An NHC-Stabilized Silicon Analogue of Acylium Ion: Synthesis, Structure, Reactivity, and Theoretical Studies

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S *Supporting Information*

ABSTRACT: The silicon analogues of an acylium ion, namely, sila-acylium ions **2a** and **2b** $[RSi(O)(NHC)_2]Cl$ stabilized by two *N*-heterocyclic carbenes (NHC = 1,3,4,5-tetramethylimidazol-2-ylidene), and having chloride as a countercation were successfully synthesized by the reduction of CO_2 using the donor stabilized silyliumylidene cations **1a** and **1b** $[RSi(NHC)_2]Cl$ (**1a**, **2a**; R = *m*-Ter = 2,6-$Mes_2C_6H_3$, Mes = 2,4,6-$Me_3C_6H_2$ 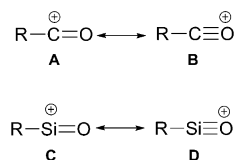and **1b**, **2b**; R = Tipp = 2,4,6-$iPr_3C_6H_2$). Structurally, compound **2a** features a four coordinate silicon center together with a double bond between silicon and oxygen atoms. The reaction of sila-acylium ions **2a** and **2b** with water afforded different products which depend on the bulkiness of aryl substituents. Although the exposure of **2a** to H_2O afforded a stable silicon analogue of carboxylate anion as a dimer form, $[m\text{-}TerSi(O)O]_2^{2-}\cdot2[NHC\text{–}H]^+$ (**3**), the same reaction with the less bulkier triisopropylphenyl substituted sila-acylium ion **2b** afforded cyclotetrasiloxanediol dianion $[\{TippSi(O)\}_4\{(O)OH\}_2]^{2-}\cdot2[NHC\text{–}H]^+$ (**4**). Metric and DFT (Density Functional Theory) evidence support that **2a** and **2b** possess strong Si=O double bond character, while **3** and **4** contain more ionic terminal Si–O bonds. Mechanistic details of the formation of different $(SiO)_n$ (n = 2, 3, 4) core rings were explored using DFT to explain the experimentally characterized products and a proposed stable intermediate was identified with mass spectrometry.
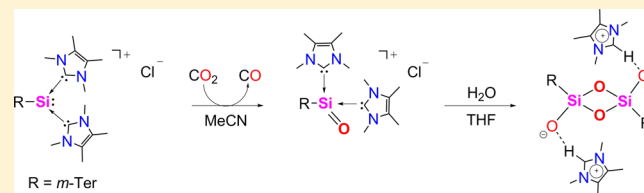
INTRODUCTION

A carbonyl (C=O) group is the core structure of several functionalities in organic chemistry including aldehydes, ketones, carboxylic acids, esters, amides, etc. The chemical transformations at the carbonyl backbone or at the neighboring functional groups by the virtue of the carbonyl group form the very basis of a bulk of organic reactivity.[1] A typical example is the generation of acylium ion $[(RCO)^+, \textbf{A}, \textbf{B}, \text{Chart 1}]^2$ in

Chart 1. Resonance Structures of an Acylium Ion (A, B) and Their Proposed Silicon Analogues (C, D) (R = Alkyl, Aryl)

$$R\text{–}\overset{\oplus}{C}\text{=}O \longleftrightarrow R\text{–}C\text{≡}\overset{\oplus}{O}$$
$$\textbf{A} \qquad\qquad \textbf{B}$$

$$R\text{–}\overset{\oplus}{Si}\text{=}O \longleftrightarrow R\text{–}Si\text{≡}\overset{\oplus}{O}$$
$$\textbf{C} \qquad\qquad \textbf{D}$$

Friedel–Crafts acylation reaction of acyl halides by a Lewis acid catalyst. Stable salts of acylium ion have been isolated by dehalogenation of acyl halides by a variety of Lewis acids.[3] An acylium ion could be represented by two resonance forms (**A** and **B**, Chart 1) with resonance structure type **B** as the most appropriate form.[2a] A silicon analogue of an acylium ion as well as its possible precursor (for example a sila-acyl halide) however could not be isolated and are still considered to be elusive. It is because, the pronounced polarity of the Si–O

bond along with weaker p_π–p_π interactions make such silacarbonyl compounds prone to polymerization and therefore hard to isolate in molecular state as a stable compound.

Although the silacarbonyl chemistry did not see much development even decades after the original work of Kipping,[4] a revival of interest in silacarbonyl compounds was observed owing to more promising, low valent silicon precursors.[5] As a result, the field has indeed seen tremendous development in recent times.[6–13]

In fact, the isolation of compounds with Si=O functionality has been achieved either through Lewis base coordination to silicon or through the combination of Lewis acid/base, so-called, donor–acceptor stabilization (Chart 2). With the help of donor–acceptor stabilization effect, crucial silacarbonyl based functionalities such as silicon acid anhydride (**I**),[6] silaformyl chloride(**II**),[7] sila-aldehyde derivative (**III**),[8] as well as donor–acceptor stabilized silanones[9] have been successfully isolated. The same methodology has been utilized toward the isolation of donor–acceptor stabilized silacarboxylic acids (**IV**[10] and **V**[11]). Apart from these donor–acceptor stabilized compounds, the donor stabilized silanones (for example donor-substituted sila-ureas, **VI**)[12] is a flourishing class of silacarbonyl compounds.[13] Very recently, the synthesis and isolation of a cationic metallosilanone complex (**VII**, Chart 2) bearing a

Chart 2. Selected Examples of Compounds Possessing Silacarbonyl Based Functional Groups[a]
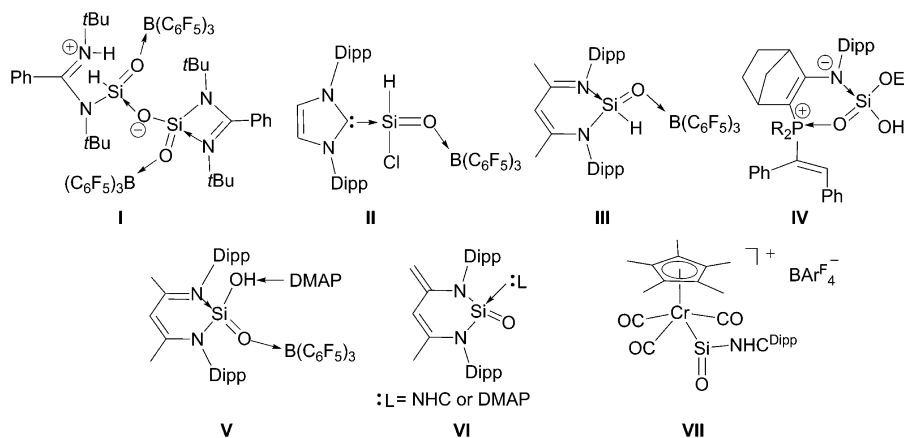
[a]Dipp = 2,6-iPr$_2$C$_6$H$_3$, NHC^{Dipp} = 1,3-bis(2,6-iPr$_2$C$_6$H$_3$)imidazolin-2-ylidene.

