

Supersilylated Tetrachlorodigermene ($t\text{Bu}_3\text{Si}$)Cl₂GeGeCl₂($\text{Si}t\text{Bu}_3$) and Triger-moxetane ($t\text{Bu}_3\text{Si}$)₃Ge₃Cl₃O

Hans-Wolfram Lerner, Frauke Schödel, Inge Sanger, Matthias Wagner, and Michael Bolte *

Institut fur Anorganische Chemie, Johann Wolfgang Goethe-Universitat Frankfurt am Main, Marie-Curie-Strae 11, D-60439 Frankfurt am Main, Germany

Reprint requests to Dr. Hans-Wolfram Lerner. E-mail: lerner@chemie.uni-frankfurt.de

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In contrast to the tetrachlorodigermene ($t\text{Bu}_3\text{Si}$)Cl₂Ge-GeCl₂($\text{Si}t\text{Bu}_3$), the *cis,trans*-cyclo-trigermene ($t\text{Bu}_3\text{SiGeCl}$)₃ is sensitive to oxygen. Its treatment with O₂ at ambient temperature leads to the triger-moxetane ($t\text{Bu}_3\text{Si}$)₃Ge₃Cl₃O. According to an X-ray structure analysis of single crystals consisting of cocrystallized ($t\text{Bu}_3\text{Si}$)₃Ge₃Cl₃O and ($t\text{Bu}_3\text{Si}$)Cl₂Ge-GeCl₂($\text{Si}t\text{Bu}_3$) the triger-moxetane contains an almost planar Ge₃O-ring while the tetrachlorodigermene ($t\text{Bu}_3\text{Si}$)Cl₂Ge-GeCl₂($\text{Si}t\text{Bu}_3$) possesses a Si-Ge-Ge-Si chain which is exactly all *trans*.

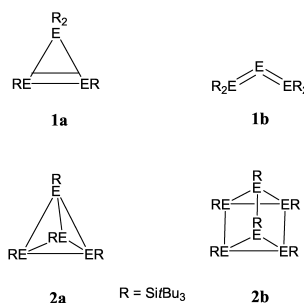
Key words: Supersilyl, Germane, Germoxane, X-Ray Structure Analysis

Introduction

Clusters containing Group 14 elements are receiving great attention due to their interesting chemical properties [1]. Various details of their reactivity are, however, still not fully elucidated and therefore subject to current investigations [2]. By using bulky ligands such as tri-*tert*-butylsilyl (supersilyl), $t\text{Bu}_3\text{Si}$, small rings and low-coordinated centers can be stabilized. When 2 equivalents of the sodium supersilanide $t\text{Bu}_3\text{SiNa}$ [3] are reacted with GeCl₂·dioxane in tetrahydrofuran several different products are formed: (i) tetrasupersilyl-trigermacyclopropene ($t\text{Bu}_3\text{Si}$)₄Ge₃ **1a** (E=Ge) [4] and (ii) supersilylated tetra-germatetrahedrane ($t\text{Bu}_3\text{SiGe}$)₄ **2a** (E=Ge) [5].

Contrary to the supersilylated tetra-germatetrahedrane ($t\text{Bu}_3\text{SiGe}$)₄ **2a** (E=Ge), the analogous tetra-stannatetrahedrane ($t\text{Bu}_3\text{SiSn}$)₄ **2a** (E=Sn) is unknown up to now. When $t\text{Bu}_3\text{SiNa}$ was reacted with [(Me₃Si)₂N]₂Sn in pentane/*tert*-butyl methyl ether, the hexasupersilyl-*prismo*-hexastannane ($t\text{Bu}_3\text{SiSn}$)₆ **2b** (E=Sn) was formed rather than the tetra-stannatetrahedrane ($t\text{Bu}_3\text{SiSn}$)₄ [6]. On the other hand, the tetrasupersilyl-tristannacyclopropene **1a** (E=Sn) was quantitatively produced by isomerisation of the tetrasupersilyl-tristannaallene **1b** (E=Sn) [7].

