

Synthesis of Alkylidenephosphiranes by Extrusion of Nitrogen from 3-Alkylidene-4,5-dihydro-3*H*-1,2,4-diazaphospholes

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The 3-alkylidene-4,5-dihydro-3*H*-1,2,4-diazaphospholes **4**, obtained from diphenylmethylene(mesityl)phosphine **3** and silyl diazo ketones **1**, undergo thermal extrusion of nitrogen to form alkenyl phosphines **7** and alkylidenephosphiranes **8**; the structures of these products have been established by single crystal X-ray structure analyses.

Three-membered rings containing a phosphorus atom have been investigated in some detail only in the last few years:¹ in particular, phosphiranes^{1,2} and 1*H*-phosphirenes.³ Phosphacyclopropanes bearing an exocyclic double bond, such as alkylidenephosphiranes,⁴ 2,3-bisalkylidenephosphiranes^{5,6} and alkylidenediphosphiranes^{6,7} are known, but their properties and chemistry have been less well studied. Structure, ring strain and inversion barriers at phosphorus of the first two systems mentioned have been determined by *ab initio* calculations for the parent compounds.⁸ The only alkylidenephosphirane so far known was obtained by addition of dichlorocarbene to a 1-phosphaallene.⁴ Herein, we describe a new synthetic route to this ring system, providing the first derivatives functionalised at the exocyclic C=C bond, and report the experimentally determined geometry.

Silyl diazo ketones maintain an equilibrium with minor (< 1%) amounts of 2-siloxy-1-diazoalkenes **2**, which can be trapped by [3 + 2] cycloaddition with suitable alkenes.⁹ Similarly, **1a,b** react readily, even at 20 °C, with phosphalkene **3** to form the 3-alkylidene-4,5-dihydro-3*H*-1,2,4-diazaphospholes **4** (**4a**, 30 min, 78% yield; **4b**, 16 h, 77%).‡ The regioselectivity of the cycloaddition step is the same as for the cycloaddition of diazoalkanes to several other phosphalkenes.^{10,11} The *E*-configuration at the exocyclic double bond is indicated by the magnitude of the coupling constant ⁴*J*_{P,CH₃} (9.3–9.4 Hz) and is confirmed by a single crystal X-ray structure determination of **4a** which will be reported elsewhere.

Thermal extrusion of nitrogen from **4a,b** occurs in boiling toluene in 16 h, yielding a mixture of the (2-siloxy-1-alkenyl)-phosphines **7a,b** and of the alkylidenephosphiranes **8a,b** (yields: **7a**, 32%; **8a**, 47%; **7b**, 33%; **8b**, 48%).§ These major products can be isolated simply by fractionating crystallisation. The solids are neither oxygen- nor moisture-sensitive. The phosphirane structure is indicated by the ³¹P NMR signal at high

field ($\delta \approx -135$); as expected, the P nucleus is more strongly shielded than in 2,2-dichloro-3-diphenylmethylene-1-(2,4,6-tri-*tert*-butylphenyl)phosphirane ($\delta -93.4$).⁴ The *cis*-relationship between the phosphorus atom and the siloxy group with respect to the exocyclic double bond (*Z*-configuration) is suggested by a ⁵*J*_{P,CH} coupling constant of 4.0 Hz.

Single crystal X-ray structure determinations of **7a** and **8a** (Figs. 1 and 2) establish that the double bond configuration is *E*

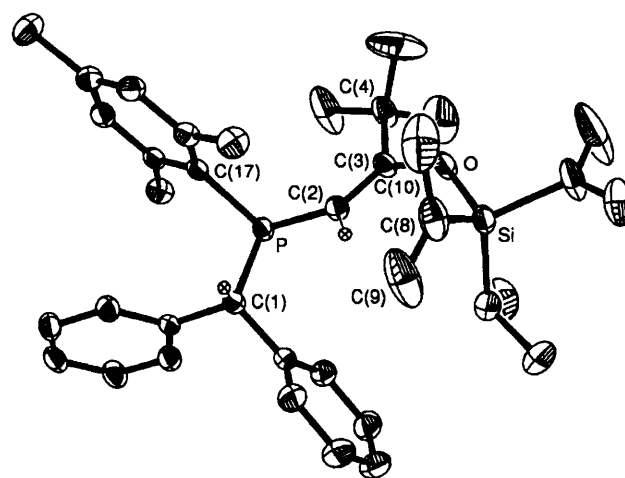
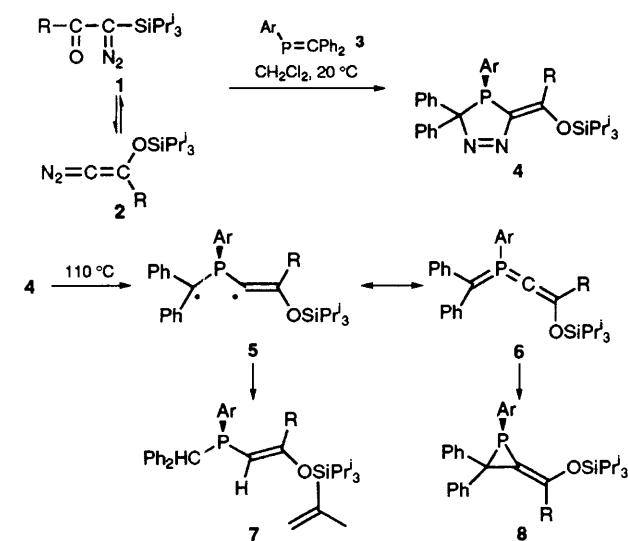


