Silicon Chemistry

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Zwitterionic Si-C-Si-P and Si-P-Si-P Four-Membered Rings with Two-Coordinate Phosphorus Atoms**

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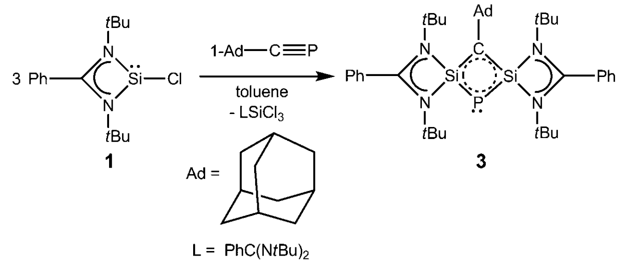
Dedicated to Professor Roald Hoffmann

In contrast to the rich and ubiquitous chemistry displayed by silicon,[1] the chemistry of unsaturated four-membered heterocycles containing silicon and phosphorus is not known. This situation is perhaps due to the instability associated with antiaromaticity for the cyclobutadiene ring systems, although it is known that the introduction of heteroatoms will substantially stabilize such rings. In a 1998 review, Bertrand clarified the bonding situation of four-membered heterocycles with four π electrons containing a phosphorus atom that has no p orbital available for contributing to the π system.[2] He showed that in these compounds either there is interrupted cyclic π delocalization or they are stable owing to a zwitterionic character, and he concluded that these compounds are not antiaromatic. This observation prompted us to design four-membered rings containing silicon and phosphorus as heteroatoms and to elucidate their bonding properties. Furthermore, nitrogen- or phosphorus-doped SiC systems have commercial applications as semiconducting materials.[3]

The easy availability of heteroleptic chlorosilylene LSiCl (**1**)[4b] and bis-silylene (LSi–SiL) (**2**)[5] ($\mathrm{L = PhC(N}t\mathrm{Bu)_2}$) creates new dimensions in silicon chemistry. The reactions of these systems with unsaturated organic compounds are thermodynamically favorable owing to the oxidation of silicon from the divalent to the tetravalent state.[4b,6] Herein we report the synthesis of the 1,3-disilacarbaphosphide **3**, containing three heteroatoms, that resulted from the reactions of **1** and **2** with RC≡P under cleavage of the C≡P bond.



Scheme 1. Preparation of compound **3**.

The synthesis of **3** is straightforward. Addition of a toluene solution of 1-Ad–C≡P to the toluene solution of **1** at −30 °C in 1:3 molar ratio resulted in the formation of **3**, which was isolated in 68.2% yield as reddish-yellow air- and moisture-sensitive crystals (Scheme 1). The constitution of **3** was unequivocally characterized by single-crystal X-ray diffraction.[7] Figure 1 depicts the molecular view of **3**, while selected bond lengths and bond angles are provided in the legend of Figure 1. Compound **3** crystallizes in the orthorhombic space group $P2_12_12_1$. The core structure consists of two silicon atoms, one carbon atom, and one phosphorus atom, which together form a Si-C-Si-P four-membered ring. The predominant structural feature of **3** is the "naked" phosphorus atom, which connects the two silicon atoms. The two silicon atoms are each four-coordinate and display a distorted tetrahedral geometry by coordination with two nitrogen atoms from the amidinato ligand. The remaining two

