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Stereochemistry of Disilanylene-Containing Cyclic Compounds. Synthesis and Reactions of *cis*- and *trans*-3,4-Benzo-1,2-di(*tert*-butyl)-1,2-dimethyl-1,2-disilacyclobut-3-ene

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The reaction of *cis*- and *trans*-3,4-benzo-1,2-di(*tert*-butyl)-1,2-dimethyl-1,2-disilacyclobut-3-ene (**1a** and **1b**) with chlorine gas in carbon tetrachloride proceeded stereospecifically to give *meso*- and *rac*-1,2-bis[(*tert*-butyl)chloromethylsilyl]benzene (**2a** and **2b**, respectively). The condensation of **2a** and **2b** with lithium and sodium produced a mixture of *cis*- and *trans*-benzodisilacyclobutene **1a** and **1b**, respectively. The reaction of **1a** and **1b** with molecular oxygen proceeded with high stereospecificity to give the respective *cis*- and *trans*-4,5-benzo-2-oxa-1,3-disilacyclopent-4-ene. The palladium-catalyzed reactions of **1a** and **1b** with phenylacetylene, 1-hexyne, *tert*-butylacetylene, phenyl-1-propyne, and diphenylacetylene proceeded in a stereospecific fashion to give the corresponding 5,6-benzo-1,4-disilacyclohexa-2,5-diene derivatives. Similar reactions of **1a** and **1b** with trimethylsilylacetylene, dimethylphenylsilylacetylene, and mesitylacetylene gave stereospecifically the *erythro*- and *threo*-1,2-bis(silyl)benzene derivatives. The structure of *trans*-5,6-benzo-1,4-di(*tert*-butyl)-1,4-dimethyl-2-phenyl-1,4-disilacyclohexa-2,5-diene was determined by single-crystal X-ray crystallography.

Introduction

The molecules bearing a silicon−silicon bond show unique properties in the photochemical and thermal reactions and also in the transition-metal-catalyzed reactions. To date, considerable attention has been devoted to investigation of the synthesis and reactions of di- and oligosilanyl-substituted compounds.[1] However, much less interest has been shown in the stereochemistry of these compounds.

We have demonstrated that the photolysis of *meso*- and *rac*-1,2-diethyl-1,2-dimethyldiphenyldisilane affords the respective silenes derived from a 1,3-silyl shift with high diastereospecificity. The reactions of the rearranged silenes thus formed with olefins proceed diastereospecifically to give the ene adducts.[2] With carbonyl compounds, however, the silenes react with high diastereoselectivity to give the ene-type adducts.[3] The photolysis of geometrical isomers of cyclic disilanylene compounds *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane in the presence of isobutene also proceeds stereospecifically to give the corresponding adducts derived from the reaction of the rearranged silenes with isobutene.[4] On the other hand, the cophotolysis of *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane with isobutene affords a *cis*-ene adduct and a *trans*-[2+2] adduct, although the similar photolysis of the *cis*-isomer proceeds stereospecifically to give a *cis*-ene adduct.[5] The palladium-catalyzed reactions of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacylopentane[6] and hexane[7a,b] with alkynes also proceed with high stereospecificity to give the products arising from insertion of a triple bond of the alkyne into a silicon−silicon bond in disilanylene-containing cyclic compounds.

The 3,4-benzo-1,2-disilacyclobut-3-enes show interesting chemical behaviors.[8a] It has been reported that the aluminum chloride-catalyzed reaction of 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene gives the ring-opened polymer with high molecular weight, while the palladium-catalyzed reactions of 1,1,2,2-tetra-

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[†] Kurashiki University of Science and the Arts.

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[1] (a) Patai, S.; Rappoport, Z. *The Chemistry of Organic Silicon Compounds;* Wiley: New York, 1989. (b) Rappoport, Z.; Apeloig, Y. *The Chemistry of Organic Silicon Compounds*; Wiley: New York, 1998; Vol. 2. (c) Rappoport, Z.; Apeloig, Y. *The Chemistry of Organic Silicon Compounds*; Wiley: New York, 2001; Vol. 3. (d) Brook, M. A. *Silicon in Organic, Organometallic, and Polymeric Chemistry*; Wiley: New York, 2000.

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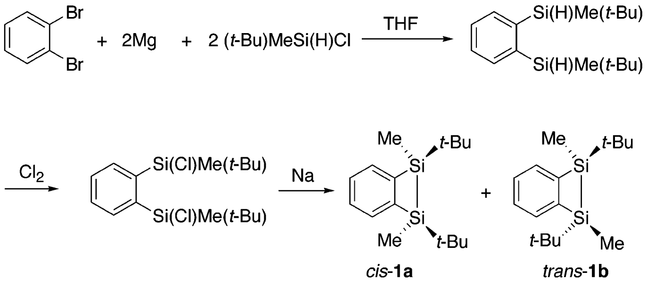
10.1021/om030508l CCC: $27.50

Scheme 1



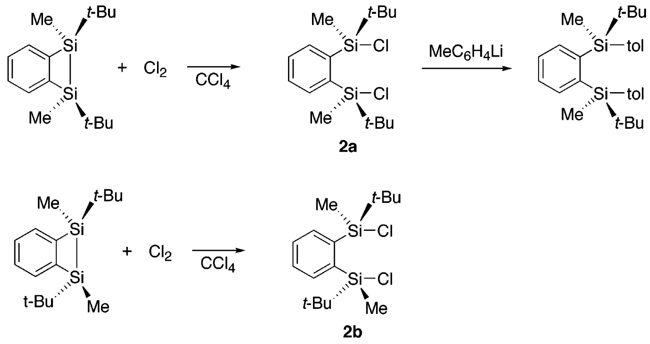
methyl-, 1,2-diethyl-1,2-dimethyl-, and 1,1,2,2-teraethyl-3,4-benzo-1,2-disilacyclobut-3-ene afford the dimerization products.[8b−e] We have also found that the transition-metal-catalyzed reactions of 3,4-benzodisilacyclobut-3-ene with aromatic compounds, carbonyl compounds, alkenes, and alkynes afford various types of products. The types of products thus formed depend highly on the nature of the metal in the complexes formed by the reactions of the benzodisilacyclobutenes with the transition-metal complexes used as the catalyst.[8a] The types of products are also influenced by the bulkiness of the substituents on the silicon atom in the benzodisilacyclobutenes. It is of interest to us to investigate the stereochemistry of the reactions of the benzodisilacyclobutenes with various substrates. We have recently reported the synthesis and some reactions of *cis*- and *trans*-3,4-benzo-1,2-di(*tert*-butyl)-1,2-disilacyclobut-3-ene.[9] In this paper we report the stereochemistry of the formation and reactions of these compounds in detail.

Results and Discussion

Recently, we have reported that *cis*- and *trans*-3,4-benzo-1,2-di(*tert*-butyl)-1,2-dimethyl-1,2-disilacyclobut-3-ene (**1a** and **1b**) can be prepared by a series of reactions using 1,2-dibromobenzene as a starting material, as shown in Scheme 1.[9] The benzodisilacyclobut-3-ene obtained from these reactions is a mixture consisting of *cis*- and *trans*-isomers. However, pure **1a** and **1b** can be separated by fractional distillation of the mixture with the use of a spinning band column, followed by recrystallization from hexane.

Using **1a** and **1b**, we could isolate pure *meso*- and *rac*-1,2-bis[(*tert*-butyl)chloromethylsilyl]benzene (**2a** and **2b**) by the reaction with chlorine gas in carbon tetrachloride, and we investigated the stereochemistry of the alkali metal condensation of the resulting *meso*- and *rac*-chloro derivatives.

Scheme 2



The reaction of **1a** with chlorine gas in carbon tetrachloride gave stereospecifically *meso*-isomer **2a** in almost quantitative yield (Scheme 2). No *rac*-isomer **2b** was detected in the reaction mixture. The structure of **2a** was confirmed by X-ray crystallographic analysis of the tolyl derivative obtained from the reaction of **2a** with *p*-tolyllithium as reported previously.[9] It has been reported that the reaction of chlorosilanes with aryllithium proceeds with inversion of configuration at the silicon center to give arylsilanes.[10] Presumably, inversion at the silicon center is involved in the present reaction. Similar treatment of **1b** with chlorine gas afforded **2b** in excellent yield. No other isomers were detected in the reaction mixture by either GLC or spectrometric analysis, indicating that cleavage of a silicon−silicon bond in **1a** and **1b** by chlorine proceeded with high stereospecificity to give **2a** and **2b**, respectively.

