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ScienceDirect
Journal of Organometallic Chemistry 691 (2006) 3976–3988
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Structures and stereochemical non-rigidity of Si-substituted *N*-(dimethylsilylmethyl)- and *N*-(methylphenylsilylmethyl)amides and -lactams

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Received 27 January 2006; received in revised form 28 May 2006; accepted 31 May 2006
Available online 20 June 2006

Abstract

Eleven new silicon-substituted *N*-(dimethylsilylmethyl)- and *N*-(methylphenylsilylmethyl)amides and -lactams bearing a chiral carbon in the amide or lactam fragment, and containing the $OSiC_3X$ (X = Hal, OTf) coordination fragment have been synthesized and their structures determined in solution by spectroscopic means. These structures are consistent with the hypervalency model. Quantum chemical calculations adequately reflect correlations between the type of monodentate ligand X and the geometric parameters of the N–C–O–Si–X fragments.

The activation parameters ($\Delta G^{\#}_{298}$, $\Delta H^{\#}$, $\Delta S^{\#}$) for enantiomerization and diastereomerization in these new compounds and the other related compounds were determined by the dynamic NMR (DNMR) method using full line-shape analysis. The free activation energy values ($\Delta G^{\#}_{298}$) in the absence of external nucleophiles vary from 9 to 27 kcal mol^{-1}. The entropies of activation ($\Delta S^{\#}$) are negative (−20 to −50 cal mol^{-1} K^{-1}) in all cases except for the chloride derivatives of 4-phenyl-2-pyrrolidone and 4-oxazolidinone that have weaker intramolecular O → Si coordination. Irregular mechanisms of permutational isomerization were proposed on the basis of the DNMR data and the results of quantum-chemical calculations carried out by ab initio (HF) and DFT (PBE, B3PW91, 6-311++G(d,p)). Depending on the coordination environment at silicon, the mechanisms proposed involve either the dissociation of the Si–X bond followed by the Berry pseudorotation or similar in the intermediate or the cleavage of intramolecular O–Si bond with subsequent inversion at the silicon atom. The apparently simple pseudorotation mechanism involving only the pentacoordinate structures **1**–**21** does not appear to be favoured in any of the examples studied.

Keywords: Compounds of pentacoordinate silicon; Intramolecular coordination; Stereochemical non-rigidity; Dynamic NMR spectroscopy; Activational parameters; Quantum-chemical analysis

1. Introduction

Stereodynamic processes in pentacoordinate silicon compounds; in particular the permutational isomerization of ligands, are the subject of intensive investigation [1–4]. These studies are important in increasing our understanding of mechanistic organosilicon chemistry, particularly for industrially important reactions such as the hydrolysis of halosilanes.

The isomerization in compounds with intramolecular N–Si coordination and zwitterionic spirocyclic O,O-bischelate organosilicates have been studied extensively, and various mechanisms for the isomerizations have been proposed [3,5]. However, there are insufficient experimentally determined data (especially $\Delta G^{\#}_{298}$, $\Delta H^{\#}$ and $\Delta S^{\#}$ values)

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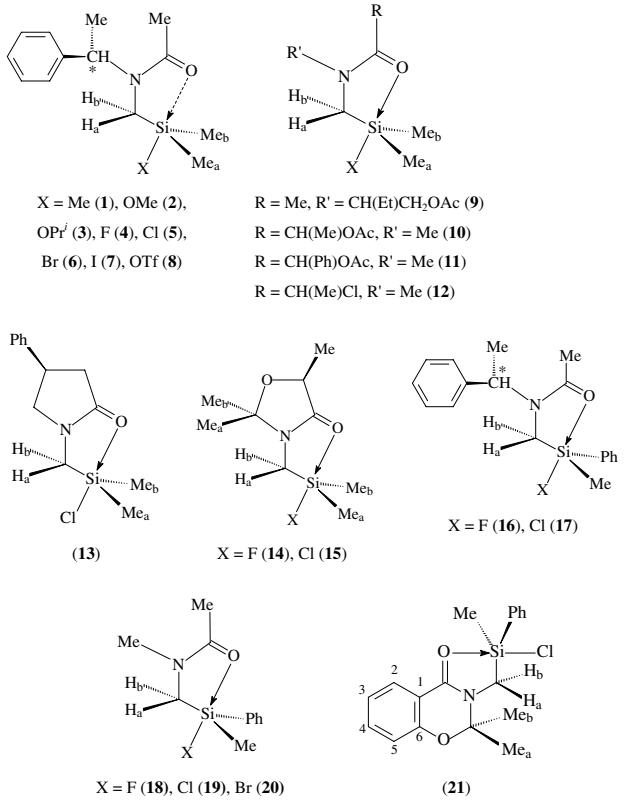
doi:10.1016/j.jorganchem.2006.05.056

for similar processes in stereochemically non-rigid compounds with C,O-coordinating ligands to enable likely mechanisms to be distinguished [3,4].

The permutational isomerization of ligands in Si-substituted (O–Si)-chelate *N*-(dimethylsilylmethyl)-*N*-[(*S*)-1-phenylethyl]amides [6–8] and 4-phenyl-*N*-(dimethylsilylmethyl)-2-pyrrolidone [9] has been previously studied by the ^{1}H dynamic NMR (DNMR) method. The calculation of free activation energy ($\Delta G^{\#}$) for this process was carried out by measuring the temperature of coalescence of the signals for the diastereomeric SiMe groups which significantly limited the extent of the mechanistic discussion owing to the absence of data on the enthalpies and entropies of activation.

In this paper we report structural studies of two series of *N*-(dimethylsilylmethyl) and *N*-(methylphenylsilylmethyl) derivatives of amides and lactams (**1**–**15** and **16**–**21**, respectively) in the liquid phase (DNMR) and using computational study methods. For the first time the ^{1}H DNMR based full line-shape analysis of the signals was carried out for pentacoordinate silicon derivatives which enabled us to calculate the stereodynamic activation parameters in solutions of the selected compounds **1**–**21**.



Thus, the present work is a logical continuation of our investigations of stereodynamic properties of pentacoordinated compounds, including reactions of nucleophilic substitution at silicon in solution [10–14].

2. Results and discussion

2.1. Structure of compounds 1–21 in solutions

The IR and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopic data confirming the structure of compounds **3**–**6**, **9**–**12**, **13**, and **15** were reported earlier [4,6–8]. The structures of new silicon derivatives **1**, **2**, **7**, **8**, **14**, and **16**–**21** were confirmed by IR and ^{1}H, ^{13}C, ^{15}N, ^{17}O, and ^{29}Si NMR spectroscopic studies (Tables 1 and 2) and elemental analysis (see Section 4).

N-Silylmethyl derivatives of amides, lactams, and related compounds can be arranged into several groups according to the strength of the O···Si interaction and the proximity of their structures to one of the five limiting structures **A**–**E** below [10,15] (Scheme 1).

According to the hypervalency model there is a correlation between the nucleofugacity of the electronegative substituent X at the silicon atom and the bond, O–Si (structure **B**) or Si–X (structure **D**) that can be termed the 'coordination bond' [15–17]. The formation of structures approximating to **A** and **E** and containing a tetracoordinate silicon may be conceptualized as the formal cleavage of either O–Si or Si–X bonds in the trigonal bipyramidal structure **C**.

An increase in the nucleofugacity of the Si-substituent in the series of alkyl-, alkoxy-, fluoro-, and chloro derivatives in the liquid state (Table 2) leads to upfield shifts of signals in the ^{29}Si NMR spectra. Further increases in the substituent nucleofugacity in bromides, triflates, and iodides decreases the upfield shift relative to that in the chlorides. This behaviour is modelled by the coordination contribution, $\Delta\delta(^{29}\mathrm{Si})$ [15]. The coordination contribution is calculated as the difference between chemical shifts of the pentacoordinate silicon and its tetracoordinate analogue, $\delta(^{29}\mathrm{Si^{V}})$–$\delta(^{29}\mathrm{Si^{IV}})$. The model tetracoordinate compounds are usually selected from chloromethylsilanes $ClCH_2SiMe_2X$ [15] or trimethylsilyl derivatives Me_3SiX [4]. In this paper the latter compounds were used (see Table 2) as the ^{29}Si NMR chemical shifts are readily available.

The silicon atom in monochlorides (Scheme 1) have the most ideal TBP configuration ($\Delta_{Si} \approx 0$; the sum of equatorial angles is ≈360°) among all neutral pentacoordinate (O–Si)-monochelates [18]. As the silicon atom moves out of the equatorial plane towards the X substituent gradually increases the Δ_{Si} value which is positive for X = Me, OAlk. Conversely, Δ_{Si} values for X = Br, OTf, I are negative.

