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Ring-Opening Reaction of Octakis(1,1,2-trimethylpropyl)octasilacubane. Chlorination with PCl_5 Leading to Stereoisomeric 4,8-Dichlorooctakis(1,1,2-trimethylpropyl)tetracyclo-$[3.3.0.0.^{2,7}.0^{3,6}]$octasilanes

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The chlorination of octakis(1,1,2-trimethylpropyl)octasilacubane (**1**) with PCl_5 resulted in skeletal rearrangement with concomitant formation of stereoisomeric 4,8-dichlorooctakis(1,1,2-trimethylpropyl)tetracyclo$[3.3.0.0.^{2,7}.0^{3,6}]$octasilanes (**2**). The three possible stereoisomers, *endo,exo*-**2**, *exo,exo*-**2**, and *endo,endo*-**2**, could be isolated in a yield of 37%, 33%, and 15%, respectively. The structures of these isomers were determined by X-ray crystallography. Crystallographic parameters are as follows. *endo,exo*-**2**: triclinic, $P\bar{1}$; a = 12.038(1) Å, b = 12.209(1) Å, c = 21.500(2) Å, α = 100.132(5)°, β = 93.723(6)°, γ = 109.443(4)°, V = 2907.2(5) Å^3, Z = 2, R = 0.037, R_w = 0.039 for 7597 reflections. *exo,exo*-**2**: monoclinic, $C2/c$; a = 27.849(9) Å, b = 11.775(7) Å, c = 22.205(9) Å, β = 127.92(1)°, V = 5744(4) Å^3, Z = 4, R = 0.081, R_w = 0.060 for 1872 reflections. *endo,endo*-**2**: monoclinic, $C2/c$; a = 23.375(4) Å, b = 11.693(1) Å, c = 21.600(3) Å, β = 102.52(1)°, V = 5763(1) Å^3, Z = 4, R = 0.046, R_w = 0.053 for 3146 reflections.

Introduction

During the last several years, an increasing number of publications have dealt with the synthesis of polyhedranes of group 14 elements, Si, Ge, and Sn.[1,2] In a preceding paper, we reported the synthesis of an alkyl-substitued octasilacubane, octakis(1,1,2-trimethylpropyl)-pentacyclo$[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]$octasilane (**1**).[2] This compound is air-stable and soluble in hydrocarbons. In addition, it possesses a low oxidation potential of 0.43 V (vs SCE in CH_2Cl_2), which is traced back to the highly strained Si_8 framework.[2] These striking properties make **1** a good choice for the study of the reactions of octasilacubane with electrophiles. In this context, we have been interested in the ring-opening chlorination of **1** as a route to related cage compounds functionalized at the silicon atoms. Here we report the reaction of **1** with PCl_5 leading to stereoisomeric 4,8-dichlorooctakis(1,1,2-trimethylpropyl)tetracyclo$[3.3.0.0^{2,7}.0^{3,6}]$-octasilanes (**2**) via the novel type of skeletal rearrangement.[3]

Results and Discussion

In 1983, Carlson and West reported that the reaction between octaethylcyclotetrasilane and PCl_5 selectively afforded 1,4-dichlorooctaethyltetrasilane as a ring-opening product.[4] Also, Hengge and Jenkner reported in 1992 that decamethylcyclopentasilane reacted with PCl_5 to give 1,5-dichlorodecamethylpentasilane and that no other ring cleavage products were found in the cleavage reaction.[5] In light of these precedents, we expected the formation of 4,7-dichlorotetracyclo$[4.2.0.0^{2,5}.0^{3,8}]$octasilane (**3**), analogous to 1,4-dichlorosecocubane, by the reaction of **1** with PCl_5. However, contrary to this expectation, when **1** was allowed to react with 2.2 equiv of PCl_5 in benzene at room temperature, stereoisomeric 4,8-dichlorooctakis(1,1,2-trimethylpropyl)tetracyclo$[3.3.0.0^{2,7}.0^{3,6}]$-octasilanes (**2**) were formed, but no compound **3** (Scheme

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(5) Hengge, E.; Jenkner, P. K. *Z. Anorg. Allg. Chem.* **1991**, *604*, 69.

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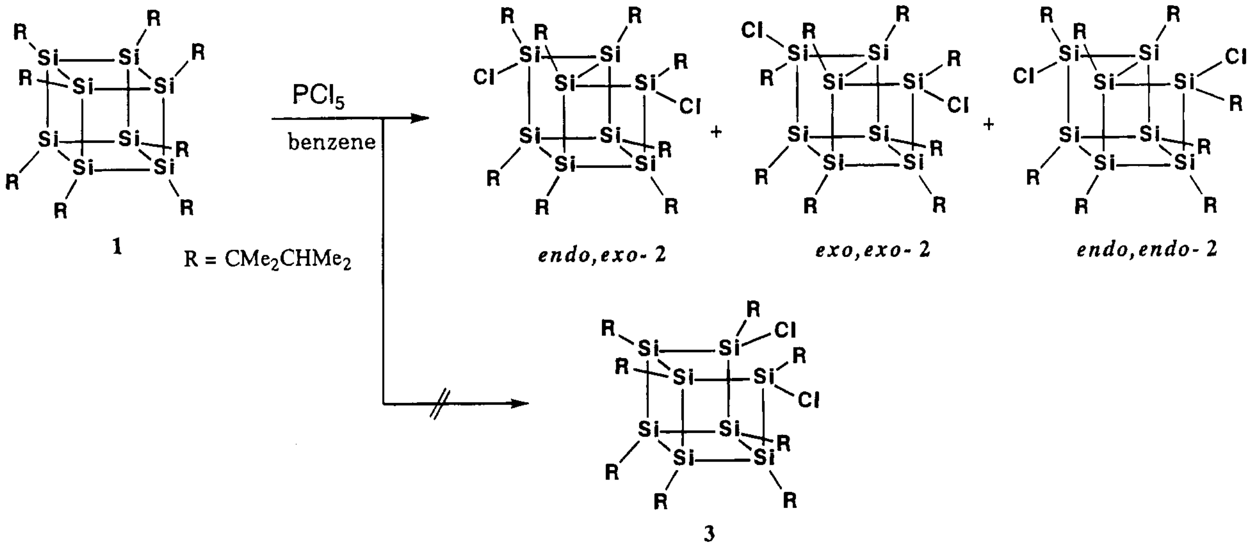
Scheme 1



1). HPLC analysis indicates that **2** exists as a mixture of the three possible isomers, *endo,exo*-**2**, *exo,exo*-**2**, and *endo,endo*-**2** (Figure 1). These isomers could easily be separated by reversed-phase recycle-type HPLC; yields of 37% (*endo,exo*-**2**), 33% (*exo,exo*-**2**), and 15% (*endo,endo*-**2**) were obtained.

The structures of *endo,exo*-**2**, *exo,exo*-**2**, and *endo,endo*-**2** were unequivocally established by X-ray crystallography. In Figures 2–4, the ORTEPII drawings of *endo,exo*-**2**, *exo,exo*-**2**, and *endo,endo*-**2** are shown.[6] Crystallographic data, positional parameters, and selected bond lengths and angles are given in Tables 1–7. As indicated by the X-ray results, the two chlorine atoms of *endo,exo*-**2**, *exo,exo*-**2**, and *endo,endo*-**2** are in endo,-exo, exo,exo, and endo,endo conformations (the positions of the chlorine atoms relative to the bridged Si–Si bonds), respectively. The structure of *endo,exo*-**2** is thus different from those of *exo,exo*-**2** and *endo,endo*-**2**. *Endo,exo*-**2** crystallizes in the $P\bar{1}$ space group with two molecules per the unit cell, while both *exo,exo*-**2** and *endo,endo*-**2** crystallize in the C2/c space group with four molecules per the unit cell and have lattice-imposed 2-fold rotation symmetry.

