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Reaction of digermanes and related Ge-Si compounds with trifluoromethanesulfonic acid: synthesis of helpful building blocks for the preparation of Ge-Ge(Si)-catenated compounds

Abstract: The reaction of a series of compounds, Ar_3Ge-MR_3, **1–4** (Ar=Ph, *p*-Tol, *M*=Si, Ge, R=Ph, Me, tBu), with one equivalent of trifluoromethanesulfonic acid (HOTf) was investigated. The corresponding triflates were isolated in several cases. The molecular structure of $Ph_3Ge-GePh_2OTf$ (**5**) in solid state was investigated by X-ray analysis. The triflates were converted to the corresponding chlorides under the action of ammonium chloride.

Keywords: σ-conjugation; digermanes; germanium; Ge-Si bond; triflate; X-ray analysis.

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Introduction

The compounds containing the chains of covalently bonded Group 14 elements (...-M-M-M-..., *M*=Si, Ge, Sn) possess the unique electronic properties. These derivatives have the structure of saturated hydrocarbons, but their electronic properties [ultraviolet (UV) absorption, conductivity, luminescence, etc.] (Amadoruge and Weinert, 2008; Marschner and Baumgartner, 2013; Marschner and Hlina, 2013; Roewe et al., 2013; Zaitsev et al., 2014) are similar to those of unsaturated carbon compounds due to the σ-conjugation (i.e., the electrons in M-M bonds are not localized between two atoms but rather are delocalized across the entire backbone). The nature of substituents (their electronic and steric properties) at the M atoms and the number of M atoms in the chain have a dramatic effect on the properties of the whole molecule.

Among these singly bonded catenated compounds, oligosilanes (Miller and Michl, 1989; Mitra and Atwood, 2006; Marschner, 2014) and oligostannanes (Davies, 2004; Sharma and Pannell, 2008) have been well studied to date. Oligogermanes have been studied in less extent due to the difficulties (low yields and mixtures of compounds) (Amadoruge and Weinert, 2008) encountered in the reactions involving the formation of germanium (Ge)-Ge bonds [germylation of halogenogermanes by germyl lithium (Mallela et al., 1999; Zaitsev et al., 2013) or germyl potassium (Fischer et al., 2005; Hlina et al., 2010) reagents, dehydrogenation of germanes (Arii et al., 2008; Tanabe et al., 2009; Tanabe and Osakada, 2010), or reduction of halogenogermanes (Azemi et al., 2005) by transition metal derivatives and by other methods]. Nowadays, hydrogermolysis may be regarded as the most convenient method for oligogermane synthesis (Weinert, 2009; Roewe et al., 2013). These Ge congeners are the objects of several current investigations (Samanamu et al., 2012; Tanabe et al., 2012; Hlina et al., 2013; Schrick et al., 2013). Besides oligogermanes, compounds with different Group 14 elements in the chain (with bonds Ge-Si, for example) have not been studied sufficiently. At the same time, the investigation of the influence of the nature of M on the chemical and physical properties of such compounds may be regarded as an actual problem for the chemistry of Group 14 elements. The other important problem in the synthetic chemistry of oligogermanes and silagermanes (Corey et al., 1995) is the development of preparative approaches to suitable synthetic building blocks (for example, monochlorodigermanes), because these derivatives are interesting starting materials for various approaches in the

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preparative catenated germane chemistry (Al-Rafia et al., 2013; Marschner and Hlina, 2013).

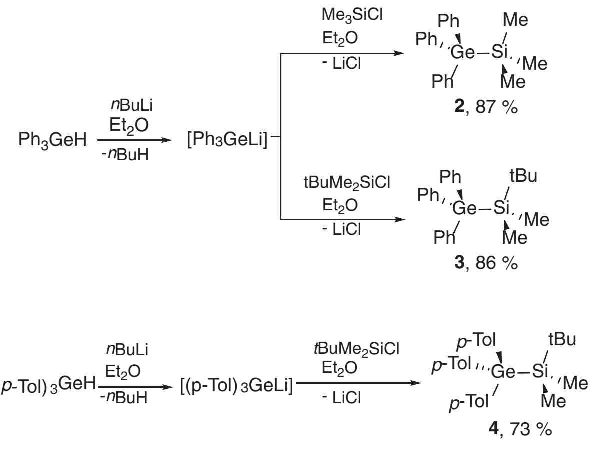
In this work, digermane **1** (hexaphenyldigermane) and three silagermanes **2**–**4** ($Ar_3Ge\text{-}SiR'R_2$: **2**, Ar=Ph, R=R′=Me; **3**, Ar=Ph, R=Me, R′=tBu; **4**, Ar=*p*-Tol, R=Me, R′=tBu) were investigated in the reaction with trifluoromethanesulfonic acid (HOTf). In the case of **1** and **3**, two novel monogermyltriflates [**5**, $Ph_2(TfO)Ge\text{-}GePh_3$, and **6**, $Ph_2(TfO)Ge\text{-}Si(tBu)Me_2$)] were isolated and characterized (X-ray data for **5**). These compounds were easily converted into corresponding monochlorides **7**, $Ph_2ClGe\text{-}GePh_3$, and **8**, $Ph_2ClGe\text{-}Si(tBu)Me_2$, via a reaction with NH_4Cl. The monochloride **9**, *p*-$Tol_2ClGe\text{-}Si(tBu)Me_2$, was also prepared according to the above two-step procedure without the isolation and characterization of the corresponding triflate. The preparation of silagermanes **2**–**4** was also reported; **3** and **4** are newly synthesized compounds.

