R group is phenyl. The presence of the bridging dppe causes a slight expansion of the Fe_2C_2 portion of the core from the unsubstituted complex, the Fe–Fe bond distance increasing to 2.622 (1) Å in **5B** from 2.597 (2) Å and the $C\equiv C$ bond distance increasing slightly from 1.232 (10) to 1.261 (11) Å in **2A**. The Fe(1)–C_α bond length also increases to 2.126 (7) Å in **5B** from 1.891 (6) Å, and the acetylide bend back-angle, C_α–C_β–C_R is more acute in **5B** (159.8 (5) vs 162.3 (8)°) than in **2A**.

In the monosubstituted complex, $Fe_2(CO)_5(\mu\text{-}PPh_2)(\mu_2\text{-}\eta^2\text{-}C\equiv CPh)(PPh_3)$, the phosphine is bound to Fe(1), which has the σ-bound acetylide atom. The phosphine is in a position trans to the phosphido bridge with an Fe(1)–P(2) distance of 2.274 (1) Å. In **5B** the dppe phosphorus atoms are also trans to the phosphido bridge, with slightly shorter Fe–P bond lengths, Fe(1)–P(2) = 2.211 (2) Å and Fe(2)–P(3) = 2.257 (2) Å.

Conclusion

In summary these results provide a rather nice illustration of the fact that in hydrocarbyl complexes where the unsaturated complex is highly activated to nucleophilic attack, by σ–π coordination, phosphorus ligands, even bidentate ones with a high affinity for bridging (dppm) or chelating (dppe) metal centers, may preferentially attack an activated carbon atom, leading initially to a phosphonium zwitterion. Although at first sight it might appear unusual that ligands normally associated with CO substitution should preferentially "coordinate" to carbon, site selectivity in these nucleophilic reactions is, at least in part, orbitally controlled and the LUMO may be principally located on a hydrocarbyl carbon atom. Only when this site is sterically inaccessible will CO substitution become dominant.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for grants (to A.J.C.) and scholarships (to A.A.C., L.H.R., and S.M.B.) in support of this work. A NATO/SERC postdoctoral fellowship to G.H. is also gratefully acknowledged.

Registry No. **1A**, 52970-25-9; **1B**, 62475-91-6; **1C**, 59584-68-8; **2A**, 139198-79-1; **2A′**, 139198-89-3; **2B**, 139198-83-7; **2B″**, 139198-91-7; **2C″**, 139198-93-9; **3A**, 139198-80-4; **3A′**, 139198-90-6; **3B**, 139198-84-8; **3B″**, 139198-92-8; **3C″**, 139198-94-0; **4A**, 139198-81-5; **4B**, 139198-85-9; **4C**, 139198-88-2; **5A**, 139198-82-6; **5B**, 139198-87-1; **5C**, 139242-49-2.

Supplementary Material Available: For both structural analyses, tables of anisotropic thermal coefficients (Tables S1 and S2), the remaining bond distances and angles (Tables S3 and S4), and hydrogen atom and solvent molecule atomic coordinates (Tables S5 and S6) (10 pages); listings of structure factors (Tables S7 and S8) (49 pages). Ordering information is given on any current masthead page.

Thiolate-Bridged Dichromium Complexes. Syntheses and Crystal Structures of $[CpCr(CO)_2(SPh)]_2$ and $[CpCr(SPh)]_2S$

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The predominant product obtained from the reaction of $[CpCr(CO)_3]_2$ with Ph_2S_2 varied with reaction temperature as follows: $[CpCr(CO)_2(SPh)]_2$ (**3**), 32.9%, ambient temperature; $[CpCr(CO)(SPh)]_2$ (**4**), 53.07%, 60 °C; $[CpCr(SPh)]_2S$ (**5**), 20.7%, 80 °C. A thermolysis study showed the degradation of **3** and **4** to **5** and eventually to $Cp_4Cr_4S_4$. The thiolate-bridged complexes have been characterized by elemental and spectral analyses. **3** and **5** have also been structurally determined. Crystal data: **3**, monoclinic, space group $P2_1/c$ (No. 14), $a = 9.138$ (2) Å, $b = 14.195$ (6) Å, $c = 18.879$ (5) Å, $\beta = 101.77$ (2)°, $V = 2397$ (1) Å^3, $Z = 4$; **5**, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.548$ (1) Å, $b = 10.122$ (2) Å, $c = 13.003$ (1) Å, $\alpha = 103.71$ (1)°, $\beta = 100.351$ (9)°, $\gamma = 98.62$ (1)°, $V = 1176.4$ (3) Å^3, $Z = 1$.

Introduction

Transition-metal complexes containing thiolate ligands have commanded a long standing interest on account of their relevance to biological[1] and catalytic[2] processes. The main interest has been concentrated on Fe, Mo, and W. Among the earliest examples of alkyl mercapto complexes were those of Fe[3] and Mo,[4] which date back to the 1960s. A commonly used synthetic route has involved the reaction of transition-metal carbonyl complexes with organic sulfides or disulfides under varying reaction conditions. Thus the reaction $[CpMo(CO)_3]_2$ with R_2S_2 led to the isolation of $[CpMo(SR)_2]_n$ (R = Me, $n = 2$;[4a] and R = Ph, $n = x$)[4b] under reflux conditions in methylcyclohexane (101 °C) and

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(2) See for example: (a) Weisser, O.; Landa, S. *Sulfide Catalysts; Their Properties and Applications*; Pergamon Press: New York, 1973. (b) Dilworth, J. R. In ref 1a, p 141. (c) Wedd, A. G. In ref 1a, p 181. (d) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 322. (e) Blower, P. J.; Dilworth, J. R. *Coord. Chem. Rev.* **1987**, *76*, 121.

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toluene (110 °C), respectively; under UV irradiation, the reaction gave $[CpMo(CO)_2(SR)]_2$ (R = Me,[6a] Ph[5a]). $[CpMo(CO)(SMe)]_2$ had also been obtained from the reaction of Me_2S_2 with $[CpMo(CO)_2]_2$ (Mo $\equiv$ Mo) under ambient-temperature conditions[6b] or with $CpMoH(CO)_3$ in pentane.[6a] Very recently, Herberhold reported the photoinduced reaction of $CpV(CO)_4$ (Cp = C_5H_5, C_5Me_5) with E_2R_2 (E = S, Se; R = Me, Ph) at 0 °C to yield $Cp_2V_2(CO)_4(\mu\text{-}ER)_2$.[7] King's early work included a study of the reaction of $[CpCr(CO)_3]_2$ and $[CpCr(CO)_3]_2Hg$ with Me_2S_2 to generate $Cp_2Cr_2(SMe)_3$.[4a] Current awareness of the rich chemistry of $[CpCr(CO)_3]_2$ (1)[8-14], and, in particular, of its high reactivity toward the chalcogens[13,14] suggests that an in-depth study of its reactions with organic dichalcogenides is warranted. In this report, we describe the results of its reaction, together with that of the related $[CpCr(CO)_2]_2$(Cr$\equiv$Cr)complex (2) with Ph_2S_2.

Experimental Section

General Procedures. All reactions were carried out either by use of conventional Schlenk techniques under nitrogen or in an argon atmosphere in a Vacuum Atmospheres Dribox equipped with a Model HE493 Dri-Train.

