ethane. The reaction mixture was warmed to room temperature and stirred for 30 min, and a white precipitate formed. The product was collected by filtration, washed with two 5-mL portions of cold THF, and dried under vacuum. The product was recrystallized from hot THF or $CH_2Cl_2/Et_2O$: yield 0.81 g (84%); $^1H$ NMR ($CD_2Cl_2$) $\delta$ 7.5–6.7 (m, 20 H, $BPh_4^-$), 5.68 (t, $J$ = 1.2 Hz, 10 H, Cp), 1.66 (m, $CH_2$), 1.30 (pseudoquartet, $|J_{P-Me}-J_{P'-Me}|$ = 7.1 Hz, 12 H, P–$CH_3$), –0.12 (pseudoquartet, $|J_{P-Me}-J_{P'-Me}|$ = 19.5 Hz, 3 H, Zr–$CH_3$) $CH_3$) $^{31}P\{^1H\}$ NMR (THF-$d_8$) AB pattern $\delta$ 7.8, 4.9 ($J_{P-P}$ = 52.8 Hz); $^{13}C$ NMR ($CD_2Cl_2$) $\delta$ 164 (q, $J_{B-C}$ = 49.5 Hz), 136, 126, 122, 107 (Cp), 26.8 (m, dmpe), 24.9 (m, dmpe), 14.8 (m, Zr–$CH_3$), 14.6 (m, P–$CH_3$), 13.3 (m, P–$CH_3$). Anal. Calcd: C, 69.77; H, 7.00; P, 8.78; Zr, 12.92. Found: C, 68.00; H, 6.82; P,

8.89; Zr, 12.82.

**Supplementary Material Available:** Tables of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates for 13 (5 pages); a listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

# Chemistry of [CpCr(CO)₃]₂. Synthesis of Cp₂Cr₂(CO)₄S, Cp₂Cr₂(CO)₄S₂, and Cp₂Cr₂(CO)₅S₂. Crystal Structure and Reactivity of Cp₂Cr₂(CO)₄S₂ and Cp₂Cr₂(CO)₅S₂

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The instantaneous reaction of [CpCr(CO)₃]₂ (Cp = $\eta^5$-C₅H₅) in tetrahydrofuran or toluene with stoichiometric amounts of elemental sulfur produced Cp₂Cr₂(CO)₄S (1) and Cp₂Cr₂(CO)₅S₂ (2) in near quantitative yields. A solution of 2 on standing 1 h at ambient temperature gave a mixture of Cp₂Cr₂(CO)₄S₂ (3) (76%) and 1. The transformation of the very labile complex 2 to 3 with the cleavage of a CO ligand thence to the linear multiple bonded Cr–S–Cr complex 1 with extrusion of a S atom and finally to Cp₄Cr₄S₄ was demonstrated by a time-dependent NMR study at 30 °C. When 2 was treated with CF₃SO₃CH₃, one of the S atoms was immediately methylated, giving [Cp₂Cr₂(CO)₅S₂(CH₃)](SO₃CF₃) (4) as a fine black unstable solid, which decomposed in solution to give 1 and [Cp₄Cr₄S₄(CH₃)](SO₃CF₃) (5). Complexes 1–3 have been characterized by elemental, spectral, and crystal structure analyses. The structure of 1 has been reported previously. Crystals of 2 are monoclinic, $P2_1/n$, with $a$ = 11.638 (4) Å, $b$ = 15.508 (5) Å, $c$ = 9.825 (3) Å, $\beta$ = 111.56 (2)°, and $Z$ = 4. Crystals of 3 are monoclinic, $P2_1/c$, with $a$ = 8.214 (1) Å, $b$ = 11.464 (2) Å, $c$ = 16.182 (3) Å, $\beta$ = 92.44 (1)°, and $Z$ = 4. The disulfur ligand bridges the two chromium centers asymmetrically $\mu$-$\eta^1,\eta^2$ in 2 and symmetrically $\mu$-$\eta^2$ in 3. S–S distances [2.010 (4) Å, 2; 1.990 (1) Å, 3] are similar to those found in other transition-metal $\mu$-S₂ complexes. Metal atoms in both complexes exhibit 4:3, 7-coordination.

## Introduction

In the last few years there has been a rapidly increasing interest in the syntheses and structural determinations of sulfur-rich transition-metal complexes. In particular, the disulfur ligand has attracted considerable attention,[1] primarily on account of its versatility in bonding and coordination modes[2] and hence its high potential in the generation of new metal-cluster complexes. Disulfur complexes are also of interest because, like their dioxygen and dinitrogen analogues, they have biological[3] and catalytic[4] implications. They are known to occur with a number of transition metals but are still relatively uncommon, and very little is known of the reactions of the S₂ ligands. Our preliminary communication[5] has described the syntheses and structures of Cp₂Cr₂(CO)₄S (1) and Cp₂Cr₂(CO)₅S₂ (2). Earlier, Legzdins[6] and co-workers had reported the preparation of 1 from the reaction of Na[CpCr(CO)₃] with S₃N₃Cl₃ together with its structure. Very recently, Herrmann[7] et al. have also synthesized the analogous compounds (C₅Me₅)₂Cr₂(CO)₄S and (C₅Me₅)₂Cr₂(CO)₅S₂ by a similar reaction. We report herein the relevant details for the preparation of 1, 2, and Cp₂Cr₂(CO)₄S₂ (3) from the reaction of [CpCr(CO)₃]₂ with

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(4) Weisser, O.; Landa, S. In *Sulfide Catalysts, Their Properties and Applications*; Pergamon: New York, 1973.

(5) Goh, L. Y.; Hambley, T. W.; Robertson, G. B. *J. Chem. Soc., Chem. Commun.* **1983**, 1458.

(6) Greenhough, T. J.; Kolthammer, B. W. S.; Legzdins, P.; Trotter, J. *Inorg. Chem.* **1979**, *18*, 3543.

(7) Herrmann, W. A.; Rohrmann, J.; Schäffer, A. *J. Organomet. Chem.* **1984**, *265*, Cl.

elemental sulfur and the structures of **2** and **3** together with some aspects of their reactivity.

## Experimental Section

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

**Reagents and Solvents.** $Cr(CO)_6$ was obtained from Strem Chemicals, Inc. Cyclooctasulfur was "S sublime" from B.D.H. $[CpCr(CO)_3]_2$ was synthesized as described previously.[8] Diethyl ether and tetrahydrofuran (THF) were dried over sodium/benzophenone and distilled before use. Other solvents were refluxed over calcium hydride and distilled prior to use. Silica gel, Merck Kieselgel 60, was activated at 140 °C overnight before chromatographic use.

**Physical Measurements and Elemental Analyses.** NMR spectra were measured on a JEOL FX100 spectrometer or on the JEOL FX200 and Bruker CXP200 spectrometers at the Research School of Chemistry, Australian National University. Chemical shifts were referenced to residual $C_6H_6$ in benzene-$d_6$ or to (C-$H_3)_4$Si. IR spectra were measured in the range 4000–200 cm$^{-1}$ by means of a Perkin-Elmer 1330 instrument. Mass spectra were performed on Kratos AEI MS3074 or VG7070 of the Australian National University. Elemental analyses were performed by the Analytical Unit of the Australian National University, Pascher Laboratories of Bonn, Germany, or in the case of the unstable complex **5**, by courtesy of Dr. K. Crouse of the University of Agriculture Malaysia.

