EurJIC
European Journal of Inorganic Chemistry

Research Article
doi.org/10.1002/ejic.202400045

Chemistry Europe
European Chemical Societies Publishing

www.eurjic.org

Isolation and Reactivity of Silepins with a Sterically Demanding Silyl Ligand

Jin Yu Liu,[a] Shigeyoshi Inoue,[b] and Bernhard Rieger*[a]

Silacycloheptatriene (silepin) species are novel silicon compounds reported in recent years. The interplay between the "closed" silepin and the "open" silylene form enables an enhanced stability of the low valent species while maintaining a high reactivity towards small molecules. In this work, two new silepins of similar structures to literature known compounds bearing modified silyl ligands are reported. A unique intramolecular activation of an aromatic hydrogen is found, and the respective formed hydrosilanes are characterized. We further synthesized iron(0) carbonyl complexes of known and new silepins in order to investigate their electronic properties relative to each other to gain more insight into substitution effect in such compounds.

Introduction

In the past decades, a series of low-valent silicon species were isolated and reported (Figure 1). Among all newly discovered silylene compounds, acyclic silylenes are attracting major focus of main-group chemists due to the particularly small energy difference of the frontier orbitals and the sterical flexibility.[1] These unique properties allow them to exhibit similar behavior towards small molecules, such as oxidative addition, which is reminiscent of transition metal complexes.[2]

Intramolecular insertions in low-valent silylene species are scarcely reported to date.[3] Usually, a steric approximation of neighboring groups within a molecule is required, as well as a highly reactive silylene atom. Due to the natural electron deficiency of the Si(II) atom,[4] such processes are usually irreversible, leading to the final Si(VI) species, e.g. **A'**, **B'**, **E'** (Figure 2), from the respective silylene **A**, **B**, **E** (Figure 2).[5]

In 2017, we described the isolation of the first silepin based on an acyclic silylene (Figure 3).[6] The ligand applied here consists of a hypersilyl group (–Si(TMS)$_3$) and a *N*-heterocyclic

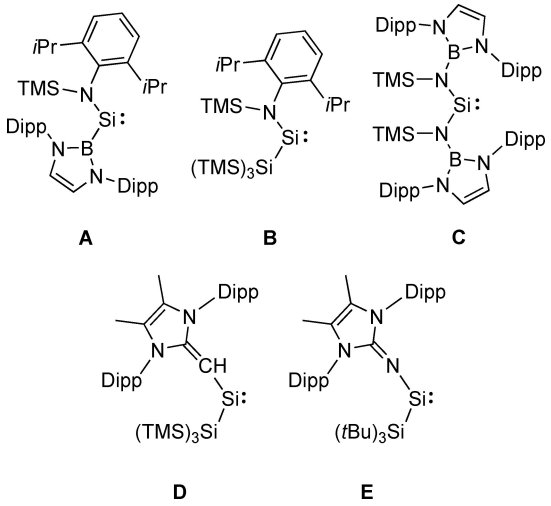


Figure 1. Selected literature known acyclic silylenes. Dipp = 2,6-Diisopropyl phenyl. TMS = Trimethylsilyl.

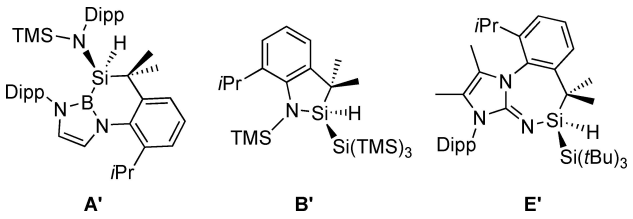
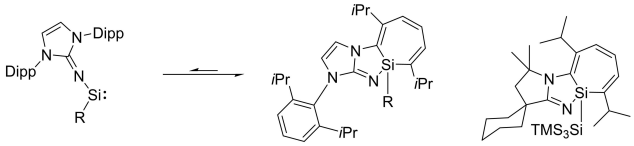


Figure 2. Literature known intramolecular insertions of Si(II) centers into the C–H bonds of attached Dipp groups.[6–8]



F: R = Si(TMS)$_3$
G: R = Si(^{t}Bu)$_3$
H: R = Si(TMS$_2$)Si(*i*Pr)$_3$

F': R = Si(TMS)$_3$
G': R = Si(^{t}Bu)$_3$
H': R = Si(TMS$_2$)Si(*i*Pr)$_3$

J'

Figure 3. Selected examples of literature known silepins in equilibrium with their acyclic silylene form. *i*Pr = *Iso*propyl.

[a] *J. Yu Liu, Prof. Dr. B. Rieger*
TUM School of Natural Sciences
Department of Chemistry
Wacker Institute for Silicon Chemistry
Technical University of Munich
Lichtenbergstraße 4, 85748 Garching bei München (Germany)
E-mail: rieger@tum.de

[b] *Prof. Dr. S. Inoue*
TUM School of Natural Sciences
Department of Chemistry
Institute of Silicon Chemistry
Technical University of Munich
Lichtenbergstraße 4, 85748 Garching bei München (Germany)

Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejic.202400045

Research Article
doi.org/10.1002/ejic.202400045

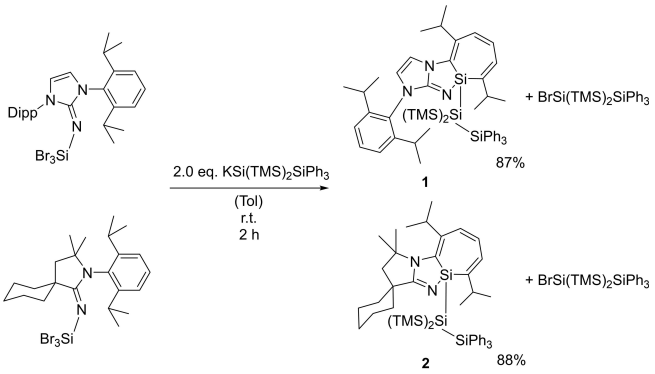
imine (NHI). NHIs, conventionally based on NHCs (*N*-heterocyclic carbenes), are σ- and π-electron donating moieties with a vast variety of steric features.[7] In this case, the NHI bearing a 2,6-diisopropyl phenyl (Dipp) group, derived from the ^{Dipp}NHC, allows a reversible insertion of **F** into its aromatic framework, thus possessing a relatively high stability as a silepin (Si(IV)) while maintaining the reactivity of an acyclic silylene (Si(II)). The significant advantage of silepin structures is, therefore, the interplay between both oxidative states (II, IV) of silicon, demonstrating a key feature for potential catalytic applications. Initial studies on substituent effects in such silepin forms were performed with compound **G/G′** bearing a modified silyl group (–Si(^{t}Bu)$_3$) as a sigma donating ligand.[8] Upon exposure of **F′** and **G′** to N_2O, the respective formed silanone species (R_2Si=O) of **G** is found to have an enhanced stability. Additionally, silepin **G′** can be used as a building block in the formation of heterodinuclear Al–Si bonds resulting in the isolation of an aluminata-silene featuring an Al=Si core with a multiple bond character,[9] thus, demonstrating an interesting utilization of silepin species in the isolation of novel main-group compounds. Further investigations on silepins were conducted throughout recent years, whereby a room temperature observable equilibrium of **H** and **H′** was reported in 2022.[10] This was mainly achieved by the application of a sterically congested bis(trimethylsilyl)triisopropylsilylsilanide. **H/H′** shows an enhanced reactivity towards small molecules, illustrating, once again, the importance of substituent effect on such structures. Subsequently, our group reported a new silepin (**J′**) with a modified imine ligand based on a cyclic alkyl amino carbene (cAAC).[11] This type of *N*-heterocyclic imine (NHI) based on cAAC has drawn attention in recent years.[12] The electronic features, as well as steric demands of cAACs relative to NHC, are distinctively different from each other, allowing effective stabilization of not only transition metal complexes but also pioneering main-group compounds.[13] Structure **J′** is found to have an increased stability in its closed silepin form compared to its related structure **F′**, and contemporary reported similar compounds as shown in reactivity studies and DFT calculations.