Condensation Reactions. We first examined the reaction of pure **2a** and **2b** with lithium in THF. Thus, treatment of **2a** with finely cut lithium in THF at room temperature for 2 h produced a mixture of **1a** and **1b** in 53% yield, along with polymeric substances. The ratio of **1a** and **1b** was determined to be 1:9 by ^{1}H NMR spectrometry. Treatment of **2b** with lithium under the same conditions again afforded a mixture consisting of both isomers in the ratio of 1:9 in 54% yield. In both cases, the abundant species was found to be *trans*-isomer **1b**.

The sodium condensation reactions of **2a** and **2b** in diethyl ether and toluene proceed cleanly to give the products in excellent yields. However, the ratio of the products **1a** and **1b** is highly dependent on the solvent used. Furthermore, as observed in the lithium condensation reactions, the ratio of **1a** and **1b** in the products obtained from **2a** and **2b** is almost the same. Thus, the reaction of **2a** with finely cut sodium metal in ether at room temperature for 2 days produced a mixture of **1a** and **1b** in the ratio of 1:4 in 92% yield. The reaction of **2b** with sodium in ether under the same conditions afforded a mixture with the same ratio of **1a** and **1b** in 93% yield. Again *trans*-isomer **1b** was produced as the abundant species. Similar treatment of **2a** and **2b** in toluene gave a mixture of **1a** and **1b** in a different ratio from that in ether. Treatment of **2a** and **2b** with sodium metal at room temperature afforded the reductive coupling products **1a** and **1b** in 90% and 93% yields. The ratio of **1a** and **1b** in both reactions was determined to be 1:2. In refluxing toluene, however, the reaction of **2a** and **2b** with sodium produced a mixture of **1a** and **1b** with a ratio of 2:3 in 95% and 97% yields, respectively.[11a]

Although Wurtz-type reactions are still mechanistically unclear, the reactions probably involve silyl radicals arising from one-electron transfer from sodium to a silicon−chlorine bond, as well as the silyl anion.[11b]

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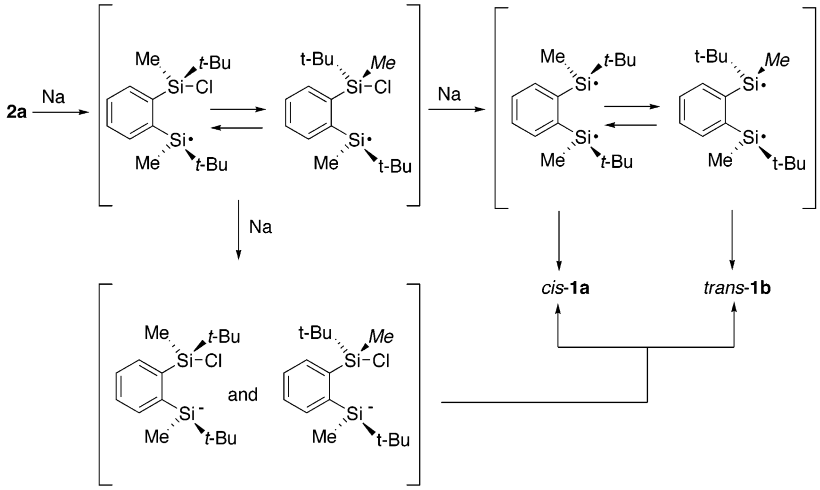
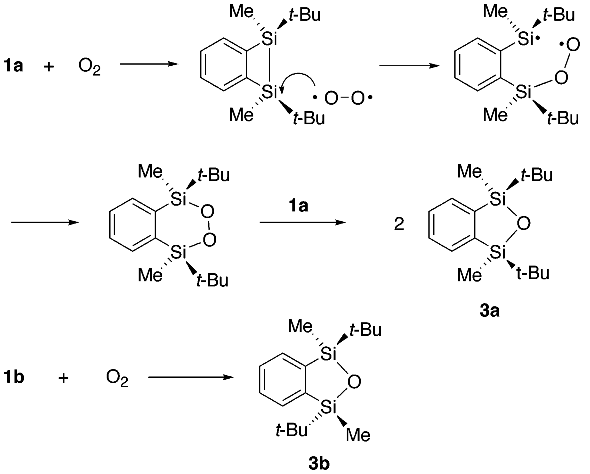
Scheme 3



Scheme 4



The present condensation reactions presumably involve both silyl radicals and silyl anions as the reactive species, as shown in Scheme 3. In a donor solvent such as ether, the silyl anions would be the favorable species, but in toluene, the silyl radicals probably play an important role for determining *cis*- and *trans*-configuration of the products.

Recently, it has been reported that the reaction of an achiral silyl anion with an optically active chlorosilane proceeds stereoselectively to give the coupling product.[11d] On the other hand, the silyl radicals are configurationally rather stable;[9,12a,b] however, inversion at the silicon center would be expected to occur at high temperature.

Oxidation Reaction. Although molecular oxygen readily reacts with **1a** and **1b** in the presence of a radical initiator to give the respective *cis*- and *trans*-4,5-benzo-1,3-di(*tert*-butyl)-1,3-dimethyl-2-oxa-1,3-disilacyclopent-4-ene (**3a** and **3b**),[9] compounds **1a** and **1b** are stable in air at room temperature and can be handled in air without decomposition. However, when a benzene solution of **1a** and **1b** was heated to reflux in an oxygen atmosphere, slow oxidation of a silicon–silicon bond in benzodisilacyclobut-3-ene took place stereospecifically to give the respective *cis*- and *trans*-4,5-benzo-2-oxa-1,3-disilacyclopent-4-enes **3a** and **3b**. Interestingly, the rate of the oxidation reaction for *cis*-isomer **1a** was found to be faster than that of *trans*-isomer **1b**. Indeed, the half-life of **1a** in the oxidation reaction was calculated to be 6 days, while that of *trans*-isomer **1b** was 21 days. The fact that the oxidation of *cis*-isomer **1a** with molecular oxygen proceeds with greater facility than that of **1b** may be ascribed to steric reasons.

The formation of cyclic siloxanes **3a** and **3b** may be best understood by a stereospecific two-step process, that is, the formation of cyclic peroxide, which would be produced by the reaction of **1a** and **1b** with molecular oxygen, and then the reaction of the resulting peroxide with **1a** and **1b** as shown in Scheme 4. In fact, it has been reported that the reaction of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane with bis(trimethylsilyl)peroxide readily proceeds in a stereospecific fashion to yield the corresponding cyclic siloxanes and hexamethyldisiloxane.[13]

Pd-Catalyzed Reaction. Benzodisilacyclobutenes **1a** and **1b** are thermally stable. When **1a** and **1b** were heated with phenylacetylene and diphenylacetylene in a sealed tube at 250 °C for 24 h, no adducts were detected in the reaction mixture. The starting compounds **1a** and **1b** were recovered unchanged. Recently, we have reported that the palladium-catalyzed reactions of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane[6] and 1,2-disilacyclohexane[7] with alkynes proceed with high stereospecificity to give the respective adducts arising from insertion of a carbon–carbon triple bond into a silicon–silicon bond in the five- and six-membered ring. The palladium-catalyzed reactions of a four-membered cyclic system with alkynes also proceed stereospecifically to give the adducts. As reported previously, the reaction of *cis*-isomer **1a** with phenyl-

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(11) (a) We reported that the reaction of **2a** with sodium in refluxing toluene gave a mixture of **1a** and **1b** in a ratio of 2:3, while **2b** afforded **1a** and **1b** in a ratio of 7:3. However, several experiments using **2b** under the same conditions indicated that the ratio of **1a**:**1b** was exactly the same as that obtained from **2a**. (b) Kochi, J. K. *Free Radicals*; John Wiley & Sons: New York, 1972; Vol. 1, pp 539–541. (c) Jones, R. G.; Benfield, R. E.; Cragg, R. H.; Swain, A. C.; Webb, S. J. *Macromolecules* **1993**, *26*, 4878. (d) Suzuki, K.; Kawakami, Y. *Organometallics* **2003**, *22*, 2367.