Scheme 1. Synthesis of NHC-Stabilized Sila-Acylium Ions 2a and 2b and Their Possible Resonance Structures (1a, 2a; R = m-Ter and 1b, 2b; R = Tipp)
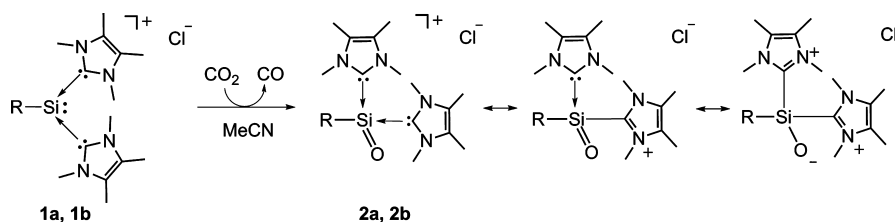
three-coordinate silicon atom stabilized by a bulky NHC and a chromium fragment in its coordination sphere has also been reported.[14]

Contrary to the generation and isolation of an acylium ion, a silicon analogue of acylium ion (RSiO)$^+$ (**C**, **D**, Chart 1) is elusive and investigated only in Mass Spectrometry as well as theoretical calculations.[15] Herein we report the synthesis, isolation and reactivity investigation of the first aryl-substituted sila-acylium ions **2a** and **2b** stabilized by two *N*-heterocyclic carbenes (NHCs). Sila-acylium ions **2a** and **2b** could be obtained by the reduction of carbon dioxide with NHC-stabilized silyliumylidene ions **1a** and **1b** (Scheme 1). The hydration of **2a** afforded the silanolate dimer dianion **3**, whereas the hydration of **2b** led to the isolation of cyclotetrasiloxane dianion **4**. The molecular structures of compounds **2a**, **3**, and **4** have been characterized by X-ray diffraction analysis. The reaction mechanisms for the formation of **2a**, **2b**, **3** and **4** have also been elucidated by DFT calculations.

■ RESULTS AND DISCUSSION

Synthesis and Characterization. *N*-Heterocyclic carbenes have proved to be effective in stabilizing reactive low valent silicon compounds including silylenes,[16] a bis(silylene),[17] a disilyne complex[18] and even a disilicon(0) compound.[17] Recently, the strategy of using two *N*-heterocyclic carbenes or a bis-carbene chelate ligand coordinated to silicon center led to the isolation of silicon(0) species, the "silylones".[19] Inspired by this methodology, we have recently reported the direct access to the NHC-stabilized silyliumylidene cations **1a** and **1b** [RSi(NHC)$_2$]Cl (R = m-Ter; **1a** and R = Tipp; **1b**) from Si(IV) precursor (dichlorosilane) and demonstrated the unusual reactivity with phenylacetylene.[20] Silyliumylidene cations can be considered as an excellent precursor for novel

organosilicon compounds.[21] However, reactivity studies of these species with organic small molecules such as carbon dioxide is yet to be investigated.[22] Therefore, we embarked on the reactivity of NHC-stabilized silyliumylidene ions **1a** and **1b** with carbon dioxide which afforded the formation of NHC-stabilized sila-acylium ions **2a** and **2b**.

The exposure of **1a** to gaseous CO$_2$ in acetonitrile at room temperature led to an immediate change in color from yellow-orange to a light brown solution with CO evolution. Removal of solvent and washing with dry THF leads to a white product which upon dissolving in acetonitrile and storing at −30 °C leads to the colorless block shaped crystals of NHC-stabilized sila-acylium ion **2a** (Scheme 1). The air and moisture sensitive crystals of compound **2a** are thermally stable (Mp = 216 °C) in the solid state. Compound **2a** shows good solubility in polar solvents such as acetonitrile and dichloromethane and shows negligible solubility in hydrocarbon as well as ethereal solvents.

In a parallel reaction, the treatment of CO$_2$ with a solution of **1b** in acetonitrile at room temperature led to discoloration of the solution with subsequent precipitation. In this case the only characterizable product in the NMR spectroscopy was the imidazolium chloride. However, when CO$_2$ was condensed in a sealed NMR tube containing frozen solution of **1b** in deuterated acetonitrile, a clean formation of the sila-acylium ion **2b** was observed when the temperature was maintained below −30 °C (Scheme 1). Compound **2b** is kinetically labile and presumably undergoes polymerization even at subzero temperatures producing amorphous precipitates insoluble in nonpolar as well as polar solvents.

The ^{1}H NMR spectrum of **2a** displays one set of signals for the m-terphenyl group. Two broad shifts for N-*Me* protons (δ = 3.06 and 3.96 ppm) were observed for **2a** at 298 K, which are transformed to sharp signals at 253 K. The ^{1}H NMR spectrum

of **2b** also displays one set of signals for the Tipp group. In contrast to **2a**, a single broad shift for N-*Me* protons (δ = 3.67 ppm) for the two coordinated NHCs was observed at 253 K. In the ^{29}Si NMR spectrum of **2a**, a sharp signal as a singlet is observed at −62.07 ppm, whereas the ^{29}Si NMR spectrum of **2b** displays a singlet at δ = −60.36 ppm. The calculated value of ^{29}Si NMR resonances for **2a** and **2b** [δ = −61.17 and −62.28 ppm, respectively, at B97-D/6-31G(2d,p) level of theory] are in good agreement with these experimental values. These experimental ^{29}Si NMR shifts are also comparable with those of the reported four-coordinate silanones (δ = −14 to −77.1 ppm)[9,12,13a] and considerably upfield shifted compared to the three-coordinate metallosilanone cation[14a] (**VII**, Chart 2, δ = 169.6 ppm).

The IR spectrum of **2a** in the solid state displays a strong Si≡O absorption band at 1098 cm^{-1}. The calculated Si≡O stretching mode at 1086 cm^{-1} fits very well to the experimentally observed band at 1098 cm^{-1}. We also performed ^{18}O isotope labeling experiments which showed that only one band at 1098 cm^{-1} shifted in this region to 1065 cm^{-1}. This change in the wavenumber is similar to that reported by Driess et al.[8,12d] and confirms that the Si≡O absorption band is at 1098 cm^{-1} in **2a**. Although this band is observed at lower wave numbers than the typical range of Si≡O stretching vibrations ($\tilde{v}$ = 1150−1300 cm^{-1}),[23] it is definitely beyond the Si−O single bond absorption bands. This somewhat lower wavenumber (1098 cm^{-1}) may be the consequence of the complicated electronic structure (vide supra) which exhibits single and double bond characters as well and is already manifested in the somewhat longer Si≡O bond length.

