

# New Insights into Hexacoordinated Silicon Complexes with 8-Oxyquinolinato Ligands: 1,3-Shift of Si-Bound Hydrocarbyl Substituents and the Influence of Si-Bound Halides on the 8-Oxyquinolinato Coordination Features

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 80<sup>th</sup> birthday

The transsilylation reaction between allyltrichlorosilane and 8-trimethylsiloxyquinoline in the molar ratio 1 : 3 yields the hexacoordinated silicon tris-chelate (oxinate)<sub>2</sub>Si(adho) (“oxinate” = 8-oxyquinolinato, “adho” = di-anion of 2-allyl-1,2-dihydro-8-oxyquinoline) comprising an SiO<sub>3</sub>N<sub>3</sub> skeleton. The identity of this complex was established by single-crystal X-ray diffraction analysis and <sup>29</sup>Si CP/MAS NMR spectroscopy of its chloroform solvate. Benzyltrichlorosilane and dibenzylchlorosilane, comprising benzyl (Bn) as an “aromatically stabilized allyl moiety” did not undergo such rearrangement. Instead, the complexes (oxinate)<sub>2</sub>SiBnCl and (oxinate)<sub>2</sub>SiBn<sub>2</sub> were obtained even upon using three molar equivalents of 8-trimethylsiloxyquinoline.

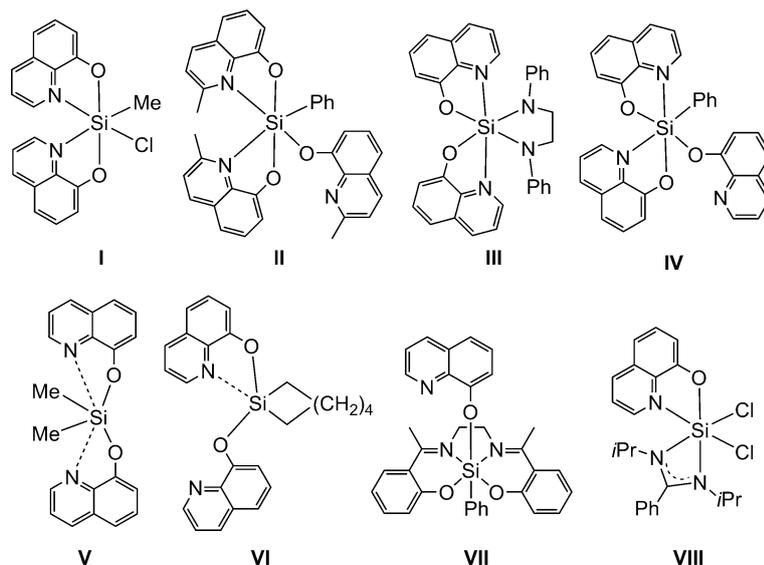
We determined the crystal structure of a non-disordered bis-chelate (oxinate)<sub>2</sub>SiBnCl with Si-bound hydrocarbyl and halogen substituents (the previously published (oxinate)<sub>2</sub>SiMeCl was disordered with alternative Me/Cl site occupancies). (Oxinate)<sub>2</sub>SiBnCl exhibits surprisingly poor response of the N–Si bonds to the different *trans*-disposed Si–X (X = Bn, Cl) bonds. For comparison and deeper insights into the coordination chemistry of oxinato silicon complexes with halide substituents, we determined the crystal structures of (oxinate)<sub>2</sub>SiPhCl·CHCl<sub>3</sub>, (oxinate)<sub>2</sub>SiCl<sub>2</sub>, (oxinate)<sub>2</sub>SiF<sub>2</sub>·1.5(CHCl<sub>3</sub>), and (8-oxyquinaldinato)<sub>2</sub>SiF<sub>2</sub>. Furthermore, the crystal structures of BnSiCl<sub>3</sub> and Bn<sub>2</sub>SiCl<sub>2</sub> (and its dibromo analog) are reported. The influence of the Si–C–C–C torsion angles of the benzyl group on the <sup>29</sup>Si NMR shift of benzylsilanes (which is noticeably upfield with respect to analogous methyl silanes) was analyzed by quantum-chemical calculations.

**Key words:** Benzylsilanes, Hypercoordination, Isomerism, Oxyquinolinato, Rearrangement

## Introduction

In 1984 Klebe and Tran Qui reported the first crystal structure of a hexacoordinated silicon bis-chelate with 8-oxyquinolinato (oxinato) ligands, *i. e.*, (oxinate)<sub>2</sub>SiMeCl (**I**) [1]. Their analysis confirmed the hexacoordination of the Si atom and revealed a silicon coordination sphere with the Si–N bonds *trans* to the monodentate substituents Me and Cl, whereas the O atoms are *trans* to each other. In our studies of silicon bis-chelates with two oxinato ligands [2–4]

we found this coordination pattern to dominate the portfolio of isomers (found for (oxinate)<sub>2</sub>SiRR' with R, R' = Ph, Ph; Ph, Me; (CH<sub>2</sub>)<sub>3</sub>; (CH<sub>2</sub>)<sub>4</sub>; (CH<sub>2</sub>)<sub>5</sub> and the related complex (8-oxyquinaldinato)<sub>2</sub>SiPh(8-oxyquinaldiny) (**II**)). By contrast, we encountered the *N,N-trans-O,O-cis* coordination mode in only one case (the tris-chelate (oxinate)<sub>2</sub>Si(PhN–CH<sub>2</sub>CH<sub>2</sub>–NPh), **III**) and the intermediate all-*cis* coordination mode with Ph, 8-oxyquinolinyl (**IV**). Furthermore, we reported three examples for silicon compounds with capped tetrahedral coordination spheres ([4+2]



or [4+1] coordination with Si...N separations  $>2.7 \text{ \AA}$ , *i. e.*, (oxinato)<sub>2</sub>SiRR' with R, R' = Me, Me (**V**); (CH<sub>2</sub>)<sub>5</sub> (**IX**, Scheme 1) and (CH<sub>2</sub>)<sub>6</sub> (**VI**). Further crystallographically confirmed hypercoordinated silicon complexes with 8-oxyquinolate among the ligands bear only one such ligand, either as a monodentate substituent (in (salen\*)SiPh(8-oxyquinoliny), **VII**, [5]) or as an *O,N*-chelating ligand (*e. g.*, in complex **VIII**, [6]) at a hexacoordinated silicon atom, and so far one pentacoordinated silicon oxinato complex (**X**, Scheme 1) has been confirmed crystallographically [4].

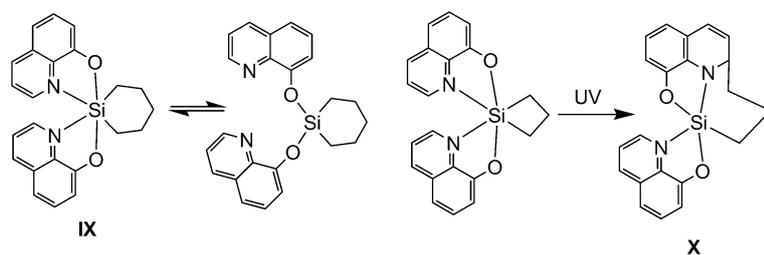
The still rather limited insights into the coordination behavior of oxinate in the ligand sphere of a silicon atom (whereas various more complex *O,N*-chelating ligands have already been utilized in silicon coordination chemistry [7–20]) and the occasional findings of surprising reactivity patterns of oxinato silicon complexes (*e. g.*, temperature-dependent coordination equilibria and UV-induced rearrangement reac-

tions, Scheme 1 [4]) served as a motivation for us to explore the chemistry of oxinato silicon compounds in more detail.

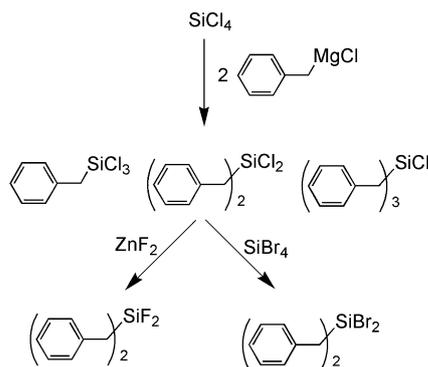
## Results and Discussion

### Benzylchlorosilanes

In the context of different investigations we had synthesized dibenzylchlorosilane (Bn<sub>2</sub>SiCl<sub>2</sub>,  $\delta^{29}\text{Si} = 22.6 \text{ ppm}$ ) and benzyltrichlorosilane (BnSiCl<sub>3</sub>,  $\delta^{29}\text{Si} = 7.6 \text{ ppm}$ ) [21], which are relevant starting materials for this study, and from Bn<sub>2</sub>SiCl<sub>2</sub> we had also prepared the fluoro and bromo derivatives Bn<sub>2</sub>SiF<sub>2</sub> ( $\delta^{29}\text{Si} = -10.7 \text{ ppm}$ ) and Bn<sub>2</sub>SiBr<sub>2</sub> ( $\delta^{29}\text{Si} = 17.2 \text{ ppm}$ ) (Scheme 2). <sup>29</sup>Si NMR investigations of these benzylsilanes revealed noticeably upfield-shifted signals with respect to those of the corresponding methylsilanes MeSiCl<sub>3</sub> ( $\delta^{29}\text{Si} = 12.2 \text{ ppm}$ ) or Me<sub>2</sub>SiX<sub>2</sub> ( $\delta^{29}\text{Si}$



Scheme 1.



Scheme 2.

= 4.4, 31.8, 19.2 ppm for X = F, Cl, Br, respectively) [22]. As we observed the same phenomenon of relatively upfield-shifted  $^{29}\text{Si}$  NMR signals during our investigation of benzyl-substituted oxinato complexes (*vide infra*), we also strived for an investigation of the molecular structures of benzylhalosilanes and the influence of the benzyl group on the  $^{29}\text{Si}$  NMR shift, which will be presented in this paragraph.

