Stereochemistry of Disilanylene-containing Cyclic Compounds – Synthesis and Palladium-catalyzed Reactions of *cis*- and *trans*-3,4-Benzo-1,2-diisopropyl-1,2-dimethyl-1,2-disilacyclobut-3-ene

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

The synthesis and palladium-catalyzed reactions of *cis*- and *trans*-3,4-benzo-1,2-diisopropyl-1,2-dimethyl-1,2-disilacyclobut-3-ene (**1a** and **1b**) are reported. Their reactions with diphenylacetylene in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) proceeded with high stereospecificity to give *cis*- and *trans*-5,6-benzo-1,4-diisopropyl-1,4-dimethyl-2,3-diphenyl-1,4-disilacyclohexa-2,5-diene, **2a** and **2b**, in 95 % and 93 % yield, respectively. Similar palladium-catalyzed reactions of **1a** and **1b** with monosubstituted acetylenes, such as 1-hexyne, *tert*-butylacetylene, phenylacetylene, and trimethylsilylacetylene, also proceeded stereospecifically to afford the respective *cis*- and *trans*-5,6-benzo-1,4-disilacyclohexa-2,5-dienes, **3a** – **6a** and **3b** – **6b**, in excellent yields and as the sole products. The palladium-catalyzed reaction of **1a** with styrene gave a mixture consisting of two stereoisomers, *cis*-2- and *trans*-2-phenyl-substituted 5,6-benzo-(*r*-1),*cis*-4-diisopropyl-1,4-disilacyclohex-5-ene **7a** and **8a** in a ratio of 5 : 3 in 72 % combined yield, while the reaction of styrene with **1b** afforded two stereoisomers, **7b** and **8b**, in a ratio of 2 : 1 in 80 % combined yield. With 1-hexene, **1a** gave two stereoisomers, 5,6-benzo-*cis*-2-(*n*-butyl)-(*r*-1),*cis*-4-diisopropyl- and 5,6-benzo-*trans*-2-(*n*-butyl)-(*r*-1),*cis*-4-diisopropyl-1,4-dimethyl-1,4-disilacyclohex-5-ene, **9a** and **10a**, in a ratio of 1 : 1 in 70 % combined yield. A similar reaction of **1b** with 1-hexene produced 5,6-benzo-*cis*-2-(*n*-butyl)-(*r*-1),*trans*-4-diisopropyl-1,4-dimethyl-1,4-disilacyclohex-5-ene in 81 % yield and as a single isomer.

Key words: Stereochemistry, Palladium-catalyzed Reaction, Disilanyl Compounds, Benzodisilacyclobutenes

Introduction

Four-membered cyclic compounds including a silicon-silicon bond are interesting because of their high strain energy and high reactivity. In fact, the 1,2-disilacyclobutene derivatives show unique chemical behavior and undergo a wide variety of reactions [1 – 9]. For example, the thermolysis of 1,2-disilacyclobutenes proceeds *via* the ring-opened 1,4-disilabutadienes as the reactive intermediates [4, 6, 11c, d]. The transition metal-catalyzed reactions of 1,2-disilacyclobutenes with various substrates afford reactive metal-containing complexes, arising from the insertion of the transition-metal complex into the silicon-silicon bond in the 1,2-disilacyclobutenes as intermediates [3, 6, 9, 11d]. The methods used for the synthesis of these compounds, however, are rather limited. They involve the reaction of silylenes with silacyclopropene or alkynes, or the reaction of disilenes with alkynes.

On the other hand, benzodisilacyclobutenes bearing various substituents at the silicon atoms can readily be prepared in high yields by the sodium condensation reaction of 1,2-bis(dialkylchlorosilyl)benzenes. To date, various types of benzodisilacyclobutenes [10 – 13] and benzobis(disilacyclobutene)s [14] have been synthe-

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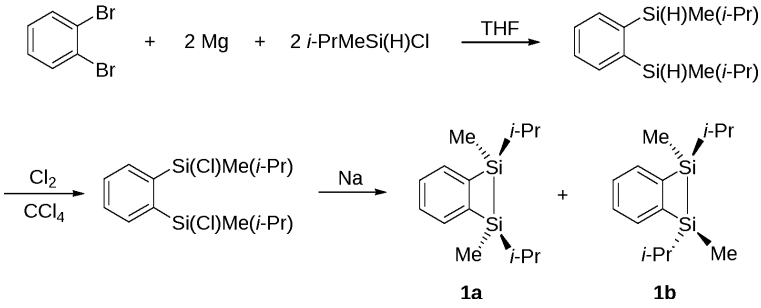


Scheme 1.

sized, and their thermal, photochemical, and transition metal-catalyzed reactions have been investigated. Theoretical treatments concerning the thermal ring-opening reaction and the platinum-catalyzed reaction of these disilacyclobutene derivatives have also been reported [15]. However, much less attention has been paid to the stereochemistry of the reactions of these compounds.

We have reported the synthesis and reactions of *cis*- and *trans*-3,4-benzo-1,2-di(*tert*-butyl)-1,2-dimethyl-1,2-disilacyclobut-3-ene and demonstrated that their palladium-catalyzed reactions with various alkynes proceed with high stereospecificity to give the 1 : 1 adducts [16]. However, on the basis of the results obtained from our investigations concerning the stereochemistry of the benzodisilacyclobutenes, it is absolutely necessary to use benzodisilacyclobutenes that are more reactive than the di(*tert*-butyl)-substituted derivatives, to be able to elucidate the stereochemistry in their reactions with various substrates. In this paper we report the synthesis and palladium-catalyzed reactions of *cis*- and *trans*-3,4-benzo-1,2-diisopropyl-1,2-dimethyl-1,2-disilacyclobut-3-ene with alkynes and alkenes.

Results and Discussion

*Synthesis of benzodisilacyclobutenes **1a** and **1b***

Cis- and *trans*-3,4-benzo-1,2-diisopropyl-1,2-dimethyl-1,2-disilacyclobut-3-ene (**1a** and **1b**) were prepared by the method used for the synthesis of *cis*- and *trans*-3,4-benzo-1,2-di(*tert*-butyl)-1,2-dimethyl-1,2-disilacyclobut-3-ene [16], as shown in Scheme 1. Thus, the reaction of *o*-dibromobenzene with 2 equiv. of magnesium in the presence of 2 equiv. of chloroisopropylmethylsilane in THF afforded 1,2-bis(isopropylmethylsilyl)benzene, consisting of a mixture of *meso*- and D,L-isomer in 77 % yield. Treatment of 1,2-bis(hydrosilyl)benzene with chlorine gas in a carbon tetrachloride solution gave a mixture of *meso*- and D,L-1,2-bis(chloroisopropylmethyl)benzene in a ratio of 1 : 1 in 92 % yield. The sodium condensation reaction of the *meso*- and D,L-isomer in refluxing toluene gave a mixture of **1a** and **1b** in a ratio of 1 : 1 in 91 % yield. **1a** and **1b** were separated by fractional distillation with the use of a spinning-band column with 50 theoretical plates and obtained in isomerically pure form.

The composition and structures of **1a** and **1b** were verified by mass spectrometry and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, as well as by elemental analysis. Because compounds **1a** and **1b** are liquid at r. t., their configuration can not be confirmed directly by X-ray crystallography. However, we assigned **1a** to have *cis* configuration on the basis of the results of an X-ray crystal structure determination of the adduct derived from the palladium-catalyzed reaction of **1a** with diphenylacetylene.

Determination of cis and trans configuration

Isomer **1a** has the higher boiling point of the two geometric isomers. It was determined to have the *cis* configuration on the basis of the following results. Treatment of isomer **1a** with diphenylacetylene in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) in a sealed glass tube at 80 °C for 24 h gave a 1 : 1 adduct in 95 % yield as white crystals. No other isomers were detected in the reaction mixture. The structure of this adduct was verified by X-ray crystallography to be *cis*-5,6-benzo-1,4-diisopropyl-1,4-dimethyl-1,4-disilacyclohexa-2,5-diene (**2a**; see Experimental Section). A drawing of the molecular structure for **2a** is shown in Fig. 1.

