

Communication

# Synthesis of a $\alpha$ -Chlorosilyl Functionalized Donor-Stabilized Chlorogermylene

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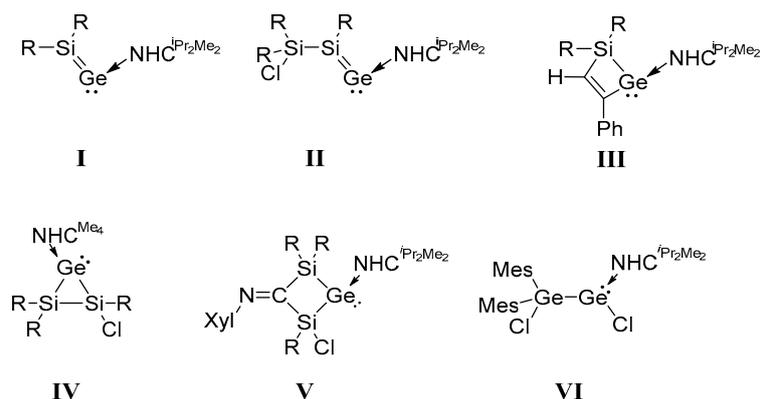
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**Abstract:** Peripherally functionalized low-valent main group species allow for the introduction/interconversion of functional groups without increasing the formal oxidation state of the main group center. Herein, we report a straightforward method for the incorporation of a  $\alpha$ -chlorosilyl moiety adjacent to the NHC-coordinated germanium(II) center.

**Keywords:** silylene; germylene; *N*-heterocyclic carbene; oxidative addition

## 1. Introduction

In recent years, the chemistry of the heavier analogues of carbenes (tetrylenes) has been expanded beyond mere synthetic curiosity [1–3] towards application in synthesis. Heavier carbene analogues are applied as a donor ligands in low-valent main group species [4,5] as well as in transition metal complexes [6,7]. An increasing number of examples show competitive catalytic activity in different organic transformations [8]. As the complexity of the tetrylenes increases with more intricate ligand architectures [9], functionalization protocols in the presence of uncompromised low-valent Group 14 centers conveniently allow for a comparatively straightforward diversification in the final stages of ligand synthesis. While the interconversion of functional groups is just beginning to emerge in the case of heavier multiple bonds [10], numerous examples have been reported for the heavier tetrylenes [11–15]. Recently, Scheschkewitz et al. have taken a similar approach with the synthesis of the multiply functional NHC-coordinated silagermylenes, **I** and **II** (Scheme 1) [16,17], which serve as precursors for cyclic NHC-coordinated germylens of type **III**, **IV**, and **V** under consumption of the Si=Ge bond, but retention of the low-valent germanium center (Scheme 1) [16,18,19]. The leaving group characteristics of the peripheral chloro functionality of **II** can be exploited for the incorporation of different organic substituents by treatment with organolithium reagents in order to fine-tune the steric requirements of the ligand scaffold of cyclic germylens of type **IV** [20,21]. Directly chloro-functionalized silylenes and germylens are readily converted to a variety of novel low-valent group 14 compounds by functional group interconversion at the low-valent tetrel center [22].

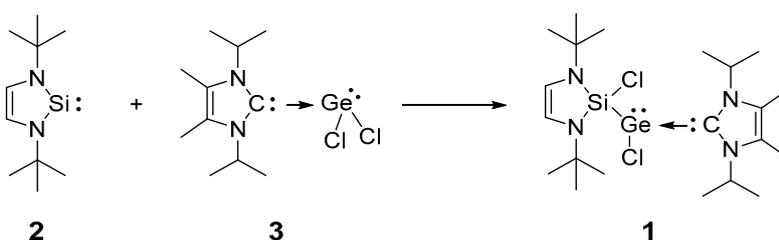


**Scheme 1.** Chemical structures of  $\alpha$ -chlorosilyl-functionalized silagermylenedene **I**, and  $\alpha$ -chloro-functionalized germylenes **II–IV** ( $R = \text{Tip} = 2,4,6\text{-}i\text{Pr}_3\text{C}_6\text{H}_2$ ,  $\text{NHC}^{i\text{Pr}_2\text{Me}_2} = 1,3\text{-diisopropyl-4,5-dimethylimidazol-2-ylidene}$ ,  $\text{NHC}^{\text{Me}_4} = 1,3,4,5\text{-tetramethylimidazol-2-ylidene}$ ,  $\text{Xyl} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ , and  $\text{Mes} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ ).

An additional leaving group adjacent to a chloro-functionalized heavier carbene center would in principle provide a precursor for the synthesis of further examples of heavier vinylidene such as **I** and **II**. The synthesis of an NHC-coordinated (chlorogermyl)chlorogermylene, **IV**, from NHC-coordinated diaryl germylene and NHC- or 1,4-dioxane coordinated dichlorogermylene has been reported by the groups of Baines and Tobitah [23,24]. Herein, we now report the synthesis of NHC-stabilized (chlorosilyl)chlorogermylene, **1**.