An interesting aspect of the structural results is the obvservation of the twisted tetracyclo[3.3.0.0^{2,7}.0^{3,6}]-octasilane frameworks. The Si–Si bond lengths vary from 2.357(1) to 2.471(1) Å in *endo,exo*-**2**, from 2.351(4) to 2.464(4) Å in *exo,exo*-**2**, and from 2.390(3) to 2.452(3) Å in *endo,endo*-**2**. The newly generated Si–Si bond lengths are 2.396(1) Å for *endo,exo*-**2**, 2.424(6) Å for *exo,exo*-**2**, and 2.400(2) Å for *endo,endo*-**2**, while average Si–Si bond lengths were 2.418 Å for *endo,exo*-**2**, 2.416 Å for *exo,exo*-**2**, and 2.421 Å for *endo,endo*-**2**. The Si–Si–Si bond angles in the three fused cyclotetrasilane rings in *endo,exo*-**2** vary from 81.21(3) to 93.63(4)°. The corresponding bond angles in *exo,exo*-**2** and *endo,endo*-**2** vary from 82.1(1) to 92.4(1)° and from 81.2(1) to 93.9(1)°, respectively. The Si–Si–C bond angles are scattered from 113.96(9) to 135.1(1)° in *endo,exo*-**2**, from 114.7(5) to 135.7(6)° in *exo,exo*-**2**, and from 113.1(2) to 129.5(3)° in *endo,endo*-**2**. Also, it is noted that the three fused cyclotetrasilane rings are folded with large dihedral angles: in *endo,exo*-**2**, 31.9° between the Si(1)–Si(3)–Si(2) and Si(1)–Si(3)–Si(4) planes, 33.7° between the Si(2)–Si(6)–Si(3) and Si(2)–Si(6)–Si(7) planes, 39.8° between the Si(5)–Si(7)–Si(6) and Si(5)–Si(7)–Si(8) planes, and in *exo,exo*-**2**, 41.5° between the Si(1)–Si(3)–Si(2) and Si(1)–Si(3)–Si(4) planes, 34.6° between the Si(2)–Si(2′)–Si(3) and Si(2)–Si(2′)–Si(3′) planes, and in *endo,endo*-**2**, 34.4° between the Si(1)–Si(3)–Si(2) and Si(1)–Si(3)–Si(4) planes and 31.7° between the Si(2)–Si(2′)–Si(3) and Si(2)–Si(2′)–Si(3′) planes. The Si–Cl bond lengths are 2.107(1) and 2.126(1) Å in *endo,exo*-**2**, 2.124(4) Å in *exo,exo*-**2**, and 2.103(3) Å in *endo,endo*-**2** and are somewhat longer than those of typical Si–Cl bonds. These structural features presumably result from the steric hindrance caused by the eight bulky 1,1,2-trimethylpropyl groups as well as the conformational requirement of the tetracyclo[3.3.0.0^{2,7}.0^{3,6}]-octasilane framework.

The NMR properties of *endo,exo*-**2**, *exo,exo*-**2**, and *endo,endo*-**2** are summarized in Table 8. In agreement with the X-ray structure, the ^{29}Si{^{1}H} NMR spectrum of *endo,exo*-**2** shows 8 resonances, indicating that all silicon atoms are nonequivalent. The ^{13}C{^{1}H} NMR spectra of this isomer consist of 44 resonances due to the nonequivalence of the eight substituents, again consistent with the molecular structure.[7] In *exo,exo*-**2** and *endo,endo*-**2**, the numbers of the resonances in the ^{29}Si{^{1}H} and the ^{13}C{^{1}H} NMR spectra are consistent with their structures, which both possess a 2-fold axis passing through the midpoints of the bridged Si–Si bond and the four-membered Si(2)–Si(3)–Si(2′)–Si(3′) ring. For example, the ^{29}Si NMR spectrum of *exo,exo*-**2** reveals only 4 resonances in the range −19.9 to +59.3 ppm. However, ^{1}H NMR spectra of the three isomers reveal complicated resonance patterns, due to crowding from the methyl–methyl interactions between the substituents.

The mechanism by which *endo,exo*-**2**, *exo,exo*-**2**, and *endo,endo*-**2** are formed from octasilacubane **1** is not

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[6] For *exo,exo*-**2**, despite several attempts at recrystallization, good quality crystals could not be obtained. However, by using the best available crystals and repeated measurement it was possible to determine unambiguously the overall structure even with a rather low accuracy of thermal parameters.

[7] When all carbon atoms are assumed to be nonequivalent, 48 resonances would be observed. In this case, four couples of carbons are thus equivalent.

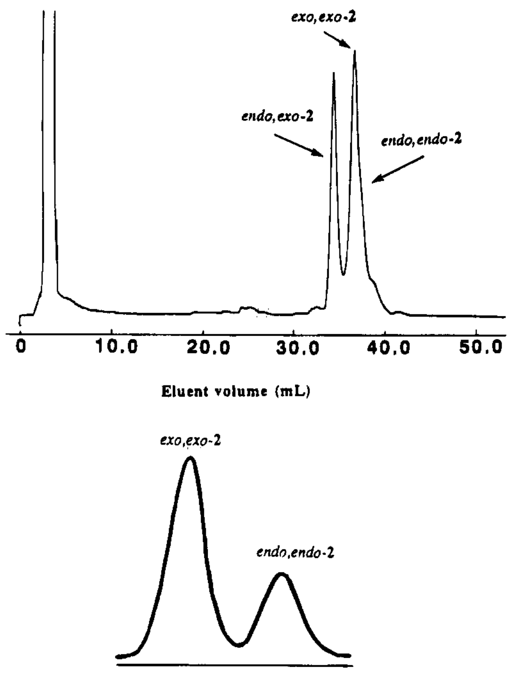

Figure 1. High-pressure liquid chromatogram of 4,8-dichlorotetracyclo[3.3.0.0^{2,7}.0^{3,6}]octasilanes (**2**): (top) reaction mixture; (bottom) after 22 times recycle (*endo,exo*-**2** was separated after four times recycle).

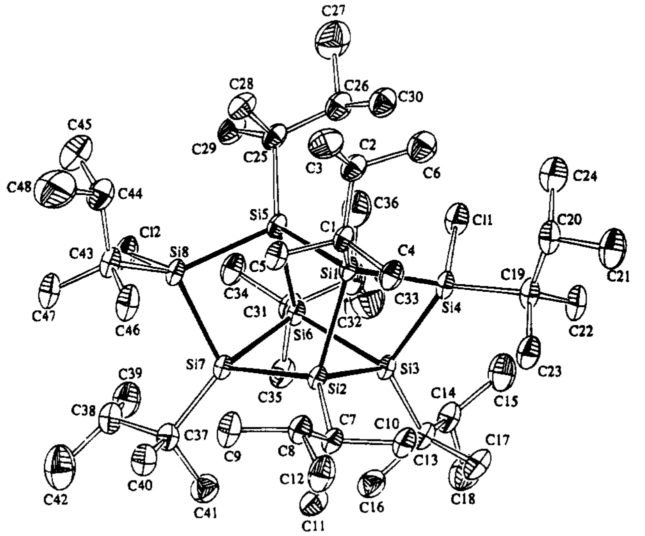

Figure 2. ORTEPII drawing of *endo,exo*-**2** projected on the *ab* plane. Thermal ellipsoids are drawn at the 30% probability level.

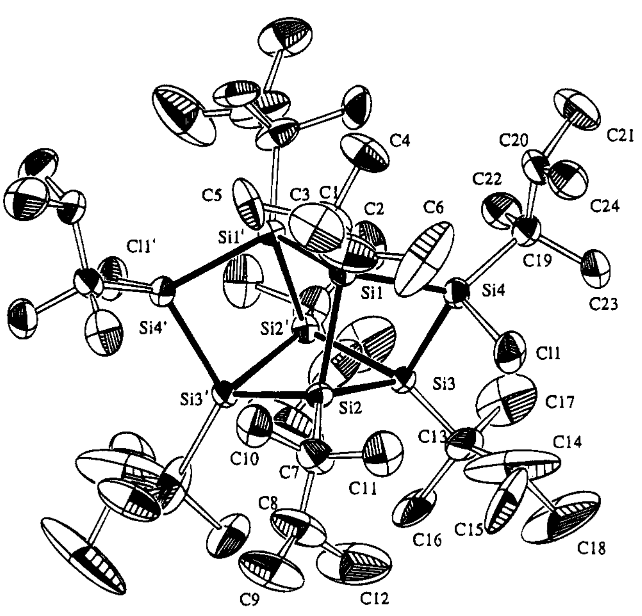

Figure 3. ORTEPII drawing of *exo,exo*-**2** projected on the *ab* plane. Thermal ellipsoids are drawn at the 30% probability level.