We have previously reported that the palladium-catalyzed reactions of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane and 1,2-disilacyclohexane with alkynes proceed with high

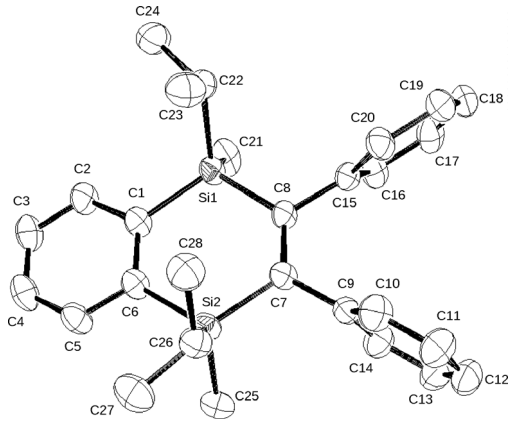


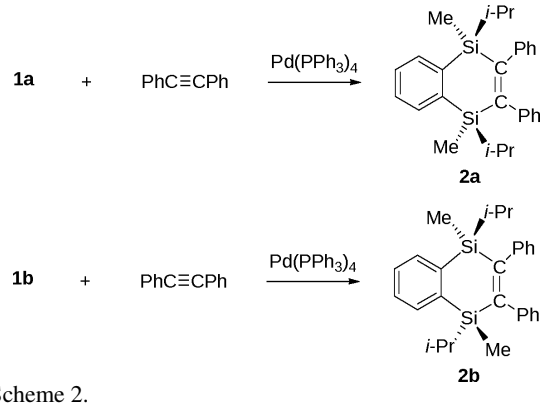
Fig. 1. ORTEP diagram of the molecular structure of **2a** in the crystal (displacement ellipsoids at the 50 % level; H atoms omitted for clarity).

stereospecificity to give the respective adducts, arising from the insertion of a carbon-carbon triple bond into a silicon-silicon bond in the five- and six-membered ring [17, 18]. We have also found that the reactions of *cis*- and *trans*-3,4-benzo-1,2-di(*tert*-butyl)-1,2-dimethyl-1,2-disilacyclobut-3-ene with diphenylacetylene in the presence of the same palladium catalyst proceed stereospecifically to give the respective adducts [16]. Therefore, in the present reaction, it seems reasonable to assume that the palladium-catalyzed reaction of the benzodisilacyclobutene **1a** with diphenylacetylene proceeds with high stereospecificity to give the *cis* adduct **2a**, and hence **1a** must have the *cis* configuration, and **1b** must be the *trans* form (Scheme 2).

The palladium-catalyzed reaction of **1b** with diphenylacetylene under the same conditions produced *trans*-5,6-benzo-1,4-diisopropyl-1,4-dimethyl-2,3-diphenyl-1,4-disilacyclohexa-2,5-diene (**2b**) in 93 % yield and as the sole product. Again, no other isomers were detected in the reaction mixture, indicating that the reaction proceeded with high stereospecificity. The structure for **2b** was confirmed by spectrometric and elemental analyses (see Experimental Section).

Palladium-catalyzed reactions with alkynes

To clarify the stereochemistry for the transition metal-catalyzed reactions of **1a** and **1b** with unsaturated compounds, we first investigated the palladium-catalyzed reactions with monosubstituted acetylenes (Scheme 3). When **1a** was treated with 1-hexyne in the presence of a catalytic amount

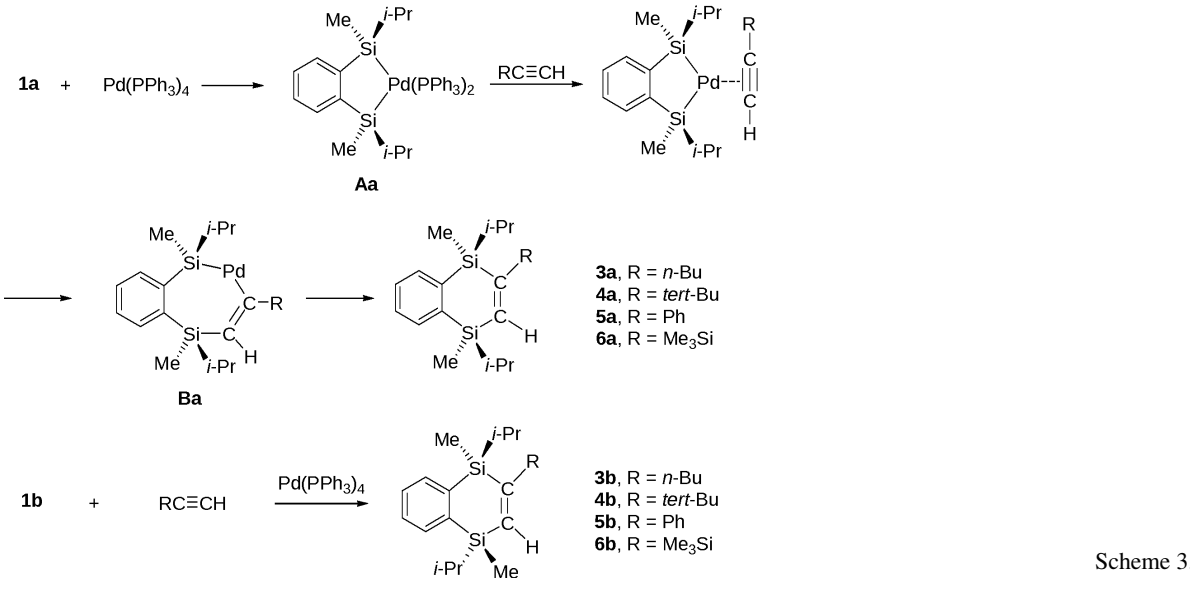


Scheme 2.

of tetrakis(triphenylphosphine)palladium(0) in a degassed sealed tube at 80 °C for 24 h, a single isomer, *cis*-5,6-benzo-2-butyl-1,4-diisopropyl-1,4-dimethyl-1,4-disilacyclohexa-2,5-diene (**3a**) was obtained in 91 % isolated yield. No other isomers were detected in the reaction mixture by spectrometric analysis. Similar treatment of **1b** with 1-hexyne afforded *trans* isomer **3b** in 93 % yield. Again, no other stereoisomers were detected in the reaction mixture. The reaction of **1a** and **1b** with *tert*-butylacetylene under the same conditions also proceeded with high stereospecificity to give the respective adducts **4a** and **4b**, in 93 % and 90 % yields, respectively. With phenylacetylene, **1a** and **1b** produced a single stereoisomer, *cis* and *trans* adducts **5a** and **5b**, respectively, as the sole products.

As reported previously, the palladium-catalyzed reactions of *cis*- and *trans*-3,4-benzo-1,2-di(*tert*-butyl)-1,2-dimethyl-1,2-disilacyclobut-3-ene [16] and also of 3,4-benzo-1,1,2,2-tetraisopropyl-1,2-disilacyclobut-3-ene [11d] with monosubstituted acetylenes bearing a bulky substituent, such as a silyl group, afford the ring-opened 1,2-bis(silyl)benzene derivatives. The benzodisilacyclobutenes **1a** and **1b**, however, reacted with trimethylsilylacetylene to give the products with the benzodisilacyclohexa-2,5-diene structure and not the 1,2-bis(silyl)benzene derivatives. Thus, treatment of **1a** with trimethylsilylacetylene at 80 °C for 24 h gave *cis*-benzodisilacyclohexadiene (**6a**) in 50 % yield, while with trimethylsilylacetylene, **1b** afforded the *trans* adduct in 77 % yield. In these reactions no other isomers were detected in the reaction mixture by spectrometric analysis.

The formation of the adducts **2a**, **b** – **6a**, **b** in the palladium-catalyzed reactions may be explained as follows (Scheme 3): (i) insertion of the palladium species



Scheme 3.

