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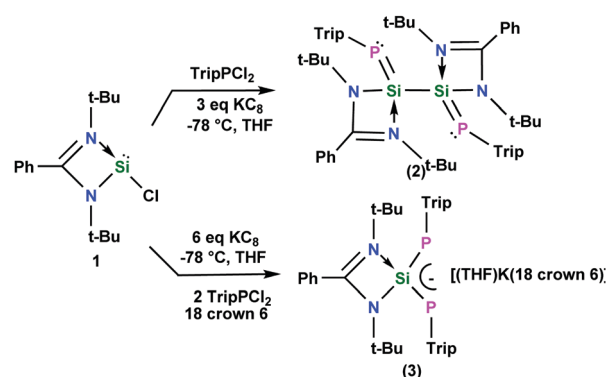
An unprecedented 1,4-diphospha-2,3-disila butadiene (–P=Si–Si=P–) derivative and a 1,3-diphospha-2-silaallyl anion, each stabilized by the amidinate ligand†

Subrata Kundu,^a Chandrajeet Mohapatra,^a Prinson P. Samuel,^a Johannes Kretsch,^a M. G. Walawalkar,^a Regine Herbst-Irmer,^a Dietmar Stalke,^{*a} Sriman De,^b Debasis Koley^{*b} and Herbert W. Roesky^{*a}

The first acyclic 4π-electron –P=Si–Si=P– motif with two four coordinate silicon substituents supported by the amidinate ligand and two coordinate phosphorus has been synthesized from the reaction of heteroleptic chlorosilylene LSiCl (1), TripPCl₂ (Trip = 2,4,6-ⁱPr₃C₆H₂) and KC₈ in a 1:1:3 ratio. The same reaction in a 1:2:6 ratio in the presence of one equivalent of 18-crown-6 ether affords the 1,3-diphospha-2-silaallyl anion.

In 1998, Dillon *et al.* published a book with the title, phosphorus: the carbon copy.¹ For decades this leitmotiv strongly influenced the research in phosphorus chemistry. In the meantime silylenes have attracted much attention due to their unique structures and bonding properties. A number of silylenes have been synthesized and structurally characterized.² Recently scientists have been fascinated with synthesizing more complex molecules using stable silylenes to unearth their interesting properties, including catalysis.^{2b} In recent years the results in silicon chemistry justify a new leitmotiv, silicon: the phosphorus copy. Compounds containing silicon and phosphorus are attracting attention due to their surprising bonding properties and their potential applications as semiconducting materials.³ After the first successful isolation of a compound with a Si=P double bond by Smit, Lock and Bickelhaupt in 1984, several derivatives having a double bond between silicon and phosphorus have been reported.⁴ In most of the cases, it has been observed that either the compounds possess a monomeric Si=P unit or a cyclic dimeric (Si₂P₂) or trimeric (Si₃P₃) arrangement.⁵ So far, only the reaction of P₄ with PhC(N(^tBu))₂SiN(TMS)₂ resulted in the formation of an

acyclic Si=P–P=P–Si chain.^{4d} Recently we reported an acyclic 4π electron delocalized butadiene analogue containing a Si–Si bonding motif (1,4-diamino-2,3-disila-1,3-butadiene).⁶ The successful isolation of a C=Si–Si=C chain inspired us to investigate whether it is possible to isolate a RP=Si–Si=PR chain, as R–P is isolobal to C.⁷ In this communication, we report the successful synthesis of an acyclic P=Si–Si=P chain and a P=Si–P anion supported by an amidinate ligand [L = PhC(N(^tBu))₂]. It is known that the Si=P bond might form when three coordinate silicon and two coordinate phosphorus are involved, although this bond is highly unstable.^{4a} So we chose amidinate silylene (1) because it will form a four coordinate silicon after the reaction with TripPCl₂. Moreover to stabilize the highly reactive Si=P bond, a bulky Trip group has been selected at the phosphorus atom. The reduction of LSiCl and TripPCl₂ with KC₈ in a molar ratio of 1:1:3 in THF resulted in compound 2 [(TripP=Si–L)₂] (Scheme 1), whereas the same reaction in a 1:2:6 ratio in the presence of one equivalent of 18-crown-6 affords compound 3 [(THF)K(18-crown-6)]⁺ [(TripP)₂SiL][–] (Scheme 1). To the best of our knowledge, a mixed phosphorus and silicon-centered chain of a stable and isolable 1,4-bisphosphino-2,3-disila butadiene has not been reported so far. In the past a 1,3-diphospha-2-silaallyl anion



Scheme 1 Syntheses of compounds 2 and 3.

