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The First X-ray Structure of a Phosphasilene: 1,3,4-Triphospha-2-silabutene-(1)

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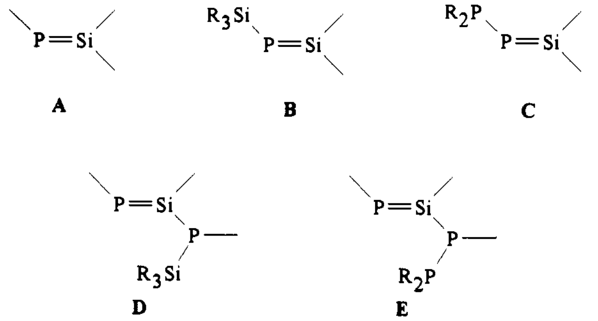
Since their first synthesis in 1984,[1] phosphasilenes have been the subject of intensive experimental and theoretical research. While the work of Bickelhaupt and co-workers yielded phosphasilenes of type **A**,[1,2] Driess et al. recently described the preparation of compounds of type **B** and **C**.[3]

In an earlier communication we reported the reaction of *tert*-butyltrichlorosilane (**1**) with 4 equiv of the lithium phosphide **2** to give the lithium 1,2-diphospha-2-silaallyl complex **3**, which was quenched with chlorotrimethylsilane to yield the thermally unstable P=Si double bond system **4**,[4] here described as type D (see Scheme I). However, until now none of the phosphasilenes **A–D** has been isolated in crystalline form, and therefore no X-ray diffraction studies of phosphorus–silicon double bond systems have been performed.

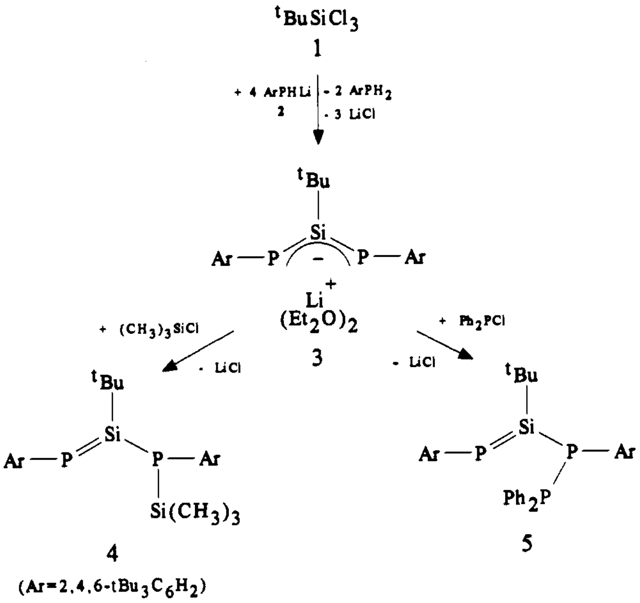
In analogy to the synthesis of **4** we found that compound **3** reacts with chlorodiphenylphosphine in diethyl ether at −78 °C, yielding the 1,3,4-triphospha-2-silabutene-(1) **5**, which represents the first phosphasilene of type **E** (see Schemes I and II). After crystallization from *n*-pentane at 4 °C, pure **5** can be isolated as a yellow solid highly sensitive to air and moisture.[5] Its constitution is determined by its mass and NMR spectra, and in managing to obtain suitable single crystals we were able to obtain the first X-ray structure of a phosphasilene.[6,7]

Compound **5** (see Figure 1) represents an (*E*)-isomer of a 1,3,4-triphospha-2-silabutene-(1), the P1–Si1–P2–P3 atoms building up a rather small dihedral angle (τ_1 = 4.9°) and forming an almost planar trapezoid (see Figure 2) with a rather short P1–P3 distance (3.68 Å).

Scheme I. Phosphasilene Types A–E



Scheme II. Synthesis of **3–5**



The alkyl and aryl substituents are all pointing outward, sterically protecting the P=Si—P—P skeleton. The P1–Si1 bond length (2.094 Å) is characteristically shorter than the neighboring Si1–P2 distance (2.254 Å), which matches very well with the average Si–P single bond distance of 2.25 Å.[9] The P2–P3 single bond length (2.251 Å) and the other bond distances are just as expected. Like in all λ^3-P=E double bonds, the angle at the dicoordinated phosphorus P1 (104.2°) shows a value smaller than 120°.

