Novel derivatives of hypervalent germanium: synthesis, structure, and stability[†]

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Received 29th January 2009, Accepted 31st March 2009 First published as an Advance Article on the web 6th May 2009 DOI: 10.1039/b901885a

Syntheses of a series of novel germanium complexes, *viz.* $RN(CH_2CH_2NC_6F_5)_2GeHal_2$ (1, R = Me, Hal = Cl; 2, R = Me, Hal = Br; 3, R = PhCH_2, Hal = Cl; 4, R = PhCH_2, Hal = Br), as well as $MeN[CH_2(2-C_4H_3N)]_2GeHal_2$ (5, Hal = Cl; 6, Hal = Br), by the reaction of GeHal_4 with dilithium salts of corresponding triamines 7–9 are presented. PhCH_2N(CH_2CH_2NSiMe_3)_2GeCl_2 (10) was prepared analogously from triamine 11. Other approaches to the synthesized compounds were also tested. Unexpected complexes $[N(CH_2CH_2NSiMe_3)_2Ge(Hal)]_2$ (12, Hal = Cl; 13, Hal = Br) were obtained by the reaction of GeHal_4 with dilithium salt of Me_3SiN(CH_2CH_2NHSiMe_3)_2 (14). DFT calculations on this reaction were carried out and discussed. Composition and structures of the novel compounds were established by elemental analyses, ¹H, ¹³C, and ¹⁹F NMR spectroscopy. The X-ray structural studies of 1–4 and 12 clearly indicated the presence of a transannular interaction N(*ax*) \rightarrow Ge for all studied compounds.

Introduction

Aminodialkyldiamide ligands based on diethylenetriamines have enjoyed intense interest of transition metal chemists due to utility of the complexes with these ligands in organic chemistry.1-11 Schrock et al. and others have prepared alkylidyne and dinitrogen complexes of different transition metals. The derivatives of Zr were found to be effective catalysts for olefin polymerization. Yttrium complexes are catalysts for hydroamination reactions. Using these ligands, main group element analogues of these complexes have already been prepared for different group 13 elements. These derivatives catalyzed the polymerization of lactide. The structural chemistry of these compounds was also studied.¹²⁻¹⁵ In contrast, the coordination chemistry of 14 group elements with these ligands is sparse, despite the importance of these elements' derivatives for many technological applications, e.g. as an elemental semiconductor and in optics and ceramics in the case of germanium.

There are four papers devoted to compounds of 14 group elements based on the ligands in question.¹⁶⁻¹⁹ Several silicon derivatives were prepared by the transamination reaction of silicon dialkyldiamides with diethylenetriamines.¹⁶⁻¹⁸ Tin complexes, $MeN(CH_2CH_2NSiMe_3)_2SnCl_2$ and $MeN(CH_2CH_2N^iPr)_2SnCl_2$

were prepared by the metathetical reaction of dilithium salts of corresponding triamines with SnCl₄.¹⁹ The structure of the former of them was confirmed by X-ray data. However, no germanium derivatives were reported to date.

As a part of our investigation program to study the complexes of main group elements as well as transition metals with $Y(CH_2CH_2Z)_2^{2-}$ and $N(CH_2CH_2Z)_3^{3-}$ ligands (Y = AlkN, ArN; Z = O, NSiMe₃, NAlk),²⁰⁻³⁰ we report herein the synthesis and crystal structures of the first examples of germanium complexes based on diethylenetriamine type ligands—1,3,6,2-triazagermocanes or "azagermocanes". An unusual intramolecular dehalosilylation process was found and discussed.

Results and discussion

Three general approaches were used for construction of the target complexes' skeleton: the reaction of halogermanes with dilithium salts of the corresponding diethylenetriamines, transamination reaction of diethylenetriamines with aminogermanes and aminodehalogenation of halogermanes with corresponding diethylenetriamines in the presence of Et_3N . Our synthetic efforts are summarized in the Schemes 1 and 2.

Triamines **8** and **11** are novel and were prepared according to the synthetic procedures presented in Experimental.

The reaction of the dilithium salt of triamines **7–9** with tetrahalogermanes expectedly led to the target compounds **1–6**. Complex **1** was also obtained by the corresponding transamination reaction. Although the second route gave the higher yield of the target compound (55% *vs.* 48%) the first route is more preferable since tetrahalogermanes are easier to handle than GeHal₂(NMe₂)₂. In addition, our attempts to prepare **5** *via* the transamination route failed (see Experimental). The reactions of GeCl₂(NMe₂)₂ with **9** and **14** as well as Ge(NMe₂)₄ with **7**, **9**, and **14** were also unsuccessful.

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[†] Electronic supplementary information (ESI) available: Calculated Cartesian coordinates of transition states and stable compounds, electronic energies, numbers of imaginary frequencies. CCDC reference numbers 718433–718437 for the structures of **1–4** and **12**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b901885a



Scheme 2 Synthesis of compound 10 and digermanium derivatives 12 and 13.

Compound **10** was prepared *via* the "lithium" method. This complex also formed in the reaction of **11** with GeCl₄ in the presence of Et₃N. It should be noted that compound **10** is very unstable. Its structure was confirmed by NMR data.

