Chemistry of Heterocyclic Compounds, Vol. 42, No. 12, 2006

8-OXYQUINOLINATE AND 8-OXYQUINALDINATE IN SILICON COMPLEX CHEMISTRY – A NEW FACE OF OLD LIGANDS

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In tris(8-oxyquinolinato)phenylsilicon a novel coordination pattern of two 8-oxyquinolinate moieties in hexacoordinate Si complexes was found: cis-(O,O')-cis-(N,N'). The product of the reaction between 1-chloro-1,2,5-triphenyl-2,5-diazasilolidine and sodium 8-oxyquinolinate [1-(8-oxyquinolinato)-1,2,5-triphenyl-2,5-diazasilolidine] bears a tetracoordinate Si atom. Replacing 8-oxyquinolinate by 8-oxyquinaldinate, however, leads to the formation of tris-(8-oxyquinaldinato)phenylsilicon with hexacoordinate Si atom, but with trans-(O,O')-cis-(N,N')-chelation. This is the first structurally and spectroscopically characterized 8-oxyquinaldinato Si complex with hypercoordinate silicon atom.

Keywords: chelates, oxyquinoline, silicon, hypercoordination.

Hypercoordinate silicon complexes with bidentate chelating ligands attract the interest of researchers for purposes such as studying stereochemical interconversions [1] and Si–E (e.g., E = Cl, Br, C) bond activation by hypercoordination [2, 3] as well as measuring the "coordination power" of various ligands [4], or *vice versa*: the lack of coordination at Lewis-acidic Si atoms bearing electron withdrawing substituents [5]. Si complexes of 8-oxyquinolinate derived bidentate ligand systems were also used for studies on potential anti-cancer drugs [6, 7]. Although UV/vis spectroscopic studies proved close N→Si contacts in some of these compounds, the exact molecular structures were not known till 1984 when Klebe et al. presented the first crystallographic study on a bis(8-oxyquinolinato)silane with hexacoordinate Si atom [8]. In recent years X-ray structure analyses delivered the first insights into the great variability of coordination spheres of hexacoordinate Si atoms within chelates of 8-oxyquinolinate [8]. This simple bidentate chelating system proved to be variable regarding the coordination modes that can generally be expected at an octahedrally coordinated Si atom. Although several examples for molecular structures of hexacoordinate tin complexes with two 8-oxyquinolinate derived ligands are known [10–17], they do not vary significantly. They underline the special role of the combination of both the Si atom together with 8-oxyquinolinato ligands as a unit of surprising coordination properties, thus as a unit of special research interest.

Starting from the known coordination modes in bis(8-oxyquinolinato) Si complexes (Scheme 1, top), the question arose whether it is possible to achieve the "missing" coordination mode (Scheme 1, bottom left) within a hexacoordinate Si complex with two chelating 8-oxyquinolinato moieties. Necessarily, the question regarding the variability of the 8-oxyquinolinate′s coordination in pentacoordinate Si complexes had to arise.

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* Dedicated to Prof. Edmunds Lukevics on the occasion of his 70th birthday

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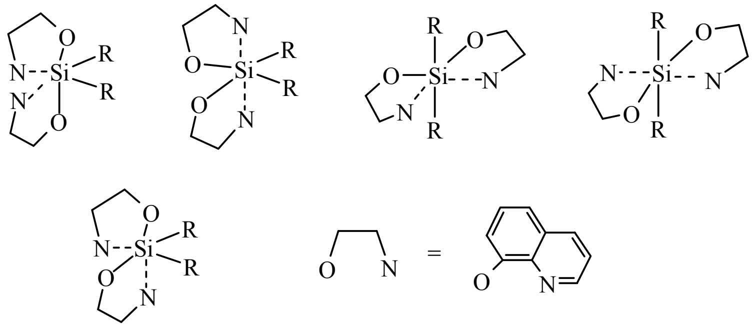
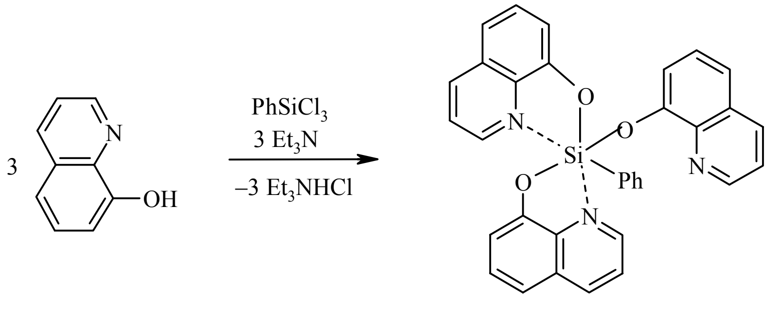
Scheme 1



The reaction of phenyltrichlorosilane with three equivalents of 8-hydroxyquinoline in the presence of triethylamine as a supporting base yielded complex **1** bearing a hexacoordinate Si atom (Scheme 2). Compound **1** crystallized from the reaction mixture (THF solution), delivering yellow needles of the THF solvate **1**·1.5 THF. These crystals were suitable for X-ray structure analysis (Fig. 1, Table 1).