Results and discussion

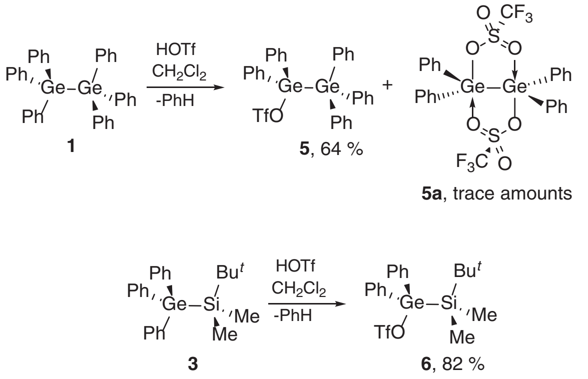
In the course of this work, we performed a synthesis of a series of Ge compounds containing silyl substituents (Scheme 1). These compounds were obtained from the reaction of *in situ* generated lithium reagents, Ph_3GeLi or $(p\text{-Tol})_3GeLi$, with corresponding trialkylsilylchlorides.

In the continuation of our works on oligogermanium compounds (Zaitsev et al., 2012, 2013), we performed an investigation of the reaction of digermane **1** and related compounds **2**–**4** containing Ge-Si bonds with triflic acid (Scheme 2).

In the case of $Ph_3Ge\text{-}GePh_3$ (**1**), the reaction with precisely measured quantity of HOTf at room temperature for 3 h led to triflate **5**, which was isolated in good yield. It should be noted that the trace amounts [according to the nuclear magnetic resonance (NMR) data of the reaction mixture] of the initial **1** and byproduct **5a** may be removed after selective crystallization. At the same time, the reaction of 'donor-acceptor' oligogermanes, $(C_6F_5)_3Ge\text{-}GePh_3$ or $(C_6F_5)_3Ge\text{-}Ge(p\text{-}Tol)_3$ (Zaitsev et al., 2013), with HOTf in similar conditions (in CH_2Cl_2 at room temperature for 3 days or at reflux for 3 h) gives only starting compounds, with no evident reaction with HOTf. In the more harsh conditions (PhMe, reflux for 3 h), the mixtures of unidentified compounds were obtained in both cases. Thus, the phenyl group is readily substituted by the OTf group in hexaphenyldigermane (**1**), but the presence of the electron-withdrawing groups at Ge atoms inhibits this reaction.



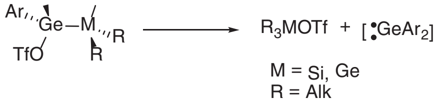
Scheme 1 Synthesis of compounds **2**–**4**.



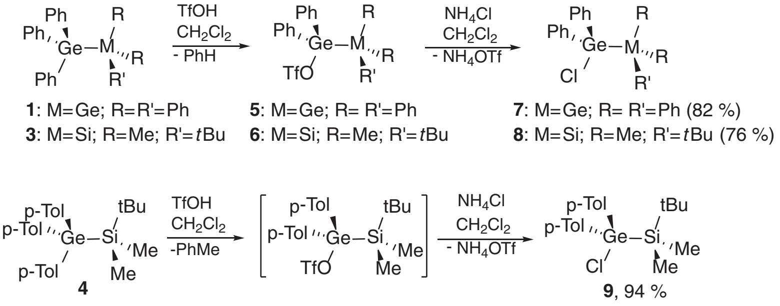
Scheme 2 Synthesis of the organoelement triflate derivatives **5** and **6**.

Analogous to what was found for **1**, the reaction of silagermane **3**, $Ph_3Ge\text{-}Si(tBu)Me_2$, led to germatriflate **6**. However, the attempts to isolate triflate derivatives from silagermanes **2** and **4** resulted to the mixtures of compounds, the composition and structure of which could not be determined. One can suppose that the corresponding triflate compounds potentially formed from **2** and **4** are unstable and decompose with the extrusion of germylenes (Zaitsev et al., 2012) (Scheme 3).

At the same time, the unstable triflate derivatives generated *in situ* from silagermane **4** may be transformed without isolation to the corresponding chloride **9** (Scheme 4). On the contrary, in the case of $Ph_3Ge\text{-}SiMe_3$, **2**, it is impossible to obtain the corresponding chloride, $Ph_2(Cl)Ge\text{-}SiMe_3$. Thus, we can conclude that at least one voluminous substituent at silicon atom is necessary for



Scheme 3 Decomposition of organoelement triflate derivatives.



