Surprising Insights in the Various Molecular Structures of Hypercoordinate Bis(oxinato)silicon Complexes

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The syntheses of two cyclic diorganosilicon enamines $RPhSi(o-O-C_6H_4-C(NCH_2Ph)=CH_2)$ [R = Ph (**2a**), Me (**2b**)] are described. These compounds react with 8-oxyquinoline leading to bis(oxinato)silicon complexes $RPhSi(oxinate)_2$ [R = Ph (**5a**), Me (**5b**)]. Their X-ray structures reveal hexacoordination of the Si atom with the monodentate substituents in *cis*-positions and N atoms as well as O atoms in *trans*-positions.

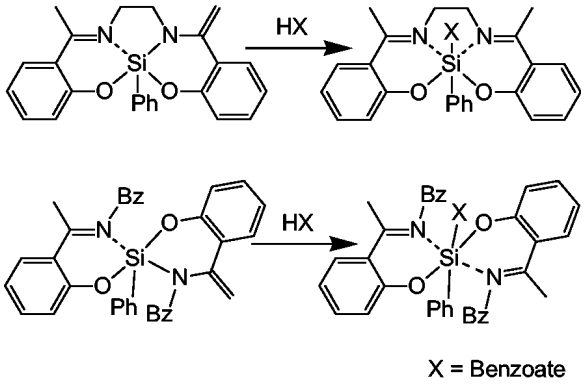
In crystalline dimethylbis(oxinato)silicon, $Me_2Si(oxinate)_2$ (**7**), the silicon atom is only bicapped tetrahedrally coordinated, while for dichlorobis(oxinato)silicon, $Cl_2Si(oxinate)_2$ (**8**), there is an octahedral coordination of the Si atom with chlorine atoms in *trans*-positions. This conclusion is based on the results of spectroscopic analysis (IR, ^{29}Si CP/MAS NMR) as well as quantum chemical calculations. The first example of a silicon-bis-oxinate with the N→Si dative bonds in a *trans*-arrangement has been detected in the hexacoordinate silicon tris-chelate $(oxinate)_2Si(PhN\text{-}CH_2CH_2\text{-}NPh)$ (**11**). Its configuration was proven by X-ray structure analysis. Thus, for hexacoordinate bis(oxinato)silicon compounds three new architectures were found which complement the previously established building pattern of the N,N'-*cis*-O,O'-*trans*-bis(oxinato)silicon complexes.

The *mer*-tris(oxinato)siliconium cation ($\mathbf{9}^+$) (its configuration being proven by ^{1}H and ^{13}C NMR spectroscopy) features at least three coordination patterns with (O,O;N,N)-*cis,cis*-, -*cis,trans*- as well as -*trans,cis*-arrangements of two oxinate ligands.

Key words: Enamine, Hypercoordination, Oxinate, Silicon

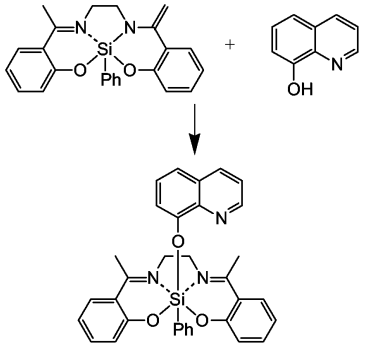
Introduction

Recently we reported the syntheses of silicon enamine complexes with ligands of the salen-type and pentacoordinate silicon atoms [1]. These compounds react with Brønsted acids to form complexes with hexacoordinate silicon atoms (Scheme 1). The addition of 8-hydroxyquinoline also leads to an octahedral coordination sphere of the Si atom in the product (Scheme 2). Regarding the installation of N→Si dative-bonds, the N-donor atom of the 8-oxyquinolinate ligand is not able to compete successfully with the N atoms of the tetradentate salen-type ligand.

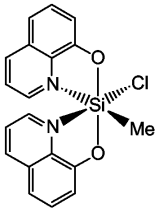


Scheme 1.

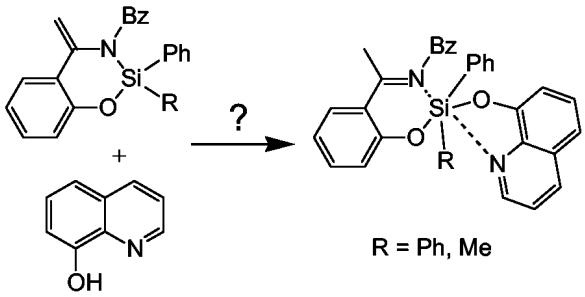
8-Oxyquinolinate, however, has previously been reported to form various silicon complexes in which the Si atom is hypercoordinated by this bidentate ligand [2]. Although there is a growing interest in silicon compounds with the oxinate ligand for purposes such as cancer therapy [3] and electronic applications [4], until now the knowledge regarding the molecular structure of bis(oxinato)silicon complexes is limited. Only the X-ray structure of one hypercoordinate



Scheme 2.



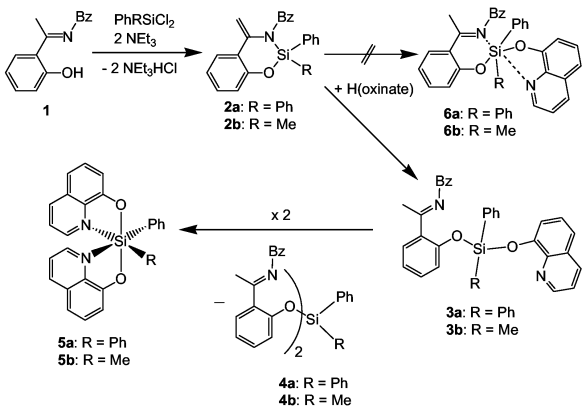
Scheme 3.



