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Stabilized germylenes based on dialkanolamines: Synthesis, structure, chemical properties

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ABSTRACT

A series of novel low valent germanium compounds RN(CHR^{2}CR^{1}R^{3}O)(CHR^{4}CHR^{5}O)Ge **1**–**13** (R = Me, Ph, Bn; R^1, R^2, R^3, R^4, R^5 = H, Me, Ph, $(CH_2)_3$, $(CH_2)_4$, $CH_2(C_6H_4)$) was obtained via the reaction between Ge[N(SiMe$_3$)$_2$]$_2$ and various dialkanolamines. All new compounds were characterized by elemental analysis, ^{1}H and ^{13}C NMR spectroscopy and in several cases by X-ray diffraction analysis (**1**, **3**, **8**, **10**). The compounds **1**, **3**, **8** are dimeric in the solid state due to the formation of intermolecular Ge–O bonds, the complex **10** is monomeric, all compounds possess a transannular Ge–N bond. The reactivity of the germylenes synthesized was investigated in reactions of oxidative insertion (with halogenation reagents, MeI, disulfides), [1 + 4]-cycloaddition, oxidation and in reactions with water and acetic anhydride. Some reactions were investigated by DFT calculations.

1. Introduction

The low valent derivatives of group IVA elements (Si, Ge, Sn) attract much attention because of interest in "heavy" carbon analogs [1]. The carbene center is very reactive, while some "heavy carbenes" are more stable due to the known "inert pair" effect and may be used as precursors for the synthesis of various metalloorganic compounds and intermediates. Especial interest may be aroused by application of such derivatives as ligands in coordination chemistry [2].

The stabilization of highly reactive "heavy carbene" centers may be accomplished using two approaches. The kinetic stabilization may be caused by the introduction of sterically demanding groups to the central atom in MR_2 (M = Si, Ge, Sn, R = *t*-Bu, N(SiMe$_3$)$_2$, 2,6-(*i*-Pr)$_2$C$_6$H$_3$) [3]. The thermodynamic stabilization may be achieved by donation of electron density from substituents to a vacant orbital of the central atom (n- and π-donation as in Ge[N(SiMe$_3$)$_2$]$_2$ or N-heterocyclic germylenes (NHGe) [4a,b,c]), or by intra- or intermolecular interaction with electron donors (for example, this type of stabilization may be caused by using N-heterocyclic carbenes (NHC) [4d,e] or β-diketiminate [5], amidinate [6], aminotroponimine [7] ligands). However application of tridentate ligands for the synthesis of stabilized germylenes is very rare [8,9]. It is evident that stabilization of Ge(II) centers with dialkanolamine dianions (RN(CH$_2$CH$_2$O$^-$)$_2$) as ligands is achieved by all these ways. So these germylenes with such ligands have to be high stable compounds. It should be noted that these germylenes may possess either a monomeric or a dimeric structure with Ge–O intermolecular coordination. At the same time it is important to investigate the chemical a reactivity of these new complexes to find out the difference in chemical behavior between monomeric and dimeric species. In the present work we used substituted diethanolamines for the synthesis of stable germylenes and performed a systematic investigation of the chemical and structural properties of these compounds.

2. Results and discussion

2.1. Synthesis of dialkanolamines

The dialkanolamines used in this work were synthesized according to the procedures published (see Experimental part) and

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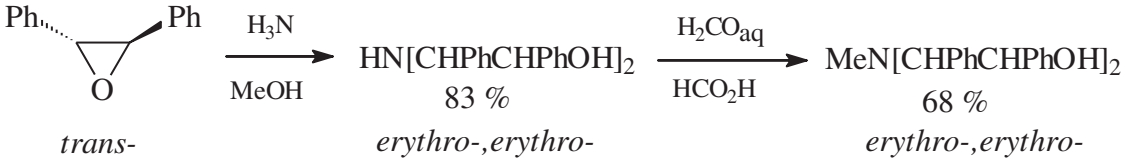


Scheme 1.

include derivatives with various substituents. The new compound *erythro*,*erythro*-MeN[CH(Ph)CH(Ph)OH]$_2$ containing sterically voluminous substituents was obtained in two steps using the conditions (formalin as a source of methyl group, formic acid as a reductant) of the Eschweiler–Clarke reaction (Scheme 1). The target compound was isolated as a mixture of two diastereomers.

2.2. Synthesis of germylenes

The most suitable method for synthesis of Ge(OR)$_2$ is a reaction of alkoxydesamination of [(Me$_3$Si)$_2$N]$_2$Ge with appropriate alcohols [10]. An alternative variant in which the unstable Ge(OEt)$_2$ * *x*EtOH is used seems undesirable [8]. Using first approach we synthesized with high yield target germanium compounds **1**–**13** (Scheme 2), containing the ligands with various substituents. The compounds **2**–**13** are novel. The previously known germylene **1** [8] was prepared for structural studies. For synthesis of **6**, **7**, **11**–**13** one diastereomer of corresponding dialkanolamine was used; in the case of compound **10** the enantiomerically pure dialkanolamine was used.

The desired compounds were obtained at long stirring (4 days) of a mixture of the corresponding reagents in toluene at room temperature. The yields of the target compounds (see Scheme 2) depend on the ligand structure.

In our work we establish that (Me$_2$N)$_2$Ge can also be used as a source of germanium for the synthesis of alkanolamine derivatives (Scheme 3). It should be noted that this approach is less favorable in spite of the high yield due to the fact that (Me$_2$N)$_2$Ge is more difficult of access than [(Me$_3$Si)$_2$N]$_2$Ge.

Also we show the possibility of germylene synthesis in the reaction of a derivative of Ge(IV) with GeCl$_2$*C$_4$H$_8$O$_2$ (Scheme 4). We believe that the formation of the strong intramolecular Ge–N and Ge–O bonds in **1** (the latter due to dimerization) is a driving force of this reaction. It should be noted that there is not appreciable Ge–N interaction in PhN(CH$_2$CH$_2$O)GeMe$_2$ [11].

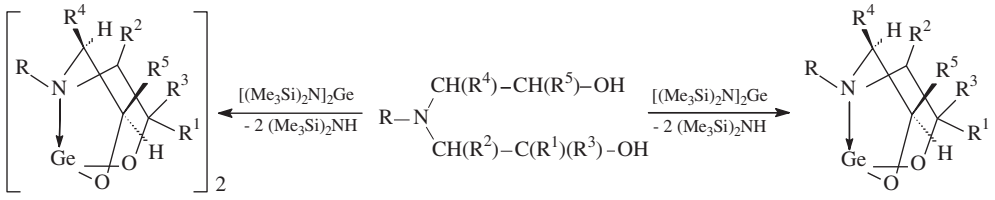
We investigated the possibility of the synthesis of germylenes by the reduction of corresponding dihalogermocanes by KC$_8$. This reduction occurs under mild conditions at stirring in THF at room temperature and gives the desired germylene with moderate yield (Scheme 5).

2.3. Investigation of the structure

There are two main methods to investigate the structure of germylenes: NMR spectroscopy (^{1}H, ^{13}C) in solution and X-ray analysis in the solid state. The basic question regarding the structural chemistry of low valent germanium compounds is establishing the coordination number of the Ge atom and investigating how the geometry depends on the nature of substituents of the central atom or the ligand (electronic and steric properties). Germylenes can be associated due to forming dimers or coordination polymers. The degree of oligomerization and the coordination geometry around the central atom in germylenes in our opinion should determine chemical properties of these compounds.

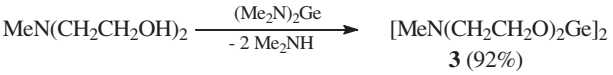
According to general considerations and quantum chemical calculations performed for simple germylenes (GeH$_2$, GeMe$_2$, GeF$_2$) [12], germylenes may exist in three possible structures (**I**–**III**) where M = Ge has oxidation state equal to +2 [13] (Fig. 1).

Structure **I** is monomeric; structure **II** is dimeric with the Ge–Ge interaction; structure **III** is dimeric, in which dimerization is observed due to O–Ge coordination. In this case there are two



1. R = Ph, R^1 = R^2 = R^3 = R^4 = R^5 = H (63%)
2. R = Bn, R^1 = R^2 = R^3 = R^4 = R^5 = H (53%)
3. R = Me, R^1 = R^2 = R^3 = R^4 = R^5 = H (89%)
4. R = Me, R^1= R^2 = R^4 = R^5=H, R^3 = Me (29%)
5. R = Me, R^1= R^2 = R^4 = R^5=H, R^3 = Ph (71%)
6. R = Me, R^1 = R^2 = Ph, R^3 = R^4 = R^5 = H (*erythro*-) (86%)
7. R = Me, R^2 = R^3 = Ph, R^1 = R^4 = R^5 = H (*threo*-) (61%)
8. R = Me, R^1 = R^3 = Ph, R^2 = R^4 = R^5= H (96%)
9. R = Me, R^1 = R^2 = R^4 = R^5 = Ph, R^3 = H (*erythro*-, *erythro*-) (42%)
10. R = Me, R^1 = R^3 = Ph, R^5 = (*R*)-Ph, R^2 = H, R^4 = (*S*)-Me (78%)
11. R = Me, R^1, R^2 = (CH$_2$)$_3$, R^3 = R^4 = R^5 = H (*threo*-) (64%)
12. R = Me, R^1, R^2 = (CH$_2$)$_4$, R^3 = R^4 = R^5 = H (*threo*-) (60%)
13. R = Me, R^1, R^2 = CH$_2$(C$_6$H$_4$), R^3 = R^4 = R^5 = H (*threo*-) (88%)

Scheme 2.



Scheme 3.

possible isomers which differ in the way in which they dimerize (*cis*-(**IIIa**) or *trans*- (**IIIb**) diastereomers).

The analysis of structural data (X-ray data, more than 30 structures) of simple germylenes (where Y, Y′ = O, N) shows that "heavy carbenes" exist as dimers **IIIa** or **IIIb**. The introduction of the ligands containing one group acting as additional donors leads to an increase in a stability of the monomeric form. Two such donor groups always stabilize the monomeric **I** form. It is important to note that increasing the steric volume of a substituent near the Ge center increases the stability of the monomeric form as well. The structures of type **II** were not known for germylenes, where germanium atom are bound to O or N.

2.3.1. X-ray analysis

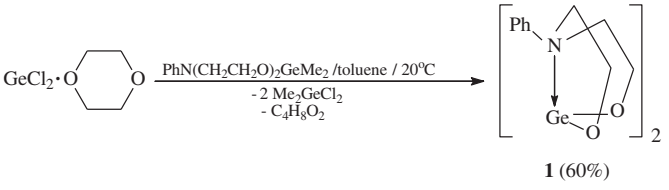
In the course of this work the structures of four germylenes **1**, **3**, **8**, **10** were investigated by X-ray analysis (Tables 1, 2, Figs. 2–5).

The diffraction studies establish that the germylenes **1**, **3** and **8** are dimeric and the germylene **10** is monomeric in the solid state.

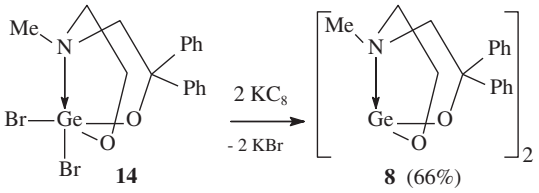
The complex **1** (Fig. 2) is a centrosymmetric dimer (type **IIIb**). The central Ge1–O2′–Ge1'–O2 ring is planar. The tetracoordinated germanium atom has a distorted trigonal bipyramidal coordination. Nitrogen and oxygen atom of another molecule are in the axial positions, and diethanolamine oxygen atoms and a lone pair occupy the equatorial positions of TBP. The Ge–N bond distance (2.584(2) Å) is significantly longer than that found in penta-coordinated $PhN(CH_2CH_2O)_2GeCl_2$ (2.202(2) Å) but less than in $PhN(CH_2CH_2O)_2GeMe_2$ (3.182(1) Å) [11]. These data correspond well to the proposition that the electronic properties of substituents on the Ge atom affect the force of the transannular Ge–N interaction. The nitrogen atom in **1** is tetrahedral. Eight membering cycles –Ge–O–C–C–N–C–C–O– are in the "chair – bath" conformation.

The complex **3** is also dimeric in the solid state (dimer of type **IIIb**) with the coordination similar to **1** (TBP). The Ge–N bond length (2.315(1) Å) is sufficiently shorter than that in the complex **1**. It should be noted that the germanium atoms in **1** and **3** are hypercoordinated. This fact significantly affects the bond distance Ge–O in **1** and **3**. The interaction in the N→Ge←O_{ax} fragment may be interpreted with the theory of three center four-electron bond. The bond length in this group is sensitive to the electronic and steric effects of the substituents. It is evident that the substitution of a Ph group for a Me group leads to stronger Ge–N interaction. The stronger N→Ge interaction in **3** in comparison with that in **1** corresponds to a weaker Ge←O_{ax} bond (2.171(1) *vs.* 2.039(1) Å). The distances for the other two Ge–O bonds in **1** and **3** are shorter than Ge←O_{ax}, where the shortest bond is Ge-$O_{uncoordinate}$ (1.838(1) *vs.* 1.856(1) Å). The same features are observed in **8** in comparison with **1** and **3**.

The introduction of the substituents to one C atom of the dialkanolamine framework near the Ge atom results in a dimeric



Scheme 4.



Scheme 5.

structure for **8** but the type of the dimer is changed (**IIIa**) perhaps due to packing effects. The germanium atom has the distorted trigonal bipyramidal coordination where the base of the pyramid is formed by one oxygen atom of the dialkanolaminate framework, a bridging O atom from neighboring alcoholate and a lone pair in one vertex. It is interesting to note that changing the dimer type (**8** *vs.* **3**) does not lead to significant changes in the geometric characteristics of Ge center.

Increasing the coordination number of the germanium atom in **3** and **8** in comparison with **10** (see below) results to the elongation of the Ge–O and Ge–N bonds in dimeric complexes **3**, **8**.

