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Stereochemistry of Disilanylene-Containing Cyclic Compounds. Synthesis and Reactions of *cis*- and *trans*-1,2-Dimethyl-1,2-diphenyl-1,2-disilacyclopentanes

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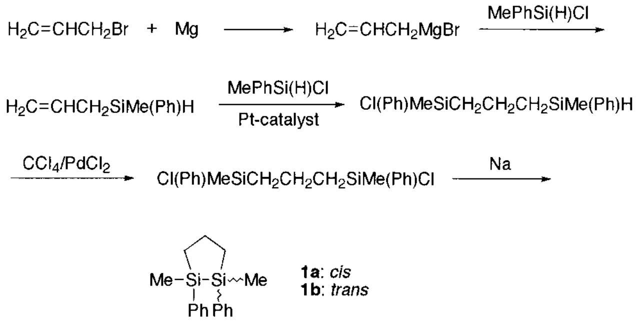
The Wurtz type coupling of a mixture of *meso*- and *dl*-1,3-bis(chloromethylphenylsilyl)-propanes with sodium metal afforded a mixture of *cis*- and *trans*-disilacyclopentanes (**1a** and **1b**) in a ratio of 1:1. Pure **1a** and **1b** obtained by fractional distillation reacted with molecular oxygen in the presence of AIBN stereospecifically to give the respective *cis*- and *trans*-cyclic siloxanes (**2a** and **2b**), with retention of configuration. The reactions of **1a** and **1b** with MCPBA produced cleanly **2a** and **2b** in high yields, respectively. The palladium-catalyzed reactions of **1a** and **1b** with phenylacetylene gave stereospecifically *cis*- and *trans*-1,4-dimethyl-1,2,4-triphenyl-1,4-disilacyclohept-2-enes (**3a** and **3b**), in high yields. Similar treatment of **1a** and **1b** with diphenylacetylene also proceeded with high stereospecificity to give *cis*- and *trans*-1,4-dimethyl-1,2,3,4-tetraphenyl-1,4-disilacyclohept-2-enes (**4a** and **4b**), respectively. The results of an X-ray crystallographic study for products **4a** and **4b** are described.

Introduction

The stereochemisty of the reactions on a silicon center has been investigated in detail using optical active silicon compounds by Sommer and co-workers[1] and later by Corriu et al.[2] Many papers dealing with the stereochemistry of silicon compounds have been published. However, little interest has been shown in the stereochemistry of the disilacyclic system, which involves geometric isomerism. To our knowledge, the synthesis and some reactions of *cis*- and *trans*-1,1,2,2-tetrasubstituted-1,2-disilacyclohexanes have been reported so far.[3]

Recently, we have found that *cis*- and *trans*-3,4-benzo-1,2-di(*tert*-butyl)-1,2-dimethyl-1,2-disilacyclobut-3-enes react with molecular oxygen in the presence of a catalytic amount of azobis(isobutyronitrile) to give the respective *cis*- and *trans*-4,5-benzo-2-oxa-1,3-disilacyclopent-4-enes with high stereospecificity.[4] We have also found that the palladium-catalyzed reactions of the *cis*- and *trans*-isomer of the benzodisilacyclobutene with monosubstituted acetylenes proceed to give the respective *cis*- and *trans*-5,6-benzo-1,4-disilacyclohexa-2,5-dienes with high stereospecificity.[4] It is of interest to us to investigate the stereochemistry of the five-membered cyclic system. In this paper, we report the first synthesis and stereochemistry of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentanes.

Scheme 1



Results and Discussion

Synthesis. The starting compounds, *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentanes (**1a** and **1b**), were prepared by a series of reactions shown in Scheme 1. Treatment of allylmagnesium bromide, prepared from the reaction of allyl bromide with magnesium in THF, with chloromethylphenylsilane afforded allylmethylphenylsilane in 77% yield. Hydrosilylation of allylmethylphenylsilane with chloromethylphenylsilane in the presence of a catalytic amount of hydrogen

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(1) Sommer, L. H. *Stereochemistry, Mechanism and Silicon: An Introduction to the Dynamic Stereochemistry and Reaction Mechanisms of Silicon Centers*; McGraw-Hill: New York, 1965.

(2) (a) Corriu, R. J. P.; Guérin, C.; Moreau, J. J. E. *Top. Stereochem.* **1984**, *15*, 43. (b) Colomer, E.; Corriu, R. J. P. *Top. Curr. Chem.* **1981**, *96*, 79.

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

(4) Ishikawa, M.; Ikadai, J.; Naka, A.; Ohshita, J.; Kunai, A.; Yoshizawa, K.; Kang, S.-Y.; Yamabe, T., in press.

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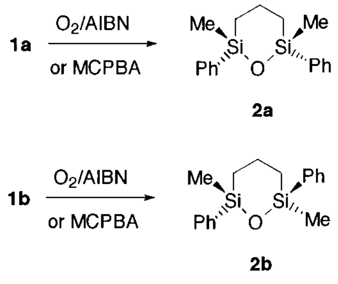
Scheme 2



hexachloroplatinate hexahydrate produced 1-(chloromethylphenylsilyl)-3-(methylphenylsilyl)propane in 54% yield.

