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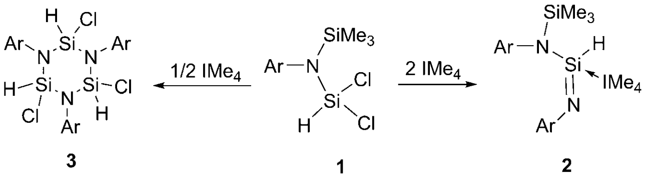
Synthesis of a Base-Stabilized 1-Hydrosilanimine via NHC-Mediated Dehydrohalogenation of Hydrochlorosilane

Haiyan Cui and Chunming Cui*[a]

In recent years, unsaturated silicon compounds (silylenes and silicon multiple-bonding species) have attracted much attention owing to their significant roles in the development of silicon chemistry.[1] Silanimines ($R_2Si=NR$), as silicon analogues of imines, are, in general, short-lived and highly reactive species in the absences of efficient protecting groups on both the silicon and nitrogen atoms.[2] By taking advantage of donor–acceptor stabilization concepts, a fair number of donor-stabilized silanimines have been isolated and structurally characterized since the first isolable silanimine was reported in 1986.[3,4] It is well-known that organosilicon hydrides have been widely used as hydrosilylation reagents in organic synthesis. However, unsaturated silicon hydrides, in which the hydride ligands are bonded to an unsaturated silicon atom, are extremely rare.[5] The lack of these species may be related to their intrinsic high reactivity arising from a reactive hydride ligand being attached to the unsaturated silicon atom. Among these, hydrosilanimines ($RHSi=NR$) are interesting and attractive synthetic targets because of their fundamental interest considering the relative stability of hydrosilanimines and their corresponding silylene isomers (RSiNHR).[6] Furthermore, it has been recently shown that transition-metal–hydrosilanimine complexes are useful for some stoichiometric and catalytic transformations.[7] However, stable hydrosilanimines are still elusive, presumably owing to their high reactivity and lack of synthetic methods for their synthesis.

Herein, we report the first donor-stabilized hydrosilanimine prepared by the reaction of $RSiHCl_2$ (**1**, $R=Ar(SiMe_3)N^-$, $Ar=2,6\text{-}i\text{Pr}_2C_6H_3$) with N-heterocyclic carbenes (NHCs; Scheme 1). In addition, we demonstrate that the reactions of **1** with NHCs are significantly influenced by the steric effects of the substituents on the NHC nitrogen atoms.



Scheme 1. Synthesis of **2** and **3**. IMe_4 = 1,3,4,5-tetramethylimidazol-2-ylidene.

We and others have previously reported NHC-mediated dehydrochlorination reactions for the generation of stable and transient silylenes.[8] To extend that methodology, we examined the reactions of the silylamino-substituted dichlorosilane $RSiHCl_2$ (**1**) with NHCs. As previously observed in the reactions of various N-heterocyclic chlorosilanes with NHCs,[8a] the products varied largely depending on the reaction conditions and the substrates employed. Therefore, it is essential to probe the steric effects of NHCs on the reaction. Thus, the less-hindered 1,3,4,5-tetramethylimidazol-2-ylidene (IMe_4) and the bulky 1,3-bis(*tert*-butyl)imidazol-2-ylidene ($ItBu_2$) were chosen for this study.[9] The reaction of **1** with one equivalent of IMe_4 in C_6D_6 at room temperature gave a complicated mixture of products as indicated by NMR analysis. However, unexpectedly, the reaction of **1** with two equivalents of IMe_4 in tetrahydrofuran at low temperature gave 1-hydrosilanimine **2** (Scheme 1) as yellow crystals in 26% yield along with some insoluble materials. Compound **2** is air and moisture sensitive, and it is soluble in common hydrocarbon solvents such as *n*-hexane and toluene. The proton NMR spectrum of **2** indicated the presence of one Si–*H* ($\delta=6.21$ ppm, $^1J_{Si\text{-}H}=218$ Hz) bond, two Ar rings, one $SiMe_3$ group, and one IMe_4 group in the structure. The detailed structure of **2** was finally determined by single-crystal X-ray analysis.

