

Syntheses, Structures, and Properties of Tricyclo[5.1.1.1^{3,5}]tetrasilachalcogenanes (Thex₂Si₂E₂)E₂ (E = S, Se) and Tricyclo[5.1.1.1^{3,5}]tetragermachalcogenanes (Thex₂Ge₂E₂)E₂ (E = S, Se)

Masafumi Unno, Yuuki Kawai, Hiroaki Shioyama, and Hideyuki Matsumoto*

Department of Applied Chemistry, Faculty of Engineering, Gunma University, Kiryu,
Gunma 376, Japan

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Reactions of ThexSiCl₃ (Thex = 1,1,2-trimethylpropyl) with Li₂S and Li₂Se in tetrahydrofuran at room temperature afforded the tricyclo[5.1.1.1^{3,5}]tetrasilachalcogenanes (Thex₂Si₂S₂)S₂ (**1**) and (Thex₂Si₂Se₂)Se₂ (**2**), respectively. Similar reactions of ThexGeCl₃ with Li₂S and Li₂Se gave the tricyclo[5.1.1.1^{3,5}]tetragermachalcogenanes (Thex₂Ge₂S₂)S₂ (**3**) and (Thex₂Ge₂Se₂)Se₂ (**4**), respectively. X-ray crystallography of **1–4** reveals that these molecules were isomorphous and possess strained “double-decker”-like frameworks (Candiani structure). Compounds **1** and **3** show isomerization at 190 °C to the adamantane-like systems, tricyclo[3.3.1.1^{3,7}]tetrasilathiane (**5**) and tricyclo[3.3.1.1^{3,7}]tetragermathiane (**6**), respectively. For **4**, isomerization to the adamantane cage takes place at much lower temperature (e.g., 80 °C), indicating that Ge–Se double-decker-like cage is more reactive than Si–S and Ge–S cages.

Introduction

Silicon and germanium sesquichalcogenides are of interest because of their intriguing structure and properties.¹ For tetrasilachalcogenanes (RSiE_{1.5})₄ and tetragermachalcogenanes (RGeE_{1.5})₄, two structures are possible: adamantane-like cages and “double-decker”-like cages. From the consideration of ring strain, the adamantane cage has been expected to be more likely than the double-decker-like one, and most of the previous work dealt with the synthesis of silicon–sulfur,² silicon–selenium,³ germanium–sulfur,⁴ and germanium–selenium⁵ adamantane cage structures. The synthesis of compounds with the double-decker structure had not been reported until 1992,⁶ when Ando and co-workers prepared the tricyclo[5.1.1.1^{3,5}]tetragermathiane (*t*-Bu₂Ge₂S₂)S₂ in 30% yield by the reaction of *t*-BuGeCl₃ with (NH₄)₂S₅ in THF.⁷ A similar structure was also observed in 1995 by Merzweiler in the transition metal-

substituted compounds, [(Cp'(CO)₂FeSi)₄E₆] (Cp' = methylcyclopentadienyl, E = S, Se).⁸ As a part of our study of the chemistry of polyhedral compounds containing silicon and germanium,⁹ we attempted to prepare tetrasilchalcogenides and tetragermsesquichalcogenides with double-decker structures. In a previous communication, we reported the synthesis of tetrathexyl-2,4,6,8,9,10-hexathia-1,3,5,7-tetrasilatrimethylenecyclo[5.1.1.1^{3,5}]decane (**1**),¹⁰ which is the first example of the double-decker-like cage composed of silicon and sulfur (thexyl or Thex denotes 1,1,2-trimethylpropyl hereafter). In this paper, we present the syntheses, structures, and properties of silicon–chalcogenide and germanium–chalcogenide double-decker cages, (Thex₂Si₂S₂)S₂ (**1**), tetrathexyl-2,4,6,8,9,10-hexaselena-1,3,5,7-tetrasilatrimethylenecyclo[5.1.1.1^{3,5}]decane ((Thex₂Si₂Se₂)Se₂, **2**), tetrathexyl-2,4,6,8,9,10-hexasila-1,3,5,7-tetragermatrimethylenecyclo[5.1.1.1^{3,5}]decane ((Thex₂Ge₂S₂)S₂, **3**), and tetrathexyl-2,4,6,8,9,10-hexaselena-1,3,5,7-tetragermatrimethylenecyclo[5.1.1.1^{3,5}]decane ((Thex₂Ge₂Se₂)Se₂, **4**). (see Chart 1.)

Results and Discussion

Synthesis. Ando and co-workers reported that, in the reactions of *t*-BuGeCl₃ with (NH₄)₂S₅ and H₂S/C₅H₅N, reactions proceeded via completely different

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Scheme 1

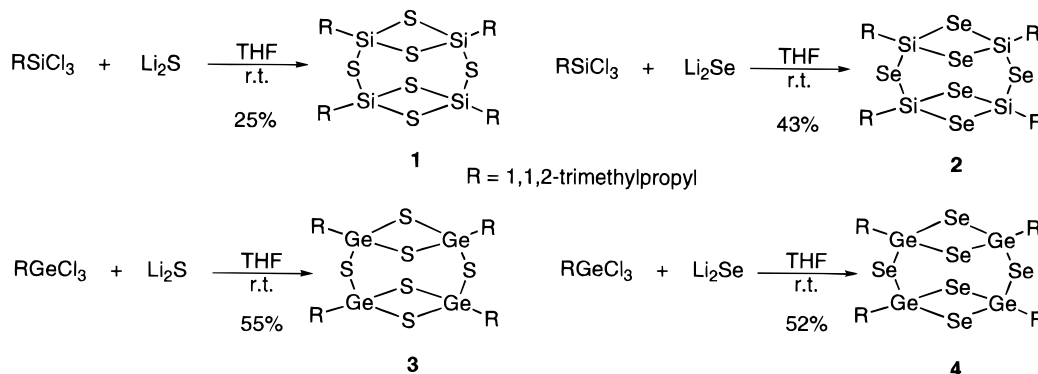
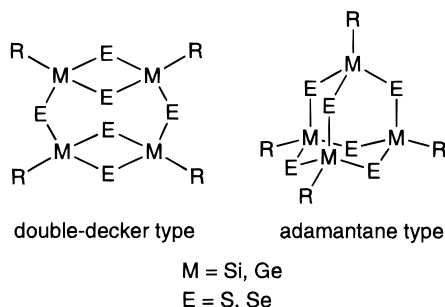


