

Reactivity of $[\text{CpCr}(\text{CO})_3]_2$ towards thione ($\text{C}=\text{S}$) moieties in some sulfur-containing substrates

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Abstract

The reaction of $[\text{CpCr}(\text{CO})_3]_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) (**1**) with 1 mol equivalent of 2,5-dimercapto-1,3,4-thiadiazole ($\equiv\text{DMcTH}_2$) at ambient temperature led to the isolation of a reddish-brown crystalline solid of $\text{CpCr}(\text{CO})_3(\eta^1\text{-DMcTH})$ (**5**) and a green solid of $\text{CpCr}(\text{CO})_3\text{H}$ (**2**) in yields of ca. 28% and 30%, respectively, along with some $[\text{CpCr}(\text{CO})_2]_2$ (**3**) and $[\text{CpCr}(\text{CO})_2]_2\text{S}$ (**4**). The reaction of **1** with 1 mol equivalent of vinylene trithiocarbonate ($\text{SCS}(\text{CH}_2)_2\text{S}$) ($\equiv\text{VTTC}$) at 90 °C led to the isolation of a red crystalline solid of $\text{CpCr}(\text{CO})_2(\eta^2\text{-SCHSC}_2\text{H}_2)$ (**6**) in ca. 15% yield while the reaction of **1** with isopropylxanthic disulfide ($(\text{CH}_3)_2\text{CHOCS}_2$) resulted in the formation of $\text{CpCr}(\text{CO})_2(\eta^2\text{-S}_2\text{COCH}(\text{CH}_3)_2)$ (**8**) in ca. 80% yield. The complexes **5**, **6** and **8** have been determined by single crystal X-ray diffraction analysis.

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Keywords: Cyclopentadienylchromium; 2,5-Dimercapto-1,3,4-thiadiazole; Vinylene trithiocarbonate; Isopropylxanthic disulfide; X-ray crystal structures

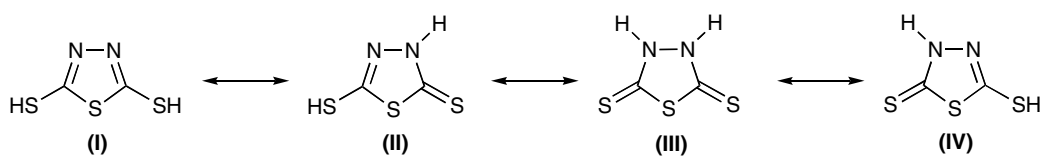
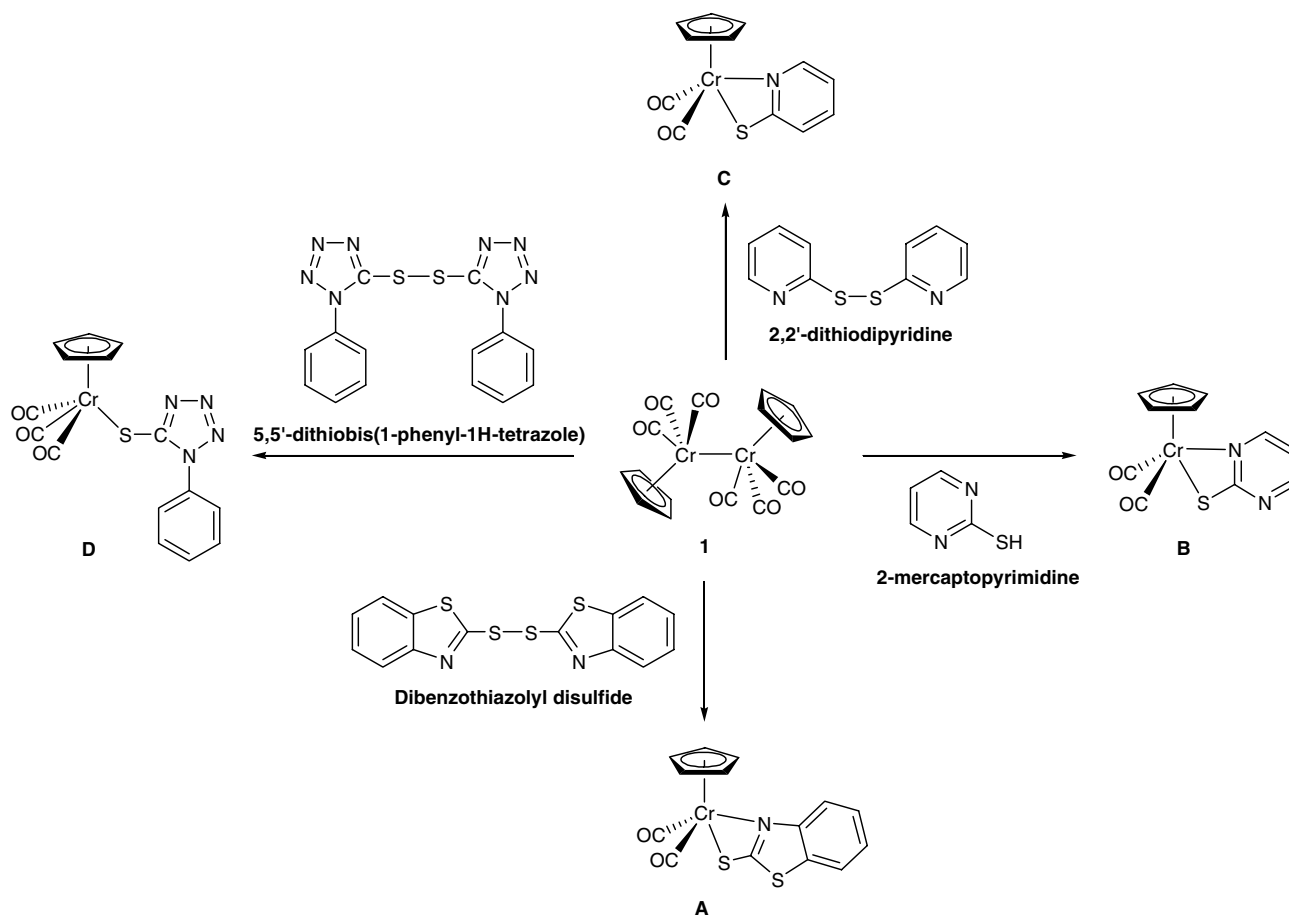
1. Introduction

In continuing investigations on the reactivity of $[\text{CpCr}(\text{CO})_3]_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) (**1**) with organic chalcogenides [1], we have recently studied its reactions with N- and S-containing heterocyclic disulfides or mercaptans, e.g., dibenzothiazolyl disulfide $[(\text{C}_6\text{H}_4)\text{NSCS}]_2$ [2], 2,2'-dithiopyridine (SPy)₂ and 2-mercaptopyrimidine (HSPy) [3], and 5,5'-dithiobis(1-phenyl-1*H*-tetrazole) (STz)₂ (Chart 1) [4]. The presence of these heterocycles in many bioactive molecules [5], renders them biologically relevant. Containing both an endocyclic hard donor N atom and an exocyclic soft donor S atom, these ligands form metal complexes, which belong to a class of heterocyclic thionates which have attracted much interest in biomedical and numerous other applications [6].

