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

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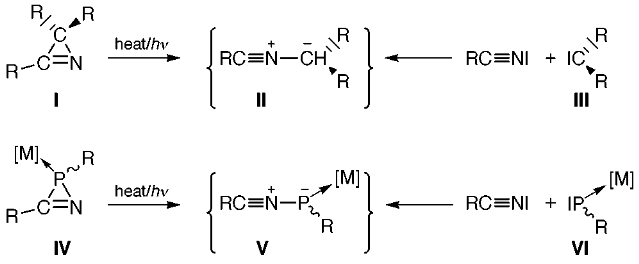
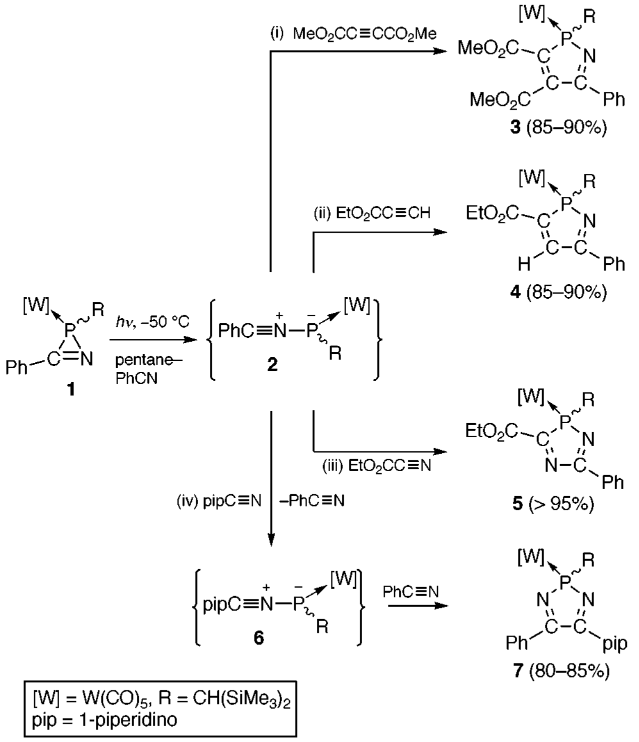
The photochemically generated nitrilium phosphane-ylid tungsten complex 2 reacts with different activated alkynes, dimethyl acetylenedicarboxylate (DMAD) (i) and ethyl acetylenecarboxylate (ii), and nitriles, ethyl cyanoformate (ECF) (iii) and 1-piperidinonitrile (iv), giving [3+2] cycloaddition products such as the 2*H*-1,2-azaphosphole complexes 3 (i) and 4 (ii), the 2*H*-1,4,2-diazaphosphole complex 5 (iii) and the 2*H*-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 2*H*-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 thermally[1] or photochemically[2] induced ring opening of 2*H*-azirenes **I** or by *N*-terminal 1,1-addition of singlet carbenes **III** to nitriles[3] (Scheme 1). So far, nitrilium phosphane-ylid complexes **V** have been transiently formed only by thermal ring opening of 2*H*-azaphosphirene 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 transylidation. Although the yields are sometimes unsatisfactory, thermally induced ring opening of 2*H*-azaphosphirene complexes provides access to, *e.g.*, 2*H*-1,2-azaphosphole,[4] 2*H*-1,4,2-diazaphosphole[6] and 2*H*-1,3,2-diazaphosphole complexes.[6] In order to broaden the synthetic applicability of 2*H*-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 1-piperidinonitrile was irradiated at −50 °C for 1 h; evaporation of the solvent yielded **7** as a yellow oil.

