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Strain-Driven, Non-Catalysed Ring Expansion of Silicon Heterocycles

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Silacycles are ubiquitous building blocks. Small silacycles can typically be expanded catalytically. A silirane, silirene and phosphasilirene as well as a siletane and a silolene were prepared starting from the base-free bromosilylene \( (\text{H}_{29}\text{Cbz})\text{SiBr} \) \( (\text{H}_{29}\text{Cbz} = 1,8\text{-bis}(3,5\text{-ditertbutylphenyl})\text{-3,6\text{-ditertbutylcarbazolyl})} \). As these heterocycles were derived from a dicoordinated silylene, they are susceptible to reactions with an external base. The three-membered silacycles readily undergo non-catalysed ring expansion reactions with isonitriles yielding the related four-membered silacycles. Surprisingly, the ring-expanded derivatives of the silirane undergo up to two further isomerisation reactions, first by enamine formation and then by another ring expansion. DFT computations were utilised to gauge the scope of this reactivity pattern. Three-membered silacycles should essentially universally undergo a ring expansion with isonitriles, while for four-membered silacycles, only very few instances are predicted to accommodate more challenging kinetic requirements of this ring expansion. Larger silacycles lack the ring strain energy required for this ring expansion reaction and are not expected to be expanded.

Introduction

Cyclic organosilicon compounds have been intensively researched in the last decades as these heterocyclic systems find applications as odorants, pharmaceuticals, agrochemicals, dyes or polymers.[1–7] The smaller and thus strained silicon-containing heterocycles are also of fundamental interest due to their high reactivity.[8] Siletane, four-membered silacycles, were already discovered by Sommer and Baum in 1954 and prepared by reduction of chloro(3-bromopropyl)dimethylsilane.[9] The three-membered silacycles, siliranes, were first synthesised by Seyferth in 1972[10] and three years later, they also obtained hexamethylsilirane (Scheme 1, A).[11] These siliranes attracted great attention because dialkylsilylenes (B) could be transiently generated by thermal or photolytical treatment.[12] These silylenes, in turn, could be trapped by other substrates such as alkynes (C), allowing access to even more strained silirene heterocycles as reported by Seyferth and Gaspar.[13,14] The same effect could also be utilised in the photolysis of dimethylalkynesilanes, as under photolytic conditions dimethylsilylène would be liberated and react with the remaining alkyne.[15] [2 + 1] cycloaddition reactions of transient silylenes were studied with many silylenes, such as dimethylsilylene MesSi by Sekiguchi and Conlin.[16,17] Tokito’s TbtSiMes (Tbt = 2,4,6-tris[trimethylsilyl]methyl)phenyl)[18]

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Scheme 1. Hexamethylsilirane as silylene source as well as addition products of silylenes to alkynes and aromatics.

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References:

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silylene was shown to undergo the [2 + 1] cycloaddition reaction already at low temperature (F), and then isomerise to an alkynylhydroxilane (G)\(^{[36]}\) of which the rearrangement could be suppressed by coordination of B\((C_6F_5)\)_3\(^{[37]}\). Work by Kato who prepared phosphine-stabilised aminosilylenes demonstrated thermal reversibility of the [2 + 1] cycloaddition reaction at ambient temperature.\(^{[38,39]}\)

For both silacycles and carbocycles, their diverse reactivity is due to their large ring strain energy. For instance, the ring strain energy of the parent cyclopropane ring is estimated at 115 kJ/mol.\(^{[40]}\) A major difference between carbocycles and silacarbo- cycles is that the bonds in carbocycles have a lower degree of polarization than in silacycles. Therefore, carbocycles are generally modified by introduction of substituents to enable the desired reaction.\(^{[37]}\) These substituents can be for example fused ring systems,\(^{[39]}\) ketones\(^{[38]}\) or alkali metals.\(^{[41]}\) In contrast, silacycles do not rely on the introduction of specific functional groups or substituents due to a greater polarization of the bonds in the ring system and the presence of a Lewis acidic site.

