Coordination of *N*-Heterocyclic Carbene to H_2SiX_2 (X = Cl, OTf) and H_3SiOTf (OTf = OSO_2CF_3): Synthesis of Donor-stabilized Parent Silylium Salts with Four- and Five-coordinate Silicon Atoms

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Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

The reactivity of the *N*-heterocyclic carbene (NHC) 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene towards dichlorosilane H_2SiCl_2, bis(trifluoromethanesulfonato)silane $H_2Si(OTf)_2$ (OTf = OSO_2CF_3), and silyl trifluoromethanesulfonate H_3SiOTf has been investigated. It turned out that the coordination of the NHC ligand can occur stepwise to form the three neutral compounds $(NHC)SiH_2Cl_2$ (**1**), $(NHC)_2SiH_2Cl_2$ (**2**), $(NHC)SiH_2(OTf)_2$ (**3**), as well as the two ion pairs $[(NHC)SiH_3]^+(OTf^-)$ (**4**) and $[(NHC)_2SiH_3]^+(OTf^-)$ (**5**); the latter represent the first NHC adducts of the parent silylium cation (H_3Si^+). The multinuclear NMR and IR spectroscopic data of the products reflect the characteristics of four-, five-, and six-coordinate silane complexes. All new compounds were structurally characterized by single-crystal X-ray diffraction analyses.

Key words: Silicon, Silane Complexes, Hypercoordination, Main Group Elements

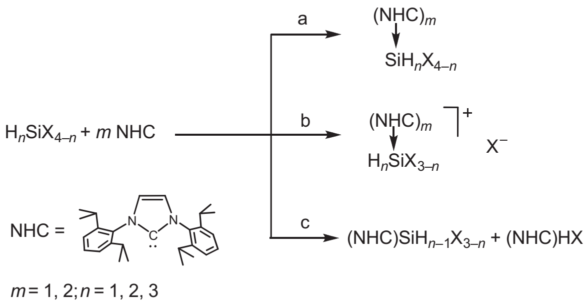
Introduction

Hydridohalosilane adducts of the type $L_mSiH_nX_{4-n}$ (L = Lewis base donor ligands, $m = 1, 2$; $n = 1, 2, 3$; X = Cl, *etc.*) with higher-coordinate silicon(IV) centers have scarcely been reported in the literature [1], perhaps in part due to their poor solubility in common organic solvents [2 – 4]. Over the last two decades several of these adducts (L = pyridine, substituted pyridine, NHC, $m = 1,2$, $n = 2$; L = N,N'-chelating ligand, $m = 1$; $n = 1$, 2) could be synthesized and structurally characterized [5 – 12]. Recently, the application of *N*-heterocyclic carbenes (NHCs) as ligands towards trichlorosilane has led to impressive synthetic advances in organosilicon chemistry. For example, the reaction of NHCs led to dehydrochlorination and subsequent formation of the first isolable NHC-dichlorosilylene complex [13]. In addition, the reactions of NHCs with halosilanes SiX_4 (X = F, Cl, Br) and R_nSiX_{4-n} (R = Me, Ph, $n = 2$, 3, X = Cl, I) have also been investigated, furnishing in most cases five-coordinate silicon(IV) adducts [14 – 17]. Some of the thus-formed higher-coordinate silane complexes have proven to be important precursors for novel silicon compounds. Utilizing the fascinating donor ability and the steric protecting effect of NHCs, we recently succeeded in synthesizing several novel NHC-supported silicon species such as NHC-stabilized silanones and dioxasiliranes [18 – 20]. Recently, Roesky and coworkers investigated the different reactivity of so-called “normal” and “abnormal” NHCs toward dichloro- and trichlorosilane which revealed the first NHC-hydridochlorosilane adducts with five- and six-coordinate silicon atoms [8]. The latter study showed that an “abnormal” NHC is capable to facilitate the dismutation of trichlorosilane to give the corresponding NHC-dichlorosilane adduct and $SiCl_4$. In addition, they reported that dichlorosilane reacts with the NHC 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene to give exclusively the corresponding bis-NHC adduct of H_2SiCl_2 bearing a six-coordinated silicon(IV) atom. In our experiments we observed that even the mono-NHC complex of H_2SiCl_2 can be isolated. Furthermore, we extended the reactivity studies of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene toward the triflate-substituted silanes H_3SiOTf

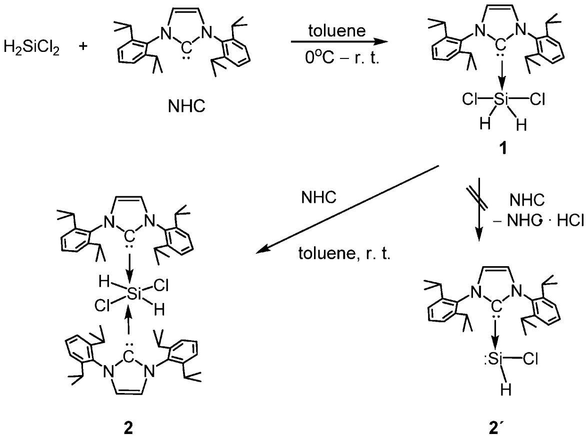
and $H_2Si(OTf)_2$ (OTf = OSO_2CF_3), aiming at synthesizing compounds with the NHC-stabilized parent silylium cation (SiH_3^+) with four- and five-coordinate silicon atoms, and with the triflatosilylium cation (H_2SiOTf^+), respectively.

