2738 *Organometallics* **1999,** *18,* 2738−2740

Addition Reactions of the Novel Mononuclear Dithio-*o*-carboranylcobalt(III) Complex (η^5-C_5H_5)Co(η^2-$S_2C_2B_{10}H_{10}$)

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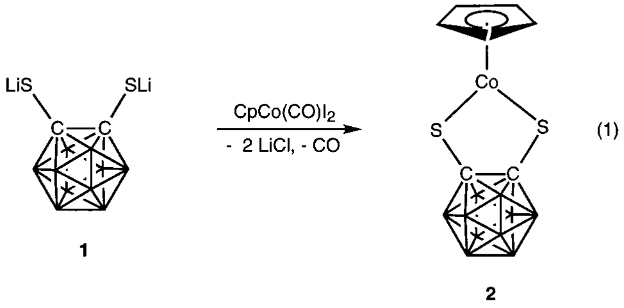
Received April 16, 1999

*Summary: The mononuclear 16-electron dithio-o-carboranylcobalt(III) complex CpCo($S_2C_2B_{10}H_{10}$) (**2**) was obtained by the reaction of CpCo(CO)I_2 with dilithium dithio-o-carborane, $Li_2[S_2C_2B_{10}H_{10}]$ (**1**). Complex **2** reacts with a variety of substrates such as CpCo(C_2H_2)$_2$, alkynes, and a diazoalkane, generating a new class of dithio-o-carboranylcobalt(III) compounds incorporating a CpCo unit and alkene and alkylidene ligands.*

The synthesis and study of organometallic complexes possessing an ancillary dithio-*o*-carboranyl ligand have continued to receive attention.[1] To further develop the chemistry of dithio-*o*-carborane and assess its ability to form reactive transition-metal complexes, we examined its reactions with a selection of cyclopentadienyl transition-metal complexes. In particular, we have been interested in obtaining coordinatively unsaturated low-valent cobalt compounds, capable of binding biologically interesting substrates such as acetylene, CO, diazenes, or dinitrogen. It was, therefore, of interest to investigate the possibility of synthesizing such coordinatively unsaturated low-valent cobalt compounds bearing both bulky *o*-carborane[2] and cyclopentadienyl units that might potentially stabilize the 16-electron metal center.[3] Here we report the synthesis of the mononuclear 16-electron dithio-*o*-carboranylcobalt(III) complex CpCo($S_2C_2B_{10}H_{10}$) (**2**), as well as its reactivity. Included are the addition of organic and organometallic compounds into the Co−S bond of **2**.

The reaction of CpCo(CO)I_2 (3 mmol) with the lithium salt $Li_2[S_2C_2B_{10}H_{10}]$ (**1**) (3.2 equiv) in tetrahydrofuran (THF) afforded an 83% yield of **2** as an air-stable green solid (eq 1).



Analytical and spectroscopic data[4] support the formulation of **2** as a mononuclear 16-electron dithio-*o*-carboranylcobalt(III) complex, and this formulation has been confirmed by an X-ray structural study[5] which showed coordinative unsaturation in the steric sense around the cobalt center in the two-legged piano-stool geometry (Figure 1). Such a monomeric 16-electron thiolatocobalt(III) structure has been reported for the benzenedithiolate complex CpCo(μ-$S_2C_6H_4$).[6] A reversible mononuclear−dinuclear interconversion in the benzenedithiolate complexes was also reported by Miller et al. for CpCo(μ-$S_2C_6H_4$).[7] We have isolated the mononuclear cobalt(III) analogue **2** and have found that it exists only in the monomeric form. Formation of a dinuclear species in solution was not observed. It is recognized that π donation by a lone pair of electrons on the coordinated sulfur atom alleviates such electron deficiency and thus the coordinative unsaturation around the transition-metal center.[8] Consequently, this geometry suggests that some of multiple-bond character is present in the Co−S bonds of complex **2**. To verify the nature of the Co−S bonds, the addition reactions of several organic and organometallic compounds to **2** have been investigated.

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(4) Data for **2**. Anal. Calcd for $C_7H_{15}B_{10}S_2Co$: C, 25.45; H, 4.58. Found: C, 25.51; H, 4.63. IR (KBr, cm^{-1}): ν(BH), 2554. ^{1}H NMR (200.13 MHz, ppm, CDCl$_3$): 5.26 (s, 5H, C_5H_5). ^{13}C{^{1}H} NMR (50.3 MHz, ppm, CDCl$_3$): 81.81 (s, C_5H_5).

