Bull. Chem. Soc. Jpn., *73*, 2093—2097 (2000)

Synthesis, Structure, and Reactions of Octakis(1,1,2-trimethylpropyl)octagermacubane

Masafumi Unno, Koichi Higuchi, Koji Furuya, Hiroaki Shioyama, Soichiro Kyushin, Midori Goto,[†] and Hideyuki Matsumoto[*]

Department of Applied Chemistry, Faculty of Engineering, Gunma University, Kiryu 376-8515

[†]National Institute of Materials and Chemical Research, Tsukuba 305-8565

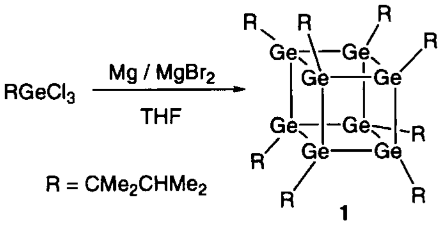
(Received February 10, 2000)

Octathexyloctagermacubane (**1**, thexyl = 1,1,2-trimethylpropyl) was synthesized by the condensation of trichlorothexylgermane with Mg/MgBr$_2$, and structurally characterized by X-ray crystallography. As in the case of the thexyl-substituted octasilacubane, a ring-opening reaction followed by skeletal rearrangement of **1** took place with PCl$_5$ to give *endo*, *exo*- and *exo*,*exo*-4,8-dichlorooctathexyltetracyclo[3.3.0.0^{2,7}.0^{3,6}]octagermanes. Treatment of these dichlorides with sodium afforded octagermacubane **1**.

Since the first synthesis of the octasilapentacyclo-[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane (octasilacubane, (t-BuMe$_2$Si)$_8$Si$_8$) in 1988,[1] the synthesis and properties of polyhedranes of group 14 elements (Si, Ge, and Sn) have been reported from several research groups.[2,3] Recently, we reported studies on the synthesis,[4] electronic properties,[5] halogenative ring-opening reactions,[6] their reverse reactions,[7] and mono- and di-oxidation[8] of the alkyl-substituted octasilacubane Thex$_8$Si$_8$, **2**.[9] We have then been interested in comparing the chemical and physical properties of octasilacubane **2** with those of the corresponding octagermacubane, Thex$_8$Ge$_8$ (**1**). To allow such a comparison, octagermacubane **1** has now been made. Here, we report the synthesis, X-ray structure, electronic properties, and reactions of **1**. To date, only two alkyl- and aryl-substituted octagermacubane R$_8$Ge$_8$ (R = 2, 6-diethylphenyl and 1-ethyl-1-methylpropyl) have been reported by Sakurai and Sekiguchi,[2] and they showed the crystal structure of octakis(2,6-diethylphenyl)octagermacubane. However, no X-ray structure of the alkyl-substituted octagermacubane was published so far.

Results and Discussion

Synthesis of Octagermacubane. Octagermacubane (**1**) was obtained by the reaction of trichlorothexylgermane (thexyl or Thex denotes 1,1,2-trimethylpropyl hereafter) with Mg in the presence of MgBr$_2$[10] in THF (Scheme 1). In the case of octasilacubane with same substituents, Thex$_8$Si$_8$, the target compound was obtained with the reaction of trichlorothexylsilane and sodium in toluene,[4] however no octagermacubane was given under similar conditions. We also examined the reaction with lithium or sodium naphthalenide; the reaction gave a complex mixture, from which **1** could not be isolated. The cubic structure of **1** was deduced on the basis of the following spectral data: The field desorption mass spectrum showed a molecular ion cluster in the range m/z 1249—1278, in agreement with that calculated for C$_{48}$H$_{104}$Ge$_8$. The NMR spectra were fully consistent with the highly symmetrical geometry; compound **1** exhibits three resonances in ^{1}H NMR and four in ^{13}C{^{1}H} NMR spectra, indicating that all thexyl groups are equivalent. No absorptions attributed to Ge–H and Ge–O bonds were observed in the IR spectrum.



Scheme 1.