In this work, we want to present two new silepin structures contributed to the question whether we can influence the electronic properties and reactivity of the silepin with simple ligand modifications.

Results and Discussion

Synthesis of New Silepins

After our previously reported silepins **F′**, **G′** and **J′**, we intended to further investigate the impact of silyl ligand modification. For this purpose, we first isolated the silyl ligand KSi(TMS)$_2$SiPh$_3$ with comparably different electronics and steric features than the previously applied KSi(TMS)$_3$ following literature known procedures.[14] Silepins **1** and **2** (Scheme 1) are obtained analogously to our reported synthetic route with the inseparable side product BrSi(TMS)$_2$SiPh$_3$ due to their identical solubility.



Scheme 1. Last synthesis step towards the isolation of silepins **1** and **2**.

Various purification attempts were made to separate silepins **1** and **2** from their side product. Crystallization in common organic solvents (Hexane, pentane, toluene, THF, Et_2O) and PMe_3, sometimes working for compounds that don't crystallize in common solvents, did not lead to pure precipitated product nor crystals suitable for SC-XRD analysis. Washing the oily mixture consisting of silepin and side product with HMDSO (hexamethyl disiloxane) and MeCN, the latter reported by us to be able to wash out the side product during the synthesis of silepin **J′**, only resulted in a homogeneous solution. Thus, a suitable purification method has not been found yet.

Analyzing the ^{1}H NMR spectrum of **1**, we observed three asymmetrical aromatic protons (6.08 ppm–6.48 ppm) due to the formed silepin ring with one of the diisopropyl phenyl (Dipp) groups. Additionally, the imidazole ring protons are split into two different doublets at 5.93 ppm and 6.63 ppm with an integral of 1, which is likewise found in its related structure **F′** due to the asymmetric electronic environment after an intramolecular insertion of the silylene atom. Similar aromatic proton shifts are determined in the ^{1}H NMR spectrum of **2**. The Dipp protons are split and found at 5.79 ppm–6.45 ppm, hinting at a successful intramolecular insertion. Relevant ^{29}Si NMR shifts are listed in Table 1. We will be referring the silicon atom embedded in the silepin ring as "central Si or $Si_{central}$" and the silicon atom bound to it as "silyl Si or $Si_{silyl\ ligand}$" for convenience. We found identical ^{29}Si shifts of the central silicon atom for related structures **F′** and **1** as well as **J′** and **2** bearing the same imine ligand motif. Thus, the shift of the central Si in the "closed" silepin form seems not to be affected by the silyl ligand modification from hypersilyl to bis(TMS)triphenylsilyl silyl ligand. $Si_{silyl\ ligand}$ in **1** and **2** show typical values in the high field shifted area as a result of the electron-rich environment.

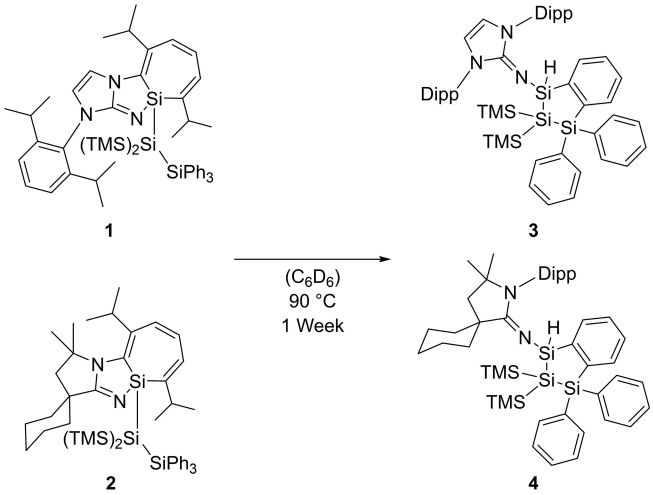
Table 1. ^{29}Si NMR shifts (ppm) of the "central" and "silyl" silicon atom.

Silepin	Si(central)	Si(silyl ligand)
F′	16.1	−135.5
1	16.1	−132.6
J′	17.6	−135.7
2	17.5	−134.1

Research Article
doi.org/10.1002/ejic.202400045

Interestingly, silepins **1** and **2** can selectively undergo a sp^2C–H activation of the aromatic proton in the triphenylsilyl moiety at elevated temperatures, forming the hydrosilane species **3** and **4**, respectively (Scheme 2). Insertions into aliphatic and aromatic C–H bonds of transition metal centers have been known for decades.[15] It is, however, rarely found regarding silylenes. Examples of aliphatic C–H cleavage, inter- or intramolecularly, are reported moderately to date, while aromatic C–H bonds are only cleaved intermolecularly to our knowledge.[16] Due to the previously mentioned purification problems in the synthesis of **1** and **2**, the existing side product, $BrSi(TMS)_2SiPh_3$, could not be successfully removed from **3** and **4** either with the mentioned procedures. Even though the side product stays extensively inactive during the heating process of **1** and **2**, it causes a minor H/Br exchange reaction, forming the respective Si–Br species and $HSi(TMS)_2SiPh_3$. This can be observed in the crystal structure of **4**, whereby a bromide atom with a 2% occupancy is bonding to the Si1 instead of a hydride.

^1H NMR spectra show a proton shift for SiH at 5.23 ppm (**3**) and 6.56 ppm (**4**) with ^{29}Si satellites. Both signals possess an almost identical $^1J_{SiH}$ coupling constant (193.0 Hz for **3**, 190.1 Hz for **4**), which is in a similar range found in related hydrosilane structures **A′**, **B′**, and **E′**. The central silicon atom adjacent to the hydrogen atom is found at a ^{29}Si NMR shift of −35.5 ppm (**3**) and −42.2 ppm (**4**), displaying, once again, particular similarity to each other. In great contrast to **A′**, **B′** and **E′**, no insertion into the *iso*propyl C–H bond of the Dipp moiety was found. Thus, it is noteworthy that a bond cleavage of a sp^2C–H is preferred to the sp^3C–H in case of silepins **1** and **2**. We assume that a highly reactive silylene atom, as well as a steric approximation of an existing phenyl or aryl group bearing an ortho hydrogen, are crucial for this reactivity, which explains why **A**, **B**, and **E** do not display such behaviors due to the lack of suitable functional groups. The final structure of **4** is supported by SC-XRD analysis (Figure 4). We proposed a likewise structure for **3** because of the similar chemical shifts and coupling constants in the ^1H and ^{29}Si NMR spectrum, as discussed above.



Scheme 2. Reaction path to hydrosilanes **3** and **4**.

