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Pentacoordinate Silicon(IV): Cationic, Anionic and Neutral Complexes Derived from the Reaction of NHC→SiCl₄ with Highly Lewis Acidic (C₂F₅)₂SiH₂.

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T. Böttcher,^{*a} S. Steinhauer,^a B. Neumann,^a H.-G. Stammer,^a G.-V. Rösenthaller,^{*b}
and B. Hoge^{*a}

Addition of NHC→SiCl₄ to the highly Lewis acidic bis(pentafluoroethyl)silane ((C₂F₅)₂SiH₂) afforded the salt [(NHC)₂SiCl₂H][(C₂F₅)₂SiCl₃] with pentacoordinate silicon in the cation and the anion. The anion represents the first example of a chlorosilicate structurally characterized in the solid state. In this reaction, the long sought pentacoordinate NHC-adduct of silicochloroform was identified as an intermediate and its crystal structure is presented.

The addition of neutral ligands, such as pyridine-type nitrogen donors, to tetrachlorosilane yields neutral or positively charged hexacoordinate complexes.¹ For halohydrosilanes, this process is accompanied by well described dismutation processes.² In 1995, Kuhn et al. reported the addition reactions of free NHC ligands with tetrachlorosilane to afford pentacoordinate 1:1 adducts.³ In 2012, Roesky et al. reported the addition of an abnormal NHC (aNHC) to silicochloroform to yield aNHC→SiCl₂H₂ as the first example of a neutral pentacoordinate complex of a halohydrosilane.^{2b} Very recently, Driess et al. reported the addition of free NHC^{Dipp} to H₃SiOTf to afford the pentacoordinate cation [(NHC^{Dipp})₂SiH₃]⁺ (see **I** – **III**, Figure 1).⁴

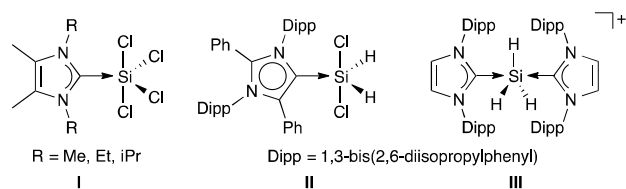
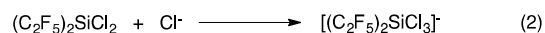


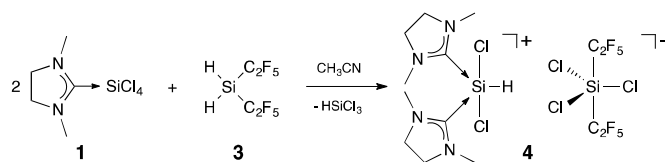
Figure 1. Neutral and cationic pentacoordinate carbene adducts of silicon(IV).⁵

For the addition reaction of free NHC^{Dipp} to SiBr₄, on the other hand, two different products were reported independently. Roesky et al. obtained the neutral adduct NHC^{Dipp}→SiBr₄, whereas Filippou et al. characterized the salt [(NHC^{Dipp})SiBr₃][Br], suggesting a low ionization barrier for the neutral adduct.⁶ While the analogous iodine compound [(NHC^{Dipp})SiI₃][I] was reported recently, the carbene adduct of SiCl₄ is only known in its neutral form so far.⁷ Our group reported an improved synthesis of NHC→SiCl₄ (NHC = 1,3-dimethylimidazolidin-2-ylidene) (**1**) based on silicochloroform and its utilization as a carbene transfer reagent.⁸ However, the NHC ligand increases the electron density at the central silicon making it prone to release chloride (eqn 1). As appropriate chloride-acceptors the electron poor and highly Lewis-acidic bis(pentafluoroethyl)silanes (C₂F₅)₂SiCl₂ (**2**) (eqn 2) and (C₂F₅)₂SiH₂ (**3**) were chosen to synthesize NHC-stabilized chlorosilyl cations.⁹



