Reviews

Dynamic stereochemistry of hypervalent silicon, germanium and tin compounds containing amidomethyl C,O-chelating ligands

Vad. V. Negrebetsky and Yu. I. Baukov**

Russian State Medical University, 1 ul. Ostrovityanova,
117869 Moscow, Russian Federation.
Fax: 007 (095) 434 4787
E-mail: vvnmeduni@glasnet.ru

The results of NMR-spectroscopy studies of the structure, dynamic stereochemistry, and intermolecular interactions in solutions of organic derivatives of penta- and hexacoordinated silicon, germanium, and tin containing amidomethyl, lactamomethyl, and related bidentate ligands are surveyed.

Key words: hypervalent silicon, germanium, and tin; structure and stereochemical flexibility; intramolecular and intermolecular coordination; dynamic and multinuclear NMR spectroscopy.

1. Introduction

Stereochemical flexibility is one of the most remarkable properties of derivatives of hypervalent silicon, germanium, and tin; however, up to now, this property has been studied to a substantially lesser degree than, for example, structural features, specific reactivities, and biological activities of these compounds (see, for example, a number of reviews[1—4] and references therein). In addition, the majority of studies devoted to the dynamic stereochemistry of derivatives of the above-mentioned hypervalent elements are concerned with silicon and tin derivatives with C,N-chelating ligands in which the central pentacoordinated atom forms no less than two covalent bonds with electronegative substituents.

In connection with the hypervalence model developed in recent years,[5,6] trigonal-bipyramidal (TBP) derivatives with one electronegative substituent has attracted particular attention. In these compounds, which incorporate markedly "milder" coordination units than their analogs containing several electronegative substituents, an important consequence of hypervalence[6] is manifested most clearly: the "coordination" component Y→M of the hypervalent bond in an Y—M—X axial fragment is enhanced not only upon an increase in the electronegativity of substituent X but also upon weakening of the "covalent" component M—X (Y is the coordinating donor atom in a C,Y-chelating ligand, for ex-

---

* For the series of works "Dynamic stereochemistry of hypervalent compounds of silicon, germanium, and tin," the author was awarded the Academia Europea Prize for young scientists from CIS in 1996.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 1912—1934, November, 1997.

1066-5285/97/4611-1807 $18.00

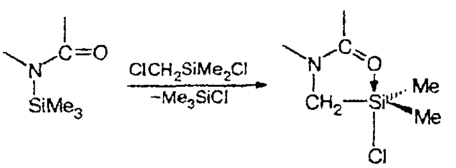
ample, an N or O atom; M = Si, Ge, or Sn; and X is an electronegative substituent, for example, halogen).* Compounds or this type are assumed to act as intermediates in S_N2 reactions at tetracoordinated silicon[8] and tin[9] atoms.

Therefore, in recent years, considerable study has been made of methods of synthesis, structure, and reactivity of organic derivatives of pentacoordinated silicon[7] and germanium[10] with C,O-chelating ligands, namely, *N*-(dimethylsilylmethyl) and *N*-(dimethylgermylmethyl) derivatives of cyclic and acyclic amides, and some related compounds as well as to their hexacoordinated analogs, including Sn derivatives, containing two C,O-chelating ligands and two monodentate electronegative ligands.[11,12]

In this review, we briefly consider the current state of research in this field and survey the results of our studies on the structure and dynamic stereochemistry of the above-listed compounds in solutions carried out by multinuclear (^1H, ^{13}C, ^{15}N, ^{17}O, ^{29}Si, ^{119}Sn), 2D-correlation (COSY, HETCOR), homonuclear *J*-resolved (HOM2DJ), exchange (NOESY), and dynamic (^1H) NMR spectroscopy.

2. Objects of studies: synthesis and structure

By now, methods for the synthesis of the main types of penta- and hexacoordinated Si, Ge, and Sn derivatives containing amidomethyl and related C,O-chelating ligands have been developed fairly well. Most of these methods are based on the reaction of chloro(chloromethyl)dimethylsilane with trimethylsilyl (TMS) derivatives of amides to give (O—Si)-chelate *N*-(chlorodimethylsilylmethyl)amides discovered by Yoder *et al.*[13–15] (transsilylation):



(1)

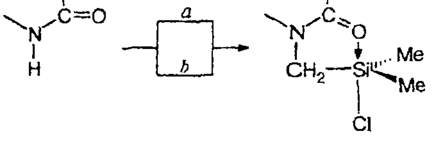
Similar reactions of *N*-TMS derivatives of lactams[16] readily occur at room temperature or upon short-term heating of the reactants without catalysts. The reactions of *N*-TMS-amides and -lactams with $ClCH_2GeMe_2Cl$ afford the corresponding (O—Ge)-chelate *N*-(chlorodimethylgermylmethyl)amides and lactams.[17]

The scheme of reaction (1) was studied by NMR monitoring. The first step in the reaction of *N*-TMS-*N*-methylacetamide and *N*-TMS-lactams with $ClCH_2MMe_2Cl$ (M = Si, Ge) is transmetallation with formation of Me_3SiCl. In the case of $ClCH_2SiMe_2Cl$, this step is completed over a period of several minutes even at low temperatures (−60 to −80 °C).[18] When the temperature increases (−20 to −30 °C), the resulting intermediates undergo intramolecular *O*-alkylation to yield the corresponding imidates, which isomerize into the final *N*-alkylation products upon a further increase in the temperature (to 0—25 °C). According to ^{29}Si NMR spectroscopy, the products of *O*- and *N*-alkylation contain pentacoordinated silicon atoms.[7,15,18,19]

In the case of $ClCH_2GeMe_2Cl$, similar transformations occur under somewhat more harsh conditions.[17] The intermediate formation of the transmetallation products is observed at ~−20 °C, the transformation into the *O*-alkylation product occurs at −10 to 10 °C, and the isomerization into the final product of *N*-alkylation proceeds at 60 °C or at higher temperatures. The trigonal-bipyramidal structures of some of the (N—Ge)- and (O—Ge)-chelate intermediate and final products of *O*- and *N*-alkylation, respectively,[17] and also of the (O—Si)-chelate final products of *N*-alkylation[8,13] containing chlorine and oxygen or nitrogen atoms in axial positions have been established by X-ray diffraction analysis. The IR spectra of isostructural (O—Si)- and (O—Ge)-chelates resulting from *N*-alkylation exhibit intense absorption bands at 1500—1510 and 1580—1620 cm^{-1} corresponding to the strongly coupled ν(C=O) and ν(C=N) vibrations of the chelate ligand.[13,14,16,17]

It has been shown for few examples that $ClCH_2SnMe_2Cl$ reacts with *N*-TMS-amides and -lactams under even more drastic conditions to give, according to ^{119}Sn spectroscopy, mixtures of *O*- and *N*-alkylation products.[19]

Another method for *N*-chlorodimethylsilylmethylation of amides and lactams consists of direct amination of chloro(chloromethyl)dimethylsilane in the presence of Et_3N [14–16,20] (reaction (2), *a*). However, better results from the synthetic viewpoint can be achieved in a one-pot-procedure using the hexamethyldisilazane—chloro(chloromethyl)dimethylsilane[21,22] system (reaction (2), *b*) in which *N*-TMS-amides or *N*-TMS-lactams are formed intermediately.



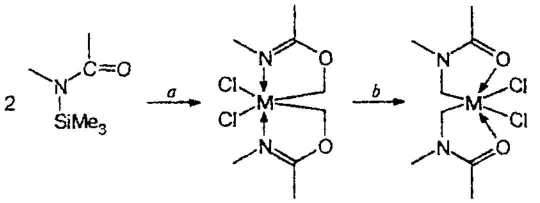
(2)

a. $ClCH_2SiMe_2Cl/Et_3N$
b. $ClCH_2SiMe_2Cl/(Me_3Si)_2NH$

The multistep scheme for reaction (1) also roughly describes the interaction of *N*-TMS-lactams with dichlorobis(chloromethyl)silane and -germane; however, when the ratio of the reactants is 2 : 1, this reaction yields derivatives of hexacoordinated Si and Ge atoms as the final products:

---

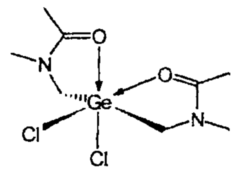
* The hypervalence model is discussed in more detail in Ref. 7.



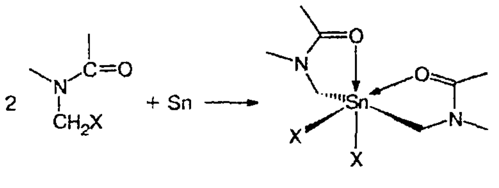
(3)

M = Si, Ge
Reagent: $(ClCH_2)_2MCl_2$

The reaction with $(ClCH_2)_2GeCl_2$ leads to relatively stable products of two types; under the conditions of kinetic control (an inert solvent, 80—100 °C), dichlorobis(lactimo-*O*-methyl)germanes are formed (reaction (3), *a*), while under more drastic conditions, the reaction yields thermodynamically more stable dichlorobis(lactamomethyl)germanes[23,24] (reaction (3), *a*, *b*). When *N*-TMS-lactams reacted with $(ClCH_2)_2SiCl_2$, only dichlorobis(lactamomethyl)silanes were isolated.[25] The hexacoordinated state of the central atom in all of the above-listed products was established using the data of IR spectroscopy, and in the case of dichlorobis(lactamomethyl)germanes, an X-ray diffraction study was carried out.[24] According to X-ray diffraction data, the Ge atom in dichlorobis(lactamomethyl)germanes has a somewhat distorted octahedral configuration and forms two intramolecular O→Ge coordination bonds. The carbon atoms occupy *trans*-positions, and the chlorine atoms as well as the coordinating oxygen atoms are in the *cis*-positions with respect to each other.



To obtain isostructural Sn-analogs, a much more convenient synthetic method has been proposed:[11,12]



(4)

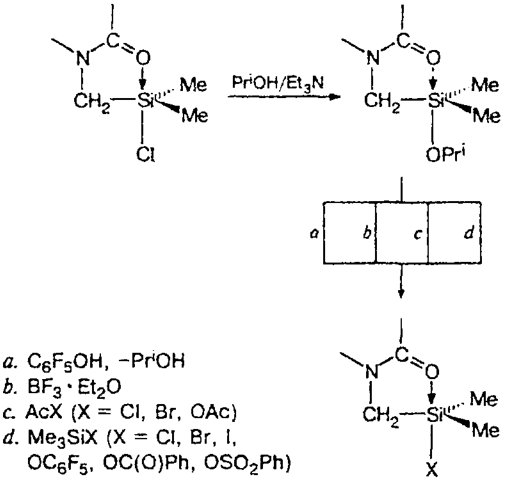
X = Cl, Br.

These reactions occur under relatively mild conditions (refluxing solutions of *N*-halomethyllactams in toluene or *o*-xylene in the presence of metallic tin for 1—2 h), and the yields of products are ~80%.

The chlorine atoms in *N*-(chlorodimethylsilylmethyl)amides and -lactams and in related compounds can be replaced by other substituents by treating these compounds with trimethylsilane derivatives Me_3SiX (X = Br, I, OSO_2R, OC(O)R′, OAlk, OAr), $(Me_3Si)_2O$, silyl ethers of enols,[16,26,27] potassium fluoride and acetate,[16] anhydrides of carboxylic acids,[16] sodium alkoxides,[26] or trialkyl(alkoxy)stannanes.[28] These transformations occur especially readily in the case where X is a better leaving group than Cl, *i.e.*, when the reaction yields compounds with a stronger O→Si coordination bond.

Alkoxy- and enoxy-derivatives and also 1,1,3,3-tetramethyl-1,3-bis(amidomethyl)- and 1,1,3,3-tetramethyl-1,3-bis(lactamomethyl)-1,3-disiloxanes can be easily obtained by the reactions of chlorides with alcohols, with enolyzable carbonyl compounds, or with water in the presence of triethylamine.[26,27] In turn, alkoxy derivatives and disiloxanes in which intramolecular O→Si interaction is extremely weak (if it occurs at all) have been used to develop alternative approaches to various Si-substituted derivatives of *N*-(dimethylsilylmethyl)amides and -lactams. The most efficient method for the synthesis of these compounds *via* the corresponding isopropoxides is shown in Scheme 1.[22,29]

Scheme 1

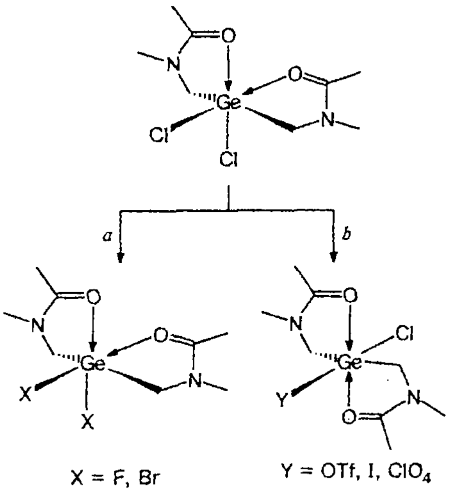


a. C_6F_5OH, $-Pr^iOH$
b. $BF_3 \cdot Et_2O$
c. AcX (X = Cl, Br, OAc)
d. Me_3SiX (X = Cl, Br, I, OC_6F_5, OC(O)Ph, OSO_2Ph)

By now, a method for the synthesis of compounds of hexacoordinated germanium with monodentate ligands other than chlorine has been developed fairly thoroughly. The method is based on the reactions of dichlorobis(lactamomethyl)germanes with trimethylsilyl triflate, halotrimethylsilanes (Me_3SiBr, Me_3SiI), and lithium or silver salts (LiBr, LiI, $LiClO_4$, AgF).[30–32] These reactions give rise to two types of compounds, *viz.*, the products of replacement of both chlorine atoms, in which the configuration of the coordination unit is similar to that in the initial dichlorides (Scheme 2, *a*), and the products of replacement of one chlorine atom by a nucleophile containing *trans*-arranged carbon atoms, oxygen atoms, and monodentate ligands (Scheme 2, *b*).

Various nucleophilic reagents incorporating identical nucleophiles (*i.e.*, Me_3SiX and LiX) lead to the same reaction products; in addition, reaction (*b*) yields mono-

Scheme 2



a. Me_3SiX, LiX, AgX
b. Me_3SiY, LiY

substitution products, irrespective of the ratio of the reactants (1 : 1 or 1 : 2).

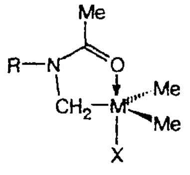
The reaction of (O—Sn)-bis-chelate dichlorobis(lactamomethyl)stannanes with lithium salts LiX (X = Br, I), unlike that of germanium derivatives, results in the replacement of both monodentate ligands by nucleophiles with the retention of the configuration of the initial dichloride.[33]

Thus, the preparative methods outlined here make it possible to synthesize a fairly broad range of model derivatives of penta- and hexacoordinated silicon, germanium, and tin (**1**—**25**) with amidomethyl and related C,O-chelating ligands including compounds with chiral labels (in particular, 4-phenyl-2-pyrrolidone and *N*-(1-phenylethyl)acetamide), which are convenient models for investigating the processes of permutational isomerization.

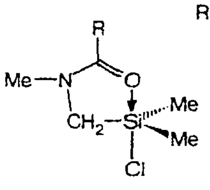
3. Spectral indications of the occurrence of O→M intramolecular interaction in solution (M = Si, Ge, Sn)

3.1. Derivatives of pentacoordinated silicon

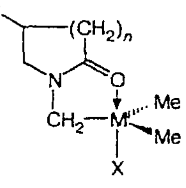
Reliable evidence for the existence of pentacoordinated Si atoms, carrying relatively electronegative substituents, in *N*-(dimethylsilylmethyl)amides and -lactams in solutions were obtained by NMR spectroscopy (see Refs. 7 and 15 and references therein and also Refs. 19, 34, and 35). Up to now, criteria permitting one to establish the presence of an O→Si intramolecular coordination bond (IntraCB) in the molecules of these compounds have been developed rather thoroughly. The formation of a hypervalent X—Si—O bond in Si-substituted *N*-(dimethylsilylmethyl)amides and -lactams **1**—**7** causes redistribution of the electron density on the N, O, Si, and C atoms in the five-membered chelate ring $\overline{SiCH_2NC(O)}$ with respect to that characterizing the corresponding model compounds with tetracoordinated Si atoms in which there is no O→Si interaction.[36—38]



1—**3**



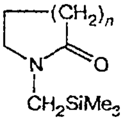
4—**6**



7a—**d**

1: R = Me
2: R = Ph
3: R= MeCH(Ph)
4: R = MeCH(OAc)
5: R = PhCH(OAc)
6: R = MeCH(Cl)
a: *n* = 1, R = H
b: *n* = 1, R = Ph
c: *n* = 2, R = H
d: *n* = 3, R = H

M = Si, Ge, Sn
X = F, Cl, Br, I, O/2, OMe, OPr^i, OPh, OC_6F_5, OCOMe, OCOPh, $OCOCF_3$, OSO_2Me, OSO_2Ph, OTf



The formation of an IntraCB is accompanied by deshielding of the ^{13}C nucleus of the carbonyl group; as a result, the ^{13}C NMR signal shifts downfield by 2—3 ppm (Table 1) in relation to this signal for compounds containing tetracoordinated Si atom. However, the change in the ^{13}C chemical shifts cannot be used for quantitative estimation of the strength of this coordination bond, because it is difficult to choose an appropriate model compound and because the range of variation of $\delta^{13}C(=O)$ upon the formation of the O→Si IntraCB is relatively small. Additional complications arise due to the necessity to take into account the ratio of the paramagnetic and diamagnetic contributions to the shielding constant.