Scheme 2



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The asymmetric unit of **1**·1.5 THF bears two molecules of **1** as well as three THF molecules which are two-fold disordered each. The bond lengths and angles of the crystallographically independent molecules of **1** differ only little; thus, only one of them is depicted in Fig. 1 and discussed herein. The molecules of compound **1**

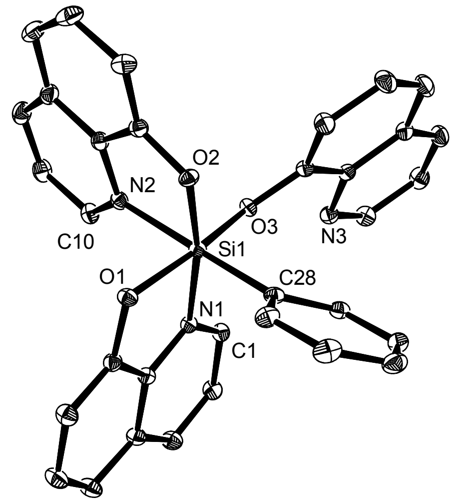


Fig. 1. ORTEP plot of one of the two crystallographically independent molecules of compound **1** in a crystal of **1**·1.5 THF (50% probability ellipsoids, selected atoms labelled, and hydrogen atoms omitted for clarity).

feature the coordination mode given in Scheme 1 (bottom left), which has not been encountered with 8-oxyquinolinato Si complexes so far. The length of the "dative" bonds N→Si strongly depends on the *trans*-situated ligand's donor atom. The significantly shorter distance N(1)–Si(1) [1.966(1) Å] is expected to originate from a more Lewis-acidic σ* MO of the Si(1)–O(2) bond in comparison with the σ* MO of the Si(1)–C(28) bond. Thus, the coordination of N(2) is remarkably weaker (N(2)–Si(1): 2.034(1) Å). *Vice versa*, the forced attack of N(1)→Si(1) results in a weaker Si–O bond to the same bidentate ligand (O(1)–Si(1) 1.796(1) Å) contrary to the other two Si–O bonds in the same molecule (O(2)–Si(1) 1.754(1), O(3)–Si(1) 1.749(1) Å).

In comparison with other bis(8-oxyquinolinato)-Si -complexes with two *cis*-(N,N')-*trans*-(O,O')-arranged bidentate ligands with C,C' or C,Cl as mono-dentate donor combinations, complex **1** bears O(3) as a small electronegative atom which may generally act as a hydrogen bridge acceptor. Supporting the hypothesis that the arrangement of the 8-oxyquinolinato ligands in complex **I** (Scheme 3) is driven by the formation of hydrogen contacts (one of them is indicated by a thin arrow) between the N atoms of the diazasilolidine ring the H atoms in α-position at the bidentate ligands, the same can be concluded for one of the ligands in **1**. Owing to the presence of only one additional hydrogen bridge acceptor (O(3)) besides the O atoms of the bidentate (ON)-chelating ligands, only one of the 8-oxyquinolinato ligands forms such a hydrogen contact to O(3) which

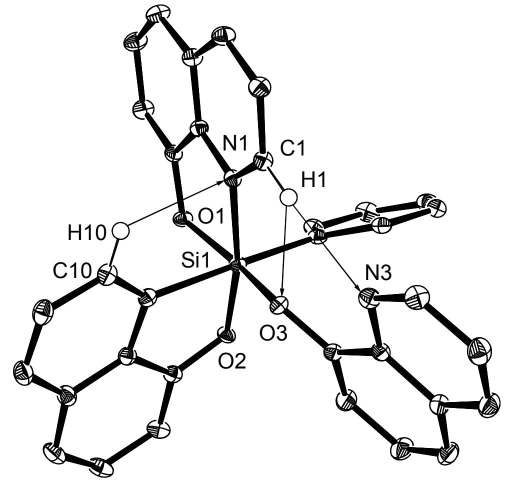
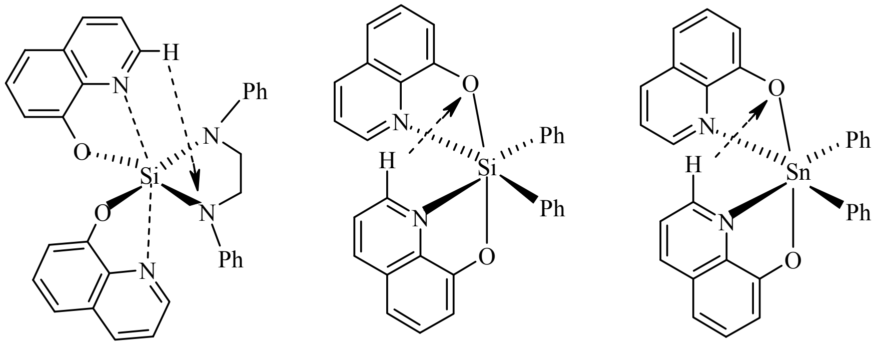


Fig. 2. Short intramolecular interligand H–O and H–N contacts in one of the crystallographically independent molecules of compound **1** (indicated by thin arrows).

