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Strong evidence for stereoselective 1,3-additions of transient nitrilium phosphane-ylide complexes: synthesis of the first 1-aza-3-phosphabuta-1,3-diene complexes†

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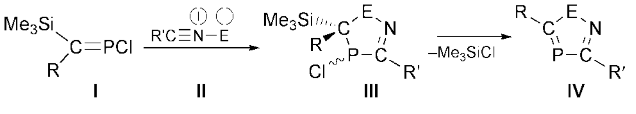
Synthesis of the first 1-aza-3-phosphabuta-1,3-diene complexes was achieved by heating solutions of 2*H*-azaphosphirene tungsten complexes, 1-piperidinonitrile and [bis(trimethylsilyl)methylene]chlorophosphane; X-ray structure analysis of one new complex revealed a *cisoid* position of the chlorine atom and the phosphaalkene unit at the C,N,P-core of the trapped nitrilium phosphane-ylide complex and a distorted heterobutadiene π-system.

[3+2] cycloaddition reactions of *P*-chlorophosphaalkenes[1] **I** with nitrilium betaines **II** such as nitrile ylides[2] and sulfides[3] are very useful in phosphorus heterocycle synthesis, especially if an elimination of chlorotrimethylsilane occurs subsequently (**III** → **IV**), thus yielding aromatic heterocycles **IV** (Scheme 1). Recently, we reported trapping reactions of nitrilium phosphane-ylide complexes with alkynes,[4] nitriles[5] and phosphaalkynes[6] giving five-membered phosphorus heterocycle complexes. If phenylacetylene was used as trapping reagent and solvent we obtained a product mixture that consisted of a 1*H*-phosphirene and a 2*H*-1,2-azaphosphole complex and two acyclic compounds, which, at least formally, resulted from two differently orientated 1,3-addition reactions of the C–H bond of phenylacetylene to the 1,3-dipole system of a transient nitrilium phosphane-ylide complex.[7] Because of this complicated situation, we were not sure about the mechanism and/or the concertedness of these 1,3-addition reactions.

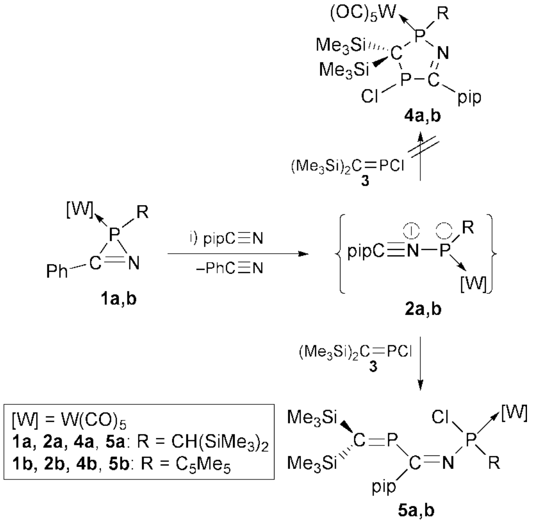
Here we report the synthesis of the first 1-aza-3-phosphabuta-1,3-diene complexes using our thermal three-component methodology: 2*H*-azaphosphirene complexes, 1-piperidinonitrile and a *P*-chlorophosphaalkene. The products were obtained in pure form by column chromatography and fully characterized by various means; one complex was characterized additionally by an X-ray diffraction study.

Heating toluene solutions of the 2*H*-azaphosphirene tungsten complexes **1a**[8] and **1b**[9] with 1-piperidinonitrile and [bis(trimethylsilyl)methylene]chlorophosphane[10] (**3**) for 2 h afforded selectively the 1-aza-3-phosphabuta-1,3-diene complexes **5a,b** as trapping products of the transiently formed nitrilium phosphane-ylide complexes **2a,b** (Scheme 2). Complexes **5a**,**b** were confirmed by elemental analyses, NMR spectroscopy and mass spectrometry.‡ Only traces ($<5\%$) of other phosphorus-containing products were observed by ^{31}P NMR spectroscopy displaying resonances at δ 106.2 and 337.4 (reaction of **1a**) and at δ 104.1 and 349.9 (reaction of **1b**); complexes **4a**,**b** could not be detected. It is remarkable that the attack at the P–Cl σ-bond is preferred to that at the π-system of the *P*-chlorophosphaalkene, which might be caused by strong steric repulsion between the substituents of the carbon centre of the P=C unit and those of the phosphorus centre of the 1,3-dipole in the transition state of the cycloaddition reaction; if this interpretation of the reaction course is correct this example would be unprecedented in nitrilium betaine chemistry.



