A Mono-Substituted Silicon(II) Cation: A Crystalline “Supersilylene”

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Abstract: Mono-coordinated silicon(II) cations are predicted to be reactive ambiphiles, combining the typically high Lewis acidity of silicon cations with nucleophilicity due to the presence of an electron pair at the same atomic centre. Here, a carbazole-derived scaffold was used to isolate salts with a mono-coordinated silicon(II) cation, $[\text{RSi}]^+$ ($R =$ bulky carbazolyl substituted), by halide abstraction from a base-free halosilylene, $\text{RSiI}$, with $\text{Ag}[\text{Al(OtBuF)}_4]$. Despite the bulk of the carbazolyl moiety, the silylenium cation $[\text{RSi}]^+$ retains high reactivity. It was shown to react with an amine to form three bonds at the silicon atom in one reaction which conforms with the notion of a “supersilylene”. The resulting silylium cation $[\text{RSi}(\text{H})\text{NR}_2]^+$ (in the formal oxidation state $\text{Si}^{VI}$) obtained by oxidative addition of an NH bond at $[\text{RSi}]^+$ is even more acidic than the silylenium cation ($\text{Si}^{VI}$) due to the absence of a lone pair of electrons the silicon atom.

Silylenes ($[\text{RSi}]^+$, $R =$ monodentate monoanionic substituent) are of great interest as they are considerably more Lewis acidic than their lighter congeners, carbenium cations ($R,C^=$). In 1993, crystallographic evidence for the existence of adducts of such silicon cations was provided for the first time by the groups of Reed and Lambert with the examples of $[\text{Pr}_3\text{Si(McCN)}]^+$ and $[\text{Pr}_3\text{Si(CB}_{11}\text{H}_{12}\text{Br}_2)]$ as well as $[\text{Et}_3\text{Si(toluene)}]^+$. In these three examples, the silicon atom adopts tetracoordination and the positive charge is predominantly localized on the coordinated donor moieties. It took the groups nine more years to achieve the isolation of salts with the donor-free genuine silylium cation $[\text{Mes}_3\text{Si}]^+$ ($\text{Mes} = 2,4,6$-trimethylphenyl). Since then, the reactivity of silylium cations has been intensively studied and was found to be dominated by extreme Lewis acidity which makes them suitable catalysts for reactions such as hydrodefluorinations, $\text{C–H}$ arylation and $\text{C–H}$ alkylation. In contrast, $\text{Si}^{IV}$ compounds in their singlet ground state are generally ambipolar, as their $\text{Si}$ atom has a lone pair of electrons but only possesses an electron sextet. West’s landmark report detailing the isolation of the first silylène in 1994 initiated the investigation of their reactivity. Three general reactivity patterns can be distinguished as follows: a) Silylenes can act as Lewis acids. For instance, Roesky and Filippou found independently that simple silylenes such as $\text{SiCl}_2$ and $\text{SiBr}_2$ can be stabilized by suitable carbene donors to make molecular synthetic equivalents of $\text{Si}^{IV}$ available. b) Silylenes can act as a base themselves. Silylenes are strong donor ligands which can be incorporated in transition metal complexes to be utilized in catalysis. c) The presence of both Lewis acidic and basic properties at the silicon atom can make them reactive ambiphiles. Many silylenes react with small molecules such as $\text{H}_2$, $\text{CH}_2$, $\text{NH}_2$, or $\text{CO}_2$ as shown by Aldridge, Driess, Iwamoto, Roesky, and Inoue.

A combination of enhanced Lewis acidity and ambiphilicity was predicted for cationic $\text{Si}^{IV}$ species. These molecules of the general formula $[\text{RSi}]^+$ have been referred to with a variety of names, such as silanetriyl, silyne, or silyliumylium cations, among which the latter is the currently dominating term. More consistently, they could be called silaylidenylium or silylenylium ions, the latter of which will be used in this article. These $\text{Si}^{IV}$ cations have been pursued intensively. A mass-spectrometric study by Gaspar targeting the reactivity of $[\text{HSi}]^+$ with diethylamine ($\text{HNEt}_2$) in the gas phase indicated that three bonds are formed in a single reactive encounter which prompted the authors to coin the phrase “supersilylenes” for these cations. Numerous attempts to isolate such mono-coordinated cations were unsuccessful, but $\text{Si}^{IV}$ cations with a higher coordination number could be obtained, such as Jutzi’s $[\text{Cp}^*\text{Si}]^+$ and masked $\text{Si}^{IV}$ cations of the general formula $[\text{RSi(L)}]^+$ ($\text{L} =$ neutral donor ligand). In all these examples, the donor-stabilisation causes a coordination number greater than one which prevents the envisaged three-bond-forming-reactivity. Müller spectroscopically observed that by thermal decomposition of a dibenzosilanorbornadienyl cation in benzene solution an aryl diphenyl silylium ion was formed which indicates that a $\text{Si}^{IV}$ cation benzene had been intermediately present. To date, the lack of substituents which provide sufficient shielding for the stabilisation of free silylimyliidenes has led to the notion that “Clearly, such steric protection cannot be achieved by the lonely substituent of silylimyliidenes” ($R^*\text{Si}^{IV}$).

