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1,2,3-Triphenyl-1,2,3-trithexylcyclotrisilanes: Synthesis and Ring-Opening by Halogens

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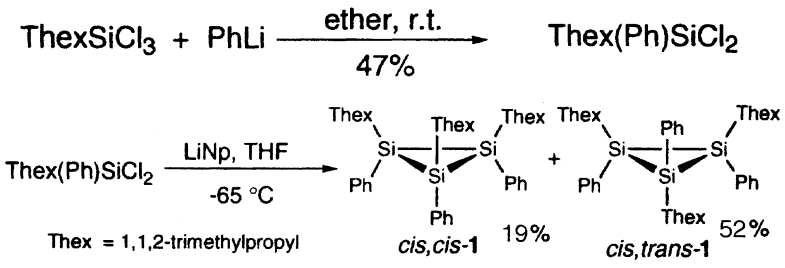
Reaction of dichlorophenylthexylsilane (thexyl = 1,1,2-trimethylpropyl) with lithium naphthalenide in tetrahydrofuran at −65 °C gave *cis,cis*- and *cis,trans*-1,2,3-triphenyl-1,2,3-trithexylcyclotrisilane **1** (*cis,cis*-**1** and *cis,trans*-**1**) in yields of 19 and 52%, respectively. The structures of both isomers were determined by X-ray crystallography. The ring-opening reaction of each isomer with bromine leads to the formation of 1,3-dibromo-1,2,3-triphenyl-1,2,3-trithexyltrisilane (**2**); *cis,cis*-**1** gave only (1*R*,3*R*)/(1*S*,3*S*)-1,3-dibromo-1,2,3-triphenyl-1,2,3-trithexyltrisilane ((1*R*,3*R*)/(1*S*,3*S*)-**2**) (87% yield). While *cis,trans*-**1** formed (1*R*,2*s*,3*S*)- and (1*R*,2*r*,3*S*)-1,3-dibromo-1,2,3-triphenyl-1,2,3-trithexyltrisilane ((1*R*,2*s*,3*S*)-**2** and (1*R*,2*r*,3*S*)-**2**, in 13 and 31% yields) as well as (1*R*,3*R*)/(1*S*/3*S*)-**2** (44% yield). The structures of (1*R*,3*R*)/(1*S*,3*S*)-**2** and (1*R*,2*r*,3*S*)-**2** were confirmed by X-ray crystallography. From the stereochemical results observed in the ring-opening reactions, it is concluded that the cleavage of the Si–Si bonds occurs with retention–inversion of the configuration of the silicon atoms. In the chlorination, *cis,cis*-**1** gave (1*R*,3*R*)/(1*S*,3*S*)-1,3-dichloro-1,2,3-triphenyl-1,2,3-trithexyltrisilane ((1*R*,3*R*)/(1*S*,3*S*)-**3**, 40% yield) and (1*R*,2*r*,3*S*)-1,3-dichloro-1,2,3-triphenyl-1,2,3-trithexyltrisilane ((1*R*,2*r*,3*S*)-**3**, 30% yield); *cis,trans*-**1** gave (1*R*,3*R*)/(1*S*,3*S*)-**3** (33% yield), (1*R*,2*r*,3*S*)-**3** (14% yield), and (1*R*,2*s*,3*S*)-1,3-dichloro-1,2,3-triphenyl-1,2,3-trithexyltrisilane in 40% yield. The structure of (1*R*,2*r*,3*S*)-**3** was confirmed by X-ray crystallography. The result indicates that stereoselectivity was lower in the ring-opening by chlorine than in that by bromine.

As a part of our ongoing research of the syntheses and reactions of the strained cyclopolysilanes,[1—3] we have prepared the cyclotrisilanes bearing two different substituents, $(PhThexSi)_3$ (*cis,cis*-**1** and *cis,trans*-**1**, thexyl or Thex denotes 1,1,2-trimethylpropyl group hereafter). This type of cyclotrisilanes is of interest because they are good models for studying the stereochemical behavior of the cleavage reactions of Si–Si bonds. Several reports have appeared on the cleavage reactions of cyclotrisilanes and related compounds with halogens.[4] However, in all cases, the starting compounds were symmetrically substituted $(R_2M)_3$ (M = Si, Ge), and thus no discussion about the stereochemical course was possible.

In a pioneering work on the cleavage reactions of Si–Si bonds by electrophiles, Kumada and co-workers suggested the existence of halonium ion intermediates for the reaction of disilanes with halogens.[5] The ring-opening halogenation of cyclopolysilanes is one of the major pathways for the preparation of α,ω-dihalosilanes.[4] However, no report has dealt with the stereochemistry of the reaction so far as we know. In this paper, the following new information is presented: (1) synthesis and X-ray structures of cyclotrisilanes *cis,cis*-**1** and *cis,trans*-**1**; (2) stereochemistry of ring-opening reaction of **1** with bromine leading to 1,3-dibromo-1,2,3-triphenyl-1,2,3-trithexyltrisilane (**2**); (3) stereochemistry of the corresponding reaction of **1** with chlorine leading to 1,3-dichloro-1,2,3-triphenyl-1,2,3-trithexyltrisilane (**3**). The structures of the dibromo- and dichlorotrisilanes were determined by X-ray crystallography and/or spectroscopic methods.

Results and Discussion

Synthesis, Separation, and Structures of *cis,cis*-1 and *cis,trans*-1. The cyclotrisilanes, *cis,cis*-**1** and *cis,trans*-**1**, were prepared by use of dichloro(phenyl)(thexyl)silane with lithium naphthalenide in THF. Thus, treatment of the dichlorosilane with two molar amounts of lithium naphthalenide in THF at −65 °C afforded 1,2,3-triphenyl-1,2,3-trithexylcyclotrisilane (**1**) in 80% yield as a mixture of *cis,cis*-**1** and *cis,trans*-**1**. From the product mixture, these isomers were separated by a column chromatography (silica, hexane/benzene = 9/1), and subsequent recrystallization from acetone gave analytically pure *cis,cis*-**1** (19% yield) and *cis,trans*-**1** (52% yield) as air stable crystals (Scheme 1). The structures of *cis,cis*-**1** and *cis,trans*-**1** were confirmed unequivocally by X-ray crystallography. The ORTEP drawings are shown in Fig. 1. Crystallographic data, selected bond lengths, and bond angles are given in Tables 1, 2, and 3. The asymmetric units of *cis,cis*-**1** and *cis,trans*-**1** contain two crystallographically independent molecules. In the case of *cis,trans*-**1**, one molecule of acetone was incorporated in the lattice. The Si–Si bond lengths of *cis,cis*-**1** (2.404(5) and 2.391(5) Å) are slightly longer than those of *cis,trans*-**1** (2.404(5) and 2.377(8) Å). The vicinal steric repulsion between the thexyl groups in *cis* position is responsible for the longer Si–Si bond lengths. This is also evident from the slightly larger Si–Si–C(thexyl) bond angles in *cis,cis*-**1** (125.8(6)—132.3(5)°) than those in *cis,trans*-**1** (122.7(6)—129.8(7)°). However, the Si–C(thexyl) bond lengths observed in *cis,cis*-**1** (1.90(2)—



Scheme 1.

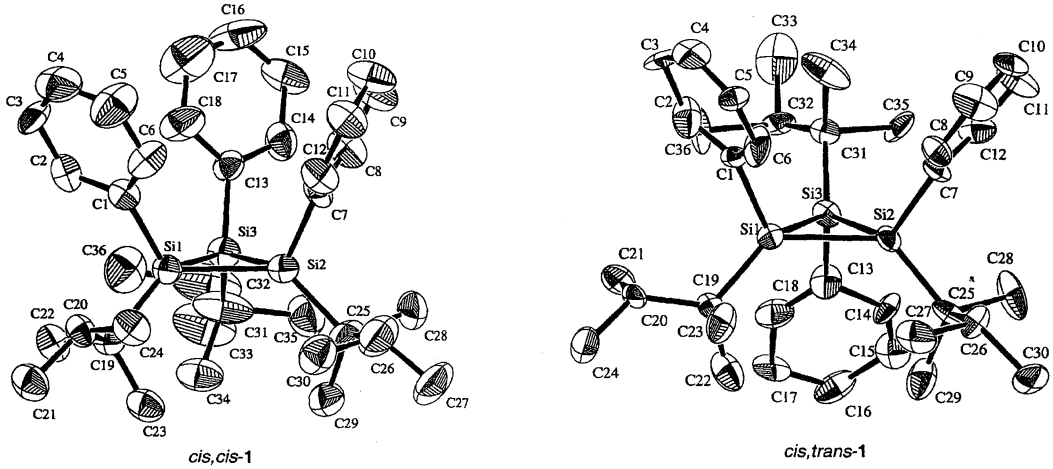


Fig. 1. ORTEP drawings of *cis,cis*-**1** and *cis,trans*-**1**. Thermal ellipsoids are drawn at the 30% probability level.

