**PAPER**

# Double N–H bond activation of N,N′-bis-substituted hydrazines with stable N-heterocyclic silylene†

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The reaction of N-heterocyclic silylene (NHSi) **L** [**L** = CH{(C=CH$_2$)(CMe)(2,6-$i$Pr$_2$C$_6$H$_3$N)$_2$}Si] with benzoylhydrazine, 1,2-dicarbethoxyhydrazine, 1,2-diacetylhydrazine and 1,2-bis($tert$-butoxycarbonyl)-hydrazine in 1 : 1 molar ratio resulted in compounds **1–4** with an almost quantitative yield and five coordinate silicon atoms. Compounds **1–4** were formed by double N–H bond activation by deliberate selection of N,N′-bis-substituted hydrazine compounds bearing the –C(O)NHNH– unit. Compounds **1–4** were characterized by NMR spectroscopy, EI-MS and elemental analysis. The molecular structures of compounds **1–3** were unambiguously established by single crystal X-ray structural analysis.
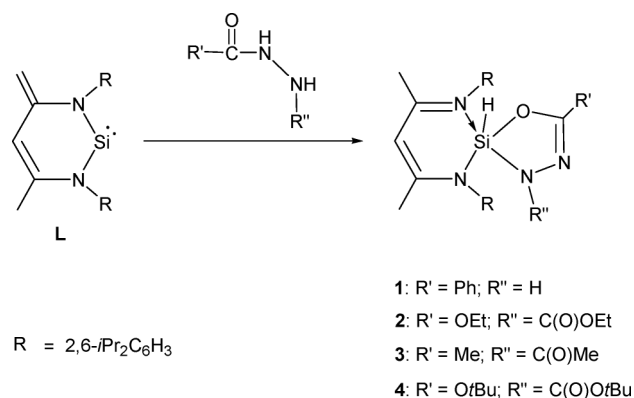
## Introduction

N–H bond activation has been the subject of many studies because of the prevalence of nitrogen-containing compounds for pharmaceutical and other fine chemicals.[1] Moreover, the activation of N–H bonds is less studied compared to the activation of C–H[2] or O–H[3] bonds. Finally the double N–H bond activation of hydrazine based molecules is still rare.[4] Recently Hartwig *et al.* reported double N–H bond activation by an iridium(I) complex.[4] Previously we published studies on the N–H bond activation of ammonia[5] and hydrazines,[6,7] and Driess *et al.* outlined the activation for organoamines[1g] by utilizing the stable N-heterocyclic silylene (NHSi) **L** [**L** = CH{(C=CH$_2$)(CMe)(2,6-$i$Pr$_2$C$_6$H$_3$N)$_2$}Si]. In the case of ammonia, hydrazine and *N*-methyl hydrazine we observed only a single N–H bond activation. However, in the reaction of **L** with 1,2-diphenylhydrazine, a spirocyclic product formed with the elimination of molecular hydrogen. Formation of this product occurred by the activation of one N–H and one C(aromatic)–H bond instead of another N–H bond, which is attributed to the steric strain within the ring.[7] With this in mind, we selected the N,N′-bis-substituted hydrazine molecules, benzoylhydrazine, 1,2-dicarbethoxyhydrazine, 1,2-diacetylhydrazine and 1,2-bis(*tert*-butoxycarbonyl)hydrazine bearing the –C(O)NHNH– unit, that would favor the double N–H bond cleavage. The choice of the above mentioned substituted hydrazines is based on the fact that the presence of the –NHNH– unit leads to activation of one of the N–H bonds and the presence of the carbonyl group with the –C(O)NHNH– unit ultimately favors the formation of a five-membered ring with **L** leading to the spirocyclic compound and

the activation of the other N–H bond. The reaction of the four hydrazine derivatives with **L** proceeds as expected, *i.e.* with the activation of two N–H bonds. Herein, we report on the double N–H bond activation of N,N′-bis-substituted hydrazines by NHSi (**L**) leading to compounds **1–4** with five coordinate silicon atoms.

