Metal carbonyl complexes of some aromatic *ortho* bis(methylthio)ethers

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Various complexes of the type $M(CO)_4L$ and $[M(CO)_4]_2L$, M = Cr, Mo, W, have been prepared and characterized. A series of aromatic *ortho* bis(methylthio)ethers were used as the ligand L. The crystal structures of the free ligand $C_6(SCH_3)_6$ and of the complex $Cr(CO)_4C_6(SCH_3)_6$ are reported.

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On a préparé divers complexes du type $M(CO)_4L$ et $[M(CO)_4]_2L$, où M = Cr, Mo, W, et on les a identifiés. On a utilisé une série d'*ortho* bis (méthylthio) éthers aromatiques comme ligand L. On rapporte la structure cristalline du ligand libre $C_6(SCH_3)_6$ et celle du complexe $Cr(CO)_4C_6(SCH_3)_6$.

[Traduit par le journal]

The ligating properties of several chelating sulfur ligands, particularly with various metal carbonyls and the platinum group metals, are the subject of continuing study (1–13). It has been shown that aromatic *ortho* bisthioethers form complexes with a number of metal ions (1). All of the complexes with simple metal ions were polymeric and could not be purified by recrystallization.

Various chromium, molybdenum, and tungsten carbonyl complexes can be formed by potentially chelating sulfur ligands. The aliphatic bisthioethers, $RS(CH_2)_xSR(L)$, give the complexes $M(CO)_5L$, $[M(CO)_5]_2L$, and $M(CO)_4L$ (2–6). However, the latter complex, $M(CO)_4L$, is only obtained when $x = 2$, and the complex contains a five-membered ring. Similar complexes have been prepared with some *ortho* bisthioethers (L1, L3, L9, L10) (1, 7, 8) and tetrakis(alkylthio)ethenes (9). The tetrakis(alkylthio)ethenes could form two five-membered chelate rings in complexes such as $[M(CO)_4]_2L$, although these were not reported (9). The crystal structure of $W(CO)_4L$, L = o-$(MeS)_2C_6H_4$, has been noted (7).

Molybdenum and tungsten hexacarbonyls react with the macrocyclic ligand 2,6,15,19-tetrathia-[7.7]paracyclophane (TTPH) to form the complexes $TTPH[M(CO)_4]_2 \cdot 2C_6H_6$ (M = Mo, W) and $TTPH[W(CO)_5]_2$ (10). The former two involve the coordination of the $M(CO)_4$ unit to two sulfur atoms and the formation of a six-membered ring, basically $M(CO)_4RS(CH_2)_3SR'$. However, with chromium hexacarbonyl several products are formed, the main one being the π complex (η^6TTPH) chromium tricarbonyl (11). Other

products characterized include elimination of the 1,3-propanedithia unit, and coordination of $Cr(CO)_4$ or $Cr(CO)_5$ units to sulfur atoms.

A further series of potential sulfur containing ligands of formula $C_6(SMe)_xH_{6-x}$ has been prepared (14). This paper is an extension of previous studies of the ligand properties of aromatic *ortho* bis(methylthio)ethers (1), with particular reference to the chromium, molybdenum, and tungsten carbonyl complexes. The ligands studied (L1, L2, L3, L4, L5, L6, L7, and L8) are shown below.
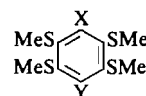
L1, X = Y = SMe
L2, X = SMe, Y = H
L3, X = Y = F
L4, X = Y = Cl
L5, X = Y = H
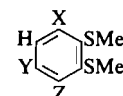
L6, X = Z = SMe, Y = H
L7, X = Y = SMe, Z = H
L8, Y = Z = H, Y = SMe
L9, X = Z = F, Y = SMe
L10, X = Z = F, Y = H

Various carbonyl complexes can be postulated, depending on the specific ligand. All the ligands should form the simple complexes $M(CO)_4L$ (1),

whereas the ligands L1, L2, L3, L4, L5, and L6 have two potentially chelating functions and the
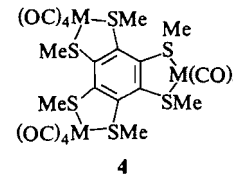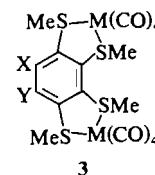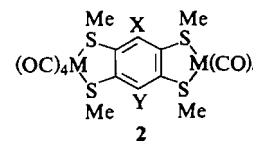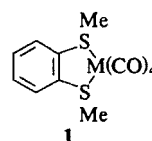
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TABLE 1. Products and analyses