Scheme 4.

oxinato-Si-complex, $(oxinate)_2SiMeCl$, has been published (Scheme 3) [5]. It exhibits a hexacoordinate Si atom with the monodentate substituents in *cis*-position. Unlike most of the known hexacoordinate silicon compounds involving two monodentate and two *(O,N)*-chelating bidentate ligands [6, 7], the covalent Si-O bonds are *trans* and the dative Si-N contacts are *cis* in this molecule. Applying the Brønsted acid addition reaction (according to Scheme 2), we now tried to prepare hexacoordinate Si complexes with mixed *(O,N)*-chelating ligands, one of them being the oxinate ligand (Scheme 4). Initially, we expected the formation of complexes such as **3a** and **3b** or **6a** and **6b**, respectively. The formation of the bis(oxinato)silicon complexes **5a** and **5b** was therefore surprising (Scheme 5).

The easy access to crystals of bis(oxinato)silicon complexes suitable for X-ray structure analysis *via* this route tempted us to strive for a deeper insight into the dative silicon-oxinate interactions.



Scheme 5.

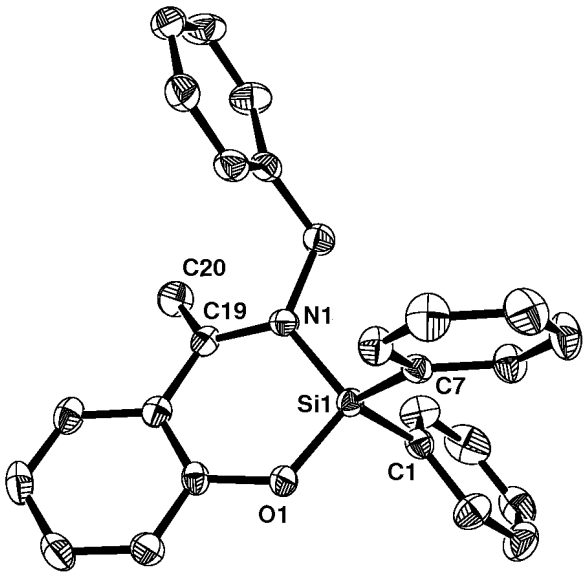
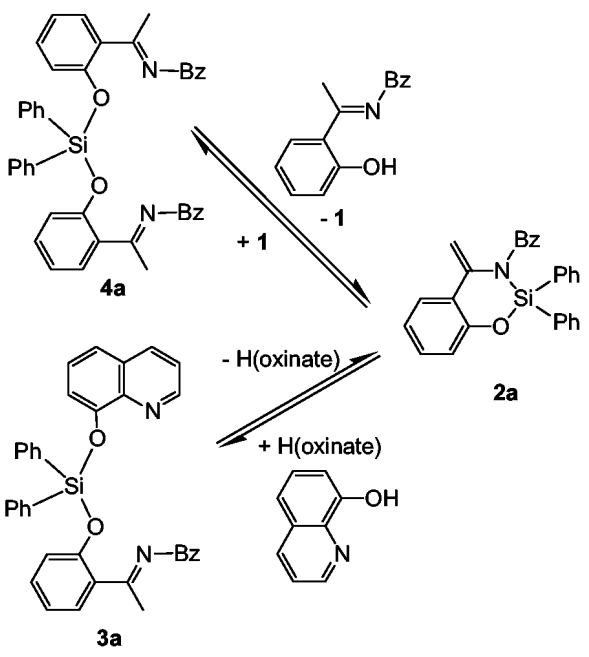


Fig. 1. Molecular structure of **2a** (ORTEP plot with 50% probability ellipsoids, hydrogen atoms omitted).

Results and Discussion

Enamines **2a** and **2b** (Scheme 5) were synthesized by reacting the 2-iminomethylphenol ligand **1** with diphenyldichlorosilane and methylphenyldichlorosilane, respectively, in the presence of an excess of triethylamine. While **2b** was obtained as an oil, **2a** formed crystals suitable for X-ray structure analysis (Fig. 1). Details of structure determination and refinement are given in the experimental section (Table 3).

The bond lengths C19=C20 and C19-N1 within the enamine moiety are similar to those of enamine-Si complexes with pentacoordinate silicon atom. The



Scheme 6.

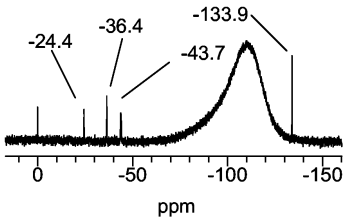


Fig. 2. ^{29}Si NMR spectrum of a 1 : 1 molar mixture of **2a** and 8-hydroxyquinoline in $CDCl_3$.

bonds Si1-N1, and especially Si1-O1, are significantly shortened as compared to the enamine complexes shown in Scheme 1 due to the Si-coordination number 4. The Si-C bond lengths, however, are not notably influenced in comparison with enamine complexes which involve a silicon atom having a higher coordination number.

Mixing of a solution of **2a** in chloroform with the 1 : 1 stoichiometric amount of 8-hydroxyquinoline delivered the bis(oxinato)silicon complex **5a** in high yield within one day. Immediately after mixing **2a** with 8-hydroxyquinoline in $CDCl_3$, a ^{29}Si NMR spectrum was recorded (Fig. 2). The signal at -133.9 ppm arises from **5a**, the peak at -24.4 ppm from the educt **2a**. The signal at -36.4 ppm was assigned to the byproduct **4a** which was also detected in the mixture of **2a** and **1** in $CDCl_3$. **4a** was coexisting with **2a** and **1** based on an equilibration process in this solvent (Scheme 6, top), compare also [7].

Thus, the remaining signal in the ^{29}Si NMR spectrum, at -43.7 ppm, can be assigned to **3a**, which may represent the intermediate furnishing **5a**. As proposed in the equilibrium depicted in Scheme 6, bottom, **3a** may also partly dissociate into its educts **2a** and 8-hydroxyquinoline, thus providing free 8-hydroxyquinoline to substitute the 2-iminomethylphenolate ligand of **3a** in a competitive reaction to yield **5a**. (An analogous dissociation equilibrium was observed for the hexacoordinate salen+oxinate silicon complex in Scheme 2.) The substitution of the 2-iminomethylphenolate ligand in **3a** by an oxinate ligand *via* free 8-hydroxyquinoline appears to be more facile than direct ligand redistribution between two molecules of **3a**. As proven by the ^{29}Si NMR spectrum, the intermediate **3a** has a tetracoordinate silicon atom. There was no indication of an intermediate **6** with a hypercoordinate Si atom.