Results and Discussion

As shown in Scheme 1, we anticipated three possible pathways for the reaction of the 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene NHC with hydridosilanes of the type H_nSiX_{4-n} which could furnish (a) neutral $(NHC)_mSiH_nX_{4-n}$ adducts through simple addition (Scheme 1a), (b) $[(NHC)_mSiH_nX_{3-n}]^+X^-$ ion pairs by NHC-mediated salt formation (Scheme 1b), or (c) $(NHC)SiH_{n-1}X_{3-n}$ adducts with divalent silicon through reductive elimination of HX by NHC (Scheme 1c). We now learned that the outcome of the reaction of the 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene with H_2SiCl_2, $H_2Si(OTf)_2$ and H_3SiOTf is depending on the nature of the substituents of the different hydrosilanes.



Scheme 1. Three possible pathways for the reaction of the 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene NHC with hydridohalosilanes and hydridosilyltriflates H_nSiX_{4-n} (X = halide, OTf).



Scheme 2. Formation of **1** and **2**.

Step-by-step coordination of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene to H_2SiCl_2

When a molar excess of H_2SiCl_2 was passed through a solution of 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene in toluene at −10 °C, the 1 : 1 adduct $(NHC)SiH_2Cl_2$ (**1**) was formed immediately as the sole product (Scheme 2) as shown by the ^1H NMR spectrum of the resulting mixture at room temperature. The adduct **1** can be isolated in the form of colorless crystals in 85 % yield.

We further examined the reactivity of **1** towards a second equivalent of NHC to give the known hexacoordinate adduct **2** [8]. Indeed, this led to the $(NHC)_2SiH_2Cl_2$ adduct **2** as the sole product (Scheme 2). The formation of **2** is reminiscent to that of $(NHC)_2SiF_4$ [21]. Consistent with the results of Roesky *et al.*, the desired dehydrochlorination of **1** to form **2′** could not be achieved even under drastic reaction conditions (refluxing toluene). This is in contrast to the reaction of 2 molar equivalents of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene with trichlorosilane, $SiHCl_3$, which furnishes the corresponding NHC-dichlorosilylene complex [13]. Obviously, the lower proton acidity of SiH_2Cl_2 hampers the desired HCl elimination in the presence of the NHC.

As expected, the Si–H resonances in the ^1H NMR spectrum and the Si–H stretching vibration modes in the IR spectrum are diagnostic for such NHC-hydridosilane adducts **1** and **2**. The proton resonance for the SiH_2 subunit in **1** appears at $\delta = 6.42$ ppm (C_6D_6) as a broad signal, while the corresponding protons in **2** give a broad signal at $\delta = 5.58$ ppm [8] (Table 1). This upfield shift of **2** is caused by the donor effect of the additional NHC ligand. A related drastic upfield shift has also been observed in the CP/MAS ^{29}Si solid-state NMR spectra ($\delta = -123.8$ ppm for **1** *vs.* −225.2 ppm for **2**). The latter ^{29}Si NMR resonance of **2** is even more shifted than those of $^Rpy_2SiH_2Cl_2$ ($\delta = -145 \sim -152$ ppm, R = 3-Br, 4-Me, 4-Et, 4-vinyl, 4-*t*Bu, 4-NMe_2) [9–12]. In line with that, the Si–H stretching vibration of **1** in the IR spectrum

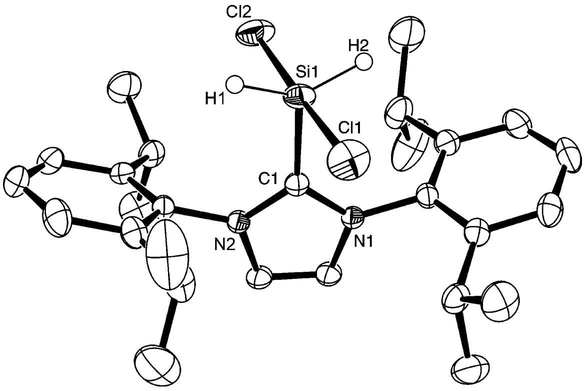


Fig. 1. Molecular structure of **1**. Displacement ellipsoids are drawn at 50 % probability level. H atoms (except SiH_2) are omitted for clarity. Selected bond lengths (pm) and angles (deg): Si1–C1 190.4(3), Si1–Cl1 227.0(1), Si1–Cl2 227.0(1), C1–N1 134.4(2), C1–N2 134.4(2); Cl1–Si1–Cl2 176.3(1), C1–Si1–Cl1 91.8(1); N1–C1–Si1 126.9(1), N2–C1–N1 106.1(2); N1–C1–Si1–Cl1 74.2.

appears at a higher wave number ($\tilde{\nu} = 2214\,cm^{-1}$) than that of **2** ($\tilde{\nu} = 2118\,cm^{-1}$). The latter value is close to those observed for the related octahedral silicon compounds of the type $^{R}py_2SiH_2Cl_2$ ($\tilde{\nu}$ = 2050–2103 cm^{-1}) [9–12].