1.92(1) Å) are not significantly different from those observed in *cis,trans*-**1** (1.85(2)—1.92(1) Å).[6]

Ring-Opening Reaction of Cyclotrisilane 1 with Br_2. When *cis,cis*-**1** was allowed to react with Br_2 in benzene at room temperature, the reaction completed in 5 min and 1,3-dibromo-1,2,3-triphenyl-1,2,3-trithexyltrisilane (**2**) was formed. HPLC analysis indicated that the reaction proceeded selectively (Fig. 2).[7] Purification by recycle-type preparative HPLC (ODS (octadecylsilanized silica), MeOH/THF = 9/1) resulted in the isolation of **2** in 87%. Dibromide **2** was identified to be an enantiomeric mixture of (1*R*,3*R*)- and (1*S*,3*S*)-1,3-dibromo-1,2,3-triphenyl-1,2,3-trithexyltrisilane by the combination of $^{29}Si\{^1H\}$ NMR spectroscopy and X-ray crystallography. In the ^{29}Si NMR spectrum, **2** shows three resonances at −14.37, 18.52, and 22.33 ppm, indicating that three silicon atoms are nonequivalent. Out of three possible diastereomers, only (1*R*,3*R*) and (1*S*,3*S*) structures are chiral and have no symmetry plane and would be expected to show three resonances in ^{29}Si NMR. On the other hand, the other two isomers with (1*R*,2*s*,3*S*) and (1*R*,2*r*,3*S*) structures have symmetry plane and are expected to show two peaks in ^{29}Si NMR. The observed ^{29}Si NMR spectrum thus allows the assignment of the dibromide to be (1*R*,3*R*) and (1*S*,3*S*) structures. This assignment is confirmed by X-ray crystallography, which discloses that two enantiomers were included in a lattice.

The reaction of *cis,trans*-**1** with bromine led to the formation of the three diastereomers of 1,3-dibromo-1,2,3-triphenyl-1,2,3-trithexyltrisilane (HPLC chart is shown in Fig. 2). Each isomer was separated by recycle-type preparative HPLC (ODS, MeOH/THF = 9/1) and the second fraction was identified to be a mixture of (1*R*,3*R*)-**2** and (1*S*,3*S*)-**2** from its NMR spectra (44%). The other two diasteromers exhibit two signals in the ^{29}Si NMR (−10.68 and 19.82 ppm for the first fraction and −8.76 and 19.87 ppm for the third fraction, respectively), indicating the presence of a symme-

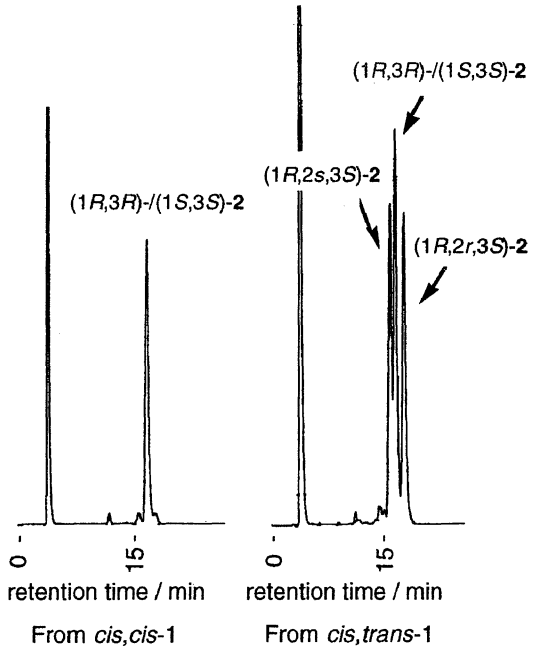


Fig. 2. HPLC chromatogram of **2** (7-ODS-H, MeOH/THF = 9/1).

Table 1. Summary of Crystal Data, Data Collection, and Refinement of *cis,cis*-**1** and *cis,trans*-**1**

	cis,cis-**1**	*cis,trans*-**1**
	Crystal data	
Formula	$C_{36}H_{54}Si_3$	$C_{36}H_{54}Si_3 \cdot 1/2C_2H_6CO$
Mol wt	571.08	600.12
Cryst. descript	Colorless prisms	Colorless prisms
Cryst. size/mm	$0.4 \times 0.4 \times 0.1$	$0.2 \times 0.2 \times 0.1$
Cryst. syst.	Triclinic	Triclinic
Space group	$P\bar{1}$	$P1$
a/Å	18.715(3)	13.174(2)
b/Å	21.360(4)	13.763(2)
c/Å	10.132(2)	10.956(2)
α/deg	91.25(2)	93.42(1)
β/deg	101.60(1)	109.81(1)
γ/deg	109.59(1)	96.87(1)
V/Å^3	3720(1)	1844.8(6)
Z	4	2
d_{calc}/g cm^{-3}	1.020	1.080
	Data collection	
Diffractometer	Rigaku AFC7S	Rigaku AFC7S
Radiation (λ, Å)	Cu $K\alpha$ (1.5418)	Cu $K\alpha$ (1.5418)
Monochromator	Graphite	Graphite
μ/cm^{-1}	13.10	13.52
2θ range/deg	4—120.1	4—120.1
Scan type	ω–2θ	ω–2θ
No. of reflns measd	8767	5774
No. of ind reflns	8412	5494
No. of obsd reflns ($\lvert F_o \rvert \geq 3\sigma(F_o)$)	3274	2980
R	0.079	0.049
R_w	0.067	0.042
Weighting scheme	$w = 1/\sigma^2(F_o)$	$w = 1/\sigma^2(F_o)$
S	3.71	1.89
$(\Delta/\sigma)_{max}$	0.04	2.34
$(\Delta\rho)_{max}$eÅ^{-3}	0.52	0.27
$(\Delta\rho)_{min}$eÅ^{-3}	−0.31	−0.20
No. of parms	704	737

try plane in these molecules. The X-ray crystallography of the third fraction indicates that it is (1*R*,2*r*,3*S*)-**2** (31% yield) and therefore the first fraction is (1*R*,2*s*,3*S*)-**2** (13% yield) (Scheme 2). The molecular structures of (1*R*,3*R*)/(1*S*,3*S*)-**2** and (1*R*,2*r*,3*S*)-**2** are shown in Fig. 4.

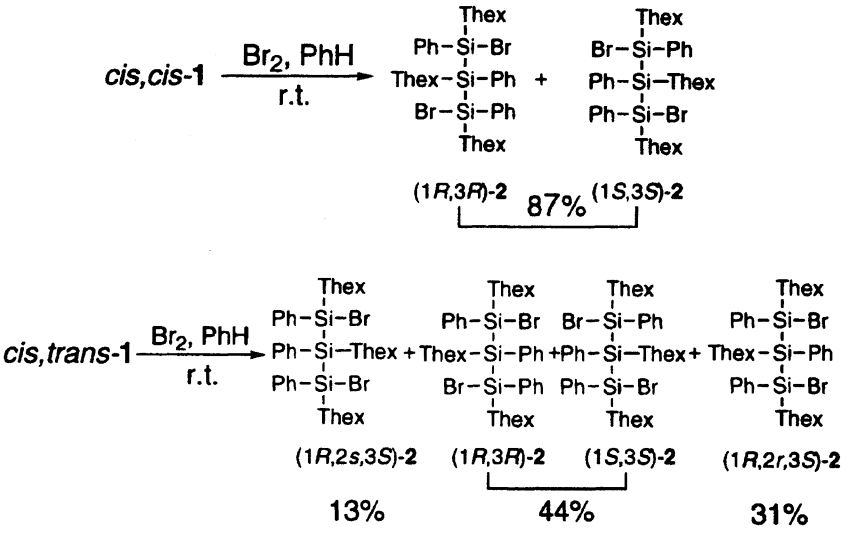
Ring-Opening Reaction of Cyclotrisilane 1 with Cl_2. Treatment of the cyclotrisilane **1** with Cl_2 in benzene at room temperature afforded 1,3-dichloro-1,2,3-triphenyl-1,2,3-trithexyltrisilane (**3**). The high-pressure liquid chromatogram of the reaction mixture is shown in Fig. 3, which indicates that the two diasteromers formed from *cis,cis*-**1**, and all three diastereomers formed from *cis,trans*-**1**. Separation was carried out in a similar way as in the case of the bromination reaction. Each isomer was assigned by NMR spectroscopy and X-ray analysis. In ^{29}Si NMR, the first fraction from *cis,cis*-**1** showed three resonances (−14.08, 18.93, and 21.39 ppm); thus it was assigned to be (1*R*,3*R*)/(1*S*,3*S*)-**3** as in the case of (1*R*,3*R*)/(1*S*,3*S*)-**2**. From *cis,trans*-**1**, the second fraction was identified to be (1*R*,3*R*)/(1*S*,3*S*)-**3**. The second fraction from

