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COMMUNICATION

Tris(dimethylamino)silylium ion: structure and reactivity of a dimeric silaguanidinium

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Although several strategies for the stabilization of silylium ions have been established, the "π-stabilization" by directly attached π-donor heteroatoms at silicon has not been developed yet. Hydride abstraction from $(Me_2N)_3SiH$ generates dicationic $[(Me_2N)_3Si^+]_2$ in solution and in the solid state – constituting the dimer of an elusive silaguanidinium ion. The compound can be synthesized on gram scale and is compatible with common organic solvents. However, it readily undergoes spontaneous electrophilic silylation of electron-rich aromatic compounds or initiates a catalytic hydro-defluorination reaction.

Silylium ions $[R_3Si^+]$ are tricoordinated, positively charged silicon species with enormous electrophilicity.[1] They may be stabilized by suitable external donors and form adducts like silylated oxonium,[2] nitrilium[3] or phosphonium[2c] ions. In less coordinating environments, they even attract weaker donors such as aromatic solvents,[4] weakly coordinating anions,[3b, 5] silanes[6] or silicon halides.[7] Silylium ions can be stabilized also by intramolecular donor coordination, as was demonstrated for nearby arene,[8] olefine,[9] C-F,[8b, 10] Si-H, Si-F or Si-C,[11] Fe(II),[12] chalcogen[13] or B-Cl[14] groups. As a third strategy, the thermodynamic stabilization by direct attachment of π-donors (π-stabilization) was suggested already in 1977.[15] Theoretical studies revealed significant impact for such donors and consistently identified the amino group as most efficient for π-stabilization.[15-16] It was found, that the hydride ion and the fluoride ion affinities of $Si(NMe_2)^{3+}$ (Figure 1a) in comparison to the parent SiH_3^+ are reduced by 311 and 251 kJ mol^{-1}, respectively.[16c, 16f] Although this resonance stabilization amounts to only 40% in comparison to the analog carbocation (the well-known guanidinium), it is clearly superior to the stabilization in the commonly used alkyl/aryl-substituted silylium ions.[16c] Despite such encouraging predictions, the synthetic realization of threefold amino- or other heteroatom substituted silylium ions are still missing in the literature. One attempt by reacting $(Me_2N)_3SiCl$ with $AlCl_3$ was reported in 1980, but it led solely to donor-acceptor complex formation (Figure 1b).[17] Preliminary studies on tris(dimethylamino) silicon perchlorate were mentioned in a review article by Lambert, but any details remained unpublished.[18] The formation of a threefold sulfur-substituted silylium ion was indicated by conductivity measurements, but no further evidence was provided.[19] Structurally related, twofold amino-substituted silylium ions were obtained in the form of silaimidazolium ions, but no solid state structure was reported.[20] A formal dimeric species of a monoamino substituted silylium ion was generated by the double protonation of a cyclodisilazane (Figure 1c).[21]

Herein, we describe the synthesis and characterization of a threefold amino-substituted silylium ion in its dimeric form in solution and in the solid state (Figure 1d). It can be handled in common organic solvents but retains some of the peculiar reactivity known for silylium ions.

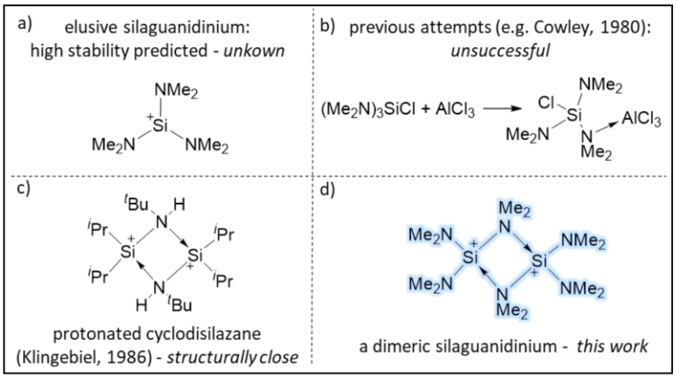

Figure 1: a) The elusive silaguanidinium, b) a previously attempted synthesis and c) the structurally closest species to the d) dimeric silaguanidinium presented in this work.

