Syntheses, Reactivities and Molecular Structures of Tungsten Complexes containing the Diphenylphosphinodithioformato Ligand†

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Treatment of $[NEt_4][W(CO)_5(PPh_2)]$ **1** with CS_2 afforded $[NEt_4][W(CO)_5(PPh_2CS_2)]$ **3** which was also synthesized from the reaction of $[W(CO)_5(MeCN)]$ with $[NEt_4][PPh_2CS_2]$ **2**. The reactions of **3** with various alkyl halides gave the neutral complexes $[W(CO)_5\{PPh_2(CS_2R)\}]$ [R = Me(**4a**), Et, C_2H_4OH, C_3H_5, CH_2CN, C_2H_4CN or C_3H_6CN], and the reactions of **3** with acyl halides gave $[W(CO)_5\{PPh_2(CS_2COR)\}]$ (R = Me or Ph). Both alkylation and acylation reactions occur at the sulfur atom. Treatment of **3** with $[Re(CO)_5Br]$ afforded $[(OC)_5W(\mu\text{-}PPh_2CS_2)Re(CO)_5]$ in which the two metal atoms were bridged by the $PPh_2CS_2^-$ ligand. The reaction of **3** with $[W(pip)_2(CO)_4]$ (pip = piperidine) yielded $[W(CO)_5(PPh_2H)]$ and the dithiocarbamato tungsten complex $[NEt_4][W(CO)_4(S_2CNC_5H_{10})]$. Complex **3** reacted with organic α,ω-diiodides (CH_2I_2, $C_2H_4I_2$, $C_3H_6I_2$), giving the phosphine bridged dinuclear complexes $[\{W(CO)_5(PPh_2CS_2)\}_2(\mu\text{-}CH_2)_n]$ (n = 1–3), and only in the reaction of $C_3H_6I_2$, was a mononuclear complex $\{[W(CO)_5\{PPh_2(CS_2C_3H_6I)\}]\}$ seen as a minor product. Complex $[\{W(CO)_5(PPh_2CS_2)\}_2(CO)_2]$ was obtained from the reaction of **3** with oxalyl bromide in CH_2Cl_2. Thermolysis of **3** in tetrahydrofuran (thf) gave an anionic product identified as $[NEt_4][W(CO)_4(PPh_2CS_2)]$. All of the complexes were identified by spectroscopic methods. The structures of complexes **2**, **3** and **4a** were confirmed by single-crystal X-ray diffraction analyses. Crystal data: **2**, monoclinic, space group $P2_1$, a = 10.244(4), b = 9.877(4), c = 11.124(3) Å, β = 102.02(2)°, Z = 2, R = 0.062, R' = 0.073 based on 1180 reflections with $I > 2\sigma(I)$; **3**, triclinic, space group $P\bar{1}$, a = 10.688(3), b = 11.070(2), c = 12.785(2) Å, α = 88.26(1), β = 81.87(2), γ = 74.081(17)°, Z = 2, R = 0.028, R' = 0.025 based on 4557 reflections with $I > 2\sigma(I)$; **4a**, triclinic, space group $P\bar{1}$, a = 9.177(5), b = 9.403(3), c = 12.461(6) Å, α = 90.00(3), β = 103.85(4), γ = 94.79(3)°, Z = 2, R = 0.041, R' = 0.041 based on 2442 reflections with $I > 2\sigma(I)$.

The chemistry of complexes containing the zwitterionic trialkylphosphonium dithiocarboxylate ligand,[1] $R_3P^+CS_2^-$, or heteroallylic anionic ligands $R_2P(X)C(Y)NR^-$ or $R_2PC(Y)NR^-$ (X = O or S, Y = O or S)[2] or dithiocarbamate ligand[3] have attracted considerable attention in recent years. One of the objectives for studying these complexes is to find different bonding modes of such ligands and to explore their chemistry. Three possible co-ordination sites are known for the $R_3P^+CS_2^-$ ligand, and a variety of bonding modes have been observed; these include monodentate co-ordination through one S atom,[1a–c] bidentate through two S atoms by chelation[1c–f] or bridging between two metal centres,[1g,h] dinuclear pseudoallylic bridging form *i.e.* η^3, σ-mode with donation of six electrons,[1h–k] or η^2, η^3 mode with donation of eight electrons.[1l] The $R_2P(X)C(Y)NR^-$ or $R_2PC(Y)NR^-$ (X = O or S, Y = O or S) anionic ligands normally show bidentate co-ordination through O and S,[2a] N and S,[2c,d] S and S,[2e] P and S.[2b,d,f–i] Interestingly, in metal complexes containing the aforementioned ligands, no monodentate P-co-ordination mode has been observed. The dithiocarbamate ligand was found to bind to metal through one or two sulfur atoms. Whereas the co-ordination chemistry of the dithiocarbamato ligand ($R_2NCS_2^-$) has been much explored, virtually none is known of the phosphorus analogue $R_2PCS_2^-$. For $R_2PCS_2^-$, only one example[4] is known and, in that instance, the chelating $R_2PCS_2^-$ ligand bonds to the metal through the two sulfur atoms of the CS_2.

In our previous communication,[5] we reported the synthesis of the complex $[NEt_4][W(CO)_5(PPh_2CS_2)]$ by the reaction of $[W(CO)_2(PPh_2)]^-$ with CS_2 in the presence of NEt_4Br and found that the $PPh_2CS_2^-$ ligand was bound to the metal in an unprecedented monodentate P-co-ordination mode. Herein we report the synthesis of the anionic diphenylphosphinodithioformato $Ph_2PCS_2^-$ and a series of tungsten complexes each containing the monodentate P-co-ordinated $R_2PCS_2^-$ ligand and the reactivities of these complexes. The new bonding mode has been confirmed by single-crystal X-ray diffraction studies.

Experimental

General Procedures.—All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. NMR spectra were recorded on a Bruker AC-200, or on a AM-300 WB FT-NMR spectrometer and are reported in units of δ (ppm) with residual protons in the solvent used as an internal standard ($CDCl_3$, δ 7.24; CD_3CN, δ 1.93; C_6D_6, δ 7.15; C_2D_6CO, δ 2.04). IR spectra were measured on a Perkin-Elmer 983 instrument and were referenced to a polystyrene standard, using cells equipped with calcium fluoride windows. Mass spectra were recorded on a JEOL SX-102A spectrometer. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. n-Hexane, diethyl ether, tetrahydrofuran (thf) and benzene were distilled from sodium–benzophenone. Acetonitrile, dichloromethane were distilled from calcium hydride, and methanol from magnesium. All other solvents and reagents were of reagent grade and were used as received. Metal carbonyls $\{[W(CO)_6]$, $[Re_2(CO)_{10}]\}$, allyl bromide and iodomethane were purchased from Strem, Merck and Aldrich, respectively. CS_2, $LiBu^n$, NEt_4Br, EtI, IC_2H_4OH, CH_2I_2, ICH_2CN, IC_2H_4CN,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

IC_3H_6CN, $C_2H_4I_2$ and $C_3H_6I_2$ were purchased from Janssen. The compounds $[W(pip)_2(CO)_4]$ (pip = piperidine),[6] $[Re(CO)_5Br]$[7] and PPh_2H[8] were prepared according to the literature methods. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument located at the National Taiwan University.

Syntheses.—$[NEt_4][W(CO)_5(PPh_2)]$ **1**. To a flask containing a thf solution of $[W(CO)_5(PPh_2H)]$ (0.75 g, 1.5 mmol) and NEt_4Br (0.3 g, 1.5 mmol), an aliquot of $LiBu^n$ (1 cm^3, 1.6 mmol) was added at 0 °C. The solution was stirred for 5 min and the solvent was removed *in vacuo*. Methanol (15 cm^3) was added to the flask and the solution was stored at −18 °C for 12 h to give yellow precipitates. These precipitates were filtered off, washed with 2 × 10 cm^3 diethyl ether and then dried under vacuum to give **1** (1.0 g, 1.4 mmol) as a yellow powder in 93% yield. IR (KBr, ν_{CO}): 2070m and 1910vs cm^{-1}. NMR ($CDCl_3$): ^{31}P (81 MHz), δ −12.9 (J_{WP} = 226.95 Hz); ^1H (200 MHz), δ 1.18 (tt, 12 H, CH_3, $^3J_{NH}$ = 1.87, J_{HH} = 7.3), 3.18 (q, 8 H, CH_2, J_{HH} = 7.3 Hz), 7.47 (m, 6 H, Ph) and 7.67 (m, 4 H, Ph); ^{13}C (50 MHz), δ 7.65 (CH_3), 52.96 (CH_2), 128.16 (d, *m*-C of Ph, $^3J_{PC}$ = 9.0), 131.48 (s, *p*-C of Ph), 133.0 (d, *o*-C of Ph, $^2J_{PC}$ = 9.7), 134.61 (d, *ipso*-C of Ph, J_{PC} = 34.58 Hz) and 197.0 (CO).

$[NEt_4][PPh_2CS_2]$ **2**. A solution of $KPPh_2$ (1 mol dm^{-3}, 10 cm^3, 10 mmol) in thf was added slowly to a flask containing CS_2 (0.9 cm^3, 15 mmol) at 0 °C. The solution was stirred for 5 min then was transferred to a flask containing NEt_4Br (2.1 g, 10 mmol) in MeOH (10 cm^3) at room temperature. After solvent was removed *in vacuo*, water (10 cm^3) was added to the flask and the solution yielded red precipitates during 1 h. The mixture was filtered and the precipitates were washed with diethyl ether (3 × 10 cm^3) to give a red powder, identified as **2**. NMR (CD_3CN): ^{31}P (81 MHz), δ 44.1; ^1H (200 MHz), δ 1.17 (tt, 12 H, CH_3, $^3J_{NH}$ = 1.87, J_{HH} = 7.3), 3.14 (q, 8 H, CH_2, J_{HH} = 7.3 Hz), 7.24 (m, 6 H, Ph) and 7.49 (m, 4 H, Ph); ^{13}C (50 MHz), δ 7.70 (CH_3), 52.60 (CH_2), 127.63 (d, *m*-C of Ph, $^3J_{PC}$ = 7.0), 127.90 (s, *p*-C of Ph), 134.39 (d, *o*-C of Ph, $^2J_{PC}$ = 19.5), 141.61 (d, *ipso*-C of Ph, J_{PC} = 34.18) and 210.1 (d, CS_2, J_{PC} = 25.50 Hz). Mass spectrum: *m/z* 391 (M^+) (Found: C, 67.95; H, 2.70; N, 3.75. $C_{21}H_{10}NPS_2$ requires C, 67.90; H, 2.70; N, 3.75%).