Deshielding of the ^{17}O nuclei in compounds containing a hypervalent fragment increases by 60—70 ppm on the average, as compared to that in unsubstituted *N*,*N*-dimethylacetamide (340.2 ppm[39]), which implies a decrease in the degree of double bonding in the carbonyl group.[40] The fact that the ^{15}N NMR chemical shifts of compounds **1**—**3** (M = Si) with pentacoordinated Si atoms are somewhat greater (by 10—20 ppm) than that of *N*,*N*-dimethylacetamide (−258.1 ppm) indicates that the formation of IntraCB decreases the π-electron density on the nitrogen atom.[41,42]

The ^{29}Si NMR method provides most information and is used most frequently to detect IntraCB and to estimate its strength. The signals of the ^{29}Si nuclei in penta- and hexacoordinated silicon derivatives occur at markedly higher fields (at about −120 ppm or more) than those of the tetracoordinated silicon derivatives.

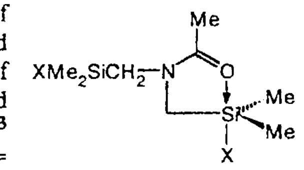
As an example, we shall consider compounds **8**[20,43] containing two silicon atoms, one of which is tetracoordinated and the other of which is pentacoordinated.

Table 1. Chemical shifts (δ) of the characteristic groups in the ^{13}C, ^{15}N, ^{17}O, ^{29}Si and ^{119}Sn NMR spectra of compounds **1—11,13,14,16** (20 °C)[12,22,36–38]

Compound	M	X	Solvent	δ			
				$^{13}C(O)$	^{15}N	^{17}O[a]	^{29}Si or ^{119}Sn
1	Si	O/2	$CDCl_3$	169.77[b]			3.4[b]
	Si	Cl	CD_2Cl_2	173.87	−249	259	−37.8
	Si	Cl [14]	$CDCl_3$	173.2	−252[c]	258	−37.6
2	Si	O/2	$CDCl_3$	169.43			3.2
	Si	Cl	CD_2Cl_2	173.91	−230	281	−36.8
	Si	Cl [14]	$CDCl_3$	173.8	−235[c]		−34.1
3	Si	Me	$CDCl_3$	170.59			0.1
	Si	O/2	$CDCl_3$	169.61			−0.1
	Si	OPr^i	$CDCl_3$	169.92		350	7.9
	Si	OMe	$CDCl_3$	169.77	−246	320	6.0
	Si	F	$CDCl_3$	171.45	−247	258	−19.4
	Si	Cl	$CDCl_3$	173.03	−252	245	−38.1 (−37.7[d])
	Si	Br	$CDCl_3$	174.23			−28.3 (−38.6[d])
	Si	I	CD_2Cl_2	173.99	−221	230	−22.7
	Si	OTf	$CDCl_3$	175.30			−5.3
	Ge	Me	$C_6D_5CD_3$	167.93			
	Ge	Cl	$CDCl_3$	172.65		294	
	Ge	Br	$C_6D_5CD_3$	172.60			
	Sn	Cl	$CDCl_3$	173.94			−47.3
4	Si	Cl	CD_2Cl_2	173.09			−31.6
5	Si	Cl	CD_2Cl_2	172.67			−32.0
6	Si	Cl	CD_2Cl_2	172.46			−33.9
7a	Si	O/2	$CDCl_3$	173.92			5.0
	Si	Cl	$CDCl_3$	177.81			−6.7[e] (−9.7) [7]
7b	Si	Cl	$CDCl_3$	175.67			−15.0 (−5.7) [7]
	Ge	Cl	$CDCl_3$	176.79			
7c	Ge	Me	$CDCl_3$	169.76			
	Si	Me	$CDCl_3$	168.06			0.9
	Si	Cl	$CDCl_3$	172.68			−42.4[f] (−38.5) [7]
7d	Si	Me	$CDCl_3$	174.06			0.3
	Si	F	$CDCl_3$	176.80		306	−19.5 (−20.6) [7]
	Si	OC_6F_5	$CDCl_3$	177.2			−27.6
	Si	Cl	$(CD_3)_2C=O$	179.54			−41.1
	Ge	Cl	$CDCl_3$	178.14			
	Sn	Cl	$CDCl_3$	179.32			−35.3
8	Si	F [43]	$CDCl_3$				29; −23.5
	Si	Cl[g]	$CDCl_3$				25.6; −38.7
	Si	$OC(O)CF_3$	$CDCl_3$				6.8; −42.2
9	Si	Cl	$CDCl_3$				32.3; −35.2
10	Si	Cl	$CDCl_3$				10.6; −37.6
11	Si	Cl [49]	[h]	175.8			−24.2
13	Si	Cl	$CDCl_3$	173.29			5.5
14a	Si	Cl	$CDCl_3—CD_2Cl_2$	170.42			−7.3
14b	Si	Cl	$CDCl_3—CD_2Cl_2$	172.97			−10.3[i]
16	Si	Me	$CDCl_3$	160.88	−248	348	1.2
	Si	O/2	$CDCl_3$	161.26			2.0
	Si	Cl	$CDCl_3$	163.80			−31.6

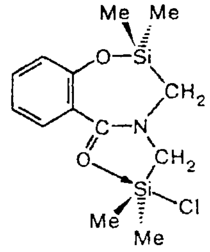
[a] At 50 °C. [b] Three sets of signals are observed; the lowest-field chemical shift for the C=O group is presented, while other signals are observed at 169.16 and 169.42 ppm, $\delta^{29}Si$: 0.1 and 3.2 ppm. [c] $\delta^{14}N$. [d] The spectrum was recorded in $C_6D_5CD_3$. [e] The spectrum was recorded in $(CD_3)_2C=O$. [f] c ~0.2 mol L^{-1}; at ~20 °C, a concentration-dependent shift is observed. [g] C. H. Yoder, private communication. [h] In a $CDCl_3—CCl_4—CH_2Cl_2$ mixture of solvents (2.5 : 1.5 : 6). [i] On prolonged keeping in $(CD_3)_2C=O$, two signals are recorded: −10.4 and −12.3 ppm.

The chemical shifts of the ^{29}Si signals ($\delta^{29}Si^{IV}$ and $\delta^{29}Si^{V}$) in the spectra of these compounds are 29 and −23.5 ppm (**8**, X = F),[43] 25.6 and −38.7 ppm (**8**, X = Cl),* and 6.8 and −42.2 ppm (**8**, X = OC(O)CF$_3$).**

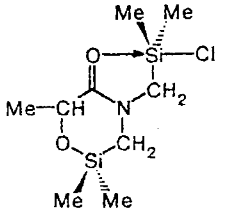


8, X = F, Cl, OC(O)CF$_3$

Chlorides **9** and **10** also can serve as examples;[44] the $\delta^{29}Si^{IV}$ and $\delta^{29}Si^{V}$ values for these compounds are 32.3, −35.2 ppm and 10.6, −37.6 ppm, respectively.



9



10

The upfield shift of the signal in the ^{29}Si NMR spectrum of *N*-(dimethylsilylmethyl)amides and -lactams **1**—**8** occurs in parallel with the increase in the nucleofugal properties of the substituent X.[7] The chemical shifts of the signals in the ^{29}Si and ^{13}C NMR spectra of alkoxides and halides **3** (M = Si) in a solution in toluene-d$_8$ are related by a linear dependence, described satisfactorily by the following equation:[37]

$$\delta^{29}Si = 1685.88 - 9.94\cdot\delta^{13}C, \quad n = 6, \ r = 0.983. \qquad (5)$$

To estimate quantitatively the degree of coordination interaction, it is significant to choose correctly the appropriate model compounds with tetracoordinated Si atoms. The difference between the chemical shifts ($\Delta\delta = \delta Si^{V} - \delta Si^{IV}$) is determined by the contribution of the coordination constituent of the hypervalent fragment to the shielding of the silicon atom. In particular, chloromethylsilanes $ClCH_2SiMe_2X$ are regarded as model compounds for Si-substituted *N*-(dimethylsilylmethyl)amides and -lactams **1**—**7** (M = Si).[7,19,34,35] As in other derivatives of hypervalent silicon,[7,45,46] the degree of shielding of ^{29}Si nuclei in compounds **1**—**7** (M = Si) is greater than that in the model compounds $ClCH_2SiMe_2X$. The coordination contributions ($\Delta\delta_1 = \delta Si^{V} - \delta Si(ClCH_2SiMe_2X)$) for compounds **3** (M = Si) and **7a**—**d** (M = Si) are listed in Table 2. However, the model compounds $ClCH_2SiMe_2X$ are known to rearrange readily into isomeric chlorosilanes XCH_2SiMe_2Cl;[47] therefore, it should be noted that in some cases, synthesis of these compounds can prove to be a fairly complicated task.

Therefore, the TMS derivatives Me_3SiX can also be used as adequate models (it is also significant that published data on ^{29}Si NMR chemical shifts for these compounds containing various electronegative substituents are more accessible[42]). The corresponding coordination contributions ($\Delta\delta_2 = \delta Si^{V} - \delta Si(Me_3SiX)$) are also included in Table 2.

Table 2. The coordination contributions ($\Delta\delta$)[7,37,49] to the ^{29}Si NMR chemical shifts of compounds **3**, **7a**—**d**, and **11** (M = Si)

Compound	X	Solvent	$-\Delta\delta_1$	$-\Delta\delta_2$	Ref.
3	Me	CDCl$_3$		0.1	37
	O/2	»		7.5	
	OPr^i	»	5.0	9.3	
	OMe	»	6.9	11.2	
	F	»	43.0	49.9	
	Cl	»	62.4	68.0	
	Br	»	46.0	54.3	
	OTf	»		49.0	
	I	»	23.4	31.3	
7a	OCOMe	CH$_2$Cl$_2$	8.8	14.7	7
	F	»	9.4	16.3	
	Cl	»	34.0,	39.6,	
		»	31.0^a	36.6^a	
	OSO$_2$Me	»	40.3	50.3	
	OSO$_2$Ph	»	41.0	51.2	
	OCOCF$_3$	»	42.6	51.1	
	Br	»	28.1	36.4	
7b	OCOMe	CH$_2$Cl$_2$	4.0	9.9	7
	F	»	7.1	14.0	
	Cl	»	30.0,	35.6,	
		CDCl$_3$	39.3^a	44.9^a	
	OSO$_2$Me	»	36.6	46.7	
	OCOCF$_3$	»	38.8	47.3	
	Br	»	29.5	37.8	
7c	OCOMe	CH$_2$Cl$_2$	50.8	56.7	7
	F	»	44.4	51.3	
	Cl	»	62.2,	68.4,	
		(CD$_3$)$_2$C(O)	66.7^{a,b}	72.3^b	
	OSO$_2$Me	CH$_2$Cl$_2$	60.3		
	OSO$_2$Ph	»	56.5	66.7	
	OCOCF$_3$	»	66.5	75.1	
	Br	»	40.3	48.6	
7d	OCOMe	CH$_2$Cl$_2$	50.8	56.7	7
	OC$_6$F$_5$	»		56.5	
	F	»	45.4	52.3	
	Cl	»	59.3,	64.9,	
		(CD$_3$)$_2$C(O)	65.4^{a,b}	71.0^b	
	OSO$_2$Me	CH$_2$Cl$_2$	58.8	68.8	
	OSO$_2$Ph	»	55.4	65.6	
	OCOCF$_3$	»	66.1	74.7	
	Br	»	45.5	53.8	
11	OCOMe	^{c}	26.2	32.1	49
	Cl	»	47.7	0.16	
	OCOCF$_3$	»	54.6	55.3	
	Br	»	48.0	56.3	
	I	»	15.6	23.5	

Note. $\Delta\delta_1$ is referred to the model compounds $ClCH_2SiMe_2X$ and $\Delta\delta_2$ is refered to the model compounds Me_3SiX. The $-\Delta\delta_1$ ($-\Delta\delta_2$) values for compounds **1**, **2**, **4**—**6** (M = Si; X = Cl) were 62.1 (67.7), 61.1 (66.7), 55.9 (61.5), 56.3 (61.9), and 58.2 (63.8). ^{a} Our data. ^{b} The increase in $-\Delta\delta$ is due to the increase in the coordination number of silicon upon interaction with the solvent. ^{c} In a CDCl$_3$—CCl$_4$—CH$_2$Cl$_2$ solvent mixture (2.5 : 1.5 : 6).

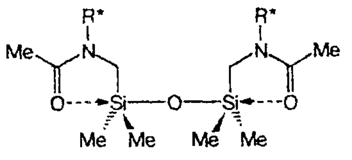
---

* C. H. Yoder, private communication.

** Our results.

It is noteworthy that compounds **8** also could serve as convenient models; however, at present, these derivatives are quite limited in number. It should also be mentioned that alkoxy derivatives (X = OAlk), which have been assumed to incorporate no O→Si IntraCB, had also been considered as model compounds for *N*-(dimethylsilylmethyl)lactams **7** (M = Si).[7] However, our most recent results suggest the hypervalent state of the silicon atom in, at least, some of these derivatives.[38] For example, the occurrence of the O→Si intramolecular interaction in alkoxides **3** (M = Si, X = OMe, OPr^i) is indicated by the fact that their NMR spectra contain only one set of signals (*i.e.*, there are no signals due to the second rotamer that would result from the hindered rotation around the C—N bond in aliphatic amides). Nevertheless, this interaction is much weaker than that in the corresponding halides, triflates, acylates, and aryl oxides as indicated by a comparison of the ^{29}Si NMR spectral parameters of alkoxides **3** (M = Si; X = OMe, OPr^i) (δ^{29}Si ~4—7) with those of the model compound $ClCH_2SiMe_2OMe$ (δ^{29}Si 12.9, $-\Delta\delta_1$ ~7, see Table 2) and also by the fact that the ^{17}O NMR signals for the alkoxides in question (δ^{17}O ~340—350, $CDCl_3$, 50 °C) are exhibited in a markedly lower field (by ~100 ppm) than the corresponding signals of chlorides of pentacoordinated silicon (240—270 ppm). At the same time, the NMR spectra of TMS derivatives **3** (M = Si, Ge; X = Me) contain two sets of signals, whose ratio depends on the nature of the solvent. The spectrum recorded in nonpolar toluene-d_8 exhibits only one set of signals, which has been assigned to the *E*-rotamer. The less intense set of signals includes the lower-field signal of the C atom of the carbonyl group. Therefore, we assigned these signals to the *Z*-rotamer.

A comparison of the chemical shifts of the low-field ^{29}Si signals for the corresponding disiloxanes (previously, they had been considered to contain no O→Si IntraCB based on the data of IR spectroscopy[26]) with those for the model disiloxane $(Me_3Si)_2O$ ($\delta(^{29}Si)$ 4.0[42]) shows that $-\Delta\delta_2$ varies from −2 to +8 ppm; this can indicate that weak O→Si interaction does occur in some of these compounds. In particular, the occurrence of this interaction in the solid state has been confirmed by an X-ray diffraction study of disiloxane **3** (M = Si, X = O/2) in which weak O...Si contacts (2.82 Å) have been found.



3

R* = (*S*)-CH(Ph)Me

Analysis of the corresponding coordination contributions (see Table 2) indicates that an increase in the nucleofugal properties of substituent X, estimated from the pK_a value of the conjugated acid, is generally accompanied by an upfield shift of the signal in the ^{29}Si NMR spectrum and by an increase in $|\Delta\delta|$. The difference between the ^{29}Si chemical shifts of $ClCH_2Me_2SiX$ and Me_3SiX ($\Delta\delta_1$) is smaller in magnitude than the corresponding value for the compound with a pentacoordinated silicon atom ($\Delta\delta_2$) by ~5—9 ppm; the general tendency of the variation of $\Delta\delta_1$ and $\Delta\delta_2$ as functions of the nature of the substituent X is retained. Note that there is also a fairly good correlation with the strengths of IntraCB in the solid phase estimated from the X-ray data based on the deviation of the silicon atom from the equatorial plane (Δ_{Si}) (Table 3).[1,8,22,48] In compounds **3** and **7a—d** (M = Si) containing rather poor leaving groups (X = OPh, OCOPh, F), the silicon atom deviates from the equatorial plane toward the substituent X (Δ_{Si} ~0.15—0.30 E); in the case of good leaving groups (X = Br, OTf, I), this atom deviates toward the coordinating oxygen atom (Δ_{Si} ~−0.15 to −0.30 E); the properties of Cl as a leaving group are intermediate (see Table 3; deviation toward the substituent X is taken as positive).

However, in the case of substituents X possessing high nucleofugal capacities (Br^-; I^-; RSO_2O^-; R = Me, Ph; TfO^-; CF_3COO^-; pK_a of the conjugate acid is less than 1), in most cases in relatively polar solvents (CD_2Cl_2, $CDCl_3$), the upfield shift of the ^{29}Si NMR signal and the coordination contribution become smaller than those for the corresponding chlorides, although the degree of O...Si interaction in the crystal obviously increases[1,8,22,48] (according to X-ray diffraction data). As a result, chlorides are normally characterized by larger $\Delta\delta$ parameters (except for compounds with weaker IntraCB, *viz.*, 2-pyrrolidone derivatives **7a,b** (M = Si, X = Cl), see below).

