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Pentacoordinate Silicon Complexes with *N*-(2-pyridylmethyl)salicylamide as a Dianionic (*ONN′*) Tridentate Chelator

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Dedicated to Professor Klaus Jurkschat on the Occasion of His 60th Birthday

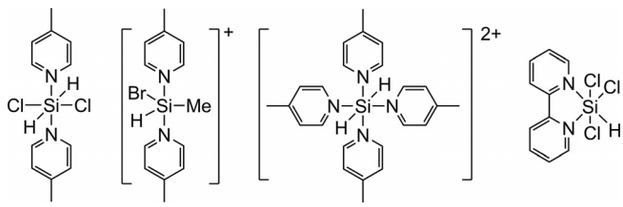
Keywords: Hypercoordination; Organosilicon complexes; Pentacoordination; Pyridine; Silicon

Abstract. The title compound, *N*-(2-pyridylmethyl)salicylamide (**1**), was synthesized by ester aminolysis of methyl salicylate and 2-picolylamine. In the presence of triethylamine as a supporting base, the salicylamide moiety reacts with the organodichlorosilanes $RR'SiCl_2$ to form the desired six-membered heterocycles of the type RR'Si–O–(*o*-C_6H_4)–C(=O)N(pic), with pic being the 2-pyridylmethyl (i.e., 2-picolyl) moiety and RR' = Me,Me (**2a**); Me,Ph (**2b**); Ph,Ph (**2c**); Bn,Bn (**2d**); All,Ph (**2e**) and Ph,H (**2f**). Despite the absence of notable ring strain release Lewis acidity (i.e., only a six-membered chelate is formed by the dianion, and smaller rings are not present in the compound), the poor electron withdrawal from silicon by its C– or H–substituents and the flexible methylene bridge between the salicylamide and the pyridine moiety, the pyridine N donor atom furnishes pentacoordinate silicon coordination spheres in all of these compounds **2a**–**2f**. The coordination number of the silicon atom was confirmed by single-crystal X-ray diffraction analysis for the solid state and by ^{29}Si NMR spectroscopy for the solution state.

Introduction

Among the ligands reported to be capable of forming hypercoordinate silicon complexes[1] pyridine is well known to react with halosilanes to form adducts with an increased coordination number of the silicon atom,[2] and a variety of 4- or 3-substituted pyridines was found to exhibit related ligand properties,[3] whereas the greater steric bulk of 2- or 2,6-substituted pyridines lowers the stability of those Lewis acid base adducts dramatically.[3b,4] The examples in Scheme 1 outline the general coordination patterns encountered with pyridine silane complexes, which may involve ionic dissociation of silicon halide (Si–*X*) bonds. The use of chelating ligands with pyridine functionality, e.g., 2,2′-bipyridyl or 1,10-phenanthroline, supports the formation of such Lewis acid base adducts.[2c,5]

Even though a large portfolio of halogen rich pyridine halosilane complexes are known (mostly of silanes of the type SiX_4, $HSiX_3$, H_2SiX_2; *X* = halide), the role of pyridine as an additional lone pair donor towards silicon is evident for an



Scheme 1. Examples of neutral and cationic halosilane pyridine adducts with hexa- or pentacoordinate silicon atom.

even greater variety of silanes from the catalytic influence of pyridines on substitution reactions at silanes, which include mono-, di- and triorganosilane derivatives.[6] Structural evidence for neutral pyridine adducts of monoorganosilanes, however, is limited to a few examples,[7] and to the best of our knowledge there is no crystallographic evidence for neutral pyridine diorganosilane adducts.[8] Some hypercoordinate silicon complexes with X_2SiC_2 skeleton and pyridine donor moiety have been reported, but in most cases the pyridine nitrogen atom was part of a rigid chelate construction, which forced the pyridine nitrogen lone pair to point in a similar direction like a lone pair of the second donor atom, e.g., 8-oxyquinolinate, 1,10-phenanthroline, the anion of 1,2,3,4-tetrahydro-1,10-phenanthroline, and others (Scheme 2, top).[9] *Gómez* et al. and *Holmes* et al. already reported on neutral pentacoordinate diorganosilicon complexes with an additional pyridine donor moiety bound to the ligand backbone via a flexible alkyl group, but they needed to clamp the pyridine donor to silicon by using two anionic anchors in 2,6-position of the pyridine (Scheme 2, bottom left).[10] Recently, *Tacke* et al. reported on pentacoordi-

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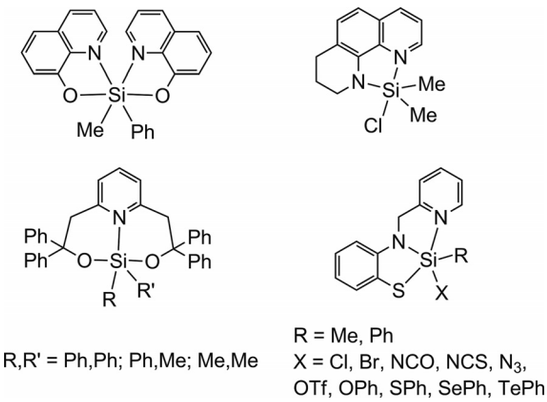
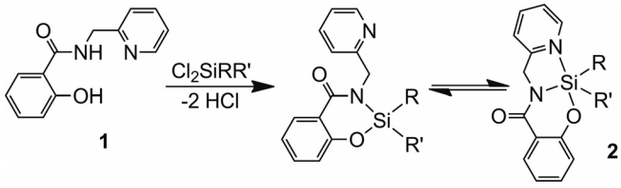
nate monoorganosilicon complexes with a pyridine donor moiety, which was anchored to silicon via only one –CH_2–N– arm in 2-position, which offers rotational degrees of freedom, thus not forcing the pyridine to bind to silicon (Scheme 2, bottom right).[11]



Scheme 2. Silicon complexes with pyridine moieties anchored to silicon via anionic ligand backbones.

In the course of our investigations of (*ONN′*) donor systems in the coordination sphere of silicon,[12] now we also have included the neutral pyridine donor moiety as a dangling arm. In contrast to the (*SNN′*) ligand system utilized by *Tacke* et al., the dianionic (*ONN′*) donor ligand **1** depicted in Scheme 3, left,[13] should primarily give rise to (*ON*)-chelated silacycles devoid of notable ring strain, as a six-membered chelate is formed, and we want to minimize effects such as ring strain release Lewis acidity[14] for our current investigation. Therefore, this ligand appeared suitable to study the influence of different diorgano substitution patterns at silicon on the coordination behavior of the pendant pyridine moiety.



Scheme 3. Syntheses of silicon complexes with the dianion of **1** as an (ONN′) donor ligand. *R,R′* = Me,Me (**2a**), Me,Ph (**2b**), Ph,Ph (**2c**), Bn,Bn (**2d**), Ph,All (**2e**), Ph,H (**2f**).

