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Carbonyl complexes of molybdenum and tungsten with sulfur donors

VI *. Reactions of carbonyl complexes of molybdenum(0) and tungsten(0) with uninegative (S,X)-donor ligands (X = S, N, P).

A.E. Sánchez-Peláez, M.F. Perpiñán *,

Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid (Spain)

E. Gutierrez-Puebla, A. Monge and C. Ruiz-Valero

Instituto de Ciencias de Materiales, Sede D., Serrano 113, 28006 Madrid and Laboratorio de Difraccion de Rayos X, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid (Spain)

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Abstract

The reactions of the zerovalent carbonyl complexes, $M(CO)_6$, $M(CO)_5(Rpy)$, $M(CO)_4(Rpy)_2$ ($M = Mo, W$, $R = 2-Me, H$) with a series of potentially mono- or bi-dentate uninegative (S,X)-donor ligands ($S, X =$ xanthates, dithiocarbamates, pyridine-2-thiol, *P, P*-diphenyl-*N*-phenylphosphinothioformomido, *P, P*-diphenylphosphinedithioformamide) have given two types of anionic complexes: $[M(S,X)(CO)_5]^-$ and $[M(S,X)(CO)_4]^-$ ($M = Mo^0, W^0$). These anions, which contain the (S,X)-ligand as a mono- or bi-dentate group, respectively, were isolated as their tetraphenylphosphonium or triethylammonium salts. Reactions of some of these species with allyl bromide and HgX_2 are described. The crystal structure of $[PPh_4][W(S_2COEt)(CO)_5]$ has been determined. The crystals are monoclinic, space group $P2_1/n$ with a 14.555(4), b 12.44(1), c 17.950(2) Å, U 3145.9(3) Å³, $Z = 4$; D_c 1.65 g cm⁻³, $\mu(Mo-K_\alpha)$ 39.68 cm⁻¹, $F(000) = 1544$, $R = 0.042$ for 4278 observed reflections. In this complex the xanthate ligand is monodentate.

* For part V see ref. 8.

Introduction

Few examples of reactions of the Group VI metal(0) carbonyl complexes with anionic potentially mono- or bi-dentate ligands have been reported [1–7]. We previously investigated the reactions of $\text{Mo}(\text{CO})_6$, $\text{Mo}(\text{CO})_4\text{bpy}$, and $\text{Mo}(\text{CO})_5\text{py}$ with uninegative (X,Y)-donor ligands (X, Y = N, S, O) [8] to give complexes of the type $[\text{Mo}(\text{X,Y})(\text{CO})_4]^-$, in which the (X,Y)-ligand acts as a bidentate group. Sometimes, traces of a pentacarbonyl species were detected. We have also studied the reactions of $\text{W}(\text{CO})_4(\text{Rpy})_2$ with anionic (N,O)-donor ligands, such as 2-picolinate and 2-quinaldinate, to give the $[\text{W}(\text{N,O})(\text{CO})_4]^-$ complexes [9].

We describe below a study of the reactions of $\text{M}(\text{CO})_6$, $\text{M}(\text{CO})_5(\text{Rpy})$ and $\text{M}(\text{CO})_4(\text{Rpy})_2$ ($\text{M} = \text{Mo}, \text{W}$; $\text{R} = \text{H}, 2\text{-Me}$) with several uninegative (S,X)-donor ligands (X = S, N, P): ROCS_2^- (xanthates, $\text{R} = \text{CH}_3(\text{Me})$; $\text{C}_2\text{H}_5(\text{Et})$; C_6H_{11} (cyclohexyl)); R_2NCS_2^- (*N,N*-dialkyldithiocarbamates, $\text{R}_2 = 2\text{Et}$, C_4H_8 (pyrrolidyl)dithiocarbamate)); Ph_2PS_2^- (*P,P*-diphenylphosphinedithioformate), and the deprotonated form of $\text{Ph}_2\text{PC}(\text{S})\text{N}(\text{H})\text{Ph}$ (*P,P*-diphenyl-*N*-phenyl(phosphinethioformamido) and 2- $\text{HSC}_5\text{H}_4\text{N}$ (pyridine-2-thiol = 2-Spy6). All these species can act as mono- or bi-dentate ligands. Since several of them may ligate in a variety of ways, we thought it of interest to study in detail the products of its reactions with the Mo^0 and W^0 derivatives mentioned above. The coordination mode can be determined by IR and NMR spectroscopy.

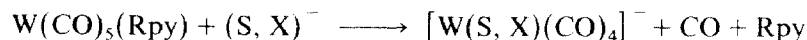
Very few crystal structures of organometallic complexes containing xanthate ligands have been resolved [10,11], and we present below the crystal structure of $[\text{PPh}_4][\text{W}(\text{S}_2\text{COEt})(\text{CO})_5]$.

Results and discussion

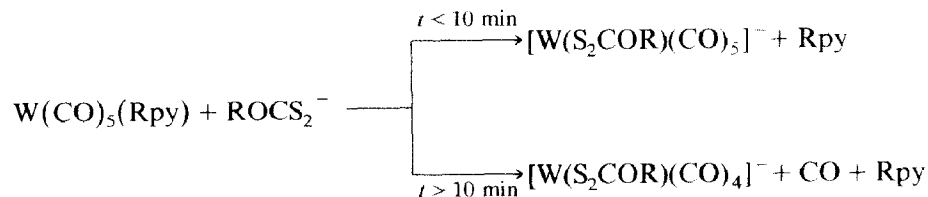
1. Reactions of $\text{M}(\text{CO})_6$, $\text{M}(\text{CO})_5(\text{Rpy})$ and $\text{M}(\text{CO})_4(\text{Rpy})_2$ ($\text{R} = 2\text{-Me}, \text{H}$; $\text{M} = \text{Mo}, \text{W}$) with anionic (S,X)-donor ligands

Analytical, infrared, ^1H , ^{31}P and ^{13}C NMR, and electronic spectral data are summarized in Tables 1–4. Scheme 1 shows the reactions observed.