Unlike the reactions described above, the treatment of tetrahalogermanes with dilithium salt of 14 as well as with 14 in the presence of Et_3N gave very unusual results. Digermanium derivatives 12 and 13 formed in both processes instead of the

Table 1	DFT	calculations on	12,	15,	and	16
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expected "Me₃SiN(CH₂CH₂NSiMe₃)₂GeHal₂". To gain a better understanding of the driving force behind these unusual reactions we carried out density functional calculations at the PBE level of theory on a geometry of **12** and Me₃SiN(CH₂CH₂NSiMe₃)₂GeCl₂ (**15**). The structure of hypothetical $N(CH_2CH_2NSiMe_3)_2Ge(Cl)$ (**16**) with covalent N–Ge^{TV} bond was also optimized (see Table 1).

It was found that the most thermodynamically stable molecule among the three studied species is digermanium derivative 12. We can suppose that 15 forms in the course of reaction but due to instability transforms into 12. The calculation results on 16 confirm that this compound is a believable intermediate in the transformation $15 \rightarrow 12$. The activation energy of this process (28.99 kcal mol⁻¹) demonstrates that this reaction may take place at room temperature. The value of *Eact* for the second transition state (TS2) is expectedly low. Thus, this process falls into a very rare transformation of transannular bond (in 15) into covalent bond (in 16) and back into transannular bond (in 12).

We believe that the main driving force for this reaction is steric proximity of the halogen atom and Me₃Si group bound to the nitrogen atom of $N(CH_2...)_2$ which appears due to the formation of transannular Ge–N bond. It should be noted that the covalent Si–N bond in Me₃SiN group weakens also due to the presence of transannular bond.

In order to estimate the ability of the prepared dihalogermanium complexes to serve precursors for the preparation of novel germanium compounds we studied the reactions of **1** with MeN(CH₂CH₂NLiC₆F₅)₂, PhCH₂N(CH₂CH₂OSiMe₃)₂, and *n*-BuLi. It was found that Ge–Cl bond in **1** is unreactive towards MeN(CH₂CH₂NLiC₆F₅)₂ and PhCH₂N(CH₂CH₂OSiMe₃)₂, while the reaction with *n*-BuLi leads to destruction of "ocane" skeleton. This behaviour is similar to the previously found for azagermatranes with bulky substituents at the equatorial nitrogen atoms, for example, for N(CH₂CH₂NC₆F₅)₃GeCl.³¹

The structure of the prepared compounds was confirmed by NMR spectroscopy and elemental analysis data. The structures of **1–4** and **12** in the solid state were studied by X-ray crystallography. The molecular structures of **1–4** and **12** are shown in Fig. 1–5, respectively. Tables 2 and 3 summarize the significant geometrical parameters of these compounds.

The coordination polyhedron of the Ge atom in compounds 1–4 represents a distorted trigonal bipyramid with N(1) (for compound 1–3) or N(11) (for compound 4) and halogen atoms Cl(1) (for 1 and 3), Br(1) (for 2) or Br(11) (for 4) occupying the axial positions. The two nitrogen atoms and one halogen atom form the equatorial plane in each molecule. The Ge-Hal(ax) bond is expectedly longer than the Ge-Hal(eq) bond in the same molecule. This is in accordance with the hypervalent bond theory. The strength of the intramolecular transannular

System	E/Hartree	$\Delta E/\text{kcal mol}^{-1}$
15 (two molecules)	-9090.472254	11.40
TS1 (15 \rightarrow 16 + Me ₃ SiCl) (two pairs of molecules)	-9090.379871	$40.39 (Eact 15 \rightarrow 16 = 28.99)$
16 (two molecules) + $2Me_3SiCl$	-9090.455830	21.70
TS2 $(2 16 \rightarrow 12) + 2 Me_3 SiCl$	-9090.446120	27.79 (Eact $16 \rightarrow 12 = 6.09$)
$12 + 2Me_3SiCl$	-9090.490413	0.00
^{<i>a</i>} See ESI for details of structure calculations [†]		



Fig. 1 Molecular structure of complex 1. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.



Fig. 2 Molecular structure of complex **2**. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

interaction (in this case $N(ax) \rightarrow Ge$) in the hypervalent main group element derivatives is the most intriguing aspect of their structure. For compounds 1-4 these distances vary within the range 2.118(2) Å (1) to 2.169(3) Å (4). These values testify to the presence of strong hypervalent interactions in these compounds and are close to those previously found in dihalogermocanes, MeN(CH₂CH₂O)₂GeBr₂, 2.166(5) Å,²² PhN(CH₂CH₂O)₂GeHal₂, 2.202(4) Å (Hal = Cl), 2.202(2) Å (Hal = Br).²³ At the same time N(ax) \rightarrow Ge distances in 1-4 are significantly shorter than that in *iso*-BuN(CH₂CH₂CH₂)₂GeCl₂ (2.389(4) Å).³² Therefore, the nature of groups bound to germanium atom in dihalogermocanes crucially influences the N(ax) \rightarrow Ge bond length, while the nature of substituent at the N(ax) atom is not so important.



Fig. 3 Molecular structure of complex **3**. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.