For example, the difference between the δ^{29}Si values of the chloride and bromide **3** (M = Si) in nonpolar toluene-d_8 is relatively small and amounts to ~1 ppm

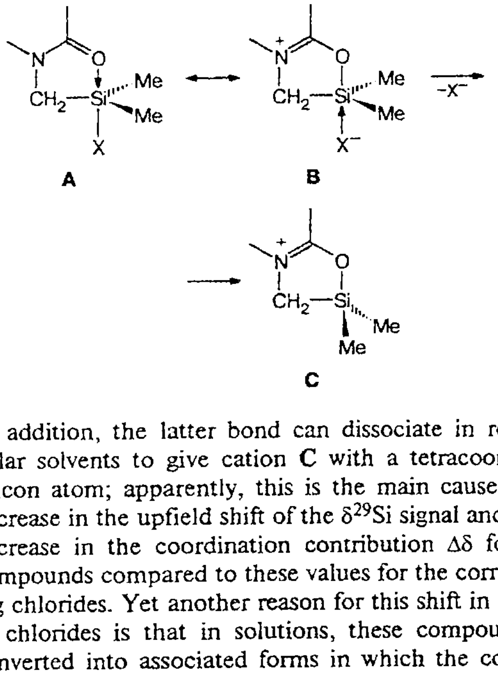
Table 3. Deviations of the silicon atom from the equatorial plane (Δ_{Si}/Å)[8,22,48] in compounds **3**, **7a—d**, and **11** (M = Si)

Compound	X	Δ_{Si}
3	F	0.20
	Cl	0.05
7a	OPh	0.30
	F	0.29
	OCOPh	0.205
7b	Cl	0.10
7c	Cl	0.06
	Br	−0.22
	OTf	−0.30
	I	−0.35
7d	OC_6F_5	0.16
	Cl	0.05
11	Cl	0.16
	Br	0.05
	I	−0.09

(unlike the corresponding value for model trimethylsilyl derivatives Me_3SiX) (see Table 1). However, in $CDCl_3$, the ^{29}Si signal of bromide **3** (−28.3 ppm) occurs at a lower field than that of chloride **3** (−38.1 ppm). On going to the iodide and triflate **3** (M = Si) in $CDCl_3$, the $\delta(^{29}Si)$ signal continues to shift downfield (−22.7 and −5.3 ppm, respectively) and the coordination contributions $\Delta\delta$ decrease (see Table 2).

The transition from X = Cl to substituents with higher nucleofugal capacities (Br, I, and Tf) results in characteristic changes in the 1500—1700 cm^{-1} region of the IR spectra of these compounds (a broadened medium-intensity absorption band at 1620—1640 cm^{-1} appears instead of the two medium-intensity bands at 1500—1520 cm^{-1} and the highly intense band at 1600—1610 cm^{-1}) and also leads to a sharp increase in the electrical conductivities of their solutions in CH_2Cl_2.[10,16,30]

Thus, the whole set of data obtained by ^{29}Si NMR and IR spectroscopy, X-ray diffraction analysis, and conductometry indicates that when substituent X is a relatively poor nucleofuge, the O—Si bond is the "coordination" bond (canonical structure **A**), whereas in compounds in which X is a good leaving group, Si—X becomes the "coordination" bond (canonical structure **B**).



(6)

In addition, the latter bond can dissociate in relatively polar solvents to give cation **C** with a tetracoordinated silicon atom; apparently, this is the main cause for the decrease in the upfield shift of the $\delta^{29}Si$ signal and for the decrease in the coordination contribution $\Delta\delta$ for these compounds compared to these values for the corresponding chlorides. Yet another reason for this shift in the case of chlorides is that in solutions, these compounds are converted into associated forms in which the coordination number of silicon is greater (see Section 4).

In particular, the assumption that iodide **3** (M = Si) in solution is mostly ionic is supported by the parameters of the ^{15}N and ^{17}O NMR spectra. Thus, the fact that the ^{17}O signal of iodide **3** (230 ppm, CD_2Cl_2, 50 °C) occurs at a higher field than that of chloride **3** (M = Si) (245 ppm) points to enhancement of shielding of the oxygen atom caused by a decrease in the degree of double bonding in the carbonyl group. Conversely, the ^{15}N signal of iodide **3** (M = Si) is exhibited at a somewhat lower field (−221 ppm, CD_2Cl_2) than that for chloride **3** (M = Si) (−252 ppm, see Table 1).

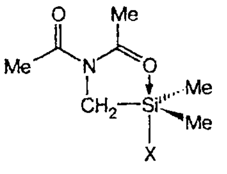
A comparison of the data of ^{29}Si NMR spectroscopy (see Tables 1 and 2 and Ref. 7) and X-ray diffraction data[1,8,22,48] made it possible to arrange substituents X, in terms of their effect on the strength of the O→Si coordination interaction in *N*-(dimethylsilylmethyl)amides and -lactams **1**—**8** (M = Si), in the following sequence:

Me << O/2, AlkO < PhO, F < PhCOO, MeCOO, C_6F_5O < $PhSO_2O$ < $MeSO_2O$ < Cl < CF_3COO << Br < TfO < I.

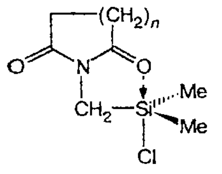
This series demonstrates one of the important consequences of the hypervalence model:[6] the degree of O—Si bonding of pentacoordinated silicon in a hypervalent O—Si—X fragment depends not only on the electronegativity of substituent X but it depends more appreciably on its nucleofugal capacity.

The few data currently available on the effects of the nature of the substituents at the nitrogen atom and at the carbonyl C atom of the amide group as well as the effects of the size of the lactam ring and of the heteroatoms incorporated into it on the degree of the O→Si intramolecular interaction indicate that electron-withdrawing groups decrease the donor ability of the coordinating oxygen atom in the chelating ligand. In fact, a chlorine atom or an acetoxy group in the α-position of substituent R in compounds **4**—**6** (see Table 1) somewhat weakens the O→Si coordination bond as indicated by the fact that the ^{29}Si signals of chlorides **4**—**6** occur at a lower field than those of chlorides **1**—**3** (M = Si).

An additional *N*-acetyl group exerts a more appreciable effect. The fact that the O→Si intramolecular interaction in *N*-(dimethylsilylmethyl)-*N*-acetylacetamides **11** is weaker than that in the corresponding derivatives of amides and lactams **1**—**3** and **7a**—**d** (M = Si) is indicated by the decrease in the upfield shift of the ^{29}Si NMR signal and in the coordination contribution for pairs of compounds with identical substituents X (see Table 3).[49] This is also confirmed by the X-ray diffraction data for halides **11** (M = Si; X = Cl, Br, I) in which the displacements of the Si atoms toward the oxygen atom were found to be smaller[7,8] than those for halides **7c** (M = Si) (see Table 3). Hence, only in iodide **11**, Si—X can be regarded as an "additional" bond, *i.e.*, as a bond with a coordination nature, whereas in bromide **11**, unlike bromide **7c** (M = Si), this is a covalent bond.



11



12a,c

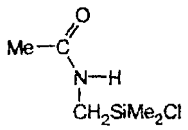
X = Cl, Br, I, OCOMe, $OCOCF_3$

n = 1 (**a**), 2 (**c**)

Note that for compounds **11**, a new type of stereodynamic transformations in derivatives of pentacoordinated silicon, namely, migration of a silicon atom bound by an O→Si intramolecular coordination bond between two donor centers, was discovered.

Weakening of the O→Si IntraCB is also observed in the case of derivatives of imides **12a,c**. The δ^{29}Si values for these compounds are 24.2 and 6.1 ppm,[50] and the $|\Delta\delta|$ values (in relation to $ClCH_2SiMe_2Cl$ and Me_3SiCl) are 0.1 and 5.7 ppm and 18.2 and 23.8 ppm, respectively. Thus, occurrence of an IntraCB in succinimide **12a** seems unlikely.

Steric factors can also be significant for the formation of IntraCB. For example, the ^{29}Si NMR spectrum of *N*-(chlorodimethylsilylmethyl)acetamide (**13**) in a dilute solution at room temperature contains one low-field signal (5.5 ppm in acetone-d_6 and 5.1 ppm in $CDCl_3$); this points to the presence of a tetracoordinated Si atom in this compound. In our opinion, this may be caused by the increase in the relative stability of the *E*-conformer owing to steric factors.[51]

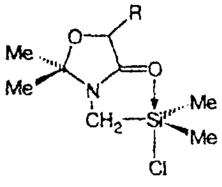


$Me{-}C({=}O){-}N(H){-}CH_2SiMe_2Cl$

13

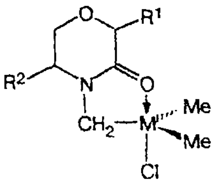
According to X-ray diffraction data, the variation of the size of the ring in lactams **7a—d** (M = Si) in the crystalline state exerts a relatively weak influence on the degree of the O→Si coordination interaction. On going from derivatives of five-membered lactams **7a,b** (M = Si) to the corresponding derivatives of six- and seven-membered lactams **7c,d** (M = Si), the coordination interaction tends to slightly increase (the $|\Delta\delta|$ value increases, see Table 2).[8,22] Since the strengths of the O→Si IntraCB in the derivatives of acyclic, six-membered, and seven-membered lactams **1—3** and **7c,d** (M = Si) are close (see Table 2), the smaller $|\Delta\delta|$ values found in the case of 2-pyrrolidone derivatives are caused apparently by the known fact that the electron-donating ability of the carbonyl O atom in the five-membered lactam ring is lower (because this ring is strained) than those for the O atoms in the six- and seven-membered rings. In particular, the pK_a values of the conjugated acids of five-, six-, and seven-membered lactams are −0.33, 0.75, and 0.36, respectively.[52]

According to X-ray diffraction, the introduction of an oxygen atom as an additional heteroatom into a lactam ring weakens the O→Si coordination bond in the case where this atom exhibits only electron-withdrawing effect and cannot be conjugated with the amide fragment. Thus in 4-oxazolidinone **14b** and morpholin-3-one **15** derivatives (M = Si), the deviations of the silicon atoms from the equatorial plane are 0.25[26] and 0.08 Å,[53] respectively (whereas those in chlorides **7b** and **7c** (M = Si) are 0.10 and 0.06 Å).[8] As a result, the O→Si interaction in the crystal of oxazolidinone **14b** is the weakest among those in *N*-(chlorodimethylsilylmethyl)amides and -lactams. In turn, the $\delta(^{29}Si)$ and $|\Delta\delta|$ values in oxazolidinones **14a,b** and 2-pyrrolidone derivatives **7a,b** (M = Si; X = Cl) are quite close to one another and are smaller than those for chlorides **1—3** (M = Si) and **7c,d** (M = Si) (see Table 2). Apparently, this is due a common reason associated with the possible formation of intermolecular homoassociates in solutions of compounds of pentacoordinated silicon with weak IntraBC (see Section 4).



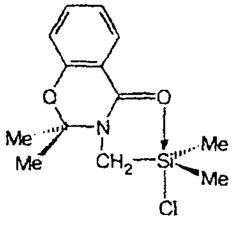
14a,b

R = H (**a**), Me (**b**)



15

M = Si, R^1 = Et, R^2 = H
M = Ge, R^1 = H, R^2 = Et



16

It is noteworthy that, according to X-ray diffraction[26] and ^{29}Si NMR data (see Tables 2 and 3), the electron-donating capacity of the carbonyl oxygen atom in 1,3-oxazin-4-one derivative **16** virtually does not decrease (Δ_{Si} = 0.06 Å, $|\Delta\delta_i|$ = 55.9). This can be explained by conjugation of the endocyclic oxygen atom and the C=O group with the π-electrons of benzannelated aromatic ring resulting in increased electron density on the oxygen atom of the lactam carbonyl group.

3.2. Derivatives of pentacoordinated germanium and tin

The above-considered regularities of variation of the spectral parameters and geometric characteristics of the hypervalent fragment in pentacoordinated silicon derivatives are also typical of their Ge and Sn analogs. In particular, the IR spectra of chlorides **7a—d** (M = Ge; X = Cl), like the spectra of isostructural silicon compounds,[16] exhibit two absorption bands in the 1500—1750 cm^{-1} region characterizing the N=C=O fragment, namely, a more intense band at ~1600 cm^{-1} and a less intense band at ~1510 cm^{-1}. This implies a (O—Ge)-chelate structure of chlorides **7a—d** (M = Ge).[17] The formation of O→Ge IntraCB in chlorides **3** (M = Ge) and **7a** (M = Ge) and in bromide **3** (M = Ge) results in a downfield shift (equal to ~6—8 ppm) of the signal of the C=O group in the ^{13}C NMR spectra with respect, for example, to the signal of the carbonyl C atom in *N*-(trimethylgermylmethyl)-2-piperidone (**7c**, M = Ge; X = Me) containing a tetracoordinated Ge atom.[33,54,55] The ^{17}O NMR signal of chloride **3** (M = Ge) is manifested at a lower field (294 ppm in $CDCl_3$) than the corresponding signals of chlorides of pentacoordinated silicon (see Section 3.1); this points to a lower electron-donating ability of the oxygen atom in chloride **3** (M = Ge).

The increase in the nucleofugal capacity of substituent X on going from the corresponding chloride to bromide is accompanied by a slight downfield shift of the ^{13}C NMR signal of the carbonyl group (172.12 ppm for chloride **3** (M = Ge) and 172.60 ppm for bromide **3** (M = Ge) in toluene-d_8, Table 1).[33] The X-ray diffraction data on the deviations of the germanium atom from the equatorial plane (Δ_{Ge}/Å) proved to be much more valuable.[10] In fact, the Δ_{Ge} values for chloride and bromide **3** (M = Ge) are 0.13 and 0.07, while those for chloride and triflate **7c** (M = Ge) are 0.15 and −0.18 Å, respectively. These results, together with conductometric data indicating that the electrical conductivity of triflate **7c** (M = Ge) is appreciably higher than that of chloride **7c** (M = Ge),[10] provide grounds for believing that the increase in the strength of the O→Ge intramolecular interaction following an increase in the nucleofugal capacity of substituent X occurs in the same order as that for the structurally similar derivatives of pentacoordinated silicon.

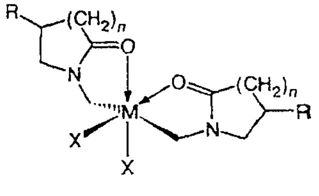
The strength of the O→Ge IntraCB in chlorides **7a—d** (M = Ge), as in the case of the corresponding Si derivatives,[8] increases on going from the five-membered lactam ring to six- or seven-membered rings and decreases when an electron-withdrawing oxygen heteroatom is introduced into the lactam ring (morpholin-3-one derivative **15** (M = Ge)).[10] In turn, a comparison of chlorides and triflates **7c** (M = Si, Ge; X = Cl, OTf) shows that, at least in these cases, interaction with the coordinating oxygen atom in silicon compounds is more efficient than that in their Ge analogs (*cf.* Δ_{Si} values for chloride and triflate **7c** (M = Si) given in Table 3 with the above-presented Δ_{Ge} values for their Ge analogs).

Unlike their Si and Ge analogs, *N*-(dimethylstannylmethyl)amides and -lactams have scarcely been studied to date. The pentacoordinated state of the tin atom in chlorides **1**, **3**, and **7d** (M = Sn) follows from the fact that the ^{119}Sn NMR signals of these compounds (−40.6, −47.3, and −35.3 ppm, respectively) are markedly shifted upfield with respect to this signal for the model dichloride $ClCH_2SnMe_2Cl$ (112.3 ppm, $CDCl_3$).[19,54,55] The resonance of the carbonyl group in the ^{13}C NMR spectra, as in the case of Si and Ge analogs, is displaced downfield with respect to $\delta^{13}C(=O)$ in *N*,*N*-dimethylacetamide.[33,56]

3.3. Derivatives of hexacoordinated silicon, germanium, and tin

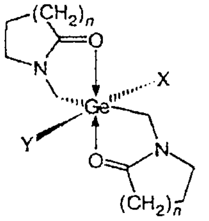
The hexacoordinated state of the central atom in bis(lactamomethyl)silanes, -germanes, and -stannanes L_2MXY (L is the lactamomethyl bidentate chelating ligand; M = Si, Ge, Sn; X, Y are halogens or some other identical or different monodentate ligands) is indicated by the fact that the positions and numbers of absorption bands in the 1500—1750 cm^{-1} regions of the IR spectra of these compounds are virtually identical to those of their isostructural pentacoordinated analogs containing one chelating ligand.[10,25] In fact, the IR spectra exhibit two characteristic absorption bands at ~1500—1510 and at ~1580—1620 cm^{-1} and contain no additional absorption bands that could be attributed to the monodentate lactamomethyl ligand. The presence of hexacoordinated silicon and, hence, an (O—Si)-bis-chelate structure, has been suggested (based on the data of IR spectroscopy) for bis(lactamomethyl)dichlorosilanes, which are the only silicon derivatives with two amidomethyl C,O-chelating ligands described to date. These compounds are amorphous hygroscopic powders,[25] whose structures have not yet been confirmed by NMR spectroscopy or X-ray diffraction analysis.

The available data concerning bis(lactamomethyl)-dihalogermanes and -stannanes and related compounds make it possible to discuss the effect of the increase in the coordination number of the central atom (from five to six) on the spectral and structural parameters.



17a—d

M = Ge, Sn;
X = F, Cl, Br, I



18a,c,d

X = Cl, Br;
Y = OTf, ClO_4, I

n = 1, R = H (**a**); *n* = 1, R = Ph (**b**);
n = 2, R = H (**c**); *n* = 3, R = H (**d**)

According to X-ray diffraction data, the central atom in compounds **17** (M = Ge, Sn) with two identical monodentate ligands in the crystalline state is hexacoordinated and forms an octahedral environment in which the carbon atoms occupy *trans*-positions and the coordinating oxygen atoms as well as halogen atoms occupy *cis*-positions with respect to each other.[12,24,32] Compounds **18** in which monodentate ligands X and Y possess markedly different nucleofugal capacities are actually ionic.[30–32] The Ge atom has an octahedral coordination, strongly distorted toward a trigonal one-cap bipyramid, with *trans*-arranged carbon atoms, oxygen atoms, and monodentate ligands.