## Results and discussion

Reaction of **L** with benzoylhydrazine, 1,2-dicarbethoxyhydrazine, 1,2-diacetylhydrazine and 1,2-bis(*tert*-butoxycarbonyl)hydrazine in 1 : 1 molar ratios resulted in the formation of compounds **1–4** with five coordinate silicon atoms in quantitative yield (Scheme 1) and the proposed mechanism is given in Scheme 2. In all the cases, N,N′-bis-substituted hydrazines have been converted to hydrazone derivatives. The formation of compounds **1–4** was supported by NMR spectroscopy, EI-MS and elemental analysis. The molecular structures of compounds **1–3** were unequivocally confirmed by single crystal X-ray structural analysis.



R = 2,6-$i$Pr$_2$C$_6$H$_3$

**1**: R′ = Ph; R″ = H
**2**: R′ = OEt; R″ = C(O)OEt
**3**: R′ = Me; R″ = C(O)Me
**4**: R′ = O$t$Bu; R″ = C(O)O$t$Bu

**Scheme 1** Double N–H bond activation of benzoylhydrazine, 1,2-dicarbethoxyhydrazine, 1,2-diacetylhydrazine and 1,2-bis(*tert*-butoxycarbonyl)hydrazine by **L** to form compounds **1–4**.

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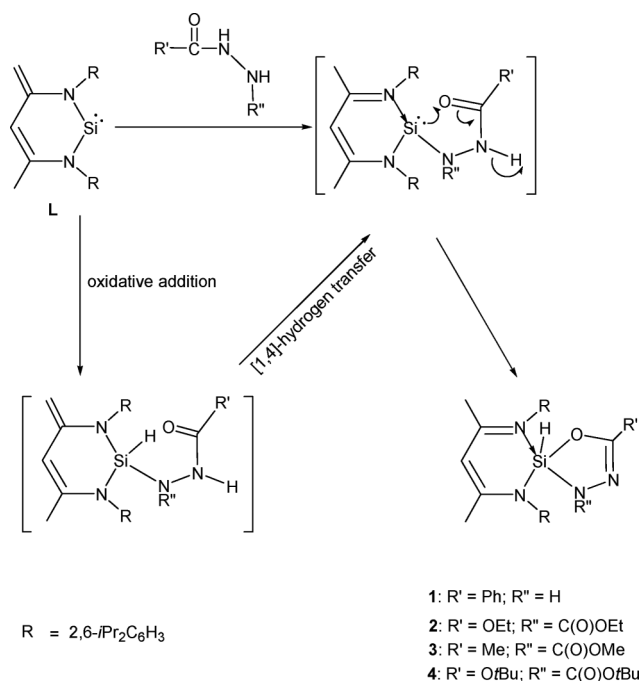
**Scheme 2** Proposed mechanism for the formation of compounds **1–4**.

R = 2,6-*i*Pr$_2$C$_6$H$_3$

**1**: R' = Ph; R" = H
**2**: R' = OEt; R" = C(O)OEt
**3**: R' = Me; R" = C(O)OMe
**4**: R' = O*t*Bu; R" = C(O)O*t*Bu

Compounds **1–4** are soluble in *n*-hexane, *n*-pentane, toluene and benzene. They are stable in the solid state as well as in solution without any decomposition under an inert gas atmosphere. The $^{29}$Si NMR spectra of **1–4** each exhibit a single resonance between $\delta -110.92$ and $-103.75$, which are upfield shifted compared to **L** ($\delta$ 88.4). This is due to the higher coordination of the silicon atoms in **1–4**. The resonances are upfield shifted compared to those of the other species with four coordinate silicon,[5–8] but they are in agreement with those formed for other five coordinate silicon compounds obtained from **L**.[9] A further proton resonance of NCC*H*$_3$ in the region of $\delta$ 1.45 to 1.49 for six hydrogen atoms and the absence of a signal for the protons in NCC*H*$_2$ of **1–4**, indicates the protonation of the methylene group in the ligand backbone of **L**. The Si–H proton in the $^1$H NMR spectra of **1–4** shows a single resonance in the $\delta$ 6.36 to 6.47 region, which was corroborated by a $^1$H–$^{29}$Si HSQC (heteronuclear single-quantum correlation) experiment. In **1** the resonances for both γ-C*H* and N–*H* protons in the $^1$H NMR spectrum are observed at $\delta$ 4.93. The $^1$H–$^{15}$N HSQC experiment shows strong coupling between the resonance at $\delta$ 4.93 and a $^{15}$N resonance, indicating that the proton is nitrogen bound. In **2–4** the resonances for γ-C*H* are observed as a single resonance each in the region at $\delta$ 4.88 to 4.92. Compounds **1–4** exhibit their molecular ion in the mass spectra at *m/z* 580, 620, 560 and 676.