X-ray structural analysis of **2** revealed that it was an NHC-stabilized 1-hydrosilanimine (Figure 1). The central silicon atom was four-coordinate and adopted a distorted

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[a] H. Cui, Prof. Dr. C. Cui
State Key Laboratory of Elemento-organic Chemistry
Nankai University
Tianjin, 300071 (China)
Fax: (+86)-22-23503461
E-mail: cmcui@nankai.edu.cn

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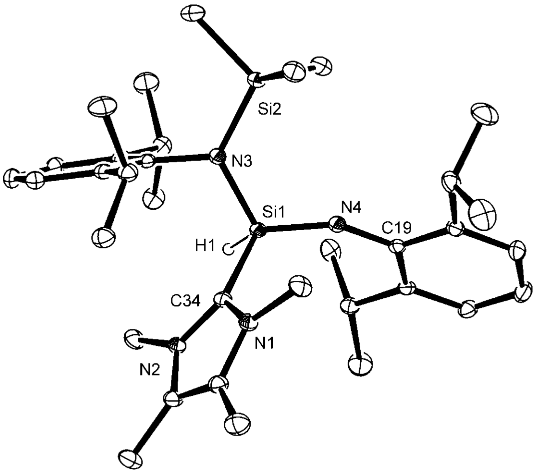


Figure 1. ORTEP of **2**. Selected bond lengths (Å) and angles (deg): Si1–N4 1.6209(13), Si1–N3 1.7442(13), Si1–C34 1.9429(16), Si1–H1 1.376(18), N4–C19 1.363(2), N3–C7 1.4490(19), N1–C34 1.349(2), N2–C34 1.3557(18), C2–C3 1.360(2); Si1-N4-C19 148.09(11), N3-Si1-N4 112.49(6), N3-Si1-C34 108.30(6), N4-Si1-C34 110.23(7), N3-Si1-H1 102.4(7), N4-Si1-H1 123.9(7), C34-Si1-H1 97.8(7).

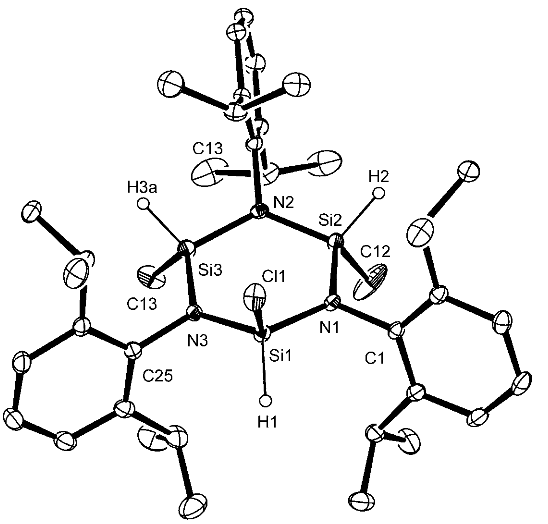
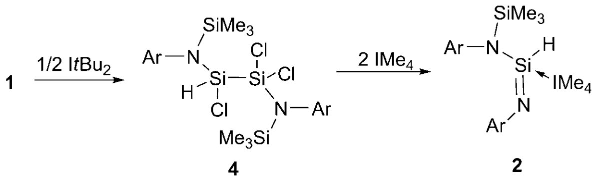


Figure 2. ORTEP of **3**. Selected bond lengths (Å) and angles (deg): Si1–N1 1.7211(17), Si1–N3 1.7144(16), Si1–Cl1 2.0682(8), Si2–N1 1.721(2), Si2–N2 1.726(2), Si2–Cl2 2.0532(16), Si3–N2 1.7184(17), Si3–N3 1.7168(16), Si3–Cl3 1.9921(11); Si1-N1-Si2 127.23(10), N1-Si2-N2 108.67(10), Si3-N2-Si2 127.68(10), N3-Si3-N2 108.72(8), Si1-N3-Si3 127.66(10), N3-Si1-N1 110.49(8).

