

(Amidomethyl)dimethylsilanol hydrohalides: Synthesis, NMR and IR studies. Characteristic features of the electronic structure from high-resolution X-ray study and quantum chemical calculation

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Abstract

(C,O)-chelate silanol hydrohalides $\text{RC(O)NHCH}_2\text{SiMe}_2\text{OH} \cdot \text{HHal}$ (**2a,b** and **5b**), and their precursors, (C,O)-chelate chlorosilanes $\text{RC(O)NHCH}_2\text{SiMe}_2\text{Cl}$ (**6a,b**) and disiloxanes $[\text{RC(O)NHCH}_2\text{SiMe}_2\text{O}]_2$ (**8a,b**) (R = Me (**a**), Ph (**b**); Hal = Cl (**2**), Br (**5**)), were obtained by several routes. The original scheme of hydrolysis of the above chlorides was discussed in detail. X-ray analysis has shown that the silanol hydrohalogenides $\text{PhC(O)NHCH}_2\text{SiMe}_2\text{OH} \cdot \text{HX}$ (**2b** and **5b**) in the crystal exist in the form of cation–anion pairs $[\text{PhC(O)NHCH}_2\text{SiMe}_2(\text{OH}_2)]^+ \cdot \text{X}^-$ (**14b** · Cl[−] and **14b** · Br[−]) assembled by H-bonds in a 3D framework. The Si atom in the cation has a trigonal bipyramidal configuration with the oxygen atom of the carbonyl group and protonated hydroxyl *exo*-substituent in axial positions. The endocyclic Si–O bonds are equal with an average of 1.905 Å while the exocyclic Si–O bonds are 1.979 and 2.009 Å, for Hal = Cl and Br, respectively.

Quantum chemical calculations have shown that the cation $[\text{PhC(O)NHCH}_2\text{SiMe}_2(\text{OH}_2)]^+$ (**14b**) is stable only in the crystal. Based on a high-resolution X-ray study and a quantum chemical calculation, it was found that the chemical bonding pattern in the OSiO axial fragment of the cation **14b** corresponds to a three-centred four electron interaction. The cation **14b** should be considered as a silylium cation stabilized by coordinated H₂O molecules rather than a silyloxonium ion.

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1. Introduction

At present, the *N*-silylmethyl derivatives of the amides and related compounds have been relatively well studied [1a,1b]. Most of them include at least one sufficiently electronegative substituent group at the silicon atom and are

characterized by the (C,O)-chelate structure with an intramolecular coordinate bond $\text{O} \rightarrow \text{Si}$ [1a,1b]. Much less is known about the corresponding intermolecular homoassociates [1b].

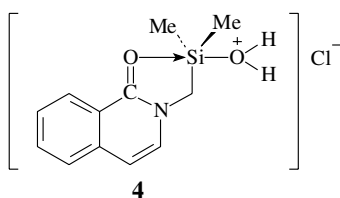
Recently, we have reported preliminary data on the synthesis and structure of the first representatives of monosubstituted amides of the general type $\text{RC(O)NHCH}_2\text{SiMe}_2\text{X}$ (R = Alk, Ar; X = Hal) [2a,2b]. The coordinate interaction in these compounds can be achieved by the participation of

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both the oxygen atom of the amide group and the hydrogen atom of the NH group. Thus, such compounds are useful as models for the investigation of the inter- and intramolecular processes of coordinate bonding. Indeed, both types of coordinate interaction have been detected in the crystals of the fluorides $\text{RC(O)NHCH}_2\text{SiMe}_2\text{F}$ (**1a**, $\text{R} = \text{Me}$; **1b**, $\text{R} = \text{Ph}$) [2b].

Preliminary data concerning the formation and oxonium structure of the first representative of another type of monosubstituted amide derivatives, the hydrochloride $\text{PhC(O)NHCH}_2\text{SiMe}_2\text{OH} \cdot \text{HCl}$ (**2b**), have been reported in a short communication [3]. An X-ray investigation revealed the nature of the pentacoordinate silicon atom in **2b**. Note, that both tetra- and pentacoordinated protonated silanols are of interest as intermediate products in the hydrolysis of organohalosilanes, of particular theoretical and practical importance in the chemistry of organosilicon compounds. At present, similar compounds containing water molecules as ligands have not been investigated in detail. In particular, the cation–anion complex $[\text{Bu}_3\text{SiOH}_2]^+ [\text{Br}_6\text{CB}_{11}\text{H}_6]^-$ (**3**) [4a], containing a tetracoordinated silicon as the cation and the non-nucleophilic brominated *closo*-carborane anion as well as the pentacoordinated protonated silanol **4** [4b] are rare examples of such compounds that have been characterized by X-ray data.



In this paper, the modified technique for the synthesis of the hydrochloride **2b**, and the synthesis of its analogs, the hydrochloride **2a** and hydrobromide **5b**, are given. We also discuss the results of an X-ray investigation and quantum

chemical calculations of the molecular and crystalline structure, and the electronic structure of the hydrohalides **2b** and **5b**.

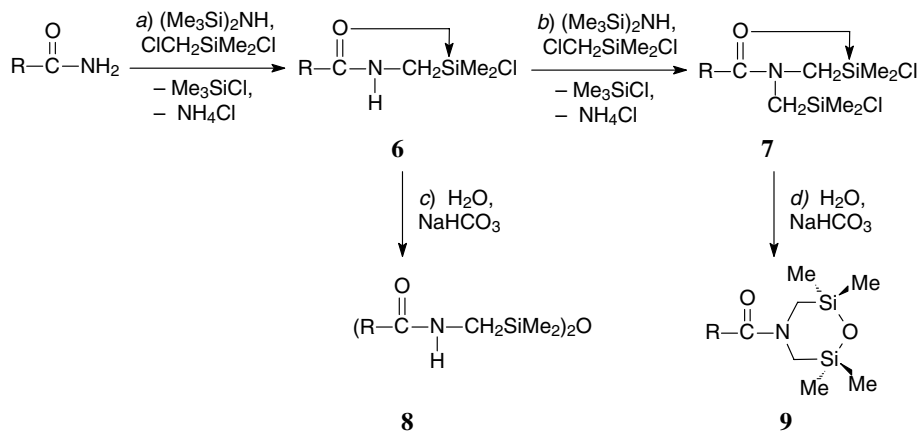
2. Results and discussion

2.1. Synthesis

The hydrochloride **2b** described in the short communication [3] was obtained as a result of a lengthy (about 8 months) storage of the *N*-(dimethylchlorosilylmethyl)benzamide under conditions which failed to completely exclude the presence of atmospheric moisture. Accordingly, we considered that the hydrolysis of the chlorides $\text{RC(O)NHCH}_2\text{SiMe}_2\text{Cl}$ (**6**) and corresponding bromides was the most rational route to the hydrohalides of the silanols. However, the preparation of the individual compounds proved to be a more complex task. We investigated several approaches to the chlorides **6** (see previous papers [2b,3,5a,5b]). The first one is based on the reaction of the amides RC(O)NH_2 with dimethyl(chloromethyl)chlorosilane $\text{ClCH}_2\text{SiMe}_2\text{Cl}$ in the presence of hexamethyldisilazane, i.e. a one pot synthesis for the *N*-chloromethylsilylmethylation of the non-substituted and monosubstituted amides using the $\text{ClCH}_2\text{SiMe}_2\text{Cl}-(\text{Me}_3\text{Si})_2\text{NH}$ system (Scheme 1) [5a,5b]. In the case of a twofold excess of the latter the reaction leads to the *N,N*-bis(dimethylchlorosilylmethyl)amides (**7**), via intermediate formation of the monochlorides **6**.

Hydrolysis of the monochlorides **6** by aqueous NaHCO_3 proceeds practically quantitatively (see below) with formation of the disiloxane **8** (see Scheme 1, equation (c)). The analogous hydrolysis of the dichloride **7**, as described earlier, yields products of the intermolecular cyclocondensation, 4-acyl-2,6-disilamorpholines (**9**) (see Scheme 1, equation (d)) [5b,6a,6b].

The dichlorides **7**, for example, compound **7a** ($\text{R} = \text{Me}$) [5b], can be obtained according to Scheme 1, equations (a) and (b), in high yield. In contrast, the products of the



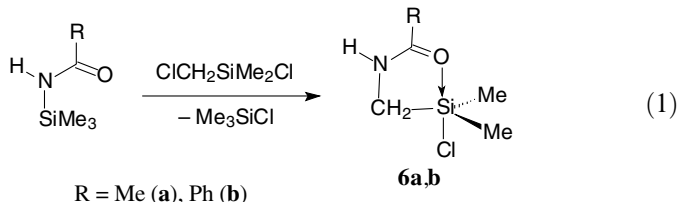
$\text{R} = \text{H}, \text{Alk}, \text{Ar}$

Scheme 1.

mono-*N*-dimethylchlorosilylmethylation **6** could not be isolated from the reaction mixture in acceptable yields even on varying the reagent ratios. Thus, the reaction of acetamide with an equimolecular amount of $\text{ClCH}_2\text{SiMe}_2\text{Cl}$ and the required amount of $(\text{Me}_3\text{Si})_2\text{NH}$ in boiling benzene gives the *N*-dimethylchlorosilylmethylacetamide (monochloride **6a**) in only 23% yield. The reason for such a low yield was found to be the formation of a significant amount of the dichloride **7a**. In addition, we established that the bissilylmethylation product **7a** could be formed using both the $\text{ClCH}_2\text{SiMe}_2\text{Cl}-(\text{Me}_3\text{Si})_2\text{NH}$ system and the reaction of the acetamide with $\text{ClCH}_2\text{SiMe}_2\text{Cl}$ in the presence of Et_3N , i.e. by the known general methods of preparation of mono-(C,O)-chelate pentacoordinated chlorosilanes [7]. The ratio of products of mono- and bissilylmethylation of acetamide depends on the nature and relative amount of the silylmethylation reagent as shown in Table 1.