Fig. 4 Molecular structure of complex **4**. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

This conclusion is supported by X-ray data obtained early for three azagermatranes. The N(*ax*) \rightarrow Ge bond distances in these compounds vary in broad interval due to varying of the equatorial groups at Ge atom: N(CH₂CH₂N₆F₅)₃GeCl (2.148(7) Å),³¹ N(CH₂CH₂NMe)₃Ge–Cl (2.167(4) Å), N(CH₂CH₂NSiMe₃)₃GeCl (2.278(2) Å).²⁰

The coordination polyhedron of the N(eq) atoms in compounds 1–4 is a slightly distorted trigonal plane while the environment of the N(ax) atoms is approximately tetrahedral. For these

	1 (R = Me, Hal = Cl)	2 (R = Me, Hal = Br)	3 (R = PhCH ₂ , Hal = Cl)	4^{a} (R = PhCH ₂	, Hal = Br)
$N(ax) \rightarrow Ge$	2.118(2)	2.132(6)	2.157(2)	2.161(4)	2.169(3)
Ge-Hal(ax)	2.2400(6)	2.414(1)	2.2269(7)	2.4100(7)	2.4226(7)
Ge-Hal(eq)	2.1719(6)	2.333(1)	2.1798(8)	2.3442(7)	2.3328(7)
N(eq)-Ge	1.833(2)	1.834(6)	1.832(2)	1.834(4)	1.831(4)
	1.839(2)	1.848(6)	1.836(2)	1.837(4)	1.842(4)
$N(ax) \rightarrow Ge-Hal(ax)$	174.35(6)	175.0(2)	176.91(7)	177.0(1)	171.7(1)
$N(ax) \rightarrow Ge-Hal(eq)$	92.24(6)	92.3(2)	90.01(7)	91.0(1)	94.0(1)
$N(ax) \rightarrow Ge-N(eq)$	82.37(8)	82.4(2)	82.41(9)	82.0(2)	81.9(2)
	83.11(8)	81.8(2)	82.8(1)	82.8(2)	81.6(2)
$N(eq) \rightarrow Ge-Hal(eq)$	118.60(6)	120.5(2)	120.30(8)	122.0(1)	121.0(1)
	113.11(6)	113.4(2)	113.90(8)	114.1(1)	113.2(1)
$N(eq) \rightarrow Ge-Hal(ax)$	94.15(6)	95.1(2)	95.85(7)	95.6(1)	93.3(1)
	95.52(6)	96.1(2)	96.16(8)	97.0(1)	95.8(1)
$N(eq) \rightarrow Ge-N(eq)$	12655(8)	124.1(3)	123.5(1)	121.8(2)	124.1(2)
$\operatorname{Hal}(eq) \rightarrow \operatorname{Ge-Hal}(ax)$	93.34(3)	92.69(4)	93.07(3)	91.83(2)	94.27(2)

Table 2 Selected bond lengths (Å) and angles (°) for 1-4 [$RN(ax)(CH_2CH_2N(eq)C_6F_5)_2Ge(Hal(eq))Hal(ax)$]

Table 3 Selected bond lengths (Å) and angles (°) for 12^a

Ge(1)-N(13)	2 118(3)	Ge(2)-N(23)	2 113(3)
Ge(1) = N(13) #1	1.949(3)	Ge(2) - N(23) = 2	1.945(3)
Ge(1) - N(12)	1.832(3)	Ge(2) - N(21)	1.833(3)
Ge(1)-N(11)	1.836(3)	Ge(2) - N(22)	1.840(3)
Ge(1)–Cl(1)	2.2872(9)	Ge(2)–Cl(2)	2.2837(9)
N(13)-Ge(1)-Cl(1)	171.57(7)	N(23)–Ge(2)–Cl(2)	171.08(7)
N(12)-Ge(1)-N(11)	123.6(1)	N(21)-Ge(2)-N(22)	123.4(1)
N(12)-Ge(1)-N(13)#1	120.0(1)	N(21)-Ge(2)-N(23)#2	118.9(1)
N(11)-Ge(1)-N(13)#1	113.2(1)	N(22)-Ge(2)-N(23)#2	114.5(1)
N(12)-Ge(1)-N(13)	85.9(1)	N(21)-Ge(2)-N(23)	86.2(1)
N(11)-Ge(1)-N(13)	85.7(1)	N(22)-Ge(2)-N(23)	85.7(1)
N(13)#1-Ge(1)-N(13)	80.2(1)	N(23)#2-Ge(2)-N(23)	80.0(1)
N(12)–Ge(1)–Cl(1)	98.22(9)	N(21)-Ge(2)-Cl(2)	98.65(9)
N(11)-Ge(1)-Cl(1)	98.00(9)	N(22)-Ge(2)-Cl(2)	97.67(9)
N(13)#1-Ge(1)-Cl(1)	91.41(8)	N(23)#2-Ge(2)-Cl(2)	91.08(8)
#1_x + 1 _v + 1 _z + 1	$1 \cdot #2 - x - y$	$\pm 1 = 7$ "Two independent	nt molecules

compounds, the axial nitrogen atoms are displaced from the plane defined by the three carbon atoms toward the germanium atom.

The same structural trends discussed above for 1–4 were found in compound 12. It should be especially noted that the transannular $N(ax) \rightarrow Ge$ distance in 12 is the shortest among those found for studied azagermocanes and azagermatranes.³³ This short bond corresponds to long covalent bond Ge(1)–N(13A), thus compound 12 should be considered as two mesomeric forms (Scheme 3).



Scheme 3 Two mesomeric forms for 12.