Structure of Octagermacubane. The X-ray crystal structure determination unequivocally established the structure of **1** (Fig. 1). Crystallographic data are shown in Table 1, and the selected bond lengths and angles are listed in Table 2. The molecule possesses only one two-fold axis passing the midpoint of Ge(1)–Ge(1′) and Ge(3)–Ge(3′) bonds, and is crystallographically isomorphous to octathexyloctasilacubane **2**.[4] The Ge–Ge bond lengths range from 2.494 to 2.540 Å (average 2.516 Å). They are approximately 0.026 Å longer than in the peraryl derivative, Ar$_8$Ge$_8$ (Ar = 2, 6-Et$_2$C$_6$H$_3$) (av. 2.490 Å).[2] The Ge–Ge–Ge bond angles lie between 88.0 and 91.9° (av 90.0°). The exocyclic Ge–C bonds are slightly elongated (2.037–2.056 Å, av 2.046 Å) relative to Ar$_8$Ge$_8$ (av 1.982 Å). The Ge–Ge–C bond angles vary from 116.1 to 132.7° (av 125.2°). This distortion may be the result of the strain of the substituents, which requires the least steric repulsion of eight thexyl groups.

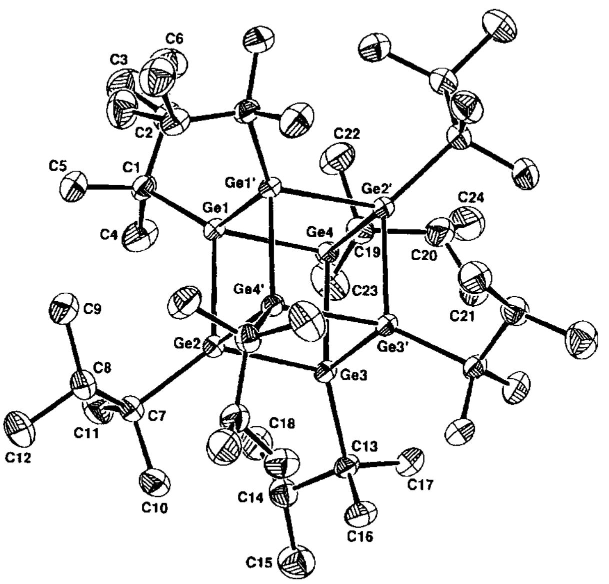


Fig. 1. ORTEP drawing of **1**. Thermal ellipsoids are drawn at the 30% probability level.

Table 1. Data of X-Ray Diffraction Analysis for **1**

Crystal data	
Formula	$C_{48}H_{104}Ge_8$
Mol wt	1262.24
Cryst descript, mm	0.16 × 0.20 × 0.43
Cryst syst	Monoclinic
Space group	*C2/c*
a/Å	13.955(1)
b/Å	19.482(1)
c/Å	21.228(2)
β/deg	99.907(4)
V/Å^3	5685.3(8)
Z	4
$d_{\mathrm{obsd}}/\mathrm{g\,cm^{-3}}$	1.473
$d_{\mathrm{calc}}/\mathrm{g\,cm^{-3}}$	1.475
Data collection	
Diffractometer	Enraf–Nonius CAD-4
Radiation	Cu $K\alpha$ (1.54184 Å)
μ/cm^{-1}	54.41
Variation of stds/%	−2.1
2θ range/deg	4—130
Scan type	ω–2θ
No. of reflns measd	5034
No. of ind rflns	4684
No. of obsd refln ($\lvert F_o \rvert \geq 3\sigma(F_o)$)	3807
R	0.035
R_w	0.062
Weighting scheme	$w = 1/\delta^2(F_o)$
$(\Delta/\sigma)_{\max}$	0.06
$(\Delta\rho)_{\max}$, eÅ^{-3}	0.59

Properties of Octagermacubane. Compound **1** forms yellow prisms, which are moderately soluble in organic solvents (benzene, toluene, hexane, THF, and dichloromethane). The result of thermogravimetric analysis is shown in Fig. 2. The result discloses that octagermacubane **1** is thermally stable and decomposes only above 190 °C. By comparison, $Thex_8Si_8$ decomposes at 200 °C. From TGA-mass spectrum, the weight loss is the result of the elimination of thexyl groups.