Chart 1



intermediates, depending on the sulfurization reagent. They indicated that a mild sulfurization reagent like $(\text{NH}_4)_2\text{S}_5$ might make a kinetically controlled reaction possible, affording the double-decker cage compound $(t\text{-Bu}_2\text{Ge}_2\text{S}_2)_2\text{S}_2$. In our work, we employed Li_2S or Li_2Se (generated in situ in tetrahydrofuran, THF)¹¹ for the reaction with RSiCl_3 and RGeCl_3 and found that the selection of the substituents is also important in the formation of the double-decker structure. For example, the sulfurization of $t\text{-BuSiCl}_3$ with Na_2S in THF afforded the adamantane cage compound tetra-*tert*-butyl-2,4,6,8,9-hexathia-1,3,5,7-tetrasilatricyclo[3.3.1.1^{3,7}]decane in 11% yield.¹⁰ However, on treatment of ThexSiCl_3 with 1.5 equiv of Li_2S in THF, $(\text{Thex}_2\text{Si}_2\text{S}_2)_2\text{S}_2$ (**1**) was formed in 25% yield. We feel that the less symmetrical structure of the thexyl group as well as its steric congestion may favor the formation of the Si_2S_2 four-membered ring. By the reaction of ThexSiCl_3 and ThexGeCl_3 with Li_2S and Li_2Se , $(\text{Thex}_2\text{Si}_2\text{Se}_2)_2\text{Se}_2$ (**2**), $(\text{Thex}_2\text{Ge}_2\text{S}_2)_2\text{S}_2$ (**3**), and $(\text{Thex}_2\text{Ge}_2\text{Se}_2)_2\text{Se}_2$ (**4**) were obtained in good yields. The results are summarized in Scheme 1. Isolation of these compounds was easily affected (see Experimental Section).

X-ray Structures. The structures of **1–4** were unequivocally established by X-ray crystallography. Crystallographic data, selected bond lengths and angles and nonbonding atom distances are given in Tables 1–5. The ORTEP drawings are shown in Figure 1. All the compounds crystallize in the $C2/c$ space group and have a twofold symmetry axis in the center of the eight-membered ring, and the lattice parameters are very close each other. The Si_4S_6 core of **1** consists of two planar Si_2S_2 rings which are linked by two bridging sulfur atoms. The Si–S bond lengths in **1** showed no difference between four- and eight-membered rings

(2.132(2) vs 2.136(2) Å). The average bond length of 2.133(2) Å is slightly longer than that of adamantane-type $\text{Me}_4\text{Si}_4\text{S}_6$ (2.129 Å).^{2c} An interesting feature of this compound is the very close intramolecular atom distance. In the four-membered rings, the distance of the opposite silicon atoms ($\text{Si}(1)\cdots\text{Si}(2)$) was 2.82 Å. This value is much lower than the sum of van der Waals radii (4.10 Å). Also for sulfur, the $\text{S}(2)\cdots\text{S}(3)$ distance was 3.19 Å and much less than the sum of van der Waals radii (3.60 Å). Obviously this phenomenon resulted from the formation of four-membered rings where bond lengths could not compensate for the atom repulsion. In addition, electronic repulsion of two sulfur atoms might be the reason for shorter Si–Si distance. Very close atom distances were also observed in $(\text{Me}_2\text{SiO})_2$ (2.31 Å for Si atoms)¹² and the Si–O–C–O skeleton of $[(\text{Me}_5\text{C}_5)_2\text{SiO}_2]_2\text{C}$ (2.18 Å for Si and C atoms),¹³ both in four-membered rings. For **2**, the average Si–Se bond length was 2.278(2) Å, slightly shorter than that of $[\text{Cp}'(\text{CO})_2\text{Fe}]_4\text{Si}_4\text{Se}_6$ (2.291(3)–2.306(3) Å).⁸ The nonbonding distances for Si atoms are more than that of **1**, while the distance between Se atoms is slightly shorter than the sum of van der Waals radii (3.53 vs 3.80 Å). Compared with the double-decker tetragermathiane $t\text{-Bu}_4\text{Ge}_4\text{S}_6$ (average 2.234 Å for Ge–S),⁷ **3** possesses slightly shorter Ge–S lengths (average 2.227(2) Å). This length is longer than those of adamantane-type tetragermathiane: 2.218(2) Å for $\text{Me}_4\text{Ge}_4\text{S}_6$,^{4b} and 2.210(2) Å for $(\text{CF}_3)_4\text{Ge}_4\text{S}_6$.^{4f} For **4**, the Ge–Se bond lengths were 2.358(2)–2.364(2) Å (average 2.361(2) Å), for $(\text{CF}_3\text{-Ge})_4\text{Se}_6$,^{4f} the Ge–Se bond length was reported to be 2.344(1) Å, and **4** showed a little longer value presumably reflecting the bulkier thexyl groups.

Properties. The obtained tricyclo[5.1.1.1^{3,5}]tetrasilachalcogenanes and tricyclo[5.1.1.1^{3,5}]tetragermachalcogenanes form colorless (**1–3**) and pale yellow (**4**) crystals which are soluble in common organic solvents (benzene, toluene, cyclohexane, THF, chloroform). They are surprisingly stable toward hydrolysis, and the exceptional inertness of the Si–S, Si–Se, Ge–S, and Ge–Se bonds in **1–4** can be seen in their stability even in concentrated hydrochloric acid. For example, **3** remained undecomposed upon exposure to concentrated hydrochloric acid for 1 week at room temperature, indicating the thexyl group is an efficient protective moiety for conferring kinetic stability upon the double-decker framework.

