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The transannular interaction germanium–nitrogen in germocanes: The influence of substituents

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Abstract

The reaction of $RN(CH_2CH_2OH)CHR^1CR^2R^3OH$ (**1**–**8**) with a stoichiometric amount of tetrachloro(bromo)germane leads to the corresponding $RN(CH_2CH_2O)(CHR^1CR^2R^3O)GeHal_2$ (**9**–**21**). Difluorenylgermocane **22** was prepared by treatment of diethoxydifluorenylgermane with *N*-methyldiethanolamine. Different dialkanolamines were found to be successive precursors of dimethylgermocanes, $RN(CH_2CH_2O)(CHR^1CR^2R^3O)GeMe_2$ (**23**–**26**). The chemical properties of simple and easy to access germocanes $RN(CH_2CH_2O)_2GeX_2$ [X = OH, Br (**28**), Cl (**29**)] were studied and the difluoro (**27**), haloalkoxy (**30**–**32**), and dialkoxy (**33**, **34**) derivatives were prepared. The structures of the compounds **16**, **20**–**22**, and **26** were confirmed by X-ray diffraction and the structural features in solution of **23** and **26** were studied by NMR spectroscopy (NOEs). The relationship between the nature of substituents at different positions of the germocane skeleton and the strength of the intramolecular Ge ← N bond is discussed.

Keywords: Germocanes; Germanium; Intramolecular interaction; Alkoxides; Dialkanolamines

1. Introduction

One of the most important points of interest in the chemistry of main group elements is the study of the structure and properties of derivatives of so-called hypervalent atoms. The coordination number of the central atom in these compounds exceeds that permitted according to the ''octet'' rule [1,2]. The hypercoordination results from the intermolecular contact of main group element with free Lewis base or from the formation of intramolecular transannular bond with donor group. The main focus of the research is the elucidation of the nature of the transannular M ← donor bond, which is strongly affected by the design of the substituents at the metal atom and donor block [3–5]. On the other hand, hypervalent compounds have found application in organic synthesis as intermediates in several coupling reactions [6,7] and in medicinal chemistry and pharmacology as compounds displaying a wide range of biological activity [8,9]. The alkanolamine moiety is a part of the widespread ligands for the formation of hypervalent compounds of Group 14 elements [10,11]. Among these species, compounds of silicon and tin are the most heavily investigated, while the derivatives of germanium have been less studied [3,4,12].

Germatranes, $N(CH_2CH_2O)_3Ge–X$, as well as their analogues with substituents at carbon atoms in atrane skeleton,

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are the most intensively and systematically studied class of compounds with hypervalent germanium atom [3,12]. The information concerning germocanes, $RN(CH_2CH_2O)_2Ge(X)Y$ – closely related analogues of germatranes – is rather limited [13–28]. However, one might expect that germocanes possess greater chemical and structural flexibility since they have more possibilities to vary substituents R, X, and Y and, hence, to modulate the effect that these groups have on the transannular Ge ← N bond strength. This conclusion was supported by a series of works by Dräger et al., Cea-Olivares et al., Tschach et al. and others in which the closely related systems such as $RN(CH_2CH_2CH_2)_2Ge(X)Y$, $O(CH_2CH_2Z)_2Ge(X)Y$, $S(CH_2CH_2Z)_2Ge(X)Y$ ($Z = CH_2$, O, S) and their Sn, As, Sb, Bi analogues were studied and some conclusions about the nature of transannular bonds have been drawn [4,29–38]. Dräger has proposed that several factors are responsible for the strength of intramolecular bond in these systems: the nature of donor (its donor capacity), the nature of the axial substituent at the metal centre (its electronegativity and ability of lone pair interaction), the type of equatorial ligands, the geometrical flexibility of donor group. However, in general, the mutual influence of these factors depends on the nature of central atom and should be an object of investigations in each specific case.

Several synthetic methods have been used for the formation of germocane skeleton. Most of them represent the reaction between dialkanolamines and suitable germanium derivatives [13,18–20,22–28]. A different approach, viz., the reaction of $GeHal_4$ with trimethylsilyl ethers of diethanolamines, $RN(CH_2CH_2OSiMe_3)_2$, leading to the corresponding 2,2-dihalogermocanes, was used by us [28] and others [15]. No chemical properties of germocanes were investigated to date except the reaction of 2,2-dihydroxygermocanes with bidentate ligands and the germocane–germatrane rearrangement [14,22–25]. Although the structure of germocanes was explored by X-ray diffraction studies in the solid state, by ^1H, ^{13}C, ^{73}Ge NMR spectroscopy in solution, and by mass-spectrometry (electron impact) in gas phase [13,15–17,19–23,26], the relationships between key structural parameters of germocanes and the electronic and steric properties of substituents bound to the Ge and N atoms are still not clarified due to the narrow scope of R, X, Y groups [28].

In continuation of our investigations in the chemistry of metallatranes [39–44] and metallocanes [28] we focused our efforts on the synthesis and characterization of germocanes bearing various substituents at the Ge and N atoms, as well as at the carbon atoms of ocane skeleton. It should be noted that the latter compounds with substituents at C atoms are almost unexplored to date. Herein we report the synthesis of novel 2,2-dihalo-, 2,2-dimethyl-, 2,2-difluorenyl-, and 2,2-dialkoxygermocanes which contain different substituents at N and C atoms of ocane skeleton. Some of them were obtained from the substitution reactions at the Ge atom proceeding with the retention of ocane skeleton. Their structures in the solid state and in solution were established by X-ray diffraction and NMR spectroscopy, respectively. Our motivation was to prepare germocanes with the strength of intramolecular Ge–N interaction varying in the wide range and to estimate the influence of substituents nature on the degree of this interaction. This report is the first systematic investigation upon the variation of wide range substituents at different positions of metallocane, $RN(CH_2CH_2O)_2M(X)Y$, skeleton where M is a Group 14 element.

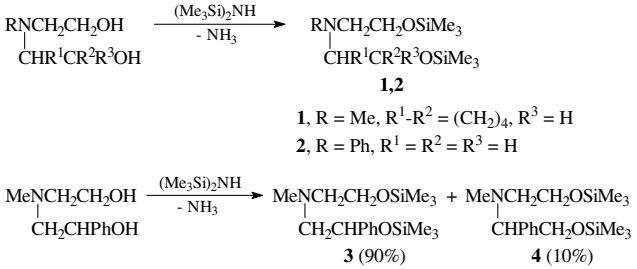
2. Results and discussion

2.1. Synthesis

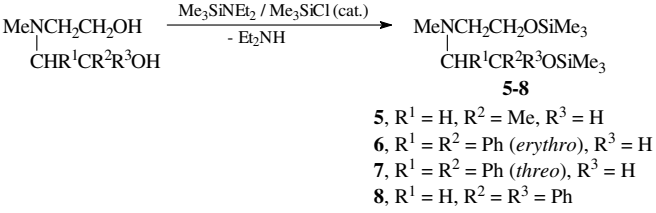
According to the literature, trimethylsilyl ethers of dialkanolamines are the most suitable intermediates for the preparation of dihalogermocanes [15,28]. In this study, we used two methods for the preparation of ethers **1**–**8**: silylation of dialkanolamines with hexamethyldisilazane (**A**, Scheme 1) or with the system Me_3SiNEt_2/Me_3SiCl (cat.) (**B**, Scheme 2) [45]. These derivatives were prepared in high yields. Compound **3** contains a small amount of **4** due to the presence of parent dialkanolamine in starting material [46]. This mixture was used in further reactions without purification.

Silyl ethers **1**–**8** react with an equimolar amount of $GeHal_4$ at reflux temperature in chloroform or toluene solution to give the corresponding 2,2-dihalogermocanes **9**–**21** in 12–87% yields (Scheme 3).

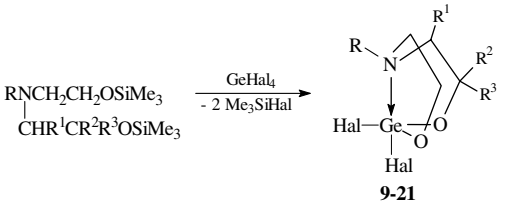
Our efforts to prepare germocane **22** with donor fluorenyl substituents at the Ge atom by an analogous metathetical reaction of $MeN(CH_2CH_2OSiMe_3)_2$ with Flu_2GeCl_2 failed. We believe that this method is successful only for the synthesis of germocanes containing acceptor substituents at the Ge atom. The compound **22** was obtained using



Scheme 1.



Scheme 2.



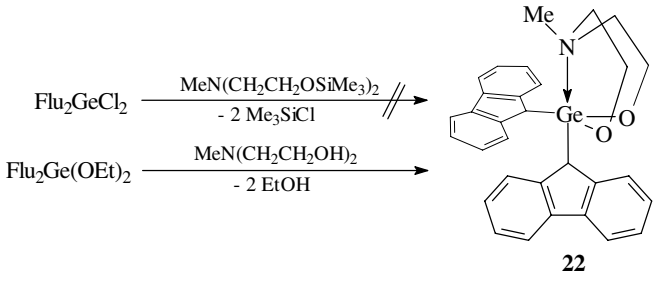
	R	R^1	R^2	R^3	Hal		R	R^1	R^2	R^3	Hal
9	Me	H	Me	H	Br	**15**	Me	Ph	Ph	H	Cl (*erythro*)
10	Me	$(CH_2)_4$		H	Br	**16**	Me	Ph	Ph	H	Br (*erythro*)
11	Me	H	Ph	H	Cl	**17**	Me	Ph	Ph	H	Br (*threo*)
12	Me	Ph	H	H	Cl	**18**	Me	H	Ph	Ph	Cl
13	Me	H	Ph	H	Br	**19**	Me	H	Ph	Ph	Br
14	Me	Ph	H	H	Br	**20**	Ph	H	H	H	Cl
						21	Ph	H	H	H	Br

Scheme 3.

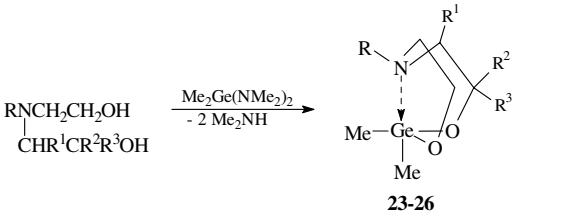
transalkoxylation reaction as an alternative approach (Scheme 4).

Recently, we reported the preparation of $MeN(CH_2CH_2O)_2GeMe_2$ by the reaction of $Me_2Ge(NMe_2)_2$ with *N*-methyldiethanolamine [28]. Following this approach, diverse 2,2-dimethylgermocanes **23**–**26** were synthesized in almost quantitative yields (Scheme 5).

As it was found previously in metallatrane, especially germatrane, chemistry the compounds containing a simple but reactive group X at the metal atom serve as convenient intermediates for the preparation of more complicated structures. We have found that the treatment of $MeN(CH_2CH_2O)_2Ge(OH)_2$ with boron trifluoride etherate led to difluoride **27** in moderate yield (Scheme 6). This difluoro derivative seems difficult to access *via* other methods.

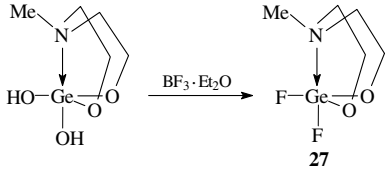


Scheme 4.



	R	R^1	R^2	R^3
23	Me	H	Ph	H
24	Me	Ph	H	H
25	Me	Ph	Ph	H (*erythro*)
26	Ph	H	H	H

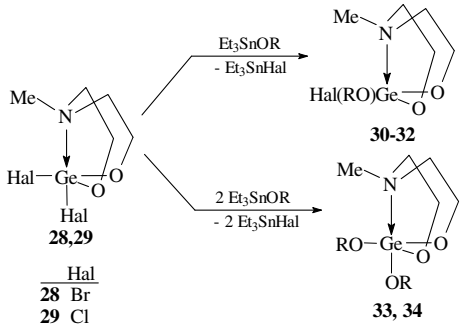
Scheme 5.



Scheme 6.