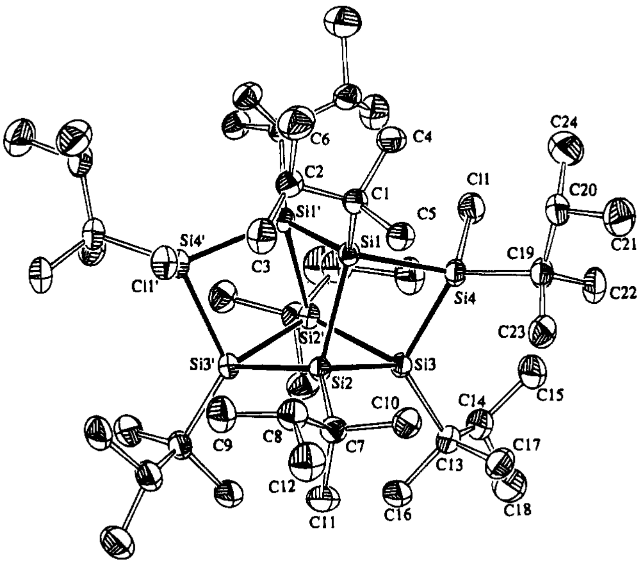

Figure 4. ORTEPII drawing of *endo,endo*-2 projected on the *ab* plane. Thermal ellipsoids are drawn at the 30% probability level.

clear at present, but it is possible to propose a mechanism to account for the reaction. Scheme 2 shows the reaction pathway for the formation of **2**. The first step involves the electrophilic attack of the Si–Si bond in **1** by PCl_5, which is known to act as a strong Lewis acid toward Si–Si bonds.[5] The attack by PCl_5 induces a heterolytic cleavage of the Si–Si bond with the formation of a transient cationic intermediate, such as the 4-chlorooctasilasecocubyl cation (**4**) which undergoes an intramolecular rearrangement to give the 4-chlorotetracyclo[3.3.0.0^{2,7}.0^{3,6}]octasilanyl cation (**5**). The latter is trapped by the chlorine atom to give **2** before it can rearrange further. Silyl cation intermediates seem likely because recent reports have provided evidence for the existence of silyl cations as reactive intermediates and quite recently Lambert *et al.* reported the isolation and the crystal structure of a stable silyl cation, $Et_3Si^+(C_6H_5)_4B^-$.[8] The fact that no traces of 4,7-dichlorotetracyclo[4.2.0.0^{2,5}.0^{3,8}]octasilane **3** had been detected under the conditions employed may suggest that the rearrangement of **4** to **5** is very rapid. The ratio of the isomers found in the chlorination shows a slight deviation from the statistical ratio expected from random ring-opening. In this case a 50 (*endo,exo*-**2**):**25** (*exo,exo*-**2**):25 (*endo,endo*-**2**) ratio is predicted, while that found experimentally is 44:39:17.[9] A kinetic preference for *exo,exo*-**2** and against the other two isomers suggests that there is a slight steric effect on the chlorine transfer step, due to the bulky, 1,1,2-trimethylpropyl groups.[10]

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(8) Lambert, B. J.; Zhang, S.; Ciro, S. M. *Organometallics* **1994**, *13*, 2430 and references cited therein.

(9) The stereochemical course of the reaction was unaffected by the reaction times, indicating that three isomers formed as kinetic products under nonequilibrium conditions.

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

	endo,exo-2	*exo,exo*-2	*endo,endo*-2
Crystal Data			
formula	$C_{48}H_{104}Cl_2Si_8$	$C_{48}H_{104}Cl_2Si_8$	$C_{48}H_{104}Cl_2Si_8$
mol wt	976.95	976.95	976.95
cryst descript	colorless prisms	colorless prisms	colorless prisms
cryst size, mm	0.2 × 0.5 × 0.2	0.4 × 0.4 × 0.2	0.1 × 0.5 × 0.1
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$C2/c$
a, Å	12.038(1)	27.849(9)	23.375(4)
b, Å	12.209(1)	11.775(7)	11.693(1)
c, Å	21.500(2)	22.205(9)	21.600(3)
α, deg	100.132(5)		
β, deg	93.723(6)	127.92(1)	102.52(1)
γ, deg	109.443(4)		
V, Å^3	2907.2(5)	5744(4)	5763(1)
Z	2	4	4
Data Collection			
diffractometer	Enraf-Nonius CAD-4	Rigaku AFC7S	Enraf-Nonius CAD-4
radiation (λ, Å)	Cu Kα (1.5418)	Mo Kα (0.710 69)	Cu Kα (1.5418)
μ, mm^{-1}	2.71	3.10	2.75
variation of stds, %	<1	−0.68	−0.9
2θ range, deg	4−130	5−120	4−120
range of h, k, l	0−14, 0−10, −14 to +14	0−36, 0−15, −29 to +29	0−26, 0−13, −24 to +24
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-\theta$
scan width, deg	$0.7 + 0.15 \tan\theta$	$0.84 + 0.30 \tan\theta$	$0.80 + 0.15 \tan\theta$
no. of reflns measd	9856	7064	4312
no. of ind reflns	9856	6921	4112
no. of obsd reflns ($\lvert F_o \rvert \geq 3\sigma(F_o)$)	7597	1872	3146
Refinement			
R	0.037	0.081	0.046
R_w	0.039	0.060	0.053
weighting scheme	$w = 1/\sigma^2(F_o)$	$w = 1/\sigma^2(F_o)$	$w = 1/[0.00305\lvert F_o \rvert^2 - 0.14643\lvert F_o \rvert + 6.2859]^{-1}$
S	0.98	2.12	1.03
$(\Delta/\sigma)_{max}$	0.73	0.29	0.13
$(\Delta\varrho)_{max}$, e Å^{-3}	0.28	0.52	0.50
$(\Delta\varrho)_{min}$, e Å^{-3}	−0.10	−0.38	−0.38
no. of params	940	262	262

Endo,exo-**2**, *exo,exo*-**2**, and *endo,endo*-**2** form colorless crystals. They are soluble in hydrocarbons and stable to air oxidation and moisture both in the solid state and in solution. In Figure 5, UV/vis spectra of *endo,exo*-**2**, *exo,exo*-**2**, and *endo,endo*-**2** are shown, together with that of octasilacubane **1**. These isomers show virtually the same spectra. The absorption bands have been curve-fitted to four skewed Gaussian peaks in the case of *endo,exo*-**2**. These Gaussians have their maxima at 254, 267, 285, and 354 nm. The longest wavelength peak (354 nm) may be compared with the lowest energy transition of **1** (λ_{max} around 500 nm[2]). Probably, decreasing the strain in the silicon framework in *endo,exo*-**2** is responsible for the shift of the absorption maxima to a much shorter wavelength.

