The Co-ordination Chemistry of Electron-rich Poly(organosulphur) Compounds. Part 1. Chromium(o), Molybdenum(o), and Tungsten(o) Complexes having Tetrakis(thioalkyl)olefins as Two- or Four-electron Donors: the Crystal and Molecular Structure of Tetracarbonyl[tetrakis(methylthio)ethene-*SS''*]chromium †

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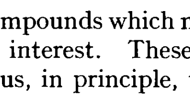
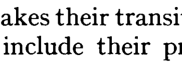
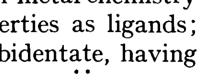
Treatment of [Cr(CO)$_6$] with $C_2(SR)_4$ ($L^{SR}{}_2$) under photolysis in tetrahydrofuran affords *cis*-[M(CO)$_4$($L^{SR}{}_2$)] (9; M = Cr, R = Me); analogues (9; M = Cr, Mo, or W; R = Et) have been obtained in better yield from the appropriate hexacarbonyl and $C_2(SEt)_4$ in EtOH in the presence of Na[BH$_4$]. In contrast, the olefin ($\dot{:}CSCH_2CH_2S)_2$ and [Cr(CO)$_6$] gave [Cr(CO)$_5${S(CH$_2$)$_2$SC=CS(CH$_2$)$_2$S}], which on heating reverts to the olefin and [Cr(CO)$_6$]; a related complex [Cr(CO)$_5${C$_2$(SEt)$_4$}] can be obtained from [NEt$_4$][Cr(CO)$_5$Cl] and the olefin in the presence of [OEt$_3$][BF$_4$], but the Mo or W analogue was unstable, affording complex (9). Complexes *fac*-[M(CO)$_3$-(PPh$_3$)($L^{SEt}{}_2$)] (10) have been prepared from [M(CO)$_3$(NCMe)$_3$] by successive treatment with $C_2(SEt)_4$ and PPh$_3$ in toluene. Infrared [ν(CO)] and ^{13}C n.m.r. spectra support the assigned configurations for complexes (9) and (10) and indicate some M–S π interaction; ^{1}H n.m.r. spectra show two sets of inequivalent groups R in these complexes. These features are confirmed by a single-crystal *X*-ray analysis of the title complex, showing an approximately octahedral geometry around the metal, with Cr–S(av.) = 2.379(2), Cr–CO(*trans* to S) = 1.886(9), Cr–CO(*trans* to CO) = 1.833(7), and C=C = 1.335(9) Å. Crystals are monoclinic, a = 12.487(1), b = 21.838(2), c = 13.686(1) Å, β = 117.32°, T = 21° C, space group $P2_1/c$, with two molecules per asymmetric unit. The structure was solved by direct methods and refined to R 0.049 by full-matrix least squares using 3 246 independent terms.

FOR the purpose of this Series, electron-rich poly(organosulphur) compounds are defined as molecules in which more than one alkyl- or aryl-thio-group is in conjugation with a neighbouring π centre, which may be a C=C bond, a tertiary nitrogen atom, or a carbanion. Examples of such molecules which will be discussed in this and subsequent papers are (1)—(5).


(1) abbreviated as $L^{SR}{}_2$


(2) abbreviated as L^{S}_2


(3) abbreviated as ttf

$M^+[C(SR)_3]^-$
(4)

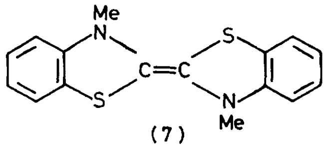
$\ddot{N}(SPh)_3$
(5)

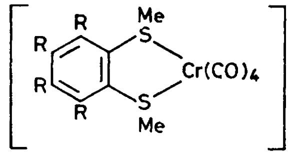
There are a number of features possessed by such compounds which makes their transition-metal chemistry of interest. These include their properties as ligands; thus, in principle, they may be (*i*) ambidentate, having not only sulphur atoms but also >C=C<, C$^-$, or $\ddot{N}$ as potential ligating sites; (*ii*) uni-, bi-, or poly-dentate; (*iii*) terminal, chelating, or bridging with respect to one or two metal centres; (*iv*) sources of electron-rich carbenes, such as $\ddot{C}(SR)_2$; and (*v*) reducing agents, by virtue of their low first-ionisation potentials and/or the stability of their conjugate acids, such as [ttf]$^+$. Other factors, which may influence reactivity in certain cases, are (*vi*) the ability of sulphur to stabilise a neighbouring carbanion or radical (whether, for example, carbon- or nitrogen-centred), and (*vii*) the high polarisability (or soft character) of sulphur-centred ligands which make them particularly attractive to a metal acceptor when in a low oxidation state.

Earlier transition-metal chemistry of compounds (1)—(5) refers to: (*a*) the $C_2(SEt)_4$–[{PtCl$_2$(PEt$_3$)}$_2$] system (leading to C–SEt cleavage),[1] to be discussed in the wider context of tetrakis(thioalkyl)olefins or bis(alkylthio)dithiolates as bridging ligands in binuclear complexes of Pd^{II} or Pt^{II};[2] (*b*) the ttf–CuCl$_2$·2H$_2$O system, which yields [ttf]$^+$ and [ttf]$^{2+}$;[3] and (*c*) the reaction of [M(CO)$_5$(thf)] with Li[C(SPh)$_3$] (M = Cr or W, thf = tetrahydrofuran) to give the bis(phenylthio)carbene complex [M(CO)$_5${C(SPh)$_2$}].[4] Compounds related to those from (*a*), [M(CO)$_5${C(SEt)$_2$}], were obtained from [M(CO)$_5$(NCMe)] and Na[*p*-MeC$_6$H$_4$SO$_2$NNC(SEt)$_2$] (M = Cr or W).[5]

