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PAPER

Silylation of N-heterocyclic carbene with aminochlorosilane and -disilane: dehydrohalogenation *vs.* Si–Si bond cleavage†

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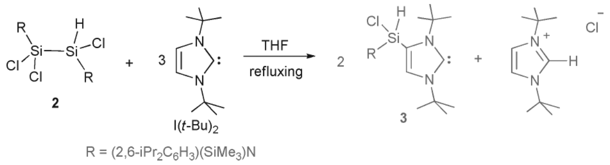
Reactions of the aminochlorosilane $RSiHCl_2$ and disilane $R_2Si_2HCl_3$ (R = (2,6-*i*$Pr_2C_6H_3$)($SiMe_3$)N) with an excess of 1,3-bis(*tert*-butyl)imidazol-2-ylidene resulted in the silylation of the NHC while reaction with the less hindered 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene yielded an NHC-stabilized aminochlorosilylene.

Introduction

Stable N-heterocyclic carbenes (NHCs) have been widely used as ligands for transition metal catalysis and stabilization of molecules with unusual bonding and reactivity.[1] It has been shown that the substituents on the 4 and 5 positions of Arduengo type carbenes have pronounced effects on their properties. Thus, the functionalization of NHCs with various groups has attracted considerable recent attention for tuning their electronic properties. Bertrand and co-workers have reported an efficient method for the introduction of several types of groups to the 4 and 5 positions *via* abnormal carbene intermediates.[2] Gates and Roesky have reported 4-phosphino- and 4-silyl-substituted NHCs by the reactions of phosphaalkenes with NHCs and an NHC-stabilized dichlorosilylene with an organic azide, respectively.[3] A few carbene-silylene adducts have also been synthesized and structurally characterized.[4b,4c,9] We have previously shown that a 4-diaminosilyl-substituted NHC can be obtained as a side product in the dehydrochlorination of diaminochlorosilanes for the generation of silylenes.[4a] However, this reaction appeared to be complicated since silylenes, disilanes and other unsaturated silicon species can be obtained in some cases.[4a,5–9] In order to develop a practical and selective method for the silylation of NHCs and synthesis of silylenes from simple chlorosilanes, the detailed investigation of the reaction is highly desirable since both silylated NHCs and silylenes are desired useful products. Herein, we report on reaction of the aminochlorosilane $RSiHCl_2$ (**1**, R = (2,6-*i*$Pr_2C_6H_3$)($SiMe_3$)N) and the disilane $(R)_2Si_2HCl_3$ (**2**) with different NHCs, leading to the selective silylation of an NHC and formation of an NHC-stabilized aminochlorosilylene, respectively, under optimized conditions (Schemes 1 and 3).

Results and discussion

We recently reported that reaction of **1** with 1,3-bis(*tert*-butyl)-imidazol-2-ylidene (I*t*Bu_2) proceeded rapidly at room temperature to yield the disilane **2** in an excellent yield.[6] It is anticipated that **2** could be the suitable precursor for the synthesis of aminochlorosilylene or its oligomer by dehydrochlorination reaction with NHCs. Heating a mixture of **2** with 1 equiv of I*t*Bu_2 in C_6D_6 led to the formation of a new species and regeneration of **1** as indicated by the NMR analysis. Thus, the reaction of **2** with an excess of I*t*Bu_2 was investigated for the clean synthesis of the new species. Refluxing a mixture of **2** and 3 equiv of I*t*Bu_2 in THF yielded the new compound, which was isolated as colorless crystals in good yield and has been identified as the silylated NHC **3** by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy, elemental analysis and an X-ray single-crystal analysis (Scheme 1).