Product	Color	Decomp. temp. (°C)	Method	Ratio M:L	Solvent†	Time	Yield‡ (%)	Found (%)		Calcd. (%)	
								C	H	C	H
$Cr(CO)_4L$	Yellow	113	A	2:1	tol	20d	32	37.2	3.37	37.1	3.50
$Mo(CO)_4L$	Green–yellow	95	A	1:1	tol	16h	77	34.6	3.06	34.2	3.22
				2:1	hex	2d	56				
$W(CO)_4L1$	Lemon	110–111*	B	1.2:1	THF	12m	4	30.2	3.00	29.5	2.79
			C	1.2:1	THF	1.5h	25				
			C	1:1	CH_2Cl_2	5h	11				
$[Cr(CO)_4]_2L1$	Orange	170	D	2:1	EtOH,P	18h	62	33.6	2.92	35.2	2.64
$[Mo(CO)_4]_2L1$	Yellow	155	A	2:1	tol	2d	80	31.0	2.83	31.2	2.35
$[W(CO)_4]_2L1$	Yellow–brown	130	C	3:1	THF	2h	9	26.3	2.11	25.4	1.92
$Cr(CO)_4L2$	Yellow	135	A	1:1	tol	6d	33	38.0	3.56	38.1	3.41
			B	2:1	THF	45m	54				
			D	2:1	EtOH,P	21h	83				
$Mo(CO)_4L2$	Green–yellow	125	A	2:1	hex,P	2d	31	34.8	2.79	34.9	3.12
			A	2:1	tol,P	1d	23				
$W(CO)_4L2$	Yellow–brown	130	C	1:1	THF	1h	24	29.4	3.46	29.8	2.67
$Mo(CO)_4L3$	Light brown	66–68*	A	1:1	tol	1d	70	33.4	2.41	33.1	2.39
$[Cr(CO)_4]_2L3$	Orange	115	D	2:1	EtOH	2d	25	34.4	2.17	34.5	1.93
$[Mo(CO)_4]_2L3$	Yellow–brown	120	A	4:1	CH_2Cl_2	10d	77	30.1	1.94	30.3	1.69
$Cr(CO)_4L4$	Yellow	135	A	1:1	tol	5d	50	33.5	3.40	33.9	2.44
$Cr(CO)_4L5$	Yellow	145	A	2:1	tol	5d	38	39.7	3.47	39.4	3.31
			D	2:1	EtOH,P	22h	84				
$Mo(CO)_4L5$	Pale green	70	A	1:1	tol,P	2d	43	35.4	2.94	35.7	3.00
$W(CO)_4L5$	Lemon	135	C	1:1	THF	1h	10	30.4	3.19	30.1	2.53
$Cr(CO)_4L6$	Yellow	130	A	1:1	tol	4d	23	39.6	3.38	39.4	3.31
			D	2:1	EtOH,P	1d	30				
$Mo(CO)_4L6$	Yellow–brown	125	A	1:1	tol	5h	53	35.3	3.19	35.7	3.00
$W(CO)_4L6$	Lemon	130	C	1.2:1	THF	2h	37	30.3	2.80	30.1	2.53
$Cr(CO)_4L7$	Orange	122–124*	A	1:1	tol	2d	43	39.5	3.30	39.4	3.31
$Mo(CO)_4L7$	Brown–yellow	128	A	1:1	tol	20h	75	36.6	3.15	35.7	3.00
$W(CO)_4L7$	Yellow	120	C	1.2:1	THF	2h	49	30.7	2.61	30.1	2.53
$Cr(CO)_4L8$	Orange–yellow	75–77*	A	1:1	tol	5d	55	41.0	3.30	41.0	3.18

*Melting point.
†tol = toluene, hex = n-hexane, P = precipitate formed.
‡Based on amount of ligand taken.

complexes $[M(CO)_4]_2L$, structure **2** or **3**, can be postulated. Similarly, it might be possible to prepare the complexes $[M(CO)_4]_3L$ (**4**) from L1.

The complexes $M(CO)_4L$ were readily prepared. Several attempts, mostly unsuccessful, were made to prepare the complexes $[M(CO)_4]_2L$ using an excess of the carbonyl reactant. Although analogous complexes with one polyfunctional sulfur ligand bonded to two metals are not known, some similar complexes with two metals and two ligands have been prepared, such as $Rh_2Cl_2(\mu\text{-CO})$-$(PhSCH_2SPh)_2$ (**13**) and the group V ligand complexes, $(OC)_4M(EMe_2—EMe_2)_2M(CO)_4$, M = Cr, W, Mo; E = P, As, with six-membered rings (**15**).

The complexes were obtained from *cis* metal tetracarbonyls, $M(CO)_4X_2$, specifically norbornadiene chromium and molybdenum tetracarbonyls and bis(acetonitrile)tungsten tetracarbonyl and the desired ligand in hexane, toluene, or THF solution (tungsten complexes). Some complexes were also prepared by irradiation of chromium hexacarbonyl

to form $Cr(CO)_5$.THF, which then reacted with the ligand or from $Et_4N[Cr(CO)_5Cl]$ in ethanol. The yields were very low when tungsten hexacarbonyl was irradiated. The tungsten complexes could not be prepared from *cis*-bis(piperidine)molybdenum tetracarbonyl (**16**) as the free piperidine generated in the reaction reacted with the sulfur-containing ligand, presumably nucleophilically displacing a methylthio group.

The complexes isolated were mainly of the type $M(CO)_4L$, see Table 1, and did not usually depend on the reactant stoichiometry. Although the chromium complex $Cr(CO)_4L$ was readily prepared the complex $[Cr(CO)_4]_2L$ was not obtained from an excess of $C_7H_8Cr(CO)_4$ or $Cr(CO)_5THF$ with L. The complexes $[Cr(CO)_4]_2L$ (L = L1, L3) were precipitated from ethanol solutions of Et_4N-$[Cr(CO)_5Cl]$ and L, in stoichiometry 2:1; under the same conditions with L2, L5, and L6 the complex $Cr(CO)_4L$ precipitated. Even with reactant stoichiometry 3:1 $W(CO)_4(MeCN)_2$:L in THF solution

it was generally only possible to isolate or detect in solution the complexes [W(CO)$_4$L]. However, depending on the stoichiometry, the complexes W(CO)$_4$C$_6$(SMe)$_6$ and [W(CO)$_4$]$_2$C$_6$(SMe)$_6$ could be prepared. The reactions of C$_7$H$_8$Mo(CO)$_4$ with the various ligands were usually studied in toluene solution where precipitation of Mo(CO)$_4$L sometimes occurred. The reactions with molar ratios C$_7$H$_8$Mo(CO)$_4$:L, 2:1, were studied in either toluene or methylene chloride, depending on the solubility of Mo(CO)$_4$L. The nmr spectra of the initial products indicated that although small amounts of [Mo(CO)$_4$]$_2$L may have been formed in several reactions, it was only possible to isolate this product when L = L1 or L3. The molybdenum complexes were often formed with incorporation of some solvent in the crystal lattice. This was detected in the nmr spectra and thermal analysis showed a loss of weight (less than 5%) accompanied by an endothermic change before decomposition. Incorporation of solvent benzene in some molybdenum complexes Mo(CO)$_4$L with sulfur-containing ligands has been noted previously (10).

