suggests stable trap site for the hole, the position of which is not far from the acceptor. The slow recombination of the geminate ion pair with the relatively short distance would be related to the trap-site structure or some sorts of reorganizations because of the charge shift in the PVCz film.

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C–S Bond Cleavage and C–C Coupling in Cyclopentadienylchromium Complexes To Give the First Dithiooxamide-Bridged and Doubly Dithiocarbamate-Bridged Double Cubanes: $[Cp_6Cr_8S_8\{(C(S)NEt_2)_2\}]$ and $[Cp_6Cr_8S_8(S_2CNEt_2)_2]$**

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There have been extensive studies on the use of the dithiocarbamate ligand in a variety of bonding modes for stabilizing a wide range of oxidation states in coordination compounds of main-group and transition metals.[1] Although generally unreactive in the majority of its complexes, this ligand can undergo C–S bond cleavage, a phenomenon first observed in a Mo complex in 1972 and becoming increasingly common in the last two decades.[2] In most cases, the cleaved S atom takes on a distinctly different coordination role in the complex, except where it is abstracted by an S acceptor such as PEt_3.[2c] For example, the cleaved S atom can assume a bridging mode (M-S-M),[2a,b,f, 3] form an M=S bond,[2d,g] or interact with a neighboring ligand (e.g., the M≡C bond of a coordinated alkyne).[2e] Cleavage of both C–S bonds of the ligand was reported for reactions with $[Ru_3(CO)_{12}]$[2h] and $[Mo_2(\mu\text{-}O_2CMe)_4]$.[3] Other reactions of the dithiocarbamate ligand include oxidative addition of a C–S bond to alkynes[4] and coupling reactions with coordinated alkyne,[2c, 5] alkylidene,[6] vinylidene/allenylidene,[7] and cyanide[8] ligands. Most of these studies involved Mo and W complexes, except for a few examples containing Cu,[4d] Nb and Ta,[2g] and Ru.[2h, 7] In the course of our investigations on the reactivity of $[\{CpCr(CO)_3\}_2]$ ($Cp = \eta^5\text{-}C_5H_5$) towards the E–E bonds of organic substrates such as diphenyl dichalcogenides Ph_2E_2 (E = S, Se, Te),[9] and bis(diphenylthiophosphinyl)disulfane $[Ph_2P(S)S]_2$,[10] we studied reactions with tetraalkylthiuram disulfides $[R_2NC(S)S]_2$, and here we report the first organochromium complexes containing dithiocarbamate and dithiooxamide ligands.

The instantaneous reaction of $[\{CpCr(CO)_3\}_2]$ with one molar equivalent of tetraethylthiuram disulfide $[Et_2NC(S)S]_2$ in toluene at ambient temperature gave a dark red solution, which upon concentration yielded air-stable deep red crystals of $[CpCr(CO)_2(S_2CNEt_2)]$ (**1**) in 87 % yield. A similar reaction at 90 °C for 2 h gave a dark brown mixture, from which were obtained, in order of elution from a silica gel column, the following compounds: $[\{CpCr(CO)_2\}_2S]$ (**7**) as a dark green solid (ca. 1 % yield), (**1**) (22 % yield), $[CpCr(CO)_2(SCNEt_2)]$ (**2**) as a dark red crystalline solid (11 % yield), $[Cp_4Cr_4S_4]$ (**3**) as a dark solid (22 % yield), $[Cp_6Cr_8S_8\{(C(S)NEt_2)_2\}]$ (**4**) as a brown solid (6.8 % yield),

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$[Cr(S_2CNEt_2)_3]$ (**5**) as a dark blue crystalline solid (19% yield), and $[Cp_6Cr_8S_8(S_2CNEt_2)_2]$ (**6**) as a dark brown solid (11% yield). Heating **1** at 90 °C for 2 h gave **1**–**6** in similar yields (Scheme 1). All compounds were spectroscopically characterized, and satisfactory elemental analyses were obtained for **1, 2**, and **4**–**6**, but only data for **4** and **6** are presented here.[11] Dark brown rhombus-shaped crystals of **4** and **6** were obtained at −29 °C by diffusion of hexane into a toluene solution after 7 d, and by layering a toluene solution with hexane after 5 d, respectively. They were structurally characterized by X-ray diffraction analysis.[12]

