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Journal of Organometallic Chemistry 676 (2003) 8–21

Journal of Organo metallic Chemistry

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Synthesis and characterization of 3- and 4-phenylgermatranes: X-ray crystal structures of $N(CH_2CH_2O)_2(CH_2CHPhO)GeZ$ (Z = F, $OSiMe_3$, C≡CPh) and $N(CH_2CH_2O)_2(CHPhCH_2O)GeOH$

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Received 28 October 2002; received in revised form 15 January 2003; accepted 10 March 2003

Abstract

Reaction of excess of product **A** [$(HOCH_2CH_2)_2NCH_2CH(Ph)OH$ (**1**):$(HOCH_2CH_2)_2NCH(Ph)CH_2OH$ (**2**) = 9:1] with $GeCl_4$ led to a mixture of 1-chloro-3-phenylgermatrane (**3**) and 1-chloro-4-phenylgermatrane (**4**). Compound **4** was isolated in yield 9% from this mixture. Reaction of $(EtO)_3GeCl$ with product **A** gave **3** in yield 55%. 1-(Phenylethynyl)-3-phenylgermatrane (**5**) was prepared in yield 31% by treatment of $(EtO)_3GeC≡CPh$ with product **A**. Reaction of product **A** with mixture of GeO_2 and H_2O produced $N(CH_2CH_2O)_2(CH_2CHPhO)GeOH$ (**6**) in yield 73%. The presence of $N(CH_2CH_2O)_2(CHPhCH_2O)GeOH$ (**7**) among the products of this reaction was confirmed by ^1H-, ^{13}C-NMR spectroscopy and X-ray analysis. $N(CH_2CH_2O)_2(CH_2CHPhO)GeF$ (**8**) is formed by the treatment of **6** with $BF_3 \cdot Et_2O$. $N(CH_2CH_2O)_2(CH_2CHPhO)GeOSiMe_3$ (**9**) was obtained by silylation of **6** with $(Me_3Si)_2NH$ or $Me_3SiCl–Et_3N$. Refluxing of a suspension of **6** in xylene with continuous removal of water by azeotropic distillation afforded $[N(CH_2CH_2O)_2(CH_2CHPhO)Ge]_2O$ (**10**). **9** reacted with $SOCl_2$, Me_3SiBr and Me_3SiOTf to give $N(CH_2CH_2O)_2(CH_2CHPhO)GeX$ (**3**, X = Cl; **11**, X = Br; **12**, X = OTf), respectively. Reaction of **11** with Et_3SnOMe led to the formation of $N(CH_2CH_2O)_2(CH_2CHPhO)GeOMe$ (**13**). Germatranes $N(CH_2CH_2O)_2(CH_2CHPhO)GeY$ [**14**, Y = Flu (fluorenyl); **15**, Y = $N(SiMe_3)_2$] were obtained from the nucleophilic substitution of the substituent X in $N(CH_2CH_2O)_2(CH_2CHPhO)GeX$ (X = $OSiMe_3$, Br) with the corresponding LiY. All compounds were characterized by ^1H- and ^{13}C-NMR spectroscopy and mass spectrometry. Single-crystal structures of **5** and **7**–**9** were determined by X-ray diffraction studies.

Keywords: Germatrane; NMR spectroscopy; Crystal structures

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1. Introduction

The chemistry of metal derivatives of aminoalcohols such as trialkanolamine—metallatranes—has attracted considerable attention mostly from the theoretical point of view, the nature of intramolecular N→M interaction being the subject of interest. The chemistry of metallatranes with different substituents in atrane moiety has been studied to a very limited extent. Among them 3,7,10-trimethyl-substituted germatranes are the most known [1]. There are only few reports concerning germatranes bearing other groups attached to carbon atoms of atrane fragment. At the same time, one could expect that the presence of phenyl group at 3- or 4-position of atrane skeleton can considerably influence the nature of the N→Ge bond and affect the reactivity, structure and physical properties of these molecules.

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doi:10.1016/S0022-328X(03)00225-0

In our opinion, successful synthesis of 3- and 4-phenyl-substituted derivatives will provide an opportunity to prepare more complex molecules by functionalization owing to not only apical group at the germanium atom but also substituents in atrane moiety.

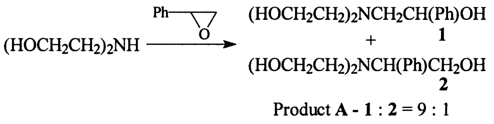
Among 3-phenyl-substituted germatranes, only 1-hydroxy, 1-methyl and 1-phenyl derivatives have been reported in the literature when we began this study. The syntheses of these compounds as well as IR data have been described [2–4]. Mass spectra of 1,3-diphenylgermatrane were also studied [2]. However, no NMR spectroscopy and X-ray diffraction have been reported so far. To the best of our knowledge, no 4-phenylgermatranes have been investigated prior to our study.

In this context, we describe synthesis and characterization of a series of functionally substituted 3- and 4-phenylgermatranes and crystal structures determination of **5** and **7**–**9**.

2. Results and discussion

2.1. Starting 2-[bis(2-hydroxyethyl)amino]-1-phenyl-1-ethanol (*1*) and 2-[bis(2-hydroxyethyl)amino]-2-phenyl-1-ethanol (*2*)

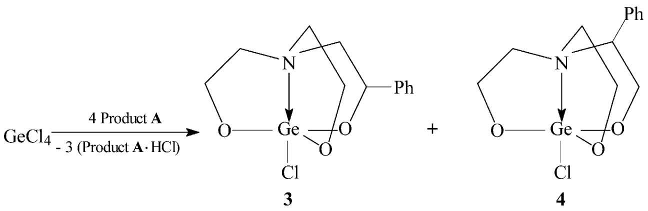
For the synthesis of C-phenyl-substituted trialkanolamines **1** and **2**, we examined reaction of diethanolamine with styrene oxide [5]. A mixture of reagents was maintained at reflux for 4 h. In actuality, the ring opening reaction imposes the formation of two isomers, and in fact, ^{1}H- and ^{13}C-NMR spectroscopy shows the reaction product (product **A**) to contain a mixture of isomeric aminoalcohols **1** and **2** in a ca. 9:1 ratio (Eq. (1)).



(1)

2.2. Synthesis of 3- and 4-phenyl-substituted germatranes by reaction of product *A* with $GeCl_4$, $(EtO)_3GeCl$ and $(EtO)_3GeC{\equiv}CPh$

Reaction of excess of product **A** with $GeCl_4$ gave a mixture of 1-chloro-3-phenylgermatrane (**3**) and 1-chloro-4-phenylgermatrane (**4**). After a number of manipulations (see Section 3), germatrane **4** was obtained as an analytically pure sample in yield 9% (Eq. (2)). However, we were unable to obtain the major isomer **3** as an individual product in this reaction.



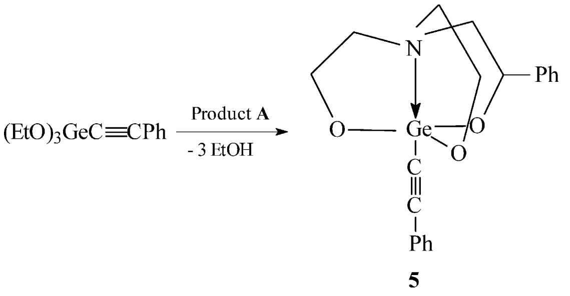
(2)

It should be noted that only one germatrane containing a substituent in the position 4 of the atrane fragment has previously been reported—1-hydroxy-4-ethylgermatrane; its structure was determined by X-ray diffraction studies [6].

Compound **3** was obtained in moderate yield in the case of the interaction of triethoxychlorogermane with product **A** (Eq. (3)).

$$(EtO)_3GeCl \underset{-3EtOH}{\overset{\text{product }\mathbf{A}}{\rightarrow}} \mathbf{3} \qquad (3)$$

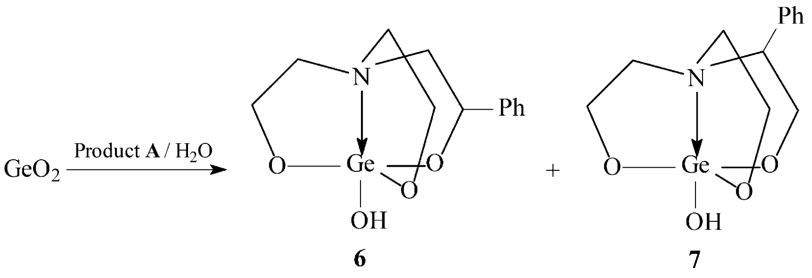
The transesterification of (triethoxygermyl)phenylacetylene with trialkanolamines (**1**:**2** = 9:1) led to 1-(phenylethynyl)-3-phenylgermatrane (**5**) in yield 31% (Eq. (4)).