The determination of the mole ratio of the chlorides **6a** and **7a** was performed by ^1H NMR spectroscopy after hydrolysis of the reaction mixture by aqueous NaHCO_3 , which resulted in their almost quantitative conversion into the acyclic disiloxane **8a** (see below) and disilamorpholine **9a** ($\text{R} = \text{Me}$), respectively.

The second approach to the monochlorides **6** is based on the use of the general method for the preparation of (C,O)-chelate Si-substituted *N*-(silylmethyl)amides and -lactams [7–9],¹ using a transsilylation reaction, i.e. the reaction of *N*-TMS-amides $\text{RC}(\text{O})\text{NHSiMe}_3$ with $\text{ClCH}_2\text{SiMe}_2\text{Cl}$



In this case the yield of the monochlorides **6a,b** were higher than those obtained by the reaction shown in Scheme 1, equation (a). However, the samples of the chlorides **6a,b** isolated from the reaction mixture were rather unstable, deliquescent powders. Their hydrolysis by aqueous NaHCO_3 gave quite stable acyclic disiloxanes **8a,b** (see Scheme 1, equation (c)). The latter were obtained without isolation of the intermediate monochlorides by hydrolysis of the reaction mixture immediately following heating of the *N*-TMS-amides with $\text{ClCH}_2\text{SiMe}_2\text{Cl}$. Thus, the conversion of **6** into the disiloxane **8** essentially provides a method for the identification of the hydrolytically labile chlorides **6** (Scheme 1, equation (a), and reaction (1)).

In addition, the disiloxanes **8** are of interest because their reactions lead to pentacoordinated silicon compounds containing a stable intramolecular coordinate bond $\text{O} \rightarrow \text{Si}$. In particular, their interaction with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ results in the fluorides **1** mentioned above [2b]. We now

Table 1

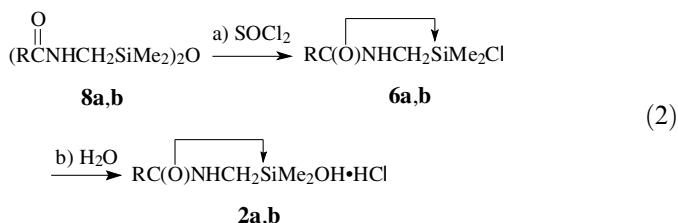
The ratio of products of mono- and bissilylmethylation of acetamide, **6a** and **7a**, depending on the nature and relative amount of the silylmethylation reagent

Reagents	The ratio of acetamide and reagents	The ratio of chlorides 6a and 7a
$\text{ClCH}_2\text{SiMe}_2\text{Cl}-(\text{Me}_3\text{Si})_2\text{NH}$	1:1:0.4	1.74:1
$\text{ClCH}_2\text{SiMe}_2\text{Cl}-(\text{Me}_3\text{Si})_2\text{NH}$	1:1:1	1.08:1
$\text{ClCH}_2\text{SiMe}_2\text{Cl}-\text{Et}_3\text{N}$	1:1:1	1.94:1
$(\text{Me}_3\text{Si})_2\text{NH}, \text{ClCH}_2\text{SiMe}_2\text{Cl}^a$	1:0.4:1	1.28:1

^a Successive addition of reagents to acetamide.

report the reactions of the disiloxanes **8** with electrophilic reagents such as SOCl_2 , Me_3SiBr and HCl .

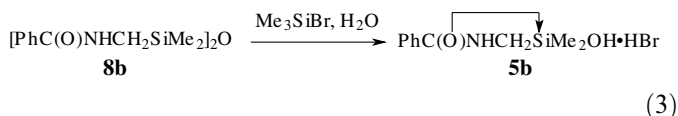
The disiloxanes **8a,b** were found to react readily with thionylchloride in benzene leading to the formation of purer samples of the chlorides **6a,b** (equation (2a)) in higher yields (~80%) than in previous cases



Unlike the reaction of *N*-(dimethylchlorosilylmethyl)amides **6a,b** with aqueous NaHCO_3 which gave the corresponding disiloxanes **8a,b** (see Scheme 1, equation (c)), hydrolysis of the chlorides **6a,b** in the absence of an HCl acceptor gives the hydrochlorides **2a,b** which are previously unknown (equation (2b)).

So, as mentioned earlier [3], when storing the chloride **6b** for long periods under conditions where moisture was not completely excluded, its conversion into the hydrochloride **2b** took place. The same compound was isolated by treatment of the freshly prepared chloride **6b** with the appropriate amount of water in boiling acetonitrile in practically quantitative yield. The interaction of the disiloxane **8a** with thionylchloride in heptane in contact with atmospheric moisture yielded the extremely unstable hydrochloride **2a**. The transformation of the silanol hydrochlorides **2** into the disiloxanes **8** proceeds easily as was established when compound **2b** was treated with excess of aqueous NaHCO_3 .

The reaction of the disiloxane **8b** with Me_3SiBr when in contact with atmospheric moisture does not lead to expected bromide $\text{PhC}(\text{O})\text{NHCH}_2\text{SiMe}_2\text{Br}$ but gives the product of its subsequent hydrolysis, the hydrobromide **5b**



Treatment of the disiloxane **8b** by an HCl solution in acetonitrile (obtained “*in situ*” from the calculated amounts of thionylchloride and water) on heating to 90 °C yielded a

¹ The multistage nature of these transsilylation reactions is discussed in detail in the review [1a].

mixture of chloride **6b** and silanol hydrochloride **2b**. Recrystallization of this mixture from damp acetonitrile yielded only one substance, the silanol hydrochloride **2b**, in a yield of 94%.

It may be suggested that the first stage in this case is the formation of the disiloxane $[\text{PhC}(\text{O})\text{NHCH}_2\text{SiMe}_2]_2\text{O} \cdot 2\text{HCl}$ (**10b**), where both amide oxygen atoms are protonated. This process is analogous to the formation of the adduct $(\text{L}^5\text{SiMe}_2)_2\text{O} \cdot 2\text{CCl}_3\text{COOH}$ (where L^n is a lactamomethyl n -membered C,O-coordinating ligand) from the corresponding disiloxane and CCl_3COOH [10a]. Other evidence for the presence of the intermediate adduct **10b** comes from comparison with the structurally characterized products of partial hydrolysis of the chloride $\text{L}^5\text{SiMe}_2\text{Cl}$, the dihydrochloride $(\text{L}^5\text{SiMe}_2)_2\text{O} \cdot 2\text{HCl}$ [10b] and of the chloride $\text{MeC}(\text{O})\text{N}(\text{Me})\text{CH}_2\text{SiMe}_2\text{Cl}$ (**6c**) and the dihydrochloride $[\text{MeC}(\text{O})\text{N}(\text{Me})\text{CH}_2\text{SiMe}_2]_2\text{O} \cdot 2\text{HCl}$ (**10c**), which will be discussed in a subsequent paper. Heating the dihydrochloride **10b** leads to rupture of the disiloxane bond with the formation of hydrochloride **2b**.

Thus, the results obtained provide evidence that the pentacoordinated silanol hydrochlorides **2** are primary products of hydrolysis of the pentacoordinated chlorosilanes in the absence of HCl acceptors and that the dihydrochlorides of the disiloxanes **10** which contain tetracoordinated silicon atoms are also possibly secondary products (Scheme 2).

The final stage of the process resulting in the formation of disiloxane **8** only requires the presence of suitable HCl acceptors. The structure of the chlorides **6**, disiloxanes **8** and silanol hydrohalides **2** and **5b** were confirmed by IR and ^1H , ^{13}C , ^{29}Si NMR spectroscopy, and X-ray crystallography. The presence of the intramolecular coordinate bond $\text{O} \rightarrow \text{Si}$ in the chlorides **6a,b** and the absence of the

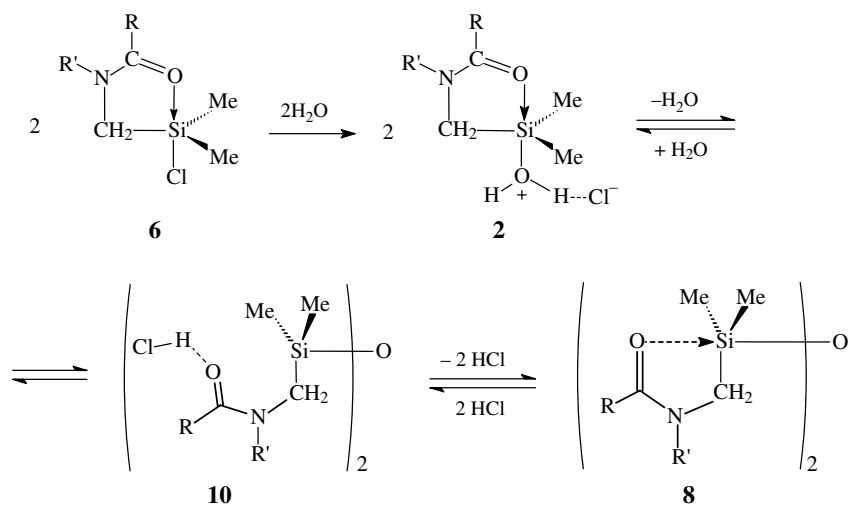
similar interaction in the disiloxanes **8a,b** were established on the basis of the IR and ^{29}Si NMR spectral characteristics of these compounds as described below.

