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# Note

# Reaction of germanes and digermanes with triflic acid: The route to novel organooligogermanes

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## A R T I C L E I N F O

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# 1. Introduction

# In the last few years chemistry of organogermanium compounds attracts intent attention of researchers and especially interest is given to oligogermanes [1,2]. This interest is based not only on academic investigations [3-5] but also on a search of new unique properties of these compounds such as thermochromism, absorption in UV/visible spectral region [6–15], conductivity, luminescence [16]. Besides organogermanium compounds may be used as precursors for synthesis of new materials for example nanostructures [17]. The main problem in chemistry of oligogermans consists in limitation of reliable synthetic methods for obtaining compounds with required structure and properties. The reaction of hydrogermolysis developed by Weinert et al. [15] and also application of alkaline organogermanium reagents investigated by Marschner, Baumgartner et al. [14] partially solved this problem. Meanwhile, a search of new techniques for modification of organogermanium compounds and improvement of synthesis of known widely used compounds may be regarded as a topic for investigation.

#### ABSTRACT

Novel germanium containing triflates were prepared from the reactions of trifluoromethanesulfonic acid with tetraphenylgermane (1) and digermanes (Ph<sub>3</sub>GeGeMe<sub>3</sub> (4), Ph<sub>3</sub>GeGePh<sub>3</sub> (5)). The improved procedures for synthesis of known organogermanium compounds (Ph<sub>4</sub>Ge (1), Ph<sub>3</sub>GeGeI (2), Ph<sub>3</sub>GeGeMe<sub>3</sub> (4), Ph<sub>3</sub>GeGePh<sub>3</sub> (5)) were also presented. The crystal structure of Ph<sub>3</sub>GeOTf (6) and Ph<sub>2</sub>Ge(OTf)Ge(OTf) Ph<sub>2</sub> (7) was studied by X-ray analysis. In 7 each germanium atom is pentacoordinated due to intramolecular interaction with O atom of the neighboring triflate group.

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It is known that the action of trifluoromethanesulfonic acid (HOTf) on organogermanium compounds containing aromatic groups results to electrophilic substitution of one Ar group [6,18] but commonly triflates obtained are used subsequently without isolation in reactions occurring with nucleophilic substitution of OTf group. The investigations of such intermediate triflate compounds are very rare [6]. Meanwhile, triflate group is strong electron acceptor and it's introduction in organogermanium molecule, especially in oligogermane substances, may result to substantial changing of structural parameters of these molecules, for example of Ge–Ge bond. In this work we used modified procedures for synthesis of mono- and digermanes. The compounds obtained were investigated in reaction with trifluoromethanesulfonic acid.

# 2. Results and discussion

Using modified procedures we synthesized several germanes and digermanes (Scheme 1) which would be used than for interaction with triflic acid. All compounds were obtained in high yields as analytically pure samples.

In the course of this work we interested in the investigation of substitution of two aryl groups at one germanium atom in oligogermanes by action of HOTf. As a model compound for studying of

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this process we used tetraphenylgermane  $Ph_4Ge(1)$ . The possibility of substitution of two phenyl groups in tetraphenylgermane was shown earlier [19], but methods of structure establishing were not reliable. It is significant that in such reaction the mild conditions (room temperature, short time) are necessary especially in the case of oligogermanes due to lability of Ge–Ge bond.

We established that action of two equivalents of HOTf on  $Ph_4Ge$ (1) results exclusively to formation of  $Ph_3GeOTf$  (6) (Scheme 2). The increase of the time of the reaction to several days did not result to changing the product nature. According to NMR the byproducts formed in the course of this reaction represent a mixture of unidentified compounds. In the control experiment with one equivalent of HOTf the triphenylgermaniumtriflate (6) was also obtained but with greater yield.

Evidently, introduction of two triflate groups to one Ge atoms is impossible in the course of this method due to the electron acceptor ability of OTf that complicate sequential electrophilic substitution at C atom.

The crystal structure of the compound (**6**) was investigated by X-ray analysis (Fig. 1, Table 2).