Single crystals of **1** suitable for an X-ray diffraction analysis were obtained from a toluene solution at ambient temperature. The compound crystallizes in the tetragonal space group $P4_22_12$ (Fig. 1). The Si atom is five-coordinated in a trigonal bipyramid with the two chlorine atoms in the axial positions. The NHC carbon atom and both SiH_2 hydrogen atoms occupy the equatorial positions. This coordination geometry is similar to those of $(NHC)SiX_4$ (X = Cl, Br) [14–16], but in sharp contrast to that of $(NHC)SiF_4$ [21], where the NHC carbon atom resides in an axial position. The Cl–Si–Cl angle of 176.3(1)° in **1** indicates a slight distortion of the trigonal-bipyramidal geometry. Owing to the steric demand of the isopropyl substituents in the NHC molecule, the N1–C1–Si1–Cl1 torsion angles amount to 74.2°. The Si–C distance of 190.4(3) pm in **1** is shorter than that in $(NHC)SiF_4$ (200.4(2) pm [21]), but close to those in $(NHC)SiCl_4$ derivatives (191–193 pm) [14, 16]. In contrast, the Si–Cl bonds (227.03(6) pm) in **1** are longer than the $Si–Cl_{axial}$ bonds in the $(NHC)SiCl_4$ system (219–222 pm [14, 16]).

Single crystals of **2** suitable for X-ray diffraction analysis have been obtained from hexane solutions at ambient temperature. The molecular structure of **2** has already been reported [8], revealing that the Si atom is six-coordinated, and the ligands are arranged in a distorted octahedral geometry with the two chlorine atoms and two NHC ligands in *trans* positions. While the Si–Cl distances in **2** are similar to those observed in **1**, the Si–C distance of 204.9(2) pm is much longer than that in **1** (190.4(3) pm) owing to the higher coordination number of the silicon atom in **2**.

Reaction of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene with $H_2Si(OTf)_2$

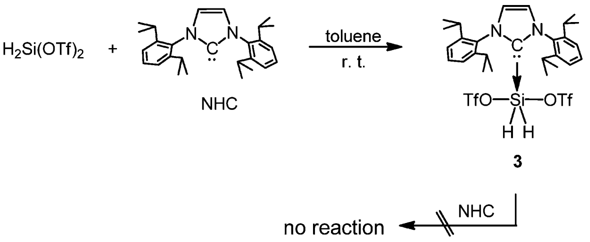
Since the triflate group OTf is a better leaving group than chloride, we investigated the reaction of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene with $H_2Si(OTf)_2$ [22]. When $H_2Si(OTf)_2$ was treated with an equivalent of the NHC in toluene at room temperature, a colorless precipitate was formed immediately. The ^1H NMR spectrum of the resulting mixture showed the formation of the desired 1 : 1 adduct $(NHC)SiH_2(OTf)_2$ (**3**), which could be isolated in 75 % yield (Scheme 3).

Unexpectedly, and in contrast to **1**, compound **3** does not react with a second equivalent of NHC, presumably because of the steric demand of the two OTf groups. The ^1H NMR spectrum of **3** shows a signal for the SiH_2 protons at $\delta = 4.77$ ppm (CD_2Cl_2), exhibiting an upfield shift in comparison with that observed for **1** (6.42 ppm in C_6D_6) (Table 1). In con-

Table 1. Comparison of selected parameters for compounds **1**–**5**^{a}.

Compounds	**1**	**2**	**3**	**4**	**5**
	$(NHC)SiH_2Cl_2$	$(NHC)_2SiH_2Cl_2$	$(NHC)SiH_2(OTf)_2$	$(NHC)SiH_3(OTf)$	$(NHC)_2SiH_3(OTf)$
$\delta(^1H)$ (SiH), ppm	6.42	5.58^b	4.77	3.69	4.19
$\delta(^{29}Si)$, ppm	−123.8	−225.2	−102.5	−80.4	−171.0
IR: $\tilde{\nu}$ (Si–H), cm^{-1}	2214	2118	2211	2230	2179
d(Si–C), pm	190.4(3)	204.9(2) 204.9(2)	190.1(4)	192.0(2)	208.3(2) 209.3(2)

^{a} NMR data for **1** and **2** were measured in C_6D_6, for **3**, **4** and **5** in CD_2Cl_2; ^{b} ref. [8] and this work.



Scheme 3. Formation of (NHC)$SiH_2(OTf)_2$ (**3**).

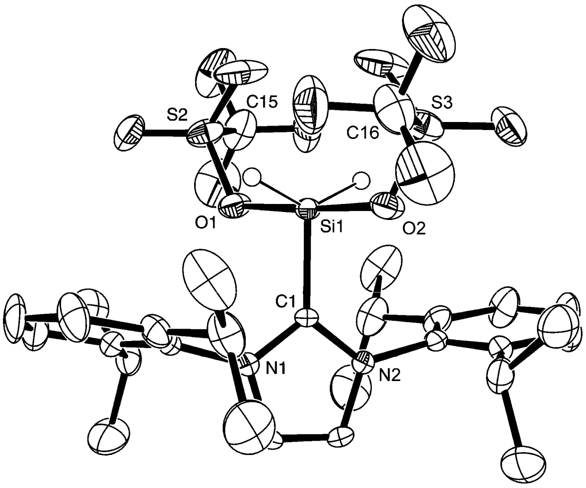


Fig. 2. Molecular structure of **3**. Displacement ellipsoids are drawn at 50 % probability level. H atoms (except SiH_2) are omitted for clarity. Selected bond lengths (pm) and angles (deg): Si1–C1 190.1(4), Si1–O1 191.3(2), Si1–O2 191.3(2), C1–N1 134.3(3); O1–Si1–O2 176.7(2), C1–Si1–O1 91.7(1), N1–C1–N2 106.4(4), N1–C1–Si1 126.8(2); O1–Si1–C1–N1 66.1.

