Reactions of silamorpholinones and acylsilamorpholines with electrophilic reagents. X-ray structure of products including a pentacoordinated silicon compound

Aleksandr G. Shipov [a], Evgeniya P. Kramarova [a], Elizaveta A. Mamaeva [a],
Oksana A. Zamyshlyaeva [a], Vadim V. Negrebetsky [a], Yuri E. Ovchinnikov [b],
Sergey A. Pogozhikh [b], Alan R. Bassindale [c,*1], Peter G. Taylor [c,*2], Yuri I. Baukov [a,*3]

[a] *Russian State Medical University, Ostrovityanov Street 1, Moscow 117813, Russia*
[b] *Nesmeyanov's Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova Street 28, Moscow 117813, Russia*
[c] *Chemistry Department, Open University, Walton Hall, Milton Keynes MK7 6AA, UK*

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Abstract

Reactions of 2-sila-5-morpholinones, 4-acyl-2-silamorpholines and 4-acyl-2,6-disilamorpholines with electrophilic reagents generally lead to the opening of the sila- or disilacycle by cleavage of the Si–O bond with subsequent rearrangement to form five-membered chelate derivatives where the amide oxygen atoms coordinate with the silicon to form pentacoordinate silicon species. Multinuclear NMR spectroscopy and X-ray diffraction studies were used for structural investigation of the products. 4-Acyl-2,6-disilamorpholines initially form adducts with strong acids where the amide oxygen is protonated by the acid as demonstrated by X-ray crystallography. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silicon; Pentacoordinate; Morpholines

1. Introduction

The structure and reactivity of pentacoordinate organosilicon compounds has attracted a great deal of interest in recent years [1–4]. As part of a continuing study of silicon derivatives of *N*-silylamides and lactams [5–9] we have previously shown that silamorpholinones (**1**), acylsilamorpholines (**2**) and acyldisilamorpholines (**3**) can be synthesized readily in one-pot reactions [5]. It was also shown that pentacoordinate silicon compounds are intermediates in these reactions even though the silicon atoms in **1–3** are tetracoordinate as their structures preclude intramolecular coordination with the amido oxygen atoms (Scheme 1).

Pentacoordinate silicon compounds are key intermediates in industrially important reactions and they are also interesting structurally, theoretically and for their enhanced reactivity in substitution reactions [2–4]. Pentacoordinate silicon derivatives of amides are almost all highly moisture sensitive and can be difficult to handle and store. In contrast the heterocyclic silicon compounds **1–3** are much more inert and easy to handle. The work presented in this paper was carried out to determine whether the reactions shown in Eqs. 1–3 could be made reversible so that a range of different pentacoordinate silicon compounds might easily be prepared. The approach taken was to react **1–3** with a variety of electrophilic reagents and attempt to isolate the products, usually by distillation.

We found that **1–3** were very reactive towards electrophilic reagents and that the Si–O bond was broken exclusively. Reactions analogous to the reverse of the final step in Eqs. 1–3 were indeed found to occur in high yield, but in some cases isolation of the pentacoordinate species by distillation was not possible owing to reversion to starting materials. A very unusual reaction was observed for **3** with strong acids where protonation

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[1] *Corresponding author. E-mail: a.bassindale@open.ac.uk
[2] *Corresponding author.
[3] *Corresponding author.

R = H (a), Me (b), Et (c), Ph (d), ClCH$_2$ (e)
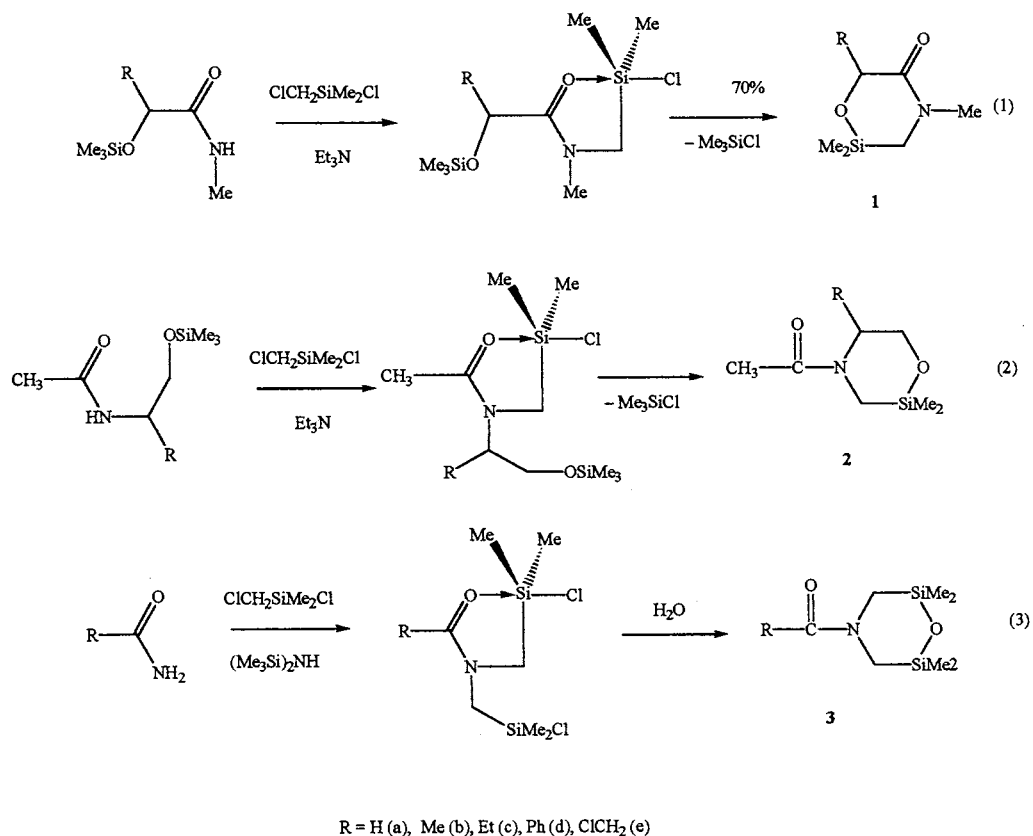
Scheme 1.

of the amido oxygen gave stable adducts in solution, which, in the case of **3** with CF_3SO_3H, was characterized by X-ray crystallography.

2. Results and discussion

The 2-sila-4-acetylmorpholines (**2**), and 2-sila-5-morpholinones (**1**), were reacted with acetyl chloride and the reactions monitored by IR spectroscopy. While the silamorpholines (**2**) reacted almost instantly, the reaction of the silamorpholinones (**1**) with acetylchloride required 3 h at 50°C. Analogous reactions with acetyl bromide all required heating for complete reaction. In all cases the initial products were the pentacoordinate compounds **4**–**7** (Scheme 2).

The presence of the pentacoordinate silicon compounds in the reaction mixtures was easily demonstrated from IR and NMR spectral data. Along with the bands of ester carbonyl fragments (1700–1720 cm^{-1}), two characteristic bands of chelated five-membered ring with pentacoordinate silicon atom at 1515–1530 and 1590–1620 cm^{-1} were observed [10]. The low frequency shifts observed in the ^{29}Si-NMR spectra for compounds **4c**, **6b** and **7b** (-38.2 ppm (CDCl$_3$), -32.0 ppm (CDCl$_3$) and -29.7 ppm (CD$_3$CN), respectively) confirm the presence of a pentacoordinate

silicon [10]. The products of the ring opening reactions with acetylchloride **4a**, **4c**, **6b** and **6d** are thermally stable and were able to be distilled in vacuo, in contrast to the products of the analogous reaction with acetylbromide **5a** and **7b**. The latter decompose on distillation giving the starting materials.

