

Palladium-catalyzed reactions of 1,1,2,2-tetraethyl- and 1,1,2,2-tetra(isopropyl)-3,4-benzo-1,2-disilacyclobut-3-ene with alkynes¹

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Abstract

The reactions of 3,4-benzo-1,1,2,2-tetra(isopropyl)-1,2-disilacyclobut-3-ene (**2**) with acetylene, phenylacetylene, 1-hexyne, and *o*-tolylacetylene in the presence of tetrakis(triphenylphosphine)palladium gave the respective 5,6-benzo-1,4-disilacyclohexa-2,5-dienes **3–6**. Similar reactions of **2** with mesitylacetylene, trimethylsilylacetylene, and dimethylphenylsilylacetylene afforded 1-alkynyl(diisopropylsilyl)-2-(diisopropylsilyl)benzenes **7–9** arising from *sp*-hybridized C–H bond activation of acetylenes. The reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene with mesitylacetylene, trimethylsilylacetylene, and dimethylphenylsilylacetylene produced 5,6-benzo-1,4-disilacyclohexa-2,5-dienes **10–12** as the sole product. The stoichiometric reaction of **2** with tetrakis(triphenylphosphine)palladium gave a yield of 3,4-benzo-2,2,5,5-tetra(isopropyl)-1-pallada-2,5-disilacyclopent-3-ene (**A**), arising from insertion of a palladium species into a silicon–silicon bond in **2**.

Keywords: Silicon; Palladium; 3,4-Benzo-1,2-disilacyclobut-3-ene; Alkyne insertion; C–H activation; Catalyst

1. Introduction

Recently, we found that 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1**) shows interesting behavior toward organic substrates such as aromatic compounds, carbonyl compounds, alkenes, and alkynes in the presence of a catalytic amount of a transition-metal complex [1]. In these reactions, *o*-quinodisilane–transition-metal complexes and 3,4-benzo-2,2,5,5-tetraethyl-1-metala-2,5-disilacyclopent-3-enes are produced as reactive species. The type of product formed from transition-metal catalyzed reactions of **1** with the organic substrates depends strongly on the nature of the metal in the reactive species. The nickel-catalyzed reactions of **1** with diphenylacetylene and 3-hexyne afford two adducts, 5,6-benzo-1,1,4,4-tetraethyl-1,4-disilacyclohexa-2,5-dienes and 5,6-benzo-1,1,2,2-tetraethyl-1,2-disilacyclohexa-3,5-dienes [2], while the palladium- and platinum-catalyzed reactions [3,4] produce only 5,6-benzo-

1,4-disilacyclohexa-2,5-dienes. Similar nickel-catalyzed reactions with mono-substituted acetylenes, such as phenylacetylene and 1-hexyne, do not give adducts, but yield involatile products. The palladium- and platinum-catalyzed reactions with these acetylenes, however, give adducts arising from insertion of a triple bond into the silicon–silicon bond in **1** as the sole products.

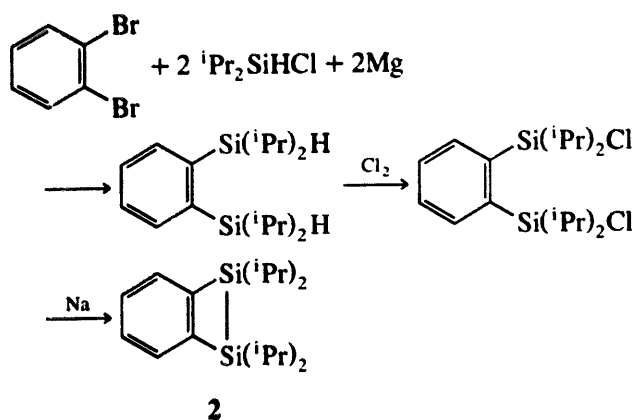
It seemed interesting to investigate the chemical behavior of the benzodisilacyclobutene with bulky substituents on the silicon atoms toward alkynes in the presence of the transition-metal catalyst. In this paper we report the palladium-catalyzed reactions of 3,4-benzo-1,1,2,2-tetra(isopropyl)-1,2-disilacyclobut-3-ene (**2**) with various types of mono-substituted alkyne. We also investigated the reactions of **1** with mono-substituted acetylenes bearing a bulky substituent in order to compare the reactivity of **1** with that of **2** toward these acetylenes.

2. Results and discussion

The starting 3,4-benzo-1,1,2,2-tetra(isopropyl)-1,2-disilacyclobut-3-ene **2** was synthesized by a method

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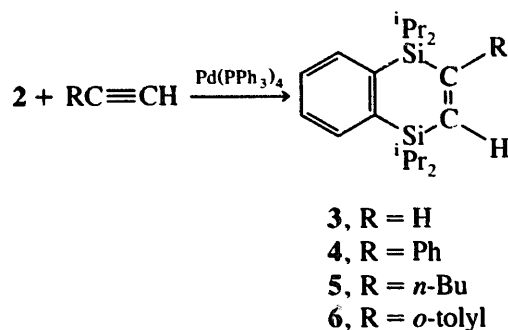
¹ Dedicated to Professor Robert Corriu in recognition of his outstanding contributions to organosilicon chemistry.



