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The Novel Redox Reaction and Thiolato Ligand Transfer between $Cp_2Ti(SCMe_3)_2$ and $CpCo(CO)_2$. Preparation and Structure of $[CpCo(\mu\text{-}SCMe_3)]_2$

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Introduction

Dimers of the type $[CpM(CO)_xSR]_2$ are an important class of molecules containing bridging thiolato ligands.[2] There are several geometric isomers possible for such complexes.[2,3] Briefly, the Cp rings can be cis or trans with respect to the M-M vector and the R groups can be axial or equatorial with respect to a nonplanar M_2S_2 "butterfly" ring.[4] Only a few complexes of the type $[CpCoSR]_2$ have been prepared, where R = CH_3,[5] Ph,[5] CF_3,[6] and C_6F_5;[6] however, they are unstable for R = Ph and CF_3. We report here the preparation and structural characterization of $[CpCoSCMe_3]_2$, the product of an unusual redox reaction between $CpCo(CO)_2$ and $CpTi(SCMe_3)_2$.

Results

UV irradiation of a solution of $CpCo(CO)_2$ and $Cp_2Ti(SCMe_3)_2$ in hexanes caused a color change from red to green and the precipitation of a red solid. The latter was identified as $[Cp_2TiSCMe_3]_2$ by elemental analysis, mass spectroscopy, and its NMR spectrum.[7] Green crystals of $[CpCoSCMe_3]_2$ were isolated from the hexane solution and characterized by elemental analysis, mass spectroscopy, and its VT ^1H NMR spectra. The NMR spectrum shows one peak for the Cp protons and a broad peak for the Me protons. Heating the sample causes the broad peak to sharpen, while cooling causes the peak to broaden even more, pass through a coalescence temperature, and reemerge as two sharp peaks of equal intensity at low temperature.[8]

On the basis of the NMR data, one would predict a structure for $[CpCoSCMe_3]_2$ wherein the Cp rings are mutually cis and the CMe_3 groups axial and equatorial with respect to the Co_2S_2 ring. The first X-ray structure of a cobalt complex of this type is depicted in Figure 1, and it confirms the assignment. The crystallographic data, atomic coordinates, and selected structural

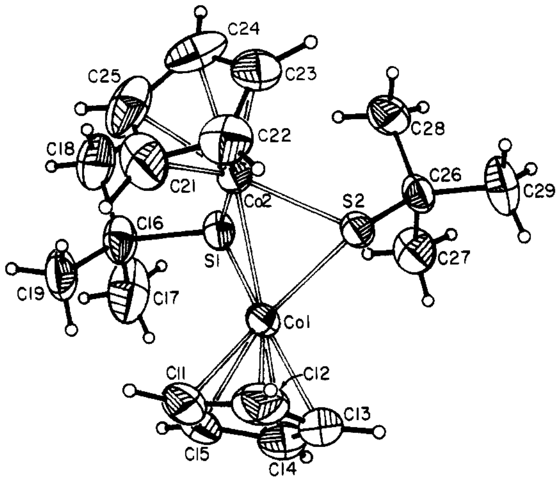

Figure 1. ORTEP view of $[CpCoSCMe_3]_2$ showing the numbering scheme.

Table I. Crystallographic Data for $[CpCoSCMe_3]_2$

chem formula: $C_{18}H_{28}Co_2S_2$
fw = 456.64
space group: $P2_1/n$
a = 14.770 (3) Å
b = 9.145 (1) Å
c = 15.483 (2) Å
β = 109.51 (1)°
V = 1971.4 (5) Å^3
Z = 4
T = 20 ± 1 °C
λ = 0.71073 Å
ρ_{calcd} = 1.539 g cm^{-3}
μ(Mo Kα) = 2.72 mm^{-1}
R_1 = 0.037
R_2 = 0.047

Table II. Positional Parameters (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[CpCoSCMe_3]_2$

atom	x	y	z	U
Co(1)	1812 (1)	2108 (1)	4729 (1)	30 (1)
Co(2)	2350 (1)	−128 (1)	5649 (1)	27 (1)
S(1)	3240 (1)	1126 (1)	5035 (1)	30 (1)
S(2)	1247 (1)	−92 (1)	4286 (1)	27 (1)
C(11)	1563 (4)	3797 (5)	5516 (3)	61 (2)
C(12)	698 (3)	3146 (5)	5016 (3)	56 (2)
C(13)	584 (3)	3298 (4)	4082 (3)	47 (1)
C(14)	1359 (3)	4050 (4)	3997 (3)	53 (1)
C(15)	1990 (4)	4341 (4)	4895 (4)	59 (2)
C(16)	4295 (3)	2113 (5)	5848 (3)	42 (1)
C(17)	4632 (4)	3157 (7)	5248 (3)	75 (2)
C(18)	5058 (3)	967 (6)	6275 (3)	55 (1)
C(19)	4047 (3)	2956 (5)	6589 (3)	51 (1)
C(21)	2254 (4)	112 (5)	6956 (3)	57 (2)
C(22)	1524 (3)	−793 (5)	6419 (3)	44 (1)
C(23)	1960 (3)	−2011 (4)	6160 (3)	44 (1)
C(24)	2943 (3)	−1866 (5)	6525 (3)	55 (2)
C(25)	3132 (3)	−538 (6)	7009 (3)	59 (2)
C(26)	1570 (2)	−1017 (4)	3335 (2)	32 (1)
C(27)	1872 (3)	89 (5)	2764 (3)	47 (1)
C(28)	2363 (3)	−2121 (4)	3749 (3)	45 (1)
C(29)	649 (3)	−1797 (5)	2776 (3)	57 (1)

