



O,O-Monochelate complexes of silicon and germanium halides: The derivatives of *L*-mandelic *N,N*-dimethylamide

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ARTICLE INFO

Article history:

Received 1 August 2008

Received in revised form 2 October 2008

Accepted 13 October 2008

Available online 22 October 2008

Keywords:

Hypervalent silicon and germanium

Synthesis

Monoanionic (*O,O*)-didentate ligands

X-ray diffraction study

Quantum-chemical calculations

ABSTRACT

Reactions of *O*-trimethylsilyl-*L*-mandelic *N,N*-dimethylamide (**1**) with tetrachlorosilane and tetrachlorogermane lead to *O,O*-monochelate complexes, [1-(dimethylcarbamoyl)-1-phenylmethoxy]trichlorosilane (**2**) and [1-(dimethylcarbamoyl)-1-phenylmethoxy]trichlorogermane (**3**). Pentacoordination of silicon and germanium in these complexes was confirmed by X-ray studies.

X-ray data show that the Si and Ge atoms in **2** and **3** have TBP environments where the ether oxygen and two halogens are equatorial while the third halogen and the amide oxygen occupy axial positions. The axial O–M and Cl–M (M = Si, Ge) distances are somewhat longer than those in similar compounds of tetracoordinate silicon and germanium.

Intramolecular coordination in compounds **1–3** and relative stabilities of different conformations of their molecules were studied by quantum-chemical calculations.

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1. Introduction

Compounds of hypercoordinate silicon and germanium have attracted particular attention owing to their structural features, reactivity and non-rigidity in solution. The complexes of these elements with (*C,O*)-, (*O,S*)-, (*N,O*)-monoanionic and (*O,O*)-, (*S,S*)-, (*C,O*)-, (*O,S*)-dianionic ligands have been studied in some detail [1,2]. In particular, we have reported several synthetic approaches to neutral penta- and hexacoordinate chlorosilanes and chlorogermanes with amidomethyl, lactamomethyl and similar (*C,O*)-chelate monoanionic ligands (see, for example, Refs. [3,4] and references therein). The chelates with (*O,O*)-monoanionic ligands have been less comprehensively studied [1b,2a]. These compounds are represented by the derivatives of acetylacetone [4], tropolone [5] and similar symmetrical ligands [6,7] and also by the derivatives of 2-hydroxypyridine *N*-oxide and acylamides [8] (see also [4c,9] and the citations therein). The synthesis, structure and chemical transformations of another (*O,O*)-monochelate of pentacoordinate germanium, [1-(dimethylcarbamoyl)-1-phenylmethoxy]dichloro(chloromethyl)germane, were reported by us in a preliminary communication [10]. The latter complex was prepared

from chloromethyltrichlorogermane and racemic *N,N*-dimethyl-*O*-trimethylsilylmandelic amide [10].

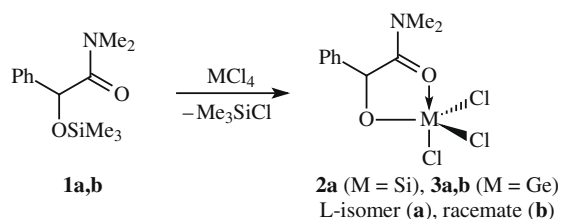
We have found previously that unsubstituted and *N*-mono-substituted amides of hydroxy acids could be used for the preparation of pentacoordinate silicon [11] and germanium [12] complexes with (*C,O*)-chelate amidomethyl ligands. In the present paper we report the use of an *N,N*-disubstituted amide of *L*-mandelic acid as the starting compound for the synthesis of new (*O,O*)-monochelate complexes of pentacoordinate silicon and germanium.

2. Results and discussion

We have found that reactions of SiCl₄ and GeCl₄ with *N,N*-dimethyl-2-trimethylsiloxyamide (**1**) could be used as convenient synthetic approaches to new complexes of pentacoordinate silicon (**2**) and germanium (**3**) with monoanionic (*O,O*)-chelate ligands. The reactions proceed in inert organic solvents at room temperature and require about 24 h for completion. In the case of *L*-mandelic amide the type of the complex is independent of the ratio of reagents; reactions of one equivalent of GeCl₄ with one or two equivalents of the amide led to the same monochelate (**3**). In all experiments the yields of the complexes **2** and **3** with respect to MCl₄ (M = Si, Ge) were from 81% to 86%.

