Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202302311

Chemistry
Europe
European Chemical
Societies Publishing

www.chemeurj.org

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

Maximilian P. Müller[a] and Alexander Hinz*[a]

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 [(dtbpCbz)SiBr] (dtbpCbz = 1,8-bis(3,5-ditertbutylphenyl)-3,6-ditert-butylcarbazolyl). 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 photolytic 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 dimesityl-alkinylsilanes, as under photolytic conditions dimesitylsilylene would be liberated and react with the remaining alkyne.[15] [2 + 1] cycloaddition reactions of transient silylenes were studied with many silylenes, such as dimesitylsilylene Mes₂Si by Sekiguchi and Conlin,[16,17] Tokitoh's TbtSiMes (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl),[18]
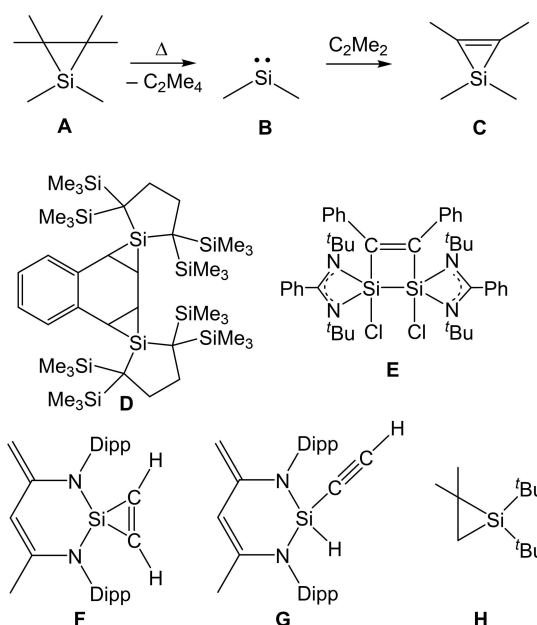


Scheme 1. Hexamethylsilirane as silylene source as well as addition products of silylenes to alkynes and aromatics.

bis(diisopropylamino)silylene,[19] tBu₂Si[20,21] and, more recently, NHI-substituted (NHI = N-heterocyclic imine),[22] silyl-substituted[23,24] or allylaminosilylenes.[7] The [2 + 1] cycloaddition was also studied with stable silylenes, for instance with Power's acyclic (TerS)₂Si (Ter = terphenyl)[25] or Kira's dialkylsilylene.[26] Remarkably, even such cycloadditions with aromatic compounds were observed with dialkyl[27–29] and diaryl[30] substituents (**D**). Base-stabilised silylenes showed different behaviour than dicoordinated ones: Roesky's amidinato-chlorosilylene was treated with diphenylacetylene, and surprisingly, no 1:1 product was formed. Instead, the alkyne reacted with two equivalents of the silylene (**E**).[31] Driess' zwitterionic

[a] M. P. Müller, Dr. A. Hinz
Karlsruhe Institute of Technology
Institute for Inorganic Chemistry
Engesserstr. 15, 76131 Karlsruhe (Germany)
E-mail: alexander.hinz@kit.edu

Chem. Eur. J. 2023, 29, e202302311 (1 of 10)

© 2023 The Authors. Chemistry - A European Journal published by Wiley-VCH GmbH

**Chemistry–A European Journal**

Research Article
doi.org/10.1002/chem.202302311

**Chemistry Europe**
European Chemical
Societies Publishing

silylene was shown to undergo the [2+1] cycloaddition reaction already at low temperature (**F**), and then isomerise to an alkynylhydrosilane (**G**)[32] of which the rearrangement could be suppressed by coordination of $B(C_6F_5)_3$.[33] Work by Kato who prepared phosphine-stabilised aminosilylenes demonstrated thermal reversibility of the [2+1] cycloaddition reaction at ambient temperature.[34,35]

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.[36] A major difference between carbocycles and silacarbocycles 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,[37] ketones[38] or alkali metals.[39] 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.[2,40–43] To date, this work could be extended to asymmetric products[43–45] 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 phenylisonitrile, 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 (dtbpCbz) 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 [(dtbpCbz)SiBr] with small molecules were targeted to prepare three-, four- and five-membered silacycles. The reactions with ethylene, acetylene, tertbutyl 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 $SiC_2$ 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**
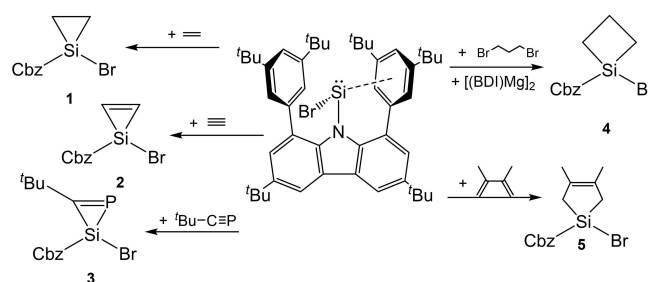


**Scheme 2.** Synthetic strategies to access silicon-containing heterocycles employing the carbazolyl bromosilylene as starting material (BDI = β-diketiminate).
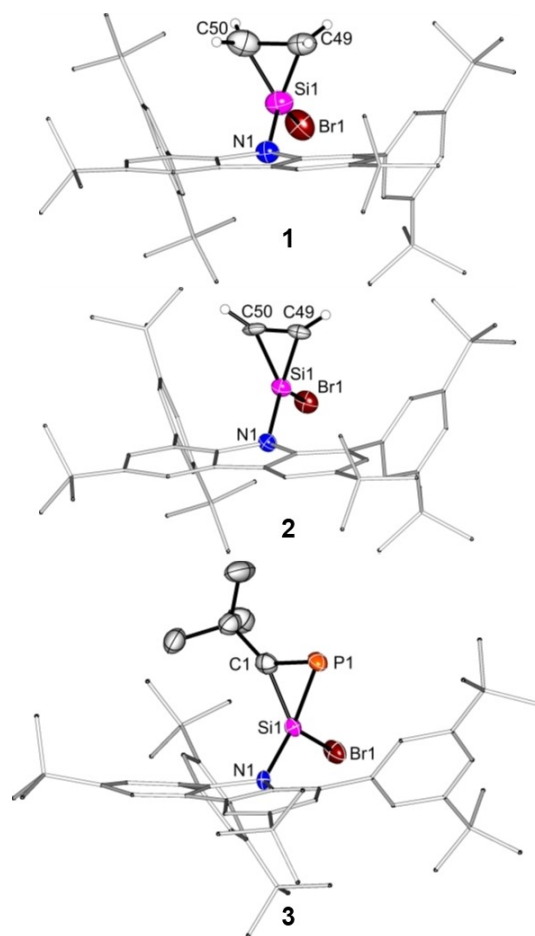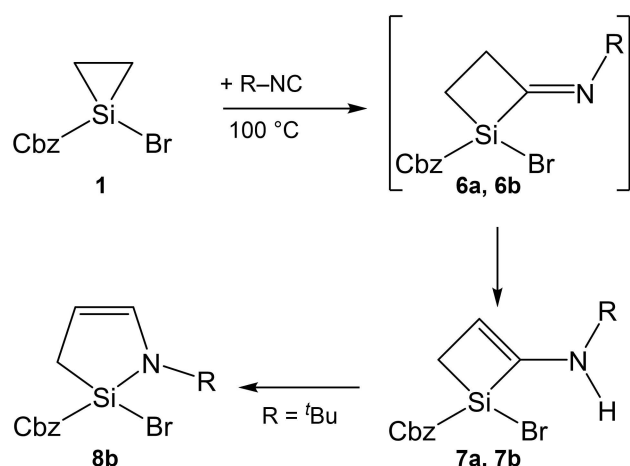


**Figure 1.** Crystal structure of silirane (**1**), silirene (**2**) and phosphasilirene (**3**). Thermal ellipsoids at probability level 50%.

(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 $C_2$ 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 $^{31}$P NMR spectrum. Structurally, the PCSi triangle shows a short P–C bond of 1.741(2) Å, as well as C–Si and P–Si bonds of 1.792(3) and 2.1463(9) Å length, respectively.