**Preparation of $Cp_2Cr_2(CO)_4S$ (1).** To a deep green solution of $[CpCr(CO)_3]_2$ (100 mg, 0.25 mmol) in THF (20 mL) was added a suspension of $S_8$ (8 mg, 0.25 mmol S) in THF (7 mL) at ambient temperature. There was an instantaneous color change to a deep greenish brown. Stirring was continued for 1 h and the solution was filtered, although there was no visible residue. The above reaction in a reduced volume of solvent (ca. 5 mL of THF or toluene) under heterogeneous conditions gave similar results after only a few minutes workup. Concentration of the filtrate to 5 mL and subsequent overnight cooling at $-17$ °C gave air-stable deep green crystals of **1** (30 mg, 0.08 mmol, 32% yield). The mother liquor was concentrated to dryness, redissolved in benzene–ether (1:1, ca. 1 mL), and transferred to a column (1 cm × 11 cm) of silica gel that had been deactivated with ether and washed with $n$-hexane. Elution with 1:1 benzene–ether (30 mL) gave a yellow solution, leaving behind a little immovable deep green rim on the top of the column. Concentration of the eluent to dryness followed by redissolution in hexane–ether and cooling overnight at $-17$ °C yielded a further 50 mg (0.13 mmol) of **1** while the mother liquor was found to contain another 13 mg (0.034 mmol), giving a total yield of 99%. Crystals of **1** melted at 111–112 °C (reported[6] 112–113 °C), accompanied by decomposition with effervescence to a dark brown liquid. $^1$H NMR (toluene-$d_8$): $\delta$(+30 °C) 4.36 (s, $C_5H_5$); $\delta$(–90 °C) 4.06 (s, $C_5H_5$). $^{13}$C NMR (toluene-$d_8$): $\delta$ (+30 °C) 89.20 (s, $C_5H_5$), 246.7 (s, CO); $\delta$ (–90 °C) 89.32 (s), 247.6 (s). IR: $\nu$(CO) 1994 vs, 1955 vs, 1938 vs, 1916 s, sh, 1906 vs, 1885 vs cm$^{-1}$ (KBr), or 2001 m, 1955 s, 1926 s, 1919 sh cm$^{-1}$ ($n$-hexane); other bands, 815 s, 637 s, 613 s, 601 m, sh, 552 m, 533 s, 520 m, sh, 485 w, sh, 477 s cm$^{-1}$ (KBr). [Reported[6] IR: $\nu$(CO) 2000, 1960, 1932, 1924 cm$^{-1}$ ($n$-hexane).] MS: $m/z$ 377.9110 [$Cp_2Cr_2(CO)_4S$, calcd 377.9110], 321.9214 [$Cp_2Cr_2(CO)_2S$], 293.9258 [$Cp_2Cr_2(CO)S$], 265.9314 [$Cp_2Cr_2S$], 200.91 [$CpCr_2S$], 182.03 [$Cp_2Cr$], 135.86 [$Cr_2S$]. Anal. Calcd for $C_{14}H_{10}Cr_2O_4S$: C, 44.45; H, 2.66; Cr, 27.49; S, 8.48. Found: C, 44.56; H, 2.77; Cr, 26.9; S, 8.27.

**Preparation of $Cp_2Cr_2(CO)_5S_2$ (2).** To a deep green solution of $[CpCr(CO)_3]_2$ (200 mg, 0.50 mmol) in THF (28 mL) was added a solution of sulfur (32 mg, 1.0 mmol) in THF (20 mL). The solution turned deep blood-red instantaneously and was immediately filtered, but there was no residue. Concentration of the filtrate to ca. 2 mL under reduced pressure, followed by addition of $n$-hexane (2 mL) and cooling at $-17$ °C for 15 min, gave a fine reddish brown air-stable crystalline product (**2**) (130 mg, 0.30

mmol, 60% yield). A second crop (60 mg, 0.14 mmol, 28%) was obtained with addition of more $n$-hexane followed by cooling. $^1$H NMR (toluene-$d_8$): $\delta$ (+30 °C) 4.17 (s, $C_5H_5$), 4.51 (s, $\nu_{1/2}$ = 12 Hz, $C_5H_5$); $\delta$ (–68 °C) 3.84 (s, $C_5H_5$), 4.42 (s, $C_5H_5$). $^{13}$C NMR (toluene-$d_8$): $\delta$ (+30 °C) 91.33 (s, $C_5H_5$), 93.28 (s, $C_5H_5$); $\delta$ (–68 °C) 90.72 (s, $C_5H_5$), 92.82 (s, $C_5H_5$), 266.50, 256.07, 246.60, 239.46, 234.03 (CO). IR: $\nu$(CO) 2014 s, 1969 vs, 1939 vs, 1924 vs, 1919 vs, 1852 s, 1821 w, sh cm$^{-1}$ (KBr), or 2025 s, 1970 vs, 1950 vs, br, 1910 w, sh, 1862 m cm$^{-1}$ (THF); other bands, 850 w, 824 m, 639 m, 627 w, sh, 615 m, 575 s, 549 s, 522 m, 502 w, 484 w, 465 vw, 415 vw cm$^{-1}$ (KBr). MS: $m/z$ as observed for complex **1**. Anal. Calcd for $C_{15}H_{10}Cr_2O_5S_2$: C, 41.10; H, 2.30; Cr, 23.72; S, 14.63. Found: C, 41.05; H, 2.46; Cr, 22.8; S, 14.0. The reaction was found to be equally facile under heterogeneous conditions in <5 mL of THF or toluene. A 10 M excess of S to $[CpCr(CO)_3]_2$ gave the same compound **2** in a similar yield.

A reaction using $[CpCr(CO)_3]_2$ (21.56 mg, 0.0536 mmol) and $S_8$ (3.72 mg, 0.116 mmol S) in toluene (1 mL) was found to evolve $1.4 \pm 0.1$ mL of CO (0.054 mmol) as the solution turned blood-red. This confirmed that $Cp_2Cr_2(CO)_5S_2$ was indeed the primary product of the reaction and had not been formed from intermediate $Cp_2Cr_2(CO)_6S_2$ by loss of one CO molecule during crystallization.

**Preparation of $Cp_2Cr_2(CO)_4S_2$ (3).** When the blood-red solution of **2** in THF (10 mL), prepared from $[CpCr(CO)_3]_2$ (200 mg) as described above, was stirred for 1 h at ambient temperature, the color changed to brown. The NMR spectrum of the solution then showed the presence of **3** (ca. 80%) as well as **1**, **2**, and $Cp_4Cr_4S_4$.[9] The mixture was concentrated to dryness, redissolved in toluene (2 mL), and loaded on to a silica gel column (1 × 18 cm) prepared in $n$-hexane–toluene. Elution with 30% $n$-hexane in toluene (30 mL) gave a greenish brown solution from which was obtained green-black solids (170 mg) consisting of a mixture of **3**, **1**, and $Cp_4Cr_4S_4$ in the relative molar proportion (estimated from $^1$H NMR spectra) of 38:10:1. Recrystallization from THF–$n$-hexane (1:1, ca. 3 mL) gave black crystals (120 mg) consisting of a mixture of **3** and $Cp_4Cr_4S_4$ in the molar ratio ($^1$H NMR) of 20:1. A solution of these crystals in toluene (4 mL) was loaded on to a Florisil column (1 × 12 cm). Elution with toluene (30 mL) and evaporation to dryness gave green solids (93 mg). A second recrystallization from THF–$n$-hexane gave the pure compound **3** as needle-shaped crystals (62 mg, 0.15 mmol, 30% yield). Further elution of the column with toluene–ether (1:1, 10 mL) gave a mixture (10 mg) of **3** and $Cp_4Cr_4S_4$ in molar proportion ($^1$H NMR) 24:1. Complex **2**, which had remained on the silica gel column, was recovered subsequently by elution with toluene (20 mL) and toluene–THF (1:1, 5 mL) to yield 20 mg of solid (0.046 mmol, 9% based on starting material). Data for **3** are as follows. $^1$H NMR (toluene-$d_8$): $\delta$ (+30 °C) 4.14 (s, $C_5H_5$); $\delta$ (–68 °C) 3.95 (s, $C_5H_5$). $^{13}$C NMR (toluene-$d_8$): $\delta$ (+30 °C) 91.33 (s, $C_5H_5$), 258.67 (s, CO, in $C_6D_6$ with $(CH_3)_2CO$ as internal standard at $\delta$ 204.00); $\delta$ (–68 °C) 91.29 (s, $C_5H_5$), 258.88 (s, CO). IR: $\nu$(CO) 1960 vs, 1925 vs, 1910 vs, 1828 vw cm$^{-1}$ (KBr), or 1963 vs, 1920 m, 1888 vs, 1850 w, sh cm$^{-1}$ (toluene); other bands, 1422 vs, 1360 vw, 1260 vw, 1060 m, 1010 m, 910 vw, 860 w, 835 m, sh, 828 s, 640 m, 570 s, 565 m, sh, 540 m, 480 m, 408 w, 390 vw cm$^{-1}$ (KBr). Anal. Calcd for $C_{14}H_{10}Cr_2O_4S_2$: C, 40.98; H, 2.46; Cr, 25.34; S, 15.63. Found: C, 40.77; H, 2.43; Cr, 24.90; S, 15.79.