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Table 1. Summary of Crystal Data, Data Collection, and Refinement

	1	2	3	4
Crystal Data				
formula	C ₂₄ H ₅₂ Si ₄ S ₆	C ₂₄ H ₅₂ Si ₄ Se ₆	C ₂₄ H ₅₂ Ge ₄ S ₆	C ₂₄ H ₅₂ Ge ₄ Se ₆
mol wt	645.38	926.78	823.39	1104.79
cryst description	colorless prisms	colorless prisms	colorless prisms	pale yellow prisms
cryst size, mm	0.2 × 0.2 × 0.2	0.4 × 0.4 × 0.3	0.4 × 0.4 × 0.3	0.3 × 0.3 × 0.1
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	C2/c	C2/c	C2/c	C2/c
a, Å	15.669(3)	15.862(3)	15.875(3)	16.139(2)
b, Å	17.007(2)	17.360(3)	17.293(3)	17.471(2)
c, Å	13.302(2)	13.227(2)	13.161(2)	13.234(1)
β, deg	97.28(1)	99.54(1)	99.33(1)	100.665(7)
V, Å ³	3516.1(8)	3592.0(9)	3565.4(7)	3667.3(5)
Z	4	4	4	4
Data Collection				
diffractometer	Rigaku AFC7S	Rigaku AFC7S	Rigaku AFC7S	Rigaku AFC7S
radiation (λ, Å)	Cu Kα (1.5418)	Cu Kα (1.5418)	Cu Kα (1.5418)	Cu Kα (1.5418)
μ, mm ⁻¹	4.991	8.575	7.262	10.674
variation of stds, %	0	0	0	0
2θ range, deg	4–120	4–120	4–120	4–120
scan type	ω–2θ	ω–2θ	ω–2θ	ω–2θ
scan width, deg	1.05 + 0.30 tan θ	1.10 + 0.30 tan θ	1.26 + 0.30 tan θ	1.52 + 0.30 tan θ
no. of reflns measd	2824	2893	2869	2953
no. of indep reflns	2779	2755	2839	2953
no. of obsd reflns	1770	2425	2428	2217
(F _o ≥ 3σ(F _o))				
Solution and Refinement				
structure soln	SHELXS86	SHELXS86	SHELXS86	SHELXS86
R	0.052	0.040	0.039	0.042
R _w	0.047	0.044	0.046	0.038
weighting scheme	w = 1/σ ² (F _o)	w = 1/σ ² (F _o)	w = 1/σ ² (F _o)	w = 1/σ ² (F _o)
S	2.35	3.30	3.24	2.58
(Δ/σ) _{max}	0.08	0.01	0.01	0.01
(Δρ) _{max} , e Å ⁻³	0.39	0.90	0.93	0.97
(Δρ) _{min} , e Å ⁻³	–0.33	–0.81	–0.51	–0.59
no. of params	227	155	155	155

Table 2. Selected Bond Lengths (Å), Nonbonding Distances (Å), and Bond Angles (deg) for 1

Bond Lengths			
Si(1)–Si(1)	2.139(2)	Si(1)–Si(2)	2.132(2)
Si(2)–Si(1)	2.128(2)	Si(2*)–Si(2)	2.139(2)
Si(3)–Si(1)	2.135(2)	Si(3*)–Si(2)	2.125(2)
Si(1)–C(1)	1.893(6)	Si(2)–C(7)	1.895(7)
Nonbonding Atom Distances			
Si(1)–Si(2*)	2.82	Si(2)–S(3)	3.19
Si(1)–S(1*)	5.25		
Bond Angles			
Si(1)–S(1)–Si(2)	110.68(9)	Si(1)–S(1)–Si(2)	82.91(9)
Si(1)–S(3)–Si(2*)	83.08(9)	Si(1)–Si(1)–S(2)	114.54(9)
S(1)–Si(1)–S(3)	114.2(1)	S(1)–Si(1)–C(1)	103.0(2)
S(2)–Si(1)–S(3)	96.82(9)	S(2)–Si(1)–C(1)	117.6(3)
S(3)–Si(1)–C(1)	111.2(3)	S(1)–Si(2)–S(2*)	114.37(10)
S(1)–Si(2)–S(3*)	113.9(1)	S(1)–Si(2)–C(7)	104.1(2)
S(2*)–Si(2)–S(3*)	96.80(9)	S(2*)–Si(2)–C(7)	116.5(3)
S(3*)–Si(2)–C(7)	111.5(3)		

Table 3. Selected Bond Lengths (Å), Nonbonding Distances (Å), and Bond Angles (deg) for 2

Bond Lengths			
Si(2)–Se(2)	2.282(2)	Si(2)–Se(3)	2.273(2)
Si(2)–C(7)	1.911(7)	Si(2)–Se(1*)	2.279(2)
Si(1)–Se(1)	2.282(2)	Si(1)–Se(2)	2.275(2)
Si(1)–Se(3)	2.276(2)	Si(1)–C(1)	1.912(7)
Nonbonding Atom Distances			
Si(1)–Si(2)	2.99	Se(2)–Se(3)	3.43
Se(1)–Se(1*)	5.66		
Bond Angles			
Se(2)–Si(2)–Se(3)	97.59(5)	Se(2)–Si(2)–C(7)	116.7(2)
Se(2)–Si(2)–Se(1*)	115.17(8)	Se(3)–Si(2)–C(7)	110.1(2)
Se(3)–Si(2)–Se(1*)	113.48(7)	C(7)–Si(2)–Se(1*)	104.0(2)
Se(1)–Si(1)–Se(2)	114.50(8)	Se(1)–Si(1)–Se(3)	114.45(7)
Se(1)–Si(1)–C(1)	103.0(2)	Se(2)–Si(1)–Se(3)	97.69(6)
Se(2)–Si(1)–C(1)	117.9(3)	Se(3)–Si(1)–C(1)	109.8(2)
Si(1)–Se(1)–Si(2*)	108.39(6)	Si(2)–Se(2)–Si(1)	82.14(6)
Si(2)–Se(3)–Si(1)	82.30(6)		

The NMR spectra of **1–4** are consistent with the X-ray crystal structures. Reflecting their high symmetry, **1** and **2** showed only one resonance in the ²⁹Si-{¹H} NMR spectrum, indicating that all silicon atoms are equivalent. The ⁷⁷Se NMR spectra of **2** and **4** are worthy of note. The corresponding spectrum reveals two resonances at –51.7 and –122.2 ppm for **2** and at 154.0 and –3.2 ppm for **4**. The data indicate that the selenium atoms in the four-membered rings and those bridging the two four-membered rings are not equivalent.¹⁴ In ¹H and ¹³C NMR spectra, one kind of thexyl groups is observed for all **1–4**.