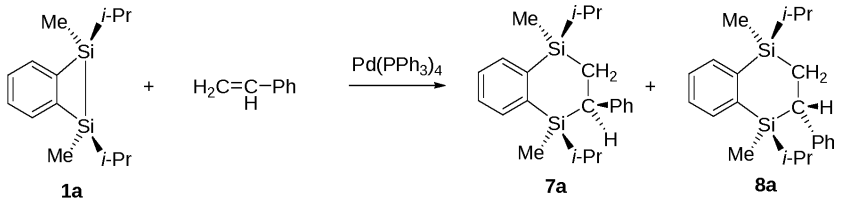
into a silicon-silicon bond in **1a**, producing *cis*-3,4-benzo-1-pallada-2,5-disilacyclopent-3-ene intermediates (**Aa**); (ii) coordination of an alkyne molecule at a palladium atom in **Aa**, followed by insertion of a triple bond of the alkyne into a palladium-silicon bond, to give complexes (**Ba**); (iii) reductive elimination of the palladium species from the resulting complex **Ba**. With **1a** as starting benzodisilacyclobutene the reaction proceeds with high stereospecificity to give the corresponding adducts, as shown in Scheme 3.

Palladium-catalyzed reactions with alkenes

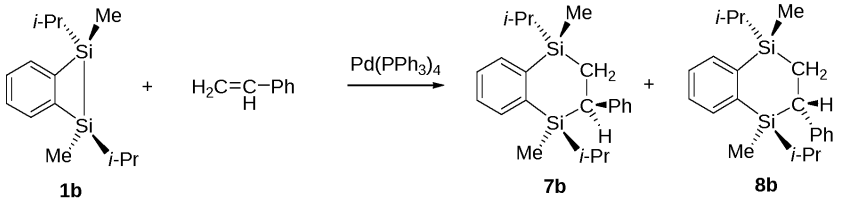
We investigated the palladium-catalyzed reaction of **1a** with alkenes under the same conditions as described above for the reactions with alkynes, however, a large amount of the starting compound **1a** was recovered unchanged. Treatment of **1a** with styrene at 80 °C for 24 h indicated that 1 : 1 adducts as a mixture of two stereoisomers were produced only in 20 % combined yield, and 80 % of **1a** was recovered unchanged. Therefore, we carried out the reactions of **1a** and **1b** with alkenes at higher temperature.

The palladium-catalyzed reaction of **1a** with styrene at 110 °C for 24 h gave two stereoisomers of the adducts, 5,6-benzo-(*r*-1),*cis*-4-diisopropyl-*cis*-2-phenyl- and 5,6-benzo-(*r*-1),*cis*-4-diisopropyl-*trans*-2-phenyl-1,4-dimethyl-1,4-disilacyclohex-5-ene (**7a** and **8a**), in a ratio of 5 : 3 in 72 % combined yield (Scheme 4). Products **7a** and **8a** were isolated by MPLC, and their configurations were confirmed by ^{1}H NMR NOE-FID difference experiments at 300 MHz. For the major product **7a**, which seems to be the sterically unfavorable isomer, irradiation of the signal at 2.84 ppm, attributed to the proton on the carbon atom attached to the phenyl group in the 1,4-disilacyclohexenyl ring, led to an enhancement of the signals at 0.12 and 0.29 ppm, due to two different kinds of methylsilyl protons, together with the signals attributed to the phenyl, phenylene and methylene protons. These results clearly indicate that the substituents, two different kinds of methyl groups at the silicon atoms, and the irradiated hydrogen atom are located in the *cis* position. For **8a**, saturation of the signal at 1.75 ppm, attributed to one of the protons of the methylene unit in the disilacyclohexenyl ring, resulted in an enhancement of the signals at 0.25, 1.21, and 7.26 ppm, due to the methyl protons, the other proton of the ring methylene unit, and the phenyl protons, indicating that the isopropyl group of the silicon at the 1-position in the six-membered ring and the phenyl group are located in a *cis* fashion.

The reaction of *trans* isomer **1b** with styrene at 110 °C produced a mixture consisting of two stereoisomers of the adducts, 5,6-benzo-(*r*-1),*trans*-4-diisopropyl-*cis*-2-phenyl- and 5,6-benzo-(*r*-1),*trans*-4-diisopropyl-*trans*-2-phenyl-1,4-dimethyl-1,4-disilacyclohex-5-ene (**7b** and **8b**), in a ratio of 2 : 1 and in 80 % combined yield. Again, the sterically unfavorable compound **7b**, but not **8b**, was obtained as the

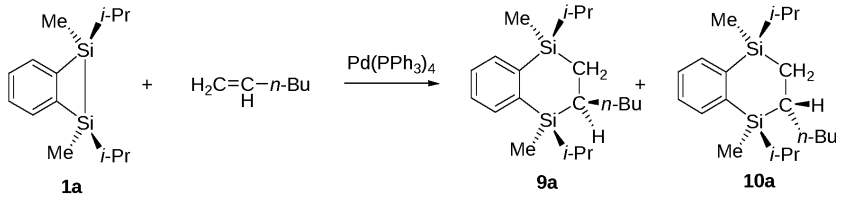


7a : **8a** = 5 : 3

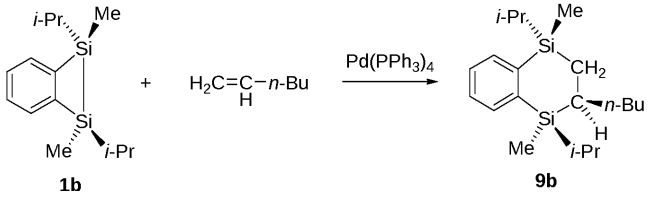


7b : **8b** = 2 : 1

Scheme 4.



9a : **10a** = 1 : 1



Scheme 5.

major product. All attempts to separate **7b** and **8b** were unsuccessful, but their structures were verified by spectrometric analysis of the mixture. The configurations for **7b** and **8b** were confirmed by NOE-FID difference experiments at 300 MHz. For the minor product **8b**, saturation of the signal at 0.28 ppm, due to methyl protons, led to an enhancement of the signals at 1.21 and 7.35 ppm, attributed to the isopropyl and phenyl protons, as well as the phenylene protons, indicating that the methyl group at the ring silicon atom at the 1-position and the phenyl group at the adjacent carbon atom are located in a *cis* fashion. Although we could not obtain clear-cut results for the configuration of **7b**, we tentatively assigned it as 5,6-benzo-(*r*-1),*trans*-4-diisopropyl-*trans*-2-phenyl-1,4-dimethyl-1,4-disilacyclohex-5-ene.

When a mixture of **1a** and 1-hexene was heated in a sealed tube at 110 °C for 24 h, two products in a ratio of 1 : 1 were obtained in 70 % combined yield. Unfortunately, all attempts to separate these two products were unsuccessful. However, we could assign these compounds tentatively as 5,6-benzo-*cis*-2-(*n*-butyl)-(*r*-1),*cis*-4-diisopropyl- and 5,6-benzo-*trans*-2-(*n*-butyl)-(*r*-1),*cis*-4-diisopropyl-1,4-dimethyl-1,4-disilacyclohex-5ene (**9a** and **10a**) by MS, and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy (see Experimental Section). To our surprise, the reaction of the *trans* isomer **1b** with 1-hexene at 110 °C afforded

5,6-benzo-*cis*-2-(*n*-butyl)-(*r*-1),*trans*-4-diisopropyl-1,4-dimethyl-1,4-disilacyclohex-5-ene (**9b**) as a single isomer, and in 81 % yield, which seems to be the sterically unfavorable isomer. No other regio- and stereoisomers were detected (Scheme 5).

