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Synthesis and characterization of alkylgermasesquioxanes

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Abstract

Alkyl(chloro)ethoxygermanes, $RGe(OEt)_nCl_{3-n}$ (R = *i*-Pr, $n = 0$; R = *t*-Bu, $n = 0$–3; R = *cyclo*-C_6H_{11}, $n = 0$) were hydrolyzed with aqueous NaOH in xylene at 130–140 °C to give cage hexakis(alkylgermasesquioxane)s, $(RGe)_6O_9$. These structures of cage $(RGe)_6O_9$ were fully confirmed by spectroscopic and X-ray diffraction methods. *t*-Butyldichloro(ethoxy)germane, *t*-$BuGe(OEt)Cl_2$, was carefully treated with water at 5 °C for 3 h to afford *cis*, *trans*-1,3,5-tri-*t*-butyl-1,3,5-trichlorocyclotrigermoxane, (*t*-$BuClGeO)_3$. Hydrolysis of (*t*-$BuClGeO)_3$ at 5 °C for additional 33 h gave a tricyclic *anti*-form ladder 5,7-dichloro-1,3,5,7,9,11-hexa-*t*-butyltricyclo[$7.3.1.1^{3,7}$]hexagermoxanes, (*t*-$BuGe)_6O_8Cl_2$. The tricyclic ladder (*t*-$BuGe)_6O_8Cl_2$ was also prepared by hydrolysis of *t*-butyl(chloro)diethoxygermane, *t*-$BuGe(OEt)_2Cl$, at 5 °C for 6 h, and its structure was determined by spectroscopic and X-ray diffraction analysis. The tricyclic ladder germoxane reacted with aqueous NaOH in xylene at 130–140 °C for 3 h to afford hexakis(*t*-butylgermasesquioxane), (*t*-$BuGe)_6O_9$. The formation mechanism of the germasesquioxane, (*t*-$BuGe)_6O_9$ from *t*-butyl(chloro)ethoxygermanes, *t*-$BuGe(OEt)_nCl_{3-n}$ ($n = 0$–3) is also discussed.

Keywords: Germoxane; Germasesquioxane; Structures; X-ray diffraction; Cage compound

1. Introduction

Spherical organosilsesquioxanes with the formula $(RSiO_{1.5})_n$ and related compounds containing Si–O bonds in a main chain have been a subject of considerable interest because of their unique structures, chemical, physical properties, and potential technological utility [1]. Matsumoto and co-workers [2], and several groups [3–7] reported the synthesis of cage, ladder, and sheet-like oligomers and polymers of $(RSiO_{1.5})_n$ and established their structures by X-ray analysis. They are organometallic analogues of silicate anions, $(Si_nO_{2.5n})^{n-}$. The modified silicate can be used as preceramic building blocks [8], organolithic macromolecular materials [9], heterogeneous silica-supported metal catalyst [10] and potential photoresists [11–13], and so on. While the organosilsesquioxanes have been amply investigated, there have been few reports on organogermasesquioxanes [14]. To the best of our knowledge, Puff and co-workers first reported the hexakis(*t*-butylgermasesquioxane), (*t*-$BuGe)_6O_9$ by hydrolysis of *t*-$BuGeCl_3$, and its structure was confirmed by X-ray diffraction analysis [14]. In this paper, we describe the synthesis and characterization of hexakis(alkylgermasesquioxane)s and their intermediates in hydrolysis of alkyl(chloro)ethoxygermanes by utilization of the difference in reactivity between the chlorine and alkoxy groups on the germanium atom.

2. Results and discussion

2.1. *Preparation and structures of hexakis(alkylgermasesquioxane)s (1)*

When a xylene solution of one mole equivalent of alkyltrichlorogermane, $RGeCl_3$ (R = *i*-Pr (**a**), *t*-Bu (**b**), *cyclo*-C_6H_{11} (**c**)) containing three mole equivalents of NaOH in water was heated at 130–140 °C for 3 h, the corresponding hexakis(alkylgermasesuquioxane) ((R-$Ge)_6O_9$, **1**) were obtained as the sole products in isolated 70–98% yields.

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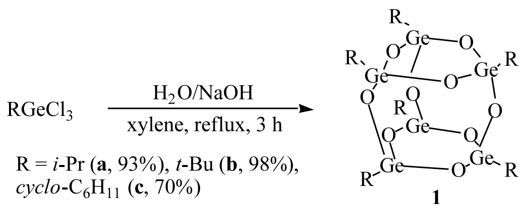

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Concentration of the reaction mixture by evaporation of xylene followed by recrystallization from diethyl ether gave a colorless crystal with the composition of germoxanes, $(RGe)_6O_9$ (**1a**–**c**). These structures of germasesquioxanes were fully established by spectroscopic (^{1}H-, ^{13}C-NMR, IR, and MS) and X-ray diffraction methods. A xylene solution of one mole equivalent of *t*-butyltriethoxygermane, *t*-BuGe(OEt)$_3$ containing three mole equivalents of NaOH in water at 130–140 °C for 3 h under similar reaction conditions also gave **1b** in isolated 64% yield, together with small amounts of unidentified products. The colorless crystal **1b** was obtained by the recrystallization from diethyl ether. The ORTEP drawings of **1a** and **1c** are shown in Figs. 1 and 2. The crystal structure of **1b**, prepared by hydrolysis of *t*-BuGeCl$_3$, has been reported by Puff and co-workers [14].