Scheme 4 Synthesis of the organoelement chloride derivatives **7**–**9**.

the formation of sufficiently stable monotriflate from silatriarylgermanes; otherwise, the generated triflates decompose.

The structure of all compounds obtained in this work was investigated in solution by multinuclear (^{1}H, ^{13}C, ^{19}F, and ^{29}Si) NMR and UV spectroscopy. Compounds **5** and **5a** were studied by infrared (IR) spectroscopy. The crystal structure of **5** was investigated by X-ray analysis (Figure 1, Experimental Part).

It should be noted that, before this work, only one crystal structure containing $(C)_3$Ge-$(C)_3$Ge-O fragment, **A** (Valentin et al., 1999), was known. The crystal structures of the two Ge triflates, **B** and **5a** (Zaitsev et al., 2012), were also investigated (Scheme 5).

The Ge-Ge bond in **5** is typical for digermanes [2.4181(4) vs. 2.40–2.50 Å] (Amadoruge and Weinert, 2008; Marschner and Hlina, 2013; Zaitsev et al., 2013) and is slightly shorter than that in parent Ph_3Ge-$GePh_3$, **1**

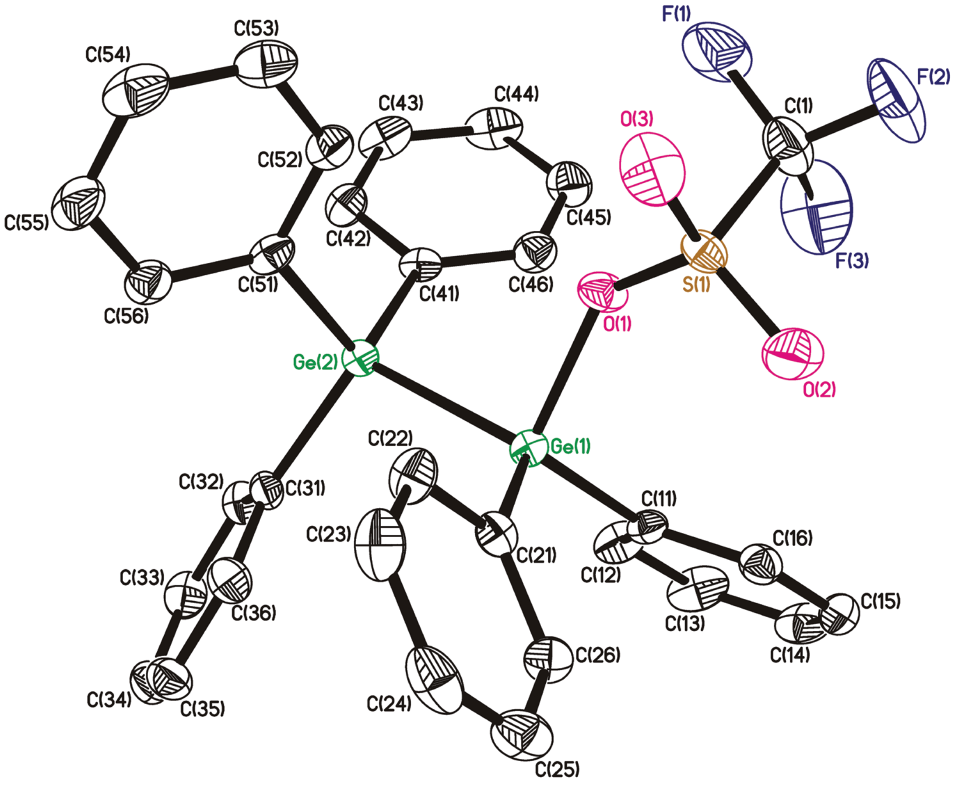
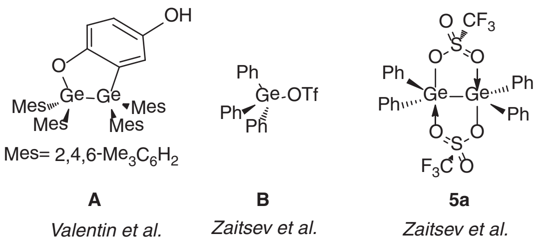


Figure 1 Molecular structure of compound **5**.

Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)-Ge(2) 2.4181(4), Ge(1)-O(1) 1.9169(19), Ge(1)-C(11) 1.928(3), Ge(1)-C(21) 1.925(3), Ge(2)-C(31) 1.948(3), Ge(2)-C(41) 1.944(3), Ge(2)-C(51) 1.955(3); O(1)-Ge(1)-C(21) 103.12(10), O(1)-Ge(1)-C(11) 105.66(10), C(21)-Ge(1)-C(11) 113.74(11), O(1)-Ge(1)-Ge(2) 94.68(6), C(21)-Ge(1)-Ge(2) 116.82(8), C(11)-Ge(1)-Ge(2) 118.56(8), C(41)-Ge(2)-C(31) 114.80(12), C(41)-Ge(2)-C(51) 110.13(11), C(31)-Ge(2)-C(51) 111.88(12), C(41)-Ge(2)-Ge(1) 109.42(8), C(31)-Ge(2)-Ge(1) 104.78(8), C(51)-Ge(2)-Ge(1) 105.23(8).