Two compounds, (6) and (7), related to (1)—(5) have previously been examined in a transition-metal context. Compound (6) generally behaved as a unidentate ligand L when caused to react with [M(CO)$_3$-

MeS—C≡C—SMe
(6)


(7)


(8) R = SMe

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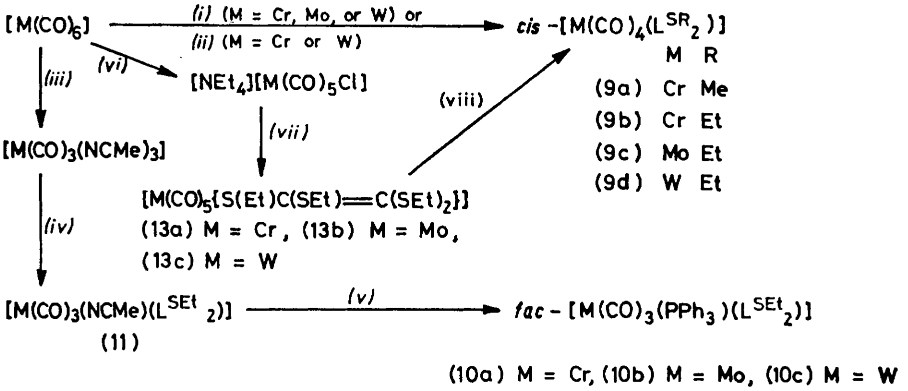
† No reprints are available.



SCHEME Preparation of Group 6 metal(0) carbonyl complexes from $C_2(SR)_4$ (R = Me or Et). (*i*) *hν*, L^{SR}_2 (R = Me or Et), thf, 25 °C, 5 h; (*ii*) L^{SEt}_2, trace $Na[BH_4]$, EtOH, 80 °C, 5 h; (*iii*) *cf.*, D. P. Tate, W. R. Knipple, and J. M. Augl, *Inorg. Chem.*, 1962, **1**, 433; (*iv*) L^{SEt}_2, PhMe, 25 °C, 1 h; (*v*) PPh_3, PhMe, 25 °C, 1 h; (*vi*) *cf.*, ref. 13; (*vii*) L^{SEt}_2, $[OEt_3][BF_4]$, CH_2Cl_2, 25 °C; (*viii*) M = Mo or W and procedure (*vii*) or, for M = Cr, n-C_8H_{18}, 80 °C

$(NCMe)_3]$ (M = Mo or W) in ethanol; the products $[M(CO)L_3]$ had the triple bond as donor site;[6] however, when M = Cr the initial product was $[Cr(CO)_2L_2]$ and then (8). For $[W(CO)L_3]$, addition of $Me_2PCH_2CH_2PMe_2$ (dmpe) gave $[W_2(dmpe)_5L]$, which was believed to be dimeric with μ-L and μ-dmpe bridges. In no case was there evidence of sulphur co-ordination. Compound (7), L'_2, behaved as a source of the carbene *N*-methylbenzothiazolinylidene (L′), when treated with, for example, $[\{PtCl_2(PEt_3)\}_2]$ to give *trans*-(primarily) *and* *cis*-$[PtCl_2(PEt_3)L']$; again there was no evidence of sulphur co-ordination.[7]

TABLE 1

Selected physical data for complexes of the type *cis*-$[M(CO)_4(L^{SR}_2)]$ and *fac*-$[M(CO)_4(PPh_3)(L^{SR}_2)]$

Complex	Yield (%)	M.p. (θ_c/°C)	Colour	Analysis (%) [a] C	H
$[Cr(CO)_4(L^{SMe}_2)]$ [b]	25	91—93	Yellow	32.1 (31.9)	3.3 (3.2)
$[Cr(CO)_4(L^{SEt}_2)]$	25	48—49	Yellow	38.8 (38.8)	4.5 (4.6)
$[Mo(CO)_4(L^{SEt}_2)]$	20	45—48	Yellow-green	28.0 (27.9)	5.0 (5.0)
$[W(CO)_4(L^{SEt}_2)]$	35	38—40	Yellow-green	23.0 (23.2)	4.3 (4.2)
$[Mo(CO)_3(PPh_3)(L^{SEt}_2)]$	60	148—150 (decomp.)	Yellow-green	52.4 (52.4)	4.9 (5.1)
$[Cr(CO)_3(PPh_3)(L^{SEt}_2)]$	80	137—139 (decomp.)	Orange	56.1 (55.8)	5.5 (5.3)
$[W(CO)_3(PPh_3)(L^{SEt}_2)]$	50	>300 (decomp.)	Black	45.9 (46.6)	4.5 (4.4)
$[Cr(CO)_5(L^{SEt}_2)]$	50	52—55	Yellow	39.1 (39.1)	4.35 (4.4)
$[Cr(CO)_5(L^{S}_2)]$	60	94—98	Pale yellow	33.0 (32.9)	2.0 (2.0)

[a] Calculated values are given in parentheses. [b] Ref. 1.

With regard to electron-richness, comparisons with olefins such as $C_2(NMe_2)_4$, $[\overline{:CN(R)CH_2CH_2N}R]_2$, C_2H_4, and C_2F_4 are informative. Their first-ionisation potentials (i.p.s) are respectively 5.95, 5.95 (R = Me), 10.6, and 10.6 eV,[8,*] and not surprisingly the first two compounds are strong reducing agents. The tetrakis(thioalkyl)olefins (1), (2), and (3) are not quite so electron-rich, having first i.p.s of 7.75 (R = Me),[9a] 7.17,[9b] and 6.83 eV,[9b] respectively.

