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Thermal Isomerization of Silicon and Germanium Sesquichalcogenides, $Thex_4M_4E_6$ (M = Si, Ge; E = S, Se)

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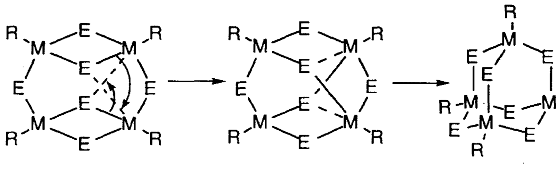
The isomerization of the sesquichalcogenides $Thex_4M_4E_6$ (Thex = 1,1,2-trimethylpropyl, **1**: M = Si, E = S; **2**: M = Si, E = Se; **3**: M = Ge, E = S; **4**: M = Ge, E = Se) with the "double-decker"-type structures $(Thex_2M_2E_2)_2E_2$, (**1dd**—**4dd**) to the corresponding compounds with the adamantane-type structures $Thex_4M_4E_6$ (**1ad**—**4ad**) was studied. The skeletal rearrangement has been observed to be reversible in the case of sesquichalcogenides **1**, **2**, and **4**; for **1** and **4**, the isomerization has reached an equilibrium with preference for adamantane-type structures **1ad** and **4ad**, respectively, while the equilibrium in **2** has lain more to "double-decker"-type **2dd**. On the other hand, the isomerization of **3dd** to **3ad** has been observed to be irreversible under the condition employed. In the temperature ranges 433—453 K (**1dd**), 373—393 K (**3dd**), and 358—383 K (**4dd**), the equilibrium has followed reversible first-order kinetics. The thermodynamic parameters determined for the forward isomerization, the "double-decker"-type structures (**dd**)→adamantane-type structures (**ad**), are as follows: for **1dd**→**1ad**, $E_a = 35.9\pm0.1$ kcal mol^{-1}, $\ln A = 30.8\pm0.2$ s^{-1}, $\Delta H^{\ddagger} = 35.0\pm0.1$ kcal mol^{-1}, $\Delta S^{\ddagger} = -0.044$ cal mol^{-1} K^{-1}; for **3dd**→**3ad**, $E_a = 35.9\pm0.1$ kcal mol^{-1}, $\ln A = 38.3\pm0.2$ s^{-1}, $\Delta H^{\ddagger} = 34.6\pm0.1$ kcal mol^{-1}, $\Delta S^{\ddagger} = 13.7$ cal mol^{-1} K^{-1}; for **4dd**→**4ad**, $E_a = 32.3\pm0.1$ kcal mol^{-1}, $\ln A = 35.7\pm0.1$ s^{-1}, $\Delta H^{\ddagger} = 31.7\pm0.3$ kcal mol^{-1}, $\Delta S^{\ddagger} = 10.4$ cal mol^{-1} K^{-1}. The X-ray structure of new sesquichalcogenide **2ad** is also reported.

As a part of our investigation on the chemistry of silicon and germanium cage molecules,[1] we have recently reported the syntheses, X-ray structures, and properties of double-decker sesquichalcogenides (denoted double-decker hereafter) $(Thex_2M_2E_2)_2E_2$ (**1dd**: M = Si, E = S; **2dd**: M = Si, E = Se; **3dd**: M = Ge, E = S; **4dd**: M = Ge, E = Se).[2] Prior to our report, Ando and co-workers reported the first synthesis of the double-decker $(t\text{-}Bu_2Ge_2S_2)_2S_2$ in 1992,[3] which underwent the skeletal isomerization to adamantane-type above 200 °C. We reported that our compounds **1dd**, **3dd**, and **4dd** also showed the isomerization to the adamantane-types, but at lower temperatures. For example, $(Thex_2Si_2S_2)_2S_2$ **1dd** and $(Thex_2Ge_2S_2)_2S_2$ **3dd** rearrange at 195 °C, and $(Thex_2Ge_2Se_2)_2Se_2$ **4dd** reacts even at 80 °C.[2] The proposed reaction pathway for the skeletal rearrangement is shown in Scheme 1. In this paper, we report the results of reinvestigation of the isomerization **dd**→**ad** of **1**, **2**, **3**, and **4**, which includes kinetic studies, providing the supporting evidence for the previously proposed mechanistic consideration. In addition, the following new information is reported: (1) the isomerizations **dd**→**ad** are reversible except in the case of **3**; (2) the X-ray structure of new compound **2ad**. The isomerization **ad**→**dd** described here has, to our knowledge, no precedent.