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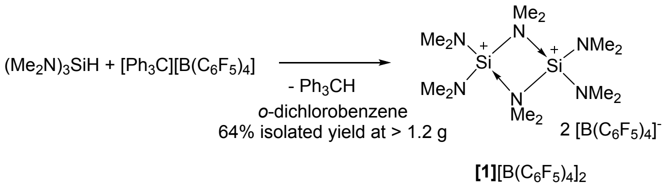

Scheme 1: Synthesis of compound **[1]**$[B(C_6F_5)_4]_2$ by hydride abstraction.

When commercially available $(Me_2N)_3SiH$ and $[Ph_3C][B(C_6F_5)_4]$ were mixed in *o*-dichlorobenzene and stored at room temperature overnight, colorless crystals formed from solution (Scheme 1). After removal of triphenylmethane by washing with *n*-pentane, [**1**]$[B(C_6F_5)_4]_2$ was isolated in 64% yield at > 1.2 g scale. The purity of the product was verified by ^1H-, ^{13}C-, ^{11}B-, ^{19}F- and ^{29}Si-NMR spectroscopy, ESI(+)-MS and elemental analysis. ESI(+)-MS indicated a monomeric, cationic species $(Me_2N)_3Si^+$ in the gas phase (m/z = 160.13). However, in a solution of *o*-difluorobenzene, two singlets at 3.57 ppm and 2.70 ppm in the ratio 1:2 were detected by ^1H-NMR spectroscopy, revealing two different types of Me_2N-groups. Surprisingly, the ^{29}Si-NMR chemical shift of -30.6 ppm was shifted upfield compared to the parent $(Me_2N)_3SiH$ (-25.4 ppm), thus in a shift range typically found for tetracoordinate silicon. The ^{29}Si-NMR chemical shift of the monomeric species $(Me_2N)_3Si^+$ was previously calculated as 42.1 ppm.[16c] An experimental ^{29}Si-NMR shift of -30.8 ppm (C_6D_6) for $[(Me_2N)_3Si][B(C_6F_5)_4]$ was mentioned as a personal communication in the same manuscript. Based on chemical shift calculations of the water adduct $(Me_2N)_3Si^+OH_2$ (-20.8 ppm), the authors concluded that rather the water adduct must have been observed. However, this interpretation would not agree with the two sets of Me_2N-groups found herein. X-ray structural analysis of [**1**]$[B(C_6F_5)_4]_2$ provided the answer. Single crystals suitable for X-ray diffraction were obtained directly from a saturated *o*-dichlorobenzene solution or by performing the reaction in toluene and recrystallizing the resulting oil in dichloromethane.

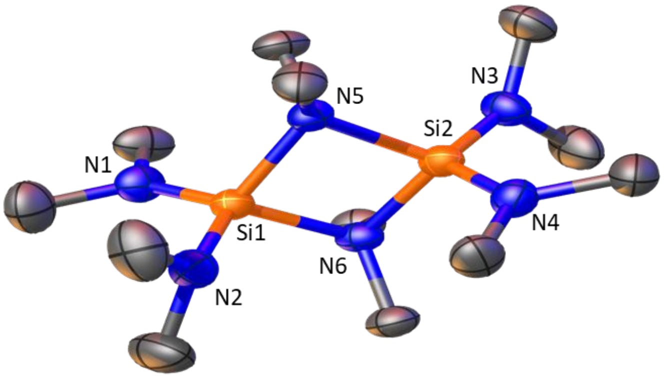

Figure 2: Molecular structure of [**1**]$^{2+}$ (anions and hydrogen atoms are omitted for clarity). Ellipsoids 50% probability, selected bond lengths [Å] and angles [deg]: Si(1)-N(1): 1.661(4), Si(1)-N(2): 1.656(4), Si(1)-N(5): 1.849(3), Si(1)-N(6): 1.871(4), Si(1)-Si(2): 2.7231(15), N(1)-Si(1)-N(2): 116.3(2), N(5)-Si(1)-N(6): 85.10(15), N(1)-Si(1)-N(5): 113.00(17), Si(1)-N(5)-Si(2): 94.30(15).

