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Hydrosilylation of RN=C*H* imino-substituted pyridines without a catalyst

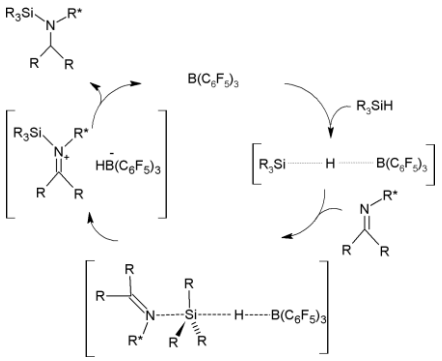
Miroslav Novák,[a] Hana Hošnová,[a] Libor Dostál,[a] Britta Glowacki,[b] Klaus Jurkschat,[b] Antonín Lyčka,[c] Zdenka Ruzickova[a] and Roman Jambor*[a]

Abstract: Treatment of the neutral pyridine based ligands $\mathbf{L^1}$ - $\mathbf{L^3}$ containing either one or two RN=CH imine moieties (where $\mathbf{L^1}$ and $\mathbf{L^2}$ are *N*,*N*-chelating ligands 2-(RN=C*H*)C_5H_4N (R = Ph ($\mathbf{L^1}$) or R = 2,4,6-$Ph_3C_6H_2$ ($\mathbf{L^2}$)) and $\mathbf{L^3}$ is the *N*,*N*,*N*-chelating ligand 2,6-(RN=C*H*)$_2C_5H_3N$ (R = 2,6-^{i}Pr$_2$C$_6$H$_3$) with $HSiCl_3$ yielded N→Si-coordinated silicon (IV) amides 2-{$Cl_3SiN(R)CH_2$}C_5H_4N (**1**, R = Ph; **2**, R = 2,4,6-$Ph_3C_6H_2$), and 2-{$Cl_3SiN(R)CH_2$}-6-(RN=C*H*)C_5H_4N (**3**, R = 2,6-^{i}Pr$_2$C$_6$H$_3$). The organosilicon amides **1** - **3** are products of the spontaneous hydrosilylation of the RN=C*H* imine moiety induced by N→Si coordination of the proposed *N*,*N*-chelated chlorosilanes $\mathbf{L^1}$→$SiHCl_3$ (**1a**), $\mathbf{L^2}$→$SiHCl_3$ (**2a**), and $\mathbf{L^3}$→$SiHCl_3$ (**3a**). In addition, the reaction of $\mathbf{L^3}$ with an excess of $HSiCl_3$ provided the intramolecularly coordinated chlorosilicon diamide *cyclo*-{(C_5H_3N)-1,3-($CH_2NR)_2$}$SiCl_2$ (**4**) (R = 2,6-^{i}Pr$_2$C$_6$H$_3$), a product of the spontaneous reduction of both RN=C*H* imine moieties. The compounds were characterized by NMR spectroscopy (**1** – **4**) and single crystal X-ray diffraction analysis (**1**, **3**, **4**). The mechanism for the hydrosilylation of the second RN=C*H* imine moiety in **3** by an excess of $SiHCl_3$ was studied as well. The experimental work is accompanied by DFT calculations.

Keywords: silicon • hydrosilylation • intramolecular coordination • NMR • DFT

Introduction

Hydrosilylation reactions[1] are usually catalysed by i) low-valent transition metal complexes[2] or by ii) nucleophilic/electrophilic synergistic mechanism, where a nucleophile polarizes the Si-H bond of the silane.[3] The hydrosilylation process is thus powerful tool for the reduction of various functional groups such as aldehydes, ketones, esters or olefins.[4] Recently, Piers and co-workers discovered a $B(C_6F_5)_3$ Lewis acid-catalyzed hydrosilylation of C*H*=N[5] and related imine functions.[6] As the reduction of imines to amines mostly involves borohydride reagents or transition metal hydrides,[7] the mechanism for the above-mentioned hydrosilylation of the imine moiety was further studied. Piers et al and Oestreich et al clarified that $B(C_6F_5)_3$ activates the Si-H bond and predicted an important role of an *inter*molecular interaction of C=N bond with polarized Si-H bond (Scheme 1).[8] Furthermore, N→Si coordinate hydrosilanes bearing azobenzene moieties have been prepared an the *intra*molecular 1,3-hydride shift to the latter was facilitated b addition of fluoride anion.[9c] The reduction of azo- t hydrazobenzene was thus promoted by the conversion of four- t five-coordinated silicon atom.[9c]



Scheme 1. Mechanism of the $B(C_6F_5)_3$-catalyzed hydrosilylation of imines (R* = H or organic substituent)

In contrast to these catalysed hydrosilylation reactions, hypercoordinated hydrosilanes exhibit an enhanced reactivity of the silicon-bound hydrogen atom.[9] As observed for the 1,3-hydride shift, the hypercoordinate silicon hydride complexes[10] reduce carbonyl or related compounds by hydride transfer in the absence of any metal catalyst.[11] Recently, Kano *et al.* reported N→Si *intra*molecularly coordinated hydrosilanes with the ability to reduce

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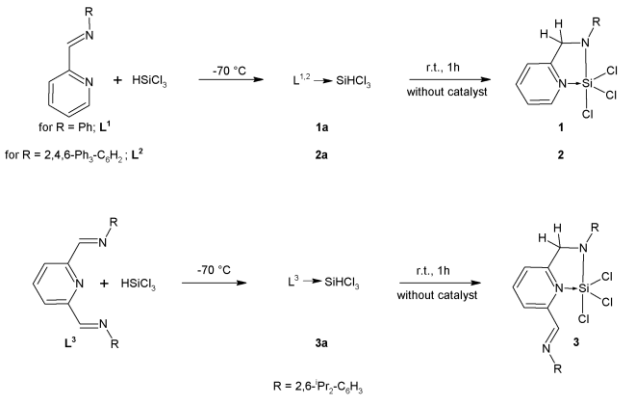
phosphine imide moieties.[12b] Kost *et al.* also developed an non-catalyzed *intra*molecular 1,3-hydride transfer from N→Si hexacoordinated silanes to imino carbon atom.[12a] In this manner, studies on the spontaneous hydrosilylation of the C*H*=N imine moiety induced by the N→Si *intra*molecular coordination have recently been reported[13]

These rare examples of the non-catalysed hydrosilylation reactions involving hypercoordinated organosilanes raise the question, whether these can be true alternatives for the catalytic hydrosilylation processes. The preparation of *intra*molecularly N→Si-coordinated silicon hydrides involves the synthesis of the parent N→Li-coordinated organolithium compounds.[13a,b] This is not really convenient especially when applications in industrial processes are envisaged. For this reason, it is meaningful to omit the metalation step and to use mixtures containing silanes and neutral C=Y-functionalized ligands (Y = O or NR). Recently, Wagler and Kroke used this concept and reported on the reactivity of 2-acylpyrroles with $HSiCl_3$ or H_2SiCl_2.[13e] They found H_2 elimination instead of a reduction of the unsaturated C=O moiety. This motivated us to use neutral pyridine-based ligands of the type 2-(RN=C*H*)C_5H_4N (**L**^{1}, R = Ph; **L**^{2}, R = 2,4,6-$Ph_3C_6H_2$) containing one and 2,6-(RN=C*H*)$_2C_5H_3N$ (**L**^{3}, R = 2,6-$^{i}Pr_2C_6H_3$) containing two imine moieties (Scheme 2) for reactions with the parent organosilanes.

