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[1 + 4]-Cycloaddition of a stable silylene to 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene

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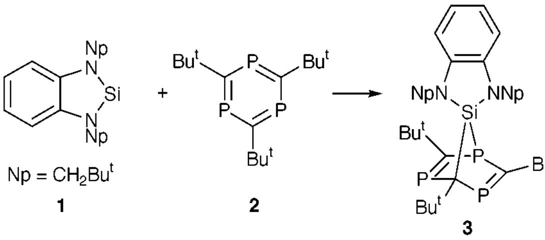
The stable bis(amino)silylene Si[(NCH$_2$Bu^t)$_2$C$_6$H$_4$-1,2] 1 undergoes [1 + 4]-cycloaddition with 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene 2 to afford compound 3: the molecular structure of 3 is supported by NMR spectroscopic data and confirmed by a single crystal X-ray diffraction study.

Addition reactions of transient as well as stable silylenes to CX (X = N or O) multiple bonds have been well documented in recent years.[1–8] Little is known, however, about the reactions of R$_2$Si: species with CP multiple bonds.[9] So far, it has been shown that R$_2$Si: (R = Bu^t) gives a phosphasilirene[10] in a [1 + 2]-cycloaddition with the CP triple bond of a phosphaalkyne; with R$_2$Si: (R = mesityl), the initially formed three-membered ring undergoes subsequent insertion of another R$_2$Si: moiety to afford a phosphadisilacyclobutene.[11] In our studies on the reactions of the stable silylene Si[(NCH$_2$Bu^t)$_2$C$_6$H$_4$-1,2] **1** we became interested in the reaction of **1** with 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene **2**. The latter has only recently been synthesised by metal-induced cyclotrimerisation of the phosphaalkyne Bu^{t}CP[12,13] and although its structure and PE spectrum have been reported,[14] its chemistry has not been studied in depth. Binger and coworkers[15] have described the synthesis of tetraphosphabarrelene and semibulvalene derivatives by addition of different phosphaalkynes to **2**. The former products resulted from a conventional [4 + 2]-cycloaddition reaction and the latter most likely from nucleophilic attack at one of the ring C atoms, followed by ring closure.



Scheme 1

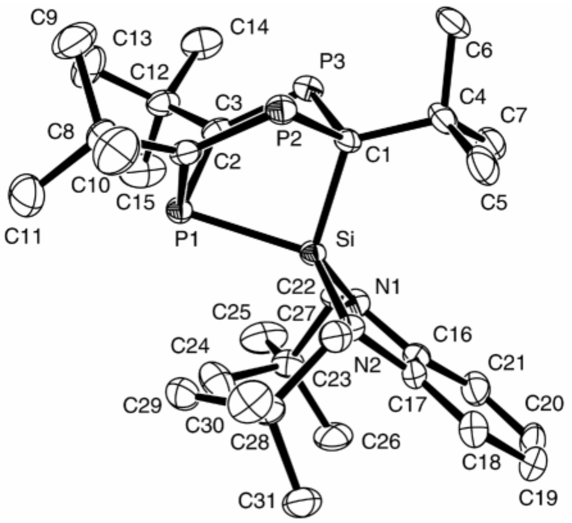


Fig. 1 Molecular structure of **3**. Selected bond lengths (Å) and angles (°): Si–N(2) 1.736(3), Si–N(1) 1.738(3), Si–C(1) 1.935(3), Si–P(1) 2.289(2), P(1)–C(2) 1.850(4), P(1)–C(3) 1.857(4), P(2)–C(2) 1.685(4), P(2)–C(1) 1.858(4), P(3)–C(3) 1.680(4), P(3)–C(1) 1.853(4), N(1)–C(16) 1.408(5), N(2)–C(17) 1.417(5); N(2)–Si–N(1) 91.71(14), C(1)–Si–P(1) 90.27(11), C(2)–P(1)–C(3) 98.67(16), C(2)–P(2)–C(1) 102.67(16), C(3)–P(3)–C(1) 102.00(17).

