

π -ARENE COMPLEXES

II*. SYNTHESIS, CHARACTERIZATION AND REACTIVITY TOWARDS ARENE AND THIOETHER SUBSTITUTION OF π -ARENEDICARBONYL(THIOETHER)CHROMIUM(0) COMPLEXES. CRYSTAL STRUCTURE OF *cis*-TETRACARBONYL(METHYL-1,3-DITHIAN-2-METHYL-2-DITHIOCARBOXYLATE)CHROMIUM(0)

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Summary

A carbonyl ligand of π -arenetricarbonylchromium(0) complexes is photochemically displaced to give π -arenedicarbonyl complexes of chromium(0) with thio-ether ligands. In contrast, irradiation of π -arenetricarbonylchromium compounds with dithio-ester and trithiocarbonate ligands yields only pentacarbonyl complexes. Substitution of the π -arene ring, the thio-ether ligand, or both, is easily achieved at room temperature and in polar solvents. The crystal structure of *cis*-tetracarbonyl(methyl-1,3-dithian-2-methyl-2-dithiocarboxylate)chromium(0) shows remarkably similar Cr–S bond distances of 2.379(2) and 2.383(2) Å for the respective thio-ether and dithio-ester sulphur-donor atoms of the bidentate ligand.

Introduction

The replacement of both the π -arene and carbonyl ligands in $\text{Cr}(\pi\text{-arene})(\text{CO})_3$ complexes by nucleophiles can easily be achieved. Thermal reaction conditions generally favour arene displacement, while photochemical procedures usually lead to carbonyl loss [2,3]. Recently the thermal labilization of a carbonyl in $\text{Cr}(\pi\text{-arene})(\text{CO})_3$ by means of catalyst mixtures was reported for isocyanide ligands [4].

Little work has been done in the field of π -arene complexes of chromium(0) with sulphur-donor ligands. An interesting aspect reported is the different modes of

* For part I see ref. 1.

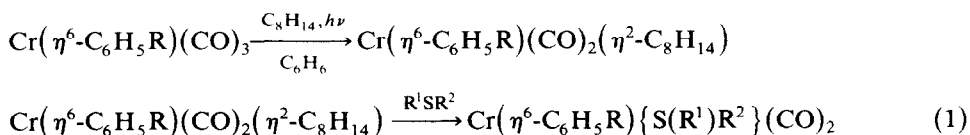
coordination found for carbon disulphide and the ease of desulphurization of $\text{Cr}(\pi\text{-arene})(\text{CO})_2(\eta^2\text{-CS}_2)$ by tertiary phosphines to give the corresponding thio-carbonyl complexes [5,6].

Thio-ether ligands in $\text{Cr}\{\text{S}(\text{CH}_2\text{R}^1)\text{R}^2\}(\text{CO})_5$, with activated α -protons are modified by BuLi to give bidentate thio-carbene ligands after alkylation, or, in the presence of the Lewis acid CS_2 , a tridentate ligand with two thioketonic and one thio-ether sulphur-donor atom [7,8]. Replacement of the poorer coordinated thio-ether ligand by other stronger π -acceptor ligands present, was found in the preparation of $\text{Cr}\{\text{C}(\text{NH}_2)\text{Ph}\}(\text{CNPh})(\text{CO})_4$ [9]. Pursuing our interest in this area we have synthesized and studied π -arene thio-ether complexes of chromium(0).

Conformations adopted by π -arene ligands with respect to the $\text{Cr}(\text{CO})_2\text{L}$ moiety in $\text{Cr}(\pi\text{-arene})(\text{CO})_2\text{L}$ complexes are of interest [4,10,11]. Recently we reported the crystal structures of $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{R})\{\text{S}(\text{CH}_2)_3\text{SCH}_2\}(\text{CO})_2$ ($\text{R} = \text{H}, \text{COOMe}$) [1].

Results and discussion

The complexes, $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{R})\{\text{S}(\text{R}^1)\text{R}^2\}(\text{CO})_2$ ($\text{R} = \text{Me}, \text{R}^1 = \text{R}^2 = \text{CH}_2\text{Ph}$ and $\text{R}^1\text{R}^2 = (\text{CH}_2)_3\text{SCH}_2$; $\text{R} = \text{COOMe}, \text{R}^1 = \text{R}^2 = \text{Ph}, \text{CH}_2\text{Ph}$ and $\text{R}^1\text{R}^2 = (\text{CH}_2)_3\text{-SCH}_2$), were synthesized by either direct or indirect photochemical procedures [12,13]. Although quantitative yields are not obtained with the indirect method (eq. 1), less decomposition occurs.