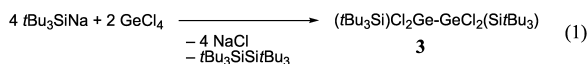
In this paper we describe the syntheses and chemical properties of the tetrachlorodigermene



($t\text{Bu}_3\text{Si}$)Cl₂Ge-GeCl₂($\text{Si}t\text{Bu}_3$) and the triger-moxetane ($t\text{Bu}_3\text{Si}$)₃Ge₃Cl₃O and report the crystal structures of these two compounds.

Results and Discussion

When two equivalents of $t\text{Bu}_3\text{SiNa}$ were reacted with GeCl₄ the tetrachlorodigermene ($t\text{Bu}_3\text{Si}$)Cl₂Ge-GeCl₂($\text{Si}t\text{Bu}_3$) (**3**) was formed in low yield (eq. (1)). However, the *cis,trans*-cyclo-trigermene ($t\text{Bu}_3\text{SiGeCl}$)₃ (**4**) could be synthesized by the reaction of GeCl₂ with one equivalent of $t\text{Bu}_3\text{SiNa}$ in 85% yield [8, 9].



In contrast to the tetrachlorodigermene **3**, the *cis,trans*-cyclo-trigermene **4** is sensitive to oxygen, but only moderately sensitive to moisture. When a solution of *cis,trans*-cyclo-trigermene **3** and **4** in benzene

* X-ray structure analysis.

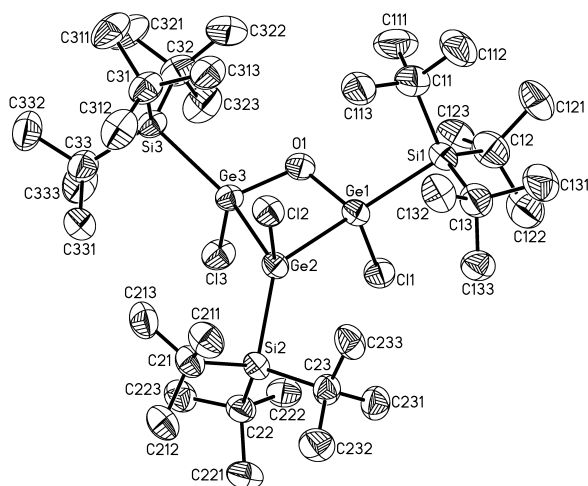
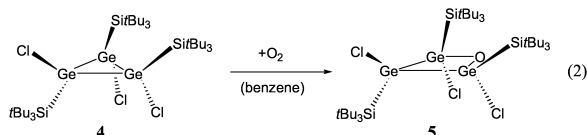