Ring expansion reactions of small silacycles frequently are catalysed by transition metals, and a plethora of substitution patterns and ring sizes is accessible among which the expansion of siletanes with alkynes is probably the best investigated example.\(^{[42–44]}\) To date, this work could be extended to asymmetric products\(^{[44–46]}\) and Si–N heterocycles recently.\(^{[46,47]}\) A notable exception is the non-catalysed insertion of CO\(_2\) into siletanes.\(^{[48]}\) Moreover, in the reactions of transient silylenes with alkynes, occasionally silole formation was observed, even though this is not a generally applicable way of preparing them.\(^{[49,50]}\) Serendipitously, Weidenbruch found an example for the expansion of silacyclopropane (H) with phenylisocyanate, and later, Woerpel and coworkers studied the diastereoselectivity of this process.\(^{[51,52]}\) Our group prepared a dicoordinated bromosilylene in 2020 and used a bulky carbazole (\(6^\text{th}\)Cz) for stabilisation.\(^{[53]}\) We have investigated the reactivity towards alkenes and alkynes. To exploit reactivity that is not accessible with base-stabilised silylenes, we then attempted the coordination of isonitriles as additional bases. Non-catalysed ring expansions were observed. DFT calculations were employed to rationalise the behaviour and explore the limitations of this strain-driven ring expansion reaction.

## Results and Discussion

In the first step, reactions of the bromosilylene [(\(6^\text{th}\)Cz)SiBr] with small molecules were targeted to prepare three-, four- and five-membered silacycles. The reactions with ethylene, acetylene, tert-butyl phosphaacetylene proceeded smoothly and allowed the isolation of the corresponding cycloaddition products (Scheme 2, 1–3).

The silirane 1 (Figure 1) is spectroscopically characterised by a \(^{29}\)Si NMR resonance at \(-40.1\) ppm, as well as a \(^{13}\)C NMR resonance at \(10.19\) ppm for the SiC2 ring. In the \(^{1}\)H NMR spectrum, an AA’BB’ spin system is observed with resonances at \(0.41\) (trans to Br) and \(0.67\) (cis to Br) ppm. The silirene 2 (Figure 1) features a resonances at \(-101.0\) ppm in the \(^{29}\)Si NMR, \(162.5\) ppm in the \(^{13}\)C NMR and \(7.27\) ppm in the \(^{1}\)H NMR for the silirene moiety. The structural data obtained for 1 and 2 show disorder of Br and the C2 moiety, and therefore, experimentally determined bond metrics are unreliable.

The phosphasilirene 3 (Figure 1) is identified by resonances at \(-59.3\) ppm in the \(^{29}\)Si NMR, \(265.6\) ppm in the \(^{13}\)C NMR as well as \(337.5\) ppm in the \(^{1}\)H NMR for the silirene moiety. The structural data obtained for 1 and 2 show disorder of Br and the C2 moiety, and therefore, experimentally determined bond metrics are unreliable.
The internal angles amount to 53.67(9)° at P, 51.51(8)° at Si, and 74.83(10)° at C. As \( \text{[CbdBr2]SiBr} \) did not appear to react with cyclopropanes, it was treated with 1,3-dibromopropane and subsequently reduced to afford the silatane 4 (Scheme 2). The \([\text{[Cbz]SiBr}]+[\text{[CbdBr2]SiBr}]\) yielded the 3-silolene 5. The siletane 4 features a signal at 3.2 ppm in the \( ^{29}\text{Si} \) NMR, as well as two resonances at 14.39 and 28.10 ppm in the \( ^{13}\text{C} \) NMR, while in the \( ^{1}\text{H} \) NMR spectrum three multiplets at 1.04, 1.22 and 1.33 ppm in a 2:2:2 ratio were observed. The five-membered silacycle 5 shows characteristic resonances at 19.8 ppm in the \( ^{29}\text{Si} \) NMR, as well as at 33.12 and 128.39 ppm in the \( ^{13}\text{C} \) NMR spectrum. In the \( ^{1}\text{H} \) NMR spectrum, the methylene protons of the silacycle are observed at 1.40 and 1.77 ppm, showing a ^2J_{\text{Si-H}} coupling of 18 Hz.

In the second step, the silacycles 1–5 were subjected to reactions with the isonitriles CNDmp (Scheme 3, a, Dmp = 2,6-dimethylphenyl) and CNBu (b). In general, the reactions with the latter isonitrile proceed faster than with the former.