2.2. IR studies

The IR spectra of the chlorides **6a,b** in solution show two absorption bands with frequencies 1635 and 1540 cm^{-1} for the chloride **6a**, as well as two bands with frequencies 1618 and 1520 cm^{-1} for the chloride **6b**. Taking into account the ^{29}Si NMR data (see below) we suggest that these bands relate to coupled stretching vibrations of the amide fragment $\text{N}=\text{C}=\text{O}$. As with the related (C,O)-chelate pentacoordinated chlorosilanes [7b–9], this confirms the presence of an intramolecular coordinate bond $\text{O} \rightarrow \text{Si}$ in **6a,b**.

The frequencies of the two strong absorption bands in the region $1670\text{--}1520\text{ cm}^{-1}$ detected in IR spectra of the disiloxanes **8a,b** are similar to those in the spectra of the chlorides **6a,b**. However, taking into account the ^{29}Si NMR data which show the absence of an intramolecular coordinate bond $\text{O} \rightarrow \text{Si}$ in **8a,b** (see below) we suggest that these bands arise from the stretching vibration of the non-coordinated carbonyl group of the amide fragment (NCO) ($\sim 1640\text{ cm}^{-1}$, amide I, $\nu_{\text{C}=\text{O}}$) and the NH-deformation vibration ($\sim 1530\text{ cm}^{-1}$, amide II, δ_{NH}).

In the IR-spectra of the silanol hydrohalides **2b** and **5b**, (KBr disks), characteristic bands for intramolecular coordinate bonds $\text{O} \rightarrow \text{Si}$ and intermolecular H-bonds with chlorine and bromine atoms were observed (see Section 3). The presence of bands in the region $1700\text{--}1500\text{ cm}^{-1}$ assigned to stretching vibrations which are strongly coupled as a result of delocalization in the $\text{N}=\text{C}=\text{O}$ fragments [7b–9] is evidence for the intramolecular



R, R' = H, Alk, Ar

R = Me, R' = H(**a**); R = Ph, R' = H (**b**); R = Me, R' = Me (**c**); R = Me, R' = CH(Ph)Me(**d**)

Scheme 2.

coordinate bond O → Si in these compounds. There were no adsorptions corresponding to uncoordinated amide groups indicating stable O → Si coordination.

A broad intense absorption in the range 3600–2600 cm⁻¹ (O–H stretching vibration, perturbed by intermolecular H-interactions) was observed in the IR spectra of the hydrohalides **2b** and **5b**. In both spectra, a narrow band for the N–H stretching frequency at 3225 and 3215 cm⁻¹ for the hydrochloride **2b** and the hydrobromide **5b**, respectively, was observed. These lower N–H frequencies compared to “free” secondary amides (3450–3400 cm⁻¹) show hydrogen bonding involving the halide ion.

2.3. NMR studies

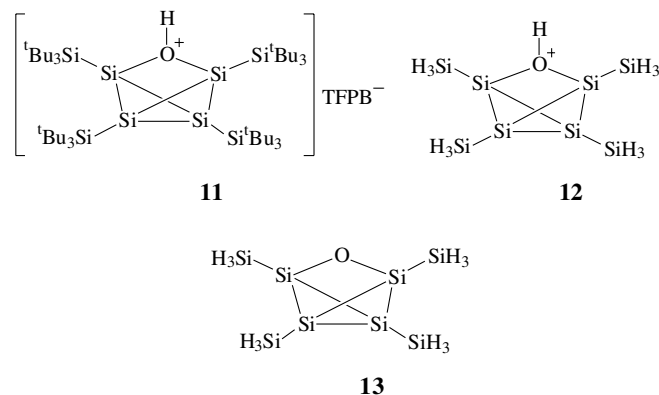
In principle, ²⁹Si NMR data is more informative concerning the extent of silicon coordination in the solution in the compounds discussed. Indeed, resonances detected in the ²⁹Si NMR spectra of the compounds **6a,b** (–27.4, –26.5 (br. s) ppm) and **8a,b** (4.5, 4.7 ppm) were found to be in the range of chemical shifts corresponding to the pentacoordinated state of the silicon atom in chlorides **6a,b** and close to the tetracoordinated state of silicon in the disiloxanes **8a,b** [cf. silicon resonances in chlorides **6c** (–37.6 ppm) and MeC(O)N(CHMePh)CH₂SiMe₂Cl (**6d**, –38.1 ppm) and disiloxanes **8c,d** (3.4 and –0.1 ppm) [11a].

Due to the limited solubility of the silanol hydrohalides **2a,b** and **5b** in solvents such as CDCl₃ or CD₂Cl₂, we have failed to determine NMR spectra under conditions where there is a low probability of hydrolysis or the formation of higher coordinate complexes. The ¹H and ¹³C NMR spectral data (CD₃CN) for compounds **2a,b** were consistent with the proposed structures. In particular, in the ¹H NMR spectrum, broadened singlets at 5.21 and 8.09 ppm, respectively, corresponding to the three slowly exchanging protons of the OH₂ and the NH groups were observed. Note that protons of the OH₂ group of the protonated silanol **3** were observed at 8.04 ppm (CD₂Cl₂) [4a].

By comparison, in the case of complexes [Bu₃Si(OH₂)⁺][Br₆CB₁₁H₆][–] (**3**), [Me₃Si(OEt₂)⁺TFPB[–]] (TFPB[–] = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate), [Me₃Si(MeCN)⁺TFPB[–]], and [Prⁱ₃Si(MeCN)⁺][Br₅CB₉H₅][–] containing the tetracoordinated Si atom, the silicon resonance was observed at 46.7 ppm (CP–MAS) [4a], 66.9 ppm (CD₂Cl₂, at –70 °C), 38.5 ppm (CD₂Cl₂, at –10 °C) and 33.8 ppm (CD₂Cl₂) [11b], respectively.

In turn, for the protonated tetracoordinated disiloxane [(^tBu₃Si)₄Si₄OH]⁺TFPB[–] (**11**), the structure of which was confirmed by X-ray crystallography, the chemical shifts of the (Si–O⁺(H)–Si) silicon atoms were found to be 44.2 ppm [12]. Thus, the resonance of the silicon atoms connected to the oxygen atom in **11** is shifted downfield by approximately 50 ppm compared with that of the corresponding non-protonated species. The chemical shifts of the silicon atoms calculated by the authors for the model

compounds **12** and **13** were 40.5 ppm (Si–O⁺(H)–Si) and –23.4 ppm (Si–O–Si), respectively (cf. 67.6 ppm calculated for the silicon atoms in [(Me₃Si)₂OH]⁺TFPB[–] [11b])



2.4. X-ray structural studies and analysis of the electron density distribution of crystals **2b** and **5b**

2.4.1. The crystal and molecular structure of **2b** and **5b**

Silanol hydrohalogenides **2b** and **5b** are isostructural cation–anion pairs assembled in the crystal into three-dimensional framework via intramolecular H-bonds (Fig. 1). The Si atom has a trigonal bipyramidal (TBP) configuration with a deviation from the plane of the equatorial carbon atoms (Δ Si) of –0.02 Å and –0.04 Å for **2b** and **5b**, respectively (the minus sign means a deviation towards the O(1) atom). The O(1) and O(2) atoms occupy the axial positions (Fig. 2). The average lengths of the Si(1)–O(1) and Si(1)–O(2) bonds are 1.902 and 1.994 Å, respectively. The shortest interatomic Si...Cl and Si...Br distances are 4.047 and 4.239 Å, respectively (Table 2).

Thus, the Si(1)–O(1) bonds in **2b** and **5b** which are commonly described as “coordinate” are significantly shorter than the Si(1)–O(2) bond. In this respect the hydrohalogenides of the silanols are significantly different from the majority of hypervalent silicon compounds. Analysis of the geometry of the silicon atom coordination polyhedra allowed us to conclude that the water ligand may be described as a “good” leaving group, such as I, Br and OTf [13]. In particular, one of the shortest Si–O coordinate bonds (1.753 Å) was found in the chelate compound L⁶SiMe₂OTf with triflate group as the *exo*-substituent. This molecule may be considered to be a close cation–anion pair with a Si(1)...O(2) interatomic distance of 2.78 Å. The ability of the triflate group to act as a “good” leaving group is closely related to high extent of delocalization of the negative charge due to electron-withdrawing effect of the fluorine atoms. It should be noted that the O(2) atom in **2b** and **5b** has a formal positive charge and the water ligand may be described as an oxonium fragment. The latter statement contradicts the results of a topological analysis of electron density [14]. According to this topological analysis, the positive charge in hypervalent silicon

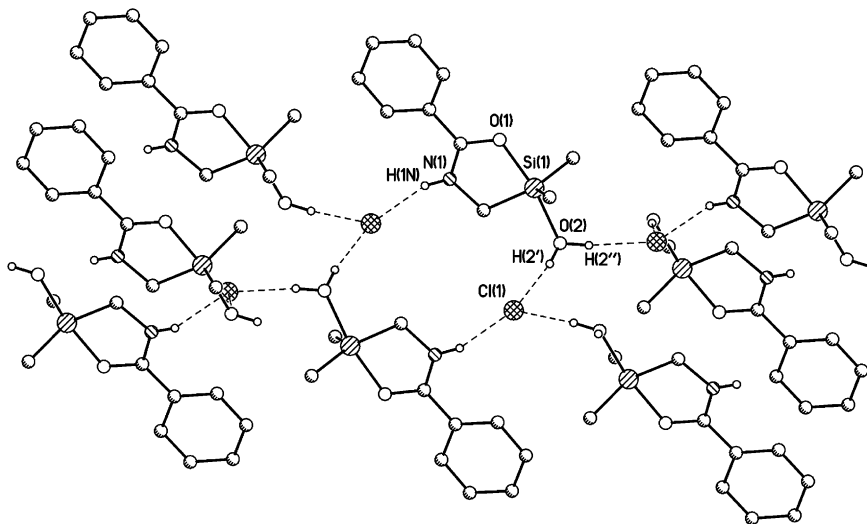


Fig. 1. Three-dimensional framework in crystal of **2b** constructed via H-bonds cations **14b** and Cl^- anions. Hydrogen with exception of $\text{H}(2'')$, $\text{H}(2')$ and $\text{H}(1\text{N})$ atoms are omitted for clarity. The parameters of H-bonds are presented in Table 2.