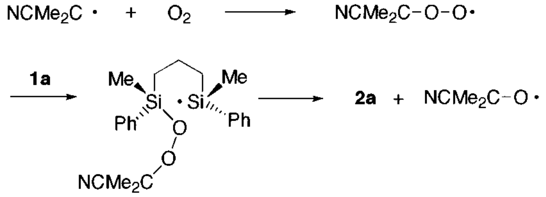
The Cl−H exchange reaction of the resulting hydrosilylation product with carbon tetrachloride in the presence of a palladium chloride catalyst gave 1,3-bis(chloromethylphenylsilyl)propane in 93% yield. Finally, Wurtz type coupling of the resulting 1,3-bis(chloromethylphenylsilyl)propane with sodium metal in refluxing toluene yielded a mixture of *cis*- and *trans*-1,2-disilacyclopentanes **1a** and **1b** in 52% combined yield. The ratio of **1a** and **1b** in the reaction mixture was calculated to be 1:1 by ^{1}H NMR spectrometric analysis of the mixture.

The pure *cis*- and *trans*-isomers could readily be isolated by fractional distillation using a spinning band distillation column with 50 theoretical plates. The geometrical configurations of the isomers **1a** and **1b** were readily established on the basis of ^{1}H NMR spectrometric analysis. Thus, in the *cis*-isomer, two hydrogens on the C_4 carbon in the 1,2-disilacyclopentane ring are nonequivalent and appear at 1.80 and 2.06 ppm as multiplet signals, while in the *trans*-isomer, two hydrogens on C_4 ring carbon are equivalent and appear at 1.96 ppm as a quintet. Both ^{13}C and ^{29}Si NMR spectra for **1a** and **1b** are also consistent with the proposed structures.

Oxidation Reaction. *cis*- and *trans*-1,2-Disilacyclopentanes **1a** and **1b** are stable toward molecular oxygen in air. They do not react with oxygen in air at room temperature. However, **1a** and **1b** react with molecular oxygen in the presence of α,α′-azobis(isobutyronitrile) (AIBN) in refluxing toluene to give the respective 1,3-dimethyl-1,3-diphenyl-2-oxa-1,3-disilacyclohexanes (**2a** and **2b**). Thus, treatment of **1a** with molecular oxygen in the presence of a catalytic amount of AIBN in refluxing toluene proceeded to give a cyclic siloxane in 27% yield, as a single stereoisomer, in addition to 73% of the starting compound **1a** (Scheme 2). No other isomer was detected in the reaction mixture by spectrometric analysis.

As reported recently, we found that oxidation of an Si−Si bond in a cyclic four-membered system by *m*-chloroperoxybenzoic acid (MCPBA) proceeded stereospecifically to give the cyclic siloxane with retention of configuration.[4] To confirm the configuration of the product obtained from the reaction of **1a** with molecular oxygen, we carried out the reaction of **1a** with MCPBA.[3b,5] Treatment of **1a** with 1 equiv of MCPBA in refluxing benzene afforded stereospecifically *cis*-1,3-dimethyl-1,3-diphenyl-2-oxa-1,3-disilacyclohexane (**2a**) in 88% yield, as the sole product. All spectral data for **2a** were identical with those of the product obtained from the reaction of molecular oxygen in the presence of AIBN. This result clearly indicates that the reaction of **1a** with oxygen in the presence of AIBN proceeds stereospecifically to give *cis*-siloxane **2a** with retention of the configuration.

Scheme 3



Similarly, treatment of **1b** with oxygen in the presence of AIBN in refluxing toluene gave *trans*-1,3-dimethyl-1,3-diphenyl-2-oxa-1,3-disilacyclohexane (**2b**) in 29% yield, together with 64% of the starting compound **1b**. In fact, all spectral data for **2b** were identical with those of the product obtained from the reaction of **1b** with MCPBA in refluxing benzene in 87% yield.

We have carried out computational analyses for the reaction of 1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene with molecular oxygen in the presence of a radical catalyst and proposed a mechanism for the formation of the cyclic siloxane.[4] We have also concluded that this reaction proceeds with retention of configuration. In fact, we found that oxidation of a silicon−silicon bond in *cis*- and *trans*-3,4-benzo-1,2-di(*tert*-butyl)-1,2-dimethyl-1,2-disilacyclobut-3-ene by the use of oxygen-AIBN afforded the respective *cis*- and *trans*-4,5-benzo-2-oxa-1,3-disilacyclopent-4-enes stereospecifically.

The present reaction of **1a** and **1b** with oxygen-AIBN probably proceeds in the same manner as that of the *cis*- and *trans*-benzodisilacyclobut-3-ene. For example, in the reaction of **1a** with oxygen-AIBN, the radical generated thermally from AIBN would react with molecular oxygen to give a peroxy radical in the initial step. The resulting peroxy radical presumably attacks a silicon atom in the 1,2-disilacyclopentane ring of **1a**, producing a ring-opened silyl radical, which undergoes ring closure to give *cis*-cyclic siloxane **2a**, with retention of configuration, as shown in Scheme 3.