1-4dd **1-4ad**

Scheme 1.

Results and Discussion

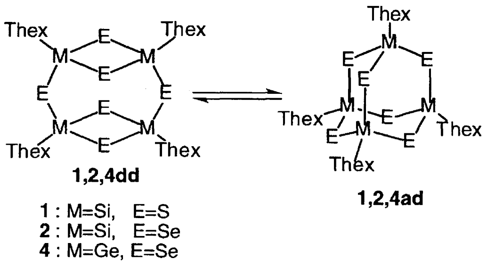
Double-Decker → Adamantane-Type Isomerization of 1, 2, 3, and 4. In the preceding paper,[2] we reported that refluxing of Si–S double-decker **1dd** in decahydronaphtalene (decalin) for 24 h resulted in the isolation of adamantane-type **1ad** in 57% yield. We reinvestigated the isomerization **1dd**→**1ad**, and found that the moderate yield of **1ad** is due to the concurrent occurrence of the reverse isomerization **1ad**→**1dd**.[4] For example, heating of a solution of **1dd** in decalin at 200 °C for 10 h led to the formation of a 27 : 73 mixture of **1dd** and **1ad**, and the ratio of these sesquichalcogenides observed did not change after prolonged heating. It is thus indicated that the isomerization reached equilibrium with the equilibrium constant (K_{eq} = [**1ad**]/[**1dd**]) of 2.7 under the condition employed.

Also in the preceding paper,[2] we reported that Si–Se double-decker **2dd** was stable to its melting point (272 °C) and no rearrangement was observed. In a solution, however, we could find that the isomerization **2dd**→**2ad** occurred at lower temperatures. For example, heating a decalin solution of **2dd** at 150 °C for 3 h resulted in the formation of a 69 : 31 mixture of **2dd** and **2ad**. In a separate experiment, **2ad** was found to be converted to **2dd** under similar conditions; heating a decalin solution of **2ad** at 150 °C for 3 h gave a 69 : 31 mixture of **2dd** and **2ad**. The equilibrium constant (K_{eq} = [**2ad**]/[**2dd**]) was 0.45 at 150 °C, indicating that **2dd** is favored in this equilibrium. However, the choice of reaction temperature is crucial in this case: no forward and reverse reactions occurred at any temperature lower than 140 °C. At the temperatures higher than 155 °C, the decomposition of **2dd** occurred, giving a complex mixture of products, whose structures were not identified.

For Ge–Se compound **4**, the isomerization was also observed to be reversible (Scheme 2). Thus, heating of **4dd** or **4ad** at 200 °C resulted in the equilibrium mixture of **4dd** (12%) and **4ad** (88%). The equilibrium constant from double-decker (K_{eq} = [**4ad**]/[**4dd**]) was 8.3.

Unlike compounds **1**, **2**, and **3**, the isomerization of Ge–S sesquichalcogenide **3** is not reversible; heating of **3dd** at 200 °C resulted in the complete conversion to **3ad**, and at the same temperature **3ad** showed no isomerization to **3dd**.

The isomerization **ad**→**dd** is very unusual and has no precedent to our knowledge. From the consideration of the ring strain, the adamantane-type has been expected to be more stable than the double-decker.[2] However, this is not the case in the combination of **2dd** and **2ad**. Then, compound **2ad** was subject to X-ray crystallography in order to obtain its structural features. The ORTEP drawing is shown in Fig. 1. Crystallographic data, selected bond lengths, and angles are given in Tables 1 and 2. In **2ad** the Si–Se bond lengths are 2.279(4)—2.297(5) Å and average 2.289 Å The Si–Se–Si bond angles are 102.5(1)—105.5(2)° and average 104.1°. The Se–Si–Se bond angles are 109.3(2)—114.5(2)° and average 112.0°. By comparing these structural parameters with those of **2dd**,[2] we can see that the bond angles of **2ad** were less strained. Moreover, it is noted that for **2dd**, the nonbonding distance of the opposite atoms Se and Si in the Si_2Se_2 four-membered ring is very short (3.43 and 2.99 Å, respectively).[2] These structural features of **2dd** seem to be one of the reasons for the isomerization to the adamantane-type, in which the nonbonding atom distance is within the normal range, being inconsistent with the experimental result. We thus tried the MM2 calculations on **2dd** and **2ad**, but no satisfactory results were obtained for the relative stability of these sesquichalcogenides, presumably because of the lack of parameters for higher-row elements. The repulsion of bulky thexyl groups also plays a role for the stability, and the energy of repulsion greatly diminished due to the longer bond lengths. In addition to these structural features, electronic properties also determine the stability. In the cases of **1**, **2**, and **4**, the difference of the energy of two isomers is smaller than the case of **3**, which resulted in the reverse isomerization. We are currently performing some calculations to explain the different stability situations.



