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Carbon–sulfur bond cleavage by cobalt. Reaction of $Cp^*Co(C_2H_4)_2$ with dibenzothiophene *

William D. Jones and Robert M. Chin

Department of Chemistry, University of Rochester, Rochester, NY 14627 (USA)

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Abstract

The thermal reaction of $Cp^*Co(C_2H_4)_2$ with thiophene yields the C–S insertion product $[Cp^*Co]_2(\mu\text{-}\eta^2,\eta^3\text{-}C_4H_4S)$. Reaction with dibenzothiophene produces the analogous dinuclear C–S insertion adduct $[Cp^*Co]_2(\mu\text{-}\eta^2,\eta^3\text{-}C_{12}H_8S)$ the crystal structure of which was determined. Reaction of the thiophene insertion adduct with H_2S gives a new butadienedithiolate compound in which sulfur has inserted into the metal–carbon bond, $[Cp^*Co]_2(\mu\text{-}\eta^2,\eta^2\text{-}S_2C_4H_4)$.

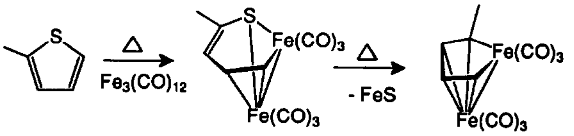
Key words: Cobalt; Cyclopentadienyl; Thiolate; Thiophene; Crystal structure; Desulfurization

1. Introduction

The hydroprocessing of petroleum represents one of the largest scale industrial chemical processes in the world today. In this procedure, crude oil is treated with high pressures of hydrogen gas (150–3000 psi) over a hot heterogeneous catalyst (500–825°C) to remove nitrogen, sulfur, and residual metals prior to further processing. The removal of sulfur from thiophene and mercaptan residues in oil is commonly referred to as hydrosulfurization (HDS), and has important ramifications both for preventing catalyst poisoning (*e.g.* in automobiles) and for decreasing contributions to acid rain upon fuel combustion (from SO_2) [1].

A great deal of fundamental work has been done in trying to understand the salient features of the HDS process. Studies range from those aimed at identifying intermediates under actual reactor conditions with industrial HDS catalysts [2–9] to surface studies of the interaction of thiophene with clean and sulfided metal surfaces [10], to homogeneous modeling of the types of steps that may be involved in the industrial catalysts. It is worthwhile to point out that while many metals are active as HDS catalysts, molybdenum and cobalt as a mixture, are the metals of choice for industrial use.

In this paper, studies of a homogenous system that cleaves the C–S bond of thiophene and dibenzothiophene are described. Homogeneous modeling chemistry has provided examples for various types of mechanisms. An excellent overview of this chemistry has been recently published [11]. One of the earliest reports was that in which $Fe_3(CO)_{12}$ was treated with thiophene to give a product in which the sulfur had been removed as iron sulfide [12–15]. In a more recent examination of this system by Rauchfuss, a thiaferrole intermediate was identified (eqn. (1)) [16].



(1)

2. Results and discussion

Reaction of $Cp^*Co(C_2H_4)_2$ with thiophene at 70°C in benzene resulted in a color change from red-orange to dark black. Removal of solvent led to the isolation of a black solid which was characterized as $[Cp^*Co]_2(\mu\text{-}\eta^2,\eta^3\text{-}C_4H_4S)$ (**1**) in which a cobalt metal center had inserted into the thiophene C–S bond and a sec-

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Correspondence to: Professor W.D. Jones.

* Dedicated to Prof. Dr. Helmut Werner on the occasion of his 60th birthday.

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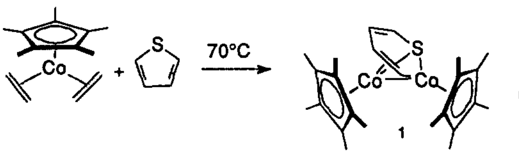
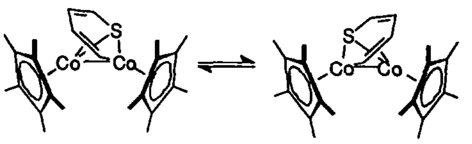
ond Cp*Co unit had complexed to the cobalt, sulfur, and C–C double bond (eqn. (2)). A single crystal X-ray structure of 1, reported earlier, confirmed this geometry, showing the asymmetric binding of the C_4H_4S unit [17].