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *cis,cis*-**1**

	Bond lengths		
Si(1)–Si(2)	2.404(5)	Si(1)–Si(3)	2.391(5)
Si(1)–C(1)	1.89(1)	Si(1)–C(19)	1.93(1)
Si(2)–Si(3)	2.376(5)	Si(2)–C(7)	1.89(1)
Si(2)–C(25)	1.92(1)	Si(3)–C(13)	1.90(1)
Si(3)–C(31)	1.90(2)	Si(4)–Si(5)	2.414(5)
Si(4)–Si(6)	2.387(5)	Si(4)–C(37)	1.88(2)
Si(4)–C(55)	1.93(1)	Si(5)–Si(6)	2.374(4)
	Bond angles		
Si(2)–Si(1)–Si(3)	59.4(1)	Si(2)–Si(1)–C(1)	117.7(5)
Si(2)–Si(1)–C(19)	128.0(4)	Si(3)–Si(1)–C(1)	112.7(4)
Si(3)–Si(1)–C(19)	126.2(5)	Si(1)–Si(2)–Si(3)	60.0(1)
Si(1)–Si(2)–C(7)	112.4(5)	Si(1)–Si(2)–C(25)	132.3(5)
Si(3)–Si(2)–C(7)	113.3(6)	Si(3)–Si(2)–C(25)	125.8(6)
Si(1)–Si(3)–Si(2)	60.6(2)	Si(1)–Si(3)–C(13)	115.3(7)
Si(1)–Si(3)–C(31)	127.0(7)	Si(2)–Si(3)–C(13)	111.1(4)
Si(2)–Si(3)–C(31)	127.2(8)	Si(5)–Si(4)–Si(6)	59.3(1)
Si(5)–Si(4)–C(37)	114.2(6)	Si(5)–Si(4)–C(55)	128.7(5)
Si(6)–Si(4)–C(37)	113.8(5)	Si(6)–Si(4)–C(55)	126.4(5)
Si(4)–Si(5)–Si(6)	59.8(1)	Si(4)–Si(5)–C(43)	114.4(5)
Si(4)–Si(5)–C(61)	128.4(6)	Si(6)–Si(5)–C(43)	113.5(5)
Si(6)–Si(5)–C(61)	129.1(5)	Si(4)–Si(6)–Si(5)	60.9(1)
Si(4)–Si(6)–C(49)	113.7(6)	Si(4)–Si(6)–C(67)	129.7(4)
Si(5)–Si(6)–C(49)	112.8(4)	Si(5)–Si(6)–C(67)	125.0(5)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for *cis,trans*-**1**

	Bond lengths		
Si(1)–Si(2)	2.404(5)	Si(1)–Si(3)	2.377(8)
Si(1)–C(1)	1.89(1)	Si(1)–C(19)	1.85(2)
Si(2)–Si(3)	2.376(5)	Si(2)–C(7)	1.86(2)
Si(2)–C(25)	1.92(1)	Si(3)–C(13)	1.81(2)
Si(3)–C(31)	1.90(2)	Si(4)–Si(5)	2.407(9)
Si(4)–Si(6)	2.387(5)	Si(4)–C(37)	1.84(2)
Si(4)–C(55)	1.93(1)	Si(5)–Si(6)	2.372(9)
Si(5)–C(43)	1.90(1)	Si(5)–C(61)	1.98(2)
Si(6)–C(49)	1.96(2)	Si(6)–C(67)	2.00(2)
	Bond angles		
Si(2)–Si(1)–Si(3)	60.0(3)	Si(2)–Si(1)–C(1)	113.6(7)
Si(2)–Si(1)–C(19)	129.6(8)	Si(3)–Si(1)–C(1)	114.2(6)
Si(3)–Si(1)–C(19)	129.3(8)	Si(1)–Si(2)–Si(3)	60.6(3)
Si(1)–Si(2)–C(7)	118.8(8)	Si(1)–Si(2)–C(25)	129.8(7)
Si(3)–Si(2)–C(7)	119.8(8)	Si(3)–Si(2)–C(25)	122.7(6)
Si(1)–Si(3)–Si(2)	59.4(3)	Si(1)–Si(3)–C(13)	116.3(8)
Si(1)–Si(3)–C(31)	124.3(7)	Si(2)–Si(3)–C(13)	114.7(9)
Si(2)–Si(3)–C(31)	125.4(8)	Si(5)–Si(4)–Si(6)	59.7(3)
Si(5)–Si(4)–C(37)	110.0(6)	Si(5)–Si(4)–C(55)	124.5(8)
Si(6)–Si(4)–C(37)	117.7(7)	Si(6)–Si(4)–C(55)	129.1(6)
Si(4)–Si(5)–Si(6)	59.1(3)	Si(4)–Si(5)–C(43)	116.1(7)
Si(4)–Si(5)–C(61)	128.6(7)	Si(6)–Si(5)–C(43)	114.6(7)
Si(6)–Si(5)–C(61)	121.9(7)	Si(4)–Si(6)–Si(5)	61.2(3)
Si(4)–Si(6)–C(49)	118.8(6)	Si(4)–Si(6)–C(67)	128.4(6)
Si(5)–Si(6)–C(49)	113.4(6)	Si(5)–Si(6)–C(67)	122.2(6)



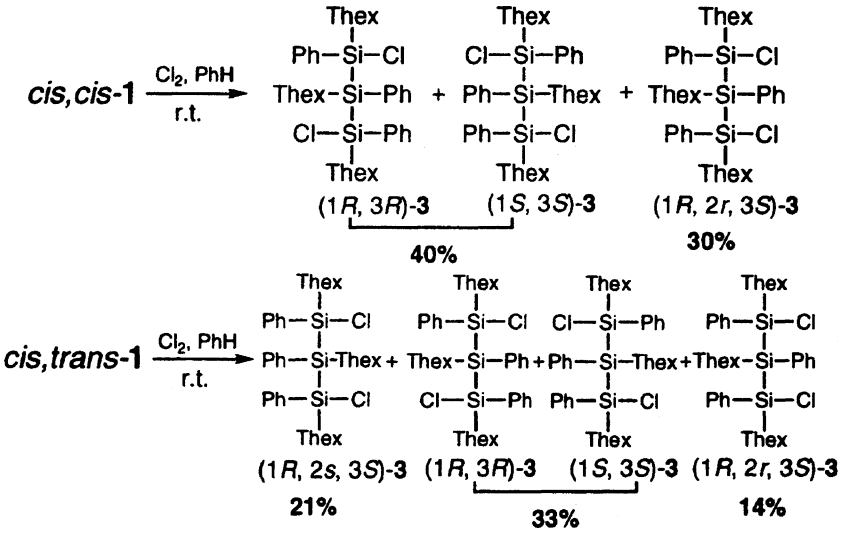
Scheme 2.

cis,cis-**1** and the first and the third fractions from *cis,trans*-**1** showed two peaks in ^{29}Si NMR (−11.07, 19.48 ppm and −8.95, 19.46 ppm). As the spectroscopic methods cannot determine the structures of these two diastereomers, we performed the X-ray crystallography of the second fraction from *cis,cis*-**1**. The result unequivocally showed the structure was (1*R*,2*r*,3*S*) form. From *cis,cis*-**1**, (1*R*,3*S*)/(1*S*,3*S*)-**3** (40% yield) and (1*R*,2*r*,3*S*)-**3** (30% yield) were obtained, and from *cis,trans*-**1**, (1*R*,2*s*,3*S*)-**3** (21%), (1*R*,3*R*/(1*S*,3*S*)-**3** (33%), and (1*R*,2*r*,3*S*)-**3** (14% yield) were given (Scheme 3).