Scheme 5 Ge triflates and oligogermane with O substituent investigated by X-ray analysis.

[2.437(2) (Dräger and Ross, 1980a), 2.446(1) Å (Dräger and Ross, 1980b)] or in **A** (2.461 Å). Both Ge atoms in **5** have a distorted tetrahedral geometry, but the presence of a highly electron-withdrawing OTf at Ge(1) atom results in a significant change of angles (decreasing down to 94.68°) and bond lengths [decreasing Ge-C, compare Ge(1)-C_{av} 1.927(3) Å with Ge(2)-C_{av} 1.949(3) Å]. In general, the structural parameters for Ge(1) in **5** are similar to Ph_3GeOTf, **B** [compare d(Ge-O) and d(Ge-C)$_{av}$: 1.9169(19) vs. 1.9225(17) and 1.927(3) vs. 1.924(2) Å]. The increase of the Ge-O bond length in **5** in comparison with that in **A** [1.9169(19) vs. 1.828 Å] may be explained by the more ionic nature of Ge-O bond in the triflate derivative. The substituents at Ge atoms are in almost ideal staggered conformation (the torsion angles O-Ge-Ge-C are 176.19°, 58.07°, and 60.25°).

According to UV spectra, the introduction of electron-withdrawing groups (OTf, Cl) to the Ge atom instead of Ph or *p*-Tol groups results in a weak bathochromic shift. The NMR spectra compounds **2**–**9** correspond to their structure.

The data of the IR spectroscopy for compounds **5** and **5a** are presented in Figure 2. In Table 1, there are IR data for compounds **5** and **5a** and the related **B**, AgOTf (Angus-Dunne et al., 2006), which are given for comparison.

In general, the IR spectra of Ge triflates are very complex, reflecting a varied coordination of OTf group. Furthermore, the correct assignment is difficult, because the SO_3 and CF_3 bands occur between 1400 and 900 cm^{-1}.

Sharp intense bands at 735 and 695 cm^{-1} are caused by the nonplanar deformation vibrations of C-H in monosubstituted aromatic rings. Intense bands in the region 1203–1240 cm^{-1} are caused by stretching degenerate vibrations of C-F in the CF_3 group. The breathing vibration of C-F (A1) appeared in the form of bands of medium and low intensity in the region 1148–1190 cm^{-1}. The bands of the stretching degenerate vibrations of the SO_3 (in the region of 1300 cm^{-1}) have medium intensity and overlap with the intense bands of stretching vibrations C-F. The intense band at 632–633 cm^{-1} may be attributed to the breathing out-of-plane deformation vibration of the SO_3 group. From the data obtained, it is evident that the breathing vibrations of SO_3 (956–997 cm^{-1}) are sensitive to the coordination to the Ge atom.

From Table 1, it is evident that, for **5**, the bands typical for monodentate (1306, 1240, 1203, 1189, and 1026 cm^{-1}) and bidentate (1153, 1087, 1066, 997, and 956 cm^{-1}) OTf coordination to Ge are present, which is similar to Ph_3GeOTf, **B** (Angus-Dunne et al., 2006). At the same time, the bands of