$[NEt_4][W(CO)_5(PPh_2CS_2)]$ **3**. *Method A*. To a thf solution of **1** (0.51 g, 1 mmol), CS_2 (1 cm^3) was added at room temperature. The colour changed from bright yellow to red immediately accompanied with the formation of red precipitates. The solution was filtered and the precipitates were washed with hexane to gave a red powder **3** (0.62 g) in 87% yield.

Method B. A MeCN solution (5 cm^3) of $[W(CO)_5(MeCN)]$ (0.364 g, 1 mmol) was added slowly at room temperature to a MeCN solution (20 cm^3) of $[NEt_4][PPh_2CS_2]$ **2** (0.391 g, 1 mmol). The solution was stirred for 1 h. The reaction was monitored by ^{31}P NMR spectroscopy. After complete disappearance of the ^{31}P resonance of **2**, acetonitrile was removed under vacuum to give a red-brown powder. The crude product was recrystallized from CH_2Cl_2–MeOH (1 : 1) to give microcrystalline complex **3** (0.6 g, 84%). IR (KBr, ν_{CO}): 2062m, 1979s, 1947s and 1904vs cm^{-1}. ν_{CS} 1027s and 990w cm^{-1}. NMR ($CDCl_3$): ^{31}P (81 MHz), δ 59.08 (J_{WP} = 238.24 Hz); ^1H (200 MHz), δ 1.18 (tt, 12 H, CH_3, $^3J_{NH}$ = 1.87, J_{HH} = 7.3), 3.10 (q, 8 H, CH_2, J_{HH} = 7.3 Hz), 7.35 (m, 6 H, Ph) and 7.66 (m, 4 H, Ph); ^{13}C (50 MHz), δ 7.56 (CH_3), 52.95 (CH_2), 128.25 (d, *m*-C of Ph, $^3J_{PC}$ = 9.76), 129.93 (s, *p*-C of Ph), 134.61 (d, *o*-C of Ph, $^2J_{PC}$ = 9.77), 134.61 (d, *ipso*-C of Ph, J_{PC} = 34.18), 199.62 (d, *cis*-CO, $^2J_{PC}$ = 7.50), 200.1 (d, CS_2, J_{PC} = 25.50) and 255.41 (d, *trans*-CO, $^2J_{PC}$ = 7.40 Hz). Mass spectrum: *m/z* 845 (M^+ + NEt_4), 714 (M^+ + NEt_4 − 2CO − CS_2) (Found: C, 43.45; H, 4.30; N, 1.95. $C_{26}H_{30}NO_5PS_2W$ requires C, 43.65; H, 4.25; N, 1.95%).

Reactions of Complex **3**.—*With* MeI. To a solution of **3** (0.71 g, 1 mmol) in CH_2Cl_2 (20 cm^3), MeI (0.1 cm^3, 1 mmol) was added and the mixture was stirred at room temperature for 1 min. The solvent was removed and the residue was extracted with hexane (2 × 10 cm^3), and the extracts were filtered through Celite. The filtrate was concentrated to *ca.* 5 cm^3 and cooled to −18 °C for 12 h to give the red crystalline product $[W(CO)_5\{PPh_2(CS_2Me)\}]$ **4a**. Yield = 0.51 g, 85%. IR (KBr, ν_{CO}): 2071m, 1988s, 1957sh and 1911vs cm^{-1}. NMR ($CDCl_3$): ^{31}P (81 MHz), δ 59.05 (J_{WP} = 247.95 Hz); ^1H (200 MHz), δ 2.71 (s, 3 H, SCH_3), 7.50 (m, 6 H, Ph) and 7.66 (m, 4 H, Ph); ^{13}C (50 MHz), δ 21.86 (CH_3), 129.62 (d, *m*-C of Ph, $^3J_{PC}$ = 9.72), 132.28 (s, *p*-C of Ph), 134.63 (d, *o*-C of Ph, $^2J_{PC}$ = 12.2), 134.88 (d, *ipso*-C of Ph, J_{PC} = 36.6), 198.04 (d, *cis*-CO, $^2J_{PC}$ = 7.50), 200.00 (d, CS_2, J_{PC} = 25.50), 240.28 (d, *trans*-CO, $^2J_{PC}$ = 7.40 Hz). Mass spectrum: *m/z* 600.7 (M^+), 571 (M^+ − CO), 543.6 (M^+ − 2CO), 515.6 (M^+ − 3CO), 487 (M^+ − 4CO), 459.7 (M^+ − 5CO), 444.7 (M^+ − 5CO − CH_3) and 368.9 (M^+ − 5CO, CH_3, CS_2) (Found: C, 38.00; H, 2.25. $C_{19}H_{13}O_5PS_2W$ requires C, 38.00; H, 2.20%).

With EtI. The synthesis and work-up were similar to those used in the preparation of complex **4a**. The pure complex $[W(CO)_5\{PPh_2(CS_2Et)\}]$ **4b** was isolated in 89% yield as a red microcrystalline solid. IR (thf, ν_{CO}): 2072m and 1934vs cm^{-1}. NMR ($CDCl_3$): ^{31}P (81 MHz), δ 58.81 (J_{WP} = 245.96 Hz); ^1H (200 MHz), δ 1.34 (t, 3 H, CH_3, J_{HH} = 7.35), 3.28 (q, 2 H, CH_2, J_{HH} = 7.35 Hz), 7.53 (m, 6 H, Ph) and 7.68 (m, 4 H, Ph); ^{13}C (50 MHz), δ 11.82 (CH_3), 32.23 (CH_2), 128.44 (d, *m*-C of Ph, $^3J_{PC}$ = 9.0), 130.98 (s, *p*-C of Ph), 133.74 (d, *o*-C of Ph, $^2J_{PC}$ = 13.5), 134.34 (d, *ipso*-C of Ph, J_{PC} = 38.78), 197.13 (d, *cis*-CO, $^2J_{PC}$ = 7.50), 199.00 (d, CS_2, J_{PC} = 25.50) and 220.28 (d, *trans*-CO, $^2J_{PC}$ = 7.80 Hz). Mass spectrum: *m/z* 614 (M^+), 586 (M^+ − CO), 558 (M^+ − 2CO), 530 (M^+ − 3CO), 502 (M^+ − 4CO), 474 (M^+ − 5CO), 445 (M^+ − 5CO − Et), 369 (M^+ − 5CO − Et − CS_2) (Found: C, 39.30; H, 2.60. $C_{20}H_{15}O_5PS_2W$ requires C, 39.10; H, 2.45%).

With IC_2H_4OH. The synthesis and work-up were similar to those used in the preparation of complex **4a**. The pure complex $[W(CO)_5\{PPh_2(CS_2C_2H_4OH)\}]$ **4c** was isolated in 90% yield as a red microcrystalline solid. IR (thf, ν_{CO}): 2072m and 1935vs cm^{-1}. NMR ($CDCl_3$): ^{31}P (81 MHz), δ 60.40 (J_{WP} = 250.66 Hz); ^1H (200 MHz), δ 3.54 (t, 2 H, SCH_2, J_{HH} = 6.03), 3.81 (t, 2 H, CH_2OH, J_{HH} = 6.03 Hz), 7.53 (m, 6 H, Ph) and 7.68 (m, 4 H, Ph); ^{13}C (50 MHz), δ 39.93 (SCH_2), 59.70 (CH_2OH), 128.53 (d, *m*-C of Ph, $^3J_{PC}$ = 13.5), 131.13 (s, *p*-C of Ph), 133.77 (d, *o*-C of Ph, $^2J_{PC}$ = 17.25), 134.26 (d, *ipso*-C of Ph, J_{PC} = 38.78) and 197.07 (d, *cis*-CO, $^2J_{PC}$ = 7.50 Hz). Mass spectrum: *m/z* 631 (M^+), 602 (M^+ − CO), 547 (M^+ − 3CO), 518 (M^+ − 4CO), 490 (M^+ − 5CO), 445 (M^+ − 5CO − EtO), 369 (M^+ − 5CO − EtO − CS_2).

With C_3H_5Br. The synthesis and work-up were similar to those used in the preparation of complex **4a**. The pure complex $[W(CO)_5\{PPh_2(CS_2C_3H_5)\}]$ **4d** was isolated in 88% yield as a red microcrystalline solid. IR (KBr, ν_{CO}): 2070m, 1988s and 1929vs cm^{-1}. NMR ($CDCl_3$): ^{31}P (81 MHz), δ 64.49 (J_{WP} = 248.56 Hz); ^1H (200 MHz), δ 3.90 (d, 2 H, SCH_2, J_{HH} = 7.2), 5.16, 5.24 (dd, 2 H, =CH_2, J_{HH} = 16.94, J_{HH} = 13.34 Hz), 5.78 (m, 1 H, CH=), 7.53 (m, 6 H, Ph) and 7.68 (m, 4 H, Ph); ^{13}C (50 MHz), δ 41.03 (SCH_2), 120.99 (CH=), 129.57 (d, *m*-C of Ph, $^3J_{PC}$ = 15.6), 130.63 (=CH_2), 132.27 (s, *p*-C of Ph), 134.59 (d, *o*-C of Ph, $^2J_{PC}$ = 19.78), 134.66 (d, *ipso*-C of Ph, J_{PC} = 38.78), 197.95 (d, *cis*-CO, $^2J_{PC}$ = 7.50), 199.90 (d, CS_2, J_{PC} = 25.50), and 238.40 (d, *trans*-CO, $^2J_{PC}$ = 7.50 Hz). Mass spectrum: *m/z* 626 (M^+), 598 (M^+ − CO), 542 (M^+ − 3CO), 514 (M^+ − 4CO), 486 (M^+ − 5CO) and 445 (M^+ − 5CO − C_3H_5).

With ICH_2CN. The synthesis and work-up were similar to those used in the preparation of complex **4a**. The complex $[W(CO)_5\{PPh_2(CS_2CH_2CN)\}]$ **4e** was isolated in 92% yield as a red microcrystalline solid. IR (thf, ν_{CO}): 2072m and 1937vs cm^{-1}. NMR ($CDCl_3$): ^{31}P (81 MHz), δ 61.46 (J_{WP} = 251.99 Hz); ^1H (200 MHz), δ 4.00 (s, 2 H, CH_2), 7.48 (m, 6 H, Ph) and 7.69 (m, 4 H, Ph); ^{13}C (50 MHz), δ 22.26 (CH_2), 113.59 (CN), 128.88 (d, *m*-C of Ph, $^3J_{PC}$ = 10.1), 131.66 (s, *p*-C of Ph), 132.91 (d, *ipso*-C of Ph, J_{PC} = 38.95), 133.76 (d, *o*-C of Ph, $^2J_{PC}$ =

11.85), 196.65 (d, *cis*-CO, $^2J_{PC}$ = 7.00), 198.20 (d, CS_2, J_{PC} = 25.50) and 234.46 (d, *trans*-CO, $^2J_{PC}$ = 7.40 Hz). Mass spectrum: *m/z* 626 (M^+), 597 (M^+ − CO), 569 (M^+ − 2CO), 542 (M^+ − 3CO), 513 (M^+ − 4CO), 485 (M^+ − 5CO), 443 (M^+ − 5CO − CH_2CN) and 369 (M^+ − 5CO − CH_2CN − CS_2).