**Crystal Structure Analyses.** Single crystals of **2** suitable for X-ray diffraction analysis were obtained as follows: [CpCr-$(CO)_3]_2$ (19.2 mg, 0.0478 mmol) was treated under heterogeneous conditions with $S_8$ (3.8 mg, 0.119 mmol S) in THF (1 mL). The solution was filtered to remove excess $S_8$ and kept at $-78$ °C. A few drops of $n$-pentane was added after 8 days, and dark brown rectangular prisms, often with curved faces, were collected after 21 days.

Diffraction quality acicular crystals of **3** were obtained by overnight recrystallization from toluene layered with $n$-hexane at $-28$ °C.

Details of the data collection are summarized in Table I. Both structures were solved by conventional Patterson and Fourier synthesis techniques and were refined by full-matrix least-squares analysis with SHELX.[10] The cyclopentadienyl ligands in **2** were

(8) Goh, L. Y.; D'Aniello, M. J.; Slater, S., Jr.; Muetterties, E. L.; Tavanaiepour, I.; Chang, M. I.; Fredrich, M. F.; Day, V. W. *Inorg. Chem.* **1979**, *18*, 192.

(9) Chen Wei; Goh, L. Y.; Bryan, R. F.; Sinn, E. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 796.

### Table I. Crystal Data

| | 2 | 3 |
|---|---|---|
| cryst system | monoclinic | monoclinic |
| space group | $P2_1/n$ | $P2_1/c$ |
| $a$, Å | 11.638 (4) | 8.214 (1) |
| $b$, Å | 15.508 (5) | 11.464 (2) |
| $c$, Å | 9.825 (3) | 16.182 (3) |
| $\beta$, deg | 111.56 (2) | 92.44 (1) |
| $V$, Å³ | 1649.2 | 1522.4 |
| $D_{calcd}$, g cm⁻³ | 1.765 | 1.790 |
| empirical formula | $C_{15}H_{10}Cr_2O_5S_2$ | $C_{14}H_{10}Cr_2O_4S_2$ |
| fw | 438.4 | 410.4 |
| $Z$ | 4 | 4 |
| $F(000)$, electrons | 880 | 824 |
| abs coeff, cm⁻¹ | 136.2 | 16.25 |
| habit | needle | needle |
| dimens, mm | 0.23 × 0.11 × 0.10 | 0.10 × 0.11 × 0.28 |
| faces | ±110, ±Ī10, ±11Ī | ±0Ī1, ±011, ±101 |
| abs cortn | num. integratn[a] | num. integratn[b] |
| transmissn factor range | 0.15, 0.37 | 0.76, 0.87 |
| cryst degradatn, % | 18[c] | <2[d] |
| temp, K | 296 | 294 |
| diffractometer | Philips PW1100/20 | Enraf-Nonius CAD4-F |
| radiation, Å | Cu K$\alpha$, $\lambda$ = 1.5418 | Mo K$\alpha$, $\lambda$ = 0.71069 |
| monochromator | graphite | graphite |
| scan mode | $\omega$–2$\theta$ | $\omega$–4/3$\theta$ |
| 2Θ range, deg | 2.0–120.0 | 1.0–50.0 |
| reflcns measd | +$h$,+$k$,±$l$ | +$h$,+$k$,±$l$ |
| reflcns used ($I > 2.5\sigma(I)$) | 1729 | 2184 |
| no. of variables | 176 | 239 |
| $R$ | 0.067 | 0.025 |
| $R_w$ | 0.081 | 0.031 |
| shift/esd | <0.06 | <0.04 |
| residual extrema in final difference map, e Å⁻³ | ±0.8 | ±0.35 |

[a] Numerical integration with SHELX[10]. [b] Method of Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* 1965, *18*, 1035. [c] A linear time-dependent correction for the mean degradation averaged over all three standards was employed. [d] No degradation correction applied.
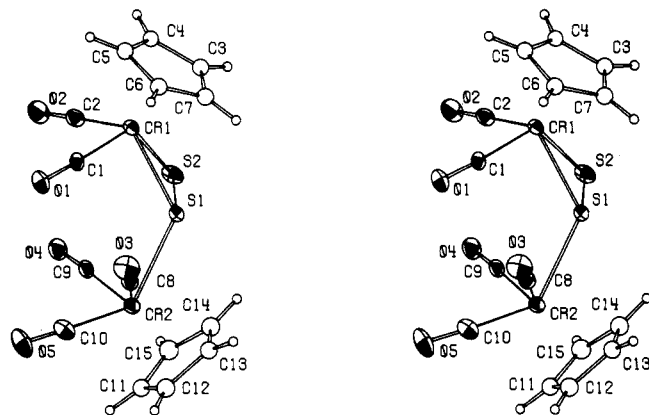


**Figure 1.** Molecular structure of Cp₂Cr₂(CO)₅S₂ (2). High occupancy ring sites only are shown. Thermal ellipsoids depict 20% probability surfaces; hydrogen atoms drawn as 0.11 Å radius hard spheres.

rotationally disordered between two mutually staggered sites, each of which was modeled as a rigid planar group (C–C = 1.378 Å, C–H = 0.97 Å) with individual isotropic thermal parameters for carbons and group parameters (2) for hydrogen atoms. All remaining atoms were assigned anisotropic thermal parameters. All non-hydrogen atoms in 3 were refined anisotropically, and hydrogen atoms were refined isotropically. Refinement converged with $R$ = 0.067 and $R_w$ = 0.081 for 2 and $R$ = 0.025 and $R_w$ = 0.031

(10) Sheldrick, G. M. *SHELX-76, Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