The silicon is tricoordinated to a carbon atom of the *tert*-butyl group and two phosphorus atoms, showing a quite unusual sum of angles (356.7°), which leaves Si1 about 0.21 Å under the P1–P2–C19 plane. Looking at the molecule along the P1=Si1 bond axis (see Figure 2), the atoms C1 and C19 form an angle of τ_2 = 3.4°, indicating a nearly planar arrangement of C1–P1–Si1–C19 as expected for a normal double bond; however, C1 and P2 show an angle of only τ_3 = 161.0°, leaving P2 displaced out of this plane.

Compared with the bond distance in the allyl system **3** (r_{PSi} = 2.11 Å),[4] the P1=Si1 distance is a little shorter (2.094 Å), but it exceeds the values predicted by theoretical studies on phosphorus–silicon double bonds (2.04–2.06 Å).[10] The shortening in relation to an average single bond is smaller (0.16 Å) than reported

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(1) Smit, C. N.; Bickelhaupt, F. *Tetrahedron Lett.* **1984**, *25*, 3011.

(2) (a) Smit, C. N.; Bickelhaupt, F. *Organometallics* **1987**, *6*, 1156. (b) van den Winkel, Y.; Bastiaans, H.; Bickelhaupt, F. *J. Organomet. Chem.* **1991**, *405*, 183.

(3) Driess, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1022.

(4) Niecke, E.; Klein, E.; Nieger, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 751.

(5) For **5**: A solution of 2.38 g (3 mmol) of **3**[4] in 20 mL of dry diethyl ether in a 50-mL three-neck flask was cooled to −78 °C (MeOH/CO_2), mixed with a solution of 0.66 g (3 mmol) of chlorodiphenylphosphine in 5 mL of diethyl ether, and stirred for 2 h at this temperature. The color of the reaction mixture changed from dark red to orange. After the mixture was heated up to 25 °C the solvent was removed by vacuum and 30 mL of dry *n*-pentane was added. The solution was filtered, and the LiCl was washed several times with fresh *n*-pentane. The filtrate was concentrated to 20 mL and left for crystallization at 4 °C. After 1 day, the phosphasilene **5** was isolated as yellow crystals: 1.41 g (57%); mass spectrum *m/z* 822(4) [M]$^+$; ^{31}P NMR (25 °C, C_6D_6) δP1 128.7 (dd, $^3J_{P1P3}$ = 102.1 Hz, $^2J_{P1P2}$ = 23.9 Hz), δP2 69.1 (dd, $^1J_{P2P3}$ = 215.2 Hz, $^2J_{P2P1}$ = 23.9 Hz), δP3 26.1 (dd, $^1J_{P3P2}$ = 215.2 Hz, $^3J_{P3P1}$ = 102.1 Hz); ^{29}Si NMR (25 °C, C_6D_6) δSi1 180.2 (ddd, $^1J_{P1Si1}$ = 203.0 Hz, $^1J_{P2Si1}$ = 141.3 Hz, $^2J_{P3Si1}$ = 13.1 Hz).

(6) Bender, H. R. G.; Klein, E.; Niecke, E.; Nieger, M.; Ranaivonjatovo, H. Unusual Coordination in Phosphorus–Silicon Compounds. *Abstracts of Posters*, 12th International Conference on Phosphorus Chemistry, Toulouse, France, July 6–10, 1992; II-26.

(7) Crystal data for **5**: $C_{52}H_{77}P_3Si$, MW = 823.1, yellow crystals, dimensions 0.15 × 0.20 × 0.30 mm; triclinic, space group $P\bar{1}$ (No. 2), a = 11.269(1) Å, b = 14.153(1) Å, c = 17.569(1) Å, α = 112.86(1)°, β = 96.13(1)°, γ = 99.07(1)°, V = 2.506 nm^3, Z = 2, d_{calc} = 1.09 g cm^{-3}, μ(Cu Kα) = 1.55 mm^{-1}, F(000) = 896. A total of 6280 symmetry-independent reflections ($2\theta_{max}$ = 110°, ω scans) were recorded on an Enraf–Nonius CAD4 diffractometer at T = 293 K. Of these, 3839 reflections with $F > 3\sigma(F)$ were used for the structure solution (direct methods) and refinement (503 parameters) using the SHELXTL-Plus program system. Non-hydrogen atoms were refined anisotropically (full-matrix least-squares, disordered p-^{t}Bu group isotropically); H atoms were refined using a riding model. R = 0.068 (R_w = 0.065, $w^{-1} = \sigma^2(F) + 0.0010F^2$). An absorption correction was applied using the DIFABS program.[8] One p-^{t}Bu-group was disordered (s.o.f. = 0.60(1)).

