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Hypercoordinate Silicon Complexes of (O,N,N′ vs. O,N,O′) Schiff Base Type *N*-(2-Carbamidophenyl)imines: Examples of Exclusively *O*-Silylated Carbamides

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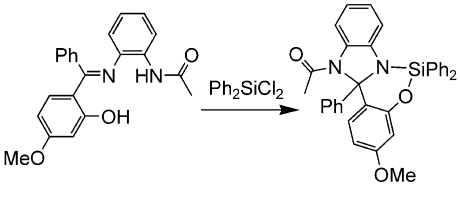
Keywords: Chelates / Coordination modes / Tridentate ligands / Silicon

Tridentate salphen-type O,N,N′ chelators, upon acylation of the NH_2 group, are capable of engaging an O,N,O′ coordination mode in addition to their inherent O,N,N′ donor character. In six-coordinate silicon complexes of the type SiL_2 [L = *N*-(2-carbamidophenyl)imine], these ligands were found to exclusively form SiN_2O_4 coordination spheres by engaging their tridentate O,N,O′ donor capability. Selected ligands L were also shown to preferably engage the O,N,O′ coordination mode when incorporated in five- and four-coordinate silicon compounds of the type LSiPhX (X = Cl, F) and $LSiPh_2$, respectively. The coordination modes of the herein presented six-, five-, and four-coordinate silicon compounds represent the first examples of X-ray structurally confirmed *O*-silylated carbamides, which hence adopt structural features of C-siloxyimines.

Introduction

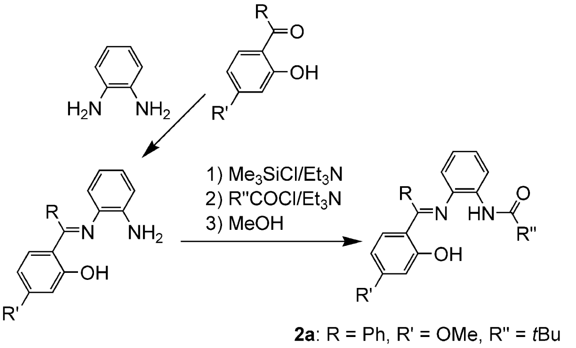
The class of hypercoordinate silicon complexes[1] comprises a great variety of such bearing bi-, tri-, and tetradentate chelating ligands. Although a wide range of oligodentate chelators with O, N, and C donor sites has already been explored,[2] the group of tridentate (O,N,N) donor ligands has apparently missed the entrance into silicon coordination chemistry, and thus they come into focus for our further investigations.[3] Surprisingly, in a preliminary study, an *N*-acylated salphen-type ligand revealed extraordinary behavior when attached to a diphenylsilicon moiety. The initial O,N,N chelator underwent isomerization to yield a benzimidazoline backbone of a now Si-bound bidentate (O,N) chelator (Scheme 1).[3a] This finding tempted us to further explore silicon compounds of *N*-acylated Schiff base type *o*-iminomethylphenols.



Scheme 1. Benzimidazoline formation upon silylation.

Results and Discussion

Tridentate salphen-type ligands such as **1a**–**c** (Scheme 2) are accessible from *o*-phenylenediamine and an *o*-hydroxyphenyl ketone (or aldehyde) in a 1:1 molar ratio.[4] The anilino group of these ligands allows further modification, that is, acylation. Thus, three such ligands (**1a**–**c**) were synthesized and *N*-acylated to afford ligands **2a**–**f** as a starting point for our study (Scheme 2). ^1H and ^{13}C NMR spectra revealed the existence of only one isomer (the *o*-iminomethylphenol) in solution. Furthermore, single-crystal X-ray analyses of **2a**, **2b**, **2d**, and **2e** (Figure 1) confirm the existence of the *o*-iminomethylphenol isomer in the solid state also (well in accord with the molecular structure of a related *N*-acetylated compound[3a]).



1a: R = Ph, R' = OMe
1b: R = Me, R' = H
1c: R = R' = H

2a: R = Ph, R' = OMe, R'' = *t*Bu
2b: R = Ph, R' = OMe, R'' = Ph
2c: R = Me, R' = H, R'' = *t*Bu
2d: R = Me, R' = H, R'' = Ph
2e: R = R' = H, R'' = *t*Bu
2f: R = R' = H, R'' = Ph

Scheme 2. Syntheses of *N*-acylated salphen ligands.

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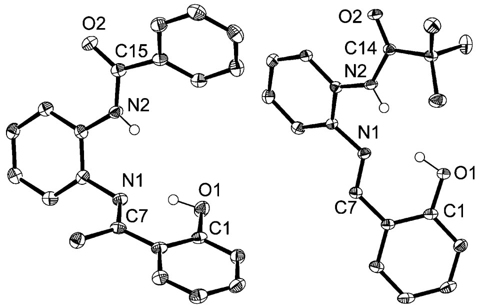
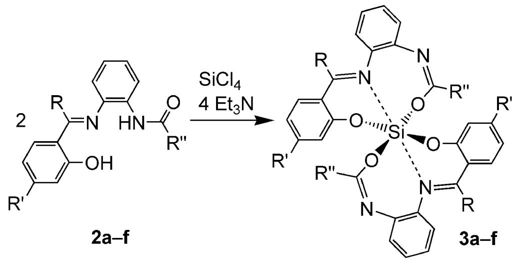


Figure 1. Molecular structures of **2d** (left) and **2e** (right). Thermal ellipsoids with 50% probability, C-bound H-atoms omitted, selected atoms labeled. Selected bond lengths [Å] for **2d**: O1–C1 1.362(2), O2–C15 1.229(2), N1–C7 1.301(2), N2–C15 1.371(2); for **2e**: O1–C1 1.355(1), O2–C14 1.223(1), N1–C7 1.286(1), N2–C14 1.366(1). The molecular structures of **2a** and **2b** (not depicted) exhibit similar features of the iminomethylphenol and the carbamide moieties.

Reaction of ligands **2a**–**f** with $SiCl_4$ in a 2:1 molar ratio (in the presence of triethylamine as supporting base) delivered hexacoordinate silicon complexes **3a**–**f** (Scheme 3) as pale-yellow solids, all of which exhibited poor solubility in chloroform and dimethyl sulfoxide. In order to confirm the hexacoordination of the Si atoms in each of these complexes, ^{29}Si CP/MAS NMR spectra were recorded (Table 1).



Scheme 3. Syntheses of hexacoordinate Si compounds **3a**–**f**. The same substitution pattern R,R′,R′′ applies to **2a**–**f** and **3a**–**f**.

Table 1. ^{29}Si NMR shifts δ_{Si} [ppm] of complexes **3a**–**f** in the solid state.

Compound	δ_{Si}	Compound	δ_{Si}
3a	–178.0	**3d**	–178.6
3b	–178.2	**3e**	–181.1
3c	–182.5	**3f**	–176.3,–177.3

Although the ^{29}Si NMR shifts indicate hexacoordination of the silicon atoms, the coordination mode of the tridentate chelating ligand cannot be assigned by this method. Hence, the solid-state structures of **3a**, **3c**, **3d**, and **3f** were determined by single-crystal X-ray structural analyses (Figure 2, Table 2). All of these complexes exhibit similar coordination spheres about their silicon atoms. In most of these structures (except **3a**) the silicon atom is situated on a crystallographically imposed center of inversion. Despite this missing center of symmetry in **3a**, the bonding parameters of the Si coordination sphere are very similar to those of **3c**, **3d**, and **3f**.