Structures of the Dihalotrisilanes 2 and 3. Crystals of (1*R*,3*R*)/(1*S*,3*S*)-**2**, (1*R*,2*r*,3*S*)-**2**, and (1*R*,2*r*,3*S*)-**3** for X-ray analysis were obtained by slow evaporation of their saturated solution at room temperature. ORTEP drawings are shown in Fig. 4. Crystallographic data, selected bond lengths, and bond angles are give in Tables 4, 5, 6, and 7. (1*R*,2*r*,3*S*)-**2** and (1*R*,2*r*,3*S*)-**3** crystallize in the same space group and have similar unit cells. The unit cell of (1*R*,3*R*)/(1*S*,3*S*)-**2** contains two molecules of (1*R*,3*R*)-**2** and (1*S*,3*S*)-**2**. Average Si–Si bond lengths were 2.453 Å for (1*R*,3*R*)/(1*S*,3*S*)-**2**, 2.457 Å for (1*R*,2*r*,3*S*)-**2**, and 2.446 Å for (1*R*,2*r*,3*S*)-**3**. Interestingly, all three compounds possess much longer Si–Si bonds than those of cyclotrisilanes **1**. Because of the difference of the size of halogen atoms, bond lengths of (1*R*,3*R*)/(1*S*,3*S*)-**2** and (1*R*,2*r*,3*S*)-**2** are slightly longer than those of (1*R*,2*r*,3*S*)-**3**. And the Si–Si–Si bond angles of (1*R*,3*R*)/(1*S*,3*S*)-**2** (115.15(7)°) and (1*R*,2*r*,3*S*)-**2** (110.0(1)°) are slightly larger than that of (1*R*,2*r*,3*S*)-**3** (109.5(1)°) (Table 8).

(1*R*,3*R*)/(1*S*,3*S*)-**2**, (1*R*,2*r*,3*S*)-**2**, and all the isomers of dichlorosilane **3** are stable in the air. However, (1*R*,2*s*,3*S*)-**2** is not stable in solution and slowly hydrolyzed to give *cis,cis*-1,2,3-triphenyl-1,2,3-tris(1,1,2-trimethylpropyl)-4-oxacyclotetrasilane.[8]

Plausible Mechanism of Ring Cleavage Reaction of 1. With Bromine. As aforementioned, when *cis,cis*-**1** was allowed to react with bromine, the only product that was obtained is (1*R*,3*R*)/(1*S*,3*S*)-**2**. The result indicates that the cleavage takes place in a highly stereoselective way. To account for the reaction, it is possible to propose an ionic mechanism as shown in Scheme 4. The first step involves the



Scheme 3.

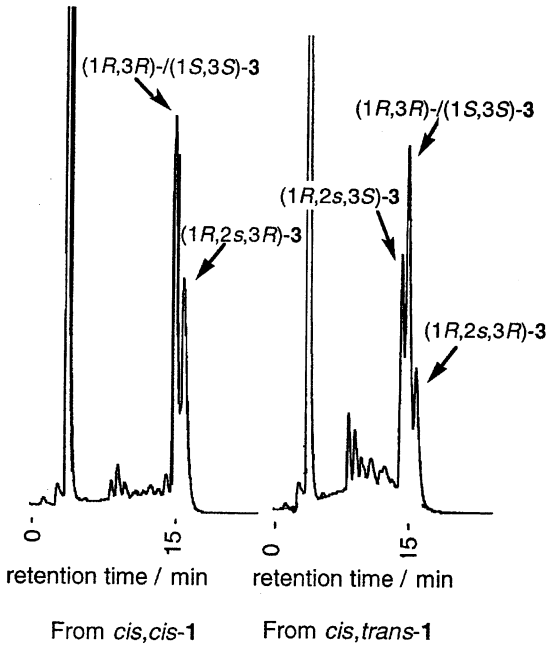
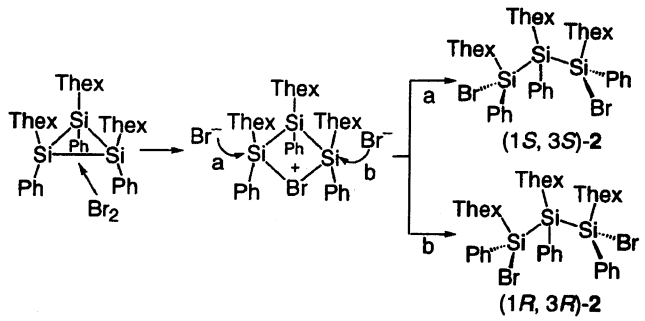


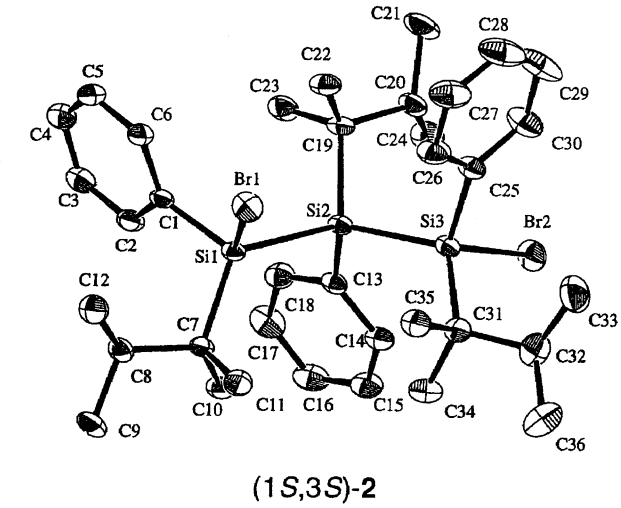
Fig. 3. HPLC chromatogram of **3** (7-ODS-H, MeOH/THF = 9/1).

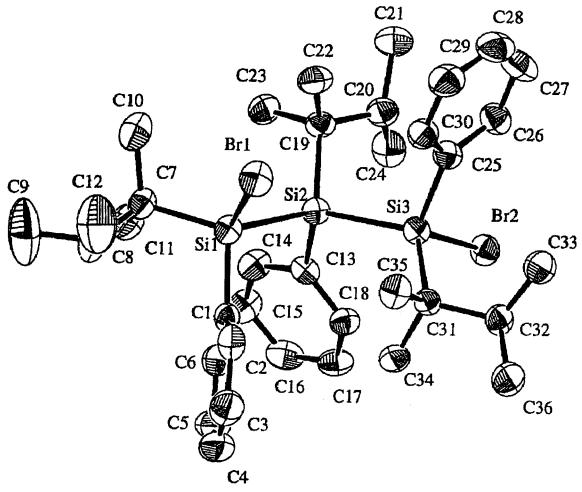


Scheme 4.

electrophilic attack to the Si–Si bond in *cis,cis*-**1** by bromine to form bromonium ion intermediate. In the next step, a nucleophilic attack by Br^- with inversion of configuration affords (1*R*,3*R*)-**2** and (1*S*,3*S*)-**2**. As a result, the overall configuration was retention–inversion (*anti*-addition). This explanation can be also applied to the case of *cis,trans*-**1** as shown in (Scheme 5). Since there are two different kinds of bonds in *cis,trans*-**1**, two pathways (a and b) are possible for the first step. From these intermediates, the attack of Br^- gave (1*R*,3*R*)/(1*S*,3*S*)-**2**, (1*R*,2*r*,3*S*)-**2**, and (1*R*,2*s*,3*R*)-**2**. In the bromination of olefin, bromonium ion intermediates are of recent interest in the calculation studies, and several reports have appeared.[9] An addition product (halonium ion) consisting of halogen and Si–Si bond was proposed by Kumada and co-workers,[5] but in our work, this type of ion was suggested experimentally.

With Chlorine. The treatment of *cis,cis*-**1** with Cl_2 gave not only (1*R*,3*R*)/(1*S*,3*S*)-**3** as an *anti*-addition product but also (1*R*,2*r*,3*S*)-**3** as a *syn*-addition product; therefore this case seems to be different from that of bromination. The proposed mechanism is shown in Scheme 6. When the reaction proceeded as in the case of bromination, an *anti*-





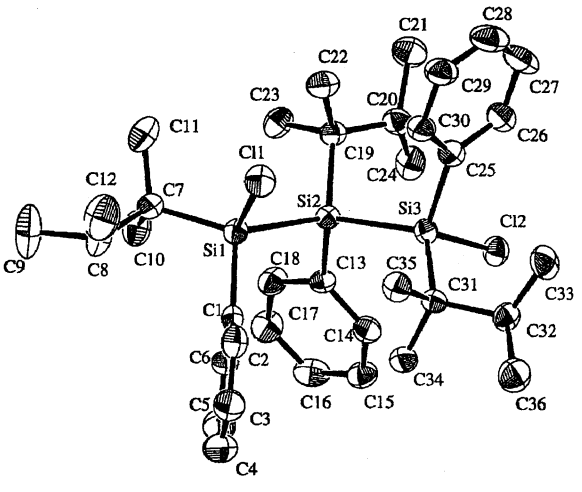
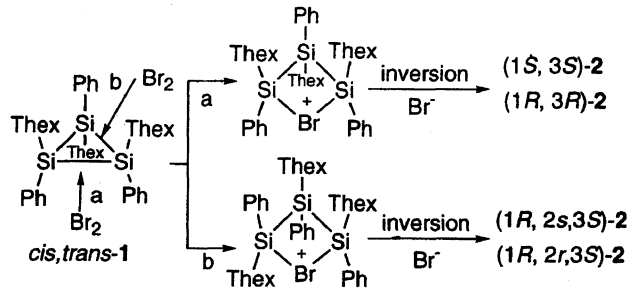


Fig. 4. ORTEP drawings of (1*R*,3*R*)/(1*S*,3*S*)-**2**, (1*R*,2*r*,3*S*)-**2**, and (1*R*,2*r*,3*S*)-**2**. Thermal ellipsoids are drawn at the 30% probability level.