$$t\text{-BuGe(OEt)}_3 \xrightarrow[\text{xylene, reflux, 3 h}]{\text{H}_2\text{O/NaOH}} \mathbf{1b}$$

Selected bond lengths, angles, and crystallographic data are summarized in Tables 1, 2 and 4. The hexakis(alkylgermasesquioxane)s, **1a** and **1c**, adopt cage structures. Two six-membered Ge_3O_3 rings are joined co-facially by Ge–O bridges, generating three further eight-membered Ge_4O_4 rings. The average Ge–O bond length in six-membered ring is 1.752 Å, and that in eight-membered ring is 1.760 Å. The average O–Ge–O bond angle in six- and eight-membered rings is 108°, and that Ge–O–Ge bond angle is 131° in six- and eight-membered rings. The observed Ge–O bond length, O–Ge–O and Ge–O–Ge bond angles for **1a** and **1c** are consistent with those of **1b** reported previously [14]. The Ge–O bond lengths of $(Ph_2GeO)_3$ and $(t\text{-}Bu_2GeO)_3$ are 1.77 and 1.78 Å, respectively. The O–Ge–O and Ge–O–Ge bond angles of $(Ph_2GeO)_3$ and $(t\text{-}Bu_2GeO)_3$ are 107.4 and 128.6, and 107.0 and 133.0°, respectively [15,16]. The Ge–O bond length of **1a** and **1c** is just a little shorter than those of $(Ph_2GeO)_3$ and $(t\text{-}Bu_2GeO)_3$. The O–Ge–O and Ge–O–Ge bond angles of **1a** and **1c** are somewhat wider, possibly due to distortion brought about by the cage structures. In contrast to $(R_2GeO)_3$ (R = Ph, *t*-Bu) where the Ge_3O_3 ring is invariably near-planar, the two six-membered Ge_3O_3 rings in **1a** and **1c** adopt a chair conformation. The bond angles about germanium for **1a** and **1c** show some deviation from the ideal tetrahedral value. The three eight-membered Ge_4O_4 in **1a** and **1c** adopt a crown configuration with the four oxygen atoms lying above the Ge_4 plane.

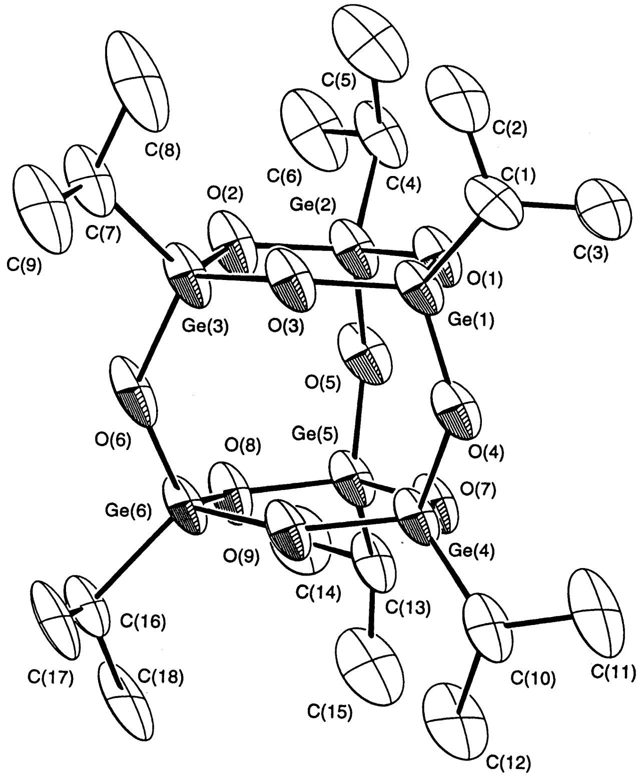


Fig. 1. ORTEP drawing of **1a**. Thermal ellipsoids are drawn at the 30% probability level.

In the hydrolysis reaction of RGeCl$_3$ and RGe(OEt)$_3$, several germoxanes are postulated to be possible intermediates for the formation of the cage germoxanes. To obtain further information we attempted the spectroscopic detection of an intermediate species involved in hydrolysis of RGeCl$_3$ and RGe(OEt)$_3$, but without success. Therefore, we tried to isolate intermediates in hydrolysis of *t*-butyl(chloro)ethoxygermane, *t*-BuGe(OEt)$_n$Cl$_{3-n}$ ($n = 0$–3) by utilization of the difference in reactivity between the chlorine and ethoxy groups on the germanium atom.