The reaction of  $\text{SiCl}_4$  with a commercially available benzylmagnesiumchloride solution in a 1 : 2 stoichiometric ratio (aiming at maximum yield in dibenzylchlorosilane) afforded a mixture of  $\text{BnSiCl}_3$ ,  $\text{Bn}_2\text{SiCl}_2$  and  $\text{Bn}_3\text{SiCl}$ , the components of which were isolated in yields of 5, 68 and 0.6%, respectively (based on  $\text{BnMgCl}$ ). Whereas the mono- and disubstituted silanes were separated by vacuum distillation,  $\text{Bn}_3\text{SiCl}$  was recrystallized from the residue. The solid-state structure of  $\text{Bn}_3\text{SiCl}$  has already been reported by Osakada *et al.* [23].  $\text{Bn}_2\text{SiCl}_2$  crystallized upon cooling to room temperature, and a single-crystalline shard thereof proved suitable for X-ray diffraction analysis (Fig. 1).  $\text{BnSiCl}_3$ , obtained as the first fraction of the vacuum distillation, was placed in a freezer ( $-20^\circ\text{C}$ ), whereupon a solid formed which also allowed for manual extraction of single-crystalline pieces on an ice-cooled Petri dish, thus giving access to their X-ray diffraction analysis (Fig. 1). The molecular structures of  $\text{BnSiCl}_3$  and  $\text{Bn}_2\text{SiCl}_2$  reveal a special arrangement of one phenyl group with respect to the Si-bound chlorine atoms (axis through the *o*-carbon atoms almost parallel to  $\text{Cl1}-\text{Cl2}$  in  $\text{Bn}_2\text{SiCl}_2$  and to  $\text{Cl}_2-\text{Cl}_3$  in  $\text{BnSiCl}_3$ ), which can alternatively be described as an almost perpendicular arrangement of the phenyl ring with respect to the plane created by the Si-C-

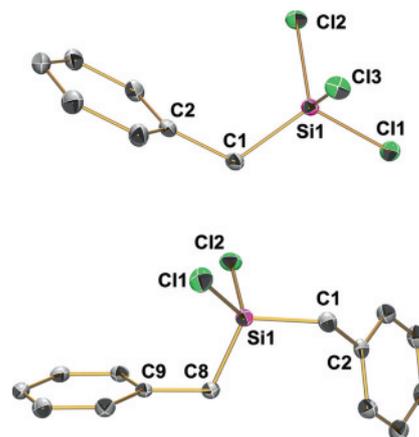


Fig. 1 (color online). Molecular structure of (from top) benzyltrichlorosilane and dibenzylchlorosilane in the crystal. (Displacement ellipsoids are shown at the 50% probability level, hydrogen atoms are omitted). Selected bond lengths (Å) and angles (deg):  $\text{BnSiCl}_3$ : Si1–C11 2.031(1), Si1–C12 2.032(1), Si1–C13 2.032(1), Si1–C1 1.849(2); Si1–C1–C2 113.6(2), C11–Si1–C1–C2 172.2(2);  $\text{Bn}_2\text{SiCl}_2$ : Si1–C11 2.052(1), Si1–C12 2.060(1), Si1–C1 1.857(1), Si1–C8 1.854(2); Si1–C1–C2 114.1(1), Si1–C8–C9 115.0(1), C1–Si1–C8–C9 171.4(1);  $\text{Bn}_2\text{SiBr}_2$  (atomic labels correspond to those in  $\text{Bn}_2\text{SiCl}_2$ ): Si1–Br1 2.210(1), Si1–Br2 2.223(1), Si1–C1 1.866(2), Si1–C8 1.861(2); Si1–C1–C2 114.6(1), Si1–C8–C9 115.3(1), C1–Si1–C8–C9 170.5(1).

C sequence of the respective benzyl group. This arrangement was also found for  $\text{Bn}_2\text{SiBr}_2$  (not depicted), which is isostructural with its chloro analog. The preferred arrangement of electron-donating groups in  $\alpha$ -position of silanes towards the positively polarized silicon atom (*e. g.*, in  $(\text{F}_3\text{C})\text{F}_2\text{Si}-\text{O}-\text{NMe}_2$  the *N*-lone pair is directed towards the silicon atom [24]) is well-known from the literature. This so-called  $\alpha$ -effect results in particular features of these so-called  $\alpha$ -silanes, *e. g.*, high-field shifted  $^{29}\text{Si}$  NMR resonances due to additional electron donation. The Si–C–C bond angles found in the molecular structures of  $\text{BnSiCl}_3$  ( $113.6(2)^\circ$ ) and  $\text{Bn}_2\text{SiCl}_2$  ( $114.1(1)$  and  $115.0(1)^\circ$ ), which are significantly wider than the tetrahedral angle, cannot support the concept of  $\alpha$ -silanes with benzyl being a special  $\alpha$ -substituent. Thus, minimization of intermolecular repulsive forces might render the present positions of the benzyl groups more favorable rather than the action of significant electrostatic attractions. In order to analyze the reasonability of retention of this  $\text{Ph-CH}_2\text{-SiX}_2$  arrangement in solution and its effect on the  $^{29}\text{Si}$  NMR shift, the gas-phase molecular

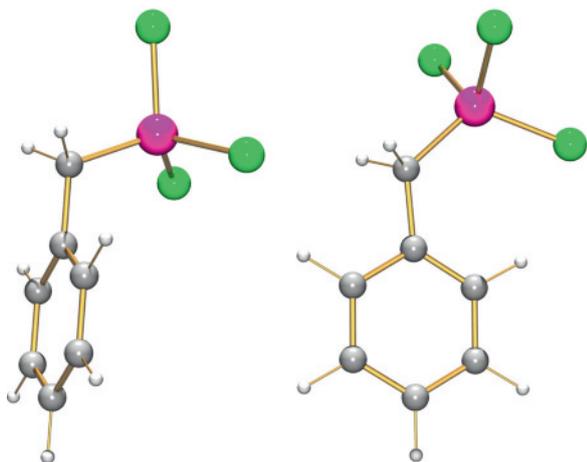


Fig. 2 (color online). Molecular conformation of benzyltrichlorosilane with minimum (left) and maximum energy (right) in the potential energy surface scan (see Fig. 3).

structures of benzyltrihalosilanes  $\text{BnSiX}_3$  ( $X = \text{F}, \text{Cl}, \text{Br}$ ) were optimized at the B3LYP/6-311G(d,p) level of theory. All of them revealed a minimum energy conformation similar to that found for  $\text{BnSiCl}_3$  in the solid state (Fig. 2, left). A potential energy surface scan was then performed, in which the  $\text{SiX}_3$  group was rotated about the Si–C bond in increments of  $2^\circ$  ( $60^\circ$  in total), in conjunction with a  $180^\circ$  rotation of the phenyl group about the (Si)C–C(Ph) bond (in increments of  $2^\circ$ ). Each rotation was followed by relaxation of the atomic coordinates (only keeping the two angles of interest restrained). The resulting energy surface profile for  $\text{BnSiCl}_3$  ( $\Delta E_{\text{max}} = 8.3 \text{ kcal mol}^{-1}$ ) is depicted in Fig. 3. Benzyltrifluoro- and -tribromosilane delivered similar energy surface patterns with  $\Delta E_{\text{max}}$  being 4.1 and  $8.9 \text{ kcal mol}^{-1}$ , respectively. For  $\text{BnSiCl}_3$  the molecular conformation of highest energy with respect to the above energy surface scan is depicted in Fig. 2, right. One can easily conclude that repulsive forces result from intramolecular interactions between one chlorine atom and an *ortho*-hydrogen atom of the benzyl group. The energy differences of about  $4\text{--}8 \text{ kcal mol}^{-1}$  give rise to the assumption that the most likely molecular structures of benzyltrihalosilanes in solution may differ only slightly from the molecular shape found for  $\text{BnSiCl}_3$  in the solid state and in the optimized gas-phase structures  $\text{BnSiX}_3$ , as far as the orientation of the benzene ring with respect to the silicon atom is concerned, but rotation of the phenyl group is still easily possible at room temperature. Rotations

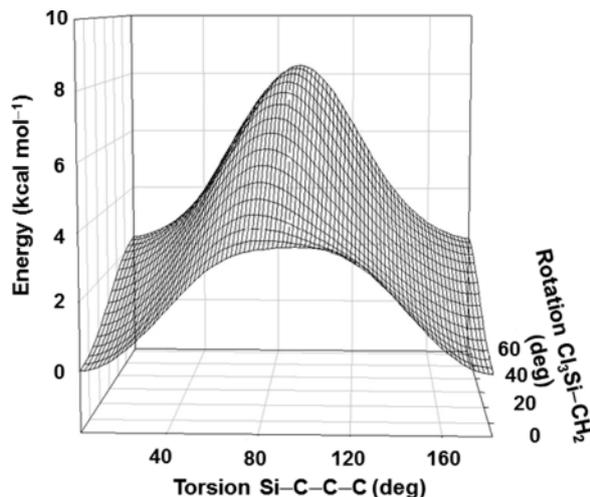
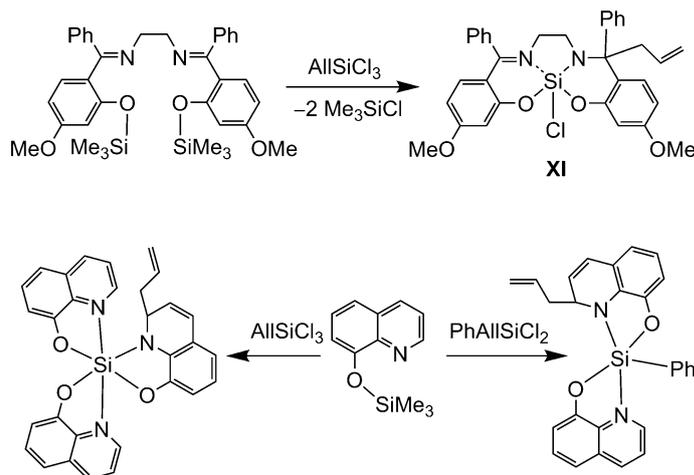


Fig. 3. Potential energy surface scan of benzyltrichlorosilane for the rotation about the Si–C bond (front to back) and variation of the Si–C–C–C dihedral angle (left to right).

of the  $\text{SiX}_3$  moiety about the Si–C bond, however, are significantly less hindered ( $2 \text{ kcal mol}^{-1}$ ). Thus, at least the relative arrangement of the benzene ring with respect to the silicon atom as depicted in Fig. 2 (left) should noticeably contribute to the predominant molecular arrangement of benzyltrihalosilanes in solution.

The magnetic anisotropy of  $\pi$ -electron systems, *e. g.*, benzene, and the shielding *vs.* deshielding effects resulting therefrom can significantly contribute to the overall shielding of the nuclei, *e. g.*, protons, which are situated in plane with or orthogonal to the benzene ring current. Hence, the so-called shielding cone of the benzene ring might provide an explanation for high-field shifted  $^{29}\text{Si}$  NMR resonances in benzylhalo- *vs.* alkylhalosilanes. Quantum-chemical calculations at the B3LYP/6-311G+(2d,p) and HF/6-311G+(2d,p) levels predicted  $^{29}\text{Si}$  NMR shifts of 31.6 and 19.8 ppm, respectively, for  $\text{BnSiCl}_3$  in the molecular conformation shown in Fig. 2, left, and shifts of 35.3 and 21.8 ppm, respectively, for the conformation shown in Fig. 2, right. Even though the chemical shifts calculated are noticeably off the experimental value (7.6 ppm) and depend on the method and basis set used, the rather small differences between the shifts calculated for the different molecular conformations clearly indicate that the arrangement of the benzyl group found in the solid state contributes only to a limited extent to an upfield shift of the  $^{29}\text{Si}$  resonance.



Scheme 3.