Scheme 3



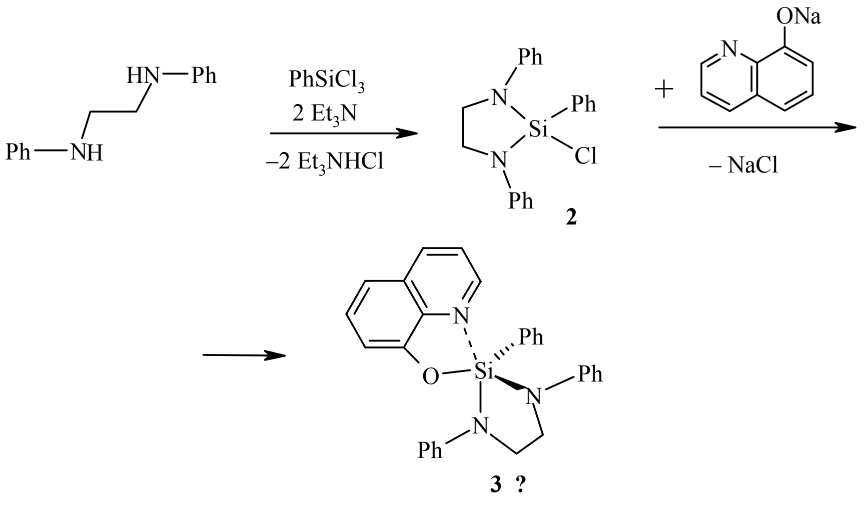
I **II** **III**

system and yields this special coordination pattern. In Fig. 2 the H(1)–O(3) and H(10)–N(1) contacts are depicted. Atoms H(1) and H(10) were refined in idealized positions; however, at the rather rigid sp^2-hybridized C-atoms C(1) and C(10) their idealized locations are expected to provide a representative base for discussion. The distance O(3)–H(1) is about 2.43 Å and therefore even shorter than the H–N contacts in **I** which are approximately 2.62-2.65 Å. The other hydrogen contact in molecule **1**, H(10)–N(1) (2.60 Å), represents the same interatomic distance. The favored formation of the hydrogen contact H(1)–O(3), neglecting the contact H(1)–O(2) upon formation of a *cis*-(N,N')-*trans*-(O,O')-shaped complex (configuration found in **II**, Scheme 3; one of the hydrogen contacts is indicated by a thin arrow), should be due to the additional hydrogen-acceptor N(3) (H(1)–N(3): 2.44 Å) in the case of the present H(1)–O(3) contact which involves the lone pair of the quinoline atom N(3). Thus, these hydrogen atoms in α-position at the 8-oxyquinolinato ligand and their intramolecular interligand-buttressing effect can be referred to as major driving forces in shaping molecule **1** as well as the other structurally confirmed bis(8-oxyquinolinato) Si complexes known so far. The outstanding influence of hydrogen bridges on the coordination sphere of hypercoordinate silicon complexes was also reported for sugar alcohols as multidentate ligands by Klüfers et al. [18] The lack of variety in the coordination patterns of bis(8-oxyquinolinato) Sn(IV) complexes, on the other hand, can be considered a result of the larger central atom which separates the 8-oxyquinolinato ligands from each other and, therefore, weakens structure-determining intramolecular interligand hydrogen contacts. For example, the intramolecular interligand O–H contacts as depicted in Scheme 3 are 2.74 and 2.80 Å in (8-oxyquinolinate)$SnPh_2$ (**III**) and much shorter (2.57 and 2.62 Å) in (8-oxyquinolinate)$SiPh_2$ (**II**).

This special molecular structure of **1**, however, is only fixed in the solid state. One cannot distinguish between the three different 8-oxyquinolinato ligands in **1** in chloroform solution at 20°C. The Si atom of **1** remains clearly hexacoordinate in solution (in $CDCl_3$: δ^{29}Si -149.8, in solid state: δ^{29}Si –147.4 ppm), but the emerging of only one set of signals for the 8-oxyquinolinate moiety in the ^{13}C NMR spectrum of **1** indicates a fluxional behavior, a rapid exchange between the mono- and bidentate coordination modes of the 8-oxyquinolinato ligands.

Starting from this variety of coordination modes in hexacoordinate bis(8-oxyquinolinato) Si complexes, the structures of pentacoordinate Si complexes bearing one of those bidentate ligands are unknown so far and were the object of the synthesis depicted in Scheme 4.