The mass spectrometric data for **2a** gave an insight into the nature of **2a** toward hydration and subsequent dimerization. The ESI-MS spectrum of **2a** (performed in the presence of moisture) displays the molecular ion fragment of the cation **2a** [*m*-TerSi(O)(NHC)$_2$]$^+$ (*m/z* = 605) as the base peak and along with it three important fragments. These include a silanoic acid monomer [{*m*-TerSi(O)OH}(NHC)]H$^+$ (*m/z* = 499), hydrated form of **2a** (*m/z* = 623) (the formation of these intermediates is supported by the DFT calculations, vide infra), and the dimer **3** [{*m*-TerSi(O)O}$_2${NHC−H}$_2$]H$^+$ (**3**) (*m/z* = 997). The ESI-MS spectrum of **2b** displays a silaanhydride fragment [(TippSiO)$_2$O(NHC)]H$^+$ (*m/z* = 635) as the base peak along with the molecular ion fragment for the cationic part of **2b** (*m/z* = 495).

Compound **2a** crystallizes in triclinic space group $P\bar{1}$ as separated ion pairs (the Si−Cl distance is 6.21 Å). Molecular structure of **2a** is depicted in Figure 1. The silicon center is 4-fold coordinated to the two N-heterocyclic carbenes and *ipso* carbon (C1) of the *m*-terphenyl group and the oxygen atom in a distorted tetrahedral fashion. The Si1−O1 bond length (1.548(2) Å) of **2a** falls well in the range of reported tetracoordinate silanones.[12,13a,24] The Si−C bond distances in **2a** for the coordinated carbenes [1.938(3) and 1.9547(3) Å] are slightly shorter than the precursor **1a** [1.948(19) and 1.967(19) Å].[20]

We carried out DFT calculations employing B97-D/6-31G(d) level of theory to elucidate the electronic structure of **2a** and **2b**, especially the nature of the silicon−oxygen bond. Calculated metric parameters of **2a** and **2b** are in good agreement with the experimentally observed data (Table 1), although it shows slightly longer Si−O bond lengths: 1.573 and 1.572 Å, respectively. According to NBO charge, Si atom of
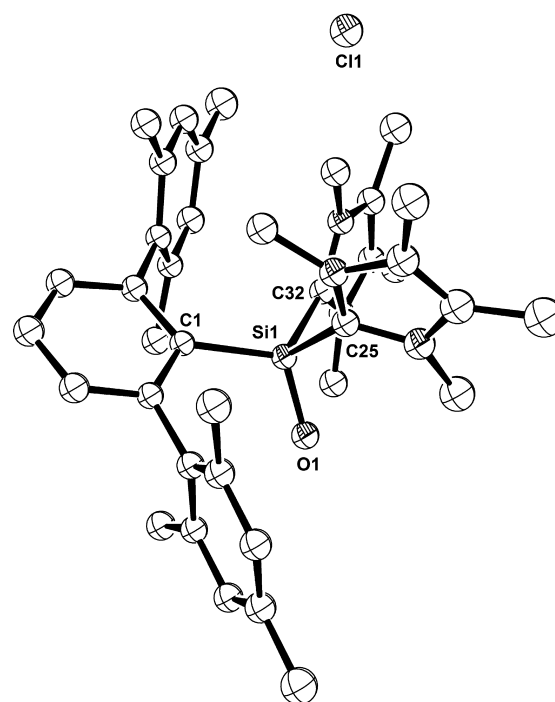

Figure 1. Molecular structure of **2a**. Thermal ellipsoids represent 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Si1−O1 1.548(2), Si1−C1 1.901(3), Si1−C32 1.954(3), Si1−C25 1.938(3), O1−Si1−C25 111.71(12), O1 −Si1−C32 106.95(12), O1−Si1−C1 115.18(13), C1−Si1−C32 116.23(12), C1−Si1−C25 107.36(13), C32−Si1−C25 98.18(13).

Table 1. Calculated Si−O Bond Lengths, NBO Charges, Mayer Bond Orders, and Natural Resonance Theory Analysis of 2a and 2b

	Si−O bond length [Å]	Si charge	O charge	MBO	NRT Si−O bond
2a	1.573(calc.) 1.548 (exp.)	+1.89	−1.17	1.58	Si≡O: 2.1% Si=O: 56.7% Si−O: 41.2%
2b	1.572	+1.91	−1.15	1.63	Si≡O: 3.8% Si=O: 58.1% Si−O: 38.1%

these compounds bears a large positive net charge (+1.89 for **2a**, +1.91 for **2b**), while the O atom has negative charge (−1.17 for **2a**, −1.15 for **2b**). Mayer Bond Orders (MBO) indicate significant multiple bond character of the Si≡O bond (1.58 for **2a** and 1.63 for **2b**). In addition, we calculated Natural Resonance Theory (NRT) for related compounds to gain deeper insight into the nature of Si−O bond. NRT suggests a very complicated picture of **2a** and **2b** where the main bonding motif is a Si≡O double bond (56.1% and 58.8%, respectively) whereas the Si−O single bond has also considerable weight (41.2% and 38.1%, respectively). Interestingly, even Si−O triple bond nature has non-negligible role in the description of the **2a** and **2b** (2.1% and 3.8%, respectively). The HOMO of **2a** and **2b** are depicted in Figure 2 showing considerable extension of the Si−O π-orbital toward the silicon center supporting a double bond between silicon and oxygen atoms. Along with MBO and NRT analysis, these molecular orbitals may also suggest the multiple bond character of the Si−O bond which could be best described as Si≡O double bond. We also
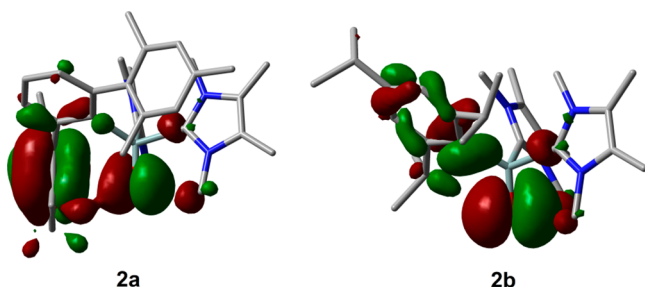
Figure 2. HOMO of **2a** (−7.14 eV, left) and **2b** (−7.30 eV, right) (isovalue: 0.02).

calculated model compounds [Me−SiO]⁺, Me₂Si=O, and Me₃Si−O⁻ (see details for Supporting Information) which we used for comparison with **2a** and **2b** as reference values of triple, double and single Si−O bonds, respectively, and it also enhanced our conclusion about multiple bond character.