Scheme 1

The ^{29}Si NMR spectrum of **3** exhibits two resonances at δ −29.24 and 9.71 ppm. The former resonance is noticeably high-field shifted compared to that observed in **1** due to the less electronegative olefinic carbon atom compared to the chloride ligand. The ^{13}C NMR spectrum signal for the central carbene carbon atom appears at 213.4 ppm, which is comparable to the value found for the free carbene.[10] Single crystals of **3** suitable for an X-ray diffraction study were obtained from *n*-hexane. The structure of **3** is shown in Fig. 1 with relevant bond parameters. The C–C and C–N bond lengths in the five-membered ring are consistent with those observed in free carbenes. **3** represents a rare example of a chlorosilyl-substituted NHC and could be further derivatised by simple metalation reactions. Attempted

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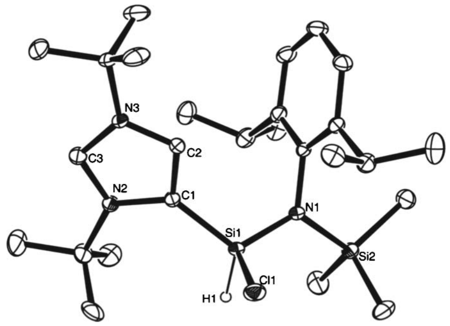
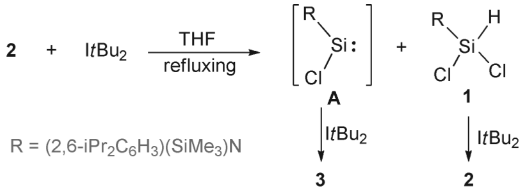


Fig. 1 Ortep drawing of **3** with ellipsoids given at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Cl1–Si1 2.0833(10), Si1–N1 1.713(2), Si1–C1 1.851(2), Si1–H1 1.40(2), C1–C2 1.357(3), N2–C1 1.419(3), N2–C3 1.367(3), N3–C3 1.365(3), N3–C2 1.377(3), N1–Si1–C1 113.37(10), N1–Si1–Cl1 111.50(7), C1–Si1–Cl1 106.03(9).

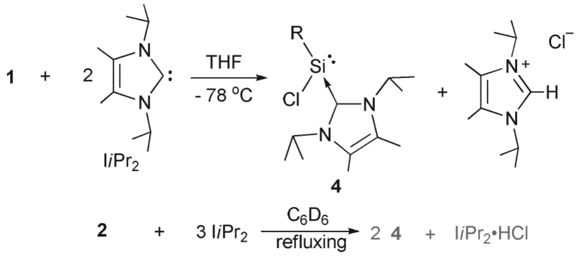
dehydrohalogenation of **3** with NHCs has been unsuccessful to date.

The most reasonable explanation for the silylation reaction is the formation of the aminochlorosilylene intermediate RClSi (**A**, Scheme 2) by the reaction of **2** with the NHC. The silylation of the NHC with **2** and regeneration of $RSiHCl_2$ as observed in NMR scale reaction suggested that the reaction proceeded through the disproportionation of **2** rather than the dehydrohalogenation of **2** by the NHC. The regenerated **1** can be converted to **2** by the dehydrogenation pathway. Therefore, it is expected that the silylation reaction could be more conveniently and practically furnished by the reaction of **1** with an excess of the NHC at high temperature. Indeed, the reaction of **1** with 3 equiv of I*t*Bu$_2$ in refluxing THF afforded **3**, which was isolated as colorless crystals from *n*-hexane in good yield. Although the disproportionation of disilanes to silylenes and silanes in the presence of Lewis bases has been proposed previously,[11] no Lewis base stabilized silylenes have been isolated from these reactions. In addition, reactions of disilanes with N-heterocyclic carbenes have not been described in the literature. Therefore, it is interesting and desirable to design a suitable route and select appropriate precursors for the isolation of proposed intermediates.



Scheme 2

Since I*t*Bu$_2$ easily undergoes a C–H bond insertion reaction, the less bulky 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (I*i*Pr$_2$), which does not possess olefinic C–H bonds on the NHC ring, was chosen for trapping the proposed silylene intermediate. Furthermore, the steric effects of the N-substituents of NHCs on this type of reaction can be explored by employing different carbenes. It was found that **2** did not react with an excess of I*i*Pr$_2$ in C_6D_6 at room temperature. However, upon heating the mixture to 80 °C for 12 h, the formation of a new compound was observed by NMR analysis. Since the new compound was slowly decomposed at the high temperature, the alternative low temperature route starting from **1** by dehydrohalogenation with the NHC has been investigated for the isolation of the new compound. As expected, reaction of **1** with two equiv of I*i*Pr$_2$ in THF from low temperature to room temperature afforded the same compound as that obtained at high temperature with **2** (Scheme 3). The new compound can be isolated as yellow powder in 75% yield from the reaction. It has been fully characterized by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy and elemental analysis. The structure of **4** has been confirmed as an NHC-silylene complex by an X-ray single crystal analysis.



