Competitive formation of η¹-1-phosphaallene and 1*H*-phosphirene complexes

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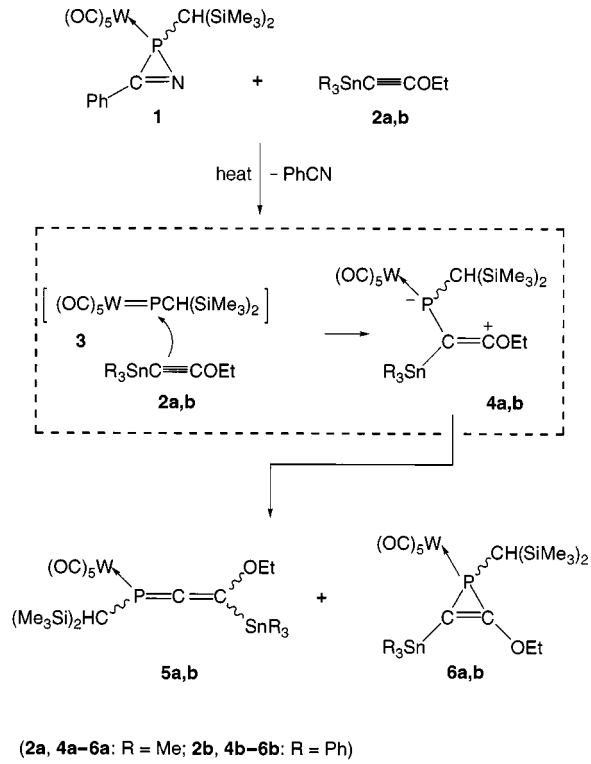
The 2*H*-azaphosphirene complex 1 reacts with triorganostannyl(ethoxy)acetylenes 2a,b to yield bifunctional η¹-1-phosphaallene 5a,b and 1*H*-phosphirene complexes 6a,b; 5a,b and 6a,b are characterized by NMR spectroscopy (^{13}C, ^{31}P) and complex 6b by single crystal X-ray diffraction.

1-Phosphaallenes[1] and their isomers, 1*H*-phosphirenes,[2] and complexes of both,[1,2] have attracted interest because of their synthetic applications in heterocyclic chemistry. At present, there are three main routes to 1-phosphaallenes: elimination of silanolate, reactions of phosphaketenes with phosphoranyl ylides or 1,3-shift reactions of alkinylphosphanes.[1] Despite current research activities, only one example of an η¹-1-phosphaallene complex is known, obtained from a complexation reaction with nickel tetracarbonyl.[3] Furthermore, in contrast to thermally induced rearrangements of cyclopropenes to allenes,[4] related transformations of 1*H*-phosphirene complexes into η¹-1-phosphaallene complexes, or *vice versa*, have not been reported.

We now report the first example of competitive formation of η¹-1-phosphaallene and 1*H*-phosphirene complexes, which has been found to proceed upon thermal decomposition of the 2*H*-azaphosphirene complex **1**[5] in the presence of triorganostannyl(ethoxy)acetylenes **2a**,**b**.[7]



Scheme 1 *Reagents and conditions*: **5a**,**b** and **6a**,**b**: 1 mmol **1** was treated with 2 mmol **2a** at 80 °C for 1.5 h or with 2 mmol **2b** at 70 °C for 2.5 h, respectively. Work-up by column chromatography at low temperature afforded **5a** and **6a** as a mixture, which could not be further separated, and **5b**, **6b**, which have been fully characterized (**5b**: 58%, mp 116 °C; **6b**: 33%, mp 128 °C); the dotted lines indicate the reaction course proposed.

Complex **1** reacts on heating in solution with the acetylene derivatives **2a**,**b** to give the η¹-1-phosphaallene complexes **5a**,**b** and the corresponding 1*H*-phosphirene complexes **6a**,**b** (Scheme 1). The product formation is explained as followed: thermally induced ring-cleavage of the 2*H*-azaphosphirene complex yields benzonitrile, determined by IR spectroscopy, and the phosphanediyl complex [(OC)$_5$W=PCH(SiMe$_3$)$_2$] **3** in the first reaction step. As illustrated in Scheme 1, reaction of **3** with the alkynes **2a**,**b** leads to zwitterionic products **4a**,**b**, which can be regarded as common precursors of the final products **5** and **6**. Furthermore, because the complexes **5b** and **6b** remain unchanged upon heating of pure samples, subsequent rearrangements (**5**–**6** and/or **6**–**5**) can be excluded with reasonable certainty.