Conclusions

We have prepared and structurally characterized a novel class of germanium complexes—azagermocanes. The strong hypervalent interaction $N \rightarrow Ge$ was found in these compounds. In the course of the preparation of tris(silyl) derivatives an unusual intramolecular dehalosilylation process was found. The DFT calculation data support the suggestion about consecutive order of bond transformation during this reaction: hypervalent bond–covalent bond–hypervalent bond.

Experimental

All manipulations were performed under dry, oxygen-free argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. GeHal₄ (Cl, Br) (Aldrich) were distilled prior to use. Starting materials MeN(CH₂CH₂NHC₆F₅)₂ (7),² bis-pyrrol derivative (9),³⁴ Me₃SiN(CH₂CH₂NHSiMe₃)₂ (14),³⁵ Ge(NMe₂)₄,³⁶





Fig. 5 Molecular structure of complex **12**. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

 $Cl_2Ge(NMe_2)_4$,³⁷ PhCH₂N(CH₂CH₂OSiMe₃)₂,²⁹ and *N*,*N*-bis(2phthalimidoethyl)amine³⁸ were prepared according to the literature. C₆D₆ was obtained from Deutero GmbH and dried over sodium. ¹H, ¹³C, and ¹⁹F NMR spectra were recorded with Bruker AC300 and Bruker Avance 400 spectrometers at room temperature. ¹H and ¹³C chemical shifts are reported in ppm relative to Me₄Si as external standard; in ¹⁹F NMR experiments CFCl₃ 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) 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.

PhCH₂N(CH₂CH₂NHC₆F₅)₂ (8)

A mixture of HN(CH₂CH₂NHC₆F₅)₂ (12.07 g, 0.028 mol), K₂CO₃ (21.30 g, 0.150 mol), PhCH₂Cl (4.20 g, 0.033 mol), and 120 ml CH₃CN was stirred at 60 °C for two weeks. All volatiles were removed under vacuum. Water (200 ml) was added to the residue and the mixture was extracted with ethyl acetate (3 × 200 ml). Combined organic extracts were dried over MgSO₄. All volatiles were removed under vacuum to give **8** as a deep-brown oil which was used without further purification. Yield: 10.41 g (71%). ¹H NMR (C₆D₆, 300 MHz) δ = 7.02–7.20 (m, 5H, Ph), 3.82 (br s, 2H, NH), 3.11 (s, 2H, NH₂Ph), 2.91–2.96 (m, 4H, NH₂), 2.15–2.19 '(m, 4H, NH₂). An analytically pure sample (colourless oil) was obtained after chromatography (eluent: hexane). Refluxing of a reaction mixture (first stage) led to the crude **8** (yield = 58%), which contained a considerable amount of undesirable PhCH₂OOCN(CH₂CH₂NHC₆F₅)₂ (X-ray data).³⁹

PhCH₂N(CH₂CH₂NHSiMe₃)₂ (11)

Benzyl-bis(2-phthalimidoethyl)amine. A mixture of *N*,*N*-bis(2-phthalimidoethyl)amine (7.27 g, 0.020 mol), Na₂CO₃ (2.12 g, 0.020 mol) and PhCH₂Cl (3.16 g, 0.025 mol) in EtOH (abs., 300 ml) was refluxed for 25 h. The warm solution was filtered and chilled (-30 °C). A white precipitate was separated by filtration and dried in vacuum. Yield: 6.08 g (67%). ¹H NMR (C₆D₆, 400 MHz) δ = 7.39–7.42, 7.07–7.12, 6.93–6.95, 6.85–6.89 (m, 13H, aromatic protons), 3.55 (t, 4H, NH₂), 3.43 (s, 2H, Ph*CH*₂), 2.58 (t, 4H, NH₂). ¹³C NMR (C₆D₆, 100 MHz) δ = 167.80 (CO), 139.36, 133.11, 132.93, 129.34, 128.20, 126.92, 122.78, (aromatic carbons), 58.28 (CH₂Ph), 52.02, 35.80 (NCH₂).

PhCH₂**N(CH**₂**CH**₂**NH**₂)₂. A suspension of benzyl-bis(2phthalimidoethyl)amine (3.70 g, 8.0 mmol) in 36% HCl (aq.) was refluxed for 25 h. Two thirds of the volatiles were evaporated in vacuum and the precipitate was filtered off. The filtrate was evaporated in vacuum and the residue was refluxed for 5 h in a solution of NaOH (2.4 g, 0.060 mol) in 50 ml H₂O. Two thirds of the volatiles were evaporated in vacuum and the residue was extracted with toluene (3 × 30 ml). Combined organic extracts were dried over MgSO₄. All volatiles were removed under vacuum to give a yellow oil which was used without further purification. Yield: 1.03 g (65%). ¹H NMR (C₆D₆, 400 MHz) δ = 7.23–7.25, 7.14–7.19, 6.99–7.12 (m, 5H, Ph), 3.49 (br s, 4H, NH₂), 3.34 (s, 2H, Ph*CH*₂), 2.51 (q, 4H, NH₂), 2.25 (t, 4H, NH₂).

