a similar coordination sphere, with each metal bonded to two μ_3-S atoms, one sulfur atom of the individual carborane dithiolato ligands and one Cp ligand, giving rise to a three-legged piano-stool geometry. The Co···Co distance of 3.316 Å between the two CpCo units is much longer than a typical Co−Co bond length in a range of 2.30−2.95 Å reported in literature.[21,22] The third cobalt atom has a coordination environment consisting of six sulfur atoms in a distorted octahedral geometry, being coordinated by four μ_3-S atoms and two sulfur atoms from the two different carborane thiolato ligands. The Co···Co distances between each CpCo unit and the third cobalt atom are 2.919 and 2.927 Å, respectively. Note that a butyl unit is linked to one carborane thiolato ligand at the sulfur site. The ^{1}H NMR data show a *n*-butyl unit and two types of Cp groups, and the mass spectrum gives a molecular ion peak. These are indicative of the consistence of both the solid-state structure and the structure in solution.

Table 2. Selected Bond Lengths and Bond Angles for the Cations in **5** and **6**

5 (symmetry code: 1 − *x*, − *y*, 2 − *z*)		**6**		Δ[a]
		Bond Lengths (Å)		
Co2−Co3	2.9549(14)	Co2−Co3	2.9618(8)	−0.0069
Co2−Co3A	2.9549(14)	Co3−Co4	2.9929(8)	−0.038
Co2−S3	2.2661(17)	Co3−S5	2.3435(11)	−0.0774
Co2−S4	2.2556(14)	Co3−S7	2.2387(12)	0.0169
Co2−S5	2.2626(15)	Co3−S6	2.2700(11)	−0.0074
Co2−S3A	2.2661(17)	Co3−S9	2.2490(11)	0.0171
Co2−S4A	2.2556(14)	Co3−S10	2.2812(11)	−0.0256
Co2−S5A	2.2626(15)	Co3−S8	2.2685(11)	−0.0059
		Bond Angles (deg)		
Co3−Co2−Co3A	180.0	Co2−Co3−Co4	175.47(2)	4.53
S4−Co2−S3	80.06(5)	S7−Co3−S5	78.84(4)	1.22
S4−Co2−S5	79.72(5)	S7−Co3−S6	81.70(4)	−1.98
S5−Co2−S3	80.73(4)	S6−Co3−S5	79.72(4)	1.01
S4A−Co2−S3A	80.06(5)	S9−Co3−S10	80.35(4)	−0.29
S4A−Co2−S5A	79.72(5)	S8−Co3−S10	80.38(4)	−0.66
S5A−Co2−S3A	80.73(4)	S9−Co3−S8	81.45(4)	−0.72

[a] Δ is the difference of the value between **5** and **6**.

Compounds 5 and 6. In contrast to the generation of complexes **3** and **4**, if excess *n*-butyl lithium and sulfur are used, for instance, the reaction of *ortho*-carborane, *n*-butyl lithium, sulfur, and $CpCo(CO)I_2$ in a ratio of 1:5:5:2 leads to products **1** (13%), **5** (26%), and **6** (6%) (Scheme 1). The solid-state structures of **5** and **6** were determined by X-ray analysis as shown in Figures 3a and 4a, and the selected bond distances and bond angels are listed in Table 2 for comparison. Both are unprecedented ionic compounds, consisting of a sulfur-bridged trinuclear cobalt cation and a four-coordinate $[Co(S_2C_2B_{10}H_{10})_2]^-$ anion.

In **5**, the three cobalt atoms of the cation are in a linear-type arrangement bridged by six *n*-butyl thiolato ligands (Figure 3a and b). The two outer cobalt atoms are

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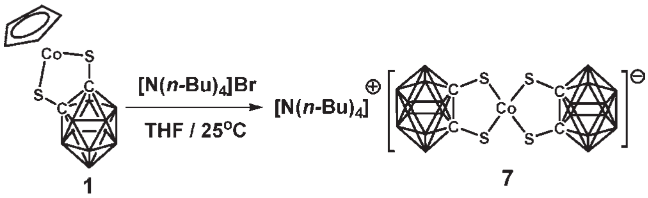
coordinated by three $(n\text{-BuS})^-$ ligands and one Cp ligand, respectively, generating a half-sandwich structure with the $\text{CpCo}(n\text{-BuS})_3$ moiety. Whereas the central cobalt atom, occupying a crystallographic inversion center, is coordinated by six $(n\text{-BuS})^-$ ligands in a distorted octahedral geometry. The Co···Co···Co angle is 180°, and the Co···Co distance is 2.955 Å, longer than 2.30−2.95 Å for a typical Co−Co bond.[21,22] Each cobalt has a charge of +3, thus the cation has a charge of −1. Such a cation is the first example, even though linear-type trinuclear cobalt species[23] and sulfur-bridged trinuclear cobalt compounds have been previously reported.[5,24] Alkanethiolato ligand is still rarely utilized to design thiolate-bridged supramolecular structures.[25]

