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Synthetic and Structural Study of Cyclopentadienylchromium Dithiocarbamate Complexes and Their Thermolytic Derivatives

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The reaction of $[CpCr(CO)_3]_2$ (**1**) with the tetraalkylthiuram disulfides $[R_2NC(S)S]_2$ (R = Me, Et, *i*-Pr) has been investigated. At ambient temperature, $CpCr(CO)_2(\eta^2\text{-}S_2CNR_2)$ (**3**) was obtained as air-stable dark red crystals in 81−87% yields from reactions in solution and in quantitative yield from a reaction in the solid state (**3a**, R = Me); the precursor complex $CpCr(CO)_3(\eta^1\text{-}S_2CNMe_2)$ (**2a**) crystallized out in a 1:1 admixture with **3a** from a product solution after 3 days at −29 °C. At 90 °C for 2 h, the same reaction or the thermal degradation of **3** led to the isolation of the thiocarbenoid complex $CpCr(CO)_2(\eta^2\text{-}SCNR_2)$ (**4**) as dark red crystals (ca. 10%), double cubanes $Cp_6Cr_8S_8(\eta^2{:}\eta^4\text{-}SCNR_2)_2$ (**5a**, R = Me; **5b**, R = Et) as dark brown crystals (3−7%), $Cp_6Cr_8S_8(\eta^1{:}\eta^2\text{-}S_2CNR_2)_2$ (**6**) as dark crystals (7−14%), $Cr(\eta^2\text{-}S_2CNR_2)_3$ (**7**) as dark blue crystals (16−21%), $Cp_2Cr_2(CO)_4S$ as dark green crystals (1−3%), and $Cp_4Cr_4S_4$ (12−22%) as dark green solids. The crystal structures of **2**−**6** were reported. Unprecedented bridging modes were found in the double cubanes: in **5**, two Cr_4S_4 cubane clusters were linked by a $\mu\text{-}\eta^2{:}\eta^4$-dithiooxamide ligand as well as a Cr−Cr bridge with bond distances of 3.101 and 3.118 Å in the two independent molecules of the compound, and in **6**, the cubanes were linked by two $\mu\text{-}\eta^1{:}\eta^2$-dithiocarbamate ligands.

1. Introduction

We have been interested in the cleavage of S−S bonds in inorganic[1] and organic substrates[2] by $[CpCr(CO)_3]_2$ (Cp = $\eta^5\text{-}C_5H_5$). Recently we encountered very facile reactions with the thiophosphorus compounds bis(diphenylthiophosphinyl)disulfane $Ph_2P(S)SSP(S)Ph_2$[3a] and the analogous bis(thiophosphoryl)disulfane $(RO)_2P(S)SSP(S)(OR)_2$ (R = *i*-Pr).[3b] At the same time, we have initiated a study with the tetraalkylthiuram disulfides $R_2NC(S)SSC(S)NR_2$ (R = Me, Et, *i*-Pr). It is anticipated that the reaction will lead to metal dithiocarbamates[4] and contribute to the organometallic chemistry of this class of compounds, in particular of cyclopentadienylmetal complexes, which to date remain scarce, in contrast to the plethora of coordination compounds known.[5] In fact, only a few cyclopentadienyl dithiocarbamate complexes have been reported, viz. the much-investigated Fe complex $CpFe(CO)_2(S_2CNR_2)$ (R = Me, Et),[6] the analogous complexes of Mo and W,[6a,7] and some recently reported Ru complexes.[8] Considering that there exists much current interest in dithiocarbamate complexes as precursors to metal sulfides,[9] this investigation is timely. In the course of this study, a preliminary communication has been published;[10] this paper describes the comprehensive results, which include numerous new cyclopentadienylchromium complexes.

2. Experimental Section

2.1. General Procedures. All reactions were carried out using conventional Schlenk techniques under an inert atmosphere of nitrogen or under argon in an M. Braun Labmaster 130 inert gas system. NMR spectra were measured on a

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Bruker 300 MHz FT NMR spectrometer (^{1}H at 300.14 MHz and ^{13}C at 75.43 MHz); ^{1}H chemical shifts were referenced to residual C_6H_6 in C_6D_6 and ^{13}C chemical shifts to the triplet of C_6D_6. IR spectra in Nujol mulls or KBr pellets were measured in the range 4000−400 cm^{-1} on a BioRad FTS-165 FTIR instrument. Mass spectra were obtained on a Finnigan Mat 95XL-T spectrometer. Elemental analyses were performed by the microanalytical laboratory in house. $[CpCr(CO)_3]_2$ (**1**) was synthesized as described by Manning[11] from chromium hexacarbonyl (98% purity from Fluka). The tetraalkylthiuram disulfides $[R_2NC(S)S]_2$ (98% purity) were obtained commercially and used as supplied (for R = Me, Et, from Fluka; for R = *i*-Pr, from Aldrich). All solvents were dried over sodium/benzophenone and distilled before use. Silica gel (Merck Kieselgel 60, 230−400 mesh) was dried at 140 °C overnight before chromatographic use.

2.2. Reactions of $[CpCr(CO)_3]_2$ (1) with Tetraalkylthiuram Disulfides, $[R_2NC(S)S]_2$.

(a) At Ambient Temperature. A deep green mixture of $[CpCr(CO)_3]_2$ (**1**) (121 mg, 0.30 mmol) and $[R_2NC(S)S]_2$ (0.30 mmol; 72, 89, and 106 mg for R = Me, Et, *i*-Pr, respectively) in toluene (8 mL) was stirred at ambient temperature for 1 h. The resultant dark red product solution was filtered, although there was no visible residue. Concentration of the filtrate to 3 mL followed by addition of *n*-hexane (ca. 2 mL) and subsequent overnight cooling at −29 °C gave air-stable dark red crystals of $CpCr(CO)_2(\eta^2\text{-}S_2CNR_2)$ (R = Me (**3a**), 151 mg, 0.52 mmol, 86% yield; R = Et (**3b**), 167 mg, 0.52 mmol, 87% yield; R = *i*-Pr (**3c**), 171 mg, 0.49 mmol, 82% yield).

(b) At 90 °C. A deep green mixture of **1** (201 mg, 0.50 mmol) and $[R_2NC(S)S]_2$ (0.50 mmol; 120, 148, and 176 mg for R = Me, Et, *i*-Pr, respectively) in toluene (10 mL) was stirred at 90 °C for 2 h. The resultant dark brown reaction mixture was filtered, to remove deep blue solids of $Cr(\eta^2\text{-}S_2CNR_2)_3$ (R = Me (**7a**), 15 mg, 0.036 mmol, 4% yield; R = Et (**7b**), 21 mg, 0.042 mmol, 4% yield) *or* dark red solids of $CpCr(CO)_2(\eta^2\text{-}S_2CNR_2)$ (R = *i*-Pr (**3c**), 31 mg, 0.089 mmol, 9% yield). The filtrate was then concentrated to ca. 4 mL and loaded onto a silica gel column (2.5 × 16 cm) prepared in *n*-hexane. A typical chromatographic workup is described for R = Me as follows. Elution gave seven fractions (i) A yellow eluate in *n*-hexane/toluene (2:1, 5 mL) was obtained, which on concentration gave deep green crystalline solids of $Cp_2Cr_2(CO)_4S$ (3 mg, 0.008 mmol, 2% yield), identified by its color characteristics and its Cp proton resonance in benzene-d_6 at δ 4.36.[1] (ii) A dark red eluate in *n*-hexane/toluene (3:1, 10 mL) was then obtained, which on concentration gave dark red crystalline solids of $CpCr(CO)_2(\eta^2\text{-}S_2CNMe_2)$ (**3a**) (44 mg, 0.15 mmol, 15% yield). (iii) A brown eluate in toluene (10 mL) was obtained, from which was isolated dark brown solids (54 mg), the ^{1}H NMR spectra of which indicated the presence of a 1:2 molar mixture of $Cp_4Cr_4S_4$ and **4a**. The mixture was extracted with *n*-hexane/toluene (1:1, 3 × 3 mL), leaving behind on the walls of the flask a dark green solid of $Cp_4Cr_4S_4$ (ca. 19 mg, 13% yield). The combined extracts were concentrated to dryness, yielding dark red crystalline solids of $CpCr(CO)_2(\eta^2\text{-}SCNMe_2)$ (**4a**) (29 mg, 0.11 mmol, 11% yield). (iv) A red brown eluate in toluene (5 mL) was obtained, from which was isolated brown solids of $Cp_6Cr_8S_8(\mu\text{-}\eta^2{:}\eta^4\text{-}SCNMe_2)_2$ (**5a**) (4 mg, 0.003 mmol, 3% yield). (v) A brown eluate in toluene (10 mL) was obtained, from which was isolated a brown solid of $Cp_6Cr_8S_8(\mu\text{-}\eta^1{:}\eta^2\text{-}S_2CNMe_2)_2$ (**6a**) (12 mg, 0.01 mmol, 7% yield). (vi) A blue eluate in THF (20 mL) was obtained, which on concentration yielded dark blue crystalline solids of $Cr(\eta^2\text{-}S_2CNMe_2)_3$ (**7a**) (85 mg, 0.21 mmol, 21% yield). FAB$^+$ mass spectrum: *m*/*z* 412 [M$^+$], 292 $[Cr(S_2CNMe_2)_2]$. (vii) A dark brown eluate in THF (10 mL) was obtained, from which was isolated a dark unidentified solid (18 mg). Similarly for R = Et and *i*-Pr were isolated analogous complexes, the yields of which are indicated in Scheme 1.