X = Cl (4, 6), Br (5, 7)

R = H (a), Me (b), Et (c), Ph (d)
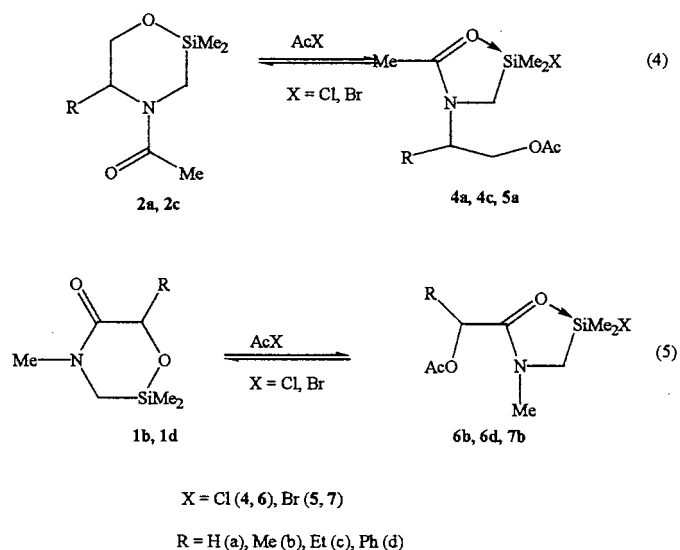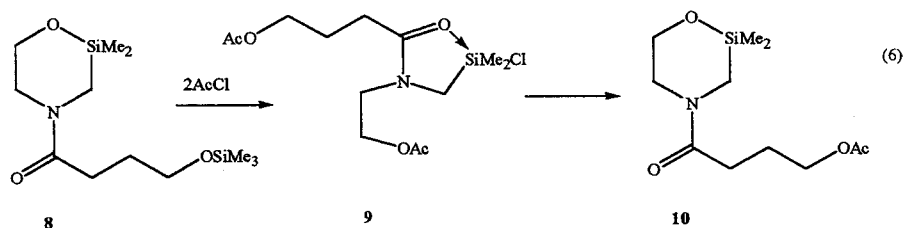
Scheme 2.

Scheme 3.

We believe that Eqs. 4 and 5 are equilibria and that the ability to isolate the pentacoordinate silicon compound as opposed to the silamorpholine or related compound depends upon the effect of temperature on these equilibria and the boiling temperature of the starting electrophilic reagent. If, at the distillation temperature, the more volatile starting material is present in sufficient quantity to be removed preferentially from the reaction mixture, then eventually the pentacoordinate silicon compound will be consumed and the pure silamorpholine will be the final product to distil. It is not a simple matter to predict a priori whether the pentacoordinate compound will be isolable by distillation. For example, reaction of 2-sila-4-acylmorpholine (8) with the excess of acetylchloride leads to the pentacoordinate silicon ring diacetate (9) as shown by the IR spectra of the reaction mixture which contains two bands at 1510 and 1592 cm^{-1}. However, after distillation only the O-acetyl derivative of the initial acylsilamorpholine, the monoacetate (10), was obtained. It is not completely clear why the presence of an AcO(CH$_2$)$_3$ group on the carbonyl carbon, as opposed to a methyl group in 4a, should affect the equilibrium. It may be that the presence of the acetyl group increases the boiling temperature of 9 so that at these higher temperatures the acetyl chloride is more easily removed (Scheme 3).

Similarly, we found that trimethylchlorosilane readily cleaves the O–Si bond in 2a giving the pentacoordinate chloride (11) which undergoes recyclisation to 2a in the course of distillation (Scheme 4).

The same thermal cyclisation of chloride 11 into 2a was observed on reaction of O-trimethylsilyl-N-acetylcholamine and dimethylchloromethylchlorosilane [5].

Reactions of 2a and 1b with thionyl chloride are less vigorous and lead to acyclic C,Si-dichlorides 12 and 13 that also contain pentacoordinate silicon (bands at 1540, 1590 and 1520, 1612 cm^{-1} for dichlorides 12a and 13b, respectively) (Scheme 5).

The ^{1}H- and ^{13}C-NMR spectra of dichlorides 12a and 13b are consistent with their structures. The presence of a pentacoordinate silicon in 13b is confirmed by the low frequency shift of the signal in the ^{29}Si-NMR spectrum (-33.9 ppm in CD$_2$Cl$_2$). We note that, the reactivity of 2-sila-4-acylmorpholines 2a,c and 2-sila-5-morpholinones 1b,d towards electrophilic reagents is

similar to that of N-(dimethylalkoxysilylmethyl)lactams [8].

The Si–O(Si) bond in 3 can also be cleaved readily by electrophiles in a similar manner to the cleavage of the Si–O bonds in 1 and 2. The cleavage of the Si–O(Si) bond by boron trifluoride was demonstrated by the reactions of disilamorpholines 3a,b with BF$_3$·Et$_2$O. The reaction led to the stable difluorides 14a,b. The structure of difluoride 14b was confirmed by X-ray crystallography (see below) (Scheme 6).

Scheme 4.

Scheme 5.

X = F (14), Cl (15), OC(O)CF$_3$ (16)
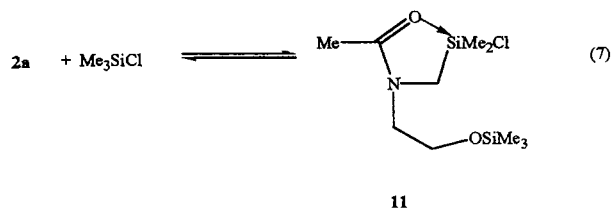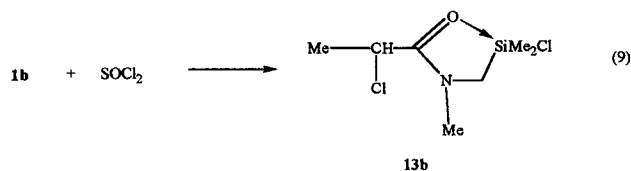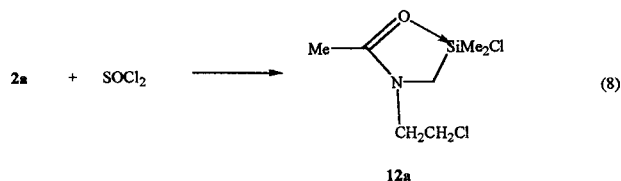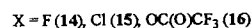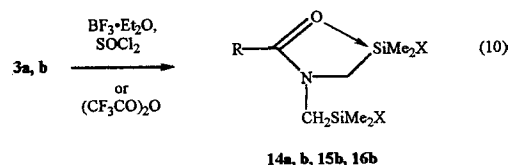
Scheme 6.

Scheme 7.

Table 1
Chemical shifts in ^{13}C-, ^{15}N-, ^{17}O- and ^{29}Si-NMR spectra of amide (NCO) and disiloxane fragments of disilamorpholine **3b** and hydrochloride **3b·HCl** in CD_3COCD_3

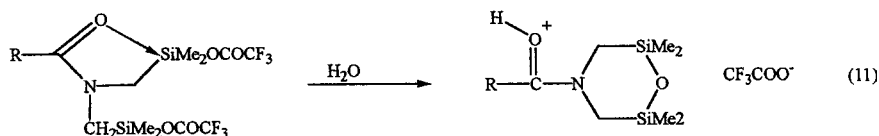| Compound	Chemical shift, δ (ppm)				
	^{13}C	^{15}N	^{17}O		^{29}Si
			(C=O)	(Si–O)	
3b	168.16	−278.5	352	50	−0.8; −1.7 [a]
3b·HCl [b]	171.32	−243.8	235	51	10.7
[c]			275	14	6.7, −43.4

[a] In $CDCl_3$: $c \cong 0.3$ M.
[b] In diluted solution: $c \cong 0.2$ mol l^{-1}.
[c] Additional signals in concentrated solution: $c \cong 0.6$ mol l^{-1}.

