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De- and Rearomatisation of Pyridine in Silylene Chemistry

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Traditional methods relying on metal-ligand cooperation for activating pyridine bonds in de- and rearomatisation are being challenged by the abundant metal-free element species as alternatives. Here, we investigated the de/re-aromatisation of pyridine facilitated by pyridylamino-functionalised silylene reactions with ketones and ketene. The reactivity outcome is highly dependent on the substituents on the ketones. By carefully tuning the steric demand of the ketone, each intermediate of the reaction sequence could be isolated. At room temperature, benzophenone and acetophenone substrates led to dearomatisation of the pyridine moiety, with the case of acetophenone showing an intermediate silaoxirane preceding dearomatisation. However, when subjected to acetone or diphenylketene, only silaoxiranes were formed without dearomatisation of the pyridine moiety. Notably, only benzophenone-derived dearomatised species demonstrated rearomatisation upon heating. Furthermore, the reduced steric bulk of the ketene facilitated further ring expansion with another equivalent of the substrate, forming sila-1,3-dioxolanes. Both steric hindrance and aromatic groups collectively influence the dearomatisation of pyridine in pyridylaminosilylene reactions.

Introduction

As one of the representatives of aromatic heterocyclic species, pyridine and its derivatives are ubiquitous in numerous natural and synthetic compounds. Besides being frequently utilised structure motifs in agrochemicals, drugs and functional materials,[1] they also play dominant roles acting as ligands in coordination chemistry and catalysis.[2] Dearomatisation of pyridines can convert the aromatic pyridines to partially saturated structure motifs that are important N-containing ring systems for further applications.[3] For example, dihydropyridines are widely used building blocks for pharmaceutical compounds.[4] Hence, the development of efficient dearomatisation pathways that enable the construction of such N-heterocycles is of particular interest. However, the direct functionalisation and dearomatisation of pyridines remain particularly challenging due to the low energy of the aromatic π-system. Dearomatisation and consequent rearomatisation of pyridine moieties in a chemical reaction have been previously documented.[5] One of the benchmark systems is Milstein's pyridine-based PNP and PNN pincer-type transition metal complexes.[6] In these examples, deprotonation by a base at benzylic carbon led to dearomatisation of the pyridine ring. Metal-ligand cooperativity can further lead to bond activation, resulting in rearomatisation of the pyridine moiety (Figure 1).

Traditionally, these bond activation processes in the de- and rearomatisation are facilitated by metal-ligand cooperation. The use of abundant p-block element species as substitutes for transition metal systems has garnered significant attention in recent years.[7] This focus emphasizes the pursuit of environmentally benign metal-free catalysts as substitutes for transition metal-based catalysts. In the past three decades, there have been big strides in developing isolable divalent silicon species (silylenes), which show interesting reactivity with small molecules and could be useful for metal-free catalysis.[8]

While the reactivity of silylenes towards ketones has been investigated previously,[9] the chemistry with ketenes has remained largely unexplored. Notably, the dearomatisation of pyridine moieties in the silylene chemistry is still rare. For instance, this was observed when a β-diketiminate-functionalised silylene was reacted with benzolylpyridine.[19] However, no rearomatisation of the pyridine was observed in this case. In silicon chemistry, one example involving de/rearomatisation of pyridine was reported by Kato. The reaction of a 1-silaketene undergoes a [2+2] cycloaddition with the solvent pyridine, yielding a sila-β-lactam due to the presence of a reactive Si=O

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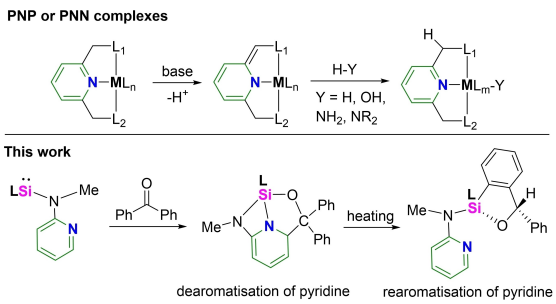


Figure 1. Typical LNL pincer compounds involving de/rearomatisation system of pyridine and this work.

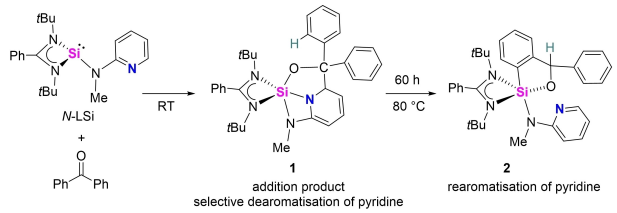
unit.[10] This sila-β-lactam further reacts with benzaldehyde at high temperature, releasing pyridine.

In this work, we showcase our findings regarding the dearomatisation and rearomatisation pathways based on a pyridylamino-functionalised silylene *N*-LSi (N=*N*-methyl-2-pyridinamine, L=PhC(N*t*Bu)$_2$),[11] which can of course also be viewed as silylenylamino-functionalised pyridine. The silylene is reacted with different ketones and diphenylketene, depending on the substituents, the observed reactivity is distinct. By carefully tuning the steric demand of the ketone, each intermediate of the reaction sequence could be isolated and characterised by single crystal X-ray diffraction.

Results and Discussion

As an initial experiment, the reaction between benzophenone and the silylene *N*-LSi was examined (Scheme 1). Interestingly, according to ^{1}H NMR spectroscopy, immediately a clean reaction occurred, leading to the selective formation of a single reaction product **1** with immense highfield-shift of the pyridine proton signals (6.33, 5.35, 4.83, 4.64 ppm). The latter three signals are rather in the typical range of alkene protons than classical aromatic ones.[12] In the ^{29}Si{^{1}H} NMR spectrum, the singlet signal was detected at −94.0 ppm, which is shifted to lower frequencies compared to the silylene *N*-LSi (−12.0 ppm).[11]

Compound **1** was crystallised from a concentrated THF solution (85% yield) at room temperature and its molecular structure was analysed by single crystal X-ray diffraction experiments (Figure 2). A prominent structural feature, the six-membered C_5N heterocycle, has lost its planarity and shows alternating C–C single (C1–C2 1.509(6) and C3–C4 1.443(6) Å) and double bond lengths (C2–C3 1.334(6) and C4–C5 1.346(6) Å). This serves to explain the observed NMR spectroscopic data, as the aromaticity is lost in the C_5N heterocycle.



Scheme 1. Reaction of silylene *N*-LSi with benzophenone.

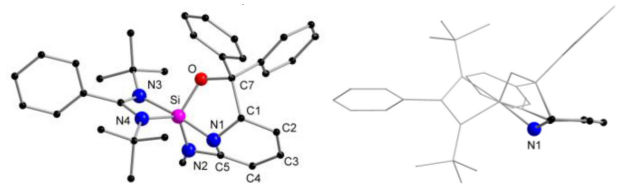
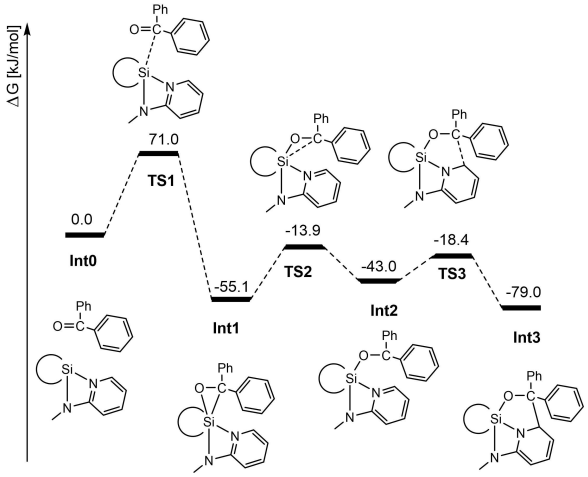


Figure 2. Left: molecular structure of the compound **1** in the solid state. Right: side-view of the dearomatized pyridine ring. All hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Si–O 1.671(3), Si–N1 1.803(4), Si–N2 1.764(4), Si–N3 1.819(3), Si–N4 1.881(4), N1–C1 1.465(5), N1–C5 1.408(5), N2–C5 1.393(5), C1–C7 1.633(6), C1–C2 1.509(6), C2–C3 1.334(6), C3–C4 1.443(6), C4–C5 1.346(6); N1–Si–N2 74.5(2), N3–Si–N4 70–90(15).

