## Photochemically generated nitrilium phosphane-ylid tungsten complexes and their reactivity towards alkyne and nitrile derivatives

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The photochemically generated nitrilium phosphane-ylid tungsten complex 2 reacts with different activated alkynes, dimethyl acetylenedicarboxylate (DMAD) (i) and ethyl acetylenecarboxylate (ii), and nitriles, ethyl cyanoformate (ECF) (iii) and 1-piperidinonitrile (iv), giving [3+2] cycload-dition products such as the 2H-1,2-azaphosphole complexes 3 (i) and 4 (ii), the 2H-1,4,2-diazaphosphole complex 5 (iii) and the 2H-1,3,2-diazaphosphole complex 7 in good to excellent yields, the latter complexes, 4–7, being formed regioselectively; the structure of the first ester-functionalized 2H-1,4,2-diazaphosphole complex 5 was established by X-ray analysis.

Nitrile ylides II, which are useful reactive intermediates in synthetic chemistry, can be generated by thermally1 or photochemically<sup>2</sup> induced ring opening of 2H-azirenes I or by Nterminal 1,1-addition of singlet carbenes III to nitriles<sup>3</sup> (Scheme 1). So far, nitrilium phosphane-ylid complexes V have been transiently formed only by thermal ring opening of 2Hazaphosphirene complexes  $IV^4$  or by N-terminal 1,1-addition of singlet type terminal phosphanediyl complexes VI to nitriles:5 we have termed the latter process C.N.P-1,3-dipole transvlidation. Although the yields are sometimes unsatisfactory, thermally induced ring opening of 2H-azaphosphirene complexes provides access to, e.g., 2H-1,2-azaphosphole, 42H-1,4,2-diazaphosphole<sup>6</sup> and 2H-1,3,2-diazaphosphole complexes.<sup>6</sup> In order to broaden the synthetic applicability of 2H-azaphosphirene complexes in synthetic chemistry, we have now started to investigate their photochemistry in the presence of activated alkynes and nitriles as trapping reagents; the first results are reported here.



Scheme 1 Synthetic routes to nitrile ylides and nitrilium phosphane-ylid complexes ([M] = metal complex fragment, R denotes ubiquitous organic substituents).

Photochemical ring opening of the 2*H*-azaphosphirene complex  $1^7$  in pentane–benzonitrile (50–100:1) at -50 °C in the presence of 2 equiv. of dimethyl acetylenedicarboxylate (DMAD) (i), ethyl acetylenecarboxylate (ii), ethyl cyanoformate (ECF) (iii) and 1-piperidinonitrile (iv) furnished the [3+2] cycloaddition products in good to excellent yields (80–95%), which are significantly higher than those obtained by thermal reactions. Reactions (i) and (ii) yielded 2*H*-1,2-azaphosphole complexes  $3^4$  and 4, and (iii) and (iv) the 2*H*-1,4,2-diazaphosphole complex 5 and the 2*H*-1,3,2-diazaphosphole complex 7.6 Of note is the very high regioselectivity of reactions (ii) and (iii) and also that of (iv); in the latter case the

regioisomer 7 provides support for the assumption of a transylidation process, giving complex 6 and a subsequent [3+2] cycloaddition of this reactive intermediate to benzonitrile. It is also remarkable that satisfying results were obtained only if pentane–benzonitrile mixtures were employed as solvent for these low-temperature photochemical reactions (Scheme 2).



Scheme 2 *Reagents and conditions*: (i), (ii) a solution of 0.14 mmol of 1, 80 mL *n*-pentane, 0.5 mL benzonitrile and 0.5 mmol alkyne was irradiated at -50 °C for 1.5 h (low-pressure Hg-lamp, Heraeus TQ150); evaporation of the solvent yielded complexes 3 and 4 as orange to red oils, which, in the case of complex 4, yielded 4 as an orange solid (mp 61 °C, decomp.) after work-up by column chromatography at low temperature and crystallization from pentane; (iii) a solution of 0.28 mmol of 1, 80 mL *n*-pentane, 0.5 mL benzonitrile and 16 mmol ethyl cyanoformate was irradiated at -50 °C for 2 h, work-up by column chromatography at low temperature and crystallization from pentane afforded 5 as red crystals (mp 67 °C, decomp.); (iv) a solution of 0.14 mmol of 1, 80 mL *n*-pentane, 0.5 mL benzonitrile and 0.5 mmol of 1, 90 mL *n*-pentane, 0.5 mL benzonitrile and 0.5 mmol of 1, 80 mL *n*-pentane, 0.5 mL benzonitrile and 0.5 mmol of 3 as red crystals (mp 67 °C, decomp.);

