VIP Main-Group Triple Bonds

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Synthesis and Structure of a Base-Stabilized *C*-Phosphino-*Si*-Amino Silyne**

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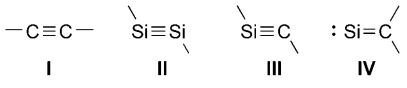
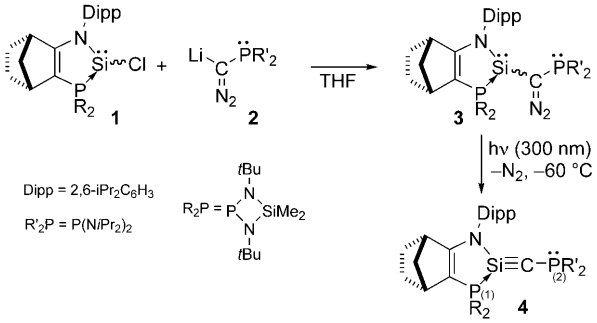
The carbon–carbon triple bond **I** is a ubiquitous functional group in organic chemistry.[1] In marked contrast, the



chemistry of heavier derivatives with triple bonds to silicon has only recently emerged, although numerous silicon–silicon and silicon–carbon double-bond species have been synthesized[2] since the discovery of the first stable silene[3] and disilene[4] in 1981. Indeed, the first stable disilynes **II** have been recently reported independently by the groups of Sekiguchi and of Wiberg.[5,6] More recently, a disilyne with bulky aryl substituents has also been isolated.[7] These molecules present two nondegenerate π bonds owing to their unique *trans*-bent structure, and have a highly reactive Si–Si multiple bond[8] with an energetically low π* orbital[9] and bis-silylene-like reactivity.[10]

Meanwhile, the synthesis of silynes **III** featuring a silicon–carbon triple bond remains a major challenge. In fact, silynes are still elusive intermediates that have been only detected in the gas phase using mass spectroscopy.[11] Several computational studies predict a *trans*-bent geometry for **III**, similar to disilynes **II**, and a linear structure that is not a minimum on the potential-energy surface.[12–14] One major obstacle for their synthesis is the energetically favored isomerization of **III** into silylidene **IV**, which has been calculated, for the parent system HSiCH, to have an activation energy of only 6 kcal mol^{-1} and to be 32.9 kcal mol^{-1} more stable than **III**.[13] It was also predicted that the order of stability of **III** and **IV** can be reversed, making the silyne more stable, by introducing a more electronegative substituent on silicon[13] or by using bulky substituents.[11,14] An alternative approach could be the use of Lewis base ligands, as low-coordinate silicon species, such as silenes,[15] disilynes,[16] or disilicon(0)[17] species, have been reported to form stable donor–acceptor complexes. Herein we present the synthesis and characterization of the first persistent and isolable phosphine-stabilized silyne **4** (Scheme 1).



Scheme 1. Synthesis of phosphino(silyl)diazomethane **3** and silyne **4**.

Several transient metallaacetylenes (–E≡C–), such as germa- and stannaacetylenes, have been generated by photolysis of the corresponding divalent germanium(II) and tin(II) (trimethylsilyl)diazomethanes.[18] We decided to adopt a similar synthetic strategy, and the precursor phosphino(silyl)diazomethane **3** was prepared by the reaction of chlorosilylene–phosphine complex **1** with the lithiated phosphinodiazomethane **2**.[19] The diazomethane derivative **3** was obtained as a mixture of two diastereomers (3:1),[20] and was isolated as orange crystals (yield 42%) from a saturated pentane solution at −30 °C. It was fully characterized by spectroscopic methods and by an X-ray diffraction analysis[21] (Figure 1). The ^{31}P NMR spectrum of **3** shows two sets of signals (AX systems: $\delta = 70.6$–69.5 ppm, $^3J_{PP} = 107.6$ Hz, and $\delta = 70.1$–69.2 ppm, $^3J_{PP} = 81.5$ Hz) in the same proportions as those of **1**, in agreement with the presence of two diastereomers. In the ^{29}Si NMR spectrum, the signal for the silicon(II) center of the major isomer appears as a doublet of doublets at $\delta = -20$ ppm with two large phosphorus–silicon coupling constants ($^2J_{Si,P} = 240$ Hz, $^1J_{Si,P} = 204$ Hz). An intense IR absorption band at 2016 cm^{-1} confirms the presence of a diazo functional group in **3**.

