9-Silyl(-Germyl,-Stannyl) Substituted Derivatives of 1-(9-Fluorenyl)-germatranes. Synthesis, Characterisation, and Crystal Structures

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9-Trimethylsilyl- and 9-trimethylgermyl substituted derivatives of 1-(9-fluorenyl)germatranes $C_{13}H_8(R)Ge(OCH_2CH_2)_3N$ (**1** - **3**) (**1**: R = H; **2**: R = Me_3Si; **3**: R = Me_3Ge) were prepared by the reaction of 9-tribromogermyl derivatives of fluorene $C_{13}H_8(R)GeBr_3$ (**4** - **6**) with $N(CH_2CH_2OSnAlk_3)_3$ (**7**: Alk = Et; **8**: Alk = Bu). 1-(9-Trimethylstannyl-9-fluorenyl)germatrane (**14**) was synthesised by the reaction of the germatrane (**1**) with Me_3SnNMe_2. Formulas and structures were established by elemental analyses, (^1H, ^{13}C) NMR spectroscopy and mass spectrometry; crystal structures of **2** and **14** are reported.

Introduction

Metallatranes are a well-known and intensively studied class of compounds comprising a number of hypervalent Main Group Elements [1]. Metallatranes of the Group 14 elements $N(CH_2CHRO)_3MX$ (M = Si, Ge, Sn) received particular attention due to the question about the nature of (N→M)-transannular interaction [1 - 3].

Hypercoordination in the Group 14 metallatranes leads to some unique chemical properties of the compounds which render them significantly different from simply tetracoordinated derivatives of these elements. In addition, interest in metallatranes arises from their potential pharmacological activity [3, 4]. Since germatranes are much less toxic then isostructural silatranes, hence some examples have already found practical application [5].

As yet, however, all reported examples of germatranes are restricted to rather simple structures and very little is known about functionally substituted derivatives.

The main object of our studies is to functionalise the relatively simple and readily available metallatranes. In the course of our investigations [6 - 12] we have focussed our efforts on the synthesis, structural characterisation, and reactivity studies of (5-aza-2,8,9-trioxa-1-germabicyclo-[3.3.3]undecanes) with fluorenyl substituents in the 1-position, including germatranes bearing an organoelement group Me_3M (M = Si, Ge, Sn) in the 9-position of the fluorenyl fragment. Some preliminary work has recently been published [13]. A combination of a germatrane moiety with the sterically demanding, electronegative fluorenyl fragment should allow us to study this combination with respect to special properties of these molecules, particularly to the nature of the Ge←N transannular bond and, last but not least, for further functionalisation of germatranes.

Results and Discussion

Organotin compounds are common reagents in organic synthesis [14]. Our recent synthetic studies showed, that an "organotin route" for the formation of the "'atrane"' framework [10 - 13], *e. g.* the reaction of organotrihalogermanes with organotin derivatives of tris(2-hydroxyalkyl)amines, is a general pathway and allows syntheses of various germatranes bearing a functional group, including

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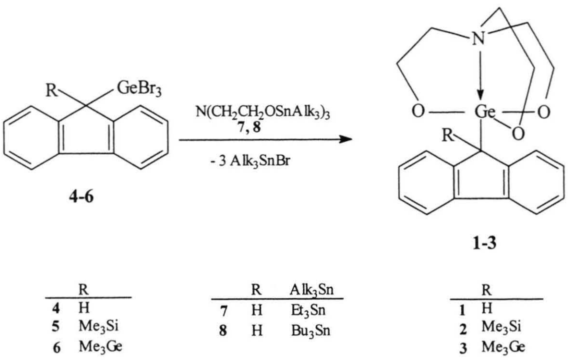
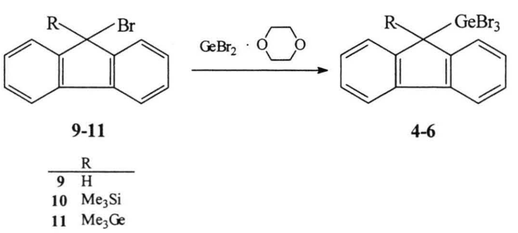


Scheme 1.

germatranes with Ge-C bonds which are sensitive towards nucleophilic or electrophilic attack [11, 12].

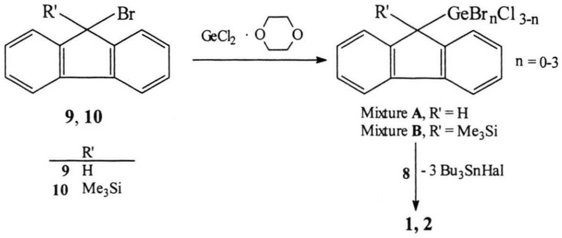
This method was used for the construction of the "atrane" skeleton in our present work: Reactions of the corresponding tribromogermylfluorenes **4 - 6** with tris(2-trialkylstannoxyethyl)amines **7, 8** under mild conditions afford germatranes **1-3** in good to excellent yields (Scheme 1). These reactions proceed smoothly after mixing of the reagents in $CHCl_3$, followed by stirring the reaction mixture for 4 - 5 h at room temperature. After addition of *n*-hexane the resulting germatranes are precipitated and separated by filtration. Analytically pure samples are obtained by washing the precipitates with *n*-hexane, recrystallisation from *n*-hexane, and finally drying *in vacuo*. Trialkylbromostannanes are formed as by-products of this transmetallation reaction and can be recovered almost quantitatively.