With IC_2H_4CN. The synthesis and work-up were similar to those used in the preparation of complex **4a**. The complex $[W(CO)_5\{PPh_2(CS_2C_2H_4CN)\}]$ **4f** was isolated in 92% yield as a red microcrystalline solid. IR (thf, ν_{CO}): 2073m and 1935vs cm^{-1}. NMR ($CDCl_3$): ^{31}P (81 MHz), δ 61.86 (J_{WP} = 252.08 Hz); ^1H (200 MHz), δ 2.68 (t, 2 H, CH_2CN, J_{HH} = 7.05), 3.53 (t, 2 H, SCH_2, J_{HH} = 7.05 Hz), 7.53 (m, 6 H, Ph) and 7.68 (m, 4 H, Ph); ^{13}C (50 MHz), δ 15.1 ($\mathit{C}\mathrm{H_2CN}$), 31.6 (SCH_2), 128.56 (d, *m*-C of Ph, $^3J_{PC}$ = 10.5), 131.28 (s, *p*-C of Ph), 133.76 (d, *o*-C of Ph, $^2J_{PC}$ = 18.0), 133.79 (d, *ipso*-C of Ph, J_{PC} = 38.78) and 196.79 (d, *cis*-CO, $^2J_{PC}$ = 7.00 Hz). Mass spectrum: *m/z* 640 (M^+), 611 (M^+ − CO), 583 (M^+ − 2CO), 555 (M^+ − 3CO), 527 (M^+ − 4CO), 499 (M^+ − 5CO), 445 (M^+ − 5CO − C_3H_4N) and 369 (M^+ − 5CO − C_3H_4N − CS_2).

With IC_3H_6CN. The synthesis and work-up were similar to those used in the preparation of complex **4a**. The complex $[W(CO)_5\{PPh_2(CS_2C_3H_6CN)\}]$ **4g** was isolated in 82% yield as a red microcrystalline solid. IR (thf, ν_{CO}): 2073m and 1934vs cm^{-1}. NMR ($CDCl_3$): ^{31}P (81 MHz), δ 60.51 (J_{WP} = 252.8 Hz); ^1H (200 MHz), δ 1.96 (m, 2 H, $\mathrm{SCH_2}\mathit{CH_2}$), 2.37 (t, 2 H, CH_2CN, J_{HH} = 10.8), 3.49 (t, 2 H, SCH_2, J_{HH} = 9.21 Hz), 7.53 (m, 6 H, Ph) and 7.68 (m, 4 H, Ph); ^{13}C (50 MHz), δ 17.05 ($\mathrm{SCH_2}\mathit{C}\mathrm{H_2}$), 23.86 ($\mathit{C}\mathrm{H_2CN}$), 35.87 ($SCH_2$), 129.11 (d, *m*-C of Ph, $^3J_{PC}$ = 9.35), 131.74 (s, *p*-C of Ph), 134.28 (d, *o*-C of Ph, $^2J_{PC}$ = 12.3), 134.22 (d, *ipso*-C of Ph, J_{PC} = 39.5), 197.51 (d, *cis*-CO, $^2J_{PC}$ = 7.00) and 199.03 (d, CS_2, J_{PC} = 25.50 Hz). Mass spectrum: *m/z* 654 (M^+), 625 (M^+ − CO), 597 (M^+ − 2CO), 569 (M^+ − 3CO), 541 (M^+ − 4CO), 513 (M^+ − 5CO), 445 (M^+ − 5CO − C_4H_6N) and 369 (M^+ − 5CO − C_4H_6N − CS_2) (Found: C, 40.25; H, 2.70; N, 2.30. $C_{22}H_{16}NO_5PS_2W$ requires C, 40.45; H, 2.45; N, 2.15%).

With MeCOCl. The synthesis and work-up were similar to those used in the preparation of complex **4a**. The complex $[W(CO)_5\{PPh_2(CS_2COMe)\}]$ **5a** was isolated in 85% yield as a green microcrystalline solid. IR (thf, ν_{CO}): 2073m, 1936vs and 1726s cm^{-1}. NMR ($CDCl_3$): ^{31}P (81 MHz), δ 67.64 (J_{WP} = 246.3 Hz); ^1H (200 MHz), δ 2.40 (s, 3 H, CH_3), 7.53 (m, 6 H, Ph) and 7.68 (m, 4 H, Ph); ^{13}C (50 MHz), δ 33.47 (CH_3), 128.49 (d, *m*-C of Ph, $^3J_{PC}$ = 8.0), 131.15 (s, *p*-C of Ph), 132.3 (d, *ipso*-C of Ph, J_{PC} = 39.5), 133.68 (d, *o*-C of Ph, $^2J_{PC}$ = 12.3), 170.0 ($\mathit{C}\mathrm{OCH_3}$), 196.32 (d, *cis*-CO, $^2J_{PC}$ = 7.00), 196.47 (d, CS_2, J_{PC} = 25.50) and 226.00 (d, *trans*-CO, $^2J_{PC}$ = 7.40 Hz).

With PhCOCl. The synthesis and work-up were similar to those used in the preparation of complex **4a**. The complex $[W(CO)_5\{PPh_2(CS_2COPh)\}]$ **5b** was isolated in 87% yield as a green microcrystalline solid. IR (thf, ν_{CO}): 2073m, 1933vs and 1726s cm^{-1}. NMR ($CDCl_3$): ^{31}P (81 MHz), δ 67.46 (J_{WP} = 246.8 Hz); ^1H (200 MHz), δ 7.33–7.77 (m, 15 H, Ph); ^{13}C (50 MHz), δ 127.6–135.4 (Ph), 168.3 (COPh), 196.40 (d, *cis*-CO, $^2J_{PC}$ = 7.00) and 197.00 (d, CS_2, J_{PC} = 25.50 Hz). Mass spectrum: *m/z* 690 (M^+), 661 (M^+ − CO), 634 (M^+ − 2CO), 607 (M^+ − 3CO), 579 (M^+ − 4CO), 551 (M^+ − 5CO), 445 (M^+ − 5CO − PhCO) and 369 (M^+ − 5CO − PhCO − CS_2).

With $[Re(CO)_5Br]$. A mixture of $[Re(CO)_5Br]$ (0.41 g, 1 mmol) and complex **3** (0.71 g, 1 mmol) in thf (50 cm^3) was heated to reflux for 1 h, the solution was cooled and the solvent was removed *in vacuo*. Recrystallization using cold 1 : 1 MeOH–CH_2Cl_2 gave the red crystalline product **6** (0.53 g, 62%). IR (KBr, ν_{CO}): 2071m, 1988s, 1980m and 1923vs cm^{-1}. NMR ($CDCl_3$): ^{31}P (81 MHz), δ 53.4 (J_{WP} = 240.9 Hz); ^1H (200 MHz), δ 7.33 (m, 6 H, Ph) and 7.66 (m, 4 H, Ph); ^{13}C (50 MHz), δ 129.6 (d, *m*-C of Ph, $^3J_{PC}$ = 9.72), 132.3 (s, *p*-C of Ph), 134.6 (d, *o*-C of Ph, $^2J_{PC}$ = 12.2) and 134.9 (d, *ipso*-C of Ph, J_{PC} = 36.6 Hz). Mass spectrum: *m/z* 884 (M^+ − CO), 856 (M^+ − 2CO), 828 (M^+ − 3CO), 800 (M^+ − 4CO), 772 (M^+ − 5CO), 744 (M^+ − 6CO), 716 (M^+ − 7CO), 688 (M^+ − 8CO), 660 (M^+ − 9CO) and 631 (M^+ − 10CO) (Found: C, 30.50; H, 1.55. $C_{23}H_{10}O_{10}PReS_2W$ requires C, 30.30; H, 1.10%).

With $[W(pip)_2(CO)_4]$. Solid $[W(pip)_2(CO)_4]$ (0.384 g, 1 mmol) was added to a solution of **3** (0.71 g, 1 mmol) in MeCN (50 cm^3). After the solution was heated to reflux for 2 h, the IR spectrum indicated that the reaction was complete. The solution was cooled and the solvent was removed *in vacuo*. Recrystallization using cold MeOH–CH_2Cl_2 (1 : 1) gave the yellow crystalline product **7** (0.62 g, 84% yield). IR (KBr, ν_{CO}): 1987m, 1854m, 1830vs, 1800vs and 1783s cm^{-1}; $\nu_{C=N}$ 1476m cm^{-1}. NMR (CD_3CN): ^1H (200 MHz), δ 1.21 (tt, 12 H, CH_3, $^3J_{NH}$ = 1.87, J_{HH} = 7.3), 1.59 (m, 6 H, $\mathrm{NCH_2C}\mathit{H_2}$), 3.15 (q, 8 H, $\mathrm{NC}\mathit{H_2}\mathrm{CH_3}$, J_{HH} = 7.3 Hz), 3.82 (m, 4 H, $\mathrm{NC}\mathit{H_2}\mathrm{CH_2}$); ^{13}C (50 MHz), δ 7.55 (CH_3), 24.68 ($\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_2}$), 25.99 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$), 47.53 ($NCH_2$), 52.89 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_3}$), 204.01 (CO), 212.98 ($CS_2$) and 213.83 (CO). Mass spectrum: *m/z* 716 (M^+ + NEt_4) and 688 (M^+ + NEt_4 − CO) (Found: C, 36.70; H, 5.25; N, 4.85. $C_{18}H_{30}N_2O_4S_2W$ requires C, 36.85; H, 5.15; N, 4.80%).

With CH_2I_2. Diiodomethane (0.1 cm^3, 3 mmol) was added slowly to a solution of **3** (0.71 g, 1 mmol) in CH_2Cl_2 (20 cm^3) at room temperature and the solution was stirred for 5 min. The solvent was removed in vacuum and the residue was extracted with hexane, and the extracts were filtered through Celite. The filtrate was concentrated to 5 cm^3 and stored at −18 °C for 12 h to give the red-brown crystalline product $[\{W(CO)_5(PPh_2CS_2)\}_2(\mu\text{-}CH_2)]$ **8** (0.48 g, 0.41 mmol, 82%). IR (CH_2Cl_2, ν_{CO}): 2070m and 1937vs cm^{-1}. NMR ($CDCl_3$): ^{31}P (81 MHz), δ 59.55 (J_{WP} = 250.96 Hz); ^1H (200 MHz), δ 5.01 (s, 2 H, CH_2) and 7.40–7.66 (m, 10 H, Ph); ^{13}C (50 MHz), δ 42.7 (CH_2), 128.45 (d, *m*-C of Ph, $^3J_{PC}$ = 8.3), 131.32 (s, *p*-C of Ph), 133.63 (d, *o*-C of Ph, $^2J_{PC}$ = 11.8), 133.3 (d, *ipso*-C of Ph, J_{PC} = 46), 196.74 (d, *cis*-CO, $^2J_{PC}$ = 6.50), 198.50 (d, CS_2, J_{PC} = 25.50) and 235.96 (d, *trans*-CO, $^2J_{PC}$ = 5.00 Hz). Mass spectrum: *m/z* 1073 (M^+ − 4CO), 1045 (M^+ − 5CO), 1017 (M^+ − 6CO), 988 (M^+ − 7CO), 960 (M^+ − 8CO), 932 (M^+ − 9CO) and 904 (M^+ − 10CO) (Found: C, 37.40; H, 1.95. $C_{37}H_{22}O_{10}P_2S_4W_2$ requires C, 37.50; H, 1.85%).