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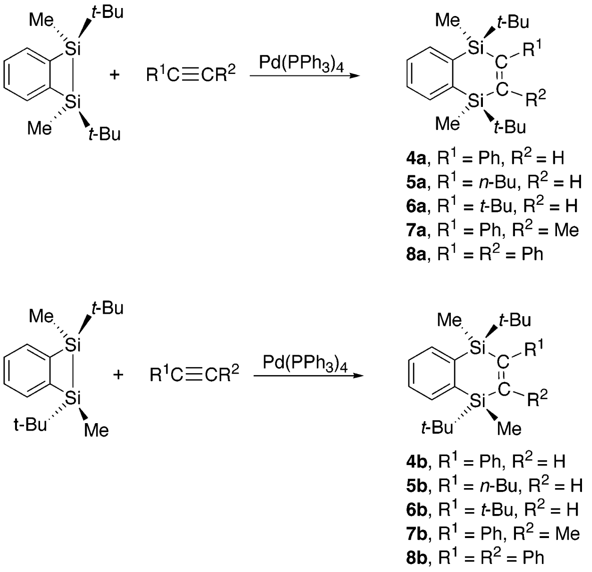
Scheme 5



4a, R^1 = Ph, R^2 = H
5a, R^1 = *n*-Bu, R^2 = H
6a, R^1 = *t*-Bu, R^2 = H
7a, R^1 = Ph, R^2 = Me
8a, R^1 = R^2 = Ph

4b, R^1 = Ph, R^2 = H
5b, R^1 = *n*-Bu, R^2 = H
6b, R^1 = *t*-Bu, R^2 = H
7b, R^1 = Ph, R^2 = Me
8b, R^1 = R^2 = Ph

acetylene in the presence of the palladium catalyst in a sealed glass tube at 150 °C for 24 h proceeded stereospecifically to afford an adduct derived from insertion of a carbon−carbon triple bond into a silicon−silicon bond in **1a**, *cis*-5,6-benzo-1,4-di(*tert*-butyl)-1,4-dimethyl-2-phenyl-1,4-disilacyclohexa-2,5-diene (**4a**) in 84% isolated yield (Scheme 5).[9] Similar reaction of *trans*-isomer **1b** with phenylacetylene gave *trans*-isomer (**4b**) in 89% isolated yield. No *cis*-isomer **4a** was detected in the reaction mixture by spectrometric analysis. Treatment of **1a** and **1b** with 1-hexyne also proceeded with high stereospecificity to give the respective adducts **5a** and **5b** in 95% and 90% yields. With *tert*-butylacetylene under the same conditions, **1a** and **1b** reacted to give the respective adducts **6a** and **6b** in 82% and 80% yields. The structures of **4a**,**b**−**6a**,**b** were verified by spectrometric and elemental analyses. Their configurations were confirmed by NOE-FID difference experiments at 300 MHz. Furthermore, we carried out X-ray crystallographic analysis for **4b** and confirmed that this compound must have the *trans* configuration. The ORTEP drawing for **4b** is depicted in Figure 1, together with selected bond lengths and angles.

Benzodisilacyclobut-3-ene **1a** and **1b** readily reacted stereospecifically with disubstituted acetylenes to give the respective adducts in high yields. The palladium-catalyzed reaction of **1a** with 1-phenyl-1-propyne at 200 °C for 24 h produced *cis*-5,6-benzo-1,4-di(*tert*-butyl)-1,3,4-trimethyl-2-phenyl-1,4-disilacyclohexa-2,5-diene (**7a**) in 79% isolated yield, as the sole product. Similarly, the reaction of **1b** with 1-phenyl-1-propyne gave *trans*-isomer **7b** in 73% yield. No *cis*-isomer **7a** was detected in the reaction mixture. Again, the configuration of **7a** and **7b** was confirmed by NOE-FID difference experiments at 300 MHz. Treatment of **1a** with diphenylacetylene under the same conditions afforded *cis*-5,6-benzo-1,4-di(*tert*-butyl)-1,4-dimethyl-2,3-diphenyl-1,4-disilacyclohexa-2,5-diene (**8a**) in 68% yield, while **1b** with diphenylacetylene produced *trans*-isomer **8b** in 65% yield. In both cases, no other isomers were detected in the reaction mixtures.

The palladium-catalyzed reactions of **1a** and **1b** with monosubstituted acetylenes bearing a bulky substituent, such as trimethylsilylacetylene, dimethylphenylsilylacetylene, and mesitylacetylene gave the respective 1:1 adducts. However, these adducts have no benzodisilacyclohexa-2,5-diene structure, but the ring-opened 1,2-bis(silyl)benzene structure. Thus, treatment of **1a** with trimethylsilylacetylene in the presence of tetrakis(triphenylphosphine)palladium at 150 °C for 24 h gave 1-[*tert*-butylmethyl(trimethylsilylethynyl)silyl]-2-(*tert*-butylmethylsilyl)benzene (**9a**) in 90% isolated yield (Scheme 6). No other isomers were detected in the reaction mixture, indicating that the reaction proceeded with high stereospecificity. We tentatively assigned **9a** as an *erythro*-isomer, according to the mechanism shown in Scheme 7. Similarly, treatment of **1b** with trimethylsilylacetylene afforded compound **9b**, a different stereoisomer from **9a**, in 94% yield. The reaction of **1a** and **1b** with dimethylphenylsilylacetylene under the same conditions also afforded the ring-opened products *erythro*-isomer **10a** and *threo*-isomer **10b** in 63% and 61% yields, respectively. Mesitylacetylene also reacted with **1a** and **1b** under the same conditions to give the adducts **11a** and **11b**, analogous to **9a**,**b** and **10a**,**b**. The structures

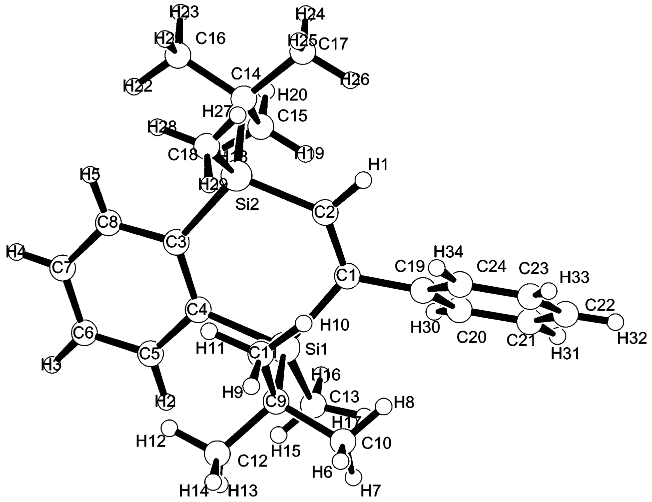
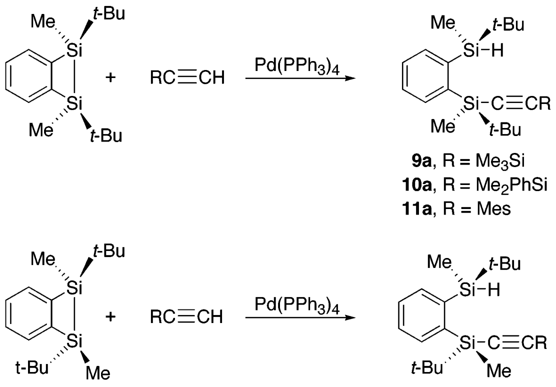


Figure 1. ORTEP diagram for **4b** showing thermal ellipsoids at the 50% level. Selected bond lengths (Å) and angles (deg): C1−C2 = 1.346, C2−Si2 = 1.861, Si2−C3 = 1.877, C3−C4 = 1.412, C4−Si1 = 1.878, Si1−C1 = 1.879, C1−C2−Si2 = 129.08, C2−Si2−C3 = 109.20, Si2−C3−C4 = 122.54, C3−C4−Si1 = 124.86, C4−Si1−C1 = 109.34, Si1−C1−C2 = 121.03.