Enamine **2b** reacts with 8-hydroxyquinoline in a similar manner to give **5b**. **5a** is nearly insoluble in chloroform, but **5b** was analyzed by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy in $CDCl_3$ solution. The ^{29}Si chemical shift value of -27.8 ppm clearly indicates a compound with a tetracoordinate silicon atom in solution. ^{29}Si solid state NMR spectra of **5a** and **5b**, however, reveal hexacoordination of the Si atoms in both complexes (**5a**: $\delta = -137.4$ ppm, **5b**: $\delta = -126.2$ ppm). In a previous report, based on UV/vis spectra, **5a** was found to have two N→Si dative bonds. Unlike this, in a solution of **5b** the presence of coordinating as well as non-coordinating oxinate-N-atoms was monitored [2b]. The latter result points to an equilibrium between tetra- and hypercoordinate species in solution. The fact that only one ^{29}Si NMR signal of **5b**

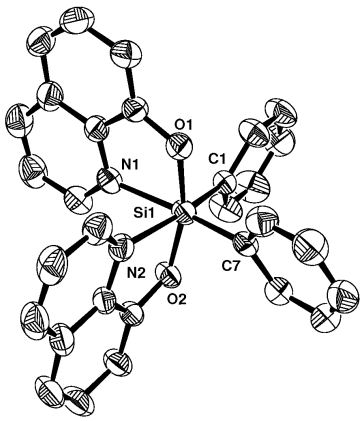


Fig. 3. Molecular structure of **5a** (ORTEP plot with 50% probability ellipsoids, hydrogen atoms omitted).

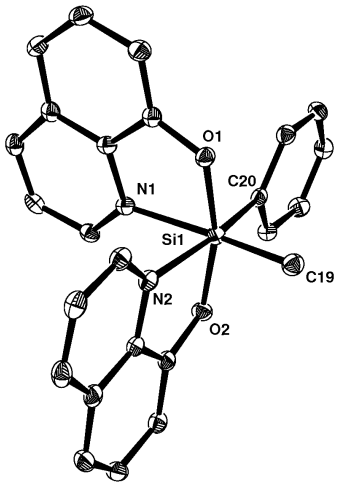
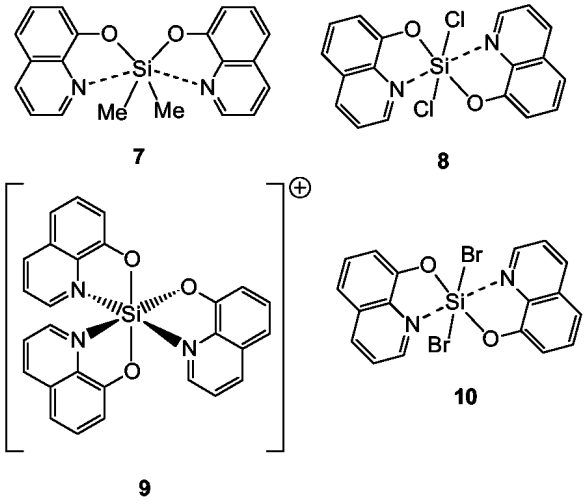


Fig. 4. Molecular structure of one of the two crystallographically independent molecules of **5b** (ORTEP plot with 50% probability ellipsoids, hydrogen atoms omitted).



Scheme 7.

at −27.8 ppm was found may arise from a rapid Si-N dissociation process in **5b** with the species containing a tetracoordinate silicon atom being dominant. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ also show only the characteristic set of signals for compound **5b** with tetracoordinate Si atom.

The crystal structures of **5a** and **5b** have been determined (Fig. 3 and 4). Details of structure determination and refinement are given in Table 3.

The asymmetric unit of **5b** consists of two molecules exhibiting nearly identical structural parameters. Therefore, only one of them is shown in Fig. 4 and included in the discussion. While both Si-C bond lengths in **5a** are similar [1.921(3) and 1.914(3) Å], in **5b** the bond with the methyl carbon atom Si1-C19 [1.902(2) Å] is notably shorter than that with the phenyl *ipso* carbon atom Si1-C20 [1.925(2) Å]. The Si-N distances in both complexes are comparable [2.099(3) and 2.108(3) Å in **5a**; 2.090(2) and 2.092(2) Å in **5b**], but important differences in bond lengths are found regarding the Si-O bonds. One of these in **5b**, Si1-O1, [Si1-O1: 1.791(1), Si1-O2: 1.778(1) Å] is slightly but significantly longer than those in the diphenylsilicon complex **5a** [Si1-O1: 1.768(2), Si1-O2: 1.769(2) Å]. In both molecules a distorted octahedral coordination of the Si atom is found. The bond angles C-Si-C [C1-Si1-C7 = 102.3(1)° in **5a**, C19-Si1-C20 = 100.58(8)° in **5b**] are notably widened while the N-Si-N angles [N1-Si1-N2 = 80.04(9)° in **5a**, 80.55(6)° in **5b**] are significantly smaller than 90°. Both molecular structures exhibit the building pattern of the bis(oxinato)silicon complexes described by Klebe *et al.* [5], suggesting that this architecture is a general type in this class of complexes. Even hexacoordinate bis(oxinato)tin complexes with two monodentate substituents exhibit the same coordination mode of the oxinate ligand [8]. In order to probe this hypothesis, two further bis(oxinato)silicon complexes **7** and **8** have been prepared (Scheme 7).

Bis(oxinato)dimethylsilicon **7**, reported to bear only non-coordinating N atoms [2b, 2f], was ^{29}Si NMR spectroscopically characterized in $CDCl_3$ solution ($\delta = -11.2$ ppm) as well as in the solid state ($\delta = -17.4$ ppm). Both signals indicate tetracoordination of the silicon atom. The remarkable upfield shift in the solid state (by −6.2 ppm), however, is indicative of significant differences between the conformations of the molecules in solution and in the solid state.