### Table II. Positional Parameters (×10⁴) for 2

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| CR(1) | 761 (1) | 1240 (1) | 8254 (1) |
| CR(2) | 3924 (1) | 1472 (1) | 7033 (1) |
| S(1) | 1973 (2) | 799 (1) | 6925 (2) |
| S(2) | 2102 (2) | 16 (1) | 8605 (3) |
| C(1) | 1387 (7) | 2313 (5) | 8303 (9) |
| O(1) | 1791 (6) | 3007 (4) | 8398 (7) |
| C(2) | 1575 (8) | 1355 (6) | 10238 (11) |
| O(2) | 2073 (7) | 1465 (5) | 11470 (8) |
| C(3) | −825 (10) | 328 (4) | 7516 (23) |
| C(4) | −945 (10) | 876 (4) | 8560 (23) |
| C(5) | −1055 (10) | 1704 (4) | 8020 (23) |
| C(6) | −1004 (10) | 1668 (4) | 6642 (23) |
| C(7) | −862 (10) | 817 (4) | 6330 (23) |
| C(3') | −1053 (27) | 1823 (7) | 7228 (47) |
| C(4') | −1009 (27) | 1390 (7) | 8471 (47) |
| C(5') | −854 (27) | 525 (7) | 8266 (47) |
| C(6') | −802 (27) | 424 (7) | 6896 (47) |
| C(7') | −925 (27) | 1226 (7) | 6255 (47) |
| C(8) | 2704 (8) | 2241 (6) | 5898 (10) |
| O(3) | 2013 (6) | 2722 (5) | 5233 (8) |
| C(9) | 4170 (8) | 1428 (5) | 9007 (10) |
| O(4) | 4386 (6) | 1401 (4) | 10233 (8) |
| C(10) | 4610 (7) | 2543 (6) | 7623 (10) |
| O(5) | 5025 (7) | 3219 (4) | 8024 (9) |
| C(11) | 5697 (7) | 1074 (14) | 7005 (24) |
| C(12) | 4958 (7) | 1343 (14) | 5624 (24) |
| C(13) | 3959 (7) | 795 (14) | 5113 (24) |
| C(14) | 4080 (7) | 187 (14) | 6180 (24) |
| C(15) | 5154 (7) | 359 (14) | 7349 (24) |
| C(11') | 5582 (20) | 687 (24) | 7419 (27) |
| C(12') | 5516 (20) | 1293 (24) | 6367 (27) |
| C(13') | 4461 (20) | 1136 (24) | 5164 (27) |
| C(14') | 3874 (20) | 433 (24) | 5472 (27) |
| C(15') | 4567 (20) | 155 (24) | 6866 (27) |

### Table III. Selected Bond Distances (Å) and Bond Angles (deg) for 2

| | | | |
|---|---|---|---|
| Cr(1)–S(1) | 2.348 (3) | Cr(2)–C(10) | 1.842 (11) |
| Cr(1)–S(2) | 2.399 (3) | Cr(2)–C(11) | 2.163 (11) |
| Cr(1)–C(1) | 1.811 (9) | Cr(2)–C(12) | 2.152 (21) |
| Cr(1)–C(2) | 1.836 (11) | Cr(2)–C(13) | 2.172 (16) |
| Cr(1)–C(3) | 2.226 (11) | Cr(2)–C(14) | 2.195 (15) |
| Cr(1)–C(4) | 2.190 (16) | Cr(2)–C(15) | 2.190 (19) |
| Cr(1)–C(5) | 2.165 (13) | Cr(2)–C(11') | 2.194 (17) |
| Cr(1)–C(6) | 2.187 (13) | Cr(2)–C(12') | 2.198 (28) |
| Cr(1)–C(7) | 2.224 (16) | Cr(2)–C(13') | 2.208 (22) |
| Cr(1)–C(3') | 2.176 (17) | Cr(2)–C(14') | 2.210 (23) |
| Cr(1)–C(4') | 2.162 (25) | Cr(2)–C(15') | 2.201 (31) |
| Cr(1)–C(5') | 2.186 (21) | S(1)–S(2) | 2.010 (4) |
| Cr(1)–C(6') | 2.215 (21) | O(1)–C(1) | 1.164 (10) |
| Cr(1)–C(7') | 2.209 (26) | O(2)–C(2) | 1.147 (11) |
| Cr(2)–S(1) | 2.466 (3) | O(3)–C(8) | 1.115 (11) |
| Cr(2)–C(8) | 1.876 (10) | O(4)–C(9) | 1.137 (11) |
| Cr(2)–C(9) | 1.855 (10) | O(5)–C(10) | 1.161 (11) |

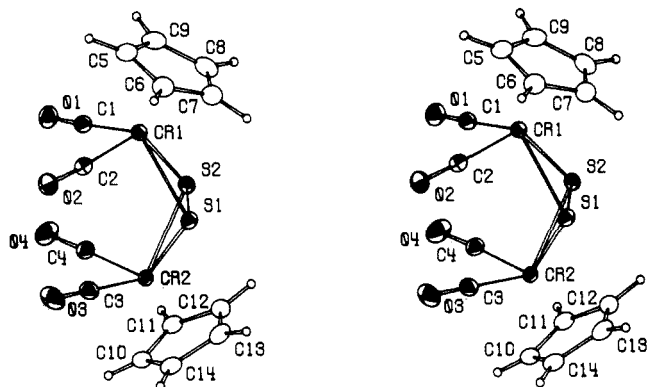| | | | |
|---|---|---|---|
| S(1)–Cr(1)–S(2) | 50.1 (1) | C(9)–Cr(2)–C(10) | 79.7 (4) |
| S(1)–Cr(1)–C(1) | 88.0 (3) | Cr(1)–S(1)–Cr(2) | 125.8 (1) |
| S(1)–Cr(1)–C(2) | 116.0 (3) | Cr(1)–S(1)–S(2) | 66.3 (1) |
| S(2)–Cr(1)–C(1) | 119.3 (3) | Cr(2)–S(1)–S(2) | 115.5 (1) |
| S(2)–Cr(1)–C(2) | 82.5 (3) | Cr(1)–S(2)–S(1) | 63.6 (1) |
| C(1)–Cr(1)–C(2) | 80.6 (4) | Cr(1)–C(1)–O(1) | 176.9 (8) |
| S(1)–Cr(2)–C(8) | 76.1 (3) | Cr(1)–C(2)–O(2) | 176.9 (9) |
| S(1)–Cr(2)–C(9) | 79.4 (3) | Cr(2)–C(8)–O(3) | 177.3 (9) |
| S(1)–Cr(2)–C(10) | 132.9 (3) | Cr(2)–C(9)–O(4) | 176.4 (8) |
| C(8)–Cr(2)–C(9) | 115.9 (4) | Cr(2)–C(10)–O(5) | 178.1 (10) |
| C(8)–Cr(2)–C(10) | 76.1 (4) | | |

for 3. Refined site distribution (occupancy) parameters for each ring pair of 2 were identical within experimental error [preferred site occupancy = 0.62 (2)], and atom thermal parameters were well-behaved. Scattering factors and dispersion corrections for Cr were taken from ref 11; for S, O, C, and H SHELX supplied values were employed. Non-hydrogen atom coordinates are listed