Palladium-Catalyzed Reaction. Recently, we found that *cis*- and *trans*-3,4-benzo-1,2-di(*tert*-butyl)-1,2-dimethyl-1,2-disilacyclobut-3-enes reacted with alkynes in the presence of a palladium catalyst to give the respective *cis*- and *trans*-5,6-benzo-1,4-di(*tert*-butyl)-1,4-dimethyl-1,4-disilacyclohexa-2,5-dienes.[4,6] To learn more about the stereochemistry of the disilacyclopentane system, we carried out the palladium-catalyzed reactions of **1a** and **1b** with alkynes.[7] Thus, the reaction of **1a** with 3-fold excess of phenylacetylene in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) in a sealed glass tube at 200 °C produced

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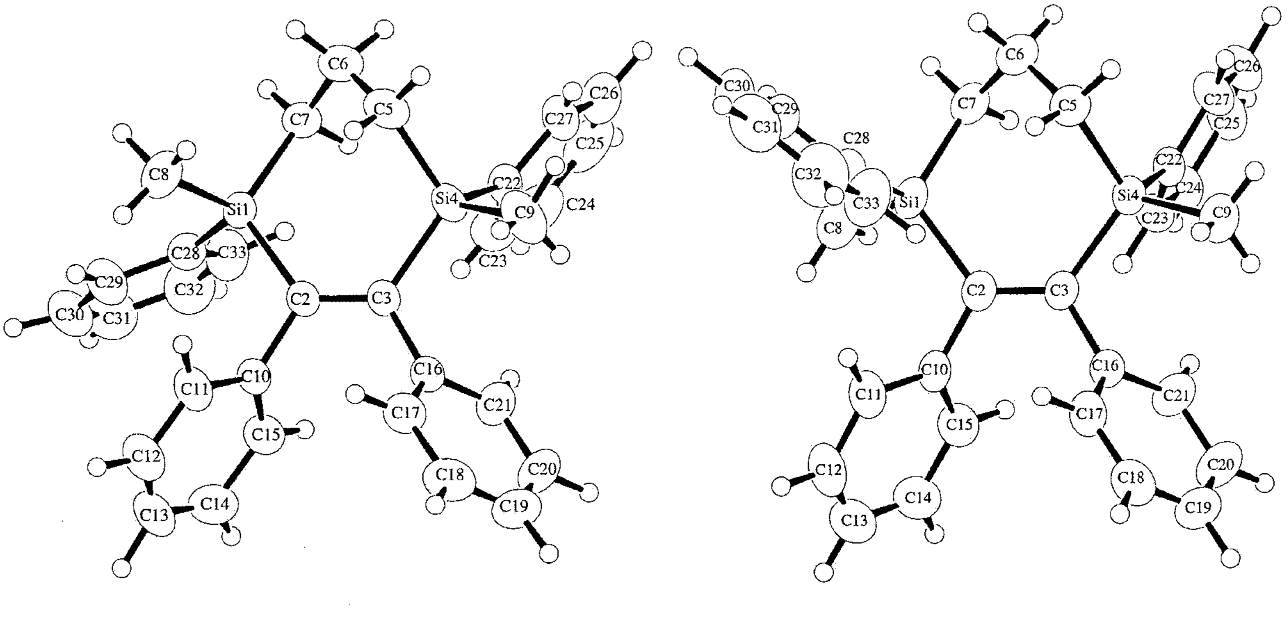
(5) Sakurai, H.; Imoto, T.; Hayashi, N.; Kumada, M. *J. Am. Chem. Soc.* **1965**, *87*, 4001.

(6) The transition-metal-catalyzed reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene have been reported in the following review article: Naka, A.; Ishikawa, M. *Synlett* **1995**, 794.

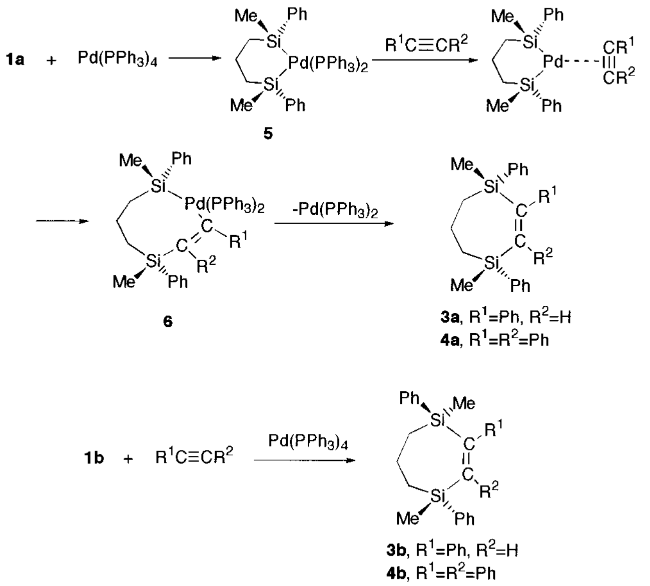
(7) Palladium-catalyzed reactions of 1,1,2,2-tetramethyl-1,2-disilacyclopentane and insertion of phenylacetylene into a silicon−silicon bond in the trimer have been reported, see: Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, *97*, 931. And also: Suginome, M.; Oike, H.; Shuff, H.; Ito, Y. *Organometallics* **1996**, *15*, 2170.