The X-ray structure of **7** reveals a tetrahedral coordination sphere of the Si atom consisting of the two methyl groups and the two oxinato oxygen atoms (Fig. 5). In the crystal, the molecules are disordered (Fig. 5, Top) in a 3 : 2 ratio. The dominating part is drawn in Fig. 5, bottom. Because of this disorder, anisotropic refinement of all non-hydrogen atoms was only possible with restrained oxinato ring systems (four same fragments) and equal anisotropic displacement parameters for atoms in similar positions. The structural details of the most interesting part of the molecule – the environment of the Si atom – are not strongly affected by the disorder. One can discern a bicapped tetrahedral coordination sphere if one includes the oxinato nitrogen atoms [Si-N distances *ca.* 2.78 Å]

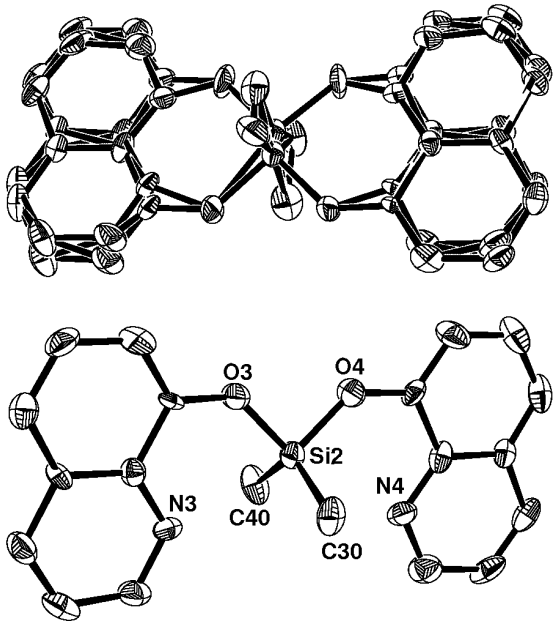


Fig. 5. Molecular structure of **7** (ORTEP plot with 50% probability ellipsoids, hydrogen atoms omitted). Top: Superposition of the disordered molecular sites. Bottom: One molecule of **7** (60% site occupation).

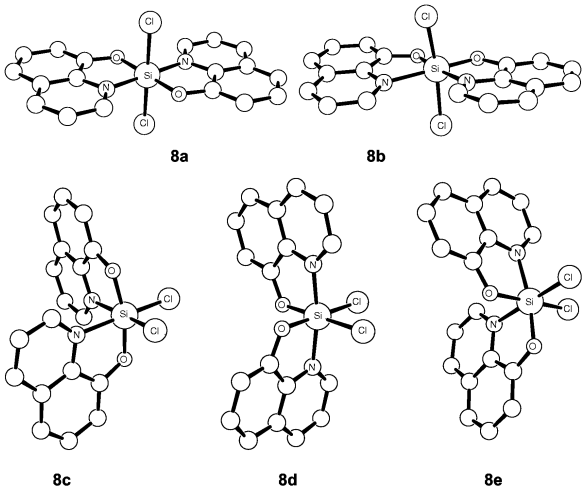


Fig. 6. Isomers of **8** optimized with B3LYP/6-31G*.

and the widened angle C30-Si2-C40 [125.3(3)°] may be seen as a result of this [4+2]-coordination.

Bis(oxinato)silicon dichloride **8** was described as a tetracoordinate dicationic complex in a very early report [9], but hexacoordination of the Si atom in **8** was finally proven by ^{29}Si NMR in the present investigations. Because crystals suitable to perform an X-ray structure analysis were not obtained, IR and ^{29}Si CP/MAS NMR spectroscopic data of **8** were recorded and compared with the results of quantum chemical calculations. Five conformational isomers of **8** were optimized and their relative energies were calculated (**8a**–**8e**, Fig. 6 and 7). The IR frequencies and ^{29}Si chemical shift tensors were also calculated and experimentally determined. Tables 1 and 2 offer the comparison between the calculated and experimentally obtained data.

Table 1. ^{29}Si NMR parameters (δ in ppm referring to TMS, Ω in ppm, κ) calculated for **8a**–**8e** and found for **8**.

	8	**8a**	**8b**	**8c**	**8d**	**8e**
δ_{iso}	−157.9	−157.3	−141.2	−140.8	−146.8	−140.9
δ_{11}	−116.9	−131.7	−120.4	−120.1	−143.4	−131.9
δ_{22}	−140.0	−132.3	−150.3	−133.6	−146.3	−134.0
δ_{33}	−216.7	−207.8	−153.0	−168.8	−150.7	−156.6
Ω	99.8	76.1	32.6	48.7	7.3	24.7
κ	0.54	0.99	−0.84	0.44	0.21	0.84

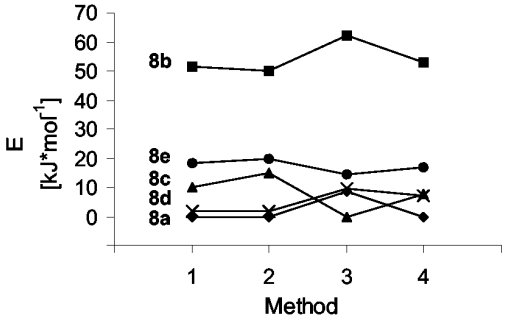


Fig. 7. Relative energies of the conformations of molecule **8** [calculated with 1.: B3LYP/6-31+G(d); 2.: B3LYP/6-311+G(2d,p); 3.: MP2/6-31+G(d,p); 4.: MP2/6-311+G(2d,p)].

The ^{29}Si solid state NMR data of **8** correlate well with the ^{29}Si NMR parameters calculated for the molecular geometry **8a**. The values for the isotropic chemical shift are nearly identical, only **8a** having such a large span Ω, suggesting that **8** has a conformation similar to **8a** in the solid state. The values of the skew κ of the ^{29}Si chemical shift tensors of **8c** and **8e** are compatible with the signal of **8**, but the other parameters deviate to such an extent that the unusual coordination geometry **8e** and the more conventional coordination mode of **8c** are unacceptable solutions.

A comparison between the IR data calculated for **8a**–**8e** was done in such a way that the most intense IR bands (IR intensities ranging between 80 and 530 as given by GAUSSIAN) were analyzed (Table 2). Referring to these data, the absorption bands of the experimental IR spectrum of **8** within a range of devi-

Table 2. IR frequencies ν [cm^{-1}] calculated for **8a**–**8e** and found for **8**.