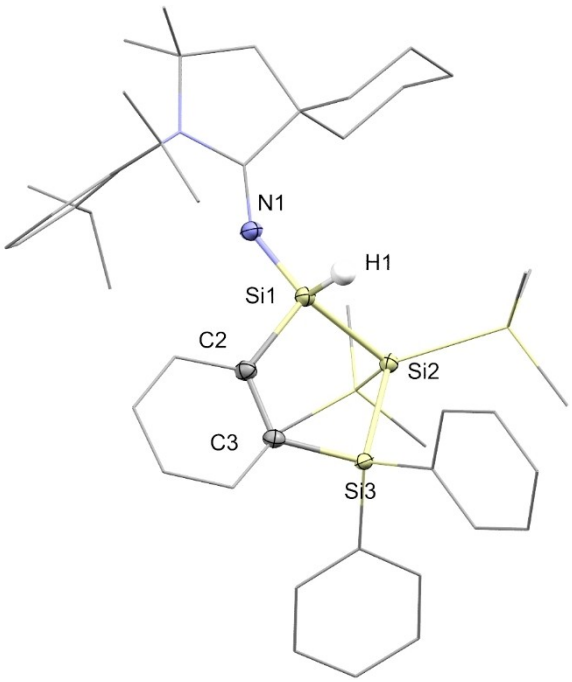


Figure 4. Molecular structure of compound **4** with ellipsoids set at the 50% probability level. The bromide atom (2% occupancy) attached to the Si1 and hydrogen atoms are omitted for clarity. Part of the ^{Cy}cAAC moiety and silyl groups are simplified as wireframes. Selected bond length: Si1–H1 1.402(8) Å, Si1–N1 1.687(2) Å, Si1–Si2 2.3608(8) Å, Si2–Si3 2.3575(9) Å, Si3–C3 1.886(2) Å, C2–C3 1.405(3) Å, Si1–C2 1.891(2) Å. Selected angles: C2–Si1–Si2 99.89(7)°, Si1–Si2–Si3 88.83(3)°, C3–Si3–Si2 102.47(7)°, C2–C3–Si3 119.0(2)°, C3–C2–Si1 120.3(2)°.

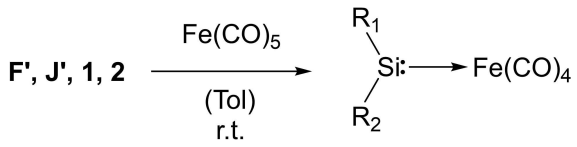
Structures **3** and **4** can be interpreted as the thermodynamically more stable product of the silepin synthesis. This phenomenon also indicates an enhanced stability of **F′**, **J′** in their silepin form compared to **1**, **2** since no activity of **F′**, **J′** in C_6D_6 could be determined even after heating at 90 °C for several days.

$Fe(CO)_4L$ Complexes

As reported by our group beforehand, silepins of this type are commonly known as "masked silylenes", which are able to perform small molecule activation. Therefore, we are also interested in the electronic properties of the respective "open" silylene species of **1** and **2**. For this purpose, the respective iron(0) carbonyl complexes of all silepins (**F′**, **J′**, **1**, **2**) reported by our group were synthesized. We expected the formation of a dative bond, as shown in Scheme 3, due to the previously mentioned silylene reactivity.

The straightforward syntheses at room temperature yielded one sole product each as the reaction outcome (**5**, **6**, **7**, **8**). Thereby, we could successfully remove the inseparable side product ($BrSi(TMS)_2SiPh_3$) derived from the last synthesis step of **1** and **2** by precipitating the final product (**7**, **8**) in cold pentane due to the extensive insolubility of the formed iron complex. The ^{29}Si NMR spectra show a significantly downfield shifted signal for the central Si atom in all complexes (Table 2),

Research Article
doi.org/10.1002/ejic.202400045



5: R_1 = ^{Dipp}NHCN, R_2 = $Si(TMS)_3$
6: R_1 = ^{Cy}cAACN, R_2 = $Si(TMS)_3$
7: R_1 = ^{Dipp}NHCN, R_2 = $Si(TMS)_2SiPh_3$
8: R_1 = ^{Cy}cAACN, R_2 = $Si(TMS)_2SiPh_3$

Scheme 3. Reaction of silepins **F′**, **J′**, **1**, **2** with iron(0)pentacarbonyl to complexes **5**–**8**.

Table 2. Selected analytical data of the respective silylene-iron(0) carbonyl complexes.

Complex	Si(central)	CO vibration bands	Si1–Fe1
5	272.7	2007, 1927, 1876	2.246(1)
6	253.1	2005, 1927, 1881	2.2331(7)
7	273.1	2021, 1953, 1920, 1894	2.2345(5)
8	247.5	2027, 1954, 1926, 1900	2.2574(6)

suggesting a formation of the desired open silylene form and the presence of a dative bond. Additionally, we determined similar shifts of the $Si_{central}$ in complexes with the same imine ligand (**5**, **7**, and **6**, **8**). The deviation in the values is thus solely dependent on the silyl ligand. While the difference in the ^{29}Si shifts in **5** and **7** is almost negligible, we can observe a slightly deshielded silylene atom in **6** compared to **8** under consideration of the standard deviation in ^{29}Si NMR spectra. All newly isolated iron complexes could also be characterized with SC-XRD analysis for definite proof (Figure 5). These structures also implement a successful isolation of **1** and **2**.

Closer investigations of the Fe1–Si1 bond, we can determine values in the range of comparable, literature reported compounds with no deviation from the norm.[17,18]

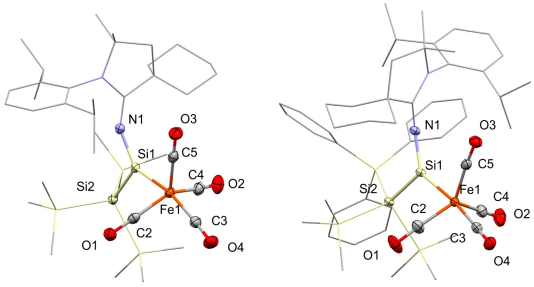


Figure 5. Molecular structure of compound **6** (left) and compound **8** (right) with ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. Part of the ^{Cy}cAAC moiety and the silyl groups are simplified as wireframes. Selected bond length in structure **6**: Fe1–Si1 2.2331(7) Å, Fe1–C2 1.774(2) Å, Fe1–C3 1.795(3) Å, Fe1–C4 1.779(2) Å, Fe1–C5 1.782(3) Å, Si1–Si2 2.3466(9) Å, Si1–N1 1.642(2) Å. Selected angles in structure **6**: N1–Si1–Si2 112.56(7)°, Si1–Fe1–C3 165.42(8)°. Selected bond length in structure **8**: Fe1–Si1 2.2574(7) Å, Fe1–C2 1.768(2) Å, Fe1–C3 1.785(2) Å, Fe1–C4 1.783(2) Å, Fe1–C5 1.800(2) Å, Si1–Si2 2.4038(6) Å, Si1–N1 1.648(2) Å. Selected angles in structure **8**: N1–Si1–Si2 115.04(6)°, Si1–Fe1–C3 172.54(7)°.

To draw conclusions on the electronic properties of the $Si_{central}$ and to compare the donor strength of the silylenes to their lighter congener, we added a conventional NHC (IMe_4) to complexes **7** and **8**. A ligand exchange can't be determined, thus also excluding the route to possibly obtain pure silepin **1** and **2** by releasing the silylene ligand from their iron carbonyl complexes.

