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Unlocking Some Si-Centered Reactivity of a 4,4′-Dichloro-1,4-di-hydro-1,4-phosphasiline

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To establish some steric protection at the P center of a tricyclic 1,4-dihydro-1,4-phosphasiline, the potassium salt of a tricyclic 1,4-dihydro-1,4-phosphasilin-1-ide was treated with triphenylmethyl chloride. Subsequently, the two Si-bound diethylamino groups, were converted to give the $SiCl_2$ derivative using HCl. The Si-functionality could be used in substitution reactions thus giving Si-dimethyl and Si-dimethoxy derivatives. Reduction of the $SiCl_2$ derivative at low temperature gave transient tricyclic silylene which could not be detected by NMR spectroscopy but successfully trapped by 1,3-butadiene to give a P-containing spiro-silolene derivative. DFT studies provide insight into reduction and the silylene formation.

Introduction

The field of mixed-substituted hetarenes with one phosphorus atom center is an unchartered territory, in general. First studies on 1,4-dihydro-1,4-phosphasilines[1] had been focused on organoelectronic properties but not giving much attention to heteroatom-centered reactions.[2] On the other hand, numerous reports on saturated and/or partially saturated heterocyclic systems having P and Si in 1,4-positions have been thoroughly discussed since the last century.[3] Recently, stable tricyclic 1,4-diphosphinines[4,5] have been successfully isolated relying on the smooth reduction of 1,4-dichloro-1,4-diphosphinine derivatives as the final step. Profiting from the stabilising effect of the two fused imidazole-2-thiones units and the electrophilicity of the P centers, a manifold of reactions could be established. One example is the synthesis of anionic derivatives and their conversion into P–P "pseudo-dimeric" derivatives,[5,6] followed by investigations of the corresponding phosphanide/diphosphane redox chemistry.[6] Very recently, the latter study was expanded to not only access new 1,4-dihydro-1,4-phosphasilines, but also the corresponding potassium 1,4-dihydro-1,4-phosphasilin-1-ides.[7] Despite this, their P/Si-centered reactivity features remained largely unexplored[7] although the versatility of $SiCl_2$ substituted Si-heterocycles towards substitution reactions is well established, in general.[8,9]

One remarkable offspring is also silylene chemistry that has flourished worldwide since the ground breaking discovery by West in 1994, *i.e.*, the synthesis of the first isolable N-heterocyclic silylene **I**, using steric protection and intramolecular electronic stabilization (Figure 1).[10] A related concept then enabled access to **II**[11] while the first non-cyclic dialkyl tetrelenes **III**[12] and cyclic dialkylsilylene/stannylene **IV**[13] still represent a largely electronically unperturbed divalent silicon species. The latter **II** and **IV** were both synthesized from their $SiBr_2$ precursors using KC_8 as reducing agent. Silylenes, transient and stable derivatives, can be trapped, e.g. using 1,3-butadiene derivatives, to form silolenes[14] or spiro-silolenes via [4 + 1] cycloaddition.[15,16] Ando discussed the *in situ* silylene trapping of a tricyclic sila-azaanthracene system with 1,3-butadiene derivatives to form spiro-silolene derivative **VI**.[17]

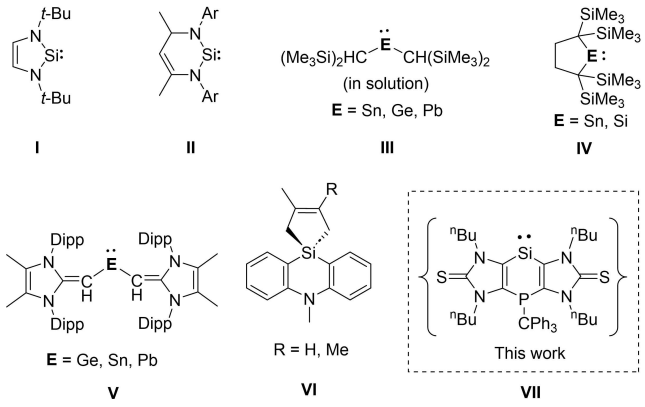

Figure 1. Examples of heterocyclic and cyclic silylenes, acyclic dialkyl tetrelenes **III**, divinylsilylenes **V** and an example of a tetracyclic spiro-silolene **VI**; targeted compound 1,4-dihydro-1,4-phosphasilin-4-ylidene **VII.**

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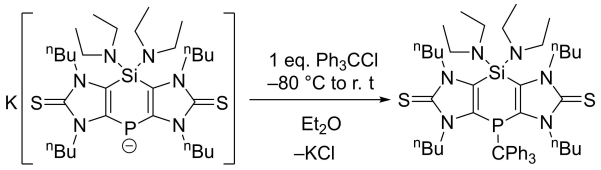
It should be noted that the N-substituted silylenes such as **I** and **II** are less reactive due to the donation of electron density from the lone pairs of the adjacent N atoms towards the vacant 3p orbital of the silylene center. Conversely, dialkylsilylene **IV** exhibits high reactivity which makes it difficult to handle, especially as it undergoes intramolecular $SiMe_3$ migration to give the corres-ponding silene (>Si=C<). In consideration of the balance between the reactivity and stability of a silylene, a carbon-substituted silylene stabilized by the adjacent C=C π electrons should be one of the interesting research targets, such as a unique divinylsilylene[18] (**V**), profiting from the employed strong donor capacity of N-heterocyclic olefines (NHOs).

Herein, synthesis and reactions of $SiCl_2$ functional 1,4-dihydro-1,4-phospha-silines is reported including nucleophilic substitution and reduction; in the latter a transient tricyclic silylene derivative was formed and trapped in-situ to yield a spiro-silolene.