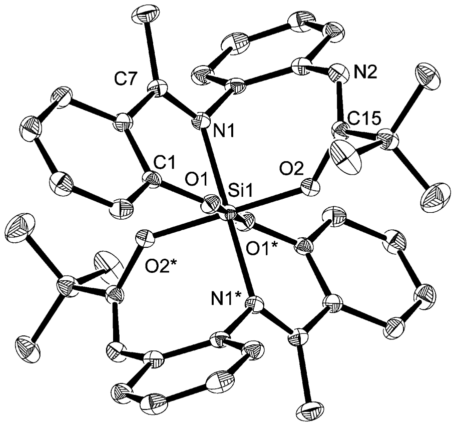
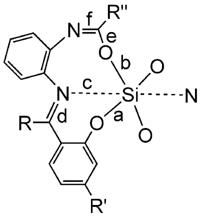


Figure 2. Molecular structure of **3c** in a crystal of **3c**·$(CHCl_3)_2$. Thermal ellipsoids with 50% probability, hydrogen atoms and chloroform molecules omitted for clarity, selected atoms labeled.

Table 2. Selected bond lengths [Å] of compounds **3a**, **3c**, **3d**, and **3f**.

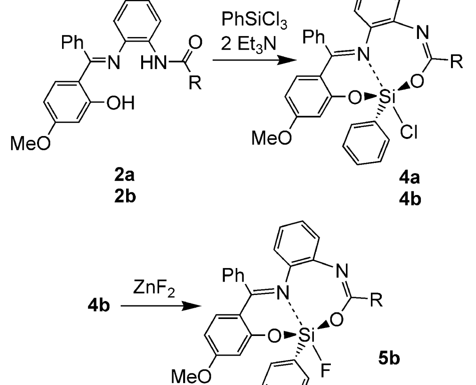


	a	b	c	d	e	f
3a	1.734(2)	1.757(2)	1.908(3)	1.322(4)	1.328(4)	1.283(4)
	1.736(2)	1.762(2)	1.915(3)	1.310(4)	1.330(4)	1.279(4)
3c	1.732(1)	1.748(1)	1.918(1)	1.309(1)	1.325(1)	1.287(1)
3d	1.734(2)	1.758(2)	1.925(2)	1.305(3)	1.326(3)	1.285(3)
3f	1.749(3)	1.752(3)	1.910(3)	1.302(4)	1.325(4)	1.294(4)
	1.741(2)	1.761(2)	1.907(3)	1.300(4)	1.329(4)	1.294(4)

To the best of our knowledge, these are the first structures of hexacoordinate silicon complexes with two tridentate O,N,O′ ligands in a *fac* coordination mode.[5,6] Concluding from the data in Table 2, one can find a number of common features regarding the coordination of the *N*-acylated salphen ligands with the silicon atom. In addition to exclusively engaging the O,N,O′ mode, the Si–O bond to the phenoxy moiety is slightly shorter than the bond to the O atom of the former carbonyl group, which is now part of a *C*-siloxyimine. The formal dative Si–N bonds are in the expected range for hexacoordinate silicon complexes with a SiN_2O_4 skeleton. Substituent R (Scheme 3) did not reveal any significant influence on the Si–N coordination behavior within this class of complexes. As regards selected bonds within the ligand molecules, the former carbonyl group of the *N*-acylated salphen ligand now exhibits features that can be described as a C–O and a C=N bond, and this C=N bond is even shorter than the C=N bond to the Si-coordinated Schiff base imine N atom. These features are similar for the benzoyl- and pivaloyl-substituted ligands. It is noteworthy that the molecular structures of **3a**–**f** are in contrast to our initial expectations for the following reasons: (i) In the above compounds, the silicon atom favors a situation within a seven-membered chelate ring rather than forming a five-membered ring system. (ii) The bonding character within the carbamide moiety (bonding situation C–N and C=O) was converted into a *C*-siloxyimine group (bonding situation C–O and C=N). Although it can be regarded as a general principle that Si–O bonds appear favorable, up to now X-ray diffraction analyses revealed the predominance of *N*-silylated carbamides.[7] Examples for such *C*-siloxyimine tautomeric forms bearing a two-coordinate siloxyimine N atom were not encountered so far.

In order to rule out that this coordination mode mainly depends on the rather bulky acyl groups at the ligand backbones, complex **3g** (Scheme 3; R = Ph, R′ = OMe, R′′ = Me) was synthesized in a similar manner and analyzed by X-ray diffraction analysis. The structural features of **3g** were found to be very similar to those of the above complexes and thus are not further discussed here.

To elucidate the coordination behavior of *N*-acylated salphen ligands further, compounds **2a** and **2b** were treated with phenyltrichlorosilane to afford **4a** and **4b**, respectively (Scheme 4, top). ^{29}Si NMR spectroscopic analysis of the product solutions revealed the near-exclusive formation of a product comprising a pentacoordinate silicon atom in both cases. Although all attempts to isolate **4a** and **4b** in good yields as solids failed so far, one single crystal of **4b** suitable for X-ray analysis formed from a residual drop of chloroform solution left in a Schlenk tube. Cl versus F exchange (Scheme 4, bottom) of **4b**, however, afforded complex **5b**, which was isolated as a crystalline solid in moderate yield. The solid-state structure of **5b** was also determined by single-crystal X-ray diffraction analysis. As a result of its isostructural relationship with **4b**, only the molecular structure of **5b** is depicted in Figure 3.



Scheme 4. Syntheses of pentacoordinate silicon complexes from *N*-acylated salphen ligands (**a**: R = *t*Bu, **b**: R = Ph).

The silicon atom of **5b**, as for **4b**, is housed within a trigonal-bipyramidal coordination sphere with the imine nitrogen atom N1 in an axial position *trans* to the halide. This arrangement has also been found for a SiMeCl-substituted silicon complex bearing a tridentate O,N,O′ ligand.[1r] A comparison of selected bond lengths and angles of **4b** and **5b** is given in Table 3.

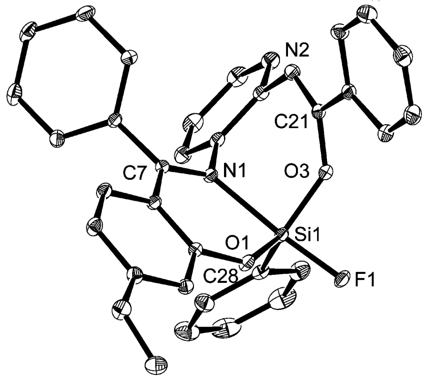


Figure 3. Molecular structure of **5b** in the solid state. Thermal ellipsoids with 30% probability, hydrogen atoms and chloroform molecule omitted for clarity, selected atoms labeled.

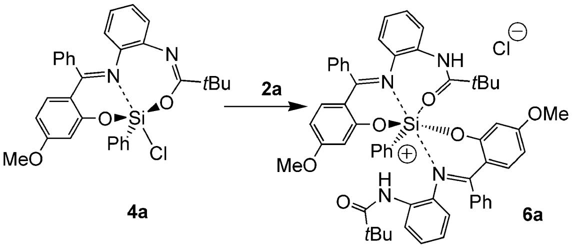
Table 3. Selected bond lengths [Å] and angles [°] of **4b** (X = Cl) and **5b** (X = F).

	4b	5b		4b	5b
Si1–O1	1.656(2)	1.663(1)	N2–C21	1.272(3)	1.279(2)
Si1–O3	1.662(2)	1.669(1)	O1–Si1–O3	119.4(1)	119.8(1)
Si1–N1	1.980(2)	2.026(1)	O1–Si1–C28	116.1(1)	116.6(1)
Si1–C28	1.863(3)	1.866(1)	O3–Si1–C28	124.5(1)	123.3(1)
Si1–X	2.204(1)	1.649(1)	N1–Si1–X	174.2(1)	175.4(1)
N1–C7	1.307(3)	1.305(2)			

In general, the tridentate ligand exhibits two similarities to the above-mentioned hexacoordinate silicon complexes, as both O,N,O′ coordination modes of this chelator are observed with only slightly shorter Si–O bonds to the phenoxy oxygen O1 than to the original carbonyl oxygen atom O3. These Si–O bonds are, due to their equatorial position, noticeably shorter than the Si–O bonds in the hexacoordinate complexes. The Si–N bonds are noticeably longer than in hexacoordinate silicon complexes **3**, and one can find a significant Si–N bond lengthening upon replacing the Si-bound chlorine atom for a fluorine atom. This effect was also observed for other Si–Cl/Si–F pairs of N-donor-substituted hypercoordinated silicon complexes and is not limited to such compounds bearing *trans*-disposed N–Si–X bonds.[8]

Surprisingly, the ^{29}Si NMR spectrum of the crude product solution of **4a** exhibited a small signal at δ = –172.5 ppm, indicative of the presence of a hexacoordinate silicon compound. During our attempts to crystallize **4a** from this solution, some crystals formed that, upon X-ray diffraction analysis, provided an answer as to which additional hypercoordinate silicon complex had formed in this reaction (Scheme 5, Figure 4).

