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Versatile Reactivity of a Zwitterionic Isolable Silylene toward Ketones: Silicon-Mediated, Regio- and Stereoselective C–H Activation

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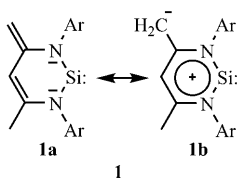
Abstract: Reactions of the isolable, ylide-like silylene LSi: (**1**) (L = CH[(C=CH_2)CMe][N(Ar)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) with different ketones (benzophenone, benzylideneaceton, acetophenone) have been investigated. The metastable dearomatized siloxindane **2**, which was suggested previously as reaction intermediate but could not be detected in related reactions, has been obtained for the first time from the regio- and stereoselective addition of silylene **1** to benzophenone at low temperature. By variation of the reaction temperature, the initial product **2** rearranges under re-aromatization stereoselectively to the corresponding siloxindane **3**, which has also been isolated in high yield. In contrast, reactions of **1** with benzylidenacetone and acetophenone furnish the [4+1] cycloaddition product **4** and the silyl enol ether **5**, respectively. It is proposed that in all reactions the 1,4-dipolar nature of **1** plays key role, leading to highly reactive donor–acceptor adducts, which undergo rearrangement (tautomerization) to the final products. The new compounds **2**, **3**, **4**, and **5** were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, EI-MS, and elemental analysis, and their structures determined by single-crystal X-ray diffraction analysis.

Keywords: cycloaddition · siloxindanes · silyl enol ethers · silylation · stereoselective addition

Introduction

Silylenes are divalent dicoordinate silicon species typically with a singlet ground state. They feature a lone pair of electrons and an empty 3p-valence orbital localized at silicon, which represent the HOMO and LUMO, respectively. Thus, silylenes can act both as Lewis acids, for example, in reactions with nucleophiles, and as Lewis bases, for example, in reactions with electrophiles.[1] Moreover, their carbene-like electron deficiency enables a variety of facile insertion reactions into X–Y σ- bonds of substrates to yield heteroatom-substituted silanes[2,3] and new classes of organosilicon compounds that are otherwise difficult to achieve. Since the successful synthesis and isolation of several stable silylenes,[4] including the zwitterionic silylene **1** (Scheme 1),[5] their fascinating reactivity toward a variety of substrates, such as haloalkanes, halosilanes,[6] alkali metal amides,[7,8] alkenes, alkynes,[9,10] alcohols,[11–13] as well as white phosphorus,[14] has been a matter of numerous investigations. Accordingly, silylenes can be valuable building blocks in organic synthesis, for which the generated organosilicon group can serve as a protecting group for further chemical transformations. Likewise, the direct formation of Si–C bonds through insertion and cycloaddition reactions of silylenes with unsaturated organic precursors in the vicinity to other functional groups and at the same time encoding stereochemical information is a challenging tool in synthetic chemistry.[15] Unexpectedly, data on the reactivity of stable silylenes toward heteroatomic C=X bonds, in particular to the C=O bond in ketones, is relatively scarce. In the latter case, merely one isolable N-heterocyclic silylene,[16] transient silylenes generated in situ either by thermolysis[17] or photolysis of the corresponding precursors,[18] and decamethylsilocene[19,20] were employed to study the reactivity of divalent silicon toward ketones. The conversions led to unexpected new Si–C- and Si–O-functionalized products, including siloxindanes[17–20] and silyl enol ethers,[17] depending on the electronic nature of the applied silylenes and the ketones. The mechanism is unknown and intermediates could not be observed but it has been pro-



Scheme 1. Zwitterionic, ylide-like silylene **1**.

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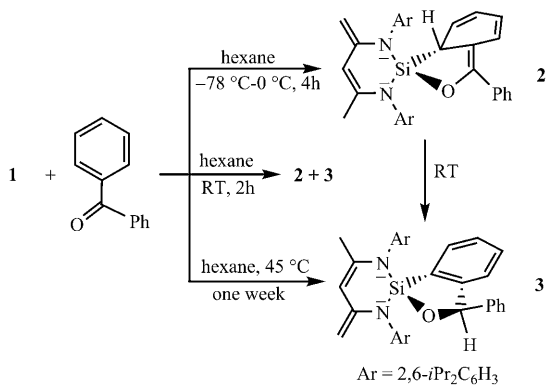
posed that [2+1] cycloaddition occurs as an initial step to give the respective three-membered SiCO cycles, which subsequently rearrange to the final products. Since the new Si–C- and Si–O-functionalized heterocyclic products could be valuable precursors for organic transformations in natural product synthesis,[21] it seems desirable to extend their synthetic access for facile applications in regio- and stereoselective synthesis by using other silylenes.