In further extension of this investigation to heterocyclic ring systems with multiple donor sites, we have selected some thione-containing ring compounds for study, viz. 2,5-dimercapto-1,3,4-thiadiazole (DMcTH_2) and vinylene trithiocarbonate (VTTC).

DMcTH_2 , commonly known as “Bismuthiol I”, exists in a solvent-dependent mixture [7] of tautomers, viz. 2,5-dimercapto-1,3,4-thiadiazole (DMcTH_2) (I), 1,3,4-thiadiazole-2-thiol-5-thione (II)/(IV) and 1,3,4-thiadiazoline-2,5-dithione (TDzTH_2) (III) (Scheme 1). The combination of hard and soft donor sites in DMcTH_2 has given rise to a rich coordination chemistry of both the main-group and transition metals, leading to the development of wide ranging applications in analytical chemistry, medical-biological systems and metal treatment, and as polyolefin stabilisers in polymers and plastics [6a]. Herein lies the major stimulus for research in the complexation chemistry of thiones. However, many of the metal complexes reported were insoluble powders, rendering

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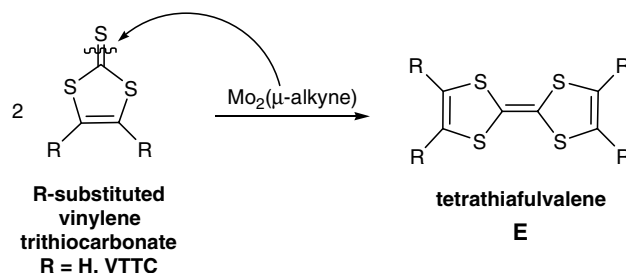
impossible any solid state structural elucidation. Such structural studies to date are confined to a few of the late transition metals, e.g., Ru, Pt, Au and Hg [8], and to the main-group metals Tl and Sn [9].

Vinylene trithiocarbonate, VTTC, belongs to the family of 1,3-dithiole-2-thiones. These classes of compounds are used often as therapeutic agents for hepatic diseases, e.g., cirrhosis or virus-derived hepatitis. VTTC is known to undergo reductive coupling by cleavage of the C=S bond to form tetrathiafulvalenes (E), (Scheme 2) which are used in a wide variety of applications such as cation sensors, liquid crystals and supramolecular switches [10].

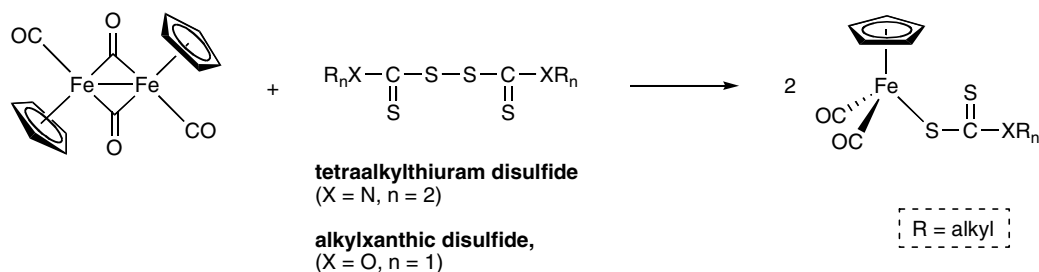
However, reactions of 1,3-dithiole-2-thione with organometallic complexes are rare and the focus of studies on VTTC is mainly centered on organic syntheses. It is also of interest to us to explore the reactivity of **1** towards the exocyclic C=S moiety in DMcTH₂ and VTTC

since the reactivity of these C—S and C=S bonds bears relevance to many significant biological and industrial processes [11].

Included in this study is the reactivity of **1** towards isopropylxanthic disulfide, since it contains a C=S bond in



Scheme 2.



Scheme 3.

addition to a S—S bond. While considerable interest surrounds the chemistry of transition metal dithiocarbamate complexes, much less is focused on xanthate complexes. Transition metal complexes of dithiocarbamate and xanthate ligands show, in general, many similarities in their synthesis as well as their structural, electronic and chemical features, as illustrated for instance, between the complexes $\text{CpFe}(\text{CO})_2(\eta^1\text{-S}_2\text{CNR}_2)$ and $\text{CpFe}(\text{CO})_2(\eta^1\text{-S}_2\text{COR})$ (Scheme 3) [12]. Furthermore, we have previously obtained the $\text{CpCr}(\text{CO})_2(\eta^2\text{-S}_2\text{CNR}_2)$ complex [13] and would like to extend a study into its xanthate counterpart.

The results presented in this paper will illustrate the multi-faceted reactivity of $[\text{CpCr}(\text{CO})_3]_2$ (**1**) towards these sulfur-containing substrates.