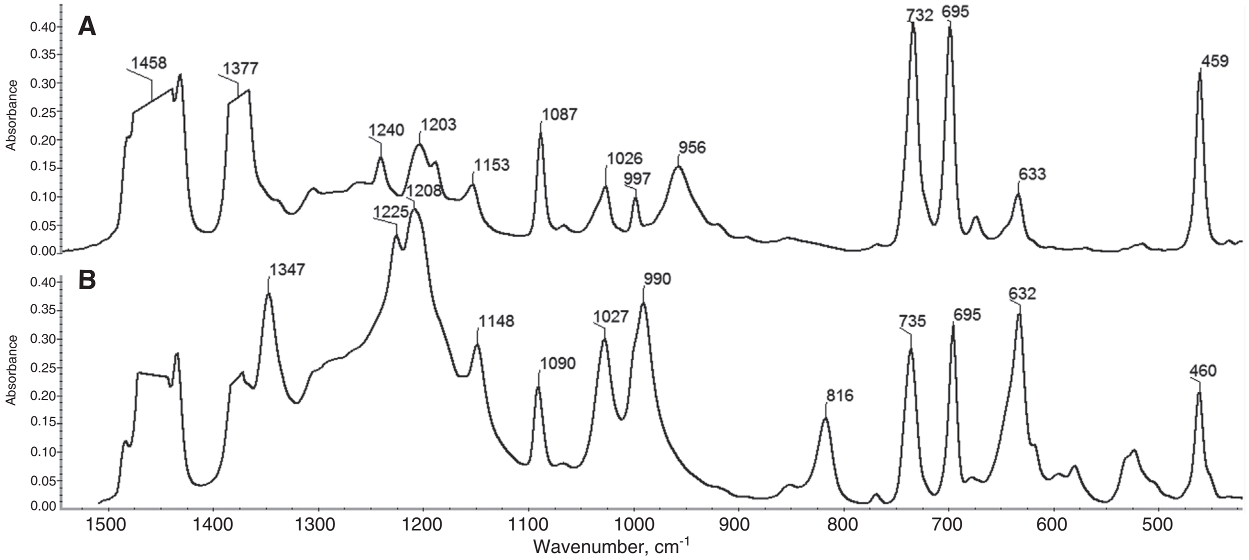


Figure 2 IR spectra of compounds **5** (A) and **5a** (B) in Nujol.
The bands of Nujol (1458 and 1377 cm^{-1}) have been removed.

Table 1 Data of IR spectroscopy for compounds **5**, **5a**, **B**, and AgOTf.

Bands assignment	Compound 5[a]	Compound 5a[a]	Compound B[b]	AgOTf[b]
$\nu[CF_3(E)]$	1240 s	1225 s	1241 s	1215 s
	1203 s	1208 s	1201 s	
$\nu[CF_3(A_1)]$	1189 w	Shoulder	1184 s	1175 s
	1153 m	1148 m	1154 m	
$\nu[SO_3(E)]$	1306 w	Shoulder	1299 m	1252 s
			1276 m s	
$\nu[SO_3(A_1)]$	1087 s	1090 s	1097 s	1033
	1066 w	1068 w	1051 m	
	1026 m	1027 m	1028 m	
	997 m	Shoulder	998 w	
	956 s	990 s	958 s	

[a] s (strong), m (medium), and w (weak).
[b] Data from Angus-Dunne et al. (2006).

the monodentate OTf coordination are more pronounced, which correlates with the X-ray analysis data (see before). Thus, it may be concluded that, in **5**, there are inequivalent triflate groups, among which the monodentate likely dominates over bidentate bridging coordination.

On the contrary, in **5a**, the bands of monodentate coordination are very weak (only 1208 and 1027 cm^{-1} may be found) and the bands of bidentate (1148, 1090, and 990 cm^{-1}) triflate coordination are stronger, which corresponds to bridging bidentate coordination. This result corresponds to the X-ray analysis data for **5a** (Zaitsev et al., 2012).

The increase in frequency and splitting of the higher-frequency $\nu(SO_3(E))$ band (~1300 cm^{-1}) may indicate the less ionic character of the Ge-O bond (Angus-Dunne et al., 2006). According to the IR data obtained, it may be concluded that the ionic character of Ge-O bond is increased in the range **5**<**B**. Apparently, the Ge-Ge fragment may be regarded as a donor fragment in relation to triflate.

At the same time, using IR in the case of **5a**, it is difficult to conclude the character of the Ge-O bond; however, using the X-ray analysis data, it may be confirmed that, in **5a**, the Ge-O bond is the most ionic in the range **5**, **B**, and **5a** [compare d(Ge-O): 1.9169(19), 1.9225(17), and 2.065(3) Å].

Conclusions

According to the data obtained in this work, it is established that one aryl group bound to Ge atom may be removed from Ar_3Ge-MR_3 (Ar=Ph, *p*-Tol, *M*=Si, Ge, R=Alk, Ar) by the action of one equivalent of HOTf. The identity of the substituents at the Si and Ge atoms has a significant effect on the isolation of the corresponding triflate derivative.

Experimental

General considerations and analyses

All operations with Ge derivatives were conducted in a dry argon atmosphere using standard Schlenk techniques. NMR spectra ^1H (400.130 MHz), ^{13}C (100.613 MHz), ^{29}Si (79.495 MHz), and ^{19}F (376.498 MHz) were registered at room temperature (298 K) on a Bruker Avance 400 or Agilent 400 spectrometer. Chemical shifts are given in ppm relative to internal Me_4Si (^1H, ^{13}C, and ^{29}Si NMR spectra) or external $CFCl_3$ (^{19}F spectra). IR spectra were recorded on 200 ThermoNicolet spectrometer. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University using Heraeus Vario Elementar instrument. UV-visible spectra were obtained using the two-ray spectrophotometer Evolution 300 (Thermo Scientific) with a cuvette of 0.10 cm long.

Solvents were dried using usual procedures. Tetrahydrofuran (THF) and diethyl ether were stored under solid KOH and then distilled under sodium/benzophenone. Toluene and n-hexane were refluxed and distilled under sodium. Dichloromethane was distilled under CaH_2. C_6D_6 was distilled over sodium under argon. $CDCl_3$ was distilled over CaH_2 under argon.

nBuLi, $tBuSiMe_2Cl$, and HOTf (all from Aldrich) are commercial reagents and were used as received.

