Ring-Opening Reactions of *anti*-Dodecaisopropyltricyclo[4.2.0.$0^{2,5}$]octasilane. Formation of Novel Bicyclo[3.3.0]octasilane and Bicyclo[4.2.0]octasilane Systems

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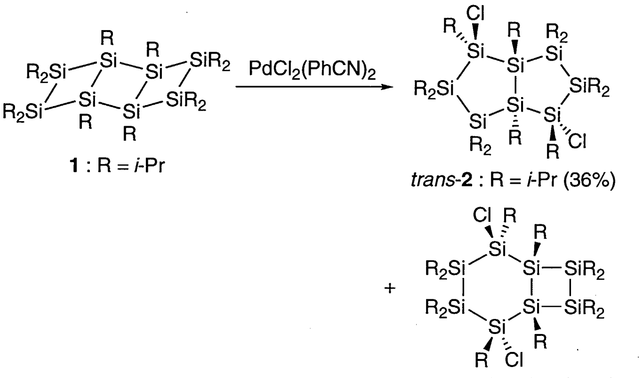
The reaction of *anti*-dodecaisopropyltricyclo[4.2.0.$0^{2,5}$]octasilane (**1**) with $PdCl_2(PhCN)_2$ gave bicyclo[3.3.0]octasilane (*trans*-**2**) and bicyclo[4.2.0]octasilane (*trans*-**3**). In the reaction of **1** with PCl_5, only the bicyclo[4.2.0]octasilanes (*cis*-**3** and *trans*-**3**) were formed. The structures of the novel rings, *trans*-**2**, *cis*-**3**, and *trans*-**3**, were investigated by X-ray crystallography.

Following the construction of ladder polysilanes,[1] we have been interested in the structures,[2] optical properties,[3] and reactions[4] of these particular compounds. We report herein the ring-opening reactions of a tricyclic ladder polysilane, *anti*-dodecaisopropyltricyclo[4.2.0.$0^{2,5}$]octasilane (**1**), with the electrophiles $PdCl_2(PhCN)_2$ and PCl_5 leading to the bicyclo[3.3.0]octasilane and bicyclo[4.2.0]octasilane systems. Despite of the rapid development in studies on polycyclopolysilanes,[5] the known bicyclic systems have still been limited to the rings such as bicyclo[1.1.0]tetrasilane,[6a] bicyclo[1.1.1]pentasilane,[6b] bicyclo[2.2.0]hexasilane,[1] bicyclo[2.2.1]heptasilane,[6c] bicyclo[2.2.2]octasilane,[6c,d] and bicyclo[4.4.0]decasilane.[6d,e] The X-ray structures of the novel ring systems, *trans*-**2**, *cis*-**3**, and *trans*-**3**, disclose unique structural features of the bicyclooctasilane frameworks.

The reaction of **1** with a small excess amount of $PdCl_2(PhCN)_2$ in benzene under reflux gave *trans*-2,6-dichlorododecaisopropylbicyclo[3.3.0]octasilane (*trans*-**2**)[7] and *trans*-2,5-dichlorododecaisopropylbicyclo[4.2.0]octasilane (*trans*-**3**)[8] in 36 and 25% yields, respectively. The formation of *trans*-**2** shows that both bridgehead Si–Si bonds of **1** were cleaved and rearranged to the bicyclo[3.3.0]octasilane system,[9] while in *trans*-**3**, one of the bridgehead Si–Si bonds of **1** was simply cleaved to form the bicyclo[4.2.0]octasilane system. Formation of other products in which peripheral Si–Si bonds are cleaved was negligibly small, indicating the high reactivity of the bridgehead Si–Si bonds of **1**.



1 : R = *i*-Pr

trans-**2** : R = *i*-Pr (36%)

trans-**3** : R = *i*-Pr (25%)

The structures of *trans*-**2** and *trans*-**3** were determined by X-ray crystallography (Figures 1 and 2).[10,11] The bicyclo[3.3.0]octasilane framework of *trans*-**2** has a trans-fused structure of cyclopentasilane rings. The trans-fused structure is notable because in bicyclo[3.3.0]octane, the cis-fused structure has been reported to be more stable than the trans-fused structure.[12,13] In fact, the MM2 calculation shows that the cis-fused isomer of *trans*-**2** is more stable than *trans*-**2** itself. Therefore, the ring-opening reaction is considered to be kinetically controlled. The cyclopentasilane rings have an intermediate conformation between the envelope and twist forms. The peripheral Si–Si bonds (average 2.428 Å) are longer than the bridgehead Si–Si bond (2.373(2) Å), probably due to the steric hindrance of the isopropyl groups.