Results and Discussion

To establish some steric protection at the P-center, the 1,4-dihydro-1,4-phosphasilin-1-ide salt **1** was treated with triphenylmethyl (trityl) chloride at −80 °C to form the P-alkylated derivative **2** in a clean fashion (Scheme 1). The product was isolated as a yellow powder via extraction with *n*-pentane and filtration to remove lithium chloride as well as traces of the "pseudo-dimeric" product.[7] Significant $^{29}Si\{^1H\}$-dept20- and $^{31}P\{^1H\}$-NMR signals are collected in Table 1.

To enable Si-centered reactivity studies, the Si-bound amino groups of **2** were then replaced by two Cl atoms using an HCl diethyl ether solution to form the derivative **3** (Scheme 2). Noteworthy is that there was hardly any change in the $^{31}P\{^1H\}$-NMR chemical shifts of **3** compared to **2** and no resonance signal in the $^{29}Si\{^1H\}$-dept20 as well as complete $^{29}Si\{^1H\}$-NMR spectrum was observed, probably due to its lability in solution during long-time NMR measurements. A comparison of ^1H NMR spectrum of **3** with that of **2** showed the absence of triplets at 0.98 and 1.07 ppm corresponding to the diethylamino groups on the Si center, signified the exchange of the amide groups with chlorides; relevant NMR spectral data are shown in Table 1. The disappearance of strong bands at 1025 and 799 cm^{-1} in the IR spectrum of **3** compared to that of **2** also pointed to the removal of Si–(NCH_2–CH_3) (Figure S5 and S9 in SI).[8] For both **2** and **3**, a sharp band was observed at 699 cm^{-1}, corresponding to the P–C stretching mode of P–C^{trityl} bond.



1 **2**

Scheme 1. Reaction of **1** to form the *P*-trityl derivative **2**.

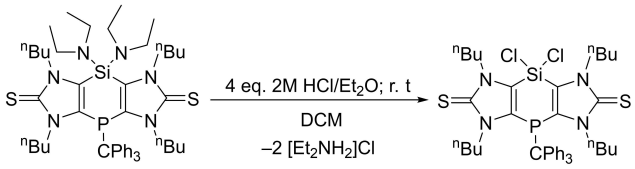
Table 1. $^{29}Si\{^1H\}$-dept20- and $^{31}P\{^1H\}$-NMR data ($CDCl_3$) of **2**, **3**, **4**, **5** and **7**.

Compound	NMR/ppm	
	δ $^{29}Si\{^1H\}$ dept20	δ $^{31}P\{^1H\}$
2	−42.1	−57.2
3	no signal was observed	−55.8
4	−25.3	−56.7
5	−47.6	−56.8
7	no signal was observed	−58.0

To test some nucleophilic substitution reactions, methyl lithium was added to compound **3** at −80 °C or an excess of methanol at room temperature. Both led to clean reactions at the Si center and the formation of derivatives **4** and **5**, respectively (Scheme 3).

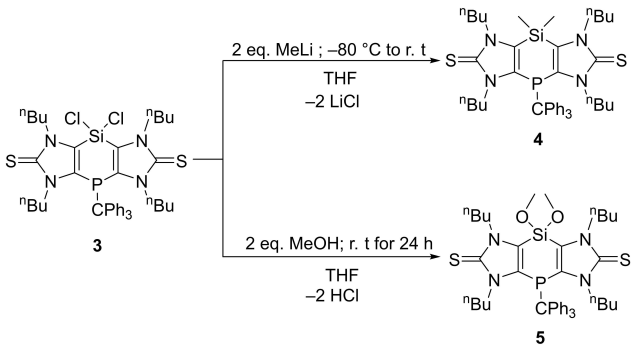
Products **4** and **5** were isolated as white powders, and the relevant NMR data are shown in Table 1.

The introduction of methyl groups on Si was also confirmed by the ^1H NMR spectrum with the appearance of a doublet at 0.68 ppm corresponding to the Si–CH_3 protons, in the case of **4**. In addition, the appearance of the strong bands at 1218, 875, 806 cm^{-1} in the IR spectrum of **4** (Figure S14 in SI) also signified the existence of groups with Si–C bonds.[19] The presence of Si–OCH_3 protons were also confirmed by the singlets at 3.50 and 3.66 ppm in the ^1H NMR spectrum of **5** compared to that of **3**. Additional structural confirmation was also obtained from the IR spectra of **5**, where strong bands corresponding to the Si–O bond containing groups at 1152, 984 cm^{-1} and a strong band corresponding to C–O bond containing group at 1241 cm^{-1} were observed, that weren't observed for **3** (Figure S19 in SI).[8] For both **4** and **5**, a sharp band was observed at 699 cm^{-1}, corresponding to the P–C stretching mode of P–C^{trityl} bond.



2 **3**

Scheme 2. Conversion of **2** to form the tricyclic Si-dichloro derivative **3**.



3 **4** **5**

Scheme 3. Substitution reactions of **3** to form **4** with methyl lithium and **5** with methanol.

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The reported derivatives **VIII**, **IX**[2] showed overall low-field-shifted heteronuclear NMR resonances (for **VIII**; δ ^{29}Si{^{1}H} dept20 = −17.7 ppm, δ ^{31}P{^{1}H} = −20.7 ppm; for **IX**; δ ^{29}Si{^{1}H} dept20 = −16.9 ppm, δ ^{31}P{^{1}H} = −36.5 ppm) compared to **4** (Figure 2). Recently discovered tricyclic imidazol-2-thione based 1,4-disilacyclohexa-2,5-diene **X** was observed to have similar ^{29}Si{^{1}H} dept20 resonance at −24.1 ppm.[20] The reported Si-dialkoxy compounds **XI**, by West[9] also showed low field-shifted ^{29}Si{^{1}H}-dept20-NMR resonance at δ = −20.7 ppm compared to **5** (Table 1). These observations could be attributed to the electron-donating feature of N-vinyl-ring systems of **4** and **5**.