The structure of the product **9b** was verified by MS and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, and also by elemental analysis. For example, the ^{13}C NMR spectrum for **9b** shows two signals at −5.8 and −4.7 ppm, a single signal at 11.8 ppm, three signals at 12.9, 14.0, and 14.1 ppm, and five signals at 17.8, 18.3, 19.0, 19.3, and 21.0 ppm, due to methyl carbons on the ring silicon atoms, the ring methylene carbon, CH-Si carbons, and methyl-C carbons, as well as the signals attributed to the methylene and phenylene carbon atoms. The ^{29}Si NMR spectrum reveals two signals at −4.0 and −3.9 ppm, due to the different ring silicon atoms. The configuration of the substituents on the benzodisilacyclohexenyl ring in **9b** was confirmed by NOE-FID difference experiments at 300 MHz. Irradiation of the signal at 0.19 ppm, due to the methyl protons on one silicon atom in the 1,4-disilacyclohexenyl ring, revealed an enhancement of the signals at 0.78, 1.00, and 7.48 – 7.52 ppm, attributed to the methyl protons of the *n*-butyl group, isopropyl, and phenylene ring protons, respectively. Saturation of a signal at 0.25 ppm, due to the methyl protons attached to the other ring silicon atom resulted in an enhancement of the signals at 1.06, 1.69 – 1.74, and 7.48 – 7.52 ppm, attributable to the isopropyl protons, the proton on the ring carbon attached to the butyl group, and the phenylene ring protons, respectively. These results are consistent with the structure proposed for **9b**.

Although the reason for the production of the unfavorable stereoisomers as major products is unclear at present, the stereochemistry for the formation of the products is considered to be determinated in the steps involving the coordination of a carbon-carbon double bond to the palladium atom in **A** (Scheme 3), and the insertion of the double bond into a palladium-silicon bond. Presumably, in these two steps, the formation of the intermediates leading to the sterically unfavorable isomers is of greater advantage than that of the others.

In conclusion, the palladium-catalyzed reactions of *cis*- and *trans*-benzodisilacyclobut-3-enes **1a** and **1b** with alkynes proceeded with high stereospecificity to give the respective adducts, *cis*- and *trans*-benzodisilacyclohex-2,5-dienes. In the reactions of **1a** and **1b** with alkenes, the *cis* and *trans* configurations of the starting compounds were maintained in all adducts. However, insertion of a carbon-carbon double bond of alkenes into a silicon-palladium bond in the palladium complex **Aa** does not proceed stereospecifically, with one exception of the reaction of **1b** with 1-hexene, to give the two stereoisomers.

Experimental Section

General procedure

All palladium-catalyzed reactions were carried out in a degassed sealed tube (1.0 cm × 15 cm). NMR spectra were measured on JNM-LA300 and JNM-LA500 spectrometers. Infrared spectra were recorded on a Jeol JIR-Diamond 20 infrared spectrophotometer. Mass spectra were measured on a Jeol model JMS-700 instrument. *Cis*- and *trans*-3,4-benzo-1,2-diisopropyl-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 used as a solvent was dried over sodium/benzophenone under a nitrogen atmosphere, and carbon tetrachloride was dried over P_4O_{10}, and distilled prior use. Benzene and toluene were dried over sodium and distilled prior use.

Preparation of 1,2-bis(isopropylmethylsilyl)benzene

In a 2 L three-necked flask fitted with a stirrer, a reflux condenser, and a dropping funnel were placed 80.4 g (3.3 mol) of magnesium and 629.8 g (5.1 mol) of chloroisopropylmethylsilane in 1.5 L of dry THF. To this mixture was added dropwise a solution of 352.7 g (1.5 mol) of *o*-dibromobenzene in 100 mL of dry THF over a period of 14 h at r. t. The mixture was heated to reflux for 1 d. 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 287.8 g (77 % yield) of a 1 : 1 mixture of *meso*- and *rac*-1,2-bis(isopropylmethylsilyl)benzene. – B. p. 76 – 80 °C/1.33 mbar. – IR (film): ν = 3046, 2953, 2890, 2862, 2137, 1461, 1250, 1120, 1004, 881, 824, 733 cm^{-1}. – ^{1}H NMR: ($CDCl_3$): δ = 0.21 – 0.22 (m, 12H, MeSi), 0.89 – 0.95 (m, 24H, Me_2CH), 1.02 – 1.12 (m, 4H, $HCMe_2$), 4.28 – 4.37 (m, 4H, HSi), 7.23 – 7.25 (m, 4H, phenylene ring protons), 7.44 – 7.46 (m, 4H, phenylene ring protons). – ^{13}C NMR ($CDCl_3$): δ = −6.8, −6.3 (MeSi), 12.7, 12.9 ($CHMe_2$), 17.87, 17.94, 18.8, 18.9 (Me_2CH), 128.06, 128.09, 134.9, 135.0, 143.35, 143.44 (phenylene ring carbon). – ^{29}Si NMR ($CDCl_3$): δ = −9.2, −8.5. – MS: *m/z* = 235 $[M–Me]^+$. – $C_{14}H_{26}Si_2$ (250.5): calcd. C 67.12, H 10.46; found C 67.14, H 10.41.

Preparation of 1,2-bis(chloroisopropylmethylsilyl)benzene

In a 1 L three-necked flask fitted with a stirrer, a reflux condenser, and an inlet tube for chlorine gas were placed 287.1 g (1.2 mol) of 1,2-bis(isopropylmethylsilyl)-benzene containing two diastereomers in a ratio of 1 : 1, in 800 mL of dry carbon tetrachloride. Dry chlorine gas was introduced into the stirred solution with ice cooling until the solution became slightly yellow. 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(chloroisopropylmethylsilyl)benzene. The solvent was distilled off, and the residue was distilled under reduced pressure to give 340.0 g (92 % yield) of 1,2-bis(chloroisopropylmethylsilyl)benzene. – B. p. 137 – 140 °C /1.33 mbar. – IR (film): ν = 2958, 2867, 1463, 1257, 1118, 998, 881, 794, 744 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.75 (s, 6H, MeSi), 0.77 (s, 6H, MeSi), 1.00 – 1.08 (m, 24H, Me_2CH), 1.50 – 1.60 (m, 4H, $HCMe_2$), 7.43 (dd, 4H, phenylene ring protons, J = 5.5 Hz, J = 3.4 Hz), 7.87 (dd, 4H, phenylene ring protons, J = 5.5 Hz, J = 3.4 Hz). – ^{13}C NMR ($CDCl_3$): δ = 1.4, 1.7 (MeSi), 16.4, 16.6 ($CHMe_2$), 16.8, 16.85, 16.91 (2C) (Me_2CH), 128.8 (2C), 136.2, 136.3, 140.4, 140.5 (phenylene ring carbons). – ^{29}Si NMR ($CDCl_3$): δ = 25.9, 26.0. – MS: *m/z* = 303 $[M - Me]^+$. – $C_{14}H_{24}Cl_2Si_2$ (319.4): calcd. C 52.64, H 7.57; found C 52.74, H 7.53.

*Preparation of cis- and trans-3,4-benzo-1,2-diisopropyl-1,2-dimethyl-1,2- disilacyclobut-3-ene (**1a** and **1b**)*

In a 1 L flask fitted with a stirrer, a reflux condenser, and a dropping funnel were placed 104.2 g (4.5 mol) of sodium and 700 mL of dry toluene. The mixture was heated to reflux, and then a solution of 340.0 g (1.1 mol) of a mixture of *meso*- and *rac*-1,2-bis(chloroisopropylmethylsilyl)benzene in 100 mL of toluene was added over a period of 7 h. After the mixture was heated to reflux for 18 h, it was filtered under a nitrogen atmosphere. The solvent toluene was distilled off, and the residue was distilled under reduced pressure to give 238.7 g (91 % yield) of a mixture of **1a** and **1b**. This mixture was fractionally distilled by using a spinning-band column with 50 theoretical plates to give pure **1a** (41.5 g, 17 % yield) and **1b** (70.4 g, 25 % yield).

