

Preparation, structure, and some coordination properties of 2-chloro-3,3-diphenyl-3-thioxo-1-(2,4,6-tri-*t*-butylphenyl)-1,3-diphosphapropene

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A sterically encumbered 3-thioxo-1,3-diphosphapropene, bearing a P=C–P=S skeleton, was prepared, characterised, and allowed to react with a carbonyltungsten(0) reagent and iodine affording the corresponding chelate tungsten(0) complex and charge-transfer complex with iodine, respectively, which were analysed by the X-ray crystallography.

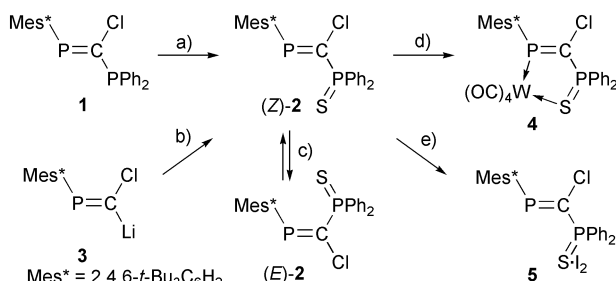
Recently we have reported the coordination properties of the kinetically stabilised 1,3-diphosphapropene **1** on the carbonyltungsten(0) moieties.¹ Compound **1** possesses two different types of phosphorus atoms within the system; an unsaturated $\lambda^3\sigma^2$ -phosphorus atom² and a common $\lambda^3\sigma^3$ -phosphorus atom, possibly regarded as a difunctional ligand. The $\lambda^3\sigma^3$ -phosphorus atom in **1** predominantly coordinated on the tungsten due to the higher basicity than the unsaturated phosphorus atom, besides **1** could behave as a chelating ligand. On the other hand, there are a number of heterofunctional ligands containing phosphorus and sulfur atoms.³ For example, a diphosphine sulfide Ph₂PCH₂P(S)Ph has been employed as catalyst ligand for methanol carbonylation.⁴ Additionally, compounds containing the unsaturated phosphorus atom(s) have been paid considerable attention as a novel class of ligands for synthetic catalysts.^{5–7} Here we report on the sulfuration of **1** to afford a 3-sulfide **2** possessing the P=C–P=S skeleton (Scheme 1), and the coordination properties of **2** using carbonyltungsten(0) reagents or iodine together with their structural determinations by the X-ray analyses.

1,3-Diphosphapropene **1** was allowed to react with an equivalent amount of sulfur affording the corresponding product **Z-2** in an excellent yield (88%) without sulfuration on the unsaturated 1-phosphorus atom.[†] In the ³¹P NMR spectrum, the P=C phosphorus of **Z-2** appeared at δ_p 322.4 and the P(S)Ph₂ phosphorus was observed at δ_p 49.1 with a ²J_{PP} value of 104 Hz. Alternatively, **Z-2** was obtained by a reaction of **3** with Ph₂P(S)Cl in a poor yield (ca. 10%). The structure of **Z-2** was confirmed by X-ray crystallography and the molecular structure is shown in Fig. 1.[‡] The P=C(Cl)–P=S skeleton displays almost a planar *s*-cis conformation, which is similar to the case of diphenylvinylphosphine sulfide.⁸ The distances of the P1–C1 and the P2–S are close to the average values for the P=C and P=S bonds, respectively.^{2,8}

A 3-sulfide **Z-2** was isomerised to afford the *E*-isomer, **E-2**, as a *Z*:*E* ratio of 4:1 upon irradiation, whereas no *E*/*Z* isomerisation of **Z-2** was observed by heating in the refluxing toluene, in contrast to the case of **1** showing no *E*/*Z* isomerisation. In the ³¹P NMR spectrum, the P=C phosphorus of **E-2** appeared at δ_p 344.0 in a lower field than that of the *Z*-isomer and the P(S)Ph₂ phosphorus appeared at δ_p 42.1.[†] The ²J_{PP} value of **E-2** (53 Hz) is smaller than that of the *Z*-isomer, which supports the *E*-configuration.¹

