New Fluxional Seven-co-ordinate Molybdenum(II) and Tungsten(II) Complexes: X-Ray Structure of the Pyridine-2-thionato Complex $[W(C_5H_4NS)_2(CO)_2(PMe_2Ph)]$†

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The reaction of $[W(CO)_3(MeCN)_3]$ with pyridine-2-thione (pySH) at room temperature gives the tungsten(II) compound $[W(pyS)_2(CO)_3]$ (**1**) and the tungsten(0) compound $[W(CO)_5(pySH)]$ (**2**). To slow the rate of intramolecular exchange of the pyS ligands in (**1**), PMe_2Ph was introduced to give $[W(pyS)_2(CO)_2(PMe_2Ph)]$ (**4**). Crystals of (**4**) are monoclinic, space group $C2/c$, $a = 30.738(9)$, $b = 9.867(2)$, $c = 16.048(9)$ Å, $\beta = 121.04(3)°$, and $Z = 8$, and the X-ray structure was refined to $R = 0.0330$ and $R' = 0.0335$. Molecules of (**4**) contain two chelating pyS ligands and the tungsten is seven-co-ordinated. Approximately determined exchange rates for the diastereotopic Me groups of PMe_2Ph and of the non-equivalent pyS ligands are the same indicating that both exchanges result from the same process. The corresponding molybdenum compound is isostructural and shows similar fluxionality.

Seven-co-ordinated complexes of tungsten(II) and molybdenum(II) are known to adopt several different stereochemistries:[1–4] pentagonal bipyramidal,[5] rectangular-face-capped trigonal prismatic,[6] 4:3 piano-stool,[7] and face-capped octahedral[8] geometries. Generally these complexes are stereochemically non-rigid which is a consequence of the small energy differences between the different forms and commonly there are distortions from idealised geometries which can lead to ambiguities in describing structure. In particular, chelating ligands with small bite angles are expected to cause distortions from idealised geometries. We have been studying pyridine-2-thionato (pyS) complexes intending to synthesize cage compounds with bridging pyS ligands. Attempting to make mononuclear complexes as starting materials for cage compounds, we have prepared and structurally characterised the first tungsten compounds containing pyridine-2-thione (pySH) and pyridine-2-thionate (pyS) which are described in this paper.

Results and Discussion

Syntheses.—Treatment of $[W(CO)_3(MeCN)_3]$ with pySH in acetonitrile solution at room temperature gives the seven-co-ordinate tungsten(II) compound $[W(pyS)_2(CO)_3]$ (**1**) and the tungsten(0) compound $[W(CO)_5(pySH)]$ (**2**) which were separated by t.l.c. on silica. Compound (**2**) was straightforwardly characterised by its ^1H n.m.r. and i.r. spectra (Table 1) as a six-co-ordinate complex containing a pySH ligand in the thione form co-ordinated through the sulphur atom. Compound (**1**) gave only two strong $\nu(CO)$ absorptions in the i.r. spectrum consistent with a facial tricarbonyl arrangement with effective local C_{3v} symmetry. As a co-ordinatively saturated complex, it has both pyS ligands bidentate and ^1H n.m.r. spectra show only one set of pyS resonances even down to -90 °C, the lowest temperature we could conveniently obtain. It is likely, however, that the seven-co-ordinate species is fluxional and that the apparent equivalence of the pyS ligands results from exchange. We could not pursue this aspect further, being unable to obtain frozen-out n.m.r. spectra nor good single crystals for X-ray structure determination.

Neither compound (**1**) nor (**2**) was formed in very good yield and brown decomposition material accompanies their formation. Compound (**2**) does not react with pySH under the conditions of the preparation to give (**1**). We suspect that an intermediate such as $[W(CO)_3(MeCN)_2(pySH)]$ is formed initially which either reacts with more pySH to give (**1**) with displacement of H_2 and MeCN, or partially decomposes with the loss of CO which is scavenged by the intermediate to give (**2**).