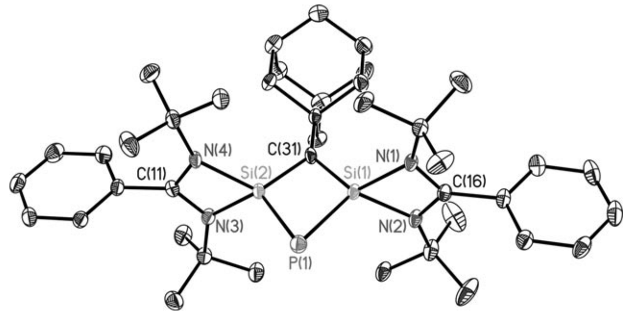


Figure 1. Molecular structure of compound **3**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms have been removed for clarity. Selected bond lengths [Å] and angles [°] N(1)–Si(1) 1.8646(17), N(2)–Si(1) 1.8653(18), P(1)–Si(2) 2.1894(7), P(1)–Si(1) 2.2012(7), Si(1)–C(31) 1.7808(18), Si(2)–C(31) 1.7834(18); Si(2)-P(1)-Si(1) 68.86(3), C(31)-Si(1)-P(1) 101.23(6), N(1)-Si(1)-P(1) 117.63(6), N(2)-Si(1)-P(1) 119.32(7), C(31)-Si(2)-P(1) 101.59(6), N(3)-Si(2)-P(1) 119.44(7), N(4)-Si(2)-P(1) 120.78(7).

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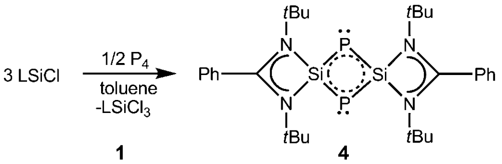
sites of the tetrahedron are occupied by the carbon and phosphorus atoms. The bond lengths of the phosphorus atom to the atoms Si(1) and Si(2) are 2.2012(7) and 2.1894(7) Å, respectively, with a Si-P-Si angle of 68.86°. The bond lengths are between the average Si–P single bond lengths of 2.25 Å[8a] and Si–P double bond length of 2.09 Å.[8b] Moreover, the Si(1)–C(31) and Si(2)–C(31) bonds (1.7808(18) and 1.7834(18) Å) are significantly shorter than the Si–C single bond length reported in literature (1.86–1.93 Å)[6b,9a] and slightly longer than the Si–C double bond found in $(TMS)_2Si{=}C(OTMS)$-2-Ad (1.764 Å; TMS = trimethylsilyl).[9b] This finding can be interpreted in terms of a zwitterionic electronic structure in which the positive charge is located on the Si-C-Si fragment and the negative charge at the two-coordinate phosphorus atom. A similar explanation was given by Frank et al. for a mixed-valent tetraphosphete, and they confirmed the predominance of the bis-ylidic formulation over the delocalized-double-bond description by charge density calculation of the P_4 ring.[10] It is noteworthy that the Si–C bond lengths in **3** match excellently with those of the 1,2-disilabenzene derivative (1.804(4) and 1.799(5) Å) reported by Sekiguchi and co-workers[11] and the recently published 1,4-disilabenzene (1.800(3) Å) in which the electron density within the Si–C bonds is delocalized.[6d] The geometry of the three-coordinate C(31) atom can be best described as distorted trigonal planar, with the sum of bond angles around C(31) of 359.96°. Atom P(1) also adopts a distorted trigonal-planar geometry when the lone pair is also considered. A similar type of naked bridging phosphorus atom is very unusual in the literature.[10,12] Another interesting feature is the interatomic Si···Si distance (2.48 Å), which conclusively demonstrated that there is no Si–Si bond in **3**. Compound **3** contains a chain of three four-membered rings, and in the spirocyclic structure each silicon atom is part of two four-membered rings.

Additionally, **3** was characterized by solution and solid-state NMR spectroscopy, EI-MS, and elemental analysis. In the ^1H NMR spectrum, four sets of resonances are observed. The *t*Bu protons appear at $\delta = 1.26$ ppm and are thus shifted downfield compared to **1** ($\delta = 1.08$ ppm). An additional set of resonances is also found in the ^1H NMR spectrum ($\delta = 1.17$ ppm). This signal indicates the formation of $LSiCl_3$ as the side product. The ^1H-coupled and ^1H-decoupled ^{31}P NMR spectra of **3** show a sharp singlet at $\delta = -243$ ppm, which can be assigned to the naked phosphorus atom. The value of the chemical shift is consistent with the assumption of a zwitterionic structure for **3**. In the ^{29}Si NMR spectrum, a sharp doublet is detected at $\delta = -5.1$ ppm with a coupling constant of $^1J_{Si\text{-}P} = 75.45$ Hz, which is quite small compared to the Si–P coupling constants found in literature.[8] The formation of $LSiCl_3$ was confirmed by ^{29}Si NMR spectroscopy by a sharp resonance detected at $\delta = -98.4$ ppm, which corresponds to the five-coordinate silicon atom of $LSiCl_3$.[4a] In the ^{31}P solid-state NMR spectrum of **3**, the most intense resonance appears at an isotropic chemical shift of $\delta = -326.1$ ppm (see the Supporting Information, Figure S4.2). The ^{29}Si NMR spectral resonance with the highest intensity appears at $\delta = -8.4$ ppm. The cross-polarization (CP) build-up curves (see the Supporting Information, Figure S4.1) show that both the silicon and the phosphorus atoms are not protonated, since maximal intensity is reached after a long contact time of 5.6 ms (^{31}P) or 5.1 ms (^{29}Si). This finding confirms the presence of a lone pair of electrons at P(1). In the EI-MS spectrum, the molecular ion is detected as the most abundant species with highest relative intensity at *m*/*z* 696. The absorption maximum of the UV/Vis spectrum in THF was detected at 259 nm ($\varepsilon = 18\,300\ cm^{-1}M^{-1}$).