Recently we reported the reactivity of silylene **1** towards a variety of saturated and unsaturated substrates.[5,6e,10,13,14,22] Owing to its 1,4-dipolar nature, **1** shows a markedly distinct reactivity compared with other stable silylenes. For instance, H^+ addition to **1** occurs solely in position 4 leading to a silyliumylidene cation,[22] and a siloxy silylene is formed through addition of water onto **1**.[13] Moreover, the ylide-like nature of **1** opens up new reaction channels for silylene transformations with unsaturated substrates such as terminal alkynes (C–H insertion vs. [2+1] cycloaddition).[10] Thus we anticipated that the versatile reactivity of **1** (ylide vs. silylene reactivity) has a drastic influence on the nature of products yielded by the reaction of **1** with heteroatomic C=X bonds. In fact, utilization of **1** facilitates for the first time the isolation of a reaction intermediate for the conversion of a stable silylene with a ketone. Herein, we describe the striking reactivity of **1** toward ketones, which proceeds via silicon-mediated C–H activation and an unprecedented tautomerization.

Results and Discussion

The reaction of silylene **1** with an equimolar amount of benzophenone in hexane proceeds readily even at −78 °C. When the reaction mixture is allowed to warm up to 0 °C within 4 h, quantitative formation of the remarkable silyl enol ether **2** is observed, which is isolated in the form of colorless crystals in 87 % yield. However, performing the reaction at ambient temperature produces a mixture of **2** and its silyl ether tautomer **3** (Scheme 2). The amount of **3** can be easily increased at the expense of **2** by prolonging the reaction time and increasing the temperature. In other words, **2** rearranges completely to **3**, which has been proven by separate experiments using isolated **2** dissolved in hexane. Quantitative formation of **3** can be achieved after one week at 45 °C, and colorless crystals of the desired product are accessible by fractional crystallization in 85 % yield.



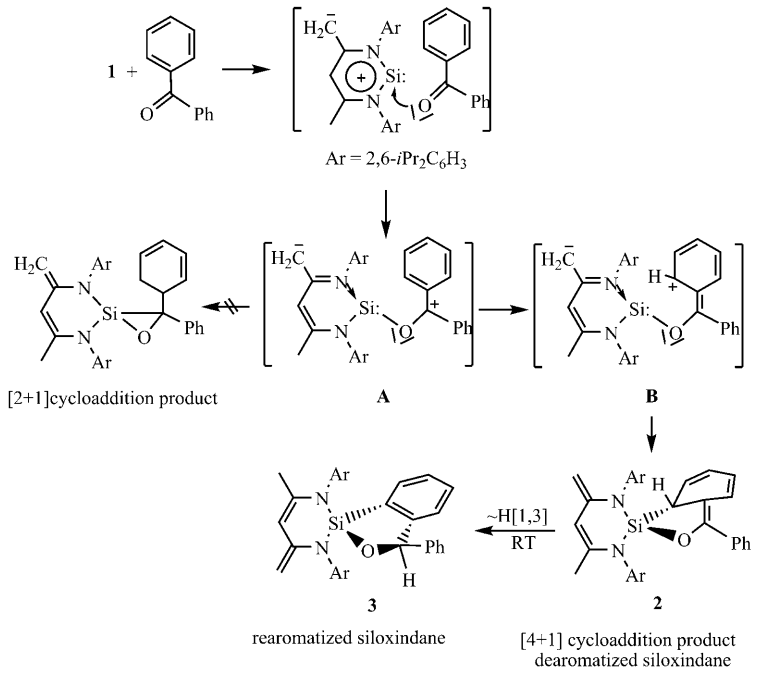
Scheme 2. Formation of **2** and **3** from silylene **1** and benzophenone.

Apparently, **2** represents the kinetic product and results from a [4+1] cycloaddition under concomitant de-aromatization of one phenyl group, whereas **3** is the thermodynamic product, which benefits from re-aromatization of the cross-conjugated methylene–cyclohexadiene π-system in **2**. Related intermediates of **2** with a non-aromatic siloxindane ring system have been previously proposed but could not be detected for similar reactions of transient silylenes[17,18] and a stable silylene[16] with benzophenone, respectively. A close example shows decamethylsilicocene which reacts slowly with benzophenone in toluene to give the corresponding analogue of **2**. However, the latter product does not undergo re-aromatization and formation of the corresponding analogue of **3**.[20]

Although the mechanism is still unknown, it is proposed that the 1,4-dipolar nature of **1** plays an important role in the reaction: First, the charge separation in **1** favors a nucleophilic attack of the oxygen atom in benzophenone at the positively charged, divalent Si atom, leading to the donor–acceptor adduct **A** as an initial product (Scheme 3). Owing to the high Lewis basicity of the Si^{II} lone pair electrons, the formation of a [2+1] cycloaddition compound in the following step seems possible but unlikely due to steric congestion and strain energy of the Si-O-C three-membered ring. Therefore, we propose that **A** isomerizes to **B** and subsequently to the [4+1] cycloaddition product **2**. The latter rearranges through silicon-mediated C–H activation and re-aromatization to give compound **3**.