Results and Discussion

A synthesis route towards ligand **1** is reported in the literature,[13] but the authors report the crystallization of the hydrate of this ligand, which needs to be circumvented when preparing a ligand for silicon coordination chemistry. Furthermore, the original procedure involved dimethylformamide as a solvent for the reaction and chloroform as a second solvent for extraction. We pursued a straightforward synthesis of **1**, and the condensation of methyl salicylate and picolylamine in *n*-pentanol turned out to be successful yielding the crystalline anhydrous ligand **1** directly from the reaction solution.

Whereas the presence of one or a half water molecule per ligand molecule could be camouflaged in the ^{1}H NMR spectra by rapid exchange with other acidic protons, the new crystal structure of **1** (Figure 1) revealed that it crystallizes in an anhydrous manner. Thus, the X-ray diffraction analysis underlines the results of the elemental analysis, which are in accord with the anhydrous nature of the gross product. In the crystal packing the asymmetric unit consists of one molecule of **1**. Together with an inversion-related molecule it forms a dimer via intermolecular O–H···N hydrogen bonds to the pyridine nitrogen atom. The configuration of the molecule of **1** itself is furthermore stabilized by an intramolecular N–H···O hydrogen bond from the amide NH group to the hydroxyl oxygen atom. The torsion angle C7–N1–C8–C9 [–82.7(1)°] indicates that the pyridine nitrogen atom N2 is significantly out of the least-squares plane of atoms C1–C7, O1, N1 [2.282(2) Å] and a conformational change is required for in-plane coordination of a silicon atom within the (*ONN′*) donor set.

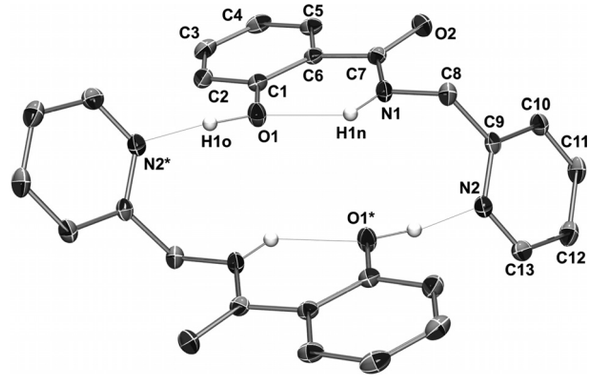


Figure 1. ORTEP[15] diagram of the molecular structure of **1** in the crystal (carbon bound hydrogen atoms are omitted for clarity, thermal displacement ellipsoids represent the 50 % probability level, selected atoms are labeled). The asymmetric unit consists of one molecule of **1**, which forms a centrosymmetric dimer with the (*–x*, 2*–y*, *–z*) symmetry related molecule via intermolecular O–H···N hydrogen bonds.

The reactions of **1** with the dichlorosilanes depicted in Scheme 3 (using triethylamine as a supporting base) did proceed rapidly, as was obvious from the amount of triethylamine hydrochloride which formed instantly upon addition of the silane to a solution of ligand and triethylamine in tetrahydrofuran (THF). In all of the above cases the silicon complexes were soluble in THF, thus allowed for separation from the hydrochloride by filtration. Upon removal of the solvent from the filtrate (by trap condensation under reduced pressure) the products remained as viscous oils, which required different solvents for successful crystallization (see Experimental Section). All compounds **2a**–**2f** gave rise to crystals of good quality for single-crystal X-ray diffraction analyses (Figure 2, Figure 3, Figure 4, Figure 5, Figure 6, and Figure 7). Whereas compounds **2a**–**2e** crystallized in a solvent free lattice, compound **2f** crystallized as THF solvate **2f**·THF. Further noteworthy features of the crystal structures were found with **2c**, which comprises three molecules of this complex in the asymmetric unit, and with **2e**, the allyl group of which is twofold disordered in a cross-wise manner in ratio 0.917(4):0.083(4).

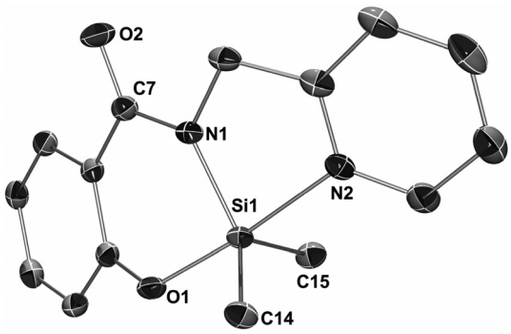


Figure 2. ORTEP[15] diagram of the molecular structure of **2a** in the crystal (hydrogen atoms are omitted for clarity, thermal displacement ellipsoids represent the 50% probability level, selected atoms are labeled). The asymmetric unit consists of one molecule of **2a**. Selected bond lengths /Å and angles /°: Si1–O1 1.742(1), Si1–N1 1.802(1), Si1–N2 2.069(1), Si1–C14 1.874(2), Si1–C15 1.876(2), O1–Si1–N2 172.96(5), N1–Si1–C14 121.58(6), N1–Si1–C15 115.50(6), C14–Si1–C15 121.12(7).

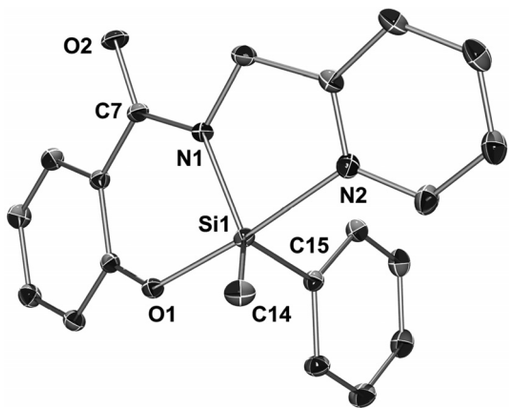


Figure 3. ORTEP[15] diagram of the molecular structure of **2b** in the crystal (hydrogen atoms are omitted for clarity, thermal displacement ellipsoids represent the 50% probability level, selected atoms are labeled). The asymmetric unit consists of one molecule of **2b**. Selected bond lengths /Å and angles /°: Si1–O1 1.734(1), Si1–N1 1.798(1), Si1–N2 2.053(1), Si1–C14 1.875(1), Si1–C15 1.881(1), O1–Si1–N2 174.18(2), N1–Si1–C14 121.27(2), N1–Si1–C15 117.17(2), C14–Si1–C15 119.81(2).