Thus, as hypercoordination ( $\alpha$ -effect) and magnetic anisotropy of the aromatic system do not play the key role for the upfield-shifted  $^{29}\text{Si}$  NMR signals of benzylsilanes, we attribute it to the properties of the Si–C bond to the Bn substituent (*i. e.*, the dia- and paramagnetic (de)shielding contributions associated therewith).

#### Reactions of allyl- and benzylchlorosilanes with 8-trimethylsilyloxyquinoline

Inspired by the allyl 1,3-shift from allylsilanes to an imine ligand (*e. g.*, formation of **XI**, Scheme 3, [25, 26]) and the UV-driven rearrangement of the complexes (oxinate) $_2\text{Si}(\text{CH}_2)_n$  ( $n = 3, 4, 5, 6$ ) [4] (as shown for **X** in Scheme 1), which proves the oxinate-2-position to be an “aromatically camouflaged” imine C atom, we investigated the reaction of allyltrichlorosilane with 8-trimethylsilyloxyquinoline (Scheme 3). To our surprise, despite using the rather mild ligand transfer reagent (oxinate) $\text{SiMe}_3$  and allyltrichlorosilane in a 1.8 : 1.0 molar ratio, we obtained the complex (oxinate) $_2\text{Si}(\text{adho})$  (which requires three equivalents of the oxinate for its formation) as chloroform solvate in 60% yield. Its molecular structure is shown in Fig. 4.

Both the crystallographic analysis and the  $^{29}\text{Si}$  CP/MAS NMR spectroscopic data ( $\delta_{\text{iso}} = -146.6$  ppm) confirmed the rearrangement of the allyl group to the formal imine C atom of one oxinate ligand with formation of the hexacoordinated silicon tris-chelate. Changing the molar ratio of the starting materials to 2.7 : 1.0 had only a marginal impact on the yield (62%), and

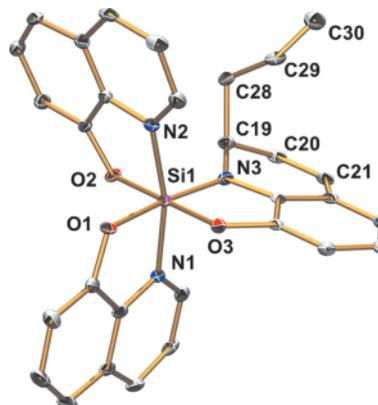
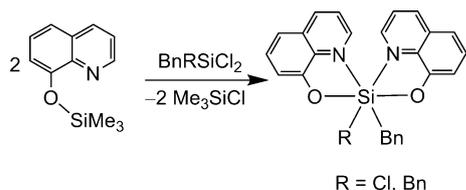


Fig. 4 (color online). Molecular structure of (oxinate) $_2\text{Si}(\text{adho})$  in a crystal of its 1.5( $\text{CHCl}_3$ ) solvate. (Displacement ellipsoids are shown at the 50% probability level, hydrogen atoms are omitted). The asymmetric unit comprises two molecules of the complex and three  $\text{CHCl}_3$  molecules, but the doubled size of the unit cell mainly arises from partial ordering of the otherwise (at room temperature) disordered solvent molecules, while the two complex molecules are pseudo-symmetry-related and thus exhibit basically identical structural features. Selected bond lengths ( $\text{\AA}$ ): Si1–O1 1.783(2), Si1–O2 1.769(2), Si1–O3 1.767(2), Si1–N1 1.961(2), Si1–N2 1.947(2), Si1–N3 1.811(2), N3–C19 1.482(3), C19–C20 1.505(4), C20–C21 1.337(4), C19–C28 1.548(3), C28–C29 1.499(4), C29–C30 1.313(4). The sum of the angles about N3 amounts to  $359.9^\circ$ .

we thus conclude that the allyl rearrangement product (oxinate) $_2\text{Si}(\text{adho})$  is the favored reaction product in this system of reactants under these conditions. Kost *et al.* [27] had reported the rearrangement of a *t*Bu



Scheme 4.

group to an unsaturated ligand moiety upon the entry of a third chelating ligand into the Si coordination sphere. In order to check whether the third oxinate ligand is essential to induce allyl rearrangement from the Si atom to the oxinate C2 atom or whether the rearrangement would also proceed at the stage of a bis-chelate  $(\text{oxinate})_2\text{SiAlCl}$ , we performed the analogous reaction with allylphenyldichlorosilane (Scheme 3), which should result either in the formation of a bis-chelate  $(\text{oxinate})_2\text{SiAlPh}$  or of its rearrangement product  $(\text{oxinate})\text{SiPh(adho)}$  with a pentacoordinated silicon atom. As found in the reaction with allyltrichlorosilane, we also observed the formation of a red product solution in this case, and  $^{29}\text{Si}$  NMR spectroscopic investigations of the crude product solution confirmed the formation of compounds with a pentacoordinated silicon atom ( $\delta^{29}\text{Si} = -84.3, -87.9, -90.9$  ppm). The presence of three signals in the characteristic shift range of pentacoordinated silicon atoms gives rise to the assumption that different isomers of  $(\text{oxinate})\text{SiPh(adho)}$  coexist in solution.

As an oxinate ligand contains a “camouflaged imine moiety” which can react in an imine-like manner in this allyl-1,3-shift reaction, we aimed at introducing benzyl as a “camouflaged allyl moiety” into the complex as well. In sharp contrast, the reactions of the benzylchlorosilanes  $\text{BnSiCl}_3$  and  $\text{Bn}_2\text{SiCl}_2$  with two equivalents of 8-trimethylsilyloxyquinoline only afforded the transsilylation products  $(\text{oxinate})_2\text{SiBnCl}$  and  $(\text{oxinate})_2\text{SiBn}_2$ , respectively (Scheme 4, Fig. 5). Even the reaction of  $\text{BnSiCl}_3$  with three equivalents of 8-trimethylsilyloxyquinoline only afforded  $(\text{oxinate})_2\text{SiBnCl}$ , and the third equivalent of the ligand did not react with the Si-bound Cl atom of this bis-chelate complex.

In addition to underlining that benzyl does not reflect a “camouflaged allyl” in terms of the intended 1,3-shift reaction, the formation of  $(\text{oxinate})_2\text{SiBnCl}$  provides support for the hypothesis that the allyl 1,3-shift reaction already proceeds at the bis-chelate

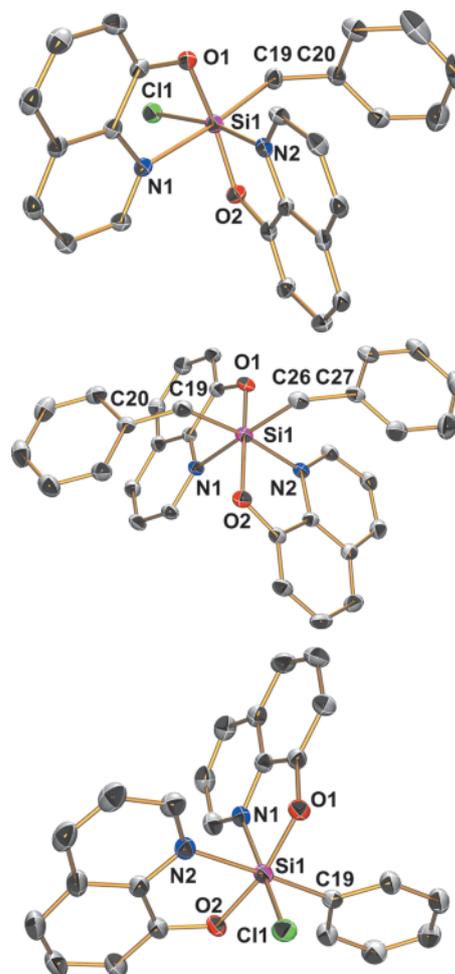


Fig. 5 (color online). Molecular structures of (from top)  $(\text{oxinate})_2\text{SiBnCl}$ ,  $(\text{oxinate})_2\text{SiBn}_2$  (in its  $\text{CHCl}_3$  solvate) and  $(\text{oxinate})_2\text{SiPhCl}$  (in its  $\text{CHCl}_3$  solvate) with displacement ellipsoids set at the 50%, 50% and 30% probability level, respectively (hydrogen atoms are omitted). Selected bond lengths (Å) and angles (deg):  $(\text{oxinate})_2\text{SiBnCl}$ : Si1–Cl1 2.230(1), Si1–O1 1.767(2), Si1–O2 1.771(2), Si1–N1 2.013(2), Si1–N2 1.982(2), Si1–C19 1.915(2); Si1–C19–C20 118.1(2);  $(\text{oxinate})_2\text{SiBn}_2$ : Si1–O1 1.784(1), Si1–O2 1.789(1), Si1–N1 2.073(2), Si1–N2 2.055(2), Si1–C19 1.931(2), Si1–C26 1.933(2); Si1–C19–C20 121.8(1), Si1–C26–C27 120.9(1);  $(\text{oxinate})_2\text{SiPhCl}$ : Si1–Cl1 2.203(1), Si1–O1 1.763(2), Si1–O2 1.753(2), Si1–N1 2.013(2), Si1–N2 2.012(2), Si1–C19 1.903(3).

stage  $(\text{oxinate})_2\text{SiAlCl}$  (which is generally possible as shown by the reaction of 8-trimethylsilyloxyquinoline with allylphenyldichlorosilane, *vide supra*), because the rearrangement product  $(\text{oxinate})\text{SiCl(adho)}$  with

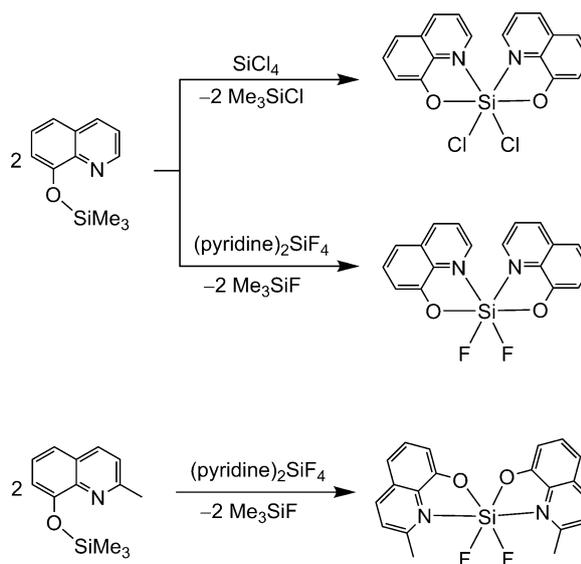
a pentacoordinated silicon atom can be expected to be more susceptible to further ligand exchange reactions, *i. e.*, transsilylation with a third equivalent of 8-trimethylsiloxyquinoline, whereas the hexacoordinated Si complex (oxinate)<sub>2</sub>SiAlCl should be rather inert towards further transsilylation (in analogy to (oxinate)<sub>2</sub>SiBnCl).