2. Results and discussion

2.1. Reaction of $[\text{CpCr}(\text{CO})_3]_2$ (**1**) with DMcTH_2 at ambient temperature

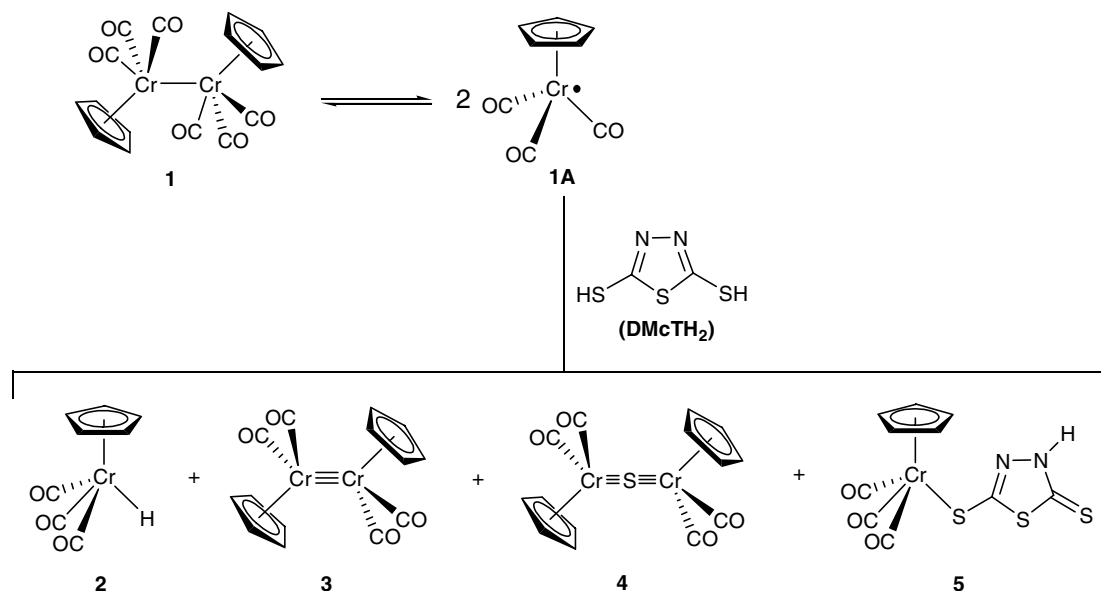
Since the 17-electron organometallic fragment, $\text{CpCr}(\text{CO})_3$ (**1A**), the incumbent monomer of **1**, is a very

efficient hydride abstractor [1,3], it is anticipated that 1 mol equivalent of **1** could react with 1 mol equivalent of DMcTH_2 to yield a mononuclear Cr–DMcTH complex with the concurrent formation of $\text{CpCr}(\text{CO})_3\text{H}$ (**2**). Indeed, the facile reaction between **1** and 1 mol equivalent of DMcTH_2 in toluene at ambient temperature produced a deep red solution, which gave a moderate yield of $\text{CpCr}(\text{CO})_3(\eta^1\text{-DMcTH})$ (**5**) as red crystals (28%), together with the known complexes, $\text{CpCr}(\text{CO})_3\text{H}$ (**2**), $[\text{CpCr}(\text{CO})_2]_2$ (**3**) and $[\text{CpCr}(\text{CO})_2]_2\text{S}$ (**4**) (Scheme 4), and an uncharacterisable green oil.

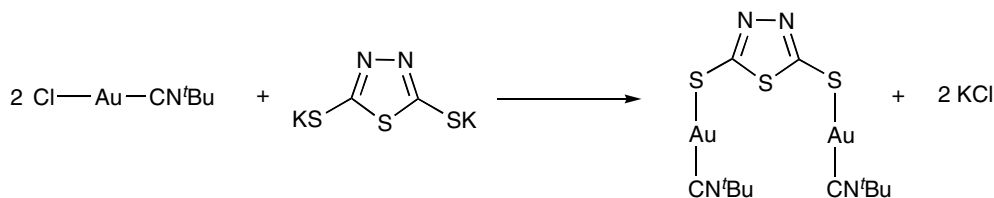
Since binuclear gold complexes have been synthesised using the potassium salt of DMcTH_2 with 2 mol equivalents of chloro-gold complexes (Scheme 5) [8c,8d], we probed the possibility of obtaining a dichromium analogue via the reaction of 2 mol equivalents of **1** with DMcTH_2 (Scheme 6). However, such a reaction did not occur; instead decomposition of the excess **1** added was observed.

2.2. Reaction of $[\text{CpCr}(\text{CO})_3]_2$ (**1**) with $\text{SCS}(\text{CH})_2\text{S}$ (VTTC) at 90 °C

A reaction between **1** and one mol equivalent of $\text{SCS}(\text{CH})_2\text{S}$ in toluene at 90 °C produced a reddish



Scheme 4.



Scheme 5.

brown solution. From this solution, a moderate yield of $\text{CpCr}(\text{CO})_2(\eta^2\text{-SCHSC}_2\text{H}_2)$ (**6**) was obtained as orange-red crystals (15%) (Scheme 7). It is noteworthy that **1** has abstracted a thione-sulfur atom from the organic ligand effectively generating complex **4** and **6**. Such a reaction holds implications for desulfurisation processes.

The thioether nature of coordinated sulfur in the VTTC fragment renders it a 2e donor, thus enabling a stable 18-electron configuration at Cr. Such a synthesis suggests the possibility of a new route to achieve coordination of a S-heterocyclic alkyl group to Cp-metal. In fact, to the best of our knowledge, there is only one other example of such a synthesis [14] in which Dixneuf and co-workers protonated a Fischer-type carbene of Fe to give a cationic complex in which Fe is bonded to a heterocyclic alkyl group (Scheme 8). The origin of the hydrogen atom attached on the heterocyclic alkyl carbon in **6** is unknown; it could originate from residual water present in the solvents used, or the Cp ligand on the chromium complex, as postulated in a previous report of ours [15].

In the absence of a sulfur-abstractor, we have previously obtained a VTTC-coordinated ruthenium complex (Scheme 9) [16], which involves chloride substitution in $[\text{CpRu}(\text{dppf})\text{Cl}]$ by VTTC.

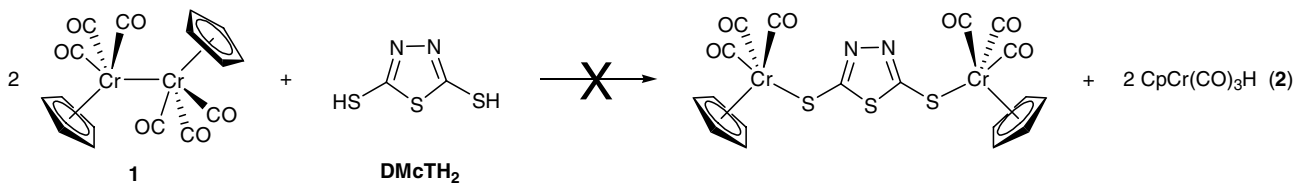
In other reported cases, the reaction of the VTTC ligand with metal fragments resulted in extensive ring opening and rearrangements as demonstrated by Morris

and co-workers [17] in reactions of CpMo complexes (Scheme 10).