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The structures of all complexes were confirmed by IR spectroscopy, ^1H , ^{13}C , ^{29}Si NMR and elemental analysis. The chemical shifts of ^{29}Si in CDCl_3 solutions of **1** and **2** (21.30 and -93.84 ppm, respectively) confirm the tetracoordinated state of the Si atom in *O*-TMS derivatives **1a,b** and the pentacoordination of the central atom in monochelates **2a,b** [13]. The resonances of the NMe_2 protons in NMR ^1H spectra of **1** and **2** appear as two singlets owing to the presence of chiral carbon centers in their molecules.

The IR spectrum of *O*-trimethylsilyl amide **1** contains two strong bands at 1672 and 1652 cm^{-1} (NCO fragment) and a weaker band at 1620 cm^{-1} (Ph group). The spectra of monochelates contain two strong bands at 1676 and 1456 cm^{-1} (**2**) or 1655 and 1484 cm^{-1} (**3**) of the NCO vibrations.

3. Single crystal X-ray studies

The details of the molecular structures of **1a–3a** in the crystals were investigated by single crystal X-ray studies. All molecules crystallize in chiral space groups with the *S* configuration of C(2) asymmetric atoms. Isostructural trichlorides **2a** and **3a** in the crystals are characterized by pentacoordination of Si and Ge atoms. The coordination polyhedron of the Si atom in **2a** can be described as a nearly ideal trigonal bipyramid, the deviation of this atom from the plane formed by equatorial atoms O(2), Cl(2) and Cl(3) is 0.07 \AA while the O(1)Si(1)Cl(1) angle is $176.00(5)^\circ$. In molecule **3a** the deviation of the Ge atom from the plane formed by equatorial atoms is greater (0.12 \AA) than that for Si(1) atom in **2a**. Five-membered chelate rings in both compounds adopt envelope conformations with the deviation of O(2) atom of 0.09 and 0.14 \AA , respectively.

Data concerning pentacoordinate *C,O*- and *O,O*-chelated compounds containing a Si(Ge)Cl₃ moiety in the literature is limited to a few complexes [14–18], in which the Ge–O distances vary in the range of 2.08 – 2.51 \AA . These data indicate that the Ge(1)–O(1) coordination bond in **3a** ($1.9972(8)\text{ \AA}$) is the strongest for this class of compounds, probably due to the increased donor ability of the NMe_2 fragment as compared to the substituents at the C(1) atom in other compounds. Despite this fact, the elongation of the axial Ge(1)–Cl(1) bond in **3a** (0.07 \AA) is almost identical to that in previously reported complexes [14–19].

The length of the Si–O coordination bond in **2a** ($1.858(1)\text{ \AA}$) is close to Si–O distances in two complexes with *C,O*-ligands [20]. The axial Si(1)–Cl(1) bond is elongated in comparison with equatorial Si–Cl distances by 0.1 \AA , which is noticeably shorter than in *N*-(trichlorosilylmethyl)-hexahydroazepin-2-one (0.16 \AA) [20].

In contrast to trichlorides **2a** and **3a**, the coordination Si–O bond in trimethylsilyl ether **1a** is absent, the interatomic separation of Si(1) and O(2) atom is 3.33 \AA , which is close to the sum of the respective van der Waals radii [21]. The configuration of the Si(1)C(2)C(1)O(1) moiety is non-planar; the value of the respective torsion angle (67.8°) suggests that the Si(1)–O(2) coordination bond is unfavorable due to significant conformational distortions.

4. Quantum-chemical calculations

According to the literature, there is a number of complexes with $\text{O}\cdots\text{GeCl}_3$ in which the Ge–O coordination is virtually absent (the

respective distance is more than 3.0 \AA , the angle between carbonyl oxygen and the axial Ge–Cl bond is 160 – 180°) [17,22–24]. A possible reason for this is the participation of the carbonyl O atom in intermolecular interactions which prevent the formation of the Ge–O bond.