On the other hand, irradiation with dithio-ester, $\text{SC}(\text{SMe})\text{Ph}$, and trithio-carbonate, $\text{SCS}(\text{CH}_2)_2\text{S}$, ligands did not lead to the corresponding π -arene complexes, but afforded the pentacarbonyl(thio)chromium(0) compounds, $\text{Cr}\{\text{SC}(\text{R}^1)\text{R}^2\}(\text{CO})_5$ ($\text{R}^1 = \text{Ph}, \text{R}^2 = \text{SMe}; \text{R}^1\text{R}^2 = \text{S}(\text{CH}_2)_2\text{S}$). Attempts to isolate a π -arene intermediate were unsuccessful, but evidence from infrared spectra for the trithiocarbonate indicated a blue tetracarbonyl compound, probably $\text{Cr}\{\text{SCS}(\text{CH}_2)_2\text{S}\}(\text{CO})_4$, which rapidly decomposes to $\text{Cr}\{\text{SCS}(\text{CH}_2)_2\text{S}\}(\text{CO})_5$. The same results were found using the indirect photochemical method. The π -arene compounds with thio-ether ligands, their melting points, yields and some analytical data are summarised in Table 1.

Two important factors, excluding steric effects, need to be considered when comparing the stability of $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{R})(\text{CO})_2\text{L}$ complexes. They are the role of the substituent R in the arene ring and the bonding properties of the ligand L [14,15]. The π -arene complexes of chromium(0) with thio-ether ligands containing an electron-donating substituent (Me) in the arene ring are less stable compared to those with an electron-withdrawing substituent (COOMe).

Aryl thio-ether compounds are more readily oxidized than their analogous alkyl derivatives. π -Arene complexes of chromium(0) with thio-ether ligands easily oxidize in air and decompose slowly when in solution, as shown in Scheme. 1. The products formed are the parent tricarbonyl, a pentacarbonyl complex with a thio-ether ligand and other oxidized chromium compounds. These results correlate with conclusions

TABLE 1

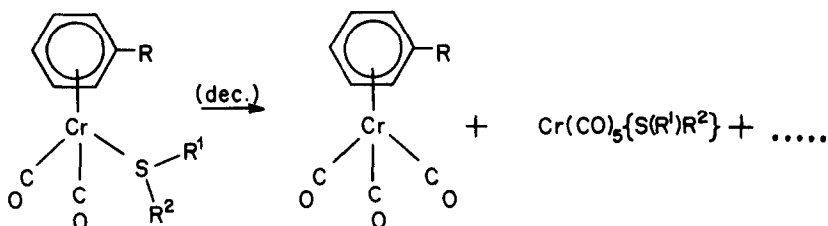
YIELDS ^a, MELTING POINTS AND ANALYTICAL DATA FOR THE COMPLEXES Cr(η^6 -C₆H₅R)(CO)₂L

Compounds			Yield (%)	M.p. (°C)	Analysis (Found (calcd.) (%))		
R	L = R ¹ SR ²				C	H	S
COOMe	$\overline{\text{S}(\text{CH}_2)_3\text{SCH}_2}$		62	92	46.38 (46.13)	4.57 (4.43)	17.48 (17.61)
Me	$\overline{\text{S}(\text{CH}_2)_3\text{SCH}_2}$		46	63	48.91 (48.73)	5.17 (5.04)	19.89 (20.01)
	R	R					
Me	CH ₂ Ph	CH ₂ Ph	53	47	66.87 (66.65)	5.52 (5.36)	7.52 (7.73)
COOMe ^b	Ph	Ph	40	48	—	—	—
COOMe	CH ₂ Ph	CH ₂ Ph	61	62	62.91 (62.82)	4.87 (4.84)	6.79 (7.11)

^a Yields obtained are of the crude products after separation, just before recrystallization. ^b This product is fairly unstable and could not be obtained analytically pure.

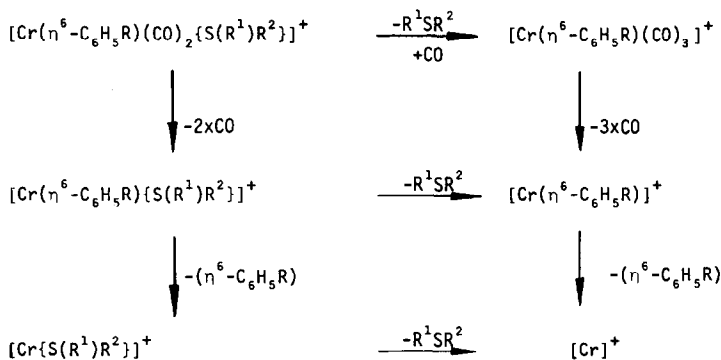
drawn from spectroscopic measurements (vide infra) of the Cr(π -arene)-{S(R¹)R²}(CO)₂ complexes.