(2)

The ^1H NMR spectrum of 1 at 23°C, however, showed a broad singlet at δ 1.892 for two equivalent Cp* groups in addition to multiplets for the olefinic hydrogens. Upon cooling a THF-d_8 solution of 1 to −50°C, the Cp* resonance is observed to broaden and then separate into two distinct resonances at δ 1.900 and 1.568, consistent with the static X-ray structure. Complete bandshape analysis of the spectra at intermediate temperatures allowed determination of the activation parameters for the exchange process shown in eqn. (3), $\Delta H^{\ddagger} = 8.6$ (3) kcal/mol and $\Delta S^{\ddagger} = -13.8$ (1.3) e.u. [17]. The $^{13}C\{^1H\}$ NMR spectrum of 1 at −50°C shows four downfield singlet resonances for the C_4H_4 unit and two distinct sets of Cp* resonances.



(3)

Reaction of dibenzothiophene with $Cp^*Co(C_2H_4)_2$ in benzene also results in a color change from red-orange to black. Removal of the volatiles under vacuum and the dibenzothiophene by sublimation (70°C) followed by recrystallization of the residue gives a black product. The ^1H NMR spectrum of this complex shows a single Cp* resonance (30H) and 8 distinct aromatic multiplets, suggesting a fluxional structure similar to that of 1 (eqn. (4)). Indeed, single crystal

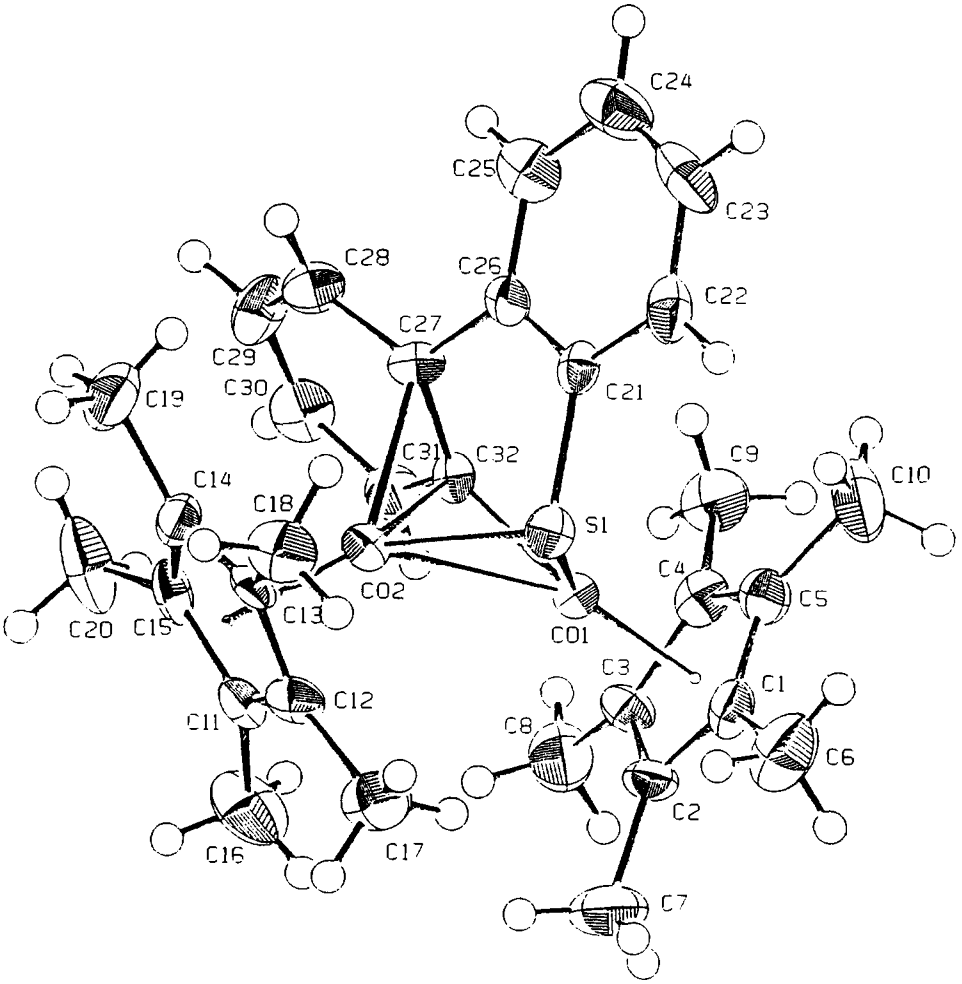
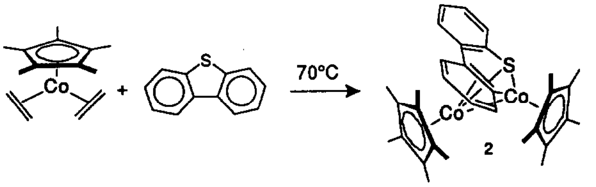


