The unexpected head-to-head dimerisation of 1*H*-phosphirenes

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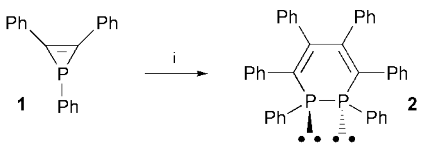
Both 1*H*-phosphirenes and their P-W(CO)$_5$ complexes readily dimerise in the presence of Ni(II) or Pd(0) catalysts to give the corresponding 1,2-dihydro-1,2-diphosphinines.

The ready dimerisation of borirenes into 1,4-diboracyclohexadienes is well documented and has been studied in some depth from a theoretical standpoint.[1] Similarly, silirenes readily give 1,4-disilacyclohexadienes in the presence of a palladium catalyst.[2] In both cases, no head-to-head dimers were detected. In the silicon case, although no mechanism was proposed for the dimerisation, the intermediacy of a 1-metalla-2-silacyclobutene appeared likely.[3] Since we knew from preceding experiments that both Pd(0) and Pt(0) readily insert into the P–C bonds of 1*H*-phosphirenes and phosphirene complexes,[4,5] it was tempting to explore the possible dimerisation of these phosphirenes in the presence of palladium catalysts.

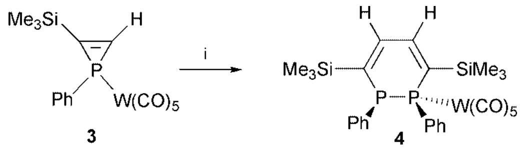
Preliminary experiments were carried out with 1,2,3-triphenylphosphirene[6] and its P-W(CO)$_5$ complex.[7] Heating 1,2,3-triphenylphosphirene with [Pd(PPh$_3$)$_4$] in toluene at 85 °C overnight led only to decomposition products. After several experiments, we finally found that clean dimerisation was achieved with a Ni(II) catalyst at room temperature (Scheme 1).

The structure of **2**† unexpectedly corresponds to a head-to-head dimer (Fig. 1).‡ The ring is highly distorted with two *trans* phosphorus lone pairs and some strain as indicated by the rather small P–P–C(ring) angles of 91.09(5) and 91.27(5)°. The P–P bond is short for a single bond at 2.193(2) Å. Compound **2** displays surprising instability. It decomposes completely upon heating at 65 °C for 20 min in toluene. Looking for more stable derivatives, we decided to investigate the dimerisation of phosphirene P-W(CO)$_5$ complexes. The complex of **1** appeared to be rather inert. We reasoned that a 1,2-disubstituted species would be more reactive. Accordingly, we prepared the (1-phenyl-2-trimethylsilylphosphirene)pentacarbonyltungsten complex **3**† by the usual technique[7] and studied its evolution in toluene at 85 °C in the presence of [Pd(PPh$_3$)$_4$]. Overnight we observed the formation of the head-to-head dimer **4**† which was isolated in 60% yield (Scheme 2).

The dimerisation is regio- and stereo-selective (Fig. 2).‡ The regioselectivity can be easily explained by a preferential insertion of Pd(0) into the less hindered P–CH intracyclic bond.



Scheme 1 *Reagents and conditions*: (i) 150 mg of **1**, 10 mg of [NiCl$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)], CH$_3$CN, 25 °C, 2 d, 70% yield.



Scheme 2 *Reagents and conditions*: (i) 530 mg of **3**, 30 mg of [Pd(PPh$_3$)$_4$], toluene, 85 °C, 16 h.

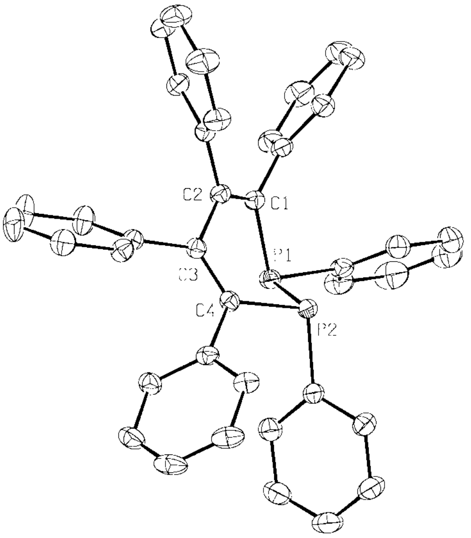


Fig. 1 Crystal structure of **2**. Significant bond distances (Å) and angles (°): P(1)–C(1) 1.857(2), P(1)–C(5) 1.831(2), P(1)–P(2) 2.193(2), P(2)–C(35) 1.839(2), P(2)–C(4) 1.855(1), C(1)–C(2) 1.357(2), C(2)–C(3) 1.493(2), C(3)–C(4) 1.355(2); C(5)–P(1)–C(1) 102.67(6), C(5)–P(1)–P(2) 101.38(5), C(1)–P(1)–P(2) 91.09(5), C(35)–P(2)–C(4) 102.04(6), C(35)–P(2)–P(1) 101.19(5), C(4)–P(2)–P(1) 91.27(5), C(2)–C(1)–P(1) 118.9(1), C(1)–C(2)–C(3) 123.1(1), C(4)–C(3)–C(2) 122.7(1), C(3)–C(4)–P(2) 119.9(1).

