

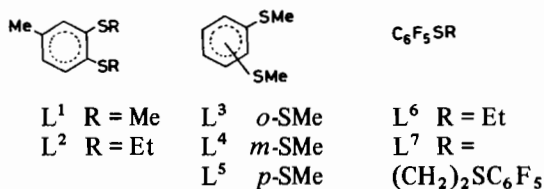
Sulphur Ligand Metal Complexes. Part 9 [1]. Aryl Sulphide Complexes of the Group 6 Metal Carbonyls

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Aryl sulphide bridged ligand complexes $[M(CO)_5]_2(\mu-L)$ ($M = Cr$ or W , $L = L^1, L^2, L^3$ or L^4) and chelated ligand complexes $M(CO)_4L$ ($M = Cr, Mo$ or W , $L = L^1$ or L^2) have been isolated and characterized by i.r., u.v.-visible and n.m.r. spectroscopy. An unusual feature of the mass spectra of Mo and W complexes of the ligand L^1 is the observation of the ions $[Mo(CO)_7]^+$, $[W(CO)_7]^+$ and $[W(CO)_8]^+$. The bonding of aryl sulphide ligands to group 6 metal carbonyls is discussed. The fluoro-substituted aryl ligands L^6 and L^7 do not form stable complexes with the group 6 metal carbonyls.

Introduction

There has been an increasing interest in the interaction of monodentate and bidentate sulphide ligands with the Group 6 metal carbonyls [2]. Recently evidence has been presented, showing that when bound to zerovalent Cr, Mo and W centres, alkyl sulphide ligands are both weaker σ donors and π acceptors than phosphine ligands [3, 4]. To date, most of the studies with bidentate sulphides have been concerned with ligands which have aliphatic [3–11], rather than aryl groups [7, 12], attached to the sulphur donor atoms. Thus, as an extension to an earlier study [3, 4] we now report the results of an investigation into the coordination properties of the bidentate aryl sulphide ligands, L^1 – L^5 , towards the carbonyls of chromium, molybdenum, and tungsten.



We find these ligands exhibit flexibility in their behaviour, in that it has been possible to synthesize both new bridged ligand complexes *viz.* $[M(CO)_5]_2(\mu-L)$ ($M = Cr$ or W), and chelated ligand complexes *viz.* $M(CO)_4L$ ($M = Cr, Mo$ or W). Only the latter type of complex was reported in a previous study using L^3 [12], and both bridged and chelated ligand complexes have been reported using the aryl sulphides $XC_6H_4SCH_2CH_2SC_6H_4X$ ($X = H, p-NO_2, p-Cl, p-Me, p-OMe$ or $p-NMe_2$) [7]. We have also attempted to prepare related complexes with the fluoro-substituted aryl sulphides C_6F_5SEt (L^6) and $C_6F_5SCH_2CH_2SC_6F_5$ (L^7), but stable compounds have not been obtained.

Experimental

I.r. spectra were recorded on a Beckman I.R. 20 spectrophotometer, 1H n.m.r. spectra on a JEOL JNM-C-60 HL spectrometer and ^{13}C n.m.r. on a JEOL FX60 fourier transform spectrometer. Electronic spectra were obtained using a Shimadzu MPS-5000 instrument and mass spectra on an A.E.I. M.S.9 spectrometer at 70 eV. Microanalyses (Table I) were carried out by Professor A. D. Campbell (University of Otago). The complexes were prepared in a 100 cm^3 water cooled, pyrex glass, annular photochemical reactor using a 125 watt Hg lamp. The reaction was continuously flushed with dinitrogen.

All solvents were dried according to established procedures. Reactions were carried out under oxygen-free dinitrogen and all complexes were routinely dried *in vacuo*.

The Ligands

These were prepared following a general method for aryl sulphides [13] using the appropriate thiol, sodium ethoxide, and iodomethane (L^1, L^3 – L^5), iodoethane (L^2 and L^6) or 1,2-dibromoethane (L^7). Toluene-3,4-dithiol was obtained from B.D.H. Chemicals Ltd. and pentafluorothiophenol from Aldrich Chemical Co. 2-methylthiobenzenethiol was prepared from 2-methylthioaniline [14], benzene-1,3-dithiol

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TABLE I. Analytical Data and Melting Points of the Complexes.