Scheme 4



1-Chloro-1,2,5-triphenyl-2,5-diazasilolidine (**2**) was prepared from N,N'-diphenylethylenediamine and phenyltrichlorosilane in the presence of triethylamine. Silane **2** seemed to be the ideal starting compound to realize the aimed synthesis from the following point of view: the five-membered cycle should support the coordination of a further donor atom at the Si atom in order to decrease the ring strain Lewis acidity. The substituents at the Si atom (phenyl group, N atoms) are more electron withdrawing than alkyl groups but are not prone to intermolecular exchanges or subsequent substitution steps that might lead to the formation of bis(8-oxyquinolinato) Si complexes.

The conversion of aminosilane **2** with 1 eq. of sodium 8-oxyquinolinate yielded the monosubstituted product **3** with one 8-oxyquinolinato group at the Si atom. In the latter one, however, the Si atom is only tetracoordinate in both the solid state and in solution. To analyze the reason for this behavior, the molecular structures of both compounds were determined by X-ray crystallography (Figs. 3 and 4).

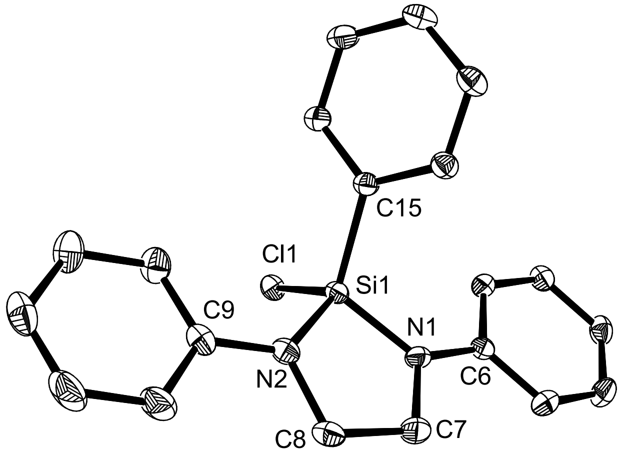


Fig. 3. Molecular structure of compound **2** in the crystal (ORTEP plot with 50% probability ellipsoids, selected atoms labelled, hydrogen atoms omitted).

The bond angle N(1)–Si(1)–N(2) in compound **2** (94.76(5)°) is by far smaller than the tetrahedral angle. This suggests the general tendency of this 2,5-diazasilolidine unit to bear ring strain which could be released *via* addition of a donor atom. This ring strain release, however, would be successfully accomplished only in the case of a trigonal bipyramidal coordination sphere as depicted in Scheme 5, left. The aimed angle N(1)–Si(1)–N(2) would be then close to 90°, which is easily realized in this heterocyclic system. The equatorial situation of both diazasilolidine N atoms (Scheme 5, **b**) would result in such a molecule bearing even higher ring strain due to upscaled bond angle discrepancy (aimed angle N(1)–Si(1)–N(2): 120°).

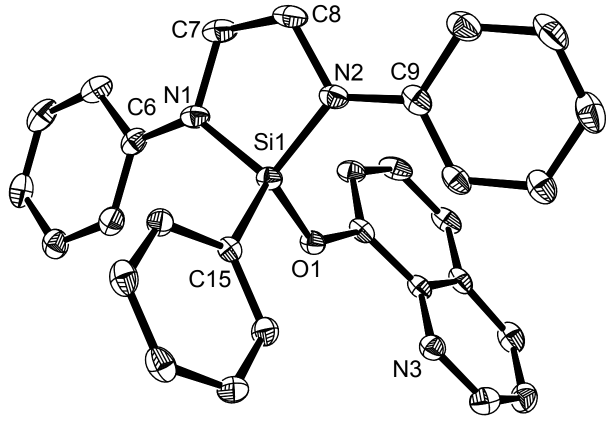
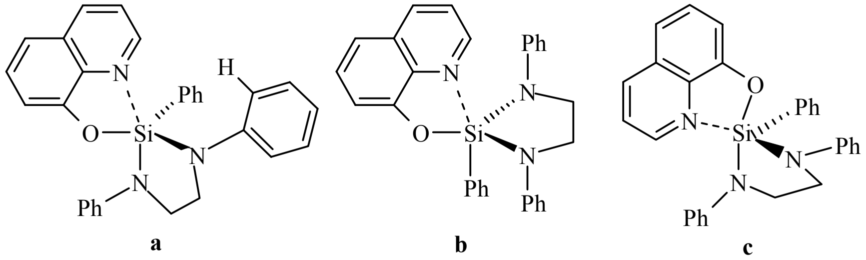


Fig. 4. Molecular structure of compound **3** in the crystal (ORTEP plot with 50% probability ellipsoids, selected atoms labelled, hydrogen atoms omitted).

