# Reversible oxidation of [$Mo_nW_{3-n}(\eta^5\text{-}C_5H_5)_3(CO)_6(\mu_3\text{-}P)$] ($n$ = 0–3) by sulfur; synthesis and characterisation of [$Mo_nW_{3-n}(\eta^5\text{-}C_5H_5)_3(CO)_6(\mu_3\text{-}PS)$] ($n$ = 0–3)

**John E. Davies, Martin J. Mays,* Elizabeth J. Pook, Paul R. Raithby and Peter K. Tompkin**

*Department of Chemistry, Cambridge University, Lensfield Road, Cambridge, UK CB2 1EW*

**The trimetallic tetrahedrane complexes [$Mo_nW_{3-n}(\eta^5\text{-}C_5H_5)_3(CO)_6(\mu_3\text{-}P)$] ($n$ = 0–3) are oxidised in carbon disulfide solution by elemental sulfur to the corresponding $\mu_3$-PS complexes [$Mo_nW_{3-n}(\eta^5\text{-}C_5H_5)_3(CO)_6(\mu_3\text{-}PS)$]; the new complexes lose the sulfur atom upon standing in solution at room temp. to regenerate [$Mo_nW_{3-n}(\eta^5\text{-}C_5H_5)(CO)_6(\mu_3\text{-}P)$]; the X-ray crystal structure of [$W_3(\eta^5\text{-}C_5H_5)_3(CO)_6(\mu_3\text{-}PS)$] is determined.**

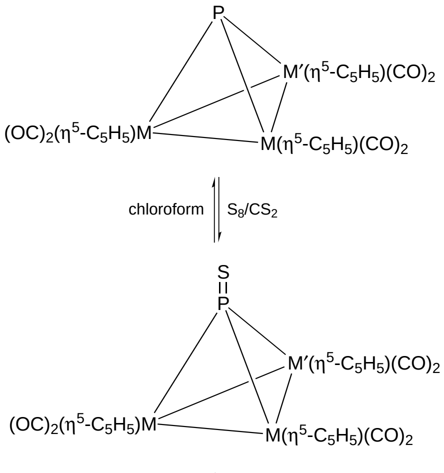
The synthesis of complexes containing naked group 15 ligands has been the subject of much research over recent years.[1] The reported chemistry of such complexes is, however, rather sparse, being limited in the main to the further coordination of 16-electron organometallic fragments to lone pairs present on the group 15 atom.[2] We recently reported that the trimetallic complexes [$Mo_nW_{3-n}(\eta^5\text{-}C_5H_5)_3(CO)_6(\mu_3\text{-}P)$] ($n$ = 0–3) could be oxidised to the respective $\mu_3$-PO complexes by standing in air,[3] although attempts to prepare the $\mu_3$-PS complexes by oxidation with sulfur using toluene as the solvent were unsuccessful. Complexes featuring the phosphorus sulfide ligand are extremely uncommon; to the best of our knowledge there exist only three previous examples with the PS ligand coordinated through phosphorus in the $\mu_3$ mode,[4–7] two examples in which it adopts the $\mu,\eta^2$ mode of coordination[6–8] and one example where the ligand is terminally coordinated through phosphorus.[9] We now report that the trimetallic species complexes [$Mo_nW_{3-n}(\eta^5\text{-}C_5H_5)_3(CO)_6(\mu_3\text{-}P)$] ($n$ = 0–3) can be oxidised by sulfur in $CS_2$ solution to the complexes [$Mo_nW_{3-n}(\eta^5\text{-}C_5H_5)_3(CO)_6(\mu_3\text{-}PS)$] ($n$ = 0–3) and that this oxidation may be reversed simply by dissolution in organic solvents in the absence of excess dissolved sulfur. None of the previously prepared PS complexes have been reported to undergo such a spontaneous self-reduction.

Reaction of elemental sulfur with carbon disulfide solutions of the phosphorus capped trimetallics [$Mo_nW_{3-n}(\eta^5\text{-}C_5H_5)_3(CO)_6(\mu_3\text{-}P)$] ($n$ = 3 **1**, $n$ = 2 **2**, $n$ = 1 **3**, $n$ = 0 **4**)[3] affords in good yield the unstable trimetallic complexes [$Mo_nW_{3-n}(\eta^5\text{-}C_5H_5)_3(CO)_6(\mu_3\text{-}PS)$] ($n$ = 3 **5**, $n$ = 2 **6**, $n$ = 1 **7**; $n$ = 0 **8**), featuring a capping phosphorus monosulfide ligand (Scheme 1).