Fig. 1. ORTEP drawing of one independent molecule of $[Cp^*Co]_2(\mu-\eta^2,\eta^3-C_{12}H_8S)$. Ellipsoids are shown at the 50% probability level.

TABLE 1. Data collection parameters for $[Cp^*Co]_2(\mu\text{-}\eta^2,\eta^3\text{-}C_{12}H_8S)$

Chemical formula	$Co_2SC_{32}H_{38}$
Formula weight	572.6
Space group (No.)	$P\bar{1}$ (No. 2)
Z	4
a (Å)	11.790 (4)
b (Å)	15.061 (3)
c (Å)	16.961 (3)
α (°)	99.90 (2)
β (°)	108.83 (2)
γ (°)	100.02 (2)
Vol (Å^3)	2721.8 (2.9)
ρ_{calc} (g cm^{-3})	1.40
Crystal dimensions (mm)	0.08 × 0.15 × 0.15
Temperature (°C)	−20
Radiation (monochrom.)	Mo, 071073 Å (graphite)
2θ range (°)	4−44
Data collected	$+h$, $\pm k$, $\pm l$
No. of data collected	7040
No. of unique data $F^2 > 3\sigma(F^2)$	3728
No. of parameters varied	631
μ (cm^{-1})	13.09
Range of transmission factors	0.82–1.18
$R(F_o)$	0.0486
$R_w(F_o)$	0.0508

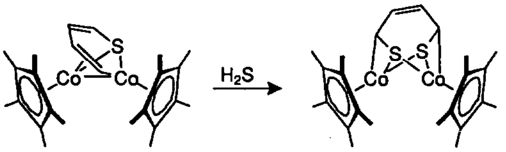
X-ray structural studies showed the product to be $[Cp^*Co]_2(\mu\text{-}\eta^2,\eta^3\text{-}C_{12}H_4S)$, **2** (Fig. 1). Data collection parameters are listed in Table 1, distances and angles are given in Table 2 and structural parameters are listed in Table 3.



(4)

Unlike **1**, however, the ^1H NMR spectrum of complex **2** does not change upon cooling to −80°C. The $^{13}C\{^1H\}$ NMR spectrum at −70°C also displays resonances for only one type of Cp* ligand, indicating that the low temperature limiting spectrum consistent with the structure found in the solid state had not yet been obtained. Two of the quaternary resonances appeared as broad singlets, and were assigned as the carbon atoms coordinated to the quadrupolar cobalt metal center. The inability to freeze out the static structure of **2** is interpreted in terms of a lowering of the transition state energy for the flip-flop of the ring, rather than as a destabilization of the ground state of **2**. This conclusion arises from examination of the X-ray structural parameters for the π-binding of the dibenzothiophene carbons in **2** (Co2–C_{ave} = 2.12 Å), which show little difference from those of **1** (Co–C_{ave} = 2.14 Å). A weaker interaction of the arene π-system with the metal atom in **2** would be expected to display itself in terms of longer metal–carbon π-bond distances.

Reaction of **1** with H_2S occurs readily at ambient temperature. NMR characterization of the product, formed in quantitative yield, shows it to be a symmetric species, with two doublets of doublets appearing in the ^1H NMR spectrum at δ 7.31 and 4.49 of area 2H each and a large Cp*singlet at 1.58 (30H). A ^1H-^{13}C HETCOR spectrum shows correlation of the olefinic hydrogens with carbon resonances at δ 128.28 and 52.45, respectively. A JMOD ^{13}C spectrum shows that the carbons have only one attached hydrogen. These data lead to the formulation of the product as the sulfur insertion adduct $[(C_5Me_5)Co]_2(\mu_2\text{-}\eta^2,\eta^2\text{-}S{=}CHCH{=}CHCH{=}S)$ as indicated in eqn. (5). The mass spectrum confirms this formulation, displaying a parent ion at $m/e = 504$.



