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An Amplified Ylidic "Half-Parent" Iminosilane LSi═NH

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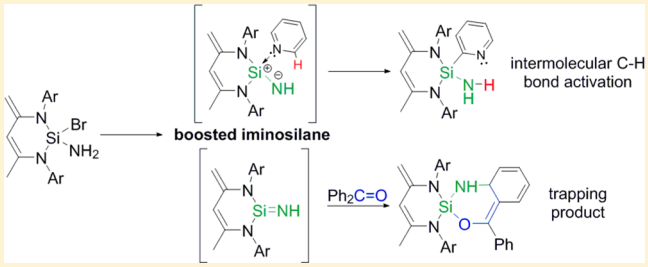
Supporting Information

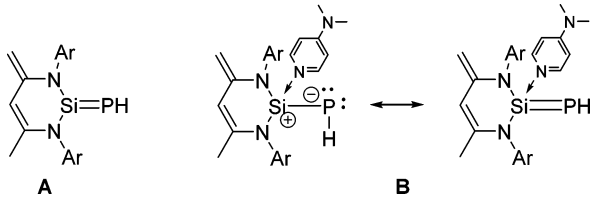
ABSTRACT: The reaction of LSiBr(NH$_2$) (**4**) (L = CH-[(C═CH$_2$)CMe(NAr)$_2$]; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) with lithium bis(trimethylsilyl)amide in the presence of pyridine or 4-dimethylaminopyridine (DMAP) resulted in the activation of the α C−H bond of pyridine or DMAP, affording the products LSi(dmap)NH$_2$ (**6**) and LSi(pyridine)NH$_2$ (**7a**), respectively. Remarkably, this metal-free aromatic C−H activation occurs at room temperature. The emerging aminosilanes were isolated and fully characterized. Isotope labeling experiments and detailed DFT calculations, elucidating the reaction mechanism, were performed and provide compelling evidence of the formation of the "half-parent" iminosilane **1**, LSi═NH, which facilitates this transformation due to its amplified ylidic character by the chelate ligand L. Furthermore, the elusive iminosilane **1** could be trapped by benzophenone and trimethylsilylazide affording the corresponding products, **8** and **9**, respectively, thereby confirming its formation as a key intermediate.



INTRODUCTION

Recently, we reported the syntheses of the highly ylidic "half-parent" phosphasilenes **A** and **B** (Scheme 1), which remarkably act as transfer reagents of the elusive parent phosphinidene (:PH) to an unsaturated organic substrate.[1,2] In analogy to the parent phosphinidene, the parent carbene (:CH$_2$) and imidogene (:NH) both exhibit triplet ground states, although the value of the singlet−triplet gap of :NH (ΔE_{ST} = −51.3 kcal·mol^{-1}) is substantially larger than in CH$_2$ and :PH (ΔE_{ST} = −32.9 kcal·mol^{-1} and ΔE_{ST} = −9.05 kcal·mol^{-1}), respectively,[3,4] highlighting its even greater reactivity.

Scheme 1. "Half-Parent" Ylidic Phosphasilenes A and B[a]

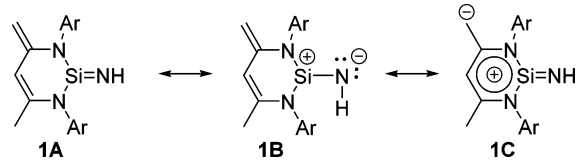


[a]Ar = 2,6-*i*Pr$_2$C$_6$H$_3$.

The imidogene was first observed by trapping experiments in an Ar matrix as early as 1958 by McCarty and Robinson.[5] Metal-mediated transfer reactions of this highly reactive fragment to unsaturated organic substrates are rarely known from the literature and require gas-phase reactions at extremely low pressures. In 1988, Freiser and co-workers reported the transfer of [:NH] from an iron-imido complex to ethylene at a pressure of 6 × 10^{-7} Torr.[6] Some 20 years later, Schwarz et al. described a dicationic nitrido-iron species, which was generated as an intermediate using electrospray ionization mass spectrometry and can transfer an :NH unit in bimolecular reactions with activated olefins.[7] Indeed, the metal-free imine-compound R$_3$N$^+$-$^-$NH, synthesized in 1966 by Schöllhorn et al., is able to transfer the [:NH] moiety to triphenylphosphine, but transfer reactions to unsaturated compounds were hitherto unsuccessful.[8]

Encouraged by our earlier results on the synthesis and reactivity of **A**, involving :PH transfer, and given the apparently intractable nature of :NH, we envisaged the synthesis of its "half-parent" nitrogen analogue **1** (Scheme 2), which could then, in analogy, potentially act as an :NH transfer reagent. To the best of our knowledge, no example of an "half-parent" iminosilane with three-coordinate silicon exists to date,

Scheme 2. Amplified Ylidic Si═N Bond of 1 Represented by the Resonance Structures 1A/1B/1C[a]



[a]Ar = 2,6-*i*Pr$_2$C$_6$H$_3$.

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presumably due to the pronounced polarity of the $Si^{\delta+}$-$N^{\delta-}$ σ- and π-bonds. Only one example of a donor-stabilized hydro(imino)silane has been reported recently.[9] All isolable iminosilanes are kinetically stabilized by bulky substituents on both the silicon and nitrogen centers. For example, the first iminosilane $(t\mathrm{Bu})_2(\mathrm{thf})\mathrm{Si{=}NSi}(t\mathrm{Bu})_3$ was reported in 1985 by Wiberg et al., where *tert*-butyl and tri(*tert*-butyl)silyl groups are protecting the Si=N double bond.[10]

Herein we report the *in situ* generation of the highly reactive amplified ylidic iminosilane **1**, starting from the aminosilane precursors **2**–**4** (Scheme 2). We pursued the same synthetic route using salt elimination reactions in analogy to the formation of **A**.[1] The unexpected reactivity of **1** renders it unisolable even in form of a donor–acceptor adduct with pyridines, in contrast to its phosphorus analogue **A**. However, trapping experiments, deuteration labeling studies and DFT investigations prove its existence as a key intermediate.

RESULTS AND DISCUSSION

To become acquainted with the remarkable electronic structure of the "half-parent" iminosilane LSi=NH **1** (L = CH[(C=CH_2)CMe(NAr)$_2$]; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$), density functional theory (DFT) studies at the B97-D/6-31G(d) level of theory were performed and compared with that of **A** and those of the parent iminosilane and the "half-parent" compounds $(CH_3)_2$Si=NH and $(NH_2)_2$Si=NH, respectively. The natural bond orbital (NBO) analysis of **1** reveals that the Si–N bond consists of an σ- and π-bond. Both σ- and π-bonds are strongly polarized toward the nitrogen atom by 75% and 78%, respectively, contrary to the phosphasilene **A**, where only the π-bond is significantly polarized. In the σ-bond of **1** (HOMO-49), the orbital of the silicon atom mainly has strong s character (65.9% s, 33.4% p), whereas the orbital of the nitrogen atom exhibits something between sp^2 and sp^3 character (28.4% s, 71.5% p) (Figure 1). The HOMO-1 illustrates the strongly

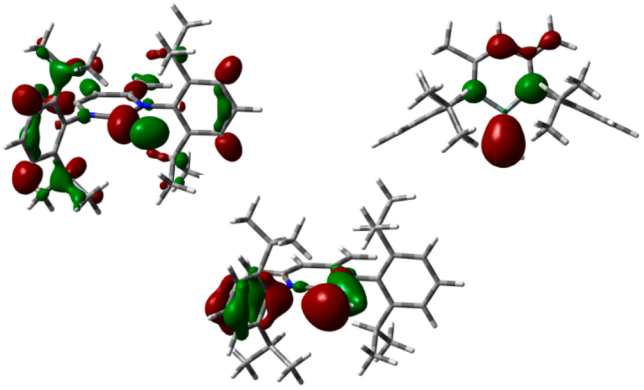


Figure 1. HOMO-49 (left), HOMO-1 (right), HOMO-6 (below, middle) of compound **1**.

