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Isolation of a New Silepin with an Imine Ligand Based on Cyclic Alkyl Amino Carbene

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To date, there are solely a handful of silacycloheptatriene structures (silepins) based on acyclic silylenes described in the literature. The unique property of such compounds is the interconversion between their silepin and silylene forms, which has raised great interest due to their potential catalytic applications. Herein, we want to report a new silyl substituted silepin with an implemented Cy-cAAC moiety, presumably enhancing the stability of the respective low-valent species. In this work, we will demonstrate the synthesis and facile purification of a newly isolated silepin with an imine ligand based on a cyclic alkyl amino carbene as well as its typical silylene-like behavior towards small molecules.

Introduction

Extraordinary advances have been made in the past decades regarding the chemistry of low-valent silicon compounds. With the isolation of the first-ever room temperature stable divalent silicon species (**A**) by *Jutzi et al.* (Figure 1),[1] silylenes received particular interest from main group chemists due to their amphiphilic character: As a result of their extensively reduced tendencies to hybridize, the lone pair orbital (HOMO) of silylenes possesses a high *s* character and can act as an electron density donor while the vacant *p*-orbitals (LUMO) can functionalize as electron density acceptor.[2] This phenomenon is reminiscent of frontier orbitals of *d*-block metals, thus allowing silylenes to mimic the reactivity of complexes bearing a transition metal center.[3] Extensive syntheses and studies of acyclic silylenes demonstrated their unique properties due to narrow HOMO-LUMO gaps and open coordination sites enabling easy accessibility of the frontier orbitals.[4] Sterical flexibility furthermore allows facile coordination of small molecules to the Si(II) center, thus enhancing the reactivity towards oxidative addition.[5] The first ever stable acyclic silylenes under ambient temperatures, **B** and **C**, were separately reported in 2012.[6] One year later, *Aldridge et al.* reported another room-temperature stable silyl silylene (**D**) with a hypersilyl group instead of the previously applied boron carbenoid ligand in **C**.[7]

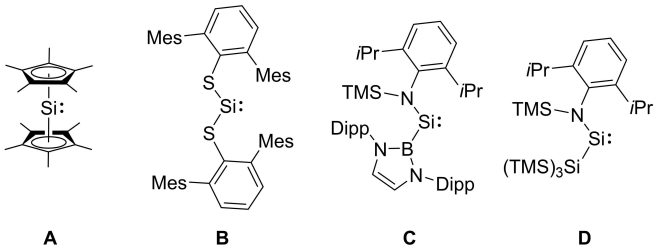

Figure 1. Selected examples of acyclic silylenes (Dipp = Diisopropyl phenyl, TMS = trimethylsilyl).

The divalent silicon atom in **C** and **D** is observed to insert into one of the methine C–H bonds of the diisopropyl phenyl moiety at elevated temperatures, forming the respective heterocyclic ring (Figure 2). In both cases, the intramolecular C–H bond cleavage was found to be an irreversible process.

Similar intramolecular insertion of silylene atoms was reported in 2017. *Rieger* and *Inoue et al.* have isolated an acyclic iminosilylsilylene (**E**), which undergoes an insertion into the C=C bond of its own aromatic ligand framework, forming a

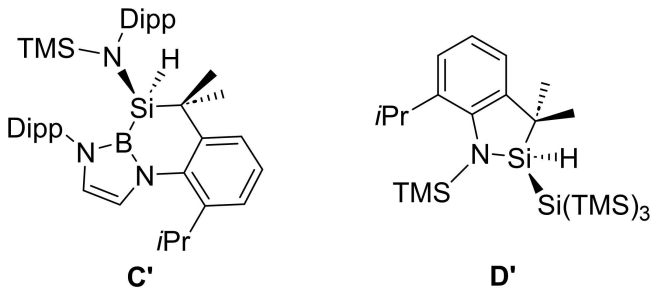

Figure 2. Intramolecular C–H insertion product of **C** and **D**, respectively.

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Research Article
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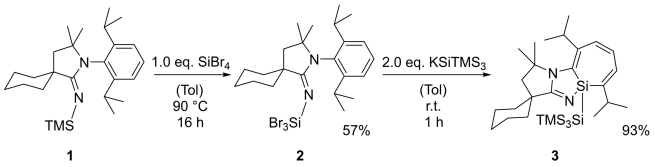
silepin (sila-cycloheptatriene) at room temperature (Figure 3).[8] Silepin **E** acts like a "masked" acyclic silylene and shows characteristic silylene-like behavior, e.g., oxidative addition of small molecules such as dihydrogen, CO_2, and ethylene. This illustrates the first reversible intramolecular insertion of a silylene center. Related compounds, such as **F** and **G**, were consecutively investigated by *Rieger*'s and *Inoue*'s group, whereby the latter demonstrated a room-temperature observable equilibrium between the respective silepin (**G**) and silylene species (**G'**), highlighting the importance of substituent effects on the reactivity of silepins.[8,9] In 2019, *Cui et al.* isolated two more silacycloheptatriene species by an electrophilic substitution of an anionic silanorcaradienyllithium structure with MeOTf and NEt_3Cl yielding **H** and **I**, whereby the silicon center can be released from its silepin form by adding an NHC.[10] Even though other examples of compounds bearing a silacycloheptatriene moiety were isolated, e.g., **J** and **K**, their reactivity is not as thoroughly investigated as the ones mentioned, and no reversibility was determined to our knowledge.[10,11]