4a 4b

Figure 1. ORTEP diagram for **4a** and **4b** showing thermal ellipsoids at the 40% level. One of two independent molecules in the crystal of a *trans* form is displayed, since these two molecules have quite the same structure. Selected torsional angles (deg): (**4a**) C5−C6−C7−Si1 = 47.9(3), C6−C7−Si1−C2 = −74.7(2), C7−Si1−C2−C3 = 13.9(2), Si1−C2−C3−Si4 = 8.8 (3), C2−C3−Si4−C5 = 29.2(2), C3−Si4−C5−C6 = −83.2(2), and Si4−C5−C6−C7 = 39.4(3); (**4b**) C5−C6−C7−Si1 = 47.6(2), C6−C7−Si1−C2 = −76.1(2), C7−Si1−C2−C3 = 19.4(2), Si1−C2−C3−Si4 = 2.2 (2), C2−C3−Si4−C5 = 33.5(2), C3−Si4−C5−C6 = −83.5(2), and Si4−C5−C6−C7 = 39.3(3).

Scheme 4



cis-1,4-dimethyl-1,2,4-triphenyl-1,4-disilacyclohept-2-ene (**3a**) in 86% yield, in addition to 11% of the unchanged compound **1a** (Scheme 4). No other stereoisomer was detected in the reaction mixture. Similar treatment of **1b** with phenylacetylene under the same conditions afforded *trans*-1,4-disilacyclohept-2-ene (**3b**) in 89% yield, as a single stereoisomer. The structures of **3a** and **3b** were verified by mass and ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analysis, as well as by elemental analysis. Compounds **1a** and **1b** also reacted stereospecifically with diphenylacetylene to give the respective adducts. Treatment of **1a** with diphenylacetylene in a degassed sealed tube at 200 °C produced *cis*-1,4-dimethyl-1,2,3,4-tetraphenyl-1,4-disilacyclohept-2-ene (**4a**) in 55% yield as white crystals, in addition to 41% of the unreacted starting compound **1a**.

Similarly, the reaction of **1b** with diphenylacetylene under the same conditions gave *trans*-adduct **4b** in 55% yield, as white crystals, together with 33% of the starting compound **1b**. Again, the reaction proceeded with high stereospecificity. No other isomer was detected in the mixture by spectrometric analysis. The structure of **4b** was confirmed by mass, IR, and ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analysis, as well as by elemental analysis. Molecular structures of **4a** and **4b** were determined by X-ray crystallographic methods as shown in Figure 1. The atoms Si1, C2, C3, and Si4 of **4a** and **4b** are coplanar within 0.045(1) and 0.011(1) Å, with C5, C6, and C7 deviating by 1.005(3), 0.342(4), and −0.594(3) Å, and 1.003(3), 0.321(4), and −0.614(3) Å, respectively, indicating that the conformation of the seven-membered rings in both forms are essentially the same. This result clearly indicates that the reaction of **1a**,**b** with diphenylacetylene proceeds to give the adduct with retention of configuration.

Scheme 4 shows a mechanism for the stereospecific production of *cis*-1,4-disilacyclohept-2-enes **3a** and **4a** using **1a** as an example.

The formation of **3a**,**b** and **4a**,**b** may be explained in terms of insertion of a palladium species into a silicon−silicon bond in **1a**,**b** to give a 2-pallada-1,3-disilacyclohexane with retention of the configuration, followed by coordination of an alkyne to the palladium atom in the intermediate **5**. Insertion of the alkyne on the palladium atom into a silicon−palladium bond affords stereospecifically 2-pallada-1,5-disilacyclooct-3-ene (**6**). Finally, reductive elimination of the palladium species gives the 1,4-disilacyclohept-2-ene with retention of the configuration.

In conclusion, Wurtz type condensation of 1,3-bis(chloromethylphenylsilyl)propane afforded a 1:1 mixture of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentanes **1a** and **1b** in high yields. The reactions of **1a** and **1b** with oxygen in the presence of AIBN produced *cis*- and *trans*-2-oxa-1,2-disilacyclohexanes, respectively, with high stereospecificity. The palladium-catalyzed reactions of **1a** and **1b** with phenylacetylene and diphenylacetylene proceeded stereospecifically to give the respective adducts arising from insertion of a triple bond into a silicon−silicon bond in **1a** and **1b**.

Experimental Section

General Procedure. All palladium-catalyzed reactions were carried out in a degassed sealed tube (1.0 cm × 15 cm). Yields of the products **2a**, **2b**, **3a**, and **3b** were calculated on the basis of the isolated products. Yields for **4a** and **4b** were determined by analytical GLC with the use of *n*-pentadecane as an internal standard, on the basis of the starting materials used. NMR spectra were recorded on a JNM-LA300 spectrometer and JNM-LA500 spectrometer. Infrared spectra were recorded on a JEOL Model JIR-DIAMOND 20 infrared spectrophotometer. Low- and high-resolution mass spectra were measured on a JEOL Model JMS-700 instrument. Pure *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane were separated by a TSA-SB2 spinning band type distillation column (Taika Kogyo). Melting points were measured with a Yanaco-MP-S3 apparatus. Column chromatography was performed by using Wakogel C-300 (WAKO). Tetrahydrofuran, ether, and toluene used as a solvent were dried over sodium/benzophenone under a nitrogen atmosphere and distilled just before use. Carbon tetrachloride was dried over diphosphorus pentoxide and distilled before use.

