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Reviews

Synthesis, structure and chemical properties of hypervalent germanium compounds, derivatives of lactams with a $\mathrm{C(\overset{}{O})NCH_2Ge}$ fragment*

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The results of studies aimed at elaborating methods for synthesizing penta- and hexacoordinated organogermanium derivatives containing lactamo-*N*-methyl and related bidentate ligands and investigating their structure and reactivity are reviewed. In these compounds the germanium coordination units include one or two O(or S)—Ge—X or N—Ge—X (X — an electron-deficient group) hypervalent fragments.

Key words: hypervalent organogermanium compounds, synthesis and structure; lactamo-*N*-methyl bidentate ligands; S_N reactions of penta- and hexacoordinated organogermanium compounds; germacenium ions stabilized by intramolecular coordination bonds.

The interest in hypervalent organogermanium and organosilicon compounds is caused mainly by their structural peculiarities, specific reactivity, and biological activity. Moreover, these compounds may also be regarded as possible intermediates in S_N reactions. At present, pentacoordinated organosilicon compounds have been comparatively well studied[1—3] and convenient methods for their synthesis have been elaborated. On the other hand, with the exception of germatranes,[4] the analogous organogermanium compounds are considerebly less well known. It is clear, however, that in some cases the germanium derivatives have undoubted advantages in experimental work due to their higher stability.

The results of recent studies of new penta- and hexacoordinated organogermanium compounds prepared by the reaction of trimethylsilyl derivatives of lactams and thiolactams with dimethylchloromethylchlorogermane and bis(chloromethyl)dichlorogermane are summarized in the present review and compared with the analogous silicon compounds.

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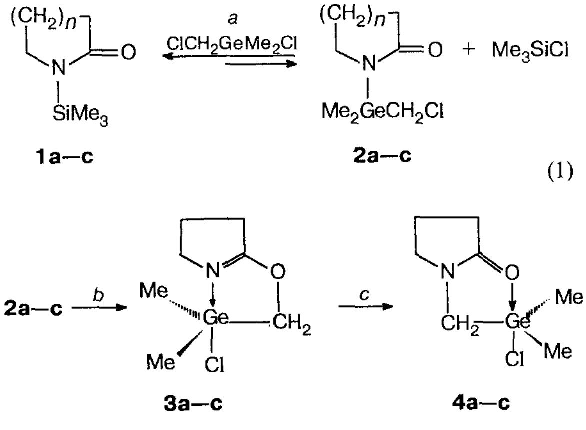
Pentacoordinated germanium compounds with the $\mathrm{C(O)NCH_2Ge}$ fragment and their analogs

First of all, the general pathway to final products by the reaction of *N*-trimethylsilyl (TMS) derivatives of lactams (**1**) with $ClCH_2GeMe_2Cl$ will be considered. ^1H NMR monitoring (in collaboration with M. G. Voronkov, V. A. Pestunovich and co-workers[5]) revealed that the first stage of the process is transmetallation with the concommitant elimination of Me_3SiCl (reaction (1), stage *a*). The transmetallation products (**2**) are formed immediately when the reagents are mixed in an inert solvent, $CDCl_3$, at −20 °C. Under these conditions the reaction is evidently reversible and, moreover, the equilibrium is shifted towards the starting compounds.

As the temperature increases, the transmetallation products **2** become unstable and undergo (at *ca.* −10 °C to +10 °C) a gradual conversion to the *O*-alkylation (*O*-germylmethylation) products, *i.e.* lactim ethers (**3**). This conversion is accompanied by migration of the chlorine atom from the carbon to the germanium atom (stage *b*). Thus, at room temperature compounds **2** practically do not exist.

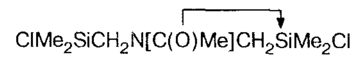
When the temperature is further increased, (up to ~60 °C) the lactim ethers **3** undergo intramolecular conversion to the *N*-alkylation (*N*-germylmethylation) products of lactams (**4**) (stage *c*). This conversion is analogous to the well-known Chapman rearrangement. However, it occurs under remarkably milder conditions. Thus, at 80 °C the period corresponding to 50 % conversion **3** → **4** amounts to 13 and 25 min for compounds **3b** and **3c**, respectively.



n = 1 (**a**), 2 (**b**), 3 (**c**)

Lactim ethers **3** can be isolated on a preparative scale (in ~80 % yields) if the reaction is carried out in an inert solvent (*e.g.*, in heptane) at 20 °C. In such experiments the reaction is "frozen" when bands related to compounds **4** appear in the IR spectrum of the reaction mixture. The thermodynamically more stable products of *N*-alkylation **4** were obtained (in 80 % yields) by heating the initial reactants at 60—100 °C for several hours. Under the same conditions the isolated lactim ethers **3** undergo isomerization into compounds **4**.

Conversions similar to **2** → **3** → **4** occur under much milder conditions for the corresponding Si-analogs. In this case, not only the transsilylation products (**Si-2**) but also the respective lactim ethers (**Si-3**) are formed as intermediates; this can be proved by NMR monitoring only.[6] Note that the reaction between $ClCH_2SiMe_2Cl$ and silylamide (*viz.* bis-TMS-acetamide) was first examined by Kowalski and Lasocki,[7] who proposed the transsilylation structure $MeC(O)N(SiMe_2CH_2Cl)_2$ for the resulting compound when the initial reagents were taken in the 2 : 1 ratio. However, an X-ray structural study showed that this compound had the structure of a bis-*N*,*N*-silylmethylation product (**5**) with the pentacoordination of one Si-atom due to the formation of the intramolecular coordination O→Si bond with an oxygen atom of the amido group.[8]


$ClMe_2SiCH_2N[C(O)Me]CH_2SiMe_2Cl$

5

($l_{Si^{IV}—Cl}$ 2.050 Å, $l_{Si^{IV}—Cl}$ 2.348 Å)

According to Yoder and co-workers,[9] the driving force of the process is the pentacoordination of the silicon atom in *N*-(dimethylhalogenosilylmethyl)amides which have been isolated as the only products of the reaction between acyclic TMS-amides and bifunctional silanes XCH_2SiMe_2Cl (X = Cl, Br; Y = Cl, Br, NEt_2). On the other hand, Sheludyakov and co-workers[10] believed that, when *N*-TMS-amides and -urethanes reacted with $ClCH_2SiMe_2Cl$, transsilylation preceded the silylmethylation stage; however, these authors did not discuss the possibility of the pentacoordination of the silicon atom in the final products. Finally, in parallel with our work[5], the synthesis of *N*-(dimethylchlorogermylmethyl)amides by the reaction of *N*-TMS-amides with $ClCH_2GeMe_2Cl$ has been published; however, neither intramolecular coordination in the final products, nor the scheme of their formation were discussed.[11]

An intramolecular O→Ge interaction in chlorides **4a—c** may be detected even from IR spectral data. As in the case of isostructural silicon compounds,[12] the N⩦C⩦O fragment in compounds **4a—c** is characterized by two absorption bands in the range of 1500—1750 cm^{-1}: a more intense band with a frequency of about 1600 cm^{-1} and a less intense band at ~1510 cm^{-1} which is typical of the (O—Ge)-chelate structure of such chlorides.[5]

