

Cite this: *Dalton Trans.*, 2024, **53**, 10220Received 9th May 2024,
Accepted 28th May 2024

DOI: 10.1039/d4dt01367k

rsc.li/dalton

Reactivities of phosphalkynes towards diverse bis-silylenes†

Xiaofei Sun,^a Da Jin,^a Stefanie Maier,^a Alexander Hinz^a and Peter W. Roesky^{a,b}*

Bis-silylenes do not only act as strong chelating σ -donor ligands, but also exhibit cooperative behaviour in the activation of small molecules. Three different P–Si containing molecules were prepared from the reaction between $t\text{BuC}\equiv\text{P}$ and different bis-silylenes, which are bridged by ferrocenediyl, diaminobenzene, or *o*-carborane.

Introduction

The chemistry of silylenes has witnessed significant advancements since Jutzi's seminal report on the first divalent silicon compound¹ and West's ground-breaking discovery of the first stable N-heterocyclic silylene.² Over recent decades, several examples of bis-silylenes have emerged,^{3–11} primarily utilising the amidinate-based Si(II) fragment, owing to the straightforward functionalisation starting from the parent chlorosilylene $[\text{LSiCl}]^{12,13}$ ($\text{L} = \text{PhC}(t\text{BuN})_2$). Altering the spacer moiety allows for adjusting the electronic properties as well as the Si...Si distance, which has led to varied reactivities.^{10,14} Apart from serving as strong σ -donating chelate ligands, bis-silylenes exhibit the capability to cooperatively activate small molecules owing to the two Si(II) centres in close proximity. This distinctive feature cannot be achieved using mono-silylenes. In addition to different small molecules such as P_4 , CO_2 , N_2O , whose reactivity has been studied using bis-silylenes, attention has recently shifted towards organic substrates with triple bonds.^{15–17}

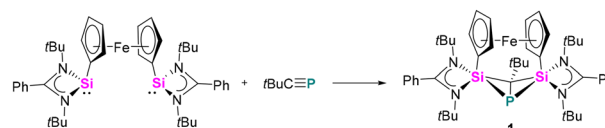
As a heavier congener of nitriles, phosphalkynes feature a polarised $\text{C}^{\delta-}\equiv\text{P}^{\delta+}$ triple bond. Since the isolation of the first stable phosphalkyne $t\text{BuC}\equiv\text{P}$ by Becker in 1981,¹⁸ this major breakthrough has paved the way for scientists to achieve a series of kinetically stable phosphalkynes.^{19,20} Their versatility as building block in synthetic chemistry has been demonstrated. In the area of low-valent silicon chemistry, earlier reports showcased the diverse reactivities with phosphalkynes

to form Si–P heterocycles *via* cycloaddition^{21–23} and insertion reactions.^{16,24–27} Intrigued by this, we started our investigation of reactions between different bis-silylenes towards $t\text{BuC}\equiv\text{P}$.

Results and discussion

Synthesis and characterisation of 1

The reaction between the ferrocenediyl-bridged bis-silylene $[\text{LSiFcSiL}]^6$ ($\text{Fc} = \text{ferrocenediyl}$) and $t\text{BuC}\equiv\text{P}$ yielded the double [1 + 2] cycloaddition product **1** in 83% yield (Scheme 1). The molecular structure was unequivocally determined by single crystal X-ray diffraction (SCXRD) analysis and is depicted in Fig. 1. Compound **1** crystallises in the orthorhombic space group *Pbca*. It consists of a four-membered “butterfly-shaped” 1-phospha-2,4-disilabicyclo[1.1.0]butane as central structural motif, in which the SiPCSi ring is folded about the P–C axis by 64.49° . The strongly bent core structure might arise from the steric constraints from the ferrocene-based linker. Structurally, the interatomic Si...Si separation of 2.97 Å clearly rules out any bonding interaction. The P–C bond (2.056(2) Å) is slightly longer than classical P–C single bond lengths, but the P–Si bonds (2.2716(9) and 2.2310(9) Å) and the Si–C1 bonds (1.867(2) and 1.875(2) Å) fall within the range of the respective single bond lengths.²⁸ The two Si atoms are pentacoordinated by two C atoms, one P atom and two N atoms and the P atom is in a trigonal pyramidal coordination environment. At first glance, the structure motif of **1** resembles

Scheme 1 Reaction of $[\text{LSiFcSiL}]$ and $t\text{BuC}\equiv\text{P}$.

^aInstitute for Inorganic Chemistry, Karlsruhe Institute of Technology (KIT), Engesserstr. 15, 76131 Karlsruhe, Germany. E-mail: roesky@kit.edu

^bInstitute for Nanotechnology, Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany

† Electronic supplementary information (ESI) available. CCDC 2345640–2345643. For ESI and crystallographic data in CIF or other electronic format see DOI:

<https://doi.org/10.1039/d4dt01367k>



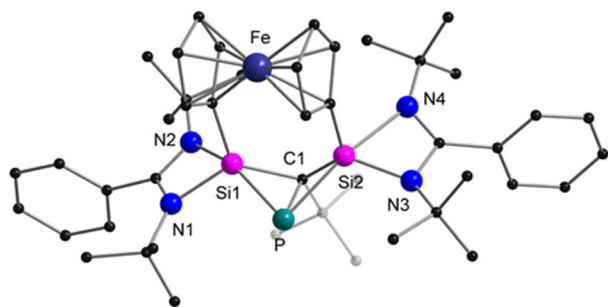


Fig. 1 Molecular structure of compound **1** in the solid state. Hydrogen atoms and non-coordinating solvent molecules are omitted for clarity. Selected bond distances [Å] and angles [°]: P–C1 2.056(2), P–Si1 2.2716(9), P–Si2 2.2310(9), Si1–C1 1.867(2), Si2–C1 1.875(2), Si1–N1 1.858(2), Si1–N2 2.080(2), Si2–N3 1.817(2), Si2–N4 2.221(2); N1–Si1–N2 66.49(8), N3–Si2–N4 65.22(8), Si1–C1–Si2 105.07(11), Si1–P–Si2 82.54(3), Si1–C1–P 70.58(8), Si2–C1–P 68.97(8), Si1–P–C1 50.81(7), Si2–P–C1 51.68(7).