The 9-tribromogermylfluorenes **4 - 6** were obtained by oxidative addition of the corresponding 9-bromofluorenes **9 - 11** to $GeBr_2$ · dioxane in boiling dioxane (Scheme 2).



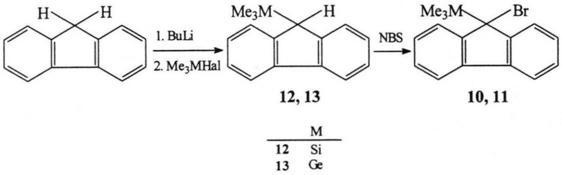
Scheme 2.

Germatranes **1** and**2** can also be successfully synthesised by transesterification of a mixture of 9-trihalogermylfluorenes (**A**, **B**) with ester **8**. For this reaction completion needs a longer period of time (25 - 30 h) than that for the 9-tribromogermylfluorenes. However, this method allows a preparation of the corresponding germatranes in reasonable yields (~ 60%). A synthesis of mixtures (**A, B**) was carried out by treatment of 9-bromofluorenes **9** and **10** with $GeCl_2$·dioxane which is more readily available than the dibromo analogue (Scheme 3).



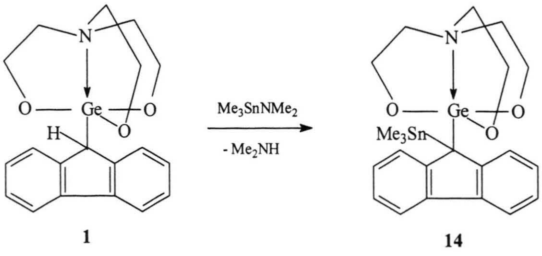
Scheme 3.

9-Bromo-9-trimethylsilylfluorene (**10**) and 9-bromo-9-trimethylgermylfluorene (**11**) can be prepared starting from compounds **12** and **13**, respectively (Scheme 4).



Scheme 4.

The tin analogue 1-(9-trimethylstannyl-9-fluorenyl)germatrane (**14**) can be synthesised from germatrane **1** (Scheme 5) by reaction of the acidic hydrogen atom at the C(9) atom of the fluorene with a strong base like trimethyltin dimethylamide.



Scheme 5.

The chemical potential of compounds **1** - **3** and **14** as useful precursors for newly functionalised germatranes is based on the presence of an acidic C(9)

Table I. ^1H and ^{13}C NMR data for fluorenyl derivatives **1** - **6**, **9** - **14**.

	^1H [δ, ppm]		^{13}C [δ, ppm]	
Comp.	Me_3M	C(9)H	Me_3M	C(9)
12	0.03	3.30	−2.68	42.73
13	0.02	3.97	−3.07	42.23
9	—	5.99	—	46.00
10	0.02	—	−3.35	54.00
11	0.08	—	−3.27	53.03
4	—	4.96	—	54.17
5	0.09	—	−1.29	57.80
6	0.29	—	−1.21	57.23
1	—	4.12	—	44.50
2	−0.23	—	−1.59	50.42
3	−0.08	—	−1.81	49.85
14	−0.16	—	−8.15	48.75

hydrogen atom, on a reactive metal-to-carbon bond C-M (M = Si, Ge, Sn), and on the properties of the aromatic ring system.

Synthesis and characterisation of compounds **1** and **4** were already described in a preliminary report [13].

New compounds **2**,**3**, **5**,**6**, and **14** were characterised by elemental analyses and (^1H, ^{13}C) NMR spectroscopy. Compounds **2**, **3**, **5**, **6**, **11**, **13**, and **14** were also characterised by mass spectrometry.

The ^1H and ^{13}C NMR spectra are in accordance with the suggested structures of the compounds: In the ^1H NMR spectra of **2**, **3** and **14** the signals of the methylene protons of the germatrane skeleton appear as a set of two pseudo-triplets at 2.66 - 2.71 (NCH_2) and 3.6 - 3.71 (OCH_2) ppm, a AA'XX' spin system (J = 5.5 -.5.8 Hz). This pattern is a general feature of the "atrane" framework for a variety of germatranes. In the ^{13}C NMR spectra of **2**, **3** and **14** the signals of the carbon atoms of the "atrane" skeleton appear at 52.1 - 52.8 (NCH_2) and 57.0 - 57.3 (OCH_2) ppm [1, 3, 6 - 13]. Chemical shifts of the hydrogen and carbon atoms of the Me_3M and fluorenyl groups are found in the expected range; a selection of NMR data is presented in Table I.