The comparison of the Si–N bonds in (oxinate)<sub>2</sub>–SiBnCl (2.01 and 1.98 Å) and (oxinate)<sub>2</sub>SiBn<sub>2</sub> (2.07 and 2.06 Å) indicates that the *trans*-disposed Si–X bond (X = Cl *vs.* C) plays a less pronounced role than the overall (“spherical”) Lewis acidity caused by the more or less electron-withdrawing substituents (*i. e.*, introduction of one Cl substituent causes shortening of both Si–N bonds and has only a marginal effect on the particular shortening of the *trans*-Si–Cl-located Si–N bond). As the available literature data of Si–N bond lengths in (oxinate)<sub>2</sub>SiRX complexes are only of limited value for a comparison (heavy disorder of the structure with R, X = Me, Cl [1], similar bonds in the structure with R, R' = Me, Ph [2], O *trans* to X for R, X = Ph, 8-oxyquinoliny [3]), we synthesized (oxinate)<sub>2</sub>SiPhCl as another example of complexes of the type (oxinate)<sub>2</sub>SiRX with two Si–N bonds *trans* to the two different monodentate substituents (Fig. 5). In case of this compound we found basically identical (both 2.01 Å) Si–N bond lengths despite the two different *trans*-disposed substituents. Furthermore, the Si–N bond lengths for the compounds with R, X = Bn, Cl and Ph, Cl are similar to one another, and the Si–N bond lengths in the compounds with R, R' = Ph, Ph (2.09 Å) [2], Ph, Me (2.09–2.11 Å) [2], (CH<sub>2</sub>)<sub>5</sub> (2.09–2.13 Å) [4], and Bn, Bn (2.07, 2.06 Å) are also similar.

#### Syntheses of bis-chelates with two Si–X (X = F, Cl) bonds

Motivated by the successful preparation of crystalline bis-oxinato silicon complexes suitable for X-ray diffraction *via* the transsilylation route and the still present lack of crystal structure data of complexes of the type (oxinate)<sub>2</sub>SiX<sub>2</sub> (X = halide), we synthesized (oxinate)<sub>2</sub>SiCl<sub>2</sub> and (oxinate)<sub>2</sub>SiF<sub>2</sub> (Scheme 5, Fig. 6).

Both complexes exhibit the same coordination mode (*O,O-trans*, N atoms *trans* to the monodentate substituents) as most of the other crystallographically characterized oxinato silicon bis-chelates. In 2005 [2] we had analyzed the potential isomers of the hexacoor-



Scheme 5.

dinated silicon complex (oxinate)<sub>2</sub>SiCl<sub>2</sub> by quantum-chemical calculations, <sup>29</sup>Si CP/MAS NMR and IR spectroscopy, and we had come to the conclusion that this complex most likely crystallizes as the all-*trans* isomer. In order to solve this contradiction, we recorded a <sup>29</sup>Si CP/MAS NMR spectrum of the (oxinate)<sub>2</sub>SiCl<sub>2</sub> obtained in the current study. The spectrum basically resembles that of the previous study (*i. e.*, only one signal located at –158.7 ppm). In contrast to the previously recorded spectrum (with a signal located at –157.9 ppm) the signal is slightly shifted upfield. We cannot rule out contributions of experimental errors and the effect of crystal size to cause this shift, but the width of the signal (caused by the chloro substituents) would at least allow for the appearance as a single signal even in case of a superposition of signals of two isomers. Therefore, we also recorded a powder X-ray diffractogram of our product (oxinate)<sub>2</sub>SiCl<sub>2</sub> and found a good match with the pattern predicted from the single-crystal structure. Some reflections of moderate intensity, however, could not be assigned, neither to the crystal structure of (oxinate)<sub>2</sub>SiCl<sub>2</sub> nor to the crystal structure of the potential contaminant 8-oxyquinoline hydrochloride [28] (see Supporting Information). These findings, and the very similar relative energies calculated for the herein found isomer of (oxinate)<sub>2</sub>SiCl<sub>2</sub> and its all-*trans* alternative [2] now give rise to the assumption that both

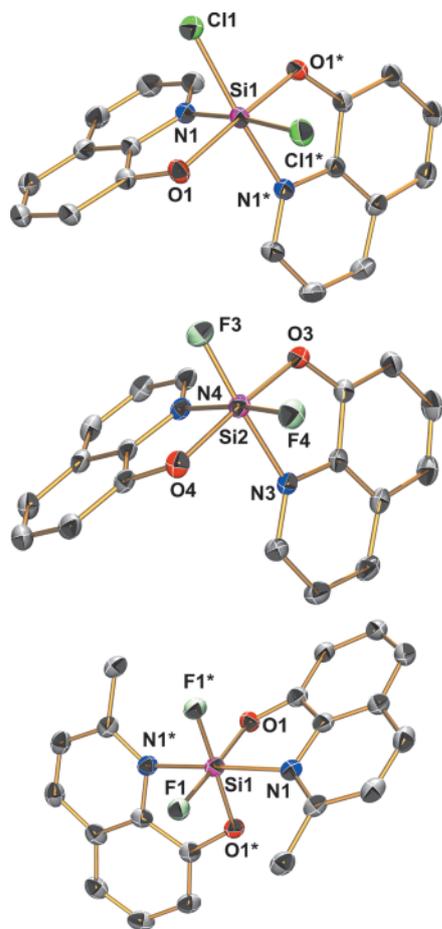
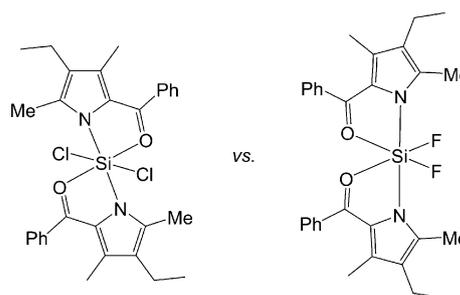


Fig. 6 (color online). Molecular structures of (from top)  $(\text{oxinate})_2\text{SiCl}_2$ ,  $(\text{oxinate})_2\text{SiF}_2$  (in its solvate  $\cdot 1.5(\text{CHCl}_3)$ ) and  $(8\text{-oxyquinaldinate})_2\text{SiF}_2$  with displacement ellipsoids set at the 50% probability level (hydrogen atoms are omitted). The structure of  $(\text{oxinate})_2\text{SiF}_2$  contains four independent complex molecules in the asymmetric unit, but only one of them is depicted as a representative example. The asymmetric units of each of the other two structures consist of half a molecule, with the Si atom located on a two-fold axis. Atom labels with asterisks indicate symmetry equivalent positions. Selected bond lengths ( $\text{\AA}$ ):  $(\text{oxinate})_2\text{SiCl}_2$ : Si1–Cl1 2.187(1), Si1–O1 1.749(1), Si1–N1 1.966(2);  $(\text{oxinate})_2\text{SiF}_2$ : Si2–F3 1.644(1), Si2–F4 1.642(1), Si2–O3 1.765(1), Si2–O4 1.752(1), Si2–N3 1.983(1), Si2–N4 1.977(1);  $(8\text{-oxyquinaldinate})_2\text{SiF}_2$ : Si1–F1 1.658(1), Si1–O1 1.769(2), Si1–N1 1.947(2).

isomers coexist in solution and precipitate/crystallize as mixtures with the fractions of the isomers depending on subtle differences between the individual syntheses performed.



Scheme 6.

Another surprising finding is that both complexes  $(\text{oxinate})_2\text{SiCl}_2$  and  $(\text{oxinate})_2\text{SiF}_2$  crystallize as the same isomer (*O,O-trans* mode). In studies of hexacoordinated silicon bis-chelates with other (*O,N*)-bidentate chelators (Scheme 6 [29, 30]) the size difference of Cl vs. O vs. F led to the formation of different isomers for the dichloro vs. the difluoro complex. That is, the substituent in close proximity to the  $sp^2$ -hybridized N atom prefers to face the smaller O atom in case of the chloro complex but faces the F atom in the difluoro complex because of the lower steric repulsion with the smaller F atom (relative to the O atom). In case of the oxinato complexes we have shown [2, 3] that hydrogen contacts between the H atom in 2-position of the oxinate and a lone-pair donor atom stabilize the Si coordination sphere. Apparently, the H contact to the neighboring oxinate O atom is favored over the alternative H contact to a fluorine atom, thus over-compensating the influence of steric repulsion by the slightly bigger O atom. Replacement of the CH moiety in 2-position by a CMe moiety (*i. e.*, using the 8-oxyquinaldinate ligand) eventually drives the still hexacoordinated silicon complex into the alternative *N,N-trans* coordination mode, now with the CMe moieties facing the F atoms (Scheme 5, Fig. 6).

For comparison of the energetics of these two alternative isomers (depending on the chelating ligand oxinate vs. 8-oxyquinaldinate and on the size of the halide Cl vs. F) we have performed quantum-chemical calculations (full optimization of the gas-phase molecular conformation at the DFT MPW1PW91 6-311G(d,p) level, single-point energy calculations at the MP2 6-31G(d) level). The relative energies are shown in Table 1, atomic coordinates of the optimized molecular structures are available in the Supporting Information (available online, see note at the end of the paper for availability). This analysis confirms that the complexes

Table 1. Relative energies of sets of two isomers *O,O-trans* and *N,N-trans* (kcal mol<sup>-1</sup>) of the complexes (chelator)<sub>2</sub>SiX<sub>2</sub>. The first entry corresponds to the optimized structure at the DFT MPW1PW91 6-311G(d,p) level, the entry in parentheses corresponds to the single-point calculation at the MP2 6-31G(d) level.

Chelator	X	<i>O,O-trans</i>	<i>N,N-trans</i>
Oxinate	F	2.7 (0)	0 (0.7)
	Cl	1.8 (0)	0 (1.9)
8-Oxyquinaldinate	F	6.7 (2.4)	0 (0)
	Cl	0 (0)	2.0 (5.9)

(oxinate)<sub>2</sub>SiX<sub>2</sub> exhibit similar energies for their alternative *O,O-trans* and *N,N-trans* coordination modes, whereas for (8-oxyquinaldinate)<sub>2</sub>SiX<sub>2</sub> the response to the steric demand of the halide is clearly reflected in *N,N-trans* being the favored coordination mode for the fluoro derivative, whereas *O,O-trans* is more favorable for the chloro derivative.

In the crystal structures of the complexes shown in Fig. 6 we find surprisingly similar bond lengths. Neither the transition from (oxinate)<sub>2</sub>SiCl<sub>2</sub> to its fluoro analog caused any noteworthy changes in Si–O and Si–N bond lengths, nor did the change of coordination mode and steric repulsion by a different ligand cause any significant changes to the Si–F, Si–O and Si–N separations (upon switching to (8-oxyquinaldinate)<sub>2</sub>SiF<sub>2</sub>). In comparison with the complexes (oxinate)<sub>2</sub>SiRR' and (oxinate)<sub>2</sub>SiRX we find systematically shorter Si–N bonds in the (oxinate)<sub>2</sub>SiX<sub>2</sub> compounds (to a less pronounced extent this trend is also reflected in the Si–O bond lengths), with the shortest Si–N separation encountered in (8-oxyquinaldinate)<sub>2</sub>SiF<sub>2</sub> (1.95 Å). This bond length corresponds nicely to the Si–N(oxinate) bond lengths in (oxinate)<sub>2</sub>Si(PhN(CH<sub>2</sub>)<sub>2</sub>NPh) [2] and (oxinate)<sub>2</sub>Si(adho), which are also 1.95/1.96 Å; this compound exhibits the same *N,N-trans* coordination mode of the *O,N*-chelators.