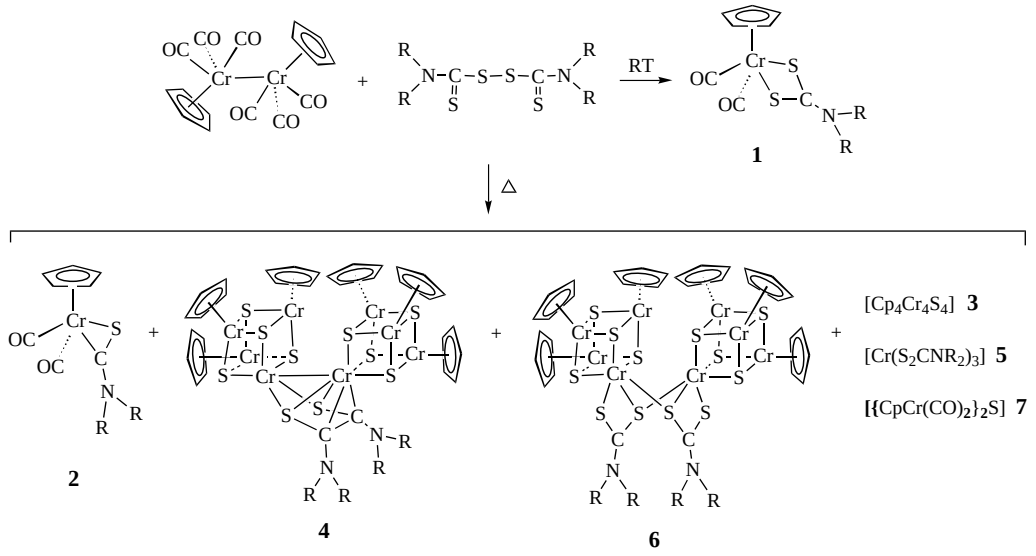
The structures of **4** and **6**, illustrated in Figure 1, consist of two $[(\eta^5\text{-CpCr})_3CrS_4]$ cubes, linked at the Cr atoms Cr(1) and Cr(5), from which the η^5-Cp ligands have been cleaved. In the molecule of **6**, the double cubane is doubly bridged by two dithiocarbamate ligands, each of which is coordinated in a μ-η^1-*S*,η^2-*S*,*S*′ mode. Whilst such a bonding mode has been found in some dinuclear coordination compounds of Mo,[13a] Re,[13b] Fe,[13c] Ru,[13d–f] Rh,[13g] Pt,[13h] and other metals, this is unprecedented for double-cubane structures. However, numerous examples of bridging S ligands are found in the $[Fe_4S_4]$ and FeMoS clusters, studied extensively by Holm et al. and Coucouvanis et al., including sulfide or disulfide,[14a–c] alkyl thiolates,[14d,e] and 1,2-ethane-dithiolates.[14f,g]

If the μ-η^1,η^2-dithiocarbamate ligand is regarded as a five-electron donor, each of the $[Cr_4S_4]$ units in **6** has 60 valence electrons. The average Cr–Cr distances are (2.86 ± 0.07) and (2.87 ± 0.06) Å for the cubes containing Cr(1) and Cr(5), respectively. The $(C_2N)C(S)_2$ units of both bridging dithiocarbamate ligands in **6** have a planar conformation. Planarity at C(1), C(2), N(1), and N(2) indicates sp^2 character of the C and N atoms. This is consistent with a double-bond nature of the C–N bond, which is reflected in the bond lengths of 1.37(3) and 1.40(3) Å for the two dithiocarbamate ligands; as expected, these bonds are shorter than the N–C(alkyl) single bonds in **6** (1.46(4)–1.51(3) Å); the values are within the reported range of 1.288(8)–1.52(9) Å for dithiocarbamate complexes.[13d,g] The C–S distances (1.62(3) and 1.78(3) Å) are also within the reported range (1.700(7)–1.79(2) Å).[13d,g,h]