(11) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

### Table IV. Postional Parameters (×10⁴) for 3

| atom | x | y | z |
|------|------|------|------|
| Cr(1) | 2442 (1) | 7018 (1) | 3827 (1) |
| Cr(2) | 2876 (1) | 10293 (1) | 3558 (1) |
| S(1) | 2505 (1) | 8817 (1) | 4581 (1) |
| S(2) | 857 (1) | 8771 (1) | 3644 (1) |
| C(1) | 2637 (3) | 7073 (2) | 2699 (2) |
| O(1) | 2755 (3) | 7074 (2) | 1996 (1) |
| C(2) | 4671 (4) | 7098 (2) | 3807 (2) |
| O(2) | 6067 (3) | 7091 (2) | 3786 (2) |
| C(3) | 5036 (4) | 9885 (2) | 3581 (2) |
| O(3) | 6394 (3) | 9653 (2) | 3565 (2) |
| C(4) | 3131 (4) | 9853 (2) | 2484 (2) |
| O(4) | 3373 (4) | 9597 (2) | 1817 (1) |
| C(5) | 2516 (4) | 5134 (3) | 3967 (2) |
| C(6) | 2708 (4) | 5645 (3) | 4756 (2) |
| C(7) | 1269 (5) | 6242 (3) | 4912 (2) |
| C(8) | 198 (5) | 6123 (3) | 4232 (3) |
| C(9) | 955 (5) | 5439 (3) | 3647 (2) |
| C(10) | 3246 (4) | 12125 (2) | 3314 (2) |
| C(11) | 1613 (4) | 11875 (2) | 3143 (2) |
| C(12) | 915 (4) | 11531 (2) | 3881 (2) |
| C(13) | 2113 (5) | 11569 (3) | 4504 (2) |
| C(14) | 3576 (4) | 11934 (2) | 4165 (2) |

### Table V. Selected Bond Distances (Å) and Bond Angles (deg) for 3

| | | | |
|------|------|------|------|
| S(1)-Cr(1) | 2.396 (1) | S(2)-Cr(1) | 2.406 (1) |
| C(1)-Cr(1) | 1.840 (3) | C(2)-Cr(1) | 1.835 (3) |
| C(5)-Cr(1) | 2.171 (3) | C(6)-Cr(1) | 2.180 (3) |
| C(7)-Cr(1) | 2.223 (3) | C(8)-Cr(1) | 2.232 (3) |
| C(9)-Cr(1) | 2.196 (3) | S(1)-Cr(2) | 2.397 (1) |
| S(2)-Cr(2) | 2.416 (1) | C(3)-Cr(2) | 1.834 (3) |
| C(4)-Cr(2) | 1.830 (3) | C(10)-Cr(2) | 2.161 (3) |
| C(11)-Cr(2) | 2.180 (3) | C(12)-Cr(2) | 2.226 (3) |
| C(13)-Cr(2) | 2.227 (3) | C(14)-Cr(2) | 2.188 (3) |
| S(2)-S(1) | 1.990 (1) | O(1)-C(1) | 1.146 (3) |
| O(2)-C(2) | 1.149 (3) | O(3)-C(3) | 1.148 (3) |
| O(4)-C(4) | 1.143 (4) | C(6)-C(5) | 1.408 (5) |
| C(9)-C(5) | 1.406 (5) | C(7)-C(6) | 1.397 (5) |
| C(8)-C(7) | 1.387 (6) | C(9)-C(8) | 1.395 (6) |
| C(11)-C(10) | 1.388 (5) | C(14)-C(10) | 1.410 (5) |
| C(12)-C(11) | 1.402 (4) | C(13)-C(12) | 1.380 (5) |
| C(14)-C(13) | 1.406 (5) | | |
| S(2)-Cr(1)-S(1) | 49.0 (0) | C(1)-Cr(1)-S(1) | 118.3 (1) |
| C(1)-Cr(1)-S(2) | 85.3 (1) | C(2)-Cr(1)-S(1) | 88.1 (1) |
| C(2)-Cr(1)-S(2) | 119.4 (1) | C(2)-Cr(1)-C(1) | 81.5 (1) |
| S(2)-Cr(2)-S(1) | 48.8 (0) | C(3)-Cr(2)-S(1) | 87.5 (1) |
| C(3)-Cr(2)-S(2) | 118.7 (1) | C(4)-Cr(2)-S(1) | 119.0 (1) |
| C(4)-Cr(2)-S(2) | 87.9 (1) | C(4)-Cr(2)-C(3) | 78.4 (1) |
| Cr(2)-S(1)-Cr(1) | 104.9 (0) | S(2)-S(1)-Cr(1) | 65.8 (0) |
| S(2)-S(1)-Cr(2) | 66.1 (0) | Cr(2)-S(2)-Cr(1) | 103.9 (0) |
| S(1)-S(2)-Cr(1) | 65.2 (0) | S(1)-S(2)-Cr(2) | 65.1 (0) |
| O(1)-C(1)-Cr(1) | 178.1 (2) | O(2)-C(2)-Cr(1) | 176.7 (2) |
| O(3)-C(3)-Cr(2) | 177.1 (3) | O(4)-C(4)-Cr(2) | 176.4 (3) |
| C(9)-C(5)-C(6) | 107.1 (3) | C(7)-C(6)-C(5) | 107.7 (3) |
| C(8)-C(7)-C(6) | 108.8 (3) | C(9)-C(8)-C(7) | 107.9 (3) |
| C(8)-C(9)-C(5) | 108.5 (3) | C(14)-C(10)-C(11) | 107.8 (3) |
| C(12)-C(11)-C(10) | 108.4 (3) | C(13)-C(12)-C(11) | 108.0 (3) |
| C(14)-C(13)-C(12) | 108.6 (3) | C(13)-C(14)-C(10) | 107.2 (3) |



**Figure 2.** Molecular structure of Cp₂Cr₂(CO)₄S₂ (3).

in Tables II and IV and selected bond lengths and angles in Tables III and V. Listings of H atom coordinates, anisotropic thermal parameters, and observed and calculated structure factor amplitudes have been deposited. The atomic nomenclature is defined in Figures 1 and 2. All figures were drawn with ORTEP.[12]

**Reaction of Cp₂Cr₂(CO)₅S₂ (2) with Ph₃P.** To a filtered red-brown solution of Cp₂Cr₂(CO)₅S₂ (2) made from [CpCr(CO)₃]₂ (20 mg, 0.05 mmol) and excess S₈ (3.85 mg, 0.12 mmol S) in THF (5 mL) was added solid Ph₃P (13 mg, 0.05 mmol), and the mixture was stirred. There was an instantaneous color change to greenish brown. Evaporation to dryness under vacuum was followed by extraction with 5% ether in *n*-hexane to give a brownish white solid residue (15 mg) consisting of Ph₃PS contaminated with unreacted Ph₃P and a trace of the starting material 2. Evaporation of the extract gave a green solid (ca. 19 mg). Chromatography of this on a silica gel column (1 × 10 cm) gave pure Cp₂Cr₂(CO)₄S 1 (ca. 4 mg, 0.01 mmol, 20%) on elution with *n*-hexane. Further elution with toluene–*n*-hexane (1:4) yielded 12 mg of yellow-green solids consisting of a mixture of 1, 2, and Cp₄Cr₄S₄ in the molar proportion (¹H NMR) of 15:6:1.

A solution of 1 made from [CpCr(CO)₃]₂ (12.6 mg, 0.031 mmol) and S₈ (1.0 mg, 0.031 mmol S) was found to be unreactive toward Ph₃P (8.01 mg, 0.031 mmol) over 4.5 days at room temperature.