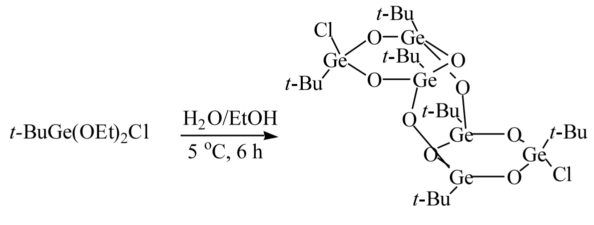
2.2. Preparation and structures of tricyclic anti-form ladder hexagermoxanes (2)

The *tert*-butyl(chloro)diethoxygermane, *t*-BuGe(OEt)$_2$Cl, prepared by treatment of *tert*-butyltrichlorogermane, *t*-BuGeCl$_3$ with ethanol in the presence of stoichiometric amounts of pyridine at room temperature for 2 weeks, was carefully hydrolyzed in ethanol at 5 °C for 6 h. After GC examination of the disappearance of *t*-BuGe(OEt)$_2$Cl, the reaction mixture was concentrated by evaporation of ethanol. The residue was dissolved in benzene at 5 °C and the generated solids were filtered off. Concentration of the organic layer by evaporation of benzene followed by recrystallization from hexane gave 5,7-dichloro-1,3,5,7,9-hexa-*tert*-butyltricyclo[7.3.1.1^{3,7}]octagermoxane ($(t\text{-}BuGe)_6O_8Cl_2$ **2**) in 29% isolated yield. The ^{1}H-NMR spectrum of **2** displayed two

Table 1
Selected bond lengths (Å) and angles (°) of **1a**

Bond lengths					
Ge1–O4	1.746(4)	Ge1–O3	1.758(4)		
Ge1–O1	1.763(4)	Ge1–C1	1.916(5)		
Ge2–O1	1.751(3)	Ge2–O5	1.751(3)		
Ge2–O2	1.755(3)	Ge2–C4	1.941(5)		
Ge3–O6	1.750(3)	Ge3–O3	1.760(4)		
Ge3–O2	1.763(4)	Ge3–C7	1.926(5)		
Bond angles					
O4–Ge1–O3	107.95(18)	O4–Ge1–O1	108.27(17)	O3–Ge1–O1	107.26(17)
O4–Ge1–C1	111.2(2)	O3–Ge1–C1	111.9(2)	O1–Ge1–C1	110.0(2)
O1–Ge2–O5	109.68(17)	O1–Ge2–O2	107.65(17)	O5–Ge2–O2	108.72(17)
O1–Ge2–C4	110.5(2)	O5–Ge2–C4	109.81(19)	O2–Ge2–C4	110.4(2)
O6–Ge3–O3	108.47(18)	O6–Ge3–O2	109.00(18)	O3–Ge3–O2	107.68(17)
O6–Ge3–C7	110.5(2)	O3–Ge3–C7	110.5(2)	O3–Ge3–C7	110.6(2)

tert-butyl signals at 1.29 and 1.32 ppm in 1:2 ratio. The ^{13}C-NMR showed four signals at 25.9, 26.5, 30.5, and 34.7 ppm. These NMR data indicated that germoxane **2** was a symmetrical structure. The structure of **2** had determined unequivocally by X-ray crystallography.



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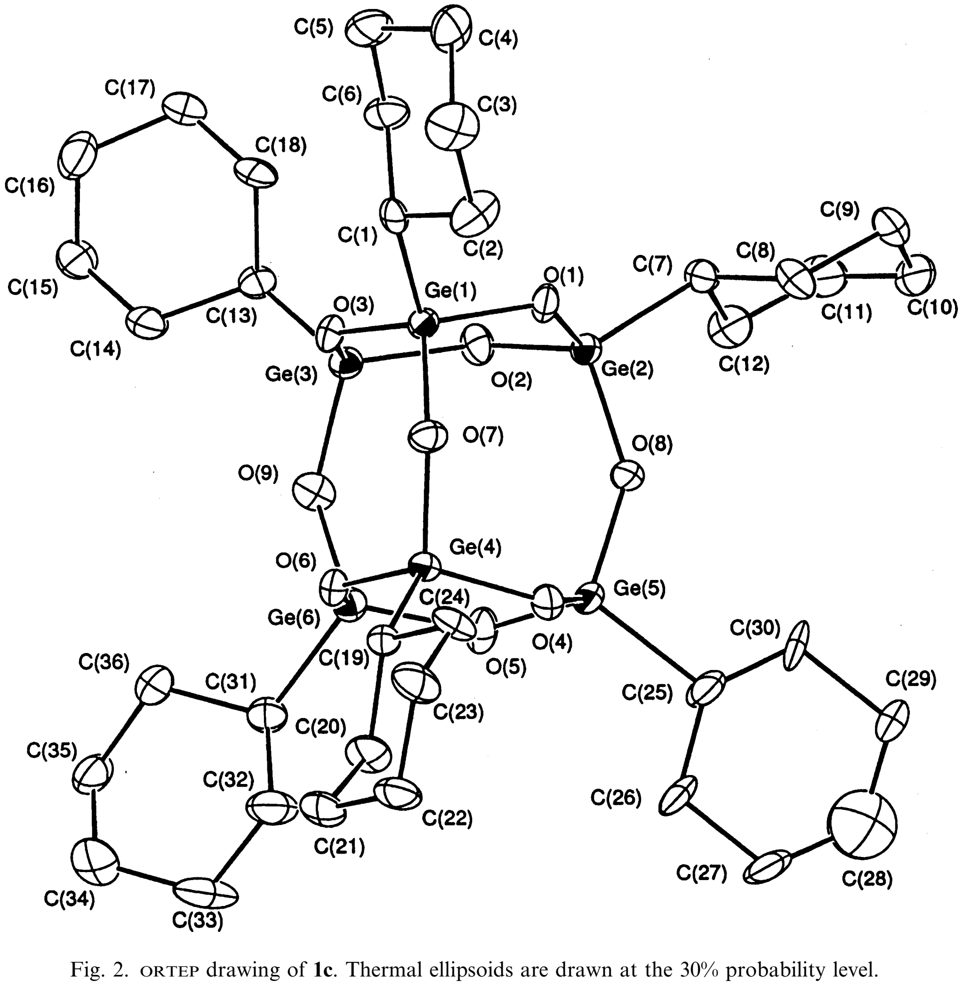


