DOI: 10.1002/zaac.201300523

Neutral Pentacoordinate Silicon(IV) Complexes with a Tridentate Dianionic O,N,O or N,N,O Ligand, an Anionic PhX Ligand (X = O, S, Se), and a Phenyl Group: Synthesis and Structural Characterization in the Solid State and in Solution

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Dedicated to Professor Werner Uhl on the Occasion of His 60th Birthday

Keywords: Chalcogens; Coordination chemistry; Pentacoordination; Silicon; Tridentate ligands

Abstract. A series of neutral pentacoordinate silicon(IV) complexes with a SiO_3NC , SiO_2SNC , SiO_2SeNC , SiO_2N_2C , $SiOSN_2C$, or $SiOSeN_2C$ skeleton was synthesized and structurally characterized by multinuclear NMR spectroscopy in the solid state and in solution and by single-crystal X-ray diffraction. The compounds studied contain a

Introduction

Recently, we have reported on the synthesis and characterization of the neutral pentacoordinate silicon(IV) complexes 1a-g.^[1,2] These compounds contain a tridentate dianionic *S*,*N*,*O* ligand, an (pseudo)halogeno ligand, and a phenyl group. Formal replacement of the S,N,O ligand by an analogous O,N,O or N,N,O ligand (formal S/O or S/NMe exchange) leads to compounds 2a-g and 3a-g.^[3,4] All these pentacoordinate silicon(IV) complexes contain a distorted trigonal-bipyramidal silicon coordination polyhedron, with the imino-nitrogen atom of the tridentate ligand and the (pseudo)halogeno ligand in the two axial positions.^[5] Some of the respective S/O/NMe analogues of the series 1-3 were found to differ significantly in their chemical properties; i.e., replacement of the soft sulfur ligand atom by a hard oxygen or nitrogen ligand atom strongly affects the bonding characteristics at the silicon atom, which could also be demonstrated by quantum-chemical studies.^[4]

In context with our investigations on compounds **1a–g**, we have also synthesized and structurally characterized the related neutral pentacoordinate silicon(IV) complexes **4b–d**. Attempts to prepare the oxygen analogue **4a** failed; instead, the isomeric tetracoordinate species **4a**' was obtained.^[6] Compounds **4b–d** contain a distorted trigonal-bipyramidal silicon coordination

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97074 Würzburg, Germany tridentate dianionic O,N,O or N,N,O ligand, an anionic PhX ligand (X = O, S, Se), and a phenyl group. The structures, NMR spectroscopic parameters, and chemical properties of these silicon(IV) complexes were compared with those of related compounds that contain a tridentate dianionic *S*,*N*,*O* ligand instead of the *O*,*N*,*O* or *N*,*N*,*O* ligand.

polyhedron; however, unlike **1a–g** the oxygen and sulfur atoms of the tridentate *S,N,O* ligand occupy the two axial positions. In light of the different chemical properties observed for some of the S/O/NMe analogues of series **1–3**, we have now been interested in the synthesis and characterization of the corresponding O and NMe analogues of **4a–d**, compounds **5a–d** and **6a–d**, with a special focus on the comparison of the respective S/O/NMe analogues (comparison between series **4–6**). These studies were performed as part of our systematic investigations on higher-coordinate silicon(IV) complexes.^[7–9] We report herein on the synthesis of compounds **5a–c** and **6a–c** and their structural characterization in the solid state (crystal structure analyses and NMR spectroscopic studies) and in solution (NMR spectroscopic studies) and the failed synthesis of **5d** and **6d**.







Scheme 2. Synthesis of compounds 5b, 5c, 6b, and 6c.

Results and Discussion

Compounds **5a** and **6a** were synthesized according to Scheme 1 by treatment of dichloro(phenoxy)phenylsilane (**7**) with one molar equivalent of the O,N,O pre-ligand **8**^[10] or the N,N,O pre-ligand **9** and two molar equivalents of triethylamine. The syntheses were performed in tetrahydrofuran, and the products were isolated after crystallization from acetonitrile (yields: **5a** 65% and **6a** 68%).



Scheme 1. Synthesis of compounds 5a and 6a.

Compounds **5b**, **5c**, **6b**, and **6c** were synthesized according to Scheme 2 by reaction of the respective chlorosilicon(IV) complexes **2b** and **3b** with one molar equivalent of benzenethiol or benzeneselenol and one molar equivalent of triethylamine. The syntheses were performed in tetrahydrofuran, and the products were isolated after crystallization from acetonitrile (yields: **5b**·CH₃CN 54%, **5c**·CH₃CN 47%, **6b** 72%, and **6c** 63%).

All attempts to prepare the tellurium analogues **5d** and **6d** analogously to the synthesis of **4d** (treatment of **2b** or **3b** with PhTeSiMe₃) failed so far. Also, treatment of **2b** or **3b** with PhTeNa did not yield the target compounds **5d** and **6d**. The reasons for this are unclear.

Compound 7 was synthesized according to Scheme 3 by treatment of trichloro(phenyl)silane with one molar equivalent each of phenol and triethylamine in tetrahydrofuran (58%)

yield). Compound **9** was obtained according to Scheme 3 by reaction of *N*-methylbenzene-1,2-diamine with acetylacetone (excess) in ethanol (73 % yield).



Scheme 3. Synthesis of compounds 7 and 9.

Compounds **5a**, **5b**·CH₃CN, **5c**·CH₃CN, **6a–c**, and **9** were isolated as crystalline solids, whereas **7** was obtained as a liquid. The identities of all these compounds were established by elemental analyses (C, H, N, S) and multinuclear NMR spectroscopic studies in the solid state (15 N, 29 Si; except **7**) and in solution (1 H, 13 C, 29 Si, 77 Se). In addition, compounds **5a**, **5b**·CH₃CN, **5c**·CH₃CN, and **6a–c** were studied by crystal structure analyses.

Compounds **5a**, **5b**·CH₃CN, **5c**·CH₃CN, and **6a–c** were structurally characterized by single-crystal X-ray diffraction. The crystal data and experimental parameters used for the crystal structure analyses are given in Table 1. The molecular structures of **5a–c** and **6a–c** are shown in Figure 1, Figure 2, Figure 3, Figure 4, Figure 5, and Figure 6, respectively. Selected bond lengths and angles are given in the respective captions.

The silicon coordination polyhedra of **5b** and **5c** (O,N,O) as well as **6b** and **6c** (N,N,O) are strongly distorted trigonal bipyramids (Table 2), with the phenolato-oxygen or amidonitrogen atom and the enolato-oxygen atom in the two axial

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Table 1. Crystallographic data for compounds 5a, 5b·CH₃CN, 5c·CH₃CN, and 6a–c.

