Stereochemical non-rigidity of N-(dimethylhalogenosilylmethyl)-N-(1-phenylethyl) acetamides in solutions

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Abstract

The structure and dynamic behavior of (O–Si)-chelate N-(dimethylhalogenosilyl)methyl acetamides of the type $MeC(O)N(CH(Ph)Me)CH_2SiMe_2X$, where X = F, Cl, Br with the $OSiC_3X$ coordination set, were studied by multinuclear (^1H, ^{13}C, ^{17}O, ^{29}Si) and dynamic ^1H NMR spectroscopy. Ligand permutation at silicon was detected. The observed influence of the solvent, nucleofugacity of the X substituent and the external nucleophile on the calculated values of the free energies of activation testify to the dissociative and/or associative mechanisms of the process, but including the stages in which the regular (pseudo-rotation or 'turnstile') mechanism takes place. At lower temperatures (up to $-90\,°C$) the ^1H, ^{13}C, ^{29}Si NMR spectra of N-(dimethylchlorosilyl)methyl acetamide contain the signals of two species of unequal intensity. This effect was explained by an equilibrium between monomers containing the intramolecular O → Si bond and dimers with a hexacoordinate silicon and the bridging chlorine atoms.

Keywords: Pentacoordinated organosilicon compounds; Intramolecular coordination; Intermolecular coordination; Dynamic NMR; Permutational isomerization

1. Introduction

The stereodynamic processes in pentacoordinate organosilicon compounds, in particular permutational isomerization, has recently become the object of intensive investigation. For compounds with the intramolecular N → Si coordination such processes are now well studied and their mechanisms have been established [1–4]. However, the stereochemical non-rigidity of the O → Si coordinated compounds has been less well investigated. The majority of papers report the calculation of the free energies of activation $\Delta G^{\ddagger}$ for the permutational isomerization without a detailed discussion of the possible mechanisms. For example, by dynamic ^1H and ^{19}F NMR spectroscopy the $\Delta G^{\ddagger}$ values were obtained for [α-(N-pyrrolidonyl-2)ethyl]trifluorosilane (ca. $9.5\,kcal\,mol^{-1}$) [5], substituted (aroyloxymethyl)trifluo-rosilanes (ca. $6.7–8.3\,kcal\,mol^{-1}$) [6] and the hypervalent organosilicon derivatives of acylhydrazines and polychlorosilanes (ca. $8–11\,kcal\,mol^{-1}$) [7]. In the course of a ^{19}F NMR investigation of the stereodynamic processes in organyl [β-(trifluorosilyl)ethyl]sulfoxides, the coalescence temperatures of the equatorial fluorine atoms and the axial and equatorial fluorine atoms were determined (from -90 to $-105\,°C$ and from -80 to $-95\,°C$ respectively) [8].

There is little information on the barriers to permutational isomerization in compounds with the coordinated unit $OSiC_3X$. 4-Phenyl-N-(dimethylsilylmethyl)-2-pyrrolidone chloride and trifluoroacetate ($11\,kcal\,mol^{-1}$ and $14\,kcal\,mol^{-1}$ respectively) [9], and N-methyl-N-[methylphenyl(N-methylimidazolyl)silylmethyl] acetamide) [10] represent exceptions.

We have studied the structure and dynamic behavior of N-(dimethylhalogenosilylmethyl)-N-(1-phenylethyl) acetamides in solutions by multinuclear and dynamic NMR spectroscopy.

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2. Results and discussion

2.1. ^1H, ^{13}C, ^{17}O, ^{29}Si NMR spectra

The compounds under investigation are N-(dimethyl-halogenosilylmethyl)- and N-(dimethylisopropoxysilyl-methyl)-N-(1-phenylethyl) acetamides **1–4** containing a chiral α-phenylethyl substituent at the nitrogen atom.
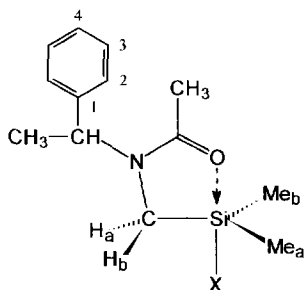
X = Br (1), Cl (2), F (3), OPr-*i* (4)

Assignment of the ^1H and ^{13}C NMR spectra was achieved by 2D NMR COSY and HETCOR ($^1J_{CH}$) methods. The spectra are largely similar to those described previously for (O–Si)-chelate N-(dimethyl-silylmethyl) amides and lactams with the $OSiC_3X$ coordination unit [11,12]. The ^1H, ^{13}C and ^{29}Si chemical shifts, given in Tables 1–3, are in agreement with the values obtained previously [11,12].

Pentacoordination of silicon in the compounds **1–3** is confirmed by greater shielding of the Si and O resonances, detected by an upfield shift in the NMR spectra of ^{29}Si ($\delta \sim -25$ to -38 ppm for bromide **1**; -31 to -42 ppm for chloride **2**; and -19 to -24 ppm for fluoride **3** in different solvents) and ^{17}O (260.8 ppm for chloride **2** in $CDCl_3$ at 50 °C). These are close to the values obtained previously for N-(dimethylhalogenosi-lylmethyl)-2-hexahydroazepinone (bromide, ^{29}Si, -27.7 ppm; chloride, -35.0 ppm; fluoride, -20.6 ppm [11]) and for N-methyl-N-(dimethylchlorosilyl-methyl)acetamide (^{29}Si, -37.6 ppm in $CDCl_3$ [12]; -37.8 ppm in CD_2Cl_2 [13]; ^{17}O, -258 ppm [12]; -259 ppm [13]). For comparison, tetracoordinate Me_3SiX (X = Br, Cl, F) nuclei resonate in the ^{29}Si NMR at $\delta\ 25 \pm 5$ ppm [14] and the amide oxygen of N,N-dimethylacetamide resonates in the ^{17}O NMR at $\delta\ 340$ ppm in C_6D_6 [15]. Also, the O → Si coordination results in a considerable downfield shift of the carbonyl carbon signal in the ^{13}C NMR (up to ca. 176 ppm) in comparison with a value for N,N-dimethylacetamide (169.36 ppm in C_6D_6 [15]).

As with N-(dimethylalkoxysilylmethyl) lactams [16], the intramolecular interaction O → Si in isopropoxide **4**

is practically absent (^{29}Si, ca. 5–6 ppm; ^{17}O, 350.2 ppm, $CDCl_3$, 50 °C, Table 3). By comparison, the ^{29}Si shift of the model compound $(CH_2Cl)(CH_3)_2SiOCH_3$ with the tetracoordinate Si is 12.9 ppm [17].

The least upfield shift in the ^{29}Si NMR spectra of N-(dimethylhalogenosilylmethyl) acetamides **1–3** in different solvents shows that fluoride **3** has the weakest O → Si coordination (Table 3). In a similar manner to the previously studied N-(dimethylchlorosilyl)methyl derivatives of amides and lactams [11,13], a decrease of temperature leads to an upfield shift in the ^{29}Si NMR spectra of halogenides **2** and **3**. In contrast to these compounds, and similar to N-(dimethylbromosi-lylmethyl) lactams [11], a greater (up to 8 ppm) downfield shift of the ^{29}Si resonance was observed for bromide **1** in some solvents at low temperatures (Table 3). These effects conform to the model of hypervalence, which assumes a parallel correlation between the nucle-ofugacity of the electronegative substituent X and the coordination D → Si in the hypervalent fragment D–Si–X (where D is the electron-releasing atom, such as N, O, S, etc.). The Si–Hal bond in halogenides **2** and **3** is 'covalent' and the O–Si bond is 'coordination', while in bromide **1** the O–Si bond has a 'covalent' character and the Si–Hal bond is 'coordination' [11,18].

