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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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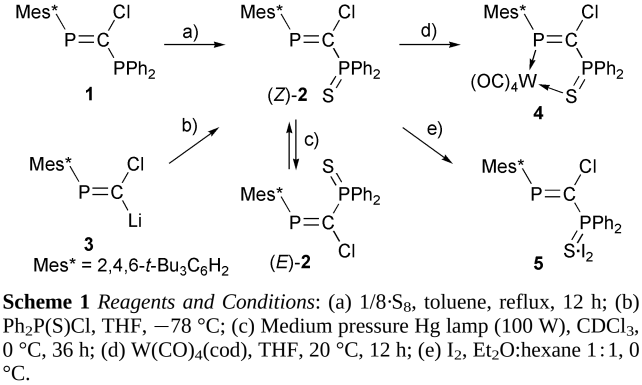
A sterically encumbered 3-thioxo-1,3-diphosphapropene, bearing a P=C–P=S skeleton, was prepared, characterised, and allowed to react with a carbonyltungsten(0) reagent and iodine affording the corresponding chelate tungsten(0) complex and charge-transfer complex with iodine, respectively, which were 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 atom[2] 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 $Ph_2PCH_2P(S)Ph$ 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 sulfurisation 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**[1] was allowed to react with an equivalent amount of sulfur affording the corresponding product *Z*-**2** in an excellent yield (88%) without sulfurisation on the unsaturated 1-phosphorus atom.† In the ^{31}P NMR spectrum, the P=C phosphorus of *Z*-**2** appeared at δ_P 322.4 and the $P(S)Ph_2$ 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 $Ph_2P(S)Cl$ 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]



Scheme 1 *Reagents and Conditions*: (a) 1/8·S_8, toluene, reflux, 12 h; (b) $Ph_2P(S)Cl$, THF, −78 °C; (c) Medium pressure Hg lamp (100 W), $CDCl_3$, 0 °C, 36 h; (d) $W(CO)_4(cod)$, THF, 20 °C, 12 h; (e) I_2, Et_2O:hexane 1 : 1, 0 °C.

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 ^{31}P 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 $P(S)Ph_2$ 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 ^{31}P NMR spectrum, the P = C phosphorus of **4** was observed at δ_P 319.0 with the satellite peaks for ^{183}W ($^1J_{PW}$ 290 Hz), whereas the $P(S)Ph_2$ phosphorus was observed at δ_P 48.4 without the satellite peaks for ^{183}W.† 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 $Ph_2PCH_2P(S)Ph_2$.[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 $Ph_2PCH_2P(S)Ph_2$.[10]

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

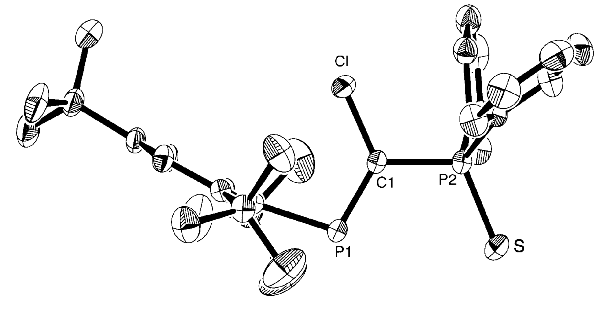


Fig. 1 An ORTEP drawing of *Z*-**2** with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C1 1.675(4), C1–Cl 1.737(3), P1–C_{Mes^*} 1.852(4), P2–C1 1.821(4), P2–S 1.946(1), C1–P1–C_{Mes^*} 101.7(2), P1–C1–P2 119.1(2), P1–C1–Cl 126.5(2),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

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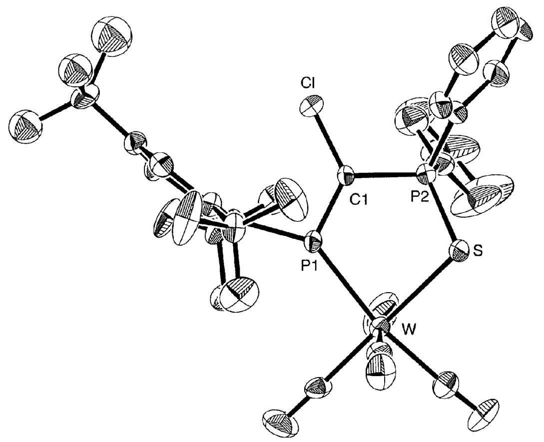