To estimate the coordination properties of **Z-2**, at first, the reactions with carbonyltungsten(0) reagents were performed. Compound **Z-2** was allowed to react with W(CO)₄(cod) (cod = cycloocta-1,5-diene) affording the corresponding chelate complex **4** almost quantitatively. In the ³¹P NMR spectrum, the P=C phosphorus of **4** was observed at δ_p 319.0 with the satellite peaks for ¹⁸³W (¹J_{PW} 290 Hz), whereas the P(S)Ph₂ phosphorus was observed at δ_p 48.4 without the satellite peaks for ¹⁸³W.[†] On the other hand, **Z-2** was allowed to react with W(CO)₅(thf) to give **4** in 20% yield through the unstable monocoordinated complex, where the sulfur solely coordinates on the tungsten (δ_p 331.7, 54.6, ²J_{PP} 96 Hz). The structure of **4** was analysed by X-ray crystallography as shown in Fig. 2.[‡] The two independent molecules were found in the unit cell and one of them is displayed. The P=C–P=S system forms the five-membered chelate ring with the tungsten. The P1–C1–P2–S torsion angle is 26.7(7)°, whereas the W–P1–C1–P2 skeleton is almost planar with the angle of 0.8(7)°. Such an envelope structure was reported for a rhodium(i) complex ligated with a diphosphine sulfide Ph₂PCH₂P(S)Ph₂.⁴ The S–W distance is similar to that of the tetracarbonyltungsten(0) complex of [*o*-(methylsulfanyl)phenyl]diphenylphosphine [2.527(2) Å].⁹ The P–W distance is comparable to that of the tetracarbonyltungsten(0) complex of 1,3-diphosphapropene **1** [2.489(3) Å].¹ Compared with **Z-2**, the P=S bond of **4** is elongated due to the coordination by the tungsten atom and accordingly the ν (P=S) value of **4** becomes lower (604 cm^{−1}) than that of **Z-2** (646 cm^{−1}). The ν (C≡O) values, 2019, 1913, and 1869 cm^{−1}, are similar to the corresponding complex of Ph₂PCH₂P(S)Ph₂.¹⁰

The charge-transfer complexes of phosphine chalcogenide with halogens have been paid considerable attention, because



Scheme 1 Reagents and Conditions: (a) 1/8-S₈, toluene, reflux, 12 h; (b) Ph₂P(S)Cl, THF, −78 °C; (c) Medium pressure Hg lamp (100 W), CDCl₃, 0 °C, 36 h; (d) W(CO)₄(cod), THF, 20 °C, 12 h; (e) I₂, Et₂O:hexane 1:1, 0 °C.

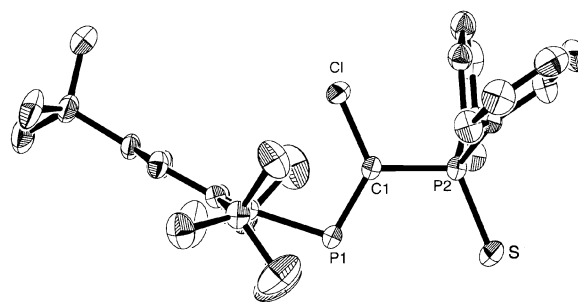


Fig. 1 An ORTEP drawing of **Z-2** with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C1 1.675(4), C1–C1 1.737(3), P1–C_{Mes*} 1.852(4), P2–C1 1.821(4), P2–S 1.946(1), C1–P1–C_{Mes*} 101.7(2), P1–C1–P2 119.1(2), P1–C1–C1 126.5(2), P2–C1–C1 114.1(2), S–P2–C1 112.5(1).

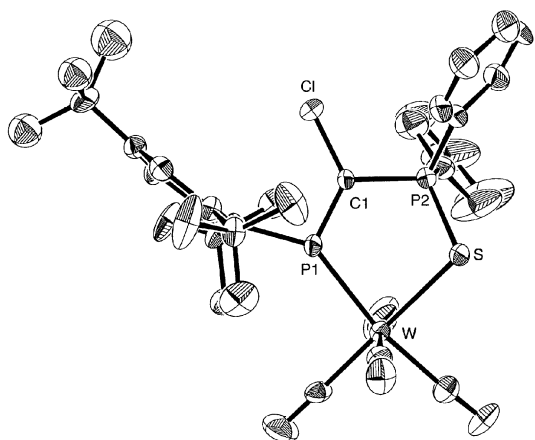


Fig. 2 An ORTEP drawing of **4** with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. The *p*-*t*-butyl group is disordered and the atoms with a predominant occupancy factors (0.55), which are refined isotropically, are shown. Selected bond lengths (Å) and angles (°): W–P1 2.442(2), W–S1 2.566(3), Cl–C1 1.746(9), S–P2 1.990(4), P1–C1 1.65(1), P1–C_{Mes}^{*} 1.82(1), C1–P2 1.81(1), S–W–P1 82.80(9), W–S–P2 102.9(2), W–P1–C1 115.3(3), W–P1–C_{Mes}^{*} 143.3(3), C1–P1–C_{Mes}^{*} 101.3(4), P1–C1–P2 117.5(5), P1–C1–Cl 127.4(6), P2–C1–Cl 114.9(6), S–P2–C1 108.2(3).