Reagents and Solvents. $[CpCr(CO)_3]_2$ was synthesized from $Cr(CO)_6$ (Strem Chemicals, Inc.) by the method of Manning et al.[15] Ph_2S_2 was from Fluka Ltd. and was used without purification. Silica gel (Merck Kieselgel 60, 35–70 mesh) and Florisil (Sigma Chemical Company, 100–200 mesh), were dried at 140 °C overnight before chromatographic use. All solvents used were distilled from sodium/benzophenone prior to use.

Physical Measurements and Elemental Analysis. ^1H and ^{13}C NMR spectra were measured on a JEOL FX100 100-MHz spectrometer, and chemical shifts were referenced to residual C_6H_6 in benzene-d_6 or to $(CH_3)_4Si$. IR spectra were measured in the range 4000–200 cm^{-1} by means of a Perkin-Elmer 1330 instrument. Elemental analyses were performed by the Analytical Unit of the Research School of Chemistry, Australian National University, except for Cr, which was analyzed as CrO_4^{2-}[16] in our own laboratory.

Reaction of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ with Ph_2S_2. (a) At Ambient Temperature. A deep green suspension of $[CpCr(CO)_3]_2$ (1) (400 mg, 0.99 mmol) in toluene (20 mL) containing Ph_2S_2 (216 mg, 0.99 mmol) was stirred at ambient temperature. After 20 min, a homogeneous brown solution was obtained, but the reaction was allowed to proceed for 2.5 h. The resultant brown solution was filtered through a 1-cm-thick disk of Celite and concentrated to ca. 2 mL. Cooling at −78 °C for 0.5 h gave brownish green crystals (133 mg) consisting of a mixture of unreacted $[CpCr(CO)_3]_2$ (1) and $[CpCr(CO)_2(SPh)]_2$ (3), followed by a second crop of brown crystals (245 mg) on further concentration of the mother-liquor and addition of ether. An NMR spectrum of this in C_6D_6 showed a 5:1 molar mixture of (3) (δ 5.17) and an unidentified Cp-containing species (δ 3.31). Recrystallization by dissolution in toluene (5 mL) followed by concentration to ca. 1 mL and addition of a little *n*-hexane removed brown crystals (10 mg) of an unidentified Cp-containing species (δ 12.73), after cooling at −30 °C for 1.5 h. Addition of more *n*-hexane to the mother-liquor and cooling at −30 °C then yielded fine brown crystals of **3** (185 mg, 32.9%). Anal. Calcd for $[(\eta^5\text{-}C_5H_5)Cr(CO)_2(SPh)]_2$: C, 55.31; H, 3.58; Cr, 18.42; S, 11.36. Found: C, 55.02; H, 3.58; Cr, 18.29; S, 12.21. Mass spectra, *m/z*: 226, [CpCr(SPh)]; 218, $[Ph_2S_2]$; 201, $[CpCr(CO)_3]$; 173, $[CpCr(CO)_2]$; 149, [CpCrS]; 109, [SPh]. ^1H NMR (C_6D_6): $\delta(C_5H_5)$ 5.17; $\delta(C_6H_5)$ 8.25, 8.17, 7.39, 7.32, 7.31. ^{13}C NMR ($CDCl_3$): $\delta(C_5H_5)$ 98.59; $\delta(C_6H_5)$ 124.81, 128.02, 128.71, 133.78; δ(CO) 236.02, 248.88. IR: ν 1945 (vs), 1920 (vs), 1870 (vs), 1850 (s), 1570 (w), 1065 (w), 1015 (w), 820 (m), 750 (w), 735 (m), 690 (w), 625 (w), 560 (m), 575 (w) cm^{-1} (Nujol).

(b) At Elevated Temperatures. A deep green suspension of $[CpCr(CO)_3]_2$ (200 mg, 0.497 mmol) in toluene (18 mL), containing Ph_2S_2 (108 mg, 0.495 mmol) was stirred at 60 °C for 3 h. The greenish brown suspension was filtered to remove fine brown particles which were recrystallized from THF-hexane to give $[CpCr(CO)(SPh)]_2$ (4) as brown crystals (134 mg, 0.264 mmol, 53.0% yield). Anal. Calcd for $[(C_5H_5)Cr(CO)(SPh)]_2$: C, 56.68; H, 3.97; S, 12.61; Cr, 20.45. Found: C, 56.64; H, 3.47; S, 11.74; Cr, 20.36. IR ν(CO) 1865 (vs), 1745 (vs, br) cm^{-1} (Nujol). ^1H NMR ($CDCl_3$): $\delta(C_5H_5)$ 9.59 ($\nu_{1/2}$ 24 Hz): $\delta(C_6H_5)$ 7.36, 7.19, 7.16, 7.40 (partially obscured by solvent). Mass spectrum: the EI spectrum only shows the fragmentation pattern of Ph_2S_2.

The filtrate was concentrated to ca. 1 mL and loaded onto a silica gel column (5 × 1.5 cm) prepared in *n*-hexane. Elution gave two fractions: (i) a green eluate in toluene (5 mL) which yielded $[CpCr(CO)_2]_2$ (4 mg, 0.012 mmol, 2.32%), identified by its ^1H NMR spectrum in benzene-d_6 (δ 4.23)[17] and TLC chromatography on Merck Kieselgel 60 F_{254}, 0.25-mm SiO_2 (R_f = 0.60 with 1:1 *n*-hexane–toluene as eluent), and (ii) a purple fraction in ether (5 mL) which yielded fine purple crystals of $[CpCr(SPh)]_2S$ (5) (6 mg, 0.012 mmol, 2.49%) (data given below).

A similar reaction for 0.5 h at 60 °C followed by 1.5 h at 80 °C gave a dark green product solution. A chromatographic workup on a (1- × 9-cm) silica gel column gave three fractions: (a) a green solution in toluene (5 mL) which gave green crystals of $[CpCr(CO)_2]_2$ (10 mg, 0.029 mmol, 5.8%), (b) a yellowish brown solution in 1:9 toluene–ether (15 mL) which yielded $[CpCr(CO)_2(SPh)]_2$ (3) (14 mg, 0.025 mmol, 5.0%), and (c) a purple solution in ether (10 mL), which yielded fine purple crystals of $[CpCr(SPh)]_2S$ (5) (50 mg, 20.7%). Anal. Calcd for $[(C_5H_5)Cr(SPh)]_2S$: C, 54.33; H, 4.17; Cr, 21.45; S, 19.84. Found: C, 54.22; H, 4.02; Cr, 20.95; S, 20.76. Mass spectrum, *m/z*: 484, $[CpCr(SPh)]_2S$; 375, $[Cp_2Cr_2(SPh)]S$; 298, $[Cp_2Cr_2S]S$; 186, $[Ph_2S_2]$; 154, $[Ph_2]$. ^1H NMR (C_6D_6): $\delta(C_5H_5)$ 13.24 ($\nu_{1/2}$ 78 Hz); $\delta(C_6H_5)$ 8.20, 7.66, 7.01, 6.38. IR: ν 1060 (w), 1016 (w), 800 (s), 750 (m), 690 (w) cm^{-1} (Nujol). ^{13}C NMR ($CDCl_3$): $\delta(C_5H_5)$ 100.44; $\delta(C_6H_5)$ 134.44, 131.16, 129.22, 128.90, 128.12, 125.24.