	5a	5b·CH ₃ CN	5c·CH ₃ CN	6a	6b	6c
Empirical formula	C ₂₃ H ₂₁ NO ₃ Si	C ₂₅ H ₂₄ N ₂ O ₂ SSi	C ₂₅ H ₂₄ N ₂ O ₂ SeSi	C ₂₄ H ₂₄ N ₂ O ₂ Si	C ₂₄ H ₂₄ N ₂ OSSi	C ₂₄ H ₂₄ N ₂ OSeSi
M _r	387.50	444.61	491.51	400.54	416.60	463.50
T/K	173(2)	100(2)	193(2)	173(2)	173(2)	173(2)
λ (Mo- K_a) /Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group (no.)	$P\overline{1}(2)$	$P2_1/c$ (14)	$P2_1/c$ (14)	$P\bar{1}$ (2)	$P2_1/c$ (14)	$P2_1/c$ (14)
a /Å	10.297(3)	10.8288(3)	11.0467(13)	7.7687(12)	13.109(2)	13.195(3)
b /Å	10.3614(19)	22.4627(5)	22.488(4)	11.560(2)	10.9701(13)	11.0155(15)
<i>c</i> /Å	10.525(2)	9.7599(2)	9.8776(11)	23.392(4)	14.690(2)	14.723(3)
$a /^{\circ}$	106.55(2)	90	90	100.18(2)	90	90
β /°	97.37(3)	107.5170(10)	107.501(13)	91.50(2)	91.05(2)	90.36(2)
γ /°	111.39(3)	90	90	95.28(2)	90	90
$V/Å^3$	967.8(4)	2263.95(9)	2340.2(5)	2056.9(6)	2112.1(6)	2139.8(7)
Ζ	2	4	4	4	4	4
$\rho_{\rm calcd}$ /g·cm ⁻³	1.330	1.304	1.395	1.293	1.310	1.439
μ / mm^{-1}	0.146	0.221	1.680	0.137	0.228	1.829
F(000)	408	936	1008	848	880	952
Crystal dimensions /mm	$0.25 \times 0.2 \times 0.1$	$0.25 \times 0.15 \times 0.1$	$0.3 \times 0.3 \times 0.2$	$0.4 \times 0.4 \times 0.2$	$0.4 \times 0.2 \times 0.2$	$0.5 \times 0.4 \times 0.3$
2 range /°	4.52-52.04	3.62-66.62	4.26-55.98	4.58-56.56	4.64-58.26	5.54-58.32
Index ranges	$-12 \le h \le 12$,	$-16 \le h \le 16$,	$-14 \le h \le 14$,	$-10 \le h \le 10,$	$-17 \le h \le 17$,	$-18 \le h \le 18,$
e	$-12 \le k \le 12,$	$-34 \le k \le 34,$	$-29 \le k \le 29,$	$-14 \le k \le 15,$	$-15 \le k \le 14$,	$-14 \le k \le 14,$
	$-12 \le l \le 12$	$-15 \le l \le 14$	$-12 \le l \le 12$	$-31 \le l \le 31$	$-20 \le l \le 19$	$-20 \le l \le 20$
Reflns collected	7928	142768	30384	20076	29573	23039
Independent reflns	3568	8680	5552	9452	5608	5683
R _{int}	0.0851	0.0533	0.0884	0.0510	0.0399	0.0596
Restraints	0	0	0	84	0	0
Parameters	255	283	283	529	265	265
S ^{a)}	0.848	1.046	0.947	0.877	1.066	0.929
Weight parameters <i>a/b</i> ^{b)}	0.0700/0.0000	0.0518/0.8253	0.0426/0.0000	0.0485/0.0000	0.0552/0.5987	0.0545/0.0000
$R_1 \stackrel{c)}{=} [I > 2\sigma(I)]$	0.0515	0.0340	0.0342	0.0404	0.0380	0.0347
$wR_2^{(d)}$ (all data)	0.1363	0.0988	0.0822	0.1033	0.1031	0.0869
Max./min. residual elec- tron density /e·Å ^{-3}	+0.327/-0.428	+0.600/-0.437	+0.542/-0.460	+0.350/-0.478	+0.370/-0.311	+0.608/-0.684

 $\overline{a) S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{0.5}; n = \text{number of reflections}; p = \text{number of parameters. b}) w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP; P = [\max(F_o^2, 0) + 2F_c^2] / 3. c) R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|. d) wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{0.5}.$





Figure 1. Molecular structure of **5a** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths /Å and angles /°: Si–O1 1.680(2), Si–O2 1.679(2), Si–O3 1.687(2), Si–N 2.060(3), Si–C1 1.858(3); O1–Si–O2 132.59(13), O1–Si–O3 91.58(10), O1–Si–N 87.77(10), O1–Si–C1 111.85(13), O2–Si–O3 87.43(11), O2–Si–N 81.72(10), O2–Si–C1 114.63(13), O3–Si–N 164.57(12), O3–Si–C1 102.32(12), N–Si–C1 92.20(12).

Figure 2. Molecular structure of **5b** in the crystal of **5b**·CH₃CN (probability level of displacement ellipsoids 50%). Selected bond lengths /Å and angles /°: Si–S 2.1694(3), Si–O1 1.7675(6), Si–O2 1.7668(6), Si–N 1.8698(7), Si–C1 1.8838(8); S–Si–O1 93.71(2), S–Si–O2 83.29(2), S–Si–N 125.62(2), S–Si–C1 121.21(3), O1–Si–O2 170.13(3), O1–Si–N 89.12(3), O1–Si–C1 92.96(3), O2–Si–N 85.06(3), O2–Si–C1 96.64(3), N–Si–C1 112.82(3).



Figure 3. Molecular structure of **5c** in the crystal of **5c**·CH₃CN (probability level of displacement ellipsoids 50%). Selected bond lengths /Å and angles /°: Si–Se 2.3097(7), Si–O1 1.7718(15), Si–O2 1.7699(15), Si–N 1.8738(17), Si–C1 1.893(2); Se–Si–O1 93.36(5), Se–Si–O2 82.79(5), Se–Si–N 127.20(5), Se–Si–C1 120.44(6), O1–Si–O2 169.22(7), O1–Si–N 89.44(7), O1–Si–C1 93.60(8), O2–Si–N 84.96(7), O2–Si–C1 97.03(8), N–Si–C1 111.95(8).