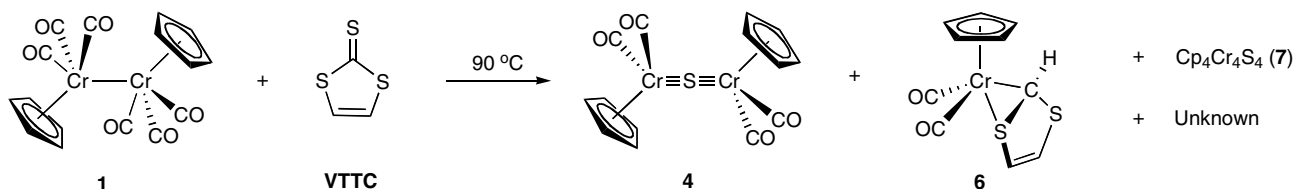
2.3. Reaction of $[\text{CpCr}(\text{CO})_3]_2$ (**1**) with $((\text{CH}_3)_2\text{CHOCS}_2)_2$ isopropylxanthic disulfide at ambient temperature

A facile reaction between **1** and one mol equivalent of $((\text{CH}_3)_2\text{CHOCS}_2)_2$ in toluene at ambient temperature produced a dark brown solution, from which $\text{CpCr}(\text{CO})_2(\eta^2\text{-S}_2\text{COCH}(\text{CH}_3)_2)$ (**8**) was obtained as reddish-brown crystals in 80% yield. The progress of the reaction was monitored via ^1H NMR spectral scans at intervals. These scans showed an initial formation of a Cp peak at δ 4.37, possibly belonging to the monodentate intermediate species, $\text{CpCr}(\text{CO})_3(\eta^1\text{-S}_2\text{COCH}(\text{CH}_3)_2)$ (**8***). Concurrent with the collapse of this signal was the growth of the Cp peak of **8** at δ 4.40 (Scheme 11).

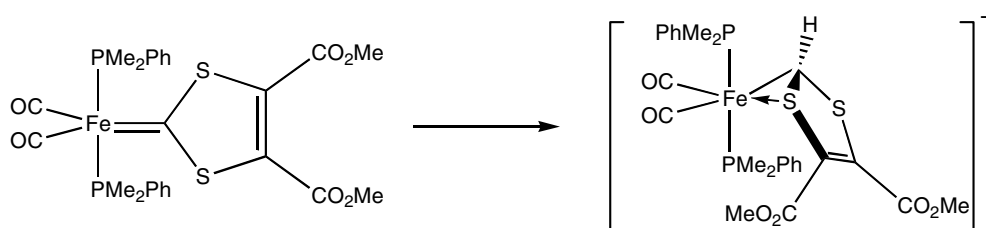
This observation is analogous to that found in the reaction of **1** with tetraalkylthiuram disulfide $((\text{R}_2\text{NCS}_2)_2; \text{R} = \text{Me}, \text{Et})$, which we have previously reported [13]; in that instance, the monodentate complex was isolated and structurally characterised. Bidentate complex **8** and its “ R_2NCS_2 ” analogue are both substantially thermodynamically more stable than their monodentate analogues. This contrasts with observations on the Cp/Cp*Fe system. Thus, Morán and co-workers found that monodentate complexes,



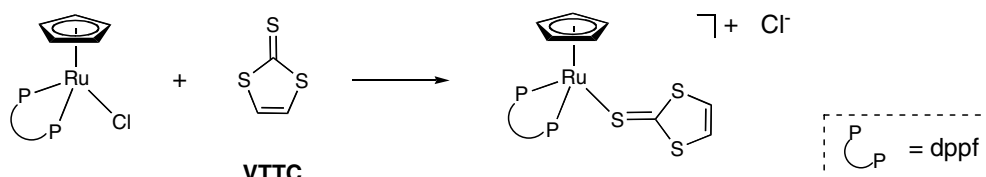
Scheme 6.



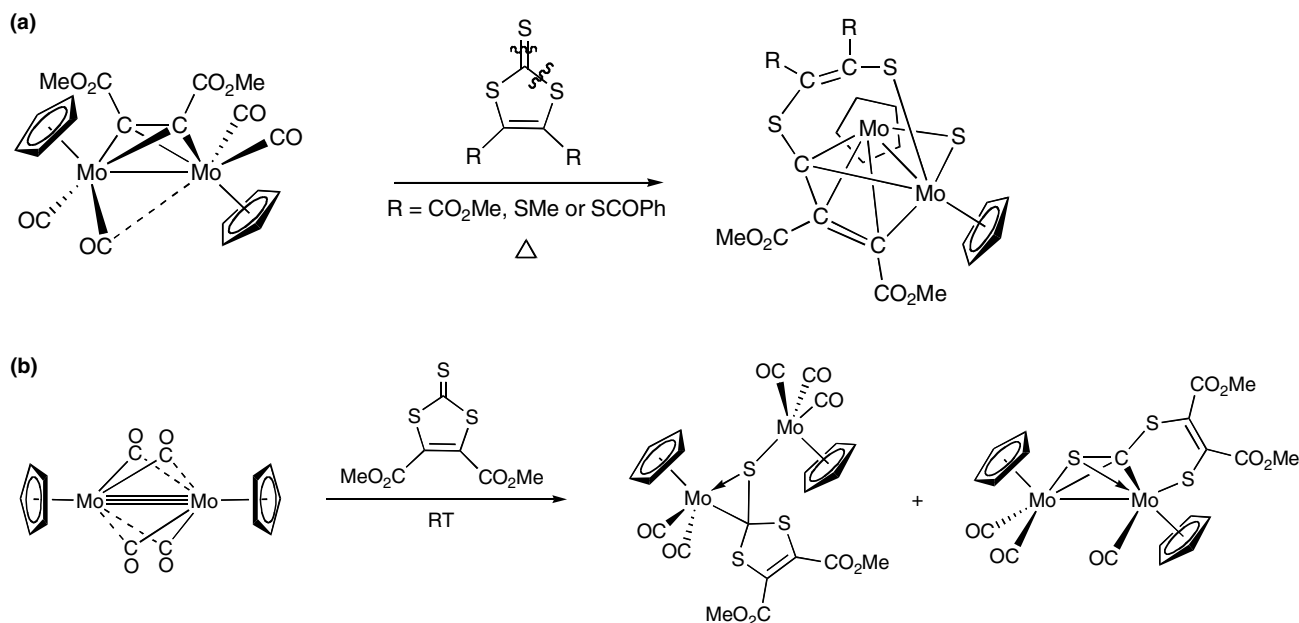
Scheme 7.