(5) Crystallographic data for **2**: $a = 11.2866(12)$ Å, $b = 12.677(6)$ Å, $c = 13.2760(19)$ Å, $\alpha = 114.12(3)°$, $\beta = 104.985(10)°$, and $\gamma = 107.18(3)°$ with $Z = 2$ in space group $P1$ (No. 2). R1 (wR2) = 0.1751 (0.5016) for 5070 data with $I > 2.0\sigma(I)$ and anisotropic refinements of the model with idealized hydrogen atoms.

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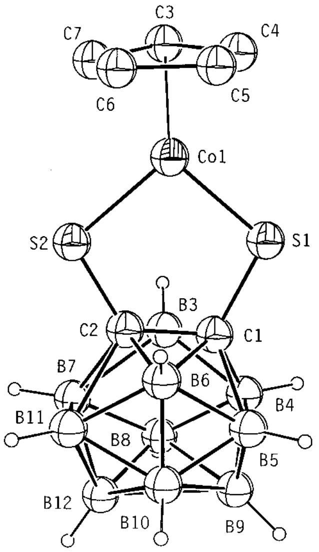

Figure 1. ORTEP drawing of **2** with the numbering scheme.

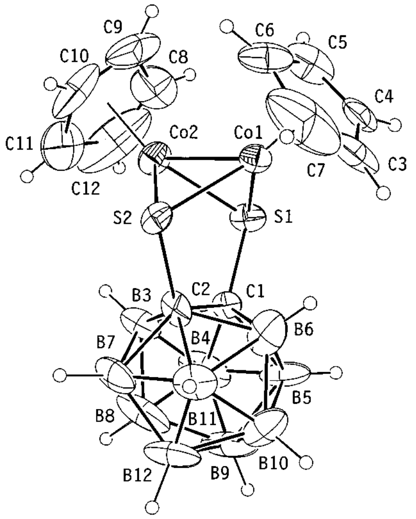

Figure 2. ORTEP drawing of **3** with the numbering scheme.

The reaction of **2** with 1 equiv of $CpCo(C_2H_4)_2$ in toluene at −78 °C proceeded smoothly, as monitored by the change of the green solution to blue. The blue complex **3** was isolated in 90% yield as a crystalline solid after precipitation from toluene/hexanes. Exact mass measurements on the parent ion of **3** support the formulation of the compound as $[(C_5H_5)Co]_2S_2C_2B_{10}H_{10}$, indicating that a CpCo unit has been incorporated into the Co−S bond of the cobaltadithia-*o*-carborane ring.[9]

Indeed, an X-ray study[10] of **3** showed it to be the product of the addition of a CpCo unit into the Co−S bond in **2**. As shown in Figure 2, the structure of **3** consists of binuclear $(CpCo)_2$ fragments in which each CpCo unit is attached to both sulfur atoms of a 1,2-dithio-*o*-carboranyl ligand **1**.

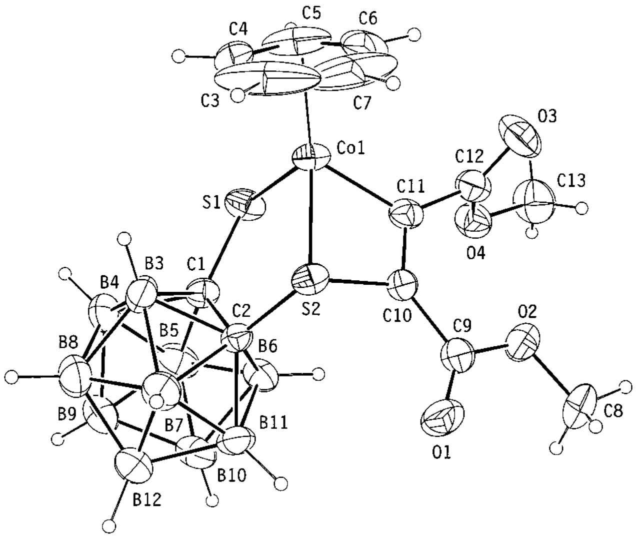

Figure 3. ORTEP drawing of adduct **4a**. Selected bond lengths (Å) and angles (deg): Co(1)−S(1) 2.247(2), Co(1)−S(2) 2.246(1), Co(1)−C(11) 1.912(5), C(10)−C(11) 1.340(7), S(2)−C(10) 1.777(5), S(1)−C(1) 1.778(5), S(2)−C(2) 1.794(5), C(1)−C(2) 1.659(6); S(1)−Co(1)−S(2) 93.51(5), S(2)−Co(1)−C(11) 72.4(2), S(1)−Co(1)−C(11) 92.8(1). The centers of the five atoms of the CoS_2C_2 moiety [Co(1), S(1), S(2), C(1), C(2)] are within 0.15 Å of a plane. The angle between planes [Co(1), S(2), C(10), C(11)] and CoS_2C_2 is 81.0(1)°.