trast, the ^{29}Si NMR spectrum exhibits a downfield shift [$\delta = -102.5$ ppm in CD_2Cl_2 *vs.* -123.8 ppm for **1** (CP/MAS)]. Moreover, the valence vibration of Si–H in the IR spectrum of **3** (2211 cm^{-1}) is slightly shifted to lower wave numbers (*vs.* 2214 cm^{-1} for **1**). Obviously, the variation of these spectroscopic data in **3** is correlated with the weaker Si–OTf bonding in **3** as compared to the Si–Cl bonding in **1**.

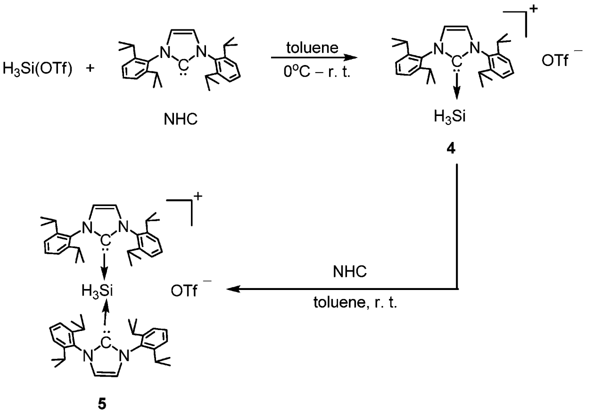
Compound **3** is insoluble in *n*-hexane and toluene, but soluble in dichloromethane. Single crystals of **3** suitable for X-ray diffraction analysis were obtained from a dichloromethane solution at ambient temperature. The compound crystallizes in the monoclinic space group $C2/c$ (Fig. 2). Similar to **1**, the Si atom in **3** is five-coordinated in a distorted trigonal-bipyramidal environment. The O1 and O2 atoms are located in the axial positions with an O1–Si1–O2 angle of 176.7(2)°, close to that in **1** (176.3(1)°). The Si–C bond length of 190.1(4) pm is also close to that in **1** (190.4(3) pm) (Table 1). Owing to the steric demand of the NHC ligand, the N1–C1–Si1–O1 torsion angle is 66.1°. As expected, the Si–O distance (191.3(2) pm) in **3** is longer than those observed for related Si–OTf containing compounds with four-coordinate silicon atoms [23–25], indicating a weaker covalent Si–O interaction due to the higher coordination number of the silicon atom. In line with that, the moderate solubility of **3** in toluene reflects a somewhat ionic character.

Reaction of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene with H_3SiOTf

To compare the reactivity of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene toward other triflate-substituted silanes, the silyltrifluoromethanesulfonate H_3SiOTf [26] was synthesized, and its reactions with NHCs were examined. The equimolar reaction of the NHC with H_3SiOTf in toluene led to the formation of the [(NHC)SiH_3]$^+$(OTf$^-$) ion pair **4** in quantitative yield (Scheme 4). The ^{1}H NMR spectrum of **4** gives a singlet at $\delta = 3.69$ ppm (CD_2Cl_2) for the SiH_3 protons. The ^{29}Si NMR spectrum exhibits a downfield shifted resonance signal at $\delta = -80.4$ ppm as compared with that of the molecular, five-coordinate NHC-bis(triflato)silane adduct **3** ($\delta = -102.5$ ppm, Table 1), but a significant upfield shift as compared with donor-stabilized, four-coordinate silylium species [(^{Et}NHC)$SiMe_3$]$^+$I$^-$ (^{Et}NHC =1,3-diethylimidazol-2-ylidene) ($\delta = -5.1$ ppm) [16].

The donor-stabilized parent silylium salt **4** is insoluble in hexane and toluene, but soluble in dichloromethane. Single crystals suitable for X-ray diffraction analysis could be grown from dichloromethane solutions. Compound **4** crystallizes in the orthorhombic space group *Pbca* (Fig. 3). The structure comprises the four-coordinate silylium cation [(NHC)SiH_3]$^+$ and the OTf$^-$ anion and is thus significantly different from that of **3**. The closest Si···O contact in **4** amounts to 266.1 pm. The silicon atom in **4** adopts a distorted tetrahedral coordination geometry. The Si–C distance of 192.0(2) pm is similar to that of the related five-coordinate silicon species **3** (190.1(4) pm) and **1** (190.4(3) pm) (Table 1).

Akin to the reactivity of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene towards **1**, the equimolar



Scheme 4. Formation of **4** and **5**.