In summary, we showed that the Si−Si cleavage of octasilacubane **1** with PCl_5 resulted in the unusual skeletal rearrangement leading to the formation of *endo,endo*-, *exo,exo*- and *endo,endo*-4,8-dichloroocta-kis(1,1,2-trimethylpropyl)tetracyclo[3.3.0.0^{2,7}.0^{3,6}]-octasilane. It may be pointed out that the cleavage reaction provides an attractive route for the synthesis of the tetracyclo[3.3.0.0^{2,7}.0^{3,6}]octasilane system. Synthesis of the tetracyclic compound analogous to **2** has been reported. Thus, Masamune and co-workers reported that the reductive coupling of 1,2-di-*tert*-butyl-1,1,2,2-tetrachlorodisilane with lithium naphthalenide gave rise to *exo,exo*-4,8-dichloroocta-*tert*-butyltetracyclo-[3.3.0.0^{2,7}.0^{3,6}]octasilane in 6% yield.[1i] The present reaction provides **2** in high yield and permits the synthesis of the endo,exo, exo,exo-, and endo,endo isomers. The reaction is also unique from a mechanistic point of view, since the skeletal rearrangement described here has no precedent in polysilane chemistry.[11,12] However, further study is required to elucidate the detailed mechanism for the rearrangement.

Experimental Section

NMR spectra were recorded on a JEOL Model α-500 (^{1}H, 500 MHz; ^{13}C, 125.7 MHz; ^{29}Si, 99.3 MHz). Chemical shifts are reported as δ units (ppm) relative to $SiMe_4$ as an internal standard. For ^{29}Si NMR, $SiMe_4$ was used for the external standard. Mass spectrometry was performed by a JEOL JMS-D300. Infrared spectra were measured with a JASCO A-102 spectrometer. Analytical HPLC was done by JASCO 875UV/

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(10) The MM2 calculations were carried out using the X-ray structures of *endo,exo*-**2**, *exo,exo*-**2**, and *endo,endo*-**2** as input structures. The force field parameters developed in our laboratory for the calculations of cyclotetrasilanes[20] were employed in the calculations. The results satisfactorily reproduced the X-ray structures (for example, 2.385−2.554 Å for Si−Si bond lengths and 80.3−95.5° for four-membered ring Si−Si−Si bond angles for *endo,exo*-**2**). The steric energies for *endo,exo*-**2**, *exo,exo*-**2**, and *endo,endo*-**2** are 250, 231, and 269 kcal mol^{-1}. The calculated energies suggest that *exo,exo*-**2** is more stable than *endo,exo*-**2** and *endo,endo*-**2**, in agreement with the preferential formation of *exo,exo*-**2**. In the relevant work, Kabe *et al.* reported that reductive coupling of $Cl_2Bu^tSiSiBu^tCl_2$ with lithium naphthalenide gave only the *exo,exo* isomer of 4,8-dichloroocta-*tert*-butyltetracyclo[3.3.0.0^{2,7}.0^{3,6}]octasilane.[1i] Also Weidenbruch *et al.*[1k] and Sekiguchi *et al.*[1m] have described *exo,exo*-4,8-dibromo- or *exo,exo*-4,8-dichloroocta-*tert*-butyltetracyclo[3.3.0.0^{2,7}.0^{3,6}]octagermane. These examples again indicate that when bulky substituents are present, the *exo,exo* isomer is favored in the tetracyclo[3.3.0.0^{2,7}.0^{3,6}]ocatsilane and -octagermane systems.

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for *endo,exo*-2

atom	x	y	z	B_{eq},[a] Å^2
Si(1)	0.09231(6)	0.51790(6)	0.30631(3)	2.63(1)
Si(2)	0.27915(6)	0.47512(6)	0.31168(3)	2.66(1)
Si(3)	0.36376(7)	0.67923(6)	0.30408(3)	2.88(2)
Si(4)	0.20383(7)	0.72897(6)	0.34475(3)	3.17(2)
Si(5)	0.06838(6)	0.49766(6)	0.19283(3)	2.74(2)
Si(6)	0.28354(7)	0.59466(6)	0.19249(3)	2.70(2)
Si(7)	0.29056(7)	0.40167(6)	0.20038(3)	2.80(2)
Si(8)	0.09513(7)	0.31287(6)	0.14642(3)	3.08(2)
Cl(1)	0.16531(8)	0.83550(6)	0.28538(4)	4.48(2)
Cl(2)	0.12272(8)	0.33141(7)	0.05150(3)	4.56(2)
C(1)	−0.0370(2)	0.4196(2)	0.3458(1)	3.09(6)
C(2)	−0.1600(3)	0.4331(3)	0.3332(1)	3.86(7)
C(3)	−0.2653(3)	0.3262(4)	0.3422(2)	6.2(1)
C(4)	0.0012(3)	0.4430(3)	0.4182(1)	3.93(7)
C(5)	−0.0481(3)	0.2928(3)	0.3152(1)	3.90(7)
C(6)	−0.1686(3)	0.5457(3)	0.3719(2)	5.21(9)
C(7)	0.3321(3)	0.4194(2)	0.3857(1)	3.29(6)
C(8)	0.2452(3)	0.3011(3)	0.3976(1)	3.94(7)
C(9)	0.2254(4)	0.1951(3)	0.3448(2)	5.34(9)
C(10)	0.3485(3)	0.5177(3)	0.4443(1)	4.39(8)
C(11)	0.4545(3)	0.4115(3)	0.3777(2)	4.60(8)
C(12)	0.2789(4)	0.2708(3)	0.4611(2)	5.8(1)
C(13)	0.5328(3)	0.7773(3)	0.3273(1)	3.88(7)
C(14)	0.5694(3)	0.8902(3)	0.2978(2)	4.73(8)
C(15)	0.5103(4)	0.9784(3)	0.3203(2)	6.4(1)
C(16)	0.6026(3)	0.6983(3)	0.3034(2)	5.01(9)
C(17)	0.5621(3)	0.8130(3)	0.4005(2)	5.33(9)
C(18)	0.7048(4)	0.9543(4)	0.3046(2)	7.5(1)
C(19)	0.2116(3)	0.8181(2)	0.4312(1)	3.90(7)
C(20)	0.0883(3)	0.8102(3)	0.4518(2)	4.52(8)
C(21)	0.0961(4)	0.8685(4)	0.5224(2)	6.6(1)
C(22)	0.2911(3)	0.9475(3)	0.4351(2)	5.02(9)
C(23)	0.2730(3)	0.7654(3)	0.4764(2)	4.88(8)
C(24)	0.0163(3)	0.8605(3)	0.4120(2)	6.1(1)
C(25)	−0.0620(3)	0.5274(3)	0.1460(1)	3.64(7)
C(26)	−0.0802(3)	0.6456(3)	0.1725(1)	4.37(7)
C(27)	−0.1668(4)	0.6752(4)	0.1280(2)	7.4(1)
C(28)	−0.1743(3)	0.4201(3)	0.1447(2)	4.79(9)
C(29)	−0.0356(3)	0.5249(3)	0.0767(1)	4.68(8)
C(30)	−0.1235(3)	0.6519(3)	0.2375(2)	4.84(8)
C(31)	0.3550(3)	0.6878(2)	0.1297(1)	3.57(7)
C(32)	0.3502(3)	0.8148(3)	0.1486(2)	4.71(8)
C(33)	0.4462(5)	0.9090(3)	0.1236(2)	8.5(1)
C(34)	0.2946(3)	0.6286(3)	0.0612(1)	4.44(8)
C(35)	0.4848(3)	0.6931(3)	0.1325(2)	4.58(8)
C(36)	0.2304(4)	0.8218(3)	0.1316(2)	5.8(1)
C(37)	0.4063(3)	0.3262(2)	0.1748(1)	3.80(7)
C(38)	0.3931(3)	0.2846(3)	0.1007(2)	4.56(8)
C(39)	0.4270(4)	0.3842(3)	0.0650(2)	5.8(1)
C(40)	0.3795(3)	0.2167(3)	0.2047(2)	4.87(8)
C(41)	0.5322(3)	0.4101(3)	0.2018(2)	5.17(9)
C(42)	0.4628(4)	0.2039(4)	0.0791(2)	8.2(1)
C(43)	0.0002(3)	0.1436(3)	0.1345(1)	3.93(7)
C(44)	−0.1339(3)	0.1156(3)	0.1151(2)	5.34(9)
C(45)	−0.1648(4)	0.1393(4)	0.0504(2)	7.6(1)
C(46)	0.0204(4)	0.1031(3)	0.1963(2)	5.29(9)
C(47)	0.0512(3)	0.0746(3)	0.0841(2)	5.13(9)
C(48)	−0.2082(5)	−0.0155(5)	0.1150(3)	10.8(2)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for *endo,exo*-2

