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From a Stable Silanone Complex to Isolable, Donor-Supported Silicoxonium Halides $[LSi(dmap)=O{-}SiMe_3]^+X^-$**

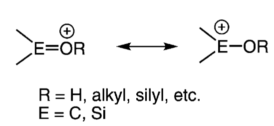
Yun Xiong, Shenglai Yao, Elisabeth Irran, and Matthias Driess*[a]

Abstract: The first donor-stabilized silylated silicoxonium species $[\mathbf{L}Si{=}O{-}SiMe_3]^+$ ($\mathbf{L} = (RN)C({=}CH_2)CH{=}CMe(NR)$, $R = 2,6\text{-}i\text{Pr}_2C_6H_3$) have been synthesized from the reaction of the dmap-supported (dmap = *p*-dimethylaminopyridine) silanone complex $[\mathbf{L}Si(dmap){=}O]$ (**1**) with trimethylsilyl halides. Although the reaction with Me_3SiCl leads directly to the Si=O addition product $[\mathbf{L}Si(Cl)OSiMe_3]$ (**2**), the ionic silicoxonium bromide $[\mathbf{L}(dmap)Si{=}O{-}SiMe_3]^+Br^-$ (**3**) can be obtained as a primary product of the reaction with Me_3SiBr, which affords $[\mathbf{L}Si(Br)OSiMe_3]$ (**4**) with release of the dmap ligand at room temperature in THF. In the case of Me_3SiI, the reaction furnishes the silicoxonium iodide $[\mathbf{L}(dmap)Si{=}O{-}SiMe_3]^+I^-$ (**5**) as the most stable species. Compounds **2**–**5** were isolated and fully characterized through multinuclear NMR spectroscopy, mass spectrometry, elemental analyses, and single-crystal X-ray diffraction analyses.

Keywords: dimethylaminopyridine · halides · Lewis bases · silanones · silicoxonium ion

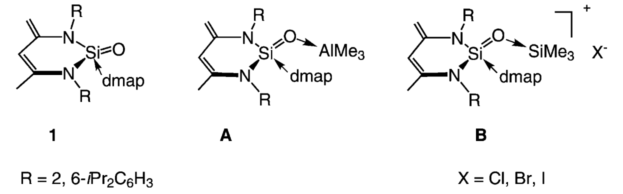
Introduction

Carboxonium ions, in which the positive charge can delocalize into the neighboring carbon atom through a resonance interaction, exhibit both carboxonium and carbenium ion character (Scheme 1, E = C). They are important intermediates in many acid-catalyzed reactions.[1] To date, long-lived protonated as well as alkylated carboxonium ions are readily prepared by protonation of the carbonyl compounds with strong acids or by alkylation of the carbonyl compounds using alkyl triflates and so on.[2,3] Even the silylated carboxonium ions,[4] also named siloxycarbenium ions,[5] have been prepared by generation of the trialkylsilyl cation in situ by using the Corey hydride transfer[6] in the presence of ketones, although none of the structures have been proven crystallographically as yet.



Scheme 1. The carboxonium ions (E = C) and silicoxonium (E = Si) ions.

In contrast, the corresponding heavier silicon analogues, that is, silicoxonium ions $[{>}Si{=}OR]^+$ (R = H, alkyl, silyl) are scarcely investigated on account of the difficulty in synthesizing suitable Si=O-containing silanone species.[7] By taking advantage of kinetic protection and thermodynamic stabilization, we recently succeeded in synthesizing a series of donor- and/or acceptor-stabilized silicon species that bear the Si=O subunit,[8–11] among which the 4-dimethylaminopyridine (dmap)-supported silanone (silaurea) species **1** (Scheme 2) represents an isolable silicon analogue of ketones suitable for reactivity studies of the Si=O moiety.[12] Although the Si=O double bond in **1** is highly polar and an Si−O single bond is favored in its resonance structures, interestingly, **1** reacts with NH_3[12] and H_2S[13] across the Si=O bond to give unique silanoic acid derivatives. In addition, the Si=O moiety in **1** also shows coordination ability by reacting with Lewis acids such as $AlMe_3$, thus leading to the stable Lewis acid–base adduct **A** with a $[Si{=}O{\rightarrow}AlMe_3]$ moiety (Scheme 2).[14] The latter reactions prompted us to investigate the reactivity of **1** toward trimethylsilyl halides Me_3SiX (X = Cl, Br, and I). Since the Me_3Si^+ is isoelectronic to $AlMe_3$, the addition of Me_3SiX to **1** was expected to give isolable silylated silicoxonium species **B** (Scheme 2). Herein we wish to report the successful isolation and characterization of the first donor-stabilized silicoxonium species $[\mathbf{L}(dmap)Si{=}O{-}SiMe_3]^+X^-$ ($\mathbf{L} = RNC({=}CH_2)CH{=}CMeNR$; $R = 2,6\text{-}i\text{Pr}_2C_6H_3$; X = Br, **3**; X = I, **5**) along with the Si=O addition products $[\mathbf{L}Si(X)OSiMe_3]$ (X = Cl, **2**; X = Br, **4**).