(14) In ref 2f, Bahr and Boudjouk pointed out that ⁷⁷Se NMR would discriminate adamantane-like and double-decker-like structures.

Compounds **1**, **3**, and **4** are thermally unstable. When **1** or **3** was heated in decahydronaphthalene at 190 °C for 24 h, the starting materials disappeared and single products were generated. From the results of mass and NMR spectra, both compounds could be assigned as the adamantane-type hexasulfides **5** and **6**. The ²⁹Si chemical shift of **5** was 26.0 ppm, and this value is in good agreement with those of adamantane-type tetrasilathianes (17.0 ppm for Me₄Si₄S₆,^{2f} 21.5 ppm for Et₄Si₄S₆,^{2f} and 29.3 ppm for *t*-Bu₄Si₄S₆¹⁰). The yields were 57% for **5** and quantitative for **6**. Such an isomerization of double-decker to adamantane-type structure was first observed for (*t*-Bu₂Ge₂S₂)₂S₂ over 200 °C.⁷ Interestingly, germanium–selenium derivative **4** showed skeletal rearrangement to **7** at a much lower temperature, 80

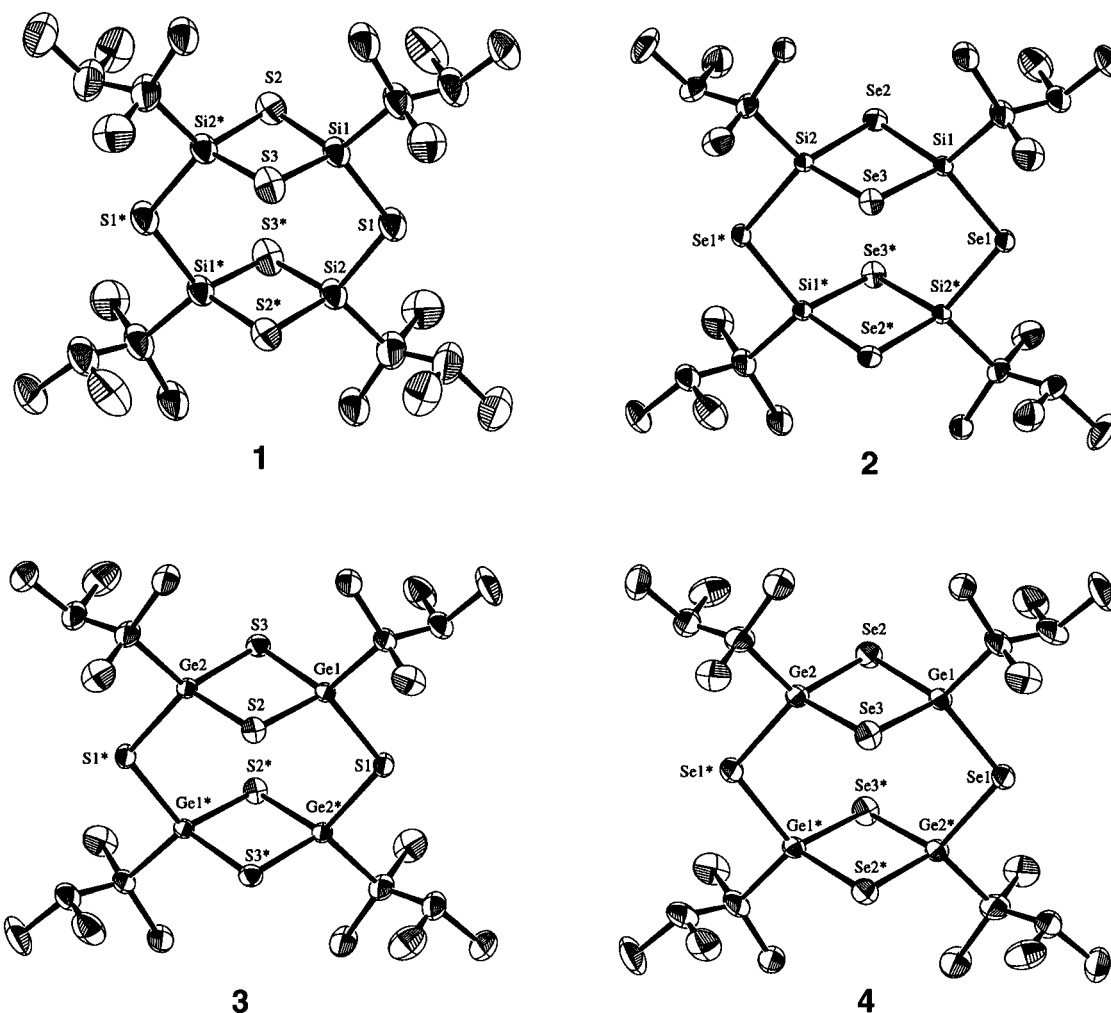


Figure 1. ORTEP drawing of 1–4. Thermal ellipsoids are drawn at the 30% probability level.