SCHEME 1



The most striking feature in the mass spectra for the compounds Cr(η^6 -C₆H₅R){S(R¹)R²}(CO)₂ is the loss of the thio-ether ligand and uptake of a carbonyl to form the parent tricarbonyl, Cr(η^6 -C₆H₅R)(CO)₃. The spectrum shown in Fig. 1 for the complex Cr(η^6 -C₆H₅COOMe){ $\overline{\text{S}(\text{CH}_2)_3\text{SCH}_2}$ }(CO)₂ is representative for this group of complexes. A general fragmentation pattern emerges from the spectra

SCHEME 2



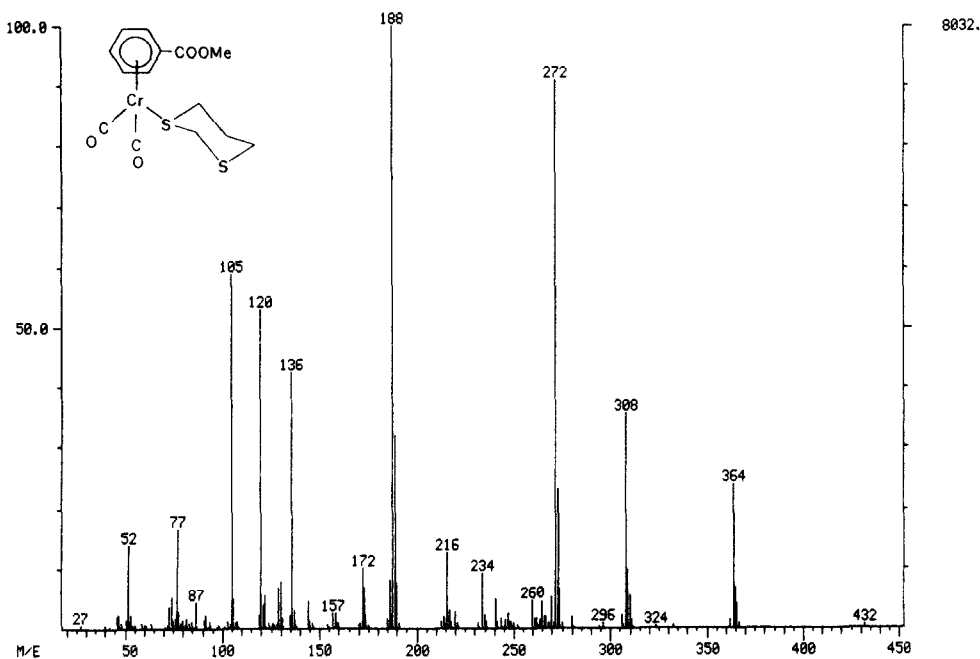


Fig. 1. Mass spectrum of $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{COOMe})\{\text{S}(\text{CH}_2)_3\text{SCH}_2\}(\text{CO})_2$.

and is explained in Scheme 2. After initial loss of the carbonyl ligands, two possible routes exist for the order of fragmentation of the π -arene and thio-ether ligand. Correlation is found with fragmentation patterns observed for analogous complexes $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{R})(\text{CO})_2\text{L}$ ($\text{L} = \text{CO}, \text{CS}, \text{PR}_3, \text{P}(\text{OR})_3$) [16].

Chemical shifts of the $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{R})\{\text{S}(\text{R}^1)\text{R}^2\}(\text{CO})_2$ complexes are given in Table 2. The chemical shift to higher fields of the protons in the π -arene ligands of the complexes $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{R})(\text{CO})_2\text{L}$ is ascribed to a reduction in the ring current due to the transfer of electron density from the π -arene ring to the metal [17,18]. The upfield shifts for the aromatic protons of the π -arene thio-ether complexes are greater compared to those for the parent tricarbonyl compounds. It is known that the electron density in $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{R})(\text{CO})_3$ compounds may be influenced considerably by the nature of ring substituents attached to the arene ring [19,20]. This is clearly reflected in the carbonyl stretching frequencies of $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{R})\{\text{S}(\text{R}^1)\text{R}^2\}(\text{CO})_2$ given in Table 2.

A change from an electron-withdrawing ($\text{R} = \text{COOMe}$) to an electron-donating group ($\text{R} = \text{Me}$) in the π -arene ring leads to a considerable lowering ($\Delta\nu$ 16 cm^{-1} (A') and $\Delta\nu$ 20 cm^{-1} (A'')) of the carbonyl frequencies, supporting conclusions drawn from the effects due to ring substituents. However, variation of substituents in the thio-ether ligand has little effect, and changes of less than 8 cm^{-1} ($\Delta\nu$ for A' , A'') are found. The thio-ether ligands with poorer π -acceptor/ σ -donor bonding properties compared to a carbonyl in $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{R})(\text{CO})_2\text{L}$, result in greater π -interaction for the remaining carbonyl ligands, leading to lower carbonyl frequencies.

