

## ***In situ* Synthesis of Phenyltrithiophosphonate: Isolation and Structure of $[\text{PPh}_4]_2[\text{W}_2\text{S}_4\{\text{S}_2(\text{S})\text{PPh}\}_2]$**

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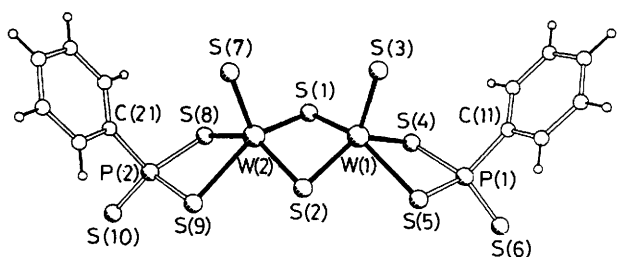
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$\text{PhP}(\text{S})\text{S}_2^{2-}$  has been prepared directly by the reaction of  $[\text{PPh}_4]_2[\text{WS}_4]$  with  $\text{PhPCl}_2$ ;  $[\text{PPh}_4]_2[\text{W}_2\text{S}_4\{\text{S}_2(\text{S})\text{PPh}\}_2]$  has been isolated and the anion shown to involve a  $\text{W}_2\text{S}_4$  core to which are ligated two bidentate  $\text{PhP}(\text{S})\text{S}_2$  moieties.

The  $d^0$  tetrathiometalates  $[\text{MS}_4]^{2-}$  ( $\text{M} = \text{Mo}, \text{W}$ ) have proved to be versatile synthetic reagents, especially for the generation of a host of metal-sulphur clusters.<sup>1</sup> Reactions of these anions with non-metallic species are rather limited. However, we have explored several of these and herein report that  $[\text{PPh}_4]_2[\text{WS}_4]$  reacts with  $\text{PhPCl}_2$  at ambient temperature to form  $[\text{PPh}_4]_2[\text{W}_2\text{S}_4\{\text{S}_2(\text{S})\text{PPh}\}_2]$ , which contains phenyltrithiophosphonate ligands.

The title compound was obtained by the addition of  $[\text{PPh}_4]_2[\text{WS}_4]$  (3.1 g, 3.13 mmol) in MeCN (30 cm<sup>3</sup>) to  $\text{PhPCl}_2$  (0.56 g, 3.13 mmol) at room temperature. The resultant mixture was stirred for *ca.* 6 h under an atmosphere of purified dinitrogen, during which time a yellow powder was deposited. This precipitate was separated by filtration, washed with  $\text{Et}_2\text{O}$ , dried, and redissolved in dried dimethylformamide (DMF); orange crystals were obtained by the slow diffusion of



**Figure 1.** Structure of the anion of  $[\text{PPh}_4]_2[\text{W}_2\text{S}_4\{\text{S}_2(\text{S})\text{PPh}\}_2]$ . Selected dimensions:  $\text{W}(1)\text{--}\text{W}(2)$  2.828(1),  $\text{W--S}_\mu$  2.321(3)—2.331(2),  $\text{W--S}_t$  2.115(3) and 2.120(3),  $\text{W--S}_{\text{ligand}}$  2.429(3)—2.463(2),  $\text{P--S}_\mu$  2.050(4)—2.073(4),  $\text{P--S}_t$  1.929(3) and 1.945(4) Å;  $\text{S}_\mu\text{--W--S}_\mu$  105.1(1)—110.5(1),  $\text{S}_\mu\text{--W--S}_\mu$  101.1(1) and 101.2(1),  $\text{S}_t\text{--W--S}_{\text{ligand}}$  103.4(1)—108.8(1),  $\text{S}_{\text{ligand}}\text{--W--S}_{\text{ligand}}$  76.7(1) and 77.6(1);  $\text{S}_t\text{--P--S}_{\text{ligand}}$  116.4(2)—118.1(2)°.

$\text{Et}_2\text{O}$  into this solution. The analytically pure product was obtained in ca. 30% yield.

Crystals, obtained as described above, proved suitable for examination by X-ray crystallography† and the structure of the anion in the  $[\text{PPh}_4]^+$  salt is shown in Figure 1. The anion consists of a central  $\text{W}_2\text{S}_4^{2+}$  core, in which each metal is bound to a bidentate  $\text{PhP}(\text{S})\text{S}_2^{2-}$  ligand which has a free  $\text{P}=\text{S}$  bond. Each tungsten is bound to a square pyramidal arrangement of five sulphur atoms and the two square pyramids share a common edge  $[\text{S}(1), \text{S}(2)]$  to form a dimer with a *syn* configuration and a  $\text{W}\cdots\text{W}$  separation of 2.828(1) Å. This geometry closely resembles that of the other structurally characterised complexes which contain a  $\text{W}_2\text{S}_4\{\text{S}_4\}$  centre, viz.  $[\text{W}_2\text{S}_4\{\text{WS}_4\}_2]^{2-}$ ,<sup>2</sup>  $[\text{W}_2\text{S}_4\{\text{SCH}_2\text{CH}_2\text{S}\}_2]^{2-}$ ,<sup>3</sup>  $[\text{W}_2\text{S}_4\{\text{S}_2\text{CNEt}_2\}_2]$ , and  $[\text{W}_2\text{S}_4\{\text{S}_2\text{P}(\text{OEt})_2\}_2]$ .<sup>4</sup> The  $\text{W}\cdots\text{W}$  separation of this last system (2.82 Å) bears the closest resemblance to that of  $[\text{W}_2\text{S}_4\{\text{S}_2(\text{S})\text{PPh}\}_2]^{2-}$ .