We reasoned that an increase in steric crowding might affect the rate of the fluxional process, probably lowering it, so we carried out a similar preparation using $[W(CO)_3(MeCN)_3]$ and 6-methylpyridine-2-thione (mpySH) but this gave only the less interesting tungsten(0) compound $[W(CO)_5(mpySH)]$ (**3**) and none of the tungsten(II) species. Presumably the increased crowding prevents the formation of $[W(mpyS)_2(CO)_3]$ by this route. A possible alternative was to suppress the supposed fluxionality of (**1**) by phosphine substitution. We have prepared the derivative $[W(pyS)_2(CO)_2(PMe_2Ph)]$ (**4**) by reaction of (**1**) with PMe_2Ph in cyclohexane at room temperature and have determined its single-crystal X-ray structure. As expected the fluxionality of (**4**) is suppressed to the extent that ^1H n.m.r. coalescences occur at higher temperatures which are experimentally accessible (see next section).

The molybdenum compound $[Mo(pyS)_2(CO)_3]$ was synthesized similarly to the tungsten compound but is rather more sensitive so we did not isolate it but treated it directly with PMe_2Ph to give $[Mo(pyS)_2(CO)_2(PMe_2Ph)]$ (**5**) which is analogous spectroscopically to the tungsten compound (**4**) and is much more stable than the tricarbonyl compound both thermally and in air.

Structure and Fluxional Behaviour of Compound (**4**).—The single-crystal X-ray structure of (**4**) is shown in Figure 1 and selected bond lengths and angles are in Table 2. The structure is as we predicted with two chelating pyS ligands, a PMe_2Ph, and two CO ligands; an 18-electron structure is therefore adopted. The monodentate ligands are facially arranged like the three CO ligands of the parent compound (**1**). Figure 2 shows two representations of the tungsten co-ordination sphere. For the face-capped octahedral representation (*a*) the atom in the capping position, C(41), should have three similarly small angles to adjacent ligands (around 75°) and three similarly large ones (around 130°). Of the seven co-ordinated atoms only C(41)

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† Dicarbonyl(dimethylphenylphosphine)bis(pyridine-2-thionato-*NS*)-tungsten.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Proton n.m.r. and i.r. spectroscopic data

	I.r.[a]	^{1}H N.m.r.,[b] δ					
Compound	ν(CO)/cm^{-1}	H^6	H^5	H^4	H^3	NH	^3J/Hz
(1)	2 023s, 1 933s	8.44	6.85	8.22	6.80		J(H^{3}H^4) 8.2 J(H^{4}H^5) 7.5 J(H^{5}H^6) 5.6
(2)	2 069m, 1 987m, 1 941s, 1 926s, 1 914 (sh)	7.84	6.94	7.50	7.77	11.2	J(H^{3}H^4) 8.6 J(H^{4}H^5) 7.2 J(H^{5}H^6) 6.0
(3)	2 069m, 1 987m, 1 940s, 1 923s, 1 909 (sh)	2.59 (Me)	6.72	7.42	7.60	11.1	J(H^{3}H^4) 8.7 J(H^{4}H^5) 7.1
(4)[c]	1 937s, 1 850s	8.15 7.79	6.79 6.62	7.33 7.03	6.72 6.27		J(H^{3}H^4) 8.8 J(H^{4}H^5) 8.0 J(H^{5}H^6) 5.6
(5)[d]	1 948s, 1 865s	8.02 7.66	6.78 6.52	7.31 6.99	7.18 6.78		J(H^{3}H^4) 8.0 J(H^{4}H^5) 7.9 J(H^{5}H^6) 5.4

[a] Compounds (1)—(3) in cyclohexane, (4) and (5) in dichloromethane. [b] Recorded in $CDCl_3$ or CD_2Cl_2. [c] Recorded in $CDCl_3$ at −53 °C; Me doublets at δ 1.79 (J 9.2) and 1.86 (J 8.8 Hz). [d] Recorded in CD_2Cl_2 at −80 °C; Me doublets at δ 1.70 (J 8.3) and 1.57 (J 8.9 Hz).

