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Different thermal reactivity of a 1,2-thiaphospholo[*a*]phosphirane in free and metal carbonyl complexed form†

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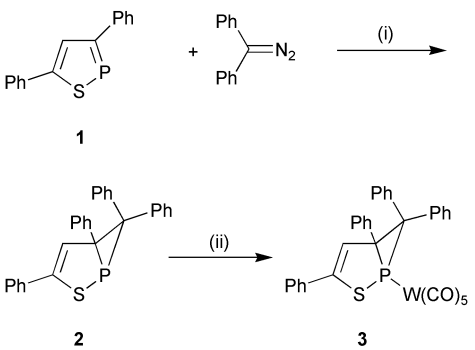
The $W(CO)_5$ and $Fe(CO)_4$ complexes of the bicyclic phosphirane 3,5,6,6-tetraphenyl-1-phospha-2-thiabicyclo-[3.1.0]hex-3-ene undergo a thermal 2-phenylphosphirane → dihydrophosphaisoindole ring expansion, while the free phosphirane suffers both a [2 + 1] cycloreversion and a fragmentation yielding a butadienyl sulfide.

The general reactivity patterns of the strained three-membered phosphirane ring system are well established.[1] Recent interest in these cyclic phosphines has focused on their ligand properties in catalytically active transition-metal complexes.[2,3] For this application, however, phosphiranes incorporated in polycyclic frameworks appear to be better suited due to their lower reactivity compared to many monocyclic phosphiranes.[3]

In this context, we became interested in bicyclic phosphiranes which are [*a*]-annelated with the P–C bond of a heterophosphole. Only a few such systems were known before we found, both experimentally[4] and computationally,[5] that the P=C double bond of 3,5-diphenyl-1,2-thiaphosphole[6] (**1**) is an excellent acceptor for the diazo dipole and cyclopropanation of this bond occurs easily. In fact, thiaphosphole **1** reacts with diazodiphenylmethane to give the (1,2-thiaphospholo)phosphirane **2**‡ in good yield (Scheme 1).† The progress of the reaction is easily monitored by ^{31}P NMR: δ_p(**1**) = 204.2 ppm, δ_P(**2**) = −81.4 ppm.

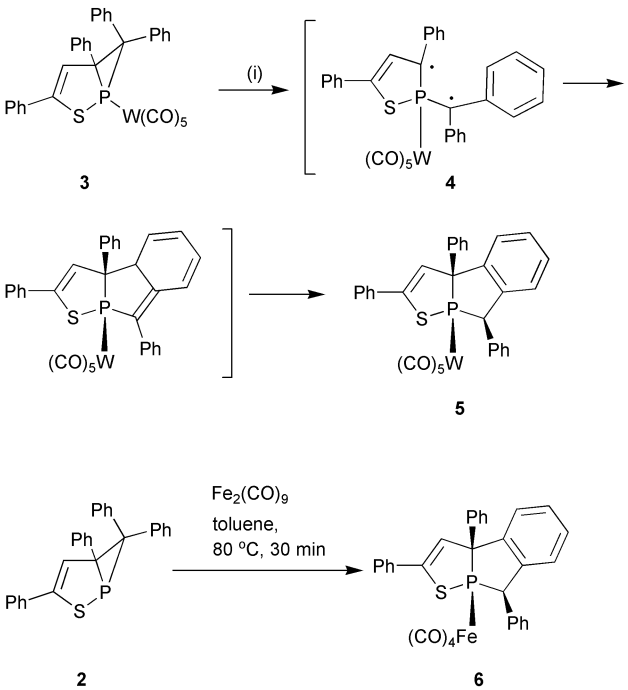
Phosphirane **2** readily formed the pentacarbonyltungsten complex **3** (Scheme 2) which was characterised by single-crystal X-ray diffraction analysis (Fig. 1).‡§ This complex (δ_P = −55.4 ppm) has a surprisingly low thermal stability and undergoes a rearrangement already at 80 °C to form the thienoisophosphindole derivative **5**‡ (δ_P = 125.1 ppm) which was identified by XRD analysis (Fig. 2).§ The tetracarbonyliron complex of phosphirane **2** is obviously even less stable thermally, because treatment of **2** with diiron nonacarbonyl at 80 °C/30 min directly yielded the ironcarbonyl-complexed rearrangement product **6** (δ_P = 195.2 ppm). Complex **6** is a rather unstable red oil which after column chromatography was obtained in only 17% yield.‡



Scheme 1 *Reactions and conditions*: (i) dry toluene, 70 °C, 24 h, 74% yield; (ii) $W(CO)_5$(THF), dry THF, 20 °C, 24 h, 71% yield.