In the mass spectra of **2** and **3**, the peak of highest intensity corresponds to the germatranyl ion, resulting from the loss of the apical substituent from the parent ion. This behaviour is analogous to that observed for 1-allylgermatrane [11] and for germatrane **1** [13] and is assumed to reflect the relative bond strength of the Ge-O ring bonds. In the case of **14** the base peak corresponds to the ion resulting from the loss of one methyl group. A cluster of peaks at m/z 130 has been attributed to the ion $GeN(CH_2)_3^+$, which is consistent with the germatrane structure. In the case of **14** the molecular ion peak is only 6% of the base peak. In the case of **2** and **3** the molecular ion peak is observed with an intensity of 45%. Other intensities > 5% of the base peak are quoted without assignment.

X-ray crystal structure determination of $N(CH_2CH_2O)_3Ge(Me_3Si)C_{13}H_8$ (**2**) *and* $N(CH_2CH_2O)_3Ge(Me_3Sn)C_{13}H_8$ (**14**)

The crystal structures of germatranes **2** and **14** were determined by single crystal X-ray diffractometry. Experimental data are summarised in Table II, important atomic distances and bond angles in Tables III - VI. The molecular structures of the two (isostructural) compounds are shown in Fig. 1 and Fig. 2.

The coordination polyhedra of the germanium atoms in **2** and **14** have the same structural features common for germatrane derivatives [6b, 11 - 13, 15 - 20], *i. e.* a distorted trigonal bipyramidal coordination at germanium with N and C atoms in the apical positions and three oxygen atoms in equatorial positions. The germanium atoms are displaced by 0.22 and 0.24 Å, respectively, from the plane defined by three oxygen atoms. The N-Ge-C fragments in both molecules are almost linear (177.99(11)° and 176.6(2)°). The N-Ge distances (2.202(3) and 2.206(6) Å) are in the normal range for germatranes containing the N-Ge-C moiety (2.16 - 2.32 Å) [11, 13]. The $Ge-C_{fluorene}$ bond lengths of 1.987(3) **2** and 1.964(6) Å **14** are somewhat smaller, but in the case of the silylated derivative this distance is almost identical to that observed for a closely related germatrane $N[CH_2CH_2O]_3GeC_{13}H_9$ (1.991(3) Å) [13].

Typical conformational disorder of the germatrane cage has been observed for both **2** and **14** [11, 12]. All five-membered rings of the atrane skeleton possess "envelope"-like conformation. The carbon atoms in the α-positions with respect to the nitrogen atom form the "flaps" of these "envelopes" [21].

Interestingly, a second form of disorder has been found for the stannylated compound: The position of oxygen atom O(3) is split into two different sites in the equatorial plane of the trigonal bipyramid. To the best of our knowledge, this type of disorder is the first case for atrane molecules. The proximity of the Me_3Sn substituent to this oxygen atom

Table II. Crystal data, data collection, structure solution and refinement parameters for **2** and **14**.

Empirical formula	$C_{22}H_{29}GeNO_3Sn$	$C_{22}H_{29}GeNO_3Si$
Formula weight	546.74	456.14
Colour, habit	Colourless block	Colourless nugget
Crystal size [mm]	0.40 × 0.30 × 0.20	0.16 × 0.13 × 0.12
Crystal system	Orthorhombic	Orthorhombic
Space group	Pbcn, Z = 8	Pbcn, Z = 8
Unit cell dimensions [Å]	$a = 14.6386(2)$	$a = 14.538(3)$
	$b = 20.7826(2)$	$b = 20.622(4)$
	$c = 14.6409(1)$	$c = 14.637(3)$
Volume [$Å^3$]	4454.17(8)	4388.2(15)
Density (calculated) [g cm^{-3}]	1.631	1.381
Absorption coefficient [mm^{-1}]	2.493	1.473
F(000)	2192	1904
Diffractometer	Siemens SMART	Stoe-IPDS
Temperature [K]	100.0(2)	190(2)
Radiation (λ [Å])	— graphite monochromatised MoKα (0.71073) —	
Scan mode	omega	phi
Θ-Range [deg]	1.70 to 24.99	2.21 to 25.90
Index ranges	$-13 \leq h \leq 18, -26 \leq k \leq 26, -18 \leq l \leq 19$	$-17 \leq h \leq 17, -22 \leq k \leq 25, -17 \leq l \leq 17$
Reflections collected	25508	24304
Independent reflections	3923 [R(int) = 0.0557]	4247 [R(int) = 0.0825]
Data reduction	Siemens SAINT (Siemens Analytical X-ray Instruments, 1995)	Stoe-INTEGRATE
Absorption correction	Multi-scan (SHELXTL, 1994) [29]	none
Min. and max. transmission	0.26 and 0.38	0.80 and 0.84
Solution method	Direct methods (SHELX-86) [30]	Direct methods (SHELXS-97) [32]
Refinement method	— Full-matrix least-squares on F^2 —	
Program	SHELXL-93 [31]	SHELXL-97 [33]
Hydrogen atoms treatment	All H atoms were placed in calculated positions and refined using a riding model	
Data / parameters	3845 / 288	4247 / 284
Goodness-of-fit on F^2	1.314	0.934
R_1, wR_2, [$I > 2\sigma(I)$]	0.0454, 0.1015	0.0394, 0.0829
R_1, wR_2 (all data)	0.0547, 0.1078	0.0680, 0.0905
Extinction coefficient	0.00046(6)	none
Largest diff. peak	1.67	0.46
hole [e / $Å^{-3}$]	–0.84	–0.51

(C(14)-O(3b) (2.90 Å) may be a plausible explanation for this phenomenon.