Scheme 5

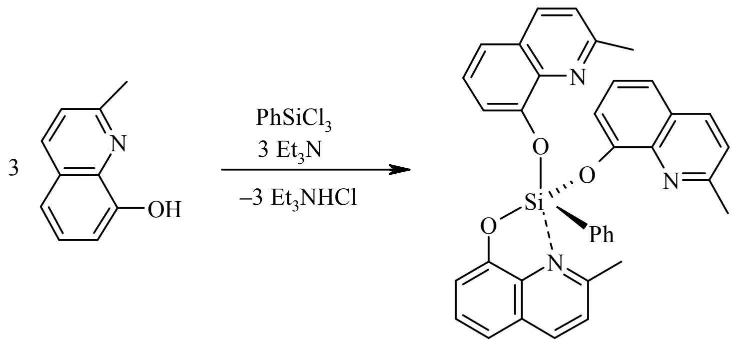


The preference of axial positions within a trigonal bipyramid for setting up "dative" N→Si bonds was demonstrated with various examples [19-25]. A major effect preventing the 8-oxyquinolinate from coordinating the Si atom in the aimed manner (Scheme 5, **a**) should be the potential repulsion emerging from the H atom in *o*-position at the phenyl group of the equatorially located diazasilolidine N atom, which points to the 8-oxyquinolinate moiety. This repulsion could eventually be minimized by a rotation of this N-linked phenyl group. *Vice versa*, this rotation would turn the phenyl ring′s π-electron system out of the conjugation with the lone pair of its aniline N atom. In both molecules **2** and **3** the bond angles around the diazasilolidine N atoms indicate their *sp*^{2}-hybridization (sums of angles: in **2** 360° at N(1) and 359° at N(2), in **3** 357° at N(1), and 359° at N(2)) and thus their π-conjugation with the electron systems of the phenyl groups attached. It can be concluded that the ring strain Lewis acidity in 2,5-diphenyl-2,5-diazasilolidines cannot overwhelm the gain in energy provided by π-conjugation between the N-atoms and the phenyl substituents. Turning around the 8-oxyquinolinato ligand to coordinate with the N-atom in equatorial position (Scheme 5, **c**) would be negatively influenced by both the lack of a suitable σ*-acceptor MO as well as repulsion between the 8-oxyquinolinate′s α-hydrogen atom with the phenyl substituent at the axially situated diazasilolidine N atom.

Recently, Voronkov et al. published the synthesis of the complex 8-thioquinolinatophenyldifluorosilane [26]. The pentacoordination of its Si atom was proven by ^{29}Si NMR spectroscopy. An X-ray crystallographic determination of the structure of this compound, however, has not been published to date. The structurally related compound 8-oxyquinolinatotrifluorosilane easily achieves hexacoordination of its Si atom by addition of a DMF molecule as additional donor. The preparation and isolation of pentacoordinate Si complexes with the 8-oxyquinolinate ligand is still a big challenge in silicon coordination chemistry.

Because of the less successful strategy of preparing a pentacoordinate 8-oxyquinolinato Si complex by avoiding ligand exchange and secondary substitution reactions and only offering one 8-oxyquinolinato ligand, a novel strategy was proposed. Based on the assumption that the hexacoordination of the Si atom in compound **1** is mainly determined by two impacts – electron withdrawing substituents at the Si atom and intramolecular hydrogen contacts – the latter may be suppressed by using 8-oxyquinaldinate instead of the oxyquinolinate. Rather repulsive interligand interactions on intramolecular level should be the result, but only if the Si atom is octahedrally coordinated. Both the transition to penta- and tetracoordinate isomers would result in a degradation of these repulsive interactions, and pentacoordination of the Si atom would account for its Lewis acidity due to its three aryloxy substituents. Indeed, the conversion of phenyltrichlorosilane with three equivalents of 8-hydroxyquinaldine (Scheme 6) leads to the formation of compound **4,** which bears a less shielded Si atom in the solid state (δ^{29}Si -114.4 ppm). As found for **1** in chloroform solution, the coordination modes of the three 8-oxyquinaldinate ligands interchange rapidly, thus producing one set of signals in both the ^{1}H and the ^{13}C NMR spectra. The donor action of the 8-oxyquinaldinato ligand retreats in solution, as indicated by a shift of the ^{29}Si

Scheme 6



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NMR signal to lower field (δ^{29}Si -81.6 ppm), but the ^{29}Si chemical shift still demonstrates the presence of hypercoordinate silicon atoms in solution, although in equilibrium with their tetracoordinate counterparts (compare δ^{29}Si -69.8 ppm for phenyltriphenoxysilane).*