According to the liquid-state ^{29}Si NMR and solid-state X-ray data (Δ_{Si}), the compounds reported in this paper may be divided into several groups. Group (*a*) includes methyl and alkoxy derivatives **1**–**3** with either absent or very weak O···Si coordination. Fluorides **4**, **16**, and **18** comprise group (*b*) that are compounds with relatively weak but noticeable interaction between the silicon and oxygen atoms. Group (*c*) contains chlorides **5**, **9**–**12**, **17**, **19**, and **21** with strong O···Si coordination and nearly TBP environment of the silicon atom. Finally, group (*d*)

Table 1
Chemical shifts (δ, ppm) of signals in ^{1}H and ^{13}C NMR spectra of Si-substituted *N*-(dimethylsilylmethyl)- and *N*-(methylphenylsilylmethyl)amides **1**, **2**, **7**, and **8** in $CDCl_3$ (≈0.1 M solutions)

Compound		δ (ppm)							
		$Si(Me)_2$	NCH_2	CH_3	CH_3CH	CH	(C^1)	H^2 (C^2)	H^3 (C^3)	H^4(C^4)	C=O
1	^{1}H	s, −0.05	dd, 2.28, 2.44 ($^1J_{HH}$ 14.7)	s, 2.25	d, 1.58 ($^3J_{HH}$ 6.8)	qu, 5.08 ($^3J_{HH}$ 6.8)		d, 7.24 ($^3J_{HH}$ 7.8)	t, 7.37 ($^3J_{HH}$ 7.8)	t, 7.29 ($^3J_{HH}$ 7.8)	
	^{13}C	0.50	35.35	22.68	18.85	57.60	141.62	129.81	128.06	129.04	169.77
2[a]	^{1}H	s, 0.23	dd, 2.18, 2.29 ($^1J_{HH}$ 14.5)	s, 2.23	d, 1.63 ($^3J_{HH}$ 6.5)	qu, 5.12 ($^3J_{HH}$ 6.5)		d, 7.26 ($^3J_{HH}$ 7.7)	t, 7.38 ($^3J_{HH}$ 7.7)	t, 7.32 ($^3J_{HH}$ 7.7)	
	^{13}C	−1.74	31.30	20.52	17.07	55.99	139.65	128.45	126.44	127.41	170.59
7	^{1}H	s, 0.38	dd, 2.53, 2.80 ($^1J_{HH}$ 14.5)	s, 2.24	d, 1.72 ($^3J_{HH}$ 6.9)	qu, 5.24 ($^3J_{HH}$ 6.9)		d, 7.29 ($^3J_{HH}$ 7.7)	t, 7.44 ($^3J_{HH}$ 7.7)	t, 7.38 ($^3J_{HH}$ 7.7)	
	^{13}C	3.51	35.44	18.88	17.94	57.83	137.65	129.35	126.93	128.77	174.99
8[b]	^{1}H	s, 0.51	dd, 2.64, 2.99 ($^1J_{HH}$ 16.6)	s, 2.38	d, 1.71 ($^3J_{HH}$ 6.8)	qu, 5.18 ($^3J_{HH}$ 6.8)		d, 7.22 ($^3J_{HH}$ 7.6)	t, 7.42 ($^3J_{HH}$ 7.6)	t, 7.37 ($^3J_{HH}$ 7.6)	
	^{13}C	1.52	33.88	17.82	17.48	57.87	137.13	129.39	126.22	128.93	175.30

[a] The ^{1}H, ^{13}C NMR chemical shifts (δ, ppm): CH_3O 3.25 (s, 3H), 49.69.
[b] The ^{13}C NMR chemical shifts of CF_3 signal (δ, ppm): t, 119.70 ($^1J_{CF}$ 318.7 Hz).

Table 2
The ^{15}N, ^{17}O, and ^{29}Si NMR chemical shifts (δ, ppm) and estimated values of coordination contribution [$\Delta\delta(^{29}Si)$] of Si-substituted *N*-(dimethylsilylmethyl)- and *N*-(methylphenylsilylmethyl)amides and -lactams **1**–**21** in $CDCl_3$

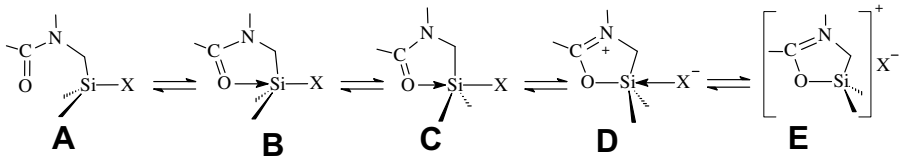
Compound	X	δ (ppm)			$-\Delta\delta(^{29}Si)$[b] (ppm)
		^{15}N	^{17}O[a]	^{29}Si	
1	Me	−279	361	8.9	−8.9
2	OPr^i	−270	350	7.9	9.3
3	OMe	−273	355	6.0	11.2
4	F	−247	258	−19.4 [4]	49.9
5	Cl	−252	245	−38.1 [4]	68.0
6	Br			−28.3 [4]	54.3
7	I	−221	201	−21.9	31.3
8	OTf			−15.3	28.3
9	Cl			−33.5	63.4
10	Cl			−31.6	61.5
11	Cl			−32.0	61.9
12	Cl			−33.9	63.8
13	Cl			−9.7 [4]	39.6
14	F			−3.0	33.5
15	Cl			−10.5 [6]	40.4
16	F			−38.9	69.4
17	Cl			−53.8	83.7
18	F			−40.3	70.8
19	Cl			−49.6	79.5
20	Br			−42.4	68.4
21	Cl			−47.2	77.1

[a] The chemical shift was measured at 50 °C.
[b] $\delta(^{29}Si^V)$–$\delta(Me_3{}^{29}SiX)$.

comprises the complexes **6**–**8** with predominantly covalent O–Si bonds with the X substituent capable of dissociation in polar solvents.

The intramolecular O···Si interactions in halides **13**–**15**, the derivatives of 4-phenyl-2-pyrrolidone and 4-oxazolidinone, are the weakest (see Table 2) among all fluorides and chlorides of pentacoordinate silicon with C,O-chelating ligands [8,9b]. This fact could be attributed to a substantial steric strain in chelate fragments in these compounds caused by the presence of a five-membered lactam ring [4]. This group will be discussed separately from the other derivatives.

The comparison of chemical shifts of signals in the ^{29}Si NMR spectra of compounds **1**–**3** [$\delta(^{29}Si) \approx 4$–7 ppm] and the corresponding tetracoordinate silanes suggest that the coordination interaction, O···Si, in these compounds [$-\Delta\delta(^{29}Si) \approx -8$ to +12 ppm] is either absent or at least is much weaker than that in other (O–Si)-chelate halides, triflates, acylates, and aryloxides of pentacoordinate silicon [4]. This conclusion is also supported by more downfield (up to 100 ppm) shift of signals in ^{17}O NMR spectra of compounds **2** and **3** [$\delta(^{17}O) \approx 340$–350 ppm, $CDCl_3$, 50 °C] in comparison to fluoride **4**, chlorides of the (*c*) group (240–270 ppm) [4,18], and iodide **7** (Table 2) and also by the upfield shift of $\delta[^{13}C(=O)]$ in compounds **1**–**3** (≈170 ppm, see [4] and Table 1) which is similar to that observed for *N*,*N*-dimethylacetamide **22** (169.36 ppm [19]) used as a model compound [20].



X	Me, OAlk	F, OPh, OC(O)Ph	Cl	Br, OTf, I	
$\delta(^{29}Si)$	15 ÷ –5	–5 ÷ –25	–10 ÷ –45	–5 ÷ –25	ppm
$\Delta\delta(^{29}Si)$		–0.1 ÷ –12	–45 ÷ –60	–50 ÷ –70	ppm
Δ_{Si}	0.3 ÷ 0.5	0.17 ÷ 0.25	0.01 ÷ 0.16	–0.18 ÷ –0.35	Å

Scheme 1.

The increase of $-\Delta\delta(^{29}Si)$ values (in comparison to compounds **1**–**3**) in difluorides **4**, **16**, and **18** to ≈50–70 ppm indicates the presence of noticeable O–Si coordination (Table 2). The subsequent transition to chlorides **5**, **9**–**12**, **17**, **19**, and **21** further increases the $-\Delta\delta(^{29}Si)$, especially for the derivatives of *N*-(methylphenylsilylmethyl)amides **17**, **19**, and **21** (see Table 2).

The increase in nucleofugacity of monodentate electronegative substituent where X is bromide, triflate, and iodide leads to downfield shifts (in comparison to chlorides) of ^{29}Si NMR signals. At the same time the appropriate $-\Delta\delta(^{29}Si)$ values decrease (see Table 2). The more upfield signal in the ^{17}O NMR spectrum of the iodide **7** (201 ppm, CD_2Cl_2, 50 °C) in comparison to chlorides of group (*c*) is a result of increased shielding of the oxygen atom [4,21] while the downfield shift of the signal in ^{15}N NMR (−220.9 ppm, CD_2Cl_2, compared to ≈−250 ppm for chlorides [4]) indicates an increased positive charge on the nitrogen atom [22]. Such changes in the spectra of (*d*) group compounds are probably caused by the increase of the contribution of ionic tetracoordinate structures **E** formed as a result of dissociation of the **X** substituent in solutions. This suggestion is in agreement with the observed increase of electroconductivity of pentacoordinate neutral monochelate complexes in the series of Cl < Br < I, OTf [4].