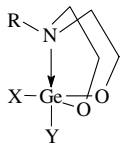
2,2-Dihalogermocanes, like 1-halogermatranes, are good starting materials for the preparation of alkoxy derivatives (Scheme 7). It should be noted that previously this type of compounds possessing one or two alkoxy groups was inaccessible except for the cyclic diolates (see, for example, Scheme 8). We have found that the treatment of the compound **28** with an equimolar amount of Et_3SnOMe led to the selective substitution of one bromine atom with a methoxy group; in the case of two equivalents of organotin compound dimethoxygermocane **33** is formed as the only ocane product. Analogously, the formation of **31** and **34** was established in the reaction of dichloride **29** with one or two equivalents of organotin L-(−)-menthol derivative, respectively. The treatment of the compound **28** with an equimolar amount of $Et_3SnOCH_2CH_2NMe_2$ led to the exchange of one chlorine atom for alkoxy group. The formation of the stable complex of **32** with one molecule of Et_3SnCl was confirmed by NMR spectroscopy and elemental analysis data.

We also investigated the reaction of dibromide **28** with two equivalents of FluLi, which led to difluorenyl derivative



	Hal	R
30	Br	Me
31	Cl	Menth
32	Cl	$CH_2CH_2NMe_2$
33		Me
34		Menth

Scheme 7.



	R	X	Y	Ref.
28	Me	Br	Br	[28]
35	H	OH	OH	[20]
36	Me	2-thienyl	2-thienyl	[26]
37	Me	OCH_2CH_2O		[18]
38	Me	$OCPh_2C(O)O$		[23]
39	*n*-Bu	$CH_2CH_2C(O)O$		[17]
40	$HOCH_2CH_2$	$CH_2CH_2C(O)O$		[16]

Scheme 8.

22 only in trace amount. Very recently we have found that the expected bis(phenylacetylenyl)germocane did not form in the reaction of **28** with two equivalents of PhC≡CLi [47]. Thus, this method is not appropriate for the preparation of novel germocanes in contrast to the previous findings in germatrane chemistry where bromo derivatives were successfully converted into germatranes with fluorenyl, phenylacetylenyl and other groups [48–50].

2.2. Solid-state structures (X-ray diffraction data)

The main purpose of the present study was to estimate how the nature of substituents at different positions of a germocane skeleton influences the strength of the intramolecular Ge ← N bond. In a series of closely related compounds, such as germocanes, the strength of the bond correlates with its length. Accordingly, the basic method for the study of hypervalent compounds is X-ray diffraction. Among previously reported germocanes, seven compounds have been structurally characterized (see Scheme 8).

In the course of our studies, the solid-state structures of **16**, **20**–**22**, and **26** were determined by single-crystal X-ray analysis. The molecular structures of these compounds are shown in Figs. 1–5. Important bond lengths and angles for **16**, **20**–**22**, and **26** are summarized in Table 1. The studied compounds may be divided into groups according to the character of the substituents at the Ge and N atoms. Germocanes **16**, **20**, and **21** possess acceptor substituents (halogens) at the Ge atom, however, **16** possesses the donor group (Me) at the N atom, while in **20** and **21** the N atom is bound to the acceptor group (Ph). In the compound **22** having the donor methyl group at the N atom the Ge atom

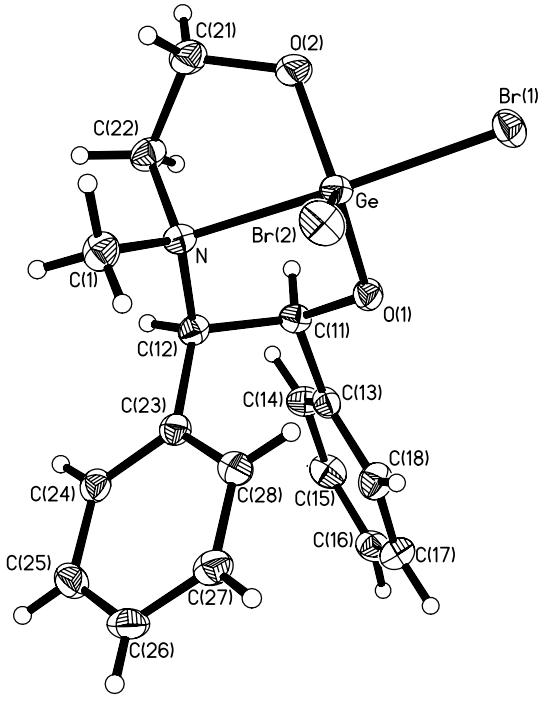


Fig. 1. Molecular structure of **16**.

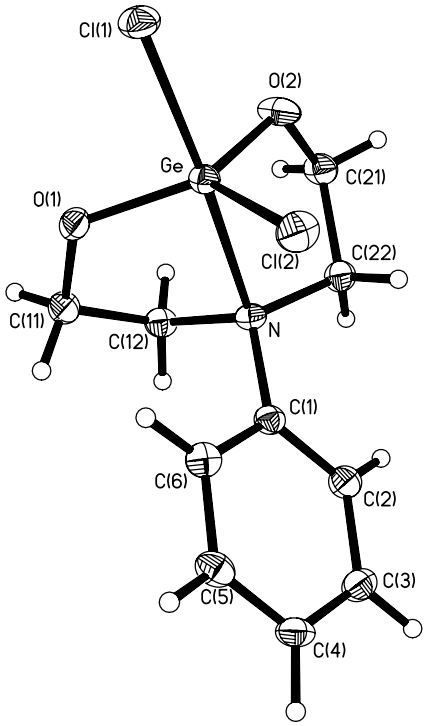


Fig. 2. Molecular structure of **20**.

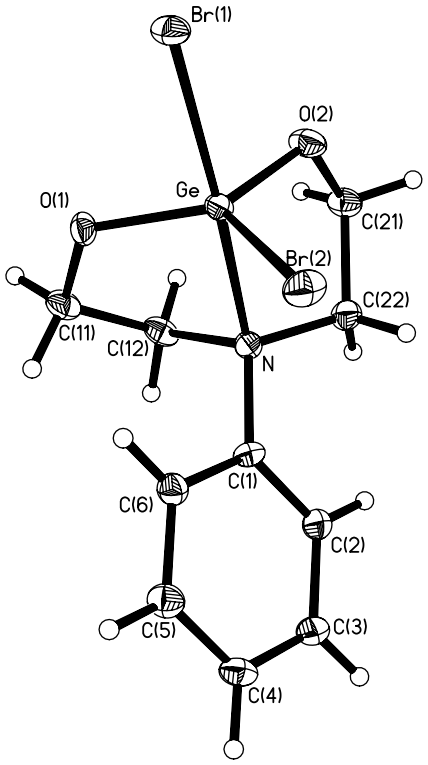


Fig. 3. Molecular structure of **21**.

is adjacent to two donor and bulky fluorenyl groups. Finally, germocane **26** contains the donor methyl groups at the Ge atom and the acceptor phenyl group at the N atom. It should be noted that **16** is the first X-ray structurally studied germocane with substituents at the carbon

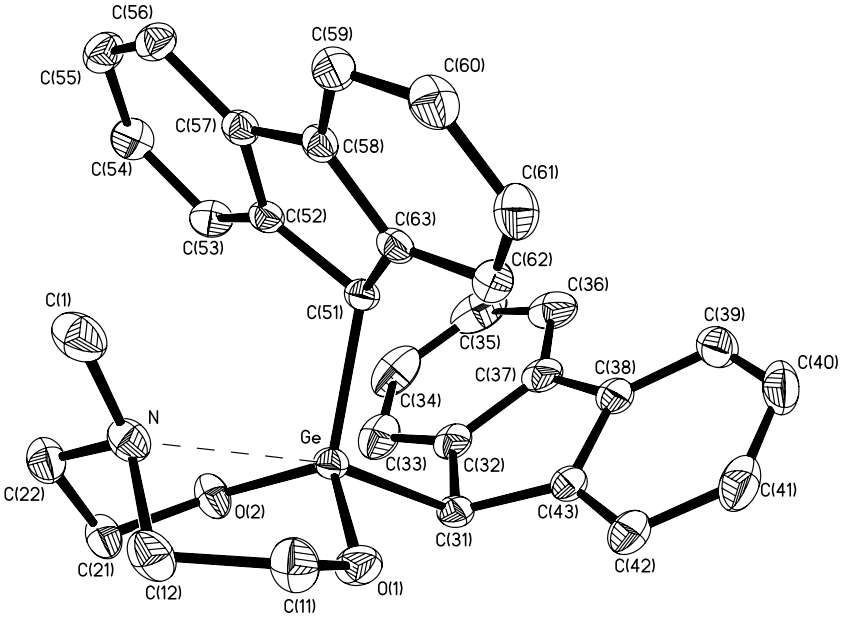


Fig. 4. Molecular structure of **22**; hydrogen atoms are omitted for clarity.

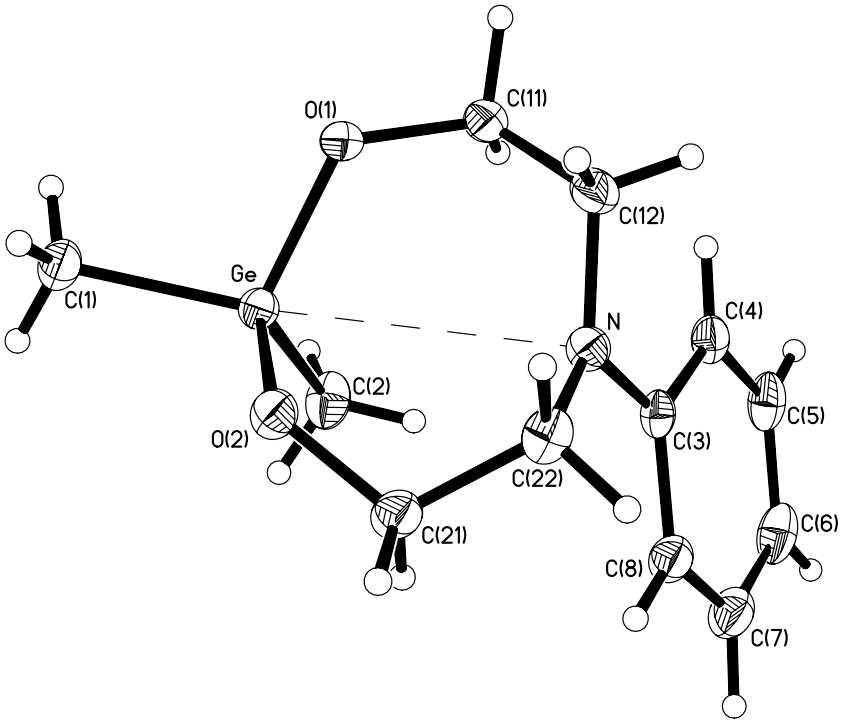


Fig. 5. Molecular structure of **26**.

atoms of ocane moiety. We believed that the analysis of the geometry parameters for **16**, **20**–**22**, and **26** and the comparison with those previously found for **28**, **35**–**40** would provide a better insight into the influence of substituents on the strength of the Ge–N intramolecular bond. Here, it should be noted that the usual values of the Ge–N covalent bond vary in the range 1.80–1.90 Å [41], while the sum of the van der Waals radii of Ge and N is 3.72 Å [51]. Another important value is the sum of the non-bonding radii of Ge and N (2.72 Å), according to the Glidewell approach [52].