Scheme 2.

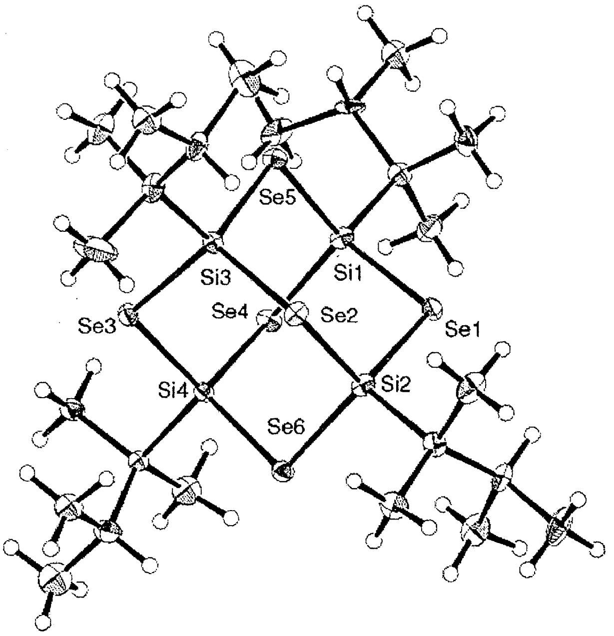


Fig. 1. ORTEP drawing of **2ad**. Thermal ellipsoids are drawn at the 30% probability level.

Table 1. Crystallographic Data for **2ad**

Crystal data	
Formula	$C_{24}H_{52}Si_4Se_6$
Mol wt	926.78
Cryst. descript	Colorless prism
Cryst. size/mm	$0.2 \times 0.2 \times 0.2$
Cryst. syst.	Orthorhombic
Space group	$Pna2_1$
a/Å	12.3703(5)
b/Å	16.8745(6)
c/Å	17.0179(6)
V/Å^3	3552.4(2)
Z	4
Data collection	
Diffractometer	Rigaku RAXIS-IV
Radiation (λ/Å)	Mo$K\alpha$ (0.71070)
Monochromator	Graphite
Temperature/°C	-100 ± 1
μ/cm^{-1}	63.3
No. of rflns. measd	4358
No. of ind reflns.	4358
No. of obsd reflns. ($\lvert F_o \rvert \geq 3\sigma(F_o)$)	3376
Refinement	
R	0.059
R_w	0.079
No. of params	274

Rates of Isomerization of the Si–S, Ge–S, Ge–Se Double-Deckers (1dd, 3dd, and 4dd). At the temperatures shown in the previous section, the thermal isomerization of **1**, **2**, and **4** gave an equilibrium mixture; however, at lower