The present paper is concerned with aspects of the chemistry of the olefins (1) and (2) with respect to Cr^0, Mo^0, and W^0 as acceptors. In principle the olefins may be two-, four-, six-, eight-, or ten-electron donors, unless the C=C bond is cleaved, when it could act as a bis(alkylthio)methylidene (carbene) ligand. Here, we shall describe their behaviour as four-electron chelating ligands with the *SS″* atoms as donor centres, or as unidentate two-electron sulphur ligands. The results may be compared with those on $C_2(NMe_2)_4$ or $[\overline{:CN(R)CH_2CH_2N}R]_2$ (L''_2) with Group 6 metal carbonyls or their derivatives,[10,11] and the $C_2(OMe)_4$–$[Mn(\eta\text{-}C_5H_5)(CO)_3]$ system.[12] Whereas (*i*) the enamines give *NN″* complexes $[\overline{M(CO)_4(olefin})]$ or, with the bicyclic L''_2, carbenemetal complexes $[M(CO)_5L'']$, *cis*- and *trans*-$[M(CO)_4L''_2]$, or $[W(CO)_3L''_3]$,[10,11] (*ii*) $C_2(OMe)_4$ yields $[Mn(\eta\text{-}C_5H_5)(CO)_2(olefin)]$, in which ligation is from the double bond.[12] A preliminary communication mentioned the reaction between $C_2(SMe)_4$ (1; R = Me) and $[Cr(CO)_6]$.[2]

RESULTS AND DISCUSSION

The reactions between a tetrakis(thioalkyl)olefin $C_2(SR)_4$ (or L^{SR}_2, 1) and a Group 6 metal(0) or metallate(0) carbonyl complex are summarised in the Scheme. It will be noted that the olefin generally behaves as a bidentate *SS″* ligand, yielding the *cis*-$[M(CO)_4(L^{SR}_2)]$ (9), or *fac*-$[M(CO)_3(PPh_3)(L^{SEt}_2)]$ (10) and *fac*-$[M(CO)_3(NCMe)(L^{SEt}_2)]$ (11) complexes. Analytical and pre-

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[*] Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

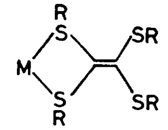
TABLE 2

Selected spectroscopic data for complexes of the type *cis*-$[M(CO)_4(L^{SR}{}_2)]$, *fac*-$[M(CO)_3(PPh_3)(L^{SR}{}_2)]$, and $[Cr(CO)_5(olefin)]$

Complex	^{1}H N.m.r. $(CDCl_3)$* τ(Me)	τ(CH_2)	^{13}C N.m.r. (CD_2Cl_2) (p.p.m.)* Olefinic C	CO_{trans}	CO_{cis}	I.r.(cm^{-1}) ν(CO) (hexane solution)
$[Cr(CO)_4(L^{SMe}{}_2)]$	7.35 (s), 7.50 (s)	7.0 (qa), 7.05 (qa)	141.6	227.0	215.9	2 015, 1 916, 1 905, 1 892
$[Cr(CO)_4(L^{SEt}{}_2)]$	8.65 (t), 8.85 (t)	7.0 (qa), 7.05 (qa)				2 021, 1 918, 1 902, 1 890
$[Mo(CO)_4(L^{SEt}{}_2)]$	8.6 (t), 8.75 (t)	7.05 (qa), 7.1 (qa)				2 029, 1 927, 1 912, 1 897
$[W(CO)_4(L^{SEt}{}_2)]$	8.65 (t), 8.8 (t)	6.85 (m), 7.45 (qa)				2 025, 1 920, 1 902, 1 894
$[Cr(CO)_3(PPh_3)(L^{SEt}{}_2)]$	8.55 (t), 8.95 (t)	6.8 (m), 7.4 (qa)				1 928 1 825 (CH_2Cl_2)
$[Mo(CO)_3(PPh_3)(L^{SEt}{}_2)]$	8.5 (t), 8.9 (t)	6.9 (m), 7.45 (qa)	138.9	218.9 (d) ^2J 35,	222.85 (d) ^2J 9 Hz	1 937 1 833 (CH_2Cl_2)
$[W(CO)_3(PPh_3)(L^{SEt}{}_2)]$	8.55 (t), 8.9 (t)					1 931 1 828 (CH_2Cl_2)
$[Cr(CO)_5(L^{SEt}{}_2)]$	8.5 (m)	6.9 (m)				2 066, 1 947, 1 941, 1 929
$[Cr(CO)_5(L^{S}{}_2)]$		6.4 (d)				2 073, 1 952m, 1 945m, 1 933

* s = Singlet, d = doublet, t = triplet, qa = quartet, and m = multiplet.

parative data for complexes (9) and (10) are in Table 1, and spectroscopic details in Table 2; on the basis of the latter *SS''* ligation is preferred over the alternative formulation of *SS'* chelation, (12), or bonding involving the >C=C< moiety, as confirmed in $[Cr(CO)_4\{C_2(SMe)_4\}]$ (9a) by *X*-ray crystallography. Complexes (11) are exceedingly hygroscopic and were not fully characterised, but (9) and (10) are stable in air, crystalline, and decompose only slowly in solution. Mass spectra, even at low source temperature and low beam energies, were not successfully recorded, but were those of the ligand and $[M(CO)_6]$.