Two units of $[(Me_2N)_3Si]^+$ dimerize in a *head-to-tail* fashion, forming a Si_2N_2 tetracycle, analog to the isoelectronic $Al_2(NMe_2)_6$.[22] The silicon atoms are coordinated by two terminal and two bridging dimethylamino groups. The coordination sphere around silicon is distorted-tetrahedral with N-Si-N bond angles between 116° (terminal/terminal), 113° (terminal/bridged) and 94° (bridged/bridged). The Si(1)-N(5)-(Si(2) plane vs. Si(1)-N(6)-(Si(2) plane has a fold angle of 16°. The terminal Si-N bond lengths with 1.66 Å are significantly shorter than common Si-N single bonds (1.75 Å).[23] In contrast, the bridging Si-N bonds with 1.87 and 1.85 Å are clearly elongated and much longer than in the structurally related, double protonated cyclodisilazane (1.79 Å, Figure 1 c).[21] This observation indicated a significant stabilization of the cationic charge at silicon due to the threefold donation of the free electron pairs from nitrogen to silicon, raising the question if dissociation might be detectable at elevated temperature. Therefore, VT-NMR-spectroscopy in *o*-dichlorobenzene was performed up to 120°C. However, no change in lineshape or product composition could be observed, revealing a substantial dimerization free energy. To support the experimental results, the respective association enthalpy and free energy was computed at the highly accurate DLPNO-CCSD(T)/cc-pVQZ level of theory.[24] In vacuum, the dimerization process is not favored (ΔH = 111 kJ mol^{-1}, ΔG = 181 kJ mol^{-1}), whereas upon consideration of solvation (*o*-dichlorobenzene, COSMO-RS), the process gets indeed favored decisively (ΔH_{sol} = -104 kJ mol^{-1}, ΔG_{sol} = -35 kJ mol^{-1}). Energy decomposition analysis for the two interacting closed shell monomeric units $(Me_2N)_3Si^+$ revealed 54% orbital and 6% London dispersive attraction besides – despite the dicationic nature – 40% of electrostatic attraction.[25] These results are inverse to dimerizing *neutral* aminosilanes, constituting 60% electrostatic and 40% orbital + London dispersive contribution.[26] ETS-NOCV analysis disclosed the orbitals that contribute mainly to this efficient dimerization.[27] As expected, the interaction between the lone pair at the bridging nitrogen atom and the $p_z(Si)/\sigma^*(Si\text{-}N)$-type acceptor orbital at silicon plays the major role (ETS-NOCV1, Fig. SI1). However, a second interaction was found, in which also the terminal nitrogen lone pairs contribute as electron density donors (ETS-NOCV2, Fig. SI1). Although the tendency for dimerization should be diminished due to the π-stabilization within the monomeric $(Me_2N)_3Si^+$ units, the three amino groups favor dimerization by mutually pushing their intermolecular donor capability through intrafragment Y-conjugation ($LP(N) \rightarrow \pi^*(Si\text{-}N)$) and negative hyperconjugation ($LP(N) \rightarrow \sigma^*(Si\text{-}N)$) at the same time.[16c, 28] Intriguingly, this might be an additional cause for the higher intrinsic basicity of silaguanidine in comparison to guanidine.[16c]

Having established theoretical insights, the stability and reactivity of [**1**]$[B(C_6F_5)_4]_2$ were considered. The dication appeared stable towards organic solvents like dichloromethane, toluene, benzene, chlorobenzene, fluorobenzene, *o*-dichlorobenzene and *o*-difluorobenzene at room temperature. The Lewis acidity of [**1**]$[B(C_6F_5)_4]_2$ was assessed by adduct formation with triethylphosphine oxide according to Gutmann-Beckett.[29] Addition of 2 eq. Et_3PO to

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1 eq. of [**1**][$B(C_6F_5)_4$]$_2$ in CD_2Cl_2 yielded a clean adduct [Et_3PO-$Si(NMe_2)_3$][$B(C_6F_5)_4$], with a ^{31}P-NMR chemical shift of $\delta = 85.2$ ppm ($\Delta\delta^{31}$P vs. free Et_3PO = 34.2 ppm).[30] The induced shift change $\Delta\delta^{31}$P is indeed smaller as for carbon-substituted silylium ions ($\Delta\delta^{31}$P = 40 - 45 ppm),[31] indicating a tamed *effective*[32] Lewis acidity due to π-stabilization – thus spectroscopically supporting the computed diminished ion affinities. Although the Lewis acidity within [**1**]$^{2+}$ is decreased by both the intra- and intermolecular donation effects, it still initiates a catalytic hydrodefluorination reaction. With 6 mol% of [**1**][$B(C_6F_5)_4$]$_2$, 1-adamantylfluoride was fully converted to adamantane in presence of Et_3SiH within <12 h at rt. Finally, the reaction of [**1**][$B(C_6F_5)_4$]$_2$ towards electron-rich aromatic compounds was tested at NMR scale. An immediate electrophilic aromatic silylation of ferrocene in CD_2Cl_2 was observed under very mild conditions, providing the protonated product salt [**2a**][$B(C_6F_5)_4$] (Figure 3a and 3b for molecular structure). In analogy, the reaction of [**1**][$B(C_6F_5)_4$]$_2$ towards *N*-methyl indole gave the C3-silylation product [**2b**][$B(C_6F_5)_4$] in perfect regioselectivity. With dimethylaniline, a highly regioselective *para*-silylation to [**2c**][$B(C_6F_5)_4$] was observed.[33] Such spontaneous and quantitative conversions are remarkable, since Friedel-Crafts type electrophilic aromatic silylations usually suffer from competing protodesilylation back-reactions.[34]