Table 2. Selected Bond Lengths and Distances of **2ad**

	Bond lengths		
Se(1)–Si(1)	2.299(4)	Se(1)–Si(2)	2.272(4)
Se(2)–Si(2)	2.292(5)	Se(2)–Si(3)	2.282(4)
Se(3)–Si(3)	2.286(5)	Se(3)–Si(4)	2.279(5)
Se(4)–Si(1)	2.297(5)	Se(4)–Si(4)	2.292(4)
Se(5)–Si(1)	2.291(5)	Se(5)–Si(3)	2.308(4)
Se(6)–Si(2)	2.297(5)	Se(6)–Si(4)	2.276(4)
Si(1)–C(1)	1.93(2)	Si(2)–C(7)	1.91(1)
Si(3)–C(13)	1.87(1)		
	Bond angles		
Si(1)–Se(1)–Si(2)	104.4(1)	Si(2)–Se(2)–Si(3)	105.5(2)
Se(4)–Si(4)–Se(6)	112.1(2)	Si(3)–Se(3)–Si(4)	104.3(1)
Si(1)–Se(4)–Si(4)	104.2(2)	Si(1)–Se(5)–Si(3)	103.5(2)
Si(2)–Se(6)–Si(4)	102.5(1)	Se(1)–Si(1)–Se(4)	108.2(2)
Se(1)–Si(1)–Se(5)	112.9(2)	Se(4)–Si(1)–Se(5)	114.5(2)
Se(1)–Si(2)–Se(2)	111.7(2)	Se(1)–Si(2)–Se(6)	115.1(2)
Se(2)–Si(2)–Se(6)	109.3(2)	Se(2)–Si(3)–Se(3)	113.7(2)
Se(2)–Si(3)–Se(5)	112.3(2)	Se(3)–Si(4)–Se(4)	110.5(2)
Se(3)–Si(4)–Se(6)	114.9(2)		

temperatures, we found the isomerization of **1dd**, **3dd**, and **4dd** followed the first-order reaction. The isomerization reactions (Scheme 3) were monitored by reverse phase HPLC. For Si–S compound **1dd**, the rate constants were determined at 433, 438, 443, 448, and 453 K.[5] As aforementioned, Ge–S and Ge–Se compounds **3dd** and **4dd** undergo the isomerization at lower temperature. Thus, the rates of the isomerization for **3dd** were determined at 373, 378, 383, 388, and 393 K, and those for **4dd** were determined at 358, 363, 373, and 383 K. The thermal isomerization of **1dd**, **3dd**, and **4dd** to the corresponding adamantane-types shows clear first-order dependence of the concentration of **1dd**, **3dd**, and **4dd** in accord with Eq. 1, as shown in Fig. 2.

$$\ln([\mathbf{1dd}]_0/[\mathbf{1dd}]) = kt. \qquad (1)$$

Arrhenius plots of the isomerizartion from **1dd**, **3dd**, and **4dd** are shown in Fig. 3. In all the cases, plots of both $\ln k$ and $\ln(k/T)$ vs. $1/T$ were linear over the temperature range measured. Rate constants and the values of $\Delta G^{\ddagger}$ are shown in Table 3, and the other kinetic and thermodynamic parameters are shown in Table 4.

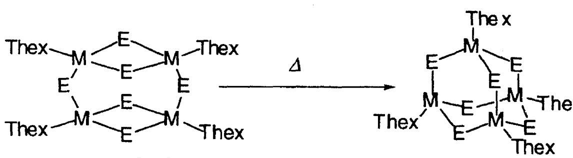
Table 3. Rate Constants and Free Energy of Activation

Compounds	Temp/K	$k/10^5\ \mathrm{s^{-1}}$	$\Delta G^{\ddagger}/\mathrm{kcal\ mol^{-1}}$
1	433	1.89±0.04	35.06±0.02
1	438	2.96±0.08	35.04±0.02
1	443	4.47±0.07	35.09±0.02
1	448	7.61±0.26	35.04±0.05
1	453	11.3±0.3	35.06±0.02
3	373	4.05±0.23	29.50±0.04
3	378	7.28±0.16	29.46±0.02
3	383	14.3±0.5	29.35±0.03
3	388	27.5±0.6	29.24±0.02
3	393	49.8±0.9	29.16±0.02
4	358	6.22±0.62	28.00±0.07
4	363	11.6±0.2	27.95±0.01
4	373	38.3±1.1	27.85±0.01
4	383	119±9	27.76±0.06

Table 4. Thermodynamic Parameters of Isomerization

Compounds	E_a [a)]	$\ln A/\mathrm{s^{-1}}$	$\Delta H^{\ddagger}$ [b)]	$\Delta S^{\ddagger}$ [c)]
1	35.9±0.1	30.8±0.2	35.0±0.1	−0.044
3	35.9±0.1	38.3±0.2	34.6±0.1	13.7
4	32.3±0.1	35.7±0.1	31.7±0.3	10.4

a,b) $\mathrm{kcal\ mol^{-1}}$. c) $\mathrm{cal\ mol^{-1}\ K^{-1}}$.