Scheme 3

The resonance for the Si(II) atom in the ^{29}Si NMR spectrum of **4** was found at δ = 3.14 ppm, which is slightly downfield shifted compared to those observed for the NHC-stabilized arylchlorosilylenes (0.77 to 1.34 ppm) that have been reported.[9] The ^{13}C NMR signal for the NHC central carbon atom in **4** appears at 164.08 ppm, consistent with those found in the NHC→Si donor–acceptor complexes.[7–9] The molecular structure of **4** (Fig. 2) features the trigonal-pyramidal three-coordinate silicon atom (the sum of angles at the Si1 atom = 305.22°). The Si1–C20 bond length (2.0023(19) Å) is slightly longer than those reported for NHC-stabilized dihalosilylenes (1.985(4) and 1.989(3) Å).[7,12] Compound **4** is the first example of a donor-stabilized aminochlorosilylene, as far as we know.

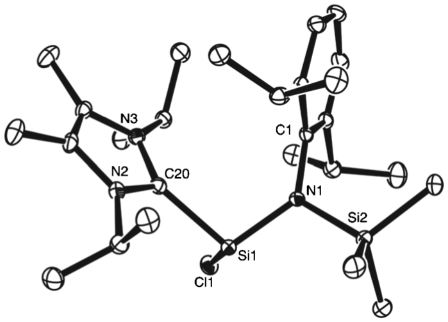


Fig. 2 Ortep drawing of **4** with ellipsoids drawn at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–N1 1.7861(15), Si1–Cl1 2.2274(7), Si1–C20 2.0023(19), Si2–N1 1.7603(15), N2–C20 1.369(2), N3–C20 1.358(2); N1–Si1–C20 103.18(7), N1–Si1–Cl1 105.92(5), C20–Si1–Cl1 96.12(5).

The isolation of **4** strongly supports the aminochlorosilylene **A** (Scheme 2) as the intermediate for the silylation of I*t*Bu$_2$. In addition, the steric factor afforded by the substituents on the NHC nitrogen atoms has noticeable effects on the reaction conditions. In the case of I*t*Bu$_2$, the reaction of **1** below room temperature yielded the disilane **2** as an isolable product, with the formation of a very small amount of the silylated product **3** that can be only observed by the proton NMR analysis of the crude product and could not be isolated, indicating the initial formed intermediate **A** by the dehydrohalogenation of **1** is prone to react with **1** to give the disilane **2** rather than I*t*Bu$_2$. In contrast, the less hindered I*i*Pr$_2$ can trap the intermediate **A** at low temperature to afford the NHC-stabilized aminochlorosilylene **4** in good yield. Reactions of the disilane **2** with NHCs proceed through initial Si–Si bond cleavage and disproportionation to generate **A** and **1** at more harsh conditions. The reaction of **2** with the bulky I*t*Bu$_2$ only proceeds at high temperature and does not follow the initial dehydrohalogenation pathway. On the other hand, the similar reaction of **2** with I*i*Pr$_2$ appears to be more complicated since **4** is thermally sensitive and partially decomposed at the high temperature.

Conclusions

We have established that the disilane **2** generated by the dehydrohalogenation of **1** with NHCs at low temperatures does not undergo a dehydrohalogenation reaction at ambient temperature but a Si–Si bond cleavage reaction at high temperatures to yield **1** and the aminochlorosilylene RClSi, the key intermediate for silylation of NHCs that can be trapped and stabilized by I*i*Pr$_2$ to give the NHC stabilized aminochlorosilylene **4**. The mechanistic information provided by the results should contribute to the selective and facile access to desired silylenes or silylated NHCs from simple chlorosilanes.