^a Institut für Anorganische Chemie, Georg-August-Universität, Tammannstraße 4D-37077, Göttingen, Germany. E-mail: hroesky@gwdg.de, dstalke@chemie.uni-goettingen.de

^b Department of Chemical Sciences, IISER-Kolkata, Mohanpur Campus, Mohanpur 741252, India. E-mail: koley@iiserkol.ac.in

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$[\{\text{Li}(15\text{-crown-5})^+\text{BuSi}(2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2)_2\}^-]^8$ has been reported by Niecke *et al.*, where a tertiary butyl group is attached to the silicon atom. In the present case we have applied a different synthetic strategy to isolate the 1,3-diphospha-2-silaallylic anion. In comparison to the literature reported 1,3-diphospha-2-silaallylic anion where the silicon center is three coordinate with two phosphorus and one carbon, in compound **3**, the silicon center is four coordinate with two nitrogen and two phosphorus atoms. The composition is therefore quite different.

Compounds **2** and **3** were stable in an inert atmosphere for three months at room temperature both in the solid state and in solution. However, in the open atmosphere both compounds immediately decomposed with the formation of a mixture of products. In the ^{29}Si NMR spectrum, compound **2** displays a doublet of doublets at $\delta = 23.3$ ppm ($^1J_{\text{SiP}} = 231$ Hz, $^2J_{\text{SiP}} = 44$ Hz) thus indicating the presence of two phosphorus atoms in the molecule and the kinetic stability in the solution. The $^1J_{\text{SiP}}$ (231 Hz) coupling constant is comparable with the highest coupling constant (234.8 Hz)⁹ reported for any multiple bonded phosphorus–silicon compound in the literature supporting a more stronger and less polarized Si=P bond. As expected, the ^{29}Si NMR spectrum of **3** displays a triplet at $\delta = 43.4$ ppm ($^1J_{\text{SiP}} = 181$ Hz). The ^{31}P NMR spectra of **2** and **3** each exhibit a singlet at $\delta = -133.9$ and -161.5 ppm, respectively. These data are in good agreement with a symmetrical environment of the molecules.

The molecular structures of **2** and **3** were determined by single-crystal X-ray diffraction studies (Fig. 1, Fig. S3, ESI† and Fig. 2, Fig. S4, ESI†). The P1–Si1–Si2–P2 skeleton of **2** has a *trans*-bent geometry (torsion angle 2.67°). The average Si–P bond length in **2** is $2.123(1)$ Å, hence it is shorter than a Si–P single bond distance previously reported for a *e.g.* $\text{LSiP}(\text{i-Pr})_2$ ($2.307(8)$ Å)¹⁰ derivative but only slightly longer than the Si=P double bond lengths found for phosphasilenes, *e.g.* as in $\text{LSi}(\text{SiMe}_3)=\text{PSiMe}_3$ ($2.095(3)$ Å).^{4c} The average Si–P bond length of **2** and quantum chemical calculations (*vide infra*) indicate that the Si–P double bonds are significantly polarized.