The highly strained Ge_8 framework of **1** gives rise to unusual electronic properties. The oxidation potential of **1**, 0.22 V (CH_2Cl_2, Bu_4NClO_4, saturated calomel electrode (SCE)), is much lower in value than that of $Thex_8Si_8$ **2** (0.43 V, CH_2Cl_2, Bu_4NClO_4, SCE), suggesting that the highest occupied molecular orbital (HOMO) of **1** lies at a higher level in energy than that of $Thex_8Si_8$ does. However, in comparison of the UV-visible spectrum of **1** with that of $Thex_8Si_8$,

Table 2. Selected Bond Lengths (Å) and Angles (deg) of **1**

Bond lengths			
Ge(1)–Ge(2)	2.517(1)	Ge(1)–Ge(4)	2.510(1)
Ge(1)–Ge(1′)	2.540(1)	Ge(2)–Ge(3)	2.510(1)
Ge(2)–Ge(4′)	2.494(1)	Ge(3)–Ge(4)	2.515(1)
Ge(3)–Ge(3′)	2.527(1)	Ge(1)–C(1)	2.047(4)
Ge(2)–C(7)	2.037(4)	Ge(3)–C(13)	2.045(4)
Ge(4)–C(19)	2.056(5)		
Bond angles			
Ge(2)–Ge(1)–Ge(4)	90.3(1)	Ge(2)–Ge(1)–Ge(1′)	88.0(1)
Ge(4)–Ge(1)–Ge(1′)	91.0(1)	Ge(1)–Ge(2)–Ge(3)	89.7(1)
Ge(1)–Ge(2)–Ge(4′)	91.9(1)	Ge(3)–Ge(2)–Ge(4′)	89.6(1)
Ge(2)–Ge(3)–Ge(4)	90.3(1)	Ge(2)–Ge(3)–Ge(3′)	90.5(1)
Ge(4)–Ge(3)–Ge(3′)	88.7(1)	Ge(1)–Ge(4)–Ge(3)	89.7(1)
Ge(1)–Ge(4)–Ge(2′)	89.1(1)	Ge(3)–Ge(4)–Ge(2′)	91.1(1)
Ge(2)–Ge(1)–C(1)	127.0(1)	Ge(4)–Ge(1)–C(1)	116.1(1)
Ge(1′)–Ge(1)–C(1)	132.7(1)	Ge(1)–Ge(2)–C(7)	124.0(1)
Ge(3)–Ge(2)–C(7)	128.3(1)	Ge(4′)–Ge(2)–C(7)	122.7(1)
Ge(2)–Ge(3)–C(13)	121.3(1)	Ge(4)–Ge(8)–C(13)	131.3(1)
Ge(3′)–Ge(3)–C(13)	128.3(1)	Ge(1)–Ge(4)–C(19)	128.5(1)
Ge(8)–Ge(4)–C(19)	124.5(1)	Ge(2′)–Ge(4)–C(19)	122.8(1)
Ge(1)–C(1)–C(2)	109.0(3)	Ge(1)–C(1)–C(4)	104.7(3)

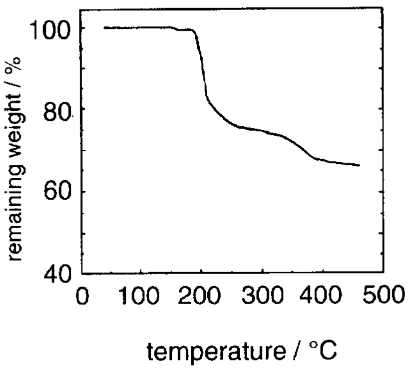


Fig. 2. Thermogravitic analysis of **1**.

one may note that the absorption of **1** (235 nm shoulder) exhibits a hypsochromic shift from that of $\mathrm{Thex_8Si_8}$ (252 nm). Thus, $\mathrm{Thex_8Si_8}$ shows absorption maxima at 252 nm (ε 30800), at 350 nm (ε 850), and at 502 nm (ε 70); the spectrum of $\mathrm{Thex_8Ge_8}$ shows absorption maxima at 236 nm (ε 68600) and tails into the visible region, but it does not show any absorption maxima around 500 nm (Fig. 3). The hypsochromic shift observed for **1** is likely caused by a greater energy separation between the HOMO and the lowest unoccupied molecular orbital (LUMO), presumably due to the high-lying LUMO in **1**. The experimental support for higher-lying LUMO ($\sigma^*_{\mathrm{Ge-Ge}}$) of oligogermanes was provided by Moldelli and coworkers,[11] who found by electron transmission spectroscopy that the LUMO ($\sigma^*_{\mathrm{Ge-Ge}}$) of $\mathrm{Me_3GeGeMe_3}$ shifts 0.30 eV to higher energy in comparison with $\sigma^*_{\mathrm{Si-Si}}$ of $\mathrm{Me_3SiSiMe_3}$.