Data for **1a**: B. p. 76 – 77 °C/1.33 mbar. – ^1H NMR ($CDCl_3$): δ = 0.34 (s, 6H, MeSi), 1.09 (d, 6H, Me_2CH, J = 7.4 Hz), 1.14 (d, 6H, Me_2CH, J = 7.4 Hz), 1.25 (hept, 2H, $CHMe_2$, J = 7.4 Hz), 7.31 (dd, 2H, phenylene ring protons, J = 5.4 Hz, J = 3.1 Hz), 7.45 (dd, 2H, phenylene ring protons, J = 5.4 Hz, J = 3.1 Hz). – ^{13}C NMR ($CDCl_3$): δ = −6.5 (MeSi), 14.6 ($CHMe_2$), 18.5, 18.9 (Me_2CH), 129.0, 132.0, 156.0 (phenylene ring carbons). – ^{29}Si NMR ($CDCl_3$): δ = 7.1. – MS: *m/z* = 248 $[M]^+$. – $C_{14}H_{24}Si_2$ (248.5): calcd. C 67.66, H 9.73; found C 67.36, H 9.70.

Data for **1b**: B. p. 73 – 74 °C/1.33 mbar. – ^1H NMR ($CDCl_3$): δ = 0.39 (s, 6H, MeSi), 1.05 – 1.09 (m, 12H, Me_2CH), 1.13 – 1.24 (m, 2H, $CHMe_2$), 7.31 (dd, 2H, phenylene ring protons, J = 5.4 Hz, J = 3.1 Hz), 7.44 (dd, 2H, phenylene ring protons, J = 5.4 Hz, J = 3.1 Hz). – ^{13}C NMR ($CDCl_3$): δ = −5.4 (MeSi), 14.8 ($CHMe_2$), 18.6, 18.8 (Me_2CH), 128.9, 131.9, 155.9 (phenylene ring carbons). – ^{29}Si NMR ($CDCl_3$): δ = 6.9. – MS: *m/z* = 248 $[M]^+$. – $C_{14}H_{24}Si_2$ (248.5): calcd. C 67.66, H 9.73; found C 67.46, H 9.62.

*Palladium-catalyzed reactions of **1a** with diphenylacetylene*

A mixture of 0.140 g (0.56 mmol) of **1a**, 0.357 g (2.00 mmol) of diphenylacetylene, and 0.0321 g (0.028 mmol) of tetrakis(triphenylphosphine)palladium(0) in 0.5 mL of benzene was heated in a degassed sealed tube at 80 °C for 24 h. The resulting mixture was chromatographed on silica gel eluting with hexane to give 0.229 g (95 % yield) of **2a**. No other stereoisomers were detected by GLC and spectrometric analyses.

Data for **2a**: M. p. 112 – 113 °C. – IR (KBr disk): ν = 3060, 2957, 2863, 1484, 1463, 1262, 1119, 1002, 908, 855, 795, 734 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.28 (s, 6H, MeSi), 1.00 (d, 6H, MeCH, J = 7.4 Hz), 1.08 (d, 6H, MeCH, J = 7.4 Hz), 1.16 – 1.20 (m, 2H, CMe_2), 6.86 (d, 4H, phenyl ring protons, J = 7.6 Hz), 6.95 – 6.98 (m, 2H, phenyl ring protons), 7.06 – 7.09 (m, 4H, phenyl ring protons), 7.42 – 7.44 (m, 2H, phenylene ring protons), 7.63 – 7.65 (m, 2H, phenylene ring protons). – ^{13}C NMR ($CDCl_3$): δ = −4.0 (MeSi), 14.0 ($CHMe_2$), 18.2, 18.8 (Me_2CH), 124.9, 127.2, 127.8, 128.3, 134.4, 142.9, 143.5, 157.6 (phenyl and phenylene ring carbons, and olefinic carbons). – ^{29}Si NMR ($CDCl_3$): δ = −16.7. – MS: *m/z* = 426 $[M]^+$. – $C_{28}H_{34}Si_2$ (426.7): calcd. C 78.81, H 8.03; found C 78.59, H 7.98.

*Palladium-catalyzed reactions of **1b** with diphenylacetylene*

A mixture of 0.292 g (1.18 mmol) of **1b**, 0.591 g (3.32 mmol) of diphenylacetylene, and 0.0520 g (0.045 mmol) of tetrakis(triphenylphosphine)palladium(0) in 0.75 mL of dry benzene was heated in a sealed tube at 80 °C for 24 h. The mixture was chromatographed on silica gel eluting with hexane to give 0.468 g (93 % yield) of **2b**. M. p. 67 – 68 °C. – IR (KBr disk): ν = 3050, 2942, 2862, 1483, 1462, 1254, 1120, 1001, 855, 794, 736, 701 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.41 (s, 6H, MeSi), 0.72 (d, 6H, MeCH, J = 7.0 Hz), 0.81 – 0.90 (m, 2H, $HCMe_2$), 0.93 (d, 6H, MeCH, J = 7.0 Hz), 6.81 (d, 4H, phenyl ring protons, J = 8.3 Hz), 6.92 – 6.95 (m, 2H, phenyl ring protons), 7.02 – 7.05 (m, 4H, phenyl ring protons), 7.38 (dd, 2H, phenylene ring protons, J = 5.5 Hz, J = 3.3 Hz), 7.57 (dd, 2H, phenylene ring protons, J = 5.5 Hz, J = 3.3 Hz). – ^{13}C NMR ($CDCl_3$): δ = −3.6 (MeSi), 13.3 ($CHMe_2$), 17.4, 17.6 (Me_2CH), 125.0, 127.3, 127.9, 128.4, 133.7, 142.7, 143.4, 156.9 (phenyl and phenylene ring carbons, and olefinic carbons). – ^{29}Si NMR ($CDCl_3$): δ = −16.5. – MS: *m/z* = 426 $[M]^+$. –

$C_{28}H_{34}Si_2$ (426.7): calcd. C 78.81, H 8.03; found C 78.69, H 7.76.

*Palladium-catalyzed reaction of **1a** and **1b** with 1-hexyne*

A mixture of 0.180 g (0.73 mmol) of **1a**, 0.211 g (2.57 mmol) of 1-hexyne, and 0.028 g (0.024 mmol) of tetrakis(triphenylphosphine)palladium(0) in 0.5 mL of dry benzene was heated in a sealed glass tube at 80 °C for 24 h. The mixture was chromatographed on silica gel, using hexane as the eluent, to give 0.219 g (91 % yield) of **3a**. No other isomers were detected by GLC and spectrometric analyses. – IR (film): ν = 2953, 2862, 1464, 1250, 1120, 998, 919, 881, 742, 714 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.23 (s, 3H, MeSi), 0.34 (s, 3H, MeSi), 0.89 – 1.02 (m, 17H, *n*-Bu and *i*-Pr protons), 1.33 – 1.37 (m, 2H, *n*-Bu protons), 1.44 – 1.49 (m, 2H, *n*-Bu protons), 2.25 – 2.30 (m, 2H, *n*-Bu protons), 6.63 (s, 1H, HC=C), 7.33 (dd, 2H, phenylene protons, J = 5.5 Hz, J = 3.3 Hz), 7.52 (dd, 2H, phenylene protons, J = 5.5 Hz, J = 3.3 Hz). – ^{13}C NMR ($CDCl_3$): δ = −5.1, −5.0 (MeSi), 14.9, 15.1 ($CHMe_2$), 18.0, 18.2, 18.3, 18.4 (Me_2CH), 14.1, 22.7, 30.9, 39.1 (*n*-Bu), 127.56, 127.58, 133.8, 134.1, 139.3, 143.5, 143.9, 161.6 (phenylene and olefinic carbons). – ^{29}Si NMR ($CDCl_3$): δ = −16.8, −16.3. – MS: *m/z* = 287 $[M - i\text{-}Pr]^+$. – $C_{20}H_{34}Si_2$ (330.7): calcd. C 72.65; H 10.36; found C 72.59, H 10.16.