In spite of the rather low stability of lactim ethers **3**, we succeeded in preparing a single crystal of the caprolactam derivative **3c**. An X-ray structural study shows that both in this compound and in the *N*-alkylation products **4a—c** the Ge atom has a trigonal bipyramidal (TBP) coordination with the N and Cl (in lactim ether

Table 1. Main characteristics of the TBP hypervalent fragments N—MC_3—Cl (M = Ge, Si) in molecules **3c**, **20a** and **Si-20a**: the displacement of the central atom M from the equatorial plane (Δ_M), the bond angle N—M—Cl, the bond lengths (*l*), and the relative bond lengthening (Δl) with respect to the corresponding bonds of the tetracoordinated atom

Compound	M	N—M—Cl /deg	Δ_M /Å	*l* (M—N) /Å	Δl (%)	*l* (M—Cl) /Å	Δl (%)	Ref.
3c	Ge	164.9(5)	0.00	2.15(2)	16	2.458(8)	14	13
20a	Ge	170.3(1)	−0.05	2.064(5)	11	2.566	19	13
Si-20a	Si	172.5(8)	−0.05	1.945(1)	11	2.423	18	27

Table 2. Main characteristics of the hypervalent fragments O—MC_3—Cl (M = Ge, Si) in chlorides **4a—c**, and their Si-analogs **Si-4a—c**: the displacement of the central atom M from the equatorial plane (Δ_M), the bond angle O—M—Cl, the bond lengths (*l*), and the relative bond lengthening (Δl) with respect to the corresponding bonds of the tetracoordinated atom

Chloride	Δ_M /Å	O—M—Cl /deg	*l* (M—O) /Å	Δl (%)	*l* (M—Cl) /Å	Δl (%)	Ref.
4a	0.192	171.3(1)	2.311(4)	32	2.324(2)	8	13
4b	0.147	170.6(2)	2.181(7)	25	2.363(3)	10	20
4c	0.154	170.6(2)	2.194(5)	25	2.354(2)	9	13
Si-4a*	0.096	172.2(6)	2.050(2)	25	2.284(1)	11	16
Si-4b	0.058	171.2(5)	1.954(2)	19	2.307(2)	13	16
Si-4c	0.055	171.7(7)	1.950(2)	19	2.315(1)	13	16

* 1-(dimethylchlorosilylmethyl)-4-phenyl-2-pyrrolidone.

3c) or O and Cl (in compounds **4a—c**) atoms in axial positions.[5,13,14] The main structural characteristics of the hypervalent fragments of these compounds are given in Tables 1, 2 and in Fig. 1.

As expected, the lone electron pair (LEP) of the nitrogen atom is a stronger electron donor than the LEP of the oxygen atom, and the N→Ge interaction in **3c** proved stronger than the O→Ge interaction in **4c**. This is confirmed by the values of the deviation, Δ, of the Ge atom from the equatorial plane: this atom has a symmetrical TBP configuration with Δ = 0 in compound **3c** and is distorted towards the Cl atom (Δ = 0.15 Å) in **4c**.

In accordance with the rule of the constancy of total order of the axial bonds in a hypervalent fragment,[15] the Cl—Ge bond is longer in **3c** (2.458 Å) than in **4c** (2.354 Å).

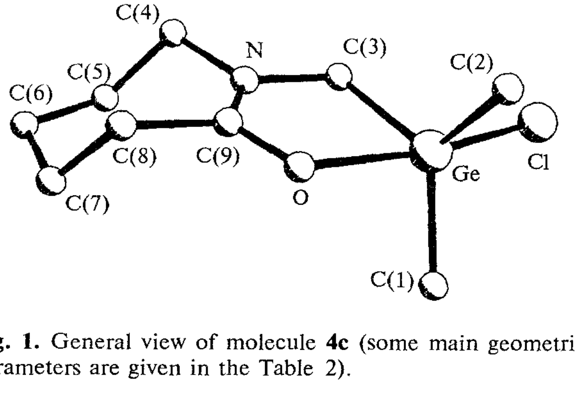
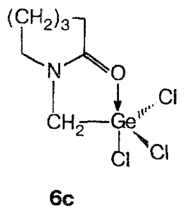


Fig. 1. General view of molecule **4c** (some main geometrical parameters are given in the Table 2).

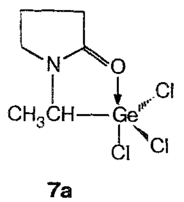
According to the criteria proposed on the basis of the X-ray structural data,[13] the intramolecular O→Ge coordination in chlorides **3c** and **4a—c** is rather "strong" (for a "strong" interaction the O(N)→Ge distances are 2.06—2.31 Å and the Ge—Cl distances are 2.57—2.24 Å, whereas in case of a "weak" interaction these distances are 2.48—3.23 and 2.33—2.13 Å, respectively).

An increase in the intramolecular O→Ge interaction in compounds **4a—c**, like their Si-analogs,[16] is observed when the lactam ring is enlarged from 5- to 6- and 7-membered (the relative lengthening of the O—Ge bond is 32 % in **4a** and 25 % in **4b,c**, respectively).

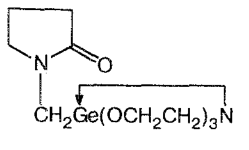
In the course of systematic studies of germatranes and their analogs (see review[4]), Mironov, Gar and coworkers synthesized series of amides, lactams and amides containing germatranyl, trihalogenogermyl or trialkoxygermyl groups. The structures of three compounds containing the lactam ring were confirmed by X-ray crystallography.



6c



7a



8a

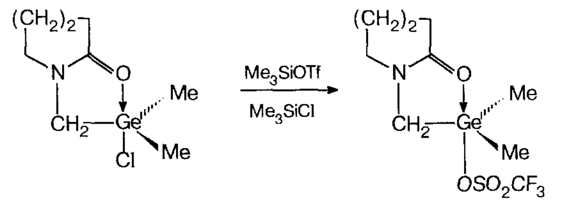
Table 3. Deviation of the central atom M from the equatorial plane (Δ_M), the bond angle O—M—X, the bond lengths (*l*), and the relative bond lengthening (Δl) with respect to the corresponding bonds of the tetracoordinated atom in the axial fragments $O—MC_3—X$ (M = Ge, Si; X = OTf, Cl) in mononuclear triflates **9b** and **Si-9b** and in binuclear chlorides and triflates **14**, **Si-14**, **15**, **Si-15** [20]

Compound	X	Δ_M /Å	O—M—X /deg	*l* (M—O) /Å	Δl (%)	*l* (M—X) /Å	Δl (%)
9b	OTf	−0.18	167.3(5)	1.90(1)	9	2.58(1)	47
Si-9b	OTf	−0.30	165.0(9)	1.753(18)	7	2.784(2)	70
14	Cl	0.20	168.8(1)	2.310(2)	32	2.322(1)	8
Si-14	Cl	0.11	170.5(1)	2.050(1)	25	2.271(1)	11
15	OTf	−0.09	169.1(1)	1.995(3)	14	2.335(3)	34
Si-15	OTf	−0.12	170.3(1)	1.843(2)	12	2.241(2)	37

The O→Ge (2.049 and 2.140 Å) and Ge—Cl(*a*) (2.268 and 2.253 Å) distances in trichlorides (**6c**)[17] and (**7a**)[18] are shorter than those in monochlorides **4a—c** examined by us and having a weaker coordination $O—Ge(C_3)—Cl$ unit. The equatorial Ge—Cl bonds are shorter than the axial ones by ~0.14—0.11 Å. The Ge atom in **6c** is displaced by 0.16 Å from the equatorial plane towards the chlorine atom, *i.e.*, in fact the same as in monochloride **4c**.