8	8a	8b	8c	8d	8e
		438			
		450			
		458			
487 / 497	**480 / 484**	**494**	**479 / 497**	**479**	**490 / 501**
		559	556	554	553
596	**580**				
		661			
765	**775**	**770**	**756**	**750**	**750 / 763**
805	**803**				
		1095	1096		
1121	**1104**			**1101**	
1272	**1275**	**1276**	**1272**	**1279**	**1278**
1333	**1330**	**1327**		**1328**	**1328**
			1365		
					1366
1387	**1372**	**1373**		**1370**	**1371**
1471	**1459**	**1457**	**1458**	**1456**	**1456**
1504	**1494**	**1493**	**1494**	**1494**	**1493**
		1575			
1617	**1602**	**1602**		**1600**	**1599**

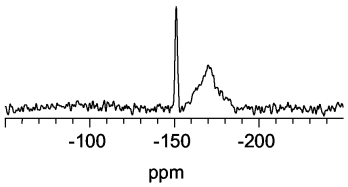
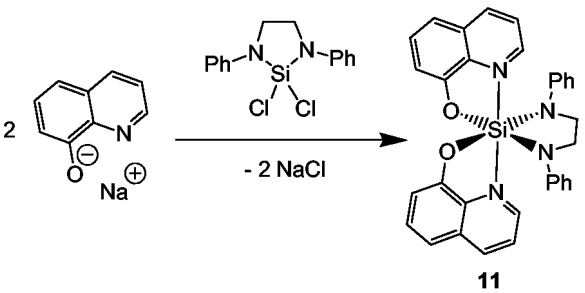


Fig. 8. ^{29}Si CP/MAS NMR spectrum of **10** [$(oxinate)_2SiBr_2$ in mixture with $(oxinate)_3Si^+Br^-$].

ations ± 20 cm^{-1} (intensity: transmittance between 0 and 50%) were assigned. The IR data of **8a** correlate well with those found in the spectrum of **8**. Compounds **8b**–**8e** are expected to give rise to absorption bands not observed in the experimental spectrum and *vice versa*.

NMR spectroscopic characterization of **8** in solution failed, because this compound is nearly insoluble in $CDCl_3$. It is rapidly dissolved in DMSO-d_6, but the ^{1}H, ^{13}C and ^{29}Si NMR data of this solution indicate decomposition and formation of the *mer*-isomer of the ionic complex $\mathbf{9}^+$ (Scheme 7). The third equivalent of the 8-oxyquinolinato ligands is probably generated in the reaction of **8** with DMSO to give chloromethylmethylsulfide, colloidal SiO_2 and 8-hydroxyquinoline. The deuterated chloromethylmethylsulfide was ^{13}C NMR spectroscopically identified in the solution. It was also recognized by its odour when the NMR sample tube was opened. This reaction of DMSO with chlorosilanes to give chloromethylmethylsulfide has already been described [10]. The SiO_2 slowly precipitated from the solution within a few days. To prove the formation of the cationic complex $\mathbf{9}^+$, the bromo analogue of **8**, compound **10** (Scheme 7), was synthesized and ^{29}Si NMR spectroscopically characterized in solution and in the solid state. The ^{29}Si CP/MAS NMR spectrum of **10** (Fig. 8) reveals the formation of the desired dibromocomplex with hexacoordinate Si atom by the signal at -170 ppm which is significantly broadened due to dipolar coupling between the ^{29}Si nucleus and the Br nuclei. The signal at -151.2 ppm points to the formation of **9Br** as a byproduct. A DMSO-d_6 solution of this product mixture shows only one signal at -151.8 ppm. It is identical with that of **9Cl**. The identity of the ^{29}Si NMR signals of **9Cl** and **9Br** in DMSO-d_6 and the unbroadened ^{29}Si CP/MAS signal of **9Br** in the solid state clearly indicate the non-coordination of the halide in those complexes and thus prove that the hexacoordination of the Si atoms in **9Cl** and **9Br** arises from the connection of the Si atom with three oxinato ligands. Evidence for the *mer*-configuration in the cation $\mathbf{9}^+$ is obtained from the ^{1}H and ^{13}C NMR spectra. There are three sets of signals of the oxinato ligands. For the *fac*-configuration which leads to a molecule with a threefold axis, only one set of signals is to be expected. To close this circle, the *mer*-configuration is derived from the *cis*-configuration found in compounds **5a** and **5b** by replacing the organic substituents at the Si atom (Me, Ph) by one oxinato ligand. Once again, this arrangement of two oxinato ligands in a hexacoordinate Si complex with two axial O atoms and two N-donor atoms in equatorial *cis*-positions is the preferred arrangement of those chelates. The coordination pattern of the Si atom in $\mathbf{9}^+$, however, may also be derived from the octahedral building patterns of **8d** and **8e** by replacing the monodentate *cis* substituents by a third oxinate ligand.

The reaction between the sodium 8-oxyquinolinate and 1,1-dichloro-2,5-diphenyl-2,5-diazasilolidine [11]



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Scheme 8.

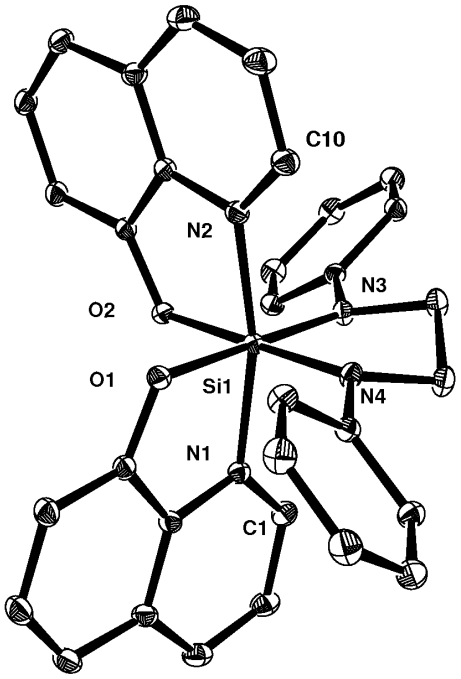

Fig. 9. Molecular structure of **11** (ORTEP plot with 50% probability ellipsoids, hydrogen atoms and chloroform molecule omitted).