With ICH_2CH_2I. The synthesis and work-up were similar to those used in the preparation of complex **8**. The complex $[\{W(CO)_5(PPh_2CS_2)\}_2(\mu\text{-}CH_2CH_2)]$ **9** was isolated in 80% yield as a red-brown microcrystalline solid. IR (CH_2Cl_2, ν_{CO}): 2074m and 1936vs cm^{-1}. NMR ($CDCl_3$): ^{31}P (81 MHz), δ 61.27 (J_{WP} = 254.05 Hz); ^1H (200 MHz), δ 4.08 (s, 4 H, CH_2), 7.45 (m, 6 H, Ph) and 7.78 (m, 4 H, Ph); ^{13}C (50 MHz), δ 61.3 (CH_2), 128.7 (d, *m*-C of Ph, $^3J_{PC}$ = 10.05), 131.56 (s, *p*-C of Ph), 133.58 (d, *o*-C of Ph, $^2J_{PC}$ = 10.0), 133.5 (d, *ipso*-C of Ph, J_{PC} = 36.6), 196.55 (d, *cis*-CO, $^2J_{PC}$ = 7.00), 198.26 (d, CS_2, J_{PC} = 25.55) and 229.36 (d, *trans*-CO, $^2J_{PC}$ = 7.40 Hz). Mass spectrum: *m/z* 1056 (M^+ − 5CO), 1028 (M^+ − 6CO), 1000 (M^+ − 7CO), 972 (M^+ − 8CO), 944 (M^+ − 9CO) and 916 (M^+ − 10CO).

With $ICH_2CH_2CH_2I$. The synthesis and work-up were similar to those used in the preparation of complex **8**. Two complexes were isolated, $[\{W(CO)_5(PPh_2CS_2)\}_2(\mu\text{-}CH_2CH_2CH_2)]$ **10a** (56%) and $[W(CO)_5\{PPh_2CS_2(CH_2)_3I\}]$ **10b** (18%). If a CH_2Cl_2 solution of **3** was added to $C_3H_6I_2$ in excess, complex **10b** was obtained as the only product. The spectroscopic data of the two complexes **10a** and **10b** were distinguishable. Therefore, no attempt was made to separate the two complexes. **10a**: IR (CH_2Cl_2, ν_{CO}) 2070m and 1931vs cm^{-1}. NMR ($CDCl_3$): ^{31}P (81 MHz), δ 59.64 (J_{WP} = 250.13 Hz); ^1H (200 MHz), δ 1.97 (m, 2 H, $\mathrm{CH_2C}\mathit{H_2}\mathrm{CH_2}$), 3.34 (m, 4 H, SCH_2), 7.50 (m, 6 H, Ph) and 7.66 (m, 4 H, Ph); ^{13}C (50 MHz), δ 24.95 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2}$), 35.86 ($SCH_2$), 128.44 (d, *m*-C of Ph, $^3J_{PC}$ = 9.75), 131.06 (s, *p*-C of Ph), 133.45 (d, *o*-C of Ph, $^2J_{PC}$ = 11.85), 133.65 (d, *ipso*-C of Ph, J_{PC} = 38.7), 196.93 (d, *cis*-CO, $^2J_{PC}$ = 7.00), 198.65 (d, CS_2, J_{PC} = 24.50) and 237.20 (d, *trans*-CO, $^2J_{PC}$ = 7.00 Hz). Mass spectrum: *m/z* 1184 (M^+ − CO), 1016 (M^+ − 7CO), 988 (M^+ − 8CO), 960 (M^+ −

Table 1 Crystal data and refinement details for complexes **2**, **3** and **4a**

	$[NEt_4][PPh_2CS_2]$ **2**	$[NEt_4][W(CO)_5(PPh_2CS_2)]$ **3**	$[W(CO)_5(PPh_2CS_2Me)]$ **4a**
Formula	$C_{21}H_{10}NPS_2$	$C_{26}H_{30}NO_5PS_2W$	$C_{19}H_{13}O_5PS_2W$
M	371.41	715.48	600.25
Crystal system	Monoclinic	Triclinic	Triclinic
Crystal size (mm)	0.30 × 0.30 × 0.40	0.40 × 0.50 × 0.50	0.30 × 0.30 × 0.40
Space group	$P2_1$	$P\bar{1}$	$P\bar{1}$
a/Å	10.244(4)	10.688(3)	9.177(5)
b/Å	9.877(4)	11.0697(19)	9.403(3)
c/Å	11.124(3)	12.7850(16)	12.461(6)
$\alpha/^\circ$		88.255(12)	90.00(3)
$\beta/^\circ$	102.020(23)	81.870(16)	103.85(4)
$\gamma/^\circ$		74.081(17)	94.79(3)
U/Å^3	1100.8(6)	1440.0(5)	1040.1(8)
Z	2	2	2
D_c/g cm^{-3}	1.121	1.650	1.917
μ(Mo-Kα)/mm^{-1}	0.3245	4.32	5.9663
F(000)	548	708	576
$2\theta_{max}/^\circ$	45	49.8	45
Unique data	1529	5052	2717
Indices explored	$\pm h$ (10), $+k$ (10), $+l$ (11)	$\pm h$ (11), $+k$ (13), $\pm l$ (15)	$\pm h$ (9), $+k$ (10), $\pm l$ (13)
Data with $F_o^2 > 2\sigma(F_o^2)$	1180	4557	2442
Parameters refined	202	326	253
R^a	0.062	0.028	0.041
R'^b	0.073	0.025	0.041
Transmission (min., max.)	1.000, 1.000	0.800, 0.999	0.523, 1.000
Quality-of-fit indicator^c	1.52	2.66	3.66
(D-map) max., min. residual electron density (e Å^{-3})	−0.20, 0.44	−0.78, 0.78	−1.74, 1.54

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{par})]^{\frac{1}{2}}$.

9CO) and 932 ($M^+ - 10CO$). **10b**: IR (CH_2Cl_2, ν_{CO}) 2070m and 1931vs cm^{-1}. NMR ($CDCl_3$): ^{31}P (81 MHz), δ 59.08 (J_{WP} = 250.11 Hz); ^1H (200 MHz), δ 2.14 (t, 2 H, CH_2CH_2I), 3.17 (t, 2 H, CH_2I, J_{HH} = 6.7), 3.43 (t, 2 H, SCH_2, J_{HH} = 6.7 Hz), 7.48 (m, 6 H, Ph) and 7.70 (m, 4 H, Ph); ^{13}C (50 MHz), δ 3.72 (CH_2I), 30.27 (CH_2CH_2I), 37.75 (SCH_2), 128.44 (d, *m*-C of Ph, $^3J_{PC}$ = 9.75), 131.06 (s, *p*-C of Ph), 133.45 (d, *o*-C of Ph, $^2J_{PC}$ = 11.85), 133.65 (d, *ipso*-C of Ph, J_{PC} = 38.7), 196.93 (d, *cis*-CO, $^2J_{PC}$ = 6.50), 198.96 (d, CS_2, J_{PC} = 25.50) and 236.55 (d, *trans*-CO, $^2J_{PC}$ = 6.50 Hz). Mass spectrum: *m*/*z* 628 ($M^+ - I$), 600 ($M^+ - I - 2CH_2$), 572 ($M^+ - I - 2CH_2 - CO$), 544 ($M^+ - I - 2CH_2 - 2CO$), 516 ($M^+ - I - 2CH_2 - 3CO$) and 488 ($M^+ - I - 2CH_2 - 4CO$).

With BrCOCOBr. The synthesis and work-up were similar to those used in the preparation of complex **8**. The pure complex $[\{W(CO)_5(PPh_2CS_2)\}_2(CO)_2]$ **11** was isolated in 40% yield as a green microcrystalline solid. IR (thf, ν_{CO}): 2071m, 1933vs and 1705s cm^{-1}. NMR ($CDCl_3$): ^{31}P (81 MHz), δ 60.67 (J_{WP} = 253.77 Hz); ^1H (200 MHz), δ 7.45–7.78 (m, 20 H, Ph). Mass spectrum: *m*/*z* 1226 (M^+), 946 ($M^+ - 10CO$), 471 ($M^+ - 10CO - WPPh_2CS_2CO$), 445 ($M^+ - 10CO - WPPh_2CS_2$-$CO - CO$) and 369 ($M^+ - 10CO - WPPh_2CS_2CO - CO - CS_2$).

Synthesis of $[NEt_4][W(CO)_4(PPh_2CS_2)]$ **12**.—Compound **3** (0.71 g, 1 mmol) was dissolved in thf (40 cm^3) and the solution heated to reflux and the reaction monitored by IR spectroscopy. After refluxing for 1 h, the IR spectrum indicated that the starting material was completely consumed. The solution was cooled and the solvent was removed *in vacuo*. Recrystallization using cold hexane–CH_2Cl_2 (1 : 1) gave the red crystalline product **12** (yield, 0.62 g, 84%). IR (thf, ν_{CO}): 1993m, 1879vs, 1859sh and 1833s cm^{-1}. NMR ($CDCl_3$): ^{31}P (81 MHz), δ 24.23 (J_{WP} = 187.4 Hz); ^1H (200 MHz), δ 1.17 (tt, 12 H, CH_3, $^3J_{NH}$ = 1.87, J_{HH} = 7.3), 3.13 (q, 8 H, NCH_2, J_{HH} = 7.3 Hz), 7.43 (m, 6 H, Ph) and 7.69 (m, 4 H, Ph); ^{13}C (50 MHz), δ 7.51 (CH_3), 52.8 (NCH_2), 129.06 (d, *m*-C of Ph, $^3J_{PC}$ = 7.16), 131.85 (s, *p*-C of Ph), 133.91 (d, *o*-C of Ph, $^2J_{PC}$ = 12.07), 134.61 (d, *ipso*-C of Ph, J_{PC} = 26.4), 205.70 (d, *cis*-CO, $^2J_{PC}$ = 7.50), 214.27 (d, CS_2, J_{PC} = 24.00 Hz) and 264.63 (*trans*-CO). Mass spectrum: *m*/*z* 817.0 ($M^+ + NEt_4$), 550 ($M^+ - NEt_4 - Ph - CO - S$), 522 ($M^+ - NEt_4 - Ph - 2CO - S$) and 494 ($M^+ - NEt_4 - Ph - 3CO - S$) (Found: C, 43.80; H, 4.20; N, 2.00. $C_{25}H_{30}NO_4PS_2W$ requires C, 43.70; H, 4.40; N, 2.05%).