At the same time, the observed signal shift in the ^{29}Si NMR spectra can be assigned to the partial dissociation of bromide **1**, as is evident from the electroconductivity of N-(dimethylbromosilylmethyl) lactams [11], and to a shift of equilibrium in the direction of the formation of cation $[LSi^{IV}Me_2]^+$ with the tetracoordinate silicon atom at low temperatures (where L is a bidentate chelate ligand, Eq. (2), see below).

A plot of the ^{13}C and ^{29}Si chemical shifts for compound **2** in different solvents (Fig. 1) shows a poor correlation between their values. This is not surprising, since the model discussed regards the chemical shift of the ^{29}Si resonance as a result of the processes in both components of the hypervalent fragment. For example, the downfield shift of carbonyl carbon signal (by 2–3 ppm) observed in high-donor solvents (acetonitrile-d_3 and methanol-d_4) testifies to the strengthening of the O → Si bond as a result of the Si–Hal bond polarization (ionization) (Table 2). The downfield shift of the corresponding ^{29}Si resonance reveals the decreasing of the coordination contribution into the hypervalent fragment (Table 3). Another explanation of this effect may be an interaction between molecules of the compounds studied and the solvent.

However, for the solvents with a comparable donor ability a partial (solid line in Fig. 1) but reasonable correlation can be established. It should be noted that for bromide **1**, with a more ionic Si–Hal bond than in chloride **2**, a correlation between the ^{13}C and ^{29}Si chemical shifts was not detected. In toluene-d_8 the influence of solvation effects is practically absent, and

the ^{13}C and ^{29}Si chemical shifts for the compounds **1–4** can be approximated by a single line (Fig. 2).

At room temperature in toluene-d_8 the ^{1}H resonances of Si(Me)$_2$ group in fluoride **3** were observed as a multiplet peak due to the coupling with the fluorine nucleus ($^3J_{HF}$ 7.4 Hz). The replacement of toluene by more polar solvents (chloroform, methanol) leads to a broadening of the signals and to the disappearance of a coupling constant which may be caused by known intermolecular exchange of fluoride ions [19]. Decreasing the temperature of the chloroform-d solution to −60 °C reduces the rate of this exchange, and the SiMe$_2$ group resonance appears in the ^{1}H NMR spectra

as a doublet of doublets ($^3J_{HF}$ 7.9 Hz). The coupling interaction between the fluorine and silicon atoms of fluoride **3** was also detected in the ^{29}Si NMR spectra. As shown in Table 3, the decrease of the coupling constant $^1J_{SiF}$ in C$_6$D$_5$CD$_3$, CDCl$_3$ and CD$_3$OD solutions from 261 to 215 Hz proceeds in accordance with the increase of the solvent polarity.

2.2. Intermolecular coordination

In the case of chloride **2**, reducing the temperature from −70 °C to −90 °C leads to a broadening of the ^{1}H, ^{13}C and ^{29}Si NMR signals and results in two sets of

Table 1

^{1}H NMR chemical shifts (spin-coupling constants in hertz) of compounds 1–4 in different solvents

Compound	Solvent	δ (ppm)							
		Si(Me)$_2$	NCH$_2$	CH$_3$	CH_3CH	CH	H^2	H^3	H^4
1	C$_6$D$_5$CD$_3$ [a]	br. s, 0.88	dqu, 2.93, 2.69 (15.9, 1.0)	t, 1.57 (1.0)	d, 1.17 (6.5)	qu, 4.41 (6.5)		7.01–7.25	
	CDCl$_3$	br. s, 0.65	dqu, 3.06, 2.74 (16.6, 1.0)	t, 2.33 (1.0)	d, 1.70 (7.1)	qu, 5.11 (7.1)	d, 7.21 (7.8)	t, 7.40 (7.8)	t, 7.35 (7.8)
	CD$_3$CN	br. s, 0.51	dqu, 2.91, 2.40 (16.2, 1.0)	t, 2.34 (1.0)	d, 1.64 (7.0)	qu, 5.27 (7.0)	d, 7.35 (7.5)	t, 7.43 (7.5)	t, 7.37 (7.5)
	CD$_2$Cl$_2$	s, 0.71 s, 0.64	dqu, 2.97, 2.67 (16.4, 1.0)	t, 2.32 (1.0)	d, 1.68 (7.1)	qu, 5.13 (7.1)	d, 7.25 (7.4)	t, 7.42 (7.4)	t, 7.37 (7.4)
	(CD$_3$)$_2$C(O)	br. s, 0.58	dqu, 2.92, 2.45 (16.6, 0.9)	t, 2.47 (0.9)	d, 1.73 (6.9)	qu, 5.43 (6.9)	7.36–7.46		
	CD$_3$OD	s, 0.30	dqu, 2.70, 2.19 (16.2, 1.0)	t, 2.42 (1.0)	d, 1.71 (6.9)	qu, 5.39 (6.9)	d, 7.38 (6.9)	t, 7.44 (7.3)	t, 7.37 (7.3)
2	C$_6$D$_5$CD$_3$	s, 0.94 s, 0.83	dqu, 2.66, 2.43 (16.2, 1.0)	t, 1.40 (1.0)	d, 0.98 (6.9)	qu, 4.16 (6.9)	6.98–7.11		
	CDCl$_3$	s, 0.57	dqu, 2.75, 2.47 (16.2, 1.0)	t, 2.26 (1.0)	d, 1.68 (6.9)	qu, 5.05 (6.9)	d, 7.20 (7.6)	t, 7.40 (7.6)	t, 7.35 (7.6)
	CD$_3$CN	s, 0.47	dqu, 2.66, 2.14 (16.2, 1.0)	t, 2.25 (1.0)	d, 1.63 (6.9)	qu, 5.20 (6.9)	d, 7.33 (7.6)	t, 7.43 (7.6)	t, 7.36 (7.6)
	CD$_2$Cl$_2$	s, 0.46	dqu, 2.66, 2.32 (16.2, 1.0)	t, 2.21 (1.0)	d, 1.63 (6.9)	qu, 5.03 (6.9)	d, 7.20 (7.5)	t, 7.38 (7.5)	t, 7.31 (7.5)
	(CD$_3$)$_2$C(O)	s, 0.46	dqu, 2.62, 2.18 (16.2, 1.0)	t, 2.36 (1.0)	d, 1.68 (6.9)	qu, 5.33 (6.9)	d, 7.39 (7.6)	t, 7.41 (7.6)	t, 7.33 (7.6)
	CD$_3$OD	s, 0.29	dqu, 2.69, 2.19 (16.2, 1.0)	t, 2.41 (1.0)	d, 1.71 (6.9)	qu, 5.38 (6.9)	d, 7.38 (7.6)	t, 7.44 (7.6)	t, 7.36 (7.6)
3 [b]	C$_6$D$_5$CD$_3$	s, 0.62 s, 0.52	dd, 2.23, 2.01 (15.4)	s, 1.52	d, 1.02 (7.0)	qu, 4.27 (7.0)	6.95–7.10		
	CDCl$_3$	s, 0.27 s, 0.20	dd, 2.32, 2.02 (15.5)	s, 2.22	d, 1.64 (6.9)	qu, 5.05 (6.9)	d, 7.20 (7.5)	t, 7.39 (7.5)	t, 7.32 (7.5)
	CD$_3$OD	s, 0.17 s, 0.07	dqu, 2.30, 1.88 (15.6, 0.8)	s, 2.24	d, 1.64 (6.9)	qu, 5.23 (6.9)	d, 7.30 (7.5)	t, 7.40 (7.5)	t, 7.32 (7.5)
4 [c]	C$_6$D$_5$CD$_3$	s, 0.42 s, 0.30	s, 2.25	s, 1.81	d, 1.20 (6.8)	qu, 4.56 (6.8)	d, 6.97 (7.5)	t, 7.16 (7.5)	t, 7.03 (7.5)
	CDCl$_3$	s, 0.20 s, 0.09	s, 2.24	s, 2.23	d, 1.61 (6.9)	qu, 5.09 (6.9)		7.24–7.39	
	CD$_3$OD	s, 0.16 s, 0.03	dd, 2.33, 2.16 (15.0)	s, 2.26	d, 1.62 (6.9)	qu, 5.24 (6.9)		7.24–7.41	

