Forging a Cage into a Chain: Stepwise Transformation of P_4 by Silylenes to a Si_3P_4 Motif

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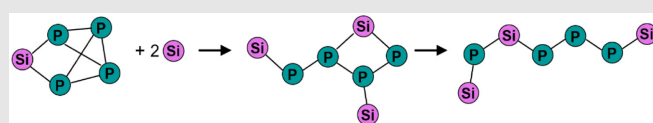*Institute of Inorganic Chemistry, Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe*

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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 (P_4) 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, P_4 activation, silylene, silicon, main group, synthesis
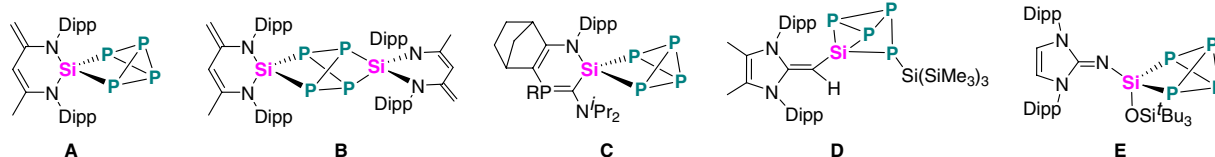
Introduction

The industrial production of organophosphorus compounds relies on the oxidation of white phosphorus (P_4) with chlorine gas, yielding PCl_3 or PCl_5 as versatile intermediates.[1,2] 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 P_4, which commonly involves the reduction of the P_4 moiety.[3–7] In main group chemistry, the synthetic access to monophosphines, which relies on intermediarily utilizing Bu_3SnH for the activation of P_4, was reported recently.[8] The more conventional approach employs low-valent compounds such as tetrylenes for the initial activation step.[9–23] Silylenes were found to be efficient agents to form unusual and exotic silicon-functionalized polyphosphides via reactions with P_4. In common pathways of P_4 activations, the P_4 unit could be retained or broken down into P_1 or P_2 building blocks (Figure 1).
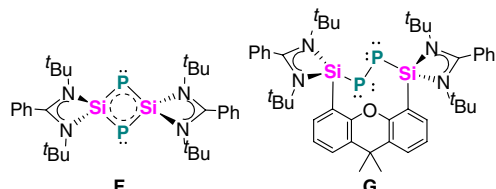
For instance, tetramesityldisilene was shown to activate white phosphorus to form a butterfly-like Si_2P_2 bicyclobutane core.[16] Silylenes can react with P_4 through an insertion of Si(II) center into one or two σ-P–P bonds to give strained SiP_4 or Si_2P_4 cage compounds (**A–E**, Figure 1).[17–19,22] The monochloro(silylene) $L^{Ph}SiCl$ ($L^{Ph} = PhC(N^tBu)_2$) and the interconnected Si(I) species $L^{Ph}SiSiL^{Ph}$ were found to react with P_4 forming compound **F** comprising a four-membered planar Si_2P_2 ring.[20] The degradation of P_4 into a zero-valent P_2 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**).[21] In general, chain structures

(a) P₄ cages

(b) P₁ or P₂ fragments
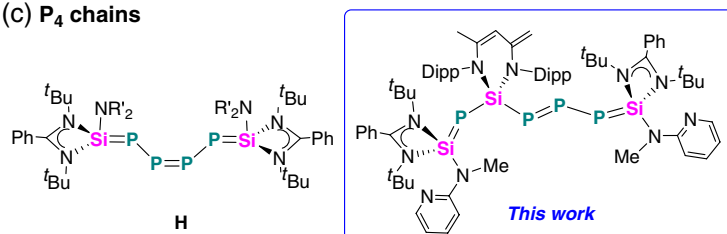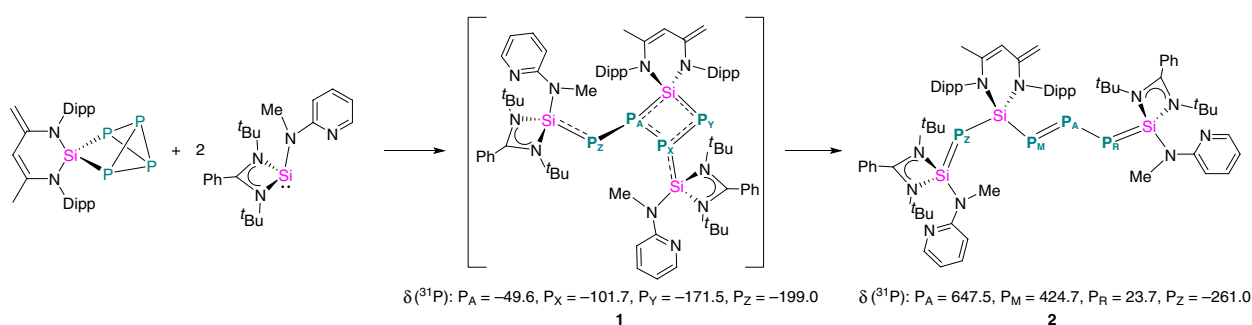