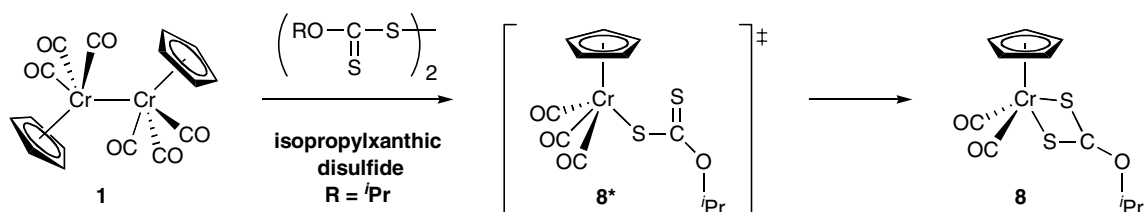
Scheme 8.



Scheme 9.



Scheme 10.



Scheme 11.

$(C_5R_5)Fe(CO)_2(\eta^1-S_2COEt)$ ($R = H, Me$), the primary product of the reaction of dicarbonylcyclopentadienyl-iron dimer, $[(C_5R_5)Fe(CO)_2]_2$ ($R = H, Me$) with ethylxanthic disulfide $(EtOCS_2)_2$ [12a,12b,12c] required photolytic activation to effect chelation [12a].

3. Crystallographic studies

The molecular structure of **5** is depicted in Fig. 1. The unit cell contains two independent molecules possessing different orientation of the heterocyclic rings. Selected

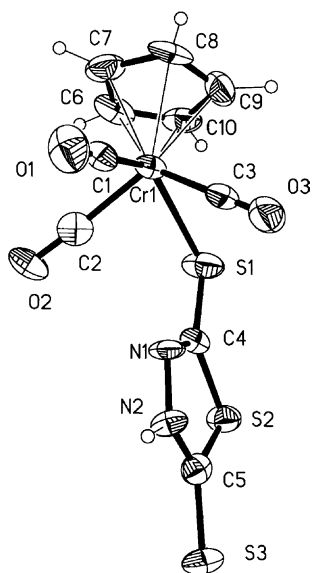


Fig. 1. Ortep plot of **5**. Thermal ellipsoids are drawn at the 50% probability level.

Table 1
Selected bond lengths (Å) and angles (°) for **5**

	Molecule 1 ^a	Molecule 2 ^a
<i>Bond distances (Å)</i>		
Cr(1)–S(1)	2.460(2)	2.484(2)
S(1)–C(4)	1.719(7)	1.739(6)
S(2)–C(4)	1.764(7)	1.744(6)
S(2)–C(5)	1.733(7)	1.718(7)
S(3)–C(5)	1.683(7)	1.658(7)
N(1)–N(2)	1.372(7)	1.365(7)
N(1)–C(4)	1.289(8)	1.269(7)
N(2)–C(5)	1.321(8)	1.346(8)
<i>Bond angles (°)</i>		
Cr(1)–S(1)–C(4)	108.0(3)	109.4(2)
S(2)–C(5)–S(3)	124.6(4)	127.4(4)
N(2)–C(5)–S(3)	127.5(5)	127.2(5)
N(2)–C(5)–S(2)	107.8(5)	105.4(5)

^a Two independent molecules in the unit cell.

bond lengths and angles are listed in Table 1. The molecule possesses a four-legged piano-stool configuration at Cr, which is coordinated to a monodentate 2,5-dimercapto-1,3,4-thiadiazolate and three CO ligands. The lengths of the exocyclic S(3)–C(5) bond (1.683(7) and 1.658(7) Å) are within the range of a C=S double bond [18a], and are shorter than the C–S bonds (1.718(7)–1.764(7) Å) in the heterocycle. These distances are comparable to those in the DMcTH complexes [Pt(trpy)₂(η¹-DMcTH)](PF₆) (1.64(1) and 1.75(1) Å) [16] and [Ru(CO)(PPh₃)₂(η¹-DMcTH)(η²-DMcTH)] (1.67(2) and 1.71(2) Å) [19]. The N(1)–C(4) distances (1.289(8) and 1.269(7) Å) are shorter than that of N(2)–C(5) (1.321(8) and 1.346(8) Å), indicative of more C=N double bond character [pure C–N single bond 1.432 Å; C–N 1.32 Å in the resonance structures

(C–N ↔ C=N) of amide groups]. [18b] The N(1)–N(2) distances (1.372(7) and 1.365(7) Å) are very close to that of a single bond (1.40 Å) [18c]. The Cr(1)–S(1)–C(4) angles are 108.0(3) and 109.4(2)°, indicative of a bent geometry. In addition, the bond angles of S(2)–C(5)–S(3) (124.6(4) and 127.4(4)°), N(2)–C(5)–S(3) (127.5(5) and 127.2(5)°) and N(2)–C(5)–S(2) (107.8(5) and 105.4(5)°), indicate a distorted trigonal geometry at C(5).

The molecular structure of **6** is depicted in Fig. 2. Selected bond lengths and angles are listed in Table 2. The molecule possesses a four-legged piano-stool configuration at Cr, which is coordinated to a chelating desulfurised-vinylene trithiocarbonate ligand and two CO ligands. The desulfurised-vinylene trithiocarbonate bonds to the CpCr fragment in a side-on manner through the C and S atom of the organic fragment, forming a three-membered chelate ring. The bite angle (46.26(9)°) for this three-membered chelate ring is comparable to that of 3-membered chelate rings in various metal carbenoid complexes [13]. The Cr(1)–C(2) bond length (2.145(3) Å) is much longer than that which we have reported for the Cr carbenoid, CpCrSCN(Me)₂ (1.953(2) Å) [13] indicating metal-alkyl characteristics.

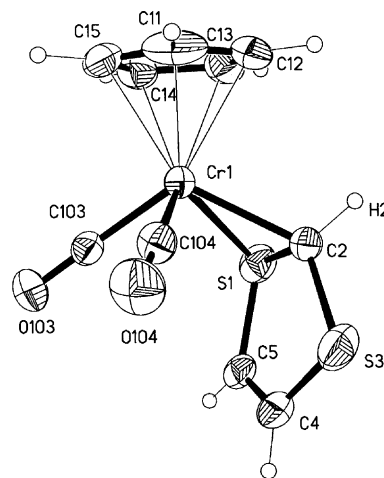


Fig. 2. Ortep plot of **6**. Thermal ellipsoids are drawn at the 50% probability level.