they have displayed various intriguing molecular assemblies which are dependent on the reaction conditions.¹¹ For example, triphenylphosphine sulfide has been reported to react with iodine to form charge-transfer complexes^{11,12} and it prompted us to investigate the reaction of **Z-2** with iodine. Compound **Z-2** was mixed with an equivalent amount of iodine in ether at 20 °C and a deep red solution was obtained after 3 h. This solution was diluted with hexane and cooled to 0 °C to obtain compound **5** as red-brown plates. The elemental analysis revealed that **5** is a 1 : 1 charge-transfer complex of **Z-2** and iodine. In the IR spectrum (KBr), **5** displayed a peak at $\nu(\text{P}=\text{S})$ 611 cm⁻¹, which is lower than that of **Z-2**. On the other hand, the ³¹P NMR spectrum in chloroform-*d* indicated the value of δ_{p} 325.8, 48.4; ²J_{PP} = 106 Hz, which is similar to the corresponding data of **Z-2**. The structure of **5** was finally established by the X-ray crystallography and the structure is shown in Fig. 3.† The I2–I1–S skeleton is almost straight in shape.¹² The S–I1 distance is longer than that of Ph₃PS–I₂ [2.753(2) Å], whereas the I1–I2 and P1–S distances are close to those of Ph₃PS–I₂.¹² The P=C distance is almost identical with that for **Z-2**. The molecule displays a weak intermolecular interaction to form a dimer and the intermolecular S⋯S and S⋯I1 distances, 3.320(4) and 3.838(2) Å respectively, are shorter than the corresponding sums of the van der Waals radii [S, 1.85 Å; I, 2.15 Å].¹³

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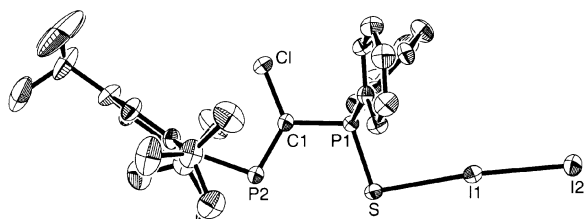


Fig. 3 An ORTEP drawing of **5** with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): I1–I2 2.8122(9), I1–S 2.809(2), Cl–C1 1.723(8), S–P1 1.990(3), P1–C1 1.822(8), 1.811(9), P2–C1 1.678(8), P2–C_{Mes}^{*} 1.843(3), I2–I1–S 174.90(5), I1–S–P1 98.44(10), S–P1–C1 109.2(3), Cl–C1–P1 112.4(4), Cl–C1–P2 118.7(5), P1–C1–P2 118.7(5), C1–P2–C_{Mes}^{*} 100.2(4).