The intramolecular formation of silepin rings is assumed to improve the respective species' stability while maintaining an acyclic silylene's reactivity. In this work, we want to further investigate ligand influences on the silicon center by applying a cyclic alkyl amino carbene (cAAC) based imine ligand to isolate the respective low-valent silicon compound. Due to their improved σ-donating and π-accepting abilities compared to NHCs, cAACs have received vast attention ever since their isolation and are widely applied in the field of small molecule activation and the stabilization of reactive main group and transition metal complexes.[12] Hence, we want to present a synthetic route to a new silepin with a modified imine ligand bearing a Cy-cAAC moiety, capable of activating small molecules as a "masked" silylene despite the enhanced stability compared to contemporary reported structures as suggested by DFT calculations.

Results and Discussion

The syntheses to the respective imine ligand precursor (**1**) were carried out according to the procedures reported by *Braunschweig et al.* (Scheme 1),[13] whereby silicon tetrabromide was added in a following step yielding **2**.[14] The final product, silepin **3**, is isolated by substitution and a subsequent reduction with two equivalents of potassium hypersilanide ($KSiTMS_3$). As stated by our group, the side product ($BrSiTMS_3$) of the final step could not be separated from silepin **E**. However, we found an easy method to purify the new silepin **3**: The bromide species can be extensively removed by washing the mixture with acetonitrile. We assume that this method couldn't be applied to silepin **E** due to the sigma donation of MeCN inducing an adduct formation leading to the undesired open silylene form of **E**.

After the purification, the formation of the desired silepin **3** is firstly analyzed by NMR spectroscopy: ^{1}H NMR spectrum shows asymmetrical aromatic proton shifts of the Dipp group around 6.3 to 6.6 ppm, which is likewise found in reported structures (**E**–**G**) hinting a successful intramolecular insertion of the silicon atom into its aromatic ligand framework. The ^{29}Si NMR spectrum displays the characteristic silepin silicon atom (Si1, Figure 4) signal at 17.6 ppm. This shift is remarkably similar to the known species (e.g. 16.1 ppm for **E**), supporting our findings. The high field shifted signal at −135.7 ppm is typical for the electron-rich hypersilyl silicon atom (Si2, Figure 4). Single crystal XRD analysis could confirm the silacycloheptatriene



Scheme 1. Final steps of the synthetic pathway to **3**.

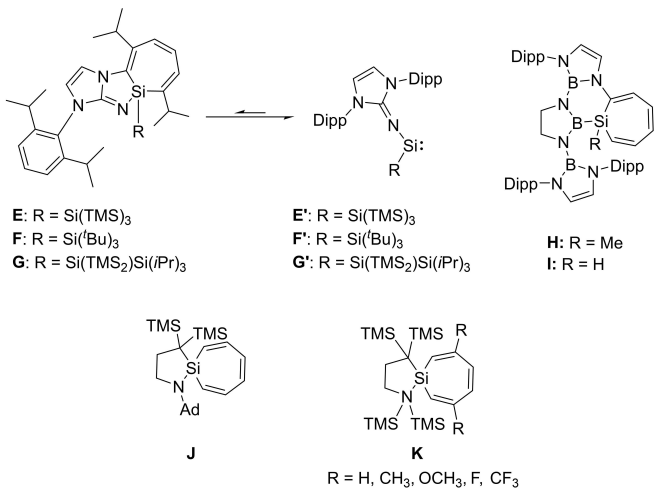


Figure 3. Structures of selected silacycloheptatriene species.

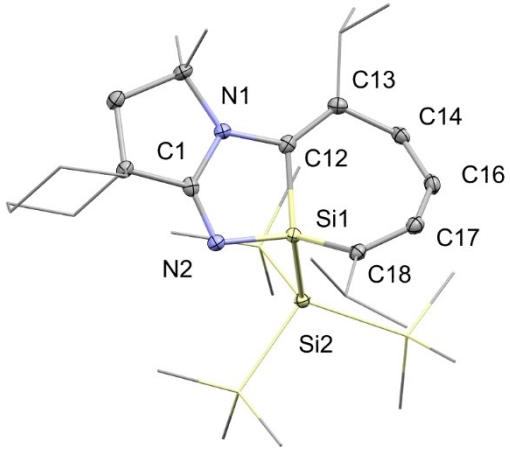


Figure 4. Molecular structure of compound **3** with ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. Part of the Cy-cAAC moiety and the TMS groups are simplified as wireframes. Selected bond lengths: Si1-C12 1.895(2) Å, Si1-C18 1.863(2) Å, Si1-N2 1.754(2) Å, Si1-Si2 2.355(1) Å, N2-C1 1.278(2) Å. Selected angles: C12-Si1-C18 106.86°, N2-Si1-C18 111.83°, Si1-C12-C13 123.91°, Si1-C18-C17 115.66°.