The unit cell of **4** contains two independent molecules (A and B). Significant features are a dithiooxamide ligand (DTO = $Et_2NC(S)$–$C(S)NEt_2$) that links the two cubes in a μ-η^2,η^4 bonding mode and a weak M–M bond between the two cubes. The Cr(1)–Cr(5) bond lengths of 3.101 and 3.118 Å in molecules A and B, respectively, are within the observed range of 2.676–3.310 Å for Cr–Cr bonds;[9a] the longest bond is the one found in $[\{Cp^*Cr(CO)_3\}_2]$ ($Cp^* = \eta^5\text{-}C_5Me_5$).[15] Interestingly, the η^4-chromadithiacyclopentenyl ring [Cr(1)S(9)C(1)C(2)S(11)] is isoelectronic with the 26-electron $C_5H_5^-$ ligand that it displaced at Cr(5).

The bonding of C(1) and C(2) of the thioamidic ligand to Cr(5), but not to Cr(1), renders Cr(5) and Cr(1) formally eight- and six-coordinate, respectively. This unsymmetrical linking mode of the bridging ligand is reflected in the presence of three Cr–S bridging bonds (2.331(7)–2.364(7) Å) which are much shorter than the Cr(5)–S(9) bond (2.469(7) Å), which lies in the range of the six Cr–S bridging bonds (av (2.50 ± 0.07) Å) in the dithiocarbamate complex **6**. With the thioamidic bridge as an eight-electron donor and the presence of a bridging Cr–Cr bond, each of the cubane skeletons in **4** has 60 valence electrons, consistent with the observation of diamagnetic behavior in the complex. The Cr–Cr distances in the two cubes [av (2.83 ± 0.02) Å in molecule A for the cube containing Cr(1) and (2.82 ± 0.06) Å for the cube containing Cr(5)] are similar to those in **6**. The C(1)–C(2) distances in molecules A and B of **4** are 1.41(3) and 1.35(3) Å, respectively, which are intermediate between those of a C–C single (1.532(2) Å) and C=C double bond (1.335(3) Å) and agree well with those in complexes in which an alkene ligand exhibits the metallacyclopropane mode of coordination, for example, 1.43 Å in $[Pt(C_2H_4)(PPh_3)_2]$,[16a] 1.46(6) Å in $[Fe(C_2H_4)(CO)_4]$,[16b] 1.44 Å in $[Pt(C_2F_4)(C_2H_4)_2]$,[16c] and 1.45 Å in the metallacyclopentene structure of [Cp_2Zr(dimethylbutadiene)].[16d]

The C(1)–C(2) distances are shorter than those in bidentate (η^2-*S*,*S*) DTO ligands, for which C–C bond lengths have been reported in the range 1.496(17)–1.526(13) Å.[17] The C–S distances (1.72(3) and 1.81(2) Å in molecule A) are compa-



Scheme 1. Synthesis of **1**–**6**. R = Et.