1, 3, 4dd

1, 3, 4ad

1 : M=Si, E=S (433–453 K)
3 : M=Ge, E=S (373–393 K)
4 : M=Ge, E=Se (358–383 K)

Scheme 3.

The rate constants of the isomerization follow the order **4dd**>**3dd**>**1dd**. The difference between silicon and germanium cages was mostly characterized by the values of $\Delta S^{\ddagger}$ and $\ln A$. The $\Delta S^{\ddagger}$ values were all close to zero or positive; this was similar to the values in the unimolecular reaction of carbon compounds.[6] However, $\Delta S^{\ddagger}$ values of **3dd** and **4dd** are greater than that of **1dd**. The difference of entropy between silicon and germanium sesquichalcogenides is expected by considering the degree of freedom at the transition state, where germanium compounds are less tightly bound than silicon compounds. The order of the $\Delta H^{\ddagger}$ was **4dd**<**3dd**<**1dd**, and this is same as the order of rate constants. Thus, this isomerization reaction could be explained as under enthalpy control and not entropy control. Actually, the rate constants were in good harmony with the order of

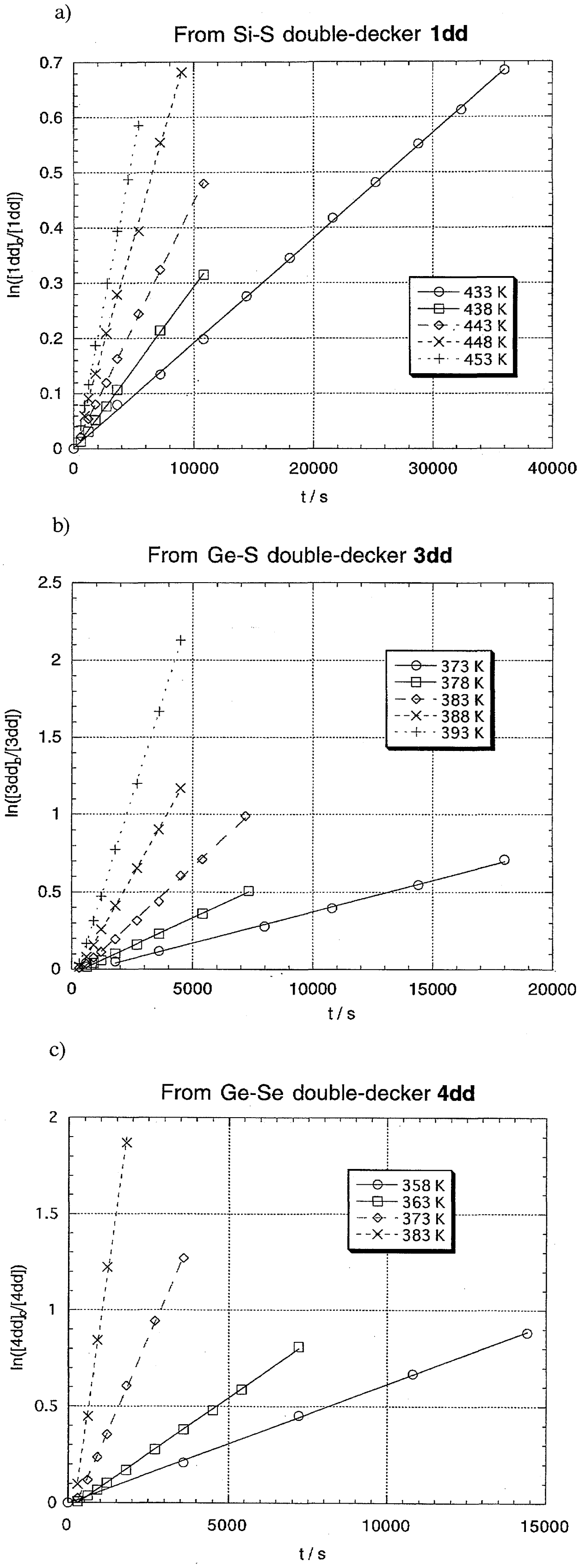


Fig. 2. Plots for the relative concentration vs. reaction time.