The germylene **10** contains substituents at different C atoms that results in a monomeric structure. In the complex **10** germanium atom has a distorted tetrahedral geometry where the electron lone pair of Ge occupies one coordination place. The values of the O–Ge–O and N–Ge–O angles exhibit the significant s-character of this pair. For the germanium atom in **10** the "octet rule" is followed so the Ge–N bond is a classical donor–acceptor interaction. The geometrical characteristics of **10** are close to those found earlier in the related monomeric structure of $[2,6\text{-}C_5H_3N(CH_2CPh_2O)_2]Ge$ (d(Ge–O) 1.827(1), 1.881(1), d(Ge–N) 2.110(1) Å) which contains not penta- but hexamembered chelate cycles [9]. It should be noted that the d(Ge–O) in **10** are close to the distances found by X-ray analysis in single monomeric dialkoxygermane $(Ge[OC(t\text{-}Bu)_3]_2$ (1.833(3), 1.855(3) *vs.* 1.83(1) Å)) where the coordination number of Ge atom is equal to 2 [14]. As it may be expected enantiomerically pure compound **10** crystallized in chiral space group ($P2_1$).

Previously we have studied the structure of various germylenes by DFT calculations (as single molecules) [13], and the X-ray results presented above are completely in agreement with the calculated results regarding which structure type is preffered (monomeric or dimeric). So we believe that the presence of one or two free OCH_2 groups in the dialkanolaminate structure results in a dimeric structure for germylenes. In other cases the germylenes of presented type are monomeric [9].

2.3.2. ^1H and ^{13}C NMR spectroscopy

The compounds obtained were investigated by ^1H and ^{13}C NMR spectroscopy. The spectral data unambiguously confirm the

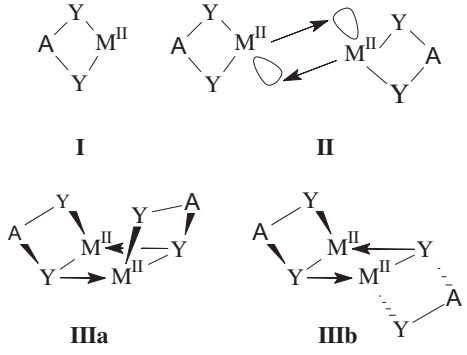


Fig. 1. Possible structures for germylenes (M = Ge).

Table 1
Selected bond lengths (Å) and angles (degrees) in **1** and **3**.

1			
Ge(1)–N(1)	2.584(2)	O(1)–Ge(1)–O(2)	97.68(6)
Ge(1)–O(1)	1.838(1)	O(1)–Ge(1)–O(2′)	87.85(5)
Ge(1)–O(2)	1.982(2)	O(2)–Ge(1)–O(2′)	74.60(6)
Ge(1)–O(2′)	2.039(1)	N(1)–Ge(1)–O(2′)	142.5(2)
N(1)–Ge(1)–O(1)	74.2(2)	C–N–C	112.9(2)–117.0(2)
N(1)–Ge(1)–O(2)	76.2(2)	C–N–Ge	98.7(2)–107.3(2)
3			
Ge(1)–O(1)	1.856(1)	O(1)–Ge(1)–O(2)#1	85.66(4)
Ge(1)–O(2)	1.933(1)	O(2)–Ge(1)–O(2)#1	72.61(4)
Ge(1)–O(2)#1	2.171(1)	O(1)–Ge(1)–N(1)	80.12(4)
Ge(1)–N(1)	2.315(1)	O(2)–Ge(1)–N(1)	78.54(4)
O(1)–Ge(1)–O(2)	100.46(5)	O(2)#1–Ge(1)–N(1)	144.80(4)

compositions of the complexes synthesized but do not clarify the degree of oligomerization of the compounds in a solution. We can state that the presence of voluminous groups in a germylene molecule result in monomeric structures. The introduction of substituents to C atoms results to magnetic nonequivalence of all protons in the dialkanolamine framework and resonance signals appear as a complex sets of multiplets.

It is known that metalloorganic derivatives of unsubstituted dialkanolamines are divided into two groups in accordance with external view of signals in ^{1}H NMR spectra [15]. The first group includes compounds for which NMR spectra give AA'XX′ system (two triplets for NCH_2CH_2O). This situation is characteristic for flexibility of dialkanolamine framework in a solution. The second group includes germylenes in which the NCH_2CH_2O group forms ABXY system (two multiplets for NCH_2 and one multiplet for OCH_2). Such compounds exist as one "frozen" conformation in a solution at room temperature. There are compounds of an intermediate type which are characterized as an AA'XY system (triplet for OCH_2 group and one or two multiplets for NCH_2).

The germylenes **1**–**3** belong to second group or may be characterized as an AA'XY system (see Experimental part). So in these compounds the conformational processes in penta- or eight membering cycles are very slow. On the basis of external view of ^{1}H NMR spectra of unsubstituted germylenes one may estimate the conformational processes in a solution but these data were not sufficient for the investigation of transannular Ge←N interaction.

2.4. Reactivity of germylenes

The systematic investigation of the reactivity of monomeric and dimeric germylenes obtained in this work and the determination of the structural factors effecting on the reaction activity are the main purposes of this work. We have investigated the reactivity of germylenes in the reactions which either involve changing the oxidation state (insertion reactions, oxidation, cycloaddition) or do not involve changes in the Ge oxidation state. It is established that

Table 2
Selected bond lengths (Å) and angles (degrees) in **8** and **10**.

8			
Ge(1)–O(1)	1.8653(9)	O(1)–Ge(1)–O(2A)	88.12(4)
Ge(1)–O(2)	1.9259(9)	O(2)–Ge(1)–O(2A)	74.18(4)
Ge(1)–O(2A)	2.1473(10)	O(1)–Ge(1)–N(1)	78.36(4)
Ge(1)–N(1)	2.3822(11)	O(2)–Ge(1)–N(1)	78.01(4)
O(1)–Ge(1)–O(2)	98.68(4)	O(2A)–Ge(1)–N(1)	146.75(4)
10			
Ge(1)–O(2)	1.833(3)	O(2)–Ge(1)–O(1)	98.8(1)
Ge(1)–O(1)	1.855(3)	O(2)–Ge(1)–N(1)	85.6(1)
Ge(1)–N(1)	2.113(3)	O(1)–Ge(1)–N(1)	84.0(1)

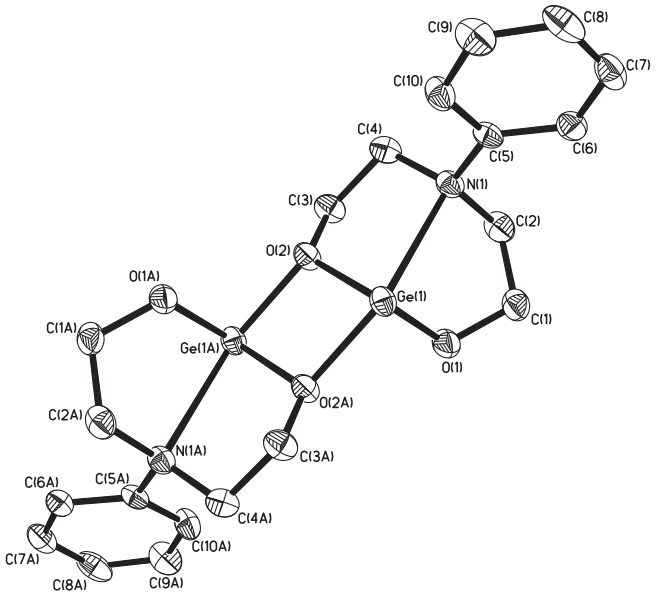


Fig. 2. Molecular structure of complex **1**. Hydrogen atoms are omitted for clarity.

the monomeric derivatives under the studied reaction conditions leads to the expected products with increasing metal oxidation state. In contrast, the reactions of dimeric derivatives often results to mixtures of unidentified compounds. This fact may be explained by a primary reaction on one metal center but simultaneous presence of two metal atoms with different oxidation states results to polymerization or decomposition.

2.4.1. Reactions with changing of germanium oxidation state

The reactions were studied for both monomeric and dimeric germylenes by experiment and DFT calculations. We tested several different model compounds prepared in the course of this work.

2.4.1.1. Oxidative insertion reactions

2.4.1.1.1. Halogenation by action of bromine, germanium tetrachloride and $KICl_2$. In this work we investigated the insertion reaction of dimeric germylene **8** with bromine (Scheme 6). The similar monomeric germylene based on pyridine-contained dialcohols was

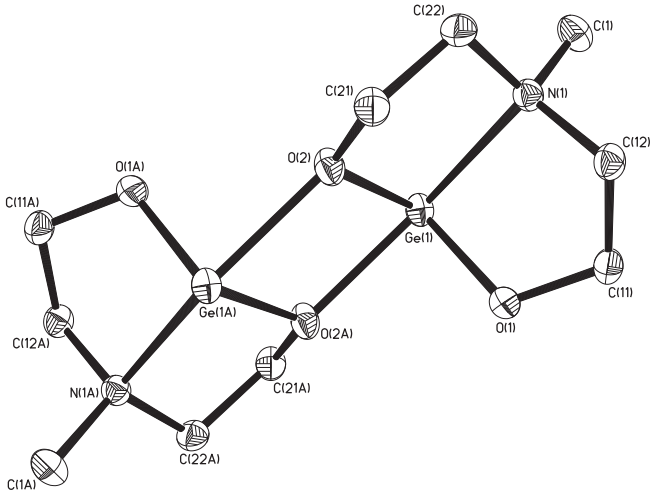


Fig. 3. Molecular structure of complex **3**. Hydrogen atoms are omitted for clarity.

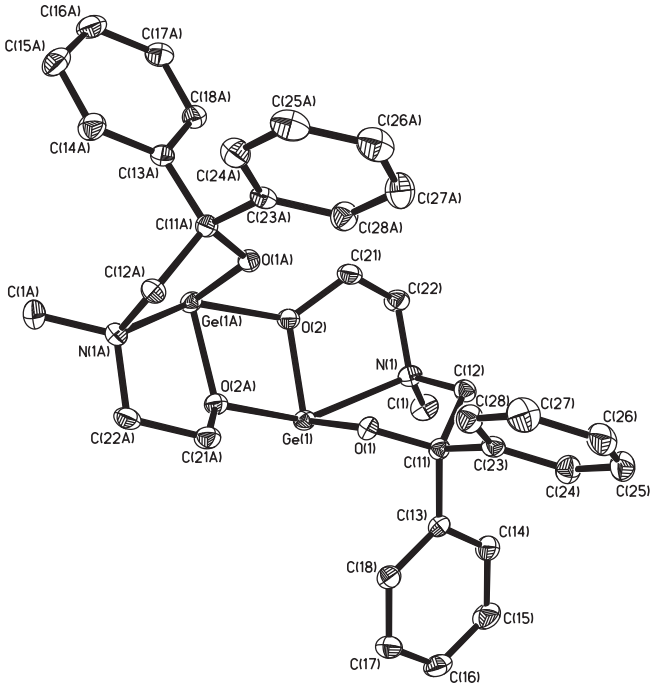
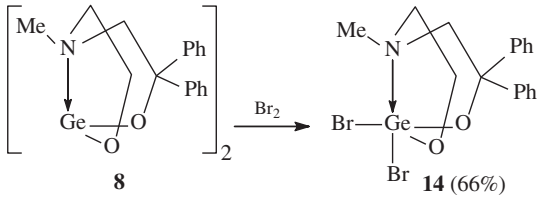


Fig. 4. Molecular structure of complex **8**. Hydrogen atoms are omitted for clarity.

studied previously in this reaction [9], the formation of dibromide was also found.

The reaction of "heavy" analogs of carbenes with bromine is very useful reaction for the investigation of the reactivity of such compounds [16]. At the moment it is common that the insertion of germylenes in the X–Y bond includes two steps (Scheme 7).

At the first stage the complex of "heavy carbene" with substrate is formed due to donation of substrate electron density on vacant orbital at Ge. In the case of Ge compounds with additional intermolecular interaction such a complex may be not formed. In the case of insertion of the "heavy carbene" into O–H or N–H bonds the bond forming in complex is short and strong enough because oxygen and nitrogen atoms have lone electron pair which are involved in the interaction with the vacant Ge orbital. In the case of



Scheme 6.

insertion into C–Hal bond the complex is formed owing to generation of Hal–Ge contact. The insertion product is formed then from a three-membered intermediate cycle. According to theoretical works the insertion reaction is more energetically favored than more electropositive substituents bound to Ge atom [17].

The mechanism of reaction of germylenes with bromine is studied by DFT method in the case of dimeric ((**3**)$_2$, *trans*-**III**, **IIIb**), monomeric form of **3** and dicoordinated (*t*-BuO)$_2$Ge **3a**. The data are present in Table 3 and Figs. 6–8.

Interaction of dimeric (**3**)$_2$ results to a complex containing simultaneously M(4+) and M(2+). This complex decomposes with the formation of free dibromide and germylene. This situation is true not only for bromination but also for following studied reactions.

All investigated reactions are thermodynamically favored. It should be noted that bromination of (*t*-BuO)$_2$Ge is more energetically favored ($\Delta H = -58.5$ kcal/mol), than bromination of monomeric **3**. This fact may be explained by the stabilizing effect of additional intramolecular interaction Ge–N in **3**. The activation energies of these reactions are not very high and significantly decrease with increasing of coordination number of Ge atoms [for example E_{act} **3a** (Ge^{II}) > E_{act} **3** (Ge^{III}) > E_{act} (**3**)$_2$ (Ge^{IV}), where Ge^{II}, Ge^{III}, Ge^{IV} are di-, tri- and tetracoordinated Ge atom]. The latter fact is in accord with the presented mechanism and with the supposition that more electronic depletion on the metal atom may be found with an increase of its coordination number.

There is interaction of the lone electron pairs of the Br atom and suitable orbitals of the Ge atom in the transition state of bromination reaction. For example, in the reaction of monomeric **3** with Br_2 (Fig. 5) a three-centered four-electron bond with the participation of vacant $4p_z$ orbital of Ge atom is formed in Br···Ge←N fragment.