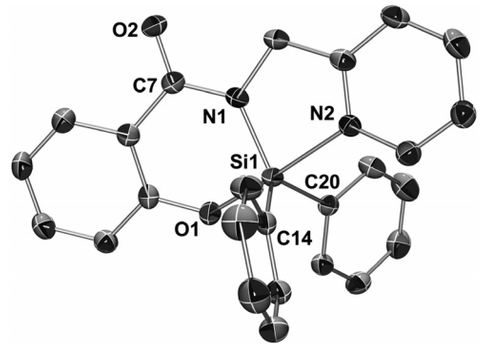


Figure 4. ORTEP[15] diagram of the molecular structure of one molecule of **2c** in the crystal (hydrogen atoms are omitted for clarity, thermal displacement ellipsoids represent the 50% probability level, selected atoms are labeled). The asymmetric unit consists of three molecules of **2c**, which reveal similar conformation, major differences can be found in the relative orientation of the Si-bound phenyl groups. Selected bond lengths /Å and angles /° of the depicted molecule: Si1–O1 1.720(1), Si1–N1 1.796(1), Si1–N2 2.041(1), Si1–C14 1.879(2), Si1–C20 1.898(2), O1–Si1–N2 174.60(6), N1–Si1–C14 114.16(7), N1–Si1–C20 123.32(7), C14–Si1–C20 120.64(8).

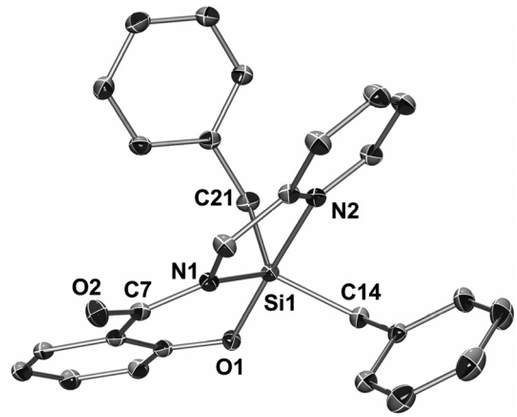


Figure 5. ORTEP[15] diagram of the molecular structure of **2d** in the crystal (hydrogen atoms are omitted for clarity, thermal displacement ellipsoids represent the 50% probability level, selected atoms are labeled). The asymmetric unit consists of one molecule of **2d**. Selected bond lengths /Å and angles /°: Si1–O1 1.750(1), Si1–N1 1.799(1), Si1–N2 2.043(1), Si1–C14 1.897(1), Si1–C21 1.904(1), O1–Si1–N2 173.33(5), N1–Si1–C14 122.68(5), N1–Si1–C21 115.79(5), C14–Si1–C21 120.16(6).

The mutual feature of the silicon complex molecules **2a**–**2f** in their crystal structures is the distorted trigonal bipyramidal coordination sphere about the silicon atom. Hence, the ligand has adopted a different conformation than in the solid-state structure of its protonated form compound **1**. The torsion angles which correspond to C7–N1–C8–C9 in the structure of **1** are now ranging from 160.9(1)° (**2a**, **2d**) via 164.3(1)° (**2b**), 167.3(1)° (**2e**) and 167.5(1)°, 171.2(1)°, 174.3(1)° (**2c**) to 179.5(1)° (**2f**). This order does not hint at any particular steric influence of the Si-bound substituents, and is therefore most likely dominated by the intermolecular packing in the crystal structure.

The greatest deviation from a trigonal bipyramidal coordination sphere is found in **2f**, with an O1–Si1–N2 angle of 164.01(4)°, whereas the corresponding angles in compounds **2a**–**2e** range from 172.83(4)° (**2e**) to 175.94(7)° (one of the three independent molecules of **2c**). The notable deviation of **2f** from this general coordination pattern can be rationalized by the lower steric demand of the Si-bound hydrogen atom. The decreased axial angle in **2f** is accompanied by a notable shortening of the bond Si1–N2 [1.993(1) Å in **2f**], which ranges between 2.041(1) Å and 2.069(1) Å in compounds **2a**–**2e**. The pyridine donor *trans*-influenced bond O1–Si1 [lengths in the range of 1.720(1) Å to 1.750(1) Å] is notably longer than the related Si–O bond of 1.648(1) Å in the pyridine donor free molecule **3c** depicted in Scheme 4.[9a] The Si1–N1 bonds [lengths in the range of 1.794(1) Å to 1.802(1) Å in **2a**–**2f**] are affected by the pyridine donor action to a similar extent, thus

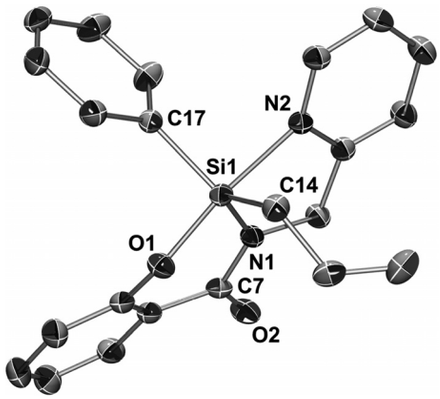


Figure 6. ORTEP[15] diagram of the molecular structure of **2e** in the crystal (hydrogen atoms are omitted for clarity, thermal displacement ellipsoids represent the 50% probability level, selected atoms are labeled). The asymmetric unit consists of one molecule of **2e**. The allyl group is twofold disordered (in a cross-wise manner about the C=C bond, site occupancies refined to 0.917(4) and 0.083(4)), only the predominant part is depicted. Selected bond lengths /Å and angles /°: Si1–O1 1.733(1), Si1–N1 1.794(1), Si1–N2 2.069(1), Si1–C14 1.891(1), Si1–C17 1.880(1), O1–Si1–N2 172.83(4), N1–Si1–C14 120.06(5), N1–Si1–C17 119.47(5), C14–Si1–C17 118.95(5).

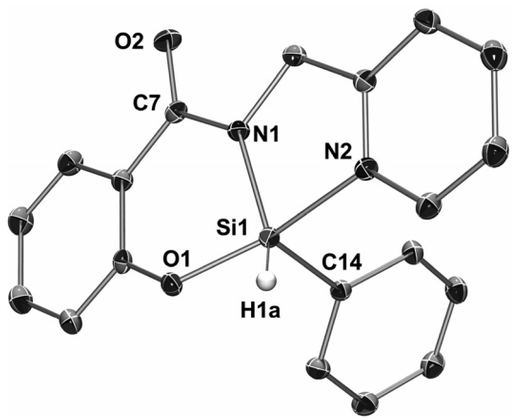
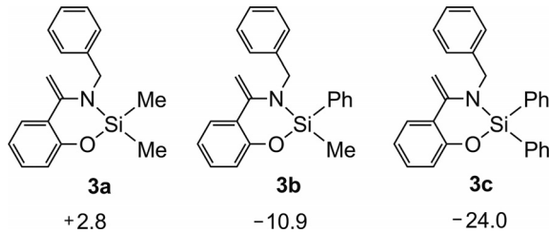


Figure 7. ORTEP[15] diagram of the molecular structure of **2f** in the crystal structure of **2f**·THF (solvent molecule as well as carbon-bound hydrogen atoms are omitted for clarity, thermal displacement ellipsoids represent the 50% probability level, selected atoms are labeled). The asymmetric unit consists of one molecule of **2f** and one molecule of tetrahydrofuran. Selected bond lengths /Å and angles /°: Si1–O1 1.723(1), Si1–N1 1.802(1), Si1–N2 1.993(1), Si1–C14 1.881(1), Si1–H1a 1.388(14), O1–Si1–N2 164.01(4), N1–Si1–C14 111.60(4), N1–Si1–H1a 132.8(6), C14–Si1–H1a 113.7(6).

being also notably longer than the Si–N bond in the reference molecule **3c** in Scheme 4 [1.720(2) Å]. Only the Si–C bonds [1.850(2) and 1.861(2) in **3c**] are elongated to lesser extent, resulting in Si–C(Ph) bond lengths of up to 1.90 Å in above pentacoordinate silicon compounds.