Finally, X-ray structure analysis of a tiny single crystal of compound **4** revealed the coordination pattern of the 8-oxyquinaldinato ligands around the Si atom (Fig. 5). Surprisingly, the Si atom is not pentacoordinate as one could expect from the ^{29}Si chemical shift of –114.4 ppm in the CP/MAS NMR spectrum. The coordination sphere is extremely distorted octahedral (axial angles: O(1)–Si(1)–O(2) 160.6(1)°, O(3)–Si(1)–N(1) 166.3(1)°, C(31)–Si(1)–N(2) 172.6(1)°), and the arrangement of the donor atoms of the two chelating 8-oxyquinolinato ligands is related to this in bis(8-oxyquinaldinato) Si complexes such as **II** (Scheme 3). The N→Si bonds are significantly longer than those in **1** (**1**: Si(1)–N(1) 1.966(1), Si(1)–N(2) 2.034(1); **4**: Si(1)–N(1) 2.258(3), Si(1)–N(2) 2.183(3) Å). This is expected to be the main reason for the extremely downfield-shifted ^{29}Si NMR signal in the solid state. The intramolecular interaction between the 8-oxyquinaldinato ligands methyl groups with the donor atoms

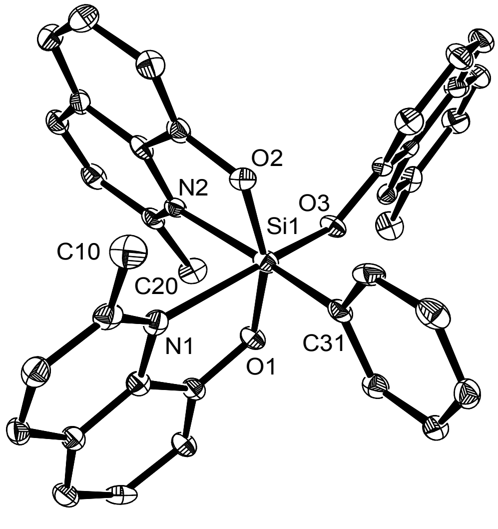

Fig. 5. ORTEP plot of one molecule of compound **4** in the crystal
(50% probability ellipsoids, selected atoms labelled and hydrogen atoms omitted for clarity).

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[*] Phenyltriphenoxysilane was prepared by reacting phenyltrichlorosilane with 3 eq. of phenol in THF at ambient temperature. Triethylamine in excess was used as supporting base. The hydrochloride, which precipitated immediately after addition of PhSiCl$_3$ to the phenol solution, was then filtered off after 1 h, the THF was removed from the filtrate, and the residual oil was dissolved in CDCl$_3$ for ^{29}Si NMR spectroscopy.

O(1) and O(2) causes a remarkable out-of-plane shift of the methyl groups (C(10) 0.195(4) and C(20) 0.268(4) Å) from the least-squares-planes of the 8-oxyquinaldine backbones (N atom and C atoms). In the monodentate 8-oxyquinaldinato ligand the methyl group C(30) remains in plane with the atoms of the oxyquinolinate system (N(3), C(21)–C(29)). The structural comparison between compounds **1** and **4** allows the following conclusions. Hexacoordination of Si atoms in bis(8-oxyquinolinato) Si complexes is not only supported by intramolecular interligand hydrogen contacts, but also by the formation of N→Si bonds as a driving force. Thus, bis(8-oxyquinaldinato) Si complexes may also achieve octahedral coordination as demonstrated in compound **4**. The formation of intramolecular hydrogen bridges between the 8-oxyquinolinato ligands, however, strengthens the chelating system to such an extent that the Si atom of compound **1** remains hexacoordinate in chloroform solution, but notable N→Si bond dissociation can be ^{29}Si NMR spectroscopically observed in solutions of compound **4**. Despite the stronger coordination of the bidentate ligands in **1**, a rapid coordination-interchange was NMR-spectroscopically observed in both complex **4** and **1**.

Silicon complexes bearing 8-oxyquinolinato ligands were shown to exhibit a great variety of coordination patterns of two oxinato ligands. The missing link, *cis*-(O,O')-*cis*-(N,N') coordination, was found with complex **1** furnishing the complete set of coordination modes in these bis-chelates. Analysis of each coordination mode in the context of the further ligand shift around the hypercoordinate Si atom revealed a notable influence of intramolecular hydrogen bridges in setting up these various coordination environments. Both weakening intramolecular interligand hydrogen bridges by larger central atoms (Sn instead of Si) as well as avoidance of such hydrogen contacts by substituting 8-oxyquinolinate for 8-oxyquinaldinate lead to *trans*-(O,O')-*cis*-(N,N') chelation of the hexacoordinate central atom by two of these bidentate ligands. Thus, this coordination pattern seems to be the sterically favored one in these cases. Although many new insights into the coordination behavior of oxinato ligands at Si atoms were gained, such complexes with pentacoordinate Si atom have not been isolated and structurally characterized in the solid state so far.

EXPERIMENTAL

Commercially available reagents were used. All manipulations were carried out under an inert atmosphere of dry argon. Triethylamine was distilled from calcium hydride and stored over molecular sieve 3 Å. Chloroform (stabilized with amylene) was dried over molecular sieve 3 Å. THF, diethylether, toluene, and hexane were distilled from sodium/benzophenone and stored over sodium wire. NMR spectra were recorded on a Bruker DPX 400 instrument ($CDCl_3$ solutions with TMS as internal standard) and a Bruker Avance 400 WB spectrometer (solid state). Elemental analyses were carried out on a Foss Heraeus CHN-O-Rapid.

