Triisopropylcyclotrisiloxanetriol: An Unprecedented Cyclic Siloxanetriol with Relatively Small Substituents

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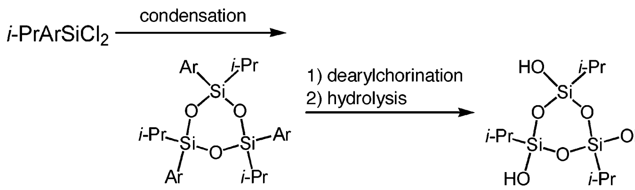
cis,trans-1,3,5-Trihydroxy-1,3,5-triisopropylcyclotrisiloxane was prepared as the first example of a cyclotrisiloxanetriol stabilized by relatively small substituents. A new synthetic pathway including dearylchlorination and subsequent hydrolysis of each stereoisomer of the cyclotrisiloxanes $[Ar(i\text{-}Pr)SiO]_3$ (Ar = Ph, *o*-$CH_3C_6H_4$) led to exclusive formation of *cis,-trans*-cyclotrisiloxanetriol in good yield.

Polyhydroxycyclooligosiloxanes have received much attention in recent years because of their potential applications as precursors for silsesquioxanes. During the course of our investigation on the construction of silsesquioxanes with well-defined structures, we have found the cyclotetrasiloxane $[i\text{-}PrSi(OH)O]_4$ to be a versatile precursor of cage silsesquioxanes,[1] laddersiloxanes,[2] and nanosize aggregates.[3] These earlier results prompted us to develop a convenient method for the synthesis of its smaller analogue, the cyclotrisiloxanetriol $[i\text{-}PrSi(OH)O]_3$. Because of their ring strain and the high reactivity of their hydroxy groups, cyclotrisiloxanetriols have been regarded as labile compounds, and thus the introduction of bulky substituents on silicon atoms may be required to isolate these compounds as stable sila-functional cyclotrisiloxanes. Until now, only a few reports have appeared concerning the synthesis of cyclotrisiloxanetriols. In 1996, Roesky and co-workers isolated the cyclotrisiloxanetriol $[Ar(Me_3Si)NSi(OH)O]_3$ (cis,trans form, Ar = 2,6-dimethylphenyl), taking advantage of kinetic stabilization by the bulky $Ar(Me_3Si)N-$ groups.[4a] However, the X-ray crystal structure was not reported. Subsequently in 2002, they also reported the synthesis and crystal structure of *cis,-cis*-$[(Me_3SiCH_2)Si(OH)O]_3$.[4b] In 2000 and 2002, Fujita's group reported the structure of *cis,cis*-$[ArSi(OH)O]_3$ (Ar = phenyl, *m*-tolyl, naphthyl) with the aid of Pd(II)-linked coordination hosts.[5] We recently reported the structure of *cis,trans*-$[TipSi(OH)O]_3$ (Tip = 2,4,6-triisopropylphenyl).[6] Unfortunately, in all these cases, no reactions starting from the triols with bulky substituents have been recorded, obviously because of the steric hindrance of the substituents. In this paper, we describe the preparation and crystal structure of $[i\text{-}PrSi(OH)O]_3$, which is stabilized by much smaller substituents compared to the cyclotrisiloxanetriols reported earlier.

Scheme 1. Synthesis of Cyclotrisiloxanetriol by Dearylchlorination and Hydrolysis



Our tactics toward the synthesis of trihydroxycyclotrisiloxanes include the following two steps: (1) construction of aryl-substituted cyclotrisiloxanes and (2) dearylchlorination and hydrolysis of the products of the first step, leading to the targeted trihydroxycyclotrisiloxanes (Scheme 1).

In the first step, we applied two methods: (a) instead of conventional hydrolytic condensation, reaction of the dichlorosilane with ZnO was used; (b) chlorosilanes with a bulkier aryl group (e.g., an *o*-tolyl group) were utilized. The result is summarized in Scheme 2. The condensation of dichlorosilanes with ZnO was first used by Takiguchi et al.[7] and was shown to be effective in the synthesis of $(MePhSiO)_3$ from $MePhSiCl_2$.[8] In our reaction of *i*-$PrPhSiCl_2$ with ZnO, cyclotrisiloxane **1**, cyclotetrasiloxane **2**, and higher oligomer **3** were obtained. Separation of products was performed with recycle-type HPLC. The identification of *cis,trans*- and *cis,cis*-**1** was based on spectroscopic analysis; the stereostructure was determined by NMR spectroscopy. Thus, two kinds of substituents and silicon atoms are observed in the ^1H, ^{13}C, and ^{29}Si NMR spectra for *cis,trans*-**1**, while single peaks appear for *cis,cis*-**1**. The yields of *cis,trans*- and *cis,cis*-cyclotrisiloxanes were 18% and 6%, respectively.