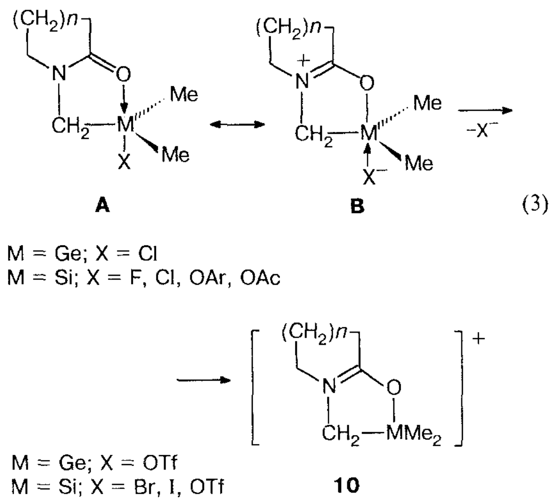
In the case of germatrane (**8a**)[19] the Ge atom is already pentacoordinate owing to the formation of the intramolecular coordination N→Ge bond and has no ability to interact further with the oxygen atom of the lactam ring.

Until now the reactivity of chlorides **4** has been studied only for a few examples. Thus, the reaction of chloride **4b** and trimethylsilyltriflate gives the corresponding triflate **9b** in a 69 % yield.[20]



4b **9b**

The X-ray structural data show that in crystals this compound, like its Si-analog **Si-9b**,[20] has considerably distorted but still TBP (4+1)-coordination; moreover the Ge—OTf bond is considerably elongated (2.258 Å). In accordance with the previously dicussed criteria, the intramolecular (C=)O→Ge interaction is, as expected, stronger than that in the initial chloride **4b**, but this interaction is still considerably weaker than in the Si-analog **Si-9b**.[20] In compound **9b** the lengtheninig of the M—O(Tf) bond (Table 3) is equal to 0.83 Å, against 1.146 Å for the Si-analog, **Si-9b** (one should also take into account that the M^{IV}—O bond in the case of Ge is longer by ~0.1 Å). The Ge atom deviates from the equatorial plane towards the oxygen atom of the lactam ring by Δ_{Ge} = −0.18 Å, whereas the Si atom deviates by Δ_{Si} = −0.30 Å. Thus, in contrast to chlorides **4** and **Si-4**, in triflates **9b**, **Si-9b**, the "additional bond", *i.e.*, the bond having a coordinative character, is M←OTf (canonical form **B**) rather than (C=)O→M (canonical form **A**).



A **B** (3)

M = Ge; X = Cl
M = Si; X = F, Cl, OAr, OAc

M = Ge; X = OTf
M = Si; X = Br, I, OTf

10

The electroconductivity of the hypervalent silicon compounds is higher than that of their Ge analogs (Table 4).[12,21] Nevertheless, the relatively high electroconductivity of triflate **9b** indicates that Ge-substituted *N*-(dimethyl-germylmethyl)lactams containing Ge-substituents, which are good leaving groups in S_N2 reactions, have the ability to dissociate, though this ability is probably somewhat lower than that of their pentacoordinated Si analogs with a similar structure.

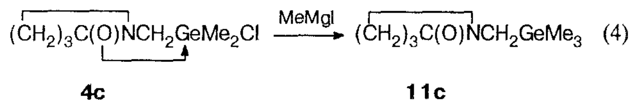
Therefore, as in the case of the $S_N—Si^V$ reaction of their Si-analogs, a *dissociative mechanism* is very probable for reactions of hexacoordinated germanium compounds, containing triflate or other relatively good leaving groups at the Ge atom. It should be noted that in the cations (**10**) formed, the germanium (or silicon) atom is tetracoordinated.

The study of the interaction between chlorides **3c** and **4c** with methylmagnesium iodide revealed that in the case of the thermodinamically more stable *N*-germyl-

Table 4. Molar conductivity (Λ) of the hypervalent silicon and germanium compounds in CH_2Cl_2 at 25 °C [21,33]

Compound	c /mmol L^{-1}	Λ /mSm cm^2 mol^{-1}
4b	18.9	6.4
9b	7.8	358
25a	6.9	39.1
25b	6.7	92.5
25c	5.0	262
26a	7.4	971
26b	5.7	1554
26c	10.0	1592
27c	0.8	6700
Si-4b	17.8	165
Si-9b	9.0	1151
Si-25a	10.4	2500
Si-25c	10.0	3660
Si-39a	4.9	5270
28c	1.6	3220
29c	1.9	1200
30c	1.4	4040

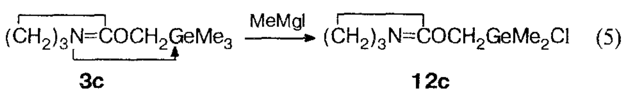
methylation product of lactam **4c** the reaction proceeds with a high degree of chemoselectivity at the Ge—Cl bond to give 1-(trimethylgermylmethyl)hexahydro-2-azepinone (**11c**) in ~80 % yield. According to the IR spectral data, the central atom in **11c** is tetracoordinated as in the structurally similar *N*-(trimethylsilylmethyl)lactams.[12,23]



$$(CH_2)_3C(O)NCH_2GeMe_2Cl \xrightarrow{MeMgI} (CH_2)_3C(O)NCH_2GeMe_3 \quad (4)$$

4c **11c**

By contrast, the similar reaction of the less stable lactim ether **3c** gives the corresponding methylated product (**12c**) in a low yield (~20 % only). Thus, either this process proceeds with less chemoselectivity or partial hydrolysis of the final reaction product (lactim ether **12c**) occurs during its isolation.