Potentially three sites for ligand displacement reactions exist for π -arene-dicarbonyl(thio-ether)chromium(0) complexes, i.e. the π -arene, thio-ether or carbonyl

TABLE 2

PROTON NMR DATA AND INFRARED CARBONYL STRETCHING FREQUENCIES OF THE COMPLEXES $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{R})(\text{CO})_2\text{L}$

(Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, S = strong, M = medium. The number of protons established by integration are either given in parentheses or are in accord with the given structures for the proton NMR data)

Compounds		^1H NMR chemical shifts ^b (acetone- d_6) (δ , ppm)			IR, $\nu(\text{CO})$ (hexane) (cm^{-1})		
R	L	L			CO	A' (S)	A'' (M)
		π -arene	$\eta^6\text{-C}_6\text{H}_5$	Me			
Me	$\text{S}(\text{CH}_2\text{Ph})_2$ $\text{S}(\text{CH}_2)_3\text{SCH}_2$	(m, 3) 4.79	(m, 2) 4.50	(s, 3) 2.08	7.32 (Ph); 3.70 (SCH_2) 7.32 (SCH_2 S); 2.68 (SCH_2); 2.09 ($\text{CH}_2\text{CH}_2\text{CH}_2$)	1899	1845
COOMe	$\text{S}(\text{CH}_2\text{Ph})_2$ $\text{S}(\text{Ph})\text{Ph}$ $\text{S}(\text{CH}_2)_3\text{SCH}_2$	(m, 2) 5.48 5.68	(m, 1) 4.90 5.24	(m, 2) 4.59 4.82	7.29 (Ph); 3.68 (SCH_2) 7.34 (SPH) 3.56 (SCH_2 S); 2.71 (SCH_2); 2.09 ($\text{CH}_2\text{CH}_2\text{CH}_2$)	1899	1847
		5.72	5.26	4.90		1917	1865
		6.28	5.93	5.65		1925	1872
	CO ^a			3.88		1994	1928

^a NMR: ref. 19; IR: ref. 21, solvent CCl_4 . ^b Internal standard: TMS.

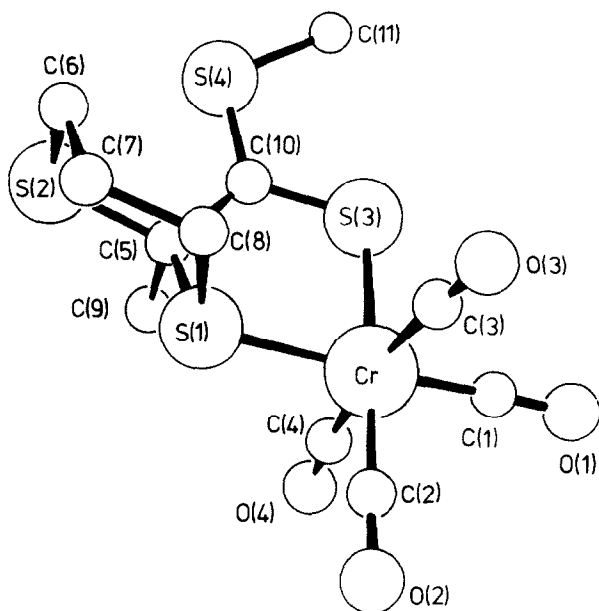
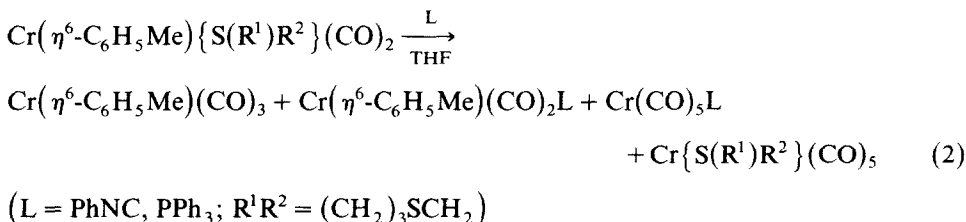


Fig. 2. A perspective view of $\text{Cr}\{\text{SC}(\text{SMe})\text{C}(\text{CH}_3)\text{S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4$ (**A**) showing the atomic numbering.

ligand. Substitution of another carbonyl from $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{R})(\text{CO})_2\text{L}$ was reported for ligands **L** (**CS**, **PR**₃, etc.) by means of UV-irradiation [22,23]. In polar solvents and at room temperature the π -arene ring, thio-ether ligand or both of $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{R})\{\text{S}(\text{R}^1)\text{R}^2\}(\text{CO})_2$ were displaced, when stirred overnight in the presence of another ligand **L**, according to eq. 2.