Reaction of $[CpCr(CO)_2]_2$ with Ph_2S_2. (a) At 40 °C. No reaction was observed at ambient temperature. At 40 °C, a deep green solution of $[CpCr(CO)_2]_2$ (200 mg, 0.578 mmol) in toluene (15 mL), containing Ph_2S_2 (126 mg, 0.578 mmol) gave, after 90 h, a dark green suspension. Filtration removed a green precipitate (126 mg) sparingly soluble in most organic solvents.

The filtrate was concentrated to ca. 1 mL and chromatographed on a silica gel column (5 × 1.5 cm) prepared in *n*-hexane. Elution gave two fractions: (i) a greenish-yellow solution in 8 mL of toluene which gave 5 mg of a 3:1 molar mixture of $[CpCr(CO)_2(SPh)]_2$ (3) and $[CpCr(CO)_2]_2$, the starting material (equivalent to 1.2 and 0.5% yields, respectively) and (ii) a purple solution in 5 mL of ether which gave $[CpCr(SPh)]_2S$ (5) (40 mg, 0.083 mmol, 14.3% yield).

(b) At 80 °C. A deep green solution of $[CpCr(CO)_2]_2$ (100 mg, 0.289 mmol) in toluene (5 mL) containing Ph_2S_2 (63 mg, 0.289 mmol) was stirred at 80 °C for 4.5 h. The resultant dark purplish

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Table I. Data Collection and Processing Parameters

	3	5
molecular formula	$(\mu\text{-}C_6H_5S)_2(C_5H_5)_2Cr_2(CO)_4$	$2[(\mu\text{-}C_6H_5S)_2(\mu\text{-}S)(C_5H_5)_2Cr_2]\cdot C_6H_6$
mol wt	564.58	1047.32
color and habit	black polyhedron, unstable in radiation	black parallelepiped
unit cell params		
a, Å	9.138 (2)	9.548 (1)
b, Å	14.195 (6)	10.122 (2)
c, Å	18.879 (5)	13.003 (1)
α, deg		103.71 (1)
β, deg	101.77 (2)	100.351 (9)
γ, deg		98.62 (1)
V, Å^3	2397 (1)	1176.4 (3)
Z	4	1
$F(000)$	1152	538
dens (calcd), g cm^{-3}	1.56	1.48
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
radiation; λ, Å	graphite-monochromatized Mo Kα; 0.71073	graphite-monochromatized Mo Kα; 0.71073
std reflns	$(22\bar{5})$, (231)	$(2\bar{1}\bar{1})$, $(10\bar{3})$
intens variation	a decline of about 40% for standards	±4%
R_{int} (from merging of equiv reflns)	0.060	0.010
abs coeff, cm^{-1}	10.82	11.68
cryst size, mm^3	0.26 × 0.36 × 0.38	0.16 × 0.24 × 0.30
mean μr	0.180	0.14
transm factors	0.406–0.745	0.704–0.826
scan type; rate, deg min^{-1}	ω–2θ; 2.00–11.72	ω; 3.005–15.625
scan range, deg	0.60 below Kα_1 to 0.70 above Kα_2	0.65 below Kα_1 to 0.65 above Kα_2
bckgd counting	stationary counts for one-fifth of scan time at each end of scan range	stationary counts for one-fifth of scan time at each end of scan range
collcn range; $2\theta_{max}$, deg	$h,k,\pm l$; 45	$h,\pm k,\pm l$; 55
no. of unique data measd	3148	5393
no. of obs data with $\lvert F_o\rvert \geq 6\sigma(\lvert F_o\rvert)$, n	2178	3432
no. of variables, p	307	271
$R_F = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0.058	0.045
weighting scheme	$w = [\sigma^2(F_o) + 0.0010\lvert F_o\rvert^2]^{-1}$	$w = [\sigma^2(F_o) + 0.0002\lvert F_o\rvert^2]^{-1}$
$R_G = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.075	0.048
$S = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n-p)]^{1/2}$	1.737	1.622
residual extrema in final diff map, e Å^{-3}	+0.70 to –0.74	+0.36 to –0.42

solution was concentrated to ca. 1 mL and loaded onto a silica gel column (6 × 1 cm) prepared in *n*-hexane. Elution gave two fractions: (a) a purple solution in ether (7 mL) which yielded $[CpCr(SPh)]_2S$ (**5**) (67 mg, 0.138 mmol, 47.9%) and (b) a blue solution in 1:1 THF–CH_3CN (3 mL) which yielded an unidentified blue solid (7 mg).

Thermolysis Reactions. $[CpCr(CO)_2(SPh)]_2$ (3). An orange-brown solution of $[CpCr(CO)_2(SPh)]_2$ (**3**) (50 mg, 0.089 mmol) in toluene (3.5 mL) was heated at 80 °C for 2.5 h. The resultant dark purple solution was concentrated to ca. 1 mL. Chromatography on a silica gel column (7 × 1 cm) afforded two fractions: (a) a purple solution in ether (15 mL) which gave (**5**) (21 mg, 48.93%) and (b) a blue solution in 1:1 THF–CH_3CN (3 mL) which yielded an unidentified blue solid (5 mg).

$[CpCr(CO)(SPh)]_2$ (4). A reddish-brown saturated solution of **4** in THF was maintained at 60 °C under nitrogen for 2.5 h. Examination of the resulting green-purple solution by TLC on a silica gel plate showed only the presence of $[CpCr(SPh)]_2S$ (R_f value = 0.25 with toluene as eluent).

$[CpCr(SPh)]_2S$ (5). A solution of **5** in toluene-d_8 was maintained at 110 °C and its decomposition monitored by its ^1H NMR spectrum. After 24 h, it was completely converted to $Cp_4Cr_4S_4$, identified by its Cp resonance at δ 4.84 and its IR characteristics.[18]

Crystal Structure Determinations. Diffraction-quality crystals of **3** were obtained as dark brown chunky crystals in cluster aggregates from *n*-hexane–THF, after 14 days at –30 °C, and those of **5** as dark purple cuboidal diamond-shaped crystals from a saturated solution in C_6D_6 in a 5-mm NMR tube after 20 days at ambient temperature.