The analysis of the intramolecular $\text{O}\cdots\text{SiMe}_3$ distances in the Cambridge Structural Database (981 ordered compounds) [8] shows that these distances vary in the range of 2.51 – 3.48 \AA and the angles between the O atom and axial Si–Me bond from 150 to 180° . The number of compounds with the non-bonded intramolecular $\text{O}\cdots\text{SiMe}_3$ distance less than 3.0 \AA is 281. Unfortunately, there is a lack of information concerning the $\text{O}\cdots\text{SiCl}_3$ distances. We believe that the Si(Ge)–O distance can be affected by crystal packing at least in the cases of SiMe_3 and GeCl_3 complexes.

According to quantum-chemical studies of complexes with the COSiMe_2Cl coordination centre [25], the potential energy curve (PEC) of the Si–O coordination bond is rather flat (the relative changes in energy do not exceed 5 kcal/mol in the range of 2.0 – 2.5 \AA), so molecules of **2a** and **3a** can exist both as coordinated and non-coordinated isomers. In the present paper we report the quantum-chemical study of possible isomers for compounds **1a–3a**. All calculations were performed for isolated molecules using PBE0/6-311G(d) and MP2/6-311G(d) levels of theory.

The calculations confirm that non-coordinated isomers of compounds **2a** and **3a** are less favorable than the respective chelates. In contrast, the chelate of **1** would have a considerably higher potential energy than the acyclic isomer.

The relaxed potential energy scan [PBE0/6-311G(d)] performed using Si(1)–O(1) and Ge(1)–O(1) distances in **2a** and **3a** as coordinates revealed two local minima corresponding to coordinated and non-coordinated isomers. The calculated Si(Ge)–O(1) distances in chelates are elongated by 0.15 – 0.3 \AA as compared to the experimental values found in structures **2a** and **3a** (Table 2). The optimization of atomic coordinates using PBE0 and MP2 methods gives the similar values (2.166 and 2.187 \AA) for the Ge(1)–O(1) bond while the calculated values for Si(1)–O(1) bonds differ by 0.08 \AA . In non-coordinated isomers of molecules **2a** and **3a** the interatomic distances differ by 0.2 \AA (Table 2). The C(1)–O(1) bonds are shortened by 0.02 \AA and the C(1)–N(1) bonds are shortened by the same value in comparison with those in chelates. Also, the absence of Si(Ge)–O(1) coordination leads to significant shortening of Si(Ge)–Cl and Si(Ge)–O(2) bonds (by 0.05 \AA on average). The differences in potential energy between two isomers of molecule **2a** are 3.9 and 1.5 kcal/mol , for PBE0/6-311G(d) and MP2/6-311G(d), respectively. In the case of **3a** these differences are somewhat larger (8.9 and 8.1 kcal/mol). Neither for **2a** nor for **3a** the transition states corresponding to the formation of coordination bond were located. This can be explained by the flexibility of five-membered chelate rings in molecules **2a** and **3a**: the increase of potential energy due to the elongation of Si(Ge)–O coordination bonds is partially compensated by the rotation of OCNMe_2 group around the C(1)–C(2) bond.

In the case of **1a** the only one local minimum was found. The Si–O distances calculated on PBE0 and MP2 level differ by 0.07 \AA (Table 2). However, the calculated distances are considerably (by as much as 0.4 \AA) shorter than the experimental one. Taking into account the flattened PEC of Si(1)–O(2) distance, the possibility of significant coordination between these atoms can be excluded. Thus the interatomic separation of Si and O atoms is mainly a result of crystal packing forces. In particular, the O(2) atom in the crystal forms three weak $\text{C–H}\cdots\text{O}$ interactions with the adjacent molecule (symmetry operation $-x, 0.5 + y, 0.5 - z$; the $\text{H}\cdots\text{O}$ distances are 2.50 – 2.58 \AA). The energies of these interactions (several kcal/mol) can be sufficient for a significant increase of the Si–O distance (Figs. 1–3).