With respect to the tetracoordinate silicon compounds in Scheme 4, the additional pyridine donor action in **2a**–**2f** can be interpreted along the coordinate of a capping of the tetrahedral face opposite the Si–O bond, which results in planarization of the Si–N1 and Si–C bonds around the silicon atom.



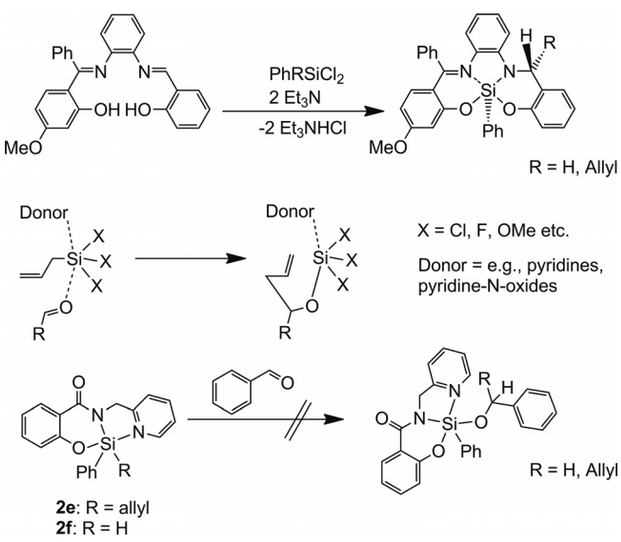
Scheme 4. Pyridine-free "benchmark" compounds, which are structurally related to **2a**, **2b**, and **2c**, respectively, with their ^{29}Si NMR shifts.

Within the margins of 328.5° for an ideal tetrahedron and 360° for a trigonal bipyramid, the sum of angles N1–Si1–C and C–Si1–C provide a measure for the progress of the transition from the tetrahedral to the trigonal bipyramidal coordination sphere. With sums of equatorial angles ranging between 357.79° (in one of the three independent molecules of **2c**) and 358.63° (**2d**), corresponding to 93.0% and 95.7% progress along this idealized reaction coordinate, respectively, the above complexes **2a**–**2f** reflect similar donor influence from the pyridine moiety.

With reference to the complexes reported by *Tacke* et al. (Scheme 2, bottom right),[11] the pyridine donor influence appears to be pronounced in their complexes, with Si–N(pyridine) bond lengths ranging between 1.970(1) Å (for *R*/*X* = Ph/O_3SCF_3) and 2.029(2) Å (for *R*/*X* = Me/SePh). These slightly shorter bond lengths can be attributed to various differences in the substitution pattern, i.e., a more electronegative substituent in the equatorial plane, an additional five-membered chelate in the complex and, last but not least, the sulfur atom *trans* to the pyridine donor. As to the role of sulfur versus oxygen, in a previous study we had found similar behavior of an N-donor, i.e., N–Si bond length shortening upon replacing the *trans*-disposed substituent (F) by the heavier congener (Cl), and *Tacke* et al. had found that in one of their silicon complexes a thiophenolate substituent supported silicon pentacoordination, whereas the corresponding phenoxy derivative formed a compound with tetracoordinate silicon atom.[16] With reference to the sum of equatorial angles about silicon the above mentioned compounds from the report by *Tacke* et al. exhibit similar features, i.e., sum of angles = 358.42° (for *R*/*X* = Ph/O_3SCF_3) and 358.02° (for *R*/*X* = Me/SePh).

The pentacoordination of the silicon atoms of above compounds is generally retained in $CDCl_3$ solution, as is apparent from their ^{29}Si NMR shifts [δ^{29}Si($CDCl_3$)/δ_{iso}^{29}Si(CP/MAS)]: **2a** –46.1/–63.1, **2b** –65.2/–75.7, **2c** –81.2/–88.8, **2d** –66.2/–71.3, **2e** –74.2/–77.2, **2f** –90.7/–94.2. Without the additional donor action of the pyridine nitrogen atom, compounds **2a**, **2b**, and **2c** should exhibit ^{29}Si chemical shifts similar to those of the compounds **3a**, **3b**, and **3c**, respectively, which are depicted in Scheme 4.[9a] The latter comprise a similar di-anionic chelate around the silicon atom, which furnishes a six-membered heterocycle. Even though the ^{29}Si NMR shifts in $CDCl_3$ solution indicate pentacoordination of the silicon atom, some resonances already appear noticeably down-field shifted with respect to the resonance in the solid state. This feature is particularly pronounced for compounds **2a** and **2b** (with down-field

shifts $\Delta\delta$ of 17 ppm and 10.5 ppm, respectively). ^{29}Si variable temperature (VT) NMR studies of these two compounds revealed significant response of the chemical shift to the temperature, i.e., up-field shift upon cooling, down-field shift upon heating. This temperature dependence indicates the existence of equilibria between tetra- and pentacoordinate silicon compounds (as depicted in Scheme 3). Using the ^{29}Si chemical shifts of compounds **3a** and **3b** as approximate reference values for the chemical shifts of **2a** and **2b**, respectively, with tetracoordinate silicon atom, and the chemical shifts from solid state NMR experiments as references for the conformers with pentacoordinate silicon atom, the temperature dependence of the equilibrium constant K can be determined from the position of δ^{29}Si(T). From ln(K) vs. 1/T plots the thermodynamic data ΔH and ΔS for the N(pyridine)→Si coordination of these two compounds were determined (for details see the Supporting Information). The results (**2a**: ΔH = –16.4 kJ·mol^{-1}, ΔS = –46.5 J·mol^{-1}·K^{-1}; **2b**: ΔH = –15.0 kJ·mol^{-1}, ΔS = –36.0 J·mol^{-1}·K^{-1} for the formation of the $N_{pyridine}$→Si coordination) appear counterintuitive. One would expect similar behavior of the reaction entropies because of the similar degrees of freedom gained upon $N_{pyridine}$–Si bond dissociation. We need to point out that the data obtained for **2b** has to be handled with care because of the small fraction (ca. 20%) of its chemical shift range (i.e., between the boundaries for the chemical shifts of the isomers with tetra- and pentacoordinate silicon atom) covered by the VT NMR experiment, whereas the data for **2a** cover more than 30% of its chemical shift range. With respect to the reaction enthalpy, which appears to be similar for **2a** and **2b**, we find that the pyridine coordination is significantly less exothermic than the coordination of a diimine moiety to a silicon atom with SiO_2Ph_2 substitution pattern within a ligand system as depicted in Scheme 5 top.[17a] In the latter case we found ΔH = –65.3 kJ·mol^{-1} (for the formation of two N_{imine}→Si bonds, i.e., –32.65 kJ·mol^{-1} for one N_{imine}→Si bond).