To get some insight into the electronic situation at the Si- as well as P-center of **3**, DFT calculations were performed at the PW6B95-D3BJ/def2-QZVP(CPCM$_{THF}$)//TPSS-D3BJ/def2-TZVP(CPCM$_{THF}$) level of theory before experiments were performed. Here, models were used in which the *N*–^{n}Bu groups were truncated to *N*–Me, and indicated by **3′** (Figure 3).

The LUMO showed large coefficients at the P- and Si-center, with slight delocalisation to the neighbouring carbon atoms and also included P–C^{trityl} σ*-orbital character, while no significant contribution of the σ*(Si–Cl)-orbitals, suggesting the rather possible cleavage of the P–C^{trityl} bond upon reduction relative to that of the Si–Cl bond under reductive conditions. Considering these frontier orbitals of **3**, it should be of great importance to choose an appropriate reducing agent facilitating the reductive elimination of chloride ions at the Si-center. Thus, theoretical calculations were performed to investigate an Si-centered reduction and the potential of silylene formation. Here, models were used where the *N*–^{n}Bu groups were truncated to *N*–Me, and the trityl group truncated to Me (denoted by ″) as we only wanted to focus on the Si-centered reactivity.

The calculations revealed that the reduction reaction (Scheme 4) to form the corresponding Si(II) species, with 2 eq. of Na (Na was taken here just as a typical and somehow arbitrary electron source), accompanied by the elimination of sodium chloride (2 eq.), was an exergonic process with a significant reaction Gibbs free energy of −19 kcal/mol (neglecting the lattice energy of formed sodium chloride).

The FMO calculations on the model **6″** (singlet state) showed that the HOMO^{-4} with a high *s*-character has a huge contribution from the in-plane non-bonding orbital at silicon, exhibiting lone-pair character (Figure 4). The LUMO was observed to be dominated by a *p*-orbital contribution of the Si(II) center which is expected for silylenes with a singlet ground state. The highly electrophilic reactivity of the silylene derivative **6″** was also expected, too, owing to the presence of a vacant *p*-orbital.[21]

Based on these theoretical results, the possibility of a (selective) reduction of the Si center in **3** was investigated. These attempts were made initially at room temperature and included strong reducing agents such as KC_8 as well as bare metals (Na, K, Mg) (Scheme 5). But the P–C^{trityl} bond was always

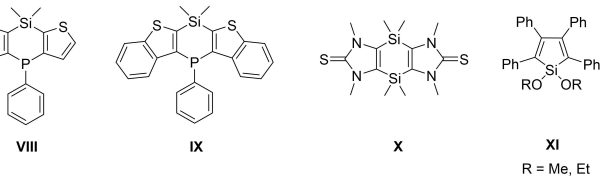


Figure 2. Selected examples of Si-dimethyl compounds **VIII**, **IX**, **X** and Si-dimethoxy compounds **XI**.

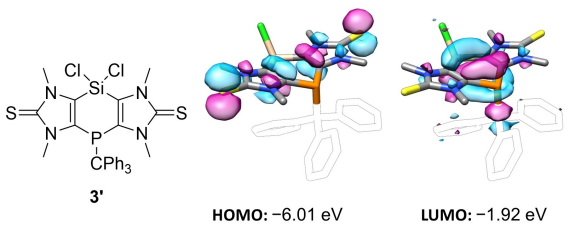
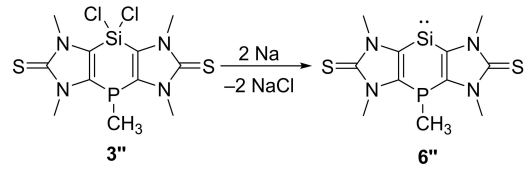


Figure 3. Selected calculated FMO of the model compound **3′**; trityl groups are given as silhouettes and hydrogen atoms are omitted for clarity.



Scheme 4. Theoretical depiction of the reduction of **3″** to form the silylene **6″**.

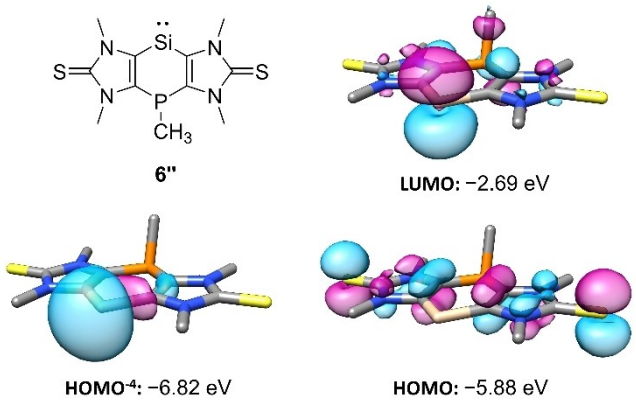
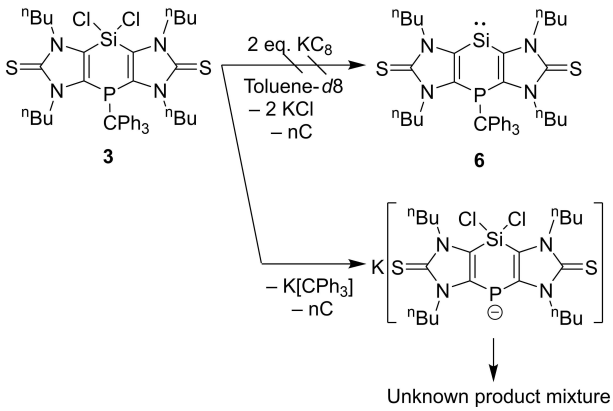


Figure 4. Selected calculated FMOs of the model compounds **6″**.



