Forging a Cage into a Chain: Stepwise Transformation of P₄ by Silylenes to a Si₃P₄ Motif

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We have discovered a route to access the longest low-valent molecular silaphospha-chain, a seven-membered chain structure that incorporates three silicon and four phosphorus atoms by stepwise activation of white phosphorus (P₄) using two different silylene precursors. The chain species was formed via a highly reactive polyphosphide intermediate. The isolation of a stable analogue of this reaction intermediate was achieved by stepwise reaction with mono and bis(silylenes). Due to the rigidity of the ferrocenediyl framework of the bis(silylene), the isomerization process of the chain structure was hampered. Theoretical studies such as natural bond orbital and atoms in molecules analyses of the seven-membered chain species indicated some degree of delocalization of the double bond system.

Keywords: phosphorus, P₄ activation, silylene, silicon, main group, synthesis

Introduction

The industrial production of organophosphorus compounds relies on the oxidation of white phosphorus (P₄) with chlorine gas, yielding PCl₃ or PCl₅ as versatile intermediates. Considering sustainability aspects, it is highly desirable to construct phosphorus-containing compounds in an efficient and controlled way directly from white phosphorus. A well-established alternative utilizes transition metals to coordinate and functionalize P₄, which commonly involves the reduction of the P₄ moiety. In main group chemistry, the synthetic access to monophosphines, which relies on intermediarily utilizing Bu₃SnH for the activation of P₄, was reported recently. The more conventional approach employs low-valent compounds such as tetrylenes for the initial activation step. Silylenes were found to be efficient agents to form unusual and exotic silicon-functionalized polyphosphides via reactions with P₄. In common pathways of P₄ activations, the P₄ unit could be retained or broken down into P₁ or P₂ building blocks (Figure 1).

For instance, tetramesityldisilene was shown to activate white phosphorus to form a butterfly-like Si₂P₂ bicyclobutane core. Silylenes can react with P₄ through an insertion of Si(II) center into one or two σ-P–P bonds to give strained SiP₄ or Si₂P₄ cage compounds (A–E) in common pathways of P₄ activations. The degradation of P₄ into a zero-valent P₂ complex G was reported most recently using a xanthene-bridged bis(silylene).

From these examples, it is apparent that typical products of these activation processes are heterocycles and cages, while chain-type structures are rare. In fact, to the best of our knowledge, the specific example is disilatetraphospha-hexatriene (H). In general, chain structures...
constituting by main group elements such as phospha-
zenes do not only play an essential role in polymer chem-
istry but also as inorganic materials. Recently, a P₆ chain obtained by activation of P₄ was reported. In-
trigued by the possibility of generating a longer chain from the third row of the periodic table, we attempted to assemble a silaphospha-chain structure by stepwise activation of P₄ by silylenes.

Results and Discussion

In the initial experiment, we synthesized the SiP₄ cage compound [LSi(η²-P₄)] to study its re-
action with the amido-substituted monosilylene [L¹⁹Si
{N(SiMe₃)₂}], but no transformation occurred, even when the mixture was heated at 80 °C for 3 days. This was rather surprising, as Si(SiMe₃)₃ had previously been found to react with P₄ forming the six-membered chain species H. To reduce steric strain and enhance polarization effects, we considered another experiment, where amido(pyridyl)-functionalized silylene [L¹⁹Si(N(2-
py)Me)] was employed in a reaction with [LSi(η²-P₄)] (Scheme 1). In an NMR-scale reaction in C₆D₆, two sets of ³¹P NMR patterns, assignable to two different reaction products 1 and 2 (ca. 1:2 ratio) were observed [see Supporting Information Figure S11, minor component δ = –49.6, –101.7, –171.5, and –199.0; major component: δ 647.5, 424.7, 23.7, and –261.0] after only 10 min of reaction time. In solution, the signals of the minor species 1 decreased rapidly within an hour, with a quantitative formation of 2 from which an isomerization process could be inferred. The NMR pattern suggested that both compounds contained four chemically inequivalent phosphorus nuclei, and the large differences in their ³¹P coupling constants, indicating the presence of a typical polyphosphide structural motif. In contrast, two of the ³¹P NMR resonances of 2 appear at very low

Scheme 1 | Formation of diphosphene 2 via intermediate 1 (see Supporting Information Scheme S1 for a proposed mechanism and Supporting Information Table S1 for more NMR data).

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Figure 1 | (a–c) Activation products of P₄ by mono- and bis(silylenes) (Dipp = 2,6-iPr-C₆H₃,R = (N tBu₂)SiMe₂, R’ = SiMe₃).
fields (δ 647.5 and 424.7 ppm), characteristic of diphosphenes. Furthermore, the resonance at −261.4 ppm showed no large coupling constants, indicating the presence of a P atom isolated from a polyphosphide moiety.