In this reaction, upon the addition of benzophenone, a concomitant dearomatisation of pyridine occurred and a five-membered $SiNOC_2$ heterocycle was formed. The Si atom is pentacoordinated by two nitrogen atoms of the amidinate ligand (Si–N3 1.819(3), Si–N4 1.881(4) Å), two nitrogen atoms from the amidopyridine[13] (Si–N1 1.803(4), Si–N2 1.764(4) Å) and one oxygen atom with a Si–O bond length of 1.671(3) Å. Occasionally, reactions between silylenes and aromatic ketones have been shown to undergo dearomative cycloaddition and furnish the cycloadduct, in which one of the aryl substituents of the ketone is dearomatised.[14] A closely related example is Driess' zwitterionic silylene that reacts with benzophenone furnishing the [4+1] cycloaddition product with concomitant dearomatisation of a phenyl group.[14a] However, in comparison to that, in our reaction, surprisingly, the two phenyl groups of the benzophenone remain intact and in a highly selective way, the pyridine moiety has undergone dearomatisation.

The activation and isomerisation processes were studied by DFT calculations (Gaussian16, PBE0-GD3/def2SVP) at a model compound *N*-L^{M}Si where amidinate was N,N-dimethylformamidinate. Furthermore, as starting conformer of *N*-L^{M}Si the one with an interaction of the pyridine N atom with the silicon atom is anticipated (Scheme 2).

The initial step is the attack of Int0 to the nucleophilic C atom of benzophenone, which initially leads the formation of the [2+1] cycloaddition product Int1. It is generally expected that silylenes react with carbonyl compounds *via* [2+1] cycloaddition forming oxasiliranes (for mechanistic studies see Scheme 2).[14,15] For example, the parent chlorosilylene [PhC(N*t*Bu)$_2$SiCl][16] and the N-heterocyclic carbene (NHC)-stabilized silylene [(NHC)SiCl$_2$][17] both react with benzophenone to give the respectively corresponding oxasilirane.[15b] The strained heterocycle can undergo ring-opening *via* Si–C dissociation yielding Int2. The C atom can subsequently attack the α-C atom of the coordinated pyridine moiety to dearomatise the heteroaromatic cycle (Int3/compound **1**). The sequence from Int1 to



Scheme 2. Modelled reaction of silylene *N*-L^{M}Si with benzophenone (Int0).

Int3 appears in principle reversible, as there is a small difference in Gibbs energy and only small activation barriers.

Compound **1** is stable at ambient temperature both in the solid state and solution under inert atmosphere. Interestingly, when a solution of **1** was heated at 80 °C, slowly, an isomerisation process could be observed by following the reaction *via* NMR spectroscopy and the reaction was complete after 60 h (Scheme 1). Colourless crystals of the reaction product **2** could be isolated in 47% yield. The molecular structure has been confirmed by single crystal X-ray diffraction analysis (Figure 3). Compound **2** crystallises in the triclinic space group $P\bar{1}$ and the Si centre is now hexacoordinated by four nitrogen atoms N1, N2, N3 and N4, one O atom and the *ortho*-carbon atom C19 from the benzophenone phenyl group in a distorted trigonal bipyramidal geometry. Compared to compound **1**, the Si–N1, Si–N2 and Si–N3 bond distances in compound **2** are elongated. In the isomerisation reaction, the C1–C7 in compound **1** is cleaved, C–H activation takes place and the thermolysis reaction features a 1,3-hydrogen migration (from C19 to C7). Upon thermolysis, the pyridine moiety is rearomatised, which can be indicated by its planarity and bonding metrics as well as the ^{1}H NMR shifts (see ESI, Figure S4).

The thermal rearrangement of **1** was also studied in silico with a model compound in which the N,N′-dimethylformamidinate ligand was incorporated instead of L (see ESI, Figure S43). No direct transformation of the isolated compound **1**/Int3 could be found. However, starting from Int1 a possible reaction pathway could be identified. As Int1 and Int3 are interconnected via Int2 with only small activation barriers, this formal equilibrium provides the option for Int1 to be part of the rearrangement from Int3 to Int7. The intermediate [2 + 1] cycloaddition product Int1 can undergo dissociation of the pyridine ligand, which then can deprotonate the benzophenone phenyl group to yield Int4, a [2.1.0] bicyclic species. The high calculated activation barrier for this process is in line with prolonged heating being required for completion of the reaction. The [2.1.0] bicycle Int4 can be flattened into Int5 by stretching the transannular Si–C bond, which forms a five-membered silacycle. The rotation of the pyridylamido group to form rotamer Int6 with O···H–N hydrogen bonding that stabilises the species by 55.7 kJ/mol. From Int6 there is only a small activation barrier for the transfer of the H atom to the benzophenone-C atom in Int7/compound **2** which releases 165.8 kJ/mol.

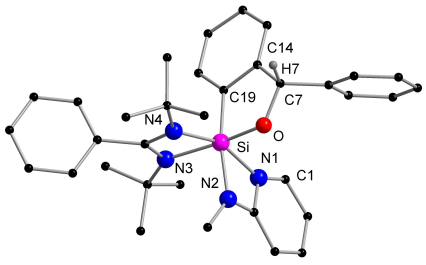


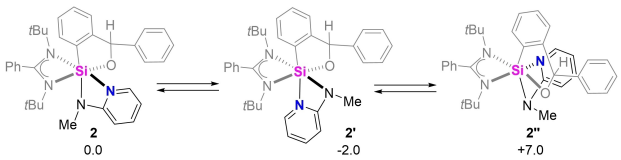
Figure 3. Molecular structure of the compound **2** in the solid state. Hydrogen atoms (except H7) are omitted for clarity. Selected bond distances [Å] and angles [°]: Si–O 1.7238(12), Si–C19 1.905(2), Si–N1, 2.0026(2), Si–N2 1.8796(15), Si–N3 1.9878(15), Si–N4 1.8764(15), C14–C19 1.395(2), C7–C14 1.517(2), C7–O 1.425(2); N3–Si–N4 67.88(6), Si–O–C7 118.23(10), Si–C19–C14 110.48(12), C19–C14–C7 113.84(15), C14–C7–O 108.46(14), O–Si–C19 88.60(7).

According to the NMR spectra measured at 298 K in C_6D_6, two isomers are present in approximately 1 : 2.4 molar ratio in solution. The respective *CH* NMR signals are found at 6.25 (minor species) and 6.38 ppm (major species), and the corresponding ^{13}C NMR signals at 79.4 and 78.7 ppm, which could be corroborated by ^{1}H-^{13}C HMQC correlation spectroscopy. We would like to find out the origin of the two isomers, therefore, variable temperature ^{1}H NMR experiments were carried out. The interconversion between the two isomers **2** (major isomer) and **2′** (minor isomer) occurred while increasing the temperature (from 298 K to 348 K) as the molar ratio of **2′**:**2** changes from 1 : 2.4 to 1 : 1.9 (see Figures S8 and S9), showcasing the amount of the minor slowly increases relative to the major isomer while increasing the temperature. This process is reversible since upon cooling back to room temperature, the molar ratio **2′**:**2** is back to 1 : 2.4. Furthermore, the ^{29}Si{^{1}H} NMR signals were found at −104.4 (minor species, **2′**) and −108.3 ppm (major species, **2**; Figure S7).