The germanium atom in Ph<sub>3</sub>GeOTf (**6**) has a slightly distorted tetrahedral coordination. The Ge–O bond length is sufficiently increased in comparison with related compounds containing Ge–O bond (1.9225(17) vs. 1.86(1) Å in Ph<sub>3</sub>GeO<sub>2</sub>CCF<sub>3</sub> [20], 1.767(2) Å in (Ph<sub>3</sub>Ge)<sub>2</sub>O [21]) what denotes the significant ionic character of this bond in **6**. Similar increasing the length of the covalent Ge–O bond was found in pentacoordinated germanium compounds (for example, in  $C_{10}H_6(OMe)(Ge(H)(OTf)(NpOMe))$ , 1.988(3) Å [22]) where weakening covalent bonds are admitted.

At the action of two equivalents of HOTf on the hexaphenyldigermane (**5**) the new complex (OTf)Ph<sub>2</sub>GeGePh<sub>2</sub>(OTf) (**7**) was obtained with high yield (Scheme 3).

In this case it is interesting to note the retention of Ge–Ge bond and the rupture of two Ge–C<sub>6</sub>H<sub>5</sub> bonds at the neighboring germanium atoms (compare bond energy Ge–C (255 kJ/mol) and Ge–Ge (163 kJ/mol)) [23]. We believed that the main reasons of predominant rupture of Ge–C bonds consist in steric hindrances for attack on the Ge–Ge bond and the formation of the thermodinamically advantageous product which contained two strong





**Fig. 1.** Molecular structure of compound Ph<sub>3</sub>GeOTf (**6**). Selected bond length (Å) and angles (°): Ge(1)–O(11) 1.9225(17) Å, Ge(1)–C(21) 1.919(2) Å, Ge(1)–C(11) 1.921(2) Å, Ge(1)–C(31) 1.931(2) Å, O(11)–Ge(1)–C(11) 06.99(9)°, O(11)–Ge(1)–C(21) 102.73(9)°, O(11)–Ge(1)–C(31) 107.21(9)°, C(21)–Ge(1)–C(11) 116.98(10)°, C(21)–Ge(1)–C(31) 116.38(10)°, C(11)–Ge(1)–C(31) 113.31(10)°. There are two independent molecules in crystal. Only one independent molecule is presented in Figure.

intramolecular interactions. It should be noted that this reaction is occurred under more mild conditions (room temperature) than the synthesis of related derivative of the trichloroacetic acid **8** (prolonged reflux in toluene; see Scheme 4) [24].

The structure of the compound **7** was established by X-ray analysis (Figs. 2 and 3, Table 2).

In the centrosymmetric structure of **7**, both germanium atoms possess trigonal bipyramidal coordination environment. The triflate oxygen atoms occupy axial positions, while phenyl groups and neighboring germanium atom lie in equatorial sites. The Ge–O bond lengths in almost linear O–Ge–O fragment are significantly different (2.065(3) and 2.344(4) Å). This fragment may be considered as **3c–4e** bond. As expected, both the Ge–O bonds are longer than ordinary germanium-triflate **2c–2e** bond in the complex **6** (1.9225(17) Å).

The Ge–Ge distance in **7** (2.4635(12) Å) is somewhat longer than in parent compound Ph<sub>3</sub>GeGePh<sub>3</sub> (**1**) (Ph<sub>3</sub>GeGePh<sub>3</sub> (2.437(2) Å) [25], Ph<sub>3</sub>GeGePh<sub>3</sub>\*2C<sub>6</sub>H<sub>6</sub> (2.446(1) Å) [26]). The latter may be caused by sterical requirements of the bridging triflate ligands.



Scheme 2.



Both phenyl and trifluoromethyl groups were found to be rotationally disordered over two positions with equal occupancies (Fig. 2). In crystal, the same disorder components of Ph-rings belonging to adjacent molecules form short intermolecular C···C contacts (C(15A)···C(16A) - 3.156 Å, C(12B)···C(13B) - 3.319 Å). Thus, different orientations of phenyl groups are mutually alternating along the crystal and the occupancies of both disordered sites are equal. The latter was independently confirmed by structure refinement.

The related derivative of trichloroacetic acid  $(Cl_3CCO_2)Ph_2Ge-GePh_2(O_2CCCl_3)$  (**8**) was obtained using published procedure (Scheme 4) [10,24] for investigation of it's UV/visible properties (see below).