PhCH₂N(CH₂CH₂NHSiMe₃)₂ (11). To a stirred solution of PhCH₂N(CH₂CH₂NH₂)₂ (1.90 g, 9.8 mmol) in 20 ml of toluene 12.25 ml of a 1.6 M n-BuLi solution (19.6 mmol) in hexane was added dropwise at -78 °C. The reaction mixture was stirred for 1 h and allowed to warm to room temperature. The reaction mixture was chilled to -78 °C and Me₃SiCl (2.14 g, 19.6 mmol) was added with stirring. After an additional stirring within 24 h at room temperature a white precipitate of LiCl was separated by filtration. The precipitate was extracted with toluene (50 ml) and organic solutions were combined. The volatiles were evaporated in vacuum and the residue was fractionated. Yield: 2.17 g (66%), vellow oil. Bp = 105–107 °C (0.3 mmHg). ¹H NMR (C₆D₆, 400 MHz) δ = 7.30-7.32, 7.17-7.21, 7.07-7.10 (m, 5H, Ph), 3.43 (s, 2H, PhCH₂), 2.75 (q, 4H, NH₂), 2.37 (t, 4H, NH₂), 0.07 (s, 18H, SiMe₃). ¹³C NMR (C₆D₆, 100 MHz) δ = 140.26, 128.97, 128.25, 126.94 (Ph), 59.42, 58.28 39.81 (PhCH₂, NCH₂), 0.06 (SiMe₃).

MeN(CH₂CH₂NC₆F₅)₂GeCl₂ (1)

Method 1. To a stirred solution of 7 (2.40 g, 5.3 mmol) in 30 ml of toluene was 7.50 ml of a 1.6 M n-BuLi solution (12.0 mmol) in hexane added dropwise at -78 °C. The reaction mixture was stirred for 1 h and allowed to warm to room temperature. The reaction mixture was chilled to -78 °C and GeCl₄ (1.14 g, 5.3 mmol) in 10 ml of toluene was added with stirring. After an additional stirring within 24 h at room temperature a white precipitate of LiCl was separated by filtration. The precipitate was extracted with toluene (50 ml) and organic solutions were combined. Half of the volatiles were evaporated in vacuum and 30 ml of diethyl ether were added. A white crystalline solid was separated by filtration, washed by cold diethyl ether $(3 \times 5 \text{ ml})$ and dried in vacuum. Yield: 1.50 g (48%). ¹H NMR (C₆D₆, 300 MHz) δ = 2.77–2.83 (m, 2H, CH₂), 2.69–2.75 (m, 2H, CH₂), 2.20–2.26 (m, 2H, CH₂), 1.92–1.98 (m, 2H, CH₂), 1.93 (s, 3H, Me). ¹³C NMR (C₆D₆, 75 MHz) δ = $50.99, 45.04, (CH_2), 43.37 (Me).$ ¹⁹F NMR (C₆D₆, 376.4 MHz) $\delta =$ -163.60-163.14 (m, 2F), -157.54 (t, 1F), -146.52-146.47 (m, 1F), -146.05 - 145.97 (m, 1F). EI m/z 252 (M-GeCl₂-CH₂NC₆F₅, 100%). Anal. calcd for C₁₇H₁₁Cl₂F₁₀GeN₃ (590.79): C, 34.57; H, 1.88. Found: C, 34.65; H, 2.06%.

An analogous reaction of GeCl_4 (0.60 g, 2.8 mmol) with two equivalents of 7 (2.52 g, 5.6 mmol) and 7.00 ml of a 1.6 M *n*-BuLi solution (11.2 mmol) gave 1. Yield: 0.40 g (24%).

Method 2. A mixture of 7 (2.25 g, 5.0 mmol) and $Cl_2Ge(NMe_2)_2$ (1.16 g, 5.0 mmol) was heated at 130 °C for 25 h. Toluene (15 ml) was added to the mixture at room temperature. White solid was separated by filtration, washed by cold diethyl ether (3 × 5 ml) and dried in vacuum. Yield: 1.62 g (55%).

MeN(CH₂CH₂NC₆F₅)₂GeBr₂ (2)

The procedure was analogous to that for **1**, Method 1: reaction of **7** (1.79 g, 4.0 mmol) with 5.13 mL of a 1.6 M *n*-BuLi solution (8.2 mmol) in hexane and then with GeBr₄ (1.57 g, 4.0 mmol) gave **2** as a beige solid. Yield: 0.79 g (29%). ¹H NMR (C₆D₆, 300 MHz) $\delta = 2.68-2.80$ (m, 4H, CH₂), 2.14–2.20 (m, 2H, CH₂), 1.90–1.96 (m, 2H, CH₂), 1.85 (s, 3H, Me). ¹³C NMR (C₆D₆, 75 MHz) $\delta = 50.48, 45.27, (CH₂), 43.64$ (Me). ¹⁹F NMR (C₆D₆, 376.4 MHz) $\delta = -163.34-163.05$ (m, 2F), -156.82 (t, 1F), -146.03-145.98 (m, 1F), -145.14-145.22 (m, 1F). EI *m*/*z* 599 (M–Br, 4%), 485

 $\begin{array}{l} (M-CH_2NC_6F_5,\,3\%)^*,\,252\;(M-GeCl_2-CH_2NC_6F_5,\,100\%).\;Anal.\\ calcd\;for\;C_{17}H_{11}Br_2F_{10}GeN_3\;(679.69):\;C,\;30.05;\;H,\;1.63;\;N,\;6.18.\\ Found:\;C,\;30.37;\;H,\;1.81;\;N,\;5.85\%. \end{array}$

PhCH₂N(CH₂CH₂NC₆F₅)₂GeCl₂ (3)