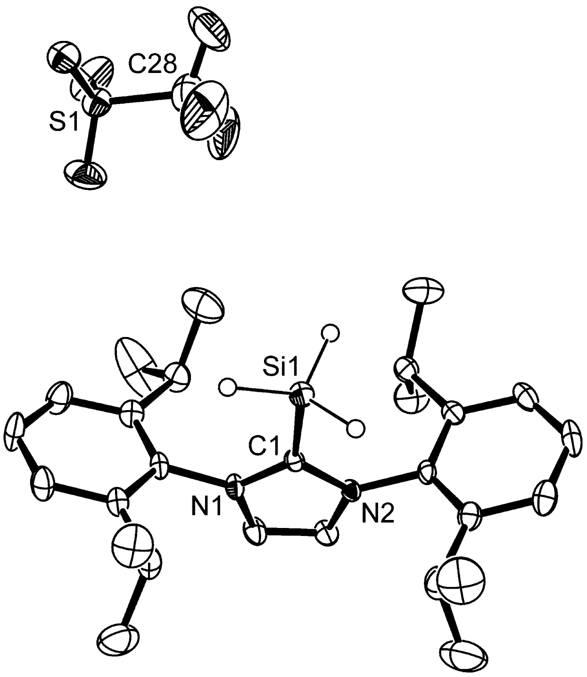


Fig. 3. Molecular structure of **4**. Displacement ellipsoids are drawn at 50% probability level. H atoms (except SiH_3) are omitted for clarity. Selected bond lengths (pm) and angles (deg): Si1–C1 192.0(2), C1–N1 138.1(3); N1–C1–Si1 129.2(1), N2–C1–Si1 125.7(1), N1–C1–N2 105.1(2).

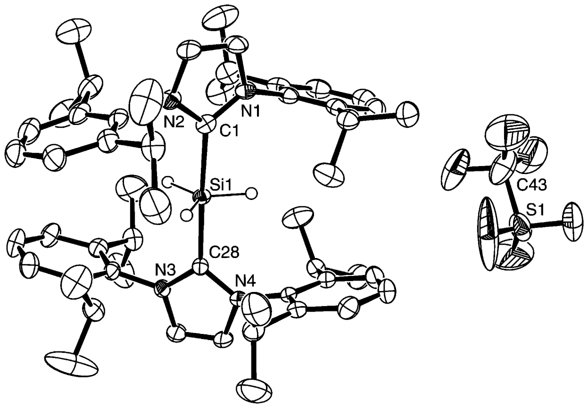


Fig. 4. Molecular structure of **5**. Displacement ellipsoids are drawn at 50% probability level. H atoms (except SiH_3) are omitted for clarity. Selected bond lengths (pm) and angles (deg): Si1–C1 209.3(2), Si1–C28 208.3(2), C1–N1 135.9(3), C1–N2 136.4(3), C28–N3 135.4(3), C28–N4 136.2(3); C1–Si1–C28 178.0(1), N1–C1–N2 104.3(2), N4–C28–N3 104.3(2), N1–C1–Si1 127.4(2), N2–C1–Si1 128.1(2), N3–C28–Si1 128.4(2), N4–C28–Si1 127.2(2).

reaction of the NHC with **4** led to the formation of the 2 : 1 coordination product $(NHC)_2SiH_3(OTf)$ **5** (Scheme 4). Interestingly, the ^1H NMR spectrum of **5** exhibits a downfield shift for the SiH_3 protons ($\delta = 4.19$ ppm) in comparison to that of **4** ($\delta = 3.69$ ppm) (Table 1). As expected, the Si–H stretching vibration in the IR spectrum of **5** ($\tilde{\nu} = 2179\ cm^{-1}$) appears at lower wave numbers compared with that in **4** ($\tilde{\nu} = 2230\ cm^{-1}$) due to the increased coordination number of silicon. The ^{29}Si NMR spectrum of **5** exhibits a singlet at $\delta = -171.0$ ppm, consistent with the higher coordination number of the silicon atom in comparison to **4** ($\delta = -80.4$ ppm).

As expected, the donor-stabilized silylium ion pair **5** is insoluble in hexane and toluene, but soluble in dichloromethane, similar to the solubility of **4**. Single crystals suitable for X-ray diffraction analysis of **5** were obtained from dichloromethane solutions. Compound **5** crystallizes in monoclinic space group $P2_1/n$. The closest Si···O distance between the $[(NHC)_2SiH_3]^+$ cation and the OTf^- anion amounts to 723.6 pm (Fig. 4).

The silicon center of the silylium cation of **5** is five-coordinated and adopts a distorted trigonal-bipyramidal geometry. The two NHC molecules occupy the axial positions and the imidazol-like rings of the NHC ligands are tilted by 37.7° with respect to each other. The C1–Si1–C28 bond angle of 178.0(1)° deviates only slightly from that in the ideal trigonal-bipyramidal geometry. The two Si–C distances of 208.3(2) and 209.3(2) pm are significantly longer than that of **4** (192.0(2) pm) (Table 1), and even longer than those in **2** (204.9(2) pm [8]) and in $(NHC)_2SiF_4$ (av. 201.0(2) pm [21]).

In summary, by examining the reactivity of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene toward H_2SiX_2 (X = Cl, OTf) and H_3SiOTf we were able to synthesize the new series of tetra-, penta- and hexa-coordinate NHC-hydrosilanes and their parent silylium complexes. The products **1**, **3**, **4**, and **5** could be fully characterized, including single-crystal X-ray diffraction analyses. Despite of the fact that the OTf substituent can serve as a good anionic leaving group, remarkably, the bis(triflato)silane forms only the covalent 1 : 1 adduct **3**. In contrast, the silyltriflate is capable to produce the NHC-stabilized silylium ion pairs **4** (1 : 1 adduct) and **5** (2 : 1 adduct) with four- and five-coordinate silicon atoms, respectively. All new complexes are expected to serve as promising precursors for the synthesis of value-added organosilicon compounds through reduction or ligand exchange. Respective investigations are currently in progress.