The ^{119}Sn NMR signals of compounds **17a,c,d** (M = Sn; X = F, Cl, Br, I) are observed in a higher field (−190 to −340 ppm,[12] Table 4) than those of compounds of pentacoordinated tin (see Table 1). An increase in the nucleofugal capacity of substituent X normally results in an upfield shift of the ^{119}Sn signal; the $\delta(^{119}Sn)$ values for fluorides and chlorides with identical bidentate ligands are virtually identical.[54,55]

The chemical shifts of the signals in the ^{119}Sn NMR spectra depend also on the size of the lactam ring. The upfield shifts of the ^{119}Sn signals of dichlorides **17c,d** (M = Sn) with respect to those of dichlorides **17a,b** (M = Sn) suggest that the O→Sn coordination interaction in the six- and seven-membered lactam derivatives is stronger than that in five-membered derivatives. This is consistent with the results of X-ray diffraction analysis of dichlorides **17a,c,d** (M = Sn) and with the data on their electrical conductivities[12] and is also in line with the above-discussed effect of the size of the lactam ring on the strength of the intramolecular interaction in isostructural compounds of pentacoordinated silicon and germanium with one chelating ligand.

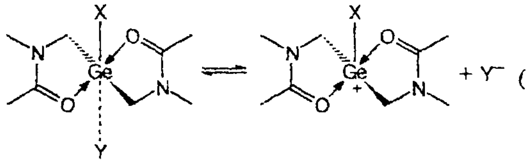
Table 4. ^{13}C NMR chemical shifts of the C=O groups and ^{119}Sn NMR chemical shifts for (O—Ge)- and (O—Sn)-bis-chelate bis(lactamomethyl)dichlorogermanes and -stannanes **17a—d** (M = Ge, Sn) and **18a,c,d** (20 °C, $CDCl_3$)[12,33,54,55]

Compound	M	X_2	$\delta^{13}C(=O)$	$\delta^{119}Sn$
			ppm	
17a	Ge	F_2	176.66	
	Ge	Cl_2	176.62	
	Ge	Br_2	176.81	
	Sn	F_2	177.78	−194.6
	Sn	Cl_2	177.35	−194.6
	Sn	Br_2	177.29	−241.3
	Sn	I_2	177.07	−272.5
17b	Sn	Cl_2	176.60	−195.9
17c	Ge	F_2	171.53	
	Ge	Cl_2	172.67	
	Ge	Br_2	174.78[a]	
	Sn	F_2	173.24	−271.6
	Sn	Cl_2	172.98	−270.2
	Sn	Br_2	172.97	−312.7
	Sn	I_2	172.87	−336.5
17d	Ge	F_2	177.31	
	Ge	Cl_2	177.61	
	Ge	Br_2	177.85[b]	
	Sn	Cl_2	178.72	−256.2
	Sn	Br_2	178.64	−293.7
	Sn	I_2	178.65	−294.5
18a	Ge	(Cl)OTf	180.71	
	Ge	$(Cl)ClO_4$	180.74	
18c	Ge	(Cl)OTf	174.84	
18d	Ge	(Cl)OTf	180.47	
	Ge	$(Cl)ClO_4$	180.39	
	Ge	(Br)OTf	180.35	
	Ge	(Br)I	180.39	

[a] A second less intense set of signals with $\delta^{13}C(=O)$ 172.30 is observed. [b] A second less intense set of signals with $\delta^{13}C(=O)$ 180.08 is observed.

The ^{13}C NMR spectra of *cis*-dihalides **17a—d** (M = Ge, Sn) are characterized by substantial (180 ppm and larger) downfield shifts of the ^{13}C signals of the carbonyl group (see Table 4). The spin-spin coupling of the tin atom with the carbonyl carbon atom and with some carbon atoms of the lactam rings, which has been observed in the ^{13}C NMR spectra of *cis*-dichlorides **17a—d** (M = Sn; X = Cl), is also retained at low temperatures.[12] The $J(^{13}C-^{119}Sn)$ value for the C atom of the carbonyl group increases following an increase in the degree of the O→Sn coordination in the following series of tin dichlorides **17a**, **17b** << **17d** < **17c**. In the case of dichloride **17c**, which contains, according to ^{119}Sn NMR spectroscopy, the strongest O→Sn coordination bond, spin-spin coupling of the tin atom with the carbon atom in position 3 of the lactam ring is observed. Based on this finding, it is believed that the $^{13}C-^{119}Sn$ spin-spin coupling in dichlorides **17a—d** (M = Sn) is transferred directly through the coordination bond.

The $^{13}C(=O)$ signals for compounds **18a,c,d** (M = Ge) with the *trans*-configuration of the coordination unit occur at lower field (up to ~180 ppm) than those of compounds of hexacoordinated germanium with the *cis*-arrangement of monodentate ligands (up to ~177 ppm).[54] This is apparently due to the deshielding of the carbonyl carbon atom caused by the substantial delocalization of the positive charge resulting from (partial) dissociation of these compounds in solutions to give germacenium ions, which is indicated by the data of conductometry.[10,30]



(7)

It has been found in ^{13}C NMR studies that the signals of the carbonyl carbon atoms of Ge and Sn six-membered lactam derivatives are markedly shifted upfield (in some cases, by up to 6 ppm) with respect to the corresponding signals of derivatives of five- and seven-membered lactams.[12,54,55] An upfield displacement of the ^{13}C NMR signal for the carbonyl carbon atom is also observed for pentacoordinated chloride **7c** (M = Si) with respect to chlorides **7a,d** (M = Si).[38]

The upfield displacement of the $^{13}C(=O)$ signals of six-membered lactam derivatives with penta- and hexacoordinated central atoms with respect to the corresponding signals for the derivatives of five- and seven-membered lactams is apparently due to more efficient delocalization of the π-electron density in the N—C—O—M fragment in the six-membered lactam ring. In this case, owing to the decrease in the length of the O→M coordination bond, the paramagnetic contribution to the constant of shielding of the carbonyl carbon atom changes more rapidly than the diamagnetic contribution. This effect was observed for the first time in a study dealing with the reactivity of some highly basic aromatic ketones, phenalenone and tropone derivatives, in acid media.[41]

4. Intermolecular coordination interactions in solutions of *N*-(halodimethylsilylmethyl)amides and -lactams

4.1. Low-temperature studies

The chemical shifts of the NMR signals for compounds of pentacoordinated silicon depend on the temperature and on the nature of solvents.[7,34—38] When solutions of fluorides **3** (M = Si), **7d** (M = Si), chlorides **1**—**7** (M = Si), and iodide **3** (M = Si) are cooled, the signals in their ^{29}Si NMR spectra shift upfield.[36—38]

The magnitudes of the upfield shifts of the ^{29}Si NMR signals at low temperatures depend on the nature of the solvent. The greatest shifts of the ^{29}Si signals of fluorides and chlorides at −90 °C are observed in a low-polarity solvent exhibiting no electron-donating properties (toluene-d_8), while the smallest shifts are observed in solvents with high electron-donating abilities such as acetone-d_6, CD_3CN, and CD_3OD.[38]

The ^{29}Si signals of bromides **3** (M = Si) and **7c**,**d** (M = Si) and iodide **11**,[49] unlike those of chlorides and fluorides, were found to substantially (by up to 12 ppm) shift downfield in solvents with relatively low electron-donating abilities (toluene-d_8, CD_2Cl_2, $CDCl_3$) at −90 °C.[7,38] An increase in the electron-donating ability of the solvent (CD_3CN, CD_3OD), on the contrary, causes an upfield shift (2—4 ppm) of signals in the ^{29}Si NMR spectra,[38] which may be due to association of the halide with solvent molecules.

In terms of the model of the effect of the medium and the temperature on the structures of pentacoordinated silicon derivatives developed by V. A. Pestunovich and M. G. Voronkov,[57] the solvent—solute interaction strengthens the coordination in the case where the dipole moment μ of the molecule increases as the coordination bond becomes shorter and weakens the coordination if the μ value and the length of IntraCB vary in parallel. Thus, the change in the shielding of the silicon atom following a decrease in the temperature is due to the increase in the dielectric constant of the solvent and to the fact that the more polar state of the halide is stabilized as a result of shortening of the O→Si coordination bond (in fluorides and chlorides) or the $Si \leftarrow Hal^-$ bond (in bromides and iodide **11**) and/or a decrease in the degree of its dissociation.[7,49] In terms of the hypervalence model,[6] these data imply the "coordination" character of the O→Si bond and the "covalent" character of the Si—Hal bond in the axial fragment of fluorides and chlorides and, conversely, the "covalent" and "coordination" characters of the O—Si and $Si \leftarrow Hal^-$ bonds, respectively, in the case of bromides and iodide **11**. Iodide **3** (M = Si) and triflate **3** do not fit in this dependence: for these compounds, shielding of the ^{29}Si nuclei increases as the temperature decreases. Note that the preliminary results obtained in conductometric studies of halides **3** (M = Si, Hal = F, Cl, Br, I) demonstrate that in all cases, the electrical conductivity at low temperatures (down to the freezing point of the solvent; ~−95 °C for CH_2Cl_2) is somewhat lower (by a factor of 1.5—2) rather than higher than that at room temperature; this is inconsistent with the assumption that the degree of dissociation of the coordination bonds in bromides and iodides increases.

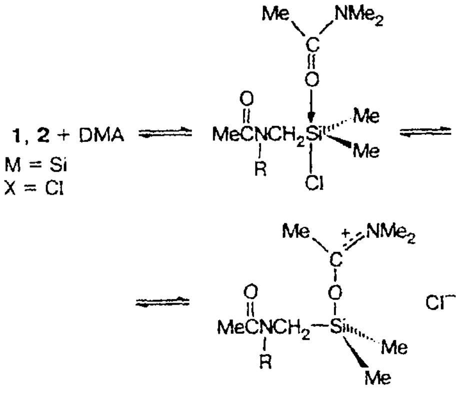
In the ^{13}C NMR spectra of fluorides **3** and **7d** (M = Si) recorded at low temperatures (−50 °C, $CDCl_3$), long-range spin-spin coupling between the F and C(=O) atoms ($^nJ_{F,C(O)}$ = 1.8 and 1.7 Hz, respectively) was detected.[58] This coupling can be accomplished in two ways: across four bonds in the F—Si—C—N—C fragment of the five-membered chelate ring ($^4J_{F,C(O)}$) or directly through the O—Si—F hypervalent bond. The latter seems more likely because the ^{19}F—^{13}C(=O) spin-spin coupling is recorded only at low temperatures, which can be due to the increase in the strength of the O→Si coordination bond after cooling of the solution.

4.2. Homo- and heteroassociation of pentacoordinated silicon derivatives in solution

Derivatives of pentacoordinated silicon with O→Si IntraCB relatively easily form complexes with rather strong nucleophiles such as dimethyl sulfoxide, hexamethyltriamidophosphate, *N*-methylimidazole, pyridine, or fluoride ions (see, for example, Refs. 59 and 60 and references therein). Using IR spectroscopy, it has been found that the complex formation between chlorides **7a**,**c**,**d** (M = Si) and tertiary amines (triethylamine, *N*-methylmorpholine) proceeds to equilibrium. The silyl chloride—amine ratio in the complexes with a non-coordinated carbonyl group amounts to 1 : 2.[27]

The formation of intermolecular associates between chlorides **1**, **2** (M = Si) and *N*,*N*-dimethylacetamide (DMA) in a solution in CD_2Cl_2 has been studied by NMR spectroscopy.[36] The ^{1}H and ^{13}C NMR chemical shifts are relatively insensitive to complex formation. Only the slight downfield displacement (~1 ppm) of the signal corresponding to the C atom of the carbonyl group of DMA in the assoiciate with respect to this signal for free DMA can be regarded as characteristic. A similar slight downfield shift of the signal of the carbonyl group has been observed upon deuteration of DMA in a solution in CF_3COOD.[39] The ^{29}Si signal of the associate is manifested at room temperature as a substantially broadened singlet with δ −32±2 ($\Delta\nu_{1/2} \approx$ 100—

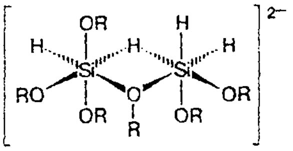
200 Hz). At low temperatures (−90 °C), the spectrum contains only one narrow singlet, which is shifted ~10 ppm upfiled in relation to the signal of the corresponding chloride. This provides grounds to believe that the coordination number of silicon does not increase upon the formation of the associate. Taking into account the fact that in the presence of DMA, the electrical conductivity of *N*-(halodimethylsilylmethyl)acetamides and -lactams increases ~3-fold, it can be assumed that associates partially dissociate in solution.



(8)

R = Me, Ph

The formation of homoassociates of derivatives of pentacoordinated silicon in solutions has not been studied in detail until recently, although species of this type with a bridging alkoxy or aryloxy group and a hydrogen atom have been assumed[2] as intermediates in the migration of OR and H groups between two pentacoordinated silicon atoms in anionic pentacoordinated hydridosilicates $[H_2Si(OR)_3]^-$ (R = OMe, OEt, OPh).



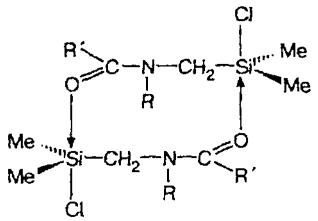
It has also been noted that dimers with bridging halogen atoms can play a crucial role in stereoisomerization with inversion of the configuration at the pentacoordinated tin atom in the optically active bromide 2-[1-(*S*)-$Me_2NCH(Me)]C_6H_4SnMePhBr$.[9]

A determination of the molecular weight of *N*,*N*-bis(chlorodimethylsilylmethyl)acetamide (**8**, X = Cl) in benzene has shown that in highly concentrated solutions, it exists as an associate;[13,14] the structure of the associate has not been discussed in detail. In a study of difluoro(aroyloxymethyl)methylsilanes carried out by IR spectroscopy, it has been found that the intensities of the absorption bands corresponding to the Si—F stretching vibrations depend on the concentration; in the opinion of the authors,[61] the form of this dependence indicates the presence of boat-shaped six-membered cyclic dimers stabilized by intermolecular (InterCB) O→Si coordination bonds in the solutions. The occurrence of the concentration dependence of the chemical shifts in the ^{29}Si NMR spectra of fluorides[62] **7a,b** (M = Si) has been explained by high sensitivity of the intramolecular O→Si interaction to the polarity of the medium, whereas the hypothesis about the formation of associates stabilized by InterCB has not been considered.

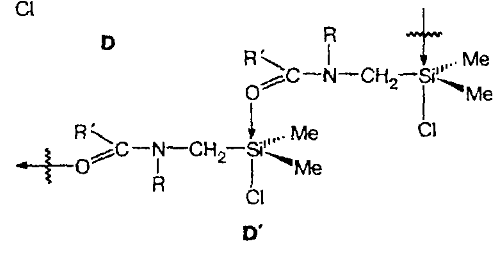
We have obtained data confirming the existence of homoassociates with hypervalent silicon, stabilized by intermolecular coordination, in a study of two series of Si-substituted *N*-(dimethylsilylmethyl)amides and -lactams $R'C(O)N(R)CH_2SiMe_2X$ by NMR spectroscopy at low temperatures.[36,38] In the first series that included *N*-(α-phenylethyl)acetamide **3** (M = Si) and lactam **7** (M = Si) derivatives, the nature of substituent X varied (X = F, Cl, Br, OPr^i), while in the second series comprising compounds **1—7** (M = Si; X = Cl), the structure of the chelating ligand varied.

The low-temperature (from −70 to −95 °C) ^1H, ^{13}C, and ^{29}Si NMR spectra of chlorides **1—6**, **7c,d** (M = Si) in relatively polar aprotic solvents possessing virtually no donor ability ($CDCl_3$, CD_2Cl_2) and in acetone-d$_6$ contained double sets of signals with different integrated intensities. Both signals recorded at low temperatures in the ^{29}Si NMR spectra occur at a very high field (in the region of −35 to −42 ppm), which indicates the hypervalent state of the silicon atom. The concentration and temperature dependences of spectral parameters imply the existence of a dynamic equilibrium between monomers in which the silicon atom is pentacoordinated owing to the O→Si intramolecular interaction and the intermolecular homoassociates. The fact that the ^1H signals of the $SiMe_2$ groups in chlorides **3** and **4—6** (M = Si) containing chiral carbon atoms remain nonequivalent is due either to the fact that the process occurs without inversion of the silicon configuration or to the fact that the process is slow on the NMR time scale.

Based on the analysis of the spectral data, one set of signals was assigned to type **A** monomer incorporating a O→Si IntraCB, and the other set of signals characterized by a higher-field position of the ^{29}Si NMR signal



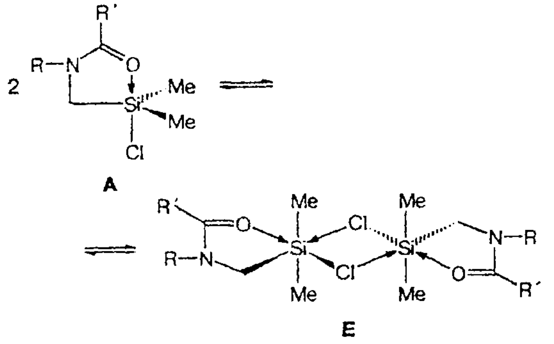
D



D'

was attributed to a homoassociate stabilized by an InterCB. Dimers **D** and *n*-mers **D′** containing O→Si InterCB can be considered as possible structures for these homoassociates.[36]

The higher-field position of the ^{29}Si signal for the intermolecular associate does not rule out the possibility that species characterized by a higher coordination number of the silicon atom, in particular, dimer **E** with bridging chlorine atoms and hexacoordinated silicon, are present in the solution. The formation of the latter can be thermodynamically preferable, because it does not include the energetically unfavorable cleavage of the O→Si IntraCB. It should be noted that the presence of bridging fluorine atoms in pentacoordinated anionic bis(siliconates)[63] and hexakis(dimethylfluorosilyl)benzene[64] has been confirmed by X-ray diffraction data.