The formation of the complexes Cr(CO)$_4$L clearly depends on the bulk of the methyl group. When p-F$_2$C$_6$(SBu^t)$_4$ was used as a potential ligand no reaction occurred in four days at 45°C with C$_7$H$_8$Cr(CO)$_4$, although C$_7$H$_8$Cr(CO)$_4$ reacted within 2 days with other ligands containing the methyl group at 45°C. It can be inferred that the large tertiary butyl group blocks the coordination of the metal to the sulfur.

The number of *ortho* methylthio groups in a ligand also determines the ease of the reaction. In a reaction of 1 mmol of C$_7$H$_8$Cr(CO)$_4$ with 1 mmol of each of L1 and L5 in toluene at 45°C, the C$_7$H$_8$Cr(CO)$_4$ had all reacted within one day. The nmr spectrum of the product, after removal of the solvent, showed that approximately 75% of L1 had formed the complex Cr(CO)$_4$L1. The ligand L1 with six possible *ortho* bis(methylthio) sites for coordination clearly forms the complex Cr(CO)$_4$L more readily than L5 which has only two *ortho* bis(methylthio) sites.

The structures of the products in solution were determined from their infrared and nmr (H-1) spectra. The spectroscopic data cannot, however, distinguish between the simple monomeric complex, M(CO)$_4$L, and a dimer, such as 5. However, as the solutions used in the preparations were relatively concentrated (0.05 M ~ 0.02 M), the possibility of the formation of 5 can be excluded. The crystal structure of Cr(CO)$_4$L1 shows that it is monomeric in the solid state.

The carbonyl vibrations, tabulated in Table 2,
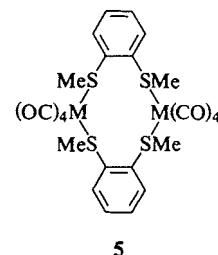
5

are all consistent with the established values for *cis*-tetracarbonyl complexes, *cis*-M(CO)$_4$X$_2$ (1, 9). The proton nmr spectra were normally recorded in benzene or methylene chloride solutions (see Table 2). The complexes decomposed readily in solvents such as deuterochloroform in which they are readily soluble. The structure 1 is clearly indicated for the complexes M(CO)$_4$L1 as three distinct methyl groups are observed in the proton nmr spectra with intensity ratio 1:1:1. Similarly, with the ligands L3, L4, L5, L7, and L8 where only one isomeric product is possible, the structure 1 is clearly indicated by the nmr spectra. The possibility of a π complex, as occurs in bis(methylthio-η-benzene) chromium (18) and the η^6 arene compound Cr(CO)$_3$C$_6$H$_5$—SC$_6$H$_5$ (19) can be excluded.

Comparison of the nmr spectra of the complexes and the free ligand in CH$_2$Cl$_2$ or CDCl$_3$ solution shows that the protons of the methyl group bonded to the ligand sulfur in the complexes M(CO)$_4$L are deshielded by approximately 0.30 ppm (Cr), 0.38 ppm (Mo), and 0.57 ppm (W) and that there is somewhat greater deshielding in the complexes [M(CO)$_4$]$_2$L. Similar deshielding has been observed in the complexes M(CO)$_5$SRR^1 (M = Cr, Mo, W), with the magnitude of the deshielding Cr < Mo < W (19, 20). The chemical shifts of the other methyl protons are relatively unchanged in comparison with the free ligand. This deshielding effect is not as clearly observed in benzene solution, with respect to the free ligand, but the magnitude of the deshielding is still Cr < Mo < W.

With the ligands L2 and L6, two isomeric products M(CO)$_4$L can be postulated, 6 and 7.
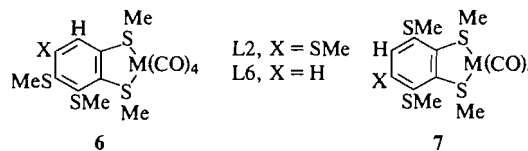
6   7

The nmr spectra of both the M(CO)$_4$L (L = L2, L6) complexes indicate that only one isomeric product is formed. The structure 7 is clearly shown in the spectrum of the L6 complexes as only two methyl proton signals are observed. Similarly, it can be postulated from the observed spectrum of L2 and