Preparation of Allylmethylphenylsilane. In a 1 L four-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed allylmagnesium bromide prepared from 28.2 g (1.16 mol) of magnesium and 139.0 g (1.15 mol) of allyl bromide in a mixed solvent of THF (350 mL) and ether (50 mL). To this was added 130.7 g (0.84 mol) of chloromethylphenylsilane over a period of 3 h at room temperature. The mixture was stirred at room temperature for 12 h and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and extracts were combined and washed with water and then dried over magnesium sulfate. The solvents were evaporated off, and the residue was fractionally distilled under reduced pressure to give 100.0 g (0.62 mmol) of allylmethylphenylsilane (74% yield): bp 85−93 °C/15 Torr; MS *m*/*z* 162 (M$^+$); ^{1}H NMR δ (CDCl$_3$) 0.38 (d, 3H, MeSi, J = 3.7 Hz), 1.81−1.91 (m, 2H, CH$_2$Si), 4.39 (sextet, 1H, HSi, J = 3.7 Hz), 4.90−4.96 (m, 2H, C*H$_2$*═C), 5.79−5.88 (m, 1H, C*H*═CH$_2$), 7.36−7.42 (m, 3H, phenyl ring protons), 7.55−7.75 (m, 2H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −6.29 (MeSi), 21.05 (CH$_2$Si), 114.02 (CH$_2$═), 127.83, 129.38, 134.09, 134.32, 135.60 (phenyl ring and olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −15.12. Anal. Calcd for $C_{10}H_{14}Si$: C, 74.00; H, 8.69. Found: C, 74.05; H, 8.63.

Preparation of 1-Chloromethylphenylsilyl-3-methylphenylsilylpropane. In a 500 mL three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 133.0 g (0.85 mol) of chloromethylphenylsilane and 0.1 mL (0.02 mmol) of an isopropyl alcohol solution of hydrogen hexachloroplatinate hexahydrate. To this was added 100.0 g (0.62 mol) of allylmethylphenylsilane at 155 °C over a period of 3 h. The mixture was heated at 180 °C for 12 h and then cooled to room temperature. The mixture was fractionally distilled under reduced pressure to give 106.0 g (0.33 mmol) of 1-chloromethylphenylsilyl-3-methylphenylsilylpropane (54% yield): bp 170−172 °C/2 Torr; MS *m*/*z* 317 (M$^+$ − 1); IR 3070, 3021, 2960, 2919, 2115 (Si−H), 1429, 1255, 1114, 910, 877, 788, 732, 698 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.43 (d, 3H, MeSi, J = 3.7 Hz), 0.73 (s, 3H, MeSi), 1.01−1.11 (m, 2H, CH$_2$), 1.24−1.39 (m, 2H, CH$_2$), 1.68−1.75 (m, 2H, CH$_2$), 4.48 (sextet, 1H, HSi, J = 3.7 Hz), 7.43−7.71 (m, 10H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −5.71, 0.38 (MeSi), 17.19, 18.16, 21.72 (CH$_2$), 127.85, 128.02, 129.22, 130.23, 133.26, 134.25, 135.40, 136.24 (phenyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) −14.15, 20.2. Anal. Calcd for $C_{17}H_{23}Si_2Cl$: C, 64.01; H, 7.27. Found: C, 64.28; H, 7.21.

Preparation of 1,3-Bis(chloromethylphenylsilyl)propane. In a 500 mL three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 0.0344 g (0.195 mmol) of palladium chloride and 300 mL of carbon tetrachloride. To this solution was added 137.7 g (0.42 mol) of 1-chloromethylphenylsilyl-3-methylphenylsilylpropane at room temperature over a period of 1 h. The mixture was heated to reflux for 6 h, and then the resulting chloroform and unchanged carbon tetrachloride were evaporated off. The residue was distilled under reduced pressure to give 137.6 g (0.39 mmol) of 1,3-bis(chloromethylphenylsilyl)propane (93% yield): MS *m*/*z* 352 (M$^+$); IR 3070, 3050, 3025, 2962, 2925, 2873, 1429, 1257, 1114, 900, 788, 734, 698, 649 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.69 (s, 6H, MeSi), 1.16−1.26 (m, 4H, CH$_2$Si), 1.72 (quint, 2H, CH$_2$, J = 7.9 Hz), 7.38−7.55 (m, 6H, phenyl ring protons), 7.62−7.64 (m, 4H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) 0.39 (MeSi), 16.95, 21.61 (CH$_2$), 128.07, 130.31, 133.26, 135.22 (phenyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) 20.1. Anal. Calcd for $C_{17}H_{22}Si_2Cl_2$: C, 57.77; H, 6.27. Found: C, 57.56; H, 5.97.

