

Reactions of Stable Amidinate Chlorosilylene and [1+4]-Oxidative Addition of N-Heterocyclic Silylene with *N*-Benzylideneaniline

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The reaction of $\text{PhC}(\text{NtBu})_2\text{SiCl}$ (**L**) with N_2O afforded the trimer $\{\text{PhC}(\text{NtBu})_2\text{Si}(\text{O})\text{Cl}\}_3$ (**1**), which contains a Si_3O_3 six-membered ring. In the molecular structure of **1**, the $\text{PhC}(\text{NtBu})_2$ moieties are arranged around the Si_3O_3 six-membered ring in a paddle-wheel fashion. Further the reaction of **L** with $\text{B}(\text{C}_6\text{F}_5)_3$ and 9-BBN (9-borobicyclo[3.3.1]nonane) yielded the chlorosilylene–boron adducts **L**· $\text{B}(\text{C}_6\text{F}_5)_3$ (**2**) and **L**·9-BBN (**3**). The reaction of $\text{CH}[(\text{C}=\text{CH}_2)(\text{CMe})(2,6-$

$i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_2\text{Si}$ (**L'**) with *N*-benzylideneaniline resulted in **4**, a [1+4]- rather than a [1+2]-cycloaddition product. Compounds **1–4** were characterized by elemental analyses and spectroscopic methods. The molecular structures of **1**, **2**, and **4** were established unequivocally by single-crystal X-ray structural analysis. The formation of products **1** and **4** was supported by DFT calculations.

Introduction

Silylenes are neutral compounds with divalent silicon that are considered to be silicon analogues of carbenes.^[1] Many stable *N*-heterocyclic silylenes (NHSis)^[1b–d,2,3] have been prepared after the first report in 1994. The HOMO of a silylene is nonbonding and possesses nucleophilic character. Its LUMO is an empty *p*-orbital exhibiting electrophilic character. Accordingly silylenes are considered to have an ambiphilic character and behave as Lewis acids as well as Lewis bases.^[4] Owing to the presence of both, nucleophilic and electrophilic reaction centers, the chemistry of silylenes is quite fascinating.^[5–16] The reactivity of NHSis is comparable with that of the *N*-heterocyclic carbenes (NHCs), the latter having given rise to rapid research activities and numerous applications in chemistry.^[17,18] Many highly reactive compounds with low-valent and zero-valent elements, which are stabilized by NHCs have been documented.^[3b,19] Recently we synthesized the dichlorosilylene stabilized by a stable *N*-heterocyclic carbene (NHC) by employing a new synthetic procedure comprising the reductive elimination of HCl from trichlorosilane in the presence of NHC under mild reaction conditions.^[3b]

Furthermore, we reported the synthesis of $\text{PhC}(\text{NtBu})_2\text{SiCl}$ (**L**) in high yield using lithium bis(trimethylsilyl)amide

as a dehydrochlorinating agent.^[3c] Currently there is active research in the chemistry of NHSis.^[6–16] In addition we reported treatment of N_2O with $\text{PhC}(\text{NtBu})_2\text{Si}-\text{Si}(\text{NtBu})_2\text{-CPh}$ which resulted in the formation of two Si_2O_2 four-membered rings connected with two oxygen atoms^[20] and also the formation of a stable silaaziridine by reaction of *N*-benzylideneaniline with **L**.^[21] Consequently we were eager to know the reaction of **L** with N_2O and study the reactivity of *N*-benzylideneaniline with the stable NHSi (**L'**) [**L'** = $\text{CH}[(\text{C}=\text{CH}_2)(\text{CMe})(2,6-i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_2]\text{Si}$].^[3c] Previously, we had shown *N*–H bond activation of ammonia,^[7b] hydrazines,^[7c] formation of spirocyclic compounds,^[7c,13b] C–H as well as C–F bond activation of fluoroarenes,^[16a] regioselective C–H activation of ylide^[16b], and reactivity of ketones and quinone^[16c] with **L'**. Interestingly, the reaction of **L** with N_2O afforded compound **1** comprising a Si_3O_3 six-membered ring. N_2O has attracted considerable attention as a precursor for an ideal mono-oxygen donor in oxidative reactions, which proceeds with elimination of dinitrogen as the single side product.^[20,22] The molecular structure of **1** features a paddle-wheel arrangement. Further, we reported the chlorosilylene–boron adducts **L**· $\text{B}(\text{C}_6\text{F}_5)_3$ (**2**) and **L**·9-BBN (**3**) by the reaction of equivalent amounts of **L** with $\text{B}(\text{C}_6\text{F}_5)_3$ and 9-BBN, respectively. The reaction of *N*-benzylideneaniline with **L'** afforded the [1+4]-cycloaddition product **4**, involving dearomatization of the benzene ring. In organic chemistry, dearomatizing of arenes provides an efficient way of generating reactive synthons from inexpensive precursors.^[23]

Results and Discussion

Compound **1** was obtained by adding gaseous N_2O to a toluene solution of **L** for 10 min at room temperature

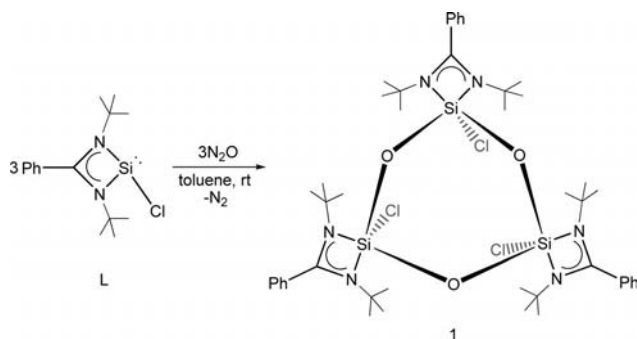
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(Scheme 1). Compound **1** is soluble in benzene, toluene, *n*-hexane, and THF and it is stable in both the solid state and in solution for a long time without any decomposition under an inert gas atmosphere.



