Dual reaction behaviour of an *in situ* generated nitrilium phosphane ylide complex towards carbon–sulfur π-systems

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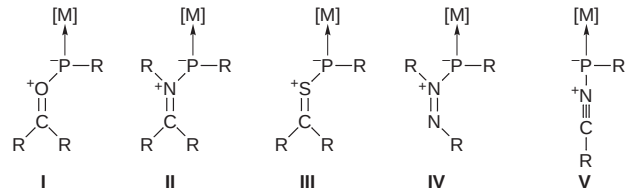
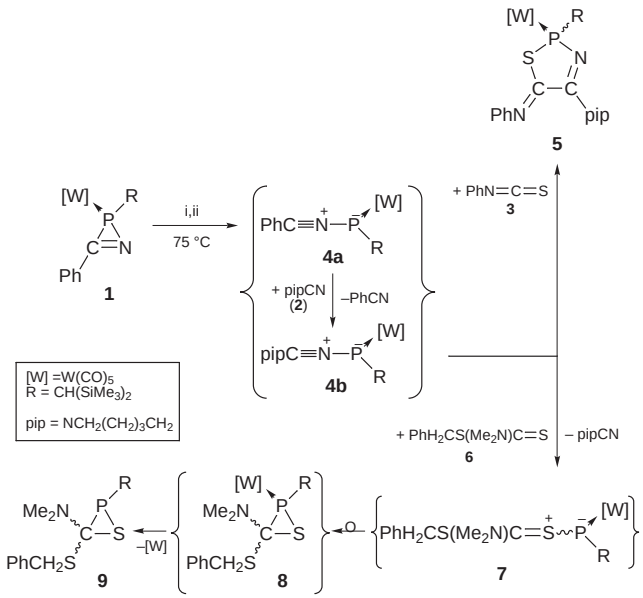
[3 + 2] Cycloaddition of *in situ* generated nitrilium phosphane ylide complex 4b with phenylisothiocyanate yielded *N*-piperidino-substituted Δ³-1,3,2-thiazaphospholene complex 5 regioselectively, whereas with benzyl *N*,*N*-dimethyl dithiocarbamate ester the thiaphosphirane 9 is obtained; these reactions, a 1,3-dipolar cycloaddition and a transylidation, shed first light on the reactivity of a nitrilium phosphane ylide complex towards different C,S π-systems.

Betaines **I**,[1] **II**,[1b,2] **III**, **IV**[3] and **V**[4] with a phosphorus atom in the central 1,3-dipole skeleton are of increasing interest in phosphorus and heterocyclic chemistry (Scheme 1).[5] Recently, we gained strong evidence for the transient formation of nitrilium phosphane ylide complexes (**V**) by employing dialkyl cyanamides and different trapping reagents such as dimethyl acetylene dicarboxylate[6] or nitriles.[7] Although we gained some evidence that transiently formed 2*H*-azaphosphirene complexes[7] and, under some circumstances, transition states of the 2 : 1 donor–acceptor adduct-type, with nitriles as donors and a terminal phosphanediyl complex as acceptor,[8] may be involved in transylidation processes, those reactions are not completely understood. To shed more light on this process and to exploit synthetically the transylidation methodology, we have now started to investigate the reaction behaviour of transiently formed nitrilium phosphane ylide complexes towards different C,S π-systems such as isothiocyanates and dithiocarbamates.



Scheme 1 1,3-Dipole complexes ([M] = metal complex fragment, R denotes ubiquitous organic substituents).

Thermal ring-opening of the 2*H*-azaphosphirene complex **1**[9] in toluene in the presence of 2 equiv. of 1-piperidinonitrile **2** and 2 equiv. of phenylisothiocyanate **3** furnished the Δ³-1,3,2-thiazaphospholene complex **5**, regioselectively; neither regioisomers nor isomers resulting from a cycloaddition reaction of intermediately formed **4b** with the C,N π-system of **3** have been observed. Employment of benzyl *N*,*N*-dimethyl dithiocarbamate ester **6** under the same reaction conditions gave the thiaphosphirane **9** exclusively; neither five-membered heterocycles, formed by reaction of **4b** with **6**, nor the corresponding thiaphosphirane complex **8** could be detected spectroscopically (Scheme 2). It is remarkable that this reaction did not change, even when benzonitrile was employed as solvent. Therefore, the formation of both heterocycles is explained by reactions of the *in situ* generated nitrilium phosphane ylide complex **4b**, which leads either to **5** *via* [3 + 2] cycloaddition or to **9** *via* an intersystem-transylidation-type reaction giving 1,3-dipole complex **7**, which undergoes ring-closure to **8** and subsequent decomplexation to give **9** as the final product. Because a transient formation of terminal phosphanediyl complex $[(OC)_5WPCH(SiMe_3)_2]$ can be achieved *via* thermally induced