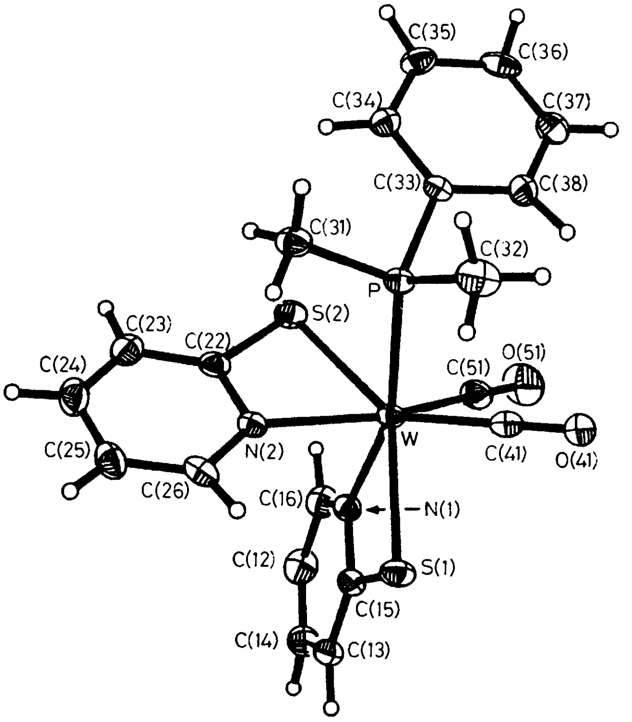
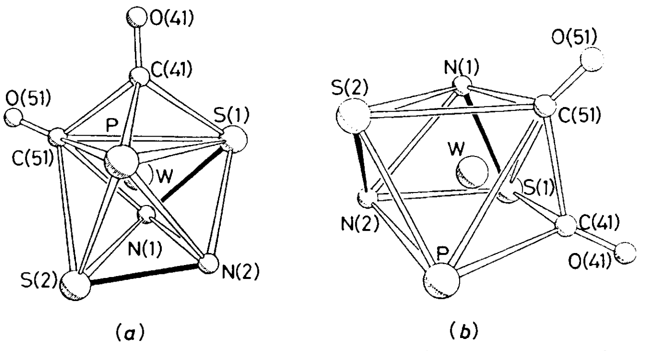


Figure 1. Molecular structure of [W(pyS)$_2$(CO)$_2$(PMe$_2$Ph)] **(4)**



(*a*) (*b*)

Figure 2. Representations of the geometry of the co-ordination sphere around W in compound **(4)** illustrating capped octahedral (*a*) and 4:3 piano-stool (*b*) descriptions

Table 2. Selected bond lengths (Å) and angles (°) for [W(pyS)$_2$(CO)$_2$(PMe$_2$Ph)] **(4)**

W–P	2.508(2)	W–S(1)	2.520(3)
W–S(2)	2.538(2)	W–N(1)	2.198(6)
W–N(2)	2.242(6)	W–C(41)	1.956(7)
W–C(51)	1.943(8)	P–C(31)	1.820(7)
P–C(32)	1.832(7)	P–C(33)	1.825(9)
S(1)–C(15)	1.750(6)	S(2)–C(22)	1.749(8)
N(1)–C(15)	1.33(1)	N(2)–C(22)	1.37(1)
C(41)–O(41)	1.16(1)	C(51)–O(51)	1.17(1)
W–S(1)–C(15)	81.5(3)	W–S(2)–C(22)	81.9(2)
W–N(1)–C(15)	105.2(4)	W–N(2)–C(22)	102.6(5)
S(1)–C(15)–N(1)	109.1(6)	S(2)–C(22)–N(2)	110.7(5)
C(41)–W–C(51)	71.5(3)	C(41)–W–P	75.3(3)
C(41)–W–S(1)	76.8(3)	C(41)–W–S(2)	143.1(2)
C(41)–W–N(1)	122.3(3)	C(41)–W–N(2)	134.9(2)
C(51)–W–P	103.2(3)	C(51)–W–S(1)	110.4(3)
C(51)–W–S(2)	92.1(2)	C(51)–W–N(1)	83.9(3)
C(51)–W–N(2)	153.5(2)	P–W–S(1)	126.0(1)
P–W–S(2)	76.9(1)	P–W–N(1)	162.4(1)
P–W–N(2)	84.9(2)	S(1)–W–S(2)	139.9(1)
S(1)–W–N(1)	64.1(2)	S(1)–W–N(2)	83.3(2)
S(2)–W–N(1)	86.9(2)	S(2)–W–N(2)	64.8(2)
N(1)–W–N(2)	82.1(2)		