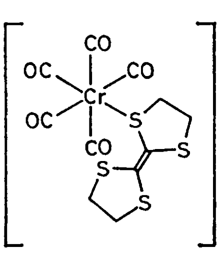
(12)

A second series of complexes (13), in which the olefin behaves as a unidentate ligand with *S* ligation, was isolated from the pentacarbonylchlorometallate(0) precursor, a procedure similar to that used previously for preparing corresponding complexes from diphosphane ligands.[13] A chromium complex $[Cr(CO)_5\{S(Et)C(SEt)=C(SEt)_2\}]$ (13a) was isolated analytically pure by dry-column chromatography, but similar work-up of the Mo and W analogues gave the chelate complexes *cis*-$[M(CO)_4(L^{SEt}{}_2)]$ [M = Mo (9c) or W (9d)]. Similarly, when a pure sample of complex (13a), $[Cr(CO)_5(L^{SEt}{}_2)]$ was warmed to 80 °C in n-octane and the reaction monitored by i.r. spectroscopy, ν(CO) bands present in $[Cr(CO)_4(L^{SEt}{}_2)]$ (9b) and $[Cr(CO)_6]$ gradually developed in intensity, but the decomposition was inhibited by excess of the olefin. We therefore propose the following decomposition path:

$$\begin{tikzcd}
{[M(CO)_5(L^{SEt}{}_2)]} \arrow[r, leftrightharpoons] \arrow[d] & {[M(CO)_5] + L^{SEt}{}_2} \arrow[d, "CO"] \\
{[M(CO)_4(L^{SEt}{}_2)] + CO} & {[M(CO)_6]}
\end{tikzcd}$$

Irradiation of the cyclic olefin (2) with $[Cr(CO)_6]$ in thf affords complex (14) (Tables 1 and 2) which on heating does not undergo chelation with CO loss, but instead at *ca.* 60 °C yields $[Cr(CO)_6]$ and the olefin (2).

The i.r. spectra (Table 2) of the *cis*-complexes $[M(CO)_4(L^{SR})_2]$ (9) show the expected four bands, appropriate for A_1'', B_1, E, and A_1' symmetry modes in an octahedral complex of the C_{2v} point group. The values are 10—20 cm^{-1} to higher energy compared with related olefin-*NN''* complexes,[11] consistent with some M–S π-interaction. Likewise, the *fac* complexes $[M(CO)_3(PPh_3)(L^{SEt}{}_2)]$ (11) have i.r. bands (three, consistent with the structure) 15—20 cm^{-1} higher than related complexes of *N*-donors.



(14)

The ^{1}H and ^{13}C n.m.r. spectra (Table 2) of the *cis* complexes (9) show that the alkyl groups attached to co-ordinated or free sulphur are magnetically inequivalent. Moreover, the single olefinic ^{13}C signal is inconsistent with the alternative to *SS''* chelation, namely the *SS'* of structure (12). At 141 p.p.m. this signal is very close to that (137 p.p.m.) observed for the free ligand, which makes any metal–olefinic bond interaction unlikely.

The ^{1}H n.m.r. spectra for *fac*-$[M(CO)_3(PPh_3)(L^{SEt}{}_2)]$ (10) are most clearly diagnostic of the *SS''* mode of co-ordination of the olefin $L^{SR}{}_2$ (1). This is illustrated in Figure 1 for (10b; M = Mo): thus, there are two magnetically distinct Et groups, but second-order effects give an ABX_3 pattern for the co-ordinated SEt groups [in contrast to (9), which give an A_2B_3 spectrum],

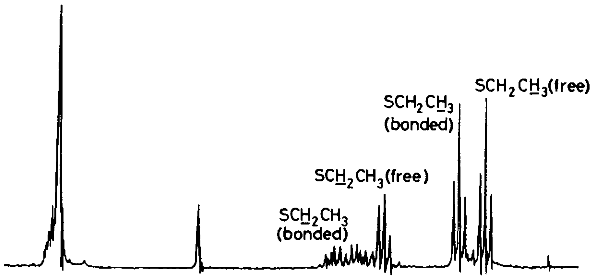
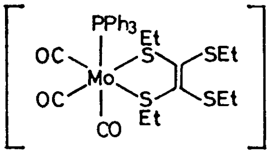


FIGURE 1 Hydrogen-1 n.m.r. spectrum of *fac*-$[Mo(CO)_3(PPh_3)(L^{SEt}{}_2)]$ in CD_2Cl_2 solutions at 30 °C

which is attributed to hindered rotation about the S–Et bond. This is probably mainly due to the bulk of the PPh_3 ligand (but alternatively the *cis*-PPh_3 ligand may



(15)

lower the rate of inversion at S rather than affect the S–Et rotational barrier), whereas the non-co-ordinating SEt groups, which are remote from the metal, show free rotation and a first-order Et ^{1}H n.m.r. spectrum. The ^{13}C n.m.r. spectrum shows a pair of doublets centred on 223 and 219 p.p.m., in a *ca.* 2 : 1 intensity ratio, which suggest that these arise from the *C*O resonances ***trans*** and ***cis*** to SEt groups respectively. The $^{2}J(^{31}P-^{13}C)$ value of 35 Hz for the latter doublet indicates a ***trans*** coupling, whereas the former has the expected smaller (9 Hz) *cis* coupling; hence structure (15) is proposed.

The Crystal and Molecular Structure of cis-$[Cr(CO)_4\{C_2(SMe)_4\}]$.—Figure 2 is an ORTEP[14] drawing of one of the two chemically equivalent molecules in the asymmetric unit, showing the 50% thermal vibration

TABLE 3

Intramolecular distances and angles (estimated standard deviations in parentheses)

(*a*) Bond lengths (Å)