[a] Chemical shifts and spin-coupling constants at −75 °C: s, 1.15, 1.01 ppm (SiMe$_2$, 6-H); dqu, 2.66, 2.43 ppm (NCH$_2$, 2-H, 16.2, 1.0 Hz); t, 1.14 ppm (CH$_3$, 3-H, 1.0 Hz); d, 0.79 ppm (CH_3CH−, 3-H, 6.9 Hz); qu, 3.77 ppm (CH, 1-H, 6.9 Hz); 6.93–7.11 ppm (C$_6$H$_5$−, 5-H).

[b] Spin-coupling constant ($^3J_{HF}$, Hz): 7.4 (C$_6$D$_5$CD$_3$); 7.9 (CDCl$_3$, −60 °C).

[c] Chemical shifts and spin-coupling constants of OPr-i group: d, 1.05 ppm (CH$_3$, 3-H, 5.9 Hz); d, 1.01 ppm (CH$_3$, 3-H, 5.9 Hz); sept. 3.92 ppm (CH, 1-H, 6.1 Hz) (C$_6$D$_5$CD$_3$); d, 1.03 ppm (CH$_3$, 3-H, 6.0 Hz); d, 0.99 ppm (CH$_3$, 3-H, 6.0 Hz); sept. 3.74 ppm (CH, 1-H, 6.1 Hz) (CDCl$_3$); d, 1.15 ppm ((CH$_3$)$_2$, 6-H, 6.1 Hz); sept. 3.70 ppm (CH, 1-H, 6.1 Hz) (CD$_3$OD).

Table 2
^{13}C NMR chemical shifts of compounds 1–4 in different solvents

Compound	Solvent	δ (ppm)									
		Si(Me)$_2$	NCH$_2$	CH$_3$C(O)	C=O	CH$_3$	CH	C^1	C^2	C^3	C^4
1	C$_6$D$_5$CD$_3$	8.11	37.64	17.87	173.73	17.49	56.85	139.09	131.20	126.47	129.07
	CDCl$_3$	5.89	36.25	18.24	174.23	17.87	57.24	137.67	129.37	126.28	128.73
	CD$_3$CN	5.60	36.22	18.17	176.10	17.47	57.88	138.90	129.92	128.03	129.36
	CD$_2$Cl$_2$	7.57, 7.53	37.30	18.10	174.70	17.98	57.26	138.03	129.53	126.83	128.92
	(CD$_3$)$_2$C(O)	8.12	37.17	17.86	175.62	17.37	57.21	139.40	129.79	127.81	129.08
	CD$_3$OD ^{a}	0.73	31.89	17.85	176.17	17.18	58.15	139.48	130.16	128.08	129.55
2	C$_6$D$_5$CD$_3$	7.96	35.64	17.36	172.80	17.35	56.02	139.10	129.13	126.26	128.24
	CDCl$_3$	7.01	35.09	18.04	173.03	17.83	56.40	138.47	129.26	126.28	128.48
	CD$_3$CN	7.68	35.73	18.20	174.95	17.33	56.99	139.79	129.88	127.91	129.13
	CD$_2$Cl$_2$	6.56	35.21	18.37	173.55	17.88	56.78	138.83	129.43	126.84	128.65
	(CD$_3$)$_2$C(O)	7.87	35.41	17.94	174.63	17.30	56.71	139.81	129.69	127.69	128.87
	CD$_3$OD ^{a}	0.74	31.80	17.81	176.09	17.18	58.08	139.50	130.16	128.08	129.55
3 ^{b}	C$_6$D$_5$CD$_3$	2.51, 2.23	31.06	18.29	171.33	17.22	55.78	139.96	129.43	126.42	128.89
	CDCl$_3$	1.57	30.37	18.90	171.45	17.62	55.99	139.21	128.98	126.33	128.01
	CD$_3$OD	1.89, 1.71	30.88	18.60	173.78	17.51	57.25	140.83	129.91	127.79	128.95
4 ^{c}	C$_6$D$_5$CD$_3$	2.22, −0.26	33.32	19.03	169.09	17.30	56.20	141.11	128.75	126.99	127.53
	CDCl$_3$	1.94, −1.00	33.51	21.16	169.74	17.53	56.37	140.36	128.67	126.72	127.56
	CD$_3$OD	1.54, −1.11	36.08	20.54	172.52	17.43	57.77	141.24	129.75	128.12	128.80

^{a} The upfield shift of SiMe$_3$ signals (by 3 ppm) was also observed in CD$_3$CN solution in the presence of N,N-dimethylacetamide.
^{b} Spin-coupling constant ($^2J_{CF}$, Hz): 47.4 (C$_6$D$_5$CD$_3$); 44.4 (CDCl$_3$, −60 °C); 31.4 (CD$_3$OD).
^{c} Chemical shifts of OPr-i group: 64.17 ppm (CH), 26.23 ppm ((CH$_3$)$_2$) (C$_6$D$_5$CD$_3$); 64.20 ppm (CH), 25.81 ppm ((CH$_3$)$_2$ (CDCl$_3$); 64.69 ppm (CH); 25.27 ppm ((CH$_3$)$_2$) (CD$_3$OD).

Table 3
^{29}Si NMR chemical shifts of compounds 1–4 in different solvents at variable temperatures

Compound	T (°C)	δ (ppm)					
		C$_6$D$_5$CD$_3$	CDCl$_3$	CD$_3$CN	CD$_2$Cl$_2$	(CD$_3$)$_2$C(O)	CD$_3$OD
1	20	−38.6	−28.3	−25.1	−29.0	−36.4	−32.8
	−40			−34.1			
	−60	−27.3	−32.8		−26.3		
	−90	−26.5			−20.4		−48.2
+ LiBr	−40						
2	20	−37.7	−38.1	−40.5	−39.4	−42.0	−31.6
	−40			−44.5			
	−60		−47.4	−42.8			
	−90	−47.4			−39.8 ^{a}	−44.2 ^{a}	−39.2
					−44.6 ^{b,c}	−46.7 ^{b}	
+ LiCl	−40			−46.4			−33.3
3	20	−20.9	−19.3				−23.7
		$^1J_{SiF}$ 261	$^1J_{SiF}$ 256				$^1J_{SiF}$ 215
	−40		−24.7				
			$^1J_{SiF}$ 256				
+ KF	20						−31.4
							$^1J_{SiF}$ 249
4	20	4.7	7.9				5.6