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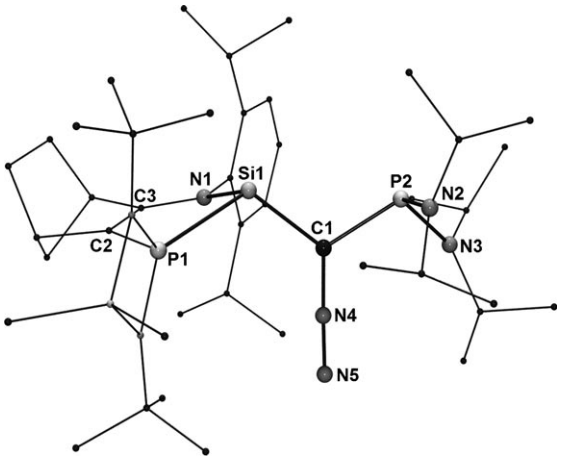


Figure 1. Structure of **3** (H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: C1–Si1 1.884(3), C1–P2 1.844(2), Si1–P1 2.3450(8), P1–C2 1.724(2), C2–C3 1.382(3), C3–N1 1.350(3), Si1–N1 1.853(2), P2–N2 1.694(2), P2–N3 1.702(2), C1–N4 1.299(3), N4–N5 1.152(3); Si1-C1-P2 112.51(12), C1-Si1-N1 106.39(10), C1-Si1-P1 112.27(8), N1-Si1-P1 88.02(6), Si1-P1-C2 92.21(9), P1-C2-C3 116.47(19), C2-C3-N1 124.1(2), C3-N1-Si1 114.36(15), N2-P2-N3 108.99(12), C1-P2-N2 105.73(12), C1-P2-N3 101.09(11), C1-N4-N5 178.8(3), N4-C1-P2 120.42(19), N4-C1-Si1 127.02(18).

Photolysis of **3** ($\lambda = 300$ nm) at −60 °C in THF afforded a dark red solution of silyne **4**. Monitoring the reaction by ^{31}P NMR spectroscopy at −80 °C shows the complete disappearance of the starting diazomethane derivative **3** after 12 h of irradiation, and the appearance of a new set of signals for silyne **4** (AX system: $P_{(1)} = 46.2$ ppm, $P_{(2)} = 3.1$ ppm, ($^3J_{PP} = 47.3$ Hz)). In the ^{29}Si NMR spectrum, the signal for the silyne fragment is shifted significantly upfield ($\delta = -89.4$ ppm, $^2J_{Si,P} = 103.0$ Hz, $^1J_{Si,P} = 155.4$ Hz). This upfield shift is probably related to the hypervalency of the silicon center in silyne **4**. Similarly, phosphinocarbenes, featuring a short P–C multiple bond, have a characteristic upfield chemical shift in ^{31}P NMR spectroscopy.[22] In the ^{13}C NMR spectrum, the silyne carbon appears at $\delta = 216$ ppm as a broad signal. Similar downfield signals were observed for carbons in silaallene derivatives ($\delta = 214$–268 ppm).[23] Only one set of signals was observed by NMR spectroscopy, even at low temperature (−90 °C), suggesting the formation of **4** as a single diastereomer.

Silyne **4** was successfully isolated as dark red crystals from an ether solution at −80 °C. The molecular structure of **4** determined by X-ray crystallography reveals an almost linear geometry around the central carbon (Si1-C1-P2 178.2°). This indicates the central carbon atom is sp-hybridized (Figure 2). The fragment N1-Si1-C1 is strongly bent (128.45°), with a very short silicon–carbon bond (Si1–C1 1.667 Å), consistent with substantial triple bonding. Indeed, this bond is significantly shorter than Si=C_{sp} double bonds (ca. 1.70 Å),[23,24] and is in the range predicted for Si≡C triple bonds (1.63–1.67 Å).[11,14] The three-coordinate silicon center becomes more planar ($\Sigma\theta_{Si\alpha}$: 345°) in comparison with the strongly pyramidalized silicon(II) center in **3** ($\Sigma\theta_{Si\alpha}$: 307°). The P2–C1 distance is shorter than that in the precursor **3** (1.844 Å and 1.682 Å for **3** and **4**, respectively), and the value is in the range between a

