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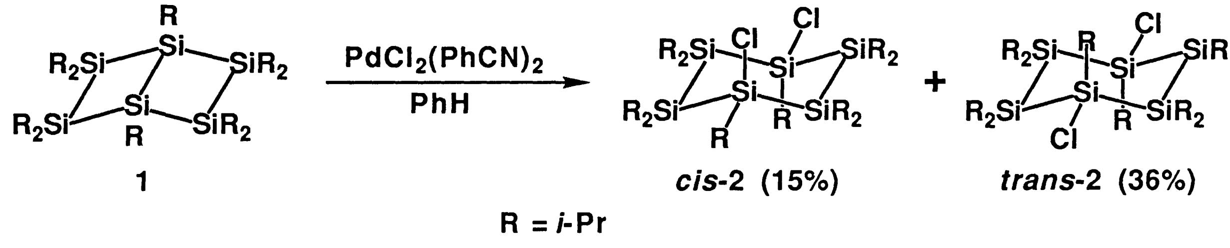
Selective Si-Si Bond Cleavage in Decaisopropylbicyclo[2.2.0]hexasilane. A Route to Sterically Hindered 1,4-Dichlorocyclohexasilanes

Soichiro KYUSHIN, Hiroyuki YAMAGUCHI, Toshiaki OKAYASU, Yusuke YAGIHASHI,
Hideyuki MATSUMOTO,* and Midori GOTO†
Department of Applied Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376
†National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305

The Si-Si bond cleavage reaction of decaisopropylbicyclo[2.2.0]hexasilane with $PdCl_2(PhCN)_2$ gave *cis-* and *trans-*1,4-dichlorocyclohexasilanes. X-ray crystallography of these products show sterically distorted chair conformations of the Si_6 rings. The *cis-* and *trans-*cyclohexasilane show rather different absorptions in the UV spectra. By treatment with sodium, both isomers reproduced the bicyclo[2.2.0]hexasilane quantitatively.

Recently, the synthesis and molecular structure of decaisopropylbicyclo[2.2.0]hexasilane (**1**), the first ladder polysilane, were reported from this laboratory.[1)] We found that **1** possesses the low oxidation potential of 0.87 V (*vs.* SCE in CH_2Cl_2). The ease with which **1** is oxidized has prompted us to explore the reactivity of this particular molecule toward electrophiles. We have been particularly interested in the cleavage of the central Si-Si bond in **1** as a route to sterically hindered cyclohexasilanes with novel properties. In this communication, we describe the selective Si-Si cleavage of **1** with a divalent palladium complex, dichlorobis(benzonitrile)palladium(II), leading to *cis-* and *trans-*1,4-dichlorodecaisopropylcyclohexasilanes (*cis-***2** and *trans-***2**).[2)] These 1,4-dichlorinated perisopropyl compounds exhibit remarkable structural features and reactivity that have not been observed with other 1,4-dichlorocyclohexasilane systems.

When **1** was allowed to react with the Pd(II) complex at room temperature in benzene, *cis-***2** and *trans-***2** were formed in 15 and 36% yields, respectively.[3)] Although the *cis-* and *trans-*1,4-dichlorodecamethylcyclohexasilanes have not been separated,[4)] *cis-***2** and *trans-***2** could be easily separated.[5)] Chlorinated products in which the peripheral Si-Si bonds of **1** were cleaved were not formed. The selective cleavage of the central Si-Si bond of **1** is explained by the MO calculation.[6)] The lobes of the HOMO of **1** are preferentially localized in the central Si-Si bond. During the first step of the reaction, the central Si-Si bond of **1** is coordinated to the palladi-