	Bond Lengths		
Si(1)−Si(2)	2.471(1)	Si(1)−Si(4)	2.4337(9)
Si(1)−Si(5)	2.396(1)	Si(2)−Si(3)	2.396(1)
Si(2)−Si(7)	2.431(1)	Si(3)−Si(4)	2.375(1)
Si(3)−Si(6)	2.4320(9)	Si(5)−Si(6)	2.462(1)
Si(5)−Si(8)	2.433(1)	Si(6)−Si(7)	2.420(1)
Si(7)−Si(8)	2.357(1)	Si(4)−Cl(1)	2.107(1)
Si(8)−Cl(2)	2.126(1)	Si(1)−C(1)	1.965(3)
Si(2)−C(7)	1.984(3)	Si(3)−C(13)	1.963(3)
Si(4)−C(19)	1.960(3)	Si(5)−C(25)	1.976(3)
Si(6)−C(31)	1.972(3)	Si(7)−C(37)	1.966(4)
Si(8)−C(43)	1.960(3)		
	Bond Angles		
Si(2)−Si(1)−Si(4)	90.35(3)	Si(2)−Si(1)−Si(5)	95.12(4)
Si(2)−Si(1)−C(1)	116.3(1)	Si(4)−Si(1)−Si(5)	103.02(4)
Si(4)−Si(1)−C(1)	125.90(8)	Si(5)−Si(1)−C(1)	118.86(7)
Si(1)−Si(2)−Si(3)	82.53(4)	Si(1)−Si(2)−Si(7)	102.88(4)
Si(1)−Si(2)−C(7)	120.9(1)	Si(3)−Si(2)−Si(7)	93.28(3)
Si(3)−Si(2)−C(7)	120.56(7)	Si(7)−Si(2)−C(7)	126.0(1)
Si(2)−Si(3)−Si(4)	93.63(4)	Si(2)−Si(3)−Si(6)	81.68(3)
Si(2)−Si(3)−C(13)	124.7(1)	Si(4)−Si(3)−Si(6)	101.58(4)
Si(4)−Si(3)−C(13)	125.1(1)	Si(6)−Si(3)−C(13)	119.8(1)
Si(1)−Si(4)−Si(3)	83.76(4)	Si(1)−Si(4)−Cl(1)	113.12(4)
Si(1)−Si(4)−C(19)	124.92(9)	Si(3)−Si(4)−Cl(1)	105.03(4)
Si(3)−Si(4)−C(19)	124.6(1)	Cl(1)−Si(4)−C(19)	103.8(1)
Si(1)−Si(5)−Si(6)	92.13(3)	Si(1)−Si(5)−Si(8)	107.25(4)
Si(1)−Si(5)−C(25)	122.82(9)	Si(6)−Si(5)−Si(8)	86.55(4)
Si(6)−Si(5)−C(25)	127.16(9)	Si(8)−Si(5)−C(25)	113.96(9)
Si(3)−Si(6)−Si(5)	104.85(4)	Si(3)−Si(6)−Si(7)	92.69(4)
Si(3)−Si(6)−C(31)	117.00(7)	Si(5)−Si(6)−Si(7)	83.85(3)
Si(5)−Si(6)−C(31)	124.7(1)	Si(7)−Si(6)−C(31)	125.7(1)
Si(2)−Si(7)−Si(6)	81.21(3)	Si(2)−Si(7)−Si(8)	108.09(4)
Si(2)−Si(7)−C(37)	122.0(1)	Si(6)−Si(7)−Si(8)	89.26(4)
Si(6)−Si(7)−C(37)	130.66(9)	Si(8)−Si(7)−C(37)	117.33(8)
Si(5)−Si(8)−Si(7)	85.83(3)	Si(5)−Si(8)−Cl(2)	102.86(5)
Si(5)−Si(8)−C(43)	135.1(1)	Si(7)−Si(8)−Cl(2)	101.64(4)
Si(7)−Si(8)−C(43)	124.2(1)	Cl(2)−Si(8)−C(43)	102.26(9)

Table 4. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for *exo,exo*-2

atom	x	y	z	B_{eq},[a] Å^2
Si(1)	0.4519(1)	0.0074(3)	0.1863(2)	4.03(8)
Si(2)	0.4626(1)	0.2052(3)	0.1600(2)	3.78(8)
Si(3)	0.4321(1)	0.2500(3)	0.2385(2)	3.82(8)
Si(4)	0.3763(1)	0.0797(3)	0.1975(2)	4.43(9)
Cl(1)	0.2989(1)	0.1211(3)	0.0849(2)	7.04(9)
C(1)	0.4370(7)	−0.129(1)	0.1264(8)	7.2(4)
C(2)	0.3956(10)	−0.122(1)	0.046(1)	12.6(7)
C(3)	0.3972(7)	−0.209(1)	−0.0055(8)	10.7(6)
C(4)	0.4190(7)	−0.228(1)	0.1516(7)	8.7(5)
C(5)	0.4992(6)	−0.168(1)	0.1405(8)	8.9(5)
C(6)	0.3313(9)	−0.110(2)	0.018(1)	19.5(9)
C(7)	0.4285(6)	0.242(1)	0.0538(7)	6.8(4)
C(8)	0.4390(8)	0.358(2)	0.0425(9)	11.4(6)
C(9)	0.4319(8)	0.378(1)	−0.0325(8)	13.9(7)
C(10)	0.4624(6)	0.158(1)	0.0318(7)	8.0(5)
C(11)	0.3602(6)	0.215(1)	−0.0011(7)	9.2(5)
C(12)	0.405(1)	0.443(2)	0.054(2)	22(1)
C(13)	0.3978(6)	0.391(2)	0.254(1)	11.4(5)
C(14)	0.342(2)	0.400(2)	0.192(1)	23(1)
C(15)	0.3232(7)	0.416(2)	0.127(1)	15.4(7)
C(16)	0.4356(7)	0.494(1)	0.255(1)	16.5(6)
C(17)	0.3895(9)	0.364(2)	0.3167(9)	13.4(8)
C(18)	0.320(1)	0.520(2)	0.219(2)	29(1)
C(19)	0.3422(5)	0.015(1)	0.2439(7)	5.6(4)
C(20)	0.3258(5)	−0.112(1)	0.2244(8)	5.9(4)
C(21)	0.3137(7)	−0.172(1)	0.2747(9)	10.8(6)
C(22)	0.3916(6)	0.033(1)	0.3317(8)	7.7(5)
C(23)	0.2853(5)	0.082(1)	0.2175(7)	7.4(4)
C(24)	0.2739(6)	−0.136(1)	0.1433(9)	9.5(5)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$.

880PU and UV-970/880PU with Chemco 4.6 mm × 250 mm 5-ODS-H columns. Preparative (recycle-type) HPLC was carried out using JAI LC-908 and LC-09 with Chemco 20 mm × 250 mm 7-ODS-H columns. Octasilacubane 1 was prepared as previously reported.[2] PCl_5 was purchased from Kanto Chemical Ltd. and sublimed before use. Benzene was dried, distilled, and deoxygenated prior to use.