^{a} The chemical shift of Si$^V_{intra}$; ^{b} the chemical shift of Si$^{VI}_n$; ^{c} the Si$^V_{intra}$ to Si$^{VI}_n$ ratios are about 72:28 at −70 °C and 65:35 at −90 °C.
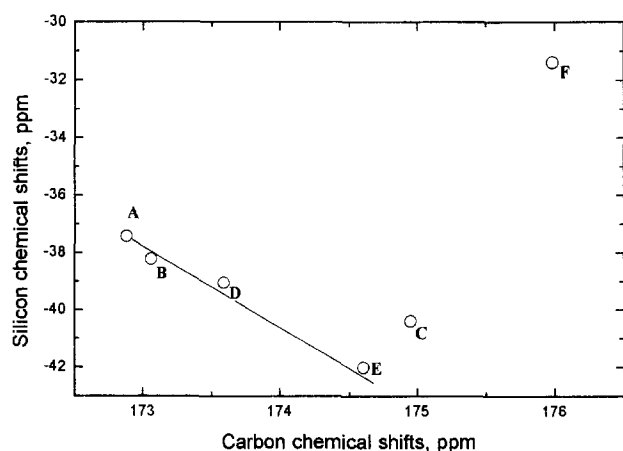
Fig. 1. Extrapolation of the ^{13}C chemical shifts of the carbonyl carbon of compound **2** in $C_6D_5CD_3$ (A), $CDCl_3$ (B), CD_3CN (C), CD_2Cl_2 (D), $(CD_3)_2CO$ (E), CD_3OD (F) against the ^{29}Si chemical shifts.
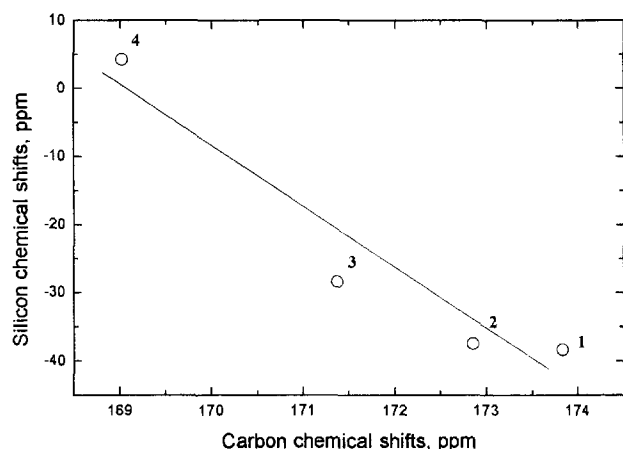

Fig. 2. Extrapolation of the ^{13}C chemical shifts of the carbonyl carbon of compounds **1–4** in $C_6D_5CD_3$ against the ^{29}Si chemical shifts.

signals of unequal intensity (Table 3). In both cases, the upfield ^{29}Si shifts (−36 ppm or more) are consistent with the hypervalent species in solution. As with *N*-methyl- and *N*-phenyl-*N*-(dimethylchlorosilylmethyl) acetamides [13], the contributions of both species depend on the concentration and temperature, which testify to the intermolecular nature of the observed process (Table 3). Thus, for the ca. 0.5 M solution of compound **2** in CD_2Cl_2 at −90 °C the ^{29}Si NMR data show that

the signal intensities are 65 ± 4 mol% and 35 ± 4 mol%, and independent of the procedure for the solution preparation (dilution or concentration). Chemical shifts of the signals in the ^1H and ^{13}C NMR of both species are almost identical.

At present we suppose that the dimers with the intramolecular O → Si coordination containing a hexacoordinate silicon and the bridged chlorine atoms predominate over the other possible oligomers (Scheme 1).

The signals of the $SiMe_2$ groups in the ^1H NMR spectra and signals of C=O groups in the ^{13}C NMR spectra of hexacoordinated dimer B are shifted downfield by ca. 0.2 ppm and ca. 0.4 ppm respectively.

It should be noted that an analogous hexacoordinate intermediate (transition state) was earlier preferred by van Koten et al. [20] in explaining slow epimerization of the $(S)_C(S)_{Sn}$ {2[[1-(dimethylamino)ethyl]-phenyl]methylphenyltin bromide diastereomer, which involves inversion of configuration at the tin atom.

The fact that the methyl groups at the silicon are diastereotopic under the experimental conditions suggests that such exchange proceeds with exclusive retention of configuration (at least on the NMR time scale). It seems likely that at room temperature and higher the equilibrium between two species is largely shifted to the monomer.

Two species for *N*-(dimethylchlorosilylmethyl) acetanilides were also observed by Yoder et al. most recently [12]. The ^1H NMR spectra of most of the acetanelides in $CDCl_3$ contained a broad peak for the $SiMe_2$ protons. At lower temperatures (up to −30 °C) this peak separated into two sharp peaks of unequal intensity. This phenomenon was attributed by the authors to rotamers due to hindered rotation about the carbon–nitrogen bond. It should be noted that no similar dynamic processes were observed for compounds **1–4** in the temperature range from 100 °C to −40 °C.

2.3. Permutation isomerization

Owing to the presence of a chiral center in the substituent at the nitrogen atom in the compounds **1–4**, the protons of the NCH_2 group, H_a and H_b, and the $SiMe_2$ group, Me_a and Me_b, are diastereotopic. As a result, in the ^1H NMR spectra, at room temperature and
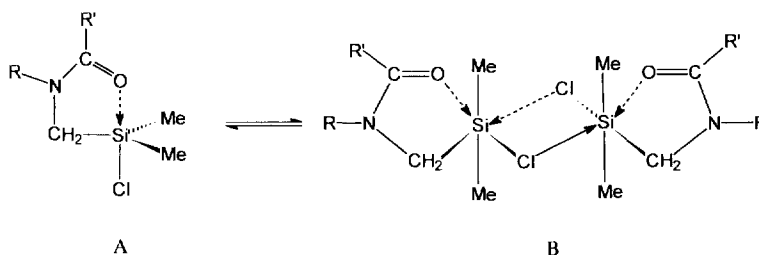
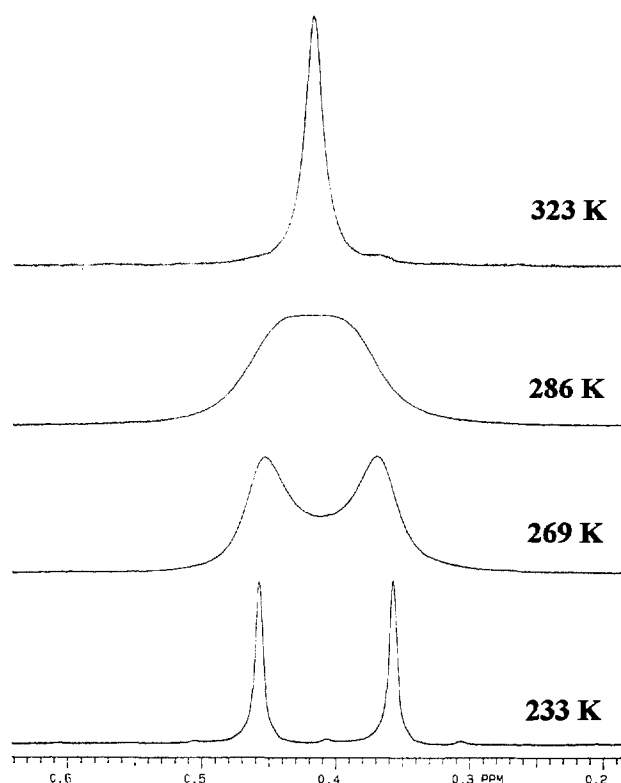Scheme 1. Mechanism for intermolecular interactions in solutions at low temperature.

