

# **Pentacoordinate Silicon(IV): Cationic, Anionic and Neutral Complexes Derived from the Reaction of NHC→SiCl<sub>4</sub> with Highly Lewis Acidic (C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>SiH<sub>2</sub>.**

T. Böttcher,\* S. Steinhauer, B. Neumann, H.-G. Stammler, G.-V. Röschenthaler,\* and B. Hoge\*

## **Supporting Information**

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# 1. Experimental Section

## General remarks

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk-line techniques unless mentioned otherwise. Solvents were dried using a Braun MB-SPS 800 system. Acetonitrile and dichloromethane were stored under 3 Å molecular sieves. Deuterated acetonitrile ( $\text{CD}_3\text{CN}$ ) was distilled over  $\text{CaH}_2$ . All other chemicals were purchased from available commercial sources and were used as received. NMR spectra were recorded on a Bruker Model Avance III 300 spectrometer (Operating frequencies:  $^{29}\text{Si}$  59.63 MHz,  $^{19}\text{F}$  282.40 MHz,  $^{13}\text{C}$  75.47 MHz,  $^1\text{H}$  300.13 MHz) with positive shifts being downfield from the external standards ( $\text{CCl}_3\text{F}$  ( $^{19}\text{F}$ ),  $\text{Si}(\text{CH}_3)_4$  ( $^{29}\text{Si}$ ,  $^{13}\text{C}$ ,  $^1\text{H}$ )). The  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR shifts were acquired by  $^1\text{H},^{13}\text{C}$  and  $^1\text{H},^{29}\text{Si}$  2D HMBC NMR correlation experiments. Elemental analyses were performed by the microanalytical laboratory of the department of Inorganic Chemistry II (ACII), University of Bielefeld, Bielefeld, Germany. Compounds  $\text{NHC-SiCl}_4$  (**1**),  $\text{Cl}_2\text{Si}(\text{C}_2\text{F}_5)_2$  (**2**) and  $\text{H}_2\text{Si}(\text{C}_2\text{F}_5)_2$  (**3**) were prepared according to procedures reported elsewhere.<sup>[1,2]</sup>

## Synthesis of $[(\text{NHC})_2\text{SiCl}_2\text{H}][(\text{C}_2\text{F}_5)_2\text{SiCl}_3]$ (**4**)

A solution of **1** (2.34 g, 8.73 mmol) in acetonitrile (60 ml) was placed in a 100 ml Schlenk flask. The solution was cooled to  $-196\text{ }^\circ\text{C}$  and **3** (5.0 mmol, 1.1 eq.) was condensed into the flask. The reaction mixture was allowed to reach room temperature over a period of 12 h under constant stirring. All volatile components were removed under reduced pressure. The residue was washed three times with 20 ml of diethyl ether. Drying in vacuo gave **4** (2.85 g, 4.26 mmol, 98% raw yield, based on **1**). Single crystals of **4** were obtained from a solution of **4** in acetonitrile stored at  $-28\text{ }^\circ\text{C}$  (1.20 g, 1.79 mmol, 41% based on **1**).

Yield: 41% (based on **1**). Elemental analysis calcd (%) for  $\text{C}_{14}\text{H}_{21}\text{N}_4\text{F}_{10}\text{Si}_2\text{Cl}_5$  (668.76): C 25.14, H 3.17, N 8.38; found: C 24.94, H 3.70, N 8.49.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  = 3.30 (s, 12H,  $-\text{CH}_3$ ), 3.85 (s, 8H,  $-\text{CH}_2-$ ), 6.71 (s, 1H, Si-H,  $^1J_{\text{SiH}} = 352$  Hz).  $^1\text{H},^{13}\text{C}$  HMBC NMR ( $\text{CD}_3\text{CN}$ )  $\delta(^1\text{H})/\delta(^{13}\text{C})$ : 3.30/36.5 (d,  $-\text{CH}_3/-\text{CH}_3$ ,  $^1J_{\text{CH}} = 141$  Hz), 3.30/51.7 (s,  $-\text{CH}_3/-\text{CH}_2-$ ), 3.85/51.7 (d,m,  $-\text{CH}_2/-\text{CH}_2-$ ,  $^1J_{\text{CH}} = 153$  Hz), 3.30/171.2 (s,  $-\text{CH}_3/\text{C}_{\text{carbene}}$ ), 3.85/171.2 (s,  $-\text{CH}_2/\text{C}_{\text{carbene}}$ ).  $^{19}\text{F}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  =  $-118.6$  (s, 4F,  $-\text{CF}_2-$ ),  $-75.8$  (s, 6F,  $-\text{CF}_3$ ).  $^1\text{H},^{29}\text{Si}$  HMBC NMR ( $\text{CD}_3\text{CN}$ )