In this work we investigated reactivity of Ph<sub>3</sub>GeGeMe<sub>3</sub> (**4**) with triflic acid under similar conditions (Scheme 5).

The substitution of one phenyl group results to desired compound under mild conditions, but the reaction of **4** with two equivalents of HOTf results to a mixture of unidentified compounds in contrast to the interaction of  $GePh_4(1)$  with HOTf (2 equivalents) which gives the isolated monotriflate product **6**. We believed that in the case of the compound **4** there are several reaction pathways including simultaneous substitution phenyl- and methyl groups. The substitution of methyl groups in the presence of geometrically strained aryl groups was published for related Sn compounds [27].

Under prolonged storage of sample of Ph<sub>2</sub>(TfO)GeGeMe<sub>3</sub> (**9**) it's transformation to trigermane Me<sub>3</sub>GeGePh<sub>2</sub>GePh<sub>2</sub>(OTf) (**9a**) was occurred with very low yield (Scheme 6). It should be noted that in this case the reaction was attended by precipitation of colored insoluble solids which may present side polymeric products. Appears that **9** decomposes with the liberation of diphenylgermylene which inserts into the Ge–Ge bond or into the Ge–O bond of the initial compound **9**. The second way looks more reliable due to more ionic character of this bond.

It should be noted that the similar results were found for decomposition of oligogermanes by Satge et al. (for EtGeCl<sub>2</sub>GeCl<sub>3</sub>, (PhCl<sub>2</sub>Ge)<sub>3</sub>GePh or ( $C_6F_5$ )\_3GeGe(F)ClGe( $C_6F_5$ )\_3) and others (for MesGeCl<sub>2</sub>GeCl<sub>2</sub>Mes) but no structural characterization of the products was presented [28]. The poor quality of the crystals **9a** was unsatisfactory to establish the exact geometrical parameters of the structure. However, the composition and molecular connectivity were determined unambiguously (Fig. 4).

It is well known that the triflate group at Ge atom is readily substituted by nucleophiles for example by chloride. We established that the action of excess of ammonium chloride on **9** results to the novel compound **10** with high yield (Scheme 7). Unfortunately, the further substitution with the action of *O*-nucleophile (*N*,*N*-dimethylethanolamine) in presence of Et<sub>3</sub>N failed due to the formation of mixture of unidentified compounds. The formation of hypothetical Me<sub>3</sub>Ge–Ph<sub>2</sub>Ge–OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> with possible intermolecular Ge–N interaction may facilitate the liberation of germylene.



**Fig. 2.** Molecular structure of complex Ph<sub>2</sub>(OTf)GeGe(OTf)Ph<sub>2</sub> (**7**). Selected bond length (Å) and angles (°): Ge(1)–Ge(1A) 2.4635(12) Å, Ge(1)–C(11) 1.934(5) Å, Ge(1)–C(21) 1.934(5) Å, Ge(1)–O(2A) 2.344(4) Å; O(1)–Ge(1)–O(2A) 177.89(13)°, Ge(1A)–Ge(1)–C(21) 120.29(15)°, Ge(1A)–Ge(1)–C(11) 121.68(15)°, C(11)–Ge(1)–C(21) 117.20(20)°. Hydrogen atoms are omitted for clarity.



Fig. 3. Intermolecular contacts in complex Ph<sub>2</sub>(OTf)GeGe(OTf)Ph<sub>2</sub> (7).

The high intensive ( $\varepsilon > 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$ ) electronic absorption in UV/visible region is unique speciality of oligogermanes ( $\sigma$ -delocalization like in oligosilanes and oligostannanes) in comparison with similar carbon derivatives [1,29]. In Table 1 there are values of absorption bands of several oligogermanes. UV/visible spectra of the compounds obtained in the course of this work are presented in Fig. 5. It is interesting to note that additional bands corresponding to  $\pi \rightarrow \pi^*$  transition in phenyl groups are less intensive and are overlapped with more intensive  $\sigma \rightarrow \sigma^*$  band or appeared as shoulders to corresponding bands [8]. It is evident that reported earlier UV/visible absorption for Ph<sub>3</sub>GeGePh<sub>3</sub> (240 nm) [10,26] was not correctly referred to  $\sigma \rightarrow \sigma^*$  band typical for Ge–Ge bond but corresponds to absorption of phenyl group.