The procedure was analogous to that for **1**, Method 1: reaction of **8** (4.29 g, 8.0 mmol) with 10.13 mL of a 1.6 M *n*-BuLi solution (16.2 mmol) in hexane and then with GeCl₄ (1.70 g, 8.0 mmol) gave **3** as a beige solid. Yield: 1.17 g (22%). ¹H NMR (C₆D₆, 300 MHz) $\delta = 6.99-7.12$ (m, 3H, Ph), 6.64–6.66 (m, 2H, Ph), 3.84 (s, 2H, Ph*CH*₂), 2.88–2.93 (m, 2H, NCH₂), 2.77–2.82 (m, 2H, NCH₂), 2.21–2.36 (m, 4H, CH₂). ¹³C NMR (C₆D₆, 75 MHz) $\delta = 131.64$, 130.71, 129.26, 128.51 (Ph), 56.74 (Ph*CH*₂), 45.81, 45.03 (NCH₂). ¹⁹F NMR (C₆D₆, 376.4 MHz) $\delta = -164.04-163.72$ (m, 2F), -157.89 (t, 1F), -147.16 (br s, 1F), -146.61–-146.54 (m, 1F). Anal. calcd for C₂₃H₁₅Cl₂F₁₀GeN₃ (666.88): C, 41.42; H, 2.27; N, 6.30. Found: C, 40.97; H, 2.43; N, 5.92%.

PhCH₂N(CH₂CH₂NC₆F₅)₂GeBr₂ (4)

The procedure was analogous to that for 1, Method 1: reaction of **8** (2.80 g, 5.0 mmol) with 6.38 mL of a 1.6 M *n*-BuLi solution (10.2 mmol) in hexane and then with GeBr₄ (1.97 g, 5.0 mmol) gave **4** as a beige solid. Yield: 0.50 g (13%). ¹H NMR (C₆D₆, 300 MHz) $\delta = 6.99-7.12$ (m, 3H, Ph), 6.64–6.66 (m, 2H, Ph), 3.86 (s, 2H, Ph*CH*₂), 2.92–2.87 (m, 2H, NCH₂), 2.79–2.85 (m, 2H, NCH₂), 2.35–2.41 (m, 2H, NCH₂), 2.24–2.30 (m, 2H, NCH₂). ¹³C NMR (C₆D₆, 75 MHz) $\delta = 131.65$, 130.37, 129.40, 128.95 (Ph), 56.98 (Ph*CH*₂), 45.29 (2NCH₂). ¹⁹F NMR (C₆D₆, 376.4 MHz) $\delta = -164.22-164.03$ (m, 2F), -157.91 (t, 1F), -146.51-146.46 (m, 1F), -145.83-145.85 (m, 1F). Anal. calcd for C₂₃H₁₅Cl₂F₁₀GeN₃ (755.79): C, 36.55; H, 2.00; N, 5.56. Found: C, 36.23; H, 2.21; N, 5.31%.

$MeN(CH_2-C_4H_3N)_2GeCl_2 (5)$

The procedure was analogous to that for **1**, Method 1: reaction of **9** (0.62 g, 3.0 mmol) with 3.81 mL of a 1.6 M *n*-BuLi solution (6.1 mmol) in hexane and then with GeCl₄ (0.70 g, 3.0 mmol) gave **3** as a beige solid. Yield: 0.52 g (52%). ¹H NMR (C₆D₆, 300 MHz) $\delta = 7.50-7.51$ (m, 2H, pyrrole ring protons), 6.27–6.31 (m, 2H, pyrrole ring protons), 5.91–5.95 (m, 2H, pyrrole ring protons), 2.78–3.01 (dd, 4H, NCH₂), 1.73 (s, 3H, Me). ¹³C NMR spectrum was not registered due to very low solubility in C₆D₆. Anal. calcd for C₁₁H₁₃Cl₂GeN₃ (330.76): C, 39.94; H, 3.96; N, 12.70. Found: C, 40.07; H, 3.81; N, 12.98%.

$MeN(CH_2-C_4H_3N)_2GeBr_2$ (6)

The procedure was analogous to that for **1**, Method 1: reaction of **9** (1.09 g, 6.0 mmol) with 7.63 mL of a 1.6 M *n*-BuLi solution (12.2 mmol) in hexane and then with GeBr₄ (2.26 g, 6.0 mmol) gave **3** as a beige solid. Yield: 0.41 g (16%). ¹H NMR (C₆D₆, 300 MHz) $\delta = 7.50-7.51$ (m, 2H, pyrrole ring protons), 6.27-6.31 (m, 2H, pyrrole ring protons), 5.91-5.95 (m, 2H, pyrrole ring protons), 2.78-3.01 (dd, 4H, NCH₂), 1.73 (s, 3H, Me). ¹³C NMR (C₆D₆, 75 MHz) $\delta = 129.38$, 123.83, 112.00, 107.76 (pyrrole ring), 52.66 (CH₂), 44.20 (Me). Anal. calcd for C₁₁H₁₃Br₂GeN₃ (419.66): C, 31.48; H, 3.12; N, 10.01. Found: C, 31.44; H, 3.30; N, 9.82%.