Compound **2** was found to be a good precursor for other addition reactions. Thus, treatment of **2** with 1−2 equiv of an alkyne in refluxing benzene for 2 h gave novel alkyne adduct complexes, $CpCo(R_1C{=}CR_2)(S_2C_2B_{10}H_{10})$, **4**, in moderate yield (Scheme 1).[11] Adducts **4a**−**c** were isolated as air-stable, microcrystalline solids and were spectroscopically characterized.[12] Each of the adducts shows the expected ^1H and ^{13}C NMR signals and is a 1:1 adduct of the cobaltadithia-*o*-carborane and alkene groups by elemental analyses. The ^1H NMR spectrum of adduct **4a** showed two nonequivalent ^1H signals of the OCH_3 groups of the ester and two nonequivalent ^{13}C signals of the ester CO groups, in agreement with molecular structure of this adduct as determined by single-crystal X-ray analysis (Figure 3).[13]

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(9) Data for **3**. Exact mass calcd. for $^{11}B_{10}{}^{12}C_{12}{}^{59}Co_2{}^{1}H_{20}{}^{32}S_2$ 456.0601, found 456.0607. Anal. Calcd for $C_{12}H_{20}B_{10}S_2Co_2$: C, 31.72; H, 4.44. Found: C, 31.69; H, 4.49. IR (KBr, cm^{-1}): ν(BH), 2586. ^1H NMR (200.13 MHz, ppm, $CDCl_3$): 5.00 (s, 5H, $C_5\mathit{H}_5$). $^{13}C\{^1H\}$ NMR (50.3 MHz, ppm, $CDCl_3$): 77.79 (s, C_5H_5).

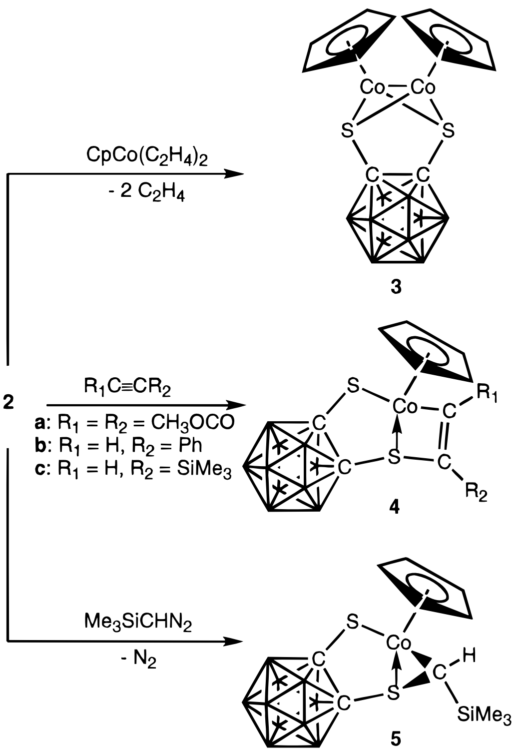
(10) Crystallographic data for **3**: $a = 15.981(4)$ Å, $b = 55.478(17)$ Å, $c = 12.0562(17)$ Å, and $\beta = 115.063(16)°$ with $Z = 4$ in space group *Cc* (No. 9). R1 (wR2) = 0.0630 (0.1685) for 9948 data with $I > 2.0\sigma(I)$ and anisotropic refinements of the model with idealized hydrogen atoms.

(11) In a typical run, **2** (0.33 g, 1.0 mmol) and dimethyl acetylenedicarboxylate (0.25 mL, 2.0 mmol) were dissolved in benzene (10 mL) under N_2, and the solution was heated ar reflux for 2 h. Addition of hexane to the resulting dark red solution afforded **4a** as dark red crystals (0.43 g, 0.91 mmol, 91%). Complexes **4b** and **4c** were obtained with essentially the same procedure in 87% and 23% yields, respectively.