Scheme 2. The dmap-stabilized silanone (silaurea) **1** and its Lewis adducts **A** and **B**.

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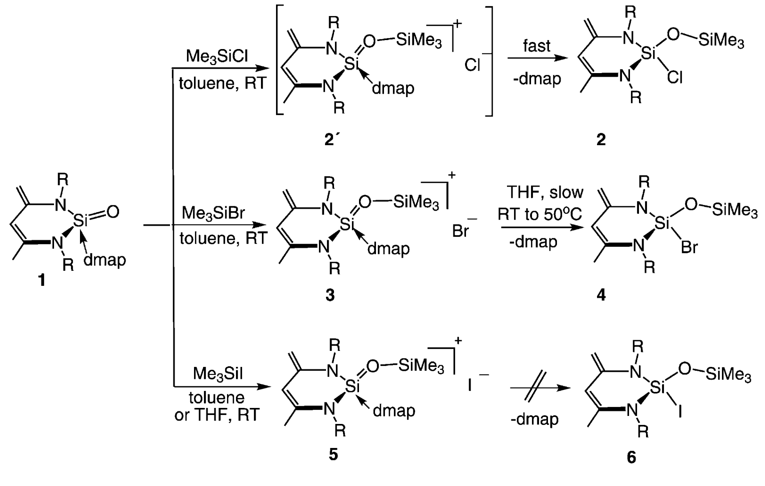
[a] Dr. Y. Xiong, Dr. S. Yao, Dr. E. Irran, Prof. Dr. M. Driess
Technische Universität Berlin
Institute of Chemistry
Metalorganic and Inorganic Materials
Sekr. C2, Strasse des 17. Juni 135
10623 Berlin (Germany)
Fax: (+49) 30-314-29732
E-mail: matthias.driess@tu-berlin.de

[**] dmap = *p*-dimethylaminopyridine; X = Br, I.

Results and Discussion

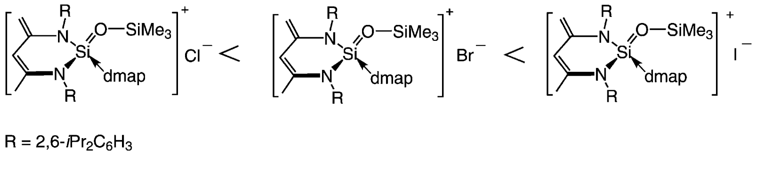
All the reactions of **1** with Me_3SiX ($X=Cl$, Br, I) are summarized in Scheme 3. When equimolar amounts of Me_3SiCl were added to a suspension of **1** in toluene at room temperature, the reaction mixture turned to a clear solution immediately, thus indicating the complete conversion of **1**. The proton NMR spectrum of the resulting mixture shows the corresponding resonance signals for the 'free' dmap molecule and the Si=O addition product **2** (Scheme 3).

We propose that the silicoxonium chloride **2′** (Scheme 3) is formed initially, which subsequently liberates dmap to afford the addition product **2** on account of the formation of a strong Si–Cl bond. Since the analogous Si–Br and Si–I bond formation is less favored, the corresponding silicoxonium halides **3** and **5** (Scheme 3) were expected to be more stable than **2′**. This is confirmed by addition of equimolar amounts of Me_3SiBr and Me_3SiI to solutions of **1** in toluene, which leads to facile formation of a saltlike precipitate of **3** and **5**, respectively (Scheme 3). The ion pair **3** is stable in the solid state; however, it slowly converts to the more stable Si–Br addition product **4** under release of the dmap ligand in THF solutions at room temperature. In contrast, the ion pair **5** is stable even in boiling THF. This underlines that the conversion of the ionic species **2′**, **3**, and **5** to the addition products depends on the nucleophilicity of the halide anion towards silicon as portrayed in Scheme 4. The composition and constitution of all isolated compounds **2**–**5** were determined by MS, multinuclear NMR spectroscopy, elemental (C, H, N) analyses, and single-crystal X-ray diffraction studies.



$R = 2{,}6\text{-}iPr_2C_6H_3$

Scheme 3. Reactions of **1** with Me_3SiX ($X=Cl$, Br, I).



$R = 2{,}6\text{-}iPr_2C_6H_3$

Scheme 4. Stability of silylated silicoxonium species.

The EIMS spectrum of **2** shows the molecular ion M at m/z 566 (9 %) along with the most intensive peak at m/z 551 assignable to $[M-Me]^+$. The proton NMR spectrum of **2** in $[D_8]$THF shows the characteristic feature of the ligand **L** and a singlet at $\delta=-0.43$ ppm for the $SiMe_3$ group. Its ^{29}Si NMR spectrum exhibits a singlet at $\delta=-67$ ppm for the silicon nucleus of the L*Si* moiety and a singlet at $\delta=14$ ppm for the *Si*Me$_3$ subunit. Some of the NMR spectroscopic data for **2**–**5** and for $[Ph_2C{=}O{-}SiMe_3]^+TFPB^-$ (TFPB = tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate)[5] are compared in Table 1.

Table 1. Comparison of selected chemical shifts in the ^1H and ^{29}Si NMR spectra of compounds **2**–**5** and $[Ph_2C{=}O{-}SiMe_3]^+TFPB^-$ (TFPB = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate); δ in ppm.