Scheme 5. Reduction of compound **3** at room temperature.

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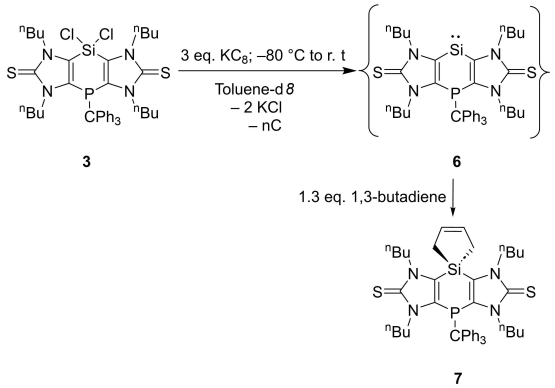
easily cleaved thus allowing for further reactions to occur, as expected from the FMO calculations on **3′**. This reaction of **3** with KC_8 was monitored by $^{31}P\{^1H\}$-NMR spectroscopy (starting material: $\delta = -55$ ppm, in toluene-d*8*) and, after 2 days, a signal was observed at $\delta = -118$ ppm ($^1J_{P,H} = 237$ Hz) (Figure S26 in SI). Apparently, the large coupling constant indicate a product with a P–H functionality, which must have been formed after reductive P–C bond cleavage and reaction with traces of water. Unfortunately, the product could not be isolated.

When the reaction was performed at −80 °C no reductive P–C^{trityl} bond cleavage occurred. In case of 2 eq. of KC_8 the reaction mixture was kept stirring overnight, and the formed graphite was removed by filtration and the solution was concentrated to dryness. The residue was dissolved in toluene-d_8 for NMR spectroscopic studies but the $^{31}P\{^1H\}$-NMR spectrum revealed hardly any change of the chemical shift compared to **3** (Figure S27 in SI), and no further evidence for a stable silylene **6** could be obtained.

As already mentioned in the beginning, reactions of 1,3-butadienes with stable silylenes as well as transient silylenes have been established previously. Therefore, we added 1,3-butadiene to a clear yellow solution of **3** at −80 °C (after reduction) and warmed it to room temperature (Scheme 6). The reaction mixture was filtered to remove graphite and potassium chloride and the residue dried to get a cream-colored powder. The product **7** was characterized by $^{31}P\{^1H\}$-, ^1H-NMR spectroscopy and EI–MS spectrometry.

Unexpectedly, no resonance signal in the complete $^{29}Si\{^1H\}$-NMR spectrum was observed in the NMR solvent ($CDCl_3$). All analytical data indicate clearly the presence of the spiro-silolene **7**, e.g., the $^{31}P\{^1H\}$-NMR spectrum showed a slight highfield shifted signal compared to that of compound **3** (Table 1) indicating the replacement of the Cl atoms on the Si-center. Although other unknown products were also observed in the crude mixture, we concluded that the formation of **7** points to the intermediacy of silylene **6**. The product was isolated as a white powder by washing the dried residue with a 3:1 solvent mixture of *n*-pentane and diethyl ether. The IR spectrum showed strong bands at 1089 and 1016 cm^{-1}, corresponding to the presence of Si–CH_2–CH containing groups in **7** and a sharp band was observed at 699 cm^{-1}, corresponding to the P–C stretching mode of P–C^{trityl} bond (Figure S24 in SI). The EI–MS spectrum showed strong evidence for the molecular ion peak at m/z 776.4 (20%) (Figure S25 in SI) and the HRMS yielded for $C_{45}H_{57}N_4PS_2Si$ [**7**] *m/z* 776.3531/776.3526 (theor./exp.).



3 **6** **7**

Scheme 6. Reduction of compound **3** and trapping reaction of the transient silylene **6** to form the spiro-silolene compound **7**.

Conclusions

Facile synthesis of the first example of a $SiCl_2$ functional tricyclic 1,4-dihydro-1,4-phosphasiline allowed for Si-centered substitution reactions. Of special interest is the plausible formation of a transient silylene under reductive conditions which was trapped to yield an unusual spiro-silolene derivative containing phosphorus. The reductive silylene formation has been computationally studied using bare sodium as electron source.

Experimental Section

General Considerations: All manipulations and reactions of air and moisture sensitive compounds were performed under inert gas atmosphere (argon) using standard Schlenk line apparatus or working in a glove box. Removal of oxygen traces from Argon gas was done by a copper catalyst (BTS) while silica gel and phosphorus pentoxide was used for drying. Purification of solvents was ensured by boiling them over Na wire and benzophenone (in the case of dichloromethane over calcium hydride) under argon atmosphere prior to use. A MAT 90 or MAT 95 XL spectrometer (70 eV) was used to record mass spectra. The progress of the reactions was monitored via $^{31}P\{^1H\}$ NMR spectroscopy. NMR measurements were performed on a Bruker AVI (300 MHz for ^1H) and Bruker AVI (400 MHz for ^1H). The calibration of the ^1H and ^{13}C NMR spectra were done according to the solvent residual signals relative to tetramethylsilane (< 1% in $CDCl_3$). ^{31}P NMR spectra were measured relative to 85% H_3PO_4 in water as external reference. For ^{29}Si NMR spectra were measured relative to tetramethylsilane as external reference. Infrared spectra was recorded on a Nicolet 380 (FT-IR) instrument or on a Bruker Alpha Diamond ATR FTIR spectrometer. Elemental analyses were per-formed using an elementary vario EL analytical gas chromatograph. Electron ionization mass spectra (70 eV). were recorded on a *Thermo Finnigan* MAT 90 or a *Thermo Finnigan* MAT 95 XL spectrometer. Electrospray Ionization (ESI +/−) mass spectra were recorded in a Thermo Fisher Scientific Orbitrap XL Mass spectrometer .MALDI mass spectra were recorded in a Bruker Daltonik ultrafleXtreme TOF/TOF time-of-flight spectrometer.