Several attempts to identify the intermediate 1 were made, but difficulties arose from the short lifetime of this species. Only in instances where a very small amount of benzene was added to a mixture of [LSi(η²-P₃)] and [Li⁸⁵Si(NMe)(2-py)] (1:2) did the formation of tiny orange needles occur. From these, X-ray diffraction (XRD) analysis allowed the identification of 1 as a compound that incorporated two pyridylaminosilylenes and a P₄ chain (Figure 2a), despite the low quality of the diffraction data. None of the attempts to recrystallize compound 1 were successful due to the formation of isomeric species 2. Nevertheless, the structural data obtained for 1 were used as a starting point for density functional theory (DFT) optimization. The molecular geometry remained essentially unchanged, and the NMR parameters predicted from this model were in excellent agreement with a set of resonances observed spectroscopically (obs. −50, −102, −172, −199; calc. −65, −105, −171, −220 ppm, see Supporting Information Table S4).

Considering the crystallographic parameters, the molecular structure of 1 showed the presence of a four-membered SiP₃ heterocycle (Si₂-P₂-P₃-P₄) and a phosphasilene moiety coordinated through P₂ to the four-membered SiP₃ ring. In addition, another pyridylaminosilylene moiety was connected to P₃ with a distance of 2.198 Å (Si3-P3). All P-P and Si-P bond distances ranged between single and double bonds, indicating that the electrons were delocalized over all the silicon and phosphorus atoms. This view was also supported by DFT analysis (see Supporting Information Table S6).

Figure 2 | Molecular structure of compounds 1 (a) and 2 (b) in the solid state. H atoms and non-coordinating solvent molecules are omitted for clarity. Structural features are summarized in the Supporting Information.

The relatively short P-P bond distances of 2.0577(4) Å is typical for P-P double bonds, supporting the presence of a diphosphone. The Si-P bond length of 2.1157(4) Å is only marginally longer than typical Si-P double bonds (2.06–2.09 Å). In contrast, the Si2-P2 distance (2.2517(4) Å) compared well with classical Si-P single bonds (2.24–2.27 Å). The Si2-P1 (2.1940(4) Å) and Si3-P4 (2.1628(4) Å) bond distances fell in a range between average Si-P single and double bond length, indicating some degree of delocalization of the double bond system. This view was supported by our DFT calculations with natural bond orbital (NBO) and atoms in molecules (AIM) analyses (see Supporting Information Tables S7–S9). Within the NBO formalism, all π-bond occupations were significantly lower than 2 e, and
π*-occupation was found. The Wiberg bond indices (WBI) along the Si3P4 chain ranged from 0.96 to 1.24 for Si-P bonds and 1.30 to 1.57 for P-P bonds. The magnitude of WBI hinted at a strong covalent component of the interactions; however, the clear distinction between Si-P and P-P bonds also indicated a significant electrostatic contribution. The NBO charges for Si were found between +1.40 and 1.74 e, while the adjacent P atoms bore charges between −0.40 and −0.87 e. These values were comparable with data obtained for H (see Supporting Information Table S7). Comparisons with model systems revealed that (see Supporting Information Table S9) this strong polarization effect was induced by the N-containing substituents of the Si atoms. Topological analysis of the electron density at the bond critical points showed ellipticity (0.09–0.32) for all bonds, corroborating double bond delocalization. The formation of the diphosphene 2 is likely to have proceeded via insertion of the (LSi) fragment into the P1–P2 bond. Related [3+1] fragmentations of the P4 moiety were observed for the other functionalized P4 derivatives,36,37 and from the direct reaction of mesoionic carbenes with P4.14

The 31P{1H} NMR spectrum of 2 reveals an AMRZ spin system (see Scheme 1 for the assignment of the P atoms). Simulations using an iterative fitting process revealed four sets of multiplets for the four inequivalent P atoms (see Supporting Information Figures S4 and S15). The PI atom between the two silicon atoms Si1 and Si2 was found at δ = −261.0 as a doublet (J(P1P2) = 23.8 Hz) with the presence of different Si satellites (J(PSi) = 70 Hz, 154 Hz). Accordingly, in the 29Si NMR spectrum, the signals for Si1 and Si2 were found at 6.8 and −6.9 ppm. The third 29Si NMR signal was detected at 2.5 ppm as a doublet with a 1J(SiP) = 146 Hz and could be assigned to Si3. The observed NMR signals were in agreement with the computed data (2 obs. 648, 425, 24, −261; calc. 666, 432, 42, −254 ppm, see Supporting Information Table S4).