Research Article
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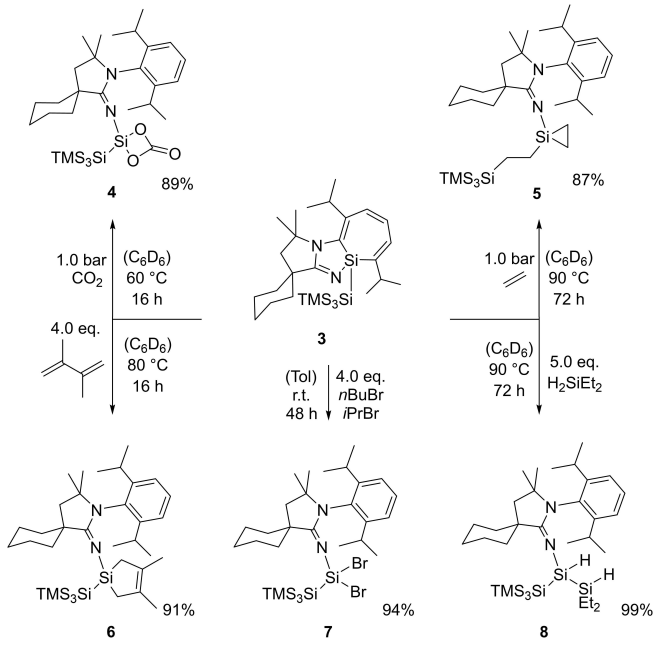
structure of **3**. The seven-membered silepin ring, as suggested by selected bond lengths and angles, is found to be in a "folded" conformation with a C12-Si1-C18 angle of 106.86° which is roughly in accordance with silepin **E** (105.3°) as reported by our group in 2017.

Due to its related structure motives to literature known silepins **E**–**G**, we were convinced of its direct usage as an acyclic silylene. As a matter of fact, **3** is found to react in a similar fashion towards small molecules as common acyclic silylenes: In the presence of a suiting reactant, **3** is capable of cleaving covalent bonds thus oxidatively activating small molecules, as shown in Scheme 2.

Over the past decades, the binding of CO_2 by metal-free compounds has raised the particular interest of main-group chemists. *Jutzi et al.* were the first to describe the formation of the silicon biscarbonato complex **L** (Figure 5).[15] Monomeric coordinating carbonato groups are a scarce occurrence with silylenes, and only a few are described in the literature to the present day, e.g., in **M, N** by *Tacke et al.*[16] and **O, P, Q** by *Inoue* and co-workers. Silepin **3**, mechanistically analogous to *Jutzi*'s descriptions, can convert one equivalent of CO_2 to CO while forming the respective silanone as the intermediate, which subsequently reacts with one additional equivalent of CO_2 to **4**. The formation of the Si(IV) carbonato moiety was confirmed with SC-XRD analysis. Furthermore, we observed an ethylene insertion into the Si-Si bond at room temperature after 30 days, forming silirane **5** (Figure 6). This process can be significantly accelerated by elevating the temperatures to 90 degrees Celsius. Comparable structures (**S, T**) were recently reported in the literature.[17] Such reactivity of acyclic silylenes towards ethylene was extensively studied by our group beforehand: The formation of **R** is spectroscopically proven with deuterated ethylene, whereby a migratory insertion mechanism could be determined.[18] A likewise reaction is assumed with silepin **3**. Not only are there hardly any examples of such compounds in the field of low-valent silicon chemistry reported, but the respective molecular depiction is even more scarce. To our best knowledge, the only literature-known crystal structure of ethylene insertion products is the one of compound **R**. In our case, we could isolate single crystals suitable for SC-XRD analysis in pentane.

Interestingly, silepin **3** does not show insertion of any kind towards 2,3-Dimethyl-1,3-butadiene. Instead, we could determine the silacyclopentene **6** as the product of a [4 + 1] cycloaddition reaction. Analogous reactivity is reported and investigated by our group before with silylsilylene **D**, which, again, underlines the silylene-like reactivity of Cy-cAAC imine-based silepin **3**.

Regarding the reactivity towards C–X bonds, we added *iso*propyl bromide and *n*-butyl bromide to **3** in two separate



Scheme 2. Reactivity of Cy-cAAC silepin **3** towards various small molecules.

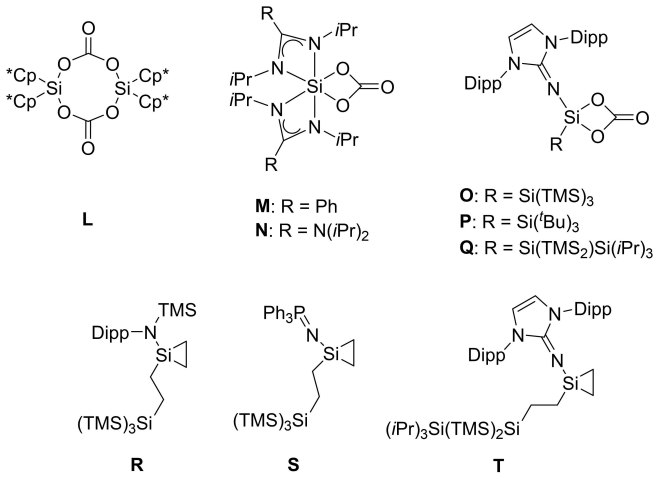


Figure 5. Selected literature known silicon carbonato and silirane compounds.