A slight excess of the ligand led to the addition of a second equivalent of **2a** to complex **4a** to yield ionic compound **6a** comprising a hexacoordinate siliconium cation. The *o*-iminomethylphenolate O,N braces are situated in one plane with their N and O atoms *trans* to one another, an arrangement also found for other hexacoordinate silicon complexes of bidentate Schiff base ligands.[8,9] The position *trans* to the Si-bound phenyl group is occupied by a carb-



Scheme 5.

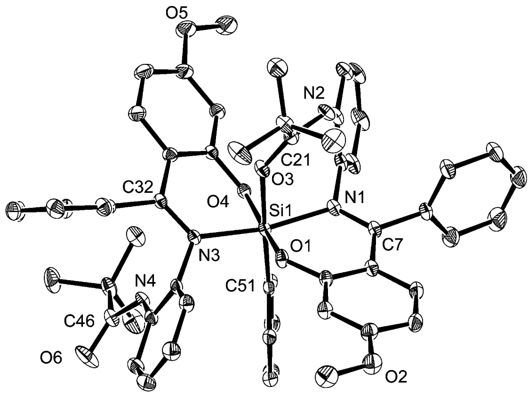
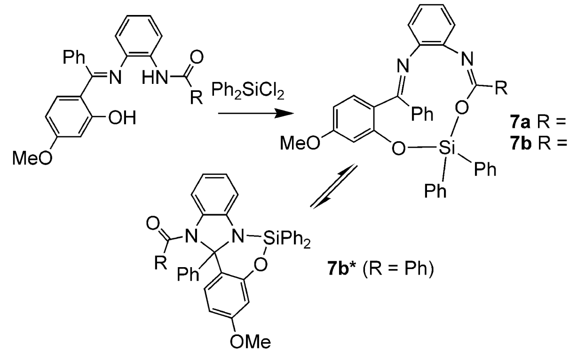


Figure 4. Molecular structure of **6a** in the solid state. Thermal ellipsoids with 20% probability, hydrogen atoms, chloride anion, and chloroform molecules omitted for clarity, selected atoms labeled. Selected bond lengths [Å] and angles [°]: Si1–O1 1.725(2), Si1–O3 1.938(2), Si1–O4 1.727(2), Si1–N1 1.943(3), Si1–N3 1.948(2), Si1–C51 1.912(3), N1–C7 1.312(4), N3–C32 1.308(4), O3–C21 1.256(4), N2–C21 1.329(4), O6–C46 1.224(4), N4–C46 1.355(4), O1–Si1–O4 170.4(1), N1–Si1–N3 168.0(1), O3–Si1–C51 178.3(1).

amide carbonyl O atom, which renders this compound a further example of a hexacoordinate Si complex with a *fac*-coordinated O,N,O′ ligand. In sharp contrast to the previously presented hexacoordinate silicon complexes, this Si1–O3 bond is remarkably longer, which thus gives rise to its interpretation as a formal dative bond. This altered bonding pattern, together with the now *N*-bound hydrogen atom at N2, is accompanied by typical carbamide bonding features, that is, a short C=O bond and a significantly longer C–N bond. Although representing an unexpected side product, **6a** complements a wide range of silicon coordination compounds bearing carbamide carbonyl oxygen donor atoms in their coordination sphere.[10]

In contrast to the pentacoordination of the silicon atoms in **4a**, **4b**, and **5b**, the products obtained from the reactions of ligands **2a** and **2b** with diphenyldichlorosilane did not give any indication of the presence of hypercoordinate silicon compounds, neither in solution nor in the solid state. Ligand **2a**, upon reaction with Ph_2SiCl_2 in the presence of triethylamine, afforded a product mixture, which as solution in $CDCl_3$, produced one predominant signal in the ^{29}Si NMR spectrum at δ = –43.2 ppm (**7a**). The absence of a signal at $\delta_{Si} \approx -25$ ppm in solutions of **7a** indicates hindrance of benzimidazoline formation, most likely due to the sterically more-demanding *t*Bu substituent. In the product solution obtained from ligand **2b** in an analogous procedure the presence of two species bearing tetracoordinate silicon atoms became apparent from ^{29}Si NMR signals at δ = –25.9 and –36.2 ppm, the first originating from the major component. The signal at δ = –25.9 ppm was attributed to the presence of benzimidazoline **7b**′ (which was supported by a ^{13}C NMR signal at δ = 90.0 ppm originating from the benzimidazoline quaternary carbon atom, as reported previously[3a]), and the signal at δ = –36.2 ppm was assigned to compound **7b**. The molecular structures of **7a** and **7b** were confirmed by X-ray crystallographic analyses of single crystals obtained from product solutions (Scheme 6, Figure 5). In spite of only a small difference at the ligand back-



Scheme 6.

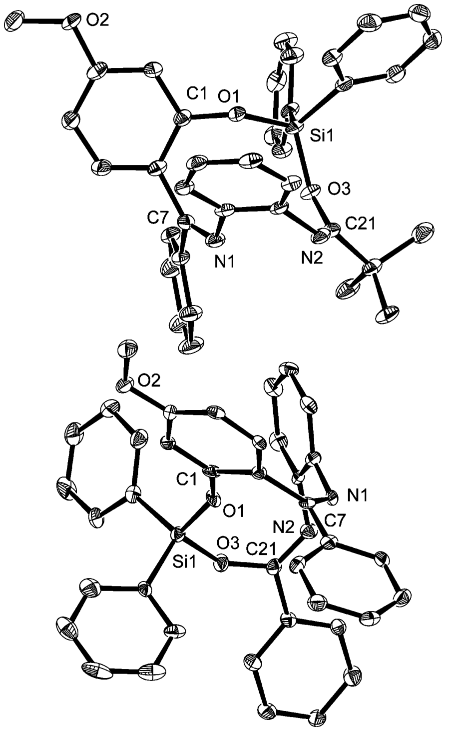


Figure 5. Molecular structures of **7a** (top) and **7b** (bottom). Thermal ellipsoids with 50% probability, hydrogen atoms omitted for clarity, selected atoms labeled. Selected bond lengths [Å] and angles [°] for **7a**: Si1–O1 1.637(2), Si1–O3 1.647(1), O3–C21 1.367(2), N1–C7 1.276(3), N2–C21 1.261(3); O1–Si1–O3 112.8(1); Si1–O1–C1 137.3(1), Si1–O3–C21 139.9(1); for **7b**: Si1–O1 1.626(3), Si1–O3 1.653(3), O3–C21 1.369(5), N1–C7 1.304(6), N2–C21 1.259(5); O1–Si1–O3 105.1(2); Si1–O1–C1 143.2(3), Si1–O3–C21 142.8(3).

bone (pivaloyl vs. benzoyl substituent), the bonding features in closer proximity of the silicon atoms in compounds **7a** and **7b** in the solid state differ significantly from each other. Although both compounds exhibit slightly distorted tetrahedral coordination spheres about the silicon atom, the O1–Si1–O3 angle is larger than the tetrahedral angle for **7a**, whereas it is noticeably smaller in **7b**. In addition, the Si–O–C angles in **7b** are significantly wider than their analogues in **7a**. As common features of **7a** and **7b**, the slightly shorter Si–O bonds to the phenoxy O atoms and the pronounced C=N double bond character within the *C*-siloxyimine moiety (N2=C21) are to be mentioned. The latter clearly distinguishes **7a** and **7b** from the above hexa- and pentacoordinate silicon compounds, the *C*-siloxyimine C=N bonds of which range between 1.272(3) and 1.294(4) Å.