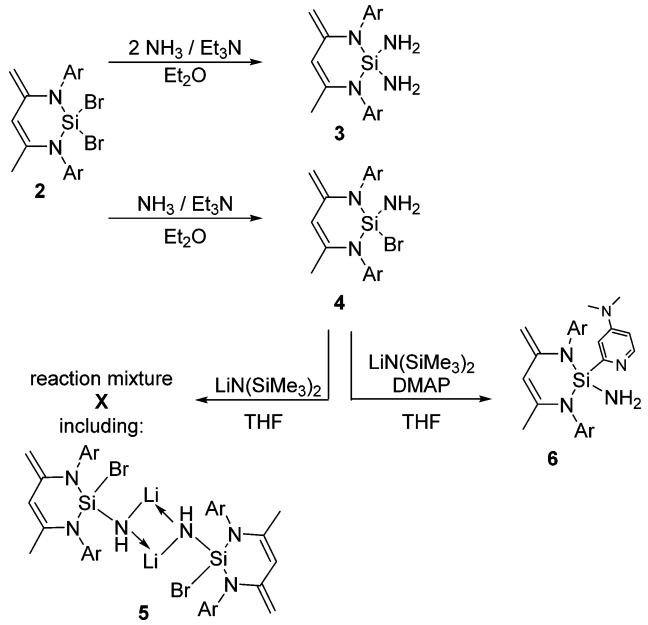
polarized π-bond, where only p-orbitals are involved. The lone pair of the nitrogen atom (45.1% s, 54.8% p) is represented in the HOMO-6 (Figure 1). The Wiberg bond index (WBI) of the Si–N bond of the "half-parent" iminosilane is 1.47, 0.21 lower than the WBI of the corresponding phosphasilene **A** (1.68). Comparison of the parent iminosilane (H_2Si=NH) to the "half-parent" compounds $(CH_3)_2$Si=NH, $(NH_2)_2$Si=NH, and **1** reveal the polarization of the Si=N bond increases with concomitant strengthening of the π-donor ability of the substituents at silicon (Table 1).[11,12] Because of the presence of the zwitterionic C_3N_2 ligand backbone[13] in **1**, its NBO charges and the WBI are slightly larger than those of (NH_2)Si=NH (Table 1).

Table 1. NBO Charges and WBIs of H_2Si=NH vs "Half-Parent" Iminosilanes

	NBO charges		WBI
	Si	N	
H_2Si=NH	1.19	−1.18	1.72
$(CH_3)_2$Si=NH	1.71	−1.25	1.62
$(NH_2)_2$Si=NH	1.92	−1.34	1.50
LSi=NH (**1**)	2.04	−1.35	1.47

Starting with the dibromosilane precursor **2**,[13] the reaction with an excess of ammonia gas and Et_3N as a mild base affords the diaminosilane **3**, whereas the reaction of **2** with only 1 equiv of NH_3 resulted in the selective formation of the mono-substituted aminosilane **4** (Scheme 3). Compounds **3** and **4**

Scheme 3. Synthesis of Compounds 2–6[a]



[a]Ar = 2,6-*i*Pr$_2$C$_6$H$_3$.

were isolated as colorless crystals and characterized by multinuclear NMR spectroscopy, high-resolution electron impact mass spectrometry (HR-EI-MS), IR spectroscopy, and single-crystal X-ray diffraction (XRD) analysis.[14] The conversion of the aminobromosilane precursor **4** with lithium bis(trimethylsilyl)amide at low temperatures (−80 °C) did not afford the desired iminosilane **1**. Instead, a reaction mixture with several undefined products **X** (Scheme 3) was observed. After several months, crystals suitable for XRD analysis were obtained from this mixture in concentrated *n*-hexane solutions upon storage at −30 °C. The latter product turned out to be the lithiated dimer compound **5** (Figure 2). The Si1–Br1 bond length of 230.95(12) pm is elongated by 7.35 pm compared to the starting material, aminobromosilane **4**, whereas the Si1–N3 bond distance of 164.0(4) pm is shorter by 5.2 pm. This is due to the interaction between lithium, N3, and bromine.

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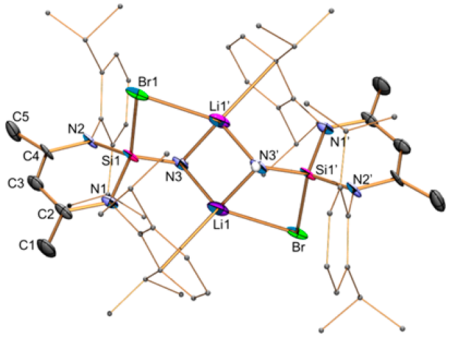


Figure 2. ORTEP representation of **5** (one of two independent molecules of one asymmetric unit). Equivalent atoms were generated by using symmetry transformations: #1 $-x + 2, -y + 1, -z + 2$; #2 $-x + 2, -y + 2, -z + 1$. Thermal ellipsoids are shown with 50% probability; hydrogen atoms are omitted for clarity, except those of N3. Selected bond distances (pm) and angles (deg.) of **5**: Si1−N3, 164.0(4); Si1−N1, 172.7(4); Si1−N2, 172.6(4); Si1−Br1, 230.95(12); N3−Li1, 202.5(10); Br1−Li1′, 277.7(11); Li1−C7, 250.2(10); C1−C2, 138.0(6); C4−C5, 146.8(7); N1−Si1−N2, 105.00(19); N1−Si1−N3, 114.2(2); N2−Si1−N3, 121.6(2); N3−Si1−Br1, 103.51(14); Si1−N3−Li1′, 116.0(4), Li1−N3−Li1′, 102.7(4); N3−Li1′−N3′, 77.3(4).

Additionally, there exists a π interaction between the phenyl group of the ligand and the Li atom.