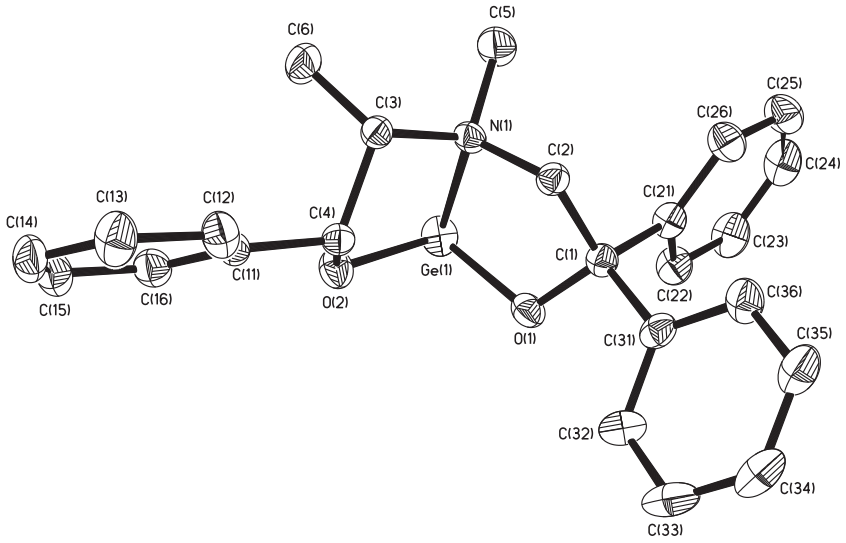
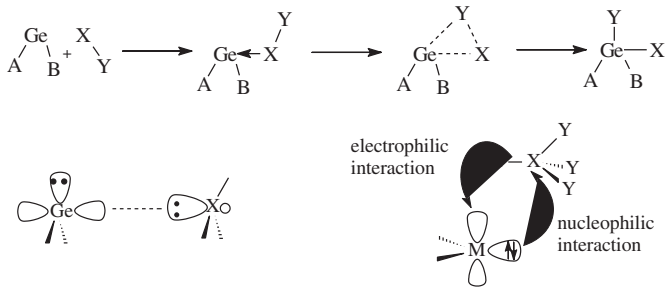


Fig. 5. Molecular structure of complex **10**. Hydrogen atoms are omitted for clarity.



Scheme 7.

Halogenation of "heavy carbenes" may be occurred by action of others reagents (for example $BiCl_3$ [18]). For the first time we investigate reaction of germylenes with $GeCl_4$. It was found that in this reaction dimeric **2** gives pentacoordinated **15**. The driving force for this reaction is formation of polymeric insoluble $GeCl_2$ and compound **15** with transannular interaction (Scheme 8).

Interaction of germylene **2** with $KICl_2$ results in complex reaction mixture from which we can isolate substituted dichlorogermocane **15** with low yield. It is known that $KICl_2$ is a source of ICl [19]. Formation of **15** may be explained by the higher thermodynamic stability of the symmetric derivative which formes under action of KCl on intermediate $ClGe(OCH_2CH_2)_2NMe$ (Scheme 9).

2.4.1.1.2. Interaction with methyl iodide. The results obtained earlier in the course of the investigation of the reactivity of dialkoxy/diaryloxy- and diamidogermylenes and stannylenes indicate that the structure of such "heavy carbenes" determines the pathway of reaction. For example $(ArO)_2Ge$ [Ar = 2,4,6-$(Me_2NCH_2)_3C_6H_2$] with transannular interaction Ge–N adds MeI with forming mixture of insoluble compounds probably possessing quaternized N [20]. The reaction of MeI with complex of dimesityloxygermylene with TMEDA at room temperature results in a product of insertion on C–I bond [21]. At the same time interaction of $(Me_2NCH_2CH_2O)_2Ge$ with methyl iodide results in $[(Me_2NCH_2CH_2O)_2GeMe]^+I^-$ [22]. In this work we investigate the reaction of synthesized monomeric (**10**) and dimeric (**3**) germylenes with MeI (Scheme 10). Reaction of dimeric germylene **3** gives mixture of unidentified compounds. On contrary, interaction of monomeric enantiomerically pure complex **10** gives the expected compound with pentacoordinated Ge atom.

In this reaction mixture of two possible diastereomers (**16a** and **16b**, 2:1) is formed. We assume that these isomers are differed in substituent disposition at the nitrogen atom.

Table 3
ΔH and E_{act} (kcal/mol) in reaction of germylenes with Br_2.

Reaction		**3**	$(\mathbf{3})_2$[a]	**3a**[b]
$M(2+)_{monomer} + Br_2 \rightarrow M(4+)Br_2$	ΔH	−55.5	–	−58.5
	E_{act}	14.1[c,d] 11.6	–	16.2
$M(2+)_{dimer} + Br_2 \rightarrow [M(4+)Br_2\ M(2+)_{monomer}]$	ΔH	–	−63.6	–
	E_{act}	–	8.2 2.7	–
$[M(4+)Br_2\ M(2+)_{monomer}] \rightarrow$ $M(4+)Br_2 + M(2+)_{monomer}$	ΔH	–	−8.6	–
	E_{act}	–	0[e]	–

[a] Dimeric *trans*-structure (**IIIb**).
[b] $(t\text{-BuO})_2Ge$.
[c] Two transition states differed in orientation of bromine atoms.
[d] TS1.
[e] Reaction has no barrier.

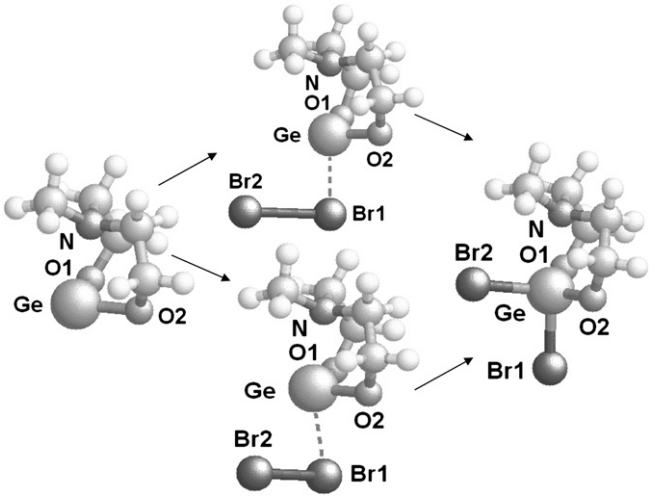


Fig. 6. Reaction of monomeric **3** with bromine (structures of reagents, intermediates, product) according to DFT.

We investigate the mechanism of the reaction of MeI with germylenes by DFT. The results are presented in Table 4.

In our opinion in this reaction there are three possible directions: 1) insertion of germylene into C–I bond; 2) quaternization of nitrogen atom; 3) cleavage of the Ge–O bond while retaining the oxidation state of the germanium atom (2+). Formation of the ionic complex $[MeN(CH_2CH_2O)_2GeMe]^+I^-$ is unlikely due to the ligand structure giving only one additional bond. The product of reaction must contain short covalent a Ge–I bond with a pentacoordinated germanium atom so the first direction of reaction is the most probable.

According to the data in Table 4 there are possible formation of insertion product on C–I bond (thermodynamic control) and formation of ate-complex of type $Me_2N^+(CH_2CH_2O)_2Ge^-I$ (kinetic control). It should be noted that the difference between E_{act} of formation of ate-complexes in case of $(\mathbf{3})_2$ and **3** wider than the difference between E_{act} of formation insertion products. This result is correlated with experimental data about formation of unidentified product mixture in case of $(\mathbf{3})_2$. The formation of the unstable $Me_2N^+(CH_2CH_2O)_2Ge^-I$ compound is more preferred in the case of $(\mathbf{3})_2$. The main reason is the more basic nitrogen atom in $(\mathbf{3})_2$ due to the fact that the Ge atom forms a dimeric structure two additional interaction, and the Ge–N interaction is weaker than that in monomeric germylenes.

The values of activation energy for insertion reactions are significantly more than the energies found earlier in reaction with bromine. This fact corresponds to higher bond energy for C–I in comparing with the energy of the Br–Br bond. Besides in the interaction of "heavy carbene" with MeI (insertion reaction) the activation energy with decreasing coordination number of the central atom is decreased but in the case of bromination the inverse relationship is found.

2.4.1.1.3. Interaction with disulfides. The S–S bond in disulfides is very reactive so insertion of "heavy" analogs of carbenes in these compounds may be regarded as a way to synthesize of disulfur germanium compounds. Interaction of $Ge(OR)_2$ with disulfides is very rare in the literature [20], so it is important to investigate the behavior of the synthesized germylenes in this reaction.

We have found that the disulfide structure has a critical influence on the reactivity in this reaction. The germylenes readily insert into the S–S bond in diphenyldisulfide, but diethyldisulfide is inert

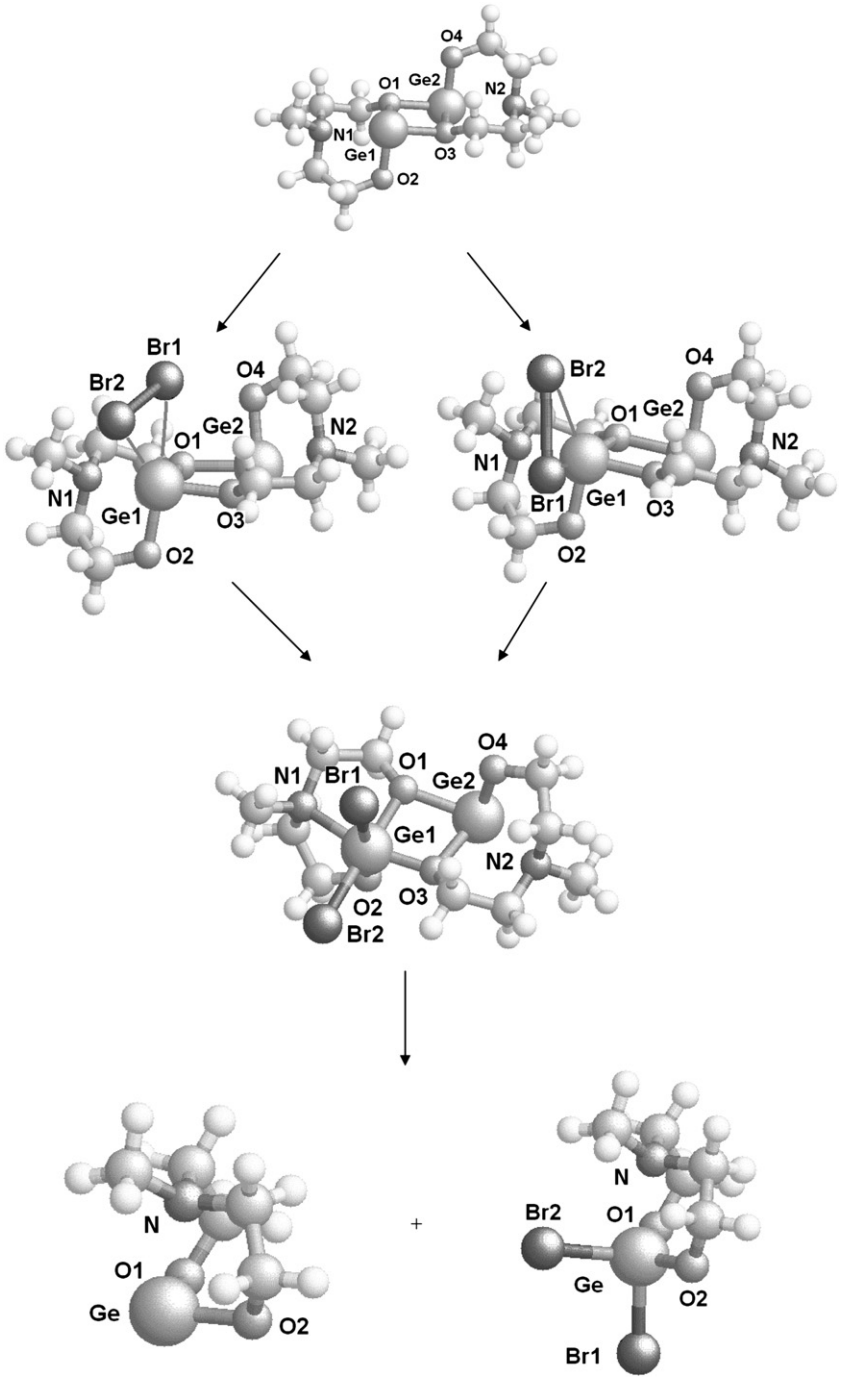


Fig. 7. Reaction of dimeric $(\mathbf{3})_2$ with bromine (structures of reagents, intermediates, products) according to DFT.

in this reaction even under UV irradiation. This fact may be explained by the stronger S–S bond in diethyldisulfide [1c] (Scheme 11). The interaction of dimeric germylene **3** with diphenyldisulfide results in a mixture of insertion product **19** and disproportionation products **17**–**18** (Scheme 11).

The structure of $Ge(SPh)_4$ (**18**) was confirmed by X-ray analysis (Fig. 9). It should be noted that in this case the crystal packing is chiral and crystal contains both enantiomers.

In our opinion, during the first stage in this reaction ocane **19** is formed exclusively. Then this compound is disproportionate into **17** and **18**. Formation of $[MeN(CH_2CH_2O)_2]_2Ge$ (**17**) is thermodynamically favorable due to the existence of four strong Ge–O bonds and two transannular interactions Ge–N [23]. In contrast, in **19** the transannular interaction is lower due to the presence of two thiolate groups at Ge.

In **18** the germanium atom has a distorted tetrahedral coordination. The geometric characteristics of the Ge center in $Ge(SPh)_4$ are close to those found previously for tetrahedral complexes [24].

It should be noted that we also found that closely related monomeric germylene based on diethylenetriamine ligand $(RN(CH_2CH_2NR'^{-})_2)$ behaves analogously to studied dimeric germylenes **3** and **8** [25].

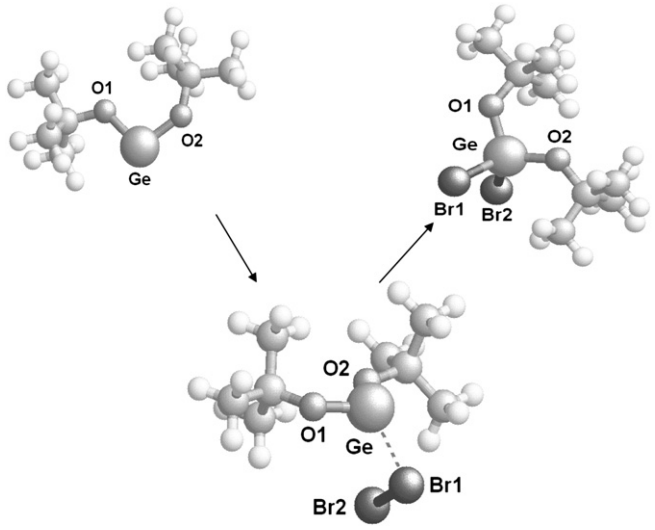


Fig. 8. Reaction of (*t*-BuO)$_2$Ge **3a** with bromine (structures of reagents, intermediates, products) according to DFT.