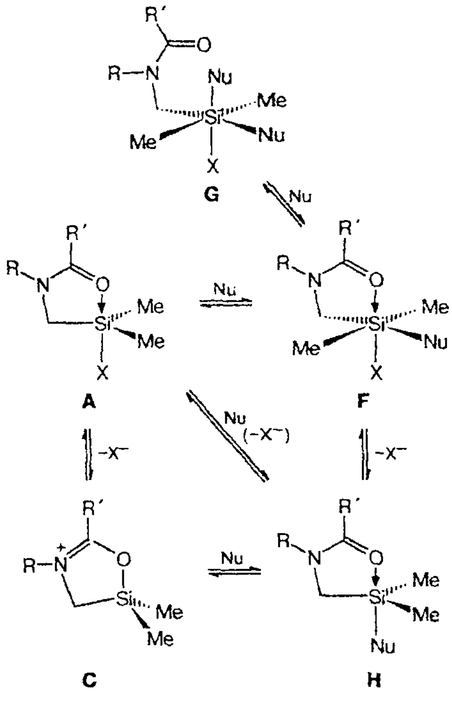
(9)

Since the the intermolecular O→Si coordination interaction in associates **D** and **D′** is weaker than the intramolecular interaction, it can hardly account for the observed upfield shift of the ^{29}Si signal of the intermolecular associate with respect to that of monomer **A**. It should be emphasized once more that the formation of associates **D** and **D′** should be preceded by the cleavage of the fairly strong O→Si IntraCB, and this is rather unlikely. This is also supported by the fact that for compounds with weak intramolecular interaction, *viz.*, fluoride **3** (M = Si), derivatives of five-membered lactams, and chlorides **7a,b** (M = Si), and for isopropoxide **3** (M = Si; X = OPr^i) in which the O→Si IntraCB appears to be very weak if existing at all (see above), no additional NMR signals can be recorded in the accessible temperature range (down to −100 °C).[38]

The results of semiempirical MNDO and MNDO/PM3 studies of electronic and spatial structures of pentacoordinated monomers and their homoassociates (dimers as models of oligomers) also support the predominant formation of type **E** associates. Quantum-chemical calculations have demonstrated that at least three main factors should be taken into account in a discussion of preferred existence of one or another structure. These factors are the heat of formation, the charge on the Si atom, and the total dipole moment of the molecule.[38] In the condensed phase, in which polar interactions between the molecules are stronger than those in the gas phase, the latter two factors are apparently more significant. The conclusion that homoassociation is a charge-controlled process was based on the fact that the charge magnitudes on the Si and Cl atoms in homoassociates **E** are greater than those in monomers **A**.

In nonpolar aprotic solvents (benzene-d_6, toluene-d_8) and in solvents with relatively high donor abilities (CD_3CN, CD_3OD), no second set of signals was observed in the spectra of chlorides **1—6**, **7c,d** (M = Si) in the temperature range studied. In the latter case, this is evidently due to the possibility of competing heteroassociation with the highly electron-donating solvent (Scheme 3) acting as an external nucleophile (Nu).[38]

Scheme 3



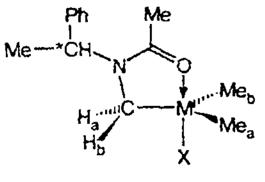
This reaction can yield both adducts with one nucleophile molecule formed without cleavage of the O→Si coordination bond (structures **F** and **H**) and those with two nucleophile molecules, whose formation requires the cleavage of the O→Si bond (structure **G**). This has been shown in a study of the complexation of chlorides **7a,c,d** (M = Si) with tertiary amines.[27] The formation of heteroassociates containing penta- and/or hexacoordinated silicon atoms may be one of the reasons for the absence of a linear correlation between the ^{13}C and ^{29}Si NMR chemical shifts for some *N*-(halodimethylsilyl)acetamides in solvents posessing high donor abilities.[37]

As has been noted previously,[38] the ^{29}Si NMR signal of bromide 3 (M = Si) in solvents with low donor abilities shifts downfield as the temperature decreases. Conversely, in CD_3OD or CD_3CN, as in the case of chlorides 1—7 (M = Si), the ^{29}Si signal shifts upfield with a decrease in the temperature. This is apparently due to the weakening of the O→Si coordination component following the formation of type **F**, **G** and/or **H** heteroassociates.

In the NMR spectra of bromide 3 (M = Si), two sets of signals were detected at low temperatures only when acetone-d_6 was employed as the solvent. The ^{29}Si NMR spectrum recorded at −90 °C exhibited two high-field signals at δ −30.8 and −44.7. Since the difference between the chemical shifts of these signals is large (for the above-discussed chlorides, this difference was no more than ~5 ppm), neither of them can be assigned to the homoassociate with hexacoordinated silicon. In our opinion, the first signal should be attributed to monomer 3 in form **A** (M = Si; X = Br), while the second (higher-field) signal refers most likely to heteroassociates **F** (M = Si; X = Br) and/or **H** (M = Si; X = Br). Apparently, in relatively highly electron-donating solvents such as CD_3OD and CD_3CN, the equilibrium shown in Scheme 3 is also shifted toward the latter heteroassociates. This is indicated by the fact that at low temperatures, the ^{29}Si signals in these solvents are displaced upfield (to −48.0 ppm) with respect to these signals in toluene-d_8 and CD_2Cl_2 (−26.5 and −20.4 ppm, respectively, at −90 °C).

5. Stereodynamic processes in compounds of pentacoordinated silicon, germanium, and tin

Since the central atom in hexacoordinated derivatives is chiral and some of the compounds of pentacoordinated silicon, germanium, and tin incorporate an additional asymmetric center, these derivatives are promising objects for the investigation of permutational isomerization. Owing to the presence of asymmetric carbon atoms in compounds **3**, **4—6**, and **7b**, the prochiral NCH_2 and MMe_2 groups become chemicaly nonequivalent in the ^{1}H NMR spectra (this is observed, for example, for compounds **3** (M = Si, Ge, Sn; X = F, Cl, Br, I, OTf)).



3

As a result, at room temperature and at lower temperatures, the protons of the NCH_2 group are manifested in the NMR spectra as a multiplet of an AB-system ($^2J_{HH}$ ~16 Hz), and the protons of the MMe_2 group are exhibited as a doublet with an intensity ratio of 1 : 1. When the temperature is increased, the nonequivalence of the protons of the CH_2 group is retained (AB spectrum), whereas the doublet of the MMe_2-group protons undergoes a temperature evolution typical of permutational processes: the components of the doublet become broader and coalesce into a singlet characterized by the average chemical shift. A decrease in the temperature is accompanied by restoration of the initial spectral pattern. The activation free energies ($\Delta G^{\#}$) found by dynamic ^{1}H NMR at the temperature of coalescence of the doublet components are listed in Table 5.

It can be seen from the presented data that in the series of halides 3 (M = Si; Hal = F, Cl, Br, I), the barrier to the permutational isomerization decreases from fluoride to iodide in parallel with the increase in the strength of the O—Si bond and the corresponding weakening of the Si—Hal bond,[7] which implies a crucial role

Table 5. The barriers to the permutational isomerization ($\Delta G^{\#}$) of amidomethyl derivatives of pentacoordinated silicon, germanium, and tin 3—7[37,54,56]

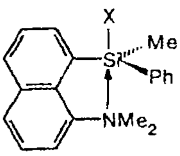
Compound	M	X	Solvent	$\Delta G^{\#}\pm0.1$ /kcal mol^{-1}
3	Si	F	$CDCl_3$	>24
	Si	Cl	$C_6D_5CD_3$	>18.6
			$CDCl_3$	14.9
			CD_3CN	14.4
			CD_2Cl_2	14.7
			$(CD_3)_2C(O)$	>16.2
			CD_3OD	12.0
	Ge	Cl[a]	CD_3CN	>21[b]
			CD_3OD	15.7
	Ge	Br	CD_3CN	17.0
			CD_3OD	15.3
	Sn	Cl	CD_3OD	12.5
	Si	Br	$C_6D_5CD_3$	15.2
			$CDCl_3$	14.6
			CD_3CN	14.2
			CD_2Cl_2	14.1
			$(CD_3)_2C(O)$	14.2
			CD_3OD	11.9
	Si	OTf	$CDCl_3$	15.4
			CD_3CN	15.9[c]
			$(CD_3)_2C(O)$	15.6
	Si	I[d]	$C_6D_5CD_3$	14.8
			$CDCl_3$	13.8
			CD_2Cl_2	12.7
4	Si	Cl	$CDCl_3$	15.6
5	Si	Cl	$C_6D_5CD_3$	>17.6
			$CDCl_3$	14.3
			CD_3CN	13.5
6	Si	Cl	$CDCl_3$	13.9
7b	Si	Cl	$CDCl_3$	11.0 (10.8)[34]
	Si	$OC(O)CF_3$		(14)[34]
	Ge	Cl	$CDCl_3$	17.8

[a] ^{1}H NMR signals of the $GeMe_2$ group in $CDCl_3$ and toluene-d_8 are recorded as a doublet with equal intensities of the components; heating of a solution in toluene-d_8 to 70 °C does not result in coalescence of the signals. [b] T_c > 76 °C. [c] At a concentration of ~0.5 mol L^{-1} (after dilution to ~0.1 mol L^{-1}, the $\Delta G^{\#}$ value was 17.1 kcal mol^{-1}). [d] The $\Delta G^{\#}$ value depends on the concentration, c ~0.4 mol L^{-1}.

of the nucleofugal properties of substituent X. For example, in 0.4—0.5 mol L^{-1} solutions in low-polarity solvents, iodide **3** (M = Si; see Table 4) is characterized by a smaller $\Delta G^{\#}$ value than bromide **3** or chlorides **3**—**6** (M = Si). In more polar and more electron-donating solvents ($CDCl_3$, CD_2Cl_2, acetone-d_6, CD_3CN, CD_3OD), these values decrease by 2—3 kcal mol^{-1}, and, simultaneously, the ^{29}Si NMR signals shift downfield by ~15—20 ppm.

In the case of fluoride **3** (M = Si), no coalescence of ^1H signals has been observed in the temperature range from 20 to 90 °C. However, in this case, too, the occurrence of ligand exchange is indicated by the cross-peak between the signals for the $SiMe_2$ group recorded by the exchange 2D NMR spectroscopy using the NOESY technique (CD_3OD, 60 °C). According to the estimates based on the slight broadening of the signals for the $SiMe_2$ group, the $\Delta G^{\#}$ value is >24 kcal mol^{-1}. Note that in non-polar toluene-d_8, the cross-peak was not observed even at 90 °C. In the case of alkoxides **3** (M = Si; X = OMe, OPr^i), unlike for halides, no dynamic exchange between the methyl groups at the silicon atoms was detected even at 100 °C.

A similar dependence of the barrier to the permutational isomerization on the nature of the halogen has been established for monofunctional halides of 1-dimethylamino-8-silylnaphthalene **19** with N→Si coordination.[45,65]



19

In the opinion of the researchers cited,[45,65] the observed relatively large $\Delta G^{\#}$ values (23, 20, and >19 kcal mol^{-1} for X = F, Cl, and Br, respectively) correspond most probably to a nonregular mechanism of the process consisting of cleavage of the N→Si coordination bond and subsequent rotation and inversion at the nitrogen atom.

The addition of external nucleophiles (LiCl, LiBr, KF, $Et_3N(CH_2Ph)Cl$, $Et_3N(CH_2Ph)I$, $Me_3N(CH_2Ph)Br$) incorporating the same halide anion as halide **3** (M = Si) in nearly stoichiometric quantities decreases the barrier to the permutation for all halides except for iodide **3** (M = Si). The $\Delta G^{\#}$ values for bromide and chloride **3** (M = Si) determined by dynamic ^1H NMR spectroscopy in CD_3CN in the presence of LiBr and LiCl, respectively, amount to 13.3 and 13.9 kcal mol^{-1}, whereas the corresponding values found in the absence of these salts are 14.2 and 14.4 kcal mol^{-1}, respectively. In addition, the signals in the ^{29}Si NMR spectra of these halides at −40 °C shift 6—7 ppm upfield with respect to their positions in CD_3CN in the absence of external nucleophiles.

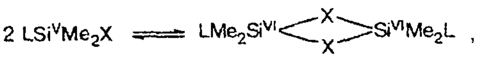
The addition of KF to a solution of fluoride **3** (M = Si) in CD_3OD decreases the $\Delta G^{\#}$ value even more substantially. In this case, the ^1H NMR signals of the $SiMe_2$ group coalesce already at 16 °C ($\Delta G^{\#}$ = 14.3 kcal mol^{-1}), and the ^{29}Si NMR spectrum exhibits a high-field signal at −31.4 ppm (−23.7 ppm in the absence of KF).

In the case of iodide **3** (M = Si), the addition of a stoichiometric amount of $Et_3N(CH_2Ph)I$ resulted in a slight increase in the barrier ($\Delta G^{\#}$ = 14.0 kcal mol^{-1}). It should be noted that the height of the barrier to the permutational isomerization in iodide **3** (M = Si) proved to depend on the concentration: as the concentration of the compound in CD_2Cl_2 increased from ~0.4 to ~0.7 mol L^{-1}, the $\Delta G^{\#}$ value increased from 12.7 to 14.5 kcal mol^{-1}.

The permutational isomerization in (O—Si)-chelate (*N*-dimethylsilylmethyl)amides and -lactams is accompanied by the inversion at the pentacoordinated silicon atom. In this respect, these compounds differ considerably from a broad range of compounds with the N→Si coordination bond, in particular, derivatives of type $Me_2NCH(Me)C_6H_4SiXYZ$, in which nondissociative permutation of ligands and processes involving cleavage of the chelate ring and inversion at the nitrogen atom have been observed, but no processes involving inversion at silicon are known.[2,45,66]

The occurrence of a regular process involving the inversion at silicon (Berry pseudo-rotation or the "turnstile" rotation mechanism equivalent to it) characterized by a relatively low activation free energy (~14—15 kcal mol^{-1}), which is normally observed for these processes, is relatively unlikely in the case of halides **3** (M = Si) and **4**—**6** (X = Cl), if one takes into account that this process requires that topomers with a diequatorial position of the chelate ligand participate in pseudo-rotation; to ensure this, the O—Si—C angle in the virtually planar five-membered ring needs to increase from ~90° to ~120°. Thus, in this case, only monodentate ligands can act as the "pivot" ligands,[8] and the process as a whole does not lead to equivalence of the methyl groups at the silicon atom (Scheme 4).

The possible equilibrium processes that require realization of nonregular mechanisms involving the initial pentacoordinated silicon halides, products of their ionization, and external nucleophiles are presented below (Eqs. (10)—(12a,b)).



$$2\,LSi^{V}Me_2X \rightleftharpoons LMe_2Si^{VI}\overset{X}{\underset{X}{<\!\!>}}Si^{VI}Me_2L\,, \qquad (10)$$

$$LSi^{V}Me_2X \rightleftharpoons [LSi^{IV}Me_2]^{+} + X^{-}, \qquad (11)$$

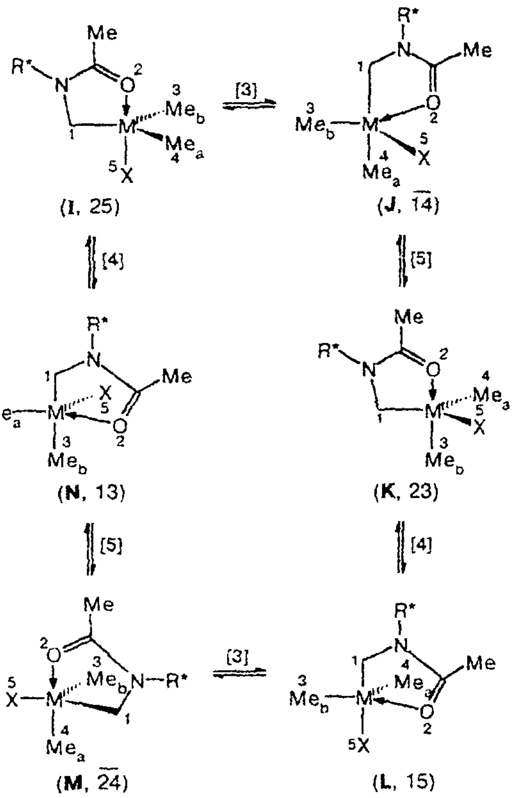
$$LSi^{V}Me_2X + X^{-} \rightleftharpoons LSi^{VI}Me_2X_2^{-}, \qquad (12a)$$

$$LSi^{V}Me_2X + X^{-} \rightleftharpoons L'Si^{V}Me_2X_2^{-}, \qquad (12b)$$

L is a bidentate chelate ligand,
L′ is a monodentate ligand, X = Hal.