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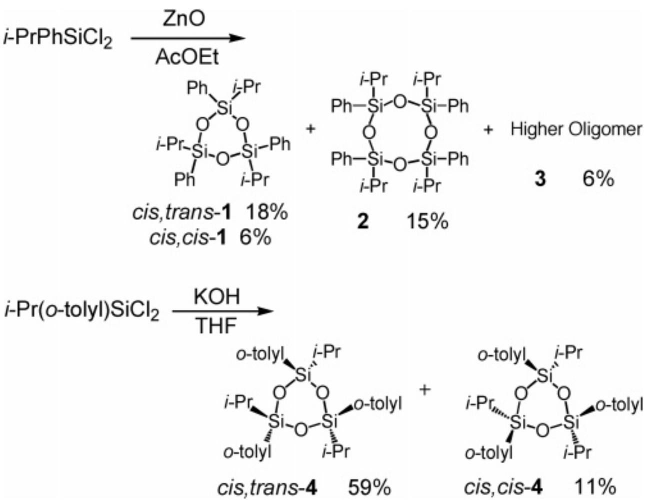
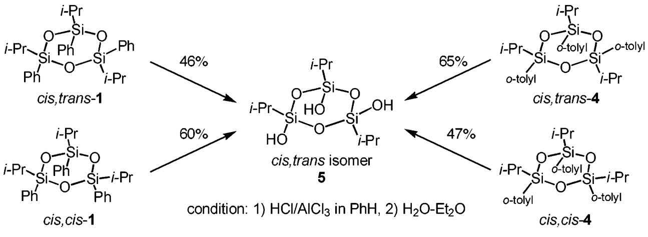
Scheme 2. Preparation of Cyclotrisiloxanes



Scheme 3. Preparation of Cyclotrisiloxanetriols



On the other hand, hydrolytic condensation of *i*-Pr(*o*-tolyl)SiCl$_2$ with aqueous KOH afforded only cyclotrisiloxane, and the yields of cis,trans and cis,cis isomers were 59% and 11%, respectively. It is noteworthy that *i*-PrPhSiCl$_2$ afforded only the cyclotetrasiloxane (*i*-PrPhSiO)$_4$ (**2**; 81%) and no trisiloxane **1** by hydrolytic condensation (see the Supporting Information). Additionally, *i*-Pr(*p*-tolyl)SiCl$_2$ and *i*-Pr(*m*-tolyl)SiCl$_2$ also gave cyclotetrasiloxanes by reaction with aqueous NaOH or KOH/THF (73% and 60%, respectively). These results clearly indicate that the bulkiness of substituents plays an important role in the ring size of the products.

The dearylchlorination of cyclotrisiloxanes was effected by HCl gas in the presence of AlCl$_3$. Because of the instability toward moisture of the generated chlorosilanes, we subsequently treated the products with water to generate the corresponding silanols. This reaction sequence was performed with the following separated stereoisomers: *cis,cis*-**1**, *cis,trans*-**1** and *cis,cis*-**4**, *cis,trans*-**4**. Surprisingly, all four compounds gave the *cis,trans*-cyclotrisiloxanetriol **5** exclusively, regardless of the structure of starting materials. The yields were as shown in Scheme 3. The product, **5**, has the smallest substituents of the known cyclotrisiloxanetriols, but it is stable toward air and moisture and could be handled under ambient conditions without problems.

The reason for the stereoselectivity shown in Scheme 3 is not clear. However, we presume that the isomerization occurs during the dearylchlorination step. Recently, the reaction of the cyclotetrasiloxane (Me$_2$SiO)$_4$ with AlCl$_3$, resulting in an aluminum complex of the siloxane, was reported.[9] In our case, even with the bulkier isopropyl groups, the increased ring strain may cause ring opening and ring closure during the course of the dearylchlorination process, resulting in the observed isomerization.