323 K

286 K

269 K

233 K

Fig. 3. ^{1}H DNMR (400 MHz, $(CD_3)_2C(O)$) spectra of compound **1** for Si(Me)$_2$ resonance.

lower, the NCH_2 protons appear as the AB pattern ($^2J_{HH} \sim 16\,Hz$) and the $SiMe_2$ protons appear as an equal doublet.

At higher temperatures the NCH_2 protons remain chemically unequal, while the doublet of $SiMe_2$ protons in the case of halogenides **1** and **2** undergoes broadening and coalescence of the doublet components, resulting in a frequency-averaged singlet that is characteristic of permutational processes. Reducing the temperature returns to the primary spectrum (Fig. 3).

The free energies of activation $\Delta G^{\ddagger}$ for halogenides **1** and **2** (Table 4) were calculated by means of dynamic ^{1}H NMR from the coalescence temperatures of the equal doublets of the $SiMe_2$ group.

In most cases the values of $\Delta G^{\ddagger}$ are greater for chloride **2** than for bromide **1**, especially in less polar solvents (Table 4). For example, in toluene-d_8 solution the free energy of activation is more than $18.6\,kcal\,mol^{-1}$ for chloride **2** and $15.2\,kcal\,mol^{-1}$ for bromide **1** (Table 4). In more polar and more electron-odonor solvents ($CDCl_3$, CD_2Cl_2, $(CD_3)_2CO$, CD_3CN and CD_3OD), these values decrease by ca. 2–3 kcal mol^{-1}; this leads to a downfield shift of the ^{29}Si resonance by ca. 20 ppm (Table 3).

The decrease in the barrier to permutational isomerization in the presence of acetonitrile-d_3 was also observed for the solution of chloride **2** in toluene-d_8 (Table 4).

For fluoride **3** the coalescence of signals in the ^{1}H NMR spectra was not observed in the range 20–90 °C ($\Delta G^{\ddagger} > 24\,kcal\,mol^{-1}$). Nevertheless, a ligand exchange for this compound was detected by a cross-peak between the $Si(Me)_2$ signals in the 2D NMR NOESY spectrum (CD_3OD, 60 °C). The analogous cross-peak in less polar toluene-d_8 was not observed, even at 90 °C.

In the case of the isopropoxide **4**, the signals of the $SiMe_2$ group appear in the ^{1}H NMR spectrum as an equal doublet. Unlike the halogenides, dynamic exchange of methyl groups at the silicon was not observed right up to 100 °C. In the NMR spectra the signals of the second rotamer were absent in the temperature range studied. It seems likely that the stabilization of the observed rotamer is due to the weakest O–Si intramolecular interaction which still persists in isopropoxide **4**.

Hence, in the series of halogenides **1–3**, the barrier to permutational isomerization decreases from fluoride to bromide in accordance with an increase in the O–Si bond strength (and a corresponding decrease in the Si–Hal bond strength) [11], so the nucleofugacity of halogen appears to be the main factor affecting the process.

An analogous dependence between the barrier to permutation isomerization and the halogen nature has been established by Corriu and co-workers [3,4] in the monofunctional 8-dimethylamino-1-silylnaphthalene compounds (**5**) with the N → Si coordination ($\Delta G^{\ddagger} =$

Table 4
Activation parameters for permutation isomerization of compounds **1** and **2**

Compound	Solvent	T_c (°C)	$\Delta G^{\ddagger} \pm 0.1$ (kcal mol^{-1})	Compound	T_c (°C)	$\Delta G^{\ddagger} \pm 0.1$ (kcal mol^{-1})
1	$C_6D_5CD_3$	34	15.2	**2**	> 100	> 18.6 [a]
	$CDCl_3$	21	14.6		24	14.9
	CD_3CN	13	14.2		17	14.4
+ LiBr	CD_3CN	−4	13.4	+ LiCl	9	13.9
	CD_2Cl_2	10	14.1		23	14.7
	$(CD_3)_2C(O)$	13	14.2		> 50	> 16.2
	CD_3OD	−28	11.9		−27	12.0

[a] At stoichiometric ratio of toluene-d_8 and acetonitrile-d_3 the $\Delta G^{\ddagger}$ value is $17.2\,kcal\,mol^{-1}$.

23 kcal mol^{-1}, 20 kcal mol^{-1} and greater than 19 kcal mol^{-1} for Hal = F, Cl and Br respectively).

(5)
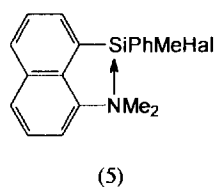
The authors suppose that the high $\Delta G^{\ddagger}$ values observed result from an irregular mechanism including the N → Si bond rupture accompanied by rotation and inversion at nitrogen.

In connection with the solvent effect observed for the barrier to permutational isomerization, which in the case of electronodonor solvents can be related to their action as the external nucleophiles, the influence of the more effective nucleophiles on the $\Delta G^{\ddagger}$ value was then studied.

It was found that the presence of external nucleophiles (KF, LiCl and LiBr) in equimolar quantities decreases the $\Delta G^{\ddagger}$ value of the process (Table 4). In CD$_3$CN, the barriers to permutational isomerization in the compounds 1 and 2, in the presence of LiBr and LiCl respectively, are 13.4 kcal mol^{-1} and 13.9 kcal mol^{-1} (14.2 kcal mol^{-1} and 14.4 kcal mol^{-1} respectively without LiX). When LiX was added to a solution of halogenides 1 and 2 the ^{29}Si NMR resonance

broadened so much that it almost disappeared into the base-line. In the ^{29}Si NMR spectra of these compounds at $-40\,°C$ the presence of an external nucleophile leads to an upfield shift (by 6–7 ppm) compared with the CD$_3$CN solution (Table 3). A similar effect was observed in the case of bis-halo *N,N*-bisdimethylsilyl-methylacetamides for the ^{29}Si NMR signal from pentacoordinate silicon in the presence of *N*-methylimidazole (NMI) [21].

An even greater decrease of the $\Delta G^{\ddagger}$ value was observed for the CD$_3$OD solution of fluoride 3 in the presence of KF. In this case the coalescence of the ^{1}H NMR resonances of the SiMe$_2$ group was detected at $16\,°C$ ($\Delta G^{\ddagger} = 14.3$ kcal mol^{-1}). The ^{29}Si NMR spectrum shows an upfield shift with δ -31.4 ppm (-23.7 ppm without KF).

