Synthesis and Structure of the first *trans*-1,2-Dihydro-1,2,3-triphosphete–Tungsten Complex

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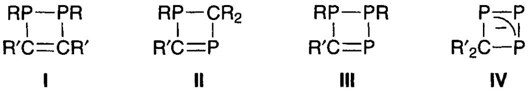
Thermal decomposition of the 2*H*-azaphosphirene complex **1** in the presence of kinetically stabilised phosphalkynes **2a,b** yields the 1*H*-diphosphirene complex **4a** and the 1,2-dihydro-1,2,3-triphosphete complex **5**; for the latter the overall reaction may be described as an insertion of a phosphanediyl complex into a ring bond of a transiently formed 1*H*-diphosphirene complex, with loss of one pentacarbonyltungsten moiety.

Buta-1,3-dienes and cyclobutenes that contain fragments of low-coordinated phosphorus in the central skeleton are of synthetic[1] and theoretical[2] interest in phosphorus chemistry. Thus, for example, recently Mathey and coworkers have shown that 1,2-dihydrophosphete complexes react on heating as masked phosphabutadiene derivatives in Diels–Alder reactions.[3] In contrast to the chemistry of 1,2-dihydro-1,2-diphosphetes[4] (**I**) and 1,2-dihydro-1,3-diphosphetes[5] (**II**), little is known about the synthesis and reactivity of 1,2-dihydro-1,2,3-triphosphetes (**III**); only an anionic derivative of type **IV** has been identified in solution[6] (Scheme 1).

The first use of phosphanediyl complexes in the synthesis of 1*H*-diphosphirene complexes was reported recently.[7] Interestingly, only the *C*-*tert*-butyl-substituted complex showed ring-opening by P–P bond cleavage followed by a dimerisation–rearrangement reaction.[7a] No evidence for a ring enlargement under the reaction conditions by insertion of a phosphanediyl complex has been reported. We now describe a reaction of this type, affording the first 1,2-dihydro-1,2,3-triphosphete derivative.

Our interest in unsaturated, small-ring phosphorus heterocycles[8] prompted us to investigate the thermal decomposition of the 2*H*-azaphosphirene complex **1**[†] (toluene, 80 °C, 2 h) in the presence of the kinetically stabilised phosphaalkynes **2a**[9] and **b**.[10] In the case of **2a** a clean reaction occurred to give the 1*H*-diphosphirene complex **4a** (yellow-orange solid, mp 97–98 °C; yield: 82%), whereas, under the same reaction conditions with **2b**, the 1,2-dihydro-1,2,3-triphosphete–tungsten complex **5** (yellow solid, mp 111 °C; yield: 86%) was obtained. Although the 1*H*-diphosphirene complex **4b** could not be observed by ^{31}P NMR spectroscopy, the assumption of its formation, by reaction of the transiently formed terminal phosphanediyl–tungsten complex $[(CO)_5W{=}PCH(SiMe_3)_2]$ **3**[11] with the phosphaalkyne **2b** in the first step, seems plausible. Subsequent insertion of phosphanediyl complex **3** into the ring of a 1*H*-diphosphirene derivative in combination with rearrangement and loss of one pentacarbonyltungsten moiety may be a rationale for the generation of the 1,2-dihydro-1,2,3-triphosphete complex **5** (Scheme 2).

The composition of **4a** and **5** is confirmed by elemental analysis and mass spectrometric investigations.[‡] The structural formulation of **4a** and **5** in solution is based on their characteristic NMR spectra[‡] and was confirmed for the solid state by an X-ray crystal structure analysis of **5**.[§] The $^{31}P\{^1H\}$ NMR spectrum of **5** displays three distinct resonances and coupling constants indicating a four-membered ring system with three types of phosphorus nuclei. Only the P(1) nucleus of compound **5** exhibits ^{183}W satellites, thus giving further support for the structural proposal of **5** as a mono-pentacarbonyltungsten complex.



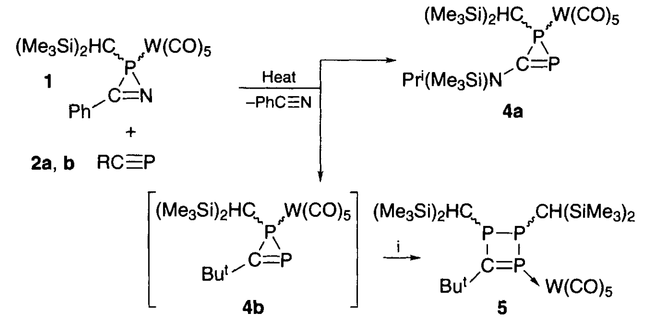
I **II** **III** **IV**

Scheme 1 Diphosphetes and triphosphetes

The X-ray crystal structure analysis of **5** reveals the molecular structure shown in Fig. 1, with a 1,2-dihydro-1,2,3-triphosphete ring system.