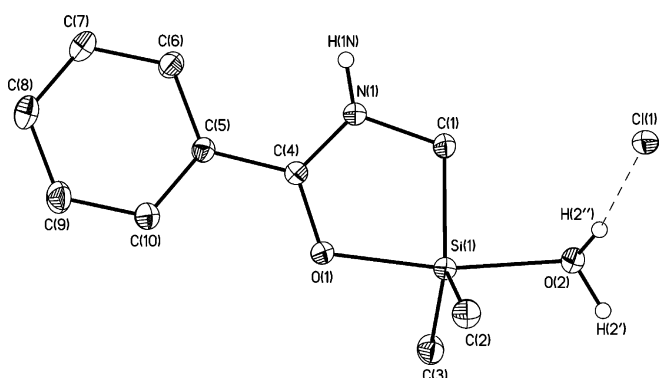


Fig. 2. The molecular structure of **2b**. Atoms are presented as thermal ellipsoids at 50% probability. Hydrogen with exception of $\text{H}(2'')$, $\text{H}(2')$ and $\text{H}(1\text{N})$ atoms are omitted for clarity.

Table 2
Important bond lengths (Å) and angles ($^\circ$) in the experimental crystal structures **2b** and **5b**

	2b	5b
Si(1)–O(1)	1.906(1)	1.898(4)
Si(1)–O(2)	1.979(1)	2.009(4)
Si(1)–C(1)	1.902(1)	1.903(5)
Si(1)–C(2)	1.863(1)	1.859(5)
Si(1)–C(3)	1.858(1)	1.855(5)
O(2)–H (averaged)	0.87(2)	0.85
Hal(1) ^a ...O(2)	3.061(1)	3.254(4)
Hal(1)...O(2) ^b	3.014(1)	3.186(4)
Hal(1)...N(1) ^c	3.141(1)	3.284(4)
Hal(1)...Si(1)	4.047(1)	4.239(1)
O(1)–Si(1)–O(2)	169.17(2)	169.0(2)

^a Hal = Cl (**2b**), Hal = Br (**5b**).

^b Atoms are generated by symmetry operations: $1 - x, 1/2 + y, 1/2 - z$.

^c Atoms are generated by symmetry operations: $x, 1 + y, z$.

compounds is mainly localized at the silicon atom. The absence of information about the exact electron structure of the organosilicon compounds with a water ligand does

not allow us to discuss the nature of this group. So, the nature of water group in the cation $[\text{PhC}(\text{O})\text{NHCH}_2\text{SiMe}_2(\text{OH}_2)]^+$ (**14b**) in the structures of **2b** and **5b** is still an open question.

With the exception of **2b** and **5b** there are only a few examples of compounds where the silicon atom is bonded to a water moiety [4a,4b,15]. All of these compounds are characterized by a significant elongation of the Si–O(H₂) bond in comparison with its standard value for tetracoordinated silicon (1.64 Å [16]). For example, in the tris(*t*-butyl)silyloxonium cation of complex **3** in which the silicon atom is tetracoordinated, the Si–O bond is 1.779 Å [4a]. In salts of pentafluoro-aquasilicon or tetrafluoro-aquasilicon with protonated azacrown-ethers the Si–O bonds are much longer than in the previous case (1.84–1.85 and 1.917 Å [15], respectively). Inspection of the Cambridge structural database (CSD [17]) has shown that the influence of the water group as a ligand is very similar to that of OR₂ moieties (R = Me, Et [18]).

It should be noted that the oxygen atom of an OEt₂ group in $[\text{Me}_3\text{Si}(\text{OEt}_2)]^+\text{B}(\text{C}_6\text{F}_5)_4^-$ [19] has an almost planar configuration while in the pentacoordinated silicon species $\text{ClSiH}_3\text{OMe}_2$ [18a] and $[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si}(\text{OMe}_2)]^+\text{BF}_4^-$ [18b], the OMe₂ groups are pyramidal. Possibly, the water moiety is also planar in the case of tetracoordination at the Si atom [4a] and it is more likely to be pyramidal when the Si atom is pentacoordinate (as in **4** [4b]). The O(2) atom in the structures **2b** and **5b** adopts a pyramidal configuration. However, due to the problems related to localization of hydrogen atoms it is difficult to prove this statement.

The only structure which is similar to **2b** and **5b** which can be found in the CSD [17] is the hydrochloride monohydrate **4** [4b]. The Si(1)–O(1) bond in **4** (1.960 Å) is somewhat longer than those in **2b** (while the Si(1)–O(2) is

slightly shorter (1.911 Å)). The value of ΔSi is 0.04 Å in **4** vs. -0.02 Å and -0.04 Å for **2b** and **5b**, respectively.

Such a difference may be explained both by the different type of five-membered chelate cycle and crystal packing effects. Undoubtedly, crystal packing will affect the geometry of the silicon atom coordination centre. The hydrogen atoms in **2b**, **5b** and **4** participate in the rather strong H-bonds with halogen atoms (Table 2) so that the organosilicon cations $[\text{PhC}(\text{O})\text{NHCH}_2\text{SiMe}_2(\text{OH}_2)]^+$ (**14b**) and in **4** form a three-dimensional network in the crystal. The O(2) atom is not involved in any H-bonding and participates only in weak van der Waals interactions. The quality of the collected X-ray data in the case of **2b** (high resolution and collection at low temperature) allows us to locate the position of H(2') and H(2'') atoms with high accuracy. Even in the presence of heavy bromine atom (**5b**) the H(2') and H(2'') atoms are localized with sufficient accuracy. According to CSD [17] the H_2O molecules do not forms contacts with Cl^- for which H...Cl and O...Cl distances shorter than 1.8 and 2.9 Å, respectively. We found in CSD [17] approximately 500 structures where H...Cl and O...Cl distances fall in ranges $2.0 \div 2.2$ and $2.9 \div 3.1$ Å. The H-bonding in structure of **2b** (averaged distances H...Cl and O...Cl are equal 2.18 and 3.04 Å) is typical for crystals of organic and organoelement compounds. Thus, one may conclude the absence of proton transfer between Cl^- and H_2O moiety in crystal of **2b**. The same conclusion holds for the structure of **5b** (H...Br and O...Br distances are 2.38 and 3.22 Å, on average). The CSD search reveals 137 structures where H...Br and O...Br distances vary in ranges of $2.1 \div 2.4$ and $3.0 \div 3.3$ Å.

It is noteworthy that the silicon atom can be coordinated with other electron pair donors, such as nitriles [20]. The silicon atom in these compounds has a tetrahedral configuration where the bond between the silicon atom and the nitrogen atom of the nitrile group is longer than a standard Si–N bond [16], up to 0.15 Å.

Unfortunately, our structural studies can give one only limited information about the nature of chemical bonding in the cation **14b**. So, we carried out quantum chemical calculations and high-resolution X-ray studies in

order to investigate the chemical bonding pattern in the axial fragment O(1)Si(1)O(2) in **2b** and **5b** as described later.

2.4.2. The stability of the $[\text{PhC}(\text{O})\text{NHCH}_2\text{SiMe}_2(\text{OH}_2)]^+$ cation (**14b**) in the crystal and isolated state

We carried out quantum chemical calculations of crystals **2b** and **5b** as well as on isolated cation–anion pairs **14b** · Hal[−] (Hal = Cl, Br) using density functional theory (DFT) with CPMD [21] code (exchange–correlation functional PBE [22], plane wave basis set). The energies of the isolated cation–anion pairs **14b** · Hal[−] (Hal = Cl, Br) and isolated cation **14b** were also calculated using the PRIRODA program [23] (PBE functional, cc-pVTZ basis set). For details see the respective Section 3.

The calculated Si(1)–O(1) and Si(1)–O(2) bond lengths (Table 3) in the crystals **2b** and **5b** agree with the experimental values. Differences are observed in the case of **2b** where the calculated Si(1)–O(2) bond length is elongated by 0.06 Å compared to the experimental value. In **5b** the deviations between the experimental and calculated bond lengths do not exceed 0.02 Å.