Compounds **2** and **3** have been unambiguously characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, mass spectrometry, and elemental analysis. Since two chiral centers are present in both compounds, the formation of two diastereomers is possible in each case. However, only one diastereomer of **2** is formed with the *R*,*S* configuration as shown by ^1H NMR spectroscopy of the resulting reaction mixture. Apparently, the formation of **2** proceeds in a regio- and stereoselective manner. Similarly in the case of **3**, one diastereomer (with *S*,*S* or *R*,*R* configuration) dominates (>93 %) in the resulting reaction mixture. The characteristic multiplet at $\delta = 3.35$ ppm in the ^1H NMR spectrum of **2** results from the proton bound to a sp^3-hybridized γ-C atom of the cyclohexadiene ring. Accordingly, this signal is absent in the ^1H NMR spectrum of **3**. Instead, two new singlets at $\delta = 5.10$ (93 % of a diastereomer) and 5.02 ppm (7 % of another diastereomer) appear for the corresponding resonances of the benzylic α-protons. The molecular structures of **2** and **3** have been confirmed by single-crystal X-ray diffraction analyses (Figure 1 and Figure 2).

Compound **2** crystallized in the monoclinic space group $P2_1/c$ with *R*,*S* configuration (Figure 1). The silicon center is tetrahydrally coordinated, featuring a Si–O (166.3(2) pm) and a Si–C (186.1(2) pm) single bond. The non-aromatic cyclohexadiene-like six-membered ring (C30 to C35) in **2** is



Scheme 3. Proposed mechanism for the formation of **2** and **3** via the intermediate **B**.

Compound **3** with *S*,*S* and *R*,*R* configuration crystallizes in the triclinic space group $P\bar{1}$ (Figure 2). Similar to the molecular structure of **2**, the silicon atom possesses a tetrahedral coordination. The two annelated rings of the siloxindane skeleton are almost coplanar and the C35–C36 distance of 152.6(2) pm represents a typical single bond. Despite the aforementioned difference, the geometric parameters within the six-membered C_3N_2Si ring are comparable to those observed in **2**.

Treatment of the stable silylene **1** with one equivalent of benzylideneacetone at room temperature leads to the quantitative formation of the [4+1] cycloaddition product **4** (Scheme 4), which is analogous

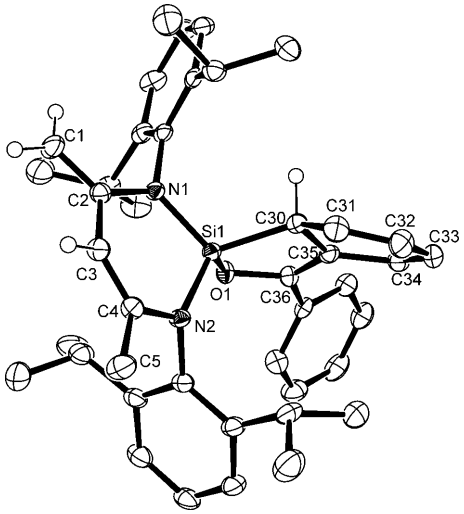


Figure 1. Molecular structure of (*R*,*S*)-**2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms (except for those at C1, C3, and C30) are omitted for clarity. Selected bond lengths [pm] and angles [°]: Si1–O1 166.3(2), Si1–N1 171.8(2), Si1–N2 171.3(2), Si1–C30 186.1(2), O1–C36 140.2(3), C36–C35 135.0(3), C35–C34 144.8(3), C34–C33 134.4(3), C33–C32 144.7(4), C32–C31 132.7(3), C31–C30 149.4(3), C35–C30 150.3(3); N2-Si1-N1 105.11(10), O1-Si1-C30 93.86(9).