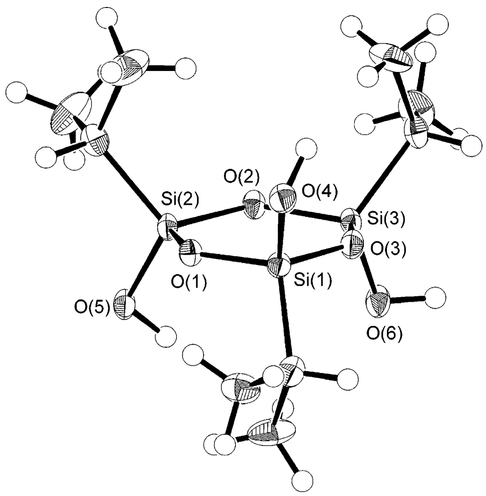


Figure 1. Molecular drawing of **5**. Thermal ellipsoids are drawn at the 30% probability level.

Table 1. Crystallographic Data for 5

formula	$C_9H_{24}O_6Si_3$
mol wt	312.54
cryst descripn	colorless prisms
cryst size, mm	0.30 × 0.30 × 0.05
cryst syst	orthorhombic
a, Å	18.832(4)
b, Å	6.332(1)
c, Å	13.685(3)
V, Å^3	1631.8(6)
space group	$Pna2_1$ (No. 33)
Z	4
D_{calcd}, g cm^{-3}	1.272
μ(Mo Kα), cm^{-1}	3.04
no. of rflns measd	6856
no. of indep rflns	2381 (R(int) = 0.072)
no. of obsd rflns ($I > 2.00\sigma(I)$)	1871
function minimized	$\sum w(F_o^2 - F_c^2)^2$
$2\theta_{\max}$ cutoff, deg	55.0
no. of params	187
rfln/param ratio	16.30
R (all rflns)	0.070
R1 ($I > 2.00\sigma(I)$)	0.062
wR2 (all reflns)	0.153
S	1.021
$(\Delta/\sigma)_{\max}$	0.000
$(\Delta\rho)_{\max}$, e Å^{-3}	0.49
$(\Delta\rho)_{\min}$, e Å^{-3}	−0.67

The structure of **5** was established on the basis of spectroscopic data and further corroborated by X-ray crystallographic analysis. In Figure 1, the molecular structure is shown, and crystallographic parameters are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. The average Si−O length was 1.638 Å, and average Si−O−Si and O−Si−O angles were 132.5 and 107.8°, respectively. These values are similar to those of the reported cyclotrisiloxanetriols,[4−6,10] indicating that steric repulsion is not severe in these compounds, even with very bulky substituents. Although there is no symmetric element in the molecule, the six-membered ring is virtually planar. Thus, the deviations of O(1), O(2), and O(3) atoms from the Si(1)···Si(2)···Si(3) plane are 0.018(5), 0.163(5), and 0.044(5)

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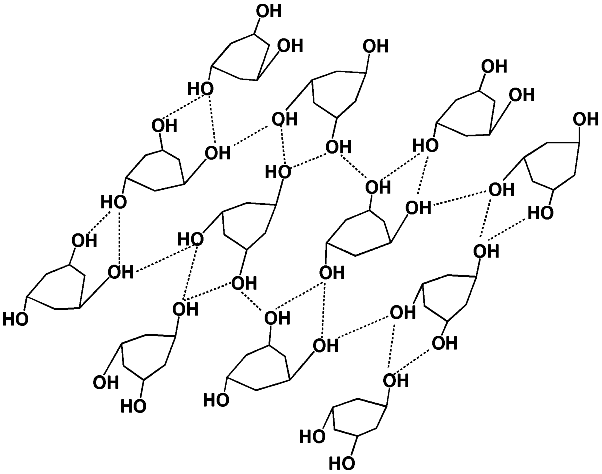

Figure 2. Hydrogen-bonding scheme. The cyclotrisiloxane ring is shown by solid lines.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5