Details of crystal parameters, data collection, and structure refinement are given in Table I. Raw intensities collected on a Nicolet R3m/V four-circle diffractometer at room temperature (294 K) were processed with the profile-fitting procedure of Diamond[19] and corrected for absorption using ψ-scan data.[20] Patterson superposition yielded the positions of the two chromium and two sulfur atoms of **3**, whereas the two chromium and three sulfur atoms of **5** were located by direct phase determination. The coordinates of the other non-hydrogen atoms of **3** and **5** were derived from successive difference Fourier syntheses. The non-hydrogen atoms were subjected to anisotropic refinement, and the H atoms were generated geometrically (C–H bonds fixed at 0.96 Å) and assigned the same isotropic temperature factor of U = 0.08 Å^2. Computations were performed using the SHELTXL-PLUS program package[21] on a DEC MicroVAX-II computer. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.[22]

Results and Discussion

Synthetic Studies. A deep green suspension of $[CpCr(CO)_3]_2$ (**1**) in toluene reacted with Ph_2S_2 at ambient temperature within 20 min to give a brown homogeneous solution from which was isolated pure brown crystals of $[CpCr(CO)_2(SPh)]_2$ (**3**) in 32.9% yield. Under thermolytic conditions at 60 °C, the same reaction for 3 h gave a greenish brown suspension, which gave brown crystals of $[CpCr(CO)(SPh)]_2$ (**4**), green crystals of $[CpCr(CO)_2]_2$ (**2**), and purple crystals of $[CpCr(SPh)]_2S$ (**5**) in 53.0, 2.3, and 2.5% yields, respectively. A similar reaction for 0.5 h at 60 °C and 1.5 h at 80 °C resulted in the isolation of **2**, **3**, and **5** in 5.8, 5.0, and 20.7% yields, respectively. The reaction of $[CpCr(CO)_2]_2$ with Ph_2S_2 was much less facile

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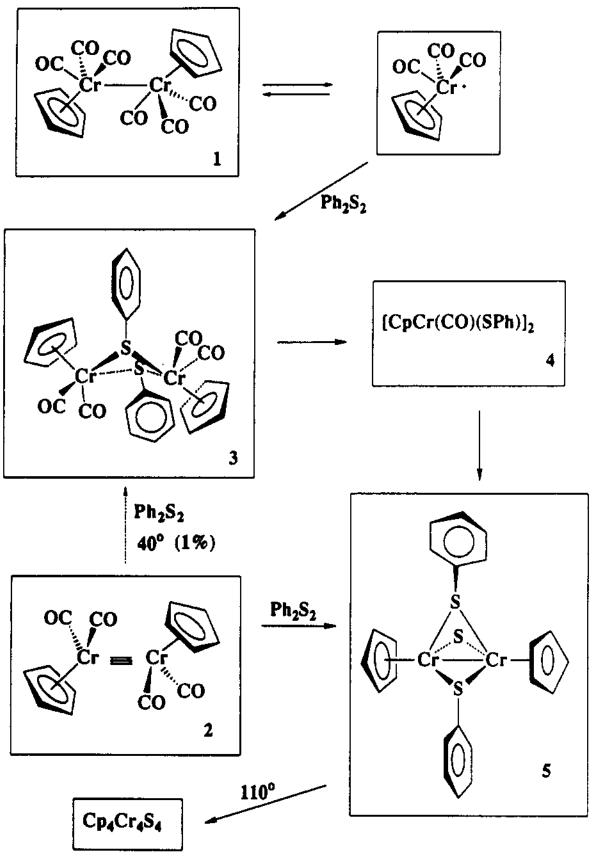
Scheme I



and did not proceed at all at ambient temperature. A reaction at 40 °C took ca. 90 h to reach completion, giving **3** (1.2%), **5** (14.3%), and an unidentified blue species.

The thermolytic degradation of **3** was complete after 2.5 h at 80 °C, giving a dark purple solution from which was isolated **5** in ca. 49% yield and a small amount of an uncharacterizable blue solid. Likewise, **4** was thermolyzed to **5** after 2.5 h at 60 °C. A solution of **5** in toluene-d_8 was found to be stable at ambient temperature, but after 24 h at 110 °C, was completely converted into $Cp_4Cr_4S_4$.

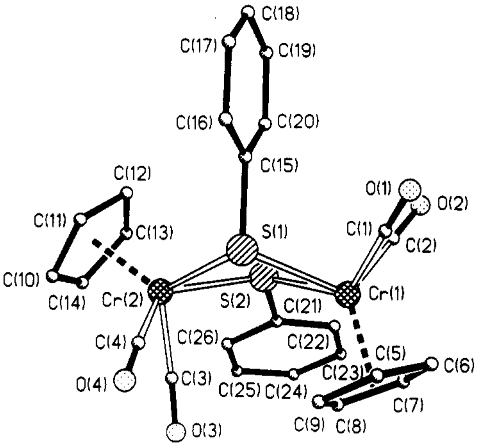


Figure 1. Perspective view of the molecular structure of $[CpCr(CO)_2(SPh)]_2$ (**3**).

Reaction Pathways. The synthetic and reaction pathways as described above are illustrated in Scheme I. We have earlier postulated that the facile reactions of **1** with elemental S_8,[13] Se_8,[14] P_4,[42] and As_4,[43] arises from the documented high tendency of **1** to dissociate into 17e radical species in solution.[9,11,23] In view of this and the known susceptibility of the S–S bond in organic disulfides to cleavage by nucleophilic, electrophilic, and radical processes,[24] it is conceivable that the initial step here also involves the attack of the $CpCr(CO)_3$ radical on the S–S bond of Ph_2S_2, resulting in thiolate-bridged dimers. Indeed, the effectiveness of many transition-metal complexes in S–S bond cleavage has long been recognized.[25] In fact, studies on the reaction of various transition-metal complexes with organic disulfides show that in cases where dissociation of the dimeric complex does not occur readily in solution, photochemical or thermal activation is necessary. Thus, the reaction of $[CpMo(CO)_3]_2$ with various R_2S_2 had to be carried out under UV irradiation[4a,5b,26,27] and that of $[CpFe(CO)_2]_2$ with Me_2S_2, under UV irradiation or thermolytic conditions.[3a,4c]

The isolation as major products of $[CpCr(CO)_2(SPh)]_2$ (**3**) under mild reaction conditions and of $[CpCr(CO)(SPh)]_2$ (**4**) and $[CpCr(SPh)]_2S$ (**5**) under thermolytic conditions indicates that **3** is the primary product. Indeed, the thermal degradation of **3** and **4** to give **5** as the sole isolable major product was independently demonstrated. This observed complete loss of CO ligands to form **5** seems to suggest that the non-carbonyl-containing complexes obtained from previous reported exhaustive cothermolysis reactions of $[CpM(CO)_3]_2$ with R_2S_2, viz. $Cp_2Cr_2(SMe)_3$ and $[CpMo(SMe)_2]_2$ from Me_2S_2 in refluxing methylcyclohexane (101 °C)[4a] and $[CpMo(SPh)_2]_x$ from Ph_2S_2 in refluxing toluene,[4b] could derive from carbonyl-containing intermediates, e.g. $[CpM(CO)_x(SR)]_2$. Partial decarbonylation occurs under mild thermolysis in toluene at 60 °C for 30 min, giving $[CpCr(CO)(SPh)]_2$ (**4**). This has been observed before in the high-temperature thermolysis of $[CpMo(CO)_2(SR)]_2$ (R = Me, ^{t}Bu, Ph, *p*-tolyl)[5b] and the mild thermolysis in vacuo of $[(\eta^5\text{-MeCp})Mo(CO)_2(EPh)]_2$ (E = Se, Te).[26]

