

**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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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 (CD_3CN) was distilled over 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}Si 59.63 MHz, ^{19}F 282.40 MHz, ^{13}C 75.47 MHz, ^1H 300.13 MHz) with positive shifts being downfield from the external standards (CCl_3F (^{19}F), $\text{Si}(\text{CH}_3)_4$ (^{29}Si , ^{13}C , ^1H)). The ^{13}C and ^{29}Si NMR shifts were acquired by ^1H , ^{13}C and ^1H , ^{29}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 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.^[1,2]

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 °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 °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. ^1H NMR (CD_3CN) δ = 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). ^1H , ^{13}C HMBC NMR (CD_3CN) $\delta(^1\text{H})/\delta(^{13}\text{C})$: 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}F NMR (CD_3CN): δ = -118.6 (s, 4F, $-\text{CF}_2-$), -75.8 (s, 6F, $-\text{CF}_3$). ^1H , ^{29}Si HMBC NMR (CD_3CN)

$\delta(^1\text{H})/\delta(^{29}\text{Si}) = 3.30/-125.4$ (s, -CH₃/Si), 3.85/-125.4 (s, -CH₂-/Si), 6.71/-125.4 (d, Si-H/Si, ¹J_{SiH} = 352 Hz). ¹⁹F, ²⁹Si HMBC NMR (CD₃CN) $\delta(^{19}\text{F})/\delta(^{29}\text{Si}) = -118.6/-96.6$ (d, -CF₂-/Si, ²J_{SiF} = 44 Hz).

Synthesis of NHC-SiCl₃H (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 ¹H NMR and as observed in XRD).

Yield: 50% (based on **1**). ¹H NMR (CD₃CN) $\delta = 3.30$ (s, 6H, -CH₃), 3.77 (s, 4H, -CH₂-), 6.80 (s, 1H, Si-H, ¹J_{SiH} = 393 Hz). ¹³C, ¹H HMBC (CD₃CN) $\delta(^{13}\text{C})/\delta(^1\text{H}) = 3.30/34.5$ (d, -CH₃/-CH₃, ¹J_{CH} = 140 Hz), 3.30/51.1 (, -CH₃/-CH₂-), 3.77/51.1 (d,m, -CH₂-/-CH₂-, ¹J_{CH} = 152 Hz), 3.30/173.1 (s, -CH₃/C_{carbene}), 3.77/173.1 (s, -CH₂/C_{carbene}), 6.80/173.1 (d, Si-H/C_{carbene}, ²J_{CH} = 8 Hz). ²⁹Si, ¹H HMBC NMR (CD₃CN) $\delta(^{29}\text{Si})/\delta(^1\text{H}) = 3.30/-104.5$ (s, -CH₃/Si), 6.80/-104.5 (d, -Si-H/Si, ¹J_{SiH} = 393 Hz). ²⁹Si, ¹H DEPT NMR (CD₃CN) $\delta = -104.5$ (d, ¹J_{SiH} = 393 Hz).

Synthesis of NHC-SiCl₂H₂ (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**). ^1H NMR (CD_3CN) δ = 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 (CD_3CN) $\delta(^1\text{H})/\delta(^{13}\text{C})$ = 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}Si NMR (CD_3CN) δ = -125.2 (t, $^1J_{\text{SiH}} = 333$ Hz). $^1\text{H}, ^{29}\text{Si}$ HMBC NMR (CD_3CN) $\delta(^1\text{H})/\delta(^{29}\text{Si})$ = 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/Si, $^1J_{\text{SiH}} = 333$ Hz). $^{29}\text{Si}, ^1\text{H}$ DEPT NMR (CD_3CN) δ = -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 α or Cu-K α radiation (multilayer mirror monochromator, $\lambda = 0.71073 \text{ \AA}$ resp. 1.5418 \AA) at 100 K. Crystallographic programs used for structure solution and refinement were from SHELX -97.^[3] 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 $U(H) = 1.5 U_{\text{eq}}$ for CH_3 groups and $U(H) = 1.2 U_{\text{eq}}$ 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.