Fig. 1. Thermal ellipsoid plot of **5** showing the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: O(1)-Ge(3) 1.800(3), O(1)-Ge(1) 1.808(3), Ge(1)-Cl(1) 2.2089(13), Ge(1)-Si(1) 2.4599(14), Ge(1)-Ge(2) 2.5310(7), Si(1)-C(13) 1.899(6), Si(1)-C(12) 1.931(7), Si(1)-C(11) 1.952(6), Ge(2)-Cl(2) 2.2227(12), Ge(2)-Si(2) 2.4736(14), Ge(2)-Ge(3) 2.5134(7), Si(2)-C(23) 1.934(5), Si(2)-C(21) 1.937(5), Si(2)-C(22) 1.937(5), Ge(3)-Cl(3) 2.2131(12), Ge(3)-Si(3) 2.4625(14), Si(3)-C(33) 1.922(6), Si(3)-C(31) 1.934(5), Si(3)-C(32) 1.949(6), Ge(3)-O(1)-Ge(1) 110.36(16), O(1)-Ge(1)-Cl(1) 104.71(11), O(1)-Ge(1)-Si(1) 111.22(11), Cl(1)-Ge(1)-Si(1) 107.70(5), O(1)-Ge(1)-Ge(2) 87.28(10), Cl(1)-Ge(1)-Ge(2) 103.71(4), Si(1)-Ge(1)-Ge(2) 137.35(4), C(13)-Si(1)-C(12) 115.5(3), C(13)-Si(1)-C(11) 114.4(3), C(12)-Si(1)-C(11) 111.1(3), C(13)-Si(1)-Ge(1) 102.75(19), C(12)-Si(1)-Ge(1) 108.2(2), C(11)-Si(1)-Ge(1) 103.6(2), Cl(2)-Ge(2)-Si(2) 105.00(5), Cl(2)-Ge(2)-Ge(3) 99.85(4), Si(2)-Ge(2)-Ge(3) 135.09(4), Cl(2)-Ge(2)-Ge(1) 100.69(4), Si(2)-Ge(2)-Ge(1) 136.42(4), Ge(3)-Ge(2)-Ge(1) 71.92(2), C(23)-Si(2)-C(21) 112.9(2), C(23)-Si(2)-C(22) 114.0(2), C(21)-Si(2)-C(22) 113.1(2), C(23)-Si(2)-Ge(2) 105.18(16), C(21)-Si(2)-Ge(2) 106.09(18), C(22)-Si(2)-Ge(2) 104.53(16), O(1)-Ge(3)-Cl(3) 102.67(11), O(1)-Ge(3)-Si(3) 111.67(11), Cl(3)-Ge(3)-Si(3) 106.17(5), O(1)-Ge(3)-Ge(2) 88.00(10), Cl(3)-Ge(3)-Ge(2) 102.33(4), Si(3)-Ge(3)-Ge(2) 140.23(4), C(33)-Si(3)-C(31) 112.5(3), C(33)-Si(3)-C(32) 113.4(3), C(31)-Si(3)-C(32) 112.9(3), C(33)-Si(3)-Ge(3) 105.30(18), C(31)-Si(3)-Ge(3) 107.15(17), C(32)-Si(3)-Ge(3) 104.72(18).

was exposed to air, only **4** was oxidized as shown in eq. (2).

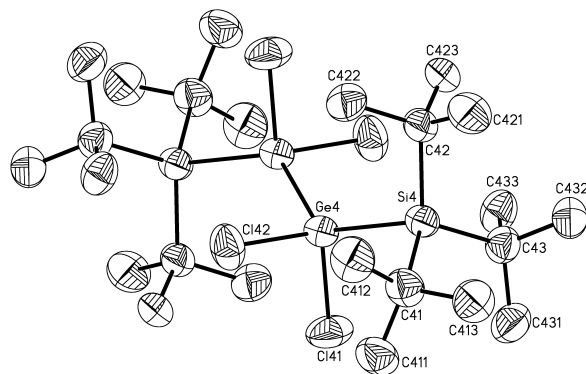


Fig. 2. Thermal ellipsoid plot of **3** showing the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ge(4)-Cl(41) 2.1920(14), Ge(4)-Cl(42) 2.1956(15), Ge(4)-Ge(4)^{#1} 2.4647(10), Ge(4)-Si(4) 2.4672(15), Si(4)-C(42) 1.918(5), Si(4)-C(43) 1.937(5), Si(4)-C(41) 1.958(5), Cl(41)-Ge(4)-Cl(42) 101.87(7), Cl(41)-Ge(4)-Ge(4)^{#1} 102.33(5), Cl(42)-Ge(4)-Ge(4)^{#1} 101.52(5), Cl(41)-Ge(4)-Si(4) 107.82(5), Cl(42)-Ge(4)-Si(4) 108.06(6), Ge(4)^{#1}-Ge(4)-Si(4) 131.61(4), C(42)-Si(4)-C(43) 113.5(2), C(42)-Si(4)-C(41) 114.2(3), C(43)-Si(4)-C(41) 113.3(2), C(42)-Si(4)-Ge(4) 103.82(18), C(43)-Si(4)-Ge(4) 105.24(17), C(41)-Si(4)-Ge(4) 105.58(18).

