Synthesis, crystal and molecular structures, and stereochemical nonrigidity of *N*-(chlorodimethylgermylmethyl)- and *N*-(bromodimethylgermylmethyl)-*N*-[(*S*)-1-phenylethyl]acetamides and *N*-(chlorodimethylgermylmethyl)-4-phenyl-2-pyrrolidone

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Racemic *N*-(chlorodimethylgermylmethyl)-4-phenyl-2-pyrrolidone and the first optically active amide derivatives containing the asymmetrical carbon atom and the five-coordinate germanium atom, *viz.*, *N*-(chlorodimethylgermylmethyl)- and *N*-(bromodimethylgermylmethyl)-*N*-[(*S*)-1-phenylethyl]acetamides, were synthesized. Their structures were established by X-ray diffraction analysis. The geometric characteristics of the trigonal-bipyramidal valence environment about the germanium atoms are compared with those of analogous enantiomeric silicon compounds and the related five-coordinate germanium compounds. The barriers to permutational isomerization of the title compounds were determined by dynamic ^{1}H NMR spectroscopy. It was found that these barriers are higher than those of the corresponding silicon analogs.

Key words: five-coordinate germanium compounds, synthesis, X-ray diffraction study; stereochemical nonrigidity, dynamic and multinuclear NMR spectroscopy; optical activity.

Compounds containing chiral labels attract the attention of researchers, in particular, as objects for studying stereodynamic processes and asymmetric induction. However, only a few representatives of these compounds are presently known among numerous hypervalent silicon[1,2] and germanium[3] derivatives. In the case of the coordination number of 5, [α-(*N*-pyrrolidon-2-yl)ethyl]trifluorosilane,[4] the chloride and trifluoroacetate of *N*-(dimethylsilylmethyl)-4-phenyl-2-pyrrolidone,[5] *N*-(methyl-α-chloronaphthylsilylmethyl)-hexahydro-2-azepinone,[6] *N*-methyl-*N*-(chloromethylphenylsilylmethyl)acetamide,[7] and phenyl[2-(methoxymethyl)phenyl]silyltriflate[8] can serve as examples of these compounds with the O→Si coordination bond.

Previously, we have reported the syntheses and the structures of the fluoride and chloride of *N*-(dimethylsilylmethyl)-*N*-[(*S*)-1-phenylethyl]acetamide (**1** and **2**, respectively), which contain the achiral five-coordinate silicon atom and the asymmetrical carbon center,[9,10] as well as racemic *N*-(chlorodimethylsilylmethyl)-4-phenyl-2-pyrrolidone (**3**).[11] In the present work, we report on the preparation of their Ge analogs and the results of studies of these compounds by X-ray diffraction analysis and dynamic NMR spectroscopy. The compounds under study are the first optically active amide derivatives, *viz.*, *N*-(chlorodimethylgermylmethyl)- and *N*-(bromodimethylgermylmethyl)-*N*-[(*S*)-1-phenylethyl]acetamides (**4** and **5**, respectively) and racemic *N*-(chlorodimethylgermylmethyl)-4-phenyl-2-pyrrolidone (**6**), containing the asymmetrical carbon atom and the five-coordinate germanium atom. Compound **6** is of particular interest here as a derivative of five-membered lactam. In this connection, the intramolecular O→Ge coordination bond in molecule **6** would be expected to be weaker compared to those in the corresponding derivatives of amides of carboxylic acids and six- and seven-membered lactams.

Results and Discussion

Synthesis and structures of compounds 4—6. Five-coordinate germanium derivatives with the chiral carbon atom, like their Si-analogs,[9] were prepared with the use of *N*-[(*S*)-1-phenylethyl]acetamide[12] as the starting compound. *N*-Chlorodimethylgermylmethylation of the latter compound was performed according to two proce-

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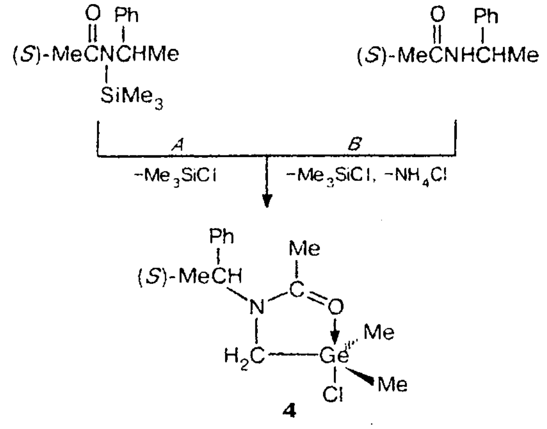
dures, *viz.*, by the reaction of the *N*-trimethylsilyl derivative of the above-mentioned amide with $ClCH_2GeMe_2Cl$ under thermodynamically controlled conditions* (transmetallation reaction (1), path *A*) and by the one-pot procedure with the use of the amide, hexamethyldisilazane, and $ClCH_2GeMe_2Cl$ (reaction (1), path *B*). Note that transmetallation has been used previously for preparing *N*-chlorodimethylgermyl derivatives of amides and lactams,[13,14] whereas *N*-chlorodimethylgermylmethylation of amides by the one-pot procedure was performed for the first time (recently, we have proposed this procedure for *N*-chlorosilylmethylation of amides and lactams).[15]