	2	3	4	5	$[Ph_2C{=}O{-}SiMe_3]^+$ TFPB[5]
$\delta(^1H)$ SiMe_3	−0.43[a] −0.45[b]	−0.19[a]	−0.39[a]	−0.20[a]	0.54[b]
$\delta(^{29}Si)$ **L**Si	−67[a] (−65[b])	−76[a]	−70[a]	−75[a]	
$\delta(^{29}Si)$ SiMe$_3$	14[a] (16[b])	18[a]	16[a]	18[a]	52.3[b]

[a] Recorded in $[D_8]$THF. [b] Recorded in $[D_2]$dichloromethane.

Compound **2** is soluble in toluene and THF. Single crystals of **2** suitable for X-ray diffraction analysis could be obtained in THF at room temperature. Compound **2** crystallized in the monoclinic space group $P2_1/m$ (Figure 1). The two Si atoms are tetrahedrally coordinated and bridged by an oxygen atom. The Si1–Cl1 bond length of 2.055(1) Å falls in the normal range of Si–Cl single bonds.[15] The same is true for the two Si–N bonds (1.707(2) Å). Remarkably, the Si1–O1 distance of 1.587(2) Å is significantly shorter than that of Si2–O1 (1.650(2) Å), thus reflecting the larger electrophilic character of the Si1 atom on account of its more electronegative substituents. The Si1-O1-Si2 bond angle of 152.8(2)° is similar to values observed for other disiloxanes.[16a] Selected metric parameters are summarized in Table 2.

The cation in **3** represents the first isolated Lewis base stabilized silylated silicoxonium that contains an $[Si{=}O{-}SiMe_3]^+$ moiety. The HR-ESI spectrum of **3** in cation mode showed a peak at m/z 655.42310 (calcd 655.42219) that is assignable to $[\mathbf{L}Si(dmap){=}O{-}SiMe_3]^+$. In the proton NMR spectrum of **3**, the

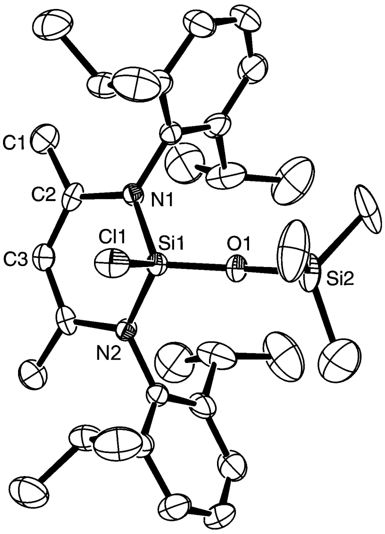


Figure 1. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity. The methyl groups of the $SiMe_3$ each adopts two positions in the crystal structure due to the disordering and only one of them is shown. Selected bond lengths [Å] and angles [°]: Si1–O1 1.587(2), Si2–O1 1.650(2), Si1–N1 1.707(2), Si1–N2 1.707(2), Si1–Cl1 2.055(1), C1–C2 1.417(4), C2–C3 1.406(3), N1–C2 1.425(3); Si1-O1-Si2 152.8(2).

Table 2. Comparison of selected metric parameters of compounds **2**–**5**. Distances in Å and angles in °.

	2	3	4	5
Si1–N1	1.707(2)	1.713(2)	1.715(2)	1.709(3)
Si1–N2	1.707(2)	1.707(2)	1.715(2)	1.713(3)
Si1–N3	–	1.808(2)	–	1.811(3)
Si1–O1	1.587(2)	1.584(1)	1.585(2)	1.582(3)
Si2–O1	1.650(2)	1.677(1)	1.646(2)	1.662(3)
Si1-O1-Si2	152.8(2)	159.1(1)	156.2(1)	165.1(2)

characteristic resonances for the ligands **L** and dmap can be assigned unambiguously. The sharp singlet at $\delta = -0.19$ ppm for the protons of the Si*Me*$_3$ group exhibits a slight downfield shift relative to that of **2** ($\delta = -0.43$ ppm, Table 1). Similar trends can be observed for the resonance of the Si atom in *Si*Me$_3$ ($\delta = 18$ ppm vs. 14 ppm in **2**) and for the Si nucleus of L*Si* ($\delta = -76$ ppm vs. -67 ppm in **2**).