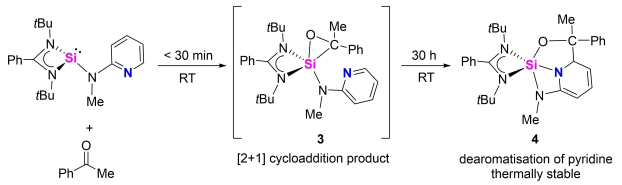
To further elucidate the two isomeric species in solution, quantum chemical calculations were carried out (see ESI IV.2). Several isomers can be considered which only differ by the relative arrangement of aminopyridyl and 2-(phenylmethoxy)-phenyl moiety. The compounds are very similar in energy of those, **2**, **2′** and **2″** are the most stable (Scheme 3), even though by a small margin (relative G: **2** 0.0, **2′** −2.0, **2″** +7.0 kJ/mol). The calculated ^{29}Si NMR data are similar as well (**2** −115, **2′** −112, 2″ −115 ppm, referenced to *N*-LSi at −12 ppm). **2′** and **2″** are closely related to **2** and differ from it by the relative orientation of the pyridylamido moiety (**2′**) and the chirality of Si (**2″**), respectively, and are candidates for the second isomer present in solution.

The deromatisation of the pyridine moiety of *N*-LSi by reaction with benzophenone and its rearomatisation upon thermolysis further prompt us to study the scope of the reaction. Therefore, we felt challenged to investigate the electronic effect of the ketone substituents on the reaction pathway with silylene *N*-LSi.

The reaction between acetophenone and the pyridylamino-silylene *N*-LSi was carefully followed by NMR spectroscopy (Scheme 4). In the ^{29}Si{^{1}H} NMR spectrum recorded after approximately 30 min, the signal of the three-membered silaoxirane **3** appears at −115.0 ppm (calc. −106 ppm) while the signal of the new species **4** is found at −93.9 ppm (calc. −91 ppm). The latter signal is comparable to the ^{29}Si{^{1}H} NMR signal of compound **1** (−94.0 ppm). Again, highfield-shift of the pyridine ^{1}H NMR signals (6.13, 5.15, 4.45, 3.96 ppm) was found



Scheme 3. Isomerisation of **2**, relative energies in kJ/mol.



Scheme 4. Reaction of silylene *N*-LSi with acetophenone.

for compound **4**. After keeping that solution for 30 h at room temperature, clean and selective conversion from **3** to **4** was observed.

Compound **4** could be crystallised from a concentrated *n*-pentane solution in 44% yield and its molecular structure was analysed by single crystal X-ray diffraction analysis (Figure 4). In the reaction, the silaoxirane **3** underwent ring-opening reaction forming the compound **4** as thermodynamic reaction product. Compound **4** crystallises in the triclinic space group $P\bar{1}$ with two molecules and one co-crystallised *n*-pentane in the asymmetric unit. The outcome of the reaction with acetophenone is similar to that with benzophenone. However, when the ketone comprises two phenyl substituents, the dearomative reaction pathway is much faster and no intermediate could be detected. When one of the phenyl groups is substituted by the methyl group, we could see that in the first step, the three-membered silaoxirane is formed which further undergoes ring-opening that is accompanied by the pyridine dearomatisation. In contrast to the thermal rearomatisation of compound **2**, the dearomatised species **4** is thermally stable since no change was observed after heating the C_6D_6 solution of **4** at 80 °C for one week.

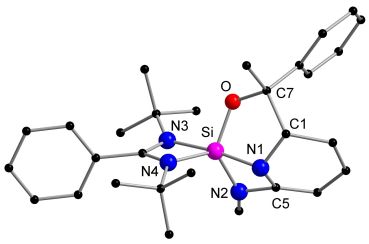
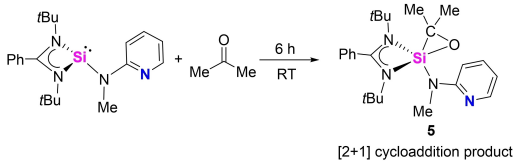


Figure 4. Molecular structure of the compound **4** in the solid state. All hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Si1–O1 1.6537(10), Si1–N1 1.804(2), Si1–N2 1.753(2), Si1–N3 1.867(2), Si1–N4 1.815(2), N1–C1 1.447(3), C1–C7 1.607(3), O1–C7 1.442(2), N1–C5 1.405(2), N2–C5 1.381(3); N3–Si1–N4 70.75(7), Si1–O1–C7 118.89(12), Si1–N1–C1 115.10(13), O1–C7–C1 107.9(2), C7–C1–N1 106.23(15), C1–N1–Si1 115.10(13), C1–N1–C5 116.6(2), N1–Si1–N2 74.48(8), N1–C5–N2 101.2(2), O1–Si1–N1 90.36(7).



Scheme 5. Reaction of silylene *N*-LSi with acetone.

Changing one Ph group to Me group of the ketone has significantly changed the reaction behaviour towards silylene *N*-LSi. Subsequently, the reaction was tested with the ketone having two Me groups, namely acetone, and the reaction progress was monitored by NMR spectroscopy (Scheme 5). Based on the ^{1}H NMR spectrum, a clean conversion to a single reaction product took place and no signals were detected between 4 and 6.5 ppm. Analysis of the pyridine ^{1}H NMR signals revealed no significant upfield shift, indicating that the pyridine moiety did not undergo dearomatisation. Besides, in the ^{1}H NMR spectrum, two singlets were detected at 3.49 and 1.82 ppm, corresponding to the NMe and $OCMe_2$ protons, respectively. In the ^{29}Si{^{1}H} NMR spectrum, a singlet signal was observed at −110.1 ppm, similar to that of **3**. These observations suggest that a three-membered Si-epoxide **5** was formed *via* [2 + 1]-cycloaddition.

Confirmation was achieved by analysing the molecular structure of compound **5** using single crystal X-ray diffraction analysis (Figure 5). As expected, compound **5** consists of a three-membered silaoxirane Si–C7–O ring and the Si atom is in a pentacoordinated environment. The Si–O bond distance (1.696(2) Å) is comparable to that observed in other literature-reported silaoxiranes.[14b]

In contrast to the intermediately-formed oxasilirane **3** observed with acetophenone, the oxasilirane compound **5** demonstrated remarkable thermal stability. These results indicate that the choice of ketone significantly influences the outcome of the reaction with silylene *N*-LSi. Selected computations were repeated with acetophenone as substrate. While the overall thermodynamics of Int1/Int3/Int5/Int7 are closely related, the rearrangement intermediate Int4 is considerably higher in energy (by approx. 40 kJ/mol) which puts it beyond thermal access (see ESI, Table S4). This hints at electronic effects of the alkyl substituent that prevent the rearrangement. With acetone as substrate, Int2 is considerably higher in energy, as stabilising and pre-organising p-p interactions between the substrate (ketone) and the pyridine are absent. The overall thermodynamics between Int1 and Int3 are similar, so it is a kinetic difference in this case. However, steric effects can not be excluded, but are expected to be less relevant as the calculations were carried out with a model with smaller substituents.