So the introduction of electron acceptor or electron acceptor groups forming hypervalent interaction with Ge atom in molecule of oligogermanes does not render significant influence on value of UV/visible absorption.

In summary, germane and digermanes containing triflate group at Ge atom were obtained. The compound  $Ph_2(OTf)GeGe(OTf)Ph_2$ (7) in solid state is characterized by pentacoordinated germanium atom. These compounds are perspective precursors for synthesis of more complex organogermanium structures.

# 3. Experimental

#### 3.1. General methods and remarks

All manipulations were performed under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. GeCl<sub>4</sub> (Aldrich), PhBr (Aldrich), *N*,*N*-dimethylethanolamine (Aldrich)

$$\begin{array}{c} \text{HOTf} \\ \text{Ph}_3\text{Ge-GeMe}_3 \xrightarrow{\text{HOTf}} & \text{Ph}_2\text{Ge-GeMe}_3 \\ \textbf{4} & \text{CHCl}_3 & \downarrow \\ \textbf{-PhH} & \text{OTf} \\ \textbf{9} & 39\% \end{array}$$

Scheme 5.

were distilled prior to use. HOSO<sub>2</sub>CF<sub>3</sub> (Aldrich), HO<sub>2</sub>CCCl<sub>3</sub> (Aldrich) and powdered Li (Aldrich) were used as supplied. Me<sub>3</sub>GeBr was obtained using published procedure [30]. <sup>1</sup>H NMR (400 MHz), <sup>13</sup>C NMR (100 MHz) and <sup>19</sup>F (376.4 MHz) spectra were recorded with a Bruker 400 spectrometer (in CDCl<sub>3</sub> at 295 K). Chemical shifts are given in ppm relative to internal Me<sub>4</sub>Si (<sup>1</sup>H and <sup>13</sup>C NMR spectra) or internal CFCl<sub>3</sub> (<sup>19</sup>F spectra). Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University. UV/visible spectra were obtained using two ray spectrophotometer Evolution 300 «Thermo Scientific» with cuvette of 0.10 cm long. Mass spectra (EI-MS, 70 eV) were recorded on a quadropoule mass spectrometer FINNIGAN MAT INCOS 50 with direct insertion; all assignments were made with reference to the most abundant isotopes.

All solvents were purified using standard procedures. Tetrahydrofuran, diethyl ether, triethylamine were stored under solid KOH and than distilled under sodium/benzophenone. Toluene was refluxed and distilled under sodium. Dichloromethane was distilled under CaH<sub>2</sub>.

#### 3.1.1. Synthesis of Ph<sub>4</sub>Ge (**1**) [31]

The solution of GeCl<sub>4</sub> (6.43 g, 29.0 mmol) in THF (40 ml) was added over 10 min to the solution of PhMgBr (prepared from PhBr (56.47 g, 360.0 mmol) and Mg (10.00 g, 420.0 mmol) in THF (115 ml)) in THF. The reaction mixture was heating under reflux for 18 h. Raw product was filtered off, washed carefully with diluted acetic acid and recrystallized from toluene. Tetraphenylgermane (1) was isolated as a white solid. Yield 10.20 g (57%). Analytically pure samples for subsequent experiments were obtained by sublimation (0.4 mm Hg, external bath 310 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.55–7.52, 7.47–7.41 (2m, 20H, aromatic hydrogens). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 136.06, 135.37, 129.08, 128.24 (aromatic carbons).

#### 3.1.2. Synthesis of Ph<sub>3</sub>GeCl (2) [32]

The mixture of  $Ph_4Ge(1)$  (2.00 g, 5.35 mmol),  $AlCl_3$  (0.07 g, 0.49 mmol) and  $GeCl_4$  (0.35 g, 1.60 mmol) was heated at  $120^{\circ}C$  for 4 h. The reaction melt was cooled to room temperature and the



solid formed was twice recrystallized from hexane. Triphenylchlorogermane (**2**) was isolated as a white solid. Yield 1.95 g (81%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.67–7.65, 7.49–7.43 (2m, 15H, aromatic hydrogens). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 134.70, 134.04, 130.48, 128.63 (aromatic carbons).