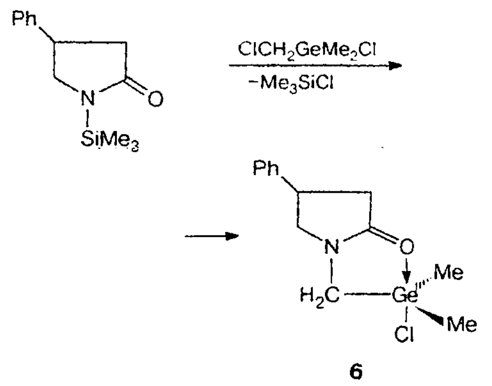


(1)

Reagents. *A*. $ClCH_2GeMe_2Cl$; *B*. $(Me_3Si)_2NH$, $ClCH_2GeMe_2Cl$.

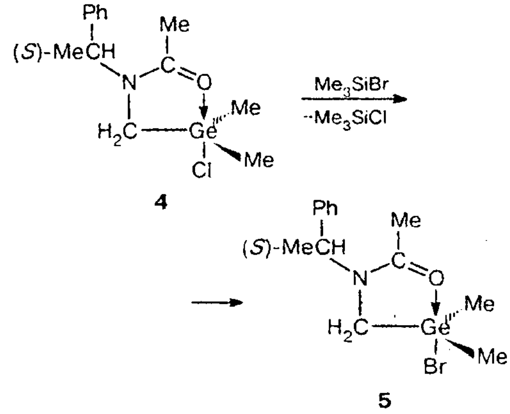
The yield of chloride **4**, which was prepared according to the second procedure (see reaction (1), path *B*), was higher (79%) than that obtained by transmetallation (64% with respect to the initial amide; see reaction (1), path *A*) taking into account the preliminary stage of silylation of *N*-[(*S*)-1-phenylethyl]-acetamide, which was necessary in the last-mentioned case.

Racemic chloride **6** was obtained by transmetallation (reaction (2)) in 77% yield.



(2)

Using conversions of chloride **4** into bromide **5** under the action of Me_3SiBr as an example, we performed substitution of the Br atom for the Cl atom in five-coordinate germanium chloride for the first time (reaction (3)). This reaction proceeded under rather mild conditions to give bromide **5** in 97% yield.



(3)

Satisfactory results of elemental analysis were obtained for halides **4**—**6**, which are described for the first time in the present work. The structures of these compounds were established based on the data of NMR and IR spectroscopy and confirmed by X-ray diffraction analysis.

In halides **4**—**6**, as in the other known *N*-(chlorodimethylgermylmethyl)amides and -lactams,[3] the Ge atoms are five-coordinate due to O→Ge intramolecular interaction. This is evidenced by the presence of two characteristic absorption bands of strongly coupled ν(C=O) and ν(C=N) stretching vibrations of the amide fragments in the 1500—1700 cm^{-1} region of the IR spectra of these compounds (see Ref. 13). The ν(C=O) absorption bands of the nonchelated amide (lactam) fragments are absent, which is indicative of a rather strong O→Ge coordination bond.

The parameters of the ^1H and ^{13}C NMR spectra of halides **4**—**6** confirming their structures are given in Tables 1 and 2, respectively. Reliable spectral (NMR) criteria which allow one to judge the presence of an intramolecular O→Ge coordination bond and the strength of this interaction in the compounds under study, unlike the Si analogs, are lacking. The five-coordinate state of the Ge atom in these compounds in solutions may be evidenced only by a downfield shift of the signal for the carbon atom of the carbonyl group in the ^{13}C NMR spectra of the compounds under consideration (see Table 2) compared to the chemical shifts of the corresponding signals in the spectra of model compounds containing the four-coordinate Ge atom. The replacement of the chlorine atom by the bromine atom on going from chloride **4** to its Br analog **5** is accompanied by an insignificant downfield shift of the signal for the carbon atom of the carbonyl group (see Tables 1 and 2).

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* The multistage scheme of analogous reactions of transmetallation has been discussed in detail previously.[13]

Table 1. Chemical shifts (δ) and spin-spin coupling constants ($^2J_{HH}$) in the ^{1}H NMR spectra of halides **4—6**