positions. The imino-nitrogen atom, the PhX ligand (X = S,Se), and the phenyl group occupy the three equatorial positions. An analogous coordination mode was also observed for the corresponding sulfur analogues 4b and 4c (S,N,O).^[6] Quite surprisingly, a totally different structure was observed for compounds 5a(O,N,O) and 6a(N,N,O) with their PhO ligand. The silicon coordination polyhedra of these two compounds are also strongly distorted trigonal bipyramids (Table 2); however, in these structures the two axial sites are occupied by the imino-nitrogen atom of the tridentate O,N,O or N,N,O ligand and the monodentate PhO ligand. I.e., replacement of the PhS or PhSe ligand in 5b, 5c, 6b, and 6c (equatorial position) by a PhO ligand (\rightarrow 5a, 6a; axial position) changes the structure. This phenomenon can be explained by the higher group electronegativity of the PhO ligand compared to the PhS and PhSe ligands. This correlates with the structures of series 1-3, where the strongly electron-withdrawing (pseudo)halogeno ligands also occupy an axial site.^[1-4] The Berry distortions (transition trigonal bipyramid \rightarrow square pyramid)^[11] of **5a–c** (*O*,*N*,*O*; 22.4–41.7%) are larger than those of the respective analogues 6a-c (N,N,O; 16.2-24.2%), and the Berry distortions of 4b and 4c (S,N,O) amount to 24.7-29.3%; i.e., the S/O/NMe exchange affects the degree of distortion of the trigonal-bipyramidal silicon coordination polyhedron.

Contrary to the different degrees of distortion observed for the respective S/O/NMe analogues (Table 2), replacement of the tridentate *S*,*N*,*O* ligand of **4b** and **4c** by the analogous $O,N,O \rightarrow 5b, 5c$ or *N*,*N*,*O* ligand $(\rightarrow 6b, 6c)$ only slightly affects the Si–SPh and Si–SePh bond lengths (Table 3). In the case of the *S*,*N*,*O* and *N*,*N*,*O* ligand, these bond lengths are almost identical, whereas for the *O*,*N*,*O* ligand a small shortening of the Si–SPh and Si–SePh bond distances was observed.



Figure 4. Molecular structures of the two crystallographically independent molecules of **6a** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths /Å and angles /° of molecule A (top): Si1–O1 1.6999(15), Si1–O2 1.7181(14), Si1–N1 2.0637(16), Si1–N2 1.7567(19), Si1–C1 1.8844(19); O1–Si1–O2 90.90(7), O1–Si1–N1 87.77(7), O1–Si1–N2 127.36(8), O1–Si1–C1 111.50(9), O2–Si1–N1 175.48(7), O2–Si1–N2 95.94(8), O2–Si1–C1 95.01(7), N1–Si1–N2 81.48(7), N1–Si1–C1 89.50(7), N2–Si1–C1 119.70(9). Selected bond lengths /Å and angles /° of molecule B (bottom): Si2–O21 1.6971(16), Si2–O22 1.7194(14), Si2–N21 2.0456(17), Si2–N22 1.7724(17), Si2–C31 1.877(2); O21–Si2–O22 90.53(7), O21–Si2–N21 87.84(7), O21–Si2–N22 127.29(8), O21–Si2–C31 114.48(8), O22–Si2–N21 171.91(7), O22–Si2–N22 93.42(8), O22–Si2–C31 95.20(8), N21–Si2–N22 81.32(7), N21–Si2–C31 92.68(8), N22–Si2–C31 117.42(9).

As can be seen from Table 4, the Si–N(imino) and Si–C bond lengths of the respective S/O/NMe analogues 4b/5b/6b and 4c/5c/6c are very similar, whereas the Si–O(enolato) bond distances of 6b/6c are slightly longer than those of 4b/4c and 5b/5c. However, the Si–O(enolato) and Si–N(imino) bond lengths of 5a/6a (axial PhO ligand) differ significantly from those of 4b/5b/6b and 4c/5c/6c (equatorial PhX ligand; X = S,



Figure 5. Molecular structure of **6b** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths /Å and angles /°: Si–S 2.1860(6), Si–O 1.8470(10), Si–N1 1.8610(12), Si–N2 1.8115(12), Si–C1 1.8867(14); S–Si–O 79.23(4), S–Si–N1 122.42(4), S–Si–N2 100.76(4), S–Si–C1 117.95(5), O–Si–N1 87.61(5), O–Si–N2 170.53(5), O–Si–C1 90.86(5), N1–Si–N2 84.43(5), N1–Si–C1 118.04(6), N2–Si–C1 97.40(6).



Figure 6. Molecular structure of **6c** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths /Å and angles /°: Si–Se 2.3313(7), Si–O 1.8451(14), Si–N1 1.8652(18), Si–N2 1.8085(17), Si–C1 1.878(2); Se–Si–O 78.55(5), Se–Si–N1 123.44(6), Se–Si–N2 100.65(6), Se–Si–C1 117.15(6), O–Si–N1 87.56(7), O–Si–N2 169.76(8), O–Si–C1 91.02(8), N1–Si–N2 84.41(8), N1–Si–C1 117.66(8), N2–Si–C1 98.32(8).

Se). In the case of **5a/6a**, a significant shortening of the Si–O(enolato) and elongation of the Si–N(imino) bonds compared to **4b/5b/6b** and **4c/5c/6c** was observed. This can be explained by the different coordination modes of the respective tridentate

Table 2. Berry distortions /% and axial bond angles /° of compounds 4b•CH₃CN, 4c•CH₃CN, 5a, 5b•CH₃CN, 5c•CH₃CN, and 6a–c.

Compound (ligand)	Berry distortion	Axial bond angle
4b (S,N,O)	29.3 ^{a)}	167.90(4) a)
4c(S,N,O)	24.7 ^{a)}	168.68(3) ^{a)}
5a (O,N,O)	41.7	164.57(12)
5b (<i>O</i> , <i>N</i> , <i>O</i>)	22.4	170.13(3)
5c (O,N,O)	27.0	169.22(7)
6a (N,N,O)	20.4, 24.2	175.48(7), 171.91(7)
6b (N,N,O)	16.2	170.53(5)
6c (N,N,O)	18.8	169.76(8)

a) Data taken from Ref. [6].

Table 3. Comparison of the Si–X (X = OPh, SPh, SePh) bond lengths /Å of compounds 4b·CH₃CN, 4c·CH₃CN, 5a, 5b·CH₃CN, 5c·CH₃CN, and 6a-c.

Compound (ligand)	Si-OPh	Si–SPh	Si-SePh
4b , 4c (<i>S</i> , <i>N</i> , <i>O</i>)		2.1881(6) a)	2.3201(3) a)
5a–c (<i>O</i> , <i>N</i> , <i>O</i>)	1.687(2)	2.1694(3)	2.3097(7)
6a–c (<i>N</i> , <i>N</i> , <i>O</i>)	1.7181(14),	2.1860(6)	2.3313(7)
	1.7194(14)		

a) Data taken from Ref. [6].

ligands. The Si–C bond lengths of **4b/4c**, **5a/5b/5c**, and **6a/6b/ 6c** are very similar.