Addition of NHC→SiCl₄ (**1**) to (C₂F₅)₂SiCl₂ (**2**) in a 1:1 molar ratio in deuterated acetonitrile was monitored by multinuclear NMR spectroscopy. According to the ¹⁹F NMR spectrum, the reaction quantitatively yielded a single product with the ¹⁹F signals (–CF₂– (δ -118.6), –CF₃ (δ -75.8)) shifted downfield relative to **2** (δ -126.5 and δ -81.0, respectively). The corresponding signal in the ²⁹Si NMR spectrum was detected at δ -97.6 (δ -14.6), which is characteristic of a pentacoordinate silicon such as the assumed trichlorobis(pentafluoroethyl)silicate(IV) anion [(C₂F₅)₂SiCl₃]⁻.¹⁰ However, attempts of isolating the product by removal of the solvent

turned out to be unsuccessful. On the other hand, when **2** was replaced by two equivalents of $(C_2F_5)_2SiH_2$ (**3**) the compound $[(NHC)_2SiCl_2H][(C_2F_5)_2SiCl_3]$ (**4**) was obtained in almost quantitative yield (Scheme 1).



Scheme 1. Synthesis of **4**.

The 1H NMR spectrum shows a singlet resonance at δ 6.71 with ^{29}Si satellites ($^1J_{SiH} = 352$ Hz). A crosspeak corresponding to the cation was detected by 2D $^1H,^{29}Si$ correlation spectroscopy at δ -125.4 which is in the expected region for pentacoordinate silicon. A second, independent crosspeak was detected by 2D $^{19}F,^{29}Si$ correlation spectroscopy at δ -97.6 (d, $^2J_{SiF} = 44$ Hz), which was already observed in the reaction mixture of **1** and **2** and is assigned to the chlorosilicate $[(C_2F_5)_2SiCl_3]^-$. Single crystals were obtained by recrystallization of the raw product from acetonitrile at -30 °C. The crystal structure of **4** was determined by single crystal XRD (Figure 2). Compound **4** crystallizes in the triclinic space group $P\bar{1}$. The structure of the cation responds to silicon in a trigonal bipyramidal geometry with the chlorides at the axial positions. The mean Si-C bond lengths (192.4(2) pm) are significantly shorter compared to those in **III** (208.8(2) pm). The Cl4-Si2-Cl5 angle is almost linear (177.28(2)°) and the equatorial angular sum is 360°. The silicon center in the anion possesses a trigonal bipyramidal coordination geometry with the two pentafluoroethyl-groups residing at the axial positions. The C1-Si1-C3 angle is almost linear (177.28(2)°) and the equatorial angular sum is 360°.

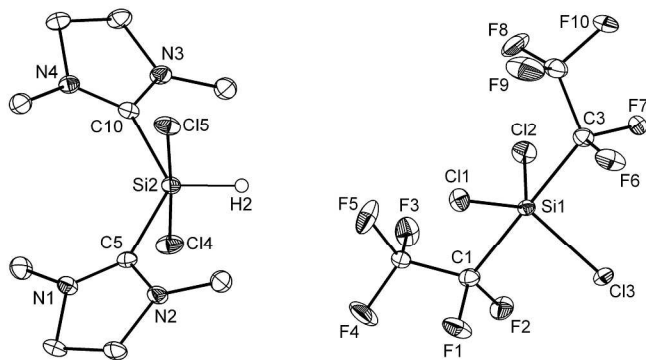
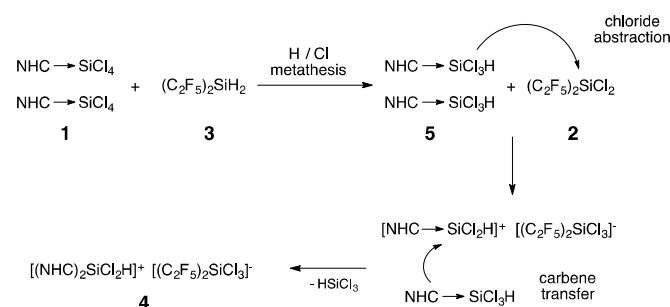