(c) At −29 °C. A deep green solution of **1** (40 mg, 0.10 mmol) in 2 mL of toluene was added to a solution of $[Me_2NC(S)S]_2$ (24 mg, 0.10 mmol) in 1 mL of toluene in a test tube, and the dark green mixture was immediately kept at −29 °C. After 3 days, a mixture of red needle-shaped crystals of $CpCr(CO)_3(\eta^1\text{-}S_2CNMe_2)$ (**2a**) and fine dark red crystals of $CpCr(CO)_2(\eta^2\text{-}S_2CNMe_2)$ (**3a**) was collected. Crystals of **2a** (28 mg, 0.087 mmol, 44% yield) were physically separated from **3a** under the microscope.

The analogous **2b** and **2c** complexes were detected in proton NMR spectra of product solutions, in an admixture with **3b** and **3c**, respectively, and considering the difficulty of isolating **2a**, no attempt has been made to isolate them.

(d) Solid State Reaction. A deep green mixture of **1** (20 mg, 0.05 mmol) and $[Me_2NC(S)S]_2$ (12 mg, 0.05 mmol) was ground in a mortar at ambient temperature for ca. 20 min; the mixture slowly turned red. After 16 h, IR and NMR spectral examination showed total conversion to $CpCr(CO)_2(\eta^2\text{-}S_2CNMe_2)$ (**3a**).

(e) Data. Compound 2a. IR (KBr, cm^{-1}): ν(CO) 2028 m, 1994 sh, 1969 s; ν(CN) 1531 m; ν(CS) 970 m. ^{1}H NMR (C_6D_6): δ 4.21 (s, 5H, C_5H_5), 3.26 (6H, CH_3). ^{13}C NMR (C_6D_6): δ 91.7 (C_5H_5), 47.3 (CH_3), 194.1 (CS_2), 251.1 (CO), 237.8 (CO). Anal. Calcd for $C_{11}H_{11}CrNO_3S_2$: C, 41.1; H, 3.5. Found: C, 40.4; H, 3.8. MS FAB$^+$ (*m*/*z*): 322 [M + H]$^+$, 293 [M − CO]$^+$, 265 [M − 2CO]$^+$, 237 [M − 3CO]$^+$.

Compounds 2b,c. These were detected in the proton NMR spectra and were not isolated. ^{1}H NMR for **2b** (C_6D_6): δ 4.19 (s, 5H, C_5H_5), 3.91 (q, *J* = 7 Hz, 4H, CH_2), 1.13 (t, *J* = 7 Hz, 6H, CH_3). ^{1}H NMR for **2c** (C_6D_6): δ 4.19 (s, C_5H_5).

Compound 3a. IR (KBr, cm^{-1}): ν(CO) 1934 vs, 1864 vs; ν(CN) 1532 m; ν(CS) 821 s; $\nu(NC_2)$ 1152 m. ^{1}H NMR (C_6D_6): δ 4.58 (s, 5H, C_5H_5), 2.40 (s, 6H, CH_3). ^{13}C NMR (C_6D_6): δ 93.0 (C_5H_5), 37.2 (CH_3), 204.1 (CS_2), 267.3 (CO). Anal. Calcd for $C_{10}H_{11}CrNO_2S_2$: C, 41.0; H, 3.8; N, 4.8. Found: C, 41.0; H, 3.7; N, 4.6. MS FAB$^+$ (*m*/*z*): 293 [M]$^+$, 265 [M − CO]$^+$, 237 [M − 2CO]$^+$.

Compound 3b. IR (KBr, cm^{-1}): ν(CO) 1935 vs, 1874 s, sh, 1858 vs; ν(CN) 1503 s; ν(CS) 828 s; $\nu(NC_2)$ 1150 m. IR(toluene, cm^{-1}): ν(CO) 1952 s, 1884 s. ^{1}H NMR (C_6D_6): δ 4.60 (s, 5H, C_5H_5), 3.16 and 3.13 (each q (unres), *J* = 7 Hz, CH_2), 0.73 (t, *J* = 7 Hz, 6H, CH_3). ^{13}C NMR (C_6D_6): δ 93.1 (C_5H_5), 43.1 (CH_2), 13.0 (CH_3), 203.5 (CS_2), 267.4 (CO). Anal. Calcd for $C_{12}H_{15}CrNO_2S_2$: C, 44.9; H, 4.7; N, 4.4. Found: C, 44.5; H, 4.7; N, 4.4. MS FAB$^+$ (*m*/*z*): 321 [M]$^+$, 265 [M − 2CO]$^+$.

Compound 3c. IR (KBr, cm^{-1}): ν(CO) 1936 vs, 1864 vs; ν(CN) 1487 s; ν(CS) 822 s; $\nu(NC_2)$ 1048 m. ^{1}H NMR (C_6D_6): δ 4.61 (s, 5H, C_5H_5), 4.22 (br, $\nu_{1/2}$ = 84 Hz, 2H, CH), 1.03 (s, 12H, CH_3). ^{13}C NMR (C_6D_6): δ 93.0 (C_5H_5), 49.9 (CH), 20.4 (CH_3), 204.6 (CS_2), 267.2 (CO). Anal. Calcd for $C_{14}H_{19}CrNO_2S_2$: C, 48.1; H, 5.5; N, 4.0. Found: C, 48.3; H, 5.5; N, 4.0. MS FAB$^+$ (*m*/*z*): 349 [M]$^+$, 293 [M − 2CO]$^+$.

Compound 4a. IR (KBr, cm^{-1}): ν(CO) 1928 vs, 1858 s, sh, 1839 vs; ν(CN) 1570 m; ν(CS) 821 m; $\nu(NC_2)$ 1170 m. IR (toluene, cm^{-1}): ν(CO) 1954 s, 1868 s. ^{1}H NMR (C_6D_6): δ 4.42 (s, 5H, C_5H_5), 3.10 (s, 3H, CH_3), 2.71 (s, 3H, CH_3). ^{13}C NMR (C_6D_6): δ 91.1 (C_5H_5), 49.1 (CH_3), 45.5 (CH_3), 255.8 (C═Cr), 254.0 (CO), 251.4 (CO). Anal. Calcd for $C_{10}H_{11}CrNO_2S$: C, 46.0; H, 4.2; N, 5.4. Found: C, 46.3; H, 4.3; N, 5.0. MS FAB$^+$ (*m*/*z*): 261 [M]$^+$, 205 [M − 2CO]$^+$.

Compound 4b. IR (KBr, cm^{-1}): ν(CO) 1943 vs, 1855 vs; ν(CN) 1537 m; ν(CS) 819 m; $\nu(NC_2)$ 1197 m. ^{1}H NMR (C_6D_6): δ 4.45 (s, 5H, C_5H_5), 3.89 (br, $\nu_{1/2}$ = 30 Hz, 1H, CH_2), 3.72 (br, $\nu_{1/2}$ = 30 Hz, 1H, CH_2), 3.25 (q, br, *J* = 7 Hz, 2H, CH_2), 0.99 (t, *J* = 7 Hz, 3H, CH_3), 0.82 (t, *J* = 7 Hz, 3H, CH_3). ^{13}C NMR (C_6D_6): δ 91.2 (C_5H_5), 54.6 (CH_2), 52.2 (CH_2), 14.4, (CH_3), 13.1 (CH_3), 254.5 (C═Cr), 253.5 (CO), 251.7 (CO). MS FAB$^+$ (*m*/*z*): 289 [M]$^+$, 233 [M − 2CO]$^+$. HR-MS FAB$^+$ (*m*/*z*): for $[C_{12}H_{15}$-