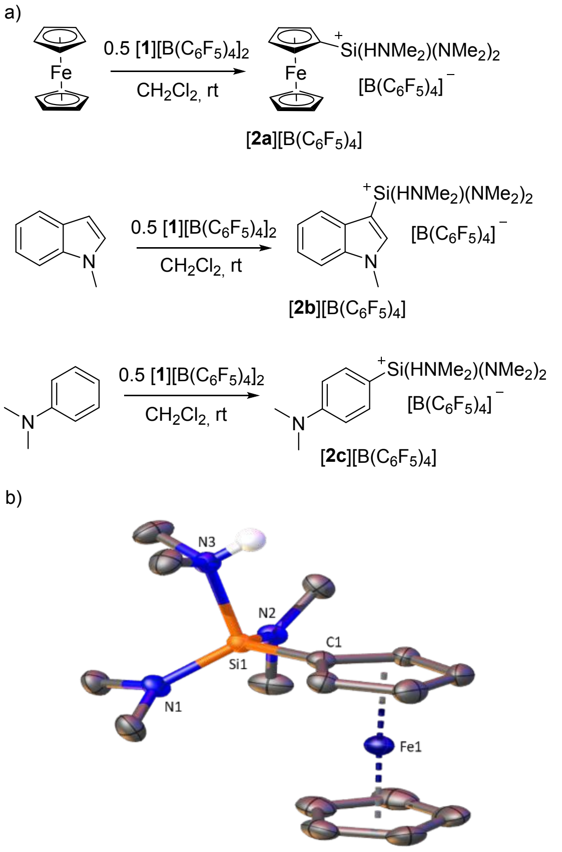

Figure 3: a) Reactivity of [**1**][$B(C_6F_5)_4$]$_2$ towards electron-rich aromatic compounds. Full conversion was verified by ^{1}H-NMR signal integration. b) molecular structure of [**2a**][$B(C_6F_5)_4$]$_2$. The $B(C_6F_5)_4$ anion and hydrogen atoms are omitted for clarity. Ellipsoids 50% probability, selected bond lengths [Å]: Si(1)-N(1): 1.682(2), Si(1)-N(2): 1.687(2), Si(1)-N(3): 1.895(2), Si(1)-C(1): 1.835(2).

A common strategy to shift the equilibrium to the product side is the addition of proton-scavengers. Obviously, the amino groups in [**1**][$B(C_6F_5)_4$]$_2$ exert two favorable effects: 1) The silylation products provide a Brønsted basic side by themselves, making the substitution reaction thermodynamically more favorable. 2) The nucleophilic attack of the aromatic at silicon might be concerted with an intramolecular hydrogen transfer process to nitrogen, thus potentially lowering the transition state energy. Although catalytic variants with $(Me_2N)_3SiH$ and $B(C_6F_5)_3$ or [Ph_3C^+] as initiators remained unsuccessful thus far, this stoichiometric methodology already provides an attractive method for the construction of more complex silanes, given the multitude of functionalization methods available for the Si-N bond.[35]

The present study provides first insights into the stabilization of silylium ions by directly attached π-donors (π-stabilization). It describes the formal dimer of the elusive silaguanidinium, isoelectronic to $Al_2(NMe_2)_6$ or related compounds, which are known for several decades.[22, 36] The dicationic compound is obtained from commercial reagents, easy to handle in common organic solvents, but still undergoes reactivity reminiscent to silylium ions. Interestingly, it performs spontaneous electrophilic aromatic substitutions of electron-rich aromatics – potentially caused by means of ligand-element cooperativity.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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The formal dimer of the elusive silaguanidinium is described. It undergoes spontaneous electrophilic aromatic silylation of electron rich π-systems