The reactions between the $\text{W}(\text{CO})_5(\text{Rpy})$ complexes and the ligands mentioned above can take two separate courses, depending on the ligand used and the reaction time. If the reaction is carried out with R_2NCS_2^- , 2-Spy or $\text{Ph}_2\text{PC}(\text{S})\text{NPh}^-$, one CO molecule and the pyridine ligand are displaced to yield anionic tetracarbonyl complexes:



When the ligand used is a xanthate, two types of compounds are isolated:



Only the pentacarbonyl derivative is obtained in the reaction with $\text{Ph}_2\text{PCS}_2^-$.

The anionic pentacarbonyl complexes can be isolated pure only for tungsten. The species $[\text{Mo}(\text{S,X})(\text{CO})_5]^-$ seem always to be contaminated with the corresponding

Table 1

Analytical and infrared data (cm^{-1}) for the new complexes.

Compound	Elemental analysis (Found (calc.)(%))			IR data		$\nu(\text{C}=\text{N})$	$\nu(\text{COR})$	$\nu(\text{C}=\text{S})$
	C	H	N	$\nu(\text{C}=\text{O})$				
$[\text{PPh}_4][\text{W}(\text{S}_2\text{COCH}_3)(\text{CO})_5]$	47.55 (48.32)	2.96 (3.00)		2060, 1968, 1913, 1891, 1870			1182	
$[\text{PPh}_4][\text{W}(\text{S}_2\text{COC}_2\text{H}_5)(\text{CO})_5]$	48.47 (48.99)	3.11 (3.21)		2055, 1963, 1916, 1886, 1870			1168	
$[\text{PPh}_4][\text{W}(\text{S}_2\text{COC}_6\text{H}_{11})(\text{CO})_5]$	49.47 (51.56)	3.54 (3.72)		2058, 1958, 1925, 1912, 1870			1172	
$[\text{PPh}_4][\text{W}(\text{S}_2\text{CPhPh}_2)(\text{CO})_5]$	67.80 (68.09)	3.90 (4.08)		2060, 1974, 1930, 1908, 1900				1032
$[\text{PPh}_4][\text{W}(\text{S}_2\text{COCH}_3)(\text{CO})_4]$	47.89 (48.52)	3.09 (3.12)		2002, 1872, 1845, 1803			1217	
$[\text{PPh}_4][\text{W}(\text{S}_2\text{COC}_2\text{H}_5)(\text{CO})_4]$	48.91 (49.21)	3.20 (3.33)		1995, 1868, 1852, 1807			1208	
$[\text{PPh}_4][\text{W}(\text{S}_2\text{COC}_6\text{H}_{11})(\text{CO})_4]$	50.79 (51.86)	3.79 (3.85)		1993, 1868, 1852, 1813			1200	
$[\text{PPh}_4][\text{W}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)(\text{CO})_4]$	50.08 (50.58)	3.75 (3.85)	1.70 (1.78)	1986, 1847, 1830, 1797		1488		
$[\text{PPh}_4][\text{W}(\text{S}_2\text{CNC}_4\text{H}_8)(\text{CO})_4]$	50.50 (50.71)	3.51 (3.71)	1.72 (1.79)	1988, 1850, 1835, 1788		1464		
$[\text{PPh}_4][\text{W}(2\text{-Spy})(\text{CO})_4]$	52.90 (53.16)	3.17 (3.24)	1.82 (1.87)	1991, 1980, 1861, 1832, 1802, 1796		1570		1134
$[\text{Et}_3\text{NH}][\text{W}(2\text{-Spy})(\text{CO})_4]$	34.98 (35.38)	3.79 (3.93)	5.39 (5.50)	1992, 1860, 1845, 1805, 1792		1572		1135
$[\text{PPh}_4][\text{W}(\text{Ph}_2\text{PC}(\text{S})\text{NPh})(\text{CO})_4]$	58.98 (59.06)	3.57 (3.69)	1.40 (1.46)	1995, 1870, 1860, 1810		1527		930
$[\text{PPh}_4][\text{Mo}(\alpha(2\text{-Spy})(\text{CO})_4)]$	60.12 (60.27)	3.59 (3.67)	2.09 (2.13)	1994, 1867, 1849, 1790		1569		1131
$[\text{PPh}_4][\text{Mo}(\text{Ph}_2\text{PC}(\text{S})\text{NPh})(\text{CO})_4]$	64.94 (65.05)	3.91 (4.06)	1.51 (1.61)	2000, 1880, 1858, 1815		1518		926

Table 2

¹H and ³¹P NMR data ^a (δ) for [PPh₄][M(S,X)(CO)_n] (M = Mo, W; n = 5, 4) complexes

[PPh ₄][W(S ₂ COCH ₃)(CO) ₅]	DMSO- <i>d</i> ₆	3.90 (s) 7.50–8.10 (m)	CH ₃ H _{arom} (PPh ₄ ⁺)	
[PPh ₄][W(S ₂ COC ₂ H ₅)(CO) ₅]	DMSO- <i>d</i> ₆	1.28 (t) 4.37 (q) 7.20–8.10 (m)	CH ₃ –CH ₂ – H _{arom} (PPh ₄ ⁺)	<i>J</i> 7.3 <i>J</i> 7.3
[PPh ₄][W(S ₂ COC ₆ H ₁₁)(CO) ₅]	DMSO- <i>d</i> ₆	1.0–2.0 (m) 5.0–5.5 (m) 7.27–8.30 (m)	–CH ₂ – >CH–O H _{arom} (PPh ₄ ⁺)	
[PPh ₄][W(S ₂ COC ₂ H ₅)(CO) ₄]	DMSO- <i>d</i> ₆	1.32 (t) 4.44 (q) 7.40–8.10 (m)	CH ₃ –CH ₂ – H _{arom} (PPh ₄ ⁺)	<i>J</i> 7.2 <i>J</i> 7.2
[PPh ₄][W(S ₂ CN(C ₂ H ₅) ₂)(CO) ₄]	CDCl ₃	1.20 (t) 3.66 (q) 7.40–8.10 (m)	CH ₃ –CH ₂ – H _{arom} (PPh ₄ ⁺)	<i>J</i> 7.2 <i>J</i> 7.2
[PPh ₄][W(S ₂ CNC ₄ H ₈)(CO) ₄]	CDCl ₃	1.84 (m) 3.72 (t) 7.40–8.10 (m)	–CH ₂ – CH ₂ –N H _{arom} (PPh ₄ ⁺)	<i>J</i> 6,7
[PPh ₄][W(2-Spy)(CO) ₄]	CDCl ₃	6.54–6.61 (m) 7.04–7.10 (dd of d)	H(3), H(5) H(4)	<i>J</i> _{4,6} 1.8 <i>J</i> _{3,4} 7.3 <i>J</i> _{4,5} 6.6
		7.53–8.03 (m)	H _{arom} (PPh ₄ ⁺), H(6) (7.96)	
[PPh ₄][Mo(2-Spy)(CO) ₄]	CDCl ₃	6.47–6.52 (dd of d) 6.69–6.72 (m) 7.01–7.07 (dd of d)	H(5) H(3) H(4)	<i>J</i> _{4,6} 1.8 <i>J</i> _{4,3} 7.2 <i>J</i> _{4,5} 6.6
		7.58–7.89 (m)	H _{arom} (PPh ₄ ⁺), H(6) (7.84)	
[PPh ₄][Mo(Ph ₂ PC(S)NPh)(CO) ₄]	DMSO- <i>d</i> ₆	6.90–8.10 (m)	H _{arom} (PPh ₄ ⁺ , Ph)	
[PPh ₄][W(Ph ₂ PC(S)NPh)(CO) ₄] ³¹ P ^b	DMSO- <i>d</i> ₆	8.83 (s) 18.41	PPh ₄ ⁺ P,S ligand	<i>J</i> (W–P) 250