Table 4. Selected Bond Lengths (Å), Nonbonding Distances (Å), and Bond Angles (deg) for 3

Bond Lengths			
Ge(1)–S(1)	2.224(2)	Ge(1)–S(2)	2.227(2)
Ge(1)–S(3)	2.232(1)	Ge(1)–C(1)	1.996(6)
Ge(2)–S(2)	2.229(1)	Ge(2)–S(3)	2.226(2)
Ge(2)–C(7)	1.990(6)	Ge(2)–S(1*)	2.227(2)
Nonbonding Atom Distances			
Ge(1)–Ge(2)	2.98	S(2)–S(3)	3.30
S(1)–S(1*)	5.57		
Bond Angles			
S(1)–Ge(1)–S(2)	113.41(6)	S(1)–Ge(1)–S(3)	114.69(6)
S(1)–Ge(1)–C(1)	105.0(6)	S(2)–Ge(1)–S(3)	95.64(5)
S(2)–Ge(1)–C(1)	110.1(2)	S(3)–Ge(1)–C(1)	118.1(2)
S(2)–Ge(2)–S(3)	95.76(5)	S(2)–Ge(2)–C(7)	109.8(2)
S(2)–Ge(2)–S(1*)	114.25(6)	S(3)–Ge(2)–C(7)	119.1(2)
S(3)–Ge(2)–S(1*)	114.57(6)	C(7)–Ge(2)–S(1*)	103.7(2)
Ge(1)–S(1)–Ge(2*)	109.22(6)	Ge(1)–S(2)–Ge(2)	84.22(5)
Ge(1)–S(3)–Ge(2)	84.21(5)		

Table 5. Selected Bond Lengths (Å), Nonbonding Distances (Å), and Bond Angles (deg) for 4

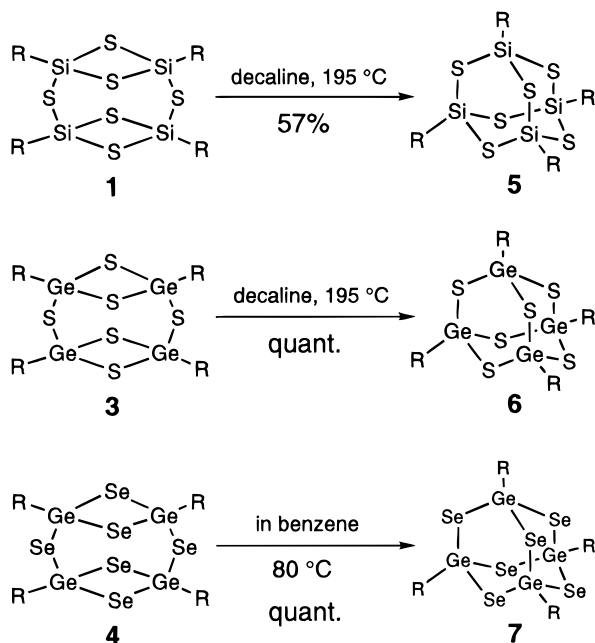
Bond Lengths			
Se(1)–Ge(1)	2.358(2)	Se(1)–Ge(2*)	2.364(2)
Se(2)–Ge(1)	2.363(1)	Se(1)–Ge(2)	2.358(2)
Se(3)–Ge(1)	2.361(2)	Se(3)–Ge(2)	2.362(1)
Ge(1)–C(1)	1.98(1)	Ge(2)–C(7)	1.98(1)
Nonbonding Atom Distances			
Ge(1)–Ge(2)	3.13	Se(2)–Se(3)	3.53
Se(1)–Se(1*)	5.94		
Bond Angles			
Ge(1)–Se(1)–Ge(2*)	107.07(5)	Ge(1)–Se(2)–Ge(2)	83.14(5)
Ge(1)–Se(3)–Ge(2)	83.09(5)	Se(1)–Ge(1)–Se(2)	115.40(6)
Se(1)–Ge(1)–Se(3)	113.48(2)	Se(1)–Ge(1)–C(1)	104.7(3)
Se(2)–Ge(1)–Se(3)	96.77(5)	Se(2)–Ge(1)–C(1)	117.0(3)
Se(3)–Ge(2)–C(1)	109.6(3)	Se(2)–Ge(2)–Se(3)	96.86(5)
Se(2)–Ge(2)–C(7)	118.7(3)	Se(2)–Ge(2)–Se(1*)	114.61(6)
Se(3)–Ge(2)–C(7)	110.0(3)	Se(3)–Ge(2)–Se(1*)	114.53(6)
C(7)–Ge(2)–Se(1*)	102.7(3)		

°C in C₆H₆. These results show that the germanium–selenium framework is more labile, probably due to a lower Ge–Se bond energy. The identification of **7** was effected by ⁷⁷Se NMR (single peak at –6.1 ppm) and other spectral data. The structures of **6** and **7** also were confirmed by X-ray crystallography.¹⁵ The skeletal rearrangement also was observed when the crystal was heated in a nitrogen atmosphere. Thus **1**, **3**, and **4** were converted to adamantane-type **5**–**7** at their melting points (Scheme 2). It is also indicated again that the double-decker compound is the kinetically controlled

product and the adamantane-type compound is the thermodynamically controlled product, as in the case of *t*-Bu₄Ge₄S₆. The proposed reaction pathway for the skeletal rearrangement is shown in Scheme 3. On the

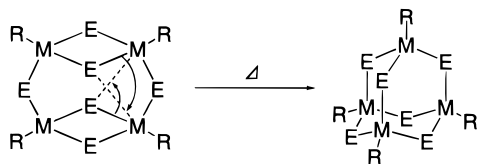
(15) Due to the severe disorder of substituents, presumably caused by sphere shape of the molecule, we could not determine the position of carbon atoms; however, the adamantane-like framework was unequivocally established. Crystal data, **6**: C₂₄H₅₂Ge₄S₆, orthorhombic, *Pna*21, *a* = 12.313(3) Å, *b* = 17.154(3) Å, *c* = 17.490(3) Å, *V* = 3694(2) Å³, *Z* = 4, *R* = 0.073, *R*_w = 0.080. **7**: C₂₄H₅₂Ge₄Se₆, orthorhombic, *P212121*, *a* = 20.572(3) Å, *b* = 20.782(3) Å, *c* = 17.026(3) Å, *V* = 7279(1) Å³, *Z* = 8, *R* = 0.092, *R*_w = 0.083.