(4)

2.3. 3- and 4-Phenyl-substituted 1-hydroxygermatranes: preparation and use for synthesis of new germatranes

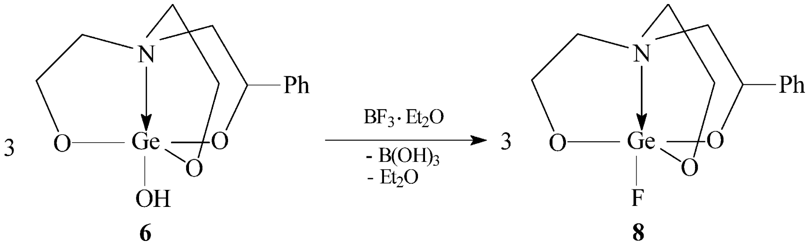
Recently, there was reported an efficient approach for the synthesis of various functionally substituted germatranes starting from the most simple and available germatranes—1-hydroxygermatranes [7]. Reaction of GeO_2 with product **A** (**1**:**2** = 9:1) in the presence of water was studied for the preparation of phenyl-substituted 1-hydroxygermatranes. Previously this reaction has been described [8]. However, composition of the product obtained in yield 89% was confirmed only by elemental analysis data. We have found that a solid precipitates after boiling of reagents mixture up to complete dissolution of GeO_2 and cooling of reaction mixture. Filtration of this precipitate followed by washing with ethanol and drying in vacuo at 1 Torr yielded analytically pure sample of 1-hydroxy-3-phenylgermatrane (**6**). ^{1}H- and ^{13}C-NMR and EI-MS studies confirm its structure. From filtrate additional amount of solid was isolated. According to the ^{1}H- and ^{13}C-NMR spectroscopy and mass spectrometry, this substance contained isomeric 1-hydroxy-4-phenylgermatrane (**7**) and compound **10** (see below) besides germatrane **6** (Eq. (5)). Crystals of compound **7** suitable for X-ray structural analysis could be found.



(5)

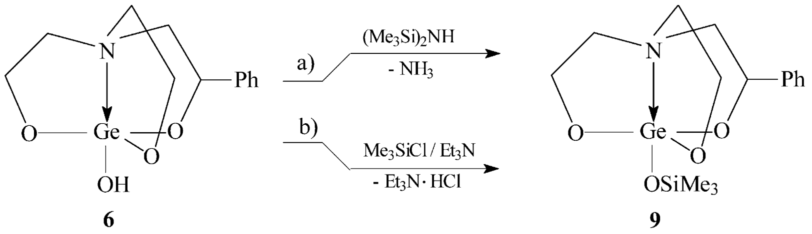
1-Hydroxygermatrane **6** was used for the preparation of 1-fluoro-3-phenylgermatrane (**8**) and 1-trimethylsiloxy-3-phenylgermatrane (**9**).

The reaction of germatrane **6** with $BF_3 \cdot Et_2O$ proceeded in mild conditions and led to compound **8** with high yield (Eq. (6)).



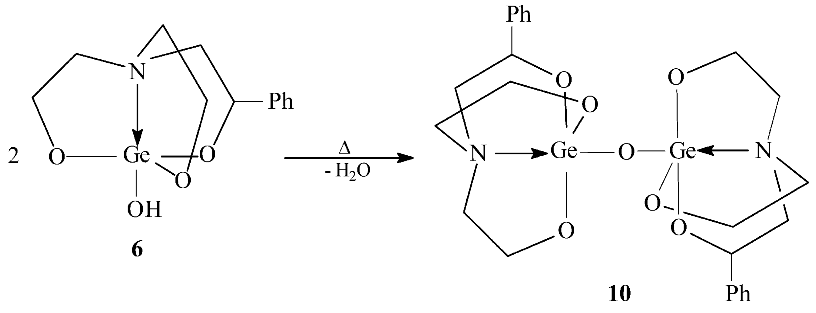
(6)

Previously silylation by means of $(Me_3Si)_2NH$ was studied for $N(CH_2CHRO)_3GeOH$ (R = H, Me) [9,10]. It was shown that in the course of boiling of a suspension of 1-hydroxygermatrane in xylene with excess of $(Me_3Si)_2NH$ dissolution of solid takes place; after cooling of the reaction mixture formation of the precipitate $N(CH_2CHRO)_3GeOSiMe_3$ (yields ~ 90%) was observed. In the case of **6**, boiling of reaction mixture for several hours have not led to the dissolution of solid. After filtration of hot reaction mixture and cooling of filtrate, compound **9** was obtained in yield 16% (Eq. (7a)). In our opinion low yield of **9** can be accounted for easiness of formation in conditions of reaction (7a) $N(CH_2CHPhO)_3GeOGe(OCHPhCH_2)_3N$ (**10**) which is inert with respect to $(Me_3Si)_2NH$. Taking it into account, we have carried out the silylation of hydroxygermatrane **6** in milder conditions. The treatment of a suspension of germatrane **6** in $CHCl_3$ with Me_3SiCl–Et_3N at room temperature gave 1-trimethylsiloxy-3-phenylgermatrane (**9**) in yield 65% (Eq. (7b)).



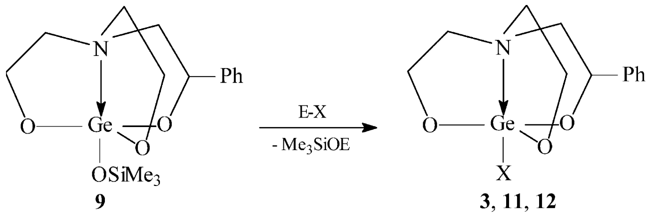
(7)

Actually, the formation of germatrane **10** was observed at refluxing of a suspension of **6** in xylene with simultaneous removing of water formed by azeotropic distillation (Eq. (8)).



(8)

Previously we have shown that $N(CH_2CHRO)_3GeX$ (R = H, Me; X = Cl, Br, OTf) can be obtained smoothly and in high yields on the basis of corresponding 1-trimethylsiloxygermatranes [10,11]. We have studied the behaviour of 1-trimethylsiloxy-3-phenylgermatrane (**9**) in analogous reactions (Eq. (9)). $N(CH_2CHRO)_3GeOSiMe_3$ (R = H, Me) easily reacts with thionyl chloride (4–8 h, room temperature) with the formation of appropriate 1-chlorogermatranes [11]. On the contrary, interaction of germatrane **9** with $SOCl_2$ proceeds more slowly (24 h) and gives 1-chloro-3-phenylgermatrane (**3**) in yield 49%. Boiling of a suspension of germatrane **9** in xylene with Me_3SiBr led to 1-bromo-3-phenylgermatrane (**11**) in yield 85%. Reaction of Me_3SiOTf with germatrane **9** at room temperature gives germatranyltriflate (**12**) in quantitative yield (Eq. (9)).

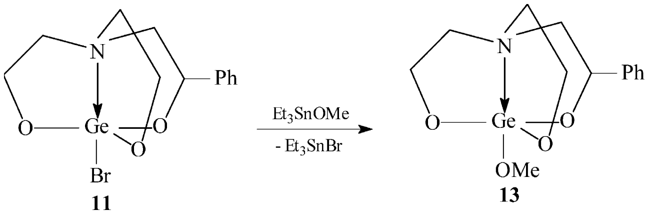


X = Cl (**3**), Br (**11**), SO_2CF_3 (**12**)
E-X = $SOCl_2$, Me_3SiBr, Me_3SiOTf

(9)

Halogenides and triflates of tetracoordinated germanium are reactive reagents for metallation and widely used as the key reagents for the synthesis of various functionally substituted organogermanium compounds [12,13]. In contrast to above, corresponding derivatives of germatranes were studied in this context to the considerably less extent. For example, their reactions with organometallic compounds have been studied only recently [11].

Reaction of 1-bromogermatrane **11** with Et_3SnOMe led to 1-methoxy-3-phenylgermatrane (**13**) in practically quantitative yield (Eq. (10)).



(10)

It should be noted that the attempted synthesis of 1-ethoxy-3-phenylgermatrane by reaction of $(EtO)_4Ge$ with product **A** (**1**:**2** = 9:1) failed.

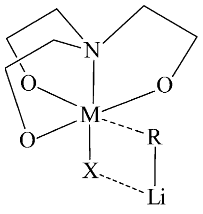
Surprisingly, but in germatrane chemistry the approach to functionalized germatranes by the reaction of simple and available germatranes with lithium reagents has not been used before work of our group [7]. Probably, hopelessness of the research like that has been assigned to the assumption about destruction of atrane moiety in the course of these transformations. Indeed, these reactions may proceed through intermediates **I** and **II** and in the case of strong nucleophilic reagents (*n*-BuLi) unselective process of cleavage of Ge–O bonds leads to destruction of atrane fragment. In the case of weaker nucleophiles, the proceeding of the reaction via intermediate **I** is more favorable and results

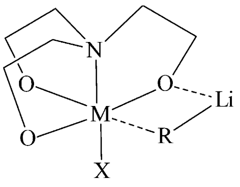
Table 1
Selected ^{1}H-NMR spectral data for **4** and **9** [a]

Proton	Chemical shift, δ (ppm)		Couple	Coupling constant, J (Hz) [b]	
	4 (4-Ph) [c]	**9** (3-Ph) [d]		**4** (4-Ph)	**9** (3-Ph)
H_a^3	4.26	4.80	$H_a^3 H_a^4$	10.7	10.8
H_e^3	3.87	–	$H_a^3 H_e^4$	–	4.1
H_a^4	4.19	2.43	$H_e^3 H_a^4$	5.0	–
H_e^4	–	3.06	$H_e^3 H_e^4$	–	–
H_a^7	3.68	3.75	$H_a^7 H_a^6$	11.0	11.3
H_e^7	3.80	3.93	$H_a^7 H_e^6$	5.7	3.8
H_a^6	3.26	2.96	$H_e^7 H_a^6$	5.7	3.4
H_e^6	2.21	2.97	$H_e^7 H_e^6$	3.8	7.4
H_a^{10}	4.07	3.71	$H_a^{10} H_a^{11}$	11.4	11.2
H_e^{10}	3.90	3.89	$H_a^{10} H_e^{11}$	4.3	5.9
H_a^{11}	2.82	2.77	$H_e^{10} H_a^{11}$	6.3	3.7
H_e^{11}	3.10	2.83	$H_e^{10} H_e^{11}$	3.7	6.0

[a] 500.132 MHz, 298 K. Abbreviations: see figure for the labeling scheme.
[b] Geminal coupling constants for OCH_2 and NCH_2 protons equal ~11.1 and ~12.5 Hz, respectively.
[c] In DMSO-d_6.
[d] In $CDCl_3$.

in 1-substituted germatranes.