Graphical correlations of $\delta(^{29}Si)$ and $\Delta\delta(^{29}Si)$ with the nucleofugacity of monodentate electronegative substituent X (estimated by the pK_a of the appropriate conjugate acid HX [23]) in the series of R^*SiMe_2X complexes (X = Me, **1**; OMe, **2**; OPr^i, **3**; F, **4**; Cl, **5**; Br, **6**; I, **7**; OTf, **8**) have a *parabola-like* shape, with the minimum and maximum, respectively, corresponding to the chloride R^*SiMe_2Cl (**5**, Fig. 1a and b, respectively). The left branch of the "*parabola*" corresponds to strong conjugate acids while weak acids are represented by the right branch. Fig. 1 shows that the gradient of $\delta(^{29}Si)$ and $\Delta\delta(^{29}Si)$ values is greater in the first case as structural changes are more sensitive to X when X is the conjugate base of a strong acid.

Increase in the nucleofugacity of the X substituent (decrease in the pK_a) in the series of compounds **1**–**5** increases the $-\Delta\delta(^{29}Si)$ value due to the higher "*covalent*" character (strong interaction) in the intramolecular O–Si coordination bond. At the same time, according to the model of hypervalency, the initially "*covalent*" Si–X interaction gradually becomes a bond of a "*coordination*" nature (longer and weaker interaction). Further increase in nucleofugacity of the X substituent in the series **6**–**8** leads to decrease of the $-\Delta\delta(^{29}Si)$ (Fig. 1b). In this case the increase of the "*covalent*" nature of the O···Si bond in comparison to the increased (as a result of dissociation,

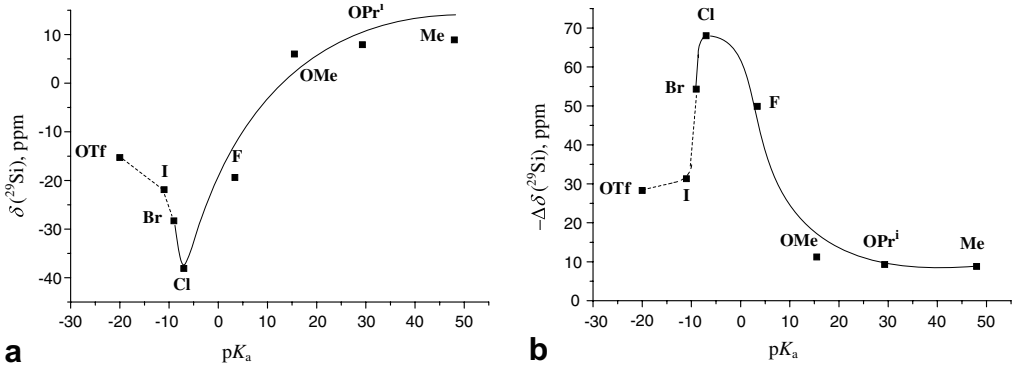


Fig. 1. Graphical interpretation of the influence of the pK_a of the appropriate HX acid (a) and the coordination contribution $[-\Delta\delta(^{29}Si)]$ (b) on experimental values of $\delta(^{29}Si)$ in Si-substituted *N*-(dimethylsilylmethyl)amides $MeC(O)CH(Ph)NCH_2SiMe_2X$, where X = Me, **1**; OMe, **2**; OPr^i, **3**; F, **4**; Cl, **5**; Br, **6**; I, **7**; OTf, **8** ($CDCl_3$).

see above) "*coordination*" nature of the Si···X interaction is relatively small.

Thus, the above correlations (Fig. 1) illustrate one of the most important observations of hypervalent compounds. An increase of the "*covalent*" character, that is a strengthening of the intramolecular O–Si interaction leads to an increase in length and decrease in strength of the corresponding Si–X bond. Thus, the "*covalent*" character of the Si–X bond decreases and the "*coordination*" character increases as illustrated in Scheme 1. Despite the obvious problems (for example the insufficient reliability of the pK_a values of very strong acids), the results obtained indicate that the acidity constants may be used as a convenient measure of nucleofugacity of the X substituent in derivatives of pentacoordinate silicon.

2.2. Quantum-chemical calculations

In order to estimate the "*coordination*" and "*covalent*" contributions in O → Si interactions in isolated molecules a quantum-chemical investigation of compounds **1**–**21** was carried out. As was shown earlier [24], the hybrid functional B3PW91 used in our calculations satisfactory represents the influence of the nature of the X substituent on structural parameters of the $OSiC_3X$ coordination set. The results of our calculations are summarized in Table 3. For comparison data obtained by ab initio methods with the basis set HF/6-311++G(d,p) and from non-empirical calculations using PBE in the TZ2P basis set are also included in Table 3.

Our calculations adequately reflect correlations between the type of the monodentate ligand X and geometric parameters of the N–C–O–Si–X fragment determined by NMR spectroscopy (see above) and X-ray analysis of compounds **4**, **5** [25], and **15** [26]. Strong intramolecular O → Si coordination in halides **4**–**7** and triflate **8** leads to significant elongation of C=O bonds and shortening of C–N distances in comparison to non-chelate compounds **1**–**3**. This indicates effective delocalization of the electronic density in amide fragments owing to additional O → Si interactions.

In contrast to other bond lengths, the calculated O–Si distances (B3PW91, PBE) are significantly larger (by 0.17–0.25 Å) than the values determined by the X-ray method (Table 3). The differences observed may be a result of deformation of coordination bonds in the crystal state compared to those in isolated molecules. Ab initio calculations give even greater values that are up to 0.3 Å longer than actual O–Si bond lengths. Similar influences of the aggregate state of substances on intramolecular coordination bonds have been observed earlier, for example, in (aroyloxymethyl)trifluorosilanes [27].

The nature of the monodentate substituent X at the silicon atom directly affects the O–Si coordination bond length: an increase in the nucleofugacity of the monodentate substituent X from fluoride **4** to triflate **8** leads to a gradual decrease of the coordination bond length (see Table 3). This behaviour is generally reflected by quantum-chemical studies of compounds **1**–**8** and these results augment the study of halides and triflate of 1-(dimethylsilylmethyl)piperidone-2 that we have previously published [28–30].

Table 3
Bond lengths (d) of the N–C–O–Si–X fragment in Si-substituted *N*-(dimethylsilylmethyl)- and *N*-(methylphenylsilylmethyl)amides and -lactams **1**–**21**, according to the quantum-chemical calculations (DFT, ab initio)

Compound	X	*d* (Å)			
		O → Si	Si–O	C=O	C(O)–N
1a B3PW91/6-311++G(d,p)	Me			1.227	1.364
1b B3PW91/6-311++G(d,p)	OPr^i			1.232	1.355
1c B3PW91/6-311++G(d,p)	OMe			1.231	1.354
1d B3PW91/6-311++G(d,p)	F	2.311	1.674	1.238	1.350
HF/6-311++G(d,p)		2.453	1.641	1.211	1.345
PBE		2.285	1.692	1.254	1.355
PCA[21]		2.149	1.668	1.260	1.336
1e B3PW91/6-311++G(d,p)	Cl	2.215	2.204	1.243	1.345
HF/6-311++G(d,p)		2.358	2.180	1.215	1.340
PBE		2.227	2.218	1.258	1.351
PCA[21]		1.975	2.306	1.269	1.326
1f B3PW91/6-311++G(d,p)	Br	2.184	2.395	1.245	1.343
PBE		2.183	2.418	1.261	1.349
1g B3PW91/6-311++G(d,p)	I	2.113	2.689	1.251	1.339
PBE		2.123	2.709	1.266	1.345
1h B3PW91/6-311++G(d,p)	OTf	2.034	1.894	1.258	1.334
PBE		2.174	1.845	1.260	1.350
2a B3PW91/6-311++G(d,p)	Cl	2.270	2.181	1.237	1.339
2b B3PW91/6-311++G(d,p)	Cl	2.190	2.191	1.241	1.339
2c B3PW91/6-311++G(d,p)	Cl	2.262	2.179	1.250	1.344
2d B3PW91/6-311++G(d,p)	Cl	2.355	2.174	1.236	1.341
3 B3PW91/6-311++G(d,p)	Cl	2.535	2.157	1.227	1.346
4a B3PW91/6-311++G(d,p)	F	2.661	1.658	1.224	1.343
4b B3PW91/6-311++G(d,p)	Cl	2.603	2.148	1.226	1.340
HF/6-311++G(d,p)		2.771	2.132	1.202	1.332
PCA[9]		2.425	2.147	1.218	1.297
5a B3PW91/6-311++G(d,p)	F	2.304	1.678	1.242	1.345
5b B3PW91/6-311++G(d,p)	Cl	2.197	2.202	1.245	1.362
5c B3PW91/6-311++G(d,p)	Br	2.204	2.384	1.245	1.339
6a B3PW91/6-311++G(d,p)	F	2.270	1.676	1.242	1.342
PCA		2.055	1.668	1.255	1.323
6b B3PW91/6-311++G(d,p)	Cl	2.228	2.196	1.244	1.340
PCA		1.948	2.298	1.278	1.305
7 B3PW91/6-311++G(d,p)	Cl	2.239	2.195	1.243	1.347

2.3. Dynamic ^1H NMR spectroscopy

2.3.1. Enantiomer and diastereomer interconversions

All DNMR studies were carried out in the same solvent, $CDCl_3$, to minimise the influence of differential solvation on the mechanisms of the observed stereodynamic processes.