**Chemistry–A European Journal**

Research Article
doi.org/10.1002/chem.202302311

**Chemistry Europe**
European Chemical
Societies Publishing

The internal angles amount to 53.67(9)° at P, 51.51(8)° at Si, and 74.83(10)° at C. As [(dtbpCbz)SiBr] did not appear to react with cyclopropanes, it was treated with 1,3-dibromopropane and subsequently reduced to afford the siletane **4** (Scheme 2). The [4+1] cycloaddition between dimethyl butadiene and [(dtbpCbz)SiBr] yielded the 3-silolene **5**. The siletane **4** features a signal at 3.2 ppm in the $^{29}$Si NMR, as well as two resonances at 14.39 and 28.10 ppm in the $^{13}$C NMR, while in the $^{1}$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 $^{29}$Si NMR, as well as at 33.12 and 128.39 ppm in the $^{13}$C NMR spectrum. In the $^{1}$H NMR spectrum, the methylene protons of the silacycle are observed at 1.40 and 1.77 ppm, showing a $^{2}J_{HH}$ coupling of 18 Hz.
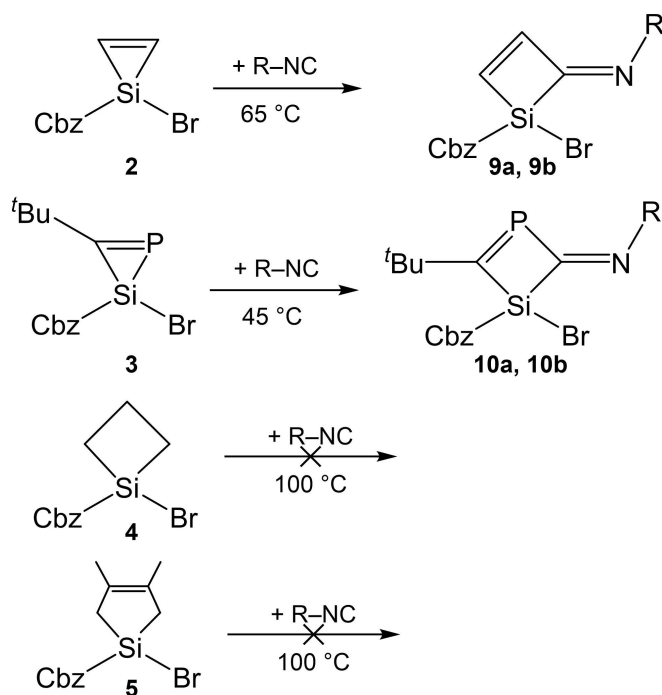
In the second step, the silacycles **1–5** were subjected to reactions with the isonitriles CNDmp (Scheme 3, **a**, Dmp=2,6-dimethylphenyl) and CN$^{t}$Bu (**b**). In general, the reactions with the latter isonitrile proceed faster than with the former.

When silirane **1** was treated with DmpNC or $^{t}$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 $^{t}$BuNC, direct conversion to **7b** was found. However, in this case, further isomerisation to **8b** was observed. The ring expansion of the unsaturated silirene **2** proceeded more straightforwardly, required lower reaction temperature than the saturated analogs. The resulting siletes **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)[54] compared to a silicon-carbon bond (507.5±8.8 kJ/mol)[54] 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 $^{13}$C NMR spectrum at 21.09 (α-C), 34.34 (β-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 α-CH$_2$, while two more downfield-shifted multiplets at 1.10 and 1.82 ppm were assigned to the β-CH$_2$. The bond metrics determined by XRD also corroborate the presence of C–C single bonds in the silacycle (1.524(6), 1.541(6) Å) and an exocyclic C=N double bond (1.232(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 $^{13}$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 $^{1}$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 $v_{NH}$ stretching mode at 3402 (**7a**) and 3418 cm$^{-1}$ (**7b**). Both compounds feature consimilar $^{29}$Si 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 $^{29}$Si NMR



**Scheme 3.** Ring expansions of the silicon heterocycles (**1**) with isonitriles R–NC (**a**: R=Dmp, **b**: R=$^{t}$Bu,) and subsequent rearrangements.



**Scheme 4.** Ring expansions of the silicon heterocycles (**2–5**) with isonitriles R–NC (**a**: R=Dmp, **b**: R=$^{t}$Bu).

**Figure 2.** Crystal structure of siletane **6a** (top), silete **7b** (middle) and silolene **8b** (bottom). Thermal ellipsoids at probability level 50%.
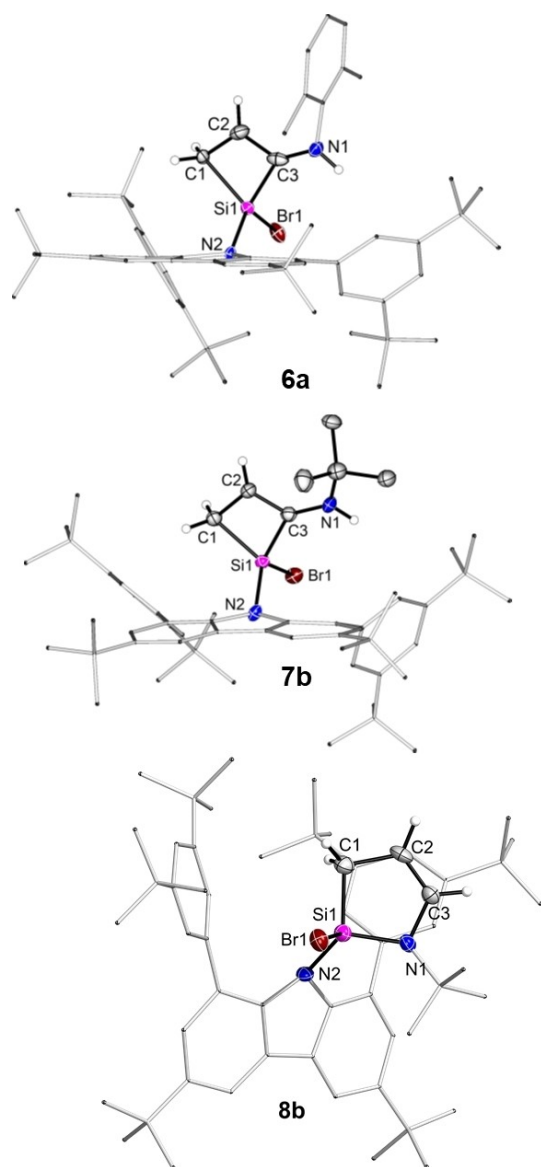
$^{29}$Si NMR resonances were found at −9.4 and −10.3 ppm, respectively. The bond metrics show localised double and single bonds along the CCCN scaffold (**9a** C1–C2 1.330(7), C2–C3 1.494(7), N1–C3 1.246(6); **9b** C1–C2 1.301(6), C2–C3 1.488(6), C3–N1 1.259(5) Å; Figure 3).

The phosphasiletes 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

resonance is now observed at −1.0 ppm, while the $^{13}$C NMR signals were found at 21.01, 99.79 and 137.30 ppm (calc. 24, 95, 138 ppm). The corresponding $^{1}$H NMR resonances were observed at 1.32, 1.75, 4.34 and 5.78 ppm (calc. 0.81, 1.95, 3.85, 5.64 ppm). Remarkably, an alkene moiety is still present, but the amine-H is now absent. The structure of **8b** consistent with the observed NMR data was eventually confirmed by single crystal XRD. The central structural motif features a five-membered heterocycle with localised single (C1–C2 1.522(8), N1–C3 1.411(7) Å) and double bonds (C2–C3 1.323(8) Å).

The siletes **9a** and **9b** are characterised by a typical set of two doublets in the $^{1}$H NMR spectrum (**9a** 6.38, 7.32 ppm, $J_{HH}$ = 7.1 Hz, **9b** 7.01, 7.13 ppm, $J_{HH}$ = 7.1 Hz). The $^{13}$C NMR resonances were all observed at low field in good agreement with the calculated values (**9a** 156.89, 166.43, 179.78, calc. 152, 176, 179, **9b** 156.84, 161.46, 176.93, calc. 159, 160, 175 ppm) and the
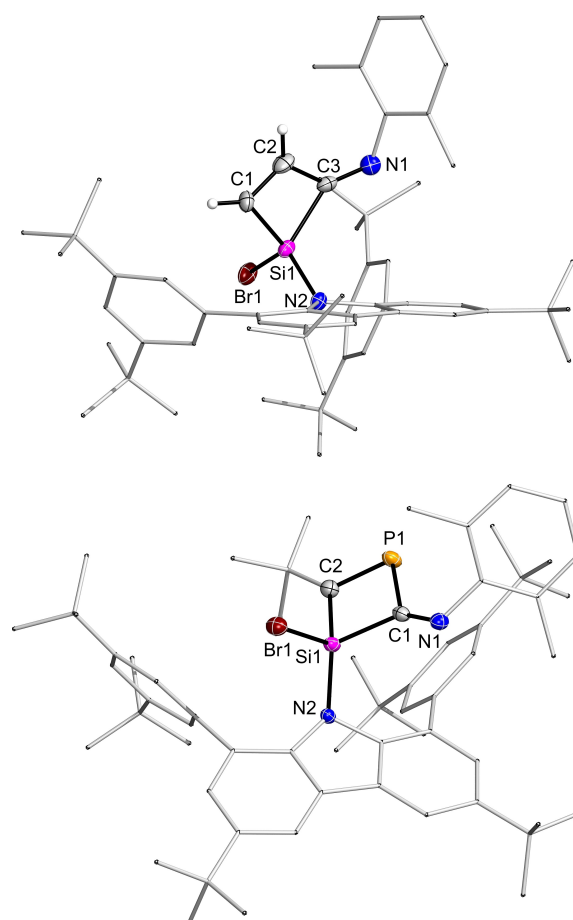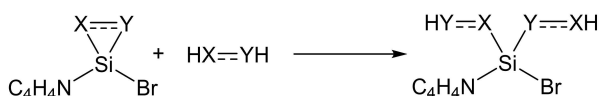


**Figure 3.** Crystal structure of silete **9a** (top) and phosphasilete **10a** (bottom). Thermal ellipsoids at probability level 50%.