$\delta(^1\text{H})/\delta(^{29}\text{Si}) = 3.30/-125.4$  (s,  $-\text{CH}_3/\text{Si}$ ),  $3.85/-125.4$  (s,  $-\text{CH}_2^-/\text{Si}$ ),  $6.71/-125.4$  (d,  $\text{Si}-\text{H}/\text{Si}$ ,  $^1J_{\text{SiH}} = 352$  Hz).  $^{19}\text{F},^{29}\text{Si}$  HMBC NMR ( $\text{CD}_3\text{CN}$ )  $\delta(^{19}\text{F})/\delta(^{29}\text{Si}) = -118.6/-96.6$  (d,  $-\text{CF}_2^-/\text{Si}$ ,  $^2J_{\text{SiF}} = 44$  Hz).

### Synthesis of NHC-SiCl<sub>3</sub>H (5)

A solution of **1** (2.81 g, 10.48 mmol) in dichloromethane (50 ml) was placed in a 100 ml Schlenk flask. Silicochloroform (1.42 g 10.48 mmol, 1 eq.) was condensed into the solution at  $-196$  °C. The reaction mixture was allowed to reach room temperature and was stirred for another 2.5 h. Removal of all volatile components gave a colorless solid (2.36 g). The raw product was then dissolved in acetonitrile (20 ml) and diethyl ether was slowly condensed into the solution at  $-30$  °C. After 7 days single crystals suitable for XRD of **5** were obtained. In solution, a dismutation process to compounds **1** and **6** takes place. Compound **5** co-crystallizes with compound **1**. Yield: 1.22 g (with 10% of compound **1** according to  $^1\text{H}$  NMR and as observed in XRD).

Yield: 50% (based on **1**).  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta = 3.30$  (s, 6H,  $-\text{CH}_3$ ),  $3.77$  (s, 4H,  $-\text{CH}_2^-$ ),  $6.80$  (s, 1H,  $\text{Si}-\text{H}$ ,  $^1J_{\text{SiH}} = 393$  Hz).  $^{13}\text{C},^1\text{H}$  HMBC ( $\text{CD}_3\text{CN}$ )  $\delta(^{13}\text{C})/\delta(^1\text{H}) = 3.30/34.5$  (d,  $-\text{CH}_3^-/\text{CH}_3$ ,  $^1J_{\text{CH}} = 140$  Hz),  $3.30/51.1$  (,  $-\text{CH}_3^-/\text{CH}_2^-$ ),  $3.77/51.1$  (d,m,  $-\text{CH}_2^-/\text{CH}_2^-$ ,  $^1J_{\text{CH}} = 152$  Hz),  $3.30/173.1$  (s,  $-\text{CH}_3/\text{C}_{\text{carbene}}$ ),  $3.77/173.1$  (s,  $-\text{CH}_2^-/\text{C}_{\text{carbene}}$ ),  $6.80/173.1$  (d,  $\text{Si}-\text{H}/\text{C}_{\text{carbene}}$ ,  $^2J_{\text{CH}} = 8$  Hz).  $^{29}\text{Si},^1\text{H}$  HMBC NMR ( $\text{CD}_3\text{CN}$ )  $\delta(^{29}\text{Si})/\delta(^1\text{H}) = 3.30/-104.5$  (s,  $-\text{CH}_3/\text{Si}$ ),  $6.80/-104.5$  (d,  $-\text{Si}-\text{H}/\text{Si}$ ,  $^1J_{\text{SiH}} = 393$  Hz).  $^{29}\text{Si},^1\text{H}$  DEPT NMR ( $\text{CD}_3\text{CN}$ )  $\delta = -104.5$  (d,  $^1J_{\text{SiH}} = 393$  Hz).

### Synthesis of NHC-SiCl<sub>2</sub>H<sub>2</sub> (6)

A solution of **1** (1.50 g, 5.60 mmol) in tetrahydrofuran (30 ml) was placed in a 100 ml Schlenk flask. Silicochloroform (23 mmol, 4 eq.) was condensed into the solution at  $-196$  °C. The reaction mixture was allowed to reach room temperature and was stirred for additional 12 h. After removal of all volatile components, the crude product was dissolved in a minimum amount of acetonitrile and diethyl ether was slowly condensed into the solution. Removal of all volatile components gave compound **6** (1.09 g, 5.47 mmol). Single crystals were obtained by slow diffusion of diethyl ether into a saturated solution of **6** in acetonitrile.