				Average	
Cr(1)–S(1)	2.379(2)	Cr(2)–S(5)	2.381(2)	Cr–S *trans* CO	2.379(2)
Cr(1)–S(2)	2.385(2)	Cr(2)–S(6)	2.370(2)		
Cr(1)–C(1)	1.879(9)	Cr(2)–C(5)	1.897(11)	Cr–CO *trans* CO	1.886(9)
Cr(1)–C(2)	1.877(9)	Cr(2)–C(6)	1.891(12)		
Cr(1)–C(3)	1.822(7)	Cr(2)–C(7)	1.838(10)	Cr–CO *trans* S	1.833(7)
Cr(1)–C(4)	1.832(8)	Cr(2)–C(8)	1.839(9)		
S(1)–C(9)	1.778(8)	S(5)–C(19)	1.777(7)	(Cr)S–C<	1.780(7)
S(2)–C(10)	1.779(7)	S(6)–C(20)	1.784(7)		
S(3)–C(9)	1.752(7)	S(7)–C(19)	1.755(7)	(Me)S–C<	1.751(7)
S(4)–C(10)	1.754(7)	S(8)–C(20)	1.744(7)		
S(1)–C(11)	1.838(9)	S(5)–C(15)	1.845(9)	>S–Me	1.830(8)
S(2)–C(12)	1.823(8)	S(6)–C(16)	1.815(8)		
S(3)–C(13)	1.820(10)	S(7)–C(17)	1.827(11)	–S–Me	1.821(8)
S(4)–C(14)	1.813(9)	S(8)–C(18)	1.824(8)		
C(9)–C(10)	1.337(9)	C(19)–C(20)	1.332(9)	>C=C<	1.335(9)
C(1)–O(1)	1.148(9)	C(5)–O(5)	1.165(10)	(Cr)C≡O	1.147(7)
C(2)–O(2)	1.146(9)	C(6)–O(6)	1.117(11)		
C(3)–O(3)	1.156(7)	C(7)–O(7)	1.153(10)		
C(4)–O(4)	1.154(8)	C(8)–O(8)	1.133(9)		

(*b*) Angles (°)

S(1)–Cr(1)–S(2)	84.0(1)	S(5)–Cr(2)–S(6)	83.6(1)	S–Cr–S	83.8(1)
S(1)–Cr(1)–C(1)	95.5(3)	S(5)–Cr(2)–C(5)	94.3(3)	S–Cr–CO *trans* CO	94.7(2)
S(2)–Cr(1)–C(1)	94.6(3)	S(6)–Cr(2)–C(5)	94.5(3)		
S(1)–Cr(1)–C(2)	89.2(3)	S(5)–Cr(2)–C(6)	89.6(4)	S–Cr–CO *trans* CO	90.0(2)
S(2)–Cr(1)–C(2)	91.0(2)	S(6)–Cr(2)–C(6)	90.2(3)		
S(1)–Cr(1)–C(3)	174.8(3)	S(5)–Cr(2)–C(7)	175.0(3)	S–Cr–CO	175.6(2)
S(2)–Cr(1)–C(4)	177.0(3)	S(6)–Cr(2)–C(8)	175.5(4)		
S(1)–Cr(1)–C(4)	93.6(2)	S(5)–Cr(2)–C(8)	93.3(3)	S–Cr–CO *trans* S	92.8(2)
S(2)–Cr(1)–C(3)	92.3(2)	S(6)–Cr(2)–C(7)	91.8(3)		
C(1)–Cr(1)–C(2)	173.0(3)	C(5)–Cr(2)–C(6)	174.1(4)	OC–Cr–CO	173.6(3)
C(1)–Cr(1)–C(3)	88.4(4)	C(5)–Cr(2)–C(7)	88.0(4)	OC–Cr–CO *trans trans* CO S	87.8(3)
C(1)–Cr(1)–C(4)	87.2(4)	C(5)–Cr(2)–C(8)	89.0(4)		
C(2)–Cr(1)–C(3)	87.2(4)	C(6)–Cr(2)–C(7)	88.4(5)		
C(2)–Cr(1)–C(4)	87.4(4)	C(6)–Cr(2)–C(8)	86.4(5)		
C(3)–Cr(1)–C(4)	90.0(3)	C(7)–Cr(2)–C(8)	91.2(4)	OC–Cr–CO *trans trans* S S	90.6(3)
Cr(1)–S(1)–C(9)	106.1(2)	Cr(2)–S(5)–C(19)	106.6(2)	Cr–S–C	106.7(2)
Cr(1)–S(2)–C(10)	106.6(2)	Cr(2)–S(6)–C(20)	107.3(2)		
Cr(1)–S(1)–C(11)	113.0(3)	Cr(2)–S(5)–C(15)	112.9(3)	Cr–S–Me	113.0(3)
Cr(1)–S(2)–C(12)	113.1(3)	Cr(2)–S(6)–C(16)	113.1(3)		
C(9)–S(1)–C(11)	99.9(4)	C(19)–S(5)–C(15)	99.9(4)	C–S–Me	100.2(3)
C(10)–S(2)–C(12)	100.1(4)	C(20)–S(6)–C(16)	100.9(4)		
C(9)–S(3)–C(13)	102.6(4)	C(19)–S(7)–C(17)	101.2(4)	C–S–Me	102.9(3)
C(10)–S(4)–C(14)	103.6(4)	C(20)–S(8)–C(18)	104.2(3)		
Cr(1)–C(1)–O(1)	174.3(8)	Cr(2)–C(5)–O(5)	176.6(8)	Cr–C–O	176.1(7)
Cr(1)–C(2)–O(2)	173.3(7)	Cr(2)–C(6)–O(6)	173.4(12)		
Cr(1)–C(3)–O(3)	177.4(7)	Cr(2)–C(7)–C(7)	179.5(10)		
Cr(1)–C(4)–O(4)	176.6(7)	Cr(2)–C(8)–C(8)	177.6(9)		
S(1)–C(9)–S(3)	118.0(4)	S(5)–C(19)–S(7)	116.5(4)	S–C–S	117.4(3)
S(2)–C(10)–S(4)	117.8(4)	S(6)–C(20)–S(8)	117.4(4)		
S(1)–C(9)–C(10)	122.0(6)	S(5)–C(19)–C(20)	121.5(6)	S–C–C	121.3(5)
S(2)–C(10)–C(9)	120.6(6)	S(6)–C(20)–C(19)	120.5(6)		
S(3)–C(9)–C(10)	119.9(6)	S(7)–C(19)–C(20)	121.9(6)		
S(4)–C(10)–C(9)	121.6(6)	S(8)–C(20)–C(19)	122.1(6)		

ellipsoids and the numbering scheme. The bond lengths and angles are listed in Table 3, and relevant mean planes and dihedral angles in Table 4. The electron-rich olefin is seen to act as a bidentate ligand with its two sulphur-donor (*SS''*) atoms occupying *cis* positions of an octahedral carbonylchromium(0) complex.