Scheme 5. Hydrogen- and allyl-shift reactions in hypercoordinate silicon complexes and attempted analogous reaction with the compounds **2e** and **2f**.

As the Si–X (X = C, H) bond activation in hexacoordinate silicon complexes is a well-known phenomenon, and resultant Si–X bond cleavage reactions have been observed in different complex systems (Scheme 5, top and middle),[17] we probed the reactivity of compounds **2e** and **2f** towards benzaldehyde. The respective complex was dissolved in $CDCl_3$, benzaldehyde (50% excess) was added, and the solution was monitored by ^{29}Si and ^{1}H NMR spectroscopy over several days. The ^{29}Si NMR spectra did not hint at significant additional donor action arising from the aldehyde oxygen atom, as we found the resonance signals of the starting materials. Furthermore, a shift of X (H or allyl) should have given rise to new characteristic peaks in the ^{1}H NMR spectrum, but we only observed the signals of the starting materials.

Conclusions

We have shown that the flexible pyridine moiety of *N*-(2-pyridylmethyl)salicylamide coordinates to the silicon atom of diorganosilicon groups within the salicylamide (*ON*) chelate. The pyridine donor action is observed for both those complexes with the more electronegative phenyl substituents and those with the less electronegative methyl substituents in a similar manner with respect to bond lengths in the silicon coordination sphere. In general, the pentacoordination of the silicon atom is retained in $CDCl_3$ solution, but a more or less pronounced down-field shift of the ^{29}Si resonance relative to the ^{29}Si chemical shift of the solid hints at $N_{pyridine}$–Si bond dissociation in dynamic equilibria. This hypothesis was confirmed by VT NMR studies.

Experimental Section

Syntheses were performed in an inert atmosphere of dry argon using Schlenk line techniques and anhydrous solvents. NMR spectra (of $CDCl_3$ solutions) were recorded with a BRUKER DPX 400 spectrometer (10 mm probe) using $SiMe_4$ as internal standard for ^{1}H, ^{13}C and ^{29}Si spectra. ^{29}Si VT NMR spectra were recorded with a BRUKER AVANCE 500 spectrometer (5 mm probe). The temperature was adjusted by the internal spectrometer temperature control system together with a BCU extreme cooling unit (BRUKER). Low temperature calibration was done using a sample of 4% methanol in [D_4]methanol, high temperature calibration using a sample of 80% 1,2-ethandiol in [D_6]DMSO according to the procedure given in the literature.[18] ^{29}Si solid state NMR spectra were recorded with a BRUKER AVANCE 400 WB spectrometer using a 7 mm probe with zirconia spinners. Elemental microanalyses were performed with a Vario Micro Cube (ELEMENTAR). X-ray diffraction data were recorded with a BRUKER NONIUS X8 diffractometer with APEX II CCD detector (in combinations of phi and omega scans) using graphite monochromated Mo-K_α radiation. The structures were solved by direct methods (SHELXS) and refined with full-matrix least-squares on F^2 (SHELXL).[19] All non-hydrogen atoms were refined anisotropically. C-bound hydrogen atoms were refined isotropically in idealized positions (riding model), Si-, O- and N-bound hydrogen atoms were located from the residual electron density map and were refined without restraints.

Dedicated Cluster

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-867781 (**1**), -867782 (**2a**), -867783 (**2b**), -867784 (**2c**), -867785 (**2d**), -867786 (**2e**), and -867787 (**2f**·THF) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Synthesis of Compound 1: In the literature [13], a method for the preparation of this ligand is reported, but the yield is not provided, the final product crystallized as mono-hydrate (which would be unsuitable for subsequent reactions with chlorosilanes), and the procedure involved reaction in dimethylformamide and extraction with chloroform. Thus, we aimed at a more convenient synthesis which should give access to anhydrous compound **1** along a straightforward procedure. In an atmosphere of dry argon a solution of 2-picolylamine (10.0 g, 92.6 mmol), methylsalicylate (14.0 g, 92.1 mmol), and two drops of *N*-methylimidazole in *n*-pentanol (20 mL) was stirred at 165 °C (oil bath temperature) for 8 h and the methanol formed was distilled off the reaction flask. The initially colorless solution turned brownish-yellow within this time. Upon cooling to room temperature the solution was stored at 8 °C for 3 weeks to afford beige crystals of **1**, which were separated by decantation, repeatedly washed with ethanol (3 × 10 mL) and dried in air. Yield 6.65 g (29.1 mmol, 33 %). M.p. 118 °C, Anal. found: C 68.43, H 5.09, N 12.25 %, calcd. for $C_{13}H_{12}N_2O_2$: C 68.41, H 5.30, N 12.27 %. In $CDCl_3$ solution the chemical shifts of some 1H resonances are particularly concentration dependent, the herein reported data refer to a concentration of 0.15 mol·L^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 12.44 (s broad, 1 H, OH), 8.58 (d 5.0 Hz, 1 H, aryl), 8.06 (s broad, 1, NH), 7.71 (m, 1 H, aryl), 7.57 (d 8.7 Hz, 1 H, aryl), 7.39 (m, 1 H, aryl), 7.33 (d 7.8 Hz, 1 H, aryl), 7.25 (m, 1 H, aryl), 6.98 (d 8.7 Hz, 1 H, aryl), 6.87 (m, 1 H, aryl), 4.61 (d 4.5 Hz, 2 H, CH_2). **^{13}C NMR** ($CDCl_3$): δ = 169.9 (C=O), [161.5, 155.3, 148.9, 137.0, 134.2, 126.0, 122.7, 122.2, 118.7, 118.4, 114.4 (aryl)], 44.0 (CH_2) ppm.

Crystal Structure Analysis of 1: Single crystals were obtained directly from the synthesis. $C_{13}H_{12}N_2O_2$, M_r = 228.25, T = 100(2) K, monoclinic, space group $P2_1/c$, a = 10.7455(3), b = 13.2524(2), c = 7.5870(2) Å, β = 97.332(2)°, V = 1071.58(5) Å^3, Z = 4, $\rho_{calcd.}$ = 1.415 Mg·m^{-3}, μ(Mo-K_α) = 0.097 mm^{-1}, F(000) = 480, $2\theta_{max}$ = 64.0°, 17157 collected reflections, 3682 unique reflections (R_{int} = 0.0420), 162 parameters, S = 1.088, R_1 = 0.0480, wR_2 = 0.1191 [$I > 2\sigma(I)$], R_1 = 0.0718, wR_2 = 0.1274 (all data), max./min. residual electron density +0.469/–0.259 e·Å^{-3}.