To further investigate the impact of aromatic groups and steric effects on the pyridine dearomatization of *N*-LSi, additional investigations were conducted using di-*tert*-butyl-ketone (tBu_2CO) and diphenylketene.[18] While for di-*tert*-butyl-ketone

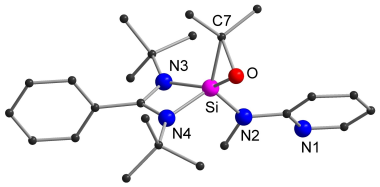
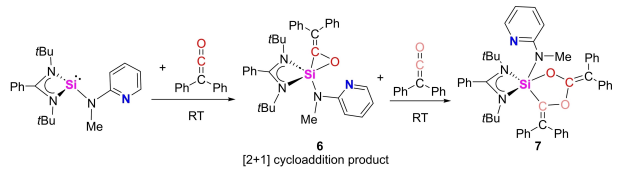


Figure 5. Molecular structure of **5** in the solid state. All hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Si–O 1.696(2), Si–C7 1.812(3), Si–N2 1.738(2), Si–N3 1.922(2), Si–N4 1.794(2); N3–Si–N4 69.70(9), Si–O1–C7 68.62(12), Si–C7–O1 60.59(11), O1–Si–C7 50.79(10).

no reaction was detected, upon careful addition of one equivalent diphenylketene to the silylene *N*-LSi, a signal at −127.6 ppm was observed in the $^{29}Si\{^1H\}$ NMR spectrum, which is slightly upfield-shifted compared to the values of **3** and **5**. In addition, no dearomatization of the pyridine moiety could be observed according to the ^1H NMR spectrum (Scheme 6).

Suitable single crystals for X-ray diffraction analysis were obtained by concentrating the C_6D_6 solution of the reaction mixture and the silaallene oxide compound **6** was formed *via* [2 + 1] cycloaddition (Figure 6). The central structure motif of **6** is similar to that of **5**, except for the substitution of two methyl groups by a [Ph_2C=] moiety. The dihedral angle defined by (SiN3N4) and (SiOC6) is 55.13°, slightly smaller than that in **5** (63.01°). Moreover, the bond distances of Si–O and Si–C observed in **6** are comparable to those observed in **5**.

Interestingly, compound **6** is thermally stable but could undergo ring-expansion reaction with another molar equivalent



Scheme 6. Reaction of silylene *N*-LSi with diphenylketene [Ph_2C=C=O].

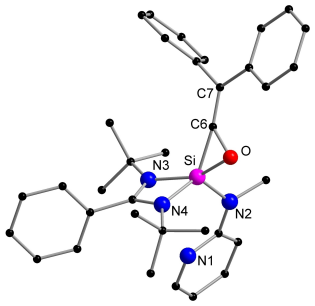


Figure 6. Molecular structure of **6** in the solid state. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles [°]: Si–O 1.7483(9), Si–C6 1.8026(13), Si–N2 1.7481(11), Si–N3 1.8702(11), Si–N4 1.8094(11), C6–C7 1.345(2); N3–Si1–N4 70.89(5), Si–O–C6 68.52(6), Si1–C6–O1 64.49(6), O1–Si1–C6 46.99(5).

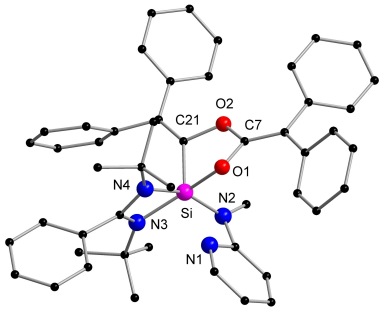


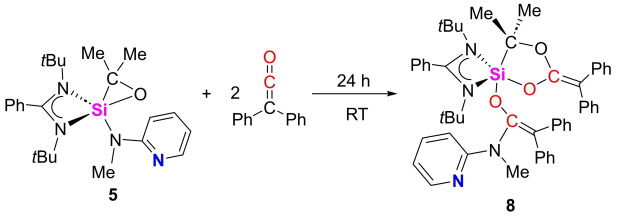
Figure 7. Molecular structure of **7** in the solid state. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles [°]: Si–O1 1.757(2), Si–C21 1.921(3), Si–N2 1.855(3), Si–N3 1.902(2), Si–N4 1.856(2), C21–O2 1.429(3), O2–C7 1.378(3), C7–O1 1.326(3); N3–Si–N4 69.44(10), Si–O1–C7 112.3(2), Si–C21–O2 104.8(2), C21–O2–C7 113.1(2), O2–C7–O1 113.2(2), C7–O1–Si 112.3(2), O1–Si–C21 84.10(11).

of diphenylketene to form compound **7** (Scheme 6, Figure 7). The newly-formed five-membered SiO_2C_2 ring is nonplanar with the sum of inner angles being 527.52°. The bond distance of Si–C21 (1.921(3) Å) is significantly longer than the corresponding bond distance of Si–C6 (1.8026(13) Å) in **6**. However, redissolving the isolated crystals of **7** in C_6D_6 led to the formation of three sets of signals in the ^1H NMR spectrum (see ESI, Figure S24) and variable temperature NMR spectroscopy did not lead to significant changes in the ratio of the three compounds. The formation of several isomers of **7** may be a result of the formation of several isomers, which differ in the relative orientations of the pyridylamino and the diphenylketene moieties in the octahedral environment of the Si central atom (see ESI IV.1).

The successful isolation of compound **7** prompted us to investigate whether a comparable ring-expansion could also occur for the three-membered silaoxirane **5** when reacting with diphenylketene. Although compound **5** exhibited no reactivity towards acetone, it was able to further react with two molecules of diphenylketene to form the ring-expansion product **8** (Scheme 7). This reaction involves the ring opening of compound **5** by one diphenylketene molecule and the insertion of the second diphenylketene into the Si–N bond to a Si–O–C–N chain. The five-membered SiO_2C_2 heterocycle formed in the ring-expansion reaction is comparable to that motif in compound **7** and the bonding metrics are similar.

The NMR spectrum of compound **8** was recorded in C_6D_6 and two species exist in solution according to the ^1H NMR spectrum measured at room temperature. Upon heating at 70 °C, isomerisation to a single species proceeded which suggests that the two species at room temperature are closely related isomers. In the $^{29}Si\{^1H\}$ NMR spectrum measured at 70 °C, a signal was detected at −88.6 ppm. In the molecular structure of **8** (Figure 8), the bond length of Si–C7 (1.9178 (12) Å) is elongated compared with that in **5** (1.812(3) Å), while the bond distance of Si with the bridged O3 (1.6699(9) Å) is shorter than that of Si with O2 (1.7461(9) Å) in the heterocycle. Both distances are within the range of Si–O single bond length.[19] The five-membered heterocycle core (SiC_2O_2) is much more planar than in **7** with the sum of inner angles being 538.73°.

In these subsequent reactions with diphenylketene, no dearomatisation of the pyridine moiety was observed, which means that both steric hindrance and aromatic groups collectively affect the dearomatisation of pyridine in pyridylaminosilylene reactions.



Scheme 7. The reaction of **5** with diphenylketene.

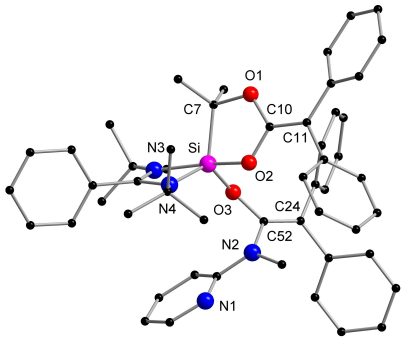


Figure 8. Molecular structure of **8** in the solid state. All hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Si–O2 1.7461(9), Si–O3 1.6699(9), Si–C7 1.9178(12), Si–N3 1.9585(11), Si–N4 1.8086(11), C7–O1 1.4734(15), O1–C10 1.3624(14), C10–O2 1.3323(15), C10–C11 1.356(2), O3–C52 1.3745(14), C52–C24 1.335(2); N3–Si–N4 69.55(5), Si–C7–O1 104.21(7), C7–O1–C10 115.90(9), O1–C10–O2 114.23(11), C10–O2–Si 115.82(7), O2–Si–C7 88.56(5), Si–O3–C52 127.17(7).