As shown in Figure 3a, the anion $[\text{Co}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10})_2]^-$ in **5** has a square-planar geometry.[26] It is known that the majority of Co(III) compounds are observed with an octahedral configuration at the metal center.[27] This is the second example after the one in the compound $(\text{Cp}_2\text{Co})^+[\text{Co}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10})_2]^-$ (**2** in Scheme 1),[15] where the generation of the anion is driven by the generation of the stable cation $(\text{Cp}_2\text{Co})^+$. Here the unusual cation $[\text{CpCo}(n\text{-BuS})_3\text{Co}(n\text{-BuS})_3\text{CoCp}]^+$ may also play the same role in the generation of **5** as $(\text{Cp}_2\text{Co})^+$ in **2**.

In contrast to **5**, the only difference in **6** lies in the replacement of a *n*-butyl thiolato ligand by an *ortho*-carborane monothiolato ligand $(\text{SC}_2\text{B}_{10}\text{H}_{11})^-$ in the cation (Figure 4a). This leads to asymmetry of the sulfur-bridged trinuclear cobalt core (Figure 4b). And the arrangement of Co···Co···Co is no longer linear, changing from 180° in **5** to 175.5° in **6**. The mean Co···Co distance is 0.022 Å longer than that of the cation in **5**. In the ^{1}H NMR spectrum the *n*-butyl groups in **6** show much more peaks than those in **5**, reflecting the change in symmetry of the cation. An *ortho*-carborane monothiolato group has been reported as a μ-S bridge.[13a] However, in our system all attempts to achieve more *ortho*-carborane monothiolato ligands instead of *n*-butyl thiolato ligands in **6** were unsuccessful. It should be noted that the immediate surroundings of cobalt in the anion $[\text{Co}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10})_2]^-$ deviate from planarity. The dihedral angle between the planes Co1/S1/S2/C1/C2 and Co1/S3/S4/C3/C4 is 6.3°. Some selected bond lengths and angles are presented in Table 2 in comparison with those in **5**.

Scheme 2. Synthesis of Compound **7**



Both **5** and **6** were also studied by spectroscopic techniques. The ESI spectra demonstrate the cations at 842 for $[(\text{CpCo})_2\text{Co}(\text{SC}_4\text{H}_9)_6]^+$ in **5** and at 928 for $[(\text{CpCo})_2\text{Co}(\text{SC}_2\text{B}_{10}\text{H}_{11})(\text{SC}_4\text{H}_9)_5]^+$ in **6** and the anions at 472 for $[\text{Co}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10})_2]^-$ in both compounds as the only molecular ion peaks, respectively. Both ^{11}B NMR spectra show three characteristic signals around 80, 35, and −25 ppm, out of the typical range of 0∼−15 ppm for an unsubstituted carborane cage.[14,15,28] In the ^{1}H NMR spectra four characteristic broad signals around −9.80, −2.28, 4.00, and 7.81 ppm were observed, corresponding to the B−H units of the carborane cage in both **5** and **6**. The unusual NMR data are attributed to the paramagnetic behavior of the anion $[\text{Co}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10})_2]^-$, where the Co(III) metal center has unpaired electrons caused by the strong coordination capability of the chelating *ortho*-carborane dithiolato ligand. Related anionic square-planar cobalt(III) and other transition-metal dithiolene or dithiolate compounds have been extensively investigated both in magnetic behavior and theoretical calculations.[8,29,30]

The ionic compounds of **5** and **6** are unusual, thus their origins are of interest. We assume that the generation of the stable and soluble cations in **5** and **6** is the driving force, as proposed in the generation of compound **2**.[15] To testify this we designed a experiment shown in Scheme 2.