Scheme 1 Phosphaalkenes **I**, nitrilium betaines **II** and phosphorus heterocycles **III**, **IV** (**I–IV**: R, R′ = organic substituents; E = CR_2 or S).

The ^{31}P NMR spectra of complexes **5a**,**b** showed resonances at low field (**5a**: δ 339.5, $|^3J(PP)|$ 15.5 Hz; **5b**: δ 342.3, $|^3J(PP)|$ 8.0 Hz), which can be assigned to the phosphaalkene nuclei, and those at higher field (**5a**: δ 111.8, $|^3J(PP)|$ 15.5, $|^1J(PW)|$ 284.7 Hz; **5b**: δ 112.9, $|^3J(PP)|$ 8.0 Hz, $|^1J(PW)|$ 305.1 Hz) to the *N*-bonded phosphorus nuclei. With respect to the resonances of the low-coordinated phosphorus centres, the ^{31}P NMR data of **5a**,**b** are quite different from those found for non-coordinated 1-aza-3-phosphabuta-1,3-dienes, which have been synthesized using trimethylsilyl shift reactions, and which show resonances in the range δ 0–100.[11,12] These differences are probably associated with the different substituents at the P=C carbon atoms, which, in our case, represent acceptor groups and in the other cases donor groups. The structure of the complexes **5a**,**b** were unambiguously confirmed by the $^{13}C\{^1H\}$ NMR spectra, which displayed resonances of the C=N and C=P carbon atoms with two phosphorus–carbon couplings each, whereby the greater magnitude values establish the direct bonding of one phosphorus centre to two different sp^2-carbon centres. The molecular structure of complex **5a** (Fig. 1), as established for the solid state by X-ray crystallography,§ shows a significantly distorted heterobutadiene π-system [N(1)–C(6)–P(2)–C(7) −106.6°] with bond lengths typical of localized double bond systems



Scheme 2 *Reagents and conditions*: 615 mg of complex **1a** or 534 mg of complex **1b**, 100 μL 1-piperidinonitrile, 449 mg phosphaalkene **2**, 2.5 mL toluene, 75 °C, 2 h; column chromatograpy (Al_2O_3, −20 °C, *n*-hexane); **5a**: yellow solid, yield: 44%, mp 128 °C (decomp.); **5b**: yellow solid, yield: 34%, mp 118 °C (decomp.).

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† This work is dedicated to Professor Henning Hopf on the occasion of his 60th birthday.

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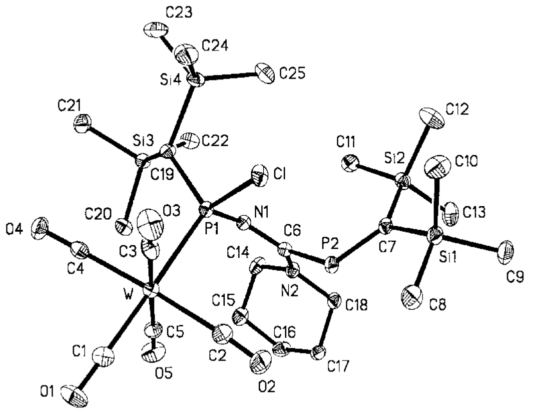

Fig. 1 Molecular structure of **5a** in the crystal (ellipsoids represent 30% probability levels; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): W–C(1) 1.999(6), W–P(1) 2.5332(13), P(1)–N(1) 1.626(4), P(1)–C(19) 1.820(4), N(1)–C(6) 1.303(5), P(2)–C(6) 1.880(5), N(2)–C(6) 1.333(6), P(2)–C(7) 1.669(5); C(1)–W–P(1) 178.43(15), W–P(1)–C(19) 116.35(16), P(1)–N(1)–C(6) 134.4(3), N(1)–C(6)–P(2) 119.2(3), C(6)–P(2)–C(7) 110.7(2).

[N1–C6 1.303(5) and P2–C7 1.669(5) Å]. The P(2)–C(6) distance 1.880(5) Å represents a P–C single bond (average value: 1.885).[13] The coordination environment of the P1 atom is tetrahedral with a P1–Cl distance of 2.143(1) Å and a P1–W distance of 2.5323(16) Å. Furthermore, the structure confirmed the *cisoid* position of the chlorine atom and the phosphaalkene unit at the C,N,P-core of the trapped nitrilium phosphane-ylide complex and thereby strengthened the assumption of a concerted 1,3-addition process that is responsible for the product formation.

Currently we are investigating the role of sterically less bulky P-substituents of transient nitrilium phosphane-ylide complexes (*cf.* ref. 4*c*), in three-component reactions on the reaction course.