Compound	Solvent	δ ($^2J_{HH}$/Hz)								
		GeMe$_2$ (s)	NCH$_2$Ge (dd)	CH$_3$ (s)	$\underline{CH}CH_3$ (q)	$\underline{CH_3}CH$ (m)	Ph (m)	CH$_2$C(O) (m)	PhC$\underline{H}$NCH$_2$ (q)	(m)
4	CD$_2$Cl$_2$	0.79, 0.87	2.40, 2.77 (13.9)	2.23	5.13 (6.9)	1.67 (6.9)	7.2—7.4			
	[a]	0.84, 0.93	2.37, 2.83 (13.9)	2.35	5.17 (6.9)	1.69 (6.9)	7.3—7.4			
	CDCl$_3$	0.86, 0.93	2.51, 2.81 (14.0)	2.25	5.12 (6.9)	1.68 (6.9)	7.2—7.4			
	C$_6$D$_5$CD$_3$	0.97, 1.08	2.45, 2.68 (13.8)	1.54	4.32 (6.9)	1.02 (6.9)	6.8—7.1			
	CD$_3$OD	0.73, 0.84	2.40, 2.91 (13.9)	2.36	5.37 (6.9)	1.70 (6.9)	7.3—7.4			
	CD$_3$CN	0.71, 0.83	2.22, 2.75 (13.9)	2.23	5.23 (6.9)	1.63 (6.9)	7.3—7.4			
	[b]	0.65[c]	2.09, 2.63 (14.0)	2.11	5.11 (6.9)	1.51 (6.9)	7.2—7.3			
	[d]	0.69	2.09, 2.63 (14.0)	2.11	5.11 (6.9)	1.51 (6.9)	7.2—7.3			
5	C$_6$D$_5$CD$_3$	1.10, 1.22	2.58, 2.82 (13.9)	1.53	4.31 (6.9)	1.03 (6.9)	6.9—7.1			
	CD$_3$OD	0.74, 0.87	2.46, 3.04 (13.8)	2.43	5.44 (6.9)	1.74 (6.9)	7.3—7.4			
	CD$_3$CN	0.88, 0.99	2.46, 3.04 (13.8)	2.43	5.44 (6.9)	1.74 (6.9)	7.3—7.4			
	[e]	0.93	2.36, 2.89 (13.8)	2.43	5.44 (6.9)	1.74 (6.9)	7.3—7.4			
6	CDCl$_3$	0.96, 0.98	2.58, 2.85 (14.0)				7.2—7.3	3.49	3.67	3.84
	CD$_3$OD	0.90	2.58, 2.86 (13.9)				7.2—7.3	3.54	3.74	3.90
	CD$_3$CN	0.92[c]	2.46, 2.76 (13.9)				7.3—7.4	3.54	3.74	3.90

[a] At −90 °C.

[b] With the addition of an equimolar amount of LiCl.

[c] Br.s.

[d] With the addition of an equimolar amount of DMA.

[e] With the addition of an equimolar amount of LiBr.

Table 2. Chemical shifts (δ) in the ^{13}C NMR spectra of halides **4—6**

Compound	Solvent	δ												
		GeMe$_2$	NCH$_2$	$\underline{C}H_3C(O)$	C=O	$CH_3\underline{C}H$	$\underline{C}H_3CH$	C$_i$	C$_o$	C$_m$	C$_p$	C(3)	C(4)	C(5)
4	CD$_2$Cl$_2$	8.55, 8.72	35.80	19.94	173.18	57.02	17.54	139.18	129.36	126.85	128.48			
	CDCl$_3$	8.34, 8.52	35.69	19.72	172.65	56.74	17.57	138.52	129.14	126.28	128.29			
	C$_6$D$_5$CD$_3$	8.45, 8.64	36.28	19.30	172.12	56.48	17.10	139.45	129.07	126.42	128.09			
	CD$_3$OD	6.18	35.14	19.17	176.08	58.43	17.22	139.85	130.12	127.95	129.39			
	CD$_3$CN	8.57, 8.70	36.08	19.84	174.28	57.31	17.11	140.23	127.81	129.74	128.86			
5	C$_6$D$_5$CD$_3$	10.39	37.35	19.18	172.60	56.45	17.11	139.16	130.1	127.97	128.07			
	CD$_3$OD	4.14	33.89	18.92	177.18	58.85	17.21	139.37	130.21	128.08	129.59			
	CD$_3$CN	10.23, 10.36	37.57	19.78	175.11	57.53	17.16	139.97	129.89	127.93	129.08			
6	CDCl$_3$	8.08, 8.17	37.02		176.79			141.59	129.03	126.56	127.38	38.52	37.52	57.05
	CD$_3$OD	7.24	37.70		178.57			143.38	129.99	127.88	128.25	39.00	38.54	58.18
	CD$_3$CN	8.69, 8.99	37.89		175.99			142.99	130.01	127.89	129.01	38.78	38.03	58.09

The ^{17}O signal of chloride **4** is observed at lower field (at δ 294, CDCl$_3$, 50 °C) compared to the analogous signal of its Si analog **1** (δ 261),[16] which is indicative of the lower donor ability of the oxygen atom with respect to the central atom in chloride **4**.

When the temperature was decreased to −100 °C, the ^{1}H and ^{13}C NMR spectra of chlorides **4** and **6** (in an equimolar mixture of CDCl$_3$ and CD$_2$Cl$_2$) have one set of signals. This fact distinguishes the compounds under consideration from the corresponding silicon derivatives, whose NMR spectra measured under analogous conditions have two sets of signals with different integrated intensities. The latter fact was interpreted[10] as the presence of an equilibrium between the five-coordinate monomer and the dimeric homoassociate with the six-coordinate Si atoms and bridging Cl atoms.

X-ray diffraction study. As can be seen from Tables 3—5, compounds **4** and **5** are isostructural. In addition, the molecular packings of their Si analogs **1** and **2**[9] are also virtually identical, which is obviously determined by the similarity of their rather rigid conformations. Chloride **6** (Tables 6 and 7) and its Si analog **3**[11] are also isostructural.