^a Chemical shifts (δ) in ppm, coupling constants in Hz. ^b 85% H₃PO₄ as external reference.

tetracarbonyl derivatives previously described [8]. The [PPh₄][W(S₂COMe)(CO)₅] complex is analogous to that obtained by displacement of halogen from the anions [WX(CO)₅][–] [4].

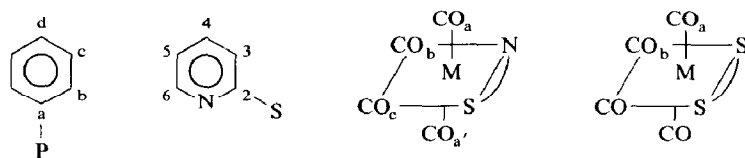
The reactions of W(CO)₆ or W(CO)₄(Rpy)₂ with the salts (or the free ligand in a basic medium) give the tetracarbonyl complexes [PPh₄][W(S,X)(CO)₄], analogous to those obtained from W(CO)₅(Rpy). Xanthate and tungsten dithiocarbamate derivatives are similar to those reported for molybdenum [8]. Two new molybdenum complexes, [PPh₄][Mo(S,X)(CO)₄] (S,X = 2-Spy, Ph₂PC(S)NPh[–]) have also been obtained.

The new anionic complexes isolated behave as 1/1 electrolytes in acetone and are diamagnetic and moderately stable to air and moisture. The stability is much lower in solution; e.g. rapid conversion of [W(S₂COR)(CO)₅][–] into the corresponding tetracarbonyl derivative takes place in acetone solution. Complete replacement of CO occurs in solutions of [PPh₄][W(S₂CPh₂)(CO)₅].

Table 3

¹³C NMR data ^a for some [PPh₄][M(S, X)(CO)₄] complexes

Compound	Solvent	PPh ₄ ⁺		δ(S, X)	δ(CO)
		δ	J		
[PPh ₄][Mo(S ₂ COC ₂ H ₅)(CO) ₄]	DMSO- <i>d</i> ₆	117.6(d)	89.2(P-C ^a)	13.7(s) CH ₃	206.7 CO ^a
		130.3(d)	13.0(P-C ^b)	66.8(s) -CH ₂ -	221.5 CO ^b
		134.5(d)	10.7(P-C ^c)	226.3(s) OCS ₂	
		135.2(d)	2.7(P-C ^d)		
[PPh ₄][W(S ₂ COC ₂ H ₅)(CO) ₄]	DMSO- <i>d</i> ₆	117.7(d)	89.2(P-C ^a)	13.6(s) CH ₃	202.2 CO ^a
		130.5(d)	12.7(P-C ^b)	66.6(s) -CH ₂ -	211.7 CO ^b
		134.6(d)	10.4(P-C ^c)	228.3(s) OCS ₂	
		135.4(d)	2.7(P-C ^d)		
[PPh ₄][Mo(2-Spy)(CO) ₄]	CDCl ₃	117.4(d)	89.4(P-C ^a)	114.9(s) C(5)	207.4 CO ^a
		130.8(d)	13.1(P-C ^b)	126.3(s) C(4) ... C(3)	209.4 CO ^a
		134.4(d)	10.3(P-C ^c)	133.1(s) C(4) ... C(3)	223.6 CO ^b
		135.8(d)	2.8(P-C ^d)	146.0(s) C(6)	225.1 CO ^c
				149.9(s) C(2)	
[PPh ₄][W(2-Spy)(CO) ₄]	CDCl ₃	117.4(d)	89.6(P-C ^a)	115.6(s) C(5)	203.8 CO ^a
		130.8(d)	12.6(P-C ^b)	127.4(s) C(4) ... C(3)	207.9 CO ^a
		134.4(d)	10.3(P-C ^c)	132.6(s) C(4) ... C(3)	214.6 CO ^b
		135.8(d)	3.0(P-C ^d)	145.2(s) C(6)	217.2 CO ^c
				149.4(s) C(2)	

^a carbons are assigned:

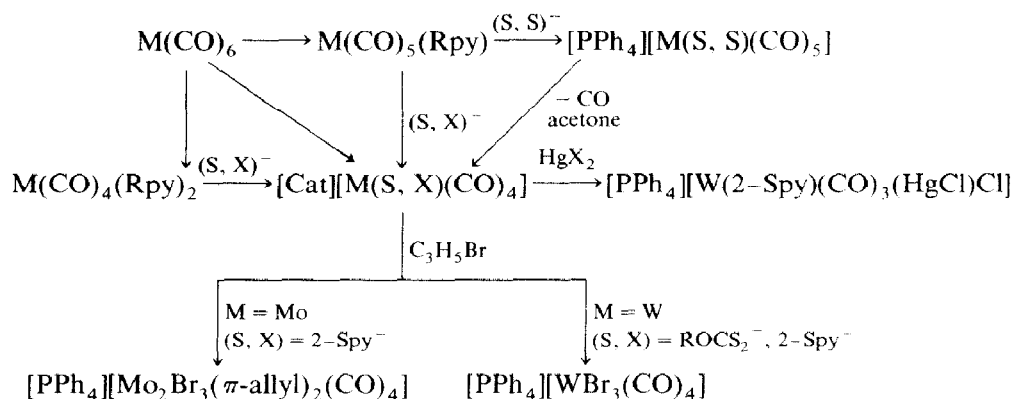
Infrared spectra of [W(S,X)(CO)₅]⁻ complexes in CH₂Cl₂ solution in the carbonyl stretching region show four bands (*A*₁, *B*₁, *E*, *A*) typical of M(CO)₅L [12–14], but five peaks are observed for the solids possibly owing to restricted rotation of the ligand in the solid, which reduces their pseudosymmetry [15] (for example, [W(S₂COMe)(CO)₅]⁻, $\nu(\text{CO})$ (CH₂Cl₂): 2040, 1972, 1920, 1862 cm⁻¹; $\nu(\text{CO})$ (KBr): 2060, 1968, 1913, 1891, 1870 cm⁻¹). All [M(S,X)(CO)₄]⁻ complexes show the four $\nu(\text{CO})$ bands (2*A*₁, *B*₂, *B*₂) typical of the *cis*-M(CO)₄L₂ complexes [16]. Sometimes only three bands appear, because of an overlap of the two central bands to produce a broad, very intense band.

Table 4

Electronic spectral data ^a

Compound	Solid, λ_{max} (nm)	Solution ^b λ_{Max} (nm) (ϵ) ^c
[PPh ₄][W(S ₂ COC ₂ H ₅)(CO) ₄]	450, 390, 382, 315, 270	450h(583), 386(3113), 314(12894)
[PPh ₄][W(S ₂ COC ₂ H ₅)(CO) ₅]	425, 400, 314, 262	
[PPh ₄][W(S ₂ CN(C ₂ H ₅) ₂)(CO) ₄]	620, 460, 350, 290	458h(400), 338(12743), 280(16258)
[PPh ₄][W(2-Spy)(CO) ₄]	550h, 468h, 419, 330, 278, 242	
[PPh ₄][W(Ph ₂ PC(S)NPh)(CO) ₄]	417, 340, 273	

^a sh = shoulder. ^b In DMF solution (10⁻⁴ M). ^c ϵ values in dm³ mol⁻¹ cm⁻¹.



Scheme 1

If an almost constant donor ability of the sulfur ligands is assumed the $\nu(\text{CO})$ frequencies reflect a decreasing π acceptor ability (or increased π donor ability) in the sequence: $\text{ROCS}_2^- \approx \text{Ph}_2\text{PCS}_2^- > 2\text{-Spy}^- > \text{R}_2\text{NCS}_2^-$.

The infrared spectra of all the complexes show a band of medium intensity in the $350\text{--}390\text{ cm}^{-1}$ region, which is assigned to $\nu(\text{M--CO})$.

The values, of the $\nu(\text{C--OR})$ stretching frequencies of xanthate and those for the $\nu(\text{C=N})$ of the dithiocarbamate for the $[\text{PPh}_4][\text{M}(\text{S}, \text{S})(\text{CO})_4]$ complexes are indicative of a chelating coordination of the ligand to a metal(0) in an octahedral environment. The frequencies are lower than those observed in Mo^{II} complexes [17]. As expected, the $[\text{W}(\text{S}_2\text{COR})(\text{CO})_5]^-$ species show lower $\nu(\text{C--OR})$ frequencies as a result of the monodentate character of the xanthate in these compounds (see Table 1).

For the $[\text{PPh}_4][\text{W}(\text{S}_2\text{CPPh}_2)(\text{CO})_5]$ complex the S-donor ligand shows a band at 1032 cm^{-1} , attributable to C=S type stretching vibration, which is at lower frequency than for complexes in which the anion occurs as P,S-bonded chelate [18].

When Et_3N is present in the reaction of $\text{M(CO)}_4(\text{py})_2$ with $\text{Ph}_2\text{PC(S)N(H)Ph}$ the N–H bond is broken and a chelate ring is formed to give the $[\text{PPh}_4][\text{M}(\text{Ph}_2\text{PC(S)NPh})(\text{CO})_4]$ complexes. No N–H stretching frequency and no N–H proton resonance signal could be found in the IR and ^1H NMR spectra of the complexes, indicating that the ligand is deprotonated. The $\text{Ph}_2\text{PC(S)N(H)Ph}$ is an ambidentate ligand because of the presence of three hetero atoms with coordinating properties. The mode of coordination can be determined by IR and ^{31}P NMR spectroscopy. The deprotonated ligand vibrations in the IR spectra are similar to those for other complexes in which P,S coordination was assumed [19–21]. The coordination of the phosphorus atom is confirmed by the observation of a $^{31}\text{P}\text{--}^{183}\text{W}$ coupling constant of 250 Hz in the ^{31}P NMR spectrum of the tungsten complex (see Table 2).

In the $[\text{Cat}][\text{M}(2\text{-Spy})(\text{CO})_4]$ complexes ($\text{Cat} = \text{PPh}_4, \text{Et}_3\text{NH}$) the deprotonated ligand acts as a (N,S)-chelate in spite of its small bite [22], to form a four-membered ring similar to that formed by the other (S,X)-ligands. This type of complex could not be obtained by Broomhead from the reaction of W(CO)_6 with 2-HSpy in presence of Et_3N [23]. The Et_3NH^+ salt of $[\text{W}(2\text{-Spy})(\text{CO})_4]^-$ was isolated in order to observe clearly the ligand vibrations in absence of other aromatic groups.