Reactivity Studies. The reaction of **2a** and **2b** with 1 equiv of H_2O afforded the cyclodisiloxane dianion **3** from **2a** (Scheme 2) and the cyclotetrasiloxanediol dianion **4** from **2b**

Scheme 2. Synthesis of 3 (R = *m*-Ter)
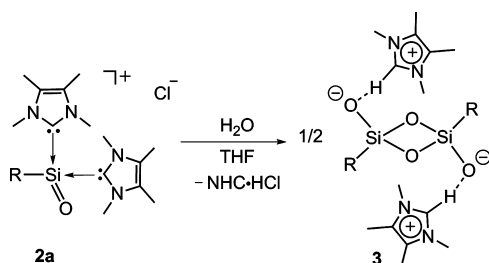
Scheme 3. Synthesis of 4 (R = Tipp)
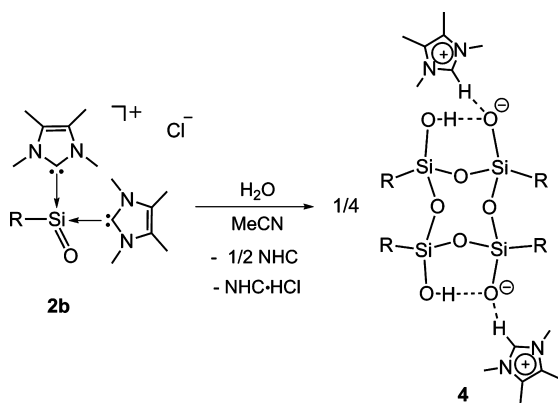
(Scheme 3), both having imidazolium ions as countercation. These results are in contrary to the hydration reaction of the cationic metallosilanone complex (**VII**, Chart 2) which led to the formation of a cationic dihydroxysilyl complex.[14a]

Direct exposure of one equivalent of H_2O toward **2a** in acetonitrile led to Si−C(*m*-Ter) bond cleavage. However, upon the addition of 1 equiv of H_2O solution in THF to a suspension of **2a** in dry THF led to formation of **3** in 5% yield (Scheme 2). The ¹H NMR of the crude mixture displayed one set of broad shifts for N-*Me* and C-*Me* protons. The acidic C-*H* group of the imidazolium countercation is observed as a broad singlet at 9.61

ppm. The compound **3** is insoluble in hydrocarbon as well as ethereal solvents and shows negligible solubility in more polar solvents once it crystallizes out from the solution. We therefore performed the solid state NMR measurement of compound **3** which displayed one signal at $\delta = -58.20$ ppm in ²⁹Si MAS NMR spectrum. This value is in good agreement with the calculated chemical shifts of $\delta = -60.11$ and -60.17 ppm for **3**. We were also able to improve the yield of **3** by charging a reaction flask containing **2a** with wet, degassed THF, which results in the initial formation of a clear solution followed by precipitation of **3** in 72% yield.

In the ESI-MS spectrum, the dianion core fragment [*m*-TerSi(O)O]₂ was observed in the anionic mode ($m/z = 747$) by performing Collision Induced Dissociation (CID-ESI-MS) of the hydrated dianion core fragment {$m/z = 747 + 18$ (H_2O) = 765}. An interesting structural feature of **3** is its behavior as a neutral species since the whole molecule [*m*-TerSi(O)O-(NHC−H]₂ acts as an individual cationic fragment in cationic mode of ESI-MS ($m/z = 997$).[25a] This is because the imidazolium cations in ionic liquids display high degree of directionality and tend to form intimate ion pairs with their counteranions primarily through hydrogen bonding thus providing additional stabilization.[25] The generation of imidazolium ion pairs during this reaction plays a crucial role in stabilizing the dianionic silanolate core of **3**; the calculated stabilization energy of the ion-pair formation is 45.7 kcal/mol at B97-D/cc-pVTZ//B97-D/6-31G(d) level of theory.

Compound **3** crystallizes in monoclinic space group $P2_1/n$ and molecular structure of **3** is depicted in Figure 3. The central
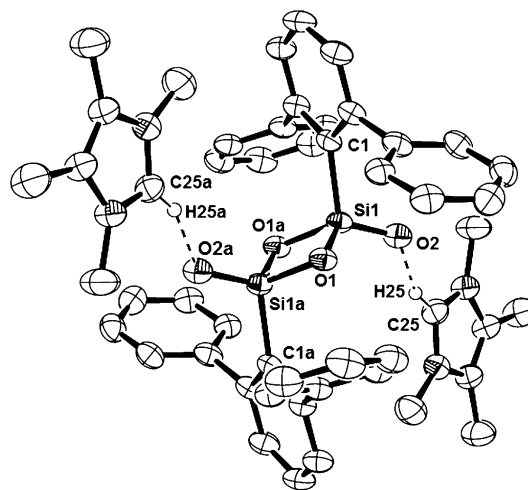
Figure 3. Molecular structure of **3**. Thermal ellipsoids represent 50% probability level. Solvent molecules, methyl groups at the mesityl substituents and hydrogen atoms except for that on C25 and C25a are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Si1−O1 1.687(2), Si1−O1a 1.676(2), Si1−O2 1.556(3), Si1−C1 1.895(3), O2···H25 1.864, C1−Si1−O2 113.09(13), C1−Si1−O1a 107.18(12), C1−Si1−O1 107.34(12), O1−Si1−O1a 88.49 (10), O1−Si1−O2 119.18(12), O1a−Si1−O2 118.64(12).

disilanolate unit $(SiO_2)_2$ is stabilized by bulky *m*-terphenyl groups. The compound **3** can be described as a dimeric silanolate with a central cyclodisiloxane (Si_2O_2) four-membered ring with tetracoordinate silicon atoms and two imidazolium ions as counter cations. The Si_2O_2 core ring is planar with the terminal oxygen atoms in *trans* position to each other. The geometry around the silicon atoms is distorted tetrahedral with

the smallest bond angle of 88.50° at the O1−Si1−O1a. The terminal oxygen atoms at the silicon centers are interacting with the protons of the two imidazolium moieties (O⋯H bond distance 1.864 Å). This pattern of hydrogen bonding is comparable with the sila-hemiaminal and silanoic amide tautomers interacting with each other through Si−O−H⋯O−Si hydrogen bonding where the O⋯H bond distance between the coordinated tautomers is 1.721 Å.[12b] Interestingly, the terminal Si−O bonds lengths (1.556 (1) Å) in **3** are considerably shorter than the endocyclic Si−O bonds in the disiloxane ring (1.676(1)-1.687(1) Å). This structural observation indicates a significant double bond character of these terminal Si−O bonds in **3** compared with the endocyclic Si−O bonds. These terminal bonds are shorter than the Si=O terminal bond in the silanoic silyl ester (1.579(3) Å) reported by Driess and co-workers.[26] Moreover, the calculated MBO values for endocyclic and exocyclic Si−O bonds (0.85 and 1.48) also support partial double bond character for the exocyclic Si−O bonds. Comparison with the Me_3Si-O^- model compound (MBO = 1.17), the terminal Si−O bond in **3** may possess partial double bond character as well as ionic character.