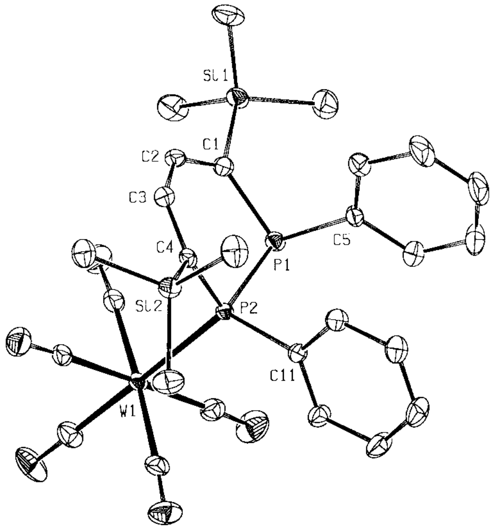


Fig. 2 Crystal structure of **4**. Significant bond distances (Å) and angles (°): P(1)–C(1) 1.817(3), P(1)–C(5) 1.828(3), P(1)–P(2) 2.227(1), P(2)–C(4) 1.815(3), P(2)–C(11) 1.824(3), P(2)–W(1) 2.5277(7), Si(1)–C(1) 1.896(3), Si(2)–C(4) 1.905(3), C(1)–C(2) 1.352(4), C(2)–C(3) 1.463(4), C(3)–C(4) 1.351(4); C(1)–P(1)–P(2) 101.3(1), C(1)–P(1)–C(5) 102.3(1), C(5)–P(1)–P(2) 105.7(1), C(4)–P(2)–C(11) 106.7(1), C(4)–P(2)–P(1) 105.7(1), C(11)–P(2)–P(1) 100.9(1), C(4)–P(2)–W(1) 114.2(1), C(11)–P(2)–W(1) 119.2(1), P(1)–P(2)–W(1) 108.52(3).

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The ring is almost undistorted. The intracyclic angles at phosphorus are normal at 101.3(1) (P_{III}) and 105.7° (P_W). The P–P bond is also in the normal range at 2.227 Å. In contrast to **2**, the stereochemistry at the phosphorus atoms is *cis* and **4** is quite stable.

At the moment, we have no precise explanation for this unexpected head-to-head dimerisation. The only argument which can be pointed out has a thermodynamic basis. The formation of one P–P and one C–C bond is more energetically favourable than the formation of two P–C bonds: $61 + 88 > 2 \times 65$ kcal mol^{-1}.[8] Unlike phosphorus, both silicon and boron have much lower electronegativities than carbon and the dimerisation of silirenes and borirenes is probably controlled by the polarity of the Si–C and B–C ring bonds. Whatever its origin, this head-to-head dimerisation of phosphirenes provides a direct access to the almost unknown 1,2-dihydro-1,2-diphosphinine ring. At the moment, only a 1,2-disulfide has appeared in the literature, prepared by a low-yield multi-step procedure.[9] The chemistry of this ring is now open for investigation.