Results and discussion

The reaction of **L**^{1} – **L**^{3} with $HSiCl_3$ gave the N→Si coordinated silicon (IV) amides 2-{$Cl_3SiN(R)CH_2$}C_5H_4N (**1**, R = Ph; **2**, R = 2,4,6-$Ph_3C_6H_2$), and 2-{$Cl_3SiN(R)CH_2$}-6-(RN=C*H*)C_5H_4N (**3**, R = 2,6-$^{i}Pr_2C_6H_3$) as white (**1**) or yellow (**2**, **3**) crystalline materials, respectively, in moderate to good yields. Compounds **1** - **3** are the result of the spontaneous hydrosilylation of the C*H*=N imine moiety in the proposed *N*, *N*-chelated chlorosilane complexes **L**^{n}→$SiHCl_3$ (**1a**, n = 1; **2a**, n = 2; **3a**, n = 3). The latter are suggested to be intermediates along this reaction path (Scheme 2), because it is well known that $HSiCl_3$ can be easily coordinated by various nitrogen based ligands.[14]



Scheme 2. Neutral N,N-chelating ligands L^1 – L^3 and their reactions towards $HSiCl_3$ providing, via the suggested intermediates **1a** - **3a**, the hydrosilylation products **1** – **3**.

The ^{1}H NMR spectra of the isolated compounds **1** - **3** showed resonances at δ 3.83 (**1**), 3.96 (**2**) and 4.21 ppm (**3**) assigned to the NCH_2 protons. In case of **3**, there was also a resonance at δ 9.86 ppm belonging to a RN=C*H* proton of the non-reacted imino group. The ^{29}Si NMR spectra of **1** – **3** revealed signals at δ –103.4 (**1**), –95.7 (**2**) and –97.2 (**3**) ppm. The ^{13}C NMR spectra of **1** - **3** revealed signals at δ 55.4 ppm (**1**), 49.7 ppm (**2**) and δ 54.9 ppm (**3**) belonging to the corresponding NCH_2 carbon atoms. A ^{13}C NMR spectrum of **3** also revealed a signal at δ 158.3 ppm that is assigned to the RN=*C*H imine moiety.

The molecular structures of **1** and **3,** as determined by single crystal X-ray diffraction analyses, are shown in Figures 1 and 2, respectively. Selected interatomic distances and angles are given in the figure captions. Crystallographic data are summarized in Table S1 (see SI).

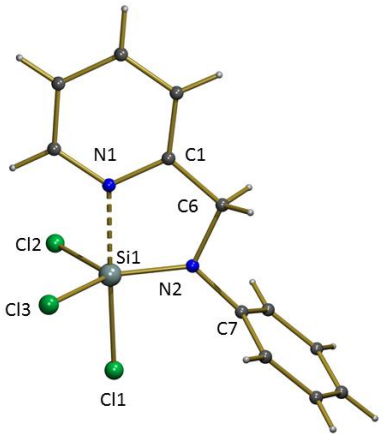


Figure 1. Molecular structure of **1**. The crystal structure contains two independer molecules only one of which is shown for clarity. Selected interatomic distances (Å Cl1–Si1 2.1593(10), Cl2–Si1 2.0838(11), Cl3–Si1 2.0848(11), Si1–N2 1.708(2), Si1 N1 1.949(2), N2–C7 1.433(4), N2–C6 1.462(3). Selected interatomic angles (°): N1 Si1–Cl1 178.14(8), N1–Si1–N2 83.56(11), Cl2–Si1–Cl3 110.15(5), Cl2–Si1 N2 123.75(10), Cl3–Si1–N2 125.16(10), Cl2–Si1–Cl1 92.46(4), Cl3–Si1–Cl1 92.01(4 N2–C6–C1 107.9(2).

In both compounds **1** and **3**, the Si1 atoms are five-coordinate and show each a distorted trigonal bipyramidal environment wit N1 and Cl1 occupying the axial and N2, Cl2, and Cl3 occupying th equatorial positions. The Si1–N2 distances (1.708(2) Å in 1 1.704(2) Å in **3**) are shorter than the sum of the covalent radii of S and N ($\sum_{cov}$(Si,N) = 1.87 Å) and are close to a Si=N double bon ($\sum_{covDB}$(Si,N) = 1.67 Å).[15] The Si1–N1 distances (1.949(2) Å in 1 2.058(2) Å in **3**) are longer and indicate strong N→Si intramolecula coordination in both compounds. The N2–C6–C1 angles (107.9(2) in **1**, 109.3(2)° in **3**) suggest sp^3 hybridization at the carbon atom C6. In addition, the C6–N2 distances (1.462(4) Å in **1**, 1.451(3) Å i **3**) fall in the range being typical for single covalent C–N bonds.[1 In contrast, the C19–N3 distance (1.265(3) Å) falls in the range tha is typical for C=N double bonds. The N3–C19–C1 (119.0(2)° suggest the sp^2 hybridization of carbon C19 in **3**.[15]

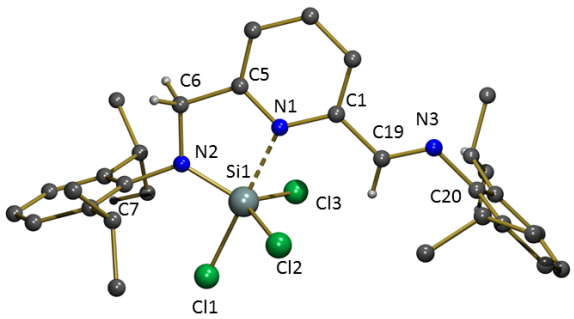


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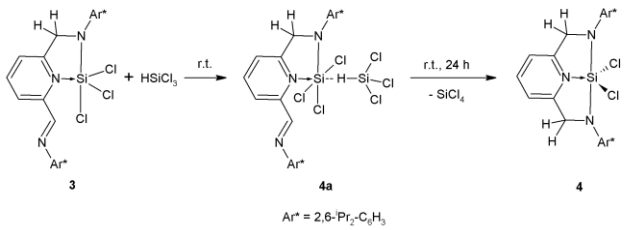
Figure 2. Molecular structure of **3**. Selected interatomic distances (Å) and angles (°): Si1–N2 1.704(2), Si1–N1 2.058(2), Si1–Cl3 2.0734(9), Si1–Cl2 2.0772(9), Si1–Cl1 2.1372(9), N3–C19 1.265(3), N3–C20 1.430(3), N2–C6 1.451(3), N2–C7 1.452(3). Selected interatomic angles (°): N2–Si1–N1 83.42(9), Cl3–Si1–Cl2 116.21(4), Cl3–Si1–Cl1 93.26(4), Cl2–Si1–Cl1 92.86(4), N2–C6–C5 109.3(2), N3–C19–C1 119.0(2).