The successful isolation of **3** prompted us to verify whether it is possible to substitute the remaining carbon atom in **3** by another phosphorus atom. Theoretically, the replacement of the RC fragment in **3** with another phosphorus atom is possible, because these two fragments are isolobal,[13] and Scherer and co-workers reported a myriad of polycyclic phosphorus compounds using this relationship.[14] Herein we report the synthesis and structure of the first complex with a $\overline{\text{Si-P-Si-P}}$ core through activation of the P_4 molecule[15] by silylene (Scheme 2).

Treatment of **1** and P_4 in toluene overnight resulted in the formation of the $\overline{\text{Si-P-Si-P}}$ unit stabilized by the amidinato ligand ($L_2Si_2P_2$; L = PhC(N*t*Bu)$_2$; **4**). After recrystallization from THF, **4** was isolated as air- and moisture-sensitive yellow crystals in 60% yield. The ^1H NMR spectrum shows a singlet at $\delta = 1.36$ ppm, which is shifted downfield in comparison to that of **1** ($\delta = 1.08$ ppm). The ^{31}P NMR spectrum of **4** displays a sharp singlet at $\delta = -166$ ppm. This downfield shift is presumably due to the presence of two naked phosphorus atoms. A similar trend is observed in the ^{29}Si NMR spectrum, which shows a resonance at $\delta = 25.6$ ppm that is shifted about 30 ppm downfield compared with that of **3**, although the magnitude of the coupling constant ($^1J_{Si\text{-}P} = 109.02$ Hz) remains comparable. The solid-state ^{31}P NMR spectrum of **4** shows a sharp resonance with an isotropic chemical shift of $\delta = -166.4$ ppm. In the solid-state ^{29}Si NMR spectrum, a triplet is observed at $\delta = 24.0$ ppm, with a coupling constant of $^1J_{Si\text{-}P} = 97.7$ Hz (see the Supporting Information, Figure S4.2). The CP build-up curves reach maximal intensity after 11.6 ms (^{31}P) or 7.8 ms (^{29}Si), thus confirming that silicon and phosphorus atoms are not protonated (see the Supporting Information, Figure S4.1). The absorption maximum of the UV/Vis spectrum in THF was detected at 234 nm ($\varepsilon = 15\,600\ cm^{-1}M^{-1}$). In the EI-MS spectrum, the molecular ion is detected as the most abundant species, with highest relative intensity at *m*/*z* 580.



1 **4**

Scheme 2. Preparation of compound **4**.

The proposed constitution of **4** was confirmed by single-crystal X-ray diffraction (Figure 2). Crystals of **4** were grown by cooling a concentrated THF solution to −32 °C. Compound **4** crystallizes in the monoclinic space group *C*2/*c* with a mirror plane bisecting the molecule.[7] The most apparent