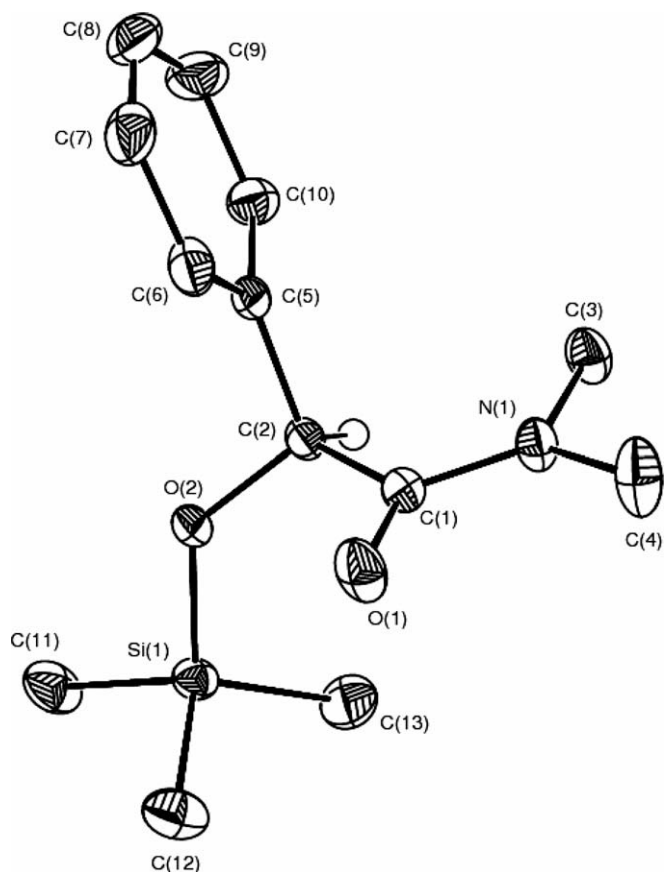


Fig. 1. Molecular structure of **1a**. Atoms are presented as thermal ellipsoids at 50% probability.

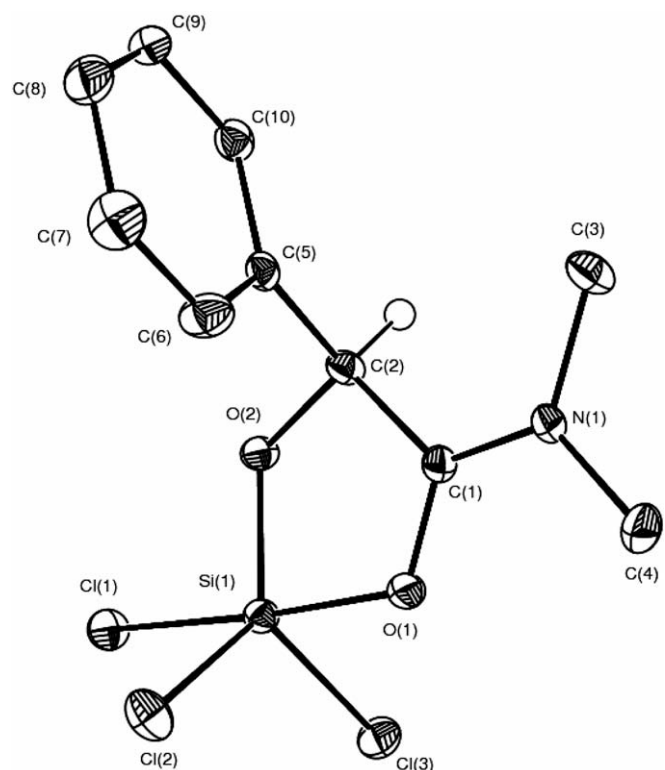


Fig. 2. Molecular structure of **2a**. Atoms are presented as thermal ellipsoids at 50% probability.