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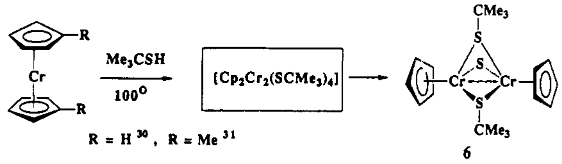
Table II. Atomic Coordinates (×10⁵ for Cr, ×10⁴ for Other Atoms) and Equivalent Isotropic Temperature Factors[a] (Å² × 10⁴ for Cr and S, Å² × 10³ for Other Atoms) for Complex 3

atom	x	y	z	U_{eq}
Cr(1)	19482 (15)	18211 (9)	11727 (7)	312 (5)
Cr(2)	−11826 (15)	25525 (9)	21145 (6)	294 (5)
S(1)	1290 (3)	1777 (1)	2367 (1)	320 (7)
S(2)	278 (2)	3150 (1)	1270 (1)	314 (7)
O(1)	4878 (8)	1285 (5)	2141 (4)	66 (3)
O(2)	3967 (8)	3372 (4)	871 (4)	56 (3)
O(3)	−3280 (8)	1832 (5)	795 (3)	59 (3)
O(4)	−1842 (8)	532 (4)	2390 (3)	53 (3)
C(1)	3768 (12)	1499 (6)	1774 (5)	46 (4)
C(2)	3186 (11)	2777 (6)	986 (4)	38 (3)
C(3)	−2455 (11)	2136 (6)	1289 (5)	39 (3)
C(4)	−1582 (10)	1316 (6)	2302 (4)	35 (3)
C(5)	1772 (11)	327 (6)	929 (4)	40 (3)
C(6)	2452 (11)	788 (6)	417 (5)	46 (4)
C(7)	1393 (11)	1411 (6)	19 (4)	44 (4)
C(8)	69 (11)	1312 (6)	286 (5)	46 (4)
C(9)	315 (11)	643 (6)	849 (4)	38 (3)
C(10)	−2650 (14)	2899 (7)	2860 (6)	63 (5)
C(11)	−1217 (14)	2984 (7)	3217 (5)	52 (4)
C(12)	−521 (12)	3696 (6)	2912 (5)	51 (4)
C(13)	−1551 (15)	4065 (6)	2346 (5)	56 (4)
C(14)	−2871 (13)	3584 (9)	2305 (6)	67 (5)
C(15)	2635 (9)	2441 (6)	2999 (4)	33 (3)
C(16)	3233 (11)	2026 (7)	3657 (4)	48 (4)
C(17)	4296 (12)	2503 (8)	4163 (5)	60 (4)
C(18)	4723 (12)	3384 (8)	4023 (5)	59 (4)
C(19)	4149 (11)	3815 (7)	3377 (5)	49 (4)
C(20)	3081 (10)	3340 (6)	2853 (5)	42 (3)
C(21)	−709 (10)	3619 (5)	425 (4)	35 (3)
C(22)	19 (11)	3734 (5)	−138 (4)	37 (3)
C(23)	−712 (12)	4170 (6)	−781 (4)	47 (4)
C(24)	−2142 (13)	4471 (6)	−844 (5)	50 (4)
C(25)	−2907 (12)	4360 (6)	−297 (5)	55 (4)
C(26)	−2179 (11)	3933 (6)	340 (5)	46 (4)

[a] U_{eq} defined as one-third of the trace of the orthogonalized **U** tensor.

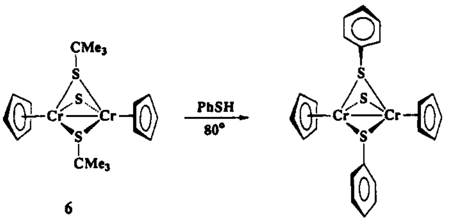
The formation of M–S bonds is often a feature of the reaction of transition-metal complexes with mercaptans e.g. of $Co_2(CO)_8$ with $C_6H_5CH_2SH$[28] or thermolysis of metallic mercaptides, e.g. $Hg(SCMe_3)_2$.[29] The first example of the Cr_2S_3 framework containing a Cr–S–Cr bridge, as found in **5**, was obtained by Pasynskii[30] from the reaction of chromocene with *tert*-butyl mercaptan in heptane reflux, presumably via $Cp_2Cr_2(SCMe_3)_4$, as depicted in (i).



6

(i)

On reacting **6** with PhSH in refluxing benzene, Pasynskii was able to replace the rather labile *tert*-butylthiolate groups with thiophenolate groups (eq ii), converting it to



6 **5**

(ii)

5 which was found to be antiferromagnetic (−2J = 430 cm^{-1}).[32] Like $(CpCrSCMe_3)_2S$,[33] **5** was totally converted, after prolonged thermolysis in refluxing toluene, to the cubane-like cluster $Cp_4Cr_4S_4$, the ultimate degradation product of numerous other cyclopentadienylchromium complexes of S.[13,18,34]

Structures. The perspective view of the molecular structure of **3** is illustrated in Figure 1. Its atomic coordinates are given in Table II and bonding parameters given in Table III.

Thiolate ligands show a high tendency to utilize an additional sulfur lone-pair of electrons to form dinuclear