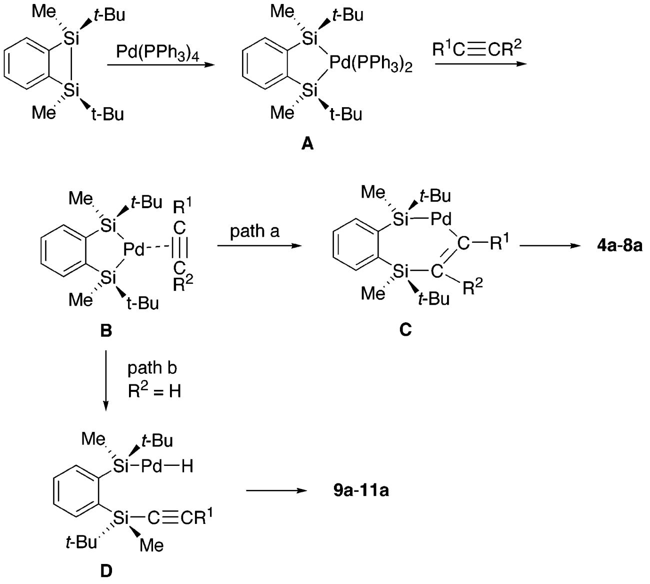
Scheme 6



9a, R = Me_3Si
10a, R = Me_2PhSi
11a, R = Mes

9b, R = Me_3Si
10b, R = Me_2PhSi
11b, R = Mes

Scheme 7



of **9a**,**b**, **10a**,**b**, and **11a**,**b** were verified by spectrometric analysis, as well as by elemental analysis.

On the basis of the results obtained from the palladium- and platinum-catalyzed double silylation of disilanes to alkynes,[14,15] a possible mechanistic interpretation of the observed reaction course is shown in Scheme 7, using **1a** as the starting benzodisilacyclobut-3-ene. The starting compound **1a** presumably reacts with a tetrakis(triphenylphosphine)palladium catalyst to produce 3,4-benzo-1-pallada-2,5-disilacyclopent-3-ene (**A**), and then an alkyne adds onto the palladium atom in the intermediate **A**, producing complex **B**. 5,6-Benzo-1,4-disilacyclohexa-2,5-dienes **4a**, **5a**, **6a**, **7a**, and **8a** are probably produced by insertion of a triple bond of the alkyne coordinating to the palladium atom in the complex **B** into a silicon−palladium bond, giving 3,4-benzo-1-pallada-2,5-disilacyclohepta-3,6-diene (**C**), followed by reductive elimination of the palladium species from the complex **C** (path a).

On the other hand, the formation of the ring-opened products **9a**, **10a**, and **11a** may be understood in terms of sp-hybridized C−H bond activation of the coordinated alkyne in the complex **B** (path b),[16] followed by a 1,2-shift of an alkynyl group to one of two silicon atoms to afford complex **D**. Finally, reductive elimination of the palladium species from complex **D** takes place to give the products **9a**−**11a**.[17] All steps shown in Scheme 7 probably proceed with high stereospecificity to give the final products, *cis*-isomers **4a**−**8a** and *erythro*-isomers **9a**−**11a**.

Experimental Section

All palladium-catalyzed reactions were carried out in a degassed sealed tube (1.0 cm × 15 cm). NMR spectra were recorded on JNM-LA300 and JNM-LA500 spectrometers. 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*-3,4-benzo-1,2-di(*tert*-butyl)-1,2-dimethyl-1,2-disilacyclobut-3-ene (**1a** and **1b**) 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 and ether used as a solvent were dried over sodium/benzophenone under a nitrogen atmosphere and distilled just before use. Benzene and toluene were dried over sodium and distilled before use. Carbon tetrachloride was dried over diphosphorus pentoxide and distilled before use.

Preparation of 1,2-Bis(*tert*-butylmethylsilyl)benzene. In a 1 L four-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 150.4 g (1.10 mol) of *tert*-butylchloromethylsilane and 14.6 g (0.60 mol) of magnesium in 350 mL of THF. To this was added dropwise 65.0 g (0.28 mol) of *o*-dibromobenzene dissolved in 100 mL of THF over a period of 1.5 h. The mixture was heated to reflux for 12 h. The resulting magnesium salts were removed by filtration and washed with ether. The solvents were evaporated, and the residue was distilled under reduced pressure to give 27.5 g (36% yield) of a 1:1 mixture of *meso*- and *rac*-1,2-bis(*tert*-butylmethylsilyl)benzene: bp 132−133 °C/10 Torr; MS m/z 277 ($M^+ - H$); ^{1}H NMR δ ($CDCl_3$) 0.37 (d, 6H, MeSi, $J = 3.7$ Hz), 0.38 (d, 6H, MeSi, $J = 3.7$ Hz), 0.98 (s, 18H, tBu), 1.04 (s, 18H, tBu), 4.52 (q, 2H, HSi, $J = 3.7$ Hz), 4.74 (q, 2H, HSi, $J = 3.7$ Hz), 7.56−7.57 (m, 2H, phenylene ring protons), 7.64−7.66 (m, 2H, phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) −7.38, −5.56 (MeSi), 17.32, 17.38 (CMe_3), 27.40, 27.91 (Me_3C), 127.74, 127.79, 134.88, 135.71, 143.06, 143.39 (phenylene ring); ^{29}Si NMR δ ($CDCl_3$) −9.4, −4.9. Anal. Calcd for $C_{16}H_{30}Si_2$: C, 68.98; H, 10.86. Found: C, 68.94; H, 11.01.

Preparation of 1,2-Bis(*tert*-butylchloromethylsilyl)benzene. In a 300 mL three-necked flask fitted with a stirrer, reflux condenser, and inlet tube for chlorine gas was placed 36.5 g (0.13 mol) of 1,2-bis(*tert*-butylmethylsilyl)benzene containing two diastereomers in a ratio of 1:1, in 250 mL of dry carbon tetrachloride. Dry chlorine gas was introduced into the stirred solution with ice cooling until the solution became a slight yellow color. At this point GLC analysis of the mixture showed that the starting hydrosilane was transformed completely into a 1:1 mixture of *meso*- and *rac*-1,2-bis(*tert*-butylchloromethylsilyl)benzene. The solution was distilled off, and the residue was distilled under reduced pressure to give 40.4 g (89% yield) of 1,2-bis(*tert*-butylchlorodimethylsilyl)benzene.

Preparation of a Mixture of *cis*- and *trans*-3,4-Benzo-1,2-di(*tert*-butyl)-1,2-dimethyl-1,2-disilacyclobut-3-ene (1a and 1b). In a 500 mL three-necked flask fitted with a stirrer,

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reflux condenser, and dropping funnel were placed 7.93 g (0.35 mol) of sodium and 150 mL of dry toluene. The contents of the flask were heated to reflux, and then a solution of 43.9 g (0.13 mol) of **2a** and **2b** (*meso*/*dl* = 1:1) in 30 mL of toluene was added over a period of 1 h. After the mixture was heated to reflux for 7 h, it was filtered under a nitrogen atmosphere. The solvent toluene was distilled off, and the residue was distilled under reduced pressure to give 25.3 g (73% yield) of a mixture of **1a** and **1b**.

Isolation of Pure 1a and 1b. A mixture of **1a** and **1b** (60 g) (*cis*/*trans* = 6/4) was fractionally distilled using a spinning-band column with 50 theoretical plates, to give 10 g of pure **1a** as white crystals and 6 g of pure **1b** as a colorless liquid. Pure **1a** was recrystallized from hexane. For **1a**: Anal. Calcd for $C_{16}H_{28}Si_2$: C, 69.49; H, 10.20. Found: C, 69.48; H, 10.17. Bp 61−62 °C/2 Torr; mp 49−50 °C; MS *m*/*z* 276 (M^+); IR 3089, 3041, 2924, 2854, 1463, 1427, 1387, 1248, 1007, 924, 820, 779, 760, 742, 712 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.37 (s, 6H, MeSi), 1.11 (s, 18H, *t*-Bu), 7.31 (dd, 2H, phenylene ring protons, $J = 5.3$ Hz, $J = 3.3$ Hz), 7.46 (dd, 2H, phenylene ring protons, $J = 5.3$ Hz, $J = 3.3$ Hz); ^{13}C NMR δ ($CDCl_3$) −4.52 (MeSi), 18.69 (CMe_3), 28.49 (Me_3C), 128.94, 131.85, 155.77 (phenylene ring); ^{29}Si NMR δ ($CDCl_3$) 14.0. For **1b**: Anal. Calcd for $C_{16}H_{28}Si_2$: C, 69.49; H, 10.20. Found: C, 69.23; H, 10.32. Bp 59−60°C/1 Torr; MS *m*/*z* 276 (M^+); IR 3045, 2952, 2925, 2892, 2854, 1469, 1461, 1361, 1243, 1006, 919, 819, 782, 754, 742, 709 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.45 (s, 6H, MeSi), 1.02 (s, 18H, *t*-Bu), 7.31 (dd, 2H, phenylene ring protons, $J = 5.6$ Hz, $J = 3.1$ Hz), 7.44 (dd, 2H, phenylene ring protons, $J = 5.6$ Hz, $J = 3.1$ Hz); ^{13}C NMR δ ($CDCl_3$) −4.67 (MeSi), 19.21 (CMe_3), 27.93 (Me_3C), 128.97, 131.72, 155.82 (phenylene ring); ^{29}Si NMR δ ($CDCl_3$) 11.0.