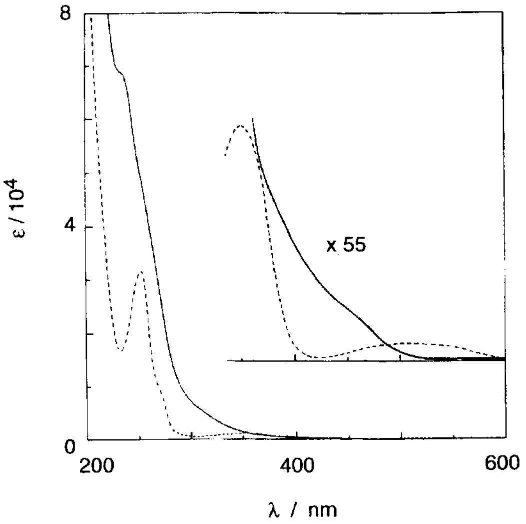
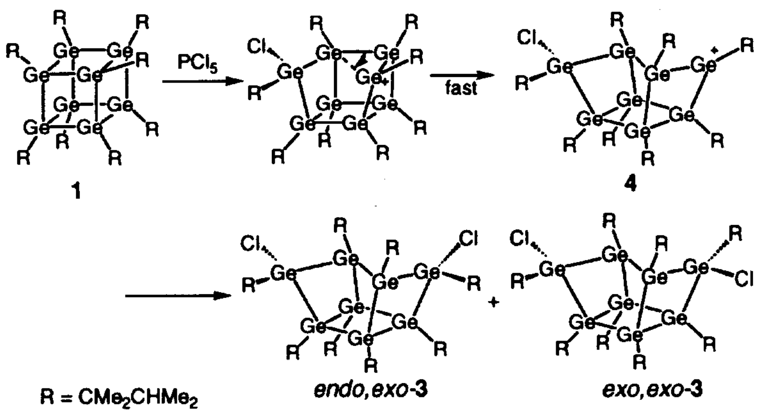


Fig. 3. UV-vis Spectrum of **1** and **2** in hexane. $\mathrm{Thex_8Ge_8}$ (**1**) : —, $\mathrm{Thex_8Si_8}$ (**2**) : ·····.

Chlorination Reaction of 1. Due to the low oxidation potential, compound **1** is reactive with electrophiles. Chlorination of **1** with $\mathrm{PCl_5}$ in benzene reached completion in 10 h at room temperature. After separation by a recycle-type preparative HPLC, *endo,exo*- and *exo,exo*-4,8-dichlorooctakis(1,1,2-trimethylpropyl)tetracyclo[3.3.0.0^{2,7}.0^{3,6}]octagermane (**3**) (7% and 37% yields, respectively) were obtained. These compounds were identified by the following spectral results. The mass spectra showed similar fragmentation patterns for both compounds and the mass numbers supported the formula $\mathrm{Thex_8Ge_8Cl_2}$. The IR spectra showed no absorption bands ascribed to Ge–O and Ge–H bond. In ^{1}H NMR, *endo,exo*-**3** showed 16 sets of singlets and doublets, and 48 peaks in ^{13}C NMR. These results indicated the eight thexyl groups were not equivalent. On the other hand, 8 sets of singlets and doublets in ^{1}H NMR and 24 peaks in ^{13}C NMR were observed for *exo,exo*-**3**, showing the symmetrical structure of *exo,exo*-isomer. In the case of $\mathrm{Thex_8Si_8}$, the similar reaction gave three isomers: *endo,exo*-, *endo,endo*-, and *exo,exo*-dichlorides.[6] Comparing the NMR data of **3** with those of silyl analogues showed that the products were *exo,exo*-**3**. The reason of the absence of *endo,endo*-isomer could be explained by the exclusive generation of the intermediate **4** (Scheme 2). Also, the less steric hindrance of exo-isomer accounts for the higher yield of *exo,exo*-**3**. The frameworks of **3** are known in fact; Sekiguchi, Sakurai et al. reported $t\text{-}\mathrm{Bu_8Ge_8Cl_2}$[13] and Weidenbruch et al. reported $t\text{-}\mathrm{Bu_8Ge_8Br_2}$[14] both in 1989. They prepared these compounds by reductive coupling from substituted halogermanes with lithium naphthalenide. Interestingly they isolated only *exo,exo*-isomers, which were thought to be the most thermodynamically stable.