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(11) There are a few precedents of Lewis acid catalyzed rearrangements of alkylpolysilanes in which the two distinctive reactions take place: intramolecular rearrangement of the silicon skeleton and intramolecular redistribution of the alkyl substituents. For example, Blinka and West reported in 1986 that, in the presence of $Al(Fe)Cl_3$ catalyst, $(Me_2Si)_n$ (n = 5−12) rearranged to form isomeric branched permethylpolysilanes. For the reaction they proposed a mechanism involving a cyclopolysilane−$Al(Fe)Cl_3$ complex which leads to a positively charged pentavalent silicon intermediate. See: Blinka, T. A.; West, R. *Organometallics* **1986**, *5*, 128.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for *exo,exo*-2[a]

	Bond Lengths		
Si(1)−Si(2)	2.464(4)	Si(1)−Si(4)	2.421(4)
Si(1)−Si(1′)	2.424(6)	Si(1)−C(1)	1.96(1)
Si(2)−Si(3)	2.419(4)	Si(2)−Si(3′)	2.415(4)
Si(2)−C(7)	1.97(1)	Si(3)−Si(4)	2.351(4)
Si(3)−C(13)	2.08(2)	Si(4)−Cl(1)	2.124(4)
Si(4)−C(19)	1.93(1)		
	Bond Angles		
Si(2)−Si(1)−Si(4)	86.1(1)	Si(2)−Si(1)−Si(1′)	93.9(1)
Si(2)−Si(1)−C(1)	128.4(4)	Si(4)−Si(1)−Si(1′)	106.7(2)
Si(4)−Si(1)−C(1)	121.2(5)	Si(1′)−Si(1)−C(1)	114.7(5)
Si(1)−Si(2)−Si(3)	83.6(1)	Si(1)−Si(2)−Si(3′)	103.9(2)
Si(1)−Si(2)−C(7)	116.7(5)	Si(3)−Si(2)−Si(3′)	92.4(1)
Si(3)−Si(2)−C(7)	119.1(4)	Si(3′)−Si(2)−C(7)	133.4(4)
Si(2)−Si(3)−Si(4)	88.7(2)	Si(2)−Si(3)−Si(2′)	82.1(1)
Si(2)−Si(3)−C(13)	135.7(6)	Si(4)−Si(3)−Si(2′)	108.1(2)
Si(4)−Si(3)−C(13)	119.2(5)	Si(2′)−Si(3)−C(13)	115.8(5)
Si(1)−Si(4)−Si(3)	86.0(1)	Si(1)−Si(4)−Cl(1)	106.0(2)
Si(1)−Si(4)−C(19)	131.1(4)	Si(3)−Si(4)−Cl(1)	102.2(2)
Si(3)−Si(4)−C(19)	123.6(4)	Cl(1)−Si(4)−C(19)	104.1(4)

[a] Symmetry code: (i) $-x, y, {}^1/_2 - z$.

Table 6. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for *endo,endo*-2

atom	*x*	*y*	*z*	$B_{eq}{}^a$ Å^2
Si(1)	0.0104(1)	0.4242(2)	0.3069(1)	3.0(1)
Si(2)	−0.0216(1)	0.2259(2)	0.3144(1)	3.1(1)
Si(3)	0.0736(1)	0.1828(2)	0.2934(1)	3.2(1)
Si(4)	0.1121(1)	0.3647(2)	0.3324(1)	3.7(1)
Cl(1)	0.1569(1)	0.4266(2)	0.2648(1)	5.1(1)
C(1)	−0.0048(3)	0.5598(6)	0.3546(3)	3.6(2)
C(2)	−0.0678(4)	0.6077(7)	0.3383(4)	4.3(2)
C(3)	−0.1098(4)	0.5433(10)	0.3683(5)	6.2(3)
C(4)	0.0387(4)	0.6498(7)	0.3396(4)	4.8(2)
C(5)	0.0132(4)	0.5304(7)	0.4251(3)	4.5(2)
C(6)	−0.0703(6)	0.7360(10)	0.3579(6)	7.8(4)
C(7)	−0.0402(3)	0.1688(7)	0.3935(4)	4.0(2)
C(8)	−0.0926(4)	0.2293(8)	0.4125(4)	5.3(3)
C(9)	−0.1484(4)	0.2206(10)	0.3636(5)	6.5(3)
C(10)	0.0149(4)	0.1933(8)	0.4454(4)	5.2(3)
C(11)	−0.0482(4)	0.0392(8)	0.3888(4)	5.3(3)
C(12)	−0.1037(5)	0.1859(11)	0.4768(5)	7.3(4)
C(13)	0.1162(3)	0.0382(7)	0.3125(4)	4.2(2)
C(14)	0.1655(4)	0.0236(8)	0.2747(4)	5.1(3)
C(15)	0.2137(4)	0.1132(9)	0.2898(5)	6.2(3)
C(16)	0.0715(4)	−0.0580(7)	0.2933(5)	5.3(3)
C(17)	0.1406(4)	0.0294(8)	0.3844(4)	5.6(3)
C(18)	0.1945(5)	−0.0961(10)	0.2831(7)	7.6(4)
C(19)	0.1692(3)	0.3925(8)	0.4126(4)	4.8(2)
C(20)	0.1765(4)	0.5218(8)	0.4324(4)	5.3(3)
C(21)	0.2130(5)	0.5368(11)	0.5005(5)	8.0(4)
C(22)	0.2284(4)	0.3420(9)	0.4058(5)	6.1(3)
C(23)	0.1486(4)	0.3239(9)	0.4644(4)	5.6(3)
C(24)	0.2019(5)	0.6013(10)	0.3901(6)	7.7(4)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for *endo,endo*-2[a]

	Bond Lengths		
Si(1)−Si(2)	2.452(3)	Si(1)−Si(4)	2.422(3)
Si(1)−Si(1′)	2.400(2)	Si(1)−C(1)	1.965(8)
Si(2)−Si(3)	2.419(3)	Si(2)−Si(3′)	2.435(3)
Si(2)−C(7)	1.968(9)	Si(3)−Si(4)	2.390(3)
Si(3)−C(13)	1.960(8)	Si(4)−Cl(1)	2.103(3)
Si(4)−C(19)	1.971(8)		
	Bond Angles		
Si(2)−Si(1)−Si(4)	90.7(1)	Si(2)−Si(1)−Si(1′)	94.1(1)
Si(2)−Si(1)−C(1)	129.5(3)	Si(4)−Si(1)−Si(1′)	101.8(1)
Si(4)−Si(1)−C(1)	113.1(2)	Si(1′)−Si(1)−C(1)	121.2(2)
Si(1)−Si(2)−Si(3)	83.0(1)	Si(1)−Si(2)−Si(3′)	103.2(1)
Si(1)−Si(2)−C(7)	120.4(2)	Si(3)−Si(2)−Si(3′)	93.9(1)
Si(3)−Si(2)−C(7)	118.5(2)	Si(3)−Si(2)−C(7)	126.9(2)
Si(2)−Si(3)−Si(4)	92.3(1)	Si(2)−Si(3)−Si(2′)	81.2(1)
Si(2)−Si(3)−C(13)	125.9(3)	Si(4)−Si(3)−Si(2′)	103.0(1)
Si(4)−Si(3)−C(13)	124.0(2)	Si(2′)−Si(3)−C(13)	120.4(3)
Si(1)−Si(4)−Si(3)	84.3(1)	Si(1)−Si(4)−Cl(1)	110.8(1)
Si(1)−Si(4)−C(19)	126.7(3)	Si(3)−Si(4)−Cl(1)	105.5(1)
Si(3)−Si(4)−C(19)	126.0(3)	Cl(1)−Si(4)−C(19)	102.0(3)

[a] Symmetry code: (i) $-x, y, {}^1/_2 - z$.