Reaction of 1a and 1b with Chlorine Gas. In a 100 mL two-necked flask was placed 1.082 g (3.91 mmol) of **1a** in 60 mL of carbon tetrachloride. To this was introduced chlorine gas with ice-cooling until the solution showed a yellow color of chlorine. The solvent carbon tetrachloride was evaporated, and the residue was distilled under reduced pressure (3 Torr) to give 1.286 g (95% yield) of **2a** as a colorless liquid. Anal. Calcd for $C_{16}H_{28}Si_2Cl_2$: C, 55.31; H, 8.12. Found: C, 55.27; H, 8.39. MS *m*/*z* 331 ($M^+ - Me$); IR 2962, 2933, 2894, 2861, 1473, 1463, 1415, 1392, 1363, 1259, 1112, 1008, 939, 821, 794, 746, 719, 703 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.87 (s, 6H, MeSi), 0.98 (s, 18H, *t*-Bu), 7.41 (dd, 2H, phenylene ring protons, $J = 5.8$ Hz, $J = 3.4$ Hz), 7.91 (dd, 2H, phenylene ring protons, $J = 5.8$ Hz, $J = 3.4$ Hz); ^{13}C NMR δ ($CDCl_3$) 2.60 (MeSi), 20.81 (CMe_3), 26.79 (Me_3C), 128.13, 137.58, 139.66 (phenylene ring carbons); ^{29}Si NMR δ ($CDCl_3$) 25.6. Similar treatment of 1.092 g (3.95 mmol) of **1b** with chlorine gas in carbon tetrachloride gave 1.307 g (95% yield) of **2b** as a colorless liquid. Anal. Calcd for $C_{16}H_{28}Si_2Cl_2$: C, 55.31; H, 8.12. Found: C, 55.38; H, 8.14. MS *m*/*z* 331 ($M^+ - Me$); IR 2962, 2933, 2894, 2861, 1473, 1463, 1415, 1392, 1363, 1257, 1112, 1008, 939, 821, 794, 746, 719, 703 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.82 (s, 6H, MeSi), 1.05 (s, 18H, *t*-Bu), 7.41 (dd, 2H, phenylene ring protons, $J = 5.8$ Hz, $J = 3.4$ Hz), 7.95 (dd, 2H, phenylene ring protons, $J = 5.8$ Hz, $J = 3.4$ Hz); ^{13}C NMR δ ($CDCl_3$) 2.05 (MeSi), 21.01 (CMe_3), 26.96 (Me_3C), 128.16, 137.34, 140.29 (phenylene ring carbons); ^{29}Si NMR δ ($CDCl_3$) 24.3.

Reaction of 2a and 2b with Lithium in THF. In a 100 mL two-necked flask was placed 0.384 g (0.055 mol) of finely cut lithium in 25 mL of THF. To this was added 4.370 g (0.013 mol) of **2a** in 5 mL of THF. The mixture was stirred for 2 h at room temperature and then filtered. The filtrate was concentrated and the residue was distilled under reduced pressure (3 Torr) to give 1.920 g (53% yield) of a mixture of **1a** and **1b**. The ratio of **1a** and **1b** was calculated to be 1:9 by ^1H NMR spectrometric analysis. Similar reaction of 4.785 g (0.014 mol) of **2b** with 0.400 g (0.058 mol) of lithium in 30 mL of THF gave 2.076 g (54% yield) of a mixture of **1a** and **1b** in a ratio of 1:9.

Reaction of 2a and 2b with Sodium in Ether. In a 100 mL two-necked flask was placed 1.934 g (0.084 mol) of finely cut sodium in 25 mL of ether. To this was added 1.330 g (0.038 mol) of **2a** in 5 mL of ether. The mixture was stirred at room temperature for 2 days, and the resulting mixture was filtered. The filtrate was concentrated, and the residue was distilled under reduced pressure to give 0.970 g (92% yield) of **1a** and **1b** in the ratio of 1:4. Similar reaction of 1.340 g (0.039 mol) of **2b** with 2.066 g (0.090 mol) of sodium in 30 mL of ether at room temperature afforded 0.987 g (93% yield) of **1a** and **1b** in the ratio of 1:4.

Reaction of 2a and 2b with Sodium in Toluene. The reaction of 1.649 g (0.048 mol) of **2a** with 3.593 g (0.156 mol) of sodium in 30 mL of toluene at room temperature for 2 days gave 1.187 g (90% yield) of **1a** and **1b** in a ratio of 1:2. Similar reaction of 1.344 g (0.039 mol) of **2b** with 1.883 g (0.082 mol) of sodium produced 0.995 g (93% yield) of **1a** and **1b** in a ratio of 1:2. In refluxing toluene **2a** with sodium afforded a 2:3 mixture of **1a** and **1b** in 95% yield, while **2b** produced the same mixture in 97% yield.

Oxidation of 1a and 1b. In a 100 mL three-necked flask was placed 0.966 g (3.49 mmol) of **1a** in 80 mL of dry benzene. The mixture was heated to reflux under an oxygen atmosphere. A small aliquot was taken from the mixture at about 3-day intervals and analyzed by ^1H NMR spectrometry. The results showed that the half-life of **1a** was determined to be 6 days. After 49 days, the solvent benzene was evaporated, and the residue was chromatographed on silica gel using hexane as the eluent to give 0.858 g (84% yield) of **3a** as a colorless liquid. All spectral data for **3a** were identical with those of the authentic sample.[9] Similar treatment of 0.963 g (3.48 mmol) of **1b** with oxygen in refluxing benzene produced 0.800 g (79% yield) of **3b** (half-life: 21 days).

Palladium-Catalyzed Reaction of 1a and 1b with Phenylacetylene. A mixture of 0.1019 g (0.37 mmol) of **1a**, 0.1339 g (1.31 mmol) of phenylacetylene, and 0.0278 g (0.024 mmol) of tetrakis(triphenylphosphine)palladium(0) was heated in a degassed sealed tube at 150 °C for 24 h. The mixture was chromatographed on silica gel eluting with hexane to give 0.1168 g (84% yield) of **4a**. Exact mass calcd for $C_{20}H_{25}Si_2$ ([$M^+ - t$-Bu]) 321.1495, found 321.1502; MS *m*/*z* 363 ($M^+ - Me$); IR 3062, 2927, 2896, 2854, 1594, 1486, 1473, 1440, 1415, 1390, 1359, 1251, 1114, 1008, 871, 817, 786, 746, 701 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.30 (s, 3H, MeSi), 0.62 (s, 3H, MeSi), 0.80 (s, 9H, *t*-Bu), 1.11 (s, 9H, *t*-Bu), 6.86 (s, 1H, HC=C), 7.25−7.41 (m, 7H, phenyl and phenylene ring protons), 7.65−7.69 (m, 2H, phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) −3.78, −2.87 (MeSi), 18.61, 19.07 (CMe_3), 27.98, 28.22 (Me_3C), 126.22, 126.90, 127.54, 127.58, 128.11, 134.61, 135.64, 142.97, 143.19, 150.22 (phenyl and phenylene ring carbons), 147.12, 161.65 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −15.1, −14.6. Similar treatment of 0.0550 g (0.20 mmol) of **1b** with 0.0830 g (0.81 mmol) of phenylacetylene in the presence of 0.0095 g (0.0082 mmol) of tetrakis(triphenylphosphine)palladium(0) at 150 °C for 24 h gave 0.0673 g (89% yield) of **4b**. Anal. Calcd for $C_{24}H_{34}Si_2$: C, 76.12; H, 9.05. Found: C, 76.14; H, 9.26. Mp 95−96 °C; MS *m*/*z* 321 ($M^+ - (t$-Bu)); IR 2952, 2925, 2852, 1683, 1652, 1635, 1558, 1540, 1471, 1457, 1259, 1116, 819, 786 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.39 (s, 3H, MeSi), 0.62 (s, 3H, MeSi), 0.64 (s, 9H, *t*-Bu), 0.89 (s, 9H, *t*-Bu), 6.86 (s, 1H, HC=C), 7.22−7.39 (m, 7H, phenyl and phenylene ring protons), 7.60−7.65 (m, 2H, phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) −5.91, −5.23 (MeSi), 18.10, 18.29 (CMe_3), 27.15, 27.35 (Me_3C), 126.17, 126.98, 127.36, 127.40, 128.10, 133.86, 134.81, 142.60, 142.68, 149.82 (phenyl and phenylene ring carbons), 146.58, 161.35 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −15.3, −13.9.