Reaction of 1 with [N(*n*-Bu)$_4$]Br. Addition of 1 equiv of $[\text{N}(n\text{-Bu})_4]\text{Br}$ to the tetrahydrofuran (THF) solution of $\text{CpCoS}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ (**1**) at ambient temperature caused an immediate color change from deep-red to deep-green, and a new compound **7**, $[\text{N}(n\text{-Bu})_4]^+[\text{Co}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10})_2]^-$, was isolated in a yield of 43% based on **1** (Scheme 2). In **7**, the square-planar cobalt(III) monoanion, $[\text{Co}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10})_2]^-$, can be isolated as a $[\text{N}(n\text{-Bu})_4]^+$ salt in a ratio of 1:1, as determined by X-ray crystallography shown in Figure 5. Its NMR data demonstrate a paramagnetic species as well since they are exactly parallel to the observations in the compounds **5** and **6**. Thus the paramagnetic property in **7** obviously arises from the

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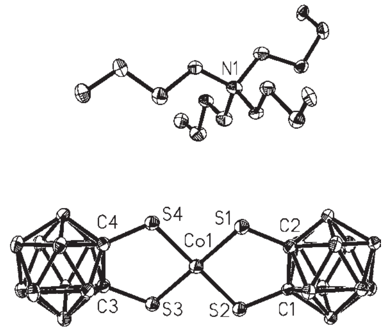

Figure 5. Molecular structure of **7** with 30% probability ellipsoids. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): C1−C2 1.638(4), Co1−S1 2.1785(10), Co1−S2 2.1581(11), Co1−S3 2.1624(11), Co1−S4 2.1653(10), S2−Co1−S1 94.82(4), and S3−Co1−S4 95.22(4).

square-planar anion $[Co(S_2C_2B_{10}H_{10})_2]^-$. This further verifies that the unconventional magnetic behavior in **5** and **6** is generated from the anion $[Co(S_2C_2B_{10}H_{10})_2]^-$, rather than their metallic cations.

More importantly, the facile conversion from **1** to **7** in the presence of [N(*n*-Bu)$_4$]Br gives experimental evidence on the generation of $[Co(S_2C_2B_{10}H_{10})_2]^-$ driven by a comparable countercation.[31] Thus the same occurs in the cases of compounds **2**, **5**, and **6**, while the individual cation is copresent with $CpCoS_2C_2B_{10}H_{10}$, **1**, in the reaction system. Therefore, a square-planar coordination geometry of $[Co(S_2C_2B_{10}H_{10})_2]^-$ is favored in comparison with the neutral 16*e* complex **1**. In addition, **7** can be isolated after chromatograph by elution with CH_2Cl_2/petroleum ether if [N(*n*-Bu)$_4$]Br is added to **2**, since **7** vs **2** is less polar and more soluble in CH_2Cl_2.

Summary

Compounds **1**−**6**, including the new products **3**−**6**, were isolated from the reaction system of *ortho*-carborane, *n*-butyl lithium, sulfur, and $CpCo(CO)I_2$. The product type is dependent on the ratio of the reactants used. Compounds **5** and **6**, topologically precedent, display an unusual class of multinuclear cobalt(III) species consisting of a large sulfur-bridged trinuclear cobalt(III) cation and a four-coordinate cobalt(III) anion $[Co(S_2C_2B_{10}H_{10})_2]^-$. The generation of compound **7** provides the insight into understanding the charge, paramagnetic origin of the ionic compounds as well as the driving force for the generation of the ionic compounds.

Experimental Section

General Procedures. The preparative work was carried out under an argon atmosphere using standard Schlenk techniques. Solvents were freshly distilled under nitrogen from either sodium or calcium hydride prior to use. *n*-Butyllithium (2.0 M in cyclohexane, Aldrich), *ortho*-carborane (1,2-$C_2B_{10}H_{12}$), and other chemicals were used as commercial products without further purification. $CpCo(CO)I_2$ was prepared according to literature.[32] Elemental analysis was performed in an elementar vario EL III elemental analyzer. NMR data were obtained on a Bruker DRX-500 spectrometer. Chemical shifts were given with respect to $CHCl_3/CDCl_3$ (δ ^1H = 7.24, δ ^{13}C = 77.0) and external Et_2O-BF_3 (δ ^{11}B = 0). The IR spectra were recorded on a Bruker Vector 22 spectrophotometer with KBr pellets in the 4000−400 cm^{-1} region. Matrix-assisted laser desorption/ionization (MALDI) in a linear time-of-flight mass spectrometry (MS) was recorded in a Bruker autoflex TOF/TOF equipped with an acquisition operation mode of reflector and signal averaging of 30 laser shots. Finnigan MAT TSQ7000 was used for ESI-MS.