Similarly the reaction of disilamorpholine **3b** with $SOCl_2$ in benzene at 50–60°C leads to *N,N*-bis-(dimethylchlorosilylmethyl)acetamide **15b** first characterized by Yoder [11]. The reaction of **3b** with trifluoroacetic anhydride proceeds at room temperature yielding the highly moisture sensitive *N,N*-bis-{[(dimethyltrofluoroacetoxy)silyl]methyl}acetamide **16b**. The IR spectrum of a freshly prepared sample of the di(trifluoroacetae) (**16b**), contains an absorbtion band characteristic of esters (1739 cm^{-1}) and two bands characteristic of the five-membered chelate ring (1517 and 1598 cm^{-1}). In the NMR spectra, in addition to the signals of bis(trifluoroacetate) **16b**, there is a set of signals belonging to a hydrolysis product. The intensity of this second set increases in time and reaches almost 100% after standing overnight. The progress of the reaction between disilamorpholine **3b** and trifluoroacetic acid in C_6D_6 was monitored by NMR spectroscopy which showed that immediately after addition of the reagents the signals corresponding to the di(trifluoroacetae) **16b** appeared in ^{1}H-NMR and ^{29}Si spectra (δ, ppm: ^{1}H; 0.09 s (SiMe$_2$), 0.44 s (SiMe$_2$), 1.77 s (CH$_3$), 2.68 s and 2.70 s (2CH$_2$); ^{29}Si; −42.2 (Si^V), 6.8 (Si^{IV})). Compound **16b** proved resistant to isolation and on attempted distillation underwent further reaction to give the trifluoroacetic acid adduct of 2,2,6,6-tetramethyl-4-acetyl-2,6-disilamorpholine **3b·CF$_3$COOH**, which was confirmed by ^{1}H-NMR spectra and elemental analysis (Scheme 7).

We were able to demonstrate that the predominant species formed on initial addition of an acid to disilamorpholines (**3**) arose from protonation at the amido oxygen. Nevertheless, the subsequent opening of the disilamorpholine ring is likely to occur through the intermediacy of a small amount of the species in which disiloxane oxygen is protonated. The initial amide protonation was demonstrated in two ways. The reaction of disilamorpholine (**3b**) with an ethereal solution of HCl leads to the corresponding hydrochloride **3b·HCl**. The structure of this adduct was confirmed by multinuclear NMR spectroscopy. A comparison of ^{13}C-, ^{15}N-, ^{17}O- and ^{29}Si-NMR chemical shifts of the disilamorpholine (**3b**) and the hydrochloride **3b·HCl** demonstrates clearly that the amide oxygen is protonated (Table 1).

The formation of the hydrochloride **3b·HCl** from compound **3b** is accompanied by a high frequency shift of the ^{13}C- and ^{15}N-NMR signals and a low frequency shift of the amide ^{17}O-NMR signal. The ^{17}O-NMR chemical shifts of the C=O oxygen shows the greatest change while the chemical shifts of the disiloxane oxygen nuclei are almost identical in each compound. Over time the HCl adduct of **13b** undergoes further reaction to give the pentacoordinated silicon compound **17**, which results from simple ring opening of the disilamorpholine ring (Eq. 12). This is accelerated by higher concentrations of acid. The ^{29}Si-NMR spectrum (CD_3COCD_3) of the acid solution is consistent with this proposal since there are two ^{29}Si-NMR resonances at δ 6.7ppm (tetracoordinated) and −43.4 ppm (pentacoordinated). The ^{17}O-NMR spectra showed new signals at δ 275 and 14 ppm, consistent with the resonances expected for oxygen atoms of the C=O → Si and Si–O–R fragments, respectively (Scheme 8).

A further experiment confirmed that initial protonation occurred at the amide oxygen atom. The reaction
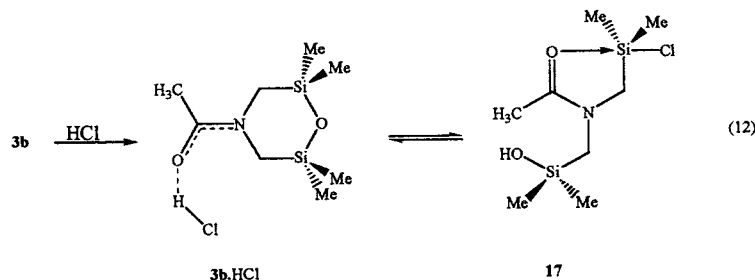
Scheme 8.

of 4-chloroacetyl-2,6-disilamorpholine (**3e**) with tri-fluoromethansulphonic acid gave the adduct (**3e·CF₃SO₃H**), the structure of which was confirmed by X-ray crystallography.

S=O distances in the anion. All others geometric parameters in structures (**3a**) and (**3e·CF₃SO₃H**) are as expected.

3. X-ray crystallography

3.1. Comparison of a disilamorpholine (3a) and a protonated disilamorpholine 3e·CF₃SO₃H

A comparison of the molecular structures of 2,2,6,6-tetramethyl-4-formyl-2,6-disilamorpholine **3a** (Fig. 1) and the protonated disilamorpholine **3e·CF₃SO₃H** (Fig. 2) shows that the geometric parameters of the rings in these structures are almost identical (Tables 2 and 3). In both compounds the rings adopt chair conformations with the planes of the CNC and SiOSi fragments achieving angles with the main plane of 63 and 26° in **3a** and of 65 and 25° in **3e·CF₃SO₃H**.

The structures of the amide fragments, however, are obviously different. The N–C and C=O bond lengths in the neutral molecule (**3a**) are as expected [12], however, the $C^3–N^1$ distance in the adduct **3e·CF₃SO₃H** corresponds to a double bond and the $C^3–O^2$ bond is significantly shorter than the average value (1.33 Å) for enols [12]. This indicates that the positive charge of the [**3e·H**]⁺ cation is localized at the N atom. A slight elongation (by 0.01–0.02 Å) of the endocyclic N–C bonds in the cation [**3e·H**]⁺ relative to the molecule **3a** is also probably a consequence of the charge location on the nitrogen atom.

It is known that some cations with $X^+C(R)OH$ fragments exist as keto-tautomers while the corresponding enols may be stabilized only by strong H-bonding with an anion [13]. Indeed, in our case the H-bond in adduct **3e·CF₃SO₃H** is particularly strong: the $O^2\cdots O^5$ distance is of 2.537(5) Å and the $O^2H^{02}O^5$ angle is of 172(4)° along with an almost standard $O^2–H^{02}$ distance (0.91(6) Å — generally X-ray diffraction gives an artificially lowered value for this distance as a result of a significant shift of electron density from the H to the O atom). There is also a small (ca. 0.02 Å) but noticeable elongation of the $S^1=O^5$ bond in comparison with other
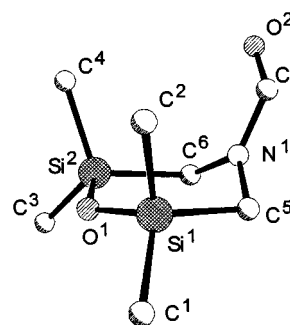

Fig. 1. Molecular structure of **3a**.
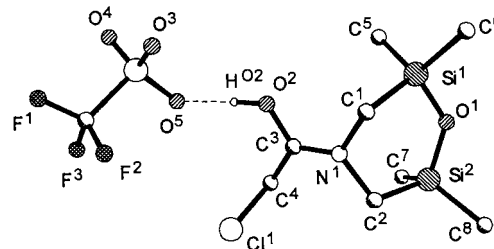
Fig. 2. Molecular structure of the adduct **3e·CF₃SO₃H**.