These data prove unambiguously the isolated compounds **1 - 3** being intramolecularly N→Si coordinated trichlorosilicon(IV) amides. Thus, compounds **1 - 3** are the products of the catalyst-free hydrosilylation of the N=CH imine moiety.

To get a better inside into the reaction mechanism, the reaction of $\mathbf{L^1}$ with $HSiCl_3$ was studied as NMR tube experiment. However, as the compound **1** is moderately soluble in toluene-d_8 or C_6D_6 only, the NMR tube experiments in these solvents provided immediate partial precipitation of **1**. In THF-d_8, the reaction was completed within 1 min (Figure S1 in SI). The reaction of $\mathbf{L^2}$ with $HSiCl_3$ in toluene-d_8 showed, within 1 min, a 26% conversion of L^2 to compound **2**. The conversion increased to 42% within 10 min (see Figures S2 – 6 in SI). After this time, the precipitation of **2** from toluene-d_8 was again observed. It should be also noted that the excess of $HSiCl_3$ or an addition of stoichiometric amount of F^- anion did not accelerate the rate of $\mathbf{L^2}$ to **2** conversion (see Figure S7 in SI). Importantly, a ^{29}Si NMR spectrum of the mixture revealed a doublet at δ –69.9 ppm ($^1J(^{29}Si\text{-}^1H)$ 458 Hz) indicating the presence of the suggested intermediate **2a** (Scheme 1, Figure S8 in SI). The signal is, however, shifted downfield in comparison to closely related *N,N*-chelated bipyridine or phenanthroline complexes of $SiHCl_3$ (range of –170 to –160 ppm),[10d] indicating the silicon atom in **2a** having a lower coordination number. The reaction in THF-d_8 proceeds faster with a 68% molar conversion of $\mathbf{L^2}$ within 10 min (see Figures S9 – 10 in SI). It gave as final product, however, a mixture consisting of compounds **2** and **5** (see Figure S11 in SI) (*vide infra*).

As the compound **3** still contains one RN=CH imine moiety, attempts to reduce this moiety have been performed. The treatment of **3** with $HSiCl_3$ provided the completely reduced N→Si coordinated dichlorosilicon(IV) diamide *cyclo*-{(C_5H_3N)-1,3-($CH_2NR)_2$}$SiCl_2$ (**4**) (R = 2,6-^{i}Pr$_2$C$_6$H$_3$), as colourless crystalline material (Scheme 3). It is worth to note that compound **4** has been also obtained by the direct reaction of ligand $\mathbf{L^3}$ with an excess of $HSiCl_3$ (see experimental part).



Scheme 3. Reaction of compound **3** with $HSiCl_3$ providing, via the suggested intermediate **4a**, the silicon amide **4**.

A ^{1}H NMR spectrum of **4** showed an AX spin system at δ_A 3.85 and δ_X at 4.57 ppm that is assigned to the NCH_2 protons. It also proved the absence of both Si*H* and RN=C*H* protons. A $^{13}C\{^1H\}$ NMR spectrum of **4** revealed signals at δ 54.1 ppm belonging to NCH_2 carbon atoms. A ^{29}Si NMR spectrum of **4** showed a resonance at δ –104.6 ppm. A ^{29}Si NMR spectrum of the crude reaction mixture according to Scheme 3 showed, in addition to the resonance belonging to **4**, a signal at δ –18.8 ppm that is assigned to silicon tetrachloride, $SiCl_4$. A tentative mechanism for the reaction may involve the intermediate formation of complex **4a**, where the Lewis acidic silicon atom of **3** may coordinate the Si*H* proton of $HSiCl_3$ (see Scheme 3). To some extent, the lot resembles the situation reported by Piers et al[8a, c] and Oestreich et al[8b] for the $B(C_6F_5)_3$-catalyzed hydrosilylation of imines (Scheme 1).

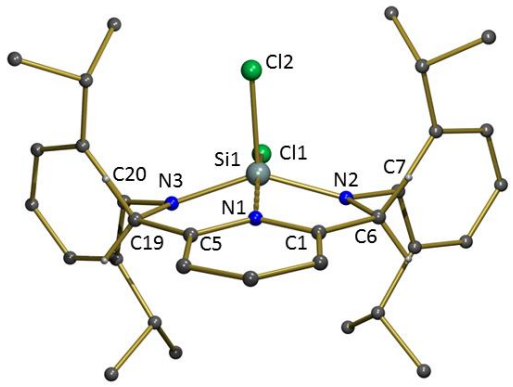


Figure 3. Molecular structure of **4**·C_7H_8. Hydrogen atoms (except those of the amid NCH_2 group) and the toluene solvate molecule are omitted for clarity. Selecte interatomic distances (Å): Si1-N1 1.8972(14), Si1-N2 1.7622(14), Si1-N3 1.7714(15 Si1-Cl1 2.1300(6), Si1–Cl2 2.1237(6), N2-C7 1.444(2), N2-C6 1.469(2), C19-N 1.462(2). Selected interatomic angles (°): N1-Si1-Cl1 165.14(5), N2-Si1-Cl2 106.4 N3-Si1-Cl2 104.60(5), N2-Si1-N3 145.75(7), N3-C19-C5 108.07(14), N2-C6-C 107.96(14)

The molecular structure of **4**, as its toluene solvate **4**·C_7H (Figure 3), was established by single crystal X-ray diffractio analysis. Selected interatomic distances and angles are given in th figure captions. Crystallographic data are summarized in Table S (Supplementary material). The Si1 atom is five-coordinated an shows a distorted square pyramidal environment. The Si1 atom i displaced by 0.3736(4) Å from the mean square plane defined by th Cl1, N1, N2 and N3 atoms in direction of Cl2. The Cl2 ator occupies the apical position. The Si1–N2 (1.7622(14) Å) and Si1 N3 (1.7714(15) Å) distances are shorter than a Si–N covalent singl bond ($\sum_{cov}$(Si,N) = 1.87 Å). They are close to a Si=N double bon ($\sum_{covDB}$(Si,N) = 1.67 Å).[15] In contrast, the Si1–N1 distance c 1.8972(14) Å is longer but still shorter that those found in relate N→Si coordinated silicon(IV) amides (range of 1.936(2) – 2.134(8) Å).[14g,i,16] The N3–C19–C5 (108.07(14)°) and N2–C6–C (107.96(14)°) angles suggest sp^3 hybridization for both C19 and C carbon atoms. In addition, the C6–N2 (1.469(2) Å) and C19–N (1.462(2) Å) distances fall in the range being typical for singl covalent C–N bonds.[15] The results clearly demonstrate that th concept of non-catalysed hydrosilylation can even be used for th reduction of both CH=N imine moieties of the ligand $\mathbf{L^3}$ yieldin new symmetrical N→Si coordinated dichlorosilicon(IV) amide **4**.