Yield: 98% (based on **1**).  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  = 3.25 (s, 6H,  $-\text{CH}_3$ ), 3.77 (s, 4H,  $-\text{CH}_2-$ ), 6.11 (s, 2H, Si-H,  $^1J_{\text{SiH}} = 333$  Hz).  $^1\text{H}, ^{13}\text{C}$  HMBC ( $\text{CD}_3\text{CN}$ )  $\delta(^1\text{H})/\delta(^{13}\text{C})$  = 3.25/34.5 (d,  $-\text{CH}_3/-\text{CH}_3$ ,  $^1J_{\text{CH}} = 140$  Hz), 3.25/51.1 (s,  $-\text{CH}_3/-\text{CH}_2-$ ), 3.77/51.1 (d,m,  $-\text{CH}_2-/-\text{CH}_2-$ ,  $^1J_{\text{CH}} = 153$  Hz), 3.25/175.4 (s,  $-\text{CH}_3/\text{C}_{\text{carbene}}$ ), 3.77/175.4 (s,  $-\text{CH}_2-/\text{C}_{\text{carbene}}$ ), 6.11/175.4 (s, Si-H/ $\text{C}_{\text{carbene}}$ ).  $^{29}\text{Si}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  = -125.2 (t,  $^1J_{\text{SiH}} = 333$  Hz).  $^1\text{H}, ^{29}\text{Si}$  HMBC NMR ( $\text{CD}_3\text{CN}$ )  $\delta(^1\text{H})/\delta(^{29}\text{Si})$  = 3.25/-125.2 (s,  $-\text{CH}_3/\text{Si}$ ), 3.77/-125.2 (s,  $-\text{CH}_2-/\text{Si}$ ), 6.11/-125.2 (d, Si-H/ $\text{Si}$ ,  $^1J_{\text{SiH}} = 333$  Hz).  $^{29}\text{Si}, ^1\text{H}$  DEPT NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  = -125.2 (t,  $^1J_{\text{SiH}} = 333$  Hz).

## 2. Crystallographic section

### X-ray crystallography

Single crystals were coated with a layer of hydrocarbon oil and attached to a MicroMount™. Crystallographic data were collected with a SuperNova, Dual, Cu at zero, Atlas diffractometer with Mo-K $\alpha$  or Cu-K $\alpha$  radiation (multilayer mirror monochromator,  $\lambda = 0.71073 \text{ \AA}$  resp.  $1.5418 \text{ \AA}$ ) at 100 K. Crystallographic programs used for structure solution and refinement were from SHELX -97.<sup>[3]</sup> The structures were solved by direct methods and were refined by using full-matrix least squares on  $F^2$  of all unique reflections with anisotropic thermal parameters for all non-hydrogen atoms, except disordered atoms of the lower occupancy in compound **4**. All hydrogen atoms bonded to silicon were refined isotropically. All hydrogen atoms bonded to carbons were refined isotropically using a riding model with  $U(\text{H}) = 1.5 U_{\text{eq}}$  for CH<sub>3</sub> groups and  $U(\text{H}) = 1.2 U_{\text{eq}}$  for all others, excluding the hydrogen atoms of compound **4** which were all refined isotropically.

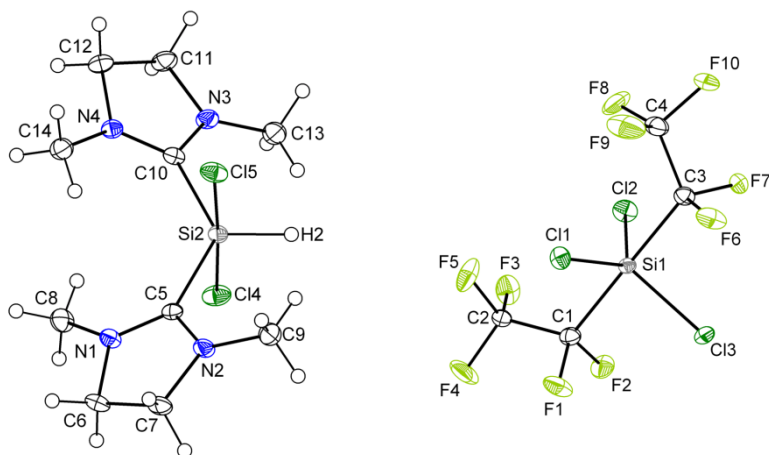
CCDC contains supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

The crystal data, refinement parameters and CCDC depositions numbers for all complexes are given in Table S1.