**Methylation of Cp₂Cr₂(CO)₅S₂ (2).** To a filtered solution of 2 made from [CpCr(CO)₃]₂ (100 mg, 0.25 mmol) and S₈ (17 mg, 0.531 mmol S) in benzene (5 mL) was injected CF₃SO₃CH₃ (56 μL, 0.51 mmol). The red-brown solution of 2 rapidly lost its reddish tinge, becoming dark greenish brown after 5 min, with precipitation of some fine solid. After the mixture was left standing for 10 min at room temperature, filtration gave a fine

black solid consisting of [Cp₂Cr₂(CO)₅S₂(CH₃)](SO₃CF₃) 4, which was washed with benzene and dried, yield 84 mg (0.140 mmol, 56%). ¹H NMR (CDCl₃): δ (+30 °C) 5.26 (ν₁/₂ = 52 Hz); δ (−60 °C) 5.32 and 5.04 (unresolved, combined ν₁/₂ = 78 Hz) (C₅H₅).[13] IR: ν(CO) 2020 s, 1970 vs, 1955 vs, 1940 s, sh, 1870 s cm⁻¹ (KBr), or 2045 s, 1965 vs, 1942 vs, sh, 1896 w, 1854 m cm⁻¹ (THF) with similar relative intensity to those of 2; ν(SO₃CF₃⁻) 1275 s, sh, 1260 s cm⁻¹; other bands, 3090 w, b, 1420 m, 1220 w, 1145 s, b, 1030 s, 1010 w, sh, 860 m, 840 vw, 825 m, b, 730 vw, 635 m, 624 m, 610 w, sh, 600 vw, sh, 570 s, 535 w, 520 w, 510 s, b, 440 vw, 420 vw, 400 vw, 350 w, 325 vw cm⁻¹. Anal. Calcd for [(C₅H₅)₂Cr₂-(CO)₅S₂(CH₃)]SO₃CF₃: C, 33.89; H, 2.17; Cr, 17.26. Found: C, 34.18; H, 2.45; Cr, 17.27. The solid complex 4 decomposed after a couple of days at room temperature and hence was too unstable to be sent overseas for analysis of S and F. Solutions of 4 decompose rapidly, and attempted recrystallizations were unsuccessful.

After some hours at room temperature the mother liquor from the filtration described above deposited an apparently pure solid (ca. 20 mg), which analyzed as [Cp₄Cr₄S₄(CH₃)](SO₃CF₃) (5). Anal. Calcd: C, 34.73; H, 3.05; S, 21.07; F, 7.49. Found: C, 34.50; H, 3.11; S, 20.6; F, 7.17. IR: ν(SO₃CF₃³⁻) 1275 s, sh, 1260 s cm⁻¹ (KBr); other bands, 3090 w, b, 1420 m, 1220 w, 1145 s, b, 1025 s, 1010 w, sh, 825 mb, 635 s, 580 w, 520 w cm⁻¹. The ¹H NMR spectrum in CDCl₃ of the sparingly soluble complex 5 showed a C₅H₅ resonance at δ 5.04 (ν₁/₂ = 12 Hz). As with 4, and for apparently similar reasons,[13] no methyl resonance could be observed.

Subsequent evaporation of the mother liquor of 5 to dryness yielded a final residue (ca. 30 mg) consisting of a mixture of 1 and an unidentified complex possessing δ (C₅H₅) 4.27 in the ¹H NMR spectrum in benzene-d₆. Cp proton signals for 1 and for the unknown were in 1:1 ratio.

Reaction of a 5:1 molar excess of CF₃SO₃CH₃ with 2 gave 4 in similar yield to that described above.

(12) Johnson, C. K. *ORTEP-II*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976; report ORNL-5138.

(13) No δ (CH₃) could be observed in either CDCl₃ or CD₂Cl₂. The complex is only sparingly soluble in those solvents, and, apparently, the resonance is masked by those (δ 0.88–1.22) due to traces of hexanes in the solutions. Attempted measurement in CD₃CN solution was also unsuccessful because of near instantaneous decomposition of the complex on dissolution.
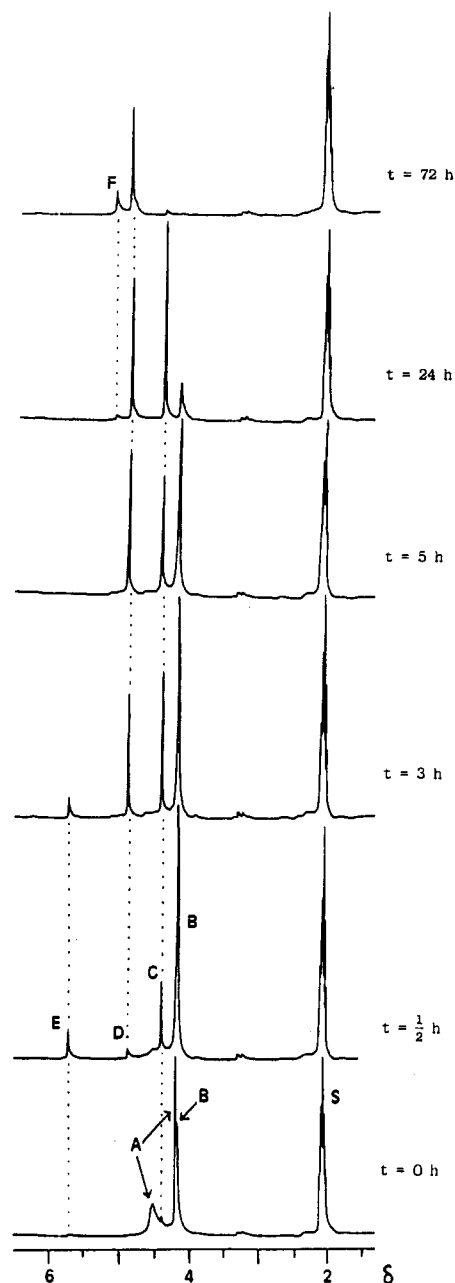
**Figure 3.** 100-MHz $^1$H NMR spectra of 0.016 M solution of $Cp_2Cr_2(CO)_5S_2$ in toluene-$d_8$ as a function of time at 30 °C. Peaks are as follows: S, $C_6D_5CHD_2$ of solvent; A, $Cp_2Cr_2(CO)_5S_2$ (2), B, $Cp_2Cr_2(CO)_4S_2$ (3); C, $Cp_2Cr_2(CO)_4S$ (1); D, $Cp_4Cr_4S_4$; E, $Cp_4Cr_4(CO)_2S_2$; F, unknown.

**Conversion of 2 to 1—An NMR Study.** The slow decomposition of **2** was monitored by its NMR spectrum as follows. A 0.016 M solution of **2**, generated from [CpCr(CO)₃]₂ (3.9 mg) and excess S₈ (2.3 mg) in toluene-$d_8$ (0.6 mL), was filtered directly into a 5-mm NMR tube and capped with a septum cap under argon. The tube was immediately cooled to -60 °C and allowed to warm up to 30 °C in the NMR probe. The first $^1$H NMR spectrum was recorded ca. 20 min after preparation of the sample and is given as the spectrum labeled $t = 0$ h in Figure 3. Spectral changes were followed at intervals during a period of 5 days, and those spectra illustrating significant changes are reproduced in the figure.