## 2. Results and Discussions

We anticipated that West's *N*-heterocyclic silylene, **2** [25] would insert into the Ge–Cl bond of the NHC-germanium(II)dichloride adduct **3** [26] as it is well known for the oxidative addition of different types of bonds e.g., C–Cl [27] and Ge–N [28]. Indeed, the reaction of **2** and **3** in a 1:1 ratio in toluene at room temperature afforded the NHC-stabilized (chlorosilyl)chlorogermylene **1** which was isolated as a crystalline compound (Scheme 2). We did not obtain any indication for the formation of donor–acceptor adducts between **2** and **3** or rearrangement products as often described for reactions of silylenes and germylenes [29,30].

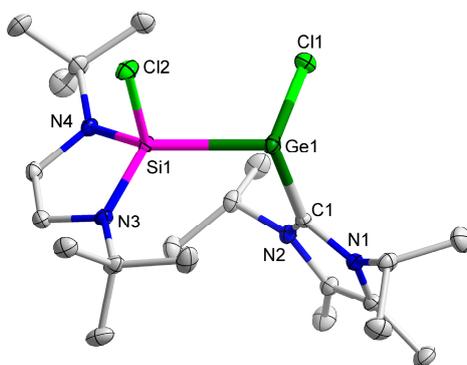


**Scheme 2.** Synthesis of **1**.

Compound **1** was characterized in solution state by NMR spectroscopy as well as in solid state by single crystal X-ray molecular structure determination. The insertion of the silylene into the Ge–Cl bond turns the germanium atom into a center of chirality. As a result the two diastereotopic C–H protons of  $\text{C}_2\text{N}_2\text{Si}$ -moiety give rise to two doublets at  $\delta = 5.87$  and  $6.03$  ppm ( $^1J_{(\text{H}, \text{H})} = 3.92$  Hz) in the  $^1\text{H}$  NMR. Similarly, the two *t*Bu groups show  $^1\text{H}$  NMR resonances at  $\delta = 1.29$  and  $1.65$  ppm. Hindered rotation can be excluded as the explanation for the doubling of these resonances. Despite the increased congestion about the germanium center, the NHC retains the local rotational  $\text{C}_2$ -symmetry in solution: the  $^1\text{H}$  NMR shows only a single septet for the two CH moieties of the isopropyl groups. In contrast,

there are again two signals for the adjacent diastereotopic methyl groups of the *N*-isopropyl moiety. In  $^{13}\text{C}\{^1\text{H}\}$  NMR, the carbenic carbon shows a resonance at  $\delta = 171.01$  ppm, which is similar to the chemical shifts observed for other NHC-coordinated Ge(II) compounds [18,19]. In  $^{29}\text{Si}\{^1\text{H}\}$  NMR, the singlet at  $\delta = -3.39$  ppm is strongly highfield shifted compared with that of the free *N*-heterocyclic silylene ( $\delta = +78.3$  ppm) [25]. Notably, even repeated crystallization of **1** did not yield NMR spectra uncontaminated by residual **2**, which led us to speculate about the reversibility of the oxidative Ge–Cl addition to the silylene. NMR at variable temperatures, however, did not show any temperature dependence of the sample composition.

Nonetheless, single crystals of **1** suitable for a X-ray diffraction study were obtained from saturated toluene solution at  $-20$  °C after one day. Compound **1** crystallizes in the monoclinic  $P2_1/c$  space group. However in the obtained single crystal X-ray diffraction data we did not see any residual electron density for the cocrystallization of **2** along with **1**. Analysis of molecular structure determination reveals the presence of  $\alpha$ -chlorosilyl moiety adjacent to the NHC-coordinated germanium(II) center; which was anticipated from the solution state structure (Figure 1). The Si–Ge bond length is 2.4969(7) Å which is close to reported Si(IV)–Ge(II) bond length [19]. The distance between carbenic carbon and germanium(II) center is 2.081(2) Å, which is slightly shorter than that of the corresponding NHC-coordinated germanium(II)dichloride (2.106(3) Å) [26].



**Figure 1.** Molecular structure of **1** at 30% probability level, all H-atoms were deleted for clarity. Selected bond lengths (Å) and bond angles (deg.): Ge1–C1 2.081(2), Ge1–Cl1 2.2891(8), Ge1–Si1 2.4969(7); Cl1–Ge1–Cl1 92.58(7), Cl1–Ge1–Si1 101.83(3), C1–Ge1–Si1 102.56(7).

### 3. Materials and Methods

#### 3.1. General Information

All manipulation were carried out under an argon atmosphere using either a Schlenk line technique or inside a GloveBox. All solvents were dried by Innovative Technology solvent purification system. Compounds **2** [25] and **3** [26] were prepared according to literature procedures. Benzene- $d_6$  was dried and distilled over potassium under argon. NMR spectra were recorded on a Bruker Avance III 300 MHz NanoBay NMR spectrometer (Bruker, Switzerland).  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were referenced to the peaks of residual protons of the deuterated solvent ( $^1\text{H}$ ) or the deuterated solvent itself ( $^{13}\text{C}\{^1\text{H}\}$ ).  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra were referenced to external  $\text{SiMe}_4$ .