Table III. Selected Bond Lengths (Å) and Angles for $[CpCoSCMe_3]_2$

Co(1)–Co(2)	2.467 (1)	Co(2)–C(21)	2.087 (5)
Co(1)–S(1)	2.194 (1)	Co(2)–C(22)	2.063 (5)
Co(1)–S(2)	2.198 (1)	Co(2)–C(23)	2.056 (4)
Co(2)–S(1)	2.187 (1)	Co(2)–C(24)	2.083 (5)
Co(2)–S(2)	2.194 (1)	Co(2)–C(25)	2.070 (4)
Co(1)–C(11)	2.075 (5)	S(1)–C(16)	1.874 (4)
Co(1)–C(12)	2.073 (5)	S(2)–C(26)	1.892 (4)
Co(1)–C(13)	2.065 (4)		
Co(1)–C(14)	2.092 (4)		
Co(1)–C(15)	2.064 (4)		
S(1)–Co(1)–S(2)	86.0	C(16)–S(1)–Co(1)	118.2 (1)
S(1)–Co(2)–S(2)	86.3	C(16)–S(1)–Co(2)	166.5 (1)
Co(1)–S(1)–Co(2)	68.5	C(26)–S(2)–Co(1)	118.9 (1)
Co(1)–S(2)–Co(2)	68.3	C(26)–S(2)–Co(2)	116.2 (1)

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(8) The activation energy for this process was calculated[9] to be 60 kJ mol^{-1}. The range observed for pyramidal inversion at the sulfur atom for a variety of dimers with bridging thiolato groups is 40–80 kJ mol^{-1}.[10]

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parameters are given in Tables I–III, respectively. The Co_2S_2 ring forms a shallow butterfly-type ring with a metal distance of 2.467 ± 1 Å, consistent with the presence of a metal–metal bond[11] and with the diamagnetism observed in the NMR spectrum.

The reaction between $CpCo(CO)_2$ and $Cp_2Ti(SCMe_3)_2$ in room-temperature hexanes does not proceed without irradiation. The reaction with $Cp_2Ti(SCHMe_2)_2$ gave a green crude product, the NMR spectrum of which was consistent with the presence of $[CpCoSCHMe_2]_2$, but pure product could not be isolated. Starting $Cp_2Ti(SCH_2Ph)_2$ was recovered from the reaction of this complex with $Cp_2Co(CO)_2$.

Discussion

The structure of $[CpCoSCMe_3]_2$ is the same as $[CpRhSPh]_2$;[12] however, it is interesting that the latter is static on the NMR time scale whereas the former is stereochemically nonrigid. Also of interest is the production of an additional isomer (possibly the equatorial–equatorial) in the preparation of the rhodium complex.[12] No evidence for the presence of any other isomers of the cobalt dimer was detected.

The routes to Cp–metal thiolate complexes have recently been discussed;[13] however, the preparation of $[CpCoSCMe_3]_2$ is quite novel. The irradiation of $CpCo(CO)_2$ in the presence of $Cp_2Ti(SCMe_3)_2$ was intended to produce the thiolato-bridged mixed-metal dimer $Cp_2Ti(\mu\text{-}SCMe_3)_2CoCp$, but instead a redox reaction occurred to give two homometal dimers: $[Cp_2TiSCMe_3]_2$ and $[CpCoSCMe_3]_2$ (eq 1). It is of interest that $[CpCoSCMe_3]_2$ could not be isolated from reaction of $CpCo(CO)_2$ with $S_2(CMe_3)_2$,[11a] the route that reportedly gave the methyl and phenyl analogues.[5]

$$2CpCo(CO)_2 + 2Cp_2Ti(SCMe_3)_2 \rightarrow [CpCoSCMe_3]_2 + [Cp_2TiSCMe_3]_2 + 4CO \quad (1)$$

Experimental Section

The general preparative methods and spectroscopic characterization techniques have been described.[14] The complex $CpCo(CO)_2$ (Strem) was used as received, and $Cp_2Ti(SCMe_3)_2$ was prepared from Cp_2TiCl_2 and $LiSCMe_3$.[15]

