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## Base-Stabilized Silimine and its Donor-Free Dimer Derived from the Reaction of NHC-Supported Silylene with SiCl<sub>4</sub><sup>†</sup>

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**Reaction of the N-heterocyclic carbene (NHC)-stabilized silylene ArN(SiMe<sub>3</sub>)Si(iPr)Cl (**1**, Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, *i*Pr = 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene) with SiCl<sub>4</sub> resulted in the formation of the three different products NHC-stabilized dichlorosilimine ArN=Si(iPr)Cl<sub>2</sub> (**2**), aminotrichlorosilane ArN(SiMe<sub>3</sub>)SiCl<sub>3</sub> (**3**) and silimine dimer (ArNSiCl<sub>2</sub>)<sub>2</sub> (**4**) under different conditions. The products can be controlled by reaction conditions. Compound **2** is the first example of less bulky NHC-supported silimines via the reaction of a silylene with SiCl<sub>4</sub>.**

### Introduction

Silylenes, as the heavier analogues of carbenes, have attracted much attention in the past two decades on account of their fundamental interest and potential applications in transition metal catalysis.<sup>1</sup> Since the first stable N-heterocyclic silylene (NHSi) was reported by West group<sup>2</sup> in 1994, stable silylenes have emerged as versatile building blocks for novel organosilicon compounds, which were otherwise difficult to access with conventional methods.<sup>3-5</sup> Studies on the formation of silimines (R<sub>2</sub>Si=NR) are among the most fascinating topics in organosilicon chemistry.<sup>6</sup> As the silicon analogues of imines, silimines are considered to be as extremely reactive species arising from the highly polarized Si<sup>δ+</sup>-N<sup>δ-</sup> double bond. The first silimines were reported independently by Wiberg<sup>7a,7b</sup> and Klingebiel<sup>7c</sup>. Since then, a handful of silimines were synthesized from the direct reactions of silylenes with organic azides<sup>8,9b</sup> and carbodiimides.<sup>9</sup> Our group reported on a donor-stabilized 1-hydrosilimine<sup>10a</sup> via the reaction of ArN(SiMe<sub>3</sub>)SiHCl<sub>2</sub> (Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) and IMe<sub>4</sub> (IMe<sub>4</sub> = 1,3,4,5-tetramethylimidazol-2-ylidene) in 2011. Recently, we reported a series of NHC-stabilized vinylsilimines via reactions of a

donor-stabilized aminochlorosilylene and alkynes.<sup>10b</sup> However, direct methods for the synthesis of silimines are still restricted, and silimines with less bulky terminal groups are quite rare. In addition, the reactions of silylenes with silicon tetrachloride or halosilanes, in general, underwent Si-X (X = Cl, Br) or Si-H insertions<sup>11</sup> to give disilanes, which would be promising precursors for functionalized disilenes and novel low-coordinated silicon species via reduction reactions.<sup>12</sup> Thermal<sup>13</sup> and base-induced<sup>14</sup> disproportionation of disilanes to silylenes and silanes have also been reported in the literature. Nevertheless, to the best of our knowledge, there are no example of silimines prepared by reaction of silylenes with SiCl<sub>4</sub>.

Herein, we reported an NHC-stabilized silimine and its base-free dimer via the reaction of an NHC-stabilized silylene ArN(SiMe<sub>3</sub>)SiCl(iPr)<sup>14a</sup> (**1**, Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, *i*Pr = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) with SiCl<sub>4</sub>. Furthermore, we demonstrate that the reactions of **1** with SiCl<sub>4</sub> are significantly influenced by the solvents, temperatures and addition sequences. This represents the first approach for the generation of silimines via reactions of silylene and SiCl<sub>4</sub>.

### Results and Discussion

We have recently reported the synthesis of the NHC-stabilized aminochlorosilylene Ar(SiMe<sub>3</sub>)NSiCl(iPr) (**1**). It was anticipated that removal of the *i*Pr coordinated to the Si(II) center would lead to the corresponding donor-free aminochlorosilylene or its oligomer by the reaction of **1** with suitable Lewis acids.<sup>10c</sup> We examined the reaction of **1** with SiCl<sub>4</sub>. Unexpectedly, the products varied largely depending on the reaction conditions (Scheme 1). Treatment of **1** with SiCl<sub>4</sub> in Et<sub>2</sub>O at room temperature resulted in the rapid formation of a new species **2** as white precipitate in 21.2% yield (Scheme 1, path a). Analysis of the soluble materials by proton NMR spectroscopy indicated a complicated mixture containing the adduct *i*Pr-SiCl<sub>4</sub>.

