

Phosphadisilacyclobutenes by stepwise silylene additions to phosphalkynes

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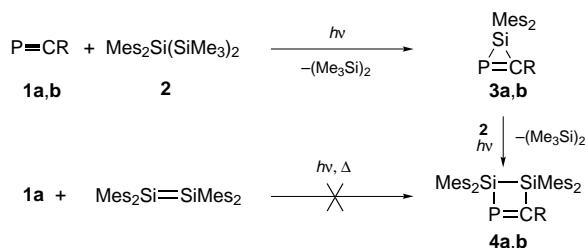
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The phosphalkynes $\text{RC}\equiv\text{P}$ [$\text{R} = 1\text{-adamantyl}$ (**1a**) or $\text{R} = 2\text{-methylcyclohexyl}$ (**1b**)] react with dimesitylsilylene, presumably by [2+1] cycloaddition followed by silylene insertion, to furnish phosphadisilacyclobutenes; the molecular structure of the adamantyl derivative was determined by X-ray crystallography.

Since the synthesis of the first thermally stable phosphalkyne¹ in 1981, the chemistry of this class of compounds has experienced an explosive development which is reflected in several review articles.² However, there are only a few examples of [2+1] cycloadditions to the $\text{P}=\text{C}$ triple bond and concrete evidence for [2+2] cycloadditions is still lacking. It has been shown that reaction of the silylene R_2Si : ($\text{R} = \text{CMe}_3$) with **1a** proceeds smoothly to furnish the phosphasilirene³ as an oily liquid, similar to the 2*H*-phosphirenes⁴ accessible by other routes and for which crystals suitable for X-ray structural analyses can only be obtained after formation of the corresponding $\text{W}(\text{CO})_5$ complexes. A crystalline germaphosphirene has been prepared by addition of the germylene R_2Ge : [$\text{R} = \text{CH}(\text{SiMe}_3)_2$]⁵ to *tert*-butylphosphaacetylene.⁶ Addition of the stannylene R_2Sn : [$\text{R} = \text{CH}(\text{SiMe}_3)_2$] to the same triple bond system appears to proceed by a different course since the formation of the phosphadistannacyclobutene obtained was interpreted as being more indicative of a [2+2] addition of the distannene,⁷ $\text{R}_2\text{Sn}=\text{SnR}_2$, to the phosphalkyne.⁸ However, as can be seen from the present results, the formation of this four-membered ring system may also be explained in terms of an initial [2+1] cycloaddition and subsequent insertion of a further stannylene unit into an intermediate three-membered ring system.

Reaction of dimesitylsilylene, generated photochemically from the trisilane **2**, with the phosphalkynes **1a,b**^{9,10} afforded the phosphadisilacyclobutenes **4a** (pale yellow crystals, mp 285 °C, yield 18 %) and **4b** (yellow crystals, mp 275 °C, yield 14%) (Scheme 1). The structures of these two representatives of a new four-membered ring system were confirmed by their analytical and spectroscopic data.† Of high diagnostic value are the positions of their ³¹P NMR signals, which are strongly deshielded and appear at δ 441 (**4a**) and 443 (**4b**) in the region typical of silyl-substituted phosphalkenes.¹¹ In the ²⁹Si NMR spectra the two silicon atoms give rise to doublets with ¹ $J_{29\text{Si},31\text{P}}$ and ² $J_{29\text{Si},31\text{P}}$ couplings.

Final confirmation of the structures of these molecules was provided by an X-ray crystallographic analysis of **4a** (Fig. 1) which revealed an almost planar ring (angular sum: 359.1°).‡



The largest endocyclic angle occurred at the carbon atom and the two smallest at the silicon atoms. In comparison to the only currently known phosphasilirene,³ all endocyclic bond lengths are elongated to some extent, indicating the differing bonding situations in the three- and four-membered ring systems.

The different behaviour of di-*tert*-butylsilylene and dimesitylsilylene towards **1a** are assumed to be due to the larger spatial requirements of the *tert*-butyl groups which effectively shield the three-membered ring from further attack. The reactions of **1a,b** with **2** probably also proceed through the three-membered ring intermediates **3**, which undergo subsequent insertion of a second silylene molecule to furnish the four-membered ring products isolated. However, a second possibility, in which the photochemically generated silylene **2** undergoes primary dimerisation to the disilene with a $\text{Si}=\text{Si}$ double bond and subsequent [2+2] cycloaddition with the phosphalkyne, is also feasible. Thus, we have prepared tetramesityldisilene¹² and examined its behaviour towards **1a** under both photochemical and thermal conditions. In neither case could any reaction be detected. Hence, not only have we obtained evidence in favour of the proposed [2+1] cycloaddition to the $\text{P}=\text{C}$ triple bond with subsequent rapid silylene insertion into the three-membered ring, but also further illustrated the absence of unequivocally demonstrated [2+2] cycloadditions to phosphalkynes.²