I

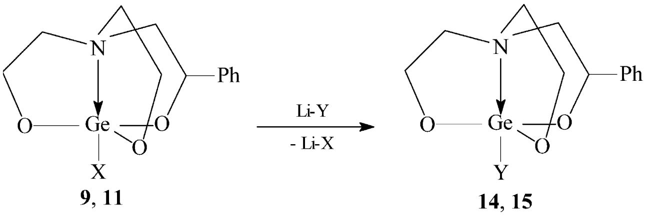

II

We tested germatranes **9** and **11** in the reactions with fluorenyllithium and $LiN(SiMe_3)_2$. Corresponding germatranes **14** and **15** were obtained in yields 60–70% (Eq. (11)).

Table 2
Selected ^{13}C-NMR Spectral Data for **4** and **9** [a]

Carbon	δ (ppm)	
	4 [b]	**9** [c]
C^3	60.10	68.57
C^7	57.24	56.92
C^{10}	57.46	56.85
C^4	61.13	59.02
C^6	47.42	52.93
C^{11}	46.13	52.37
Ph	131.67 (C_i)	141.48 (C_I)
	129.72 (C_o)	128.50 (C_o)
	129.41 (C_p)	127.76 (C_p)
	128.66 (C_m)	125.43 (C_m)

[a] 125.77 MHz, 298 K. Abbreviations: see figure for the labeling scheme.
[b] In DMSO-d_6.
[c] In $CDCl_3$, δ $^{13}C(SiMe_3)$ 2.25 ppm.



9, **11** → **14**, **15**

(11)

	X		Y
9	OsiMe$_3$	**14**	Flu
11	Br	**15**	N(SiMe$_3$)$_2$

The new compounds **3**–**15** were characterized by elemental analyses, IR (**5**), ^{1}H-, ^{13}C-NMR spectroscopy and mass spectrometry.

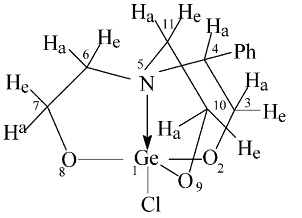
2.4. NMR spectra

^{1}H- and ^{13}C-NMR spectra are in accord with the suggested structures. The proton spectra of **3**–**15** are evidently complicated by the asymmetric carbon atoms C^4 or C^3. The signals of the protons of the germatrane skeleton appear as complex multiplets: two AA′XX′ spin systems for $N(CH_2CH_2O)_2$ and one ABX for $NCHCH_2O$ or NCH_2CHO.

The ^{1}H and ^{13}C data for **4** and **9** are collected in Tables 1 and 2, respectively. The assignments of the signals have been made on the basis of 2D ^{1}H NOESY, 2D ^{1}H COSY, and 2D ^{1}H, ^{13}C correlations.

Table 3
Selected bond lengths (Å) and angles (°) for **5**

Ge(1)–O(3)	1.775(4)	O(1)–C(12)	1.400(7)
Ge(1)–O(1)	1.787(3)	O(2)–C(13)	1.423(5)
Ge(1)–O(2)	1.789(4)	O(3)–C(14)	1.423(6)
Ge(1)–C(1)	1.914(7)	C(2)–C(3)	1.445(7)
Ge(1)–N(1)	2.166(6)	C(9)–C(14)	1.504(7)
C(1)–C(2)	1.192(9)	C(10)–C(13)	1.527(6)
N(1)–C(9)	1.451(8)	C(11)–C(12)	1.503(8)
N(1)–C(10)	1.481(7)	C(13)–C(15)	1.504(6)
N(1)–C(11)	1.484(7)		
O(3)–Ge(1)–O(1)	116.8(2)	C(10)–N(1)–Ge(1)	105.0(3)
O(3)–Ge(1)–O(2)	118.6(2)	C(11)–N(1)–Ge(1)	104.7(3)
O(1)–Ge(1)–O(2)	120.7(2)	C(12)–O(1)–Ge(1)	120.1(3)
O(3)–Ge(1)–C(1)	98.6(3)	C(13)–O(2)–Ge(1)	118.6(3)
O(1)–Ge(1)–C(1)	94.5(2)	C(14)–O(3)–Ge(1)	117.0(3)
O(2)–Ge(1)–C(1)	96.9(2)	C(1)–C(2)–C(3)	176.8(5)
O(3)–Ge(1)–N(1)	83.7(2)	N(1)–C(9)–C(14)	107.6(4)
O(1)–Ge(1)–N(1)	82.6(2)	N(1)–C(10)–C(13)	108.4(4)
O(2)–Ge(1)–N(1)	83.7(2)	N(1)–C(11)–C(12)	107.8(5)
C(1)–Ge(1)–N(1)	176.9(2)	O(1)–C(12)–C(11)	109.9(4)
C(2)–C(1)–Ge(1)	169.3(6)	O(2)–C(13)–C(15)	109.9(3)
C(9)–N(1)–C(10)	114.7(4)	O(2)–C(13)–C(10)	109.0(4)
C(9)–N(1)–C(11)	114.2(5)	C(15)–C(13)–C(10)	110.4(4)
C(10)–N(1)–C(11)	112.2(5)	O(3)–C(14)–C(9)	109.9(4)
C(9)–N(1)–Ge(1)	104.8(4)		



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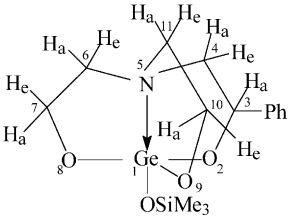

9

In ^{1}H-NMR spectrum of 1-chloro-4-phenylgermatrane (**4**), the proton H_a^4 have two various proton–proton coupling constants 10.7 Hz (with axial H_a^3) and 5.2 Hz (H_e^3). The similar values of constants (10.9 and 5.9 Hz) were observed for closely related silatranes $N(CHMeCH_2O)_3SiX$ (X = OMe, Ph) [14].

For 1-trimethylsiloxy-3-phenylgermatrane (**9**) protons H_a^3 have likewise vicinal coupling constants 10.8 (with axial H_a^4 proton) and 4.1 Hz (H_e^4). For other germatranes with the same structure, the constants are similar—11.1 and 3.7 Hz [$N(CH_2CH_2O)_2(CH_2CHMeO)GeH$] [15] and 10.4 and 4.3 Hz [$N(CH_2CH_2O)_2(CH_2CHRO)GeH$, R = OCH_2Ph] [16]. Two considerably different vicinal proton–proton coupling constants at the *exo*-substituted carbon atom in germatranes **4** and **9** should be explained by the fact that this fragment exists in a single frozen conformation. The proton adjusted to C^3 atom is located axial and, hence, Ph group occupies the equatorial position. For non-substituted rings $N(CH_2CH_2O)_2$ in **4** and **9** similar values of two vicinal coupling constants for axial–axial and axial–equatorial protons (11.0–11.4 and 3.4–6.3 Hz, Table 1) were observed. Thus compounds **4** and **9** possess the rigid structure.

It should be noted that ^{1}H-NMR spectra of germatranes $N(CH_2CH_2O)_3GeX$ contain two triplets due to the fast conversion on the NMR time scale of their five-membered rings. Vicinal coupling constants are averaged ($J \approx 8$ Hz) because of an exchange process between two states where each proton occupies alternately equatorial and axial positions [15].

The values of proton chemical shifts in germatranes **4** and **9** confirm a rigid structure, too. Two rings $Ge(OCH_2CH_2)_2N$ with frozen conformation in **9** have average values of proton chemical shifts (OCH_2: 3.82 ppm and NCH_2: 2.88 ppm) which are close to the values (3.84 and 2.85 ppm, respectively) for chemically equivalent protons in model germatrane $N(CH_2CH_2O)_3GeOSiMe_3$ with fast interconversion [17]. Thus, the Ph group in position 3 of atrane skeleton does not affect shielding of other rings protons, i.e. it is placed on maximum long distances from unsubstituted rings (in the equatorial place).

For germatrane **4**, the average values of chemical shifts in non-substituted rings 3.86 ppm $(OCH_2)_2$ and 3.06 ppm (only three NCH protons) are close to 3.97 and 2.98 ppm for 1-chlorogermatrane [17]. However, the rest of NCH proton has abnormal great shielding ($\delta(H_e^6)$ 2.21 ppm) caused by its close contact to Ph group.

Thus the NMR spectroscopy data show that compound **9** maintains in solution the primary geometry found in the solid state. The structure of **4** in solution is similar to that found for closely related germatrane **7** in the solid state.