Ph_3GeH (Batchelor and Birchall, 1983), $(p\text{-Tol})_3GeH$ (Lee et al., 2007), $Ph_3Ge-GePh_3$ (**1**) (Zaitsev et al., 2012), $Ph_3Ge-SiMe_3$ (**2**) (Eaborn and Mahmoud, 1981), and $Ph_2Ge(OTf)-GePh_2(OTf)$ (**5a**) (Zaitsev et al., 2012) were obtained according to the procedures published earlier.

Single crystal X-ray diffraction studies

Crystal data for **5:** $C_{31}H_{25}F_3Ge_2O_3S$, *M*=679.75, monoclinic, *a*=9.9624(6), *b*=16.0168(9), *c*=18.3195(7) Å, *β*=91.207(4)°, *V*=2922.5(3) $Å^3$, space group $P2_1/n$, Z=4, D_c=1.545 g/cm^3, *F*(000)=1368, $m(MoK_a)$=2.178 mm^{-1}. A total of 29,466 reflections (7046 unique, R_{int}=0.0549) were measured on a Gemini Ultra diffractometer (graphite monochromatized MoK_a radiation, l=0.71073 Å) using a *ω*-scan mode at 120 K. The structure was solved by direct methods and refined by full matrix least squares on F^2 (Sheldrick, 2008) with anisotropic thermal parameters for all nonhydrogen atoms. All H atoms were placed in calculated positions and refined using a riding model. The final residuals were R_1=0.0379, wR_2=0.0830 for 5673 reflections with $I>2s(I)$ and 0.0544 and 0.0920 for all data and 361 parameters. Goof=1.050, maximum Dr=1.277e×$Å^{-3}$.

The crystallographic data for **5** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications under the CCDC number 1002293. This information may be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $Ph_3Ge-SiMe_3$ (2)

Synthesis was performed by literature procedure using Ph_3GeH (1.55 g, 5.08 mmol), nBuLi (2.5 M in hexane, 2.10 mL, 5.20 mmol), Me_3SiCl (0.57 mL, 5.30 mmol) in ether (30 mL) giving compound **1** as a white solid (1.67 g, 87%). ^1H NMR (400.130 MHz, $CDCl_3$) δ: 7.53–7.46

(m, 6H, aromatic hydrogens), 7.41–7.35 (m, 9H, aromatic hydrogens), 0.39 (s, 9H, $SiMe_3$). ^{13}C NMR (100.613 MHz, $CDCl_3$) δ: 138.44, 135.36, 128.25, 128.15 (aromatic carbons), -0.34 ($SiMe_3$). ^{29}Si (79.495 MHz, $CDCl_3$) δ: -13.93. UV (CH_2Cl_2): λ_{max}, nm (ε, M^{-1} cm^{-1}): 224 (2.2×10^4).

Synthesis of $tBuSiMe_2$-$GePh_3$ (3)

(a) Synthesis of Ph_3GeLi: At room temperature, the solution of nBuLi in hexane (2.5 M, 2.10 mL, 5.20 mmol) was added dropwise to the solution of Ph_3GeH (1.55 g, 5.08 mmol) in ether (20 mL). The reaction mixture was stirred for 2 h. The reagent was used without further purification.

(b) Synthesis of $tBuSiMe_2$-$GePh_3$ (**3**): The above-mentioned solution of Ph_3GeLi in ether was added dropwise to the solution of $tBuSi(Me)_2Cl$ (0.81 g, 5.30 mmol) in THF (10 mL). The reaction mixture was stirred overnight. Then, the water was added, the organic phase was isolated, the aqueous phase was extracted with EtOAc (3×20 mL), and the combined organic phases were dried over Na_2SO_4. The volatiles were removed under reduced pressure and the residue was recrystallized from hexane. Compound **3** (1.83 g, 86%) was isolated as white crystals. ^1H NMR (400.130 MHz, $CDCl_3$) δ: 7.54–7.47 (m, 6H, aromatic hydrogens), 7.37–7.32 (m, 9H aromatic hydrogens), 0.91 (s, 9H, CMe_3), 0.33 (s, 6H, $SiMe_2$). ^{13}C NMR (100.613 MHz, $CDCl_3$) δ: 139.11, 135.58, 128.16, 128.06 (aromatic carbons), 27.74 (CMe_3), 18.73 (CMe_3), -3.58 ($SiMe_2$). ^{29}Si (79.495 MHz, $CDCl_3$) δ: 1.60. UV (hexane), λ_{max}, nm (ε, M^{-1} cm^{-1}): 218 (2.4×10^4), 230 (2.0×10^4). Elemental analyses: calculated (%) for $C_{24}H_{30}GeSi$ (419.1905 g/mol): C 68.77, H 7.21; found: C 68.65, H 7.18.