#### 3.1.3. Synthesis of Ph<sub>3</sub>GeLi (**3**) [33]

The solution of  $Ph_3GeCl$  (**2**) (0.37 g, 1.10 mmol) in THF (20 ml) was added dropwise to suspension of powdered Li (0.05 g, 5.40 mmol) in THF (20 ml) at room temperature. The reaction mixture was stirred overnight and then was filtered yielding a dark brown solution used consequently as obtained.

## 3.1.4. Synthesis of Ph<sub>3</sub>GeGeMe<sub>3</sub> (4)

At  $-78^{\circ}$ C the solution of Me<sub>3</sub>GeBr (0.22 g, 1.10 mmol) in ether (20 ml) was added dropwise to the solution of Ph<sub>3</sub>GeCl (**3**) in THF (20 ml) prepared as described above. The reaction mixture was slowly heated to room temperature and was stirred overnight. Then water (20 ml) was added, the water phase was extracted with ether (3 × 20 ml), dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated at reduced pressure. The residue was recrystallized from hexane/CH<sub>2</sub>Cl<sub>2</sub> mixture. The Ph<sub>3</sub>GeGeMe<sub>3</sub> (**4**) was isolated as a white solid. Yield 0.38 g (82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.48–7.42 (m, 6H, aromatic hydrogens), 7.38–7.33 (m, 9H, aromatic hydrogens), 0.45 (s, 9H, Ge(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 138.16, 135.21, 128.43, 128.19 (aromatic carbons), -0.84 (CH<sub>3</sub>).

#### 3.1.5. Synthesis of Ph<sub>3</sub>GeGePh<sub>3</sub> (**5**) [31]

The solution of PhBr (54.60 g, 348.00 mmol) in ether (110 ml) was added dropwise to suspension of Mg (10.00 g, 417.00 mmol) in



Fig. 4. Molecular structure of compound  $Me_3GeGe(Ph)_2Ge(Ph)_2OTf$  (9a). Hydrogen atoms are omitted for clarity.

ether (35 ml). After violent reaction the mixture was heated under reflux for 1 h. At room temperature the solution of GeCl<sub>4</sub> (5.32 g, 24.80 mmol) in toluene (60 ml) was added dropwise to the solution of Grignard reagent. The reaction mixture was heated under reflux for 4 h, then cooled to room temperature and toluene (50 ml), 10% HCl were added. The white solid was filtered off, washed with hot toluene and water. The purification was performed by extraction with CHCl<sub>3</sub> in Soxlett apparatus for 40 h. Hexaphenyldigermane (**5**) was isolated as a white powder. Yield 5.20 g (69%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.32–7.21 (m, 30H, aromatic hydrogens). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 137.31, 135.53, 128.74, 128.25 (aromatic carbons). UV/visible (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  222 nm ( $\varepsilon$ 2.8 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>), 238 nm ( $\varepsilon$  1.9 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>).

# 3.1.6. Reaction of $Ph_4Ge(\mathbf{1})$ with one equivalent of

trifluoromethanesulfonic acid. Synthesis of Ph<sub>3</sub>GeOTf (6) [18]

Trifluoromethanesulfonic acid (0.04 ml, 0.47 mmol) was added at 0°C to the solution of Ph<sub>4</sub>Ge (1) (0.18 g, 0.47 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml). The reaction mixture was heated to room temperature and stirred overnight. The volatiles were removed under vacuum, hexane (5 ml) and trace amounts of CH<sub>2</sub>Cl<sub>2</sub> were added and the solution was stored at  $-30^{\circ}$ C overnight. The crystals formed were isolated and dried under reduced pressure. Triphenylgermyltriflate (**6**) was isolated as a white solid. Yield 0.20 g (91%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta = 7.76-7.66$  (m, 6H, aromatic hydrogens), 7.58–7.48 (m, 9H, aromatic hydrogens). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta = 134.68$ , 131.94, 130.46, 129.10 (aromatic carbons), 118.58 (q, *J* = 318.0 Hz, CF<sub>3</sub>). <sup>19</sup>F NMR (376.4 MHz, CDCl<sub>3</sub>, ppm):  $\delta = -77.03$  (s, CF<sub>3</sub>).