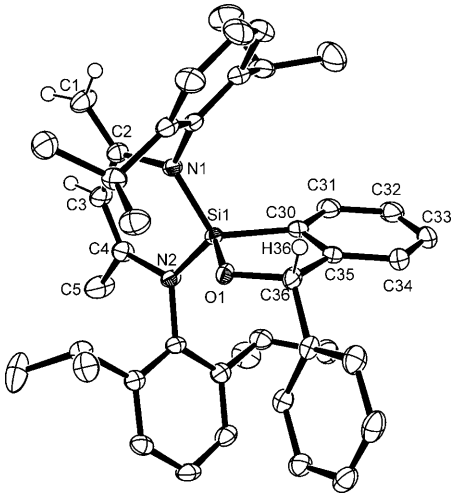
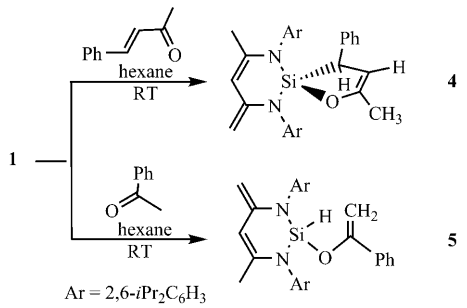


Figure 2. Molecular Structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms (except for those at C1, C3, and C36 are omitted for clarity. Selected bond lengths [pm] and angles [°]: Si1–O1 164.5(1), Si1–N1 171.4(1), Si1–N2 172.2(1), Si1–C30 184.9(1), O1–C36 143.8(1), C36–C35 152.6(2), C35–C30 139.5(2); N2-Si1-N1 105.11(10), O1-Si1-C30 93.86(9), N1-Si1-N2 104.91(6), O1-Si1-C30 94.03(6).

puckered with a folding angle of 17.6° between the planes defined by C30, C31, C35, and the plane defined by C31–C35. In line with that, the distances of C30–C31 (149.4 pm) and C30–C35 (150.3 pm) show typical single-bond character, whereas that of C35–C36 (135.0 pm) is indicative for a C=C double bond.

to that observed with another stable silylene.[16] The reaction mechanism should be similar to that for compound **2**. Compound **4** was isolated in the form of colorless crystals in 94% yield. The latter was fully characterized by NMR spectroscopy, EI-MS, and elemental analysis. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of the resulting reaction solution show



Scheme 4. Synthesis of **4** and **5**.

only one set of signals, indicating a highly regio- and stereospecific reaction. The doublet of doublets at $\delta = 1.49$ ppm in the ^{1}H NMR spectrum can be assigned to the resonance of the methyl group of the OC*Me* protons, which undergo long-range coupling with the two protons on the five-membered ring. The latter protons in turn resonate at $\delta = 3.22$ and 4.52 ppm, respectively. The molecular structure of **4** was established by a single-crystal X-ray diffraction analysis (Figure 3). Compound **4** crystallizes in the triclinic space

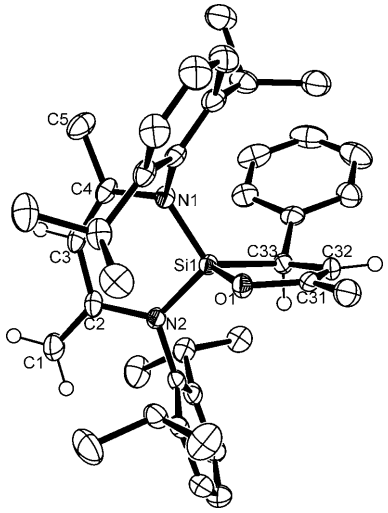
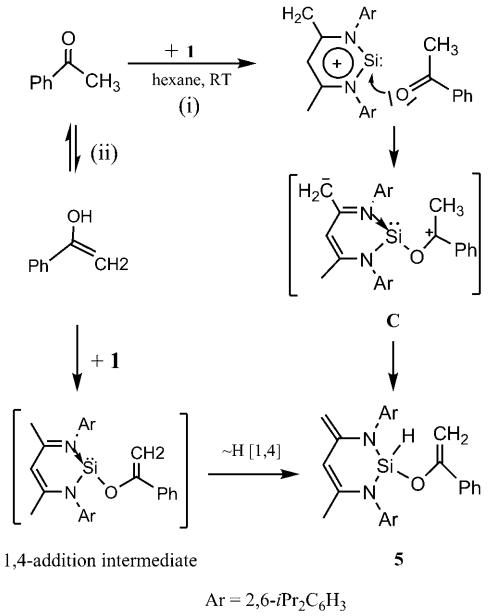


Figure 3. Molecular Structure of **4**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms (except for those at C1, C3, C32, and C33) are omitted for clarity. Selected bond lengths [pm] and angles [°]: Si1–O1 166.4(1), Si1–N1 171.8(1), Si1–N2 172.0(1), Si1–C33 188.7(2), O1–C31 139.3(2), C31–C32 132.5(2), C32–C33 151.1(2); N1-Si1-N2 105.15(6), O1-Si1-C33 95.00(6).