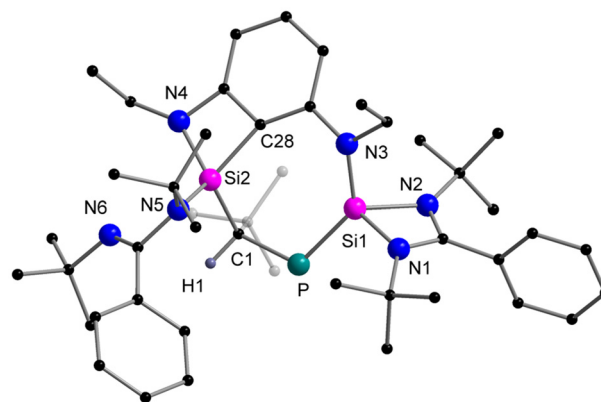


Fig. 2 Molecular structure of compound **2** in the solid state. Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Si1–P 2.1322(8), Si1–N1 1.835(2), Si1–N2 1.889(2), Si1–N3 1.728(2), P–C1 1.897(2), Si2–C1 1.881(2), Si2–C28 1.855(2), Si2–N4 1.777(2), Si2–N5 1.748(2), N1–Si1–N2 70.42(8), Si1–P–C1 116.28(7), P–C1–Si2 106.15(10), N4–Si2–C28 75.40(9).

that of the zwitterionic SiPSiC ring²⁶ formed from the reaction between the mono-silylene [LSiCl]^{12,13} and 1-AdC≡P.

However, the predominant difference lies in the geometry of the SiPSiC cycle which is in this case perfectly planar (sum of inner angles 360°) and the phosphorus atom is only dicoordinated by two Si atoms, due to the cleavage of the P–C bond. In contrast, the P–C bond in compound **1** is intact.

In the ¹H NMR spectrum of **1**, the *t*Bu protons appear as three singlets at 1.53, 1.34, and 1.31 ppm. The singlet signal at –294.2 ppm in the ³¹P{¹H} NMR spectrum is assigned to the tri-coordinated P atom, which is shifted to lower frequencies compared to *t*BuC≡P (–69 ppm).²⁹ In the ²⁹Si{¹H} NMR spectrum, a doublet signal is detected at –76.4 ppm with ¹J_{SiP} of 44.8 Hz. The addition of the bis-silylene moiety to the phosphalkyne induces a significant highfield shift of the resonance.⁶

Synthesis and characterisation of **2**

Next, we investigated the reaction between the diamino-benzene-functionalised bis-silylene [LSiCSiL]⁹ (C = 2,6- $\{(\text{EtN})_2\text{C}_6\text{H}_3\}$) and *t*BuC≡P²⁹ (Scheme 2). After stirring both precursors at room temperature for 30 min, all the starting materials were consumed. Concentrating the solution and storing in a –40 °C freezer resulted in the formation of single crystals of the cyclic reaction product **2**, which significantly differs from **1**. The molecular structure of compound **2** was determined *via* SCXRD analysis and is depicted in Fig. 2. Compound **2** crystallises in the triclinic space group *P* $\bar{1}$ and the core structure comprises a seven-membered SiC₂N₂SiPc



Scheme 2 Reaction of [LSiCSiL] and *t*BuC≡P.

heterocycle. Notably, the Si1–P bond distance of 2.1322(8) Å is significantly shorter than the reported Si–P single bonds (~2.25 Å)³⁰ but only marginally longer than the Si–P double bond (~2.09 Å), indicating its double bond character. The Si1–P bond length found in compound **2** is comparable with other literature-reported Si–P heterocycles^{26,31} or chain-type species.^{32,33}