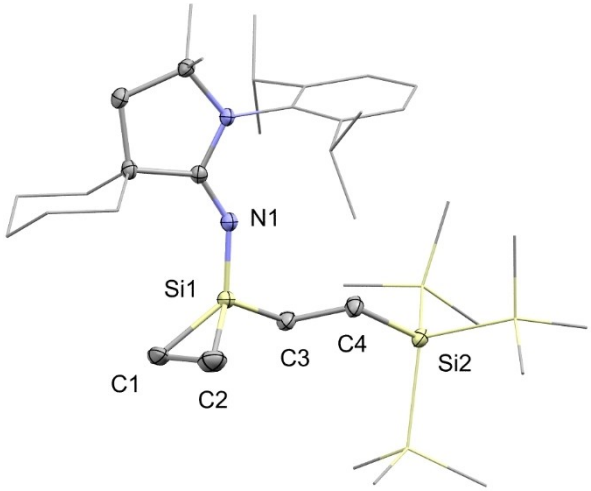


Figure 6. Molecular structure of silirane **5** with ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. Part of the Cy-cAAC moiety and the TMS groups are simplified as wireframes. Selected bond length: Si1-C1 1.867(1) Å, Si1-C2 1.831(2) Å, Si1-C3 1.861(1) Å, Si2-C4 1.907(1) Å, C1-C2 1.607(2) Å, C3-C4 1.543(2) Å.

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attempts. A complete conversion could be achieved readily at room temperature after 20 hours. However, ^{1}H and ^{29}Si NMR suggested an identical product in both attempts. Additional SC-XRD analysis supported the assumed outcome of the reaction: Instead of an oxidative addition of the alkyl bromides cleaving the C–Br bond, we found a full bromination of silepin **3** to the respective dibromo species **7**. Herein, we assume a mechanism involving radicals due to the enhanced stability of bromine radicals. Additionally, to C–X bonds, we were especially interested in the oxidative addition of silanes due to potential applications in hydrosilylation as an industrial usage. Therefore, as the simplest representative, diethyl silane was applied as a model compound for investigations. A successful conversion to **8** could be determined, resulting in two Si-H bonds potentially able to react with double bonds. We applied a variety of substrates bearing C=C bonds as well as aldehydes, ketones, and imines. Unfortunately, decomposition or inactivity was determined as the reaction outcome, leading to the assumption that a transfer from such Si(IV) species is not feasible.

Despite being a "masked" silylene, **3** is inert towards the strong and nonpolar bond of dihydrogen compared to silepin **E** or reported silylenes **C** and **D** with related structure motifs, which suggests an overall improved stabilization of the Si1 atom in **3** after our application of a Cy-cAAC containing imine ligand. This phenomenon is assumed to be affected by the increased silepin silylene interconversion energy barrier and the higher HOMO-LUMO gap of the respective silylene. The exact mechanism of the conversion from silepin to the silylene structure is fully calculated with the known compounds **E/E'** and **G/G'**, whereby both compounds are found to be reactive towards H_2. This led to our assumption that compound **3** presumably possesses a higher energy barrier between both forms. For further understanding of the inert nature of **3**, we investigated the HOMO-LUMO gap. We utilized the crystal structure of **7** by using the respective silylene fragment as the starting point of the structural optimization for the open silylene form of **3** (Figure 7).

The calculated HOMO-LUMO gap of 3.188 eV is comparably on the larger side than that of reported silylenes (typical values between 2–4 eV). Additionally, the measured melting point of compound **3** (122 °C) is well above the value of silepin **E** (99.2 °C), being the pre-modified version of **3**. These data validate our observations and support the hypothesis that silepin **3** indeed possesses an advanced stability after the ligand modification, emphasizing the impact of substituent effects on the reactivity of silepins.

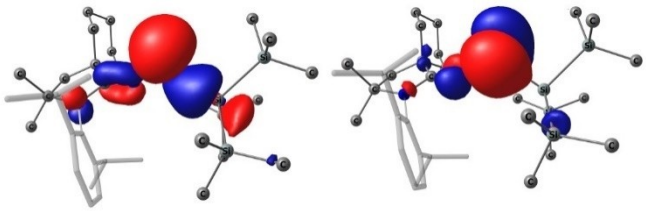

Figure 7. Visualization of the structure optimization. Calculation of HOMO and LUMO energy Levels at the B3LYP/6-311 + G(d,p) level of theory for the open silylene form of **3**. HOMO: 445.2797 kJ/mol (−4.615 eV), LUMO: −137.6845 kJ/mol (−1.427 eV).

Conclusions

In summary, we have reported a new silepin (**3**) with a modified imine ligand based on a cyclohexyl cyclic alkyl amino carbene. The reactivity of **3** as a "masked" silylene is verified by reactivity studies with various small molecules, whereby, in great contrast to its closely related structure **E**, an inactivity of **3** towards oxidative addition of dihydrogen was observed. We assume a larger silepin silylene interconversion energy barrier in molecule **3** compared to structures **E/E'** and **G/G'**. This observation and the calculated HOMO-LUMO gap of 3.188 eV supported our theory that the ligand modification from an NHC- to a Cy-cAAC-containing imine moiety led to enhanced stability of the resulting silepin **3**, which underlines the significance of substituent effects on low-valent silicon species.