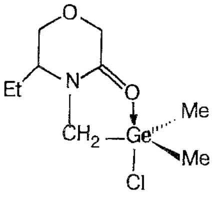


$$(CH_2)_3N{=}COCH_2GeMe_3 \xrightarrow{MeMgI} (CH_2)_3N{=}COCH_2GeMe_2Cl \quad (5)$$

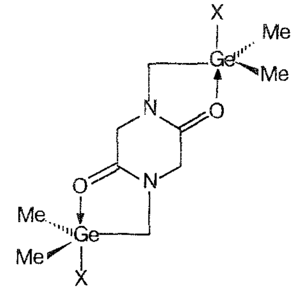
3c **12c**

In view of the vast possibilities for structural variation of the starting compounds in these reactions, it seemed interesting to examine the scope of the applicability of the general scheme (reaction (1), *a—c*) using the interacton of *N*-TMS-amides and -lactams with $ClCH_2GeMe_2Cl$[5] and $ClCH_2SiMe_2Cl$ as examples.[3,6] Thus, a thermodynamically controlled interaction of *N*-TMS-5-ethyl-3-morpholinone with $ClCH_2GeMe_2Cl$ affords the corresponding product of *N*-germylmethylation (**13**).[24]

A comparision of the main structural characteristics of compounds **13** and **4b** shows (see Table 2) that the replacement of the ^4C atom in the six-membered lactam cycle by an oxygen atom results in some weakening of the O→Ge coordinative interaction (the O→Ge bond becomes 0.084 Å longer and the Ge—Cl bond becomes 0.023 Å shorter, and the displacement of the germanium atom from the equatorial plane towards the chlorine atom increases from 0.147 Å to 0.176 Å). Similar weakening of the O→M interaction occurs also in 4-(dimethylchlorosilylmethyl)-2-ethyl-5-morpholinone (**Si-13**).[24]



13



14, 15, Si-14, Si-15

M = Ge, X = Cl (**14**), OTf (**15**);
M = Si, X = Cl (**Si-14**), OTf (**Si-15**)

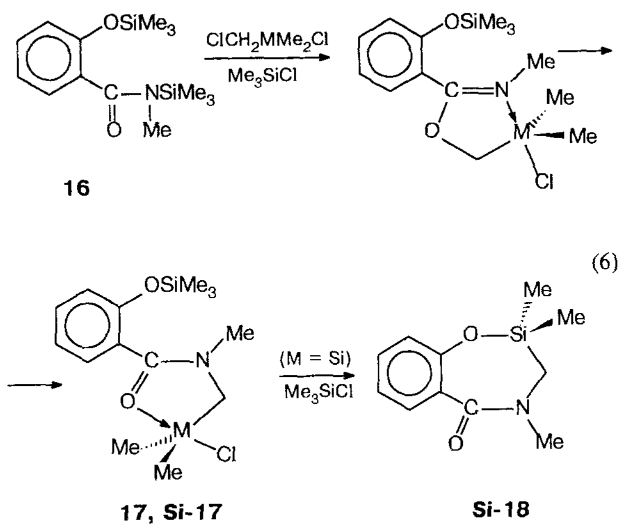
The thermodynamically controlled interaction of bis-*N*-TMS-2,5-piperazinedione with $ClCH_2GeMe_2Cl$ and $ClCH_2SiMe_2Cl$ also yields the formally tricyclic binuclear dichlorides (**14**) and (**Si-14**), whose reaction with excess trimethylsilyltriflate affords the corresponding ditriflates (**15**) and (**Si-15**).[14,20]

A comparison of the main structural characteristics of binuclear (**14**, **15**, **Si-14**, **Si-15**) and mononuclear (**4b**, **9b**, **Si-4b**, **Si-9b**) compounds shows (see Table 3) a weakening of the O→M (M = Si, Ge) interaction and a strengthening of the second axial bond in the binuclear structures. Indeed, in the latter compounds the O→M distances are always 0.09—0.13 Å longer, whereas the M—Cl distances are 0.04 Å shorter and the M—O(Tf) bonds are much shorter (by 0.24 Å and 0.54 Å for Ge- and Si-analogs, respectively). In the case of dichlorides **14** and **Si-14**, the displacement of the central atom from the equatorial plane is larger than for monochlorides **4b**, **Si-4b** (the difference of Δ_M values is equal to 0.05 Å); in ditriflates the Δ_M differences are 0.09 Å and 0.18 Å for Ge and Si analogs, respectively.

The reaction of the bis-*O*,*N*-TMS-derivative of the *N*-methylamide of salicylic acid (**16**) with $ClCH_2GeMe_2Cl$ and its Si-analog exemplifies a process involving an acyclyc amide derivative having an additional functional group (Eq. 6). These reactions were shown to proceed in accordance with the general scheme (reactions (1), *a—c*).

While in the case of $ClCH_2GeMe_2Cl$ the reaction affords the *N*-germylmethylated derivative (**17**) as a final product, which is sufficiently stable and can be distilled without decomposition, the corresponding

N-silylmethylated product (**Si-17**) is very unstable and on standing or distillation undergoes heterocyclization with elimination of Me_3SiCl and formation of the seven-membered silaoxaazaheterocycle (**Si-18**).[25]



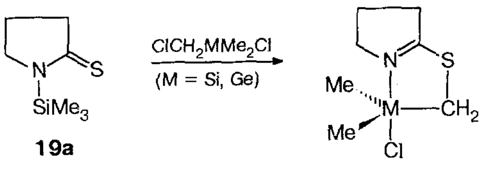
16

17, Si-17

Si-18

(M = Si, Ge)

As is shown by the example of the thiopyrrolidone derivative (**19a**), *N*-TMS-silylthiolactams, unlike *N*-TMS-lactams **1a—c**, react with $ClCH_2GeMe_2Cl$ to yield a sufficiently stable (N—Ge)-chelated product of S-germylmethylation (**20a**) as the final substance.[13] The chloride $ClCH_2SiMe_2Cl$ reacts similarly.[26,27]

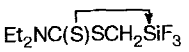


19a

20a, Si-20a

(7)

It should be noted that the hypervalent silicon and germanium compounds with (C=)S→M coordinate bonds have not been studied much. Our attempts to isomerize thiolactim ethers **20a** and **Si-20a** into the *N*-alkylation products were unsuccessful. At present the only example of such compounds is *N*,*N*-diethyldithiocarboamino-methyltrifluorosilane **Si-21**[28] with the intramolecular S—Si distance 2.697 Å, which is approximately by 1.2 Å shorter than the sum of the Si and S Van der Waals radii.[29]



$Et_2NC(S)SCH_2SiF_3$

Si-21

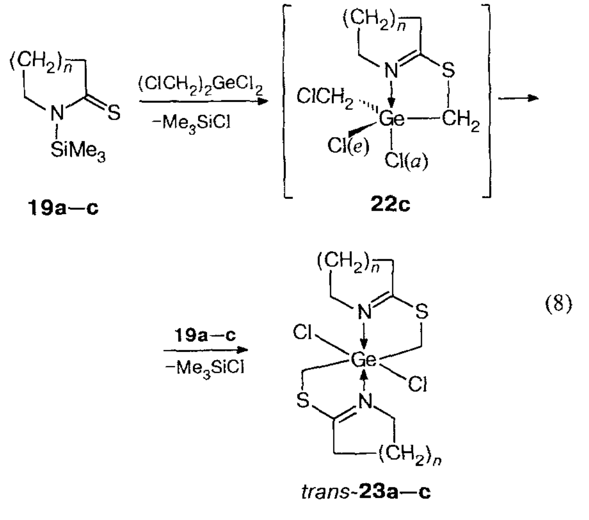
According to X-ray structural data, the N→Ge (2.054 Å) and Ge—Cl (2.566 Å) distances in thiolactim ether **20a** are the shortest and the longest, respectively, among the values known for pentacoordinated germanium derivatives. Moreover, the Ge atom is displaced from the equatorial plane towards the N(*a*) atom (Δ_{Ge} = −0.048 Å), *i.e*,. the Ge—Cl bond represents an "additional" bond.