Preparation of *cis*- and *trans*-1,2-Dimethyl-1,2-diphenyl-1,2-disilacyclopentane. In a 500 mL three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 27.9 g (1.21 mol) of sodium and 300 mL of toluene. The mixture was heated to reflux and stirred to prepare a sodium dispersion. To this was added 137.6 g (0.39 mol) of 1,3-bis(chloromethylphenylsilyl)propane over a period of 4 h. After the mixture was heated to reflux for 2 h, the solvent was distilled off. The residue was distilled under reduced pressure to give 57.0 g (0.20 mol) of a mixture of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane (52% yield). Pure *cis*- and *trans*-compounds were separated by a spinning band type distillation column. For *cis*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane (**1a**): bp 144.0 °C/2 Torr; MS *m*/*z* 282 (M$^+$); IR 3066, 3020, 3008, 2898, 2846, 1427, 1249, 1106, 1072, 998, 914, 790, 775, 723, 698 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.45 (s, 6H, MeSi), 0.97−1.17 (m, 4H, CH$_2$Si), 1.72−1.87 (m, 1H, CH$_2$), 1.99−2.12 (m, 1H, CH$_2$), 7.15−7.26 (m, 6H, phenyl ring protons), 7.32−7.35 (m, 4H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −4.98 (MeSi), 18.09 (CH$_2$Si), 23.03 (CH$_2$), 127.59, 128.45, 134.46, 137.48 (phenyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) −14.9. Anal. Calcd for $C_{17}H_{22}Si_2$: C, 72.27; H, 7.85. Found: C, 72.42; H, 7.75. For *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane (**1b**): bp 149.7 °C/2 Torr; MS *m*/*z* 282 (M$^+$); IR 3066, 3020, 2994, 2898, 2846, 1427, 1247, 1106, 997, 914, 800, 765, 730, 711, 698 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.31 (s, 6H, MeSi), 0.97 (dt, 2H, CH$_2$Si, J = 13.4 Hz, 6.7 Hz), 1.20 (dt, 2H, CH$_2$Si, J = 13.4 Hz, 6.7 Hz), 1.96 (quint, 2H, CH$_2$, J = 6.7 Hz), 7.33−7.37 (m, 6H, phenyl ring protons), 7.50−7.53 (m, 4H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −4.76 (MeSi), 18.02 (CH$_2$Si), 23.43 (CH$_2$), 127.85, 128.53, 134.29, 138.08 (phenyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) −14.6. Anal. Calcd for $C_{17}H_{22}Si_2$: C, 72.27; H, 7.85. Found: C, 71.93; H, 7.87.

Reaction of 1a with Oxygen in the Presence of α,α′-Azobis(isobutyronitrile). In a 30 mL two-necked flask fitted with a stirrer and reflux condenser attached to an oxygen balloon was placed a mixture of 0.1586 g (0.53 mmol) of **1a** and 0.0056 g (0.034 mmol) of α,α′-azobis(isobutyronitrile) in 10 mL of dry toluene. The mixture was heated to reflux under an oxygen atmosphere for 24 h, and then an additional 0.0027 g (0.016 mmol) of α,α′-azobis(isobutyronitrile) was added to the mixture. Again the mixture was heated to reflux for 24 h.

The solvent was evaporated off, and the residue was chromatographed on a silica gel column eluting with hexane to give product **2a** (0.0434 g, 27%) and unchanged **1a** (0.1152 g, 73%). For **2a**: MS *m/z* 298 (M$^+$); IR 3068, 3048, 2954, 2904, 2850, 1427, 1253, 1116, 987, 796, 777, 732, 698 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.46 (s, 6H, MeSi), 0.89−1.02 (m, 4H, CH$_2$Si), 1.96−2.09 (m, 2H, CH$_2$), 7.34−7.41 (m, 6H, phenyl ring protons), 7.57−7.59 (m, 4H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −0.15 (MeSi), 16.19 (CH$_2$Si), 17.83 (CH$_2$), 127.70, 129.39, 133.15, 138.64 (phenyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) 3.05. Anal. Calcd for $C_{17}H_{22}Si_2O$: C, 68.40; H, 7.43. Found: C, 68.10; H, 7.41.

Reaction of 1b with Oxygen in the Presence of α,α′-Azobis(isobutyronitrile). In a 30 mL two-necked flask fitted with a stirrer and reflux condenser attached to an oxygen balloon was placed a mixture of 0.1870 g (0.66 mmol) of **1b** and 0.0011 g (0.0067 mmol) of α,α′-azobis(isobutyronitrile) in 10 mL of dry toluene. The mixture was heated to reflux for 24 h, and an additional 0.0012 g (0.0073 mmol) of α,α′-azobis(isobutyronitrile) was added to the mixture. Again, the mixture was heated to reflux for 24 h under an oxygen atmosphere. The solvent was evaporated off, and the residue was chromatographed on silica gel to give **2b** (0.056 g, 29%) and unchanged **1b** (0.1189 g, 64%). For **2b**: MS *m/z* 298 (M$^+$); IR 3068, 3048, 2954, 2904, 2850, 1427, 1253, 1118, 1002, 989, 929, 802, 779, 700 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.42 (s, 6H, MeSi), 0.88 (dt, 2H, CH$_2$Si, J = 14.0 Hz, 7.0 Hz), 1.00 (dt, 2H, CH$_2$Si, J = 14.0 Hz, 7.0 Hz), 1.95 (quint, 2H, CH$_2$, J = 7.0 Hz), 7.41−7.43 (m, 6H, phenyl ring protons), 7.64−7.66 (m, 4H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) 0.00 (MeSi), 16.31 (CH$_2$Si), 17.64 (CH$_2$), 127.79, 129.41, 133.07, 138.96 (phenyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) 3.08. Anal. Calcd for $C_{17}H_{22}Si_2O$: C, 68.40; H, 7.43. Found: C, 68.22; H, 7.33.