**Molecular structure of 1**

Compound **1** forms as yellow crystals in the monoclinic space group *P*2$_1$/*n* (Table 1), and the molecular structure is shown in Fig. 1. The silicon atom is five coordinate and features a distorted trigonal bipyramidal geometry (TBP), made up from three nitrogen atoms, a single oxygen atom and a hydrogen atom. The three nitrogen atoms arranged at the silicon atom originate from the hydrazone moiety and from the β-diketiminate ligand.
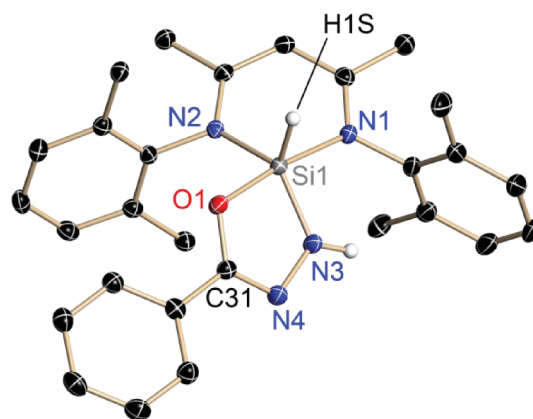


**Fig. 1** Molecular structure of **1**·0.52 hexane with anisotropic displacement parameters depicted at the 50% probability level. The solvent hexane molecule, the methyl carbons of isopropyl groups and all of the hydrogen atoms except at Si1 and N3 are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Si1–N1 1.9437(12), Si1–N2 1.8371(11), Si1–N3 1.7391(12), Si1–O1 1.7667(10), Si1–H1S 1.376(15), N3–N4 1.4021(16), N4–C31 1.2873(17), C31–O1 1.3395(16); N1–Si1–N2 91.74(5), N3–Si1–O1 83.70(5), N2–Si1–N3 128.58(6), N1–Si1–O1 172.69(5), N3–Si1–H1S 126.5(6), O1–Si1–H1S 94.6(6), N2–Si1–H1S 104.9(6), N1–Si1–H1S 91.3(6).

The structural index τ which defines the extent of deviation from trigonal bipyramidal to square pyramidal geometry (τ = 1 for perfect trigonal bipyramidal; τ = 0 for perfect square based pyramid[10]) is 0.74 indicating small deviation from the regular TBP geometry. The overall geometrical features of **1** correspond to those determined earlier.[11] The sum of angles of the equatorial atoms around Si1 equals 360.0°. The silicon atom is shifted out of the plane defined by N1, C1, C2, C3 and N2 significantly by 0.7116(15) Å. There are two types of Si–N bonds present in **1**, one is shorter (N2–Si1: 1.8371(11) Å) and the other one is longer (N1–Si1: 1.9437(12) Å). There is an appreciable change in the N1–Si1–N2 bite angle of **1** (128.58(6)°), when compared with that of **L** (99.317(54)°). These changes are attributed to the protonation of the methylene group at the backbone of the β-diketiminate ligand. The Si1–N3 bond length is 1.7391(12) Å indicating a single bond character.[12] The Si1–O1 bond length is 1.7667(10) Å, which is comparable to the Si–O single bond distances observed in five coordinate silicon complexes.[13a] The position of the silicon bound hydrogen atom was taken from the Fourier difference map and was refined freely. The Si–H distance of 1.376(15) Å is considerably shorter than the related distance in the structurally characterized silicon(II) monohydride of 1.47342(11) Å determined from charge density investigations.[13b] The higher coordination around Si1 and the higher formal oxidation state of Si1 in **1** indicates much more covalent bonding when compared with the latter where the Si–H bond is highly polar. The N3–N4 bond length is 1.4021(16) Å, indicating a N–N single bond of hydrazine or of a hydrazone derivative as reported in literature.[14] The C31–N4 distance of 1.2873(17) Å compares well with a C=N double bond[14] and the C31–O1 bond length of 1.3395(16) Å with a single bond.[15]

