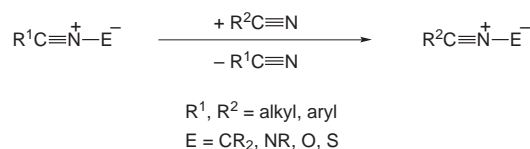# Transylidation of a transiently formed nitrilium phosphane ylide complex

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Thermal decomposition of the 3-phenyl-substituted 2*H*-azaphosphirene complex 1 in the presence of dimethyl cyanamide and dimethyl acetylenedicarboxylate (DMAD) yielded dimethylamino-substituted products, the 2*H*-1,2-azaphosphole complex 4b and the diastereoisomeric Δ³-1,3,2-oxazapholene complexes 5a,b; this represents the first example of 1,3-dipolar cycloaddition reactions of a nitrilium phosphane ylide complex that is generated *in situ* by transylidation.

Recently, we reported the first evidence for transiently formed nitrilium phosphane ylide complexes by two different trapping experiments. Thermal ring opening of the 2*H*-azaphosphirene complex 1 in toluene in the presence of dimethyl acetylenedicarboxylate (DMAD) yielded a product mixture consisting of the 1*H*-phosphirene complex 3 and the 2*H*-1,2-azaphosphole complex 4a.[1,2] With dimethyl cyanamide in benzonitrile the trapping resulted in the formation of a 2*H*-1,3,2-diazaphosphole complex;[3] based on the observed selectivity and non-formation of a 4,5-diphenyl-substituted 2*H*-1,3,2-diazaphosphole complex, we assumed a transylidation during the reaction course. To the best of our knowledge transylidation processes among nitrilium betaines have been reported so far only for nitrile sulfides[4] (Scheme 1); neither is their mechanism known nor has this methodology been synthetically exploited. With respect to the enormous potential of 1,3-dipoles such as nitrilium betaines in [3 + 2] cycloaddition reactions and, therefore, in heterocyclic chemistry,[5] we decided to examine this aspect more thoroughly for the case of nitrilium phosphane ylide complexes and performed a trapping experiment with two suitable, but different trapping reagents, DMAD and dimethyl cyanamide.

$$R^1C\equiv\overset{+}{N}-E^- \xrightarrow[-\,R^1C\equiv N]{+\,R^2C\equiv N} R^2C\equiv\overset{+}{N}-E^-$$

$$R^1, R^2 = \text{alkyl, aryl}$$
$$E = CR_2, NR, O, S$$

Scheme 1

Thermal decomposition of the 2*H*-azaphosphirene tungsten complex 1 in the presence of 2 equiv. of DMAD and 2 equiv. of dimethyl cyanamide yielded the 2*H*-1,2-azaphosphole complex 4b and the two diastereoisomeric Δ³-1,3,2-oxazapholene complexes 5a,b (*meso* and racemate) in an estimated ratio of 1 : 1 : 1 (³¹P NMR integration). The formation of both five-membered heterocycles is rationalized by 1,3-dipolar cycloaddition reactions of the *in situ* generated nitrilium phosphane ylide complex 2b to the C≡C triple bond and the C=O double bond of dimethyl acetylenedicarboxylate [Scheme 2, path (*b*)].

This result has several noteworthy aspects. It is a rare example of a dual reactivity of DMAD towards a 1,3-dipole and it is remarkable that neither the 1*H*-phosphirene complex 3 nor the phenyl-substituted five-membered heterocycle complex 4a was detected [path (*a*)]. Furthermore, during the reaction course a transylidation must have taken place, such that the benzonitrile unit in 2a was substituted, at least formally, by dimethyl

cyanamide, thus forming the nitrilium phosphane ylide complex 2b. We performed additionally control experiments to check this interpretation. Firstly, we heated a solution of 1*H*-phosphirene complex 3 and dimethylcyanamide to exclude a subsequent ring enlargement reaction, but up to 85 °C no reaction was observed. Secondly, we examined the possible reaction sequence: DMAD gives initially an azete derivative with dimethyl cyanamide, which then could yield 2*H*-1,2-azaphosphole complex 4b by insertion of transiently formed terminal phosphanediyl complex [(OC)₅WPCH-(SiMe₃)₂] (*cf.* ref. 2) into a C–N bond of the azete ring; but azete formation could not be detected upon heating a solution of DMAD and dimethyl cyanamide for 2 h at 85 °C.

