# Synthesis of a Dichlorosilaimine Coordinated by an N-Heterocyclic Carbene from ArN(SiMe<sub>3</sub>)SiHCl<sub>2</sub>

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NHC-stabilized dichlorosilaimine ArN=Si(I*i*Pr)Cl<sub>2</sub> (**2**) (Ar=2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, I*i*Pr=1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) and disilane LSiHCl-SiCl<sub>2</sub>L (L=ArNSiMe<sub>3</sub>) (**3**) could be synthesized from the reaction of aminodichlorosilane ArN(SiMe<sub>3</sub>)SiHCl<sub>2</sub> (**1**) with I*i*Pr under different conditions. This represents the first route to the generation of donor-stabilized dichlorosilaimine from substituted chlorosilane in the presence of an NHC via dehydrosilylation.

Keywords silaimine, dehydrosilylation, silane, N-heterocyclic carbene

# Introduction

The chemistry of unsaturated silicon compounds (silylenes and silicon multiple-bonding species) has been of great interest to chemists throughout the last decades owing to their significant roles in the development of silicon chemistry.<sup>[1,2]</sup> Silaimines ( $R_2Si=NR$ ), silicon analogues of imines, are considered as one of the most intriguing topics in organosilicon chemistry.<sup>[2-9]</sup> With highly polarized  $\mathrm{Si}^{\delta^+} - \mathrm{N}^{\delta^-}$  double bond, silaimines are extremely reactive species. The first silaimines were reported independently by Wiberg<sup>[4a,4b]</sup> and Klingebiel<sup>[4c]</sup> in 1980's via salt elimination. Since then, a fair number of silaimines were isolated from direct reactions of silylenes towards organic azides<sup>[5,6b]</sup> and carbodiimides.<sup>[6a,6b]</sup> In 2012, Inoue and his co-worker isolated the zwitterionic silaimine from the reaction of silylene with  $(C_6F_5)_3B$ .<sup>[6c]</sup> Very recently, we reported the N-heterocyclic carbene (NHC)-stabilized vinylsila-imines<sup>[7]</sup> and dichlorosilaimine<sup>[8]</sup> through reactions of a donor-stabilized silvlene with alkynes and SiCl<sub>4</sub>, respectively. Subsequently, controlled oxidation of an NHC-stabilized phosphinosilylene Ar(SiMe<sub>3</sub>)NSi(NHC)-PPh<sub>2</sub> with dioxygen was reported to afford donor-stabilized dioxysilaimine and oxysilaimine.<sup>[9]</sup> However, direct access to silaimines is still restricted.

Substituted chlorosilanes are important building blocks in silicon chemistry. Cui's group and Roesky's group reported a dehydrohalogenation route for the generation of a series of silylenes by NHCs under very mild conditions from substituted chlorosilanes<sup>[10]</sup> and

HSiCl<sub>3</sub>.<sup>[11]</sup> Soon several silylenes have been isolated with similar methods by other groups.<sup>[12]</sup> Inoue's group recently reported an NHC-stabilized silyliumylidene ion by dehydrochlorination from chlorosilanes.<sup>[6d]</sup> Base-stabilized 1-hydrosilaimine ArN=SiH(NHC)N(SiMe<sub>3</sub>)-Ar could also be isolated from reactions of a less hindered N-heterocyclic carbene with substituted chlorosilanes.<sup>[13]</sup> To the best of our knowledge, there is no example of dichlorosilaimine which could be synthesized via dehydrosilylation by NHCs from substituted chlorosilanes.

Herein, we reported the synthesis of NHC-stabilized dichlorosilaimine  $ArN = Si(IiPr)Cl_2$  (2,  $Ar = 2,6-iPr_2-C_6H_3$ , IiPr = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) from the reaction of aminodichlorosilane  $ArN(SiMe_3)SiHCl_2$  (1) with an N-heterocyclic carbene IiPr. This is the first route to the synthesis of donor-stabilized dichlorosilaimine from substituted chlorosilane in the presence of an NHC via direct dehydrosilylation. In addition, we demonstrate that the reactions of 1 with IiPr are significantly influenced by the reaction conditions.

## Experimental

All operations were carried out under an atmosphere of dry argon or nitrogen by using modified Schlenck line and glovebox techniques. All solvents were freshly distilled from Na and degassed immediately prior to use. The <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectroscopic data were recorded on Bruker Mercury Plus 300, 400 and 600 MHz

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# COMMUNICATION.

NMR spectrometers.  $ArN(SiMe_3)Si(IiPr)Cl (1)^{[13a]}$  and  $IiPr^{[15]}$  were synthesized according to published procedures.