The formation of **4** motivated us to study the interaction c $HSiCl_3$ with compounds **1** and **2** in more detail. The reaction of containing a sterically demanding substituent R with excess HSiCl was studied as a NMR tube experiment. A ^{29}Si NMR spectrum measured in C_6D_6 of the crude reaction mixture containing excess of $HSiCl_3$ and **2** (measured after 5 min; Supporting Information, Figure S12) showed three signals at δ –9.3 ($^1J(^{29}Si\text{-}^1H)$ 372 Hz), –18.8 and –95.6 ($^1J(^{29}Si\text{-}^1H)$ 369 Hz) ppm, respectively. The doublet at –9.3 ppm corresponds to the excess of $HSiCl_3$, the singlet at δ –18.8 ppm indicates the presence of $SiCl_4$, and the doublet at δ –95.6 ppm was assigned to the N→Si-coordinated silicon(IV) hydride 2-{$Cl_2HSiN(R)CH_2$}C_5H_4N (**5**, R = 2,4,6-$Ph_3C_6H_2$) (Scheme 4). In addition, the above mentioned reaction of $\mathbf{L^2}$ with $HSiCl_3$ performed in THF-d_8 and monitored by ^{1}H NMR spectroscopy, also revealed the conversion of **2** to **5** (Supporting Information, Figure S11). The

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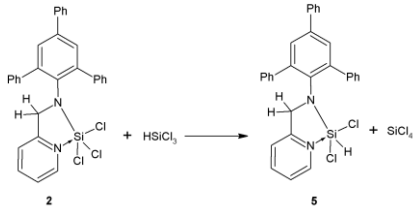
NCH_2 protons of **5** resonated as broad signal at δ 4.22 ppm, while the signal for the Si*H* proton appeared at δ 5.50 ppm.

Compound **5** was directly prepared by the stoichiometric reaction of **2** with $HSiCl_3$ and obtained as white crystalline material in good yield (Scheme 4). Alternatively, it was also prepared by the reaction of $\mathbf{L}^2$ with 2 molar equiv. of $HSiCl_3$.



Scheme 4. The reaction of the N→Si coordinated silicon amide **2** with $HSiCl_3$.

A ^{1}H NMR spectrum (toluene-d_8) of **5** showed a broad signal at δ 4.05 ppm that is assigned to the NCH_2 protons. At 280 K, de-coalescence of this signal into an AX spin-type system (δ_A 3.75, δ_X 4.06 ppm) was observed. The dynamic process may involve either a Berry pseudorotation or de-coordination of the pyridine moiety. The singlet resonance at δ 6.00 ppm ($^1J(^1H–^{29}Si)$ = 369 Hz) is assigned to the Si*H* proton. A $^{13}C\{^1H\}$ NMR spectrum of **5** revealed a signal at δ 49.6 ppm belonging to the NCH_2 carbon atom.

Figure 4 shows the molecular structure of **5**, as its toluene solvate **5**·½C_7H_8, as determined by single crystal X-ray diffraction analysis. Crystallographic data are summarized in the Table S1 (see SI).

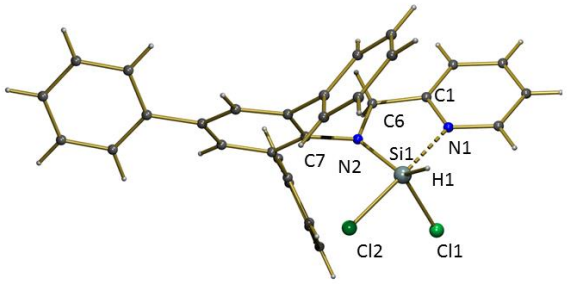
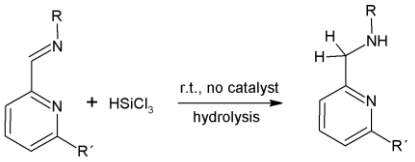


Figure 4. Molecular structure of **5**·½C_7H_8. The crystal structure contains two independent molecules. Only one molecule is shown and the toluene solvate molecule is omitted for clarity. Selected interatomic distances (Å): Si1–Cl1 2.1850(12), Si1–Cl2 2.1077(12), Si1–N1 1.977(2), Si1–N2 1.725(2), Si1–H1 1.7420. Selected interatomic angles (°): N2–Si1–N1 82.98(10), N2–Si1–Cl1 117.15(9), N1–Si1–Cl1 87.17(8), N2–Si1–Cl2 95.86(9), N1–Si1–Cl2 178.79(8), Cl2–Si1–Cl1 93.69(5), N2-Si1-H1 127.9, N1–Si1–H1 96.6.

The molecular structure of **5** closely resembles those found for **1** and **2**. The Si1 atom is five-coordinated with N1 and Cl2 in axial and N2, Cl1 and H1 in equatorial positions of a distorted trigonal bipyramid. The Si1–N1 (1.977(2) Å) and Si1–N2 (1.725(2) Å) distances are different, like those in **1** and **2**.

The formation of compound **5** thus demonstrates that the silicon centers in the N→Si coordinated silicon amides **1**, **2**, and **3** are sufficiently Lewis acidic to activate the Si–*H* bond of $HSiCl_3$ and also corroborates the mechanism proposed for the **3** → **4** conversion. The reaction in THF-d_8 of **1** with an excess of $HSiCl_3$ is slower, but after a reaction time of one week, a ^{29}Si NMR spectrum also showed a low-intense doublet at δ – 93.5 ppm ($^1J(^{29}Si-^1H)$ 369 Hz) suggesting the formation of a new species containing a Si*H* proton (Supporting Information, Figure S13 and for another example also Figure S14). The isolation of compound **5** also allowed investigating, whether **5** is able to act as a hydride donor in an intermolecular reaction. However, the reactions of **5** with ligands containing RN=CH groups were unsuccessful (Supporting Information, Schemes S1 -2 and Figures S15 - 16).