The composition of the 2*H*-1,2-azaphosphole complex 4b and the Δ³-1,3,2-oxazapholene complexes 5a,b are confirmed by elemental analysis and mass spectrometry;‡ the structural formulation is based on their characteristic NMR spectral data‡ in solution and that of 5a was confirmed by X-ray structure analysis.§ The phosphorus nucleus of 4b displays a resonance at δ 85.6, which is significantly high-field shifted compared to other 2*H*-1,2-azaphosphole complexes (δ 102–105[2]) with a markedly increased phosphorus–tungsten coupling constant of 249.7 Hz (*vs.* 236–238 Hz[2]). The ³¹P NMR parameters of the diastereoisomeric Δ³-1,3,2-oxazapholene complexes are δ 191.6 [¹J_{PW} 303.1 Hz (5a)] and δ 198.6 [¹J_{PW} 305.9 Hz (5b)]. In view of the strong influence of the phosphorus-bonded oxygen atom on the
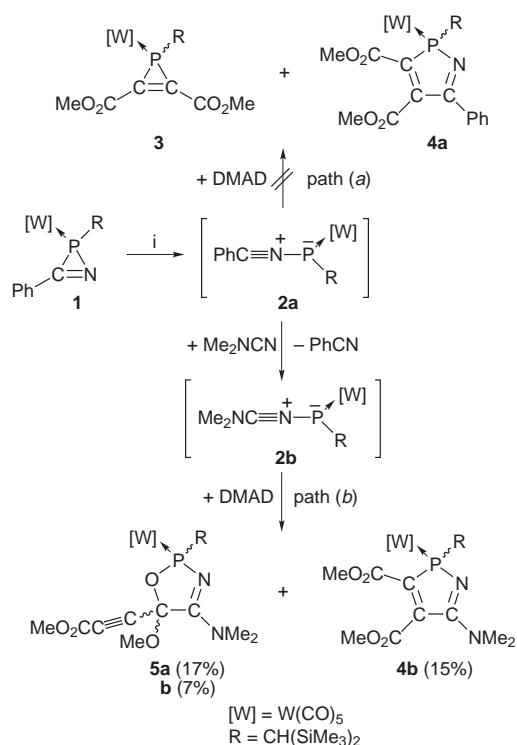
Scheme 2 *Reagents and conditions*: i, DMAD (2 equiv.), Me₂NCN (2 equiv.), toluene (3 ml), 75 °C, 1.5 h.
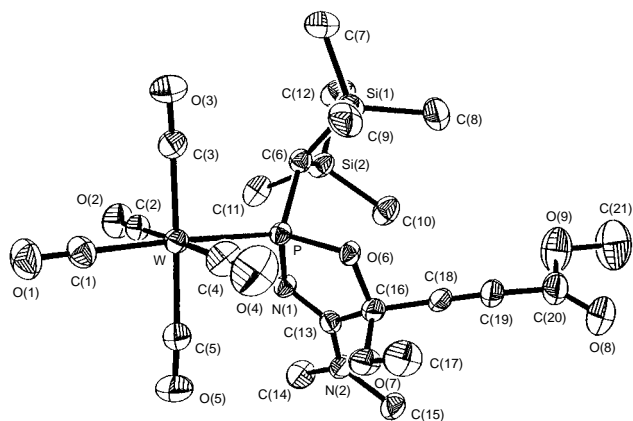
Fig. 1 Molecular structure of complex **5a** in the crystal. Radii are arbitrary. Selected bond lengths (Å) and angles (°): P–W 2.4748(9), P–N(1) 1.677(3), N(2)–C(13) 1.337(4), O(6)-C(16) 1.413(4), C(13)–C(16) 1.552(4), C(18)–C(19) 1.180(5), P–O(6) 1.683(2), N(1)–C(13) 1.301(4); N(1)–C(13)–N(2) 1.242(3), N(1)–P–O(6) 95.23(12), C(13)–N(1)–P 111.5(2), C(16)–O–P 111.9(2), N(1)–C(13)–C(16) 114.8(3), O(6)–C(16)–C(13) 105.3(2).