The coordination polyhedron of the germanium atom in **16**, **20**, and **21** is the common one for germocane derivatives **28**, **35**–**40** and represents a slightly distorted trigonal bipyramid (TBP) with the N and one halogen atoms in the apical positions. The oxygen atoms O(1), O(2) and

Table 1
Selected bond lengths (Å) and angles (°) for germocanes, $N(CH_2CH_2O)(CHR^1CR^2R^3O)GeX_2$ (**16**, **20**–**22**, and **26**)

	16	20	21	22	26
Ge–N	2.217(2)	2.202(2)	2.202(4)	2.739(1)	3.182(1)
Ge–O	1.771(2)	1.773(2)	1.775(4)	1.776(1)	1.781(1)
	1.788(2)	1.775(2)	1.777(3)	1.785(1)	1.781(1)
$Ge–X_{ax}$	2.3790(4)	2.2180(6)	2.3848(6)	1.994(2)	1.926(2)
$Ge–X_{eq}$	2.3282(4)	2.1658(6)	2.3200(7)	1.982(1)	1.925(2)
ΔGe[a]	0.103	0.095	0.086	0.346	0.553
ΔN[b]	0.468	0.442	0.442	0.451	0.148
$N–Ge–X_{ax}$	169.10(6)	171.75(5)	170.9(1)	168.32(5)	165.37(6)
$N–Ge–X_{eq}$	94.40(6)	92.61(5)	93.4(1)	88.47(5)	79.22(6)
N–Ge–O	83.15(8)	84.26(7)	84.4(2)	74.51(4)	68.68(4)
	84.11(8)	84.72(7)	84.8(1)	74.70(5)	69.12(4)
O–Ge–O	126.55(9)	122.83(8)	122.0(2)	115.61(5)	108.23(5)
$O–Ge–X_{eq}$	116.24(6)	114.08(6)	114.5(1)	115.19(6)	112.65(7)
	116.35(7)	122.33(5)	122.9(1)	118.90(6)	112.90(7)
$O–Ge–X_{ax}$	90.48(6)	91.00(5)	90.6(1)	98.36(6)	102.75(7)
	92.57(6)	92.23(5)	91.4(1)	100.88(6)	104.06(7)
$X_{ax}–Ge–X_{eq}$	96.49(1)	95.63(2)	95.78(2)	103.17(6)	115.37(8)
C–N–C	108.0(2)	109.4(2)	109.6(4)	109.3(1)	118.16(13)
	110.3(2)	112.7(2)	112.6(4)	110.0(1)	119.26(13)
	113.9(2)	112.9(2)	112.6(4)	113.6(1)	119.46(13)
C–N–Ge	101.2(2)	99.3(1)	99.3(3)	94.02(9)	86.75(9)
	105.6(1)	101.4(1)	101.1(3)	96.36(9)	85.99(9)
	117.1(2)	120.4(1)	120.8(3)	132.5(1)	114.50(9)

[a] Displacement of the Ge atom from the plane defined by the two oxygen atoms and the X_{eq} atom towards the X_{ax} atom.
[b] Displacement of the N atom from the plane defined by the three carbon atoms towards the Ge atom.

the other halogen atom occupy equatorial sites. The N–Ge–X_{ax} fragment is close to linear (169.10(6)–171.75(5)°). The germanium atom is displaced from the equatorial plane defined by the two oxygen atoms and the X_{eq} atom towards X_{ax} by 0.086–0.103 Å. These ΔGe values correspond to a very slight distortion of TBP geometry and consequently to strong Ge ← N interaction. The Ge ← N distances in **16**, **20**, and **21** (2.217(5)–2.202(4) Å) slightly exceed those previously found in germocanes **28**, **35**, **37**–**40** (2.080(3)–2.16(1) Å) [17,23] with electronegative substituents adjusted to the germanium atom and are sufficiently shorter than that in **36** (2.446(8) Å) [26], where the thienyl substituents are weak electron acceptor groups but their steric bulkiness is considerably greater than that for other studied compounds. The formal replacement of the donor methyl group at nitrogen in **28** with the phenyl group in **20** and **21** decreases the basicity of the N atom due to the possibility for the nitrogen lone pair to interact with the aromatic ring. However, in the case of acceptor substituents at the germanium atom such replacement does not drastically change the length of the Ge ← N bond. This result is unexpected because previously in silocane chemistry a considerable elongation of the Si ← N bond distance was found in $PhN(CH_2CH_2O)_2SiPh_2$ (3.08(1) Å) in comparison with that in $MeN(CH_2CH_2O)_2SiPh_2$ (2.68(1) Å) [53]. This difference between germanium and silicon derivatives may be explained, on the one hand, by steric reason as the radius of silicon atom is smaller than that of germanium atom. On the other hand, the $GeHal_2$ groups are unambiguously more attractive for the formation of additional interaction than $SiPh_2$ group.

The same trend of invariability of Ge ← N bond distance was observed in germocanes with substituents at the carbon atoms of ocane skeleton. The formal replacement of two hydrogen atoms in **28** [*d*(Ge ← N) = 2.166(5) Å] [28] with two phenyl groups in **16** [*d*(Ge ← N) = 2.217(2) Å] leads to only slight elongation of Ge ← N bond, probably due to the steric reasons. A more appreciable effect results from the replacement of the equatorial oxygen atoms with the donor CH_2 groups. The Ge ← N bond in **20** (2.202(2) Å) is notably shorter than that in *i*-$C_4H_9N(CH_2CH_2CH_2)_2GeCl_2$ (2.389(4) Å) [31]. This is also in accordance with the general trend observed in atrane structures: more electronegative equatorial groups yield shorter M ← N transannular distances.

The replacement of two bromine atoms in **28** with two donor and bulky fluorenyl groups causes a sizeable elongation of the Ge ← N distance in **22** (2.739(1) Å). Although this distance is shorter than the sum of the van der Waals radii of Ge and N, according to the Glidewell approach [52], this compound possesses very weak Ge ← N bond. The coordination polyhedron of Ge represents a strongly distorted TBP with the nitrogen and one carbon in the apical positions and the oxygen atoms and the other carbon atom occupying equatorial sites. The ΔGe value in **22** (0.346 Å) is expectedly greater than those in dihalogermocanes **16**, **20**, and **21** (ΔGe = 0.086–0.103 Å).

In germocane **26**, where the acceptor phenyl group is bound to the N atom and two donor Me groups are bound to the Ge atom the Ge ← N interaction is absent. The value of the Ge···N distance is 3.182(1) Å. The coordination polyhedron of Ge represents a slightly distorted tetrahedron.

Thus, the variation of substituents in different positions of germocane molecules allows the preparation of germocanes with a strong transannular germanium–nitrogen interaction (**16**, **20**, and **21**), with a weak one (**22**), and without this interaction (**26**). Our data and the analysis of the previously reported results on X-ray diffraction studies carried out by Cea-Olivares et al. [4] testify to the very great sensitivity of the Ge ← N bonding in germocanes and closely related structures $[Z'(CH_2CH_2Z)_2Ge(X)Y$, where Z = CH_2, O, S and Z′ = RN, O, S] primarily to the nature of substituents at the Ge atom and secondly to the nature of substituents at the N atom when Z′ = RN.

In the dihalogermocanes **16**, **20**, and **21** possessing the noticeable Ge ← N interaction the Ge–X_{ax} bond distances are considerably longer than the Ge–X_{eq} ones. The weakening of the Ge ← N bond in **22** and **26** leads to the levelling of these values. The previously reported data for **28**, **35** and **36** confirm this tendency [20,26,28]. This difference in **37** is small due to the considerable steric requirements for substituents where $X_{ax} + X_{eq}$ are OCH_2CH_2O group [18].

Of interest, the comparison of the Ge–Cl_{ax} bond distance in **20** (2.2180(6) Å) with that in closely related

i-$C_4H_9N(CH_2CH_2CH_2)_2GeCl_2$ (2.319(4) Å) [31] shows a large difference between these two values, the longer bond being observed in the compound with weaker transannular Ge ← N interaction. In our opinion, two factors should be considered when these values are discussed. The first one is the transannular interaction (''trans''-effect) which makes the Ge–X_{ax} bond longer, the second is the influence of equatorial groups. According to Bent's rule, more electronegative groups (oxygen atoms in the pair O and CH_2) stimulate the shortening of the Ge–X_{ax} bond [54]. Thus, in the case of **20** these factors do not act in concert, while in *i*-$C_4H_9N(CH_2CH_2CH_2)_2GeCl_2$ both factors lead to the elongation of the Ge–X_{ax} bond. The values of Ge–O bonds (1.771(2)–1.788(2) Å) are close in all the compounds **16**, **20**–**22**, and **26**. The latter may be explained by the combined influence of two above named factors: the strong Ge ← N interaction elongates the Ge–O distances, while the presence in the axial position at the Ge atom of an acceptor group which causes this strong intramolecular interaction shortens the Ge–O distances.

The nitrogen atom in **16** and **20**–**22** possesses an approximately tetrahedral environment. The considerable shifts of the nitrogen atom towards the Ge atom from the plane defined by the three carbon atoms (ΔN = 0.442–0.468 Å) were found in these compounds. On the contrary, in the compound **26** the nitrogen atom is nearly planar and the shift towards the Ge atom is smaller (ΔN = 0.148 Å). All the five-membered metallacycles –Ge–O–C–C–N– are not planar with the C atoms in α-positions to the N atoms maximally deviated from the least-squares planes. The exceptions are the phenyl substituted cycle in compound **16** and both –Ge–O–C–C–N– cycles in **26** where β-carbon atoms deviate from the plane. Conformation of the eight-membered cycles –Ge–O–C–C–N–C–C–O– in **16** and **20**–**22** may be considered as ''boat–chair'', while in **26** it is a ''crown''.

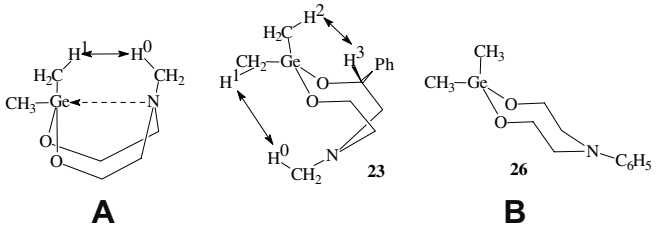
2.3. Solution structures (NMR spectroscopy data)

The ^1H and ^{13}C NMR spectra of the prepared compounds are in accord with the suggested structures. The germocanes without substituents at the carbon atoms of the ocane skeleton may be divided into two groups, according to the appearance of the signals of the germocane skeleton protons. The methylene protons of the first group compounds (**20**–**22**, **26** and $MeN(CH_2CH_2O)_2GeMe_2$) appear as two triplets of the AA′XX′ spin system. These spectra indicate the non-rigidity of ocane skeleton in these compounds in solution. On the contrary, ABXY system as a set of three multiplets (two multiplets for NCH_2 groups and one for OCH_2) of NCH_2CH_2O moiety appears in the ^1H NMR spectra of **27**, **30**–**32** and, for example, previously studied **28** and **29**. These compounds are in one ''frozen'' conformation in $CDCl_3$ solution at room temperature. The compounds **32** and **33** with two alkoxy groups at the Ge atoms mediate with the spectra showing one triplet for OCH_2 groups and one or two multiplets for NCH_2 groups (AA′XY system). However, we cannot judge the strength of the Ge ← N interaction in these compounds in solution on the basis of the appearance of their ^1H NMR spectra. An additional argument for the rigidity of the compound **27** in solution is provided by the ^{19}F NMR spectrum, which exhibits two resonances for two non-equivalent axial and equatorial fluorine atoms. Consequently, Berry pseudorotation is hindered in this compound.

The ^1H NMR spectra of the germocanes with substituents at carbon atoms of ocane skeleton are more complicated due to the non-equivalence of all protons of ocane skeleton (as previously found for germatranes [50]). Moreover, these compounds were prepared as mixtures of diastereomers. According to Dräger and Engler [55], such compounds, when they possess the ''boat–chair'' conformation of eight-membered ring exist as racemic mixture of two enantiomers. Thus, all protons of these compounds are diastereotopic, and the appearance of the asymmetric centre in ocane skeleton due to the presence of substituent(s) results in the formation of diastereomeric mixtures of **9**–**19**.

In our opinion, two approaches may be used for the estimation of the strength of the Ge ← N interaction in germocanes in solution. The first one is the analysis of the ^1H NMR chemical shifts for the protons bound with carbon atoms at the N atom. Of interest, the NCH_2 and NMe proton signals in ^1H NMR spectra of dichloro and dibromo derivatives **11**–**16** are shifted to lower field compared to those of the corresponding dimethylgermocanes **23**–**25**. According to Tandura et al. [56], this implies strengthening of the Ge ← N bond in **11**–**16** in comparison with **23**–**25** in $CDCl_3$ solution. However, this approach has some limitations such as in the case of **22**. The presence of the aromatic fragments (fluorenyl groups) at the Ge atom accounts for the considerable upfield shift of the NCH_2 and NMe proton signals.