Fig. 2. ORTEP drawing of **1c**. Thermal ellipsoids are drawn at the 30% probability level.

Table 2
Selected bond lengths (Å) and angles (°) of **1c**

Bond lengths					
Ge1–O7	1.753(7)	Ge1–O3	1.765(6)		
Ge1–O1	1.768(6)	Ge1–C1	1.920(9)		
Ge2–O8	1.745(6)	Ge2–O2	1.757(7)		
Ge2–O1	1.761(7)	Ge2–C7	1.942(9)		
Ge3–O2	1.756(7)	Ge3–O3	1.760(6)		
Ge3–O9	1.765(7)	Ge3–C13	1.936(9)		
Bond angles					
O7–Ge1–O3	109.8(3)	O7–Ge1–O1	109.1(3)	O3–Ge1–O1	107.5(3)
O7–Ge1–C1	107.2(3)	O3–Ge1–C1	113.3(3)	O1–Ge1–C1	109.9(3)
O8–Ge2–O2	109.8(4)	O8–Ge2–O1	108.8(3)	O2–Ge2–O1	106.4(3)
O8–Ge2–C7	106.4(3)	O2–Ge2–C7	111.1(4)	O1–Ge2–C7	114.3(4)
O2–Ge3–O3	107.3(3)	O2–Ge3–O9	109.1(4)	O3–Ge3–O9	109.7(3)
O2–Ge3–C13	111.1(4)	O3–Ge3–C13	112.5(4)	O9–Ge3–C13	107.1(4)

The ORTEP drawing is shown in Fig. 3 as an *anti*-form ladder germoxane. Selected bond lengths, angles, and crystallographic data are summarized in Tables 3 and 4. The average Ge–O bond length in the six- and eight-membered rings is same (1.76 Å). The average O–Ge–O is 107°; the average Ge–O–Ge bond angle is 126.5°. The structural parameters of **2** (e.g. Ge–O bond lengths, Ge–O–Ge angles, O–Ge–O angels) are similar with those for **1**. All these values are within the normal range, showing that this molecule is strain-free.

A xylene solution of one mole equivalent of **2** containing 10 mol equivalents of NaOH in water was

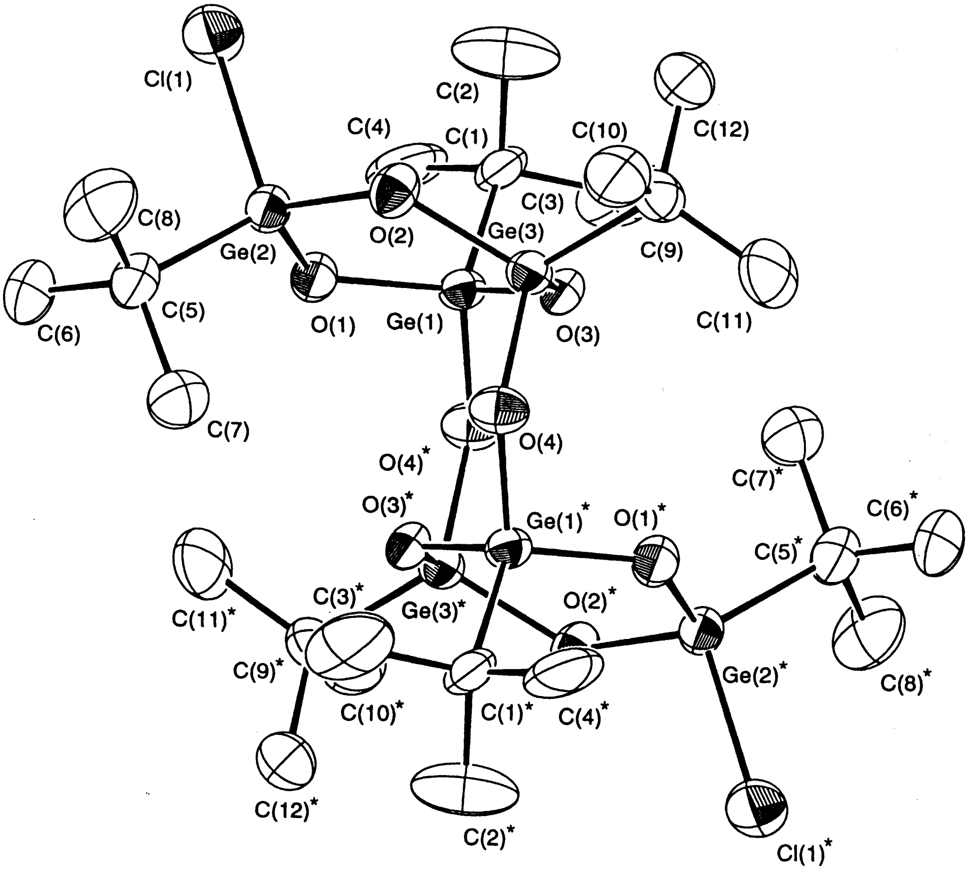


Fig. 3. ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 30% probability level.