Conclusions

In conclusion, we report here the reactions of an aminopyridyl -silylene towards several types of ketones and diphenylketene. The reactivity outcome is highly dependent on the substituents on the ketones. When the ketone comprises two phenyl groups (benzophenone), the direct dearomatisation of the pyridine is observed. Interestingly, this dearomatised species can undergo rearomatisation at elevated temperature. Using instead the monoarylketone (acetophenone) allows the direct comparison of the reactivity. In the first step, the [2+1] cycloaddition reaction generates the three-membered silaoxirane ring, which is unstable at room temperature and further undergoes ring-opening and forms the respective dearomatised species. This compound is extremely thermally stable and no rearomatisation could be obtained. Reactions with acetone and diphenylketene led the formation of [2+1] cycloaddition and further ring expansion product. These observations shed light on novel reactivities of donor-functionalized silylenes towards carbonyl species and enriched the methods availabilities for the de- and rearomatisation of pyridine moieties.

Experimental Section

All air- and moisture-sensitive manipulations were performed under dry N_2 or Ar atmosphere using standard Schlenk techniques or in an argon-filled MBraun glovebox, unless otherwise stated. Et_2O, *n*-pentane, and toluene were dried using an MBraun solvent purification system (SPS-800) and degassed. THF and *n*-hexane were distilled under nitrogen from potassium benzophenone ketyl. C_6D_6 was dried over Na–K alloy and degassed by freeze-pump-thaw cycles. Acetone and benzaldehyde were dried over 3 Å molecular sieves. Silylene *N*-LSi[11] and diphenylketene[20] were prepared according to the literature procedures. All other chemicals were obtained from commercial sources and used without further purification. Elemental analyses were carried out with an Elementar vario MICRO cube. NMR spectra were recorded on Bruker spectrometers (Avance III 300 MHz, Avance Neo 400 MHz or Avance III 400 MHz). Chemical shifts are referenced internally using signals of the residual protio solvent (^{1}H) or the solvent (^{13}C{^{1}H}) and are reported relative to tetramethylsilane (^{1}H, ^{13}C{^{1}H}), or externally relative to tetramethylsilane (^{29}Si). All NMR spectra were measured at 298 K, unless otherwise specified. The multiplicity of the signals is indicated as s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet and br = broad. Assignments were determined based on unambiguous chemical shifts, coupling patterns and ^{13}C-DEPT experiments or 2D correlations. Infrared (IR) spectra were recorded in the region 4000–400 cm^{-1} on a Bruker Tensor 37 FTIR spectrometer equipped with a room temperature DLaTGS detector, a diamond attenuated total reflection (ATR) unit and a nitrogen-flushed chamber. In terms of their intensity, the signals were classified into different categories (vs = very strong, s = strong, m = medium, w = weak, and sh = shoulder).

Synthesis of 1

To a mixture of *N*-LSi (0.101 g, 0.274 mmol) and Ph_2CO (0.050 g, 0.274 mmol) was condensed toluene (5 mL) at −88 °C. The resulting mixture was stirred at room temperature for 6 h. All volatiles were removed under reduced pressure. The resulting solid was washed with cold *n*–pentane (5 mL) and dried *in vacuo* for 10 min, affording the title compound as a white solid. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of THF at room temperature. Yield: 0.144 g (0.233 mmol), 85 %. Anal. Calcd. for $C_{34}H_{40}N_4OSi$ (548.81 g/mol): C, 74.41; H, 7.35; N, 10.21. Found: C, 74.77; H, 7.02; N, 10.07. ^{1}H NMR (400.3 MHz, C_6D_6): δ (ppm) = 7.87–7.84 (m, 2H, CH_{Ph}), 7.58–7.56 (m, 2H, CH_{Ph}), 7.38–7.34 (m, 2H, CH_{Ph}), 7.21–7.18 (m, 3H, CH_{Ph}), 7.08–7.05 (m, 1H, CH_{Ph}), 6.97–6.90 (m, 2H, CH_{Ph}), 6.87–6.82 (m, 3H, CH_{Ph}), 6.33 (ddd, $^3J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, CH_{Py}), 5.35 (dd, $^3J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 5.5 Hz, 1H, CH_{Py}), 4.83 (dd, $^4J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, CH_{Py}), 4.64, (d, $^4J_{HH}$ = 5.5 Hz, 1H, CH_{Py}), 3.08 (s, 3H, NCH_3), 1.19 (s, 9H, $C(CH_3)_3$), 0.90 (s, 9H, $C(CH_3)_3$). ^{13}C{^{1}H} NMR (100.67 MHz, C_6D_6): δ (ppm) = 176.5 (NCN), 154.9 ($C_{q\ Py}$), 150.0 ($C_{q\ Ph}$), 147.2 ($C_{q\ Ph}$), 132.4 ($C_{q\ Ph}$), 130.1 (C_{Ph}), 128.63 (C_{Ph}), 128.58 (C_{Ph}), 128.2 (C_{Ph}), 128.0 (C_{Ph}), 127.9 (C_{Ph}), 127.5 (C_{Ph}), 127.0 (2 C_{Ph}), 126.6 (C_{Ph}), 126.2 (C_{Py}), 110.8 (C_{Py}), 90.3 (CO), 72.5 (C_{Py}), 64.7 (C_{Py}), 54.0 ($C(CH_3)_3$), 53.9 ($C(CH_3)_3$), 31.1 ($C(CH_3)_3$), 30.8 ($C(CH_3)_3$), 30.1 (NCH_3). ^{29}Si{^{1}H} NMR (79.52 MHz, C_6D_6): δ (ppm) = −94.0. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3059 (w), 3028 (w), 2970 (m), 2896 (w), 2867 (w), 1628 (s), 1553 (s), 1527 (m), 1475 (m), 1411 (vs), 1361 (s), 1323 (w), 1300 (s), 1272 (s), 1237 (m), 1196 (s), 1147 (s), 1085 (s), 1018 (s), 992 (m), 925 (m), 884 (m), 840 (s), 781 (s), 736 (s), 700 (s), 674 (s), 647 (s), 612 (m), 577 (w), 544 (m), 507 (w), 485 (s), 417 (w).

Synthesis of 2

A toluene solution (5 mL) of compound **1** (0.120 g, 0.219 mmol) was heated at 80 °C for 60 h. All volatiles were removed under reduced pressure. The residue was washed with a small amount of *n*-pentane and dried under vacuum for 30 min. Recrystallisation from a concentrated toluene solution led to the formation of colorless crystals. Redissolving the crystals in C_6D_6 indicated the presence of two closely related isomers (ca 1 : 2.4 molar ratio). Yield (based on crystals): 0.057 g (0.104 mmol), 47 %. Anal. Calcd. for $C_{34}H_{40}N_4SiO$ (548.81 g/mol): C, 74.41; H, 7.35; N, 10.21. Found: C, 74.97; H, 7.03; N, 10.24. ^{1}H NMR (400.3 MHz, C_6D_6): δ (ppm) = 7.99–6.00 (CH_{Ar}, *ca.* 26H), 6.38 (s, 1H, *CH*, major isomer **2**), 6.25 (s, 0.4H, *CH*, minor isomer **2'**), 2.76 (s, 1.24H, NCH_3, minor isomer **2'**), 2.54 (s, 3H, NCH_3, major isomer **2**), 1.06 (s, 18H, $C(CH_3)_3$, major isomer **2**), 1.05 (s, *ca.* 7.5H, $C(CH_3)_3$, minor isomer **2'**). ^{13}C{^{1}H} NMR (100.67 MHz, C_6D_6): δ (ppm) = 168.6 (NCN, minor isomer **2'**), 167.5 (NCN, major isomer **2**), 161.6, 161.3, 152.3, 152.0, 146.7, 146.2, 145.8, 144.5, 143.7, 142.8, 140.9, 139.6, 138.8, 138.3, 137.3, 136.5, 132.1, 131.7, 131.6, 130.2, 129.51, 129.48, 129.1, 128.9, 128.6, 128.5, 128.4, 128.3,