Compounds **5a**, **5b**·CH₃CN, **5c**·CH₃CN, and **6a–c** were characterized by solid-state ¹⁵N, ²⁹Si, and ⁷⁷Se (**5c**·CH₃CN and **6c**) NMR spectroscopy (see Table 5 and Experimental Section). The NMR spectroscopic data obtained are in accordance with the experimentally established crystal structures. The isotropic ²⁹Si chemical shifts clearly indicate the presence of pentacoordinate silicon atoms.

As shown by ¹H, ¹³C, and ²⁹Si NMR spectroscopic studies, compounds **5a–c** and **6a–c** also exist in solution (solvent, CD_2Cl_2 ; see Experimental Section). The stereochemistry of these compounds in the solid state and in solution is very similar. As shown by the X-ray diffraction studies, two different types of structures exist in the crystal, depending on the type of ligands (structures **A** and **B**; Figure 7). The isotropic ²⁹Si chemical shifts of **5a** (PhO, *O*,*N*,*O*) and **6a** (PhO, *N*,*N*,*O*) in the solid state and in solution are very similar (Table 5), indicating the presence of structure **A** both in the solid state and in solution. The isotropic ²⁹Si chemical shifts in solution for **5b** (PhS, *O*,*N*,*O*), **6b** (PhS, *N*,*N*,*O*), **5c** (PhSe, *O*,*N*,*O*), and **6c** (PhSe, *N*,*N*,*O*) (Table 5) indicate that these compounds exist



Figure 7. Structures A and B discussed for compounds 4b, 4c, 5a-c, and 6a-c.



Table 4. Comparison of the Si–O(enolato), Si–N(imino), and Si–C bond lengths /Å of 4b·CH₃CN, 4c·CH₃CN, 5a, 5b·CH₃CN, 5c·CH₃CN, and 6a–c.

Compound (ligand)	Si-O(enolato)	Si–N(imino)	Si–C
4b (<i>S</i> , <i>N</i> , <i>O</i> , SPh)	1.7676(10) ^{a)}	1.8592(12) ^{a)}	1.8782(16) ^{a)}
4c (<i>S</i> , <i>N</i> , <i>O</i> , SePh)	$1.7644(8)^{(a)}$	1.8545(10) ^{a)}	1.8757(12) ^{a)}
5a (O,N,O, OPh)	1.680(2)	2.060(3)	1.858(3)
5b (<i>O</i> , <i>N</i> , <i>O</i> , SPh)	1.7675(6)	1.8698(7)	1.8838(8)
5c (O,N,O, SePh)	1.7718(15)	1.8738(17)	1.893(2)
6a (N.N.O, OPh)	1.6999(15), 1.6971(16) ^{b)}	2.0637(16), 2.0456(17) ^{b)}	1.8844(19), 1.877(2) ^{b)}
6b (<i>N</i> , <i>N</i> , <i>O</i> , SPh)	1.8470(10)	1.8610(12)	1.8867(14)
6c (N,N,O, SePh)	1.8451(14)	1.8652(18)	1.878(2)

a) Data taken from Ref. [6]. b) Data for two crystallographically independent molecules.

Table 5. Isotropic ¹⁵N (imino-nitrogen atom) and ²⁹Si chemical shifts of compounds **4b**·CH₃CN, **4c**·CH₃CN, **5a**, **5b**·CH₃CN, **5c**·CH₃CN, and **6a–c** in the solid state ($T = 22 \degree$ C) and ²⁹Si chemical shifts of **4b**, **4c**, **5a–c**, and **6a–c** in solution (CD₂Cl₂, $T = 23 \degree$ C).

Compound (ligand)	δ ¹⁵ N /ppm	δ^{29} Si (solid state) /ppm	δ^{29} Si (solution) /ppm
4b (<i>S</i> , <i>N</i> , <i>O</i> , SPh)	-190.3 ^{a)}	-79.3 ^{a)}	-79.7 ^{a)}
4c (<i>S</i> , <i>N</i> , <i>O</i> , SePh)	-186.4 ^{a)}	-82.6 ^{a)}	-82.7 ^{a)}
5a (O,N,O, OPh)	-152.8	-109.5	-108.7
5b (<i>O</i> , <i>N</i> , <i>O</i> , SPh)	-204.5	-93.2	-88.3
5c (<i>O</i> , <i>N</i> , <i>O</i> , SePh)	-201.7	-93.9	-88.7
6a (N,N,O, OPh)	-156.5, -151.9 ^{b)}	-109.1, -106.1 ^{b)}	-107.5
6b (<i>N</i> , <i>N</i> , <i>O</i> , SPh)	-205.8	-78.9	-84.4
6c (N,N,O, SePh)	-203.3	-78.5	-84.2

a) Data taken from Ref. [6]. b) Data for two crystallographically independent molecules.

as pentacoordinate silicon(IV) complexes in solution as well; however, the shifts in the solid state and in solution differ by about 5 ppm. The magnitude of this shift difference is not unusual and was already reported in one of our earlier publications and discussed extensively with support of computational studies.^[7e] In this context it is also interesting to note that the solid-state ²⁹Si chemical shifts of the two crystallographically independent molecules of **6a**, which have very similar structures, differ by 3.0 ppm (Table 5, Figure 4).

As shown by the NMR spectroscopic studies in solution, there is another striking difference in the properties of the S/ O/NMe analogues 4a/5a/6a (PhO), 4b/5b/6b (PhS), and 4c/ 5c/6c (PhSe). As already reported earlier, the pentacoordinate compound 4a (S,N,O, PhO) does not exist in the solid state and in solution; instead, the tetracoordinate isomer 4a' (existing as two diastereomers) was observed.^[6] In addition, for the analogues 4b (S,N,O, PhS) and 4c (S,N,O, PhSe) a dynamic equilibrium between the pentacoordinate complexes and the corresponding tetracoordinate species 4b' and 4c' was detected in solution (solvent, CD₂Cl₂; Scheme 4).^[6] Interestingly, such kind of equilibrium was not observed for the corresponding analogues with an O,N,O or N,N,O ligand, compounds 5b, 5c, **6b**, and **6c**. The same holds true for compounds **5a** (O,N,O), PhO) and **6a** (N,N,O, PhO), the sulfur analogue of which (**4a**) does not exist. These results can be explained in terms of a more favored cleavage of the Si-S bond of compounds 4a, 4b, and 4c (S.N,O) compared to the cleavage of the stronger Si-O bond of 5a, 5b, and 5c (O,N,O) and the stronger Si-N bond of 6a, 6b, and 6c (N,N,O).