The much higher yields of the pentacarbonyl species indicate that π -arene substitution is preferred and enhanced due to the bonding properties of the thioether ligand in the π -arene complexes. When excess of **L** or a bidentate ligand were used, tetracarbonyl complexes $\text{Cr}(\text{CO})_4\text{L}_2$ (**L** = **PhNC**, **L**₂ = **SC(SMe)C(CH₃)S(CH₂)₃S**) also formed in relative high yields.

Crystal structure of $\text{Cr}\{\text{SC}(\text{SMe})\text{C}(\text{CH}_3)\text{S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4$ (**A**)

The molecular geometry of **A** is shown in the perspective drawing in Fig. 2, which also serves to define the atomic numbering scheme. Selected bond distances and angles are given in Table 3.

The remarkably similar Cr–S bond lengths of 2.383(2) and 2.379(2) Å for the *sp*²-dithio-ester and *sp*³-thio-ether sulphur-donor atoms could be ascribed either to

TABLE 3

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR THE NON-HYDROGEN ATOMS OF $\text{Cr}\{\text{SC}(\text{SMe})\text{C}(\text{CH}_3)\text{S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4$ (A)

Bond lengths			
Cr–S(1)	2.379(2)	S(1)–C(8)	1.823(8)
Cr–S(3)	2.383(2)	S(2)–C(5)	1.824(8)
Cr–C(1)	1.809(9)	S(2)–C(6)	1.819(9)
Cr–C(2)	1.818(9)	S(3)–C(10)	1.697(8)
Cr–C(3)	1.918(9)	S(4)–C(10)	1.710(7)
Cr–C(4)	1.872(9)	S(4)–C(11)	1.792(9)
C(1)–O(1)	1.171(9)	C(5)–C(10)	1.436(10)
C(2)–O(2)	1.181(9)	C(5)–C(9)	1.578(10)
C(3)–O(3)	1.143(9)	C(6)–C(7)	1.518(11)
C(4)–O(4)	1.151(9)	C(7)–C(8)	1.537(10)
S(1)–C(5)	1.848(8)		
Bond angles			
S(3)–Cr–S(1)	82.3(1)	C(10)–C(5)–S(1)	111.8(5)
C(3)–Cr–S(1)	93.8(2)	C(10)–C(5)–S(2)	116.0(6)
C(3)–Cr–S(3)	88.3(2)	C(9)–C(5)–S(1)	106.8(5)
C(1)–Cr–S(1)	175.9(3)	C(9)–C(5)–S(2)	103.0(5)
C(1)–Cr–S(3)	93.7(3)	C(9)–C(5)–C(10)	108.5(7)
C(1)–Cr–C(3)	86.8(4)	C(6)–S(2)–C(5)	102.6(4)
C(2)–Cr–S(1)	94.2(3)	C(7)–C(6)–S(2)	111.7(6)
C(2)–Cr–S(3)	175.5(3)	C(8)–C(7)–C(6)	110.6(7)
C(2)–Cr–C(3)	89.1(4)	C(7)–C(8)–S(1)	111.4(6)
C(2)–Cr–C(1)	89.8(4)	S(3)–C(10)–C(5)	121.2(6)
C(4)–Cr–S(1)	92.8(3)	S(4)–C(10)–C(5)	117.4(6)
C(4)–Cr–S(3)	97.1(3)	S(4)–C(10)–S(3)	121.4(5)
C(4)–Cr–C(3)	171.9(4)	C(10)–S(3)–Cr	107.9(3)
C(4)–Cr–C(1)	86.8(4)	C(11)–S(4)–C(10)	104.6(4)
C(4)–Cr–C(2)	85.9(4)	O(3)–C(3)–Cr	174.7(7)
C(5)–S(1)–Cr	104.0(3)	O(1)–C(1)–Cr	176.4(7)
C(8)–S(1)–Cr	106.7(3)	O(2)–C(2)–Cr	178.3(8)
C(8)–S(1)–C(5)	99.8(4)	O(4)–C(4)–Cr	173.7(8)
S(2)–C(5)–S(1)	109.9(4)		