Si(1)−O(1)	1.638(5)	Si(3)−O(2)	1.636(6)
Si(1)−C(1)	1.866(6)	Si(3)−C(7)	1.834(7)
Si(2)−C(4)	1.850(7)	Si(1)−O(4)	1.639(4)
Si(3)−O(6)	1.636(6)	Si(2)−O(2)	1.646(6)
Si(1)−O(3)	1.643(5)	Si(3)−O(3)	1.629(5)
Si(2)−O(1)	1.633(5)		
O(1)−Si(1)−O(3)	107.3(3)	O(6)−Si(3)−O(2)	105.8(3)
O(1)−Si(2)−O(2)	106.9(3)	Si(2)−O(2)−Si(3)	132.3(3)
O(3)−Si(3)−O(2)	106.6(3)	O(3)−Si(1)−O(4)	109.8(3)
Si(1)−O(1)−Si(2)	132.5(3)	O(2)−Si(2)−O(5)	108.8(3)
O(1)−Si(1)−O(4)	107.9(3)	O(6)−Si(3)−O(3)	109.5(3)
O(1)−Si(2)−O(5)	109.6(3)	Si(1)−O(3)−Si(3)	132.8(3)

Å, respectively. This feature is similar to the situation in *cis,cis*-[*m*-tolylSi(OH)O]$_3$[10] and *cis,cis*-[(Me$_3$Si)$_2$CHSi(OH)O]$_3$[4b] but in contrast to the *cis,cis,cis*-cyclotetrasiloxanetetraol [*i*-PrSi(OH)O]$_4$, which forms a folded siloxane ring.[1a,3]

For previously reported cyclotrisiloxanetriols, crystallographic analyses were performed only for all-cis compounds, except for our recent Tip-substituted one.[6] As expected, *all-cis*-[(Me$_3$Si)$_2$CHSi(OH)O]$_3$ forms a dimeric structure in the crystal; encapsulated triols are, of course, monomeric.[5] The most intriguing point for the cis,trans triol **5** is a possibility of supramolecular aggregation by hydrogen bonding. As shown in Figures 2 and 3, **5** forms a connected-column (triangular prism) structure. In the case of *cis,trans*-[TipSi(OH)O]$_3$, a similar packing of the molecules was observed. However, the columns are not connected because of the bulky Tip groups. This result shows that the hydroxyl groups of **5** are not shielded by bulky substituents, promising the potential of **5** as a precursor of siloxanes or metallosiloxanes. In Figure 3, the packing structure of **5** is depicted. The hydrogen-bonded triangular prism as well as the "column-connecting" hydroxyl groups can be seen.

In summary, we have demonstrated the novel synthesis of a cyclotrisiloxanetriol by the dearylchlorination−hydrolysis method and succeeded in the preparation of the so far least bulky triisopropylcyclotrisiloxanetriol (**5**). The structure of **5** was determined by X-ray crystallography, and its unique hydrogen-bonded cluster was elucidated. The reactivity for this promising compound will be reported in due course.

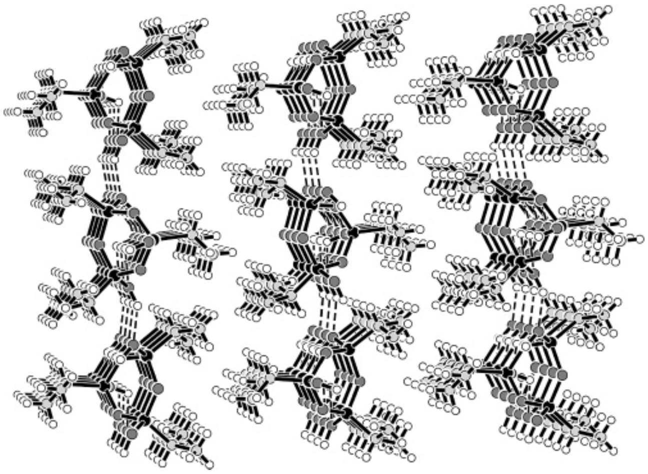

Figure 3. Packing diagram of **5**: (black) Si; (dark gray) O; (light gray) C; (white) H.

Experimental Section

GLC analyses were performed on a Shimadzu GC-8A model using a 3.5 mm × 1000 mm glass column packed with 10% silicon KF-96 on 60−80 mesh Celite 545sk. HPLC analysis was carried out a Jasco 880-PU with a Jasco Chemicosorb 4.6 mm × 250 mm 5-ODS-H column detected by a Jasco 875-UV instrument. Preparative recycle-type HPLC was carried out using a JAI LC-908 instrument with a Chemco 20 mm × 250 mm 7-ODS column. Wet column chromatography was performed with silica gel 60N. Preparative thin-layer chromatography (PTLC) was carried out with Merck Kieselgel 60 PF$_{254}$. FT-NMR spectra were obtained on JEOL Model α-500 and λ-500 spectrometers (^{1}H at 500.00 MHz, ^{13}C at 125.65 MHz, and ^{29}Si at 99.25 MHz). Chemical shifts were reported in δ units (ppm) relative to SiMe$_4$, and residual solvent peaks were used for standards; J values are given in Hz. For ^{29}Si NMR, SiMe$_4$ was used as an external standard. EI mass spectrometry was performed with JEOL JMS-DX302 and JMS-700 instrument. Infrared spectra were measured with a Shimadzu FTIR-8700 spectrometer.