Synthesis of Compound 2a: A solution of ligand **1** (1.00 g, 4.63 mmol) and triethylamine (1.41 g, 13.9 mmol) in tetrahydrofuran (THF, 30 mL) was stirred at room temperature and dimethyldichlorosilane (0.66 g, 5.10 mmol) was added within 10 s. The mixture was stirred for 1 h and stored at room temperature overnight, whereupon the hydrochloride precipitate was filtered off and washed with THF (10 mL). From the combined filtrate and washings the solvent was removed under reduced pressure and the resultant brownish oily residue was dissolved in toluene (1.2 mL) and hexane (0.5 mL). Upon storage at 8 °C for 3 d the first beige crystals appeared, whereupon further hexane (0.6 mL) was added and the mixture was stored at 8 °C for 4 weeks. Afterwards, the crystals were filtered off, washed with 4 mL of a mixture of toluene and hexane (1:1) and dried in vacuo. Yield 0.30 g (1.05 mmol, 23 %). M.p. 139 °C, Anal. found: C 63.05, H 5.49, N 9.86 %, calcd. for $C_{15}H_{16}N_2O_2Si$: C 63.35, H 5.67, N 9.85 %. **^{1}H NMR** ($CDCl_3$): δ = 8.40 (d 5.4 Hz, 1 H, aryl), 8.04 (dd 1.6 Hz, 7.7 Hz, 1 H, aryl), 7.87 (m, 1 H, aryl), 7.49–7.25 (mm, 3 H, aryl), 6.95–6.86 (mm, 2 H, aryl), 5.11 (s, 2 H, CH_2), 0.45 (s, 6 H, CH_3). **^{13}C NMR** ($CDCl_3$): δ = 169.2 (C=O), [157.0, 155.2, 143.7, 138.9, 133.6, 129.9, 123.4, 121.9, 120.5, 119.6, 119.4 (aryl)], 47.2 (CH_2), 4.2 (CH_3). **^{29}Si NMR** ($CDCl_3$): δ = –46.1, (CP/MAS): δ_{iso} = –63.1 ppm.

Crystal Structure Analysis of 2a: Single crystals were obtained directly from the synthesis. $C_{15}H_{16}N_2O_2Si$, M_r = 284.39, T = 100(2) K, monoclinic, space group $P2_1/c$, a = 7.3258(4), b = 13.3140(7), c = 14.3057(8) Å, β = 90.386(2)°, V = 1395.28(13) Å^3, Z = 4, $\rho_{calcd.}$ = 1.354 Mg·m^{-3}, μ(Mo-K_α) = 0.171 mm^{-1}, F(000) = 600, $2\theta_{max}$ = 60.0°, 14028 collected reflections, 4078 unique reflections (R_{int} = 0.0386), 183 parameters, S = 1.037, R_1 = 0.0428, wR_2 = 0.1055 [$I > 2\sigma(I)$], R_1 = 0.0672, wR_2 = 0.1141 (all data), max./min. residual electron density +0.594/–0.330 e·Å^{-3}.

Synthesis of Compound 2b: A solution of ligand **1** (1.00 g, 4.63 mmol) and triethylamine (1.41 g, 13.9 mmol) in THF (30 mL) was stirred at room temperature and methylphenyldichlorosilane (0.97 g, 5.10 mmol) was added within 10 s. The mixture was stirred for 2 h, whereupon the hydrochloride precipitate was filtered off and washed with THF (10 mL). From the combined filtrate and washings the solvent was removed under reduced pressure and the resultant brownish oily residue was dissolved in warm toluene (1 mL) and THF (4 mL). Upon storage at room temperature, crystallization commenced within a few minutes. After 11 d the beige crystals were filtered off, washed with 2.5 mL of a mixture of toluene and THF (1:4) and dried in vacuo. Yield 1.0 g (3.5 mmol, 65 %). M.p. 185 °C, Anal. found: C 69.47, H 5.25, N 8.08 %, calcd. for $C_{20}H_{18}N_2O_2Si$: C 69.34, H 5.24, N 8.09 %. **^{1}H NMR** ($CDCl_3$): δ = 7.99 (dd 1.5 Hz, 7.6 Hz, 1 H, aryl), 7.88 (d, 5.1 Hz, 1 H, aryl), 7.83 (m, 1 H, aryl), 7.48 (d 7.9 Hz, 1 H, aryl), 7.40–7.36 (mm, 2 H, aryl), 7.27–7.17 (mm, 5 H, aryl), 6.82 (m, 1 H, aryl), 6.75 (d 8.2 Hz, 1 H, aryl), 5.47, 5.06 (2d 19.6 Hz, 2 H, CH_2), 0.68 (s, 3 H, CH_3). **^{13}C NMR** ($CDCl_3$): δ = 170.1 (C=O), [157.2, 154.6, 143.5, 140.6, 139.5, 133.6, 132.7, 129.6, 128.5, 127.5, 123.4, 121.6, 120.2, 119.6, 119.2 (aryl)], 47.7 (CH_2), 4.5 (CH_3). **^{29}Si NMR** ($CDCl_3$): δ = –65.2, (CP/MAS): δ_{iso} = –75.7 ppm.

Crystal Structure Analysis of 2b: Single crystals were obtained directly from the synthesis. $C_{20}H_{18}N_2O_2Si$, M_r = 346.45, T = 97(2) K, monoclinic, space group $P2_1/c$, a = 12.6835(3), b = 8.5894(2), c = 15.8348(3) Å, β = 98.486(1)°, V = 1706.21(7) Å^3, Z = 4, $\rho_{calcd.}$ = 1.349 Mg·m^{-3}, μ(Mo-K_α) = 0.154 mm^{-1}, F(000) = 728, $2\theta_{max}$ = 104.0°, 118597 collected reflections, 19400 unique reflections (R_{int} = 0.0318), 227 parameters, S = 1.072, R_1 = 0.0373, wR_2 = 0.1147 [$I > 2\sigma(I)$], R_1 = 0.0618, wR_2 = 0.1238 (all data), max./min. residual electron density +0.669/–0.350 e·Å^{-3}.

Synthesis of Compound 2c: A solution of ligand **1** (1.00 g, 4.63 mmol) and triethylamine (1.41 g, 13.9 mmol) in THF (30 mL) was stirred at room temperature and diphenyldichlorosilane (1.29 g, 5.10 mmol) was added within 10 s. The mixture was stirred for 2 h, whereupon the hydrochloride precipitate was filtered off and washed with THF (7.5 mL). From the combined filtrate and washings the solvent was removed under reduced pressure and the resultant brownish oily residue was dissolved in warm toluene (1.5 mL) and the solution was stored at 8 °C for crystallization. After 4 d the beige crystals were filtered off, washed with 1.5 mL of a mixture of toluene and THF (2:1) and dried in vacuo. Yield 1.64 g (4.01 mmol, 90 %). M.p. 278 °C, Anal. found: C 72.89, H 4.94, N 6.71 %, calcd. for $C_{25}H_{20}N_2O_2Si$: C 73.50, H 4.93, N 6.86 %. **^{1}H NMR** ($CDCl_3$): δ = 7.97 (dd 1.5 Hz, 7.8 Hz, 1 H, aryl), 7.83 (m, 1 H, aryl), 7.70 (d 5.4 Hz, 1 H, aryl), 7.56–7.51 (mm, 5 H, aryl), 7.27 (mm, 7 H, aryl), 7.15–7.09 (m, 1 H, aryl), 6.82–6.76 (mm, 2 H, aryl), 5.41 (s, 2 H, CH_2). **^{13}C NMR** ($CDCl_3$): δ = 170.7 (C=O), [157.3, 154.7, 144.4, 140.5, 139.9, 133.7, 133.5, 129.5,

128.6, 127.7, 123.2, 121.4, 120.1, 119.8, 119.1 (aryl)], 47.7 (CH_2). **^{29}Si NMR** ($CDCl_3$): δ = –81.2, (CP/MAS): δ_{iso} = –88.8 ppm.