Experimental Section

Material and Methods: All manipulations were carried out under argon atmosphere using standard *Schlenk* or glovebox techniques. Glassware was heat-dried under vacuum prior to use. Unless otherwise stated, all chemicals were purchased commercially and used as received. All solvents were refluxed over sodium, distilled, and deoxygenated. Deuterated solvents were obtained commercially and were dried over 3 Å molecular sieves. All NMR samples were prepared under argon in *J. Young* PTFE tubes. Cy-cAAC and $KSiTMS_3$ were synthesized according to procedures described in the literature.[19] Carbon dioxide (5.0) and ethylene (3.5) were purchased from Westfalen AG and used as received. NMR spectra were recorded on Bruker AV-500 C or AV-400 spectrometers at ambient temperature (300 K) unless otherwise stated. ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopic chemical shifts (δ) are reported in ppm. $\delta(^{1}H)$ and $\delta(^{13}C)$ were referenced internally to the relevant residual solvent resonances. $\delta(^{29}Si)$ was referenced to the signal of tetramethylsilane (TMS) ($\delta = 0$ ppm) as the external standard. Liquid Injection Field Desorption Ionization Mass Spectrometry (LIFDI-MS) was measured directly from an inert atmosphere glovebox with a *Thermo Fisher Scientific* Exactive Plus Orbitrap equipped with an ion source from Linden CMS. Melting points were determined in sealed glass capillaries under inert gas with a *Büchi* Melting Point B-540.

Synthesis of 1: Cy-cAAC (1.34 g, 4.12 mmol, 1.0 eq.) is dissolved in toluene (20 mL), and $TMSN_3$ (1.37 mL, 10.3 mmol, 2.5 eq.) is added. The mixture is stirred at 90 °C for 16 h. The product is obtained upon evaporation of the solvent as an off-white solid (1.62 g, 95 %). ^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 7.20 (dd, J = 8.5, 6.8 Hz, 1H, H_{Ar}), 7.15–7.10 (m, 2H, H_{Ar}), 3.16–3.04 (m, 2H, $CH(CH_3)_2$), 1.90–1.85 (m, 1H, H_{Cy}), 1.84 (s, 1H, CH_2), 1.79 (s, 1H, CH_2), 1.77–1.33 (m, 9H, H_{Cy}), 1.32–1.22 (m, 12H, CH_3), 1.19 (d, J = 6.9 Hz, 3H, CH_3), 1.14 (d, J = 6.7 Hz, 3H, CH_3), 1.02 (s, 4H, H_{TMS}), 0.27 (s, 5H, H_{TMS}). ^{13}C NMR (126 MHz, C_6D_6): δ [ppm] = 173.16 (C=N), 150.92 (C_{Ar}), 133.87 (C_{Ar}), 124.96 (C_{Ar}), 123.89 (C_{Ar}), 62.20 (C-N), 47.32 (N–C–*C*), 38.03 (*C*-C=N), 30.23 (C_{Cy}), 29.15 (C_{Cy}), 26.80 (C_{Cy}), 26.03 (CH_3), 23.29 (CH_3), 4.44 (TMS). ^{29}Si NMR (99 MHz, C_6D_6): δ [ppm] = −18.74. LIFDI-MS: m/z = 412.3258 $[1]^+$. Melting point: 91.9 °C.

Synthesis of 2: Cy-cAACNTMS (1.63 g, 3.94 mmol, 1.0 eq.) is dissolved in toluene (25 mL), and $SiBr_4$ (0.49 mL, 3.94 mmol, 1.0 eq.) is added. The mixture is stirred at 90 °C for 16 h. The solvent is

evaporated in *vacuo*. After *Whatman* filtration, the product is obtained as a powder (1.36 g, 57%). ^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 7.24–7.22 (m, 2H, H_{Ar}), 7.14 (d, J = 1.0 Hz, 1H, H_{Ar}), 2.89 (hept, J = 6.8 Hz, 2H, C*H*(CH_3)$_2$), 2.40–2.32 (m, 2H, CH_2), 1.71 (s, 2H, H_{Cy}), 1.66–1.50 (m, 5H, H_{Cy}), 1.46 (d, J = 6.7 Hz, 6H, CH_3), 1.41–1.33 (m, 1H, H_{Cy}), 1.24 (d, J = 6.7 Hz, 6H, CH_3), 1.21–1.10 (m, 2H, H_{Cy}), 0.95 (s, 6H, CH_3). ^{13}C NMR (126 MHz, C_6D_6): δ [ppm] = 172.32 (C=N), 147.62 (C_{Ar}), 130.75 (C_{Ar}), 129.05 (C_{Ar}), 124.29 (C_{Ar}), 63.50 (C–*C*–N), 48.81 (*C*–C–N), 45.65 (C–*C*=N), 35.21 (C_{Cy}), 29.30 (C_{Cy}), 28.95 (CH), 26.70 ((C_{Cy})), 25.02 (CH_3), 23.11 (CH_3), 22.15 (CH_3). ^{29}Si NMR (99 MHz, C_6D_6): δ [ppm] = −107.85. LIFDI-MS: m/z = 604.0107 $[2]^+$. Melting point: 159.5 °C.