The presence of chiral carbon (**1**–**15**) or silicon (**16**–**21**) atoms in molecules of pentacoordinate derivatives **1**–**21** leads to chemical non-equivalency of the NMR signals of the prochiral groups NCH_2, $SiMe_2$ and CMe_2. As a result, in the ^1H NMR spectra at room and lower temperatures the signals of NCH_2 protons appear as multiplets of AB-system ($^2J_{HH} \approx 14$–16 Hz) while the protons of $SiMe_2$ and CMe_2 groups appear as pairs of singlets. This indicates

interconversions between the topomers (enantiomers for compounds **1**–**15**, **18**–**21** and diastereomers for halides **16** and **17**) that are slow on the NMR time scale.

At higher temperatures in derivatives of *N*-(dimethylsilylmethyl)amides and -lactams the quartets of NCH_2 protons retain their chemical non-equivalency while the doublet of $SiMe_2$ groups demonstrate a temperature evolution typical for permutational processes: components of a doublet broaden and gradually coalesce into a singlet with averaged chemical shift [3,4,6,7]. Decrease in temperature reverses the evolution and restores the initial spectrum.

^{1}H NMR spectra of *N*-(methylphenylsilylmethyl)amides **16**–**21** demonstrate similar temperature evolution in the accessible temperature range (up to 60 °C): increase in temperature leads to broadening and, in some cases, coalescence of AB-systems into a broad, averaged singlet.

Activation parameters of permutational isomerization for compounds **1**–**21** (Table 4) were determined by the full line-shape analysis of two singlets of $SiMe_2$ groups (compounds **1**–**15**) and AB-system quartets of NCH_2 protons (halides **16**–**21**).

The highest barriers of permutational isomerization were found for the fluorides **4**, **14**, **16**, **18** and chlorides **17**, **19**, **21**. In the ^{1}H NMR spectra of fluorides in $CDCl_3$ the coalescence of the relevant signals was not observed even at 60 °C. The coalescence of the AB-system quartet in chloride **19** [31] is achieved at significantly lower temperatures. At 50 °C in the ^{1}H NMR spectrum of this compound the NCH_2 protons appear as a broad singlet with averaged chemical shift. However, the free activation energy of enantiomerization for compound **19** was not determined [31].

The presence of 1,8-bis(dimethylamino)naphthalene "*proton sponge*" does not affect activational parameters of chloride **5** while for bromide **6**, iodide **7**, and triflate **8** the $\Delta G^{\#}$ values decrease by 0.5, 1.0, and 1.5 kcal mol^{-1}, respectively (Table 4). Thus, the presence of acidic products of hydrolysis may affect the barriers of permutational isomerization, so in this paper we will discuss only those results that were obtained with "*proton sponge*".

Analysis of the data in Tables 2, 4 shows an inverse dependence of $\Delta G^{\#}$ values for compounds **4**–**8** on the nucleofugacity (pK_a) of the monodentate ligand X and the coordination contribution of the appropriate bond (Fig. 2a and b).

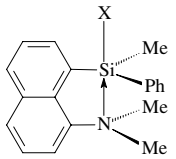
Fig. 2b illustrates that the increase of $-\Delta\delta(^{29}Si)$ on the transition from fluoride **4** to chloride **5** is accompanied by a decrease of $\Delta G^{\#}$. The decreasing of value $-\Delta\delta(^{29}Si)$ (compounds **6**–**8**) shows a minor increase $\Delta G^{\#}$. This suggests that there may be a different permutation mechanism for compounds on different branches of the parabola shown in Fig. 2b.

Table 4
Activational parameters of permutational isomerization in Si-substituted *N*-(dimethylsilylmethyl)- and *N*-(methylphenylsilylmethyl)amides and -lactams **4**–**21** ($CDCl_3$, $c \approx 0.1$ M)

Compound	X	$\Delta G^{\#}_{298}$ (kcal mol^{-1})	$\Delta H^{\#}$ (kcal mol^{-1})	$\Delta S^{\#}$ (cal mol^{-1} K^{-1})	$\Delta G^{\#}_c$ (kcal mol^{-1})	T_c (°C)
4	F	25.3 ± 0.2	19.3 ± 0.2	−20 ± 6	>24[c]	>60
	[a]	14.4 ± 0.1	6.7 ± 0.1	−26 ± 8		
5	Cl	14.6 ± 0.1	5.0 ± 0.2	−32 ± 6	14.9 ± 0.1	24
	[b]	14.5 ± 0.1	4.2 ± 0.2	−35 ± 5		
6	Br	14.2 ± 0.1	7.4 ± 0.3	−23 ± 6	14.6 ± 0.1	21
	[b]	13.7 ± 0.1	4.2 ± 0.2	−35 ± 5		
7	I	13.8 ± 0.1	1.2 ± 0.2	−42 ± 10	13.8 ± 0.1	−7
	[b]	12.9 ± 0.1	4.9 ± 0.3	−27 ± 6		
8	OTf	15.0 ± 0.1	0.2 ± 0.4	−50 ± 12	15.4 ± 0.1	40
	[b]	13.5 ± 0.1	4.4 ± 0.4	−31 ± 8		
9	Cl	14.2 ± 0.1	6.8 ± 0.1	−25 ± 3	12.5 ± 0.1[d]	−7[d]
10	Cl	14.0 ± 0.1	4.8 ± 0.1	−31 ± 6	15.6 ± 0.1	57
11	Cl	14.3 ± 0.1	8.0 ± 0.2	−21 ± 2	14.3 ± 0.1	31
12	Cl	14.1 ± 0.1	6.4 ± 0.1	−26 ± 3	13.9 ± 0.1	22
13	Cl	10.6 ± 0.1	7.8 ± 0.2	10 ± 3	10.8	
14	F	29.4 ± 0.2	25.8 ± 0.2	−12 ± 5		
	[a]	15.1 ± 0.1	7.0 ± 0.1	−27 ± 6		
15	Cl	9.6 ± 0.1	6.2 ± 0.2	12 ± 4	9.8 ± 0.1	−85
16	F	28.9 ± 0.2	26.2 ± 0.2	−9 ± 5		
17	Cl	17.9 ± 0.2	9.0 ± 0.2	−30 ± 6		
18	F	26.9 ± 0.2	23.3 ± 0.2	−12 ± 5		
19	Cl	18.4 ± 0.2	8.6 ± 0.1	−33 ± 8		
20	Br	15.2 ± 0.1	3.0 ± 0.2	−41 ± 10		
21	Cl	17.8 ± 0.1	9.5 ± 0.2	−28 ± 5		

[a] In present of $Bu_4N^+F^- \cdot 3H_2O$ (0.01 M).
[b] In present of 1,8-bis(dimethylamino)naphtalene (0.01 M).
[c] Is estimated by a DNMR method on observed broadering of signals.
[d] In CD_3CN solution.

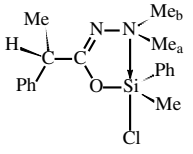
A similar dependence of the permutational isomerization barrier on the nature of the halogen was found for monofunctional halides of 8-dimethylamino-1-silylnaphtalene (**22**) (X = F, Cl, and Br) with intramolecular N → Si coordination [32].