Furthermore, we measured IR spectra of all $FeCO_4L$ (L = silylene ligand, Scheme 3). The experimentally determined CO stretching frequencies are all within expected ranges.[18,19] Similar C=O vibrations of complexes **5** and **6** were found, indicating that the imine ligand modification from ^{Dipp}NHC to ^{Cy}cAAC does not seem to have a significant impact on the silylene atom. However, the increased wavenumber of complexes **7** and **8** show an overall slightly reduced donor strength of the silylene atom, most likely deriving from the altered silyl ligand (from $-Si(TMS)_3$ to $-Si(TMS)_2SiPh_3$). This observation is assumed to be caused by the decreased σ-donation of the silyl ligand to the silylene atom after replacing a TMS with a $SiPh_3$ group. The ligand modification simultaneously results in a comparably increased π-acceptance of the silylene atom (due to π-acceptor properties of the phenyl groups in $SiPh_3$), withdrawing electron density from the iron center, leading to higher wavenumbers.[20]

Conclusions

In summary, we have isolated two new silepin structures **1**, **2** bearing a sterically demanding silyl ligand with their inseparable side product $BrSi(TMS)_2SiPh_3$ at room temperature. An intramolecular sp^2C–H cleavage forming the respective hydrosilanes was found in both species at elevated temperatures, which are determined as the thermodynamically more stable product of the silepin synthesis. Furthermore, we isolated the $Fe(CO)_4L$ (L=:SiR_2) complexes of compounds **F′**, **J′**, **1**, **2**. Subsequent infrared spectroscopy showed an overall decreased σ-donation and increased π-acceptance of the silylene atom carrying the modified silyl ligand. The altered electronic effects of the stabilizing ligand from a hypersilyl group to a bis(trimethylsilyl)triphenylsilyl silyl group are assumed to cause the observed wavenumbers in the IR spectra. These findings, therefore, show the notable impact of small and simple ligand modifications in novel low-valent silicon compounds.

Experimental Section

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 prior to use. Deuterated solvents were obtained commercially and were dried over 3 Å molecular sieves prior to use. All NMR samples were prepared under argon in *J. Young* PTFE tubes. $KSi(TMS)_3$, $KSi(TMS)_2SiPh_3$, ^{Dipp}NHC silepin **F′** and ^{Cy}cAAC silepin **J′** were synthesized according to procedures described in the literature.[6,11,14] NMR spectra were recorded on Bruker AV-500C or

AV-400 spectrometers at ambient temperature (300 K) unless otherwise stated. ^{1}H, ^{13}C{H}, and $^{29}Si_{ig}${H} 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, δ = 0 ppm) as external standard. All $^{29}Si_{ig}$ NMR spectra underwent auto baseline correction (*Whittaker* Smoother). FT-IR spectra were recorded on a Vertex 70 from Bruker with a Platinum ATR unit. A solution of the sample in pentane was drop-casted onto the ATR crystal and dried under a stream of nitrogen. 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: ^{Dipp}NHC–$SiBr_3$ (120 mg, 198 mmol, 1.0 eq.) and $KSi(TMS)_2SiPh_3$ (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 compound 1 (135 mg, 156 μmol, 87%) is obtained with its side product $BrSi(TMS)_2SiPh_3$ (81 mg, 155 μmol, 87%) as a 1:1 inseparable mixture. The yield is calculated with the measured mass of the mixture (216 mg). **^{1}H NMR** (500 MHz, C_6D_6): δ [ppm] = 7.80–7.77 (m, 7H, H_{Ph}), 7.76–7.71 (m, 8H, H_{Ph}), 7.18–7.16 (m, 15H, $H_{Ph\ sideproduct}$), 7.16–7.15 (m, 3H, H_{Ar}), 6.63 (d, *J* = 3.2 Hz, 1H, N–C–H), 6.46 (d, *J* = 12.9 Hz, 1H, H_{Ar}), 6.43 (dd, *J* = 6.5, 1.2 Hz, 1H, H_{Ar}), 6.13–6.07 (m, 1H, H_{Ar}), 5.93 (d, *J* = 2.9 Hz, 1H, N–C–H), 3.29–3.13 (m, 2H, C*H*$(CH_3)_2$), 3.04–2.89 (m, 2H, C*H*$(CH_3)_2$), 1.39 (d, *J* = 6.8 Hz, 3H, CH_3), 1.22–1.20 (m, 8H, CH_3), 1.14 (dd, *J* = 6.8, 2.4 Hz, 4H, CH_3), 1.09 (dd, *J* = 6.8, 4.7 Hz, 6H, CH_3), 0.92 (d, *J* = 6.8 Hz, 3H, CH_3), 0.29 (s, 9H, H_{TMS}), 0.23 (s, 9H, H_{TMS}), 0.17 (s, 18H, $H_{TMS\ sideproduct}$). **^{13}C{H} NMR** (126 MHz, C_6D_6): δ [ppm] = 156.81 (C=N), 148.12 (C_{Ar}), 147.04 (C_{Ar}), 144.95 (C_{Ar}), 137.57 (C_{Ar}), 137.43 (C_{Ph}), 136.75 ($C_{Ph\ sideproduct}$), 135.00 ($C_{Ph\ sideproduct}$), 133.68 (C_{Ph}), 130.58 (C_{Ph}), 129.99 ($C_{Ph\ sideproduct}$), 129.45 (C_{Ph}), 129.33 (C_{Ar}), 129.17 (C_{Ar}), 128.57 ($C_{Ph\ sideproduct}$), 128.43 (C_{Ar}), 125.70 (C_{Ar}), 124.20 (C_{Ar}), 124.14 (C_{Ar}), 117.65 (C–N), 110.12 (C–N), 32.00 (*C*H$(CH_3)_2$), 29.37 (*C*H$(CH_3)_2$), 28.81 (CH_3), 28.48 (CH_3), 26.40 (CH_3), 25.84 (CH_3), 25.40 (CH_3), 23.68 (CH_3), 23.27 (CH_3), 22.91 (CH_3), 22.66 (CH_3), 21.31 (CH_3), 3.89 (C_{TMS}), 3.58 (C_{TMS}), 0.03 ($C_{TMS\ sideproduct}$). **^{29}Si{H} NMR** (99 MHz, C_6D_6): δ [ppm] = 16.07 ($Si_{central}$), −8.50 (Si_{TMS}), −9.53 (Si_{TMS}), −9.55 ($SiPh_3$), −11.54 ($Si_{TMS\ sideproduct}$), −20.27 ($Si_{Ph\ sideproduct}$), −26.48 (Br*Si*$(TMS)_2SiPh_3$), −132.58 (*Si*$(TMS)_2SiPh_3$). **LIFDI-MS**: Calculated: m/z = 863.4338; Experimental: m/z = 863.4311 $[\mathbf{1}]^+$ (+ 6.65 ppm error).