Very recently we have found that dimethylgermocane $MeN(CH_2CH_2O)_2GeMe_2$ possesses a short Ge ← N contact in $CDCl_3$ solution [28]. This fact has been established by the presence of the strong NOE from H^0 protons of Me–N group to the H^1 protons of Me–Ge groups, which is possible on assuming the conformation **A** in solution (Scheme 9). On the contrary, our investigation of the compounds **23** and **26** has shown no NOE from protons of Me–N group to the protons of Me–Ge groups in **26** ($CDCl_3$ solution) and only weak NOE from H^0 protons of Me–N group to H^1 protons of one Me–Ge group in **23**. NOE was also detected between H^2 and H^3 protons in **23**. Thus,



Scheme 9.

the conformations **B** may be considered as prevailing for these compounds in solution (Scheme 9). The compound **26** retains the solid-state structure (see above) in solution. Of interest, as previously pointed out, the replacement of hydrogen atoms in $MeN(CH_2CH_2O)_2GeBr_2$ (**28**) [28] with phenyl groups does not noticeably affect the strength of the Ge ← N interaction in *erythro*-$MeN(CH_2CH_2O)$-$(CHPhCHPhO)GeBr_2$ (**16**). On the contrary, the analogous replacement in $MeN(CH_2CH_2O)_2GeMe_2$ leads to a substantial elongation of the Ge···N contact in $MeN(CH_2$-$CH_2O)(CH_2CHPhO)GeMe_2$ (**23**).

In conclusion, the combined X-ray diffraction and NMR studies of the germocane structures allowed to state the relationships between the strength of the Ge ← N interaction and the nature of substituents in different positions of ocane skeleton. The determining factor is the nature of substituents at the Ge atom: a strong acceptor group leads to strong interaction; no important influence of substituents at the N and C atoms was detected in this case. The presence of donor substituents at the Ge atom generally results in the weakening of the Ge ← N interaction along with a considerable increase of the influence of substituents at the N and C atoms on its strength. In this case, an acceptor substituent at the N atom and bulky substituents at carbon atoms stimulate the weakening of the Ge ← N interaction.

3. Experimental

All manipulations were performed under dry, oxygen-free argon atmosphere using standard Schlenk techniques. $PhN(CH_2CH_2OH)_2$ (Aldrich) was used as supplied. $(Me_3Si)_2NH$, Me_3SiCl, and $BF_3 \cdot Et_2O$ (Aldrich) were distilled before use. $MeN(CH_2CH_2OH)CH_2CH(Me)OH$ [57], $MeN(CH_2CH_2OH)CH_2CH(Ph)OH + MeN(CH_2CH_2OH)$-–$CH(Ph)CH_2OH$ as a 9:1 mixture [44], *erythro*-$MeN(CH_2$-$CH_2OH)CH(Ph)CH(Ph)OH$, *threo*-$MeN(CH_2CH_2OH)$-$CH(Ph)CH(Ph)OH$, $MeN(CH_2CH_2OH)CH_2C(Ph)_2OH$ and $MeN(CH_2CH_2OH)CH(C_4H_8)CHOH$ [46], Me_3SiNEt_2 [45], Flu_2GeCl_2 [58], $MeN(CH_2CH_2OSiMe_3)_2$ [59], MeN-$(CH_2CH_2O)_2GeCl_2$ and $MeN(CH_2CH_2O)_2GeBr_2$ [28], $Me_2Ge(NMe_2)_2$ [60], $Et_3SnOMenth$ [61], and $MeN(CH_2$-$CH_2O)_2Ge(OH)_2$ [24] were prepared according to the literature. Solvents were dried by standard methods and distilled prior to use. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC200, DRX 300, DPX 500, and Varian VXR 400 spectrometers at 300 K. ^1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. Mass spectra (EI-MS) were recorded on a VARIAN CH-7a device using electron impact ionization at 70 eV; all assignments were made with reference to the most abundant isotopes. Elemental analyses were carried out at the Microanalytical Laboratory of the Chemistry Department of Moscow State University.

3.1. General procedures for the synthesis of bis(trimethylsilyl)ethers of dialkanolamines

A: A mixture of dialkanolamine (0.05 mol) and $HN(SiMe_3)_2$ (0.13 mol) was heated under reflux (Table 2). All volatile materials were evaporated, and the residue was distilled in vacuum or was used without additional purification for the synthesis of germocanes.

B: A mixture of dialkanolamine (0.01 mol), Me_3SiNEt_2 (0.04 mol), Me_3SiCl (0.004 mol), and ethylacetate (25 mL) was heated under reflux (Table 2). The solvent and all volatile materials were evaporated, and the residue was distilled in vacuum or was used without additional purification for the synthesis of germocanes.

3.1.1. $MeN(CH_2CH_2OSiMe_3)CH(C_4H_8)CHOSiMe_3$ (1)

^1H NMR ($CDCl_3$, 400 MHz): $\delta = 0.08$ (s, 9H, $SiMe_3$), 0.09 (s, 9H, $SiMe_3$), 1.07–1.29 (m, 4H), 1.56–1.72 (m, 3H), 1.82–1.89 (m, 1H) ($4CH_2$ groups), 2.33 (s, 3H, MeN), 2.27–2.36 (m, 1H), 2.67–2.71 (m, 2H), 3.53–3.61 (m, 3H) (NCH_2, OCH_2, NCH, and OCH groups). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.44$ ($SiMe_3$), 0.87 ($SiMe_3$), 24.58, 25.34, 28.04, 36.05 (CH_2 groups), 38.87 (MeN), 57.05 (NCH_2), 61.86 (OCH_2), 68.72 (NCH), 72.46 (OCH). MS (EI, *m*/*z*, %): 317 (<1) [M^+], 302 (2) [M^+-Me], 214 (57) [$M^+-SiMe_3-CH_2O$], 171 (8) [$M^+-2SiMe_3$], 73 (100) [$SiMe_3^+$]. Anal. Calc. for $C_{15}H_{35}NO_2Si_2$ (317.62): C, 56.72; H, 11.11; Si, 17.69. Found: C, 56.88; H, 11.32; Si, 17.89%.

3.1.2. $PhN(CH_2CH_2OSiMe_3)_2$ (2)

^1H NMR ($CDCl_3$, 400 MHz): $\delta = 0.10$ (s, 18H, $2SiMe_3$), 3.49 (t, $^3J = 7$ Hz, 4H, $2NCH_2$), 3.71 (t, $^3J = 7$ Hz, 4H, $2OCH_2$), 6.63–6.69, 7.17–7.21 (2m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.56$ ($SiMe_3$), 53.44 (NCH_2), 59.29 (OCH_2), 111.35, 115.73, 129.31, 147.60 (Ph). MS (EI, *m*/*z*, %): 325 (4) [M^+], 222 (100) [$M^+-SiMe_3-CH_2O$],

Table 2
Synthesis of bis(trimethylsilyl)ethers of dialkanolamines

Compound	Method	Refluxing time (h)	Isolated yield (%)	B.p. (°C)
$MeN(CH_2CH_2OSiMe_3)CH(C_4H_8)CHOSiMe_3$ (**1**)	A	70	86	90–92 (1 mm Hg)
$PhN(CH_2CH_2OSiMe_3)_2$ (**2**)	A	9	87	144–145 (1 mm Hg)
$MeN(CH_2CH_2OSiMe_3)CH_2CH(Ph)OSiMe_3$ (**3**) + $MeN(CH_2CH_2OSiMe_3)CH(Ph)CH_2OSiMe_3$ (**4**)	A	21	76	78–82 (0.2 mm Hg)
$MeN(CH_2CH_2OSiMe_3)CH_2CH(Me)OSiMe_3$ (**5**)	B	40	79	56–61 (1 mm Hg)
erythro-$MeN(CH_2CH_2OSiMe_3)CH(Ph)CH(Ph)OSiMe_3$ (**6**)	B	33	98	–
threo-$MeN(CH_2CH_2OSiMe_3)CH(Ph)CH(Ph)OSiMe_3$ (**7**)	B	39	97	–
$MeN(CH_2CH_2OSiMe_3)CH_2C(Ph)_2OSiMe_3$ (**8**)	B	65	98	–

73 (26) [$SiMe_3^+$]. Anal. Calc. for $C_{16}H_{31}NO_2Si_2$ (325.59): C, 59.02; H, 9.60; Si, 17.25. Found: C, 59.10; H, 9.92; Si, 17.06%.

3.1.3. MeN(CH$_2$CH$_2$OSiMe$_3$)CH$_2$CH(Ph)OSiMe$_3$ (3) and MeN(CH$_2$CH$_2$OSiMe$_3$)CH(Ph)CH$_2$OSiMe$_3$ (4)

The approximate ratio of isomers is **3**:**4** = 9:1 (according to ^{1}H NMR). NMR data for MeN($CH_2CH_2OSiMe_3$)CH_2-CH(Ph)$OSiMe_3$ (**3**): ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.01$ (s, 9H, $SiMe_3$), 0.08 (s, 9H, $SiMe_3$), 2.34 (s, 3H, MeN), 2.51–2.76 (m, 4H, 2NCH_2 groups), 3.60 (t, $^3J = 7$ Hz, 2H, OCH_2), 4.78 (dd, $^3J = 8$ Hz, $^3J = 5$ Hz, 1H, OCH), 7.18–7.32 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = -0.52$ ($SiMe_3$), 0.23 ($SiMe_3$), 43.65 (MeN), 59.77, 60.69 (2NCH_2 groups), 66.92 (OCH_2), 73.54 (OCH), 126.19, 127.11, 128.01, 144.01 (Ph). NMR data for MeN($CH_2CH_2OSiMe_3$)CH(Ph)CH_2OSiMe_3 (**4**): ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = -0.02$ (s, 9H, $SiMe_3$), 0.05 (s, 9H, $SiMe_3$), 2.29 (s, 3H, MeN), 3.75–3.99 (m, 2H, OCH_2). Other proton resonances could not be located due to the overlap with those for major isomer. ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = -0.61$ (2$SiMe_3$), 40.39 (MeN), 56.80, 60.85, 64.46 (2OCH_2 and NCH_2 groups), 70.54 (NCH), 127.04, 127.96, 128.61 (Ph). The fourth aromatic signal was not observed, probably due to the low concentration of minor isomer. MS (EI, *m*/*z*, %): 324 (5) [M^+−Me], 236 (35) [MeN($CH_2CH_2OSiMe_3$)$CH(Ph)^+$], 160 (100) [MeN($CH_2CH_2OSiMe_3$)CH_2^+], 147 (10) [MeN$CH_2CH_2OSiMe_3^+$], 117 (11) [$CH_2CH_2OSiMe_3^+$], 73 (28) [$SiMe_3^+$]. Anal. Calc. for $C_{17}H_{33}NO_2Si_2$ (339.62): C, 60.12; H, 9.79; N, 4.12. Found: C, 60.10; H, 9.68; N, 4.40%.

3.1.4. MeN(CH$_2$CH$_2$OSiMe$_3$)CH$_2$CH(Me)OSiMe$_3$ (5)

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.07$ (s, 9H, $SiMe_3$), 0.08 (s, 9H, $SiMe_3$), 1.11 (d, $^3J = 6$ Hz, 3H, Me), 2.25 (s, 3H, MeN), 2.26–2.38 (m, 2H), 2.44–2.57 (m, 2H) (2NCH_2 groups), 3.61 (t, $^3J = 7$ Hz, 2H, OCH_2), 3.79–3.86 (m, 1H, OCH). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.50$ ($SiMe_3$), 0.26 ($SiMe_3$), 22.26 (Me), 44.02 (MeN), 60.36, 60.81 (2NCH_2 groups), 66.30, 66.99 (OCH_2 and OCH groups). MS (EI, *m*/*z*, %): 277 (<1) [M^+], 262 (2) [M^+−Me], 174 (15) [M^+−$SiMe_3$−CH_2O], 160 (73) [M^+−$SiMe_3$−MeCHO], 73 (100) [$SiMe_3^+$]. Anal. Calc. for $C_{12}H_{31}NO_2Si_2$ (277.55): C, 51.93; H, 11.26; Si, 20.24. Found: C, 52.20; H, 11.40; Si, 19.73%.