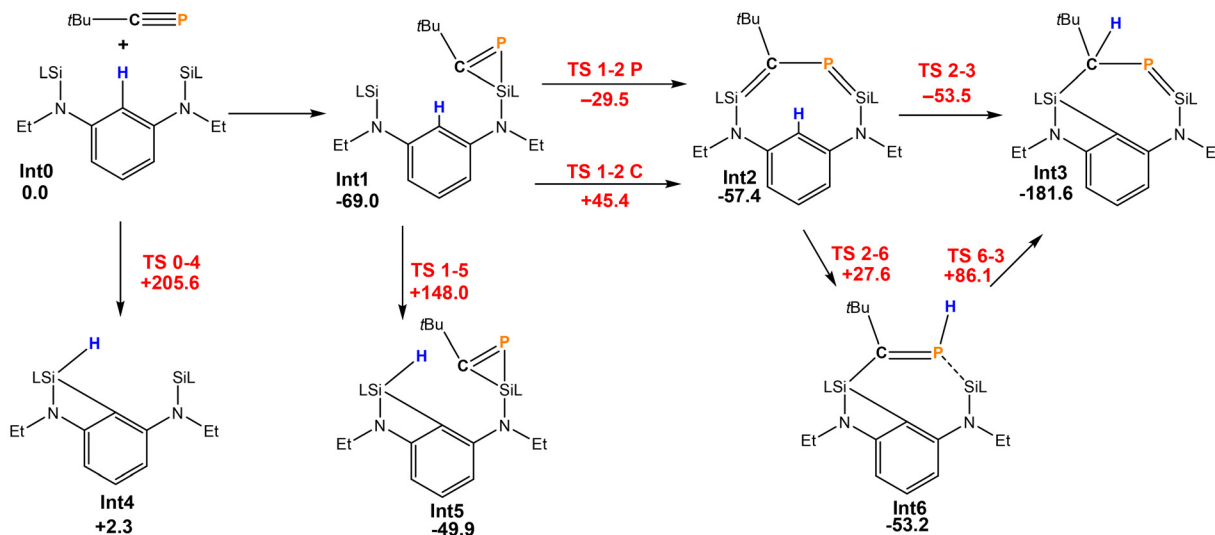
In contrast, the P–C1 bond distance (1.897(2) Å) falls within the range of P–C single bonds.²⁸ The formation of the seven-membered ring is facilitated by an intramolecular C–H bond activation. Si2 in compound **2** is coordinated by two amido groups and two C-substituents C1 and C28 in a distorted tetrahedral environment. The presence of the proton at C1 was detected at 2.21 ppm as a doublet signal due to the ²J_{HP} (23.2 Hz) coupling with the ³¹P nucleus. Correspondingly, the ³¹P NMR resonance was observed at –173.0 ppm as a doublet (²J_{HP} = 23.2 Hz) and the ²⁹Si{¹H} NMR resonances were found at 2.5 ppm and –28.1 ppm as two doublets with coupling constants of 209.3 Hz (¹J_{SiP}) and 10.8 Hz (²J_{SiP}), respectively.

Critically, there is no suitable C–H proton available in the ferrocenediyl-bridged bis-silylene [LSiFcSiL], which leads to the formation of **1**. Thus, the C–H bond activation in [LSiCSiL] is a key factor for the formation of the two different products **1** and **2**. Therefore, we aimed to investigate the reactivity of the diaminopyridine-bridged bis-silylene [LSiNSiL] (N = 2,6- $\{(\text{EtN})_2\text{C}_5\text{H}_3\text{N}\}$),⁴ which is analogous to [LSiCSiL] but lacks a proton at 1-position of the aromatic ring. However, the NMR-scale reaction in C₆D₆ revealed the formation of a mixture of several reaction products, and unfortunately, no single product could be crystallised and identified.

DFT calculations for the reaction pathway of the formation of **2**

The reaction pathway for the formation of **2** was investigated by DFT calculations (Scheme 3). The initial step is most likely to be well-established the [2 + 1] cycloaddition of the P≡C





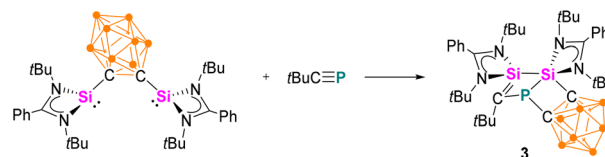
Scheme 3 Reaction of [LSiCSiL] and $t\text{BuC}\equiv\text{P}$ (energies in kJ mol^{-1} , intermediates in black, transition states in red).

triple bond on one of the silylenes. This is exergonic by $-69.0 \text{ kJ mol}^{-1}$ and leads to **Int1**. Subsequently, the strained phosphasilirene²¹ is opened to give the nine-membered cyclic species **Int2** in which both a P–C bond order is reduced to 1 and both a Si–C and Si–P double bond exist. This step can proceed by opening either the Si–C or a Si–P bond of **Int1**. Both are feasible, but the activation barrier for the latter path is considerably lower ($\Delta G = 39.5 \text{ kJ mol}^{-1}$). From **Int2** there is a path with a very low activation barrier that directly leads to **Int3** (=2) where simultaneously, the former phosphalkyne C atom abstracts a hydrogen atom from the central phenyl ring and the nine-membered heterocycle contracts to the seven-membered cyclic **Int3**. Alternatively, the H atom could be transferred to the phosphorus atom (**Int6**), but the subsequent H atom migration has a rather high activation barrier, which makes the direct process the most probable one.

It should be noted that without the C–P unit bridging both silylenes, the C–H activation barrier by the silylene of 148.0 or 205.6 kJ mol^{-1} is much too large to be feasible. Therefore, the rigid linker of the bis-silylene first enables the formation of the unusual intermediate **Int2**. The additional strain enforced closer proximity of the silylene moiety and the Ph group that allows then C–H activation. The more flexible ferrocenediyl backbone can facilitate closer Si...Si distances so that the bicyclic **1** can form. This is inhibited in the formation of **2**.

Synthesis and characterisation of **3**

When the *o*-carborane-substituted bis(silylene) [LSiBSiL]¹¹ ($\text{B} = \text{C}_2\text{B}_{10}\text{H}_{10}$) was treated with $t\text{BuC}\equiv\text{P}$, a single reaction product **3** was formed and isolated in 51% yield as yellow crystals (Scheme 4). Compound **3** crystallises in the monoclinic space group $P2_1/n$ and consists of two fused four-membered heterocycles Si_2PC and SiC_2P (Fig. 3). In this transformation, one of the Si–C bonds is cleaved and a Si–Si single bond (2.352(2) Å) is newly formed. Notably, the C–P bond of the phosphalkyne remains intact and the P–C1 bond of 1.780(5) Å is slightly



Scheme 4 Reaction of [LSiBSiL] and $t\text{BuC}\equiv\text{P}$.