2.4.1.2. Reaction of [1 + 4]-cycloaddition. The reactions of [1 + 4]-cycloaddition with participation of "heavy" analogs of carbenes have been known for a long time and include interaction with various organic substrates with conjugated double bonds [26,1c]. In this work we systematically investigate a number of such molecules to find the dependence of the reaction pathways from substrate structure. The polymeric or oligomeric materials are the main side products in these reactions.

2.4.1.2.1. Interaction with benzil. Benzil is a typical reagent for reaction of "heavy" carbene analogs in [1 + 4]-cycloaddition reactions [27]. In reaction of dimeric germylene **3** with benzyl the expected complex **21** is formed (Scheme 12).

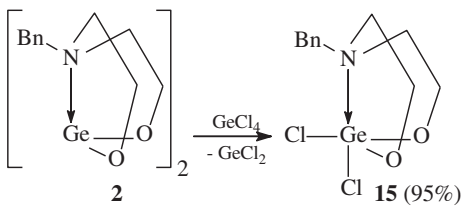
Reactions of germylenes were investigated by DFT calculations (Table 5, Figs. 10–12).

It is established that the activation energies for the compounds studied are low and are close to the energies found for bromination reaction. The reaction occurs as single stage process with transition states presented on Figs. 10–12, so the reaction proceeds as a concerted process and metal atom simultaneously attached to both O atoms.

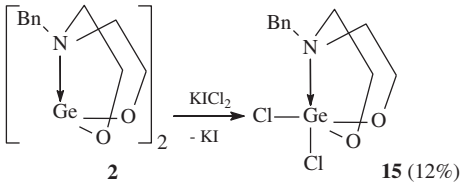
2.4.1.2.2. Interaction with trans-chalcone and its ferrocenic analog. Germylenes **3** and **8** react with *trans*-chalcone and *trans*-FcCH = CHC(O)Ph forming products of a [1 + 4]-cycloaddition (Scheme 13).

The reaction of chalcone with germylene was investigated by DFT calculations (Table 6). All studied reactions are thermodynamically favorable.

It should be noted that we also found that closely related monomeric germylene based on diethylenetriamine ligand (RN($CH_2CH_2NR'^-$)$_2$) behaves analogously to studied dimeric germylenes **3** and **8** in both reactions with benzyl and chalcone [25]. So cycloaddition reactions of studied monomeric and dimeric germylenes should result in desired products with high yield.



Scheme 8.



Scheme 9.

2.4.1.3. Oxidation. All attempt to oxidize dimeric germylene **3** with different oxidizing agents such as trimethylamine oxide, diphenylphosphoryl azide and sulfur failed. In the cases of Me_3NO and DPPA the reactions led to unidentified product mixtures, while germylene **3** with S_8 didn't react. It should be noted that we also found that closely related monomeric germylene based on the diethylenetriamine ligand (RN($CH_2CH_2NR'^-$)$_2$) gave in these three reactions expected products of Ge(4+) [25].

2.4.2. Reactions without changes of germanium oxidation state

The reactions of germylenes which do not change the oxidation state of Ge are important because in such reactions germylenes may be used as catalysts. In this work we investigated the reactivity of the synthesized germylenes in reactions of nucleophilic substitution (Scheme 14).

It was found that the interaction of dimeric **3** with acetic anhydride results in ester of dialkanolamine and $Ge(OAc)_2$. It should be noted that **25** is difficult to access.

The interaction of dimeric germylene **2** with water results in the formation of free ligand $BnN(CH_2CH_2OH)_2$ and solid which was insoluble in common organic solvents. According to reaction mechanism the last compound seems to be germanium hydroxide. So in this reaction there is no formation of the germanol compound (Scheme 15).

It is evident that in this reaction the formation of insoluble germanium hydroxide is thermodynamically favorable.

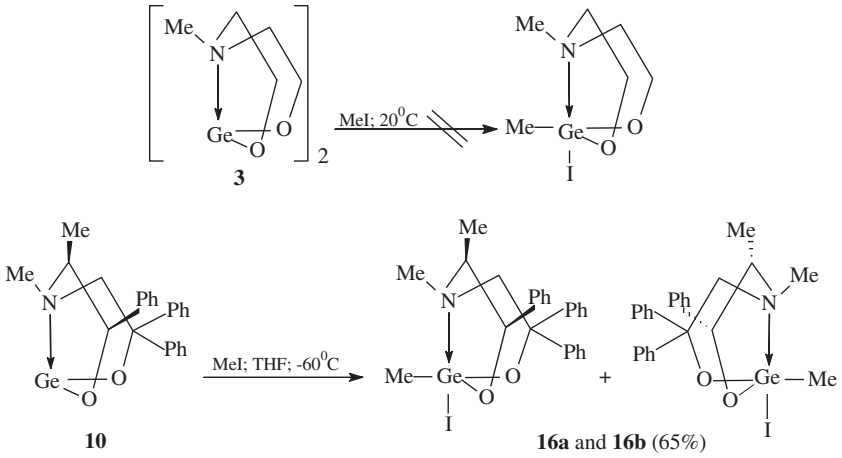
3. Conclusions

In summary, a number of germylenes based on dialkanolamine ligands was synthesized. Therefore, dialkanolamines may be regarded as a good ligand for the stabilization of low valent germanium derivatives. Compounds in which the dialkanolamine ligand contains one or two unsubstituted OCH_2 groups are dimeric. In other cases the complexes are monomeric. Accordingly, germylenes **1**, **3** and **8** are dimeric and **10** is monomeric in the solid state. The studied germylenes participate in reactions of insertion and cycloaddition with the formation of the corresponding desired products.

4. Experimental part

4.1. General methods and remarks

All manipulations were performed under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. *trans*-Stilbene oxide [28], $GeCl_2{*}C_4H_8O_2$ [29], $Ge[N(SiMe_3)_2]_2$ [14], $(Me_2N)_2Ge$ [30], $PhN(CH_2CH_2O)_2GeMe_2$ [11], $BnN(CH_2CH_2OH)_2$ [31], $MeN(CH_2CH_2OH)_2$ [32], $MeN(CH_2CH_2OH)(CH_2CHMeOH)$ [33], $MeN(CH_2CH_2$



Scheme 10.

OH)(CH$_2$CHPhOH) (**a**)/MeN(CH$_2$CH$_2$OH)(CHPhCH$_2$OH)(**b**) (**a**:**b** = 9:1) [34], *erythro*–MeN(CH$_2$CH$_2$OH)(CHPhCHPhOH) [35], *threo*–MeN(CH$_2$CH$_2$OH)(CHPhCHPhOH) [35], MeN(CH$_2$CH$_2$OH)(CH$_2$CPh$_2$OH) [35], *threo*–MeN(CH$_2$CH$_2$OH)[CH(CH$_2$)$_4$CHOH] [35], (*1R,2S*)–MeN(CHMeCHPhOH)(CH$_2$CPh$_2$OH) [36], *threo*–MeN(CH$_2$CH$_2$OH)[CH(CH$_2$)$_3$CHOH] [35], *threo*–MeN(CH$_2$CH$_2$OH)[CHCH$_2$(C$_6$H$_4$)CHOH] [35], (*E*)-FcC(O)CH=CHPh [37] were synthesized according to the literature procedures. GeCl$_4$ (Aldrich), Et$_2$S$_2$ (Aldrich) were distilled prior to use. PhN(CH$_2$CH$_2$OH)$_2$ (Aldrich), Ph$_2$S$_2$ (Aldrich), (PhO)$_2$P(O)N$_3$ (Aldrich), PhC(O)C(O)Ph (Aldrich), trimethylamine oxide (Aldrich) and sulfur (Aldrich) were used as supplied. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with a Bruker 400 spectrometer (in CDCl$_3$ or C$_6$D$_6$ at 295 K). Chemical shifts in the ^{1}H and ^{13}C NMR spectra are given in ppm relative to internal Me$_4$Si. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University. Mass spectra (EI-MS, 70 eV) were recorded on a VARIAN CH-7a device (Philipps-University Marburg, Germany); all assignments were made with reference to the most abundant isotopes.

4.2. Synthesis of compounds

4.2.1. Synthesis of erythro,erythro-MeN(CHPhCHPhOH)$_2$

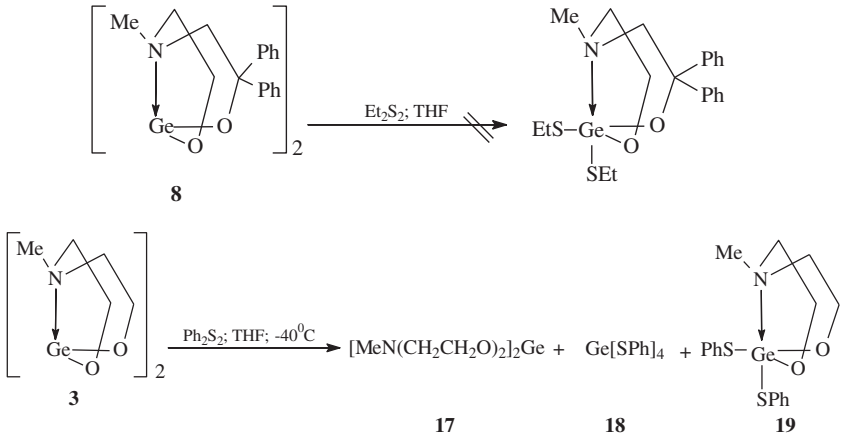
4.2.1.1. Synthesis of erythro,erythro-HN[CH(Ph)CH(Ph)OH]$_2$. The solution of ammonia in methanol (5.5 ml of 2.0 M solution, 0.01 mol) and *trans*-stilbene oxide (5.89 g, 0.03 mol) were mixed in the thick walled bulb. The mixture was stirred overnight, then it was heated at 60 °C during 107 h. The precipitate was filtered off, washed with hexane (3 × 10 ml) and vucuum dried. The HN[CH(Ph)CH(Ph)OH]$_2$ was obtained as a white solid. Yield 3.43 g (83%). According to NMR data, compound was obtained as a mixture of diastereomers in the ratio 1:1. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 2.54 (br s, 1H, NCH), 3.55, 3.77 (2d, 2H, NCH), 4.59, 4.84 (2d, 2H, OCH), 6.72–7.21 (20H, aromatic hydrogens). Anal. Calc. for C$_{28}$H$_{27}$NO$_2$ (409.520): C 82.12, H 6.65, N 3.42. Found: C 82.40, H 6.84, N 3.25.

4.2.1.2. Synthesis of erythro,erythro-MeN[CH(Ph)CH(Ph)OH]$_2$. A solution of 30% solution of CH$_2$O (0.30 ml, 3.00 mmol) was added to *erythro,erythro*-HN[CH(Ph)CH(Ph)OH]$_2$. Formic acid (0.14 g,

Table 4
ΔH and E_{act} (kcal/mol) in reaction of germylenes with MeI.

Reaction		**3**	(**3**)$_2$[a]	**3a**[b]
M(2+)$_{monomer}$ + MeI → M(4+)(Me)I	ΔH	−26.2[c] −28.5	–	−33.0
	E_{act}	40.4[c] 41.1 57.3	–	38.1
M(2+)$_{monomer}$ + MeI → MeN(CH$_2$CH$_2$OMe)CH$_2$CH$_2$O–Ge–I	ΔH	−10.1	–	–[e]
	E_{act}	43.1	–	–[e]
M(2+)$_{monomer}$ + MeI → Me$_2$N$^+$(CH$_2$CH$_2$O)$_2$Ge$^-$I	ΔH	0.1	–	–[e]
	E_{act}	32.0	–	–[e]
M(2+)$_{dimer}$ + MeI → [M(4+)(Me)I M(2+)$_{monomer}$]	ΔH	–	−18.2[c] −16.8	–
	E_{act}	–	37.9[c] 40.0	–
[M(4+)(Me)I M(2+)$_{monomer}$] → M(4+)(Me)I + M(2+)$_{monomer}$	ΔH	–	−1.6[c] −0.3	–
	E_{act}	–	–[d]	–
M(2+)$_{dimer}$+ MeI → MeN(CH$_2$CH$_2$OMe)CH$_2$CH$_2$O–Ge–I M(2+)$_{monomer}$	ΔH	–	6.2	–
	E_{act}	–	50.8	–
M(2+)$_{dimer}$+ MeI → Me$_2$N$^+$(CH$_2$CH$_2$O)$_2$Ge$^-$I M(2+)$_{monomer}$	ΔH	–	5.3[c] 5.9	–
	E_{act}	–	26.8	–

[a] *Trans*-dimer (**IIIb**).
[b] (*t*-BuO)$_2$Ge.
[c] Structures with different orientation of methyl group and iodide.
[d] Reaction without barrier.
[e] Reactions were not studied.



Scheme 11.

3.00 mmol) was added during 1 h, and then mixture was stirred at 75 °C for 5 h. Volatiles were removed in vacuum, the residue was extracted with Et_2O. The water (50 ml) was added to organic extract and the precipitate obtained was filtered off. *erythro*,*erythro*-MeN[CH(Ph)CH(Ph)OH]$_2$ was obtained as white solid. Yield 0.90 g (68%). According to NMR data, compound was obtained as a mixture of diastereomers in the ratio 5:4. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): $\delta = 2.06, 2.58$ (2s, 6H, NH_3), 3.57, 3.95 (2d, 2H, NCH), 5.20, 5.44 (2d, 2H, OCH), 7.00–7.04, 7.11–7.25 (2m, 20H, aromatic hydrogens). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 35.26, 35.90$ (NCH_3), 70.63, 71.40, 72.26, 72.43 (NCH, OCH), 126.30, 126.43, 127.33, 127.52, 127.55, 127.58, 127.62, 127.86, 127.96, 129.89, 129.95, 134.69, 135.42, 141.49, 141.57 (aromatic carbons). Signal of one carbon atom was not found. Anal. Calc. for $C_{29}H_{29}NO_2$ (423.546): C 82.24, H 6.90, N 3.31. Found: C 82.01, H 7.07, N 3.08.