Synthesis of 3: Cy-cAAC-$SiBr_3$ (120 mg, 198 mmol, 1.0 eq.) and $KSiTMS_3$ (113 mg, 396 mmol, 2.0 eq.) is dissolved in toluene (3 mL) and stirred at r.t. for 1 h. After evaporation of the solvent, pentane (5 mL) is added, and the suspension is filtered through a PE syringe filter. Pentane is then removed, and the product is precipitated with MeCN (8 mL). Pure Cy-cAAC silepin is obtained after centrifugation and separation of the solvent (113 mg, 93%). ^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 6.61 (d, J = 13.0 Hz, 1H, H_{Ar}), 6.38 (dd, J = 5.8, 1.2 Hz, 1H, H_{Ar}), 6.33 (dd, J = 13.0, 6.1 Hz, 1H, H_{Ar}), 3.25 (hept, J = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 3.04 (hept, J = 6.7 Hz, 1H, C*H*(CH_3)$_2$), 2.19–2.11 (m, 1H, CH), 2.08–2.01 (m, 1H, CH), 1.84–1.77 (m, 2H, H_{Cy}), 1.69–1.46 (m, 8H, H_{Cy}), 1.25–1.19 (m, 15H, CH_3), 1.05 (d, J = 6.8 Hz, 3H, CH_3), 0.41 (s, 27H, H_{TMS}). ^{13}C NMR (126 MHz, C_6D_6): δ [ppm] = 179.53 (C=N), 146.54 (C_{Ar}), 135.61 (C_{Ar}), 133.72 (C_{Ar}), 128.93 (C_{Ar}), 123.71 (C_{Ar}), 58.28 (C–N), 52.75 (*C*–C–N), 42.38 (*C*–C=N), 37.51 (C_{Cy}), 36.79 (C_{Cy}), 33.98 (C_{Cy}), 31.17 (*C*H(CH_3)$_2$), 31.12 (*C*H(CH_3)$_2$), 29.03 (C_{Cy}), 25.96 (C_{Cy}), 24.88 (CH_3), 23.21 (CH_3), 22.99 (CH_3), 22.84 (CH_3), 22.67 (CH_3), 20.65 (CH_3), 3.36 (C_{TMS}). ^{29}Si NMR (99 MHz, C_6D_6): δ [ppm] = 17.25, −9.29, −135.71. LIFDI-MS: m/z = 614.3743 $[3]^+$. Melting point: 122.4 °C.

Synthesis of 4: Cy-cAAC silepin (15 mg, 24.4 μmol) is solved in C_6D_6 (0.5 mL) and filled into a PTFE *JYoung* tube. The solution is frozen with liquid nitrogen and degassed. Subsequently, gaseous CO_2 (1 bar) is introduced, and the tube is sealed afterward. The mixture is heated to 60 °C for 16 hours. After evaporation of the solvent, the product is obtained as a pale-yellow oil (15.7 mg, 88% purity) containing compound 4 (14.7 mg, 89% yield) and $SiTMS_4$ (0.93 mg) as the impurity.

^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 7.16–7.14 (m, 1H, H_{Ar}), 7.06 (d, J = 7.3 Hz, 2H, H_{Ar}), 2.84 (hept, J = 6.9 Hz, 2H, C*H*(CH_3)$_2$), 2.12 (td, J = 13.1, 3.8 Hz, 2H, C–CH_2), 1.67–1.59 (m, 5H, H_{Cy}), 1.56–1.45 (m, 5H, H_{Cy}), 1.29 (d, J = 6.7 Hz, 6H, CH_3), 1.16 (d, J = 6.7 Hz, 6H, CH_3), 0.88 (s, 6H, CH_3), 0.29 (s, 27H, H_{TMS}). ^{13}C NMR (126 MHz, C_6D_6): δ [ppm] = 174.20 (C=N), 150.97 (C_{Ar}), 148.15 (C_{Ar}), 131.53 (C_{Ar}), 129.22 (C_{Ar}), 124.78 (C=O), 63.77 (*C*(CH_3)$_2$), 48.72 (*C*–C(CH_3)$_2$), 46.20 (*C*–C=N), 35.95 (C_{Cy}), 29.39 (*C*H(CH_3)$_2$), 29.29 (*C*H(CH_3)$_2$), 28.03 (C_{Cy}), 25.22 (C_{Cy}), 23.53 (CH_3), 22.73 (CH_3), 2.79 (C_{TMS}). ^{29}Si NMR (99 MHz, C_6D_6): δ [ppm] = −9.64 (TMS), −28.31 (SiO_2C=O), −134.20 (*Si*TMS_3). LIFDI-MS: m/z = 675.3645 $[4 + H]^+$.