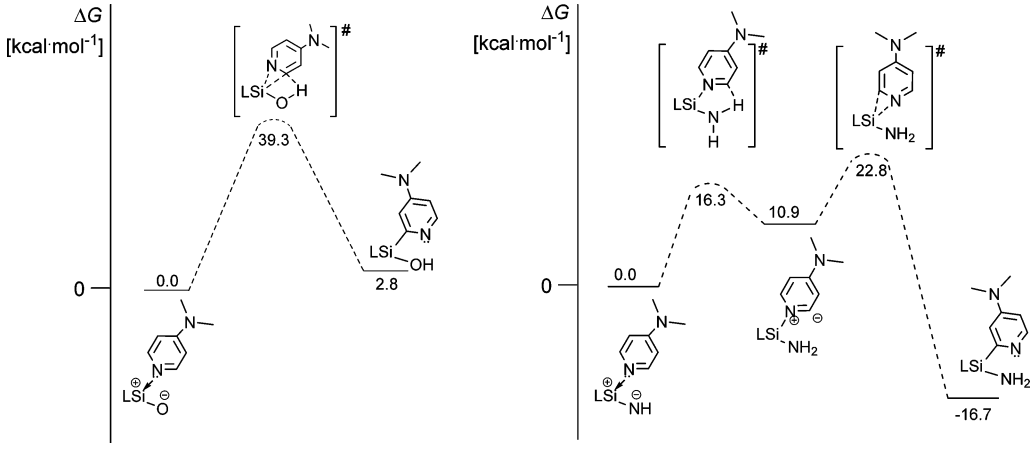
Since we were unable to detect the desired iminosilane **1** via LiBr elimination, starting from **4**, we attempted stabilization of **1** in the presence of 4-dimethylaminopyridine (DMAP) as a donor-stabilizing agent, a strategy we employed before resulting in the DMAP-stabilized phosphasilene **B** (Scheme 1).[2] Strikingly, the conversion of the aminobromosilane **4** with lithium bis(trimethylsilyl)amide in the presence of DMAP did not afford the expected donor-stabilized iminosilane adduct, in contrast to the phosphorus analogue **B**. Instead, facile room temperature activation of the α-C−H bond of the DMAP occurs, resulting in aminosilane **6** as colorless crystals in a 50% yield. A similar activation of the α-positioned C−H bond in pyridine was observed by Klingebiel and co-workers in 1998, although elevated temperatures were required.[15] For comparison, it seems instructive to note that the isolable DMAP-stabilized silanone analogue LSi(dmap)=O[16] does not activate the α-C−H bond of the DMAP, although the Si−O double bond is strongly polarized toward the oxygen atom (WBI = 1.17).[14,12,17] The Gibbs free energy of activation of the transition state which would afford the α-positioned C−H bond activation product in LSi(dmap)=O is with $\Delta G^{\ddagger}$ = 39.3 kcal·mol^{-1} rather high and the product is thermodynamically disfavored by ΔG = 2.8 kcal·mol^{-1}, in contrast to the hypothetical LSi(dmap)=NH adduct (ΔG = −16.7 kcal·mol^{-1}; Scheme 4).

In the ^{1}H NMR spectrum of **6**, the broad signal at δ = 1.63 ppm, corresponding to the amine group at the silicon center, is shifted to low field by 1.02 ppm compared to **4** and by 1.17 ppm compared to **3**, indicating reduced electron density at the nitrogen atom in **6**. A ^{1}H−^{1}H homonuclear correlation spectroscopy (COSY) experiment, where only three cross-peaks in the aryl area of the DMAP could be observed, proves that an α-carbon atom of the DMAP is bonded to the silicon center. The ^{13}C{^{1}H} resonance signal of this carbon atom at δ = 163.1 ppm is shifted 14.4 ppm to lower field compared to the second α-^{13}C nucleus of the DMAP. The ^{29}Si{^{1}H} NMR spectrum of **6** exhibits a singlet at δ = −47.8 ppm, which is similar to those of compounds **3** and **4** (**3**: δ(^{29}Si) = −51.1 ppm, **4**: δ(^{29}Si) = −48.5 ppm). The IR spectrum of **6** displays two weak sharp bands corresponding to the symmetric and asymmetric stretching vibrations of the NH_2 group (υ = 3495 and 3370 cm^{-1}).[18]

The molecular structure of **6** was confirmed by XRD analysis (Figure 3). The silicon center is coordinated in a distorted tetrahedral fashion. The Si1−N3 bond length of 168.33(17) pm is rather similar to those in the aminosilanes **3** (Si1−N3 168.57(14) pm; Si1−N4 169.32(14) pm) and **4** (Si1−N3 169.3(3) pm). The Si1−C31(DMAP) distance of 186.9(2) pm in **6** is in the characteristic range of Si−C single bonds in organosilanes.[19]

To investigate the mechanism of the formation of compound **6**, we used deuterium-labeling techniques and repeated the reaction with pyridine and pyridine-d_5, respectively. The conversions of **4** with lithium bis(trimethylsilyl)amide in the presence of pyridine or pyridine-d_5 selectively affords the aminosilane **7a** and **7b**, respectively (Scheme 5). Suitable crystals of **7a** for single-crystal XRD analysis were obtained from a concentrated *n*-hexane solution upon storage at 5 °C for 3 days (Figure 3). As expected, the molecular structure of **7a** is similar to that of **6**. Interestingly, the nitrogen atom of the

Scheme 4. DFT-Derived Gibbs Free Energies of the Activation of the α-C−H Bond of DMAP in the Iminosilane-Dmap Complex (right) vs Its Silanone Analogue LSi(dmap)=O (left)



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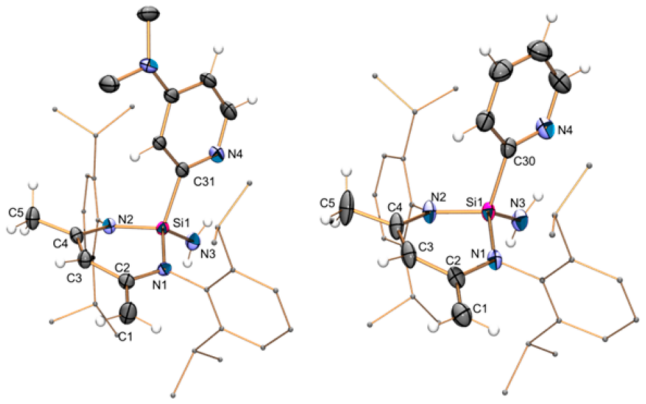


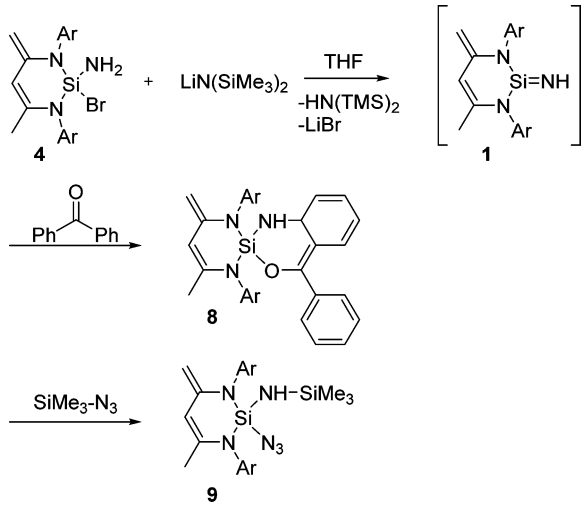
Figure 3. ORTEP representation of **6** and **7a**; thermal ellipsoids are shown with 50% probability; hydrogen atoms are omitted for clarity, except those of C1, C3, C5, N3 and aryl-DMAP/pyridine. Selected bond distances (pm) and angles (deg.) of **6**: Si1–N3, 168.33(17); Si1–N1, 173.81(16); Si1–N2, 173.37(15); Si1–C31, 186.9(2); C1–C2, 135.7(3); C4–C5, 148.5(3); N1–Si1–N2, 103.42(8); N1–Si1–N3, 114.08(9); N2–Si1–N3, 112.31(8); N3–Si1–C31, 104.55(10). Selected bond distances (pm) and angles (deg.) of **7a**: Si1–N3, 168.50(13); Si1–N1, 174.19(13); Si1–N2, 173.10(12); Si1–C31, 188.07(16); C1–C2, 135.1(2); C4–C5, 150.3(2); N1–Si1–N2, 102.96(6); N1–Si1–N3, 114.27(7); N2–Si1–N3, 112.67(6); N3–Si1–C31, 103.92(7).