Table 2
Selected bond lengths (Å) and bond angles (°) for **3a**

Bond length [a]			
$Si^1–O^1$	1.637(2)	$Si^2–C^4$	1.849(2)
$Si^1–C^1$	1.840(2)	$O^2–C^7$	1.213(3)
$Si^1–C^2$	1.850(3)	$N^1–C^7$	1.340(3)
$Si^2–O^1$	1.648(2)	$Si^2–C^3$	1.838(2)
Bond angles [a]			
$O^1Si^1C^1$	109.4(1)	$Si^1O^1Si^2$	130.60(9)
$O^1Si^1C^2$	109.1(1)	$C^7N^1C^6$	120.9(2)
C^1Si^1C2	110.6(1)	$C^7N^1C^5$	121.9(2)
$O^1Si^1C^5$	104.9(1)	$C^6N^1C^5$	116.8(2)
$O^2C^7N^1$	125.7(2)	$N^1C^6Si^2$	110.1(1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3
Selected bond lengths (Å) and bond angles (°) for **3e**·CF$_3$SO$_3$H

Bond length [a]			
Si^1–O^1	1.646(3)	N^1–C^2	1.492(4)
Si^1–C^1	1.900(4)	N^1–C^3	1.288(4)
Si^2–O^1	1.637(2)	C^3–C^4	1.503(4)
Si^2–C^2	1.902(4)	O^2–C^3	1.306(4)
Cl^1–C^4	1.774(4)	O^2–H^{O2}	0.95(6)

Bond angles [a]			
O^{1}Si^{1}C^1	102.7(1)	O^{2}C^{3}N^1	117.5(3)
Si^{1}O^{1}Si^2	132.2(2)	O^{2}C^{3}C^4	119.2(3)
C^{3}O^{2}H^{O2}	113(3)	N^{1}C^{3}C^4	123.2(3)
C^{1}N^{1}C^2	113.3(3)	C^{1}N^{1}C^3	121.8(3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.
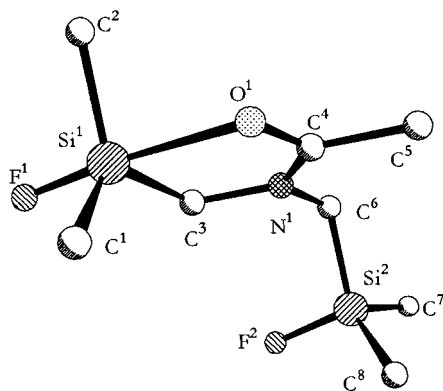

Fig. 3. Molecular structure of **14b**.

3.2. Comparison of the X-ray structure of two bis(dimethylhalosilylmethyl)acetamides

The structure of the product of the reaction of **3b** with BF$_3$·Et$_2$O, *N,N*-bis(dimethylfluorosilylmethyl)acetamide, was determined by X-ray diffraction. This is of interest because we had shown previously that there is a significant difference in reactivity between the bis-(dimethylfluorosilylmethyl)acetamide and the bis-(dimethylchlorosilylmethyl)acetamide [14]. The hyper-coordinated Si–Cl bond is significantly more labile than the tetracoordinated Si–Cl bond towards nucleophilic substitution whereas the reverse is true for the fluoro compound. The difference in bonding between the two compounds, as revealed by X-ray crystallography, should help in understanding the different reactivities.

The environment of the Si^1 atom in the difluoride **14b** (see Scheme 6) is close to trigonal bipyramidal (TBP) with displacement of the central atom from the equatorial plane by 0.23 Å towards the F^1 substituent (Fig. 3). The distortion of the TBP environment may be measured as a deviation $\Delta\Omega$ of a space angle formed by all the equatorial bonds from this angle in an ideal TBP (360°), i.e. $\Delta\Omega = 2\pi - \Omega$ [15]. In **14b** this deviation is

72°, much greater than that in *N*-(dimethylchlorosilyl-methyl)amides and -lactams with OSiC$_3$Cl coordination environments (10–20°) [11,15,16]. The $d_{O \to Si}$ distance in **14b** is 2.19 Å as expected for this type of coordination bond. We have reported previously the X-ray structure of the monofluoride MeC(O)N(CHPhMe)CH$_2$SiMe$_2$F which has a similar coordination environment to **14b** [16]. The lengths of the axial bonds are $d_{O \to Si} = 2.15$ Å and $d_{Si-F} = 1.67$ Å and the $\Delta\Omega$ value is 62°. This suggests that the O → Si coordination in the difluoride **14b** is slightly weaker than in this monofluoride as a result of the electron-withdrawing dimethylfluorosilyl-methyl substituent on the nitrogen.

It is interesting to compare the geometric parameters of the Si^1 environment with those of the almost ideal tetrahedral coordination of the Si^2 atom (Table 4) in the difluoride **14b** and with the geometric parameters of the TBP silicon centre in the dichloride **15b** [11]. The equatorial bond lengths of the pentacoordinate Si atom in the difluoride are slightly shorter than in the second silicon. The elongation of the axial Si–F bond relative to the tetrahedral value is 0.045 Å. In the case of dichloride **15b** the hypervalent state of the central atom does not affect the lengths of the Si–C bonds but the Si–Cl distance increases significantly, from 2.05 to 2.35 Å ($d_{Si-O} = 1.92$ Å). As we have shown earlier the hypercoordination of a fluorosilyl centre has an insignificant effect on the strength of the Si–F bond, whereas the Si–Cl bond is considerably weakened by the additional coordination of the silicon atom with a nucleophilic group [16].

4. Experimental

Crystal and X-ray diffraction study parameters are summarized in Table 5. The structures were resolved by direct methods and refined using F^2 by full-matrix least-squares in anisotropic approximation for non-hydrogen atoms. A profile analysis was carried out for the structure of **14b** using 'PROFIT' software [17]. Hydrogen atoms were located by difference synthesis and refined isotropically. All calculations were performed on PC/AT computers using SHELXTL PLUS software [18]. The main bond lengths and bond angles are presented in Tables 2–4. Other geometric parameters and atomic

Table 4
Selected bond lengths (Å) and bond angles (°) for **14b**

Bond length [a]

Si^1–F^1	1.668(2)	Si^2–F^2	1.603(3)
Si^1–C^1	1.853(3)	Si^2–C^7	1.843(3)
Si^1–C^2	1.869(5)	Si^2–C^6	1.884(5)
Si^1–C^3	1.887(3)	O^1–C^4	1.252(3)
Si^1–O^1	2.187(3)	N^1–C^4	1.327(3)
Si^2–C^8	1.836(3)	N^1–C^6	1.471(3)

Bond angles [a]

$C^1Si^1C^2$	118.6(2)	$F^2Si^2C^6$	107.0(2)
$F^1Si^1C^3$	93.3(1)	$C^4O^1Si^1$	110.8(2)
$C^1Si^1C^3$	120.4(2)	C^4N^1C3	116.1(2)
$C^2Si^1C^3$	116.6(1)	$N^1C^3Si^1$	114.6(2)
$F^1Si^1O^1$	172.1(1)	$O^1C^4N^1$	119.6(2)
$F^2Si^2C^8$	107.6(1)	$N^1C^6Si^2$	115.9(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

coordinates are available from Cambridge Structural Database.