Table 2
Selected bond lengths (Å) and angles (°) for **6**

<i>Bond distances (Å)</i>			
Cr(1)–C(2)	2.145(3)	C(2)–S(3)	2.066(3)
Cr(1)–S(1)	2.3451(11)	C(4)–C(5)	1.338(5)
S(1)–C(5)	1.765(4)	Cr(1)–C(104)	1.821(4)
S(1)–C(2)	1.773(4)	Cr(1)–C(105)	1.838(4)
S(3)–C(4)	1.776(3)		
<i>Bond angles (°)</i>			
C(2)–Cr(1)–S(1)	46.26(9)	C(4)–S(3)–C(2)	95.57(18)
C(5)–S(1)–C(2)	96.90(17)	S(1)–C(2)–S(3)	110.97(19)

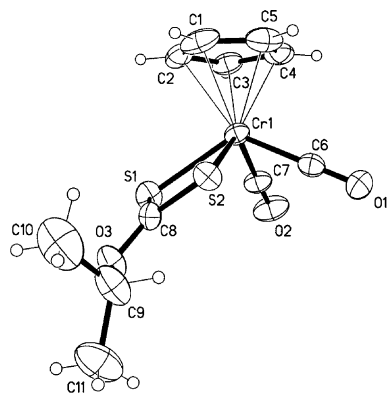


Fig. 3. Ortep plot of **8**. Thermal ellipsoids are drawn at the 50% probability level.

Table 3
Selected bond lengths (Å) and angles (°) for **8**

	Molecule 1 ^a	Molecule 2 ^a
<i>Bond distances (Å)</i>		
Cr(1)–S(1)	2.4217(9)	2.4024(8)
Cr(1)–S(2)	2.4157(8)	2.4232(9)
C(8)–S(1)	1.686(3)	1.678(3)
C(8)–S(2)	1.680(3)	1.684(3)
C(8)–O(3)	1.319(3)	1.324(4)
C(9)–O(3)	1.465(4)	1.468(3)
<i>Bond angles (°)</i>		
S(1)–Cr(1)–S(2)	70.80(3)	70.77(3)
S(1)–C(8)–S(2)	112.72(17)	112.46(18)
S(1)–C(8)–O(3)	119.4(2)	119.91(19)
S(2)–C(8)–O(3)	127.7(2)	127.5(2)
C(8)–O(3)–C(9)	118.8(2)	119.6(2)

^a Two independent molecules, which are related by (almost) a center of inversion.

Hence, we deduce that the Cr–C bond in **3** has a bond order of one, supporting the presence of a hydrogen atom at C(2), which is indeed confirmed by ¹H NMR spectroscopy. The C(2)–S(1) bond of 1.773 (4) Å is comparable to that of the non-coordinated C(2)–S(3) (1.776(3)) Å.

The molecular structure of **8** is depicted in Fig. 3. Selected bond lengths and angles of the two independent molecules in the unit cell are listed in Table 3. The molecule possesses a four-legged piano-stool configuration at Cr, which is coordinated to a chelating η²-xanthate and two terminal CO ligands, isoelectronic with CpCr(CO)₂(η²-S₂CNR₂) (R = Me, Et, ^tPr) [13]. The C–S distances (1.678(3)–1.686(3) Å) are between the C–S (1.718(6)–1.725(12) Å) and C=S distances (1.642(5)–1.650(12) Å) in (C₅R₅)Fe(CO)₂(η¹-S₂COEt) (R = H, Me) [12a,12b,12c], indicative of a partial double-bond character, and are comparable to previous reported values (1.702(2)–1.7201 Å) for the CpCr-dithiocarbamate analogues, CpCr(CO)₂(η²-S₂CNR₂) (R = Me, Et, ^tPr) [13]. The pairs of C–OR distances of 1.319(3)–1.324(4) Å and 1.465(4)–1.468(3) Å are also comparable

to the pairs in the (C₅R₅)Fe(CO)₂(η¹-S₂COEt) (R = H, Me) (1.331(14)–1.335(7) Å and 1.441(17) and 1.457(8) Å) [12a,12b,12c].

4. Conclusion

The reaction of [CpCr(CO)₃]₂ (**1**) with 2,5-dimercapto-1,3,4-thiadiazole (DMcTH₂), demonstrates facile S–H homolytic bond cleavage by the 17-electron organometallic species **1A**, providing an efficient route to 2,5-dimercapto-1,3,4-thiadiazolate (DMcTH) cyclopentadienyl chromium complexes. CpCr(CO)₃(η¹-DMcTH) (**5**) is the first example of a Cp-containing 2,5-dimercapto-1,3,4-thiadiazolate complex. The reaction of [CpCr(CO)₃]₂ with vinylene trithiocarbonate at elevated temperature causes a C=S cleavage of the sulfur-containing organic ligand giving a metal-alkyl complex **6**, CpCr(CO)₂(η²-SCHSC₂H₂). In reacting with **1**, isopropylxanthic disulfide, ((CH₃)₂CHOCS₂)₂ only undergoes S–S bond cleavage, followed/accompanied by metal chelation with assistance from the C=S moiety, thus forming the complex CpCr(CO)₂(η²-S₂COCH(CH₃)₂) (**8**) which was obtained in relatively high yields.

5. Experimental

5.1. 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 Bruker 300 MHz FT NMR spectrometer; ¹H and ¹³C chemical shifts were referenced to residual C₆H₆ in C₆D₆. IR spectra in KBr discs were measured in the range of 4000–600 cm⁻¹ by means of a BioRad FTS-165 FTIR instrument. Mass spectra were run on a Finnigan Mat 95XL-T spectrometer. Elemental analyses were carried out by the microanalytical laboratory in-house. [CpCr(CO)₃]₂ (Cp = η⁵-C₅H₅) (**1**) was synthesised as described by Manning et al. [20] from chromium hexacarbonyl (98% purity from Fluka). The ligands vinylene trithiocarbonate, 2,5-dimercapto(1,3,4-thiadiazole) and isopropylxanthic disulfide were obtained from Sigma–Aldrich and used as supplied. All solvents were dried over sodium-benzophenone and distilled before use. Celite (Fluka AG) and silica gel (Merck Kieselgel 60, 230–400 mesh) were dried at 140 °C overnight before chromatographic use.