2: A solution of 1 (0.35 g, 1 mmol) in THF (5 mL) was added slowly to a solution of IiPr (0.27 g, 1.5 mmol) in THF (5 mL) at -78 °C. The color of the solution soon changed from colorless to yellow. The mixture was allowed to warm to room temperature and stirred overnight. After filtration and removal of solvents, the remaining residue was washed successively with hexane (5 mL) and Et<sub>2</sub>O (10 mL) to afford white powder 2 (0.11 g, 24.2%). m.p. 197-199 °C; <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$ : 0.95 [d, J=7.0 Hz, 12H,  $CH(CH_3)_2$ ], 1.34 (s, 6H, CCH<sub>3</sub>), 1.56 [d, J = 6.8 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>], 4.13 [m, 2H, Ar-CH(CH<sub>3</sub>)<sub>2</sub>], 6.62 [m, 2H, N-CH(CH<sub>3</sub>)<sub>2</sub>], 7.09 (m, 1H, Ar-H), 7.39 (d, J=7.5 Hz, 2H, Ar-H); <sup>13</sup>C NMR (100.61 MHz,  $d_8$ -THF)  $\delta$ : 10.69 (=CCH<sub>3</sub>), 21.08 [CH(CH<sub>3</sub>)<sub>2</sub>], 24.16 [CH(CH<sub>3</sub>)<sub>2</sub>], 28.47 [Ar-CH(CH<sub>3</sub>)<sub>2</sub>], 51.73 [NCH(CH<sub>3</sub>)<sub>2</sub>], 116.06, 122.01, 129.73, 139.90, 145.78 (Ar-C), 145.99 (NCN); <sup>29</sup>Si NMR (79.49 MHz, *d*<sub>8</sub>-THF) δ: -107.03.

**3**: A solution of **1** (0.35 g, 1 mmol) in  $Et_2O$  (5 mL) was added slowly to a solution of IiPr (0.18 g, 1 mmol) in Et<sub>2</sub>O (5 mL) at room temperature. Soon a white suspension formed. The mixture was allowed to stir for 1 h. After filtration, the residue was washed with cold CHCl<sub>3</sub> (3 mL $\times$ 2) to yield white power 3 (0.22 g, 66.7%). Sublimated at 219 °C (1 mbar); <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ: 0.17 (s, 9H, Me<sub>3</sub>Si), 0.28 (s, 9H, Me<sub>3</sub>Si), 1.15-1.42 (m, 24H, Me<sub>2</sub>CH), 3.66 (m, 1H, CHMe<sub>2</sub>), 3.76 (m, 2H, CHMe<sub>2</sub>), 3.98 (m, 1H, CHMe<sub>2</sub>), 5.47 (s, 1H, Si-H), 7.05 (m, 6H, Ar-H); <sup>13</sup>C NMR (100.61 MHz, C<sub>6</sub>D<sub>6</sub>) δ: 1.01, 2.36, 2.59, 23.88, 24.30, 24.35, 25.02, 25.24, 26.01, 26.67, 26.80, 27.34, 27.42, 28.07, 28.27, 29.70, 77.20, 124.13, 124.26, 124.36, 125.90, 126.00, 146.83, 147.58,162.35; <sup>13</sup>C NMR (100.61 MHz, CDCl<sub>3</sub>) *δ*: 1.64, 2.49, 2.70, 24.01, 24.41, 24.53, 25.17, 25.40, 26.15, 26.91, 27.01, 27.44, 27.52, 28.06, 28.22, 28.42, 30.53, 124.23, 124.39, 124.48, 126.00, 126.08, 138.63, 143.13, 146.87, 147.52, 147.66; <sup>29</sup>Si NMR (59.62 MHz, CDCl<sub>3</sub>) δ: -19.25.

#### **Results and Discussion**

We have recently reported reactions of ArN(SiMe<sub>3</sub>)-SiHCl<sub>2</sub> **1** with different NHCs.<sup>[13,14a]</sup> And the products were influenced by steric hindrance of NHCs and reaction conditions. Donor-stabilized silylene Ar(SiMe<sub>3</sub>)-NSiCl(*Ii*Pr) (**A**) was synthesized from dropping ArN-(SiMe<sub>3</sub>)SiHCl<sub>2</sub> **1** into two equivalents of *Ii*Pr<sup>[15]</sup> at -78 °C in THF.<sup>[14a]</sup> To examine the effects of reaction condition on products, we changed the ratios of the reactants. It was found that dropping **1** into 1.5 equiv. of *Ii*Pr in THF from low temperature to ambient temperature led to a complicated mixture. Analysis of the soluble materials by proton NMR spectroscopy indicated the formation of **A** and a different species **2** with a ratio of 1 : 0.47. **2** was isolated as white powder in 24.2% yield (Scheme 1).