Table 4
Selected bond lengths (Å) and angles (°) for **7**

Ge–O(4)	1.767(2)	C(11)–C(12)	1.498(5)
Ge–O(1)	1.773(2)	O(2)–C(22)	1.414(3)
Ge–O(3)	1.781(2)	O(2)–H(1)#1	2.19(4)
Ge–O(2)	1.805(2)	C(21)–C(22)	1.498(4)
Ge–N	2.187(2)	C(21)–C(1)	1.514(4)
N–C(11)	1.471(3)	O(3)–C(32)	1.403(4)
N–C(31)	1.479(4)	C(31)–C(32)	1.487(5)
N–C(21)	1.482(3)	O(4)–H(1)	0.71(4)
O(1)–C(12)	1.413(4)		
O(4)–Ge–O(1)	96.4(1)	C(21)–N–Ge	104.0(2)
O(4)–Ge–O(3)	97.6(1)	C(12)–O(1)–Ge	117.5(2)
O(1)–Ge–O(3)	117.5(1)	N–C(11)–C(12)	108.3(2)
O(3)–Ge–O(2)	120.7(1)	C(22)–O(2)–H(1)#1	100(1)
O(4)–Ge–N	178.4(1)	Ge–O(2)–H(1)#1	134.5(9)
O(1)–Ge–N	84.11(9)	N–C(21)–C(22)	106.9(2)
O(3)–Ge–N	83.54(9)	N–C(21)–C(1)	116.0(2)
O(2)–Ge–N	82.88(9)	C(22)–C(21)–C(1)	114.9(2)
C(11)–N–C(31)	113.6(3)	O(2)–C(22)–C(21)	110.4(2)
C(11)–N–C(21)	116.7(2)	C(32)–O(3)–Ge	118.3(2)
C(31)–N–C(21)	112.8(2)	N–C(31)–C(32)	108.6(3)
C(11)–N–Ge	103.8(2)	O(3)–C(32)–C(31)	111.9(3)
C(31)–N–Ge	104.1(2)	Ge–O(4)–H(1)	107(3)

Table 5
Selected bond lengths (Å) and angles (°) for **8**

Ge–F(1)	1.749(2)	N(1)–C(3)	1.477(4)
Ge–O(3)	1.765(2)	N(1)–C(2)	1.480(3)
Ge–O(2)	1.766(2)	N(1)–C(6)	1.486(4)
Ge–O(1)	1.774(2)	C(1)–C(7)	1.516(4)
Ge–N(1)	2.108(2)	C(1)–C(2)	1.523(4)
O(1)–C(1)	1.432(4)	C(3)–C(4)	1.516(4)
O(2)–C(5)	1.426(4)	C(5)–C(6)	1.503(5)
O(3)–C(4)	1.421(4)		
F(1)–Ge–O(3)	93.9(1)	C(3)–N(1)–C(6)	114.2(3)
F(1)–Ge–O(2)	94.1(1)	C(2)–N(1)–C(6)	112.8(2)
O(3)–Ge–O(2)	117.4(1)	C(3)–N(1)–Ge	104.4(2)
F(1)–Ge–O(1)	93.81(9)	C(2)–N(1)–Ge	105.3(2)
O(3)–Ge–O(1)	121.4(1)	C(6)–N(1)–Ge	104.7(2)
O(2)–Ge–O(1)	119.9(1)	O(1)–C(1)–C(7)	109.2(2)
F(1)–Ge–N(1)	179.4(1)	O(1)–C(1)–C(2)	109.3(2)
O(3)–Ge–N(1)	85.99(9)	C(7)–C(1)–C(2)	110.7(2)
O(2)–Ge–N(1)	86.5(1)	N(1)–C(2)–C(1)	108.5(2)
O(1)–Ge–N(1)	85.73(9)	N(1)–C(3)–C(4)	107.3(3)
C(1)–O(1)–Ge	116.9(2)	O(3)–C(4)–C(3)	109.8(3)
C(5)–O(2)–Ge	115.0(2)	O(2)–C(5)–C(6)	111.0(3)
C(4)–O(3)–Ge	115.9(2)	N(1)–C(6)–C(5)	107.7(3)
C(3)–N(1)–C(2)	114.1(2)		

2.5. Mass spectra

We have found major fragmentation pathways of 3-phenyl-substituted germatranes under EI conditions. The received data testify to two opportunities of fragmentation of these molecules. The first way is connected to dissociative ionization of Ge–X bond with formation of germatranyl cation at m/e 296. Further subsequent fragmentation proceeds through consecutive elimination of PhCHO (m/e 190) and then of CH_2O (m/e 160) or group (OCH_2CH_2) (m/e 146) or $2CH_2O$ (m/e 130). A cluster of peaks at m/e 130 has been attributed to the ion $GeN(CH_2)_3^+$, which is consistent with the germatrane structure. This way is realized for germatranes containing labile Ge–X bond as compound **14** where the peak of highest intensity corresponds to the germatranyl ion. This behaviour is analogous to that observed for 1-(9-fluorenyl)germatranes [7,18–20] and assumed to reflect the relative weakness of the Ge–C bond. No ions contained N–Ge–X fragment were found in mass spectrum of **14**.

The second way is observed in 3-phenyl-substituted germatranes with strong X–Ge–N interaction. The first step of fragmentation is elimination of PhCHO. For compounds **5**, **6**, **8** and **9**–**13**, the intensities of this peak are 30–100%. There are intensive peaks of ions resulting from the further loss of CH_2O (13–94%). On the

Table 6
Selected bond lengths (Å) and angles (°) for **9**

Ge–O(1)	1.776(3)	O(3)–C(32)	1.412(4)
Ge–O(3)	1.789(2)	C(21)–C(22)	1.508(7)
Ge–O(2)	1.793(3)	C(32)–C(31A)	1.286(8)
Ge–N	2.170(4)	C(32)–C(31B)	1.619(8)
Si–O(1)	1.631(3)	C(22)–C(11)	1.492(7)
Si–C(1)	1.861(4)	C(11)–C(16)	1.36(1)
Si–C(2)	1.882(5)	C(11)–C(13)	1.43(1)
N–C(31B)	1.325(7)	C(16)–C(15)	1.38(1)
N–C(21)	1.455(5)	C(15)–C(14)	1.41(2)
N–C(31A)	1.678(7)	C(14)–C(12)	1.39(2)
O(2)–C(22)	1.486(5)	C(12)–C(13)	1.39(1)
O(1)–Ge–O(3)	97.66(9)	C(31A)–C(32)–O(3)	120.1(5)
O(3)–Ge–O(3)#1	116.5(2)	C(32)–C(31A)–N	107.6(5)
O(1)–Ge–O(2)	92.4(1)	O(2)–C(22)–C(11)	108.0(4)
O(3)–Ge–O(2)	120.19(8)	O(2)–C(22)–C(21)	105.8(4)
O(1)–Ge–N	176.1(1)	C(11)–C(22)–C(21)	115.8(4)
O(3)–Ge–N	84.35(9)	C(16)–C(11)–C(13)	118.5(7)
O(2)–Ge–N	83.7(1)	C(16)–C(11)–C(22)	123.1(7)
Si–O(1)–Ge	140.6(2)	C(13)–C(11)–C(22)	118.4(6)
C(21)–N–C(31A)	101.8(3)	C(11)–C(16)–C(15)	122(1)
C(21)–N–Ge	105.4(2)	C(16)–C(15)–C(14)	121(2)
C(31A)–N–Ge	100.0(3)	C(15)–C(14)–C(12)	118(2)
C(22)–O(2)–Ge	115.9(3)	C(13)–C(12)–C(14)	120(1)
C(32)–O(3)–Ge	117.4(3)	C(12)–C(13)–C(11)	120.4(8)
N–C(21)–C(22)	112.4(3)		

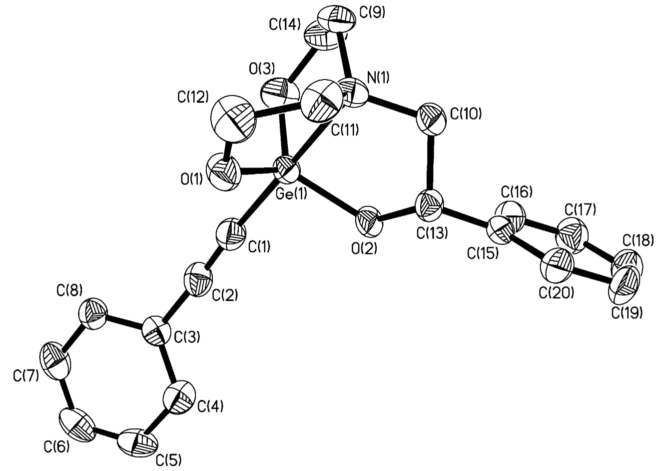

Fig. 1. Molecular structure of **5**. Hydrogen atoms are omitted for clarity.

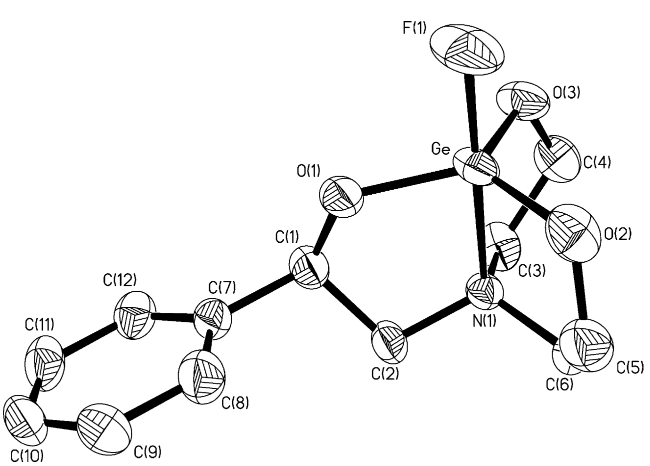

Fig. 2. Molecular structure of **8**. Hydrogen atoms are omitted for clarity.