Scheme 4. Dynamic equilibrium between the pentacoordinate complexes 4b (X = S) and 4c (X = Se) and the corresponding tetracoordinate species 4b' and 4c'.

Conclusions

With the synthesis of compounds 5a-c and 6a-c, a series of novel neutral pentacoordinate silicon(IV) complexes with an SiO_3NC , SiO_2SNC , SiO_2SeNC , SiO_2N_2C , $SiOSN_2C$, or $SiOSeN_2C$ skeleton was made available. These compounds contain a tridentate dianionic O,N,O (series 5) or N,N,O ligand (series 6), an anionic PhX ligand (X = O, S, Se), and a phenyl group. They represent analogues of the silicon(IV) complexes 4a-c that contain a tridentate dianionic S,N,O ligand, with a soft sulfur ligand atom instead of the hard oxygen (series 5) or nitrogen ligand atom (series 6). Comparison of the respective S/O/NMe analogues of the series 4-6 revealed insight into the impact of the soft sulfur ligand atom on (i) the chemical properties and (ii) the molecular structure.

The S/O/NMe analogues 4a/4b/4c with their PhO ligand show striking differences in their chemical properties. The pentacoordinate silicon(IV) complex 4a (*S*,*N*,*O*) does not exist in the solid state and in solution; instead, the tetracoordinate

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isomer 4a' was observed. In contrast, the pentacoordinate analogues 5a (O,N,O) and 6a (N,N,O) are stable both in the solid state and in solution and do not isomerize to the corresponding tetracoordinate species. The S/O/NMe analogues 4b/5b/6b (PhS) and 4c/5c/6c (PhSe) also exist in the solid state and in solution; however, the pentacoordinate silicon(IV) complexes 4b and 4c (S,N,O) isomerize in a dynamic equilibrium upon dissolution in organic solvents to give the tetracoordinate species 4b' and 4c'. In contrast, compounds 5b and 5c (O,N,O) as well as 6b and 6c (N,N,O) do not undergo such kind of isomerization, which can be explained by the stronger Si–O and Si–N bonds compared to the weaker Si–S bond.

Both the different tridentate S,N,O, O,N,O, and N,N,O ligands and the different PhX ligands (X = O, S, Se) control the structures of the pentacoordinate silicon(IV) complexes studied. As shown by the X-ray diffraction studies, the silicon coordination polyhedra of 5a and 6a are strongly distorted trigonal bipyramids with the PhO ligand and the imino-nitrogen atom of the tridentate O,N,O or N,N,O ligand in the two axial sites. Replacement of the strongly electron-withdrawing PhO ligand by the less electronegative PhS or PhSe ligands changes the structures completely. The S/O/NMe analogues 4b/5b/6b (PhS) and 4c/5c/6c (PhSe) have also distorted trigonal-bipyramidal structures; however, in these structures the PhS and PhSe ligands and the imino-nitrogen atom of the tridentate O.N.O or N.N.O ligand occupy equatorial positions, together with the phenyl group. Analysis of the Berry distortions of the S/O/NMe analogues 4b/5b/6b and 4c/5c/6c reveals that the different tridentate S,N,O, O,N,O, and N,N,O ligands affect the degree of distortion, which can be explained by the different nature of the Si-S, Si-O, and Si-N bond. The ²⁹Si NMR spectroscopic data of all the silicon(IV) complexes studied suggest that the structures of these compounds in the solid state and in solution are very similar.

Experimental Section

General Information: All syntheses were carried out under dry argon. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. The solution-state ¹H, ¹³C, ²⁹Si, and ⁷⁷Se NMR spectra were recorded at 23 °C with a Bruker Avance 500 NMR spectrometer (¹H, 500.1 MHz; ¹³C, 125.8 MHz; $^{29}\text{Si},~99.4~\text{MHz};~^{77}\text{Se},~95.4~\text{MHz}).$ CD_2Cl_2 served as the solvent. Chemical shifts (ppm) were determined relative to internal CHDCl₂ (¹H, δ = 5.32 ppm), internal CD₂Cl₂ (¹³C, δ = 53.8 ppm), external TMS $(^{29}\text{Si}, \delta = 0 \text{ ppm})$, or external Me₂Se with 5% w/w C₆D₆ (⁷⁷Se, $\delta =$ 0 ppm). Assignment of the ¹³C NMR spectroscopic data was supported by DEPT 135 experiments and 13C,1H correlation experiments. Solidstate ¹⁵N, ²⁹Si, and ⁷⁷Se VACP/MAS NMR spectra were recorded at 22 °C with a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO2 (diameter, 4-7 mm) containing ca. 80-300 mg of sample [15N, 40.6 MHz; 29Si, 79.5 MHz; 77Se, 76.3 MHz; external standard, TMS (¹³C, ²⁹Si; $\delta = 0$ ppm), glycine (¹⁵N, $\delta = -342.0$ ppm), or Me₂Se (⁷⁷Se, $\delta = 0$ ppm); spinning rate, 5–10 kHz; contact time, 1–2 ms (13C), 3 ms (15N), 3-5 ms (29Si), or 5 ms (77Se); 90° 1H transmitter pulse length, 2.8 µs (4 mm), 3.6 µs (7 mm); repetition time, 4 s].

Synthesis of 5a: Triethylamine (1.03 g, 10.2 mmol) and **7** (1.36 g, 5.05 mmol) were added sequentially in single portions at 20 °C to a

stirred suspension of 8 (970 mg, 5.07 mmol) in tetrahydrofuran (40 mL), and the reaction mixture was stirred at 20 °C for 1 h. The resulting solid was filtered off, washed with tetrahydrofuran (10 mL), and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, and acetonitrile (10 mL) was added to the residue. The solvent was removed in vacuo, acetonitrile (12 mL) was added to the residue, and the resulting mixture was heated until a clear solution was obtained, which was kept undisturbed at -20 °C for 16 h. The resulting precipitate was isolated by filtration, washed with npentane (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 1 h) to give 5a in 65% yield (1.28 g, 3.30 mmol) as a yellow crystalline solid. ¹H **NMR** (500.1 MHz, CD₂Cl₂): $\delta = 1.90$ [d, ${}^{4}J({}^{1}H, {}^{1}H) = 0.3$ Hz, 3 H, CCH_3], 2.50 (s, 3 H, CCH_3), 5.69 [q, ${}^{4}J({}^{1}H, {}^{1}H) = 0.3$ Hz, 1 H, CCHC], 6.75-6.79, 6.80-6.84, 6.88-6.92, 7.13-7.18, 7.22-7.25, 7.27-7.31, and 7.70–7.74 ppm (m, 14 H, C_6H_4 , SiC_6H_5 , OC_6H_5). ¹³C NMR $(125.8 \text{ MHz}, \text{CD}_2\text{Cl}_2)$: $\delta = 24.0 (\text{CCH}_3), 24.3 (\text{CCH}_3), 104.6 (\text{CCHC}),$ 115.1, 118.7, 120.9, 121.0, 121.4 (2 C), 127.7 (2 C), 128.3, 129.1 (2 C), 129.7, 131.8, 135.9 (2 C), 138.4, 153.3, and 157.0 (C₆H₄, SiC₆H₅, OC₆H₅), 171.1 [C(N)CH₃], 179.9 ppm [C(O)CH₃]. ²⁹Si NMR (99.4 MHz, CD₂Cl₂): δ = -108.7 ppm. ¹⁵N VACP/MAS NMR: δ = -152.8 ppm. ²⁹Si VACP/MAS NMR: $\delta = -109.5$ ppm. C₂₃H₂₁NO₃Si: calcd. C 71.29; H 5.46; N 3.61%; found: C 71.0; H 5.4; N 3.9%.