Reaction of 1a with *m*-Chloroperoxybenzoic Acid. In a 30 mL two-necked flask fitted with a stirrer and reflux condenser was placed a mixture of 0.1566 g (0.55 mmol) of **1a** and 0.1345 g (0.78 mmol) of *m*-chloroperbenzoic acid in 15 mL of dry benzene. The mixture was heated to reflux for 72 h, and the solvent was evaporated off. Compound **2a** (0.1448 g, 88%) was isolated by silica gel column chromatography. All spectral data for **2a** were identical with those of an authentic sample obtained from the above reaction.

Reaction of 1b with *m*-Chloroperoxybenzoic Acid. In a 30 mL two-necked flask fitted with a stirrer and reflux condenser was placed a mixture of 0.1822 g (0.65 mmol) of **1b** and 0.1457 g (0.84 mmol) of *m*-chloroperbenzoic acid in 15 mL of dry benzene. The mixture was heated to reflux for 72 h, and the solvent was evaporated off. Compound **2b** (0.1670 g, 87%) was isolated by silica gel column chromatography. All spectral data for **2b** were identical with those of an authentic sample obtained from the above reaction.

Palladium-Catalyzed Reaction of 1a with Phenylacetylene. A mixture of 0.2130 g (0.75 mmol) of **1a**, 0.2559 g (2.51 mmol) of phenylacetylene, and 0.0241 g (0.021 mmol) of tetrakis(triphenylphosphine)palladium(0) was heated in a degassed sealed tube at 200 °C for 24 h. The palladium species in the resulting mixture was removed by passing through a short silica gel column. Compound **3a** (0.2491 g, 86%) was isolated by column chromatography, together with **1a** (0.0236 g, 11%). For **3a**: MS *m/z* 384 (M$^+$); IR 3066, 3016, 2898, 1594, 1486, 1427, 1251, 1110, 908, 867, 821, 784, 736, 715, 698 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.17 (s, 3H, MeSi), 0.33 (s, 3H, MeSi), 0.97−1.18 (m, 4H, CH$_2$Si), 1.55−1.83 (m, 2H, CH$_2$), 6.94 (s, 1H, HC═C), 7.01−7.07 (m, 5H, phenyl ring protons), 7.12−7.20 (m, 6H, phenyl ring protons), 7.40−7.44 (m, 4H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −2.45, −1.72 (MeSi), 15.71, 17.26, 18.13 (CH$_2$), 126.26, 126.60 (2C), 127.74, 127.81, 127.89, 128.89, 133.92, 134.44, 138.09, 138.93, 148.26 (phenyl ring carbons), 149.37, 162.50 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −11.5, −6.0. Anal. Calcd for $C_{25}H_{28}Si_2$: C, 78.06; H, 7.34. Found: C, 78.30; H, 7.37.

Palladium-Catalyzed Reaction of 1b with Phenylacetylene. A mixture of 0.3211 g (1.14 mmol) of **1b**, 0.3105 g (3.04 mmol) of phenylacetylene, and 0.0124 g (0.011 mmol) of tetrakis(triphenylphosphine)palladium(0) was heated in a degassed sealed tube at 200 °C for 24 h. The palladium species in the resulting mixture was removed by passing through a short silica gel column. Compound **3b** (0.3882 g, 89%) was isolated by column chromatography. For **3b**: MS *m/z* 384 (M$^+$); IR 3066, 3016, 2956, 2898, 2861, 1486, 1427, 1251, 1110, 908, 867, 823, 782, 734, 715, 698 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.21 (s, 3H, MeSi), 0.31 (s, 3H, MeSi), 1.04−1.17 (m, 4H, CH$_2$Si), 1.59−1.68 (m, 1H, CH$_2$), 1.75−1.83 (m, 1H, CH$_2$), 7.08 (s, 1H, HC═C), 7.13−7.22 (m, 5H, phenyl ring protons), 7.34−7.39 (m, 6H, phenyl ring protons), 7.59−7.63 (m, 4H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −1.56, −1.52 (MeSi), 16.12, 17.39, 18.21 (CH$_2$), 126.31, 126.61 (2C), 127.82, 127.88, 127.94, 128.99, 133.95, 134.55, 138.26, 138.76, 148.37 (phenyl ring carbons), 149.15, 162.54 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −10.9, −5.3. Anal. Calcd for $C_{25}H_{28}Si_2$: C, 78.06; H, 7.34. Found: C, 78.01; H, 7.24.