Compound **3** is sparingly soluble in toluene and diethyl ether but soluble in THF. It crystallized as colorless cubes in the monoclinic space group $P2_1/c$. A single-crystal X-ray diffraction analysis revealed that **3** is an ion pair (Figure 2) as shown by the closest Si⋯Br contacts of 4.700 and 6.227 Å for Si2⋯Br1 and Si1⋯Br1, respectively. Thus the structural features resemble that of the ionic compound $[py\rightarrow SiMe_3]^+ Br^-$ (py = pyridine) with a Si⋯Br distance of 4.359 Å.[16b] The dmap molecule remains coordinated to the Si1 atom, which thus adopts a distorted tetrahedral coordination environment. The Si1–N3 distance of 1.808(2) Å is significantly longer than the other Si–N distances (Si1–N1 (1.713(2) Å) and Si1–N2 (1.707(2) Å)). The positive charge in **3** is presumably thoroughly delocalized as represented by the resonance structures shown in Scheme 5. Accordingly, the Si1–O1 distance of 1.584(1) Å is slightly longer than that of the Si=O bond in **1** (1.545(2) Å,[12] whereas the Si2–O1 bond (1.677(1) Å) is comparable to the Si–O σ-bond length in **L**SiO_2(NHC) (1.682(2) Å).[17] Notably, the latter Si1–O1 distance is also marginally longer than the corresponding Si–O length in [**L**Si(dmap)=O→$AlMe_3$] (1.547(2) Å).[14] This observation may reflects the electronically less positive character of silicon relative to aluminum.

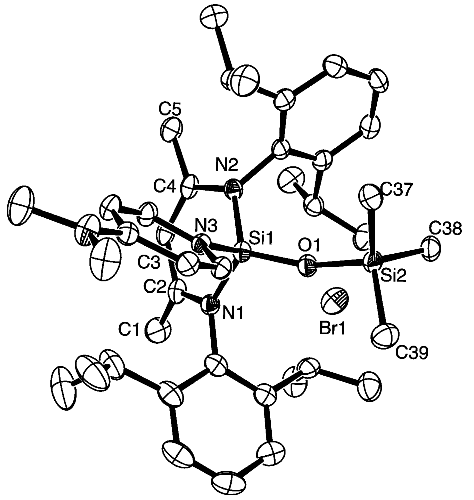
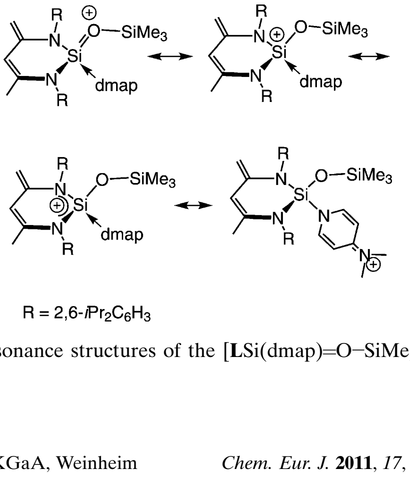


Figure 2. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–O1 1.584(1), Si2–O1 1.677(1), Si1–N1 1.713(2), Si1–N2 1.707(2), Si1–N3 1.808(2), Si2–C37 1.842(2), Si2–C38 1.848(2), Si2–C39 1.858(2), C1–C2 1.339(3), C2–C3 1.456(3), C3–C4 1.341(3), C4–C5 1.500(3); Si1-O1-Si2 159.1(1), N2-Si1-N3 107.8(1), N1-Si1-N3 108.4(1), N1-Si1-N2 106.7(1).

As mentioned above, the ion pair **3** is more stable in the solid state and reacts slowly at ambient temperature in THF to form the corresponding silyl bromide **4** with release of the dmap molecule (Scheme 3). The EIMS spectrum of isolated **4** shows a peak of the molecular ion *M* at *m*/*z* 614 (9 %), whereas the most intensive peak at *m*/*z* 599 corresponds to $[M{-}Me]^+$. As shown in Table 1, the chemical shift of the protons of the Si*Me*$_3$ group in the ^1H NMR spectrum appears at $\delta = -0.39$ ppm, similarly to that of **2** ($\delta = -0.43$ ppm). Likewise, the ^{29}Si resonances are comparable to those observed for **2**.



Scheme 5. Resonance structures of the $[\mathbf{L}Si(dmap){=}O{-}SiMe_3]^+$ cation in **3** and **5**.

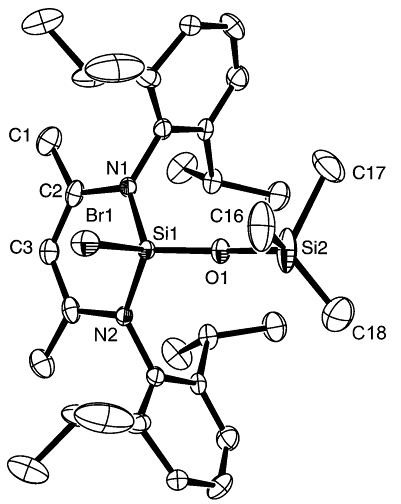


Figure 3. Molecular structure of **4**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. The methyl groups of the SiMe$_3$ and the aryl groups each adopts two positions in the crystal structure due to the disordering and only one of them is shown. Selected bond lengths [Å] and angles [°]: Si1−O1 1.585(2), Si2−O1 1.646(2), Si1−Br1 2.240(1), Si1−N1 1.715(2); Si1−N2 1.715(2), C1−C2 1.417(4), C2−C3 1.406(3), N1−C2 1.425(3); Si1-O1-Si2 156.2(1), O1-Si1-Br1 108.9(1), O1-Si1-N1 112.1(1).