Synthesis of 2: ^{Cy}cAAC–$SiBr_3$ (120 mg, 198 μmol, 1.0 eq.) and $KSiTMS_2SiPh_3$ (187 mg, 396 μmol, 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 compound 2 (139 mg, 173 μmol, 88%) is obtained with its side product $BrSiTMS_2SiPh_3$ (88.8 mg, 173 μmol, 88%) as a 1:1 inseparable mixture. The yield is calculated with the measured mass of the mixture (227 mg). **^{1}H NMR** (500 MHz, C_6D_6): δ [ppm] = 7.86–7.70 (m, 15H, $H_{Ph\ sideproduct}$), 7.26–7.22 (m, 6H, H_{Ph}), 7.21–7.17 (m, 5H, H_{Ph}), 7.14 (d, *J* = 5.6 Hz, 4H, H_{Ph}), 6.43 (d, J = 13.1 Hz, 1H, H_{Ar}), 6.31 (d, *J* = 5.8 Hz, 1H, H_{Ar}), 5.81 (dd, *J* = 13.5, 5.4 Hz, 1H, H_{Ar}), 3.26 (h, *J* = 6.8 Hz, 1H, C*H*$(CH_3)_2$), 2.76 (hept, *J* = 7.2, 6.7 Hz, 1H, C*H*$(CH_3)_2$), 2.09 (d, *J* = 17.7 Hz, 3H, H_{Cy}), 1.86–1.77 (m, 2H, CH), 1.73–1.65 (m, 2H, H_{Cy}), 1.57 (dd, *J* = 13.1, 2.4 Hz, 2H, H_{Cy}), 1.50 (s, 3H, H_{Cy}), 1.28–1.23 (m, 9H, CH_3), 1.08 (d, *J* = 6.8 Hz, 3H, CH_3), 1.01 (d, J = 5.0 Hz, 3H, CH_3), 1.00 (d, J = 5.2 Hz, 3H, CH_3), 0.34 (s, 9H, H_{TMS}), 0.29 (s, 9H, H_{TMS}), 0.15 (s, 18H, $H_{TMS\ sideproduct}$). **^{13}C{H} NMR** (126 MHz, C_6D_6): δ [ppm] = 179.90 (C=N), 144.99 (C_{Ar}), 137.52 ($C_{Ph\ sideproduct}$), 136.75 ($C_{Ph\ sideproduct}$), 135.00 (C_{Ph}), 134.29 (C_{Ph}), 133.65 (C_{Ar}), 129.99 ($C_{Ph\ sideproduct}$), 129.32 (C_{Ph}), 129.13 (C_{Ph}), 128.75 (C_{Ph}), 128.57 (C_{Ar}), 128.43 ($C_{Ph\ sideproduct}$), 125.70 (C_{Ar}), 124.54 (C_{Ar}), 58.54 (C–N), 52.87 (*C*–C–N), 42.40 (*C*–C=N), 37.24 (C_{Cy}), 37.15 (C_{Cy}), 32.24 (C_{Cy}), 31.26 (C_{Cy}), 30.88 (*C*H$(CH_3)_2$), 29.20 (*C*H$(CH_3)_2$), 26.14 (C_{Cy}), 25.70 (CH_3), 22.97 (CH_3), 22.83 (CH_3), 22.77 (CH_3), 21.94 (CH_3), 21.30 (CH_3), 3.92 (C_{TMS}), 3.85 (C_{TMS}), 0.04 ($C_{TMS\ sideproduct}$). **^{29}Si{H} NMR** (99 MHz, C_6D_6): δ [ppm] = 17.53 ($Si_{central}$), −8.48 (Si_{TMS}), −8.54 (Si_{TMS}), −9.48 (Si_{Ph}), −11.54 ($Si_{TMS\ sideproduct}$), −20.28 ($Si_{Ph\ sideproduct}$), −26.50 (Br*Si*$(TMS)_2SiPh_3$), −134.08 (*Si*$(TMS)_2SiPh_3$). **LIFDI-MS**: Calculated: m/z = 800.4229; Experimental: m/z = 800.4213 $[\mathbf{2}]^+$ (+ 1.99 ppm Error).

Synthesis of 3: A solution of a 1:1 mixture of **1** and $BrSi(TMS)_2SiPh_3$ (33 mg) in C_6D_6 is heated to 90 °C for 1 week, forming the intramolecular insertion product 3 in quantitative yield. **^{1}H NMR** (400 MHz, C_6D_6) δ 7.87–7.83 (m, 3H, H_{Ar}), 7.81–7.62 (m, 9H, H_{Ph}), 7.58–7.53 (m, 2H, H_{Ar}), 7.35 (td, *J* = 7.4, 1.2 Hz, 1H, H_{Ar}), 7.24–7.16 (m, 10H, $H_{Ph\ sideproduct}$), 7.15–7.11 (m, 5H, $H_{Ph\ sideproduct}$), 7.11–7.06 (m, 6H, H_{Ph}), 6.05 (s, 2H, N–C–H), 5.23 (s, 1H, with ^{29}Si satellites ^{1}J(SiH) = 193.0 Hz, SiH), 3.31 (hept, *J* = 6.7 Hz, 4H, C*H*$(CH_3)_2$), 1.31 (dd, *J* = 6.8, 1.8 Hz, 12H, CH_3), 1.19 (dd, *J* = 6.9, 2.3 Hz, 12H, CH_3), 0.16 (s, 18H, $H_{TMS\ sideproduct}$), 0.14 (s, 9H, H_{TMS}), −0.14 (s, 9H, H_{TMS}). **^{13}C{H} NMR** (101 MHz, C_6D_6): δ [ppm] = 153.78 (C=N), 148.06 ($C_{Ar,\ Si\text{-}ring}$), 147.52 ($C_{Ar,\ Si\text{-}ring}$), 146.67 ($C_{Ar,\ Si\text{-}ring}$), 145.14 ($C_{Ar,\ Si\text{-}ring}$), 138.59 ($C_{Ar,\ Si\text{-}ring}$), 137.73 ($C_{Ar,\ Si\text{-}ring}$), 136.88 ($H_{Ph\ sideproduct}$), 136.76 (C_{Ar}), 136.53 (C_{Ar}), 136.44 (C_{Ph}), 135.03 ($H_{Ph\ sideproduct}$), 134.89 (C_{Ph}), 134.79 (C_{Ph}), 134.53 (C_{Ph}), 129.99 ($H_{Ph\ sideproduct}$), 129.65 (C_{Ph}), 129.34 (C_{Ph}), 129.01 (C_{Ph}), 128.65 (C_{Ph}), 128.43 ($H_{Ph\ sideproduct}$), 124.30 (C_{Ar}), 124.15 (C_{Ar}), 115.04 (C–N), 29.06 (*C*H$(CH_3)_2$), 29.02 (*C*H$(CH_3)_2$), 25.66 (CH_3), 25.11 (CH_3), 23.84 (CH_3), 23.78 (CH_3), 2.60 (C_{TMS}), 2.46 (C_{TMS}), 0.05 ($C_{TMS\ sideproduct}$). **^{29}Si{H} NMR** (99 MHz, C_6D_6): δ [ppm] = −4.60 (Si_{TMS}), −9.01 (Si_{TMS}), −10.11 ($SiPh_3$), −11.54 ($Si_{TMS\ sideproduct}$), −20.27 ($Si_{Ph\ sideproduct}$), −26.49 (Br*Si*$(TMS)_2SiPh_3$), −35.48 ($Si_{central}$), −134.67 (*Si*$(TMS)_2SiPh_3$). **LIFDI-MS**: Calculated: m/z = 863.4338; Experimental: m/z = 863.4261 $[\mathbf{3}]^+$ (+ 12.45 ppm error).