Reaction of Octakis(1,1,2-trimethylpropyl)octasilacubane (1) with PCl_5. Reaction was carried out under an atmosphere of argon. To a solution of 50 mg (0.055 mmol) of octasilacubane **1** in benzene (5.0 mL) was added PCl_5 (0.05 mol/L solution in benzene, 2.4 mL, 0.12 mmol) dropwise with stirring at room temperature. The color of the solution changed from pink to colorless in 2 h. The reaction was monitored by HPLC. The isomeric distribution remained unchanged (*endo,exo*-**2**:*exo,exo*-**2**:*endo,endo*-**2** = 44:39:17) while the reaction progressed. The resulting solution was passed through a short silica gel column. Removal of the solvent by evaporation gave 51 mg of a colorless semisolid. Each isomer was isolated by recycle-type preparative HPLC (MeOH/THF = 6/4 elution). The yields of *endo,exo*-**2**, *exo,exo*-**2**, and *endo,endo*-**2** were 20 mg (37%), 17 mg (33%), and 8 mg (15%), respectively.[13]

endo,exo-**2**: colorless prisms, mp (sealed) 192 °C dec; IR (KBr) 2955, 2865, 1465, 1375, 1125, 1085, cm^{-1}; MS (30 eV) *m/z* 890 ($M^+ - CMe_2CHMe_2$, 3), 805 ($M^+ - CMe_2CHMe_2 - CMe_2CMe_2$, 10), 721 (7), 637 (6), 553 (7), 469 (10), 385 (21), 301 (9), 69 (100); HRMS calcd for $C_{36}H_{79}Si_8Cl_2$ 805.3713, found 805.3690.

exo,exo-**2**: colorless prisms, mp (sealed) 200 °C dec; IR (KBr) 2955, 2865, 1460, 1370, 1125, 1090 cm^{-1}; MS (30 eV) *m/z* 890 ($M^+ - CMe_2CHMe_2$, 2), 805 ($M^+ - CMe_2CHMe_2 - CMe_2CMe_2$, 7), 721 (6), 637, (5), 553 (7), 469 (9), 385 (17), 301 (6), 69 (100); HRMS calcd for $C_{36}H_{79}Si_8Cl_2$ 805.3713, found 805.3702.

endo,endo--**2**: colorless prisms, mp (sealed) 199 °C dec; IR (KBr) 2925, 2860, 1450, 1370, 1125, 1070 cm^{-1}; MS (30 eV) *m/z* 890 ($M^+ - CMe_2CHMe_2$, 4), 805 ($M^+ - CMe_2CHMe_2 - CMe_2CMe_2$, 10), 721 (8), 637 (6), 553 (7), 469 (9), 385 (22), 301 (10), 69 (100); HRMS calcd for $C_{36}H_{79}Si_8Cl_2$ 805.3713, found 805.3752.

X-ray Crystallographic Analysis of *endo,exo*-2. Colorless crystals of *endo,exo*-4,8-dichlorooctakis(1,1,2-trimethylpropyl)tetracyclo[3.3.0.0^{2,7}.0^{3,6}]octasilane were obtained from 2-butanone−hexane (3:1) by slow evaporation. A crystal specimen of dimensions 0.16 × 0.46 × 0.23 mm was sealed in a glass capillary and used for data collection on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Cu Kα radiation. Cell parameters were refined by the least-squares method using 25 reflections ($31 < 2\theta < 58°$). Intensity data were collected in the range $4 < 2\theta < 130°$ by the $\omega-2\theta$ scan technique at room temperature. Three standard reflections were measured after every 1 h and varied less than 1%. The space group $P\bar{1}$ was determined from the lack of systematic absences, statistical analysis of the intensity distribution, and successful solution and refinement of the structure. A total of 9856 unique reflections were collected, and 7597 nonzero observed reflections ($|F_o| \geq 3\sigma(F_o)$) were obtained and corrected for Lorentz-polarization and empirical absorption on the basis of a ψ scan. The structure was solved by direct methods using *MULTAN78*.[14] Non-hydrogen atoms were

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(12) Also, no example has been reported for the reactions of cubanes wherein the tetracyclo[3.3.0.0^{2,7}.0^{3,6}]octane framework had been formed. For reactions of cubanes and related compounds, see: (a) Griffin, G. W.; Marchand, A. P. *Chem. Rev.* **1989**, *89*, 997. (b) Marchand, A. P. *Chem. Rev.* **1989**, *89*, 1011. (c) Eaton, P. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1421.

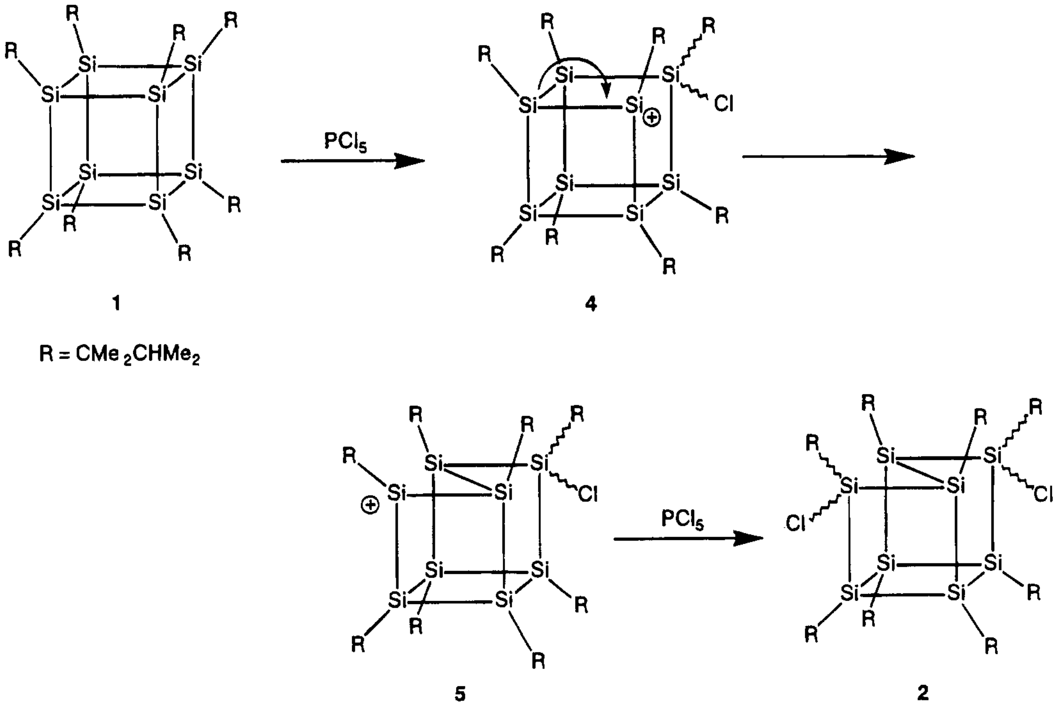
(13) An attempt to obtain good elemental analyses met with failure due to the formation of silicon carbide. For example, a microcombustion of *endo,exo*-**2** afforded the values of C, 56.03, and H, 10.77 (Calcd for $C_{48}H_{104}C_{12}Si_8$: C, 59.00; H, 10.73), and left ashes.

(14) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq. J.-P.; Woolfson, M. M. *MULTAN78, A system of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*; Universities of York, England, and Louvain, Belgium, 1978.

