

P₄ ActivationConsecutive Insertion of a Silylene into the P₄ Tetrahedron: Facile Access to Strained SiP₄ and Si₂P₄ Cage Compounds**

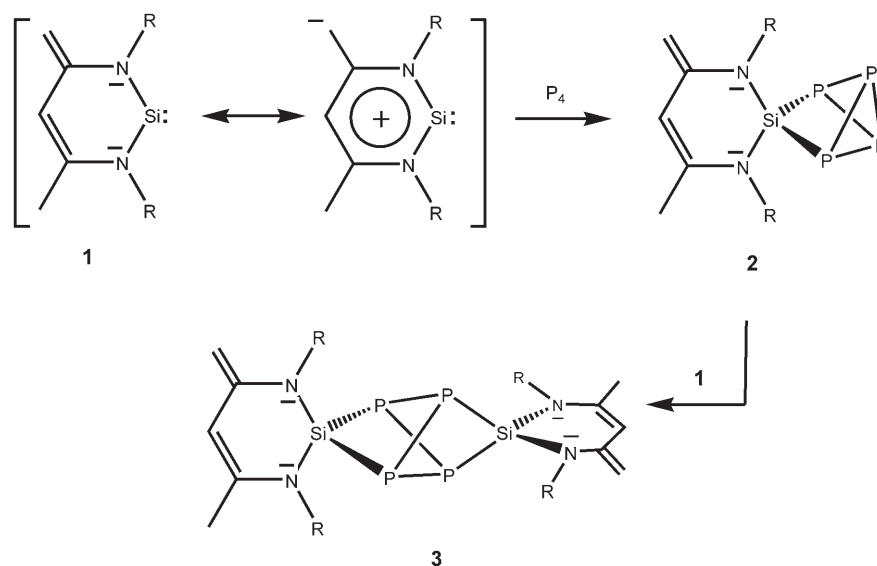
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Dedicated to Professor Michael F. Lappert

Organosilicon–phosphorus compounds are versatile building blocks in contemporary organophosphorus chemistry^[1] and for the synthesis of metal phosphide semiconducting materials or respective molecular clusters.^[2]

Likewise, cyclic silicon–phosphorus compounds can serve as chelating electron-rich ligands in transition-metal complexes, modeling unusual coordination modes of metal centers in catalysts.^[3] The formation of silicon–phosphorus compounds is commonly achieved by salt metathesis reactions using silicon halides and main-group-metal phosphides (for example, lithium phosphides).^[1,4] However, the latter method is hardly suitable for the synthesis of strained silicon–phosphorus cycles and cages because of facile skeletal rearrangement reactions (for example, intermolecular ring enlargement)^[5] under the reaction conditions.^[5] Hence, other synthetic methods are desirable to gain access to well-defined, strained silicon–phosphorus cycles and cages. A promising alternative strategy represents the utilization of unsaturated silicon compounds and white phosphorus (P₄) as shown by the gentle reaction of disilenes (R₂Si=SiR₂) and phosphasilenes (R₂Si=PR') with P₄ at 40 °C, leading to the unusual butterfly-shaped Si₂P₂ and SiP₃ heterobicyclo-[1.1.0]butanes,^[6a,7] respectively. The mechanism of this remarkably mild P₄ activation and degradation process, initiated by low-valent silicon, is not clearly understood as yet.^[6b] The latter results prompted us to investigate whether stable silylenes (R₂Si:) are also capable of P₄ activation to give novel strained silicon–phosphorus cycles. Herein we report

the first SiP₄ and Si₂P₄ cage compounds which result from consecutive P₄ activation with the stable silylene **1** (Scheme 1).



Scheme 1. Synthesis of **2** and **3** from **1** and P₄. R = 2,6-*i*-Pr₂C₆H₃.

Although several stable silylenes have been described thus far, to our knowledge, both the highly electrophilic silylene (CH₂)₂[C(SiMe₃)₂]₂Si:^[8] and the silicon analogues of nucleophilic Arduengo-type carbenes^[9] seemed to be unsuitable for P₄ activation. In contrast, the zwitterionic silylene **1**^[10a] reacts gently with P₄ in the molar ratio of 1:1 at ambient temperature to give solely the compound **2**. Remarkably, the germylene analogue of **1**,^[10b] in turn, is resistant towards P₄ even in boiling toluene owing to the lower reduction potential of Ge^{II} versus Si^{II} (inert-pair effect). Compound **2** can be isolated in the form of colorless crystals in 60 % yield.^[11]

According to EI-MS spectra and combustion analysis, **2** is a 1:1 adduct of **1** and P₄. Its ¹H NMR spectrum proves the integrity of the C₃N₂ chelate ligand at the silicon atom. As shown by ³¹P NMR spectroscopy, **2** bears three chemically different sorts of ³¹P nuclei (A, B, and X), giving rise to temperature-invariant resonance signals at δ_X = 131.9, δ_A = −342.4, and δ_B = −348.0 ppm. The low-field resonance signal at δ_X splits into a doublet (¹J(P_X,P_A) = 146.8, ¹J(P_X,P_B) = 144.7 Hz) while each of the two high-field signals exhibits a doublet of triplets (¹J(P_X,P_A) = 144.7, ¹J(P_A,P_B) = 188.0 Hz), indicating an ABX₂ splitting pattern.^[11] The

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[**] We thank the Deutsche Forschungsgemeinschaft for financial support and Prof. Dr. Konstantin Karaghiosoff (University of Munich) for his help on spectra simulations.