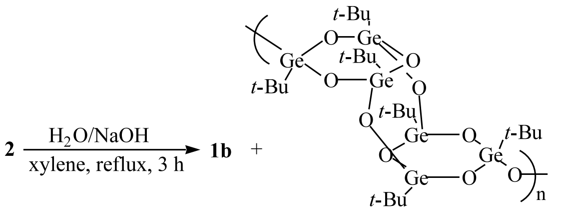
Table 3
Selected bond length (Å) and angles (°) of **2**

Bond lengths					
Ge1–O4*	1.751(3)	Ge1–O3	1.765(3)		
Ge1–O1	1.780(3)	Ge1–C1	1.947(4)		
Ge2–O1	1.746(3)	Ge2–O2	1.755(3)		
Ge2–C5	1.946(4)	Ge2–C1	2.1739(12)		
Ge3–O4	1.768(3)	Ge3–O3	1.759(3)		
Ge3–O2	1.776(3)	Ge3–C9	1.939(4)		
Bond angles					
O4*–Ge1–O3	107.39(13)	O4*–Ge1–O1	106.43(13)	O3–Ge1–O1	107.68(13)
O4*–Ge1–C1	109.80(15)	O3–Ge1–C1	112.05(16)	O1–Ge1–C1	113.18(16)
O1–Ge2–O2	108.32(13)	O1–Ge2–C5	114.97(17)	O2–Ge2–C5	113.14(17)
O1–Ge2–Cl1	106.12(10)	O2–Ge2–Cl1	105.68(10)	C5–Ge2–Cl1	109.97(14)
O4–Ge3–O3	108.59(13)	O4–Ge3–O2	106.90(14)	O3–Ge3–O2	107.13(13)
O4–Ge3–C9	110.95(16)	O3–Ge3–C9	111.75(16)	O2–Ge3–C9	111.30(16)
Ge2–O1–Ge1	128.13(16)	Ge2–O2–Ge3	125.70(16)	Ge1–O3–Ge3	127.80(15)

Table 4
Crystallographic data for **1a**, **1c**, and **2**

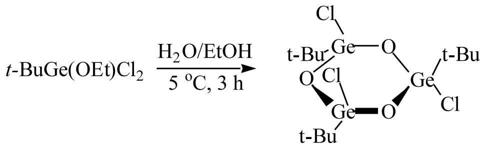
	1a	**1c**	**2**
Formula	$C_{18}H_{42}Ge_6O_9$	$C_{36}H_{66}Ge_6O_9$	$C_{24}H_{54}Cl_2Ge_6O_8$
Molecular weight	838.06	1078.43	977.11
Crystal description	Colorless prism	Colorless prism	Colorless prism
Crystal size (mm)	0.40 × 0.20 × 0.20	0.20 × 0.20 × 0.20	0.40 × 0.30 × 0.30
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	$P\bar{1}$	$P212121$	$P\bar{1}$
a (Å)	11.9140(11)	11.6520(4)	10.2730(10)
b (Å)	12.5490(11)	17.6130(6)	10.8580(10)
c (Å)	13.2720(15)	21.2470(9)	10.9450(10)
β (°)	64.205(5)	90	71.909(5)
V (Å^3)	1559.9(3)	4360.5(3)	986.84(16)
Z	2	4	1
Radiation (λ (Å))	Mo–K$_\alpha$ (0.71070)	Mo–K$_\alpha$ (0.71070)	Mo–K$_\alpha$ (0.71070)
Temperature (K)	295	200	200
D_{calc} (g cm^{-3})	1.784	1.643	1.644
Unique reflections	4280	3511	2604
Goodness-of-fit	1.048	1.041	1.113
R	0.0479	0.0443	0.0371
R_w	0.0388	0.0377	0.0354

heated at 130–140 °C for 3 h. After concentration of the reaction mixture by evaporation of xylene, the crude products were identified by NMR, GC, and GC–MS spectra. The cage germoxane **1b** was formed in 18% isolated yield together with oligogermoxanes. The structure of the oligogermoxanes may suppose to be oligomers of **2** from NMR, GC–MS, and GPC data. The presence of **1b** suggests that the *anti*-form ladder germoxane **2** is clearly an intermediate for the formation of cage germoxanes, (t-BuGe)$_6$O$_9$.