Conclusions

In addition to the previously reported benzimidazoline formation upon silylation of an *N′*-acetylated tridentate O,N,N′ salphen-type ligand, this isomerization was now shown to also proceed with *N*-bound acyl groups other than acetyl. Increasing steric bulk, however, may prevent benzimidazoline formation, that is, for ligands carrying a *t*Bu-substituted acyl group. In these cases, and upon formation of hypercoordinate silicon complexes (five- and six-coordinate) *N′*-acylated salphen-type ligands were shown to swap from the inherent O,N,N′ to the tautomeric O,N,O′ coordination mode. The herein presented examples of hexa-, penta-, and tetracoordinate silicon compounds, which were characterized by single-crystal X-ray diffraction analyses, represent the first such evidence for solely *O*-silylated carbamides comprising a two-coordinate nitrogen atom, and hence exhibiting *C*-siloxyimine structural features. Additionally, some of the herein reported complexes are the first to exhibit tridentate (O,N,O′) chelators in a *fac* coordination mode in the coordination sphere of hexacoordinate silicon atoms.

Experimental Section

General Methods: All syntheses were carried out under an inert atmosphere of dry argon in dry solvents by using Schlenk techniques. ^{1}H, ^{13}C, and ^{29}Si NMR spectra (solution) were recorded with a Bruker DPX 400 instrument by using $SiMe_4$ as an internal standard. Solid-state NMR spectra (^{29}Si CP/MAS) were recorded with a Bruker AVANCE 400WB instrument. Single-crystal X-ray diffraction data were collected with a Bruker-Nonius X8 APEXII CCD instrument by using Mo-K_α radiation. The structures were solved with direct methods (SHELXS97) and refined with full-matrix least-squares methods on F^2 (SHELXL97).[11] The syntheses of compounds **1a**[3a] and **1c**[4] were described in the literature.

1b: *O*-Phenylenediamine (20.0 g, 185 mmol), *o*-hydroxyacetophenone (25.2 g, 185 mmol), and piperidine (15.7 g, 185 mmol) were dissolved in isobutyl alcohol (120 mL) and stirred under reflux for 14 h. The resulting orange-red solution was cooled to room temperature before stored at 8 °C overnight, whereupon **1b** crystallized. The orange solid product was separated from the still-cold solution by vacuum filtration, washed with isobutyl alcohol (20 mL) and dried in air. Yield: 33.2 g (147 mmol, 79 %). M.p. 108 °C. $C_{14}H_{14}N_2O$ (226.28): calcd. C 74.31, H 6.24, N 12.38; found C 74.30, H 6.19, N 12.31. ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ = 2.37 (s, 3 H, CH_3), 3.63 (s br., 2 H, NH_2), 6.70–7.05 (mm, 6 H), 7.37 (m, 1 H), 7.64 (dd, J = 8.0 Hz, 1 H, 1.2 Hz), 14.76 (s, 1 H, OH) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 17.2 (CH_3), 115.7, 118.2, 118.3, 118.5, 119.7, 121.5, 126.2, 129.0, 133.2, 133.3, 138.2, 162.1, 173.7 ppm.

2a: To a solution of compound **1a** (6.00 g, 18.8 mmol) and triethylamine (5.00 g, 49.5 mmol) in thf (80 mL) was added chlorotrimethylsilane (2.10 g, 19.3 mmol) dropwise, whereupon $[Et_3NH]Cl$ precipitated. The resulting mixture was stirred at ambient temperature for 10 min, whereafter pivaloic chloride (2.50 g, 20.7 mmol) was added, and the mixture was stirred for a further 10 min. $[Et_3NH]Cl$ was then removed by filtration, washed with thf (20 mL), and discarded. From the combined filtrate and washings the solvent was removed under reduced pressure. The residue was dissolved in methanol (20 mL) under gentle heating to yield a clear yellow solution, wherefrom crystallization of **2a** commenced within a few minutes. After 1 d the supernatant was decanted from the yellow crystalline product, which was washed with small portions of methanol (5 mL) and dried in air. Yield: 5.44 g (13.5 mmol, 72 %). M.p. 144 °C. $C_{25}H_{26}N_2O_3$ (402.48): calcd. C 74.61, H 6.51, N 6.96; found C 74.98, H 6.60, N 6.75. ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ = 1.31 [s, 9 H, $C(CH_3)_3$], 3.85 (s, 3 H, OCH_3), 6.30–7.30 (mm, 11 H), 7.98 (s, 1 H, NH), 8.29 (d, J = 8.0 Hz, 1 H), 14.32 (s, 1 H, OH) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 27.7 [$C(CH_3)_3$], 40.1 [$C(CH_3)_3$], 55.5 (OCH_3), 101.4, 106.7, 113.4, 119.9, 122.0, 123.2, 125.5, 128.4, 128.5, 129.4, 131.4, 134.0 (2×), 136.5, 164.3, 164.8, 175.5, 176.6 ppm. A single crystal of dimensions $0.70 \times 0.50 \times 0.40$ mm obtained by slow evaporation of a solution in ethanol was chosen for data collection. Selected crystallographic data for **2a**: $C_{25}H_{26}N_2O_3$, M_r = 402.48, T = 90(2) K, triclinic, space group $P\bar{1}$, a = 9.4917(3) Å, b = 9.8900(3) Å, c = 12.6894(3) Å, α = 111.162(1)°, β = 104.971(1)°, γ = 96.357(2)°, V = 1045.28(5) Å^3, Z = 2, $\rho_{calcd.}$ = 1.279 Mg m^{-3}, μ(Mo–K_α) = 0.084 mm^{-1}, F(000) = 428, $2\theta_{max}$ = 70.0°, 36473 collected reflections, 9127 unique reflections (R_{int} = 0.0219), 283 parameters, S = 1.076, R_1 = 0.0406 [$I > 2\sigma(I)$], wR_2(all data) = 0.1260, max./min. residual electron density +0.552/–0.257 e Å^{-3}.

2b: The same procedure as for **2a** applies. Starting materials used: **1a** (6.00 g, 18.8 mmol), triethylamine (5.00 g, 49.5 mmol), Me_3SiCl (2.10 g, 19.3 mmol), PhCOCl (2.70 g, 19.2 mmol) in thf (80 mL). After removal of the solvent and upon treatment of the crude product with methanol (30 mL) **2b** precipitated immediately. The yellow solid obtained was filtered off with suction and dried in air. Yield: 6.12 g (14.5 mmol, 77 %). M.p. 180 °C. $C_{27}H_{22}N_2O_3$ (422.47): calcd. C 76.76, H 5.25, N 6.63; found C 76.73, H 5.23, N 6.63. ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ = 3.84 (s, 3 H, OCH_3), 6.30–8.50 (mm, 18 H), 14.40 (s, 1 H, OH) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 55.5 (OCH_3), 101.5, 106.7, 113.7, 120.2, 122.3, 123.6, 125.6, 127.1, 128.4, 128.6, 128.9, 129.4, 131.5, 131.8, 134.1 (2×), 135.0, 136.8, 164.4, 164.9, 165.2, 175.7 ppm. A single crystal of dimensions $0.65 \times 0.55 \times 0.40$ mm obtained by slow evaporation of a solution in methanol and tetrahydrofuran was chosen for data collection. Selected crystallographic data for **2b**: $C_{27}H_{22}N_2O_3$, M_r = 442.47, T = 90(2) K, monoclinic, space group $P2_1/c$, a = 10.1615(3) Å, b = 14.5152(4) Å, c = 15.5414(4) Å, β = 108.589(1)°, V = 2172.71(10) Å^3, Z = 4, $\rho_{calcd.}$ = 1.292 Mg m^{-3}, μ(Mo–K_α) = 0.085 mm^{-1}, F(000) = 888, $2\theta_{max}$ = 70.0°, 41321 collected reflections, 9573 unique reflections (R_{int} = 0.0277), 297 parameters, S =

1.080, R_1 = 0.0432 [$I > 2\sigma(I)$], wR_2(all data) = 0.1324, max./min. residual electron density +0.561/–0.464 e Å^{-3}.