The asymmetrical centers in halides **4** and **5**, as in their Si analogs **1** and **2**, have the *S* absolute configuration (Fig. 1). On the whole, the molecules of compounds **4** and **5** and their Si analogs **1** and **2** have two internal rotational degrees of freedom, *viz.*, rotation both about the N(1)—C(3) and C(3)—C(31) bonds is possible. In molecules **3** and **6** (Fig. 2), this rotation is realized only for the Ph ring except for the slight conformational lability of the C(3)C(4)C(5) lactam fragment. However, the average difference between the corresponding torsion angles about the above-mentioned bonds (four angles per bond) are 2° and 4° for molecules **4** and **5**, respectively (in the Si analogs, 3° and 10°,

Table 3. Principal details of X-ray diffraction study and crystal-structural data for halides **4—6**

Parameter	**4**	**5**	**6**
Diffractometer	Siemens P3/PC		Syntex P2$_1$
Molecular formula	$C_{13}H_{20}ClGeNO$	$C_{13}H_{20}BrGeNO$	$C_{13}H_{18}ClGeNO$
Radiation	Mo-Kα	Mo-Kα	Mo-Kα
T/K	150	140	180
Scan mode	θ/2θ	θ/2θ	θ/2θ
$2\theta_{max}$/deg	60	54	60
a/Å	10.674(2)	10.737(2)	6.422(2)
b/Å	11.424(3)	11.587(3)	12.007(3)
c/Å	11.872(4)	11.902(4)	18.388(4)
α/deg	90	90	90
β/deg	90	90	97.55(2)
γ/deg	90	90	90
V/Å^3	1448(1)	1481(1)	1406(1)
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/n$
Z	4	4	4
d_{calc}/g cm^{-3}	1.442	1.610	1.476
Number of measured reflections	2429	1875	5176
Number of reflections used in the least-squares refinement	2021 ($I > 3\sigma(I)$)	1498 ($I > 2\sigma(I)$)	2732 ($I > 3\sigma(I)$)
R and R_w	0.030; 0.031	0.038; 0.036	0.039; 0.039
R and R_w for the inverted structure	0.051; 0.054	0.049; 0.048	—

Table 4. Principal bond lengths (d) in molecules **4** and **5**

Bond	d/Å	
	4	**5**
Ge(1)—Cl(1)	2.359(1)	—
Ge(1)—Br(1)	—	2.558(1)
Ge(1)—O(1)	2.203(3)	2.138(5)
Ge(1)—C(1)	1.946(4)	1.950(7)
Ge(1)—C(4)	1.933(4)	1.906(9)
Ge(1)—C(5)	1.927(4)	1.937(8)
O(1)—C(2)	1.258(4)	1.260(8)
N(1)—C(1)	1.474(5)	1.489(9)
N(1)—C(2)	1.342(4)	1.332(9)

respectively), and is only 1° for molecules **3** and **6**. Apparently, the conformational similarity indicates that this conformation is favorable regardless of the packing effects.

Table 5. Principal bond angles (ω) in molecules **4** and **5**

Angle	ω/deg	
	4	**5**
Cl(1)—Ge(1)—O(1)	169.5(1)	—
Br(1)—Ge(1)—O(1)	—	169.4(1)
Cl(1)—Ge(1)—C(1)	90.6(1)	—
Br(1)—Ge(1)—C(1)	—	89.0(2)
Cl(1)—Ge(1)—C(4)	96.7(1)	—
Br(1)—Ge(1)—C(4)	—	95.0(2)
Cl(1)—Ge(1)—C(5)	93.9(1)	—
Br(1)—Ge(1)—C(5)	—	91.9(2)
O(1)—Ge(1)—C(1)	79.1(1)	80.6(2)
O(1)—Ge(1)—C(4)	90.2(1)	92.1(3)
C(1)—Ge(1)—C(4)	118.0(2)	118.9(3)
O(1)—Ge(1)—C(5)	89.4(1)	91.3(3)
C(1)—Ge(1)—C(5)	120.7(2)	120.4(3)
C(4)—Ge(1)—C(5)	120.1(2)	120.4(3)
Ge(1)—O(1)—C(2)	110.6(2)	111.1(4)
C(1)—N(1)—C(2)	116.9(3)	116.5(5)
Ge(1)—C(1)—N(1)	112.3(2)	110.4(4)
O(1)—C(2)—N(1)	120.0(3)	120.4(6)

Table 6. Principal bond lengths (d) in molecule **6**

Bond	d/Å	Bond	d/Å
Ge(1)—Cl(1)	2.322(1)	Ge(1)—C(7)	1.921(5)
Ge(1)—O(1)	2.348(2)	O(1)—C(2)	1.239(4)
Ge(1)—C(1)	1.959(3)	N(1)—C(1)	1.447(4)
Ge(1)—C(6)	1.923(4)	N(1)—C(2)	1.325(4)

Table 7. Principal bond angles (ω) in molecule **6**

Angle	ω/deg	Angle	ω/deg
Cl(1)—Ge(1)—O(1)	170.6(1)	O(1)—Ge(1)—C(7)	87.0(1)
Cl(1)—Ge(1)—C(1)	92.0(1)	C(1)—Ge(1)—C(7)	120.5(2)
O(1)—Ge(1)—C(1)	78.6(1)	C(6)—Ge(1)—C(7)	118.4(2)
Cl(1)—Ge(1)—C(6)	97.5(2)	Ge(1)—O(1)—C(2)	105.3(2)
O(1)—Ge(1)—C(6)	87.1(2)	C(1)—N(1)—C(2)	120.7(2)
C(1)—Ge(1)—C(6)	118.1(2)	Ge(1)—C(1)—N(1)	111.0(2)
Cl(1)—Ge(1)—C(7)	97.8(1)	O(1)—C(2)—N(1)	122.7(3)