The ^1H -NMR spectra (see Table 2) of the new compounds are consistent with the proposed formulae. The ethyl groups of the *N,N*-diethyldithiocarbamate ligand give a single resonance, and so are equivalent on the NMR time scale because of free rotation around the C–N bond. As expected, the δ values for the R groups of ROCS_2^- and R_2NCS_2^- in these anionic metal(0) complexes are generally lower

Table 5

Atomic coordinates for $[\text{PPh}_4][\text{W}(\text{S}_2\text{COEt})(\text{CO})_5]$, with thermal parameters as $U_{\text{eq}} = \frac{1}{3}\Sigma[(U_{ij} + a_i a_j + a_i a_j \cos a_i a_j)] \times 10^4$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
W	0.69128(3)	0.01955(4)	0.31823(3)	438(2)
P	0.43056(20)	−0.44302(24)	0.32421(16)	386(9)
S(1)	0.53633(23)	0.12432(28)	0.30793(19)	539(12)
S(2)	0.38557(26)	0.24305(33)	0.19724(25)	748(15)
O(1)	0.64714(75)	−0.14021(102)	0.44158(63)	927(50)
O(2)	0.76322(70)	0.17276(81)	0.20262(57)	719(41)
O(3)	0.80707(71)	0.17182(85)	0.45096(56)	759(41)
O(4)	0.87831(71)	−0.11327(84)	0.34242(63)	794(45)
O(5)	0.58390(87)	−0.13313(97)	0.18051(64)	951(52)
O(6)	0.52570(61)	0.13952(72)	0.16300(49)	586(33)
C(1)	0.66092(81)	−0.08191(112)	0.39634(73)	548(47)
C(2)	0.73200(80)	0.11936(97)	0.24158(69)	465(42)
C(3)	0.76465(90)	0.11747(116)	0.40486(77)	579(51)
C(4)	0.80887(90)	−0.06127(111)	0.33246(75)	569(48)
C(5)	0.61972(97)	−0.07641(119)	0.22883(84)	638(55)
C(6)	0.48221(82)	0.16830(98)	0.21684(73)	505(44)
C(7)	0.48642(111)	0.17221(134)	0.08419(83)	767(62)
C(8)	0.55595(142)	0.14319(155)	0.04016(91)	966(82)
C(9)	0.41537(74)	−0.31549(90)	0.36621(63)	410(38)
C(10)	0.40708(99)	−0.31193(108)	0.44155(76)	597(53)
C(11)	0.40301(101)	−0.21294(119)	0.47675(80)	665(57)
C(12)	0.40646(94)	−0.12080(106)	0.43791(89)	633(55)
C(13)	0.41315(98)	−0.12239(102)	0.36353(87)	627(55)
C(14)	0.41622(86)	−0.21934(98)	0.32671(71)	513(45)
C(15)	0.34660(78)	−0.53520(98)	0.34624(59)	450(40)
C(16)	0.24978(85)	−0.50043(108)	0.33382(71)	562(48)
C(17)	0.18475(82)	−0.56599(130)	0.34825(77)	622(53)
C(18)	0.20921(111)	−0.67385(138)	0.37348(79)	703(62)
C(19)	0.29984(118)	−0.70602(112)	0.38525(79)	682(60)
C(20)	0.37019(89)	−0.63888(101)	0.37103(71)	526(46)
C(21)	0.54945(71)	−0.49058(88)	0.36259(58)	397(36)
C(22)	0.61208(79)	−0.43694(104)	0.42262(63)	482(41)
C(23)	0.70029(86)	−0.47613(144)	0.44849(69)	689(55)
C(24)	0.73157(84)	−0.56854(112)	0.41622(74)	559(47)
C(25)	0.67056(89)	−0.61819(101)	0.35664(75)	550(48)
C(26)	0.57952(79)	−0.57895(90)	0.32858(67)	458(41)
C(27)	0.41452(71)	−0.43387(88)	0.22149(60)	383(35)
C(28)	0.33717(85)	−0.47577(116)	0.17078(67)	564(45)
C(29)	0.32977(107)	−0.47299(128)	0.09276(74)	706(56)
C(30)	0.40168(100)	−0.42700(121)	0.06610(72)	625(53)
C(31)	0.47897(95)	−0.38168(116)	0.11631(77)	610(53)
C(32)	0.48720(81)	−0.38700(108)	0.19437(69)	526(46)

than those reported for M^{II} neutral complexes [17]. The chemical shifts and multiplicity of the resonance signals in the $[Cat][M(2-Spy)(CO)_4]$ complexes are similar to those for other compounds which contain anionic chelating (N,S)-ligands [24,25].

The ^{13}C NMR spectra for $[PPh_4][M(S,X)(CO)_4]$ complexes ($M = Mo, W$; $X = S, N$) (see Table 3) show signals for all the different carbon atoms, present in the complexes. For the ethylxanthate derivatives the signal at lowest field can be assigned to carbon atom of the group OCS_2 [26]. As expected, only two types of CO ligands are observed in these complexes. However, four different CO ligands are observed in the pyridine-2-thiolate complexes. The δ values for the CO resonances are as observed for other compounds of Mo^0 and W^0 [27]. The chemical shifts are lower for the tungsten complexes than for the analogous molybdenum derivatives owing to the more basic character of tungsten.

Electronic spectra in DMF solution (270–900) and diffuse reflectance spectra (190–900 nm) were recorded for some of the products (see Table 4). The nature of the absorption maxima were assigned by comparison with literature data [28,29]. The band or shoulder in the 450–470 nm region was assigned to LF spin-forbidden singlet $\rightarrow$ triplet transition. The enhanced intensity of this transition in the tungsten complex is the expected result of the larger spin-orbital coupling in the heavier metals. The absorption maxima between 386–420 nm are assigned to $d \leftarrow d$ permitted transitions. Likewise the absorption bands at higher energies include $\pi^*(CO) \leftarrow M$ charge-transfer transitions probably accompanied by $d \leftarrow d$ or intraligand transitions.