An exchange process involving dimeric homoassociates containing hexacoordinated silicon atoms (Eq. (10)) has already been discussed for a series of

Scheme 4



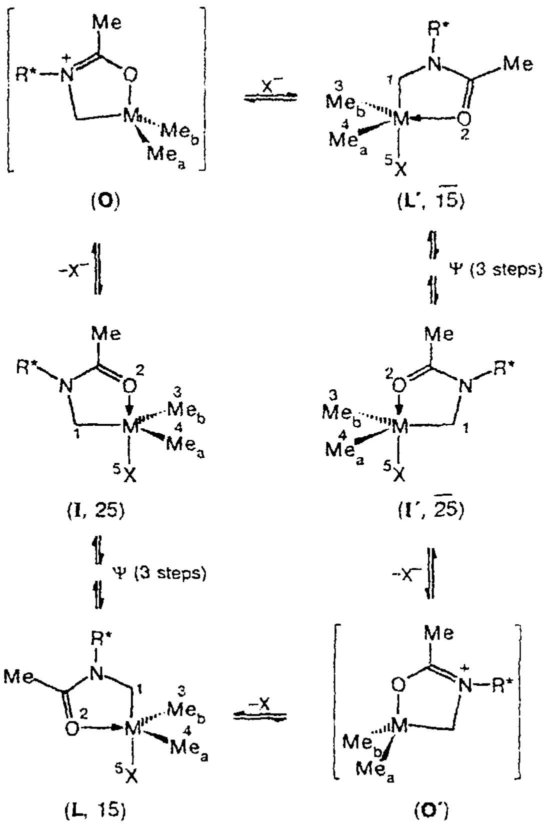
Note. In this review, we use a known system for designation of TBP stereoisomers. Substituents bound directly to the central atom are arbitrarily denoted by digits (from 1 to 5). The configuration of a particular isomer is specified by the digits corresponding to the numbers of axial ligands (for example, 15 and 25) if the ordinal numbers of equatorial ligands increase clockwise. If the ordinal numbers of the equatorial ligands increase counterclockwise (as in the case of the corresponding enantiomers), a bar is placed over the digit denoting an axial ligand (for example, $\overline{15}$, $\overline{25}$, see Scheme 5).

From here on, the number of the "pivot" ligand, which retains its equatorial position during pseudo-rotation, is given in brackets at the arrows.

pentacoordinated chlorides including chloride **3** (M = Si) (see Eq. (9)). In our opinion, this process can hardly be responsible for the observed exchange of the diastereotopic methyl groups at the silicon atom, which is relatively slow (on the NMR time scale). In fact, in the absence of external nucleophiles, the rate of this exchange in toluene-d_8 is sufficient for detecting it on the NMR time scale only at temperatures above 100 °C ($\Delta G^{\neq}$ >18.6 kcal mol^{-1}) (see Table 5) at which the homoassociate is virtually missing in the equilibrium (according to the above-discussed data on the position of the equilibrium between the monomers and the dimeric homoassociates).

Based on the obvious difference between the heights of the barriers in halides **3** (M = Si; X = Cl, Br, I) (~12—15 kcal mol^{-1}) in most solvents without external nucleophiles, on the one hand, and those for fluoride and chloride **3** (M = Si) in toluene-d_8, on the other hand ($\Delta G^{\neq}$ >24 and >18.6 kcal mol^{-1}, respectively) (see Table 4), it can be assumed that the nonregular dissociative mechanism of permutational isomerization (Eq. (11), Scheme 5) can be realized under these conditions. Apparently, this mechanism can be accomplished for chlorides **3—6** and bromide **3** (M = Si) in relatively polar solvents without external nucleophiles added. In the case of iodide **3** (M = Si), this mechanism is apparently retained in the presence of I$^-$ ions as external nucleophiles, which suppress the dissociation of iodide **3** and thus shift equilibrium (11) to the left. Consequently, the barrier to the permutational isomerization increases.

Scheme 5

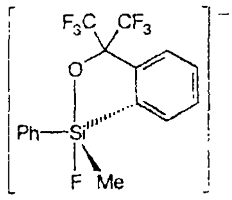


Note. Ψ is pseudo-rotation.

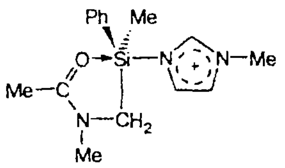
Taking into account the above-mentioned ability of substituted *N*-(dimethylsilylmethyl)lactams with relatively good leaving groups X to exhibit high electrical conductivities in appropriate solvents,[10,16,30] it can be assumed that dissociation to give ionic intermediate **O** with a tetrahedral silicon atom is the first step of the nonregular dissociative mechanism. The subsequent attack of this intermediate by a halide ion should occur not only from the rear but also from the front with respect to oxygen leading to intermediate L′ and should be followed by pseudo-rotation (three steps). Only in this case, the configuration of the silicon atom would be inverted.

The practicality of this assumption is supported by the fact that, depending on the natures of the nucleophile and the nucleofuge, bimolecular nucleophilic substitution at a tetrahedral silicon atom can occur both with inversion and retention of the configuration.[45] In the latter case, it is assumed that the nucleophile attacks the molecule from the frontal side with respect to the nucleofuge to give a TBP-intermediate (or a transition state) in which the entering group occupies an axial position, while the nucleofuge occupies an equatorial position; after that, pseudo-rotation occurs resulting in the nucleophile passing into an equatorial position and the nucleofuge passing into an axial position.[67]

Note that the dissociative exchange of ligands in siliconate **20** occurring without racemization of silicon is believed to involve an equilibrium between derivatives of tetra- and pentacoordinated silicon, which is responsible for the fast intermolecular exchange of fluorine atoms.[68]



20



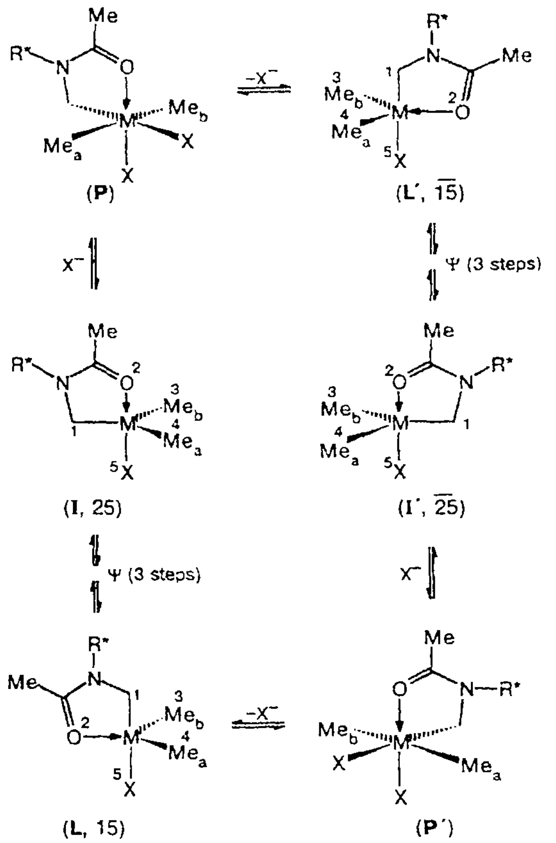
21

Data on the stereochemistry of nucleophilic substitution at a pentacoordinated silicon atom are few in number. It is known that reactions involving Si—Cl bonds occur with the retention of configuration.[45] An NMR study of the kinetics and stereochemistry of the degenerate exchange between derivative of pentacoordinated silicon **21** and *N*-methylimidazole has shown[69] that processes occurring with the inversion and with retention of the configuration at the silicon atom both contribute to the overall rate of the exchange. The following activation parameters of this reaction were found from kinetic measurements: $\Delta H \sim 10$ kcal mol^{-1} and $\Delta S \sim -4.8$ cal mol^{-1} K^{-1}.

The dissociative mechanism shown in Scheme 5 is close in some aspects to one of the two competing mechanisms discussed for the racemization of halosilanes $\mathrm{PhMeCHSiMe_2X}$ catalyzed by nucleophiles.[67] This mechanism involves a nucleophilic attack followed by inversion of the configuration in the silane complex with a nucleophile $[\mathrm{PhMeCHSiMe_2Nu}]^+$ (Nu = $\mathrm{Et_3N}$, HMPA, DMF, *N*-methylimidazole, *etc.*) formed at the preceding stage as a result of the replacement of the halogen atom by the nucleophile. Note that in the case of (O—Si)-chelate (N-dimethylsilylmethyl)amides and -lactams, the NC(O) fragment in the bidentate chelate ligand acts as the neutral nucleophile bound in a complex with the silane, while the nucleophilic attack of the complex is accomplished by a halide ion.

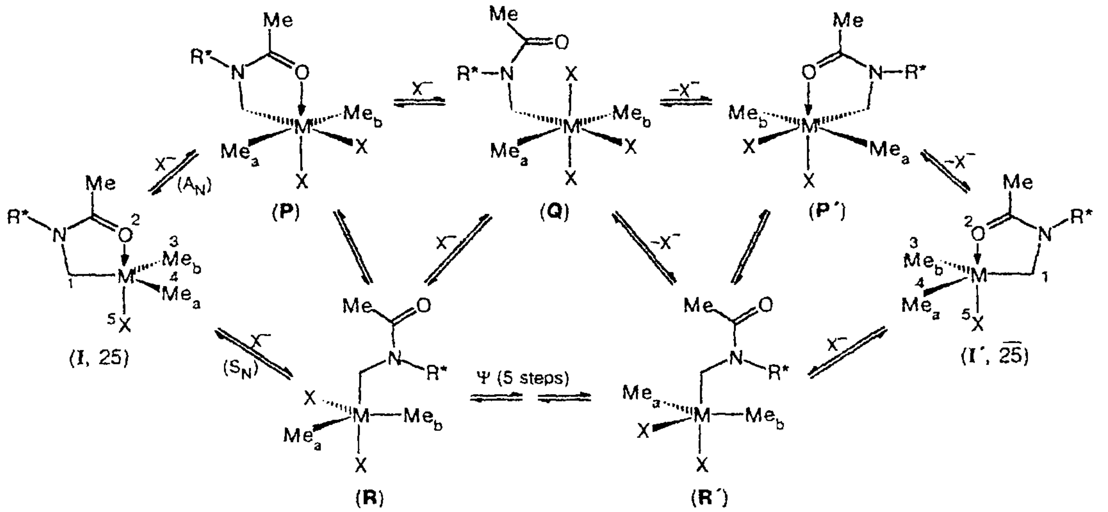
The decrease in the barrier to the permutational isomerization in halides **3** (M = Si; X = F, Cl, Br) in the presence of an external nucleophile indicates that this process might occur by an associative mechanism involving the formation of intermediates with hexacoordinated silicon atom. This mechanism can be realized with or without cleavage of the O→Si bond. The mechanism of the exchange of diastereotopic methyl groups $\mathrm{Me_a}$ and $\mathrm{Me_b}$ without cleavage of the coordination bond (Eq. (12a), Scheme 6, $\mathbf{I} \rightleftharpoons \mathbf{I'}$) includes a frontal attack, with respect to oxygen, on the silicon atom by the nucleophile that occurs from the side opposite to the $\mathrm{CH_2}$ group of the chelate ligand, the subsequent elimination of the halide ion from the axial position in hexacoordinated intermediate **P**, and pseudo-rotation (three steps) in the resulting pentacoordinated intermediate **L**′.

Scheme 6



The nonregular mechanism with cleavage of the O→Si bond (Eq. (12b), Scheme 7) can follow two alternative pathways: the intermediate hexacoordinated

Scheme 7

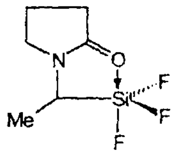


adducts can contain either one (P) (I $\rightleftharpoons$ P or I $\rightleftharpoons$ R $\rightleftharpoons$ P´) two (Q) nucleophilic species (I $\rightleftharpoons$ P $\rightleftharpoons$ Q or I $\rightleftharpoons$ R $\rightleftharpoons$ Q). The (R $\rightleftharpoons$ R´) transformation by pseudo-rotation (5 steps) is quite probable in view of the fact that all the five ligands in these intermediates are monodentate. In turn, data supporting the possible formation of 1 : 2 adducts (*i.e.*, adducts Q) have been obtained in a study of the reaction between *N*-(chlorodimethylsilylmethyl)lactams with tertiary amines.[27]

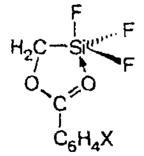
In our opinion, the mechanism of permutational isomerization that includes cleavage of the O—Si bond as the first step appears less likely. First, in the case of fluoride 3 (M = Si) and alkoxides 3 (M = Si; X = OMe, OPr^i), *i.e.*, compounds with the weakest O→Si coordination, realization of this mechanism should be associated with the lowest energy barrier; however, this is not observed in reality (see Table 5). Second, the cleavage of the O—Si bond followed by the recoordination could result in the inverted configuration at the silicon atom either as a result of the subsequent inversion in the tetrahedral intermediate due to exchange with a nucleophile or as a result of recoordination including an attack on the oxygen atom, frontal in relation to the electronegative substituent X, which is relatively unlikely.

The processes of permutational isomerization in *N*-(dimethylgermylmethyl)- and *N*-(dimethylstannylmethyl)amides and -lactams, unlike similar processes in their Si analogs, have been little studied by now. A comparison of the barriers to the permutational isomerization in chlorides 3 (M = Ge), **7b** (M = Ge), and 3 (M = Sn) with the corresponding parameters of chlorides of pentacoordinated silicon (see Table 5, CDCl$_3$) indicates that $\Delta G^{\#}$ increases on going from silicon derivatives to their Ge-analogs and then to Sn-analogs.[54,56] However, since the Lewis acidity of germanium and tin halides is higher than that of silicon halides, an increase in the donor properties of the solvent (transition from CDCl$_3$ to CD$_3$OD) leads to a more substantial decrease in the barrier to isomerization (to 15.7 kcal mol^{-1} for 3 (M = Ge; X = Cl) and 12.5 kcal mol^{-1} for 3 (M = Sn; X = Cl)). As in the case of Si analogs, an increase in the nucleofugal capacity of the substituent X at the Ge atom decreases the barrier to the permutational isomerization (for bromide 3 (M = Ge), the $\Delta G^{\#}$ value in CD$_3$CN is 17.0 kcal mol^{-1}).

According to the ^{19}F NMR spectra of trifluorides **22** [70] and **23**, [34,71] the axial and equatorial fluorine atoms are nonequivalent. The geminal F$_a$—F$_e$ spin-spin coupling constants vary in the 40—50 Hz range. The nonequivalence of the equatorial F atoms and their spin-spin coupling was observed for the first time for trifluoride **22**. The barrier to the inversion of the SiF$_3$ group was estimated from the coalescence temperature (~9.5 kcal mol^{-1}).



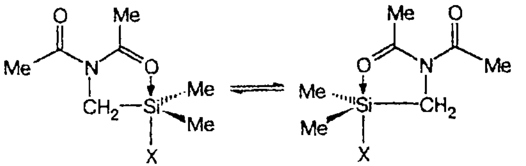
22



23

The fast (on the NMR time-scale) exchange between the fluorine atoms in (aroyloxymethyl)trifluorosilanes **23** is due either to pseudo-rotation involving the silicon atom or to consecutive cleavage and formation of the O→Si coordination bond.[71] The fact that the ^{29}Si—^{19}F and ^{19}F—^{1}H constants are retained rules out the possibility of intermolecular exchange of fluorine atoms. The results obtained indicate that the thermodynamic stability and the strength of the O→Si IntraCB in trifluorides increase as the electron-donating ability of substituents in the aromatic ring increases.

A new type of dissociative-associative stereodynamic transformations, namely, migration of silicon bound by an intramolecular O→Si coordination bond between two donor centers, was described for the first time in relation to the degenerate isomerization of (O—Si)-chelate dimethyl(*N*-acetylacetamidomethyl)silanes **11**.[49]



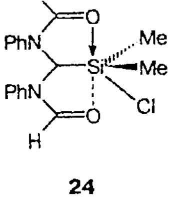
(13)

11

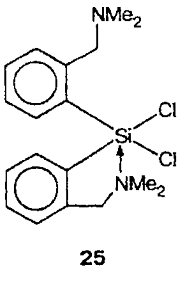
X = Cl, Br, I, OCOMe, $OCOCF_3$

Based on the data of ^{13}C and ^{29}Si NMR spectroscopy, the authors[49] suggested that the migration of silicon between the two oxygen atoms of the two acetyl groups occurs *via* dissociation of the IntraCB, rotation of the silylmethyl fragment and the two acetyl fragments through 180° around the corresponding C—N bonds, and formation of the new O→Si bond with the oxygen atom of the second acetyl group. Note that the free energy of activation of the degenerate isomerization (7.7—10.5 kcal mol^{-1}) is slightly higher than the typical barriers to the hindered rotation around the amide bond of *N*-diacetyl derivatives of aliphatic amines.[72] Depending on the substituent X, the height of the barrier to the stereodynamic process increases in the sequence OC(O)Me << Cl < $OC(O)CF_3$, Br << I, which matches the order in which the interaction between the silicon and oxygen atoms is enhanced. Therefore, it was assumed that it is the energy required for the dissociation of the O→Si bond that determines the thermodynamics of the degenerate isomerization and the ability of the silicon atom to migrate.

A similar migration has also been observed for dimethyl(*N*,*N*′-diformanilidomethyl)chlorosilane (**24**).[73]



24



25

According to ^{29}Si NMR spectroscopy, the Si atom in this compound is pentacoordinated (δ −33.7). However, the pairwise isochronism of the ^1H and ^{13}C NMR signals of the methyl and formyl groups up to −60 °C suggests the occurrence of rapid O(1)...Si←O(2) $\rightleftharpoons$ O(1)→Si...O(2) exchange (conversion of coordination) in solution. According to X-ray diffraction data, the silicon atom in solid chloride **24** has a distorted TBP-environment with two nonequivalent O—Si bonds (1.99 and 3.12 Å).