Synthesis of $tBuSi(Me)_2$-$Ge(p\text{-}Tol)_3$ (4)

(a) Synthesis of $(p\text{-}Tol)_3GeLi$: At room temperature, the solution of nBuLi in hexane (2.5 M, 4.70 mL, 11.75 mmol) was added dropwise to the solution of $(p\text{-}Tol)_3GeH$ (4.00 g, 11.53 mmol) in ether (30 mL). The reaction mixture was stirred for 2 h. The reagent was used without further purification.

(b) Synthesis of $tBuSi(Me)_2$-$Ge(p\text{-}Tol)_3$ (**4**): The above-mentioned solution of $(p\text{-}Tol)_3GeLi$ in ether was added dropwise to the solution of $tBuSi(Me)_2Cl$ (1.74 g, 11.53 mmol) in ether (25 mL). The reaction mixture was stirred overnight. Then, the water was added, the organic phase was isolated, the aqueous phase was extracted with EtOAc (3×20 mL), and the combined organic phases were dried over Na_2SO_4. The volatiles were removed under reduced pressure and the residue was recrystallized from hexane. Compound **4** (3.88 g, 73%) was isolated as white crystals. ^1H NMR (400.130 MHz, $CDCl_3$) δ: 7.40 (d, 6H, *J*=7.8 Hz, aromatic hydrogens), 7.17 (d, 6H, *J*=7.3 Hz, aromatic hydrogens), 2.37 (s, 9H, $C_6H_4CH_3$), 0.92 (s, 9H, CMe_3), 0.33 (s, 6H, $SiMe_2$). ^{13}C NMR (100.613 MHz, $CDCl_3$) δ: 137.68, 135.69, 135.53, 128.86 (aromatic carbons), 27.79 (CMe_3), 21.38 ($C_6H_4CH_3$), 18.70 (CMe_3), -3.57 ($SiMe_2$). ^{29}Si (79.495 MHz, $CDCl_3$) δ: 1.23. UV (CH_2Cl_2), λ_{max}, nm (ε, M^{-1} cm^{-1}): 235 (4.5×10^4). UV (hexane), λ_{max}, nm (ε, M^{-1} cm^{-1}): 208 (5.4×10^4), 233 (3.2×10^4). Elemental analyses: calculated (%) for $C_{27}H_{36}GeSi$ (461.2702 g/mol): C 70.30, H 7.87; found: C 70.18, H 7.77.

Synthesis of Ph_3Ge-$GePh_2OTf$ (5)

At 0°C, HOTf (0.175 mL, 1.97 mmol) was added to the slurry of Ph_3Ge-$GePh_3$, **1** (1.20 g, 1.97 mmol), in CH_2Cl_2 (40 mL). The reaction mixture was slowly warmed to room temperature and stirred for 3 h, giving a yellowish solution. Then, all volatile materials were removed under reduced pressure and the residue was recrystallized (-30°C) twice from hexane/CH_2Cl_2 mixture, giving **5** (0.86 g, 64%) as a white powder. ^1H NMR (400.130 MHz, $CDCl_3$) δ: 7.77–7.70 (m, 2H, aromatic hydrogens), 7.56–7.50 (m, 8H, aromatic hydrogens), 7.46–7.40 (m, 6H, aromatic hydrogens), 7.39–7.35 (m, 9H, aromatic hydrogens). ^{13}C NMR (100.613 MHz, $CDCl_3$) δ: 137.59, 135.39, 134.41, 133.27, 131.26, 129.98, 128.90, 128.85 (aromatic carbons), 118.33 (quart, *J*=315.0 Hz, CF_3). ^{19}F (376.498 MHz, $CDCl_3$) δ: -76.96. UV (CH_2Cl_2), λ_{max}, nm (ε, M^{-1} cm^{-1}): 222 (3.1×10^5), 236 (shoulder, 2.1×10^5). Elemental analyses: calculated (%) for $C_{31}H_{25}F_3Ge_2O_3S$ (679.8096 g/mol): C 54.77, H 3.71; found: C 55.12, H 3.82. The crystals suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2/octane mixture at -30°C.

Synthesis of $tBuSi(Me)_2$-$GePh_2OTf$ (6)

At room temperature, HOTf (0.25 mL, 2.80 mmol) was added to the solution of $tBuSi(Me)_2$-$GePh_3$ (**3**) (1.18 g, 2.80 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 2 h, and then all volatile materials were removed under reduced pressure. The residue was dissolved in pentane and stored at -30°C, yielding a yellowish oil of **6** (1.13 g, 82%, purity more than 95%). ^1H NMR (400.130 MHz, $CDCl_3$) δ: 7.67–7.60 (m, 4H, aromatic hydrogens), 7.52–7.46 (m, 6H, aromatic hydrogens), 0.95 (s, 9H, CMe_3), 0.60 (s, $SiMe_2$). ^{13}C NMR (100.613 MHz, $CDCl_3$) δ: 136.35, 134.31, 130.98, 128.83 (aromatic carbons), 118.53 (q, *J*=318.5 Hz, CF_3), 27.23 (CMe_3), 18.73 (CMe_3), -4.77 ($SiMe_2$). ^{19}F (376.498 MHz, $CDCl_3$) δ: -77.80. ^{29}Si (79.495 MHz, $CDCl_3$) δ: 11.28. UV (CH_2Cl_2), λ_{max}, nm (ε, M^{-1} cm^{-1}): 222 (1.6×10^4), 227 (1.4×10^4).

