Synthesis and structure of the first 2*H*-1,3,2-diazaphosphole complex

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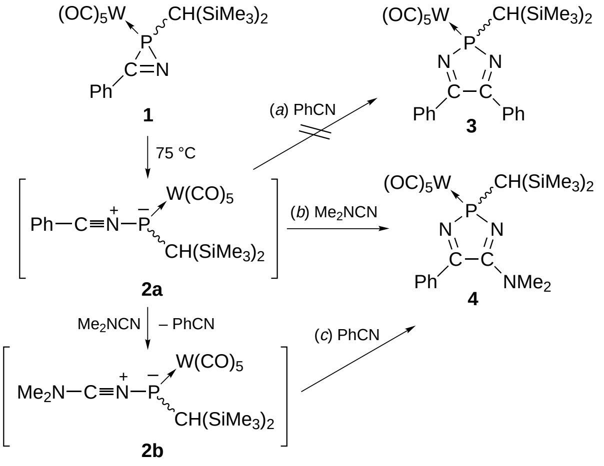
Thermal decomposition of the 2*H*-azaphosphirene tungsten complex 1 in benzonitrile and in the presence of dimethylcyanamide yields the 2*H*-1,3,2-diazaphosphole tungsten complex 4, containing a novel five-membered heterocyclic ligand; the overall reaction may be described as a 1,3-dipolar cycloaddition of an *in situ* generated nitrilium phosphane ylide complex to benzonitrile.

Nitrilium ylides, like nitrile oxides,[1] sulfides[2] and nitrile-imines,[1,3] are versatile building blocks in heterocyclic chemistry. Very recently, we obtained the first evidence of a nitrilium phosphane ylide complex as a reactive intermediate in the thermolysis of 2*H*-azaphosphirene tungsten complexes in the presence of dimethylacetylenedicarboxylate (DMAD) in toluene.[4] The formation of the 2*H*-1,2-azaphosphole tungsten complexes, which were obtained as by-products, was explained as a 1,3-dipolar cycloaddition of a nitrilium phosphane ylide complex to the trapping reagent.[4]

We now report the first synthesis of a 2*H*-1,3,2-diazaphosphole tungsten complex **4**, which has been obtained in good yield by thermal decomposition of the 2*H*-azaphosphirene tungsten complex **1** in benzonitrile and in the presence of 2 equiv. of dimethylcyanamide. Under these reaction conditions the 1,3-dipolar cycloaddition is stereoselective and the exclusive formation of this regioisomer was observed.

This reaction is interpreted as a further example of a 1,3-dipolar cycloaddition of the transiently formed nitrilium phosphane ylide tungsten complex **2b** to benzonitrile (Scheme 1, pathway (*c*)]. Pathways (*a*) and (*b*) seem less plausible, especially, if taken into account that under these reaction conditions the formation of the diphenyl-substituted 2*H*-1,3,2-diazaphosphole tungsten complex **3** was not observed [pathway (*a*)].

The composition of 2*H*-1,3,2-diazaphosphole tungsten complex **4** is confirmed by elemental analysis and mass spectrometry;† the structural formulation is based on the characteristic NMR spectral data† in solution and was confirmed for the solid state by a X-ray crystal structure analysis.‡ In comparison to related 2*H*-1,2-azaphosphole tungsten complexes,[4] the 2*H*-1,3,2-diazaphosphole tungsten complex **4** displays a low-field shifted resonance signal of the phosphorus nucleus at δ 149.8 (*cf.* δ 102–105[4]) and a markedly increased phosphorus tungsten coupling constant of 257.1 Hz (*cf.* $^1J_{WP}$ 236–238 Hz[4]). The phosphorus–carbon coupling constants of the quaternary ring carbon atoms are 2–10 Hz, which are characteristically small for both five-membered heterocycles.



Scheme 1 *Reagents and conditions*: 1 mmol **1** was treated with 2 mmol dimethylcyanamide in benzonitrile at 75 °C for 1.5 h. Work-up by column chromatography at low temperature afforded **4** in good yield (67%, mp 90 °C).