Initial compounds (2,2-dimethyl-4-acetyl-2-silamorpholine (**2a**); 2,2-dimethyl-4-acetyl-5-ethyl-2-silamorpholine (**2c**); 2,2,4,6-tetramethyl-2-sila-5-morpholinone (**1b**); 2,2,4-trimethyl-6-phenyl-2-sila-5-morpholinone (**1d**); 2,2-dimethyl-4-(4-trimethylsiloxybutryl)-2-silamorpholine (**8**); 2,2,6,6-tetramethyl-4-acetyl-2,6-disilamorpholine (**3b**) and 2,2,6,6-tetramethyl-4-chloroacetyl-2,6-disilamorpholine (**3e**) were prepared by standard methods. The physical properties and yields of the compounds were in accordance with literature data [5,9].

4.1. 2,2,6,6-Tetramethyl-4-formyl-2,6-disilamorpholine (*3a*)

Formamide (4.50 g) and hexamethyldisilazane (12.9 g) were dissolved in benzene (50 ml), the solution was cooled and dimethylchloromethylsilane (28.6 g) was added dropwise under vigorous stirring. The mixture was refluxed for 1 h, cooled and a solution of $NaHCO_3$ (16.8 g) in water (40 ml) was added. The organic layer was separated, the aqueous phase was extracted with $CHCl_3$ (50 ml) and the combined organic extracts were reduced under vacuum and distilled to yield 10.05 g (50%) of disilamorpholine (**3a**); b.p. 123–125°C (10 mmHg); m.p. 82–85°C (hexane). IR spectrum ($CHCl_3$, v, cm^{-1}): 1670 (C=O). ^{1}H-NMR spectrum ($CDCl_3$, δ, ppm): 0.20 (6H, s, $SiCH_3$), 0.21 (6H, s, $SiCH_3$), 2.78 (2H, s, CH_2), 2.99 (2H, s, CH_2), 8.03 (1H, s, CH). ^{29}Si-NMR spectrum ($CDCl_3$, δ, ppm): 8.2, 9.7. Anal. Calc. (%): C 41.30, H 8.43. $C_7H_{17}NO_2Si_2$. Found (%): C 41.33, H 8.47.

4.2. N-(2-Acetoxyethyl)-N-(dimethylchlorosilylmethyl)-acetamide (*4a*)

Acetyl chloride (35.3 g) was added to silamorpholine (**2a**) (25.8 g). The reaction mixture was heated for 3 h at 50°C, then the excess of acetyl chloride was removed under reduced pressure, and the residue was distilled to yield 30 g (81%) of the required product (**4a**); b.p. 164–165°C (2 mmHg). IR spectrum (v, cm^{-1}): 1535, 1590 (NCO), 1710 (COO). ^{1}H-NMR spectrum ($CDCl_3$, δ, ppm): 0.09 (6H, s, Me_2Si), 1.64 (3H, s, $CH_3C(O)N$), 1.79 (3H, s, CH_3CO), 2.36 (2H, s, NCH_2Si), 3.32 (2H,

Table 5
Main parameters of the X-ray diffraction study of compounds **3a**, **14b**, and **3d**·CF_3SO_3H

Compound	**3a**	**14b**	**3d**·CF_3SO_3H
Empirical formula	$C_7H_{17}NO_2Si_2$	$C_8H_{19}F_2NOSi_2$	$C_8H_{18}NO_2ClSi_2$·CF_3SO_3H
Diffractometer	Syntex P2$_1$	Siemens P3/PC	Syntex P2$_1$
Radiation, T (K)	Mo–K$_\alpha$, 190	Mo–K$_\alpha$, 173	Mo–K$_\alpha$, 180
Scan type, $2\theta_{max}$ (°)	$\theta/2\theta$, 50	$\omega/2\theta$, 50	$\theta/2\theta$, 54
a (Å)	12.23(3)	8.70(1)	8.476(2)
b (Å)	11.546(4)	6.938(6)	10.686(3)
c (Å)	8.210(2)	21.63(5)	11.347(4)
α (°)	90	90	108.49(2)
β (°)	107.35(2)	101.03(11)	94.89(3)
γ (°)	90	90	109.59(2)
V (Å^3)	1106.7(6)	1282(4)	897(1)
D_{calc} (g cm^{-3})	1.221	1.241	1.488
Space group, Z	$P2_1/c$, 4	$P2_1/n$, 4	$P\bar{1}$, 2
Reflections collected	1913	2258	3200
Observed reflections ($I > 2\sigma(I)$)	1521	2004	2403
Least squares parameters	177	203	275
Absorption coefficient (cm^{-1})	2.88	2.74	5.09
R_1 (observed reflections)	0.039	0.046	0.047
R_1 (all the data)	0.058	0.075	0.080

t, J 7.2 Hz, NCH$_2$), 3.90 (2H, t, J 7.2 Hz, OCH$_2$). Anal. Calc. (%): C 42.93, H 7.21. C$_9$H$_{18}$NO$_3$Si. Found (%): C 43.62, H 7.47.

4.3. N-(1-Acetoxy-2-butyl)-N-(dimethylchloro-silylmethyl)acetamide (4c)

Acetyl chloride (5.3 g) was added to silamorpholine (2c) (4.5 g). The reaction mixture was left to stay for 3 h at room temperature (r.t.) and distilled to recover (4c), 4.5 g (72%); b.p. 162–172°C (2 mmHg). IR spectrum (v, cm^{-1}): 1510, 1580 (NCO), 1710 (COO). ^{1}H-NMR spectrum (CDCl$_3$, δ, ppm): 0.49 (6H, s, Me$_2$Si), 0.9 (3H, t, J 7.0 Hz, CH_3CH$_2$), 1.62 (2H, br. s, CH$_3$CH_2), 2.04 (3H, m, CH$_3$C(O)N), 2.12 (3H, s, H$_3$C(O)), 2.50 (1H, br. d, J 16.3 Hz, NCH$_A$HSi) 2.54 (1H, br. d, J 16.3 Hz, NCHH$_B$Si), 3.8–3.9 (1H, br. m, CHN), 4.0–4.1 (2H, m, $^2J_{HH}$ 14.1 Hz, $^3J_{HH}$ 2.2 Hz, OCH$_2$). ^{13}C-NMR spectrum (CDCl$_3$, δ, ppm): 5.61 (Me$_2$Si), 9.66 (CH_2CH$_2$), 7.34 (CH$_3$CH_2), 20.73 (2 CH$_3$CO), 32.11 (NCH$_2$), 57.89 (CH), 61.96 (OCH$_2$), 169.40 (NCO), 173.71 (COO). ^{29}Si-NMR spectrum (CDCl$_3$, δ, ppm): -38.3. Anal. Calc. (%): C 47.21, H 7.93, Si 10.04. C$_{11}$H$_{22}$ClNO$_3$Si. Found (%): C 46.86, H 8.11, Si 10.20.