Scheme 5. Aminosilanes 7a and 7b

pyridine or DMAP is turned in the direction of the amine group, in both molecules. The ^{1}H NMR spectra of **7a** and **7b** exhibit at δ = 1.50 ppm the signals of the amine group. For compound **7b**, this signal integrates to 1.2, indicating that the amine group is partially deuterated. Moreover the ^{2}H NMR spectrum of **7b** exhibits a resonance signal at δ = 1.55 ppm corresponding to the deuterated amine group. Signals in the aromatic region are also observed for the deuterated pyridine moiety. In the aryl region of the ^{1}H NMR spectra of **7b**, no signals corresponding to pyridine were observed. Consequently, no exchange/scrambling between the deuterium of the pyridine and the protons of the amine occur. The high-resolution atmospheric pressure chemical ionization mass spectrum (HR-APCI-MS) indicates the presence of the deuterated compound **7b**, with some nondeuterated compound concomitantly present. Additional evidence is provided by the IR spectra, which exhibits N–D stretching vibrations at υ = 2560 and 2515 cm^{-1}.[20] The presence of the deuterium atom on the nitrogen therefore provides some evidence that deprotonation of the pyridine-d$_5$ occurs via the iminosilane **1** at low temperatures.

To further prove the "half-parent" iminosilane **1** is in fact generated as an intermediate during the reaction, benzophenone and trimethylsilylazide were employed as trapping agents, respectively (Scheme 6). It is known that these reactants readily undergo cycloaddition reactions or that benzophenone can stabilize a compound bearing a Si=N double bond.[21−26] The reaction of **4** with lithium bis(trimethylsilyl)amide and 1 equiv

Scheme 6. Synthesis of Compounds 8 and 9



of benzophenone in THF at low temperatures (−80 °C) indeed resulted in the selective formation of the cyclized product **8**, where dearomatization of one phenyl group took place, in analogy to the addition of benzophenone to the silylene LSi:.[22] Similarly, by employing trimethylsilylazide as a trapping agent, the insertion adduct **9** was afforded. Both compounds, **8** and **9**, were characterized by multinuclear NMR spectroscopy and by HR-APCI MS, and additionally, compound **9** was studied by XRD analysis. The ^{29}Si signal of **8** (δ(^{29}Si) = −65.0 ppm) is shifted almost 20 ppm to higher field in comparison to the aminobromosilane **4**. In the ^{1}H NMR spectrum of **8**, the proton at the amine group could be found at δ = 1.27 ppm using 2D-NMR-spectroscopy (HMBC and COSY). The protons of the resulting dearomatized phenyl group appear between δ = 4.47 ppm and δ = 6.12 ppm as isolated multiplets. The ^{29}Si{^{1}H} spectrum of **9** reveals two signals; one singlet of the SiMe$_3$ group at δ = 6.4 ppm and a second singlet resonance signal at δ = −57.8 ppm (L*Si*(N$_3$)-NHSiMe$_3$). The molecular structure of **9** was confirmed by XRD analysis (Figure 4). Compound **9** exhibits a high

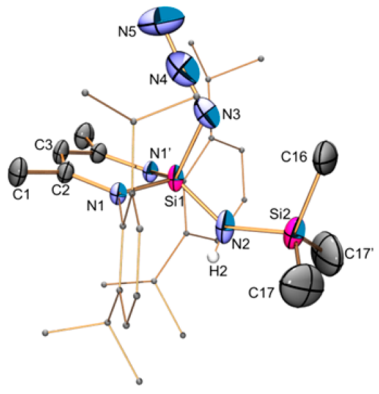


Figure 4. ORTEP representation of **9**. Equivalent atoms were generated by using symmetry transformations: #1 x, $-y$ + 3/2, z. Thermal ellipsoids are shown with 50% probability; hydrogen atoms are omitted for clarity, except those of N2. Selected bond distances (pm) and angles (deg.) of **9**: Si1–N2, 164.4(4); Si1–N3, 173.2(4); Si2–N2, 171.4(4); N3–N4, 115.3(7); N4–N5, 119.7(8); N1–Si1–N2, 104.79(15); N2–Si1–N3, 104.0(2); Si1–N3–N4, 122.1(4); N3–N4–N5, 175.5(7); Si1–N2–Si2, 140.6(3).

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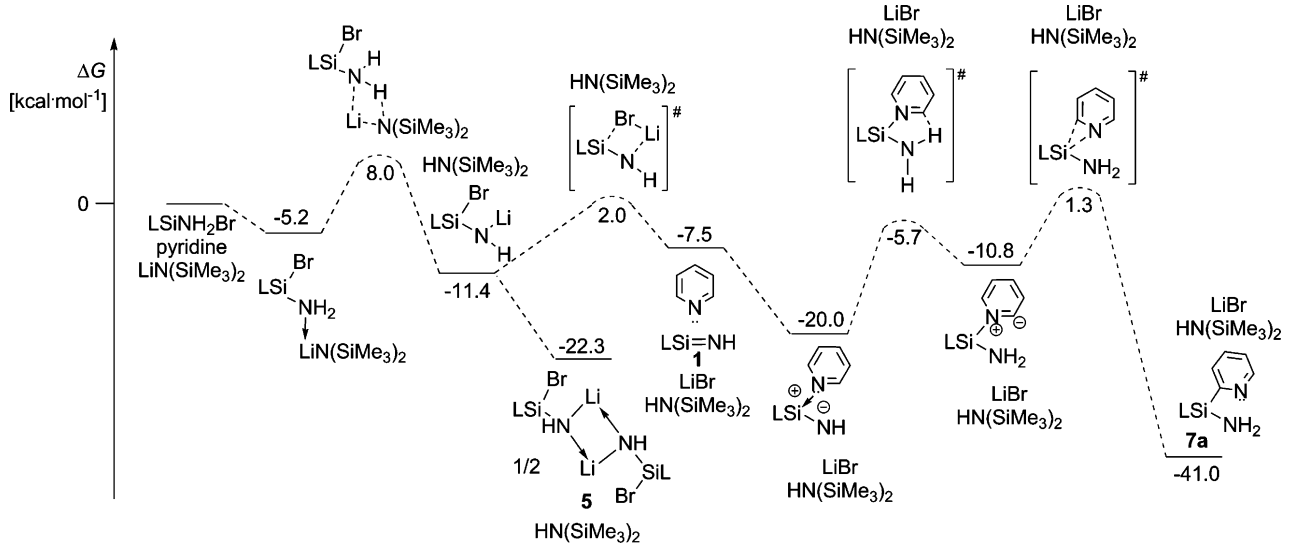
Scheme 7. Calculated Gibbs Free Energies for the Reaction Mechanism of the Conversion of 4 with $LiN(SiMe_3)_2$ in the Presence of Pyridine via Iminosilane 1 and the Dimeric Precursor 5



symmetry, and a mirror plane is located between C3, Si1, N3, N4, N5, N2, Si2, and C16. The silicon center Si1 exhibits a distorted tetrahedral coordination geometry. The azide group is positionated almost orthogonal to the plane defined by the ligand backbone, and it is nearly linear with an N3−N4−N5 bond angle of 175.5(7)°. The trapping products **8** and **9** provide additional evidence that the desired iminosilane **1** is generated *in situ* at low temperatures and then reacts with the trapping agents, benzophenone and trimethylsilylazide, respectively.