2.4. The nature of fluxional processes

Certain of the stereochemical processes observed for halogenides 1–3 were accompanied by the inversion of configuration at the pentacoordinate silicon center. This sets them apart from the wide range of the N → Si chelated compounds, in particular Me$_2$NCH(Me)C$_6$H$_4$SiXYZ, which undergo a non-dissociative ligand permutation as well as processes associated with rupture of the chelate ring and the nitrogen inversion, but without the silicon inversion [4]. The dependence of the barriers to permutational isomerization from the nucleofugacity of halogen, solvent nature and the presence of an external nucleophile suggest that the associative and/or dissociative mechanism of the
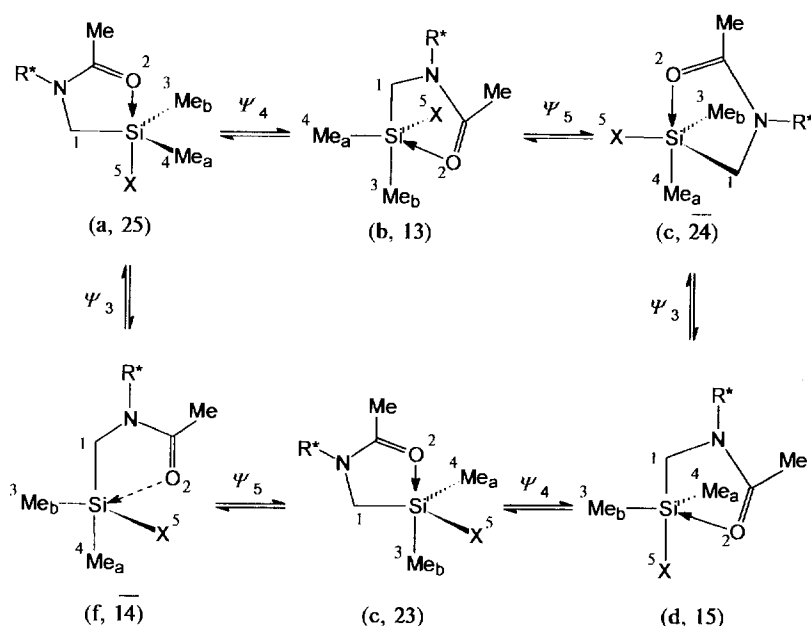
Scheme 2. Regular mechanism for site exchange of acyclic ligands by pseudo-rotation in a pentacoordinate chelate without ring-opening and inversion at silicon. (Ψ indicates Berry pseudo-rotation or similar process, R$^* = $ CH(Ph)Me).

process is more preferable than the regular mechanism for compounds **1–3**.

It should be noted that the compounds studied are not favorable for the regular processes because of the presence of the bidentate chelated ligand and only one monodentate electronegative ligand at the central coordination set. The latter distinguishes the compounds **1–3** from those discussed above [α-(N-pyrrolidonyl-2)ethyl]silane [5] and (aroyloxymethyl)silanes [6] trifluorides and also organyl [β-(trifluorosilyl)ethyl]sulfoxides [8] containing three monodentate electronegative fluorine atoms for which, without detailed discussion, the regular mechanism was suggested as an alternative.

Indeed, the regular process including an inversion at silicon (Berry pseudo-rotation or 'turnstile' mechanism) for halogenides **1** and **2** with the sufficiently low energies of activation $(14-15\,\text{kcal}\,\text{mol}^{-1})$ seems to be unlikely, since it must involve an intermediate formation of topomers with a diequatorial chelate ligand; this requires an increase of the O–Si–C angle in five-membered ring from ca. 90° to ca. 120°.

Thus, the monodentate substituents can be the only 'pivot' ligands, and the process does not lead to an equivalence for the methyl groups at silicon (Scheme 2, **a ⇌ b**, etc.).

It should be mentioned that comparatively high barriers to permutational isomerization in bicyclic pentacoor-

dinate silicates (**6**) (Y = CN, F, PhO, $\Delta G^\ddagger = 17-22\,\text{kcal}\,\text{mol}^{-1}$; Y = n-Bu, Ar, $\Delta G^\ddagger = 25-29\,\text{kcal}\,\text{mol}^{-1}$) [22], as well as energies for inversion in initial spirosilane (**7**) [23] caused by external nucleophiles (MeOH, pyridine, benzaldehyde; $\Delta G^\ddagger = 10-12\,\text{kcal}\,\text{mol}^{-1}$), were observed. These data were regarded by authors (see also review in Ref. [4]) as an indication of the regular mechanism; however, the dissociative and/or associative mechanism of the inversion was not completely excluded.
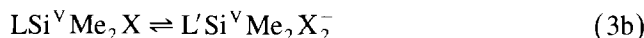

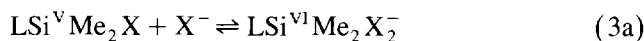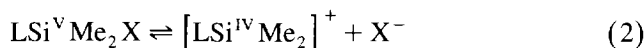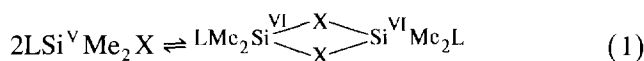(6)   (7)
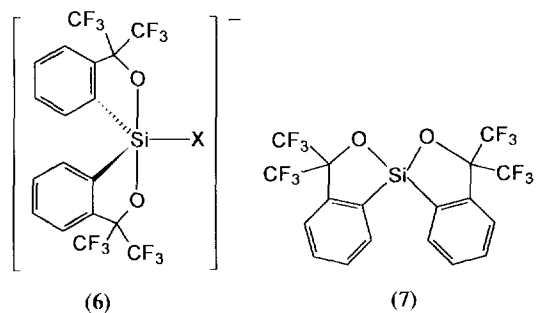
The possible equilibria involving the halogenides **1–3**, the products of their ionization, and the external
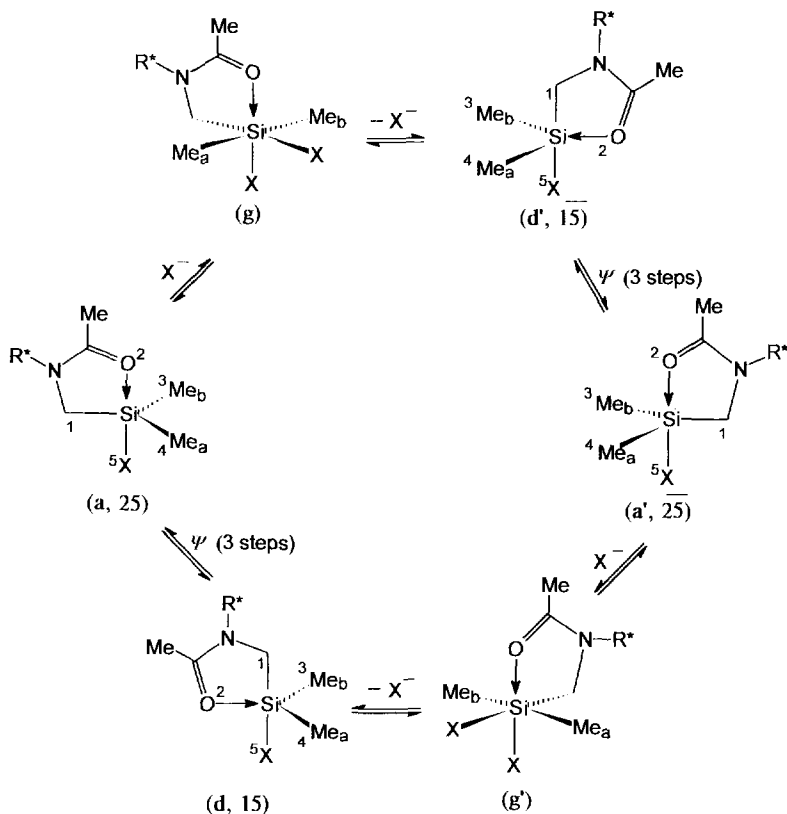
Scheme 3. Associative mechanism for Si-methyl groups equivalence without rupture of O → Si bond.

halogenide ions added are summarized in Eqs. (1), (2), (3a) and (3b)).

$$2LSi^V Me_2 X \rightleftharpoons LMe_2 Si \overset{VI}{\underset{X}{\overset{X}{<}}} Si^{VI} Me_2 L \qquad (1)$$

$$LSi^V Me_2 X \rightleftharpoons \left[LSi^{IV} Me_2\right]^+ + X^- \qquad (2)$$

$$LSi^V Me_2 X + X^- \rightleftharpoons LSi^{VI} Me_2 X_2^- \qquad (3a)$$

$$LSi^V Me_2 X \rightleftharpoons L'Si^V Me_2 X_2^- \qquad (3b)$$

(L = bidentate chelated ligand, L' = monodentate ligand).