The calculated interatomic O(N)...Br and H...Br distances in structure **5b** reproduce the experimental data by better than 0.05 Å. The calculated O...Cl distances are up to 0.2 Å shorter than the experimental values (Tables 2 and 3). This overestimation of the strength of the H-bonds may have an effect on the effective charge of the O(2) atom that may result in the above-mentioned elongation of the Si(1)–O(2) bond.

The calculated structures of the isolated cation–anion pairs **14b** · Hal[−] (Hal = Br, Cl) differ considerably from the experimental crystal structures. The H...Cl and H...Br distances in **14b** · Hal[−] are shortened by up to 1.37 and 1.56 Å, which essentially means the elimination of the H-atom from the coordinated water molecule. Such a transformation leads to a change of geometry of the axial fragment O(1)Si(1)O(2), i.e. the Si(1)–O(2) bond is shortened by 0.2 Å while the Si(1)–O(1) bond is elongated by up to 0.3 Å in comparison with the corresponding values in the crystal. The opposite distribution of bond lengths

Table 3
Calculated structural parameters of **2b** and **5b**

	A		B		C
	2b	5b	2b	5b	
Si(1)–O(1)	1.886	1.895	2.379/2.397	2.319/2.257	1.838
Si(1)–O(2)	2.045	2.006	1.774/1.755	1.794/1.789	2.487
Si(1)–C(1)	1.909	1.918	1.935/1.927	1.937/1.930	1.925
Si(1)–C(2)	1.870	1.867	1.881/1.870	1.881/1.872	1.873
Si(1)–C(3)	1.876	1.884	1.889/1.880	1.880/1.881	1.874
O(2)–H(2')	0.980	1.006	0.971/0.974	0.973/0.975	0.973
O(2)–H(2'')	1.056	1.006	1.558/1.598	1.464/1.432	0.973
Hal(1)...O(2)	2.865	3.219	2.928/2.955	3.020/3.000	
O(1)–Si(1)–O(2)	171.7	171.3	177.3/176.2	170.7/176.1	165.8

A, crystal; B, cation–anion pairs **14b** · Hal[−] (Hal = Cl, Br) (CPMD/PRIRODA calculated values); C, isolated cation $[\text{PhC}(\text{O})\text{NHCH}_2\text{SiMe}_2(\text{OH}_2)]^+$ (**16b**).

in the axial fragment O(1)Si(1)O(2) is observed in the isolated cation **14b**. The Si(1)–O(2) is very long (2.49 Å) so one may assume that a coordinated water molecule can be easily eliminated from the silicon coordination sphere. To confirm our assumption we calculated the energies of decomposition of the cation–anion pairs **14b** · Hal[−] into the silanol PhC(O)NHCH₂SiMe₂OH (**15b**) and HHal, as well as the energy of decomposition of the cation **14b** into PhC(O)NHCH₂SiMe₂⁺ (**16b**) and H₂O. The calculated values are 6.43 and 7.74 kcal/mol for the cation–anion pairs **14b** · Hal[−] (Hal = Cl, Br) and 7.99 kcal/mol for cation **14b**, respectively. Thus, the quantum chemical calculations allowed us to conclude that cation **14b** is only stable in the crystalline state.

The calculations of the lattice energies are useful to estimate the effect of crystal packing on the geometry of the cation **14b**. The lattice energy was determined as the difference between the energy of the full crystal and the energy of the formula unit (obtained separately by a single point energy calculation, its geometry extracted from the unit cell) multiplied by the number of formula units. The values of the lattice energy are 24.75 and 20.43 kcal/mol for **2b** and **5b**, respectively. However, the difference between the energy of the full crystal and the energy corresponding to the optimized ionic pairs **14b** · Hal[−] multiplied by number of formula units was 9.92 and 7.12 kcal/mol, respectively. The discrepancies between the two sets of lattice energies may reflect the strengthening of the H...Hal bonds by up to 13–14 kcal/mol in the crystalline state compared to the isolated state.

However, the values of the lattice energy may be only used as a rough guide to show the influence of the crystal packing on the structure of cation **14b**. The contribution of each of the intermolecular interactions in the crystal and the energy of the coordinative O → Si bonds can be estimated from a topological analysis of the experimental and calculated electron density distribution functions ($\rho(r)$). The comparison of the results from the topological

analysis of $\rho(r)$ and the lattice energy calculation allow us to provide a good description of the chemical bonding pattern in **2b** and **5b**.

2.4.3. Chemical bonding in cation **14b**

Qualitative analysis of the chemical bonding of **2b** and **5b** on the basis of the deformation electron density (DED) has demonstrated the presence of two maxima in the $\rho(r)$ ($0.4 \text{ e } \text{Å}^{-3}$) localized at 0.45 Å from the oxygen atoms along the OSiO line. The maximum in the $\rho(r)$ corresponds to the lone pair of the O(2) atom which is localized at the vertex of the imaginary tetrahedra constructed from the Si(1)–O(2), O(2)–H(2') and O(2)–H(2'') bonds, while the maximum corresponding to the lone pair of the O(1) atom is localized along the line C(1)O(1). The distribution of DED in region of O(2)–H(2'')...Cl(1) intermolecular bond supports the conclusion about absence of proton transfer between Cl[−] and H₂O moiety (Fig. 3).

It should be noted that the observed distribution of DED is similar to that observed in the acetylhydrazine derivative **17** [24]. On the basis of an experimental study of $\rho(r)$ we showed that the chemical bonding pattern in the axial fragment OSiO of the above compound corresponds to a similar (3c–4e) bond. Based on the similar distribution of DED functions one may propose the presence of a three centre one electron bond in **2b** and **5b**

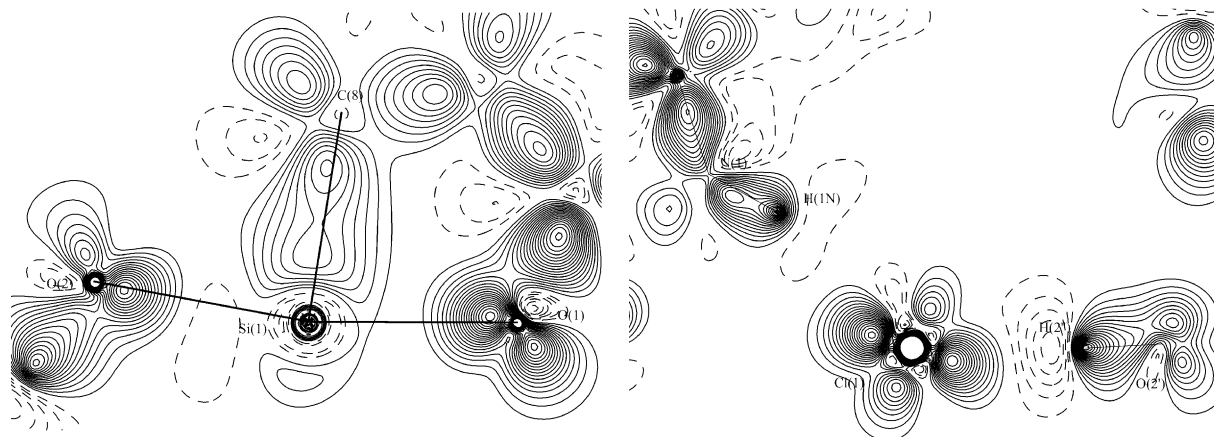
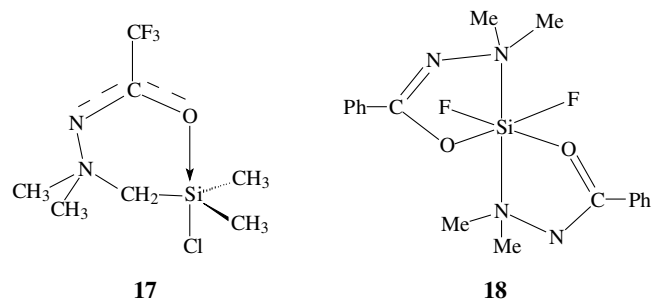


Fig. 3. Multipole static DED maps for the compounds **2b** in O(1)–Si(1)–C(1) (left) and O(2)–Cl(1)–H(2'') planes (right). Isolines are drawn through $0.1 \text{ e } \text{Å}^{-3}$, negative contours are dashed.

Table 4

Topological characteristics of the electron density distribution in cation $[\text{PhC}(\text{O})\text{NHCH}_2\text{SiMe}_2(\text{OH}_2)]^+$ (**16b**)

	Experiment			CPMD/ABINIT calculation					
	$\rho(r)$	$\nabla^2\rho(r)$	$E(r)$	$\rho(r)$		$\nabla^2\rho(r)$		$E(r)$	
	2b	2b	2b	2b	5b	2b	5b	2b	5b
Si(1)–O(1)	0.55	3.86	–0.20	0.43	0.56	3.25	6.95	–0.11	–0.12
Si(1)–O(2)	0.42	3.43	–0.11	0.40	0.43	2.32	3.25	–0.07	–0.06
Si(1)–C(1)	0.89	–2.85	–0.73	0.84	0.82	0.46	1.22	–0.75	–0.74
Si(1)–C(2)	0.89	–2.11	–0.73	0.89	0.87	2.05	1.27	–0.74	–0.74
Si(1)–C(3)	0.89	–0.88	–0.69	0.89	0.89	1.45	1.74	–0.70	–0.70

A more detailed description of the chemical bonding was obtained by a topological analysis of the electron density distribution functions in terms of Bader's "Atom in molecules" (AIM) theory² [25]. The usage of this approach allowed us to investigate the chemical bonding pattern in silatranes and monochelate compounds which contain the pentacoordinated silicon atom [26]. The CPs (3, –1) are located at all chemical bonds including Si(1)–O(1) and Si(1)–O(2). Also the CP (3, –1) corresponding to the O(N)–H...Hal bonds have also been found (Table 4). The character sets of the CPs satisfied the Poincarre–Hopf equation [25].