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unusual low-field shift of P_X is similar to values observed for M–P-bonded P atoms in isovalent $[L_nMP_4]$ complexes with a tricyclo[3.1.0]pentane-like core ($[L_nM]$ = diamagnetic transition-metal complex fragment^[12a–c] and PI_2 ^[12d]). Likewise, the high-field shifts of P_A and P_B in **2** signalize similar electronic features as observed for bridgehead P atoms in $[L_nMP_4]$ complexes^[12] and related butterfly-shaped Si₂P compounds (Scheme 1).^[6,7] The ²⁹Si NMR spectrum of **2** displays a broadened triplet resonance at $\delta = -40.4$ ppm ($^1J(^{29}\text{Si}, ^{31}\text{P}) = 32.0$ Hz), which is in the typical range of related cyclosilaphosphanes with silicon–phosphorus single bonds.^[13] The molecular structure of **2** deduced from ¹H, ³¹P, and ²⁹Si NMR spectroscopy was confirmed by a single-crystal X-ray diffraction analysis.^[11] Compound **2** consists of a tricyclic SiP₄ core with pyramidally coordinated phosphorus atoms and silicon atoms in a tetrahedral environment (Figure 1). The six-membered C₃N₂Si skeleton is almost planar and possesses endocyclic C–N and C–C bond lengths typical for its π -conjugated C₃N₂ backbone.^[10] The exocyclic C1–C2 and C4–C5 bond lengths are identical owing to orientation disorder. As expected, both the Si–P (av. 224.7 pm) and P–P bond

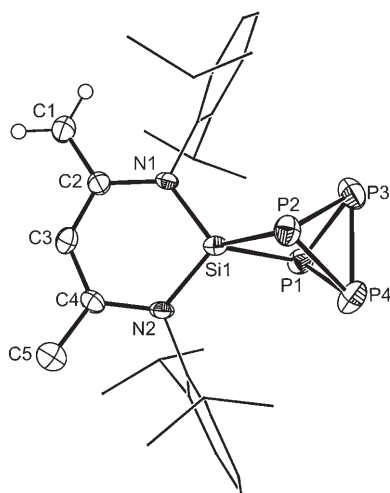


Figure 1. Molecular structure of **2**. Thermal ellipsoids (C1 through C5, P atoms, N1, N2, Si1) are drawn at the 50% probability level. Hydrogen atoms (except for those at C1) are omitted for clarity. Selected bond lengths [pm] and angles [°]: Si1–N1 172.8(3), Si1–N2 172.4(3), Si1–P2 225.0(1), Si1–P1 224.6(1), P3–P2 223.2(1), P1–P3 223.5(2), P3–P4 215.9(2), P2–P4 222.7(1), P1–P4 222.1(2), N1–C2 141.2(4), N2–C4 142.2(4), C1–C2 141.8(4), C2–C3 139.7(5), C3–C4 139.2(4), C4–C5 141.6(5); N1–Si1–N2 104.1(1), P1–Si1–P2 87.32(5), P4–P3–P2 60.94(5), P4–P3–P1 60.70(5), P2–P3–P1 88.03(5), P4–P2–P3 57.91(5), P4–P2–Si1 84.82(5), P3–P2–Si1 83.85(5).

lengths (av. 222.9 pm) are similar to those observed in related strained silaphosphanes^[13] and isostructural η^2 -P₄ transition-metal complexes,^[12a–c] respectively, except for the P3–P4 bridgehead bond length of 215.9(2) pm, which is even shorter than that in P₄ (220 pm). This result is reminiscent of the situation in related bicyclo[1.1.0]tetraphosphanes, R₂P₄ (R = organyl), which have relatively short P–P bridgehead bonds (212 pm) owing to partial P–P π -bond character.^[14] Apparently, this bonding situation favors the insertion of a Si^{II} atom

into the P3–P4 bond in **2**. Thus, **1** reacts slowly with **2** in toluene at 25 °C to give the insertion product **3** (Scheme 1), which was isolated in 27% yield in the form of colorless crystals.^[11] The reaction progress for the second insertion step of **1** into a P–P bond of the P₄ core is kinetically hampered because of steric congestion.