Palladium-Catalyzed Reaction of 1a with Diphenylacetylene. A mixture of 0.0769 g (0.27 mmol) of **1a**, 0.1333 g (0.75 mmol) of diphenylacetylene, and 0.0144 g (0.013 mmol) of tetrakis(triphenylphosphine)palladium(0) was heated in a degassed sealed tube at 200 °C for 24 h. The palladium species in the resulting mixture was removed by passing through a short silica gel column. The mixture was then analyzed by GLC as being **4a** (55% yield) and unchanged **1a** (41% yield). Compound **4a** was isolated by recrystallization from methanol. For **4a**: mp 115−116 °C; MS *m/z* 460 (M$^+$); IR 3066, 3016, 2896, 2879, 1592, 1483, 1427, 1251, 1116, 987, 792, 698 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.24 (s, 6H, MeSi), 1.19 (ddd, 2H, CH$_2$Si, ^2J = 14.0 Hz, ^3J = 7.0 Hz, ^3J = 7.0 Hz), 1.47 (ddd, 2H, CH$_2$Si, ^2J = 14.0 Hz, ^3J = 7.0 Hz, ^3J = 7.0 Hz), 1.82 (dtt, 1H, CH$_2$, ^2J = 14.0 Hz, ^3J = 7.0 Hz, ^3J = 7.0 Hz), 1.92 (dtt, 1H, CH$_2$, ^2J = 14.0 Hz, ^3J = 7.0 Hz, ^3J = 7.0 Hz), 6.65 (d, 4H, J = 7.3 Hz, phenyl ring protons), 6.80 (t, 2H, J = 7.3 Hz, phenyl ring protons), 6.88 (t, 4H, J = 7.3 Hz, phenyl ring protons), 7.24−7.33 (m, 6H, phenyl ring protons), 7.44−7.46 (m, 4H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −2.33 (MeSi), 17.04 (CH$_2$), 17.12 (CH$_2$Si), 124.50, 126.89, 127.52, 128.34, 128.70, 134.33, 138.27, 144.57 (phenyl ring carbons), 159.21 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −7.69. Anal. Calcd for $C_{31}H_{32}Si_2$: C, 80.81; H, 7.00. Found: C, 80.88; H, 7.05.

Palladium-Catalyzed Reaction of 1b with Diphenylacetylene. A mixture of 0.0726 g (0.26 mmol) of **1b**, 0.1327 g (0.75 mmol) of diphenylacetylene, and 0.0149 g (0.013 mmol) of tetrakis(triphenylphosphine)palladium(0) was heated in a degassed sealed tube at 200 °C for 24 h. The palladium species in the resulting mixture was removed by passing through a short silica gel column. The mixture was then analyzed by GLC as being **4b** (33% yield) and unchanged **1b** (55% yield). Compound **4b** was isolated by recrystallization from hexane. For **4b**: mp 125−126 °C; MS *m/z* 460 (M$^+$); IR 3056, 3006, 2915, 2877, 2861, 1592, 1483, 1427, 1251, 1105, 989, 904, 852, 786, 700 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.13 (s, 6H, MeSi), 1.21 (dt, 2H, CH$_2$Si, ^2J = 15.6 Hz, ^3J = 4.6 Hz), 1.40 (dt, 2H, CH$_2$Si, ^2J = 15.6 Hz, ^3J = 9.2 Hz), 1.68 (tt, 2H, CH$_2$, ^3J = 9.2 Hz, ^3J = 4.6 Hz), 6.84−6.85 (m, 4H, phenyl ring protons), 6.90−6.93 (m, 2H, phenyl ring protons), 6.97−7.00 (m, 4H, phenyl ring protons), 7.45−7.49 (m, 6H, phenyl ring protons), 7.76−7.78 (m, 4H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −1.73 (MeSi), 17.01 (CH$_2$), 17.77 (CH$_2$Si), 124.73, 127.13, 127.75, 128.47, 128.90, 134.66, 138.30, 145.01 (phenyl ring carbons), 159.18 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −6.39. Anal. Calcd for $C_{31}H_{32}Si_2$: C, 80.81; H, 7.00. Found: C, 80.71; H, 7.02.

X-ray Crystallographic Analysis. The X-ray data were collected on a Rigaku AFC7R four-circle diffractometer, using $\omega/2\theta$ scan mode. All calculations were performed with the crystallographic software package teXsan (Molecular Structure

Corp., 1985, 1992). The structures were solved by direct methods[8] and subsequent Fourier recycling[9] and refined by full-matrix least-squares refinement against $|F|$, with all hydrogen atoms fixed at the calculated positions. The empirical absorption corrections were applied.[10] Crystal data for **4a**: $C_{31}H_{32}Si_2$, monoclinic, space group $P2_1/a$, Mo Kα radiation, $2\theta_{max} = 55.0°$, $a = 12.544(1)$ Å, $b = 15.320(2)$ Å, $c = 15.387(2)$ Å, $\beta = 113.550(6)°$, $U = 2710.7(4)$ Å^3, $D_c = 1.129$ g cm^{-3}, $\mu = 1.47$ cm^{-1}, 6217 independent intensities, 4935 observed ($I > 1.00\sigma(I)$), $T = 296$ K, $R = 0.054$, $R_w = 0.077$, GOF = 1.83, maximum residual electron density 0.31 e Å^{-3}. Crystal data for **4b**: $C_{31}H_{32}Si_2$, triclinic, space group $P\bar{1}$, Mo Kα radiation, $a = 12.903(2)$ Å, $b = 18.245(2)$ Å, $c = 11.947(1)$ Å, $\alpha = 90.351(9)°$, $\beta = 104.197(8)°$, $\gamma = 94.460(9)°$, $U = 2717.3(5)$ Å^3, $D_c = 1.126$ g cm^{-3}, $\mu = 1{,}47$ cm^{-1}, $2\theta_{max} = 55.0°$, 12 488 independent intensities, 9827 observed ($I > 2.00\sigma(I)$), $T = 296$ K, $R = 0.047$, $R_w = 0.080$, GOF = 1.69, maximum residual electron density 0.32 e Å^{-3}.

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Supporting Information Available: Tables of crystallographic data, atom coordinates, bond lengths and angles, and anisotropic thermal parameters for **4a** and **4b**. An X-ray crystallographic file in CIF format is also available. This material is available free of charge via the Internet at http://www.pubs.acs.org.

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