(12) Data for **4a**. Anal. Calcd for $C_{13}H_{21}B_{10}O_4S_2Co$: C, 35.05; H, 4.48. Found: C, 35.10; H, 4.52. IR (KBr, cm^{-1}): ν(BH) 2580; ν(C=O), 1710; ν(C=C), 1579. ^1H NMR (200.13 MHz, ppm, $CDCl_3$): 5.23 (s, 5H, $C_5\mathit{H}_5$), 3.94 (s, 3H, $OC\mathit{H}_3$), 3.77 (s, 3H, $OC\mathit{H}_3$). $^{13}C\{^1H\}$ NMR (50.3 MHz, ppm, $CDCl_3$): 171.07 (s, $CH_3O\mathit{C}O$), 155.25 (s, $CH_3O\mathit{C}O$), 118.84 (CH_3-$OCO\mathit{C}{=}$), 98.40 ($CH_3OCO\mathit{C}{=}$), 86.70 (s, C_5H_5), 52.85 (s, $O\mathit{C}H_3$), 52.71 (s, $O\mathit{C}H_3$). Data for **4b**. Anal. Calcd for $C_{15}H_{21}B_{10}S_2Co$: C, 41.66; H, 4.89. Found: C, 41.73; H, 4.95. IR (KBr, cm^{-1}): ν(BH), 2600; ν(C=C), 1488; ν(C=C), 1442. ^1H NMR (200.13 MHz, ppm, $CDCl_3$): 7.30 (s, 5H, $C_6\mathit{H}_5$), 4.51 (s, 5H, $C_5\mathit{H}_5$), 2.36 (s, 1H, $C{=}C\mathit{H}$). $^{13}C\{^1H\}$ NMR (50.3 MHz, ppm, $CDCl_3$): 192.05 (s, $HC{=}\mathit{C}{-}C_6H_5$), 176.64 (s, $H\mathit{C}{=}C{-}C_6H_5$), 127.58 (m, C_6H_5), 84.96 (s, C_5H_5). Data for **4c**. Anal. Calcd for $C_{12}H_{25}B_{10}S_2SiCo$: C, 33.63; H, 5.88. Found: C, 33.68; H, 5.93. IR (KBr, cm^{-1}): ν(BH), 2586; ν(C=C), 1401. ^1H NMR (200.13 MHz, ppm, $CDCl_3$): 5.00 (s, 5H, $C_5\mathit{H}_5$), 1.91 (s, 1H, $C{=}C\mathit{H}$), 0.29 (s, 9H, $Si(C\mathit{H}_3)_3$). $^{13}C\{^1H\}$ NMR (50.3 MHz, ppm, $CDCl_3$): 146.51 (s, $H\mathit{C}{=}C{-}Si(CH_3)_3$), 77.92 (s, C_5H_5), 1.78 (s, $Si(\mathit{C}H_3)_3$).

(13) Crystallographic data for **4a**: $a = 10.0447(7)$ Å, $b = 11.5109(6)$ Å, $c = 12.0399(5)$ Å, $\alpha = 115.980(3)°$, $\beta = 106.281(5)°$, and $\gamma = 102.960(5)°$ with $Z = 2$ in space group *P*1 (No. 2). R1 (wR2) = 0.0480 (0.1205) for 4325 data with $I > 2.0\sigma(I)$ and anisotropic refinements of the model with idealized hydrogen atoms.

Scheme 1



This structure results from the addition of $R_1C{\equiv}CR_2$ into the Co−S bond of $CpCo(S_2C_2B_{10}H_{10})$, **2**. In adduct **4a**, the alkene moiety thus formed bridges between Co and S of the metalladithia-*o*-carborane ring without breaking the Co−S bond [Co(1)−S(1) = 2.247(2) Å, Co(1)−S(2) = 2.246(1) Å]. This adduct has a piano-stool structure consisting of a four-membered and a five-membered ring. The central metal is coordinatively saturated, in contrast to the pentacoordinate structure of complex **2**. In this adduct, the plane of the C(11)−Co(1)−S(2)−C(10) four-membered ring is almost perpendicular to the plane of the almost planar dithia-*o*-carborane ring. Such an addition of an alkyne into an M−S bond has been observed in Sugimori's work on the chemoselective addition of dimethyl acetylenedicarboxylate to the Rh−S bond in a rhodium-catalyzed reaction.[14]