TABLE 2. CO absorptions and summary of nmr data

Compound	CO absorptions (cm^{-1})*	H nmr chemical shifts (ppm) and intensity ratios†
L1		2.49s
Cr(CO)$_4$L1	2014s, 1912sh, 1902vs, 1881s	2.76s, 2.54s, 2.52s(1:1:1)
Mo(CO)$_4$L1	2021s, 1915sh, 1910vs, 1886s	2.83s, 2.53s, 2.51s(1:1:1)
W(CO)$_4$L1	2018s, 1905sh, 1901vs, 1882(C$_6$H$_6$)	2.99s, 2.55s, 2.54s(1:1:1)
[Cr(CO)$_4$]$_2$L1	2015s, 1915sh, 1908vs, 1878(CH$_2$Cl$_2$)	2.90s, 2.65s(2:1)
[Mo(CO)$_4$]$_2$L1	2024s, 1923vs, 1920s, 1881s(CH$_2$Cl$_2$)	2.92s, 2.61s(2:1)
[W(CO)$_4$]$_2$L1	2016s, 1912sh, 1905vs, 1883s(THF)	3.16s, 2.65s(2:1)
L2		2.49s, 2.45s, 2.37s, 6.41s(3:6:6:1)
Cr(CO)$_4$L2	2015s, 1915sh, 1902vs, 1880s	2.79s, 2.64s, 2.57s, 2.49s, 2.40s, 6.90s(3:3:3:3:3:1)
Mo(CO)$_4$L2	2022s, 1914sh, 1911vs, 1884s	2.85s, 2.74s, 2.57s, 2.48s, 2.40s, 6.91s(3:3:3:3:3:1)
W(CO)$_4$L2	2018s, 1910sh, 1901vs, 1877s(C$_6$H$_6$)	3.01s, 2.90s, 2.55s, 2.46s, 2.37s, 6.84s(3:3:3:3:3:1)
L3		2.45T(J(H—F) 1.0Hz)‡
Cr(CO)$_4$L3	2020s, 1925s, 1910s, 1890s(ref. 1)	2.77s, 2.59T(J(H—F)0.55Hz) (ref. 1) (1:1)
Mo(CO)$_4$L3	2028s, 1920sh, 1916vs, 1891s	2.81s, 2.55T(J(H—F)1.1Hz) (1:1)‡
W(CO)$_4$L3	2018s, 1925m, 1907m, 1901m(ref. 1)	2.98s, 2.54T(J(H—F)1.3Hz) (ref. 1) (1:1)
[Cr(CO)$_4$]$_2$L3	2022s, 1922sh, 1918vs, 1886s(CH$_2$Cl$_2$)	2.81s
[Mo(CO)$_4$]$_2$L3	2026s, 1926vs, 1920sh, 1887s(CH$_2$Cl$_2$)	2.87s
L4		2.47s
Cr(CO)$_4$L4	2018s, 1920sh, 1902vs, 1888s	2.74s, 2.50s(1:1)
L5		2.46s, 7.05s(6:1)
Cr(CO)$_4$L5	2016s, 1915sh, 1903vs, 1879s	2.72s, 2.54s, 7.42s(3:3:1)
Mo(CO)$_4$L5	2024s, 1916sh, 1913vs, 1884s	2.77s, 2.51s, 7.42s(3:3:1)
W(CO)$_4$L5	2018s, 1903sh, 1899vs, 1876s(THF)	2.94s, 2.52s, 7.45s(3:3:1)
L6		2.39s, 7.05s(6:1)
Cr(CO)$_4$L6	2012s, 1913sh, 1904vs, 1880s	2.71s, 2.55s, 7.25s(3:3:1)
Mo(CO)$_4$L6	2022s, 1915sh, 1911vs, 1883s	2.75s, 2.51s, 7.23s(3:3:1)
W(CO)$_4$L6	2017s, 1908sh, 1901vs, 1879s(C$_6$H$_6$)	2.95s, 2.54s, 7.27s(3:3:1)
L7		2.47s, 2.39s, 2.24s, 6.67s(3:6:3:2)
Cr(CO)$_4$L7	2017s, 1907sh, 1904vs, 1879s	2.72s, 2.60s, 2.25s, 7.25d, 6.95d(3:3:6:1:1)§
Mo(CO)$_4$L7	2024s, 1920sh, 1910vs, 1883s	2.83s, 2.70s, 2.55s, 7.26d, 6.94d(3:3:6:1:1)§
W(CO)$_4$L7	2019s, 1908sh, 1901vs, 1874s	2.97s, 2.86s, 2.54s, 7.28d, 6.96d(3:3:6:1:1)§
L8		2.44s, 2.42s, 2.39s, 7.06m(1:1:1:1)
Cr(CO)$_4$L8	2016s, 1920sh, 1902vs, 1888s	2.72s, 2.67s, 2.50s, 7.50m(1:1:1:1)

*Measured in toluene solution.
†Measured in CH$_2$Cl$_2$ solution.
‡F-19 L3, 101.4s (CFCl$_3$/CCl$_4$ ref. 17); Mo(CO)$_4$L3, 99.84s(CFCl$_3$/CDCl$_3$).
§M(CO)$_4$L7, J(H—H) (Hz): M = Cr, 2.0; M = Mo, 1.8; M = W, 1.7.

the magnitude of the deshielding found in the other complexes that the probable structure of the M(CO)$_4$L2 complexes is also 7, rather than 6.

In the free ligand L3, the methyl protons are coupled to the fluorine, and appear as a triplet (17). This can be attributed to steric through space coupling, with free rotation about both the aromatic carbon–sulfur and the methyl carbon–sulfur bonds. In the complexes there is increasing rigidity of the aromatic carbon–sulfur bond, so that no coupling to fluorine is observed in [M(CO)$_4$]$_2$L3. However, in the complexes M(CO)$_4$L3, two distinct methyl groups are observed. The methyl group bonded to the coordinated sulfur is a singlet, whereas the methyl group bonded to non-coordinated sulfur still appears as a triplet.

While the structures of the complexes [M(CO)$_4$]$_2$L3 must be unambiguously assigned as 2, it is not clear from the nmr spectra whether the complexes [M(CO)$_4$]$_2$L1 have structure 2 or 3. Two distinct methyl groups are observed in the proton nmr spectrum, with intensity ratio 2:1.

Similarly, any complexes of the type [M(CO)$_4$]$_2$L could have structure 2, when L = L2, L5, and structure 3, when L = L2 or L6. There was no indication of any complexes [M(CO)$_4$]$_2$L being formed with L2, L5, or L6. If the complexes were formed with L6, some rearrangement must have occurred in the solution as the complexes M(CO)$_4$L6 all have structure 7. The different abilities of the somewhat analogous ligands L3 and L5 to form the [M(CO)$_4$]$_2$L complexes may be due to the differences in size of hydrogen and fluorine.

The crystal structures of the free ligand C$_6$(SCH$_3$)$_6$, L1, and the chromium complex Cr(CO)$_4$L1 have been examined and compared.

They are shown in Figs. 1, 2, and 3 and some bond lengths and angles are tabulated in Tables 3 and 4.