Table III. Bond Lengths (Å) and Bond Angles (deg) for Complex 3

(i) Coordination Geometry about Cr Atoms			
Cr(1)–S(1)	2.449 (3)	Cr(2)–S(1)	2.471 (3)
Cr(1)–S(2)	2.457 (3)	Cr(2)–S(2)	2.431 (3)
Cr(1)–C(1)	1.87 (1)	Cr(2)–C(3)	1.842 (8)
Cr(1)–C(2)	1.85 (1)	Cr(2)–C(4)	1.842 (9)
Cr(1)–Cp(1)[a]	1.857 (9)	Cr(2)–Cp(2)	1.865 (9)
O(1)–C(1)	1.15 (1)	O(3)–C(3)	1.16 (1)
O(2)–C(2)	1.15 (1)	O(4)–C(4)	1.16 (1)
Cr(1)···Cr(2)	3.808 (2)		
S(1)–Cr(1)–S(2)	71.2 (1)	S(1)–Cr(2)–S(2)	71.3 (1)
S(1)–Cr(1)–C(1)	77.9 (3)	S(1)–Cr(2)–C(3)	114.5 (3)
S(2)–Cr(1)–C(1)	129.2 (3)	S(2)–Cr(2)–C(3)	83.9 (3)
S(1)–Cr(1)–C(2)	118.0 (3)	S(1)–Cr(2)–C(4)	75.4 (3)
S(2)–Cr(1)–C(2)	82.2 (3)	S(2)–Cr(2)–C(4)	128.0 (3)
C(1)–Cr(1)–C(2)	78.0 (4)	C(3)–Cr(2)–C(4)	75.0 (4)
S(1)–Cr(1)–Cp(1)	119.1 (3)	S(1)–Cr(2)–Cp(2)	123.2 (3)
S(2)–Cr(1)–Cp(1)	116.5 (3)	S(2)–Cr(2)–Cp(2)	115.7 (3)
C(1)–Cr(1)–Cp(1)	113.6 (4)	C(3)–Cr(2)–Cp(2)	122.2 (4)
C(2)–Cr(1)–Cp(1)	122.9 (4)	C(4)–Cr(2)–Cp(2)	115.8 (4)
Cr(1)–C(1)–O(1)	178.8 (8)	Cr(2)–C(3)–O(3)	176.0 (8)
Cr(1)–C(2)–O(2)	179.6 (8)	Cr(2)–C(4)–O(4)	177.2 (7)
S(1)–Cr(1)···Cr(2)	39.5 (1)	S(1)–Cr(2)···Cr(1)	39.1 (1)
S(2)–Cr(1)···Cr(2)	38.6 (1)	S(2)–Cr(2)···Cr(1)	39.1 (1)
C(1)–Cr(1)···Cr(2)	116.3 (3)	C(3)–Cr(2)···Cr(1)	85.5 (3)
C(2)–Cr(1)···Cr(2)	115.9 (3)	C(4)–Cr(2)···Cr(1)	91.5 (3)
Cp(1)–Cr(1)···Cr(2)	107.8 (3)	Cp(2)–Cr(2)···Cr(1)	144.2 (3)
(ii) Geometry about Bridging S Atoms			
S(1)–C(15)	1.796 (8)	S(2)–C(21)	1.793 (8)
S(1)···S(2)	2.857 (5)		
Cr(1)–S(1)–Cr(2)	101.4 (1)	Cr(1)–S(2)–Cr(2)	102.3 (1)
Cr(1)–S(1)–C(15)	109.6 (3)	Cr(1)–S(2)–C(21)	115.2 (3)
Cr(2)–S(1)–C(15)	111.6 (3)	Cr(2)–S(2)–C(21)	118.0 (3)
S(2)···S(1)–C(15)	101.6 (4)	S(1)···S(2)–C(21)	158.1 (4)
(iii) Cyclopentadienyl Groups			
C(5)–C(6)	1.41 (1)	C(10)–C(11)	1.35 (2)
C(5)–C(9)	1.38 (1)	C(10)–C(14)	1.41 (2)
C(6)–C(7)	1.41 (1)	C(11)–C(12)	1.38 (2)
C(7)–C(8)	1.41 (2)	C(12)–C(13)	1.38 (1)
C(8)–C(9)	1.41 (1)	C(13)–C(14)	1.37 (2)
C(6)–C(5)–C(9)	108.9 (7)	C(11)–C(10)–C(14)	107 (1)
C(5)–C(6)–C(7)	107.8 (9)	C(10)–C(11)–C(12)	109.9 (9)
C(6)–C(7)–C(8)	107.1 (8)	C(11)–C(12)–C(13)	107.6 (9)
C(7)–C(8)–C(9)	108.6 (8)	C(12)–C(13)–C(14)	108.0 (9)
C(5)–C(9)–C(8)	107.6 (9)	C(10)–C(14)–C(13)	108.0 (9)
(iv) Phenyl Groups			
C(15)–C(16)	1.38 (1)	C(21)–C(22)	1.38 (1)
C(15)–C(20)	1.39 91)	C(21)–C(26)	1.39 (1)
C(16)–C(17)	1.39 (1)	C(22)–C(23)	1.40 (1)
C(17)–C(18)	1.35 (2)	C(23)–C(24)	1.36 (2)
C(18)–C(19)	1.37 (1)	C(24)–C(25)	1.37 (2)
C(19)–C(20)	1.41 (1)	C(25)–C(26)	1.39 (1)
S(1)–C(15)–C(16)	117.7 (7)	S(2)–C(21)–C(22)	119.8 (7)
S(1)–C(15)–C(20)	122.7 (6)	S(2)–C(21)–C(26)	121.3 (7)
C(16)–C(15)–C(20)	119.6 (7)	C(22)–C(21)–C(26)	118.7 (7)
C(15)–C(16)–C(17)	120.2 (9)	C(21)–C(22)–C(23)	120.0 (9)
C(16)–C(17)–C(18)	120.4 (8)	C(22)–C(23)–C(24)	119.7 (9)
C(17)–C(18)–C(19)	120.9 (9)	C(23)–C(24)–C(25)	121.9 (8)
C(18)–C(19)–C(20)	119.7 (9)	C(24)–C(25)–C(26)	118.3 (9)
C(15)–C(20)–C(19)	119.3 (7)	C(21)–C(26)–C(25)	121.4 (9)

[a] Cp(1) is the center of the ring composed of carbon atoms C(5)–C(9), and Cp(2) is the center of the C(10)–C(14) ring.

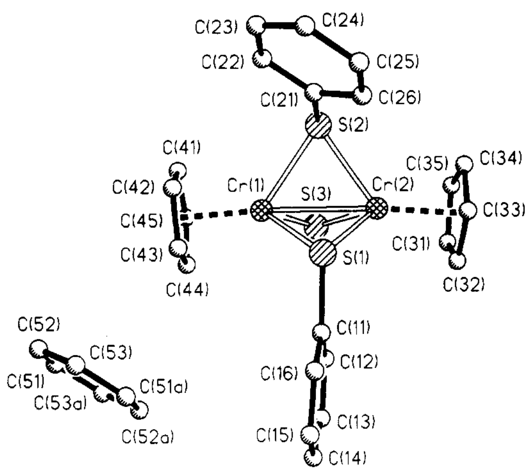


Figure 2. Perspective view of the molecular structure of $[CpCr(SPh)]_2S$ (**5**).

Table IV. Atomic Coordinates (×10⁵ for Cr Atoms, ×10⁴ for Other Atoms) and Equivalent Isotropic Temperature Factors[a] ($Å^2 \times 10^4$ for Cr and S Atoms, $Å^2 \times 10^3$ for Other Atoms) for 5

atom	x	y	z	U_{eq}
Cr(1)	694 (7)	22984 (6)	17781 (5)	351 (2)
Cr(2)	−23095 (7)	30875 (7)	8928 (5)	376 (3)
S(1)	−1175 (1)	3828 (1)	2763 (1)	370 (4)
S(2)	−2224 (1)	788 (1)	1016 (1)	419 (4)
S(3)	−307 (1)	2930 (1)	221 (1)	457 (4)
C(11)	−150 (4)	5562 (4)	3156 (3)	37 (2)
C(12)	492 (5)	6171 (4)	2469 (3)	53 (2)
C(13)	1315 (6)	7501 (5)	2849 (4)	62 (2)
C(14)	1515 (6)	8243 (5)	3910 (4)	59 (2)
C(15)	860 (6)	7652 (5)	4588 (4)	65 (2)
C(16)	17 (5)	6324 (4)	4217 (3)	52 (2)
C(21)	−2971 (5)	301 (4)	2073 (3)	43 (2)
C(22)	−2469 (6)	−717 (5)	2479 (4)	60 (2)
C(23)	−3077 (7)	−1174 (6)	3259 (5)	76 (3)
C(24)	−4173 (7)	−637 (6)	3623 (5)	78 (3)
C(25)	−4666 (6)	368 (6)	3223 (4)	72 (3)
C(26)	−4078 (5)	846 (5)	2450 (4)	56 (2)
C(31)	−3075 (6)	4331 (8)	−203 (6)	82 (3)
C(32)	−3349 (6)	4888 (6)	818 (5)	77 (3)
C(33)	−4352 (6)	3859 (6)	1004 (5)	67 (3)
C(34)	−4672 (5)	2730 (6)	127 (5)	64 (2)
C(35)	−3893 (6)	3006 (7)	−607 (4)	70 (3)
C(41)	1442 (6)	718 (6)	1820 (5)	70 (2)
C(42)	1260 (6)	1260 (6)	2878 (5)	67 (2)
C(43)	1891 (6)	2653 (6)	3199 (4)	64 (2)
C(44)	2450 (5)	2984 (6)	2359 (5)	65 (2)
C(45)	2174 (6)	1781 (7)	1514 (4)	69 (3)
C(51)	5962 (7)	4374 (10)	4574 (9)	101 (4)
C(52)	5454 (11)	3984 (7)	5376 (10)	108 (4)
C(53)	4461 (11)	4621 (11)	5790 (5)	99 (4)