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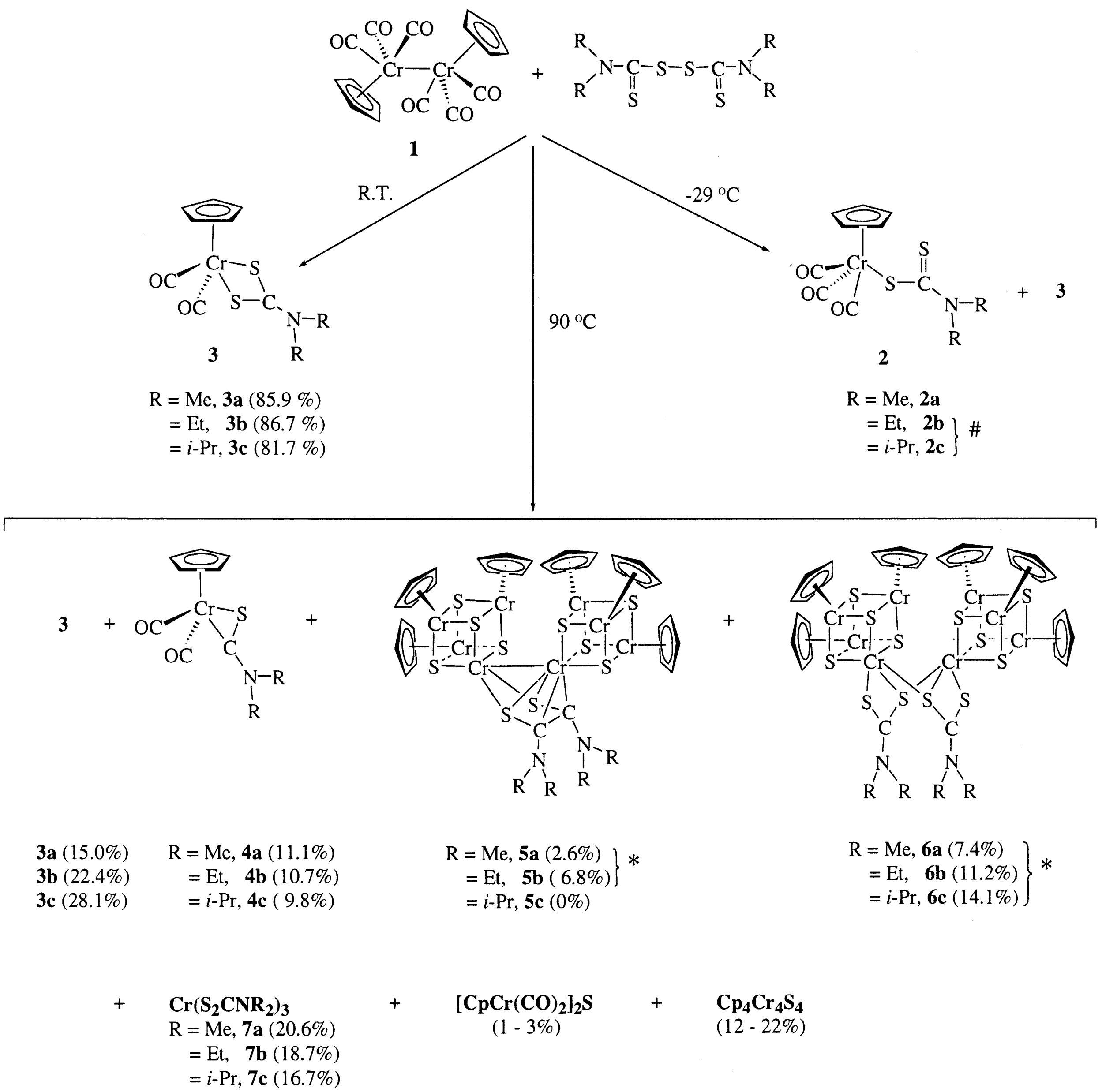
Scheme 1[a]



[a] Legend: (#) detected in solution; (*) the six Cr−Cr bonds in each of the cubanes are omitted for clarity.

$CrNO_2S$] 289.0222 (found), 289.0229 (calcd). This compound was an oil (mp −29 °C). No satisfactory elemental analysis was obtained. The proton NMR spectrum of a pure sample is given as Supporting Information.

Compound 4c. IR (KBr, cm^{-1}): ν(CO) 1944 vs, sh, 1932 vs, 1866 vs, 1838 vs; ν(CN) 1537 s; ν(CS) 820 m; $\nu(NC_2)$ 1147 m. IR (toluene, cm^{-1}): ν(CO) 1948 s, 1861 s. ^{1}H NMR (C_6D_6): δ 4.46 (s, 5H, C_5H_5), 5.37 (septuplet, J = 7 Hz, 1H, CH), 3.35 (septuplet, J = 7 Hz, 1H, CH), 1.14 (d, J = 7 Hz, 6H, CH_3), 0.89 (d, J = 7 Hz, 6H, CH_3). ^{13}C NMR (C_6D_6): δ 91.2 (C_5H_5), 63.8 (CH), 52.3 (CH), 20.8 (CH_3), 20.5 (CH_3), 254.8 (C=Cr), 252.0 (CO), 245.5 (CO). Anal. Calcd for $C_{14}H_{19}CrNO_2S$: C, 53.0; H, 6.0; N, 4.4. Found: C, 53.5; H, 6.4; N, 4.5. MS FAB$^+$ (m/z): 317 [M]$^+$, 261 [M − 2CO]$^+$, 117 [CrCp]$^+$, 52 [Cr]$^+$.

Compound 5a. ^{1}H NMR (C_6D_6): δ 5.19 (s, 5H, C_5H_5), 5.15 (s, 10H, C_5H_5), 5.07 (s, 10H, C_5H_5), 5.03 (s, 5H, C_5H_5), 2.88 (s, 12H, CH_3). The ^{1}H NMR spectrum of a sample is given in Supporting Information.

Compound 5b. IR (KBr, cm^{-1}): ν(CN) 1434 m; ν(CS) 802 s; $\nu(NC_2)$ 1115 w. ^{1}H NMR (C_6D_6): δ 5.20 (s, 5H, C_5H_5), 5.14 (s, 10H, C_5H_5), 5.08 (s, 10H, C_5H_5), 5.06 (s, 5H, C_5H_5), 3.44 (q, J = 7 Hz, 4H, CH_2), 3.21 (q, J = 7 Hz, 4H, CH_2), 1.21 (t, J = 7 Hz, 12H, CH_3). ^{13}C NMR (C_6D_6): δ 92.2 (C_5H_5), 91.9 (C_5H_5), 91.5 (C_5H_5), 91.4 (C_5H_5), 48.6 (CH_2), 14.0 (CH_3). Anal. Calcd for $C_{40}H_{50}Cr_8N_2S_{10}\cdot C_4H_8O$: C, 38.7; H, 4.3; N, 2.1. Found: C, 39.0; H, 4.3; N, 2.2. MS FAB$^+$ (m/z): 1295 [M]$^+$, 1063 [$Cp_6Cr_8S_8$]$^+$, 531 [$Cp_3Cr_4S_4$]$^+$.

5c was not detected in the proton NMR spectrum of the product solution.

Compound 6a. IR (Nujol, cm^{-1}): ν(CN) 1572 m; ν(CS) 801 s; $\nu(NC_2)$ 1151 m. ^{1}H NMR (C_6D_6): δ 5.24 (s, 30H, C_5H_5), 2.95 (s, 12H, CH_3). ^{13}C NMR (C_6D_6): δ 92.0 (C_5H_5), 40.8 (CH_3). Anal. Calcd for $C_{36}H_{42}Cr_8N_2S_{12}\cdot{}^3/_4C_7H_8$: C, 36.1; H, 3.5; N, 2.1. Found: C, 35.9; H, 3.6, N, 2.6. MS FAB$^+$ (m/z): 651 $^1/_2$[M]$^+$, 586 [$Cp_2Cr_4S_4(S_2CNMe_2)$]$^+$, 531 [$Cp_3Cr_4S_4$]$^+$.

Compound 6b. IR (KBr, cm^{-1}): ν(CN) 1495 s; ν(CS) 801 s; $\nu(NC_2)$ 1145 m. ^{1}H NMR (C_6D_6): δ 5.09 (br, $\nu_{1/2}$ = 22 Hz, 30H, C_5H_5), 3.55 (d, J = 7 Hz, 8H, CH_2), 0.95 (t, J = 7 Hz, 12H, CH_3). VT ^{1}H NMR ($C_6D_5CD_3$, 223 K): δ 5.40 (s, 10H, C_5H_5), 5.28 (s, 10H, C_5H_5), 5.06 (s, 10H, C_5H_5). ^{13}C NMR (C_6D_6): δ 91.7 (C_5H_5), 45.5 (CH_2), 13.5 (CH_3). Anal. Calcd for $C_{40}H_{50}Cr_8N_2S_{12}\cdot{}^1/_2C_6H_{14}$: C, 36.8; H, 4.1; N, 2.0. Found: C, 37.1; H,

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4.2; N, 1.2. MS FAB$^+$ (m/z): 679 $^1/_2$[M]$^+$, 614 [$Cp_2Cr_4S_4(S_2CNEt_2)$]$^+$, 563 [$Cp_2Cr_3S_4(S_2CNEt_2)$]$^+$, 531 [$Cp_2Cr_3S_3(S_2CNEt_2)$]$^+$.