tetrahedral geometry. The Si1−N4 bond length (1.6209(13) Å) was the longest observed so far for structurally characterized free- and donor-stabilized silanimines (1.568–1.611 Å);[3,4] however, it was shorter than other Si−N single bonds (1.64–1.78 Å) in a variety of silanamines. The Si1−C34 bond length (1.9429(16) Å) was longer than Si−C single bonds in organosilanes (average 1.86 Å) but in the reported range for NHC-supported silicon halides (1.935–2.0088 Å).[8d,10] As is the case for all known stable silanimines, the Si1−N4−C19 bond angle (148.09(11)°) was much larger than the analogous C-N-C bond angles in imines owing to highly polarized Si−N double bonds. However, it is much smaller than those in silyl-substituted (both on the silicon and nitrogen atoms of the Si=N moiety) silanimines, in which the interaction of the lone pair on the nitrogen atom with the silyl group on the nitrogen atom has been proposed by calculations as well as based on X-ray crystal analy sis.[4a,11] The N4−C19 bond length (1.363 (2) Å) was significantly shorter than a C−N single bond, thus suggesting an interaction of the nitrogen electrons with the aryl ring. Compound **2** is the first example of donor-stabilized 1-hydrosilanmines. Recent studies have shown that NHCs could stabilize some interesting silicon multiple-bonding species, such as the formally silicon(0) species (NHC)Si=Si(NHC) reported by Robinson and co-workers and a NHC-supported silanone reported by Driess and co-workers.[12]

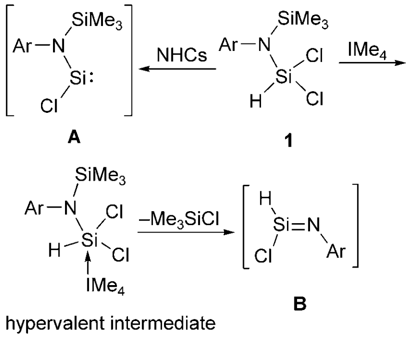
In order to better understand the reaction mechanism for the formation of **2**, various experimental conditions (different stoichiometries, temperatures, and addition sequences) were been examined. In most cases, it is impossible to isolate pure products even from repeated crystallizations from different solvents. However, compound **3** was obtained from the slow addition of a solution of IMe_4 in tetrahydrofuran to two equivalents of **1** in tetrahydrofuran at low temperature. Compound **3** has been fully characterized by multinuclear NMR and IR spectroscopy, and X-ray single-crystal analysis (Figure 2). The Si_3N_3 six-membered ring is twisted in a similar fashion to those in the known cyclotrisilazanes.[13] The aryl rings are almost perpendicular to the mean Si_3N_3 ring.

For comparison, the reaction of **1** with the bulky N-heterocyclic carbene I*t*Bu$_2$ was investigated. As with our previously reported results, disilane **4** was isolated from the reaction (Scheme 2). Compound **4** has been characterized by ^1H and ^{13}C NMR and IR spectroscopy, and elemental analysis. The different products observed in the reactions with small IMe_4 and bulky I*t*Bu$_2$ indicated either that the reactions proceeded through different initial mechanisms or that product **4** underwent further reactions with the less-hindered IMe_4. To test the latter pathway, the reaction of **4** with IMe_4 was studied. Indeed, the reaction of **4** with one equivalent of IMe_4 in tetrahydrofuran afforded a mixture containing **2** and **3** in the molar ratio of 1:0.57, as estimated from the proton NMR spectrum. In contrast, the reaction of **4** with two equivalents of IMe_4 exclusively yielded **2** as a major product, whilst **3** was not observed by ^1H NMR analysis. These results strongly indicated that **2** was formed following the ini-



Scheme 2. Synthesis of **2** from **4**. I*t*Bu$_2$ = 1,3-bis(*tert*-butyl)imidazol-2-ylidene.

tial formation of **4** as an intermediate in the reaction of **1** with IMe_4. In this case, the small size of IMe_4 may attack the disilane **4**, thereby resulting in the elimination of insoluble $(SiCl_2)_n$ and Me_3SiCl (Scheme 3). The extrusion of **1** from **4** to form the chlorosilylene RSiCl could also be operating. Therefore, an excess of IMe_4 favors the formation of **2**, as **1** could again be converted into **2** in this case. These observations were consistent with the conditions for the preparation of **2** from **1**. Compound **3** can be viewed as the elimination product from **1** through loss of Me_3SiCl, as the small IMe_4 may coordinate to **1** to form a hypervalent silicon species (Scheme 3), which facilitates the elimination reaction to give **B** followed by its trimerization.



Scheme 3. Proposed initial reactions of **1** with IMe_4.