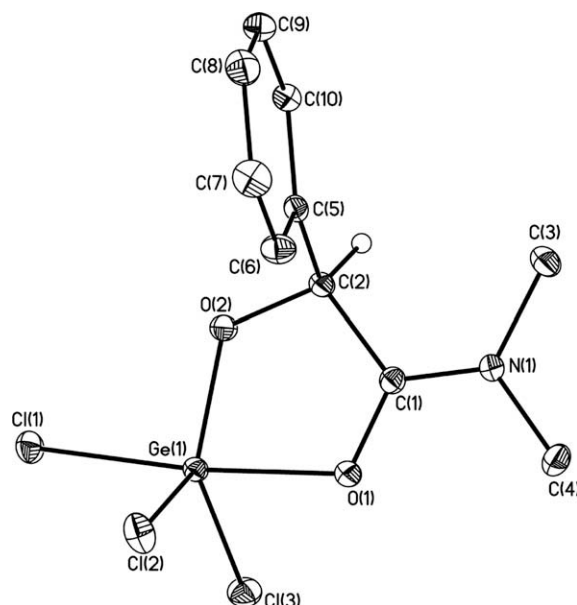


Fig. 3. Molecular structure of **3a**. Atoms are presented as thermal ellipsoids at 50% probability.

The calculated elongation of the Si(Ge)–O(1) bonds in isolated molecules **2a** and **3a** in comparison with the experimental values can be explained similarly. The O(1) atom does not form intermolecular contacts. On the other hand, the Cl(1) atoms in **2a** and **3a** participate in 2–3 weak C–H···Cl interactions (the H···Cl distances are 2.84–2.94 Å). Interactions of the same type are also observed for equatorial Cl atoms. Their overall energy is comparable to the energy needed for the shortening of the Si(Ge)···O distances down to their experimental values (2–3 kcal/mol, Fig. 4). The formation of similar contacts in solution might cause the additional stabilization of cyclic isomers and decrease the possibility of stereodynamic processes involving the cleavage of the Si(Ge)–O(1) coordination bond. Alternatively, in the case of molecule **1a** intramolecular interactions might hinder the Si(1)–O(2) bond formation and thus prevent some dynamic processes (such as SiMe₃ group exchange) from taking place in solution.

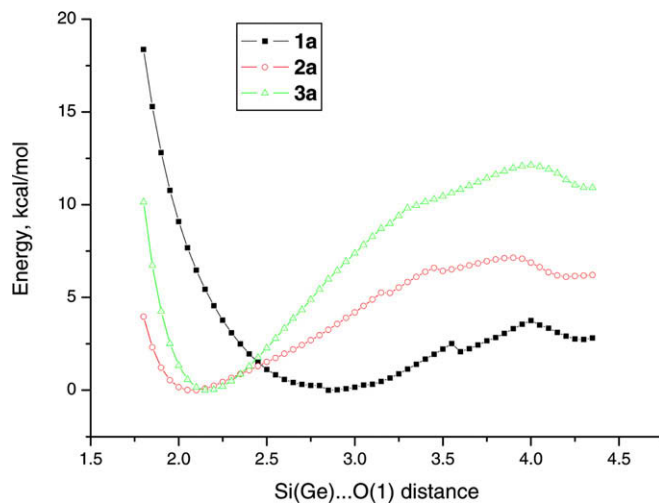


Fig. 4. Potential energy curves calculated as potential energy surface scan of molecules **1a–3a** using Si(Ge)···O(1) distance as coordinate at PBE0/6-311G(d) level (range 1.8–4.35 Å, step size 0.05 Å).

5. Experimental

IR spectra of compounds were recorded in KBr cells using a Specord IR-75 instrument. The ^1H , ^{13}C and ^{29}Si NMR spectra in CDCl_3 and CD_3CN were recorded on a Jeol JNM-EX400 and a Varian VXR-400 instruments (400.1, 100.6 and 79.5 MHz, respectively). ^1H , ^{13}C and ^{29}Si chemical shifts were measured using tetramethylsilane as internal reference. All solvents were dried over molecular sieves.

X-ray diffraction measurements of **1a–3a** were carried out with a Bruker Smart Apex II and Nonius Kappa CCD diffractometers. The details of crystallographic data and experimental conditions are presented in Table 1. Important structural parameters of structures **1a–3a** are summarized in Table 2.

The structures were solved by direct method and refined by full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Hydrogen atoms were located from difference electron density syntheses and refined in the rigid body model. All calculations were performed using the SHELXTL PLUS 5.10 program package [26]. Atomic coordinates, bond lengths, bond angles and thermal parameters of **1a–3a** have been deposited at the Cambridge Crystallographic Data Base (deposition numbers 694513, 694514 and 694628, respectively).