Apart from the known complexes **3** and **7**, the composition of complex **4** and the ester-functionalized 2H-1,4,2-diazaphosphole complex **5** were confirmed by elemental analyses and mass spectrometry<sup>†</sup> and the structural formulation is based on the characteristic NMR spectral data<sup>†</sup> in solution. Furthermore, the ring constitution of complex **5** was confirmed by X-ray structure analysis<sup>‡</sup> (Fig. 1).

The phosphorus nuclei of **4** and **5** display resonances at  $\delta$ 94.4 and 122.4, which are in the expected range of such heterocycle complexes, with phosphorus–tungsten coupling constants



**Fig. 1** Molecular structure of complex **5** in the crystal. Radii are arbitrary. Selected bond lengths (Å) and angles (°): P–W 2.5039(5), N1–P 1.7007(16), P–C6 1.8678(19), C6–N2 1.284(2), N2–C7 1.438(2), C7–N1 1.287(2), P–C8 1.8221(19); N1–P–C6 89.05(8), P–C6–N2 110.61(13), N2–C7–N1 119.60(16), C7–N1–P 110.08(13), W–P–C8 121.98(6).

|J(W,P)| of 227.2 and 233.6 Hz, respectively. The assignment of the resonances to the carbon atoms of the heterocyclic system in complexes 4 and 5 is unambiguous, if the carbon atoms are bonded either to phosphorus or to hydrogen leading in the first case to significantly greater magnitudes of |J(P,C)| (in general) and/or to characteristic spectra if DEPT experiments were performed. The carbon atom resonances of the heterocycle in complex **4** appear at  $\delta$  138.0 (C<sup>3</sup>), 162.4 (C<sup>4</sup>) and 170.5 (C<sup>5</sup>) with phosphorus–carbon coupling constants |J(P,C)| of 23.5, 9.0 and 9.6 Hz, respectively. The <sup>1</sup>H resonance at  $\delta$  8.41 with a 32.7 Hz coupling to phosphorus is also structurally important; it is significantly low-field shifted compared to 4-substituted constitutional isomers, which have resonances at  $\delta$  ca. 7.5.<sup>8</sup> As in the 3,5-diphenyl-substituted 2H-1,4,2-diazaphosphole tungsten complex  $\mathbf{8}$ ,<sup>6</sup> the ester-functionalized complex  $\mathbf{5}$  displays a typical phosphorus resonance ( $5:\delta$  122.4, |J(W,P)| 233.6 Hz;  $8:\delta$  110.6, |J(W,P)| 227.8 Hz<sup>6</sup>). The ester group effectively increases not only the coupling constant |J(W,P)|, but also |J(P,C)|, which was observed in the <sup>13</sup>C NMR spectra of complex 5 for the C<sup>3</sup>- and C<sup>5</sup>-resonances (5: $\delta$  195.6, |J(P,C)|29.8 Hz and 167.2, |J(P,C)| 7.0 Hz; 8: & 198.5, |J(P,C)| 22.3 Hz and 169.5, |J(P,C)| 5.1 Hz<sup>6</sup>).

The five-membered ring system of the 2*H*-1,4,2-diazaphosphole complex **5** is almost planar and the phenyl group subtends an interplanar angle to the five-membered ring of 4.2°, thus enabling an efficient  $\pi$ - $\pi$  electron interaction of the two rings. The N–C distances, N1–C7 1.287(2) and N2–C6 1.284(2) Å, are in the typical range of nitrogen–carbon double bonds;<sup>9</sup> the latter is somewhat shorter than the value of 1.302(9) Å in complex **8**.<sup>6</sup> The coordination spheres of the phosphorus atoms

in **5** and **8** are both distorted tetrahedral, displaying identical  $\Sigma^{\circ}P_{PR_3}$  values [310.9° (**5**) and 311° (**8**)], identical N1–P–C6 angles [89.05(8)° (**5**) and 90.2(3)° (**8**)<sup>6</sup>] and only slightly different W–P–C8 angles [121.98(6)° (**5**) and 119.6(3)° (**8**)<sup>6</sup>], but different phosphorus–tungsten distances of 2.5039(5) Å (**5**) and 2.532(2) Å (**8**).<sup>6</sup> Together with the other distances and angles, this shows a predominant electronic effect of the ester group on these structural parameters.