Single-crystal X-Ray Diffraction Analyses of **2**, **3** *and* **4a**.—Single crystals of **2**, **3** and **4a** suitable from X-ray diffraction analysis were all grown by recrystallization from hexane–CH_2Cl_2 (20 : 1). The diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo-Kα (λ = 0.7107 Å) radiation. The raw intensity data were converted to structure factor amplitudes and their estimated standard deviations after correction for scan speed, background, Lorentz, and polarization effects. An empirical absorption correction, based on the azimuthal scan data, was applied to the data. Crystallographic computations were carried out on a Microvax III computer using the NRCC-SDP-VAX structure determination package.[9]

A suitable single crystal of **2** was mounted on the top of a glass fibre with glue. Initial lattice parameters were determined from 24 accurately centred reflections with 2θ values in the range 19.50–24.38°. Cell constants and other pertinent data were collected and are recorded in Table 1. Reflection data were collected using the θ–2θ scan method. The final scan speed for each reflection was determined from the net intensity gathered during an initial prescan and ranged from 2 to 7° min^{-1}. The θ scan angle was determined for each reflection according to the equation $0.75 \pm 0.25 \tan \theta$. Three check reflections were measured every 30 min throughout the data collection and showed no apparent decay. The merging of equivalent and duplicate reflections gave a total of 1529 unique measured data in which 1180 reflections with $I > 2\sigma(I)$ were considered observed. The structure was first solved by using the heavy-atom method (Patterson synthesis), which revealed the positions of P and S atoms. The remaining atoms were found in a series of alternating Fourier difference maps and least-squares refinements. The quantity minimized by the least-squares

Table 2 Selected bond distances (Å) and angles (°) for compound **2**

S(1)–C	1.658(15)	C(4)–C(5)	1.41(3)
S(2)–C	1.660(14)	C(5)–C(6)	1.375(23)
P–C	1.870(16)	C(7)–C(8)	1.392(23)
P–C(1)	1.833(13)	C(7)–C(12)	1.383(21)
P–C(7)	1.823(14)	C(8)–C(9)	1.370(23)
C(1)–C(2)	1.395(20)	C(9)–C(10)	1.37(3)
C(1)–C(6)	1.381(21)	C(10)–C(11)	1.38(3)
C(2)–C(3)	1.369(21)	C(11)–C(12)	1.36(3)
C(3)–C(4)	1.363(25)		
C–P–C(1)	101.5(7)	C(3)–C(4)–C(5)	118.4(14)
C–P–C(7)	106.8(7)	C(4)–C(5)–C(6)	119.3(15)
C(1)–P–C(7)	100.2(6)	C(1)–C(6)–C(5)	121.6(14)
S(1)–C–S(2)	128.7(10)	P–C(7)–C(8)	125.3(11)
S(1)–C–P	120.6(8)	P–C(7)–C(12)	117.2(12)
S(2)–C–P	110.7(9)	C(8)–C(7)–C(12)	117.3(13)
P–C(1)–C(2)	124.3(11)	C(7)–C(8)–C(9)	121.3(15)
P–C(1)–C(6)	117.1(11)	C(8)–C(9)–C(10)	119.9(17)
C(2)–C(1)–C(6)	118.6(13)	C(9)–C(10)–C(11)	119.9(15)
C(1)–C(2)–C(3)	119.7(14)	C(10)–C(11)–C(12)	120.0(17)
C(2)–C(3)–C(4)	122.4(15)	C(7)–C(12)–C(11)	121.6(16)

Table 3 Selected bond distances (Å) and angles (°) for complex **3**

W–P	2.5533(14)	C(4)–O(4)	1.152(6)
W–C(1)	2.004(5)	C(5)–O(5)	1.143(6)
W–C(2)	1.997(5)	C(11)–C(12)	1.393(7)
W–C(3)	2.001(5)	C(11)–C(16)	1.394(7)
W–C(4)	2.007(5)	C(12)–C(13)	1.386(7)
W–C(5)	2.025(5)	C(13)–C(14)	1.358(8)
P–C	1.872(5)	C(14)–C(15)	1.350(8)
P–C(11)	1.831(5)	C(15)–C(16)	1.383(7)
P–C(21)	1.833(5)	C(21)–C(22)	1.386(6)
S(1)–C	1.669(5)	C(21)–C(26)	1.379(6)
S(2)–C	1.650(5)	C(22)–C(23)	1.389(7)
C(1)–O(1)	1.168(7)	C(23)–C(24)	1.375(7)
C(2)–O(2)	1.142(6)	C(24)–C(25)	1.364(7)
C(3)–O(3)	1.157(7)	C(25)–C(26)	1.393(7)
P–W–C(1)	87.89(14)	W–P–C(21)	119.26(15)
P–W–C(2)	175.77(14)	C–P–C(11)	106.68(21)
P–W–C(3)	93.33(14)	C–P–C(21)	102.59(20)
P–W–C(4)	97.49(13)	C(11)–P–C(21)	102.13(21)
P–W–C(5)	87.02(14)	P–C–S(1)	112.7(3)
C(1)–W–C(2)	91.82(22)	P–C–S(2)	119.6(3)
C(1)–W–C(3)	175.53(21)	S(1)–C–S(2)	127.6(3)
C(1)–W–C(4)	89.49(21)	W–C(1)–O(1)	176.8(4)
C(1)–W–C(5)	92.99(22)	W–C(2)–O(2)	178.8(5)
C(2)–W–C(3)	87.28(22)	W–C(3)–O(3)	175.5(4)
C(2)–W–C(4)	86.73(19)	W–C(4)–O(4)	174.8(4)
C(2)–W–C(5)	88.78(20)	W–C(5)–O(5)	177.7(4)
C(3)–W–C(4)	86.09(21)	P–C(11)–C(12)	119.7(4)
C(3)–W–C(5)	91.37(22)	P–C(11)–C(16)	122.2(4)
C(4)–W–C(5)	174.93(19)	P–C(21)–C(22)	120.7(3)
W–P–C	112.22(15)	P–C(21)–C(26)	120.6(3)
W–P–C(11)	112.65(15)		

program was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weight of a given operation. The analytical forms of the scattering factor tables for the neutral atoms were used.[10] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations in their expected positions on the basis of idealized bonding geometry but were not refined in least squares. The NEt_4 cation was found disordered and the refinement was carried out with 50% occupancy for the disordered group. The final residuals of this refinement were $R = 0.062$ and $R' = 0.073$. Final values of selected bond distances and angles are listed in Table 2.

The procedures for **3** and **4a** were similar to those for **2**. The unit-cell constants were also determined from 24 accurately centred reflections. Cell constants and other pertinent data are collected in Table 1. The final residuals of the refinements were $R = 0.028$ and $R' = 0.025$ for **3** and $R = 0.041$ and $R' = 0.041$ for **4a**. Final values of selected bond distances and angles of **3** and **4a** are listed in Tables 3 and 4. The atomic coordinates of **2**, **3** and **4a** are given in Tables 5–7.

Table 4 Selected bond distances (Å) and angles (°) for complex **4a**

W–P	2.533(3)	C(6)–O(6)	1.217(19)
W–C(3)	1.970(14)	C(7)–O(7)	1.124(15)
W–C(4)	2.014(12)	C(11)–C(12)	1.392(17)
W–C(5)	1.967(16)	C(11)–C(16)	1.428(17)
W–C(6)	1.932(16)	C(12)–C(13)	1.393(20)
W–C(7)	2.008(12)	C(13)–C(14)	1.35(3)
P–C(1)	1.879(11)	C(14)–C(15)	1.40(3)
P–C(11)	1.823(11)	C(15)–C(16)	1.360(19)
P–C(21)	1.826(11)	C(21)–C(22)	1.387(17)
S(1)–C(1)	1.638(12)	C(21)–C(26)	1.402(15)
S(2)–C(1)	1.673(11)	C(22)–C(23)	1.373(19)
S(2)–C(2)	1.780(13)	C(23)–C(24)	1.364(21)
C(3)–O(3)	1.161(17)	C(24)–C(25)	1.345(23)
C(4)–O(4)	1.131(14)	C(25)–C(26)	1.371(19)
C(5)–O(5)	1.185(19)		
P–W–C(3)	175.3(4)	W–P–C(21)	121.0(4)
P–W–C(4)	93.6(3)	C(1)–P–C(11)	103.8(5)
P–W–C(5)	89.2(4)	C(1)–P–C(21)	102.6(5)
P–W–C(6)	96.0(4)	C(11)–P–C(21)	101.1(5)
P–W–C(7)	88.5(3)	C(1)–S(2)–C(2)	103.5(7)
C(3)–W–C(4)	88.9(4)	P–C(1)–S(1)	117.4(6)
C(3)–W–C(5)	86.8(6)	P–C(1)–S(2)	114.7(6)
C(3)–W–C(6)	88.1(5)	S(1)–C(1)–S(2)	127.7(6)
C(3)–W–C(7)	89.1(5)	W–C(3)–O(3)	176.9(11)
C(4)–W–C(5)	89.3(5)	W–C(4)–O(4)	177.8(11)
C(4)–W–C(6)	90.6(5)	W–C(5)–O(5)	179.4(10)
C(4)–W–C(7)	177.8(4)	W–C(6)–O(6)	172.7(10)
C(5)–W–C(6)	174.8(5)	W–C(7)–O(7)	176.3(10)
C(5)–W–C(7)	91.4(5)	P–C(11)–C(12)	124.5(9)
C(6)–W–C(7)	88.5(5)	P–C(11)–C(16)	116.2(9)
W–P–C(1)	110.6(3)	P–C(21)–C(22)	120.5(8)
W–P–C(11)	115.8(4)	P–C(21)–C(26)	121.4(9)