This reaction sequence is in contrast to the spontaneous multiple insertions of subvalent main-group-metal centers into the P₄ cage. For example, a related β -diketiminato Al^I complex reacts with P₄ to give a double-insertion product with a Al₂P₄ core.^[15a] Likewise, the tetrameric Al^I compound $[(\text{Cp}^*\text{Al})_4]$ reacts with P₄ in a 1.5:1 ratio to give $[(\text{Cp}^*\text{Al})_6\text{P}_4]$,^[15b] whereas the isovalent Ga^I atom in $[(\text{Me}_3\text{Si})_3\text{CGa}]$ affords an insertion product with a Ga₃P₄ core.^[15c]

The composition of **3** is proven by EI-MS (molecular ion m/z 1013) and a correct combustion analysis while its constitution is evident by NMR spectroscopy. As expected, the ³¹P{¹H} NMR spectrum displays two multiplets at $\delta_A = 153$ and $\delta_B = 158$ ppm, representing a AA'BB' splitting pattern of higher order with unusually small magnitudes of the respective $^1J(^{31}\text{P}, ^{31}\text{P})$ coupling constants.^[11] The ²⁹Si NMR spectrum displays a multiplet at $\delta = -15.9$ ppm, about 24 ppm to lower field in comparison with **2**. The molecular structure of **3** was confirmed by an X-ray diffraction analysis (Figure 2).^[11] The P–P bond lengths in the asterane-shaped P₄ core in **3** are similar (av. 228.5(1) pm) but somewhat longer than those in **2**, presumably because of the steric congestion from the substituents at the silane moieties. The same is true for the Si–P bond lengths (av. 228.5(1) pm), which are slightly longer than those in **2**. Both C₃N₂Si moieties are practically planar

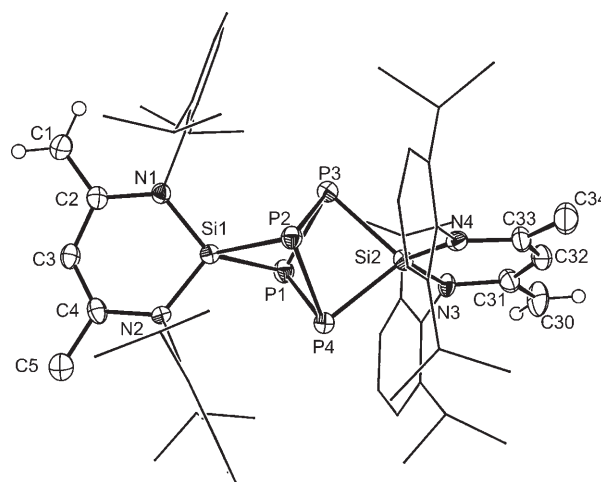


Figure 2. Molecular structure of **3**. Thermal ellipsoids (C1 through C5, C30 through C34, P atoms, N1 through N4, Si1, Si2) are drawn at the 50% probability level. Hydrogen atoms (except for those at C1 and C30) are omitted for clarity. Selected bond lengths [pm] and angles [°]: Si1–N1 172.6(3), Si1–N2 172.9(3), Si2–N3 172.5(3), Si2–N4 173.4(3), Si1–P1 229.1(1), Si1–P2 227.5(1), Si2–P3 229.5(1), Si2–P4 227.5(1), P1–P3 228.0(1), P1–P4 229.7(1), P2–P3 229.6(1), P2–P4 228.0(1), C1–C2 138.9(5), C2–C3 142.0(5), C3–C4 136.6(5), C4–C5 145.5(5); N1–Si1–N2 102.9(1), N3–Si2–N4 102.8(1), P2–Si1–P1 82.1°(4), P4–Si2–P3 82.30(5), P3–P1–Si1 82.42(5), P3–P1–P4 82.16(5), Si1–P1–P4 80.00(5), P1–P3–Si2 82.31(5), P1–P3–P2 81.90(5), Si2–P3–P2 79.75(5).

and the endo- and exocyclic C–C bond lengths of the ligand backbone indicate alternating C–C single and double bonds. This situation suggests only little perturbation of the buta-1,3-diene π system by the nitrogen atoms, similar to the situation in other compounds with tetravalent silicon.^[10a]

In summary, the novel strained tricyclic silaphosphans **2** and **3** are readily accessible by the first insertion reaction of a stable silylene into the P–P bonds of P_4 . Owing to the intrinsic $Si^{\delta+}-P^{\delta-}$ σ -bond polarity, the compounds **2** and **3** could serve as nucleophilic reagents for a mild transfer of formally P_4^{2-} (in **2**) and P_4^{4-} moieties (in **3**) to transition metals, leading to phosphorus-rich metal clusters or complexes with “naked” polyphosphorus ligands.^[16] Respective investigations are currently underway.

Received: March 19, 2007

Published online: May 4, 2007

Keywords: N ligands · phosphorus · silicon · silylenes · strained molecules

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