Complex	Analyses (%) ^a			M.p. (°C)
	C	H	S	
[Cr(CO) ₅] ₂ (μ-L ¹)	40.4(40.2)	2.4(2.1)	11.45(11.3)	104–7
[W(CO) ₅] ₂ (μ-L ¹)	27.9(27.45)	1.95(1.45)	8.9(7.7)	108–11
Cr(CO) ₄ L ¹	44.9(44.8)	3.5(3.5)	18.7(18.4)	81–2
Mo(CO) ₄ L ¹	40.1(39.8)	3.2(3.1)	16.25(16.35)	65–7
W(CO) ₄ L ¹	31.5(32.5)	3.1(2.5)	13.4(13.4)	78–81
[Cr(CO) ₅] ₂ (μ-L ²)	42.5(42.3)	2.9(2.7)	10.45(10.8)	94–7
[W(CO) ₅] ₂ (μ-L ²)	30.1(29.4)	2.1(1.9)	8.7(7.5)	96–7
Cr(CO) ₄ L ²	47.8(47.9)	4.5(4.3)	17.25(17.0)	72–4
Mo(CO) ₄ L ²	43.7(42.9)	4.5(3.8)	14.9(15.25)	66–9
W(CO) ₄ L ²	36.9(35.5)	3.6(3.2)	12.7(12.6)	86–8
[Cr(CO) ₅] ₂ (μ-L ³) ^b	41.6(41.3)	2.4(2.4)	14.6(15.0)	84–5
[W(CO) ₅] ₂ (μ-L ³)	26.8(26.4)	1.2(1.2)	8.2(7.8)	109
[Cr(CO) ₅] ₂ (μ-L ⁴)	40.0(39.0)	2.1(1.8)	–	35
[W(CO) ₅] ₂ (μ-L ⁴)	26.7(26.4)	1.4(1.2)	8.0(7.8)	82–3

^aCalculated values are given in parentheses. ^bContains 0.5 mol L³ of solvation.

from 1,3-benzenedisulphonyl chloride [15] and benzene-1,4-dithiol from 1,4-dibromobenzene [16].

The Complexes [M(CO)₅]₂(μ-L) (M = Cr or W; L = L¹–L⁴)

These were obtained by similar methods of which the following is typical.

The complex Cr(CO)₆ (0.880 g, 4 mmol) was dissolved in 60 cm³ tetrahydrofuran (thf) and the solution irradiated in a u.v. cell for 1 hr. The ligand, L¹ (0.377 g, 2 mmol), dissolved in thf (20 cm³) was added to the orange solution and the mixture stirred for 5 min, before filtering through Kieselguhr. The solvent was completely removed under vacuum and the excess of Cr(CO)₆ sublimed from residue *in vacuo* at room temperature. The resulting yellow crystals were washed with n-pentane. Yield 0.594 g (57%).

For L = L³ and M = Cr, the thf residue was extracted into cyclohexane and chromatographed on a silica gel (100–200 mesh) column, eluting with 20% benzene/cyclohexane. The product, which was recrystallized from benzene, always contained approximately 0.5 mol L³ of solvation. The previously reported complex, Cr(CO)₄L³, was obtained in a second fraction by eluting with 50% benzene/cyclohexane. For L = L³ and M = W, the thf residue was extracted with the minimum volume of benzene, to remove the contaminating W(CO)₄L³ complex, recrystallized from benzene, and washed with cyclohexane. For L = L⁴ and M = Cr, the product was recrystallized from n-hexane and for M = W from cyclohexane. For L = L⁵ and M = Cr or W, only

unstable solids were obtained, identified as pentacarbonyl species, from their i.r. spectra.

Electronic spectral data, λ_{max}/nm (log ε), for the [M(CO)₅]₂(μ-L) complexes in ethanol are as follows: for M = Cr and L = L¹ 252 (4.22), 300 (3.51), 445 (3.22); M = Cr and L = L² 268 (4.22), 288 (3.88), 423 (3.50); M = W and L = L¹ 265 (4.26), 277 sh (3.90), 298sh (3.80), 395 (3.62), 417 (3.64), 422sh (2.98); M = W and L = L² 265 (4.28), 281sh (3.90), 293sh (3.81) 306sh (3.69), 382 (3.51), 411 (3.43), 443sh (2.63).

The Complexes M(CO)₄L (L = L¹ or L²; M = Cr, Mo or W)

These were obtained by similar methods of which the following is typical.