3.1.5. erythro-MeN(CH$_2$CH$_2$OSiMe$_3$)CH(Ph)CH(Ph)OSiMe$_3$ (6)

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = -0.15$ (s, 9H, $SiMe_3$), 0.03 (s, 9H, $SiMe_3$), 2.17 (s, 3H, MeN), 2.33–2.40 (m, 1H), 2.61–2.68 (m, 1H) (NCH_2), 3.31–3.41 (m, 2H, OCH_2), 3.64 (d, $^3J = 7$ Hz, 1H, NCH), 5.14 (d, $^3J = 7$ Hz, 1H, OCH), 7.16–7.29 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.56$ ($SiMe_3$), 0.12 ($SiMe_3$), 40.06 (MeN), 56.35 (NCH_2), 60.93 (OCH_2), 75.26 (NCH), 75.42 (OCH), 126.67, 126.95, 127.10, 127.24, 127.51, 129.98, 137.17, 143.94 (2Ph). Anal. Calc. for $C_{23}H_{37}NO_2Si_2$ (415.72): C, 66.45; H, 8.97; Si, 13.51. Found: C, 66.65; H, 8.83; Si, 13.50%.

3.1.6. threo-MeN(CH$_2$CH$_2$OSiMe$_3$)CH(Ph)CH(Ph)OSiMe$_3$ (7)

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = -0.01$ (s, 9H, $SiMe_3$), 0.10 (s, 9H, $SiMe_3$), 2.37 (s, 3H, MeN), 2.59–2.66 (m, 1H), 2.88–3.00 (m, 1H) (NCH_2), 3.65 (t, $^3J = 7$ Hz, 2H, OCH_2), 3.83 (d, $^3J = 8$ Hz, 1H, NCH), 5.11 (d, $^3J = 8$ Hz, 1H, OCH), 7.02–7.14 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.50$ ($SiMe_3$), 0.30 ($SiMe_3$), 40.33 (MeN), 56.38 (NCH_2), 61.42 (OCH_2), 75.39 (NCH), 76.10 (OCH), 126.67, 126.87, 127.48, 127.52, 129.40, 138.25, 142.88 (2Ph). Anal. Calc. for $C_{23}H_{37}NO_2Si_2$ (415.72): C, 66.45; H, 8.97; Si, 13.51. Found: C, 66.33; H, 8.84; Si, 13.25%.

3.1.7. MeN(CH$_2$CH$_2$OSiMe$_3$)CH$_2$C(Ph)$_2$OSiMe$_3$ (8)

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = -0.09$ (s, 9H, $SiMe_3$), 0.07 (s, 9H, $SiMe_3$), 2.16 (s, 3H, MeN), 2.51 (t, $^3J = 7$ Hz, 2H, NCH_2), 3.33 (s, 2H, NCH_2), 3.40 (t, $^3J = 7$ Hz, 2H, OCH_2), 7.19–7.30, 7.35–7.38 (2m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.51$ ($SiMe_3$), 2.05 ($SiMe_3$), 44.55 (MeN), 60.66, 61.40, 68.69 (2NCH_2 and OCH_2 groups), 81.69 ($C(Ph)_2$), 126.67, 127.40, 127.72, 146.70 (Ph). Anal. Calc. for $C_{23}H_{37}NO_2Si_2$ (415.72): C, 66.45; H, 8.97; Si, 13.51. Found: C, 66.29; H, 8.91; Si, 13.72%.

3.2. The synthesis of the 2,2-dihalogermocanes 9–21

3.2.1. MeN(CH$_2$CH$_2$O)(CH$_2$CH(Me)O)GeBr$_2$ (9)

0.50 ml (4.0 mmol) of germanium tetrabromide were added to a stirred solution of 1.11 g (4.0 mmol) of MeN($CH_2CH_2OSiMe_3$)CH_2CH(Me)$OSiMe_3$ (**5**) in $CHCl_3$ (10 ml). The reaction mixture was refluxed for 20 h, and the solvent was then removed under reduced pressure. To the residue as a brown oil diethyl ether (10 ml) was added. Upon vigorous stirring the product transferred into a solid, which was filtered, washed with diethyl ether (2 × 5 ml), and dried in vacuum to give 0.61 g (42%) of **9** as a light brown powder, m.p. 129–134 °C (dec.). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 1.30$ (d, $^3J = 6$ Hz, 3H, Me), 1.33 (d, $^3J = 6$ Hz, 3H, Me), 2.63 (s, 3H, MeN), 2.64 (s, 3H, MeN), 2.47–2.55 (m, 2H), 2.74–2.78 (m, 2H), 2.88–3.13 (m, 4H) (4NCH_2 groups), 3.85–3.91, 3.99–4.11, 4.18–4.26 (3m, 6H, 2OCH_2 and 2OCH groups). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 20.13$ (Me), 21.03 (Me), 45.14 (MeN), 45.85 (MeN), 54.73, 56.56, 59.23, 59.42 (4NCH_2 groups), 60.86, 61.90, 65.27, 65.89 (2OCH_2 and 2OCH groups). Two diastereomers. MS (EI, *m*/*z*, %): 283 (3) [M^+−Br], 102 (7) [M^+−CH_2O−$GeBr_2$+1], 88 (97) [M^+−MeCHO−$GeBr_2$+1], 57 (24) [MeN$CH_2CH_2^+$], 28 (100). Anal. Calc. for $C_6H_{13}Br_2GeNO_2$ (363.59): C, 19.82; H, 3.60; Ge, 19.97. Found: C, 20.27; H, 3.91; Ge, 19.44%.

3.2.2. MeN(CH$_2$CH$_2$O)(CH(C$_4$H$_8$)CHO)GeBr$_2$ (10)

Analogously to the synthesis of **9**, germocane **10** was prepared from 0.63 ml (5.0 mmol) of $GeBr_4$ and 1.59 g

(5.0 mmol) of $MeN(CH_2CH_2OSiMe_3)CH(C_4H_8)CHOSiMe_3$ (**1**) by reflux for 30 h in 10 ml of $CHCl_3$. The product (1.19 g, 59%) was isolated in form of a beige powder, m.p. 201–202 °C (dec.). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.12$–1.47 (m, 8H), 1.75–1.80 (m, 4H), 1.85–1.91 (m, 4H) (8CH_2 groups), 2.46 (s, 3H, MeN), 2.55 (s, 3H, MeN), 2.00–2.05, 2.25–2.32, 2.37–2.61, 2.83–3.02, 3.57–3.64, 3.69–3.75, 3.82–3.89, 4.01–4.05 (8m, 12H, NCH_2, OCH_2, NCH, and OCH groups). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 22.73$, 23.24, 23.38, 23.47, 24.82, 24.91, 33.23, 33.32 (CH_2 groups), 39.04, 42.29 (MeN), 49.87, 53.48 (NCH_2), 59.25, 59.32 (OCH_2), 66.39, 67.88 (NCH), 71.93, 72.78 (OCH). Two diastereomers. MS (EI, *m*/*z*, %): 373 (14) [M^+-CH_2O], 324 (41) [M^+-Br], 294 (18) [$M^+-Br-CH_2O$], 170 (15) [M^+-GeBr_2-H], 141 (22) [$M^+-CH_2O-GeBr_2$], 112 (19) [$NCH(C_4H_8)CHO^+$]. Anal. Calc. for $C_9H_{17}Br_2GeNO_2$ (403.66): C, 26.78; H, 4.24; N, 3.47. Found: C, 26.89; H, 4.23; N, 3.33%.

3.2.3. *MeN(CH$_2$CH$_2$O)(CH$_2$CH(Ph)O)GeCl$_2$ (**11**)*

1.26 ml (11.0 mmol) of germanium tetrachloride were added to a stirred solution of 3.40 g (10.0 mmol) of the mixture of bis(trimetylsilyl)ethers (**3** + **4**) in 15 ml of toluene. The reaction mixture was refluxed for 3 h. The precipitated solid was filtered, washed with pentane (2 × 10 ml), and dried in vacuum to give 2.23 g (66%) of **11** as a white powder. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 2.66$ (s, 3H, MeN), 2.80 (s, 3H, MeN), 2.68–2.85 (m, 2H), 2.89–3.09 (m, 4H), 3.14–3.29 (m, 2H) (4NCH_2 groups), 3.89–4.14 (m, 4H, 2OCH_2 groups), 4.98 (dd, $^3J = 11$ Hz, $^3J = 4$ Hz, 1H, OCH), 5.04 (dd, $^3J = 11$ Hz, $^3J = 4$ Hz, 1H, OCH), 7.28–7.40 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 44.42$ (MeN), 45.01 (MeN), 54.55, 56.20, 58.67, 58.73 (4NCH_2 groups), 61.32, 61.81 (2OCH_2 groups), 70.47, 70.78 (2OCH groups), 125.60, 125.83, 128.48, 128.78, 129.26, 129.54 (2Ph). Two diastereomers. The quaternary carbons of phenyl groups were not detected due to the poor solubility of **11** in $CDCl_3$. MS (EI, *m*/*z*, %): 307 (5) [M^+-CH_2O], 300 (19) [M^+-Cl], 231 (67) [$M^+-PhCHO$], 106 (6) [$PhCHO^+$], 57 (100) [$MeN(CH_2)_2^+$]. Anal. Calc. for $C_{11}H_{15}Cl_2GeNO_2$ (336.76): C, 39.23; H, 4.49; N, 4.16. Found: C, 39.31; H, 4.47; N, 3.99%. The reaction mixture also contained small amount (10–15%) of $MeN(CH_2CH_2O)(CH(Ph)CH_2O)GeCl_2$ (**12**). ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 2.24$–2.29 (m, 1H, NCH_2), 2.30 (s, 3H, MeN), 2.49 (s, 3H, MeN). Two diastereomers. Other proton resonances could not be located due to the overlap with those for major isomer.

3.2.4. *MeN(CH$_2$CH$_2$O)(CH$_2$CH(Ph)O)GeBr$_2$ (**13**)*

Analogously to **11**, germocane **13** was prepared from 1.15 ml (9.1 mmol) of $GeBr_4$ and 3.10 g (9.1 mmol) of the mixture of bis(trimetylsilyl)ethers (**3** + **4**) by reflux for 30 h in 15 ml of $CHCl_3$. The product (1.03 g, 27%) was isolated as a slightly yellow powder. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 2.63$ (s, 3H, MeN), 2.76 (s, 3H, MeN), 2.69–2.78 (m, 2H), 2.83–2.97 (m, 3H), 2.99–3.07 (m, 1H), 3.08–3.16 (m, 1H), 3.22–3.32 (m, 1H) (4NCH_2 groups), 3.89–3.99 (m, 1H), 4.01–4.11 (m, 3H) (2OCH_2 groups), 4.99 (dd, $^3J = 11$ Hz, $^3J = 4$ Hz, 1H, OCH), 5.10 (dd, $^3J = 11$ Hz, $^3J = 5$ Hz, 1H, OCH), 7.27–7.40 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 44.82$ (MeN), 45.51 (MeN), 54.44, 55.95, 59.26, 59.39 (4NCH_2 groups), 60.78, 61.90 (2OCH_2 groups), 71.24, 71.43 (2OCH groups), 125.62, 125.85, 128.44, 128.76 (three unresolved signals), 139.20, 139.79 (2Ph). Two diastereomers. MS (EI, *m*/*z*, %): 346 (37) [M^+-Br], 319 (63) [$M^+-PhCHO$], 240 (100) [$M^+-PhCHO-Br$], 226 (8) [$M^+-CH_2CH(Ph)O-Br$], 196 (5) [$CH_2=CHOGeBr^+$], 153 (7) [$GeBr^+$], 86 (32) [$M^+-PhCHO-GeBr_2-H$], 57 (92) [$MeN(CH_2)_2^+$]. Anal. Calc. for $C_{11}H_{15}Br_2GeNO_2$ (425.66): C, 31.04; H, 3.55; N, 3.29. Found: C, 30.99; H, 3.65; N, 3.20%. The reaction mixture also contained small amount (10–15%) of $MeN(CH_2CH_2O)(CH(Ph)CH_2O)GeBr_2$ (**14**). ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 2.28$ (s, 3H, MeN), 2.45 (s, 3H, MeN). Two diastereomers. Other proton resonances could not be located due to the overlap with those for major isomer.