fits this condition well with angles 71.5(3), 75.3(3), and 76.8(3)° to the three atoms in the capped face of the octahedron [C(51), P, and S(1)] and with angles 143.1(3), 122.3(3), and 134.9(2)° to the atoms in the opposite face [S(2), N(1), and N(2)]. The capped face C(51)PS(1) has expanded as expected relative to the opposite face S(2)N(1)N(2). The edges N(1)–S(1) and N(2)–S(2) are shown with solid lines to indicate that these are shorter than the others because of the chelate rings. The small angles in the chelate rings [N(1)–W–S(1) 64.1(2), N(2)–W–S(2) 64.8(2)°] are the main causes for the distortions from an idealised capped-octahedral geometry. Representation (*b*) in Figure 2 shows that the 4:3 piano-stool arrangement is an alternative having the ligand distribution PN(2)S(1)C(41):S(2)N(1)C(51). A quantitative assessment of the extent of deviation from the two idealised geometries would be necessary to decide which is the better description.

Compound **(4)** is asymmetric in the crystal; the pyS ligands are non-equivalent and the Me groups are diastereotopic. This

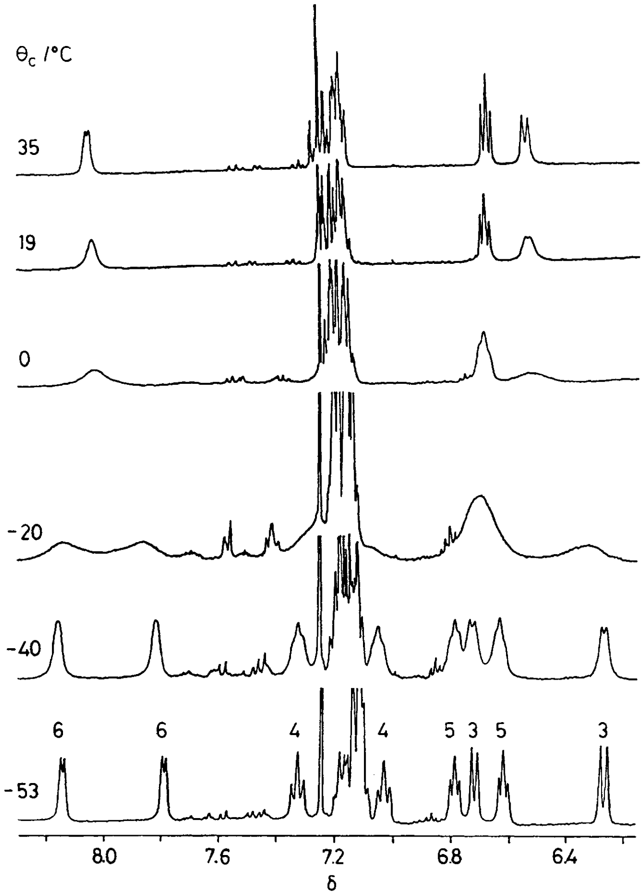


Figure 3. Proton n.m.r. spectra of compound (4) in $CDCl_3$ at 400 MHz. The weak absorptions observed in the ranges δ 6.8—7.0 and 7.4—7.8 are probably due to an impurity containing co-ordinated pyS. The numbers above the signals are assignments to the hydrogen atoms in the 3- to 6-positions of the pyS rings