group $P\bar{1}$ with *R*,*R* or *S*,*S* configurations. The five-membered $SiOC_3$ ring is nearly planar and perpendicular to the six-membered SiN_2C_3 ring. The spiro-silicon atom is tetrahedrally coordinated, featuring four single bonds, which are each within the respective normal bond length range.[23]

To learn whether the possible keto–enol tautomerism in acetophenone changes the nature of the addition product, we probed the conversion of silylene **1** with one molar equivalent of acetophenone at room temperature. In fact, sole formation of **5** is a result of the relatively high C–H acidity of the α-methyl group (Scheme 4).

The formation of **5** is analogous to that observed with a transient silylene and acetophenone.[17] Its generation can be rationalized by a reaction pathway involving prior formation of donor–acceptor adduct **C** followed by intramolecular proton abstraction and enolization through the divalent Si atom (Scheme 5, pathway i). An alternative pathway to **5** is the formation of a 1,4-addition intermediate based on reaction of silylene **1** with the enol form of the acetophenone (Scheme 5, pathway ii). Unfortunately, attempts to detect a reaction intermediate by means of low-temperature ^{1}H NMR spectroscopy (−80 °C) failed.



Scheme 5. Proposed mechanism for the formation of **5**.

Compound **5** was isolated as colorless crystals in 86% yield and fully characterized by ^{1}H, ^{13}C, ^{29}Si NMR spectroscopy, mass spectrometry, and elemental analysis. The doublets at $\delta = 3.06$ and 4.49 ppm in the ^{1}H NMR spectrum with a coupling constant of $J = 2$ Hz can be assigned to the germinal protons of the PhCCH_2 moiety, while the singlet at $\delta =$ 5.37 ppm represents the SiH proton of the silyl enol ether. According to X-ray diffraction analysis (Figure 4), compound **5** crystallizes in the monoclinic space group *C*2/*c*. The short C30–C31 distance of 131.4(3) pm is indicative for a double bond. The metric parameters for **5** are similar to those of other silyl enol ether.[23]

Conclusions

In conclusion, reaction of the zwitterionic stable silylene **1** with benzophenone at −78 °C leads to the isolation of the

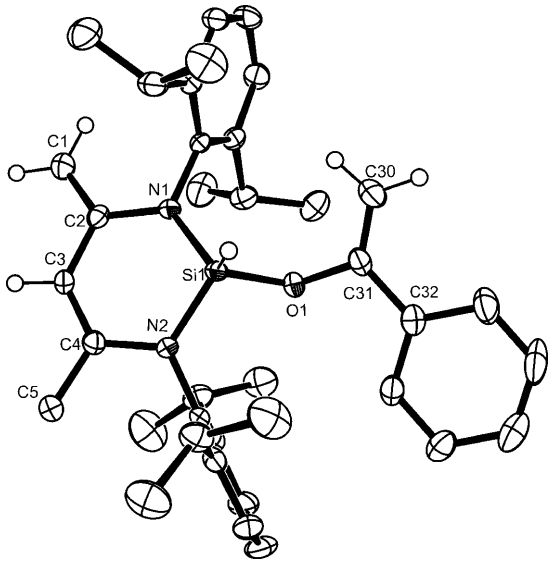


Figure 4. Molecular Structure of **5**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms (except for those at C1, C3, Si1, and C30) are omitted for clarity. Selected bond lengths [pm] and angles [°]: Si1–O1 163.2(1), Si1–N1 171.6(2), Si1–N2 171.8(2), O1–C31 133.8(2), C30–C31 131.4(3); N2-Si1-N1 104.18(8), O1-Si1-C31 127.5(1), O1-C31-C30 120.7(2), O1-C31-C32 113.2(2), C30-C31-C32 126.0(2).

unusual [4+1] cycloaddition product **2**, which contains a methylenecyclohexadiene moiety that results from de-aromatization of a phenyl group. The tendency of **2** to undergo re-aromatization facilitates its slow tautomerization to **3** already at room temperature. The latter has also been isolated and structurally characterized. Reaction of **1** with benzylideneacetone and the higher C–H acidic acetophenone yields the expected [4+1] cycloaddition product **4** and the corresponding silyl enol ether **5**, respectively. Remarkably, formation of **2**, **3**, and **4** occurs regio- and stereospecifically. It is proposed that in all reactions the 1,4-dipolar nature of **1** plays a key role in facilitating the facile attack of the oxygen atom on the silicon atom, leading to the formation of donor–acceptor intermediates, which subsequently undergo rearrangement (tautomerization) to yield the respective thermodynamic products.