4.2.2. Synthesis of PhN(CH_2CH_2O)$_2$Ge (**1**)

Method A. A solution of PhN(CH_2CH_2OH)$_2$ (0.14 g, 0.76 mmol) in toluene (10 ml) was added to a stirred solution of Ge[N(TMS)$_2$]$_2$ (0.30 g, 0.76 mmol) in toluene (10 ml), and the mixture was stirred at room temperature. After 4 days the reaction mixture was concentrated under vacuum (approximately third part was removed), and the solid formed was filtered off to give **1** as a white solid. Yield 0.12 g (63%). ^{1}H NMR (400 MHz, C_6D_6, ppm): $\delta = 2.62–2.99$ (m, 4H, NCH_2), 3.94 (br s, 4H, OCH_2), 6.82–6.87, 7.07–7.16 (2m, 5H, aromatic hydrogens). ^{13}C NMR (100 MHz, C_6D_6, ppm): $\delta = 56.54$ (NCH_2), 61.82 (OCH_2), 115.32, 118.95, 128.87, 129.27 (aromatic carbons).

Method B. A solution of PhN(CH_2CH_2OH)$_2$GeMe$_2$ (0.12 g, 0.43 mmol) in toluene (20 ml) was added to a stirred solid of $GeCl_2$*$C_4H_8O_2$ (0.10 g, 0.43 mmol). The reaction mixture was stirred for 3 days at room temperature and all volatiles were removed under reduced pressure. Then ether (10 ml) was added to the residue, the precipitate was filtered off to give **1** as a white powder. Yield 0.11 g (60%).

4.2.3. Synthesis of BnN(CH_2CH_2O)$_2$Ge (**2**)

Analogously to **1** (Method A), complex **2** was prepared from BnN(CH_2CH_2OH)$_2$ (0.23 g, 1.20 mmol) and Ge[N(TMS)$_2$]$_2$ (0.47 g, 1.20 mmol) in toluene (20 ml). The mixture was stirred for 4 days at room temperature and all volatiles were removed under reduced pressure. Then ether (10 ml) was added to the residue, the precipitate was filtered off to give **2** as a white solid. Yield 0.17 g (53%). ^{1}H NMR (400 MHz, C_6D_6, ppm): $\delta = 1.88–1.96, 2.50–2.56$ (2m, 4H, NCH_2), 3.56 (s, 2H, CH_2Ph), 3.56–3.60, 3.87–3.92 (2m, 4H, OCH_2), 6.81–6.87, 7.03–7.06 (2m, 5H, aromatic hydrogens). ^{13}C NMR (100 MHz, C_6D_6, ppm): $\delta = 50.38, 57.39, 58.06$ (NCH_2, OCH_2), 128.23, 128.59, 131.50, 135.12 (aromatic carbons). Anal. Calc. for $C_{11}H_{15}GeNO_2$ (265.8523): C 49.70, H 5.69, N 5.27. Found: C 49.55, H 5.45, N 5.36.

4.2.4. Synthesis of MeN(CH_2CH_2O)$_2$Ge (**3**)

Method A. Analogously to **2**, complex 3 was prepared from MeN(CH_2CH_2OH)$_2$ (0.15 g, 1.25 mmol) and Ge[N(TMS)$_2$]$_2$ (0.49 g,

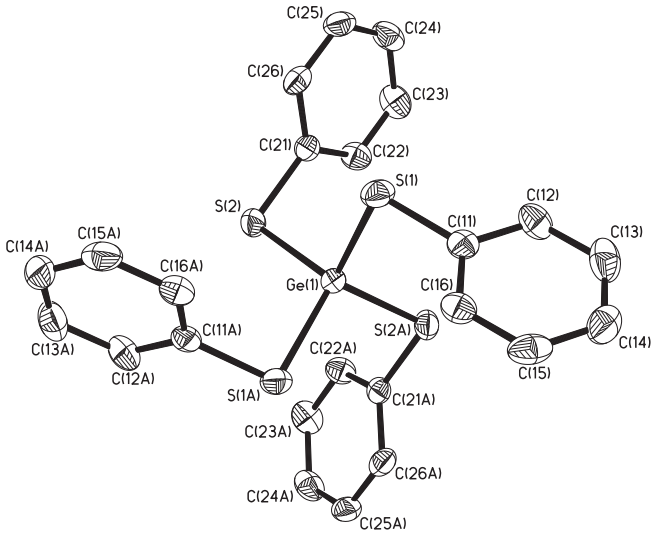
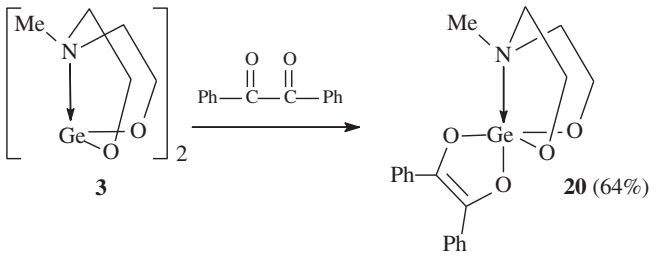


Fig. 9. Molecular structure of complex Ge(SPh)$_4$ (**18**). Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (°): Ge(1)–S(1) 2.2149(6), Ge(1)–S(2) 2.2191(5), S(1)–C(11) 1.7873(19), S(2)–C(21) 1.7927(19), S(1)–Ge(1)–S(1A) 115.15(4), S(1)–Ge(1)–S(2) 105.461(19), S(1)–Ge(1)–S(2) 107.848(19), C(11)–S(1)–Ge(1) 99.67(6), C(21)–S(2) Ge(1) 98.13(6).



Scheme 12.

Table 5
ΔH and E_{act} (kcal/mol) in interaction of germylenes with benzil.

Reaction		**3**	$(\mathbf{3})_2$[a]	**3a**[b]
$M(+2)_{monomer}$+ PhC(O)-C(O)Ph →M(+4)[(Ph)C(O−) = C(O−)Ph]	ΔH	−24.2	–	−21.7
	E_{act}	10.8[c]	–	6.2
		8.5		
$M(+2)_{dimer}$ + PhC(O)-C(O)Ph→ [M(+4)[(Ph)C(O−) = C(O−)Ph]$M(+2)_{monomer}$]	ΔH	–	−14.9	–
	E_{act}	–	4.0[c]	–
			2.8	
[M(+4)[(Ph)C(O−) = C(O−)Ph]$M(+2)_{monomer}$] → M(4+)[(Ph)C(O−) = C(O−)Ph] + $M(2+)_{monomer}$	ΔH	–	−9.3	–
	E_{act}	–	0[d]	–

[a] *Trans*-dimer **IIIb**.
[b] (*t*-BuO)$_2$Ge.
[c] There are two transition states differed in orientation of O atoms.
[d] Reaction without energetic barrier.

1.25 mmol) in toluene (20 ml). The product was isolated by filtration to give **3** as a white solid. Yield 0.21 g (89%). ^{1}H NMR (400 MHz, C_6D_6, ppm): $\delta = 1.87$ (s, 3H, NCH_3), 1.89–2.01 (m, 4H, NCH_2), 3.85–4.05 (m, 4H, OCH_2). ^{13}C NMR (100 MHz, C_6D_6, ppm): $\delta = 45.16$ (CH_3), 60.81 (NCH_2), 66.27 (OCH_2). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): $\delta = 2.74$ (s, 3H, CH_3N), 2.73–2.80 (m, 4H, NCH_2), 3.96–4.18 (m, 4H, OCH_2). ^{13}C NMR (100 MHz, C_6D_6, ppm): $\delta = 45.58$ (CH_3N), 60.50 (NCH_2), 65.54 (OCH_2). EI MS (rel. int.): $[M]^+$ 192 (**1**); $[M-CH_2O]^+$ 161 (**5**).

Method B. A solution of $MeN(CH_2CH_2OH)_2$ (0.13 g, 1.10 mmol) in toluene (10 ml) was added to a stirred solution of $(Me_2N)_2Ge$ (0.17 g, 1.10 mmol). The reaction mixture was stirred for 4 days at room temperature and all volatiles were removed under reduced pressure. Then ether (10 ml) was added to the residue, the precipitate was filtered off to give **3** as a white powder. Yield 0.16 g (92%).

4.2.5. Synthesis of $MeN(CH_2CH_2O)(CH_2CHMeO)Ge$ (**4**)

Analogously to **2**, complex **4** was prepared from $MeN(CH_2CH_2OH)(CH_2CHMeOH)$ (0.14 g, 1.04 mmol) and $Ge[N(TMS)_2]_2$ (0.41 g, 1.04 mmol) in toluene (20 ml). The product was isolated by

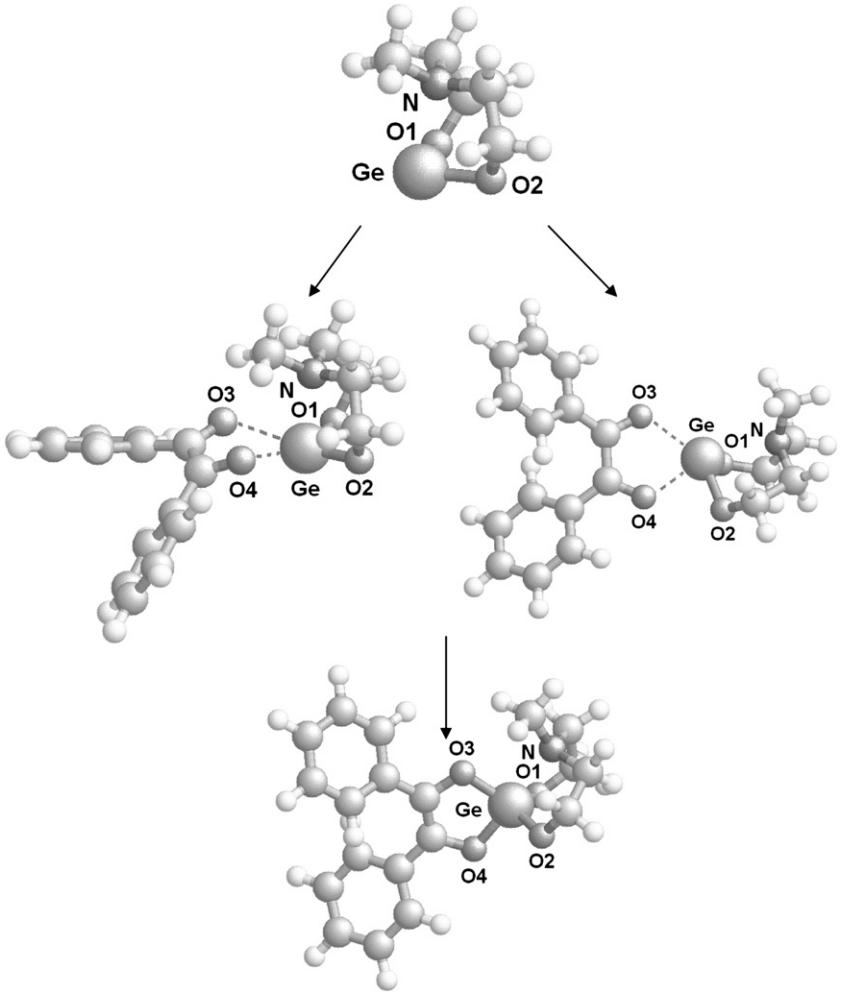


Fig. 10. Reaction of monomeric **3** with benzil (structures of reagents, intermediates, product) according to DFT.

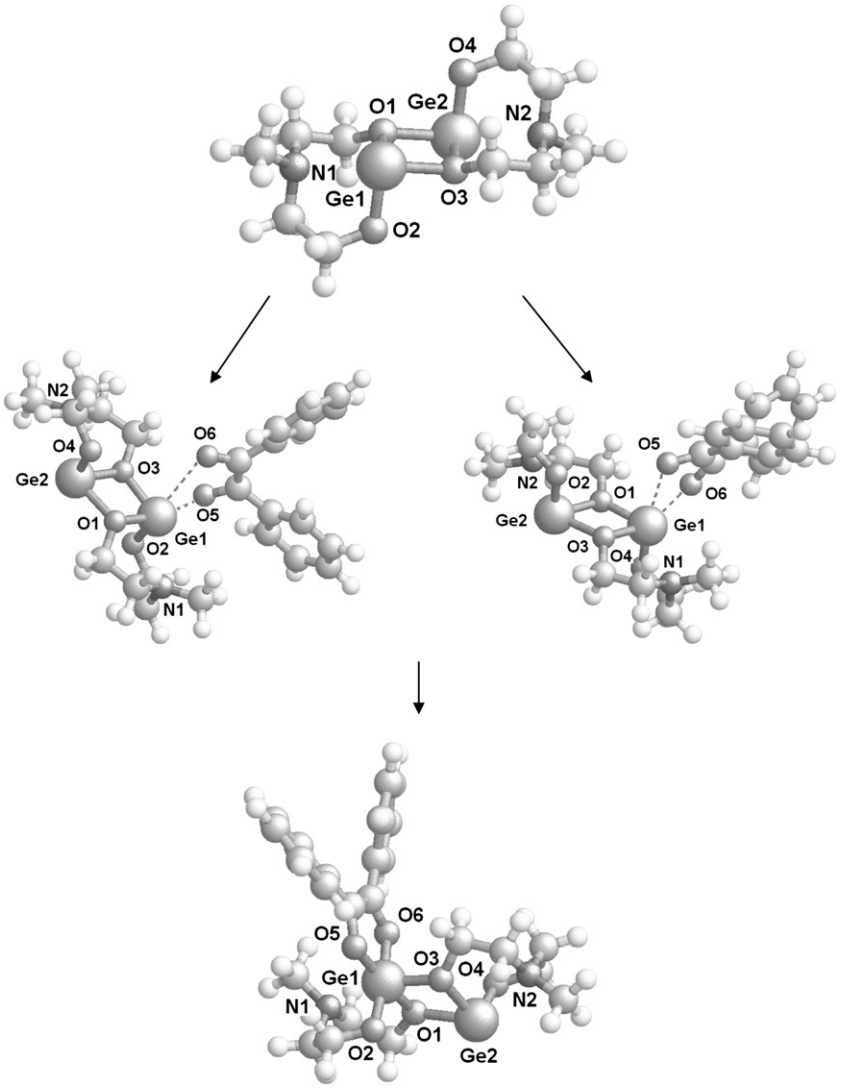


Fig. 11. Reaction of dimeric $(\mathbf{3})_2$ with benzil (structures of reagents, intermediates, product) according to DFT.

filtration to give **4** as a white solid. Yield 0.06 g (29%). ^{1}H NMR (400 MHz, C_6D_6, ppm): δ = 1.12 (d, 3H, J = 5.8 Hz, C$\underline{H}_3$CH), 1.93 (s, 3H, CH_3N), 1.89–2.04 (m, 4H, NCH_2), 3.94–4.13 (m, 2H, OCH_2), 4.31–4.41 (m, 1H, OCH). ^{13}C NMR (100 MHz, C_6D_6, ppm): δ = 22.63 ($\underline{C}H_3CH$), 46.76 (CH_3N), 61.82, 67.97 (NCH_2), 68.95 (OCH_2), 74.38 (OCH). Anal. Calc. for $C_6H_{13}GeNO_2$ (203.783): C 35.36, H 6.43, N 6.87. Found: C 35.40, H 6.41, N 6.89.