Compound 6c. IR (KBr, cm^{-1}): ν(CN) 1483 s; ν(CS) 802 s; $\nu(NC_2)$ 1149 m. ^{1}H NMR (C_6D_6): δ 5.39 (br, $\nu_{1/2} = 55$ Hz, 30H, C_5H_5), 1.24 (br, $\nu_{1/2} = 52$ Hz, 24H, CH_3). VT ^{1}H NMR ($C_6D_5CD_3$, 223 K): δ 5.39 (s, 10H, C_5H_5), 5.27 (s, 10H, C_5H_5), 5.11 (s, 10H, C_5H_5). ^{13}C NMR (C_6D_6): δ 91.6 (C_5H_5), 52.3 (CH), 20.9 (CH_3). Anal. Calcd for $C_{44}H_{58}Cr_8N_2S_{12}\cdot{}^1/_2C_7H_8$: C, 39.0; H, 4.3; N, 1.9. Found: C, 39.2; H, 4.6; N, 1.9. MS FAB$^+$ (m/z): 707 $^1/_2$[M]$^+$, 642 [$Cp_2Cr_4S_4(S_2CN$-i-$Pr_2)$]$^+$.

2.3. Thermolysis of $CpCr(CO)_2(\eta^2$-$S_2CNR_2)$ (3) at 90 °C. Red solutions of $CpCr(CO)_2(\eta^2$-$S_2CNR_2)$ (R = Me (**3a**), 117 mg, 0.40 mmol; R = Et (**3b**), 289 mg, 0.90 mmol; R = i-Pr (**3c**), 87 mg, 0.25 mmol) in toluene (8 mL) was stirred at 90 °C for 2 h. The workup of this product solution, as described in section 2.2, gave the same complexes in similar yields, in addition to some recovered starting material (**3a**, 27%; **3b**, 19%; **3c**, 18%).

2.4. NMR Tube Reactions. The following reactions were monitored in septum-capped 5 mm tubes under argon via ^{1}H NMR spectral analysis for purposes of detection of intermediates and/or products.

(a) Reaction of $[CpCr(CO)_3]_2$ (1) with $[R_2NC(S)S]_2$. A deep green mixture of $[CpCr(CO)_3]_2$ (**1**) (8 mg, 0.02 mmol) and $[R_2NC(S)S]_2$ (R = Me, 5 mg; R = Et, 6 mg; R = i-Pr, 7 mg) in benzene-d_6 (0.5 mL) was shaken up for 2 min and then its ^{1}H NMR spectrum scanned at intervals, to monitor the time-dependent change in the relative concentration of complexes **2** and **3**. This was found to be as follows (time in min (relative concentration)): R = Me, 5 (2:1), 10 (3:2), 40 (5:6), 60 (1:3), and 180 (1:50); R = Et, 5 (2:1), 10 (1:1), 15 (3:4), 30 (1:4), 60 (1:9), and 120 (1:100); R = i-Pr, 5 (1:1), 10 (1:4), 20 (1:6), 30 (1:7), 60 (1:8), and 120 (1:50).

(b) Reaction of $[CpCr(CO)_2]_2(Cr{\equiv}Cr)$ with $[Et_2NC(S)S]_2$. A deep green mixture of $[CpCr(CO)_2]_2(Cr{\equiv}Cr)$ (7 mg, 0.02 mmol) and $[Et_2NC(S)S]_2$ (6 mg, 0.02 mmol) in benzene-d_6 (0.5 mL) was shaken up for 10 min and then its ^{1}H NMR spectrum scanned at intervals (10 min, 120 min, 100 h).

(c) Reaction of $Cp_4Cr_4S_4$ with [i-$Pr_2NC(S)S]_2$ at 80 °C. A dark green mixture of $Cp_4Cr_4S_4$ (12 mg, 0.02 mmol) and [i-$Pr_2NC(S)S]_2$ (3.5 mg, 0.01 mmol) in benzene-d_6 (0.5 mL) was maintained at ca. 80 °C for 1 h, and its ^{1}H NMR spectrum was scanned.

(d) Thermolysis of $CpCr(CO)_2(SCNEt_2)$ (4b). A red solution of $CpCr(CO)_2(SCNEt_2)$ (**4b**) (9 mg, 0.03 mmol) in toluene-d_8 (0.5 mL) in a septum-capped 5 mm NMR tube under argon was maintained at ca. 110 °C, and its proton NMR spectrum was scanned at intervals of 2 h.

(e) Thermolysis of $Cp_6Cr_8S_8(S_2CNEt_2)_2$ (6b). A red-brown solution of $Cp_6Cr_8S_8(S_2CNEt_2)_2$ (**6b**) (4 mg, 0.003 mmol) in benzene-d_6 (0.5 mL) was maintained at ca. 80 °C, and its ^{1}H NMR spectrum was monitored at intervals (30, 60, and 120 min).

2.5. Crystal Structure Analyses. Diffraction-quality single crystals were obtained from solutions in toluene layered with hexane at −29 °C as follows: **2a** as red needles as described in section 2.2, **3a** as a dark red rhombus after 3 days, **3b** as dark red prisms after 2 days, **3c** as dark red needles after 2 days, **4a**,**c** as dark red rhombuses after 7 and 5 days, respectively, **6b**,**c** as dark blue rhombuses after 5 and 8 days, respectively, and **5b** as a dark blue rhombus by diffusion of n-hexane into a THF solution after 7 days.

The crystals were mounted on quartz fibers. X-ray data were collected on a Siemens SMART diffractometer, equipped with a CCD detector, using Mo Kα radiation (λ = 0.710 73 Å).

The data were corrected for Lorentz and polarization effcts with the SMART suite of programs[12] and for absorption effects with SADABS.[13] Structure solution and refinement were carried out with the SHELXTL suite of programs.[14] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. The Cp and alkyl hydrogens were placed in calculated positions. Data collection and processing parameters are given in Table 1.

3. Results and Discussion

3.1. Reaction of $[CpCr(CO)_3]_2$ (1) with $[R_2NC(S)S]_2$ (R = Me, Et, i-Pr). At ambient temperature, a deep green suspension of $[CpCr(CO)_3]_2$ (**1**) in toluene reacted with 1 mol equiv of tetraalkylthiuram disulfide $[R_2NC(S)S]_2$ (R = Me, Et, i-Pr) within 1 h, giving dark red solutions, from which were obtained in high yields air-stable dark red crystals of $CpCr(CO)_2(\eta^2$-$S_2CNR_2)$ (**3**), as shown in Scheme 1. This reaction also proceeded between the reactants in the solid state. When the progress of the reaction was monitored via time-dependent proton NMR spectral scans, it was observed that **3** was formed either concurrently with or via the intermediate compound $CpCr(CO)_3(\eta^1$-$S_2CNR_2)$ (**2**), which converted to **3** within 2−3 h at ambient temperature. This slower rate of conversion in a *sealed* NMR tube is in agreement with suppression of the reaction by the released carbon monoxide. Indeed, red needle-shaped crystals of **2a** in an approximately 1:1 admixture with fine crystals of **3a** were obtained after mixing the reactants and keeping the solution at −29 °C for 3 days. At 90 °C for 2 h, the reaction led to the isolation of **3** together with $CpCr(CO)_2(\eta^2$-$SCNR_2)$ (**4**) as dark red crystals (R = Me, i-Pr) or a dark red oil (R = Et), $Cp_6Cr_8S_8(\eta^2{:}\eta^4$-$SCNR_2)_2$ (**5**) as dark brown crystals, $Cp_6Cr_8S_8(\eta^1{:}\eta^2$-$S_2CNR_2)_2$ (**6**) as dark brown crystals, $Cr(\eta^2$-$S_2CNR_2)_3$ (**7**) as dark blue crystals, $Cp_2Cr_2(CO)_4S$ as dark green crystals, and $Cp_4Cr_4S_4$ as deep green solids, with yields as presented in Scheme 1. A similar product composition was obtained from a thermolytic degradation of **3** at 90 °C for 2 h.

3.2. Reaction Pathways. The reaction pathways are illustrated in Scheme 1. In view of the facile dissociation of the Cr dimer (**1**) into the monomeric 17-electron radical species,[15] and the known susceptibility of the S−S bond in organic disulfides to cleavage by nucleophilic, electrophilic, and radical processes,[16] it is conceivable that the reaction is initiated by the attack of $CpCr(CO)_3$ on the S−S bond of thiuram disulfide, as shown in eq i, forming the complex **2**, which contains a monodentate dithiocarbamate ligand. A terminating

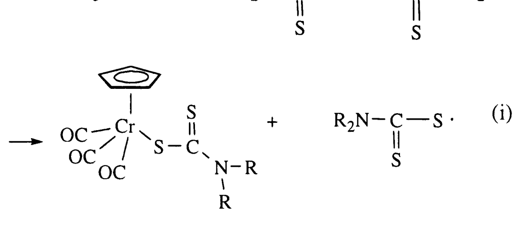

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Table 1. Data Collection and Processing Parameters