Experimental Section

General considerations: All experiments and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or in an MBraun inert atmosphere dry box, containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior to use. The starting material silylene **1** was prepared according to a literature procedure.[5] The NMR spectra were recorded with Bruker spectrometers ARX200, AV400, and with residual solvent signals as internal reference (^{1}H and ^{13}C{H}) or with an external reference ($SiMe_4$ for ^{29}Si). Abbreviations: s = singlet; d = doublet; t = triplet; sept = septet; m = multiplet; br = broad.

Single-crystal X-ray structure determination: Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data of **2**–**5** were collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97[24] software package (Table 1). The positions of the H atoms were calculated and considered isotropically according to a riding model (exception is the hydrogen atom on silicon in **5** which has been found in the electron density map). CCDC-719074, CCDC-719075, CCDC-719076, and CCDC-719077 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table 1. Crystal and refinement data for **2**, **3**, **4**, and **5**.

Compound	**2**	**3**	**4**	**5**
empirical formula	$C_{42}H_{50}N_2SiO$	$C_{42}H_{50}N_2SiO$	$C_{39}H_{50}N_2SiO$	$C_{37}H_{48}N_2SiO$
M	626.93	626.93	90.90)	564.86
crystal system	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a [Å]	9.3263(3)	11.3945(3)	8.9500(2)	21.2473(5)
b [Å]	22.0602(7)	11.8961(4)	12.7001(6)	10.1482(2)
c [Å]	17.9069(7)	14.8824(3)	15.5694(5)	30.7649(8)
α [°]	90	78.296(2)	95.481(3)	90
β [°]	104.129(4)	82.767(2)	96.704(3)	91.980(2)
γ [°]	90	68.200(3)	97.307(3)	90
V [Å^{-3}]	3572.7(2)	1831.26(9)	1732.36(11)	6629.4(3)
Z	4	2	2	8
d_{calcd} [Mg m^{-3}]	1.166	1.137	1.133	1.132
μ ($Mo_{K\alpha}$) [mm^{-1}]	0.100	0.098	0.099	0.101
reflections collected	18951	17089	15096	26495
independent reflections	6261	6447	6086	5805
R(int)	0.0569	0.0167	0.0263	0.0371
reflections with $I > 2\sigma(I)$	4468	5597	4877	4936
data/parameters	6261/424	6447/424	6086/398	5805/382
final R indices [$I > 2\sigma(I)$] R_1	0.0615	0.0380	0.0421	0.0561
R indices (all data) wR_2	0.1107	0.1087	0.1041	0.1121

Syntheses: **2**: Ph_2CO (0.14 g, 0.77 mmol) was added to a solution of silylene **1** (0.34 g, 0.77 mmol) in hexane (10 mL) at −78 °C. The reaction temperature was allowed to warm slowly to 0 °C within 4 h. At 4 °C compound **2** crystallized from concentrated hexane solution (5 mL) as colorless plates in a yield of 0.42 g (0.67 mmol, 87%). M.p. 159 °C (decomp); ^{1}H NMR (200.13 MHz, [D$_6$]benzene, 25 °C): δ = 1.15 (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.28 (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.30 (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.32 (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.33 (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.35 (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.39 (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.47 (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.59 (s, 3H; NCMe), 3.35 (m, 1H; OSiC*H*–CH=), 3.47 (s, 1H; NCCH_2), 3.60 (sept., ^3J(H,H) = 7.0 Hz, 1H; C*H*Me$_2$), 3.88 (m, 3H; C*H*Me$_2$), 4.06 (s, 1H; NCCH_2), 5.39 (m, 1H; OSiCHC*H*=), 5.50 (s, 1H; γ-C*H*), 5.56 (m, 2H; OSiCH–CH=C*H*C*H*=), 6.37 (d, ^3J(H,H) = 9.7 Hz, 1H; PhC=CC*H*=), 7.01–7.22 ppm (m, br, 11H; C_6H_5, 2,6-iPr$_2$C$_6$*H*$_3$), 7.69 (m, 1H); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$]benzene, 25 °C): δ = 21.7 (NC*C*H$_3$), 23.6, 24.3, 25.1, 25.4, 25.5, 25.8, 26.6, 26.7 (CH*Me*$_2$, OSi*C*HCH=), 28.4, 28.8, 28.9 (*C*HMe$_2$), 88.7 (NC*C*H$_2$), 108.9 (γ-*C*), 114.5, 123.3, 123.8, 124.9, 124.4, 124.6, 124.7, 125.5, 127.4, 127.8, 127.9, 128.1, 128.7, 134.3, 135.4, 137.2, 141.4, 147.4, 148.1, 148.2, 149.0, 149.1, 149.8 ppm (N*C*Me, NC*C*H$_2$, vinyl –*C*H=(cyclohexadiene system), *CPh*, 2,6-iPr$_2$*C*$_6$H$_3$); ^{29}Si{^{1}H} NMR (79.49 MHz, [D$_6$]benzene, 25 °C): δ = −22.0 ppm (s); EI-MS: m/z (%): 626.5 (31) [M^+], 611.4 (100) [M^+–Me],