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	4	5	6
Empirical formula	C ₁₄ H ₂₁ Cl ₅ F ₁₀ N ₄ Si ₂	0.9 x C ₅ H ₁₁ Cl ₃ N ₂ Si 0.1 x C ₅ H ₁₀ Cl ₄ N ₂ Si ₂	C ₅ H ₁₂ N ₂ SiCl
Formula weight	668.78	236.88	199.16
Temperature [K]	100.0(1)	100.0(1)	100.0(1)
Radiation used	Cu-K α	Mo-K α	Mo-K α
Crystal system	triclinic	orthorhombic	monoclinic
Space group	<i>P</i> -1	<i>Pbca</i>	<i>P2₁/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)
α [°]	89.833(2)	90	90
β [°]	81.713(2)	90	90.020(2)
γ [°]	79.902(2)	90	90
Volume [Å ³]	1307.57(6)	2053.65(4)	950.45(4)
Z	2	8	4
ρ_{calc} [mg/mm ³]	1.699	1.532	1.392
μ [mm ⁻¹]	6.743	0.979	0.745
F(000)	672.0	972.0	416.0
Crystal size [mm ³]	0.38 × 0.10 × 0.09	0.26 × 0.24 × 0.18	0.16 × 0.14 × 0.11
2 Θ 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 ²	1.101	1.184	1.057
<i>R</i> ₁ [I > 2 σ (I)] ^a	0.0240	0.0289	0.0507
<i>R</i> _w (all data) ^b	0.0625	0.0766	0.1323
Largest diff. peak/hole / eÅ ⁻³	0.54/-0.34	0.44/-0.48	1.16/-0.78
CCDC deposition no.	965803	965804	965805

^a $R_1 = \sum ||F_{\text{o}}| - |F_{\text{c}}|| / \sum |F_{\text{o}}|$. ^b $R_w = \{\sum [w(F_{\text{o}}^2 - F_{\text{c}}^2)^2] / \sum [w(F_{\text{o}}^2)^2]\}^{1/2}$

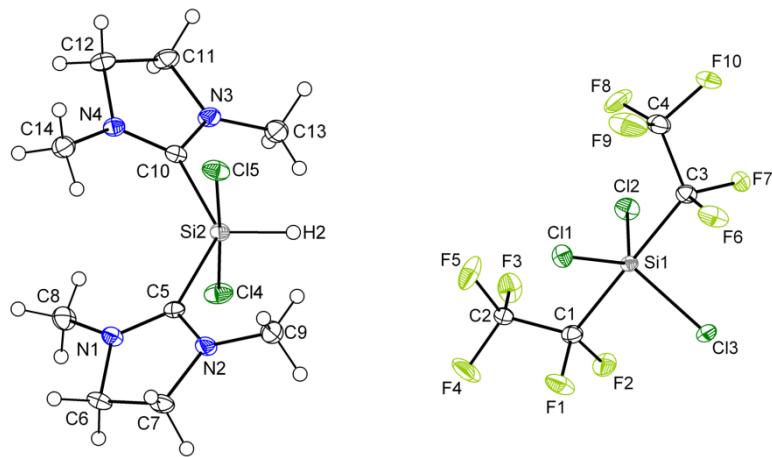


Figure S1. Atom labeling for the crystal structure of **4** (cation and anion are depicted independently).

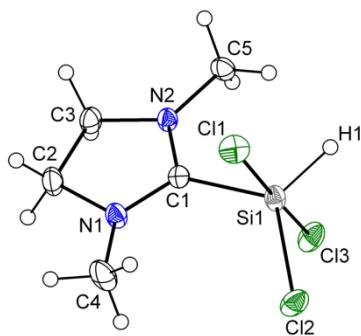


Figure S2. Atom labeling for the crystal structure of **5**.

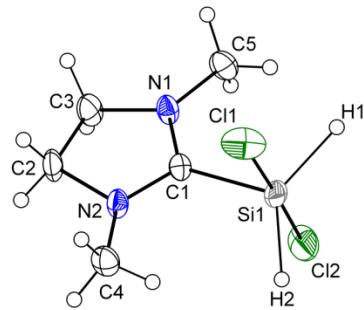


Figure S3. Atom labeling for the crystal structure of **6**.

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. Röschenhalar, *Chem. Sci.* 2013, **4**, 77.
- [3] Sheldrick, G. M., *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2008, **64**, 112.