In the crystal all $C_6(SCH_3)_6$ molecules are found to have a crystallographic centre of symmetry in their middle. The C_6S_6 fragment is only roughly planar. With the carbon atoms deviating from a best plane through the origin by ±0.03 Å (signs alternating) the benzene ring is slightly puckered. Deviations of the sulfur atoms from this plane are considerably higher (S1: 0.22 Å, S2: 0.25 Å; S3: 0.24 Å), probably caused by short non-bonding S...S-contacts (Table 3).

While the low temperature nmr spectrum of $C_6(SCH_3)_6$ ($-75°C$ in CS_2) indicates that all the methyl groups are equivalent, in the solid state three adjacent methyl groups are situated above the plane, the other three below. The aromatic C—S bond length and S—CH$_3$ bond lengths are as expected, but the aromatic C—S bond length, average 1.78 Å, is approximately 0.05 Å lower than the anticipated sum of the covalent radii (21); however, values of 1.74 and 1.76 Å are reported in di-p-toly sulfide (22).

The structure of $Cr(CO)_4C_6(SCH_3)_6$ does not show fundamental changes within the ligand. Still some changes in the SCCS torsion angles can be observed, possibly due to complexation, though it cannot be excluded that intermolecular packing gives rise to similar effects. Bonding to the chromium atom apparently reduces the angle S1C1C2S2 from the range of 11.7°–13.6° in the free ligand to 5.4° in the complex, thus enabling the chelate ring to be more planar. Contrary to that, the carbon–sulfur bonds to S4 and S5 opposite the bonded part of the ligand enclose a torsion angle of 19.8° which is unusual for adjacent sp^2-centres normally being
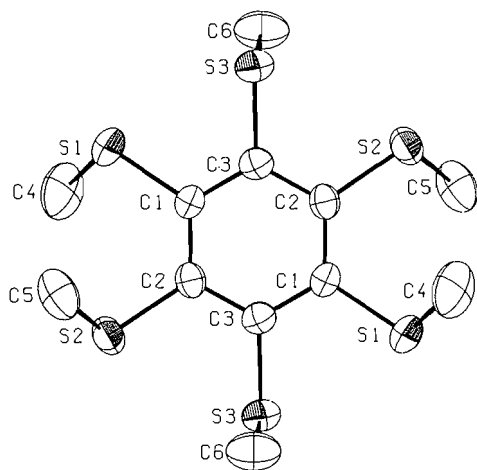
Fig. 3. ORTEP-plot (50% probability) of the complex Cr(CO)$_4$L1 direction of view from atom S1 to atom S2.

coplanar. As for the aromatic carbon-bridging sulfur bond lengths, however, there is virtually no change from those observed in the free ligand.

In the crystal three of the methyl groups bonded to non-coordinated sulfur are on one side of the ligand plane and only one on the other. This may be due to packing as the room temperature nmr spectrum (CH_2Cl_2) shows that there are three distinct methyl groups of equal intensity. On cooling the peaks broaden somewhat and below $-25°C$ the peaks due to the methyl attached to non-coordinated sulfur coalesce and a single broad peak is observed.

The methyl groups bonded to the coordinated sulfur are on the same side of the ligand plane. This was also observed in $W(CO)_4L$ where $L = o$-$(MeS)_2C_6H_4$ (7) and in the complex $Cr(CO)_4L$, where L is tetrakis(methylthio)ethene (9). However, in the complexes $Cr(CO)_4L$ where L is $RS(CH_2)_nSR$ ($n = 2, 3$) and the bridging $(CH_2)_n$ unit is saturated the groups R are $anti$ (5, 6).

Fig. 1. ORTEP-plot (50% probability) of the molecule $C_6(SCH_3)_6$ direction of view perpendicular to the C_6-plane.

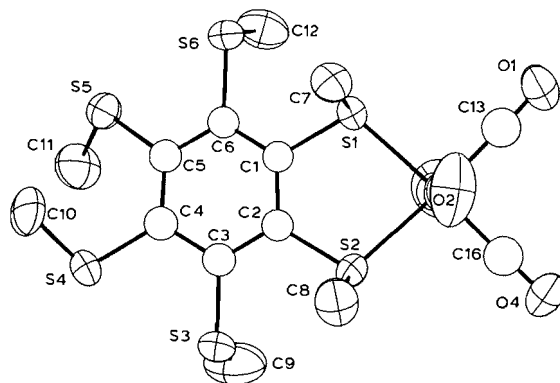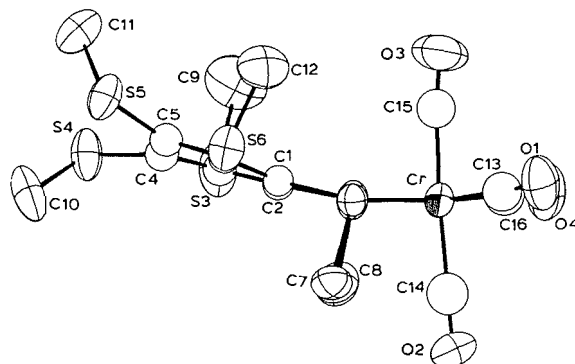TABLE 3. Some bond lengths and angles in $C_6(SMe)_6$

Bond	Length (Å)	Bond'	Angle (deg)
S1—C1	1.778(2)	C1—S1—C4	103.8(2)
S1—C4	1.805(4)	C2—S2—C5	102.4(1)
S2—C2	1.778(2)	C3—S3—C6	101.8(1)
S2—C5	1.795(3)	C1—C2—S2	123.5(2)
S3—C3	1.779(2)	C3—C2—S2	117.2(2)
S3—C6	1.794(4)	C2—C1—S1	124.3(2)
C1—C2	1.402(3)	C3—C1—S1	116.4(2)
C1—C3	1.403(3)	C1—C3—S3	119.4(2)
C2—C3	1.405(3)	C2—C3—S3	119.7(2)