These results, however, show that the reduction of the neutral ligands $\mathbf{L}^1$ - $\mathbf{L}^3$ with $HSiCl_3$ is a straightforward method to yield the novel N→Si coordinated silicon amides **1** - **4**. In addition, the hydrolysis of **1** and **2** provided the corresponding unsymmetrically substituted secondary amines 2-{R(H)NCH_2}C_5H_4N (R = Ph, 2,4,6-$Ph_3C_6H_2$). Therefore, we extended the number of neutral pyridine-based ligands containing a CH=N imine moiety (substrate) an reacted these with $HSiCl_3$ in toluene. The resulting insolubl materials were hydrolysed providing the correspondin unsymmetrically substituted secondary amines (see Table 1, entrie 1 – 6; details for the syntheses and characterization of all substrate and products are given in the Supporting Information, Figures S17 29). This synthetic protocol is rather convenient. *Proof-of-principc* examples are given in Scheme 5.



R = Ph; 2,6-*i*Pr$_2$-C_6H_3, 2,4,6-Ph_3-C_6H_2

R´ = H; Ph,4-(CN)-C_6H_4

Scheme 5. A straightforward protocol for the synthesis of unsymmetrically substitute secondary amines.

It was demonstrated that the reduction takes place either for nor substituted or for *ortho* substituted imino pyridines. The outcome c the reactions substantially depends on both the steric shielding an electronic effects of the substituents. While the reduction i relatively fast for non-substituted imino pyridines (Table 1, entries – 3), the substitution of the imino pyridines in *ortho* position slowe down the reduction process (Table 1, entries 4 – 6, Figure S29 in SI Importantly, the reduction of the RN=CH imine function by HSiCl is selective leaving other functional groups (C≡N or C=C unaffected (Supporting Information, Table 1, entries 5 – 6; substrate containing a second RN=CH moiety was prepared, Figure S22 - 21 and reduced as well, but the hydrolysis gave a product tha was always contaminated with CH=O group, see Figure S28). Fc comparison, the reduction of the substrate containing a C=C functional group with $LiAlH_4$ was also performed. It revealed reduction of both functional groups (Scheme S3 and Figure S30 i SI).

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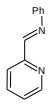
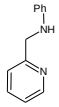
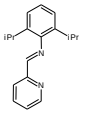
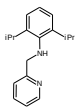
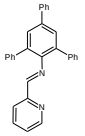
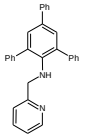
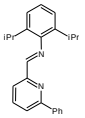
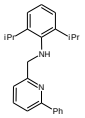
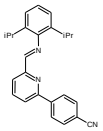
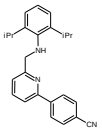
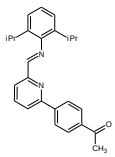
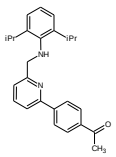
Table 1. Representative examples for the synthesis of unsymmetrically substituted secondary amines by the subsequent reaction of imine moiety-containing substrates with $HSiCl_3$ and water.

Entry	Substrate	Product	Reaction time [a]	Isolated Yield
1			5 min	96
2			5 min	96
3			60 min	90
4			24 h	90
5			24 h	84
6			24 h	82[b]

[a] reaction times were determined by ^{1}H NMR spectroscopy, [b] heated at 50°C see SI

As the proposed neutral *N,N*-chelated chlorosilanes **1a - 3a** have not been isolated, the geometries of **1a** and its corresponding hydrosilylated product **1** were optimized via density functional theory (DFT) calculations with Gaussian09[17] at B3LYP[18]/6-31++G(d,p)[19] (A) and B3LYP-D3[20]/6-31++G(d,p) (B) level of theory. The calculated structures of **1** obtained with B3LYP and B3LYP-D3 (which contains dispersive interactions) fit to the molecular structure determined for the solid state (Table 2; Supporting Information, Figure S31). The Si–N distances are slightly longer in the calculated structures (Si(1)–N(1) 2.0933 (A), 2.1041 (B) Å and Si(1)–N(2) 1.7502 (A) and 1.7462 (B) Å) than in the measured solid state structure (Si(1)-N(1) 1.949(2), Si(1)–N(2) 1.708(2) Å). The same trend is observed for the Si(1)-Cl(2) and Si(1)-Cl(3) distances. The interatomic angles of calculated **1** fit well with the corresponding angles of the solid state structure.

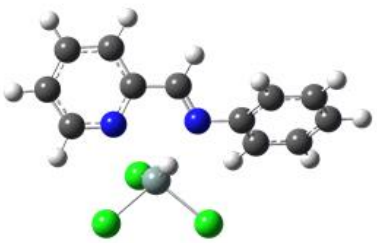


Figure 5. Optimized geometry of complex **1a**.

DFT calculations of the complexation of $\mathbf{L^1}$ with $HSiCl_3$ suggested formation of complex **1a** as the only one of three possible diastereomers with an octahedral structure differing mutually by the position of the Si*H* hydrogen atom (Supporting Information, Figure S32). The isomer **1a** as shown in Figure 5 was calculated using both DFT methods A and B. Selected interatomic distances and angles of the optimized structures are collected in Table 2. The $HSiCl_3$ is coordinated by two nitrogen atoms at Si–N distances ranging between 2.2249 and 2.3165 Å. These are longer than the values found in **1** and longer than a Si–N covalent single bond ($\sum_{cov}$(Si,N) = 1.87 Å).[15] The Si-H distance is about 1.48 Å. As the result, the silicon atom is hexa-coordinated and its geometry can be best described as distorted octahedron. The proposed intermediate **1a** is significantly higher in energy (128 (method A) and 125 (method B kJ/mol, zero point corrected) than **1**, which was calculated based o the molecular structure (Supporting Information, Table S2).

Table 2. Selected interatomic distances (Å) and angles (°) for **1, 1a.** Method A: B3LYP/6-31++G(d), Method B: B3LYP-D3/6-31++G(d)

	1 X-ray	**1 A**	**1 B**	**1a A**	**1a B**
Si(1)-N(1)	1.949(2)	2.0933	2.1041	2.2252	2.224
Si(1)-N(2)	1.708(2)	1.7502	1.7462	2.3165	2.272
Si(1)-Cl(1)	2.159(1)	2.1435	2.1462	2.1453	2.146
Si(1)-Cl(2)	2.084(1)	2.1281	2.1253	2.1539	2.15
Si(1)-Cl(3)	2.085(1)	2.1282	2.1253	2.1693	2.17
Si(1)-H				1.4764	1.477
N(1)-Si(1)-N(2)	83.56(11)	81.13	80.66	73.39	73.7
Cl(1)-Si(1)-Cl(2)	92.46(4)	95.25	95.74	100.99	100.9
Cl(2)-Si(1)-Cl(3)	110.15(5)	112.55	112.52	97.68	97.4
Cl(3)-Si(1)-Cl(1)	92.01(4)	95.26	95.74	96.85	97.2
Cl(1)-Si(1)-H				95.91	95.9
Cl(2)-Si(1)-H				97.27	96.7
Cl(3)-Si(1)-H				158.10	158.3
N(1)-Si(1)-Cl(1)	178.14(8)	178.42	177.95	166.71	166.7
N(1)-Si(1)-Cl(2)	89.28(8)	85.62	85.39	92.02	91.8
N(1)-Si(1)-Cl(3)	87.98(8)	85.62	85.39	84.00	83.9
N(1)-Si(1)-H				79.57	79.3
N(2)-Si(1)-Cl(1)	94.94(9)	97.29	97.29	93.47	93.2
N(2)-Si(1)-Cl(2)	123.75(10)	122.11	121.95	165.09	165.3
N(2)-Si(1)-Cl(3)	125.16(10)	122.11	121.96	84.07	83.8
N(2)-Si(1)-H				77.45	78.2