Fig. 1 Crystal structure of **7a** with 30% thermal ellipsoids. Selected bond distances (Å) and angles (°): P–C(1) 1.886(4), P–C(2) 1.805(4), P–C(17) 1.853(4), C(2)–C(3) 1.342(5), C(3)–O 1.378(4), O–Si 1.647(3), C(8)–C(9) 1.314(9), C(8)–C(10) 1.500(9); C(1)–P–C(2) 99.3(2), C(1)–P–C(17) 98.7(2), C(2)–P–C(17) 109.1(2), P–C(2)–C(3) 132.6(3), C(2)–C(3)–C(4) 130.2(4), C(2)–C(3)–O 120.1(3), C(3)–O–Si 133.8(2). Selected torsion angles (°): P–C(2)–C(3)–C(4) 13.1(8), P–C(2)–C(3)–O –169.8(3), C(2)–C(3)–O–Si 10.2(6). See footnote¶ for disorder of the isopropyl group [C(14), C(15), C(16)].



4–8: Ar = 2,4,6-Me₃-C₆H₂; **a:** R = Bu^t; **b:** R = 1-adamantyl

Scheme 1

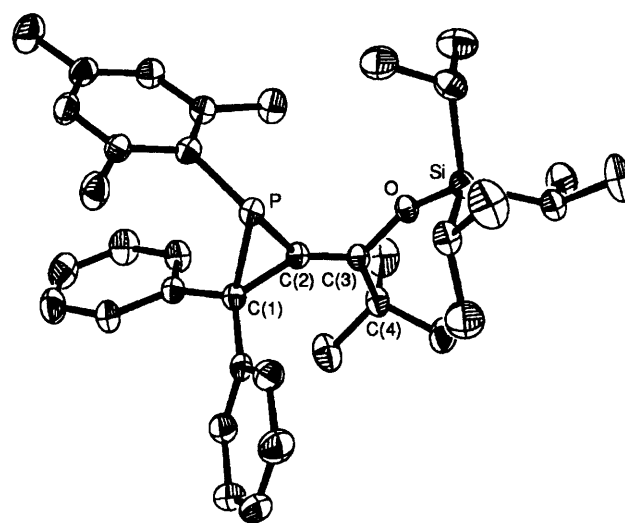


Fig. 2 Crystal structure of **8a**. For selected bond lengths and angles, see Fig. 3.

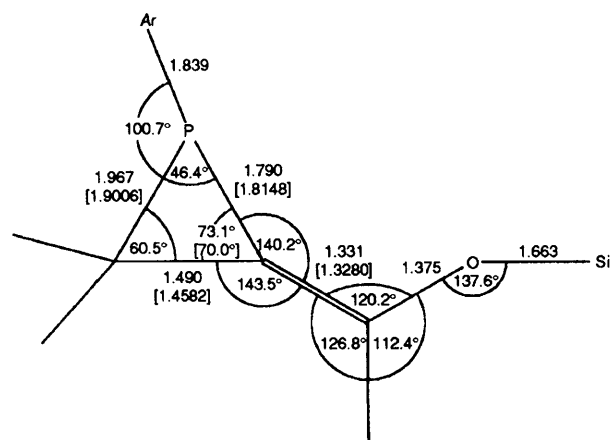


Fig. 3 Bond lengths (Å) and angles (°) in **8a**. Estimated standard deviations are 0.003–0.004 Å for bond lengths, 0.1° for bond angles at P, and 0.2–0.3° for the other angles. Values obtained for the geometry-optimised MP2/6-31G* structure of the parent compound⁸ are given in brackets. The angle between the plane of the three-membered ring and the P–C–aryl bond vector (or P–H bond vector) is 82.5° (83.9°).

in **7a**, but Z in **8a**.[¶] Thus, formation of phosphine derivatives **7** from **4** occurs with retention, whereas formation of alkylidene-phosphiranes **8** occurs with inversion of the configuration at the silyloxy-substituted C=C bond. These observations suggest that thermolysis of **4** initially generates the diradical **5**, which can either abstract hydrogen atoms from a silicon-attached isopropyl group or undergo isomerisation to the 2-phosphabutatriene **6**. By analogy to the 2-phosphaallene → phosphirane isomerisation,¹² a (conrotatory) 4π -cyclisation¹³ leads to **8**, whereby the obviously thermodynamically more favourable Z-diastereoisomer is formed exclusively.