As (oxinate)<sub>2</sub>SiF<sub>2</sub> and (8-oxyquinaldinate)<sub>2</sub>SiF<sub>2</sub> contain Si–F bonds *cis* to each other, we expected a <sup>29</sup>Si CP/MAS NMR signal shape similar to that of other hexacoordinated difluorosilicon complexes [6, 30, 31], *i.e.*, a dublettoid signal caused by dipolar coupling of the *cis*-arranged fluorine atoms instead of an intentionally expected triplet-like signal. Indeed, this signal shape was observed in both cases (spectra available in the Supporting Information), but at different chemical shifts ( $\delta_{\text{iso}} = -163$  ppm

Table 2. Solid-state <sup>29</sup>Si NMR shifts  $\delta_{\text{iso}}$  (in ppm relative to TMS) of various hexacoordinated silicon chelates with two oxinato (or related) ligands.

	$\delta_{\text{iso}}^{\text{29Si}}$	remarks	Lit.
(oxinate) <sub>2</sub> SiPhMe	-126		[2]
(oxinate) <sub>2</sub> SiPh <sub>2</sub>	-137		[2]
(oxinate) <sub>2</sub> SiBn <sub>2</sub>	-124/-130	<sup>a</sup>	this work
(oxinate) <sub>2</sub> Si(CH <sub>2</sub> ) <sub>3</sub>	-130		[4]
(oxinate) <sub>2</sub> Si(CH <sub>2</sub> ) <sub>4</sub>	-99		[4]
(oxinate) <sub>2</sub> Si(CH <sub>2</sub> ) <sub>5</sub>	-112/-114	<sup>b</sup>	[4]
(oxinate) <sub>2</sub> SiPhCl	-152		this work
(oxinate) <sub>2</sub> SiBnCl	-140		this work
(oxinate) <sub>2</sub> SiPh (8-oxyquinoliny)	-147		[3]
(oxinate) <sub>2</sub> SiF <sub>2</sub>	-163		this work
(oxinate) <sub>2</sub> SiCl <sub>2</sub>	-158/-159	<sup>c</sup>	[2] and this work
(oxinate) <sub>2</sub> SiBr <sub>2</sub>	-170	<sup>d</sup>	[2]
(oxinate) <sub>2</sub> Si(PhN(CH <sub>2</sub> ) <sub>2</sub> NPh)	-152		[2]
(oxinate) <sub>2</sub> Si(adho)	-147		this work
(oxinate) <sub>3</sub> Si <sup>+</sup>	-151	<sup>e</sup>	[2]
(8-oxyquinaldinate) <sub>2</sub> SiPh (8-oxyquinoliny)	-114	<sup>f</sup>	[3]
(8-oxyquinaldinate) <sub>2</sub> SiF <sub>2</sub>	-158		this work

<sup>a</sup> We attribute the presence of two signals to a phase transformation upon partial loss of solvent of crystallization; <sup>b</sup> the crystallographic asymmetric unit comprises two independent molecules; <sup>c</sup> only for the 2<sup>nd</sup> entry the crystal structure has been determined; <sup>d</sup> broad signal, no crystal structure reported; <sup>e</sup> the counter ion is chloride, no crystal structure reported; <sup>f</sup> the Si–N bonds in this complex are noticeably longer (2.18 and 2.26 Å) than in the other complexes (1.95–2.12 Å).

for (oxinate)<sub>2</sub>SiF<sub>2</sub>·1.5(CHCl<sub>3</sub>), -158 ppm for (8-oxyquinaldinate)<sub>2</sub>SiF<sub>2</sub>).

With the current study the portfolio of crystallographically and <sup>29</sup>Si NMR spectroscopically (solid state) characterized bis-chelates (oxinate)<sub>2</sub>SiRR' and analogs has grown noticeably. Table 2 shows their <sup>29</sup>Si CP/MAS NMR shifts ( $\delta_{\text{iso}}$ ), which now allow for further comparison within this class of complexes. The hydrocarbyl-substituted compounds with Si(CH<sub>2</sub>)<sub>5</sub>, SiMePh and SiPh<sub>2</sub> moieties reflect the trend of upfield-shifted <sup>29</sup>Si NMR signals upon replacing alkyl by aryl substituents, which has also been observed with other silicon compounds [32]. The “outlier” complexes with Si(CH<sub>2</sub>)<sub>4</sub> and Si(CH<sub>2</sub>)<sub>3</sub> moieties simply reflect the trend of alternating up- and downfield-shifted signals of homologous silacycloalkanes, which has already been reported [4]. The complex (oxinate)<sub>2</sub>SiBn<sub>2</sub> seems to represent another outlier from this series, but the investigation of other benzylhalosilanes (*vide supra*) already shows that benzyl does not reflect typical alkyl

character in terms of its influence on  $^{29}\text{Si}$  NMR shifts but causes an upfield shift of the resonance with respect to “regular” alkyl groups. Replacing one hydrocarbyl group by a more electronegative substituent (Cl or aryloxy) causes a further upfield shift of the  $^{29}\text{Si}$  resonance, and the same is observed even more pronounced for systems with both hydrocarbyls replaced by ligands with more electronegative donor atoms. In the series  $(\text{oxinate})_2\text{SiX}_2$  ( $X = \text{F}, \text{Cl}, \text{Br}$ ) some kind of “sagging pattern” is observed as in case of the silicon halides  $\text{SiX}_4$  with  $\text{SiCl}_4$  exhibiting the most downfield resonance. This behavior can be attributed to the different dia- and paramagnetic and relativistic contributions to the  $^{29}\text{Si}$  shielding in silicon halides [33].

## Conclusion

Our continuation of the exploration of syntheses of hypercoordinated silicon compounds with oxinate and 8-oxyquinadinate ligands has proven oxinate susceptible to an allyl-1,3-shift from silicon to the oxinate C2 atom. Benzyl, although resembling a camouflaged allyl group, was retained bound to the hexacoordinated silicon atom, *e. g.*, in  $(\text{oxinate})_2\text{SiBnCl}$ . New insights into oxinate coordination patterns (coordination modes and Si–N bond lengths depending on the other Si-bound substituents) were obtained from this and other halide-substituted silicon complexes which have been prepared in the course of this study. Last but not least, the solid-state structures of  $\text{BnSiCl}_3$ ,  $\text{Bn}_2\text{SiCl}_2$  and  $\text{Bn}_2\text{SiBr}_2$  were determined, which enhance the portfolio of crystallographically characterized benzylsilanes significantly, and which allowed a closer look at the influence of the Si-bound benzyl group on the  $^{29}\text{Si}$  NMR shift.

## Experimental Section

General considerations: Most of the starting materials were commercially available and were used as received without further purification. Triethylamine and some solvents were distilled from sodium benzophenone (THF and diethyl ether) or sodium (hexane and toluene) and were stored over sodium wire (diethyl ether, hexane, toluene) or activated molecular sieves 3 Å under argon atmosphere (THF). Amylene-stabilized chloroform and acetonitrile were received in spectroscopic grade and were stored over activated molecular sieves 3 Å. All reactions were carried out under an atmosphere of dry argon utilizing standard Schlenk techniques. Solution-state  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra

were recorded on a Bruker Avance III 500 MHz spectrometer or on a Bruker DPX 400 spectrometer ( $\text{Me}_4\text{Si}$  as internal standard), solid-state  $^{29}\text{Si}$  NMR spectra were recorded on a Bruker Avance<sup>TM</sup> 400 MHz WB spectrometer in 4 mm  $\text{ZrO}_2$  rotors or in 7 mm  $\text{ZrO}_2$  rotors with Kelf inserts. Elemental analyses were performed using an Elementar vario MICRO cube.

### Dibenzylchlorosilane

A solution of benzylmagnesiumchloride (100 mL of a 2.0 M solution in THF, 200 mmol) was added dropwise to a cooled solution ( $-10^\circ\text{C}$ ) of tetrachlorosilane (19.5 g, 115 mmol) in THF (350 mL). The resulting cloudy yellow solution was allowed to reach room temperature and was stirred for another 2 h. The clear and almost colorless solution thus obtained was stored at room temperature for 1 d. Then the solvent was removed under reduced pressure, and the colorless oily residue was dissolved in hexane (200 mL). Immediately magnesium chloride precipitated. After stirring at room temperature for 1 h the precipitate was filtered off and washed with hexane ( $3 \times 40$  mL). From the combined filtrate and washings the solvent was removed in a vacuum, and the cloudy oily residue was again dissolved in hexane (100 mL), whereupon more magnesium chloride precipitated which, after stirring at room temperature for 1 h, was filtered off and washed with hexane (30 mL). Again, from the clear colorless filtrate the solvent was removed under reduced pressure, and the resulting oily product was distilled in a vacuum (3.0 mm Hg). Fraction 1 (benzyltrichlorosilane, yield: 2.36 g, 10.5 mmol, 5% with respect to benzylmagnesiumchloride) was obtained between 65 and  $75^\circ\text{C}$ . Some drops of an intermediate fraction (from 75 to  $140^\circ\text{C}$ ) were discarded before fraction 2 (dibenzylchlorosilane, yield: 19.1 g, 68.0 mmol, 68%) was received between 140 and  $147^\circ\text{C}$  as a colorless liquid which crystallized upon cooling to room temperature. The yellow oily residue was dissolved in hexane (19 mL), and colorless crystals of tribenzylchlorosilane were obtained at room temperature (yield: 1.40 g, 0.42 mmol, 0.6% with respect to benzylmagnesiumchloride).

The identity of benzyltrichlorosilane was confirmed by  $^{29}\text{Si}$  NMR (79.49 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta = 7.6$  ppm [10].

Dibenzylchlorosilane: Yield: 19.1 g (68.0 mmol, 68%).  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta = 2.60$  (s, 4 H,  $\text{CH}_2$ ), 7.05–7.35 ppm (m, 10 H, ar).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.62 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta = 28.7$  ( $\text{CH}_2$ ), 125.8 (*p*), 128.6, 129.1 (*o* and *m*), 133.8 ppm (*i*) (ar).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (79.74 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta = 22.6$  ppm.  $-\text{C}_{14}\text{H}_{14}\text{SiCl}_2$  (281.25): calcd. C 59.79, H 5.02; found C 59.20, H 5.08.