The calculation of the possible mechanism of the **1a** to **1** transformation provided two further intermediates **Int_1** and **Int_2** (zero point corrected energies, Figure 6; Supporting Information, Table S3). In the intermediate **Int_1**, the Si*H* hydrogen atom is localized at the aromatic nitrogen atom N1 and the $SiCl_3$ moiety is coordinating the imine nitrogen atom N2. In the second intermediate **Int_2**, the hydrogen atom is bound to the nitrogen atom N2 while the $SiCl_3$ group coordinates to N1. Also, the non-coordinated $\mathbf{L^1}$ and $SiHCl_3$ were placed at a distance of approx. 10 Å and allowed to approach to each other. A local minimum was found for a N···H distance of 2.60 Å (Si···N 3.95 Å). The relative zero point-corrected

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energies of the optimized local minima (intermediates) **1a**, **Int_1** and **Int_2** as well as of the isolated **1** are referred to this (see Figure 6). The complex **1a** is 34 kJ/mol higher in energy and **1** 94 kJ/mol lower. Intermediate **Int_1** has a lower energy level (15 kJ/mol) and **Int_2** a higher energy level (47 kJ/mol). While the first intermediate **Int_1** is 79 kJ/mol higher in energy than compound **1**, it is 49 kJ/mol lower than the complex **1a**. The second intermediate **Int_2** is 141 kJ/mol higher in energy than **1**, but it is also 13 kJ/mol higher in energy than complex **1a**. As a result of the calculations, we only found the intermediates **Int_1** and **Int_2** but no intermediate showing direct transfer of the Si*H* hydrogen to the carbon atom. For the reaction pathway from **1a** via **Int_1** to **1** we obtained two transition states **TS1** (activation energy 190 kJ/mol) and **TS2** (activation energy 126 kJ/mol). Given that the reaction takes place between –78 °C and room temperature, these energies are far too high (Supporting Information, Figures S33 - 34). Unfortunately, meaningful transition states for the proposed reaction pathway ($HSiCl_3$ + **L**^{1}) → **1a** → **Int_1** → **1** were not found. Based on the experimental finding, we suppose that the transformation of **1a** → **1** may proceed via **Int_1**. However, alternative mechanisms (for example a bimolecular mechanism, where the $HSiCl_3$ molecule attacks the **1a**) cannot be excluded either.

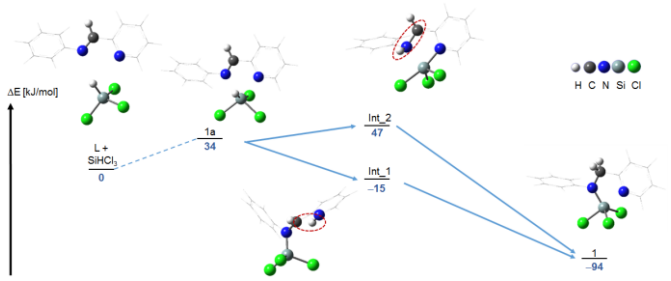

Figure 6. Stationary points and intermediates for a possible mechanism of the **1a** → **1** transformation proceeding via two possible intermediates **Int_1** and **Int_2** (zero point corrected energies method A).

Conclusion

We have demonstrated that the neutral pyridine-based ligands L^1 - L^3 containing either one or two RN=C*H* imine moieties react with $HSiCl_3$ in terms of a hydrosilylation to provide N→Si-coordinated silicon (IV) amides. In course of the reaction and induced by N→Si intermolecular coordination, the imine function is transformed into a NCH_2 moiety. In addition, the reaction of **L**^{3} with an excess of $HSiCl_3$ provided the intramolecularly coordinated chlorosilicon diamide *cyclo*-(C_5H_3N)-1,3-(CH_2NR)$_2SiCl_2$ (**4**) (R = 2,6-^{i}Pr$_2$C$_6$H$_3$), a product of the spontaneous reduction of both RN=C*H* C*H*=N imine moieties. It has been also shown that the complexes **1** – **3** are sufficiently Lewis acidic to activate the Si–*H* bond of second $SiHCl_3$ molecule. To some extent, the lot resembles the situation reported by Piers and Oestreich for the B(C_6F_5)$_3$-catalyzed hydrosilylation of imines. [8] Therefore, the stoichiometric reaction of the silicon amide **2** with $HSiCl_3$ provides compound **5**.

As the compounds **1** – **4** can be easily hydrolysed, a number of neutral pyridine based ligands containing RN=C*H* imine moiety (substrate) were treated with $HSiCl_3$ in toluene and the resulting insoluble material was hydrolysed to give the corresponding unsymmetrically substituted secondary amines. This is a rather straightforward protocol for the synthesis of unsymmetrically substituted pyridine-based secondary amines.

Experimental Section

All reactions were carried out under argon, using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. The ligands **L**^{1} – **L**^{3} were prepared according to the literature.[21] All starting compounds were purchased from Sigma Aldrich. The ^{1}H, ^{13}C, ^{29}Si NMR spectra were recorded in C_6D_6 at 300K on a Bruker Avance500 spectrometer. The ^{1}H, ^{13}C, ^{29}Si NMR chemical shifts δ are given in ppm and referenced to external Me_4Si. Elemental analyses were performed on an LECO-CHNS-932 analyzer.