Scheme 5.

addition product (1*R*,3*R*)/(1*S*,3*S*)-**3** is given (path a and b). In addition, the generation of silyl cation intermediates[10] could explain the formation of a *syn*-addition product (path c).

If the chloronium ion intermediate was not involved, the theoretical production ratio of (1*R*,3*R*)/(1*S*,3*S*)-**3** and (1*R*,2*r*,3*S*)-**3** is calculated to be 1 : 1. However, the observed product ration was 40 : 30; thus a certain pathway which proceeded via chloronium ion intermediate (path a and b) is thought to be included. This assumption can be also applied to *cis,trans*-**1** as in the case of the bromination.

In summary, ring cleavage reaction of **1** proceeded via ionic reaction conditions, and gave certain stereoisomers selectively. Reaction mechanisms were proposed and postulation of a cyclic bromonium ion explains the results well.

Experimental

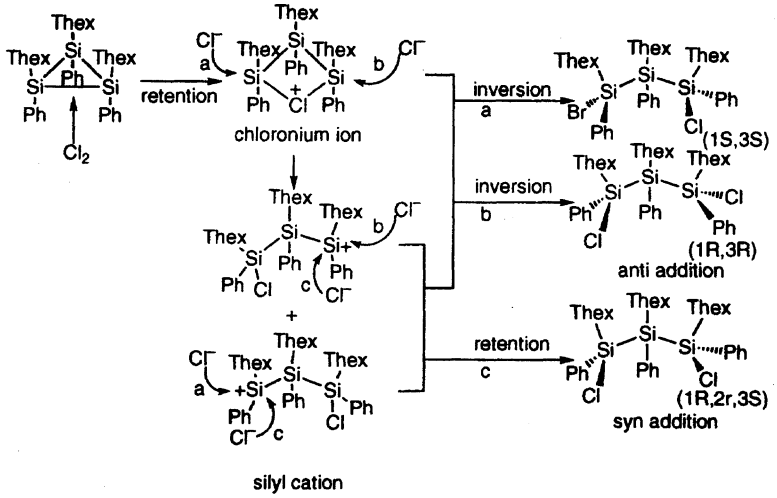
NMR spectra were recorded on a JEOL Model α-500 (^{1}H, 500.0 MHz; ^{13}C, 125.7 MHz; ^{29}Si, 99.3 MHz). Mass spectrometry was performed by JEOL JMS-D300. Infrared spectra were measured with a JASCO A-102 spectrometer. Analytical HPLC was done by JASCO 875UV/880PU and UV-970/880PU with Chemco 4.6 mm×250 mm 5-ODS-H column. Preparative (recycle-type) HPLC was carried out using JAI LC-908 and LC-09 with Chemco 20 mm×250 mm 7-ODS-H columns. All reactions were carried out under an atmosphere of argon or nitrogen.

Preparation of Dichlorophenyl(1,1,2-trimethylpropyl)silane: A solution of bromobenzene (17.3 g, 0.110 mol) in ether (20 ml) was added dropwise to a mixture of finely cut lithium lumps (1.8 g, 0.26 mol) in ether (15 ml). The mixture was stirred for next 2 h. To a solution of ThexSiCl$_3$[11] (18.8 g, 0.0858 mol) in ether (80 ml), the solution of PhLi was added dropwise. After 12 h of stirring at room temperature, the solvent was removed by evaporation. Then hexane was added to the residue and the salt was removed by filtration. The filtrate was concentrated and distilled under reduced pressure to give ThexPhSiCl$_2$ (10.6 g, 47%). ThexPhSiCl$_2$: Colorless liquid, bp 85 °C/3 mmHg (1 mmHg = 133.322 Pa); ^{1}H NMR (acetone-d_6) δ = 0.90 (d, J = 6.7 Hz, 6H), 1.10 (s, 6H), 1.86 (sept, J = 6.7 Hz, 1H), 7.52 (t, J = 7.0 Hz, 2H), 7.57 (t, J = 7.0 Hz, 1H), 7.80 (d, J = 7.0 Hz, 2H); ^{13}C NMR (acetone-d_6) δ = 18.83, 20.15, 30.98, 34.17, 129.13, 132.33, 133.04, 135.15; ^{29}Si NMR (acetone-d_6) δ = 23.03; MS (70 eV) m/z 260 (M$^+$; 1 %), 175 (33 %), 85 (100 %); IR (neat) 3080, 3060, 2970, 2880, 1465, 1430, 1390, 1380, 1365, 1110, 765, 735, 700, 690 cm^{-1}.

Preparation of 1,2,3-Triphenyl-1,2,3-tris(1,1,2-trimethylpropyl)cyclotrisilane, (ThexPhSi)$_3$ (1): To a solution of lithium naphthalenide prepared from naphthalene (3.86 g, 30.1 mmol) and finely cut lithium lumps (0.21 g, 30 mmol) in THF (25 ml), a solution of ThexPhSiCl$_2$ (3.40 g, 13.0 mmol) in THF was added dropwise around −65 °C. The mixture was allowed to warm to room temperature. Excess lithium naphthalenide was quenched by exposing to air. The solvent was removed by evaporation. Hexane was added to the residue and the salt was removed by passing the mixture through a short silica-gel column. Hexane was evaporated and naphthalene was removed by sublimation. A pale-yellow solid was obtained as an isomeric mixture of **1**. Both isomers were isolated by silica-gel chromatography (hexane/benzene = 9/1) and recrystallized from acetone. The yields of *cis,cis*-**1** and *cis,trans*-**1** were 0.46 g (19%) and 1.28 g (52%), respectively.

cis,cis-**1**: Pale-yellow prisms, mp 179.0—181.5 °C; ^{1}H NMR (CD_2Cl_2) δ = 1.01 (d, J = 6.7 Hz, 18H), 1.43 (s, 18H), 1.51 (sept, J = 6.7 Hz, 3H), 6.98 (t, J = 7.3 Hz, 6H), 7.07 (t, J = 7.3 Hz, 3H), 7.44 (d, J = 7.3 Hz, 6H); ^{13}C NMR (CD_2Cl_2) δ = 17.97, 24.33, 29.81, 34.06, 126.28, 127.42, 135.18, 137.73; ^{29}Si NMR (99.25 MHz, CD_2Cl_2) δ = −34.81; MS (30 eV) m/z 570 (M$^+$; 2 %), 486 (14%), 402 (53%), 318 (100%); UV/vis (λ_{max} in hexane) 333 (ε 457), 362 nm (408); IR (KBr) 3040, 2940, 2890, 2850, 1455, 1420, 1385, 1370, 1355, 725, 690 cm^{-1}. Anal. Calcd for $C_{36}H_{54}Si_3$: C, 75.72; H, 9.53%. Found: C, 75.32; H, 9.59%.

cis,trans-**1**: Colorless prisms, mp 177.0—179.0 °C; ^{1}H NMR (CD_2Cl_2) δ = 0.82 (s, 6H), 0.96 (d, J = 6.7 Hz, 6H), 0.97 (d,



Scheme 6.