After the complex Cr(CO)₆ (0.660 g, 3 mmol) in thf (60 cm³) was irradiated for 1 hr, the ligand L¹ (0.566 g, 3 mmol) was added and the irradiation continued for a further 1¼ hr. The thf was removed under vacuum and the unreacted Cr(CO)₆ sublimed *in vacuo* from the residue. The i.r. spectrum showed the presence of both tetracarbonyl and pentacarbonyl species. Their separation was achieved on a silica gel (100–200 mesh) column eluting with n-pentane and then benzene. The complex Cr(CO)₄L¹ (benzene fraction) was isolated by reducing the solvent volume and washing the resulting yellow crystals with cold n-pentane. Recrystallization was achieved using n-pentane. Yield 0.43 g (42%). The complex [Cr(CO)₅]₂(μ-L¹) was isolated from the n-pentane fraction in low yield (0.040 g, 5%).

TABLE II. I.r. and ¹H n.m.r. Spectral Data for the Complexes.

Compound	CO stretching frequencies (cm ⁻¹) ^a				Chemical shifts, δ (p.p.m.) ^c
	A ₁ '	B ₂	E	A ₁ '	
L ¹					
[Cr(CO) ₅] ₂ (μ-L ¹)	2072w	1989w	1948s	1933m	2.02s(ArCH ₃), 2.05s(SCH ₃), 6.9m(Ar) ^d
[W(CO) ₅] ₂ (μ-L ¹)	2065w	1987s	1942w	1947sh	1.46s(ArCH ₃), 1.57s(SCH ₃), 6.7m(Ar) ^d
L ²					
[Cr(CO) ₅] ₂ (μ-L ²)	2076w	1990w	1948s	1938sh	1.90s(ArCH ₃), 2.24s(SCH ₃), 6.5m(Ar) ^d
[W(CO) ₅] ₂ (μ-L ²)	2074w	1986w	1947s	1936sh	1.18t(SCH ₂ CH ₃), 2.22s(ArCH ₃), 2.81q(SCH ₂ CH ₃), 6.8(Ar) ^d
L ³					
[Cr(CO) ₅] ₂ (μ-L ³)	2073w	1988w	1948s	1935sh	0.96t(SCH ₂ CH ₃), 1.83s(ArCH ₃), 2.57q(SCH ₂ CH ₃), 6.5m(Ar) ^d
[W(CO) ₅] ₂ (μ-L ³)	2076w	1982w	1944s	1949sh	0.92t(SCH ₂ CH ₃), 2.00s(ArCH ₃), 2.81q(SCH ₂ CH ₃), 6.7m(Ar) ^d
L ⁴					
[Cr(CO) ₅] ₂ (μ-L ⁴)	2070w	1984w	1945s	1932sh	2.45s(SCH ₃), 7.15s(Ar) ^e
[W(CO) ₅] ₂ (μ-L ⁴)	2070w	1985w	1949s	1940sh	3.04s(SCH ₃), 7.49s(Ar)
Cr(CO) ₅ L ⁶	2073w	b	1950s	1954sh	2.42s(SCH ₃), 7.0m(Ar)
W(CO) ₅ L ⁶	2079w	b	1948s	1942sh	2.77s(SCH ₃), 7.6m(Ar)
					3.00s(SCH ₃), 7.6m(Ar) ^e
					^e
	A ₁	A ₁ '	B ₁	B ₂	
L ¹					
Cr(CO) ₄ L ¹	2020w	1920m	1908s	1888s	2.28s(ArCH ₃), 2.40s, 2.42s(SCH ₃), 7.0m(Ar)
Mo(CO) ₄ L ¹	2027m	1925sh	1916s, 1909sh	1894s	2.41s(ArCH ₃), 2.69s, 2.72s(SCH ₃), 7.4m(Ar)
					2.40s(ArCH ₃), 2.74s, 2.78s(SCH ₃), 7.4m(Ar)
W(CO) ₄ L ¹	2025w	1918m	1907s	1893s	2.41s(ArCH ₃), 2.88s, 2.91s(SCH ₃), 7.2m(Ar)
L ²					
Cr(CO) ₄ L ²	2020m	1925s, 1918s	1909s, 1903s	1889s	1.30t, 1.35t(SCH ₂ CH ₃), 2.35s(ArCH ₃), 2.89q, 2.92q(SCH ₂ CH ₃), 6.9m(Ar)
Mo(CO) ₄ L ²	2022m	1928s	1920s, 1914s	1896s	1.46t(SCH ₂ CH ₃), 2.47s(ArCH ₃), 3.09q(SCH ₂ CH ₃), 7.4m(Ar)
W(CO) ₄ L ²	2027m	1924m, 1919m	1907s, 1903s	1895s	1.50t(SCH ₂ CH ₃), 2.56s(ArCH ₃), 3.14q(SCH ₂ CH ₃), 7.4m(Ar)

^aIn cyclohexane, w = weak, s = strong, m = medium, sh = shoulder. ^bObscured by M(CO)₆ absorption. ^cIn CDCl₃ unless otherwise stated, s = singlet, t = triplet, q = quartet, m = multiplet. ^dIn C₆D₆. ^eDecomposed.