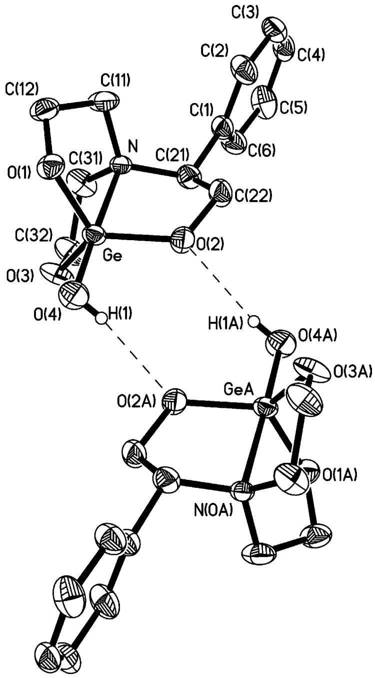

Fig. 3. Molecular structure of **7**. Two symmetry-related molecules forming dimer are shown. Hydrogen atoms (except H(1)) are omitted for clarity.

contrary, intensities of germatranyl cation peak (*m*/*e* 296) for these compounds are smaller than 12%.

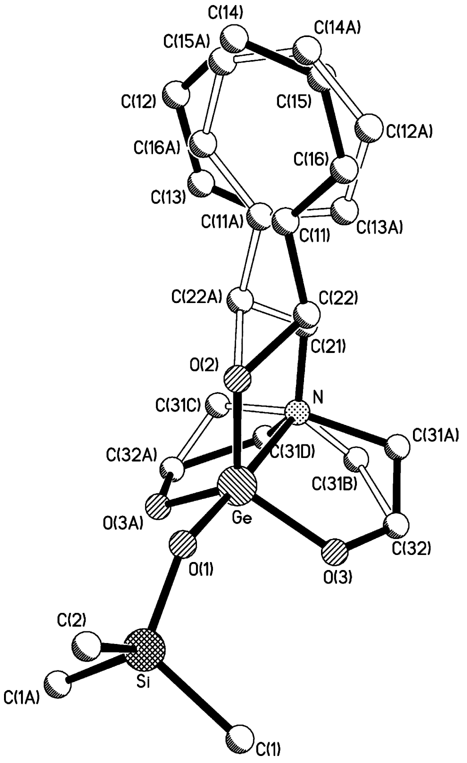

Fig. 4. Molecular structure of **9**. Hydrogen atoms are omitted for clarity.

However, in the case of **15** the base peak corresponds to the ion resulting from the loss of one Me group. Analogously, the same ion $[M^+ - Me]$ was detected for compound **9** (49%).

It should be noted that the fragmentation pathway of compound **4** containing phenyl substituent in position 4 of atrane skeleton is different from that found for 3-phenyl-substituted analogue **3**. Thus, the first step of fragmentation is elimination of CH_2O. The intensity of this peak is 63%. The intensity of the peak corresponding to the ion resulting from the loss of another CH_2O group is 28%. Of interest, the peaks corresponding to ions $[M^+ - CH_2O - Ph]$ and $[M^+ - 2CH_2O - Ph]$ are sufficiently intensive, too. Analogously, for compound **3** intensity of germatranyl cation peak (*m*/*e* 296) was found to be 11%.

For all studied compounds, the molecular ion peak is not observed or its intensity is smaller than 1% of the ion current, except compound **8** (8%).

2.6. Crystal structures

To the best of our knowledge, compounds **5** and **7**–**9** are the first structurally characterized germatrane derivatives with Ph substituent in atrane skeleton. Selected bond lengths and angles for **5** and **7**–**9** are listed in Tables 3–6, respectively.

The molecular structures of **5** and **8** are shown in Figs. 1 and 2. The main geometrical parameters of **5** and **8** are close to those previously reported for $N(CH_2CH_2O)_3$-$GeC{\equiv}CPh$ [21] and $N(CH_2CH_2O)_3GeF$ [22], respectively. The coordination polyhedron of the germanium atom in both compounds represents a distorted trigonal bipyramid with N(1) and C(1) (for compound **5**) or F(1) (for compound **8**) atoms in the axial positions and the three oxygen atoms occupying equatorial sites. The value of $Ge-N_{ax}$ distance in **5** (2.166(6) Å) lies within the typical range for germatranes (2.081(5)–2.32(1) Å) [23,24] and clearly verifies the existence of Ge–N transannular bond in **5**. The germanium atom in compound **5** is displaced by 0.21 Å (ΔGe) towards the phenylethynyl substituent from the equatorial plane defined by three oxygen atoms.

The value of $Ge-N_{ax}$ distance in **8** (2.108(2) Å) is noticeably shorter than that in **5**. This is in accordance with the general trend observed in atrane structures: more electronegative groups X yield shorter M–N transannular distances. It should be noted that ΔGe (0.12 Å) is smaller than that in compound **5**. Thus, the coordination polyhedron of the germanium atom in compound **8** is closer to an ideal trigonal bipyramid than in **5**.

The molecular structure of **7** is shown in Fig. 3. The main geometrical parameters of **7** are very close to those previously reported for $N(CH_2CH_2O)_2(CHEtCH_2O)$-$GeOH$ [6] and $N(CH_2CH_2O)_3GeOH \cdot H_2O$ [25]. Thus, the presence of alkyl or aryl groups in position 4 of atrane skeleton does not influence on coordination polyhedron of germanium atom. It should be noted that the value of Ge–O(4)$_{ax}$ distance (1.767(2) Å) is noticeably smaller than the values of Ge–O$_{eq}$ distances (1.773(2), 1.781(2), 1.805(2) Å). In crystal two molecules of **7** form centrosymmetric dimers by H-bonding (O(2)–O(4A) distance is 2.90 Å).

The molecular structure of **9** is shown in Fig. 4. In contrast to above, the key geometrical parameters of **9** are different to those previously reported for closely related $N(CH_2CH_2O)_3GeOSiMe_3$ [26]. The value of Ge–N transannular distance (2.170(4) Å) is noticeably longer than the values of Ge–N distances in $N(CH_2CH_2O)_3GeOSiMe_3$ (2.128(5) Å). On the contrary, Ge–O$_{ax}$ bond in **9** (1.776(3) Å) is shorter than that in 1-trimethylsiloxygermatrane (1.810(5) Å). Other main geometrical parameters of **9** and $N(CH_2CH_2O)_3GeOSiMe_3$ are very close with the exception of Si–O–Ge angle. The value of this angle in compound **9** (140.6(2)°) is larger than that in $N(CH_2CH_2O)_3GeOSiMe_3$ (133.0(4)°) as well as in $N(CH_2CH_2O)_3GeOSiMe_2$(2-thienyl) (134.8(3)°), $N(CH_2CH_2O)_3GeO$–SiMe(2-thienyl)$_2$ (139.6(3)°) [26] and $N(CH_2CH_2O)_3GeOSiMe_2$Vin (136.5(4)°) [27].

According to X-ray data phenyl substituent (compounds **5** and **7**–**9**) lies in equatorial position with respect to corresponding five-membered rings (solid state). The same results were found for the solution from NMR data (see above).

In conclusion, synthetic approaches to 3-phenyl-substituted germatranes were investigated and the structure and the chemical behaviour of these compounds were studied. In general, no significant difference, which could appear due to the steric effect of the phenyl group, was detected in reactivity of 3-phenyl-substituted germatranes and their unsubstituted or 3,7,10-trimethyl-substituted analogues. However, we note the increased easiness of germanoxane **10** formation from 1-hydroxygermatrane **6** in comparison with unsubstituted 1-hydroxygermatrane. Complete analysis of the ^{1}H and ^{13}C spectra of 3- and 4-phenyl-substituted germatranes has been performed. All protons and carbons of atrane skeleton (substituted and unsubstituted rings) were found non-equivalent. The structure of 3-phenyl- and 4-phenyl-substituted germatranes in solution (NMR data) strongly differs from the structure of unsubstituted germatranes. The latter undergoes the intramolecular conformation conversions while the introduction of phenyl group in atrane framework leads to "freezing" of these processes. This "frozen" conformation is the same in solution and in solid state (X-ray data). It should be noted that the structure of germatrane **9** in solid state is notably different from that of unsubstituted analogue. Other phenyl-substituted germatranes studied by X-ray analysis demonstrate the same structural trends as unsubstituted derivatives.

3. Experimental

3.1. General comments

The synthesis of **3**–**5** and **8**–**15** were carried out under argon atmosphere and standard Schlenk techniques. All solvents were dried by standard methods and distilled before use. Solutions of *n*-butyllithium in hexane were commercially obtained and analyzed regularly by the Gilman double titration method [28]. NMR spectra were recorded at 25 °C in $CDCl_3$ and DMSO-d_6 with internal deuterium lock, on Varian VXR 400, Bruker DRX 500, Bruker AC 300 spectrometers. Chemical shifts in the ^{1}H- and ^{13}C-NMR spectra are given in ppm relative to internal TMS; in ^{19}F-NMR experiments $CFCl_3$ was used as an external standard. 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; all assignments were made with reference to the most abundant isotopes.

3.2. Reaction of diethanolamine with 2-phenyloxirane: synthesis of product A [$(HOCH_2CH_2)_2NCH_2CH(Ph)OH$ (1):$(HOCH_2CH_2)_2NCH(Ph)CH_2OH$ (2) = 9:1]

A mixture of $(HOCH_2CH_2)_2NH$ (19.03 g, 0.181 mol) and 2-phenyloxirane (21.08 g, 0.181 mol) was refluxed for 4 h. The distillation gave 35 g (85%) of product **A** as a mixture of **1** (90%) and **2** (10%); b.p. 205–207 °C per 1 Torr [5]: 218–222 °C per 3 Torr. ^{1}H-NMR ($CDCl_3$): δ 5.14 (broad s, 3H, OH); 7.22, 7.30 (2m, aromatic protons); multiplets of $(AA'XX')_2$ and ABX systems of NCH_2CH_2O, NCH_2CHO and $NCHCH_2O$ groups protons—for **1**: 2.46, 2.81, 3.53, 3.72, 4.76; for **2**: 2.35, 2.64, 3.49, 3.61, 3.93, 4.03. ^{13}C-NMR ($CDCl_3$): 125.86, 127.42, 128.27, 141.89 (aromatic C for **1**); 127.59, 128.20, 128.49, 136.31 (aromatic C for **2**); 57.25, 59.40, 64.05, 70.98 [$N(CH_2CH_2OH)_2(CH_2$–$CHOH)$ in **1**]; 51.74, 59.18, 61.35, 64.62 [$N(CH_2CH_2OH)_2(CH$-$CH_2OH)$ in **2**].