Scheme 1. Synthesis of **1**.

The ^{29}Si NMR spectrum of **1** shows a single resonance at $\delta = -114.51$ ppm, which is upfield shifted compared to **L** ($\delta = 14.6$ ppm),^[3c] because in **1** the silicon atom is shielded upon attachment of oxygen atoms to silicon. DFT calculations also reveal a similar upfield shift ($\Delta\delta_{\text{calcd.}} = 134$, $\Delta\delta_{\text{exp.}} = 129$ ppm) for ^{29}Si in **1**. The *t*Bu protons for compound **1** in the ^1H NMR spectrum display a broad singlet, which is observed at $\delta = 1.45$ ppm and is shifted downfield compared to that of **L** ($\delta = 1.08$ ppm). In its mass spectrum compound **1** exhibits its fragment ions at m/z 629 [$\text{M}^+ - \{\text{PhC}(\text{N}t\text{Bu})_2 + 2\text{Cl}\}$] and 594 [$\text{M}^+ - \{\text{PhC}(\text{N}t\text{Bu})_2 + 3\text{Cl}\}$].

Compound **1** crystallizes in the triclinic space group $P\bar{1}$ (Table 1). The molecular structure of **1** is shown in Figure 1. In **1** all silicon atoms are five-coordinate with τ values ($\tau = 1$ for perfect trigonal-bipyramidal arrangement; $\tau = 0$ for perfect square-based pyramid)^[24] of 0.78 (Si1), 0.77 (Si2), and 0.73 (Si3), and are arranged in a distorted trigonal bipyramidal geometry comprising two nitrogen atoms from the supporting amidinato ligand, one chlorine, and two oxygen atoms. The Si_3O_3 six-membered ring is very well known in silicon chemistry.^[25] The $\text{PhC}(\text{N}t\text{Bu})_2$ moieties in **1** are placed in such a way that it gives a paddle-wheel structure (Figure 1, a). In **1**, the $\text{PhC}(\text{N}t\text{Bu})_2$ and Cl moieties are aligned in the opposite direction to the plane of the Si_3O_3 six-membered ring (Figure 1, b). The Si_3O_3 ring in **1** is slightly distorted from planarity, with the largest deviations being 0.1108 and 0.1044 Å for atoms O3 and Si3. There exist two types of Si–N (amidinate ligand) bond lengths, one being shorter [$\text{Si}-\text{N}_{\text{av}}$ 1.813(3) Å] corresponding to the equatorial position and one longer [$\text{Si}-\text{N}_{\text{av}}$ 2.001(3) Å] to the axial position. Similarly two types of Si–O bond lengths are present; the average length of the shorter bond is 1.621(2) Å and the average length of the longer one is 1.670(2) Å. The average Si–O–Si and O–Si–O bond angles are 136.84(14)° and 100.95(11)°. The average Si–Cl bond length in **1** is 2.1125(14) Å [$\text{Si}-\text{Cl}$ of **L** 2.156(1) Å], and the N–Si–N cone angles are 67.84(12)°, 67.64(11)°, and 68.39(12)° [N–Si–N of **L** 71.15(7)°].

The reaction of equimolar amounts of **L** with $\text{B}(\text{C}_6\text{F}_5)_3$ and 9-BBN afforded the colorless crystalline chlorosilylene–

Table 1. Crystal and structure refinement parameters for compounds **1**, **2**, and **4**.

Parameters	1 ·0.5 hexane	2	4
Empirical formula	$\text{C}_{48}\text{H}_{76}\text{Cl}_3\text{N}_6\text{O}_3\text{Si}_3$	$\text{C}_{33}\text{H}_{23}\text{BClF}_{15}\text{N}_2\text{Si}$	$\text{C}_{42}\text{H}_{51}\text{N}_3\text{Si}$
Formula weight	975.77	806.88	625.95
Temperature [K]	133(2)	133(2)	133(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
Unit cell dimensions	$a = 8.6167$ (17) Å $b = 13.912$ (3) Å $c = 23.625$ (5) Å $\alpha = 97.99$ (3)° $\beta = 98.86$ (3)° $\gamma = 107.30$ (3)°	$a = 11.636$ (2) Å $b = 18.945$ (3) Å $c = 15.316$ (3) Å $\alpha = 90^\circ$ $\beta = 100.36$ (3)° $\gamma = 90^\circ$	$a = 11.077$ (2) Å $b = 12.485$ (3) Å $c = 13.109$ (3) Å $\alpha = 87.44$ (3)° $\beta = 86.97$ (3)° $\gamma = 87.99$ (3)°
Volume, Z	2619.9 (9) Å ³ , 2	3321.3 (12) Å ³ , 4	1807.6 (6) Å ³ , 2
Density (calculated)	1.237 g/cm ³	1.614 g/cm ³	1.150 g/cm ³
Absorption coefficient	0.288 mm ^{−1}	0.265 mm ^{−1}	0.098 mm ^{−1}
$F(000)$	1046	1624	676
Crystal size	0.49 × 0.17 × 0.08 mm ³	0.19 × 0.14 × 0.12 mm ³	0.36 × 0.25 × 0.15 mm ³
θ range for data collection	1.56 to 25.95°	1.73 to 27.05°	1.56 to 27.14°
Limiting indices	$-10 \leq h \leq 9$, $-17 \leq k \leq 17$, $-28 \leq l \leq 28$	$-13 \leq h \leq 14$, $-24 \leq k \leq 24$, $-19 \leq l \leq 19$	$-14 \leq h \leq 13$, $-16 \leq k \leq 15$, $-13 \leq l \leq 16$
Reflections collected	23306	29474	15340
Independent reflections	10059 ($R_{\text{int}} = 0.0674$)	7236 ($R_{\text{int}} = 0.0544$)	7672 ($R_{\text{int}} = 0.0590$)
Completeness to θ	98.0% ($\theta = 25.95$)	99.2% ($\theta = 27.05$)	95.8% ($\theta = 27.14$)
Refinement method		full matrix least-squares on F^2	
Data / restraints / parameters	10059 / 10 / 591	7236 / 0 / 484	7672 / 15 / 443
Goodness of fit on F^2	0.981	1.031	1.010
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0566$, $wR2 = 0.1197$	$R1 = 0.0465$, $wR2 = 0.0772$	$R1 = 0.0624$, $wR2 = 0.1349$
R indices (all data)	$R1 = 0.0972$, $wR2 = 0.1340$	$R1 = 0.0765$, $wR2 = 0.0846$	$R1 = 0.1012$, $wR2 = 0.1515$
Largest diff. peak and hole	0.893 and -0.488 e Å ^{−3}	0.290 and -0.266 e Å ^{−3}	0.695 and -0.307 e Å ^{−3}