All four $\mu_3$-PS complexes lose sulfur on standing in solution in common organic solvents in the absence of excess sulfur to give the corresponding $\mu_3$-P complex. The rate of this reverse reaction increases with an increasing number of molybdenum atoms in the complexes. Time-lapse $^1$H NMR studies on [$W_3(\eta^5\text{-}C_5H_5)_3(CO)_6(\mu_3\text{-}PS)$] **8** revealed the formation of [$W_3(\eta^5\text{-}C_5H_5)_3(CO)_6(\mu_3\text{-}P)$] **4** as the only significant cyclopentadienyl-containing product. The stabilities of the PS capped complexes in solution decrease in the order **8** > **7** > **6** > **5**. A study of the kinetics of this decomposition is being undertaken and will be the subject of a later paper. The oxidation of naked phosphorus ligands by sulfur has previously been reported both for ligands consisting of a single phosphorus atom[5,9] and for the $P_2$ ligand, this latter oxidation giving $P_2S_2$ coordinated to a tetrairon core.[10]

The spectroscopic data for the new complexes† are in accord with the proposed structures. All the complexes exhibit a similar IR absorption pattern in the carbonyl region, with the frequencies being similar to those observed for the corresponding phosphorus monoxide complexes.[3] The $^{31}$P NMR spectra of **5**–**8** show more positive chemical shifts and smaller $^1J_{PW}$ coupling constants as the number of tungsten atoms is decreased, as was also observed for the $\mu_3$-PO complexes.[3]

The molecular structure of [$W_3(\eta^5\text{-}C_5H_5)_3(CO)_6(\mu_3\text{-}PS)$] **8** has been determined by X-ray diffraction,‡ and is shown in Fig. 1 along with selected bond lengths and angles. The complex crystallises along with 1 equiv. of $CH_2Cl_2$ in the space group $P2_12_12_1$, whereas [$Mo_3(\eta^5\text{-}C_5H_5)_3(CO)_6(\mu_3\text{-}PO)$]$\cdot CH_2Cl_2$ crystallises in space group $Pna2_1$.[3] Each $W(\eta^5\text{-}C_5H_5)(CO)_2$ fragment is distinct in the solid state on account of the differing relative geometry of the $\eta^5$-$C_5H_5$ and CO ligands with respect to the PS capping ligand, as also observed for [$Mo_3(\eta^5\text{-}C_5H_5)_3(CO)_6(\mu_3\text{-}PO)$].[3] Only one cyclopentadienyl signal is observed in the $^1$H NMR spectrum of **8**, indicating a fluxional process in solution. The P=S bond is essentially perpendicular to the plane defined by the three tungsten atoms. The P=S separation of 1.992(7) Å is at the long end of the range for phosphorus–sulfur double bonds, these being typically observed to fall in the range 1.85–1.95 Å for alkyl and aryl phosphine sulfides,[11] and is in agreement with the observed weakness of this bond. As compared to the alkyl and aryl phosphine sulfides, back-donation from the filled metal d orbitals to vacant d orbitals on phosphorus is likely to reduce the effectiveness of the S → P π component of the PS bond. The W–W and W–P distances correspond to the presence of single bonds, as requires by simple electron counting schemes.



**5** M = M′ = Mo
**6** M = Mo, M′ = W
**7** M = W, M′ = Mo
**8** M = M′ = W

**Scheme 1**

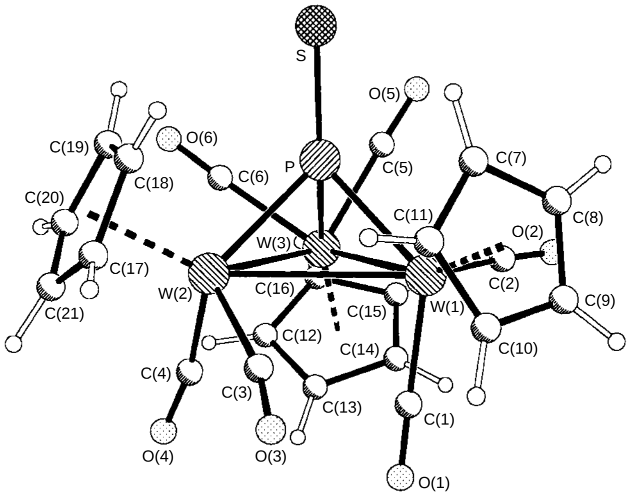


**Fig. 1.** Molecular structure of **8**, showing the atom labelling scheme adopted. Selected bond lengths (Å) and angles (°): P–S 1.992(7), P–W(1) 2.377(5), P–W(2) 2.403(5), P–W(3) 2.441(5), W(1)–W(2) 3.153(2), W(1)–W(3) 3.122(2), W(2)–W(3) 3.109(2); W(1)–W(2)–W(3) 59.79(3), W(1)–W(3)–W(2) 60.80(4), W(2)–W(1)–W(3) 59.41(3), W(1)–P–W(2) 82.5(2), W(1)–P–W(3) 80.7(2), W(2)–P–W(3) 79.9(2), P–W(1)–W(2) 49.09(13), P–W(1)–W(3) 50.52(13), P–W(2)–W(1) 48.38(12), P–W(2)–W(3) 50.60(13), P–W(3)–W(1) 48.74(12), P–W(3)–W(2) 49.54(12), W(1)P–S 132.0(3), W(2)–P–S 128.7(3), W(3)–P–S 133.3(3).