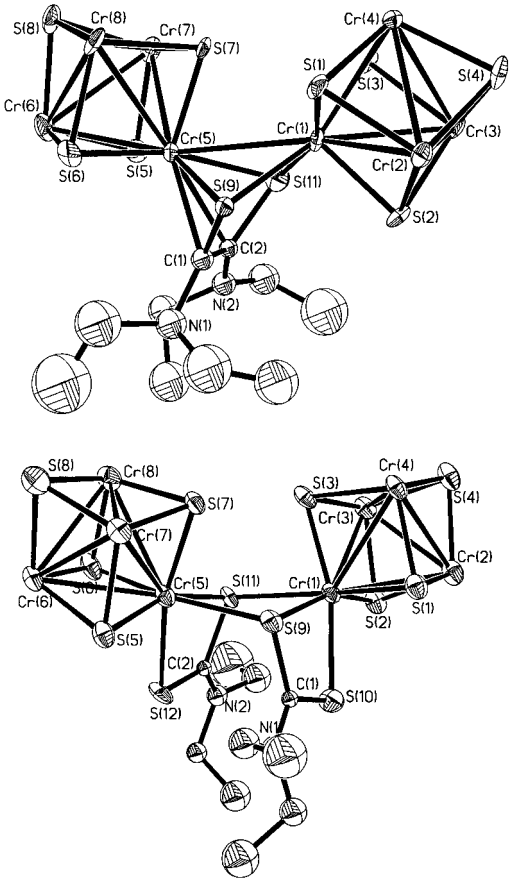
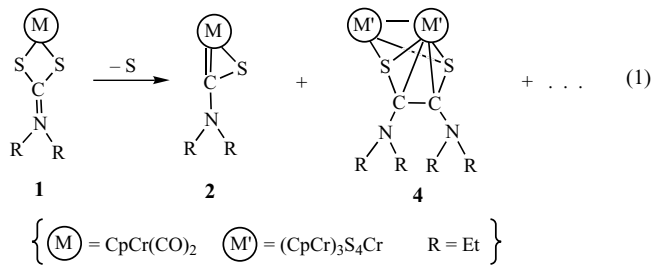


Figure 1. Ortep diagrams of **4** (top) and **6** (bottom). Cp rings on Cr(2)–Cr(4) and Cr(6)–Cr(8) are omitted for clarity. Selected distances [Å] and angles [°] in molecule A of **4** for the bridging dithiooxamide ligand: Cr(1)-Cr(5) 3.101(6), Cr(1)-S(9) 2.331(7), Cr(1)-S(11) 2.340(8), Cr(5)-S(9) 2.364(7), Cr(5)-S(11) 2.469(7), Cr(5)-C(1) 2.32(3), Cr(5)-C(2) 2.45(2), C(1)-S(9) 1.72(3), C(2)-S(11) 1.81(2), C(1)-C(2) 1.41(3), C(1)-N(1) 1.44(3), C(2)-N(2) 1.38(3); S(9)-Cr(1)-S(11) 81.4(3), S(9)-Cr(5)-S(11) 78.1(2), 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), Cr(1)-S(9)-Cr(5) 82.7(2), S(9)-C(1)-Cr(5) 69.8(9), C(1)-S(9)-Cr(5) 67.1(9), C(2)-S(11)-Cr(1) 109.1(8), C(2)-C(1)-Cr(5) 77.8(15), C(1)-C(2)-Cr(5) 67.8(14), C(2)-S(11)-Cr(5) 67.8(8), S(11)-C(2)-Cr(5) 69.0(8), N(1)-C(1)-S(9) 122.8(19), N(2)-C(2)-Cr(5) 135.0(17), C(1)-C(2)-S(11) 114.2(18), 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). For the Cr_4S_4 cubes: Cr-S 2.208(7)–2.264(7), Cr-Cr 2.764(6)–2.887(6); S-Cr-S 98.6(2)–104.1(3), Cr-S-Cr 75.4(2)–79.2(3), Cr-Cr-Cr 57.70(13)–61.95(15). Selected distances [Å] and angles [°] for the bridging dithiooxamide ligand in **6**: Cr(1)···Cr(5) 3.853(7), Cr(1)-S(9) 2.495(9), Cr(1)-S(10) 2.443(10), Cr(1)-S(11) 2.552(10), Cr(5)-S(9) 2.581(10), Cr(5)-S(11) 2.505(9), Cr(5)-S(12) 2.441(9), C(1)-S(9) 1.77(3), C(1)-S(10) 1.71(3), C(2)-S(11) 1.78(3), C(2)-S(12) 1.62(3), C(1)-N(1) 1.37(3), C(2)-N(2) 1.40(3); S(9)-Cr(1)-S(10) 71.5(3), S(11)-Cr(5)-S(12) 71.1(3), Cr(1)-S(9)-Cr(5) 98.7(3), Cr(1)-S(11)-Cr(5) 99.2(3), Cr(1)-S(11)-C(2) 112.0(10), Cr(5)-S(9)-C(1) 109.2(10), C(1)-S(9)-Cr(1) 86.7(9), C(1)-S(10)-Cr(1) 89.8(9), C(2)-S(11)-Cr(5) 83.8(9), C(2)-S(12)-Cr(5) 89.3(10), S(9)-C(1)-S(10) 112.1(15), S(9)-C(1)-N(1) 121(2), S(10)-C(1)-N(1) 127(2), S(11)-C(2)-S(12) 115.7(15), S(11)-C(2)-N(2) 119(2), S(12)-C(2)-N(2) 125(2). For the Cr_4S_4 cubes: Cr-S 2.218(11)–2.290(11), Cr-Cr 2.783(8)–2.926(7); S-Cr-S 97.5(4)–103.2(4), Cr-S-Cr 75.8(3)–80.4(3), Cr-Cr-Cr 57.34(18)–61.88(18).