TABLE III. Force Constant Data and Low Energy Absorption Maxima for the Complexes.

Complex ^a	CO force constants (N m ⁻¹) ^b		λ_{\max} (nm) ^c	References
	k ₁	k ₂		
Cr(CO) ₅ (PPh ₃)	1551	1585	359 ^d	39, 31
Cr(CO) ₅ L ⁶	1563	1601		j
[Cr(CO) ₅] ₂ (μ -L ²)	1538	1600	423	j
[Cr(CO) ₅] ₂ (μ -pte)	1533	1600	430 ^d	7 ^k
[Cr(CO) ₅] ₂ (μ -L ³)	1532	1597		j
[Cr(CO) ₅] ₂ (μ -dto)	1530	1592	398	3 ^k
[Cr(CO) ₅] ₂ (μ -L ¹)	1529	1598	445	j
Cr(CO) ₅ (SEt ₂)	1528	1581	393 ^d	36
[Cr(CO) ₅] ₂ (μ -nte)			450	7 ^k
Cr(CO) ₅ (SPMe ₃)	1494	1590	424	3 ^k
Cr(CO) ₅ (H ₂ NC ₆ H ₁₁)	1508	1577		39
Cr(CO) ₅ (HNC ₅ H ₁₀)			426 ^e	31
W(CO) ₅ (PPh ₃)	1557	1589		39
W(CO) ₅ (PBu ₃ ⁿ)			351 ^f	24
W(CO) ₅ L ⁶	1556	1590		j
[W(CO) ₅] ₂ (μ -L ¹)	1556	1595	395	j
[W(CO) ₅] ₂ (μ -L ³)	1556	1587		j
[W(CO) ₅] ₂ (μ -L ⁴)	1533	1576	405	j
[W(CO) ₅] ₂ (μ -L ²)	1533	1594	382	j
[W(CO) ₅] ₂ (μ -dto)	1531	1590	371 ^g	3 ^k
[W(CO) ₅] ₂ (μ -tmdto)			368 ^g	3
W(CO) ₅ (H ₂ NC ₆ H ₁₁)	1513	1572		40
W(CO) ₅ (HNC ₅ H ₁₀)			403 ^h	25
Cr(CO) ₄ (diphos)	1492	1566		41 ^k
Cr(CO) ₄ (aphos)			373 ⁱ	24
Cr(CO) ₄ L ¹	1404	1542	374	j
Cr(CO) ₄ L ³	1396	1559		12 ^k
Cr(CO) ₄ (dto)	1386	1557	372	3 ^k
Cr(CO) ₄ (Me ₄ en)	1338	1506		42 ^k
Cr(CO) ₄ (en)			424 ⁱ	43
W(CO) ₄ (diphos)	1404	1579		41 ^k
W(CO) ₄ (aphos)			363 ⁱ	24
W(CO) ₄ L ¹	1397	1571	368	j
W(CO) ₄ L ²	1393	1571	365	j
W(CO) ₄ L ³	1388	1581		12 ^k
W(CO) ₄ (dto)	1367	1585	364	3 ^k
W(CO) ₄ (en)			397 ⁱ	43

^aLigand abbreviations : pte = 1,2-bis(phenylthio)ethane, dto = 3,6-dithiaoctane, nte = 1,2-bis(*p*-nitrophenylthio)ethane, tmdto = 2,2,7,7-tetramethyl-3,6-dithiaoctane, diphos = 1,2-bis(diphenylphosphino)ethane, aphos = bis(diphenylphosphine)methylamine, Me₄en = N,N,N',N'-tetramethylethylenediamine, en = ethylenediamine. ^bCalculated from CO stretching frequencies obtained in saturated hydrocarbon solvents. Estimated errors are 3 and 4 N m⁻¹ for pentacarbonyl and tetracarbonyl complexes respectively. ^cIn ethanol, unless otherwise stated. ^dIn n-hexane. ^eIn cyclohexane. ^fIn methylcyclohexane/isopentane. ^gIn chloroform. ^hIn benzene. ⁱIn methanol. ^jThis work. ^kForce constants calculated from data published in reference.