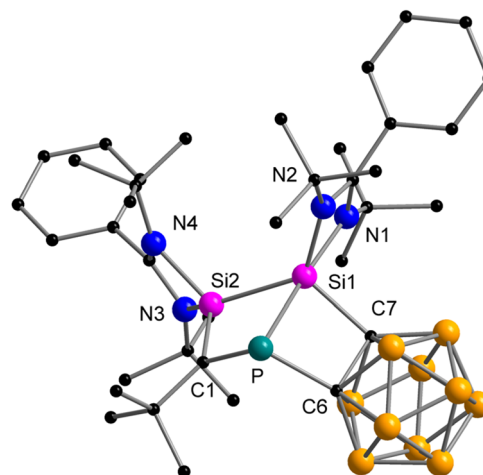


Fig. 3 Molecular structure of compound **3** in the solid state. Hydrogen atoms and non-coordinating solvent molecules are omitted for clarity. Selected bond distances [Å] and angles [°]: Si1–Si2 2.352(2), Si2–C1 1.761(5), C1–P 1.780(5), P–Si1 2.343(2), P–C6 1.964(5), Si1–C7 1.969(5), Si1–N1 1.956(4), Si1–N2 1.857(4), Si2–N3 1.894(4), Si2–N4 1.884(4); N1–Si1–N2 68.7(2), N3–Si2–N4 69.2(2), Si1–P–C1 89.5(2), Si1–P–C6 79.93(14), Si1–Si2–C1 89.7(2), Si2–Si1–P 73.84(6), Si2–Si1–C7 118.53(14), Si2–C1–P 105.6(3), C1–P–C6 110.9(2), C7–Si1–P 80.64(14).

shorter compared to classical P–C single bonds ($\sim 1.87 \text{ Å}$). In contrast, the P–C6 bond distance of 1.964(5) Å is elongated than typical P–C single bonds.



Moreover, the Si2–C1 bond distance of 1.761(5) Å is much shorter than literature-known Si–C single bonds (1.86–1.93 Å)³⁴ but well-comparable to that of Brook's silene [(Me₃Si)₂Si=C(OSiMe₃)Ad] (1.764(3) Å)³⁵ and other cyclic silenes.^{25,36} During the preparation of this work, the group of Li and Su reported a similar reaction between the bis-silylene [LSiBSiL] and 1-AdC≡P, which gave a comparable product.¹⁶ The bonding metrics of the two compounds are very similar. In their work, DFT calculations were performed to elucidate the mechanistic pathway, which is initiated by the [2 + 2] cycloaddition between the P≡C bond and one Si–C bond. Following this, one C–C bond is formed and one Si–C bond is cleaved to rearrange to the reaction product.

In the ¹H NMR spectrum of **3**, five singlet signals (0.93, 1.08, 1.18, 1.26, 1.54 ppm) were found for the five *t*Bu groups, and at 3.15 ppm a broad signal was detected for the ten remaining protons of the *o*-carborane. In the ³¹P{¹H} NMR spectrum, a singlet signal appeared at 96.9 ppm and in the ²⁹Si{¹H} NMR spectrum, two doublet signals were detected at –21.0 and –59.1 ppm, with coupling constants of 31.8 and 7.3 Hz due to the ¹J_{SiP} and ²J_{SiP} coupling with the ³¹P atom. These resonances are similar to that found in the Ad-functionalised species.¹⁶ A generalisation of reactivity patterns is difficult, because the characteristics of the ligand scaffolds are quite distinct: in [LSiFcSiL], a high degree of flexibility is enabled by rotation of the Fc moiety, allowing for both large and small Si...Si distances without reactive sites in close proximity. In contrast, with the more rigid [LSiCSiL], a longer Si...Si distance is enforced, but the reactive C–H opens up a pathway independent of the Si...Si distance. Lastly, with the [LSiBSiL] scaffold a short Si...Si contact is enforced, but the anchoring bond between backbone and silylene is broken upon reaction with the phosphalkyne. This is not a frequently observed mode of reaction and is likely a property owing to the carborane scaffold than the bis-silylene.

Conclusions

In summary, we have prepared three P–Si containing molecules starting from the reaction between the different bis-silylenes [LSiFcSiL], [LSiCSiL] and [LSiBSiL] with *t*BuC≡P. When the ferrocenediyl-functionalised bis-silylene was employed, a double cycloaddition took place, giving rise to compound **1** featuring a butterfly-shaped SiPCSi molecule. When changing from the ferrocene-linker to a diaminobenzene unit, C–H activation at the benzene ring occurred and compound **2** was isolated. With the *o*-carborane-bridged bis-silylene, compound **3** with two fused four-membered heterocycles formed. Thus, subtle changes in ligand structure and properties can significantly impact the behaviour in small molecule activation by changing Si...Si distances and Si–linker bond stability. This study provides valuable insights into the reactivity of bis-silylenes with phosphalkynes, expanding the synthetic possibilities of silicon–phosphorus heterocycles and contributing to the field of low-valent silicon chemistry.