3.3. Reaction of $GeCl_4$ with product A

Product **A** (4.46 g, 20 mmol) was added dropwise to a solution of $GeCl_4$ (1.06 g, 4.94 mmol) in 20 ml of THF. Immediately formation of the salts [(**1**:**2** = 9:1)·HCl] was observed. The precipitate was filtered off and washed with CH_3CN. After removal of all volatiles from combined filtrates in vacuo, the residue was dried in vacuo and dissolved in 50 ml of boiling CH_3CN. The solution was cooled; the precipitate was filtered off and recrystallized from CH_2Cl_2–hexane. Yield of $N(CH_2CH_2O)_2(CHPhCH_2O)GeCl$ (**4**): 0.15 g (9%). ^1H- and ^{13}C-NMR spectra (DMSO-d_6) (Tables 1 and 2). EI-MS *m/e* (rel. int.): $[M^+]$ 331 (0.2); $[M^+-CH_2O]$ 301 (63); $[M^+-Cl]$ 296 (11); $[M^+-2CH_2O]$ 271 (28); $[M^+-CH_2O-Cl]$ 266 (12); $[M^+-CH_2O-Ph]$ 224 (45); $[M^+-2CH_2O-Ph]$ 194 (39); $[N(CH_2)(CHC_6H_5)(CH_2CH_2O)]$ 162 (73); $[N(CH_2)(CHC_6H_5)]$ 118 (40); $[M^+-3CH_2O-N(CH_2)_2(CHC_6H_5)]$ 109 (52); $[C_7H_7]$ 91 (100); $[HN(CH)(CH_2)-(CH_2CH_2O)]$ 86 (92). Anal. Found: C, 43.79; H, 4.80; Ge, 21.61. Calc. for $C_{12}H_{16}ClGeNO_3$ (330.22): C, 43.63; H, 4.88; Ge, 21.98%.

CH_3CN was removed in vacuo from filtrate after separation of **4**, the residue was dried in vacuo. In ^1H-NMR ($CDCl_3$) spectra the signals of protons of $N(CH_2CH_2O)_2(CH_2CHPhO)GeCl$ (**3**) (mainly), [(**1**:**2** = 9:1)·HCl] and **4** were founded.

3.4. Synthesis of 1-chloro-3-phenylgermatrane, $N(CH_2CH_2O)_2(CH_2CHPhO)GeCl$ (3)

3.4.1. From reaction of $(EtO)_3GeCl$ with product A

Product **A** (1.48 g, 6.57 mmol) was added dropwise to a solution of $(EtO)_3GeCl$ (1.6 g, 6.58 mmol) in 20 ml of benzene. Immediate formation of the precipitate was observed. The reaction mixture was stirred for 24 h, the white solid was filtered off, washed with hexane and dried in vacuo to give 1.19 g (55%) of **3**. ^1H-NMR ($CDCl_3$): δ 2.64, 2.94, 3.12, 3.21, 3.89, 4.06, 4.95 (H-3) [7 m, $(AA'XX')_2$ and ABX systems of NCH_2CH_2O and NCH_2CHPhO groups protons], 7.28–7.45 (m, 5H, aromatic protons). ^{13}C-NMR ($CDCl_3$): atrane C—52.43, 52.98, 57.85, 57.98, 58.79, 69.75 (C-3); aromatic C—122.91, 125.73, 127.78, 127.90, 128.21, 128.49, 132.39, 141.13. EI-MS *m/e* (rel. int.): $[M^+-Cl]$ 296 (3); $[M^+-C_6H_5CHO]$ 225 (63); $[M^+-C_6H_5CHO-CH_2O]$ 195 (41); $[N(CH_2)_2CH_2CH_2O]$ 86 (100). Anal. Found: C, 43.81; H, 4.75; Ge, 21.90. Calc. for $C_{12}H_{16}ClGeNO_3$ (330.32): C, 43.63; H, 4.88; Ge, 21.98%.

3.4.2. From reaction of 9 with $SOCl_2$

$SOCl_2$ (0.096 g, 0.8 mmol) was added dropwise to a solution of **9** (0.31 g, 0.8 mmol) in 6 ml of $CHCl_3$. The reaction mixture was stirred for 24 h, then the precipitate was filtered off, washed with hexane (3 × 3 ml) and dried in vacuo for 2 h. Yield of **3**: 0.13 g (49%).

3.5. Synthesis of 1-(phenylethynyl)-3-phenylgermatrane, $N(CH_2CH_2O)_2(CH_2CHPhO)GeC\equiv CPh$ (5)

$(EtO)_3GeC\equiv CPh$ (4.4 g, 14 mmol) was added to a solution of product **A** (2.9 g, 13 mmol) in 50 ml of benzene. The reaction mixture was stirred for 24 h at r.t. A white solid was filtered off, washed with hexane (5 × 10 ml), dried in vacuo and recrystallized from $CHCl_3$–hexane to give 1.57 g (31%) of **5**. IR (thin film): ν 2172 cm^{-1} ($C\equiv C$). ^1H-NMR ($CDCl_3$): δ 2.52, 2.83, 3.00, 3.06, 3.79, 3.95, 4.83 (H-3) [7 m, $(AA'XX')_2$ and ABX systems of NCH_2CH_2O and NCH_2CHPhO groups protons], 7.07–7.50 (m, 10H, aromatic protons). ^{13}C-NMR ($CDCl_3$): atrane C—51.69, 52.31, 56.8, 56.7, 58.26, 68.53 (C-3); 90.91 ($GeC\equiv$); 99.29 ($\equiv CPh$); aromatic C—122.91, 125.73, 127.78, 127.90, 128.21, 128.49, 132.39, 141.13. EI-MS *m/e* (rel. int.): $[M^+]$ 397 (0.3); $[M^+-C_6H_5CHO]$ 291 (48); $[M^+-C_6H_5CHO-CH_2O]$ 261 (13); $[M^+-C_6H_5CHO-2CH_2O-N(CH_2)_3]$ 175 (31); $[M^+-C_6H_5CHO-C_6H_5C\equiv C-CH_2CH_2O]$ 146 (100); $[N(CH_2)_2CH_2CH_2O]$ 86 (14). Anal. Found: C, 60.92; H, 5.17; N, 3.28. Calc. for $C_{20}H_{21}GeNO_3$ (396.0): C, 60.66; H, 5.35; N, 3.54%.

3.6. Reaction of GeO_2–H_2O with product A: synthesis of 1-hydroxy-3-phenyl-germatrane, $N(CH_2CH_2O)_2(CH_2CHPhO)GeOH$ (6)

A mixture of product **A** (18.69 g, 83 mmol), GeO_2 (8.72 g, 83 mmol) and H_2O (25 ml) was heated at reflux. GeO_2 has dissolved within 1 h. A precipitate was filtered off, washed with EtOH (4 × 10 ml) and dried in vacuo; 19 g (73%) of **6** was obtained. ^1H-NMR ($CDCl_3$): δ 1.62 (s, 1H, OH); 2.55, 2.89, 3.05, 3.13, 3.81, 3.97, 4.85 (H-3) [7 m, $(AA'XX')_2$ and ABX systems of NCH_2CH_2O and NCH_2CHO groups protons]; 7.30–7.39 (m, 5H, aromatic protons). ^{13}C-NMR ($CDCl_3$): atrane C—52.38, 52.94, 56.81, 56.93, 58.87, 68.66 (C-3); aromatic C—125.63, 128.05, 128.60, 140.83. EI-MS *m/e* (rel. int.): $[M^+]$ 313 (0.2); $[M^+-C_6H_5CHO]$ 207 (77); $[M^+-C_6H_5CHO-CH_2O]$ 177 (61); $[M^+-C_6H_5CHO-CH_2CH_2O-OH]$ 146 (7); 134 (24); $[M^+-C_6H_5CHO-2CH_2O-N(CH_2)_3]$ 91 (39); $[N(CH_2)_2CH_2CH_2O]$ 86 (100). Anal. Found: C, 46.49; H, 5.43; N, 4.65. Calc. for $C_{12}H_{17}GeNO_4$ (311.88): C, 46.21; H, 5.49; N, 4.49%.

From filtrate the volatiles were evaporated in vacuo. A precipitate was dried in vacuo. A white solid was obtained (6.62 g, 26%) as the mixture of **6**, $N(CH_2CH_2O)_2(CHPhCH_2O)GeOH$ (**7**) and **10**. ^1H-NMR ($CDCl_3$) for **7**: δ 1.84 (s, 1H, OH); 2.23 (m, H_e^6). ^{13}C-NMR ($CDCl_3$) for **7**: atrane C—47.46, 48.67, 56.65, 56.88 59.83, 62.34. Crystals of **7** suitable for X-ray diffraction study were found in this mixture.