In the hypervalent OGeHal fragments of molecules **4—6**, the O—Ge distances (2.14—2.35 Å, see Tables 4 and 6) fall within the region of the average coordination distances; the corresponding Ge—Cl and Ge—Br bond lengths (2.32—2.36 and 2.56 Å, respectively) are larger than the standard (tetrahedral) bond lengths[17,18] by only 0.2—0.3 Å. In this case, the deviation of the geometry of this fragment from the ideal trigonal bipyramid is characterized by the value $\Delta\Omega = 2\pi - \Omega$ (Ω is the solid angle formed by the directions of the three equatorial bonds about the Ge atom[19]). This value is 39, 19, and 59 deg of the solid angle in molecules **4—6**, respectively.

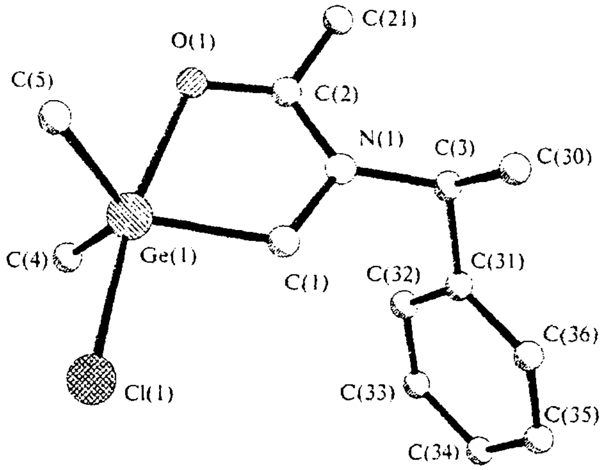


Fig. 1. Structure of molecule **4** in the crystal (the H atoms are omitted). Molecule **5** has an analogous structure; the atomic numbering schemes are identical.

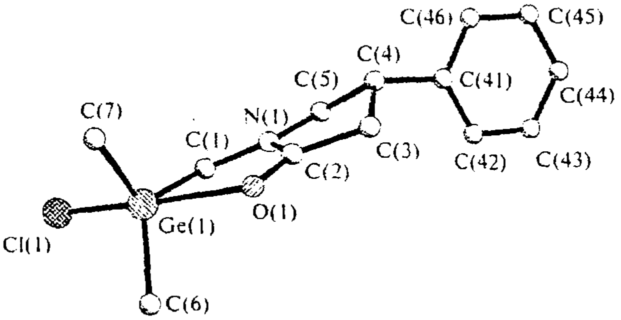


Fig. 2. Structure of molecule **6** in the crystal (the H atoms are omitted).

Apparently, the reason for an increase in the $\Delta\Omega$ values and the Ge—O distances in the case of the bidentate five-membered lactam ligand is identical to that in the case of the analogous five-coordinate silicon compounds.[11] The $\Delta\Omega$ values and the Ge—O distances in bromide **5** are smaller than the corresponding values in chloride **4** due to the fact that the bromide ion is a more readily leaving group than the chloride ion.

It is of interest to compare the parameters of the hypervalent bond in the pairs of molecules **2** and **4** and molecules **3** and **6**, which differ from each other only in the type of the hypervalent M atom. In both pairs, the asymmetry of the hypervalent O—M—Cl bond increases when the silicon atom is replaced by the germanium atom. In the pair of molecules **3** and **6**, which are characterized by the larger deviation of the coordination environment about the M atom from the ideal trigonal bipyramid, the increase in the asymmetry is also larger.

Let us also compare halides **4—6** and their Si analogs **1—3** with respect to another parameter, *viz.*, the relative deviations of the Ge and Si atoms from the plane through the three substituents $(\Delta_{M_s} - \Delta_M)/\Delta_{M_s}$ (where Δ_M is the deviation of the five-coordinate M atom from the equatorial plane toward the Hal atom and Δ_{M_s} is the deviation of the tetrahedral M atom from the plane through the three substituents in the model compound) on formally going from the four-coordinate state of the central atom to the five-coordinate state. The calculated values of this parameter along with the O—M and M—X bond lengths in the hypervalent OMX fragment (M = Si or Ge; X = Hal) and the Δ_M and Δ_{M_s} values are given in Table 8. Previously, we have suggested that this parameter be used for estimating the ability of the four-coordinate Si atom to deviate from the plane through the three substituents when subjected to the attack of the nucleophilic reagent (the O atom of the amide fragment) yielding a five-coordinate intermediate (*i.e.*, for estimating geometric rigidity of the Si substrate) and the donor ability of the oxygen atom in the C,O-chelating ligand with respect to the corresponding electrophilic center.[20] The deviation of the M atom from the plane through the three carbon atoms in the Me_3MHal molecules was used as the standard value of Δ_{M_s}. Since reliable structural data for the majority of these compounds are lacking, the Δ_{M_s} value was calculated from the geometry of Me_3MHal optimized by the AM1 method.[21]