**Chemistry–A European Journal**

Research Article
doi.org/10.1002/chem.202302311

**Chemistry Europe**
European Chemical
Societies Publishing

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 ($C_3H_6$) and silirane ($SiC_2H_6$) 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 $SiC_3$, $SiC_2N$, $SiC_2O$ $-64.3$--$-75.6$ kJ/mol, and only slightly lower for the heavier $SiC_2Si$, $SiC_2P$ and $SiC_2S$ rings ($-40.5$--$65.9$ kJ/mol). In contrast, the RSE for the five-membered ring is approximating zero ($-0.4$ kJ/mol) and even positive for the larger rings ($SiC_5$ 20.1, $SiC_6$ 5.4 kJ/mol).

From this, one can draw the expectation that three and four-membered rings should undergo a ring expansion reaction to alleviate some ring strain. Five-membered and larger rings should not benefit significantly from ring expansion and therefore no reaction is expected.

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 $SiC_3$ 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 $SiC_3$ 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 $CN^tBu$ 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 hexa-coordinated 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.[55–57]

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

**Scheme 5.** General isodesmic reaction to estimate the ring strain energy RSE for both saturated and unsaturated heterocycles.

**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), $[Si] = Si(NC_4H_4)Br$ fragment. The G data refer to the reaction depicted in Scheme 6.
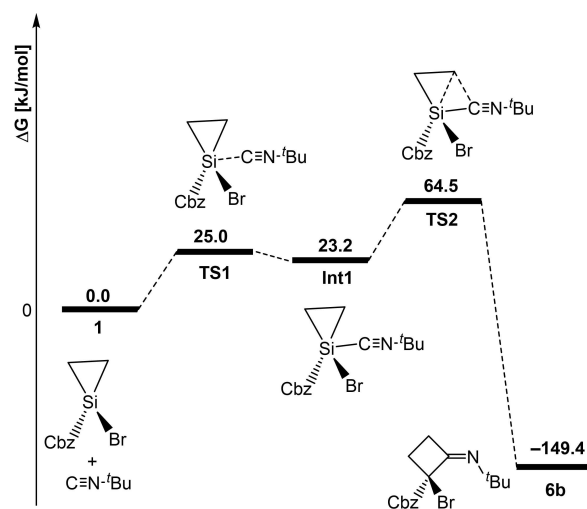
| heterocycle | RSE [kJ/mol] | $\Delta G_{Int1}$ [kJ/mol] | $\Delta G^{\#}_{TS2}$ [kJ/mol] | $\Delta_R G$ [kJ/mol] |
|---|---|---|---|---|
| [Si] (SiC₂) | −158.0 | 17.8 | 73.0 | −158.0 |
| [Si] (SiC₂) | −156.8 | 23.2 | 64.5 | −149.4 |
| [Si]·NH | −172.8 | 6.7 | 68.5 | −131.5 |
| [Si]·O | −165.7 | −7.4 | 45.3 | −77.5 |
| [Si]·P | −87.3 | 23.9 | 43.7 | −91.4 |
| [Si] (SiC₃) | −65.5 | 32.2 | 121.4 | −113.5 |
| [Si]·NH | −64.3 | 24.4 | 109.3 | −75.8 |
| [Si]·O | −75.6 | 15.5 | 120.7 | −18.1 |
| [Si]·SiH₂ | −65.9 | 37.9 | 65.0 | −100.7 |
| [Si]·PH | −56.7 | 31.5 | 89.2 | −72.2 |
| [Si]·S | −40.5 | 18.6 | 69.6 | −41.7 |
| [Si] (5-ring) | −0.4 | – | – | – |
| [Si] (6-ring) | 20.1 | – | – | – |
| [Si] (7-ring) | 5.4 | – | – | – |

**Scheme 6.** Ring expansion of the silicon heterocycle (**1**) with $^tBu$-NC (**b**) to give **6b**.

**Chemistry–A European Journal**

Research Article
doi.org/10.1002/chem.202302311

**Chemistry Europe**
European Chemical
Societies Publishing

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 $SiC_3$ 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 $SiC_2S$ heterocycle, the computational activation barrier amounts to 69.6 kJ/mol, just in the same range as for the silirene expansion.

We have attempted the synthesis of a $SiC_2S$ heterocycle starting from the bromosilylene via addition of 2-bromoethanethiol and thiirane, 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 silirane. To account for that, a silirane derived Weidenbruch's **H**, $^tBu_2SiC_2H_4$, 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 silirane but nonetheless higher than for our carbazole-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) Electronegative 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 [($^{dtbp}$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 silirane 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-thiasiletanes 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 $^{dtbp}$CbzSiBr (220 mg, 0.288 mmol) in toluene was degassed. Subsequently, the evacuated reaction vessel was filled with ethylene and the reaction mixture was stirred over night at room temperature. After removal of a colorless precipitate, the solvent was removed in vacuo and the residue was dissolved n-hexane. 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 yellowish solid was washed with n-hexane and dried in vacuo (16 mg, 0.020 mmol, 7%).

$^1$H NMR (400.3 MHz, $C_6D_6$): $\delta$ (ppm) = 0.41 (m, 2 H, $H_2CCH_2$), 0.67 (m, 2 H, $H_2CCH_2$), 1.34 (s, 36 H, Ar–$^tBu$), 1.36 (s, 18 H, Carb–$^tBu$), 7.54 (d, 4 H, $^4J_{HH}$ = 1.6 Hz, o-CH), 7.58 (t, 2 H, $^4J_{HH}$ = 1.7 Hz, p-CH), 7.62 (d, 2 H, $^4J_{HH}$ = 2.0 Hz, $C^{2,7}H$), 8.34 (d, 2 H, $^4J_{HH}$ = 2.0 Hz, $C^{4,5}H$). $^{13}$C{$^1$H} NMR (100.7 MHz, $C_6D_6$): $\delta$ (ppm) = 10.19 (s, $C_2H_4$), 31.71 (s, Ar–C($CH_3$)$_3$), 32.00 (s, Carb–C($CH_3$)$_3$), 34.82 (s, Carb–$C$($CH_3$)$_3$), 35.04 (s, Ar–$C$($CH_3$)$_3$), 115.67 (s, $C^{4,5}$), 122.80 (s, p-C), 125.62 (s, o-C), 127.40 (s, $C^{2,7}$), 128.69 (s, $C^{4a,4b}$), 131.52 (s, $C^{1,8}$), 140.16 (s, i-C), 143.92 (s, $C^{8a,9a}$), 145.35 (s, $C^{3,6}$), 150.74 (s, m-C). $^{15}$N NMR (40.6 MHz, $C_6D_6$): $\delta$ (ppm) = 107.9 (s). $^{29}$Si NMR (79.5 MHz, $C_6D_6$): $\delta$ (ppm) = −40.1 (s).

**Synthesis of 2**: 161 mg $^{dtbp}$CbzSiBr (0.211 mmol) were dissolved in 10 mL of n-hexane. Acetylene gas was introduced into this solution, which was produced by hydrolysis of $CaC_2$. 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 deposited. 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%).

$^1$H NMR (400.3 MHz, $C_6D_6$): $\delta$ (ppm) = 1.32 (s, 36 H, Ar–$^tBu$), 1.38 (s, 18 H, Carb–$^tBu$), 7.27 (s, 2 H, $^2J_{SiH}$ = 3.4 Hz, $^1J_{CH}$ = 190 Hz, $C_2H_2$), 7.57

**Chemistry–A European Journal**

Research Article
doi.org/10.1002/chem.202302311

**Chemistry Europe**
European Chemical
Societies Publishing

(t, 2 H, $^4J_{HH}=1.9$ Hz, p-CH), 7.68 (m, 6 H, o-CH/$C^{2,7}H$), 8.35 (d, 2 H, $^4J_{HH}=2.0$ Hz, $C^{4,5}H$). $^{13}$C{$^1$H} NMR (100.7 MHz, $C_6D_6$): δ (ppm) = 31.72 (s, Ar–C(CH$_3$)$_3$), 31.97 (s, Carb–C(CH$_3$)$_3$), 34.85 (s, Carb–C(CH$_3$)$_3$), 35.10 (s, Ar–C(CH$_3$)$_3$), 115.93 (s, $C^{4,5}$), 122.33 (s, p-C), 125.31 (s, o-C), 127.53 (s, $C^{2,7}$), 129.96 (s, $C^{4a,4b}$), 131.57 (s, $C^{1,8}$), 140.84 (s, i-C), 141.89 (s, $C^{8a,9a}$), 145.80 (s, $C^{3,6}$), 151.49 (s, m-C), 162.51 (s, $C_2H_2$). $^{15}$N NMR (40.6 MHz, $C_6D_6$): δ (ppm) = 118.6 (s). $^{29}$Si NMR (79.5 MHz, $C_6D_6$): δ (ppm) = −101.0 (s).