2.3. Preparation of cyclic germoxanes (3)

The *tert*-butyldichloro(ethoxy)germane, t-BuGe(OEt)Cl$_2$, prepared by treatment of t-BuGeCl$_3$ with ethanol at room temperature for 2 weeks, was in control of hydrolysis at 5 °C for 3 h to give a new cyclic germoxane, (t-BuGeOCl)$_3$ (**3**). The cyclic germoxane **3** was isolated by distillation in 31% yield. The ^{1}H-, ^{13}C-NMR examination of **3** showed a single isomer; ^{1}H-NMR (CDCl$_3$) spectrum of **3** displayed two *tert*-butyl signals at 1.29 and 1.33 ppm in 1:2 ratio. ^{13}C-NMR of **3** showed four signals at 25.2, 25.5, 35.4, and 39.6 ppm. A fragment peak (M$^+$ $-t$-Bu) with m/z 487 was observed. The NMR (^{1}H and ^{13}C{^{1}H}) and GC–MS spectra indicate that **3** exists as a single isomer. The geometry is *cis*,*trans*-1,3,5-tri-*tert*-butyl-1,3,5-trichlorocyclotrigermoxane.



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After careful control of hydrolysis of **3** at 5 °C for an additional 33 h, the *anti*-form ladder germoxane **2** was formed in 45% GC yield. A small amount of the cage germoxane **1b** was also detected by GC–MS.

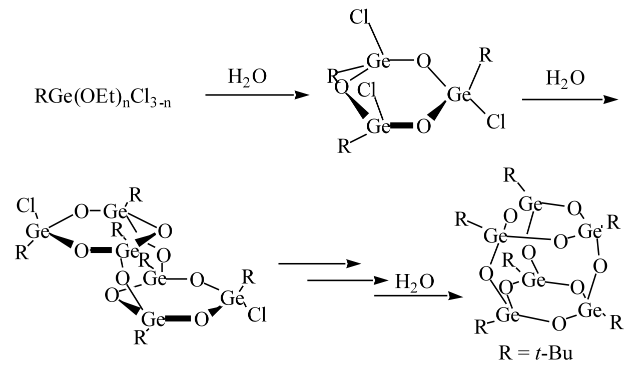
$$\mathbf{3} \xrightarrow[5\ ^\circ\mathrm{C},\ 33\ \mathrm{h}]{H_2O/EtOH} \mathbf{2}$$

The formation of **1b** was identified with NMR, GC, and GC–MS spectra in comparison with those of authentic sample. The presence of **2** suggests that the germoxane **3** is clearly an intermediate for the formation of tricyclic *anti*-form ladder germoxanes, (t-BuGe)$_6$O$_8$Cl$_2$.

2.4. Reaction mechanism

The simplest rationalization of the above results is shown below. At first, *t*-butyldichloro(ethoxy)germane, t-BuGe(OEt)Cl$_2$, may be hydrolyzed to give *t*-butyldichloro(hydroxyl)germane, t-BuGe(OH)Cl$_2$, by the difference in reactivity between the chlorine and ethoxy groups on the germanium atom and then, cyclic trigermoxane, (t-BuGeOCl)$_3$, **3** is formed by the dehydrative condensation of t-BuGe(OH)Cl$_2$. The cyclization product **3** exists as *cis*,*trans* geometry. No all-*cis* isomer is formed probably due to the steric hindrance of *t*-butyl groups. Subsequently, two **3** easily couple cofacially to give a tricyclic *anti*-form ladder 5,7-dichloro-1,3,5,7,9,11-hexa-*t*-butyltricyclo[7.3.1.1^{3,7}]hexagermoxane **2**, which undergoes isomerization under these experimental conditions to give a *syn*-isomer after the cleavage of Ge–O bond in the eight-membered ring. Further condensation occurs to give a most stable cage germoxane **1b** after several steps (Scheme 1).

In summary, we have synthesized cage hexakis(alkylgermasesquioxane)s, (RGe)$_6$O$_9$, (R = *i*-Pr, *t*-Bu. *cyclo*-C$_6$H$_{11}$), from hydrolysis of RGe(OEt)$_n$Cl$_{3-n}$ (R = *i*-Pr, $n = 0$; R = *t*-Bu, $n = 0$–3; R = *cyclo*-C$_6$H$_{11}$, $n = 0$), and these structures were determined by spectroscopic and X-ray diffraction methods. Cyclic germoxanes are hydrolyzed to form tricyclic *anti*-form ladder germoxanes, and additional hydrolysis of tricyclic germoxanes afford cage germoxanes.



Scheme 1.

3. Experimental

3.1. General methods

The NMR spectra were obtained on a Varian Unity Inova 400 MHz NMR spectrometer. The GC–MS spectra were measured on a JEOL JMS-DX 303 mass spectrometer. Gas chromatography was performed on a Shimadzu GC 8A with 1 m 20% SE30 column. Liquid chromatography was performed on a Twincle with an Asahipak GS 310 column. X-ray crystallographic data and diffraction intensities were collected on a MacScience DIP2030 diffractometer utilizing graphite-monochromated Mo–K$_\alpha$ ($\lambda = 0.71073$ Å) radiation. The structures were solved by direct methods using the program system SIR-92. A refinement was performed by full-matrix least-square using program a SILICON Graphics O$_2$ with maXus.