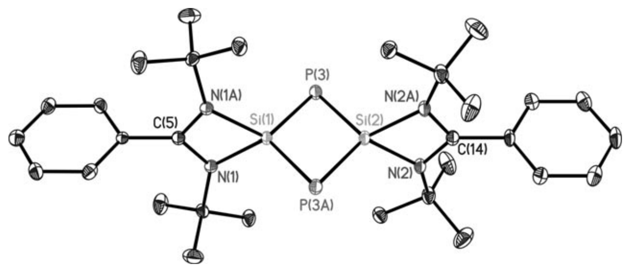
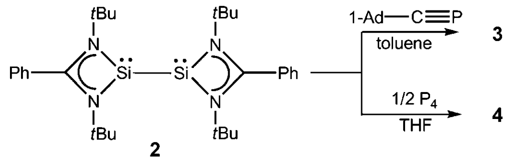


Figure 2. Molecular structure of compound **4**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms have been removed for clarity. Selected bond lengths [Å] and angles [°] N(1)–Si(1) 1.8585(14), N(2)–Si(2) 1.8524(15), P(3)–Si(2) 2.1737(6), P(3)–Si(1) 2.1742(6), Si(1)–N(1A) 1.8586(14), Si(1)-P(3A) 2.1742(6), Si(2)–P(3A) 2.1737(6); Si(2)-P(3)-Si(1) 72.45(2), N(1)-Si(1)-N(1A) 170.53(9), N(1)-Si(1)-P(3) 118.61(4), N(1A)-Si(1)-P(3) 119.11(4), N(1)-Si(1)-P(3A) 119.11(4), N(1A)-Si(1)-P(3A) 118.61(4), P(3)-Si(1)-P(3A) 107.54(3), P(3)-Si(2)-P(3A) 107.57(3). Symmetry generated A: −*x*, *y*, −*z*+1/2.

feature of **4** is the planar Si-P-Si-P four-membered ring. The planar ring consists of four equivalent Si−P bonds of 2.174 Å. The value is roughly the intermediate between the normal Si−P single bond (2.25 Å) and normal Si=P bond (2.09 Å)[8] and matches well with that of **3**. The Si⋯Si interatomic separation is 2.57 Å, which shows there is no Si−Si bond in **4**. Like **3**, the silicon atoms in **4** exhibit a distorted tetrahedral geometry, whereas both the phosphorus atoms adopt a trigonal-planar geometry when the lone pairs are considered. Another important feature are the two equivalent Si-P-Si bond angles of 72.45(2)°. The value is increased slightly compared to that of **3**. The two P-Si-P bond angles are exactly the same (107.5(3)°). These data indicate the formation of a bis-ylide structure in which the two silicon atoms are formally positively charged, whereas the two phosphorus atoms carry partial negative charges.

Moreover, we probed the reactions of **2** with phosphaalkyne and with P_4 (Scheme 3). The advantage of **2** over **1** is that the former has two lone pairs of electrons and a labile Si−Si bond, so it is expected that **2** would be more reactive than **1**. Accordingly, we treated **2** with equimolar amounts of 1-Ad−C≡P in toluene and one-half equivalent of P_4 at room temperature in THF, respectively. In the former case a color change of the solution from dark to pale red was observed, whereas the latter reaction resulted in the formation of a bright yellow solution within minutes. Multinuclear NMR spectroscopic and EI-MS data showed that the reactions led quantitatively to products **3** and **4**, respectively. It must be noted that unlike in previous cases, no formation of any side product was detected by NMR spectroscopy.

To elucidate the nature of the bonding and to investigate whether the Si-C-Si-P ring of **3** and the Si-P-Si-P ring of **4** are of antiaromatic character with two delocalized double bonds or if there is only one delocalized double bond in the Si-C-Si moiety and two lone pairs of electrons at the phosphorus atoms, we performed DFT gas-phase structural optimizations and frequency calculations at the B3LYP/6-311G* level of theory.[16] The Si−P bond lengths (2.21372/2.21238 Å) in **3** are slightly elongated compared to the experimental results and are clearly more in the range of a Si−P single bond than of a Si−P double bond, while the Si−C bond lengths are in the range between a single and a double bond (1.79472/1.79371 Å). Isotropic and anisotropic ^{31}P chemical shieldings as determined by theory are in agreement with values extracted from the spinning sideband pattern of solid-state NMR spectra (see the Supporting Information, Table S4.1 and Figure S4.2).



Scheme 3. Alternate synthesis of **3** and **4**.

