Synthesis and Stereochemistry of *cis*- and *trans*-3,4-Benzo-1,2-di(*tert*-butyl)-1,2-dimethyl-1,2-disilacyclobutene

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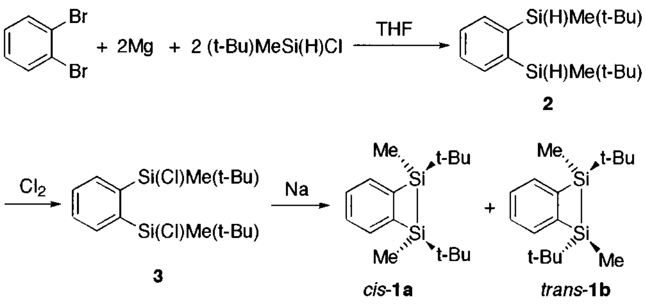
*Summary: The reactions of pure cis- and trans-3,4-benzo-1,2-di(tert-butyl)-1,2-dimethyl-1,2-disilacyclobut-3-ene (**1a** and **1b**) with oxygen in the presence of AIBN proceeded stereospecifically to give the respective siloxanes. The palladium-catalyzed reactions of **1a** and **1b** with phenylacetylene and 1-hexyne produced stereospecifically cis- and trans-5,6-benzo-1,4-disilacyclohexa-2,5-dienes.*

Although considerable attention has been devoted to investigations of the small-ring compounds involving a silicon−silicon bond in the ring system,[1,2] much less interest has been shown in the stereochemistry of these small-ring compounds. In this paper we report the first synthesis and stereochemistry of *cis*- and *trans*-3,4-benzo-1,2-di(*tert*-butyl)-1,2-dimethyl-1,2-disilacyclobut-3-ene (**1a** and **1b**).[3]

Cis- and *trans*-isomers **1a** and **1b** were prepared by a series of the reactions shown in Scheme 1. The reaction of *o*-dibromobenzene with 2 equiv of magnesium in the presence of 2 equiv of *tert*-butylchloromethylsilane in THF gave 1,2-bis[(*tert*-butyl)methylsilyl]benzene (**2**), consisting of *meso*- and *dl*-isomers in a ratio of 1:1 in 35% yield. Treatment of **2** with chlorine gas in carbon tetrachloride afforded a mixture of *meso*- and *dl*-1,2-bis[(*tert*-butyl)chloromethylsilyl]benzene (**3**, *meso*/*dl* = 1:1) in 90% yield. The sodium condensation reaction of pure *meso*- and *dl*-**3** in refluxing toluene proceeded stereoselectively, but not stereospecifically to give a mixture of *cis*- and *trans*-1,2-disilacyclobut-3-ene **1a** and **1b**, respectively, in high yields (Scheme 1).[4] Both **1a** and **1b** were separated by fractional distillation of the mixture with the use of a spinning-band column with 50-theoretical plates, followed by recrystallization from hexane, as an isomerical pure form.

Scheme 1



The structures of **1a** and **1b** were verified by mass and ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analysis, and also by elemental analysis. X-ray crystallographic analysis for **1a** clearly indicates that this compound must have the *cis* configuration as shown in Figure 1.

In contrast with tetramethyl- and tetraethyl-substituted benzodisilacyclobutenes,[5,6] **1a** and **1b** are stable toward atmospheric oxygen. They can be handled in air without decomposition. However, when a benzene solution of **1a** and **1b** was stirred under an oxygen atmosphere in the presence of a catalytic amount of azobis(isobutyro)nitrile (AIBN) at refluxing temperature, the reaction took place to give 4,5-benzo-1,3-di(*tert*-butyl)-1,3-dimethyl-2-oxa-1,3-disilacyclopent-4-enes, arising from oxidation of an Si−Si bond in **1a** and **1b**. To our surprise, oxidation of the Si−Si bond in **1a** and **1b** proceeded stereospecifically to give the respective cyclic siloxanes in high yields. Thus, the reaction of **1a** with oxygen in the presence of AIBN in refluxing benzene gave only one stereoisomer, *cis*-4,5-benzo-1,3-di(*tert*-butyl)-1,3-dimethyl-2-oxa-1,3-disilacyclopent-4-ene (**4a**) in 84% isolated yield, while with **1b**, the *trans*-isomer (**4b**) was isolated in 80% yield as a single product. Treatment of **1a** and **1b** with MCPBA in benzene at room temperature proceeded stereospecifically to give the corresponding cyclic siloxanes, quantitatively. All spectral data for the cyclosiloxanes were consistent with those obtained by the reaction with oxygen-AIBN.