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

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

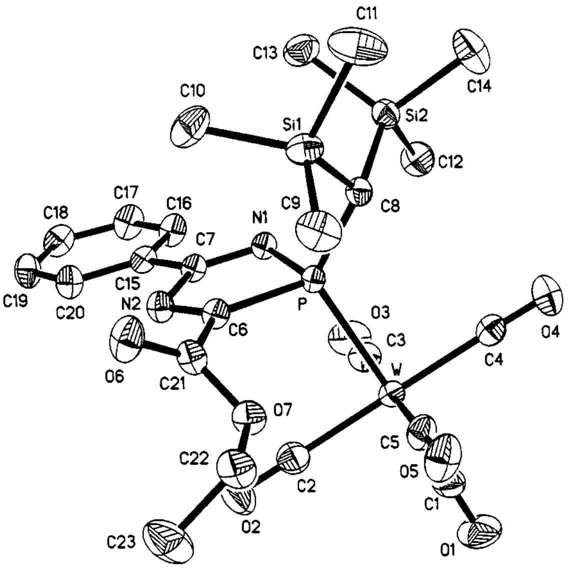


Fig. 1 Molecular structure of complex **5** in the crystal. Radii are arbitrary. Selected bond lengths (Å) and angles (°): P–W 2.5039(5), N1–P 1.7007(16), P–C6 1.8678(19), C6–N2 1.284(2), N2–C7 1.438(2), C7–N1 1.287(2), P–C8 1.8221(19); N1–P–C6 89.05(8), P–C6–N2 110.61(13), N2–C7–N1 119.60(16), C7–N1–P 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 δ 138.0 (C^3), 162.4 (C^4) and 170.5 (C^5) with phosphorus–carbon coupling constants |*J*(P,C)| of 23.5, 9.0 and 9.6 Hz, respectively. The ^1H resonance at δ 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 δ *ca.* 7.5.[8] As in the 3,5-diphenyl-substituted 2*H*-1,4,2-diazaphosphole tungsten complex **8**,[6] the ester-functionalized complex **5** displays a typical phosphorus resonance (**5**: δ 122.4, |*J*(W,P)| 233.6 Hz; **8**: δ 110.6, |*J*(W,P)| 227.8 Hz[6]). The ester group effectively increases not only the coupling constant |*J*(W,P)|, but also |*J*(P,C)|, which was observed in the ^{13}C NMR spectra of complex **5** for the C^3- and C^5-resonances (**5**: δ 195.6, |*J*(P,C)| 29.8 Hz and 167.2, |*J*(P,C)| 7.0 Hz; **8**: δ 198.5, |*J*(P,C)| 22.3 Hz and 169.5, |*J*(P,C)| 5.1 Hz[6]).

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 π–π 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;[9] the latter is somewhat shorter than the value of 1.302(9) Å in complex **8**.[6] The coordination spheres of the phosphorus atoms in **5** and **8** are both distorted tetrahedral, displaying identical $\Sigma°P_{PR_3}$ values [310.9° (**5**) and 311° (**8**)], identical N1–P–C6 angles [89.05(8)° (**5**) and 90.2(3)° (**8**)[6]] and only slightly different W–P–C8 angles [121.98(6)° (**5**) and 119.6(3)° (**8**)[6]], but different phosphorus–tungsten distances of 2.5039(5) Å (**5**) and 2.532(2) Å (**8**).[6] 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 π-systems.

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Notes and references

† Satisfactory elemental analyses were obtained for complexes **4** and **5**. NMR data were recorded in $CDCl_3$ solution at 50.3 MHz (^{13}C) and 81.0 (^{31}P), using $SiMe_4$ and 85% H_3PO_4 as standard references; *J*/Hz. Selected spectroscopic data: **4**: ^{13}C NMR: δ 19.1 (d, $^1J_{PC}$ 4.4, P*C*H), 138.0 (d, $^{(2+3)}J_{PC}$ 23.5, P–*C*=C), 162.4 (d, $^{(2+3)}J_{PC}$ 9.0, P–C=*C*), 163.8 (d, $^3J_{PC}$ 17.2, *C*O$_2$Et), 170.5 (d, $^{(2+3)}J_{PC}$ 9.6, P–N=*C*), 196.3 (d, $^2J_{PC}$ 6.4, *cis*-CO), 198.4 (d, $^2J_{PC}$ 21.0, *trans*-CO); *m/z* (EI) 715 (M+, 10). **5**: ^{13}C NMR: δ 21.9 (d, $^1J_{PC}$ 3.8, P*C*H), 167.2 (d, $^{(2+3)}J_{PC}$ 7.0, P–N=*C*), 163.3 (d, $^3J_{PC}$ 28.2, *C*O$_2$Et), 195.6 (d, $^{(1+4)}J_{PC}$ 29.8, P–*C*=N), 196.3 (d, $^2J_{PC}$ 6.2, *cis*-CO), 198.6 (d, $^2J_{PC}$ 23.1, *trans*-CO); *m/z* (EI) 716 (M^+, 32).

‡ *Crystal data* for **5**: $C_{23}H_{29}N_2O_7PSi_2W$; M = 716.48, triclinic, space group group $P\bar{1}$, a = 10.5466(10), b = 10.7010(11), c = 13.8717(14) Å, α = 79.915(3), β = 82.215(3), γ = 75.406(3)°, U = 1484.8(3) Å^3, Z = 2, D_c = 1.603 Mg m^{-3}, μ = 4.065 mm^{-1}, $F(000)$ = 708, 7327 independent reflections to 2θmax. 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^{-3}.

The X-ray data set was collected with monochromated Mo-Kα radiation (λ = 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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