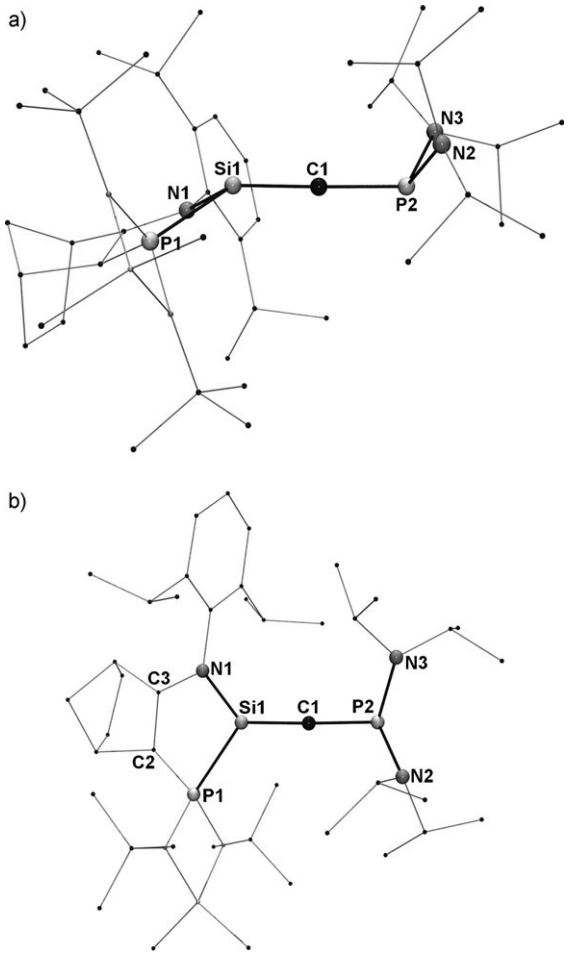


Figure 2. Two mutually orthogonal views of structure of **4** (H atoms and a molecule of diethyl ether solvent are omitted for clarity). Selected bond lengths [Å] and angles [°]: Si1–C1 1.667(3), C1–P2 1.682(3), Si1–P1 2.253(5), P1–C2 1.718(6), C2–C3 1.422(9), C3–N1 1.345(7), N1–Si1 1.8139(19), P2–N2 1.706(3), P2–N3 1.708(3); Si1-C1-P2 178.2(3), C1-Si1-N1 128.45(18), C1-Si1-P1 125.54(17), C1-P2-N2 108.53(17), C1-P2-N3 113.1(2), N1-Si1-P1 91.27(13), Si1-P1-C2 94.2(3), P1-C2-C3 114.0(6), C2-C3-N1 122.0(7), C3-N1-Si1 113.4(4), N2-P2-N3 102.93(19).

P=C_{sp} double bond (ca. 1.63 Å)[25] and P-C_{sp} single bond (1.76–1.77 Å).[26] Furthermore, the two pyramidalized three-coordinate silicon and phosphorus centers show a *trans*-bent geometry, which implies an interaction between the phosphorus lone pair and the π^*_{Si-C} (3-center-4-electron system). However, this interaction is relatively weak, as the phosphine moiety remains strongly pyramidalized ($\Sigma\theta_{p\alpha}$: 324° for **4** versus 315° for **3**). The P1–Si1 distance (2.253 Å) is shorter than that in the precursor **3** (2.345 Å).

To gain more insight into **4**, DFT calculations have been performed. The calculated geometry of **4** agrees quite well with experiment, except that in the calculations, the Si1-C1-P2 angle is slightly more bent (170.9°).[27] Calculations predict a singlet ground state for **4** with a small singlet–triplet energy gap ($\Delta E_{S-T} = 10.2$ kcal mol^{-1}). The highest-occupied molecular orbital (HOMO) corresponds to the Si–C in-plane π bond (Figure 3). In marked contrast to disilynes stabilized by two Lewis bases, such as imines or *N*-heterocyclic carbenes,

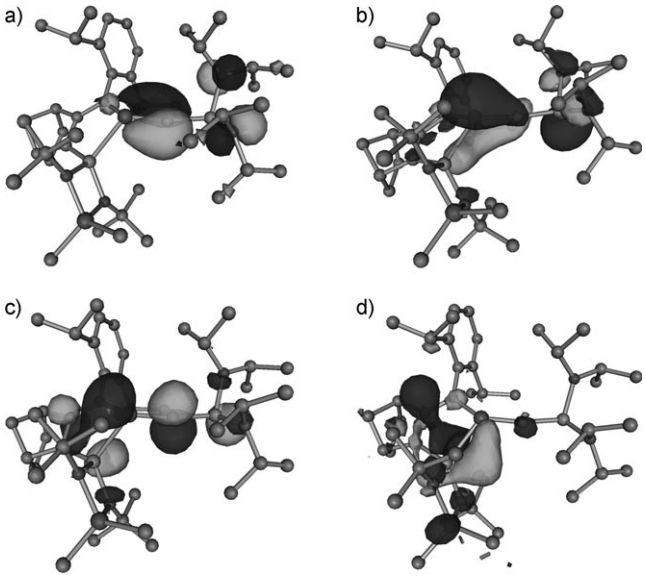
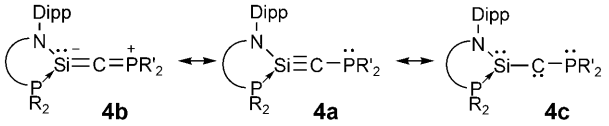