On the other hand, the hydrolysis of **2b** led to the formation of tetrasiloxane dianion **4** with terminal oxide and hydroxide groups (Scheme 3). Since **2b** is kinetically labile in solution because of less sterically hindering Tipp group and it is prone to self-oligomerization which occurs even at −30 °C. Therefore, the hydrolysis of **2b** was performed by in situ addition of one equivalent of degassed water with concomitant exchange of the atmosphere of **1b** with CO_2. This led to quantitative crystallization of **4** from the acetonitrile solution. The low solubility of **4** even in polar solvents such as acetonitrile and dichloromethane could be attributed to the higher degree of agglomeration as well as the ionic nature of **4** (Scheme 3). ^1H NMR displays a single set of signals for the Tipp groups. The analytically pure compound **4** led to the ill-defined ^1H NMR spectrum in CD_3CN after half an hour. The low solubility of **4** hampered the measurement of ^{13}C and ^{29}Si NMR in solution. The ^{29}Si MAS NMR of **4** displays four signals at $\delta = -66.73$ ($Si-O^-$), −67.96 ($Si-O^-$), −71.16 ($Si-OH$) and −72.43 ppm ($Si-OH$) bonds, respectively. The GIAO calculation of **3** [GIAO/B97-D/cc-pVTZ//B97-D/6-31G(d)] is in good agreement with the experimental values and confirmed the assignment (−67.18, −68.45, −71.85, and −73.01 ppm). The molecular ion peak is observed in the cationic mode of the ESI-MS spectrum (m/z = 1306) whereas the central dianion core $[\{TippSi(O)\}_4\{(O)OH\}_2]$ without the imidazolium counter cations is observed in the anionic mode (m/z = 1056).

Compound **4** crystallizes in monoclinic space group $P2_1/c$ and molecular structure of **4** is shown in Figure 4. The central core of **4** is 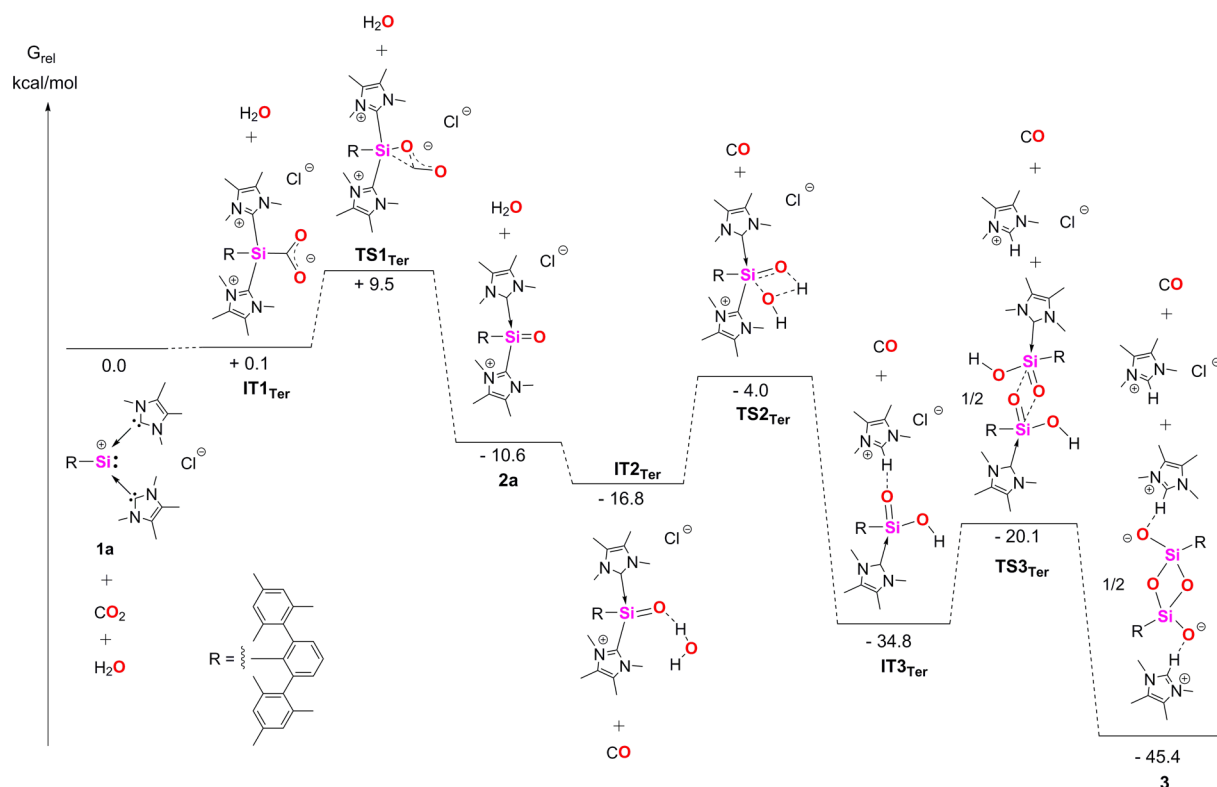composed of Si_4O_4 cyclotetrasiloxane core unit as an eight-membered ring structure with silicon−oxygen bond lengths varying between 1.62 and 1.65 Å. These bond lengths are much shorter than bridging Si−O bond lengths in **3** (1.68(4)−1.69(4) Å). Moreover, the terminal Si−O bond lengths represent two sets of bonds for the four terminal Si−O bonds. The longer Si−O bonds (1.60(3) and 1.61(3) Å) correspond to the Si−OH bonds of silanol function. Interestingly, the shorter Si−O bonds (1.58(3) Å) have the slightly larger MBO values (1.15 and 1.16) than that of endocyclic bonds (0.80−0.82). However, model compound Me_3Si-O^- also has high bond order of 1.17 (Table 1); therefore, compound **4** possesses rather ionic terminal Si−O⁻