[a] U_{eq} defined as one-third of the trace of the orthogonalized **U** tensor.

complexes with two bridging ligands.[35] The $M(\mu\text{-}SR)_2M$ unit in these complexes may be planar as in $[CpMo(CO)(\mu\text{-}SCMe_3)]_2$,[5b] $[CpCr(\mu\text{-}SPh)(NO)]_2$,[36] $[Mn_2(SC_2H_4S)_4]^{2-}$,[37] and $[Fe(\mu\text{-}SEt)(CO)_3]_2$,[40] depending on the central metal and the strength of the metal–metal bond. In **3**, the Cr_2S_2 fragment is nonplanar and the dihedral angle between Cr(1)–S(1)–Cr(2) and Cr(1)–S(2)–Cr(2) is 44.9 (2)° (Figure 1). Each chromium atom is in a tetragonal-pyramidal coordination environment, with the cyclopentadienyl group occupying the axial position. The two tetragonal pyramids share a basal edge [S(1)···S(2)] in an anti relationship, the dihedral angle between the two basal planes being 36.3 (8)°. Cr(1) and Cr(2) are each displaced from the respective basal plane by 0.983 (8) and 1.015 (8) Å in the direction of the cyclopentadienyl group.

Table V. Bond Lengths (Å) and Bond Angles (deg) for Complex 5

(i) Coordination Geometry about Cr Atoms			
Cr(1)–Cr(2)	2.676 (1)		
Cr(1)–S(1)	2.368 (1)	Cr(2)–S(1)	2.365 (1)
Cr(1)–S(2)	2.369 (1)	Cr(2)–S(2)	2.383 (1)
Cr(1)–S(3)	2.248 (1)	Cr(2)–S(3)	2.251 (2)
Cr(1)–Cp(1)[a]	1.876 (6)	Cr(2)–Cp(2)	1.885 (6)
Cr(2)–Cr(1)–S(1)	55.5 (1)	Cr(1)–Cr(2)–S(1)	55.6 (1)
Cr(2)–Cr(1)–S(2)	56.0 (1)	Cr(1)–Cr(2)–S(2)	55.5 (1)
S(1)–Cr(1)–S(2)	86.7 (1)	S(1)–Cr(2)–S(2)	86.5 (1)
Cr(2)–Cr(1)–S(3)	53.6 (1)	Cr(1)–Cr(2)–S(3)	53.4 (1)
S(1)–Cr(1)–S(3)	98.4 (1)	S(1)–Cr(2)–S(3)	98.4 (1)
S(2)–Cr(1)–S(3)	84.6 (1)	S(2)–Cr(2)–S(3)	84.2 (1)
Cr(2)–Cr(1)–Cp(1)	174.4 (2)	Cr(1)–Cr(2)–Cp(2)	174.6 (2)
S(1)–Cr(1)–Cp(1)	125.1 (2)	S(1)–Cr(2)–Cp(2)	125.2 (2)
S(2)–Cr(1)–Cp(1)	128.8 (2)	S(2)–Cr(2)–Cp(2)	129.0 (2)
S(3)–Cr(1)–Cp(1)	122.0 (2)	S(3)–Cr(2)–Cp(2)	122.2 (2)
(ii) Geometry about Bridging S Atoms			
S(1)–C(11)	1.783 (4)	S(2)–C(21)	1.791 (5)
S(1)···S(2)	3.252 (2)	S(1)···S(3)	3.469 (2)
S(2)···S(3)	3.109 (2)		
Cr(1)–S(1)–Cr(2)	68.9 (1)	Cr(1)–S(1)–C(11)	110.2 (2)
Cr(2)–S(1)–C(11)	112.2 (1)	Cr(1)–S(2)–Cr(2)	68.6 (1)
Cr(1)–S(2)–C(21)	109.6 (1)	Cr(2)–S(2)–C(21)	115.6 (2)
S(2)···S(1)–C(11)	149.4 (2)	S(1)···S(2)–C(21)	84.1 (2)
Cr(1)–S(3)–Cr(2)	73.0 (1)		
(iii) Phenyl Groups			
C(11)–C(12)	1.378 (7)	C(21)–C(22)	1.373 (7)
C(11)–C(16)	1.380 (5)	C(21)–C(26)	1.377 (7)
C(12)–C(13)	1.378 (6)	C(22)–C(23)	1.390 (9)
C(13)–C(14)	1.369 (6)	C(23)–C(24)	1.36 (1)
C(14)–C(15)	1.365 (8)	C(24)–C(25)	1.354 (9)
C(15)–C(16)	1.384 (6)	C(25)–C(26)	1.383 (8)
S(1)–C(11)–C(12)	124.0 (3)	S(2)–C(21)–C(22)	118.3 (4)
S(1)–C(11)–C(16)	117.4 (3)	S(2)–C(21)–C(26)	122.9 (4)
C(12)–C(11)–C(16)	118.6 (4)	C(22)–C(21)–C(26)	118.8 (5)
C(11)–C(12)–C(13)	120.3 (4)	C(21)–C(22)–C(23)	119.9 (5)
C(12)–C(13)–C(14)	121.2 (5)	C(22)–C(23)–C(24)	121.1 (6)
C(13)–C(14)–C(15)	118.7 (4)	C(23)–C(24)–C(25)	119.0 (6)
C(14)–C(15)–C(16)	120.9 (4)	C(24)–C(25)–C(26)	121.2 (6)
C(11)–C(16)–C(15)	120.3 (5)	C(21)–C(26)–C(25)	120.1 (5)
(iv) Cyclopentadienyl Groups			
C(31)–C(32)	1.40 (1)	C(41)–C(42)	1.407 (8)
C(31)–C(35)	1.374 (9)	C(41)–C(45)	1.371 (9)
C(32)–C(33)	1.401 (9)	C(42)–C(43)	1.379 (8)
C(33)–C(34)	1.360 (7)	C(43)–C(44)	1.385 (9)
C(34)–C(35)	1.365 (9)	C(44)–C(45)	1.387 (7)
C(32)–C(31)–C(35)	107.6 (6)	C(42)–C(41)–C(45)	107.9 (5)
C(31)–C(32)–C(33)	106.6 (5)	C(41)–C(42)–C(43)	107.4 (5)
C(32)–C(33)–C(34)	108.3 (6)	C(42)–C(43)–C(44)	108.5 (5)
C(33)–C(34)–C(35)	108.8 (5)	C(43)–C(44)–C(45)	107.8 (5)
C(31)–C(35)–C(34)	108.8 (5)	C(41)–C(45)–C(44)	108.5 (5)
(v) Benzene (Solvent)			
C(51)–C(52)	1.34 (2)	C(51)–C(53a)	1.31 (2)
C(52)–C(53)	1.34 (2)	C(53)–C(51a)	1.31 (2)
C(52)–C(51)–C(53a)	121.3 (9)	C(51)–C(52)–C(53)	119.0 (9)
C(52)–C(53)–C(51a)	120 (1)		

Symmetry transformation: a $(1 - x, 1 - y, 1 - z)$

[a] Cp(1) is the center of the ring composed of carbon atoms C(41)–C(45), and Cp(2) is the center of the C(31)–C(35) ring.