Similar to the reactions between **2** and alkynes, the cobaltadithia-*o*-carborane ring in **2** undergoes the addition of a methylene group between Co and S in its reaction with a diazoalkane. The reaction of **2** with trimethylsilyldiazomethane in dichloromethane solution at room temperature for 1 h gave the trimethylsilylmethylene adduct **5**[15] in 84% yield. To establish the exact conformation of the adduct, the structure of **5** was determined by single-crystal X-ray analysis.[16] The molecular structure of **5** is shown in Figure 4, together with important bond parameters. The plane of the C−Co−S three-membered ring is almost perpendicular to the plane of the cobaltadithia-*o*-carborane ring. In **5**, the trimethylsilyl group is located in the anti-position with respect to the cobaltadithia-*o*-carborane ring. The formation of a methylene bridge between a metal and a chalcogen in a reaction with a diazoalkane compound is a typical result due to unsaturation.[17] These cycloaddition reactions suggest that a certain degree of multiple-bond character is present in the Co−S bond of complex **2**.

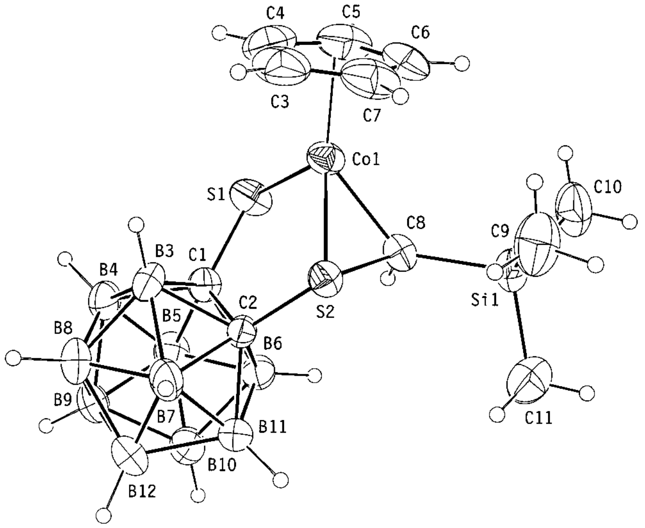


Figure 4. ORTEP drawing of adduct **5**. Selected bond lengths (Å) and angles (deg): Co(1)−S(1) 2.264(1), Co(1)−S(2) 2.1567(9), Co(1)−C(8) 1.994(4), S(2)−C(8) 1.760(3), S(1)−C(1) 1.776(3), S(2)−C(2) 1.808(8), C(1)−C(2) 1.647(4); S(1)−Co(1)−S(2) 94.78(3), S(2)−Co(1)−C(8) 50.0(1), S(1)−Co(1)−C(8) 91.9(1), Co(1)−C(8)−S(2) 69.8(1), Co(1)−S(2)−C(8) 60.2(1). The centers of the five atoms of the CoS_2C_2 moiety [Co(1), S(1), S(2), C(1), C(2)] are within 0.16 Å of a plane. The angle between planes [Co(1), S(2), C(8)] and CoS_2C_2 is 83.0(1)°.

Acknowledgment. We gratefully acknowlege the financial support from the Korean Ministry of Education through the Basic Science Research Institute Program (BSRI-98-3407).

Supporting Information Available: Tables describing the X-ray analysis (data collection and analysis), crystal data, atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and least-squares planes for **4a** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] Data for **5**. Anal. Calcd for $C_{11}H_{25}B_{10}S_2SiCo$: C, 31.72; H, 6.05. Found: C, 31.77; H, 6.09. IR (KBr, cm^{-1}): ν(BH), 2596; ν(BH), 2568. ^{1}H NMR (200.13 MHz, ppm, $CDCl_3$): 4.99 (s, 5H, C_5H_5), 3.49 (s, 1H, $(CH_3)_3SiCH$), 0.24 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (50.3 MHz, ppm, $CDCl_3$): 83.10 (s, C_5H_5), 43.93 (s, $(CH_3)_3SiCH$), 0.00 (s, $Si(CH_3)_3$).

[16] Crystallographic data for **5**: $a = 7.8599(4)$ Å, $b = 9.7306(8)$ Å, $c = 14.7510(7)$ Å, $\alpha = 102.517(5)°$, $\beta = 104.820(4)°$, and $\gamma = 96.329(5)°$ with $Z = 2$ in space group $P\bar{1}$ (No. 2). R1 (wR2) = 0.0374 (0.1028) for 4107 data with $I > 2.0\sigma(I)$ and anisotropic refinements of the model with idealized hydrogen atoms.

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