**Synthesis of 3**: Tert-butyl phosphaacetylene ($^t$BuCP) (180 mg, 1.8 mmol) was added to a solution of $^{dtbp}$CbzSiBr (534 mg, 0.700 mmol) in toluene. Subsequently, all volatile compounds were removed in vacuo and the colorless residue was dissolved hot n-hexane. 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 colorless solid was washed with n-hexane and dried in vacuo (208 mg, 0.324 mmol, 46%).

$^1$H NMR (400.3 MHz, $C_6D_6$): δ (ppm) = 0.80 (s, 9 H, $^t$BuCP), 1.35 (s, 18 H, Carb–$^t$Bu), 1.46 (s, 36 H, Ar–$^t$Bu), 7.68 (t, 2 H, $^4J_{HH}=1.8$ Hz, p-CH), 7.70 (br, 2 H, $C^{2,7}H$), 7.94 (br, 4 H, o-CH), 8.20 (d, 2 H, $^4J_{HH}=2.0$ Hz, $C^{4,5}H$). $^{13}$C{$^1$H} NMR (100.7 MHz, $C_6D_6$): δ (ppm) = 29.21 (s, (CH$_3$)$_3$–C–CP), 31.85 (s, Ar–C(CH$_3$)$_3$), 31.87 (s, Carb–C(CH$_3$)$_3$), 34.78 (s, Carb–C(CH$_3$)$_3$), 35.20 (s, Ar–C(CH$_3$)$_3$), 43.22 (s, (CH$_3$)$_3$–C–CP), 115.45 (s, $C^{4,5}$), 123.26 (s, p-C), 125.17 (s, o-C), 128.10 (s, $C^{2,7}$), 129.97 (s, $C^{4a,4b}$), 132.10 (s, $C^{1,8}$), 140.81 (s, i-C), 143.99 (s, $C^{8a,9a}$), 146.01 (s, $C^{3,6}$), 151.23 (s, m-C), 265.92 (d, $^1J_{CP}=102$ Hz, SiC$^t$BuP). $^{15}$N NMR (40.6 MHz, $C_6D_6$): δ (ppm) = n. obs. $^{29}$Si NMR (79.5 MHz, $C_6D_6$): δ (ppm) = −59.3 (d, $^2J_{SiP}=54$ Hz). $^{31}$P{$^1$H} (162.0 MHz, $C_6D_6$): δ (ppm) = 337.5 (s).

**Synthesis of 4**: The compound (10) (395 mg, 0.409 mmol) was dissolved in 8 mL toluene and added slowly to a suspension of [($^{Mes}$NacNac)Mg]$_2$ (308 mg, 429 mmol) in 7 mL toluene. Subsequently, the reaction mixture was stirred for one hour at room temperature. Afterwards, all volatiles were removed under reduced pressure and 6 mL of n-hexane were added. After filtration, 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 (35.0 mg, 0.043 mmol, 11%).

$^1$H NMR (400.3 MHz, $C_6D_6$): δ (ppm) = 1.04 (m, 2 H, (SiCH$_2$CH$_2$CH$_2$)), 1.22 (m, 2 H, (SiCH$_2$CH$_2$CH$_2$)), 1.33 (m, 2 H, (SiCH$_2$CH$_2$CH$_2$)), 1.39 (s, 36 H, Ar–$^t$Bu), 1.40 (s, 18 H, Carb–$^t$Bu), 7.60 (t, 2 H, $^4J_{HH}=1.8$ Hz, p-CH), 7.62–7.64 (m, 6 H, $C^{2,7}H$ and o-CH), 8.37 (d, 2 H, $^4J_{HH}=2.0$ Hz, $C^{4,5}H$). $^{13}$C{$^1$H} NMR (100.7 MHz, $C_6D_6$): δ (ppm) = 14.39 (s, (SiCH$_2$CH$_2$CH$_2$)), 28.10 (s, (SiCH$_2$CH$_2$CH$_2$)), 31.75 (s, Ar–C(CH$_3$)$_3$), 31.99 (s, Carb–C(CH$_3$)$_3$), 34.80 (s, Carb–C(CH$_3$)$_3$), 35.07 (s, Ar–C(CH$_3$)$_3$), 115.69 (s, $C^{4,5}$), 122.80 (s, p-C), 125.37 (s, o-C), 127.91 (s, $C^{2,7}$), 129.80 (s, $C^{4a,4b}$), 132.03 (s, $C^{1,8}$), 140.49 (s, i-C), 142.54 (s, $C^{8a,9a}$), 145.47 (s, $C^{3,6}$), 150.70 (s, m-C). $^{15}$N NMR (40.6 MHz, $C_6D_6$): δ (ppm) = n. obs. $^{29}$Si NMR (79.5 MHz, $C_6D_6$): δ (ppm) = 3.2 (s).

**Synthesis of 5**: 2,3-Dimethyl-1,3-butadiene (dmb) (31 mg, 0.377 mmol) was added to a solution of $^{dtbp}$CbzSiBr (199 mg, 0.261 mmol) in toluene. Subsequently, 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 colorless solid was washed with n-hexane and dried in vacuo (55 mg, 0.065 mmol, 25%).

$^1$H NMR (400.3 MHz, $C_6D_6$): δ (ppm) = 1.25 (s, 6 H, dmb-CH$_3$), 1.39 (s, 18 H, Carb–$^t$Bu), 1.40 (d, 2 H, $^2J_{HH}=18$ Hz, dmb-CH$_2$), 1.44 (s, 36 H, Ar–$^t$Bu), 1.77 (d, 2 H, $^2J_{HH}=18$ Hz, dmb-CH$_2$), 7.63 (t, 2 H, $^4J_{HH}=1.8$ Hz, p-CH), 7.66 (d, 2 H, $^4J_{HH}=2.1$ Hz, $C^{2,7}H$), 7.77 (d, 4 H, $^4J_{HH}=1.7$ Hz, o-CH), 8.33 (d, 2 H, $^4J_{HH}=2.1$ Hz, $C^{4,5}H$). $^{13}$C{$^1$H} NMR (100.7 MHz, $C_6D_6$): δ (ppm) = 18.39 (s, dmb-CH$_3$), 31.79 (s, Ar–C(CH$_3$)$_3$), 31.98 (s, Carb–C(CH$_3$)$_3$), 33.12 (s, dmb-CH$_2$), 34.74 (s, Carb–C(CH$_3$)$_3$), 35.14 (s, Ar–C(CH$_3$)$_3$), 115.55 (s, $C^{4,5}$), 122.66 (s, p-C), 125.75 (s, o-C), 128.39 (s, dmb-C–CH$_3$), 128.63 (s, $C^{2,7}$), 130.10 (s, $C^{4a,4b}$), 132.05 (s, $C^{1,8}$), 140.91 (s, i-C), 143.95 (s, $C^{8a,9a}$), 145.57 (s, $C^{3,6}$), 150.62 (s, m-C). $^{15}$N NMR (40.6 MHz, $C_6D_6$): δ (ppm) = 111.8 (s). $^{29}$Si NMR (79.5 MHz, $C_6D_6$): 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-dimethylphenylisonitrile (DmpNC) (10.6 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 deposited. The supernatant 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%).

$^1$H NMR (400.3 MHz, $C_6D_6$): 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). $^{13}$C{$^1$H} NMR (100.7 MHz, $C_6D_6$): δ (ppm) = 21.09 (s, C1H$_2$), 34.34 (s, C2H$_2$), 187.06 (s, C3 N).

**Synthesis of 7a**: The silirane **1** (230 mg, 0.291 mmol) and 2,6-dimethylphenylisonitrile (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 deposited. The supernatant was removed with a syringe, the colorless solid was washed with n-hexane and dried in vacuo (21.5 mg, 0.023 mmol, 8%).