Synthesis of 5b·CH₃CN: Triethylamine (305 mg, 3.01 mmol) and benzenethiol (332 mg, 3.01 mmol) were added sequentially in single portions at 20 °C to a stirred solution of 2b (994 mg, 3.01 mmol) in tetrahydrofuran (20 mL), and the reaction mixture was stirred at 20 °C for 1.5 h. The resulting solid was filtered off, washed with tetrahydrofuran $(2 \times 5 \text{ mL})$, and discarded. The solvent of the filtrate (including the wash solutions) was removed in vacuo, and acetonitrile (1 mL) was added to the residue. The solvent was removed in vacuo, acetonitrile (6 mL) was added to the residue, and the resulting mixture was heated until a clear solution was obtained, which was kept undisturbed at 20 °C for 2 h and then at -20 °C for a further 48 h. The resulting precipitate was isolated by filtration, washed with n-pentane (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 10 min) to give 5b·CH₃CN in 54% yield (723 mg, 1.63 mmol) as an orange-colored crystalline solid. ¹H NMR (500.1 MHz, CD₂Cl₂): $\delta = 1.50$ (s, 3 H, CCH_3), 1.97 (s, 3 H, N= CCH_3), 2.46 (s, 3 H, CCH_3), 5.59 (s, 1 H, CCHC), 6.73-6.80, 7.06-7.19, 7.27-7.37, and 7.72-7.77 ppm (m, 14 *H*, C₆*H*₄, SiC₆*H*₅, SC₆*H*₅). ¹³C NMR (125.8 MHz, CD₂Cl₂): $\delta = 2.0$ (N≡CCH₃), 23.3 (CCH₃), 24.3 (CCH₃), 104.0 (CCHC), 116.9 $(N \equiv CCH_3)$, 115.0, 118.4, 121.2, 126.5, 127.8 (2 C), 128.3 (2 C), 128.4, 129.7, 131.2, 135.7 (2 C), 136.1, 136.3 (2 C), 139.5, and 154.7 (C₆H₄, SiC₆H₅, SC₆H₅), 172.7 [C(N)CH₃], 182.5 ppm [C(O)CH₃]. ²⁹Si **NMR** (99.4 MHz, CD_2Cl_2): $\delta = -88.3$ ppm. ¹⁵N VACP/MAS NMR: $\delta = -204.5 \text{ ppm.}^{[12]}$ ²⁹Si VACP/MAS NMR: $\delta = -93.2 \text{ ppm.}^{[12]}$ C25H24N2O2SSi: calcd. C 67.53; H 5.44; N 6.30; S 7.21%; found: C 66.9; H 5.3; N 5.9; S 6.9%.^[13]

Synthesis of 5c·CH₃CN: Triethylamine (283 mg, 2.80 mmol) and benzeneselenol (440 mg, 2.80 mmol) were added sequentially in single portions at 20 °C to a stirred solution of **2b** (924 mg, 2.80 mmol) in tetrahydrofuran (20 mL), and the reaction mixture was stirred at 20 °C for 1 h. The resulting solid was filtered off, washed with tetrahydrofuran (2×5 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed in vacuo, and acetonitrile (1 mL) was added to the residue. The solvent was removed in vacuo, acetonitrile (5 mL) was added to the residue, and the resulting mixture was heated until a clear solution was obtained, which was slowly cooled to 20 °C and kept undisturbed at 20 °C for 3 h and then at -20 °C for a further 48 h. The resulting precipitate was isolated by filtration, washed with *n*-pentane (10 mL), and dried in vacuo (0.01 mbar, 20 °C,



10 min) to give 5c·CH₃CN in 47 % yield (647 mg, 1.32 mmol) as an orange-colored crystalline solid. ¹H NMR (500.1 MHz, CD₂Cl₂):^[14] δ = 1.50 (s, 3 H, CCH₃), 1.97 (s, 3 H, N=CCH₃), 2.45 (s, 3 H, CCH₃), 5.58 (s, 1 H, CCHC), 6.73-6.82, 7.06-7.23, 7.24-7.39, 7.46-7.52, and 7.70–7.76 ppm (m, 14 H, C_6H_4 , SiC_6H_5 , SeC_6H_5). ¹³C NMR $(125.8 \text{ MHz}, \text{ CD}_2\text{Cl}_2)$:^[14] $\delta = 2.0 \text{ (N=CCH}_3), 23.2 \text{ (CCH}_3), 24.4$ (CCH₃), 104.1 (CCHC), 116.9 (N≡CCH₃), 115.0, 118.6, 121.2, 126.6, 127.8 (2 C), 128.4 (2 C), 129.8, 131.2, 132.5, 133.7, 136.1 (2 C), 137.0 (2 C), 139.7, and 154.7 (C₆H₄, SiC₆H₅, SeC₆H₅), 172.7 [C(N)CH₃], 182.2 ppm [C(O)CH₃]. ²⁹Si NMR (99.4 MHz, CD_2Cl_2):^[14] δ = -88.7 ppm [⁷⁷Se satellites, ¹J(²⁹Si,⁷⁷Se) = 101 Hz]. ⁷⁷Se NMR (95.4 MHz, CD₂Cl₂):^[14] δ = 131.1 ppm. ¹⁵N VACP/MAS NMR:^[15] δ = -201.7 ppm (SiNCCH₃); N=CCH₃ not detected. ²⁹Si VACP/MAS **NMR**: $\delta = -93.9 \text{ ppm} [^{77}\text{Se satellites}, {}^{1}J({}^{29}\text{Si}, {}^{77}\text{Se}) = 109 \text{ Hz}]. {}^{77}\text{Se}$ **VACP/MAS NMR**: δ = 144.8 ppm. C₂₅H₂₄N₂O₂SeSi: calcd. C 61.09; H, 4.92; N, 5.70%; found: C 60.8; H, 4.8; N, 5.1%.[13]