583.3 (55) [M^+-iPr]; elemental analysis calcd (%) for $C_{42}H_{50}N_2SiO$: C 80.46, H 8.04, N 4.47; found: C 80.21, H 7.94, N 4.45.

3: Ph_2CO (0.26 g, 1.41 mmol) was added to a solution of silylene **1** (0.63 g, 1.41 mmol) in hexane (15 mL) at room temperature and the solution was warmed to 45 °C. After one week the reaction was completed and the solution was concentrated to 5 mL and cooled at 4 °C. The collected colorless crystals amounted to 0.76 g (1.20 mmol, 85 %). M.p. 207 °C (decomp); ^{1}H NMR (200.13 MHz, [D$_6$]benzene, 25 °C): $\delta = 0.01$ (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 0.04 (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.12–1.22 (3 × d, ^3J(H,H) = 7.0 Hz, 9H; CHMe_2), 1.35–1.43 (3 × d, ^3J(H,H) = 7.0 Hz, 9H; CHMe_2), 1.57 (s, 3H; NCMe), 3.28 (s, 1H; NCCH_2), 3.34 (m, 2H; CHMe$_2$), 3.88 (m, 2H; CHMe$_2$), 3.95 (s, 1H; NCCH_2), 5.10 (s, 1H; PhCH), 5.38 (s, 1H; γ-H), 5.93 (d, ^3J(H,H) = 6.5 Hz, 2H; C$_6H_4$), 6.32 (d, ^3J(H,H) = 7.6 Hz, 1H; C$_6$H$_4$), 6.74–7.24 (m, br, 12H; C$_6H_5$, 2,6-iPr$_2$C$_6H_3$), 7.66 ppm (d, ^3J(H,H) = 7.2 Hz, 1H; C$_6$H$_4$); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$]benzene, 25 °C): $\delta = 22.1$ (NCCH_3), 24.5, 24.6, 24.7, 24.9, 25.2, 25.4, 26.4, 26.8 (CHMe_2), 27.8, 28.2, 29.1, 29.2 (CHMe$_2$), 80.3 (CHPh), 86.2 (NCCH_2), 103.8 (γ-*C*), 123.6, 124.5, 124.6, 124.8, 124.9, 126.8, 127.4, 127.6, 127.7, 128.1, 128.2, 128.3, 130.1, 133.5, 134.6, 136.0, 141.5, 142.4, 148.2, 148.7, 148.9, 149.7, 150.5, 155.0 ppm (NCMe, NCCH_2, C_6H_4, C_6H_5, 2,6-iPr$_2C_6H_3$); ^{29}Si{^{1}H} NMR (79.49 MHz, [D$_6$]benzene, 25 °C): $\delta = -33.3$ ppm (s); EI-MS: *m*/*z* (%): 626.3 (31) [M^+], 611.4 (100) [M^+−Me], 583.2 (56) [M^+-iPr]; elemental analysis calcd (%) for $C_{42}H_{50}N_2SiO$: C 80.46, H 8.04, N 4.47; found: C 80.21, H 7.96, N 4.53.

