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†

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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.2c 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)2)SiN(TMS) resulted in the formation of an acyclic Si–P=P=P=P=Si chain.6d 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. In this communication, we report the successful synthesis of an acyclic P–Si–Si–P chain and a P–Si–P–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.6e 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)], (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–Si–L]. (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

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[Scheme 1 Syntheses of compounds 2 and 3]
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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): S1–P1 2.1201(9) [2.133]; S1–S2 2.3825(11) [2.375]; S2–P2 2.1256(9) [2.125]; S1–N1 1.8331(16) [1.861]; S1–N2 1.8763(16) [1.890]; S2–N3 1.8378(16); S2–N4 1.8787(16); P1–S1–P2 110.87(4) [114.4]; P2–S2–S1 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): S1–P1 2.1662(7) [2.146]; S1–P2 2.1677(6) [2.166]; S1–N1 1.8870(12) [1.906]; S1–N2 1.8829(12) [1.890]; P1–S1–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). The formation of both complexes 2 and 3 from precursor 1 is highly exergonic with energy values (ΔE) of −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. The Si–Si bond exhibits a σ-occupancy of 1.878e with equal contributions from the bonding partners (Si ~ 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 [P(σ) ~ 57%, P(π) ~ 79%], as pictorially represented by natural bond orbitals (Fig. S2 and Table S2, ESIF). 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...
1.862e, where the electron density of this bond is mostly localized on the N center (∼87%), which indicates that it is a very polar electron sharing bond (Table S1). 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 well as to the other N atom containing a lone pair which suggests a closed shell interaction.

The electron density at the BCP (ρ) is given in Table S1 (ESI†). The electron density at the BCP of the Si–P bond (ρ(r) = 0.111) along with the respective Laplacian (∇²ρ(r) = 0.059) indicates a covalent interaction. The calculated ellipticity of the Si–P bond [εBCP = 0.335] is much higher than that of the Si–N single bond [εBCP = 0.14] previously reported, indicating a significant double bond character in this case.

The Laplacian value, ∇²ρ(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(σ) ~ 59%, P(π) ~ 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 [∇²ρ(r) = −0.044]. Here also the ellipticity value (εBCP = 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 polarized Si–P bonds with a significant double bond character.

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