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PhCH₂N(CH₂CH₂NSiMe₃)₂GeCl₂ (10)

Method 1. The procedure was analogous to that for 1, Method 1: reaction of 11 (0.32 g, 1.0 mmol) with 1.25 mL of a 1.6 M *n*-BuLi solution (2.0 mmol) in hexane and then with GeCl₄ (0.20 g, 1.0 mmol) gave a red oil which contained 10 according to ¹H NMR. Yield (crude): 0.21 g (43%). All attempts to purify or investigate this compound with other analytical methods failed. ¹H NMR (C₆D₆, 300 MHz) δ = 7.09–7.14 (m, 3H, Ph), 6.82–6.86 (m, 2H, Ph), 3.61 (s, 2H, Ph*CH*₂), 2.65–2.88 (m, 4H, NCH₂), 2.29–2.39 (m, 2H, NCH₂), 1.68–1.79 (m, 2H, NCH₂), 0.40 (s, 18H, SiMe₃).

Method 2. To a stirred solution of GeCl_4 (0.49 g, 2.3 mmol) in 10 ml of toluene a solution of **14** (0.76 g, 2.3 mmol) and Et₃N (0.47 g, 4.6 mmol) in toluene (10 ml) was added dropwise at -78 °C. The stirring reaction mixture was allowed to warm to room temperature overnight. The precipitate (Et₃N·HCl) was separated by filtration. Volatiles were evaporated in vacuum. A red oil contained **10** according to ¹H NMR.

[N(CH₂CH₂NSiMe₃)₂Ge(Cl)]₂ (12)

Method 1. The procedure was analogous to that for 1, Method 1: reaction of 14 (2.95 g, 9.0 mmol) with 11.25 mL of a 1.6 M *n*-BuLi solution (18.0 mmol) in hexane and then with GeCl₄ (1.93 g, 9.0 mmol) gave 12 as a white solid (after recrystallisation from toluene). Yield: 1.12 g (35%). ¹H NMR (C₆D₆, 300 MHz) $\delta = 3.23-3.29$ (m, 4H, CH₂), 2.94–3.00 (m, 4H, CH₂), 2.74–2.80 (m, 4H, CH₂), 2.06–2.12 (m, 4H, NCH₂), 0.38 (s, 36H, SiMe₃). ¹³C NMR (C₆D₆, 75 MHz) $\delta = 51.62$ (CH₂), 43.28 (CH₂), 3.63 (SiMe₃). EI *m*/*z* 352 (1/2M, 4%), 252 (1/2M – CH₂NSiMe₃, 9%); 237 (16) (1/2M – CH₂CH₂NSiMe₃, 16%). Anal. calcd for C₂₀H₅₂Cl₂Ge₂N₆ (705.13): C, 34.07; H, 7.43; N, 11.92. Found: C, 34.41; H, 7.70; N, 11.65%.

Method 2. To a stirred solution of GeCl₄ (0.99 g, 4.6 mmol) in 10 ml of toluene a solution of **14** (1.47 g, 4.6 mmol) and Et₃N (0.93 g, 9.2 mmol) in toluene (20 ml) was added dropwise at -78 °C. The stirring reaction mixture was allowed to warm to room temperature. The precipitate (Et₃N·HCl) was separated by filtration. Half of the volatiles were evaporated in vacuum and 10 ml of diethyl ether were added. A white crystalline solid was separated by filtration, washed by cold diethyl ether (3 × 5 ml) and dried in vacuum. Yield: 1.00 g (62%).

$[N(CH_2CH_2NSiMe_3)_2Ge(Br)]_2$ (13)

The procedure was analogous to that for 1, Method 1: reaction of 14 (2.11 g, 6.6 mmol) with 8.25 mL of a 1.6 M *n*-BuLi solution (13.2 mmol) in hexane and then with GeCl₄ (2.60 g, 6.6 mmol) gave 13 as a white solid (after recrystallisation from toluene) Yield: 1.12 g (35%). ¹H NMR (C₆D₆, 300 MHz) δ = 3.23–3.28 (m, 4H, CH₂), 2.95–3.02 (m, 4H, CH₂), 2.75–2.81 (m, 4H, CH₂), 1.99–2.04 (m, 4H, NCH₂), 0.40 (s, 36H, SiMe₃). ¹³C NMR spectrum was not registered due to very low solubility in C₆D₆. EI *m/z* 397 (1/2M, 1%), 296 (1/2M – CH₂NSiMe₃, 9%), 217 (16) (1/2M – Br – CH₂NSiMe₃, 5%), 147 (1/2M – Br – SiMe₃ – CH₂NSiMe₃, 100%). Anal. calcd for C₂₀H₅₂Br₂Ge₂N₆ (794.04): C, 30.25; H, 6.60; N, 10.58. Found: C, 30.75; H, 7.03; N, 10.93%.

Reaction of Ge(NMe₂)₄ with 7

The mixture of 7 (1.51 g, 3.0 mmol) and $Ge(NMe_2)_4$ (0.84 g, 3.0 mmol) was heated at 130 °C for 72 h. According to ¹H NMR spectroscopy data, only starting materials were found in the reaction mixture.

Reaction of Cl₂Ge(NMe₂)₂ with 9

The mixture of **9** (0.19 g, 1.0 mmol) and $Cl_2Ge(NMe_2)_2$ (0.23 g, 1.0 mmol) was heated at 80 °C for 24 h. According to ¹H NMR spectroscopy data, only starting materials were found in the reaction mixture.

Reaction of Ge(NMe₂)₄ with 9

The mixture of **9** (0.19 g, 1.0 mmol) and Ge(NMe₂)₄ (0.25 g, 1.0 mmol) was heated at 80 °C for 24 h. According to ¹H NMR spectroscopy data, only starting materials were found in the reaction mixture.