The identity of tribenzylchlorosilane was confirmed NMR spectroscopically:  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta = 2.33$  (s, 6 H,  $\text{CH}_2$ ), 7.05 (d, 6 H, ar,  $^3J_{\text{HH}} =$

7.6 Hz), 7.14–7.30 ppm (mm, 9 H, ar). –  $^{29}\text{Si}\{^1\text{H}\}$  NMR (79.74 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 21.1$  ppm.

#### Dibenzylidifluorosilane

To a solution of dibenzylidichlorosilane (1.57 g, 5.58 mmol) in THF (10 mL) zinc fluoride (1.15 g, 11.2 mmol) was added. After stirring at room temperature for 3 d the solvent was removed under reduced pressure. The colorless residue was dissolved in a mixture of hexane (10 mL) and toluene (5 mL) and allowed to stand overnight, and the zinc halides were filtered off. Removal of the solvents from the clear filtrate under reduced pressure afforded dibenzylidifluorosilane as a colorless oil. Yield: quantitative. –  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 2.26$  (s, 4 H,  $\text{CH}_2$ ), 7.02 (d, 4 H, ar,  $^3J_{\text{HH}} = 7.2$  Hz), 7.10–7.25 ppm (mm, 6 H, ar). –  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.62 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 21.0$  (t,  $^2J_{\text{FC}} = 14.0$  Hz,  $\text{CH}_2$ ), 125.6 (*p*), 128.7, 128.8 (*o* and *m*), 133.7 (*i*) ppm (ar). –  $^{29}\text{Si}\{^1\text{H}\}$  NMR (79.74 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = -10.7$  ppm (t,  $^1J_{\text{SiF}} = 310$  Hz).

#### Dibenzylidibromosilane

To a solution of dibenzylidichlorosilane (2.03 g, 7.21 mmol) in toluene (5 mL) tetrabromosilane (2.51 g, 7.21 mmol) was added at room temperature. The mixture was stirred under reflux for 2 h. After cooling to room temperature the volatiles were removed *in vacuo*, the viscous residue was again dissolved in toluene (4 mL), and tetrabromosilane (1.30 g, 3.74 mmol) was added. After stirring under reflux for 1 h and cooling to room temperature the volatiles were again removed under reduced pressure, and toluene (4 mL) and tetrabromosilane (1.50 g, 4.31 mmol) were added to the residue once again, followed by stirring the mixture under reflux for 1 h. Final removal of volatiles under reduced pressure afforded an oil which solidified at room temperature to yield beige crystals. Yield: quantitative. –  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 2.83$  (s, 4 H,  $\text{CH}_2$ ), 7.14 (d, 4 H, ar,  $^3J_{\text{HH}} = 6.8$  Hz), 7.17–7.30 ppm (mm, 6 H, ar). –  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.62 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 30.6$  ( $\text{CH}_2$ ), 125.9 (*p*), 128.5, 129.2 (*o* and *m*), 134.0 (*i*) ppm (ar). –  $^{29}\text{Si}\{^1\text{H}\}$  NMR (79.74 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 17.5$  ppm.

#### (Oxinate) $_2$ Si(adho)-1.5( $\text{CHCl}_3$ )

**Reaction 1:** To a stirred solution of 8-oxyquinoline (2.00 g, 13.7 mmol) and triethylamine (2.10 g, 20.6 mmol) in THF (50 mL) chlorotrimethylsilane (1.78 g, 16.4 mmol) was added at 0 °C. After 1 h stirring at this temperature the precipitated triethylammonium chloride was filtered off and washed with THF (10 mL). From the combined filtrate and washings the solvent was removed under reduced pressure, and the remaining oil was dissolved in chloroform (20 mL).

To this solution allyltrichlorosilane (1.32 g, 7.50 mmol) was added at 0 °C to afford a yellow solution, which turned orange and red within one day. The product was obtained after 3 d as a red crystalline solid which was filtered off, washed with chloroform (10 mL) and dried *in vacuo*. Yield: 1.93 g (2.84 mmol, 62%). –  $^{29}\text{Si}$  CP/MAS NMR (79.5 MHz,  $\nu_{\text{spin}} = 4$  kHz):  $\delta_{\text{iso}} = -146.6$  ppm. –  $\text{C}_{63}\text{H}_{49}\text{Cl}_9\text{N}_6\text{O}_6\text{Si}_2$  (1361.31): calcd. C 55.58, H 3.63, N 6.17; found C 55.62, H 3.61, N 6.20. (The characterization of this compound in solution was hampered by the very poor solubility in solvents such as chloroform or DMSO.)

**Reaction 2:** 8-Trimethylsiloxyquinoline (from 2.00 g, 13.7 mmol of 8-oxyquinoline) was prepared as described above, and it was dissolved in chloroform (20 mL). To this solution allyltrichlorosilane (0.88 g, 5.0 mmol) was added at 0 °C to afford a yellow solution, which turned orange and red within one day. The product was obtained after 3 d as a red crystalline solid which was filtered off, washed with chloroform (10 mL) and dried *in vacuo*. Yield: 1.86 g (2.73 mmol, 60%). –  $^{29}\text{Si}$  CP/MAS NMR (79.5 MHz,  $\nu_{\text{spin}} = 4$  kHz):  $\delta_{\text{iso}} = -146.6$  ppm.

#### (Oxinate)SiPh(adho)

To a stirred solution of 8-oxyquinoline (2.00 g, 13.7 mmol) and triethylamine (2.10 g, 20.6 mmol) in THF (50 mL) chlorotrimethylsilane (1.64 g, 15.1 mmol) was added at 0 °C. After 1 h stirring at this temperature the precipitated triethylammonium chloride was filtered off and washed with THF (10 mL). From the combined filtrate and washings the solvent was removed under reduced pressure, and the remaining oil was dissolved in chloroform (25 mL). To this solution allylphenyldichlorosilane (1.49 g, 6.86 mmol) was added at 0 °C to afford a yellow solution, which turned orange and red within few days. The volume of this still clear product solution was reduced to about 10 mL (by condensation of volatiles into a cold trap under reduced pressure), and a  $^{29}\text{Si}$  NMR spectrum was recorded (79.74 MHz,  $\text{D}_2\text{O}$  insert, 25 °C):  $\delta = 31.0$  ( $\text{Me}_3\text{SiCl}$ ), 20.4 (residual 8-trimethylsiloxyquinoline),  $-84.3$ ,  $-87.9$ ,  $-90.9$  ppm. So far, we have not been able to isolate one or more of the products from this solution by crystallization.

#### (Oxinate) $_2$ SiBnCl

8-Oxyquinoline (1.00 g, 6.85 mmol) and triethylamine (1.00 g, 9.78 mmol) were dissolved in THF (30 mL) and the mixture cooled to 0 °C; chlorotrimethylsilane (0.78 g, 7.2 mmol) was added dropwise. The triethylammonium chloride precipitate was filtered off and washed with THF (6 mL). From the filtrate and washings the solvent was removed under reduced pressure. The residue was dissolved in chloroform (3 mL), and benzyltrichlorosilane (0.78 g, 3.42 mmol) was added. The yellow product, which crystallized within

2 d, was filtered off, washed with THF and dried *in vacuo*. Yield: 1.42 g (3.21 mmol, 94%). – M. p. > 200 °C (decomposition without melting). – <sup>29</sup>Si CP/MAS NMR (79.5 MHz,  $\nu_{\text{spin}} = 5$  kHz):  $\delta_{\text{iso}} = -139.8$  ppm. – C<sub>25</sub>H<sub>19</sub>ClN<sub>2</sub>O<sub>2</sub>Si (442.96): calcd. C 67.78, H 4.32, N 6.32; found C 67.68, H, 4.42, N 6.23. (The characterization of this compound in solution was hampered by the very poor solubility in solvents such as chloroform or DMSO.)

(Oxinate)<sub>2</sub>SiBn<sub>2</sub>·CHCl<sub>3</sub>

To an ice-cooled stirred solution of 8-oxyquinoline (1.00 g, 6.85 mmol) and triethylamine (1.00 g, 9.78 mmol) in THF (30 mL) chlorotrimethylsilane (0.79 g, 7.3 mmol) was added. After 1 h the triethylammonium chloride precipitate was filtered off, washed with THF (6 mL) and discarded. From the combined filtrate and washings the solvent was removed under reduced pressure, and the remaining oil was dissolved in chloroform (3 mL), and solid dibenzylchlorosilane (0.98 g, 3.5 mmol) was added to the solu-

tion. The mixture was stored at a temperature of –50 °C, and the product was obtained as a crystalline solid (0.62 g, 1.0 mmol), which was filtered off, washed with chloroform (6 mL) and dried *in vacuo*. The filtrate and washings were concentrated by removing some solvent under reduced pressure, and a second charge of product was obtained upon storage at 6 °C (0.38 g, 0.62 mmol). Combined yield: 1.00 g (1.62 mmol, 46%). – <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 2.56$  (bs, 2 H; CH<sub>2</sub>); 6.57 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 2 H); 6.66 (m, 3 H); 6.90 (m, 1 H); 7.05 (d, <sup>3</sup>J<sub>HH</sub> = 8.22 Hz, 1 H); 7.12 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 1 H); 7.46 (t, <sup>3</sup>J<sub>HH</sub> = 8.08 Hz, 1 H); 7.90 (d, <sup>3</sup>J<sub>HH</sub> = 8.48 Hz, 1 H); 8.10 ppm (m, 1 H, HC=N). – <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 36.8$  (CH<sub>2</sub>), 111.4, 114.1, 121.3, 122.0, 126.8, 128.0, 128.7, 129.9, 135.9, 137.6, 141.7, 144.8, 154.4 ppm (HC=N). – <sup>29</sup>Si CP/MAS NMR (79.5 MHz,  $\nu_{\text{spin}} = 5$  kHz):  $\delta_{\text{iso}} = -124.3, -129.8$  ppm (two signals were detected because of loss of chloroform from the crystalline product upon drying; loss of chloroform was also confirmed by elemental analy-

Table 3. Crystal structure data for BnSiCl<sub>3</sub>, Bn<sub>2</sub>SiCl<sub>2</sub> and Bn<sub>2</sub>SiBr<sub>2</sub>.