2c: The same procedure as for **2a** applies. Starting materials used: **1b** (3.00 g, 13.3 mmol), triethylamine (4.00 g, 39.6 mmol), Me_3SiCl (1.44 g, 13.3 mmol), *t*BuCOCl (1.75 g, 14.5 mmol) in thf (40 mL). After removal of the solvent and upon treatment of the crude product with methanol (25 mL) all our attempts to crystallize **2c** failed. Thus, the yellow oil obtained (yield: 3.53 g, 11.4 mmol, 85.7%) was used for further reactions as a thf solution (50%). ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ = 1.18 [s, 9 H, $C(CH_3)_3$], 2.35 (s, 3 H, $N{=}CCH_3$), 6.75–8.25 (mm, 9 H), 13.8 (s br., 1 H, OH) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 17.1 ($N{=}C\mathit{C}H_3$), 27.0 [$C(\mathit{C}H_3)_3$], 39.3 [$\mathit{C}(CH_3)_3$], 117.8, 118.1, 119.0, 120.8, 121.5, 123.8, 125.5, 128.9, 129.6, 133.2, 136.9, 161.4, 174.1, 176.1 ppm.

2d: The same procedure as for **2a** applies. Starting materials used: **1b** (3.00 g, 13.3 mmol), triethylamine (4.00 g, 39.6 mmol), Me_3SiCl (1.44 g, 13.3 mmol), PhCOCl (2.10 g, 14.9 mmol) in thf (40 mL). After removal of the solvent and upon treatment of the crude product with methanol (10 mL) **2d** precipitated as a yellow fine crystalline powder. The yellow solid obtained was filtered off with suction, washed with methanol (5 mL) and dried in air. Yield: 3.34 g (10.1 mmol, 76%). M.p. 152 °C. $C_{21}H_{18}N_2O_2$ (330.37): calcd. C 76.34, H 5.50, N 8.48; found C 76.10, H 5.48, N 8.49. ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ = 2.43 (s, 3 H, CH_3), 6.87 (d, J = 7.6 Hz, 1 H), 6.93 (t, J = 7.4 Hz, 1 H), 7.07 (d, J = 8.0 Hz, 1 H), 7.18 (t, J = 7.4 Hz, 1 H), 7.20–7.50 (mm, 5 H), 7.67 (d, J = 8.0 Hz, 1 H), 7.82 (d, J = 2 H, 7.2 Hz), 8.02 (s, 1 H, NH), 8.53 (d, J = 8.0 Hz, 1 H), 14.24 (s, 1 H, OH) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 17.8 (CH_3), 118.5, 118.7, 119.6, 121.3 (2×), 124.3, 126.3, 127.0, 128.9, 129.3, 130.2, 131.9, 133.8, 134.6, 136.6, 161.9, 165.2, 175.0 ppm. A single crystal of dimensions 0.55 × 0.18 × 0.14 mm obtained by slow evaporation of a solution in methanol was chosen for data collection. Selected crystallographic data for **2d**: $C_{21}H_{18}N_2O_2$, M_r = 330.37, T = 90(2) K, orthorhombic, space group *Pbca*, a = 19.7096(13) Å, b = 7.8678(4) Å, c = 21.9221(14) Å, V = 3399.5(4) Å^3, Z = 8, $\rho_{\text{calcd.}}$ = 1.291 Mg m^{-3}, μ(Mo–K_α) = 0.084 mm^{-1}, F(000) = 1392, $2\theta_{\max}$ = 50.0°, 18293 collected reflections, 2995 unique reflections (R_{int} = 0.0803), 233 parameters, S = 1.010, R_1 = 0.0378 [$I > 2\sigma(I)$], wR_2(all data) = 0.0914, max./min. residual electron density +0.200/–0.225 e Å^{-3}.

2e: The same procedure as for **2a** applies. Starting materials used: **1c** (3.00 g, 14.1 mmol), triethylamine (4.00 g, 39.6 mmol), Me_3SiCl (1.55 g, 14.3 mmol), *t*BuCOCl (1.85 g, 15.4 mmol) in thf (70 mL). After removal of the solvent and upon treatment of the crude product with methanol (20 mL) crystallization of **2e** commenced. The supernatant was decanted, the crystals were washed with methanol (5 mL) and dried in air. Yield: 2.48 g (8.38 mmol, 59%). M.p. 136 °C. $C_{18}H_{20}N_2O_2$ (296.36): calcd. C 72.94, H 6.81, N 9.45; found C 72.86, H 6.70, N 9.46. ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ = 1.33 (s, 9 H, CH_3), 6.90–7.50 (mm, 7 H), 8.16 (s, 1 H, NH), 8.45 (d, J = 8.0 Hz, 1 H), 8.63 (s, 1 H, $N{=}CH$), 12.43 (s, 1 H, OH) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 27.6 [$C(\mathit{C}H_3)_3$], 40.1 [$\mathit{C}(CH_3)_3$], 117.3, 117.9, 119.2, 119.6, 120.6, 124.2, 128.0, 132.3, 132.8, 133.9, 138.2, 160.8, 164.2, 176.6 ppm. single crystal of dimensions 0.40 × 0.28 × 0.22 mm obtained directly from the above synthesis was chosen for data collection. Selected crystallographic data for **2e**: $C_{18}H_{20}N_2O_2$, M_r = 296.36, T = 90(2) K, monoclinic, space group $P2_1/c$, a = 13.8500(6) Å, b = 9.2073(3) Å, c = 12.3970(4) Å, β = 99.952(2)°, V = 1557.09(10) Å^3, Z = 4, $\rho_{\text{calcd.}}$ = 1.264 Mg m^{-3}, μ(Mo–K_α) = 0.083 mm^{-1}, F(000) = 632, $2\theta_{\max}$ = 60.0°, 17698 collected reflections, 4499 unique reflections (R_{int} = 0.0335), 209 parameters, S = 1.063, R_1 = 0.0407 [$I > 2\sigma(I)$], wR_2(all data) = 0.1160, max./min. residual electron density +0.381/–0.251 e Å^{-3}.

2f: The same procedure as for **2a** applies. Starting materials used: **1c** (3.00 g, 14.1 mmol), triethylamine (4.00 g, 39.6 mmol), Me_3SiCl (1.55 g, 14.3 mmol), PhCOCl (2.16 g, 15.4 mmol) in thf (70 mL). After removal of the solvent and upon treatment of the crude product with methanol (20 mL) **2e** precipitated. The yellow solid obtained was filtered off with suction, washed with methanol (5 mL) and dried in air. Yield: 3.41 g (10.8 mmol, 77%). M.p. 160 °C. $C_{20}H_{16}N_2O_2$ (316.36): calcd. C 75.93, H 5.10, N 8.85; found C 75.61, H 5.10, N 8.81. ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ = 6.97 (t, J = 7.4 Hz, 1 H), 7.05 (d, J = 8.0 Hz, 1 H), 7.10–7.55 (mm, 8 H), 7.91 (d, J = 2 H, 8.0 Hz), 8.58–8.65 (m, 3 H, NH, ar, $N{=}CH$), 12.47 (s, 1 H, OH) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 117.4, 118.1, 119.3, 119.6, 120.7, 124.6, 127.0, 128.1, 128.9, 131.9 ppm. 132.2, 132.9, 133.9, 134.6, 138.3, 160.9, 164.5, 165.1 ppm.