Synthesis of 6a: Triethylamine (1.21 g, 12.0 mmol) and 7 (1.61 g, 5.98 mmol) were added sequentially in single portions at 20 °C to a stirred suspension of 9 (1.22 g, 5.97 mmol) in tetrahydrofuran (50 mL), and the reaction mixture was stirred at 20 °C for 30 min. The resulting solid was filtered off, washed with tetrahydrofuran (10 mL), and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, acetonitrile (20 mL) was added to the solid residue, and the resulting mixture was heated until a clear solution was obtained, which was kept undisturbed at -20 °C for 20 h. The resulting precipitate was isolated by filtration, washed with *n*-pentane (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 1 h) to give 6a in 68% yield (1.63 g, 4.07 mmol) as a yellow crystalline solid. ¹H NMR $(500.1 \text{ MHz}, \text{CD}_2\text{Cl}_2)$: $\delta = 1.95 \text{ [d, } {}^4J({}^1\text{H}, {}^1\text{H}) = 0.6 \text{ Hz}, 3 \text{ H}, \text{CCH}_3\text{]},$ 2.41 (s, 3 H, CCH₃), 3.23 (s, 3 H, NCH₃), 5.60 [q, ${}^{4}J({}^{1}H, {}^{1}H) = 0.6$ Hz, 1 H, CCHC], 6.65-6.69, 6.72-6.76, 6.77-6.81, 6.83-6.87, 7.10-7.15, 7.17–7.22, and 7.25–7.29 ppm (m, 14 H, C₆H₄, SiC₆H₅, OC₆H₅). ¹³C **NMR** (125.8 MHz, CD_2Cl_2): $\delta = 23.4$ (CCH₃), 24.6 (CCH₃), 34.0 (NCH₃), 105.8 (CCHC), 110.7, 115.9, 119.4, 120.6, 120.9 (2 C), 127.5 (2 C), 128.4, 128.7, 128.9 (2 C), 130.6, 133.3 (2 C), 140.5, 146.5, and 158.4 (C₆H₄, SiC₆H₅, OC₆H₅), 166.6 [C(N)CH₃], 170.8 ppm $[C(O)CH_3]$. ²⁹Si NMR (99.4 MHz, CD₂Cl₂): $\delta = -107.5$ ppm. ¹⁵N VACP/MAS NMR (data for two crystallographically independent molecules): $\delta = -305.8/-302.9$ (NCH₃), -156.5/-151.9 ppm (SiNCCH₃). ²⁹Si VACP/MAS NMR (data for two crystallographically independent molecules): $\delta = -109.1/-106.1$ ppm. C₂₄H₂₄N₂O₂Si: calcd. C 71.97; H, 6.04; N, 6.99%; found: C 72.0; H, 6.1; N, 7.0%.

Synthesis of 6b: Triethylamine (1.12 g, 11.1 mmol) and benzenethiol (1.22 g, 11.1 mmol) were added sequentially at 20 °C to a stirred solution of 3b (3.79 g, 11.1 mmol) in tetrahydrofuran (50 mL), and the reaction mixture was stirred at 20 °C for 2 h. The resulting solid was filtered off, washed with tetrahydrofuran (10 mL), and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, and acetonitrile (5 mL) was added to the residue. The solvent was removed in vacuo, acetonitrile (60 mL) was added to the residue, and the resulting mixture was heated until a clear solution was obtained, which was kept undisturbed at 20 °C for 1 h and then at -20 °C for a further 16 h. The resulting precipitate was isolated by filtration, washed with *n*-pentane $(2 \times 15 \text{ mL})$, and dried in vacuo (0.01 mbar, 20 °C, 3 h) to give **6b** in 72 % yield (3.34 g, 8.02 mmol) as a dark-red crystalline solid. ¹H NMR (500.1 MHz, CD_2Cl_2): $\delta = 1.58$ (s, 3 H, CCH₃), 2.42 (s, 3 H, CCH₃), 2.52 (s, 3 H, NCH₃), 5.00 (s, 1 H, CCHC), 6.46-6.50, 6.57-6.62, 7.04-7.05, 7.12-7.16, 7.17-7.20, 7.25-7.33, 7.37–7.43, and 7.51–7.54 ppm (m, 14 H, C₆H₄, SiC₆H₅, SC₆H₅). ¹³C NMR (125.8 MHz, CD₂Cl₂): δ = 23.5 (CCH₃), 24.4 (CCH₃), 32.6 (NCH₃), 104.6 (CCHC), 108.2, 114.1, 120.9, 126.1, 127.6 (2 C), 128.1

(2 C), 128.2, 128.4, 129.0, 134.9 (2 C), 135.8 (2 C), 136.9, 140.7, and 148.2 (C_6H_4 , Si C_6H_5 , S C_6H_5), 171.4 [C(N)CH₃], 181.9 ppm [C(O)CH₃]. ²⁹Si NMR (99.4 MHz, CD₂Cl₂): δ = -84.4 ppm. ¹⁵N VACP/MAS NMR: δ = -290.1 (NCH₃), -205.8 ppm (SiNCCH₃). ²⁹Si VACP/MAS NMR: δ = -78.9 ppm. $C_{24}H_{24}N_2OSSi$: calcd. C 69.19; H, 5.81; N, 6.72; S, 7.70%; found: C 69.1; H, 5.8; N, 6.8; S, 7.6%.