$^1$H NMR (400.3 MHz, $C_6D_6$): δ (ppm) = 1.38 (br, 18 H, Carb–$^t$Bu), 1.40 (br, 36 H, Ar–$^t$Bu), 1.52 (dd, 1 H, $J_{HH}=1.8$ Hz and 14.3 Hz, (SiCHHCHC)), 1.62 (dd, 1 H, $J_{HH}=1.9$ Hz and 14.3 Hz, (SiCHHCHC)), 1.89 (br, 6 H, Dmp-(CH$_3$)$_2$), 4.64 (t, 1 H, $J_{HH}=1.5$ Hz, $^3J_{SiH}=40$ Hz, (SiCH$_2$CHC)), 5.14 (s, 1 H, DmpNH), 6.81-6.85 (m, 3 H, Dmp-CH), 7.62 (br, 1 H, $C^{2/7}H$), 7.66 (t, 2 H, $^4J_{HH}=1.6$ Hz, p-CH), 7.66 (br, 2 H, o-CH), 7.68 (br, 1 H, $C^{2/7}H$), 8.00 (br, 2 H, o-CH), 8.29 (d, 2 H, $^4J_{HH}=2.0$ Hz, $C^{4,5}H$). $^{13}$C{$^1$H} NMR (100.7 MHz, $C_6D_6$): δ (ppm) = 17.97 (s, DMP-CH$_3$), 26.49 (s, SiCH$_2$CHC), 31.68 (br, Ar–C(CH$_3$)$_3$), 31.77 (br, Ar–C(CH$_3$)$_3$), 31.96 (s, Carb–C(CH$_3$)$_3$), 34.76 (s, Carb–C(CH$_3$)$_3$), 35.12 (s, Ar–C(CH$_3$)$_3$), 106.95 (s, SiCH$_2$CHC), 115.64 (br, $C^{4/5}$), 115.92 (br, $C^{4/5}$), 123.11 (br, p-C), 123.67 (br, p-C), 125.48 (br, o-C), 126.08 (s, Dmp-p-C), 128.25 (s, $C^{2/7}$), 128.35 (s, $C^{2/7}$), 128.69 (br, Dmp-m-C), 130.52 (s, $C^{4a/4b}$), 130.80 (s, $C^{4a/4b}$), 132.25 (br, $C^{1,8}$), 135.22 (br, Dmp-o-C), 138.43 (s, Dmp-i-C), 140.10 (br, i-C), 140.40 (br, i-C), 143.27 (br, $C^{8a/9a}$), 143.89 (br, $C^{8a/9a}$), 145.50 (br, $C^{3/6}$), 145.80 (br, $C^{3/6}$), 148.51 (s, SiCH$_2$CHC), 150.77 (br, m-C), 151.59 (br, m-C). $^{15}$N NMR (40.6 MHz, $C_6D_6$): δ (ppm) = 79.5 (s, DmpNH). $^{29}$Si NMR (79.5 MHz, $C_6D_6$): 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-butylisonitrile ($^t$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 deposited. The supernatant was removed with a syringe, the off-white solid was washed with n-hexane and dried in vacuo (120 mg, 0.137 mmol, 24%).

$^1$H NMR (400.3 MHz, $C_6D_6$): δ (ppm) = 0.88 (s, 9H, $^t$BuNC), 1.39 (s, 9 H, Carb–$^t$Bu), 1.43 (s, 18 H, Ar–$^t$Bu), 1.45 (s, 18 H, Ar–$^t$Bu), 1.51 (dd, 1 H, $^2J_{HH}=1.7$ Hz, 14 Hz, (SiCHHCHC)), 1.85 (dd, 1 H, $^2J_{HH}=2.0$ Hz, 14 Hz

(SiCH*H*CHC)), 3.65 (s, 1 H, N*H*), 4.98 (m, 1 H, $^3J_{SiH}=43$ Hz, (SiCH$_2$C*H*C)), 7.58 (d, 1 H, $^4J_{HH}=1.8$ Hz, $C^{2/7}H$), 7.62 (t, 1 H, $^4J_{HH}=1.7$ Hz, *p*-C*H*), 7.66 (d, 1 H, $^4J_{HH}=1.8$ Hz, $C^{2/7}H$), 7.68 (t, 1 H, $^4J_{HH}=2.0$ Hz, *p*-C*H*), 7.77 (br, $\nu_{1/2}=6.9$ Hz, 2 H, *o*-C*H*), 7.87 (d, 2 H, $^4J_{HH}=1.4$ Hz, *o*-C*H*), 8.24 (d, 1 H, $^4J_{HH}=1.8$ Hz, $C^{4/5}H$), 8.27 (d, 1 H, $^4J_{HH}=1.8$ Hz, $C^{4,5}H$). **$^{13}$C{$^1$H} NMR** (100.7 MHz, C$_6$D$_6$): $\delta$ (ppm) = 28.47 (s, SiCH$_2$CHC), 28.64 (s, CN–C(CH$_3$)$_3$), 31.84 (s, Ar–C(CH$_3$)$_3$), 31.89 (s, Ar–C(CH$_3$)$_3$), 32.01 (s, Carb–C(CH$_3$)$_3$), 34.77 (s, Carb–C(CH$_3$)$_3$), 35.10 (s, Ar–C(CH$_3$)$_3$), 35.25 (s, Ar–C(CH$_3$)$_3$), 51.52 (s, N–C(CH$_3$)$_3$), 105.69 (s, SiCH$_2$CHC), 115.68 (s, $C^{4,5}$), 122.67 (s, *p*-C), 123.47 (s, *p*-C), 124.87 (s, *o*-C), 127.60 (s, $C^{2/7}$), 128.00 (s, $C^{2/7}$), 129.93 (s, $C^{4a/4b}$), 131.14 (s, $C^{4a/4b}$), 131.39 (s, $C^{1/8}$), 132.26 (s, $C^{1/8}$), 140.40 (s, *i*-C), 140.50 (s, *i*-C), 143.53 (s, $C^{8a/9a}$), 144.08 (s, $C^{8a/9a}$), 145.64 (s, $C^{3/6}$), 145.79 (s, $C^{3/6}$), 149.58 (SiCH$_2$CHC), 150.80 (s, *m*-C), 151.39 (s, *m*-C). **$^{15}$N NMR** (40.6 MHz, C$_6$D$_6$): $\delta$ (ppm) = 93.7 (s, N*H*). **$^{29}$Si NMR** (79.5 MHz, C$_6$D$_6$): $\delta$ (ppm) = –17.6 (s).

**Synthesis of 8b:** The silirane **1** (600 mg, 0.758 mmol) was dissolved in 10 mL toluene. After addition of a solution of *tert*-butylisonitrile (ᵗBuNC) (95.6 mg, 1.150 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 The supernatant was removed with a syringe, the off-white solid was washed with *n*-hexane and dried in vacuo. Then, the residue was dissolved in 5 mL benzene and 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 off-white solid was washed with *n*-hexane and dried in vacuo (120 mg, 0.137 mmol, 24%).

**$^1$H NMR** (400.3 MHz, C$_6$D$_6$): $\delta$ (ppm) = 0.78 (s, 9H, ᵗBuNC), 1.32 (ddd, 1 H, $J_{HH}=1.7$ Hz, 3.8 Hz, 19 Hz, (SiC*H*HCHCHN)), 1.37 (s, 18 H, Carb–ᵗBu), 1.38 (s, 18 H, Ar–ᵗBu), 1.43 (s, 18 H, Ar–ᵗBu) 1.75 (m, 1 H, (SiCH*H*CHCHN)), 4.34 (m, 1 H, (SiCH$_2$C*H*CHN)), 5.78 (m, 1 H, (SiCH$_2$CHC*H*N)), 7.51 (t, 1 H, $^4J_{HH}=1.8$ Hz, *p*-C*H*), 7.52 (d, 1 H, $^4J_{HH}=2.0$ Hz, $C^{2/7}H$), 7.60 (t, 1 H, $^4J_{HH}=1.8$ Hz, *p*-C*H*), 7.64 (d, 2 H, $^4J_{HH}=1.4$ Hz, *o*-C*H*), 7.74 (d, 1 H, $^4J_{HH}=2.0$ Hz, $C^{2/7}H$), 7.89 (br, $\nu_{1/2}=2.2$ Hz, 2 H, *o*-C*H*), 8.22 (d, 1 H, $^4J_{HH}=2.0$ Hz, $C^{4/5}H$), 8.24 (d, 1 H, $^4J_{HH}=2.0$ Hz, $C^{4/5}H$). **$^{13}$C{$^1$H} NMR** (100.7 MHz, C$_6$D$_6$): $\delta$ (ppm) = 21.01 (s, SiCH$_2$CHCHN), 28.93 (s, N–C(CH$_3$)$_3$), 31.86 (s, Ar–C(CH$_3$)$_3$), 31.88 (s, Carb–C(CH$_3$)$_3$), 32.04 (s, Ar–C(CH$_3$)$_3$), 34.70 (s, Carb–C(CH$_3$)$_3$), 34.74 (s, Carb–C(CH$_3$)$_3$), 35.07 (s, Ar–C(CH$_3$)$_3$), 35.17 (s, Ar–C(CH$_3$)$_3$), 52.97 (s, N–C(CH$_3$)$_3$), 99.79 (s, SiCH$_2$CHCHN), 114.75 (s, $C^{4/5}$), 115.38 (s, $C^{4/5}$), 121.45 (s, *p*-C), 122.49 (s, *p*-C), 124.64 (s, *o*-C), 125.34 (s, *o*-C), 128.82 (s, $C^{2/7}$), 129.11 (s, $C^{2/7}$), 131.40 (s, $C^{4a/4b}$), 131.77 (s, $C^{4a/4b}$), 133.45 (s, $C^{1/8}$), 134.21 (s, $C^{1/8}$), **137.30** (s, SiCH$_2$CHCHN), 141.86 (s, *i*-C), 143.67 (s, $C^{8a/9a}$), 143.73 (s, $C^{8a/9a}$), 144.24 (s, *i*-C), 146.26 (s, $C^{3/6}$), 146.29 (s, $C^{3/6}$), 150.34 (s, *m*-C), 150.69 (s, *m*-C). **$^{15}$N NMR** (40.6 MHz, C$_6$D$_6$): $\delta$ (ppm) = 94.8 (s, ᵗBuN). **$^{29}$Si NMR** (79.5 MHz, C$_6$D$_6$): $\delta$ (ppm) = –1.0 (s).