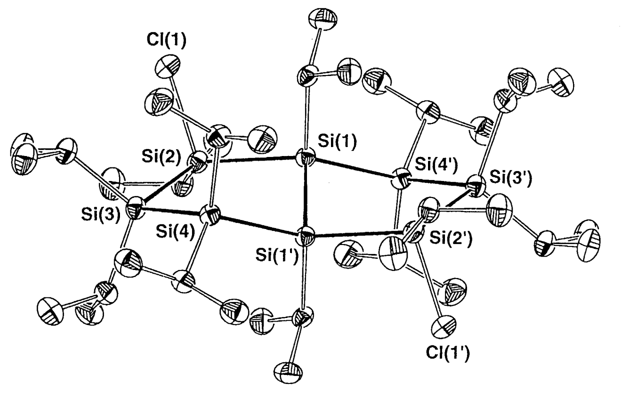


Figure 1. Molecular structure of *trans*-**2**. Selected bond lengths (Å): Si(1)–Si(2) 2.429(2), Si(1)–Si(1') 2.373(2), Si(1)–Si(4') 2.429(2), Si(2)–Si(3) 2.433(2), Si(3)–Si(4) 2.422(2).

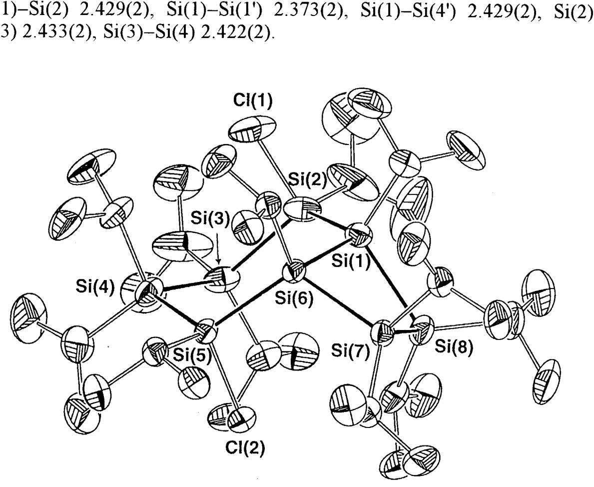


Figure 2. Molecular structure of *trans*-**3**. Selected bond lengths (Å): Si(1)–Si(2) 2.395(3), Si(1)–Si(6) 2.388(2), Si(1)–Si(8) 2.427(3), Si(2)–Si(3) 2.392(3), Si(3)–Si(4) 2.413(3), Si(4)–Si(5) 2.409(3), Si(5)–Si(6) 2.398(2), Si(6)–Si(7) 2.415(2), Si(7)–Si(8) 2.381(3).

In *trans*-**3**, the cyclohexasilane ring has a chair form and both chlorine atoms occupy axial positions. The cyclotetrasilane ring has a folded structure with fold angles of 33.0° and 33.6°.[14]

The ring-opening reaction of **1** also proceeded using PCl_5 to give *cis*-2,5-dichlorododecaisopropylbicyclo[4.2.0]octasilane (*cis*-**3**)[15] and *trans*-**3** in 47 and 11% yields, respectively. In this reaction, the bridgehead Si–Si bonds of **1** are also highly reactive toward PCl_5. However, rearrangement products such as *trans*-**2** were not formed, and *cis*-**3** was produced in preference to *trans*-

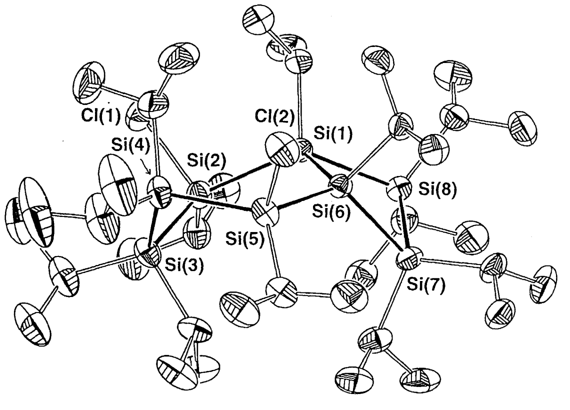
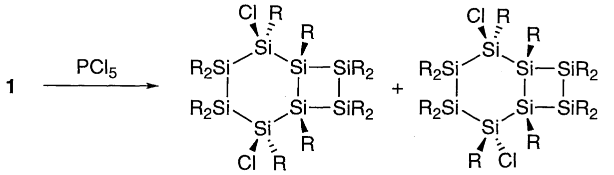


Figure 3. Molecular structure of *cis*-**3**. Selected bond lengths (Å): Si(1)–Si(2) 2.430(4), Si(1)–Si(6) 2.427(5), Si(1)–Si(8) 2.420(4), Si(2)–Si(3) 2.402(6), Si(3)–Si(4) 2.415(4), Si(4)–Si(5) 2.398(4), Si(5)–Si(6) 2.415(5), Si(6)–Si(7) 2.426(4), Si(7)–Si(8) 2.390(6).