4.4. Reaction of 2,2-dimethyl-4-acetyl-2-silamorpholine (2a) with acetylbromide

Acetylbromide (24.6 g) was added to silamorpholine (2a) (35 g). After the exothermic reaction the mixture was heated for 3 h at 50°C which led to crystallization. Two bands at 1535 and 1590 cm^{-1} in IR spectrum and the ^{1}H-NMR signals at (δ, ppm) 0.04 (6H, br. s, Me$_2$Si), 1.68 br. (3H, s, CH$_3$C(O)N), 1.87 (3H, s, CH$_3$CO), 2.40 (2H, br. s, NCH$_2$Si) 3.51 (2H, t, J 7.0 Hz, NCH$_2$), 3.88 (2H, t, J 7.0 Hz, OCH$_2$ were observed and attributed to bromide (5a). The attempt to distill it in vacuo yielded 32 g (92%) of initial silamorpholine (2a), b.p. 103–104°C (2 mmHg). IR spectrum (v, cm^{-1}): 1650 (NCO).

4.5. N-Methyl-N-(dimethylchlorosilylmethyl)amide of 2-acetoxypropionic acid (6b)

Acetyl chloride (23.6 g) was added to silamorpholinone (1b) (17.1 g). The reaction mixture was heated for 3 h at 50°C, cooled down and the excess of acetyl chloride was removed under reduced pressure. The crystalline residue was distilled to yield 23.1 g (92%) of compound (6b); b.p. 146–148°C (5 mmHg), m.p. 68°C. IR spectrum (v, cm^{-1}): 1540, 1615 (NCO), 1710 (COO). ^{1}H-NMR spectrum (CDCl$_3$, δ, ppm): 0.50 (6H, br. d, Me$_2$Si), 1.12 (3H, d, J 7.0 Hz, CH_3CH$_2$), 2.08 (3H, s, CH$_3$CO), 2.79 (2H, s, NCH$_2$Si), 3.14 (2H, s, CH$_2$N), 5.22 (3H, q, J 7.0 Hz, CH$_3$CH). ^{29}Si-NMR

spectrum (CD$_2$Cl$_2$, δ, ppm, -75°C): -42.6, -38.3. Anal. Calc. (%): C 42.93, H 7.21, Si 11.15. C$_9$H$_{18}$ClNO$_3$Si. Found (%): C 42.74, H 7.36, Si 10.70.

4.6. Reaction of 2,2,4,6-tetramethyl-2-silamorpholin-5-one (1b) with acetylbromide

Acetylbromide (3.7 g) was added to silamorpholinone (1b) (3.5 g). In 5 min after the addition in IR spectrum of the mixture (v, CHCl$_3$) the intensity of the C=O band of initial silamorpholinone decreased and two new bands at 1515 and 1620 cm^{-1} appeared. The reaction mixture was heated for 3 h at 85°C. The subsequent cooling down led to crystallisation of 7b. ^{1}H-NMR spectrum of the reaction mixture (CDCl$_3$, δ, ppm): 0.3 (6H, br. s, Me$_2$Si), 1.43 (3H, d, CH_3CH), 2.12 (3H, s, CH$_3$CO), 2.88 (1H, br. d, J 15.0 Hz, NCH$_A$HSi) 2.92 (1H, br. d, J 15.0 Hz, NCHH$_B$Si), 3.15 (3H, br. s, CH$_3$N), 5.31 (1H, q, J 7.0 Hz, CH$_3$CH). ^{13}C-NMR spectrum (CDCl$_3$, δ, ppm): 1.5 (Me$_3$Si), 16.3 (CH_3CH), 20.4 (CH$_3$CO), 37.1 (NCH$_2$Si), 42.3 (CH$_3$N), 65.7 broad s (CH$_3$CH), 170.2 broad (2 C=O). The fractional distillation yielded 3.3 g (95%) of initial silamorpholinone (1b).

4.7. N-Methyl-N-(dimethylchlorosilylmethyl)amide of 2-acetoxy-2-phenylacetic acid (6d)

Acetyl chloride (7.9 g) was added to silamorpholinone (1d) (6.5 g). The reaction mixture was heated for 3 h at 50°C, cooled down and the excess of acetyl chloride was removed under reduced pressure. The residue was distilled to yield 7.8 g (83%) of compound (6d): b.p. 180–182°C (2 mmHg). IR spectrum (v, cm^{-1}): 1620, 1526 (NCO), 1710 (COO). ^{1}H-NMR spectrum (CDCl$_3$, δ, ppm): 0.47 (6H, d, Me$_2$Si), 1.98 (3H, d, CH_3CO), 2.62 (1H, d, J 15.0 Hz, NCH$_A$HSi) 2.66 (1H, d, J 15.0 Hz, NCHH$_B$Si), 2.92 (3H, s, CH$_3$N), 6.01 (1H, s, CHPh), 7.2–7.3 (5H, m, C$_6$H$_5$CH). ^{13}C-NMR spectrum (CDCl$_3$, δ, ppm): 6.30, 6.46 (Me$_2$Si), 19.8 (CH$_3$CO), 35.8 (CH$_3$N), 44.2 (CH$_2$N), 70.6 (CH), 127.6, 128.7 (C$_o$, C$_m$), 129.5 (C$_p$), 131.3 (C$_{ipso}$), 169.6 d q (COO, $^2J_{CH}$ 1.7 Hz, $^3J_{CH}$ 7.0 Hz), 170.6 quintet (NCO, $^2J_{CH} = {}^3J_{CH}$ 3.0 Hz). ^{29}Si-NMR spectrum (CD$_3$CN, δ, ppm): -29.7, -38.3. Anal. Calc. (%): C 53.53, H 6.42, Si 8.95. C$_{14}$H$_{20}$ClNO$_3$Si. Found (%): C 53.15, H 6.87, Si 9.05.

4.8. 2,2-Dimethyl-4-(4-acetoxy)butiryl-2-silamorpholine (10)

Acetyl chloride (7.85 g) was added to silamorpholine (8) (3.5 g). In IR spectrum of the mixture (v, CHCl$_3$) two new bands at 1510 and 1592 cm^{-1} were observed and attributed to diacetate (9). The reaction mixture was heated for 3 h at 70°C, cooled down and the excess

of acetyl chloride was removed under reduced pressure. The residue was distilled to yield 6.6 g (82%) of compound **10**: b.p. 162–164°C (3 mmHg), n_D^{20} 1.4735. IR spectrum (v, cm^{-1}): 1628, (NCO), 1724 (COO). ^{1}H-NMR spectrum (CD$_3$CN, δ, ppm; two sets of signals in a 2:3 ratio): 0.12, 0.16 (6H, s, Me$_2$Si), 1.84 (2H, m, CCH$_2$C), 1.96 (3H, s, CH$_3$COO), 2.34 (2H, t, CH$_2$CO), 2.85, 3.03 (2H, s, NCH$_2$Si), 3.57, 3.46 (2H, br. t, J 7.0 Hz, NCH$_2$), 3.64 (2H, t, J 7.0 Hz, CH$_2$OC(O)), 3.8, 4.04 (2H, br. t, J 7.0 Hz, OCH$_2$). Anal. Calc. (%): C 54.37, H 8.69, Si 11.56. C$_{11}$H$_{21}$NO$_3$Si. Found (%): C 55.47, H 9.20, Si 12.19.