Similar treatment of a mixture consisting of 0.241 g (0.97 mmol) of **1b**, 0.231 g (2.81 mmol) of 1-hexyne, and 0.028 g (0.024 mmol) of tetrakis(triphenylphosphine)-palladium(0) in 0.5 mL of benzene at 80 °C for 24 h afforded 0.299 g (93 % yield) of **3b**. – IR (film): ν = 2954, 2862, 1461, 1245, 1120, 998, 881, 848, 823, 786, 735 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.25 (s, 3H, MeSi), 0.36 (s, 3H, MeSi), 0.83 – 1.04 (m, 17H, *n*-Bu and *i*-Pr protons), 1.33 – 1.54 (m, 4H, *n*-Bu protons), 2.21 – 2.34 (m, 2H, *n*-Bu protons), 6.60 (s, 1H, HC=C), 7.33 (dd, 2H, phenylene ring protons, J = 5.5 Hz, J = 3.3 Hz), 7.51 (dd, 2H, phenylene ring protons, J = 5.5 Hz, J = 3.3 Hz). – ^{13}C NMR ($CDCl_3$): δ = −4.8, −3.5 (MeSi), 14.1, 14.3 ($CHMe_2$), 17.8 (2C), 17.9, 18.1, (Me_2CH), 14.4, 22.6, 31.0, 39.5 (*n*-Bu), 127.5, 127.7, 133.1, 133.7, 138.5, 143.4, 143.8, 161.9 (phenylene and olefinic carbons). – ^{29}Si NMR ($CDCl_3$): δ = −16.8, −16.2. – MS: *m/z* = 315 $[M–Me]^+$. – $C_{20}H_{34}Si_2$ (330.7): calcd. C 72.65, H 10.36; found C 72.54, H 10.35.

*Palladium-catalyzed reactions of **1a** and **1b** with tert-butylacetylene*

A mixture of 0.138 g (0.56 mmol) of **1a**, 0.193 g (2.35 mmol) of *tert*-butylacetylene, and 0.0330 g (0.029 mmol) of tetrakis(triphenylphosphine)palladium(0) in 0.5 mL of benzene in a sealed tube was heated at 80 °C for 24 h. The mixture was chromatographed on silica gel eluting with hexane to give 0.171 g (93 % yield) of **4a**. No other isomers were detected by GLC and spectrometric analyses. – IR (film): ν = 2956, 2863, 1462, 1361, 1258, 1131, 1115, 999, 881, 858, 833, 799, 788, 740, 710, 703 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.22 (s, 3H, MeSi), 0.56 (s, 3H, MeSi), 0.76 (d, 3H, MeCH, J = 7.3 Hz), 0.93 – 1.15 (m, 11H, *i*-Pr protons), 1.17 (s, 9H, *t*-Bu protons), 6.80 (s, 1H, HC=C), 7.31 – 7.36 (m, 2H, phenylene ring protons), 7.52 – 7.56 (m, 2H, phenylene ring protons). – ^{13}C NMR ($CDCl_3$): δ = −5.7, −0.7 (MeSi), 15.1, 15.6 ($CHMe_2$), 18.1, 18.3, 18.4, 18.8 (Me_2CH), 31.1 (Me_3C), 40.1 (CMe_3), 127.3, 127.5, 133.7, 134.6, 138.1, 143.6, 143.8, 168.9 (phenylene and olefinic carbons). – ^{29}Si NMR ($CDCl_3$): δ = −16.0 (2Si). – MS: *m/z* = 315 $[M - Me]^+$. – $C_{20}H_{34}Si_2$ (330.7): calcd. C 72.65, H 10.36; found C 72.54, H 10.26.

Similar treatment of a mixture consisting of 0.137 g (0.56 mmol) of **1b**, 0.211 g (2.56 mmol) of *tert*-butylacetylene, and 0.032 g (0.028 mmol) of tetrakis(triphenylphosphine)palladium(0) in a sealed tube at 80 °C for 24 h gave 0.166 g (90 % yield) of **4b**. – IR (film): ν = 2953, 2863, 1461, 1326, 1256, 1246, 1223, 1132, 1116, 1000, 880, 856, 832, 785, 742 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.26 (s, 3H, MeSi), 0.59 (s, 3H, MeSi), 0.68 (d, 3H, MeCH, J = 7.3 Hz), 0.81-0.82 (m, 3H, MeCH), 0.94 (d, 3H, MeCH, J = 7.3 Hz), 0.99 – 1.11 (m, 5H, MeCH and $HCMe_2$), 1.17 (s, 9H, *t*-Bu), 6.80 (s, 1H, HC=C), 7.30 – 7.35 (m, 2H, phenylene ring protons), 7.50 – 7.54 (m, 2H, phenylene ring protons). – ^{13}C NMR ($CDCl_3$): δ = −3.6, −1.2 (MeSi), 14.5, 15.3 ($CHMe_2$), 17.8, 17.9, 18.0, 18.3 (Me_2CH), 31.0 (Me_3C), 40.2 (CMe_3), 127.38, 127.42, 132.7, 134.2, 136.2, 143.3, 143.6, 169.5 (phenylene and olefinic carbons). – ^{29}Si NMR ($CDCl_3$): δ = −16.1, −15.6. – MS: *m/z* = 287 $[M - i\text{-}Pr]^+$. – $C_{20}H_{34}Si_2$ (330.7): calcd. C 72.65, H 10.36; found C 72.69, H 10.32.

*Palladium-catalyzed reaction of **1a** and **1b** with phenylacetylene*

A mixture of 0.234 g (0.94 mmol) of **1a**, 0.333 g (3.26 mmol) of phenylacetylene, and 0.039 g (0.034 mmol) of tetrakis(triphenylphosphine)palladium(0) in 0.5 mL of benzene was heated in a sealed tube at 80 °C for 24 h. The mixture was chromatographed on silica gel eluting with hexane to give 0.312 g (94 % yield) of **5a**. No other stereoisomers were detected by GLC and spectrometric analyses. – IR (film): ν = 3057, 2956, 2862, 1488, 1462, 1251, 1117, 998, 880, 815, 789, 768, 714 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.31 (s, 3H, MeSi), 0.42 (s, 3H, MeSi), 0.81 (d, 3H, MeCH, J = 7.1 Hz), 0.96 – 1.09 (m, 11H, *i*-Pr, MeCH, and $CHMe_2$), 6.84 (s, 1H, HC=C), 7.20 – 7.25 (m, 3H, phenyl ring protons), 7.30 – 7.33 (m, 2H, phenyl ring protons), 7.36 – 7.39 (m, 2H, phenylene ring protons), 7.57 – 7.59 (m, 2H, phenylene ring protons). – ^{13}C NMR ($CDCl_3$): δ = −5.0, −3.5 (MeSi), 14.9, 15.0 ($CHMe_2$), 18.0 (2C), 18.25, 18.31 (Me_2CH), 126.3, 126.6, 127.80, 127.83, 128.1, 133.9, 134.4, 143.0, 143.3, 145.5, 148.4, 161.9 (phenyl, phenylene and olefinic car-

bons). – ^{29}Si NMR ($CDCl_3$): δ = −16.5, −15.8. – MS: *m/z* = 307 $[M - i\text{-Pr}]^+$. – $C_{22}H_{30}Si_2$ (350.6): calcd. C 75.36, H 8.62; found C 75.66, H 8.63.

Similar treatment of a mixture consisting of 0.194 g (0.78 mmol) of **1b**, 0.338 g (3.31 mmol) of phenylacetylene, and 0.0290 g (0.025 mmol) of a palladium catalyst produced 0.259 g (94 % yield) of **5b**. – IR (film): ν = 3057, 2954, 2890, 1488, 1463, 1246, 1120, 998, 880, 867, 818, 788, 736, 700 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 0.35 (s, 3H, MeSi), 0.46 (s, 3H, MeSi), 0.73 (d, 3H, MeCH, *J* = 7.1 Hz), 0.88 – 1.08 (m, 11H, *i*-Pr, MeCH, and $CHMe_2$), 6.81 (s, 1H, HC=C), 7.22 – 7.26 (m, 3H, phenyl ring protons), 7.31 – 7.38 (m, 4H, phenyl and phenylene ring protons), 7.56 – 7.57 (m, 2H, phenylene ring protons). – ^{13}C NMR ($CDCl_3$): δ = −3.8, −3.4 (MeSi), 14.39, 14.40 ($CHMe_2$), 17.6, 17.75, 17.81, 17.9 (Me_2CH), 126.3, 126.6, 127.8, 127.9, 128.1, 133.2, 134.0, 143.0, 143.2, 144.6, 148.4, 162.1 (phenyl, phenylene and olefinic carbons). – ^{29}Si NMR ($CDCl_3$): δ = −16.2, −15.9. – MS: *m/z* = 307 $[M - i\text{-Pr}]^+$. – $C_{22}H_{30}Si_2$ (350.6): calcd. C 75.36, H 8.62; found C 75.41, H 8.62.