**Synthesis of 9a:** The silirene **2** (400 mg, 0.507 mmol) was dissolved in 15 mL toluene. After addition of a solution of *tert*-butylisonitrile (ᵗBuNC) (49.6 mg, 0.597 mmol) in benzene, the reaction mixture was stirred over night at 35 °C in the oil bath. Afterwards, 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 off-white solid was washed with *n*-hexane and dried in vacuo (228 mg, 0.261 mmol, 51%). **$^1$H NMR** (400.3 MHz, C$_6$D$_6$): $\delta$ (ppm) = 0.92 (s, 9H, ᵗBuNC), 1.37 (s, 18 H, Ar–ᵗBu), 1.40 (br, $\nu_{1/2}=4.4$ Hz, 18 H, Carb–ᵗBu), 1.44 (s, 18 H, Ar–ᵗBu), 7.01 (d, 1 H, $^3J_{HH}=7.1$ Hz, (SiC(ᵗBuN)C*H*CH)), 7.13 (d, 1 H, $^3J_{HH}=7.1$ Hz, (SiC(ᵗBuN)CHC*H*)), 7.47 (t, 1 H, $^4J_{HH}=1.8$ Hz, *p*-C*H*), 7.53 (d, 1 H, $^4J_{HH}=2.0$ Hz, $C^{2/7}H$), 7.57 (d, 2 H, $^4J_{HH}=1.8$ Hz, *o*-C*H*), 7.64 (t, 1 H, $^4J_{HH}=1.8$ Hz, *p*-C*H*), 7.76 (d, 1 H, $^4J_{HH}=2.0$ Hz, $C^{2/7}H$), 7.94 (d, 2 H, $^4J_{HH}=1.8$ Hz, *o*-C*H*), 8.23 (d, 1 H, $^4J_{HH}=2.0$ Hz, $C^{4/5}H$), 8.24 (d, 1 H, $^4J_{HH}=2.0$ Hz, $C^{4/5}H$). **$^{13}$C{$^1$H} NMR** (100.7 MHz, C$_6$D$_6$): $\delta$ (ppm) = 28.76

(s, CN–C(CH$_3$)$_3$), 31.87 (s, Ar–C(CH$_3$)$_3$), 32.03 (s, Carb–C(CH$_3$)$_3$), 32.08 (s, Ar–C(CH$_3$)$_3$), 34.76 (s, Carb–C(CH$_3$)$_3$), 34.80 (s, Carb–C(CH$_3$)$_3$), 35.12 (s, Ar–C(CH$_3$)$_3$), 35.23 (s, Ar–C(CH$_3$)$_3$), 59.05 (s, CN–C(CH$_3$)$_3$), 115.17 (s, $C^{4/5}$), 115.73 (s, $C^{4/5}$), 121.64 (s, *p*-C), 122.70 (s, *p*-C), 125.21 (s, *o*-C), 125.70 (s, *o*-C), 128.85 (s, $C^{2/7}$), 129.06 (s, $C^{2/7}$), 130.92 (s, $C^{4a/4b}$), 131.53 (s, $C^{4a/4b}$), 132.08 (s, $C^{1/8}$), 133.82 (s, $C^{1/8}$), 140.56 (s, *i*-C), 143.08 (s, $C^{8a/9a}$), 143.12 (s, *i*-C), 143.37 (s, $C^{8a/9a}$), 146.62 (s, $C^{3/6}$), 146.85 (s, $C^{3/6}$), 151.06 (s, *m*-C), 156.84 (s, (SiC(ᵗBuN)CHCH)), 161.46 (s, (SiC(ᵗBuN)CHCH)), 176.93 (s, SiC(ᵗBuN)CHCH). **$^{15}$N NMR** (40.6 MHz, C$_6$D$_6$): $\delta$ (ppm) = 109.3 (s, ᵈᵗᵇᵖCbz-*N*), 375.4 (s, ᵗBuN). **$^{29}$Si NMR** (79.5 MHz, C$_6$D$_6$): $\delta$ (ppm) = –10.3 (s).

**Synthesis of 10a:** The phosphasilirene (**3**) (150 mg, 0.174 mmol) and 2,6-dimethylphenylisonitrile (DmpNC) (23.0 mg, 0.175 mmol) were dissolved in 6 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%). **$^1$H NMR** (400.3 MHz, C$_6$D$_6$): $\delta$ (ppm) = 0.85 (s, 9 H, ᵗBuCP), 1.24 (s, 18 H, Ar–ᵗBu), 1.32 (s, 9 H, Carb–ᵗBu), 1.34 (s, 9 H, Carb–ᵗBu), 1.40 (s, 18 H, Ar–ᵗBu), 2.15 (br, 6 H, DmpNC–CH$_3$), 6.95 (br, 3 H, *m*-/*p*-C*H* of DmpNC), 7.41 (d, 1 H, $^4J_{HH}=1.8$ Hz, $C^{2/7}H$), 7.45 (t, 1 H, $^4J_{HH}=1.7$ Hz, *p*-C*H*), 7.50 (d, 1 H, $^4J_{HH}=1.8$ Hz, $C^{2/7}H$), 7.51 (br, 2 H, *o*-C*H*), 7.59 (t, 1 H, $^4J_{HH}=1.8$ Hz, *p*-C*H*), 7.79 (br, 2 H, *o*-C*H*), 8.13 (m, 2 H, $C^{4,5}H$).

**$^{13}$C{$^1$H} NMR** (100.7 MHz, C$_6$D$_6$): $\delta$ (ppm) = 19.71 (s, DmpNC–CH$_3$), 31.78 (s, Ar–C(CH$_3$)$_3$), 31.82 (s, Carb–C(CH$_3$)$_3$), 31.87 (s, Ar–C(CH$_3$)$_3$), 32.97 (d, $^3J_{CP}=8$ Hz, PC-(CH$_3$)$_3$), 34.72 (s, Carb–C(CH$_3$)$_3$), 34.73 (s, Carb–C(CH$_3$)$_3$), 35.06 (s, Ar–C(CH$_3$)$_3$), 35.11 (s, Ar–C(CH$_3$)$_3$), 41.02 (d, $^2J_{CP}=6$ Hz, P-C-(CH$_3$)$_3$), 116.03 (s, $C^{4/5}$), 116.51 (s, $C^{4/5}$), 122.55 (s, *p*-C), 123.65 (s, *p*-C), 124.81 (s, DmpNC–CH), 124.96 (s, *o*-C), 126.42 (br, *o*-C), 128.59 (s, $C^{2/7}$), 128.78 (s, DmpNC–CH), 129.36 (s, $C^{2/7}$), 131.84 (s, $C^{4a,4b}$), 132.14 (s, $C^{1/8}$), 134.96 (s, DmpNC–C–CH$_3$), 142.22 (s, *i*-C), 142.36 (s, *i*-C), 144.29 (s, $C^{8a/9a}$), 144.81 (s, $C^{8a/9a}$), 146.30 (s, $C^{3/6}$), 146.54 (s, $C^{3/6}$), 150.60 (s, *m*-C), 152.07 (d, $^3J_{CP}=10$ Hz, DmpNC-*i*-C), **196.79** (d, $^1J_{CP}=61$ Hz, SiᵗBuCP-C), **238.28** (d, $^1J_{CP}=48$ Hz, SiᵗBuCPC). **$^{15}$N NMR** (40.6 MHz, C$_6$D$_6$): $\delta$ (ppm) = n. obs. **$^{29}$Si NMR** (79.5 MHz, C$_6$D$_6$): $\delta$ (ppm) = -9.1 (d, $^2J_{SiP}=17$ Hz). **$^{31}$P{$^1$H} NMR** (162.0 MHz, C$_6$D$_6$): $\delta$ (ppm) = 378.9 (br, $\nu_{1/2}=118$ Hz).