Experimental Section

General considerations

All experiments and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or in an MBraun inert atmosphere dry-box containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior to use. The starting materials, $H_2Si(OTf)_2$ [22], $H_3Si(OTf)$ [26] and NHC [27] were prepared according to literature procedures. H_2SiCl_2 (ABCR) was commercially available and used as received. The NMR spectra were recorded with Bruker spectrometers ARX200, AV400 and with residual solvent signals as internal reference (^1H and $^{13}C\{H\}$) or with an external reference ($SiMe_4$ for ^{29}Si). Abbreviations: s = singlet; d = doublet; t = triplet; sept = septet; m = multiplet; br = broad. Elemental analyses were performed on a FlashEA 1112 CHNS Analyzer. (+)-ESI mass spectra were measured on a Thermo Scientific LTQ orbitrap XL instrument. The infrared spectra were taken on a Nicolet Magna 750 spectrometer with nitrogen gas purge.

*Synthesis of (NHC)SiH$_2$Cl$_2$ (**1**)*

A molar excess of SiH_2Cl_2 was introduced into the solution of NHC (0.63 g, 1.6 mmol) in toluene (20 mL) at −10 °C. The reaction mixture was allowed to warm to room temperature and stirred at room temperature for 30 min. The excess of SiH_2Cl_2 and the solvent were evaporated in a vacuum, and the residue was washed with *n*-hexane (5 mL) and extracted with toluene to afford compound **1** with a yield of 0.67 g (85 %). X-Ray-qualified single crystals were grown in toluene at 4 °C; m. p. 165 °C (decomposed). – ^1H NMR (200.13 MHz, C_6D_6, 25 °C): δ = 0.95 (d, ^3J(H,H) = 6.6 Hz, 12 H; $CHMe_2$), 1.50 (d, ^3J(H,H) = 6.6 Hz, 12 H; $CHMe_2$), 3.18 (sept, ^3J(H,H) = 6.6 Hz, 4 H; $CHMe_2$), 6.42 (s, 2 H; SiH_2), 6.51 (s, br, 2 H; CH=CH in C_3N_2 ring), 7.15 – 7.22 ppm (m, 6 H; arom. H in 2,6-iPr$_2$C$_6$H$_3$). – $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 25 °C): δ = 22.7, 26.5, 29.2 ($CHMe_2$, $CHMe_2$), 123.8, 124.5, 129.3, 131.8, 132.5, 146.6 ppm (in C_3N_2 ring, and arom. C in 2,6-iPr$_2$C$_6$H$_3$). – CP/MAS $^{29}Si\{^1H\}$ NMR (79.49 MHz, C_6D_6, 25 °C): δ = − 123.8 ppm. – HR ((+)-ESI): m/z = 389 $[NHC+H]^+$. – Elemental analysis (%) for $C_{27}H_{38}N_2SiCl_2$: calcd. C 66.24, H 7.82, N 5.72; found C 66.17, H 7.80, N 5.78. – IR: (KBr, cm^{-1}): ν = 3141 (w), 3114 (w), 3081 (w), 2961 (vs), 2928 (s), 2869 (s), 2756 (w), 2214 (w, $\nu_{(Si-H)}$), 1533 (s), 1467 (vs), 1443 (s), 1422 (m), 1385 (m), 1365 (m), 1327 (s), 1255 (w), 1206 (m), 1139 (m), 1126 (m), 1060 (s), 956 (vs), 802 (s), 786 (vs), 753 (s), 641 (w), 533 (w).

*Synthesis of (NHC)$_2$SiH$_2$Cl$_2$ (**2**)*

To a solution of **1** (0.45 g, 0.92 mmol) in toluene (20 mL) was added a solution of NHC (0.36 g, 0.92 mmol) in toluene (10 mL) at room temperature under stirring. After 4 h the volatiles were evaporated, and the residue was extracted with *n*-hexane. From *n*-hexane the X-ray-qualified single crystals were obtained at room temperature. The collected crystals amounted to 0.70 g (0.80 mmol, 87 %). The analytical data for the isolated compound **2** (m. p., NMR data, MS, X-ray structure determination) are identical with those reported by Roesky and coworkers [8]. – IR (KBr, cm^{-1}): ν = 3175 (w), 3144 (w), 3065 (w), 3030 (w), 2961 (vs), 2927 (vs), 2867 (vs), 2118 (m, $\nu_{(Si-H)}$), 1533 (w), 1465 (vs), 1406 (s), 1380 (s), 1360 (s), 1330 (s), 1205 (s), 1177 (w), 1114 (s), 1082 (w), 1060 (m), 1017 (vs), 941 (s), 801 (s), 755 (vs), 743 (s), 695 (w), 639 (w).