*4.2.6. Synthesis of MeN(CH_2CH_2O)(CH_2CHPhO)Ge (**5**)*

Analogously to **2**, complex **5** was prepared from the inseparable mixture of MeN(CH_2CH_2OH)($CH_2CHPhOH$) (**a**)/MeN(CH_2-CH_2OH)($CHPhCH_2OH$) (**b**) (0.17 g, 0.87 mmol, **a**:**b** = 9:1) and Ge$[N(TMS)_2]_2$ (0.34 g, 0.87 mmol) in toluene (20 ml). The product was isolated by filtration to give **5** as a white solid. Yield 0.17 g (71%). ^{1}H NMR (400 MHz, C_6D_6, ppm): δ = 1.86 (s, 3H, CH_3N), 1.89–2.14, 2.23–2.36 (2m, 4H, NCH_2), 3.92–4.29 (m, 2H, CH_2O), 5.35–5.45 (m, 1H, OCHPh), 7.20–7.30, 7.41–7.58 (2m, 5H, aromatic hydrogens). ^{13}C NMR (100 MHz, C_6D_6, ppm): δ = 46.13 (CH_3N), 61.21, 67.33 (NCH_2), 68.93 (OCH_2), 80.12 (OCH), 127.37, 128.41, 128.61, 144.29 (aromatic carbons). Anal. Calc. for $C_{11}H_{15}GeNO_2$ (265.8523): C 49.70, H 5.69, N 5.27. Found: C 49.67, H 5.40, N 5.07.

*4.2.7. Synthesis of erythro-MeN(CH_2CH_2O)(CHPhCHPhO)Ge (**6**)*

Analogously to **2**, complex **6** was prepared from *erythro*–MeN(CH_2CH_2OH)(CHPhCHPhOH) (0.38 g, 1.40 mmol) and Ge$[N(TMS)_2]_2$ (0.55 g, 1.40 mmol) in toluene (20 ml). The product was isolated by filtration to give **6** as a white solid. Yield 0.41 g (86%). ^{1}H NMR (400 MHz, C_6D_6, ppm): δ = 1.81 (s, 3H, CH_3), 2.03–2.13, 2.58–2.69 (2m, 2H, NCH_2), 3.46 (d, 1H, J = 3.8 Hz, NCH), 3.86–3.97, 4.17–4.28 (2m, 2H, OCH_2), 5.98 (d, 1H, J = 3.8 Hz, OCH), 6.77–6.90, 6.99–7.07, 7.27–7.33 (3m, 10H, aromatic hydrogens). ^{13}C NMR (100 MHz, C_6D_6, ppm): δ = 42.42 (CH_3), 62.08 (NCH_2), 64.47 (OCH_2), 80.02 (NCH), 80.95 (OCH), 126.38, 126.58, 127.88, 131.12, 134.97 (aromatic carbons). The signals of three carbon atoms were not found due to overlap with the solvent signals. Anal. Calc. for $C_{17}H_{19}GeNO_2$ (341.9483): C 59.71, H 5.60, N 4.10. Found: C 59.50, H 5.46, N 4.15.

*4.2.8. Synthesis of threo-MeN(CH_2CH_2O)(CHPhCHPhO)Ge (**7**)*

Analogously to **2**, complex **7** was prepared from *threo*–MeN(CH_2CH_2OH)(CHPhCHPhOH) (0.18 g, 0.66 mmol) and Ge$[N(TMS)_2]_2$ (0.26 g, 0.66 mmol) in toluene (20 ml). The product was isolated by filtration to give **7** as a white solid. Yield 0.14 g (61%). ^{1}H NMR (400 MHz, C_6D_6, ppm): δ = 1.87 (s, 3H, CH_3N), 1.93–2.09, 2.82–2.99, 3.38–3.55, 3.95–4.11, 4.37–4.50, 5.70–5.89 (6m, 6H,

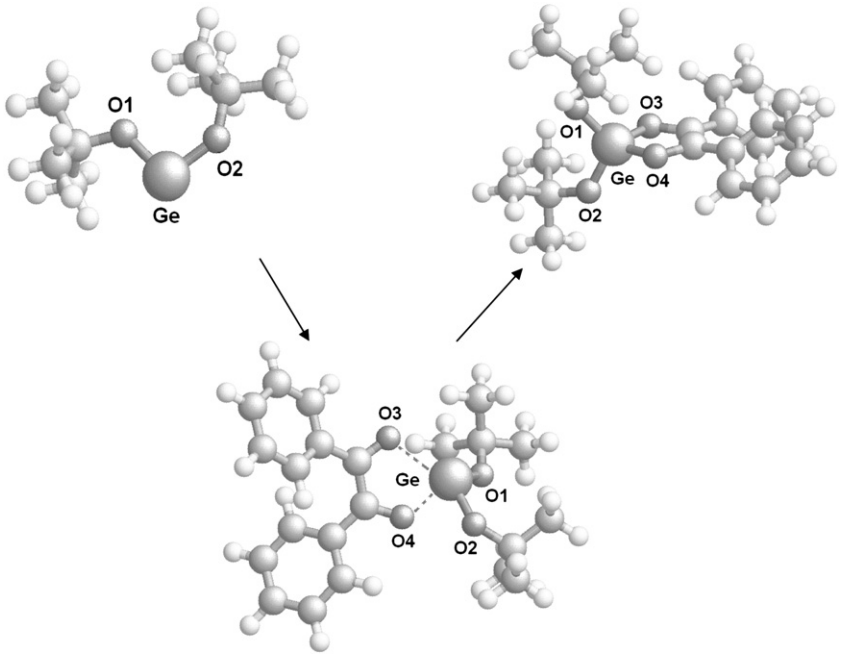


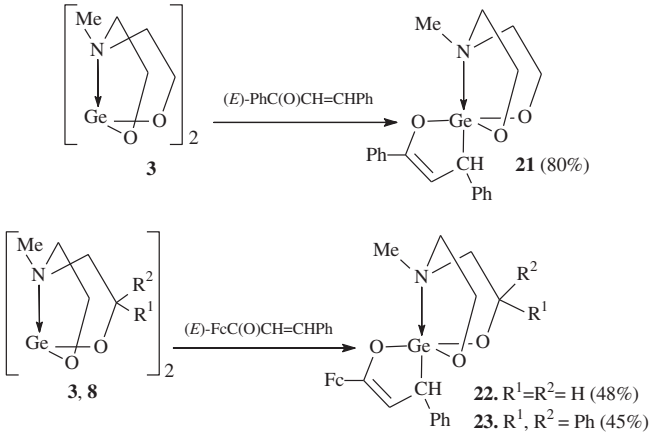
Fig. 12. Reaction of (*t*-BuO)$_2$Ge **3a** with benzil (structures of reagents, intermediates, product) according to DFT.

NCH_2, NCH, OCH_2, OCH), 6.60–6.70, 6.81–6.98, 7.01–7.08, 7.31–7.40 (4m, 10H, aromatic hydrogens). ^{13}C NMR spectra is not recorded due to insolubility of **7**. Anal. Calc. for $C_{17}H_{19}GeNO_2$ (341.9483): C 59.71, H 5.60, N 4.10. Found: C 59.80, H 5.51, N 4.13.

*4.2.9. Synthesis of MeN(CH$_2$CH$_2$O)(CH$_2$CPh$_2$O)Ge (**8**)*

Method A. Analogously to **2**, complex **8** was prepared from $MeN(CH_2CH_2OH)(CH_2CPh_2OH)$ (0.38 g, 1.42 mmol) and Ge$[N(TMS)_2]_2$ (0.56 g, 1.42 mmol) in toluene (20 ml). The product was isolated by filtration to give **8** as a white solid. Yield 0.47 g (96%). ^{1}H NMR (400 MHz, C_6D_6, ppm): δ = 1.84 (s, 3H, CH_3), 1.75–1.87 (m, 2H, NCH_2), 2.57, 3.14 (2d, 2H, J = 13.0 Hz, AM system of NCH_2CPh_2 group protons), 3.89–3.95, 3.99–4.10 (2m, 2H, OCH_2), 6.93–7.04, 7.08–7.17, 7.60–7.74 (3m, 10H, aromatic hydrogens). ^{13}C NMR (100 MHz, C_6D_6, ppm): δ = 45.45 (CH_3), 63.69, 64.58, 66.48 (2NCH_2, OCH_2), 84.20 ($OCPh_2$), 125.74, 126.78, 126.93, 127.09, 128.31, 128.36, 147.95, 148.88 (aromatic carbons). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.40 (s, 3 H), 2.67–2.73, 2.84–2.92 (2m, 2H, NCH_2CH_2), 3.55–3.58 (m, 2H, NCH_2CPh_2), 3.79–3.89, 3.91–3.98 (2m, 2H, CH_2O), 7.17–7.23, 7.27–7.34, 7.53–7.62 (3m, 10H, Ph). Anal. Calc. for $C_{17}H_{19}GeNO_2$ (341.9483): C 59.71, H 5.60, N 4.10. Found: C 59.64, H 5.43, N 4.42.

Method B. KC_8 (0.22 g, 1.60 mmol) was added to solution of $MeN(CH_2CH_2O)(CH_2CPh_2O)GeBr_2$ (14) (0.16 g, 0.32 mmol) in THF (30 ml) at room temperature. Reaction mixture was stirred for 4 days. Volatiles were evaporated under reduced pressure, toluene (20 ml) was added to mixture, slurry was filtered and solvent was evaporated. The residue was recrystallized from toluene. The product was isolated as white solid. Yield 0.07 (66%). NMR spectra were identical to above mentioned.



Scheme 13.

*4.2.10. Synthesis of erythro,erythro-MeN(CHPhCHPhO)$_2$Ge (**9**)*

Analogously to **2**, complex **9** was prepared from *erythro*,*erythro*-$MeN(CHPhCHPhOH)_2$ (0.45 g, 1.07 mmol) and Ge$[N(TMS)_2]_2$ (0.42 g, 1.07 mmol) in toluene (20 ml). The product was isolated by filtration to give **9** as a yellow solid. Yield 0.22 g (42%). Compound **9** was obtained as a mixture of diastereomers in the ratio 2:1. ^{1}H NMR (400 MHz, C_6D_6, ppm): δ = 1.89, 2.25 (2s, 6H, CH_3N), 3.86 (d, J = 4.8 Hz), 4.03 (d, J = 4.8 Hz), 4.52 (d, J = 5.3 Hz), 5.50 (d, J = 4.3 Hz), 6.49 (d, J = 3.5 Hz), 6.49 (d, J = 5.0 Hz) (8H, NCH, OCH), 6.61–6.74, 6.77–7.12, 7.39–7.47, 7.54–7.62 (4m, 40H, aromatic hydrogens). ^{13}C NMR (100 MHz, C_6D_6, ppm): δ = 45.70, 45.74 (CH_3N), 71.94, 72.77, 78.09, 78.70, 81.35, 82.77 (NCH, OCH), 125.95, 126.09, 126.23, 126.35, 126.56, 127.09, 127.38, 127.68, 127.92, 128.14, 131.67, 131.72, 141.60, 141.99, 142.63, 142.96 (aromatic carbons). Anal. Calc. for $C_{29}H_{27}GeNO_2$ (494.1402): C 70.49, H 5.51, N 2.83. Found: C 69.99, H 5.13, N 3.10.

*4.2.11. Synthesis of MeN((S)-CHMe-(R)-CHPhO)(CH$_2$CPh$_2$O)Ge (**10**)*

Analogously to **2**, complex **10** was prepared from (*1R*,*2S*)-$MeN(CHMeCHPhOH)(CH_2CPh_2OH)$ (0.87 g, 2.41 mmol) and Ge$[N(TMS)_2]_2$ (0.95 g, 2.41 mmol) in toluene (20 ml). The product was isolated by filtration to give **10** as a white solid. Yield 0.81 g (78%). ^{1}H NMR (400 MHz, C_6D_6, ppm): δ = 0.46 (d, 3H, J = 6.8 Hz, $NCHC\underline{H}_3$), 1.88 (s, 3H, NCH_3), 2.39–2.48 (m, 1H, $NC\underline{H}CH_3$), 3.22, 3.45 (2d, 2H, J = 13.1 Hz, AM system of NCH_2CPh_2 group protons), 5.80 (d, 1H, J = 2.0 Hz, OCHPh), 6.96–7.04, 7.06–7.23, 7.31–7.37,

Table 6
ΔH and E_{act} (kcal/mol) in reaction of germylenes with chalcone.

Reaction		**3**	$(\mathbf{3})_2$[a]	**3a**[b]
$M(+2)_{monomer}$ + PhCH = CH-C(O)Ph → M(+4)[(Ph)C(O−) = CHCH(Ph)−]	ΔH	−14.1[c] −14.6	−	−16.3
	E_{act}	6.4[c] 3.6	−	1.6[c] 4.1
$M(+2)_{dimer}$+ PhCH = CHC(O)Ph → [M(+4)[(Ph)C(O−) = CHCH(Ph)−]$M(+2)_{monomer}$]	ΔH	−	−4.7[c] −4.6 −4.9 −6.4	−
	E_{act}	−	8.3[c] 9.2 9.2 4.7	−
[M(+4)[(Ph)C(O−) = CHCH(Ph)−]$M(+2)_{monomer}$] → M(+4)[(Ph)C(O−) = CHCH(Ph)−] + $M(2+)_{monomer}$	ΔH	−	−2.1[c] −2.0 −2.3 −3.8	−
	E_{act}	−	0[d]	−

[a] *Trans*-dimer (**IIIb**).
[b] $(t\text{-BuO})_2$Ge.
[c] It is found several structures which are differed in orientation of substituent.
[d] Reaction without energetic barrier.