128.21, 128.19, 128.16, 128.08, 127.8, 127.6, 127.5, 127.1, 126.8, 126.5, 126.3, 124.2, 123.7, 109.9, 109.2, 105.7, 104.5, 79.4 (*CH*, minor isomer **2'**), 78.7 (*CH*, major isomer **2**), 54.07 ($C(CH_3)_3$, minor isomer **2'**), 54.06 ($C(CH_3)_3$, major isomer **2**), 32.48 (s, $C(CH_3)_3$, minor isomer **2'**), 32.43 (s, $C(CH_3)_3$, major isomer **2**), 30.7 (NCH_3, minor isomer **2'**), 30.3 (NCH_3, major isomer **2**). $^{29}Si\{^1H\}$ NMR (79.52 MHz, C_6D_6): δ (ppm) = −104.4 (minor isomer **2'**), −108.3 (major isomer **2**). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3062 (w), 3029 (w), 3004 (w), 2965 (w), 2927 (w), 2905 (w), 2865 (w), 2813 (w), 2783 (w), 1619 (w), 1597 (m), 1557 (w), 1509 (m), 1477 (m), 1445 (m), 1416 (m), 1389 (m), 1358 (m), 1299 (w), 1251 (w), 1198 (m), 1147 (m), 1073 (m), 1053 (m), 1017 (m), 920 (w), 882 (m), 829 (m), 799 (w), 740 (s), 698 (s), 668 (m), 614 (m), 589 (m), 528 (m), 495 (m), 467 (m), 441 (m).

Synthesis of 4

To a toluene solution (5 mL) of *N*-LSi (0.101 g, 0.274 mmol) [Ph(Me)CO] (0.033 g, 0.274 mmol) was added at room temperature, and the resulting mixture was stirred at room temperature for 30 h. All volatiles were removed under reduced pressure. The solid residue was redissolved in *n*-pentane and the *n*-pentane solution was concentrated. The solution was kept at room temperature for two days and colorless crystals suitable for X-ray diffraction analysis were obtained. Yield (based on crystals): 59 mg (0.121 mmol), 44%. Anal. Calcd. for $C_{29}H_{38}N_4SiO$ (486.74 g/mol): C, 71.56; H, 7.87; N, 11.51. Found: C, 72.08; H, 7.98; N, 12.01. ^1H NMR (400.3 MHz, C_6D_6): δ (ppm) = 7.58 (d, $^3J_{HH}$ = 7.8 Hz 2H, CH_{Ph}), 7.29 (t, $^3J_{HH}$ = 7.8 Hz, 2H, CH_{Ph}), 7.14 (t, $^3J_{HH}$ = 7.2 Hz, 1H, CH_{Ph}), 6.96–6.92 (m, 1H, CH_{Ph}), 6.86–6.84 (m, 4H, CH_{Ph}), 6.12 (dd, $^3J_{HH}$ = 9.0 Hz, $^3J_{HH}$ = 5.4 Hz, 1H, CH_{Py}), 5.15 (dd, $^3J_{HH}$ = 9.0 Hz, $^3J_{HH}$ = 5.5 Hz, 1H, CH_{Py}), 4.46 (d, $^3J_{HH}$ = 5.5 Hz, 1H, CH_{Py}), 3.96, (d, $^3J_{HH}$ = 5.6 Hz, 1H, CH_{Py}), 3.03 (s, 3H, NCH_3), 1.80 (s, 3H, CCH_3), 1.16 (s, 9H, $C(CH_3)_3$), 1.13 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100.67 MHz, C_6D_6): δ (ppm) = 176.5 (*N*CN), 155.0 ($C_{q\ Py}$), 148.6 ($C_{q\ Ph}$), 132.6 ($C_{q\ Ph}$), 130.1 (C_{Ph}), 128.6 (C_{Ph}), 128.3 (C_{Ph}), 128.0 (C_{Ph}), 127.1 (C_{Ph}), 126.1 (C_{Py}), 125.9 (C_{Ph}), 109.8 (C_{Py}), 85.4 (*C*O), 72.8 (C_{Py}), 63.0 (C_{Py}), 55.2 ($C(CH_3)_3$), 53.9 ($C(CH_3)_3$), 31.4 (CCH_3), 31.09 ($C(CH_3)_3$), 31.10 ($C(CH_3)_3$), 30.0 (NCH_3). $^{29}Si\{^1H\}$ NMR (79.52 MHz, C_6D_6): δ (ppm) = −93.9. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3058 (w), 3026 (w), 2966 (w), 2930 (w), 2862 (w), 2797 (w), 1627 (m), 1552 (m), 1476 (w), 1446 (w), 1411 (s), 1353 (m), 1324 (w), 1296 (w), 1272 (w), 1235 (w), 1200 (m), 1143 (w), 1087 (m), 1056 (m), 1025 (w), 990 (w), 942 (m), 858 (w), 785 (m), 771 (m), 743 (m), 710 (m), 678 (m), 642 (m), 600 (w), 556 (w), 534 (w), 493 (m).

Synthesis of 5

To a toluene solution (5 mL) of *N*-LSi (120.0 mg, 0.327 mmol) acetone (19.1 mg, 0.329 mmol) was added at room temperature and the resulting mixture was stirred at room temperature for 6 h. All volatiles were removed under reduced pressure. The solid residue was washed with a small amount of *n*-pentane and dried under vacuum for 30 min. According to NMR spectroscopy, compound **5** was isolated in pure form. Crystals of compound **5** suitable for X-ray diffraction analysis were obtained after concentrating the C_6D_6 solution of **5** in the NMR tube. Yield: 81 mg (0.191 mmol), 58%. Anal. Calcd. for $C_{24}H_{36}N_4SiO$ (424.66 g/mol): C, 67.88; H, 8.55; N, 13.19. Found: C, 67.85; H, 8.29; N, 13.18. ^1H NMR (400.3 MHz, C_6D_6): δ (ppm) = 8.37–8.35 (m, 1H, CH_{Py}), 7.33–7.31 (m, 1H, CH_{Ph}), 7.26–7.21 (m, 1H, CH_{Py}), 7.14–7.12 (m, 2H, $CH_{Py} + CH_{Ph}$), 7.03–6.93 (m, 3H, CH_{Ph}), 6.55–6.52 (m, 1H, CH_{Py}), 3.49 (s, 3H, NCH_3), 1.82 (s, 6H, $C(CH_3)_2$), 1.28 (s, 9H, $C(CH_3)_3$), 0.83 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100.67 MHz, C_6D_6): δ (ppm) = 173.9 (*N*CN), 164.2 (C_{Py}), 147.6 (C_{Py}), 136.4 (C_{Py}), 133.7 ($C_{q\ Ph}$), 129.8 (C_{Ph}), 128.9 (C_{Ph}), 128.6 (C_{Ph}), 128.1 (C_{Ph}), 127.7 (C_{Ph}), 114.8 (C_{Py}), 113.9 (C_{Py}), 65.3 ($OC(CH_3)_2$), 53.8 ($C(CH_3)_3$), 53.4 ($C(CH_3)_3$), 36.4 (NCH_3), 31.3 ($C(CH_3)_3$), 30.6 ($C(CH_3)_3$), 29.5 ($C(CH_3)_2$), 26.9 ($C(CH_3)_2$). $^{29}Si\{^1H\}$ NMR (79.52 MHz, C_6D_6): δ (ppm) = −110.1. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2967 (w), 2929 (w), 2867 (w), 1648 (w), 1569 (w), 1478 (m), 1446 (w), 1409 (w), 1385 (w), 1360 (w), 1297 (w), 1203 (w), 1138 (m), 1020 (s), 930 (w), 880 (m), 855 (w), 805 (w), 773 (m), 736 (m), 705 (m), 662 (m), 584 (w), 466 (m), 417 (w).