**Molecular structure of 2**

Compound **2** crystallizes in the monoclinic space group *P*2$_1$/*c* and the molecular structure is shown in Fig. 2. Similar to **1**, the

**Table 1** Crystal and structure refinement parameters for compounds **1**, **2** and **3**

| Parameters | **1**·0.52 *n*-hexane | **2** | **3** |
|---|---|---|---|
| Empirical formula | $C_{39.12}H_{55.24}N_4OSi$ | $C_{35}H_{52}N_4O_4Si$ | $C_{33}H_{48}N_4O_2Si$ |
| Formula weight | 625.65 | 620.90 | 560.84 |
| Crystal system | Monoclinic | Monoclinic | Orthorhombic |
| Space group | $P2_1/n$ | $P2_1/c$ | $P2_12_12_1$ |
| Unit cell dimensions | $a = 11.4828(8)$ Å | $a = 13.2681(14)$ Å | $a = 13.816(2)$ Å |
| | $b = 12.0258(9)$ Å | $b = 12.0341(12)$ Å | $b = 14.387(2)$ Å |
| | $c = 26.1609(19)$ Å | $c = 21.837(2)$ Å | $c = 15.751(3)$ Å |
| | $\beta = 94.746(2)°$ | $\beta = 94.780(5)°$ | |
| Volume, Z | 3600.2(5) Å$^3$, 4 | 3476.6(6) Å$^3$, 4 | 3130.8(9) Å$^3$, 4 |
| Density (calcd) | 1.154 g cm$^{-3}$ | 1.187 g cm$^{-3}$ | 1.190 g cm$^{-3}$ |
| Absorption coefficient | 0.101 mm$^{-1}$ | 0.065 mm$^{-1}$ | 0.110 mm$^{-1}$ |
| F (000) | 1360 | 1344 | 1216 |
| Crystal size | $0.22 \times 0.16 \times 0.12$ mm$^3$ | $0.18 \times 0.14 \times 0.11$ mm$^3$ | $0.1 \times 0.05 \times 0.04$ mm$^3$ |
| $\theta$ range for data collection | 1.56 to 26.11° | 1.22 to 21.06° | 1.92 to 27.13° |
| Limiting indices | $-14 \leq h \leq 14, -14 \leq k \leq 14,$ | $-16 \leq h \leq 16, -15 \leq k \leq 15,$ | $-14 \leq h \leq 17, -18 \leq k \leq 18,$ |
| | $-32 \leq l \leq 32$ | $-27 \leq l \leq 27$ | $-20 \leq l \leq 18$ |
| Reflections collected | 57531 | 97129 | 26322 |
| Independent reflections | 7146 ($R_{int} = 0.0368$) | 7620 ($R_{int} = 0.0576$) | 6906 ($R_{int} = 0.0778$) |
| Completeness to $\theta$ | 99.8% ($\theta = 26.11$) | 99.7% ($\theta = 21.07$) | 99.8% ($\theta = 27.13$) |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 7146/2/434 | 7620/4/440 | 6906/2/379 |
| Goodness-of-fit on $F^2$ | 1.042 | 1.099 | 1.023 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1 = 0.0367$, w$R2 = 0.0908$ | $R1 = 0.0456$, w$R2 = 0.1119$ | $R1 = 0.0393$, w$R2 = 0.0873$ |
| $R$ indices (all data) | $R1 = 0.0452$, w$R2 = 0.0955$ | $R1 = 0.0600$, w$R2 = 0.1181$ | $R1 = 0.0461$, w$R2 = 0.0914$ |
| Absolute structure parameter[21] | | | 0.04(8) |
| Largest diff. peak and hole | 0.306 and $-0.363$ e Å$^{-3}$ | 0.337 and $-0.334$ e Å$^{-3}$ | 0.324 and $-0.258$ e Å$^{-3}$ |
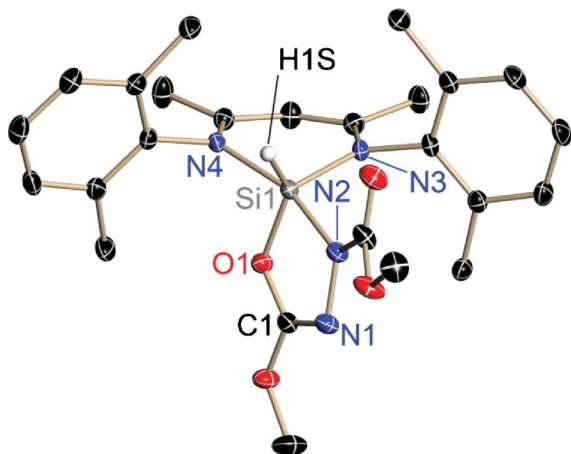