## Results and Discussion

**Preparative Results.** Deep green solutions of [CpCr(CO)₃]₂ in THF or toluene react rapidly at room temperature with 1 mol equiv of S to give a green-brown solution from which **1** was isolated as a dark green crystalline solid in 99% yield. **1** has been isolated previously

**Scheme I**
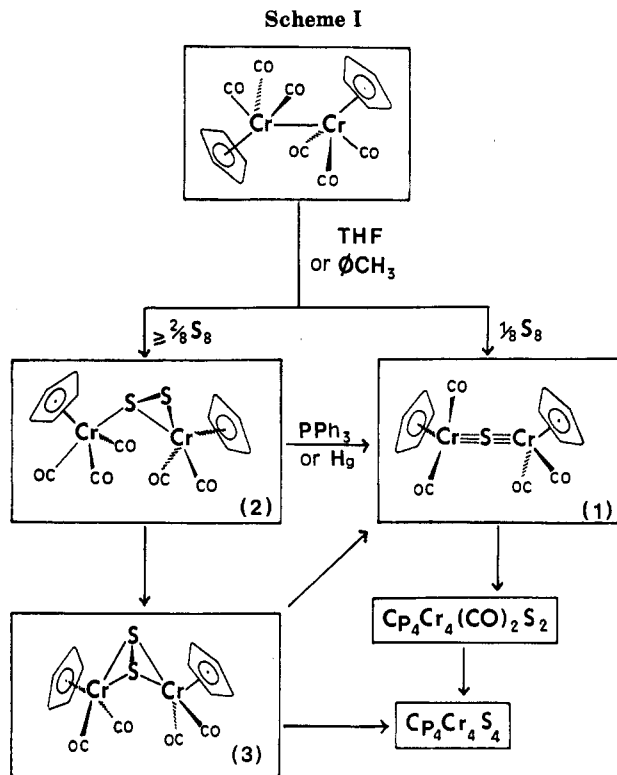


(in 34% yield) from the reaction of Na[CpCr(CO)₃] with $S_3N_3Cl_3$ in THF at -78 °C[6] and was shown by single-crystal X-ray diffraction analyses[5,6] to possess an unusual Cr≡S≡Cr linkage.

With *two or more* mole equivalents of S per mole of [CpCr(CO)₃]₂ the reaction in THF or toluene produces, instantaneously, a deep blood-red solution. An immediate workup gives, after ca. 30 min, complex **2** as fine reddish brown air-stable crystals in 88% yield. The reaction proceeds with simultaneous evolution of 1 mol of CO/mol of [CpCr(CO)₃]₂ confirming that the immediate product is indeed **2** rather than $Cp_2Cr_2(CO)_6S_2$. The yield and purity of the product were found to decrease rapidly with longer workup time. After 1 h the product solution had changed color to greenish brown and contained mainly **3** (ca. 80%) with minor amounts of **1**, **2**, and $Cp_4Cr_4S_4$. This mixture was very difficult to separate. However, repeated chromatography coupled with fractional crystallization finally gave pure **3** in 30% yield. (See Scheme I.) Like **1**, complexes **2** and **3** have been fully characterized by total elemental, spectral, and crystal structure analyses.

The present reactions are much more facile than similar reactions of transition-metal complexes with elemental sulfur, which generally require either thermal[14] or photochemical activation[15] or long reaction times (extending to days) at ambient temperature.[16]

**Structures of 2 and 3.** Single molecules of **2** and **3** are shown in Figures 1 and 2, respectively. In **2** the Cp rings are each rotationally disordered between two sites, and, for clarity, only the preferred ring orientations (62% occupancy)[17] are shown in Figure 1. The $S_2$ ligand bridges the two chromium atoms asymmetrically in **2** and symmetrically in **3**, corresponding to $S_2$ bonding types Ib and III in Müller's classification[1,2] or $\mu$-$\eta^1$,$\eta^2$ and $\mu$-$\eta^2$ in that

(14) Lincoln, S.; Soong, S.-L.; Koch, S. A.; Sato, M.; Enemark, J. H. *Inorg. Chem.* **1985**, *24*, 1355.

(15) Giannotti, C.; Ducourant, A. M.; Chanaud, H.; Chiaroni, A.; Riche, C. *J. Organomet. Chem.* **1977**, *140*, 289 and references therein.

(16) Ginsberg, A. P.; Lindsell, W. E.; Spinkle, C. R.; West, K. W.; Cohen, R. L. *Inorg. Chem.* **1982**, *21*, 3666.
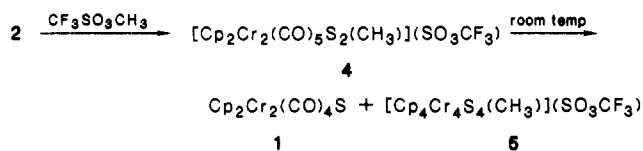
(17) Low occupancy sites have 38% occupancy.

of Bolinger et al.[18] The structure of the pentamethyl-cyclopentadienyl analogue of **3** has been reported recently.[19] Reported bond lengths and angles for that complex agree closely with those in **3**. The S–S distance in **2** [2.010 (4) Å] is within the range of values reported previously for $\mu$-$\eta^1,\eta^2$-$S_2$ ligands [1.980 (8)–2.048 (7) Å].[15,20-22] The S–S distance in **3** [1.990 (1) Å] is shorter than that in **2** and is at the low end of the reported range for $\mu$-$\eta^2$-$S_2$ complexes.[19,23-32] The one shorter value reported [1.956 (2) Å in $(C_5H_4CH_3)V_2S_5$] derives from a disordered structure and is slightly suspect.[18] The shortened S–S distance in **3**, compared with that in **2**, may reflect additional depopulation of the ligand $\pi^*$ orbitals. Attainment of 18e configurations at each of the metal centers requires the $S_2$ ligand to function as a 4e donor (to zerovalent chromiums) in **2**[33] and as a 6e donor in **3**. As in the majority of other $\mu$-$\eta^1,\eta^2$-$S_2$ complexes, the Cr–S distances in the $\eta^2$ fragment of **2** are significantly different [2.348 (3), 2.399 (3) Å]. Smaller, but still substantial, Cr–S bond-length differences [$\Delta_{max}$ = 0.020 (2) Å] are also observed in **3**, despite the formal chemical equivalence of both the sulfur and the metal centers in the molecule. The average Cr–S distance in **3** is 2.404 Å. Metal–C(carbonyl) distances are unexceptional [average 1.84 (2) Å (**2**), 1.835 (4) Å (**3**)]. Metal–ring plane distances [average 1.85 (1) Å (**2**), 1.848 (2) Å (**3**)] are equivalent to within experimental error and do not differ significantly from those in $(C_5Me_5)_2Cr_2(CO)_4S_2$ [average 1.849 (2) Å].[19] The low-occupancy ring sites in **2** are approximately staggered and slightly inclined (average 1.4°) relative to those shown in Figure 1.

**NMR and IR Spectra.** At both +30 and –90 °C in toluene-$d_8$, complex **1** exhibits singlet ¹H and ¹³C resonances arising from the Cp rings and a singlet ¹³C resonance for the CO ligands. This is in agreement with the theoretical predictions of Kostić and Fenske[34] for a very low-energy barrier to intramolecular rotation about the Cr≡S≡Cr axis.

Complex **3**, like **1**, also shows one singlet for the Cp rings in both the ¹H and ¹³C NMR spectra at +30 ($\delta$ 4.14 and 91.33) or –68 °C ($\delta$ 3.95 and 91.29). The CO ligands also exhibit only one singlet at $\delta$ 258.67 (+30 °C) and 258.88 (–68 °C).

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(33) Contrary to our earlier suggestion[5] both metal centers in **2** have 18e configurations.

(34) Kostić, N. M.; Fenske, R. F. *J. Organomet. Chem.* **1982**, *233*, 337.

**Scheme II**

$$2 \xrightarrow{CF_3SO_3CH_3} [Cp_2Cr_2(CO)_5S_2(CH_3)](SO_3CF_3) \xrightarrow{\text{room temp}}$$

**4**

$$Cp_2Cr_2(CO)_4S + [Cp_4Cr_4S_4(CH_3)](SO_3CF_3)$$

**1**                              **5**

Owing to the labile nature of **2**, (discussed below) its NMR spectra must be measured immediately after dissolution of the complex or immediately after its preparation in situ. Its NMR spectra indicate the presence of two magnetically nonequivalent Cp rings. At +30 °C in toluene-$d_8$, these are observed as a sharp singlet at $\delta$ 4.17 and a broad singlet at $\delta$ 4.51 ($\nu^{1/2}$ = 12 Hz) in the ¹H spectrum and at $\delta$ 91.37 and 93.30 in the ¹³C spectrum. At –68 °C, these peaks appear at $\delta$ 3.84 and 4.42 (¹H) and at $\delta$ 90.72 and 92.82 (¹³C), while the CO resonances are observed at $\delta$ 266.50, 256.07, 246.60, 239.46, and 234.03.