Additionally, the nucleus-independent chemical shift (NICS) at 1 Å above the ring centers was calculated.[17] The NICS(1) of the Si-C-Si-P ring is −4.17 (NICS(0) = −12.42, NICS(2) = +0.14), which clearly shows that the ring has no antiaromatic character.

To investigate the electronic situation in the vicinity of the phosphorus atom more closely, the electron localizability index (ELI-d) was calculated (Figure 3).[18] There are two monosynaptic basins at the phosphorus atom which are populated with 1.95 and 1.97 electrons. This finding indicates two lone pairs of electrons at the phosphorus atom. These conclusions are supported by topology investigations,[19] because two non-bonding valence shell charge concentrations (VSCCs) are found at the phosphorus atom. Additionally, the two disynaptic basins between the silicon and phosphorus atoms are occupied by 1.96 electrons each, which indicates two single bonds. On the other hand, the disynaptic basins between the silicon and carbon atoms are occupied by 2.84 and 2.97 electrons, thus indicating a delocalized double bond. This result is confirmed by the leading natural lewis structure as given by a natural bond orbital (NBO) analysis,[20] which shows that there are 1.91 electrons distributed between each silicon atom and the phosphorus atom and 1.94 electrons between each silicon atom and the carbon atom, and additional 1.74 electrons between one silicon atom and the carbon atom, thus indicating electron delocalization over the Si-C-Si moiety but not over the Si-P-Si skeleton. The natural charges from the NBO analysis are −0.75 for the phosphorus atom, +1.56 for each silicon atom, and −1.44 for the carbon atom, thus confirming the zwitterionic character of the ring system.

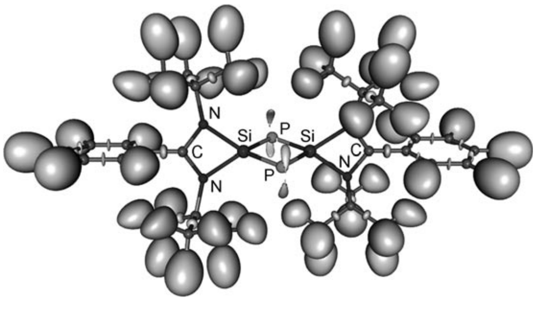


Figure 3. Representation of the ELI-d of compound **4** (isosurface value, $\eta = 1.8$).

In **4** the Si–P bond lengths are slightly shortened compared to **3** (2.19835/2.19838/2.19835/2.19838 Å), but they are again still in the range of a Si–P single bond. The NICS(1) value is −2.56 (NICS(0) = −5.92, NICS(2) = +0.44), which shows that the ring has no antiaromatic character. The ELI-d investigations reveal two monosynaptic basins at each of the phosphorus atoms, which are occupied by 1.86 and 1.88 electrons each, again indicating two lone pairs of electrons at each of the phosphorus atoms. The disynaptic basins between the silicon and phosphorus atoms are occupied by 2.02, 2.03, 2.03, and 2.03 electrons, thus indicating four single bonds in the ring. In accordance with the ELI-d findings, topological investigations show two non-bonding VSCCs at each of the phosphorus atoms. The shorter P–Si bond and the lower occupation of the monosynaptic basins at the phosphorus atoms indicate that the delocalization in the ring is more prominent than in **3**. This result is confirmed by a NBO analysis, which shows that besides the 1.92 electrons between each silicon and phosphorus atom, there are another 1.77 electrons each shared between Si(1) and P(3) and Si(2) and P(3A), thereby indicating electron delocalization over the whole Si-P-Si-P skeleton. The natural charges obtained from the NBO analysis are +1.12 for the silicon atoms and −0.69 for the phosphorus atoms, which shows that there is still a strong charge separation and thus a zwitterionic contribution.

In conclusion, we have prepared a Si-C-Si-P and a Si-P-Si-P ring, each stabilized by bulky benzamidinato ligands with *t*Bu substituents on the nitrogen atoms. X-ray structural data, theoretical calculations, and solid-state NMR spectroscopy showed conclusively that these two rings are stabilized by their zwitterionic character. Currently we are investigating the reactivity of **3** and **4**, and the results will be published in due course.

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