However, an alternative mechanism for the formation of **4a,b**, in which—according to Scheme 2—the silylene is trapped by addition to the phosphorus atoms of **1a,b** to furnish an ylide intermediate, followed by the addition of a second silylene molecule and ring closure cannot be excluded.§

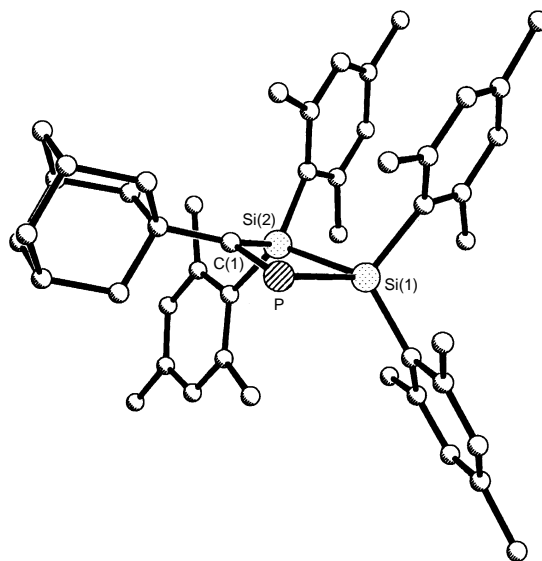
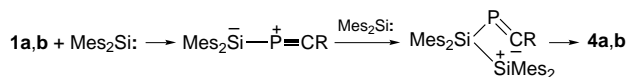


Fig. 1 Molecular structure of **4a** in the crystal (hydrogen atoms omitted). Selected bond lengths (pm) and angles (°): C(1)–P 170.1(3), P–Si(1) 228.8(1), Si(1)–Si(2) 239.1(1), Si(2)–C(1) 190.3(3), Si(1)–P–C(1) 90.1(1), P–Si(1)–Si(2) 77.6(1), Si(1)–Si(2)–C(1) 85.5(1), P–C(1)–Si(2) 108.9(2).



Scheme 2

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Footnotes

† Selected spectroscopic data for **4a**: δ_{H} 1.55 (m, 6 H), 1.87 (m, 3 H), 2.04 (s, 6 H), 2.06 (s, 6 H), 2.18 (m, 6 H), 2.43 (s, 12 H), 2.63 (s, 12 H), 6.59 (s, 8 H); δ_{C} 20.89 (C_p), 26.04 (C_p), 26.17 (C_p), 29.82 (CH), 36.88 (CH₂), 46.05 (CH₂), 46.20 (CH₂), 129.05 (CH), 138.22 (C_q), 143.37 (C_q), 144.87 (C_q) (C_p and C_q refer to primary and quaternary carbon atoms); δ_{P} 441.2 (s); δ_{Si} 2.15 (d, $^2J_{\text{Si}^{29}\text{Si}^{31}\text{P}}$ 8 Hz), -20.2 (d, $^1J_{\text{Si}^{29}\text{Si}^{31}\text{P}}$ 67 Hz); MS (CI, isobutane) m/z 711 (MH⁺, 48%). For **4b**: δ_{H} 1.40 (m, 10H), 1.45 (s, 3 H), 2.02 (s, 6 H), 2.06 (s, 6 H), 2.44 (s, 12 H), 2.62 (s, 12 H), 6.59 (s, 8 H); δ_{C} 20.95, 23.23, 25.99, 26.30, 41.75, 48.29, 129.18, 129.73, 132.57, 134.29, 138.29, 143.41, 144.89; δ_{P} 442; δ_{Si} 2.2 (d, $^2J_{\text{Si}^{29}\text{Si}^{31}\text{P}}$ 8.2 Hz), -22.7 (d, $^1J_{\text{Si}^{29}\text{Si}^{31}\text{P}}$ 42 Hz); MS (CI, isobutane) m/z 673 (MH⁺, 100 = %).

‡ Crystal data for **4a**: C₄₇H₅₉PSi₂, $M = 711.1$, crystal dimensions 0.70 × 0.60 × 0.30 mm, monoclinic, space group $P2_1/n$, $a = 1318.3(1)$, $b = 1923.2(1)$, $c = 1652.4(1)$ pm, $\beta = 98.589(6)^\circ$, $V = 4142.4(5)$ pm³, $Z = 4$, $D_{\text{c}} = 1.140$ g cm⁻³, $\lambda(\text{Mo-K}\alpha) = 71.073$ pm, $T = 296(2)$ K, $2\theta_{\text{max}} = 55^\circ$, unique reflections 9513, observed [$F > 2\sigma(F)$] 6884, data-to-parameter ratio 15.23. The structure was solved by direct phase determination using the Siemens SHELXTL PLUS program system and refined by full-matrix least-squares techniques. Hydrogen atoms were placed in calculated positions, and all other atoms were refined anisotropically; $R = 0.066$, $R_w = 0.062$. CCDC 182/516.

§ We thank one of the referees for drawing our attention to this possibility.

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