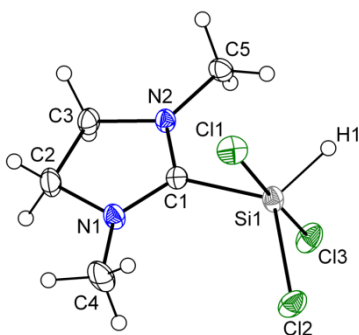
**Table S1.** Crystallographic parameters for compounds **4**, **5**, and **6**.

Parameter	<b>4</b>	<b>5</b>	<b>6</b>
Empirical formula	C <sub>14</sub> H <sub>21</sub> Cl <sub>5</sub> F <sub>10</sub> N <sub>4</sub> Si <sub>2</sub>	0.9 x C <sub>5</sub> H <sub>11</sub> Cl <sub>3</sub> N <sub>2</sub> Si 0.1 x C <sub>5</sub> H <sub>10</sub> Cl <sub>4</sub> N <sub>2</sub> Si	C <sub>5</sub> H <sub>12</sub> N <sub>2</sub> SiCl 2
Formula weight	668.78	236.88	199.16
Temperature [K]	100.0(1)	100.0(1)	100.0(1)
Radiation used	Cu-K $\alpha$	Mo-K $\alpha$	Mo-K $\alpha$
Crystal system	triclinic	orthorhombic	monoclinic
Space group	<i>P</i> -1	<i>Pbca</i>	<i>P2</i> <sub>1</sub> / <i>c</i>
a [Å]	8.1924(2)	13.05642(14)	9.9722(3)
b [Å]	12.5273(3)	10.62115(11)	12.2770(3)
c [Å]	13.0812(3)	14.80917(14)	7.76332(14)
$\alpha$ [°]	89.833(2)	90	90
$\beta$ [°]	81.713(2)	90	90.020(2)
$\gamma$ [°]	79.902(2)	90	90
Volume [Å <sup>3</sup> ]	1307.57(6)	2053.65(4)	950.45(4)
Z	2	8	4
$\rho_{\text{calc}}$ [mg/mm <sup>3</sup> ]	1.699	1.532	1.392
$\mu$ [mm <sup>-1</sup> ]	6.743	0.979	0.745
F(000)	672.0	972.0	416.0
Crystal size [mm <sup>3</sup> ]	0.38 × 0.10 × 0.09	0.26 × 0.24 × 0.18	0.16 × 0.14 × 0.11
2 $\theta$ range for data collection	6 to 144°	6 to 60°	6 to 60°
Reflections collected	22010	136389	56379
Independent reflections	5116	3005	2767
<i>R</i> (int)	0.0246	0.0375	0.0732
Data/restraints/parameters	5116/0/430	3005/0/125	2767/1/100
Goodness-of-fit on F <sup>2</sup>	1.101	1.184	1.057
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	0.0240	0.0289	0.0507
<i>R</i> <sub>w</sub> (all data) <sup>b</sup>	0.0625	0.0766	0.1323
Largest diff. peak/hole / eÅ <sup>-3</sup>	0.54/-0.34	0.44/-0.48	1.16/-0.78
CCDC deposition no.	965803	965804	965805

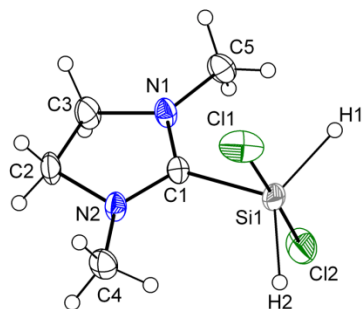
$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b R_w = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$



**Figure S1.** Atom labeling for the crystal structure of **4** (cation and anion are depicted independently).



**Figure S2.** Atom labeling for the crystal structure of **5**.



**Figure S3.** Atom labeling for the crystal structure of **6**.

### 3. References

- [1] a) B. Hoge, S. Steinhauer, J. Bader, N. Ignati'ev, *20th Symposium on Fluorine Chemistry, Kyoto, Japan 2012*; b) B. Hoge, S. Steinhauer, N. Ignati'ev, *6th European Silicon Days, Lyon, France 2012*; c) B. Hoge, S. Steinhauer, Manuscript in preparation.
- [2] T. Böttcher, B. S. Bassil, L. Zhechkov, T. Heine, G.-V. Rösenthaller, *Chem. Sci.* 2013, **4**, 77.
- [3] Sheldrick, G. M., *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2008, **64**, 112.