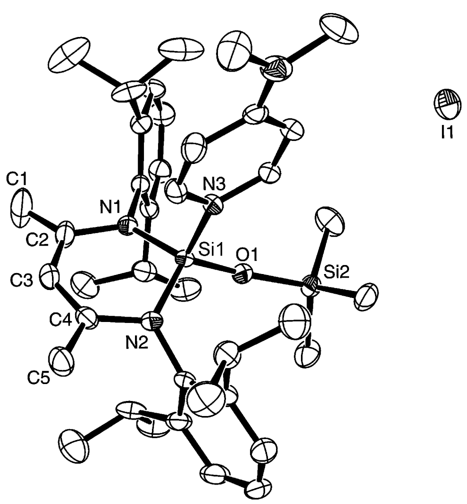


Figure 4. Molecular structure of **5**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and THF molecules are omitted for clarity. The iodide anion and solvent THF molecules are in disorder. Selected bond lengths [Å] and angles [°]: Si1−O1 1.582(3), Si2−O1 1.662(3), Si1−N1 1.709(3), Si1−N2 1.717(3), Si1−N3 1.811(3); Si1-O1-Si2 165.1(2), N2-Si1-N3 106.8(2), N1-Si1-N3 109.4(2), N1-Si1-N2 106.0(2), O1-Si1-N1 114.4(2), O1-Si1-N2 115.3(2), O1-Si1-N3 104.6(2).

Single crystals of **4** suitable for X-ray diffraction analysis could be obtained from THF solutions; the compound crystallized in a monoclinic space group $P2_1/m$ with similar disorders as those that occurred in **2**. As expected, the compound is isostructural to the chloride analogue **2** (Figure 3). The Si1−Br1 distance of 2.240(1) Å, which is significantly shorter than that in the silicoxonium bromide **3** (6.227 Å), falls in the common range of Si−Br distances in related silyl bromides.[15] Despite the different halogen atoms connected to Si1 in **4** relative to **2**, their respective metric parameters are quite similar (Table 2).

The aforementioned treatment of **1** with Me$_3$SiI both in toluene and in THF at room temperature led immediately to the formation of the ionic compound **5** (Scheme 3). No further elimination of dmap and coordination of I$^-$ to the silicon center to give **6** was observed, even in boiling THF. The HR-ESI spectrum of **5** (cation mode) showed a peak at *m*/*z* 655.42316 (calcd 655.42219) assignable to the cation [**L**Si(dmap)=O−SiMe$_3$]$^+$. The ^{1}H and ^{13}C NMR spectra of **5** in [D$_8$]THF show very similar patterns to those of **3** for the supporting ligand **L** and the coordinated dmap. The same is true for the ^{29}Si NMR spectroscopic resonances of **5** and **3** (Table 1). Pale yellow rhombic crystals of **5** suitable for X-ray diffraction analysis could be obtained from a THF solution at room temperature. The compound crystallized in the monoclinic space group $P2/c$ with several THF molecules in the asymmetric unit. Similar to **3**, compound **5** features an ionic structure, although they are not isostructural (Figure 4). The shortest Si−I contact amounts to 5.176 Å. The conformation and the geometric parameters of the cation of **5** are very similar to those of **3** (Table 2). Unexpectedly, the corresponding metric parameters around the silicon atom of the **L**Si subunit in **3** and **5** do not differ significantly from those of the neutral species **2** and **4** (Table 2). This observation may be ascribed in large part to the strong donor effect of the supporting dmap ligand in **3** and **5**, respectively.

Conclusion

In summary, by examining the reactivity of the donor-stabilized silanone complex [**L**Si(dmap)=O] (**1**) towards trimethylsilyl halides Me$_3$SiX (X = Cl, Br, and I) under mild conditions, the first Lewis base supported silicoxonium halides species with [>Si=O−SiMe$_3$]$^+$ have been synthesized and isolated successfully. The stability of these silicoxonium species depends on the nature of the respective halide counterion. Although the corresponding silicoxonium chloride **2′** is elusive during the formation of [**L**Si(Cl)OSiMe$_3$] (**2**), the silicoxonium bromide [**L**(dmap)Si=O−SiMe$_3$]$^+$Br$^-$ (**3**) could be isolated and structurally characterized but transforms in solutions to afford [**L**Si(Br)OSiMe$_3$] (**4**) and 'free' dmap. In contrast, the corresponding iodide salt [**L**(dmap)Si=O−SiMe$_3$]$^+$I$^-$ **5** is stable both in the solid state and in THF. The first Lewis base stabilized silicoxonium compounds **3** and **5** are expected to serve as promising precursors for the synthesis of value-added organosilicon compounds. Respective investigations are currently in progress.

Experimental Section

General: All experiments and manipulations were carried out under dry oxygen-free nitrogen by using standard Schlenk techniques or using an

MBraun inert atmosphere dry box that contained an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior to use. The starting material **1** was prepared according to literature procedures.[12,18] The NMR spectra were recorded using Bruker spectrometers ARX200 and AV400 and with residual solvent signals as internal references (^{1}H and ^{13}C{H}) or with an external reference (SiMe$_4$ for ^{29}Si). Abbreviations: s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet, br = broad. Elemental analyses were performed using a FlashEA 1112 CHNS analyzer.