The composition and constitution of **5a**,**b** and **6a**,**b** are confirmed by NMR spectroscopic and **5b**, **6b**, additionally, by mass spectrometric investigations.‡ The typical ^{13}C NMR data of **6a**,**b** (**6a**: δ 226.5, $^1J_{PC}$ 90.9 Hz; **6b**: δ 228.2, $^1J_{PC}$ 90.7 Hz) unambigously establish the existence of the 1-phosphaallene moiety in **5a**,**b**. The coordination mode is confirmed by the $^1J_{WP}$ coupling constant values of 262.6 Hz (**5a**) and 265.5 Hz (**5b**), which are in the expected range of η¹-P-coordinated ligands with low-coordinated phosphorus.[7]

In comparison to the related 2-ethoxy substituted 1*H*-phosphirene complex **6c**,[8] the complexes **6a**,**b** show high-field shifted resonances of the phosphorus nuclei at δ −107.4 (**6a**) and −98.2 (**6b**) (*cf.* δ −90.8[8]). Compared to **6c** the carbon-13 resonance values of the three-membered ring in **6a**,**b** are remarkably downfield shifted [C^2: δ 175 ± 3 (*cf.* 158.8), C^3: δ 100 ± 5 (*cf.* 88.1)]. Furthermore, the $^{(1+2)}J_{PC}$ coupling constants of these carbon atoms of **6a**,**b** show greater differences in magnitudes than those observed for 1*H*-phosphirene complex

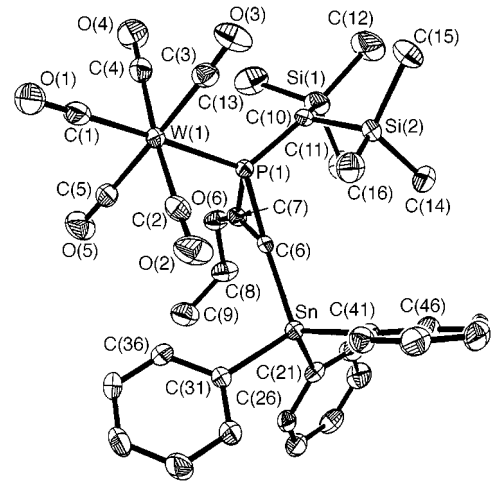


Fig. 1 Molecular structure of complex **6b** in the crystal. Selected bond lengths (pm) and angles (°): W(1)–P(1) 249.83(11), P(1)–C(7) 176.8(4), P(1)–C(6) 182.8(4), P(1)–C(10) 182.2(4), O(6)–C(7) 132.6(5), Sn–C(6) 213.5(4), Sn–C(25) 213.8(4); W(1)–P(1)–C(10) 119.04(14), C(7)–P(1)–C(6) 43.14(19), C(6)–C(7)–P(1) 70.9(3), C(7)–C(6)–P(1) 66.0(2), O(6)–C(7)–C(6) 146.0(4).

6c (**6a**,**b**: C^3: $^{(1+2)}J_{PC}$ 25 ± 3 Hz, C^2: $^{(1+2)}J_{PC}$ ⩽ 3 Hz; **6c**: 4.9 and 2.0 Hz[8]).

The X-ray crystal structure analysis of the complex **6b** confirms the molecular structure (Fig. 1).§ In comparison to the structure [8] of **6c** (values given in square brackets) the endocyclic P–C bond lengths of **6b** are lengthened {P(1)–C(6) 1.828(4) [1.792(8)], P(1)–C(7) 1.768(4) [1.753(8)], C(6)–C(7) 1.323(6) [1.298(11)] Å}, probably because of increased steric strain in **6b**.