(5)

3. Conclusions

In conclusion, both thiophene and dibenzothiophene are found to react with $Cp^*Co(C_2H_4)_2$ to give dinuclear C–S insertion adducts. The bridging SC_4 unit is fluxional in both molecules, giving apparent symmetry in the averaged NMR spectra. The thiophene insertion adduct reacts with H_2S to give a product in which the sulfur inserts into the Co–C bond, giving the symmetrical bridging ligand S=CH-CH=CHCH=S.

4. Experimental details

4.1. General

All operations and routine manipulations were performed under a nitrogen atmosphere, either on a high vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corporation dri-lab. Tetrahydrofuran (THF), benzene, and toluene were distilled from dark purple solutions of benzophenone ketyl. Hexanes were stirred over concentrated H_2SO_4 overnight, washed with aqueous $KMnO_4$ and water and then distilled from a dark purple solution of benzophenone ketyl. Benzene-d_6 and THF-d_8 were distilled under vacuum from dark purple solutions of benzophenone ketyl and stored in ampules with Teflon sealed vacuum line adapters.

TABLE 2. Selected bond distances (Å) and angles (°) for $[Cp^*Co]_2(\mu\text{-}\eta^2,\eta^3\text{-}C_{12}H_8S)$ [a]

Distances			
Co1–Co2	2.517(2)	Co3–Co4	2.513(2)
Co1–S1	2.174(3)	Co4–S2	2.177(3)
Co1–C32	1.910(9)	Co4–C64	1.910(8)
Co2–S1	2.196(3)	Co3–S2	2.191(3)
Co2–C27	2.21(1)	Co3–C59	2.23(1)
Co2–C32	2.038(8)	Co3–C64	2.043(8)
S1–C21	1.77(1)	S2–C53	1.76(1)
C21–C22	1.40(1)	C53–C54	1.41(1)
C21–C26	1.39(1)	C53–C58	1.38(1)
C22–C23	1.42(1)	C54–C55	1.39(2)
C23–C24	1.36(1)	C55–C56	1.36(2)
C24–C25	1.39(1)	C56–C57	1.39(1)
C25–C26	1.41(1)	C57–C58	1.41(1)
C26–C27	1.48(1)	C58–C59	1.49(1)
C27–C28	1.44(1)	C59–C60	1.44(1)
C27–C32	1.47(1)	C59–C64	1.46(1)
C28–C29	1.35(1)	C60–C61	1.34(1)
C29–C30	1.40(1)	C61–C62	1.42(1)
C30–C31	1.37(1)	C62–C63	1.37(1)
C31–C32	1.43(1)	C63–C64	1.44(1)
Angles			
Co2–Co1–S1	55.23(8)	Co3–Co4–S2	55.13(8)
Co2–Co1–C32	52.7(2)	Co3–Co4–C64	52.9(2)
S1–Co1–C32	90.6(3)	S2–Co4–C64	90.6(3)
Co1–Co2–S1	54.41(8)	Co4–Co3–S2	54.64(8)
Co1–Co2–C27	78.3(2)	Co4–Co3–C59	77.7(2)
Co1–Co2–C32	48.2(2)	Co4–Co3–C64	48.2(2)
S1–Co2–C27	85.1(3)	S2–Co3–C59	85.0(3)
S1–Co2–C32	86.7(3)	S2–Co3–C64	86.9(3)
C27–Co2–C32	40.3(3)	C59–Co3–C64	39.6(3)
Co1–S1–Co2	70.36(9)	Co3–S2–Co4	70.23(9)
Co1–S1–C21	103.1(3)	Co4–S2–C53	103.4(3)
Co2–S1–C21	101.4(3)	Co3–S2–C53	101.0(3)
S1–C21–C22	121.8(8)	S2–C53–C54	120.5(8)
S1–C21–C26	116.8(7)	S2–C53–C58	118.2(7)
C22–C21–C26	121(1)	C54–C53–C58	121(1)
C21–C22–C23	119(1)	C53–C54–C55	119(1)
C22–C23–C24	120(1)	C54–C55–C56	121(1)
C23–C24–C25	120(1)	C55–C56–C57	121(1)
C24–C25–C26	122(1)	C56–C57–C58	119(1)
C21–C26–C25	117(1)	C53–C58–C57	119(1)
C21–C26–C27	122(1)	C53–C58–C59	120.5(9)
C25–C26–C27	121(1)	C57–C58–C59	120(1)
Co2–C27–C26	107.5(6)	Co3–C59–C58	106.5(6)
Co2–C27–C28	117.7(7)	Co3–C59–C60	118.8(7)
Co2–C27–C32	63.6(5)	Co3–C59–C64	63.4(5)
C26–C27–C28	116.3(9)	C58–C59–C60	115.2(8)
C26–C27–C32	120.4(8)	C58–C59–C64	122.0(8)
C28–C27–C32	119.0(8)	C60–C59–C64	118.8(8)
C27–C28–C29	122(1)	C59–C60–C61	123.0(9)
C28–C29–C30	121(1)	C60–C61–C62	119.7(9)
C29–C30–C31	119(1)	C61–C62–C63	119.1(9)
C30–C31–C32	125(1)	C62–C63–C64	124.8(9)
Co1–C32–Co2	79.2(3)	Co3–C64–Co4	78.8(3)
Co1–C32–C27	124.0(7)	Co4–C64–C59	124.1(7)
Co1–C32–C31	121.5(7)	Co4–C64–C63	121.5(7)
Co2–C32–C27	76.1(5)	Co3–C64–C59	77.0(5)
Co2–C32–C31	118.8(6)	Co3–C64–C63	117.1(6)
C27–C32–C31	114.4(8)	C59–C64–C63	114.4(8)