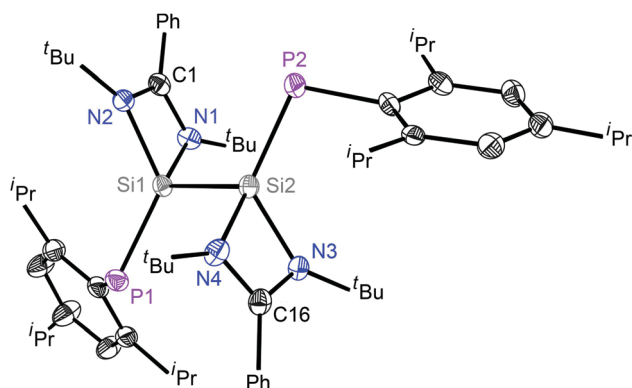


Fig. 1 Molecular structure of **2**; hydrogen atoms are omitted for clarity. Anisotropic displacement parameters are depicted at the 50% probability level. Selected experimental [calculated at R-M06-2X/def2-SVP for the singlet state] bond lengths (Å) and angles (deg): Si1–P1 $2.1201(9)$ [2.133]; Si1–Si2 $2.3825(11)$ [2.375]; Si2–P2 $2.1256(9)$ [2.125]; Si1–N1 $1.8331(16)$ [1.861]; Si1–N2 $1.8763(16)$ [1.890]; Si2–N3 $1.8378(16)$; Si2–N4 $1.8787(16)$; P1–Si1–Si2 $110.87(4)$ [114.4]; P2–Si2–Si1 $111.29(4)$ [114.4].

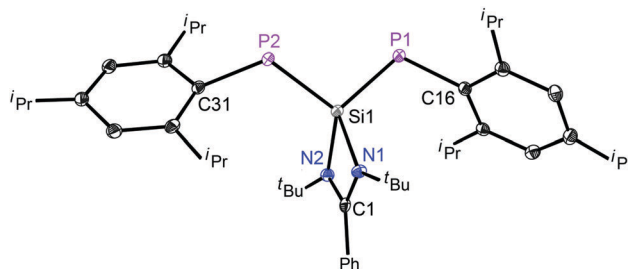


Fig. 2 Molecular structure of the anion in **3**; the *t*-butyl groups, the cationic part, the isopropyl groups and hydrogen atoms are omitted for clarity. Anisotropic displacement parameters are depicted at the 50% probability level. Selected experimental [calculated at R-M06-2X/def2-SVP for the singlet state] bond lengths (Å) and angles (deg): Si1–P1 $2.1662(7)$ [2.146]; Si1–P2 $2.1677(6)$ [2.166]; Si1–N1 $1.8870(12)$ [1.906]; Si1–N2 $1.8829(12)$ [1.890]; P1–Si1–P2 $103.12(2)$ [108.5].

The Si–Si bond distance in **2** is 2.383 Å, which is slightly shorter than the parent bis-silylene L–Si–Si–L ($2.413(2)$ Å).¹¹

The structure of **3** (Fig. 2) consists of a 1,3-diphospha-2-silaallylic anion and a potassium cation, which is bonded to an 18-crown-6 ether and a THF molecule in one of the axial positions. The Si(1)–P(1) and Si(1)–P(2) bond lengths are $2.166(7)$ and $2.168(6)$ Å, respectively, indicating the extensive delocalization of the anion. Thus, the Si–P bond distances in **3** are significantly shorter than an average Si–P single bond distance ($2.307(8)$ Å)¹⁰ but longer than the Si=P double bond lengths found in the literature for phosphasilenes, (2.053 – 2.095 Å).^{4c,12} The P1–Si1–P2 angle in the free anion in **3** is $103.12(2)^\circ$, which is more acute than the P–Si–P angle of $125.7(1)$ found in $[\{\text{Li}(15\text{-crown-5})^+\text{BuSi}(2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2)_2\}^-]^8$.

In order to explain the electronic structure and bonding scenario of **2** and **3**, DFT calculations were performed at the M06-2X/def2-SVP level of theory (see Computational details, ESI†). Computed singlet and triplet states of **2** and **3** showed that the singlet is the ground electronic state with energy differences of ($\Delta E_{\text{S} \rightarrow \text{T}}$) 42.3 and 33.7 kcal mol^{−1}, respectively. The geometrical parameters are in good agreement with the X-ray crystal structures as seen from the alignment and superposition of the conformers (Fig. S1 and Table S1, ESI†).