To have a better understanding of the results obtained in the present experiments, computational analyses of the adduct of 1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene (**5**) and $CH_3OO^{\bullet}$ radical were carried out using the

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[1] Brook, A. G. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 2, Chapter 17.

[2] Naka, A.; Ishikawa, M. *Synlett* **1995**, 794, and references therein.

[3] Tamao, K.; Ishikawa, M.; Kumada, M. *Chem. Commun.* **1969**, 73. (b) Tamao, K.; Kumada, M.; Ishikawa, M. *J. Organomet. Chem.* **1971**, *31*, 17.

[4] The reaction of pure *meso*-**3** with sodium in refluxing toluene gave a mixture of **1a** and **1b** in a ratio of 4:6 in 94% yield, while pure *dl*-**3** afforded **1a** and **1b** in the ratio of 7:3 in 97% yield.

[5] Shiina, K. *J. Organomet. Chem.* **1986**, *310*, C57.

[6] Ishikawa, M.; Sakamoto, H.; Tabuchi, T. *Organometallics* **1991**, *10*, 3173.

10.1021/om000909q CCC: $20.00

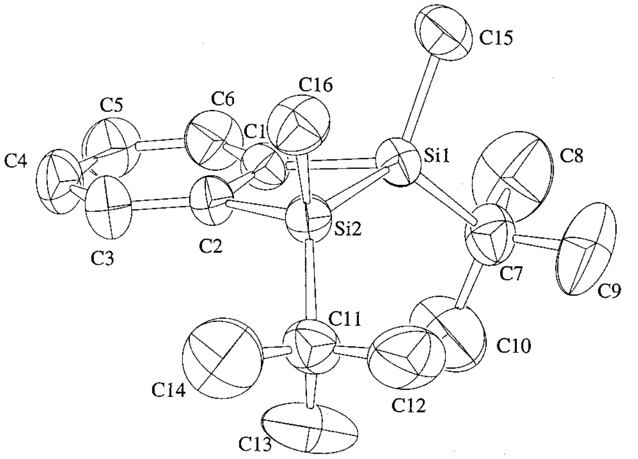

Figure 1. ORTEP diagram for **1a** showing thermal ellipsoids at the 50% level; hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Si(1)–Si(2) 2.355(1), Si(1)–C(1) 1.892(2), Si(2)–C(2) 1.892(2), C(1)–C(2) 1.413(3); Si(2)–Si(1)–C(1) 75.72(8), Si(1)–Si(2)–C(2) 75.42(8), Si(1)–C(1)–C(2) 104.2(2), Si(2)–C(2)–C(1) 104.7(2).

Gaussian 98 program[8] at the UB3LYP/6-311+G** level of density functional theory.[9–11] A computed potential energy profile, including zero-point energy corrections, along the reaction pathway is presented in Figure 2. Since the energy profile is highly exothermic, this reaction is expected to proceed spontaneously. The first step of the reaction is the formation of $CH_3OO^{\bullet}$ radical from methyl radical and dioxygen, which takes place at no cost of energy.[12] The resultant $CH_3OO^{\bullet}$ radical readily attacks **5** to lead to the dissociation of the Si–Si bond; this process should occur with no potential energy barrier. The final step of the reaction is the formation of the Si–O–Si bridge, and at the same time the O–O bond is cleaved to produce the $CH_3O^{\bullet}$ radical, which can continue this type of the radical reaction.

The activation barrier for the transition state was computed to be only 2.8 kcal/mol. If this barrier is lower than the energy required for the rotation of the dihedral angle C=C–Si–CH_3, we can reasonably conclude that this oxidation should proceed with retention of stereochemistry. Thus, we decided to compare the two quantities. Figure 3 shows computed potential energies as a function of the dihedral angle while the other geometrical parameters are fixed. The torsional barrier was calculated to require an activation barrier higher than that of the formation of the Si–O–Si bridging. The cause for the torsional barrier is the steric repulsion between the methyl groups on the neighboring silicon atoms. Therefore the oxidation of benzodisilacyclobutene is likely to occur stereospecifically despite the involvement of radical species.