Notes and references

† *Physical data*: **Z-2**: Colourless crystals, mp 111–112 °C, ¹H NMR (400 MHz, CDCl₃) δ = 7.93 (4H, m, arom), 7.50 (2H, m, arom), 7.46 (4H, m, arom), 7.42 (2H, m, arom), 1.45 (18H, s, *o*-*t*-Bu), 1.34 (9H, s, *p*-*t*-Bu); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ = 159.4 (dd, ¹J_{PC} 84 Hz, ¹J_{PC} 62 Hz, P=C), 154.0 (d, ²J_{PC} 2 Hz, *o*-Mes*), 151.7 (s, *p*-Mes*), 134.7 (dd, ¹J_{PC} 62 Hz, ³J_{PC} 13 Hz, *ipso*-Mes*), 132.9 (d, ²J_{PC} 11 Hz, *m*-Ph), 132.4 (d, ⁴J_{PC} 3 Hz, *p*-Ph), 132.0 (dd, ¹J_{PC} 88 Hz, ³J_{PC} 3 Hz, *ipso*-Ph), 128.8 (d, ³J_{PC} 13 Hz, *o*-Ph), 123.0 (brs, *m*-Mes*), 38.3 (brs, *o*-CMe₃), 35.5 (s, *p*-CMe₃), 33.5 (d, ⁴J_{PC} 7 Hz, *o*-CMe₃), 31.8 (s, *p*-CMe₃). **E-2**: ¹H NMR (400 MHz, CDCl₃) δ = 7.75 (4H, m, arom), 7.38 (8H, m, arom), 1.51 (18H, s, *o*-*t*-Bu), 1.39 (9H, s, *p*-*t*-Bu). **4**: Deep red prisms (hexane), mp 173 °C (decomp); ¹H NMR (400 MHz, CDCl₃) δ = 7.74 (4H, m, arom), 7.62 (2H, m, arom), 7.53 (6H, m, arom), 1.63 (18H, s, *o*-*t*-Bu), 1.35 (9H, s, *p*-*t*-Bu); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ = 209.4 (dd, ²J_{PC} 46 Hz, ³J_{PC} 6 Hz, CO_{eq}), 204.8 (d, ³J_{PC} 4 Hz, CO_{ax}), 202.4 (d, ²J_{PC} 10 Hz, CO_{ax}), 155.5 (s, *o*-Mes*), 153.5 (s, *p*-Mes*), 142.6 (dd, ¹J_{PC} 89 Hz, ¹J_{PC} 16 Hz, P=C), 133.5 (d, ⁴J_{PC} 3 Hz, *p*-Ph), 133.0 (d, ²J_{PC} 11 Hz, *m*-Ph), 130.1 (m, *ipso*-Ph), 129.3 (d, ³J_{PC} 13 Hz, *o*-Ph), 128.3 (dd, ¹J_{PC} 87 Hz, ³J_{PC} 5 Hz, *ipso*-Mes*), 123.5 (d, ³J_{PC} 7 Hz, *m*-Mes*), 39.1 (brs, *o*-CMe₃), 35.7 (s, *p*-CMe₃), 33.8 (brs, *o*-CMe₃), 31.5 (s, *p*-CMe₃). Anal. Calc. for C₃₅H₃₉ClO₄P₂SW: C, 50.23; H, 4.70. Found: C, 50.24, H, 4.66%. **5**: Red plates (ether-hexane), mp 102 °C (decomp). Anal. Calc. for C₃₁H₃₉ClI₂P₂S: C, 46.83; H, 4.91. Found: C, 46.79; H, 4.84%.
‡ *Crystal data*: **Z-2**: C₃₁H₃₉ClI₂P₂S, *M* = 541.11, colourless prism, 0.50 × 0.50 × 0.20 mm, monoclinic, *P*2₁/*n* (no. 14), *a* = 16.294(2), *b* = 11.480(4), *c* = 17.142(3) Å, β = 105.38(1)°, *V* = 3091(4) Å³, *Z* = 4, *T* = 288 K, 2 θ _{max} = 50.0°, ρ = 1.163 g cm⁻³, $\mu(\text{Mo-K}\alpha)$ = 0.312 mm⁻¹, 0.4562 measured reflections, 4520 unique reflections (*R*_{int} = 0.052), *R*1 = 0.062 [*I* > 2 σ (*I*)], *R*_w = 0.087 (all data), *S* = 1.29 for 316 parameters (CCDC-196480). **4**: C₃₅H₃₉ClO₄P₂SW, *M* = 837.00, deep red prism, 0.30 × 0.30 × 0.20 mm, triclinic, *P*1 (no. 2), *a* = 17.180(2), *b* = 20.019(1), *c* = 10.807(1) Å, α = 90.023(6), β = 91.993(2), γ = 89.968(6)°, *V* = 3714.6(6) Å³, *Z* = 4, *T* = 296 K, 2 θ _{max} = 55.0°, ρ = 1.497 g cm⁻³, $\mu(\text{Mo-K}\alpha)$ = 3.362 mm⁻¹, 28035 measured reflections, 14887 unique reflections (*R*_{int} = 0.119), *R*1 = 0.064 [*I* > 2 σ (*I*)], *R*_w = 0.148 (all data), *S* = 1.28 for 789 parameters (CCDC-196481). **5**: C₃₁H₃₉ClI₂P₂S, *M* = 794.92, red plate, 0.40 × 0.50 × 0.08 mm, orthorhombic, *P*_{bc}a (no. 61), *a* = 11.751(1), *b* = 38.246(3), *c* = 15.542(1) Å, *V* = 6985(1) Å³, *Z* = 8, *T* = 243 K, 2 θ _{max} = 55.0°, ρ = 1.512 g cm⁻³, $\mu(\text{Mo-K}\alpha)$ = 2.047 mm⁻¹, 59303 measured reflections, 8504 unique reflections (*R*_{int} = 0.043), *R*1 = 0.045 [*I* > 3 σ (*I*)], *R*_w = 0.053 (all data), *S* = 1.19 for 334 parameters (CCDC-196482). See <http://www.rsc.org/suppdata/cc/b2/b211230b/> for crystallographic files in CIF or other electronic format.

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