Crystal Structure Analysis of 2c: Single crystals were obtained directly from the synthesis. $C_{25}H_{20}N_2O_2Si$, M_r = 408.52, T = 150(2) K, monoclinic, space group $P2_1/n$, a = 15.2057(3), b = 14.7503(3), c = 27.2041(5) Å, β = 100.592(1)°, V = 5997.6(2) Å^3, Z = 12, $\rho_{calcd.}$ = 1.357 Mg·m^{-3}, μ(Mo-K_α) = 0.143 mm^{-1}, F(000) = 2568, $2\theta_{max}$ = 50.0°, 55511 collected reflections, 10433 unique reflections (R_{int} = 0.0391), 811 parameters, S = 1.073, R_1 = 0.0419, wR_2 = 0.1037 [$I > 2\sigma(I)$], R_1 = 0.0729, wR_2 = 0.1139 (all data), max./min. residual electron density +0.354/–0.271 e·Å^{-3}.

Synthesis of Compound 2d: A solution of ligand **1** (1.23 g, 5.70 mmol) and triethylamine (1.73 g, 6.30 mmol) in THF (20 mL) was stirred at room temperature and a solution of dibenzyldichlorosilane[6a] (1.76 g, 6.30 mmol) in THF (10 mL) was added within 10 s. The mixture was stirred for 2 h, whereupon the hydrochloride precipitate was filtered off and washed with THF (10 mL). From the combined filtrate and washings the solvent was removed under reduced pressure and the resultant brownish oily residue was dissolved in warm toluene (1 mL) and the solution was stored at –25 °C for crystallization. After 4 weeks the beige crystals were filtered off, washed with 9 mL of toluene and dried in vacuo. Yield 1.27 g (2.91 mmol, 65 %). M.p. 135 °C, Anal. found: C 73.93, H 5.33, N 6.36 %, calcd. for $C_{27}H_{24}N_2O_2Si$: C 74.28, H 5.54, N 6.42 %. **^{1}H NMR** ($CDCl_3$): δ = 8,42 (d 5.4 Hz, 1 H, aryl), 7.95 (d 7.9 Hz, 1 H, aryl), 7.82 (m, 1 H, aryl), 7.42 (t, 7.9 Hz, 1 H, aryl), 7.35 (m, 1 H, aryl), 7.16 (d 8.1 Hz, 1 H, aryl), 6.99–6.86 (mm, 7 H, aryl), 6.80 (d 8.2 Hz, 1 H, aryl), 6.70 (d 6.6 Hz, 4 H, aryl), 4.37 (s, 2 H, N-CH_2), 2.68 (d 13.1 Hz, 2 H, SiCH_2), 2.49 (d 13.1 Hz, 2 H, SiCH_2). **^{13}C NMR** ($CDCl_3$): δ = 169.9 (C=O), [157.5, 155.5, 142.8, 139.5, 139.0, 133.5, 129.5, 128.3, 127.9, 124.3, 123.1, 121.2, 119.9, 119.3, 119.0 (aryl)], 47.2 (N-CH_2), 30.2 (SiCH_2). **^{29}Si NMR** ($CDCl_3$): δ = –66.2, (CP/MAS): δ_{iso} = –71.3 ppm.

Crystal Structure Analysis of 2d: Single crystals were obtained directly from the synthesis. $C_{27}H_{24}N_2O_2Si$, M_r = 436.57, T = 100(2) K, orthorhombic, space group $Pna2_1$, a = 8.7355(2), b = 19.3266(4), c = 13.0917(2) Å, V = 2210.24(8) Å^3, Z = 4, $\rho_{calcd.}$ = 1.312 Mg·m^{-3}, μ(Mo-K_α) = 0.134 mm^{-1}, F(000) = 920, $2\theta_{max}$ = 64.0°, 30364 collected reflections, 7551 unique reflections (R_{int} = 0.0317), 289 parameters, S = 1.033, χ(Flack) = 0.02(7), R_1 = 0.0328, wR_2 = 0.0792 [$I > 2\sigma(I)$], R_1 = 0.0386, wR_2 = 0.0820 (all data), max./min. residual electron density +0.302/–0.194 e·Å^{-3}.

Synthesis of Compound 2e: A solution of ligand **1** (1.00 g, 4.63 mmol) and triethylamine (1.41 g, 13.9 mmol) in THF (30 mL) was stirred at room temperature and allylphenyldichlorosilane (1.10 g, 5.10 mmol) was added within 10 s. The mixture was stirred for 2 h, whereupon the hydrochloride precipitate was filtered off and washed with THF (10 mL). From the combined filtrate and washings the solvent was removed under reduced pressure and the resultant brownish oily residue was dissolved in chloroform (5 mL) and the solution was stored at room temperature for crystallization. After 3 d the beige crystals were filtered off, washed with 3 mL of chloroform and dried in vacuo. Yield 1.19 g (5.88 mmol, 66 %). M.p. 226 °C, Anal. found: C 70.92, H 5.41, N 7.48 %, calcd. for $C_{22}H_{20}N_2O_2Si$: C 70.94, H 5.41, N 7.52 %. **^{1}H NMR** ($CDCl_3$): δ = 7.96 (m, 1 H, aryl), 7.90–7.84 (mm, 2 H, aryl), 7.39 (d 7.8 Hz, 1 H, aryl), 7.37 (mm, 2 H, aryl), 7.30–7.10 (mm, 5 H, aryl), 6.78 (mm, 2 H, aryl), 5.85 (m, 1 H, CH_2–C*H*=CH_2), 5.48 (d 19.5 Hz, 1 H, NCH_2), 4.90 (d 19.5 Hz, 1 H, NCH_2), 4.59 [d 10.2 Hz, 1 H, CH_2–CH=CH*H*(E)], 4.31 [d 17.2 Hz, 1 H, CH_2–CH=CH*H*(Z)], 2.39 (m, 1 H, C*H*$_2$–CH=CH_2), 1.88 (m, 1 H, C*H*$_2$–CH=CH_2). **^{13}C NMR** ($CDCl_3$): δ = 170.5 (C=O), [157.6, 155.5, 143.3, 140.5, 139.7, 134.5, 133.6, 129.5, 128.5, 123.3, 121.2, 120.2, 119.6, 119.0, 113.3 (aryl, allyl C=C)], 48.0 (N-CH_2), 30.2 (allyl CH_2). **^{29}Si NMR** ($CDCl_3$): δ = –74.2, (CP/MAS): δ_{iso} = –77.2 ppm.