3.2. Materials

i-PrGeCl$_3$ [17] and *cyclo*-C$_6$H$_{12}$GeCl$_3$ [18], were prepared as reported in the literature.

3.3. Preparation of tert-butyltrichlorogermane (t-BuGeCl$_3$)

To a solution of trichlorogermane (46.0 g, 0.25 mol) in Et$_2$O (125 ml) was added a Et$_2$O solution (25 ml) of *tert*-butyl chloride (23.4 g, 0.25 mol) at 0 °C. The mixture was stirred at 0 °C for 1 day and the solution was concentrated to ca. 10 ml. After pentane (50 ml) was slowly added, colorless solid was formed. Recrystallization from Et$_2$O formed pure t-BuGeCl$_3$ (38.0 g, 0.15 mol, 60%) [17].

3.4. Preparation of tert-butyldichloro(ethoxy)germane, t-BuGe(OEt)Cl$_2$

t-BuGeCl$_3$ (0.1 g, 0.4 mmol) and dry EtOH (20 ml) were placed in two-necked 100 ml flask. The mixture was stirred at room temperature (r.t.) for 2 weeks. Crude t-BuGe(OEt)Cl (> 70%) was obtained by distillation. ^{1}H-NMR (δ, C$_6$H$_6$) 0.85 (t, $J = 7.0$ Hz, 3 H), 1.05 (s, 9 H), 3.94 (q, $J = 7.0$ Hz, 2 H). GC–MS (70 eV) *m*/*z* (relative intensity) 246 (M$^+$, 13), 231 (34), 211 (13), 201 (56), 189 (24), 157 (100).

3.5. Preparation of tert-butyl(chloro)diethoxygermane, t-BuGe(OEt)$_2$Cl

To a solution of t-BuGeCl$_3$ (7.08 g, 0.03 mol) in dry EtOH (10 ml) was added pyridine (2.40 g, 0.03 mol) at r.t. The mixture was stirred at r.t. for 1 week. Pure t-BuGe(OEt)$_2$Cl (1.09 g, 4.3 mmol, 14% yield) was obtained by distillation, b.p. 50 °C/50 mmHg. ^{1}H-

NMR (δ, C_6H_6) 0.93 (t, $J = 7.0$ Hz, 6 H), 1.12 (s, 9 H), 3.94 (q, $J = 7.0$ Hz, 4 H); ^{13}C-NMR (δ, C_6H_6) 18.8, 25.9, 26.7, 61.3. GC–MS (70 eV) *m/z* (relative intensity) 256 (M^+, 4), 231 (34), 211 (53), 199 (64), 164 (25), 154 (100). Found: C, 37.90; H, 7.25. Calc. for $C_8H_{19}ClGeO_2$: C, 37.64; H, 7.50%.

3.6. Preparation of tert-butyltriethoxygermane, t-BuGe(OEt)$_3$

To a solution of *t*-$BuGeCl_3$ (7.12 g, 0.03 mol) in dry EtOH (100 ml) was added pyridine (7.22 g, 0.10 mol) at r.t. The mixture was stirred at r.t. for 5 days. Pure *t*-$BuGe(OEt)_3$ (3.28 g, 12.4 mmol, 41% yield) was obtained by distillation, b.p. 70 °C/24 mmHg. ^{1}H-NMR (δ, C_6H_6) 1.24 (s, 9 H), 1.25 (t, $J = 7.0$ Hz, 9 H), 3.94 (q, $J = 7.0$ Hz, 6 H); ^{13}C-NMR (δ, C_6H_6) 18.5, 25.9, 33.4, 61.1. GC–MS (70 eV) *m/z* (relative intensity) 266 (M^+, 2), 251 (4), 221 (14), 209 (28), 164 (100), 119 (60). Found: C, 45.70; H, 8.95. Calc. for $C_{10}H_{24}GeO_3$: C, 45.35; H, 9.13%.

3.7. Hydrolysis of iso-propyltrichlorogermane

Aqueous NaOH (NaOH, 3.62 g, H_2O, 80 ml) was added to a stirred solution of *i*-$PrGeCl_3$ (7.11 g, 0.03 mol) in xylene (200 ml). The mixture was heated to reflux for 3 h. The organic layer was washed with water. The aqueous phase was extracted with xylene. The combined organic phase was dried over anhydrous magnesium sulfate and evaporated. The residue was recrystallized from Et_2O to give hexakis(*i*-propylgermasesquioxane) **1a** (3.90 g, 4.65 mmol, 93%). ^{1}H-NMR (δ, $CDCl_3$) 1.25 (d, $J = 7.5$ Hz, 36 H), 1.73 (sept, $J = 7.5$ Hz, 6 H); ^{13}C-NMR (δ, $CDCl_3$) 17.4, 21.6; IR (KBr, cm^{-1}) 499.5, 794.6, 875.6, 1465.8, 2869.9. GC–MS (70 eV) *m/z* (relative intensity) 795 (M^+, 100), 752 (4), 709 (9), 660 (9); Found: C, 25.67; H, 5.23. Calc. for $C_{18}H_{42}Ge_6O_9$: C, 25.79; H, 5.05%.