the geometry of the chelate ring or an electronic effect in the dithio-ester moiety. Furthermore, the Cr–S–C bond angle of 107.9° deviates considerably from the expected 120° for an sp^2 -hybridized sulphur atom, the 120.8° in $\text{Cr}\{\text{SCMe}_2\}(\text{CO})_5$ or the 123.1° in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mn}\{\text{SC}(\text{Ph})\text{C}_5\text{H}_4\}\text{Mn}(\text{CO})_3$ [24,25]. A significant difference in the Cr–S values for $\text{Cr}(\text{SCMe}_2)(\text{CO})_5$ (2.377(4) Å) and $\text{Cr}\{\text{S}(\text{Et})\text{CH}_2\text{-Ph}\}(\text{CO})_5$ (2.458(2) Å) was found [24,26]. Replacement of alkyl groups in SCMe_2 by more electro-negative groups, $\text{Cr}\{\text{SCOC}(\text{Me}_2)\text{C}(\text{Me}_2)\text{O}\}(\text{CO})_5$, leads to Cr–S bond lengthening, 2.438(1) Å [27]. The Cr–S(dithiane) distance 2.379(2) Å compares well with the corresponding distance 2.384(4) Å in $\text{cis-Cr}\{\text{C}(\text{OEt})\text{C}(\text{OH})\text{CS}(\text{CH}_2)_3\text{S}\}(\text{CO})_4$ and is a little shorter than the values of 2.425(1) and 2.412(1) Å found for $\text{Cr}\{\text{S}(\text{Et})\text{CH}_2\text{CH}_2\text{SEt}\}(\text{CO})_4$ [28,29]. Similar thio-ether and dithio-ester Cr–S distances 2.338(2), 2.322(2) and 2.338(2) Å was also reported for $\text{fac-Cr}\{\text{S}(\text{CH}_2)_3\text{SC}[\text{C}(\text{S})\text{SEt}]_2\}(\text{CO})_3$ [8].

The C–S(thione) distances in A of 1.697(8) Å differ slightly from those in $(\eta^5\text{-C}_5\text{H}_6)(\text{CO})_2\text{Mn}\{\text{SC}(\text{Ph})\text{C}_5\text{H}_4\}\text{Mn}(\text{CO})_3$ (1.656(6) Å) and $\text{Cr}\{\text{SCOC}(\text{Me}_2)\text{-}$

$\text{C}(\text{Me}_2\text{O})(\text{CO})_5$ (1.659(3) Å but is significantly longer than the value of 1.618(8) Å found for $\text{Cr}\{\text{SCMe}_2\}(\text{CO})_5$ [25,27,24].

An interesting feature of the structure of **A** is the short C(10)–S(4) and C(10)–C(5) distances of 1.710(7) and 1.436(10) Å, respectively, indicating a considerable charge delocalization over the SC–SMe and SC–C moieties of the chelate ring. The expected bond distances for a C(sp^2)–C(sp^3) bond is 1.51(2) Å.

The Cr–C(carbonyl) bond lengths *trans* to the sulphur-donor atoms of 1.818(9) and 1.809(9) Å are shorter than those for the *cis* carbonyls, 1.918(9) and 1.872(9) Å, reflecting a greater *trans* influence exercised by the sulphur-donor ligands compared with a carbonyl.

Experimental

General comments

The $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{R})(\text{CO})_3$ complexes were prepared by modified literature procedures [2,30]. Solvents were carefully dried and freshly distilled under nitrogen before use. All preparations and manipulations were carried out under nitrogen atmosphere. Photolyses were run in Pyrex flasks with water cooled jackets and using a Philips medium pressure mercury arc. Column chromatography on SiO_2 (0.063–0.200 mm) was typically performed on 2 cm × 35 cm columns at -10°C . Microanalyses were performed by F. and E. Pascher, Microanalytical Laboratories, Bonn. Infrared spectra were obtained with a Beckman IR 4250 Spectrometer and calibrated against polystyrene film, ^1H NMR spectra were recorded on a Bruker WP 80 MHz instrument (reported δ values are in ppm relative to TMS) and mass spectra on a Perkin–Elmer RMU-6H instrument operating at 70 eV. Melting points were recorded on a Kofler hot-stage apparatus and are uncorrected.

Data collection and structure determination

Suitable single crystals of **A** were identified by standard photographic techniques. Intensity measurements were made using Mo- K_α radiation (λ 0.7107 Å, graphite monochromator) on a Philips PW 1100 four circle diffractometer in the ω – 2θ mode

TABLE 4

CRYSTAL DATA AND DETAILS OF THE STRUCTURE ANALYSIS OF **A**

Molecular formula	$\text{CrC}_{11}\text{H}_{12}\text{O}_4\text{S}_4$
a (Å)	16.404(4)
b (Å)	13.850(4)
c (Å)	14.154(4)
V (Å ³)	3215
Space group	$Pbcn$
Z	8
D_c (g cm ^{−3})	1.58
$F(000)$	1288
μ (Mo- K_α) mm ^{−1}	11.43
N (measured)	2183
N (unobserved)	232
R_w (σ_F^{-2})	0.060
Res. background (e Å ^{−3})	0.42