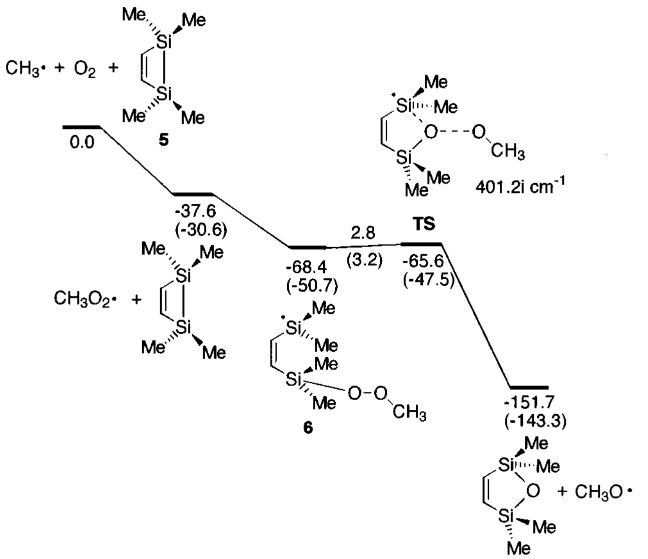

Figure 2. Potential energy diagram for the oxidation of disilacyclobutene (**5**) at the UB3LYP/6-311+G** level. Relative energies are in kcal/mol. The values in parentheses are free energies at 298 K.

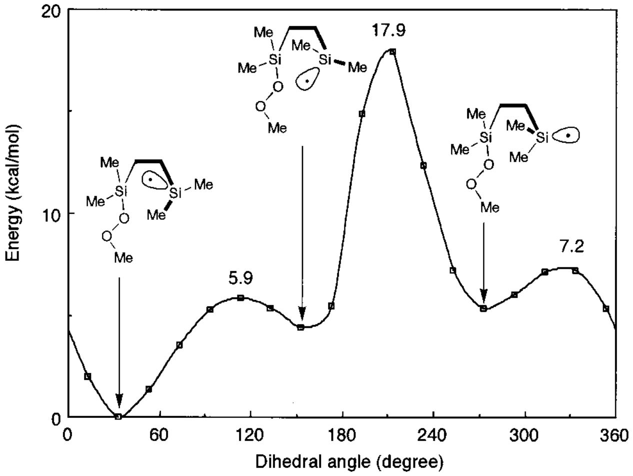

Figure 3. Energy profiles along C–$SiMe_2$ torsional coordinate for **6** at the UB3LYP/6-311+G** level. The dihedral angle is defined by a thick line.

Treatment of a carbon tetrachloride solution of **1a** with chlorine gas[13] at 0 °C afforded the *meso*-isomer of **3** in almost quantitative yield (Scheme 3). ^{1}H and ^{13}C NMR spectrometric analysis of the reaction mixture shows no *dl*-isomer, indicating that cleavage of the Si–Si bond in **1a** by chlorine proceeds with high stereospecificity. Similar treatment of **1b** with chlorine under the same conditions gave *dl*-**3** quantitatively.

The fact that the structure of the chlorosilane formed from the reaction of **1a** with chlorine is a *meso*-form was

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(7) It has been reported that the reaction of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane with peroxybenzoic acid proceeds stereospecifically to give the respective *cis*- and *trans*-cyclic siloxane; see ref 3b.

(8) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.6; Gaussian Inc.: Pittsburgh, PA, 1998.

(9) (a) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

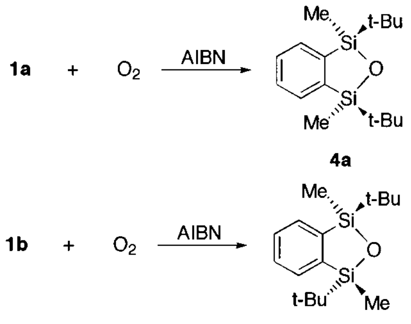
(10) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.

(11) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (c) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

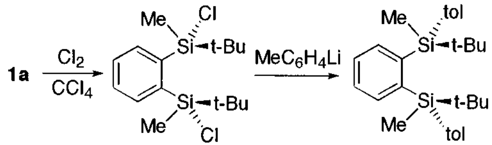
(12) Branko, S. J. *J. Phys. Chem. A* **1997**, *101*, 2345.

(13) Kumada, M.; Tamao, K. *Adv. Organomet. Chem.* **1968**, *6*, 19.