SS'' Chelation has not been extensively studied structurally, although some features are similar to the maleonitriledithiolate (mnt) systems in $[\mathrm{NBu^n_4}]_2[\mathrm{Co(S_2C_4N_2)_2}]$,[15] $[\mathrm{NBu^n_4}][\mathrm{Cu(S_2C_4N_2)_2}]$,[15] and $[\mathrm{NMe_4}]_2[\mathrm{Ni(S_2C_4N_2)_2}]$.[16] The S–C bond lengths of 1.70(1)—1.76(1) Å in the latter tend to be slightly shorter than the corresponding values in Table 3(*a*), although the C=C bond lengths [1.31(2)—1.34(2) Å] in the dithiolates are not significantly different from the C=C values in Table 3(*a*). The S–M–S′ bite, however, in the mnt systems of 91.4(2)—92.5(2)° is substantially larger than the values of 83.6(1)—84.0(1)° of Table 3(*b*); consequently the five-membered chelate ring has an envelope conformation with the chromium deviating from the plane of the other four atoms by 0.19 Å (av.) (Table 4). This compares with the almost planar conformation of the mnt complexes.

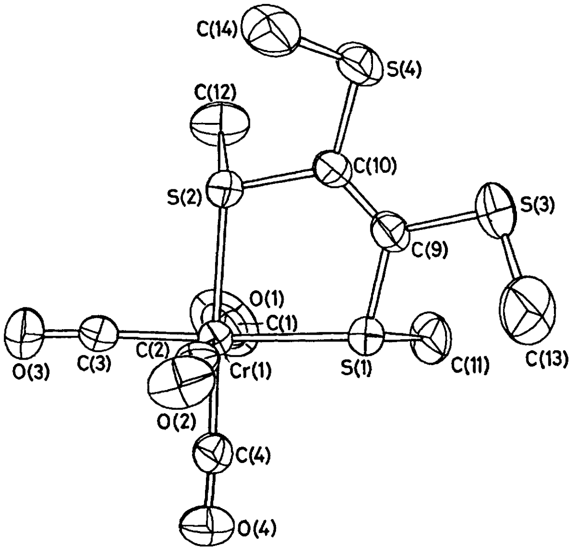


FIGURE 2 View of one of the two molecules of complex (9a) in the asymmetric unit, approximately perpendicular to the five-membered chelate ring. The thermal ellipsoids represent a 50% probability distribution

The Cr–S distances [2.370(2)—2.385(2) Å] are comparable with the values [2.38(1)—2.41(1) Å] in tris(dithiobenzoato)chromium(III).[17] They are significantly longer than the length of 2.337(2) Å in $[\mathrm{Cr(en)_2\{O_2CCH_2(SH)\}}][\mathrm{ClO_4}]_2$,[18] and substantially shorter than the value of 2.510(2) Å in $[\mathrm{Cr(CO)_5(PMe_3S)}]$,[19] indicating some Cr–S π interaction.

The Cr–CO geometry is as expected and similar to many other studies.[20] The Cr–CO bond lengths are shorter when *trans*, rather than *cis*, to S, and are not significantly different from values found in *cis*-$[\mathrm{Cr(CO)_4\{S{:}\overline{CN(Me)CH_2CH_2N}Me\}_2}]$.[11]

TABLE 4

Least-squares planes, expressed in the form $Px + Qy + Rz - S = 0$, with displacements (Å) of atoms from these planes

(*i*) Planes and deviations

(*a*)		(*b*)		(*c*)		(*d*)	
S(1)	0.001(2)	Cr(1)	0	S(5)	−0.001(2)	Cr(2)	0
S(2)	−0.001(2)	S(1)	0	S(6)	0.001(2)	S(5)	0
C(9)	−0.025(8)	S(2)	0	C(19)	0.024(8)	S(6)	0
C(10)	0.025(8)			C(20)	−0.023(8)		
Cr(1)	−0.217(1)			*Cr(2)*	0.162(1)		
S(3)	−0.003(3)			*S(7)*	0.044(3)		
S(7)	0.148(3)			*S(8)*	−0.149(3)		

Italicised atoms were not used in the derivation of the plane.

(*ii*) Equations

	(*a*)	(*b*)	(*c*)	(*d*)
P	0.356 6	0.300 7	0.499 0	0.460 1
Q	0.305 7	0.207 8	−0.143 9	−0.066 9
R	−0.882 8	−0.930 8	−0.854 6	−0.885 4
S	−5.198 6	−6.276 4	−3.150 6	−3.135 9

(*iii*) Dihedral angles (°)

(*a*)—(*b*) 7.03; (*a*)—(*c*) 27.33; (*b*)—(*d*) 18.46; (*a*)—(*d*) 22.30; (*b*)—(*c*) 23.71; (*c*)—(*d*) 5.25; av. = 6.14.