The C–C, N–C and O–C bonds are characterized by negative values of the Laplacian of the electron density ($\nabla^2\rho(r)$) and negative values of the local energy density ($E^c(r)$) in CP (3, –1). These bonds may be described as shared interactions in terms of AIM theory. On the contrary, at the CP (3, –1) of the Si(1)–O(1) and Si(1)–O(2) bonds, positive values of the $\nabla^2\rho(r)$ are observed. The values of the $E^c(r)$ for these bonds still have a negative sign and the magnitudes of the $\rho(r)$ at CP's (3, –1) are large. Thus, according to the AIM theory [25] the axial Si(1)–O(1) and Si(1)–O(2) bonds in **2b** and **5b** are classified as an *intermediate* type of interatomic interactions.

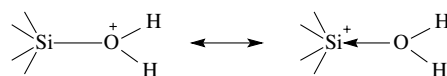
The advantage of using the AIM theory is the possibility of estimating the strength of the Si(1)–O(1) and Si(1)–O(2) bonds based on the correlation between the potential energy density in CP (3, –1) and the energy of the interatomic interaction. The estimated values are 19.2 and 21.84 kcal/mol for the Si(1)–O(2) bonds in the **2b** and **5b**, respectively. A similar calculation for the Si(1)–O(1) bonds in **2b** and **5b** gave us values of 37.66 and 35.81 kcal/mol which significantly exceed the magnitudes of the Si(1)–O(2) bond. It should be noted that the energy of the

Si(1)–O(2) bond dissociation in the isolated cation **14b** is 7.99 kcal/mol. So, we may conclude that the Si(1)–O(2) bond in **2b** and **5b** is approximately 12 kcal/mol stronger than in the isolated cation **14b**.

Based on the proposal that the overall bond order of the axial Si(1)–O(1) and Si(1)–O(2) bonds is constant one may propose that in the isolated cation **14b** the Si(1)–O(1) bond is approximately 12 kcal/mol stronger than in the crystal. The estimation of the Si(1)–O(1) and Si(1)–O(2) bond strengths according to AIM theory is in agreement with that based on the density matrix diagonalization procedure [27].

Important information about the chemical bonding in the axial fragment O(1)Si(1)O(2) may be obtained from analysis of the AIM charges on the Si and O atoms. A previous computational study [14b] of the classic species with 3c–4e bonds such as H_3^- , FHF^- , ClHCl^- showed that the charges of the terminal atoms are noticeably lower compared to diatomic molecules (HCl, HF). On the contrary, the positive charge of the central atom is increased compared to HCl and HF. In turn, in the SiF_5^- anion and the molecule PF_5 where the central atom has an ideal TBP configuration the charges of the Si and P atoms have large positive values (3.85 and 3.56 e). The corresponding value for the hexacoordinated Si atom in **18** (3.23 e) [14a] is only slightly lower than that in SiF_5^- .

In **2b** the charge on the Si atom (1.84 e) is significantly decreased while the charges of the O(1) and O(2) atoms are increased in comparison with other compounds containing a hexacoordinated Si atom [14a]. Analysis of the AIM charges verifies the formation of 3c–4e bonds in **2b** and **5b**. The magnitude of the negative charge of the O(2) atom (–1.14 e) is slightly increased compared with that of the O(1) atom (–1.06 e). So, the description of the O(2) atom as an oxonium ion is only a formal description since the main positive charge is localized at the Si(1) atom.



Thus, the cation **14b** containing a pentacoordinate silicon atom in the crystals **2b** and **5b** should be considered as a silylium cation stabilized by a coordinated H_2O molecule rather than as a silyloxonium ion.

² According to this theory the existence of interatomic interaction indicated by presence of critical point (CP) (3, –1); that is, a saddle point in electron density distribution function between two atoms. For analysis of type and energy of interatomic interactions the values of three parameters in CP (3, –1) are important: the $\rho(r)$, the Laplacian of $\rho(r)$ ($\nabla^2\rho(r)$) and the local energy density $E^c(r)$. Two latter characteristics show the contribution of kinetic and potential energy in interatomic interaction. If contribution of potential energy in CP (3, –1) dominates over kinetic one ($\nabla^2\rho(r)$ and $E^c(r) < 0$) than interatomic interaction corresponds to covalent bond (shared interaction). In case when contribution of kinetic energy dominates over potential one ($\nabla^2\rho(r)$ and $E^c(r) > 0$) the interatomic interaction have pronounced ionic character.

3. Experimental

IR spectra were recorded in tablets pressed with KBr (1 mg/200 mg KBr), in suspensions of compounds in a liquid paraffin on CaF₂ laminas, in organic solvents in KBr cells, and in a film between KBr laminas for liquid substances using Specord IR-75, M80, and M82 instruments.

The ¹H, ¹³C, and ²⁹Si NMR spectra of solutions in CDCl₃ and (CD₃)₂C(O) were measured on Varian XL-400 spectrometer operating at 400.0, 100.6 and 79.5 MHz, respectively, with Me₄Si as the internal standard.

X-ray diffraction measurements for **2b** and **5b** were carried out with a Syntex P2₁ four-circle diffractometer. Structures were solved by direct methods and non-hydrogen atoms were refined in full-matrix anisotropic approximation. The hydrogen atoms were located from differential Fourier synthesis of the electron density and refined isotropically (the exception is **5b** in which H atoms refined using rigid body model). All calculations were carried out using the SHELXTL 5.1 program package [28]. Details of crystallographic data and experimental condition are presented in Table 5.

The analytical form of the experimental electron density was obtained by a multipole refinement of **2b** based on the Hansen–Coppens [29] formalism using the XD program package [30]. C–H, N–H and O–H bonds were normalized at 1.07, 1.00 and 0.96 Å according to neutron diffraction data [16]. The level of the multipole expansion was hexadecapole for the Si, O, N, Cl atoms and dipole for hydrogens. In the case of C(1) and C(2) atoms for the refinement of values of multipole expansion population coefficients of the local symmetry *m* were used. The scattering factor of the hydrogen atoms was calculated from the contracted radial density functions ($\kappa = 1.2$). The ratio of the number of reflections to the number of refined parameters was more than 20.

The quantum chemical calculations of the crystal structures **2b** and **5b** and the isolated ionic pairs **14b** · Hal[−] (Hal = Cl, Br) have been carried out in terms of density functional theory (exchange-correlation functional PBE [22]) utilising CPMD code [21]. Vanderbilt's ultrasoft pseudopotentials [31] have been applied to account for core electrons while valence electrons were approximated by plane-wave expansion with 25 Ry cutoff. The experimental structures of **2b** and **5b** were taken as starting points in geometry optimization procedure while cell parameters were fixed at the experimental values. The isolated ionic pairs **14b** · Hal[−] (Hal = Cl, Br) were calculated in cubic cell with side length 15 Å.

Topological analysis of electron density of hydrohalides **2b** and **5b** have been carried out using ABINIT program suite [32] for the crystal structures optimized by the CPMD code. Electron density function of core electron was pre-computed whereas valence part of electron density function was described by plane-wave with 100 Ry cutoff using PBE exchange-correlation functional. The energy of Si–O bonds was estimated according to formalism by Espinosa Mollins and Lecomte [33].

Table 5
Crystallographic parameters for the compounds **2b** and **5b**

	2b	5b
Molecular formula	C ₁₀ H ₁₆ ClNO ₂ Si	C ₁₀ H ₁₆ BrNO ₂ Si
Formula weight	245.78	290.24
Temperature (K)	173(2)	173(2)
<i>a</i> (Å)	9.9334(4)	10.037(5)
<i>b</i> (Å)	6.9815(3)	7.050(3)
<i>c</i> (Å)	18.0828(7)	18.579(8)
α (°)	90	90
β (°)	104.780(1)	103.84(4)
γ (°)	90	90
<i>V</i> (Å ³)	1212.55(9)	1276.5(10)
Space group, <i>Z</i>	<i>P</i> 2 ₁ / <i>c</i> , 4	<i>P</i> 2 ₁ / <i>c</i> , 4
2 θ _{max} (°)	90	52
Scan type	$\theta/2\theta$	$\theta/2\theta$
Reflections collected	46,226	2578
Number of independent reflections (<i>R</i> _{int})	9479 (0.072)	2433 (0.044)
Number of reflections with <i>I</i> > 2 σ (<i>I</i>)	7299	2172
Parameters	200	138
Linear absorption (cm ^{−1})	3.93	33.0
Absorption correction	None	Ψ -scan
<i>T</i> _{min} / <i>T</i> _{max}		0.848/0.848
Goodness-of-fit	0.991	0.958
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.036	0.0612
<i>wR</i> ₂ (all reflections)	0.106	0.1278

PRIRODA [23] program have been applied for the quantum chemistry calculations of isolated ionic pairs **14b** · Hal[−] (Hal = Cl, Br) and cation **14b** using cc-pVTZ basis set. All calculated structures are in the local minima of their respective potential energy surfaces that have been proved by vibrational analysis. The values of dissociation energies include zero-point corrections.