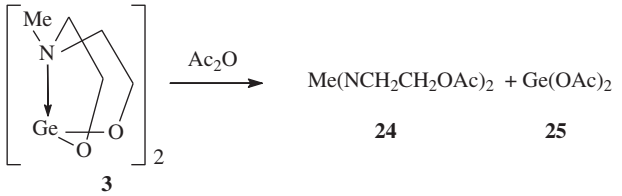
7.68−7.82 (4m, 15H, aromatic hydrogens). ^{13}C NMR (100 MHz, C_6D_6, ppm): δ = 11.00 (NCHCH$_3$), 41.00 (NCH_3), 68.75, 70.33 (NCHCH$_3$, NCH_2), 78.97 (OCHPh), 84.43 ($OCPh_2$), 125.61, 126.58, 126.84, 126.88, 126.99, 127.13, 127.88, 128.45, 128.49, 142.93, 147.92, 149.15 (aromatic carbons). Anal. Calc. for $C_{24}H_{25}GeNO_2$ (432.0708): C 66.72, H 5.83, N 3.24. Found: C 66.45, H 5.64, N 3.30.

4.2.12. Synthesis of threo-MeN(CH_2CH_2O)[$CH(CH_2)_3CHO$]Ge (**11**)

Analogously to **2**, complex **11** was prepared from *threo*-MeN(CH_2CH_2OH)[$CH(CH_2)_3CHOH$] (0.15 g, 0.97 mmol) and Ge $[N(TMS)_2]_2$ (0.38 g, 0.97 mmol) in toluene (20 ml). The product was isolated by filtration to give **11** as a white solid. Yield 0.14 g (64%). ^{1}H NMR (400 MHz, C_6D_6, ppm): δ = 1.20−1.64 (m, 6H, C_3H_6), 1.99 (s, 3H, CH_3N), 1.77−2.07, 2.27−2.56 (2m, 3H, NCH, NCH_2), 3.72−3.90, 4.00−4.11, 4.30−4.47 (3m, 3H, OCH, OCH_2). ^{13}C NMR (100 MHz, C_6D_6, ppm): δ = 19.52, 27.99, 30.16 (CH_2), 41.47 (CH_3N), 50.10 (NCH_2), 61.42, 73.34 (NCH, OCH_2), 77.09 (OCH). The satisfactory results of elemental analysis were not obtained due to hygroscopicity of **11**.

4.2.13. Synthesis of threo-MeN(CH_2CH_2O)[$CH(CH_2)_4CHO$]Ge (**12**)

Analogously to **2**, complex **12** was prepared from *threo*-MeN(CH_2CH_2OH)[$CH(CH_2)_4CHOH$] (0.18 g, 1.04 mmol) and Ge $[N(TMS)_2]_2$ (0.41 g, 1.04 mmol) in toluene (20 ml). The product was isolated by filtration to give **12** as a yellow solid. Yield 0.15 g (60%). ^{1}H NMR (400 MHz, C_6D_6, ppm): δ = 0.45−0.65, 0.67−1.01, 1.07−1.50, 1.56−1.67 (4m, 8H, C_4H_8), 1.89 (s, 3H, CH_3N), 1.69−1.82, 2.20−2.35 (2m, 3H, NCH, NCH_2), 3.73−3.85, 3.89−4.00, 4.03−4.14 (3m, 3H, OCH, OCH_2). ^{13}C NMR (100 MHz, C_6D_6, ppm): δ = 22.44, 24.06, 25.29, 36.50 (CH_2), 42.46 (CH_3N), 52.79, 65.92, 73.05, 78.82 (NCH_2, NCH, OCH_2, OCH). The satisfactory results of elemental analysis were not obtained due to hygroscopicity of **12**.



3 **24** **25**

Scheme 14.

4.2.14. Synthesis of threo-MeN(CH_2CH_2O)[$CHCH_2(C_6H_4)CHO$]Ge (**13**)

Analogously to **2**, complex **13** was prepared from *threo*-MeN(CH_2CH_2OH)[$CHCH_2(C_6H_4)CHOH$] (0.19 g, 0.92 mmol) and Ge $[N(TMS)_2]_2$ (0.36 g, 0.92 mmol) in toluene (20 ml). The product was isolated by filtration to give **13** as a yellow solid. Yield 0.23 g (88%). ^{1}H NMR (400 MHz, C_6D_6, ppm): δ = 2.38 (s, 3H, CH_3N), 2.14−2.54, 2.61−3.23, 3.52−3.95, 4.71−4.49 (4m, 8H, NCH_2, NCH, OCH_2, OCH, CH_2), 6.86−6.99 (m, 4H, aromatic hydrogens). ^{13}C NMR spectrum is not recorded due to insolubility of **13**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.91 (s, 3H, CH_3N), 2.52−2.66, 2.70−2.97, 3.05−3.16, 3.80−3.93, 3.98−4.15, 4.55−4.69 (6m, 8H, NCH_2, NCH, OCH_2, OCH, CH_2), 7.09−7.22 (m, 4H, aromatic hydrogens). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 35.09 (CH_3N), 42.93, 50.91, 60.62, 76.32, 78.84 (NCH_2, NCH, OCH_2, OCH, CH_2), 122.66, 126.26, 126.53, 127.52, 140.76 (aromatic carbons). Signal of one aromatic carbon was not found. Anal. Calc. for $C_{12}H_{15}GeNO_2$ (277.863): C 51.87, H 5.44, N 5.04. Found: C 51.83, H 5.47, N 5.06.

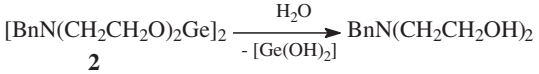
4.3. Reactions of germylenes with changing of germanium oxidation state

4.3.1. Reaction of **8** with bromine. Synthesis of MeN(CH_2CH_2O)(CH_2CPh_2O)$GeBr_2$ (**14**)

A solution of bromine (0.05 g, 0.30 mmol) in toluene (10 ml) was added to a stirred solution of **8** (0.11 g, 0.30 mmol) in toluene (10 ml). The reaction mixture was stirred for 1 day at room temperature and solvents were removed in vacuum. Then ether (10 ml) was added to the residue, the precipitate was filtered off to give **14** as a white solid. Yield 0.10 g (66%). The ^{1}H and ^{13}C NMR spectra were in accord with the data of literature [13].

4.3.2. Reaction of **2** with $KICl_2$ or $GeCl_4$. Synthesis of BnN(CH_2CH_2O)$_2GeCl_2$ (**15**)

Method A. Reaction of **2** *with* $KICl_2$. A solid $KICl_2$ (0.12 g, 0.50 mmol) was added to a stirred solution of 2 (0.13 g, 0.50 mmol)



2

Scheme 15.

in toluene (10 ml). The reaction mixture was refluxed for 15 h. The precipitated solid was filtered. The filtrate was concentrated, and the solid formed was filtered off to give **15** as a white solid. Yield 0.02 g (12%). ^{1}H NMR (400 MHz, C_6D_6, ppm): δ = 2.71–2.77, 3.01–3.07 (2m, 4H, $2NCH_2$), 3.97–4.03, 4.08–4.14 (2m, 4H, $2OCH_2$), 4.00 (s, 2H, CH_2Ph), 7.13–7.16, 7.21–7.23, 7.41–7.42 (3m, 5H, aromatic hydrogens). ^{13}C NMR (100 MHz, C_6D_6, ppm): δ = 49.18 (NCH_2), 57.29 (NCH_2Ph), 58.64 (OCH_2), 129.14, 129.44, 131.01, 131.27 (aromatic carbons). Anal. Calc. for $C_{11}H_{15}Cl_2GeNO_2$ (336.7577): *C* 39.23, H 4.49, N 4.16. Found: *C* 39.35, H 4.50, N 4.28.

*Method B. Reaction of **2** with $GeCl_4$.* A solution of $GeCl_4$ (0.12 g, 0.56 mmol) in toluene (5 ml) was added to a stirred solution of 2 (0.15 g, 0.56 mmol) in toluene (10 ml). The reaction mixture was stirred under reflux for 3 days. The solid formed ($GeCl_2$) was filtered off and all volatiles were removed in vacuum. Then ether (10 ml) was added to the residue, the precipitate was filtered off, washed with diethyl ether (2 × 2 ml) and dried under vacuum to give **15** as a white solid. Yield 0.18 g (95%).

4.3.3. Reaction of **10** with MeI. synthesis of MeN((S)-CHMe-(R)-CHPhO)(CH_2CPh_2O)GeMeI (**16a** and **16b**)

To a stirred solution of **10** (0.35 g, 0.81 mmol) in THF (8 ml) was added dropwise solution of MeI (0.23 g, 1.62 mmol) in THF (2 ml) at −60 °C. The reaction mixture was stirred for 20 min and allowed to warm to room temperature. After 7 days the solid was filtered off to give **16** as a white solid. Yield 0.30 g (65%). According to NMR data, compound **10** was obtained as a mixture of diastereomers in the ratio 2:1. Anal. Calc. for $C_{25}H_{28}GeINO_2$ (574.0098): C 52.31, H 4.92, N 2.44. Found: C 52.38, H 4.90, N 2.42. Complex (**16a**): ^{1}H NMR (400 MHz, C_6D_6, ppm): δ = 0.37 (d, 3H, J = 6.6 Hz, NCHC$\underline{H}_3$), 1.38 (s, 3H, CH_3Ge), 1.62 (s, 3H, NCH_3), 2.62–2.64 (m, 1H, C$\underline{H}CH_3$), 3.33, 3.63 (2d, 2H, J = 13.7 Hz, AM system of NCH_2 group protons), 5.10–5.15 (m, 1H, OCHPh), 6.85–7.01, 7.05–7.10, 7.57–7.67, 7.74–7.84 (4m, 10H, aromatic hydrogens). ^{13}C NMR (100 MHz, C_6D_6, ppm): δ = 10.45 (NCH$\underline{C}H_3$), 23.95 (CH_3Ge), 41.86 (NCH_3), 60.58 (N$\underline{C}H_2CPh$), 65.97 (N$\underline{C}HCH_3$), 73.65 (OCHPh), 79.76 ($OCPh_2$), 125.43, 125.99, 126.48, 126.86, 127.32, 127.56, 128.13, 128.36, 128.81, 140.90, 146.01, 147.67 (aromatic carbons). Complex (**16b**): ^{1}H NMR (400 MHz, C_6D_6, ppm): δ = 0.72 (d, 3H, J = 6.8 Hz, NCHC$\underline{H}_3$), 1.43 (s, 3H, CH_3Ge), 1.58 (s, 3H, NCH_3), 2.62–2.65 (m, 1H, C$\underline{H}CH_3$), 2.95–3.09 (m, 2H, NCH_2), 4.96 (d, 1H, J = 6.6 Hz, OCHPh), 6.85–7.01, 7.05–7.10, 7.57–7.67, 7.74–7.84 (4m, 10H, aromatic hydrogens). ^{13}C NMR (100 MHz, C_6D_6, ppm): δ = 10.71 (NCH$\underline{C}H_3$), 26.83 (CH_3Ge), 45.40 (NCH_3), 64.86 (N$\underline{C}H_2CPh$), 66.58 (N$\underline{C}HCH_3$), 73.65 (OCHPh), 77.62 ($OCPh_2$), 125.12, 125.79, 126.35, 126.77, 127.21, 127.63, 127.90, 128.45, 128.79, 139.97, 146.57, 146.95 (aromatic carbons).

4.3.4. Reaction of 3 with MeI

To a stirred solution of $MeN(CH_2CH_2O)_2Ge$ (0.15 g, 0.80 mmol) in toluene (5 ml) a solution of MeI (0.23 g, 1.60 mmol) in toluene (5 ml) was added dropwise at room temperature. After 7 days all volatiles were removed under reduced pressure. Then ether (10 ml) was added to the residue, the precipitate was filtered to give a white powder. According to NMR data, a mixture of unidentified compounds was obtained.

4.3.5. Reaction of **3** with Ph_2S_2. generation of [$MeN(CH_2CH_2O)_2]_2Ge$ (**17**), $Ge(SPh)_4$ (**18**) and $MeN(CH_2CH_2O)_2Ge(SPh)_2$ (**19**)

To a stirred solution of **3** (0.06 g, 0.32 mmol) in THF (10 ml) was added dropwise solution of Ph_2S_2 (0.07 g, 0.32 mmol) in THF (5 ml) at −40 °C. The reaction mixture was stirred for 20 min and allowed to warm to room temperature. After 4 days the solvents were removed under reduced pressure. Then THF (1 ml) was added to the residue, the precipitate was filtered off to give 0.05 g of yellow crystalline solid. According to NMR data, the yellow crystalline solid was obtained as a mixture of [$MeN(CH_2CH_2O)_2]_2Ge$ (**17**), $Ge(SPh)_4$ (**18**) and $MeN(CH_2CH_2O)_2Ge(SPh)_2$ (**19**) in the ratio 1:1:1. Complex (**17**) (^{1}H and ^{13}C NMR data were in accordance with the data of literature [34]): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.46 (s, 6H, CH_3N), 2.58 (*t*, 8H, J = 5.8 Hz, NCH_2), 3.71 (*t*, 8H, J = 5.8 Hz, OCH_2). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 45.46 (NCH_3), 57.26 (NCH_2), 58.05 (OCH_2). Complex (**18**): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 6.91–6.98, 7.45–7.50 (2m, 20H, aromatic hydrogens). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 127.08, 128.12, 128.99, 129.47 (aromatic carbons). Complex (**19**): ^{1}H NMR (400 MHz, C_6D_6, ppm): δ = 2.10 (*t*, 4H, J = 5.6 Hz, NCH_2), 2.11 (s, 3H, CH_3N), 3.73 (*t*, 4H, J = 5.6 Hz, OCH_2), 6.91–6.98, 7.45–7.50 (2m, 10H, aromatic hydrogens). ^{13}C NMR (100 MHz, C_6D_6, ppm): δ = 47.07 (CH_3N), 55.30 ($2NCH_2$), 57.61 ($2OCH_2$), 127.42, 128.82, 135.64, 136.92 (aromatic carbons).