For $L = L^1$ and $M = W$, it was necessary to irradiate for 1-3/4 hr. Chromatography on silica gel and elution with 30% benzene/n-pentane gave $[W(CO)_5]_2(\mu-L^1)$, and $W(CO)_4L^1$ was isolated after elution with benzene. For $L = L^2$ and $M = Cr$ or Mo purification was achieved by recrystallization from n-pentane. For $L = L^2$ and $M = W$, after 1½ hr irradiation, chromatography on silica gel and elution with 50% toluene/n-hexane yielded $[W(CO)_5]_2(\mu-L^2)$. Further elution with toluene gave $W(CO)_4L^2$.

Electronic spectral data, λ_{max}/nm ($\log \epsilon$), for the $M(CO)_4L$ complexes in ethanol are as follows: for $M = Cr$ and $L = L^1$ 248 (4.14), 295sh (3.56), 333sh (3.25), 375sh (3.04); $M = Cr$ and $L = L^2$ 240 (4.28), 331sh (3.44), 374sh (3.14); for $M = Mo$ and $L = L^1$ 252 (4.28), 289sh (3.77), 307sh (3.56), 407 (3.08); for $M = Mo$ and $L = L^2$ 256 (4.20), 296sh (3.84), 358 (3.24); for $M = W$ and $L = L^1$ 243 (4.31), 293sh (3.90), 368 (3.28), 410sh (2.83); for $M = W$ and $L = L^2$ 244 (4.35), 250sh (4.33), 287sh (3.95), 365 (3.30), 397sh (2.93).

The Complexes $M(CO)_5L^6$ ($M = Cr$ or W)

Addition of L^6 to $M(CO)_6$ u.v. irradiated solutions, in a 1:1 mol ratio, yielded yellow solutions which were treated as above for the bridged ligand complexes. Attempts to isolate analytically pure complexes were unsuccessful although solution i.r. spectra were characteristic of pentacarbonyl species. No evidence was found for complex formation with the ligand L^7 .

Results

Syntheses

The complexes were generally obtained as moderately air-stable, yellow solids, on addition of the sulphide ligand to u.v.-irradiated tetrahydrofuran solutions of the appropriate metal carbonyl. The bridged ligand complexes $[M(CO)_5]_2(\mu-L)$ ($M = Cr$ or W ; $L = L^1, L^2, L^3$ or L^4), were best isolated from reactions where the ligand to metal carbonyl ratio was 1:2, whereas the chelated ligand complexes $M(CO)_4L$ ($M = Cr, Mo$ or W ; $L = L^1$ or L^2), were obtained using equimolar ligand to metal carbonyl ratios and further irradiating the reaction mixtures. However, as both types of complex generally formed under the reaction conditions used, chromatography on silica gel or careful crystallization was usually required to achieve purification. Complexes prepared from the *para*-substituted ligand, 1,4-bis(methylthio)benzene (L^5), were unstable and hence could not be characterized. This lower stability may be correlated with the higher ionization energy (as determined by photoelectron spectroscopy) of the ligand's sulphur electron lone pair (8.8 eV) [17], compared with the value of 8.34 eV for the *meta*-substituted ligand, 1,3-bis(methylthio)benzene (L^4) [18]. The existence of

pentafluorophenyl sulphide ligand complexes $M(CO)_5L^6$ ($M = Cr$ or W), was inferred from spectral evidence, but they were too unstable to be fully characterized. No evidence was found for complexation by the related bidentate ligand L^7 .

Infrared Spectra

Infrared spectral data in the CO stretching region for the complexes are listed in Table II and the Cotton-Kraihanzel force constants in Table III. The $\nu(CO)$ frequencies of the bridged and chelated ligand complexes are typical of other $M(CO)_5L$ ($L =$ monodentate sulphide) and $M(CO)_4L$ ($L =$ bidentate sulphide) systems respectively [3, 7, 19] and assignments were made accordingly. In some cases splitting of the nondegenerate A_1' and B_1 modes of the $M(CO)_4L$ complexes was observed and can be attributed to conformational isomerism about the M-S bonds. Similar CO frequency doubling has been observed previously [21] for the series of dialkyl sulphide complexes $(\eta^5-C_5H_5)Mn(CO)_2SR_2$. The room temperature 1H (Table II) n.m.r. spectra do not exhibit any splittings thus showing the two conformers exist in equilibrium, only the time averaged spectra being observed. It has been shown that the barriers to inversion of configuration of sulphur are remarkably low in sulphide complexes of Cr and W pentacarbonyls [22].