Synthesis of 5: Cy-cAAC silepin (15 mg, 24.4 μmol) is solved in C_6D_6 (0.5 mL) and filled into a PTFE *JYoung* tube. The solution is frozen with liquid nitrogen and degassed. Subsequently, gaseous ethylene (1 bar) is introduced, and the tube is sealed afterward. The mixture is heated to 90 °C for 72 hours. After evaporation of the solvent, the product is obtained as a pale-yellow oil (14.3 mg, 21.3 μmol, 87%). ^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 7.21 (dd, J = 8.4, 6.9 Hz, 1H, H_{Ar}), 7.14 (d, J = 8.3 Hz, 2H, H_{Ar}), 3.01 (hept, J = 6.7 Hz, 2H, C*H*(CH_3)$_2$), 2.18 (td, J = 13.2, 3.6 Hz, 2H, C–CH_2), 1.77–1.46 (m, 10H, H_{Cy}), 1.32 (d, J = 6.7 Hz, 6H, CH_3), 1.25 (d, J = 6.8 Hz, 6H, CH_3), 1.19–1.12 (m, 4H, NSi(CH_2)$_2$), 1.09–1.04 (m, 2H, Si(CH_2)$_2$Si), 0.97 (s, 6H, CH_3), 0.94–0.89 (m, 2H, Si(CH_2)$_2$Si), 0.25 (s, 27H, H_{TMS}). ^{13}C NMR (126 MHz, C_6D_6): δ [ppm] = 170.73 (C=N), 149.04 (C_{Ar}), 133.07 (C_{Ar}), 124.09 (C_{Ar}), 122.98 (C_{Ar}), 61.14 (*C*(CH_3)$_2$), 47.70 (*C*–C(CH_3)$_2$), 47.18 (*C*–C=N), 35.94 (C_{Cy}), 29.84 (*C*H(CH_3)$_2$), 29.37 (*C*H(CH_3)$_2$), 27.02 (C_{Cy}), 25.82 (C_{Cy}), 23.13 (CH_3), 22.93 (CH_3), 12.74 (NSi(CH_2)$_2$), 1.44 (C_{TMS}), 0.77 (Si(CH_2)$_2$Si). ^{29}Si NMR (99 MHz, C_6D_6): δ [ppm] = −13.31, −72.85, −77.03. LIFDI-MS: m/z = 670.4366 $[5]^+$.

Synthesis of 6: Cy-cAAC silepin (15 mg, 24.4 μmol, 1.0 eq.) is solved in C_6D_6 (0.5 mL) and 2,3-dimethylbuta-1,3-diene (11.1 μL, 97.5 μmol, 4.0 eq.) is added. The mixture is filled into a *JYoung* PTFE tube and heated to 80 °C for 16 hours. After evaporation of the solvent, the product is obtained as a white solid (15.5 mg, 22.2 μmol, 91%).

^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 7.21–7.17 (m, 1H, H_{Ar}), 7.09 (d, J = 7.4 Hz, 2H, H_{Ar}), 3.05 (hept, J = 6.8 Hz, 2H, C*H*(CH_3)$_2$), 1.98 (td, J = 13.4, 3.7 Hz, 2H, C–CH_2), 1.80 (s, 2H, H_{Cy}), 1.72 (s, 6H, SiCH_2*C*H_3), 1.70–1.62 (m, 4H, Si*C*$H_2$$CH_3$), 1.54–1.39 (m, 4H, H_{Cy}), 1.34–1.23 (m, 4H, H_{Cy}), 1.21 (d, J = 6.8 Hz, 12H, CH_3), 1.00 (s, 6H, CH_3), 0.37 (s, 27H, H_{TMS}). ^{13}C NMR (126 MHz, C_6D_6): δ [ppm] = 166.52 (C=N), 149.29 (C_{Ar}), 134.53 (C_{Ar}), 131.07 (C_{Ar}), 127.97 (C=C), 124.74 (C_{Ar}), 61.10 (*C*(CH_3)$_2$), 47.46 (*C*–C(CH_3)$_2$), 47.29 (*C*–C=N), 36.57 (C_{Cy}), 34.61 (C_{Cy}), 30.43 (Si*C*$H_2$$CH_3$), 28.89 (*C*H($CH_3$)$_2$), 27.77 ($CH_3$), 25.50 ($C_{Cy}$), 24.29 ($CH_3$), 22.92 ($CH_3$), 19.40 (Si$CH_2$*C*$H_3$), 3.67 ($C_{TMS}$). ^{29}Si NMR (99 MHz, C_6D_6): δ [ppm] = −10.34 (TMS), −18.43 (Si$CH_2$$CH_3$), −132.75 (*Si*$TMS_3$). LIFDI-MS: m/z = 696.4501 $[6]^+$. Melting point: 185 °C.