	2a	**3a**	**3b**	**3c**	**4a**	**4c**	**5b**	**6b**	**6c**
formula	$C_{11}H_{11}CrNO_3S_2$	$C_{10}H_{11}CrNO_2S_2$	$C_{12}H_{15}CrNO_2S_2$	$C_{14}H_{19}CrNO_2S_2$	$C_{10}H_{11}CrNO_2S$	$C_{14}H_{19}CrNO_2S$	$[C_{40}H_{50}Cr_8N_2S_{10}]_2\cdot THF$	$C_{40}H_{50}Cr_8N_2S_{12}\cdot C_6H_{14}$	$C_{44}H_{58}Cr_8N_2S_{12}\cdot C_7H_8$
M_r	321.33	293.32	321.37	349.42	261.26	317.36	2658.91	1445.71	1507.78
temp, K	223(2)	223(2)	223(2)	173(2)	223(2)	223(2)	223(2)	223(2)	173(2)
cryst color. habit	red, needle	dark red, rhombus	dark red, prism	dark red, needle	dark red, rhombus	dark red, rhombus	dark blue, rhombus	dark blue, rhombus	dark blue, rhombus
cryst size, mm	0.16 × 0.26 × 0.40	0.43 × 0.39 × 0.05	0.39 × 0.27 × 0.27	0.28 × 0.26 × 0.16	0.32 × 0.28 × 0.24	0.30 × 0.24 × 0.10	0.32 × 0.14 × 0.04	0.03 × 0.08 × 0.30	0.26 × 0.09 × 0.08
cryst syst	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$Pbca$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a, Å	7.0727(3)	12.9368(4)	11.1400(2)	7.72630(10)	10.3873(7)	12.5009(9)	9.7539(3)	9.6283(9)	13.0323(6)
b, Å	13.0378(6)	7.4045(2)	11.4572(2)	10.0947(2)	19.5813(13)	13.2552(9)	50.869(2)	26.798(2)	21.6688(10)
c, Å	29.0898(14)	12.4458(3)	11.47700(10)	10.1584(2)	11.1634(7)	18.7306(12)	21.1727(9)	21.0638(19)	21.3389(10)
α, deg	90	90	90	79.4630(10)	90	90	90	90	90
β, deg	90	96.4590(10)	96.5760(10)	83.3000(10)	91.076(2)	93.444(2)	91.659(2)	99.133(4)	91.4800(10)
γ, deg	90	90	90	82.6650(10)	90	90	90	90	90
V, Å^3	2682.4(2)	1184.62(6)	1455.21(4)	769.02(2)	2270.2(3)	3098.1(4)	10500.9(7)	5365.9(8)	6024.0(5)
Z	8	4	4	2	8	8	4	4	4
density, g cm^{-3}	1.591	1.645	1.467	1.509	1.529	1.361	1.682	1.790	1.663
abs coeff, mm^{-1}	1.161	1.300	1.065	1.015	1.169	0.870	2.021	2.060	1.839
F(000)	1312	600	664	364	1072	1328	5392	2952	3080
θ range for data collecn (deg)	2.80−31.61	3.17−29.39	2.41−29.33	2.05−29.27	2.08−31.03	2.18−30.52	2.08−23.26	2.10−22.46	2.04−28.28
index ranges	$0 \le h \le 10$, $0 \le k \le 18$, $0 \le l \le 42$	$-17 \le h \le 16$, $0 \le k \le 10$, $0 \le l \le 16$	$-15 \le h \le 14$, $0 \le k \le 14$, $0 \le l \le 15$	$-9 \le h \le 10$, $-12 \le k \le 13$, $0 \le l \le 13$	$-14 \le h \le 14$, $0 \le k \le 27$, $0 \le l \le 15$	$-17 \le h \le 17$, $0 \le k \le 18$, $0 \le l \le 26$	$-10 \le h \le 10$, $0 \le k \le 56$, $0 \le l \le 23$	$-10 \le h \le 9$, $0 \le k \le 28$, $0 \le l \le 22$	$-17 \le h \le 17$, $0 \le k \le 28$, $0 \le l \le 28$
no. of rflns collected	23 500	7799	11 249	6599	19 769	25 201	69 642	13 987	84 678
no. of indep rflns	4298	2962	3581	3686	7004	8745	15 082	5828	14 961
max, min transmissn	0.863, 0.699	0.949, 0.707	0.813, 0.688	0.831, 0.679	0.802, 0.637	0.928, 0.718	0.862, 0.661	0.928, 0.508	0.875, 0.728
no. of data/ restraints/params	4298/0/207	2962/0/189	3581/0/223	3686/0/257	7004/0/359	8745/0/460	15082 /21/708	5828/73/386	14 961/0/674
final R indices ($I > 2\sigma(I)$)[a,b]	R1 = 0.0420, wR2 = 0.0889	R1 = 0.0332, wR2 = 0.0721	R1 = 0.0345, wR2 = 0.0827	R1 = 0.0279, wR2 = 0.0708	R1 = 0.0435, wR2 = 0.1263	R1 = 0.0520, wR2 = 0.0948	R1 = 0.1678, wR2 = 0.3400	R1 = 0.1319, wR2 = 03047	R1 = 0.0527, wR2 = 0.1037
R indices (all data)	R1 = 0.0570, wR2 = 0.0940	R1 = 0.0444, wR2 = 0.0777	R1 = 0.0481, wR2 = 0.0907	R1 = 0.0342, wR2 = 0.0743	R1 = 0.0526, wR2 = 0.1304	R1 = 0.1094, wR2 = 0.1086	R1 = 0.2367, wR2 = 0.3728	R1 = 0.2821, wR2 = 0.3781	R1 = 0.1024, wR2 = 0.1193
goodness of fit on F^2 [c]	0.980	1.075	1.052	1.036	1.053	0.828	1.122	0.959	0.944
large diff peak, hole, e Å^{-3}	0.513, −0.206	0.300, −0.414	0.465, −0.596	0.529, −0.367	0.507, −0.417	0.580, −0.588	1.533, −0.963	1.150, −1.396	0.699, −0.469

[a] $R1 = (\sum|F_o| - |F_c|)\sum|F_o|$. [b] $wR2 = [(\sum w|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] $GOF = [(\sum w|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

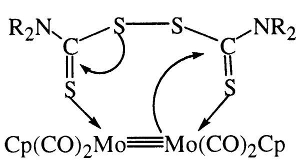
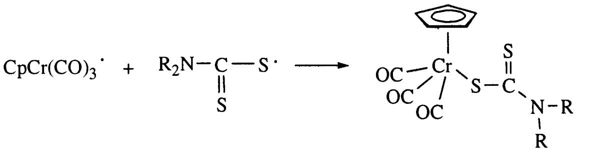


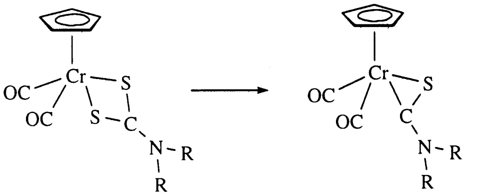
Figure 1. Intermediate **A**.

step involving direct coupling of the CpCr and the dithio-organic radicals will also generate **2** (eq ii). The radical initiation step had been postulated before for the reaction of **1** with Ph_2E_2 (E = S, Se, Te), which gave rise to complexes containing η^1-EPh and η^2-EPh ligands,[2] and for the scission of the S−S bonds in bis(thiophosphinyl) and bis(thiophosphoryl) disulfanes.[3] A similar mechanism had been demonstrated by Abrahamson and Helm for the reaction of $[CpW(CO)_3]_2$ with tetramethylthiuram disulfide, in which case the W monomeric species was generated by visible irradiation of the dimer.[7c] A subsequent facile dissociation of a CO ligand from **2** is accompanied by chelation of the ligand to produce **3**, without violation of the 18-electron rule, considering the monodentate and bidentate ligands as one- and three- electron donors, respectively. While this process was found to occur readily at ambient temperature, the same transformation in the W analogue[7c] and in $CpFe(CO)_2(\eta^1\text{-}S_2CNR_2)$[17] required higher energy activation, e.g. thermolysis, photolysis, or electron-transfer catalysis. The Mo analogue of **3** had been obtained from the reaction of thiuram disulfide with $[CpMo(CO)_3]_2$ in refluxing methylcyclohexane (101 °C) after 18 h[6a] or with the triply bonded Mo dimer $[CpMo(CO)_2]_2$ at ambient temperature after 16 h.[7a] Alper proposed for *both* of these reactions an initial coordination of the Mo atoms in the Mo≡Mo species to the sulfur atoms of the ligand, generating the intermediate **A** (Figure 1), prior to S−S and Mo−Mo bond cleavages. In our case, however, we found $[CpCr(CO)_2]_2$(*Cr*≡*Cr*) to be rather sluggish toward thiuram disulfide, with a half-life on the order of 60 h at ambient temperature; also, we saw no evidence of a species of the nature of **A** in the time-dependent proton NMR spectral scans of the reaction mixture.