When silatane 1 was treated with DmpNC or BuNC, the reaction mixtures had to be heated to 100°C for 18 h to achieve completion of the reactions. For DmpNC, the initial ring expansion product 6a could be detected and isolated, but upon redissolution, rapid isomerisation to 7a was observed. For the reaction of 1 with BuNC, direct conversion to 7b was found. However, in this case, further isomerisation to 8b was observed. The ring expansion of the unsaturated sililene 2 proceeded more straightforwardly, required lower reaction temperature than the saturated analogs. The resulting siletanes 9a and 9b (Scheme 4) did not undergo further rearrangements. Remarkably, with the phosphasilirene 3, even lower reaction temperatures were required, and 18 h at 45°C sufficed to ensure completion of the reaction, yielding 10a and 10b. The insertion reaction of the isonitriles occurred exclusively at the silicon-phosphorus bond. This might be due, on the one hand, to the lower homolytic bond dissociation energy of a silicon-phosphorus bond (363.6 kJ/mol) compared to a silicon-carbon bond (507.5 ± 8.8 kJ/mol) and, on the other hand, to the greater steric demand on the carbon atom by the bonded tert-butyl substituent. When the siletane 4 or the silolene 5 were treated with either isonitrile, no ring expansion reactivity could be observed.

The four-membered heterocyclic ring expansion products were characterised spectroscopically and by single crystal XRD. The initially formed compound 6a features three characteristic resonances in the \( ^{13}\text{C} \) NMR spectrum at 21.09 (\( \alpha \)-C), 34.34 (\( \beta \)-C) and 187.06 ppm (imino-C) in good agreement with the calculated values of 23, 33 and 189 ppm. Four distinct resonances were identified for the protons of the silacycle. Two multiplets at 0.95 and 1.01 ppm were assigned to the \( \alpha \)-CH\(_2\) groups, while two more downfield-shifted multiplets at 1.10 and 1.82 ppm were assigned to the \( \beta \)-CH\(_2\) groups. The bond metrics determined by XRD also corroborate the presence of C–N single bonds in the silicycle (1.524(5), 1.541(5) Å) and an exocyclic C–N bond (1.274(5) Å; Figure 2).

After rearrangement to 7a, the bond metrics are changed significantly: The C–C bonds are shortened (1.422(5), 1.386(5) Å) and the C–N bond (1.274(5) Å) is elongated, with similar bond metrics being observed in 7b (C–C 1.529(12), 1.358(5); C–N 1.355(5) Å). This is also reflected in the NMR spectroscopic data. The central structural motif features three \( ^{13}\text{C} \) NMR resonances at 26.49, 106.95, 148.51 (7a, calc. 27, 103, 142 ppm) and 28.47, 105.69, 149.58 ppm (7b, calc. 30, 102, 149 ppm), respectively. In the \( ^{1}\text{H} \) NMR spectrum, four related resonances appear at 1.51, 1.85, 3.65, 4.98 (7a) and 1.52, 1.62, 4.64, 5.14 ppm (7b). The presence of an N–H moiety is also corroborated by a typical ν\(_{\text{NH}}\) stretching mode at 3402 (7a) and 3418 cm\(^{-1}\) (7b). Both compounds feature consimilar 29Si NMR resonances at –17.9 (7a) and –17.6 ppm (7b). As 7b undergoes a second rearrangement to 8b, the NMR signature changes again. The 29Si NMR
The bond metrics show localised double and single bonds along the CCCN scaffold (9a C1–C2 1.330(7), C2–C3 1.494(7), N1–C3 1.246(6); 9b C1–C2 1.301(6), C2–C3 1.488(6), C3–N1 1.259(5) Å; Figure 3).

The phosphasilates feature even more deshielded NMR signals of the central heterocycle, but the analysis is complicated by the existence of 10b in two isomers which occur in 3:1 ratio in solution and are likely rotamers as the calculated values show agreement to the observed ones (see Supporting Information Figure S86, S87). The $^{13}$C NMR spectra show two strongly downfield-shifted doublets for each species (10a 196.79, 238.28, 10b major 188.05, 232.75, 10b minor 184.02, 242.76 ppm). Similarly, the $^{31}$P NMR signals are observed at low field and all three are observed as broad singlets (10a 378.9, 10b 374.8 major, 10b minor 392.3 ppm). Structurally, there is a localised double bond present in both species which is apparent from the distinct P–C bond lengths (10a P1–C2 1.693(3), P1–C1 1.869(3); 10b P1–C1 1.676(5), P1–C2 1.840(4) Å).