(**22**)

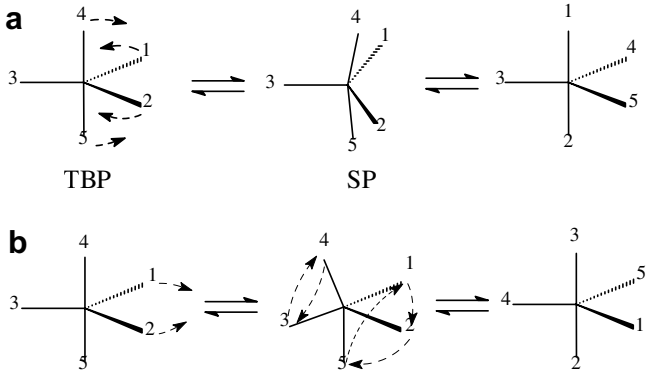
The $\Delta G^{\#}$ values calculated for **22** from the ^{1}H DNMR data at the coalescence temperature are 23, 20, and >19 kcal mol^{-1} for X = F, Cl and Br, respectively. The authors suggest an irregular mechanism for observed stereodynamic processes involving the N–Si bond cleavage with subsequent rotation and inversion at the nitrogen atom [32].

Kalikhman and co-workers [33] studied a related compound, **23**, and were able to show that at low temperatures the N–Si bond dissociated and rotation about the N–N bond rendered the NMe groups equivalent without epimerization at the silicon centre.



(**23**)

The $\Delta G^{\#}$ value for this process was measured to be 11.4 kcal mol^{-1}. This value is lower than that reported for **22** because the geometric constraints to rotation of the NMe_2 group are significantly smaller. At higher temperatures the signals from the two diastereomers coalesce through a pseudorotation process at silicon with a measured $\Delta G^{\#}$ value of 18.7 kcal mol^{-1}.



Scheme 2.

2.3.2. Mechanisms of permutational isomerization

According to the literature, there are two general types of permutational isomerization mechanisms in pentacoordinate silicon compounds [34]. *Dissociative mechanisms* involve cleavage (dissociation) of either intramolecular coordination bond heteroatom–silicon, or the covalent bond between silicon and a monodentate substituent (X). *Non-dissociative mechanisms* (*pseudorotation*) involve either a *Berry pseudorotation* [a fast interconversion between trigonal bipyramid (TBP) and square pyramid (SP), Scheme 2a] or a *Ugi turnstile rotation* (Scheme 2b [35]).

The pseudorotation mechanism of stereodynamic processes in lactamo- and amidomethyl derivatives of silicon involves topomers with the diequatorial configuration of the chelate ligand (which requires the increase of the O–Si–C angle in nearly planar five-membered ring from ≈90° to ≈120°). It is impossible to envisage structures in which the chelate ligand occupies two axial positions as this necessitates an O–Si–C bond angle close to 180°. Therefore, the role of "*pivot*" substituents in such compounds can be played only by monodentate ligands. As a result, the pseudorotation proceeds with retention of configuration at the silicon atom (Scheme 3, **a** ↔ **b**, etc.).

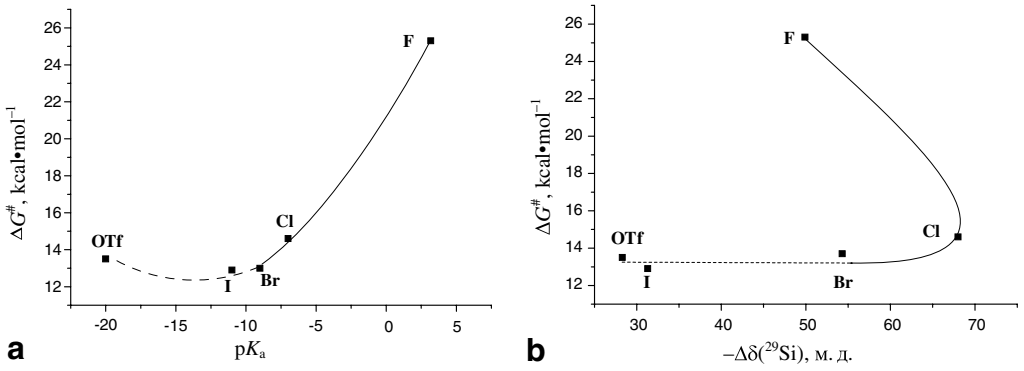
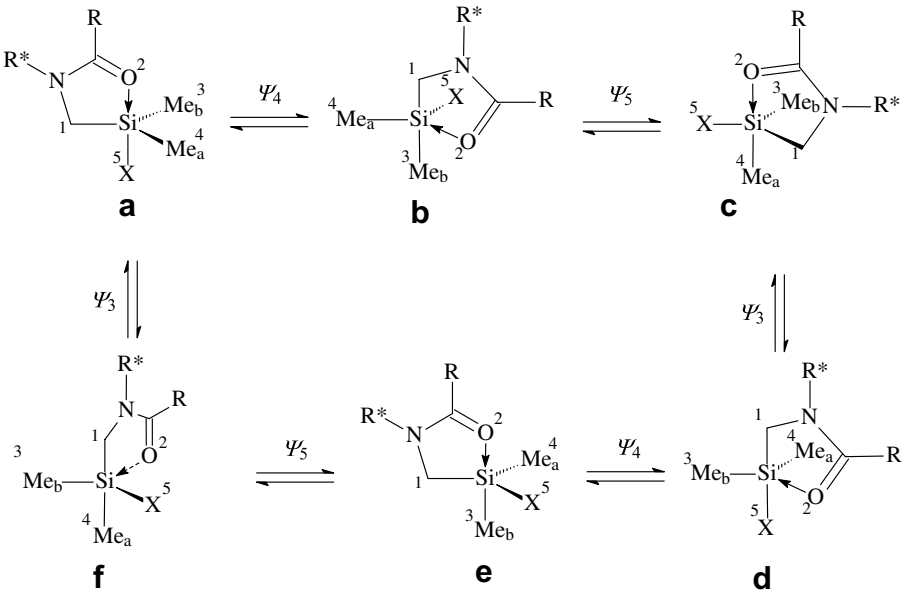


Fig. 2. Graphical interpretation of the influence of the pK_a of the appropriate HX acid (a) and the coordination contribution [$-\Delta\delta(^{29}Si)$] (b) on experimental values of $\Delta G^{\#}$ of permutational isomerization in Si-substituted *N*-(dimethylsilylmethyl)amides $MeC(O)CH(Ph)NCH_2SiMe_2X$ $SiMe_2X$, where X = Me, **11**; OMe, **13**; OPr^i, **14**; F, **15**; Cl, **16**; Br, **19**; I, **21**; OTf, **22** ($CDCl_3$).



Scheme 3.

The mechanism of permutational isomerization in derivatives of pentacoordinate silicon with good leaving groups [X = Br (**6**), I (**7**), OTf (**8**)] and chlorides **5**, **9**–**12**, **17**, **19**, **21** with relatively short O–Si distance and elongated Si–Cl bond may involve dissociation of the Si–X bond and formation of a tetracoordinate intermediate or a transition state (**b**) (Scheme 4).

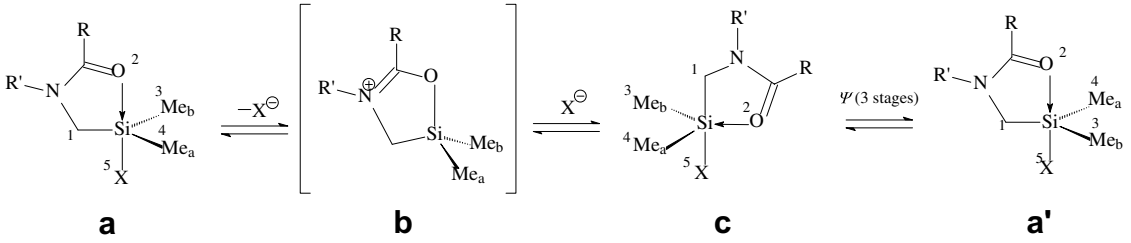
Negative $\Delta S^{\#}$ values (Table 4) indicate that the rate-limiting step of the process involves a more compact (in comparison with the initial molecule) intermediate (**b**). It has been hypothesized [3] that a high negative value of the activation entropy in hypervalent silicon derivatives might be attributed to efficient solvation of intermediates. Subsequent nucleophilic attack by the X^- anion can proceed from the rear of the C–Si bond and lead to formation of a pentacoordinate intermediate (**c**). A three-step pseudorotation starting with (**c**) produces the enantiomer (**a**′).

Another reason for the lower barriers of permutation in chlorides **13** and **15** can be also attributed to weaker intramolecular coordination O → Si in these molecules in comparison to chlorides **5**, **9**–**12**, **17**, **19**, and **21** that have shorter O–Si distances. The positive $\Delta S^{\#}$ values of the stereomutation process for chlorides **13** and **15** (Table 4) suggest that the limiting step is the formation of a more open intermediate or transition state suggested to be (**b**) (Scheme 5).