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Notes and references

‡ Satisfactory elemental analysis were obtained for complexes **5a**,**b**. NMR data were recorded in $CDCl_3$ solutions (295 K) at 50.3 MHz (^{13}C) and 81.0 MHz (^{31}P), using TMS and 85% H_3PO_4 as standard references; *J*/Hz. *Selected spectroscopic data* for **5a**,**b**: **5a**: $^{13}C\{^1H\}$ NMR: δ 1.2 [d, ^3J(PC) 2.6, CSi(CH$_3$)$_3$], 1.5 [d, ^3J(PC) 13.0, CSi(CH$_3$)$_3$], 3.4 [d, ^3J(PC) 2.7, CHSi(CH$_3$)$_3$], 4.1 [d, ^3J(PC) 2.6, CHSi(CH$_3$)$_3$], 24.4 (s, $NCH_2CH_2CH_2$), 25.2 (s, $NCH_2CH_2CH_2$), 26.0 (s, $NCH_2CH_2CH_2$), 40.8 [d, ^3J(PC) 8.5, CH(SiCH$_3$)$_2$], 45.9 (s, $NCH_2CH_2CH_2$), 50.6 [d, ^3J(PC) 4.5, $NCH_2CH_2CH_2$], 175.9 [dd, ^1J(PC) 101.1, ^2J(PC) 7.1, C=N], 199.0 [d, ^2J(PC) 8.2, ^5J(PC) 2.9, ^1J(WC) 127.0, *cis*-CO], 200.3 [d, ^1J(PC) 85.9, C=P], 201.1 [d, ^2J(PC) 33.0, *trans*-CO]. MS (pos.-CI; NH_3, ^{184}W) *m/z* (%): 851 (2) $[M+H]^+$. **5b**: $^{13}C\{^1H\}$ NMR: δ 1.0–2.3 [m, br, CSi(CH$_3$)$_3$], 11.9–14.1 [$C_5(CH_3)_4$], 22.7 [d, ^3J(PC) 36.4, $C_5(CH_3)$], 24.6 (s, $NCH_2CH_2CH_2$), 25.0 (s, $NCH_2CH_2CH_2$), 25.8 (s, $NCH_2CH_2CH_2$), 46.3 [d, ^3J(PC) 1.9, $NCH_2CH_2CH_2$], 50.4 [d, ^3J(PC) 4.8, $NCH_2CH_2CH_2$], 67.8 [d, ^1J(PC) 16.2, $C_5(CH_3)_5$-$C1$], 136.9 [d, ^2J(PC) 5.2, $C_5(CH_3)_5$-$C2/5$], 137.3 [d, ^2J(PC) 8.2, $C_5(CH_3)_5$-$C2/5$], 141.9 [d, ^3J(PC) 6.4, $C_5(CH_3)_5$-$C3/4$], 142.2 [d, ^3J(PC) 5.8, $C_5(CH_3)_5$-$C3/4$], 174.7 [dd, ^1J(PC) 101.4, ^2J(PC) 8.0, C=N], 197.0 [dd, ^2J(PC) 8.4, ^5J(PC) 2.4, ^1J(WC) 126.9, *cis*-CO], 199.5 [d, ^2J(PC) 34.7, *trans*-CO], 199.9 [d, ^1J(PC) 84.9, C=P]. MS (pos.-CI; NH_3, ^{184}W) *m/z* (%): 825 (4) $[M+H]^+$.

§ *Crystal structure determination* of **5a**: *Crystal data*: $C_{25}H_{46}ClN_2O_5P_2Si_4W$; monoclinic, space group $P2_1/c$, a = 10.854(2), b = 11.864(2), c = 29.372(4) Å, β = 94.16(2)°, U = 3772.3 Å^3, Z = 4, μ = 3.4 mm^{-1}, T = −130 °C. *Data collection*: a colourless crystal *ca.* 0.4 × 0.3 × 0.3 mm was used to record 9019 intensities on a Stoe STADI-4 diffractometer (Mo-Kα radiation, $2\theta_{max}$ = 50°); 6639 reflections were independent (R_{int} = 0.025). An absorption correction based on ψ-scans was applied, with transmissions 0.72–0.80. *Structure refinement*: the structure was solved by the heavy-atom method and refined anisotropically on F^2 (program SHELXL-97, G. M. Sheldrick, Univ. of Göttingen) to $wR2$ 0.072, $R1$ 0.033 for 373 parameters and 59 restraints; S = 1.05, max. $\Delta\rho$ 1.2 e Å^{-3}. The hydrogen atoms were included using a riding model or rigid methyl groups.

CCDC 161074. See http://www.rsc.org/suppdata/cc/b1/b102250b/ for crystallographic data in CIF or other electronic format.

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