Figure 4. Molecular structure of **4**. Hydrogen atoms (except that on O5, O6, C61 and C68) and isopropyl groups at the phenyl substituents are omitted for clarity. Thermal ellipsoids represent 50% probability level. Selected bond lengths [Å] and angles [deg]: Si1−O5 1.602(3), Si1−O1 1.626(3), Si1−O4 1.652(3), Si1−C1 1.889(4), Si3−O7 1.585(3), Si3−O3 1.630(3), Si3−O2 1.656(2), O7⋯H68A 1.961, O7⋯H5A 1.747, O8⋯H61A 1.995, O8⋯H6A 1.679, O5−Si1−O1 109.95(15), O5−Si1−O4 111.35(13), O1−Si1−O4 106.90(14), O5−Si1−C1 109.25(16), O1−Si1−C1 111.04(15), O4−Si1−C1 108.33(16), O6−Si2−O2 110.85(14).

character. The terminal oxygen atoms with silanolate character interact with the proton of the imidazolium counter cations (C−H⋯O bond distance 1.96 and 1.99 Å) as well as with the hydrogen atoms of the neighboring hydroxyl groups (O−H⋯O bond distance 1.68 and 1.75 Å). This intensive hydrogen bonding is probably the reason for the remarkable stability of **4** in the solid state when compared with similar systems.[27] Unlike **3**, the Si_4O_4 tetrasiloxane core ring is nonplanar and could be best described as the boat−boat conformation.

DFT Calculations on the Mechanism. DFT calculations were carried out at B97-D/cc-pVTZ(SMD = acetonitrile)//B97-D/6-31G* level of theory for the better understanding of the formation of **3** and **4** from NHC-stabilized silyliumylidene cations **1a** and **1b** via the sila-acylium ions **2a** and **2b**. This methodology has previously proved to provide good agreement with experiments involving silicon in special coordination modes[28] and even when applied to large systems.[29] The difference in the steric bulk of the precursors **2a** and **2b** lead to different products based on reaction kinetics. These investigations revealed the initial formation of the stable sila-acylium ion **2a** via the formation of silylcarboxylate ion $IT1_{Ter}$ that led to Si−C bond formation upon treatment with CO_2 which is known for NHCs (Figure 5).[30] This finding is consistent with the recent results that donor-stabilized low-valent silicon compounds can be stronger sigma donors than NHC.[28f] The next step is the evolution of CO (leading to the formation of **2a**) by simultaneous Si−O bond formation and Si−C(CO₂) bond cleavage with the associated energy of +9.5 kcal/mol ($TS1_{Ter}$). The hydration reaction of the sila-acylium ion **2a** toward the silanolate dimer is energetically a highly favored reaction. The coordination of water to **2a** ($IT2_{Ter}$) is followed by energetically favored intramolecular rearrangements involving **TS2-IT3-TS3**. The $TS3_{Ter}$ is followed by the proton

Figure 5. Results of DFT calculation at B97-D/cc-pVTZ(SMD = acetonitrile)//B97-D/6-31G* level of theory of the simplified mechanisms for the formation of **3**. For detailed mechanism, please see the Supporting Information, Figure S28).

abstraction by NHC leading to the imidazolium formation. This type of proton abstraction by NHC has already been reported by Cui and co-workers in the formation of anionic oxoboranes from borinic acids in the presence of NHCs.[31] The *m*-terphenyl substituted silanoic acid **IT3**$_{Ter}$ may still prove to be kinetically unstable in condensed phase and lead to dimerization with concomitant release of the imidazolium chloride. The eventual deprotonation caused by the coordinated NHC may afford the generation of the cyclodisiloxane dimer **3**. To support the mechanistic investigations on the formation of the silanolate dimer **3** from **1a**, we performed mass spectrometric analysis on **2a** in the presence of moisture. According to the calculations, the highly stable **IT3**$_{Ter}$ (−34.8 kcal/mol) was a likely candidate to be observed which we identified in the mass spectrum (*m/z*= 623) as a stable fragment (see Supporting Information).

The DFT calculations performed on the formation of **4** from **1b** suggested the formation of the sila-acylium ion **2b** as well as the dimeric silanolate with similar energy as for the formation of **3** (Supporting Information Figures S29 and S30). DFT calculations confirmed, based on reaction kinetics, that the difference in the steric bulk of the precursors **2a** and **2b** is the main driving force to lead to different products (**3** and **4**, respectively). For details see Supporting Information.

■ SUMMARY AND CONCLUSIONS

We report the first NHC-stabilized silicon analogue of an acylium ion, the four coordinate sila-acylium ions **2a** and **2b** with a bulky aryl (**2a**; terphenyl and **2b**; Tipp) group. The steric bulk of the aryl group in **2a** and **2b** proved to be of vital importance in the stability and reaction kinetics. Whereas **2b** was kinetically labile, **2a** was isolated as a stable compound in 71% yield. The crystal structure of **2a** features a tetracoordinate

silicon and a double bond between silicon and oxygen atoms. Molecular orbitals, MBO, and NRT analysis of **2a** and **2b** indicate significant double bond character for the Si≡O bond. The calculations on model compounds [Me−SiO]$^+$, Me$_2$Si≡ O, and Me$_3$Si−O$^−$ also support multiple bond character between Si≡O bond of **2a** and **2b**. Additionally, a comparison of model compounds with **2a** and **2b** elucidated a significant role of coordinated NHCs as well as the steric effect of the aryl group for the Si−O bond nature. The reactivity of **2a** and **2b** with water had different reaction kinetics based on the steric bulk of the respective aryl group. Thus, the cyclodisiloxane dianion **3** was obtained by the hydration of **2a**, whereas the tetracyclodisiloxane dianion **4** was obtained from the reaction of sila-acylium ion **2b** with water. These reaction pathways were also supported by the DFT calculations. Moreover, MBO results suggest that beside partial double bond character, the terminal Si−O bonds in **3** and **4** primarily possess ionic Si−O character. Our work introduces a simple strategy for isolating the elusive species, silicon analogue of an acylium ion and has allowed for a better understanding of nature of silicon oxygen multiple bonds. Also, we believe that this paper highlights the potential of developing reactivity of the sila-acylium ion for brand new applications toward organic and inorganic synthesis.