Table 5 Atomic coordinates for compound **2** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
S(1)	0.3733(4)	0.9441(5)	0.7754(4)
S(2)	0.2032(5)	1.0553(7)	0.9404(4)
P	0.2122(4)	1.2063(6)	0.7180(4)
C	0.2679(13)	1.0543(16)	0.8154(12)
C(1)	0.0416(12)	1.1583(15)	0.6441(12)
C(2)	−0.0094(14)	1.0273(14)	0.6434(14)
C(3)	−0.1373(15)	1.0012(17)	0.5819(15)
C(4)	−0.2175(16)	1.0989(20)	0.5189(15)
C(5)	−0.1662(15)	1.2312(19)	0.5173(15)
C(6)	−0.0393(15)	1.2586(16)	0.5821(15)
C(7)	0.2928(12)	1.1970(16)	0.5867(13)
C(8)	0.2506(16)	1.1168(16)	0.4830(15)
C(9)	0.3134(18)	1.1217(20)	0.3857(15)
C(10)	0.4176(18)	1.209(3)	0.3883(18)
C(11)	0.4607(15)	1.2897(22)	0.4897(21)
C(12)	0.4003(14)	1.2819(17)	0.5874(16)
N	0.2406(12)	0.5796(15)	−0.0086(12)
C(13)	0.272(4)	0.439(5)	0.064(4)
C(13′)	0.152(5)	0.475(6)	0.035(5)
C(14)	0.189(3)	0.381(4)	0.125(3)
C(15)	0.369(3)	0.630(4)	−0.032(3)
C(15′)	0.354(4)	0.503(5)	−0.062(4)
C(16)	0.4259(21)	0.562(3)	−0.1281(19)
C(17)	0.123(5)	0.553(6)	−0.129(5)
C(17′)	0.149(4)	0.667(5)	−0.101(4)
C(18)	0.088(3)	0.630(4)	−0.212(3)
C(19)	0.178(4)	0.690(5)	0.073(4)
C(19′)	0.328(4)	0.674(5)	0.093(4)
C(20)	0.2602(23)	0.740(3)	0.1733(22)

Table 6 Atomic coordinates for complex **3** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
W	0.388 70(2)	0.283 81(2)	0.081 46(2)
P	0.174 96(12)	0.326 93(12)	0.209 54(9)
S(1)	0.294 42(15)	0.374 69(16)	0.393 05(11)
S(2)	0.141 71(20)	0.184 94(15)	0.414 90(12)
C	0.204 6(5)	0.290 2(4)	0.349 4(4)
C(1)	0.427 2(5)	0.428 5(5)	0.148 5(4)
O(1)	0.449 7(4)	0.515 6(4)	0.183 0(3)
C(2)	0.562 4(5)	0.242 3(5)	−0.010 4(4)
O(2)	0.661 4(3)	0.216 5(4)	−0.063 4(3)
C(3)	0.347 0(5)	0.147 9(5)	0.004 8(4)
O(3)	0.325 5(4)	0.072 9(4)	−0.045 7(3)
C(4)	0.319 1(4)	0.397 5(5)	−0.034 7(4)
O(4)	0.286 8(4)	0.457 1(4)	−0.106 6(3)
C(5)	0.471 0(5)	0.159 9(5)	0.188 7(4)
O(5)	0.521 2(4)	0.089 0(4)	0.247 0(3)
C(11)	0.066 5(4)	0.234 6(4)	0.178 4(3)
C(12)	0.113 8(5)	0.104 4(5)	0.169 0(4)
C(13)	0.035 6(6)	0.033 8(5)	0.139 1(4)
C(14)	−0.087 9(6)	0.090 4(6)	0.118 1(4)
C(15)	−0.135 3(5)	0.216 5(5)	0.127 1(4)
C(16)	−0.061 0(5)	0.290 5(5)	0.157 3(4)
C(21)	0.064 4(4)	0.486 5(4)	0.220 8(3)
C(22)	−0.021 9(5)	0.526 2(5)	0.312 5(4)
C(23)	−0.113 4(5)	0.643 2(5)	0.317 0(4)
C(24)	−0.120 0(5)	0.720 7(5)	0.230 6(4)
C(25)	−0.034 8(5)	0.682 9(5)	0.140 3(4)
C(26)	0.057 3(5)	0.565 9(5)	0.135 2(4)
N	0.304 2(4)	0.778 7(4)	0.474 1(3)
C(31)	0.428 2(7)	0.712 5(7)	0.407 6(5)
C(32)	0.483 2(8)	0.791 6(7)	0.326 7(6)
C(33)	0.195 3(7)	0.834 8(7)	0.409 7(6)
C(34)	0.171 0(7)	0.756 4(7)	0.329 2(6)
C(35)	0.259 4(7)	0.680 4(6)	0.545 9(5)
C(36)	0.341 8(7)	0.620 1(6)	0.622 9(5)
C(37)	0.328 8(8)	0.876 2(7)	0.536 4(5)
C(38)	0.215 3(8)	0.945 8(6)	0.615 9(5)

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

Results and Discussion

Synthesis and Reactivities of $[NEt_4][PPh_2CS_2]$ **2** *and Synthesis of* $[NEt_4][W(CO)_5(PPh_2CS_2)]$ **3**.—Although the anionic heteroallyl ligands containing phosphorus such as $R_2P(X)C(Y)NR^-$ or $R_2PC(Y)NR^-$ (X = O or S, Y = O or S) were synthesized by Kunze, Ambrosius and co-workers,[2] no crystal structures were reported and little effort was directed toward investigating the chemistry of metal complexes containing the dialkylphosphinodithioformate ligand, $PR_2CS_2^-$. We prepared the compound $[NEt_4][PPh_2CS_2]$ **2**, from the reaction of $KPPh_2$ with CS_2 in the presence of NEt_4Br in thf at 0 °C. Recrystallization from CH_2Cl_2–MeOH (1 : 1) gave the product as a clear, red crystalline solid and the molecular structure of **2** was determined by X-ray diffraction. In order to compare the co-ordination chemistry of **2** with that of the anionic heteroallyl ligands $R_2P(X)C(Y)NR^-$ or $R_2PC(Y)NR^-$ (X = O or S, Y = O or S), we carried out the reaction of **2** with $[W(CO)_5(MeCN)]$ in MeCN at room temperature. The reaction was monitored by ^{31}P NMR spectroscopy and the monodentate P-co-ordinated complex $[NEt_4][W(CO)_5(PPh_2CS_2)]$ **3**, was observed as the sole product.

Treatment of $[NEt_4][W(CO)_5(PPh_2)]$ **1** with CS_2 also afforded **3** in 87% yield. The analytical data of **3** are in agreement with the formulation. The FAB mass spectrum of **3** shows a base peak at *m*/*z* 845. The IR spectrum of **3** shows three ν_{CO} stretchings at 2072, 1970 and 1937 cm^{-1} in thf, a typical pattern for a $LM(CO)_5$ unit in octahedral geometry. The ^{31}P NMR spectrum of **3** exhibits a resonance at δ 59.08 with a tungsten satellite (J_{WP} = 238.24 Hz) indicating phosphorus co-ordination of the ligand. From the X-ray diffraction study described below, the co-ordination of the ligand to the tungsten metal is established to be through the P atom.

Table 7 Atomic coordinates for complex **4a** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
W	0.281 01(6)	0.262 34(6)	0.056 70(4)
P	0.345 8(3)	0.147 5(3)	0.244 16(25)
S(1)	0.668 5(4)	0.271 1(4)	0.294 3(3)
S(2)	0.598 0(4)	−0.041 8(4)	0.308 1(3)
C(1)	0.553 5(11)	0.126 8(12)	0.288 5(9)
C(2)	0.798 1(14)	−0.026 2(17)	0.333 0(11)
C(3)	0.246 2(13)	0.362 0(15)	−0.085 1(12)
O(3)	0.219 2(10)	0.417 2(11)	−0.170 1(8)
C(4)	0.083 4(14)	0.322 3(13)	0.076 7(8)
O(4)	−0.026 3(10)	0.360 1(10)	0.087 1(7)
C(5)	0.381 1(15)	0.444 3(14)	0.125 6(13)
O(5)	0.442 6(11)	0.553 5(11)	0.167 2(9)
C(6)	0.179 5(17)	0.092 3(13)	−0.023 7(11)
O(6)	0.109 9(10)	−0.004 8(10)	−0.084 0(8)
C(7)	0.475 3(14)	0.203 5(14)	0.030 5(9)
O(7)	0.580 7(10)	0.170 8(12)	0.009 9(8)
C(11)	0.308 1(13)	0.247 9(12)	0.358 3(9)
C(12)	0.416 3(14)	0.293 1(14)	0.453 4(10)
C(13)	0.371 9(19)	0.365 5(17)	0.536 1(13)
C(14)	0.225 3(25)	0.385 4(16)	0.528 3(13)
C(15)	0.114 7(18)	0.338 8(17)	0.434 4(14)
C(16)	0.154 5(14)	0.272 8(14)	0.349 9(9)
C(21)	0.262 7(11)	−0.030 4(12)	0.265 7(9)
C(22)	0.226 1(12)	−0.131 7(13)	0.180 5(9)
C(23)	0.168 0(14)	−0.266 2(14)	0.199 2(12)
C(24)	0.144 7(15)	−0.305 0(15)	0.299 7(13)
C(25)	0.181 3(16)	−0.206 7(17)	0.382 2(11)
C(26)	0.239 2(13)	−0.070 4(13)	0.369 0(9)

Obviously, **3** is formed *via* abstraction of the proton by $LiBu^n$, followed by the addition of the resulting phosphido unit onto the carbon atom of CS_2. Such a strategy, namely, abstraction of a proton from the metal-co-ordinated phosphine has been reported for the synthesis of the phosphorus derivatives.[11] Until now, only one example[4] is known for the dialkylphosphinodithioformato ligand, $R_2PCS_2^-$. The bis(trimethylsilyl)phosphino zirconium complex $[Zr(\eta^5\text{-}C_5H_5)_2\{\eta^2\text{-}S_2CP(SiMe_3)_2\}Cl]$, obtained from the reaction of $[Zr(\eta^5\text{-}C_5H_5)_2(PR_2)X]X$ (R = $SiMe_3$, X = Cl or Me) with CS_2, contains a $R_2PCS_2^-$ ligand chelating through the two sulfur atoms of the CS_2 moiety. Formation of complex **3** was observed in two different synthetic routes. This observation clearly indicates that **3** is a thermodynamic product. Thermolysis of **3** causes loss of CO and changes the co-ordination mode of the PPh_2CS_2 ligand (possibily *via* P,S-chelate described below). Therefore in a tungsten carbonyl complex with only one vacant co-ordination site, P-co-ordination seems to be more favourable than S-co-ordination for the PPh_2CS_2 ligand. Attempts to obtain a similar product from the reaction of **3** with CO_2 were unsuccessful. No reaction occurred under the same reaction conditions.