3.7. Synthesis of 1-fluoro-3-phenylgermatrane, $N(CH_2CH_2O)_2(CH_2CHPhO)GeF$ (8)

A solution of $BF_3\cdot Et_2O$ (0.15 g, 0.001 mol) in 15 ml of acetonitrile was added to a solution of **6** (1 g, 0.0032 mol) in 20 ml of acetonitrile at 50 °C. After 1 h the solid precipitated. After removal of volatile in vacuo hexane was added to the residue. The precipitate was filtered off and recrystallized from ethanol–water (1:1). Colorless crystals of **8** were obtained in 52% yield. ^{1}H-NMR ($CDCl_3$): δ 2.60, 2.90, 2.99, 3.11, 3.22, 3.85, 4.05, 4.92 (H-3) [8 m, $(AA'XX')_2$ and ABX systems of NCH_2CH_2O and NCH_2CHO groups protons]; 7.28–7.39 (m, 5H, aromatic protons). ^{13}C-NMR ($CDCl_3$): atrane C—52.63, 53.16, 57.13, 57.27, 59.02, 68.96 (C-3); aromatic C—125.52, 128.25, 128.68, 140.93. EI-MS *m/e* (rel. int.): [M^+] 315 (8); [$M^+ - F$] 296 (2); [$M^+ - C_6H_5CHO$] 209 (100); [$M^+ - C_6H_5CHO - CH_2O$] 179 (91); [$M^+ - F - C_6H_5CHO - CH_2CH_2O$] 146 (8); [$N(CH_2)_2CH_2CH_2O$] 86 (91). Anal. Found: C, 45.77; H, 5.29; N, 4.53. Calc. for $C_{12}H_{16}FGeNO_3$ (313.87): C, 45.92; H, 5.14; N, 4.46%.

*3.8. Synthesis of 1-trimethylsiloxy-3-phenylgermatrane, $N(CH_2CH_2O)_2(CH_2CHPhO)GeOSiMe_3$ (**9**)*

*3.8.1. From reaction of **6** with $(Me_3Si)_2NH$*

A mixture of **6** (15 g, 48 mmol), $(Me_3Si)_2NH$ (23 g, 143 mmol) and 100 ml of xylene was heated at reflux for 8 h. The precipitate was filtered off. After cooling of a filtrate to room temperature (r.t.), white crystals formed which were filtered off, washed with hexane (5 × 10 ml), recrystallized from CH_2Cl_2–hexane and dried in vacuo to give 2.9 g (16%) of **9**. ^{1}H- and ^{13}C-NMR ($CDCl_3$) (Tables 1 and 2). EI-MS *m/e* (rel. int.): [$M^+ - CH_3$] 370 (49); [$M^+ - C_6H_5CHO$] 279 (66); [$M^+ - C_6H_5CHO - CH_2O$] 249 (27); [$M^+ - C_6H_5CHO - 2CH_2O - N(CH_2)_3$] 163 (16); [$N(CH_2)_2CH_2CH_2O$] 86 (100). Anal. Found: C, 46.64; H, 6.69; N, 3.65. Calc. for $C_{15}H_{25}GeNO_4Si$ (384.06): C, 46.91; H, 6.56; N, 3.65%.

*3.8.2. From reaction of **6** with Me_3SiCl–Et_3N*

Et_3N (0.71 g, 7 mmol) and then Me_3SiCl (0.76 g, 7 mmol) were added dropwise to a suspension of **6** (2 g, 6.4 mmol) in 20 ml of $CHCl_3$. Immediately **6** has dissolved. The reaction mixture was stirred for 24 h at r.t., then 20 ml of H_2O was added, the water layer was separated and extracted with $CHCl_3$ (3 × 20 ml). The $CHCl_3$ solutions were washed with H_2O (5 × 30 ml). The combined $CHCl_3$ extracts were dried with $CaCl_2$, $CHCl_3$ was removed in vacuo; the residue was dried in vacuo to give 1.61 g (65%) of **9**.

*3.9. Synthesis of $[N(CH_2CH_2O)_2(CH_2CHPhO)Ge]_2O$ (**10**)*

6 (0.7 g, 2.24 mmol) was heated in vacuo at 180 °C for 20 h and the water formed was continuously removed. Yield of **10**: 0.65 g (96%), m.p. 294 °C. ^{1}H-NMR ($CDCl_3$): δ 2.39, 2.75, 2.93, 3.03, 3.71, 3.93, 4.82 (H-3) [7 m, $(AA'XX')_2$ and ABX systems of NCH_2CH_2O and NCH_2CHO groups protons]; 7.17–7.42 (m, 10H, aromatic protons). ^{13}C-NMR ($CDCl_3$): atrane C—52.53, 53.02, 53.05, 53.58, 57.01, 57.11, 57.14, 57.20, 59.21, 59.63, 68.51, 68.52 (C-3); aromatic C—125.74, 125.76, 125.63, 127.15, 127.23, 128.07, 128.11, 142.27, 142.76 (two diastereomers). EI-MS *m/e* (rel. int.): [$M^+ - C_6H_5CHO$] 500 (35); [$M^+ - C_6H_5CHO - CH_2O$] 470 (28); [$M^+ - C_6H_5CHO - 2CH_2O - N(CH_2)_3$] 384 (100); [$M^+ - OGe(OCHPhCH_2)(OCH_2CH_2)_2N$] 296 (11). Anal. Found: C, 46.33; H, 5.22; N, 4.26. Calc. for $C_{24}H_{32}Ge_2N_2O_7$ (605.74): C, 47.59; H, 5.33; N, 4.62%.

*3.10. Synthesis of 1-bromo-3-phenylgermatrane, $N(CH_2CH_2O)_2(CH_2CHPhO)GeBr$ (**11**)*

Me_3SiBr (3.06 g, 20 mmol) was added dropwise to a suspension of **9** (3.84 g, 10 mmol) in 20 ml of xylene. The reaction mixture was heated at reflux. After 5 min, **9** has dissolved and after 30 min of stirring formation of a precipitate was observed. The reaction mixture was refluxed for additional 20 min. The precipitate was filtered off, washed with hexane (5 × 5 ml), dried in vacuo to give 3.1 g (83%) of **11**. ^{1}H-NMR ($CDCl_3$): δ 2.65, 2.96, 3.13, 3.21, 3.90, 4.06, 4.96 (H-3) [7 m, $(AA'XX')_2$ and ABX systems of NCH_2CH_2O and NCH_2CHO groups protons]; 7.27–7.38 (m, 5H, aromatic protons). EI-MS *m/e* (rel. int.): [$M^+ - Br$] 296 (10); [$M^+ - C_6H_5CHO$] 269 (79); [$M^+ - C_6H_5CHO - CH_2O$] 239 (34); [$M^+ - Br - C_6H_5CHO$] 190 (37); [$M^+ - Br - C_6H_5CHO - CH_2O$] 160 (32); [$M^+ - Br - C_6H_5CHO - CH_2CH_2O$] 146 (11); [$M^+ - Br - C_6H_{52}O$] 130 (5); [$N(CH_2)_2CH_2CH_2O$] 86 (100). Anal. Found: C, 38.19; H, 4.45; N, 3.91. Calc. for $C_{12}H_{16}BrGeNO_3$ (374.77): C, 38.46; H, 4.30; N, 3.74%.

*3.11. Synthesis of [1-(3-phenyl)germatranyl]triflate, $N(CH_2CH_2O)_2(CH_2CHPhO)GeOTf$ (**12**)*

Me_3SiOTf (0.71 g, 3.2 mmol) was added dropwise with stirring to a suspension of **9** (0.5 g, 1.3 mmol) in 10 ml of xylene at r.t. Immediately a formation of a precipitate was observed. A reaction mixture was stirred for 24 h. After removal of all volatiles in vacuo, 0.57 g (100%) pure **12** was obtained as a white solid. EI-MS *m/e* (rel. int.): [M^+] 445 (0.2); [$M^+ - C_6H_5CHO$] 339 (65); [$M^+ - C_6H_5CHO - CH_2O$] 309 (94); [$M^+ - OSO_2CF_3$] 296 (67); [$M^+ - OSO_2CF_3$] 266 (31); [$M^+ - OSO_2CF_3 - C_6H_5CHO$] 190 (8); [$M^+ - OSO_2CF_3 - C_6H_5CH$-$O - CH_2O$] 160 (20); [$M^+ - OSO_2CF_3 - C_6H_5CH$-$O - CH_2CH_2O$] 146 (38); [$N(CH_2)_2CH_2CH_2O$] 86 (100). Anal. Found: C, 34.97; H, 3.68; N, 2.96. Calc. for $C_{13}H_{16}F_3GeNO_6S$ (443.94): C, 35.17; H, 3.63; N, 3.16%.