■ EXPERIMENTAL SECTION

General Procedures. All experiments and manipulations were carried out under dry oxygen-free atmosphere using standard Schlenk techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. Glass junctions were coated with the PTFE-based grease Merkel Triboflon III. Solvents were dried using an M Braun purification system and stored over 3 Å molecular sieves and degassed by freeze−pump−thaw technique prior to use. The deuterated solvents were degassed and stored over 3 Å molecular

sieves. The ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra were recorded on Bruker Avance II 200 and 400 MHz Spectrometers. ^{1}H chemical shifts were referenced to the residual protons of CD$_{3}$CN at 1.94 ppm and C$_{6}$D$_{6}$ at 7.16 ppm. ^{13}C chemical shifts were referenced to the carbon atom of CD$_{3}$CN and C$_{6}$D$_{6}$ at 128.06 at 118.26 ppm, respectively. The ^{29}Si{^{1}H} NMR spectra were referenced to tetramethylsilane as an external standard. Abbreviations: s = singlet, br = broadened, d = doublet, t = triplet. Solid state NMR was measured on Bruker Avance 400 Solid-State NMR with the measurement rotation frequency of 10000 Hz. Melting points were determined on an electronic "Melting point tester" device from BSGT company and are uncorrected. High resolution ESI mass spectra were recorded on an Orbitrap LTQ XL of Thermo Scientific mass spectrometer. IR spectra for **2a** were recorded on a PerkinElmer Spectrum 100 FT-IR Spectrometer. Reagents purchased from commercial sources were used as received if not stated otherwise. NHC-stabilized silicon(II) cations **1a** and **1b** were synthesized according to literature procedures.[20]

Data for the single crystal structure determination of **2a**, **3** and **4** were collected on an Agilent SuperNova diffractometer, equipped with a CCD area Atlas detector and a mirror monochromator utilizing Cu Kα radiation (λ = 1.5418 Å). The individual crystals were mounted on a glass capillary in per-fluorinated oil and measured in a cold N$_{2}$ flow.

The crystal structures were solved by Direct Methods and refined on F^{2} using full-matrix least-squares with SHELXL-97 (G. M. Sheldrick, SHELXL-97, *Program for refinement of crystal structures*, University of Göttingen, Germany, **1997**). The positions of the H atoms of the carbon atoms were calculated by standard methods.

CCDC Numbers. **2a** (1045019), **3** (993049), **4** (1019175).

Preparation of [*m*-TerSi(O)(NHC)$_{2}$]Cl, 2a. A total of 200 mg of **1a** was dissolved in 5 mL acetonitrile. Bubbling a stream of CO$_{2}$ through the acetonitrile solution of **1a** results in an immediate change in color from yellow-orange to a light brown solution with CO evolution. After 2 min exposure, the solution was stirred for another 10 min. Afterward the solvent was removed under reduced pressure. The product was washed with dried THF and redissolved in 3 mL acetonitrile. This led to a colorless solution of **2a** in acetonitrile. Placing the solution at −30 °C afforded block shaped crystals of **2a** in 71% yield. The compound **2a** shows good solubility in dichloromethane and acetonitrile; however, it is insoluble in hydrocarbon as well as ethereal solvents. Mp 216–218 °C. ^{1}H NMR δ (200.13 MHz, 298 K, CD$_{3}$CN) = 2.01(s, 12H, 4xC-*Me*, NHC), 2.05 (s, 12H, 2xC^{2,6}-*Me*, Mes), 2.11 (s, 6H, 2xC^{4}-*Me*, Mes), 3.06, 3.96 (br, s, 12H, 4xN-*Me*, NHC), 6.67 (s, 4H, 2xC^{3,5}-*H*, Mes), 7.04 (d, ^{3}*J*H−H = 7.6 Hz, 2H, C^{3,5}-*H*, C$_{6}$H$_{3}$), 7.57 (t, ^{3}*J*H−H = 7.6 Hz, 1H, C^{4}-*H*, C$_{6}$H$_{3}$). ^{1}H NMR δ (400.13 MHz, 253 K, CD$_{3}$CN) = 1.98, 2.07(s, 12H, 4xC-*Me*, NHC), 2.02, 2.06 (s, 12H, 4xC-*Me*, NHC), 2.04 (s, 6H, 2xC^{4}-*Me*, Mes), 2.92, 3.97 (s, 12H, 4xN-*Me*, NHC), 6.58, 6.74 (s, 4H, 2xC^{3,5}-*H*, Mes), 7.01 (d, ^{3}*J*H−H = 7.6 Hz, 2H, C^{3,5}-*H*, C$_{6}$H$_{3}$), 7.57 (t, ^{3}*J*H−H = 7.6 Hz, 1H, C^{4}-*H*, C$_{6}$H$_{3}$). ^{13}C NMR δ (100.61 MHz, 298 K, CD$_{3}$CN) = 8.95 (s, 2xC^{4,5}-*Me*, NHC), 20.88 (s, C^{4}-*Me*, Mes), 22.16 (s, br, C^{2,6}-*Me*, Mes), 34.93 (s, br, 4xN-*Me*, NHC), 128.07 (s, 2xC^{4,5}-Me, NHC), 129.17 (2xC^{4}-Mes), 129.78 (s, br, 2xC^{3,5}-H, Mes), 131.38 (s, C^{3,5}-H, C$_{6}$H$_{3}$), 131.44 (s, C^{4}-H, C$_{6}$H$_{3}$), 137.34 (s, Si-C, C$_{6}$H$_{3}$), 139.72 (s, 2xC^{1}-Mes), 148.82 (s, 2xC^{2,6}-C$_{6}$H$_{3}$), 148.94 (s, 2xSi-C, NHC). ^{29}Si NMR δ (79.49 MHz, 298 K, CD$_{3}$CN) = −62.07. ESI-MS (*m/z*) = [*m*-TerSi(O)-(NHC)$_{2}$] (M)$^{+}$ 605.37.

Preparation of [TippSi(O)(NHC)$_{2}$]Cl, 2b. A total of 40 mg of **1b** was dissolved in deuterated acetonitrile and frozen in liquid nitrogen. The NMR tube was evacuated, CO$_{2}$ was condensed in the NMR tube, and the tube was sealed afterward. The NMR tube was placed in a −30 °C freezer for 4 h for the thawing of solution. Afterward the NMR tube was subjected to NMR characterization at −20 °C. Compound **2b** is kinetically unstable even at sub zero temperature and undergo polymerization which is observed even at −30 °C. By the end of 1 week most of the dissolved **2b** had already polymerized to give insoluble white precipitates. ^{1}H NMR δ (400.13 MHz, 253 K, CD$_{3}$CN) = 0.99 (d, ^{3}*J*H−H = 7.0 Hz, 12H, C^{2,6}- CH*Me*$_{2}$, *i*Pr), 1.19 (d, ^{3}*J*H−H = 7.0 Hz, 6H, C^{4}-CH*Me*$_{2}$, *i*Pr), 2.22 (s, 12H, 4xC-*Me*, NHC), 2.86 (sept, ^{3}*J*H−H = 7.0 Hz, 1H, C^{4}−CH*Me*$_{2}$, *i*Pr), 3.26 (sept, ^{3}*J*H−H = 7.0 Hz, 2H, C^{2,6}−CH*Me*$_{2}$, *i*Pr), 3.67 (br, s, 12H, 4xN-*Me*, NHC),