Synthesis of 3 and 4. To a solution of *ortho*-carborane (57.6 mg, 0.4 mmol) in dry diethylether (20 mL) at −10 °C, a 2.0 M solution of *n*-BuLi (0.44 mL, 0.88 mmol) was added. After 30 min sulfur (51.2 mg, 1.6 mmol) was added, followed by an addition of $CpCo(CO)I_2$ (324.6 mg, 0.8 mmol) in dry THF (30 mL) at −10 °C. The resulting mixture was stirred for 2 h accompanied by the temperature gradually rising to ambient temperature. Then the solvents were evaporated under reduced pressure. The residue was chromatographed on silica gel to give compounds **1** (18.5 mg, 28%), **3** (11.6 mg, 8%), and **4** (28.6 mg, 17%) based on *ortho*-carborane. Compound **3**: gray solid, mp (dec.) 173 °C. ^1H NMR ($CDCl_3$): δ 0.94 (t, 3H, CH_3), 1.14 (m, 2H, CH_2), 1.74 (m, 2H, CH_2), 2.79 (m, 2H, SCH_2) for *n*-Bu group, 4.15 (s, br, 1H, C−H of carborane), 5.10 (s, 5H, Cp), 5.32 (s, 5H, Cp). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −0.8 (2B), −4.4 (2B), −5.6 (3B), −8.3 (5B), −9.1 (5B), −11.2 (3B). MALDI-TOF-MS: (*m*/*z*) 720.329 (M + H$^+$, 40%). IR (KBr, cm^{-1}): 2588 (ν_{B-H}). Anal. calcd for $C_{18}H_{40}B_{20}Co_2S_4$: C, 30.07; H, 5.61. Found: C, 29.31; H, 5.24. Compound **4**: caesious solid, mp (dec.) 201 °C. ^1H NMR ($CDCl_3$): δ 1.02 (t, 3H, CH_3), 1.16 (m, 2H, CH_2), 1.81 (m, 2H, CH_2), 2.85 (m, 2H, SCH_2) for *n*-Bu group, 5.06 (s, 5H, Cp), 5.12 (s, 5H, Cp). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −9.2 (2B), −11.5 (12B), −14.7 (6B). ESI-MS (*m*/*z*): 829.83, [M−$CHCl_3$]. IR (KBr, cm^{-1}): 2578 (ν_{B-H}). Anal. calcd for $C_{18}H_{39}B_{20}Co_3S_6\cdot CHCl_3$: C, 23.76; H, 4.20. Found: C, 23.14; H, 3.88.