According to these results, a transfer reaction of the imidogene :NH from the *in situ* generated "half-parent" iminosilane **1** to an unsaturated organic compound seemed probable but turned out to be unsuccessful. N-heterocyclic carbenes (NHC) featuring different steric properties, such as mesityl, *tert*-butyl, *iso*-propyl, and methyl groups at the nitrogen atoms, were tested as trapping agents for the :NH moiety, in analogy to our previous studies with successful :PH transfer from **A** and **B**. The mass spectra of the resulting product mixtures after the *in situ* generation of **1** in the presence of 1 equiv of NHC did not reveal a signal corresponding to the desired imine adducts NHC═NH,[27] indicating that the transfer of the :NH did not occur. Instead, the same reaction mixture **X** could be observed in the ^{1}H NMR spectrum as without the presence of a trapping agent (Scheme 3).

To further ensure that the apparently highly reactive "half-parent" iminosilane **1** is indeed generated as an intermediate, we calculated possible reaction mechanisms using density functional theory (DFT) at the ωB97X-D/cc-pVTZ(PCM═benzene)//B97-D/6-31G* level.[14] Regarding the reaction affording the aminosilane **7a**, where the C−H bond of the pyridine was activated, the calculations verify that the base deprotonates the NH_2 group of **4** and not the α-C−H position of pyridine, in accordance with the deuterium-labeling experiments. The calculated pK_a value (in THF) of the NH_2 group in **4** is with pK_a = 35.2 lower than that of the α-C−H moiety of pyridine (pK_a = 44.6) and is therefore more acidic and preferentially deprotonated. The Gibbs free energy of the activation of the transition state resulting in the deprotonation of the pyridine by $LiN(SiMe_3)_2$ is rather high at $\Delta G^{\ddagger}$ = 29.2 kcal·mol^{-1}, implying that this route is highly unlikely (see free-energy profiles in SI).[14]

The experimentally observed dimer **5** suggests that the reaction might proceed via this intermediate, and we indeed found mechanisms that explicitly involved **5**.[14] However, considering the most favorable mechanism (Scheme 7), dimer **5** can be regarded as a resting state which also explains its experimental observation. LiBr elimination is also possible from **5**,[14] however, it exhibits a considerable activation barrier, 42.2 kcal·mol^{-1} (see Figure S19 in SI), while direct LiBr elimination from the monomer (see in Scheme 7) exhibits only a 13.4 kcal·mol^{-1} activation barrier compared to the previous step. This rather large activation barrier in the dimerized case stems from several unfavorable factors: to eliminate LiBr, the coordination of the adjacent N atom to the Li center has to be disrupted, in addition to the favorable interaction of the Li atoms with the phenyl group of the bulky ligand. These interactions offset the additional steric hindrance and entropic effects of the dimerization process and provide the stability of the dimer **5**. Further analysis of the reaction mechanisms in the presence of trapping agents, such as benzophenone, revealed their preference to react with monomeric **1** instead of **5** due to steric hindrance in the latter.[14]

Our DFT analysis also provides evidence as too why [:NH] transfer to NHCs from **1** is significantly hampered. Calculations suggest that the reaction of an NHC with **1** is a one step process, however, it exhibits a considerable activation barrier (e.g., the activation barrier of the reaction of Dipp-NHC and **1** is 29.6 kcal·mol^{-1}).[14]

These calculations, therefore, convincingly demonstrate that the iminosilane **1** can be generated as an intermediate at low temperatures, but the reaction profiles[14] along with the enormous ylidic polarity of the Si−N double bond also suggest the iminosilane **1** is to reactive, preventing its isolation.

■ CONCLUSION

In summary, the amplified ylidic "half-parent" iminosilane **1** could be generated at low temperatures as a highly reactive species from suitable aminosilane precursors. Unexpectedly, **1** is capable, in a facile way at room temperature, of activating a α-C−H bond of 4-dimethylaminopyridine and pyridine,

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respectively. This is facilitated by the stronger resonance stabilization of the Si^{+}-N^{-} ylide structure as indicated by the low WBI of only 1.47 vs 1.72 for $H_2Si{=}NH$. Mechanistic studies of this C−H activation by isotope labeling techniques and DFT calculations revealed that **1** is indeed formed as a reactive intermediate. In line with that, the iminosilane **1** could be trapped by employing benzophenone and trimethylsilylazide affording the corresponding products, **8** and **9**, respectively. Further investigations are devoted to the synthesis of related amplified ylidic iminosilanes for the activation of even less reactive sp^3 C−H moieties.

EXPERIMENTAL SECTION

General Considerations. All experiments and manipulations were conducted under dry anaerobic nitrogen using standard Schlenk techniques or in a MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior use. The starting material $LSiBr_2$ (L = CH[(C=CH_2)CMe(NAr)$_2$]; Ar = 2,6-^{i}PrC_6H_3) were prepared according to literature procedures.[13] ^{1}H, ^{2}H, ^{13}C, and ^{29}Si NMR spectra were recorded on Bruker Avance II 400 MHz (^{1}H: 400.13 MHz, ^{13}C: 100.61 MHz; ^{29}Si: 79.49 MHz), Bruker Avance II 200 MHz (^{1}H: 200.13 MHz, ^{13}C: 50.32 MHz), or on Bruker AvanceIII 700 MHz (^{1}H: 700.17 MHz, ^{2}H: 107.48 MHz) spectrometers. The NMR signals are reported relative to the residual solvent peaks (^{1}H: C_6D_6: 7.16 ppm; ^{13}C: C_6D_6: 128.0 ppm) or an external standard (^{29}Si: TMS: 0.0 ppm). EI-Mass spectra were recorded on a Finnigan MAT95S, ESI- and APCI-mass spectra on LTQ Orbitrap XL, and the raw data evaluated using the XCalibur computer program. IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR

Compound ***3***. A solution of **2** (53.3 mg, 0.09 mmol) and triethylamine (25.6 μL, 0.18 mmol) in 10 mL diethyl ether at −30 °C was placed in a Schlenk-tube and degassed by a freeze−pump−thaw cycle. The reaction vessel was charged with NH_3 at normal pressure. After stirring for 5 min, the solution was warmed to room temperature and stirred for a further 30 min. All volatiles were removed *in vacuo*, and the residue was extracted three times with *n*-hexane (3 × 5 mL). The obtained colorless filtrate was concentrated to 5 mL and left at −30 °C for 3 days to afford colorless crystalline product, which was separated from the mother liquor by filtration and dried *in vacuo* for 30 min. Yield: 31.5 mg (75%). ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C): δ [ppm] = 0.46 (br, 4 H, NH_2); 1.21, 1.26, 1.26, 1.42 (each d, ^3J(H,H)= 6.8 Hz, 6 H, CHMe_2); 1.50 (s, 3 H, NC*Me*); 3.24 (s, 1 H, NCC*H*H′); 3.49, 3.71 (each sept, ^3J(H,H) = 6.9 Hz, 2 H, C*H*Me$_2$); 3.90 (s, 1 H, NCC*H*H′); 5.40 (s, 1 H, γ-C*H*), 7.04−7.27 (m, 6 H, 2x 2,6-iPr$_2$C$_6$*H*$_3$). ^{13}C{^{1}H}-NMR (50.32 MHz, C_6D_6, 25 °C): δ [ppm] = 21.7 (NC*Me*); 24.0, 24.4, 25.0, 26.0 (CH*Me*$_2$); 27.9, 28.3 (*C*HMe$_2$); 84.3 (NC*C*H$_2$); 104.9 (γ-*C*); 124.0, 124.4, 128.0, 137.0, 138.2, 148.2, 148.3 (2,6-iPr$_2$C$_6$H$_3$); 141.2, 149.5 (NC). ^{29}Si{^{1}H}-NMR (39.76 MHz, C_6D_6, 25 °C): δ [ppm] = −51.1. IR (KBr): υ[cm^{-1}] = 3494 (w, N−H), 3475 (m, N−H), 3414 (w, N−H), 3378 (m, N−H), 3057 (w), 2964 (s), 2923 (m), 2868 (m), 1637 (s), 1624 (m), 1584 (w), 1535 (w), 1465 (m), 1451 (m), 1379 (s), 1351 (s), 1327 (m), 1310 (m) 1254 (m), 1247 (m), 1201 (s), 1177 (m), 1112 (w), 1102 (w), 1074 (s), 1057 (m), 1058 (w), 975 (w), 932 (m), 902 (s), 817 (m), 803 (s), 760 (m), 560 (w), 520 (w). MS (EI 70 eV): *m*/*z* (%) = 476 (8, [M]$^+$), 461 (100, [M − Me]$^+$), 433 (57, [M − *i*Pr]$^+$). MS (HR-EI 70 eV): *m*/*z* = 476.33299 [M]$^+$, calcd: 476.33298.

