Ring-opening and Dimerisation of a 1*H*-Diphosphirene–Tungsten Pentacarbonyl Complex

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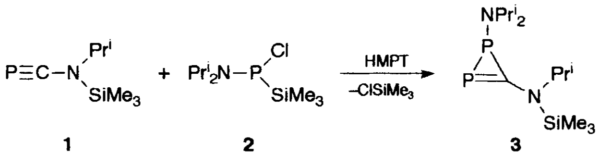
The 1*H*-diphosphirene complex **6**, generated by [2 + 1] cycloaddition of the short-lived phosphinidene species **5** to the phosphaalkyne **4**, undergoes dimerisation with elimination of a W(CO)$_5$ fragment to give the tricyclotetraphosphahexane **11**; reaction of **6** with tetrachloro-*o*-quinone gives rise to the 1 : 2-adduct **13** in which the P–P bond of the former has been cleaved.

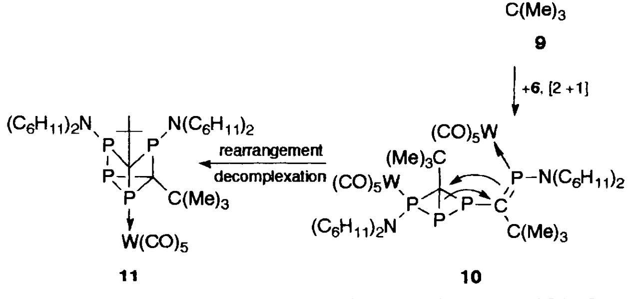
Unsaturated, three-membered phosphorus heterocycles participate significantly in the current development of phosphorus chemistry.[1,2] Thus, for example, the 1*H*-phosphirenes, which are readily accessible by [2 + 1] cycloaddition of phosphinidene complexes to alkynes and subsequent decomplexation,[3] are versatile building blocks for synthesis.[1] Furthermore, the corresponding 2*H*-isomers possessing a P=C double bond in the ring can be generated by 1,3 ring closure reactions of phosphavinylcarbenes and are thermally stable when bulky substituents are present.[4]

This stabilising effect of bulky substituents is also observed with the 1*H*-diphosphirenes; the first representative of this class of compounds **3** was recently obtained by the reaction of the donor-substituted phosphaalkyne **1** with the phosphine **2** (see Scheme 1).[5] No evidence for a ring cleavage of product **3** has been reported previously. We now describe the first process of this type, namely the P–P bond cleavage of a 1*H*-diphosphirene/tungsten complex.

The starting material for our investigations was the bis(cyclohexyl)aminophosphirane/tungsten complex **8**† which was synthesised from the aminophosphine **7** and 1,2-dichloroethane in analogy to the corresponding diethylamino compounds [**7**, **8** (C_2H_5 in place of C_6H_{11}; Scheme 2)[6]]. When the phosphinidene species **5** was generated by thermal decomposition of **8** in the presence of the kinetically stabilised



Scheme 1 HMPT = hexamethylphosphorus triamide



Scheme 2 *Reagents and conditions*: i, (*a*), for **6**: 30 min at 70 °C in C_6D_6 in a sealed tube; i, (*b*), for **11**: 30 min at 70 °C in C_6H_6 and 4 weeks at room temperature; ii, (*a*), THF, −78 °C, Bu^{n}Li (2 equiv.) in n-hexane; ii, (*b*), $ClCH_2CH_2Cl$, −78 °C for 1 h and then allow to warm to room temperature

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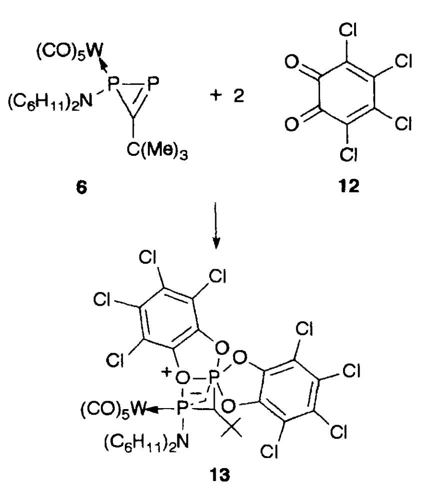
† *Selected data* for **8**: colourless crystals, m.p. 96 °C (60%); ^{13}C NMR (C_6D_6): δ 16.8 (d, $^1J_{C,P}$ 17.4 Hz, C–P); ^{31}P NMR (C_6D_6): δ −133.9 ($^1J_{P,W}$ 285.6 Hz); MS (70 eV): *m/z* 563 (M$^+$, 10%), 479 (M$^+$ −3CO, 100%); additionally characterised by mass spectroscopy and elemental analysis.