The trigermozetane **5** cocrystallizes with the tetrachlorodigermane **3** in a molar ratio of 2 : 1 from benzene. Obviously, the oxygen atom has only been inserted into the longer Ge-Ge bond of **4** with the adjacent *t*Bu₃Si substituents in a *cis*-position.

Figure 1 shows the molecular structure of **5** (monoclinic, *P*2₁/*c*). The asymmetric unit consists of one molecule of **5** and half a molecule of **3** (located on a center of inversion, *C*_i symmetry). The trigermozetane **5** is the first example of a molecule containing a four-membered ring composed of three Ge and one O atom which has been structurally characterized by X-ray determination. The GeO distance in **5** of 1.804(3) Å (average) represents a characteristic value for a germoxane bond. The ring is nearly planar (rmsd = 0.101 Å) as confirmed by small torsion angles [14.10 (15)°]. The Cl substituents are in axial positions whereas the *t*Bu₃Si groups occupy equatorial positions due to the size of the latter. The two Cl substituents adjacent to the O atom are located on the same side of the ring, the third one is in a *trans* position on the other side of the ring. The two O-Ge-Ge angles are close to 90°, while the Ge-Ge-Ge angle is much smaller and the Ge-O-Ge angle is significantly larger than 90° [5: O1-Ge1-Ge2 87.54(10)°, Ge1-O1-Ge3 110.36(16)°, Ge1-Ge2-Ge3 71.92(2)°].

The molecular structure of the tetrachlorodigermene **3** is shown in Fig. 2, and selected bond lengths and angles of **3** and **5** are listed in the corresponding figure captures. The Si-Ge-Ge-Si chain of **3** is all *trans* by symmetry. The tetrachlorodigermene **3** represents the second structurally characterized molecule containing a Si-Ge-Ge-Si chain in which all four atoms are not members of a ring. For both compounds there are no significant variations of the Ge-Cl bond lengths [**5**: Ge-Cl 2.2149(14) Å (average); **3**: Ge-Cl 2.1938(15) Å]. However, the Ge-Ge distance in **3** [2.4647(10) Å] is shorter than in **5** [2.5310(7) Å (average)] but longer than in (Me₃Si)₃SiCl₂Ge-GeCl₂Si(SiMe₃)₃ [10].

Experimental Section

All experiments were carried out under dry argon with strict exclusion of air and moisture using standard Schlenk techniques. *t*Bu₃SiNa [3] was prepared according to literature procedures. The solvents (benzene, tetrahydrofuran, heptane) were distilled from sodium/benzophenone prior to use. The NMR spectra were recorded on Bruker AM 250 (¹H/¹³C: 250.133/62.896 MHz), Bruker DPX 250 (¹H/¹³C/²⁹Si: 250.130/62.895/49.69 MHz) and Bruker AMX 400 (¹H/²⁹Si: 400.130 MHz/79.495 MHz) spectrometers. The ²⁹Si NMR spectra were recorded using the IN-EPT pulse sequence with empirically optimized parameters for polarization transfer from the *t*Bu substituents.

Synthesis of 3: A solution of 0.3 ml (0.56 g; 2.63 mmol) GeCl₄ in 6 ml pentane was added to a cooled (−78 °C) solution of 5.2 mmol *t*Bu₃SiNa(THF)₂ in 10 ml pentane. The solution was stirred for 4 h at a temperature of −78 °C and then allowed to warm slowly to ambient temperature. Then all volatile components were removed *in vacuo* and the remaining solid residue was extracted into 10 ml toluene. After filtration, **3** was separated by GPC using toluene as eluent (stationary phase: Phenogel 100 Å, 5 μm, retention time of 7.2 min) [11]. NMR data for **3** are listed in Table 1.