Experimental section

General procedures

All air- and moisture-sensitive manipulations were performed under dry N₂ or Ar atmosphere using standard Schlenk techniques or in an argon-filled MBraun glovebox, unless otherwise stated. *n*-Pentane and toluene were dried using an MBraun solvent purification system (SPS-800) and degassed. *n*-Hexane was distilled under nitrogen from potassium benzophenone ketyl. C₆D₆ and THF-*d*₈ were dried over Na–K alloy and degassed by freeze–pump–thaw cycles. *t*BuCP²⁹ (synthesised as a hexamethyldisiloxane solution, *ca.* 1130 mg solution per 1 mmol *t*BuCP, the concentration (mol g^{–1}) of the silylene solution of *t*BuCP was determined using ³¹P NMR spectroscopy: 46 mg of the *t*BuCP solution and 17.2 mg of bis(diphenylphosphino)methane (DPPM) were mixed in an NMR tube and the relaxation time (*D*₁) was set to 120 s, the concentration was calculated by comparing the integrations), [LSiFcSiL] (L = PhC(*t*BuN)₂, Fc = ferrocenediyl),⁶ [LSiCSiL] (C = 2,6-((EtN)₂C₆H₃)₂)⁹ and [LSiBSiL] (B = C₂B₁₀H₁₀)¹¹ were prepared according to the literature procedures. All other chemicals were obtained from commercial sources and used without further purification. Elemental analyses were carried out with an Elementar vario MICRO cube. NMR spectra were recorded on Bruker spectrometers (Avance Neo 300 MHz, Avance Neo 400 MHz or Avance III 400 MHz). Chemical shifts are referenced internally using signals of the residual protio solvent (¹H) or the solvent (¹³C{¹H}) and are reported relative to tetramethylsilane (¹H, ¹³C{¹H}), or externally relative to BF₃·Et₂O (¹¹B), tetramethylsilane (²⁹Si) or 85% phosphoric acid (³¹P). All NMR spectra were measured at 298 K, unless otherwise specified. The multiplicity of the signals is indicated as s = singlet, d = doublet, dd = doublet of doublets, dq = doublet of quartets, t = triplet, q = quartet, m = multiplet and br = broad. Assignments were determined based on unambiguous chemical shifts, coupling patterns and ¹³C-DEPT experiments or 2D correlations (¹H–¹H COSY, ¹H–¹³C HMQC and ¹H–¹³C HMBC). Infrared (IR) spectra were recorded in the region 4000–400 cm^{–1} on a Bruker Tensor 37 FTIR spectrometer equipped with a room temperature DLATGS detector, a diamond attenuated total reflection (ATR) unit. In terms of their intensity, the signals were classified into different categories (vs = very strong, s = strong, m = medium, w = weak, and sh = shoulder). Details on crystallography and quantum chemical calculations are provided in the ESI.†

Synthesis of compound 1

To a J. Young NMR tube containing a C₆D₆ (*ca.* 0.4 mL) solution of [LSiFcSiL] (50.0 mg, 0.07 mmol) was added *t*BuCP (8 mg (375 mg solution), 0.08 mmol). The NMR tube was carefully shaken and immediately, single crystals suitable for X-ray diffraction analysis precipitated. The solution was carefully decanted and the remaining crystals were washed twice with *n*-hexane (*ca.* 1 mL) and dried under vacuum for 30 min. Yield (based on crystals): 83% (49.8 mg, 0.06 mmol). Anal. calcd for C₄₅H₆₁FeN₄PSi₂ (0.5 C₆D₆) (843.08 g mol^{–1}): C 68.38; H 8.01; N



6.65. Found: C 68.87; H 8.52; N 6.91. ^1H NMR (400.3 MHz, THF- d_8): δ (ppm) = 7.39–7.26 (m, 10H, CH_{Ph}), 4.63–4.53 (m, 4H, CH_{Fc}), 4.19–4.15 (m, 4H, CH_{Fc}), 1.53 (s, 9H, $\text{PC}(\text{CH}_3)_3$), 1.34 and 1.31 (two br s, 36H, $\text{NC}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (101.67 MHz, THF- d_8): δ (ppm) = 171.0 (NCN), 138.1 (Ph- C_q), 130.8 (CH_{Ph}), 130.01 (CH_{Ph}), 129.95 (CH_{Ph}), 128.4 (CH_{Ph}), 128.0 (CH_{Ph}), 80.2 (Fc-CH), 76.3 (Fc-CH), 75.6 (Fc- C_q), 72.0 (Fc-CH), 70.4 (Fc-CH), 56.2 ($\text{NC}(\text{CH}_3)_3$), 54.7 ($\text{NC}(\text{CH}_3)_3$), 34.3 ($\text{NC}(\text{CH}_3)_3$), 33.7 ($\text{CC}(\text{CH}_3)_3$), 33.5 ($\text{NC}(\text{CH}_3)_3$). The two quaternary carbon atoms PCCtBu and PCCtBu could not be detected. $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.49 MHz, C_6D_6): δ (ppm) = -76.4 (d, $^1J_{\text{SiP}} = 44.8$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162.04 MHz, THF- d_8): δ (ppm) = -294.2 (s). IR (ATR): $\tilde{\nu}(\text{cm}^{-1}) = 3084$ (vw), 2959 (vs), 2933 (s), 2867 (m), 1642 (w), 1614 (w), 1538 (vw), 1477 (m), 1446 (m), 1393 (s), 1360 (s), 1245 (m), 1192 (s), 1161 (m), 1100 (vw), 1073 (w), 1036 (m), 1018 (m), 1003 (m), 975 (s), 922 (w), 799 (w), 768 (m), 705 (m), 637 (w), 616 (w), 580 (w), 573 (w), 496 (w), 475 (w).