Reductive Dechlorination of 3. In the case of silicon analogues, octasilacubane could be regenerated from the isomeric mixtures of dihalides $\mathrm{Thex_8Si_8X_2}$ (X = Cl, Br, I).[7] We first examined the reaction of **3** with $\mathrm{Mg/MgBr_2}$ in THF



Scheme 2.

as in the case of the synthesis of octagermacubane from trichlorothexylgermane. Against our expectation, no octagermacubane was obtained. Instead, treatment of **3** (mixture of isomers) with sodium in toluene at 120 °C gave octagermacubane **1** in 50% yield (Scheme 3). It is noteworthy that Weidenbruch commented that the generation of octagermacubane from t-Bu$_8$Ge$_8$Br$_2$ was not possible.[14] In our case, the higher stability of thexyl-substituted octagermacubane is one of the reasons of the generation of octagermacubane, while the regeneration of more strained cubane skeleton demanded high reaction temperature.

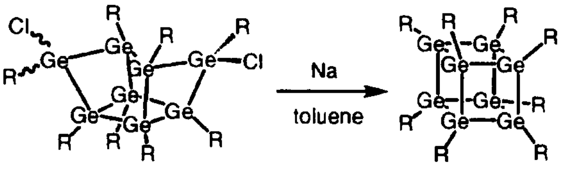
Experimental

Synthesis of Octakis(1, 1, 2- trimethylpropyl)pentacyclo-[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octagermane (1). Under argon atmosphere, magnesium (2.77 g, 114 mmol) and THF (30 mL) were placed in a 100 mL three-necked flask equipped with a condenser and a dropping funnel. With stirring, 1,2-dibromoethane (4.3 g, 23 mmol) in THF (5 mL) was dropped at room temperature. The solution color first turned black, then white MgBr$_2$ generated. To this, trichlorothexylgermane (3.97 g, 15.0 mmol) in 35 mL of THF was dropped for 3.5 h at r.t. After dropping, the black solution was stirred for 3 h. Hexane was added to the mixture and the salt was separated by filtration. Removal of the solvent gave 2.24 g of orange solid. This solid was purified by column chromatography (silica, hexane) and recrystallization from benzene gave 79 mg (3.3%) of octagermacubane (**1**).

1: yellow prisms, mp (sealed) 194 °C (decomp); ^{1}H NMR (C$_6$D$_6$) δ = 1.13 (d, J = 6.8 Hz, 48H), 1.56 (s, 48H), 2.44 (sept, J = 6.8 Hz, 8H); ^{13}C NMR (C$_6$D$_6$) δ = 20.73, 26.35, 39.31, 46.33; IR (KBr) ν 2947, 2857, 1454, 1372, 1359, 1202, 1142, 1125, 1082; UV (hexane) $\lambda_{\max}$ (ε) 235 nm (sh, 68300); MS (FD) m/z 1249—1278 (M$^+$). Calcd for C$_{48}$H$_{104}$Ge$_8$: C, 45.68; H, 8.30%. Found: C, 45.36; H, 8.29%.

X-Ray Crystallography of 1. Some crystals of **1** suitable for the X-ray analysis were obtained by recrystallization from benzene. Each crystal was mounted in a glass-capillary under dry argon atmosphere. Intensity data of **1** were collected on a Enraf–Nonius CAD-4 with graphite monochromated Cu-$K\alpha$ radiation at room temperature. The structure was solved by direct methods with Multan78 Program[15] using the reflections with $F > 3\sigma$ (F_o). The structure was refined anisotropically for non-hydrogen atoms by full-matrix least-square using the Molen[16] package system. Hydrogen atoms were not refined.