We are currently investigating the reactivity of photochemically generated nitrilium phosphane-ylid complexes towards other  $\pi$ -systems.

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## Notes and references

† Satisfactory elemental analyses were obtained for complexes **4** and **5**. NMR data were recorded in CDCl<sub>3</sub> solution at 50.3 MHz (<sup>13</sup>C) and 81.0 (<sup>31</sup>P), using SiMe<sub>4</sub> and 85% H<sub>3</sub>PO<sub>4</sub> as standard references; *J*/Hz. Selected spectroscopic data: **4**: <sup>13</sup>C NMR:  $\delta$  19.1 (d, <sup>1</sup>*J*<sub>PC</sub> 4.4, PCH), 138.0 (d, <sup>(2+3)</sup>*J*<sub>PC</sub> 23.5, P–C=C), 162.4 (d, <sup>(2+3)</sup>*J*<sub>PC</sub> 9.0, P–C=C), 163.8 (d, <sup>3</sup>*J*<sub>PC</sub> 17.2, CO<sub>2</sub>Et), 170.5 (d, <sup>(2+3)</sup>*J*<sub>PC</sub> 9.6, P–N=C), 196.3 (d, <sup>2</sup>*J*<sub>PC</sub> 6.4, *cis*-CO), 198.4 (d, <sup>2</sup>*J*<sub>PC</sub> 21.0, *trans*-CO); *m*/z (EI) 715 (M+, 10). 5: <sup>13</sup>C NMR:  $\delta$ 21.9 (d, <sup>1</sup>*J*<sub>PC</sub> 3.8, PCH), 167.2 (d, <sup>(2+3)</sup>*J*<sub>PC</sub> 7.0, P–N=C), 163.3 (d, <sup>3</sup>*J*<sub>PC</sub> 28.2, CO<sub>2</sub>Et), 195.6 (d, <sup>(1+4)</sup>*J*<sub>PC</sub> 29.8, P–C=N), 196.3 (d, <sup>2</sup>*J*<sub>PC</sub> 6.2, *cis*-CO), 198.6 (d, <sup>2</sup>*J*<sub>PC</sub> 23.1, *trans*-CO); *m*/z (EI) 716 (M+, 32).

‡ *Crystal data* for **5**: C<sub>23</sub>H<sub>29</sub>N<sub>2</sub>O<sub>7</sub>PSi<sub>2</sub>W; M = 716.48, triclinic, space group group  $P\overline{1}$ , a = 10.5466(10), b = 10.7010(11), c = 13.8717(14) Å,  $\alpha = 79.915(3)$ ,  $\beta = 82.215(3)$ ,  $\gamma = 75.406(3)^\circ$ , U = 1484.8(3) Å<sup>3</sup>, Z = 2,  $D_c = 1.603$  Mg m<sup>-3</sup>,  $\mu = 4.065$  mm<sup>-1</sup>, F(000) = 708, 7327 independent reflections to 2 $\theta$  max. 56°, T = 143 K, S = 1.019,  $R[F, > 4\sigma(F)] = 0.0186$ ,  $wR(F^2) = 0.0438$ , 25 restraints and 332 parameters, highest peak 1.142 and deepest hole -0.539 e Å<sup>-3</sup>.

The X-ray data set was collected with monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Bruker SMART 1000 CCD area detector. Absorption correction based on multiple scans. The structure was solved by the Patterson method and refined anisotropically by full-matrix least squares on  $F^{2,10}$  H atoms were included using a riding model (except methyl groups: refined as rigid groups). CCDC 182/1410. See http://www.rsc.org/ suppdata/cc/1999/2127/ for crystallographic files in .cif format.

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