Reactions of **3** *with Alkyl Halides*.—To explore the reactivity of complex **3**, we carried out reactions of **3** with several alkyl halides. The reaction of **3** with MeI in CH_2Cl_2 gave the neutral complex $[W(CO)_5\{PPh_2(CS_2Me)\}]$ **4a**. This red powder was isolated in 85% yield. Complex **4a** is stable in refluxing MeCN or in refluxing C_6H_6 under N_2. Hexane extraction of **4a** followed by removal of solvent gave the analytically pure product. The spectroscopic and analytical data of **4a** are in agreement with the formulation. The FAB mass spectrum of **4a**

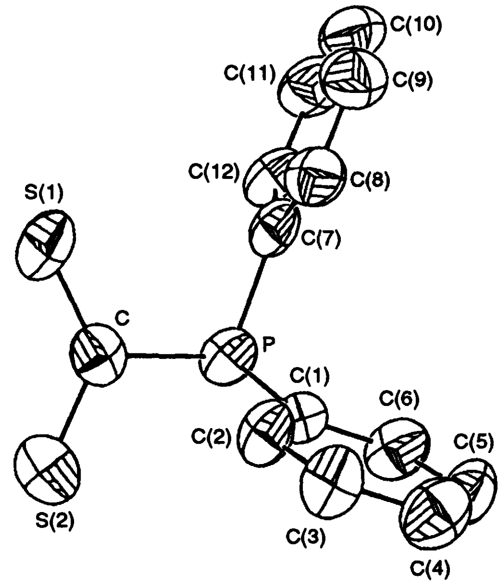


Fig. 1 An ORTEP[14] drawing with 50% thermal ellipsoids and atom-numbering scheme for $[NEt_4][PPh_2CS_2]$ **2** with hydrogen atoms and the NEt_4 cation omitted for clarity

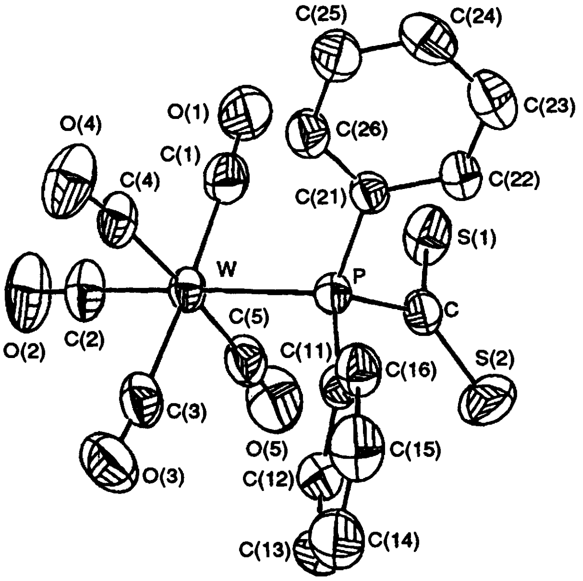


Fig. 2 An ORTEP[14] drawing with 50% thermal ellipsoids and atom-numbering scheme for $[NEt_4][W(CO)_5(PPh_2CS_2)]$ **3** with hydrogen atoms and the NEt_4 cation omitted for clarity

shows a parent peak at *m/z* 600. The ^1H NMR spectrum of **4a** exhibits a resonance at δ 2.71 attributed to the methyl protons. The corresponding resonance in the ^{13}C NMR spectrum appears at δ 21.86.[12] Lack of coupling with ^{31}P of this ^{13}C resonance contrasts with the observation of a doublet resonance with $^2J_{PC}$ = 14.7 Hz[13] for the compound $[W(\eta^5\text{-}C_5H_5)(CO_2)\{S_2C(Me)PMe_3\}]$ where the methyl group is attached to the carbon atom. The ^{31}P NMR spectrum of **4a** shows a resonance at δ 59.05 (J_{WP} = 247.95 Hz), near to the ^{31}P resonance of **3**. On the basis of these spectroscopic data, it is likely that the alkylation takes place at one of the sulfur atoms. The structure is confirmed by an X-ray diffraction analysis. The other alkylated complexes $[W(CO)_5\{PPh_2(CS_2R)\}]$ (R = Et, C_2H_4OH, C_3H_5, CH_2CN, C_2H_4CN, C_3H_6CN, **4b–4g**) have been prepared similarly. Interestingly, the chemical shifts of the ^{31}P resonances of all these complexes fall in the region δ 58–64 with J_{WP} varying from 245 to 252 Hz indicating similar structures. Although the difference is small, the ^{31}P chemical shift moves downfield with increasingly electron-withdrawing groups attached to the phosphine ligand. Using this reaction, we can impart various functional groups into the diphenyldiphosphinodithioformato ligand. Kunze[2f] and Ambrosius[2a] and co-workers have described the reactions of PPh_2H with RNCS to give PPh_2CSNRH (R = alkyl). The molecule displayed a bidentate co-ordination mode through P and S or N and S when bound to metal. Interestingly, the neutral phosphines $PPh_2(CS_2Me)$ and $PPh_2(CS_2C_3H_5)$, which are readily prepared by the alkylation of $PPh_2CS_2^-$ with iodomethane and allyl bromide, respectively, are less stable than the corresponding metal-co-ordinated ones.

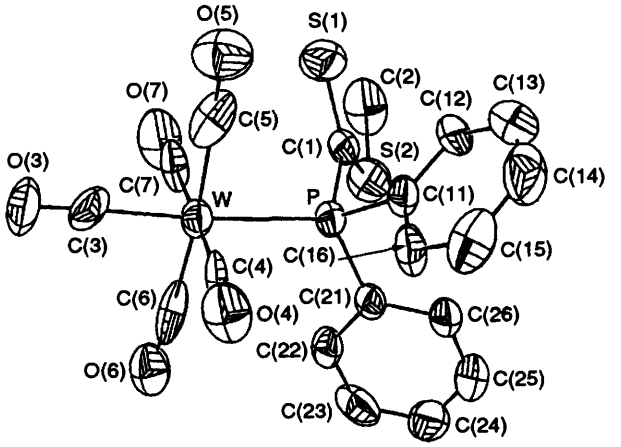
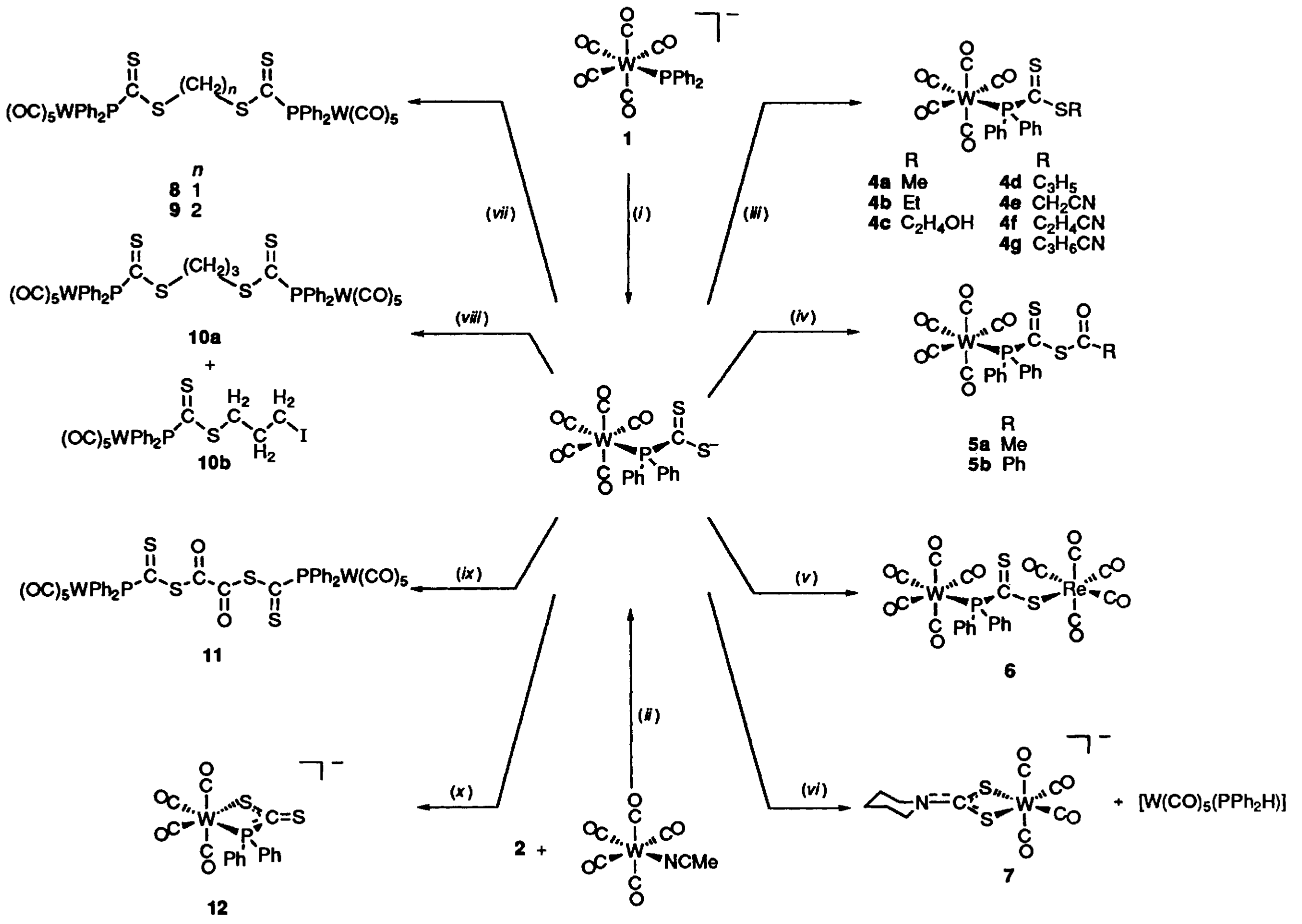


Fig. 3 An ORTEP[14] drawing with 50% thermal ellipsoids and atom-numbering scheme for $[W(CO)_5\{PPh_2(CS_2Me)\}]$ **4a** with hydrogen atoms omitted for clarity

No reaction was observed when complex **4a** was treated with amines such as ethylamine, piperidine or other strong donor ligands such as $Ph_2PCH_2PPh_2$, PPh_3 or PhC≡CPh, even in refluxing toluene. Under photolytic condition the reaction of **4a** with piperidine gave more than ten compounds. This reaction was not pursued further.