Scheme 2



R = 1,1,2-trimethylpropyl

Scheme 3

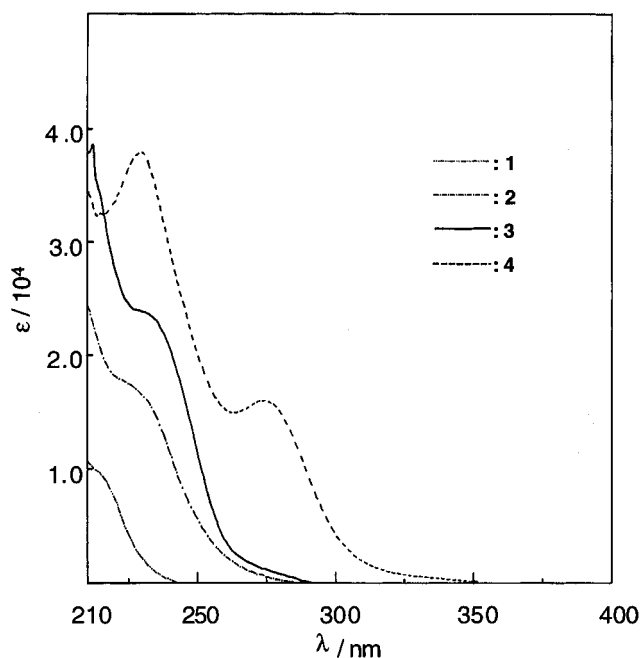
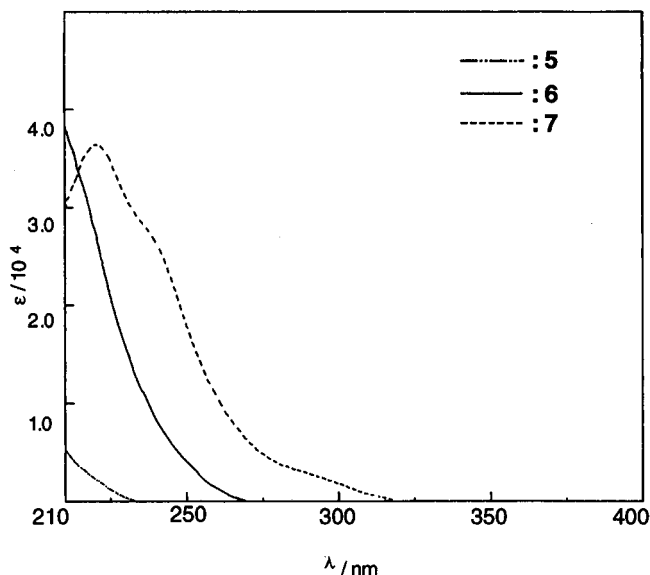


other hand, silicon-selenium analogue **2** was stable to its melting point (272 °C) and no rearrangement was observed.¹⁶

UV Spectra. The electronic spectra of silicon and germanium sesquichalcogenides have not been appeared so far to our best knowledge. We found that the double-deckers **1–4** show an absorption above 200 nm in the UV region. Data for these compounds are shown in Figure 2. Although **1** shows only end absorption, **2** and **3** exhibited absorption maxima as shoulders at 232 (ϵ 16 000) and 236 nm (ϵ 23 000), respectively. Interestingly, **4** shows two absorption maxima (274 nm, ϵ 16 000; 229 nm, ϵ 38 000), and the band edge is tailing into the visible region. UV-visible spectra of adamantane-type **5–7** in cyclohexane are shown in Figure 3. Similarly, only **7** shows an absorption maximum (221 nm, ϵ 37 000) and shoulder (238 nm, ϵ 26 000). Although the reasons why these transitions are allowed and why the double-decker compounds show higher absorption maximum are not yet understood, the optical properties of these cage systems are of considerable interest. We are now investigating their electronic properties including emission spectra for interpreting these unique systems.

In summary, treatment of hexyltrichlorogermane or hexyltrichlorosilane with lithium sulfide or selenide

(16) The reason why only **2** did not rearrange to an adamantane-type compound is not clear. We postulate that there are two factors for the rearrangement. One is the bond strength; thus, the Ge–Se compound rearranged most readily. The second is steric hindrance of the starting double-decker compounds. Compared to the Si–S bond, Si–Se bond is longer and that releases the strain and decreases reactivity.

Figure 2. UV spectra of **1–4** in cyclohexane.Figure 3. UV spectra of **5–7** in cyclohexane.

gave double-decker hexachalcogenide **1–4**, and those were stable to hydrolysis. The structures were determined by X-ray crystallography. Double-deckers were converted to the adamantane type by heating, except for the silicon-selenium system. Further reactions of these unique skeleton compounds are now investigated.

Experimental Section

All solvents used in the reactions were purified and dried by the reported methods. Lithium aluminum hydride was used in the case of hydrocarbons such as benzene and hexane. THF was purified by distillation from benzophenone ketyl prior to use. Hydrocarbons for recrystallization were used after distillation. All reactions were carried out under an argon or dry nitrogen unless otherwise noted. Lithium sulfide, selenium, LiEt_3BH , 2,3-dimethyl-2-butene, α, α' -azobis(isobutyronitrile) (AIBN), trichlorosilane, and trichlorogermane were commercially available and used without further purification.

Nuclear magnetic resonance spectra were obtained by a JEOL α -500 spectrometer. Dimethyl selenide was used as

external standard in ^{77}Se NMR. Mass spectrometry was measured by a Jeol JMS-DX302 instrument. Infrared spectra were recorded with Jasco A-102 spectrometer. GLC analysis was carried out by Shimadzu GC-8A instrument using a glass packed column (i.d. 3.5×1000 mm) with 10% silicon KF-96 on Celite 545 sk. Preparative HPLC was performed on an LC-09 instrument with JAI gel 1H+2H columns, and chloroform was used as eluent.