† Electronic Supplementary Information (ESI) available: full experimental, spectroscopic and analytical data. See http://www.rsc.org/suppdata/cc/b3/b310256d/

The thermal rearrangement **3**→**5** can be described as a 2-phenylphosphirane → dihydroisophosphindole ring expansion and requires the C–C bond of the phosphirane ring to be broken. This is unusual because, as far as we know, most thermally induced ring-opening reactions of phosphiranes described so far occur at one of the P–C bonds.[1,7] (The



Scheme 2 *Reactions and conditions*: (i) toluene, 80 °C, 3 h, 76% yield.

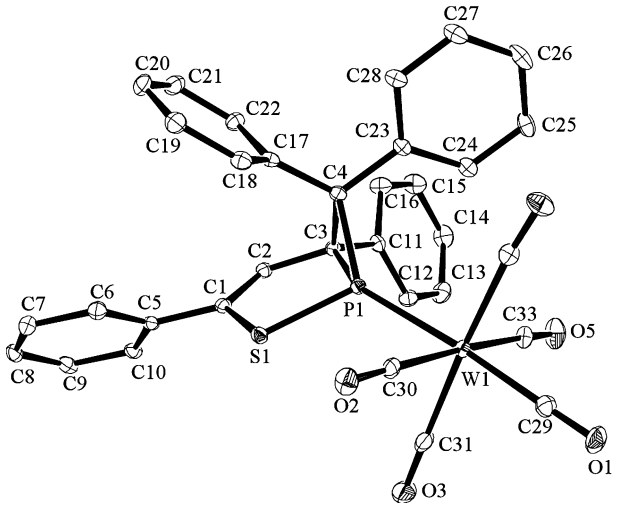


Fig. 1 Solid-state structure of **3**. Selected bond distances (Å) and angles (°): P1–C3 1.878(3), P1–C4 1.872(3), C3–C4 1.576(4), P1–S1 2.097(1), P1–W 2.480(1), W–C29 2.001(4); C3–P1–C4 49.7(1), S1–P1–C3 96.5(1), S1–P1–C4 106.1(1).

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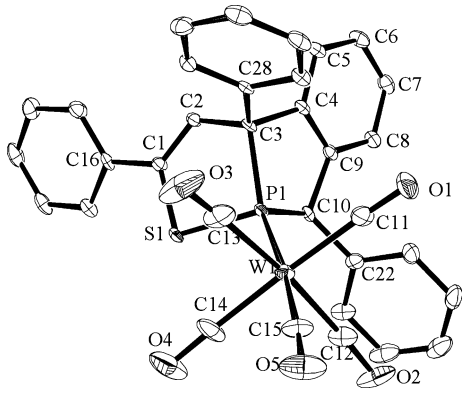
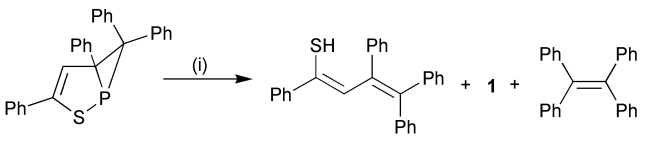


Fig. 2 Solid-state structure of **5**. Selected bond distances (Å) and angles (°): P1–S1 2.090(3), P1–C3 1.911(6), P1–C10 1.879(7), P1–W1 2.5103(16), W1–C15 1.965(7); S1–P1–C3 96.1(2), S1–P1–C10 104.9(2), C3–P1–C10 92.9(3), C3–P1–W1 127.0(2).

electrocyclic ring-opening of a 9-phosphabicyclo[6.1.0]nona-2,4,6-triene *P*-oxide is an exceptional case.[8]) Two reasons may account for the ring opening at the C–C bond: (a) this bond (C3–C4 in Fig. 1, 1.576(4) Å) is rather long; (b) homolytic cleavage of this bond yields a 1,3-diradical **4** (Scheme 2) that is exceptionally well resonance-stabilised by the adjacent π systems.