II. Description of the structure of $[PPh_4][W(S_2COEt)(CO)_5]$

Table 5 shows the final atomic parameters and Table 6 the bond lengths and

Table 6

Principal bond distances ($\text{\AA}$) and angles ($^\circ$) for $[PPh_4][W(S_2COEt)(CO)_5]$

W–S(1)	2.571(3)	O(1)–C(1)	1.144(19)
W–C(1)	2.015(14)	O(2)–C(2)	1.138(17)
W–C(2)	2.047(13)	O(3)–C(3)	1.126(16)
W–C(3)	2.054(13)	O(4)–C(4)	1.175(17)
W–C(4)	1.945(13)	O(5)–C(5)	1.138(13)
W–C(5)	2.062(14)	O(6)–C(6)	1.329(17)
S(1)–C(6)	1.718(12)	O(6)–C(7)	1.144(19)
S(2)–C(6)	1.649(12)	C(7)–C(8)	1.476(27)
C(1)–W–C(2)	176.0(5)	S(1)–W–C(14)	176.5(4)
C(1)–W–C(3)	90.4(5)	S(1)–W–C(5)	88.5(4)
C(1)–W–C(4)	85.6(4)	W–S(1)–C(6)	114.5(5)
C(1)–W–C(5)	91.3(6)	C(6)–O(6)–C(7)	119.0(1)
C(2)–W–C(3)	88.0(5)	W–C(1)–O(1)	177(1)
C(2)–W–C(4)	90.6(5)	W–C(2)–O(2)	173(1)
C(2)–W–C(5)	90.2(5)	W–C(3)–O(3)	178(1)
C(3)–W–C(4)	86.1(5)	W–C(4)–O(4)	177(1)
C(3)–W–C(5)	178.2(6)	W–C(5)–O(5)	176(1)
C(4)–W–C(5)	93.5(6)	S(2)–C(6)–O(6)	122(1)
S(1)–W–C(1)	91.5(4)	S(1)–C(6)–O(6)	114.7(9)
S(1)–W–C(2)	92.2(3)	S(1)–C(6)–S(2)	123.1(8)
S(1)–W–C(3)	92.0(3)	O(6)–C(7)–C(8)	107(1)

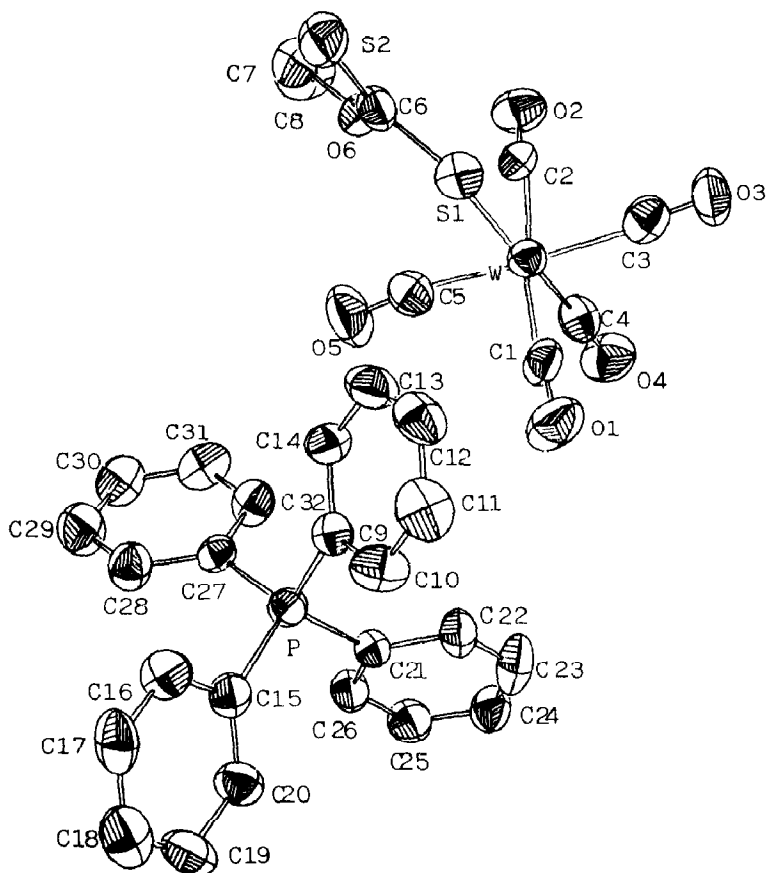


Fig. 1. The structure and atom labelling scheme of $[\text{PPh}_4][\text{W}(\text{S}_2\text{COEt})(\text{CO})_5]$.

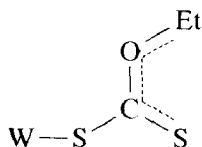
angles for this complex. Figure 1 shows the structure and atom labelling scheme [30].

Few transition-metal complexes have shown unequivocally to contain monodentate xanthate groups [10,11]. Furthermore very few crystal structures of pentacarbonyl complexes containing an S-donor ligand have been determined [31,32].

In the $[\text{PPh}_4][\text{W}(\text{S}_2\text{COEt})(\text{CO})_5]$ complex the tungsten atom is coordinated to five CO groups and a sulfur-donor monodentate ligand. Octahedral symmetry is retained around the metal atom, with angles varying between 85.6 and 93.6° . The structural parameters for the monodentate xanthate ligand resemble those determined previously [10,11]. In such compounds, including the present one, there is a rotation about the S(coordinated)–C bond to place oxygen, not the second sulfur, in the non-bonded position nearest the metal. Since the W–O distance is non-bonding, this conformation may be dictated by the smaller size of oxygen relative to that of sulfur.

Although, the C(6)–S(2) bond distance, $1.64 \text{ \AA}$, is shorter than the C(6)–S(1) bond distance, $1.71 \text{ \AA}$, these distances are neither as long nor as short as those in molecules with C=S ($1.61 \text{ \AA}$) and C–S ($1.78 \text{ \AA}$) bonds. On the other hand, the C(6)–O(6) distance, $1.329(17) \text{ \AA}$, is shorter than the corresponding distance to sp^2 carbon in methyl vinyl ether ($1.360(3) \text{ \AA}$); these observations, viewed along the

xanthate planarity and the C(6)–O(6)–C(7) bond angle ($119.0(1)^\circ$), indicate significant C(6)–O(6) double-bond character. The C–S lengthening and C–O shorting are consistent with the following delocalized structure:



The W–S distance is comparable to those observed for other tungsten complexes with sulfur-donor ligands [31]. The *trans*-W–CO bond ($1.945(13)$ Å) to W–S bond is significantly shorter than the four *cis*-W–CO bonds (average, 2.044 Å), reflecting the lower π -acceptor ability of the xanthate ligand compared with that of coordinated CO.