Synthetic protocol for compound 2: Potassium 1,4-dihydro-1,4-phosphasilin-1-ide **1** (150 mg, 0.234 mmol) was dissolved in 2 mL of Et_2O at ambient temperature to obtain a yellow solution. The clear solution was cooled to −80 °C and the temperature was kept the same with a Dewar. Triphenylmethyl chloride (65.2 mg, 0.234 mmol) was dissolved in 2.5 mL of Et_2O and added dropwise into the clear solution. The reaction rapidly became turbid orange upon addition, which gradually turned to turbid light yellow. After overnight stirring, the solvent was removed *in vacuo* (2.4×10^{-2} mbar). The residue was re-dissolved in *n*-pentane and filtered via a cannula to remove the potassium chloride salt. Then the solvent was removed *in vacuo* (1.6×10^{-2} mbar) to obtain **2** as a yellow powder.

Yield: 183 mg (0.211 mmol, 90%), yellow powder. M.p.: 100 °C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.78$ (t, 6H, $^3J_{H,H} = 7.3$ Hz, $NCH_2CH_2CH_2\underline{CH_3}$), 0.92 (t, 6H, $^3J_{H,H} = 6.9$ Hz, $NCH_2CH_2CH_2\underline{CH_3}$), 0.98 (t, 6H, $^3J_{H,H} = 7.3$ Hz, Si–(N–CH_2–$\underline{CH_3}$)$_2$), 1.07 (t, 6H, $^3J_{H,H} = 6.9$ Hz,

Si–(N–CH_2–$\underline{CH_2}$–CH_3)$_2$), 1.14–1.31, 1.36–1.50 (m, 8H, $NCH_2CH_2\underline{CH_2}CH_3$), 1.67–2.01 (m, 8H, $NCH_2\underline{CH_2}CH_2CH_3$), 2.84 (q, 4H, $^3J_{H,H}$ = 6.9 Hz, Si–(N–$\underline{CH_2}$–CH_3)$_2$), 2.95 (q, 1H, $^3J_{H,H}$ = 6.8 Hz, Si–(N–$\underline{CH_2}$–CH_3)$_2$), 3.05 (q, 3H, $^3J_{H,H}$ = 7.0 Hz, Si–(N–$\underline{CH_2}$–CH_3)$_2$), 3.82–3.90 (m, 2H, $N\underline{CH_2}CH_2CH_2CH_3$), 3.99–4.13 (m, 5H, $N\underline{CH_2}CH_2CH_2CH_3$), 4.21–4.44 (m, 1H, $N\underline{CH_2}CH_2CH_2CH_3$), 7.04 (d, 3H, $^3J_{H,H}$ = 7.2 Hz, trityl phenyl protons), 7.09 (t, 3H, $^3J_{H,H}$ = 8.2 Hz, trityl phenyl protons), 7.21 (t, 4H, $^3J_{H,H}$ = 7.2 Hz, trityl phenyl protons), 7.27 (q, 4H, $^3J_{H,H}$ = 7.2 Hz, trityl phenyl protons), 7.37 (t, 1H, $^3J_{H,H}$ = 8.3 Hz, trityl phenyl protons). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 13.4 (s, Si–(N–CH_2–$\underline{CH_2}$–CH_3)$_2$), 13.6 (s, Si–(N–CH_2–$\underline{CH_2}$–CH_3)$_2$), 13.7 (s, $NCH_2CH_2CH_2\underline{CH_3}$), 13.9 (s, $NCH_2CH_2CH_2\underline{CH_3}$), 20.1 (s, $NCH_2CH_2\underline{CH_2}CH_3$), 20.4 (s, $NCH_2CH_2\underline{CH_2}CH_3$), 29.3 (s, $NCH_2\underline{CH_2}CH_2CH_3$), 30.1 (s, $NCH_2\underline{CH_2}CH_2CH_3$), 37.5 ((s, Si–(N–$\underline{CH_2}$–$CH_3$)$_2$)), 38.2 ((s, Si–(N–$\underline{CH_2}$–$CH_3$)$_2$)), 48.7 (s, $N\underline{CH_2}CH_2CH_2Me$), 56.7 (trityl phenyl protons), 125.9–129.4 (trityl phenyl protons), 131.2 (s, C^5), 134.3 (s, C^4), 134.5 (s, C^4), 142.8 (trityl phenyl protons), 166.6 (s, C = S). $^{31}P\{^1H\}$ NMR (121.5 Hz, $CDCl_3$): δ = −57.2. $^{29}Si\{^1H\}$ dept20 (60 Hz, $CDCl_3$): δ = − 42.1 (d, ^3J = 3.8 Hz, $\underline{Si}$–(N–CH_2–CH_3)$_2$)). IR: ν̃ (cm^{-1}) = 2965 (*w*), 1403 (*s*), 1098 (*w*), 1025 (*s*, Si–N), 799 (*s*, Si–N), 699 (*s*, P–C). MALDI TOF-MS: m/z (intensity in a.u.) = 866.5 (9800) $[M]^+$, 835.5 (4000) $[C_{49}H_{72}N_6PSSi]^{+\bullet}$. HRMS: for $C_{49}H_{71}N_6PS_2Si$ theor./exp. 866.4683/866.4683. EA (%): exp. C 67.90, H 8.04, N 9.03, S 6.22. Calc. C 67.86, H 8.25, N 9.69, S 7.39.