Non-bonding S...S-contacts	Distance	Atoms	Dihedral angle (deg)
S1...S3	3.083(1)	S1C1C2S2	13.2
S2...S3	3.119(1)	S2C2C3S3	13.4
S1...S2	3.401(1)	S3C3C1S1	12.3

TABLE 4. Some bond lengths and angles in $Cr(CO)_4$-$C_6(SCH_3)_6$

Bond	Length (Å)	q Bonds	Angle (deg)
C1—S1	1.794(5)	C6—C1—S1	119.1(4)
C2—S2	1.788(5)	C2—C1—S1	119.5(4)
S1—C7	1.826(6)	C1—C2—S2	120.8(4)
S2—C8	1.827(7)	C3—C2—S2	119.7(4)
S1—Cr	2.368(2)	C1—S1—Cr	106.7(2)
S2—Cr	2.388(2)	C2—S2—Cr	106.2(2)
Cr—C13	1.834(6)	S1—Cr—S2	84.55(6)
Cr—C14	1.893(7)	C1—S1—C7	99.9(3)
Cr—C15	1.863(6)	C2—S2—C8	101.7(3)
Cr—C16	1.849(7)	C14—Cr—S1	93.6(2)
C1—C2	1.396(7)	C14—Cr—S2	94.1(2)
C1—C6	1.384(7)	C14—Cr—C13	91.6(3)
C2—C3	1.404(6)	C14—Cr—C16	89.6(3)
C3—C4	1.416(8)	C15—Cr—S1	88.6(2)
C4—C5	1.403(8)	C15—Cr—S2	88.6(2)
C5—C6	1.409(6)	C15—Cr—C13	85.8(3)
C3—S3	1.771(6)	C15—Cr—C16	88.2(3)
C4—S4	1.770(6)	C14—Cr—C15	176.6(3)
C5—S5	1.765(5)	C13—Cr—C16	90.3(3)
C6—S6	1.775(5)	O1—C13—Cr	176.3(6)
S3—C9	1.832(9)	O2—C14—Cr	178.8(7)
S4—C10	1.825(8)	O3—C15—Cr	173.3(6)
S5—C11	1.817(8)	O4—C16—Cr	177.5(6)
S6—C12	1.801(7)		
C13—O1	1.151(7)		
C14—O2	1.140(10)		
C15—O3	1.134(9)		
C16—O4	1.163(9)		

Non-bonding atoms	Distance (Å)	Atoms	Dihedral angle (deg)
S1...S2	3.199(2)	S1C1C2S2	−5.4
S2...S3	3.203(3)	S2C2C3S3	+2.4
S3...S4	3.103(3)	S3C3C4S4	+13.8
S4...S5	3.419(3)	S4C4C5S5	−19.8
S5...S6	3.089(3)	S5C5C6S6	+10.3
S6...S1	3.170(2)	S6C6C1S1	+1.5

As there is an angle of 13.3° between the plane S1CrS2 and a best plane S1C1C2S2 the chelate ring is envelope shaped. Although it would be tempting to attribute this angle to the space requirements of the methyl groups at C7 and C8, this is apparently not justified, since the chelate ring in $Cr(CO)_4L$, L = bis(t-butylthio)ethene, with far more bulky groups in the same positions is reported to be planar.[2] The structure with L = tetrakis(methyl-thio)ethene (9), however, exhibits an angle of 7.03° between corresponding planes in the ring.

The coordination around chromium in the present structure is octahedral with relatively little distortion. The S—Cr—S angle of 84.5° is in good agreement with that reported in $Cr(CO)_4L$, when L = tetrakis(methylthio)ethene (83.8°) (9) or L = 3,6-dithiaoctane (85.1°) (5).

Influence of the substituents at the sulfur atom on the environment of the metal may be detected from the S—Cr—C angles, which are greater when C = C14 and smaller when C = C15 (see Table 3). A corresponding observation has been made in similar compounds (9).[2] The carbonyl group closest to sulfur is bent to an angle O3—C15—Cr of 173.3(6)° and thus distorted most from 180° with respect to the other three. It was suggested that repulsion from lone pairs of the sulfur atom might be responsible for such a distortion (5). The angle C14—Cr—C15 (176.6°) is significantly larger than that in some other $Cr(CO)_4L$ complexes, when L = bis(t-butylthio)ethane (169.8°) (6), L = 3,6-di-thiaoctane (174.7°) (5), or L = bis(t-butyl-thio)ethene (173.5°).[2]

Much discussion has been presented about Cr—S and Cr—C(O) distances in similar compounds. Values found in the present structure fit

[2]G. M. Reisner, I. Bernal, and G. R. Dobson. To be published.

quite well with those already reported. A shortening of the average Cr—S bond (2.39 Å) (2.38 Å when L = tetrakis(methylthio)ethene, 2.42 Å when L = 2,6-dithiaoctane, and 2.44 Å when L = 2,2,7,7-tetramethyl-3,6-dithiaoctane) compared to the sum of the assumed covalent radii (1.48 Å for Cr^0 (23) and 1.04 Å for sulfur (21)) has been attributed to multiple bonding between Cr and S (5, 9). Differences in the bond lengths Cr—C(O) of carbonyl groups mutually *trans* and those *trans* to sulfur have been taken as an indicator for the lack of π-interaction in the Cr—S bond compared to the Cr—C(O) bond (5). Similar differences are observed in the present complex, Cr—C(O) mutually *trans* being slightly longer (1.878 Å ave) than Cr—C(O) *trans* to sulfur (1.842 Å ave). Corresponding, though less significant, variations of the C—O bond lengths are found as expected.