Scheme 3 *Reaction conditions*: generation of **6** as described (Scheme 2) but in CH_2Cl_2, subsequent addition of **12** at −40 °C and then allow to warm to room temperature

phosphaalkyne **4**,[7] the 1*H*-diphosphirene complex **6** was formed selectively.

Although the three-membered heterocycle **6** could not be isolated, its intermediate formation is well substantiated by NMR spectroscopy.‡ When a solution of **6** was kept at room temperature for 4 weeks and then worked-up by chromatography (silica gel, CH_2Cl_2), the diphosphirene dimer/monotungsten complex **11** was isolated as the CH_2Cl_2 adduct (30%, colourless crystals, m.p. 176 °C, decomp.). The structure of the tricyclotetraphosphahexane **11** was established unequivocally by an X-ray diffraction analysis.§ The bond distances in the diphosphirane ring are in good agreement (see Fig. 1) with those of a substituted diphosphatricyclo[3.2.1.0^{2,7}]octene [P–P: 2.183(2), P–C: 1.886(4) and 1.888(4) Å][8] which contains the same three-membered ring system.

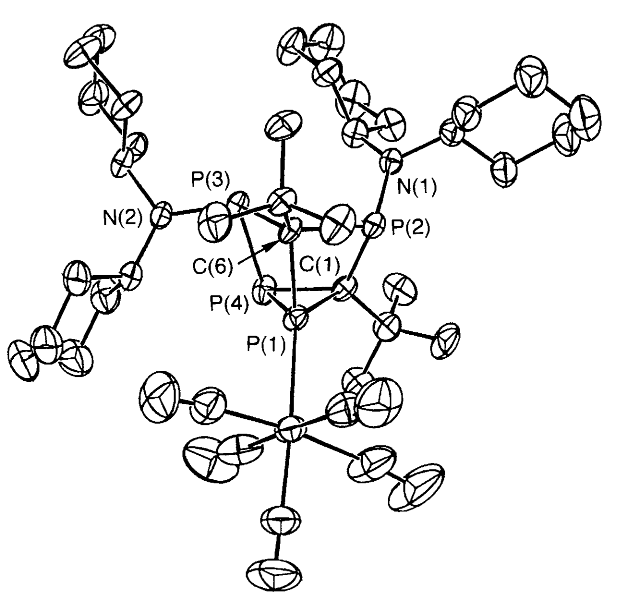


Fig. 1 Molecular structure of $C_{39}H_{62}N_2O_5P_4W{\cdot}CH_2Cl_2$, **11**. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): W(1)–P(1) 2.555(2); P(1)–P(4) 2.188(2); P(1)–C(1) 1.885(6), P(1)–C(6) 1.900(6), P(2)–N(1) 1.679(5), P(2)–C(1) 1.848(6), P(2)–C(6) 1.925(6), P(3)–P(4) 2.229(2), P(3)–N(2) 1.696(5), P(3)–C(6) 1.892(6), P(4)–C(1) 1.873(6), W(1)–P(2)–P(4) 131.4(8), W(1)–P(1)–C(1) 133.0(2), W(1)–P(1)–C(6) 137.4(2), P(4)–P(1)–C(1) 54.1(2), P(4)–P(1)–C(6) 85.8(2), C(1)–P(1)–C(6) 82.8(2), N(1)–P(2)–C(1) 114.8(3), N(1)–P(2)–C(6) 117.8(2), C(1)–P(2)–C(6) 83.1(2), P(4)–P(3)–N(2) 101.9(2), P(4)–P(3)–C(6) 84.8(2), N(2)–P(3)–C(6) 114.9(2), P(1)–P(4)–P(3) 82.8(8), P(1)–P(4)–C(1) 54.7(2), P(3)–P(4)–C(1) 94.5(2), P(1)–C(1)–P(2) 88.7(2), P(1)–C(1)–P(4) 71.2(2), P(2)–C(1)–P(4) 120.6(3), P(1)–C(6)–P(2) 86.1(2), P(1)–C(6)–P(3) 100.8(3), P(2)–C(6)–P(3) 106.3(3).