**Fig. 2** Molecular structure of **2** with anisotropic displacement parameters depicted at the 50% probability level. All hydrogen atoms except at Si1, the methyl carbons of isopropyl groups and one carbon atom of the ethyl groups are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Si1–O1 1.7205(12), Si1–N3 1.8078(14), Si1–N2 1.8405(14), Si1–N4 1.9272(14), Si1–H1S 1.371(19), N1–N2 1.4275(19), N1–C1 1.272(2), C1–O1 1.340(2); O1–Si1–N3 108.85(6), O1–Si1–N2 83.74(6), N3–Si1–N2 100.83(6), O1–Si1–N4 85.23(6), N3–Si1–N4 94.72(6), N2–Si1–N4 163.19(6), O1–Si1–H1S 135.7(8), N3–Si1–H1S 115.4(8), N2–Si1–H1S 90.7(8), N4–Si1–H1S 88.4(8).

silicon atom in **2** is five coordinate comprising three nitrogen atoms (two from the *β*-diketiminate ligand and one from the hydrazone moiety), one oxygen atom and one hydrogen atom. The structural index *τ* is 0.46. This is caused by the axial substituents N4 and N2 that have an angle of 163.19(6)° with Si1. The sum of angles between the equatorial ligands around Si1 is 360.0°. As in **1**, there are two types of Si–N bonds observed from the supporting ligand. One (equatorial) is 1.8078(14) Å and the other

one is (axial) 1.9272(14) Å. The silicon atom is shifted out of the $N_2C_3$-plane of the $SiN_2C_3$ six-membered ring by 0.4862(18) Å. Again, the position of the silicon bound hydrogen atom was taken from the Fourier difference map and refined freely. The Si–H distance of 1.371(19) Å in **2** is very similar to that determined in **1**.[13c] The N3–Si1–N4 bite angle at the silicon atom of the *β*-diketiminate ligand is 94.72(6)°. The N–N [N1–N2 1.4275(19) Å] and C–O [C1–O1 1.340(2) Å] bond lengths present in the newly formed five-membered ring of **2** are quite comparable to those in similar compounds reported in the literature.[15] The distance between C1–N1 is 1.272(2) Å indicating C=N double bond character.[14]

## Molecular structure of 3

Compound **3** crystallizes in the orthorhombic space group $P2_12_12_1$ and the molecular structure is given in Fig. 3. Like **1** and **2**, the silicon atom in **3** is five coordinate comprising three nitrogen atoms, one oxygen atom and one hydrogen atom. The bond lengths of Si–N(equatorial) and the Si–N(axial) are 1.8059(14) Å and 1.9250(14) Å. The structural index *τ* is 0.53. The silicon atom is shifted out of the $N_2C_3$–plane of the $SiN_2C_3$ six-membered ring by 0.4478(18) Å. The Si–H distance of 1.476(13) Å, was taken from the Fourier difference map and refined freely. The N–Si–N bite angle at the silicon atom with the backbone ligand is 93.94(6)°. The N–N [N3–N4 1.4107(19) Å] and C–O [C30–O1 1.365(2) Å] bond lengths present in the newly formed five-membered ring of **3** are quite comparable to those in similar compounds reported in the literature.[15] The distance between C30–N4 is 1.274(2) Å.