The Cr(1)···Cr(2) separation of 3.808 (2) Å is much longer than the normal Cr–Cr single bond found in related dinuclear complexes [2.950 (2) Å for $[CpCr(\mu\text{-}SPh)(NO)]_2$ (**7**)[36] and 2.906 (3) Å for $Cp_2Cr_2(NO)_2(\mu\text{-}SCMe_3)(\mu\text{-}S\text{-}SCMe_3)$ (**8**)[41]] so that no metal–metal bond is formed between them. The angles S(2)···S(1)–C(15) = 101.6 (4)° and S(1)···S(2)–C(21) = 158.1 (4)° indicate that the two phenyl groups attached to the thiolato bridges are in the axial–equatorial configuration. The crystals of the complex

Table VI. Comparison of Cr–Cr Bonds and Cr–S Bonds in Related Complexes

complex	Cr–Cr, Å	Cr–S(sulfido), Å		Cr–S(thiolato), Å		ref
5	2.676 (1)	2.248 (1)	2.251 (1)	2.368 (1) 2.365 (1)	2.369 (1) 2.383 (1)	this work
6	2.689 (8)	2.22 (1)	2.25 (1)	2.41 (1) 2.37 (1)	2.39 (1) 2.36 (1)	30
7	2.950 (1)			2.317 (2)	2.315 (2)	36
8	2.906 (3)			2.295 (4) 2.307 (4)	2.296 (4) 2.298 (4)	41

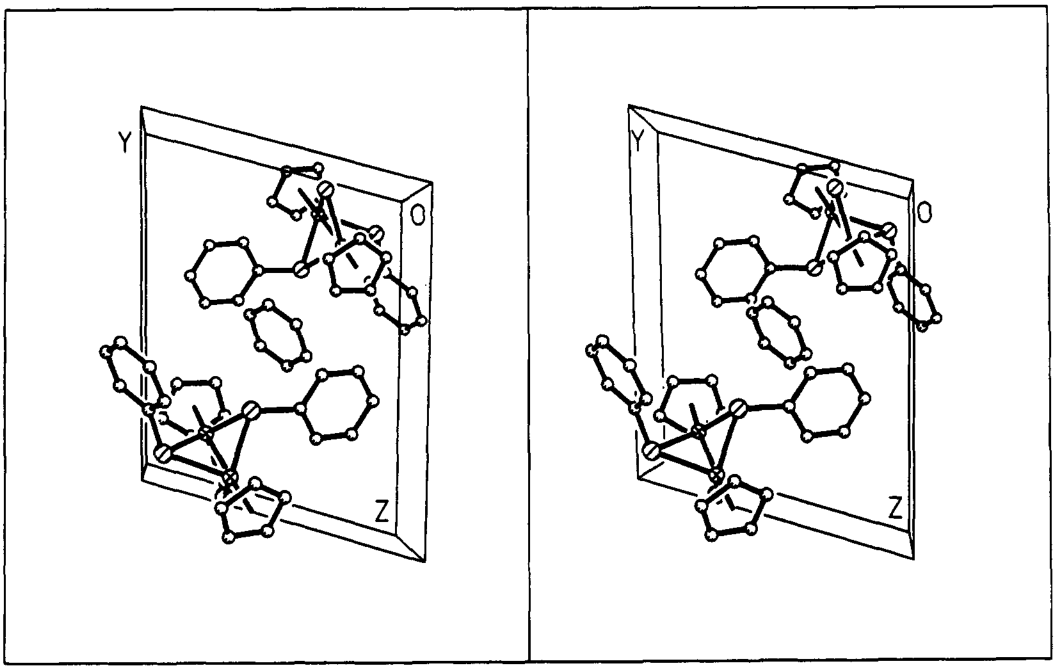


Figure 3. Stereoview of the crystal structure of $2[Cp_2Cr_2(SPh)_2S]\cdot C_6H_6$. The origin of the unit cell lies at the upper right corner, with *a* pointing toward the reader, *b* from right to left at an upward slant, and *c* vertically downward.

consist of a packing of discrete molecules with normal van der Waals separations.

A perspective view of 5, including the neighboring solvent molecule (C_6H_6), is shown in Figure 2. The atomic coordinates are given in Table IV and bonding parameters given in Table V. The structure resembles closely that of the analogous bis(μ-*tert*-butylthiolato) complex (6). In both these complexes, the formal +3 oxidation state of the Cr atoms would require the existence of a triple bond between them, in accordance with the demands of the 18e rule. This is reflected in the much shorter Cr–Cr distance [2.676 (1) Å in 5, and 2.689 (8) Å in 6] as compared with the Cr–Cr single-bond lengths in the analogous complexes 7 and 8 with the sulfido bridge substituted by two terminal NO groups. Each Cr atom in 5 is in an elongated tetrahedral coordination environment, with the Cp ligand occupying the apical position and the two coordination polyhedra sharing a common basal plane comprising three bridging S atoms; the Cp–Cr–S angles [average 125.4 (2)°] greatly exceed the S–Cr–S angles [average 89.8 (1)°]. The Cr–S(thiolato) bond distances [2.371 (1) Å] are significantly longer than the Cr–S(sulfido) distances [2.250 (1) Å], and Table VI gives a comparison of the measured Cr–Cr and Cr–S bond lengths in these complexes. The angles S(2)···S(1)–C(11) = 149.4 (2)° and S(1)···S(2)–C(31) = 84.1 (2)° indicate that the two phenyl groups attached to the thiolato bridges are in the equatorial–axial configuration. The two cyclopentadienyl ligands are approximately in an eclipsed configuration about the Cr(1)–Cr(2) bond, and the dihedral angle between their least-squares planes is 12.0 (5)°.

A stereoview of the crystal structure is given in Figure 3. The closest C···C contact between the benzene molecule, which occupies the crystallographic inversion center at ($^1/_2$, $^1/_2$, $^1/_2$), and the dinuclear complex is 3.59 (2) Å, so that the crystal consists of a packing of discrete molecules with normal van der Waals separation. As shown in Figure 3, the benzene molecules are piled up in a column in the direction of the *a* axis.

The structural character of 4 remains speculative for lack of a suitable crystal. The IR data (ν_{CO} 1865 (vs) and 1745 (vs)) are indicative of bridging CO groups, in contrast to terminal CO groups (ν_{CO} 1881 (w) and 1858 (s)) and a Mo═Mo bond (2.616 Å) in $[CpMo(CO)(\mu\text{-}SCMe_3)]_2$, the only other complex of similar empirical formula.[5b]

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Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen atom coordinates and assigned isotropic temperature factors for 3 and 5 (4 pages); tables listing observed and calculated structure factors for 3 and 5 (32 pages). Ordering information is given on any current masthead page.