Single-crystal X-ray structure determination: Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N$_2$ flow. The data of **2**–**5** were collected using an Oxford Diffraction Xcalibur S Sapphire instrument at 150 K (Mo$_{K\alpha}$ radiation, $\lambda=0.71073$ Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97[19] software package. The positions of the hydrogen atoms were calculated and considered isotropically according to a riding model.

CCDC-827047 (**2**), 827048 (**3**), 827049 (**4**), and 827050 (**5**) 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.

Crystal data for 2: Monoclinic, space group $P2_1/m$; $a=8.861(2)$, $b=19.952(3)$, $c=10.235(2)$ Å; $\beta=113.73(2)°$; $V=1656.6(5)$ Å^3; $Z=2$; $\rho_{\text{calcd}}=1.141$ Mg m^{-3}; $\mu(\text{Mo}_{K\alpha})=0.213$ mm^{-1}; 6608 collected reflections, 3003 crystallographically independent reflections ($R_{\text{int}}=0.0416$), 2096 reflections ($I>2\sigma(I)$); $\theta_{\max}=25°$; $R(F_o)=0.0501$ ($I>2\sigma(I)$), $wR(F_o^2)=0.1235$ (all data), 201 refined parameters.

Crystal data for 3: Monoclinic, space group $P2_1/c$; $a=10.8224(4)$, $b=20.9731(9)$, $c=17.9482(5)$ Å; $\beta=96.219(3)°$; $V=4049.9(3)$ Å^3; $Z=4$; $\rho_{\text{calcd}}=1.207$ Mg m^{-3}; $\mu(\text{Mo}_{K\alpha})=1.108$ mm^{-1}; 29 892 collected reflections, 7098 crystallographically independent reflections ($R_{\text{int}}=0.0381$), 5107 reflections with ($I>2\sigma(I)$), $\theta_{\max}=25°$, $R(F_o)=0.0312$ ($I>2\sigma(I)$), $wR(F_o^2)=0.0684$ (all data), 438 refined parameters.

Crystal data for 4: Monoclinic, space group $P2_1/m$; $a=8.8642(4)$, $b=19.8176(8)$, $c=10.4248(4)$ Å; $\beta=114.594(3)°'$ $V=1665.2(1)$ Å^3; $Z=2$; $\rho_{\text{calcd}}=1.224$ Mg m^{-3}; $\mu(\text{Mo}_{K\alpha})=1.332$ mm^{-1}; 14482 collected reflections, 3032 crystallographically independent reflections ($R_{\text{int}}=0.0352$), 2482 reflections with ($I>2\sigma(I)$), $\theta_{\max}=25°$, $R(F_o)=0.0309$ ($I>2\sigma(I)$), $wR(F_o^2)=0.0784$ (all data), 267 refined parameters.

Crystal data for 5: Monoclinic, space group $P2/c$; $a=19.2310(9)$, $b=11.3749(5)$, $c=23.172(1)$ Å; $\beta=106.280(5)°$; $V=4865.5(4)$ Å^3; $Z=4$, $\rho_{\text{calcd}}=1.200$ Mg m^{-3}; $\mu(\text{Mo}_{K\alpha})=0.745$ mm^{-1}; 35 224 collected reflections, 8568 crystallographically independent reflections ($R_{\text{int}}=0.0493$), 6556 reflections with ($I>2\sigma(I)$), $\theta_{\max}=25°$, $R(F_o)=0.0586$ ($I>2\sigma(I)$), $wR(F_o^2)=0.1539$ (all data), 555 refined parameters.