The comparison of structural characteristics of the thiolactim ethers **20a** and **Si-20a** (see Table 1) shows that the strength of the intramolecular N—M (M = Si, Ge) interaction is approximately the same in the coordinative N—M(C_3)—Cl units ($\Delta_{Si} \approx \Delta_{Ge}$, the relative lengthening of the N(*a*)—M^V bond in comparison with the N—M^{IV} bond and its bond order are actually equal).

Hexacoordinated germanium compounds with the C(O)NCH$_2$Ge fragment and their analogs

In our opinion, the reaction of $(ClCH_2)_2GeCl_2$ with *N*-TMS-lactams, **1** and -thiolactams, **19** is very promising, because it should make it possible to obtain the practically unknown compounds of hexacoordinated germanium. The latter are interesting, in particular, as possible models of transition states or relatively stable intermediates in reactions of pentacoordinated germanium compounds. At this time, not all types of possible intermediates have been detected in these reactions. However, it is clear that in these cases the general schemes established for analogous reactions of bifunctional germanes and silanes $ClCH_2MMe_2Cl$ (M = Ge, Si; reactions (1), *a—c*, (7)) are, for the most part, valid.

The reaction of $(ClCH_2)_2GeCl_2$ with *N*-TMS-thiolactams **19a—c** in the 1 : 2 ratio proceeds under mild conditions (the reagents were mixed at −196 °C and allowed to reach room temperature under a vacuum to remove the Me_3SiCl that evolved). In the case of the caprolactam derivative we were able in one of experiments to obtain a very small quantity of the product of the reaction in a 1 : 1 ratio, *viz*., thiolactim ether (**22c**).



19a—c

22c

(8)

trans-**23a—c**

However, in these reactions bis(thiolactimo-*S*-methyl)dichlorogermanes (**23a—c**) proved to be the main products, formed in nearly quantitative yields.[30]

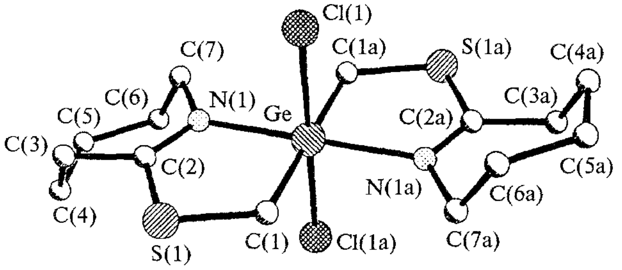


Fig. 2. General view of molecule *trans*-**23c**.

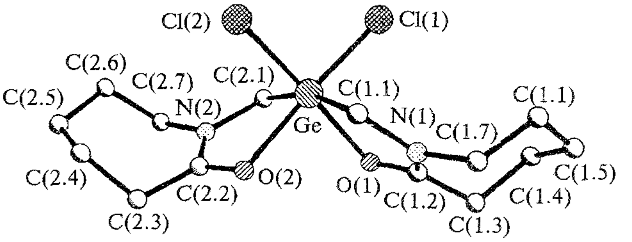


Fig. 3. General view of molecule *cis*-**25c** (some main geometrical parameters are given in the Table 5).

According to X-ray structural data the Ge atom in thiolactim ether **22c** is pentacoordinated. The geometric parameters of its coordination unit are close to those of thiolactim ethers **20a**. The distinct difference between the lengths of the axial and equatorial Ge—Cl bonds (2.41 and 2.17 Å) in the former molecule, indicating typical hypervalent interaction in the N(*a*)—Ge—Cl(*a*) fragment, should be noted. Moreover, this difference is essentially greater than that observed, for example, in (aroyloxymethyl)trifluorosilanes,[2] wherein the axial Si—F bond is longer than the equatorial one by about 0.03 Å, and somewhat longer than in the earlier discussed trichloride **3c** (0.135 Å for one chlorine atom and 0.143 Å for the other).[17]

According to X-ray structural data the Ge atoms in bis(thiolactimo-*S*-methyl)dichlorogermanes **23a—c** have slightly distorted octahedral coordination with two intramolecular N → Ge coordinate bonds, and both the chlorine atoms and the chelate rings also have a mutual *trans*-orientation (Fig. 2).

The Ge—N distances in (N—Ge)-bis-chelate compounds **23a—c** (2.03—2.12 Å) are rather close and the Ge—Cl distances (2.40—2.42 Å) are somewhat shorter than those in (N—Ge)-monochelate thioethers **20a** and **22c**, but both these distances are still essentially longer than in tetrahedral germanium compounds.

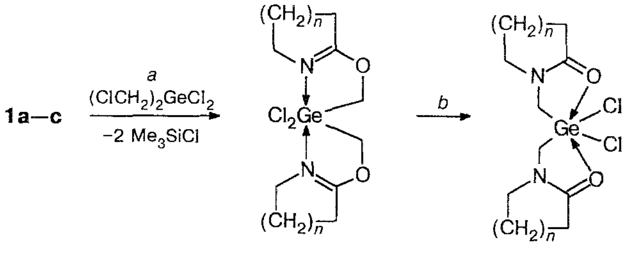
The interaction of $(ClCH_2)_2GeCl_2$ with *N*-TMS-lactams **1a—c** at a 1 : 2 molar ratio produces two types of fairly stable products. Bis(lactimo-*O*-methyl)dichlorogermanes (**24b**,**c**) are formed under kinetically controlled conditions (an inert solvent, 80—100 °C), (reaction (9), *a*). The thermodynamically more stable bis(lactamo-*N*-methyl)dichlorogermanes (**25a—c**) have been obtained under more drastic conditions, that is, by heating the starting reactants until the onset of a visible reaction (~90 °C) with evolution of Me_3SiCl and strong spontaneous heating to 155—175°C (reaction (9), *a*, *b*).[31,32]

The individual (N—Ge)-bis-chelate compounds **24b**,**c**, isolated on a preparative scale, isomerize to the corresponding (O—Ge)-bis-chelate compounds **25b**,**c** when boiled in *p*-xylene (~140 °C) for 0.5—1.5 h (reaction (9), *b*). Thus, the **24**→**25** isomerization proceeds under somewhat harsher conditions than the earlier discussed transformation **3**→**4** of mono-chelate compounds containing the pentacoordinated Ge atom.

Hexacoordination of the Ge atom in dichlorides **24** and **25** may be assumed on the basis of the IR spectra. The position and number of absorption bands in the 1500—1700 cm^{-1} region are, in fact, absolutely identical to the absorptions of the *O*- and *N*-germyl- and -silylmethylation products of *N*-TMS-lactams containing only one chelate ligand (*i.e.*, in compounds **3**, **4** and **Si-4**).[5,12]

According to X-ray structural data,[32] the germanium atoms in dichlorides **25a—c**, by analogy with bis(thiolactimo-*S*-methyl)dichlorogermanes **23a—c**, have octahedral coordination. However, both the chelate rings and the chlorine atoms have a *cis*-orientation relative to each other (Fig. 3).