TABLE 5

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS ($\text{\AA}^2 \times 10^3$) FOR THE NON-HYDROGEN ATOMS OF A

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Cr	1321(1)	2617(1)	1116(1)	35(0)
S(1)	2155(1)	3847(2)	1781(2)	35(1)
C(5)	3183(4)	3587(5)	1312(6)	33(4)
S(2)	3940(1)	4317(2)	1928(2)	46(1)
C(6)	3790(5)	3970(7)	3155(6)	54(5)
C(7)	2934(5)	4200(7)	3492(6)	52(5)
C(8)	2311(5)	3528(6)	3017(5)	45(5)
C(10)	3342(4)	2567(6)	1273(5)	36(4)
S(3)	2581(1)	1762(2)	1075(2)	41(1)
S(4)	4332(1)	2201(2)	1395(2)	50(1)
C(11)	4297(6)	916(7)	1252(9)	77(7)
C(9)	3210(5)	4001(6)	274(5)	46(5)
C(3)	1101(5)	2021(5)	2312(7)	36(5)
C(1)	753(5)	1637(7)	587(6)	40(5)
C(2)	384(5)	3307(6)	1237(6)	43(5)
C(4)	1386(5)	3150(6)	−98(7)	43(5)
O(3)	933(4)	1616(5)	2987(4)	59(4)
O(1)	348(3)	1018(5)	274(4)	57(4)
O(2)	−225(4)	3759(5)	1290(5)	65(4)
O(4)	1348(4)	3482(5)	−842(4)	69(4)

with $3 \leq \theta \leq 23^\circ$. The crystal data and details of the structure analysis are listed in Table 4. The measured reflections were corrected for background and for Lorentz and polarization effects only. Accurate cell parameters were obtained from the diffractometer settings for 25 reflections. The structure was solved uneventfully and refined by full-matrix least-squares techniques using the program SHELX with σ_F^{-2} weights [31]. All the hydrogen atoms were placed in calculated positions and included in the refinements with common isotropic thermal parameters, riding upon the associated carbon atoms. All the non-hydrogen atoms were refined anisotropically. Scattering factors for Cr^0 were taken from the literature [32]. Fractional atomic coordinates are listed in Table 5. Tables of thermal parameters and structure factors are available from the authors.

Synthesis of η^6 -arenedicarbonyl(thio-ether)chromium(0) complexes

A solution of the parent complex $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{R})(\text{CO})_3$ (3 mmol) and the thio-ether ligand R^1SR^2 (3 mmol, see Table 1) in MeOH was irradiated for 1.5 h. The yellow-orange solution changed progressively to red following the replacement of a CO group by the thio-ether ligand. At the end of the irradiation period the solvent was removed in vacuo. The required π -arene thio-ether complex can also be obtained indirectly by adding a prior irradiated mixture of the tricarbonyl complex and cyclooctene to the thio-ether ligand. The residue was purified on a silica gel column. Elution with hexane/diethyl ether (1/1) gave unreacted $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{R})(\text{CO})_3$ followed by a red zone which was concentrated and stripped of solvent under vacuum. Recrystallization of the crude product from ether/pentane (-30°C) afforded $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{R})\{\text{S}(\text{R}^1)\text{R}^2\}(\text{CO})_2$ in good yields (Table 1).

Synthesis of pentacarbonyl(thio)chromium(0) complexes

A solution of $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{COOMe})(\text{CO})_3$ (3 mmol) and $\text{R}^1\text{C}(\text{S})\text{R}^2$ (I: $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{SMe}$; II: $\text{R}^1\text{R}^2 = \text{S}(\text{CH}_2)_2\text{S}$) (3 mmol) was irradiated under the above conditions and the products purified chromatographically (SiO_2 , -10°C). Elution with hexane/ether (4/1) gave the pentacarbonyl(thio)chromium(0) complex and unreacted $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{COOMe})(\text{CO})_3$. Recrystallization from ether/pentane (-30°C) yielded $\text{Cr}\{\text{S}(\text{R}^1)\text{R}^2\}(\text{CO})_5$ which was spectroscopically characterized:

I, $\text{Cr}\{\text{SC}(\text{SMe})\text{Ph}\}(\text{CO})_5$: red crystals, yield 2.1 mmol (30%), m.p. 120°C . IR $\nu(\text{CO})$ (hexane): 2064 (w), 1957 (s), 1939 (m) cm^{-1} ; $\nu(\text{CS})$ (CS_2) 1048 (w) cm^{-1} . ^1H NMR CD_3COCD_3 (ppm): 7.46 (m, 5), *Ph*, 2.79 (s, 3) *SMe*.