Synthesis of $SiCl_2$ derivative 3 from 2: The 1,4-dihydro-1,4-phosphasiline derivative **2** (150 mg, 0.17 mmol) was dissolved in 2 mL of DCM to obtain a yellow solution. A 2 M solution of hydrogen chloride in diethyl ether (0.38 mL, 0.76 mmol) was added dropwise into the clear solution at room temperature but no color change was observed. After stirring for an hour, the solvent was removed *in vacuo* (2.1×10^{-2} mbar). The residue was re-dissolved in toluene and filtered via a cannula to remove the ammonium chloride salt formed. The solvent was then removed *in vacuo* (1.8×10^{-2} mbar) to obtain **3** as yellow powder.

Yield: 115 mg (0.145 mmol, 85%), yellow powder, M.p. : 159 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.80 (t, 6H, $^3J_{H,H}$ = 7.3 Hz, $NCH_2CH_2CH_2\underline{CH_3}$), 0.99 (t, 6H, $^3J_{H,H}$ = 7.3 Hz, $NCH_2CH_2CH_2\underline{CH_3}$), 1.18–1.32 (m, 8H, $NCH_2CH_2\underline{CH_2}CH_3$), 1.44–1.50 (m, 8H, $NCH_2CH_2\underline{CH_2}CH_3$), 1.75–2.01 (m, 8H, $NCH_2\underline{CH_2}CH_2CH_3$), 3.85–3.91 (m, 2H, $N\underline{CH_2}CH_2CH_2CH_3$), 4.01–4.08 (m, 2H, $N\underline{CH_2}CH_2CH_2CH_3$), 4.18–4.29 (m, 4H, $N\underline{CH_2}CH_2CH_2CH_3$), 7.03 (d, 3H, $^3J_{H,H}$ = 7.3 Hz, trityl phenyl protons), 7.11 (t, 2H, $^3J_{H,H}$ = 8.3 Hz, trityl phenyl protons), 7.21 (t, 6H, $^3J_{H,H}$ = 7.3 Hz, trityl phenyl protons), 7.27 (q, 3H, $^3J_{H,H}$ = 7.3 Hz, trityl phenyl protons), 7.37 (t, 1H, $^3J_{H,H}$ = 8.3 Hz, trityl phenyl protons). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 13.7 (d, ^3J = 5.4 Hz, $NCH_2CH_2CH_2\underline{CH_3}$), 20.1 (d, ^3J = 5.1 Hz, $NCH_2CH_2\underline{CH_2}CH_3$), 29.3 (s, $NCH_2\underline{CH_2}CH_2CH_3$), 30.1 (s, $NCH_2\underline{CH_2}CH_2CH_3$), 49.2 (s, $N\underline{CH_2}CH_2CH_2CH_3$), 56.8 (trityl phenyl protons), 125.9–129.4 (trityl phenyl protons), 131.2 (s, C^5), 134.1 (s, C^4), 134.5–134.7 (trityl phenyl protons), 142.5 (trityl phenyl protons), 168.2 (s, C = S). $^{31}P\{^1H\}$ NMR (121.5 Hz, $CDCl_3$): δ = − 55.8. IR: ν̃ (cm^{-1}) = 2947 (*w*), 1494 (*m*), 1448 (*m*), 1407 (*s*), 756 (*m*), 699 (*s*, P–C). FTMS + p-APCI: m/z (%) = 793.2 (45) $[M]^+$, 757.3 (40) $[M–Cl]^+$, 697.3 (100) $[C_{41}H_{55}ClN_4PSi]^{+\bullet}$. HRMS: for $C_{41}H_{51}Cl_2N_4PS_2Si$ theor/exp. 793.2512/793.2509. EA (%): exp. C 61.92, H 6.70, N 6.89, S 7.26. Calc. C 62.02, H 6.47, N 7.06, S 8.08.

Methylation of 3 to form 4: The 1,4-dihydro-1,4-phosphasiline **3** (150 mg, 0.18 mmol) was dissolved in 2 mL of THF to obtain a yellow solution, and a solution (1.6 M in diethyl ether) of methyllithium (0.23 mL, 0.37 mmol) was added dropwise into the clear solution at −80 °C. The color rapidly changed from yellow to deep red, then to deep wine red. After overnight stirring, the color turned to deep brown-orange and the solvent was removed *in vacuo* (2.3×10^{-2} mbar). The residue was re-dissolved in toluene and filtered via a cannula to remove the lithium chloride salt formed. The solvent was then removed *in vacuo* (3.7×10^{-2} mbar), washed with *n*-pentane thoroughly and dried *in vacuo* (4.2×10^{-2} mbar) to obtain **4** as yellow powder.