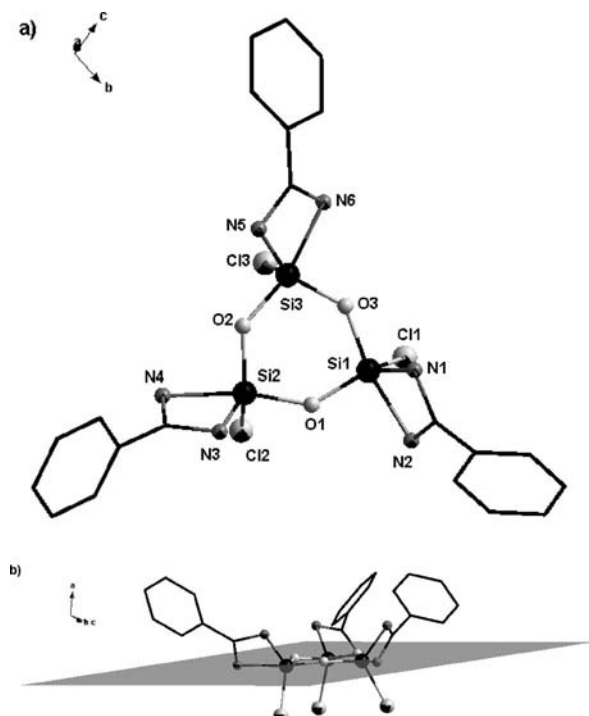


Figure 1. (a) Molecular structure of **1**, showing its paddle-wheel arrangement. (b) Side view of **1** parallel to the plane of the Si_3O_3 six-membered ring, displaying orientation of $\text{PhC}(\text{NtBu})_2$ and Cl moieties relative to this ring. Selected bond lengths [\AA] and angles [$^\circ$]: $\text{Si}(1)\text{--O}(1)$ 1.620(2), $\text{Si}(1)\text{--O}(3)$ 1.670(2), $\text{Si}(2)\text{--O}(1)$ 1.668(2), $\text{Si}(2)\text{--O}(2)$ 1.620(2), $\text{Si}(3)\text{--O}(2)$ 1.672(2), $\text{Si}(3)\text{--O}(3)$ 1.6229(19), $\text{Si}(1)\text{--N}(1)$ 1.813(3), $\text{Si}(1)\text{--N}(2)$ 2.006(3), $\text{Si}(1)\text{--Cl}(1)$ 2.1062(14), $\text{Si}(2)\text{--N}(3)$ 1.808(3), $\text{Si}(2)\text{--N}(4)$ 2.010(3), $\text{Si}(2)\text{--Cl}(2)$ 2.1104(14), $\text{Si}(3)\text{--N}(5)$ 1.818(3), $\text{Si}(3)\text{--N}(6)$ 1.987(3), $\text{Si}(3)\text{--Cl}(3)$ 2.1210(13); $\text{N}(1)\text{--Si}(1)\text{--N}(2)$ 67.84(12), $\text{N}(3)\text{--Si}(2)\text{--N}(4)$ 67.64(11), $\text{N}(5)\text{--Si}(3)\text{--N}(6)$ 68.39(12), $\text{O}(1)\text{--Si}(1)\text{--O}(3)$ 100.64(11), $\text{O}(2)\text{--Si}(2)\text{--O}(1)$ 100.93(12), $\text{O}(3)\text{--Si}(3)\text{--O}(2)$ 101.29(11), $\text{Si}(1)\text{--O}(1)\text{--Si}(2)$ 138.30(14), $\text{Si}(2)\text{--O}(2)\text{--Si}(3)$ 136.12(13), $\text{Si}(3)\text{--O}(3)\text{--Si}(1)$ 136.11(15).

boron adducts **2** and **3**, respectively in quantitative yield (Scheme 2). Both compounds **2** and **3** are stable in solution as well as in the solid state at room temperature in an inert atmosphere. The chlorosilylene–boron adducts **2** and **3** have been characterized by elemental analyses and spectroscopic methods. The molecular structure of adduct **2** has been un-

equivocally established by single-crystal X-ray structural analysis.

The coordination of the boron atom to the silicon atom can be readily noticed in the ^{29}Si NMR spectrum of **2**. Compound **2** resonates at $\delta = 29.94$ ppm with a broad signal owing to the coupling of silicon with the quadrupolar ^{11}B ($I = 3/2$) nucleus which is downfield shifted compared to that of **L**. The ^{11}B NMR spectrum of **2** exhibits a resonance at $\delta = -17.55$ ppm. The ^{19}F NMR spectrum of **2** shows multiplet resonances centered at $\delta = -125.38$, -157.47 , and -167.73 ppm. The ^1H NMR spectrum of **2** exhibits a resonance for $\text{C}(\text{CH}_3)_3$ at $\delta = 0.65$ ppm which is upfield shifted compared to that of **L**. Furthermore, **2** shows its $[\text{M}^+ - \text{C}_6\text{F}_5]$ fragment ion in its ESI-MS at m/z 638.