Tris(8-oxyquinolinato)phenylsilicon (**1**). 8-Hydroxyquinoline (2.00 g, 13.8 mmol) and triethylamine (2.0 g, 20 mmol) were dissolved in THF (120 ml). This solution was stirred at room temperature and phenyltrichlorosilane (1.00 g, 4.73 mmol) was added dropwise. The resulting mixture was stored at 8°C for 15 min, then the triethylamine hydrochloride was filtered off and washed with THF (20 ml). The clear yellow filtrate was stored at 8°C for 1 week to yield yellow crystals of **1**·1.5 THF which were filtered off, washed with THF (3 ml), and briefly dried under vacuum. Yield: 1.65 g (2.56 mmol, 56%). ^{1}H NMR ($CDCl_3$, THF signals omitted), δ, ppm (*J*, Hz): 6.95-7.35 (12H, m); 7.90 (3H, d, $^3J_{HH} = 8.4$); 8.08 (2H, d, $^3J_{HH} = 7.2$); 8.55 (3H, broad). ^{13}C NMR ($CDCl_3$), δ, ppm: 113.9, 115.1, 121.1, 126.2, 126.8, 128.7, 129.4, 135.1, 137.2, 138.0, 144.0, 150.8, 154.2. ^{29}Si NMR ($CDCl_3$), δ, ppm: -149.8. (CP/MAS), δ, ppm: -147.4. Found, %: C 72.81; H 5.72; N 6.65. $C_{78}H_{70}N_6O_9Si_2$. Calculated, %: C 72.53; H 5.46; N 6.51.

1-Chloro-1,2,5-triphenyl-2,5-diazasilolidine (**2**). A solution of phenyltrichlorosilane (15.0 g, 70.9 mmol) in toluene (75 ml) was stirred at room temperature and a solution of N,N'-diphenylethylenediamine (15.0 g, 71.0 mmol) and triethylamine (15.0 g, 14.8 mmol) in toluene (225 ml) was added dropwise. After 4 days the triethylamine hydrochloride was filtered off and washed with toluene (40 ml). The solvent was removed from the filtate under reduced pressure and the crude solid product was extracted with hexane (150 ml). From the hexane

TABLE 1. Data of Crystal Structure Determination and Refinement of **1-4***

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{78}H_{70}N_6O_9Si_2$	$C_{20}H_{19}ClN_2Si$	$C_{29}H_{25}N_3OSi$	$C_{36}H_{29}N_3O_3Si$
T, K	90(2)	93(2)	90(2)	90(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a, Å	17.1086(5)	13.293(2)	9.1605(3)	12.7303(13)
b, Å	17.2518(5)	9.5802(14)	22.5576(8)	17.2513(18)
c, Å	21.6458(6)	14.812(3)	11.6509(4)	13.0613(16)
β, °	101.843(1)	112.644(4)	105.703(2)	99.766(4)
V, $Å^3$	6252.9(3)	1740.9(5)	2317.67(14)	2826.9(5)
ρ_{calc}, $g{\cdot}cm^{-3}$	1.372	1.339	1.317	1.362
μ, mm^{-1}	0.126	0.292	0.130	0.127
F(000)	2720	736	968	1216
Crystal size, mm^3	0.55×0.15×0.11	0.50×0.30×0.20	0.20×0.10×0.05	0.16×0.06×0.01
$2\theta_{max}$, °	60	64	54	50
Index ranges	$-24 \leq h \leq 20$, $-24 \leq k \leq 24$, $-30 \leq l \leq 30$	$-19 \leq h \leq 19$, $-14 \leq k \leq 14$, $-22 \leq l \leq 21$	$-11 \leq h \leq 9$, $-28 \leq k \leq 28$, $-14 \leq l \leq 14$	$-15 \leq h \leq 15$, $-18 \leq k \leq 20$, $-15 \leq l \leq 15$
Reflections collected	76749	21487	21660	20013
R_{int}	0.0501	0.0315	0.0468	0.1165
Independent reflections	18211	6044	5058	4996
Parameters	904	217	307	388
R Indices [$I > 2\sigma(I)$]				
R_1	0.0432	0.0352	0.0436	0.0537
wR_2	0.1037	0.0917	0.0937	0.0940
R Indices (all data)				
R_1	0.0710	0.0481	0.0688	0.1375
wR_2	0.1118	0.0968	0.1005	0.1096
Largest diff. peak and hole, $e{\cdot}Å^{-3}$	0.451, -0.391	0.410, -0.285	0.292 and -0.359	0.264 and -0.334

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* **1–4** *Z* = 4.