*Synthesis of (NHC)SiH$_2$(OTf)$_2$ (**3**)*

Trifluoromethanesulfonic acid (0.30 mL, 98 %, d = 1.71 g mL^{-1}, 3.3 mmol) was dropped into diphenylsilane (0.32 mL, 97 %, d = 0.993 g mL^{-1}, 1.7 mmol) at 0 °C under stirrung. After 10 min a solution of NHC (0.65 g, 1.7 mmol) in toluene (50 mL) was added to the reaction mixture at room temperature. Large amounts of a precipitate formed immediately. The solvent toluene was separated away through filtration, and the residue was purified by recrystalllization from dichloromethane. The collected crystals amounted to 0.90 g (1.26 mmol, 75 %); m. p. 230 °C (decomp.). – ^1H NMR (200.13 MHz, CD_2Cl_2, 25 °C): δ = 1.16 (d, ^3J(H,H) = 6.7 Hz, 12 H; $CHMe_2$), 1.43 (d, ^3J(H,H) = 6.7 Hz, 12 H; $CHMe_2$), 2.60 (sept, ^3J(H,H) = 6.7 Hz, 4 H; $CHMe_2$), 4.77 (s, 2 H; SiH_2), 7.42 – 7.68 ppm (m, 8 H; CH=CH in C_3N_2 ring, arom. H in 2,6-$i$$Pr_2C_6H_3$). – $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 25 °C): δ = 21.4, 26.4, 29.0 ($CHMe_2$, $CHMe_2$), 124.9, 127.3, 127.8, 128.3, 132.2, 145.2 ppm (in C_3N_2 ring, arom. C in 2,6-$i$$Pr_2C_6H_3$). – $^{29}Si\{^1H\}$ NMR (79.49 MHz, CD_2Cl_2, 25 °C): δ = – 102.5 ppm. – ^{19}F NMR (200.13 MHz, CD_2Cl_2, 25 °C): δ = – 77.2 ppm. – HR ((+)-ESI): $m/z = 389$ $[NHC+H]^+$. – Elemental analysis (%) for $C_{29}H_{38}N_2Si_2O_6F_6S_2$: calcd. C 48.59, H 5.34, N 3.91; found C 48.56, H 5.20, N 3.94. – IR (KBr, cm^{-1}): ν = 3168 (w), 2969 (vs), 2928 (m), 2873 (w), 2211 (w, $\nu_{(Si-H)}$), 1537 (w), 1466 (m), 1390 (w), 1369 (m), 1262 (vs), 1160 (s), 1031 (vs), 957 (w), 867 (w), 807 (w), 758 (m), 638 (vs), 575 (m), 518 (m).

Synthesis of $[(NHC)SiH_3]^+(OTf^-)$ *(**4**)*

To phenylsilane (0.62 mL, 97 %, d = 0.88 g mL^{-1}, 4.9 mmol) was added dropwise trifluoromethanesulfonic acid (0.44 mL, 98 %, d = 1.71 g mL^{-1}, 4.9 mmol) at –50 °C under stirring. After 10 min a solution of NHC (1.90 g, 4.9 mmol) in toluene (50 mL) was added *in situ* into the solution of produced $H_3Si(OTf)$. A colorless precipitate was formed immediately. The solvent toluene was replaced by dichloromethane, from which compound **4** crystallized as colorless plates with a yield of 2.5 g (4.4 mmol, 90 %); m. p. 238 °C (decomp.). – ^1H NMR (200.13 MHz, CD_2Cl_2, 25 °C): δ = 1.24 (d, ^3J(H,H) = 6.8 Hz, 24 H; $CHMe_2$), 2.28 (sept, ^3J(H,H) = 6.8 Hz, 4 H; $CHMe_2$), 3.69 (s, 3 H; SiH_3), 7.41 – 7.95 ppm (m, 8 H; CH=CH in C_3N_2 ring, arom. H in 2,6-$i$$Pr_2C_6H_3$). – $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 25 °C): δ = 22.7, 24.7, 29.1 ($CHMe_2$, $CHMe_2$), 125.1, 128.9, 130.7, 132.0, 144.8, 148.4 ppm (in C_3N_2 ring, arom. C in 2,6-$i$$Pr_2C_6H_3$). – $^{29}Si\{^1H\}$ NMR (79.49 MHz, CD_2Cl_2, 25 °C): δ = – 80.4 ppm. – ^{19}F NMR (200.13 MHz, CD_2Cl_2, 25 °C): δ = – 78.9 ppm. – HR ((+)-ESI): $m/z = 389$ $[NHC+H]^+$. – Elemental analysis (%) for $C_{28}H_{39}N_2SiO_3F_3S$: calcd. C 59.13, H 6.91, N 4.93; found C 58.97, H 6.88, N 4.83. – IR (KBr, cm^{-1}): ν = 3172 (w), 2970 (vs), 2933 (m), 2874 (w), 2230 (w, $\nu_{(Si-H)}$), 1469 (s), 1370 (s), 1327 (w), 1235 (vs), 1248 (vs), 1223 (s), 1161 (vs), 1139 (s), 957 (w), 1061 (w), 1029 (vs), 885 (vs), 804 (m), 773 (m), 759 (s), 637 (vs), 573 (w), 517 (m).