3.8. Hydrolysis of cyclo-hexyltrichlorogermane

Aqueous NaOH (NaOH, 3.70 g, H_2O, 80 ml) was added to a stirred solution of *cyclo*-$HexGeCl_3$ (7.99 g, 0.03 mol) in xylene (200 ml). The mixture was heated to reflux for 3 h. The organic layer was washed with water. The aqueous phase was extracted with xylene. The combined organic phase was dried over anhydrous magnesium sulfate and evaporated. The residue was recrystallized from Et_2O to give hexakis(*cyclo*-hexylgermasesquioxane) **1c** (3.77 g, 3.50 mmol, 70%). ^{1}H-NMR (δ, $CDCl_3$) 1.3–1.9 (m); ^{13}C-NMR (δ, $CDCl_3$) 26.3, 26.9, 27.2, 32.4; IR (KBr, cm^{-1}) 489.9, 796.5, 1448.4, 2850.6, 2925.8. Found: C, 40.49; H, 6.53. Calc. for $C_{36}H_{66}Ge_6O_9$: C, 40.09; H, 6.17%.

3.9. Hydrolysis of tert-butyltriethoxygermane

Aqueous NaOH (NaOH, 0.24 g, H_2O, 30 ml) was added to a stirred solution of *t*-$BuGe(OEt)_3$ (0.62 g, 2.26 mmol) in xylene (15 ml). The mixture was heated to reflux for 3 h. The organic layer was washed with water. The aqueous phase was extracted with xylene. The combined organic phase was dried over anhydrous magnesium sulfate and evaporated. The residue was recrystallized from Et_2O to give hexakis(*t*-butylgermasesquioxane) **1b** (0.22 g, 0.24 mmol, 64%). ^{1}H-NMR (δ, $CDCl_3$) 1.22 (s); ^{13}C-NMR (δ, $CDCl_3$) 26.5, 30.2.

3.10. Hydrolysis of t-butyl(ethoxy)dichlorogermane

Water (3.0 mg, 0.17 mmol) was added to a stirred solution of *t*-$BuGe(OEt)Cl_2$ (0.03 g, 0.13 mol) in EtOH at 5 °C for 3 h. A pure *cis*,*trans*-1,2,3-tri-*t*-butyl-1,2,3-trichlorocyclotrigermoxane, (*t*-$BuGeOCl)_3$, (**3**) was obtained. ^{1}H-NMR (δ, $CDCl_3$) 1.29 (s, 9 H), 1.33 (s, 18 H); ^{13}C-NMR (δ, $CDCl_3$) 25.2, 25.5, 35.4, 39.6. GC–MS (70 eV) *m/z* (relative intensity) 487 ($M^+ - Bu$, 100), 430 (80), 415 (20), 395 (14), 372 (11), 338 (8), 268 (5)709 (9), 660 (9).

3.11. Hydrolysis of t-butyldiethoxy(chloro)germane

Water (0.14 g, 7.6 mmol) was added to a stirred solution of *t*-$BuGe(OEt)_2Cl$ (0.97 g, 3.5 mmol) in EtOH (20 ml) at 5 °C for 6 h. After the solvent was evaporated, the residue was dissolved in C_6H_6. The generated solids were filtered off. Concentration of the organic layer by evaporation of C_6H_6 followed by recrystallization from hexane gave a pure 5,7-dichloro-1,3,5,7,9-hexa-*tert*-butyltricyclo[7.3.1.1^{3,7}]octagermoxane, (*t*-$BuGe)_6O_8Cl_2$ (**2**), in 29.1% yield (0.18 g, 0.18 mmol). ^{1}H-NMR (δ, C_6D_6) 1.29 (s, 18 H), 1.32 (s, 36 H); ^{13}C-NMR (δ, C_6D_6) 25.9, 26.5, 30.5, 34.7. m.p. 233–234 °C. GC–MS (70 eV) *m/z* (relative intensity) 921 ($M^+ - Bu$, 77), 827 (15), 57 (100). Found: C, 29.75; H, 5.43. Calc. for $C_{24}H_{54}Cl_2Ge_6O_8$: C, 29.50; H, 5.57%.

3.12. Hydrolysis of 5,7-dichloro-1,3,5,7,9-hexa-tert-butyltricyclo[7.3.1.1^{3,7}]octagermoxane

Aqueous NaOH (NaOH, 4 mg, H_2O, 1 ml) was added to a stirred solution of (*t*-$BuGe)_6O_8Cl_2$ (0.01 g, 0.01 mmol) in xylene (10 ml). The mixture was heated to reflux for 3 h. After the solvent was evaporated, the residue was obtained. A pure (*t*-$BuGe)_6O_9$ (1.8 mg, 18% yield) was isolated by preparative GPC. Polygermoxane, $[(t\text{-}BuGe)_6O_9]_n$ (4.6 mg) was also obtained. ^{1}H-NMR (δ, C_6D_6) 1.25 (s); ^{13}C-NMR (δ, C_6D_6) 2.6, 29.6.

3.13. X-ray crystallography

Crystallographic data for **1a**, **1c**, and **2** are summarized in Table 4. Crystallographic data for **1a**, **1b**, and **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-192754, 193021, and 192755, respectively.

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