**Synthesis of 10b:** The phosphasilirene (**3**) (475 mg, 0.550 mmol) was dissolved in 15 mL toluene. After addition of a solution of *tert*-butylisonitrile (ᵗBuNC) (55.9 mg, 0.673 mmol) in benzene, the reaction mixture was stirred over night at room temperature. Afterwards, all volatiles were removed under reduced pressure and the orange 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 deposited. The supernatant was removed with a syringe, the orange solid was washed with *n*-hexane and dried in vacuo (153 mg, 0.162 mmol, 29%). **$^1$H NMR** (400.3 MHz, C$_6$D$_6$): $\delta$ (ppm) = 0.81 (s, 9 H, ᵗBuN), 0.87 (s, 9 H, ᵗBuCP), 0.89 (s, 9 H, ᵗBuCP), 1.26 (s, 9 H, ᵗBu), 1.28 (s, 9 H, ᵗBu), 1.28 (s, 9 H, ᵗBuN), 1.29 (s, 9 H, ᵗBu), 1.29 (s, 9 H, ᵗBu), 1.29 (s, 9 H, ᵗBu), 1.38 (s, 9 H, ᵗBu), 1.40 (s, 18 H, ᵗBu), 1.41 (s, 18 H, ᵗBu), 1.47 (s, 9 H, ᵗBu), 1.55 (s, 9 H, ᵗBu), 7.36 (m, 1 H, $C^{2/7}H$), 7.37 (m, 1 H, $C^{2/7}H$), 7.41 (d, 1 H, $^4J_{HH}=1.9$ Hz, $C^{2/7}H$), 7.44 (m, 1 H, C*H*), 7.46 (d, 1 H, C*H*), 7.49 (d, 1 H, $^4J_{HH}=2.1$ Hz, $C^{2/7}H$), 7.54 (m, 1 H, C*H*), 7.57 (m, 1 H, *o*-C*H*), 7.57 (m, 1 H, C*H*), 7.64 (d, 2 H, $^4J_{HH}=1.7$ Hz, C*H*), 7.66 (t, 1 H, $^4J_{HH}=1.6$ Hz, *p*-C*H*), 7.78 (br, $\nu_{1/2}=8$ Hz, 1 H, C*H*), 8.00 (d, 1 H, $^4J_{HH}=2.0$ Hz, $C^{4,5}H$), 8.14 (d, 1 H, $^4J_{HH}=2.0$ Hz, $C^{4,5}H$), 8.16 (t, 1 H, $^4J_{HH}=1.6$ Hz, *p*-C*H*), 8.20 (d, 1 H, $^4J_{HH}=2.1$ Hz, $C^{4,5}H$), 8.24 (d, 1 H, $^4J_{HH}=2.0$ Hz, $C^{4,5}H$). **$^{13}$C{$^1$H} NMR** (100.7 MHz, C$_6$D$_6$): $\delta$ (ppm) = 28.67 (s, N–C–(CH$_3$)$_3$), 28.67 (s, N–C–(CH$_3$)$_3$), 30.66 (d, $^3J_{CP}=4$ Hz, P–C–(CH$_3$)$_3$)), 31.74 (s, CH$_3$), 31.80 (s, CH$_3$), 31.84 (s, CH$_3$), 31.94 (s,

$CH_3$), 31.98 (s, $CH_3$), 32.05 (s, $CH_3$), 32.14 (s, $CH_3$), 32.81 (d, $^3J_{CP} = 9$ Hz, P–C–($CH_3$)$_3$), 34.66 (s, $C(CH_3)_3$), 34.75 (s, $C(CH_3)_3$), 35.05 (s, $C(CH_3)_3$), 35.12 (s, $C(CH_3)_3$), 35.18 (s, $C(CH_3)_3$), 35.30 (s, $C(CH_3)_3$), 40.42 (d, $^2J_{CP} = 7$ Hz, PC–C–($CH_3$)$_3$), 41.04 (d, $^2J_{CP} = 6$ Hz, PC–C–($CH_3$)$_3$), 61.53 (d, $^2J_{CP} = 17$ Hz, PCN–C–($CH_3$)$_3$), 61.96 (d, $^2J_{CP} = 3$ Hz, PCN–C–($CH_3$)$_3$), 115.27 (s, $C^{4/5}$), 115.46 (s, $C^{4/5}$), 115.88 (s, $C^{4/5}$), 122.38 (s, $CH$), 122.46 (s, $CH$), 122.87 (s, $CH$), 124.76 (s, $CH$), 125.67 (s, $CH$), 126.22(br, $CH$), 126.52 (s, $CH$), 128.75 (s, $CH$), 129.04 (s, $CH$), 129.56 (s, $CH$), 129.83 (s, $CH$), 131.14 (s), 132.07 (s), 132.34 (s), 132.60 (s), 132.74 (s), 133.26 (s), 134.49 (s), 135.70 (s), 142.00 (s), 142.37 (s), 142.52 (s), 142.61 (s), 144.42 (s), 144.62 (s), 144.82 (s), 145.00 (s), 146.40 (s), 146.52 (s), 146.72 (s), 146.87 (s), 149.73 (s), 150.44 (s), 150.48 (s), 151.20 (s), 151.39 (s), 153.04 (s), 184.02 (d, $^1J_{CP} = 67$ Hz, P–C–N$^t$Bu), 188.05 (d, $^1J_{CP} = 28$ Hz, P–C–N$^t$Bu), 232.75 (d, $^1J_{CP} = 53$ Hz, P–C–$^t$Bu), 242.76 (d, $^1J_{CP} = 59$ Hz, P–C–$^t$Bu). $^{15}$N NMR (40.6 MHz, $C_6D_6$): $\delta$ (ppm) = 407.1 ($^t$BuN), 414.6 ($^t$BuN). $^{29}$Si NMR (79.5 MHz, $C_6D_6$): $\delta$ (ppm) = -18.0 (d, $^2J_{SiP} = 11$ Hz), −5.7 (d, $^2J_{SiP} = 11$ Hz). $^{31}$P{$^1$H} NMR (162.0 MHz, $C_6D_6$): $\delta$ (ppm) = 374.8 (br, $v_{1/2=}26$ Hz), 392.3 (br, $v_{1/2=}57$ Hz).

## Supporting Information

Deposition Numbers 2264949 (for **1**), 2264948 (for **2**), 2264951 (for **3**), 2264939 (for [($^{dtbP}$Cbz)SiBr$_2$C$_3$H$_6$Br]), 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.[58–77]