II, $\text{Cr}\{\text{SCS}(\text{CH}_2)_2\text{S}\}(\text{CO})_5$: red crystals; yield 2.3 mmol (37%), m.p. 117°C . IR $\nu(\text{CO})$ (hexane): 2066 (w), 1952 (s), 1936 (m) cm^{-1} ; $\nu(\text{CS})$ (CS_2) 1069 (w) cm^{-1} . ^1H NMR CDCl_3 (ppm): 4.01 (s, 4), SCH_2 .

Reactions of $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{Me})\{\text{S}(\text{CH}_2)_3\text{SCH}_2\}(\text{CO})_2$ with *PhNC*, *PPh*₃ and $\text{SCS}(\text{CH}_2)_2\text{S}$

An ether solution 0.64 g (2 mmol) of $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{Me})\{\text{S}(\text{CH}_2)_3\text{SCH}_2\}(\text{CO})_2$ and 0.25 cm^3 (2.4 mmol) *PhNC* was stirred overnight at room temperature. The solvent was evaporated under reduced pressure and the residue chromatographed on SiO_2 (-10°C) with ether/hexane (1/2) as the eluent. The first yellow band afforded, after recrystallization from ether/pentane at -30°C , 71 mg (12% based on $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{Me})\{\text{S}(\text{CH}_2)_3\text{SCH}_2\}(\text{CO})_2$) of $\text{Cr}(\text{CNPh})(\text{CO})_5$ which was characterized spectroscopically. The second yellow band yielded 88 mg (14%) of $\text{Cr}\{\text{S}(\text{CH}_2)_3\text{SCH}_2\}(\text{CO})_5$ after recrystallization [33]. The next two bands gave the π -arene complexes $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{CO})_3$ (2%) and $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{CNPh})(\text{CO})_2$ (1%) in low yields.

The same method was used for the other ligands and yields were never higher than 15% for the pentacarbonyl species and less than 2% for π -arene compounds. All products were spectroscopically (mass spectra, IR and ^1H NMR) identified.

In addition to the above-mentioned products a twofold excess of *PhNC* yielded *cis*- $\text{Cr}\{\text{CNPh}\}_2(\text{CO})_4$ is less than 3%.

Synthesis of $\text{Cr}\{\text{SC}(\text{SMe})\text{C}(\text{CH}_3)\text{S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4$

(i) *Preparation of $\text{S}(\text{CH}_2)_3\text{SC}(\text{CH}_3)\text{C}(\text{S})\text{SMe}$* . A solution of 0.46 cm^3 (5 mmol) $\text{S}(\text{CH}_2)_3\text{SC}(\text{CH}_3)\text{H}$ in 100 cm^3 THF was cooled to 0°C , 3.12 cm^3 (5 mmol) 1.6 *M* BuLi in hexane was added dropwise and the mixture stirred for 2 h. Carbon disulphide 0.3 cm^3 (5 mmol) was added, the solution stirred for 0.5 h at room temperature and for a further hour after the addition of 0.32 cm^3 (5 mmol) MeI. The solvent was removed in vacuo, the residue dissolved in ether and the solution was filtered through SiO_2 . The solvent was again removed, yielding an orange oil which was used in (ii).

(ii) *Preparation of $\text{Cr}\{\text{SC}(\text{SMe})\text{C}(\text{CH}_3)\text{S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4$* . To a stirred solution of 0.32 g (1 mmol) $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{Me})\{\text{S}(\text{CH}_2)_3\text{SCH}_2\}(\text{CO})_2$ in 50 cm^3 THF, was added 0.4 cm^3 (ca. 2 mmol) $\text{SC}(\text{SMe})\text{C}(\text{Me})\text{S}(\text{CH}_2)_3\text{S}$ ((i) above). Stirring was continued for 2 h whereafter the solution was stripped of solvent under reduced pressure, the residue chromatographed on SiO_2 with hexane/ CH_2Cl_2 (2/1) and the blue band collected. This yielded, after recrystallization from pentane 66 mg (17% based on $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{Me})\{\text{S}(\text{CH}_2)_3\text{SCH}_2\}(\text{CO})_2$) of $\text{Cr}\{\text{SC}(\text{SMe})\text{C}(\text{CH}_3)\text{S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4$ (A) (m.p. 114°C (dec.); Anal., Found: C, 34.05; H, 3.3; S, 30.92.

Calcd.: C, 34.01; H, 3.11; S, 33.02%. Mass spectra $m/e(\text{Ir})$: 388(34, M^+), 360(8, $M^+ - \text{CO}$), 332(8, $M^+ - 2\text{CO}$), 304(35, $M^+ - 3\text{CO}$), 276(100, $M^+ - 4\text{CO}$); IR $\nu(\text{CO})$ (cm^{-1}): 2017 (A_1'), 1933 (A_1'), 1919 (B_1) and 1905 (B_2).

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