(c) P₄ chains

This work

Figure 1 | *(a–c) Activation products of P₄ by mono- and bis(silylenes) (Dipp = 2,6-^{i}Pr-C₆H₃, R = (N^{t}Bu₂)SiMe₂, R' = SiMe₃).*[16–23]

constituting by main group elements such as phosphazenes do not only play an essential role in polymer chemistry but also as inorganic materials.[24–26] Recently, a P₆ chain obtained by activation of P₄ was reported.[27] Intrigued 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)][17] (**A**, L = CH{C(Me)N(Dipp)}{C(CH₂)-N(Dipp)}, Dipp = 2,6-^{i}Pr-C₆H₃) to study its reaction with the amido-substituted monosilylene [L^{Ph}Si{N(SiMe₃)₂}],[28] but no transformation occurred, even when the mixture was heated at 80 °C for 3 days. This was rather surprising, as [L^{Ph}Si{N(SiMe₃)₂}] 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 [L^{Ph}Si{N(2-py)Me}][29] 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 NMR chemical shifts indicated their strikingly distinct chemical nature. The set of ³¹P NMR resonances of **1** span only the high-field region between −50 and −200 ppm and J(PP) coupling constants, which were observed in the expected range of ¹J 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

δ (³¹P): P$_A$ = −49.6, P$_X$ = −101.7, P$_Y$ = −171.5, P$_Z$ = −199.0 **1**

δ (³¹P): P$_A$ = 647.5, P$_M$ = 424.7, P$_R$ = 23.7, P$_Z$ = −261.0 **2**

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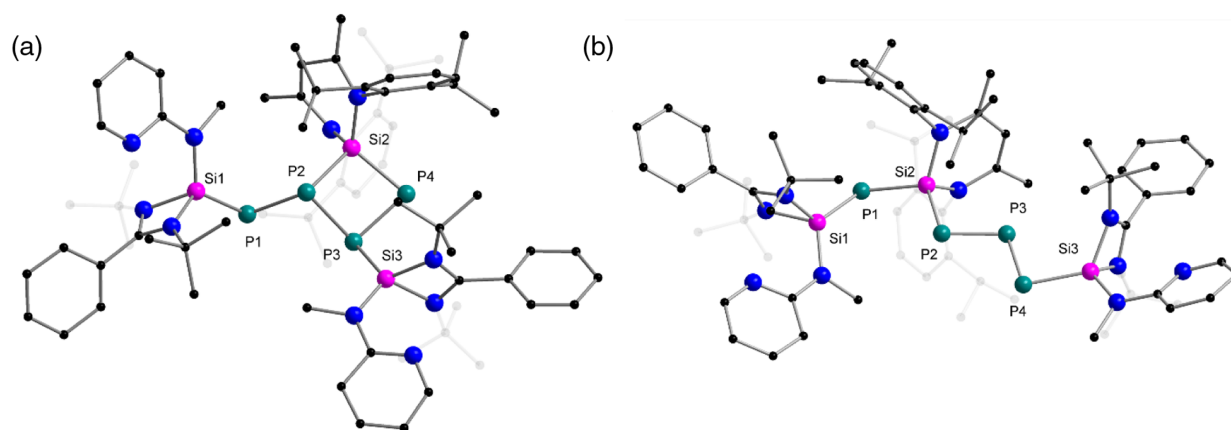
Figure 2 | *Molecular structure of compounds **1** (a) and **2** (b) in the solid state. H atoms and non-coordinating solvent molecules are omitted for clarity. Structural features are summarized in the Supporting Information.*

fields (δ 647.5 and 424.7 ppm), characteristic of diphosphenes.[9,30] 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(η^2-P$_4$)] and [L^{Ph}Si {(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 P$_4$ 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 (**1** 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 SiP$_3$ heterocycle (Si2-P2-P3-P4) and a phosphasilene moiety coordinated through P2 to the four-membered SiP$_3$ 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,[31,32] 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). Apparently, the reaction proceeded through nucleophilic attack of pyridylaminosilylene [L^{Ph}Si{(NMe)(2-py)}] with [LSi(η^2-P$_4$)] and the

cleavage of two σ-P–P bonds, which resulted in the opening of the SiP$_4$ cage in [LSi(η^2-P$_4$)], giving compound **1** as unstable intermediate.