Synthesis of 6

To a toluene solution (5 mL) of *N*-LSi (0.090 g, 0.245 mmol) diphenylketene (0.046 g, 0.237 mmol) was added at room temperature and the resulting mixture was stirred at room temperature for 12 h. All volatiles were removed under reduced pressure. The resulting solid was washed with a small amount of *n*-pentane and dried under vacuum for 30 min. According to NMR spectroscopy, the title compound **6** was formed. By concentrating the C_6D_6 solution in the J. Young NMR tube, colorless crystals suitable for X-ray diffraction analysis were obtained. Yield (based on crystals): 0.040 g (0.071 mmol), 30%. Anal. Calcd. for $C_{35}H_{40}N_4SiO$ (560.82 g/mol): C, 74.96; H, 7.19; N, 9.99. Found: C, 74.77; H, 6.61; N, 9.37. ^1H NMR (400.3 MHz, C_6D_6): δ (ppm) = 8.30 (d, $^3J_{HH}$ = 8.1 Hz, 2H, CH_{Ph}), 8.20 (br, 1H, CH_{Py}), 7.65 (d, $^3J_{HH}$ = 8.3 Hz, 2H, CH_{Ph}), 7.38 (t, $^3J_{HH}$ = 7.9 Hz, 2H, CH_{Ph}), 7.26–7.22 (m, 3H, CH_{Ph}), 7.13–7.09 (m, 2H, $CH_{Py} + CH_{Ph}$), 6.98–6.86 (m, 5H, CH_{Ph}), 6.57 (d, $^3J_{HH}$ = 8.2 Hz, 1H, CH_{Py}), 6.44 (t, 1H, CH_{Py}, $^3J_{HH}$ = 6.0 Hz), 3.13 (s, 3H, NCH_3), 1.11 (br s, 9H, $C(CH_3)_3$), 0.75 (br s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100.67 MHz, C_6D_6): δ (ppm) = 176.4 (*N*CN), 175.8 (C_q), 162.3 ($C_{q\ Py}$), 147.1 (C_{Py}), 143.9 (C_q), 140.9 (C_q), 137.5 (C_{Py}), 132.7 ($C_{q\ Ph}$), 131.0 (C_{Ph}), 130.0 (C_{Ph}), 129.5 (C_{Ph}), 128.4 (C_{Ph}), 128.35 (C_{Ph}), 128.25 (C_{Ph}), 128.22 (C_{Ph}), 128.17 (C_{Ph}), 127.8 (C_{Ph}), 127.6 (C_{Ph}), 125.7 (C_{Ph}), 125.3 (C_{Ph}), 120.6 (C_q), 113.9 (C_{Py}), 109.9 (C_{Py}), 53.8 ($C(CH_3)_3$), 32.8 (NCH_3), 30.3 (br, $C(CH_3)_3$). $^{29}Si\{^1H\}$ NMR (79.52 MHz, C_6D_6): δ (ppm) = −127.6. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3077 (w), 3054 (w), 3024 (w), 2973 (w), 2930 (w), 2866 (w), 2821 (w), 1620 (m), 1588 (m), 1492 (w), 1476 (w), 1441 (w), 1422 (m), 1392 (w), 1361 (w), 1316 (w), 1302 (w), 1198 (m), 1156 (w), 1075 (m), 1027 (m), 1006 (m), 913(w), 886 (w), 835 (w), 765 (m), 735 (m), 696 (s), 648 (m), 621 (w), 572 (w), 552 (w), 492 (m), 454 (w), 437 (w).

Synthesis of 7

To a toluene solution of compound **6** (0.104 g, 0.185 mmol) [$Ph_2C{=}C{=}O$] (0.036 g, 0.185 mmol) was added at room temperature, and the resulting mixture was stirred for 2 h. All volatiles were then removed under reduced pressure. The remaining solid was washed twice with *n*-pentane (ca. 5 mL). The colorless solid was then redissolved in toluene and colorless crystals were obtained from a highly concentrated toluene solution. The mother liquid was removed using a syringe and the crystals were washed with *n*-pentane before drying under vacuum. While the crystals appear identical, analysis of the ^1H NMR spectrum reveals a complex mixture. Despite multiple recrystallization attempts, the results remain the same. Variation in temperature or solvent choice does not alter the molar ratio of the mixture.

Synthesis of 8

To a J. Young NMR tube containing a C_6D_6 solution (*ca.* 0.4 mL) compound **5** (0.040 g, 0.094 mmol) was added $Ph_2C{=}C{=}O$ (0.038 g, 0.195 mmol) at room temperature. The resulting mixture was kept at room temperature for 24 h and followed by NMR spectroscopy, until all starting materials were converted. Concentration of the C_6D_6 solution to *ca.* 0.2 mL and leaving the solution undisturbed at room temperature led to the formation of colorless block-shaped crystals. Yield (based on crystals): 32 mg (0.039 mmol), 42%. Anal. Calcd. for $C_{52}H_{56}N_4O_3Si$ (813.13 g/mol): C, 76.81; H, 6.94; N, 6.89. Found: C, 76.93; H, 6.44; N, 6.93. ^1H NMR (400.3 MHz, C_6D_6, 343 K): δ

(ppm) = 8.26–8.24 (m, 1H, CH_{Ar}), 7.80–7.78 (m, 6H, CH_{Ar}), 7.36–7.21 (m, 9H, CH_{Ar}), 7.14–7.12 (m, 1H, CH_{Ar}), 7.10–7.06 (m, 1H, CH_{Ar}), 7.02–6.89 (m, 7H, CH_{Ar}), 6.87–6.85 (m, 2H, CH_{Ar}), 6.67 (br, 1H, CH_{Ar}), 6.44 (m, 1H, CH_{Ar}), 2.89 (s, 3H, NCH_3), 1.43 (s, 3H, $C(CH_3)_2$), 1.27 (s, 3H, $C(CH_3)_2$), 0.96 (s, 9H, $C(CH_3)_3$), 0.93 (s, 9H, $C(CH_3)_3$). Note: Ar=Ph + Py. $^{13}C\{^1H\}$ NMR (100.67 MHz, C_6D_6, 343 K): δ (ppm) = 173.8 (NCN), 159.0 (C_q), 155.3 ($C_{q\ Py}$), 148.6 (2 C_{Ph}), 146.2 (C_q), 142.8 (C_q), 142.5 (C_q), 141.8 (C_q), 140.8 (C_q), 136.6 (2 C_{Ph}), 133.4 (C_q), 131.1 (C_{Ph}), 130.5 (C_q), 130.0 (C_{Ph}), 129.8 (C_{Ph}), 129.2 (C_{Ph}), 128.8 (C_{Ph}), 128.7 (C_{Ph}), 128.6 (C_q), 128.4 (C_{Ph}), 128.3 (C_{Ph}), 128.1 (C_{Ph}), 127.7 (C_{Ph}), 127.6 (C_{Ph}), 126.62 (C_{Ar}), 126.56 (C_{Ar}), 124.7 (C_{Ar}), 124.1 (C_{Ar}), 113.1 (C_{Ar}), 109.8 (C_{Ar}), 91.6 (C_q), 70.2 (CMe_2), 55.2 ($C(CH_3)_3$), 54.4 ($C(CH_3)_3$), 37.2 (NCH_3), 32.7 ($C(CH_3)_3$), 32.0 ($C(CH_3)_3$), 25.6 ($C(CH_3)_2$), 25.5 ($C(CH_3)_2$). $^{29}Si\{^1H\}$ NMR (79.52 MHz, C_6D_6): δ (ppm) = −88.6. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3080 (w), 3050 (w), 3008 (w), 2972 (w), 2909 (w), 2867 (w), 2168 (w), 1632 (s), 1587 (s), 1562 (m), 1545 (m), 1477 (m), 1438 (m), 1388 (s), 1337 (m), 1253 (m), 1195 (s), 1129 (m), 1105 (m), 1077 (m), 1035 (m), 1013 (s), 983 (s), 941 (m), 913 (m), 842 (w), 813 (m), 789 (m), 756 (s), 698 (vs), 643 (s), 618 (m), 568 (w), 540 (m), 522 (m), 508 (m), 489 (m), 414 (m).