4.9. Reaction of 2,2-dimethyl-4-acetyl-2-silamorpholine (2a) with trimethylchlorosilane

Trimethylchlorosilane (5.4 g) was added to silamorpholine (**2a**) (8.7 g), with stirring. The IR and ^{1}H-NMR monitoring of the reaction was carried out. Two new bands at 1515 and 1620 cm^{-1} (CHCl$_3$) appeared while the C=O band of initial silamorpholine at 1625 cm^{-1} disappeared in IR spectrum. After addition of the reagents within 2 min of the signals of *N*-(trimethylsiloxyethyl)-*N*-(dimethylchlorosilylmethyl)amide of acetic acid (**11**) appeared in ^{1}H-NMR spectrum. ^{1}H-NMR spectrum (CD$_3$CN, δ, ppm, reaction mixture): 0.08 (9H, s, Me$_3$Si), 0.48 (6H, s, Me$_2$Si), 2.21 (3H, s, CH$_3$CO), 2,83 (2H, s, NCH$_2$Si), 3.53 (2H, t, J 7.0 Hz, NCH$_2$), 3.75 (2H, t, J 7.0 Hz, OCH$_2$). ^{29}Si-NMR spectrum (C$_6$D$_6$, δ, ppm): −39.7 (Me$_2$SiCl), 18.6 (Me$_3$Si). The initial compound (**2a**) 8.4 g (96%) was isolated by fractionation of the reaction mixture in vacuum: b.p. 87°C (2 mmHg.), n_D^{20} 1.4765 [5].

4.10. N-(2-Chloroethyl)-N-(dimethylchlorosilylmethyl)-amide of acetic acid (12a)

Thionyl chloride (4.8 g) was added to silamorpholine (**1d**) (6.5 g). After an exothermic reaction the mixture was heated for 3 h at 55°C, cooled down and the excess of acetyl chloride was removed under reduced pressure. The residue was distilled to give starting material (**12a**) 6.2 g (72%); b.p. 110–115°C (2 mmHg). IR spectrum (v, cm^{-1}): 1590, 1540 (NCO). ^{1}H-NMR spectrum (CD$_3$CN, δ, ppm): 0.47 (6H, s, Me$_2$Si), 2.13 (3H, s, CH$_3$C(O)N), 2.71 (2H, s, NCH$_2$Si), 3.73 (2H, t, J 5.5 Hz, NCH$_2$), 3.83 (2H, t, J 5.5 Hz, CH$_2$Cl). ^{13}C-NMR spectrum (CDCl$_3$, δ, ppm): 55.5 d (Me$_2$Si), 19.9 (CH$_3$CO), 36.5 (CH$_3$N), 44.5 (CH$_2$N), 46.3 (CH), 170.1 (C=O). Anal. Calc. (%): C 36.84, H 6.36. C$_7$H$_{15}$Cl$_2$NOSi. Found (%): C 36.84, H 6.63.

4.11. N-Methyl-N-(dimethylchlorosilylmethyl)amide of 2-chloropropionic acid (13b)

Thionyl chloride (5.1 g) was added to silamorpholi-

none (**1b**) (6.6 g). After an exothermic reaction the mixture was heated for 3 h at 60°C and cooled down. The residue was distilled to yield 6.6 g (76%) of the starting compound (**13b**); b.p. 120–123°C (2 mmHg); m.p. 49°C. IR spectrum (v, cm^{-1}): 1612, 1520 (NCO). ^{1}H-NMR spectrum (CD$_3$CN, δ, ppm): 0.47 (6H, s, Me$_2$Si), 1.58 (3H, d, J 7.0 H, CH$_3$CHz), 2.79 (2H, s, NCH$_2$Si), 3.12 (3H, s, NCH$_3$), 4.87 (1H, q, J 7.0 Hz, CH$_3$CHCl). ^{13}C-NMR spectrum (CDCl$_3$, δ, ppm): 55.5 (d, NCH$_2$Si), 19.9 (CH$_3$CO), 36.5 (CH$_3$N), 44.5 (CH), 170.1 (C=O). Anal. Calc. (%): C 36.84, H 6.36, Si 12.31. C$_7$H$_{15}$Cl$_2$NOSi. Found (%): C 36.91, H 6.81, Si 12.40.

4.12. N,N-Bis(dimethylfluorosilylmethyl)formamide (14a)

Boron trifluoride etherate (2.32 g) was added dropwise to 5 g of disilamorpholine (**3a**). The reaction mixture was refluxed until 1.2 ml of ether was condensed. The residue was distilled to yield 3.7 g (66%) of difluoride (**14a**); b.p. 128–129°C (10 mmHg); n_D^{20} 1.4545. IR spectrum (v, cm^{-1}): 1650 broad (NCO). ^{1}H-NMR spectrum (CDCl$_3$, δ, ppm): 0.1–0.3 (12H, m, Me$_2$Si), 2.29 (2H, d, NCH$_2$Si^{IV}) 2.7–2.9 (2H, m, NCH$_2$Si^V), 7.75 (1H, d, HC(O)N). ^{13}C-NMR spectrum (CDCl$_3$, δ, ppm): −2.36 to 0.98 (Me$_2$Si), 34.39, 36.99, 37.32, 39.44, 40.31, 40.47, 41.68 (NCH$_2$), 161.01, 162.37, 162.48 (C=O). ^{29}Si-NMR spectrum (CDCl$_3$, δ, ppm): −10.2 d ($^1J_{SiF}$ 268 Hz, Si^V), 16 d ($^1J_{SiF}$ 289 Hz, Si^{IV}). Anal. Calc. (%): C 37.31, H 7.60. C$_7$H$_{17}$NOSi$_2$F$_2$. Found (%): C 37.64, H 7.78.

4.13. N,N-Bis(dimethylfluorosilylmethyl)acetamide (14b)

Boron trifluoride etherate (3.1 g) was added dropwise to 7.2 g of disilamorpholine (**3b**). Reaction mixture was refluxed until 1.1 ml of ether were condensed. The residue was distilled to yield 4.1 g (52%) of difluoride (**14b**); b.p. 123–125°C (7 mmHg). FW Calc.: 239.4. FW found (cryoscopy in benzene, $b = 0.15$ mol kg^{-1}): 234.4. IR spectrum (CHCl$_3$, v, cm^{-1}): 1590, 1513 (NCO). ^{1}H-NMR spectrum (CDCl$_3$, δ, ppm): 0.19 (6H, s, Me$_2$Si^{IV}) 0.33 (6H, d, $^3J_{HF}$ 5.4 Hz, Me$_2$Si^V), 2.03 (3H, s, CH$_3$C(O)), 2.38 (2H, s, NCH$_2$Si^V) 3.01 (2H, d, $^3J_{HF}$ 5.9 Hz, NCH$_2$Si^V). ^{13}C-NMR spectrum (CDCl$_3$, δ, ppm): 1.61, −1.86 (d, $^2J_{CF}$ 14.0 Hz, Me$_2$Si), 18.19 (CH$_3$CO), 40.17, 41.60 (d, $^2J_{CF}$ 16.2 Hz, CH$_2$N), 171.05 (C=O). ^{29}Si-NMR spectrum (CDCl$_3$, δ, ppm): −23.5 (Si^V, $^1J_{SiF}$ 257 Hz), 29.0 (Si^{IV}, $^1J_{SiF}$ 287 Hz). Anal. Calc. (%): C 40.14, H 8.00, N 5.85. C$_8$H$_{19}$NOSi$_2$F$_2$. Found (%): C 40.35, H 8.01, N 5.64.

4.14. N,N-Bis(dimethylchlorosilylmethyl)acetamide [19] (15b)

The mixture of 1.08 g of disilamorpholine (**3b**) and thionyl chloride (1.78 g) in 2 ml of benzene (abs.) was

heated for 30 min at 50–60°C. The solvent was removed under reduced pressure and the residue was crystallized on addition of heptane (5 ml) to yield 1 g (73%) of dichloride (**15b**); m.p. 122–123°C. IR spectrum ($CHCl_3$, v, cm^{-1}): 1590, 1517 (NCO). ^{1}H-NMR spectrum (C_6D_6, δ, ppm; two sets of signals in a 63:37 ratio; minor set in brackets): −0.03 (6H, s, Me_2Si) (0.01 (6H, s, Me_2Si)), 1.0 (6H, s, Me_2Si) (0.99 (6H, s, Me_2Si)), 1.40 (3H, s, $CH_3C(O)$) (1.30 (3H, s, $CH_3C(O)$)), 2.40 (2H, s, NCH_2) (2.31 (2H, s, NCH_2)), 2.88 (2H, s, NCH_2Si) (2.72 (2H, s, NCH_2Si).