The molecular structure of $\text{L}\cdot\text{B}(\text{C}_6\text{F}_5)_3$ is represented in Figure 2. Compound **2** crystallizes in the monoclinic space group $P2_1/n$. Both the silicon and boron atoms are four-coordinate and display a distorted tetrahedral geometry. The silicon coordination environment is derived from two nitrogen atoms, one chlorine atom, and a boron atom, whereas boron features three carbon atoms and one silicon atom. The silicon–boron bond length in **2** is 2.108(2) \AA which is quite comparable to that in $\text{R}'\cdot\text{B}(\text{C}_6\text{F}_5)_3$, $\{\text{R}' = \text{RSiCl}_2$ [$\text{R} = 1,3\text{-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene}\}$ where it is 2.106(6) \AA . The Si–Cl distance in **2** is 2.0656(9) \AA and the N–Si–N cone angle 72.82(8) $^\circ$.

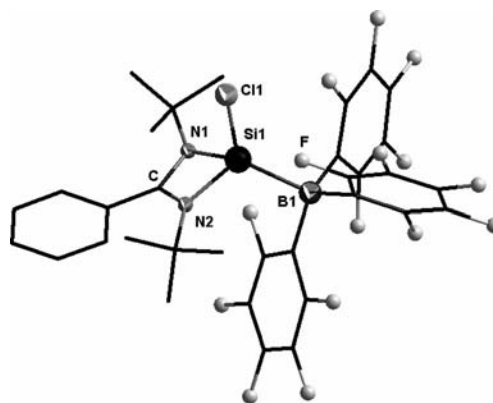
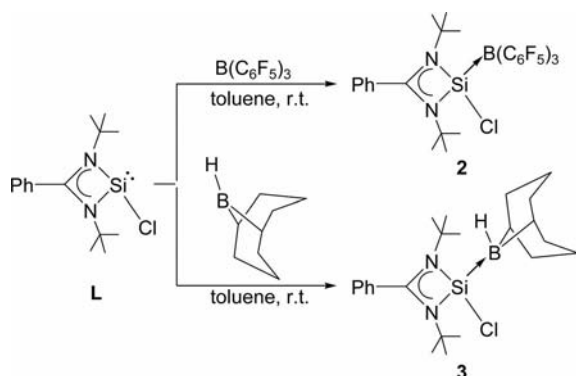


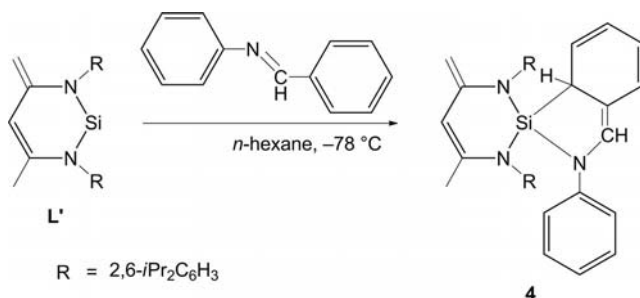
Figure 2. Molecular structure of **2**; the hydrogen atoms have been omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: $\text{Si}(1)\text{--N}(1)$ 1.8110(19), $\text{Si}(1)\text{--N}(2)$ 1.8126(19), $\text{Si}(1)\text{--Cl}(1)$ 2.0656(9), $\text{Si}(1)\text{--B}(1)$ 2.108(2); $\text{N}(1)\text{--Si}(1)\text{--N}(2)$ 72.82(8), $\text{N}(1)\text{--Si}(1)\text{--Cl}(1)$ 101.94(6), $\text{N}(2)\text{--Si}(1)\text{--Cl}(1)$ 105.67(7), $\text{N}(1)\text{--Si}(1)\text{--B}(1)$ 118.65(9), $\text{N}(2)\text{--Si}(1)\text{--B}(1)$ 117.09(9).

As for **2**, the ^{29}Si NMR spectrum of compound **3** displays a downfield chemical shift which is observed at $\delta = 29.62$ ppm with a broad signal. The ^{11}B NMR spectrum of **3** reveals a doublet resonance of equal intensity at $\delta = -15.04$ ppm ($J_{\text{BH}} = 70$ Hz). The ^1H NMR spectrum of **3** exhibits a resonance for $\text{C}(\text{CH}_3)_3$ at $\delta = 1.01$ ppm. Compound **3** shows its molecular ion in its ESI-MS spectrum at m/z 416. In the IR spectrum we were able to observe the band for the $\nu_{\text{B--H}}$ vibration at 2193 cm^{-1} which is in agreement with literature values ($\nu_{\text{B--H}} \approx 2200\text{ cm}^{-1}$).^[26]



Scheme 2. Synthesis of **2** and **3**.

The reaction of **L'** with an equimolar amount of *N*-benzylideneaniline in *n*-hexane at room temperature proceeds rapidly with the formation of the dearomatized product **4** (Scheme 3). Compound **4** is soluble in *n*-hexane, *n*-pentane, toluene, and benzene. Moreover it is stable both in the solid state as well as in solution for a long time without any decomposition under an inert gas atmosphere. The ^{29}Si NMR spectrum of **4** shows a single resonance ($\delta = -25.40$ ppm) which is upfield shifted when compared with that of **L'** ($\delta = 88.4$ ppm), because in **4** the silicon atom is more shielded. A similar trend is observed from the DFT calculations ($\Delta\delta_{\text{calcd.}} = 123$, $\Delta\delta_{\text{exp.}} = 113$ ppm). The identity of the dearomatized product has been clearly established with ^1H NMR spectroscopy, by considerable upfield shift of the hydrogen resonance of the hydrogen atom present in the former benzene ring. The dearomatized ring shows multiplets in the range of $\delta = 5.28\text{--}5.31$ (1 H), $5.34\text{--}5.38$ (1 H), $5.44\text{--}5.49$ (1 H), and $5.96\text{--}5.99$ (1 H) ppm, respectively, in its ^1H NMR spectrum. These values support the dearomatization of the benzene ring and are in agreement with those reported in the literature.^[23] The mass spectrum of compound **4** displays its molecular ion peak at m/z 625.3 confirming the composition.