Table 1

Selected experimental bond lengths, interatomic distances and bond angles in molecules **1a–3a**.

	1a	2a	3a
Si(Ge)–O(1)	1.655(1)	1.858(1)	1.9972(8)
Si(Ge)···O(2)	3.330(1)	1.665(1)	1.7872(8)
Si(Ge)–X(1) (X = C, Cl)	1.867(2)	2.1693(7)	2.2253(3)
Si(Ge)–Y(2) (Y = C, Cl)	1.856(2)	2.0740(8)	2.1495(3)
Si(Ge)–Y(3) (Y = C, Cl)	1.864(2)	2.0720(8)	2.1465(3)
O(1)–C(1)	1.227(2)	1.280(2)	1.2760(1)
C(1)–N(1)	1.351(2)	1.309(3)	1.305(2)
O(2)–C(2)	1.427(2)	1.432(2)	1.424(1)
C(1)–C(2)	1.535(2)	1.517(3)	1.526(2)
Cl(1)–Ge(1)–O(1)	152.19	176.00(5)	173.95(3)
O(1)–C(1)–C(2)	120.1(1)	114.2(2)	115.9(1)
O(2)–C(2)–C(1)	110.5(1)	110.7(2)	107.70(9)
$\Delta_{\text{Si(Ge)}}$	0.5604(4)	–0.0708(5)	0.1241(3)

Table 2

Selected calculated bond lengths, interatomic distances and bond angles in molecules **1a–3a**.

	Cyclic isomer		Acyclic isomer	
	PBE0/6-311G(d)	MP2/6-311G(d)	PBE0/6-311G(d)	MP2/6-311G(d)
Molecule 1a				
Si(1)–O(1)			1.689	1.694
Si(1)···O(2)			2.965	3.030
Si(1)–C			1.876	1.875
O(2)Si(1)C(1)			165.73	165.94
Molecule 2a				
Si(1)···O(1)	2.081	2.164	4.267	4.063
Si(1)–O(2)	1.677	1.673	1.629	1.636
Si(1)–Cl(1)	2.100	2.084	2.033	2.026
Si(1)–Cl(2)	2.080	2.062	2.040	2.033
Si(1)–Cl(3)	2.077	2.065	2.040	2.032
O(1)Si(1)C(1)	174.39	174.48	153.32	156.57
Molecule 3a				
Ge(1)···O(1)	2.166	2.187	4.208	4.057
Ge(1)–O(2)	1.795	1.799	1.751	1.761
Ge(1)–Cl(1)	2.177	2.173	2.118	2.113
Ge(1)–Cl(2)	2.162	2.156	2.127	2.122
Ge(1)–Cl(3)	2.160	2.150	2.127	2.123
O(1)Ge(1)C(1)	172.28	172.83	154.53	155.48

Table 3

Crystallographic and experimental parameters of compounds **1a–3a**.

	1a	2a	3a
Brutto formula	$\text{C}_{13}\text{H}_{21}\text{NO}_2\text{Si}$	$\text{C}_{10}\text{H}_{12}\text{Cl}_3\text{NO}_2\text{Si}$	$\text{C}_{10}\text{H}_{12}\text{Cl}_3\text{GeNO}_2$
Formula weight	251.40	312.65	357.15
Diffractometer	Nonius Kappa	Nonius Kappa	Bruker
	CCD	CCD	SmartAPEX II
Temperature (K)	120	120	100
<i>a</i> (Å)	7.23190(10)	7.38990(10)	7.4003(3)
<i>b</i> (Å)	11.0720(3)	10.4793(3)	10.4878(5)
<i>c</i> (Å)	18.1646(5)	17.0382(5)	17.0299(8)
<i>V</i> (Å ³)	1454.47(6)	1319.45(6)	1321.74(10)
<i>d</i> _{calc.} (g cm ^{−3})	1.148	1.574	1.795
Space group, <i>Z</i>	$P2_12_12_1$, 4	$P2_12_12_1$, 4	$P2_12_12_1$, 4
$2\theta_{\text{max}}$ (°)	27.47	27.48	33.14
<i>F</i> (000)	544	640	712
Scan type	Φ/ω	Φ/ω	ω
Reflections collected	17363	11013	18612
Independent reflections	3314(0.0369)	3014(0.0412)	4961(0.0198)
$[R_{\text{int}}]$			
Reflections with $ I > 2\sigma(I)$	3142	2766	4760
Parameters	160	156	156
Absorption coefficient (cm ^{−1})	1.53	7.73	29.12
R_1 [$ I > 2\sigma(I)$]	0.0457	0.0289	0.0166
wR_2 (all reflections)	0.1123	0.0616	0.0396
Absolute structure parameter	0.06(12)	0.08(6)	0.011(4)
Largest difference peak/hole (e Å ^{−3})	0.555/−0.985	0.265/−0.299	0.317/−0.748