TABLE 5. Some data of the crystals, the data set, and the refinement

Parameter	Value*	
	$C_6(SCH_3)_6$	$(CO)_4Cr \cdot C_6(SCH_3)_6$
Crystal dimensions (mm)	$0.3 \times 0.2 \times 0.15$	Sphere with $r = 0.17$
Space group, molecules/unit cell	$P2_1/n, Z = 2$	$P2_1/n, Z = 4$
a (Å)	9.513(1)	10.542(1)
b (Å)	6.218(1)	10.764(1)
c (Å)	14.404(1)	20.526(1)
β (deg)	106.95(1)	101.58(1)
V (Å^3)	815.0	2281.8
ρ_{exp} (Mg m^{-3})	1.40	1.49
ρ_{calcd} (Mg m^{-3})	1.45	1.51
2θ range	5°–46°	5°–43°
Number of reflections		
Symmetrically independent	1119	2447
Observed	1027	2260
Number of variables refined	109	194
R_1 (obs. refl. only)	0.028	0.048
(incl. unobs. refl.)	0.031	0.050
R_2 (obs. refl. only)	0.035	0.068

*Data collection: Syntex $P2_1$-Diffractometer, Mo K$_\alpha$-radiation, graphite monochromator, $\lambda = 0.71069$ Å, ω-scan, $\Delta\omega = 0.8°$, $T =$ ca. 298 K.

Experimental

All reactions are studied in dry solvents, under N_2. The ligands were prepared by literature methods (14, 24). The carbonyl complexes were available commercially or were prepared by slightly modified known procedures, $C_7H_8M(CO)_4$ (M = Cr, Mo), $Et_4N[Cr(CO)_5Cl]$ from Et_4NCl and $Cr(CO)_6$, and $(MeCN)_2W(CO)_4$ from MeCN and $W(CO)_6$.[3]

Infrared spectra were recorded in solution on a Perkin Elmer Infrared Spectrophotometer Model 283 and nmr spectra were recorded on a Varian T-60 (H-1) or XL-90 (F-19). Thermal analyses were studied on a DuPont Thermal Analyser 990.

Details of the reaction conditions, yields, analyses of products, and ir and nmr spectra are shown in Tables 1 and 2, respectively. Microanalyses were performed either by the Mikroanalytical Laboratory, University of Würzburg, or Mikroanalytisches Laboratorium Beller, Göttingen, W. Germany.

Structure investigation by X-ray methods

The crystals examined were grown from methanol (L1) and toluene/hexane (1:2 volume ratio) (Cr(CO)$_4$L1), respectively. Some of the crystal data are given in Table 5. The lattice constants and estimated standard deviations are derived from least-squares calculations based on 19 (20) centered reflections in a 2θ range of 23°–28° (23°–26°) in the case of the free ligand L1 (the complex Cr(CO)$_4$L1). Systematic extinction was observed for reflections $h0l$ with $h + l = 2n + 1$ and $0k0$ with $k = 2n + 1$ leading to the space group $P2_1/n$ (non standard setting of $P2_1/c$, No. 19 of the International Tables) with the equivalent positions $x, y, z; -x, -y, -z; x + 1/2, 1/2 - y, z + 1/2; 1/2 - x, y + 1/2, 1/2 - z$. X-ray intensity data were measured on a Syntex P 2_1-diffractometer. They were corrected for Lorentz and polarisation factors but not for absorption. The structure L1 was solved by direct methods (program MULTAN (25)). After refining positional parameters and anisotropic temperature factors[4] for the non-hydrogen atoms by full-matrix least-squares

[3] W-D. Schenk. Private communication.

[4] Tables of the observed and calculated structure amplitudes and temperature factors are available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ont., Canada K1A 0S2.

the following R-values were obtained: $R_1 = 0.047$, $R_2 = 0.074$ (observed reflections only). The quantity minimized was $\Sigma(|F_{obs}| - |F_{calc}|)^2 \cdot W$ with $W = 1/\sigma^2$ and σ derived from counting statistics. Those reflections with $I/\sigma(I) < 3.0$ were classified as unobserved and not included in the refinement.

At this stage all of the 9 hydrogen atoms could be localized among the 12 highest peaks of a difference electron density map at reasonable positions. Including these in the structure factor calculations yielded $R_1 = 0.038$. Further refinement, with hydrogens kept tied to a common isotropic temperature factor, converged at $R_1 = 0.028$ and $R_2 = 0.035$. Positional parameters are listed in Table 6.

During the last cycle change/esd was less than 0.1 for all parameters.

Concerning the complex (CO)$_4$CrL1 the position of the Cr

TABLE 6. Positional parameters for the crystal structure of the free ligand L1 $C_6(SCH_3)_6$*

Atom	x	y	z
S1	−0.20869(8)	0.35051(13)	0.12475(5)
S2	0.14793(7)	0.19090(11)	0.17760(4)
S3	0.34537(6)	0.44239(10)	0.07583(4)
C1	−0.0884(2)	0.4202(3)	0.0554(2)
C2	0.0621(2)	0.3730(3)	0.0828(2)
C3	0.1508(2)	0.4643(4)	0.0305(2)
C4	−0.1073(5)	0.4247(7)	0.2471(2)
C5	0.0315(4)	−0.0415(5)	0.1477(2)
C6	0.3794(4)	0.1984(6)	0.0195(3)
H41	−0.186(4)	0.433(6)	0.277(3)
H42	−0.060(4)	0.310(6)	0.277(2)
H43	−0.066(4)	0.562(7)	0.247(3)
H51	0.098(4)	−0.156(6)	0.188(2)
H52	−0.021(4)	−0.063(5)	0.077(3)
H53	−0.051(4)	−0.016(7)	0.162(3)
H61	0.336(4)	0.208(6)	−0.049(2)
H62	0.490(4)	0.177(6)	0.037(2)
H63	0.336(4)	0.079(5)	0.048(3)

*Estimated standard deviations are given in parentheses and correspond to the least significant digits.

atom in the unit cell could be found from a Patterson synthesis. Successive structure factor, Fourier and difference Fourier calculations revealed the positions of the lighter atoms except hydrogen. All atoms except C1, ..., C6 and C13, ..., C16 were made anisotropic. Positional parameters as resulting from full-matrix least-squares refinement are given in Table 7. The maximum change/esd during the last cycle was 0.01 and there were no values above $0.5 \, e/\text{Å}^3$ in the final difference electron density map. R-values are given in Table 5.