Figure 3. Calculated frontier orbitals of **4** contoured at 0.04 atomic units (bHandH/6-31G*). Eigenvalues of the molecular orbitals [eV]: a) HOMO −4.05, b) HOMO−1 −4.19, c) LUMO −1.26, d) LUMO + 7 +1.66. Hydrogen atoms are omitted for clarity.

which have extremely polarized structures with a lone pair localized on each silicon atom,[28] the in-plane π electrons are delocalized between the silicon and carbon atoms in spite of the coordination of the phosphine subunit on the silicon atom. The HOMO−1 corresponds to the out-of-plane Si–C π-bond orbital and the lone pair of the phosphine. The LUMO is the antibonding out-of-plane π orbital. Contrary to the energetically low LUMO (−1.26 eV), the antibonding in-plane Si–C π orbital (LUMO + 7, 1.66 eV) is much higher in energy.

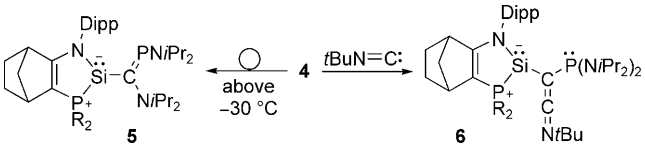
These data are in agreement with a λ^5-silyne character of **4**, which is consistent with the linear geometry around the central carbon (**4a** in Scheme 2). However, the calculated



Scheme 2. Resonance structures of **4**.

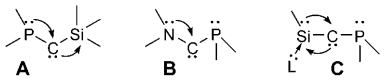
Wiberg bond order for the Si–C fragment (1.687) is much smaller than that calculated for the Si–Si triple bond (2.618)[5] This is probably due to the three-center–four-electron system of the Si-C-P fragment, with significant contribution from canonical structure **4b** (Scheme 2). Indeed, the bond order for the P–C fragment (1.219) indicates some multiple-bond character in spite of the strongly pyramidalized phosphino group. The small bond order for Si–C can also be explained by the highly polarized Si–C π bonds owing to the phosphine coordination on the silicon center, suggesting a certain carbenic character (**4c**). The bond order for the Si–P fragment (0.825) is similar to that calculated for the phosphonium sila-ylide without any P–Si π interaction (0.856),[29] despite the significantly shorter P1–Si1 bond.

Silyne **4** is stable up to −30 °C in solution and transforms into the phosphaalkene derivative **5** via the 1,2-migration of a diisopropylamino group from the phosphine to the central carbon atom, which is a typical rearrangement for singlet carbenes[30] (Scheme 3). The carbenic character of **4** (**4c**) was also highlighted by its coupling reaction with *tert*-butylisocyanide, a well-known carbene trapping agent, to cleanly afford the corresponding keteneimine **6**.



Scheme 3. Synthesis of phosphaalkene **5** and keteneimine **6**.

As indicated by its reactivity as well as by theoretical investigations, silyne **4** can also be regarded as a persistent singlet carbene bearing two π-donating substituents, one a sila-ylide and the other a phosphino group.[31] There are two main types of π-donating substituents for stable carbenes; amino groups and phosphino groups.[32] It has been demonstrated that carbenes bearing a phosphino substituent (π and σ donor) requires an additional electron-withdrawing group (push–pull; type **A**) for efficient stabilization.[33] In contrast,



the more electronegative and stronger π-donating amino group (π donor and σ acceptor) can function as the single electronically active substituent for stabilization, leaving the other substituent on the carbene center as a spectator (push–spectator; type **B**).[34] This electronic effect provides the larger structural diversity of stable monoamino carbenes.[26c,27,35] The phosphonium sila-ylide fragment, like amino groups, behaves as the single electronically active substituent towards the carbenic centre. The sila-ylide substituent with strong π-donating and π-accepting character interacts more strongly with the carbenic centre than the phosphino group. A clear consequence of these electronic effects is the linear geometry of the Si-C-P carbene scaffolding with a substantially shorter Si–C bond. The fact that the phosphino group remains pyramidalized strongly indicates that it plays a spectator role (push–pull–spectator; type **C**). It is worth noting that the structurally similar acyclic diphosphino carbenes (carbenes substituted by two electropositive π-donating groups) are only transient species.[32]

In conclusion, we have successfully synthesized the first isolable silyne stabilized by coordination of a phosphine ligand, which has a silicon–carbon bond as short as those computationally predicted for silicon–carbon triple bonds. This new species shows a certain amount of carbenic character. The results shown herein also imply that the phosphonium sila-ylide group is a strong π-donating and π-accepting substituent, which can more efficiently stabilize a

carbenic center than electronically similar phosphino substituents. Further study of the reactivity of this new species, and structural modifications, particularly by replacing the phosphino group by other electronically less active substituents, are under active investigation.

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