5.2. Reaction of [CpCr(CO)₃]₂ (**1**) with DMcTH₂ at ambient temperature

A deep red mixture was obtained instantaneously when green solid [CpCr(CO)₃]₂ (**1**) (80 mg, 0.20 mmol)

and yellow solid 2,5-dimercapto-1,3,4-thiadiazole (DMcTH₂) (30.0 mg, 0.20 mmol) were dissolved in toluene (7 mL) with stirring. After 30 min at ambient temperature, the resultant deep red homogeneous product solution was concentrated to ca. 2 mL and loaded on to a silica gel column (2 × 10 cm) prepared in *n*-hexane. Elution gave 4 fractions: (i) a yellowish-green eluate in *n*-hexane (10 mL), which yielded green crystals of CpCr(CO)₃H (**2**) (ca. 22 mg, 0.06 mmol, 30% yield), identified by its colour characteristics and ¹H NMR spectrum in benzene-*d*₆ (δ(H): -5.61 and δ(Cp): 4.06) and its FAB⁺-MS molecular ion peak at *m/z* 202 [15]; (ii) a deep green eluate in toluene (7 mL), which on concentration gave deep green crystals (ca. 18 mg), the proton NMR spectrum of which showed a 2:1 molar mixture of [CpCr(CO)₂]₂ (**3**) (ca. 6 mg, 0.02 mmol, 4% yield) and [CpCr(CO)₂]₂S (**4**) (ca. 12 mg, 0.03 mmol, 8% yield) at δ(Cp) 4.24 and 4.36, respectively [21]; (iii) a reddish-brown eluate in ether (10 mL), which yielded red crystals of CpCr(CO)₃(η¹-DMcTH) (**5**) (ca. 40 mg, 0.11 mmol, 28% yield); (iv) a deep green eluate in acetonitrile (5 mL) which yielded a deep green oil of an uncharacterisable compound (ca. 20 mg). An immovable dirty green band (ca. 1 mm thick) was left on the column.

5.3. Data for 5

IR (KBr, cm⁻¹): ν(N–H stretch) 3099s; ν(sp²-C–H stretch) 3097w and 3088w; ν(C≡O stretch) 2034s, 1954s and 1890s; ν(other bands) 1626m, 1469m, 1428m, 1384m, 1343m, 1268m, 1094s, 1048s, 1017s, 820vs, 769w, 707m, 666w, 606m, 579m and 517m. ¹H NMR (C₆D₆): δ 4.00 (s, 5H, C₅H₅); δ 8.93 (s, 1H, NH). A ¹³C NMR spectrum is not available owing to instability in solution. In addition, the elemental analysis of the complex also showed disappointing results due to its instability. ESI⁺-MS: *m/z* 350 [M⁺, C₁₀H₆CrN₂O₃S₃]; FAB⁺-MS: *m/z* 351 [M + H, C₁₀H₇CrN₂O₃S₃]⁺, 266 [M – 3CO]⁺, 182 [C₁₀H₁₀Cr]. High resolution FAB⁺-MS: *m/z* 350.9016 ([M + H]⁺, calcd *m/z* 350.9024). Compound **5** is highly unstable and readily converts to a dirty green insoluble solid (**R**) even under inert atmosphere at ambient temperature. Its elemental analytical data gave an empirical formula C_{8.34}H_{8.45}N_{1.55}S_{2.36}Cr, i.e., in the proximity of [C₅H₅CrS₃C₂N₂H]_{*n*}, indicative of a polymeric form of **5** with loss of CO.

5.4. Reaction of 2 mol equivalents of [CpCr(CO)₃]₂ (**1**) with DMcTH₂ at ambient temperature

The reaction resulted in similar product composition as that when 1 mol equivalent of **1** was reacted with DMcTH₂. They included CpCr(CO)₃H (**2**), [CpCr(CO)₂]₂ (**3**), [CpCr(CO)₂]₂S (**4**), CpCr(CO)₃(η¹-

DMcTH) (**5**) and a deep green uncharacterisable oil, together with unreacted **1**. A prolonged reaction led to the decomposition of **1** to **3**, as well as the decomposition of **5** to the insoluble green solid **R**, described above.

5.5. Reaction of [CpCr(CO)₃]₂ (**1**) with SCS(CH)₂S at 90 °C

A dark green mixture of [CpCr(CO)₃]₂ (**1**) (105 mg, 0.26 mmol) and vinylene trithiocarbonate (VTTC) (34 mg, 0.25 mmol) in toluene (10 mL) was stirred at 90 °C for 4 h. The resultant reddish brown reaction mixture was concentrated to ca. 3 mL and loaded onto a silica gel column (2.5 × 15 cm) prepared in *n*-hexane. Elution gave four fractions: (i) a brownish green eluate in *n*-hexane/toluene (3:1, 20 mL), which yielded green crystals of [CpCr(CO)₂]₂S (**4**) (ca. 39 mg, 0.13 mmol, 41% yield), identified by its colour characteristics and Cp resonance (¹H) in benzene-*d*₆ at δ 4.36 [21b,21c]; (ii) an orange-red eluate in a mixture of *n*-hexane/toluene (2:1, 20 mL), which yielded orangish-red crystals of CpCr(CO)₂(η²-SCHSC₂H₂) (**6**) (ca. 21 mg, 0.08 mmol, 15% yield); (iv) a dark brown eluant in toluene (30 mL), which yielded dark green solids of Cp₄Cr₄S₄ (**7**) (ca. 15 mg, 0.03 mmol, 20% yield), characterised by its colour and Cp (¹H) resonance in benzene-*d*₆ at δ 4.91 [22]; (iv) an uncharacterisable brown eluate in THF (15 mL, ca. 3 mg), the ¹H NMR spectrum of which shows a triplet at δ 4.31. A 3-mm thick green band was left unmoved on top of the column.