Compounds **3** were almost insoluble in solvents such as $CDCl_3$ and DMSO. Hence, they were characterized in the solid state only.

3a: To a solution of ligand **2a** (0.90 g, 2.24 mmol) dissolved in chloroform (9 mL) was added triethylamine (0.67 g, 6.6 mmol) followed by the rapid addition of $SiCl_4$ (0.19 g, 1.12 mmol) whilst stirring. Immediately a clear solution resulted, and stirring was stopped 10 s after the addition of $SiCl_4$ was complete. Within a few minutes precipitation of **3a** (as chloroform solvate) commenced. After 1 week the fine precipitate was filtered off, washed with chloroform (2 mL), and briefly dried in a vacuum. Yield: 1.15 g. This product comprises an undefined fraction of solvent of crystallization. Upon storage in a 20-mL Schlenk tube for 2 weeks large amounts of this solvent must have escaped from the crystals, as microanalysis revealed a composition matching the C/H/N contents for the solvent-free compound. $C_{50}H_{48}N_4O_6Si$ (829.06): calcd. C 72.44, H 5.84, N 6.76; found C 72.48, H 6.16, N 6.99. ^{29}Si CP/MAS NMR (79.51 MHz, 25 °C): δ = –178.0 ppm. In order to obtain single crystals of **3a** suitable for X-ray diffraction analysis, ligand **2a** (0.38 g, 0.95 mmol), triethylamine (0.15 g, 1.5 mmol), and the (compared with $SiCl_4$) less-reactive $(Et_2N)_2SiCl_2$ (0.11 g, 0.56 mmol) were dissolved in chloroform (9 mL), stored at room temperature for 1 d and then stored at 8 °C for 1 week, whereupon a precipitate of small crystals of **3a**·$(CHCl_3)_3$ had formed. A single crystal of dimensions 0.23 × 0.18 × 0.03 mm was chosen for data collection. Selected crystallographic data for **3a**·$(CHCl_3)_3$: $C_{53}H_{51}Cl_9N_4O_6Si$, M_r = 1187.12, T = 90(2) K, monoclinic, space group $P2_1/c$, a = 10.6909(3) Å, b = 18.0804(5) Å, c = 28.2333(8) Å, β = 91.019(1)°, V = 5456.5(3) Å^3, Z = 4, $\rho_{\text{calcd.}}$ = 1.445 Mg m^{-3}, μ(Mo–K_α) = 0.537 mm^{-1}, F(000) = 2448, $2\theta_{\max}$ = 50.0°, 50406 collected reflections, 9605 unique reflections (R_{int} = 0.0681), 666 parameters, S = 1.040, R_1 = 0.0535 [$I > 2\sigma(I)$], wR_2(all data) = 0.1289, max./min. residual electron density +0.354/–0.635 e Å^{-3}.

In general, for the syntheses of compounds **3b**–**f** the same procedure applies as for the synthesis of **3a** (hence starting from $SiCl_4$, triethylamine and ligand **2b**–**3f**, respectively).

3b: Starting materials used: **2b** (0.900 g, 2.13 mmol), triethylamine (0.640 g, 6.32 mmol), $SiCl_4$ (0.180 g, 1.06 mmol), chloroform (9 mL). Yield: 0.90 g. Whereas solid-state ^{29}Si NMR spectroscopy revealed the formation of a hexacoordinate silicon compound (δ = –178.2 ppm), C/H/N analysis was not conclusive: $C_{54}H_{40}N_4O_6Si$: calcd. C 74.63, H 4.69, N 6.45; found C 71.95, H 6.00, N 6.50.

3c: Starting materials used: **2c** (0.750 g, 2.42 mmol, as 1.50 g of a 50% solution in thf), triethylamine (0.730 g, 7.21 mmol), $SiCl_4$ (0.200 g, 1.18 mmol), chloroform (9 mL). Crystals of **3c**·$(CHCl_3)_2$

formed within some hours. Yield: 0.75 g (0.83 mmol, 70%). $C_{40}H_{42}Cl_6N_4O_4Si$ (883.57): calcd. C 54.37, H 4.79, N 6.34; found C 55.47, H 5.06, N 6.64. ^{29}Si CP/MAS NMR (79.51 MHz, 25 °C): δ = –182.5 ppm. A single crystal of dimensions 0.60 × 0.45 × 0.35 mm was chosen for data collection. Crystals of this compound turned out to be systematically twinned. Determination of the twin law was carried out with CELL-NOW,[12] data integration was performed with SAINTPLUS.[13] Refinement of twin contributions resulted in populations of 54 and 46%. Selected crystallographic data for **3c**·$(CHCl_3)_2$: $C_{40}H_{42}Cl_6N_4O_4Si$, M_r = 883.57, T = 150(2) K, monoclinic, space group $P2_1/c$, a = 10.8547(5) Å, b = 16.3569(7) Å, c = 12.0130(5) Å, β = 100.647(2)°, V = 2096.18(16) Å^3, Z = 2, $\rho_{calcd.}$ = 1.400 Mg m^{-3}, μ(Mo–K_α) = 0.484 mm^{-1}, $F(000)$ = 916, $2\theta_{max}$ = 64.0°, 40120 collected reflections, 7273 unique reflections (R_{int} = 0.0246), 268 parameters, S = 1.059, R_1 = 0.0381 [$I > 2\sigma(I)$], wR_2(all data) = 0.1044, max./min. residual electron density +0.558/–0.604 e Å^{-3}.

3d: Starting materials used: **2d** (0.600 g, 1.82 mmol), triethylamine (0.550 g, 5.43 mmol), $SiCl_4$ (0.160 g, 0.91 mmol), chloroform (7.5 mL). Yield: 0.97 g (0.83 mmol, 92%) of **3d**·$(CHCl_3)_4$. $C_{46}H_{36}Cl_{12}N_4O_4Si$ (1162.28): calcd. C 47.53, H 3.12, N 4.82; found C 50.18, H 4.42, N 5.90. ^{29}Si CP/MAS NMR (79.51 MHz, 25 °C): δ = –178.6 ppm. From the reaction product a single crystal of dimensions 0.28 × 0.06 × 0.06 mm was chosen for data collection. Selected crystallographic data for **3d**·$(CHCl_3)_4$: $C_{46}H_{36}Cl_{12}N_4O_4Si$, M_r = 1162.28, T = 90(2) K, monoclinic, space group $P2_1/n$, a = 9.1276(2) Å, b = 19.0043(6) Å, c = 13.9283(4) Å, β = 92.125(1)°, V = 2414.39(12) Å^3, Z = 2, $\rho_{calcd.}$ = 1.599 Mg m^{-3}, μ(Mo–K_α) = 0.763 mm^{-1}, $F(000)$ = 1180, $2\theta_{max}$ = 54.0°, 20991 collected reflections, 5264 unique reflections (R_{int} = 0.0378), 318 parameters, S = 1.071, R_1 = 0.0398 [$I > 2\sigma(I)$], wR_2(all data) = 0.1074, max./min. residual electron density +0.839/–0.488 e Å^{-3}.

3e: Starting materials used: **2e** (0.750 g, 2.53 mmol), triethylamine (0.760 g, 7.51 mmol), $SiCl_4$ (0.220 g, 1.29 mmol), chloroform (9 mL). Yield: 0.66 g (1.07 mmol, 85%). $C_{36}H_{36}N_4O_4Si$ (616.81): calcd. C 70.10, H 5.89, N 9.08; found C 69.83, H 6.19, N 9.25. ^{29}Si CP/MAS NMR (79.51 MHz, 25 °C): δ = –181.1 ppm.