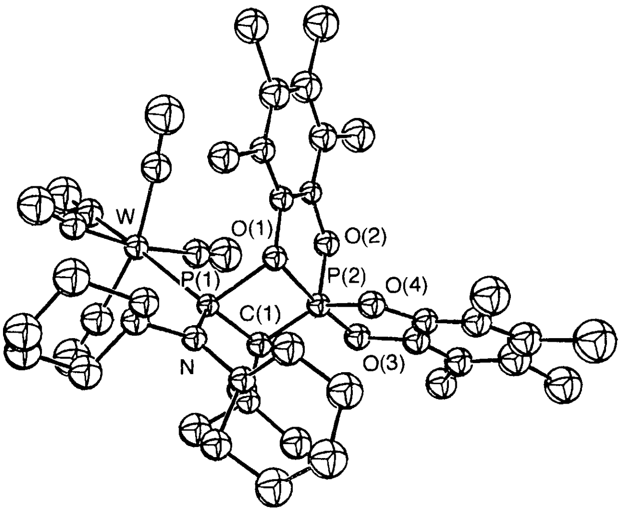


Fig. 2 Molecular structure of $C_{34}H_{31}Cl_8NO_9P_2W$, **13**. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): W–P(1) 2.542(2), P(1)–O(1) 1.906(5), P(1)–N 1.638(6), P(1)–C(1) 1.756(7), P(2)–O(1) 1.996(5), P(2)–O(2) 1.652(5), P(2)–O(3) 1.655(5), P(2)–O(4) 1.666(5), P(2)–C(1) 1.679(7); W–P(1)–O(1) 111.6(1), W–P(1)–N 124.2(2), W–P(1)–C(1) 118.2(2), O(1)–P(1)–N 101.9(2), O(1)–P(1)–C(1) 81.4(3), N–P(1)–C(1) 109.7(3), O(1)–P(2)–O(2) 85.6(2), O(1)–P(2)–O(3) 175.1(2), O(1)–P(2)–O(4) 83.2(2), O(1)–P(2)–C(1) 80.7(3), O(2)–P(2)–O(3) 91.4(3), O(2)–P(2)–O(4) 103.0(3), O(2)–P(2)–C(1) 126.2(3), O(3)–P(2)–O(4) 93.8(2), O(3)–P(2)–C(1) 104.2(3), O(4)–P(2)–C(1) 126.2(3), P(1)–O(1)–P(2) 89.9(2), P(1)–C(1)–P(2) 106.7(4), P(1)–C(1)–C(2) 126.8(5), P(2)–C(1)–C(2) 126.4(5).

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‡ ^{1}H NMR (C_6D_6): **6**, δ 1.16 (s, 9H, Bu^t), 0.62–1.73 (m, cyclohexyl CH_2), 2.68 (m, cyclohexyl CH); ^{31}P NMR (C_6D_6): δ −113.5 [d, $^1J_{P,P}$ 146.5 Hz, P--> W(CO)$_5$], +213.0 ppm [d, $^1J_{P,P}$ 146.5 Hz, P = C–Bu^t].