In all reported reactions, the SiN₂CO five-membered ring has been formed. The dihedral angles between the planes of the six- and five-membered rings are 34.31(6)°, 83.21(6)° and 79.93(5)°, in compounds **1**, **2** and **3**, respectively. A hydrogen atom has been transferred to the silicon atom in all cases.
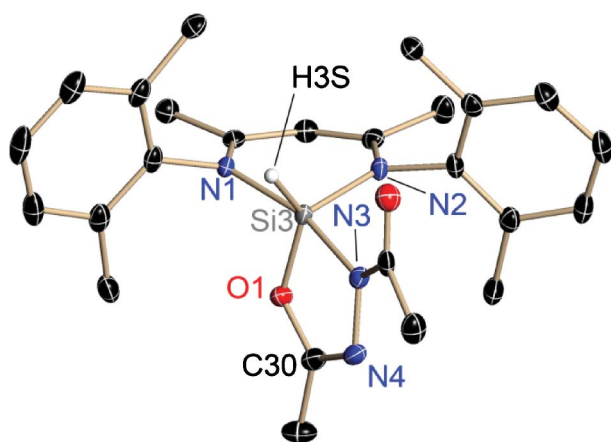
**Fig. 3** Molecular structure of **3** with anisotropic displacement parameters depicted at the 50% probability level. All hydrogen atoms except at Si3 and the methyl carbons of isopropyl groups are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Si3–O1 1.7109(12), Si3–N2 1.8059(14), Si3–N3 1.8573(14), Si3–N1 1.9250(14), Si1–H3S 1.476(13), N3–N4 1.4107(19), N4–C30 1.274(2), C30–O1 1.365(2); O1–Si3–N2 108.26(6), O1–Si3–N3 84.03(6), N3–Si3–N2 99.58(6), O1–Si3–N1 87.00(6), N2–Si3–N1 93.94(6), N3–Si3–N1 165.58(6), O1–Si3–H3S 133.6(6), N2–Si3–H3S 118.1(6), N3–Si3–H3S 90.6(7), N1–Si3–H3S 87.4(7).

## Experimental section

All manipulations were carried out in an inert atmosphere of dinitrogen gas using standard Schlenk line techniques and in a dinitrogen gas filled glove box. Solvents were purified by an MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from Aldrich, Alfa Aeser, or ABCR and used without further purification. **L** was prepared as reported in literature.[15] $^{1}$H and $^{29}$Si NMR spectra were recorded with a Bruker Avance DPX 200, a Bruker Avance DRX 300 or a Bruker Avance DRX 500 spectrometer, using $C_6D_6$ as solvent. Chemical shifts $\delta$ are given relative to $SiMe_4$. EI-MS spectra were obtained using a Finnigan MAT 8230 instrument. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Göttingen. Melting points were measured in a sealed glass tube on a Büchi B-540 melting point apparatus.

### Synthesis of 1

*n*-Hexane (60 mL) was added to a 100 mL Schlenk flask containing **L** (0.30 g, 0.68 mmol) and benzoylhydrazine (0.10 g, 0.73 mmol) and the reaction mixture was stirred at room temperature for 12 h. The solution was filtered and the solvent was reduced *in vacuo* to about 30 mL and stored at −32 °C for a week in a freezer to obtain yellow colored single crystals. (0.30 g, 77%). Mp 215–218 °C (decomp). For elemental analysis, **1**·0.52 *n*-hexane was treated under vacuum for six hours to remove the hexane molecules. Elemental analysis (%) calcd for $C_{36}H_{48}N_4OSi$ (580.88): C, 74.44; H, 8.33; N, 9.65. Found: C, 74.22; H, 8.05; N, 9.37. $^{1}$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ 1.03 (d, 3H, *J* = 7 Hz, CH(C*H$_3$*)$_2$), 1.17 (d, 6H, *J* = 7 Hz, CH(C*H$_3$*)$_2$), 1.19 (d, 3H, *J* = 7 Hz, CH(C*H$_3$*)$_2$), 1.21 (d, 6H, *J* = 7 Hz, CH(C*H$_3$*)$_2$), 1.31 (d, 3H, *J* = 7 Hz, CH(C*H$_3$*)$_2$), 1.45 (s, 6H, NC(C*H$_3$*)$_2$, 1.48 (d, 3H, *J* = 7 Hz, CH(C*H$_3$*)$_2$), 3.25 (m, 1H, C*H*(CH$_3$)$_2$), 3.30 (m, 2H, C*H*(CH$_3$)$_2$),