Palladium-Catalyzed Reaction of 1a and 1b with 1-Hexyne. A mixture of 0.1324 g (0.48 mmol) of **1a**, 0.1288 g (1.57 mmol) of 1-hexyne, and 0.0305 g (0.0264 mmol) of tetrakis(triphenylphosphine)palladium(0) was heated in a degassed sealed tube at 150 °C for 24 h. The mixture was chromatographed on silica gel eluting with hexane to give 0.1636 g (95% yield) of **5a**. Anal. Calcd for $C_{22}H_{38}Si_2$: C, 73.66; H, 10.68. Found: C, 73.60; H, 10.52. MS *m/z* 358 (M^+); IR 2958, 2929, 2894, 2856, 1463, 1429, 1116, 821, 786, 744, 709 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.26 (s, 3H, MeSi), 0.41 (s, 3H, MeSi), 0.99 (t, 3H, CH_3, $J = 7.1$ Hz), 1.04 (s, 9H, *t*-Bu), 1.08 (s, 9H, *t*-Bu), 1.39−1.46 (m, 2H, CH_2), 1.50−1.59 (m, 2H, CH_2), 2.31−2.44 (m, 2H, CH_2), 6.76 (s, 1H, HC=C), 7.33−7.39 (m, 2H, phenylene ring protons), 7.58−7.67 (m, 2H, phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) −4.85, −3.34 (MeSi), 14.19, 22.74, 31.54, 39.00 (n-Bu), 18.52, 18.73 (CMe_3), 28.05, 28.73 (Me_3C), 127.32, 127.41, 134.61, 135.22, 143.68, 143.80 (phenylene ring carbons), 140.20, 161.25 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −14.8, −14.6. Similar treatment of 0.0824 g (0.30 mmol) of **1b** with 0.0968 g (1.18 mmol) of 1-hexyne in the presence of 0.0176 g (0.0152 mmol) of tetrakis(triphenylphosphine)-palladium(0) at 150 °C for 24 h afforded 0.0966 g (90% yield) of **5b**. Anal. Calcd for $C_{22}H_{38}Si_2$: C, 73.66; H, 10.68. Found: C, 73.61; H, 10.77. MS *m/z* 358 (M^+); IR 2956, 2927, 2894, 2856, 1471, 1225, 1118, 819, 782, 744, 736, 692 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.32 (s, 3H, MeSi), 0.45 (s, 3H, MeSi), 0.82 (s, 9H, *t*-Bu), 0.92 (s, 9H, *t*-Bu), 0.95 (t, 3H, CH_3, $J = 7.0$ Hz), 1.37−1.56 (m, 4H, CH_2), 2.24−2.30 (m, 1H, CH_2), 2.39−2.45 (m, 1H, CH_2), 6.75 (s, 1H, HC=C), 7.32−7.35 (m, 2H, phenylene ring protons), 7.54−7.57 (m, 1H, phenylene ring protons), 7.62−7.64 (m, 1H, phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) −7.47, −5.75 (MeSi), 14.14, 22.76, 32.17, 39.78 (n-Bu), 18.01, 18.19 (CMe_3), 27.38, 27.43 (Me_3C), 127.19, 127.21, 133.78, 134.26, 143.15, 143.36 (phenylene ring carbons), 140.16, 161.35 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −15.9, −14.2.

Palladium-Catalyzed Reaction of 1a and 1b with *tert*-Butylacetylene. A mixture of 0.135 g (0.49 mmol) of **1a**, 0.165 g (2.01 mmol) of *tert*-butylacetylene, and 0.0316 g (0.027 mmol) of tetrakis(triphenylphosphine)palladium(0) in a degassed sealed tube was heated at 150 °C for 24 h. The mixture was chromatographed on silica gel using hexane as the eluent to give 0.144 g (82% yield) of **6a**. Anal. Calcd for $C_{22}H_{38}Si_2$: C, 73.66; H, 10.68. Found: C, 73.58; H, 10.84. MS *m/z* 343 ($M^+ - Me$); IR 2956, 2929, 2892, 2856, 1471, 1361, 1249, 1110, 833, 802, 786, 744, 705 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.20 (s, 3H, MeSi), 0.61 (s, 3H, MeSi), 0.97 (s, 9H, *t*-Bu), 1.07 (s, 9H, *t*-Bu), 1.23 (s, 9H, *t*-Bu), 6.94 (s, 1H, HC=C), 7.32−7.35 (m, 2H, phenylene ring protons), 7.58−7.62 (m, 2H, phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) −2.83, −0.14 (MeSi), 17.92, 18.53, 39.77 (CMe_3), 28.38, 30.37, 32.27 (Me_3C), 127.08, 127.32, 134.04, 135.47, 142.89, 145.73 (phenylene ring carbons), 140.59, 169.59 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −12.3 (2Si). Similar reaction of 0.135 g (0.49 mmol) of **1b** and 0.162 g (1.97 mmol) of *tert*-butylacetylene in the presence of 0.0303 g (0.026 mmol) of tetrakis(triphenylphosphine)palladium(0) afforded 0.141 g (80% yield) of **6b**. Anal. Calcd for $C_{22}H_{38}Si_2$: C, 73.66; H, 10.68. Found: C, 73.62; H, 10.85. MS *m/z* 343 ($M^+ - Me$); IR 2956, 2927, 2892, 2856, 1471, 1361, 1259, 1114, 831, 819, 800, 782, 744 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.35 (s, 3H, MeSi), 0.67 (s, 3H, MeSi), 0.76 (s, 9H, *t*-Bu), 0.91 (s, 9H, *t*-Bu), 1.23 (s, 9H, *t*-Bu), 6.95 (s, 1H, HC=C), 7.29−7.36 (m, 2H, phenylene ring protons), 7.57−7.65 (m, 2H, phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) −6.12, −3.15 (MeSi), 17.95, 18.58, 40.22 (CMe_3), 27.43, 28.57, 31.98 (Me_3C), 126.91, 127.29, 133.44, 134.27, 142.77, 144.83 (phenylene ring carbons), 139.46, 169.40 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −14.48, −13.20.