Preparation of (1,1,2-Trimethylpropyl)trichlorosilane. This trichlorosilane was prepared by a reported method.¹⁷ Trichlorosilane (40.3 g, 0.30 mol), 2,3-dimethyl-2-butene (8.9 g, 0.11 mol) and AIBN (3.0 g, 18.3 mmol) were charged in a stainless steel autoclave, and the mixture was heated to 120 °C for 24 h. After cooling the reaction mixture, the remaining AIBN was removed by filtration, and filtrate was distilled under reduced pressure to afford ThexSiCl_3 (31.8 g, 69%) as colorless liquid: bp 46–49 °C (6 mmHg); ^1H NMR (CDCl_3) δ 1.01 (d, 6H, $J = 6.8$ Hz), 1.12 (s, 6H), 1.95 (sept, 1H, $J = 6.8$ Hz); ^{13}C NMR (CDCl_3) δ 18.53, 19.32, 23.45, 33.25; ^{29}Si NMR (CDCl_3) δ 16.90.

Preparation of (1,1,2-Trimethylpropyl)trichlorogermane. This trichlorogermane was prepared by reported methods.¹⁸ Trichlorogermane (37.8 g, 0.21 mol) was slowly added to 2,3-dimethyl-2-butene (17.7 g, 0.21 mol) at 0 °C. After the addition, the reaction mixture was warmed to room temperature and stirred for 12 h. The reaction mixture was distilled under reduced pressure to afford ThexGeCl_3 (42.3 g, 77%) as colorless liquid: bp 58–62 °C (4 mmHg); ^1H NMR (CDCl_3) δ 1.06 (d, 6H, $J = 7.0$ Hz), 1.32 (s, 6H), 2.14 (sept, 1H, $J = 7.0$ Hz); ^{13}C NMR (CDCl_3) δ 18.63, 20.03, 34.59, 53.63.

Synthesis of Tetrakis(1,1,2-trimethylpropyl)-2,4,6,8,9,10-hexathia-1,3,5,7-tetrasilatricyclo[5.1.1.1^{3,5}]decane (1). To a suspension of Li_2S (1.0 g, 22.1 mmol) in THF (35 mL) was added a solution of ThexSiCl_3 (2.9 g, 13.4 mmol) in THF (20 mL) over 1 h at 0 °C. The reaction mixture was warmed to room temperature and stirred for 2 weeks. After removal of THF, benzene was added to the residue to precipitate insoluble salts and the solution was filtered. The filtrate was concentrated in vacuo. Hexane was added to the residue, resulting in precipitation of white crystals which were filtered and recrystallized from hexane to give **1** (0.55 g, 25%) as colorless crystals: mp 267–269 °C; ^1H NMR (CDCl_3) δ 0.95 (d, 24H, $J = 6.7$ Hz), 1.10 (s, 24H), 2.06 (sept, 4H, $J = 6.7$ Hz); ^{13}C NMR (CDCl_3) δ 18.49, 18.91, 33.81, 34.01; ^{29}Si NMR (CDCl_3) δ 17.43; MS (70 eV) m/z (%) 644 (M^+ , 31), 349 (base). Anal. Calcd for $\text{C}_{24}\text{H}_{52}\text{Si}_4\text{S}_6$: C, 44.66; H, 8.12. Found: C, 44.70; H, 8.30.

Synthesis of Tetrakis(1,1,2-trimethylpropyl)-2,4,6,8,9,10-hexaselena-1,3,5,7-tetrasilatricyclo[5.1.1.1^{3,5}]decane (2). A solution of LiEt_3BH (12.5 mmol in 12.5 mL of THF) was added dropwise to elemental selenium (0.45 g, 5.7 mmol) via syringe. After the addition, THF (6 mL) was added and the mixture was stirred for 1 h at room temperature. A solution of ThexGeCl_3 (0.80 g, 3.6 mmol) in THF (10 mL) was added to the Li_2Se solution over 1 h at 0 °C. After the addition, the reaction mixture was warmed to room temperature and stirred until the red color of the selenium salt had disappeared (~5 days). THF was removed in vacuo, and benzene was added to precipitate insoluble salts. The filtrate was concentrated, and residue was recrystallized from benzene to afford **2** (0.36 g, 43%): colorless crystals, mp 272–274 °C; ^1H NMR (CDCl_3) δ 0.98 (d, 24H, $J = 6.7$ Hz), 1.13 (s, 24H), 2.08 (sept, 4H, $J = 6.7$ Hz); ^{13}C NMR (CDCl_3) δ 18.80, 19.30, 33.75, 34.75; ^{29}Si NMR (CDCl_3) δ -3.80; ^{77}Se NMR (CDCl_3) δ -122.2, -51.7; MS (70 eV) m/z (%) 928 (M^+ , 7), 85 (base). Anal. Calcd for $\text{C}_{24}\text{H}_{52}\text{Si}_4\text{Se}_6$: C, 31.10; H, 5.66. Found: C, 31.49; H, 5.69.

Synthesis of Tetrakis(1,1,2-trimethylpropyl)-2,4,6,8,9,10-hexathia-1,3,5,7-tetragermatricyclo[5.1.1.1^{3,5}]decane

(**3**). To a suspension of Li_2S (1.0 g, 22.1 mmol) in THF (30 mL) was added a solution of ThexSiCl_3 (3.8 g, 14.2 mmol) in THF (15 mL) over 1 h at 0 °C. The reaction mixture was warmed to room temperature and stirred for 24 h. After removal of THF, benzene was added to the residue to precipitate insoluble salts and the mixture was filtered. The filtrate was concentrated in vacuo. Hexane was added to the residue. The resulting white crystals were filtered and recrystallized from benzene/hexane to give **3** (1.6 g, 55%) as colorless crystals: mp 217–219 °C; ^1H NMR (CDCl_3) δ 0.97 (d, 24H, $J = 6.7$ Hz), 1.26 (s, 24H), 2.15 (sept, 4H, $J = 6.7$ Hz); ^{13}C NMR (CDCl_3) δ 18.80, 19.80, 34.92, 48.15; MS (30 eV) m/z (%) 824 (M^+ , 1), 85 (base). Anal. Calcd for $\text{C}_{24}\text{H}_{52}\text{Ge}_4\text{S}_6$: C, 35.01; H, 6.36. Found: C, 35.24; H, 6.45.