Table 4. Summary of Crystal Data, Data Collection, and Refinement of (1*R*,3*R*)/(1*S*,3*S*)-**2**, (1*R*,2*r*,3*S*)-**2**, and (1*R*,2*r*,3*S*)-**3**

	(1*R*,3*R*)/(1*S*,3*S*)-**2**	(1*R*,2*r*,3*S*)−**2**	(1*R*,2*r*,3*S*)-**3**
		Crystal data	
Formula	$C_{36}H_{54}Br_2Si_3$	$C_{36}H_{54}Br_2Si_3+1/2C_6H_{14}$	$C_{36}H_{54}Cl_2Si_3+1/2CH_3OH$
Mol wt	730.89	773.98	665.02
Cryst. descript	Colorless prisms	Colorless prisms	Colorless prisms
Cryst. size/mm	0.4×0.2×0.2	0.3×0.3×0.2	0.4×0.1×0.1
Cryst. syst.	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	9.890(4)	13.763(4)	13.551(2)
b/Å	16.433(2)	14.798(2)	14.689(2)
c/Å	23.214(3)	10.896(1)	10.8231(6)
α/deg		106.319(9)	105.713(6)
β/deg	95.89(2)	98.76(1)	98.584(8)
γ/deg		68.91(2)	69.179(8)
V/Å^3	3752(1)	1983.9(8)	1935.1(4)
Z	4	2	2
d_{calc}/g cm^{-3}	1.293	1.296	1.141
		Data collection	
Diffractometer	Rigaku AFC7S	Rigaku AFC7S	Rigaku AFC7S
Radiation (λ, Å)	Cu $K\alpha$ (1.5418)	Cu $K\alpha$ (1.5418)	Cu $K\alpha$ (1.5418)
Monochromator	Graphite	Graphite	Graphite
μ/cm^{-1}	38.16	36.37	25.75
2θ range/deg	4—120.1	4—120.1	4—120.1
Scan type	ω–2θ	ω–2θ	ω–2θ
Scan width/deg	1.68+0.30tan θ	0.84+0.30tan θ	0.73+0.30tan θ
No. of reflns measd	6353	6168	6031
No. of ind reflns	5818	5882	5748
No. of obsd reflns ($\|F_o\| \geq 3\sigma(F_o)$)	4260	3912	3717
		Refinement	
R	0.040	0.066	0.073
R_w	0.038	0.078	0.087
Weighting scheme	$w=1/\sigma^2(F_o)$	$w=1/\sigma^2(F_o)$	$w=1/\sigma^2(F_o)$
S	1.98	2.95	3.20
$(\Delta/\sigma)_{max}$	0.10	0.02	0.03
$(\Delta\rho)_{max}$/eÅ^{-3}	0.32	1.01	0.65
$(\Delta\rho)_{min}$/eÅ^{-3}	−0.36	−0.78	−1.30
No. of params	563	371	371

J = 6.7 Hz, 6H), 1.00 (d, *J* = 7.0 Hz, 6H), 1.11 (overlap, s, 12H), 1.29—1.40 (overlap, m, 3H), 7.18—7.26 (overlap, m, 6H), 7.36—7.42 (overlap, m, 3H), 7.83 (d, *J* = 8.0 Hz, 4H), 8.03 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (CD_2Cl_2) δ = 18.03, 18.17, 18.19, 22.93, 23.45, 23.66, 29.67, 29.81, 33.75, 33.82, 126.47, 126.70, 127.98, 128.45, 133.74, 134.36, 138.42, 138.80; ^{29}Si NMR (CD_2Cl_2) δ = −41.25, −35.98; MS (EI, 30 eV) *m/z* 570 (M^+; 2 %), 486 (14%), 402 (48%), 318 (100%); UV/vis (λ_{max} in hexane) 241 (ε 30900), 328 (610), 357 nm (560); IR (KBr) 3040, 2940, 2880, 2850, 1455, 1420, 1380, 1365, 1360, 725, 695 cm^{-1}. Anal. Calcd for $C_{36}H_{54}Si_3 \cdot 0.5C_3H_6O$: C, 74.07; H, 9.45%. Found: C, 74.78; H, 9.44%. HRMS (30 eV) Calcd for $C_{36}H_{54}Si_3$: M, 570.3533. Found: *m/z* 570.3528.

Reaction of Cyclotrisilane 1 with Br_2: (From *cis,cis*-**1**) A 0.1 M (1 M = 1 mol dm^{-3}) benzene solution of Br_2 (0.6 ml) was added dropwise to a solution of *cis,cis*-**1** (60.9 mg, 107 μmol) in benzene (4 ml) until the solution was colored at room temperature. The reaction mixture was passed through a short silica-gel column and the solvent was removed by evaporation. Only (1*R*,3*R*)/(1*S*,3*S*)-**2** was isolated by recycle-type preparative HPLC (ODS, MeOH/THF = 9/1).

(From *cis,trans*-**1**) To *cis,trans*-**1** (74.4 mg, 130 μmol) in 5 ml of benzene, 0.1 M benzene solution of bromine (1.5 ml) was added at room temperature until the red color remained. After the work-up as described above, (1*R*,2*s*,3*S*)-**2**, (1*R*,3*R*)/(1*S*,3*S*)-**2** (racemate), and (1*R*,2*r*,3*S*)-**2** were isolated by recycle-type preparative HPLC (ODS, MeOH/THF = 9/1). The yields of (1*R*,2*s*,3*S*)-**2**, (1*R*,3*R*)/(1*S*,3*S*)-**2**, and (1*R*,2*r*,3*S*)-**2** were 12.2 mg (13%), 41.7 mg (44%), and 30.0 mg (31%), respectively.

(1*R*,2*s*,3*S*)-**2**: Colorless prisms, mp 109.6—111.0 °C; ^{1}H NMR (CD_2Cl_2) δ = 0.54 (d, *J* = 6.7 Hz, 6H), 0.61 (d, *J* = 6.7 Hz, 6H), 0.64 (d, *J* = 6.7 Hz, 6H), 1.00 (s, 6H), 1.01 (s, 6H), 1.07 (s, 6H), 1.94 (sept, *J* = 6.7 Hz, 2H), 2.42 (sept, *J* = 6.7 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.34—7.40 (overlap, m, 6H), 7.93 (d, *J* = 7.7 Hz, 4H), 7.98 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (CD_2Cl_2) δ = 17.55, 17.73, 18.36, 21.88, 22.34, 23.56, 30.03, 32.13, 34.00, 36.48, 126.60, 127.17, 128.41, 129.05, 135.05, 136.08, 137.32, 137.40; ^{29}Si NMR (CD_2Cl_2) δ = −10.68, 19.82; MS (70 eV) *m/z*

Table 5. Selected Bond Lengths (Å) and Angles (deg) for (1*R*,3*R*)/(1*S*,3*S*)-**2**

Bond lengths			
Br(1)–Si(1)	2.268(1)	Br(2)–Si(3)	2.264(1)
Si(1)–Si(2)	2.454(2)	Si(1)–C(1)	1.884(5)
Si(1)–C(7)	1.945(4)	Si(2)–Si(3)	2.452(2)
Si(2)–C(13)	1.911(5)	Si(2)–C(19)	1.970(5)
Si(3)–C(25)	1.876(5)	Si(3)–C(31)	1.928(5)
Bond angles			
Br(1)–Si(1)–Si(2)	106.08(6)	Br(1)–Si(1)–C(1)	105.4(2)
Br(1)–Si(1)–C(7)	107.5(2)	Si(2)–Si(1)–C(1)	107.0(1)
Si(2)–Si(1)–C(7)	121.0(2)	C(1)–Si(1)–C(7)	108.8(2)
Si(1)–Si(2)–Si(3)	115.15(7)	Si(1)–Si(2)–C(13)	102.8(1)
Si(1)–Si(2)–C(19)	109.4(2)	Si(3)–Si(2)–C(13)	110.9(2)
Si(3)–Si(2)–C(19)	106.8(2)	C(13)–Si(2)–C(19)	111.9(2)
Br(2)–Si(3)–Si(2)	104.90(6)	Br(2)–Si(3)–C(25)	105.4(2)
Br(2)–Si(3)–C(31)	104.0(2)	Si(2)–Si(3)–C(25)	109.8(2)
Si(2)–Si(3)–C(31)	120.0(2)		