Since intermediate 1 had an impractically short lifetime and featured two pyridylamino-monosilylene moieties, we sought to prevent its isomerization reaction by introducing geometric constraints and employing a bis(silylene) in the reaction with [LSi(η²-P₄)]. Our bis(silylene) of choice was the ferrocenediyli-bridged [L³⁰SiFc-SiL³⁰⁻],38 as the bridging ferrocene moiety was rigid and resulted in a short distance between the two nucleophilic Si(II) centers (4.048 Å).39 The equimolar reaction of [LSi(η²-P₄)] with [L³⁰SiFcSiL³⁰⁻] in benzene instantly afforded a dark orange solution. The 31P NMR spectrum revealed two AXYZ spin systems in a 6:5 ratio (Figure 3, major component 3a: δ = −60.4, −126.3, −159.0, and −191.8; minor component: 3b: δ = −57.3, −119.4, −173.9, and −178.3 ppm; see Scheme 2 for the assignment of the P atoms). The data suggested the presence of two isomers 3a and 3b in solution with similar molecular structures and ³¹P NMR chemical shifts reminiscent of intermediate 1. This hypothesis was unambiguously corroborated by single-crystal XRD (SCXRD) analysis of 3a (Figure 4). The molecular structure revealed that the central Si-polyphosphide moiety was analogous to...
intermediate 1. The assignment of the molecular structure elucidated by XRD being responsible for the major NMR pattern was corroborated by DFT computations, as the calculated NMR parameters for 3a from XRD data agree with the observed NMR shifts (calc. −72, −117, −160, −194; obs. −60, −126, −159, and −192 ppm, see Supporting Information Table S5). Other isomers were computed to establish the nature of the other component in solution. The best fit with the observed data was found with 3b (calc. −62, −105, −138, −179; obs. −57, −119, −174, and −178 ppm). The two species are cis (3a) and trans (3b) isomers with respect to the relative orientation P2 and the methyl group of the β-diketiminate backbone with a slight energy difference of 22 kJ/mol (Scheme 2).

The presence of two nucleophilic Si(II) centers in the bis(silylene) [L^nSiFcSiL^n] led to the opening of the SiP4 cage in [LSi(n^2-P4)] by cleavage into two P-P bonds. The open-caged P4 moiety in 3a is coordinated by the bis(silylene) through P1 and P3 with Si-P bond distances being 2.1258(8) Å (Si-L-P1) and 2.1973(8) Å (Si3-P3), between typical single and double bond lengths. The P-P bond distances were similar to that of intermediate 1. The newly formed SiP3 ring (Si2-P2-P3-P4) was folded about the Si2–P3 axis by 32.1°, giving a “butterfly-shaped” structure. The Si-P bond distances in the four-membered ring showed longer (Si2–P2 = 2.2813(7) Å) and shorter (Si2–P4 = 2.1658(7) Å) bonds, with the latter one to the dicordinated P4 atom. In the $^2$Si NMR spectrum of 3a and 3b, three broad signals were observed at 35.5, 33.0, and −9.0, respectively, indicating their highly dynamic nature in solution. The steric constraint and rigidity of the ferrocenediyli-bridged bis(silylene) [L^nSiFcSiL^n] made it possible to stabilize the polyphosphide moiety in 3; therefore, an analogous isomerization pathway was further hindered.

**Conclusion**

We have shown that the SiP4 cage in the tetraphosphasilatricyclopentane [LSi(n^2-P4)] could be cleaved further using different silylenes to afford highly reactive and unusual polyphosphides. In this case, while the amino-silylene [L^nSi(N(SiMe3)2)] did not show any reactivity, using the amido-pyridyl functionalized mono(silylene) [L^nSi(N(Me)(2-py))], a non-symmetrically substituted trisilatetraphospha-heptatriene 2 was formed through a highly reactive intermediate 1. The isolation of a stable analogue of this reaction intermediate was achieved using a bis(silylene) [L^nSiFcSiL^n] bearing a rigid ferrocenediyli backbone, yielding 3a and 3b. These results showcase that an introduction of geometric constraints between two reactive sites in the activation process of small molecules such as P4 could have control over the reaction product obtained.

**Supporting Information**

Supporting Information is available and includes: (1) synthesis and characterization of all compounds, (2) NMR spectra, (3) details of the simulation of the NMR spectra, (4) IR spectra, (5) SXRD data, and (6) details of the quantum chemical calculations.

**Conflict of Interest**

There is no conflict of interest.

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