Experimental

All solvents were dried by standard methods and distilled prior to use; melting points are uncorrected. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University and of the Fachbereich Chemie of the Philipps-University Marburg (Heraeus-Rapid-Analyser).

NMR spectra were recorded at 25 °C on Varian VXR-400 and Bruker AC 300 spectrometers, $CDCl_3$ was used as a solvent and for internal deuterium lock. The chemical shifts (δ) of the ^1H and ^{13}C NMR resonances are given in ppm relative to internal TMS. Assignments of the ^{13}C NMR data were supported by APT experiments. Mass spectra (EI-MS) were recorded on a Varian CH-7a instrument using electron impact with an ionisation energy of 70 eV; all assignments were made with respect to the most abundant isotopes.

Solutions of *n*-butyllitium in *n*-hexane were obtained from Aldrich Chemical Company and were analysed by the Gilman double titration method prior to use [22].

Tris(2-trialkylstannoxyalkyl)amines (**7, 8**) were prepared according to a modified procedure using an excess of trialkylmethoxystannanes [11 - 13, 23].

9-Trimethylsilylfluorene (**12**) and 9-trimethylgermylfluorene (**13**) were synthesised by the reaction of fluorenyllithium with Me_3SiCl or Me_3GeBr, respectively.

9-Trimethylsilylfluorene (**12**) *[24]*

^1H NMR ($CDCl_3$): δ = 0.03 (s, 9H, $SiMe_3$); 3.30 (s, 1H, SiCH); 7.75 - 7.70, 7.63 - 7.58, 7.39 - 7.30 (3 m,

Table III. Selected bond lengths (Å) for **2**.

Ge-N	2.202(3)	Ge-C(1)	1.987(3)
Ge-O(1)	1.793(2)	O(1)-C(17)	1.389(4)
Ge-O(2)	1.784(4)	O(3)-C(21)	1.399(5)
Ge-O(3)	1.785(2)	O(2)-C(19)	1.412(4)
N-C(18)	1.441(11)	N-C(18A)	1.445(9)
N-C(20)	1.427(8)	N-C(20A)	1.561(6)
N-C(22)	1.581(9)	N-C(22A)	1.429(7)
C(17)-C(18)	1.506(14)	C(17)-C(18A)	1.467(11)
C(19)-C(20)	1.602(8)	C(19)-C(20A)	1.470(7)
C(21)-C(22)	1.425(9)	C(21)-C(22A)	1.610(9)
Si-C(1)	1.922(3)	Ge-PL[a]	0.22[b]

[a] PL means an equatorial plane defined by O(1), O(2), O(3) atoms; [b] positive sign indicates that Ge atom is displaced towards carbon atom C(1).

Table IV. Selected bond angles (deg) for **2**.

O(2)-Ge-O(3)	119.02(14)	O(1)-Ge-C(1)	97.46(12)
O(2)-Ge-O(1)	117.53(12)	O(2)-Ge-C(1)	96.54(12)
O(1)-Ge-O(3)	118.22(14)	O(3)-Ge-C(1)	100.3(2)
O(1)-Ge-N	82.10(10)	O(3)-Ge-N	81.98(12)
O(2)-Ge-N	82.99(10)	C(1)-Ge-N	177.99(11)
C(18)-N-C(20)	120.1(6)	C(18A)-N-C(20A)	109.7(5)
C(18)-N-C(22)	111.5(6)	C(18A)-N-C(22A)	117.8(5)
C(20)-N-C(22)	109.4(5)	C(20A)-N-C(22A)	112.8(5)
C(18)-N-Ge	105.9(5)	C(18A)-N-Ge	105.4(4)
C(20)-N-Ge	105.5(3)	C(20A)-N-Ge	102.2(3)
C(22)-N-Ge	102.8(4)	C(22A)-N-Ge	107.7(3)
O(1)-C(17)-C(18)	113.6(5)	O(1)-C(17)-C(18A)	115.2(4)
O(2)-C(19)-C(20)	111.6(4)	O(2)-C(19)-C(20A)	112.8(3)
O(3)-C(21)-C(22)	114.9(4)	O(3)-C(21)-C(22A)	112.0(4)
N-C(18)-C(17)	108.7(8)	N-C(18A)-C(17)	110.6(6)
N-C(20)-C(19)	105.2(5)	N-C(20A)-C(19)	105.2(4)
N-C(22)-C(21)	106.1(6)	N-(22A)-C(21)	104.4(5)
C(17)-O(1)-Ge	120.0(2)	C(21)-O(3)-Ge	120.8(2)
C(19)-O(2)-Ge	119.5(2)		