Scheme 2



Scheme 3



meso-**3**

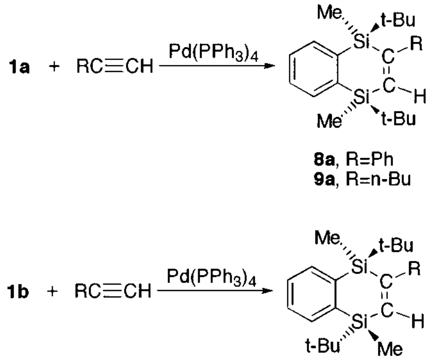
7a

verified by X-ray crystallographic analysis of the tolyl derivative (**7a**) obtained from the reaction of *meso*-**3** and *p*-tolyllithium.[14]

Previously, we reported that the transition-metal-catalyzed reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene with alkynes afforded 5,6-benzo-1,4-disilacyclohexa-2,5-dienes arising from insertion of a triple bond of the alkynes into an Si−Si bond in the starting benzodisilacyclobut-3-ene.[2] It is of interest to us to investigate the stereochemistry of the transition-metal-catalyzed reaction of the benzodisilacyclobut-3-ene with unsaturated compounds.

When **1a** and **1b** were heated with phenylacetylene in a sealed glass tube at 250 °C for 24 h, no adducts were detected in the reaction mixture. The starting compounds **1a** and **1b** were recovered unchanged. However, in the presence of a palladium catalyst, **1a** and **1b** readily reacted with monosubstituted acetylenes to give the respective adducts derived from insertion of a carbon−carbon triple bond into a silicon−silicon bond in benzodisilacyclobutenes. Thus, the reaction of **1a** with a 3.5-fold excess of phenylacetylene in the presence of a catalytic amount of tetrakis(triphenylphosphine)-palladium(0) in a sealed glass tube at 150 °C for 24 h gave *cis*-5,6-benzo-1,4-di(*tert*-butyl)-1,4-dimethyl-2-phenyl-1,4-disilacyclohexa-2,5-diene (**8a**) in 84% isolated yield. No *trans*-isomer was detected by GLC analysis and also by spectrometric analysis of the mixture. Similarly, treatment of **1b** with phenylacetylene under the same conditions afforded the *trans*-isomer (**8b**) in 89% isolated yield (Scheme 4). Again, no *cis*-isomer **8a** was detected in the reaction mixture. When **1a** was treated with 1-hexyne in the presence of the palladium catalyst under the same conditions, *cis*-5,6-benzo-2,3-di(*n*-butyl)-1,4-di(*tert*-butyl)-1,4-dimethyl-1,4-disilacyclohexa-2,5-diene (**9a**) was formed in 95% yield, as a single stereoisomer. Similar reaction of **1b** with 1-hexyne proceeded stereospecifically to give the *trans*-isomer (**9b**) in 90% yield.

Scheme 4



The structures of **8a**,**b** and **9a**,**b** were verified by mass and ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analysis, as well as by elemental analysis. The configurations of **8a**,**b** and **9a**,**b** were confirmed by NOE-FID difference experiments at 300 MHz.[15] These results clearly indicate that palladium-catalyzed reactions of **1a** and **1b** with monosubstituted acetylene proceed with retention of configuration.

In conclusion, the reaction of **1a** and **1b** with oxygen in the presence of AIBN proceeded to give the respective siloxanes **4a** and **4b** with high stereospecificity. Theoretical calculations also suggested that the reaction of **1a** and **1b** with oxygen-AIBN should proceed stereospecifically to give **4a** and **4b**. With chlorine in carbon tetrachloride, **1a** and **1b** reacted stereospecifically to give **3a** and **3b**, respectively. The palladium-catalyzed reactions of **1a** and **1b** with monosubstituted acetylenes afforded the respective 5,6-benzo-1,4-disilacyclohexa-2,4-dienes stereospecifically.

Acknowledgment. This work was supported by the Research for the Future Program from the Japan Society for the Promotion of Science (JSPS-RFTF96P00206).

Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1a** and **7a** in CIF. Experimental details and characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] It has been reported that the reaction of chlorosilanes with aryllithium proceeds with inversion of configuration; see for example: Sommer, L. H.; Korte, W. D. *J. Am. Chem. Soc.* **1967**, *89*, 5802.

[15] For **8a**: Irradiation of the *tert*-butyl protons on one silicon atom at 0.80 ppm resulted in strong enhancement of the protons in the *tert*-butyl group on the other silicon atom at 1.11 ppm, as well as the methylsilyl group at 0.62 ppm. For **8b**: Saturation of the *tert*-butyl protons at 0.89 ppm caused a positive NOE of the protons in the methylsilyl group at 0.39 ppm.