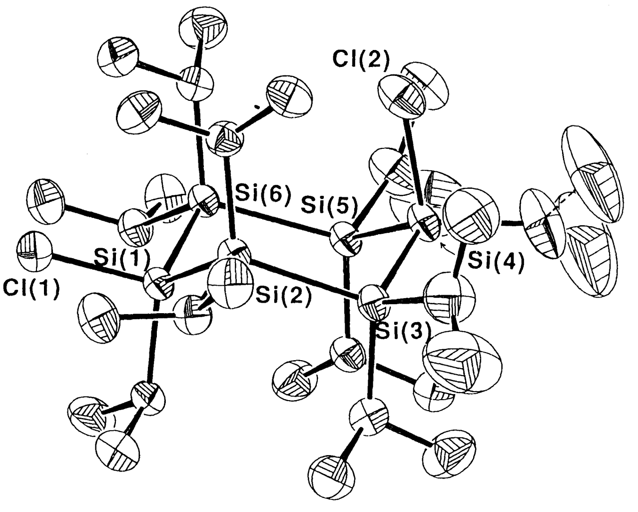


Fig. 1. Molecular structure of *cis*-**2**. Selected bond distances (Å): Si(1)-Si(2) 2.415(2), Si(1)-Si(6) 2.422(2), Si(2)-Si(3) 2.421(3), Si(3)-Si(4) 2.403(3), Si(4)-Si(5) 2.404(2), Si(5)-Si(6) 2.417(2), Si(1)-Cl(1) 2.123(3), Si(4)-Cl(2) 2.111(3).

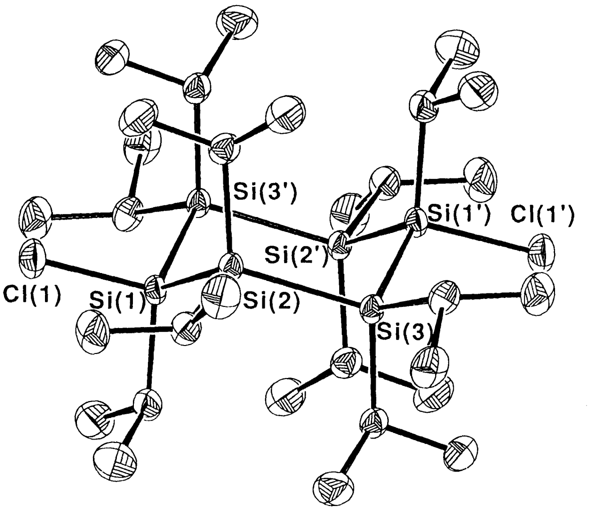


Fig. 2. Molecular structure of *trans*-**2**. Selected bond distances (Å): Si(1)-Si(2) 2.416(1), Si(1)-Si(3') 2.418(1), Si(2)-Si(3) 2.418(1), Si(1)-Cl(1) 2.114(1).

um complex and then oxidatively cleaved.

The structures of *cis*-**2** and *trans*-**2** were determined by X-ray crystallography (Figs. 1 and 2).7) The cyclohexasilane rings of both isomers exist in distorted chair conformations. The Si-Si bond distances of *cis*-**2** (2.403(3)-2.422(2) Å, av. 2.414 Å) and *trans*-**2** (2.416(1)-2.418(1) Å, av. 2.417 Å) are longer than those of cyclohexasilanes so far reported (($Me_2Si)_6$: 2.332(1)-2.342(1) Å,8) all-*trans*-$(PhMeSi)_6$: 2.356(1)-2.362(1) Å,9) $(Ph_2Si)_6$: 2.393(3)-2.396(3) Å,10) and *trans*-1,4-$Ph_2Me_{10}Si_6$: 2.348(1)-2.353(1) Å11)) due to the steric repulsion among the isopropyl groups. The Si-Si-Si bond angles are large at the silicon atoms attached to chlorine (*cis*-**2**: 113.29(8) and 114.29(8)°, *trans*-**2**: 114.23(3)°) and small at the other positions (*cis*-**2**: 104.92(8)-108.71(9)°, *trans*-**2**: 105.33(2)-105.40(3)°). It is noted that both chlorine atoms of *trans*-**2** occupy equatorial positions and the geminal isopropyl groups occupy axial positions. The conformation is explained by the fact that the 1,3-diaxial interaction among the isopropyl groups may not be very important because of the long length of the Si-Si bonds. Moreover, if the isopropyl groups occupied equatorial positions, the steric repulsion among the isopropyl group and four vicinal isopropyl groups would be significantly large because of the gauche conformation. The result is also confirmed by the MM2 calculation that the conformation of the equatorial-Cl and axial-*i*-Pr is more stable than that of the axial-Cl and equatorial-*i*-Pr in *trans*-**2**.

In Fig. 3, the UV spectra of *cis*-**2**, *trans*-**2**, and $(Me_2Si)_6$ (**3**) are described. The spectrum of **3** shows two bands at 235 nm (ε 5200) and 260 nm (ε 900). However, *cis*-**2** and *trans*-**2** show quite different absorptions extending to 300 nm. In *cis*-**2**, shoulders appear at 245 nm (ε 12400), 267 nm (ε 6600), and *ca.* 285 nm (ε 1600). In *trans*-**2**, shoulders appear at 235 nm (ε 9200), 250 nm (ε 7300), 265 nm (ε 3600), and *ca.* 280 nm (ε 1300). The absorption bands shift to the longer wavelength region and have larger extinction coefficients in the order of **3** < *trans*-**2** < *cis*-**2**. The order is in good agreement with their strain energies12) and explained by the fact that the strained Si_6 skeleton has the high energy level of the HOMO.