As the molecular structure of the intermediate **1** was established, the identity of **2** still had to be elucidated. To isolate the final reaction product **2**, [LSi(η^2-P$_4$)] was added to a benzene solution of the silylene [L^{Ph}Si{(NMe)(2-py)}]. The reaction mixture turned from orange to purple within a few minutes. When this solution was left undisturbed at 20 °C for 1 week, it led to the formation of red block-shaped single crystals of the reaction product **2** in 32% yield. The molecular structure of product **2** was unambiguously determined by XRD analysis, revealing a non-symmetrically substituted (*E*)-diphosphene isomer with [L^{Ph}Si{(NMe)(2-py)}P(LSi)] and [(P)L^{Ph}Si{(NMe)(2-py)}] coordinated to the two different phosphorus atoms (Figure 2b). The central motif consisted of a seven-membered SiPSiP$_3$Si chain; thus, the longest low-valent molecular Si-P chain reported so far. The P–P bond distances in the P$_3$ fragment were 2.0577(4) (P2–P3) and 2.1204(4) Å (P3–P4), respectively, whereas the latter one was between P–P single and double bonds.[31,32]

The relatively short P–P bond distances of 2.0577(4) Å is typical for P–P double bonds,[21,31] supporting the presence of a diphosphene. The Si1–P1 bond length of 2.1157(4) Å is only marginally longer than typical Si=P double bonds (2.06–2.09 Å).[31,33,34] In contrast, the Si2–P2 distance (2.2517(4) Å) compared well with classical Si–P single bonds (2.24–2.27 Å).[21,35] 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
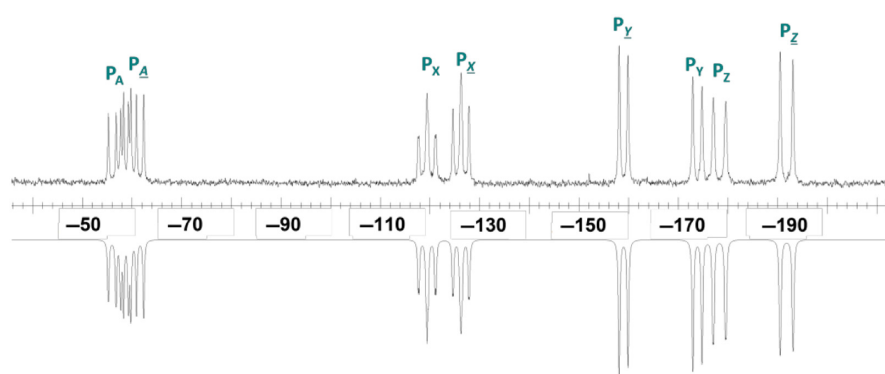
Figure 3 | $^{31}P\{^{1}H\}$ NMR spectrum (162.04 MHz) for **3a** and **3b**. Experimental (top) and simulated (bottom) spectrum.

π^*-occupation was found. The Wiberg bond indices (WBI) along the Si_3P_4 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 P_4 moiety were observed for the other functionalized P_4 derivatives,[36,37] and from the direct reaction of mesoionic carbenes with P_4.[14]