We are currently investigating the synthetic potential of this new route to η^1-1-phosphaallene complexes and the reactivity of the complexes **5a**,**b** and **6a**,**b**.

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Notes and References

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‡ Correct elemental analysis were obtained for complexes **5b** and **6b**. NMR data were recorded at room temperature in $CDCl_3$ solution at 50.3 MHz (^{13}C) and 81.0 MHz (^{31}P); *J*/Hz. *Selected spectroscopic data* for **5a**: ^{13}C NMR, δ −8.3 (s, $^1J_{119SnC}$ 356.3, $^1J_{117SnC}$ 339.3, Hz, $SnMe_3$), 156.1 (s, P=C=*C*), 196.4 (d, $^2J_{PC}$ 9.7 Hz, *cis*-CO), 200.2 (d, $^2J_{PC}$ 30.3 Hz, *trans*-CO), 226.5 (d, $^1J_{PC}$ 90.9 Hz, P=*C*=C); ^{31}P NMR, δ 76.4 (s, $^1J_{WP}$ 262.6, $^3J_{119SnP}$ 152.8, $^3J_{117SnP}$ 144.3 Hz). **5b**: ^{13}C NMR, δ 154.5 (d, $^2J_{PC}$ 2.0 Hz, P=C=*C*), 196.2 (d, $^2J_{PC}$ 9.2 Hz, *cis*-CO), 199.8 (d, $^2J_{PC}$ 30.4 Hz, *trans*-CO), 227.8 (d, $^1J_{PC}$ 90.4 Hz, P=*C*=C); ^{31}P NMR, δ 87.4 (s, $^1J_{WP}$ 265.5, $^3J_{119SnP}$ 174.7, $^3J_{117SnP}$ 167.5 Hz). **6a**: ^{13}C NMR, δ −6.8 (s, $^1J_{119SnC}$ 371.4, $^1J_{117SnC}$ 355.1 Hz, $SnMe_3$), 97.2 (d, $^{(1+2)}J_{PC}$ 23.2 Hz, PCSn), 172.5 (s, $^2J_{SnC}$ 53.4 Hz, PCO), 197.6 (d, $^2J_{PC}$ 8.2, $^1J_{WC}$ 126.4 Hz, *cis*-CO), 199.8 (d, $^2J_{WC}$ 29.3 Hz, *trans*-CO); ^{31}P NMR, δ −107.4 (s, $h_{1/2}$ 15 Hz, $^1J_{WP}$ 265.1, $^2J_{SnP}$ 49.6 Hz); MS (EI, ^{120}Sn, ^{184}W): M^+ at *m*/*z* = 934. **6b**: ^{13}C NMR, δ 94.7 (d, $^{(1+2)}J_{PC}$ 21.4 Hz, PCSn), 175.4 (d, $^{(1+2)}J_{PC}$ 3.1 Hz, PCO), 197.2 (d, $^2J_{PC}$ 8.5 Hz, *cis*-CO), 198.7 (d, $^2J_{PC}$ 28.5 Hz, *trans*-CO); ^{31}P NMR, δ −98.2 (s, $h_{1/2}$ 95 Hz); MS (EI, ^{120}Sn, ^{184}W): M^+ at *m*/*z* = 934.

§ *Crystal data* for **6b**: $C_{34}H_{39}O_6PSi_2SnW$, monoclinic, space group $P2_1/c$, a = 21.024(2), b = 9.2419(10), c = 19.619(3) Å, β = 95.753(15)°, U = 3792.8(8) Å^3, Z = 4, μ = 3.8 mm^{-1}, T = −130 °C. Colourless block 0.6 × 0.5 × 0.5 mm, Mo-Kα radiation, Stoe STADI-4 diffractometer, 8387 intensities to $2\theta_{max}$ 50°, 6681 unique (R_{int} 0.021) used for all calculations. Structure solution by heavy-atom method, anisotropic refinement on F^2 (program SHELXL-97, G. M. Sheldrick, Univ. of Göttingen). Treatment of H atoms: rigid methyls, others riding. Final $wR(F^2)$ 0.075, conventional $R(F)$ 0.030 for 412 parameters. CCDC 182/930.

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