Under recrystallization of reaction mixture from toluene a less drop of complex **18** was isolated as colorless crystals.

4.3.6. Reaction of **8** with Et_2S_2

To a stirred solution of **8** (0.20 g, 0.58 mmol) in THF (10 ml) was added dropwise solution of Et_2S_2 (0.07 g, 0.58 mmol) in THF (5 ml) at −40 °C. The reaction mixture was stirred for 20 min and allowed to warm to room temperature. After 4 days the volatiles were removed under reduce pressure to give a 0.22 g yellow solid. According to NMR data, only starting materials were found in the reaction mixture.

4.3.7. Reaction of **3** with PhC(O)C(O)Ph. synthesis of $MeN(CH_2CH_2O)_2Ge$–cyclo-(OC(Ph)C(Ph)O) (**20**)

A solid PhC(O)C(O)Ph (0.13 g, 0.63 mmol) was added to a stirred solution of **3** (0.12 g, 0.63 mmol) in toluene (10 ml). The reaction mixture was stirred for 4 days at room temperature and volatiles were removed in vacuum. Then ether (10 ml) was added to the residue, the precipitate was filtered off to give **20** as a white solid. Yield 0.16 g (64%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.05 (s, 3H, CH_3N), 3.06–3.12, 3.21–3.24 (2m, 4H, NCH_2), 4.16–4.18 (m, 4H, OCH_2), 7.32–7.40, 7.56–7.58, 7.65–7.67 (3m, 10H, aromatic hydrogens). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 44.08 (CH_3N), 55.39 (NCH_2), 57.15 (OCH_2), 126.09, 126.61, 127.07, 127.51, 127.70, 127.90, 133.88, 135.26, 135.39, 138.10 (=C and aromatic carbons). Anal. Calc. for $C_{19}H_{21}GeNO_4$ (399.9844): *C* 57.05, H 5.29, N 3.50. Found: *C* 57.26, H 5.33, N 3.68.

4.3.8. Reaction of **3** with (E)-PhC(O)CH = CHPh. synthesis of $MeN(CH_2CH_2O)_2Ge$–cyclo-(OC(Ph)CHCH(Ph)) (**21**)

A solid (*E*)-PhC(O)CH = CHPh (0.15 g, 0.74 mmol) was added to a stirred solution of **3** (0.14 g, 0.74 mmol) in toluene (10 ml). The reaction mixture was stirred for 4 days at room temperature and volatiles were removed in vacuum. Then ether (10 ml) was added to the residue, the precipitate was filtered off and recrystallized from toluene to give **21** as a white solid. Yield 0.23 g (80%). ^{1}H NMR (400 MHz, C_6D_6, ppm): δ = 1.55 (s, 3H, CH_3N), 1.94–2.20 (m, 4H, $2NCH_2$), 3.21–3.62 (m, 5H, CHPh and $2OCH_2$), 5.60–5.67 (m, 1H, CH=C(O)Ph), 6.92–7.09, 7.34–7.42, 7.99–8.10 (3m, 10H, aromatic hydrogens). ^{13}C NMR (100 MHz, C_6D_6, ppm): δ = 38.44 (CHPh), 42.61 (NCH_3), 55.43, 55.69, 58.21, 58.26 ($4OCH_2$), 98.39 (C$\underline{H}$=C(O)Ph), 125.64, 125.77, 125.93, 128.52, 129.28, 129.92 (aromatic carbons), 145.38 (PhC(O) = C$\underline{H}$). The signals of two aromatic carbons and one C(O) group were not found in spectrum. Anal. Calc. for $C_{20}H_{23}GeNO_3$ (398.012): C 60.35, H 5.82, N 3.52. Found: C 60.47, H 5.78, N 3.45.

4.3.9. Reaction of **3** with (E)-FcC(O)CH = CHPh. synthesis of $MeN(CH_2CH_2O)_2Ge$-cyclo-(OC(Fc)CHCHPh) (**22**)

A solid (*E*)-FcC(O)CH = CHPh (0.30 g, 0.95 mmol) was added to a stirred solution of **3** (0.18 g, 0.95 mmol) in toluene (10 ml). The

Table 7
Details of crystallographic experiments for **1**, **3**, **8**, **10** and **18**.

	1	**3**	**8**	**10**	**18**
Formula	$C_{20}H_{26}Ge_2N_2O_4$	$C_{10}H_{22}Ge_2N_2O_4$	$C_{34}H_{38}Ge_2N_2O_4$	$C_{24}H_{25}GeNO_2$	$C_{24}H_{20}GeS_4$
Fw	503.65	379.48	683.84	432.04	509.23
T, K	293(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	trigonal	monoclinic	monoclinic	monoclinic	orthorhombic
Space group, *Z*	*R*−3,9	*P*2$_1$/n, 2	*C*2/c, 4	*P*2$_1$, 2	*P*ba2, 2
a (Å)	27.375(5)	6.3058(9)	16.9874(8)	11.082(4)	8.5827(9)
b (Å)	27.375(5)	12.6867(18)	18.1601(8)	6.249(2)	16.7199(17)
c (Å)	7.245(5)	8.9400(13)	11.8582(5)	14.872(5)	8.0734(9)
β (°)		98.023(2)	122.365(1)	91.123(5)	
V (Å^3)	4702(3)	708.20(18)	3089.9(2)	1029.6(6)	1158.5(2)
d_{calc} (g cm^{-3})	1.601	1.780	1.470	1.394	1.460
Abs.coeff.(mm^{-1})	2.905	4.252	1.986	1.507	1.691
F(000)	2304	384	1408	448	520
θ Range (°)	2.58–25.95	2.81–27.00	2.24–27.99	1.84–28.00	2.44–27.00
Reflections collected	12,394	6571	15,812	10,156	8663
Unique reflections (R_{int})	2035 (0.0434)	1535 (0.0154)	3735 (0.0254)	4896 (0.0377)	2396 (0.0303)
Data/restraints/parameters	2035/0/127	1535/0/127	3735/0/191	4896/1/255	2396/1/132
R_1 [$I > 2\sigma(I)$]	0.0210	0.0151	0.0214	0.0472	0.0194
wR_2 (all data)	0.0548	0.0404	0.0595	0.1291	0.0471
Goof on F^2	0.830	1.079	1.061	1.072	1.018
Flack parameter	–	–	–	0.009(13)	−0.003(9)
Largest difference peak/hole (e Å^{-3})	0.429/−0.185	0.316/−0.253	0.453/−0.240	1.046/−0.391	0.373/-0.147

reaction mixture was stirred for 7 days at room temperature. The precipitate was filtered off to give **22** as an orange solid. Yield 0.23 g (48%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.43 (s, 3H, CH_3N), 2.09–2.26, 2.65–2.78, 2.94–3.08 (3m, 4H, NCH_2), 3.42–3.53 (m, 1H, CHPh), 3.68–4.23 (m, 6H, $2CH_2O$, C_5H_4), 4.26 (s, 5H, C_5H_5), 4.63–4.70 (m, 2H, C_5H_4), 5.13–5.18 (m, 1H, CH = C(O)Fc), 7.31–7.51 (m, 5H, aromatic hydrogens). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 37.33 (PhCH), 42.99 (CH_3N), 55.49, 55.80 ($2NCH_2$), 58.11, 58.20 ($2OCH_2$), 66.49, 68.10, 81.28 (C_5H_4), 69.42 (C_5H_5), 96.07 (CHPh), 125.74, 128.46, 129.29, 142.15 (aromatic carbons), 156.61 (CH = C(O)Fc). Anal. Calc. for $C_{24}H_{27}FeGeNO_3$ (505.9311): C 56.98, H 5.38, N 2.77. Found: C 56.72, H 5.34, N 2.60.

*4.3.10. Reaction of 8 with (E)-FcC(O)CH = CHPh. synthesis of MeN(CH$_2$CH$_2$O)(CH$_2$CPh$_2$O)Ge-cyclo-(OC(Fc)CHCHPh) (**23**)*

Analogously to **22**, complex **23** was prepared from **8** (0.15 g, 0.44 mmol) and (*E*)-FcC(O)CH = CHPh (0.14 g, 0.44 mmol) in toluene (20 ml). The product was isolated by filtration to give **23** as a yellow solid. Yield 0.13 g (45%). ^{1}H NMR (400 MHz, C_6D_6, ppm): δ = 1.61 (s, 3H, NCH_3), 1.44–1.55 (m, 1H, NCH_2CH_2), 1.67–1.78 (m, 1H, NCH_2CH_2), 2.67, 2.86 (2d, 2H, *J* = 13.5 Hz, AM system of NCH_2CPh_2 group protons), 3.07–3.11 (m, 1H, PhCH), 3.32–3.41 (m, 2H, CH_2O), 4.38 (s, 5H, C_5H_5), 4.02–4.14, 4.84–4.93 (2m, 4H, C_5H_4), 5.33–5.36 (m, 1H, CH = C(O)Fc), 7.04–7.10, 7.20–7.38, 7.60–7.71 (3m, 15H, aromatic hydrogens). ^{13}C NMR spectra is not recorded due to insolubility of **23**. Anal. Calc. for $C_{36}H_{35}FeGeNO_3$ (658.123): C 65.70, H 5.36, N 2.13. Found: C 65.50, H 5.23, N 2.05.

*4.3.11. Reaction of **3** with trimethylamine oxide*

To a stirred solution of MeN(CH$_2$CH$_2$O)$_2$Ge (**3**) (0.32 g, 1.70 mmol) in toluene (20 ml) trimethylamine oxide (0.13 g, 1.70 mmol) was added by small portions at room temperature. After 4 days all volatiles were removed under reduced pressure. Then ether (10 ml) was added to the residue, the precipitate was filtered to give a white powder. According to NMR data, a mixture of unidentified compounds was obtained.

*4.3.12. Reaction of **3** with S$_8$*

To a stirred solution of MeN(CH$_2$CH$_2$O)$_2$Ge (**3**) (0.15 g, 0.80 mmol) in THF (15 ml) a sulfur in THF (10 ml) (0.03 g, 0.10 mmol) was added at room temperature. After 5 days all volatiles were removed under reduced pressure. According to NMR data, a mixture of initial compounds was obtained.

*4.3.13. Reaction of **3** with (PhO)$_2$P(O)N$_3$*

To a stirred solution of MeN(CH$_2$CH$_2$O)$_2$Ge (**3**) (0.10 g, 0.53 mmol) in toluene (15 ml) a solution of (PhO)$_2$P(O)N$_3$ (0.15 g, 0.53 mmol) in toluene (5 ml) was added at room temperature. After 4 days all volatiles were removed under reduced pressure. According to NMR data, a mixture of unidentified compounds was obtained.

4.4. Reactions without changes of germanium oxidation state

*4.4.1. Reaction of **8** with acetic anhydride. synthesis of MeN[CH$_2$CH$_2$OC(O)CH$_3$]$_2$ (**24**) and Ge[OC(O)CH$_3$]$_2$ (**25**)*

The solution of acetic anhydride (0.12 g, 1.20 mmol) in toluene (10 ml) was added to solution of **3** (0.09 g, 0.50 mmol) in toluene (10 ml). The reaction mixture was stirred for 7 days, then volatiles were removed in vacuum and residue was washed with ether (10 ml). According to NMR the mixture (1:1) of MeN[CH$_2$CH$_2$OC(O)CH$_3$]$_2$ (**24**) и Ge[OC(O)CH$_3$]$_2$ (**25**) was obtained. Compound **24**: ^{1}H NMR (400 MHz, C_6D_6, ppm): δ = 1.67 (s, 6H, CH_3CO), 2.12 (s, 3H, NCH_3), 2.50–2.60 (m, 4H, NCH_2), 4.00 (*t*, 4H, *J* = 5.7 Hz, OCH_2). ^{13}C NMR (100 MHz, C_6D_6, ppm): δ = 20.39 (CH_3CO), 41.31 (CH_3N), 55.24, 58.79 (NCH_2, OCH_2), 170.00 (C=O). Compound **25**: ^{1}H NMR (400 MHz, C_6D_6, ppm): δ = 1.78 (s, 6H, CH_3). ^{13}C NMR (100 MHz, C_6D_6, ppm): δ = 21.42 (CH_3), 166.30 (C=O).

*4.4.2. Reaction of **2** with H$_2$O. generation of BnN(CH$_2$CH$_2$OH)$_2$*

Water (0.02 g, 1.10 mmol) was added to solution of **2** (0.27 g, 1.00 mmol) in THF (5 ml). The reaction mixture was stirred for 5 days, volatiles were removed in vacuum. The residue was extracted with toluene (10 ml), filtered off, washed with toluene (2 × 2 ml) and solvents were removed under reduced pressure to give a yellow oil. According to NMR spectroscopy, BnN(CH$_2$CH$_2$OH)$_2$ was obtained [31]. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.64 (*t*, 4H, *J* = 5.1 Hz, CH_2N), 3.55 (*t*, *J* = 5.1 Hz, 4H, CH_2O), 3.64 (s, 2H, $PhCH_2$), 7.16–7.23 (m, 5H, aromatic hydrogens). The solid formed during this reaction was insoluble in common organic solvents.

4.5. Single X-ray structure determination

Experimental crystallographic data for **1**, **3**, **8**, **10** and **18** are given in Table 7. The data were collected on a Bruker SMART 1K (for **1**) and on a Bruker SMART APEX II (for **3**, **8**, **10** and **18**) diffractometers using graphite monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Åa;). The structures were solved by direct methods and refined by full matrix least-squares on F^2 [38]. In the structures **1**, **8**, **10** and **18** all hydrogen atoms were placed in calculated positions and refined using a riding model. As for **3**, all hydrogen atoms were found from difference Fourier synthesis and refined isotropically.

4.6. Computational procedures

Calculations were carried out by the density functional theory (DFT) using the non-empirically generalized gradient approximation and the PBE functional [39,40] implemented in the PRIRODA program using TZ2P basis [41,42]. Geometry optimization was performed for all stable compounds and transition states. The characters of the located stationary points (minimum or saddle point) were determined by the calculation of Eigen values of the matrix of the second derivatives of the energy with respect to the coordinates of atomic nuclei. The correspondence between the transition states and a given transformation has been established by the calculation of intrinsic reaction coordinate (IRC). The zero point energy correction has been applied.

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Appendix A. Supplementary material

CCDC 836875–836879; contain the supplementary crystallographic data for **1**, **3**, **8**, **10** and **18**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2012.01.018.

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