The ring is slightly folded [dihedral angle P(1)–P(2)–P(3), P(1)–C(6)–P(3) 23.6(0.3)°] with an approximately planar W–P–C–C subunit [torsion angle 4.8(4)°]. The alkylsubstituents at phosphorus are *trans*. The two P–P bond lengths [P(1)–P(2) 215.76(11) pm and P(2)–P(3) 223.75(12) pm] are significantly different. Together with the lengthened P=C double bond [P(1)–C(6) 1.691(3) pm] an increased electron delocalisation in this ring system is probably indicated.

We are currently investigating the reactivity of **4a** and **5**.



2a; R = $Pr^i(Me_3Si)N$
2b; R = Bu^t

Scheme 2 i, + **1**, −PhCN, $-W(CO)_5$

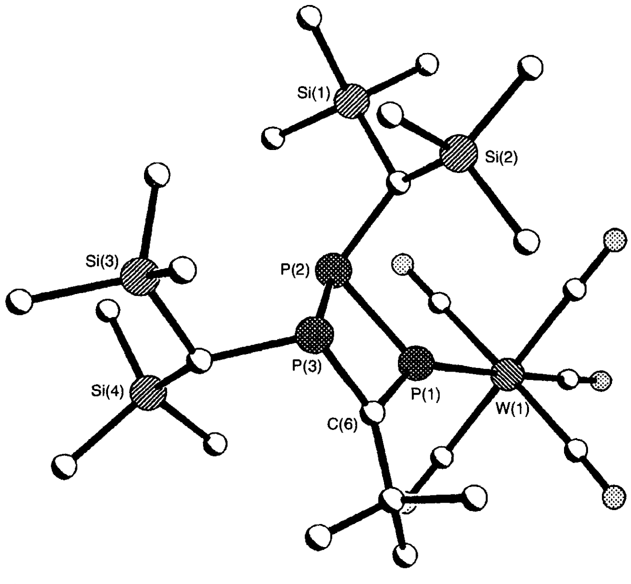


Fig. 1 Molecular structure of complex **5** in the crystal. Radii are arbitrary. Selected bond lengths (pm) and angles (°): P(1)–C(6) 169.1(3), P(1)–P(2) 215.76(11), P(2)–P(3) 223.75(12), P(3)–C(6) 181.7(3), P(1)–W(1) 247.04(9), C(6)–P(1)–P(2) 90.61(11), P(1)–P(2)–P(3) 77.11(4), P(2)–P(3)–C(6) 84.95(10), P(3)–C(6)–P(1) 102.6(2).

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Footnotes

† Compound **1** was synthesised by analogy with the corresponding *C*-aryl-substituted compounds.[8]

‡ Satisfactory elemental analyses were obtained for all complexes reported. NMR data were recorded at room temperature in C_6D_6 solution at 50.3 MHz (^{13}C) and 81.0 MHz (^{31}P); J/Hz; the J_{PC} coupling constants of **5** were assigned by selective ^{31}P decoupling experiments; atom numbering as shown in Fig. 1. *Selected spectroscopic data* for **4a**: $^{13}C\{^1H\}$ NMR δ 204.8 (dd, $^1J_{PC}$ 78.1, 44.5, C=P); $^{31}P\{^1H\}$ NMR δ −28.2 (d, $^1J_{PP}$ 115.1, $\lambda^3\sigma^2$-P), −159.2 (dd, $^1J_{PP}$ 115.1, $^1J_{PW}$ 262.1, $\lambda^5\sigma^4$-P); MS (EI): M^+ at *m/z* 687. *Selected spectroscopic data* for **5**: $^{13}C\{^1H\}$ NMR δ 213.5 (ddd, $^1J_{P(3)C}$ 54.5, $^2J_{P(2)C}$ 21.9, $^1J_{P(1)C}$ 1.9, C=P); $^{31}P\{^1H\}$ NMR: δ −18.6 [dd, P(2)], 22.9 [dd, P(3)], 225.2 [ddd, $^1J_{WP(1)}$ 230.4, P(1)], $^1J_{P(1)P(2)}$ −261.2, $^2J_{P(1)P(3)}$ 95.6, $^1J_{P(2)P(3)}$ −166.4. MS (EI): M^+ at *m/z* 804.

§ *Crystal data* for **5**: $C_{24}H_{47}O_5P_3Si_4W$, triclinic, space group $P\bar{1}$, a = 1149.56(14), b = 1215.44(12), c = 1606.9(2) pm, α = 72.938(8), β = 72.018(8), γ = 62.815(8)°, U = 1.8686(3) nm^3, Z = 2, μ = 3.376 mm^{-1}, T = −100 °C. Yellow prism 0.52 × 0.50 × 0.38 mm, Mo-Kα radiation, Siemens R4 diffractometer, 6571 intensities to $2\theta_{max}$ 50°, 6455 unique (R_{int} 0.0142) used for all calculations. Structure solution by direct methods, anisotropic refinement on F^2 (program SHELXL-93, G. M. Sheldrick, Univ. of Göttingen). Treatment of H atoms: rigid methyls, others riding. Final $wR(F^2)$ 0.054, conventional $R(F)$ 0.023 for 394 parameters. Full details may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlichtechnische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the reference number CSD 401776, the names of the authors and the journal citation. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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