	BnSiCl <sub>3</sub>	Bn <sub>2</sub> SiCl <sub>2</sub>	Bn <sub>2</sub> SiBr <sub>2</sub>
Empirical formula	C <sub>7</sub> H <sub>7</sub> Cl <sub>3</sub> Si	C <sub>14</sub> H <sub>14</sub> Cl <sub>2</sub> Si	C <sub>14</sub> H <sub>14</sub> Br <sub>2</sub> Si
<i>M</i> <sub>r</sub>	225.27	281.24	370.16
<i>T</i> , K	90(2)	90(2)	90(2)
Crystal size, mm <sup>3</sup>	0.45 × 0.42 × 0.23	0.41 × 0.32 × 0.24	0.26 × 0.24 × 0.10
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , Å	6.0773(6)	9.8002(2)	9.9011(5)
<i>b</i> , Å	7.3273(6)	13.8222(3)	13.8650(7)
<i>c</i> , Å	10.7882(10)	10.4841(3)	10.5256(5)
$\beta$ , deg	90.357(5)	102.976(1)	102.015(3)
<i>V</i> , Å <sup>3</sup>	480.39(8)	1383.91(6)	1413.29(12)
<i>Z</i>	2	4	4
<i>D</i> <sub>calcd.</sub> , g cm <sup>–3</sup>	1.56	1.35	1.74
$\mu$ (MoK $\alpha$ ), cm <sup>–1</sup>	10	5	58
<i>F</i> (000), <i>e</i>	228	584	728
<i>hkl</i> range	–8 ≤ <i>h</i> ≤ +8 –10 ≤ <i>k</i> ≤ +10 –16 ≤ <i>l</i> ≤ +16	–14 ≤ <i>h</i> ≤ +14 –20 ≤ <i>k</i> ≤ +16 –15 ≤ <i>l</i> ≤ +15	–14 ≤ <i>h</i> ≤ +12 –20 ≤ <i>k</i> ≤ +20 –13 ≤ <i>l</i> ≤ +15
((sin $\theta$ )/ $\lambda$ ) <sub>max</sub> , Å <sup>–1</sup>	0.75	0.75	0.75
$\theta$ <sub>max</sub> , deg/% completeness	32/98.5	32/100	32/95
Refl. measured	16 716	19 230	24 858
Refl. unique/ <i>R</i> <sub>int</sub>	3231/0.0254	4811/0.0332	4666/0.0406
Param. refined	101	154	154
<i>R</i> ( <i>F</i> )/ <i>wR</i> ( <i>F</i> <sup>2</sup> ) <sup>a</sup>	0.0231/0.0644	0.0323/0.0789	0.0282/0.0593
[ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]			
<i>R</i> ( <i>F</i> )/ <i>wR</i> ( <i>F</i> <sup>2</sup> ) <sup>a</sup>	0.0246/0.0662	0.0478/0.0831	0.0474/0.0622
(all refls.)			
<i>x</i> (Flack)	0.03(7) <sup>b</sup>	–	–
GoF ( <i>F</i> <sup>2</sup> ) <sup>a</sup>	1.189	1.063	1.079
$\Delta\rho_{\text{fin}}$ (max/min), e Å <sup>–3</sup>	0.30/–0.45	0.45/–0.23	0.54/–0.53

<sup>a</sup>  $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$  for the observed reflections with  $F^2 > 2 \sigma(F^2)$ ;  $wR(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ;  $\text{GoF} = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$ ;  $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ , where  $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$ ; <sup>b</sup> The structure was refined as a twin ( $\bar{1}000\bar{1}0001$ , BASF 0.331(1)).

sis). – C<sub>33</sub>H<sub>27</sub>Cl<sub>3</sub>N<sub>2</sub>O<sub>2</sub>Si (618.01): calcd. C 64.14, H 4.40, N 4.53 vs. C<sub>32</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>Si·0.18(CHCl<sub>3</sub>) (520.13): calcd. C 74.31, H 5.07, N 5.39; found C 74.37, H 5.04, N 5.45.

(Oxinate)<sub>2</sub>SiPhCl·CHCl<sub>3</sub>

8-Oxyquinoline (3.00 g, 20.6 mmol) and triethylamine (3.14 g, 30.8 mmol) were dissolved in THF (60 mL) and cooled to 0 °C, whereupon chlorotrimethylsilane (2.46 g, 22.6 mmol) was added dropwise. The triethylammonium chloride precipitate was filtered off and washed with THF (20 mL). From the filtrate and washings the solvent was removed under reduced pressure. The residue was dissolved in chloroform (30 mL) and cooled to 0 °C. At this temperature, phenyltrichlorosilane (2.39 g, 11.3 mmol) was added, and the solution was stored at room temperature. The yellow crystalline product was filtered off, washed with chloroform and dried *in vacuo*. Yield: 4.55 g (8.31 mmol, 81 %). – <sup>29</sup>Si CP/MAS NMR (79.5 MHz,  $\nu_{\text{spin}} = 4$  kHz):  $\delta_{\text{iso}} =$

– 152.1 ppm. – C<sub>25</sub>H<sub>18</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Si (548.30): calcd. C 54.76, H 3.31, N 5.11; found C 54.61, H, 3.29, N 5.09. (The characterization of this compound in solution was hampered by the very poor solubility in solvents such as chloroform or DMSO.)

(Oxinate)<sub>2</sub>SiF<sub>2</sub>·1.5(CHCl<sub>3</sub>)

To a solution of 8-hydroxyquinoline (0.58 g, 4.0 mmol) and triethylamine (0.43 g, 4.3 mmol) in THF (20 mL) was added trimethylchlorosilane (0.46 g, 4.2 mmol) dropwise, and the resulting suspension was stirred for 1 h. After filtration the colorless solid residue was washed with THF (3 × 2 mL), and from the combined filtrates and washings the volatiles were removed *in vacuo*. In another Schlenk tube SiF<sub>4</sub>Py<sub>2</sub> [34, 35] (0.53 g 2.0 mmol) was stirred in chloroform (2 mL), and the resulting suspension was layered with additional 5 mL of pure chloroform followed by a layer of the previously prepared 8-trimethylsiloxyquinoline which

Table 4. Crystal structure data for (oxinate)<sub>2</sub>SiF<sub>2</sub>·1.5 CHCl<sub>3</sub>, (oxinate)<sub>2</sub>SiPhCl·CHCl<sub>3</sub> and (oxinate)<sub>2</sub>(adho)Si·1.5 CHCl<sub>3</sub>.

	(oxinate) <sub>2</sub> SiF <sub>2</sub> ·1.5 CHCl <sub>3</sub>	(oxinate) <sub>2</sub> SiPhCl ·CHCl <sub>3</sub>	(oxinate) <sub>2</sub> (adho)Si ·1.5 CHCl <sub>3</sub>
Empirical formula	C <sub>39</sub> H <sub>27</sub> Cl <sub>9</sub> F <sub>4</sub> N <sub>4</sub> O <sub>4</sub> Si <sub>2</sub>	C <sub>25</sub> H <sub>18</sub> Cl <sub>4</sub> N <sub>2</sub> O <sub>2</sub> Si	C <sub>63</sub> H <sub>49</sub> Cl <sub>9</sub> N <sub>6</sub> O <sub>6</sub> Si <sub>2</sub>
$M_r$	1066.88	548.30	1361.31
$T$ , K	150(2)	296(2)	100(2)
Crystal size, mm <sup>3</sup>	0.30 × 0.28 × 0.18	0.20 × 0.20 × 0.10	0.38 × 0.12 × 0.06
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$a$ , Å	16.2316(5)	8.2014(3)	11.2522(3)
$b$ , Å	16.6957(6)	11.0054(4)	14.0343(3)
$c$ , Å	17.4505(6)	13.7955(5)	19.9637(5)
$\alpha$ , deg	72.468(3)	78.239(2)	77.977(1)
$\beta$ , deg	78.518(3)	88.439(2)	79.815(1)
$\gamma$ , deg	80.500(3)	85.604(2)	75.471(1)
$V$ , Å <sup>3</sup>	4391.1(3)	1215.36(8)	2958.89(13)
$Z$	4	2	1
$D_{\text{calcd.}}$ , g cm <sup>-3</sup>	1.61	1.50	1.53
$\mu$ (MoK $\alpha$ ), cm <sup>-1</sup>	7	6	5
$F(000)$ , $e$	2152	560	1396
$hkl$ range	–21 ≤ $h$ ≤ +21 –22 ≤ $k$ ≤ +22 –23 ≤ $l$ ≤ +23	–9 ≤ $h$ ≤ +10 –14 ≤ $k$ ≤ +14 –17 ≤ $l$ ≤ +17	–10 ≤ $h$ ≤ +13 –16 ≤ $k$ ≤ +16 –20 ≤ $l$ ≤ +22
$((\sin \theta)/\lambda)_{\text{max}}$ , Å <sup>-1</sup>	0.66	0.64	0.60
$\theta_{\text{max}}$ , deg/%	28/99.9	27/98.6	25/99.9
completeness			
Refl. measured	63 808	19 697	30 305
Refl. unique/ $R_{\text{int}}$	21 174/0.0298	5236/0.0359	10 054/0.0443
Param. refined	1192	355	788
$R(F)/wR(F^2)^a$	0.0394/0.0996	0.0485/0.1261	0.0433/0.0905
$[I > 2 \sigma(I)]$			
$R(F)/wR(F^2)^a$	0.0622/0.1086	0.0819/0.1387	0.0894/0.1009
(all refls.)			
GoF ( $F^2$ ) <sup>a</sup>	1.030	1.134	0.985
$\Delta\rho_{\text{fin}}$ (max/min), $e \text{ \AA}^{-3}$	0.57/–0.45	0.36/–0.45	0.40/–0.39

<sup>a</sup> See Table 3 for definition of  $R$  values and GoF, as well as information on the weighting scheme applied.

has been dissolved in chloroform (2 mL). This reaction mixture was stored undisturbed overnight at room temperature after which a yellow crystalline solid suitable for X-ray diffraction was obtained. The product was filtered off, washed with chloroform (2 × 1 mL) and dried *in vacuo*. Yield 0.66 g (1.8 mmol, 88% referring to C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>SiF<sub>2</sub> · 0.14 CHCl<sub>3</sub>). – <sup>29</sup>Si CP/MAS NMR (79.5 MHz,  $\nu_{\text{spin}} = 5$  kHz):  $\delta_{\text{iso}} = -163$  ppm (signal consists of two peaks, at  $-160.9$  and  $-165.0$  ppm). – C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>SiF<sub>2</sub> · 0.14 CHCl<sub>3</sub> (371.10): calcd. C 58.71, H 3.30, N 7.55; found C 58.56, H 3.33, N 7.93. (The characterization of this compound in solution was hampered by the very poor solubility in solvents such as chloroform or DMSO.)

#### (8-Oxyquinaldinate)<sub>2</sub>SiF<sub>2</sub>

This compound was prepared in an analogous manner from 4 mmol 8-hydroxyquinaldine and 2 mmol SiF<sub>4</sub>Py<sub>2</sub> [34, 35]. Crystals appeared after one week. Yield: 0.35 g

(0.91 mmol, 45%). – <sup>29</sup>Si CP/MAS NMR (79.5 MHz,  $\nu_{\text{spin}} = 4$  kHz):  $\delta_{\text{iso}} = -158$  ppm (signal consists of two peaks, at  $-155.6$  and  $-160.3$  ppm). – C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>SiF<sub>2</sub> (382.44): calcd. C 62.81, H 4.22, N 7.33; found C 62.86, H 4.37, N 7.50. (The characterization of this compound in solution was hampered by the very poor solubility in solvents such as chloroform or DMSO.)