Synthesis of Cyclic Siloxanes with Zinc Oxide. Isopropylphenyldichlorosilane (5.97 g, 27.2 mmol) was added to a mixture of dry ethyl acetate (10 mL) and zinc oxide (3.72 g, 45.7 mmol). This mixture was stirred at 50 °C for 2.5 days. The crude mixture was neutralized by slowly pouring it into saturated aqueous NaHCO$_3$ with vigorous stirring. The resulting mixture was filtered through a glass filter. The filtrate was extracted with ether, and the combined organic phases were dried over anhydrous MgSO$_4$ and concentrated. The resulting liquid was separated by recycle-type HPLC to afford 1,3,5-triisopropyl-1,3,5-triphenylcyclotrisiloxane (**1**), 1,3,5,7-tetraisopropyl-1,3,5,7-tetraphenylcyclotetrasiloxane (**2**; 686 mg, 15%, mixture of four isomers), and higher oligomers (**3**; 188 mg, 6%). The isomeric mixture of **1** was further separated by recycle-type HPLC to give *cis,trans*-**1** (813 mg, 18%) and *cis,cis*-**1** (284 g, 6%). Compounds **2** were identified by comparison with authentic samples obtained in a different reaction (see the Supporting Information). *cis,trans*-**1**: colorless semisolid; ^{1}H NMR (CDCl$_3$) δ 0.83 (d, 6H, $J = 7.3$), 0.92 (sept, 1H, $J = 7.3$), 1.02 (d, 12H, $J = 7.3$), 1.10 (sept, 2H, $J = 7.3$), 7.33 (m, 9H), 7.67 (d, 4H, $J = 6.4$), 7.78 (d, 2H, $J = 7.0$) ppm; ^{13}C NMR (CDCl$_3$) δ 14.75, 14.92, 16.14, 16.35, 16.37, 127.54, 127.67, 129.84, 129.94, 133.88, 133.95, 134.44, 134.81 ppm; ^{29}Si NMR (CDCl$_3$) δ −22.79, −22.55 ppm; MS (70 eV) m/z (%) 492 (M$^+$, 5), 449 (M$^+$ − *i*-Pr, 100); IR (NaCl) ν 3071, 3051, 3003, 2945, 2866, 1591, 1464, 1429, 1384, 1248, 1123, 1031, 1011, 993, 920, 883, 758, 741, 716, 698, 642 cm^{-1}. Anal. Calcd for C$_{27}$H$_{36}$O$_3$Si$_3$: C, 65.80; H, 7.36%. Found: C, 65.55; H, 7.31%. *cis,cis*-**1**: colorless solid, mp 63−64 °C; ^{1}H NMR (CDCl$_3$) δ 1.05

(d, 18H, $J = 7.1$), 1.13 (sept, 3H, $J = 7.1$), 7.07 (t, 6H, $J = 7.3$), 7.18 (t, 3H, $J = 7.3$), 7.36 (d, 3H, $J = 6.4$) ppm; ^{13}C NMR ($CDCl_3$) δ 14.94, 16.51, 127.34, 129.66, 133.92, 134.12 ppm; ^{29}Si NMR (99 MHz, $CDCl_3$) δ −23.18 ppm; MS (70 eV) *m/z* (%) 492 (M^+, 5), 449 ($M^+ - i$-Pr, 100); IR (NaCl) ν 3072, 3051, 2945, 2895, 2866, 1464, 1429, 1385, 1246, 1123, 1032, 1011, 993, 920, 885, 802, 731, 712, 637, 598, 548 cm^{-1}. Anal. Calcd for $C_{27}H_{36}O_3Si_3$: C, 65.80; H, 7.36. Found: C, 65.65; H, 7.46.