4.15. N,N-Bis(dimethyltrifluoroacetoxysilylmethyl)-acetamide (16b)

(a) Trifluoroacetic anhydride (8.4 g) was added dropwise to a solution of 6.51 g of disilamorpholine (**3b**) in benzene (5 ml) and the mixture was allowed to stand for 4 h. Distillation yielded 6.4 g (50%) of compound **16b**; b.p. 156–157°C (3 mmHg); n_D^{20} 1.4434. IR spectrum (v, cm^{-1}): 1517, 1590 (NCO), 1739 (COO).

(b) Trifluoroacetic anhydride (0.42 g) and disilamorpholine (**3b**) (0.43 g) were dissolved in C_6D_6 (0.5 ml) in NMR sample tube. In 5 min the signals of compound **16b** were found in ^{1}H-NMR spectrum: 0.09 s ($SiMe_2$), 0.44 s ($SiMe_2$), 1.77 s (CH_3), 2.68 s and 2.70 s (2 CH_2). ^{29}Si-NMR spectrum (C_6D_6, δ, ppm): −42.2 (Si^V), 6.8 (Si^{IV}).

(c) The attempt to distil 4 g of the product **16b** for the second time led to decomposition and yielded 1.18 g of a compound that, according to the elemental analysis and the ^{1}H-NMR spectrum, is an adduct of 2,2,6,6-tetramethyl-4-acetyl-2,6-disilamorpholine with trifluoroacetic acid (**3b·CF₃COOH**). ^{1}H-NMR spectrum (CD_3COCD_3, δ, ppm): 0.13 (6H, s, Me_2Si), 0.19 (6H, s, Me_2Si), 2.08 (3H, s, CH_3), 3.03 (2H, s, CH_2) and 3.11 (2H, s, CH_2). Anal. Calc. (%): C 36.90, H 6.19. $C_{10}H_{20}NO_4Si_2F_3$. Found (%): C 36.92, H 5.79.

4.16. Hydrochloride of 2,2,6,6-tetramethyl-4-acetyl-2,6-disilamorpholine (3b·HCl)

Disilamorpholine (**3b**) was added to the solution of HCl prepared by the hydrolysis of thionyl chloride (1.19 g) with water (0.18) in ether (5 ml). The solvent was removed under reduced pressure, the residue was crystallized in hexane (5 ml) to yield 1.18 g (94%) of the hydrochloride (**3b·HCl**); m.p. 114–117°C (hexane). IR spectrum ($CHCl_3$, v, cm^{-1}): 1658 (NCO). ^{1}H-NMR spectrum (CD_3COCD_3, δ, ppm): 0.24 (12H, s, 2 $SiMe_2$), 2.54 (3H, s, CH_3), 3.33 (4H, s, 2 CH_2). Anal. Calc. (%): C 37.84, H 7.93, Si 22.12. $C_8H_{20}ClNO_2Si_2$. Found (%): C 38.22, H 7.63, Si 21.98.

4.17. Adduct of 2,2,6,6-tetramethyl-4-chloroacetyl-2,6-disilamorpholine (3e) with trifluoromethanesulphonic acid (3e·CF₃SO₃H)

Trimethylsilyltrifluorosulphonic acid (1.33 g) and 1.25 g of disilamorpholine (**3e**) were dissolved in hexane (4 ml). The mixture was allowed to stand for several months in presence of atmospheric moisture, which led to formation of small amount of crystalline adduct (**3e·CF₃SO₃H**). The crystals were used for X-ray analysis without purification.

References

[1] D. Kost, I. Kalikhman, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, Ch. 23, vol. 2, Wiley, New York, 1998, pp. 1339–1445.

[2] C. Chuit, R.J.P. Corriu, C. Reye, J.C. Young, Chem. Rev. 93 (1993) 1371.

[3] R.R. Holmes, Chem. Rev. 96 (1996) 927.

[4] (a) S.N. Tandura, M.G. Voronkov, N.A. Alekseev, Topics in Current Chemistry, vol. 131, Springer-Verlag, Berlin, 1986, pp. 99–189. (b) A.G. Shipov, E.P. Kramarova, O.B. Artamkina, Yu.I. Baukov, Metalloorg. Khim. 4 (1991) 1101. (c) A.G. Shipov, E.P. Kramarova, O.B. Artamkina, G.I. Oleneva, N.A. Nepomniashaja, Yu.I. Baukov, Zh. Obshch. Khim. 65 (1995) 272.

[5] Yu.I. Baukov, A.G. Shipov, E.P. Kramarova, E.A. Mamaeva, O.A. Zamishliaeva, N.A. Anisimova, V.V. Negrebetsky, Zh. Organ. Khim. 32 (1996) 1259.

[6] O.B. Artamkina, E.P. Kramarova, A.G. Shipov, Yu.I. Baukov, A.A. Macharashvili, Yu.E. Ovchinnikov, Yu.T. Struchkov, Zh. Organ. Khim. 63 (1993) 2289.

[7] V.V. Negrebetsky, Yu.I. Baukov, Izv. Akad. Nauk, Ser. Khim. (1997) 1912.

[8] O.B. Artamkina, A.G. Shipov, Yu.I. Baukov, Zh. Obshch. Khim. 65 (1995) 2005.

[9] E.P. Kramarova, V.V. Negrebetsky, A.G. Shipov, Yu.I. Baukov, Zh. Obshch. Khim. 64 (1994) 1222.

[10] Yu.I. Baukov, E.P. Kramarova, A.G. Shipov, G.I. Oleneva, O.B. Artamkina, A.I. Albanov, M.G. Voronkov, V.A. Pestunovich, Zh. Obshch. Khim. 59 (1989) 127.

[11] K.D. Onan, A.T. McPhail, C.H. Yoder, R.W. Hillard, J. Chem. Soc. Chem. Commun. (1978) 209.

[12] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc. Perkin Trans. II (1987) 1.

[13] L.M. Epshtein, in: N.D. Sokolov (Ed.), Hydrogen Bonds, Nauka, Moscow, 1981, p. 255.

[14] A.R. Bassindale, M. Borbaruah, J. Chem. Soc. Chem. Commun. (1993) 352.

[15] Yu.E. Ovchinnikov, Yu.T. Struchkov, A.G. Shipov, L.S. Smirnova, Yu.I. Baukov, S.Yu. Bylikin, Mendeleev Commun. (1994) 178.

[16] Yu.I. Baukov, Yu.E. Ovchinnikov, A.G. Shipov, E.P. Kramarova, V.V. Negrebetsky, Yu.T. Struchkov, J. Organomet. Chem. 536–537 (1997) 399.

[17] V.A. Strel'zov, V.E. Zavodnik, Kristallografia 34 (1989) 1369.

[18] W. Robinson, G.M. Sheldrick, in: N.W. Isaaks, M.R. Taylor (Eds.), Crystallographic Computing Techniques and New Technologies, Oxford University Press, Oxford, 1988, pp. 366–372.

[19] R.W. Hillard, C.M. Ruan, C.H. Yoder, J. Organomet. Chem. 153 (1978) 369.