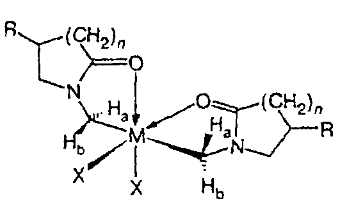
It should be noted that this type of migration of pentacoordinated silicon is also typical of compounds with N→Si coordination. For example, as shown by X-ray diffraction analysis, one 2-(dimethylaminomethyl)phenyl group in dichlorosilane **25** in the solid state is a bidentate ligand, while the other one is a monodentate ligand, and the silicon atom exists in a pentacoordinated state.[74] However, at elevated temperatures, rapid position exchange ("flip-flop"-coordination) between the chelating and nonchelating ligands occurs in solutions of this compound ($\Delta G^{\neq}$ = 11.2 kcal mol^{-1}).

6. Polytopic rearrangements in compounds of hexacoordinated germanium and tin

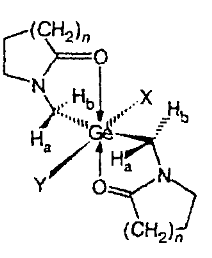
Stereochemical flexibility is a known characteristic feature of octahedral metal complexes.[75] A typical example is provided by *tris*-chelate aluminum(III), cobalt(III), and rhodium(III) complexes, stereodynamic processes in which have been investigated[76] by dynamic ^1H NMR spectroscopy. The heights of the barriers to the permutational isomerization (polytopic rearrangement) were calculated to be 11—17 kcal mol^{-1}. The barriers to the polytopic rearrangements in iron complexes containing a FeS_6 coordination unit (8—10 kcal mol^{-1}),[77] in β-ketoenolate complexes of silicon(IV), germanium(IV), tin(IV), and titanium(IV) (6—13 kcal mol^{-1}),[78—81] and in 1,4-bis{[2,6-bis((dimethylamino)methyl)phenyl]dihydrosilyl}benzene (8.3 kcal mol^{-1})[82] were determined in a similar way.

The data on the stereochemical flexibility of organic derivatives of hexacoordinated silicon with N→Si coordination accumulated by now have been presented in a review[2] and in a number of papers.[83—85] More extensive experimental information on the polytopic rearrangements in organic compounds of hexacoordinated tin has been surveyed in a review.[3] Data on the polytopic processes in organic derivatives of hexacoordinated tin and, especially, germanium characterizing their configurational stabilities are quite scarce. The effect of the nucleofugal properties of the substituents at the central atom on the height of the barrier to the isomerization has virtually not been considered until recently.

Due to the presence of an asymmetrical center, the M atom, the methylene protons of the NCH_aH_bM groups in compounds *cis*-**17a—d** (M = Ge, Sn) and *trans*-Ge-**18a,c,d** are diastereotopic. Consequently, they are nonequivalent in pairs in the ^1H NMR spectra and are exhibited as an AB-system quartet; in the case of compounds **18a,c,d**, this is observed even at room temperature, whereas for dihalides **17a—d** this is manifested at low temperatures (at a room temperature, the spectrum exhibits a somewhat broadened singlet).



cis-**17a—d**
M = Ge, Sn;
X = F, Cl, Br, I



trans-**18a,c,d**
X = Cl, Br;
Y = OTf, ClO4, I

As the temperature increases, the components of the quartet are reversibly broadened and coalesce into a singlet. This dynamic picture is typical of polytopic rearrangements in which the arrangement of ligands in octahedral complexes change.[75]

The activation free energies for dihalides **17a—d** (M = Ge, Sn) found by dynamic ^{1}H NMR spectroscopy are listed in Table 6.[12,55,56] The fact that these $\Delta G^{\#}$ values do not depend on the concentration of the solution implies a mostly intramolecular mechanism of the steps determining the rates of the polytopic processes under study.

It follows from the data presented in Table 6 that the barriers to the polytopic rearrangement for Sn derivatives are normally 1—3 kcal mol^{-1} higher than those for their Ge analogs. An increase in the size of the lactam ring in the bidentate ligand is accompanied by an increase in $\Delta G^{\#}$. This change is more pronounced in the case of Ge derivatives. As in the above-considered halides of pentacoordinated silicon and germanium **3** and **7b**, an increase in the nucleofugal capacity of the substituent X in the series Cl, Br, I results in a decrease in the $\Delta G^{\#}$ value. Note that in the case of tin dihalides, this tendency can be observed only for derivatives with five-membered lactam rings, *i.e.*, for compounds with weaker O→Sn coordinated bonds.

Table 6. The barriers to the polytopic rearrangement in (O—Ge)- and (O—Sn)-bis-chelate dihalobis(lactamomethyl)germanes and -stannanes **17a—d** ($CDCl_3$)[12,55,56]

Compound	M	X_2	$\Delta G^{\#}\pm0.2$ /kcal mol^{-1}
17a	Ge	Cl_2	10.6
	Ge	Br_2	10.2
	Sn	Cl_2	13.6
	Sn	Br_2	13.3
	Sn	I_2	12.6
17b	Sn	Cl_2	13.7
17c	Ge	Cl_2	12.8
	Ge	Br_2	12.1
	Sn	Cl_2	13.6
	Sn	Br_2	13.8
	Sn	I_2	13.8
17d	Ge	Cl_2	13.6
	Ge	Br_2	12.9
	Sn	Cl_2	13.9
	Sn	Br_2	13.9
	Sn	I_2	13.8

Our preliminary results concerning the activation free energies for compounds **18a,c,d** with *trans*-configurations make it possible to estimate the height of the barrier as >22 kcal mol^{-1} (the temperature of coalescence in $CDCl_3$ is > 55 °C),[54,55] which distinguishes these compounds from *cis*-dihalides **17a—d**.

The dynamic process observed in solutions of compounds **17a—d** and **18a,c,d** can occur by the following mechanisms: (a) abstraction of one monodentate ligand to give a TBP-intermediate followed by Berry pseudorotation; (b) cleavage of the O→M coordination bond, formation of a TBP intermediate, and subsequent Berry pseudo-rotation; (c) abstraction of one monodentate ligand or cleavage of the O→M coordination bond to give a square-pyramidal transition state; (d) a trigonal twist mechanism involving a trigonal-prismatic transition state. However, no data have yet been obtained that would permit one of these mechanisms to be preferred or rejected for the compounds in question.

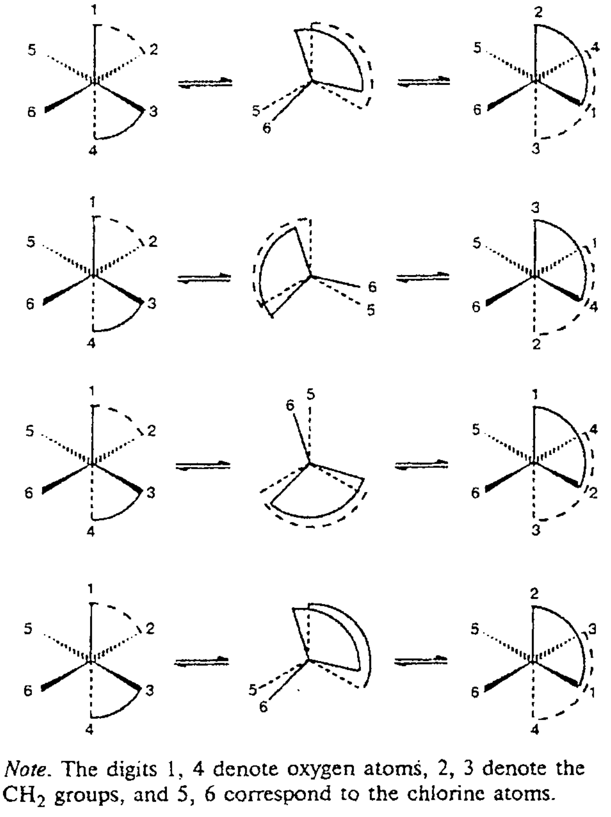
Based on the results of theoretical permutation analysis of octahedral complexes, it has been assumed that low barriers to the polytopic rearrangements are in better agreement with a regular trigonal twist mechanism.[86] The fact that a high activation free energy was found for the dichloride $Cl_2Ge(dpm)_2$ ($dpmH_2$ is dipivaloylmethane) (25.3 kcal mol^{-1}) and was not observed in the case of the monochloride $(C_6H_5)ClGe(acac)_2$ (12.8 kcal mol^{-1}) suggests, in the opinion of the authors cited,[78] that the mechanism of the process may be different depending on structural factors and on the nature of the ligands.

The sizes of the five-membered bidentate chelating ligands attached to the central atom in the compounds mentioned above are virtually identical; hence, the different $\Delta G^{\#}$ values are caused by the nature of the monodentate ligands and by the properties of the central atom, most of all, by the bond lengths in its coordination polyhedron including the O→M coordination bonds (M = Ge, Sn), whose strength depends on the size of the lactam ring (see Section 3).

The lower barriers found for five-membered lactam derivatives, *i.e.*, for compounds with weaker O→M coordination bonds (M = Ge, Sn), are not at variance with the mechanisms involving cleavage of this bond in the first step. However, the decrease in the $\Delta G^{\#}$ values following an increase in the nucleofugal capacity of the substituent at the M atom, which strengthens the coordination bond in the hypervalent fragment, is inconsistent with the above. The low electrical conductivity of solutions of **17a—d** (M = Ge, Sn)[12] is evidence against the dissociative mechanism according to which halide anions and germacenium or stannacenium cations containing a pentacoordinated germanium or tin atom, respectively, and stabilized by two O→M coordination bonds are formed during the reaction. Note that the relatively low free energies of the polytopic rearrangement in these compounds (10—14 kcal mol^{-1}) suggest that the mechanisms including pseudo-rotation steps in which the coordinating atoms of the chelate rings act as the pivot ligands are relatively unlikely,[79,81,87] as has already been discussed for the permutation of ligands in derivatives of pentacoordinated silicon and germanium (see Section 5).

The increase in the barrier to the polytopic rearrangement on going from dihalides **17a—d** to their Sn analogs suggest that in these two cases, the process follows different mechanisms. The close heights of the barriers to the polytopic rearrangements in Sn derivatives of six- and seven-membered lactams **17c,d**, indicates, in our opinion, that the trigonal twist mechanism is the most probable for these compounds (Scheme 8).

Scheme 8



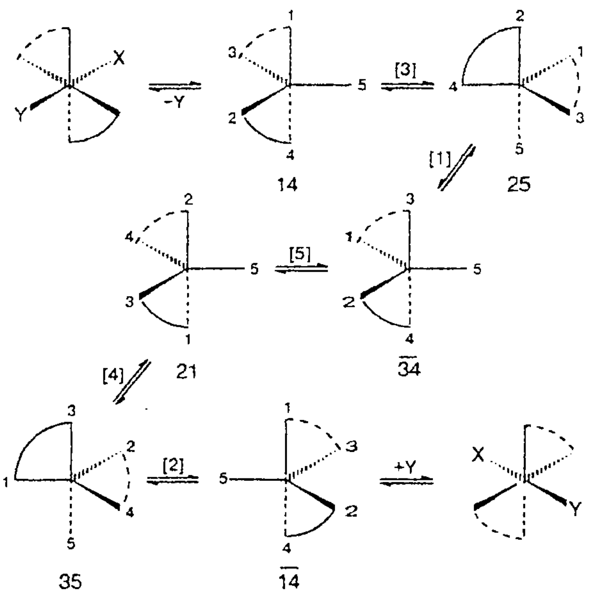
Note. The digits 1, 4 denote oxygen atoms, 2, 3 denote the CH_2 groups, and 5, 6 correspond to the chlorine atoms.

A similar mechanism of stereoisomerization has been proposed, in particular, for dibromobis[(2-dimethylaminomethyl)phenyl]stannane,[88] and also for triorganotin halides containing two C,N-chelating 8-dimethylamino-1-naphthyl ligands.[89]

Apparently, the substantial difference between the barriers to the permutational isomerization of *cis*-dihalides **17a—d** (M = Ge) and compounds **18a,c,d** with the *trans*-configuration (~10 kcal mol^{-1}) is mostly due to the different spatial structures of these compounds. The coordination polyhedron of the central atom in compounds **18a,c,d** is more "rigid," and the bonds between the germanium atom, the coordinating oxygen atoms, and one of the monodentate ligands (X) are markedly shorter than those in dihalides **17a—d** (M = Ge).[7] Conversely, the bond with the second monodentate ligand is extremely weak and, according to the results of conductometric studies,[7] it is able to dissociate under appropriate conditions to give germacenium cations stabilized by two O→Ge coordination bonds (see Eq. (7)).

Therefore, to describe the polytopic rearrangements in compounds **18a,c,d** with the *trans*-configurations of the coordination unit, we assume a two-step mechanism consisting of the dissociation of the monodentate ligand and Berry pseudo-rotation (Scheme 9). A similar mechanism of dissociative isomerization has been considered for difluorodialkoxydiarylpersulfuranes.[90]

Scheme 9



Note. The digits 1, 4 denote the oxygen atoms, 2, 3 denote the CH_2 groups, and 5 corresponds to the halogen atom.

Thus, the polytopic rearrangements in amidomethyl derivatives of hexacoordinated germanium and tin with C,O-chelating ligands can apparently occur by different mechanisms depending on the structure of the particular compound. A stricter reasoning supporting one or another mechanism requires additional experimental data and the results of quantum-chemical calculations, which is the object of our further studies.

The authors are grateful to V. A. Pestunovich and V. V. Negrebetsky for discussion of the problem of intermolecular association in solutions of compounds of pentacoordinated silicon and for recommendations concerning low-temperature NMR procedures, to L. S. Smirnova for providing the data on the electrical conductivities of compounds **3** (M = Si), **7c,d** (M = Si; X = Cl), and to Yu. E. Ovchinnikov for providing the X-ray diffraction data for disiloxane **3** (M = Si; X = O/2).

The works of the authors included in this review were carried out with the financial support of the Russian Foundation for Basic Research (Projects No. 93-03-4855 and No. 96-03-32718), the State Program "Universities of Russia," the Russian Federation State Committee on Higher Education (Science and Engineering Program "Fine Organic Synthesis," Project FT-13), and by the INTAS (Grant 93-1411).