Synthesis of 1,3,5-Triisopropyl-1,3,5-tri-*o*-tolylcyclotrisiloxane (4). An aqueous KOH solution (5 mL, 4.6 mol/l) was added to *i*-Pr(*o*-tolyl)$SiCl_2$ (1.01 g, 4.3 mmol) in 5 mL of THF. This solution was heated at reflux for 36 h. Analysis by HPLC showed two peaks, indicating the generation of an isomeric mixture. Water and ether were added to the solution, and the aqueous phase was extracted three times with ether. The combined organic phases were dried over anhydrous $MgSO_4$ and concentrated. The isomeric mixture of **4** was separated by dry column chromatography to give *cis,trans*-**4** (445 mg, 59%) and *cis,cis*-**4** (83.5 mg, 11%). *cis,trans*-[*i*-Pr(*o*-tolyl)SiO]$_3$ (*cis,trans*-**4**): colorless semisolid; ^{1}H NMR ($CDCl_3$) δ 0.70 (d, 7H, $J = 7.2$), 0.94 (d, 6H, $J = 7.2$), 0.96 (d, 6H, $J = 7.2$), 1.09 (sept, 2H, $J = 7.2$), 7.10 (t, 3H, $J = 7.0$), 7.14 (d, 2H, $J = 7.0$), 7.21 (t, 2H, $J = 7.0$), 7.26 (d, 1H, $J = 7.0$), 7.34 (t, 1H, $J = 7.0$), 7.69 (d, 2H, $J = 7.0$), 7.79 (d, 1H, $J = 7.0$) ppm; ^{13}C NMR ($CDCl_3$) δ 15.45, 15.92, 16.19, 16.54, 16.65, 22.72, 22.87, 124.47, 124.60, 129.68, 129.74, 129.87, 130.00, 133.31, 133.63, 135.23, 135.27, 143.13, 143.27 ppm; ^{29}Si NMR ($CDCl_3$) δ −20.61, −20.30 ppm; MS (70 eV) *m/z* (%) 534 (M^+, 1), 491 ($M^+ - i$-Pr, 92); IR (NaCl) 3057, 3005, 2947, 2866, 1593, 1566, 1464, 1383, 1285, 1248, 1132, 1086, 1009, 918, 883, 806, 748, 721, 692, 633 cm^{-1}. Anal. Calcd for $C_{30}H_{42}O_3Si_3$: C, 67.36; H, 7.91. Found: C, 68.82; H, 8.26. *cis,cis*-[*i*-Pr(*o*-tolyl)SiO]$_3$ (*cis,cis*-**4**): colorless semisolid; ^{1}H NMR ($CDCl_3$) δ 1.14 (d, 18H, $J = 6.9$), 1.31 (sept, 6H, $J = 6.9$), 2.49 (s, 9H), 6.99 (t, 3H, $J = 7.5$), 7.08 (d, 3H, $J = 7.5$), 7.20 (t, 3H, $J = 7.5$), 7.55 (d, 3H, $J = 7.5$) ppm; ^{13}C NMR ($CDCl_3$) δ 16.22, 16.79, 22.99, 124.33, 129.57, 129.76, 132.91, 135.21, 143.08 ppm; ^{29}Si NMR ($CDCl_3$) δ −21.39 ppm; MS (70 eV) *m/z* (%) 534 (M^+, 10), 491 ($M^+ - i$-Pr, 73), 399 (100); IR (NaCl) 3051, 3005, 2947, 2866, 1593, 1564, 1464, 1383, 1285, 1261, 1132, 1088, 1061, 1009, 883, 806, 746, 723, 689 cm^{-1}. Anal. Calcd for $C_{30}H_{42}O_3Si_3$: C, 67.36; H, 7.91. Found: C, 66.64; H, 8.31.