All quantum-chemical calculations were carried out using PC-GAMESS program [27]. For geometry optimization and relaxed potential surface scan of molecule **3a** tight angular and radial grids were utilized (NRAD = 99 and LMAX = 41) (Table 3).

6. *O*-trimethylsilyl-*L*-mandelic *N,N*-dimethylamide (**1a**)

Methyl-*L*-mandelate (50 g, 0.30 mol) and Me_2NH (50 g of 60 mass % aqueous solution, 0.62 mol) were mixed together and kept in a sealed bottle for 3 days. The precipitate formed was filtered, washed thoroughly with cold water (5×30 ml), and dried *in vacuo* to afford 26 g (0.16 mol, 52%) of *L*-mandelic *N,N*-dimethylamide. The product was dissolved in hexamethyldisilazane (52 g, 0.32 mol) and the mixture was refluxed for 3 h. The volatiles were removed *in vacuo* and the residue was distilled to afford 35 g (0.14 mol, 88%) of compound **1a**, m.p. 42–43 °C (no solvent), b.p. 87–89 °C (0.2 mm Hg). IR (CHCl_3 , ν , cm^{-1}): 1652 s, 1620 m. NMR ^1H (CDCl_3 , δ , ppm): 0.15 s (9H, OSiMe_3), 2.85 s, 2.89 s (6H, NMe_2), 5.50 s (1H, CH), 7.2–7.4 m (5H, Ph). NMR ^{13}C (CDCl_3 , δ , ppm): −0.25 (OSiMe_3), 36.29, 36.61 (NMe_2), 76.42 (CH), 125.31, 127.48, 128.36, 138.99 (Ph), 171.50 (C=O). NMR ^{29}Si (CDCl_3 , δ , ppm): 21.30. $[\alpha]_{\text{D}}^{25} = +42.8^\circ$ (589 nm, MeCN, 0.2 M). Anal. Calc. for $\text{C}_{13}\text{H}_{21}\text{NO}_2\text{Si}$ (mass %): C, 62.11; H, 8.42; N, 5.57; Si, 11.17. Found (mass %): C, 62.45; H, 8.59; N, 5.78; Si, 10.92%. The crystals for X-ray diffraction study were formed upon re-distillation of the product.

7. *O*-trimethylsilyl-*DL*-mandelic *N,N*-dimethylamide (**1b**)

5-Phenyl-1,3-dioxalan-4-one [28] (52 g, 0.31 mol) and Me_2NH (250 g of 30 mass % aqueous solution, 1.5 mol) were mixed together and kept in a sealed bottle for 2 days. The precipitate formed was filtered, washed thoroughly with cold water (5×30 ml), and dried *in vacuo* to afford 33.6 g (0.19 mol, 60.5%) of *DL*-mandelic *N,N*-dimethylamide. The crude product was dissolved in hexamethyldisilazane (100 g, 0.62 mol) and the mixture was refluxed for 3 h. The volatiles were removed *in vacuo* and the residue was distilled to

afford 42.1 g (0.17 mol, 90%) of compound **1b**, b.p. 154–155 °C (9 mm Hg), n_D^{20} 1.4971. IR (CHCl₃, ν , cm⁻¹): 1650 s, 1620 m. NMR ¹H (CDCl₃, δ , ppm): 0.17 s (9H, OSiMe₃), 2.81 s, 2.84 s (6H, NMe₂), 5.52 s (1H, CH), 7.2–7.4 m (5H, Ph). NMR ¹³C (CDCl₃, δ , ppm): -0.25 (OSiMe₃), 36.25, 36.59 (NMe₂), 75.40 (CH), 125.28, 127.48, 128.44, 138.99 (Ph), 173.20 (C=O).

