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Unexpected dimerisation of a 2*H*-azaphosphirene complex

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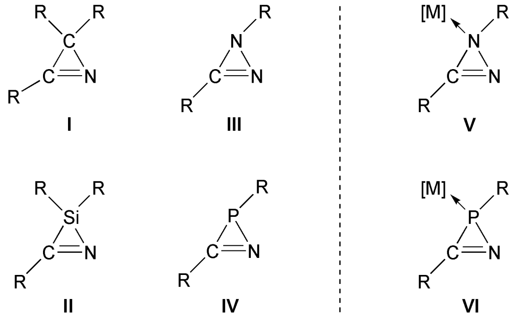
Heating a 2*H*-azaphosphirene complex in the solid state afforded the first head-to-tail dimer, a 2,5-dihydro-2,5-diphosphapyrimidine complex, a η^1-diphosphene complex and another complex having low-coordinated phosphorus centers; whereas the latter was detected only by ^{31}P NMR spectroscopy, the dimer was isolated and structurally characterized.

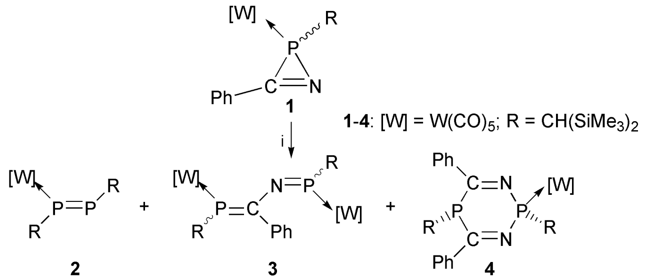
In comparison to 2*H*-azirenes[1] **I** (Scheme 1), which are versatile building blocks in heterocycle syntheses, the chemistry of heteroatom-substituted ring systems of type **II–IV** is much less explored. For example, transiently[2] formed 2*H*-azasilirenes **II** readily dimerise in solution in a head-to-head or head-to-tail manner, the orientation depending mainly on the carbon substituents.[3] Interestingly, even at low temperatures, 1*H*-diazirenes **III**[4] preferentially undergo ring enlargement[4] or rearrangement reactions,[5] but do not form dimers. Although 2*H*-azaphosphirenes **IV** have been claimed as intermediates, no dimerisation was reported; instead, ring cleavage occurred at room temperature to yield a short-lived phosphinidene and a nitrile derivative.[6] 1*H*-diazirene complexes **V** are, to the best of our knowledge, unknown. Recently, we reported syntheses[7] and reactions of 2*H*-azaphosphirene complexes **VI**, which gave access, *e.g.* to differently sized unsaturated phosphorus heterocycles either *via* ring cleavage[8] or *via* selective P–C[9] and P–N bond[10] cleavage ring expansion reactions.



Scheme 1 2*H*-azirenes (**I**), heteroazirenes (**II–IV**), 1*H*-diazirene (**V**) and 2*H*-azaphosphirene complexes (**VI**) (**I–VI**: R, R′ = alkyl, aryl; [M] = metal complex fragment).

Here we report the first dimerisation of a 2*H*-azaphosphirene complex leading to a head-to-tail dimer, a 2,5-dihydro-2,5-diphosphapyrimidine complex; a η^1-diphosphene complex and another complex having low-coordinated phosphorus centers were detected as by-products.

Heating the neat 2*H*-azaphosphirene tungsten complex **1**[11] for a short period afforded three phosphorus-containing products **2**, **3** and **4** in a ratio of *ca.* 1 : 3 : 10 (Scheme 2); heating complex **1** for longer periods, *i.e.* 1 h, did not significantly affect the ratio. Whereas the η^1-diphosphene tungsten complex **2**[12] ([d$_8$]-toluene): δ 391.3 ppm (^1J(P,P) 513.4 Hz, ^1J(P,W) 230.8 Hz, P=*P*W(CO)$_5$), 443.1 ppm (^1J(P,P) 513.4 Hz) was isolated in 8% yield by column chromatography, the dinuclear complex **3** decomposed during chromatography, but the chemical shifts, phosphorus–phosphorus and phosphorus–tungsten coupling constant magnitudes of **3** (AM-type; δ (P$_A$) 360.9 ppm, ^3J(P,P) 162.1, ^1J(W,P) 264.3 Hz) (δ (P$_M$) 160.9 ppm, ^3J(P,P) 162.1, ^1J(W,P) 272.4 Hz) revealed the existence of low-coordinated phosphorus centers,[13] thus allowing a tentative structural assignment with an atom connectivity as shown in Scheme 2 (P$_A$ = P=NR,P$_M$. = P=CR$_2$). The unusually great ^3J(P,P) value might result from the two-fold η^1-coordination mode of the two phosphorus centers.[14] The main product, the 2,5-dihydro-2,5-diphosphapyrimidine tungsten complex **4**, was confirmed by elemental analyses and NMR spectroscopy.† Further investigations using the analogous 2*H*-azaphosphirene chromium and molybdenum complexes[15] showed that the reaction course strictly depended on the nature of the metal; in contrast to the chromium (and tungsten) complex, heating the 2*H*-azaphosphirene molybdenum complex afforded the corresponding η^1-diphosphene molybdenum complex[12] as main product.