Crystal Structure Analysis of 2e: Single crystals were obtained directly from the synthesis. $C_{22}H_{20}N_2O_2Si$, M_r = 372.49, T = 150(2) K, triclinic, space group $P\bar{1}$, a = 9.8407(2), b = 9.9004(2), c = 10.7876(2) Å, α = 93.128(1), β = 91.212(1), γ = 117.923(1)°, V = 925.96(3) Å^3, Z = 2, $\rho_{calcd.}$ = 1.336 Mg·m^{-3}, μ(Mo-K_α) = 0.147 mm^{-1}, F(000) = 392, $2\theta_{max}$ = 60.0°, 21179 collected reflections, 5323 unique reflections (R_{int} = 0.0257), 263 parameters, S = 1.061, R_1 = 0.0374, wR_2 = 0.0984 [$I > 2\sigma(I)$], R_1 = 0.0487, wR_2 = 0.1034 (all data), max./min. residual electron density +0.420/–0.264 e·Å^{-3}.

Synthesis of Compound 2f: A solution of ligand **1** (1.00 g, 4.63 mmol) and triethylamine (1.41 g, 13.9 mmol) in THF (30 mL) was stirred at room temperature and phenyldichlorosilane (1.10 g, 5.10 mmol) was added within 10 s. The mixture was stirred for 2 h, whereupon the hydrochloride precipitate was filtered off and washed with THF (10 mL). From the combined filtrate and washings the solvent was removed under reduced pressure and the resultant brownish oily residue was dissolved in a mixture of toluene (1.5 mL) and THF (2 mL) and the solution was stored at room temperature for crystallization. After 2 days the colorless crystals were filtered off, washed with 6 mL of a mixture of toluene and THF (1:1) and briefly dried in vacuo. The product crystallized as the solvate **2f**·THF (according to single crystal structure analysis and ^{1}H NMR spectroscopic data of a sample prepared immediately after isolating the solid product). Yield 2.11 g (5.22 mmol, 62 %). Anal. found: C 68,26, H 5.15, N 8.72 %. This composition hints at loss of solvent during preparation of the sample, as it corresponds to the values calculated for the solvent free product. Calcd. for $C_{23}H_{24}N_2O_3Si$: C 68.29, H 5.98, N 6.92 %, calcd. for $C_{19}H_{16}N_2O_2Si$: C 68.65, H 4.85, N 8.43 %. **^{1}H NMR** ($CDCl_3$): δ = 8.15 (d 5.9 Hz, 1 H, aryl, 8.00–7.94 (mm, 2 H, aryl), 7.59 (d 7.8 Hz, 1 H, aryl), 7.40 (t 6.6 Hz, 1 H, aryl), 7.36–7.25 (mm, 3 H, aryl), 7.21–7.14 (mm, 3 H, aryl), 6.85 (mm, 2 H, aryl), 5.88 (s, 1 H, Si-H; with ^{29}Si-satellites of ^1J 290 Hz), 5.31 (d 20.5 Hz, 1 H, CH_2), 5.18 (d 20.5 Hz, 1 H, CH_2). **^{13}C NMR** ($CDCl_3$): δ = 170.5 (C=O), [157.4, 154.1, 141.9, 140.6, 133.7, 133.6, 129.7, 129.0, 127.8, 124.1, 121.9, 119.8 (2x), 119.2 (aryl)], 48.3 (CH_2). **^{29}Si NMR** ($CDCl_3$): δ = –90.7 (^1J SiH = 290 Hz), (CP/MAS): δ_{iso} = –94.2 ppm.

Crystal Structure Analysis of 2f·THF: Single crystals were obtained directly from the synthesis. $C_{23}H_{24}N_2O_3Si$, M_r = 404.53, T = 100(2) K, monoclinic, space group $P2_1/c$, a = 14.9381(3), b = 8.8942(2), c = 15.4527(3) Å, β = 105.488(1)°, V = 1978.53(7) Å^3, Z = 4, $\rho_{calcd.}$ = 1.358 Mg·m^{-3}, μ(Mo-K_α) = 0.147 mm^{-1}, F(000) = 856, $2\theta_{max}$ = 70.0°, 29248 collected reflections, 8701 unique reflections (R_{int} = 0.0369), 266 parameters, S = 1.084, R_1 = 0.0410, wR_2 = 0.1074 [$I > 2\sigma(I)$], R_1 = 0.0640, wR_2 = 0.1156 (all data), max./min. residual electron density +0.524/–0.309 e·Å^{-3}.

3a, **3b**, **3c:** The syntheses of **3b** and **3c** are reported in reference [9a], and compound **3a** was synthesized in analogy: To a solution of *N*-benzyl-2-hydroxyacetophenoneimine (0.20 g, 0.89 mmol) and triethylamine (0.25 g, 2.5 mmol) in THF (10 mL) dimethyldichlorosilane (0.13 g, 1.0 mmol) was added at room temperature, whereupon triethylamine hydrochloride precipitated immediately and the initially yellow solution turned colorless. The mixture was stored at 6 °C for 30 min, finally the hydrochloride was filtered off and from the filtrate the volatiles (THF, excess Et_3N and Me_2SiCl_2) were removed in vacuo to yield an almost colorless oil of **3a** (0.24 g, 0.85 mmol, 96 %). **^{1}H NMR** ($CDCl_3$): δ = 7.55 (dd, 8.0 Hz, 1.5 Hz, 1 H, aryl), 7.15–7.35 (mm, 6 H, aryl), 6.85–6.95 (mm, 2 H, aryl), 4.54 (d, 1.3 Hz, 1 H, C=CH_2), 4.43

(d, 1.3 Hz, 1 H, C=CH_2), 3.86 (s, 2 H, N-CH_2), 0.34 (s, 6 H, Si–CH_3). **^{13}C NMR** ($CDCl_3$): δ = 151.0 (C–O), 145.8 (C=*C*–N), 138.3, 129.5, 128.4, 127.1, 126.6, 126.4, 124.7, 121.4, 120.1, 85.1 (C=*C*H_2), 47.9 (N–CH_2), –1.0 (Si–CH_3). **^{29}Si NMR** ($CDCl_3$): δ = 2.8 ppm.

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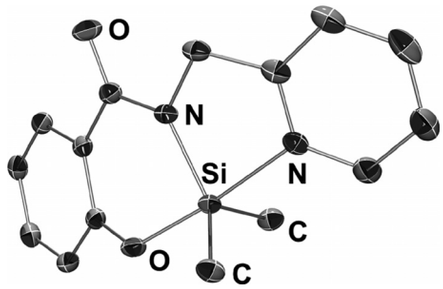

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