[a] Parameters for the two distinct molecules within the asymmetric unit are given in each column.

Dibenzothiophene, 99 + %, was purchased from Aldrich and was sublimed prior to use. Hydrogen sulfide, C.P. grade, was obtained from Scott Specialty Gases and used as received. $(C_5Me_5)Co(C_2H_4)_2$ and $[(C_5Me_5)Co]_2(\mu\text{-}SC_4H_4)$ were prepared as previously reported.

All ^1H and ^{13}C spectra were recorded on a Bruker AMX400 NMR spectrometer. All chemical shifts are reported in ppm (δ) relative to tetramethylsilane and were referenced to the chemical shifts of residual solvent resonances (^1H, ^{13}C). An Enraf-Nonius CAD4 diffractometer was used for X-ray crystal structure determination.

4.2. *Preparation of* $[Cp^*Co]_2(\mu\text{-}\eta^2\eta^3\text{-}SC_{12}H_8)$

$Cp^*Co(C_2H_4)_2$ (263 mg, 1.05 mmol) and dibenzothiophene (721 mg, 3.91 mmol) were dissolved in 20 ml of benzene and heated to 100–110°C for 6 days. A ^1H NMR spectrum of the crude reaction mixture showed no starting material remaining. The benzene was removed under reduced vacuum and the black residue was transferred into a large sublimation vessel. The excess dibenzothiophene was then removed by sublimation over 2 days at 65–70°C. The residue was redissolved in 2 ml of benzene, evaporated to dryness, and the sublimation process repeated. The residue was then suspended in 4–5 ml of hexanes and placed in a −30°C freezer for 18 h. Filtration yielded 200 mg of crude product, which was further purified by dissolving in 2 ml of toluene, layering with 6 ml of hexanes, and recrystallizing at −30°C to give 134 mg of pure product. (44% yield). ^1H NMR (400 MHz, THF-d_8, 25°C): δ 9.07 (d, $J = 8.4$ Hz, 1 H); 7.49 (d, $J = 8.4$ Hz, 1 H); 6.90 (m, 2H); 6.70 (t, $J = 6.8$ Hz, 1H); 6.62 (t, $J = 7.3$ Hz, 1H); 6.50 (t, $J = 7.3$ Hz, 1H); 6.41 (d, $J = 7.3$ Hz, 1H); 1.51 (s, 30H). JMOD $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8, 25°C): δ 160.91 (br s, C); 155.38 (s, CH); 148.83 (s, C); 138.58 (s, C); 133.36 (s, CH); 129.55 (s, CH); 127.31 (s, CH); 125.32 (s, CH); 124.92 (s, CH); 124.47 (s, CH); 118.08 (s, CH); 114.07 (br s, C); 87.18 (s, C_5Me_5); 10.28 (s, $C_5\mathit{Me}_5$).