The proposed mechanism for the formation of **2** is further supported by the previous observation that a disilane easily undergoes Si–Si bond cleavage and disproportionation in the presence of a Lewis base.[14] It is reasonably assumed that the reaction of **1** with IMe_4 may proceed through two distinct pathways because of its small size (Scheme 3). In contrast, the reaction of **1** with $It Bu_2$ can only proceed through the dehydrohalogenation pathway to give the intermediate **A**, as proposed previously by ourselves, owing to the bulkiness of the $ItBu_2$ group.

In summary, we have shown that reaction of **1** with IMe_4 and $ItBu_2$ yielded different products owing to the differing steric influence of the reactants on the initial steps. Compound **2** is the first example of a base-stabilized 1-hydrosilanimine. The presence of the reactive hydride ligand on the unsaturated silicon atom may have cooperative effects on its reactivity toward unsaturated substrates. Reactivity studies of **2** and isolation of the other products in the reaction system are currently in progress.

Experimental Section

2: A solution of **1** (0.35 g, 1.00 mmol) in THF (5 mL) was added to a solution of IMe_4 (0.25 g, 2 mmol) in THF (5 mL) at −78 °C. The mixture was allowed to warm up to room temperature and stirred overnight. All volatile compounds were removed, and the remaining residual was extracted with *n*-hexane. Removal of solvents and crystallization from toluene at −30 °C yielded yellow crystals of **2** (26 %). M.p.: 177 °C; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.05$ (d, 3 H, Me), 0.51 (s, 9 H, Si*Me*$_3$), 0.10 (s, 6 H, N*Me*), 1.17 (d, 3 H, Me) 1.35 (d, 3 H, Me), 1.48 (dd, 12 H, CH*Me*$_2$), 1.57 (d, 3 H, Me), 3.21 (m, 1 H, C*H*Me$_2$), 4.00 (m, 1 H, C*H*Me$_2$), 4.13 (m, 2 H, C*H*Me$_2$), 6.21 (s, 1 H, $^1J_{Si-H} = 218$ Hz, Si*H*), 6.86–7.19 (m, 4 H, Ar*H*), 7.36 ppm (d, 2 H, Ar*H*); ^{13}C NMR (100.61 MHz, C_6D_6): $\delta = 3.34$, 7.39, 22.56, 22.71, 24.84, 25.04, 25.65, 26.06, 26.41, 27.84, 28.58, 28.71,113.3, 123.0, 123.3, 124.9, 125.1, 125.7, 139.7, 140.5, 148.1, 149.6, 151.3, 154.3 ppm; ^{29}Si NMR (59.62 MHz, C_6D_6): $\delta = -72.01$ (SiH), 2.74 ppm (s, $SiMe_3$); EI-MS (*m*/*z*): 576.4 [M^+]; UV/Vis (λ_{max}): 282 nm (toluene, $\varepsilon =$ 1200 $cm^2 mmol^{-1}$); IR: $\tilde{\nu} = 1623$, 2962 cm^{-1}.

4: A solution of $ItBu_2$ (0.09 g, 0.5 mmol) in THF (5 mL) was slowly added to a stirred solution of **1** (0.35 g, 1 mmol) in THF (5 mL) at −78 °C. The mixture was slowly warmed to room temperature and stirred overnight, before being filtered and the volatile compounds removed. **4** was obtained as a colorless solid by sublimation at 219 °C. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.17$ (s, 9 H, *Me*$_3$Si), 0.28 (s, 9 H, *Me*$_3$Si), 1.15–1.42 (m, 24 H, CH*Me*$_2$), 3.66 (m, 1 H, C*H*), 3.76 (m, 2 H, C*H*), 3.98 ppm (m, 2 H, C*H*), 5.40 (s, 1 H, Si*H*), 7.05 (m, 6 H, Ar*H*); ^{13}C NMR (100.61 MHz, $C_6D_{6,}$): $\delta = 1.01$, 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, 124.1, 124.3, 124.4, 125.9, 126.0, 146.8, 147.6, 162.4 ppm; EI (*m*/*z*): 660.2 [M^+]; IR: $\tilde{\nu} = 2169$ cm^{-1} (Si–H).

Further details for the synthesis and characterization of compounds **1–4** are given in the Supporting Information. CCDC 761526 (**2**) and CCDC 761525 (**3**) contain the 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.

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