Synthesis of 6c: Triethylamine (544 mg, 5.38 mmol) and benzeneselenol (844 mg, 5.37 mmol) were added sequentially in single portions at 20 °C to a stirred solution of 3b (1.84 g, 5.37 mmol) in tetrahydrofuran (50 mL), and the reaction mixture was stirred at 20 °C for 2.5 h. The resulting solid was filtered off, washed with tetrahydrofuran (10 mL), and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, and acetonitrile (10 mL) was added to the residue. The solvent was removed in vacuo, acetonitrile (7 mL) was added to the residue, and the reaction mixture was heated until a clear solution was obtained, which was kept undisturbed at 20 °C for 16 h. The resulting precipitate was isolated by filtration, washed with *n*-pentane $(2 \times 9 \text{ mL})$, and dried in vacuo (0.01 mbar, 20 °C, 2 h) to give 6c in 63% yield (1.56 g, 3.37 mmol) as a dark-red crystalline solid. ¹H NMR (500.1 MHz, CD₂Cl₂):^[14] δ = 1.64 (s, 3 H, CCH₃), 2.36 (s, 3 H, CCH₃), 2.49 (s, 3 H, NCH₃), 5.50 (s, 1 H, CCHC), 6.45-6.51, 6.58-6.64, 7.01-7.07, 7.10-7.17, 7.18-7.23, 7.25-7.31, and 7.47–7.56 ppm (m, 14 H, C_6H_4 , SiC_6H_5 , SeC_6H_5). ¹³C NMR $(125.8 \text{ MHz}, \text{ CD}_2\text{Cl}_2)$;^[14] $\delta = 23.5 (\text{CCH}_3), 24.4 (\text{CCH}_3), 32.7$ (NCH₃), 104.9 (CCHC), 108.5, 114.4, 120.9, 126.3, 127.6 (2 C), 128.3 (2 C), 129.0, 129.7, 130.9, 133.7, 134.9 (2 C), 137.2 (2 C), 141.0, and 147.8 (C₆H₄, SiC₆H₅, SeC₆H₅), 171.1 [C(N)CH₃], 181.1 ppm $[C(O)CH_3]$. ²⁹Si NMR (99.4 MHz, CD₂Cl₂):^[14] $\delta = -84.2 \text{ ppm}$ [⁷⁷Se satellites, ¹*J*(²⁹Si,⁷⁷Se) = 112 Hz]. ⁷⁷Se NMR (95.4 MHz, CD₂Cl₂):^[14] $\delta = 140.0 \text{ ppm}.$ ¹⁵N VACP/MAS NMR: $\delta = -287.3 \text{ (NCH}_3),$ -203.3 ppm (SiNCCH₃). ²⁹Si VACP/MAS NMR: $\delta = -78.5$ ppm (⁷⁷Se satellites not detected). ⁷⁷Se VACP/MAS NMR: $\delta = 164.2$ ppm. C24H24N2OSeSi: calcd. C 62.19; H, 5.22; N, 6.04%; found: C 62.3; H, 5.1; N, 6.1%.

Synthesis of 7: A solution of phenol (3.40 g, 36.1 mmol) in tetrahydrofuran (50 mL) was added dropwise at -20 °C within 1 h to a stirred solution of freshly distilled trichloro(phenyl)silane (7.63 g, 36.1 mmol) and triethylamine (3.65 g, 36.1 mmol) in tetrahydrofuran (50 mL). The resulting suspension was warmed to 20 °C and stirred for 20 h. The solid residue was removed by filtration, washed with tetrahydrofuran (20 mL), and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, diethyl ether (100 mL) was added to the residue, and the resulting mixture was kept undisturbed at -20 °C for 20 h. The resulting solid was removed by filtration and discarded, the solvent of the filtrate was removed under reduced pressure, and the residue was purified by distillation in vacuo to give 7 in 58% yield (5.62 g, 20.9 mmol) as a colorless liquid. B.p. 107–111 °C/1 mbar. ¹H NMR (500.1 MHz, CD_2Cl_2): $\delta = 7.11-7.17$, 7.32-7.37, 7.51-7.56, 7.60-7.64, and 7.86-7.90 ppm (m, 10 H, C₆H₅, OC_6H_5). ¹³C NMR (125.8 MHz, CD_2Cl_2): $\delta = 120.3$ (2 C), 124.2, 128.9 (2 C), 130.1, 130.5, 132.9 (2 C), 134.1 (2 C), 152.3 ppm (SiC_6H_5, OC_6H_5) . ²⁹Si NMR (99.4 MHz, CD_2Cl_2): $\delta = -26.2$ ppm. C12H10Cl2OSi: calcd. C 53.54; H, 3.74%; found: C 53.5; H, 3.7%.

Synthesis of 8: This compound was synthesized according to Ref.^[10].

Synthesis of 9: Acetylacetone (37.5 g, 375 mmol) was added in a single portion at 20 °C to a stirred solution of freshly distilled *N*-methylbenzene-1,2-diamine (41.6 g, 341 mmol) in ethanol (200 mL), and the reaction mixture was then stirred for 10 min, cooled to -20 °C, and kept undisturbed at this temperature for 3 d. The resulting precipitate was isolated by filtration, washed with *n*-pentane (2×50 mL), and

dried in vacuo (0.01 mbar, 20 °C, 3 h) to give **9** in 73 % yield (50.8 g, 249 mmol) as a yellow crystalline solid. ¹H NMR (500.1 MHz, CD₂Cl₂): δ = 1.78 [d, ⁴*J*(¹H, ¹H) = 0.5 Hz, 3 H, CCH₃], 2.04–2.06 (m, 3 H, CCH₃), 2.82 [d, ³*J*(¹H, ¹H) = 5.0 Hz, 3 H, NCH₃], 4.05 [br. s, 1 H, N(CH₃)*H*], 5.22–5.24 (m, 1 H, CCHC), 6.62–6.70, 6.93–6.99, and 7.12–7.21 (m, 4 H, C₆H₄), 11.8 ppm (br. s, 1 H, *H*NCCH₃). ¹³C NMR (125.8 MHz, CD₂Cl₂): δ = 19.3 (CCH₃), 29.2 (CCH₃), 30.5 (NCH₃), 97.2 (CCHC), 110.6, 116.5, 124.4, 128.0, 128.6, and 145.9 (C₆H₄), 163.2 (NCCH₃), 196.4 ppm (CO). ¹⁵N VACP/MAS NMR (data for two crystallographically independent molecules): δ = –257.7/–252.1 (NCCH₃), -323.9 ppm (2 N, NCH₃). C₁₂H₁₆N₂O: calcd. C 70.56; H, 7.89; N, 13.71%; found: C 70.5; H, 7.8; N, 13.7%.

Crystal Structure Analyses: Suitable single crystals of **5a**, **5b**·CH₃CN, **5c**·CH₃CN, and **6a–c** were mounted in inert oil (perfluoropolyalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer [Stoe IPDS (**5a**, **5c**·CH₃CN, and **6a–c**; graphite-monochromated Mo- K_{α} radiation, $\lambda = 0.71073$ Å) or Bruker Nonius KAPPA APEX II (**5b**·CH₃CN; Montel mirror, Mo- K_{α} radiation, $\lambda = 0.71073$ Å)]. All structures were solved by direct methods (SHELXS-97^[16]) and refined by full-matrix least-squares methods on F^2 for all unique reflections (SHELXL-97^[16]). SHELXLE was used as refinement GUI.^[17] For the CH hydrogen atoms, a riding model was employed.

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-966387 (**5a**), CCDC-966388 (**5b**·CH₃CN), CCDC-966389 (**5c**·CH₃CN), CCDC-966390 (**6a**), CCDC-966391 (**6b**), and CCDC-966392 (**6c**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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Received: November 13, 2013 Published Online: December 16, 2013