Figure 2. Crystal structure of **4**. The cation (left) and anion (right) are depicted independently. All C-H protons have been omitted for clarity. Thermal ellipsoids set at 50% probability. Selected bond lengths [pm] and angles [°]: (cation) Si2-C5 192.3(2), Si2-C10 192.5(2), Si2-Cl5 223.87(6), Si2-Cl4 224.28(6), Si2-H2 141(2), Cl4-Si2-Cl5 177.28(2), C5-Si2-C10 126.98(6). (anion) Si1-Cl1 210.95(5), Si1-Cl2 209.64(5), Si1-Cl3 209.49(5), Si1-C1 200.7(2), Si1-C3 200.0(2), Cl1-Si1-Cl2 126.75(2), Cl2-Si1-Cl3 116.74(2), Cl3-Si1-Cl1 116.51(2), C1-Si1-C3 179.55(7).

Only one example for a cationic species containing a $\{SiCl_2H\}^+$ moiety was reported to the literature by the group of Boudjouk.¹¹ The octahedral complex $[(pmteda)SiCl_2H]^+$ (*pmteda* = *N,N,N',N',N''*-pentamethyldiethylenetriamine) was obtained by addition of *pmteda* to $HSiCl_3$ followed by precipitation of the product. In contrast, compound **4** is readily soluble in polar solvents and no phase transfer occurred

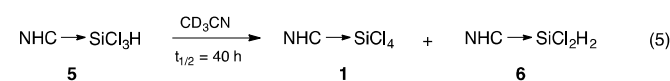
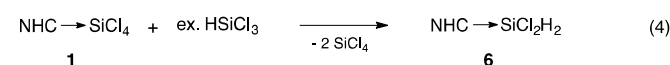
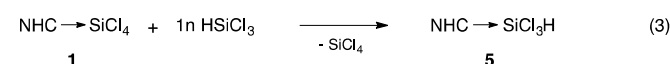
during its formation. The anion of **4** ($[(C_2F_5)_2SiCl_3]^-$) represents the first example of a chlorosilicate structurally characterized in the solid state. Due to the low chloride affinity of silanes no chlorosilicates have been obtained by the reactions described above and chloro silicates in general are unknown. Previous attempts of their synthesis and isolation failed and evidence proving their existence is limited to mass spectrometric analysis in the gas phase only.¹²

To rationalize the formation of **4** a proposed mechanism for its formation is given in Scheme 2. The first step is a chloride/hydride metathesis between the two starting compounds to give two equivalents of the pentacoordinate silicochloroform adduct $NHC \rightarrow SiCl_3H$ (**5**) and **2**. A chloride from **5** is then abstracted by **2** to give the trichlorosilicate anion with $[NHC-SiCl_2H]^+$ as the corresponding cation. The Lewis-acidity of this cation is increased compared with the neutral adduct and NHC transfer from the remaining equivalent of **5** takes place to yield the cationic biscarbene complex $[(NHC)_2SiCl_2H]^+$ under liberation of silicochloroform.



Scheme 3. Proposed mechanism for the formation of **4**.

A pentacoordinate adduct of a Lewis base and silicochloroform has not been reported yet, although Roesky et al. recently assumed such a species as an intermediate in the formation of the silylene complex $NHC^{Dipp} \rightarrow SiCl_2$ via addition of free carbene to $HSiCl_3$.^{2g} To prove the existence of this adduct, a solution of **1** in dichloromethane was treated with additional silicochloroform as a source for hydride (eqn. 3-5).



Addition of one equivalent of $HSiCl_3$ to **1** yielded $NHC \rightarrow SiCl_3H$ (**5**). Addition of two or more equivalents gave $NHC \rightarrow SiCl_2H_2$ (**6**). Both adducts were isolated as colorless and hygroscopic solids after removal of all volatile components. Compound **5** is stable as a solid, but in solution a dismutation process to compounds **1** and **6** takes place. The half-life period of **5** in CD_3CN is 40 hours as monitored by 1H NMR (see Figure 3). A similar dismutation process was also observed for octahedral adducts of $HSiCl_3$ by the groups of Boudjouk and Kroke.^{2c-e}