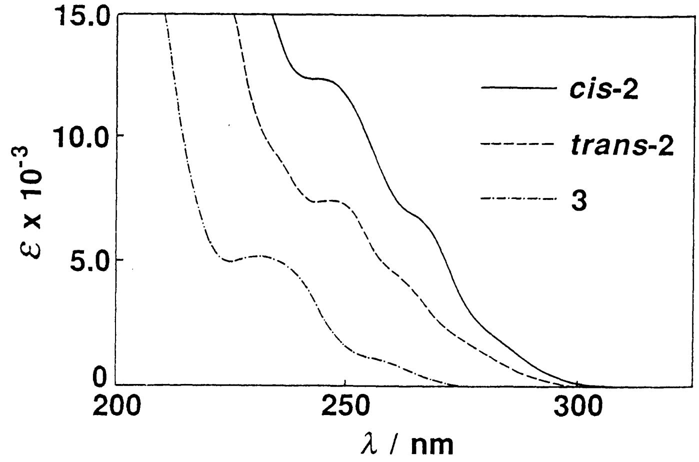
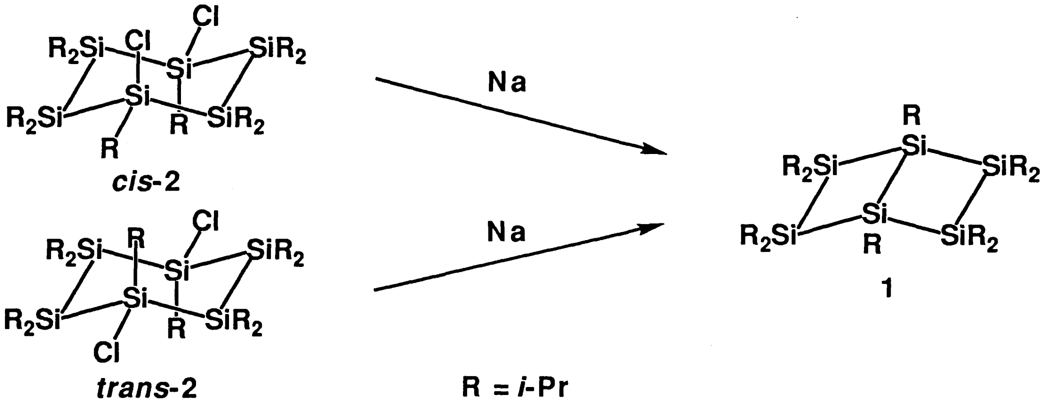


Fig. 3. UV spectra of *cis*-**2**, *trans*-**2**, and **3** in hexane.

In *cis*-**2** and *trans*-**2**, a transannular reaction occurred to quantitatively reproduce **1** by the reductive coupling with sodium under reflux in toluene.[13] The intermolecular coupling products were not formed under these conditions, indicating rapid intramolecular coupling. The result is in contrast with that of dichlorodecamethylcyclohexasilanes,[14] in which only intermolecular coupling occurs. The reaction is also unique because the stereochemistry of **2** does not influence the course of the reaction, although details of the mechanism for the stereochemistry cannot be explained at this moment. Probably, the role of the isopropyl groups is important for the transannular reaction. The intramolecular steric repulsion among the isopropyl groups on the cyclohexasilane ring facilitates the formation of the bicyclo[2.2.0]hexasilane ring and the intermolecular steric repulsion among the isopropyl groups suppresses the coupling reaction of two molecules of **2**.



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3) A solution of **1** (0.0808 g, 0.135 mmol) and $PdCl_2(PhCN)_2$ (0.0785 g, 0.205 mmol) in benzene (2 ml) was stirred at room temperature for 6 days. After filtration of palladium metal, *trans*-**2** was recrystallized from hexane. The filtrate was separated by recycle-type HPLC (ODS, MeOH/THF = 7/3) to give *cis*-**2**.

4) F. K. Mitter and E. Hengge, *J. Organomet. Chem.*, **332**, 47 (1987).