3.2.5. *erythro-MeN(CH$_2$CH$_2$O)(CH(Ph)CH(Ph)O)GeCl$_2$ (**15**)*

1.04 ml (9.0 mmol) of germanium tetrachloride were added to a stirred solution of 3.74 g (9.0 mmol) of *erythro*-$MeN(CH_2CH_2OSiMe_3)CH(Ph)CH(Ph)OSiMe_3$ (**6**) in 20 ml of toluene. The reaction mixture was refluxed for 18 h. The precipitated solid was filtered, washed with diethyl ether (2 × 5 ml), and dried in vacuum to give 3.14 g (85%) of **15** as an off-white powder. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 2.31$ (s, 3H, MeN), 2.70 (s, 3H, MeN), 2.29–2.33, 2.43–2.47, 2.81–2.82, 3.02–3.12, 3.19–3.27, 3.48–3.55 (6m, 4H, 2NCH_2), 3.80–3.87, 3.92–4.02, 4.15–4.19 (3m, 4H, 2OCH_2), 4.08 (d, $^3J = 5$ Hz, 1H, NCH), 4.29 (d, $^3J = 6$ Hz, 1H, NCH), 5.54 (d, $^3J = 6$ Hz, 1H, OCH), 5.64 (d, $^3J = 5$ Hz, 1H, OCH), 7.06–7.37 (m, 20H, 4Ph). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz, 80 °C): $\delta = 42.21$ (MeN), 57.56 (NCH_2), 58.82 (OCH_2), 70.61 (NCH), 71.53 (OCH) (one diastereomer), 45.80 (MeN), 53.68 (NCH_2), 58.97 (OCH_2), 71.73 (NCH), 73.69 (OCH) (the other diastereomer), 125.23, 125.86, 126.46, 127.56, 127.61, 127.67, 128.26, 128.40, 128.84, 130.99, 132.83, 139.35 (4Ph for both diastereomers). Two diastereomers. Other signals of aromatic carbons were not found due to the poor solubility of **15** in $(CD_3)_2SO$ and probably due to coalescence of some signals. MS (EI, *m*/*z*, %): 378 (6) [M^+-Cl], 307 (77) [$M^+-PhCHO$], 272 (22) [$M^+-PhCHO-Cl$], 162 (34) [$M^+-PhCHO-GeCl_2-H$], 132 (100) [$M^+-PhCHO-GeCl_2-CH_2O-H$], 118 (17) [CH_2NCHPh^+]. Anal. Calc. for $C_{17}H_{19}Cl_2GeNO_2$ (412.85): C, 49.46; H, 4.64; N, 3.39. Found: C, 49.81; H, 4.53; N, 3.40%.

3.2.6. *erythro-MeN(CH$_2$CH$_2$O)(CH(Ph)CH(Ph)O)GeBr$_2$ (**16**)*

Analogously to **15**, germocane **16** was prepared from 0.88 ml (7.0 mmol) of $GeBr_4$ and 2.91 g (7.0 mmol) of

erythro-MeN($CH_2CH_2OSiMe_3$)CH(Ph)CH(Ph)$OSiMe_3$ (**6**) by reflux for 35 h in 15 ml of toluene. The product (0.95 g, 27%) was isolated as dark brown crystals. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.28$ (s, 3H, MeN), 2.70 (s, 3H, MeN), 2.24–2.33, 2.41–2.45, 2.84–2.85, 3.00–3.09, 3.19–3.26, 3.45–3.54 (6m, 4H, $2NCH_2$), 3.81–4.05, 4.13–4.16 (2m, 4H, $2OCH_2$), 4.08 (d, $^3J = 5$ Hz, 1H, NCH), 4.26 (d, $^3J = 6$ Hz, 1H, NCH), 5.54 (d, $^3J = 6$ Hz, 1H, OCH), 5.67 (d, $^3J = 5$ Hz, 1H, OCH), 6.99–7.39 (m, 20H, 4Ph). ^{13}C NMR (($CD_3)_2SO$, 100 MHz, 80 °C): $\delta = 41.08$ (MeN), 41.61 (MeN), 54.81 (NCH_2), 57.42 (NCH_2), 57.98 (OCH_2), 58.11 (OCH_2), 70.38, 71.08, 71.31, 71.47 (2NCH and 2OCH groups), 125.23, 125.90, 126.58, 127.53, 127.62, 127.70, 127.84, 128.14, 128.55, 128.84, 130.34, 132.40, 139.28 (4Ph). Two diastereomers. Other signals of aromatic carbons were not found due to the poor solubility of **16** in $(CD_3)_2SO$ and probably due to coalescence of some signals. MS (EI, *m/z*, %): 422 (11) [M^+−Br], 395 (30) [M^+−PhCHO], 316 (100) [M^+−PhCHO−Br], 162 (26) [M^+−PhCHO−$GeBr_2$−H], 132 (42) [M^+−PhCHO−$GeBr_2$−CH_2O−H], 118 (9) [CH_2NCHPh^+], 58 (26) [$NCH_2CH_2O^+$]. Anal. Calc. for $C_{17}H_{19}Br_2GeNO_2$ (501.76): C, 40.69; H, 3.82; N, 2.79. Found: C, 41.02; H, 3.78; N, 2.96%.

3.2.7. *threo*-MeN(CH_2CH_2O)(CH(Ph)CH(Ph)O)$GeBr_2$ (**17**)

0.47 ml (3.73 mmol) of germanium tetrabromide were added to a stirred solution of 1.55 g (3.73 mmol) of *threo*-MeN($CH_2CH_2OSiMe_3$)CH(Ph)CH(Ph)$OSiMe_3$ (**7**) in 10 ml of chloroform. The reaction mixture was refluxed for 24 h. The precipitated solid was filtered, washed with chloroform (2 × 8 ml), and dried in vacuum to give 0.91 g (49%) of **17** as a white powder. ^{1}H NMR (($CD_3)_2SO$, 400 MHz): $\delta = 2.63$ (s, 3H, MeN), 3.43–3.49, 3.80–3.86, 4.05–4.10 (3m, 4H, NCH_2 and OCH_2 groups), 4.26 (d, $^3J = 11$ Hz, 1H, NCH), 5.53 (d, $^3J = 11$ Hz, 1H, OCH), 7.16–7.33, 7.39–7.45, 7.65–7.75, 7.84–7.88 (4m, 10H, 2Ph). The signals of MeN, NCH, and OCH groups of two other diastereomers are observed at the total rate of about 30%. ^{13}C NMR (($CD_3)_2SO$, 100 MHz): $\delta = 43.63$ (MeN), 52.18 (NCH_2), 57.63 (OCH_2), 72.79 (NCH), 73.79 (OCH), 127.36, 127.51, 127.94, 128.39, 129.59, 131.75, 139.09, 141.32 (2Ph). MS (EI, *m/z*, %): 422 (30) [M^+−Br], 395 (51) [M^+−PhCHO], 316 (100) [M^+−Br−PhCHO], 162 (11) [M^+−PhCHO−$GeBr_2$−H], 153 (22) [$GeBr^+$], 132 (72) [M^+−PhCHO−$GeBr_2$−CH_2O−H], 118 (22) [CH_2NCHPh^+], 105 (15) [$PhCO^+$], 77 (28) [Ph^+], 58 (16) [$NCH_2CH_2O^+$]. Anal. Calc. for $C_{17}H_{19}Br_2GeNO_2$ (501.76): C, 40.69; H, 3.82; N, 2.79. Found: C, 40.99; H, 3.79; N, 2.76%.

3.2.8. MeN(CH_2CH_2O)($CH_2C(Ph)_2O$)$GeCl_2$ (**18**)

Analogously to **15**, germocane **18** was prepared from 0.48 ml (4.2 mmol) of $GeCl_4$ and 1.75 g (4.2 mmol) of MeN($CH_2CH_2OSiMe_3$)$CH_2C(Ph)_2OSiMe_3$ (**8**) by reflux for 28 h in 10 ml of toluene. The product (1.51 g, 87%) was isolated as a brown powder. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.45$ (s, 3H, MeN), 2.68–2.74 (m, 1H), 2.87–2.93 (m, 1H) (NCH_2), 3.65 (AB system, $^2J = 13$ Hz, 2H, $NCH_2C(Ph)_2$), 3.83–3.94 (m, 2H, OCH_2), 7.18–7.24 (m, 2H), 7.28–7.34 (m, 4H), 7.51–7.58 (m, 4H) (2Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 46.75$ (MeN), 57.02, 58.72 ($2NCH_2$ groups), 63.69 (OCH_2), 77.56 ($OC(Ph)_2$), 125.16, 125.29, 127.57, 128.60, 128.72, 144.90, 145.41 (2Ph). A signal of aromatic carbon was not found probably due to coalescence of two signals. MS (EI, *m/z*, %): 378 (5) [M^+−Cl], 231 (57) [M^+−Ph_2CO], 161 (6) [M^+−Ph_2CO−2Cl], 105 (5) [$PhCO^+$], 57 (100) [$CH_3N(CH_2)_2^+$]. Anal. Calc. for $C_{17}H_{19}Cl_2GeNO_2$ (412.85): C, 49.46; H, 4.64; N, 3.39. Found: C, 49.81; H, 4.53; N, 3.40%.

3.2.9. MeN(CH_2CH_2O)($CH_2C(Ph)_2O$)$GeBr_2$ (**19**)

Analogously to **15**, germocane **19** was prepared from 0.72 ml (5.8 mmol) of $GeBr_4$ and 2.40 g (5.8 mmol) of MeN($CH_2CH_2OSiMe_3$)$CH_2C(Ph)_2OSiMe_3$ (**8**) by reflux for 28 h in 20 ml of toluene. The product (1.55 g, 53%) was isolated as a beige powder. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.44$ (s, 3H, MeN), 2.68–2.75 (m, 1H), 2.87–2.93 (m, 1H) (NCH_2), 3.64 (s, 2H, $NCH_2C(Ph)_2$), 3.86–3.96 (m, 2H, OCH_2), 7.19–7.24 (m, 2H), 7.29–7.35 (m, 4H), 7.53–7.59 (m, 4H) (2Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 47.22$ (MeN), 56.82, 59.31 ($2NCH_2$ groups), 63.50 (OCH_2), 125.19, 125.37, 127.57, 128.62, 128.74, 144.88, 145.49 (2Ph). The signal of $OC(Ph)_2$ group was not found due to the low solubility of the product in $CDCl_3$. One signal of aromatic carbon was not found probably due to coalescence of two signals. Anal. Calc. for $C_{17}H_{19}Br_2GeNO_2$ (501.76): C, 40.69; H, 3.82; N, 2.79. Found: C, 40.85; H, 3.73; N, 3.13%.

3.2.10. PhN(CH_2CH_2O)$_2GeCl_2$ (**20**)

Analogously to **9**, germocane **20** was prepared from 1.50 ml (13.0 mmol) of $GeCl_4$ and 4.24 g (13.0 mmol) of PhN($CH_2CH_2OSiMe_3$)$_2$ (**2**) by reflux for 3 h in 15 ml of chloroform. The product (1.10 g, 26%) was isolated as a light brown powder. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta =$ 3.48 (t, $^3J = 5$ Hz, 4H, $2NCH_2$), 4.23 (t, $^3J = 5$ Hz, 4H, $2OCH_2$), 7.03–7.10 (m, 3H), 7.31–7.35 (m, 2H) (Ph). ^{13}C NMR was not measured due to the poor solubility of germocane **20** in $CDCl_3$. MS (EI, *m/z*, %): 323 (14) [M^+], 293 (15) [M^+−CH_2O], 149 (100) [M^+−CH_2O−$GeCl_2$], 119 (96) [M^+−$2CH_2O$−$GeCl_2$], 105 (13) [$PhNCH_2^+$], 91 (33) [PhN^+]. Anal. Calc. for $C_{10}H_{13}Cl_2GeNO_2$ (322.73): C, 37.22; H, 4.06; N, 4.34. Found: C, 37.32; H, 4.33; N, 4.24%.

3.2.11. PhN(CH_2CH_2O)$_2GeBr_2$ (**21**)

Analogously to **9**, germocane **21** was prepared from 1.25 ml (10.0 mmol) of $GeBr_4$ and 3.26 g (10.0 mmol) of PhN($CH_2CH_2OSiMe_3$)$_2$ (**2**) by reflux for 30 h in 15 ml of toluene. The product (0.49 g, 12%) was isolated as a white powder. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 3.52$ (t, $^3J = 5$ Hz, 4H, $2NCH_2$), 4.20 (t, $^3J = 5$ Hz, 4H, $2OCH_2$), 6.87–6.90 (m, 2H), 6.96–7.00 (m, 1H), 7.26–7.33 (m, 2H) (Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 57.68$ (NCH_2),

65.24 (OCH_2), 116.47, 121.27, 129.17, 148.40 (Ph). MS (EI, *m/z*, %): 411 (4) [M^+], 381 (6) [M^+-CH_2O], 302 (29) [M^+-CH_2O-Br], 149 (100) [$M^+-CH_2O-GeBr_2$], 119 (17) [$M^+-2CH_2O-GeBr_2$], 105 (11) [$PhNCH_2^+$], 91 (9) [PhN^+]. Anal. Calc. for $C_{10}H_{13}Br_2GeNO_2$ (411.63): C, 29.18; H, 3.18; N, 3.40. Found: C, 29.42; H, 3.15; N, 3.24%.