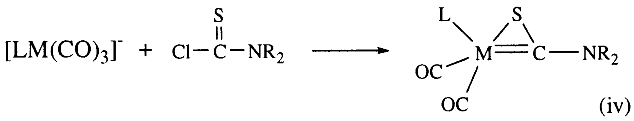


(ii)

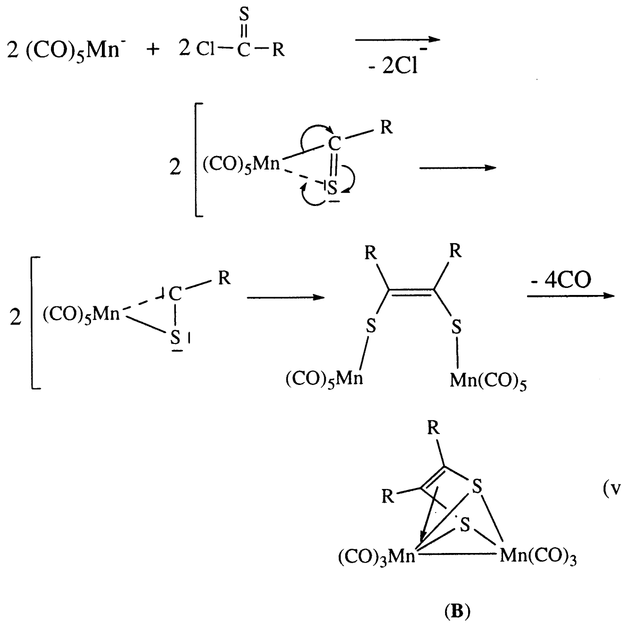
The thermolytic degradation of **3** gave a multicomponent mixture from which complexes **4**−**7** could be isolated, together with the well-known cubane $Cp_4Cr_4S_4$ and $[CpCr(CO)_2]_2S$[1,18a] in trace amounts. The formation of the carbenoid complexes **4** from **3** involves the cleavage of a S atom, resulting in the conversion of a dithiocarbamate ligand to a thiocarboxamido ligand (eq iii). A few examples of this occurrence have been reported, viz. at Re,[19] Ru,[20] Rh,[21] Mo,[22] and W,[23] though thiocarbamoyl complexes are commonly synthesized by oxidative addition of $R_2NC(S)X$ (eq iv), a method employed by Kreissl for Mo and W complexes,[24] by Weiss for an Fe complex,[22] and by Dean for Mo, Mn, and Fe complexes.[25] The thermal conversion of **3** to the double-cubanes **5** and **6** is an unprecedented reactivity feature, not observed before for the Mo or W analogues,[7] even though the synthesis of the latter complexes had also involved thermolytic conditions. In fact, thermolytic degradation of the cyclopentadienylchromium complex **3** gives rise to two classes of products, viz. complexes containing the intact dithiocarbamate ligand, as in **6** and **7**, and complexes in which the ligand has undergone one C−S bond cleavage, as in **4** and **5**. The structural features of **5** show that its formation from **3** has involved a single C−S bond cleavage cum C−C coupling, resulting in a metallacyclopropane moiety, i.e., Cr(5)C(1)C(2) in complex **5b**. There exists a striking similarity between the bridging component in **5** and the dithiolene complexes **B** obtained by Lindner from the manganese-induced reductive dimerization of the thioaroyl chlorides RC(S)Cl, for which an unstable carbenoid intermediate was proposed (eq v).[26] However, in this study an NMR tube experiment showed that the carbenoid complex **4** was thermally stable in solution. Neither was **5** derived



(iii)



(iv)



(v)

(**B**)

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 2−4

	2a	**3a**	**3b**	**3c**	**4a**	**4c**
			Bond Lengths			
Cr(1)−S(1)	2.4406(5)	2.4209(6)	2.4240(6)	2.4108(4)	2.4495(6)	2.4188(9)
Cr(1)−S(2)		2.4266(6)	2.4172(5)	2.4209(5)		
C(1)−S(1)	1.7568(18)	1.703(2)	1.7058(19)	1.7201(16)	1.675(2)	1.666(3)
C(1)−S(2)	1.6822(19)	1.709(2)	1.7116(19)	1.7171(16)		
C(1)−N(1)	1.340(2)	1.325(3)	1.326(2)	1.3353(19)	1.301(3)	1.306(3)
C(1)−Cr(1)					1.953(2)	1.978(3)
			Bond Angles			
S(1)−Cr(1)−S(2)		70.693(19)	70.608(17)	70.333(14)		
C(1)−S(1)−Cr(1)	114.00(6)	89.54(7)	89.70(6)	90.90(5)	52.53(7)	54.20(9)
C(1)−S(2)−Cr(1)		89.22(7)	89.79(7)	90.63(5)		
S(1)−Cr(1)−C(1)					42.91(6)	43.09(8)
S(1)−C(1)−Cr(1)					84.56(9)	82.72(13)
S(1)−C(1)−S(2)	123.67(11)	110.54(11)	109.91(10)	108.12(8)		
S(1)−C(1)−N(1)	113.70(13)	124.25(16)	125.47(15)	124.29(12)	129.29(17)	132.9(2)
S(2)−C(1)−N(1)	122.63(14)	125.20(16)	124.61(15)	127.58(12)	−	−
Cr(1)−C(1)−N(1)	−	−	−	−	146.04(16)	144.3(2)
C(1)−N(1)−C(2)	123.31(17)	120.55(19)	121.39(18)	118.48(13)	123.4(2)	123.7(2)
C(1)−N(1)−C(3)	121.95(18)	122.14(19)	121.08(17)	123.73(13)	121.24(19)	119.8(2)
C(2)−N(1)−C(3)	114.71(18)	117.2(2)	117.47(17)	117.60(12)	115.3(2)	116.4(2)

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from thermolysis of the dithiocarbamate-bridged double cubane **6** or thermal treatment of $Cp_4Cr_4S_4$ with the ligand. The following paper in this issue describes the role of $CpCr(CO)_3$ and/or $CpCr(CO)_2$ in the formation of **5** from **3** or $Cr(\eta^2\text{-}S_2CNR_2)_3$ (**7**), a known coordination compound previously synthesized from the direct reaction of Cr(III) salts with $Na(S_2CNR_2)$[27] and one of the thermolytic products of **3** in this study**.** The dissociation of η^5-Cp ligands from the metal atom, as evident in the formation of **7** and also of **5**, is not common but appears to be facilitated in this system, as well as the related complexes containing the bis(diphenylthiophosphinyl)-disulfane and bis(thiophosphoryl)disulfane ligands.[3] In comparison, the Cp rings remain intact in the cubane molecules $Cp_4Cr_4X_2Y_2$ (X = S, Se; Y = S, O, CO), often encountered from the thermolysis of CpCr chalcogen complexes.[1]

3.3. Properties and Spectral Characteristics. The complexes **3**−**6**, with the exception of **2b**,**c**, **4b**, and **5a**,**c**, were fully characterized by microanalytical and spectral data (see the Experimental Section). The compounds **2b**,**c** were not isolated as solids and were characterized by their proton NMR spectra. Microanalytical data were lacking for **4b**, which was an oil even at −29 °C. It was not possible to purify the low-yield compound **5a**, and its presence was based on the resemblance of its Cp proton NMR spectral characteristics to those of its analogue **5b**. The presence of **5c** was not detected in the proton NMR spectrum of the product solution. The Cp proton resonances of the 18-electron mononuclear complexes **2**−**4**, all containing chromium in oxidation state +2, are found in the range δ 4.19−4.61, within the normal range observed for other CpCr moieties;[1−3] likewise, the corresponding $^{13}C\{^1H\}$ resonances at δ 91.1−93.1 are in the normal range for diamagnetic compounds. Other ^{13}C resonances are observed for CO at δ 237.8−267.4, for CS_2 at δ 194.1−204.6, and for C=Cr at δ 254.5−255.8. The proton Cp resonances of the 60-electron double cubanes **5** and **6**, containing chromium in the +3 oxidation state, are observed at lower field than the mononuclear complexes, viz. δ 5.06−5.20 for **5b** and δ 5.06−5.40 for complexes **6a**−**c**, but the corresponding ^{13}C peaks are found in the same region as for the mononuclear compounds. The observation of four Cp signals (relative intensity 1:2:2:1) in the molecule **5b** is consistent with the structure of the molecule.[10] The spectrum confirms the presence of two cubane cores in different magnetic environments, each possessing two equivalent Cp ligands different from a third. Likewise in the carbon spectrum, four signals are observed. In the dithiocarbamate-bridged double cubane **6**, the Cp rings resonate as a single very broad peak at room temperature, indicative of fluxionality, which is often encountered with dithiocarbamate ligands.[28] In this case the fluxionality can be totally arrested at temperatures of −55 °C and below, at which temperatures three sharp signals can be observed for the three Cp rings of each cubane, thus also providing evidence for the equivalence of the two cubane cores. The IR stretching frequencies for the CO ligands in the mononuclear complexes are found in the normal carbonyl region. The stretching frequencies of the dithiocarbamate ligand in all the complexes fall in the range as follows: ν(CN) between 1487 and 1570 cm^{-1}, ν(CS) between 819 and 828 cm^{-1} for the bidentate ligands, and $\nu(NC_2)$ between 1048 and 1197 cm^{-1}.