Experimental section

General considerations

All operations were carried out under an atmosphere of dry argon or nitrogen by using modified Schlenk line and glovebox techniques. All solvents were freshly distilled from Na and degassed immediately prior to use. Elemental analyses were carried out on an Elemental Vario EL analyzer. The ^{1}H, ^{13}C and ^{29}Si NMR spectroscopic data were recorded on Bruker Mercury Plus 300, 400 and 600 MHz NMR spectrometers. Infrared spectra were recorded on a Bio-Rad FTS 6000 spectrometer. The UV-vis spectra were recorded on a Shimadzu UV-2450 spectrometer and emission spectra on an Edinburgh Analytical Instruments FL900CD spectrometer. 1,3-Bis(*tert*-butyl)-imidazol-2-ylidene I*t*Bu$_2$,[13] 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (I*i*Pr$_2$)[14] and disilane R$_2$Si$_2$HCl$_3$[4a] (R = (2,6-*i*Pr$_2$C$_6$H$_3$)(SiMe$_3$)N) were synthesized according to published procedures.

Synthesis of RSiHCl[(C$_3$N$_2$)H(Bu^t)$_2$] (3, R = (2,6-*i*Pr$_2$C$_6$H$_3$)(SiMe$_3$)N): Method a. A solution of **1** (3.46 g, 10 mmol) in THF (30 mL) was added to a stirred solution of I*t*Bu$_2$ (3.61 g, 20 mmol) in THF (30 mL) at −78 °C. Soon a white suspension formed. The mixture was slowly warmed to room temperature, and refluxed for 24 h. The volatiles were removed under vacuum. The residue was extracted with *n*-hexane (40 mL × 2). Concentration to *ca.* 2 mL and storage at room temperature afforded colorless crystals of **3** (2.3 g, 46.7%). M.p. 162–164 °C; ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 0.24 (s, 9 H, Si(C*H*$_3$)$_3$), 0.46 (d, 3H, CH(C*H*$_3$)$_2$), 1.01, (d, 3H, CH(C*H*$_3$)$_2$), 1.24 (d, 3H, CH(C*H*$_3$)$_2$), 1.39 (d, 3H, CH(C*H*$_3$)$_2$), 1.26 (s, 9H, C(C*H*$_3$)$_3$), 1.72 (s, 9H, C(C*H*$_3$)$_3$), 3.11 (m, 1H, C*H*(CH$_3$)$_2$), 3.91 (m, 1H, C*H*(CH$_3$)$_2$), 6.17 (s, 1H, C*H*═), 6.44 (s, 1H, Si-*H*), 6.82–7.08 (m, 3H, Ar-*H*) ppm; ^{13}C NMR (100.61 MHz, C$_6$D$_6$): δ 1.61 (Si(*C*H$_3$)$_3$), 23.88, 24.69, 25.43, 26.49 (CH(*C*H$_3$)$_2$), 28.35, 28.44 (*C*H(CH$_3$)$_2$), 31.17, 32.42 (C(*C*H$_3$)$_3$), 56.05, 58.33 (*C*(CH$_3$)$_3$), 130.34 (*C*H═), 120.34 (Si*C*═), 124.58, 124.84, 126.26, 140.34, 147.26, 147.66 (Ar-*C*), 213.40 (carbene) ppm; ^{29}Si NMR (59.62 MHz, C$_6$D$_6$): δ −29.24 (*Si*-H), 9.71 (*Si*(CH$_3$)$_3$) ppm; Elemental analysis (%) calcd for C$_{26}$H$_{46}$ClN$_3$Si$_2$: C, 63.43; H, 9.42; N, 8.54; Found: C, 62.99; H, 9.90; N, 8.34; IR (cm^{-1}): $\nu_{\mathrm{Si-H}}$ 2196.88.

Method b. A mixture of **2** (0.41 g, 0.622 mmol) and I*t*Bu$_2$ (0.34 g, 1.87 mmol) was treated with 20 mL of THF. The resulting suspension was refluxed for 24 h. And the reaction processed quantitatively. The volatiles were removed under vacuum. The residue was extracted with *n*-hexane (40 mL). Concentration to *ca.* 2 mL and storage at room temperature afforded colorless crystals of **3** (0.3 g, 49%).