3f: Starting materials used: **2f** (0.750 g, 2.37 mmol), triethylamine (0.720 g, 7.11 mmol), $SiCl_4$ (0.200 g, 1.18 mmol), chloroform (9 mL). Within some hours a crystalline precipitate of **3f**·$(CHCl_3)$ had formed. Yield: 0.74 g (0.95 mmol, 81%). $C_{41}H_{29}Cl_3N_4O_4Si$ (776.12): calcd. C 63.45, H 3.77, N 7.22; found C 62.01, H 4.05, N 7.17. ^{29}Si CP/MAS NMR (79.51 MHz, 25 °C): δ = –177.3 ppm. From this product a single crystal of dimensions 0.45 × 0.04 × 0.03 mm was chosen for data collection. Selected crystallographic data for **3f**·$(CHCl_3)$: $C_{41}H_{29}Cl_3N_4O_4Si$, M_r = 776.12, T = 90(2) K, triclinic, space group $P\bar{1}$, a = 11.8304(11) Å, b = 12.6157(12) Å, c = 14.285(2) Å, α = 108.473(5)°, β = 111.797(6)°, γ = 100.134(4)°, V = 1770.2(4) Å^3, Z = 2, $\rho_{calcd.}$ = 1.456 Mg m^{-3}, μ(Mo–K_α) = 0.344 mm^{-1}, $F(000)$ = 800, $2\theta_{max}$ = 50.0°, 15054 collected reflections, 6214 unique reflections (R_{int} = 0.1013), 523 parameters, S = 0.858, R_1 = 0.0584 [$I > 2\sigma(I)$], wR_2(all data) = 0.1136, max./min. residual electron density +0.318/–0.355 e Å^{-3}.

3g: Starting materials used: The N'-acetylated derivative of **1a** compound **2g**[3a] (0.700 g, 1.94 mmol), triethylamine (0.550 g, 5.43 mmol), $SiCl_4$ (0.165 g, 0.97 mmol), thf (10 mL). In contrast to previous syntheses, the initial precipitate was filtered off, the solvent was removed from the filtrate under reduced pressure, and the residue was then dissolved in chloroform (2 mL), whereupon crystals of **3g**·$(CHCl_3)_3$ formed within some hours. Upon drying the crystalline product lost some of its chloroform content to yield a compound of the composition **3g**·$(CHCl_3)$. Yield: 0.10 g (0.12 mmol, 12%). $C_{45}H_{37}Cl_3N_4O_6Si$ (864.24): calcd. C 62.54, H 4.32, N 6.48; found C 62.33, H 4.51, N 6.56. A single crystal of dimensions 0.29 × 0.08 × 0.03 mm was chosen for data collection from the crude crystalline product in chloroform. Selected crystallographic data for **3g**·$(CHCl_3)_3$: $C_{47}H_{39}Cl_9N_4O_6Si$, M_r = 1102.96, T = 90(2) K, monoclinic, space group $P2_1/c$, a = 24.7743(8) Å, b = 8.9571(2) Å, c = 22.8209(8) Å, β = 101.522(1)°, V = 4962.0(3) Å^3, Z = 4, $\rho_{calcd.}$ = 1.476 Mg m^{-3}, μ(Mo–K_α) = 0.584 mm^{-1}, $F(000)$ = 2256, $2\theta_{max}$ = 52.0°, 39100 collected reflections, 9738 unique reflections (R_{int} = 0.0694), 647 parameters, S = 0.949, R_1 = 0.0430 [$I > 2\sigma(I)$], wR_2(all data) = 0.0986, max./min. residual electron density +0.318/–0.388 e Å^{-3}.

4a and 6a: To a solution of ligand **2a** (0.700 g, 1.74 mmol) and triethylamine (0.500 g, 4.94 mmol) dissolved in thf (10 mL) at –10 °C was added phenyltrichlorosilane (0.370 g, 1.75 mmol), whereupon triethylamine hydrochloride precipitated. This precipitate was filtered off and from the filtrate the solvent was removed under reduced pressure. The crude product was dissolved in chloroform and a ^{29}Si NMR spectrum was recorded: δ = –104.3 ppm (**4a**) and δ = –172.5 ppm (**6a**), ratio 9:1. Whereas our attempts to isolate **4a** failed so far, crystals of **6a**·$(CHCl_3)_5$ formed when the crude solution in chloroform (5 mL) and diethyl ether (5 mL) was placed in a freezer (–22 °C) for 3 d. These crystals were separated by decantation and briefly dried in a vacuum. Yield of (the composition found by elemental microanalysis corresponds to) **6a**·$(CHCl_3)_{2.8}$: 0.14 g (0.30 mmol, 15%). $C_{58.8}H_{57.8}Cl_{9.4}N_4O_6Si$ (1277.87): calcd. C 55.27, H 4.56, N 4.38; found C 55.41, H 4.62, N 4.40. From the crystalline product obtained in the freezer a single crystal of **6a**·$(CHCl_3)_5$ of dimensions 0.70 × 0.60 × 0.30 mm was chosen for data collection. Selected crystallographic data for **6a**·$(CHCl_3)_5$: $C_{61}H_{60}Cl_{16}N_4O_6Si$, M_r = 1540.42, T = 200(2) K, monoclinic, space group $P2_1/c$, a = 22.3508(6) Å, b = 18.8348(5) Å, c = 17.7535(5) Å, β = 101.932(1)°, V = 7312.3(3) Å^3, Z = 4, $\rho_{calcd.}$ = 1.399 Mg m^{-3}, μ(Mo–K_α) = 0.666 mm^{-1}, $F(000)$ = 3152, $2\theta_{max}$ = 50.0°, 57101 collected reflections, 12675 unique reflections (R_{int} = 0.0335), 939 parameters, S = 1.121, R_1 = 0.0596 [$I > 2\sigma(I)$], wR_2(all data) = 0.1931, max./min. residual electron density +0.692/–0.548 e Å^{-3}.

4b: The same procedure applies as described for **4a**. Starting materials used: **2b** (0.700 g, 1.66 mmol), triethylamine (0.500 g, 4.94 mmol), $PhSiCl_3$ (0.350 g, 1.66 mmol), thf (10 mL). In analogy to **4a** the crude product was dissolved in chloroform and a ^{29}Si NMR spectrum was recorded (δ = –103.3 ppm). So far, our attempts to isolate **4b** as a crystalline solid in reasonable amounts failed. However, from a residual drop of a chloroform solution of **4b** in a Schlenk tube a crystal of **4b**·$(CHCl_3)$ of dimensions 0.45 × 0.37 × 0.08 mm had formed and was chosen for data collection. Selected crystallographic data for **4b**·$(CHCl_3)$: $C_{34}H_{26}Cl_4N_2O_3Si$, M_r = 680.46, T = 150(2) K, triclinic, space group $P\bar{1}$, a = 9.5302(4) Å, b = 12.9429(7) Å, c = 13.2766(7) Å, α = 99.397(2)°, β = 94.445(2)°, γ = 90.515(2)°, V = 1610.42(14) Å^3, Z = 2, $\rho_{calcd.}$ = 1.403 Mg m^{-3}, μ(Mo–K_α) = 0.443 mm^{-1}, $F(000)$ = 700, $2\theta_{max}$ = 52.0°, 21617 collected reflections, 6201 unique reflections (R_{int} = 0.0341), 422 parameters, S = 1.100, R_1 = 0.0472 [$I > 2\sigma(I)$], wR_2(all data) = 0.1452, max./min. residual electron density +0.456/–0.572 e Å^{-3}.