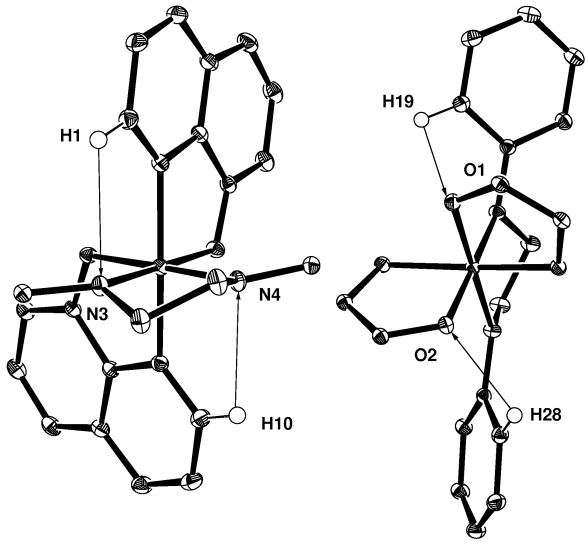

Fig. 10. Selected intramolecular hydrogen contacts in molecule **11** (non-relevant atoms omitted for clarity).

also yields a tris-chelate with a hexacoordinate silicon atom (**11**) (Scheme 8, Fig. 9.).

The N→Si dative bonds in this bis(oxinato)silicon tris-chelate are in *trans*-positions. Surprisingly, among four X-ray structurally characterized hexacoordinate bis(oxinato)silicon complexes, **11** is the only example with this configuration, but in most hexacoordinate silicon bis-chelates with other O,N-ligands the N→Si bonds are also in a *trans*-arrangement. Contrasting the coordination behavior of the oxinato ligands in compounds **5a** and **5b**, the N→Si bonds in **11** [1.9502(9) and 1.9557(9) Å] are rather short indicating a strong coordination. This arrangement may be supported by intramolecular hydrogen contacts as depicted in Fig. 10.

The hydrogen atoms in position 1 at the oxinato ligands (at C1 and C10) are directed towards the diazasilolidine nitrogen atoms N3 and N4. These contacts (H1-N3: 2.65 Å, H10-N4: 2.62 Å) cause a slight pyramidalization of the involved N atoms (sum of angles: 357.3° at N3, 355.6° at N4). This N→H interaction may also be a reason for the formation of the rather short N→Si dative bonds. (Further attractive hydrogen contacts between the oxinato O atoms and the *ortho*-H atoms of the phenyl groups (H19-O1: 2.43 Å, H28-O2: 2.34 Å) are also expected to stabilize the coordination sphere in **11**.) In complexes **5a**, **5b** and in $(oxinate)_2SiMeCl$ [5] no such interactions are possible. To realize arene π-stacking in **5a**, the phenyl groups must be forced into a coplanar arrangement which is sterically unfavorable due to the repulsion between their protons in *ortho* positions. In **5b** and in $(oxinate)_2SiMeCl$ the interactions between the H atom in position 1 of one oxinate ligand and the Si-bonded methyl group are considered to be repulsive.

Another striking feature of the structure of **11** is the similarity of Si-O and Si-N bond lengths in the equatorial plane [Si-O: 1.7893(7), 1.7933(7) Å; Si-N: 1.8138(8), 1.8224(8) Å], the former of which are expected to be much shorter.

Conclusions

The four molecular architectures of the bis(oxinato)silicon complexes presented above together with the only previously known structure of a hypercoordinate silicon complex of this class, $(oxinate)_2SiMeCl$, lead to the conclusion that the coordination of the oxinates with the N→Si dative bonds in *cis*- and the Si-O bonds in *trans*-positions result from sterical factors. The first example of a bis(oxinato)silicon complex with the *trans*-N→Si and *cis*-Si-O coordination, a dominating pattern in hexacoordinate silicon bis-chelates with other O,N-ligands, has been accom-

plished by avoiding such sterical repulsions. A [4+2]-coordination in bis(oxinato)$SiMe_2$ has been proven by X-ray structure analysis and ^{29}Si solid state NMR spectroscopy: The Si atom in this compound is bicapped tetrahedrally coordinated. The alternative *all-trans*-configuration was observed for (oxinate)$_2SiCl_2$ in the solid state and confirmed by quantum chemical calculations.

A large variety of coordination patterns was shown to exist in this class of complexes, but mainly for the solid state. The crystal structures do not necessarily represent the coordination mode of the oxinate ligand in these complexes in solution. Thus, the absence of significant N→Si coordination has been demonstrated for solutions of (oxinate)$_2SiMe_2$ and (oxinate)$_2$SiMePh by ^{29}Si NMR spectroscopy.

Experimental Section

Commercially available reagents were applied. 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 and toluene 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 400WB spectrometer (solid state). IR spectra of **8** were recorded on a Nicolet 510 FT IR spectrometer using KBr techniques. Elemental analyses were carried out on a Foss Heraeus CHN-O-Rapid.

2a: In thf (150 ml) the imine ligand **1** (10.0 g, 44.4 mmol) and triethylamine (12.0 g, 119 mmol) were stirred at room temperature and diphenyldichlorosilane (11.3 g, 44.6 mmol) was added dropwise. The resulting colorless mixture was stored at room temperature overnight. Then the precipitated hydrochloride was filtered off and washed with thf (60 ml). The volatiles were removed from the filtrate under reduced pressure and the oily residue was dissolved in chloroform (40 ml) and *n*-hexane (40 ml) was added. The solution was stored at room temperature to yield colorless crystals of **2a**. For complete crystallization the mixture was then stored in a refrigerator for 3 d. The product was filtered off, washed with hexane (30 ml) and dried in a vacuum. Yield: 12.3 g (30.3 mmol, 68%). m.p. 145 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.07$, 4.74 (2s, 2H, C=CH_2), 4.52 (s, 2H, Ph-CH_2), 6.80 – 7.75 (mm, 19H, ar). – ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 48.7$ (N-*C*H_2-Ph), 87.3 (C=*C*H_2), 120.3, 121.6, 124.7, 126.5 (2×), 127.2, 128.1 (2×), 129.6, 131.1, 131.2, 135.3, 137.7, 145.5, 151.3 (ar & *C*=CH_2). – ^{29}Si NMR (79 MHz, $CDCl_3$): $\delta = -24.0$. – $C_{27}H_{23}NOSi$ (405.55): calcd. C 79.96, H 5.72, N 3.45; found C 79.50, H 5.76, N 3.40.