The parameters of the Ge atom coordination in dichlorides *cis*-**25a—c** (Table 5) are close to those in monochlorides **4a—c** containing the pentacoordinated Ge atom (see Table 2). Though the O—Ge and Ge—Cl bonds in **25a—c** are somewhat shorter than those in the monochlorides **4a—c**, these distances are still significantly longer than those in tetracoordinated germanium compounds. Thus, *cis*-dichlorides **25a—c** have two



24b,e **25a—c** (9)

Table 5. Main geometrical parameters of the hypervalent O(1)—Ge—X(2) and O(2)—Ge—X(1) bonds in (O—Ge)-bis-chelated bis(lactamo-*N*-methyl)germanes *cis*-L_2GeX_2 (X = F, Cl, Br)

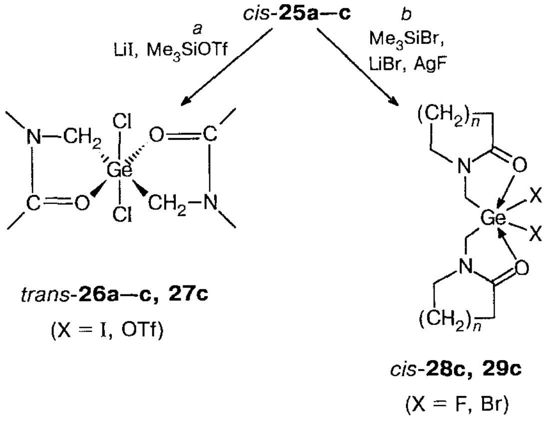
Compound	X	*l* (O(1)—Ge) /Å	*l* (Ge—X(2)) /Å	O(1)—Ge—X(2) /град	*l* (O(2)—Ge) /Å	*l* (Ge—X(1)) /Å	O(2)—Ge—X(1) /deg
25a	Cl	2.183(4)	2.284(2)	172.0(1)	2.239(4)	2.274(2)	171.6(1)
25b	Cl	2.093(7)	2.313(3)	173.2(2)	2.220(7)	2.280(2)	170.6(2)
25c	Cl	2.113(4)	2.312(2)	174.5(2)	2.137(6)	2.314(3)	174.1(2)
28c*	F	2.185(3)	1.799(2)	172.2(1)			
29c	Br	2.089(4)	2.506(1)	174.0(1)	2.087(4)	2.483(1)	173.4(1)

* The molecule on the twofold crystallographic axis.

O—Ge—Cl hypervalent fragments, and consequently one can expect their sufficiently high reactivity (although not as high as the reactivity of pentacoordinated germanium chlorides).

Indeed, regardless of the ratio of reactants (1 : 1 or 1 : 2), the reaction of dichlorides **25a—c** with trimethylsilyltriflate in MeCN proceeds with replacement of one chlorine atom and gives rise to the (O—Ge)-chelated bis(lactamo-*N*-methyl)-*trans*-(trifluorosulfonyloxy)-chlorogermanes (**26a—c**).[33] Lithium iodide reacts similarly to yield chloride-iodide (**27c**) in case of the caprolactam derivative.[34]

At the same time when excess Me_3SiBr is used or an excess of such inorganic salts as LiBr and AgF, the replacement of both chlorine atoms in dichloride **25c** is observed with the formation of dibromide (**28c**) and difluoride (**29c**), respectively. However in the case of $AgBF_4$ the product of the replacement of one chlorine by fluorine and of another by a BF_4 group, fluorotetrafluoroborate (**30c**) was unexpectly obtained.[35]



trans-**26a—c, 27c**
(X = I, OTf)

cis-**28c, 29c**
(X = F, Br)

According to X-ray structural data,[35] in the disubstituted products **28c** and **29c** with the same monodentate ligands as in initial dichlorides **25a—c**, the ligands of the same kind have a *cis*-orientation. It is very surprising that the formation of the monosubstituted products is accompanied by *cis→trans* isomerization, and the chelate rings and the monodentate ligands in compounds **26a—c** and **27c** have a *trans*-orientation.

In triflates **26a—c** the Ge atom has octahedral coordination strongly distorted towards a monocapped trigonal bipyramid (Fig. 4).

The Ge—Cl bond lengths in triflates **26a—c** (2.13—2.17 Å) are the shortest of those observed in hypervalent germanium structures, whereas the Ge—O(Tf) bond lengths (3.02—3.36 Å) are, on the contrary, the longest.

The structure of iodide **27c** crystals is almost ionic with weak Ge...I coordination (4.18 Å).[34] The coordination polyhedron of the germanium atom is a distorted trigonal bipyramid.

Finally, fluoro-tetrafluoroborate **30c** has a typical ionic structure and the configuration of the Ge atom valence bonds is a distorted trigonal bipyramid opened, as in iodide **27c**, towards the BF_4^- anion (Fig. 5).[35]

A comparison of the geometrical parameters of *trans*-bis(lactamo-*N*-methyl)germanes, *trans*-$L_2Ge(X)Y$ (L — chelate lactam ligand), (Table 6) shows that the electronic system of the Ge atom together with its valentce environment may be considered as two hypervalent O(1)—Ge—O(2) and X—Ge—Y subsystems which interact only slightly with each other. The Ge—O distances depend only weakly on the size of the lactam ring (its variation affects both oxygen atoms equally), whereas considerable variation (within 0.35 Å) of the length of the near-ionic sixth Ge...O bond takes place as a result of the first dependence.

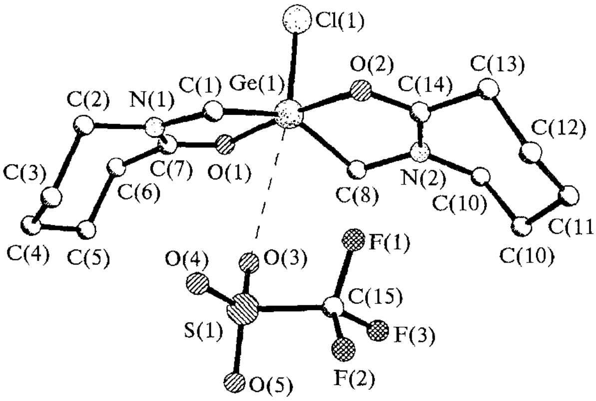


Fig. 4. General view of molecule *trans*-**26c** (some main geometrical parameters are given in the Table 6).