3.43 (m, 1H, C*H*(CH$_3$)$_2$), 4.93 (b, 2H, N*H*, γ-C*H*), 6.39(s, 1H, Si*H*), 6.91–7.12 (m, 6H, 2 × *i*Pr$_2$C$_6$*H$_3$*), 7.47–7.50 (m, 5H, C$_6$*H$_5$*) ppm. $^{29}$Si{$^{1}$H} NMR (59.63 MHz, $C_6D_6$, 25 °C): $\delta$ −110.92 ppm. EI-MS: *m/z* 580 (M$^+$).

### Synthesis of 2

*n*-Hexane (60 mL) was added to a 100 mL Schlenk flask containing **L** (0.26 g, 0.59 mmol) and 1,2-dicarbethoxyhydrazine (0.11 g, 0.62 mmol). The reaction mixture was stirred at room temperature for 12 h. The solution was filtered and the solvent was reduced *in vacuo* to 30 mL and stored in a freezer at −32 °C for 15 days to obtain colorless single crystals. (0.28 g, 76%). Mp 150–153 °C (decomp). Elemental analysis (%) calcd for $C_{35}H_{52}N_4O_4Si$ (620.90): C, 67.70; H, 8.44; N, 9.02. Found: C, 67.10; H, 8.15; N, 9.31. $^{1}$H NMR (200 MHz, $C_6D_6$, 25 °C): $\delta$ 0.83 (t, 3H, *J* = 7 Hz, CH$_2$C*H$_3$*), 1.01 (t, 3H, *J* = 7 Hz, CH$_2$C*H$_3$*), 1.06 (d, 6H, *J* = 7 Hz, CH(C*H$_3$*)$_2$), 1.18 (d, 6H, *J* = 7 Hz, CH(C*H$_3$*)$_2$), 1.43 (d, 6H, *J* = 7 Hz, CH(C*H$_3$*)$_2$), 1.46 (s, 6H, NC(C*H$_3$*)), 1.54 (d, 6H, *J* = 7 Hz, CH(C*H$_3$*)$_2$), 3.21–3.47 (m, 4H, C*H*(CH$_3$)$_2$), 3.80 (q, 2H, *J* = 7 Hz, –OC*H$_2$*), 4.12 (q, 2H, *J* = 7 Hz, –OC*H$_2$*), 4.88 (s, 1H, γ-C*H*), 6.41 (s, 1H, Si*H*), 7.10–7.23 (m, 6H, 2 × *i*Pr$_2$C$_6$*H$_3$*) ppm. $^{29}$Si{$^{1}$H} NMR (59.36 MHz, $C_6D_6$, 25 °C): $\delta$ −103.75 ppm. EI-MS: *m/z* 620 (M$^+$).

### Synthesis of 3

*n*-Hexane (60 mL) was added to a 100 mL Schlenk flask containing **L** (0.32 g, 0.72 mmol) and 1,2-diacetylhydrazine (0.09 g, 0.77 mmol). The reaction mixture was stirred at room temperature for 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 2 days to obtain colorless single crystals. (0.34 g, 84%). Mp 163–165 °C (decomp). Elemental analysis (%) calcd for $C_{33}H_{48}N_4O_2Si$ (560.85): C, 70.67; H, 8.63; N, 9.99. Found: C, 70.62; H, 8.56; N, 9.82. $^{1}$H NMR (500 MHz, $C_6D_6$, 25 °C): $\delta$ 1.07 (d, 6H, *J* = 7 Hz, CH(C*H$_3$*)$_2$), 1.20 (d, 6H, *J* = 7 Hz, CH(C*H$_3$*)$_2$), 1.28 (d, 6H, *J* = 7 Hz, CH(C*H$_3$*)$_2$), 1.49 (s, 6H, NC(C*H$_3$*)), 1.52 (d, 6H, *J* = 7 Hz, CH(C*H$_3$*)$_2$), 1.84(s, 3H, C*H$_3$*), 1.94 (s, 3H, C*H$_3$*), 3.21 (m, 2H, C*H*(CH$_3$)$_2$), 3.46 (m, 2H, C*H*(CH$_3$)$_2$), 4.92 (s, 1H, γ-C*H*), 6.47 (s, 1H, Si*H*), 7.09–7.18 (m, 6H, 2 × *i*Pr$_2$C$_6$*H$_3$*) ppm. $^{29}$Si{$^{1}$H} NMR (99.36 MHz, $C_6D_6$, 25 °C): $\delta$ −104.39 ppm. EI-MS: *m/z* 560 (M$^+$).