Footnote

Compounds **1**, **6** and **7** crystallised in the centrosymmetric space group $P2_1/c$, and compounds **2** and **4** crystallised in the centrosymmetric space group $P\bar{1}$, so racemic mixtures are present. Compounds **5** and **8** crystallised in the non-centrosymmetric space groups $P2_1$ and $P2_12_12_1$, respectively, so in the crystal, only one enantiomer was present.

Deposition Numbers 2353366 (for **1**), 2353367 (for **2**), 2353368 (for **4**), 2353369 (for **5**), 2353537 (for **6**), 2353370 (for **7**), 2353371 (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.

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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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[1] M. Baumann, I. R. Baxendale, *Beilstein J. Org. Chem.* **2013**, *9*, 2265–2319.
[2] M. N. Zafar, A. H. Atif, M. F. Nazar, S. H. Sumrra, E. S. Gul, R. Paracha, *Russ. J. Coord. Chem.* **2016**, *42*, 1–18.
[3] a) P. Kiuru, J. Yli-Kauhaluoma, *in Heterocycles in Natural Product Synthesis*, Wiley-VCH, Weinheim **2011**; b) M. Escolano, D. Gaviña, G. Alzuet-Piña, S. Díaz-Oltra, M. Sánchez-Roselló, C. del Pozo, *Chem. Rev.* **2024**, *124*, 1122–1246; c) L. M. Comparini, M. Pineschi, *Molecules* **2023**, *28*, 6186; d) C. Zheng, S.-L. You, *ACS Cent. Sci.* **2021**, *7*, 432–444.
[4] a) V. K. Sharma, S. K. Singh, *RSC Adv.* **2017**, *7*, 2682–2732; b) E. Vitaku, D. T. Smith, J. T. Njardarson, *J. Med. Chem.* **2014**, *57*, 10257–10274.
[5] C. Gunanathan, D. Milstein, *Acc. Chem. Res.* **2011**, *44*, 588–602.
[6] a) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2005**, *127*, 10840–10841; b) S. Tang, N. von Wolff, Y. Diskin-Posner, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2019**, *141*, 7554–7561; c) E. Ben-Ari, G. Leitus, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.* **2006**, *128*, 15390–15391; d) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* **2006**, *45*, 1113–1115.
[7] P. P. Power, *Nature* **2010**, *463*, 171–177.
[8] a) C. Shan, S. Yao, M. Driess, *Chem. Soc. Rev.* **2020**, *49*, 6733–6754; b) E. Fritz-Langhals, *Org. Process Res. Dev.* **2019**, *23*, 2369–2377; c) C. Weetman, S. Inoue, *ChemCatChem* **2018**, *10*, 4213–4228.
[9] a) Y. Xiong, S. Yao, M. Driess, *Chem. Eur. J.* **2009**, *15*, 5545–5551; b) Y. Li, B. Ma, C. Cui, *Dalton Trans.* **2015**, *44*, 14085–14091; c) H. Sakaba, M. Yabe-Yoshida, H. Oike, C. Kabuto, *Organometallics* **2010**, *29*, 4115–4119; d) R. Azhakar, R. S. Ghadwal, H. W. Roesky, J. Hey, D. Stalke, *Organometallics* **2011**, *30*, 3853–3858.
[10] M. L. Reyes, T. Troadec, R. Rodriguez, A. Baceiredo, N. Saffon-Merceron, V. Branchadell, T. Kato, *Chem. Eur. J.* **2016**, *22*, 10247–10253.
[11] X. Qi, T. Zheng, J. Zhou, Y. Dong, X. Zuo, X. Li, H. Sun, O. Fuhr, D. Fenske, *Organometallics* **2019**, *38*, 268–277.
[12] K. L. Miller, B. N. Williams, D. Benitez, C. T. Carver, K. R. Ogilby, E. Tkatchouk, W. A. Goddard III, P. L. Diaconescu, *J. Am. Chem. Soc.* **2010**, *132*, 342–355.
[13] a) S. Deeken, G. Motz, R. Kempe, *Z. Anorg. Allg. Chem.* **2007**, *633*, 320–325; b) X. Sun, T. Simler, K. Reiter, F. Weigend, P. W. Roesky, *Chem. Eur. J.* **2020**, *26*, 14888–14895.
[14] a) Y. Xiong, S. Yao, M. Driess, *Chem. Eur. J.* **2009**, *15*, 5545–5551; b) K. Uchida, S. Ishida, T. Iwamoto, *Eur. J. Org. Chem.* **2022**, *2022*, e202200522.
[15] a) M. K. Bisai, V. S. V. S. N. Swamy, T. Das, K. Vanka, R. G. Gonnade, S. S. Sen, *Inorg. Chem.* **2019**, *58*, 10536–10542; b) R. S. Ghadwal, S. S. Sen, H. W. Roesky, M. Granitzka, D. Kratzert, S. Merkel, D. Stalke, *Angew. Chem. Int. Ed.* **2010**, *49*, 3952–3955; c) N. Weyer, M. Heinz, C. Bruhn, M. C. Holthausen, U. Siemeling, *Chem. Commun.* **2021**, *57*, 9378–9381; d) F. M. Mück, J. A. Baus, A. Ulmer, C. Burschka, R. Tacke, *Eur. J. Inorg. Chem.* **2016**, 1660–1670; e) Y. Li, B. Ma, C. Cui, *Dalton Trans.* **2015**, *44*, 14085–14091; f) S. Ishida, T. Iwamoto, M. Kira, *Organometallics* **2010**, *29*, 5526–5534; g) Y. Gao, H. Hu, C. Cui, *Chem. Eur. J* **2011**, *17*, 8803–8806; h) V. S. V. S. N. Swamy, K. V. Raj, K. Vanka, S. S. Sen, H. W. Roesky, *Chem. Commun.* **2019**, *55*, 3536–3539; i) R. Azhakar, R. S. Ghadwal, H. W. Roesky, J. Hey, D. Stalke, *Organometallics* **2011**, *30*, 3853–3858.
[16] a) C.-W. So, H. W. Roesky, J. Magull, R. B. Oswald, *Angew. Chem. Int. Ed.* **2006**, *45*, 3948–3950; b) S. S. Sen, H. W. Roesky, D. Stern, J. Henn, D. Stalke, *J. Am. Chem. Soc.* **2010**, *132*, 1123–1126.
[17] R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn, D. Stalke, *Angew. Chem. Int. Ed.* **2009**, *48*, 5683–5686.
[18] J. M. Goll, E. Fillion, *Organometallics* **2008**, *27*, 3622–3625.
[19] W. H. Baur, *Am. Min.* **1971**, *56*, 1573–1599.
[20] N. Tsoureas, J. C. Green, F. G. N. Cloke, H. Puschmann, S. M. Roe, G. Tizzard, *Chem. Sci.* **2018**, *9*, 5008–5014.

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