Computations (Gaussian16, PBE0-GD3, Def2-SVP basis sets) were initiated to rationalise the observed reactivity (Table 1). First, isodesmic reactions were calculated to estimate the gain in Gibbs free energy by relieving the ring strain (negative value

Figure 2. Crystal structure of siletane 6a (top), silete 7b (middle) and silolene 8b (bottom). Thermal ellipsoids at probability level 50%.

Figure 3. Crystal structure of silet 9a (top) and phosphasilet 10a (bottom). Thermal ellipsoids at probability level 50%.
indicates energy gain upon ring opening) as this appears as the driving force of the ring expansion reactivity (Scheme 5).

The ring strain energy (RSE) is high for the three-membered rings, with energies for the SiC$_2$, SiCN and SiCO rings ranging from $-156.8$ to $-172.8$ kJ/mol. For comparison, the RSE for the parent cyclopropane (C$_3$H$_6$) and silirane (SiC$_2$H$_6$) were calculated with the same method and found to be $-80.6$ and $-125.6$ kJ/mol, respectively, which illustrates the effect of Si incorporation as well as the effect of the substituents. The incorporation of a second element of the third period in the heterocycle markedly reduced the ring strain to $-87.3$ kJ/mol which can be explained by the smaller degree of ideal hybridisation at the heavier element. The RSE is smaller for the four membered rings SiC$_2$, SiC$_2$N, SiC$_2$O $-64.3$ to $-75.6$ kJ/mol, and only slightly lower for the five-membered ring $-65.9$ to $-77.5$ kJ/mol.

Table 1. Calculated ring strain energies (RSE) thermodynamic gains upon isonitrile insertion and activation barrier for the insertion reaction (all in kJ/mol at 298.15 K). [Si] = Si(NC$_2$H$_4$)Br fragment. The G data refer to the reaction depicted in Scheme 6.

<table>
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<tr>
<th>heterocycle</th>
<th>RSE [kJ/mol]</th>
<th>$\Delta G_{0.0}$ [kJ/mol]</th>
<th>$\Delta G^{\ddagger}_{132}$ [kJ/mol]</th>
<th>$\Delta G$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Si]</td>
<td>$-156.8$</td>
<td>$-172.8$</td>
<td>$-125.6$</td>
<td>$-80.6$</td>
</tr>
<tr>
<td>[Si]</td>
<td>$-158.0$</td>
<td>$-156.8$</td>
<td>$-172.8$</td>
<td>$-125.6$</td>
</tr>
<tr>
<td>[NH]</td>
<td>$-172.8$</td>
<td>$-165.7$</td>
<td>$-158.0$</td>
<td>$-149.4$</td>
</tr>
<tr>
<td>[C]</td>
<td>$-156.8$</td>
<td>$-158.0$</td>
<td>$-172.8$</td>
<td>$-125.6$</td>
</tr>
<tr>
<td>[P]</td>
<td>$-87.3$</td>
<td>$-65.5$</td>
<td>$-125.6$</td>
<td>$-113.5$</td>
</tr>
<tr>
<td>[S]</td>
<td>$-64.3$</td>
<td>$-40.5$</td>
<td>$-125.6$</td>
<td>$-41.7$</td>
</tr>
<tr>
<td>[S]-NH</td>
<td>$-64.3$</td>
<td>$-40.5$</td>
<td>$-125.6$</td>
<td>$-41.7$</td>
</tr>
<tr>
<td>[S]-O</td>
<td>$-75.6$</td>
<td>$-65.9$</td>
<td>$-125.6$</td>
<td>$-18.1$</td>
</tr>
<tr>
<td>[S]-SiH$_2$</td>
<td>$-65.9$</td>
<td>$-56.7$</td>
<td>$-125.6$</td>
<td>$-72.2$</td>
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<tr>
<td>[Si]-P</td>
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<td>$-40.5$</td>
<td>$-125.6$</td>
<td>$-41.7$</td>
</tr>
<tr>
<td>[Si]-S</td>
<td>$-20.1$</td>
<td>$-0.4$</td>
<td>$-125.6$</td>
<td>$-18.1$</td>
</tr>
<tr>
<td>[Si]</td>
<td>$5.4$</td>
<td>$-20.1$</td>
<td>$-125.6$</td>
<td>$-72.2$</td>
</tr>
</tbody>
</table>