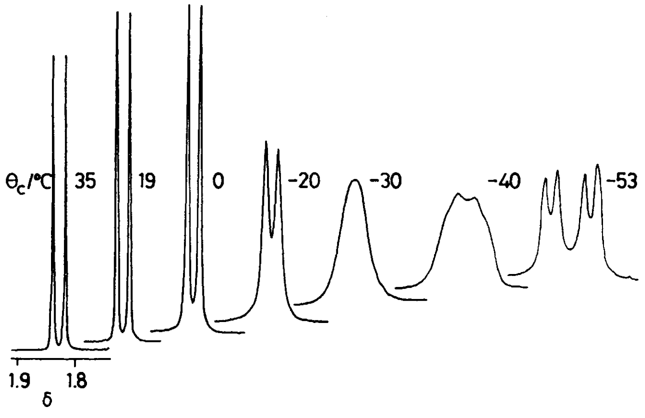
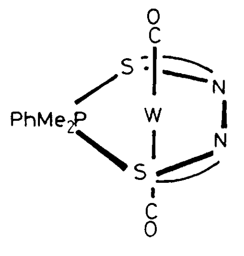
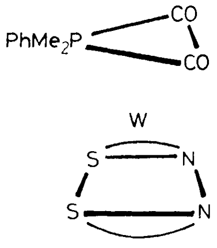


Figure 4. Proton n.m.r. spectra of compound (4) in $CDCl_3$ at 400 MHz. The scale of each spectrum is the same but they are offset with respect to each other

asymmetry is also observed in the ^1H n.m.r. spectrum in $CDCl_3$ at −53 °C (Table 1). The molybdenum analogue (**5**) also shows two sets of pyS signals and two Me doublets in the ^1H n.m.r. spectrum in CD_2Cl_2 at −80 °C. Figures 3 and 4 show the temperature dependence of the ^1H n.m.r. spectrum of (**4**). We did not make line-shape analyses of these spectra which would have given accurate kinetic data. However, estimates of the exchange rates are 316 s^{-1} at T_c (263 ± 10 K) for the pyS 6-H signals ($\Delta\nu$ = 142.4 Hz) and 60 s^{-1} at T_c (238 ± 10 K) for the methyl signals ($\Delta\nu$ = 27.2 Hz). When allowance is made for the 25 K temperature difference, these rates could be for the same process. The $\Delta G^{\ddagger}$ values are estimated to be 52 ± 2 kJ mol^{-1} for pyS ligand exchange and 50 ± 2 kJ mol^{-1} for the exchange of the diastereotopic methyl groups. We believe that these exchanges are a consequence of the same process which would require a transition state or intermediate with a plane of symmetry passing through the W–P bond and also relating the two pyS ligands. There are various possible geometries, such as (**A**) and (**B**), which would fit this but none is simply and obviously derived from the geometry found in the crystal. There may well be other processes occurring, such as a turnstile rotation of the $W(CO)_2(PMe_2Ph)$ unit, which are unobserved because they do not lead to exchange but may nonetheless be important for the fluxionality of this system.



(**A**)



(**B**)

Experimental

Tungsten and molybdenum hexacarbonyls and pyridine-2-thione were obtained from Aldrich Chemical Company and used as obtained.