Synthesis of 4: A solution of a 1:1 mixture of **2** and $BrSi(TMS)_2SiPh_3$ (33 mg) in C_6D_6 is heated to 90 °C for 1 week, forming the intramolecular insertion product **4** in quantitative yield. **^{1}H NMR** (400 MHz, C_6D_6): δ [ppm] = 7.96–7.92 (m, 2H, H_{Ar}), 7.81–7.68 (m, 10H, $H_{Ph,\ sideproduct}$), 7.34 (t, J = 7.7 Hz, 1H, H_{Ar}), 7.27–7.22 (m, 3H, $H_{Ph,\ sideproduct}$), 7.22–7.19 (m, 2H, $H_{Ph,\ sideproduct}$), 7.19–7.16 (m, 5H, H_{Ph}), 7.15–7.01 (m, 8H, H_{Ph}), 6.92–6.88 (m, 1H, H_{Ph}), 6.56 (s, 1H, with ^{29}Si satellites ^{1}J(SiH) = 190.1 Hz, SiH), 3.14 (m, 2H, C*H*$(CH_3)_2$), 2.26–2.13 (m, 2H, CH_2), 2.12 (s, 1H, H_{Cy}), 1.94–1.73 (m, 3H, H_{Cy}), 1.70–1.58 (m, 4H, H_{Cy}), 1.51–1.38 (m, 2H, H_{Cy}), 1.29–1.23 (m, 10H, CH_3), 1.13 (d, J = 6.7 Hz, 3H, CH_3), 1.07 (d, J = 9.6 Hz, 6H, CH_3), 0.41 (s, 9H, H_{TMS}), 0.16 (s, 18H, $H_{TMS\ sideproduct}$), 0.05 (s, 9H, H_{TMS}). **^{13}C{H} NMR** (101 MHz, C_6D_6): δ [ppm] = 169.94 (C=N), 152.56 ($C_{Ar,\ Si\text{-}ring}$), 149.60 ($C_{Ar,\ Si\text{-}ring}$), 149.12 ($C_{Ar,\ Si\text{-}ring}$), 144.10 ($C_{Ar,\ Si\text{-}ring}$), 138.83 ($C_{Ar,\ Si\text{-}ring}$), 137.33 ($C_{Ar,\ Si\text{-}ring}$), 137.01 (C_{Ph}), 136.88 (C_{Ph}), 136.76 ($C_{Ph\ sideproduct}$), 136.42 (C_{Ph}), 135.79 (C_{Ph}), 135.03 ($C_{Ph\ sideproduct}$), 134.45 (C_{Ph}), 134.26 (C_{Ar}), 129.99 ($C_{Ph\ sideproduct}$), 129.34 (C_{Ar}), 129.24 (C_{Ph}), 128.88 (C_{Ph}), 128.57 ($C_{Ph\ sideproduct}$), 125.70 (C_{Ar}), 124.75 (C_{Ph}), 124.62 (C_{Ar}), 61.00 (C–N), 48.22 (*C*–C–N), 47.20 (*C*–C=N), 36.63 (C_{Cy}), 35.96 (C_{Cy}), 30.92 (C_{Cy}), 29.47 (C_{Cy}), 29.30 (*C*H$(CH_3)_2$), 29.19 (*C*H$(CH_3)_2$), 27.95 (C_{Cy}), 26.77 (CH_3), 25.41 (CH_3), 23.84 (CH_3), 23.74 (CH_3), 22.72 (CH_3), 22.49 (CH_3), 2.81 (C_{TMS}), 2.78 (C_{TMS}), 0.05 ($C_{TMS\ sideproduct}$). **^{29}Si{H} NMR** (99 MHz, C_6D_6): δ [ppm] = −6.64 (Si_{TMS}), −8.94 (Si_{TMS}), −10.56 ($SiPh_3$), −11.54 ($Si_{TMS\ sideproduct}$), −20.28 ($Si_{Ph\ sideproduct}$), −26.49 (Br*Si*$(TMS)_2SiPh_3$), −42.19 ($Si_{central}$), −129.29 (*Si*$(TMS)_2SiPh_3$). **LIFDI-MS**: Calculated: m/z = 800.4229; Experimental: m/z = 800.4114 $[\mathbf{4}]^+$ (+ 14.36 ppm error).

Synthesis of 5: $FeCO_5$ (8.00 μL, 59.0 μmol, 2.0 eq.) was added to a solution of ^{Dipp}NHC silepin **F'** (20.0 mg, 29.5 μmol, 1.0 eq.) in toluene (1 mL). The mixture was stirred at r.t. for 16 h. The solvent was completely evaporated in *vacuo* to afford the product as an orange oil (18.3 mg, 73%). **^{1}H NMR** (500 MHz, C_6D_6): δ [ppm] = 7.22–7.17 (m, 4H, H_{Ar}), 7.07 (dd, *J* = 7.4, 2.0 Hz, 2H, H_{Ar}), 6.09 (s, 2H, N–C–H), 3.85 (h, *J* = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 2.82 (hept, *J* = 6.8 Hz, 2H, C*H*$(CH_3)_2$),

1.57 (d, J = 6.7 Hz, 6H, CH_3), 1.30 (d, J = 6.7 Hz, 6H, CH_3), 1.11 (d, J = 6.7 Hz, 6H, CH_3), 0.98 (d, J = 6.7 Hz, 6H, CH_3), 0.22 (s, 27H, H_{TMS}). **^{13}C{H} NMR** (126 MHz, C_6D_6): δ [ppm] = 215.58 (CO), 152.56 (C═N), 148.33 (C_{Ar}), 146.42 (C_{Ar}), 133.53 (C_{Ar}), 130.66 (C_{Ar}), 129.33 (C_{Ar}), 125.70 (C_{Ar}), 125.14 (C_{Ar}), 124.40 (C_{Ar}), 118.19 (CH–N), 28.77 (CH_3), 28.61 (CH_3), 26.54 (CH_3), 26.27 (CH_3), 23.39 (CH_3), 23.15 (CH_3), 2.96 (C_{TMS}). **^{29}Si{H} NMR** (80 MHz, C_6D_6): δ = 272.72 (Si:), −9.45 (TMS), −92.89 (*Si*(TMS)$_3$). **LIFDI-MS**: Calculated: m/z = 845.3014; Experimental: m/z = 845.2930 [**5**]$^+$ (+9.93 ppm error). **IR (cm^{-1})**: 2958 (m), 2892 (m), 2006 (s), 1906 (s), 1875 (s), 1524 (s), 1457 (m), 1243 (s), 1034 (m), 825 (s).

Synthesis of 6: $FeCO_5$ (9.95 μL, 97.5 μmol, 2.0 eq.) was added to a solution of ^{Cy}cAAC silepin **J** (30 mg, 48.7 μmol, 1.0 eq.) in toluene (1 mL). The mixture was stirred at r.t. for 10 days. The solvent was completely evaporated in *vacuo* to afford the product as an orange oil (33 mg, 91 %). **^{1}H NMR** (400 MHz, C_6D_6) δ [ppm] = 7.15–7.12 (m, 2H, H_{Ar}), 6.99 (dd, J = 5.4, 4.0 Hz, 1H, H_{Ar}), 3.43 (hept, J = 6.4 Hz, 1H, C*H*(CH_3)$_2$), 2.97 (hept, J = 6.7 Hz, 1H, C*H*(CH_3)$_2$), 2.30 (td, J = 13.1, 3.9 Hz, 1H, CH_2), 2.25–2.17 (m, 1H, H_{Cy}), 1.91 (td, J = 13.1, 3.7 Hz, 1H, CH_2), 1.86–1.55 (m, 7H, H_{Cy}), 1.50 (d, J = 6.6 Hz, 3H, CH_3), 1.42–1.26 (m, 2H, H_{Cy}), 1.22 (d, J = 6.6 Hz, 3H, CH_3), 1.16–1.11 (m, 9H, CH_3), 0.88 (s, 3H, CH_3), 0.34 (s, 27H, H_{TMS}). **^{13}C{H} NMR** (101 MHz, C_6D_6): δ [ppm] = 215.11 (CO), 170.92 (C═N), 149.30 (C_{Ar}), 147.30 (C_{Ar}), 131.17 (C_{Ar}), 129.03 (C_{Ar}), 125.46 (C_{Ar}), 124.41 (C_{Ar}), 65.35 (C–N), 49.31 (*C*–C–N), 44.86 (*C*–C═N), 39.49 (C_{Cy}), 32.87 (C_{Cy}), 31.17 (C_{Cy}), 29.24 (C_{Cy}), 28.98 (*C*H(CH_3)$_2$), 28.76 (*C*H(CH_3)$_2$), 28.51 (C_{Cy}), 27.35 (CH_3), 25.11 (CH_3), 24.30 (CH_3), 23.25 (CH_3), 22.33 (CH_3), 22.02 (CH_3), 3.16 (C_{TMS}). **^{29}Si{H} NMR** (99 MHz, C_6D_6) δ [ppm] = 253.11 (Si:), −9.73 (Si_{TMS}), −94.15 (*Si*(TMS)$_3$). **LIFDI-MS**: Calculated: m/z = 782.2905; Experimental: m/z = 782.2835 [**6**]$^+$ (+8.94 ppm error). **IR (cm^{-1})**: 2950 (w), 2890 (m), 2005 (s), 1921 (s), 1881 (s), 1436 (s), 1242 (s), 824 (s).