In line with the expectation, ring expansion was observed for all investigated three-membered rings and not observed for the five-membered ring.Somewhat unexpectedly, the SiC$_2$ ring did not show any sign of ring expansion, even though the ring strain energy is in the same order of magnitude as of the SiCP ring that underwent ring expansion. Not only the ring strain of the heterocycle but also the specific ring expansion reaction with the complete carbazolyl ligand was studied and indicated an even higher thermodynamic gain for the SiC$_2$ cycle compared to the SiCP derivative. To elucidate kinetic influences on the reaction, the pathway was studied in detail, depicted exemplarily for the reaction of 1 with CN$^-$Bu in Scheme 6. The reaction proceeds via an associative mechanism, so that the initial step is coordination of the isonitrile on the silicon atom. This is a reaction with a low activation barrier (TS1), but also an endergonic process. Therefore, it can be viewed as equilibrium reaction which disfavours the pentacoordinated intermediate (Int1). This behaviour can be understood, as in general tetracoordinated silanes are not very strong acids and usually form penta- or hexacoordinated complexes only with very hard donors such as O or F, or the use of bidentate ligands such as amidinates. However, rigid ligands introducing structural strain can make Si a potent acid as shown by Greb [56–57].

From this intermediate, there is another transition state (TS2) for the insertion of the isonitrile C atom into a Si–X bond (X=C, N, O, Si, P, S). This activation barrier depends strongly on the ring size and the X atom. The three-membered silacycles show moderate activation barriers for this insertion process, but...
for the PCSi cycle, the barrier is notably lower. This is nicely in agreement with the observation that for the latter cycle the temperature required for ring expansion is the lowest.

In contrast, the SiC₄ four-membered heterocycle has a considerably higher activation barrier for this process. Hence, while thermodynamically favourable, the kinetic parameters of this reaction prevent the ring expansion. However, as observed for the three-membered cycles, the activation barrier can be reduced drastically by introducing heteroatoms. For instance, with the hypothetical SiC₅S heterocycle, the computational activation barrier amounts to 69.6 kJ/mol, just in the same range as for the siliren expansion.

We have attempted the synthesis of a SiC₅S heterocycle starting from the bromosilylene via addition of 2-bromoethanol and thirane, but neither reaction was successful. Other routes via addition of 1,2-dibromoethane and subsequent insertion of S did not lead to the desired species either. The challenge to prepare an 1,2-cyclobutane derivative with Si and another 3rd period element remains to test our hypotheses experimentally.

It is interesting to note that instead of the expected silacycles 6a and 6b, the isomeric 7a and 7b were obtained after imine to enamine isomerisation (Scheme 3). The enamine is thermodynamically more stable by 11.6 kJ/mol. The monomolecular barrier for the tautomerisation is estimated as 258.7 kJ/mol which is not feasible. An explanation for the reaction taking place regardless could be an autocatalytic process in which the imine or amine serves as intermolecular base to reduce the activation barrier of the proton migration. Further isomerisation of 7b to 8b releases further 86.7 kJ/mol.

As the ring expansion of silacycles appeared a general process that should occur independent of the origin of the silacycle, i.e. the carbazolyl substituent, two more calculations were carried out to check the applicability of the ring expansion method to other species. For instance, with Seyferth’s silirane A, no intermediate of the type of Int1 could be located, but the activation barrier for the insertion of the isonitrile into the silacycle (TS2) amounts to 103.5 kJ/mol, which is considerably larger than the activation energy for the expansion of 1 to 6b (64.5 kJ/mol). Some of that difference may be due to the substitution pattern of the siliran. To account for that, a siliran derived Weidenbruch’s H, Bu₂SiC₆H₆ was calculated as well. Again, no Int1 could be located, but TS2 is at 93.8 kJ/mol, which is lower than for Seyferth’s siliran but nonetheless higher than for our carbazol-derived species.

Therefore, three main factors determine whether the insertion of the isonitrile into the silacycle can take place, provided the ring strain energy is sufficient: 1) Steric shielding of the silacycle should be small, substituents such as H on the carbon atoms are advantageous. 2) Electronnegative substituents stabilise Int1 and reduce TS2, therefore the insertion proceeds more readily. 3) Heteroatoms in the silacycle reduce the thermodynamic gain upon ring expansion, but reduce the required activation barrier.