5b: Starting from **2b** (1.00 g, 2.37 mmol), triethylamine (0.700 g, 6.92 mmol), and $PhSiCl_3$ (0.500 g, 2.37 mmol) the synthesis of **4b** was repeated. After removal of the triethylamine hydrochloride by filtration ZnF_2 (0.25 g, 2.4 mmol) was added to the filtrate, and the mixture was stirred at ambient temperature for 80 h. The solvent was then removed under reduced pressure, and the residue was dissolved in chloroform (5 mL) and filtered. Upon storage at room temperature for 1 week crystals of **5b**·($CHCl_3$) had formed, which were separated by decantation and briefly dried in a vacuum. Yield: 0.71 g (1.07 mmol, 45%). $C_{34}H_{26}Cl_3FN_2O_3Si$ (664.01): calcd. C 61.50, H 3.95, N 4.22; found C 59.20, H 4.13, N 4.29. ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ = 3.84 (s, 3 H, OCH_3), 5.44 (d, J = 8.0 Hz, 1 H), 6.28 (t, J = 7.2 Hz, 1 H), 6.42 (d, J = 8.8 Hz, 1 H), 6.8–6.9 (m, 4 H), 7.05 (d, J = 7.6 Hz, 1 H), 7.15–7.25 (m, 7 H), 7.34 (d, J = 2 H, 6.8 Hz), 7.45–7.50 (m, 3 H), 8.36, 8.37 (2s, 2 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 55.9 (OCH_3), 105.1, 110.0, 112.4, 123.3, 124.1, 126.4, 126.6, 127.0, 127.2, 128.0, 128.3, 128.7, 128.9, 129.3, 131.2, 133.4, 134.6, 134.9, 135.8, 138.6, 139.1, 141.1, 153.8, 159.8, 166.4, 173.9 ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 25 °C): δ = –113.8 (t, $^{1}J_{Si,F}$ = 220 Hz) ppm. A single crystal of dimensions 0.55 × 0.45 × 0.18 mm was chosen for data collection. Selected crystallographic data for **5b**·($CHCl_3$): $C_{34}H_{26}Cl_3FN_2O_3Si$, M_r = 664.01, T = 130(2) K, triclinic, space group $P\bar{1}$, a = 9.3768(3) Å, b = 12.9632(4) Å, c = 13.0210(5) Å, α = 97.397(1)°, β = 92.310(1)°, γ = 91.869(1)°, V = 1567.16(9) $Å^3$, Z = 2, $\rho_{calcd.}$ = 1.407 $Mg\,m^{-3}$, $\mu(Mo–K_\alpha)$ = 0.375 mm^{-1}, $F(000)$ = 684, $2\theta_{max}$ = 64.0°, 30198 collected reflections, 10714 unique reflections (R_{int} = 0.0204), 431 parameters, S = 1.117, R_1 = 0.0473 [$I > 2\sigma(I)$], wR_2(all data) = 0.1564, max./min. residual electron density +0.633/–0.676 $e\,Å^{-3}$.

7a: To a solution of **2a** (0.700 g, 1.74 mmol) and triethylamine (0.530 g, 5.25 mmol) in thf (10 mL) at 0 °C was added diphenyldichlorosilane (0.440 g, 1.74 mmol) dropwise. The reaction mixture was then stirred at 40 °C for 1 h, cooled to room temperature, and triethylamine hydrochloride was removed by filtration. From the filtrate the solvent was removed under reduced pressure. The yellow residue was dissolved in chloroform (3 mL) and diethyl ether (2 mL) and stored at 8 °C overnight, whereupon crystals of **7a** had formed, which were separated from the solution by decantation, washed with diethyl ether (1 mL) and dried in a vacuum. Yield: 0.29 g (0.50 mmol, 29%). M.p. 207 °C. $C_{37}H_{34}N_2O_3Si$ (582.75): calcd. C 76.25, H 4.81, N 5.88; found C 75.90, H 4.78, N 5.60. ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ = 1.05 [s, 9 H, $C(CH_3)_3$], 3.61 (s, 3 H, OCH_3), 6.06 (s, 1 H), 6.2–7.8 (mm, 21 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): δ = 28.2 [$C(CH_3)_3$], 38.8 [$C(CH_3)_3$], 55.2 (OCH_3), 106.4, 108.2, 118.1, 118.7, 123.0, 124.1, 127.6, 127.9, 129.5, 130.0, 130.9, 132.7, 134.6, 135.0, 139.2, 140.7, 142.7, 151.8, 160.5, 161.4, 163.4, 176.4 ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 25 °C): δ = –44.1 ppm. A single crystal of dimensions 0.18 × 0.14 × 0.10 mm was chosen for data collection. Selected crystallographic data for **7a**: $C_{37}H_{34}N_2O_3Si$, M_r = 582.75, T = 90(2) K, monoclinic, space group $P2_1/c$, a = 9.426(1), b = 17.749(2), c = 18.476(2) Å, β = 96.864(4)°, V = 3068.9(6) $Å^3$, Z = 4, $\rho_{calcd.}$ = 1.261 $Mg\,m^{-3}$, $\mu(Mo–K_\alpha)$ = 0.116 mm^{-1}, $F(000)$ = 1232, $2\theta_{max}$ = 50.0°, 18061 collected reflections, 5398 unique reflections (R_{int} = 0.0629), 392 parameters, S = 0.982, R_1 = 0.0447 [$I > 2\sigma(I)$], wR_2(all data) = 0.1118, max./min. residual electron density +0.420/–0.404 $e\,Å^{-3}$.

7b: The same procedure applies as described for **7a**. Starting materials used: **2b** (0.700 g, 1.66 mmol), triethylamine (0.530 g, 5.25 mmol), diphenyldichlorosilane (0.420 g, 1.66 mmol), thf (10 mL). ^{29}Si NMR spectroscopy of the crude product solution revealed two predominant signals (δ = –36.2 and –25.9 ppm) in a ratio of 1:3, which can be attributed to **7b** and its benzimidazoline isomer, respectively. In addition to the ^{29}Si shift of δ = –25.9 ppm, the presence of the latter compound was indicated by a ^{13}C resonance signal at δ = 90.0 ppm. Upon storing a solution of the crude product in chloroform (1 mL) and diethyl ether (2 mL) at 8 °C for 1 week a crystalline precipitate formed (Yield: 0.35 g), which upon dissolution in $CDCl_3$ exhibited the same ^{29}Si NMR behavior as the crude product. From the solid product a tiny single crystal of dimensions 0.16 × 0.04 × 0.03 mm was chosen for data collection. Selected crystallographic data for **7b**: $C_{39}H_{30}N_2O_3Si$, M_r = 602.74, T = 90(2) K, orthorhombic, space group $Pna2_1$, a = 18.518(5) Å, b = 19.693(6) Å, c = 8.389(3) Å, V = 3059.4(16) $Å^3$, Z = 4, $\rho_{calcd.}$ = 1.309 $Mg\,m^{-3}$, $\mu(Mo–K_\alpha)$ = 0.119 mm^{-1}, $F(000)$ = 1264, $2\theta_{max}$ = 50.1°, 8878 collected reflections, 4490 unique reflections (R_{int} = 0.0780), 407 parameters, S = 0.915, R_1 = 0.0578 [$I > 2\sigma(I)$], wR_2(all data) = 0.1059, max./min. residual electron density +0.250/–0.276 $e\,Å^{-3}$.

CCDC-710471 (for **2a**), -710472 (for **2b**), -710475 (for **2d**), -710467 (for **2e**), -710469 [for **3a**·$(CHCl_3)_3$], -710470 [for **3c**·$(CHCl_3)_2$], -710466 [for **3d**·$(CHCl_3)_4$], -710468 [for **3f**·($CHCl_3$)], -710478 [for **3g**·$(CHCl_3)_3$], -710476 [for **6a**·$(CHCl_3)_5$], -710477 [for **4b**·($CHCl_3$)], -710479 [for **5b**·($CHCl_3$)], -710473 (for **7a**), -710474 (for **7b**) 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 (see footnote on the first page of this article): ORTEP diagrams of the molecular structures of **2a**, **2b**, **3a**, **3d**, **3f**, **3g**, and **4b** with selected bond lengths and angles.

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