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## Footnotes and References

* E-mail: mjm14@cam.ac.uk

† Selected spectroscopic data [IR($\nu_{CO}$/cm$^{-1}$) recorded in $CH_2Cl_2$ solution; $^1$H and $^{31}$P NMR shifts recorded in $CDCl_3$ solution; $^{31}$P NMR shifts recorded relative to $P(OMe)_3$ at $\delta$ 0.0 with upfield shifts negative (add 140.2 ppm to convert reference to 85% $H_3PO_4$) ; *J* in Hz]. **5**: $\nu_{CO}$ 1995m, 1959vs, 1938s, 1903m ; $^1$H NMR, $\delta$ 5.17 (d, $^3J_{HP}$ 0.5); $^{31}$P NMR, $\delta$ +308.2 (s); FABMS, *m/z* 714 (M$^+$). **6**: $\nu_{CO}$ 1995m, 1957vs, 1935s, 1900m ; $^1$H NMR, $\delta$ 5.20 [s, 5 H, $(C_5H_5)$W], 5.18 [d, 10 H, $^3J_{HP}$ 0.6, $(C_5H_5)$Mo]; $^{31}$P NMR, $\delta$ +273.6 (s, $^1J_{PW}$ 534); FABMS *m/z* 803 (M$^+$ + 1). **7**: $\nu_{CO}$ 1993m, 1956vs, 1932s, 1896m ; $^1$H NMR, $\delta$ 5.23 [d, 10 H, $^3J_{HP}$ 0.8, $(C_5H_5)$W], 5.19 [d, 5 H, $^3J_{HP}$, 0.8, $(C_5H_5)$Mo]; $^{31}$P NMR, $\delta$ +237.3 (s, $^1J_{PW}$ 471); FABMS, *m/z* 891 (M$^+$ + 1). **8**: $\nu_{CO}$ 1991m, 1955vs, 1932s, 1893m ; $^1$H NMR, $\delta$ 5.23 (d, $^3J_{HP}$ 0.6, $(C_5H_5)$); $^{31}$P NMR, $\delta$ +200.7, $^1J_{PW}$ 415; FABMS, *m/z* 979 (M$^+$ + 1).

‡ *Crystal structure determination* of **8**·$CH_2Cl_2$. $C_{21}H_{15}O_6PSW_3 \cdot CH_2Cl_2$, $M_r$ = 1062.84, orthorhombic, space group $P2_12_12_1$, $a$ = 13.476(5), $b$ = 18.114(11), $c$ = 10.447(6) Å, $U$ = 2550(2) Å$^3$ (by least-squares refinement on diffractometer angles from 25 centred reflections, $15 < 2\theta < 20°$), $Z$ = 4, $D_c$ = 2.768 Mg m$^{-3}$, $\mu$(Mo-K$\alpha$) = 13.890 mm$^{-1}$, semi-empirical absorption correction based on $\psi$-scans,[12,13] relative transmission factors 0.593–1.000, $F(000)$ = 1936, dark green–brown block with dimensions 0.15 × 0.15 × 0.10 mm. Data were collected by the $\omega$–$2\theta$ scan method on a Rigaku AFC5R four-circle diffractometer at 150(2) K using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.710 73 Å) in the range $5.42 < 2\theta < 50.0°$, $+h$, $+k$, $+l$; three standard reflections showed no significant variation in intensity; 2775 reflections of which 2743 were independent ($R_{int}$ = 0.025) and used in all calculations. Structure was solved using direct methods[14] and subsequent Fourier difference syntheses and refined by full-matrix least-squares on $F^2$[15] with anisotropic thermal parameters for W, P, S and Cl atoms. Hydrogen atoms were placed geometrically in idealised positions and refined using a riding model. In the final cycles of refinement a weighting scheme of the form $w^{-1} = [\sigma^2(F_o^2) + (0.0283P)^2 + 24.032P]$, where $P = (F_o^2 + 2F_c^2)/3$, was employed which produced a flat analysis of variance. Final $R(F)$ = 0.0404, $wR(F^2)$ = 0.0912 for 2260 observed reflections [$I > 2\sigma(I)$], $R(F)$ = 0.0739, $wR(F^2)$ = 0.2048 for all data; 176 parameters; GOF = 1.041, maximum $\Delta/\sigma$ = 0.08. Maximum peak and hole in final difference electron density 2.21 and −1.81 e Å$^{-3}$, respectively. CCDC 186/590.

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