Synthesis of 2: Me$_3$SiCl (0.080 mL, $d=0.85$ g mL^{-1}, 0.63 mmol) was added to a suspension of **1** (0.37 g, 0.63 mmol) in toluene (10 mL) at room temperature. The suspension turned clear immediately. From the concentrated solution (4 mL) compound **2** crystallized as colorless plates with yield of 0.30 g (0.53 mmol, 84 %). X-ray qualified single crystals were obtained from THF at −20 °C. M.p. 213 °C; ^{1}H NMR (200.13 MHz, [D$_8$]THF, 25 °C): $\delta=-0.43$ (s, 9H; Si*Me*$_3$), 1.09–1.38 (m, 24H; CH*Me*$_2$), 1.63 (s, 3H; NC*Me*), 3.05 (s, 1H; NCC*H*$_2$), 3.15 (sept, ^{3}J(H,H) = 7.0 Hz, 1H; C*H*Me$_2$), 3.40–3.69 (m, 3H; C*H*Me$_2$), 3.76 (s, 1H; NCC*H*$_2$), 5.31 (s, 1H; γ-C*H*), 7.09–7.38 ppm (br m, 6H; 2,6-*i*Pr$_2$C$_6$*H*$_3$); ^{1}H NMR (200.13 MHz, [D$_2$]dichloromethane, 25 °C): $\delta=-0.44$ (s, 9H; Si*Me*$_3$), 1.15–1.36 (m, 24H; CH*Me*$_2$), 1.63 (s, 3H; NC*Me*), 3.05 (s, 1H; NCC*H*$_2$), 3.34–3.63 (m, 4H; C*H*Me$_2$), 3.79 (s, 1H; NCC*H*$_2$), 5.31 (s, 1H; γ-C*H*), 7.16–7.32 ppm (br m, 6H; 2,6-*i*Pr$_2$C$_6$*H*$_3$); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_8$]THF, 25 °C): $\delta=1.20$ (Si*Me*$_3$), 22.0 (NC*Me*), 23.5, 24.2, 24.5, 24.8, 25.3, 26.0, 26.1, 26.6 (CH*Me*$_2$), 28.8, 28.9, 29.5, 29.6 (*C*HMe$_2$), 87.2 (NC*C*H$_2$), 104.2 (γ-*C*), 123.7, 124.6, 124.7, 125.6, 125.9, 128.7, 128.8, 141.5, 143.1, 148.5, 148.9, 149.6, 149.9, 150.2 ppm (N*C*Me, N*C*CH$_2$, 2,6-*i*Pr$_2$*C*$_6$H$_3$); ^{29}Si{^{1}H} NMR (79.49 MHz, [D$_8$]THF, 25 °C): $\delta=-67$ (s, 1Si; N$_2$*Si*OCl), 14 ppm (s, 1Si; O*Si*Me$_3$); ^{29}Si{^{1}H} NMR (79.49 MHz, [D$_8$]dichloromethane, 25 °C): $\delta=-65$ (s, 1Si; N$_2$*Si*OCl), 16 ppm (s, 1Si; O*Si*Me$_3$); EI-MS: *m*/*z* (%): 566 (9) [*M*]$^+$, 551 (100), [*M*−Me]$^+$, 523 (55) [*M*$^+$−*i*Pr]; elemental analysis calcd (%) for C$_{32}$H$_{49}$N$_2$Si$_2$OCl: C 67.50, H 8.67, N 4.92; found: C 67.30, H 8.31, N 5.03.

Synthesis of 3: Me$_3$SiBr (0.070 mL, $d=1.16$ g mL^{-1}, 0.53 mmol) was added to a suspension of **1** (0.31 g, 0.53 mmol) in toluene (10 mL) at room temperature. The suspension turned clear immediately. In half an hour compound **3** precipitated from the solution with yield of 0.30 g (0.41 mmol, 77 %). X-ray qualified single crystals were obtained as colorless plates from THF at −20 °C. M.p. 170 °C (decomposed); ^{1}H NMR (200.13 MHz, [D$_8$]THF, 25 °C): $\delta=-0.19$ (s, 9H; Si*Me*$_3$), 0.64 (d, ^{3}J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 0.71 (d, ^{3}J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.03 (d, ^{3}J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.10 (d, ^{3}J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.21 (d, ^{3}J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.27 (d, ^{3}J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.41 (d, ^{3}J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.45 (d, ^{3}J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.79 (s, 3H; NC*Me*), 2.45 (sept, ^{3}J(H,H) = 7.6 Hz, 1H; C*H*Me$_2$), 2.74 (sept, ^{3}J(H,H) = 7.6 Hz, 1H; C*H*Me$_2$), 3.25 (s, 1H; NCC*H*$_2$), 3.47 (s, 6H; dmap), 3.51–3.68 (m, 2H; C*H*Me$_2$), 4.05 (s, 1H; NCC*H*$_2$), 5.65 (s, 1H; γ-C*H*), 6.66–6.80 (m, 1H; dmap), 7.09–7.27 (m, 6H; 2,6-*i*Pr$_2$C$_6$*H*$_3$), 7.77–8.74 ppm (m, 3H; dmap); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_8$]THF, 25 °C): $\delta=1.99$ (Si*Me*$_3$), 22.1 (NC*C*H$_3$), 24.1, 24.3, 25.0, 25.9, 26.4, 28.8, 29.6, 29.8 (CH*Me*$_2$, *C*HMe$_2$), 41.3 (dmap), 87.8 (NC*C*H$_2$), 107.1 (γ-*C*), 111.8 (dmap), 124.9, 125.0, 125.8, 126.1, 129.1, 134.8, 144.3, 148.0, 148.6, 149.1, 149.7, 149.8, 158.3, 174.7 ppm (N*C*Me, N*C*CH$_2$, dmap, 2,6-*i*Pr$_2$*C*$_6$H$_3$); ^{29}Si{^{1}H} NMR (79.49 MHz, [D$_8$]THF, 25 °C): $\delta=-76$ (s, 1Si; N$_3$*Si*O), 18 ppm (*Si*Me$_3$); HR-ESI: *m*/*z* calcd: 655.42219 [*M*−Br]$^+$; found: 655.42310; elemental analysis calcd (%) for C$_{39}$H$_{59}$N$_4$Si$_2$OBr: C 63.65, H 8.08, N 7.61; found: C 63.54, H 8.04, N 7.87.