### Synthesis of 4

*n*-Hexane (60 mL) was added to a 100 mL Schlenk flask containing **L** (0.45 g, 1.01 mmol) and 1,2-bis(*tert*-butoxycarbonyl)hydrazine (0.24 g, 1.03 mmol). The reaction mixture was stirred at room temperature for 12 h. The solution was filtered and the solvent was reduced *in vacuo* to 30 mL and stored in a freezer at −32 °C for 15 days to obtain a crystalline product of **4**. (0.52 g, 76%). Mp 145–148 °C (decomp). Elemental analysis (%) calcd for $C_{39}H_{60}N_4O_4Si$ (677.00): C, 69.19; H, 8.93; N, 8.28. Found: C, 69.12; H, 8.86; N, 8.23. $^{1}$H NMR (500 MHz, $C_6D_6$, 25 °C): $\delta$ 1.05 (d, 6H, *J* = 7 Hz, CH(C*H$_3$*)$_2$), 1.20 (d, 6H, *J* = 7 Hz, CH(C*H$_3$*)$_2$), 1.25 (s, 9H, C(C*H$_3$*)$_3$), 1.44 (d, 6H, *J* = 7 Hz, CH(C*H$_3$*)$_2$), 1.45 (s, 15H, NC(C*H$_3$*), C(C*H$_3$*)$_3$), 1.55 (d, 6H, *J* = 7 Hz, CH(C*H$_3$*)$_2$, 3.29 (m, 2H, C*H*(CH$_3$)$_2$), 3.42 (m, 2H, C*H*(CH$_3$)$_2$), 4.88 (s, 1H, γ-C*H*), 6.36 (s, 1H, Si*H*), 7.13–7.20 (m, 6H, 2 × *i*Pr$_2$C$_6$*H$_3$*) ppm. $^{29}$Si{$^{1}$H} NMR (99.36 MHz, $C_6D_6$, 25 °C): $\delta$ −104.63 ppm. EI-MS: *m/z* 676 (M$^+$).

## Crystal Structure Determination

Suitable single crystals for X-ray structural analysis of **1**, **2** and **3** were mounted at low temperature in inert oil under an argon atmosphere by applying the X-Temp2 device.[16] The data of **1**, **2** and **3** were collected at 100 K on a Bruker D8 three circle diffractometer equipped with a SMART APEX II CCD detector and an INCOATEC Mo microsource with INCOATEC Quazar mirror optics.[17] The data were integrated with SAINT[18] and an empirical absorption correction with SADABS[19] was applied. 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).[20] All non hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their $U_{iso}$ values constrained to $1.5U_{eq}$ of their pivot atoms for terminal sp³ carbon atoms and 1.2 times for all other carbon atoms. The positions of hydrogen atoms located at the silicon atoms were taken from the Fourier difference map. Their $U_{iso}$ value was constrained to be the $1.5U_{eq}$ of the silicon atom in the case of **2**, $1.2U_{eq}$ in the case of **3** and refined freely in the case of **1**. The site occupation factor for several lattice *n*-hexane molecules located on an inversion center in the unit cell was refined in the case of **1** leading to non-integer numbers in the empirical formula.

## Conclusions

In summary, we have demonstrated the double N–H bond activation by the reaction of NHSi with substituted hydrazines leading to compounds **1–4** in high yield where each silicon is five coordinate. The driving force for this reaction is the oxidative addition at the silicon(II) centers to yield the five coordinate silicon(IV) products.

## Acknowledgements

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