3.3. The synthesis of the 2,2-difluorenyl-6-methylgermocane (**22**)

3.3.1. $Flu_2Ge(OEt)_2$

A solution of 0.38 ml (2.7 mmol) of triethylamine in 15 ml of ethanol was added dropwise, at 0 °C, to a suspension of 0.85 g (1.8 mmol) of Flu_2GeCl_2 in 20 ml of THF. The reaction mixture was refluxed for 15 h, and then all volatiles were removed under reduced pressure. Diethyl ether (5 ml) was added to the residue, and the resulting suspension was stirred for 1 h. The precipitate ($Et_3N \cdot HCl$) was filtered off and washed with ether (2×2 ml). After the volume of the filtrate was reduced to ca. 2 ml, heptane (10 ml) was added. The precipitated solid was filtered and dried in vacuum to give 0.30 g of crude $Flu_2Ge(OEt)_2$ as a white powder. This compound was used in the next step without further purification. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.17$ (t, $^3J = 7$ Hz, 6H, $2CH_3$), 3.69 (q, $^3J = 7$ Hz, 4H, $2OCH_2$), 4.06 (s, 2H, 2 GeCH), 7.03–7.07 (m, 4H), 7.18–7.22 (m, 4H), 7.27–7.29 (m, 4H), 7.57–7.59 (m, 4H) (aromatic protons of two fluorenyl groups).

3.3.2. $MeN(CH_2CH_2O)_2GeFlu_2$ (**22**)

A: A mixture of 0.30 g (0.6 mmol) of $Flu_2Ge(OEt)_2$, 0.07 g (0.6 mmol) of *N*-methyldiethanolamine and 20 ml of toluene was refluxed for 4 h. After 80% of volatile materials were removed under reduced pressure, hexane (5 ml) was added. The precipitate was filtered, washed with hexane (2×3 ml), and dried in vacuum to give 0.17 g (55%) of germocane **22** as a white powder. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.40$ (s, 3H, MeN), 2.23 (t, 4H, $2NCH_2$), 3.75 (t, 6H, $2OCH_2$ + br s, 2H, GeCH), 7.12–7.20 (m, 8H), 7.38 (m, 4H), 7.56–7.58 (m, 4H) (aromatic protons of two fluorenyl groups). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 44.62$ (MeN), 49.90 (GeCH), 57.34 (NCH_2), 61.68 (OCH_2), 119.50, 125.61, 125.95, 127.55, 140.83, 143.07 (aromatic carbons of two fluorenyl groups). MS (EI, *m/z*, %): 356 (62) [$M^+-C_{13}H_9$], 165 (100) [$C_{13}H_9^+$]. Anal. Calc. for $C_{31}H_{29}GeNO_2$ (520.18): C, 71.59; H, 5.62; N, 2.69. Found: C, 72.05; H, 5.82; N, 2.51%.

B: A mixture of 0.36 g (0.8 mmol) of Flu_2GeCl_2, 0.20 g (0.8 mmol) of $MeN(CH_2CH_2OSiMe_3)_2$ and 10 ml of chloroform was refluxed for 3 h. After all volatiles were removed in vacuum, toluene (5 ml) was added to the residue. The solid was filtered off, the most part of toluene was evaporated, and then hexane (5 ml) was added. The precipitate was filtered and dried in vacuum to give 0.15 g of a pink powder, which was found to be a complex mixture of products difficult to separate and to identify (according to ^1H and ^{13}C NMR spectra).

3.4. The synthesis of the 2,2-dimethylgermocanes **23–26**

3.4.1. $MeN(CH_2CH_2O)(CH_2CH(Ph)O)GeMe_2$ (**23**)

A mixture of 0.57 g (2.93 mmol) of isomeric dialkanolamines $MeN(CH_2CH_2OH)$–$CH_2CH(Ph)OH$ + $MeN(CH_2CH_2OH)CH(Ph)CH_2OH$, 0.67 g (3.51 mmol) of $Me_2Ge(NMe_2)_2$ and 15 ml of toluene was heated at 70 °C for 15 h. All volatile materials were removed under reduced pressure, and the residue was dried in vacuum for 4 h to give 0.87 g (100%) of a mixture of germocane **23** (95%) and isomeric $MeN(CH_2CH_2O)(CH(Ph)CH_2O)GeMe_2$ (**24**) (5%) in form of a light yellow oil. ^1H NMR for **23** ($CDCl_3$, 400 MHz): $\delta = 0.48$ (s, 3H, GeMe), 0.58 (s, 3H, GeMe), 2.44 (s, 3H, MeN), 2.46–2.50 (m, 1H), 2.53–2.59 (m, 1H), 2.62–2.66 (m, 1H), 2.72–2.79 (m, 1H) ($2NCH_2$ groups), 3.73–3.85 (m, 2H, OCH_2), 4.70 (dd, $^3J = 11$ Hz, $^3J = 2$ Hz, 1H, OCH), 7.19–7.24 (m, 1H), 7.27–7.32 (m, 2H), 7.34–7.38 (m, 2H) (Ph). ^{13}C NMR for **23** ($CDCl_3$, 100 MHz): $\delta = 2.69$ (GeMe), 4.48 (GeMe), 44.00 (MeN), 61.77 (two signals) ($2NCH_2$ groups), 66.49 (OCH_2), 73.12 (OCH), 125.88, 127.08, 128.16, 143.17 (Ph). ^1H NMR for **24** ($CDCl_3$, 400 MHz): $\delta = 2.38$ (s, 3H, MeN), 3.63–3.66, 3.90–3.94, 4.12–4.18 (3m, NCH_2CH_2O and $NCH(Ph)CH_2O$ moieties). Other proton resonances could not be located due to the overlap with those for major component. ^{13}C NMR for **24** ($CDCl_3$, 100 MHz): $\delta = 2.57$ (GeMe), 4.34 (GeMe), 42.36 (MeN), 59.52 (NCH_2), 64.09 (NCH(Ph)), 69.47, 70.31 ($2OCH_2$ groups), 125.84, 127.49, 128.30 (Ph). The quaternary carbon of phenyl group was not detected due to the low concentration of minor isomer. MS (EI, *m/z*, %): 297 (18) [M^+], 282 (15) [M^+-Me], 252 (24) [$M^+-Me-CH_2O$], 191 (100) [$M^+-PhCHO$], 176 (71) [$M^+-PhCHO-Me$], 161 (35) [$M^+-PhCHO-2Me$], 147 (42) [$MeNCH_2CH_2OGe^+$], 105 (56) [$PhCO^+$], 77 (58) [Ph^+], 58 (49) [$NCH_2CH_2O^+$]. Anal. Calc. for $C_{13}H_{21}GeNO_2$ (295.92): C, 52.76; H, 7.15; Ge, 24.54. Found: C, 52.30; H, 7.48; Ge, 24.96%.

3.4.2. *erythro*-$MeN(CH_2CH_2O)(CH(Ph)CH(Ph)O)GeMe_2$ (**25**)

Analogously to **23**, germocane **25** was prepared from 0.76 g (2.8 mmol) of *erythro*-$MeN(CH_2CH_2OH)CH(Ph)CH(Ph)OH$ and 0.65 g (3.4 mmol) of $Me_2Ge(NMe_2)_2$ by heating for 20 h in 15 ml of toluene. The product (1.02 g, 98%) was isolated as a light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 0.48$ (s, 3H, GeMe), 0.81 (s, 3H, GeMe), 2.31 (s, 3H, MeN), 2.50–2.55 (m, 1H), 2.63–2.69 (m, 1H) (NCH_2), 3.48 (d, $^3J = 3$ Hz, 1H, NCH), 3.76–3.82 (m, 1H), 3.88–3.92 (m, 1H) (OCH_2), 5.47 (d, $^3J = 3$ Hz, 1H, OCH), 6.96–7.23 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 1.38$ (GeMe), 4.33 (GeMe), 43.45 (MeN), 58.78 (NCH_2), 63.51 (OCH_2), 75.00 (NCH), 76.42 (OCH), 125.88, 126.80, 127.10, 127.19, 128.15, 130.66, 137.20, 142.88 (2Ph). MS (EI, *m/z*, %): 373 (8) [M^+], 358 (7) [M^+-Me], 267 (100) [$M^+-PhCHO$], 252 (87) [$M^+-PhCHO-Me$], 162 (51) [$M^+-PhCHO-GeMe_2-H$], 132 (46) [$M^+-PhCHO-CH_2O-GeMe_2-H$], 118 (21) [$CH_2=NCHPh^+$], 105 (42) [$PhCO^+$], 77 (32) [Ph^+]. Anal. Calc.

for $C_{19}H_{25}GeNO_2$ (372.02): C, 61.34; H, 6.77; Ge, 19.52. Found: C, 61.10; H, 6.97; Ge, 19.26%.

3.4.3. $PhN(CH_2CH_2O)_2GeMe_2$ (26)

Analogously to **23**, germocane **26** was prepared from 0.41 g (2.28 mmol) of $PhN(CH_2CH_2OH)_2$ and 0.53 g (2.78 mmol) of $Me_2Ge(NMe_2)_2$ by heating for 15 h in 20 ml of toluene. The product (0.65 g, 83%) was isolated as colourless crystals upon the slow evaporation of the reaction mixture in vacuum. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.35$ (s, 6H, $GeMe_2$), 3.54 (t, $^3J = 4$ Hz, 4H, $2NCH_2$), 3.98 (t, $^3J = 4$ Hz, 4H, $2OCH_2$), 6.65–6.67 (m, 2H), 6.72–6.75 (m, 1H), 7.20–7.24 (m, 2H) (Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -1.61$ ($GeMe_2$), 57.83 (NCH_2), 63.22 (OCH_2), 112.13, 117.07, 129.34, 148.18 (Ph). MS (EI, *m*/*z*, %): 283 (34) [M^+], 238 (15) [$M^+ - Me - CH_2O$], 119 (100) [$PhN(CH_2)_2^+$], 105 (35) [$PhNCH_2^+$]. Anal. Calc. for $C_{12}H_{19}GeNO_2$ (281.90): C, 51.13; H, 6.79; N, 4.97. Found: C, 51.06; H, 6.84; N, 5.01%.

3.5. $MeN(CH_2CH_2O)_2GeF_2$ (27)

A solution of 0.21 ml (1.6 mmol) of $BF_3 \cdot Et_2O$ in 3 ml of CH_3CN was added dropwise, within 15 min, to a solution of 0.56 g (2.5 mmol) of $MeN(CH_2CH_2O)_2Ge(OH)_2$ in 5 ml of CH_3CN warmed up to 50 °C. The reaction mixture was stirred at 50 °C for 12 h, and then all volatile materials were removed under reduced pressure. Chloroform (15 ml) was added to the residue, and the resulting suspension was stirred for 2 h. The solid was filtered, washed with 4 ml of chloroform, dried in vacuum, and then recrystallized from methanol/H_2O to give 0.28 g (48%) of difluorogermocane **27** as a white powder. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 2.71$ (s, 3H, MeN), 2.83–2.93, 2.96–3.04 (2m, 4H, $2NCH_2$), 3.87–4.05 (m, 4H, $2OCH_2$). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 54.82$ (NCH_2), 57.01 (OCH_2). The signal of MeN group was not found due to the poor solubility of the compound **27** in $CDCl_3$. ^{19}F NMR ($CDCl_3$, 188 MHz): $\delta = -147.0$ (d, $^2J_{F,F} = 56$ Hz, 1F, GeF), −156.05 (d, $^2J_{F,F} = 56$ Hz, 1F, GeF). Anal. Calc. for $C_5H_{11}F_2GeNO_2 \cdot H_2O$ (245.77): C, 24.43; H, 5.33; N, 5.70. Found: C, 23.93; H, 5.28; N, 5.48%.