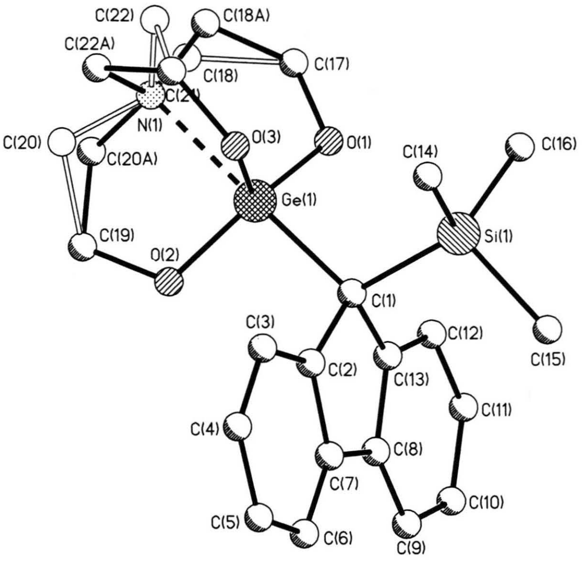


Fig. 1. Molecular structure of **2**.

Ar, 8 H). ^{13}C NMR (CDCl$_3$): $\delta = -2.68$ (SiMe$_3$), 42.73 (SiCH), 119.87 (C-4,5), 123.97, 125.93, 125.17 (C-1,8; C-2,7; C-3,6), 140.38 (C-11,12), 145.64 (C-10,13).

*9-Trimethylgermylfluorene (**13**) [25]*

^{1}H NMR (CDCl$_3$): $\delta = 0.02$ (s, 9H, GeMe$_3$); 3.97 (s, 1H, GeCH); 7.88 - 7.85, 7.49 - 7.47, 7.36 - 7.27 (3 m, Ar, 8 H). ^{13}C NMR (CDCl$_3$): $\delta = -3.07$ (GeMe$_3$), 42.23 (GeCH), 119.83 (C-4,5), 123.36, 124.99, 125.96 (C-1,8; C-2,7; C-3,6), 139.79 (C-11,12), 146.17 (C-10,13). EI-MS, *m/z* (rel. int., assign.): 284 (10%, M$^+$), 166 (8%, C$_{13}$H$_{10}$), 165 (57%, C$_{13}$H$_9$), 163 (7%, C$_{13}$H$_7$), 119 (100%, GeMe$_3$).

9-Bromofluorenes (**10**, **11**) were synthesized by the reaction of the corresponding fluorenes (**12, 13**) with NBS.

*9-Bromo-9-trimethylsilylfluorene (**10**) [26]*

^{1}H NMR (CDCl$_3$): $\delta = 0.02$ (s, 9H, SiMe$_3$); 7.74 - 7.71, 7.63 - 7.59, 7.74 - 7.71 (3 m, Ar, 8 H). ^{13}C NMR (CDCl$_3$): $\delta = -3.35$ (SiMe$_3$); 54.00 (SiCBr); 120.05 (C-4,5); 125.54, 127.25, 127.62 (C-1,8; C-2,7; C-3,6); 139.07 (C-11,12). 147.43 (C-10,13).

*9-Bromo-9-trimethylgermylfluorene (**11**)*

M. p. 135 - 137 °C. ^{1}H NMR (CDCl$_3$): $\delta = 0.08$ (s, 9H, GeMe$_3$); 7.76 - 7.69, 7.62 - 7.56, 7.38 - 7.29 (3 m, Ar, 8H). ^{13}C NMR (CDCl$_3$): $\delta = -3.27$ (GeMe$_3$); 53.03 (GeCBr); 119.93 (C-4,5); 124.77, 127.36, 127.25 (C-1,8; C-2,7; C-3,6); 138.23 (C-11,12); 147.97 (C-10,13). EI-MS, *m/z* (rel. int., assign.): 360 (8%, M$^+$), 268 (4%, M$^+$-CH$_3$-Br), 253 (4%, M$^+$-2CH$_3$-Br), 243 (7%, M$^+$-Br-GeMe$_3$); 237 (3%, M$^+$-3CH$_3$-Br), 166 (17%, C$_{13}$H$_{10}$), 165 (49%, C$_{13}$H$_9$), 164 (26%, C$_{13}$H$_8$), 163 (30%, C$_{13}$H$_7$), 119 (100%, GeMe$_3$).

GeX$_2$·dioxanes were synthesized as described in the literature [27].

Tribromogermyl derivatives **4 - 6** were obtained by refluxing a mixture of GeBr$_2$·dioxane and the corresponding 9-bromofluorene (**9** - **11**). 9-Tribromogermyl-fluorene (**4**) was prepared according to the literature [13].