4.3. *Preparation of* $[Cp^*Co]_2(\mu\text{-}SC_4H_4S)$

$[Cp^*Co]_2(\mu\text{-}SC_4H_4)$ (131 mg, 0.277 mmol) was dissolved in 10 ml of benzene and 1 atm of H_2S bubbled through the solution for 6 h at 25°C. The benzene was removed under reduced vacuum and the residue redissolved in 3 ml of hexanes and placed in a −30°C freezer. The solution was filtered to remove an unidentified precipitate. The resulting mother liquor was allowed to sit at 25°C until all of the solvent had evaporated (~ 24 h), by which time medium size crystals of $[(Cp^*)Co]_2(\mu\text{-}SC_4H_4S)$ had formed. The crystals were collected in a glass frit and washed with 2 ml of

TABLE 3. Atomic coordinates and B_{eq} for $[Cp^*Co]_2(\mu\text{-}\eta^2,\eta^3\text{-}C_{12}H_8S)$

Atom	x	y	z	B_{eq} (Å^2)
Co(1)	0.4274(1)	0.04073(9)	0.75683(8)	1.94(5)
Co(2)	0.2363(1)	0.0744(1)	0.77856(8)	2.04(5)
Co(3)	0.2598(1)	0.42378(9)	0.21878(8)	1.96(5)
Co(4)	0.1480(1)	0.45328(9)	0.32045(8)	2.00(5)
S(1)	0.4062(2)	0.0719(2)	0.8805(2)	2.4(1)
S(2)	0.3322(2)	0.4282(2)	0.3560(2)	2.5(1)
C(1)	0.5420(9)	−0.0502(7)	0.7869(7)	2.7(4)
C(2)	0.4512(9)	−0.0938(7)	0.7067(7)	2.7(4)
C(3)	0.4564(9)	−0.0314(7)	0.6518(6)	2.4(4)
C(4)	0.5574(9)	0.0473(7)	0.7004(6)	2.6(4)
C(5)	0.6093(9)	0.0376(7)	0.7833(7)	2.8(4)
C(6)	0.571(1)	−0.0937(8)	0.8626(8)	5.0(5)
C(7)	0.373(1)	−0.1907(8)	0.6760(8)	5.2(5)
C(8)	0.388(1)	−0.0553(8)	0.5568(7)	4.3(5)
C(9)	0.604(1)	0.1270(7)	0.6669(7)	3.9(5)
C(10)	0.719(1)	0.1009(9)	0.8571(7)	5.0(5)
C(11)	0.0835(8)	−0.0347(7)	0.6982(6)	2.7(4)
C(12)	0.1243(9)	−0.0442(6)	0.7820(6)	2.4(4)
C(13)	0.1116(8)	0.0348(7)	0.8379(6)	2.0(3)
C(14)	0.0663(9)	0.0903(7)	0.7856(7)	2.7(4)
C(15)	0.0494(8)	0.0503(7)	0.6991(6)	2.7(4)
C(16)	0.068(1)	−0.1039(8)	0.618(6)	4.9(5)
C(17)	0.167(1)	−0.1255(7)	0.8116(7)	4.1(5)
C(18)	0.139(1)	0.0493(7)	0.9319(6)	3.5(4)
C(19)	0.034(1)	0.1835(8)	0.8156(7)	4.5(5)
C(20)	−0.015(1)	0.0820(9)	0.6216(7)	5.2(5)
C(21)	0.4788(8)	0.1917(7)	0.9215(6)	2.2(4)
C(22)	0.5755(9)	0.2258(8)	1.0010(6)	3.1(4)
C(23)	0.628(1)	0.323(1)	1.0311(7)	4.2(5)
C(24)	0.586(1)	0.3819(8)	0.9829(8)	4.3(5)
C(25)	0.492(1)	0.3463(8)	0.9030(7)	3.4(4)
C(26)	0.4352(8)	0.2507(7)	0.8706(7)	2.6(4)
C(27)	0.3390(9)	0.2141(7)	0.7837(6)	2.3(4)
C(28)	0.268(1)	0.2772(7)	0.7505(6)	2.9(4)
C(29)	0.221(1)	0.2722(8)	0.6653(7)	3.4(5)
C(30)	0.238(1)	0.2031(8)	0.6061(6)	3.2(4)
C(31)	0.2958(9)	0.1372(7)	0.6346(6)	2.8(4)
C(32)	0.3481(8)	0.1357(6)	0.7230(5)	1.8(3)
C(33)	0.2741(1)	0.5368(6)	0.1620(6)	2.1(4)
C(34)	0.3871(9)	0.5399(6)	0.2257(6)	2.6(4)
C(35)	0.4253(8)	0.4566(7)	0.1999(6)	2.4(4)
C(36)	0.3356(8)	0.4052(7)	0.1217(6)	2.2(4)
C(37)	0.2410(8)	0.4535(7)	0.0984(6)	2.2(4)
C(38)	0.208(1)	0.6136(7)	0.1563(7)	4.3(5)
C(39)	0.459(1)	0.6182(7)	0.3043(6)	3.7(4)
C(40)	0.545(1)	0.4336(8)	0.2454(7)	4.4(5)
C(41)	0.339(1)	0.3157(7)	0.0677(7)	3.7(4)
C(42)	0.135(1)	0.4284(7)	0.0139(6)	3.5(4)
C(43)	0.135(1)	0.5872(7)	0.3783(7)	3.0(4)
C(44)	0.176(1)	0.5378(7)	0.4406(6)	3.0(4)
C(45)	0.085(1)	0.4529(7)	0.4203(6)	2.6(4)
C(46)	−0.012(1)	0.4510(7)	0.3455(7)	2.9(4)
C(47)	0.018(1)	0.5326(7)	0.3181(6)	2.9(4)
C(48)	0.193(1)	0.6859(8)	0.3819(9)	6.7(6)
C(49)	0.292(1)	0.569(1)	0.5178(7)	6.3(6)
C(50)	0.091(1)	0.3834(8)	0.4747(8)	5.8(6)
C(51)	−0.134(1)	0.3772(8)	0.3036(8)	5.5(5)
C(52)	−0.065(1)	0.5638(8)	0.2442(7)	5.2(5)
C(53)	0.3047(8)	0.3087(7)	0.3530(6)	2.4(4)
C(54)	0.365(1)	0.2778(8)	0.4253(6)	3.5(5)
C(55)	0.344(1)	0.183(1)	0.419(1)	5.5(7)
C(56)	0.264(1)	0.121(1)	0.346(1)	5.3(6)
C(57)	0.199(1)	0.1514(8)	0.2751(7)	3.6(5)
C(58)	0.2233(9)	0.2471(7)	0.2780(6)	2.3(4)
C(59)	0.1514(8)	0.2815(6)	0.2046(6)	2.2(4)
C(60)	0.1046(9)	0.2161(7)	0.1218(7)	2.8(4)
C(61)	0.005(1)	0.2188(7)	0.0570(6)	3.0(4)
C(62)	−0.0597(8)	0.2881(7)	0.0686(6)	2.9(4)
C(63)	−0.0151(9)	0.3540(7)	0.1447(7)	2.7(4)
C(64)	0.0922(8)	0.3573(6)	0.2171(5)	1.6(3)