Reactions of $[W(CO)_3(MeCN)_3]$.—*With pyridine-2-thione.* A mixture of $[W(CO)_6]$ (1.12 g, 3.17 mmol) and acetonitrile (50 cm^3) was heated under reflux under nitrogen for 40 h to generate $[W(CO)_3(MeCN)_3]$ in solution (i.r. evidence). Pyridine-2-thione (1.06 g, 9.50 mmol) was added to the cooled solution and the mixture stirred for 48 h at room temperature. The solvent was removed under vacuum and the deep yellow solid residue chromatographed on a silica gel column [60—120 mesh; eluant, light petroleum (b.p. <40 °C)–dichloromethane (7:3 v/v)] to give $[W(pyS)_2(CO)_3]$ (**1**) as red-brown crystals (0.163 g, 12%) from a dichloromethane–hexane mixture (Found: C, 32.4; H, 1.7; N, 5.6; O, 9.7; S, 13.0. Calc. for $C_{13}H_8N_2O_3S_2W$: C, 32.0; H, 1.65; N, 5.75; O, 9.8; S, 13.15%). A second band gave $[W(CO)_5(pySH)]$ (**2**) as yellow crystals (0.073 g, 6%) from a dichloromethane–hexane mixture (Found: C, 27.5; H, 1.5; N, 3.3; O, 18.4; S, 7.25. Calc. for $C_{10}H_5NO_5SW$: C, 27.6; H, 1.15; N, 3.2; O, 18.4; S, 7.35%).

With 6-methylpyridine-2-thione. A solution of the acetonitrile compound prepared from $[W(CO)_6]$ (1.00 g) as above was treated with mpyS (1.06 g) and the mixture stirred under nitrogen at room temperature for 48 h. Chromatographic separation as above gave only $[W(CO)_5(mpySH)]$ (**3**) as a yellow powder (0.273 g, 21%) from a dichloromethane–hexane mixture (Found: C, 30.6; H, 1.75; N, 3.0; S, 6.75. Calc. for $C_{11}H_7NO_5SW$: C, 29.4; H, 1.55; N, 3.1; S, 7.15%). No evidence for the formation of $[W(mpyS)_2(CO)_3]$ was obtained.

Reaction of $[W(pyS)_2(CO)_3]$ (**1**) *with Dimethylphenylphosphine.*—A solution of compound (**1**) (0.200 g, 0.40 mmol) and PMe_2Ph (0.056 g, 0.40 mmol) in cyclohexane (50 cm^3) was stirred under nitrogen at room temperature for 1 h. A deep yellow precipitate began to be deposited after a few minutes.

Table 3. Crystal data and details of intensity measurements and structure solution and refinement for [W(pyS)$_2$(CO)$_2$(PMe$_2$Ph)] (**4**)

Formula	$C_{20}H_{19}N_2O_2PS_2W$
M	598.33
Crystal system	Monoclinic
Space group	$C2/c$
a/Å	30.738(9)
b/Å	9.867(2)
c/Å	16.048(9)
β/°	121.04(3)
U/Å^3	4 167(1)
Z	8
D_c/g cm^{-3}	1.91
$F(000)$	2 320
Collection range/°	$5 \leqslant 2\theta \leqslant 50$
Rejection criterion	$F_o \leqslant 3\sigma(F_o)$
No. reflections used in refinement	3 145
R^a	0.0330
R'^b	0.0335

^{a} $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. ^{b} $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Table 4. Atomic co-ordinates (× 10^4) for [W(pyS)$_2$(CO)$_2$(PMe$_2$Ph)] (**4**)

Atom	x	y	z
W	1 331(1)	2 673(1)	4 306(1)
P	1 616(1)	2 010(2)	6 022(1)
S(2)	741(1)	727(2)	4 091(1)
S(1)	1 898(1)	3 446(2)	3 692(1)
O(51)	484(2)	4 805(7)	3 786(5)
O(41)	1 809(2)	5 325(5)	5 481(4)
C(41)	1 651(3)	4 306(7)	5 072(5)
C(51)	805(3)	4 011(7)	4 000(6)
N(1)	995(2)	2 611(5)	2 721(4)
C(12)	437(3)	2 345(8)	1 031(6)
C(13)	1 301(3)	3 050(7)	1 660(6)
C(14)	829(4)	2 728(8)	885(6)
C(15)	1 365(3)	2 987(6)	2 576(5)
C(16)	535(3)	2 289(8)	1 962(6)
C(31)	1 846(3)	284(7)	6 384(6)
N(2)	1 608(2)	609(5)	4 208(4)
C(22)	1 217(3)	−217(7)	4 071(5)
C(26)	2 016(3)	62(7)	4 245(5)
C(24)	1 658(3)	−2 144(8)	3 991(6)
C(25)	2 048(3)	−1 289(8)	4 121(6)
C(23)	1 236(3)	−1 601(8)	3 959(5)
C(38)	954(3)	3 524(7)	6 322(7)
C(33)	1 108(2)	2 214(6)	6 285(5)
C(32)	2 136(3)	2 956(9)	7 022(6)
C(35)	470(3)	1 364(8)	6 585(6)
C(36)	322(3)	2 673(9)	6 625(6)
C(34)	859(3)	1 131(7)	6 411(5)
C(37)	565(3)	3 739(8)	6 501(7)