Scheme 2 *Reagents and conditions:* (i) 615 mg of complex **1**, 130 °C, 15 min; column chromatograpy (Al$_2$O$_3$, −50 °C, light petroleum–diethyl ether 90 : 10); **4**: bright yellow solid, yield: 43%, mp 156 °C (decomp.).

The ^{31}P NMR data of complex **4** are similar to those found for non-coordinated 2,5-dihydro-2,5-diphosphapyrimidine derivatives, which have been recently synthesized for the first time using a completely different approach.[16] The line broadenings in the ^{1}H and ^{13}C{^{1}H} NMR spectra of complex **4** at ambient temperature, which disappear upon cooling to −55 °C are remarkable; *e.g.* in the ^{13}C{^{1}H,^{31}P} NMR spectra two distinct resonances appear for the imino and also for the *ipso* carbon atoms of the phenyl rings. So far, we have no explanation for this phenomenon. Furthermore, the methine carbon atom (δ 9.9 ppm) and also the protons of one trimethylsilyl group (δ −0.73 ppm) of the three-coordinated phosphorus center resonate at remarkably high field, which probably indicates a shielding caused by the ring current of a nearby phenyl group. The molecular structure of complex **4** (Fig. 1), as established for the solid state by X-ray crystallography,‡ shows a slightly distorted boat conformation of the six-membered ring with the P1 and P2 atoms in the bow and stern positions (Fig. 2). The steric situation of the P2-bonded bis(trimethylsilyl)methyl group is noteworthy; as shown by the two different distances P2–C20 1.882(9) Å and P2–C13 1.829(10) Å, this group is asymmetrically flanked by the two phenyl rings, which act like a pincer, but only for one of the two trimethylsilyl groups. If this steric situation is retained in solution, this would convincingly explain the observed shielding of the proton and carbon atoms of the respective methine and trimethylsilyl groups.

Currently we are investigating the reaction of 2*H*-azaphosphirene complexes with various nickel(II) and palladium(0) complexes; such complexes have been shown to catalyze the

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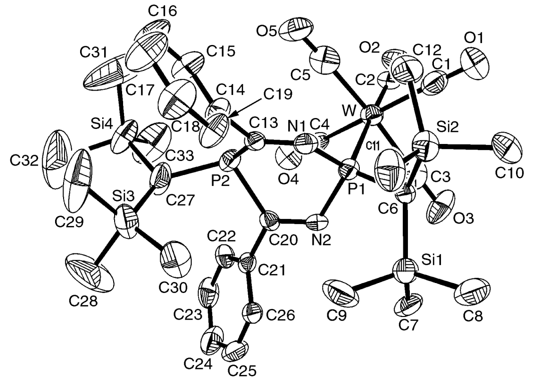

Fig. 1 Molecular structure of **4** in the crystal (ellipsoids represent 50% probability levels, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W–C(2) 1.986(10), W–P(1) 2.521(2), P(1)–C(6) 1.796(8), P(1)–N(1) 1.7107(7), P(1)–N(2) 1.698(7), N(1)–C(13) 1.280(9), N(2)–C(20) 1.267(9), P(2)–C(27) 1.852(9), C(13)–C(14) 1.514(11), C(13)–C(14) 1.482(12); C(2)–W–P(1) 176.0(3), W–P(1)–C(6) 115.7(3), N(2)–P(1)–N(1) 103.6(3), N(2)–P(1)–C(6) 107.1(4), N(1)–P(1)–C(6) 102.0(4), C(13)–P(2)–C(20) 95.5(4).