Table 8. NMR Properties of 2

compd	^{1}H NMR, ppm			^{13}C NMR, ppm	^{29}Si NMR, ppm
	CH	$CH_3(\alpha)$	$CH_3(\beta)$		
endo,exo-**2**	2.51 (sept, 2H)	1.62 (s, 3H)	1.09 (overlap, d, 12H))	37.71, 37.03, 36.29	55.74
	2.35 (sept, 2H)	1.48 (s, 3H)	1.05 (d, 3H)	36.13, 36.09, 35.99	53.23
	2.30 (sept, 2H)	1.42 (s, 3H)	1.03 (d, 3H)	35.92, 35.32, 35.32	21.00
	2.28 (sept, 2H)	1.405 (s, 3H)	0.98 (d, 3H)	35.24, 35.19, 34.80	15.28
		1.401 (s, 3H)	0.97 (overlap, d, 6H)	34.35, 34.35, 34.24	−2.55
	all $J = 6.7$ Hz	1.39 (overlap, s, 6H)	0.96 (d, 3H)	33.89, 30.35, 29.90	−7.09
		1.38 (s, 3H)	0.93 (d, 3H)	28.54, 28.32, 27.54	−25.87
		1.35 (s, 3H)	0.92 (d, 3H)	27.43, 26.50, 26.50	−27.12
		1.34 (s, 3H)	0.90 (d, 3H)	26.45, 26.02, 25.56	
		1.32 (s, 3H)	0.89 (d, 3H)	25.14, 24.17, 23.93	
		1.31 (s, 3H)	0.88 (overlap, d, 6H)	23.35, 23.18, 21.45	
		1.304 (s, 3H)		21.40, 21.30, 21.16	
		1.298 (s, 3H)		21.16, 21.07, 21.07	
		1.29 (s, 3H)	all $J = 6.7$ Hz	20.59, 20.28, 19.70	
		1.20 (s, 3H)		19.34, 19.05, 17.74	
				17.67, 17.67, 16.20	
exo,exo-**2**	2.31 (sept, 8H)	1.42 (s, 6H)	1.04 (d, 6H)	36.00, 35.02, 35.02	51.49
		1.40 (s, 6H)	1.00 (d, 6H)	34.73, 33.57, 34.50	19.93
	$J = 6.7$ Hz	1.38 (s, 6H)	0.98 (d, 6H)	33.07, 33.01, 27.55	−5.98
		1.34 (s, 6H)	0.94 (d, 6H)	27.19, 25.69, 25.40	−29.92
		1.33 (s, 6H)	0.909 (d, 6H)	25.30, 25.08, 24.94	
		1.30 (s, 6H)	0.905 (d, 6H)	20.84, 20.28, 19.96	
		1.24 (s, 6H)	0.85 (d, 6H)	19.96, 19.51, 19.01	
		1.15 (s, 6H)	0.84 (d, 6H)	18.86, 18.05, 16.73	
			all $J = 6.7$ Hz		
endo,endo-**2**	2.59 (sept, 2H)	1.51 (s, 6H)	1.09 (d, 6H)	36.49, 36.33, 36.09	59.33
	2.46 (sept, 2H)	1.45 (s, 6H)	1.07 (d, 6H)	35.76, 35.23, 35.13	13.89
	2.27 (sept, 2H)	1.35 (s, 6H)	1.03 (d, 6H)	34.57, 34.18, 30.19	−4.01
	2.25 (sept, 2H)	1.30 (overlap, s, 12H)	1.00 (d, 6H)	29.81, 28.49, 25.86	−19.90
		1.28 (s, 6H)	0.88 (d, 6H)	25.65, 25.61, 24.30	
	all $J = 6.7$ Hz	1.27 (overlap, s, 12H)	0.85 (overlap, d, 18H)	23.35, 35.20, 21.76	
			all $J = 6.7$ Hz	20.98, 20.75, 18.74	
				18.64, 17.25, 16.53	

Scheme 2



found from subsequent Fourier syntheses and refined by the full-matrix least-squares method with anisotropic thermal parameters using *Mol*EN.[15] All hydrogen atoms were located at calculated positions and refined isotropically. A secondary extinction correction was applied in the least squares. The final coefficient was 0.000 000 5. Final R and R_w values were 0.037 and 0.039, respectively, in which the final weighting scheme was $w = 1/\sigma^2(F_o)$. Atomic scattering factors were taken from ref 16. All calculations were carried out on a Micro VAXII computer. Details of crystal data, data collection, and refinement are listed in Table 1.

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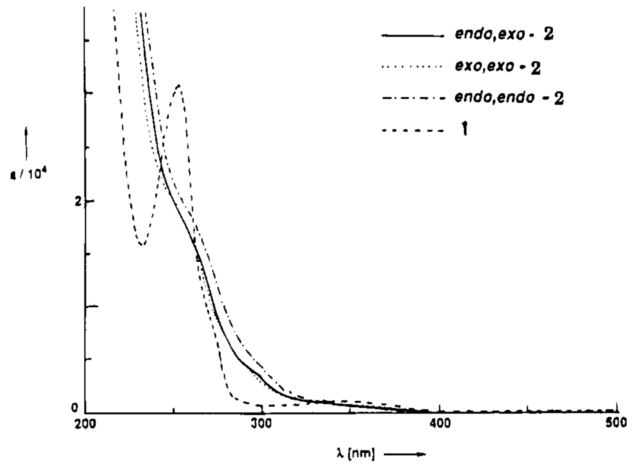

Figure 5. UV spectra of **1** and **2**.

X-ray Crystallographic Analysis of *exo,exo*-2. Colorless crystals of *exo,exo*-4,8-dichlorooctakis(1,1,2-trimethylpropyl)tetracyclo[3.3.0.0^{2,7}.0^{3,6}]octasilane were obtained from 2-butanone–hexane by slow evaporation. A crystal specimen of dimensions 0.4 × 0.4 × 0.2 mm was sealed in a glass capillary and used for data collection on a Rigaku AFC7S diffractometer using graphite-monochromated Mo Kα radiation. Cell parameters were refined by the least-squares method using 25 reflections ($24 < 2\theta < 35°$). Intensity data were collected in the range $5 < 2\theta < 120°$ by the $\omega - 2\theta$ scan technique at room temperature. Three reference reflections were measured after every 1 h and varied 0.679%. The space group *C*2/*c* was determined from systematic absences (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$) of packing considerations, a statistical analysis of the intensity distribution, and the successful solution and refinement of the structure. A total of 6921 unique reflections were collected, and 1872 non-zero observed reflections ($|F_o| \geq 3\sigma(F_o)$) were obtained and corrected for Lorentz–polarization and empirical absorption on the basis of a ψ scan. The structure was solved by direct methods using SIR88.[17] Non-hydrogen atoms were found from subsequent Fourier syntheses and refined by the full-matrix least-squares method with anisotropic thermal parameters using DIRDIF92.[18] Hydrogen atoms were located in the calculated positions and were included in the refinement but restrained to ride on the atoms to which they are bonded. All hydrogen atoms were not refined. A secondary extinction correction was applied in the least squares. Final R and R_w values were 0.081 and 0.060, respectively, in which the final weighting scheme was $w = 1/\sigma^2(F_o)$. Atomic scattering factors were taken from ref 16. All calculations were carried out on a Silicon Graphics INDY computer. Details of crystal data, data collection, and refinement are listed in Table 1.

X-ray Crystallographic Analysis of endo,endo-2. Colorless crystals of *endo,endo*-4,8-dichlorooctakis(1,1,2-trimethylpropyl)tetracyclo[3.3.0.0^{2,7}.0^{3,6}]octasilane were obtained from 2-butanone–hexane by slow evaporation. A crystal specimen of dimensions 0.13 × 0.5 × 0.13 mm was sealed in a glass capillary and used for data collection on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Cu Kα radiation. Cell parameters were refined by the least-squares method using 24 reflections ($22 < 2\theta < 48°$). Intensity data were collected in the range $4 < 2\theta < 120°$ by the $\omega - \theta$ scan technique at room temperature. Three reference reflections were measured after every 1 h and varied 0.9%. The space group *C*2/*c* was determined from systematic absences (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$). A total of 4112 unique reflections were collected, and 3146 non-zero observed reflections ($|F_o| \geq 3\sigma(F_o)$) were obtained and corrected for Lorentz–polarization and empirical absorption on the basis of a ψ scan. The structure was solved by direct methods using *MULTAN78*.[14] Non-hydrogen atoms were found from subsequent Fourier syntheses and refined by the full-matrix least-sqaures method with anisotropic thermal parameters using *UNICSIII*.[19] A total of 20 hydrogen atoms were located from difference Fourier maps, and 32 hydrogen atoms were located at calculated positions. All hydrogen atoms were not refined. Final R and R_w values were 0.046 and 0.053, respectively, in which the final weighting scheme was $w = 1/[0.00305|F_o|^2 - 0.14643|F_o| + 6.2859]$. Atomic scattering factors were taken from ref 16. All calculations were carried out on a FACOM M-380 computer. Details of crystal data, data collection, and refinement are listed in Table 1.

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Supplementary Material Available: Tables of anisotropic thermal parameters, atomic coordinates and isotropic thermal parameters involving H atoms, and bond lengths and angles for **2** and views of molecular packing and packing diagrams (27 pages). Ordering information is available on any current masthead page.

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