Synthesis of 5 and 6. To a solution of *ortho*-carborane (57.6 mg, 0.4 mmol) in dry diethylether (20 mL) at −10 °C, a 2.0 M solution of *n*-BuLi (1 mL, 2 mmol) was added and stirred for 30 min. Then sulfur (64 mg, 2 mmol) was added and stirred for 10 min at −10 °C, followed by an addition of $CpCo(CO)I_2$ (324.6 mg, 0.8 mmol) in dry THF (30 mL) at −10 °C. The resulting mixture was stirred from −10 °C to ambient temperature for 2 h. Then the solvents were evaporated, and the residue was chromatographed on silica gel to give **1** (17.2 mg, 13%), **5** (68.3 mg, 26%), and **6** (11.2 mg, 6%) based on *ortho*-carborane. Compound **5**: red solid, mp (dec.) 185 °C. ^1H NMR ($CDCl_3$): δ −9.81 (q, br, 4H), −2.27 (d, br, 4H) for carborane, 0.98 (t, 18H, CH_3), 1.17 (m, 12H, CH_2), 2.27 (m, 12H, CH_2), 2.56 (m, 12H, SCH_2) for six *n*-Bu groups, 3.92 (s, 10H, Cp), 3.97 (q, br, 8H), 7.83 (q, br, 4H) for carborane. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 80.6 (10B), 35.0 (6B), −25.4 (4B). ESI-MS (positive and negative ion modes, *m*/*z*): 472 for $[Co(S_2C_2B_{10}H_{10})_2]^-$ and 842 for $[(CpCo)_2Co(SC_4H_9)_6]^+$. IR (KBr, cm^{-1}): 2577 (ν_{B-H}). Anal. calcd for $C_{38}H_{84}B_{20}Co_4S_{10}\cdot H_2O$: C, 34.27; H, 6.51. Found: C, 33.68; H, 6.73. Compound **6**: black solid, mp (dec.) > 350 °C. ^1H NMR ($CDCl_3$): δ −9.80 (q, br, 6H), −2.28 (d, br, 6H), for carborane, 0.48 (t), 0.59 (t), 0.74−0.79 (m), 0.87−0.91 (m), 0.99 (m), 1.15 (m), 1.25 (m), 1.43 (m), 1.57 (m), 1.65 (m), 1.77 (m), 1.89 (m), 1.94 (m), 2.10 (m), 2.29 (m) for five *n*-Bu groups, 3.68 (s, 10H, Cp), 3.82 (s, 1H, C−H of carborane), 3.95 (q, br, 12H), 7.80 (q, br, 6H) for carborane. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 80.7 (15B), 35.1 (9B), −25.5 (6B). ESI-MS (positive and negative ion modes, *m*/*z*): 472 for $[Co(S_2C_2B_{10}H_{10})_2]^-$ and 928 for $[(CpCo)_2Co(SC_2B_{10}H_{11})(SC_4H_9)_5]^+$. IR (KBr, cm^{-1}): 2565 (ν_{B-H}). Anal. calcd for $C_{36}H_{86}B_{30}Co_4S_{10}\cdot 0.5H_2O$: C, 30.69; H, 6.22. Found: C, 30.11; H, 6.37.

Synthesis of 7. To a solution of $CpCoS_2C_2B_{10}H_{10}$ (**1**) (66.0 mg, 0.2 mmol) in dry THF (20 mL) at ambient temperature was added [N(*n*-Bu)$_4$]Br (64.6 mg, 0.2 mmol), the color changed immediately

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from deep-red to deep-green. Then the solvent was evaporated under reduced pressure, and the resulting residue was chromatographed on silica gel to give compound **7** (30.7 mg, 43%) based on **1**. Compound **7**: green solid, mp (dec.) 215 °C. ^{1}H NMR ($CDCl_3$): δ −9.79 (q, br, 4H), −2.29 (d, br, 4H) for carborane, −0.30 (s, br, 8H, CH_2), −0.15 (s, br, 12H, CH_3), 0.38 (s, br, 8H, CH_2), 0.99 (s, br, 8H, CH_2) for four *n*-Bu groups, 4.00 (q, br, 8H), 7.85 (q, br, 4H) for carborane. ^{11}B{^{1}H} NMR ($CDCl_3$): δ 80.4 (10B), 34.9 (6B), −25.5 (4B). ESI-MS (positive and negative ion modes, *m*/*z*): 472 for $[Co(S_2C_2B_{10}H_{10})_2]^-$ and 242 for $[N(n\text{-}Bu)_4]^+$. IR (KBr, cm^{-1}): 2580 (ν_{B-H}). Anal. calcd for $C_{20}H_{56}B_{20}CoNS_4$: C, 33.64; H, 7.90; N, 1.96. Found: C, 33.15; H, 7.61; N, 1.77.

X-ray Structure Determinations.[33] Diffraction data were collected on a Bruker SMART Apex II CCD diffractometer using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. During the intensity data collection, no significant decay was observed. The intensities were corrected for Lorentz polarization effects and empirical absorption with the SADABS program. The structures were solved by direct methods using the SHELXL-97 program. All nonhydrogen atoms were found from the different Fourier syntheses. The hydrogen (H) atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All calculations were performed using the Bruker Smart program. Crystallographic data and details of data collection and structure refinements of **3**−**7** are provided in the Table 1 and the CIF files of the Cambridge Crystallographic Data Centre (CCDC; 727873−727876 and 758892).

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Supporting Information Available: CIF files giving X-ray crystallographic data for the structure determinations of compounds **3**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[33] *SMART*, version 5.0; *SAINT*, version 6; *SHELXTL*, version 6.1; *SADABS*, version 2.03; Bruker AXS, Inc.: Madison, WI, 2000.