phosphorus resonances, the almost constant imino carbon resonances of **4b** and **5a,b** (δ 158.0–158.4) are surprising. All these carbon resonances display small carbon–phosphorus coupling constants (1.1-5.3 Hz), which seems to be characteristic for such heterocyclic ring systems; these magnitudes most probably derive from ^2J and ^3J scalar couplings.

The five-membered ring system of the Δ^3-1,3,2-oxazaphospholene complex **5a**, which is the first to be reported, is almost planar; the best plane is given by P–N(1)–C(13)–C(16) (deviation: 0.005 Å) and the oxygen atom lies 0.17 Å out of this plane. The N(1)–C(13) distance [1.301(4) Å] is in the typical range of nitrogen–carbon double bonds, while the coordination sphere of the phosphorus atom is distorted tetrahedral with a phosphorus–tungsten bond length of 2.4748(9) Å.

We are currently investigating the synthetic potential of nitrilium phosphane ylide complexes that are generated *in situ* by transylidations.

Notes and References

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‡ Satisfactory elemental analyses were obtained for complexes **4b** and **5a,b**. NMR data [CDCl₃], 30.3 MHz (^{13}C), 81.0 MHz (^{31}P), TMS and 85% H₃PO₄ were used as standard references. *Selected data* for **4b**: mp 123 °C; δ_C 139.2 (d, J_{PC} 21.1, P–*C*=C), 158.4 (d, $^{(2+3)}J_{PC}$ 5.3, P–N=*C*), 161.8 (d, $^{(2+3)}J_{PC}$ 7.3, P–*C*=C); δ_P 85.6 (d, ^{1}H$_{PW}$ 249.7); *m/z* (EI) 726 (M⁺). For **5a**: mp 158 °C; δ_C 99.1 (d, $^{(2+3)}J_{PC}$ 6.9, P–O–C), 158.1 (d, $^{(2+3)}J_{PC}$ 1.1, P–N=C); δ_P 191.6 (d, $^1J_{PW}$ 305.9); *m/z* (EI) 726 (M⁺). For **5b**: mp 164 °C; δ_C 99.2 (d, $^{(2+3)}J_{PC}$ 4.0, P–O–C), 158.0 (d, $^{(2+3)}J_{PC}$ 1.3, P–N=C); δ_P 198.6 (d, $^1J_{PW}$ 303.1); *m/z* (EI) 726 (M⁺).

§ *Crystal data* for **5a**: C₂₁H₃₁N₂O₉PSi₂W; M = 726.48, triclinic, space group $P\bar{1}$, a = 10.0074(10), b = 10.073(2), c = 15.8415 Å, α = 97.711(8), β = 92.631(8), γ = 106.817(8)°, U = 1508.8(3) Å³, Z = 2, D_c = 1.599 mg m⁻³, μ = 4.006 mm⁻¹, F(000) = 720, 5290 independent reflections to $2\theta_{max}$. = 50°, T = 173 K, S = 0.962, R [F, >4σ(F)] = 0.0217, R_w(F^2) = 0.0505, 164 restraints and 336 parameters, highest peak = 0.994, deepest hole = −0.527 e Å⁻³. The X-ray data set was collected with monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Siemens P4 four-circle diffractometer. Absorption correction was based on ψ-scans. The structure was solved by the heavy-atom method and refined anisotropically by full-matrix least-squares on F^2. H atoms were included using a riding model for all non-methyl group protons. Methyls were refined as rigid groups. CCDC 182/894.

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