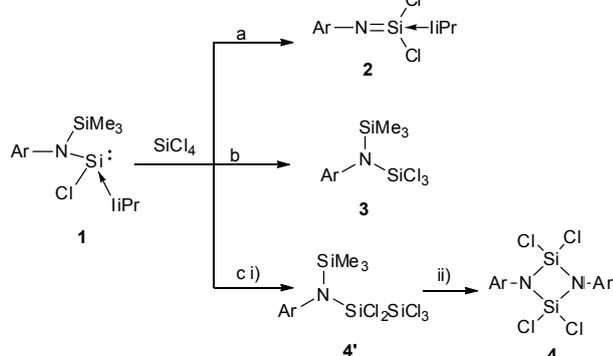
Compound **2** is air and moisture sensitive, and slowly decomposed completely in C<sub>6</sub>D<sub>6</sub> at 70 °C. It is soluble in THF and insoluble in *n*-hexane. **2** has been fully characterized by

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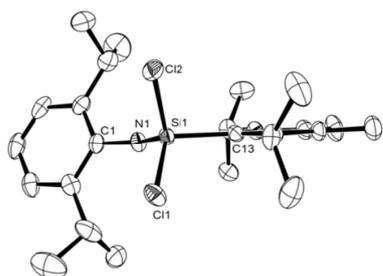
multinuclear NMR spectroscopy, elemental analysis and an X-ray single-crystal analysis. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **2** indicate the disappearance of the  $\text{SiMe}_3$  group. The  $^{13}\text{C}$  NMR signal for the carbene carbon atom in **2** appears at  $\delta$  145.99 ppm, consistent with those found in the  $\text{NHC}\rightarrow\text{Si}$  donor-acceptor complexes.<sup>5,10</sup> The  $^{29}\text{Si}$  resonance in  $d^8$ -THF occurs for the central silicon atom at  $\delta$  -107.03 ppm, similar to that for the NHC-supported silaimine ( $\delta$  -107.07 ppm)<sup>9b</sup>.



Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, NHC = 1,3-*i*Pr<sub>2</sub>-4,5-Me<sub>2</sub>-imidazol-2-ylidene

a) Et<sub>2</sub>O, rt, 2 h; b) SiCl<sub>4</sub> (excess) to **1**, hexane, rt, overnight; c) i) **1** to SiCl<sub>4</sub> (1:1), hexane, rt, overnight; ii) toluene, 80 °C, 16 h.

**Scheme 1** Synthesis of **2**, **3** and **4**.



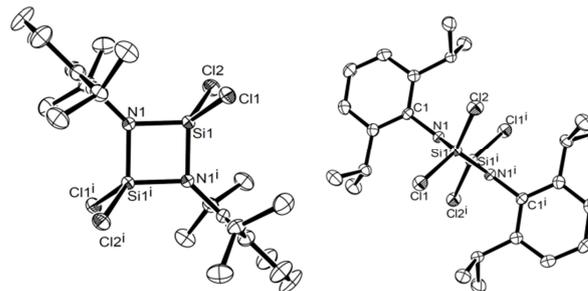
**Fig. 1** Ortep drawing of **2** with ellipsoids given at the 50% probability level. Hydrogen atoms and the solvent molecule have been omitted for clarity. Selected bond lengths (Å), angles (deg) and torsion angles (deg): Si1–N1 1.570(3), Si1–C13 1.914(3), Si1–Cl2 2.1002(14), Si1–Cl1 2.0997(13), N1–C1 1.385(4), N1–Si1–C13 112.03(13), N1–Si1–Cl2 115.69(10), C13–Si1–Cl1 102.16(9), N1–Si1–Cl1 118.47(11), C13–Si1–Cl2 105.64(10), Cl2–Si1–Cl1 101.13(5), C1–N1–Si1 149.4(2), C13–Si1–N1–C1 172.5(4)