Compound ***4***. 78.0 mL of gaseous NH_3 (3.19 mmol) was added via syringe to a stirred solution of **2** (1.93 g, 3.19 mmol) and triethylamine (486 μL, 3.51 mmol) in 200 mL diethyl ether at −60 °C. After stirring for 60 min, the solution was warmed to room temperature and stirred for further 3 h. All volatiles were removed *in vacuo*, and the residue was extracted three times with *n*-hexane (3 × 75 mL). The filtrate was concentrated to 50 mL and left at −30 °C for 3 days to afford colorless crystalline product, which was separated from the mother liquor by filtration and dried *in vacuo* for 30 min. Yield: 1.34 g (79%). ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C): δ [ppm] = 0.61 (br, 2 H, NH_2);1.14, 1.18, 1.23, 1.24, 1.31, 1.36, 1.38, 1.53 (each d, ^3J(H,H) = 6.8 Hz, 3 H, CHMe_2); 1.44 (s, 3 H, NC*Me*); 3.38 (s, 1 H, NCC*H*H′); 3.37, 3.52, 3.72, 3.94 (each sept, ^3J(H,H) = 6.9 Hz, 1 H, C*H*Me$_2$); 3.95 (s, 1 H, NCCH*H*′); 5.43 (s, 1 H, γ-C*H*), 7.00−7.27 (m, 6 H, 2x 2,6-iPr$_2$C$_6$*H*$_3$). ^{13}C{^{1}H}-NMR (50.32 MHz, C_6D_6, 25 °C): δ [ppm] = 21.1 (NC*Me*); 23.3, 24.1, 24.4, 24.9, 25.1, 25.7, 26.3, 26.3 (CH*Me*$_2$); 28.2, 28.4, 28.5, 28.7 (*C*HMe$_2$); 88.0 (NC*C*H$_2$); 107.1 (γ-*C*); 123.9, 123.9, 124.7, 125.7, 128.0, 128.0, 134.8, 136.4, 147.6, 147.7, 148.2, 149.2 (2,6-iPr$_2$C$_6$H$_3$); 140.6, 149.3 (NC). ^{29}Si{^{1}H}-NMR (39.76 MHz, C_6D_6, 25 °C): δ [ppm] = −48.5. IR (KBr): υ[cm^{-1}] = 3485 (w, N−H), 3394 (m, N−H), 3396 (w, N−H), 3058 (w), 2965 (s), 2925 (m), 2867 (m), 1645 (s), 1584 (w), 1557 (m), 1536 (m), 1464 (s), 1439 (m), 1380 (s), 1351 (s), 1339 (m), 1314 (m), 1305 (m), 1254 (m), 1244 (w), 1194 (s), 1179 (m), 1111 (w), 1101 (m), 1075 (s), 1053 (m), 1043 (w), 986 (m), 958 (w), 934 (s), 890 (w), 830 (m), 805 (s), 787 (w), 758 (m), 583 (w), 563 (w), 517 (w). MS (EI 70 eV): *m*/*z* (%) = 539 (4, [M]$^+$), 524 (95, [M − Me]$^+$), 496 (52, [M − *i*Pr]$^+$). MS (HR-EI 70 eV): *m*/*z* = 539.23220 [M]$^+$, calcd: 539,23259.

Compound ***6***. A solution of lithium bis(trimethylsilyl)amide (24.8 mg, 0.15 mmol) in 3 mL THF at −70 °C was added via a Teflon cannula to a stirred solution of 4 (73.0 mg, 0.13 mmol) and DMAP (4-dimethylamino)pyridine (16.5 mg, 0.13 mmol) in 10 mL of THF at −70 °C. After stirring for 60 min, the solution was warmed to room temperature and stirred for a further 24 h. All volatiles were removed *in vacuo*, and the residue was extracted three times with *n*-hexane (3 × 6 mL). The obtained colorless filtrate was concentrated to 5 mL and left at −30 °C for 3 days to afford a colorless crystalline product, which was separated from the mother liquor by filtration and dried *in vacuo* for 30 min. Yield: 39.3 mg (50%). ^{1}H NMR (400.26 MHz, C_6D_6, 25 °C): δ [ppm] = 0.46, 0.67, 1.09, 1.23, 1.32, 1.33, 1.36, 1.46 (each d, ^3J(H,H)= 6.8 Hz, 3 H, CHMe_2); 1.63 (br, 2 H, NH_2); 1.66 (s, 3 H, NC*Me*); 3.42 (s, 1 H, NCC*H*H′); 3.35, 3.41, 3.74, 3.94 (each sept, ^3J(H,H) = 6.9 Hz, 1 H, C*H*Me$_2$); 4.06 (s, 1 H, NCC*H*H′); 5.59 (s, 1 H, γ-C*H*), 6.11 (dd, ^3J(H,H) = 5.9 Hz, ^4J(H,H) = 2.8 Hz, 1 H, DMAP, NCHC*H*CN); 7.01−7.22 (m, 6 H, 2x 2,6-iPr$_2$C$_6$*H*$_3$); 7.40 (d, ^4J(H,H) = 2.8 Hz, 1 H, DMAP, NCC*H*N); 8.22 (d, ^3J(H,H) = 5.9 Hz, 1 H, DMAP, NC*H*CHCN). ^{13}C{^{1}H}-NMR (50.32 MHz, C_6D_6, 25 °C): δ [ppm] = 21.5 (NC*Me*); 23.2, 23.2, 23.5, 24.1, 24.4, 24.7, 25.4, 26.1 (CH*Me*$_2$); 28.0, 28.3, 28.4, 28.5 (*C*HMe$_2$); 37.9 (N*Me*$_2$); 85.9 (NC*C*H$_2$); 105.3 (γ-*C*); 106.7 (DMAP, NCHCHCN); 113.6 (DMAP, NCCHCN); 123.4, 123.5, 123.8, 124.6, 126.7, 127.0, 136.4, 137.7, 147.6, 148.2, 148.3, 148.5 (2,6-iPr$_2$C$_6$H$_3$); 142.5, 149.0 (NC); 148.7 (DMAP, NCHCHCN); 152.7 (DMAP, NCHCHCN); 163.1 (DMAP, NCCHCN). ^{29}Si{^{1}H}-NMR (39.76 MHz, C_6D_6, 25 °C): δ [ppm] = −47.8. IR (KBr): υ[cm^{-1}] = 3495 (w, N−H), 3370 (w, N−H), 3058 (w), 2970 (s), 2937 (m), 2864 (m), 1635 (m), 1588 (s), 1534 (m), 1512 (m), 1467 (m), 1440 (m), 1378 (s), 1352 (s), 1305 (m) 1253 (m), 1199 (m), 1177 (m), 1103 (m), 1068 (w), 1047 (m), 986 (m), 925 (m), 885 (m), 805 (s), 763 (m), 558 (w). MS (EI 70 eV): *m*/*z* (%) = 581 (1, [M]$^+$), 566 (10, [M − Me]$^+$), 538 (7, [M − *i*Pr]$^+$). MS (HR-EI 70 eV): *m*/*z* = 581.38910 [M]$^+$, calcd: 581.39082.