The formation of both complexes **2** and **3** from precursor **1** is highly exergonic with energy values ($\Delta G_{\text{r}}^{\text{S}}$) -363.0 and -390.5 kcal mol^{−1}, respectively, suggesting their favorable formation. To gain insight into the bonding nature of the Si–Si, Si–P and Si–N bonds in **2**, we carried out natural bond orbital analysis at the BP86/TZ2P//M06-2X/def2-SVP level of theory implemented in the ADF2013.01 program suite.¹³ The Si–Si bond exhibits a σ -occupancy of $1.878e$ with equal contributions from the bonding partners (Si $\sim 49\%$). The Si–P covalent bond shows a double bond character with σ and π occupancies of 1.940 and $1.847e$, respectively. Both the bonded electron densities (σ and π) of Si–P are polarized towards the P atom [$\text{P}(\sigma) \sim 57\%$, $\text{P}(\pi) \sim 79\%$], as pictorially represented by natural bond orbitals (Fig. S2 and Table S2, ESI†). The σ -bond is formed mainly from the *sp* hybridized orbital of Si and the almost pure *p*-orbital of the P atom. The NBO (NBO = Natural Bond Orbital) also locates a lone pair with an occupancy of $1.886e$ at the P atom. The Si atom is connected to one N atom *via* a single bond with an electron occupancy of



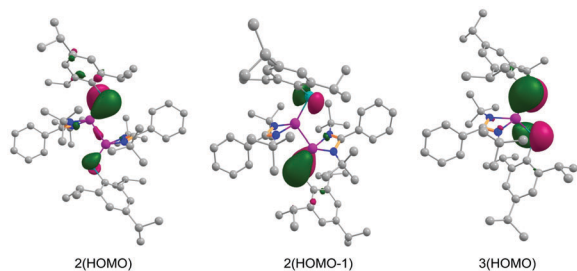


Fig. 3 Selected KS-MOs of **2** and **3** (isosurface = 0.05 a.u.). H atoms are omitted for clarity.

1.862e, where the electron density of this bond is mostly localized on the N center ($\sim 87\%$), which indicates that it is a very polar electron sharing bond (Table S7, ESI[†]). In contrast, the other N atom contains a lone pair which suggests a closed shell interaction between the Si and N atoms. The lone pair of electrons on the N atom donates an electron to the Si center as is evident from NRT calculations.¹³ An accumulation of positive and negative charges on the LSi and TripP fragments ($q_{\text{LSi}} = 0.76e$; $q_{\text{TripP}} = -0.76e$) (Table S3, ESI[†]) indicates a significant Si \rightarrow P σ donation; a similar observation was reported for carbene-dichlorosilylene stabilized phosphinidenes.¹⁴ The NBO proposed electronic scenario is further studied by QTAIM¹⁵ calculations. The important topological parameters at the (3, -1) bond critical points (BCP) are given in Table S4 (ESI[†]). The electron density at the BCP of the Si-P bond [$\rho(r) = 0.111$] along with the respective Laplacian [$\nabla^2\rho(r) = -0.059$] indicates a covalent interaction. The calculated ellipticity of the Si-P bond [$\epsilon_{\text{BCP}} = 0.335$] is much higher than that of the Si-P covalent single bond [$\epsilon_{\text{BCP}} = 0.14$] previously reported,¹⁶ indicating a significant double bond character in this case.

The Laplacian value, $\nabla^2\rho(r)$, of -0.155 for the Si-Si bond clearly suggests its covalent nature. The Wiberg bond indices (WBI) of the Si-Si and Si-P bonds are calculated to be 0.85 and 1.40, suggesting a single bond and a partial double bond, respectively. Similar to **2**, the phosphorus atom in **3** provides a major contribution towards the formation of both Si-P σ - and π -bonds [$P(\sigma) \sim 59\%$, $P(\pi) \sim 81\%$]. These bonds show occupancies of 1.891 and 1.828e, respectively (Table S2, ESI[†]). Moreover, similar to **2**, the AIM calculations of **3** show slight covalency of the Si-P bond with respect to the Laplacian value [$\nabla^2\rho(r) = -0.044$]. Here also the ellipticity value ($\epsilon_{\text{BCP}} = 0.334$) and Wiberg bond indices (WBI = 1.30) correspond fairly to a double bond character. The KS-HOMOs of compounds **2** and **3** show the π -bonding in the Si-P bonds (Fig. 3). Thus overall the observations have confirmed that both of the compounds have significantly polarized Si-P bonds with a notable double bond character.