*9-Tribromogermyl-9-trimethylgermylfluorene (**6**)*

A mixture of **11** (1.00 g, 2.76 mmol) and GeBr$_2$·dioxane 0.9 g (2.81 mmol) in 6 ml dioxane was heated to reflux for 8 h; solvent was removed *in vacuo*. Chloroform (2 ml) and *n*-hexane (3 ml) were added to the residual red oil and the mixture was stored for 12 h at −18 °C. A precipitate was filtered off and dried *in vacuo*. After recrystallisation (*n*-hexane / CHCl$_3$) 0.61 g (37%) of the product was recoverd, m. p. 119 - 121°C.

Table V. Selected bond lengths (Å) for **14**.

Ge-C(9)	1.964(6)	Ge-N	2.206(6)
Ge-O(2)	1.790(4)	Ge-O(3B)	1.811(11)
Ge-O(1)	1.797(5)	Ge-O(3A)	1.846(10)
N-C(17)	1.39(2)	N-C(170)	1.50(2)
N-C(19)	1.603(12)	N-C(190)	1.356(14)
N-C(21)	1.481(12)	N-C(210)	1.588(14)
O(1)-C(18)	1.388(8)	O(3A)-C(22)	1.351(12)
O(2)-C(20)	1.417(7)	O(3B)-C(22)	1.544(14)
C(18)-C(17)	1.56(2)	C(18)-C(170)	1.42(2)
C(20)-C(19)	1.463(13)	C(20)-C(190)	1.64(2)
C(22)-C(21)	1.68(2)	C(22)-C(210)	1.48(2)
Sn-C(9)	2.212(6)	Ge-PL[a]	0.24[b]

[a] PL means an equatorial plane defined by four oxygen atoms O(1), O(2), O(3A) and O(3B); [b] positive sign indicates that Ge atom is displaced towards carbon atom C(9).

Table VI. Selected bond angles (deg) for **14**.

O(2)-Ge-O(1)	119.4(2)	O(2)-Ge-C(9)	100.3(2)
O(2)-Ge-O(3B)	130.8(4)	O(1)-Ge-C(9)	96.0(2)
O(1)-Ge-O(3B)	106.2(4)	O(3B)-Ge-C(9)	92.2(4)
O(2)-Ge-O(3A)	107.3(4)	O(3A)-Ge-C(9)	99.7(4)
O(1)-Ge-O(3A)	126.7(4)	C(9)-Ge-N	176.6(2)
O(2)-Ge-N	83.0(2)	O(3B)-Ge-N	86.0(4)
O(1)-Ge-N	81.8(2)	O(3A)-Ge-N	79.6(3)
C(17)-N-C(21)	118.4(9)	C(170)-N-C(210)	106.6(10)
C(17)-N-C(19)	110.6(9)	C(170)-N-C(190)	122.7(10)
C(19)-N-C(21)	106.7(7)	C(190)-N-C(210)	114.6(8)
C(17)-N-Ge	108.7(7)	C(170)-N-Ge	103.7(8)
C(19)-N-Ge	103.6(5)	C(190)-N-Ge	105.9(7)
C(21)-N-Ge	107.9(6)	C(210)-N-Ge	100.4(6)
C(18)-O(1)-Ge	120.6(4)	C(22)-O(3A)-Ge	120.0(7)
C(20)-O(2)-Ge	120.0(4)	C(22)-O(3B)-Ge	111.7(7)
O(1)-C(18)-C(17)	113.9(7)	O(1)-C(18)-C(170)	115.0(9)
O(2)-C(20)-C(19)	115.4(7)	O(2)-C(20)-C(190)	109.1(7)
O(3A)-C(22)-C(21)	104.4(7)	O(3B)-C(22)-C(210)	105.4(8)
N-C(17)-C(18)	108.8(10)	N-C(170)-C(18)	110.7(11)
N-C(19)-C(20)	104.6(8)	N-C(190)-C(20)	107.8(9)
N-C(21)-C(22)	100.4(8)	N-C(210)-C(22)	104.6(8)

^{1}H NMR (CDCl):δ = 0.29 (s, 9H, GeMe$_3$); 7.95-7.93, 7.53 - 7.49, 7.45 - 7.42 (3 m, Ar, 8 H). ^{13}C NMR (CDCl$_3$): δ = –1.21 (GeMe$_3$); 57.23 (GeCGe); 120.32 (C-4,5); 124.84, 127.28, 127.01 (C-1,8; C-2,7; C-3,6); 140.70 (C-11,12); 141.40 (C-10,13). EI-MS, *m/z* (rel. int., assign.): 594 (2%, M$^+$), 396 (19%, M$^+$-Br-GeMe$_3$), 268 (9%, M$^+$-GeBr$_3$-CH$_3$), 253 (9%, M$^+$-GeBr$_3$-2CH$_3$), 243 (36%, $C_{13}H_8Br$), 180 (22%, $C_{13}H_9CH_3$), 179 (100%, $C_{13}H_8CH_3$), 178 (40%, $C_{13}H_8CH_2$), 165 (77%, $C_{13}H_9$), 164 (17%, $C_{13}H_8$), 163 (22%, $C_{13}H_7$), 119 (70%, GeMe$_3$).