Compound ***7a***. To a stirred solution of **4** (109.2 mg, 0.20 mmol) and lithium bis(trimethylsilyl)amide (37.2 mg, 0.22 mmol) in 20 mL THF at −80 °C was added dropwise 17.9 μL of pyridine (0.22 mmol). After stirring for 60 min, the solution was warmed to room temperature and stirred for a further 24 h. All volatiles were removed *in vacuo*, and the residue was extracted three times with *n*-hexane (3 × 6 mL). The obtained colorless filtrate was concentrated to 5 mL and left at −30 °C for 3 days to afford colorless crystalline product, which was separated from the mother liquor by filtration and dried *in vacuo* for 30 min. Yield: 54.4 mg (50%). ^{1}H NMR (400.26 MHz, C_6D_6, 25 °C): δ [ppm] = 0.20, 0.43, 1.03, 1.27, 1.28, 1.31, 1.34, 1.43 (each d, ^3J(H,H)= 6.8 Hz, 3 H, CHMe_2); 1.50 (br, 2 H, NH_2); 1.59 (s, 3 H, NC*Me*); 3.40 (s, 1 H, NCC*H*H′); 3.06, 3.06, 3.69, 3.89 (each sept, ^3J(H,H) = 6.9 Hz, 1 H, C*H*Me$_2$); 4.05 (s, 1 H, NCC*H*H′); 5.53 (s, 1 H, γ-C*H*), 6.63 (ddd, ^3J(H,H) = 7.7 Hz, ^3J(H,H) = 4.8 Hz, ^4J(H,H) = 1.3 Hz, 1 H, pyridine, NCHC*H*CH); 6.96−7.21 (m, 7 H, pyridine, NCHCHC*H*, 2x 2,6-iPr$_2$C$_6$*H*$_3$); 7.84 (ddd, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 1.5 Hz, ^5J(H,H) = 1.0 Hz, 1 H, pyridine, NCC*H*CH); 8.33 (ddd,

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^3J(H,H) = 4.8 Hz, ^4J(H,H) = 1.8 Hz, ^5J(H,H) = 1.0 Hz, 1 H, pyridine, NC*H*CHCH). $^{13}C\{^1H\}$-NMR (50.32 MHz, C_6D_6, 25 °C): δ [ppm] = 21.7 (NC*Me*); 23.2, 23.5, 23.6, 24.2, 24.7, 24.9, 25.8, 26.2 (CH*Me*$_2$); 28.2, 28.6, 28.7, 28.8 (*C*HMe$_2$); 86.6 (NC*C*H$_2$); 106.0 (γ-*C*); 123.2 (pyridine, NCH*C*HCH); 123.8, 123.9, 124.0, 124.9, 127.3, 128.0, 136.3, 137.6, 147.9, 148.4, 148.4, 148.6 (2,6-*i*Pr$_2$*C*$_6$H$_3$); 130.3 (pyridine, NCCHCH); 133.5 (pyridine, NCCHCH); 142.5, 149.0 (NC); 148.8 (pyridine, NCHCHCH); 164.6 (pyridine, NCCHCH). $^{29}Si\{^1H\}$-NMR (39.76 MHz, C_6D_6, 25 °C): δ [ppm] = −48.7. IR (KBr): υ[cm^{-1}] = 3489 (w, N−H), 3381 (w, N−H), 3105 (w), 3058 (w), 2967 (s), 2946 (m), 2925 (m), 2864 (m), 1639 (m), 1576 (w), 1555 (w), 1516 (m), 1461 (m), 1438 (m), 1379 (s), 1351 (s), 1306 (m) 1254 (m), 1197 (m), 1177 (m), 1102 (w), 1067 (m), 1047 (m), 970 (w), 928 (m), 885 (w), 801 (s), 757 (m), 563 (w). MS (EI 70 eV): *m*/*z* (%) = 538 (1, [M]$^+$), 523 (9, [M − Me]$^+$), 495(6, [M − *i*Pr]$^+$). APCI-MS: *m*/*z* = 539.35654 [M + H]$^+$, calcd: 539.35645.

Compound ***7b***. To a stirred solution of **4** (72.0 mg, 0.13 mmol) and lithium bis(trimethylsilyl)amide (24.5 mg, 0.15 mmol) in 20 mL THF at −80 °C was added dropwise 11.7 μL of pyridine-d$_5$ (0.15 mmol). After stirring for 60 min, the solution was warmed to room temperature and stirred for a further 24 h. All volatiles were removed *in vacuo*, and the residue was extracted three times with *n*-hexane (3 × 6 mL). The obtained colorless filtrate was concentrated to 5 mL and left at −30 °C for 3 days to afford colorless crystalline product, which was separated from the mother liquor by filtration and dried *in vacuo* for 30 min. Yield: 38.8 mg (55%). ^{1}H NMR (400.26 MHz, C_6D_6, 25 °C): δ [ppm] = 0.20, 0.43, 1.03, 1.27, 1.28, 1.31, 1.34, 1.43 (each d, ^3J(H,H)= 6.8 Hz, 3 H, CH*Me*$_2$); 1.50 (br, 1.2 H, N*H*$_2$); 1.59 (s, 3 H, NC*Me*); 3.40 (s, 1 H, NCC*H*H′); 3.06, 3.06, 3.69, 3.89 (each sept, ^3J(H,H) = 6.9 Hz, 1 H, C*H*Me$_2$); 4.05 (s, 1 H, NCC*H*H′); 5.53 (s, 1 H, γ-C*H*), 6.96−7.21 (m, 6 H, 2x 2,6-*i*Pr$_2$C$_6$*H*$_3$); ^{2}H NMR (107.48 MHz, 5% C_6D_6 and 95% C_6H_6, 25 °C): δ [ppm] = 1.55 (br, N*D*H), 6.64, 7.86, 8.33 (br, pyridine); $^{13}C\{^1H\}$-NMR (50.32 MHz, C_6D_6, 25 °C): δ [ppm] = 21.7 (NC*Me*); 23.2, 23.5, 23.6, 24.2, 24.7, 24.9, 25.8, 26.2 (CH*Me*$_2$); 28.2, 28.6, 28.7, 28.8 (*C*HMe$_2$); 86.6 (NC*C*H$_2$); 106.0 (γ-*C*); 123.8, 123.9, 124.0, 124.9, 127.3, 128.0, 136.3, 137.6, 147.9, 148.4, 148.4, 148.6 (2,6-*i*Pr$_2$*C*$_6$H$_3$); 142.5, 149.0 (NC). $^{29}Si\{^1H\}$-NMR (39.76 MHz, C_6D_6, 25 °C): δ [ppm] = −48.7. IR (KBr): υ[cm^{-1}] = 3489 (m, N−H), 3469 (w, N−H), 3406, (w, N−H), 3381 (m, N−H), 3108 (w), 3061(w), 2970 (s), 2945 (m), 2925 (m), 2864 (m), 2560 (w, N-D), 2515 (w, N-D), 1635 (m), 1583 (w), 1527 (w), 1514 (m), 1465 (m), 1439 (m), 1378 (s), 1353 (s), 1306 (m) 1255 (m), 1200 (s), 1179 (m), 1099 (m), 1066 (m), 1047 (m), 978 (w), 929 (m), 885 (w), 830 (w), 802 (s), 764 (m), 561 (w). APCI-MS: *m*/*z* = 543.38154 [M + H]$^+$ (M = $C_{34}H_{42}D_4N_4Si$), calcd: 543.38156, 544.38564 [M + H]$^+$ (M = $C_{34}H_{41}D_5N_4Si$), calcd: 544.38783.