*Palladium-catalyzed reaction of **1a** and **1b** with trimethylsilylacetylene*

A mixture of 0.160 g (0.64 mmol) of **1a**, 0.254 g (2.59 mmol) of trimethylsilylacetylene, and 0.036 g (0.031 mmol) of tetrakis(triphenylphosphine)palladium(0) in 0.5 mL of benzene was heated in a sealed tube at 80 °C for 24 h. The mixture was chromatographed on silica gel eluting with hexane to give 0.113 g (50 % yield) of **6a**. No other isomers were detected by GLC and spectrometric analyses. – IR (film): ν = 2953, 2892, 2863, 1462, 1247, 1117, 998, 899, 882, 832, 744, 709 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 0.14 (s, 9H, Me_3Si), 0.25 (s, 3H, MeSi), 0.40 (s, 3H, MeSi), 0.77 (d, 3H, MeCH, *J* = 7.3 Hz), 0.94 – 1.05 (m, 11H, *i*-Pr, MeCH, and $CHMe_2$), 7.30 – 7.34 (m, 2H, phenylene ring protons), 7.48 – 7.54 (m, 2H, phenylene ring protons), 7.72 (s, 1H, HC=C). – ^{13}C NMR ($CDCl_3$): δ = −5.9, −2.9 (MeSi), 0.1 (Me_3Si), 15.0, 15.2 ($CHMe_2$), 18.1, 18.3 (2C), 18.5 (Me_2CH), 127.5, 127.6, 134.0, 134.3, 143.5, 143.7, 162.0, 168.4 (phenylene and olefinic carbons). – ^{29}Si NMR ($CDCl_3$): δ = −22.3, −16.6, −4.2. – MS: *m/z* = 346 $[M]^+$. – $C_{19}H_{34}Si_3$ (346.7): calcd. C 65.82, H 9.88; found C 65.60, H 9.78.

Similar treatment of a mixture consisting of 0.166 g (0.67 mmol) of **1b**, 0.241 g (2.45 mmol) of phenylacetylene, and 0.0330 g (0.029 mmol) of a palladium catalyst produced 0.159 g (77 % yield) of **6b**. – IR (film): ν = 2952, 2922, 2891, 1463, 1246, 1118, 998, 899, 882, 804, 785, 743, 707 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 0.15 (s, 9H, Me_3Si), 0.27 (s, 3H, MeSi), 0.43 (s, 3H, MeSi), 0.70 (d, 3H, MeCH, *J* = 7.3 Hz), 0.84 – 1.04 (m, 11H, *i*-Pr, MeCH, and $CHMe_2$), 7.29 – 7.34 (m, 2H, phenylene ring protons), 7.48 – 7.54 (m, 2H, phenylene ring protons), 7.69 (s, 1H, HC=C). – ^{13}C NMR ($CDCl_3$): δ = −4.0, −3.0 (MeSi), 0.0 (Me_3Si), 14.2, 14.7 ($CHMe_2$), 17.8, 17.87, 17.90, 18.0 (Me_2CH), 127.5, 127.6, 133.1, 133.9, 143.4, 143.6, 160.5, 168.9 (phenylene and olefinic carbons). – ^{29}Si NMR ($CDCl_3$): δ = −22.0, −16.7, −4.3. – MS: *m/z* = 346 $[M]^+$. – $C_{19}H_{34}Si_3$ (346.7): calcd. C 65.82. H 9.88; found C 65.52, H 9.94.

*Palladium-catalyzed reactions of **1a** with styrene*

A mixture of 0.1008 g (0.406 mmol) of **1a**, 0.1180 g (1.13 mmol) of styrene, and 0.0232 g (0.0201 mmol) of tetrakis(triphenylphosphine)palladium(0) in 0.5 mL of benzene was heated in a degassed sealed tube at 110 °C for 24 h. The resulting mixture was applied to a short silica gel column to give 0.1030 g (72 % yield) of the mixture consisting of **7a** and **8a**. The ratio of **7a** and **8a** was determined to be 5 : 3 by ^{1}H NMR spectroscopy. Compounds **7a** and **8a** were isolated by MPLC.

Data for **7a**: ^{1}H NMR ($CDCl_3$): δ = 0.12 (s, 3H, MeSi), 0.29 (s, 3H, MeSi), 0.91 (d, 3H, *i*-Pr-Me, *J* = 6.6 Hz), 1.09 – 1.14 (m, 11H, *i*-Pr-Me, CHSi), 1.39 (dd, 1H, CHSi, *J* = 14.3 Hz, 3.1 Hz), 1.51 (t, 1H, CHSi, *J* = 14.3 Hz), 2.84 (dd, 1H, CHPh, *J* = 14.3 Hz, 3.1 Hz), 7.16 – 7.63 (m, 9H, phenyl and phenylene ring protons). – ^{13}C NMR ($CDCl_3$): δ = −6.0, −5.9 (MeSi), 12.6 (CH_2Si), 13.0, 14.4 (CHSi), 17.6, 17.7, 18.1, 18.2 (MeCH), 26.0 (CHPh), 124.6, 127.5, 127.8, 128.0, 128.1, 134.2, 134.3, 144.2, 144.7, 147.4 (phenyl and phenylene ring carbons). – ^{29}Si NMR ($CDCl_3$): δ = −2.33, −2.27. – MS: *m/z* = 352 $[M]^+$. – $C_{22}H_{32}Si_2$ (352.7): calcd. C 74.93, H 9.15; found C 74.64, H 9.11.

Data for **8a**: ^{1}H NMR ($CDCl_3$): δ = 0.09 (s, 3H, MeSi), 0.25 (s, 3H, MeSi), 0.77 (d, 3H, *i*-Pr-Me, *J* = 7.3 Hz), 0.80 (d, 3H, *i*-Pr-Me, *J* = 7.3 Hz), 1.01 (d, 3H, *i*-Pr-Me, *J* = 6.8 Hz), 1.10 (d, 3H, *i*-Pr-Me, *J* = 6.8 Hz), 1.00 – 1.13 (m, 2H, CHMe), 1.21 (dd, 1H, CHSi, *J* = 14.3 Hz, 2.4 Hz), 1.75 (dd, 1H, ring CHSi, *J* = 15.3 Hz, 14.3 Hz), 2.63 (dd, 1H, CHPh, *J* = 15.3 Hz, 2.4 Hz), 7.14 – 7.55 (m, 9H, phenyl and phenylene ring protons). – ^{13}C NMR ($CDCl_3$): δ = −5.7, −4.0 (MeSi), 10.6 (CH_2Si), 11.4, 13.6 (CHSi), 17.6, 18.0, 18.8, 19.4 (MeCH), 29.1 (CHPh), 124.5, 127.1, 127.7, 128.0, 128.1, 133.8, 134.7, 144.1, 144.3, 146.5 (phenyl and phenylene ring carbons). – ^{29}Si NMR ($CDCl_3$): δ = −0.96, −1.00. – MS: *m/z* = 352 $[M]^+$. – $C_{22}H_{32}Si_2$ (352.7): calcd. C 74.93, H 9.15; found C 74.77, H 9.01.