Scheme 1 Synthesis of 2 and 3



*Ii*Pr = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene

a) **1** to l/Pr (1 : 1.5), THF, –78  $\,^{\circ}\mathbb{C}$  to r.t., overnight; b) **1** to l/Pr (1 : 1), Et\_2O, r.t., 1 h

Compound **2** is air and moisture sensitive, and it is soluble in THF and insoluble in *n*-hexane. **2** has been fully characterized by <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectra. From the NMR spectra, **2** was identified as NHC-stabilized dichlorosilaimine  $ArN = SiCl_2(IiPr)$ , which was first reported by our group from the reaction of silylene **A** and SiCl<sub>4</sub> in *ca*. 21% yield.<sup>[8]</sup>

The proton NMR spectrum of **2** indicates the disappearance of the SiMe<sub>3</sub> group and the presence of one Ar ring and one *Ii*Pr group in the structure. The <sup>13</sup>C NMR resonance for the carbene carbon atom in **2** occurs at  $\delta$  145.99, similar to those found in the NHC $\rightarrow$ Si donor-acceptor complexes.<sup>[7-9,12-14]</sup> The <sup>29</sup>Si spectrum in  $d_8$ -THF for the central silicon atom exhibits a singlet signal at  $\delta$  –107.03. The multinuclear NMR is in good agreement with the values reported in the literature.<sup>[8]</sup>

In order to improve the yield of **2**, various experimental conditions (different solvents, temperatures, stoichiometries and addition sequences) have been examined. In most cases, it was impossible to isolate pure products even from repeated crystallizations from different solvents. Nevertheless, addition of a solution of **1** to one equivalent of I*i*Pr in Et<sub>2</sub>O at room temperature afforded disilane **3** as white powder in 66.7% yield after workup (Scheme 1). **3** was previously reported from the reaction of **1** and I*t*Bu<sup>[16]</sup> [1,3-bis(*tert*-butyl)imidazol-2-ylidene] in a molar ratio of 2: 1,<sup>[13a]</sup> but has not been structurally characterized.

Compound **3** is air and moisture sensitive, and exhibits high thermal stability in the solid state, as indicated by its high melting point. **3** has been fully characterized by multinuclear NMR and X-ray single-crystal analysis. The <sup>1</sup>H NMR spectrum of **3** exhibits a singlet at  $\delta$  5.47 (<sup>1</sup>*J*<sub>Si-H</sub>=247.15 Hz) for the Si-*H* proton, and two singlet resonances at  $\delta$  0.17 and 0.28 for SiMe<sub>3</sub>. Single crystals of **3** suitable for an X-ray diffraction study were obtained from toluene at ambient temperature. The X-ray crystal structure analysis confirmed compound **3** to be a disilane, consisting of two tetracoordinated silicon atoms attached respectively with one

Ar(SiMe<sub>3</sub>)N ligand (Figure 1). The Si1-N1 (1.7170(17) Å) bond length and Si3-N2 1.7157(17) bond length were shorter than the average value of Si2-N1 and Si4-N2 bond lengths (1.7762 Å), but in the range of Si-N single bond. The Si1-Si3 bond length (2.3680(8) Å) was comparable to the Si-Si single bond value reported in the literatures (2.36-2.46 Å).<sup>[17]</sup> The four atoms N1, Si1, Si3 and N2 were almost coplanar with the torsion angle N1-Si1-Si3-N2 (-172.98(9)°).



Figure 1 Ortep drawing of 3 with ellipsoids given at the 50% probability level. Carbon bound hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), angles (°) and torsion angles (°): N1-C1 1.472(2), N1-Si1 1.7170(17), N1-Si2 1.7733(18), N2-C16 1.468(2), N2-Si3 1.7157(17), N2-Si4 1.7792(18), Si1-Si3 2.3680(8), Si1-H1a 1.41(3), Si1-Cl1 2.0887(8), Si3-Cl3 2.0614(9), Si3-Cl2 2.0753(8), C1-N1-Si1 116.47(13), C1-N1-Si2 115.47(12), Si1-N1-Si2 127.95(10), C16-N2-Si3 118.57(13), C16-N2-Si4 117.80(12), Si3-N2-Si4 123.58(9), N1-Si1-Si3 117.41(6), N2-Si3-Si1 117.03(6), N1-Si1-Si3-N2 172.98(9).

The most plausible explanation for the formation of **2** may proceed through the intermediate **M**, with a hypervalent silicon centre, followed by the elimination of Me<sub>3</sub>SiH to give the final product (Scheme 2, path a).

Scheme 2 The proposed pathway for the formation of 2 and 3



While the formation of **3**, as with the previously reported literature,<sup>[10]</sup> may involve the initial generation of the transient silylene N [ArN(SiMe<sub>3</sub>)SiCl] via a dehydrochlorination reaction with *li*Pr, followed by insertion into the Si-H or Si-Cl single bond of another molecule of **1** (Scheme 2, path b).

#### Conclusions

In summary, we have shown that reaction of 1 with *Ii*Pr yielded NHC-stabilized dichlorosilaimine 2 and disilane 3 in different reaction conditions. This represents the first approach for the generation of donor-stabilized dichlorosilaimine from substituted chlorosilane via direct dehydrosilylation in the presence of an NHC. Reactivity studies of chlorosilanes and compound 2 are currently in progress.

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