Compound ***8***. A solution of benzophenone (25.1 mg, 0.14 mmol) in 2 mL THF at −70 °C was added via a Teflon cannula to a stirred solution of **4** (74.5 mg, 0.14 mmol) and lithium bis(trimethylsilyl)-amide (25.4 mg, 0.15 mmol) in 20 mL THF at −80 °C. After stirring for 2 h, the solution was warmed to room temperature and stirred for a further 3 h. All volatiles were removed *in vacuo*, and the residue was extracted three times with *n*-hexane (3 × 6 mL). The colorless filtrate was separated in two fractions: All volatiles of the first fraction were removed *in vacuo* and dissolved in C_6D_6 for NMR measurements. All volatiles of the second fraction were removed *in vacuo*, and the residue was used for HR-MS. ^{1}H NMR (400.26 MHz, C_6D_6, 25 °C): [ppm] = 1.27 (N*H*, found by COSY and HMQC); 0.99, 1.12, 1.20, 1.24, 1.31, 1.33, 1.36, 1.42 (each d, ^3J(H,H)= 6.8 Hz, 3 H, CH*Me*$_2$); 1.49 (s, 3 H, NC*Me*); 3.38 (s, 1 H, NCC*H*H′); 3.74, 3.74, 3.75, 3.76 (each sept, ^3J(H,H) = 6.9 Hz, 1 H, C*H*Me$_2$); 3.95 (s, 1 H, NCC*H*H′); 4.47 (br, 1 H, SiNH−C*H*-CH=CH−CH=CH); 5.20 (m, 2 H, SiNH−CH−CH=C*H*−C*H*=CH); 5.46 (s, 1 H, γ-C*H*); 5.53 (m, 1 H, SiNH−CH−C*H*=CH−CH=CH); 6.12 (d, ^3J(H,H) = 9.7 Hz, 1 H, SiNH−CH−CH=CH−CH=C*H*); 6.93−7.28 (m, 13 H, 2x 2,6-*i*Pr$_2$C$_6$*H*$_3$, SiOCC$_6$*H*$_5$)). $^{13}C\{^1H\}$-NMR (100.61 MHz, C_6D_6, 25 °C): δ [ppm] = 21.5 (NC*Me*); 23.7, 23.9, 24.6, 24.7, 24.7, 25.3, 25.7, 26.2 (CH*Me*$_2$); 28.0, 28.0, 28.1, 28.5 (*C*HMe$_2$); 49.4 (SiNH−CH−CH=CH−CH=CH); 86.3 (NC*C*H$_2$); 107.3 (γ-*C*); 118.5, 126.7 (SiNH−CH−CH=CH-CH=CH); 123.7 (SiNH−CH−*C*H=CH−CH=CH); 124.1 (SiOC=*C*); 124.9 (SiNH−CH−CH=CH−CH=CH); 124.3, 124.5, 125.7, 127.5, 127.7, 129.2, 135.2, 135.7, 136.3, 147.9, 148.2, 148.6, 249.2 (2,6-*i*Pr$_2$*C*$_6$H$_3$, SiOC*C*$_6$H$_5$); 141.4, 148.8 (NC). $^{29}Si\{^1H\}$-NMR (79.49 MHz, C_6D_6, 25 °C): δ [ppm] = −65.0. APCI-MS: *m*/*z* = 642.38794 [M + H]$^+$ (M = $C_{42}H_{52}N_3OSi$), calcd: 642.38742.

Compound ***9***. To a stirred solution of **4** (103.1 mg, 0.19 mmol) and lithium bis(trimethylsilyl)amide (35.1 mg, 0.21 mmol) in 20 mL THF at −80 °C was added dropwise 25.3 μL of trimethylsilyl azide (0.19 mmol). After stirring for 2 h, the solution was warmed to room temperature and stirred for a further 3 h. All volatiles were removed *in vacuo*, and the residue was extracted three times with *n*-hexane (3 × 6 mL). The obtained colorless filtrate was concentrated to 3 mL and left at −30 °C for 3 weeks to afford colorless product, which was separated from the mother liquor by filtration and dried *in vacuo* for 30 min. Yield: 44.8 mg (60%). ^{1}H NMR (400.26 MHz, C_6D_6, 25 °C): δ [ppm] = 0.38 (s, 9 H, Si*Me*$_3$); 0.24 (br, 1 H, N*H*); 1.15, 1.26, 1.28, 1.31, 1.36, 1.42, 1.54, 1.61 (each d, ^3J(H,H) = 6.8 Hz, 3 H, CH*Me*$_2$); 1.48 (s, 3 H, NC*Me*); 3.35 (s, 1 H, NCC*H*H′); 3.50, 3.56, 3.62, 3.63 (each sept, ^3J(H,H) = 6.9 Hz, 1 H, C*H*Me$_2$); 3.94 (s, 1 H, NCC*H*H′); 5.24 (s, 1 H, γ-C*H*); 6.97−7.24 (m, 6 H, 2x 2,6-*i*Pr$_2$C$_6$*H*$_3$). $^{13}C\{^1H\}$-NMR (50.32 MHz, C_6D_6, 25 °C): δ [ppm] = 1.1 (Si*Me*$_3$); 21.4 (NC*Me*); 23.2, 23.7, 24.1, 24.1, 24.6, 25.0, 26.1, 26.3 (CH*Me*$_2$); 27.9, 28.2, 28.7, 28.8 (*C*HMe$_2$); 86.4 (NC*C*H$_2$); 103.6 (γ-*C*); 123.6, 123.9, 124.5, 125.1, 127.9, 128.0, 135.2, 135.7, 147.2, 147.2, 148.4, 148.8 (2,6-*i*Pr$_2$C$_6$H$_3$); 141.1, 148.3 (NC). $^{29}Si\{^1H\}$-NMR (79.49 MHz, C_6D_6, 25 °C): δ [ppm] = −57.8 (NS*i*N), 6.4 (Si*Me*$_3$). IR (KBr): υ[cm^{-1}] = 3324 (w, N−H), 2151 (s, N_3). APCI-MS: *m*/*z* = 575.37213 [M + H]$^+$ (M = $C_{32}H_{51}N_6Si_2$), calcd: 575.37083.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details on single X-ray crystal structure analysis, selected NMR and HR-MS spectra of **3**−**9** as well as Cartesian coordinates, NBO analysis of **1**, and additional results from energy calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(14) See the SI. NMR and MS spectra, single-crystal X-ray structure determinations, and DFT calculations. CCDC-1022970 (**3**), CCDC-1022974 (**4**), CCDC-1022969 (**5**), CCDC-1022971 (**6**), CCDC-1022972 (**7a**), and CCDC-1022973 (**9**) 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.
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