Analysis for $C_{16}H_{17}Br_3Ge_2$ (594.20)
Calcd C 32.34 H 2.88%,
Found C 32.05 H 2.51%.

9-Tribromogermyl-9-trimethylsilylfluorene (**5**) was obtained according to the procedure for **6,** and recrystallised from *n*-hexane. Yield 69%, m. p. 121 - 124 °C.

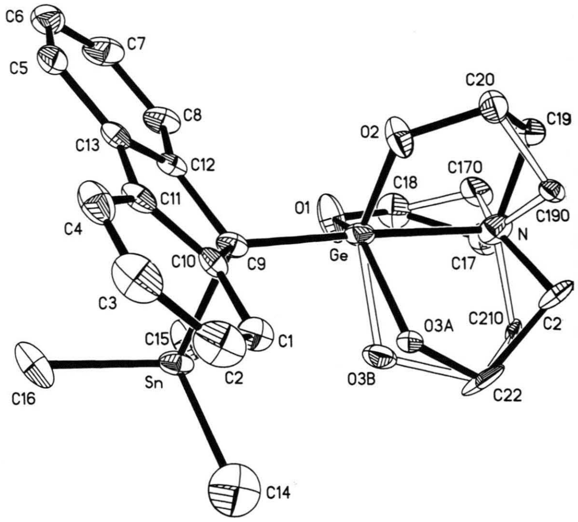


Fig. 2. Molecular structure of **14**.

^{1}H NMR (CDCl$_3$): δ = 0.09 (s, 9H, SiMe$_3$); 7.99 - 7.95, 7.55 - 7.52, 7.47 - 7.43 (3 m, Ar, 8 H). ^{13}C NMR (CDCl$_3$): δ = –1.29 (SiMe$_3$); 57.80 (GeCSi); 120.40 (C-4,5); 125.44, 127.51, 127.03 (C-1,8; C-2,7; C-3,6); 140.66 (C-11,12); 141.28 (C-10,13). EI-MS, *m/z* (rel. int., assign.): 550 (8%, M$^+$), 396 (69%, M$^+$-SiMe$_3$-Br), 243 (52%, $C_{13}H_8Br$), 237 (31%, $C_{13}H_8SiMe_3$), 222 (43%, $C_{13}H_8SiMe_2$); 180 (5%, $C_{13}H_9Me$), 179 (23%), 178 (26%), 165 (22%, $C_{13}H_9$), 164 (10%, $C_{13}H_8$), 163 (12%, $C_{13}H_7$), 73 (100%, SiMe$_3$).

Analysis for $C_{16}H_{17}Br_3GeSi$ (549.70)
Calcd C 34.96 H 3.12%,
Found C 34.83 H 3.36%.

Mixture **B** *($C_{13}H_8(SiMe_3)GeBr_nCl_{3-n}$)* was obtained according to the same procedure as for **6**, starting from 9-bromo-9-trimethylsilylfluorene (**10**) with GeCl$_2$·dioxane.

^{1}H NMR(CDCl$_3$): δ = 0.09, 0.11, 0.13, 0.14 (4s, 9H, SiMe$_3$); 7.95 - 7.85, 7.61 - 7.47, 7.45 - 7.30 (3m, 8H, Ar)

Mixture **A** *($C_{13}H_9GeBr_nCl_{3-n}$)* was obtained by an analogous reaction.

Synthesis of germatranes **1 - 3**

1 - 3 were obtained according to published procedures by reacting esters **7**, **8** with 9-tribromogermylfluorenes (**4 - 6**) [11, 12]. **1** was prepared by the reaction of **7** with **4,** as described in [13], and also by the reaction of ester **8** with mixture **A** ($C_{13}H_9GeBr_nCl_{3-n}$).

1-(9-Trimethylsilyl-9-fluorenyl)germatrane (**2**)

A mixture of 0.09 g (0.16 mmol) of 9-tribromogermyl-9-trimethylsilylfluorene (**5**), 0.24 g (0.24 mmol) of tris(2-tributylstannoxyethyl)amine (**8**) and 6 ml of chloroform was stirred at room temperature for 4 h. After removal of the solvent, addition of 4 ml *n*-hexane gave a white solid which was filtered off and washed with *n*-hexane (5x5 ml). Recrystallisation from *n*-hexane / chloroform (3:1) yielded 0.07 g (95 %), m. p. 212 - 214 °C.