Synthesis of compound 2

To a Schlenk flask containing a toluene (*ca.* 5 mL) solution of [LSiCSiL] (81.2 mg, 0.119 mmol) was added *t*BuCP (13 mg (605 mg solution), 0.130 mmol) at room temperature and the solution became immediately dark red. After stirring at room temperature for 30 min, the solution was concentrated to *ca.* one third of the original volume. Crystals of the title compound could be obtained after storing the solution in a -40 °C freezer for 3 days. The mother liquid was carefully removed *via* syringe and the obtained crystals were dried, washed with a small amount of *n*-hexane and the remaining crystals were dried under vacuum for 1 h. Yield (based on crystals): 57% (53.1 mg, 0.068 mmol). Anal. calcd for $\text{C}_{45}\text{H}_{69}\text{N}_6\text{PSi}_2$ (781.23 g mol $^{-1}$): C 69.18; H 8.90; N 10.76. Found: C 69.55; H 9.27; N 10.44. ^1H NMR (400.3 MHz, C_6D_6): δ (ppm) = 8.20 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2H, H_{Ar}), 7.31 (dd, $^3J_{\text{HH}} = 8.3$, 7.3 Hz, 1H, H_{benz}), 7.19–7.17 (m, 2H, H_{Ar}), 7.10–7.08 (m, 2H, H_{Ar}), 6.93–6.90 (m, 1H, H_{Ar}), 6.85–6.81 (m, 2H, H_{Ar}), 6.77–6.75 (m, 1H, H_{Ar}), 6.32 (d, $^3J_{\text{HH}} = 8.3$ Hz, 1H, H_{benz}), 6.20 (d, $^3J_{\text{HH}} = 7.3$ Hz, 1H, H_{benz}), 3.90–3.70 (overlapped dq, $^2J_{\text{HH}} = 13.2$ Hz, $^3J_{\text{HH}} = 6.7$ Hz, 2H, CH_2CH_3), 3.63 (dq, $^2J_{\text{HH}} = 13.2$ Hz, $^3J_{\text{HH}} = 6.7$ Hz, 1H, CH_2CH_3), 3.35 (dq, $^2J_{\text{HH}} = 14.3$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, 1H, CH_2CH_3), 2.21 (d, $^2J_{\text{HP}} = 23.2$ Hz, 1H, PCH), 1.56 (t, $^3J_{\text{HH}} = 7.1$ Hz, 3H, CH_2CH_3), 1.51 (s, 9H, C-C(CH_3) $_3$), 1.38 (s, 9H, N-C(CH_3) $_3$), 1.35–1.34 (overlapped s and t, 21H, 18H of N-C(CH_3) $_3$ + 3H of CH_2CH_3), 1.05 (s, 9H, N-C(CH_3) $_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.67 MHz, C_6D_6): δ (ppm) = 174.3 (NCN- C_q), 165.8 (NCN- C_q), 162.8 (benz- C_q), 145.2 (benz- C_q), 142.1 (Ph- C_q), 132.7 (CH_{benz}), 131.83 (Ph- C_q), 131.78 (CH_{Ph}), 131.7 (CH_{Ph}), 130.1 (CH_{Ph}), 128.9 (CH_{Ph}), 128.4 (CH_{Ph}), 128.3 (CH_{Ph}), 128.2 (CH_{Ph}), 127.5 (CH_{Ph}), 127.1 (two CH_{Ph}), 126.7 (benz- C_q), 104.9 (CH_{benz}), 97.3 (CH_{benz}), 55.5 (N-C(CH_3) $_3$), 54.6 (N-C(CH_3) $_3$), 54.3 (N-C(CH_3) $_3$), 39.2 (CH_2CH_3), 38.8 (CH_2CH_3), 34.6 (PCC(CH_3) $_3$), 34.1 (d, $^1J_{\text{CP}} = 60.6$ Hz, PCtBu), 33.1 (2 N-C(CH_3) $_3$), 32.3 (d, $^3J_{\text{CP}} = 16.1$ Hz, C-C(CH_3) $_3$), 32.2 (d, $^3J_{\text{CP}} = 4.2$ Hz, N-C(CH_3) $_3$), ^{37}Cl 31.4 (N-C(CH_3) $_3$), 16.0 (CH_2CH_3), 14.6 (CH_2CH_3). One carbon signal C_{Ar} could not be detected. $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.52 MHz, C_6D_6): δ (ppm) = 2.5 (d,

$^1J_{\text{SiP}} = 209.3$ Hz), -28.1 (d, $^2J_{\text{SiP}} = 10.8$ Hz). ^{31}P NMR (162.04 MHz, C_6D_6): δ (ppm) = -173.0 (d, $^2J_{\text{HP}} = 23.2$ Hz). ^{31}P $\{^1\text{H}\}$ NMR (162.04 MHz, C_6D_6): δ (ppm) = -173.0 (s, $^1J_{\text{SiP}} = 209.0$ Hz, determined from the ^{29}Si satellites). IR (ATR): $\tilde{\nu}(\text{cm}^{-1}) = 3059$ (vw), 2963 (vs), 2928 (s), 2865 (m), 1646 (vw), 1589 (m), 1571 (s), 1530 (w), 1474 (m), 1443 (m), 1394 (s), 1362 (s), 1313 (w), 1286 (w), 1266 (m), 1243 (s), 1198 (s), 1188 (s), 1159 (m), 1092 (m), 1071 (m), 1024 (w), 1008 (m), 975 (w), 934 (w), 905 (w), 840 (m), 790 (w), 766 (s), 731 (w), 709 (s), 633 (m), 590 (w), 575 (w), 534 (w), 469 (w), 436 (vw).