N.m.r. Spectra

1H n.m.r. spectral data for the complexes are listed in Table II. For the bridged ligand complexes, $[M(CO)_5]_2(\mu-L)$ ($M = Cr$ or W , $L = L^1-L^4$), the $-SCH_3$ and $-SCH_2CH_3$ chemical shift values compared to the free ligands establish the bridging nature (rather than monodentate) of the ligands. It is of interest that for the more stable chelated ligand complexes, $M(CO)_4L^1$ ($M = Cr, Mo$ or W), spectra were able to be recorded in $CDCl_3$ rather than C_6D_6 , giving enhanced resolution, thus enabling the inequivalence of the $-SCH_3$ protons to be observed. Values of ^{13}C carbonyl resonances for selected complexes are listed in Table IV and show the expected [23] downfield shifts when compared with the parent hexacarbonyls. That the overall net basicity of aryl sulphide ligands in certain cases is similar to that of triphenylphosphine is confirmed from ^{13}CO chemical shifts (Table IV). For example, the values for $[W(CO)_5]_2(\mu-L^1)$ and $W(CO)_5(PPh_3)$ are almost identical and chelated ligand complexes follow the same trend.

Mass spectra

An unusual feature of the mass spectra of the W bridged ligand, and the Mo and W chelated L^1 ligand complexes, was the observation of peaks corresponding to the $[W(CO)_8]^+$, $[W(CO)_7]^+$ and $[Mo(CO)_7]^+$ ions in moderate abundance. The existence of such

TABLE IV. ^{13}C n.m.r. Spectral Data for the Complexes.

Complex	Chemical Shift, δ (p.p.m.) ^a	
	<i>cis</i> -CO	<i>trans</i> -CO
$\text{Cr}(\text{CO})_4\text{L}^1$	215.1	226.8
$\text{Cr}(\text{CO})_4\text{L}^2$	215.4	226.6
$\text{W}(\text{CO})_4\text{L}^2$	200.4	207.7
<i>cis</i> - $\text{W}(\text{CO})_4(\text{PEt}_3)_2$ ^b	204.4	204.7
$[\text{W}(\text{CO})_5]_2(\mu\text{-L}^1)$	196.9	199.9
$\text{W}(\text{CO})_5(\text{PPh}_3)^c$	197.5	199.4

^aIn CDCl_3 unless otherwise stated. ^bIn CH_2Cl_2 , from ref. 44. ^cIn CHCl_3 , from ref. 45.

ions does not appear to have been noted previously but sulphide complexes of the group VI metal carbonyls are known to be readily decomposed in the mass spectrometer to the free ligand and $[\text{M}(\text{CO})_6]^+$ ions [3, 7]. Although the chelated ligand complexes show the expected parent ion, $[\text{M}(\text{CO})_4\text{L}^1]^+$, the bridged ligand complexes do not. For example, the spectrum of the complex $[\text{W}(\text{CO})_5]_2(\mu\text{-L}^1)$ gave ions corresponding to $[\text{W}(\text{CO})_6]^+$ and $\text{W}(\text{CO})_4\text{L}^1$ in high abundance. The latter ion underwent successive loss of 4 CO groups to give $[\text{WL}^1]^+$ in the normal manner. A very weak feature corresponds to the $[\text{W}(\text{CO})_5\text{L}^1]^+$ ion and this peak is also seen in the spectrum of the chelated ligand complex $\text{W}(\text{CO})_4\text{L}^1$. Ions of the type $[\text{Cr}(\text{CO})_x]^+$ where $x > 6$ were not observed for the chromium complexes. For the complex, $\text{Cr}(\text{CO})_4\text{L}^1$, the peak corresponding to the $[\text{Cr}(\text{CO})_3\text{L}^1]^+$ ion was absent although the analogous ion was observed for the Mo and W complexes. Similar behaviour has been seen previously for other phenylsubstituted phosphine and arsine ligand complexes and explained in terms of η^6 -arene type coordination [41]. An ion such as $[\text{Cr}(\text{CO})_2\text{L}^1]^+$, would be formed by preferred loss of two CO groups from $[\text{Cr}(\text{CO})_4\text{L}^1]^+$ and could have a structure with both the arene ring and one thioether sulphur bonded to the Cr atom.