Yield: 134 mg (0.17 mmol,96%), yellow powder, M.p.: 155 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.68 (d, 6H, $^3J_{H,H}$ = 12.5 Hz, Si–$\underline{CH_3}$), 0.80 (t, 6H, $^3J_{H,H}$ = 7.3 Hz, $NCH_2CH_2CH_2\underline{CH_3}$), 0.99 (t, 6H, $^3J_{H,H}$ = 7.3 Hz, $NCH_2CH_2CH_2\underline{CH_3}$), 1.18–1.32 (m, 8H, $NCH_2CH_2\underline{CH_2}Me$), 1.41–1.48 (m, 8H, $NCH_2CH_2\underline{CH_2}Me$), 1.71–1.93 (m, 8H, $NCH_2\underline{CH_2}CH_2Me$), 3.82–3.88 (m, 2H, $N\underline{CH_2}CH_2CH_2Me$), 3.98–4.11 (m, 6H, $N\underline{CH_2}CH_2CH_2Me$), 7.02 (d, 3H, $^3J_{H,H}$ = 7.3 Hz, trityl phenyl protons), 7.11 (d, 3H, $^3J_{H,H}$ = 8.4 Hz, trityl phenyl protons), 7.20 (*br.* t, 3H, trityl phenyl protons), 7.23–7.28 (m, 5H, trityl phenyl protons), 7.32 (t, 1H, $^3J_{H,H}$ = 8.4 Hz, trityl phenyl protons). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 0.3 (s, Si–$\underline{CH_3}$), 13.7 (d, ^3J = 5.4 Hz, s, $NCH_2CH_2CH_2\underline{CH_3}$), 20.1 (s, $NCH_2CH_2\underline{CH_2}Me$), 20.3 (s, $NCH_2CH_2\underline{CH_2}Me$), 29.6 (s, $NCH_2\underline{CH_2}CH_2Me$), 30.7 (s, $NCH_2\underline{CH_2}CH_2Me$), 49.1 (s, $N\underline{CH_2}CH_2CH_2Me$), 56.7 (trityl phenyl protons), 125.9–129.4 (trityl phenyl protons), 131.2 (s, C^5), 134.2 (s, C^4), 134.4 (s, C^4), 142.8 (trityl phenyl protons), 166.7 (s, C = S). $^{31}P\{^1H\}$ NMR (121.5 Hz, $CDCl_3$): δ = −56.7. $^{29}Si\{^1H\}$ dept20 NMR (60 Hz, $CDCl_3$): δ = −25.3 (s, $\underline{Si}$–$(CH_3)_2$)). IR: ν̃ (cm^{-1}) = 2965 (*w*), 1437 (*m*), 1403 (*s*), 1218 (*s*, Si–C), 1091 (*s*), 875 (*s*, Si–C), 806 (*s*, Si–C), 699 (*s*, P–C). FTMS + p-APCI: m/z (%) = 753.3 (50) $[M+H]^+$, 469.2 (75) $[C_{20}H_{34}N_4OPS_2Si]^{+\bullet}$. HRMS: for $C_{43}H_{58}N_4PS_2Si$ theor./exp. 753.3604/753.3602. EA (%): exp. C 64.61, H 7.18, N 6.70, S 7.34. Calc. C 68.58, H 7.63, N 7.44, S 8.51.

Methoxylation of 3 to form 5: The 1,4-dihydro-1,4-phosphasiline derivative **3** (150 mg, 0.18 mmol) was dissolved in 2 mL of THF to obtain a clear yellow solution. Excess of methanol was added drop wise into the clear solution at room temperature. After overnight stirring, the solvent was removed *in vacuo* (2.1×10^{-2} mbar). The residue was washed with *n*-pentane thoroughly and dried *in vacuo* (5.6×10^{-2} mbar) to obtain **5** as a white powder.

Yield: 69 mg (0.08 mmol, 49%), white powder, M.p.: 188 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.78 (t, 6H, $^3J_{H,H}$ = 7.3 Hz, $NCH_2CH_2CH_2\underline{CH_3}$), 0.99 (t, 6H, $^3J_{H,H}$ = 7.3 Hz, $NCH_2CH_2CH_2\underline{CH_3}$), 1.15–1.29 (m, 8H, $NCH_2CH_2\underline{CH_2}Me$), 1.39–1.49 (m, 8H, $NCH_2CH_2\underline{CH_2}Me$), 1.76–2.02 (m, 8H, $NCH_2\underline{CH_2}CH_2Me$), 3.50 (s, 3H, Si–(O-$C\underline{H_3}$)$_2$), 3.66 (s, 3H, Si–(O–$C\underline{H_3}$)$_2$), 3.83–3.89 (m, 2H, $N\underline{CH_2}CH_2CH_2Me$), 4.04–4.16 (m, 6H, $N\underline{CH_2}CH_2CH_2Me$), 7.02 (*br.* d, 3H, trityl phenyl protons), 7.14 (t, 5H, $^3J_{H,H}$ = 8.2 Hz, trityl phenyl protons), 7.18 (t, 5H, $^3J_{H,H}$ = 7.2 Hz, trityl phenyl protons), 7.25 (q, 1H, $^3J_{H,H}$ = 7.2 Hz, trityl phenyl protons), 7.39 (t, 1H, $^3J_{H,H}$ = 8.3 Hz, trityl phenyl protons). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 13.7 (s, $NCH_2CH_2CH_2\underline{CH_3}$), 13.9 (s, $NCH_2CH_2CH_2\underline{CH_3}$), 20.1 (s, $NCH_2CH_2\underline{CH_2}Me$), 20.2 (s, $NCH_2CH_2\underline{CH_2}Me$), 29.3 (s, $NCH_2CH_2\underline{CH_2}Me$), 30.7 (s, $NCH_2\underline{CH_2}CH_2Me$), 49.1 (s, $N\underline{CH_2}CH_2CH_2Me$), 51.1 (s, P–(O–$\underline{CH_3}$)$_2$), 51.4 (s, P–(O–$\underline{CH_3}$)$_2$), 56.7 (trityl phenyl protons), 125.9–129.4 (trityl phenyl protons), 131.2 (s, C^5), 134.2–134.4 (trityl phenyl protons), 134.7 (s, C^4), 142.7 (trityl phenyl protons), 167.2 (s, C=S). $^{31}P\{^1H\}$ NMR (121.5 Hz, $CDCl_3$): δ = −56.8. $^{29}Si\{^1H\}$ dept20 NMR (60 Hz, $CDCl_3$): δ = −47.6 (s, $\underline{Si}$–$(CH_3)_2$)). IR: ν̃ (cm^{-1}) = 3403 (*w*), 2947 (*w*), 1637 (*m*), 1407 (*s*), 1241 (*s*, C–O), 1152 (*s*, Si–OCH_3), 984 (*s*, Si–OCH_3), 699 (*s*, P–C). FTMS + pos-APCI: m/z (%) = 785.3 (25) $[M+H]^+$, 243.1 (25) $[C_{19}H_{15}]^{+\bullet}$, 213.1 (100) $[C_{11}H_{21}N_2S]^+$. HRMS: for $C_{43}H_{57}N_4O_2PS_2Si$ theor./exp. 785.3503/785.3503.