Scheme 3. Synthesis of **4**.

Product **4** was unambiguously identified by single-crystal X-ray structural analysis. Product **4** crystallizes in the triclinic space group $P\bar{1}$ and the molecular structure is shown in Figure 3. The imine compound (--N=C--C--) has been converted into the alkene derivative (--N=C=C--). We propose that the reaction of **L'** with *N*-benzylideneaniline follows the [1+4]-cycloaddition reaction (Scheme 4). The silicon atom, which is already part of the $\text{C}_3\text{N}_2\text{Si}$ six-membered ring based on **L'**, acts as a reaction center to form a new C_3NSi five-membered ring with the *N*-benzylideneaniline

keeping the six-membered ring intact and leading to the spirocyclic compound **4**. In **4**, the six- and five-membered rings are fused by the silicon center and the resulting rings are arranged nearly orthogonal to each other. The dihedral angle between the planes of the six- and five-membered ring is $86.22(5)^\circ$. Furthermore, the dearomatized benzene ring is not planar similar to those observed in the reaction of **L'** with benzophenone^[13a] and with diphenyl hydrazone.^[7c] The silicon atom is in a distorted tetrahedral geometry, consisting of three nitrogen atoms and a carbon atom. Among the three nitrogen atoms one originates from the nitrogen atom of the *N*-benzylideneaniline and the two others from the chelating ligand. The silicon atom is shifted out of the plane defined by N2, C27, C28, C29, and N3 significantly by 0.39 Å. A shortening of bonds can be observed between the silicon atom and the nitrogen atoms of the supporting ligand. The average bond length between Si--N_{av} in **4** is

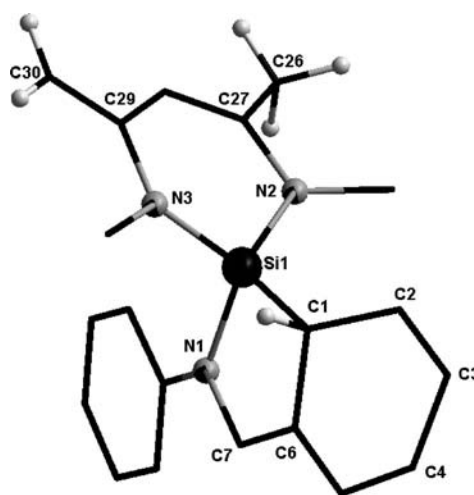
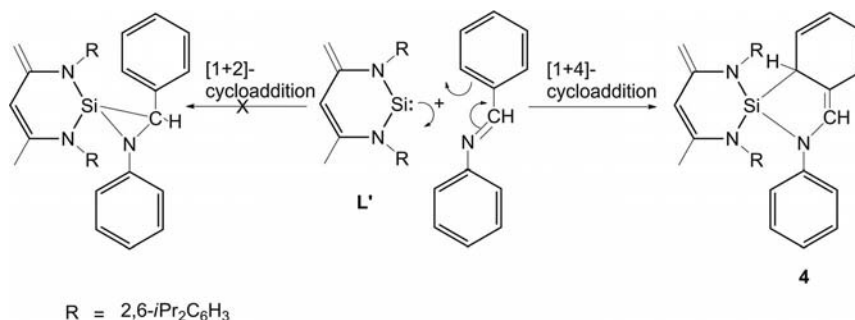


Figure 3. Molecular structure of **4**, where the substituents on the N atoms and hydrogen on the carbon atoms except on C1, C26, and C30 have been deleted for clarity. The hydrogen on C1 was found and refined freely. Selected bond lengths [Å] and angles [°]: Si(1)–N(1) 1.780(2), Si(1)–N(2) 1.720(2), Si(1)–N(3) 1.728(2), Si(1)–C(1) 1.877(3), C(1)–C(2) 1.477(4), C(2)–C(3) 1.329(4), C(3)–C(4) 1.465(4), C(4)–C(5) 1.339(4), C(5)–C(6) 1.441(3), C(6)–C(7) 1.341(3), C(7)–N(1) 1.406(3), C(6)–C(1) 1.512(3); N(1)–Si(1)–N(3) $113.96(10)$, N(2)–Si(1)–N(3) $103.36(9)$, N(1)–Si(1)–N(2) $115.11(10)$, N(3)–Si(1)–C(1) $111.18(12)$, N(2)–Si(1)–C(1) $120.85(12)$, N(1)–Si(1)–C(1) $92.79(10)$, Si(1)–C(1)–C(2) $128.60(2)$, C(6)–C(1)–C(2) $112.2(2)$.

Scheme 4. Proposed mechanism for the formation of **4**.