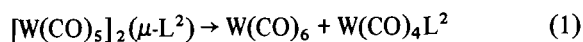
Electronic Spectra

Electronic spectral data for the L^1 and L^2 ligand complexes are given in the experimental section and all show bands of moderate intensity ($\epsilon = 1500\text{--}4400 \text{ l mol}^{-1} \text{ cm}^{-1}$) in the 350–450 nm region (Table III). For the bridged ligand complexes $[\text{M}(\text{CO})_5]_2(\mu\text{-L})$ ($\text{M} = \text{Cr}$ or W ; $\text{L} = \text{L}^1$ or L^2), following the detailed study of Braterman *et al.* [24] for $\text{M}(\text{CO})_5\text{L}$ phosphine complexes, this band can be assigned to an $e \rightarrow a_1$ transition involving charge transfer from $d(xy, yz)$ orbitals of the metal to the z -like combination of equatorial CO π^* orbitals (which will be mixed with $d(z^2)$). Shoulders observed at longer wavelengths

are probably $d\text{--}d$ in nature and for the tungsten complexes weaker shoulders can be assigned to corresponding singlet \rightarrow triplet transitions [25]. For a series of $\text{M}(\text{CO})_5\text{L}$ amine complexes, Wrighton *et al.* [25] and others [26], while agreeing with the symmetry of the transition, prefer to assign the $e \rightarrow a_1$ band to a $d\text{--}d$ type transition. Electronic spectra for complexes of the type *cis*- $\text{M}(\text{CO})_4\text{L}_2$ or $\text{M}(\text{CO})_4\text{L}$ ($\text{L} =$ bidentate ligand) have been less studied, but again the band of moderate intensity at lowest energy (Table III) appears to be intermediate in character between $d\text{--}d$ and charge transfer [24, 25].

Reactivity

The bridged ligand complexes $[\text{M}(\text{CO})_5]_2(\mu\text{-L})$, with the ligands L^1 , L^2 and L^3 (*i.e.* those which contain *ortho*-SR groups) are readily transformed into the related chelated ligand complexes. In the case of $\text{M} = \text{W}$ and $\text{L} = \text{L}^2$, the thermal decomposition has been followed by i.r. and ^1H n.m.r. and shows, as for bridged alkyl sulphide complexes [3], complete CO migration (equation 1) after 1 hr refluxing in *n*-hexane.



For a similar reaction in the presence of excess Ph_3P (6:1 mol ratio), the products are $\text{W}(\text{CO})_5(\text{PPh}_3)$, $\text{W}(\text{CO})_6$ as well as $\text{W}(\text{CO})_4\text{L}^2$, no evidence being found for the replacement of the chelate L^2 ligand. In an analogous fashion, the thermal reaction of excess $(\text{PhO})_3\text{P}$ yields $\text{W}(\text{CO})_5[\text{P}(\text{OPh})_3]$, $\text{W}(\text{CO})_6$ and $\text{W}(\text{CO})_4\text{L}^2$ as the initial products in the first 20 minutes and further reflux over a period of 2 hr, causes the complete conversion of $\text{W}(\text{CO})_4\text{L}^2$ into *cis*- $\text{W}(\text{CO})_4[\text{P}(\text{OPh})_3]_2$. Detailed kinetic studies by Dobson *et al.* [6, 8, 9], on the replacement of chelated dithioether ligands by phosphite donors, have indicated that substitution proceeds largely through a ring-opening mechanism.

Discussion

The calculation of approximate CO force constants from carbonyl stretching frequencies of substituted metal carbonyl complexes, has been the centre of controversy ever since Cotton and Kraihanzel published their approximate force constant method [27]. However, the qualitative use of data calculated by the 'approximate' method, to give a measure of total electron availability at the metal, appears to be justified [29], provided comparisons are not made between complexes of widely differing stereochemistries. The use of the data to calculate σ and π parameters for metal–ligand bonds is dubious [28, 29]. Force constant data for the

complexes prepared in this study are listed in Table III and subsequent discussion concentrated mainly on the *trans*-CO force constant, k_1 , which is affected most by changes in metal–ligand bonding. Care has been taken to ensure all data discussed have been obtained from spectral measurements made in saturated hydrocarbon solvents, thus avoiding solvent effect differences [29]. The data show that there is generally little difference between the k_1 values for the aryl sulphide and analogous alkyl sulphide pentacarbonyl complexes. However, the effect of the strongly electron withdrawing pentafluorophenyl group of L^6 is readily apparent. For the complex, $Cr(CO)_5L^6$, k_1 is higher than for all other $Cr(CO)_5L$ (L = alkyl or aryl sulphide) complexes (Table III) and for both chromium and tungsten, is comparable to the values normally observed for phosphine complexes. The fluoro substituents must increase the $M \rightarrow S \pi$ donation and decrease the $S \rightarrow M \sigma$ donation. Similar electronegative substituent effects have been shown [30] by ultraviolet photoelectron spectroscopic studies on the complexes $Cr(CO)_5L$, where the d orbital ionization potential increases from 10.00 eV to 10.27 eV, as L changes from $(CH_3)_2S$ to $CH_3(CH_2Cl)S$, in line with decreasing electron density on the chromium. In contrast to $Cr(CO)_5L^6$, the trimethylphosphine sulphide complex $Cr(CO)_5(SPM_3)$ has a k_1 value similar to amine donors, and a single crystal X-ray analysis has shown that the Cr–S bond in this complex, can be regarded as essentially single [34]. This can be attributed to the more negatively charged sulphur atom of SPM_3 , compared to thioether sulphur donors.