Conclusions

We have prepared three-, four-, and five-membered silacycles starting from the carbazolyl bromosilylene [(4-Cbz)SiBr]. As they, in contrast to products derived from amidinatosilylenes, feature four-coordinated Si atoms, isonitriles were added as external Lewis bases. In several cases of three-membered silacycles, ring expansion reactions were observed, leading to four-membered silacycles. Derivatives of the saturated siliran were found to undergo up to two further isomerisation reactions. At this stage, four- and five-membered silacycles could not be expanded. The reaction was studied in silico to gauge the scope of this ring expansion reaction. The reaction should in principle be applicable to other silacycles as well, and in particular the expansion of three-membered silacycles is predicted to occur universally. In contrast, the expansion of four-membered silacycles is kinetically hampered although thermodynamically feasible. Suitable silacycles such as 1,2-thialtelenes are predicted to undergo ring expansion with isonitriles. Larger rings lack the thermodynamic driving force for this ring expansion and are not expected to react with isonitriles.

Experimental Section

All experiments were conducted in dry glassware under an inert argon atmosphere by applying standard Schlenk techniques.

Synthesis of 1: A solution of [(4-Cbz)SiBr (220 mg, 0.288 mmol) in toluene was degassed. Subsequently, the evacuated reaction vessel was filled with ethylene and the reaction mixture was stirred overnight at room temperature. After removal of a colorless precipitate, the solvent was removed in vacuo and the residue was dissolved in n-hexane. The solvent was evaporated to incipient crystallisation and left undisturbed until single crystals suitable for X-ray diffraction deposition. The supernatant was removed with a syringe, the yellowish solid was washed with n-hexane and dried in vacuo (16 mg, 0.020 mmol, 7%).

1H NMR (400.3 MHz, CD₂Cl₂): δ (ppm) = 0.41 (m, 2 H, H₂C₂H₂), 0.67 (m, 2 H, H₂C₂H₂), 1.34 (s, 36 H, Ar-Bu), 1.36 (s, 18 H, Carb-Bu), 7.54 (d, 4 H, J=1.6 Hz, o-Ch), 7.58 (t, 2 H, J=1.7 Hz, p-Ch), 7.62 (d, 2 H, J=2.0 Hz, C⁵-H), 8.34 (d, 2 H, J=2.0 Hz, C⁵-H). 13C(CH₃) NMR (100.7 MHz, CD₂Cl₂): δ (ppm) = 10.19 (s, C₃H₃), 31.71 (s, Ar-C(Ch₂)₃), 32.00 (s, Carb-C(Ch₂)₃), 34.82 (s, Carb-C(Ch₂)₃), 35.04 (s, Ar-C(Ch₂)₃), 115.67 (s, C⁵), 122.80 (s, p-C), 125.62 (s, o-C), 127.40 (s, C⁵), 128.69 (s, C₄H₃), 131.52 (s, C₃), 140.16 (s, i-C), 143.92 (s, C₄H₃), 143.35 (s, C₃), 150.74 (s, m-C). 13N NMR (40.6 MHz, CD₂Cl₂): δ (ppm) = 107.9 (s).

Synthesis of 2: 161 mg [(4-Cbz)SiBr (0.211 mmol) were dissolved in 10 ml of n-hexane. Acetylene gas was introduced into this solution, which was produced by hydrolysis of CaC₂. Subsequently, the reaction mixture was stirred for 30 min at room temperature. Afterwards, the solvent was removed under reduced pressure and the colorless residue was dissolved in toluene. The solvent was evaporated to incipient crystallisation and left undisturbed until single crystals suitable for X-ray diffraction deposition. The supernatant was removed with a syringe, the colorless solid was washed with n-hexane and dried in vacuo (45 mg, 0.057 mmol, 27%).

1H NMR (400.3 MHz, CD₂Cl₂): δ (ppm) = 1.32 (s, 36 H, Ar-Bu), 1.38 (s, 18 H, Carb-Bu), 7.27 (s, 2 H, J=3.4 Hz, J=190 Hz, C₃H₃), 7.57
temperature. Afterwards, all volatiles were removed under reduced 0.377 mmol) was added to a solution of Ar (C=CH(3)) 31.97 (s, Carb–C(CH3)3)), 34.15 (s, Ar–C(CH3)2), 115.33 (s, 28.10 (s, (SiCH2)), 31.75 (s, Ar–C(CH3)2), 115.13 (s, C (s, 29C)), 128.39 (s, dmb–C(CH3)), 128.63 (s, C(4)), 130.10 (s, C(29)), 132.05 (s, C(5)), 140.91 (s, i-C3), 143.95 (s, C(29)), 145.57 (s, C(26)), 150.62 (s, m-C). 13C NMR (40.6 MHz, CD2Cl2): δ (ppm) = 111.8 (s). 29Si NMR (79.5 MHz, CD2Cl2): δ (ppm) = 19.8 (s).