1.724(2) Å, whereas in **L'** it is 1.7345(10) Å. In addition, there is an appreciable change in the N–Si–N bite angle at the silicon atom with the backbone ligand. In **4** it is 103.36(9)°, whereas in **L'** it is 99.317(54)°. The bond lengths of Si1–N1 and Si1–C1 are 1.780(2) and 1.877(3) Å, indicating single bond character.^[20] The bond lengths between adjacent carbon atoms in the dearomatized six-membered benzene ring (C1, C2, C3, C4, C5, C6) of compound **4** possess both single and double bond character, the bond lengths between C1–C2, C3–C4, C5–C6, and C1–C6 are 1.477(4), 1.465(4), 1.441(3), and 1.512(3) Å indicating C–C single bonds and the bond lengths between C2–C3 and C4–C5 are 1.329(4) and 1.339(4) Å representing C=C double bonds. The bond lengths of C7–N1 and N1–C8 are 1.406(3) and 1.416(3) Å, respectively. The bond length between C6–C7 is 1.341(3) Å and thus reflects a C=C double bond.^[22]

BP86/SVP optimized structures of the trimer containing a Si₃O₃ six-membered unit (**1_c**) and a dimer containing a Si₂O₂ four-membered unit (**1a_c**) are shown in Figure 4. Both the DFT-optimized structures display a good resemblance with the X-ray crystal data. The reaction of **L** with N₂O affords **1_c**, the process being highly favorable with a reaction energy of –1285.6 kJ/mol at BP86/TZVP//BP86/SVP level of theory (see Computational Details). It was previously reported that the reaction of **L** with *tert*-butylisocyanate in toluene at ambient temperature furnishes a four-membered Si₂O₂ ring species (**1a_c**).^[13g] Interestingly, the formation of the Si₂O₂ four-membered ring is not observed in the presence of N₂O, instead a paddle-wheel like Si₃O₃ six-membered ring is formed (vide supra). We envisage that the cyclization of the silanones formed from *tert*-butylisocyanate is controlled by the sterically hindered *tert*-butyl groups. While the approach of more than two such silanone units seems to be prohibitive, the exclusive formation of the four-membered Si₂O₂ fragment is nevertheless observed. On the

other hand, the reaction of N₂O allows the formation of silanones with a facile removal of N₂, henceforth providing ample steric clearance for subsequent trimerization to occur, furnishing the six-membered Si₃O₃ species. The origin of extra stabilization of **1_c** can be explained through the steric strain imposed on the four-membered ring species **1a_c**. The average bond angles O–Si–O and Si–O–Si are 100.3 and 135.9° in case of **1_c** while for **1a_c** they are 85.2 and 94.8°, respectively. These values clearly indicate an inherent ring strain present in **1a_c**. To further quantify the higher ring strain we have compared the energies of the O–Si[(*t*BuN)₂CPh]–O (**F1**) and PhC(N*t*Bu)₂Si–O–Si(N*t*Bu)₂–CPh (**F2**) fragments from the gas-phase optimized **1_c** and **1a_c** structures, respectively (see Figure S1 and Scheme S1 for fragment definition). Both fragments are relatively stable for **1_c** with higher stability of **F2**, as a direct consequence of the more relaxed ∠Si–O–Si bond angle (see Figure 4).

Additional DFT calculations were performed to elucidate the driving force for the formation of dearomatized [1+4]-cycloaddition product **4_c**. The isomeric [1+2]-cycloaddition product (**4i_c**) is not observed when **L'** reacts with an equimolar amount of *N*-benzylideneaniline. DFT-optimized structures of **4_c** and **4i_c** are depicted in Figure 5. Calculations reveal that the [1+4]-cycloaddition product is energetically more stable by 16.4 kJ/mol compared to the [1+2]-cycloaddition product. The activation energy for the formation of both **4_c** and **4i_c** were calculated at the BP86/SVP level of theory (see Computational Details). For **4_c** the activation barrier is 47.9 kJ/mol lower than for **4i_c** indicating a more facile formation of the [1+4]-cycloaddition product. The LUMO of **4_c** is predominantly the p_z orbital of silicon, which is perpendicular to the **L'** plane and is electrophilic in nature.^[27] Preferential orbital interaction will be sustained only when the orbitals of the ligands are oriented for better overlap. For the formation of **4i_c** the p_z orbital has

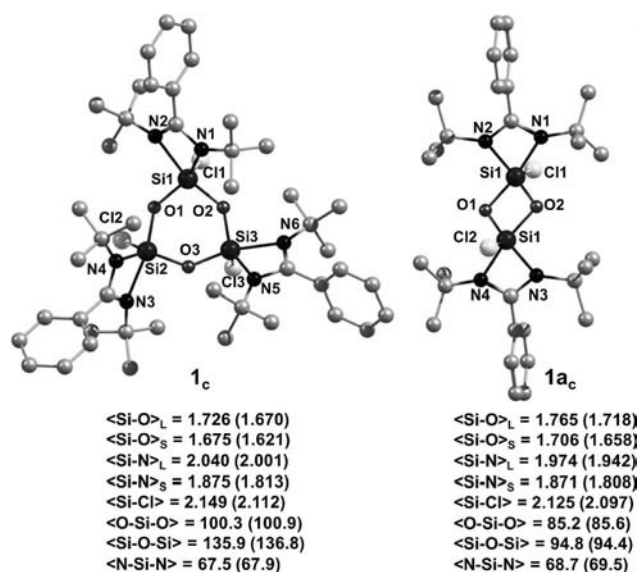


Figure 4. BP86/SVP-optimized structures of the compounds **1_c** and **1a_c** with bond lengths [Å] and bond angles [°]. Hydrogen atoms are omitted for clarity. Values in parentheses represent X-ray data.