3.4. X-ray Diffraction Analyses. The molecular structures of **2a**, **3a**−**c**, **4a**,**c**, **5b**, and **6b**,**c** have been determined. The ORTEP diagrams are shown in Figures 2−6. Selected bond parameters are given in Table 2 for the mononuclear complexes and Table 3 for the doube-cubane complexes.

The structure of **2a** (Figure 2) contains a CpCr moiety bonded to a η^1-dithiocarbamate and three CO ligands,

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complexes 5 and 6

	5b	6b	6c
Bond Distances for the Bridging Ligand			
Cr(1)−Cr(5)	3.101(6)		
Cr(1)−S(9)	2.331(7)	2.495(9)	2.4870(12)
Cr(1)−S(10)		2.443(10)	2.4131(12)
Cr(1)−S(11)	2.340(8)	2.552(10)	2.5486(13)
Cr(5)−S(9)	2.364(7)	2.581(10)	2.5501(13)
Cr(5)−S(11)	2.469(7)	2.505(9)	2.4835(12)
Cr(5)−S(12)		2.441(9)	2.4209(13)
Cr(5)−C(1)	2.32(3)		
Cr(5)−C(2)	2.45(2)		
C(1)−S(9)	1.72(3)	1.77(3)	1.769(4)
C(1)−S(10)		1.71(3)	1.696(4)
C(2)−S(11)	1.81(2)	1.78(3)	1.775(4)
C(2)−S(12)		1.62(3)	1.698(4)
C(1)−C(2)	1.41(3)		
C(1)−N(1)	1.44(3)	1.37(3)	1.322(5)
C(2)−N(2)	1.38(3)	1.40(3)	1.314(5)
Bond Angles for the Bridging Ligand			
S(9)−Cr(1)−S(10)		71.5(3)	71.41(4)
S(9)−Cr(1)−S(11)	81.4(3)		
S(9)−Cr(5)−S(11)	78.1(2)		
S(11)−Cr(5)−S(12)		71.1(3)	71.44(4)
S(9)−Cr(5)−C(1)	43.1(6)		
S(11)−Cr(5)−C(2)	43.2(6)		
C(1)−Cr(5)−C(2)	34.4(8)		
Cr(1)−S(11)−Cr(5)	80.3(2)	99.2(3)	98.34(4)
Cr(1)−S(9)−Cr(5)	82.7(2)	98.7(3)	98.21(4)
C(1)−S(9)−Cr(1)	86.7(9)	86.7(9)	86.47(15)
C(1)−S(10)−Cr(1)		89.8(9)	90.50(15)
S(9)−C(1)−Cr(5)	69.8(9)		
C(1)−S(9)−Cr(5)	67.1(9)	109.2(10)	112.12(14)
C(2)−S(11)−Cr(1)	109.1(8)	112.0(10)	113.68(15)
C(2)−S(12)−Cr(5)		89.3(10)	90.36(15)
S(9)−C(1)−S(10)		112.1(15)	111.2(2)
C(2)−C(1)−Cr(5)	77.8(15)		
S(10)−C(1)−N(1)		127(2)	125.8(3)
S(11)−C(2)−S(12)		115.7(15)	111.1(2)
C(1)−C(2)−Cr(5)	67.8(14)		
C(2)−S(11)−Cr(5)	67.8(8)	83.8(9)	86.59(14)
S(11)−C(2)−Cr(5)	69.0(8)		
N(1)−C(1)−S(9)	122.8(19)	121(2)	122.9(3)
N(2)−C(2)−Cr(5)	135.0(17)		
C(1)−C(2)−S(11)	114.2(18)		
N(2)−C(2)−S(11)	115.5(17)	119(2)	121.8(3)
S(12)−C(2)−N(2)		125(2)	126.9(3)
C(2)−C(1)−S(9)	120.9(19)		
N(1)−C(1)−C(2)	114(2)		
N(2)−C(2)−C(1	130(2)		
C(1)−N(1)−C(111)	113(3)	124(3)	121.8(4)
C(1)−N(1)−C(113)	115(3)	120(2)	123.8(4)
C(111)−N(1)−C(113)	107(3)	115(3)	114.4(4)
C(2)−N(2)−C(121)	119(2)	118(2)	123.7(4)
C(2)−N(2)−C(123)	123(2)	127(3)	121.3(4)
C(121)−N(2)−C(123)	115(2)	114(3)	114.9(4)
Bond Distances for the Cr_4S_4 Cubes			
Cr−S	2.208(7)−2.264(7)	2.218(11)−2.290(11)	2.2392(13)−2.2776(13)
Cr−Cr	2.764(6)−2.887(6)	2.783(8)−2.926(7)	2.7955(10)−2.9067(10)
Bond Angles for the Cr_4S_4 Cubes			
S−Cr−S	98.6(2)−104.1(3)	97.5(4)−103.2(4)	97.94(5)−102.67(5)
Cr−S−Cr	75.4(2)−79.2(3)	75.8(3)−80.4(3)	76.44(4)−80.20(4)
Cr−Cr−Cr	57.70(13)−61.95(15)	57.34(18)−61.88(18)	58.04(2)−61.66(2)

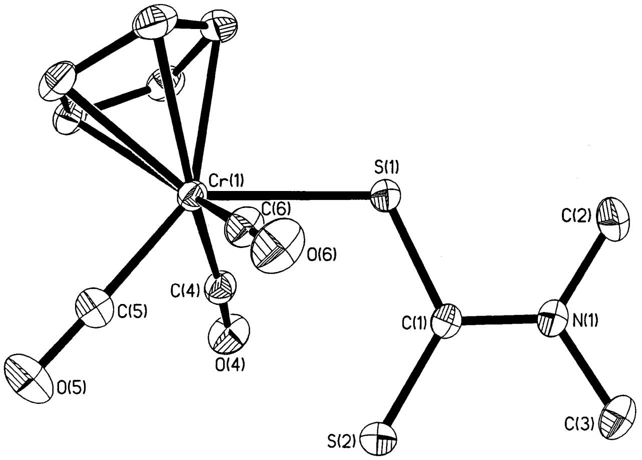

Figure 2. Molecular structure of **2a**. Thermal ellipsoids are drawn at the 50% probability level.

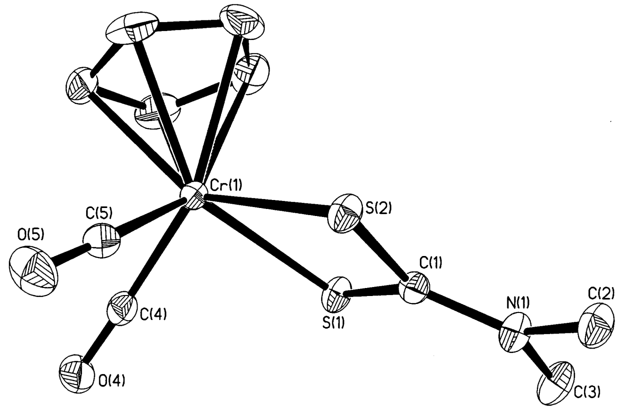

Figure 3. Molecular structure of **3a**. Thermal ellipsoids are drawn at the 50% probability level.

similar to the W analogue discussed above.[7c] There is only one other case known of η^1-bonding in dithiocarbamate organometallic compounds, i.e., $CpFe(CO)_2(\eta^1\text{-}S_2CNR_2)$ and its Cp* analogues, which have been extensively investigated by Astruc,[17,29] though a few examples have been reported for coordination compounds, viz. in $Pt(S_2CN(^tBu)_2)_2(PMe_2Ph)$, $Pt(S_2CNEt_2)(PPh_3)$, $Ru(S_2CNEt_2)_3(NO)$, and $Au(S_2CNEt_2)_3$.[30] The gross features of the structure of the molecules of **3a**−**c** are similar and are illustrated in Figure 3 for **3a**. There is present a CpCr unit bonded to a η^2-dithiocarbamate and two CO ligands, isostructural with $CpMo(CO)_2(\eta^2\text{-}S_2CN(i\text{-}Pr)_2)$.[7a] This bidentate bonding is the common coordination mode in mononuclear thiocarbamate complexes. The bond parameters of **3a**−**c** are presented in Table 2, together with those of the other mononuclear complexes for comparison. The M−S bond distances, ranging from 2.4108(4) to 2.4266(6) Å, are similar to those reported for $CpMo(CO)_2(S_2CN(i\text{-}Pr)_2)_2$ (average 2.4965(1) Å)[7a] and $CpMo(CO)_2(S_2CNMe_2)$ (average 2.503(1) Å),[7b] allowing for the difference in atomic size between Cr and Mo. The range of Cr−S distances for the series of compounds **2**−**4** (2.4108(4)−2.4495(6) Å) lie within the range observed for other CpCr com-

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Table 4. Bond Parameters of the Thiocarboxamide Carbenoid MCS Unit in Related Complexes (L = (S)CNR$_2$)