§ *Crystal data*: Single crystals of both compounds were grown by cooling from dichloromethane solutions. Data were collected at 18 ± 1 °C on an Enraf Nonius CAD4 diffractometer. The crystal structures were solved and refined using the Enraf Nonius supplied SDP package. Mo-Kα radiation (λ = 0.71073 Å) and a graphite monochromator were used for data collection. Direct methods yielded suitable solutions for both structures. The hydrogen atoms were included as fixed contribution in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.08 in $\sigma^2(F^2) = \sigma^2(I) + (pF^2)^2$.[2]

Compound **11**, $C_{39}H_{62}N_2O_5P_4W{\cdot}CH_2Cl_2$, crystallises in space group *C*2/*c*, $a = 30.402(3)$, $b = 11.401(1)$, $c = 26.863(2)$ Å, $\beta = 97.40(1)°$; $V = 9233.29\ (2.61)$ Å^3; $Z = 8$; $D_c = 1.484$ g cm^{-3}; $\mu = 28.5$ cm^{-1}; $F(000) = 4208$. A total of 8273 unique reflexions were recorded in the range $2° \leqslant 2\theta \leqslant 50.0°$ of which 2996 were considered as unobserved [$F^2 < 3.0\sigma(F^2)$], leaving 5277 for solution and refinement. The final agreement factors were $R = 0.039$, $R_w = 0.053$, G.O.F. = 1.08.

Compound **13**, $C_{34}H_{31}Cl_8NO_9P_2W$, crystallises in space group $P\bar{1}$, $a = 9.076(1)$, $b = 12.064(1)$, $c = 21.541(2)$ Å, $\alpha = 88.85(1)°$, $\beta = 82.61(1)°$, $\gamma = 76.21\ (1)°$; $V = 2271.50\ (50)$ Å^3; $Z = 2$; $D_c = 1.648$ g cm^{-3}; $\mu = 31.9$ cm^{-1}; $F(000) = 1108$. A total of 7973 unique reflexions were collected in the range $2° \leqslant 2\theta \leqslant 50.0°$. 5819 of these were regarded as observed and used in subsequent calculations. A final Fourier map revealed the presence of a dichloromethane molecule. The latter was assigned an occupancy factor of 0.25. The final *R* factors were $R = 0.041$, $R_w = 0.065$, G.O.F. = 1.29.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

When the fact that the final product crystallises with one molecule of CH_2Cl_2 and that one $W(CO)_5$ fragment is lacking are ignored, complex **11** may be considered as a dimer of the intermediate **6**. The formation of **11** can be rationalised by the assumption that P–P bond cleavage of **6** generates the phosphinidene **9**; analogous ring-opening processes of cyclopropenes to yield vinylcarbenes are well documented.[9] Then, either the electron-deficient species **9** itself or the isomeric phosphinidene complex in which the $W(CO)_5$ fragment has already migrated from the $\lambda^4\sigma^3$- to the $\lambda^1\sigma^1$-phosphorus atom [the final position of $W(CO)_5$ in **11**] undergoes immediate addition to unchanged **6** to give **10**. Rearrangement of **10**, which incorporates an energy-rich P=C bond and an angular-strained bicyclic system, as indicated by the arrows (see Scheme 2) concludes the reaction sequence.

Further evidence for the feasibility of this ring-opening mechanism of 1*H*-diphosphirene/tungsten complexes is provided by the reaction of **6** with tetrachloro-*o*-quinone **12**. Chromatographic work-up of the reaction mixture (silica gel, hexane followed by hexane–CH_2Cl_2, 9 : 1) furnishes the bis-adduct **13** (55%, colourless crystals, m.p. *ca.* 210 °C).¶ Product **13** again contains the elements of a ring-opened 1*H*-diphosphirene moiety. An X-ray diffraction analysis of **13**§ reveals a bonding interaction between O(1) and P(2) amounting to 1.996(5) Å in accordance with the depicted betaine-like bicyclic structure of the central skeleton (see Scheme 3). We have not yet been able to determine the chronological order of the cycloadditions of the two *ortho*-quinone molecules.

The formal addition of **12** to **9** is reminiscent of the reaction of a postulated phenylphosphinidene intermediate with benzil.[10]

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¶ ^{1}H NMR (CD_2Cl_2): δ 1.38 (s, 9H, Bu^t); ^{31}P NMR (CD_2Cl_2): δ 5.1 (d, $^2J_{P,P}$ 43.9 Hz, P-1), 272.0 (d, $^2J_{P,P}$ 43.9 Hz, P-2).