Synthesis of compound 3

To a J. Young NMR tube containing a C_6D_6 solution (*ca.* 0.4 mL) of [LSiBSiL] (43.0 mg, 0.075 mmol) was added *t*BuCP (8 mg (375 mg solution), 0.08 mmol). The NMR tube was carefully shaken for monitoring the reaction. A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was recorded, which confirmed the formation of a single reaction product. The solution was carefully concentrated to *ca.* 0.1 mL and kept at room temperature. After three days, yellow block-shaped crystals have formed. Yield (based on crystals): 51% (32.4 mg, 0.038 mmol). Anal. calcd for $\text{C}_{37}\text{H}_{65}\text{B}_{10}\text{N}_6\text{Psi}_2$ 0.15 ($\text{C}_6\text{H}_{18}\text{Si}_2\text{O}$) (785.56 g mol $^{-1}$): C 57.95; H 8.85; N 7.13. Found: C 57.93; H 7.85; N 6.54. ^1H NMR (400.3 MHz, C_6D_6): δ (ppm) = 7.20–7.18 (m, 1H, CH_{Ph}), 6.94–6.76 (m, 9H, CH_{Ph}), 3.15 (br, 10H, BH), 1.54 (s, 9H, C-C(CH_3) $_3$), 1.26 (s, 9H, N-C(CH_3) $_3$), 1.18 (s, 9H, N-C(CH_3) $_3$), 1.08 (s, 9H, N-C(CH_3) $_3$), 0.93 (s, 9H, N-C(CH_3) $_3$), 0.00 (s, *ca.* 2.6H, O{Si(CH_3) $_3$ } $_2$, co-crystallised solvent). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.38 MHz, C_6D_6): δ (ppm) = 26.7, 2.1, -2.2, -4.5, -5.4, -7.9, -13.5, -14.9. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, C_6D_6): δ (ppm) = 174.6 (NCN), 174.2 (NCN), 133.0 (Ph- C_q), 131.7 (Ph- C_q), 130.32 (CH_{Ph}), 130.28 (CH_{Ph}), 129.7 (CH_{Ph}), 129.4 (CH_{Ph}), 128.4 (CH_{Ph}), 128.1 (CH_{Ph}), 127.8 (CH_{Ph}), 127.72 (CH_{Ph}), 127.68 (CH_{Ph}), 126.6 (CH_{Ph}), 98.1 (d, $^1J_{\text{CP}} = 48.3$ Hz, Si=C), 91.5 (d, $^1J_{\text{CP}} = 133.7$ Hz, cage-C), 89.4 (d, $^2J_{\text{CP}} = 13.1$ Hz, cage-C), 55.7 (N-C(CH_3) $_3$), 55.1 (N-C(CH_3) $_3$), 54.4 (N-C(CH_3) $_3$), 54.1 (N-C(CH_3) $_3$), 37.4 (d, $^2J_{\text{CP}} = 10.7$ Hz, C-C(CH_3) $_3$), 35.3 (d, $J_{\text{CP}} = 7.7$ Hz, N-C(CH_3) $_3$), ^{37}Cl 33.4 (d, $J_{\text{CP}} = 13.8$ Hz, C-C(CH_3) $_3$), 32.7 (two N-C(CH_3) $_3$), 32.4 (N-C(CH_3) $_3$), 2.1 (O{Si(CH_3) $_3$ } $_2$), co-crystallised solvent). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.52 MHz, C_6D_6): δ (ppm) = -21.0 (d, $^1J_{\text{SiP}} = 31.8$ Hz), -59.1 (d, $^2J_{\text{SiP}} = 7.3$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162.04 MHz, C_6D_6): δ (ppm) = 96.9 (s). IR (ATR): $\tilde{\nu}(\text{cm}^{-1}) = 3059$ (vw), 2971 (vs), 2953 (vs), 2930 (vs), 2856 (m), 2565 (vs), 1605 (vw), 1529 (w), 1474 (m), 1456 (m), 1447 (m), 1406 (vs), 1394 (vs), 1380 (vs), 1363 (vs), 1251 (m), 1236 (m), 1222 (m), 1195 (vs), 1071 (m), 1042 (w), 1021 (m), 966 (vw), 925 (w), 894 (m), 841 (w), 786 (m), 759 (m), 747 (m), 729 (m), 706 (s), 688 (vw), 634 (w), 610 (m), 581 (vw), 493 (w), 479 (w), 440 (w).

Author contributions

X. S. - investigation, synthesis, crystallography, manuscript writing (original draft); D. J. - investigation, manuscript writing (editing); S. M. - investigation, manuscript writing (editing); A. H. - theoretical calculation, manuscript writing



(editing); P. W. R. – conceptualisation, supervision, manuscript writing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (RO 2008/25-1, 546228048).