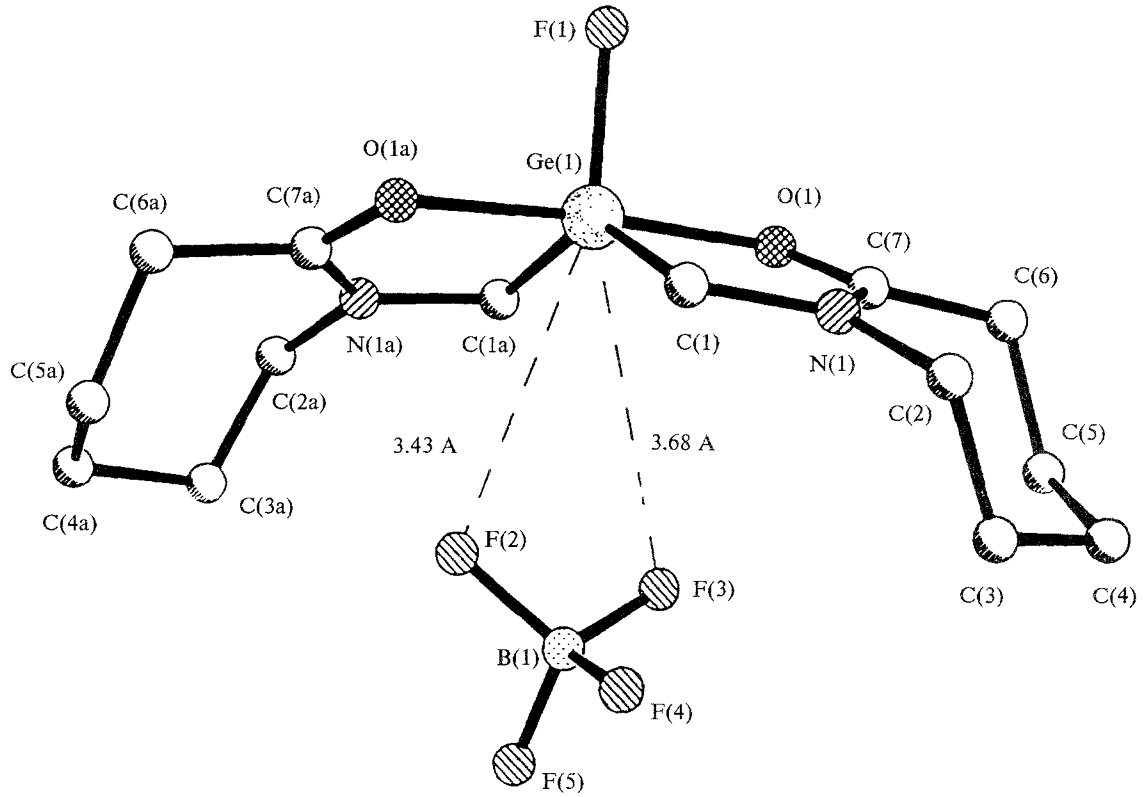


Fig. 5. General view of cation-anion pair **30c** (some main geometrical parameters are given in the Table 6).

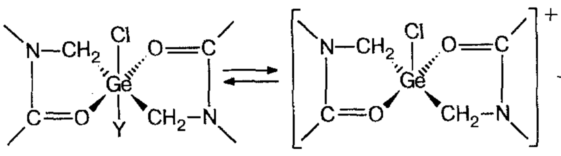
Table 6. Main geometrical parameters of the hypervalent O(1)—Ge—X(2) and X—Ge—Y bonds in (O—Ge)-bis-chelated bis(lactamo-*N*-methyl)germanes *trans*-$L_2Ge(X)Y$ (X = Cl, F; OTf, BF_4)

Compound	*l* (O(1)—Ge) /Å	*l* (O(2)—Ge) /Å	*l* (Ge—X) /Å	*l* (Ge—Y) /Å	O(1)—Ge—O(2) /deg	X—Ge—Y /deg	C(1)—Ge—C(6) /deg
26a	2.047(2)	2.028(2)	2.159(1)	3.015(2)	167.4(1)	169.1(1)	141.3(1)
26b	2.049(5)	1.984(5)	2.129(2)	3.355(5)	168.5(2)	165.3(2)	133.6(3)
26c	2.012(2)	1.980(2)	2.165(1)	3.135(5)	173.8(1)	165.5(1)	142.9(2)
27c*	2.006(4)	2.006(4)	2.178(3)	4.215(1)	171.5(3)	180	134.7(4)
	2.006(4)	2.006(4)	2.182(3)	4.219(1)	169.4(3)	180	138.1(4)
	2.006(4)	2.006(4)	2.215(2)	4.181(1)	170.7(2)	178.2(1)	135.5(3)
30c	2.001(4)	2.001(4)	1.792(8)	3.434(8)	175.8(7)	161.8(3)	136.6(6)

* Three crystallographically independent molecules.

On the existence of germacenium ions stabilized by the O→Ge coordinate bonds

The shortening of one and the considerable elongation of another of the pseudo-axial bonds with non-chelate monodentate ligands in the mixed bis-chelate compounds *trans*-$L_2Ge(X)Y$ suggests that the dissociation of these compounds may take place in sufficiently polar solvents to produce the corresponding $[L_2GeX]^+$ cations (**31**). This assumption has been confirmed by conductometric measurements (Table 4). The electroconductivity of *cis*-dichlorides **25a—c** in CH_2Cl_2 turned out to be rather low, as in the case of penta- and tetracoordinated covalent silyl- and germylhalides. When one of the halogen atoms in dichlorides **25a—c** is replaced with iodine or a triflate group the electroconductivity increases by *ca.* an order of magnitude and becomes close to the electroconductivity of fluorotetrafluoroborate **30c**, which retains a definitely ionic structure even in the crystalline state. Thus, the present data confirm the existence in solutions of germacenium cations with a pentacoordinated Ge atom, stabilized by intramolecular coordinate bonds.

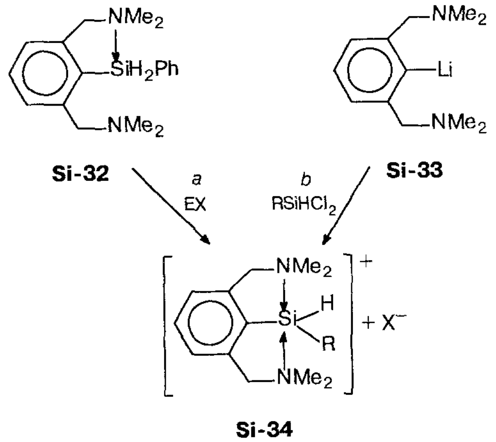


(11)

trans-**26a—c, 27c** **31**

Y = I, OTf

It should be noted that the first data concerning the formation of silycenium ions stabilized by intramolecular coordinate N→Si bonds have been published only very recently (Corriu and co-workers, 1993).[36,37] In particular, the reaction of dihydrosilane (**Si-32**), containing a pentacoordinated Si atom, with electrophilic reagents such as Me_3SiOTf, PhC(O)Cl, PhC(O)Br, $Ph_3C^+BF_4^-$, I_2 or the reaction of $RSiHCl_2$ (R = Ph, Cl) and 2,6-bis(dimethylaminomethyl)phenyllithium (**33**) produce ionic compounds (**Si-34**), which are stable at room temperature under an inert atmosphere, whose cations are the siliconium ions containing the pentacoordinated Si atoms.[36] The ionic structure of compounds **Si-34** was confirmed by conductometric titration.