Syntheses of the initial *N*-trimethylsilylacetamide and *N*-trimethylsilylbenzamide were reported earlier [34].

3.1. (*O* → *Si*)-chelate

N-(dimethylchlorosilylmethyl)acetamide (**6a**)

(a) ClCH₂SiMe₂Cl (28.6 g, 0.2 mol) was added dropwise to a solution of acetamide (11.8 g, 0.2 mol) and (Me₃Si)₂NH (12.9 g, 0.08 mol) in 100 ml of C₆H₆. The reaction mixture was refluxed for 1 h, the precipitate was filtered out, and the solvent was removed in vacuo. Double fractionation of the residue yielded 7.45 g (23%) of chloride **6a**, b.p. 156–158 °C (8 mm Hg), m.p. 87–90 °C (benzene) (cf. [2a]). IR spectrum (C₆H₆, ν , cm^{−1}): 1635, 1540 (NCO). ¹H NMR (CDCl₃, δ , ppm): 0.56 (6H, s, Me₂Si); 2.16 (3H, br. s, CH₃); 2.79 (2H, br. s, NCH₂). ¹³C NMR (CDCl₃, δ , ppm): 23.06 (Me); 0.99 (SiMe₂); 33.50 (CH₂); 175.43 (C=O). ²⁹Si NMR (CDCl₃, δ , ppm): −27.4 s. Anal. Found (%): C, 36.92; H, 6.96. C₅H₁₂NOSiCl. Calc. (%): C, 36.22; H, 7.30.

(b) Thionyl chloride (1.79 g, 15 mmol) was added dropwise to a solution of disiloxane **8a** (2.2 g, 7.96 mmol) in benzene (5 ml). The reaction mixture was distilled to yield 2.0 g (76%) of chloride **6a**, b.p. 161–163 °C (10 mm Hg).

(c) Chloro(chloromethyl)dimethylsilane (17.04 g, 0.12 mol) was added dropwise to a solution of *N*-trimethylsilylacacetamide (13.1 g, 0.10 mol) in *n*-xylene (50 ml). The reaction mixture was heated for 0.5 h at 110 °C and the solvent was removed in vacuo. The residue was distilled to yield 6.25 g (66%) of chloride **6a**, b.p. 163–170 °C (12 mm Hg).

(d) The mixture of *N*-trimethylsilylacacetamide (24 g, 0.18 mol) and ClCH₂SiMe₂Cl (28.6 g, 0.2 mol) was heated to remove Me₃SiCl (18.5 g, 94%, b.p. 58–59 °C). Distillation of the residue yielded 20.1 g (67%) of chloride **6a**, b.p. 164–167 °C (10 mm Hg).

3.2. Reaction of acetamide with (Me₃Si)₂NH and ClCH₂SiMe₂Cl (1:1:1) with subsequent hydrolysis of the reaction mixture

ClCH₂SiMe₂Cl (5.68 g, 40 mmol) was added dropwise to a solution of acetamide (2.36 g, 40 mmol) and (Me₃Si)₂NH (6.5 g, 40 mmol) in benzene (50 ml) and refluxed for 1 h. The reaction mixture was cooled down, the precipitate was filtered out, and the solvent was removed in vacuo. CHCl₃ (30 ml) was added to the residue after solvent removing. The residue was treated with CHCl₃ (30 ml) and a solution of NaHCO₃ (1.67 g) in water (20 ml). The organic layer was removed and the aqueous layer was extracted by CHCl₃ (20 ml). The volatiles from combined organic layers were removed in vacuo. ¹H NMR spectra of the residue indicated the presence of disilamorpholine **9a** and disiloxane **8a** in 1:0.54 ratio.

3.3. Reaction of acetamide with ClCH₂SiMe₂Cl and Et₃N (1:1:1) with subsequent hydrolysis of the reaction mixture

ClCH₂SiMe₂Cl (5.68 g, 40 mmol) was added dropwise to a solution of acetamide (2.36 g, 40 mmol) and Et₃N (4.05 g, 40 mmol) in benzene (50 ml). The reaction mixture was refluxed for 1 h, then cooled down and filtered. The volatiles from the filtrate were removed in vacuo. The residue was treated with CHCl₃ (30 ml) and a solution of NaHCO₃ (1.67 g) in water (20 ml). The organic layer was removed and the aqueous layer was extracted by CHCl₃ (20 ml). The volatiles from combined organic layers were removed in vacuo. ¹H NMR spectra of the residue indicated the presence of disilamorpholine **9a** and disiloxane **8a** in 1:0.97 ratio.

3.4. Reaction of acetamide with (Me₃Si)₂NH and ClCH₂SiMe₂Cl (1:0.4:1) with subsequent hydrolysis of the reaction mixture

ClCH₂SiMe₂Cl (5.68 g, 40 mmol) was added dropwise to a solution of acetamide (2.36 g, 40 mmol) and (Me₃Si)₂NH (2.6 g, 16 mmol) in benzene (50 ml). The reaction mixture was refluxed for 1 h, then cooled down and filtered. The volatiles from the filtrate were removed in vacuo. The residue was treated with CHCl₃ (30 ml) and a solution of NaHCO₃ (1.67 g) in water (20 ml). The organic

layer was removed and the aqueous layer was extracted by CHCl₃ (20 ml). The volatiles from combined organic layers were removed in vacuo. ¹H NMR spectra of the residue indicated the presence of disilamorpholine **9a** and disiloxane **8a** in 1:0.87 ratio.

3.5. Reaction of acetamide with (Me₃Si)₂NH and ClCH₂SiMe₂Cl with the subsequent hydrolysis of the reaction mixture

The mixture of acetamide (30 g, 0.5 mol), (Me₃Si)₂NH (16.1 g, 0.1 mol) and catalytic amount of Me₃SiCl was refluxed for 1.5 h. The remaining (Me₃Si)₂NH was removed in vacuo, and ClCH₂SiMe₂Cl (71 g, 0.5 mol) was added to the residue. The reaction mixture was refluxed to remove Me₃SiCl (71%, b.p. 58–90 °C). The residue was cooled down, dissolved in CHCl₃ (150 ml) and stirred with a solution of NaHCO₃ (45 g) in water (200 ml). The organic layer was removed and the aqueous layer was extracted by CHCl₃ (150 ml). The volatiles from combined organic layers were removed in vacuo. Disilamorpholine **9a** (28.6 g, 0.13 mol), b.p. 124–127 °C (10 mm Hg), m.p. 36–40 °C [6a] and disiloxane **8a** (22.9 g, 83 mmol), b.p. 230–234 °C (10 mm Hg), *n*_D²⁰ 1.4680 (ratio 1:0.64) were obtained by distillation of the residue. IR spectrum (CHCl₃, ν/cm⁻¹): 1640 (amide I, ν_{C=O}), 1520 (amide II, δ_{NH}).

3.6. (O → Si)-chelate *N*-(dimethylchlorosilylmethyl)benzamide (**6b**)

(a) Thionyl chloride (1.64 g, 14 mmol) was added dropwise to a solution of disiloxane **8b** in benzene (10 ml). The residue was filtered to yield 1.9 g (84%) of chloride **7b**, m.p. 92–95 °C (C₆H₆). IR spectrum (dioxane), ν/cm⁻¹: 1618, 1520 (NCO). ¹H NMR [(CD₃)₂C(O), δ, ppm J/Hz]: 0.51 (6H, br. s, SiMe₂); 2.87 (2H, br. s, CH₂); 7.96 (d, ³J_{HH} = 7.3), 7.63 (t, ³J_{HH} = 7.3), 7.50 (t, ³J_{HH} = 7.3), 5H, C₆H₅; 6.7 (1H, br. s, NH). ¹³C NMR [(CD₃)₂C(O), δ, ppm]: 34.44 (CH₂), 129.66 (C-ortho), 128.46 (C-meta), 129.52 (C-para), 133.38 (C-ipsi), C₆H₅. The NMR signals of SiMe₂ and C=O groups at room temperature were not observed due to broadening. ²⁹Si NMR [(CD₃)₂C(O), δ, ppm]: -26.5 (br. s). Anal. Found (%): C, 52.48; H, 6.50; N, 5.89. C₁₀H₁₄ClNOSi. Calc. (%): C, 52.73; H, 6.20; N, 6.15.

(b) A mixture of *N*-trimethylsilylbenzamide (5.0 g, 0.026 mol) and ClCH₂SiMe₂Cl (3.65 g, 0.02 mol) was refluxed to remove Me₃SiCl (2.4 g, 85%, b.p. 57–59 °C). The residue was treated with hexane (15 ml) to produce 5.2 g (88%) of chloride **7b**, m.p. 90–93 °C (hexane).

3.7. 1,1,3,3-Tetramethyl-1,3-bis(acetamidomethyl)-1,3-disiloxane (**8a**)

(a) A solution of chloride **6a** (9.8 g, 0.059 mol) in CHCl₃ (25 ml) was stirred with solution of NaHCO₃ (5 g) in water

(30 ml). The organic layer was removed and the water layer was extracted by CHCl_3 (20 ml). Distillation of combined organic layers produced 7.65 g (84%) of disiloxane **8a**, b.p. 228–230 °C (7 mm Hg), n_D^{20} 1.4680. IR spectrum (CHCl_3), ν/cm^{-1} : 1640 (amide I, $\nu_{\text{C=O}}$), 1520 (amide II, δ_{NH}). ^1H NMR (CDCl_3 , δ , ppm, J/Hz): 1.98 (6H, s, 2Me); 0.08 (6H, s, 2SiMe₂); 2.65 (4H, 2CH₂); 6.9 (2H, br. s, 2NH). ^{13}C NMR (CDCl_3 , δ , ppm): 22.56 (Me); 0.71 (SiMe₂); 31.00 (CH₂); 170.63 (C=O). ^{29}Si NMR (CDCl_3 , δ , ppm): 4.47 s. Anal. Found (%): C, 43.18; H, 8.84; N, 9.98. C₁₀H₂₄N₂O₃Si₂. Calc. (%): C, 43.44; H, 8.75; N, 10.13.