Fig. 2 An ORTEP drawing of **4** with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. The *p-t*-butyl group is disordered and the atoms with a predominant occupancy factors (0.55), which are refined isotropically, are shown. Selected bond lengths (Å) and angles (°): W–P1 2.442(2), 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–P–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 ν(P=S) 611 cm^{-1}, which is lower than that of *Z*-**2**. On the other hand, the ^{31}P 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 $Ph_3PS{\cdot}I_2$ [2.753(2) Å], whereas the I1–I2 and P1–S distances are close to those of $Ph_3PS{\cdot}I_2$.[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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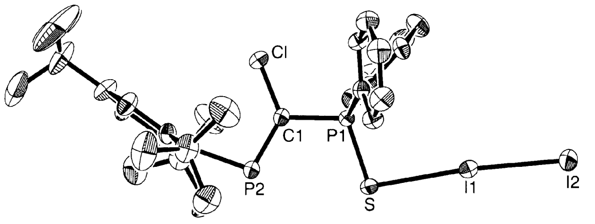

Fig. 3 An ORTEP drawing of **5** with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): I1–I2 2.8122(9), I1–S 2.809(2), Cl–C1 1.723(8), S–P1 1.990(3), P1–C1 1.822(8), 1.811(9), P2–C1 1.678(8), P2–C_{Mes*} 1.843(3), I2–I1–S 174.90(5), I1–S–P1 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, ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) 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*-*C*Me$_3$), 35.5 (s, *p*-*C*Me$_3$), 33.5 (d, $^4J_{PC}$ 7 Hz, *o*-C*Me*$_3$), 31.8 (s, *p*-C*Me*$_3$). *E*-**2**: ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 209.4 (dd, $^2J_{PC}$ 46 Hz, $^3J_{PC}$ 6 Hz, CO_{eq}), 204.8 (d, $^3J_{PC}$ 4 Hz, CO_{eq}), 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*-*C*Me$_3$), 35.7 (s, *p*-*C*Me$_3$), 33.8 (brs, *o*-C*Me*$_3$), 31.5 (s, *p*-C*Me*$_3$). Anal. Calc. for $C_{35}H_{39}ClO_4P_2SW$: 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 $C_{31}H_{39}ClI_2P_2S$: C, 46.83; H, 4.91. Found: C, 46.79; H, 4.84%.

‡ *Crystal data*: *Z*-**2**: $C_{31}H_{39}ClP_2S$, M = 541.11, colourless prism, 0.50 × 0.50 × 0.20 mm, monoclinic, $P2_1/n$ (no. 14), a = 16.294(2), b = 11.480(4), c = 17.142(3) Å, β = 105.38(1)°, V = 3091(4) Å^3, Z = 4, T = 288 K, $2\theta_{max}$ = 50.0°, ρ = 1.163 g cm^{-3}, μ(Mo-Kα) = 0.312 mm^{-1}, 4565 measured reflections, 4520 unique reflections (R_{int} = 0.052), $R1$ = 0.062 [$I > 2\sigma(I)$], R_w = 0.087 (all data), S = 1.29 for 316 parameters (CCDC-196480). **4**: $C_{35}H_{39}ClO_4P_2SW$, M = 837.00, deep red prism, 0.30 × 0.30 × 0.20 mm, triclinic, $P\bar{1}$ (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) Å^3, Z = 4, T = 296 K, $2\theta_{max}$ = 55.0° ρ = 1.497 g cm^{-3}, μ(Mo-Kα) = 3.362 mm^{-1}, 28035 measured reflections, 14887 unique reflections (R_{int} = 0.119), $R1$ = 0.064 [$I > 2\sigma(I)$], R_w = 0.148 (all data), S = 1.28 for 789 parameters (CCDC-196481). **5**: $C_{31}H_{39}ClI_2P_2S$, M = 794.92, red plate, 0.40 × 0.50 × 0.08 mm, orthorhombic, P_{bca} (no. 61), a = 11.751(1), b = 38.246(3), c = 15.542(1) Å, V = 6985(1) Å^3, Z = 8, T = 243 K, $2\theta_{max}$ = 55.0°, ρ = 1.512 g cm^{-3}, μ(Mo-Kα) = 2.047 mm^{-1}, 59303 measured reflections, 8504 unique reflections (R_{int} = 0.043), $R1$ = 0.045 [$I > 3\sigma(I)$], 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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