3 in contrast with the reaction using $PdCl_2(PhCN)_2$. These results seem to reflect different mechanisms in the ring-opening reactions of **1** with $PdCl_2(PhCN)_2$ and PCl_5, although detailed mechanisms cannot be clearly explained at this moment.



cis-**3** : R = *i*-Pr (47%) *trans*-**3** : R = *i*-Pr (11%)

The X-ray analysis of *cis*-**3** shows an unprecedented cyclohexasilane structure (Figure 3).[16] The cyclohexasilane ring does not adopt the well-known conformations such as the chair, boat, twist-boat, and half-chair forms. In this cyclohexasilane ring, the Si(1)–Si(6)–Si(5)–Si(4) atoms construct a partial boat form and the Si(1)–Si(2)–Si(3)–Si(4) atoms construct a partial twist-boat form. Therefore, the cyclohexasilane ring can be regarded as the half-twist-boat form. The cyclotetrasilane ring has a folded structure with fold angles of 32.5° and 33.8°. The Si–Si bond lengths (average 2.414 Å) are longer than those of *trans*-**3** (average 2.402 Å). Especially, the bridgehead Si–Si bond (2.427(5) Å) is far longer than that of *trans*-**3** (2.388(2) Å). These structural features reveal that *cis*-**3** is a highly strained molecule compared to *trans*-**3**.

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7 *trans*-**2**: Mp 220–221 °C; ^{1}HNMR (C_6D_6) δ 1.26 (d, 6H, J = 7.3 Hz), 1.28 (d, 6H, J = 7.3 Hz), 1.30 (d, 6H, J = 7.3 Hz), 1.38 (d, 12H, J = 7.3 Hz), 1.41 (d, 6H, J = 5.6 Hz), 1.42 (d, 6H, J = 7.0 Hz), 1.45 (d, 6H, J = 7.3 Hz), 1.467 (d, 6H, J = 7.6 Hz), 1.473 (d, 6H, J = 7.3 Hz), 1.55 (d, 6H, J = 6.6 Hz), 1.56 (d, 6H, J = 9.8 Hz), 1.74 (sep, 2H, J = 7.5 Hz), 1.78 (sep, 4H, J = 7.6 Hz), 1.79 (sep, 4H, J = 7.6 Hz), 1.87 (sep, 2H, J = 7.4 Hz); ^{13}CNMR (C_6D_6) δ 14.5, 15.9, 16.5, 16.6, 17.2, 19.2, 20.8, 21.5, 22.3, 22.5, 23.6, 23.7, 23.9, 24.2, 25.5, 25.9; ^{29}SiNMR (C_6D_6) δ –53.3, –9.2, 0.7, 41.2; IR (KBr, cm^{-1}) 2860, 1455, 1375, 1355, 875; UV (λ_{max} in hexane) 226 nm (ε 42500), 245 nm (ε 36100), 306 nm (ε 4800); MS *m*/*z* (%) 810 (M$^+$($^{35}Cl_2$), 9), 547 (^{35}Cl, 100), 441 (45); HRMS. Found: 810.4144. Calcd for $C_{36}H_{84}Cl_2Si_8$: 810.4104.