† Crystal data:  $\text{C}_{60}\text{H}_{50}\text{P}_4\text{S}_{10}\text{W}_2$ , triclinic, space group  $\bar{P}1$ ,  $Z = 2$ ,  $a = 11.925(2)$ ,  $b = 13.457(2)$ ,  $c = 21.145(3)$  Å,  $\alpha = 99.02(1)$ ,  $\beta = 90.79(1)$ ,  $\gamma = 111.89(1)^\circ$ ,  $U = 3100.0$  Å<sup>3</sup>,  $D_c = 1.696$  g cm<sup>-3</sup>,  $F(000) = 2088$ , Mo- $K_\alpha$  radiation,  $\lambda = 0.71073$  Å,  $\mu = 4.25$  mm<sup>-1</sup>. The structure was determined from a whole sphere of absorption-corrected data [ $2\theta_{\text{max}} 50^\circ$ , 21 756 reflections, 10 887 unique, 8918 with  $F > 4\sigma(F)$ ], and refined to  $R = 0.058$ ,  $R_w = 0.050$  with anisotropic thermal parameters and rigid idealised phenyl groups [ $\text{C--C}$  1.395,  $\text{C--H}$  0.96 Å,  $U(\text{H}) = 1.2U_{\text{equiv}}(\text{C})$ ]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The immediate environment of phosphorus in the anion reported here closely resembles that in Lawesson's reagent,  $[\{\text{MeO-4-C}_6\text{H}_4\text{P}(\text{S})\}_2\text{S}_2]$ .<sup>5</sup> Indeed, several complexes containing  $\text{MeO-4-C}_6\text{H}_4\text{P}(\text{S})\text{S}_2$  (=L) ligands, viz.  $[\text{Cp}_2\text{TiL}]$  ( $\text{Cp} = \text{C}_5\text{H}_5$ )<sup>6</sup> and  $[(\text{Ph}_3\text{P})_2\text{ML}]$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Et}$ ), have been prepared from Lawesson's reagent. Also, bis(dialkylthiophosphonyl)disulphanes,  $[\{\text{R}_2\text{P}(\text{S})\text{S}\}_2]$ , have been shown to react with metal carbonyls to form dithiophosphate complexes, e.g.  $[\text{Mo}_3\text{S}_7\{\text{S}_2\text{PR}_2\}_3]^+$  and  $[\text{W}_2\text{S}_4\{\text{S}_2\text{PR}_2\}_2]$  ( $\text{R} = \text{Et}, \text{Pr}^n$ ).<sup>7</sup> However, the *in situ* synthesis of an  $\text{PhP}(\text{S})\text{S}_2$  complex, from  $\text{PhPCl}_2$  and  $[\text{WS}_4]^{2-}$ , has no direct chemical precedent. Although the reaction proceeds in reasonably good (ca. 30% yields) it is not stoichiometric since (*inter alia*)  $\text{W}^{\text{VI}}$  is reduced to  $\text{W}^{\text{V}}$  with  $\text{P}^{\text{III}}$  being oxidised to  $\text{P}^{\text{V}}$ .

The <sup>31</sup>P NMR spectrum of the title complex in  $\text{CD}_2\text{Cl}_2/\text{DMF}$  contains resonances at  $\delta +22$  ( $[\text{PPh}_4]^+$ ) and  $+120$  p.p.m.  $[\text{PhP}(\text{S})\text{S}_2]$ . The latter may be compared to the corresponding resonances for  $[(\text{L}_2)\text{M}\{\text{S}_2(\text{S})\text{PC}_6\text{H}_4\text{-4-OMe}\}]$  [ $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ ;  $\text{L}_2 = (\text{Ph}_3\text{P})_2$  or 1,2-bis(diphenylphosphino)ethane]<sup>8,9</sup> of  $\delta +88$  to  $+101$  p.p.m.<sup>9</sup> The  $\nu(\text{P}=\text{S})$  stretching frequency occurs at  $666$  cm<sup>-1</sup>. This absorption remains unchanged upon exposure of the solid and solutions of the title compound to air; this observation, coupled with the lack of appearance of a  $\nu(\text{P}=\text{O})$  bond, shows that the  $\text{P}=\text{S}$  bond in this compound is stable in air, unlike that in the  $[(\text{Ph}_3\text{P})_2\text{M}\{\text{S}_2(\text{S})\text{PC}_6\text{H}_4\text{-4-OMe}\}]$  complexes.<sup>9</sup>

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