Table 6. Selected Bond Lengths (Å) and Angles (deg) for (1*R*,2*r*,3*S*)-**2**

Bond lengths			
Br(1)–Si(1)	2.258(3)	Br(2)–Si(3)	2.269(3)
Si(1)–Si(2)	2.438(4)	Si(1)–C(1)	1.90(1)
Si(1)–C(7)	1.939(8)	Si(2)–Si(3)	2.475(3)
Si(2)–C(13)	1.893(8)	Si(2)–C(19)	1.952(10)
Si(3)–C(25)	1.89(1)	Si(3)–C(31)	1.916(9)
Bond angles			
Br(1)–Si(1)–Si(2)	104.4(1)	Br(1)–Si(1)–C(1)	107.1(3)
Br(1)–Si(1)–C(7)	105.3(3)	Si(2)–Si(1)–C(1)	107.3(3)
Si(2)–Si(1)–C(7)	124.3(3)	C(1)–Si(1)–C(7)	107.4(4)
Si(1)–Si(2)–Si(3)	110.0(1)	Si(1)–Si(2)–C(13)	105.4(3)
Si(1)–Si(2)–C(19)	114.1(3)	Si(3)–Si(2)–C(13)	110.1(3)
Si(3)–Si(2)–C(19)	106.1(3)	C(13)–Si(2)–C(19)	111.2(4)
Br(2)–Si(3)–Si(2)	102.9(1)	Br(2)–Si(3)–C(25)	104.5(3)
Br(2)–Si(3)–C(31)	103.2(3)	Si(2)–Si(3)–C(25)	110.9(3)
Si(2)–Si(3)–C(31)	120.9(3)		

645 ($M^+ - C_6H_{11}$; 1%), 561 (3%), 477 (18%), 377 (71%), 197 (76%), 69 (100%); IR (neat) 3060, 2960, 2920, 2880, 1465, 1425, 1390, 1380, 1365, 735, 700 cm^{-1}. Anal. Calcd for $C_{36}H_{54}Br_2Si_3$: C, 59.16; H, 7.45; Br, 21.86%. Found: C, 58.74; H, 7.28; Br, 21.88%.

(1*R*,3*R*)/(1*S*,3*S*)-**2**: Colorless prisms, mp 141.5—142.5 °C; ^{1}H NMR (CD_2Cl_2) δ = 0.40 (d, J = 6.7 Hz, 3H), 0.49 (d, J = 6.7 Hz, 3H), 0.52 (d, J = 6.7 Hz, 3H), 0.56 (d, J = 6.7 Hz, 3H), 0.65 (d, J = 6.7 Hz, 3H), 0.72 (d, J = 6.7 Hz, 3H), 0.72 (s, 3H), 0.87 (s, 3H), 0.88 (s, 3H), 1.12 (s, 3H), 1.29 (s, 3H), 1.31 (s, 3H), 1.95—2.04 (overlap, m, 2H), 2.29 (sept, J = 6.7 Hz, 1H), 7.25—7.42 (overlap, m, 9H), 7.78 (d, J = 7.3 Hz, 2H), 7.95 (d, J = 6.4 Hz, 2H), 8.11 (d, J = 6.7 Hz, 2H); ^{13}C NMR (CD_2Cl_2) δ = 16.99, 17.04, 17.20, 17.81, 18.21, 19.01, 20.63, 22.02, 22.15, 22.49, 23.89, 24.39, 29.94, 30.32, 32.31, 33.95, 34.07, 35.37, 126.68, 127.02, 127.39, 128.51, 128.94, 129.19, 134.81, 135.07, 135.89, 136.01, 137.16, 137.55; ^{29}Si NMR (CD_2Cl_2) δ = −14.37, 18.52, 22.33; MS (70 eV) *m/z* 645 ($M^+ - C_6H_{11}$; 1%), 561 (4%), 477 (19%), 377 (63%), 197 (75%), 69 (100%); IR (KBr) 3090, 3000, 2945, 2900, 1465, 1435, 1400, 1385, 1370, 740, 705 cm^{-1}. Anal. Calcd for $C_{36}H_{54}Br_2Si_3$: C, 59.16; H, 7.45; Br, 21.86%. Found: C, 59.33; H, 7.52; Br, 21.74%.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for (1*R*,2*r*,3*S*)-**3**

Bond lengths			
Cl(1)–Si(1)	2.095(3)	Cl(2)–Si(3)	2.094(3)
Si(1)–Si(2)	2.431(3)	Si(1)–C(1)	1.877(9)
Si(1)–C(7)	1.916(8)	Si(2)–Si(3)	2.460(3)
Si(2)–C(13)	1.900(7)	Si(2)–C(19)	1.941(9)
Si(3)–C(25)	1.881(9)	Si(3)–C(31)	1.915(8)
Bond angles			
Cl(1)–Si(1)–Si(2)	103.5(1)	Cl(1)–Si(1)–C(1)	107.0(3)
Cl(1)–Si(1)–C(7)	105.7(3)	Si(2)–Si(1)–C(1)	107.7(2)
Si(2)–Si(1)–C(7)	124.7(3)	C(1)–Si(1)–C(7)	107.2(4)
Si(1)–Si(2)–Si(3)	109.5(1)	Si(1)–Si(2)–C(13)	106.6(3)
Si(1)–Si(2)–C(19)	114.0(2)	Si(3)–Si(2)–C(13)	109.9(2)
Si(3)–Si(2)–C(19)	106.1(2)	C(13)–Si(2)–C(19)	110.7(3)
Cl(2)–Si(3)–Si(2)	103.53(10)	Cl(2)–Si(3)–C(25)	104.3(3)
Cl(2)–Si(3)–C(31)	103.4(2)	Si(2)–Si(3)–C(25)	110.3(2)
Si(2)–Si(3)–C(31)	120.3(3)		

Table 8. Average Bond Lengths and Angles (1*R*,3*R*)/(1*S*,3*S*)-**2**, (1*R*,2*r*,3*S*)-**2**, and (1*R*,2*r*,3*S*)-**3**

Compound	*d*(Si–Si)/Å	*d*(Si–C)/Å	Si–Si–Si (deg)
(1*R*,3*R*)-/(1*S*,3*S*)-**2**	av. 2.453	av. 1.948 (Thex) av. 1.890 (Ph)	111.15(7)
(1*R*,2*r*,3*S*)-**2**	av. 2.457	av. 1.936 (Thex) av. 1.89 (Ph)	110.0(1)
(1*R*,2*r*,3*S*)-**3**	av. 2.446	av. 1.924 (Thex) av. 1.886 (Ph)	109.5(1)

(1*R*,2*r*,3*S*)-**2**: Colorless crystals, mp 149.0—149.8 °C; ^{1}H NMR (CD_2Cl_2) δ = 0.52 (d, J = 6.7 Hz, 6H), 0.54 (d, J = 6.7 Hz, 6H), 0.63 (d, J = 6.7 Hz, 6H), 0.85 (s, 6H), 1.11 (s, 6H), 1.13 (s, 6H), 1.92 (sept, J = 6.7 Hz, 2H), 2.31 (sept, J = 6.7 Hz, 1H), 7.21 (t, J = 7.4 Hz, 4H), 7.31 (t, J = 7.4 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.44 (t, J = 7.5 Hz, 1H), 7.65 (d, J = 7.4 Hz, 4H), 8.11 (d, J = 7.5 Hz, 2H); ^{13}C NMR (CD_2Cl_2) δ = 17.82, 18.09, 18.24, 21.14, 22.62, 23.94, 30.57, 32.20, 33.79, 34.28, 126.83, 126.97, 128.76, 129.04, 134.31, 136.26, 136.69, 138.09; ^{29}Si NMR (CD_2Cl_2) δ = −8.67, 19.87; MS (70 eV) *m/z* 645 ($M^+ - C_6H_{11}$; 1%), 561 (6%), 477 (20%), 377 (70%), 197 (77%), 69 (100%); IR (KBr) 3060, 2970, 2900, 2880, 1465, 1430, 1395, 1380, 1360, 735, 700 cm^{-1}. Anal. Calcd for $C_{36}H_{54}Br_2Si_3$: C, 59.16; H, 7.45; Br, 21.86%. Found: C, 57.95; H, 7.38; Br, 21.78%. HRMS (70 eV) Calcd for $C_{30}H_{41}Si_3Br_2$: (M^+ − Thex), 643.0873. Found: *m/z* 643.0844.

Reaction of Cyclotrisilane 1 with Cl_2: (From *cis,cis*-**1**) A saturated benzene solution of Cl_2 (0.4 ml) was added dropwise to a solution of *cis,cis*-**1** (47.7 mg, 83.5 μmol) in benzene (4 ml) until the solution was colored at room temperature. The reaction mixture was passed through a short silica-gel column and the solvent was removed by evaporation. (1*R*,3*R*)/(1*S*,3*S*)-**3** (racemate) and (1*R*, 2*r*,3*S*)-**3** was isolated by recycle-type preparative HPLC (ODS, MeOH/THF = 9/1). The yields of (1*R*,3*R*)/(1*S*,3*S*)-**3** and (1*R*,2*r*, 3*S*)-**3** were 21.5 mg (40%) and 16.1 mg (30%).