TABLE 5

Atomic positional (fractional) parameters

Atom	*x*	*y*	*z*
Cr(1)	0.394 1(1)	0.202 7(1)	0.656 9(1)
Cr(2)	0.040 2(1)	−0.056 4(1)	0.252 6(1)
S(1)	0.600 7(2)	0.229 5(1)	0.724 9(2)
S(2)	0.369 8(2)	0.308 3(1)	0.686 3(2)
S(3)	0.757 9(2)	0.339 1(1)	0.835 5(2)
S(4)	0.530 1(2)	0.418 5(1)	0.786 6(2)
S(5)	−0.166 0(2)	−0.026 1(1)	0.162 6(2)
S(6)	0.076 5(2)	0.050 3(1)	0.256 4(2)
S(7)	−0.309 5(2)	0.088 3(1)	0.066 6(2)
S(8)	−0.067 4(2)	0.166 7(1)	0.174 2(2)
O(1)	0.323 7(6)	0.214 3(3)	0.414 9(5)
O(2)	0.438 6(6)	0.166 3(3)	0.885 2(5)
O(3)	0.136 9(5)	0.173 6(3)	0.590 7(5)
O(4)	0.431 7(5)	0.070 0(3)	0.630 2(6)
O(5)	0.060 0(6)	−0.060 5(3)	0.483 8(6)
O(6)	0.046 7(11)	−0.070 1(4)	0.037 0(8)
O(7)	0.304 1(6)	−0.084 2(3)	0.359 5(8)
O(8)	−0.016 6(8)	−0.189 3(3)	0.227 7(8)
C(1)	0.354 0(7)	0.212 6(4)	0.507 7(8)
C(2)	0.424 1(7)	0.183 6(3)	0.801 0(7)
C(3)	0.236 0(7)	0.186 2(3)	0.615 2(6)
C(4)	0.420 5(7)	0.121 7(4)	0.640 6(7)
C(5)	0.048 8(8)	−0.058 3(4)	0.394 6(9)
C(6)	0.039 2(11)	−0.062 4(4)	0.114 4(10)
C(7)	0.202 4(9)	−0.073 4(4)	0.317 9(9)
C(8)	0.003 3(9)	−0.138 5(4)	0.238 0(9)
C(9)	0.613 7(6)	0.306 5(3)	0.771 0(7)
C(10)	0.517 0(7)	0.340 6(3)	0.751 4(7)
C(11)	0.645 6(7)	0.238 8(4)	0.615 3(8)
C(12)	0.304 2(8)	0.352 9(4)	0.559 6(7)
C(13)	0.851 4(8)	0.275 0(5)	0.913 0(9)
C(14)	0.430 8(9)	0.427 3(4)	0.849 4(9)
C(15)	−0.238 3(8)	−0.029 0(4)	0.253 7(9)
C(16)	0.129 0(8)	0.083 7(4)	0.392 2(7)
C(17)	−0.370 6(11)	0.043 0(5)	−0.059 6(10)
C(18)	0.065 2(8)	0.184 3(3)	0.156 0(8)
C(19)	−0.167 5(6)	0.054 2(3)	0.141 4(7)
C(20)	−0.066 3(6)	0.087 0(3)	0.183 9(6)

EXPERIMENTAL

General Procedures. All the reactions were carried out under an atmosphere of dry dinitrogen. Hydrocarbon and ether solvents were dried over sodium wire and distilled before use, and chlorinated solvents were distilled from P_4O_{10}. Analyses were carried out in our microanalytical laboratory by Mr. and Mrs. A. G. Olney, and ^{13}C n.m.r. spectra were obtained by Mr. T. M. Siverns on a JEOL PFT-100 Fourier-transform spectrometer. Infrared spectra (250—4 000 cm^{-1}) were examined as dilute Nujol mulls or as dilute solutions using a Perkin-Elmer 457 grating spectrophotometer, and ^{1}H n.m.r. spectra were recorded on Varian Associates HA-100, A60, or T60 spectrometers. Melting points were determined in evacuated sealed tubes and are uncorrected. The electron-rich olefins (1) [21] and (2) [22] were prepared by literature methods. Other starting materials were prepared by standard procedures (see Scheme), and $[M(CO)_6]$ (M = Cr, Mo, or W) were used as purchased from Alfa Ventron Ltd.

Crystal Data.—$C_{10}H_{12}CrO_4S_4$, $M = 376.46$, Monoclinic, $a = 12.487(1)$, $b = 21.838(2)$, $c = 13.686(1)$ Å, $\beta = 117.32(1)°$, $U = 3\,315.7$ Å^3, $D_m = 1.50$, $Z = 8$, $D_c = 1.508$ g cm^{-3}, $F(000) = 1\,536$, space group $P2_1/c$ (C^5_{2h}), Cu-K_α radiation, $\lambda = 1.541\,8$ Å, $\mu = 104.97$ cm^{-1}.

Cell dimensions were obtained by least-squares refinement of the setting angles of 12 carefully centred reflections having 2θ values between 90 and 120° on a Picker FACS1 automatic four-circle diffractometer using Cu-$K_{\alpha1}$ radiation (λ 1.540 51 Å) with a graphite crystal monochromator. A small well formed yellow crystal of dimensions $0.1 \times 0.1 \times 0.2$ mm was used for data collection with its *a* axis approximately coincident with the instrumental ϕ axis. Intensity data were collected by the θ—2θ continuous scan technique using a scan speed of 2° min^{-1} and scan range from $(2\theta - 0.9)°$ to $(2\theta + 0.9 + \Delta)°$ where Δ is the 2θ separation of the Cu-$K_{\alpha1}$ and -$K_{\alpha2}$ peaks for the reflection concerned. Stationary background counts of 10-s duration were made at each extreme of the scan range. Intensities of three standard reflections were monitored periodically to check crystal and electronic stability. No significant crystal decomposition was observed. Intensities were collected for reflections with $3 < 2\theta$ (Cu-K_α) $< 126°$. Of the 5 892 intensities measured, 3 589 (61%) for which $I > 3\sigma(I)$ were accepted as being significantly above background and after sorting and averaging only the unique 3 246 were used in subsequent calculations.