5) *cis*-**2**: Mp 275-285 °C; ^{1}HNMR (C_6D_6) δ 1.34 (d, 6H, J = 7.7 Hz), 1.35 (d, 6H, J = 7.3 Hz), 1.39 (d, 6H, J = 7.4 Hz), 1.40 (d, 6H, J = 7.0 Hz), 1.436 (d, 12H, J = 7.3 Hz), 1.441 (d, 12H, J = 7.6 Hz), 1.53 (d, 12H, J = 7.3 Hz), 1.62 (sep, 3H, J = 7.2 Hz), 1.72 (sep, 2H, J = 7.1 Hz), 2.10 (sep, 5H, J = 7.4 Hz); ^{13}CNMR (C_6D_6) δ 16.8, 18.1, 20.8, 21.4, 23.3, 23.5, 23.9, 24.2; IR (KBr, cm^{-1}) 2870, 1460, 1380, 1360, 1230, 1060, 1020, 1000, 990, 920, 880; MS *m/z* (%) 668 (M$^+$, 27), 519 (100), 405 (71); UV (λ_{max} in hexane) 245 nm (sh, ε 12400), 267 nm (sh, ε 6600), 285 nm (sh, ε 1600). Anal. Found: C, 52.13; H, 10.26%. Calcd for $C_{30}H_{70}Cl_2Si_6$: C, 53.76; H, 10.53%. *trans*-**2**: Mp 288-294 °C; ^{1}HNMR (C_6D_6) δ 1.376 (d, 12H, J = 7.0 Hz), 1.381 (d, 12H, J = 7.4 Hz), 1.39 (d, 12H, J = 7.0 Hz), 1.48 (d, 12H, J = 7.4 Hz), 1.50 (d, 12H, J = 7.3 Hz), 1.73 (sep, 3H, J = 7.4 Hz), 1.74 (sep, 3H, J = 7.4 Hz), 1.91 (sep, 4H, J = 7.4 Hz); ^{13}CNMR (C_6D_6) δ 17.3, 17.5, 20.6, 21.4, 23.5, 23.7, 23.9; IR (KBr, cm^{-1}) 2870, 1450, 1380, 1360, 1220, 1060, 1010, 990, 920, 870; MS *m/z* (%) 668 (M$^+$, 60), 519 (100), 405 (87); UV (λ_{max} in hexane) 235 nm (sh, ε 9200), 250 nm (ε 7300), 265 nm (sh, ε 3600), 280 nm (sh, ε 1300). Anal. Found: C, 52.75; H, 10.44%. Calcd for $C_{30}H_{70}Cl_2Si_6$: C, 53.76; H, 10.53%.

6) The *ab initio* MO calculation was carried out with the GSCF3 program[15)] using the 3-21G basis set. The X-ray structure of **1**[1)] was used, but the isopropyl groups were replaced by hydrogen atoms.

7) Crystal data for *cis*-**2**: $C_{30}H_{70}Cl_2Si_6$, F_w = 670.31, orthorhombic, space group *Pbca*, a = 14.611(1), b = 18.100(1), c = 30.761(3) Å, V = 8135(1) Å^3, Z = 8, D_o = 1.097, D_c = 1.095 g cm^{-3}, R = 0.066, R_w = 0.077 (w = $(0.00679|F_o|^2-0.39415|F_o|+17.198)^{-1}$) for 3854 observed reflections. Crystal data for *trans*-**2**: $C_{30}H_{70}Cl_2Si_6$, F_w = 670.31, monoclinic, space group $P2_1/n$, a = 9.874(1), b = 18.183(1), c = 11.892(1) Å, β = 113.09(1)°, V = 1960.1(3) Å^3, Z = 2, D_o = 1.126, D_c = 1.136 g cm^{-3}, R = 0.038, R_w = 0.070 (w = $(0.00564|F_o|^2-0.15572|F_o|+1.61165)^{-1}$) for 2486 observed reflections.

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12) In the MM2[16)] optimized structures of *cis*-**2** and *trans*-**2**, which closely resemble the X-ray structures, the strain energy of *cis*-**2** is 60.7 kJ mol^{-1} larger than that of *trans*-**2**.

13) A mixture of *cis*-**2** or *trans*-**2** and 3.3 equivalents of sodium in toluene was refluxed for 18 hours. The reaction mixture was hydrolyzed and the organic layer was separated by recycle-type HPLC (ODS, MeOH/THF = 7/3) to give **1** quantitatively.

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