We found that treatment of the silylene **1** with triphosphabenzene **2** in benzene at room temperature afforded, after evaporation of the solvent, an orange solid which was recrystallised from toluene–hexane at −25 °C to yield the [1 + 4]-cycloaddition product **3** (pale orange crystals, mp 224–225 °C, yield 66%) (Scheme 1). Compound **3** was characterised by analytical and spectroscopic techniques,† and its structure was confirmed by a single crystal X-ray diffraction study.‡

The ^{31}P, ^{29}Si, ^{13}C and ^{1}H NMR spectroscopic data are in agreement with the proposed [1 + 4]-cycloaddition product. The ^{31}P{^{1}H} NMR spectrum exhibits the expected doublet and triplet consistent with a plane of symmetry bisecting both the triphosphabenzene and silylene moieties. The doublet at δ 320.4 is characteristic of an unsaturated P environment, while the triplet at δ −63.8 is typical of a saturated P centre. These values are similar to those of δ 324.1 and −87.0 reported recently for the tetraphosphabarrelene.[14] The ^{29}Si chemical shift of δ 3.8 is consistent with a tetravalent Si centre and the $^1J_{\mathrm{SiP}}$ coupling of 7.1 Hz to the bridgehead P lies within the expected range.

The structure of **3** (Fig. 1) clearly reveals it to be the [1 + 4]-cycloaddition product of the silylene across the triphosphabenzene ring; the P=C bond distances of 1.68 Å and the longer P–C bond distances of 1.85 Å to the bridgehead atoms are appropriate for this formulation.

Compound **3** did not react further with **1**, using an excess of the silylene, even on heating up to 80 °C in a sealed NMR spectral tube. It was not possible to extend the reaction of **2** to the higher group 14 metal analogues of the silylene. Thus, no reaction was observed on treatment of M[(NCH$_2$Bu^t)$_2$C$_6$H$_4$-1,2] (M = Ge, Sn or Pb) with **2**, even at higher temperatures. The reactions of **2** with carbenes are currently under investigation and follow significantly different reaction pathways than that observed with the silylene.

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Notes and references

† *Selected spectroscopic data* for **3**: ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.95 (s, 18H), 1.38 (s, 9H), 1.55 (s, 18H), 3.23 (AB-type, 4H), 6.63–6.69 (m, 2H) and 6.73–6.79 (m, 2H). ^{13}C{^{1}H} NMR (75.48 MHz, C$_6$D$_6$): δ 29.5 [C(*C*H$_3$)$_3$, d, ^5J(^{13}C, ^{31}P) 2.7 Hz], 33.8 [C(*C*H$_3$)$_3$, t, ^3J(^{13}C, ^{31}P) 9.2 Hz], 34.5 [C(*C*H$_3$)$_3$, dd, ^3J(^{13}C, ^{31}P) 14.0, 7.0 Hz], 35.4 [*C*(CH$_3$)$_3$, d, ^4J(^{13}C, ^{31}P)

0.4 Hz], 36.9 [$C(\mathrm{CH}_3)_3$, t, $^{2}J(^{13}\mathrm{C}, ^{31}\mathrm{P})$ 16.2 Hz], 43.3–43.9 [$C(\mathrm{CH}_3)_3$, m, $^{2}J(^{13}\mathrm{C}, ^{31}\mathrm{P})$ 10.7 Hz], 54.1 (CH_2, s), 103.1 [CSi, td, $^{1}J(^{13}\mathrm{C}, ^{31}\mathrm{P})$ 64.8, $^{3}J(^{13}\mathrm{C}, ^{31}\mathrm{P})$ 8.4 Hz], 111.6, 118.4 and 138.1 (phenyl) and 218.3 (P=C, m). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (121.49 MHz, $\mathrm{C_6D_6}$): δ −63.8 [t, $^{2}J(^{31}\mathrm{P}, ^{31}\mathrm{P})$ 30.7 Hz] and 320.4 [d, $^{2}J(^{31}\mathrm{P}, ^{31}\mathrm{P})$ 30.7 Hz]. $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR (99.33 MHz, $\mathrm{C_6D_6}$): δ 3.8 [d, $^{1}J(^{29}\mathrm{Si}, ^{31}\mathrm{P})$ 7.1 Hz]. MS: *m/z* 574 (M^+).

‡ *Crystal data for* **3**: $\mathrm{C_{31}H_{53}N_2P_3Si}$, M = 574.75, specimen 0.3 × 0.3 × 0.2 mm, triclinic, space group $P\bar{1}$ (no. 2), a = 11.0632(18), b = 11.090(5), c = 15.682(7) Å, α = 77.81(4), β = 76.87(3), γ = 62.15(3)°, U = 1644.4(11) Å^3, Z = 2, μ = 0.24 mm^{-1}, T = 173(2) K, 5781 unique reflections collected, $R1$ = 0.054 for 4575 reflections with $I > 2\sigma(I)$, $wR2$ = 0.136 for all reflections. Data collection CAD4, full-matrix least-squares refinement on F^2, SHELXL-97. CCDC 182/1468. See http://www.rsc.org/suppdata/cc/1999/2451/ for crystallographic files in .cif format.

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