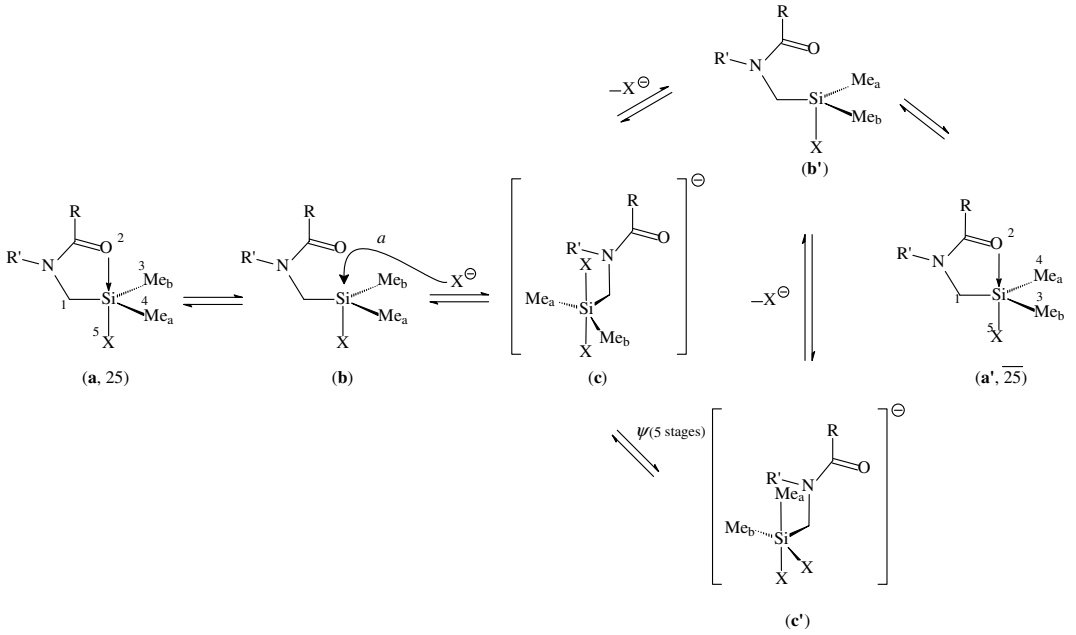
Nucleophilic attack by the anion X^- at silicon in the second stage of the process leads to a pentacoordinate species (**c**) (or in the case of fluorides, to an intermolecularly associated species). The loss of the original monodentate ligand X (**b**′) results in inversion of configuration at silicon, which with subsequent re-coordination of the intramolecular oxygen atom produces the enantiomer (**a**′).

The permutational isomerization barriers for the fluorides studied are the highest among the calculated values for pentacoordinate silicon derivatives and are virtually independent on the structure of lactamomethyl ligand (Table 4).

Taking into account the concentration dependencies of chemical shifts in NMR spectra found by us earlier [36]. Scheme 5 illustrates the most probable mechanism for stereodynamic processes in fluorides. In contrast to chlorides

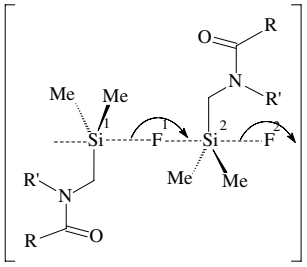


Scheme 4.



Scheme 5.

13 and **15**, permutation in fluorides may involve intermolecular associates with fluorine bridges (Si^1–F^1–Si^2).



3. Conclusion

Halides and other derivatives of *N*-(dimethylsilylmethyl)acetamides and -lactams containing a hypervalent $OSiC_3X$ fragment in solutions undergo permutational isomerization of ligands in the trigonal-bipyramidal environment of silicon. Irregular mechanisms of stereodynamic processes involving a dissociation of either the Si–X bond (the route **I**) or the O → Si intramolecular coordination bond (the route **II**) were proposed on the basis of ^{1}H DNMR data.

Permutational isomerization in fluorides and chlorides of pentacoordinate silicon with a "*coordinate*" nature of the intramolecular O → Si interaction predominantly proceeds along the route **II**.

Increase of the "*covalent*" contribution in bromides, iodides, and triflates favours the route **I** of the stereodynamic process. The apparently simple pseudorotation mechanism involving only the pentacoordinate structures **1**–**21** does not appear to be favoured in any of the examples studied.

4. Experimental

IR spectra of compounds (KBr, ≈5% solutions in $CHCl_3$) were recorded using a Specord IR-75 instrument. Specific rotations were determined using A1-EPO polarimeter using 0.5 dm samples.

The ^{1}H, ^{13}C, ^{15}N, ^{17}O, ^{19}F and ^{29}Si NMR spectra of the compounds studied in $CDCl_3$ were recorded on a Varian VXR-400 and Jeol JNM-EX400 instruments (400.1, 100.6, 40.5, 54.2, 396 and 79.5 MHz, respectively). ^{1}H, ^{13}C and ^{29}Si chemical shifts were measured using tetramethylsilane as the internal reference. Chemical shifts of ^{15}N, ^{17}O, and ^{19}F were measured using external references, 1 M CH_3NO_2 solution, H_2O, and $CFCl_3$, respectively. ^{15}N NMR spectra were obtained by DEPT method [37]. Signals in ^{1}H and ^{13}C NMR spectra were identified by 2D NMR (COSY, HETCOR $^1J_{CH}$–$^3J_{CH}$) using standard techniques of built-in software for Varian VXR-400.

Temperature calibrations were performed using the distances between non-equivalent protons of methanol (−90 to +30 °C) and ethylene glycol (+30 to +85 °C) [38]. Activation parameters of the stereodynamic processes were calculated using DNMR-SIM software [39] and modified Eyring equation [40]. The number of temperature points was from 10 to 15. The correlation coefficient varied from 0.997 to 0.999.

The quantum-chemical calculations were carried out in terms of ab initio (HF) and density functional theory

(B3PW91, 6-311++G(d,p)) by GAUSSIAN-98 software [41] and exchange-correlation functional (PBE, TZ2P) [42] by "PRIRODA" software [43]. All calculated structures are in the local minima of their respective potential energy surfaces that have been proved by vibrational analysis.

Syntheses of initial *N*-[(*S*)-1-phenylethyl]acetamide [44], *N*-trimethylsilyl-*N*-[(*S*)-1-phenylethyl]acetamide [25], 2,2,5-trimethyl-3-trimethylsilyl-4-oxazolidinone [45], 2,2-dimethyl-3-(trimethylsilyl)benzo[2*H*]-1,3-oxazin-4-one [45], and methylphenyl(chloromethyl)chlorosilane [46] were reported earlier.

4.1. *N*-(Trimethylsilylmethyl)-*N*-[(*S*)-1-phenylethyl]acetamide (**1**)

A solution of MeMgI (33 mmol) in diethyl ether (35 ml) was added dropwise to a solution of 8.1 g (30 mmol) of *N*-[(*S*)-1-phenylethyl]acetamide in benzene (50 ml). The mixture was stirred for 40 min, than treated with water (10 ml) and saturated solution of NH_4Cl (15 ml). The organic layer was separated, the water layer extracted with ether (12 ml). Combined organic phases were dried over $MgSO_4$ and the solvent was removed in vacuo. Fractionation of the residue produced 4.4 g (59%) of compound **1** as a colourless liquid, b.p. 155–156 °C (7 mm Hg), n_D^{20} 1.5133, d_{20} 0.940 g/ml. IR spectrum ($CHCl_3$, ν, cm^{-1}): 1630 (NCO). $[\alpha]_D^{20}$ −39.9 (*c* 1.3 M, CH_3CN). Anal. Calc. for $C_{14}H_{23}NOSi$: C, 67.41; H, 9.29; N, 5.62. Found: C, 67.29; H, 9.30; N, 5.47%.

4.2. *N*-(Dimethylmethoxysilylmethyl)-*N*-[(*S*)-1-phenylethyl]acetamide (**2**)

A solution of *N*-[(*S*)-1-phenylethyl]acetamide (16.3 g, 0.1 mol), hexamethyldisilazane (6.44 g, 0.04 mol), and chloro(chloromethyl)dimethylsilane (14.3 g, 0.1 mol) in benzene (100 ml) was refluxed for 3 h. The reaction mixture was cooled down, then 16 g (0.5 mol) of methanol and 24.1 g (0.15 mol) of hexamethyldisilazane was added. The precipitate formed was removed by filtration; the solvent was removed in vacuo. Fractionation of the residue produced 20.6 g (78%) of compound **2**, b.p. 181–182 °C (11 mm Hg), n_D^{20} 1.5100. IR ($CHCl_3$, ν, cm^{-1}): 1630 (NCO). $[\alpha]_D^{20}$ −34.72 (*c* 2.3, CH_3CN). Anal. Calc. for $C_{14}H_{23}NO_2Si$: C, 63.35; H, 8.73; Si, 10.58. Found: C, 63.48; H, 8.62; Si, 10.27%.