8. L-[1-(Dimethylcarbamoyl)-1-phenylmethoxy]trichlorosilane (2a)

O-trimethylsilylamide **1a** (3.77 g, 15 mmol) and SiCl₄ (2.55 g, 15 mmol) were dissolved in hexane (20 ml) and stirred for 24 h. The precipitate was filtered, washed with hexane (2 × 10 ml) and dried *in vacuo* to afford 4.15 g (13 mmol, 88%) of compound **2a**, off-white crystals, m.p. 197–198 °C (MeCN). IR (KBr, ν , cm⁻¹): 1676 s, 1456 m. NMR ¹H (CDCl₃, δ , ppm): 2.75 s, 3.17 s (6H, NMe₂), 5.76 s (1H, CH), 7.4–7.6 m (5H, Ph). NMR ¹³C (CDCl₃, δ , ppm): 38.92, 39.14 (NMe₂), 75.88 (CH), 129.02, 130.74, 136.18, 138.75 (Ph), 174.47 (C=O). NMR ²⁹Si (CDCl₃, δ , ppm): -93.84. [α_D^{25} = +35.8° (589 nm, MeCN, 0.2 M). Anal. Calc. for C₁₀H₁₂Cl₃NO₂-Si (mass %): C, 38.42; H, 3.87; N, 4.48; Si, 8.98. Found (mass %): C, 38.81; H, 4.14; N, 4.44; Si, 8.07%. The crystals for X-ray diffraction study were obtained from hot MeCN.

9. L-[1-(Dimethylcarbamoyl)-1-phenylmethoxy]trichlorogermane (3a)

O-trimethylsilylamide **1a** (3.77 g, 15 mmol) and GeCl₄ (3.22 g, 15 mmol) were dissolved in hexane (20 ml) and stirred for 24 h. The precipitate was filtered, washed with hexane (2 × 10 ml) and dried *in vacuo* to afford 4.50 g (13 mmol, 84%) of **3a**, off-white crystals, m.p. 238–239 °C (MeCN). IR (KBr, ν , cm⁻¹): 1655 s, 1484 m. NMR ¹H (CDCl₃, δ , ppm): 2.75 s, 3.14 s (6H, NMe₂), 5.72 s (1H, CH), 7.3–7.6 m (5H, Ph). NMR ¹³C (CDCl₃, δ , ppm): 38.40, 39.04 (NMe₂), 75.87 (CH), 128.97, 130.58, 137.45, 139.20 (Ph), 174.34 (C=O). [α_D^{25} = +31.2 (589 nm, MeCN, 0.2 M). Anal. Calc. for C₁₀H₁₂Cl₃GeNO₂ (mass %): C, 33.62; H, 3.39; Ge, 20.34; N, 3.92. Found (mass %): C, 33.99; H, 3.53; N, 3.86; Ge, 19.80%. The crystals for X-ray diffraction study were obtained from hot MeCN.

10. DL-[1-(Dimethylcarbamoyl)-1-phenylmethoxy]trichlorogermane (3b)

GeCl₄ (5.3 g, 25 mmol) was added dropwise to the mixture of O-trimethylsilylamide **1b** (3.58 g, 20 mmol), Et₃N (2.50 g, 25 mmol) and benzene (15 ml). The mixture was stirred for 24 h, then diluted with *o*-xylene (60 ml) and refluxed for a short time. Hot solution was filtered from the precipitate and allowed to cool down to afford 4.24 g (12 mmol, 47%) of racemate **3b**, white crystals, m.p. 241–242 °C (MeCN).

This study was supported by Russian Foundation for Basic Research (project 07-03-01067) and INTAS (project 03-51-4164).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.10.026.

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