#### 3.2. Experimental Details

**Synthesis of compound 1:** 25-mL dry and degassed toluene were added to a Schlenk flask containing **2** (0.242 g, 1.23 mmol) and **3** (0.4 g, 1.23 mmol) at  $-78$  °C. The mixture is brought to room temperature within one hour and stirred continuously for another two hours. Removal of the solvent in vacuum and washing of the solid residue with *n*-hexane was followed by extraction with 20 mL warm toluene. The resulting yellow solution was concentrated to about 15 mL and kept at  $-20$  °C for one day

to get bright yellow crystals of the desired compound, **1**, suitable for single crystal X-ray diffraction study. Despite apparently uniform crystals, a pure sample of compound **1** without free silylene **2** could not be obtained. Yield: 0.360 g (56% which include 13% of compound **2**).  $^1\text{H NMR}$  (300 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta = 1.13$  (d,  $^1J_{(\text{H}, \text{H})} = 7.02$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.24 (d,  $^1J_{(\text{H}, \text{H})} = 6.9$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.29 (s, 9H,  $\text{N}(\text{CH}_3)_3$ ), 1.51 (s, 6H,  $\text{CCH}_3$ ), 1.63 (s, 9H,  $\text{N}(\text{CH}_3)_3$ ), 5.74 (sept,  $^1J_{(\text{H}, \text{H})} = 7.02$  Hz, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 5.87 (d,  $^1J_{(\text{H}, \text{H})} = 3.92$  Hz, 1H,  $\text{CHCH}$ ) 6.03 (d, 1H,  $^1J_{(\text{H}, \text{H})} = 3.92$  Hz,  $\text{CHCH}$ ) (1.42 and 6.76 ppm refer to the resonances for compound **2**) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.4 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta = 10.35$  (2C,  $\text{CCH}_3$ ), 22.06 (4C,  $\text{CH}(\text{CH}_3)_2$ ), 31.97 (3C,  $\text{C}(\text{CH}_3)_3$ ), 32.15 (3C,  $\text{C}(\text{CH}_3)_3$ ), 51.97 (1C,  $\text{C}(\text{CH}_3)_3$ ), 52.49 (1C,  $\text{C}(\text{CH}_3)_3$ ), 54.07 (2C,  $\text{CH}(\text{CH}_3)_2$ ), 113.70 (1C,  $\text{CHCH}$ ), 115.26 (1C,  $\text{CHCH}$ ), 127.13 (2C,  $\text{CCH}_3$ ), 171.01 (1C,  $\text{NCN}$ ).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (59.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta = -3.39$  ppm.

### 3.3. X-ray Crystallographic Analysis

Single crystals of **1** were obtained from saturated toluene solution at  $-20$  °C. Intensity data were collected on a Bruker SMART APEX CCD diffractometer (Bruker, Germany with a  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073$  Å) at  $T = 182(2)$  K. The structures were solved by a direct method (*SHELXS* [31]) and refined by a full-matrix least square method on  $F^2$  for all reflections (*SHELXL*-2014 [32]). All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically. Crystallographic data (Supplementary Materials) were deposited at the Cambridge Crystallographic Data Center (CCDC; under reference number: CCDC-1587144) and can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>. X-ray crystallographic data for **1**:  $M = 520.15$ , monoclinic,  $P2_1/c$ ,  $a = 11.3853(3)$  Å,  $b = 13.1071(3)$  Å,  $c = 17.5390(5)$  Å,  $\beta = 96.2860(10)^\circ$ ,  $V = 2601.58(12)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc.}} = 1.328$  gcm<sup>-3</sup>,  $m = 1.444$  mm<sup>-1</sup>,  $2\theta_{\text{max}} = 54.20^\circ$ ,  $\text{measd.}/\text{unique refls.} = 48784/5747$  ( $R_{\text{int.}} = 0.0292$ ),  $\text{GOF} = 1.075$ ,  $R_1 = 0.0408/0.0471$  [ $I > 2\sigma(I)$ /all data],  $wR_2 = 0.1077/0.1112$  [ $I > 2\sigma(I)$ /all data], largest diff. peak and hole 3.152 and  $-0.604$  e.Å<sup>-3</sup>.

## 4. Conclusions

We have demonstrated a proof of principle study for the straightforward incorporation of a  $\alpha$ -chlorosilyl moiety adjacent to the donor-stabilized germanium(II) center. The resulting product features a 1,2-dichloro functionality and should therefore in principle be suitable as precursor for the targeted synthesis of NHC-coordinated silagermylenes, the heavier analogues of vinylidenes. So far, attempts to eliminate the two chloro substituents reductively were not met with success.

**Supplementary Materials:** The following are available online at [www.mdpi.com/2304-6740/6/1/6/s1](http://www.mdpi.com/2304-6740/6/1/6/s1), Cif, cif-checked, NMR spectra files.

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**Author Contributions:** David Scheschkewitz and Anukul Jana conceived and designed the experiments and wrote the paper; Debabrata Dhara performed the experiments; Volker Huch performed the XRD analysis.

**Conflicts of Interest:** The authors declare no conflict of interest.

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