Table 7
Crystal data, data collection and refinement parameters for **5** and **7**–**9**

Empirical formula	$C_{20}H_{21}Ge_1N_1O_3$ (**5**)	$C_{12}H_{17}Ge_1N_1O_4$ (**7**)	$C_{12}H_{16}F_1Ge_1N_1O_3$ (**8**)	$C_{15}H_{25}Ge_1N_1O_4Si_1$ (**9**)
Formula weight	395.97	311.86	313.85	384.04
Color, habit	colorless prism	colorless block	colorless prism	colorless block
Crystal size (mm^3)	0.2 × 0.2 × 0.2	0.5 × 0.2 × 0.2	0.25 × 0.25 × 0.25	0.40 × 0.30 × 0.10
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	*Cc*	$P2_1/n$	$P2_1/c$	*Pnma*
Unit cell dimensions				
a (Å)	17.075(9)	6.861(3)	9.527(2)	6.8584(1)
b (Å)	11.263(7)	10.234(3)	10.108(2)	10.9075(3)
c (Å)	11.380(8)	17.906(5)	12.976(2)	23.4761(5)
β (°)	123.61(5)	98.49(3)	99.19(2)	
Volume (Å^3)	1823(2)	1243.5(7)	1233.5(4)	1756.20(7)
Z	4	4	4	4
Absorption coefficient (mm^{-1})	1.699	2.470	2.496	1.828
Scan mode	$\omega/2\theta$	ω	$\omega/2\theta$	ω
θ range (°)	2.31–25.97	2.30–24.98	2.17–25.97	2.06–27.99
Index ranges	$-20 \le h \le 17$, $-6 \le k \le 13$, $-6 \le l \le 14$	$-8 \le h \le 8$, $-3 \le k \le 12$, $-5 \le l \le 21$	$0 \le h \le 11$, $0 \le k \le 12$, $-15 \le l \le 15$	$-8 \le h \le 9$, $-14 \le k \le 11$, $-31 \le l \le 27$
Reflections collected	2028	4046	2556	12353
Independent reflections	2028 [$R_{int} = 0.000$]	2186 [$R_{int} = 0.021$]	2415 [$R_{int} = 0.024$]	2212 [$R_{int} = 0.031$]
Data/restraints/parameters	2028/2/226	2105/0/232	2415/0/227	2212/0/154
Reflections with $I > 2\sigma(I)$	1927	1819	1958	2054
Goodness-of-fit on F^2	1.307	1.071	1.024	1.237
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0274$, $wR_2 = 0.0691$	$R_1 = 0.0290$, $wR_2 = 0.0751$	$R_1 = 0.0324$, $wR_2 = 0.0715$	$R_1 = 0.0467$, $wR_2 = 0.1089$
R indices (all data)	$R_1 = 0.0300$, $wR_2 = 0.0702$	$R_1 = 0.0406$, $wR_2 = 0.0797$	$R_1 = 0.0451$, $wR_2 = 0.0756$	$R_1 = 0.0502$, $wR_2 = 0.1101$
Absolute structure parameter	−0.012(3)	–	–	–
Largest diff. peak per hole (e Å^{-3})	0.415/−0.441	0.714/−0.428	0.289/−0.365	0.500/−1.110

*3.12. Synthesis of 1-methoxy-3-phenylgermatrane, $N(CH_2CH_2O)_2(CH_2CHPhO)GeOMe$ (**13**)*

Et_3SnOMe (0.14 g, 0.58 mmol) was added dropwise to a suspension of **11** (0.2 g, 0.53 mmol) in 10 ml of $CHCl_3$. After 15 min of stirring, a precipitate of **11** has dissolved and the reaction mixture was stirred for 24 h at r.t. $CHCl_3$ was evaporated in vacuo. 20 ml of hexane was added, a white solid was filtered off, washed with hexane (5 × 10 ml) and dried. Yield of **13**: 0.16 g (94%). ^{1}H-NMR ($CDCl_3$): δ 2.38, 2.74, 2.92, 3.03, 3.63, 3.79, 4.71 (H-3) [7 m, $(AA'XX')_2$ and ABX systems of NCH_2CH_2O and NCH_2CHO groups protons]; 3.57 (s, 3H, OMe); 7.14–7.27 (m, 5H, aromatic protons). ^{13}C-NMR ($CDCl_3$): 53.03 (OMe); atrane C—52.21, 52.77, 56.78, 56.87, 58.73, 68.37 (C-3); aromatic C—125.46, 127.83, 128.45, 141.06. EI-MS *m/e* (rel. int.): [$M^+ - OMe$] 296 (6); [$M^+ - C_6H_5CHO$] 221 (31); [$M^+ - OCH_3 - C_6H_5CHO$] 190 (17); [$M^+ - OCH_3 - C_6H_5CHO - CH_2O$] 160 (22); [$M^+ - OCH_3 - C_6H_5CHO - CH_2CH_2O$] 146 (19); 130 [$M^+ - OCH_3 - C_6H_5CHO - 2CH_2O$] (8); [$N(CH_2)_2CH_2CH_2O$] 86 (100). Anal. Found: C, 48.26; H, 5.63; N, 4.15. Calc. for $C_{13}H_{19}GeNO_4$ (325.90): C, 47.94; H, 5.88; N, 4.30%.

*3.13. Synthesis of 1-(fluorenyl)-3-phenylgermatrane, $N(CH_2CH_2O)_2(CH_2CHPhO)GeC_{13}H_9$ (**14**)*

A solution of FluLi, prepared from fluorene (0.43 g, 2.6 mmol) and *n*-BuLi (1.71 ml, 2.7 mmol) as a 1.6-M solution in hexane, was added to a solution of **9** (1.0 g, 2.6 mmol) in THF (10 ml) at r.t. The reaction mixture was stirred for 24 h at r.t; all volatiles were evaporated in vacuo. 20 ml of toluene was added. The white solid was filtered off, washed with hexane (2 × 10 ml) and dried in vacuo. Yield of **14**: 0.73 g (61%). ^{1}H-NMR ($CDCl_3$): δ 2.34, 2.64, 2.85, 2.95, 3.55, 3.61, 3.72, 3.80, 4.72 (H-3) [9 m, $(AA'XX')_2$ and ABX systems of NCH_2CH_2O and NCH_2CHO groups protons]; 4.20 (s, 1H, CHGe); 7.23–7.33, 7.79–7.84, 7.93–7.97 (3 m, 13H, aromatic protons). ^{13}C-NMR ($CDCl_3$): 44.82 (CGe); atrane C—52.25, 52.79, 56.97, 57.08, 58.80, 68.27 (C-3); aromatic C—119.42, 125.19, 125.42, 125.72, 125.90, 127.48, 128.41, 140.91, 142.54, 145.32. EI-MS *m/e* (rel. int.): [M^+] 461 (3); [$M^+ - C_{13}H_9$] 296 (100), [$M^+ - C_{13}H_9 -$

C_6H_5CHO] 190 (13); [$M^+-C_{13}H_9-C_6H_5CHO-CH_2CH_2O$] 146 (19). Anal. Found: C, 65.42; H, 5.42; N, 2.91. Calc. for $C_{25}H_{25}GeNO_3$ (460.08): C, 65.26; H, 5.48; N, 3.04%.

3.14. Synthesis of 1-[bis(trimethylsilyl)amino]-3-phenylgermatrane, $N(CH_2CH_2O)_2(CH_2CHPhO)GeN(SiMe_3)_2$ (**15**)

A solution of $(Me_3Si)_2NLi$, prepared from $(Me_3Si)_2NH$ (0.22 g, 1.36 mmol) and *n*-BuLi (0.88 ml, 1.4 mmol) as a 1.66-M solution in hexane, was added to a suspension of **11** (0.5 g, 1.33 mmol) in 10 ml of THF at r.t. The reaction mixture was stirred for 24 h at r.t; volatiles were evaporated in vacuo and then 20 ml of toluene was added. The white solid was filtered off, washed with hexane (2 × 10 ml) and dried in vacuo. Yield of **15**: 0.28 g (46%). ^{1}H-NMR (C_6D_6): δ 0.62 (s, 18H, Me_3Si); 1.89, 1.98, 2.14, 2.29, 3.38, 3.53, 4.58 (H-3) [7 m, $(AA'XX')_2$ and ABX systems of NCH_2CH_2O and NCH_2CHO groups protons]; 7.18–7.44 (m, 5H, aromatic protons). ^{13}C-NMR ($CDCl_3$): 5.45 (Me_3Si); atrane C—52.90, 53.37, 57.19, 57.29, 59.94, 69.40 (C-3); aromatic C—125.91, 127.71, 128.00, 142.57. EI-MS *m*/*e* (rel. int.): [M^+-Me] 441 (100); [$M^+-CH_3-C_6H_5CHO$] 335 (23); [$M^+-N(SiMe_3)_2$] 296 (1.8); [$M^+-C_6H_5CHO-2CH_2ON(CH_2)_3$] 234 (30); [$M^+-C_6H_5CHO-CH_2CH_2O-N(SiMe_3)_2$] 146 (44); [$HN(CH_2CH_2O)_2CH_2CH$] 130 (93). Anal. Found: C, 47.62; H, 7.42; N, 6.01. Calc. for $C_{18}H_{34}GeN_2O_3Si_2$ (455.26): C, 47.49; H, 7.53; N, 6.15%.

3.15. X-ray crystallographic study of **5** and **7–9**

Table 7 summarizes the crystal data as well as details of data collection and structure determination for compounds **5** and **7–9**. The experimental data for **5**, **7** and **8** were collected on an Enraf-Nonius CAD4 diffractometer at room temperature using graphite monochromatized Mo–K_α radiation (0.71073 Å). As for **9**, intensities were measured on Bruker SMART CCD diffractometer at 120 K. All structures were solved by direct methods (SHELXS-86 [29]) and refined by full-matrix least-squares based on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97 [30]). For structures **7** and **8**, all hydrogen atoms were found from difference Fourier synthesis and refined isotropically. In the structures of **5** and **9**, hydrogen atoms were placed in calculated positions and refined using a riding model.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 191521 for compound **5**, CCDC No. 191522 for compound **7**, CCDC No. 191523 for compound **8**, CCDC No. 196131 for compound **9**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax. +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank Dr. A.V. Yatsenko for the X-ray crystal structure determination of **5** and **8**. This work was supported by INTAS under Grant No. YSF-2001/2-135 for S.S.K., by the Fonds der Deutschen Chemischen Industrie (VCI) for J.L. as well as by the Russian Foundation for Basic Research under Grant Nos. 01-03-32474 and 02-03-06347. A.V.C. is grateful to the Royal Society of Chemistry for the RSC Journal Grants for International Authors.

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