Reaction of Cl₂Ge(NMe₂)₂ with 14

To a stirred solution of $Cl_2Ge(NMe_2)_2$ (0.58 g, 2.5 mmol) in 25 ml of toluene **14** (0.8 g, 2.5 mmol) was added. The reaction mixture was refluxed for 72 h resulting (according to ¹H NMR spectrum) in a complex mixture of products which were difficult to separate and to identify.

Reaction of Ge(NMe₂)₄ with 14

The mixture of **14** (0.35 g, 1.0 mmol) and $Ge(NMe_2)_4$ (0.27 g, 1.0 mmol) was heated at 130 °C for 24 h resulting (according to ¹H NMR spectrum) in a complex mixture of products which were difficult to separate and to identify.

Reaction of 1 with MeN(CH₂CH₂NLiC₆F₅)₂

The procedure was analogous to that for 1, Method 1 except 1 was used instead of GeCl_4 : reaction of 7 (0.57 g, 1.3 mmol) with 1.63 mL of a 1.6 M *n*-BuLi solution (2.6 mmol) in hexane

 Table 4
 X-Ray structure determination summary

Reaction of 1 with PhCH₂N(CH₂CH₂OSiMe₃)₂

A solution of **1** (0.04 g, 0.07 mmol) and PhCH₂N-(CH₂CH₂OSiMe₃)₂ (0.02 g, 0.07 mmol) in toluene (15 ml) was refluxed for 15 h resulting (according to ¹H NMR spectrum) in a complex mixture of products which were difficult to separate and to identify.

Reaction of 1 with *n*-BuLi

To a suspension of 1 (0.10 g, 0.17 mmol) in toluene (10 ml) 0.21 ml of a 1.6 M *n*-BuLi solution (0.34 mmol) in hexane was added dropwise at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for further 24 h (1 dissolved in 40 min after the treatment). A precipitate of LiCl was filtered off. The filtrate was evaporated resulting (according to ¹H NMR spectrum) in a complex mixture of products which were difficult to separate and to identify.

Computational procedure

Density functional (DFT) study was carried out using the *ab initio* generalized gradient approximation and the PBE⁴⁰ functional with the TZ2P basis set and "Priroda" software.⁴¹ Geometry optimization was carried out for all stable compounds and for the structures corresponding to the saddle points (in the case of transition states, TS). The types of the stationary points were confirmed by the vibrational frequency analysis. For the saddle points, the reaction coordinates were also calculated. All computations were performed for the gas phase.

X-Ray crystallography

Crystal data and details of X-ray analyses are given in Table 4. All experimental datasets were collected on a Bruker SMART diffractometer using graphite monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å) at 120 K. Absorption correction based on measurements of equivalent reflections was applied. The structures

Compound	1	2	3	4	12
Formula	$C_{27.5}H_{23}Cl_2F_{10}Ge_1N_3$	$C_{27.5}H_{23}Br_2F_{10}Ge_1N_3$	C_{33} $_{5}H_{27}Cl_{2}F_{10}Ge_{1}N_{3}$	$C_{24,75}H_{17}Br_2F_{10}Ge_1N_3$	C ₂₀ H ₅₂ Cl ₂ Ge ₂ N ₆ Si ₄
М	728.98	817.90	805.07	778.82	705.12
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_{1}/c$	Pbca	$P2_{1}/c$	ΡĪ	$P2_{1}/c$
a/Å	7.4562(6)	14.4325(5)	7.3340(5)	7.7668(5)	16.744(3)
b/Å	22.0794(17)	21.6686(8)	19.8573(12)	16.6310(10)	14.569(2)
c/Å	17.7878(14)	19.2039(7)	22.7800(14)	20.6711(12)	13.503(2)
$\alpha/^{\circ}$	90	90	90	83.241(1)	90
$\beta/^{\circ}$	90.241(2)	90	90.994(2)	80.160(1)	90.501(4)
γ°	90	90	90	87.979(1)	90
$V/Å^3$	2928.4(4)	6005.7(4)	3317.0(4)	2612.2(3)	3293.9(9)
Ζ	4	8	4	4	4
μ/mm^{-1}	1.317	3.768	1.171	4.326	2.154
Data collected	19 274	35 4 49	17 319	15498	18 868
Unique data (R_{int})	6279 (0.0285)	5583 (0.0748)	7198 (0.0371)	9391 (0.0343)	7896 (0.0428)
$R_1[I > 2\sigma(I)]$	0.0338	0.0667	0.0462	0.0424	0.0466
wR_2 (all data)	0.0846	0.1791	0.1111	0.0946	0.1179

were solved by direct methods⁴² and refined by full-matrix leastsquares on F^{243} with anisotropic thermal parameters for all non-hydrogen atoms (except disordered toluene molecules). All measured structures contain solvent toluene molecules disordered over crystallographic inversion centres. All hydrogen atoms were placed in calculated positions and refined using a riding model. In the monoclinic structures **1**, **3** and **12**, β angles are close to 90° and they may emulate the orthorhombic crystal system. The possibility of pseudo-merohedric twinning for these structures was checked, however, no twinning behaviour was observed. **12** contains two crystallographically independent pseudo-symmetric molecules. The refinement of **12** in higher symmetry space group *Pbca* was found to be unsatisfactory.

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