The exchange process corresponding to Eq. (1) with the participation of the dimeric species including a hexacoordinate silicon was previously discussed in connection with the detection of two species for chloride 2 at lower temperatures (see Scheme 1). It seems likely that this process is not responsible for the exchange of the diastereotopic methyl groups at the silicon on the NMR time scale.

A considerable difference between the barriers for halogenides 1 and 2 (ca. 12–15 kcal mol^{-1}) and for fluoride 3 ($\Delta G^\ddagger > 24$ kcal mol^{-1}) in the absence of the external nucleophile in most solvents, and also a $\Delta G^\ddagger > 18.6$ kcal mol^{-1}) for chloride 2 in toluene-d_8, is indicative of the possibility of a dissociative mechanism for permutational isomerization shown in Eq. (2) (and in more detail in Scheme 3).

This mechanism can be proposed for both bromide 1 and chloride 2 in sufficiently polar solvents in the case of the absence of the external nucleophiles. Taking into account the high electroconductivity of Si-substituted N-(dimethylsilylmethyl) lactams with good leaving Si-substituents in solutions [11,24], the first stage of the process may be a dissociation leading to the ionic intermediate (j) with a tetracoordinate silicon. The inversion of configuration at silicon is to be included in the attack of this intermediate by halogenide ion from the side of the oxygen atom [25] with the formation of the intermediate (d') and consequent three-stage pseudo-rotation. Notice that the attack discussed may proceed with a slower rate compared with the rate of attack from the back of the oxygen atom. However, only in this case can the inversion at the silicon and the equivalence of the diastereotopic Si-methyl groups be observed.

It should be noted once again, that the pathway leading to inversion must be a minor one compared with the route with retention of configuration at silicon. However, the possibility of such a pathway is based on the fact that bimolecular nucleophilic substitution at tetrahedral silicon can take place with either inversion or retention of configuration, depending on the nature of the nucleophile and the nucleofuge [25]. For inversion

of configuration, a trigonal bipyramidal intermediate is usually assumed in which the nucleophile attacks at the tetrahedral face opposite the nucleofuge, whereas for retention of configuration it is assumed that the nucleophile attacks at a face of the tetrahedron that contains the nucleofuge [26]. In the case of the proposed dissociative mechanism (Scheme 3), on the contrary, the nucleophile attack at the face of the tetrahedral ionic intermediate that contains the oxygen, and from the side opposite the CH_2 group, provides only a means for the inversion of configuration at trigonal bipyramidal pentacoordinate silicon.

Notice that dissociative exchange of ligands in siliconate (8) proceeds, however, without the racemization at silicon, and it includes the dynamic equilibrium between the tetra- and pentacoordinate silicon species which leads to fast intermolecular exchange of the fluorine atoms [27].

(8)   (9)
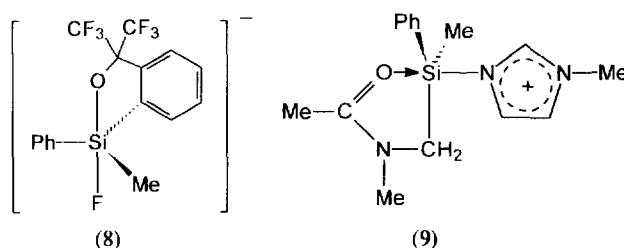
It is worth noting that the experimental data about the stereochemistry of nucleophilic substitution at pentacoordinate silicon are scarce. In particular, the retention of configuration was detected for the reactions of the Si–Cl bond [3]. The NMR investigation of dynamics and stereochemistry of degenerate exchange between the pentacoordinate silicon species (9) and NMI shows the contribution of processes with both inversion and retention of configuration at silicon into the total rate of NMI exchange [10].

The dissociative mechanism discussed above is somewhat similar to one of concurrent mechanisms proposed by Bassindale et al. on the basis of kinetic investigation of nucleophile-assisted racemization of halosilanes PhMeCHSiMe$_2$X [26]. The latter includes a nucleophile attack on a silane-nucleophile complex [PhMeCHSiMe$_2$Nu]$^+$ formed by displacement of the halide by the nucleophile, with inversion of configuration. In particular, the presence of DMF as the external nucleophile in 3 M solution of halogenosilane in benzene-d_6 leads to the fast racemization accompanied by the inversion at silicon in equimolar halogenosilane to nucleophile ratio for chloride (X = Cl) and 1:0.07 ratio for bromide (X = Br). For the compounds studied, the NC(O) fragment of the bidentate chelate ligand appears
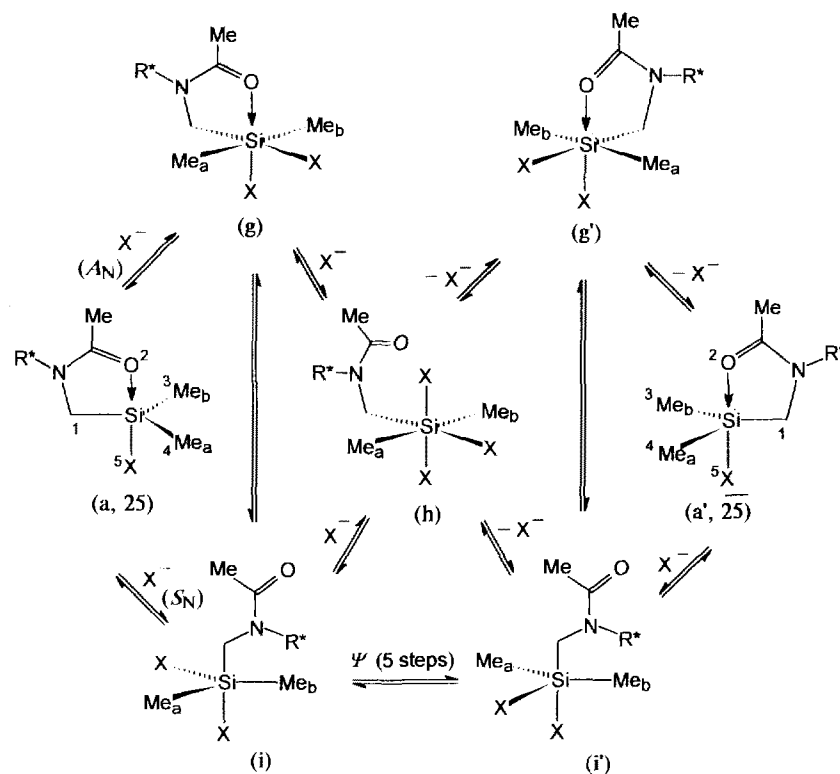
Scheme 4. Associative mechanisms for Si-methyl groups equivalence with rupture of O → Si bond.
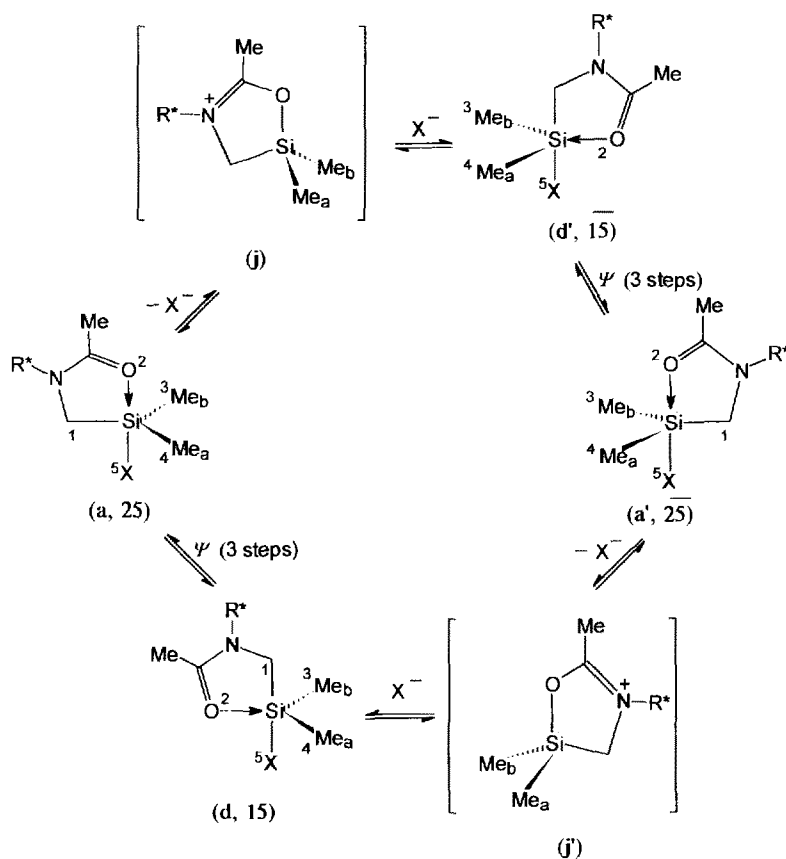
Scheme 5. Dissociative mechanisms for Si-methyl groups equivalence.