The solvent was removed under reduced pressure and the residue chromatographed [t.l.c. on SiO$_2$; eluant light petroleum (b.p. <40 °C)–dichloromethane (4:1 v/v)] to give [W(pyS)$_2$(CO)$_2$(PMe$_2$Ph)] (**4**) as deep yellow crystals (0.137 g, 54%) from a dichloromethane–methanol mixture (Found: C, 40.0; H, 3.0; N, 4.85; S, 10.9. Calc. for $C_{20}H_{19}N_2O_2PS_2W$: C, 40.15; H, 3.2; N, 4.7; S, 10.7%).

Synthesis of [Mo(pyS)$_2$(CO)$_3$] *and its Reaction with Dimethylphenylphosphine.*—A solution of [Mo(CO)$_6$] (2.00 g, 7.75 mmol) in acetonitrile was refluxed under nitrogen for 4 h to generate [Mo(CO)$_3$(MeCN)$_3$] (i.r. evidence). Pyridine-2-thione (2.52 g, 22.6 mmol) was added to the pale yellow solution and the mixture stirred for 12 h at room temperature until it was blood red. The i.r. spectrum demonstrated the presence of [Mo(pyS)$_2$(CO)$_3$]. Dimethylphenylphosphine (1.07 g, 1.02 mmol) was added and the solution stirred for 24 h. Work-up as in the tungsten case gave several t.l.c. bands, one of which yielded [Mo(pyS)$_2$(CO)$_2$(PMe$_2$Ph)] (**5**) as red crystals (0.625 g, 16%) from a dichloromethane–methanol mixture (Found: C, 46.95; H, 3.65; N, 5.35; P, 6.15; S, 12.4. Calc. for $C_{20}H_{19}N_2MoO_2PS_2$: C, 47.05; H, 3.75; N, 5.5; P, 6.05; S, 12.55%). The intermediate compound [Mo(pyS)$_2$(CO)$_3$] could not be isolated and the other products were not characterised.

X-*Ray Structure Determination for* [W(pyS)$_2$(CO)$_2$(PMe$_2$Ph)] (**4**).—A deep yellow crystal of complex (**4**) of size 0.24 × 0.14 × 0.30 mm deposited from a dichloromethane–methanol solution was chosen for study. Measurements were made at 290 K using a Nicolet R3v/m diffractometer operating in the ω—2θ scan mode with graphite-monochromated Mo-K_α radiation (λ = 0.710 73 Å). Crystal data and details of the data collection, structure solution, and refinement are in Table 3. A total of 3 934 unique intensity data were corrected for Lorentz and polarisation effects and a decay correction calculated from the intensities of three standard reflections collected periodically throughout the experiment was also applied. The data were corrected for absorption using the azimuthal scan method, μ(Mo-K_α) = 59.5 cm^{-1}.

The structure was solved by direct methods and a model containing 299 parameters was refined by alternating cycles of full-matrix least squares and by Fourier difference syntheses. All non-hydrogen atoms were refined anisotropically and hydrogen atoms included in the model for structure-factor calculations in idealised positions but their positions were not refined. The function minimised was $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ with the weight w defined as $1/[\sigma^2(F_o) + 0.000\ 396F_o^2]$. All calculations were carried out using a MicroVax II computer running SHELXTL PLUS.[9] Atomic co-ordinates are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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