References

1. V. E. Shklover, Yu. T. Struchkov, and M. G. Voronkov, *Usp. Khim.*, 1989, **58**, 353 [*Russ. Chem. Rev.*, 1989, **58** (Engl. Transl.)].
2. C. Chuit, R. J. P. Corriu, C. Reye, and J. C. Young, *Chem. Rev.*, 1993, **93**, 1371.
3. J. T. B. H. Jastrzebski and G. Van Koten, *Adv. Organometal. Chem.*, 1993, **35**, 241.
4. M. G. Voronkov and E. Ya. Lukevits, *Usp. Khim.*, 1969, **38**, 2173 [*Russ. Chem. Rev.*, 1969, **38** (Engl. Transl.)]; M. G. Voronkov, *Top. Curr. Chem.*, 1978, **84**, 77.
5. J. I. Musher, *Angew. Chem. Intern. Edit.*, 1969, **8**, 54.
6. V. F. Sidorkin, V. A. Pestunovich, and M. G. Voronkov, *Dokl. Akad. Nauk SSSR*, 1977, **235**, 1363 [*Dokl. Chem.*, 1977 (Engl. Transl.)].
7. M. G. Voronkov, V. A. Pestunovich, and Yu. I. Baukov, *Metalloorg. Khim.*, 1991, **4**, 1210 [*Organomet. Chem. USSR*, 1991, **4** (Engl. Transl.)].
8. A. A. Macharashvili, V. E. Shklover, Yu. T. Struchkov, G. I. Oleneva, E. P. Kramarova, A. G. Shipov, and Yu. I. Baukov, *J. Chem. Soc., Chem. Commun.*, 1988, 683; A. A. Macharashvili, *Ph. D. (Chem.) Thesis*, Moscow, Institute of Organoelement Compounds of the RAS, 1990 (in Russian).
9. G. Van Koten, J. T. B. H. Jastrzebski, J. G. Noltes, and A. L. Spek, *J. Am. Chem. Soc.*, 1978, **100**, 5021; D. Britton and J. D. Dunitz, *J. Am. Chem. Soc.*, 1981, **114**, 2971.
10. Yu. I. Baukov, A. G. Shipov, Yu. E. Ovchinnikov, and Yu. T. Struchkov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 982 [*Russ. Chem. Bull.*, 1994, **43**, 917 (Engl. Transl.)].
11. A. G. Shipov, S. Yu. Bylikin, Vad. V. Negrebetskii, and Yu. I. Baukov, *Zh. Obshch. Khim.*, 1995, **65**, 2066 [*J. Gen. Chem.*, 1995, **65** (Engl. Transl.)].
12. S. Yu. Bylikin, A. G. Shipov, Vad. V. Negrebetskii, L. S. Smirnova, Yu. I. Baukov, Yu. E. Ovchinnikov, and Yu. T. Struchkov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2768 [*Russ. Chem. Bull.*, 1996, **45**, 2627 (Engl. Transl.)].
13. K. D. Onan, A. T. McPhail, C. H. Yoder, and R. W. Hilliard, *J. Chem. Soc., Chem. Commun.*, 1978, 209.
14. R. W. Hillard, C. M. Ryan, and C. H. Yoder, *J. Organomet. Chem.*, 1978, **153**, 369; C. H. Yoder, C. M. Ryan, G. F. Martin, and P. S. Ho, *J. Organomet. Chem.*, 1980, **190**, 1.
15. C. H. Yoder, W. D. Smith, B. L. Buckwalter, C. D. Schaeffer, Ir., K. J. Sullivan, and M. F. Lehman, *J. Organomet. Chem.*, 1995, **492**, 129.
16. Yu. I. Baukov, E. P. Kramarova, A. G. Shipov, G. I. Oleneva, O. B. Artamkina, A. I. Albanov, M. G. Voronkov, and V. A. Pestunovich, *Zh. Obshch. Khim.*, 1989, **59**, 127 [*J. Gen. Chem.*, 1989, **59** (Engl. Transl.)].
17. I. D. Kalikhman, A. I. Albanov, O. B. Bannikova, L. I. Belousova, S. V. Pestunovich, M. G. Voronkov, V. A. Pestunovich, A. A. Macharashvili, V. E. Shklover, Yu. T. Struchkov, T. I. Khaustova, G. Ya. Zueva, E. P. Kramarova, A. G. Shipov, G. I. Oleneva, and Yu. I. Baukov, *Metalloorg. Khim.*, 1989, **2**, 637 [*Organomet. Chem. USSR*, 1989, **2** (Engl. Transl.)].
18. I. D. Kalikhman, A. I. Albanov, O. B. Bannikova, L. I. Belousova, M. G. Voronkov, V. A. Pestunovich, A. G. Shipov, E. P. Kramarova, and Yu. I. Baukov, *J. Organomet. Chem.*, 1989, **361**, 147.
19. V. A. Pestunovich, I. D. Kalikhman, Yu. I. Baukov, O. B. Bannikova, A. I. Albanov, L. I. Belousova, E. P. Kramarova, A. G. Shipov, and M. G. Voronkov, *Metalloorg. Khim.*, 1988, **1**, 719 [*Organomet. Chem. USSR*, 1988, **1** (Engl. Transl.)]; I. D. Kalikhman, *Sc. D. (Chem.) Thesis*, Irkutsk Institute of Organic Chemistry, Irkutsk, 1989 (in Russian).
20. C. H. Yoder, G. A. Gullinane, and G. F. Martin, *J. Organomet. Chem.*, 1981, **210**, 289.
21. A. G. Shipov, E. P. Kramarova, and Yu. I. Baukov, *Zh. Obshch. Khim.*, 1994, **64**, 1220 [*J. Gen. Chem.*, 1994, **64** (Engl. Transl.)].
22. Yu. I. Baukov, Yu. E. Ovchinnikov, A. G. Shipov, E. P. Kramarova, Vad. V. Negrebetsky, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1997, **536—537**, 399.
23. E. P. Kramarova, G. I. Oleneva, A. G. Shipov, and Yu. I. Baukov, *Zh. Obshch. Khim.*, 1991, **61**, 1918 [*J. Gen. Chem.*, 1991, **61** (Engl. Transl.)].
24. E. P. Kramarova, G. I. Oleneva, A. G. Shipov, Yu. I. Baukov, A. O. Mozzhukhin, M. Yu. Antipin, and Yu. T. Struchkov, *Metalloorg. Khim.*, 1991, **4**, 1016 [*Organomet. Chem. USSR*, 1991, **4** (Engl. Transl.)].
25. E. P. Kramarova, L. S. Smirnova, O. B. Artamkina, A. G. Shipov, Yu. I. Baukov, Yu. E. Ovchinnikov, A. O. Mozzhukhin, and Yu. T. Struchkov, *Zh. Obshch. Khim.*, 1993, **63**, 2275 [*J. Gen. Chem.*, 1993, **63** (Engl. Transl.)].
26. O. B. Artamkina, E. P. Kramarova, A. G. Shipov, Yu. I. Baukov, A. A. Macharashvili, Yu. E. Ovchinnikov, and Yu. T. Struchkov, *Zh. Obshch. Khim.*, 1993, **63**, 2289 [*J. Gen. Chem.*, 1993, **63** (Engl. Transl.)]; O. B. Artamkina, E. P. Kramarova, A. G. Shipov, Yu. I. Baukov, A. A. Macharashvili, Yu. E. Ovchinnikov, and Yu. T. Struchkov, *Zh. Obshch. Khim.*, 1994, **64**, 263 [*J. Gen. Chem.*, 1994, **64** (Engl. Transl.)].
27. A. G. Shipov, O. B. Artamkina, E. P. Kramarova, G. I. Oleneva, N. A. Nepomnyashchaya, and Yu. I. Baukov, *Zh. Obshch. Khim.*, 1995, **65**, 272 [*J. Gen. Chem.*, 1995, **65** (Engl. Transl.)].
28. O. B. Artamkina, A. G. Shipov, N. Mokhammad, D. P. Krut'ko, G. S. Zaitseva, and Yu. I. Baukov, *Metalloorg. Khim.*, 1991, **4**, 688 [*Organomet. Chem. USSR*, 1991, **4** (Engl. Transl.)].
29. O. B. Artamkina, A. G. Shipov, and Yu. I. Baukov, *Zh. Obshch. Khim.*, 1995, **65**, 2005 [*J. Gen. Chem.*, 1995, **65** (Engl. Transl.)].
30. Yu. I. Baukov, A. G. Shipov, L. S. Smirnova, E. P. Kramarova, S. Yu. Bylikin, Yu. E. Ovchinnikov, and Yu. T. Struchkov, *J. Organometal. Chem.*, 1993, **461**, 39.
31. Yu. E. Ovchinnikov, Yu. T. Struchkov, Yu. I. Baukov, A. G. Shipov, E. P. Kramarova, and S. Yu. Bylikin, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1421 [*Russ. Chem. Bull.*, 1994, **43**, 1346 (Engl. Transl.)].

32. Yu. E. Ovchinnikov, Yu. T. Struchkov, Yu. I. Baukov, A. G. Shipov, and S. Yu. Bylikin, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1427 [*Russ. Chem. Bull.*, 1994, **43**, 1351 (Engl. Transl.)].
33. Yu. I. Baukov, A. G. Shipov, S. Yu. Bylikin, Vad. V. Negrebetsky, and Yu. E. Ovchinnikov, *Fargo Conference on Main Group Chemistry*, North Dakota State University, USA, 1996, P-27.
34. A. I. Albanov, *Ph. D. (Chem.) Thesis*, Irkutsk Institute of Organic Chemistry, Irkutsk, 1984 (in Russian).
35. V. A. Pestunovich, *Sc. D. (Chem.) Thesis*, Irkutsk Institute of Organic Chemistry, Irkutsk, 1985 (in Russian).
36. Vad. V. Negrebetsky, V. V. Negrebetsky, E. P. Kramarova, A. G. Shipov, and Yu. I. Baukov, *J. Organometal. Chem.*, 1995, **496**, 103.
37. Vad. V. Negrebetsky, A. G. Shipov, E. P. Kramarova, V. V. Negrebetsky, and Yu. I. Baukov, *J. Organometal. Chem.*, 1997, **530**, 1.
38. Vad. V. Negrebetskii, E. P. Kramarova, A. G. Shipov, and Yu. I. Baukov, *Zh. Obshch. Khim.*, 1997, **67**, 1304 [*J. Gen. Chem.*, **67**, 117 (Engl. Transl.)].
39. Vad. V. Negrebetskii, *Zh. Obshch. Khim.*, 1997, **67**, 104 [*J. Gen. Chem.*, 1997, **67** (Engl. Transl.)].
40. Vad. V. Negrebetskii, *Zh. Obshch. Khim.*, 1993, **63**, 2059 [*J. Gen. Chem.*, 1993, **63** (Engl. Transl.)].
41. Vad. V. Negrebetskii, Ph. D. (Chem.) Thesis, D. I. Mendeleev Chemical Engineering Institute, Moscow, 1992, 163 pp. (in Russian).
42. H. Marsmann, *NMR-17 Bas. Princip. Prog.*, 1981, **17**, 64; E. A. Williams, *The Chemistry of Organic Silicon Compounds*. Eds. S. Patai, Z. Rappoport, Wiley, Chichester, 1989, Ch. 8.
43. A. R. Bassindale and M. Borbaruah, *J. Chem. Soc., Chem. Commun.*, 1993, 352.
44. Yu. I. Baukov, A. G. Shipov, E. P. Kramarova, E. A. Mamaeva, O. A. Zamyshlyaeva, N. A. Anisimova, and Vad. V. Negrebetskii, *Zh. Org. Khim.*, 1996, **32**, 1259 [*J. Organ. Chem.*, 1996, **32** (Engl. Transl.)].
45. R. J. P. Corriu, S. Guerin, and J. J. E. Moreau, *The Chemistry of Organic Silicon Compounds*. Eds. S. Patai, Z. Rappoport, Wiley, Chichester, 1989, Ch. 4; R. J. P. Corriu, *J. Organometal. Chem.*, 1990, **400**, 81.
46. A. R. Bassindale and R. G. Taylor, *The Chemistry of Organic Silicon Compounds*. Eds. S. Patai, and Z. Rappoport, Wiley, Chichester, 1989, Pt. 1, Ch. 13.
47. J. J. Eisch and C. S. Chiu, *J. Organometal. Chem.*, 1988, **358**, C1.
48. Yu. E. Ovchinnikov, A. A. Macharashvili, Yu. T. Struchkov, A. G. Shipov, and Yu. I. Baukov, *Zh. Strukt. Khim.*, 1994, **35**, 100 [*J. Struct. Chem.*, 1994, **35**, No. 1 (Engl. Transl.)].
49. I. D. Kalikhman, O. B. Bannikova, L. I. Belousova, B. A. Gostevskii, E. Liepin'sh, O. A. Vyazankina, N. S. Vyazankin, and V. A. Pestunovich, *Metalloorg. Khim.*, 1988, **1**, 683 [*Organomet. Chem. USSR*, 1988, **1** (Engl. Transl.)].
50. V. A. Pestunovich, A. I. Albanov, M. F. Larin, M. G. Voronkov, E. P. Kramarova, and Yu. I. Baukov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 2178 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1980, **29** (Engl. Transl.)].
51. Yu. I. Baukov, A. G. Shipov, Vad. V. Negrebetskii, E. P. Kramarova, and O. A. Zamyshlyaeva, *Zh. Obshch. Khim.*, 1995, **65**, 2064 [*J. Gen. Chem.*, 1995, **65** (Engl. Transl.)].
52. R. Huisgen, H. Brade, H. Wals, and J. Glogger, *Chem. Ber.*, 1957, **90**, 1437.
53. N. A. Orlova, A. G. Shipov, Yu. I. Baukov, A. O. Mozzhukhin, M. Yu. Antipin, and Yu. T. Struchkov, *Metalloorg. Khim.*, 1992, **5**, 666 [*Organomet. Chem. USSR*, 1992, **5** (Engl. Transl.)].
54. Vad. V. Negrebetsky, A. G Shipov, S. Yu. Bylikin, L. S. Smirnova, and Yu. I. Baukov, *Proc. VIII Int. Conf. on the Organometallic Chemistry of Germanium, Tin, and Lead*, Tohoku University, Japan, 1995, P-26.
55. Yu. I. Baukov, A. G. Shipov, S. Yu. Bylikin, Vad. V. Negrebetsky, Yu. E. Ovchinnikov, and Yu. T. Struchkov, *Proc. VIII Int. Conf. on the Organometallic Chemistry of Germanium, Tin, and Lead*, Tohoku University, Japan, 1995, P-25.
56. Vad. V. Negrebetsky, S. Yu. Bylikin, and Yu. I. Baukov, *Fargo Conference on Main Group Chemistry*, North Dakota State University, USA, 1996, P-21.
57. V. F. Sidorkin, V. A. Pestunovich, G. K. Balakhchi, and M. G. Voronkov, *Dokl. Akad. Nauk SSSR*, 1987, **296**, 113 [*Dokl. Chem.*, 1987 (Engl. Transl.)].
58. Vad. V. Negrebetskii and Yu. I. Baukov, *Zh. Obshch. Khim.*, 1995, **65**, 2062 [*J. Gen. Chem.*, 1995, **65** (Engl. Transl.)].
59. A. I. Albanov, L. I. Gubanova, M. F. Larin, V. A. Pestunovich, and M. G. Voronkov, *J. Organometal. Chem.*, 1990, **244**, 5.
60. Yu. L. Frolov, T. N. Aksamentova, G. A. Gavrilova, N. N. Chipanina, V. B. Modonov, L. I. Gubanova, V. M. D'yakov, and M. G. Voronkov, *Dokl. Akad. Nauk SSSR*, 1982, **267**, 646 [*Dokl. Chem.*, 1982, **267** (Engl. Transl.)].
61. O. M. Trofimova, *Ph. D. (Chem.) Thesis*, Irkutsk Institute of Organic Chemistry, Irkutsk, 1995 (in Russian).
62. A. I. Albanov, V. A. Pestunovich, E. P. Kramarova, and Yu. I. Baukov, *Tez. dokl. III Vsesoyuzn. konf. "Spektroskopiya YaMR tyazhelykh yader elementoorganicheskikh soedinenii" (III All-Union Conf. "NMR Spectroscopy of Heavy Nuclei in Heteroorganic Compounds". Abstrs.)*, Irkutsk, 1989, 20 (in Russian).
63. K. Tamao, T. Mayashi, and Y. Ito, *Organometallics*, 1992, **11**, 2099.
64. K. Ebata, T. Inada, C. Kabato, and H. Sakurai, *J. Am. Chem. Soc.*, 1994, **116**, 3595.
65. F. Carre, R. J. P. Corriu, A. Kpoton, M. Poirier, G. Royo, J. C. Young, and C. Belin, *J. Organomet. Chem.*, 1994, **470**, 43.
66. R. J. P. Corriu, A. Kpoton, M. Poirier, G. Royo, and J. Y. Corey, *J. Organomet. Chem.*, 1986, **277**, C25; J. Boyer, R. J. P. Corriu, A. Kpoton, M. Mazhar, M. Poirier, and G. Royo, *J. Organomet. Chem.*, 1986, **301**, 131.
67. A. R. Bassindale, J. C.-Y. Lau, and P. G. Taylor, *J. Organomet. Chem.*, 1995, **490**, 75.
68. W. B. Farnham and R. L. Harlow, *J. Am. Chem. Soc.*, 1981, **103**, 4608.
69. A. R. Bassindale, S. G. Glynn, J. Jiang, D. J. Parker, R. Turtle, P. G. Taylor, and S. S. D. Brown, in *Organosilicon Chemistry II. From Molecules to Matherials*, Eds. N. Auner and J. Weiss, Weinheim, New York—Bazel—Cambridge, Tokyo, 1996, 411.
70. V. A. Pestunovich, M. F. Larin, A. I. Albanov, L. I. Gubanova, V. M. Kopylov, and M. G. Voronkov, *Izv. Akad. Nauk, Ser. Khim.*, 1983, 1931 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **30**, 1755 (Engl. Transl.)]].
71. A. I. Albanov, L. I. Gubanova, M. F. Larin, V. A. Pestunovich, and M. G. Voronkov, *J. Organomet. Chem.*, 1983, **244**, 5.
72. E. A. Noe and M. Raban, *J. Am. Chem. Soc.*, 1975, **97**, 5811.
73. J. C. Otter, C. L. Adamson, C. H. Yoder, and A. L. Rheingold, *Organometallics*, 1990, **9**, 1557.

74. R. Probst, C. Lewis, S. Gampra, E. Herdtweck, C. Zybill, and N. Auner, *Angew. Chem. Int. Ed. Engl.*, 1991, **103**, 1132; H. Handwerker, C. Leis, R. Probst, P. Bissinger, A. Grohmann, P. Kiprof, E. Herdtweck, J. Blumel, N. Auner, and C. Zybill, *Organometallics*, 1993, **12**, 2162.
75. F. Basolo and R. Pearson, *Mechanisms of Inorganic Reactions*, J. Wiley and Sons, Inc., Second Ed., 1967.
76. S. S. Eaton, J. R. Hutchison, R. H. Holm, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1972, **94**, 6411.
77. L. H. Pignolet, R. A. Lewis, and R. H. Holm, *J. Am. Chem. Soc.*, 1971, **93**, 360.
78. N. Serpone and K. A. Hersh, *J. Organomet. Chem.*, 1975, **84**, 177.
79. N. Serpone and K. A. Hersh, *Inorg. Chem.*, 1974, **13**, 2901.
80. P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Am. Chem. Soc.*, 1973, **95**, 75.
81. D. G. Bickley and N. Serpone, *Inorg. Chem.*, 1974, **13**, 2908.
82. F. Carre, C. Chuit, R. J. P. Corriu, A. Mehdi, and C. Reye, *Organometallics*, 1995, **14**, 2754.
83. I. D. Kalikhman, D. Kost, and M. Raban, *J. Chem. Soc., Chem. Commun.*, 1995, 1253.
84. C. Chuit, R. J. P. Corriu, A. Mehdi, and C. Reye, *Chem. Eur. J.*, 1996, 342.
85. F. Carre, C. Chuit, R. J. P. Corriu, A. Mehdi, and C. Reye, *J. Organomet. Chem.*, 1993, **446**, C6.
86. W. G. Klemperer, *J. Am. Chem. Soc.*, 1972, **94**, 6940.
87. E. L. Muetterties, *J. Am. Chem. Soc.*, 1969, **91**, 1636.
88. G. van Koten, J. T. B. H. Jastrzebski, and J. G. Noltes, *J. Organomet. Chem.*, 1979, **177**, 283.
89. J. T. B. H. Jastrzebski, P. A. van der Schaaf, J. Boersma, G. van Koten, D. A. A. de Ridder, and D. Heijdenrijk, *Organometallics*, 1992, **11**, 1521.
90. R. S. Michalak and J. C. Martin, *J. Am. Chem. Soc.*, 1982, **104**, 1683.

Received May 7, 1997