The solution IR spectra of **1**, **2**, and **3** show, as expected, four, five, and four $\nu$(CO) bands, respectively, whereas in the solid-state IR six, seven, and four bands are observed. The additional bands in the (solid) spectra of **1** and **2** are probably due to the presence of conformational isomers in the solids. Crystals of both **1** and **2** contain at least two distinct (ring rotated) conformers.[35] In contrast crystals of **3** contain just one conformer and the solid-state IR spectrum shows no "additional" bands.

**Conversion of 2 to 1—An NMR Study.** The labile nature of **2** was indicated by its facile conversion to **3** at ambient temperature, as manifested in the preparative procedures described above. This was further illustrated by time-dependent NMR spectral changes of a 0.016 M solution of **2** in toluene-$d_8$ at +30 °C (Figure 3). The peaks, $\delta$ 4.51 and 4.17, pertaining to **2** are clearly observed at $t$ = 0 h but have largely disappeared within 0.5 h, as the peak at $\delta$ 4.14 of **3** intensifies and that at $\delta$ 4.36 of **1** begins to form. This is followed by the growth of resonances at $\delta$ 5.67 due to $Cp_4Cr_4(CO)_2S_2$ and at $\delta$ 4.85 of $Cp_4Cr_4S_4$, the final product. The mechanistic pathway for the formation of the latter two products and their structures have been discussed in earlier papers.[9,36] After 72 h, the only signals observed were those due to $Cp_4Cr_4S_4$ ($\delta$ 4.85) and an apparently small amount of an unknown $C_5H_5$-containing compound having a singlet resonance at $\delta$ 5.06. The bulk of the $Cp_4Cr_4S_4$ product had been deposited as needles on the NMR tube walls. These sequential conversion steps are illustrated in Scheme I.

**Reaction with Thiophiles.** Triphenylphosphine, $Ph_3P$, readily strips a S atom from **2**, itself forming $Ph_3PS$, while **2** undergoes a concurrent loss of a CO molecule to form **1**, which does not react further with excess $Ph_3P$. While this work was in progress,[5,37] Herrmann et al. reported that the pentamethylcyclopentadienyl analogue of **2**, isolated from the reaction of $K[(C_5Me_5)Cr(CO)_3]$ with $^1/_5$ $S_3N_3Cl_3$ in 30% yield, undergoes a similar reaction with $Ph_3P$.[7]

It is interesting to note that in contrast to $\eta^2$-bonded $S_2$ monometallic complexes, e.g. $M(\eta^2$-$S_2)(dppe)_2Cl$ (where M = Rh or Ir and dppe = bis(diphenylphosphino)ethane)[16,38] and $MoO(\eta^2$-$S_2)(S_2CNR_2)_2$,[38] which undergo loss of both S atoms to $Ph_3P$, only one S atom of the $\mu$-$S_2$ group in **2**

(35) Crystals of **1** also contain two crystallographically inequivalent molecules in the asymmetric unit.

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can be abstracted. This attests to the high stability of the multiply bonded linear Cr≡S≡Cr moiety. A "labile sulfur" in such bridging $S_2$ ligands has also been observed in $[Mo_3S(\mu$-$S_2)_3(\eta^2$:$\eta^2$-$S_2)_3]^{2-}$,[39] which undergoes nucleophilic attack by $CN^-$ at each of its three $\mu$-$S_2$ ligands. Such reactions of activated sulfur ligands are of interest in connection with bioinorganic problems like the deactivation of the Mo-containing enzyme xanthine oxidase via nucleophilic abstraction of a "labile sulfur".[40]

**Methylation.** 2 undergoes instantaneous methylation when treated with one or more equivalents of methyl trifluoromethanesulfonate in toluene, precipitating a black unstable solid 4, which in solution rapidly converts to 1 and 5 as shown in Scheme II.

Although there have been frequent reports on the methylation of side-on metal-bonded $\eta^2$-$S_2$ ligands, aimed at producing perthiolates, which are of interest in connection with enzymatic processes, little is known about the methylation of bridging $\mu$-$S_2$ ligands.[41] Our present study shows that, like the $\eta^2$-$S_2$ ligands in $Os(S_2)(CO)_2(PPh_3)_2$[41]

and $Ir(S_2)(dppe)_2Cl$,[38,42] the $\mu$-$S_2$ ligand in 2 undergoes monomethylation, presumably at S(2). Unfortunately the methylated derivative 4 is not stable enough for single crystals to be grown for a structure analysis to definitively determine the point of methylation. Attempts at crystallization gave only a mixture of 5 and 1 after several days at −28 °C. This facile loss of $CH_3S^+$ suggests that 4 might be a potential $CH_3S^+$ transfer agent.

**Conclusion.** This study highlights the high reactivity of the $\mu$-$S_2$ complex 2 with regard to decarbonylation, S atom abstraction by $Ph_3P$, and loss of the $CH_3S^+$ cation.

**Supplementary Material Available:** Listings of anistropic thermal parameters and hydrogen atom coordinates for 2 and 3 (4 pages); listing of observed and calculated structure factor amplitudes for 2 and 3 (24 pages). Ordering information is given on any current masthead page.

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# Bidentate Alkene–Carbene Complexes of Tungsten: Synthesis, Structure, and Reactivity toward Alkenes

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The reactivity of complexes of tungsten, bearing a bidentate alkene–carbene ligand, toward alkenes has been studied. These complexes very easily react photochemically with olefins to give, after decoordination of the double bond, followed by a rearrangement of the pentacoordinated intermediate, new alkene–carbene complexes in which the two functions are trans. In most of the cases, the reaction is reversible. The synthesis and X-ray diffraction studies have been completed on three derivatives. Complex 5, which contains a carbene and a free cyclohexenyl group, crystallizes in the monoclinic space group $P2_1/n$, with $a = 10.272$ (3) Å, $b = 21.918$ (9) Å, $c = 6.571$ (2) Å, $\beta = 92.20$ (3)°, $Z = 4$, and $d_{calcd} = 2.01$ g cm$^{-3}$. Complex 6, which contains a carbene ligand and a coordinated cyclohexenyl group, crystallizes in the monoclinic space group $P2_1/n$, with $a = 7.155$ (3) Å, $b = 13.062$ (3) Å, $c = 13.998$ (2) Å, $\beta = 102.48$ (2)°, $Z = 4$, and $d_{calcd} = 2.18$ g cm$^{-3}$. Complex 11, which contains a carbene ligand, a free cyclohexenyl group, and a coordinated ethene molecule, crystallizes in the monoclinic space group $P2_1/n$ with $a = 6.635$ (8) Å, $b = 21.007$ (8) Å, $c = 11.193$ (7) Å, $\beta = 90.60$ (7)°, $Z = 4$, and $d_{calcd} = 1.91$ g cm$^{-3}$.

## Introduction

The synthesis and structure of several tungsten carbene–alkene complexes have been described, and their reactivity per se has been studied.[1–6] The importance of

such species both in the cyclopropanation as well as in the metathesis reactions of olefins has been outlined. But little attention has been paid to the reactivity of such species toward external ligands such as alkenes and alkynes.

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