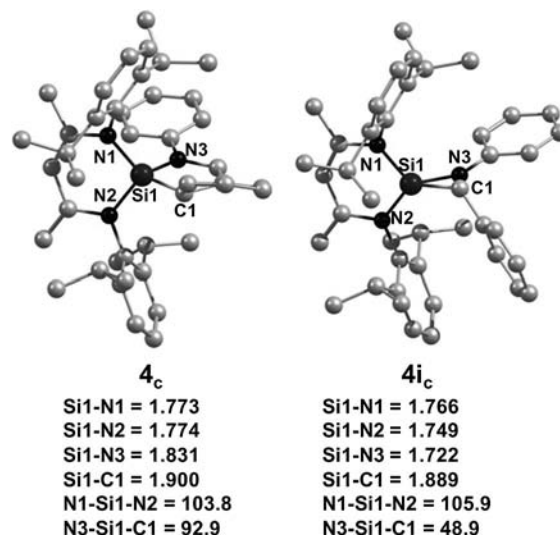


Figure 5. BP86/SVP-optimized structures of compounds **4_c** and **4i_c** with bond lengths [Å] and bond angles [°]. Hydrogen atoms are omitted for clarity.

been distorted to allow orbital overlaps with the adjacent N and C atoms furnishing a N–Si–C three-membered unit concomitant with a reduced N–Si–C bond angle of 48°.^[28] However, a similar orbital distortion is not conceptualized in the [1+4]-cycloaddition product **4_c**, where the interactions from the N and C_{ortho} atoms are more “opened” (N–Si–C bond angle: 92°). This particular regulation in orbital orientation allows the stabilization of the [1+4]-cycloaddition product **4_c**. Another important observation emanates from the fact that the relative conformation of the *N*-benzylideneaniline fragments in complexes **4_c** and **4_i** are considerably different from its free form. The conformational deformation of the complexed **L'** fragment with respect to the DFT-optimized **L'** structure is more pronounced in **4_c** than **4_i** ($\Delta E_c \approx 63$ kJ/mol). This indicates the combined effect of two factors: firstly, favorable orbital interaction (vide supra) and secondly, ring strain relief predominates in the ligand deformation calculated for **4_c** allowing its formation to be more feasible than that of **4_i**.

Conclusions

In summary, we first explored the reactivity of chlorosilylene, PhC(NtBu)₂SiCl (**L**) with N₂O, which afforded the trimer {PhC(NtBu)₂Si(O)Cl}₃ (**1**), containing a Si₃O₃ six-membered ring. In **1**, the PhC(NtBu)₂ and Cl moieties are aligned in opposite directions of the plane. In addition we reported the chlorosilylene–boron adducts **L**·B(C₆F₅)₃ (**2**) and **L**·9-BBN (**3**), yielded by the reaction of **L** with B(C₆F₅)₃ and 9-BBN. The reaction of CH{(C=CH₂)(CMe)-(2,6-*i*Pr₂C₆H₃N)₂}Si (**L'**) with *N*-benzylideneaniline afforded **4** as a [1+4]- rather than a [1+2]-cycloaddition product. Here the reaction occurred at the silicon atom, and a new five-membered ring was formed leading to a spirocyclic compound keeping the C₃N₂Si six-membered ring intact. Formation of products **1** and **4** was supported by DFT calculations.

Experimental Section

General: Syntheses were carried out under an inert atmosphere of dinitrogen in oven-dried glassware using standard Schlenk techniques and other manipulations were accomplished in a dinitrogen-filled glove box. Solvents were purified by the MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from Aldrich and used without further purification. **L**^[3a,3c] and **L'**^[3d] were prepared as reported in the literature. ¹H and ²⁹Si NMR spectra were recorded with a Bruker Avance DPX 200, or a Bruker Avance DRX 500 spectrometer, using C₆D₆ as solvent. Chemical shifts δ are given relative to SiMe₄. EI-MS spectra were obtained with a Finnigan MAT 8230 instrument and ESI-MS spectra with an Applied Biosystems API 2000 as well as with a Thermo Finnigan Ion Trap LCQ spectrometer. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Göttingen. Melting points were measured in sealed glass capillaries on a Büchi B-540 melting point apparatus.

Synthesis of 1: Toluene (60 mL) was added to a 100-mL Schlenk flask containing **L** (0.31 g, 1.05 mmol). Gaseous N₂O was passed through the solution for 10 min. After that, the solvent was completely removed and the compound redissolved in hexane (30 mL). The solution was filtered, and the filtrate was reduced in vacuo to 15 mL and stored in a freezer at –32 °C for a day to obtain colorless single crystals of **1**, yield 0.27 g, 82.0%, m.p. 220–223 °C. For elemental analysis, **1**·0.5 hexane was treated under vacuum for 6 h to remove the *n*-hexane molecules. C₄₅H₆₉Cl₃N₆O₃Si₃ (930.38): calcd. C 57.95, H 7.46, N 9.01; found C 57.85, H 7.82, N 8.80. ¹H NMR (200 MHz, C₆D₆, 25 °C): δ = 1.45 [br. s, 54 H, C(CH₃)₃], 6.80–6.99 (br., 15 H, C₆H₅) ppm. ²⁹Si{¹H} NMR (99.36 MHz, C₆D₆, 25 °C): δ = –114.51 ppm. EI-MS: *m/z* (%) = 629 [M^+ – {PhC(NtBu)₂ + 2Cl}], 594 [M^+ – {PhC(NtBu)₂ + 3Cl}].

Synthesis of 2: To a Schlenk flask containing **L** (0.30 g, 1.02 mmol) in toluene (30 mL) cooled to –78 °C, B(C₆F₅)₃ (0.52 g, 1.02 mmol) dissolved in toluene (30 mL) was added. The stirred reaction mixture was warmed to room temperature and stirred for another 12 h. The solution was filtered and the solvent was reduced in vacuo to 15 mL and stored in a freezer at –32 °C for 3 days to obtain colorless single crystals of **2**, yield 0.65 g, 79.3%, m.p. 195–198 °C (dec.). C₃₃H₂₃BClF₁₅N₂Si (806.87): calcd. C 49.12, H 2.87, N 3.47; found C 48.95, H 2.83, N 3.41. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 0.65 [s, 18 H, C(CH₃)₃], 6.57–6.85 (br., 5 H, C₆H₅) ppm. ¹⁹F{¹H} NMR (282.40 MHz, C₆D₆, 25 °C): δ = –125.38 (m), –157.47 (m), –167.73 (m) ppm. ¹¹B{¹H} NMR (96.29 MHz, C₆D₆, 25 °C): δ = –17.55 ppm. ²⁹Si{¹H} NMR (59.63 MHz, C₆D₆, 25 °C): δ = 29.94 (br) ppm. ESI-MS: *m/z* (%) = 638 [M^+ – C₆F₅].