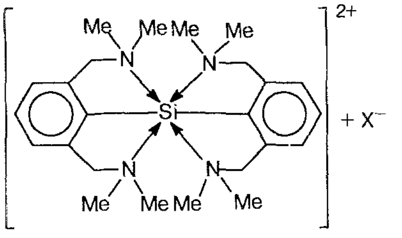


(12)

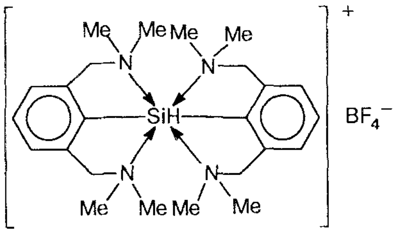
Si-34

R = Ph, Cl; X = Cl, Br, I, OTf, BF_4

The tridentate [2,6-bis(dimethylaminomethyl)phenyl] ligand was efficient at stabilizing siliconium ions (**Si-35**) and (**Si-36**) containing the hexa- and heptacoordinated Si atoms, respectively.[37]



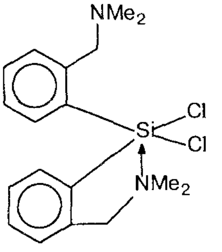
Si-35 (X = Cl, Br)



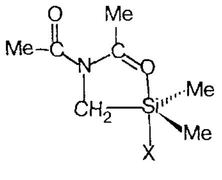
Si-36

At the same time, however, dichlorosilane (**Si-37**) is a covalent compound which, according to X-ray structural data, has one bidentate and one monodentate [2-(dimethylaminomethyl)phenyl] ligand, while the Si atom is pentacoordinated.[38] According to the NMR spectra a fast exchange between the chelated and non-chelated ligands takes place at high temperatures ($\Delta G^{\#}$ = 46.5 kJ mol^{-1}). Analogous migration of the intramolecular Si—O bond between the two oxygen atoms is characteristic of the *N*-acetylacetamide derivatives (**Si-38**).[39]

Our attempts to prepare the Si-analogs of the germacenium ions **31** discussed above containing lactamo-*N*-methyl ligands, were unsuccessful.[21] The interaction of *N*-TMS-lactams **1a,c** with $(ClCH_2)_2SiCl_2$ in a 2 : 1 ratio leads to the thermodynamically controlled products, *i.e.*, bis(lactamo-*N*-methyl)dichlorosilanes (**Si-25a,c**). According to the IR spectral data, the Si atom in these compounds is hexacoordinated (the absorption bands corresponding to the non-chelated lactamo-*N*-methyl ligands are absent).[21]



Si-37



Si-38

X = Cl, Br, MeCOO, CF_3COO

The electroconductivity of dichlorides **Si-25a,c** in CH_2Cl_2 (see Table 4) proved to be higher than that of their Ge-analogs, **25a,c**, and was comparable to that of the "ionic" adducts of amides with electrophilic silanes[40] or dimethyl(lactamo-*N*-methyl)silylbromides and -iodides, which are ionized in polar solvents.[12] This suggests the possibility of dissociation of the dichlorides **Si-25a,c** in appropriate solvents to form the siliconium cations (**Si-31**).

$$2\cdot\mathbf{1a,c}\ \xrightarrow[-2\ Me_3SiCl]{(ClCH_2)_2GeCl_2}\ (LCH_2)_2SiCl_2 \qquad (13)$$

Si-25a,c

L = $\overline{(CH_2)_nCH_2CH_2C(O)N}$—; *n* = 1 (a), 3 (c)

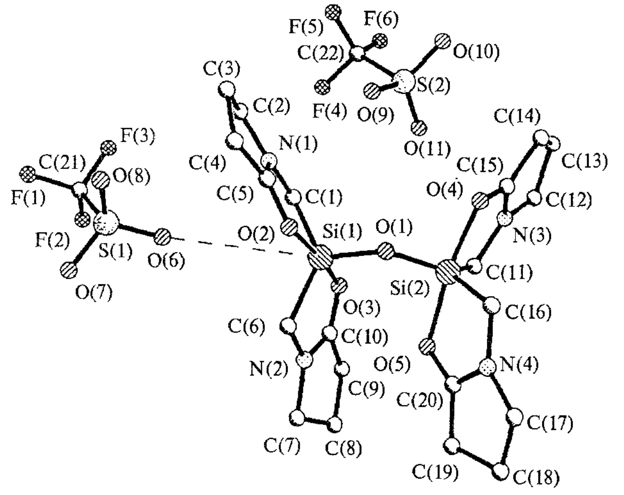
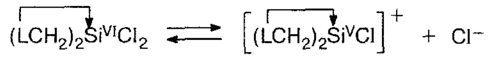


Fig. 6. General view and some main geometrical parameters of ditriflate **Si-39c** in a crystal.

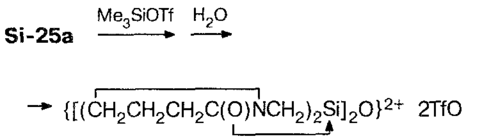
However, our attempts to prepare monocrystals of **Si-25a,c** suitable for X-ray structural study were unsuccessful. The interaction of dichloride **Si-25a** with trimethylsilyltriflate followed by hydrolysis (reaction 15) leads to the ionic product whith high electroconductivity. According to X-ray structural data, the latter is disiloxanoditrifluoromethylsulfonate (**Si-39a**).



$$(LCH_2)_2Si^{VI}Cl_2 \rightleftarrows \left[(LCH_2)_2Si^{V}Cl\right]^+ + Cl^- \qquad (14)$$

Si-25 **Si-31**

The coordination polyhedrons around the Si atoms in **Si-39a** are close to an ideal trigonal bipyramid (the displacement of the Si atom from the equatorial plane is 0.02 Å) (Fig. 6). In this case the two coordinate O→Si bonds closing the chelate rings are axial. The data obtained make it possible to consider ditriflate **Si-39a** as an analog of the siliconium cations of the $[R_2SiX]^+$ type, stabilized by intramolecular coordinate bonds. Note that ditriflate **Si-39a** is the first example of a compound containing silycenium ions stabilized by intramolecular coordinate O→Si interaction.



$$\textbf{Si-25a} \xrightarrow{Me_3SiOTf} \xrightarrow{H_2O}$$

$$\rightarrow \{[(CH_2CH_2CH_2C(O)NCH_2)_2Si]_2O\}^{2+}\ 2TfO \qquad (15)$$

Si-39a

In conclusion it should be stressed that the existence of stable compounds of hexacoordinated germanium testifies to the existence of an *associative mechanism* with formation of intermediateds with hexacoordinated Ge atoms in S_N reactions of pentacoordinated Ge compounds with such relatively poorly leaving groups as chloride.

A *dissociative mechanism* is also very probable for the reactions of hexacoordinated Ge compounds $L_2Ge(X)Y$ with the transient formation of germacenium ions such as $[L_2Ge(X)]^+$, stabilized by intraionic coordinate bonds.

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