*Palladium-catalyzed reactions of **1b** with styrene*

A mixture of 0.1050 g (0.423 mmol) of **1b**, 0.1236 g (1.19 mmol) of styrene, and 0.0230 g (0.0199 mmol) of tetrakis(triphenylphosphine)palladium(0) in 0.5 mL of dry benzene was heated in a sealed tube at 110 °C for 24 h. The mixture was purified by chromatography through silica gel column eluting with hexane to give 0.1192 g (80 % yield) of a mixture consisting of **7b** and **8b**. The ratio of **7b** and **8b** was

determined to be 2 : 1 by ^{1}H NMR spectroscopy. – ^{1}H NMR ($CDCl_3$): δ = 0.28 (s, 3H, MeSi, **8b**), 0.41 (s, 3H, MeSi, **7b**), 0.415 (s, 3H, MeSi, **7b**), 0.419 (s, 3H, MeSi, **8b**), 0.88 (d, 3H, *i*-Pr-Me, *J* = 7.0 Hz, **7b**), 0.90 (d, 3H, *i*-Pr-Me, *J* = 7.0 Hz, **7b**), 0.92 (d, 3H, *i*-Pr-Me, *J* = 7.0 Hz, **8b**), 1.10 (d, 3H, *i*-Pr-Me, *J* = 7.0 Hz, **8b**), 1.13 (d, 3H, *i*-Pr-Me, *J* = 7.0 Hz, **7b**), 1.18 (d, 3H, *i*-Pr-Me, *J* = 7.0 Hz, **8b**), 1.20 (d, 3H, *i*-Pr-Me, *J* = 7.0 Hz, **7b**), 1.21 (d, 3H, *i*-Pr-Me, *J* = 7.0 Hz, **8b**), 1.00 – 1.34 (m, 4H, CHMe, **7b** and **8b**), 1.57 (dd, 2H, ring CHSi, *J* = 15.0 Hz, 3.0 Hz, **7b** and **8b**), 1.69 (t, 1H, CH, *J* = 15.0 Hz, **8b**), 1.75 (t, 1H, CH, *J* = 15.0 Hz, **7b**), 2.81 (dd, 1H, CHPh, *J* = 15.0 Hz, 2.5 Hz, **8b**), 2.84 (dd, 1H, CHPh, *J* = 15.0 Hz, 2.5 Hz, **7b**), 7.27 – 7.72 (m, 18H, phenyl and phenylene ring protons, **7b** and **8b**). – ^{13}C NMR ($CDCl_3$): δ = −6.1 (**8b**), −5.3 (**7b**), −5.0 (**7b**), −4.3 (**8b**) (MeSi), 11.8 (**7b**), 12.1 (**8b**) (CH_2Si), 12.4 (**8b**), 12.6 (**7b**), 13.3 (**8b**), 13.7 (**7b**) (CHSi), 17.4 (**8b**), 17.6 (**8b**), 17.7 (**7b**), 17.9 (**8b**), 18.0 (**8b**), 18.3 (**7b**), 18.6 (**7b**), 19.2 (**7b**) (MeCH), 25.7 (**8b**), 29.9 (**7b**) (CHPh), 124.5 (**7b**), 124.6 (**8b**), 127.0 (**7b**), 127.5 (**7b**), 127.7 (**8b**), 127.85 (**8b**), 127.88 (**8b**), 127.97 (**8b**), 128.03 (**7b**), 128.1 (**7b**), 133.7 (**8b**), 133.9 (**8b**), 134.1 (**7b**), 134.5 (**7b**), 143.9 (**7b**), 144.1 (**7b**), 144.4 (**8b**), 144.5 (**8b**), 146.4 (**7b**), 147.5 (**8b**) (phenyl and phenylene ring carbons). – ^{29}Si NMR ($CDCl_3$): δ = −4.2, −2.6, −2.4, −1.2. – MS: *m/z* = 352 $[M]^+$. – $C_{22}H_{32}Si_2$ (352.7): calcd. C 74.93, H 9.15; found C 74.67, H 9.10.

*Palladium-catalyzed reactions of **1a** with 1-hexene*

A mixture of 0.1006 g (0.405 mmol) of **1a**, 0.1203 g (1.43 mmol) of 1-hexene, and 0.0232 g (0.0201 mmol) of tetrakis(triphenylphosphine)palladium(0) in 0.5 mL of benzene was heated in a degassed sealed tube at 110 °C for 24 h. The resulting mixture was purified by chromatography through silica gel column eluting with hexane to give 0.0943 g (70 % yield) of a mixture consisting of **9a** and **10a**. The ratio of **9a** and **10a** was determined to be 1 : 1 by ^{1}H NMR spectroscopy.

Data for **9a** and **10a**: ^{1}H NMR ($CDCl_3$): δ = 0.16 (s, 6H, MeSi), 0.19 (s, 3H, MeSi), 0.23 (s, 3H, MeSi), 0.70 – 1.11 (m, 38H, Me,CH_2), 1.22 – 1.37 (m, 10H, CHSi, CH_2), 1.54 – 1.74 (m, 4H, CH), 7.29 – 7.33 (m, 4H, phenylene ring protons), 7.46 – 7.50 (m, 4H, phenylene ring protons). – ^{13}C NMR ($CDCl_3$): δ = −7.4, −6.4, −5.3, −3.8 (MeSi), 10.3, 11.1 (CH_2Si), 12.4, 13.4 (2C), 13.7, 14.1, 14.2, 16.1, 17.55, 17.60, 17.98, 18.01, 18.2, 18.3, 19.1, 19.3, 20.4, 22.67, 22.68, 30.3, 30.6, 33.1, 33.6 (*i*-Pr, *n*-Bu, CHSi), 127.48, 127.52, 127.8 (2C), 133.7, 133.9, 134.3, 134.4, 144.6, 144.7, 144.9, 145.2 (phenylene ring carbons). – ^{29}Si NMR ($CDCl_3$): δ = −4.0, −3.4, −2.1, −1.9. – MS: *m/z* = 332 $[M]^+$. – $C_{20}H_{36}Si_2$ (332.7): calcd. C 72.21, H 10.91; found C 72.00, H 10.98.

*Palladium-catalyzed reactions of **1b** with 1-hexene*

A mixture of 0.1021 g (0.411 mmol) of **1b**, 0.1102 g (1.33 mmol) of 1-hexene, and 0.0232 g (0.0201 mmol) of tetrakis(triphenylphosphine)palladium(0) in 0.5 mL of dry benzene was heated in a sealed tube at 110 °C for 24 h. The mixture was purified by chromatography through silica gel column eluting with hexane to give 0.1107 g (81 % yield) of **9b**. – ^{1}H NMR ($CDCl_3$): δ = 0.19 (s, 3H, MeSi), 0.25 (s, 3H, MeSi), 0.78 (t, 3H, CH_3, *J* = 14.5 Hz), 0.90 – 1.06 (m, 16H, MeCH, CH_2), 1.24 – 1.42 (m, 4H, CHSi, CH_2), 1.34 (dd, 1H, CH, *J* = 15 Hz, 4 Hz), 1.58 – 1.64 (m, 1H, CH), 1.69 – 1.74 (m, 1H, CH), 7.31 – 7.34 (m, 2H, phenyl ring protons), 7.48 – 7.52 (m, 2H, phenylene ring protons). – ^{13}C NMR ($CDCl_3$): δ = −5.8, −4.7 (MeSi), 11.8 (CH_2Si), 12.9, 14.0, 14.1 (CHSi), 17.8, 18.3, 19.0, 19.3, 21.0 (Me), 22.7, 30.6, 33.6 (CH_2), 127.5, 127.6, 133.9, 134.2, 144.6, 144.7 (phenylene ring carbons). – ^{29}Si NMR ($CDCl_3$): δ = −4.0, −3.9. – MS: *m/z* = 332 $[M]^+$. – $C_{20}H_{36}Si_2$ (332.7): calcd. C 72.21, H 10.91; found C 72.11, H 10.76.

Crystal structure analysis

The structure determination of **2a** suffered from a weakly diffracting crystal and a low completeness of the data set. As a consequence, a poor data to parameter ratio precludes a detailled discussion of distances and angles, although the observed *cis* configuration could be clearly confirmed [19].

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