Synthesis of 6a: In three Young NMR tubes, the silirane 1 (64.0 mg, 0.081 mmol) and 2,6-dimethylphenylisilomorpholine (DmpNC) (106.6 mg, 0.081 mmol) were dissolved in 0.5 mL benzene, respectively. After heating at 100 °C in the oil bath for four hours, the reaction mixtures have been combined and all volatiles were removed under reduced pressure. The colorless residue was dissolved in n-hexane. The solvent was evaporated to incipient crystallisation and left undisturbed until single crystals suitable for X-ray diffraction deposition. The supematant was removed with a syringe, the off-white solid was washed with n-hexane and dried in vacuo (27.2 mg, 0.029 mmol, 12%).

1H NMR (400.3 MHz, CD2Cl2): δ (ppm) = 0.95 (m, 1 H, H1/H2), 1.01 (m, 1 H, H1/H2), 1.10 (m, 1 H, H3/H4), 1.82 (m, 1 H, H3/H4). 13C(1H) NMR (100.7 MHz, CD2Cl2): δ (ppm) = 21.09 (s, CH3), 34.33 (s, CH2), 187.06 (s, C3 N).

Synthesis of 7a: The silirane 1 (230 mg, 0.291 mmol) and 2,6-dimethylphenylisilomorpholine (DmpNC) (40.0 mg, 0.305 mmol) were dissolved in 3 mL toluene. Subsequently, the reaction mixture was stirred over night at 100 °C in the oil bath. Afterwards, all volatiles were removed under reduced pressure and the colorless residue was dissolved in fluorobenzene. The solvent was evaporated to incipient crystallisation and left undisturbed until single crystals suitable for X-ray diffraction deposition. The supematant was removed with a syringe, the colorless solid was washed with n-hexane and dried in vacuo (21.5 mg, 0.023 mmol, 8%).

1H NMR (400.3 MHz, CD2Cl2): δ (ppm) = 1.38 (br, 18 H, Carb–Bu), 1.40 (br, 36 H, Ar–Bu), 1.52 (dd, 1 H, Jαβ=1.8 Hz and 14.3 Hz, 1HCH(2CH3)), 1.62 (dd, 1 H, Jαβ=1.9 Hz and 14.3 Hz, Si(CH2CH3)), 1.89 (br, 6 H, Dmp-(CH3)), 4.64 (t, 1 H, Jαβ=1.5 Hz, Jαγ=40 Hz, Si(CH2CH3)), 5.14 (s, 1 H, DmpNH), 6.81-6.85 (m, 3 H, Dmp–CH3), 7.62 (br, 1 H, C(2)), 7.66 (t, 2 H, J=1.6 Hz, p–CH2), 7.66 (br, 2 H, o–CH2), 7.68 (br, 1 H, C(2)), 8.00 (br, 2 H, o–CH2), 8.29 (d, 2 H, Jαβ=2.0 Hz, 1HCH(2CH3)). 13C(1H) NMR (100.7 MHz, CD2Cl2): δ (ppm) = 17.97 (s, Dmp–CH3), 26.49 (s, Si(CH2CH3), 31.68 (br, Ar–C(CH3)), 31.77 (br, Ar–C(CH3)), 32.75 (s, Dmp–CH3)), 34.76 (s, Carb–C(CH3)), 35.12 (s, Ar–C(CH3)), 106.95 (s, Si(CH2CH3), 115.64 (br, C(26)), 115.92 (br, C(26)), 123.11 (br, C)), 123.67 (br, p–C), 125.48 (br, o–C), 126.08 (s, Dmp–p-C), 128.25 (s, C(29)), 128.35 (s, C(29)), 126.89 (br, Dmp–m-C), 130.52 (s, C(29)), 130.80 (s, C(26)), 132.25 (br, C(35)), 132.25 (br, Dmp–o-C), 134.83 (s, Dmp–i-C), 140.10 (br, i-C), 140.40 (br, i-C), 143.27 (br, C(4)), 143.89 (br, C(29)), 145.50 (br, C(26)), 148.50 (br, C(26)), 148.51 (s, Si(CH2CH3), 150.77 (br, m–C), 151.59 (br, m–C). 13N NMR (40.6 MHz, CD2Cl2): δ (ppm) = 79.5 (s, DmpNH). 29Si NMR (79.5 MHz, CD2Cl2): δ (ppm) = -17.9 (s).