The $^{31}P\{^{1}H\}$ 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 P1 atom between the two silicon atoms Si1 and Si2 was found at δ −261.0 as a doublet ($^{2}J(P_MP_Z)$ = 23.8 Hz) with the presence of different Si satellites (J(PSi) = 70 Hz, 154 Hz). Accordingly, in the ^{29}Si NMR spectrum, the signals for Si1 and Si2 were found at 6.8 and −6.9 ppm. The third ^{29}Si NMR signal was detected at 2.5 ppm as a doublet with a ^{1}J(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 $[LSi(\eta^2-P_4)]$. Our bis(silylene) of choice was the ferrocenediyl-bridged $[L^{Ph}SiFcSiL^{Ph}]$,[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 $[LSi(\eta^2-P_4)]$ with $[L^{Ph}SiFcSiL^{Ph}]$ in benzene instantly afforded a dark orange solution. The ^{31}P 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 ^{31}P 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
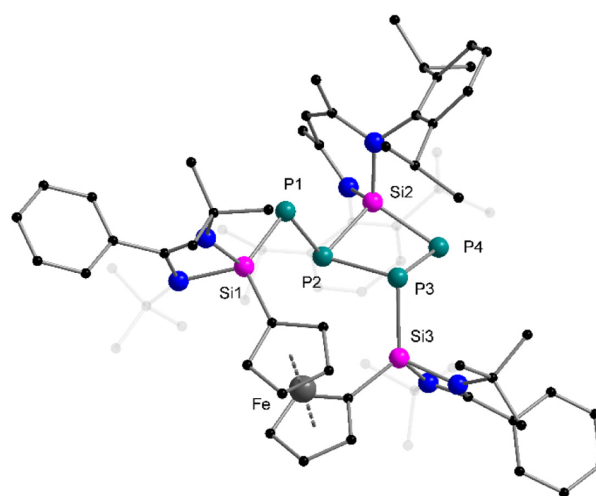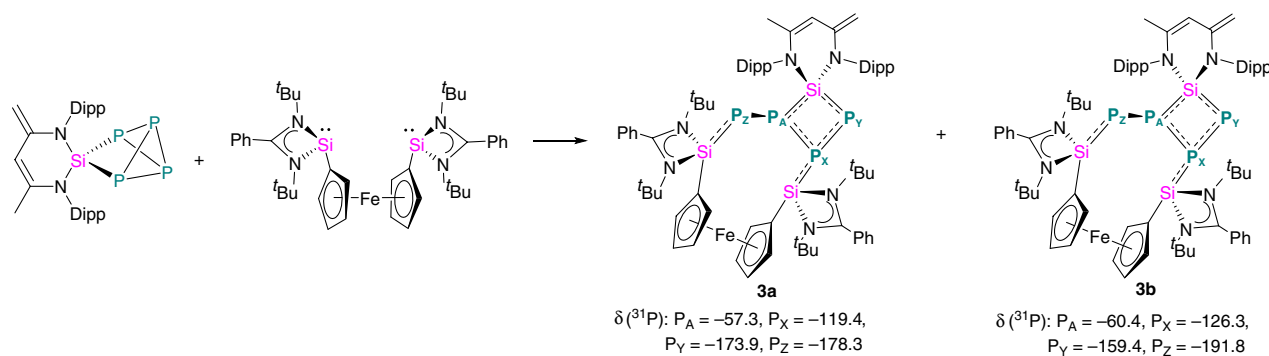

Figure 4 | Molecular structure of compound **3** in the solid state. H atoms and non-coordinating solvent molecules are omitted for clarity. Structural features are summarized in the Supporting Information.

δ (^{31}P): $P_A = -57.3$, $P_X = -119.4$,
$P_Y = -173.9$, $P_Z = -178.3$

3a

δ (^{31}P): $P_A = -60.4$, $P_X = -126.3$,
$P_Y = -159.4$, $P_Z = -191.8$

3b

Scheme 2 | *Synthesis of compound 3 (see Supporting Information Table S2 for more NMR data).*

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 P_Z 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^{Ph}SiFcSiL^{Ph}] led to the opening of the SiP$_4$-cage in [LSi(η^2-P$_4$)] by cleavage into two σ-P–P bonds. The open-caged P$_4$ moiety in **3a** is coordinated by the bis(silylene) through P1 and P3 with Si–P bond distances being 2.1258(8) Å (Si1–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 SiP$_3$ 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 dicoordinated P4 atom. In the ^{29}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 ferrocenediyl-bridged bis(silylene) [L^{Ph}SiFcSiL^{Ph}] made it possible to stabilize the polyphosphide moiety in **3**; therefore, an analogous isomerization pathway was further hindered.

Conclusion

We have shown that the SiP$_4$ cage in the tetraphospha-silatricyclopentane [LSi(η^2-P$_4$)] could be cleaved further

using different silylenes to afford highly reactive and unusual polyphosphides. In this case, while the aminosilylene [L^{Ph}Si{N(SiMe$_3$)$_2$}] did not show any reactivity, using the amido-pyridyl functionalized mono(silylene) [L^{Ph}Si{(NMe)(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^{Ph}SiFcSiL^{Ph}] bearing a rigid ferrocenediyl 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 P$_4$ 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.

Funding Information

Acknowledgments

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