Synthesis of Ph_3Ge-$GePh_2Cl$ (7)

At room temperature, finely ground NH_4Cl (1.00 g, 18.70 mmol) was added to the solution of Ph_3Ge-$GePh_2OTf$ (0.88 g, 1.30 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 3 days. The mixture was filtered, the solvent was removed in vacuo, and the residue was recrystallized from CH_2Cl_2/hexane and then from toluene/hexane, giving **7** (0.61 g, 82%) as a white powder. ^1H NMR (400.130 MHz, $CDCl_3$) δ: 7.58–7.52 (m, 4H, aromatic hydrogens), 7.50–7.46 (m, 2H, aromatic hydrogens), 7.44–7.40 (m, 2H, aromatic hydrogens), 7.38–7.33 (m, 7H, aromatic hydrogens). ^{13}C NMR (100.613 MHz, $CDCl_3$): δ 137.84, 135.40, 134.98, 133.84, 129.92, 129.42, 128.57, 128.51 (aromatic carbons). The ^{13}C NMR data correspond to the literature data (Häberle and Dräger, 1987).

Synthesis of $tBuSi(Me)_2$-$GePh_2Cl$ (8)

At room temperature, finely ground NH_4Cl (1.00 g, 18.70 mmol) was added to the solution of $tBuSi(Me)_2$-$GePh_2OTf$ (1.38 g, 2.80 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 3 days. The mixture was filtered; the solvent was removed in vacuo, extracted with hexane (20 mL), filtered, and concentrated under reduced pressure; and the residue was fractioned (boiling temperature 135–140°C, 0.4 mm Hg), giving a colorless oil of **8** (0.80 g, 76%). ^1H NMR (400.130 MHz, $CDCl_3$) δ: 7.65–7.59 (m, 4H, aromatic hydrogens), 7.42–s7.37 (m, 6H, aromatic hydrogens), 0.96 (s, 9H, CMe_3), 0.40 (s, 6H, $SiMe_2$). ^{13}C NMR (100.613

MHz, $CDCl_3$): δ 139.05, 133.64, 129.45, 128.43 (aromatic carbons), 27.30 (CMe_3), 18.79 (CMe_3), -4.90 ($SiMe_2$). ^{29}Si (79.495 MHz, $CDCl_3$) δ: 7.59. UV (hexane), λ_{max}, nm (ε, M^{-1} cm^{-1}): 220 (2.3×10^4). Elemental analyses: calculated (%) for $C_{18}H_{25}ClGeSi$ (377.5393 g/mol): C 57.26, H 6.67; found: C 56.88, H 6.56.

Synthesis of tBuSi(Me)$_2$-Ge(*p*-Tol)$_2$Cl (9)

At room temperature, HOTf (0.25 mL, 2.80 mmol) was added to the solution of tBuSi(Me)$_2$-Ge(*p*-Tol)$_3$ (**4**) (1.18 g, 2.80 mmol) in CH_2Cl_2 (20 mL). After 2 h, the volatile materials were removed under reduced pressure, giving a yellowish oil. Then, CH_2Cl_2 (20 mL) and NH_4Cl (1.00 g, 18.70 mmol) were added to tBuSi(Me)$_2$-Ge(*p*-Tol)$_2$OTf. The reaction mixture was stirred for 3 days. The mixture was filtered; the solvent was removed in vacuo, extracted with hexane (20 mL), filtered, and concentrated under reduced pressure, giving a yellowish oil of **9** (1.00 g, 94%). ^1H NMR (400.130 MHz, $CDCl_3$) δ: 7.30–7.25 (m, 2H, aromatic hydrogens), 7.22–7.16 (m, 6H, aromatic hydrogens), 2.37 (s, 6H, $C_6H_4CH_3$), 1.02 (s, 9H, CMe_3), 0.47 (s, 6H, $SiMe_2$). ^{13}C NMR (100.613 MHz, $CDCl_3$) δ: 137.87, 129.04, 128.23, 125.31 (aromatic carbons), 25.70 (CMe_3), 24.70 ($C_6H_4CH_3$), 18.13 (CMe_3), -2.96 ($SiMe_2$). ^{29}Si (79.495 MHz, $CDCl_3$) δ: 7.27. UV (hexane), λ_{max}, nm (ε, M^{-1} cm^{-1}): 212 (1.5×10^4), 221 (1.8×10^4), 228 (1.9×10^4). Elemental analyses: calculated (%) for $C_{20}H_{29}ClGeSi$ (405.5925 g/mol): C 59.23, H 7.21; found: C 58.78, H 6.89.

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