Single crystals of **2** suitable for an X-ray diffraction study were obtained from a mixture of the solvents of toluene and THF. The X-ray crystal structure analysis confirmed **2** to be an NHC-stabilized dichlorosilaimine, consisting of a tetra-coordinated silicon atom attached two chlorine atoms, one nitrogen atom from the imine moiety, and one carbon atom from the carbene (Fig. 1). The central silicon atom has adopted a tetrahedral geometry. The Si1–N1 bond length (1.570(3) Å) was comparable to the Si=N values reported in the literature (1.5329–1.678(2) Å),<sup>8d,15</sup> and as long as the Si=N bond length in Wiberg' silaimine *t*Bu<sub>2</sub>Si=N–Si*t*Bu<sub>3</sub>.<sup>7c</sup> The Si1–C13 bond length (1.914(3) Å) was similar to the structurally characterized NHC-stabilized silaimines (1.917(5) – 1.953(2) Å),<sup>9b</sup> and was significantly shorter than that in **1** (2.0023(19) Å). The N1–C1 bond length (1.385(4) Å) was remarkably shorter than the C–N single bond in **1** (1.443(2) Å), thus indicating an interaction

between the N electrons and the aryl ring. As with all the reported silaimines, the C1–N1–Si1 bond angle (149.4(2) °) was significantly larger than the C–N–C bond angles in imines due to the highly polarized Si=N double bonds. The most notable structural feature of **2** is that the carbene ring is almost coplanar with the four atoms C13, Si1, N1, C1, with the torsion angles C13–Si1–N1–C1 (172.5(4) °). And the aryl ring is nearly perpendicular to the NHC plan. That probably is the reason for the shortest Si1–C13 coordination bond, which stabilizes the less bulky dichlorosilaimine using the minimum steric hindrance NHC. Compound **2** represents the first example of NHC-stabilized dichlorosilaimines via the reaction of a silylene with SiCl<sub>4</sub>.

In order to improve the yield of **2**, the less polarized solvent *n*-hexane was employed. Unexpectedly, compound **3** was obtained in 91.4% yield from the addition of an excess of SiCl<sub>4</sub> to **1** in *n*-hexane at ambient temperature (Scheme 1, path b). Compound **2** was undetected, and the coproduct was the adduct *i*Pr–SiCl<sub>4</sub> as a white precipitate. **3** is soluble in *n*-hexane, toluene and THF, with high thermal stability in solution, with no change observed in refluxing toluene for two days. Compound **3** has been fully characterized by multinuclear NMR, which is in good agreement with the values reported in the literature.<sup>16</sup>

Nevertheless, when the suspension of **1** in *n*-hexane was added to one equiv of SiCl<sub>4</sub> solution in *n*-hexane at ambient temperature, the products became complicated. The reaction resulted in the formation of *i*Pr–SiCl<sub>4</sub> in the white precipitates as well. Removal the solvents of the filtrate afforded a colorless, solid mixture, containing **3**, disilane **4'** and undefined coproducts, which were difficult to isolated owing to the similar solubility. Compound **4'** was characterized by multinuclear NMR spectroscopy. Heating the mixture in C<sub>6</sub>D<sub>6</sub> at 75 °C for 12 hours led to the formation of a new species **4** in good yield (Scheme 1, path c), while **4'** disappeared. The signal of Me<sub>3</sub>SiSiCl<sub>3</sub> could be detected at  $\delta$  0.29 ppm.<sup>18</sup>



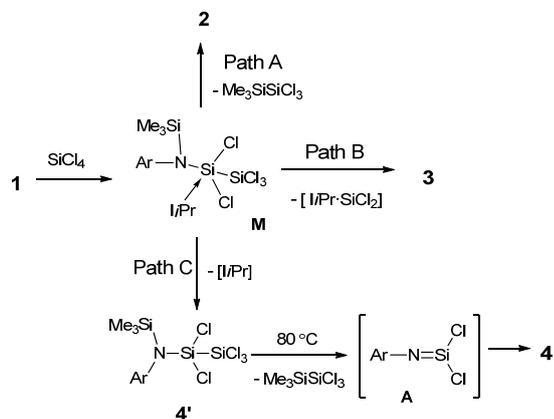
**Fig. 2** Ortep drawing of **4** with ellipsoids given at the 50% probability level (left: top view; right: side view). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), angles (deg) and torsion angles (deg): Si1–N1 1.7170(15), N1–Si1 1.7181(15), Si1–Cl1 2.0280(14), Si1–Cl2 2.0298(12), Si1–Si1' 2.4704(14), N1–C1 1.447(2), N1–Si1–N1' 88.03(7), N1–Si1–Cl1 116.20(6), N1–Si1–Cl2 115.80(5), Si1–N1–Si1' 91.97(7), N1'–Si1–N1–C1 -179.27(19), Si1'–Si1–N1–C1 -179.27(19), N1'–Si1–N1–Si1' 0.0.