2b: In thf (150 ml) the imine **1** (10.0 g, 44.4 mmol) and triethylamine (12.0 g, 119 mmol) were stirred at room temperature and methylphenyldichlorosilane (8.53 g, 44.6 mmol) was added dropwise. The resulting colorless mixture was stored at room temperature overnight. Then the precipitated hydrochloride was filtered off and washed with thf (30 ml). The volatiles were removed from the filtrate under reduced pressure to yield an oily colorless residue. Yield: 11.7 g (34.1 mmol, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.58$ (s, 3H, Si-CH_3), 3.99, 4.67 (2d, 2H, C=CH_2, $^2J_{HH} = 1.2$ Hz), 4.33 (s, 2H, Ph-CH_2), 6.80 – 7.60 (mm, 14H, ar). – ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 3.5$ (Si-CH_3), 48.2 (N-*C*H_2-Ph), 86.1 (C=*C*H_2), 120.1, 121.5, 124.4, 126.3, 126.5, 127.0, 128.0, 128.2, 129.5, 130.8, 133.8, 133.9, 137.9, 145.6, 151.0 (ar & *C*=CH_2). – ^{29}Si-NMR (79 MHz, $CDCl_3$): $\delta = -10.9$.

5a: **2a** (1.6 g, 3.9 mmol) was dissolved in chloroform (6 ml) and the solution was stirred at 0 °C. A solution of 8-hydroxyquinoline (0.57 g, 3.9 mmol) in chloroform (6 ml) was added dropwise. The resulting yellowish solution was stored at room temperature. After 1 d the crystalline product was filtered off, washed with chloroform (6 ml) and dried under reduced pressure. Yield: 0.70 g (1.5 mmol, 76%) yellowish crystals. m.p. 260 °C. – $C_{30}H_{22}N_2O_2Si$ (470.59): calcd. C 76.57, H 4.71, N 5.95; found C 75.32, H 4.81, N 5.84.

5b: **2b** (3.43 g, 10.0 mmol) was stirred in chloroform (15 ml) at 0 °C and a solution of 8-hydroxyquinoline (1.45 g, 10.0 mmol) in chloroform (15 ml) was added. The resulting solution was stored at room temperature for 2 weeks. The crystalline product was filtered off and dried in a vacuum. Yield: 0.35 g (mmol, 17%) yellowish crystals. (In the filtrate crystallization continued for many weeks.) m.p. 177 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.52$ (s, 3H, Si-CH_3), 7.10 – 7.25 (m, 7H, ar), 7.35 (d, 2H, ar, $^3J_{HH} = 8.0$ Hz), 7.49 (t, 2H, ar, $^3J_{HH} = 8.0$ Hz), 7.93 (dd, 2H, ar, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.0$ Hz), 7.99 (dd, 2H, ar, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 0.8$ Hz), 8.61 (dd, 2H, ar, $^3J_{HH} = 4.6$ Hz, $^4J_{HH} = 1.0$ Hz). – ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 6.1$ (Si-CH_3), 114.2, 116.8, 121.6, 127.1, 127.5, 129.1, 129.2, 133.8, 136.9, 138.1, 144.4, 146.0, 153.6 (ar). – ^{29}Si-NMR (79 MHz, $CDCl_3$): $\delta = -27.8$. – $C_{25}H_{20}N_2O_2Si$ (408.52): calcd. C 73.50, H 4.93, N 6.86; found C 72.47, H 4.99, N 6.83.

8: To a refluxing solution of $SiCl_4$ (1.76 g, 10.4 mmol) in chloroform (100 ml) a solution of 8-hydroxyquinoline (3.00 g, 20.6 mmol) in chloroform (40 ml) was added dropwise and the resulting suspension was refluxed for further 1.5 h. The mixture was then allowed to cool to ambient temperature, the solid product was filtered off, stirred in a solution of triethylamine in chloroform (2 ml + 30 ml) for 3 h, filtered off again and dried in a vacuum. Yield: 2.90 g (7.29 mmol, 72%) yellow powder. $C_{18}H_{12}N_2O_2SiCl_2$

Table 3. Data of crystal structure determination and refinement of **2a**, **5a**, **5b 7** and **11**∗$CHCl_3$.