Notes and references

† Selected analytical and spectroscopic data: **2**: Precipitates as yellow crystals from CH_3CN; ^{31}P NMR (CH_2Cl_2): $\delta -45.5$; *m/z* 573 (M + H, 14%), 465 (M + H − PPh, 100). **3**: ^{31}P NMR (toluene): $\delta -185.6$, $^{1}J_{PW}$ 275 Hz; ^{1}H NMR ($CDCl_3$): δ 0.29 (s, $SiMe_3$), 8.89 (d, $^{2}J_{PH}$ 24.9 Hz, ring H); ^{13}C NMR ($CDCl_3$): $\delta -1.15$ (s, $SiMe_3$), 136.95 (d, $^{1}J_{CP}$ 15.5 Hz, ring CH), 139.48 (d, $^{1}J_{CP}$ 7.6 Hz, Ph-C_{ipso}), 142.83 (d, $^{1}J_{CP}$ 36.6 Hz, *C*-$SiMe_3$), 196.54 (d, $^{2}J_{CP}$ 9.1 Hz, *cis*-CO), 198.34 (d, $^{2}J_{CP}$ 32.5 Hz, *trans*-CO); *m/z* (^{184}W) 530 (M, 23%), 388 (M − 5CO, 100); Anal. Calc. for $C_{16}H_{15}O_5PSiW$: C, 36.25; H, 2.85. Found: C, 36.87; H, 2.68%. **4**: Purified by chromatography on silica gel (hexane–CH_2Cl_2, 10 : 1); yellow crystals (60%): ^{31}P NMR ($CDCl_3$): $\delta -68.0$ (P_{III}) and 26.3 (P-W), $^{1}J_{PP}$ 277 Hz; ^{1}H NMR ($CDCl_3$): δ 0.00 (s, $SiMe_3$), 0.08 (s, $SiMe_3$); ^{13}C NMR ($CDCl_3$): $\delta -0.87$ (d, $^{3}J_{CP}$ 3.7 Hz, $SiMe_3$), 0.57 (s, $SiMe_3$), 140.59 (d, $^{2}J_{CP}$ 28.0 Hz, ring CH), 142.38 (s, ring CH), 197.58 (pseudo t, *cis*-CO); *m/z* (^{184}W) 709 (M − CO, 22%), 596 (M − 5CO, 100); Anal. Calc. for $C_{27}H_{30}O_5P_2Si_2W$: C, 44.03; H, 4.11. Found: C, 43.94; H, 4.13%.

‡ *Crystal data* for **2**: $C_{40}H_{30}P_2 \cdot 1/2CH_2Cl_2$, $M = 615.04$ g mol^{-1}, triclinic, $a = 6.069(5)$ Å, $b = 12.180(5)$ Å, $c = 22.035(5)$ Å, $\alpha = 97.030(5)°$, $\beta = 92.580(5)°$, $\gamma = 96.690(5)°$, $V = 1602.7(15)$ Å^3, $T = 150.0(1)$ K, space group $P\bar{1}$, $Z = 2$, μ(Mo-Kα) = 0.247 cm^{-1}. 14341 reflections measured, 9228 unique (R(int) = 0.0285) which were used in all calculations. The final $wR(F^2)$ was 0.1472 (all data), $R1 = 0.0482$. For **4**: $C_{27}H_{30}O_5P_2Si_2W$, $M = 736.48$ g mol^{-1}, monoclinic, $a = 12.6004(3)$ Å, $b = 12.2493(3)$ Å, $c = 20.1311(5)$ Å, $\beta = 96.1640(10)°$, $V = 3089.19(13)$ Å^3, $T = 150.0(1)$ K, space group $P2_1/c$, $Z = 4$, μ(Mo-Kα) = 3.953 cm^{-1}. 16625 reflections measured, 8897 unique (R(int) = 0.0578) which were used in all calculations. The final $wR(F^2)$ was 0.0928 (all data), $R1 = 0.0247$. CCDC 182/1641. See http://www.rsc.org/suppdata/cc/b0/b001304h/ for crystallographic files in .cif format.

1 P. H. M. Budzelaar, S. M. van der Kerk, K. Krogh-Jesperson and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1986, **108**, 3960.

2 M. Ishikawa, H. Sugisawa, M. Kumada, T. Higuchi, K. Matsui and K. Hirotsu, *Organometallics*, 1982, **1**, 1473.

3 M. Ishikawa, J. Ohshita, Y. Ito and J. Iyoda, *J. Am. Chem. Soc.*, 1986, **108**, 7417; J. Ohshita, Y. Isomura and M. Ishikawa, *Organometallics*, 1989, **8**, 2050.

4 S. S. Al Juaid, D. Carmichael, P. B. Hitchcock, S. Lochschmidt, A. Marinetti, F. Mathey and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1988, 1156; S. S. Al Juaid, D. Carmichael, P. B. Hitchcock, A. Marinetti, F. Mathey and J. F. Nixon, *J. Chem. Soc., Dalton Trans.*, 1991, 905.

5 D. Carmichael, P. B. Hitchcock, J. F. Nixon, F. Mathey and A. Pidcock, *J. Chem. Soc., Chem. Commun.*, 1986, 762.

6 S. Lochschmidt, F. Mathey and A. Schmidpeter, *Tetrahedron Lett.*, 1986, **27**, 2635.

7 A. Marinetti, F. Mathey, J. Fischer and A. Mitschler, *J. Am. Chem. Soc.*, 1982, **104**, 4484.

8 W. W. Schoeller, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Thieme, Stuttgart, 1990, pp. 5–32.

9 T. Kawashima, M. Shimamura and N. Inamoto, *Heterocycles*, 1982, **17**, 341. A 3,6-di(*tert*-butyl)-1,2-dihydro-1,2-diphosphinine has also been isolated as a byproduct from the reaction of phenylphosphine with 1,4-di(*tert*-butyl)buta-1,3-diyne: D. Carmichael and F. Mathey, unpublished results, 1993.