8 *trans*-**3**: Mp 180–182 °C; ^{1}HNMR (C_6D_6) δ 1.31 (d, 3H, J = 7.4 Hz), 1.35–1.47 (m, 63H), 1.52 (d, 3H, J = 7.4 Hz), 1.57 (d, 3H, J = 7.3 Hz), 1.68 (sep, 1H, J = 7.2 Hz), 1.69 (sep, 1H, J = 7.3 Hz), 1.75 (sep, 1H, J = 7.4 Hz), 1.87 (sep, 2H, J = 7.2 Hz), 1.91 (sep, 1H, J = 7.5 Hz), 1.96 (sep, 1H, J = 7.6 Hz), 2.01 (sep, 1H, J = 7.3 Hz), 2.02 (sep, 1H, J = 7.2 Hz), 2.03 (sep, 1H, J = 7.8 Hz), 2.08 (sep, 1H, J = 7.6 Hz), 2.12 (sep, 1H, J = 7.4 Hz); ^{13}CNMR (C_6D_6) δ 14.8, 15.2, 15.4, 15.8, 16.0, 16.5, 17.0, 17.1, 17.3, 19.9, 20.6, 20.8, 21.6, 21.9, 22.3, 22.4, 22.6, 22.89, 22.91, 22.96, 22.98, 23.26, 23.32, 23.4, 23.5, 23.56, 23.58, 23.7, 23.9, 24.3, 24.4, 24.9, 25.2, 25.3; ^{29}SiNMR (C_6D_6) δ –43.3, –30.8, –9.5, –8.6, 7.6, 11.7, 30.7, 33.0; IR (KBr, cm^{-1}) 2860, 1460, 1385, 1360, 875; UV (λ_{max} in hexane) 230 nm (sh, ε 25200), 251 nm (sh, ε 14000), 299 nm (sh, ε 2400); MS *m*/*z* (%) 810 (M$^+$($^{35}Cl_2$), 6), 547 (^{35}Cl, 100), 441 (53); HRMS. Found: 810.4072. Calcd for $C_{36}H_{84}Cl_2Si_8$: 810.4104.

9 Recently, similar rearrangement of octasilacubane has been reported. See: M. Unno, K. Higuchi, M. Ida, H. Shioyama, S. Kyushin, H. Matsumoto, and M. Goto, *Organometallics*, **13**, 4633 (1994); M. Unno, H. Shioyama, M. Ida, and H. Matsumoto, *Organometallics*, **14**, 4004 (1995).

10 Crystal data for *trans*-**2**: $C_{36}H_{84}Cl_2Si_8 \cdot C_6H_{14}$ (hexane was incorporated upon recrystallization), F_w = 898.83, monoclinic, space group $C2/c$, a = 25.342(2), b = 14.120(2), c = 20.527(2) Å, β = 132.535(4)°, V = 5413(1) Å^3, Z = 4, D_o = 1.101, D_c = 1.103 g cm^{-3}, R = 0.052, R_w = 0.048 (w = $1/\sigma^2(F_o)$) for 3288 observed reflections.

11 Crystal data for *trans*-**3**: $C_{36}H_{84}Cl_2Si_8$, F_w = 812.65, monoclinic, space group $P2_1/c$, a = 12.132(3), b = 33.704(5), c = 13.198(5) Å, β = 111.66(2)°, V = 5015(3) Å^3, Z = 4, D_o = 1.078, D_c = 1.076 g cm^{-3}, R = 0.060, R_w = 0.043 (w = $1/\sigma^2(F_o)$) for 4075 observed reflections.

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14 The structure of bicyclo[4.2.0]octane was previously reported, in which the cyclohexane ring has a chair form and the cyclobutane ring has a folded structure. See: A. Spelbos, F. C. Mijlhoff, W. H. Bakker, R. Baden, and L. Van den Enden, *J. Mol. Struct.*, **38**, 155 (1977).

15 *cis*-**3**: Mp 230 °C; ^{1}HNMR (C_6D_6) δ 1.35–1.67 (m, 78H), 1.72 (sep, 2H, J = 7.6 Hz), 2.02 (sep, 2H, J = 7.4 Hz), 2.14 (sep, 2H, J = 7.5 Hz); ^{13}CNMR (C_6D_6) δ 16.4, 17.2, 17.8, 17.9, 18.5, 20.6, 21.2, 22.1, 22.6, 23.0, 23.2, 23.9, 24.0, 24.3, 24.6, 24.7; ^{29}SiNMR (C_6D_6) δ –45.5, –18.6, 2.4, 31.7; IR (KBr, cm^{-1}) 2850, 1450, 1375, 1355, 875; UV (λ_{max} in hexane) 245 nm (sh, ε 18600), 269 nm (sh, ε 5300), 317 nm (ε 2000); MS *m*/*z* (%) 810 (M$^+$($^{35}Cl_2$), 6), 547 (^{35}Cl, 100), 441 (39); HRMS. Found: 810.4116. Calcd for $C_{36}H_{84}Cl_2Si_8$: 810.4104.

16 Crystal data for *cis*-**3**: $C_{36}H_{84}Cl_2Si_8$, F_w = 812.65, orthorhombic, space group $Pca2_1$, a = 24.458(2), b = 10.969(3), c = 18.306(2) Å, V = 4911(2) Å^3, Z = 4, D_o = 1.110, D_c = 1.099 g cm^{-3}, R = 0.052, R_w = 0.068 (w = $1/\sigma^2(F_o)$) for 2419 observed reflections.