solution colorless crystals of **2** formed which were filtered off and dried under vacuum. Yield: 20.1 g (57.3 mmol, 81%), mp 134°C. ^1H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 3.70-3.90 (4H, m, CH_2CH_2); 6.75-6.85 (6H, m); 7.10-7.20 (4H, m); 7.35-7.50 (3H, m); 7.84 (2H, d, $^3J_{HH} = 6.8$). ^{13}C NMR ($CDCl_3$), δ, ppm: 44.6 (CH_2CH_2); 115.5, 119.5, 128.6, 129.1, 130.9, 131.7, 135.1, 145.3. ^{29}Si NMR ($CDCl_3$), δ, ppm: -20.3. Found, %: C 68.30; H 6.45; N 8.18. $C_{20}H_{19}ClN_2Si$. Calculated, %: C 68.45; H 6.46; N 7.98.

1-(8-Oxyquinolinato)-1,2,5-triphenyl-2,5-diazasilolidine (**3**). A solution of sodium 8-oxyquinolinate [8] (1.15 g, 6.88 mmol) in THF (20 ml) was added to a cooled (-10°C) solution of compound **2** (2.45 g, 6.99 mmol) in THF (50 ml). Then the mixture was stirred at room temperature for 3 h, the NaCl precipitate was removed by filtration, and the volume of the filtrate was reduced to ca. 15 ml by vacuum evaporation. Compound **3** crystallized out of this solution within few minutes. After 1 day the solid product was filtered off, washed with THF (10 ml), and dried under vacuum. Yield: 1.95 g (4.25 mmol, 62%). mp 210 °C. ^1H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 3.65-3.90 (4H, m, CH_2CH_2); 6.69 (2H, t, $^3J_{HH} = 7.2$); 6.95-7.45 (15H, m); 7.97 (1H, dd, $^3J_{HH} = 8.2$, $^4J_{HH} = 1.4$); 8.10-8.20 (2H, m); 8.84 (1H, dd, $^3J_{HH} = 4.0$, $^4J_{HH} = 1.6$). ^{13}C NMR ($CDCl_3$), δ, ppm: 44.2 (CH_2CH_2); 115.4, 117.0, 118.8, 121.3, 121.8, 126.5, 128.3, 128.9, 129.7, 130.6, 131.0, 135.4, 135.9, 141.8, 146.2, 149.4, 149.9. ^{29}Si NMR ($CDCl_3$), δ, ppm: -40.3. Found, %: C 75.61; H 5.40; N 9.19. $C_{29}H_{25}N_3OSi$. Calculated, %: C 75.78; H 5.48; N 9.14.

Tris(8-oxyquinalinato)phenylsilicon (**4**). 8-Hydroxyquinaldine (2.16 g, 13.8 mmol) and triethylamine (2.0 g, 20 mmol) were dissolved in THF (60 ml). This solution was stirred at room temperature and phenyltrichlorosilane (1.00 g, 4.73 mmol) was added dropwise. The resulting mixture was stored at 8°C for 15 min, then the triethylamine hydrochloride was filtered off and washed with THF (10 ml). The volatiles from the clear colorless filtrate were removed under vacuum. Addition of diethylether (3 ml) to the oily residue initiated crystallization. The crude solid product was recrystallized from a mixture of chloroform (9 ml) and hexane (10 ml) to give **4** as a beige crystalline powder which was filtered off, washed with hexane (5 ml), and dried under vacuum. Yield: 1.60 g (2.78 mmol, 59 %). ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 2.32 (9H, s, CH_3); 6.95 (3H, d, $^3J_{HH}$ = 8.4); 7.15-7.30 (9H, m); 7.35-7.40 (3H, m); 7.75 (3H, d, $^3J_{HH}$ = 8.4); 8.15-8.20 (2H, m). ^{13}C NMR ($CDCl_3$), δ, ppm: 24.3 (CH_3); 117.2, 119.7, 122.0, 125.8, 126.9, 127.1, 129.0, 135.0, 135.3, 135.6, 140.3, 151.0, 156.9. ^{29}Si NMR ($CDCl_3$), δ, ppm: -81.6; (CP/MAS), δ, ppm: -114.4. Found, %: C 74.40; H 5.41; N 7.01. $C_{36}H_{29}N_3O_3Si$. Calculated, %: C 74.59; H 5.04; N 7.25.

X-Ray structure analyses. X-Ray structure data were recorded on a Bruker-Nonius-X8-APEX2-CCD diffractometer with MoKα-radiation (λ = 0.71073 nm) and semi-empirical correction (SADABS). The structures were solved with direct methods (SHELXS-97) and refined by full-matrix least-squares methods (refinement of F^2 against all reflections with SHELXL-97). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and refined isotropically. Selected data of structure determination and refinement are presented in Table 1. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-619445 (**1**), CCDC-619444 (**2**), CCDC-619446 (**3**), and CCDC-619447 (**4**).

The authors thank the German Chemical Industries Fund for financial support.

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