Surprisingly, the free bicyclic phosphirane **2** shows a different thermal behaviour compared with its metal complexes. The thermal stability of the free phosphirane is higher, and thermal impact at 120 °C yields a mixture of butadienyl sulfide **7**‡ (30%), thiaphosphole **1** (31%), and tetraphenylethene (38%) (Scheme 3), but no ring expansion product. Obviously, the products result from two processes: (a) a [2 + 1] cycloreversion yielding **1** and diphenylcarbene which then dimerises, and (b) a fragmentation with loss of the phosphorus atom the fate of which is not known. Perhaps, the latter process begins with a [2 + 1] cycloreversion that generates a phosphinidene R–S–P which after cleavage of the sulfur–phosphorus bond and H abstraction from the solvent yields sulfide **7**.



Scheme 3 *Conditions*: (i) mesitylene, 120 °C, 6 h.

The reason for the different thermal behaviour of free phosphirane **2** and its P-complexed counterpart **3** (as well as the analogous iron complex not shown in Scheme 2) is not clear at present. In fact, if one accepts a different behaviour, one might have expected the opposite, since it is known that some phosphirane–$W(CO)_5$ complexes easily undergo cycloreversion with elimination of a P–$W(CO)_5$ fragment.[1,9] We suggest that the elongation of the C–C bond in the metal-complexed phosphirane ring is a crucial factor: although the length of this bond in phosphirane **2** is unknown, it is generally expected that participation of the phosphorus lone pair in bonding leads to an elongation of the C–C ring bond and a shortening of the two P–C bonds.[3] However, while this effect has been documented for several Rh[2] and Pt[3] complexes of phosphiranes, comparisons between free phosphiranes and their associated $W(CO)_5$ complexes appear not to be available yet. On the other hand, the C–C bond in the calculated structure of $Cr(CO)_5$(phosphirane) complex[10] is indeed longer by *ca*. 0.02–0.03 Å than the experimental and calculated values for the free ligand.

In addition to the mode of formation, butadienyl sulfide **7** is an interesting compound per se, because it is a novel example of stable thioenols (vinyl sulfides) which is obviously not in equilibrium with the thioketone tautomer.‡ In fact, it is vinylogous to another stable thioenol, $Ph_2C{=}C(SH)Ph$.[11]