Synthesis of Tetrakis(1,1,2-trimethylpropyl)-2,4,6,8,9,10-hexaselena-1,3,5,7-tetragermatricyclo[5.1.1.1^{3,5}]decane

(**4**). Preparation of Li_2Se was effected in the same manner as described above. A solution of ThexGeCl_3 (0.99 g, 3.8 mmol) in THF (10 mL) was added to this solution over 1 h at 0 °C. After the addition, the reaction mixture was warmed to room temperature and stirred until the red color of the selenium salt had disappeared (~24 h). THF was removed, and hexane was added to precipitate insoluble materials. After the filtration, the precipitate was extracted with benzene and the insoluble salts were removed by filtration. The benzene solution was concentrated and the residue was recrystallized from benzene/pentane below 60 °C to afford **4** (0.54 g, 52%): pale yellow crystals, mp >275 °C; ^1H NMR (CDCl_3) δ 0.98 (d, 24H, $J = 6.7$ Hz), 1.21 (s, 24H), 2.13 (sept, 4H, $J = 6.7$ Hz); ^{13}C NMR (CDCl_3) δ 19.01, 19.91, 35.86, 46.66; ^{77}Se NMR (CDCl_3) δ -3.1, 154.0; MS (70 eV) m/z (%) 1106 (M^+ , 1), 85 (base). Anal. Calcd for $\text{C}_{24}\text{H}_{52}\text{Ge}_4\text{Se}_6$: C, 26.09; H, 4.74. Found: C, 26.35; H, 4.72.

Thermal Reaction of 1. A solution of **1** (137 mg, 0.21 mmol) in decahydronaphthalene (80 mL) was refluxed for 24 h. After removal of decahydronaphthalene in vacuo, the residue was separated by (GPC) and recrystallized from EtOH to afford **5** (78 mg, 57%): colorless crystals, mp 211–213 °C; ^1H NMR (CDCl_3) δ 1.01 (d, 24H, $J = 6.7$ Hz), 1.10 (s, 24H), 2.01 (sept, 4H, $J = 6.7$ Hz); ^{13}C NMR (CDCl_3) δ 19.00, 19.22, 32.48, 33.47; ^{29}Si NMR (CDCl_3) δ 26.00; MS (70 eV) m/z (%) 644 (M^+ , 13), 84 (base). Anal. Calcd for $\text{C}_{24}\text{H}_{52}\text{Si}_4\text{S}_6$: C, 44.67; H, 8.12. Found: C, 44.69; H, 8.23.

Thermal Reaction of 3. A solution of **3** (203 mg, 0.25 mmol) in decahydronaphthalene (80 mL) was refluxed for 24 h. After removal of the decahydronaphthalene in vacuo, the residue was separated by (GPC) and recrystallized from EtOH to afford **6** (quantitative) as colorless crystals: mp 232–235 °C; ^1H NMR (CDCl_3) δ 1.02 (d, 24H, $J = 7.0$ Hz), 1.22 (s, 24H), 2.08 (sept, 4H, $J = 7.0$ Hz); ^{13}C NMR (CDCl_3) δ 18.97, 20.43, 34.56, 46.45; MS (30 eV) m/z (%) 824 (M^+ , 0.3), 85 (base). Anal. Calcd for $\text{C}_{24}\text{H}_{52}\text{Ge}_4\text{S}_6$: C, 35.01; H, 6.36. Found: C, 35.18; H, 6.44.

Thermal Reaction of 4. A solution of **4** (73.1 mg, 66.2 mmol) in benzene (20 mL) was refluxed for 24 h. After removal of benzene in vacuo, the residue was separated by GPC and recrystallized from hexane to afford **7** (quantitative) as colorless crystals: mp >270 °C; ^1H NMR (CDCl_3) δ 1.06 (d, 24H, $J = 6.7$ Hz), 1.23 (s, 24H), 2.11 (sept, 4H, $J = 6.7$ Hz); ^{13}C NMR (CDCl_3) δ 19.18, 21.48, 35.48, 45.49; ^{77}Se NMR (CDCl_3) δ -3.46; MS (30 eV) m/z (%) 1095–1117 (M^+), 85 (base). Anal. Calcd for $\text{C}_{24}\text{H}_{52}\text{Ge}_4\text{Se}_6$: C, 26.09; H, 4.74. Found: C, 26.14; H, 4.80.

X-ray Crystallography (General Procedure). Intensity data were collected on a Rigaku AFC7S diffractometer at 20 ± 1 °C with Cu K α radiation ($\lambda = 1.54178$ Å) and the ω -2 θ scan technique to a maximum value of 120.1°. An empirical absorption correction was applied. The data were corrected for Lorenz and polarization effects. The structure was solved

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by SHELXS86.¹⁹ The positions of all hydrogen atoms were calculated. For **1**, 18 hydrogen atoms were refined isotropically, and the rest were included in fixed position. For **2–4**, hydrogen atoms were included but not refined. All calculations were performed using the teXsan²⁰ software of the Molecular Structure Corp.

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and Culture of Japan. We also thank Shin-Etsu Chemical Co. Ltd. and Chisso Co. Ltd for the gift of silicon reagents and Asai Germanium Research Institute Co. Ltd for germanium reagents.

Supporting Information Available: X-ray analysis experiment for **1–4** including tables of anisotropic thermal parameters, atomic coordinates and isotropic thermal parameters, bond lengths and angles, and figures showing the molecular and views of molecular packing (78 pages). Ordering information is given on any current masthead page.

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