Table 8. Dependence of the O—M and M—X bond lengths (*d*) in the hypervalent OMX fragment in compounds **1—6** on the nature of the M atom and the X substituent and the Δ_M and $(\Delta_{M_s} - \Delta_M)/\Delta_{M_s}$ parameters*

Compound	M	X	Δ_M /Å	$(\Delta_{M_s} - \Delta_M)/\Delta_{M_s}$	d_{O-M}	d_{M-X}
					Å	
1	Si	F	0.20	0.662	2.149	1.668
2	Si	Cl	0.05	0.991	1.975	2.306
3	Si	Cl	0.096	0.823	2.050	2.284
4	Ge	Cl	0.127	0.793	2.206	2.360
5	Ge	Br	0.066	0.906	2.138	2.557
6	Ge	Cl	0.197	0.679	2.349	2.916

* Δ_{M_s} = 0.592 (Me_3SiF), 0.543 (Me_3SiCl), 0.613 (Me_3GeCl), and 0.701 Å (Me_3GeBr).

The values of the relative displacements of the central Si and Ge atoms in the structurally similar compounds (see Table 8) are indicative of the higher geometric rigidity of the Ge atoms and the higher donor ability of the O atoms in amides **2** and **4** compared to those in the derivatives of five-membered lactam, *viz.*, in compounds **3** and **6**. These conclusions agree with those made previously about the influence of the nature of the central atom in the coordination unit and of the C,O-chelating ligands on the degree of intramolecular coordination in amidomethyl derivatives and related compounds of five-coordinate silicon and germanium (see, for example, Ref. 22).

Dynamic ^{1}H NMR spectroscopy. The presence of the carbon chiral lable in halides **4—6** leads to the chemical nonequivalence of the signals of the prochiral NCH_2 and $GeMe_2$ groups in the ^1H NMR spectra. As a result, in the NMR spectra measured at room temperature and at lower temperatures, the protons of the NCH_2 group are manifested as a multiplet of an AB system ($^2J_{HH}$ ≈ 14 Hz) and the protons of the $GeMe_2$ group are observed as two singlets with equal intensities. When the temperature is increased, the quartet for the protons of the NCH_2 group retains the chemical nonequivalence. At the same time, the temperature evolution typical of permutation processes is observed for the protons of the $GeMe_2$ group. Thus, both in solvents with a rather high donor ability and/or upon addition of external nucleophiles, the singlet signals are broadened and coalesce into a singlet with an averaged chemical shift (when the temperature is decreased, the spectral pattern is restored to its original form). The free activation energies ($\Delta G^{\neq}$) of the polytopic rearrangement of halides **4**—**6** and the temperatures of coalescence of the signals of the $GeMe_2$ group calculated by the dynamic ^1H NMR method are given in Table 9. The corresponding parameters for their Si analogs **1**—**3** [10,23] are given in Table 9 for comparison.

First, note an increase in the barrier to permutational isomerization, all other factors being the same, on going from the silicon atom to the germanium atom, which is indicative of the higher configurational stability of the five-coordinate Ge halides under consideration compared to their Si analogs. This is in agreement with the X-ray diffraction data on the higher rigidity of the central $OGeC_3Hal$ coordination unit compared to the structurally similar $OSiC_3Hal$ coordination unit (see above and Ref. 22).

Table 9. Barriers to permutational isomerization ($\Delta G^{\neq}$) and temperatures of coalescence (T_c) of the signals for halides **1**—**6**

Compound	M	X	Solvent	$\Delta G^{\neq}$±0.1 /kcal mol^{-1}	T_c /°C
1	Si	F	$CDCl_3$	14.9	24
			CD_3CN	14.4	17
			CD_3OD	12.0	−24
2	Si	Cl	CD_3CN	14.2	−13
			CD_3OD	11.9	−25
2 + LiBr	Si	Cl	CD_3CN	13.4	−2
3	Si	Cl	$CDCl_3$	11.0	−61
4	Ge	Cl	$CDCl_3$	> 23	
			CD_3CN	> 20	
			CD_3OD	15.7	43
4 + DMA *	Ge	Cl	CD_3CN	17.0	−67
5	Ge	Br	CD_3CN	17.0	67
			CD_3OD	15.3	36
5 + LiBr	Ge	Br	CD_3CN	13.0	−17
6	Ge	Cl	$CDCl_3$	17.8	60
			CD_3OD	11.3	21

* For DMA, $\Delta G^{\neq}$ = 21 kcal mol^{-1}, T_c = 67 °C.

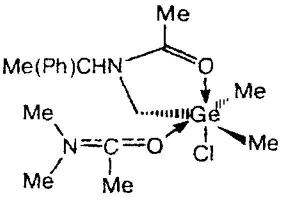
For chloride **4**, the signals of the $GeMe_2$ group are only slightly broadened in the temperature range from 20 to 90 °C in aprotic low-polarity solvents, such as $C_6D_5CD_3$, $CDCl_3$, CD_2Cl_2, and CD_3CN. In the 2D nuclear Overhauser enhancement NMR spectra (2D-NOESY) at 50 °C in $CDCl_3$ (at 90 °C in $C_6D_5CD_3$), low-intensity cross-peaks are observed between the signals of the $GeMe_2$ group, which are suggestive of the ligand positional exchange in the central coordination unit. The $\Delta G^{\neq}$ value, which was estimated based on the analysis of the total shape of the line, is >21 kcal mol^{-1}.