Crystals suitable for X-ray analysis were obtained at storage of the solution of  $Ph_3GeOTf(6)$  in  $CH_2Cl_2$  at  $-30^{\circ}C$ .

#### 3.1.7. Reaction of $Ph_4Ge(1)$ with two equivalents of

trifluoromethanesulfonic acid. Synthesis of Ph<sub>3</sub>GeOTf (6)

Trifluoromethanesulfonic acid (0.07 ml, 0.84 mmol) was added at 0°C to the solution of Ph<sub>4</sub>Ge (**1**) (0.16 g, 0.42 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml). The reaction mixture was heated to room temperature and stirred overnight. The colorless solution was carefully separated from a brown oil, the volatiles were removed under vacuum. Hexane (5 ml) and trace amounts of CH<sub>2</sub>Cl<sub>2</sub> were added to the residue and the solution was stored at  $-30^{\circ}$ C overnight. The crystals formed were isolated and dried under reduced pressure. Triphenylgermyltriflate (**6**) was isolated as a white solid. Yield 0.15 g (66%). <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were correspond to mentioned above.

#### 3.1.8. Synthesis of Ph<sub>2</sub>Ge(OTf)Ge(OTf)Ph<sub>2</sub> (7)

Trifluoromethanesulfonic acid (0.87 g, 5.90 mmol) was added at  $0^{\circ}$ C to the solution of Ph<sub>3</sub>GeGePh<sub>3</sub> (1) (1.20 g, 1.97 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 ml). The reaction mixture was heated to room temperature and stirred for 48 h. The volatiles were removed under vacuum, the residue was washed with hexane. Hexane (5 ml) and CH<sub>2</sub>Cl<sub>2</sub> were added to the solid obtained up to dissolving. After storage at  $-30^{\circ}$ C the crystals formed were isolated by filtration and dried under vacuum. Ph<sub>2</sub>Ge(OTf)Ge(OTf)Ph<sub>2</sub> (**7**) was isolated as a pale yellow



crystals. Yield 1.48 g (54%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta = 7.78-7.71$  (m, 8H, aromatic hydrogens), 7.63-7.54 (m, 4H, aromatic hydrogens), 7.54-7.47 (m, 8H, aromatic hydrogens). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta = 134.50$ , 133.56, 131.69, 129.05 (aromatic carbons), 118.15 (q, J = 318.4 Hz, CF<sub>3</sub>). <sup>19</sup>F NMR (376.4 MHz, CDCl<sub>3</sub>, ppm):  $\delta = -76.53$  (s, CF<sub>3</sub>). UV/visible (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  224 nm ( $\varepsilon 5.0 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>). Anal. Calc. for C<sub>26</sub>H<sub>20</sub>F<sub>6</sub>Ge<sub>2</sub>O<sub>6</sub>S<sub>2</sub> (751.776): C 41.54, H 2.68, S 8.53. Found: C 41.37, H 2.60, S 8.49. EI-MS *m/z* (%): 616 (1) [M - 2CF<sub>3</sub>]<sup>+</sup>, 454 (3) [M - 2H-2CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>, 377 (3) [Ph<sub>2</sub>Ge(O<sub>3</sub>SCF<sub>3</sub>)]<sup>+</sup>, 306 (100)  $B = [M - 2H-Ph_2Ge(CF_3SO_3) - CF_3]^+, 77 (75) [Ph].$ 

Crystals suitable for X-ray analysis were obtained at storage of concentrated solution of  $Ph_2Ge(OTf)Ge(OTf)Ph_2$  (7) in  $CH_2Cl_2$  at room temperature.