## 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.

**Keywords:** expansion · heterocycles · isonitrile · ring strain · silylene

[1] M. Ishikawa, A. Naka, J. Ohshita, *Asian J. Org. Chem.* **2015**, *4*, 1192–1209.
[2] J. Huang, F. Liu, X. Wu, J. Q. Chen, J. Wu, *Org. Chem. Front.* **2022**, *9*, 2840–2855.
[3] J. Liu, Q. Zhang, P. Li, Z. Qu, S. Sun, Y. Ma, D. Su, Y. Zong, J. Zhang, *Eur. J. Inorg. Chem.* **2014**, 3435–3440.
[4] S. Yoshioka, T. Takehara, T. Matsuzaki, T. Suzuki, H. Tsujino, T. Uno, Y. Tsutsumi, K. Murai, H. Fujioka, M. Arisawa, *Chem. Commun.* **2019**, *55*, 14070–14073.
[5] S. J. Barraza, S. E. Denmark, *J. Am. Chem. Soc.* **2018**, *140*, 6668–6684.
[6] J. C. Sanchez, A. G. Dipasquale, A. A. Mrse, W. C. Trogler, *Anal. Bioanal. Chem.* **2009**, *395*, 387–392.
[7] M. Nobis, S. Inoue, B. Rieger, *Chem. Commun.* **2022**, *58*, 11159–11162.
[8] G. C. Nandi, *Eur. J. Org. Chem.* **2021**, 587–606.
[9] L. H. Sommer, G. A. Baum, *J. Am. Chem. Soc.* **1954**, *76*, 5002–5002.
[10] R. L. Lambert, D. Seyferth, *J. Am. Chem. Soc.* **1972**, *94*, 9246–9248.
[11] D. Seyferth, D. C. Annarelli, *J. Am. Chem. Soc.* **1975**, *97*, 2273–2275.
[12] D. Seyferth, D. C. Annarelli, D. P. Duncan, *Organometallics* **1982**, *1*, 1288–1294.
[13] D. Seyferth, D. C. Annarelli, S. C. Vick, *J. Am. Chem. Soc.* **1976**, *98*, 6382–6384.
[14] R. T. Conlin, P. P. Gaspar, *J. Am. Chem. Soc.* **1976**, *98*, 3715–3716.
[15] K. Hirotsu, T. Higuchi, M. Ishikawa, H. Sugisawa, M. Kumada, *J. Chem. Soc. Chem. Commun.* **1982**, 726.
[16] W. Ando, M. Fujita, H. Yoshida, A. Sekiguchi, *J. Am. Chem. Soc.* **1988**, *110*, 3310–3311.
[17] S. Zhang, P. E. Wagenseller, R. T. Conlin, *J. Am. Chem. Soc.* **1991**, *113*, 4278–4281.
[18] H. Suzuki, N. Tokitoh, R. Okazaki, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2471–2481.
[19] S. Tsutsui, K. Sakamoto, M. Kira, *J. Am. Chem. Soc.* **1998**, *120*, 9955–9956.
[20] P. Boudjouk, U. Samaraweera, R. Sooriyakumaran, J. Chrusciel, K. R. Anderson, *Angew. Chem. Int. Ed.* **1988**, *27*, 1355–1356.
[21] A. Schäfer, M. Weidenbruch, W. Saak, S. Pohl, *Angew. Chem. Int. Ed.* **1987**, *26*, 776–777.
[22] D. Wendel, A. Porzelt, F. A. D. Herz, D. Sarkar, C. Jandl, S. Inoue, B. Rieger, *J. Am. Chem. Soc.* **2017**, *139*, 8134–8137.
[23] D. Reiter, R. Holzner, A. Porzelt, P. J. Altmann, P. Frisch, S. Inoue, *J. Am. Chem. Soc.* **2019**, *141*, 13536–13546.
[24] H. Zhu, F. Hanusch, S. Inoue, *Isr. J. Chem.* **2023**, *63*, e202300012.
[25] F. Lips, A. Mansikkamäki, J. C. Fettinger, H. M. Tuononen, P. P. Power, *Organometallics* **2014**, *33*, 6253–6258.
[26] S. Ishida, T. Iwamoto, M. Kira, *Heteroat. Chem.* **2011**, *22*, 432–437.
[27] M. Kira, S. Ishida, T. Iwamoto, C. Kabuto, *J. Am. Chem. Soc.* **2002**, *124*, 3830–3831.
[28] T. Fukuoka, K. Uchida, Y. M. Sung, J. Y. Shin, S. Ishida, J. M. Lim, S. Hiroto, K. Furukawa, D. Kim, T. Iwamoto, H. Shinokubo, *Angew. Chem. Int. Ed.* **2014**, *53*, 1506–1509.
[29] T. Kosai, S. Ishida, T. Iwamoto, *Chem. Commun.* **2015**, *51*, 10707–10709.
[30] H. Suzuki, N. Tokitoh, R. Okazaki, *J. Am. Chem. Soc.* **1994**, *116*, 11572–11573.
[31] S. S. Sen, H. W. Roesky, D. Stern, J. Henn, D. Stalke, *J. Am. Chem. Soc.* **2010**, *132*, 1123–1126.
[32] S. Yao, C. Van Wüllen, X. Y. Sun, M. Driess, *Angew. Chem. Int. Ed.* **2008**, *47*, 3250–3253.
[33] S. Yao, Y. Xiong, C. van Wüllen, M. Driess, *Organometallics* **2009**, *28*, 1610–1612.
[34] R. Rodriguez, D. Gau, T. Kato, N. Saffon-Merceron, A. De Cózar, F. P. Cossío, A. Baceiredo, *Angew. Chem. Int. Ed.* **2011**, *50*, 10414–10416.
[35] R. Nougué, S. Takahashi, A. Baceiredo, N. Saffon-Merceron, V. Branchadell, T. Kato, *Angew. Chem. Int. Ed.* **2023**, *62*, DOI 10.1002/anie.202215394.
[36] B. Biletskyi, P. Colonna, K. Masson, J. L. Parrain, L. Commeiras, G. Chouraqui, *Chem. Soc. Rev.* **2021**, *50*, 7513–7538.
[37] O. A. Ivanova, I. V. Trushkov, *Chem. Rec.* **2019**, *19*, 2189–2208.

**Chemistry–A European Journal**

Research Article
doi.org/10.1002/chem.202302311

**Chemistry Europe**
European Chemical
Societies Publishing

[38] J. S. Chickos, *J. Org. Chem.* **1973**, *38*, 3642–3646.

[39] G. E. Niznik, H. M. Walborsky, *J. Org. Chem.* **1974**, *39*, 608–611.

[40] Q. C. Mu, J. Chen, C. G. Xia, L. W. Xu, *Coord. Chem. Rev.* **2018**, *374*, 93–113.

[41] X. Tang, Y. Zhang, Y. Tang, Y. Li, J. Zhou, D. Wang, L. Gao, Z. Su, Z. Song, *ACS Catal.* **2022**, *12*, 5185–5196.

[42] Y. Qin, J. L. Han, C. W. Ju, D. Zhao, *Angew. Chem. Int. Ed.* **2020**, *59*, 8481–8485.

[43] X.-C. Wang, B. Li, C.-W. Ju, D. Zhao, *Nat. Commun.* **2022**, *13*, 3392.

[44] H. Chen, J. Peng, Q. Pang, H. Du, L. Huang, L. Gao, Y. Lan, C. Yang, Z. Song, *Angew. Chem. Int. Ed.* **2022**, *61*, 6–11.

[45] R. Shintani, K. Moriya, T. Hayashi, *J. Am. Chem. Soc.* **2011**, *133*, 16440–16443.

[46] W. Wang, S. Zhou, L. Li, Y. He, X. Dong, L. Gao, Q. Wang, Z. Song, *J. Am. Chem. Soc.* **2021**, *143*, 11141–11151.

[47] Y. Fan, J. Jing, R. Tong, X. Tu, L. Gao, W. Wang, Z. Song, *Org. Lett.* **2023**, *25*, 455–460.

[48] N. Ishida, S. Okumura, T. Kawasaki, M. Murakami, *Angew. Chem. Int. Ed.* **2018**, *57*, 11399–11403.

[49] D. Seyferth, D. P. Duncan, M. L. Shannon, *Organometallics* **1984**, *3*, 579–583.

[50] S. Santra, *ChemistrySelect* **2020**, *5*, 9034–9058.

[51] E. Kroke, S. Willms, M. Weidenbruch, W. Saak, S. Pohl, H. Marsmann, *Tetrahedron Lett.* **1996**, *37*, 3675–3678.

[52] P. T. Nguyen, W. S. Palmer, K. A. Woerpel, *J. Org. Chem.* **1999**, *64*, 1843–1848.

[53] A. Hinz, *Angew. Chem. Int. Ed.* **2020**, *59*, 19065–19069.

[54] Y. R. Luo, *Comprehensive Handbook of Chemical Bond Energies*, CRC Press, Boca Raton, FL **2007**.

[55] F. Ebner, L. Greb, *J. Am. Chem. Soc.* **2018**, *140*, 17409–17412.

[56] D. Hartmann, M. Schädler, L. Greb, *Chem. Sci.* **2019**, *10*, 7379–7388.

[57] F. Ebner, L. Greb, *Chem* **2021**, *7*, 2151–2159.

[58] A. Hinz, *Chem. Eur. J.* **2019**, *25*, 3267–3271.

[59] M. Baudler, G. Brauer, F. Fehér, F. Huber, R. Klement, W. Kwasnik, P. W. Schenk, M. Schmeisser, R. Steudel, *Handbuch der Präparativen Anorganischen Chemie*, Ferdinand Enke Verlag, Stuttgart **1975**, pp. 671–672.

[60] S. Kundu, S. Sinhababu, M. M. Siddiqui, A. v Luebben, B. Dittrich, T. Yang, G. Frenking, H. W. Roesky, *J. Am. Chem. Soc.* **2018**, *140*, 9409–9412.

[61] W. P. Weber, G. W. Gokel, *Tetrahedron Lett.* **1972**, *17*, 1637–1640.

[62] M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 8738–8749.

[63] J. Feldman, S. J. McLain, A. Parthasarathy, W. J. Marshall, J. C. Calabrese, S. D. Arthur, *Organometallics* **1997**, *16*, 1514–1516.

[64] S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, G. J. McIntyre, *Chem. Eur. J.* **2010**, *16*, 938–955.

[65] J. Hicks, M. Juckel, A. Paparo, D. Dange, C. Jones, *Organometallics* **2018**, *37*, 4810–4813.

[66] P. P. Power, *Inorganic Synthesis*, John Wiley & Sons **2018**, p. 45.

[67] N. C. Bruno, M. T. Tudge, S. L. Buchwald, *Chem. Sci.* **2013**, *4*, 916–920.

[68] E. Niecke, H. Westermann, *Synthesis* **1988**, *4*, 330.

[69] J. A. Barth, G. Becker, *Z. Anorg. Allg. Chem.* **1977**, *430*, 66–76.

[70] G. Becker, G. Gresser, W. Uhl, *Z. Naturforsch.* **1981**, *86*, 16–19.

[71] R. K. Harris, E. D. Becker, S. M. C. de Menezes, R. Goodfellow, P. Granger, *Solid State Nucl. Magn. Reson.* **2002**, *22*, 458–483.

[72] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.

[73] G. M. Sheldrick, **1997**, SHELXS-97.

[74] G. M. Sheldrick, *Acta Crystallogr. A* **2015**, *71*, 3.

[75] G. M. Sheldrick, **2013**, SHLEXL-2013.

[76] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281–1284.

[77] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. v Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. v Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Jr Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian 16, Revision B.01*, Gaussian Inc. Wallingford CT **2016**.