Bis(cyclopentadienyl)bis(μ-2-methylpropanethiolato)dicobalt(II), $[CpCoSCMe_3]_2$. A solution of $CpCo(CO)_2$ (0.30 g, 1.67 mmol) and $Cp_2Ti(SCMe_3)_2$ (0.59 g, 1.65 mmol) in hexanes (70 mL) was irradiated by using a mercury-vapor lamp (Hanovia, 100 W) and apparatus[16] previously described. The solution was slowly and continuously purged with N_2. The red solution became dark green, and a red precipitate formed on the walls of the apparatus. The progress of the reaction was monitored by following the decrease in intensity of the ν(CO) bands of $CpCo(CO)_2$ in infrared spectra taken at intervals. After 30 h only a trace of $CpCo(CO)_2$ was detected and the irradiation was terminated. The green supernatant was decanted under N_2 and saved. The red precipitate was washed with hexanes (3 × 20 mL), and the washings were added to the green supernatant. The red precipitate was pumped overnight and then scraped from the flask to give $[Cp_2TiSCMe_3]_2$ (0.39 g, 88%, mp 198–200 °C dec). Anal. Calcd for $C_{28}H_{38}S_2Ti_2$: C, 62.92; H, 7.16; S, 12.00. Found: C, 62.90; H, 7.18; S, 11.99.

The combined supernatant and washings were filtered under N_2, and the filtrate was reduced in volume under vacuum to about 10 mL. Cooling the solution under N_2 to −78 °C (dry ice) gave dark green microcrystals of $[CpCoSCMe_3]_2$ (0.21 g, 60%, mp 114–115 °C). ^1H NMR (toluene-d_8): δ 4.76 (s, 5, C_5H_5), 1.70–0.89 (b, 9, $C(CH_3)_3$). Mass spectrum, m/z (relative intensity, assignment): 425 (29, $M^+ - H$), 369 (14, $M^+ - C_4H_9$), 312 (238, $M^+ - C_8H_{18}$) 280 (26, $M^+ - C_8H_8S$), 248 (20, $C_8H_{18}S_2$). Anal. Calcd for $C_{18}H_{28}Co_2S_2$: C, 50.69; H, 6.23; S, 15.04. Found: C, 50.73; H, 6.74; S, 14.94.

X-ray Structure Determination. Table I contains the crystal parameters for $[CpCoSCMe_3]_2$. A large, approximately cube-shaped dark green crystal obtained by recrystallization from hexanes at −16 °C was glued with epoxy to the inside of a thin-walled glass capillary and sealed under N_2. A total of 4529 independent reflections having 2θ(Mo K$\bar{\alpha}$) < 55.0 ° (the equivalent of 1.0 limiting Cu K$\bar{\alpha}$ sphere) were collected on a computer-controlled Nicolet autodiffractometer using full (0.90° wide) ω scans and graphite-monochromated Mo K$\bar{\alpha}$ radiation. The structure was solved by using direct methods techniques with the Nicolet SHELXTL software package as modified at Crystalytics Co. The resulting structural parameters have been refined to convergence [R_1(unweighted, based on F) = 0.037 for 3160 independent reflections having 2θ(Mo K$\bar{\alpha}$) < 55.0° and $I > 3\sigma(I)$] by using counter-weighted cascade block-diagonal least-squares techniques and a structural model that incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. The six methyl groups were included in the refinement as idealized sp^3-rigid rotors. The remaining hydrogen atoms were fixed at idealized sp^2-hybridized positions with a C–H bond length of 0.96 Å.

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Supplementary Material Available: Full crystal structure analysis report (Table 4), Full tables of bond lengths and angles (Table 5), anisotropic temperature factors (Table 6), and hydrogen coordinates and temperature factors (Table 7) (11 pages); a listing of observed and calculated structure factor amplitudes for $[CpCoSCMe_3]_2$ (14 pages). Ordering information is given on any current masthead page.

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Proton NMR Spectroscopy of Flavocytochrome c_{552} from *Chromatium vinosum*†

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The anaerobic purple sulfur bacterium *Chromatium vinosum* utilizes sulfide, thiosulphate, or organic substrates as electron donors for phosphorylation.[1,2] It has been demonstrated that flavocytochrome c_{552} isolated from such a microorganism functions in vitro as a sulfide cytochrome *c* oxidoreductase and probably is the enzyme responsible for catalyzing the oxidation of sulfide to sulfur observed in vivo.[3,4]

The *C. vinosum* flavocytochrome c_{552} is one of the few proteins containing different types of redox prosthetic groups. There is still a controversy on the number of subunits composing the active enzyme and their molecular weights. Bartsch and co-workers reported the presence of three subunits tightly associated over the pH range 5–10: a covalently bound FAD- (through an 8-α-S cysteinyl linkage) containing subunit (42000 MW) and two smaller subunits (15000 MW) containing one heme-*c* each.[5–7] Yamanaka et al., conversely, suggested the flavocytochrome c_{552} to be composed by only two subunits, the flavin-containing one (46000 MW) and the other with the two hemes (21000 MW).[4,8]

Magnetic susceptibility measurements at neutral pH and low temperature indicate that the two heme irons are in a low-spin ground-state configuration ($S = {}^1/_2$).[9,10] Mössbauer spectra point

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† Abbreviations used throughout the paper: CD, circular dichroism; EPR, electron paramagnetic resonance; FAD, flavin adenine dinucleotide; NMR, nuclear magnetic resonance; ppm, parts per million; WEFT, water-eliminated Fourier transform.

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