4.3. (O–Si)-Chelate *N*-(dimethyliodosilylmethyl)-*N*-[(*S*)-1-phenylethyl]acetamide (**7**)

A solution of chloride **5** (1.35 g, 5 mmol) and trimethyliodosilane (1.1 g, 5 mmol) in CH_2Cl_2 (10 ml) was stirred for 24 h at room temperature. The volatiles were removed in vacuo to yield 1.8 g (100%) of iodide **7**. IR spectrum ($CHCl_3$, ν, cm^{-1}): 1580, 1500 (NCO). When the reaction was carried out in the NMR tube, the signals of the product appear in the reaction mixture in 2 h.

4.4. (O–Si)-Chelate *N*-(dimethyltrifluoromethansulfonylsilylmethyl)-*N*-[(*S*)-1-phenylethyl]acetamide (**8**)

A solution of compound **5** (1.5 g, 5.5 mmol) and trimethylsilyltriflate (1.33 g, 6 mmol) in toluene (10 ml) was stirred for 1 h at 40 °C. The volatiles were removed in vacuo to yield 2 g (95%) of compound **8**, m.p. 66–67 °C. IR spectrum ($CHCl_3$, ν, cm^{-1}): 1584, 1504 (NCO). $[\alpha]_D^{20}$ +13.3 (*c* 1.9, CH_3CN). Anal. Calc. for $C_{14}H_{20}F_3NO_4SSi$: C, 43.85; H, 5.25; N, 3.65. Found: C, 43.50; H, 5.59; N, 3.29%.

4.5. (O–Si)-Chelate 2,2,5-trimethyl-3-dimethylfluorosilylmethyl-4-oxazolidinone (**14**)

A mixture of 2,2,5-trimethyl-3-trimethylsilyl-4-oxazolidinone (5 g, 25 mmol [45]) and chloro(chloromethyl)dimethylsilane (3.8 g, 25 mmol) was refluxed at 80 °C until 3 ml of Me_3SiCl was distilled out. The crystalline mixture formed was dissolved in $CHCl_3$ (40 ml) and sodium hydrocarbonate (3.5 g of the salt in 30 ml of water) was added. The organic layer was separated and dried over K_2CO_3. The volatiles were removed in vacuo, the residue was treated with $BF_3 \cdot Et_2O$ (2.1 g, 14 mmol) and fractionated to produce 2.5 g (46%) of compound **14**, b.p. 97–99 °C (10 mm Hg), n_D^{20} 1.4390. IR spectrum (thin film, ν, cm^{-1}): 1700, 1500 (NCO).

^1H NMR (*c* 0.2 M, $CDCl_3$, δ, ppm): 0.2 s (6H, $SiMe_2$), 2.49 s (2H, NCH_2), 1.47 s (6H, Me_2), 1.38 d (3H, Me, $^3J_{HH}$ 7.0 Hz), 4.42 q (1H, CH, $^3J_{HH}$ 7.0 Hz). ^{13}C NMR (*c* 0.2 M, $CDCl_3$, δ, ppm): 4.83 wide ($SiMe_2$), 33.01 (NCH_2), 24.93 (Me_2), 18.12 (Me), 26.93 (CH), 94.99 (CMe_2). ^{29}Si NMR (*c* 0.2 M, $CDCl_3$, δ, ppm): −3.0 d ($^1J_{SiF}$ 254 Hz). Anal. Calc. for $C_9H_{18}FNO_2Si$: C, 49.28; H, 8.27; N, 6.38. Found: C, 49.11; H, 8.34; N, 6.67%.

4.6. (O–Si)-Chelate *N*-(methylsilylfluoromethylsilyl)-*N*-[(*S*)-1-phenylethyl]acetamide (**16**)

Trimethylchlorosilane (0.5 ml) and triethylamine (3.5 ml, 0.025 mol) were added dropwise to a solution of chloride **17** (6.6 g, 0.02 mol) in toluene (20 ml). After the reaction mixture cooled down, it was warmed again just below the boiling point and stirred for 40 min. Next day the precipitate formed was filtered out and volatiles were removed in vacuo. Fractionation of the residue produced 2.0 g (30%) of crude *N*-(methylphenylmethoxysilylmethyl)-*N*-[(*S*)-1-phenylethyl]acetamide with b.p. 170–200 °C (10 mm Hg). The crude product (2.0 g, 0.006 mol) was treated with $BF_3 \cdot Et_2O$ (0.28 g, 0.002 mol) and the reaction mixture was refluxed for 2 h, then volatiles were removed in vacuo. The residue was dissolved in chloroform, the solution was separated from the insolubles and the solvent was removed in vacuo. The residue was recrystallized from a mixture of diethyl ether–THF (1:1) to produce 1.3 g (68%) of white crystalline fluoride **16**, m.p. 118–121 °C (diethyl ether–THF, 1:1). IR spectrum ($CHCl_3$, ν, cm^{-1}): 1497, 1607 (NCO).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.41 s (3H, SiMe), 2.20 d (3H, *C–CH_3, $^3J_{HH}$ 7.0 Hz), 1.6 s (3H, CH_3CO), 2.29, 2.58 dd (2H, NCH_2, $^2J_{HH}$ 15.9 Hz), 5.04 q (1H, *C–CH, $^3J_{HH}$ 7.0 Hz), 7.2–7.8 m (10H, C_6H_5) (first diastereomer); 0.45 s (3H, SiMe), 2.20 d (3H, *C–CH_3, $^3J_{HH}$ 7.0 Hz), 1.7 s (3H, CH_3CO), 2.23, 2.53 dd (2H, NCH_2, $^2J_{HH}$ 15.9 Hz), 5.04 q (1H, *C–CH, $^3J_{HH}$ 7.0 Hz), 7.2–7.8 m (10H, C_6H_5) (second diastereomer). The signal intensities of two diastereomers were approximately in 1:1 ratio. ^{13}C NMR ($CDCl_3$, δ, ppm): 55.99 (CH); 17.73 [$CH_3C(O)$]; 18.39 (CH_3CH); broad, 1.05 (SiMe); 37.30 (NCH_2); 171.83 (C=O); 134.29 (C_{ipso}), 128.95 (C_{ortho}), 128.00 (C_{para}), 126.32 (C_{meta}) (C–C_6H_5); 134.00 (C_{ipso}), 128.49 (C_{ortho}), 128.32 (C_{para}), 127.31 (C_{meta}) (Si–C_6H_5). ^{29}Si NMR ($CDCl_3$, δ, ppm): −38.9 ($^1J_{SiF}$ 245.1 Hz), −40.7 ($^1J_{SiF}$ 245.1 Hz) (two diastereomers). Anal. Calc. for $C_{18}H_{22}FNOSi$: C, 68.53; H, 7.03; N, 4.44. Found: C, 67.60; H, 7.08; N, 4.63%.

4.7. (O–Si)-Chelate N-(methylchlorosilylmethyl)-N-[(S)-1-phenylethyl]acetamide (17)

Trimethylchlorosilane (1 ml) and hexamethyldisilazane (4.84 g, 0.03 mol) were added to a solution of *N*-[(*S*)-1-phenylethyl]acetamide (8.16 g, 0.05 mol) in benzene (60 ml). The solution was stirred for 10 min, then chloro(chloromethyl)methylphenylsilane [46] (10.25 g, 0.05 mol) was added. The reaction mixture was stirred for 4 h at room temperature and then refluxed for 1 h. The precipitate formed was filtered out and volatiles were removed in vacuo. The residual oil was treated with a mixture of diethyl ether–THF (3:2) to produce 13.2 g (80%) of chloride **17**, colourless crystals, m.p. 137–141 °C (benzene), $[\alpha]_D$ +10.6 (*c* 2.1, $CHCl_3$). IR spectrum ($CHCl_3$, ν, cm^{-1}): 1497, 1574 (NCO).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.90 s (3H, SiMe), 1.70 d (3H, *C–CH_3, $^3J_{HH}$ 5.8 Hz), 2.21 (3H, CH_3CO), 2.64, 3.05 dd (2H, NCH_2, $^2J_{HH}$ 16.6 Hz), 5.10 q (1H, *C–CH, $^3J_{HH}$ 5.8 Hz), 7.2–7.8 (10H, C_6H_5) (first diastereomer); 0.83 s (3H, SiMe), 1.70 d (3H, *C–CH_3, $^3J_{HH}$ 5.8 Hz), 2.21 (3H, CH_3CO), 2.76, 2.92 dd (2H, NCH_2, $^2J_{HH}$ 16.6 Hz), 5.10 q (1H, *C–CH, $^3J_{HH}$ 5.8 Hz), 7.2–7.8 (10H, C_6H_5) (second diastereomer). The signal intensities of two diastereomers were approximately in 1:1 ratio. ^{13}C NMR ($CDCl_3$, δ, ppm): 56.28 (CH); 17.73 [$CH_3C(O)$]; 17.48 s, 17.73 s (CH_3CH); br. s, 7.15 (SiMe); 33.82 s, 33.89 s (NCH_2); 173.17 (C=O); 137.75 (C_{ipso}), 129.05 (C_{ortho}), 128.45 (C_{para}), 127.35 (C_{meta}) (C–C_6H_5); 132.79 (C_{ipso}), 128.33 (C_{ortho}), 127.32 (C_{para}), 126.33 (C_{meta}) (Si–C_6H_5). ^{29}Si NMR ($CDCl_3$, δ, ppm): −53.8 s, −54.3 s (two diastereomers). Anal. Calc. for $C_{18}H_{22}ClNOSi$: C, 65.14; H, 6.68; N, 4.22. Found: C, 65.14; H, 6.81; N, 4.24%.