Palladium-Catalyzed Reaction of 1a and 1b with 1-Phenyl-1-propyne. A mixture of 0.138 g (0.50 mmol) of **1a**, 0.340 g (2.92 mmol) of 1-phenyl-1-propyne, and 0.0401 g (0.035 mmol) of tetrakis(triphenylphosphine)palladium(0) in a degassed sealed tube was heated at 200 °C for 24 h. The mixture was chromatographed on silica gel using hexane as the eluent to give 0.154 g (79% yield) of **7a**. Anal. Calcd for $C_{25}H_{36}Si_2$: C, 76.46; H, 9.24. Found: C, 76.35; H, 9.36. MS *m/z* 377 ($M^+ -$ Me); ^1H NMR δ ($CDCl_3$) 0.26 (s, 3H, MeSi), 0.29 (s, 3H, MeSi), 0.76 (s, 9H, *t*-Bu), 1.00 (s, 9H, *t*-Bu), 1.61 (s, 3H, Me), 6.84−7.03 (m, 2H, phenyl ring protons), 7.09−7.14 (m, 1H, phenyl ring proton), 7.21−7.28 (m, 4H, phenyl and phenylene ring protons), 7.52−7.56 (m, 2H, phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) −4.28, −2.89 (MeSi), 18.82, 19.26 (CMe_3), 21.60 (Me), 28.78, 29.03 (Me_3C), 125.50, 127.26, 127.31, 128.02 (2C), 135.05, 135.60, 143.44, 143.50, 145.16, 150.91, 156.47 (phenyl and phenylene and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −15.97, −13.41. Similar reaction of 0.138 g (0.50 mmol) of **1b** and 0.270 g (2.32 mmol) of 1-phenyl-1-propyne in the presence of 0.0475 g (0.041 mmol) of tetrakis(triphenylphosphine)-palladium(0) afforded 0.143 g (73% yield) of **7b**. Anal. Calcd for $C_{25}H_{36}Si_2$: C, 76.46; H, 9.24. Found: C, 76.42; H, 9.41. MS *m/z* 392 (M^+); ^1H NMR δ ($CDCl_3$) 0.43 (s, 3H, MeSi), 0.50 (s, 3H, MeSi), 0.63 (s, 9H, *t*-Bu), 0.78 (s, 9H, *t*-Bu), 1.78 (s, 3H, Me), 7.05−7.08 (m, 2H, phenyl ring protons), 7.16−7.22 (m, 1H, phenyl ring proton), 7.30−7.36 (m, 4H, phenyl and phenylene ring protons), 7.54−7.62 (m, 2H, phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) −7.77, −5.76 (MeSi), 18.32, 18.72 (CMe_3), 21.06 (Me), 27.93, 27.96 (Me_3C), 125.52, 126.92, 127.02, 127.90, 128.58, 133.96, 134.74, 142.52, 142.99, 144.31, 149.88, 155.15 (phenyl and phenylene and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −15.93, −13.38.

Palladium-Catalyzed Reaction of 1a and 1b with Diphenylacetylene. A mixture of 0.140 g (0.51 mmol) of **1a**, 0.382 g (2.14 mmol) of diphenylacetylene, and 0.0421 g (0.036 mmol) of tetrakis(triphenylphosphine)palladium(0) in a degassed sealed tube was heated at 200 °C for 24 h. The mixture was chromatographed on silica gel using hexane as the eluent to give 0.156 g (68% yield) of **8a**. Anal. Calcd for $C_{30}H_{38}Si_2$: C, 79.23; H, 8.42. Found: C, 79.30; H, 8.43. Mp 158−159 °C; MS *m/z* 454 (M^+); IR 3062, 3037, 2962, 2927, 2890, 2854, 1596, 1571, 1473, 1461, 1249, 1114, 856, 819, 794, 746, 700 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.28 (s, 6H, MeSi), 0.95 (s, 18H, *t*-Bu), 6.75−7.00 (m, 10H, phenyl ring protons), 7.37 (dd, 2H, phenylene ring protons, $J = 5.5$, 3.4 Hz), 7.63 (dd, 2H, phenylene ring protons, $J = 5.5$, 3.4 Hz); ^{13}C NMR δ ($CDCl_3$) −3.09 (MeSi), 19.25 (CMe_3), 29.01 (Me_3C), 124.82, 126.69, 127.32, 129.14, 135.71, 143.14, 143.93, 158.60 (phenyl and phenylene and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −15.47. Similar reaction of 0.132 g (0.48 mmol) of **1b** and 0.270 g (1.52 mmol) of diphenylacetylene in the presence of 0.0412 g (0.036 mmol) of tetrakis(triphenylphosphine)palladium(0) afforded 0.142 g (65% yield) of **8b**. Anal. Calcd for $C_{30}H_{38}Si_2$: C, 79.23; H, 8.42. Found: C, 79.33; H, 8.51. Mp 96−97 °C; MS *m/z* 454 (M^+); IR 3070, 3047, 2954, 2927, 2896, 1483, 1475, 1253, 1245, 1116, 1072, 991, 852, 817, 794, 781, 750, 727 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.57 (s, 6H, MeSi), 0.61 (s, 18H, *t*-Bu), 6.85−7.18 (m, 10H, phenyl ring protons), 7.36 (dd, 2H, phenylene ring protons, $J = 5.5$, 3.4 Hz), 7.63 (dd, 2H, phenylene ring protons, $J = 5.5$, 3.4 Hz); ^{13}C NMR δ ($CDCl_3$) −5.47 (MeSi), 18.62 (CMe_3), 27.66 (Me_3C), 125.00 (2C), 127.05 (2C), 134.67, 142.27, 144.10, 156.52 (phenyl and phenylene and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −14.80.

Palladium-Catalyzed Reaction of 1a and 1b with Trimethylsilylacetylene. A mixture of 0.139 g (0.50 mmol) of **1a**, 0.256 g (2.60 mmol) of trimethylsilylacetylene, and 0.0425 g (0.037 mmol) of tetrakis(triphenylphosphine)palladium(0) in a degassed sealed tube was heated at 150 °C for 24 h. The mixture was chromatographed on silica gel using hexane as the eluent to give 0.168 g (90% yield) of **9a** as a colorless liquid. Anal. Calcd for $C_{21}H_{38}Si_3$: C, 67.30; H, 10.22. Found: C, 67.43; H, 10.60. MS *m/z* 359 ($M^+ -$ Me); IR 2956, 2929, 2894, 2171, 1471, 1461, 1251, 1114, 889, 860, 842, 802, 744, 703 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.21 (s, 9H, Me_3Si), 0.28 (d, 3H, MeSi, $J = 3.7$ Hz), 0.60 (s, 3H, MeSi), 0.93 (s, 9H, *t*-Bu), 0.95 (s, 9H, *t*-Bu), 4.49 (q, 1H, HSi, $J = 3.7$ Hz), 7.32−7.36 (m, 2H, phenylene ring protons), 7.52−7.53 (m, 1H, phenylene ring proton), 8.11−8.13 (m, 1H, phenylene ring proton); ^{13}C NMR δ ($CDCl_3$) −6.41 (MeSi), −0.10 (Me_3Si), 0.02 (MeSi), 17.16, 18.09 (CMe_3), 27.10, 27.85 (Me_3C), 113.36, 116.50 (sp carbons), 127.71 (2C), 135.02, 137.86, 140.99, 143.04 (phenylene carbons); ^{29}Si NMR δ (CDCl$_3$) −19.04, −9.25, −7.01. Similar reaction of 0.156 g (0.56 mmol) of **1b** and 0.212 g (2.15 mmol) of trimethylsilylacetylene in the presence of 0.0409 g (0.035 mmol) of tetrakis(triphenylphosphine)palladium(0) afforded 0.198 g (94% yield) of **9b** as a colorless liquid. Anal. Calcd for $C_{21}H_{38}Si_3$: C, 67.30; H, 10.22. Found: C, 67.00; H, 10.52. MS *m*/*z* 359 (M$^+$ − Me); IR 2958, 2929, 2894, 2856, 2181, 1471, 1461, 1261, 1249, 1112, 879, 856, 842, 800, 790, 757, 744 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.17 (s, 9H, Me$_3$Si), 0.25 (d, 3H, MeSi, J = 3.7 Hz), 0.52 (s, 3H, MeSi), 0.96 (s, 9H, *t*-Bu), 0.99 (s, 9H, *t*-Bu), 4.76 (q, 1H, HSi, J = 3.7 Hz), 7.29−7.33 (m, 2H, phenylene ring protons), 7.55−7.57 (m, 1H, phenylene ring proton), 7.75−7.77 (m, 1H, phenylene ring proton); ^{13}C NMR δ (CDCl$_3$) −6.28 (MeSi), −1.76 (MeSi), −0.18 (Me$_3$Si), 17.27, 18.07 (CMe$_3$), 27.15, 28.01 (Me$_3$C), 113.80, 116.96 (sp carbons), 127.54, 127.74, 134.76, 136.70, 141.18, 144.13 (phenylene carbons); ^{29}Si NMR δ (CDCl$_3$) −19.23, −13.76, −8.18.