analogous to the neutral nucleophile while the halogenide ion performs the nucleophilic attack at the silicon.

The decrease in the permutational isomerization barrier for halogenides **1** and **2** in the presence of the corresponding lithium salts, as well as the greater influence of KF on the process in the case of fluoride **3** and also the exchange of the *Si*-methyl substituents in 2D NMR NOESY spectra in the CD_3OD (the less active external nucleophile) solution of the latter compound, is indicative of the possibility of the associative mechanism including the extra-coordinate silicon intermediates (Eqs. (3a) and (3b)).

It should be noted that, in principle, the addition of the inorganic salts into the solutions of compounds under study could have other effects, namely to drive the equilibrium in Eq. (2) to the left and the equilibria in Eqs. (3a) and (3b) to the right, with concomitant increases in the ^{29}Si NMR chemical shifts; this is supported by the experimental data (see above and Table 3). In contrast, one would expect an increase in the recombination rate for ions in Eq. (2) including the inversion at silicon as a result of the nucleophile attack from the side opposite the CH_2 group (Scheme 3), as well as the acceleration of bimolecular substitution at silicon (Eqs. (3a) and (3b)) which can also lead to the inversion at silicon.

We suppose that in the presence of the external halogenide ions the associative mechanisms for permutational isomerization mentioned above (Eqs. (3a) and (3b)) are more preferable. In this case, two different types of mechanism are possible: without the rupture of the O → Si bond (Eq. (3a), Scheme 4) and with the rupture of this bond (Eq. (3b), Scheme 5). The mechanism for exchange of the diastereotopic methyl groups, Me_a and Me_b, at the silicon without the coordination bond break (Scheme 4, **a** ⇌ **a′**) includes a frontal attack of the silicon atom from the side opposite the CH_2 group of the chelate ligand, the consequent elimination of the halide ion from an axial position at the hexacoordinate intermediate (**g**) and at finally the pseudo-rotation (three stages) of the resulting pentacoordinate structure (**d′**).

In the case of the associative mechanism with the O → Si bond break there are two possible paths: the formation of the intermediate adducts with one (**i**) (Scheme 5, **a** ⇌ **g** ⇌ **i** ⇌ **i′** or **a** ⇌ **i** ⇌ **i′**) or two (**h**) nucleophiles (Scheme 5, **a** ⇌ **g** ⇌ **h** or **a** ⇌ **i** ⇌ **h**, etc.).

The experimental data do not allow us to select one of the possible mechanisms (Scheme 5) leading to the inversion of configuration. However, for pentacoordinated intermediate (**i**) with the absence of the O → Si coordination the five-stage pseudo-rotation (**i** ⇌ **i′**) seems to be possible because all five ligands in these intermediates are monodentate. However, the experimental data provide support for the 1:2 adducts (type **h**)

on reaction of *N*-(dimethylchlorosilylmethyl) lactams with tertiary amines [28]. Moreover, for simple organosilicon [26] and -tin [29] halides it has been established that the rate of the inversion process is accelerated if external nucleophiles, e.g. pyridine, are present.

In the case of the above-mentioned degenerated exchange between the species **9** and NMI, Bassindale et al. [10], on the basis of kinetic data (zero order in NMI), proposed the mechanism in which the breaking of the O–Si bond is the rate limiting step. We suppose that such mechanism for permutational isomerization is highly probable for halogenides **1** and **2** in solutions with a high donor capability (acetonitrile, acetone, methanol), as well as for fluoride **3** in methanol in the presence of KF.

The mechanism of permutational isomerization of halogenides **1–3** via reversible dissociation of the O–Si bond as the first stage of the process seems to be less possible for the following reasons. First, the realization of such a mechanism for compounds **3** and **4** with the weakest O → Si coordination should result in the lowest barriers; this is not observed (Table 4). Second, the rupture of the O → Si bond with consequent re-coordination may lead to inversion at silicon, either by the exchange of a tetrahedral intermediate with the nucleophile or as a result of re-coordination including the hardly possible frontal attack of the oxygen atom from the side of the electronegative *Si*-substituent.

Thus, the permutational isomerization of halogenides **1–3**, in general, follows the dissociative and/or associative mechanism, including the series of tertracoordinated or/and extra-coordinated intermediates. The isomerization rate depends on the halogen and solvent nature and the presence of external nucleophiles. The main feature of the mechanisms discussed is the presence of pseudo-rotation stages.

3. Experimental details

The ^1H, ^{13}C, ^{17}O and ^{29}Si NMR spectra were recorded on a Varian XL-400 spectrometer at 400.0 MHz, 100.6 MHz, 54.2 MHz and 79.5 MHz respectively. A standard 5 mm $^{13}C/^1H$ probe head was used. Chemical shifts were measured using TMS as internal references for 0.5 M solutions (^1H, ^{13}C, ^{29}Si) and H_2O as external references for saturated solutions (^{17}O). Negative values are to high field. The 2D spectra NOESY, COSY and HETCOR were recorded using the pulse sequences suggested for the Varian XL-400 spectrometer [30–32].

Probe temperatures were measured from chemical shift differences between non-equivalent protons of methanol (− 90 to + 30 °C) or 1,2-ethanediol (30–85 °C) using Van Geet equations, unless otherwise noted, in the appropriate temperature ranges [33]. Coalescence of the separate ^1H resonances resulting from diastereotopic

$SiMe_2$ groups could be determined visually with a precision of $\pm 0.5\,^{\circ}C$.

Free activation energies for the processes of permutation isomerization resulting in coalescence of NMR signals were calculated from the Eyring equation [34].

All experiments with the external nucleophiles were carried out at stoichiometric reagent ratio. The concentration measurements were limited by the low solubility of inorganic salts in most organic solvents.

Acknowledgements

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