4: Benzylideneacetone (0.23 g, 1.53 mmol) was added to a solution of silylene **1** (0.68 g, 1.53 mmol) in hexane (15 mL) at room temperature. The reaction was completed within one hour. The solution was concentrated to about 5 mL and cooled at 4 °C. The product **4** crystallized as colorless crystals. Yield: 0.85 g (1.44 mmol, 94 %). M.p. 136 °C (decomp); ^{1}H NMR (200.13 MHz, [D$_6$]benzene, 25 °C): $\delta = 0.63$ (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 0.94 (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.22 (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.26 (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.35 (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.39 (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.41 (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.42 (s, 3H; NCMe), 1.46 (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.49 (dd, ^4J(H,H) = 3 Hz, ^5J(H,H) = 1 Hz, 3H; OCMe), 3.00 (sept. ^3J(H,H) = 7 Hz, 1H; CHMe$_2$), 3.22 (m; PhCH), 3.40 (s, 1H; NCCH_2), 3.60 (sept. ^3J(H,H) = 7.0 Hz, 1H; CHMe$_2$), 3.81 (sept. ^3J(H,H) = 7.0 Hz, 2H; CHMe$_2$), 4.02 (s, 1H; NCCH_2), 4.52 (m, 1H; OCCH), 5.44 (s, 1H; γ-CH), 6.76–7.23 ppm (m, 11H; *Ph*, iPr$_2$C$_6$H$_3$); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$]benzene, 25 °C): $\delta = 18.1$ (NCCH_3), 21.6, 23.9, 24.0, 24.6, 24.7, 25.1, 25.2, 26.2, 26.5, 28.2, 28.3, 28.4, 29.0, 31.7 (NCMe, OCMe, PhCH, CHMe$_2$), 88.4 (NCCH_2), 104.8 (OCCH), 107.0 (γ-*C*), 124.1, 124.4, 125.0, 125.1, 125.2, 127.9, 128.1, 128.4, 128.9, 136.5, 137.1, 139.7, 142.2, 147.8, 148.5, 148.6, 149.1, 149.9, 153.6 ppm (NCMe, NCCH_2, *PhC*, 2,6-iPr$_2C_6H_3$); ^{29}Si{^{1}H} NMR (79.49 MHz, [D$_6$]benzene, 25 °C): $\delta = -23.8$ ppm (s); EI-MS: *m*/*z* (%): 590.4 (100) [M^+], 575.4 (82) [M^+−Me], 547.2 (50) [M^+-iPr]; elemental analysis calcd (%) for $C_{39}H_{50}N_2SiO$: C 79.27, H 8.53, N 4.74; found: C 79.60, H 8.39, N 4.76.

5: Acetophenone (0.12 mL, $d = 1.03$ g mL^{-1}, 1.01 mmol) was added to a solution of silylene **1** (0.45 g, 1.01 mmol) in hexane (8 mL) at room temperature. The reaction mixture was completed immediately. The solution was concentrated to about 5 mL and cooled at 4 °C. The product **5** crystallized as colorless crystals. Yield: 0.49 g (0.87 mmol, 86 %). M.p. 146 °C (decomp); ^{1}H NMR (200.13 MHz, [D$_6$]benzene, 25 °C): $\delta = 0.98$ (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.07 (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.24 (d, ^3J(H,H) = 7.0 Hz, 6H; CHMe_2), 1.32 (d, ^3J(H,H) = 7.0 Hz, 6H; CHMe_2), 1.36 (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.40 (d, ^3J(H,H) = 7.0 Hz, 3H; CHMe_2), 1.51 (s, 3H; NCMe), 3.06 (d, ^2J(H,H) = 2.0 Hz, 1H; PhCCH_2), 3.45 (sept. ^3J(H,H) = 7.0 Hz, 1H; CHMe$_2$), 3.48 (s, 1H; NCCH_2), 3.57 (sept. ^3J (H,H) = 7.0 Hz, 1H; CHMe$_2$), 3.83 (sept. ^3J(H,H) = 7.0 Hz, 2H; CHMe$_2$), 4.02 (s, 1H; NCCH_2), 4.49 (d, ^2J (H,H) = 2.0 Hz, 1H; PhCCH_2), 5.35 (s, 1H; γ-CH), 5.37 (s, 1H; SiH), 6.50–7.29 ppm (m, 11H; *Ph*, iPrC$_6$H$_3$); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$]benzene, 25 °C): $\delta = 21.5$ (NCCH_3), 24.1, 24.3, 24.6, 24.8, 25.0, 25.4, 26.0, 26.1 (CHMe_2), 28.2, 28.5, 28.7, 28.8 (CHMe$_2$), 86.6 (NCCH_2), 94.7 (PhCCH_2), 103.1 (γ-*C*), 124.7, 124.8, 125.0, 125.2, 125.4, 128.1, 128.5, 134.9, 135.7, 136.4, 140.9, 148.3, 148.4, 148.7, 149.7, 149.8, 154.5 ppm (NCMe, NCCH_2, *PhC*CH_2, 2,6-iPr$_2C_6H_3$); ^{29}Si{^{1}H} NMR (79.49 MHz, [D$_6$]benzene, 25 °C): $\delta = -51.5$ ppm (s); EI-MS: *m*/*z* (%): 564.4 (14) [M^+], 549.3 (100) [M^+−Me], 521.3 (15) [M^+-iPr]; elemental analysis calcd (%) for $C_{37}H_{48}N_2SiO$: C 78.67, H 8.56, N 4.96; found: C 78.47, H 8.46, N 4.97.

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