III. Reactions of $[\text{PPh}_4][\text{M}(\text{S},\text{X})(\text{CO})_n]$ ($n = 5, 4$) compounds with allyl bromide and with HgX_2

The salts $[\text{PPh}_4][\text{M}(\text{S},\text{X})(\text{CO})_4]$ were found to react with an excess of allyl bromide to give the previously reported complex $[\text{Mo}_2\text{Br}_3(\pi\text{-allyl})_2(\text{CO})_4]^-$ [33]. The salt has thus reacted in the same way as the salt $[\text{PPh}_4][\text{Mo}(\text{S},\text{S})(\text{CO})_4]$ (S,S = xanthate or dithiocarbamate) [8]. However, the salts $[\text{PPh}_4][\text{W}(\text{S}_2\text{COR})(\text{CO})_4]$ and $[\text{PPh}_4][\text{W}(\text{2-Spy})(\text{CO})_4]$ behave differently towards the halides. Thus reaction with an excess of allyl bromide gives the reported anion $[\text{WBr}_3(\text{CO})_4]^-$ [34]. In both types of reactions there is displacement of (S,X)-ligand and oxidation of the metal.

When the $[\text{W}(\text{S}_2\text{COR})(\text{CO})_5]^-$ species reacts with $\text{C}_3\text{H}_5\text{Br}$ or HgX_2 ($\text{X} = \text{Cl}$; $\text{X}_2 = \text{Ph}, \text{Cl}$), halopentacarbonyl complexes and other unidentified compounds are obtained. The formation of $[\text{WCl}(\text{CO})_5]^-$ is also observed in the reaction of $[\text{W}(\text{SH})(\text{CO})_5]^-$ with acetyl chloride [35]. The behaviour of the anions in $[\text{PPh}_4][\text{M}(\text{2-Spy})(\text{CO})_4]$ towards HgCl_2 is similar to that of $[\text{W}(\text{N},\text{O})(\text{CO})_4]^-$ anions [9]. Thus the reaction in acetone gives the M^{II} heptacoordinate anionic complexes $[\text{PPh}_4][\text{M}(\text{2-Spy})(\text{CO})_3(\text{HgCl})\text{Cl}]$ ($\text{M} = \text{Mo}, \text{W}$).

Experimental

All manipulations were performed under oxygen-free dry nitrogen. Analytical grade solvents were used.

Reagents. $\text{M}(\text{CO})_5(\text{Rpy})$, ($\text{R} = 2\text{-Me}, \text{H}$; $\text{M} = \text{Mo}, \text{W}$) and $\text{W}(\text{CO})_4(\text{R-py})_2$ ($\text{R} = 2\text{-Me}, \text{H}$) complexes were prepared as previously described [14,36], as were methylxanthate, sodium cyclohexylxanthate [37], potassium *P,P*-diphenylphosphinedithioformate and *P,P*-diphenyl-*N*-phenyl-phosphinothioformamido [38,39]. Molybdenum and tungsten hexacarbonyl, potassium ethylxanthate, sodium *N,N*-diethyldithiocarbamate, ammonium 1-pyrrolyldithiocarbamate and pyridine-2-thiol were used as purchased.

Analysis and physical measurements. C,H,N analysis were carried out by Elemental Micro-Analysis Ltd. Laboratories, Amberley, Bearworthy, (Devon, U.K.). Infrared spectra in the $4000\text{--}200\text{ cm}^{-1}$ region were recorded on a Perkin–Elmer 1300 spectrophotometer, with KBr disks or CH_2Cl_2 solutions. The ^1H (299.95 MHz), ^{13}C (75.43 MHz) and ^{31}P (121.42) NMR spectra were recorded on a Varian VXR-300 spectrometer operating in the FT mode, and chemical shifts are relative to

Me₄Si for ¹H and ¹³C, and to 85% H₃PO₄ for ³¹P spectra in deuterodimethylsulphoxide and deuteriochloroform solutions.

Preparation of complexes

[PPh₄][W(S₂COR)(CO)₅] complexes (R = Me, Et, C₆H₁₁). A mixture of alkali metal xanthate and W(CO)₅(R-py) (R = 2-py, H) in 1/1 molar ratio in 25 ml of acetone was refluxed for 5–8 min. The solution formed was rapidly cooled to room temperature and filtered through Celite. A stoichiometric amount of PPh₄Br was added together with 2 ml of diethyl ether. After filtration and addition of cold light petroleum (b.p. 40–60°C) a yellow oil separated. After decantation of the supernatant solution, the complex was precipitated by addition of diethyl ether with vigorous stirring. The solid was filtered off, washed with diethyl ether, and dried in vacuo.

[PPh₄][W(S₂CPhPh₂)(CO)₅] complex. A mixture of W(CO)₅(2-Mepy) and K₂S₂CPhPh₂ in 1/1 molar ratio in acetone was refluxed for 3 h. The solution was filtered and an equivalent amount of PPh₄Br and 2 ml of diethyl ether were added to the filtrate. After filtration and addition of n-pentane a brown-red solid separated, and was filtered off, washed with n-pentane, and dried in vacuo.

[PPh₄][W(S₂COR)(CO)₄] and [PPh₄][W(S₂CNR'₂)(CO)₄] (R = Me, Et, C₆H₁₁; R' = Et, R'₂ = C₄H₈). *Method A.* The salt of the xanthate or dithiocarbamate was added to a suspension of W(CO)₆ in acetone in an 1/1 molar ratio and the stirred mixture was boiled for 6 h. After cooling, PPh₄Br and 3 ml of diethyl ether were added and the mixture was filtered. The solvent was removed under reduced pressure and diethyl ether was added to the residual oil to give a yellow or yellow-orange solid. This was filtered off, washed with cold EtOH; and dried in vacuo. The unchanged W(CO)₆ was removed by sublimation to 60°C and 2 mmHg. The products can also be recrystallized from an acetone/light petroleum (b.p. 40–60°C) mixture.