^{1}H NMR ($CDCl_3$): δ = –0.23 (s, 9H, $SiMe_3$); 3.62(t, 6H, OCH_2); 2.66 (t, 6H, NCH_2); 7.92 - 7.87, 7.84 - 7.80, 7.26 - 7.20(3m, 8H, Ar); ^{13}C NMR ($CDCl_3$): δ = –1.59 ($SiMe_3$), 50.42 (SiCGe), 52.77 (NCH_2), 57.30 (OCH_2), 119.24 (C-4,5), 123.91, 125.22, 125.67 (C-1,8; C-2,7; C-3,6), 139.97 (C-11,12), 147.45 (C-10,13). EI-MS, *m/z* (rel. int., assign.): 457 (45%, M^+), 237 (6%, $C_{13}H_8SiMe_3$), 220 (100%, A = $N(CH_2CH_2O)_3Ge$), 165 (14%, $C_{13}H_9$), 160 (9%, A-$2CH_2O$), 146 (44%, A-CH_2O-CH_2CH_2O), 73 (22%, $SiMe_3$).

Analysis for $C_{22}H_{29}GeNO_3Si$ (456.15)
Calcd C 57.93 H 6.41 N 3.07%,
Found C 57.26 H 6.42 N 3.10%.

Germatrane **2** was also prepared by the reaction of ester **8** with mixture **B** ($C_{13}H_8(SiMe_3)GeBr_nCl_{3-n}$).

1-(9-Trimethylgermyl-9-fluorenyl)germatrane (**3**)

This synthesis was carried out as described for **2**, starting from **6** and **8**; yield 85%, m. p. 184 - 186~°C.

^{1}H NMR ($CDCl_3$): δ = –0.08 (s, 9H, $GeMe_3$); 3.67(t, 6H, OCH_2); 2.70 (t, 6H, NCH_2); 7.92 - 7.90, 7.87 - 7.84, 7.27 - 7.25(3m, 8H, Ar); ^{13}C NMR ($CDCl_3$): δ = –1.81 ($GeMe_3$), 49.85 (GeCGe), 52.56 (NCH_2), 57.16 (OCH_2), 119.16 (C-4,5), 123.67, 125.07, 125.24 (C-1,8; C-2,7; C-3,6), 139.35 (C-11,12), 148.10 (C-10,13). EI-MS, *m/z* (rel. int., assign.): 501 (45%, M^+), 486 (33%, M^+-CH_3), 266 (30%), 220 (100%, A = $N(CH_2CH_2O)_3Ge$), 179 (69%), 165 (78%, $C_{13}H_9$), 160 (29%, A-$2CH_2O$), 146 (70%, A-CH_2O-CH_2CH_2O), 119 (37%, $GeMe_3$).

Analysis for $C_{22}H_{29}Ge_2NO_3$ (500.66)
Calcd C 52.78 H 5.84 N 2.80%,
Found C 52.38 H 5.48 N 2.65%.

1-(9-Trimethylstannyl-9-fluorenyl)germatrane (**14**)

A mixture of 0.54 g (1.3 mmol) of 1-(9-fluorenyl)germatrane (**1**) and 0.8 g (3.85 mmol) of Me_3SnNMe_2 was heated to reflux in THF (6 ml) for 10 h. After cooling to room temperature and with addition of 3 ml of *n*-hexane, colourless crystals grew at –18 °C, which were dried in a vacuum; yield 0.59 g (77%), m. p. 195 - 196 °C.

^{1}H NMR ($CDCl_3$): δ = –0.16 (s, 9H, $SnMe_3$); 3.71 (t, 6H, OCH_2); 2.71 (t, 6H, NCH_2); 7.97 - 7.8, 7.32 - 7.23 (2m, 8H, Ar); ^{13}C NMR ($CDCl_3$): δ = –8.15 ($SnMe_3$), 48.75 (GeCSn), 52.09 (NCH_2), 56.98 (OCH_2), 119.19 (C-4,5), 122.76, 124.19, 125.09 (C-1,8; C-2,7; C-3,6), 138.03 (C-11,12), 148.51 (C-10,13). EI-MS, *m/z* (rel. int., assign.): 547 (6%, M^+), 532 (100%, M^+-CH_3), 502 (4%, M^+-$3CH_3$), 283 (5%, $C_{13}H_8Sn$), 220 (39%, A = $N(CH_2CH_2O)_3Ge$), 165 (32%, $C_{13}H_9$), 160 (9%, A-$2CH_2O$), 146 (9%, A-CH_2O-CH_2CH_2O).

Analysis for $C_{22}H_{29}GeNO_3Sn$ (540.75)
Calcd C 48.33 H 5.35 N 2.56%,
Found C 48.70 H 5.24 N 2.35%.

X-ray crystal structure determination [28]

Table II [29 - 33] summarises crystal data as well as details of data collection and structure refinement for compounds **2** and **14**. All non-hydrogen atoms of **2** and – except for C(14) – of **14** were refined anisotropically; the hydrogen atoms were placed on calculated positions and refined using a riding model.

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[28] Further details of the crystal structure determination can be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) (email: crysdata FIZ-Karlsruhe.de) under the depository number CSD-408779 for **2**, and CSD-408780 for **14**.

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