Reaction of 1 with PCl$_5$. To the benzene solution (10 ml) of **1** (49.5 mg, 39 µmol), 10 mg (48 µmol) of PCl$_5$ was added at 0 to 5 °C. Then the mixture was stirred at room temperature for 10 h and filtered, and benzene was removed. The resulting pale yellow solid was separated by HPLC (ODS, MeOH/THF = 6/4) and analytically pure *endo,exo*-**3** (3.5 mg, 7%) and *exo,exo*-**3** (19.2 mg, 37%) were obtained. *endo,exo*-**3**: ^{1}H NMR (C$_6$D$_6$) δ = 0.97 (d, 6H, J = 6.7 Hz), 0.98 (d, 3H, J = 6.7 Hz), 1.02 (d, 3H, J = 6.7 Hz), 1.03 (d, 3H, J = 6.7 Hz), 1.11 (d, 3H, J = 6.7 Hz), 1.13 (d, 6H, J = 6.7 Hz), 1.16 (d, 6H, J = 6.7 Hz), 1.18 (d, 3H, J = 6.7 Hz), 1.19 (d, 3H, J = 6.7 Hz), 1.20 (d, 3H, J = 6.7 Hz), 1.24 (d, 3H, J = 6.7 Hz), 1.25 (d, 3H, J = 6.7 Hz), 1.29 (d, 3H, J = 6.7 Hz), 1.41 (s, 3H), 1.46 (s, 3H), 1.49 (s, 3H), 1.50 (s, 3H), 1.537 (s, 3H), 1.543 (s, 3H), 1.55 (s, 3H), 1.57 (s, 3H), 1.59 (s, 3H), 1.62 (s, 3H), 1.64 (s, 3H), 1.66 (s, 3H), 1.69 (s, 3H), 1.71 (s, 3H), 1.73 (s, 3H), 1.81 (s, 3H), 2.36 (sept, 1H, J = 6.7 Hz), 2.42 (sept, 1H, J = 6.7 Hz), 2.50—2.57 (m, 5H), 2.78 (sept, 1H, J = 6.7 Hz); ^{13}C NMR (C$_6$D$_6$) δ = 17.74, 18.99, 19.12, 19.20, 19.35, 19.92, 20.64, 20.99, 21.38, 21.51, 21.69, 21.78, 22.20, 22.26, 22.51, 22.65, 25.14, 25.34, 25.80, 25.95, 26.30, 26.74, 26.95, 27.25, 27.57, 27.78, 28.33, 28.40, 29.17, 29.41, 36.12, 36.72, 37.11, 37.23, 37.30, 37.82, 37.93, 47.13, 47.49, 48.57, 48.91, 49.17, 49.56, 50.24, 51.88, 58.70, 60.65, 67.26; MS (70 eV) m/z (%) 1164 (M$^+$ − 2Thex, 0.2), 69 (100); IR (KBr) ν 1085, 1125, 1375, 1450, 2880, 2960 cm^{-1}. HRMS (70 eV) Found : m/z 1342.1990. Calcd for C$_{48}$H$_{104}$C$_{12}$Ge$_8$: M, 1342.1211. *exo,exo*-**3**: colorless prisms, mp > 500 °C (sealed). ^{1}H NMR (C$_6$D$_6$) δ = 1.01 (d, 6H, J = 6.7 Hz), 1.06 (d, 12H, J = 6.7 Hz), 1.09 (d, 6H, J = 6.7 Hz), 1.12 (d, 6H, J = 6.7 Hz), 1.148 (d, 6H, J = 6.7 Hz), 1.150 (d, 6H, J = 6.7 Hz), 1.27 (d, 6H, J = 6.7 Hz), 1.51 (s, 3H), 1.49 (s, 3H), 1.50 (s, 3H), 1.537 (s, 3H), 1.543 (s, 6H), 1.57 (s, 6H), 1.58 (s, 6H), 1.59 (s, 6H), 1.60 (s, 6H), 1.62 (s, 6H), 1.64 (s, 12H), 2.51 (m, 8H); ^{13}C NMR (C$_6$D$_6$) δ = 18.90, 20.01 (overlap), 20.25, 20.62, 20.72, 20.93, 21.15, 21.48, 22.24, 25.99, 26.64, 26.92, 27.03, 27.82, 28.42, 36.04, 36.90, 37.00, 37.81, 48.46, 49.40, 49.88, 51.09; MS (70 eV) m/z (%) 1164 (M$^+$ − 2Thex, 0.9), 69 (100); IR (KBr) ν 1085, 1125, 1375, 1450, 2880, 2960 cm^{-1} ; HRMS (70 eV) Found : m/z Calcd for C$_{48}$H$_{104}$C$_{12}$Ge$_8$: M, 1342.1211. 1342.1330.