Synthesis of 7: Cy-cAAC silepin (10 mg, 16.3 μmol, 1.0 eq.) is solved in toluene (1 mL) and *n*-butyl bromide (7.0 μL, 65.0 μmol, 4.0 eq.) or *iso*-propyl bromide (6.1 μL, 65.0 μmol, 4.0 eq.) is added. The mixture is stirred at 90 °C for 24 hours. After evaporation of the solvent, the product is obtained as a yellow oil (12.1 mg, 16.6 μmol, 96% yield for reaction with *n*-butyl bromide and 11.8 mg, 15.2 μmol, 94% for reaction with *iso*-propyl bromide). ^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 7.15 (d, J = 4.8 Hz, 1H, H_{Ar}), 7.09 (d, J = 6.6 Hz, 2H, H_{Ar}), 2.95 (p, J = 6.8 Hz, 2H, C*H*(CH_3)$_2$), 2.81 (td, J = 13.4, 3.6 Hz, 2H, C–CH_2), 1.81–1.47 (m, 10H, H_{Cy}), 1.42 (d, J = 6.7 Hz, 6H, CH_3), 1.18 (d, J = 6.7 Hz, 6H, CH_3), 0.94 (s, 6H, CH_3), 0.39 (s, 27H, H_{TMS}). ^{13}C NMR (126 MHz, C_6D_6): δ [ppm] = 173.56 (C=N), 147.70 (C_{Ar}), 132.48 (C_{Ar}), 128.60 (C_{Ar}), 124.71 (C_{Ar}), 63.52 (*C*(CH_3)$_2$), 49.31 (*C*–C(CH_3)$_2$), 47.23 (*C*–C=N), 34.78 (C_{Cy}), 29.79 (C_{Cy}), 28.76 (C_{Cy}), 28.39 (*C*H(CH_3)$_2$), 24.05 (CH_3), 22.44 (CH_3), 2.83 (C_{TMS}). ^{29}Si NMR (99 MHz, C_6D_6): δ [ppm] = −10.16 (TMS), −53.00 ($SiBr_2$), −101.03 (*Si*TMS_3). LIFDI-MS: m/z = 697.4562 [7-Br]$^+$.

Synthesis of 8: Cy-cAAC silepin (10 mg, 16.3 μmol, 1.0 eq.) is solved in C_6D_6 (0.5 mL) and diethyl silane (10.5 μL, 81.3 μmol, 5.0 eq.) is added. The mixture is filled into a *JYoung* PTFE tube and heated to 80 °C for 16 hours. After evaporation of the solvent, the product is obtained as a white solid (11.3 mg, 16.6 μmol, 99%). ^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 7.19 (t, J = 7.6 Hz, 1H, H_{Ar}), 7.12 (dd, J = 7.8, 1.8 Hz, 1H, H_{Ar}), 7.09 (dd, J = 7.6, 1.8 Hz, 1H, H_{Ar}), 6.41 (d, J = 4.1 Hz, 1H, Si*H*SiHEt$_2$), 4.05 (qq, J = 4.1, 2.2 Hz, 1H, SiHSi*H*Et$_2$), 3.16–3.06 (m, J = 6.7 Hz, 2H, C*H*(CH_3)$_2$), 2.56 (m, 1H, C–CH_2), 2.47 (m, 1H, C–CH_2), 1.86 (m, 1H, H_{Cy}), 1.76–1.57 (m, 6H, H_{Cy}), 1.37 (d, J = 6.7 Hz, 3H, H_{Cy}), 1.29–1.20 (m, 18H, CH_3), 1.05 (s, 3H, CH_2*C*H_3), 1.04–0.99 (m, 1H, C*H*$_2$$CH_3$), 0.95 (s, 3H, CH_2*C*H_3), 0.94–0.78 (m, 3H, C*H*$_2$$CH_3$), 0.34 (s, 29H, H_{TMS}). ^{13}C NMR (126 MHz, C_6D_6): δ [ppm] = 170.11 (C=N), 149.28 (C_{Ar}), 148.89 (C_{Ar}), 134.13 (C_{Ar}), 124.59 (C_{Ar}), 124.17 (C_{Ar}), 61.34 (*C*(CH_3)$_2$), 48.63 (*C*–C(CH_3)$_2$), 48.31 (*C*–C=N), 37.47 (C_{Cy}), 34.84 (C_{Cy}), 30.83 (C_{Cy}), 29.32 (C_{Cy}), 29.25 (C_{Cy}), 29.20 (*C*H(CH_3)$_2$), 29.17 (*C*H(CH_3)$_2$), 28.13 (CH_3), 25.72 (CH_3), 24.24 (CH_3), 23.41 (CH_3), 23.35 (CH_3), 23.15 (CH_3), 11.31 (*C*H$_2$CH$_3$), 10.18 (*C*H$_2$CH$_3$), 3.78 (C_{TMS}). ^{29}Si NMR (99 MHz, C_6D_6): δ [ppm] = −9.50 (TMS), −18.77 (SiHEt$_2$), −60.03 (*Si*HSiHEt$_2$), −130.80 (*Si*TMS_3). LIFDI-MS: m/z = 702.4455 $[8]^+$. Melting point: 172.5 °C.

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Supporting Information

Experimental details for all newly synthesized compounds, DFT calculation details, and single crystallographic data can be found in the Supporting Information (SI). The authors have cited additional references within the SI ([20–32]).

Deposition Number(s) 2293615 (for Compound **2**), 2293616 (for Compound **3**), 2293619 (for Compound **4**), 2293620 (for Compound **5**), 2293618 (for Compound **6**), 2293617 (for Compound **7**) contain(s) 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.

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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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