## 3.1.9. Synthesis of Ph<sub>2</sub>Ge(O<sub>2</sub>CCCl<sub>3</sub>)Ge(O<sub>2</sub>CCCl<sub>3</sub>)Ph<sub>2</sub> (8) [10,24]

Trichloroacetic acid (1.17 g, 7.16 mmol) was added to the suspension of Ph<sub>3</sub>GeGePh<sub>3</sub> (**5**) (1.00 g, 1.65 mmol) in toluene (4 ml). The reaction mixture was heated at 110°C in closed bulb over 72 h and then cooled to room temperature. Hexane (15 ml) was added to the mixture, the solid formed was filtered off. Ph<sub>2</sub>Ge(O<sub>2</sub>CCCl<sub>3</sub>) Ge(O<sub>2</sub>CCCl<sub>3</sub>)Ph<sub>2</sub> (**8**) was isolated as a white solid. Yield 0.57 g (45%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.76–7.66 (m, 8H, aromatic hydrogens), 7.58–7.48 (m, 12H, aromatic hydrogens). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 166.36 (O<sub>2</sub>CCCl<sub>3</sub>), 134.25, 133.93, 130.81, 128.82 (aromatic carbons), 90.73 (O<sub>2</sub>CCCl<sub>3</sub>). <sup>1</sup>H and <sup>13</sup>C NMR spectra correspond to mentioned in literature [10]. UV/visible (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  224 nm ( $\varepsilon$  3.9 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>).

# 3.1.10. Reaction of $Ph_3GeGeMe_3$ (**4**) with one equivalent of trifluoromethanesulfonic acid. Synthesis of $Ph_2(OTf)GeGeMe_3$ (**9**)

Trifluoromethanesulfonic acid (0.11 ml, 1.19 mmol) was added at 0°C to the solution of Ph<sub>3</sub>GeGeMe<sub>3</sub> (**4**) (0.50 g, 1.19 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml). The reaction mixture was heated to room temperature and for 2 h. The volatiles were removed under vacuum, hexane and CH<sub>2</sub>Cl<sub>2</sub> were added to residue up to dissolving and solution was stored at -30 C. The crystals formed were isolated and dried under reduced pressure. Ph<sub>2</sub>(OTf)GeGeMe<sub>3</sub> (**9**) was isolated as a beige powder. Yield 0.23 g (39%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta = 7.60-7.53$  (m, 4H, aromatic hydrogens), 7.52-7.44 (m, 6H, aromatic hydrogens), 0.68 (s, 9H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta = 135.53$ , 133.88, 131.10, 128.97 (aromatic carbons), 118.59 (q, *J* = 318.4 Hz, CF<sub>3</sub>), -0.76 (CH<sub>3</sub>). Anal. Calc. for C<sub>16</sub>H<sub>19</sub>F<sub>3</sub>Ge<sub>2</sub>O<sub>3</sub>S (493.601): C 38.93, H 3.88. Found: C 38.06, H 4.15.

Under prolonged storage of the concentrated solution of  $Ph_2(OTf)GeGeMe_3$  (**9**) in  $CH_2Cl_2$  the crystals of  $Ph_2(OTf)GeGePh_2$ . GeMe<sub>3</sub> (**9a**) suitable for X-ray analysis were obtained.

The values of UV	/visible abso	rption for s	everal oligo	germanes.

Compound	λ <sub>max</sub> , nm	Reference
$Ph_3GeGePh_3$ ( <b>5</b> )	222 ( $\sigma \rightarrow \sigma^{*}$ ), 238 ( $\pi \rightarrow \pi^{*}$ )	This work
$(F_3CSO_3)Ph_2GeGePh_2(O_3SCF_3)$ (7)	224	This work
$(Cl_3CCO_2)Ph_2GeGePh_2(O_2CCCl_3)$ (8)	224	This work
ClPh <sub>2</sub> GeGePh <sub>2</sub> Cl	225	[29a]

Details of crystallographic experiments for 6 and 7.