	CpCr(CO)$_2$L (this work)				
	4a	**4c**	CpW(CO)$_2$L[24]	(HBPz$_3$)Mo(CO)$_2$L[24]	(Ph$_3$P)Mn(CO)$_3$L[25b]
C−M−S (deg)	42.91(6)	43.09(8)	41.3(3)	41.2(5)	44.0(2)
M−C (Å)	1.953(2)	1.978(3)	2.098(10)	2.09(2)	1.924(**6**)
C−S (Å)	1.675(2)	1.666(3)	1.694(1)	1.68(2)	1.68(2)
M−S (Å)	2.4495(6)	2.4188(9)	2.552(3)	2.531(5)	2.404(3)
M−C(CO) (Å)	1.817(2), 1.849(2)	1.806(4), 1.816(4)	1.964(12), 1.929(11)	1.91(2), 1.81(3)	1.815(7), 1.784(0)

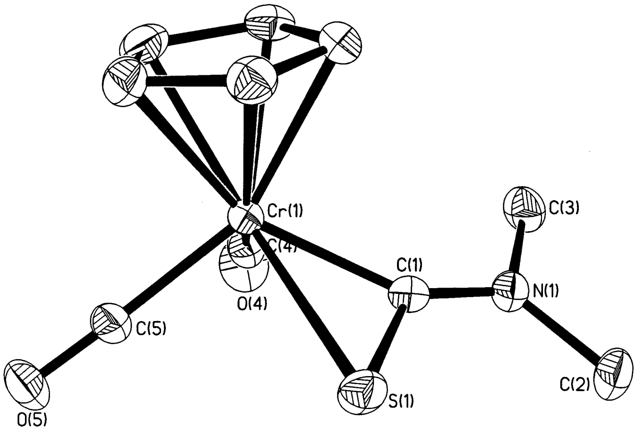

Figure 4. Molecular structure of **4a**. Thermal ellipsoids are drawn at the 50% probability level.

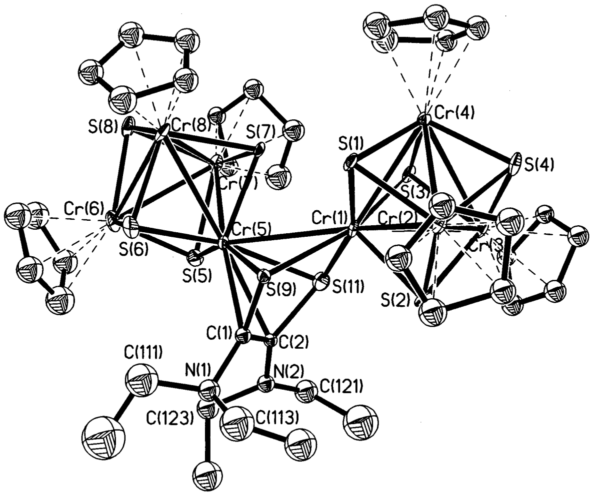

Figure 5. Molecular structure of **5b**. Thermal ellipsoids are drawn at the 50% probability level.

plexes that we have studied, i.e. 2.348−2.466 Å for complexes containing bare S ligands,[18a] 2.486−2.517 Å for complexes containing bare P/S ligands,[18b] 2.365(1)−2.471(3) Å for complexes containing bridging SPh ligands,[2a] and 2.3711(8)−2.517(8) Å for complexes containing S$_2$PR$_2$ or S$_2$P(OR)$_2$ ligands.[3] The C−S distances in **3a**−**c** (1.703(2)−1.7201(16) Å), comparable to previously reported values for dithiocarbamate ligands (1.700(7)−1.79(2) Å)[31a−c] and the C−N distances (1.325(3)−1.3353(19) Å), slightly longer than previous values (1.288(8)−1.52(9) Å) for dithiocarbamate complexes,[31a,b] are indicative of partial double-bond character (C−S, 1.81 Å; C═S, 1.61 Å; C−N, 1.47 Å; C═N, 1.27 Å).[32] In complex **2a**, the distance of C(1) to S(2), the uncoordinated S atom (1.6822(19) Å), approaches the value for a C═S double bond, in agreement with the monodenticity of the ligand.

The structures of **4a**,**c** are similar, each containing a carbenoid Cr−C bond; a representative ORTEP diagram is illustrated in Figure 4 for **4a**. These compounds complete the family of such complexes of group 6, the Mo and W members of which have recently been synthesized by Kreissl and his group, alongside analogous complexes containing pyrazolylborate ligands, HB(pz)$_3$ or HB(pzMe$_2$)$_3$, instead of Cp.[24] The bond parameters defining the cyclo-MCS unit in these carbenoid complexes are compared with those of **4** in Table 4, which also includes a Mn complex.[25b] It is seen that the bond lengths and bond angles subtended at the metal atoms all fall within a narrow range. Notable is the significantly shorter C−S bond (1.666(3)−1.675(2) Å; cf. 1.61 Å for C═S[32]) when compared with the same bonds (1.703−1.7201 Å) in the dithiocarbamate ligand in complex **3**, reflecting the stronger π-acidity of the chelating thiocarboxamido ligand. The Cr═C bond (1.953(2) and 1.978(3) Å in **4a**,**c**, respectively) is comparable to similar bonds within the range observed for Fischer-type carbene complexes.[33] We also note that it is longer than the Cr−C(carbonyl) distances 1.849(2) and 1.817(2) Å in **4a** and 1.806(4)−1.837(4) Å for the analogous distances in the two independent molecules of **4c**, indicative of its weaker interaction. In the complexes **2**−**4**, N assumes a planar configuration, in agreement with its sp^2 character.

The structures of **5b** and **6b**, illustrated in Figures 5 and 6, respectively, have been described.[10] The molecule of **6c** is isostructural with **6b**. Some selected bond parameters of these complexes are listed in Table 3. The salient feature in **6** is a double cubane doubly bridged by two dithiocarbamate ligands, each bonding in a η^1-(S):η^2(S,S′) coordination mode. The significant feature in **5b** is the presence of a dithiooxamide ligand (DTO = Et$_2$NC(S)C(S)NEt$_2$), which links the two cubanes with a η^2:η^4 bonding mode, in addition to a weak M−M bond between the two cubanes.

Concluding Remarks

Thermally induced C−S bond cleavage(s) of a S,S′-bidentate dithiocarbamate ligated to cyclopentadienylchromium led to the formation of thiocarbenoid and

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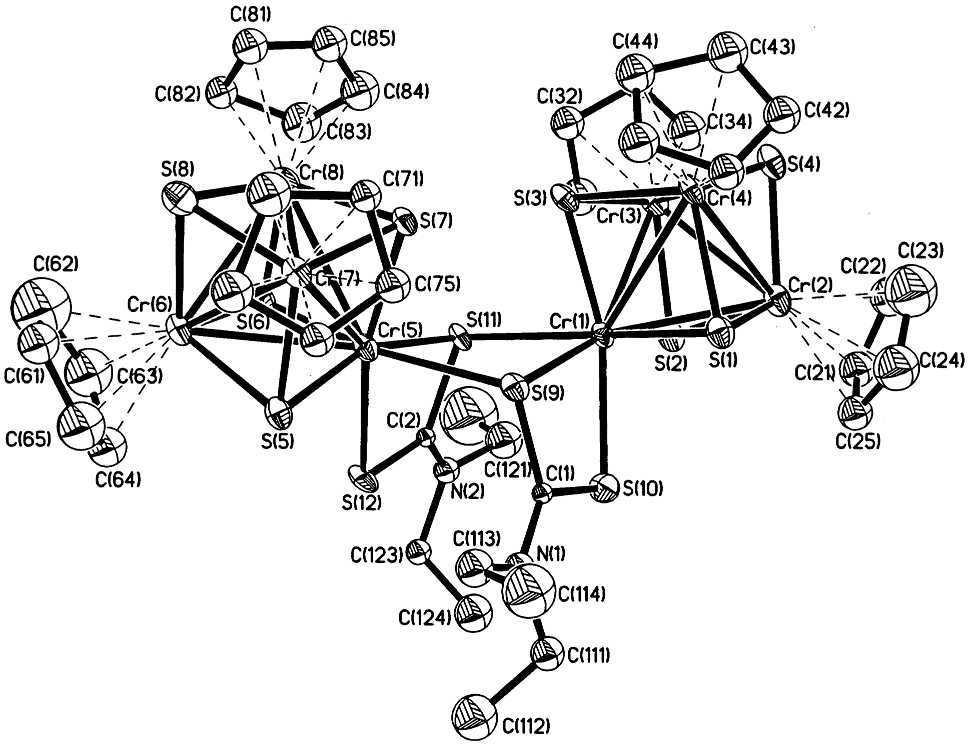

Figure 6. Molecular structure of **6b**. Thermal ellipsoids are drawn at the 50% probability level.

double-cubane complexes, doubly bridged by dithiocarbamate ligands in one case and by a dithiooxamide ligand in another.

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Supporting Information Available: ORTEP diagrams and tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and all bond lengths and angles for the structures of **2a**, **3a**–**c**, **4a**,**c**, **5b**, and **6b**,**c** and figures giving proton NMR spectra of **4b** and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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