Synthesis of 4: Me$_3$SiBr (0.073 mL, $d=1.16$ g mL^{-1}, 0.55 mmol) was added to a suspension of **1** (0.32 g, 0.55 mmol) in THF (10 mL) at room temperature. The suspension turned clear immediately. The proton NMR spectra showed a mixture of **3** and **4**. By heating the solution to 50 °C for 3 d, compound **3** converted to **4** completely. Compound **4** crystallized as colorless rods from the solution at 4 °C with a yield of 0.25 g (0.41 mmol, 74 %). M.p. 215 °C; ^{1}H NMR (200.13 MHz, [D$_8$]THF, 25 °C): $\delta=-0.39$ (s, 9H; Si*Me*$_3$), 1.14–1.36 (m, 24H; CH*Me*$_2$), 1.64 (s, 3H; NC*Me*), 3.08 (s, 1H; NCC*H*$_2$), 3.44–3.72 (m, 4H; C*H*Me$_2$), 3.80 (s, 1H; NCC*H*$_2$), 5.37 (s, 1H; γ-C*H*), 7.16–7.32 ppm (m, 6H; 2,6-*i*Pr$_2$C$_6$*H*$_3$); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_8$]THF, 25 °C): $\delta=1.36$ (Si*Me*$_3$), 21.8 (NC*C*H$_3$), 24.1, 24.5, 25.3, 25.4, 26.0, 26.1, 26.4, 27.2 (CH*Me*$_2$), 29.0, 29.1, 29.6, 29.8 (*C*HMe$_2$), 87.9 (NC*C*H$_2$), 105.1 (γ-*C*), 124.6, 124.7, 125.7, 126.3, 128.8, 128.9, 135.4, 135.8, 141.3, 148.5, 148.6, 149.7, 150.1, 150.4 ppm (N*C*Me, N*C*CH$_2$, 2,6-*i*Pr$_2$*C*$_6$H$_3$); ^{29}Si{^{1}H} NMR (79.49 MHz, [D$_8$]THF, 25 °C): $\delta=-70$ (s, 1Si; N$_3$*Si*O), 16 ppm (s, 1Si, *Si*Me$_3$); EI-MS: *m*/*z* (%): 614 (9) [*M*]$^+$, 599 (100), [*M*−Me]$^+$, 571 (65) [*M*−*i*Pr]$^+$; elemental analysis calcd (%) for C$_{32}$H$_{49}$N$_2$Si$_2$OBr: C 62.62, H 8.05, N 4.56; found: C 62.54, H 7.79, N 4.61.

Synthesis of 5: Me$_3$SiI (0.060 mL, $d=1.40$ g mL^{-1}, 0.42 mmol) was added to a suspension of **1** (0.25 g, 0.42 mmol) in toluene (10 mL) at room temperature. The suspension turned clear immediately. In half an hour compound **5** precipitated from the solution with yield of 0.30 g (0.38 mmol, 90 %). X-ray qualified single crystals were obtained as colorless plates from THF at 4 °C. M.p. 195 °C (decomposed); ^{1}H NMR (200.13 MHz, [D$_8$]THF, 25 °C): $\delta=-0.20$ (s, 9H; Si*Me*$_3$), 0.65 (d, ^{3}J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 0.72 (d, ^{3}J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.04 (d, ^{3}J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.11 (d, ^{3}J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.21 (d, ^{3}J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.25 (d, ^{3}J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.41 (d, ^{3}J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.45 (d, ^{3}J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.81 (s, 3H; NC*Me*), 2.44 (sept, ^{3}J(H,H) = 7.6 Hz, 1H; C*H*Me$_2$), 2.72 (sept, ^{3}J(H,H) = 7.6 Hz, 1H; C*H*Me$_2$), 3.26 (s, 1H; NCC*H*$_2$), 3.48 (s, 6H, dmap), 3.44–3.67 (m, 2H; C*H*Me$_2$), 4.07 (s, 1H; NCC*H*$_2$), 5.68 (s, 1H; γ-C*H*), 7.17–7.32 (m, 6H; 2,6-*i*Pr$_2$C$_6$*H*$_3$), 7.82 (br, 2H; dmap), 8.04 (br, 1H; dmap), 8.65 ppm (br, 1H; dmap); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_8$]THF, 25 °C): $\delta=2.14$ (Si*Me*$_3$), 22.2 (NC*C*H$_3$), 24.3, 24.4, 25.7, 26.1, 26.2, 26.4, 29.6, 29.7, 29.8 (CH*Me*$_2$, *C*HMe$_2$), 41.8 (dmap), 91.5 (NC*C*H$_2$), 107.2 (γ-*C*), 108.3 (dmap), 125.0, 125.2, 125.8, 126.3, 129.1, 129.2, 134.8, 135.3, 144.3, 148.0, 148.5, 149.1, 149.6, 149.7, 158.1, 174.7 ppm (N*C*Me, N*C*CH$_2$, dmap, 2,6-*i*Pr$_2$*C*$_6$H$_3$); ^{29}Si{^{1}H} NMR (79.49 MHz, [D$_8$]THF, 25 °C): $\delta=-75$ ppm (s, 1Si; N$_3$*Si*O), 18 ppm (s, 1Si; *Si*Me$_3$); HR-ESI: *m*/*z* calcd: 655.42219 [*M*−I]$^+$; found: 655.42316; elemental analysis calcd (%) for C$_{39}$H$_{59}$N$_4$Si$_2$OI: C 59.83, H 7.59, N 7.16; found: C 59.86, H 7.48, N 7.09.

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