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Notes and references

‡ Selected physical and spectroscopic data: Compound **2**: colourless needles, mp 146 °C; ^{1}H NMR: δ 6.50 (d, $^3J_{P,H}$ = 4.8 Hz, 1H, =CH), 6.78–7.50 (m, 20H, H_{Ph}); ^{13}C{^{1}H} NMR: δ 42.1 (d, $^1J_{P,C}$ = 48.6 Hz), 73.4 (d, $^1J_{P,C}$ = 40.6 Hz), 125.6, 126.4, 126.6, 127.0, 127.7, 128.2, 129.2, 129.4, 130.9, 131.5, 133.5, 137.6, 142.2 (2 C). Compound **3**: colourless prisms, m.p. 127 °C; ^{1}H NMR: δ 6.18 (d, $^3J_{P,H}$ = 17.2 Hz, 1H, =CH), 6.48 (d, J = 8.3 Hz, 2H_{Ph}), 6.90–7.50 (m, 18H_{Ph}); ^{13}C{^{1}H} NMR: δ = 39.9 (d, $^1J_{P,C}$ = 23.5 Hz), 67.1 (d, $^1J_{P,C}$ = 26.2 Hz), 126.0–135.9 (16 C), 142.9, 194.2, 195.8; ^{31}P NMR: δ −55.4 (t, ^1J(^{31}P,^{183}W) = 266 Hz). Compound **5**: colourless prisms, mp173–174 °C; ^{1}H NMR: δ 5.28 (d, $J_{P,H}$ = 14.0 Hz, 1H, PC*H*), 6.30 (d, $J_{P,H}$ = 18.3 Hz, 1H, =CH), 7.2–7.4 (m, 17H_{aryl}), 7.66 (dd, J = 8.1 and 1.9 Hz, 2H_{Ph}); ^{13}C{^{1}H} NMR: δ 62.8 (d, $^1J_{P,C}$ = 3.8 Hz), 75.3 (d, $^1J_{P,C}$ = 11.0 Hz), 125.4–134.3 (14 C), 141.7, 142.9, 194.3, 194.4, 197.7; ^{31}P NMR: δ 125.1 (t, ^1J(^{31}P,^{183}W) = 262 Hz). Compound **6**: red oil; ^{1}H NMR: δ 5.24 (d, $^3J_{P,H}$ = 14.2 Hz, 1H), 6.36 (d, $J_{P,H}$ = 20.9 Hz, 1H), 6.9–7.3 (17H_{aryl}), 7.60 (dd, J = 8.1 and 1.8 Hz, 2H_{Ph}); ^{13}C{^{1}H} NMR: δ 60.4 (d, $^1J_{P,C}$ = 9.1 Hz), 72.7 (d, $^1J_{P,C}$ = 16.3 Hz), 122.3–137.4 (9 C) and 142.1, 151.1, 210.7, 210.9; ^{31}P NMR: δ 195.2. Compound **7**: colourless solid, mp 129–130 °C; IR (KBr): ν = 2550 cm^{-1} (w, SH); ^{1}H NMR: δ 3.09 (s, 1H, SH), 6.57 (s, 1H, 2-H), 7.01–7.44 (m, 20H_{Ph}). All NMR spectra were taken from $CDCl_3$ solutions at 400.13 (^{1}H), 100.62 (^{13}C) or 161.98 Hz (^{31}P).

§ *Crystal data* for **3**: $C_{33}H_{21}O_5PSW$, M = 744.38, triclinic, space group $P\bar{1}$ (no. 2), a = 11.159(3), b = 11.268(3), c = 13.387(4) Å, α = 69.34(3), β = 79.86(3), γ = 69.31(3)°, V = 1470.9(7) Å^3, Z = 2, D_c = 1.681 g cm^{-3}, μ(Mo–$K\alpha$) = 4.09 mm^{-1}, T = 193 K; 15 692 measured reflections, 5 352 independent reflections (R_{int} = 0.0504). Refinement of 370 variables converged at $R1$ = 0.0273, $wR2$ = 0.0552 for all independent reflections and $R1$ = 0.0240, $wR2$ = 0.0542 for 4910 reflections with $I > 2\sigma(I)$. For **5**: $C_{33}H_{21}O_5PSW$, M = 744.38, monoclinic, space group $P2/n$, a = 8.875(2), b = 10.701(2), c = 30.832(5) Å, α = 90, β = 92.81(2), γ = 90°, V = 2924.7(9) Å^3, Z = 4, D_c = 1.691 g cm^{-3}, μ(Mo–$K\alpha$) = 4.12 mm^{-1}, T = 193 K; 20 349 measured reflections, 4 431 independent reflections (R_{int} = 0.0510). Refinement of 378 variables converged at $R1$ = 0.0312, $wR2$ = 0.0772 for all independent reflections and $R1$ = 0.0516, $wR2$ = 0.0816 for 3209 reflections with $I > 2\sigma(I)$. For both structures, data collection was done on a Stoe IPDS diffractometer. The structures were solved using SHELXS and refined on F^2 values using SHELX-97. Hydrogen atoms were included at calculated positions and treated as riding on their bond neighbours; H2 and H10 in **5** were refined freely. CCDC 218743 (**5**) and 218744 (**3**). See http://www.rsc.org/suppdata/cc/b3/b310256d/ for crystallographic data in .cif or other electronic format.

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