7.13 (s, 2H, C^{3,5}-*H*, C$_{6}$H$_{2}$). ^{13}C NMR δ (100.61 MHz, 253 K, CD$_{3}$CN) = 8.70 (s, 2xC^{4,5}-*Me*, NHC), 23.57 (s, C^{4}−CH*Me*$_{2}$, *i*Pr), 24.55 (s, C^{2,6}-CH*Me*$_{2}$, *i*Pr), 33.58 (C^{2,6}-CH*Me*$_{2}$, *i*Pr), 33.91 (s, br, 4xN-*Me*, NHC), 34.56 (C^{4}-CH*Me*$_{2}$, *i*Pr), 122.84 (s, C^{3,5}-H, C$_{6}$H$_{2}$), 125.24 (Si-C, C$_{6}$H$_{2}$), 130.32 (s, 2xC^{4,5}-Me, NHC), 149.50 (s, 2xSi-C, NHC), 152.58 (C^{4}-C$_{6}$H$_{2}$), 156.62 (C^{2,6}-C$_{6}$H$_{2}$). ^{29}Si NMR δ (79.49 MHz, 253 K, C$_{6}$D$_{6}$) = −60.36. ESI-MS (*m/z*) = [TippSi(O)(NHC)$_{2}$] (M)$^{+}$ 495.35.

Preparation of [*m*-TerSi(O)O]$_{2}$$^{2−}$·2[NHC−H]$^{+}$, 3. *Procedure 1*. A suspension of **2a** (180 mg) in THF was frozen under liquid nitrogen, a solution of 1 equiv of water in THF was then added to the frozen solution of **2a** and the suspension was allowed to stir overnight at room temperature. Later on, the THF solution was filtered and the solvent was removed under reduced pressure. The crude mixture containing **3** was taken up in deuterated benzene which was helpful in the determination of the proton chemical shift of the imidazolium countercation. XRD quality crystals of **2a** were grown by dissolving the same crude mixture in acetonitrile by fractional crystallization. Standing at room temperature for 2 weeks led to XRD quality crystals of **3**. These colorless plate like crystals of **3** displayed negligible solubility in polar as well as non polar solvents. (Yield = 5%)

Procedure 2. Five milliliters of wet THF was added to a Schlenk flask containing 100 mg of **2a** and the suspension was stirred for a few minutes which turned to a clear solution and afterward gave white precipitates of **3**. The stirring was stopped after 10 min and the THF was separated from the white precipitates. The white precipitates were then washed with acetonitrile to give pure **3** in 72% yield. Mp = 136– 138 °C. ^{1}H NMR δ (200.13 MHz, 298 K, C$_{6}$D$_{6}$) = 1.63 (br, s, 12H, 4xC-*Me*, NHC−H), 2.06, 2.20, 2.27 (s, 3 × 12H, C^{2}-*Me*, Mes + C^{4}-*Me*, Mes + C^{6}-*Me*, Mes), 3.37 (br, s, 12H, 4xN-*Me*, NHC−H), 6.87 (s, 4H, 2xC^{3,5}-*H*, Mes), 6.97 (d, ^{3}*J*H−H = 7.6 Hz, 2H, C^{3,5}-*H*, C$_{6}$H$_{3}$), 7.26 (t, ^{3}*J*H−H = 7.6 Hz, 1H, C^{4}-*H*, C$_{6}$H$_{3}$), 9.61 (br, 1H, NHC−*H*). CPMAS NMR δ = −58.20 ppm. ESI-MS *m/z* = [{*m*-TerSi(O)O}$_{2}${ NHC− H}$_{2}$] (M + H)$^{+}$ 997.55, [{*m*-TerSi(O)O}{NHC−H}] (M + H)$^{+}$ 499.28, [*m*-TerSi(O)O]$_{2}$ (M + H)$^{-}$ 747.33.

Preparation of [{TippSi(O)}$_{4}${(O)OH}$_{2}$]$^{2−}$·2[NHC−H]$^{+}$, 4. A solution of **1b** (50 mg) in 0.3 mL deuterated acetonitrile was frozen in an NMR tube and 1 equiv of water dissolved in 0.3 mL deuterated acetonitrile is added to the frozen **1b**. The solvent was frozen completely and afterward the NMR tube was evacuated and CO$_{2}$ was condensed in the NMR tube and sealed afterward. The solvent was allowed to thaw at −30 °C and finally placed at room temperature for overnight leading to the formation of colorless rod shaped crystals of **4** in 65% yield. Mp = 204−206 °C. ^{1}H NMR δ (200.13 MHz, 298 K, CD$_{3}$CN) = 0.97 (d, ^{3}*J*H−H = 7.0 Hz, 48H, 4xC^{2,6}-CH*Me*$_{2}$, *i*Pr), 1.13 (d, ^{3}*J*H−H = 7.0 Hz, 24H, 4xC^{4}-CH*Me*$_{2}$, *i*Pr), 2.13 (s, 12H, 4xC-*Me*, NHC−H), 2.73, 4.63 (sept, ^{3}*J*H−H = 7.0 Hz, 4H, 4xC^{4}−CH*Me*$_{2}$, *i*Pr + sept, ^{3}*J*H−H = 7.0 Hz, 8H, 4xC^{2,6}−CH*Me*$_{2}$, *i*Pr), 3.62 (s, 12H, 4xN-*Me*, NHC−H), 6.85 (s, 8H, 4xC^{3,5}-*H*, C$_{6}$H$_{2}$). The imidazolium protons are apparently involved in rapid exchange with the deuterated solvent resulting into a shift too broad to be observed in the ^{1}H NMR. ^{29}Si{^{1}H} CPMAS NMR = −66.73, −67.96, −71.16, −72.43. ESI-MS (*m/z*) = [{TippSi(O)}$_{4}${(O)OH}$_{2}${NHC-H}$_{2}$] (M + 2H)$^{+}$ 1306.83. [{TippSi(O)}$_{4}${(O)OH}$_{2}$] (M + H)$^{-}$ 1055.61.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Details on X-ray crystal structure analyses, selected NMR and mass spectra of **2a**, **3** and **4** as well as additional data on the DFT calculations, NBO analyses, optimized structures, and more elaborate mechanistic schemes. 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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