Synthesis of 7b: The silirane 1 (450 mg, 0.569 mmol) was dissolved in 10 mL toluene. After addition of a solution of tert-butyloxilisilomorpholine (BuNC) (70.9 mg, 0.853 mmol) in benzene, the reaction mixture was stirred over night at 100 °C in the oil bath. Afterwards, all volatiles were removed under reduced pressure and the yellowish residue was dissolved in n-hexane. Then, the solvent was evaporated to incipient crystallisation and left undisturbed until single crystals suitable for X-ray diffraction deposition. The supematant was removed with a syringe, the off-white solid was washed with n-}

turbed until single crystals suitable for X-ray diffraction deposited.

Then, the residue was dissolved in 15 mL toluene. After addition of a solution of tert-butylsilirane (BuNC) (55.9 mg, 0.673 mmol) in benzene, the reaction mixture was stirred over night at 110 °C in the oil bath. Afterwards, all volatiles were removed under reduced pressure and the orange residue was dissolved in benzene. The solvent was evaporated to incipient crystallisation and left undisturbed until single crystals suitable for X-ray diffraction deposited. The supernatant was removed with a syringe, the yellow solid was washed with n-hexane and dried in vacuo (46.3 mg, 0.047 mmol, 27%). 1H NMR (400.3 MHz, CD2Cl2): δ (ppm) = 0.85 (s, 9 H, Bu3C), 1.24 (s, 18 H, Ar–Bu), 1.32 (s, 9 H, Carb–Bu), 1.34 (s, 9 H, Carb–Bu), 1.40 (s, 18 H, Ar–Bu), 2.15 (d, J = 6 Hz, Ph–C(Ph)–CH2), 3.95 (s, 3 H, –CH3), 4.08 (d, J = 3 Hz, –CH2–), 7.46 (t, J = 1.8 Hz, p-CH3), 7.70 (d, J = 1.8 Hz, p-CH3), 7.88 (s, 1 H, S=O), 10.93 (s, 1 H, N=O) NMR (97.95 MHz, CD3OD): δ (ppm) = 17.6 (s, N=O).

Synthesis of 10a: The phosphasilirane (3) (150 mg, 0.174 mmol) and 2,6-dimethylphenylsilirane (DmpNC) (23.0 mg, 0.175 mmol) were dissolved in 15 mL toluene. The reaction mixture was stirred over night at 45 °C in the oil bath. Afterwards, all volatiles were removed under reduced pressure and the orange residue was dissolved in benzene. The solvent was evaporated to incipient crystallisation and left undisturbed until single crystals suitable for X-ray diffraction deposited. The supernatant was removed with a syringe, the yellow solid was washed with n-hexane and dried in vacuo (46.3 mg, 0.047 mmol, 27%). 1H NMR (400.3 MHz, CD2Cl2): δ (ppm) = 0.85 (s, 9 H, Bu3C), 1.24 (s, 18 H, Ar–Bu), 1.32 (s, 9 H, Carb–Bu), 1.34 (s, 9 H, Carb–Bu), 1.40 (s, 18 H, Ar–Bu), 2.15 (d, J = 6 Hz, Ph–C(Ph)–CH2), 3.95 (s, 3 H, –CH3), 4.08 (d, J = 3 Hz, –CH2–), 7.46 (t, J = 1.8 Hz, p-CH3), 7.70 (d, J = 1.8 Hz, p-CH3), 7.88 (s, 1 H, S=O), 10.93 (s, 1 H, N=O) NMR (97.95 MHz, CD3OD): δ (ppm) = 17.6 (s, N=O).
Supporting Information

Deposition Numbers 2264949 (for 1), 2264948 (for 2), 2264951 (for 3), 2264939 (for 4), 2264950 (for 4), 2264955 (for 5), 2265192 (for 6a), 2264934 (for 7a), 2264935 (for 7b), 2264936 (for 8b), 2264937 (for 9a), 2264938 (for 9b), 2264953 (for 10a), 2264954 (for 10b) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

The full experimental data including plots of spectra, crystallographic and computational data is given in the Supporting Information. The authors have cited additional references within the Supporting Information. [88-77]

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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 supplemental material of this article.

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