5.6. Data for 6

Anal. Found: C, 43.5; H, 3.2; S, 23.6%. Calc. for C₁₀H₈CrO₂S₂: C, 43.5; H, 2.9; S, 23.2%. IR (KBr, cm⁻¹): ν (CO) 1911s, 1829s ν (others) 1513w, 1427w, 1255w, 1157w, 1118w, 1088w, 1059w, 1010w, 915w, 872w, 821m, 782w, 724w, 682m, 676m, 665msh, 659m, 637msh, 607m, 592m, 559m, 543m, 505w, 499w. FAB⁺-MS: *m/z* 276 [M⁺; CpCr(CO)₂(SCHS(CH)₂)₂]; 219[M⁺ – 2CO; CpCr(SCHS(CH)₂)₂], 103 [(SCHS(CH)₂)₂]. ¹H NMR (C₆D₆): δ (CrCHS) 5.77 (1H, d, ²*J* = ca. 1 Hz), δ (SCH) 5.76 (1H, d, ²*J* = ca. 1 Hz), δ 5.22 (0.5H, br s), δ (CH) 5.04 (1H, s), δ (C₅H₅) 4.09 (5H, s). The ¹³C NMR spectrum was also not available owing to the instability of the complex in solution.

5.7. Reaction of [CpCr(CO)₃]₂ (**1**) with ((CH₃)₂CHOCS₂)₂ isopropylxanthic disulfide at ambient temperature

A deep green mixture of **1** (40 mg, 0.10 mmol) and isopropylxanthic disulfide (27 mg, 0.10 mmol) in toluene (5 mL) was stirred at ambient temperature for 2 h. A deep red homogeneous solution was obtained. Concentration of the filtrate to ca. 1 mL, and addition

Table 4
Data collection and processing parameters

Complexes	5	6	8
Formula	C ₁₀ H ₆ CrN ₂ O ₃ S ₃	C ₁₀ H ₈ CrO ₂ S ₂	C ₁₁ H ₁₂ CrO ₃ S ₂
<i>M_r</i>	350.35	276.28	308.33
Temperature (K)	223(2)	223(2)	223(2)
Crystal colour and habit	Bright red, plate	Orange-red, rhombus	Red, rhombus
Crystal size (mm)	0.20 × 0.12 × 0.08	0.19 × 0.22 × 0.26	0.40 × 0.38 × 0.28
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>Pca</i> 2(1)
<i>a</i> (Å)	10.131(3)	12.1704(6)	12.4696(5)
<i>b</i> (Å)	11.514(3)	15.1231(7)	10.3793(4)
<i>c</i> (Å)	13.555(3)	12.5470(7)	20.1359(8)
α (°)	90.587(8)	90	90
β (°)	104.534(6)	111.421(3)	90
γ (°)	115.999(6)	90	90
<i>V</i> (Å ³)	1362.5(6)	2149.80(19)	2606.10(18)
<i>Z</i>	4	8	8
Density (Mg m ⁻³)	1.708	1.707	1.572
Abs. coeff. (mm ⁻¹)	1.301	1.425	1.190
<i>F</i> (000)	704	1120	1264
θ range for data collection	1.57 to 25.00	2.20 to 30.03	1.96 to 30.00
Index ranges	-12 ≤ <i>h</i> ≤ 11	-16 ≤ <i>h</i> ≤ 15	-17 ≤ <i>h</i> ≤ 16
Number of reflection collected	7934	18262	20339
Independent reflections	4783	6042	7327
Max. and min. transmission	0.9031	0.8134	0.7499
No. of data/restraints/parameters	4783/2/351	6042/15/284	7327/1/307
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^{ab}	<i>R</i> ₁ = 0.0391	<i>R</i> ₁ = 0.0617	<i>R</i> ₁ = 0.0391
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1256	<i>R</i> ₁ = 0.0909	<i>R</i> ₁ = 0.0481
Goodness-of-fit on <i>F</i> ^{2c}	0.945	1.045	1.006
Large diff. peak and hole (e Å ⁻³)	0.567 and -0.439	0.936 and -0.537	0.664 and -0.255

^a $R = \sum |F_o| - |F_c| / \sum |F_o|$.

^b $wR_2 = [(\sum \omega |F_o| - |F_c|)^2 / \sum \omega |F_o|^2]^{1/2}$.

^c $\text{GoF} = [(\sum \omega |F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$.

of *n*-hexane (ca. 1 mL), followed by overnight cooling at -30 °C gave reddish-brown crystals of CpCr(CO)₂(η²-S₂COCH(CH₃)₂) (**8**) (48 mg, 0.16 mmol, 80 % yield). Anal. Found: C, 42.9; H, 3.8; S, 21.0%. Calcd for C₁₁H₁₂CrO₃S₂: C 42.9; H, 3.9; S, 20.8%. IR (KBr, cm⁻¹): ν(aromatic C-H) 3122m, 3095m. ν(CO) 1950s and 1858s. ν(other bands) 2978w, 1993m, 1245s, 1094s, 1046w, 885w, 834w, 642w, 567w, 535w, 482w. FAB⁺-MS: *m/z* 308 [M⁺; CpCr(CO)₂(S₂COCH(CH₃)₂)], 280 [M⁺ - CO; CpCr(CO)(S₂COCH(CH₃)₂)], 252 [M⁺ - 2CO; CpCr(S₂COCH(CH₃)₂)], 210 [CpCr(S₂CO)], 150 [CpCrS], 134 [S₂COCH(CH₃)₂], 43 [CH(CH₃)₂]. ¹H NMR (C₆D₆): δ 4.40 (s, 5H, C₅H₅); δ 5.20–5.29 (m, 1H, CH). ¹³C NMR (C₆D₆): δ 22.1 (s, CH₃); δ 75.3 (s, OCH); δ 92.2 (s, C₅H₅); δ 215.1 (s, S₂CO); δ 264.8 (s, C≡O).

5.8. Structure determinations

Diffraction-quality single crystals were obtained from solutions at -30 °C as follows: **5** as bright red crystals from THF/ether after 3 days; **6** as bright red rhombic crystals from *n*-hexane/toluene after 3 days; **8** as dull red rhombic crystals from toluene/*n*-hexane after 1 day.

The crystals were mounted on quartz fibres. X-ray data were collected on a Siemens SMART diffractometer, equipped with a CCD detector, using Mo Kα radiation (λ 0.71073 Å). The data were corrected for Lorentz and polarisation effects with the SMART suite of programs [23] and for absorption effects with SADABS [24]. Structure solution and refinement were carried out with the SHELXTL suite of programs [25]. The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. The Cp, DMcTH, vinylic and metal-alkyl hydrogens were placed in calculated positions. The crystallographic data together with data collection details are given in Table 4.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 261160–261162 for compounds **5**, **6** and **8**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK

(Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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