Synthesis of 1

A solution of ligand **L**^{1} (0.20 g, 1.11 mmol) in toluene (15 mL) was added to a solution of $HSiCl_3$ (0.16 g, 1.17 mmol) in toluene (15 mL) at –78 °C. A white solid precipitated immediately. The suspension was stirred for 1 hour at –78 °C and then allowed slowly adjust to room temperature. The white precipitate was filtered off, dried in vacuo an characterized as **1**. Yield: 0.30 g (86 %). m.p. = 215°C (decomposition). Anal. calcd. fo $C_{12}H_{11}Cl_3N_2Si$ (MW 317.68): C, 45.4; H 3.5. Found: C 45.6; H 3.6. ^{1}H NMR (C_6D 400.13 MHz): 3.83 (s, 2H, CH_2N), 5.89 (d, 1H, py-H, $^3J(^1H, ^1H)$ = 8 Hz), 6.35 (t, 1H py-H, $^3J(^1H, ^1H)$ = 6.8 Hz), 6.60 (t, 1H, py-H, $^3J(^1H, ^1H)$ = 8 Hz), 7.11 (t, 2H, Ph-H $^3J(^1H, ^1H)$ = 8 Hz), 7.23 (t, 1H, Ph-H, $^3J(^1H, ^1H)$ = 8 Hz), 7.29 (d, 2H, Ph-H, $^3J(^1H, ^1H$ = 8 Hz), 8.49 (d, 1H, py-H, $^3J(^1H, ^1H)$ = 6.8 Hz); ^{13}C NMR (C_6D_6, 100.61 MHz): 55. (CH_2N), 120.0, 123.2, 126.0, 128.2, 129.4, 139.4, 143.6, 147.9, 151.8 (Ar-*C*); ^{29}Si NM (C_6D_6, 99.36 MHz): -103.4.

Synthesis of 2

$HSiCl_3$ (52.8 mg, 0.39 mmol) was added to a stirred solution of ligand **L**^{2} (0.16 g, 0. 3 mmol) in toluene (15 mL). The reaction mixture was stirred for 4 hours at roo temperature and all volatiles were removed under reduced pressure. The residue wa characterized as **2**. m.p. = 230 °C (decomposition). Yield: 0.2 g (95 %). Anal. calcd. fo $C_{30}H_{23}Cl_3N_2Si$ (MW 545.96): C 66.0; H 4.3. Found: C 66.2; H 4.4. ^{1}H NMR (C_6D 500.20 MHz): 3.96 (s, 2H, CH_2N), 6.02 (d, 1H, py-H, $^3J(^1H, ^1H)$ = 7.5 Hz), 6.45 (dd, 1 py-H, $^3J(^1H, ^1H)$ = 6 Hz), 6.53 (dd, 1H, py-H, $^3J(^1H, ^1H)$ = 6.9 Hz), 7.02 (m, 2H, ArH 7.04 – 7.20 (m, 4H, ArH), 7.44 (s, 2H, ArH), 7.44 – 7.50 (m, 9H, ArH), 8.21 (d, 1H, py H, $^3J(^1H, ^1H)$ = 7.5 Hz); ^{13}C NMR (C_6D_6, 125.72 MHz): 49.7 (CH_2N), 123.5, 123. 126.7, 128.0, 128.2, 128.7, 128.8, 129.3, 129.6, 134.3, 134.8, 140.1, 140.7, 142.4, 154. (Ar-*C*); ^{29}Si NMR (C_6D_6, 99.36 MHz): -95.7.

Synthesis of 3

A solution of $HSiCl_3$ (23 mg, 0.17 mmol) in benzene (15 mL) was added to a stirre solution of ligand **L**^{3} (75.2 mg, 0.16 mmol) in benzene (15 mL) at room temperatur The reaction mixture was stirred overnight. After that all volatiles were removed unde reduced pressure to give **3** as a yellow solid of m.p. = 247-250 °C. Yield: 68.8 m (73 %). Anal. calcd. for $C_{31}H_{40}Cl_3N_3Si$ (MW 589.13): C 63.2; H 6.8. Found: C 63.5; 7.0. ^{1}H NMR (C_6D_6, 400.13 MHz): 1.31 (d, 12H, CH_3, $^3J(^1H, ^1H)$ = 6.9 Hz), 1.36 (6H, CH_3, $^3J(^1H, ^1H)$ = 6.9 Hz), 1.62 (d, 6H, CH_3, $^3J(^1H, ^1H)$ = 6.9 Hz), 3.30 (sept, 2H CH, $^3J(^1H, ^1H)$ = 6.9 Hz), 3.66 (sept, 2H, CH, $^3J(^1H, ^1H)$ = 6.9 Hz), 4.21 (s, 2H, CH_2N 6.01 (d, 1H, py-H, $^3J(^1H, ^1H)$ = 7.6 Hz), 6.74 (t, 1H, py-H, $^3J(^1H, ^1H)$ = 7.6 Hz), 7.20 7.32 (m, 6H, ArH), 8.37 (d, 1H, py-H, $^3J(^1H, ^1H)$ = 7.6 Hz), 9.86 (s, 1H, CH=N); ^{13} NMR (C_6D_6, 100.61 MHz): 23.5, 24.6, 25.3 ((CH_3)$_2$CH), 27.9, 28.4 ((CH_3)$_2$CH), 54. (CH_2N), 122.0, 123.5, 123.7, 124.4, 125.7 127.3, 136.9, 139.6, 140.8, 146.9, 148.(148.2, 151.4 (Ar-*C*), 158.3 (*C*H=N); ^{29}Si NMR (C_6D_6, 99.36 MHz): -97.2.

Synthesis of 4

Method A. An excess of $HSiCl_3$ (1.50 g, 11.06 mmol) in toluene (20 mL) was added to stirred solution of ligand **L**^{3} (1.00 g, 2.21 mmol) in toluene (20 mL) at room temperatu The reaction mixture was heated at 90 °C for 2 weeks. After that all volatiles we removed under reduced pressure and the residue was washed with hexane (5 mL) give **4** as a white solid of m.p. = 230 °C (decomposition). Yield: 1.05 g (86 %). Ana calcd. for $C_{31}H_{41}Cl_2N_3Si$ (MW 554.68): C 67.1; H 7.5. Found: C 67.4; H 7.6. ^{1}H NM (C_6D_6, 400.13 MHz): 1.05 (d, 6H, CH_3, $^3J(^1H, ^1H)$ = 7 Hz), 1.35 (d, 6H, CH_3, $^3J(^1H, ^1H)$ = 7 Hz), 1.41 (d, 6H, CH_3, $^3J(^1H, ^1H)$ = 7 Hz), 1.59 (d, 6H, CH_3, $^3J(^1H, ^1H)$ = 7 Hz), 3.58 (sept, 2H, CH, $^3J(^1H, ^1H)$ = 7 Hz), 3.85 and 4.57 (AX system, 4H, CH_2N), 4.28 (sept, 2H, CH, $^3J(^1H, ^1H)$ = 7 Hz), 6.12 (d, 2H, py-H, $^3J(^1H, ^1H)$ = 7.5 Hz), 6.69 (t, 1H, py-H, $^3J(^1H, ^1H)$ = 7.5 Hz), 7.15 – 7.19 (m, 6H, ArH); ^{13}C NMR (C_6D_6, 100.61 MHz): 24.4, 25.1, 25.3, 25.4 ((CH_3)$_2$CH), 28.1, 28.5 ((CH_3)$_2$CH), 54.1 (CH_2N), 118.1, 123.5, 124.8, 126.3, 139.9, 144.4, 146.4, 148.7, 151.3 (Ar-*C*); ^{29}Si NMR (C_6D_6, 99.36 MHz): -104.6.