Palladium-Catalyzed Reaction of 1a and 1b with Dimethylphenylsilylacetylene. A mixture of 0.126 g (0.46 mmol) of **1a**, 0.487 g (3.04 mmol) of dimethylphenylsilylacetylene, and 0.0413 g (0.036 mmol) of tetrakis(triphenylphosphine)palladium(0) in a degassed sealed tube was heated at 150 °C for 24 h. The mixture was chromatographed on silica gel using hexane as the eluent to give 0.126 g (63% yield) of **10a** as a colorless liquid. Anal. Calcd for $C_{26}H_{40}Si_3$: C, 71.48; H, 9.23. Found: C, 71.47; H, 9.33. MS *m*/*z* 421 (M$^+$ − Me); IR 2956, 2929, 2892, 2171, 1471, 1461, 1429, 1251, 1114, 939, 887, 840, 821, 800, 782, 755, 742, 721, 703 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.30 (d, 3H, MeSi, J = 3.7 Hz), 0.48 (s, 6H, Me$_2$Si), 0.67 (s, 3H, MeSi), 0.985 (s, 9H, *t*-Bu), 0.991 (s, 9H, *t*-Bu), 4.54 (q, 1H, HSi, J = 3.7 Hz), 7.35−7.42 (m, 5H, phenyl ring protons), 7.56−7.58 (m, 1H, phenylene ring proton), 7.71−7.74 (m, 2H, phenylene ring protons), 8.18−8.19 (m, 1H, phenylene ring proton); ^{13}C NMR δ (CDCl$_3$) −6.42, −0.80, −0.78, 0.06 (MeSi), 17.16, 18.18 (CMe$_3$), 27.15, 27.86 (Me$_3$C), 114.05, 115.62 (sp carbons), 127.74, 127.77, 127.85, 129.37, 133.78, 135.04, 137.10, 137.95, 140.81, 143.05 (phenyl and phenylene ring carbons); ^{29}Si NMR δ (CDCl$_3$) −22.73, −8.76, −6.90. Similar reaction of 0.145 g (0.52 mmol) of **1b** and 0.349 g (2.18 mmol) of dimethylphenylsilylacetylene in the presence of 0.0400 g (0.035 mmol) of tetrakis(triphenylphosphine)palladium(0) afforded 0.139 g (61% yield) of **10b** as a colorless liquid. Anal. Calcd for $C_{26}H_{40}Si_3$: C, 71.48; H, 9.23. Found: C, 71.31; H, 9.35. MS *m*/*z* 421 (M$^+$ − Me); IR 3068, 3047, 2956, 2929, 2892, 2177, 1471, 1461, 1249, 1114, 879, 840, 821, 800, 746, 728, 700 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.25 (d, 3H, MeSi, J = 3.7 Hz), 0.41 (s, 6H, Me$_2$Si), 0.56 (s, 3H, MeSi), 0.97 (s, 9H, *t*-Bu), 0.99 (s, 9H, *t*-Bu), 4.75 (q, 1H, HSi, J = 3.7 Hz), 7.29−7.37 (m, 5H, phenyl ring protons), 7.56−7.58 (m, 1H, phenylene ring proton), 7.64−7.66 (m, 2H, phenylene ring protons), 7.80−7.81 (m, 1H, phenylene ring proton); ^{13}C NMR δ (CDCl$_3$) −6.24, −1.65, −1.63, −0.87 (MeSi), 17.26, 18.15 (CMe$_3$), 27.25, 28.03 (Me$_3$C), 114.46, 116.06 (sp carbons), 127.57, 127.79 (2C), 129.31, 133.78, 134.77, 136.87, 137.03, 141.01, 144.15 (phenyl and phenylene ring carbons); ^{29}Si NMR δ (CDCl$_3$) −22.91, −13.03, −7.98.

Palladium-Catalyzed Reaction of 1a and 1b with Mesitylacetylene. A mixture of 0.147 g (0.53 mmol) of **1a**, 0.394 g (2.73 mmol) of mesitylacetylene, and 0.0293 g (0.025 mmol) of tetrakis(triphenylphosphine)palladium(0) in a degassed sealed tube was heated at 150 °C for 24 h. The mixture was chromatographed on silica gel using hexane as the eluent to give 0.158 g (70% yield) of **11a** as a colorless liquid. Anal. Calcd for $C_{27}H_{40}Si_2$: C, 77.07; H, 9.58. Found: C, 77.47; H, 9.30. MS *m*/*z* 420 (M$^+$); IR 3043, 2954, 2927, 2856, 2171, 1471, 1361, 1251, 1224, 1112, 887, 835, 811, 742, 705 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.32 (d, 3H, MeSi, J = 3.7 Hz), 0.74 (s, 3H, MeSi), 1.00 (s, 9H, *t*-Bu), 1.02 (s, 9H, *t*-Bu), 2.30 (s, 3H, Mes-Me), 2.50 (s, 6H, Mes-Me), 4.58 (q, 1H, HSi, J = 3.7 Hz), 6.89 (s, 2H, Mes protons), 7.35−7.39 (m, 2H, phenyl ring protons), 7.56−7.59 (m, 1H, phenylene ring proton), 8.29−8.32 (m, 1H, phenylene ring proton); ^{13}C NMR δ (CDCl$_3$) −6.46, 0.50 (MeSi), 17.17, 18.31 (CMe$_3$), 21.19, 21.33 (Mes-Me), 27.24, 27.83 (Me$_3$C), 101.12, 105.30 (sp carbons), 120.37, 127.55, 127.66, 128.33, 135.06, 137.85, 138.17, 140.76, 141.49, 142.91 (mesityl and phenylene ring carbons); ^{29}Si NMR δ(CDCl$_3$) −7.63, −6.87. Similar reaction of 0.150 g (0.54 mmol) of **1b** and 0.367 g (2.54 mmol) of mesitylacetylene in the presence of 0.0280 g (0.024 mmol) of tetrakis(triphenylphosphine)palladium(0) afforded 0.139 g (54% yield) of **11b** as a colorless liquid. Anal. Calcd for $C_{27}H_{40}Si_2$: C, 77.07; H, 9.58. Found: C, 77.00; H, 9.39. MS *m*/*z* 420 (M$^+$); IR 3043, 2956, 2927, 2856, 2173, 1471, 1361, 1249, 1224, 1112, 879, 852, 814, 744, 717, 701 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.31 (d, 3H, MeSi, J = 3.7 Hz), 0.68 (s, 3H, MeSi), 1.00 (s, 9H, *t*-Bu), 1.09 (s, 9H, *t*-Bu), 2.30 (s, 3H, Mes-Me), 2.48 (s, 6H, Mes-Me), 4.85 (q, 1H, HSi, J = 3.7 Hz), 6.88 (s, 2H, Mes protons), 7.35−7.39 (m, 2H, phenyl ring protons), 7.62−7.65 (m, 1H, phenylene ring proton), 7.98−8.00 (m, 1H, phenylene ring proton); ^{13}C NMR δ (CDCl$_3$) −5.98, −1.22 (MeSi), 17.24, 18.32 (CMe$_3$), 21.14, 21.33 (Mes-Me), 27.41, 28.07 (Me$_3$C), 101.53, 105.88 (sp carbons), 120.42, 127.54, 127.74, 128.33, 134.72, 137.23, 137.79, 140.76, 141.78, 144.07 (mesityl and phenylene ring carbons); ^{29}Si NMR δ (CDCl$_3$) −7.63, −6.87.

X-ray Structure Determination of 4b. Crystal data for $C_{24}H_{34}Si_2$: colorless block, monoclinic, space group $C2/c$, a = 16.004(3) Å, b = 11.918(4) Å, c = 24.909(4) Å, β = 94.20(2)°, V = 4738(1) Å^3, Z = 8, D_c = 1.062 g cm^{-3}, μ(Mo Kα) = 1.55 cm^{-1}. Crystal dimensions: 0.3 × 0.4 × 0.2 mm. The structure was solved by direct methods (SIR92) and developed through subsequent cycles of least-squares refinement and difference Fourier synthesis, final R_w = 0.121 for 5032 ($I > 3\sigma(I)$) with a GOF of 1.93. Data were measured on a Rigaku AFC7R diffractometer with graphite-monochoromatized Mo Kα at 296 K.

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

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