Synthesis of 7: $FeCO_5$ (5.90 μL, 43.5 μmol, 2.0 eq.) was added to an inseparable mixture (30 mg) of ^{Dipp}NHC silepin-$SiPh_3$ **1** (18.8 mg, 21.8 μmol, 1.0 eq.) and $BrSi(TMS)_2SiPh_3$ (11.2 mg) in toluene (1 mL). The mixture was stirred at r.t. for 16 h. The solvent was completely evaporated in *vacuo* and the remains dissolved in pentane to precipitate pure complex **7**. After centrifugation and separation of the solvent, the product is dried in vacuo to afford a yellow solid (11.2 mg, 50 %). **^{1}H NMR** (500 MHz, C_6D_6): δ [ppm] = 7.82–7.79 (m, 6H, H_{Ar}), 7.24–7.16 (m, 13H, H_{Ph}), 7.05 (m, 2H, H_{Ph}), 6.10 (s, 2H, CH–N), 3.97 (hept, J = 6.7 Hz, 2H, C*H*(CH_3)$_2$), 2.81 (hept, J = 6.7 Hz, 2H, C*H*(CH_3)$_2$), 1.61 (d, J = 6.7 Hz, 6H, CH_3), 1.28 (d, J = 6.7 Hz, 6H, CH_3), 1.13 (d, J = 6.7 Hz, 6H, CH_3), 0.97 (d, J = 6.6 Hz, 6H, CH_3), 0.01 (s, 18H, H_{TMS}). **^{13}C{H} NMR** (126 MHz, C_6D_6): δ [ppm] = 215.42 (CO), 153.18 (C═N), 148.38 (C_{Ar}), 146.69 (C_{Ar}), 137.60 (C_{Ar}), 136.27 (C_{Ar}), 133.82 (C_{Ar}), 130.72 (C_{Ar}), 129.60 (C_{Ph}), 127.95 (C_{Ph}), 125.04 (C_{Ph}), 124.54 (C_{Ph}), 118.49 (CH–N), 28.77 (*C*H(CH_3)$_2$), 28.75 ((*C*H(CH_3)$_2$), 26.69 (CH_3), 26.53 (CH_3), 23.17 (CH_3), 23.02 (CH_3), 3.48 (C_{TMS}). **^{29}Si{H} NMR** (99 MHz, C_6D_6): δ [ppm] = 273.09 (Si:), −8.76 (Si_{TMS}), −9.85 ($SiPh_3$), −94.41 (*Si*(TMS)$_2$$SiPh_3$). **LIFDI-MS**: Calculated: m/z = 1031.3484; Experimental: m/z = 1031.3546 [**7**]$^+$ (−6.01 ppm error). **Melting point**: 206.6 °C. **IR (cm^{-1})**: 3084 (w), 2958 (s), 2921 (s), 2021 (s), 1953 (s), 1919 (s), 1983 (s), 1548 (s), 1461 (m), 1244 (s), 1104 (s), 834 (s).

Synthesis of 8: $FeCO_5$ (6.10 μL, 44.9 μmol, 2.0 eq.) was added to an inseparable mixture (30 mg) of ^{Cy}cAAC silepin–$SiPh_3$ **2** (18.0 mg, 22.5 μmol, 1.0 eq.) and $BrSi(TMS)_2SiPh_3$ (12 mg) in toluene (1 mL). The mixture was stirred at r.t. for 16 h. The solvent was completely evaporated in *vacuo*, and the remains were dissolved in pentane to precipitate pure complex **8**. After centrifugation and separation of the solvent, the product is dried in vacuo to afford a yellow solid (12.7 mg, 58 %). **^{1}H NMR** (400 MHz, C_6D_6): δ [ppm] = 7.78–7.72 (m, 6H, H_{Ph}), 7.15–7.10 (m, 9H, H_{Ph}), 7.08 (d, J = 4.6 Hz, 1H, H_{Ar}), 7.05 (d, J = 7.8 Hz, 1H, H_{Ar}), 6.73 (dd, J = 7.4, 2.0 Hz, 1H, H_{Ar}), 3.51 (hept, J = 6.2 Hz, 1H, C*H*(CH_3)$_2$), 2.61 (hept, J = 6.9 Hz, 1H, C*H*(CH_3)$_2$), 2.37–2.20 (m, 2H, CH_2), 1.93–1.75 (m, 4H, H_{Cy}), 1.69–1.51 (m, 6H, H_{Cy}), 1.25 (d, J = 6.6 Hz, 6H, CH_3), 1.07 (s, 3H, CH_3), 0.91 (d, J = 6.8 Hz, 3H, CH_3), 0.77 (s, 3H, CH_3), 0.37 (s, 9H, H_{TMS}), 0.30 (s, 9H, H_{TMS}). **^{13}C{H} NMR** (126 MHz, C_6D_6): δ [ppm] = 215.83 (CO), 171.95 (C═N), 149.22 (C_{Ar}), 147.94 (C_{Ar}), 137.79 (C_{Ar}), 137.38 (C_{Ar}), 137.16 (C_{Ar}), 131.22 (C_{Ar}), 129.69 (C_{Ph}), 129.41 (C_{Ph}), 125.29 (C_{Ph}), 124.74 (C_{Ph}), 65.83 (C–N), 49.95 (*C*–C–N), 44.82 (*C*–C═N), 38.80 (C_{Cy}), 33.30 (C_{Cy}), 31.46 (C_{Cy}), 30.08 (C_{Cy}), 29.09 (*C*H(CH_3)$_2$), 28.92 (*C*H(CH_3)$_2$), 28.03 (C_{Cy}), 27.66 (CH_3), 24.86 (CH_3), 24.39 (CH_3), 23.08 (CH_3), 22.63 (CH_3), 22.39 (CH_3), 4.36 (C_{TMS}), 3.90 (C_{TMS}). **^{29}Si{H} NMR** (99 MHz, C_6D_6): δ [ppm] = 247.45 (Si:), −7.41 (Si_{TMS}), −7.79 (Si_{TMS}), −8.35 ($SiPh_3$), −95.69 (*Si*-(TMS)$_2$$SiPh_3$). **LIFDI-MS**: Calculated: m/z = 968.3375; Experimental: m/z = 968.3386 [**8**]$^+$ (−1.14 ppm error). **Melting point**: 216.2 °C. **IR (cm^{-1})**: 3200–3068 (w), 2959 (s), 2927 (m), 2859 (s), 2026 (s), 1953 (s), 1925 (s), 1900 (s), 1600 (s), 1459 (m), 1428 (s), 1243 (s), 1104 (s), 833 (s), 737 (s).

Supporting Information

More experimental details for all newly synthesized compounds and single crystallographic data can be found in the Supporting Information (SI). The authors have cited additional references within the SI.[21–28] CCDC: Deposition Numbers 2324672 (for **4**), 2324673 (for **5**), 2324675 (for **6**), 2324674 (for **7**), 2324676 (for **8**) 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.