Synthesis of *cis,trans*-1,3,5-Trihydroxy-1,3,5-triisopropylcyclotrisiloxane (5) from *cis,trans*-1 (General Procedure). To a solution of *cis,trans*-1,3,5-triisopropyl-1,3,5-triphenylcyclotrisiloxane (*cis,trans*-**1**; 420 mg, 0.853 mmol) and anhydrous aluminum chloride (0.603 g, 4.52 mmol) in 8 mL of dry benzene was passed gaseous hydrogen chloride for 1 h at room temperature. Analysis by GLC showed the formation of 1,3,5-trichloro-1,3,5-triisopropylcyclotrisiloxane. Acetone was added to the solution to quench aluminum chloride, and argon gas was bubbled through the solution for 25 min. Water and ether were added to the solution. The aqueous phase was extracted three times with ether, and the combined organic phases were dried over anhydrous $MgSO_4$ and concentrated. Recrystallization from hexane gave **5** (123 mg, 46%). *cis,trans*-1,3,5-Trihydroxy-1,3,5-triisopropylcyclotrisiloxane (**5**): colorless solid, mp 161−162 °C; ^{1}H NMR (DMSO-d_6) δ 0.84 (sept, 3H, $J = 7.0$ Hz), 0.95 (d, 12H, $J = 7.0$), 0.97 (d, 6H, $J = 7.0$), 6.64 (s, 1H), 6.66 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 12.17, 13.37, 17.05, 17.11, 17.16; ^{29}Si NMR (DMSO-d_6) δ −50.60, −49.75; MS (70 eV) *m/z* (%) 269 ($M^+ - i$-Pr, 27), 183 (4), 72 (100); IR (KBr) 3311, 2947, 2872, 1466, 1259, 1034 cm^{-1}. Anal. Calcd for $C_9H_{24}O_6Si_3$: C, 34.58; H, 7.74. Found: C, 34.74; H, 7.58.

Synthesis of *cis,trans*-1,3,5-Trihydroxy-1,3,5-triisopropylcyclotrisiloxane (5) from *cis,cis*-1,3,5-Triisopropyl-1,3,5-triphenylcyclotrisiloxane (*cis,cis*-1). Cyclotrisiloxanetriol **5** was obtained in a similar manner from *cis,cis*-**1** (227 mg, 0.461 mmol) with anhydrous aluminum chloride (0.323 g, 2.42 mmol) and HCl gas in 8 mL of benzene. Recrystallization from hexane gave **5** (93.6 mg, 65%).

Synthesis of *cis,trans*-1,3,5-Trihydroxy-1,3,5-triisopropylcyclotrisiloxane (5) from *cis,trans*-1,3,5-Triisopropyl-1,3,5-tri(*o*-tolyl)cyclotrisiloxane (*cis,trans*-4). Into a solution of *cis,trans*-1,3,5-triisopropyl-1,3,5-tri-*o*-tolylcyclotrisiloxane (*cis,trans*-**4**; 445 mg, 0.832 mmol) and anhydrous aluminum chloride (0.566 g, 4.25 mmol) in 15 mL of dry benzene was passed hydrogen chloride for 30 min at room temperature. The reaction mixture was separated and purified in a manner similar to that above to give **5** (155 mg, 60%).

Synthesis of *cis,trans*-1,3,5-Trihydroxy-1,3,5-triisopropylcyclotrisiloxane (5) from *cis,cis*-1,3,5-Triisopropyl-1,3,5-tri-*o*-tolylcyclotrisiloxane (*cis,cis*-4). Into a solution of *cis,trans*-1,3,5-triisopropyl-1,3,5-tri-*o*-tolylcyclotrisiloxane (*cis,cis*-**4**) (104 mg, 0.194 mmol) and anhydrous aluminum chloride (0.223 g, 1.67 mmol) in 5 mL of dry benzene was passed hydrogen chloride for 1 h at room temperature. The reaction mixture was separated and purified in a manner similar to that above to give **5** (28.6 mg, 47%).

X-ray Crystallographic Analysis of 5. A colorless prismatic crystal of $C_9H_{24}O_6Si_3$ having approximate dimensions of 0.30 × 0.30 × 0.05 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-IV++ imaging plate area detector with graphite-monochromated Mo Kα radiation. Indexing was performed from four oscillations that were exposed for 60 s. The data were collected at a temperature of −160 °C to a maximum 2θ value of 64.7°. A total of 294 oscillation images were collected. A sweep of data was done using ϕ oscillations from 7.0 to 154.0° in 0.5° steps. The exposure rate was 360.0 s/deg. The detector swing angle was 1.10°. The crystal-to-detector distance was 100.40 mm. Readout was performed in the 0.100 mm pixel mode. The linear absorption coefficient, μ, for Mo Kα radiation is 3.04 cm^{-1}. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated and refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 1871 observed reflections and 187 variable parameters and converged. All calculations were performed using the CrystalStructure software of Rigaku/MSC.

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Supporting Information Available: Text giving the experimental procedure for **2** and a CIF file giving crystallographic data for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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