4.8. (O–Si)-Chelate N-methyl-N-(methylphenylfluorosilylmethyl)acetamide (18)

Triethylamine (3.28 g, 0.032 mol) was added dropwise to a solution of chloride **19** (7.5 g, 0.031 mol), methanol (4 g, 0.125 mol), and trimethylchlorosilane (0.5 ml) in toluene (20 ml). The reaction mixture was stirred for 1 h at room temperature, then 40 min at 50–60 °C. Next day the precipitate formed was filtered out and volatiles were removed in vacuo. Fractionation of the residue yielded 3.2 g (46%) of crude *N*-methyl-*N*-(methylsilylmethoxysilylmethyl)acetamide, b.p. 152–155 °C (5 mm Hg). The crude product (3.2 g, 0.01 mol) was treated with $BF_3 \cdot Et_2O$ (0.50 g, 0.0036 mol). The ether was distilled out at 100–120 °C, the residue was dried in vacuo, then dissolved in chloroform (20 ml). The solution was decanted from insolubles, the solvent was removed in vacuo, the residual oil was treated with a hot mixture of diethyl ether–THF (1:1, 20 ml), and the final solution was cooled down. The precipitate formed was re-crystallized from the same mixture of solvents to yield 1.3 g (24%) of fluoride **18**, m.p. 97–98 °C (diethyl ether–THF, 1:1). IR spectrum ($CHCl_3$, ν, cm^{-1}): 1524, 1610 (NCO). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.44 s (3H, SiMe), 2.07 s (3H, CH_3CO), 2.63, 2.64 dd (2H, NCH_2, $^2J_{HH}$ 16.7 Hz), 3.08 s (3H, NMe), 7.3–7.7 (5H, C_6H_5). ^{13}C NMR ($CDCl_3$, δ, ppm): 37.49 (NCH_3); 17.86 [$CH_3C(O)$]; d 1.48 ($^2J_{CF}$ 25.6 Hz, SiMe); d 38.96 ($^2J_{CF}$ 46.2 Hz, NCH_2); 171.99 (C=O); 140.99 (C_{ipso}); 134.53 (C_{ortho}); 128.65 (C_{para}); 127.38 (C_{meta}). ^{29}Si NMR ($CDCl_3$, δ, ppm): −40.3 d ($^1J_{SiF}$ 257.1 Hz). Anal. Calc. for $C_{11}H_{16}NFOSi$: C, 58.63; H, 7.16; N, 6.22. Found: C, 58.66; H, 7.34; N, 6.23%.

4.9. (O–Si)-Chelate N-methyl-N-(methylphenylchlorosilylmethyl)acetamide (19)

N-Methylacetamide (3.66 g, 0.05 mol), trimethylchlorosilane (1 ml), and hexamethyldisilazane (4.84 g, 0.03 mol) were dissolved in benzene (50 ml) and stirred for 5 min, then chloro(chloromethyl)methylphenylsilane (10.25 g, 0.05 mol) was added. The reaction mixture was stirred for 4 h at room temperature and then refluxed for 1 h. The precipitate formed was filtered out and volatiles were removed in vacuo. The residual yellow oil was treated with a mixture of diethyl ether–THF (3:2, 12 ml) to produce 9.4 g (77%) of chloride **19**, m.p. 116–124 °C (benzene). IR spectrum ($CHCl_3$, ν, cm^{-1}): 1517, 1610 (NCO).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.83 s (3H, SiMe), 2.12 s (3H, CH_3CO), 3.10 s (2H, NCH_2), 3.11 s (3H, NMe), 7.3–7.7 m (5H, C_6H_5). ^{13}C NMR ($CDCl_3$, δ, ppm): 43.02 (NCH_3); 17.16 [$CH_3C(O)$]; 6.63 (SiMe); 37.06 (NCH_2); 173.57 (C=O); 141.37 (C_{ipso}); 133.06 (C_{ortho}); 128.52 (C_{para}); 127.38 (C_{meta}). ^{29}Si NMR ($CDCl_3$, δ, ppm): −49.6 s. Anal. Calc. for $C_{11}H_{16}ClNOSi$: C, 54.65; H, 6.67; N, 5.79. Found: C, 53.27; H, 6.85; N, 5.86%.

4.10. (O–Si)-Chelate N-methyl-N-(methylphenylbromosilylmethyl)acetamide (20)

A crude disiloxane (1.1 g, 0.0025 mol) obtained by hydrolysis of chloride **19** in air was dissolved in benzene (10 ml), then trimethylbromosilane (1 ml, 0.0076 mol) was

added, and the reaction mixture was stirred for 2.5 h. The crystals formed were filtered from the solution and dried in vacuo to produce 0.95 g (65%) of bromide **20**, m.p. 107–110 °C. IR spectrum ($CHCl_3$, ν, cm^{-1}): 1500, 1591 (NCO).

^1H NMR ($CDCl_3$, δ, ppm): 0.85 (3H, SiMe), 2.50 (3H, CH_3CO), 3.10 s (3H, NMe), 3.4 wide (2H, NCH_2), 7.2–7.6 (5H, C_6H_5). ^{13}C NMR ($CDCl_3$, δ, ppm): 45.03 (NCH_3); 17.13 [$CH_3C(O)$]; 7.41 (SiMe); 37.30 (NCH_2); 174.58 (C=O); 139.93 (C_{ipso}); 132.88 (C_{ortho}); 128.88 (C_{para}); 127.55 (C_{meta}). ^{29}Si NMR ($CDCl_3$, δ, ppm): −42.4. Anal. Calc. for $C_{11}H_{16}BrNOSi$: C, 46.00; H, 5.97; N, 4.88. Found: C, 45.83; H, 6.00; N, 4.68%.

*4.11. 2,2-Dimethyl-3-(methylphenylchlorosilylmethyl)benzo[2H]-1,3-oxazin-4-one (**21**)*

A solution of chloro(chloromethyl)methylphenylsilane (4.1 g, 0.02 mol) in hexane (5 ml) was added dropwise to a solution of 2,2-dimethyl-3-(trimethylsilyl)benzo[2*H*]-1,3-oxazin-4-one (5 g, 0.02 mol) in hexane (15 ml). The reaction mixture was stirred for 1 h. The crystals formed were filtered from the solution and dried in vacuo to yield 6 g (86%) of compound **21**, m.p. 139–141 °C (benzene) IR spectrum ($CHCl_3$, ν, cm^{-1}): 1618, 1517 (NCO).

^1H NMR ($CDCl_3$, δ, ppm): 1.83 s (6H, $2CH_3$); 0.78 s (3H, SiMe); 2.98, 3.49 dd (2H, $^3J_{HH}$ 14.2 Hz, NCH_2); 7.79 d (1H, $^3J_{HH}$ 7.9 Hz, H-5), 7.61 t (1H, $^3J_{HH}$ 7.9 Hz, H-4), 7.16 t (1H, $^3J_{HH}$ 7.9 Hz, H-3), 7.01 d (1H, $^3J_{HH}$ 7.9 Hz, H-2), 7.24–7.43 m (5H, C_6H_5). ^{13}C NMR ($CDCl_3$ δ, ppm): 6.51 (SiMe); 35.32 (NCH_2); 24.66 (CMe_2); 173.28 (C=O); 138.33 (C_{ipso}); 133.58 (C_{ortho}); 127.87 (C_{para}); 126.51 (C_{meta}) (C_6H_5); 100.0 (C-1); 138.03 (C-2), 128.38 (C-3), 123.03 (C-4), 117.78 (C-5); 91.55 (C-6);. ^{29}Si NMR ($CDCl_3$, δ, ppm): −47.2. Anal. Calc. for $C_{18}H_{20}ClO_2NSi$: C, 62.49; H, 5.83; N, 4.048. Found: C, 62.28; H, 5.73; N, 3.80%.

Acknowledgments

The authors are grateful to Prof. Yu.E. Ovchinnikov and Dr. S.A. Pogozhikh for the X-ray data and to Dr. A.A. Korlyukov for the assistance in quantum-chemical calculations (GAUSSIAN-98).

This study was supported by RFBR (Grants 02-03-32335 and 04-03-32557) and INTAS (Grant 03-51-4164).

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