rable to those previously observed (1.666–1.738 Å), but the C–N distances (1.44(3) and 1.38(3) Å in molecule A) are longer than earlier reported ones (1.279–1.318 Å),[17] and are close to those of the N–C(alkyl) single bonds (1.37(4)–1.49(4) Å in molecule A). The conformation of the [{$(C_2N)C(S)$}$_2$] moiety of the dithiooxamide ligand is almost planar, whereby N(1) and N(2) lie slightly out of the plane defined by the three carbon atoms (0.42 and 0.15 Å in molecule A, and 0.14 and 0.39 Å in molecule B), and only slight torsion is present in the S-C-C-S chain (−4.8 and −8.8° in molecules A and B, respectively). The deviation from planarity is possibly a result of steric interactions between the NEt_2 groups, which are brought close together by the C(1)–C(2) bond. The Cr–C distances (Cr(5)–C(1) 2.32(3) and Cr(5)–C(2) 2.45(2) Å) fall outside the range observed so far (1.93–2.19 Å) for a number of Cr "carbenoid" complexes.[18]

The thermal transformation of **1** into the double cubanes **4** and **6** is unprecedented. Such behavior has not been reported for the Mo[19] or W[20] analogues of **1**, although the W analogues were obtained by UV irradiation and thermolysis of the monodentate complex [$CpW(CO)_3(S_2CNMe_2)$]. The various reactions of related cyclopentadienyl metal complexes such as [$(\eta^5$-$C_5R_5)Fe(CO)_2(\eta^1$-$S_2CNR'_2)$] (R = H, Me; R′ = alkyl), which have been extensively investigated by Astruc et al., involve chelation of the monodentate ligand, initiated chemically, photolytically or by redox processes; ligand exchange; substitution; redox reactions; and electrophilic attack at the uncoordinated S atom of the ligand.[21] In the cyclopentadienylchromium complexes investigated here, the thermolysis of **1** gives rise to complexes containing the intact dithiocarbamate ligand (**5** and **6**), and to complexes in which the ligand has undergone C–S bond cleavage (**2** and **4**). It was experimentally demonstrated that **4** did not derive from the thiocarbenoid complex **2** or the dithiocarbamate-bridged double cubane **6**. It is conceivable that **6** may derive directly from **1** without C–S bond cleavage. Alternatively, the occurrence of a C–S bond cleavage in **1** would lead to **2**, and when accompanied by a concurrent intermolecular C(1)–C(2) coupling across two thiocarboxamido ligands, would produce the bridging unit in the cubane **4** [Eq. (1)]. Such dimerization



(1)

processes have been well-established to be one of the principal reaction pathways of carbenes.[17] A subsequent or concomitant coordination of the ethene ligand so formed to a Cr center, would then produce the metallacyclopropane [Cr(5)C(1)C(2)] moiety in complex **4**.

This first study of the reaction of an organochromium complex with tetraalkylthiuram disulfide showed that the resulting mononuclear dithiocarbamato complex has unusual reactivity, which results in the formation of cubane structures that are doubly bridged by dithiocarbamate or dithiooxamide

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ligands. We are extending our investigations by varying the transition metal complex and the ligand.