Acknowledgements

All authors want to express their appreciation towards Franziska Hanusch for the guidance on the SC-XRD analyses and Fabrizio E. Napoli for the LIFDI-MS measurements. Furthermore, we want to thank Martin E. Doleschal for the scientific discussions. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: low-valent · silylenes · silepins · main group · silicon

[1] a) S. Fujimori, S. Inoue, *Eur. J. Inorg. Chem.* **2020**, *2020*, 3131; b) C. Shan, S. Yao, M. Driess, *Chem. Soc. Rev.* **2020**, *49*, 6733; c) L. Wang, Y. Li, Z. Li, M. Kira, *Coord. Chem. Rev.* **2022**, *457*, 214413.
[2] a) S. Fujimori, S. Inoue, *Commun. Chem.* **2020**, *3*, 175; b) D. Reiter, R. Holzner, A. Porzelt, P. Frisch, S. Inoue, *Nat. Chem.* **2020**, *12*, 1131; c) P. P. Power, *Nature* **2010**, *463*, 171; d) M. M. D. Roy, M. J. Ferguson, R.

McDonald, Y. Zhou, E. Rivard, *Chem. Sci.* **2019**, *10*, 6476; e) M. M. D. Roy, S. R. Baird, E. Dornsiepen, L. A. Paul, L. Miao, M. J. Ferguson, Y. Zhou, I. Siewert, E. Rivard, *Chem. Eur. J.* **2021**, *27*, 8572..
[3] H. Zhu, S. Fujimori, A. Kostenko, S. Inoue, *Chem. Eur. J.* **2023**, *29*, e202301973.
[4] Y. Xiong, S. Yao, M. Driess, *Chem. Eur. J.* **2009**, *15*, 5545.
[5] a) A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2012**, *134*, 6500; b) A. V. Protchenko, A. D. Schwarz, M. P. Blake, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *Angew. Chem. Int. Ed.* **2013**, *52*, 568; c) H. Zhu, A. Kostenko, D. Franz, F. Hanusch, S. Inoue, *J. Am. Chem. Soc.* **2023**, *145*, 1011.
[6] D. Wendel, A. Porzelt, F. A. D. Herz, D. Sarkar, C. Jandl, S. Inoue, B. Rieger, *J. Am. Chem. Soc.* **2017**, *139*, 8134.
[7] a) A. Kostenko, S. Inoue, *Chem* **2023**, *9*, 3022; b) T. Ochiai, D. Franz, S. Inoue, *Chem. Soc. Rev.* **2016**, *45*, 6327.
[8] D. Wendel, D. Reiter, A. Porzelt, P. J. Altmann, S. Inoue, B. Rieger, *J. Am. Chem. Soc.* **2017**, *139*, 17193.
[9] M. Ludwig, D. Franz, A. Espinosa Ferao, M. Bolte, F. Hanusch, S. Inoue, *Nat. Chem.* **2023**, *15*, 1452.
[10] T. Eisner, A. Kostenko, F. Hanusch, S. Inoue, *Chem. Eur. J.* **2022**, *28*, e202202330.
[11] J. Y. Liu, T. Eisner, S. Inoue, B. Rieger, *Eur. J. Inorg. Chem.* **2024**, *27*, e202300568.
[12] a) R. Jazzar, M. Soleilhavoup, G. Bertrand, *Chem. Rev.* **2020**, *120*, 4141; b) J. T. Goettel, H. Gao, S. Dotzauer, H. Braunschweig, *Chem. Eur. J.* **2020**, *26*, 1136.
[13] a) Y. K. Loh, M. Melaimi, M. Gembicky, D. Munz, G. Bertrand, *Nature* **2023**, *623*, 66; b) Y. K. Loh, M. Melaimi, D. Munz, G. Bertrand, *J. Am. Chem. Soc.* **2023**, *145*, 2064; c) E. Welz, J. Böhnke, R. D. Dewhurst, H. Braunschweig, B. Engels, *J. Am. Chem. Soc.* **2018**, *140*, 12580; d) Y. K. Loh, L. Gojiashvili, M. Melaimi, M. Gembicky, D. Munz, G. Bertrand, *Nat. Synth* **2024**, *3*, 727..
[14] a) C. Kayser, R. Fischer, J. Baumgartner, C. Marschner, *Organometallics* **2002**, *21*, 1023; b) P. Schmidt, S. Fietze, C. Schrenk, A. Schnepf, *Z. Anorg. Allg. Chem.* **2017**, *643*, 1759.
[15] a) S. Hashimoto, N. Watanabe, S. Ikegami, *Chem. Commun.* **1992**, *20*, 1508; b) I. Hussain, T. Singh, *Adv. Synth. Catal.* **2014**, *356*, 1661; c) F. Neve, M. Ghedini, A. Tiripicchio, F. Ugozzoli, *Inorg. Chem.* **1989**, *28*, 3084.
[16] a) A. Jana, P. P. Samuel, G. Tavcar, H. W. Roesky, C. Schulzke, *J. Am. Chem. Soc.* **2010**, *132*, 10164; b) S. Takahashi, E. Bellan, A. Baceiredo, N. Saffon-Merceron, S. Massou, N. Nakata, D. Hashizume, V. Branchadell, T. Kato, *Angew. Chem. Int. Ed.* **2019**, *58*, 10310; c) R. H. Walker, K. A. Miller, S. L. Scott, Z. T. Cygan, J. M. Bartolin, J. W. Kampf, M. M. Banaszak Holl, *Organometallics* **2009**, *28*, 2744.
[17] a) B. Blom, M. Pohl, G. Tan, D. Gallego, M. Driess, *Organometallics* **2014**, *33*, 5272; b) G. Dübek, F. Hanusch, S. Inoue, *Inorg. Chem.* **2019**, *58*, 15700; c) C. Eisenhut, T. Szilvási, G. Dübek, N. C. Breit, S. Inoue, *Inorg. Chem.* **2017**, *56*, 10061; d) R. S. Ghadwal, R. Azhakar, K. Pröpper, J. J. Holstein, B. Dittrich, H. W. Roesky, *Inorg. Chem.* **2011**, *50*, 8502; e) W. Yang, H. Fu, H. Wang, M. Chen, Y. Ding, H. W. Roesky, A. Jana, *Inorg. Chem.* **2009**, *48*, 5058.
[18] A. Saurwein, T. Eisner, S. Inoue, B. Rieger, *Organometallics* **2022**, *41*, 3679.
[19] a) P. Frisch, T. Szilvási, A. Porzelt, S. Inoue, *Inorg. Chem.* **2019**, *58*, 14931; b) D. Lutters, C. Severin, M. Schmidtmann, T. Müller, *J. Am. Chem. Soc.* **2016**, *138*, 6061.
[20] a) E. W. Abel, F. G. A. Stone, *Chem. Soc.* **1969**, *23*, 325; b) L. E. Orgel, *Inorg. Chem.* **1962**, *1*, 25.
[21] *APEX suite of crystallographic software*, APEX 3, Version 2019-1.0, Bruker AXS Inc., Madison, Wisconsin, USA, **2019**.
[22] *SAINT*, Version 8.40 A and *SADABS*, Version 2016/2, Bruker AXS Inc., Madison, Wisconsin, USA, **2016**/**2019**.
[23] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3.
[24] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3.
[25] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281–1284.
[26] *International Tables for Crystallography, Vol. C* (Ed.: A. J. Wilson), Kluwer Academic Publishers, Dordrecht, The Netherlands, **1992**, Tables 6.1.1.4 (pp. 500–502), 4.2.6.8 (pp. 219–222), and 4.2.4.2 (pp. 193–199).
[27] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J. Appl. Crystallogr.* **2008**, *41*, 466.
[28] A. L. Spek, *Acta Crystallogr. Sect. D* **2009**, *65*, 148.

Manuscript received: January 23, 2024
Revised manuscript received: May 16, 2024
Accepted manuscript online: May 20, 2024
Version of record online: June 28, 2024