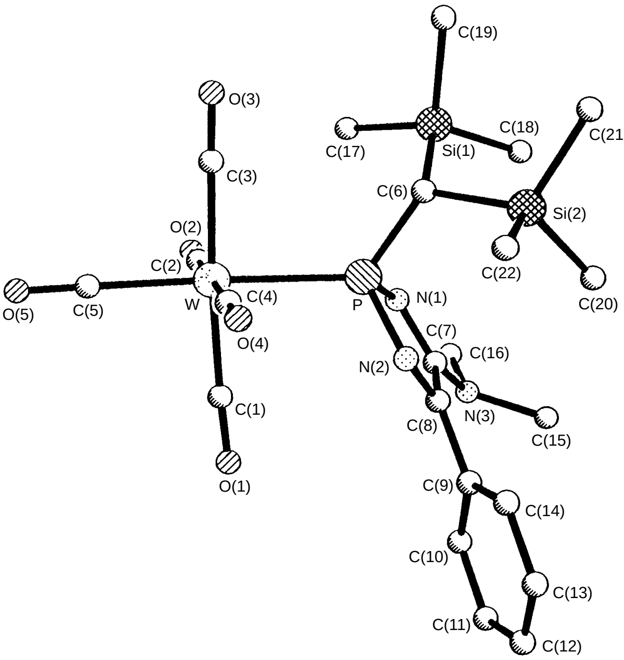


Fig. 1 Molecular structure of complex **4** in the crystal. Radii are arbitrary. Selected bond lengths (Å) and angles (°): P–W 2.479(11), P–N(1) 1.705(3), P–N(2) 1.705(3), N(1)–C(7) 1.291(5), N(2)–C(8) 1.284(5), C(7)–C(8) 1.488(5); N(1)–P–N(2) 96.3(2), P–N(1)–C(7) 108.2(3), N(1)–C(7)–C(8) 114.0(3), N(2)–C(8)–C(7) 113.4(4), P–N(2)–C(8) 107.8(3).

Remarkable features of the molecular structure of **4** and 2*H*-1,2-azaphosphole complexes[4] are the planar five-membered ring system and the localised double bonds; the latter being in contrast to the situation of aromatic heterocycles like 2*H*-1,2,3-diazaphospholes[5,6] and 2*H*-1,2,3-triazoles.[7] The coordination sphere of phosphorus is distorted tetrahedral and the phosphorus–tungsten bond length is 2.479(11) Å.

We are currently investigating the synthetic potential of nitrilium phosphane ylide complexes in 1,3-dipolar cycloaddition reactions.

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Footnotes and References

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† Satisfactory elemental analysis was obtained for complex **4**. NMR data were recorded at room temp. in $CDCl_3$ solution at 50.3 MHz (^{13}C) and 81.0

(^{31}P), using TMS and 85% H_3PO_4 as standard references; J/Hz. *Selected spectroscopic data* for **4**: ^{13}C NMR, δ 162.4 (d, ΣJ_{PC} 9.4, P–N=C), 165.0 (d, ΣJ_{PC} 2.5, P–N=C); ^{31}P NMR, δ 149.8 (5, $^1J_{WP}$ 257.1); MS (EI): M$^+$ at m/z 687.

‡ *Crystal data* for **4**: $C_{22}H_{30}N_3O_5PSi_2W$, M = 687.49; triclinic, space group $P\bar{1}$: a = 9.284(3), b = 10.359(3), c = 16.321(4) Å, α = 75.07(2), β = 88.21(2), γ = 67.67(2)°; U = 1398.9(6) Å^3; Z = 2, D_c = 1.632 Mg m^{-3}, T = 143 K, a crystal (0.7 × 0.7 × 0.6 mm) was mounted in inert oil. A total of 4946 absorption corrected intensities were measured to 2θ = 50° using Mo-Kα radiation on a STOE Stadi-4 diffractometer; 4915 were unique (R_{int} = 0.0546) and used for all calculations (program SHELXL-93). The structure was solved by direct methods and refined anisotropically on F^2. The final wR_2 was 0.0686, with conventional $R(F)$ 0.0262 for 316 parameters and 151 restraints; max. $\Delta\rho$ 2.48 e Å^{-3}. CCDC 182/666.

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