All calculations were carried out by means of the XTL-programme (26) package on a NOVA 1200 minicomputer with structure factors for uncharged atoms as given in ref. 27. Effects of anomalous dispersion were not taken into account.

Methods

Reactions with $C_7H_8M(CO)_4$, $M = Cr, Mo$ (Method A)

Equimolecular amounts (1 mmol) of $C_7H_8M(CO)_4$ and ligand were dissolved in ~20 mL toluene and heated to approximately 45°C. The reaction was monitored by observing changes in the ir spectrum in the 2100–1750 cm^{-1} region. When the reaction was approximately 90% complete, any precipitate was filtered off, and further product precipitated by addition of an equal volume of hexane. The products were recrystallized from toluene/hexane.

The nmr spectra and thermal analysis of the Mo products, $Mo(CO)_4L$, showed that they contained some solvent which was lost before the product decomposed. The excess solvent was removed by carefully heating in vacuum.

Reactions with stoichiometry 2:1 $C_7H_8Mo(CO)_4:L$ were studied in either toluene at 45°C, or methylene chloride (~35°C) when precipitation had occurred in toluene. The reaction was monitored by ir or nmr spectra. In the reactions with L2, L5, and

L6 in CH_2Cl_2, the infrared spectrum showed that approximately 50% of the $C_7H_8Mo(CO)_4$ had reacted within 20 h, and that any subsequent reaction was very slow, probably a decomposition generating increasing amounts of $Mo(CO)_6$. After 4 or 5 days, the nmr spectrum showed that the main product formed was $Mo(CO)_4L$ and only traces of possible $[Mo(CO)_4]_2L$ could be detected.

Reactions with $M(CO)_6$, $M = Cr, W$ (Method B)

The experimental details have been described previously (1).

Reactions with $W(CO)_4(MeCN)_2$ (Method C)

A solution of approximately 1.7 mmol $W(CO)_4(MeCN)_2$ in 20 mL THF was filtered into a solution of the ligand (1.0 mmol) in 10 mL THF. The infrared spectrum showed that the reaction was complete at room temperature within less than 2 h, i.e. specifically the band at 1853 cm^{-1} attributed to $W(CO)_4(MeCN)_2$ (28) had disappeared. Any $W(CO)_5MeCN$ did not react, as no change was observed in the band at 1840 cm^{-1} (28). The solvent was removed and the product extracted with 20~30 mL toluene. The product was precipitated on addition of an equal volume of hexane. It was recrystallized from a mixture of hexane and toluene.

In the reactions with approximately 3 mmol $W(CO)_4(MeCN)_2$ and 1 mmol ligand, the residue after the toluene extraction to remove $W(CO)_4L$ was further extracted with CH_2Cl_2. The product $[W(CO)_4]_2L$ was precipitated on slow addition of toluene. In reactions with L3 and L5, $W(CO)_4L$ was the only complex detected in the nmr spectra of the products.

Reactions with $Et_4N[Cr(CO)_5Cl]$ (Method D)

Approximately 1 mmol of $Et_4N[Cr(CO)_5Cl]$ was added to a solution of 0.5 mmol of ligand in 60 mL EtOH at room temperature. The solution was stirred. If precipitation had not occurred within 1 day, approximately 5 mL of H_2O was added. The volume of the solution was reduced until a precipitate had formed. The precipitate was extracted with toluene to remove $Cr(CO)_4L$ and the residue with CH_2Cl_2. The product $[Cr(CO)_4]_2L$ reprecipitated on addition of toluene.

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TABLE 7. Positional parameters ($\times 10^4$, for Cr $\times 10^5$) for non-hydrogen atoms in the crystal structure of the complex $Cr(CO)_4L1$ with esd's in parentheses

Atom	x	y	z
Cr	25965(9)	22032(8)	718(4)
S1	4233(1)	3179(1)	−385(1)
S2	2116(1)	1121(1)	−964(1)
S3	2376(2)	−365(2)	−2283(1)
S4	4493(2)	389(2)	−3062(1)
S5	7212(1)	1671(2)	−2110(1)
S6	6773(2)	3416(1)	−981(1)
C1	4382(5)	2304(4)	−1110(2)
C2	3420(5)	1450(4)	−1376(2)
C3	3536(5)	773(5)	−1946(2)
C4	4599(5)	1008(5)	−2254(3)
C5	5657(5)	1697(5)	−1914(2)
C6	5505(5)	2407(4)	−1358(2)
C7	3744(6)	4681(5)	−768(3)
C8	745(6)	1826(8)	−1529(3)
C9	3129(10)	−1751(7)	−1852(5)
C10	5145(8)	1633(8)	−3502(3)
C11	7468(7)	45(7)	−2284(4)
C12	7635(7)	2418(7)	−337(3)
C13	3152(6)	2960(6)	879(3)
C14	1373(7)	3478(7)	−210(3)
C15	3776(6)	954(6)	399(3)
C16	1362(7)	1335(6)	412(3)
O1	3547(5)	3382(4)	1395(2)
O2	651(6)	4261(6)	−373(3)
O3	4493(6)	239(5)	658(3)
O4	614(5)	794(5)	649(2)

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