Synthesis of $[(NHC)_2SiH_3]^+(OTf^-)$ *(**5**)*

To a solution of **4** (0.50 g, 0.88 mmol) in dichloromethane (15 mL) was added a solution of NHC (0.34 g, 0.88 mmol) in toluene (10 mL) at room temperature under stirring. After 16 h the reaction mixture was concentrated to 5 mL and cooled to –20 °C. From dichloromethane compound **5** crystallized as colorless plates suitable for X-ray diffraction analysis. The collected crystals amounted to 0.70 g (0.73 mmol, 83 %); m. p. 245 °C (decomp.). – ^1H NMR (200.13 MHz, CD_2Cl_2, 25 °C): δ = 0.86 (d, ^3J(H,H) = 6.7 Hz, 24 H; $CHMe_2$), 1.00 (d, ^3J(H,H) = 6.7 Hz, 24 H; $CHMe_2$), 2.19 (sept, ^3J(H,H) = 6.7 Hz, 8 H; $CHMe_2$), 4.19 (s, 3 H; SiH_3), 6.88 (s, 4 H; CH=CH in C_3N_2 ring), 7.12 – 7.49 ppm (m, 12 H; arom. H in 2,6-$i$$Pr_2C_6H_3$). – $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 25 °C): δ = 22.9, 24.5, 28.6 ($CHMe_2$, $CHMe_2$), 123.5, 123.6, 124.4, 130.8, 132.7, 144.6 ppm (in C_3N_2 ring, arom. C in 2,6-$i$$Pr_2C_6H_3$). – $^{29}Si\{^1H\}$ NMR (79.49 MHz, CD_2Cl_2, 25 °C): δ = – 171.0 ppm. – ^{19}F NMR (200.13 MHz, CD_2Cl_2, 25 °C): δ = – 78.9 ppm. – HR ((+)-ESI): $m/z = 389$ $[NHC+H]^+$. – Elemental analysis (%) for $C_{55}H_{75}N_4SiO_3F_3S$: calcd. C 69.00, H 7.90, N 5.85; found C 69.11, H 8.08, N 5.75. – IR (KBr, cm^{-1}): ν = 2966 (vs), 2931 (m), 2871 (m), 2179 (w, $\nu_{(Si-H)}$), 1465 (s), 1406 (m), 1365 (m), 1273 (vs), 1223 (m), 1150 (vs), 1103 (w), 1061 (w), 1031 (vs), 955 (s), 806 (m), 785 (m), 759 (s), 637 (vs), 575 (m), 571 (w), 517 (w).

Single-crystal X-ray structure determinations

Crystals were mounted on glass capillaries in perfluorinated oil and measured in a cold N_2 flow. The data of **1**, **3**, **4**, and **5** were collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K (MoK_α radiation, λ = 0.71073 Å). The structures were solved by Direct Methods and refined on F^2 with the SHELXS/L-97 [28, 29] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model.

CCDC 921558, 921559, 921560, and 921561 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.

1: Tetragonal, space group $P4_12_12$, $a = b = 14.2410(6)$, $c = 13.425(2)$ Å, $V = 27227(3)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.19$ Mg m^{-3}, μ(MoK_α) = 0.3 mm^{-1}, 18278 collected reflections, 2384 crystallographically independent reflections [$R_{int} = 0.1161$], 2295 reflections with $I > 2\,\sigma(I)$, $\theta_{max} = 25°$, $R(F_o) = 0.0401$ [$I > 2\,\sigma(I)$], $wR(F^2) = 0.0976$ (all data), 154 refined parameters.

3: Monoclinic, space group $C2/c$, $a = 23.332(6)$, $b = 9.201(2)$, $c = 18.102(5)$ Å, $\beta = 117.99(4)°$, $V = 3431.5(1)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.39$ Mg m^{-3}, μ(MoK_α) = 0.3 mm^{-1}, 7466 collected reflections, 3002 crystallographically independent reflections [$R_{int} = 0.0478$], 1907 reflections with $I > 2\,\sigma(I)$, $\theta_{max} = 25°$, $R(F_o) = 0.0573$ [$I > 2\,\sigma(I)$], $wR(F^2) = 0.1402$ (all data), 217 refined parameters.

4: Orthorhombic, space group $Pbca$, $a = 16.258(2)$, $b = 17.545(2)$, $c = 21.418(2)$ Å, $V = 6109.4(9)$ Å^3, $Z = 8$, $\rho_{calcd.} = 1.24$ Mg m^{-3}, μ(MoK_α) = 0.2 mm^{-1}, 25205 collected reflections, 5366 crystallographically independent reflections [$R_{\text{int}} = 0.0440$], 3961 reflections with $I > 2\,\sigma(I)$, $\theta_{\max} = 25°$, $R(F_o) = 0.0444$ [$I > 2\,\sigma(I)$], $wR(F^2) = 0.1075$ (all data), 363 refined parameters.

5: Monoclinic, space group $P2_1/n$, $a = 13.7805(9)$, $b = 23.746(2)$, $c = 16.866(2)$ Å, $\beta = 94.716(7)°$, $V = 5500.2(8)$ Å^3, $Z = 4$, $\rho_{\text{calcd.}} = 1.16\ \text{Mg m}^{-3}$, $\mu(\text{Mo}K_\alpha) = 0.1\ \text{mm}^{-1}$, 40240 collected reflections, 9664 crystallographically independent reflections [$R_{\text{int}} = 0.0482$], 6596 reflections with $I > 2\,\sigma(I)$, $\theta_{\max} = 25°$, $R(F_o) = 0.0594$ [$I > 2\,\sigma(I)$], $wR(F^2) = 0.1669$ (all data), 632 refined parameters.

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