Scheme 2 *Reagents and conditions*: i, 1 mmol of **1** was treated with 6 mmol of phenylisothiocyanate and 2 mmol 1-piperidinonitrile in 2 ml of toluene at 75 °C for 1.5 h. Work-up by column chromatography at low temperature and crystallization from pentane afforded **5** as a yellow solid (28%, mp. 98 °C); ii, 1 mmol of **1** was treated with 5 mmol of benzyl *N*,*N*-dimethyldithiocarbamate ester in 3 ml of toluene at 75 °C for 2 h.Work-up by column chromatography at low temperature afforded **9** as a pale yellow oil (13%).

ring-cleavage of **4a** in toluene,[4] we repeated the reaction of **1** and **6** in toluene in the absence of **2** and obtained, once more, thiaphosphirane **9** as the only phosphorus-containing product. This result also supports the assumption of complex **7** as a highly reactive intermediate in this reaction course.

The compositions of the Δ³-1,3,2-thiazaphospholene complex **5** and the thiaphosphirane **9** are confirmed by elemental analyses and mass spectrometry;† the structural formulation is based on their characteristic NMR spectral data† in solution. The connectivity of the heterocyclic ring atoms of complex **5** was also confirmed by X-ray structure analysis, although the refinement was unsatisfactory because of heavily disordered substituents at the five-membered ring system; therefore, the structure will not be further discussed here.

The phosphorus nucleus of **5** displays a resonance at δ 105.8, which is significantly high-field shifted compared to Δ³-1,3,2-oxazaphospholene complexes (δ 190–205[6]), with a markedly decreased phosphorus–tungsten coupling constant of 287.1 Hz (*cf.* 300–306 Hz[6]). The carbon atom resonances of the heterocycle appear at δ 157.7 and 160.9 with phosphorus–carbon coupling constants of 9.2 and 12.8 Hz, respectively. Similarly to Δ³-1,3,2-oxazaphospholene complexes, these carbon resonances display small carbon–phosphorus coupling constants; this seems to be a characteristic phenomenon for such heterocyclic ring systems. The phosphorus and the ring carbon atom of the thiaphosphirane **9** display resonances at low field

[δ(^{31}P) 36.4; δ(^{13}C) 106.5; *cf.* ref. 10], which indicates a deshielding influence of the two directly bonded electronegative N- and S-atoms of the *exo*-substituents on the atoms of the thiaphosphirane ring.

We are currently investigating the reactivity of *in situ* generated nitrilium phosphane ylide complexes towards other heterocumulene systems.

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Notes and references

† Satisfactory elemental analyses were obtained for complexes **5** and **9**. NMR data were recorded in $CDCl_3$ solution at 50.3 (^{13}C) and 81.0 MHz (^{31}P), using TMS and 85% H_3PO_4 as standard references; *J*/Hz. *Selected spectroscopic data* for **5**: ^{13}C NMR: δ 157.7 (d, $^{(2+3)}J_{PC}$ 9.2, PSC), 160.9 (d, $^{(2+3)}J_{PC}$ 12.8, PN=C), 197.5 (d, $^{2}J_{PC}$ 7.9, *cis*-CO), 200.9 (d, $^{2}J_{PC}$ 30.0, *trans*-CO); ^{31}P NMR: δ 105.8 (d, $^{1}J_{PW}$ 287.1); *m/z* (EI) 759 (M^+). **9**: ^{13}C NMR: δ 106.5 (s, PSC); ^{31}P NMR: δ 36.4; *m/z* (EI) 401 (M^+).

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