A value of 0.03 was used for the experimental uncertainty factor *p*.[23] Intensities were corrected for Lorentz and polarisation effects and later for absorption. Transmission factors for F_o, calculated using the analytical method of De Meulenauer and Tompa,[24] varied from 0.509 7 to 0.684 2.

Structure Analysis.—The crystallographic asymmetric unit consists of two molecules, which made the Patterson solution rather complicated due to the extensive overlap of Cr–S vectors. The use of the direct-methods system MULTAN [25] readily revealed the two molecules. The structure was refined by full-matrix least squares, the function minimised being $\Sigma w(|F_o| - |F_c|)^2$ where $w = I/\sigma^2(F)$. The values of R and $R'\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}\}$ at convergence of the refinement of the fully anisotropic model using absorption-corrected data were 0.049 and 0.060, respectively. Atomic scattering factors and values of the anomalous dispersion were taken from ref. 26. Hydrogen-atom positions were not clearly discernible from difference maps and were not included in any calculations. The large thermal parameters of some atoms [O(6) in particular] implies some degree of positional disorder; several unsuccessful attempts were made to resolve this.

In the final cycle of refinement no parameter shifted by more than 0.04 times its standard deviation. The adequacy of the weighting scheme was confirmed by analyses of $w(|F_o| - |F_c|)^2$ against F_o and $(\sin\theta)/2$ which showed no systematic trends. The standard deviation of an observation of unit weight was 2.04. There were no peaks in the final difference map >0.4 e Å^{-3}. Atomic positional parameters are shown in Table 5. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22377 (14 pp.).* The ANUCRYS (1975) system of crystallographic programs, as implemented on the UNIVAC 1108 at A.N.U. by P. O. Whimp and D. Taylor, was used throughout the structure analysis.

Complexes cis-$[M(CO)_4(L^{SR}{}_2)]$ (M = Cr *or* W; R = Me *or* Et). *Method* (*A*). A mixture of hexacarbonylchromium(0) (1.1 g, 5 mmol) and tetrakis(methylthio)ethene (1 g, 5 mmol) in thf (50 cm^3) was irradiated (25 °C, 5 h) using a water-cooled medium-pressure mercury 100-W Hanovia u.v. lamp. The dark solution was taken to dryness *in vacuo* to leave an oily residue which was extracted with warm hexane (2×10 cm^3). These extracts were filtered and combined. Cooling (−30 °C) afforded yellow crystals of cis-*tetracarbonyl*[*tetrakis*(*methylthio*)*ethene*-SS″]-*chromium*(0) (0.3 g). This method was used for several analogues: M = Cr, R = Me or Et, and M = Mo or W, R = Et.

Method (*B*). To a suspension of $[M(CO)_6]$ (1.1 g, 5 mmol) and tetrakis(ethylthio)ethene (1.35 g, 5 mmol) in ethanol (25 cm^3) was added a microspatula of sodium tetrahydroborate. The reaction mixture was heated under reflux for 5 h, resulting in a dark solution. The products were isolated using a similar work-up to method (A), and was used for M = Cr, Mo, or W, R = Et.

Complexes fac-$[M(CO)_3(PPh_3)(L^{SEt}{}_2)]$ (M = Cr, Mo, *or* W). To a suspension of tris(acetonitrile)tricarbonylchromium(0) (0.5 g, 2 mmol) in toluene (25 cm^3) was added $C_2(SEt)_4$ (0.54 g, 2 mmol). The orange reaction mixture was stirred for 1 h at 25 °C, followed by addition of triphenylphosphine (0.52 g, 2 mmol). Further stirring (1 h) resulted in an orange solution. Addition of hexane and cooling to −30 °C afforded orange crystals which were recrystallised from CH_2Cl_2–hexane to give fac-*tricarbonyl*[*tetrakis*(*ethylthio*)*ethene*-SS″](*triphenylphosphine*)*chromium*(0) (0.7 g). The molybdenum and tungsten adducts were prepared in a similar manner.

Complexes $[Cr(CO)_5(L^{SEt}{}_2)]$ *and* $[Cr(CO)_5\{(\colon\overline{CSCH_2CH_2S})_2\}]$. *Method* (*A*). To a solution of tetraethylammonium pentacarbonylchlorochromate(0) (1.0 g, 3 mmol) and $C_2(SEt)_4$ (0.8 g, 3 mmol) in CH_2Cl_2 (25 cm^3) was added triethyloxonium tetrafluoroborate (0.6 g, 3.1 mmol). The reaction mixture was taken to dryness and the resulting yellow oil placed on to a dry 15-cm alumina column. The column was eluted with pentane, the first yellow band being the product. Concentration of the pentane and cooling to −65 °C gave analytically pure yellow crystals of *pentacarbonyl*[*tetrakis*(*ethylthio*)*ethene*-S]-*chromium*(0) (0.4 g).

Method (*B*). A solution of $[Cr(CO)_6]$ (0.44 g, 2 mmol) and 2,2′-bi(1,3-dithiolanylidene) in a thf solution (20 cm^3) were irradiated at 25 °C for 3 h. Removal of solvent followed by extraction with warm hexane (2×10 cm^3) gave a pale-yellow solution, which on cooling gave pale-yellow crystals of [2,2′-*bi*(1,3-*dithiolanylidene*)-S]*pentacarbonylchromium*(0).

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* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

We thank Drs. B. Çetinkaya [preparation of complex (9a)] and P. L. Pye [preparation of a suitable crystal of (9a) for the *X*-ray study] for their contributions, and the S.R.C. for the award of a studentship (to D. B. S.).

[8/353 *Received, 27th February,* 1978]

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