Compound **4** is air and moisture sensitive, and is soluble in THF and insoluble in *n*-hexane. **4** has been identified as the dimer of ArN=SiCl<sub>2</sub> by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectroscopy, elemental analysis and an X-ray single-crystal analysis. The  $^1\text{H}$  NMR spectrum of **4** revealed the absence of the  $\text{SiMe}_3$  group

and carbene moiety. The  $^{29}\text{Si}$  NMR spectrum in  $d^8$ -THF of **4** exhibits one resonance at  $\delta$  -43.15 ppm, which is noticeably lowfield shifted compared to that observed in **2**, indicating the absence of NHC coordination.

Single crystals of **4** were obtained from toluene at ambient temperature. The X-ray crystal structure analysis confirmed **4** to be a dimer of dichlorosilaimine, consisting of a planar four-membered  $\text{Si}_2\text{N}_2$  central ring, on which two silicon atoms respectively were attached to two chlorine atoms and two nitrogen atoms from the amine moiety (Figure 2). The structure of **4** exhibits high symmetry. The four-membered  $\text{Si}_2\text{N}_2$  ring is almost square (the torsion angle  $\text{N1}^i\text{-Si1-N1-Si1}^i = 0.0^\circ$ ), with the very similar Si-N bond lengths (1.7170(15) Å and 1.7181(15) Å) and bond angles ( $\text{N1-Si1-N1}^i 88.03(7)^\circ$  and  $\text{Si1-N1-Si1}^i 91.97(7)^\circ$ ). The two aryl rings are almost coplanar and both perpendicular to the  $\text{Si}_2\text{N}_2$  plane. To our knowledge, the distance between Si1 and Si1<sup>i</sup> (2.4704(14)) is shorter than that in the reported  $\text{Si}_2\text{N}_2$  unit (2.48-2.79 Å).<sup>17</sup>

The formation of **2** ~ **4** prompted us to investigate the effects of experimental conditions (solvents, temperature, time, and addition sequences) on the reaction mechanism. In most cases, we failed to isolate pure products even from repeated crystallizations from different solvents. In spite of this, it was still found that **2** could be detected in polar solvent, such as THF, Et<sub>2</sub>O and toluene, together with **3**,  $\text{I}^i\text{Pr-SiCl}_4$ ,  $\text{Me}_3\text{SiSiCl}_3$  and other undefined impurities. Reduction of the temperatures increased the complexity of products. And prolongation of the reaction time led to the disappearance of **2**. However, **2** was undetected under various conditions when the nonpolar solvent *n*-hexane was employed. In addition, the reaction of **2** and  $\text{SiCl}_4$  led to the formation of  $\text{I}^i\text{Pr-SiCl}_4$  and mixture of  $(\text{ArN}=\text{SiCl}_2)_n$  ( $n \neq 2$ ). These experiments suggest that **2** and **4** were formed via different mechanisms.



**Scheme 2** The proposed three reaction pathways for the reactions of **1** with  $\text{SiCl}_4$ .

Although the mechanism is unclear, we proposed the formation of **2**, **3** and **4** may involve the initial generation of the hypervalent silicon intermediate NHC-coordinated disilane **M** via a Si-Cl insertion reaction (Scheme 2). Compound **2** can be viewed as the elimination product from **M** through loss of  $\text{Me}_3\text{SiSiCl}_3$  (path A). The formation of **3** is supported by the previous observation that disilanes easily proceeded through Si-Si bond cleavage and disproportionation in the presence of a Lewis base (path B).<sup>14</sup> While the extrusion of  $\text{I}^i\text{Pr}$  moiety from

**M** leads to the formation of **4'**, which was facilitated to eliminate  $\text{Me}_3\text{SiSiCl}_3$  by high temperature to give **A** followed by its dimerization (path C). The adduct  $\text{I}^i\text{Pr-SiCl}_2$  and free  $\text{I}^i\text{Pr}$  could react with other substrates in the system such as  $\text{SiCl}_4$  or  $\text{Me}_3\text{SiSiCl}_3$  to give the final coproduct  $\text{I}^i\text{Pr-SiCl}_4$ .

## Conclusions

In summary, the reactions of NHC-stabilized chloroaminosilylene **1** with  $\text{SiCl}_4$  afforded several different products under different reaction conditions. Compound **2** represents a rare example of an NHC-stabilized silaimine with both a less hindered terminal group and minimum NHC donor. Remarkably, **2** was isolated without metal, azides or carbodiimides under very mild conditions. Compound **4** is a dimer of silaimine with less steric hindrance, and possesses high symmetry consisting of a square bicyclic  $\text{Si}_2\text{N}_2$  central ring. Reactivity studies of the two compounds and isolation of other products in the reaction systems are currently in progress.

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