This alkylation reaction was extended to α,ω-diiodides for the synthesis of dinuclear complexes. The reaction of **3** with an excess of CH_2I_2 in CH_2Cl_2 gave the dinuclear complex $[\{W(CO)_5(PPh_2CS_2)\}_2(\mu\text{-}CH_2)]$ **8**. The FAB mass spectrum of **8** shows a base peak at *m/z* 904 corresponding to $[\{W(PPh_2CS_2)\}_2(\mu\text{-}CH_2)]^+$, formed by loss of ten CO groups from complex **8**. The spectroscopic and analytical data of **8** are in agreement with the formulation. The ^1H NMR spectrum of **8** exhibits a resonance at δ 5.01 assignable to the CH_2 group and the corresponding ^{13}C NMR signal is at δ 42.7. The ^{31}P NMR spectrum of **8** shows a resonance at δ 59.55 (J_{WP} = 250.96 Hz). Two other dinuclear complexes $[\{W(CO)_5(PPh_2CS_2)\}_2(\mu\text{-}CH_2CH_2)]$ **9** and $[\{W(CO)_5(PPh_2CS_2)\}_2(\mu\text{-}CH_2CH_2CH_2)]$ **10a** were prepared similarly. In the ^{31}P NMR spectra, the resonances for **9** and **10a** are at δ 61.3 (J_{WP} = 254.05 Hz) and δ 59.6 (J_{WP} = 250.13 Hz), respectively. In the reaction of $C_3H_6I_2$ with **3**, if $C_3H_6I_2$ was added to **3**, the mononuclear complex $[W(CO)_5\{PPh_2CS_2(C_3H_6I)\}]$ **10b** was also obtained as the minor product. The ratio of **10a** to **10b** was 5 : 1. If a solution of **3** was added at room temperature to $C_3H_6I_2$ in excess, complex **10b** was obtained as the only product. The ^1H NMR spectrum of **10b** exhibits a multiplet resonance at δ 2.14, two triplet resonances at δ 3.17 and 3.43 assignable to the centre CH_2, ICH_2 and SCH_2 units, respectively, and the corresponding ^{13}C NMR signals are at δ 30.3, 3.7 and 37.8. The ^{31}P NMR spectrum of **10b** shows a resonance at δ 59.08 (J_{WP} = 250.11 Hz). From the reactions of **3** with these α,ω-diiodide species, it is observed that the rate of formation of the dinuclear product decreases as the chain length increases.

Structure Determination of $[NEt_4][PPh_2CS_2]$ **2**, $[NEt_4][W(CO)_5(PPh_2CS_2)]$ **3** *and* $[W(CO)_5\{PPh_2(CS_2Me)\}]$ **4a**.—



Scheme 1 (*i*) CS_2; (*ii*) $PPh_2CS_2^-$; (*iii*) RX; (*iv*) RCOX; (*v*) $[Re(CO)_5Br]$; (*vi*) $[W(pip)_2(CO)_4]$; (*vii*) $(CH_2)_nI_2$; (*viii*) $(CH_2)_3I_2$; (*ix*) $C_2Br_2O_2$; (*x*) heat

The three complexes **2**, **3** and **4a** were also identified on the basis of their single-crystal X-ray diffraction analyses, as illustrated in Figs. 1, 2 and 3, respectively. Interatomic distances and angles of **2**, **3** and **4a** are recorded in Tables 2, 3 and 4, respectively. The two C–S bonds of **2** are equal [C–S(1) 1.66(2), C–S(2) 1.66(1) Å] and the P–C bond distance is 1.87(2) Å, indicating delocalization of the negative charge on CS_2. These C–S(1), C–S(2) and P–C bond distances in $PPh_2CS_2^-$ are comparable to the corresponding bond lengths [1.669(5), 1.650(5), 1.872(5) Å] in $[NEt_4][W(CO)_5(PPh_2CS_2)]$ **3**. The four atoms C, S(1), S(2), P are coplanar both in the free ligand **2** and in complex **3**. In complexes **3** and **4a**, it is clear that the co-ordination geometry about the tungsten atom can be described as distorted octahedral with a phosphorus co-ordination. The W–P distances were 2.553(1) Å for **3** and 2.533(3) Å for **4a**. As expected, the CS_2 group on the phosphorus makes the M–P bond shorter by inducing more phosphorus s character into that bond.[15] In complex **3** the CS_2 unit is attached to the phosphorus atom through carbon. The W–S(1) and W–S(2) distances of **3** [4.056(2) and 4.946(2) Å] and **4a** [4.041(4) and 4.846(4) Å] also indicate the absence of a bonding interaction between the tungsten and the two sulfur atoms. The W–C–O angles are from 174.8(4) to 178.5(5)° for **3** and from 172.7(10) to 179.4(10)° for **4a**. The W–C distances of the W–CO groups are between 1.997(5) and 2.025(5) Å for **3** and between 1.932(16) and 2.014(12) Å for **4a**, and the C–O distances are 1.142(6)–1.168(7) for **3** and 1.124(15)–1.217(19) for **4a**.

Reactions of **3** *with Acyl Halides.*—Acyl groups, similarly to alkyl groups, are easily attached to the CS_2 of **3**. For example, treatment of the complex **3** with excess acetyl chloride resulted in an immediate reaction from which the green, hexane-soluble complex, $[W(CO)_5\{PPh_2(CS_2COMe)\}]$ **5a**, was obtained in 85% yield. The ^1H NMR spectrum of **5a** exhibits a singlet at δ 2.40 attributed to the methyl protons and the corresponding ^{13}C NMR signal is at δ 33.4. The ^{31}P NMR spectrum of **5a** shows a resonance at δ 67.6 (J_{WP} = 246.3 Hz). The complex $[W(CO)_5\{PPh_2(CS_2COPh)\}]$ **5b** was prepared similarly in 87% yield. In the ^{31}P NMR spectrum of **5b**, the resonance appeared at δ 67.46 (J_{WP} = 246.8 Hz). The downfield shift of the ^{31}P resonance compared to that of **4a**–**4g** may be caused by the presence of the electron-withdrawing acyl group –COR on the phosphine. This type of reaction was extended to oxalyl bromide for diacylation. The reaction of **3** with excess BrCOCOBr in CH_2Cl_2 gave a neutral complex $[\{W(CO)_5(PPh_2CS_2)\}_2(CO)_2]$ **11**. This green, air- and water-sensitive powder was isolated in only 40% yield. Under N_2 and at low temperature, complex **11** is stable in *n*-hexane and C_6H_6. The FAB mass spectrum of **11** also shows a base peak at *m*/*z* 946 corresponding to $[\{W(PPh_2CS_2)\}_2(CO)_2]^+$, formed by loss of ten CO groups from complex **11**.

Reactions of **3** *with Metal Complexes.*—Reaction of anionic complex **3** with $[Re(CO)_5Br]$ afforded the dinuclear complex, $[(OC)_5W(\mu\text{-}PPh_2CS_2)Re(CO)_5]$ **6**. The FAB mass spectrum of **6** shows a base peak at *m*/*z* 631 corresponding to $[W(\mu\text{-}PPh_2CS_2)Re]^+$, formed by loss of ten CO groups from complex **6**. In the IR spectrum of **6**, two sets of absorptions are clearly distinguishable, the three absorptions at 2141, 2037 and 1977 cm^{-1} which are assigned to the ν_{CO} of $Re(CO)_5$ are red-shifted[16] relative to those of $[Re(CO)_5Br]$; the other two absorptions at 2068 and 1933 cm^{-1}, assigned to the ν_{CO} of $W(CO)_5$ show blue-shifting relative to that for **3**. The ^{31}P NMR spectrum of **6** exhibits a resonance at δ 53.47 with a tungsten satellite (J_{WP} = 240.9 Hz) indicating phosphorus co-ordination of the ligand to the tungsten. The $PPh_2CS_2^-$ ligand serves as a bridge in complex **6**, in which the phosphorus bonds to the tungsten centre and one of the sulfur atoms bonds to the rhenium centre.

Attempts to prepare a W–W dinuclear complex using the $R_2PCS_2^-$ unit of **3** as the bridging ligand led to cleavage of the P–CS_2 bond. In the reaction of **3** and [W(pip)$_2$(CO)$_4$] the CS_2 of the $Ph_2PCS_2^-$ ligand in complex **3** inserted into the metal–nitrogen bond of [W(pip)$_2$(CO)$_4$] to yield the alkyldithiocarbamate complex [NEt$_4$][W(CO)$_4$(S$_2$CNC$_5$H$_{10}$)] **7** and [W(CO)$_5$(PPh$_2$H)]. A recent article[17] reported the synthesis of dithiocarbamate metal complexes of the type [NEt$_4$][M(Et$_2$NCS$_2$)(CO)$_4$] (M = Mo or W) from the reaction of [M(CO)$_6$] with Na(S$_2$CNEt$_2$) in the presence of NEt$_4$Cl. The IR spectrum of **7** shows four terminal carbonyl stretchings at 1984, 1865, 1834 and 1794 cm^{-1}. The band at 1476 cm^{-1} for **7** is assigned to the C=N group. In the ^{13}C NMR spectrum, the CS_2 group shows a resonance at δ 212.98. This assignment is supported by a HMBC (^{1}H-detected heteronuclear multiple bond correlation) experiment,[18] *i.e.* the α-protons of piperidine show long-range couplings with the carbon atom of CS_2.

Thermal Reaction of **3**.—When compound **3** was heated in thf, decarbonylation occurred, affording a stable compound which can be formulated as [NEt$_4$][W(CO)$_4$(PPh$_2$CS$_2$)] **12** based on its analytical and spectroscopic data (Scheme 1). The IR spectrum of **12** shows a different pattern from that of M(CO)$_5$L. The four absorptions at 1993, 1879, 1859 and 1833 cm^{-1} are typical for a M(CO)$_4$[17] unit in pseudo-octahedral geometry. The ^{31}P NMR spectrum of **12** shows a resonance at δ 24.23 again with a tungsten satellite (J_{WP} = 187.4 Hz) indicating phosphorus co-ordination. The significant upfield shift of the ^{31}P resonance of **12** relative to that of **3** (δ 59.08) suggests a distinctively different chemical and electronic environment for the $R_2PCS_2^-$ ligand and supports the structure depicted in Scheme 1. Attempts to grow single crystals of complex **12** were unsuccessful. We believe that in **12** the $R_2PCS_2^-$ behaves as a bidentate ligand co-ordinating to the metal through the phosphorus and one of the sulfur atoms. Complexes with co-ordination *via* P and S atoms in the similar heteroallylic Ph_2PCSNR^- ligand, have been reported by Kunze, Ambrosius and co-workers.[2] Attempted reaction of complex **12** with MeI did not give any product at room temperature, and decomposition occurred at elevated temperature.

Conclusion

The $R_2PCS_2^-$ ligand of [NEt$_4$][W(CO)$_5$(PPh$_2$CS$_2$)] is bonded to the metal through the phosphorus atom. Alkylation and acylation reactions of **3** with various alkyl and acyl halides take place at the sulfur atom leading to a number of neutral complexes. The reactions of **3** with organic α,ω-diiodide reagents give dinuclear complexes, in which the two metal atoms are bridged by the chelating phosphorus ligand. Treatment of **3** with [Re(CO)$_5$Br] gave a dinuclear heterobimetallic complex, in which the bridging $R_2PCS_2^-$ ligand is bound to the two metal atoms through the phosphorus and one of the sulfur atoms. Thermolysis of **3** causes decarbonylation and leads the $R_2PCS_2^-$ ligand to bind to the tungsten metal centre through the phosphorus and one of the sulfur atoms.

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