Fig. 3 shows the experimentally determined values for the geometry of the alkylidene-phosphirane skeleton of **8a** together with those obtained for the parent 2-methylenephosphirane⁸ from *ab initio* calculations. Remarkably, the two ring-bonds involving the diphenyl-substituted ring atom in **8a** are distinctly longer than in the parent system. Presumably, this is mainly due to the steric repulsion between the two phenyl rings and the P-attached mesityl ring as well as the Bu^t group. The steric overcrowding at the three-membered ring of **8a** is also evident from the torsion angles around the exocyclic double bond [e.g. P–C(2)–C(3)–O 13.7(5)° and C(1)–C(2)–C(3)–C(4) 26.9(6)°] and is likely to be responsible for the slight pyramidalisation of the ring atom C(2) (sum of valence angles 356.8°); thus, the bond vector C(2)=C(3) forms an angle of 11.8° with the ring plane and points in the direction opposite to the P–C(17) vector which forms an angle of 82.5° with the ring.

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Footnotes

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‡ All new compounds gave satisfactory elemental analyses, and were characterised by ¹H, ¹³C (CDCl₃, 100.61 MHz), and ³¹P NMR (CDCl₃, 161.98 MHz) spectra. Selected data for **4a**: yellow, decomp. temp. 112 °C; ¹³C NMR (J/Hz) δ 29.0 (d, ⁴J_{PC} 9.4, CMe₃), 105.0 (d, ¹J_{PC} 27.3, CPh₂), 139.6 (d, ¹J_{PC} 36.1, P=C=), 176.9 (d, ²J_{PC} 25.4, =C–O); ³¹P NMR δ –55.0.

4b: yellow, decomp. temp. 111 °C; ³¹P NMR δ –55.0.

§ Selected data **7a**: colourless, mp 111 °C; ¹³C NMR (T = 333 K, J/Hz)

δ 29.1 (d, ⁴J_{PC} 9.3, CMe₃), 38.8 (d, ³J_{PC} 2.6, CMe₃), 52.2 (d, ¹J_{PC} 11.1, CHPh₂), 99.0 (d, ¹J_{PC} 21.6, P=C=), 166.9 (d, ²J_{PC} 24.9, =C–O); ³¹P NMR δ –25.3.

7b: colourless, mp 115 °C; ³¹P NMR δ –25.8.

8a: colourless, mp 135 °C; ¹³C NMR (J/Hz) δ 14.2 (d, ⁵J_{PC} 4.0, SiCH), 28.7 (s, CMe₃), 39.8 (s, CMe₃), 52.1 (d, ¹J_{PC} 21.3, CPh₂), 114.8 (d, ¹J_{PC} 47.6, P=C=), 164.5 (d, ²J_{PC} 7.2, =C–O); ³¹P NMR δ –134.5.

8b: colourless, mp 168 °C; ³¹P NMR δ –135.4.

¶ *Crystal structure determination 7a*: C₃₇H₅₁OPSi, triclinic, space group P $\bar{1}$, a = 10.947(5), b = 12.275(3), c = 15.277(4) Å, α = 66.90(2), β = 80.43(2), γ = 71.55(2)°, V = 1789.1(1.0) Å³, Z = 2, D_c = 1.060 g cm⁻³, μ(Mo-Kα) = 0.135 mm⁻¹, Siemens P4 diffractometer, ω-scan, 2θ_{max} = 46.94°; 5484 reflections measured (hemisphere), 5258 symmetry-independent reflections (R_{int} = 0.072), full-matrix least-squares refinement on F² (program SHELXLS-93; G. M. Sheldrick, Universität Göttingen, 1993) with 372 variables. H-atoms are in calculated positions and were treated as riding atoms, H-atoms at C(14) and C(15) were not located. R1 = 0.0645 for 3499 observed [I > 2σ(I)], wR2 = 0.1894 for all independent reflections, residual electron density between 0.43 and –0.22 e Å⁻³. Disorder of the isopropyl group leads to the observation of an averaged position for the C(15) methyl group, efforts to resolve which into two geometrically meaningful positions and to refine them were unsuccessful. A set of data collected at 193 K was of poor quality and the disorder could again not be treated in a meaningful way.

8a: C₃₇H₅₁OPSi, triclinic, space group P $\bar{1}$, a = 13.875(5), b = 15.467(5), c = 8.789(4) Å, α = 91.73(2), β = 100.73(2), γ = 68.54(4)°, V = 1723.3(1.3) Å³, Z = 2, D_c = 1.100 g cm⁻³, μ(Mo-Kα) = 0.140 mm⁻¹, Enraf-Nonius CAD4 diffractometer, ω–2θ-scan, 2θ_{max} = 46.92°, 5760 measured reflections (hemisphere), 5361 symmetry-unrelated reflections (R_{int} = 0.046), full-matrix least-squares refinement on F² (programme SHELXLS-93) with 373 variables, R1 = 0.0519 for 3501 observed reflections [I > 2θ(I)], wR2 = 0.1302 for all independent reflections; residual electron density between 0.20 and –0.22 e Å⁻³.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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