3 (mixture of isomers) R = CMe$_2$CHMe$_2$ **1**

Scheme 3.

Reaction of 3 with Sodium. Sodium sand (14 mg, 0.61 mmol) was added to the toluene (1.5 ml) solution of **3** (mixture of isomers, 22.3 mg, 17 µmol). The solution was stirred at 120 °C for 13 h under argon atmosphere. Upon cooling, the reaction mixture was filtered through silica gel to remove sodium chloride and excess sodium. Removal of the solvent afforded yellow semisolid, and recrystallization from hexane gave pure octagermacubane **1** (10.5 mg, 50%). Identification was made by comparing the NMR, IR, and mass spectra with those of the authentic sample.

We thank Asai Germanium Institute for the gift of germanium compounds.

References

1 H. Matsumoto, K. Higuchi, Y. Hoshino, H. Koike, Y. Naoi, and Y. Nagai, *J. Chem. Soc., Chem. Commun.*, **1988**, 1083.

2 A. Sekiguchi, T. Yatabe, H. Kamatani, C. Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, **144**, 6260 (1992).

3 A. Sekiguchi and H. Sakurai, *Adv. Organomet. Chem.*, **37**, 1 (1995), and references cited therein.

4 H. Matsumoto, K. Higuchi, S. Kyushin, and M. Goto, *Angew. Chem., Int. Ed. Engl.*, **31**, 1354 (1992).

5 a) Y. Kanemitsu, K. Suzuki, H. Uto, Y. Matsumoto, T. Matsumoto, S. Kyushin, K. Higuchi, and H. Matsumoto, *Appl. Phys. Lett.*, **61**, 2446 (1992). b) Y. Kanemitsu, K. Suzuki, H. Uto, Y. Matsumoto, K. Higuchi, S. Kyushin, and H. Matsumoto, *J. Appl. Phys. Jpn.*, **32**, 408 (1993).

6 M. Unno, K. Higuchi, M. Ida, H. Shioyama, S. Kyushin, H. Matsumoto, and M. Goto, *Organometallics*, **13**, 4633 (1994).

7 M. Unno, H. Shioyama, M. Ida, and H. Matsumoto, *Organometallics*, **14**, 4004 (1995).

8 M. Unno, T. Yokota, and H. Matsumoto, *J. Organomet. Chem.*, **521**, 409 (1996).

9 H. Matsumoto, S. Kyushin, M. Unno, and R. Tanaka, *J. Organomet. Chem.*, in press.

10 a) C. L. Smith and R. Gooden, *J. Organomet. Chem.*, **81**, 33 (1974). b) W. Ando and T. Tsumuraya, *J. Chem. Soc., Chem. Commun.*, **1987**, 1514.

11 A. Modelli, D. Jones, L. Favaretto, and G. Distefano, *Organometallics*, **15**, 380 (1995). The comparison of cyclohexasilane and cyclohexagermane was also reported in Ref. 12.

12 M. Okano and K. Mochida, *Chem. Lett.*, **1990**, 701.

13 A. Sekiguchi, H. Naito, H. Nameki, K. Ebata, C. Kabuto, and H. Sakurai, *J. Organomet. Chem.*, **368**, C1 (1989).

14 M. Weidenbruch, F. -T. Grimm, S. Pohl, and W. Saak, *Angew. Chem., Int. Ed. Engl.*, **28**, 198 (1989).

15 P. Main, S. E. Hull, K. Lassinger, G. Germain, J. -P. Declercq, and M. M. Woolfson, "A System of Computer Programs for the Automatic Solution of Crystal Structures for the X-ray Diffraction Data, Multan78," (1978).

16 C. K. Fair, "Molen. Structure Determination Package," Enraf–Nonius (1990).