As in the case of the Si analogs,[10] the nature of the electronegative substituent at the central atom substantially affects the barrier to permutational isomerization. The replacement of the Cl atom by the Br atom on going from chloride **4** to bromide **5** leads to a decrease in the $\Delta G^{\neq}$ value (for example, to 17.8 kcal mol^{-1} in $CDCl_3$), which may be associated with an increase in the nucleofugicity of the substituent at the Ge atom and/or with an increase in the Ge—Hal distance. At the same time, the effect of the nature of the halogen atom in CD_3OD (in the solvent possessing the higher solvating ability) is virtually absent. Thus, for bromide **5**, $\Delta G^{\neq}$ = 15.3 kcal mol^{-1}, which is only 0.3 kcal mol^{-1} lower than that for chloride **4**.

In the above-mentioned solvent, the $\Delta G^{\neq}$ value is even lower for chloride **6** (11.3 kcal mol^{-1}). According to the data of X-ray diffraction analysis, the O—Ge distance in molecule **6** is larger than that in molecule **4** (see above), *i.e.*, the intramolecular O→Ge coordination bond in **6** is weaker.

As we demonstrated using halides **4** and **5** as examples, the corresponding decrease in the barrier to permutational isomerization occurs upon addition of external nucleophiles (LiBr or $MeCONMe_2$) in nearly stoichiometric amounts. Thus, the $\Delta G^{\neq}$ value for compound **5** in the presence of lithium bromide is 13.0 kcal mol^{-1} (in CD_3CN).

Addition of *N*,*N*-dimethylacetamide (DMA) to a solution of chloride **4** in CD_3CN leads to a decrease in the barrier to permutational isomerization (to 17 kcal mol^{-1}) and to an increase in the barrier to hindered rotation about the partially double C—N bond in DMA (from 17.4[24] to 21 kcal mol^{-1}). These results are consistent with the coordination at the oxygen atom of DMA upon its complexation with chloride **4**.



Possible mechanisms of ligand permutation (regular nondissociative and irregular dissociative or associative) in the coordination polyhedra of five-coordinate silicon.

germanium, and tin compounds containing the amidomethyl and related C,O-chelating ligands have been discussed in detail in the review.[23] Apparently, a regular process with the inversion of germanium (Berry's pseudorotation or an equivalent mechanism of turnstyle rotation) taking into account the low conductivity of *N*-(chlorodimethylgermylmethyl)-2-piperidone in CD_2Cl_2[19] occurs only in the case of chlorides **4** and **6** in $CDCl_3$ in the absence of additives of external nucleophiles. In CD_3OD as well as in CD_3CN in the presence of external nucleophiles (LiBr or DMA), associative mechanisms are more probable. These processes are accompanied by the formation of six-coordinate germanium intermediates both without and with the cleavage of the O→Ge coordination bond (*i.e.*, with the participation of one or two equivalents of the nucleophile) as well as by the formation of five-coordinate germanium intermediates with the cleavage of the O→Ge coordination bond (one equivalent of the nucleophile). The latter can undergo subsequent permutations according to the mechanism of pseudorotation, which are characterized by substantially lower values of $\Delta G^{\neq}$ compared to the initial halides because all five ligands in these intermediates are monodentate.[23]

In our opinion, five- and (or) six-coordinate intermediates with the cleavage of the O—Ge bond, in which the electronegative substituent (halogen) at the Ge atom is replaced by an external nucleophile, are the most probable compounds under the above-mentioned conditions (and, apparently, in the presence of external nucleophiles whatsoever), which is evidenced by a noticeable decrease in the $\Delta G^{\neq}$ value in CD_3OD on going from chloride **4** to chloride **6** with a weaker O→Ge coordination bond and, in addition, by the lowering of the barrier to permutational isomerization in the case of halides **4** and **5** in this solvent.

We believe that the mechanism of polytopic rearrangement in CD_3CN in the absence of a nucleophile is more complex. In particular, in the case of bromide **5** under the above-considered conditions, the solvent can serve as an external nucleophile or promote dissociation of the initial bromide to form an ionic intermediate with the tetrahedral germanium atom and the bromide ion. The latter, in turn, either acts as an external nucleophile with respect to the nondissociated molecule of bromide **5** (see the above-considered associative mechanisms) or attacks the ionic intermediate not only on the backside but also on the front with respect to the oxygen atom, which leads to the inversion of the configuration of the germanium atom, resulting in the chemical equivalence of the Me groups.[23]

Therefore, permutational isomerization in the germanium halides under study proceeds at different rates (depending on the nature of the halogen and the solvent as well as on the presence of an external nucleophile in the solution) predominantly according to the irregular mechanism, yielding five- and/or six-coordinate germanium compounds without the O→Ge coordination bond as the most probable intermediates.

Experimental

The IR spectra of ~5% solutions of the compounds in $CHCl_3$ were recorded on a Specord IR-75 instrument in KBr cells.