After the recent synthesis of heavier chlorotetrylenes and the corresponding tetrylenium cations bearing a sterically demanding carbazolyl substituent ($R, R = 1.8$-bis(3,5- di-$\text{tetrabutyl-phenyl})$-3,6-di-$\text{tetrabutyl-carbazolyl}$) in our group, the question whether analogous silicon compounds were accessible as well, inevitably had to be asked. Initially the issue was tackled computationally (Figure 1). The calculations (Gaussian16 B.01, PBE0 hybrid functional, def2SVP basis set) revealed that the chlorosilylene $\text{RSiCl}$ is a stable molecule on the energy hypersurface (see Figure 1, SI 4.1). Then the energetics for the typical decomposition reactions, namely

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The insertion of the Si atom in one of the C–C or C–H bonds of the flanking arene groups of the substituent, were investigated. For the C–C insertion reaction of RSiCl, the activation barrier was computationally determined to be 144.4 kJ mol\(^{-1}\) which might be thermally accessible, but the product (isomer I) is less stable than the chlorosilylene isomer by 25.7 kJ mol\(^{-1}\). On the other hand, the CH insertion product (isomer II) is thermodynamically favoured over the chlorosilylene RSiCl, but the activation barrier of 202.5 kJ mol\(^{-1}\) for this reaction is too high to be feasible. Similar energy profiles were found for the other base-free halosilylenes RSiX\(_3\) (X = Cl, Br, I) and the silylenylium cation [RSi]\(^+\) (details see SI 4.1). With these data available, experiments were initiated.

The metathesis reaction of potassium carbazolide (R-K) with silicon halides SiX\(_4\) afforded the trihalosilane derivatives RSiX\(_3\) (1X = Cl, Br, I; Figure 1) in good to moderate yields (1Cl 77%, 1Br 71%, 1I 41%). The molecular structure of these trihalosilane derivatives is surprising in the regard that the N-Si bond is bent out of the plane spanned by the carbazole C atoms by more than 40° (see SI 2.1–2.3), thereby reducing the effective steric bulk of the carbazolyl substituent drastically. The \(^{29}\)Si NMR resonances were found in the expected range for the respective trihalosilanes (1Cl –23.5, 1Br –59.5, 1I –199.3 ppm). While all attempts of reduction of RSiCl to RSiCl failed, the heavier homologues RSiBr\(_3\) and RSiI\(_3\) could be reduced to afford the first base-free halosilylenes, RSiBr (2Br) and RSiI (2I), where the best results were achieved with Mg\(^+\) compounds as reducing agents. The reduction reactions were carried out by combining stoichiometric amounts of RSiX\(_3\) and [(MesBDI)Mg]\(_2\) (BDI = \(\beta\)-diketiminate, Mes = 2,4,6-trimethylphenyl) in toluene. After sonication at ambient temperature, the solvent was evaporated and the solid was extracted with \(n\)-hexane to afford RSiX in moderate yields (2Br 50%, 2I 64%). By removal of two substituents from the silicon atom the occupied space is reduced, hence the molecular structures show the silicon atom in the carbazole plane (Figure 2). The \(^{29}\)Si NMR resonances for 2Br and 2I were observed at +129.2 and +152.8 ppm, respectively, in the characteristic region for aminosilylenes. During all reduction reactions, an interesting silylene-type by-product was observed (\(\delta\)(\(^{29}\)Si) = +147.5 ppm). The compound could be isolated and identified as the bis-carbazolyl silylene R\(_2\)Si which is the bulkiest silylene known to date (see SI 2.5.1).

The halosilylenes 2Br and 2I could prove versatile starting materials for a wide range of reactions, but the focus of this study was set on halide abstraction reactions. Due to the high inherent reactivity of the silylenes and the reaction product, viable solvents for these reactions were only hydrocarbons and aromatic solvents. As a halide abstraction reagent, Ag\(^+\) salts were chosen, as neither Li\(^+\), Na\(^+\), K\(^+\) or Cs\(^+\) salts showed any reactivity in these solvents. Initial experiments of the reaction of 2Br with Ag[wca] (wca = Al(OC\(_4\)F\(_9\))\(_4\)) yielded an intractable mixture of compounds in which no [RSi]\(^+\) was
Figure 2. Molecular structure of RSiI (2I), thermal ellipsoids at 50% probability. Selected bond lengths [Å]: Si-I 2.5552(10); Si-N 1.792(3); N-Si-I 103.26(9); angle sum at N 360°.

Figure 3. Molecular structure of [RSi][wca] (3, 130 K, shortest Si-C contacts are indicated). Thermal ellipsoids at 50% probability, H atoms and counterion omitted for clarity. Bond length Si-N 1.714(2) Å, sum of angles at N: 359.5°.

Figure 4. Selected Kohn–Sham orbital representations of [RSi]− (iso-value 0.05, energies in eV).
[RSi(H)(NHBu)NH2Bu+] (6). In good agreement with the computed value, the 29Si NMR resonance was observed at -29.4 ppm (calc. -36 ppm). The 1H NMR spectrum indicates the presence of two distinct NBu groups in proximity to the SiH moiety as well as the presence of an NH and an NH2 moiety (see SI 2.7). No intermediate was observed and no reaction to 5 occurred after addition of another equivalent of [RSi-]

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Conflict of interest

The authors declare no conflict of interest.

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