(8) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(9) Rademacher, P. In Grösse und Gestalt von Molekülen, *Strukturen organischer Moleküle, Physikalische Organische Chemie*; Klessinger, M., Ed.; Verlag Chemie: Weinheim, 1987; p 55.

(10) (a) Dykema, K. J.; Truong, T. N.; Gordon, M. *J. Am. Chem. Soc.* **1985**, *107*, 4535. (b) Lee, J.-G.; Boggs, J. E.; Cowley, A. H. *J. Chem. Soc., Chem. Commun.* **1985**, 773. (c) Schleyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105.

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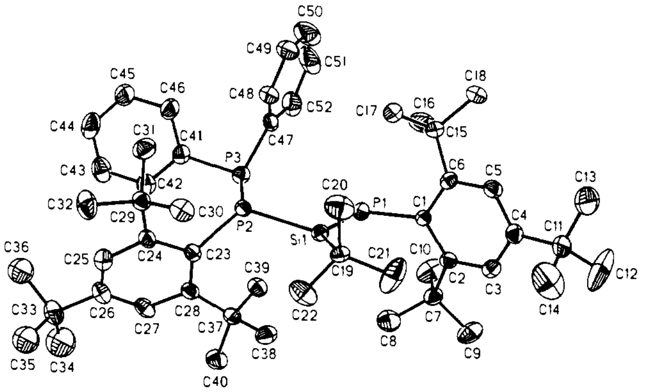

Figure 1. X-ray structure of **5**, showing the atomic numbering scheme with ellipsoids at the 30% probability level. Hydrogen atoms omitted for clarity. Important bond distances (Å) and angles (deg): P1–Si1 2.094(3); Si1–P2, 2.254(3); P2–P3, 2.251(2); C1–P1–Si1, 104.2(2); P1–Si1–P2, 115.2(1); Si1–P2–P3, 103.2(1); τ_1: P1–Si1–P2–P3, 4.9(1).

for P=C[11] and P=Ge[12] systems with 0.20 Å. The rather long P1=Si1 distance and the unusual geometry at the tricoordinated silicon may just be due to the steric crowding in the system but could also be explained by a donation of the lone pair at the P2 atom into the π^* orbital of the double bond.

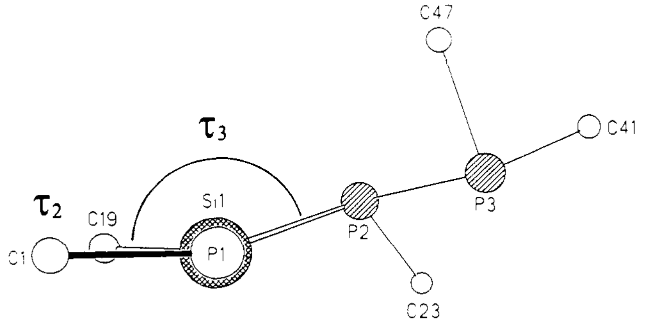

Figure 2. Reduced view of **5** and view along the double bond P1=Si1. τ_2: ∠C1–P1–Si1–C19, 3.4(3)°. τ_3: ∠C1–P1–Si1–P2, 161.0(2)°.

The ^{31}P-NMR spectrum of **5**[5] shows a characteristic AMX spin system with the downfield signal of P1 (128.7 ppm) typical for a dicoordinated phosphorus in phosphasilenes.[1-3,13] The value of the $^3J_{P1P3}$ coupling constant is unusually high (102.1 Hz), indicating a P1–P3 contact through space,[14] which is in agreement with the X-ray structure. The ^{29}Si-NMR spectrum[5] shows a large deshielding for the tricoordinated silicon atom (180.2 ppm). The coupling constants $^1J_{P1=Si}$ = 203.0 Hz and $^1J_{P2-Si}$ = 141.3 Hz are remarkably high and occur only in the phosphino-substituted phosphasilenes **D** and **E**. The corresponding $^1J_{P=Si}$ values of **A**–**C**, often used to characterize a P=Si double bond, are significantly smaller (150–160 Hz).[1-3]

The NMR spectra do not show any sign of (*E*)/(*Z*)-isomerization in solution.

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Supplementary Material Available: Tables of final atomic coordinates, anisotropic displacement parameters, bond distances and angles, and crystal data for **5** (14 pages); a listing of final observed and calculated structure factors for **5** (23 pages). Ordering information is given on any current masthead page.

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[13] Exceptions to the rule are the silyl-substituted compounds of type B, showing a greater shielding of the phosphorus (δ 10–20).[3]

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