Synthesis of RSiCl(I*i*Pr$_2$) (4, R = (2,6-*i*Pr$_2$C$_6$H$_3$)(SiMe$_3$)N). A solution of **1** (0.42 g, 1.19 mmol) in THF (10 mL) was added to a stirred solution of I*i*Pr$_2$ (0.43 g, 2.38 mmol) in THF (5 mL) at −78 °C. The mixture was slowly warmed to room temperature and stirred overnight whereupon a large quantity of precipitate formed. The volatiles were removed under vacuum. The residue was extracted with toluene (40 mL). After filtration and removal solvents, the remaining residue was washed with *n*-hexane (5 mL × 3) to afford a light yellow powder of **4**.(0.44 g, 75.16%). M.p. 149–150 °C; ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 0.33 (d, 3 H, CH(C*H*$_3$)$_2$), 0.54 (s, 3H, Si(C*H*$_3$)$_3$), 1.21, (d, 3H, CH(C*H*$_3$)$_2$), 1.25 (d, 6H, CH(C*H*$_3$)$_2$), 1.41 (d, 3H, CH(C*H*$_3$)$_2$), 1.48 (s, 6H, ═CC*H*$_3$), 1.56 (d, 3H, CH(C*H*$_3$)$_3$), 3.30 (m, 1H, C*H*(CH$_3$)$_2$), 4.55 (m, 1H, C*H*(CH$_3$)$_2$), 5.06 (br, C*H*(CH$_3$)$_2$), 6.93–7.03 (m, 2H, Ar-*H*), 7.23–7.25 (d, 1H, Ar-*H*) ppm; ^{13}C NMR (100.61 MHz, C$_6$D$_6$): δ 3.86, 9.90, 23.89, 25.88, 25.94, 26.44, 27.87, 28.46, 124.02, 124.25, 124.87, 126.40, 144.51, 147.67, 148.36, 164.08 ppm; ^{29}Si NMR (59.62 MHz, C$_6$D$_6$): δ 6.99 (*Si*(CH$_3$)$_3$), 3.14 (*Si*Cl) ppm; Elemental analysis (%) calcd for C$_{26}$H$_{46}$ClN$_3$Si$_2$: C, 63.43; H, 9.42; N, 8.54; Found: C, 63.45; H, 9.70; N, 8.49; UV-VIS: $\varepsilon_{220} = 1.63 \times 10^4$ L mol^{-1} cm^{-1} (THF); IR (cm^{-1}): ν 441.64, 541.87, 596.68, 664.25, 755.03, 802.72, 843.46, 932.26, 1054.91, 1192.06, 1250.83, 1450.58, 1553.56, 1628.75, 2180.91, 2870.54.

X-Ray structural determinations

Intensity data for compound **3** was collected with a Bruker SMART CCD diffractometer, and compound **4** was collected with a Rigaku Saturn 724 CCD diffractometer, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods (*SHELXS-97*)[15] and refined by full-matrix least squares on F^2. H1 atom for **3** was obtained from difference Fourier map Q1. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (*SHELXL-97*).[16] Crystals of **3** suitable for X-ray analysis were grown from hexane, and crystals of **4** were obtained from toluene. Crystallographic data for **3** and **4** are given in Table 1.

Table 1 Crystallographic data for **3** and **4**

Compound	**3**	**4**
CCDC number	830376	830375
Formula	$C_{26}H_{46}ClN_3Si_2$	$C_{26}H_{46}ClN_3Si_2$
M	492.29	492.29
Crystal system	Orthorhombic	Monoclinic
a/Å	10.129(2)	10.3126(17)
b/Å	17.177(3)	17.824(3)
c/Å	34.277(7)	15.921(3)
α (°)	90.00	90.00
β (°)	90.00	102.561(2)
γ (°)	90.00	90.00
V/Å^3	5964(2)	2856.4(8)
Space group	*Pbca*	$P2_1/n$
Z	8	4
R_{int}	0.0561	0.0545
R_1 ($I > 2\sigma(I)$)	0.0573	0.0448
w$R(F^2)$ ($I > 2\sigma(I)$)	0.1318	0.0964
R_1 (all data)	0.0662	0.0627
w$R(F^2)$ (all data)	0.1364	0.1040
GOF	1.145	1.016

Acknowledgements

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