Oxidation of 4: Crystals of the composition (5)₂ · **3** were grown by storing a benzene solution of (*t*Bu₃SiGeCl)₃ (0.34 mmol) [8] and (*t*Bu₃Si)Cl₂Ge-GeCl₂(*Sir*Bu₃) (0.06 mmol) on air at room temperature.

Crystal structure determination: Data collection: Stoe-IPDS-II diffractometer, graphite-monochromated Mo-K_α radiation; *T* = 173 K, empirical absorption correction using MULABS [12], structure solution by direct methods, [13] structure refinement: full-matrix least-squares on *F*² using SHELXL-97. Hydrogen atoms were placed on ideal

Table 1. NMR data for **3**, **4**, and **5**.

	¹ H NMR (C ₆ D ₆)	¹³ C NMR (C ₆ D ₆)	²⁹ Si NMR (C ₆ D ₆)
3	δ 1.39 (s; <i>Sir</i> Bu ₃)	δ 26.1 (s; CMe ₃), 32.8 (s; CMe ₃)	δ 53.8 (s; <i>Sir</i> Bu ₃), 48.4 (s; 2 <i>Sir</i> Bu ₃)
4	δ 1.39 (s; 2 <i>Sir</i> Bu ₃) 1.40 (s; <i>Sir</i> Bu ₃)	δ 25.6 (s; CMe ₃), 26.1 (s; 2 CMe ₃), 31.7 (s; CMe ₃), 31.9 (s; 2 CMe ₃)	δ 46.5 (s; <i>Sir</i> Bu ₃), 48.4 (s; 2 <i>Sir</i> Bu ₃)
5	δ 1.34 (s; 2 <i>Sir</i> Bu ₃) 1.38 (s; <i>Sir</i> Bu ₃)	δ 26.2 (s; CMe ₃), 26.8 (s; 2 CMe ₃), 32.0 (s; 2 CMe ₃), 32.4 (s; CMe ₃)	δ 44.4 (s; <i>Sir</i> Bu ₃), 39.9 (s; 2 <i>Sir</i> Bu ₃)

Table 2. Crystal data and structure refinement for (5)₂ · **3**.

Empirical formula	C ₄₈ H ₁₀₈ Cl ₅ OGe ₄ Si ₄
Color	colorless
Shape	block
Formula weight	1281.31
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	14.2019(8)
<i>b</i> [Å]	17.7934(9)
<i>c</i> [Å]	25.5342(17)
β [deg]	94.554(5)
<i>Z</i>	4
Volume [Å ³]	6432.1(6)
Density (calcd.) [g/cm ³]	1.323
Abs coeff μ(Mo-K _α) [mm ^{−1}]	2.164
<i>F</i> (000)	2692
Crystal size [mm ³]	0.32 × 0.26 × 0.23
Diffractometer	Stoe-IPDS-II
θ-Range [deg]	1.96–25.78
Index ranges	−17 ≤ <i>h</i> ≤ 17, −21 ≤ <i>k</i> ≤ 21, −31 ≤ <i>l</i> ≤ 31
No. of reflections collected	59013
No. of independent reflections	12249
<i>R</i> (int)	0.0575
Absorption correction	semi-empirical, MULABS
<i>T</i> _{min} , <i>T</i> _{max}	0.5443, 0.6359
No. of data/ restraints/ parameters	12249/0/559
Goodness of fit on <i>F</i> ²	0.922
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)], <i>R</i> ₁ , <i>wR</i> ₂	0.0498, 0.1281
Final <i>R</i> indices [<i>all data</i>], <i>R</i> ₁ , <i>wR</i> ₂	0.0729, 0.1366
Largest diff peak/ hole eÅ ^{−3}	1.787, −0.941

positions and refined with fixed isotropic displacement parameters using a riding model. Crystallographic data (excluding structure factors) for (5)₂ · **3** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 209189. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (Telefax: +1223/336 033. E-mail: deposit@ccdc.cam.ac.uk).

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