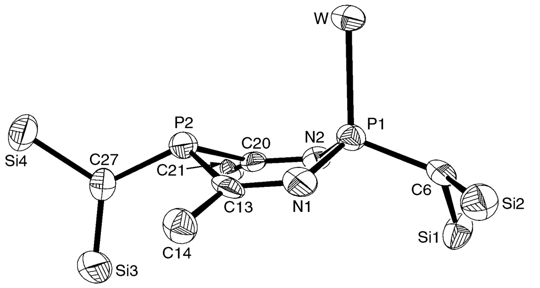

Fig. 2 Side-view showing the boat conformation of **4** (reduced molecular structure).

dimerisation of 1*H*-phosphirenes and 1*H*-phosphirene complexes.[17]

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Notes and references

† Satisfactory elemental analysis were obtained for complex **4**. NMR data were recorded in CDCl$_3$ solutions at 50.3 MHz (^{13}C) and 81.0 (^{31}P), using TMS and 85% H$_3$PO$_4$ as standard references; J/Hz. Selected spectroscopic data for **4**: ^{1}H-NMR (rt): δ −0.15 (v br, 18H, SiMe$_3$), 0.34 (s, 18H, SiMe$_3$), 0.98 (d, ^{2}J(P,H) 11.8 Hz, 1H, P^{2}C*H*), 1.87 (d, ^{2}J(P,H) 4.7 Hz, 1H, P^{1}C*H*), 7.43 (s br, 10H, C$H_{\text{aromat.}}$). ^{1}H-NMR (−55 °C): δ −0.73 (s, 9H, SiMe$_3$), 0.28 (s, 18H, SiMe$_3$), 0.31 (s, 9H, SiMe$_3$), 0.94 (d, ^{2}J(P,H) 11.8 Hz, 1H, P^{2}C*H*), 1.80 (d, ^{2}J(P,H) 4.7 Hz, 1H, P^{1}C*H*), 7.30 (s br, 4H, C$H_{\text{aromat.}}$), 7.44 (s br, 6H, C$H_{\text{aromat.}}$). ^{13}C{^{1}H}-NMR (rt): δ 2.1 (d br, ^{3}J(P,C) 3.8 Hz, SiMe$_3$), 3.3 (d, ^{3}J(P,C) 1.8 Hz, SiMe$_3$), 9.9 (d, ^{1}J(P,C) 52.6 Hz, *C*H(SiMe$_3$)$_2$), 29.2 (dd, ^{1}J(P,C) 27.0 Hz, ^{4}J(P,C) 1.5 Hz, *C*H(SiMe$_3$)$_2$), 128.2 (s br, *C*H$_{\text{aromat.}}$), 128.3 (s br, *C*H$_{\text{aromat.}}$), 129.7 (s, *C*H$_{\text{aromat.}}$), 130.1 (s br, *C*H$_{\text{aromat.}}$), 140.4 (m$_c$, $C_{\text{aromat.}}$), 184.6 (m, PN*C*), 197.8 (dd, ^{2}J(P,C) 7.4 Hz, ^{4}J(P,C) 2.2 Hz, *cis*-*C*O), 199.5 (d, ^{2}J(P,C) 24.2 Hz, *trans*-*C*O). ^{13}C{^{1}H,^{31}P}-NMR (−55 °C): δ 1.3 (s, SiMe$_3$), 2.4 (s, SiMe$_3$), 3.0 (s, SiMe$_3$), 8.9 (s, *C*H(SiMe$_3$)$_2$), 28.4 (s, *C*H(SiMe$_3$)$_2$), 128.1 (s, *C*H$_{\text{aromat.}}$), 128.7 (s, *C*H$_{\text{aromat.}}$), 129.6 (s, *C*H$_{\text{aromat.}}$), 130.6 (s, *C*H$_{\text{aromat.}}$), 138.9 (s, $C_{\text{aromat.}}$), 140.3 (s, $C_{\text{aromat.}}$), 183.6 (s, PN*C*), 185.6 (s, PN*C*), 197.6 (s, *cis*-*C*O), 200.2 (s, *trans*-*C*O). ^{31}P{^{1}H}-NMR: δ −0.6 (m$_c$, P^2), 79.9 (d, ^{3}J(P,P) 15.2 Hz, ^{1}J(P,W) 266.1 Hz, P^1).

‡ *Crystal structure determination* for **fidi1**: $C_{33}H_{48}N_2O_5P_2Si_2W$; M = 910.90, monoclinic, space group $P2/n$, a = 18.440(3), b = 9.831(3), c = 25.145(5) Å, β = 111.491(10)°, U = 4241.3(16) Å^3, Z = 4, D_c = 1.426 Mg m^{-3}, μ = 2.949 mm^{-1}, F(000) = 1840, 7430 independent reflections to $2\theta_{\text{max.}}$ 50°, T = 173 K, S = 0.763, $R(F > 4\sigma(F))$ = 0.0537, $R_w(F^2)$ = 0.0731, 171 restraints and 424 parameters, highest peak 1.162 and deepest hole −0.712 e Å^{-3}. The X-ray dataset was collected with monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Siemens P4 four-circle diffractometer. CCDC 182/1840. See http://www.rsc.org/suppdata/cc/b0/b007107m/ for crystallographic files in .cif format.

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