Synthesis of spiro-silolene 7 via assumed silylene trapping: The 1,4-dihydro-1,4-phosphasiline **3** (150 mg, 0.18 mmol) was taken in a 10 mL Schlenk tube along with KC_8 (72.9 mg, 0.54 mmol). Then, the Schlenk tube was cooled down to −80 °C and 1,3-Butadiene (15 wt % in hexane) (0.08 mL, 0.23 mmol) was added along the walls. After that, 1.5 mL of toluene was cooled down to − 80 °C in another Schlenk tube and was transferred by using a stainless steel cannula/bent-tube. After overnight stirring, the consumption of added KC_8 was observed, indicated by the formation of graphite precipitate. The solvent was removed *in vacuo* (3.1×10^{-2} mbar). The

residue was re-dissolved in diethyl ether and filtered via a cannula to remove the potassium chloride salt and graphite formed. The solvent was then removed *in vacuo* (3.9×10^{-2} mbar), washed with a 3:1 mixture of *n*-pentane and diethyl ether thoroughly and dried *in vacuo* (5.6×10^{-2} mbar) to obtain **7** as white powder.

Yield: 99 mg (0.168 mmol, 80%), white powder, M.p.: 161 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.45–0.71 (*br.* m, 4H, Si–(C*H*$_2$)–CH–), 0.81–0.96 (*br.* m, 12H, $NCH_2CH_2CH_2C\underline{H}_3$), 1.22–1.42 (*br.* m, 8H, $NCH_2CH_2C\underline{H}_2Me$), 1.61–1.91 (*br.*m, 8H, $NCH_2C\underline{H}_2CH_2Me$), 3.68–4.29 (*br.* m, 8H, $NC\underline{H}_2CH_2CH_2Me$), 4.86–5.27 (*br.* m, 1H, Si–(CH_2)–C*H*–), 5.27–5.46 (*br.* m, 1H, Si–(CH_2)–C*H*–), 6.90–7.09 (*br.* m, 6H, trityl phenyl protons), 7.17–7.21 (*br.* m, 3H, trityl phenyl protons), 7.25–7.40 (*br.* m, 4H, trityl phenyl protons), 7.40–7.50 (*br.* m, 2H, trityl phenyl protons). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 13.8 (s, Si–(C*H*$_2$)–CH–), 14.2 (s, $NCH_2CH_2CH_2C\underline{H}_3$), 20.1 (s, $NCH_2CH_2C\underline{H}_2Me$), 20.3 (s, $NCH_2CH_2C\underline{H}_2Me$), 29.8 (s, $NCH_2C\underline{H}_2CH_2Me$), 47.1 (s, Si–$(CH_2)$–C*H*–), 49.1 (s, $NC\underline{H}_2CH_2CH_2Me$), 56.6 (trityl phenyl protons), 56.8 (trityl phenyl protons), 126.0–129.6 (trityl phenyl protons), 131.3 (s, C^5), 134.6 (s, C^4), 146.9 (trityl phenyl protons), 166.1 (s, *C*=S). ^{31}P{^{1}H} NMR (121.5 Hz, CD_2Cl_2): δ = −58.0. IR: $\tilde{\nu}$ (cm^{-1}) = 2961 (*w*), 1407 (*w*), 1262 (*s*), 1089 (*s*, Si–CH_2–CH), 1016 (*s*, Si–CH_2–CH), 797 (*s*), 699 (*s*, P–C). EI–MS (70 eV): m/z (%) = 776.4 (20) $[M]^+$, 743.4 (5) $[M–S]^+$, 728.4 (40) $[C_{45}H_{57}N_4OPSi]^+$, 712.4 (40) $[M–2S]^+$. HRMS: for $C_{45}H_{57}N_4PS_2Si$ theor./exp. 776.3531/776.3526.

The EA values didn't improve within a 0.4% error bar despite multiple measurements. A recent report[22] systematically proved that the measurements should be within a deviation of 0.4% is not a realistic journal requirement with the variability attributed to random error and more than 10% of the measurements were outside this deviation. The presence of sulfur may point to missing pre-experimental arrangements usually done prior to the measurements of the samples containing sulfur. Besides, the elemental compositions were evidenced by HRMS, additionally. Apart from that, *p*-benzhydryltetraphenylmethane[23,24] couldn't be separated by column chromatography from **2** and, hence, was also present in all samples thereafter (approx 3%).

Theoretical Methods: All structures were built with the free software Avogadro.[25] Structures and orbitals were visualized with Chimera.[26] Orbitals were plotted with an isovalue of 0.04 a.u. All structures were optimized using ORCA 4.0.1[27] on the TPSS-D3BJ/def2-TZVP($CPCM_{THF}$)[28,29] level of theory. The optimized structures are characterized by frequency analysis to identify the nature of located stationary points (no imaginary frequency) and to provide thermal corrections (at 298.15 K and 1 atm) according to the modified ideal gas-rigid rotor-harmonic oscillator model. Single point energies have been computed on PW6B95-D3BJ/def2-QZVP($CPCM_{THF}$)[29,30] and Kohn–Sham molecular orbitals are taken from therein.

Supporting Information

The authors have cited additional references within the Supporting Information.[23,24]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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