References

- 1 P. Jutzi, D. Kanne and C. Krüger, *Angew. Chem., Int. Ed.*, 1986, **25**, 164.
- 2 M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner and N. Metzler, *J. Am. Chem. Soc.*, 1994, **116**, 2691.
- 3 X. Chen, H. Wang, S. Du, M. Driess and Z. Mo, *Angew. Chem., Int. Ed.*, 2021, **61**, e2021145.
- 4 D. Gallego, S. Inoue, B. Blom and M. Driess, *Organometallics*, 2014, **33**, 6885.
- 5 S. Li, Y. Wang, W. Yang, K. Li, H. Sun, X. Li, O. Fuhr and D. Fenske, *Organometallics*, 2020, **39**, 757.
- 6 W. Wang, S. Inoue, S. Enthaler and M. Driess, *Angew. Chem., Int. Ed.*, 2012, **51**, 6167.
- 7 X. Wang, B. Lei, Z. Zhang, M. Chen, H. Rong, H. Song, L. Zhao and Z. Mo, *Nat. Commun.*, 2023, **14**, 2968.
- 8 R. Yadav, X. Sun, R. Köppe, M. T. Gamer, F. Weigend and P. W. Roesky, *Angew. Chem., Int. Ed.*, 2022, **61**, e202211115.
- 9 H. Yang, A. Hinz, Q. Fan, S. Xie, X. Qi, W. Huang, Q. Li, H. Sun and X. Li, *Inorg. Chem.*, 2022, **61**, 19710.
- 10 S. Yao, A. Saddington, Y. Xiong and M. Driess, *Acc. Chem. Res.*, 2023, **56**, 475.
- 11 Y.-P. Zhou, S. Raoufmoğhaddam, T. Szilvási and M. Driess, *Angew. Chem., Int. Ed.*, 2016, **55**, 12868.
- 12 S. S. Sen, H. W. Roesky, D. Stern, J. Henn and D. Stalke, *J. Am. Chem. Soc.*, 2010, **132**, 1123.
- 13 C.-W. So, H. W. Roesky, J. Magull and R. B. Oswald, *Angew. Chem., Int. Ed.*, 2006, **45**, 3948.
- 14 C. Shan, S. Yao and M. Driess, *Chem. Soc. Rev.*, 2020, **49**, 6733.
- 15 Y. Chen, J. Li, Y. Zhao, L. Zhang, G. Tan, H. Zhu and H. W. Roesky, *J. Am. Chem. Soc.*, 2021, **143**, 2212.
- 16 R. Liu, Y. Tang, C. Wang, Z.-F. Zhang, M.-D. Su and Y. Li, *Inorg. Chem.*, 2023, **62**, 1095.
- 17 J. Schoening, A. Gehlhaar, C. Wölper and S. Schulz, *Chem. – Eur. J.*, 2022, **28**, e202201031.
- 18 G. Becker, G. Gresser and W. Uhl, *Z. Naturforsch., B: J. Chem. Sci.*, 1981, **36b**, 16.
- 19 A. Chirila, R. Wolf, J. Chris Slootweg and K. Lammertsma, *Coord. Chem. Rev.*, 2014, **270–271**, 57.
- 20 M. Regitz, *Chem. Rev.*, 1990, **90**, 191.
- 21 M. P. Müller and A. Hinz, *Chem. – Eur. J.*, 2023, **29**, e202302311.
- 22 A. Schäfer, M. Weidenbruch, W. Saak and S. Pohl, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 776.
- 23 M. Weidenbruch, S. Olthoff, K. Peters and H. Georg von Schnering, *Chem. Commun.*, 1997, 1433, DOI: [10.1039/A703054A](https://doi.org/10.1039/A703054A).
- 24 S. S. Sen, J. Hey, M. Eckhardt, R. Herbst-Irmer, E. Maedl, R. A. Mata, H. W. Roesky, M. Scheer and D. Stalke, *Angew. Chem., Int. Ed.*, 2011, **50**, 12510.
- 25 S. S. Sen, J. Hey, R. Herbst-Irmer, H. W. Roesky and D. Stalke, *J. Am. Chem. Soc.*, 2011, **133**, 12311.
- 26 S. S. Sen, S. Khan, H. W. Roesky, D. Kratzert, K. Meindl, J. Henn, D. Stalke, J.-P. Demers and A. Lange, *Angew. Chem., Int. Ed.*, 2011, **50**, 2322.
- 27 C. Wang, M.-D. Su, Z. Fang, J. Zhou, H. Zhang, X. Li, D. Zuo, Z.-F. Zhang and Y. Li, *Chem. Commun.*, 2023, **59**, 10275.
- 28 E. Wiberg, *Lehrbuch der anorganischen Chemie*, Walter de Gruyter GmbH & Co KG, 2019.
- 29 C. A. Russell and N. S. Townsend, in *Phosphorus(III) Ligands in Homogeneous Catalysis: Design and Synthesis*, ed. P. W. N. M. van Leeuwen and P. C. J. Kamer, John Wiley & Sons, West Sussex, United Kingdom, 2012, ch. 11, p. 343.
- 30 P. Pykkö and M. Atsumi, *Chem. – Eur. J.*, 2009, **15**, 12770.
- 31 Y. Xiong, S. Dong, S. Yao, C. Dai, J. Zhu, S. Kemper and M. Driess, *Angew. Chem., Int. Ed.*, 2022, **61**, e202209250.
- 32 S. Khan, R. Michel, S. S. Sen, H. W. Roesky and D. Stalke, *Angew. Chem., Int. Ed.*, 2011, **50**, 11786.
- 33 X. Sun, A. Hinz and P. W. Roesky, *CCS Chem.*, 2022, **4**, 1843.
- 34 M. Kaftory, M. Kapon and M. Botoshansky, in *The Chemistry of Organic Silicon Compounds*, ed. Z. Rappoport and Y. Apeloig, John Wiley & Sons, West Sussex, United Kingdom, 1998, ch. 5, p. 181.
- 35 A. G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst and R. K. Kallury, *J. Chem. Soc., Chem. Commun.*, 1981, 191.
- 36 X. Sun, A. Hinz, H. Kucher, M. T. Gamer and P. W. Roesky, *Chem. – Eur. J.*, 2022, **28**, e202201963.
- 37 J.-C. Hierso, *Chem. Rev.*, 2014, **114**, 4838.