#### (Oxinate)<sub>2</sub>SiCl<sub>2</sub>

To a solution of 8-trimethylsiloxyquinoline (prepared analogously as described for (oxinate)<sub>2</sub>SiF<sub>2</sub>·1.5(CHCl<sub>3</sub>) but starting from 10 mmol 8-hydroxyquinoline, 12.5 mmol Me<sub>3</sub>SiCl and 15 mmol Et<sub>3</sub>N in 50 mL THF) in acetonitrile (20 mL) was quickly added SiCl<sub>4</sub> (0.85 g, 5.0 mmol) in one portion under stirring at room temperature. Stirring was discontinued immediately after complete SiCl<sub>4</sub> addition, and the mixture was stored undisturbed overnight at room temperature yielding a yellow crystalline solid suitable for X-ray

Table 5. Crystal structure data for (oxinate)<sub>2</sub>SiBnCl and (oxinate)<sub>2</sub>SiBn<sub>2</sub>·CHCl<sub>3</sub>.

	(oxinate) <sub>2</sub> SiBnCl	(oxinate) <sub>2</sub> SiBn <sub>2</sub> ·CHCl <sub>3</sub>
Empirical formula	C <sub>25</sub> H <sub>19</sub> ClN <sub>2</sub> O <sub>2</sub> Si	C <sub>33</sub> H <sub>27</sub> Cl <sub>3</sub> N <sub>2</sub> O <sub>2</sub> Si
<i>M<sub>r</sub></i>	442.96	618.01
<i>T</i> , K	100(2)	200(2)
Crystal size, mm <sup>3</sup>	0.30 × 0.10 × 0.03	0.45 × 0.35 × 0.03
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> , Å	11.3434(3)	13.7917(4)
<i>b</i> , Å	10.2509(2)	16.4454(5)
<i>c</i> , Å	17.9446(4)	14.1748(4)
$\beta$ , deg	97.182(1)	112.868(1)
<i>V</i> , Å <sup>3</sup>	2070.23(8)	2962.30(15)
<i>Z</i>	4	4
<i>D</i> <sub>calcd.</sub> , g cm <sup>-3</sup>	1.42	1.42
$\mu$ (MoK $\alpha$ ), cm <sup>-1</sup>	3	4
<i>F</i> (000), <i>e</i>	920	1280
<i>hkl</i> range	$-13 \leq h \leq +13$ $-12 \leq k \leq +12$ $-21 \leq l \leq +22$	$-17 \leq h \leq +15$ $-18 \leq k \leq +20$ $-16 \leq l \leq +17$
$((\sin \theta)/\lambda)_{\text{max}}$ , Å <sup>-1</sup>	0.62	0.62
$\theta_{\text{max}}$ , deg/	26/99.9	26/99.9
% completeness		
Refl. measured	17 706	26 740
Refl. unique/ <i>R</i> <sub>int</sub>	4062/0.0608	5816/0.0439
Param. refined	280	386
<i>R</i> ( <i>F</i> )/ <i>wR</i> ( <i>F</i> <sup>2</sup> ) <sup>a</sup>	0.0453/0.0978	0.0414/0.0846
[ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]		
<i>R</i> ( <i>F</i> )/ <i>wR</i> ( <i>F</i> <sup>2</sup> ) <sup>a</sup>	0.0799/0.1056	0.0858/0.0941
(all refls.)		
GoF ( <i>F</i> <sup>2</sup> ) <sup>a</sup>	1.046	1.013
$\Delta\rho_{\text{fin}}$ (max/min), <i>e</i> Å <sup>-3</sup>	0.33/−0.33	0.31/−0.29

<sup>a</sup> See Table 3 for definition of *R* values and GoF, as well as information on the weighting scheme applied.

Table 6. Crystal structure data for (oxinate)<sub>2</sub>SiCl<sub>2</sub> and (oxyquinaldinate)<sub>2</sub>SiF<sub>2</sub>.

	(oxinate) <sub>2</sub> SiCl <sub>2</sub>	(oxyquinaldinate) <sub>2</sub> SiF <sub>2</sub>
Empirical formula	C <sub>18</sub> H <sub>12</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> Si	C <sub>20</sub> H <sub>16</sub> F <sub>2</sub> N <sub>2</sub> O <sub>2</sub> Si
<i>M<sub>r</sub></i>	387.29	382.44
<i>T</i> , K	150(2)	100(2)
Crystal size, mm <sup>3</sup>	0.35 × 0.30 × 0.10	0.30 × 0.20 × 0.05
Crystal system	monoclinic	monoclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> , Å	13.9866(16)	17.2309(13)
<i>b</i> , Å	8.1132(7)	7.6145(5)
<i>c</i> , Å	14.9864(16)	13.5351(11)
$\beta$ , deg	109.907(8)	112.998(5)
<i>V</i> , Å <sup>3</sup>	1599.0(3)	1634.7(2)
<i>Z</i>	4	4
<i>D</i> <sub>calcd.</sub> , g cm <sup>-3</sup>	1.61	1.55
$\mu$ (MoK $\alpha$ ), cm <sup>-1</sup>	5	2
<i>F</i> (000), <i>e</i>	792	792
<i>hkl</i> range	$-19 \leq h \leq +19$ $-11 \leq k \leq +11$ $-21 \leq l \leq +16$	$-20 \leq h \leq +20$ $-9 \leq k \leq +9$ $-16 \leq l \leq +16$
$((\sin \theta)/\lambda)_{\text{max}}$ , Å <sup>-1</sup>	0.70	0.60
$\theta_{\text{max}}$ , deg/	30/100	25/99.9
% completeness		
Refl. measured	9129	8547
Refl. unique/ <i>R</i> <sub>int</sub>	2335/0.0286	1440/0.1341
Param. refined	114	124
<i>R</i> ( <i>F</i> )/ <i>wR</i> ( <i>F</i> <sup>2</sup> ) <sup>a</sup>	0.0404/0.1068	0.0396/0.0882
[ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]		
<i>R</i> ( <i>F</i> )/ <i>wR</i> ( <i>F</i> <sup>2</sup> ) <sup>a</sup>	0.0501/0.1126	0.0639/0.0956
(all refls.)		
GoF ( <i>F</i> <sup>2</sup> ) <sup>a</sup>	1.076	1.029
$\Delta\rho_{\text{fin}}$ (max/min), <i>e</i> Å <sup>-3</sup>	0.63/−0.27	0.22/−0.23

<sup>a</sup> See Table 3 for definition of *R* values and GoF, as well as information on the weighting scheme applied.

diffraction. The product was collected by filtration, washed with diethyl ether ( $2 \times 10$  mL) and dried *in vacuo*. Yield: 1.92 g (4.96 mmol, 99%).  $^{-29}\text{Si}$  CP/MAS NMR (79.5 MHz,  $\nu_{\text{spin}} = 5$  kHz):  $\delta_{\text{iso}} = -158.7$  ppm.  $-\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_2\text{SiCl}_2$  (387.29): calcd. C 55.82, H 3.12, N 7.23; found C 55.55, H 3.39, N 7.54. (The characterization of this compound in solution was hampered by the very poor solubility in solvents such as chloroform or decomposition in DMSO.)

#### Computational analyses

Geometry optimization (at DFT MPW1PW91 6-311G(d,p) level) and single point energy analyses (at MP2 6-31G(d) level) of hexacoordinated silicon complexes with oxinato ligands were performed on isolated molecules (pseudo gas phase) using GAUSSIAN 09 [36]. For potential energy surface scans of benzyltrihalosilanes (B3LYP/6-311G(d,p)) and calculations of  $^{29}\text{Si}$  NMR shifts for different conformations of benzyltrichlorosilane and TMS (at the B3LYP/6-311G+(2d,p) and HF/6-311G+(2d,p) level) GAUSSIAN 03 was employed.

#### X-Ray structure determinations

Single-crystal X-ray diffraction data were collected on a Stoe IPDS 2/2T single-crystal diffractometer (for (oxinate) $_2$ SiCl $_2$ , (oxinate) $_2$ SiF $_2$ ·1.5(CHCl $_3$ ) and (8-oxyquinaldinate) $_2$ SiF $_2$ ) or on a Bruker X8 APEX2 CCD diffractometer (for the other crystal structures) using MoK $\alpha$  radiation. The structures were solved by Direct Methods using SHELXS-97 and refined with full-matrix least-squares methods on  $F^2$  of all reflections with SHELXL-97 [37–39] in WINGX [40, 41]. Graphics of the molecular structures were generated with ORTEP-32 [42, 43] and POV-RAY [44]. All non-hydrogen atoms were refined anisotropically. C-bound hydrogen atoms were refined isotropically in idealized positions (riding model). In the crystal structures of (oxinate) $_2$ SiF $_2$ ·1.5(CHCl $_3$ ) and (oxinate) $_2$ Si(adho)·1.5(CHCl $_3$ ) the independent molecules of the Si complex in the asymmetric unit (4 and 2, respectively) are related to one another by pseudosymmetry, but this symmetry is heavily violated by the ordering

of the solvent molecules (in case of two-fold disordered chloroform, the site occupancies are far off the 50 : 50 ratio). In addition to solvent disorder (which also applies to the chloroform molecule in (oxinate) $_2$ SiBn $_2$ ), the SiPhCl moiety of (oxinate) $_2$ SiPhCl is disordered with site occupancies of 0.961(4) and 0.039(4). The phenyl group of the low occupancy part was refined as an idealized hexagon (SHELXL code AFIX 66). Details of the structure determinations are summarized in Tables 3–6.

CCDC 999917 (for (oxinate) $_2$ SiCl $_2$ ), 999918 (for (oxinate) $_2$ SiF $_2$ ·1.5(CHCl $_3$ )), 999919 (for (8-oxyquinaldinate) $_2$ SiF $_2$ ), 999920 (for (oxinate) $_2$ SiPhCl·CHCl $_3$ ), 999921 (for (oxinate) $_2$ Si(adho)·1.5(CHCl $_3$ )), 999922 (for (oxinate) $_2$ SiBnCl), 999923 (for (oxinate) $_2$ SiBn $_2$ ·CHCl $_3$ ), 999924 (for BnSiCl $_3$ ), 999925 (for Bn $_2$ SiCl $_2$ ) and 999926 (for Bn $_2$ SiBr $_2$ ) 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](http://www.ccdc.cam.ac.uk/data_request/cif).

#### Supporting information

Cartesian coordinates of the optimized (DFT MPW1PW91/6-311G(d,p)) molecular structures of *O,O-trans* and *N,N-trans* isomers of (oxinate) $_2$ SiCl $_2$ , (oxinate) $_2$ SiF $_2$ , (8-oxyquinaldinate) $_2$ SiCl $_2$  and (8-oxyquinaldinate) $_2$ SiF $_2$ ;  $^{29}\text{Si}$  CP/MAS NMR spectra of (oxinate) $_2$ SiF $_2$  and (8-oxyquinaldinate) $_2$ SiF $_2$ ; powder X-ray diffractogram of (oxinate) $_2$ SiCl $_2$  are given as Supporting Information (16 pages) available online (DOI: 10.5560/ZNB.2014-4170).

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