	6	7
Formula	C <sub>19</sub> H <sub>15</sub> F <sub>3</sub> GeO <sub>3</sub> S	C <sub>26</sub> H <sub>20</sub> F <sub>6</sub> Ge <sub>2</sub> O <sub>6</sub> S <sub>2</sub>
Fw	452.96	751.72
Т, К	120(2)	150(2)
Crystal system	Triclinic	Triclinic
Space group, Z	P-1,4	P-1,1
a (Å)	9.7725(7)	9.389(3)
b (Å)	13.1335(10)	9.839(3)
c (Å)	14.8693(11)	10.062(3)
α (°)	93.571(1)	110.792(4)
β(°)	102.525(1)	95.733(5)
γ(°)	92.339(1)	117.674(4)
$V(Å^3)$	1856.5(2)	729.1(4)
$d_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.621	1.712
Abs. coeff. (mm <sup>-1</sup> )	1.808	2.282
F(000)	912	374
$\theta$ Range (°)	1.41-26.00	2.29-25.50
Reflections collected	16 112	5587
Unique reflections (R <sub>int</sub> )	7257 (0.0200)	2674 (0.0294)
Data/restraints/parameters	7257/0/487	2674/12/173
$R_1 \left[ l > 2\sigma(l) \right]$	0.0287	0.0545
wR <sub>2</sub> (all data)	0.0702	0.1496
Goof	1.039	1.079
Largest difference in peak/hole (e $Å^{-3}$ )	0.605/-0.340	1.402/-1.022

# 3.1.11. Reaction of $Ph_3GeGeMe_3$ (4) with two equivalents of trifluoromethanesulfonic acid

Trifluoromethanesulfonic acid (0.11 ml, 1.19 mmol) was added at  $-70^{\circ}$ C to the solution of Ph<sub>3</sub>GeGeMe<sub>3</sub> (**4**) (0.24 g, 0.59 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml). The reaction mixture was stirred for 2 h and heated to room temperature. The volatiles were removed under vacuum. According to NMR analysis the mixture of unidentified compounds was obtained.

# 3.1.12. Synthesis of $Ph_2(Cl)GeGeMe_3$ (10)

Solid NH<sub>4</sub>Cl (1.00 g, 18.70 mmol) was added to the solution of Ph<sub>2</sub>(OTf)GeGeMe<sub>3</sub> (**9**) (0.40 g, 0.81 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml). The reaction mixture was stirred for 2 days, then filtered and all volatiles were removed under vacuum. The residue was washed with hexane and dried under reduced pressure. Ph<sub>2</sub>(Cl)GeGeMe<sub>3</sub> (**10**) was isolated as a white solid. Yield 0.29 g (94%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.61–7.55 (m, 4H, aromatic hydrogens), 7.45–7.37 (6H, aromatic hydrogens), 0.54 (s, 9H, CH<sub>3</sub>). <sup>1</sup>H NMR spectrum corresponds to mentioned in literature [19]. <sup>13</sup>C NMR (100 MHz,



Fig. 5. UV/visible spectra of 5, 7, 8 in CH<sub>2</sub>Cl<sub>2</sub> solution.

CDCl<sub>3</sub>, ppm):  $\delta$  = 138.24, 133.48, 129.72, 128.53 (aromatic carbons), -1.42 (CH<sub>3</sub>).

# 3.1.13. Reaction of Ph<sub>2</sub>(Cl)GeGeMe<sub>3</sub> (10) with N,N-

## dimethylethanolamine

The solution of *N*,*N*-dimethylethanolamine (0.10 g, 1.16 mmol) and Et<sub>3</sub>N (0.16 ml, 1.16 ml) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added dropwise to the solution of Ph<sub>2</sub>ClGeGeMe<sub>3</sub> (**10**) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) at -78 C. The reaction mixture was heated slowly to room temperature and stirred overnight. All volatiles were removed under reduced pressure and residue was extracted with benzene (2+20 ml), the solvent was removed in vacuo. According to NMR analysis the mixture of unidentified compounds was obtained.

#### 3.1.14. X-ray crystallographic study

Experimental details for the structures **6** and **7** are given in Table 2. Data were collected on a Bruker SMART APEX II diffractometer (graphite monochromatized MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å). The structures **6** and **7** was solved by direct methods and refined by full matrix least-squares on  $F^2$  [34] with anisotropic thermal parameters for all non-hydrogen atoms. As for **7**, disordered atoms of Ph-rings and CF<sub>3</sub> groups were refined isotropically. In both cases, all hydrogen atoms were placed in calculated positions and refined using a riding model. In **7**, phenyl and trifluoromethyl groups were found to be rotationally disordered over two positions with equal occupancies.

#### Appendix A. Supplementary material

The crystallographic data for **6**, **7** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication under the CCDC numbers 847597 and 847598. They can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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