NMR calculations at the PBE0/TZ2P¹⁷ level reveal the ^{29}Si chemical shift of **2** at 30.0 ppm, which is more up-field shifted when compared with that of **3** (42.4 ppm). The ^{31}P NMR spectra of **2** and **3** also show chemical shifts at -141.5 and -177.8 ppm, respectively (Table S5, ESI[†]). These values demonstrate similar trends with the experimental findings.

In conclusion an unprecedented acyclic 4 π -electron $\text{P}=\text{Si}-\text{Si}=\text{P}$ motif and a 1,3-diphospha-2-silaallyl anion have been isolated and structurally characterized. The theoretical investigations of

compounds **2** and **3** indicate that both of the products have polarized Si-P bonds with a significant double bond character.

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Notes and references

† Crystal data for **2** at 100(2) K: $\text{C}_{63.50}\text{H}_{96}\text{N}_6\text{P}_2\text{Si}_2$, $M_r = 1033.56 \text{ g mol}^{-1}$, $0.490 \times 0.200 \times 0.150 \text{ mm}$, triclinic, $P\bar{1}$, $a = 12.044(5) \text{ \AA}$, $b = 14.466(6) \text{ \AA}$, $c = 19.396(8) \text{ \AA}$, $\alpha = 81.95(2)^\circ$, $\beta = 77.12(2)^\circ$, $\gamma = 69.98(2)^\circ$, $V = 3088(2) \text{ \AA}^3$, $Z = 2$, $\mu(\text{MoK}\alpha) = 0.150 \text{ mm}^{-1}$, $\theta_{\text{max}} = 25.4^\circ$, 130 813 reflections measured, 11 414 independent ($R_{\text{int}} = 0.0565$), $R_1 = 0.0382$ [$I > 2\sigma(I)$], $wR_2 = 0.1043$ (all data), res. density peaks: 0.299 to $-0.244 \text{ e \AA}^{-3}$, CCDC 1507708. Crystal data for **3** at 100(2) K: $\text{C}_{61}\text{H}_{101}\text{KN}_2\text{O}_2\text{P}_2\text{Si}_2$, $M_r = 1103.56 \text{ g mol}^{-1}$, $0.424 \times 0.279 \times 0.152 \text{ mm}$, triclinic, $P\bar{1}$, $a = 10.771(3) \text{ \AA}$, $b = 13.848(3) \text{ \AA}$, $c = 22.433(5) \text{ \AA}$, $\alpha = 101.050(10)^\circ$, $\beta = 103.860(10)^\circ$, $\gamma = 100.660(10)^\circ$, $V = 3093.4(13) \text{ \AA}^3$, $Z = 2$, $\mu(\text{AgK}\alpha) = 0.114 \text{ mm}^{-1}$, $\theta_{\text{max}} = 20.3^\circ$, 127 873 reflections measured, 12 250 independent ($R_{\text{int}} = 0.0419$), $R_1 = 0.0331$ [$I > 2\sigma(I)$], $wR_2 = 0.0813$ (all data), res. density peaks: 0.471 to $-0.247 \text{ e \AA}^{-3}$, CCDC 1507709. All crystals were selected under cold protective conditions using the X-Temp2 device.¹⁸ The data were integrated with SAINT.¹⁹ A multi-scan absorption correction and a 3λ correction²⁰ were applied using SADABS.²¹ The structures were solved by SHELXT²² and refined on F^2 using SHELXL²³ in the graphical user interface SHELXLE.²⁴

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