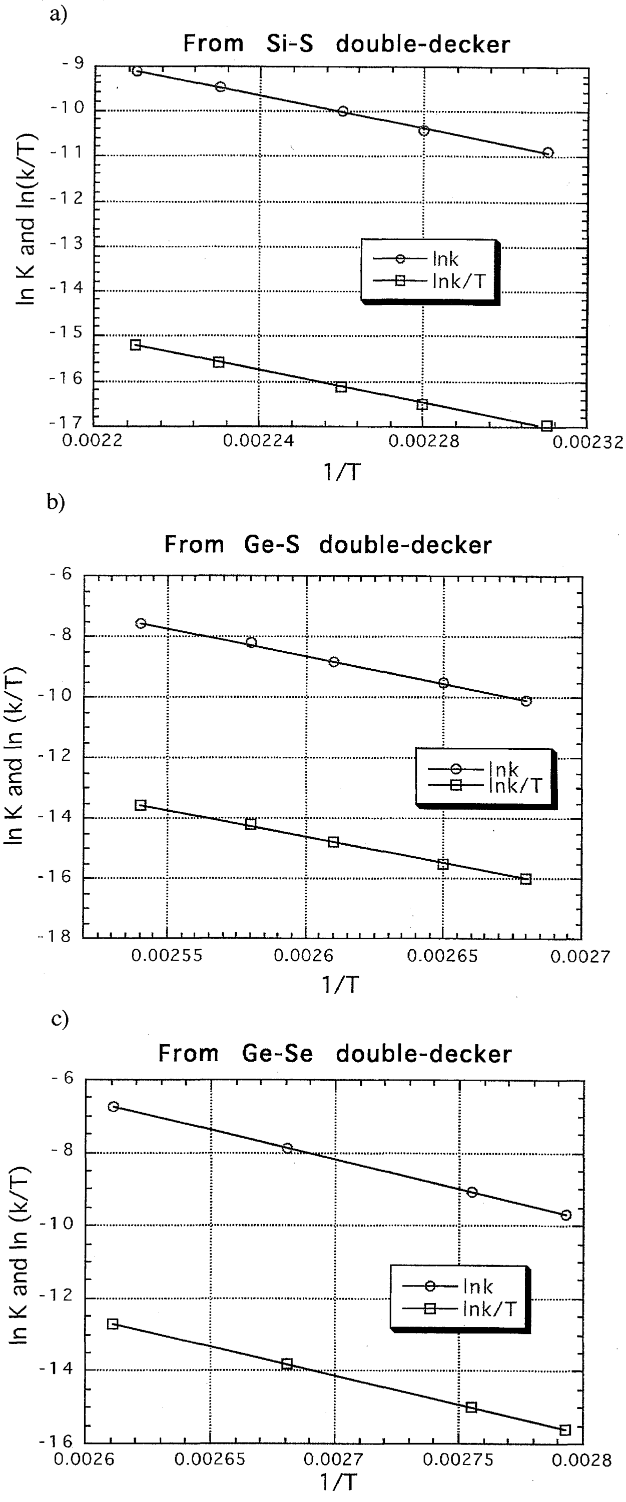


Fig. 3. Arrhenius plots for the thermodynamics and kinetics of isomerization.

bond dissociation energy (Ge–Se: 489±4, Ge–S: 551.0±2.5, Si–S: 623 kJ mol^{-1}).[8] The presented results supported the previously suggested reaction mechanism (Scheme 1).

In summary, we measured the thermodynamic and kinetic parameters for the isomerization of double-decker sesquichalcogenides. At 473 K, equilibrium was observed for **1**, **2**, and **4**, and double-decker isomer was shown to be more stable in the case of Si–Se compound **2**. At lower temperatures, the thermodynamic and kinetic parameters for the isomerization from double-decker to adamantane-type could be calculated for sesquichalcogenides **1**, **3**, and **4**, and the reaction was determined to be first-order and under enthalpy control.