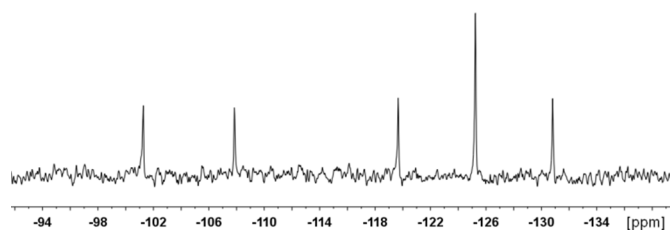
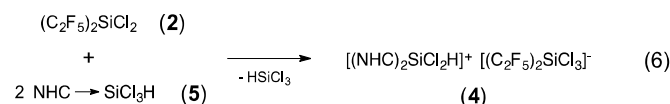


Figure 3. ^{29}Si NMR spectrum (CD_3CN) of a mixture of **5** (δ -104.5, d, $^1J_{\text{SiH}} = 393$ Hz) and **6** (δ -125.2, t, $^1J_{\text{SiH}} = 333$ Hz).

To further prove the proposed mechanism **5** was added directly to a solution of **2** which also afforded **4**, as monitored by NMR spectroscopy in solution (eqn. 6).



Crystallization of **5** yields mixed crystals containing 90% of **5** and 10% of **1**, disordered at the same crystallographic site, as determined by single crystal XRD (Figure 3). Compound **5** crystallizes in the orthorhombic space group *Pbca*. The silicon is in the expected trigonal bipyramidal coordination environment with the NHC ligand at the equatorial position. The C-Si bond length (191.4(2) pm) is little shorter compared with **1** (192.8(3) pm). The mean axial Si-Cl bond lengths (223.3(2) pm) as well as the equatorial Si-Cl bond length (207.80(8) pm) are elongated compared with **1** (220.8(2) pm and 207.3(2) pm, respectively).

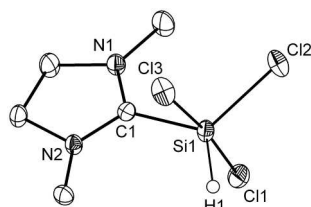


Figure 3. Crystal structure of **5**. All C-H protons have been omitted for clarity. Thermal ellipsoids set at 50% probability. Selected bond lengths [pm] and angles [°]: Si1-C1 191.4(2), Si1-Cl1 222.9(2), Si1-Cl2 207.80(8), Si1-Cl3 223.61(8), Cl1-Si1-Cl3 174.10(3).

Two derivatives of **6** have been reported recently, one with an abnormal NHC by Roesky et al. (see Figure 1, **II**) and $\text{NHC}^{\text{Dipp}} \rightarrow \text{SiCl}_2\text{H}_2$ by Driess et al.^{2b,4} All three complexes share the same trigonal bipyramidal geometry with the chlorine atoms residing at the axial positions. Despite the different classes of carbene ligands used in these examples (abnormal, bulky and unsaturated, small and saturated) the structural parameters show no significant structural deviations between each other. For more detailed crystallographic information please see the ESI.

In summary, we presented the formation of the salt $[(\text{NHC})_2\text{SiCl}_2\text{H}]^+ [(\text{C}_2\text{F}_5)_2\text{SiCl}_3]^-$. The cation represents the first example of a pentacoordinate $\{\text{SiCl}_2\text{H}\}^+$ moiety. The anion is the first example of a chlorosilicate structurally characterized in the solid state. A mechanism for the formation was proposed and studied stepwise, including the successful isolation and characterization of the involved

intermediates. Among them is $\text{NHC} \rightarrow \text{SiCl}_3\text{H}$ as the first example of a pentacoordinate adduct of silicochloroform.

Notes and references

^a Universität Bielefeld, Centrum für Molekulare Materialien, Anorganische Chemie II, Universitätsstraße 25, 33615 Bielefeld (Germany). E-mail: b.hoge@uni-bielefeld.de; tobias.bottcher@monash.edu.

^b Jacobs University Bremen, School of Engineering and Science, Campus Ring 1, 28759 Bremen (Germany). E-mail: g.roeschenthaler@jacobs-university.de.

† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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