The ^1H, ^{13}C, and ^{17}O NMR spectra of the compounds in different solvents (C = 0.5 mol L^{-1}) were obtained on a Varian XL-400 spectrometer (400.1, 100.6, and 54.2 MHz, respectively) in the pulsed mode followed by Fourier transform and ^2H-stabilization of the resonance conditions. The ^1H and ^{13}C chemical shifts were measured relative to Me_4Si (the internal standard).

The temperature was calibrated against the distance between the signals for the nonequivalent protons of methanol (from −90 to +30 °C) and ethylene glycol (30—85 °C).[25] The free activation energies of permutational isomerization were calculated using the modified Eyring equation.[26]

The initial *N*-[(*S*)-1-phenylethyl]acetamide,[12] *N*-trimethylsilyl-*N*-[(*S*)-1-phenylethyl]acetamide,[9] and *N*-trimethylsilyl-4-phenyl-2-pyrrolidone[27] were synthesized according to procedures reported previously.

(O—Ge)-Chelated *N*-(chlorodimethylgermylmethyl)-*N*-[(*S*)-1-phenylethyl]acetamide (4). ***A.*** A solution of $ClCH_2GeMe_2Cl$ (1.3 g, 7 mmol) and *N*-trimethylsilyl-*N*-[(*S*)-1-phenylethyl]acetamide (1.63 g, 7 mmol) in *o*-xylene (10 mL) was heated to boiling for 3 h and concentrated *in vacuo* to one-half of the initial volume. The crystals that precipitated were filtered off, washed with hexane, and dried. Chloride **4** was obtained in a yield of 1.76 g (81%), m.p. 86—87 °C (toluene), $[\alpha]_D^{20}$ +42° (MeCN, 12 mg mL^{-1}). IR ($CHCl_3$), ν/cm^{-1}: 1590 (s), 1500 (w). Found (%): C, 49.91; H, 6.48; Ge, 22.92. $C_{13}H_{20}ClGeNO$. Calculated (%): C, 49.67; H, 6.41; Ge, 23.10.

B. *N*-[(*S*)-1-Phenylethyl]acetamide (2.44 g, 15 mmol) and $(Me_3Si)_2NH$ (1.26 mL, 6 mmol) were added to a solution of $ClCH_2GeMe_2Cl$ (2.8 g, 15 mmol) in *o*-xylene (20 mL). The reaction mixture was heated to boiling for 3 h and the salt that precipitated was separated by filtration. The resulting solution was concentrated *in vacuo* to one-half of the initial volume. The crystals that precipitated were filtered off, washed with hexane, and dried. Chloride **4** was obtained in a yield of 3.7 g (78.5%), m.p. 85—87 °C (toluene).

(O—Ge)-Chelated *N*-(bromodimethylgermylmethyl)-*N*-[(*S*)-1-phenylethyl]acetamide (5). A solution of chloride **4** (0.81 g, 2.6 mmol) and Me_3SiBr (0.45 mL, 3 mmol) in MeCN (15 mL) was heated to boiling for 2 h. The solution was concentrated *in vacuo* and bromide **5** was obtained in a yield of 0.9 g (97%), m.p. 149—150 °C (benzene), $[\alpha]_D^{20}$ +60° (MeCN, 10 mg mL^{-1}). IR ($CHCl_3$), ν/cm^{-1}: 1590 (s), 1500 (w). Found (%): C, 43.72; H, 5.67; Ge, 20.41. $C_{13}H_{20}BrGeNO$. Calculated (%): C, 43.51; H, 5.62; Ge, 20.24.

(O—Ge)-Chelated *N*-(chlorodimethylgermylmethyl)-4-phenyl-2-pyrrolidone (6). A solution of *N*-trimethylsilyl-4-phenyl-2-pyrrolidone (3.51 g, 15 mmol) and $ClCH_2GeMe_2Cl$ (2.81 g, 15 mmol) in toluene (25 mL) was heated to boiling for 2 h and then heptane (15 mL) was added. The oil that formed was separated and crystallized under a heptane layer. Chloride **6** was obtained in a yield of 3.61 g (77%), m.p. 158—159 °C (toluene). IR ($CHCl_3$), ν/cm^{-1}: 1610 (s), 1515 (w). Found (%): C, 50.21; H, 6.03; N, 4.60. $C_{13}H_{18}ClGeNO$. Calculated (%): C, 49.99; H, 5.81; N, 4.48.

X-ray diffraction study of halides 4—6. The principal details of X-ray diffraction study and crystal-structural parameters of compounds **4—6** are given in Table 3. The structures were solved by the direct method and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The positions of the H atoms were located from difference electron density syntheses and refined isotropically in the structures of **4** and **6** and refined with fixed C—H distances and thermal parameters U = 0.05 Å^2 in the structure of **5**. In the refinement of the structure of **5**, the absorption correction (μ = 47 cm^{-1}) was applied using the DIFABS program.[28] For halides **4** and **5**, the absolute configuration of the asymmetrical center (C*HMePhN) was determined with a reliability of >0.995 according to the Hamilton test. All calculations were carried out on an IBM PC/AT computer using the SHELXTL PLUS program package (version 4.0).[29] The principal bond lengths and bond angles are given in Tables 4—7. The remaining geometric parameters and the atomic coordinates in the structures of **4—6** were deposited with the Cambridge Structural Database.

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