(From *cis,trans*-**1**) By a reaction analogous to that described for *cis,cis*-**1**, from *cis,trans*-**1** (99.5 mg, 174 μmol), (1*R*,2*s*,3*S*)-**3**, (1*R*,3*R*)/(1*S*,3*S*)-**3** (racemate), and (1*R*, 2*r*,3*S*)-**3** were isolated by

recycle-type preparative HPLC (ODS, MeOH/THF = 9/1). The yields of (1*R*,2*s*,3*S*)-**3**, (1*R*,3*R*)/(1*S*,3*S*)-**3**, and (1*R*,2*r*,3*S*)-**3** were 23.1 mg (21%), 37.3 mg (33%), and 15.6 mg (14%), respectively.

(1*R*,2*s*,3*S*)-**3**: Colorless prisms, mp 100.0—101.3 °C; ^{1}H NMR (CD_2Cl_2) δ = 0.58 (d, J = 6.7 Hz, 6H), 0.60 (d, J = 6.7 Hz, 6H), 0.65 (d, J = 6.7 Hz, 6H), 0.95 (s, 6H), 0.97 (s, 6H), 1.02 (s, 6H), 1.91 (sept, J = 6.7 Hz, 2H), 2.32 (sept, J = 6.7 Hz, 1H), 7.24—7.40 (overlap, m, 9H), 7.81 (d, J = 8.0 Hz, 4H), 7.95 (d, J = 8.0 Hz, 2H); ^{13}C NMR (CD_2Cl_2) δ = 17.39, 17.66, 18.32, 21.32, 21.52, 23.34, 30.27, 31.29, 33.51, 36.63, 126.67, 127.06, 128.30, 128.93, 135.33, 136.08, 136.89, 137.22; ^{29}Si NMR (CD_2Cl_2) δ = −11.07, 19.48; MS (70 eV) *m/z* 640 (M^+; 1%), 555 (1%), 471 (7%), 387 (27%), 331 (100%); IR (KBr) 3090, 3000, 2960, 2900, 1470, 1435, 1400, 1385, 1370, 740, 705 cm^{-1}. Anal. Calcd for $C_{36}H_{54}Cl_2Si_3$: C, 67.35; H, 8.48; Cl, 11.04%. Found: C, 67.58; H, 8.51; Cl, 11.14%.

(1*R*,3*R*)/(1*S*,3*S*)-**3**: Colorless crystals, mp 127.8—128.5 °C; ^{1}H NMR (CD_2Cl_2) δ = 0.46 (d, J = 6.7 Hz, 3H), 0.51 (d, J = 6.7 Hz, 3H), 0.56 (d, J = 6.7 Hz, 3H), 0.59 (d, J = 6.7 Hz, 3H), 0.65 (d, J = 6.7 Hz, 3H), 0.70 (d, J = 6.7 Hz, 3H), 0.76 (s, 3H), 0.87 (s, 3H), 0.94 (s, 3H), 1.07 (s, 3H), 1.16 (s, 3H), 1.18 (s, 3H), 1.90—1.98 (overlap, m, 2H), 2.22 (sept, J = 6.7 Hz, 1H), 7.24 (t, J = 7.7 Hz, 2H), 7.29—7.44 (overlap, m, 7H), 7.59 (d, J = 7.7 Hz, 2H), 7.87 (d, J = 6.7 Hz, 2H), 8.05 (d, J = 6.7 Hz, 2H); ^{13}C NMR (CD_2Cl_2) δ = 17.17, 17.20, 17.52, 17.67, 18.00, 18.46, 20.38, 21.70, 21.76, 22.53, 22.81, 23.33, 30.11, 30.45, 31.51, 33.49, 33.56, 35.83, 126.71, 126.98, 127.33, 128.40, 128.84, 129.10, 135.19, 135.22, 135.82, 136.15, 136.84, 137.44; ^{29}Si NMR; (CD_2Cl_2) δ = −14.08, 18.93, 21.39; MS (30 eV) *m/z* 640 (M^+; 1%), 555 (1%), 471 (8%), 387 (34%), 331 (100%); IR (KBr) 3100, 2900, 2950, 2920, 1470, 1435, 1400, 1390, 1370, 745, 710 cm^{-1}. Anal. Calcd for $C_{36}H_{54}Cl_2Si_3$: C, 67.35; H, 8.48; Cl, 11.04%. Found: C, 67.65; H, 8.46; Cl, 11.00%.

(1*R*,2*r*,3*S*)-**3**: Colorless prisms, mp 137.0—137.6 °C; ^{1}H NMR (CD_2Cl_2) δ = 0.51 (d, J = 6.7 Hz, 6H), 0.60 (d, J = 6.7 Hz, 6H), 0.62 (d, J = 6.7 Hz, 6H), 0.82 (s, 6H), 1.02 (s, 6H), 1.06 (s, 6H), 1.90 (sept, J = 6.7 Hz, 2H), 2.21 (sept, J = 6.7 Hz, 1H), 7.22 (t, J = 7.3 Hz, 4H), 7.31 (t, J = 7.3 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.43 (t, J = 7.5 Hz, 1H), 7.58 (d, J = 7.3 Hz, 4H), 8.08 (d, J = 7.5 Hz, 2H); ^{13}C NMR (CD_2CL_2) δ = 17.85, 17.86, 18.05, 20.63, 21.65, 23.54, 30.58, 31.26, 33.42, 34.55, 126.92, 126.95, 128.66, 128.96, 135.45, 135.55, 136.55, 137.79; ^{29}Si NMR CD_2Cl_2) δ = −8.95, 19.46; MS (30 eV) *m/z* 640 (M^+; 1%), 555 (3%), 471 (11%), 387 (40%), 331 (100%); IR (KBr) 3050, 2960, 2900, 2880, 1460, 1425, 1390, 1380, 1360, 735, 700 cm^{-1}. Anal. Calcd for $C_{36}H_{54}Cl_2Si_3 \cdot 0.5CH_4O$: C, 66.63; H, 8.57; Cl, 10.77%. Found: C, 66.67; H, 8.45; Cl, 10.97%.

X-Ray Crystallography of *cis,cis*-1: The pale yellow crystals of *cis,cis*-**1** were obtained by slow evaporation of the solvent from the acetone solution. The intensities of three representative reflection were measured after every 150 reflections. A polynomial correction factor was applied to the data to account for this phenomenon. An empirical absorption correction was applied. The data were collected for Lorentz and polarization effects. A correction for secondary extinction was applied. The structure was solved by SIR88[12] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were carried out using the teXsan crystallographic software package.[13]

X-Ray Crystallography of *cis,trans*-1: The colorless crystals of *cis,trans*-**1** were obtained by slow evaporation of the solvent from the acetone solution. The intensities of three representative reflections were measured after every 150 reflections. A polynomial correction factor was applied to the data to account for this phenomenon. An empirical absorption correction was applied. The data were collected for Lorentz and polarization effects. A correction for secondary extinction was applied. The structure was solved by SIR88[12] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were carried out using the teXsan crystallographic software package.[13]

X-Ray Crystallography of (1*R*,3*R*)/(1*S*,3*S*)-2: The colorless crystals of (1*R*,3*R*)/(1*S*,3*S*)-**2** were obtained by slow evaporation of the solvent from the ethanol solution. The intensities of three representative reflection were measured after every 150 reflections. A polynomial correction factor was applied to the data to account for this phenomenon. An empirical absorption correction was applied. The data were collected for Lorentz and polarization effects. A correction for secondary extinction was applied. The structure was solved by SAPI91[14] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were included in fixed positions. All calculations were carried out using the teXsan crystallographic software package.[13]

X-Ray Crystallography of (1*R*,2*r*,3*S*)-2: The colorless crystals of (1*R*,2*r*,3*S*)-**2** were obtained by slow evaporation of the solvent from the ethanol/hexane solution. The intensities of three representative reflections were measured after every 150 reflections. A polynomial correction factor was applied to the data to account for this phenomenon. An empirical absorption correction was applied. The data were collected for Lorentz and polarization effects. A correction for secondary extinction was applied. The structure was solved by SIR88[12] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were carried out using the teXsan crystallographic software package.[12]

X-Ray Crystallography of (1*R*,2*r*,3*S*)-3: The colorless crystals of (1*R*,2*r*,3*S*)-**3** were obtained by slow evaporation of the solvent from the ethanol/hexane solution. The intensities of three representative reflections were measured after every 150 reflections. A polynomial correction factor was applied to the data to account for this phenomenon. An empirical absorption correction was applied. The data were collected for Lorentz and polarization effects. A correction for secondary extinction was applied. The structure was solved by SAPI91[14] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were carried out using the teXsan crystallographic software package.[13]

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