Method B. 1 eq. of $HSiCl_3$ (60 mg, 0.44 mmol) was added to a stirred solution of **3** (0.26 g, 0.44 mmol) in toluene (15 mL) at room temperature. The reaction mixture was stirred 24 hours at this temperature and after that all volatiles were removed under reduced pressure. The residue was washed with small amount of hexane to afford white powder material characterized as **4**. Yield: 0.12 (51 %).

Synthesis of 5

An excess of $HSiCl_3$ (0.25 g, 1.81 mmol) was added to a stirred solution of ligand $\mathbf{L}^2$ (0.15 g, 0.36 mmol) in toluene (20 mL). The reaction mixture was stirred overnight. After that all volatiles were removed under reduced pressure to give **5** as white solid of m.p. = 217-219 °. Yield: 0.15 g (83%). Anal. calcd. for $C_{30}H_{24}Cl_2N_2Si$ (MW 511.52): C 70.4; H 4.7. Found: C 70.5; H 4.9. ^{1}H NMR (C_6D_6, 500.20 MHz): 4.05 (bs, 2H, CH_2N), 5.78 (d, 1H, py-H, $^3J(^1H, ^1H)$ = 7.8 Hz), 6.00 (s, 1H, Si-H, $^1J(^{29}Si, ^1H)$ = 369 Hz), 6.07 (t, 1H, py-H, $^3J(^1H, ^1H)$ = 6.5 Hz), 6.39 (t, 1H, py-H, , $^3J(^1H, ^1H)$ = 7.6 Hz), 7.02 – 7.71 (m, 17H, ArH), 8.15 (bs, 1H, py-H); ^{13}C NMR (C_6D_6, 125.72 MHz): 49.6 (CH_2N), 123.5, 126.7, 126.9, 128.0, 128.2, 128.7, 128.9, 129.3, 129.6, 134.4, 134.9, 140.1, 140.4, 142.4, 154.8 (Ar-*C*); ^{29}Si NMR (C_6D_6, 99.36 MHz): -95.6 (d, $^1J(^{29}Si-^1H)$ 369 Hz).
Alternative synthesis of ***5***. A solution of **2** (0.98 g, 1.81 mmol) in toluene (15 mL) was added to a solution of $HSiCl_3$ (0.25 g, 1.81 mmol) in toluene (15 mL) at room temperature. After stirring for 12 hours, the reaction mixture was filtrated. From the filtrate compound **5** precipitated as single crystalline material suitable for X-ray diffraction analysis as toluene solvate $\mathbf{5}\cdot\frac{1}{2}C_7H_8$.

Crystallography: The single crystals suitable for X-ray diffraction analysis were obtained from saturated toluene solution at room temperature (**1**, $\mathbf{5}\cdot\frac{1}{2}C_7H_8$) or at 4 °C ($\mathbf{4}\cdot C_7H_8$). The single crystals of **3** suitable for X-ray diffraction analysis were obtained from C_6D_6 solution at room temperature. Crystal structure analysis of colourless crystal of $\mathbf{1}\cdot$(0.25 x 0.12 x 0.11 mm^3), yellow of $\mathbf{3}\cdot$(0.37 x 0.23 x 0.19 mm^3), colourless of $\mathbf{4}\cdot C_7H_8$ (0.37 x 0.32 x 0.26 mm^3) and of $\mathbf{5}\cdot\frac{1}{2}C_7H_8$ (0.31 x 0.22 x 0.21 mm^3) were obtained at 150K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo K_α radiation (λ = 0.71073 Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN[22]. The absorption was corrected by integration methods.[23] Structures were solved by direct methods (Sir92)[24] and refined by full matrix least-square based on F^2 (SHELXL97)[25] Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H)$ = 1.2 U_{eq}(pivot atom) or of 1.5U_{eq} for the methyl moiety with C-H = 0.96, 0.97, and 0.93 Å for methyl, methylene, and hydrogen atoms in aromatic ring, respectively. There are residual electron maxima within the unit cell probably originated from the disordered solvent in the structure of **5**. PLATON /SQUEZZE[26] was used to correct the data for the presence of disordered solvent. A potential solvent volume of 598 Å^3 was found. 124 electrons per unit cell worth of scattering were located in the void. The calculated stoichiometry of solvent was calculated to be two molecules of toluene per unit cell which results in 100 electrons per unit cell.
Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 1431188-1431190 (**1**, **3** and **4**) and CCDC no 1454048 (**5**) 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.

Supporting Information. Crystallographic parameters of compounds **1**, **3, 4**$\cdot C_7H_8$ and $\mathbf{5}\cdot\frac{1}{2}C_7H_8$. Experimental details and NMR spectra for the synthesis of the unsymmetrical amines. Calculated coordinates of **1**, **1a_1**, **1a_2** and **Int_1** and **Int_2**. Optimized geometry of complex **1**. Calculated energies of **1, 1a_1** and **1a_2** as well as **Int_1** and **Int_2**.

Acknowledgements

We are grateful to the Czech Science Foundation (project no. P207/13-00289S) for supporting this work.

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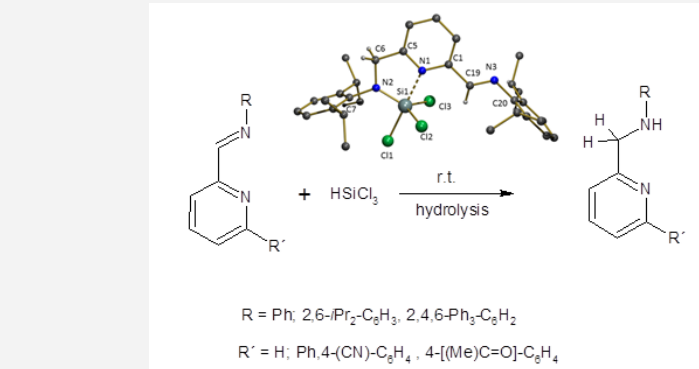
Entry for the Table of Contents

Hydrosilylation

*Miroslav Novák, Hana Hošnová, Libor Dostál, Britta Glowacki, Klaus Jurkschat, Antonín Lyčka, Zdenka Růžičková, and Roman Jambor**

Hydrosilylation of RN=C*H* imino-substituted pyridines without a catalyst



The neutral pyridine based ligands **L**^{1} - **L**^{3} containing either one or two RN=C*H* imine moieties were treated with $HSiCl_3$ to provide under reduction of the former N→Si-coordinated silicon (IV) amides. With an excess of $SiHCl_3$ the second RN=C*H* imine group is also reduced. The hydrolysis of the parent silicon amides provided the corresponding unsymmetrically substituted secondary amines 2-{R(H)NCH_2}C_5H_4N. The experimental work is also accompanied by DFT calculations.