Compound	**2a**	**5a**	**5b**	**7**	**11**∗$CHCl_3$
Empirical formula	$C_{27}H_{23}NOSi$	$C_{30}H_{22}N_2O_2Si$	$C_{25}H_{20}N_2O_2Si$	$C_{20}H_{18}N_2O_2Si$	$C_{33}H_{27}Cl_3N_4O_2Si$
T (K)	198(2)	293(2)	93(2) T (K)	198(2)	93(2)
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$Pna2_1$	$P\bar{1}$
a [Å]	9.526(1)	12.644(2)	9.0444(10)	13.057(1)	8.6169(3)
b [Å]	14.711(1)	14.748(2)	14.2541(16)	9.839(1)	12.7470(5)
c [Å]	15.446(1)	12.826(3)	15.6102(16)	13.517(1)	13.7596(6)
α [°]	90	90	74.784(5)	90	94.627(2)
β [°]	96.777(10)	91.080(10)	85.094(6)	90	92.361(2)
γ [°]	90	90	89.880(6)	90	103.967(2)
Z	4	4	4	4	2
V [Å^3]	2149.4(3)	2391.3(7)	1934.4(4)	1736.5(3)	1459.0(1)
ρ_{calc} [g cm^{-3}], μ [mm^{-1}]	1.253, 0.128	1.307, 1.108	1.403, 0.148	1.325, 0.151	1.471, 0.395
$F(000)$	856	984	856	728	668
Crystal size [mm^3]	$0.41 \times 0.36 \times 0.27$	$0.5 \times 0.4 \times 0.2$	$0.14 \times 0.12 \times 0.10$	$0.44 \times 0.37 \times 0.26$	$0.42 \times 0.38 \times 0.32$
$2\theta_{max}$ [°]	50	150	50	54	68.9
Index ranges	$-11 \le h \le 11$, $-17 \le k \le 17$, $-18 \le l \le 18$	$-15 \le h \le 15$, $-10 \le k \le 18$, $-9 \le l \le 16$	$-10 \le h \le 10$, $-16 \le k \le 16$, $-18 \le l \le 18$	$-16 \le h \le 16$, $-12 \le k \le 11$, $-17 \le l \le 15$	$-13 \le h \le 13$, $-20 \le k \le 20$, $-21 \le l \le 21$
Reflections collected, R_{int}	29992, 0.1370	5953, 0.0339	54733, 0.0494	19658, 0.0357	36218, 0.0208
Independent reflections	3774	4868	6822	3530	12296
Parameters	271	316	542	326	388
R Indices (all data)	$R_1 = 0.0746$, $wR_2 = 0.0979$	$R_1 = 0.1179$, $wR_2 = 0.1758$	$R_1 = 0.0525$, $wR_2 = 0.0892$	$R_1 = 0.0608$, $wR_2 = 0.0898$	$R_1 = 0.0414$, $wR_2 = 0.0918$
Largest diff. peak and hole [e Å^{-3}]	0.309 and −0.283	0.367 and −0.393	0.333 and −0.287	0.162 and −0.170	0.625 and −0.581

(387.30): calcd. C 55.81, H 3.12, N 7.23; found C 54.81, H 3.68, N 7.02.

10: To a refluxing solution of $SiBr_4$ (1.6 g, 4.6 mmol) in toluene (50 ml) a solution of 8-trimethylsiloxyquinoline [2f] (2.0 g, 9.2 mmol) in toluene (25 ml) was added dropwise and the resulting suspension was refluxed again for 2 h. The mixture was then allowed to cool to ambient temperature, the solid product was filtered off and dried in a vacuum. Yield: 1.7 g, yellow powder.

This crude product contains the bis(oxinato)silicon complex **10** and notable amounts of the complex **9Br** as shown by solid state ^{29}Si NMR spectroscopy and by elemental analyses.

11: A solution of 8-hydroxyquinoline (0.49 g, 3.4 mmol) was added to a stirred solution of sodium bis(trimethylsilyl)amide (0.63 g, 3.4 mmol) in thf (30 ml). After 12 h the volatiles were removed in a vacuum and the remaining solid was dissolved in thf (12 ml). Subsequently, a solution of 1,1-dichloro-2,5-diphenyl-2,5-diazasilolidine (0.51 g, 1.7 mmol) [11] in thf (6 ml) was added dropwise and the orange suspension was stirred for 1 h. The solvent was removed under reduced pressure and the solid product was extracted from the residue with chloroform (20 ml) to yield orange crystals of **11***$CHCl_3$ after 7 d. These crystals were filtered off and briefly dried in a vacuum. Yield: 0.29 g (0.45 mmol, 26%), m.p. 218 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.08, 3.39 (2s broad, 4H, N-CH_2CH_2-N), 6.40 – 6.90 (3m, 12H, ar), 7.01 (d, 2H, ar, $^3J_{HH}$ = 8.4 Hz), 7.20 – 7.30 (m, 2H, ar), 7.64 (dd, 2H, ar, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 4.8 Hz), 8.34 (d, 2H, ar, $^3J_{HH}$ = 8.4 Hz), 9.30 (d, 2H, ar, $^3J_{HH}$ = 4.8 Hz). – ^{13}C NMR (101 MHz, $CDCl_3$): δ = 46.9 (N-CH_2CH_2-N), 110.9, 112.2, 117.7, 121.1, 121.5, 127.1, 128.4, 130.8, 135.7, 139.6, 140.8, 153.1, 153.8 (ar). – ^{29}Si NMR (79 MHz, CP/MAS): δ = −152.0. – $C_{33}H_{27}N_4O_2SiCl_3$ (646.03): calcd. C 61.35, H 4.21, N 8.67; found C 64.48, H 4.53, N 9.53. The systematically higher contents of C, H and N result from partial loss of chloroform from the crystals.

Quantum chemical calculations

The quantum chemical calculations were carried out using the GAUSSIAN 03 series of programs [12]. Geometries were fully optimized at the density functional theory level (DFT), using Becke's three-parameter hybrid exchange functional and the correlation functional of Lee, Yang and Parr (B3LYP) [13, 14]. Geometry optimizations and harmonic frequencies were calculated with the polarized 6-31G* basis set for all elements [15, 16]. IR frequencies were scaled with the factor 0.9613 [17]. Further single point energies for the optimized geometries were obtained at the B3LYP/6-31+G(d), B3LYP/6-311+G(2d,p), MP2/6-31+G(d,p), and MP2/6-311+G(2d,p) level of theory [18, 19].

NMR shielding tensors were calculated with the Gauge-Independent Atomic Orbital method (GIAO) [20] at the B3LYP/6-311+G(2d,p) level of theory with the optimized

geometries (B3LYP/6-31G*). Calculated absolute shielding values were converted to relative shifts δ with the calculated shielding for tetramethylsilane at the same level of theory.

X-ray structure analyses

X-ray structure data were recorded on an Enraf Nonius CAD4 diffractometer using Cu-K_α-radiation (λ = 1.54178 nm) and psi-scans for absorption correction (**5a**), a Bruker-Nonius-KappaCCD diffractometer (**2a**, **7**) and a Bruker-Nonius-APEX2-CCD diffractometer (**5b**, **11***$CHCl_3$) with Mo-K_α-radiation (λ = 0.71073 nm) and semi-empirical correction (SADABS). The structures were solved with direct methods (SHELXS-97) and refined by 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 3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-276924 (**2a**), CCDC-194703 (**5a**), CCDC-276922 (**5b**), CCDC-276903 (**7**) and CCDC-276905 (**11***$CHCl_3$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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