3.6. The synthesis of the 2-halo-2-alkoxygermocanes 30–32 and 2,2-dialkoxygermocanes 33 and 34

3.6.1. $Me_2NCH_2CH_2OSnEt_3$

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.88$–1.23 (m, 15H, $SnEt_3$), 2.18 (s, 6H, Me_2N), 2.35 (t, $^3J = 5$ Hz, 2H, NCH_2), 3.76 (t, $^3J = 5$ Hz, 2H, OCH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 6.01$ ($SnCH_2$), 9.93 ($SnCH_2CH_3$), 46.12 (Me_2N), 63.81, 63.96 (NCH_2 and OCH_2 groups).

3.6.2. $MeN(CH_2CH_2O)_2Ge(Br)OMe$ (30) and $MeN(CH_2CH_2O)_2Ge(OMe)_2$ (33)

0.26 g (1.09 mmol) of Et_3SnOMe were added dropwise to a suspension of 0.38 g (1.09 mmol) of $MeN(CH_2CH_2O)_2GeBr_2$ (**28**) in 10 ml of chloroform. The precipitate of **28** immediately dissolved, and the reaction mixture was stirred for 24 h at room temperature. The analysis of the ^{1}H NMR spectroscopy data revealed the selective formation of $MeN(CH_2CH_2O)_2Ge(Br)OMe$ (**30**). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.63$ (s, 3H, MeN), 2.75–2.81 (m, 2H), 2.90–2.96 (m, 2H) ($2NCH_2$ groups), 3.63 (s, 3H, OMe), 3.91–3.97 (m, 4H, $2OCH_2$ groups). Upon the treatment of the reaction mixture with the second equivalent (0.26 g, 1.09 mmol) of Et_3SnOMe exclusive formation of $MeN(CH_2CH_2O)_2Ge(OMe)_2$ (**33**) was observed. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.52$ (s, 3H, MeN), 2.63–2.68 (m, 2H), 2.75–2.81 (m, 2H) ($2NCH_2$ groups), 3.57 (s, 3H, OMe), 3.63 (br s, 3H, OMe), 3.83 (t, $^3J = 6$ Hz, 4H, $2OCH_2$ groups). Removal of the solvent gave a light yellow oil.

3.6.3. $MeN(CH_2CH_2O)_2Ge(Cl)OMenth$ (31)

1.68 g (4.64 mmol) of $Et_3SnOMenth$ were added to a suspension of 1.21 g (4.64 mmol) of $MeN(CH_2CH_2O)_2GeCl_2$ (**29**) in 15 ml of chloroform. The reaction mixture was stirred for 24 h at room temperature, in 0.5 h the precipitate of **29** dissolved. After removal of the solvent in vacuum, 20 ml of hexane were added to the solid residue. The suspension was stirred for 2 h, and then the precipitate was filtered, washed with 5 ml of hexane, and dried in vacuum. According to ^{1}H NMR data, the resultant white solid (0.72 g) contained mainly $MeN(CH_2CH_2O)_2Ge(Cl)O$-Menth (**31**) with small admixtures of Et_3SnCl and menthol. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.79$ d, 0.83–0.86 m, 0.71–1.01 m, 1.11–1.19 m, 1.36–1.45 m, 1.52–1.62 m, 1.99–2.04 m, 2.07–2.14 m, 3.97–4.03 m (19H, menthoxy group), 2.60 (s, 3H, MeN), 2.70–2.77 (m, 2H), 2.87–2.93 (m, 2H) ($2NCH_2$ groups), 3.89–3.95 (m, 4H, $2OCH_2$ groups). Further attempts to remove admixtures and to obtain an analytically pure sample of **31** failed.

3.6.4. $MeN(CH_2CH_2O)_2Ge(OMenth)_2$ (34)

Analogously to described above, the reaction of 1.11 g (4.26 mmol) of $MeN(CH_2CH_2O)_2GeCl_2$ (**29**) with 3.08 g (8.52 mmol) of $Et_3SnOMenth$ was performed in 12 ml of chloroform. Analysis of the reaction mixture with NMR spectroscopy after 24 h of stirring at room temperature showed the formation of $MeN(CH_2CH_2O)_2Ge(OMenth)_2$ (**34**) and Et_3SnCl as a by-product. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.85$ d, 0.71–0.96 m, 1.04–1.12 m, 1.30–1.38 m, 1.50–1.58 m, 2.05–2.08 m, 2.16–2.22 m, 2.58–2.65 m, 3.55–3.63 m, 3.82–3.90 m (38H, two menthoxy groups), 2.46 (s, 3H, MeN), 2.61–2.70 (m, 4H, $2NCH_2$ groups), 3.78 (t, $^3J = 6$ Hz, 4H, $2OCH_2$ groups). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 16.08$, 21.44, 22.50, 23.18, 25.28, 31.83, 34.99, 45.96, 50.31, 73.12 (two menthoxy groups), 44.59 (MeN), 55.91 ($2NCH_2$), 57.85 ($2OCH_2$).

3.6.5. Complex $MeN(CH_2CH_2O)_2Ge(Cl)OCH_2CH_2NMe_2$ (32) · Et_3SnCl

1.55 g (5.26 mmol) of $Et_3SnOCH_2CH_2NMe_2$ were added to a suspension of 1.37 g (5.26 mmol) of MeN-

$(CH_2CH_2O)_2GeCl_2$ (**29**) in 15 ml of chloroform. The precipitate of starting **29** dissolved in 5 min. The reaction mixture was stirred for 24 h at room temperature, and then the solvent was removed in vacuum. The residue as a yellow oil solidified on standing. The crude product was recrystallized from CH_2Cl_2/hexane at −18 °C to give 2.12 g (73%) of a 1:1 adduct of $MeN(CH_2CH_2O)_2Ge(Cl)OCH_2CH_2NMe_2$ (**32**) with Et_3SnCl in form of a light yellow powder. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.17$–1.42 (m, 15H, $SnEt_3$), 2.75 (s, 6H, Me_2N), 2.80 (s, 3H, MeN), 3.06–3.12 (m, 2H), 3.28–3.34 (m, 2H) ($2NCH_2$), 3.14 (t, 2H, NCH_2), 3.94–4.00 (m + t, 6H, $3OCH_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 10.41$, 14.08 ($SnEt_3$), 43.80 (MeN), 46.29 (Me_2N), 55.22 ($2NCH_2$), 58.29 ($2OCH_2$), 58.61 (NCH_2), 59.06 (OCH_2). MS (EI, *m*/*z*, %): 226 (3) [$M^+ - Et_3SnCl - Me_2NCH_2CH_2O$], 213 (14) [$Et_2SnCl^+$], 153 (12) [$Ge(Cl)OCH_2CH_2^+$], 149 (7) [$EtSn^+$], 58 (100) [$Me_2NCH_2^+$]. Anal. Calc. for $C_{15}H_{36}Cl_2GeN_2O_3Sn$ (554.68): C, 32.48; H, 6.54; N, 5.05. Found: C, 32.17; H, 6.58; N, 5.10%. A solution of 0.64 g (1.15 mmol) of the adduct **32** · Et_3SnCl in 5 ml of chloroform was treated with 0.5 ml (3.59 mmol) of Et_3N, followed by crystallization from chloroform/hexane mixture. This treatment as well as the heating of the product in vacuum (1 mm Hg) at 60–70 °C failed to remove Et_3SnCl from the complex.

3.7. X-ray crystallographic study

Crystal data, data collection, structure solution and refinement parameters for compounds **16**, **20**–**22**, and **26** are presented in Table 3. Experimental intensities were measured on a Bruker SMART CCD diffractometer using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 120(2) K. Absorption correction based on measurements of equivalent reflections were applied. The structures were solved by direct methods [62] and refined by full matrix least-squares on F^2 [63] with anisotropic thermal parameters for all non-hydrogen atoms. In the structures **16**, **20**, **22**, and **26** all H atoms were found from diff. Fourier synthesis and refined isotropically; in **21** all H atoms were placed in calculated positions and refined using a riding model.

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Appendix A. Supplementary data

CCDC-247126 (for **16**), CCDC-247128 (for **20**), CCDC-247127 (for **21**), CCDC-247125 (for **22**), and

Table 3
Crystal data, data collection, structure solution and refinement parameters for **16**, **20**, **21**, **22**, and **26**

Compound	**16**	**20**	**21**	**22**	**26**
Empirical formula	$C_{17}H_{19}Br_2Ge_1N_1O_2$	$C_{10}H_{13}Cl_2Ge_1N_1O_2$	$C_{10}H_{13}Br_2Ge_1N_1O_2$	$C_{31}H_{29}Br_2Ge_1N_1O_2$	$C_{12}H_{19}Ge_1N_1O_2$
Formula weight	501.74	322.70	411.62	520.14	281.87
Colour, habit	Colourless block	Colourless needle	Colourless block	Colourless block	Colourless block
Crystal size (mm)	0.40 × 0.30 × 0.10	0.40 × 0.20 × 0.10	0.30 × 0.30 × 0.10	0.40 × 0.40 × 0.20	0.30 × 0.20 × 0.20
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$
Unit cell dimensions					
a (Å)	8.3771(2)	8.1768(6)	8.4202(7)	7.6559(1)	7.3212(3)
b (Å)	13.4619(3)	17.8615(13)	17.794(1)	24.4898(4)	9.3830(4)
c (Å)	15.5237(4)	8.4899(1)	8.6179(7)	12.9850(2)	18.6108(8)
β (°)	93.369(1)	106.407(1)	106.522(1)	96.271(1)	97.798(1)
Volume (Å^3)	1747.61(7)	1189.5(2)	1237.9(2)	2420.01(6)	1266.64(9)
Z	4	4	4	4	4
Density (calculated) [g cm^{-3}]	1.907	1.802	2.209	1.428	1.478
Absorption coefficient (mm^{-1})	6.334	3.008	8.915	1.296	2.405
$F(000)$	984	648	792	1080	584
θ Range (°)	2.00–28.00	2.28–27.00	2.52–28.00	2.29–27.00	2.21–28.00
Index ranges	$-5 \leqslant h \leqslant 11$	$-10 \leqslant h \leqslant 9$	$-11 \leqslant h \leqslant 11$	$-9 \leqslant h \leqslant 9$	$-8 \leqslant h \leqslant 9$
	$-16 \leqslant k \leqslant 17$	$-13 \leqslant k \leqslant 22$	$-23 \leqslant k \leqslant 10$	$-31 \leqslant k \leqslant 24$	$-12 \leqslant k \leqslant 9$
	$-17 \leqslant l \leqslant 20$	$-10 \leqslant l \leqslant 9$	$-9 \leqslant l \leqslant 11$	$-16 \leqslant l \leqslant 15$	$-24 \leqslant l \leqslant 22$
Reflections collected	10,850	7035	7066	16,313	7861
Independent reflections	4196 [$R_{int} = 0.0195$]	2600 [$R_{int} = 0.0277$]	2938 [$R_{int} = 0.0396$]	5268 [$R_{int} = 0.0181$]	3069 [$R_{int} = 0.0205$]
Data/restraints/parameters	4196/0/284	2600/0/197	2938/0/146	5268/0/432	3069/0/221
Goodness-of-fit on F^2	1.037	1.138	1.056	1.059	1.044
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0260$,	$R_1 = 0.0349$,	$R_1 = 0.0490$,	$R_1 = 0.0251$,	$R_1 = 0.0219$,
	$wR_2 = 0.0648$	$wR_2 = 0.0947$	$wR_2 = 0.1340$	$wR_2 = 0.0636$	$wR_2 = 0.0541$
R indices (all data)	$R_1 = 0.0346$,	$R_1 = 0.0376$,	$R_1 = 0.0586$,	$R_1 = 0.0294$,	$R_1 = 0.0275$,
	$wR_2 = 0.0675$	$wR_2 = 0.0966$	$wR_2 = 0.1395$	$wR_2 = 0.0652$	$wR_2 = 0.0559$
Extinction coefficient	–	–	0.0021(9)	–	–
Largest difference in peak/hole (e Å^{-3})	1.724/−0.403	2.301/−0.805	1.671/−1.683	0.391/−0.259	0.457/−0.261

CCDC-290247 (for **26**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

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