hexanes to give 34 mg of product (24%). The reaction is quantitative by ^1H NMR spectroscopy when done on an NMR scale. ^1H NMR (400 MHz, C_6D_6, 25°C): δ 7.31 (dd, $J = 3.1$, 5.0 Hz, 2H); 4.49 (dd, $J = 3.1$, 5.0 Hz, 2H); 1.58 (s, 30 H). JMOD $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8, 25°C): δ128.28 (s), 89.52 (s, C_5Me_5), 52.54 (s), 9.82 (s, C_5Me_5). Mass spectrum (70 eV): $m/e = 504$.

4.4. *X-Ray structural determination of $[Cp^*Co]_2(\mu\text{-}\eta^2,\eta^3\text{-}C_{12}H_8S)$*

A single black crystal of the complex was mounted with epoxy on a glass fiber and cell constants obtained from 25 centered reflections with values of χ between 0 and 70°. Routine data collection of one hemisphere of data was undertaken on the primitive triclinic cell as indicated in Table 1. The Molecular Structure Corporation TEXSAN analysis software package was used for data reduction and solution [18*]. Patterson map solution of the structure to locate the four cobalt atoms (two independent molecules in the asymmetric unit), followed by expansion of the structure with the program DIRDIF revealed all non-hydrogen atoms. Following isotropic refinement, an absorption correction was applied using the program DIFABS. Full matrix least squares anisotropic refinement of all non-hydrogen atoms (with hydrogens attached in idealized positions) was carried out to convergence. Selected distances and angles are given in Table 2 and fractional coordinates in Table 3.

Complete tables of bond distances and angles and lists of fractional atomic coordinates and thermal parameter have been deposited at the Cambridge Crystallographic Data Centre. A list of calculated and observed structure factors is available from W.D.J.

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* Reference number with asterisk indicates a note in the list of references.

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