(b) A mixture of *N*-trimethylsilylacetamide (33.6 g, 0.25 mol) and $\text{ClCH}_2\text{SiMe}_2\text{Cl}$ (35.5 g, 0.25 mol) was refluxed to remove of Me_3SiCl (21.75 g, 76%, b.p. 57–59 °C). The residue was dissolved in CHCl_3 (150 ml) and stirred for 1 h with a solution of NaHCO_3 (22.5 g) in water (150 ml). The organic layer was removed and the aqueous layer was extracted by CHCl_3 (100 ml). Disiloxane **8a** (5.0 g, 43%) was obtained by distillation of combined organic extracts; b.p. 234–236 °C (7 mm Hg), n_D^{20} 1.4680.

3.8. 1,1,3,3-Tetramethyl-1,3-bis(benzamidomethyl)-1,3-disiloxane (**8b**)

(a) Suspension of chloride **6b** (5.2 g, 23 mmol) in CHCl_3 (20 ml) was treated with a solution of NaHCO_3 (2 g) in water (25 ml). The organic layer was removed and the water layer was extracted by CHCl_3 (25 ml). The solvent from combined organic extracts was removed in vacuo and the C_6H_6 (15 ml) was added to the residue. On the next day crystals of disiloxane **8b** (2.65 g, 58%), m.p. 119–121 °C (benzene) were formed. IR spectrum (tablet with KBr), ν/cm^{-1} : 3350, 3310 (ν_{NH}), 1635 (amide I, $\nu_{\text{C=O}}$), 1545 (amide II, δ_{NH}). ^1H NMR (CDCl_3 , δ , ppm, J/Hz): 0.16 (6H, br. s, 2SiMe₂); 2.87 (4H, s, 2CH₂); 7.78 (d, $^3J_{\text{HH}} = 7.7$), 7.32 (t, $^3J_{\text{HH}} = 7.7$), 7.42 (t, $^3J_{\text{HH}} = 7.7$), 10H, 2C₆H₅; 7.15 (br. s, 2 NH). ^{13}C NMR (CDCl_3 , δ , ppm): -0.32 (SiMe₂); 31.93 (CH₂); 128.37 (*C-ortho*), 127.38 (*C-meta*), 126.99 (*C-para*), 134.79 (*C-ipso*), C₆H₅; 167.89 (C=O). ^{29}Si NMR (CDCl_3 , δ , ppm): 4.70 s. Anal. Found (%): C, 60.24; H, 6.94; N, 7.00. C₂₀H₂₈N₂O₃Si₂. Calc. (%): C, 59.96; H, 7.04; N, 6.99.

(b) A mixture of *N*-trimethylsilylbenzamide (10.1 g, 0.05 mol) and $\text{ClCH}_2\text{SiMe}_2\text{Cl}$ (7.4 g, 0.05 mol) was refluxed to remove Me_3SiCl (5.22 g, 91%, b.p. 57–59 °C), then CHCl_3 (50 ml) was added and the reaction mixture was stirred with solution of NaHCO_3 (4.5 g) in water (30 ml). The organic layer was removed and the water layer was extracted by CHCl_3 (20 ml). The solvent from combined organic layers was removed in vacuo. Benzene (20 ml) was added to the residue, and the crystals formed were isolated to yield disiloxane **8b** (7.55 g, 75%), m.p. 119–121 °C (benzene).

(c) A mixture of hydrochloride **2b** (0.35 g, 1.4 mmol) and CHCl_3 (5 ml) was treated with a solution of NaHCO_3 (0.12 g) in water (3 ml). The organic layer was removed and

the water layer was extracted by CHCl_3 (3 ml). The solvent from combined organic extracts was removed in vacuo and benzene (2 ml) was added to the residue. The crystals formed were isolated to yield disiloxane **8b** (0.26 g, 93%), m.p. 120.5–121 °C (benzene).

3.9. (*O* → *Si*)-chelate dimethyl(acetamidomethyl)silanole hydrochloride (**2a**)

Thionyl chloride (2.6 g, 22 mmol) was added to a solution of disiloxane **9a** (3.05 g, 11 mmol) in heptane (20 ml). On the next day hydrochloride **2a** (3.25 g, 80%) was isolated by filtration; m.p. 92–96 °C (heptane). ^1H NMR (δ , ppm, CD_3CN): 0.24 (6H, s, SiMe₂); 2.26 (3H, s, Me); 2.85 (2H, s, CH₂); 5.21 (3H, br. s, OH₂, NH). ^{13}C NMR (CD_3CN , δ , ppm): 20.03 (Me); -2.62 (SiMe₂); 34.45 (CH₂); 175.18 (C=O). ^{29}Si NMR (CDCl_3 , δ , ppm): 4.70 s. Anal. Found (%): C, 32.68; H, 7.49; N, 7.57. C₅H₁₄ClNO₂Si. Calc. (%): C, 32.68; H, 7.68; N, 7.62.

Hydrochloride **2a** is highly hygroscopic which makes it impossible to obtain an informative IR spectrum. The spectrum appears significantly distorted due to the presence of absorptions of water at various frequencies.

3.10. (*O* → *Si*)-chelate dimethyl(benzamidomethyl)silanole (**2b**) hydrochloride

(a) *N*-(dimethylchlorosilylmethyl)benzamide **6b** (0.45 g) was exposed to air for 8 months. Compound **2b** (0.39 g, 80%), m.p. 124–127 °C (CH_3CN) was obtained by re-crystallization from CH_3CN . IR spectrum (CaF_2 , vaseline oil), ν/cm^{-1} : 1612, 1521 (NCO), 1581 (Ph). ^1H NMR (CD_3CN , δ , ppm): 0.44 (6H, s, SiMe₂); 2.91 (2H, s, CH₂); 7.88 (d, $^3J_{\text{HH}} = 7.3$), 7.65 (t, $^3J_{\text{HH}} = 7.3$), 7.57 (t, $^3J_{\text{HH}} = 7.3$), 5H, C₆H₅; 8.09 (3H, br. s, OH₂, NH). Anal. Found (%): C, 48.59; H, 6.33; N, 5.36. C₁₀H₁₆ClNO₂Si. Calc. (%): C, 48.87; H, 6.56; N, 5.70. A single crystal of **6b** for X-ray diffraction study was obtained from CH_3CN .

(b) Chloride **6b** (0.5 g, 2.2 mmol) was added to a mixture CH_3CN (5 ml) and water (18 mg, 1.1 mmol). The reaction mixture was refluxed for several hours. The crystals formed were isolated by filtration to produce hydrochloride **2b** (0.5 g, 93%), m.p. 124–125 °C (Me_3CN). Anal. Found (%): C, 48.97; H, 6.63; N, 5.64. C₁₀H₁₆ClNO₂Si. Calc. (%): C, 48.87; H, 6.56; N, 5.70.

(c) Disiloxane **8b** (1.0 g, 2.5 mmol) was added to a solution of CH_3CN (22 ml) and thionyl chloride (0.6 g, 5.0 mmol) in water (0.09 g, 5.0 mmol). The reaction mixture was heated to 90 °C. The crystals formed were filtered and dried in vacuo. Two types of crystals were obtained: chloride **6b** (m.p. 92–94 °C) and hydrochloride **2b** (124–125 °C). The latter was isolated from the mixture by re-crystallization from CH_3CN , yield 1.15 g (94%), m.p. 124–125 °C (Me_3CN). IR spectrum (tablet with KBr), ν/cm^{-1} : 1615 (s), 1520 (s) (NCO). Anal. Found (%): C, 48.87; H, 6.63; N, 5.65. C₁₀H₁₆ClNO₂Si. Calc. (%): C, 48.87; H, 6.56; N, 5.70.

3.11. (*O* → *Si*)-chelate dimethyl(benzamidomethyl)silanol hydrobromide (**5b**)

Me₃SiBr (0.92 g, 6.0 mmol) was added dropwise to a suspension of disiloxane **8b** (1.2 g, 3 mmol) in benzene (5 ml). The reaction mixture was stirred for 1 h. The residue formed (1.55 g) was filtered and exposed to the air for 11 months. Hydrobromine **5b** (1.05 g, 60%) was obtained by re-crystallization from CH₃CN, m.p. 123–125 °C (CH₃CN). IR spectrum (tablet with KBr), ν/cm^{-1} : 1612 (s), 1520 (s) (NCO). Anal. Found (%): C, 41.13; H, 5.47; N, 4.68. C₁₀H₁₆BrNO₂Si. Calc. (%): C, 41.38; H, 5.56; N, 4.83.

Single crystals for X-ray diffraction study were obtained from CH₃CN.

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Appendix A. Supplementary data

CCDC (refcodes 293721 and 293722) contain supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.ac.uk/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033), e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.05.047](https://doi.org/10.1016/j.jorganchem.2006.05.047).

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