The energy of the $e \rightarrow a_1$ electronic spectral transition reflects the nature of the M–L bonding in $M(CO)_5L$ complexes, and since good π acceptors will stabilize the d donor orbitals, the π acceptor ability of the ligand L . It has been argued that this is the biggest single effect [31, 32] and previously we have shown for a series of pentacarbonyl complexes of Cr and W the energy of this transition decreases in the order phosphine ligand > alkyl sulphide ligand > nitrogen donor ligand [3]. The aryl sulphide ligand pentacarbonyl complexes prepared in this study however show the low energy absorptions at wavelengths closer to those expected for σ donor amine ligand complexes (390–430 nm) than those expected for phosphine complexes (330–360 nm) (Table III). Force constant data indicate that the total electron availability at the metal centres is not markedly different for the alkyl or aryl sulphide ligand complexes thus suggesting the acceptor orbital involves some aryl sulphide ligand character. Support for this idea comes from a series of bridged ligand complexes $[Cr(CO)_5]_2(\mu-L)$ (L = $XC_6H_4SCH_2CH_2SC_6H_4X$). Where X is an electron withdrawing substituent, such as

$p\text{-NO}_2$, the transition is red shifted by 38 nm compared to the spectrum where X is an electron donating group such as $p\text{-NMe}_2$ [7].

For the chelated ligand complexes less data are available, but it appears the lowest energy absorptions for both aryl and alkyl sulphide ligands are closer in energy to the range expected for phosphine ligands rather than for amine ligands. Force constant data (Table III) indicate the chelated aryl sulphides are better π acceptors than $EtS(CH_2)_2SEt$. A comparison of the single crystal X-ray structures of an aryl sulphide complex $W(CO)_4L^4$ [12] and alkyl sulphide complexes $W(CO)_4[t\text{-BuS}(CH_2)_n\text{t-Bu}]$ ($n = 2$ or 3) [8] shows that in fact, for the former complex, the W–S bonds (mean 2.52(2) Å) may actually be slightly shorter than in the latter complexes ($n = 2$, mean W–S = 2.562(5) Å and $n = 3$ mean W–S = 2.578(5) Å). However the differences are not statistically significant and there is a possibility that steric interactions may have an effect on the W–S bonding in the latter complexes. No data are available for aryl sulphide chromium complexes but the mean Cr–S distance (2.418(1) Å) for the alkyl sulphide complex $Cr(CO)_4[EtS(CH_2)_2SEt]$ [4], is significantly longer than the value of 2.379(2) Å found for the mean Cr–S bond length in the alkene sulphide ligand complex $Cr(CO)_4[(MeS)_2C=C(SMe)_2]$ [33]. In both cases the Cr–S distances are less than expected (~ 2.52 Å) for a single bond [34].

It cannot be assumed that the bonding behaviour of a specific bidentate ligand will necessarily be similar in both its chelated and bridged ligand complexes. For example, in the former case a ligand may act as a better π acceptor as compared to the latter case, because there is one less CO group competing for the metal's π bonding d electrons [35]. This means that although aryl sulphides may exhibit increased M–S π bonding in their $M(CO)_4L$ complexes (compared to alkyl sulphides) this may not be so apparent in their bridged ligand $[M(CO)_5]_2(\mu-L)$ complexes (see force constant data, Table III). Certainly the Cr–S bond length in the pentacarbonyl complex $Cr(CO)_5(EtSCH_2Ph)$ at 2.458(2) Å [36], is longer than the mean Cr–S distance (2.418(1) Å) in $Cr(CO)_4[EtS(CH_2)_2SEt]$ [4]. The same trend is seen in the phosphine complexes $Cr(CO)_5(PPh_3)$ and $Cr(CO)_4[Ph_2P(CH_2)_2PPh_2]$ (Cr–P distances are 2.422(1) and 2.360(2) respectively [37, 38]).

In conclusion then, it can be stated that while in general sulphide ligands are overall weaker π acceptors than phosphine ligands when bound to group 6 metal carbonyls, the extent of their π acidity will depend on both the substituents on the S donor atom and the nature of the metal centre to which it is bound.

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