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[11] Spectroscopic data for **4**: ^{1}H NMR (300 MHz, C_6D_6, 27 °C): $\delta = 5.17$ ($1\times$ Cp), 5.14 ($2\times$ Cp), 5.08 ($2\times$ Cp), 5.06 ($1\times$ Cp), 3.44 and 3.22 (each dq, $J = 14$, 7 Hz; $2\times CH_2$), 1.21 (t, $J = 6$ Hz; $4\times CH_3$); ^{13}C NMR (75.47 MHz, C_6D_6, 27 °C): $\delta = 92.2$, 91.9, 91.5, 91.4 (Cp), 48.6 (CH_2), 14.0 (CH_3). IR (KBr): $\tilde{\nu} = 1434$ (m, C–N), 1006 (w, NC_2), 802 cm^{-1} (vs, C–S). MS (FAB$^+$): *m*/*z*: 1295 [$Cp_6Cr_8S_8\{(C(S)NEt_2)_2\}$], 1063 [$Cp_6Cr_8S_8$], 531 [$Cp_3Cr_4S_4$], 233 [$Cp_2Cr_2$]. Spectroscopic data for **6**: ^{1}H NMR (300 MHz, $C_6D_5CD_3$, 27 °C): $\delta = 5.09$ ($\nu_{1/2} = 22$ Hz, $3\times$ Cp; at -50 °C: 5.40, 5.28, 5.06 (Cp)), 3.57 (unres. d, $J = 7$ Hz, $2\times CH_2$), 0.99 (t, $J = 7$ Hz, $2\times CH_3$). ^{13}C NMR (75.47 MHz, C_6D_6, 27 °C): $\delta =$ 91.7 (Cp), 45.5 (CH_2), 13.5 (CH_3), 353.8 (S_2CNEt_2). IR (KBr): $\tilde{\nu} = 1495$ (s, C=N), 1145 (m, NC_2), 801 cm^{-1} (s, C–S). MS (FAB$^+$): *m*/*z*: 679 [$Cp_3Cr_4S_4(S_2CN(Et)_2)$], 614 [$Cp_2Cr_4S_4(S_2CN(Et)_2)$], 563 [$Cp_2Cr_3S_4(S_2CN(Et)_2)$], 530 [$Cp_2Cr_3S_3(S_2CN(Et)_2)$], 348 [$Cr(S_2CN(Et)_2)_2$], 200 [$Cr(S_2CN(Et)_2)$], 116 $SCN(Et)_2$.

[12] Crystal data for $2\mathbf{4}\cdot C_4H_4O$: $M_r = 2658.91$, monoclinic, space group $P2_1/n$, $a = 9.7539(3)$, $b = 50.869(2)$, $c = 21.1727(9)$ Å, $\beta = 91.659(2)°$, $V = 10500.9(7)$ Å^3, $Z = 4$, $\rho = 1.682$ Mg m^{-3}, $F(000) = 5392$, $\lambda(Mo_{K\alpha}) =$ 0.71073 Å, $\mu = 2.021$ mm^{-1}, $T = -50$ °C, crystal dimensions $0.32\times 0.14\times 0.04$ mm. Siemens SMART diffractometer, equipped with a CCD detector. Of 69642 reflections measured, 15082 unique reflections were used in refinement. Final $R = 0.1678$, ($R_w = 0.3400$). Crystal data for $\mathbf{6}\cdot C_6H_{14}$: $M_r = 1445.71$, monoclinic, space group $P2_1/c$, $a =$ 9.6283(9), $b = 26.798(2)$, $c = 21.0638(19)$ Å, $\beta = 99.133(4)°$, $V =$ 5365.9(8) Å^3, $Z = 4$, $\rho = 1.790$ Mg m^{-3}, $F(000) = 2952$, $\lambda(Mo_{K\alpha}) =$ 0.71073 Å, $\mu = 2.060$ mm^{-1}, $T = -50$ °C, crystal dimensions $0.03\times 0.08\times 0.30$ mm. Siemens SMART diffractometer, equipped with a CCD detector. Of 13987 reflections measured, 5828 unique reflections were used in refinement. Final $R = 0.1319$, ($R_w = 0.3047$). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-159452 (**4**) and CCDC-159453 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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