Experimental

Rate Measurement of the Thermal Reaction from 1,3,5,7-Tetrasila-2,4,6,8,9,10-hexathiatricyclo[5.1.1.1^{3,5}]decane, ($Thex_2Si_2S_2)_2S_2$ (1dd, Typical Procedure): In the two-necked reaction tube with stopcock-equipped septum inlet, 9.3 mg of tetrasilahexathiatricyclo[5.1.1.1^{3,5}]tetrasilathiane in 5 ml of decalin was added under argon atmosphere. The reaction tube was immersed in the preheated silicone-oil constant temperature bath. An aliquot was taken every 5 min, and HPLC (ODS, MeOH/THF = 7/3, detected at 235 nm) was measured. The relative sensitivity of the starting material and reactant was measured with authentic samples, and calibrated (relative sensitivity of adamantane type was 0.544 times that of double-decker). The amount was determined by comparing the peak area of both compounds.

Equilibrium between ($Thex_2Si_2Se_2)_2Se_2$ 2dd and Adamantane-Type 2ad (Typical Procedure): Si–Se double-decker **2dd** (50.8 mg, 0.055 mmol) was dissolved in 5 ml of decalin, and the mixture was heated to 150 °C. After 3 h, the ratio of **2dd/2ad** came to an equilibrium, and then the solvent was removed. By ^{1}H NMR of the crude mixture, only **2dd** and **2ad** were observed. The mixture was separated by recycle-type reverse phase HPLC. Starting material was recovered in 43% (22 mg), and 7 mg (14%) of target **2ad** was obtained. $Thex_4Si_4Se_6$ (**2ad**): Colorless prisms, mp 239—241 °C; ^{1}H NMR ($CDCl_3$) $\delta = 1.03$ (s, 24H), 1.16 (d, $J = 6.7$ Hz, 24 H), 2.05 (sept, $J = 6.7$ Hz, 4 H); ^{13}C NMR ($CDCl_3$) $\delta = 19.27$, 20.26, 32.507, 34.31; ^{29}Si NMR ($CDCl_3$) $\delta = 16.09$ ($J_{Si-Se} = 174$ Hz); ^{77}Se NMR ($CDCl_3$) $\delta = -128.23$; MS (30 eV) *m*/*z* 928 (M^+; 100%), 843 (96), 758 (40); IR (neat) 3000, 1495, 1460, 1385 cm^{-1}. HRMS Calcd for $C_{18}H_{39}Si_4Se_6$: (M-Thex), 846.7120. Found: *m*/*z* 846.7126.

X-Ray Crystallography of Tetrakis(1,1,2-trimethylpropyl)-2,4,6,8,9,10-hexaselena-1,3,5,7-tetrasilatricyclo[3.3.1.1^{3,7}]decane (2ad): Colorless crystals of tetrakis(1,1,2-trimethylpropyl)-2,4,6,8,9,10-hexaselena-1,3,5,7-tetrasilatricyclo[3.3.1.1^{3,7}]decane (**2ad**) were obtained from hexane by slow evaporation. A colorless plate crystal having approximate dimensions of 0.2×0.2×0.2 mm was mounted on a capillary and measured by a Rigaku RAXIS-IV imaging plate diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) at -100 ± 1 °C. The structure was solved by SIR92.[9] The linear absorption coefficient, μ, for Mo $K\alpha$ radiation is 63.3 cm^{-1}. The data were corrected for Lorenz and Polarization effects. A correction for secondary extinction was applied. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3376 observed reflections ($I > 3\sigma(I)$) and 274 variable parameters and converged (largest parameter shift was 0.06 times its esd) with weighted agreement factors of $R = 0.059$, and $R_w = 0.079$.

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4 We are grateful to the reviewer who pointed out the possibility of the reverse reactions (dd⊣ ad).

5 For the silicon double-deckers, decomposition was observed in some cases. That is the reason we reported the yield of isomerization of ($Thex_2Si_2S_2)_2S_2$ (**1**) in 57% yield at 195 °C.[2] However, this time we found that at lower temperature (160—180 °C), the reaction proceeded quantitatively.

6 The thermal syn-anti isomerization of tricyclic ladder polysilane was reported from our laboratory[7] and the $\Delta S^{\ddagger}$ value was shown to be 7.6 kcal mol^{-1}K^{-1}, which is close to the values here. The thermodynamic parameters of the other unimolecular reactions of silicon compounds have not been reported to our best knowledge.

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