Synthesis of 3: To a Schlenk flask containing **L** (0.30 g, 1.02 mmol) in toluene (30 mL) was added 0.5 M 9-BBN(THF) solution (2 mL, 1.00 mmol) at –78 °C. The stirred reaction mixture was warmed to room temperature and stirred for another 12 h. The solution was filtered and the solvent was reduced in vacuo to 20 mL and stored in a freezer at –32 °C for 14 h to obtain crystalline compound **3**, yield 0.33 g, 78.6%, m.p. 202–205 °C (dec.). C₂₃H₃₈BClN₂Si (416.26): calcd. C 66.26, H 9.19, N 6.72; found C 66.16, H 9.14, N 6.68. ¹H NMR (500 MHz, C₆D₆, 25 °C): δ = 1.01 [s, 18 H, C(CH₃)₃], 6.71–6.90 (br., 5 H, C₆H₅) ppm. ¹¹B{¹H} NMR (96.29 MHz, C₆D₆, 25 °C): δ = –15.04 (d, *J*_{BH} = 70 Hz) ppm. ²⁹Si{¹H} NMR (99.36 MHz, C₆D₆, 25 °C): δ = 29.62 (br) ppm. FTIR (Nujol): ν_{B-H} 2193(w). ESI-MS: *m/z* (%) = 416 [M^+], 381 [M^+ – Cl].

Synthesis of 4: To a Schlenk flask containing **L'** (0.25 g, 0.56 mmol) in hexane (30 mL) cooled to –78 °C, *N*-benzylideneaniline (0.10 g, 0.55 mmol) dissolved in hexane (30 mL) was added. The stirred reaction mixture was warmed to room temperature and stirred for another 12 h. The solution was filtered and the solvent was reduced in vacuo to 20 mL and stored in a freezer at –32 °C for 3 days to obtain colorless single crystals of **4**, yield 0.26 g, 74%, m.p. 168–170 °C. C₄₂H₅₁N₃Si (625.39): calcd. C 80.59, H 8.21, N 6.71; found C 79.52, H 9.07, N 6.58. ¹H NMR (500 MHz, CD₃, 25 °C): δ = 0.76 [d, *J* = 7 Hz, 3 H, CH(CH₃)₂], 0.87 [d, *J* = 7 Hz, 3 H, CH(CH₃)₂], 1.02 [d, *J* = 7 Hz, 3 H, CH(CH₃)₂], 1.18 [d, *J* = 7 Hz, 3 H, CH(CH₃)₂], 1.28–1.31 [2 × d, 6 H, CH(CH₃)₂], 1.40–1.49 [m, 9 H, CH(CH₃)₂, NCCCH₃], 3.08 (m, 1 H, SiCH), 3.14 [m, *J* = 7 Hz, 1 H, CH(CH₃)₂], 3.33–3.38 [m, 2 H, CH(CH₃)₂, NCCCH₂], 3.68 [m, *J* = 7 Hz, 1 H, CH(CH₃)₂], 3.96–4.01 [m, 2 H, CH(CH₃)₂, NCCCH₂], 5.28–5.31 (m, 1 H, CH), 5.34–5.38 (m, 1 H, CH), 5.44–5.49 (m, 2 H, CH, γ -CH), 5.66 (s, 1 H, NCH), 5.96–5.99 (m, 1 H, CH), 6.88–7.29 (m, 11 H, C₆H₅, 2 × *i*Pr₂C₆H₃) ppm. ²⁹Si{¹H} NMR (99.36 MHz, C₆D₆, 25 °C): δ = –25.40 ppm. EI-MS: *m/z* (%) = 625.3 [M^+].

Crystal Structure Determination: Suitable single crystals for X-ray structural analyses of **1**, **2**, and **4** were mounted on a glass fiber, and the respective data were collected with an IPDS II Stoe image-plate diffractometer (graphite-monochromated Mo- K_α radiation, $\lambda = 0.71073$ Å) at 133(2) K. The structures were solved by direct methods (SHELXS-97) and refined against all data by full-matrix least-squares methods on F^2 (SHELXL-97).^[29] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically at calculated positions using a riding model with their U_{iso} values constrained to 1.5 U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. In compound **4** the hydrogen atoms on carbons C1 to C5 and on C7 were found and refined freely without any restraints, though their U_{iso} values were refined jointly.

CCDC-831714 (for **1**), -831715 (for **2**), and -776752 (for **4**) 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.

Computational Details: All calculations were performed in Gaussian03 quantum code.^[30] The geometries of all compounds were optimized with the generalized approximation (GGA) to DFT by using the exchange functional of Becke^[31] in addition to the correlation functional of Perdew^[32] (BP86). All the atoms were treated with Ahlrich's split valence plus polarization (SVP) basis sets^[33] of 6-31G* quality. In all our DFT treatments, the resolution-of-the-identity (RI) approximation (also called "density fitting") for the two electron integrals was employed.^[34] The geometries were optimized without any symmetry constraints. For validation, single-point energies were calculated with larger basis sets at BP86/TZVP^[35] using BP86/SVP-optimized geometries. Relative energies in this work are given at the BP86/TZVP//BP86/SVP level of theory if otherwise not mentioned. Approximate activation energy was calculated by investigating the potential energy surface scan of a specified reaction coordinate. NMR shielding tensors were calculated for the selected optimized structures using the Gauge-Independent Atomic Orbital (GIAO) method.^[30] All figures were made in the Chemcraft visualization software.^[36]

Supporting Information (see footnote on the first page of this article): DFT-optimized geometries (Cartesian coordinates) and absolute energies.

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