Method B. A mixture of W(CO)₅(2-py) or W(CO)₅(py) and the salt of the (S,S)-ligand in acetone was refluxed for 20 min (dithiocarbamates) or 30 min (xanthates). The solution was allowed to cool to room temperature and then filtered through Celite. An equimolar quantity of PPh₄Br and several drops of diethyl ether were added. After filtration through Celite, the filtrate was treated with light petroleum (b.p. 40–60°C) (xanthate derivatives) or cold diethyl ether (dithiocarbamate derivatives) to give a solid, which was filtered off, washed with MeOH or H₂O, respectively, and dried in vacuo.

Method C. The salts [PPh₄][W(S,S)(CO)₄] can be prepared from the W(CO)₄(R-py)₂ (R = 2-Me, H) species. The procedure was similar to that in method B above, but reaction times were 10 min shorter than those used for the synthesis from the pyridinepentacarbonyl derivatives.

[PPh₄][M(Ph₂PC(S)NPh)(CO)₄] complexes (M = Mo, W). A mixture of M(CO)₄(py)₂, Ph₂PC(S)N(H)Ph, and Et₃N (1/1/1 molar ratio), in acetone was refluxed for 3 min (M = Mo) or 15 min (M = W) and then cooled to room temperature and filtered. An equimolecular amount of PPh₄Br and a few ml of diethyl ether were added to the filtrate and the solution was again filtered and light petroleum (b.p. 40–60°C) was added to give an oil. The supernatant solution was decanted and the oil was kept under reduced pressure to give a yellow solid, which was washed with diethyl ether and cold ethanol and dried in vacuo.

[Cat][M(2-Spy)(CO)₄] complexes (M = Mo, W, Cat⁺ = PPh₄⁺; M = W; Cat⁺ = Et₃NH⁺). A solution of 2-HSC₅H₄N (2 mmol) in ethanolic KOH (2 mmol) was added to a solution of M(CO)₄(R-py)₂ (2 mmol) in acetone. After 15 min (M = W) or 10 min (M = Mo) refluxing, the mixture was cooled to room temperature and the solvent removed under reduced pressure. The residual oil was dissolved in acetone and PPh₄Br (2 mmol) and 10 ml of diethyl ether were added. The solution was filtered through Celite and cold n-hexane was added to give an oil. The supernatant solution was decanted and the oily residue was evaporated to dryness to give an orange-yellow solid, which was washed with cold n-hexane and dried in vacuo. A similar procedure, but without addition of PPh₄Br, was used to obtain the Et₃N⁺ salt.

Reaction of [PPh₄][Mo(2-Spy)(CO)₄] with allyl bromide. Formation of [PPh₄][Mo₂Br₃(π-allyl)₂(CO)₄]. A mixture of the molybdenum complex and an excess of allyl bromide was stirred for 10 min and few ml of acetone and cold diethyl ether were then added. The solution was filtered and the filtrate evaporated to dryness. Addition of acetone and n-pentane gave an oil, which crystallized upon addition of light petroleum (b.p. 40–60 °C). The solid was filtered off, washed with pentane, and dried in vacuo. The product was shown by analysis and IR spectroscopy to be [PPh₄][Mo₂Br₃(π-allyl)₂(CO)₄] [33].

Reaction of [PPh₄][W(S₂COR)(CO)₄] or [PPh₄][W(2-Spy)(CO)₄] with allyl bromide. Formation of [PPh₄][WBr₃(CO)₄]. A mixture of the tungsten complex in an excess of allyl bromide was stirred for 15 min (ROCS₂[−]) or 5 min (2-Spy), then filtered through Celite. Addition of cold n-hexane gave an orange solid, which was filtered off, washed with n-hexane, dried in vacuo, and shown to be [PPh₄][WBr₃(CO)₄] [34].

Reaction of [PPh₄][W(2-Spy)(CO)₄] with HgCl₂. Formation of [PPh₄][W(2-Spy)(CO)₃(HgCl)Cl]. HgCl₂ was added to a stirred acetone solution of [PPh₄][W(2-Spy)(CO)₄]. Stirring was continued for 10 min, and then the solution was filtered through Celite. The filtrate was treated with cold diethyl ether and the precipitate formed was filtered off, washed with cold diethyl ether, and dried in vacuo; $\nu(\text{CO})$: 1878, 1915, 2010 cm^{−1}.

Crystal data for [PPh₄][W(S₂COEt)(CO)₅]. *M* = 784.5, monoclinic, space group *P*2₁/*n*, *a* 14.550(4), *b* 12.44(1), *c* 17.950(2) Å; β 104.43(2)°, *V* 3145.9 Å³, *Z* = 4, *D*_c 1.656 g cm^{−3}, *F*(000) 1544, $\mu(\text{Mo-K}\alpha)$ 39.68 cm^{−1}, *T* = 295 K, *R* = 0.043 for 4278 observed reflections.

X-ray data collection, structure determination and refinement. A prismatic crystal 0.2 × 0.2 × 0.5 mm of [PPh₄][W(S₂COEt)(CO)₅] was mounted in an Enraf–Nonius CAD4-F automatic diffractometer. The cell dimensions were refined by least-squares fitting of the θ values of 25 reflections. The intensities of all 5513 unique reflections with 1 < θ < 25 and the range from (−17, 0, 0) to (17, 14, 21) were measured at 295 K with monochromated Mo-K_α radiation (λ 0.71069 Å) and an $\omega/2\theta$ scan technique. There was no appreciable change in the periodically monitored standard reflections. The intensities were corrected for Lorentz and polarization effects, and 4278 were considered as observed with *I* > 2σ(*I*). Scattering factors for neutral atoms and anomalous dispersion corrections for W, P and S were taken from ref. 40.

The structure was solved by Patterson and Fourier methods. An empirical absorption correction [41] was applied at the end of the isotropic refinement. Anisotropic full-matrix least-squares refinement with units weight, minimizing

$\sum w[|F_o| - |F_c|]^2$ gave $R = 0.043$. H atoms were fixed at calculated positions. Final refinement with fixed isotropic temperature factor and coordinates for H atoms gave $R = 0.042$. Maximum and average shifts/error were 0.017 and 0.15 respectively. Most of the calculations were carried out with program XRAY80 [42].

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