Scheme 1.

similar to that used for 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene **1** [5,6]. Thus, treatment of 1,2-dibromobenzene with magnesium in the presence of chloro(diisopropyl)silane in THF afforded 1,2-bis(diisopropylsilyl)benzene in 72% yield. Treatment of 1,2-bis(diisopropylsilyl)benzene with chlorine in carbon tetrachloride produced 1,2-bis[chloro(diisopropylsilyl)]benzene in 56% yield. Sodium condensation of the bis(chlorosilyl)benzene gave **2** in 91% yield (Scheme 1). Compound **2** is stable toward oxygen and moisture in air. Unlike that in 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene **1**, the silicon–silicon bond in **2** is not oxidized by air at room temperature, and so **2** can be handled in air without decomposition. Compound **2** is thermally very stable. Thus, when it was heated in a degassed glass tube under conditions in which **1** is readily converted into an *o*-quinodisilane intermediate there was no indication of the formation of the *o*-quinodisilane derivative. Even at 280°C no change was observed, and **2** was recovered unchanged.

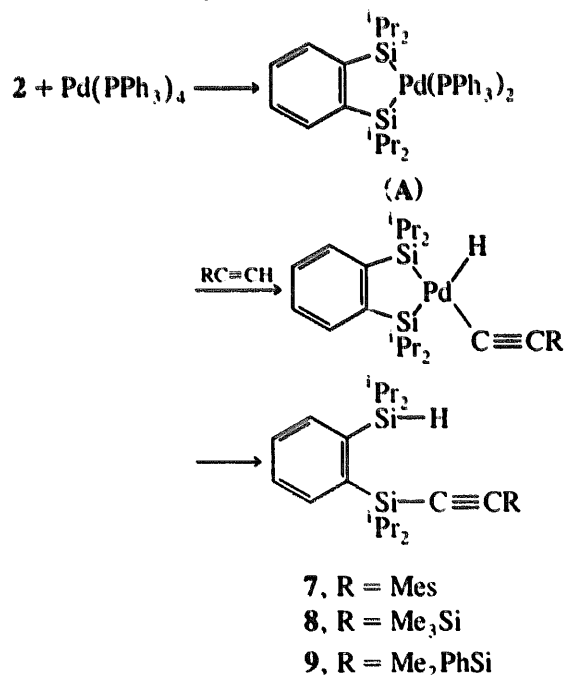
First, we investigated the palladium-catalyzed reaction of **2** with acetylene. The reaction of **2** in the presence of tetrakis(triphenylphosphine)palladium(0) with acetylene bubbled through refluxing mesitylene afforded 5,6-benzo-1,1,4,4-tetra(isopropyl)-1,4-disilacyclohexa-2,5-diene (**3**) in 75% yield as the sole product. Treatment of **2** with phenylacetylene in the presence of the palladium catalyst in refluxing benzene gave 5,6-benzo-1,1,4,4-tetra(isopropyl)-2-phenyl-1,4-disilacyclohexa-2,5-diene (**4**) quantitatively. Similar treatment of **2** with 1-hexyne again produced 5,6-benzo-1,1,4,4-disilacyclohexa-2,5-diene (**5**) in quantitative yield. With *o*-tolylacetylene, **2** also afforded the benzodisilacyclohexadiene derivative, 5,6-benzo-1,1,4,4-tetra(isopropyl)-2-*o*-tolyl-1,4-disilacyclohexa-2,5-diene (**6**) in 64% yield, along with 33% of unchanged **2** (Scheme 2). The benzodisilacyclohexadienes analogous to **3–6** were formed in the palladium-catalyzed reactions of **1** with the same alkynes.



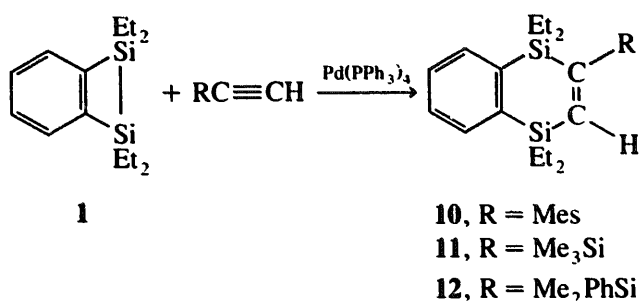
Scheme 2.

The structures of products **3–6** were verified by spectrometric analysis, as well as by elemental analysis. In the ^{29}Si NMR spectra of **3–6**, all resonances for silicon atoms appear in the range -13.8 to -12.0 ppm, indicating that **3–6** must have a benzodisilacyclohexadiene structure [2].

Interestingly, the reaction of **2** at higher temperatures with mono-substituted acetylenes bearing a bulky substituent follows a different course from that observed for phenylacetylene and 1-hexyne. Thus, the palladium-catalyzed reaction of **2** with mesitylacetylene in a degassed sealed tube at 150°C for 24 h gave exclusively 2-diisopropylsilyl-1-[diisopropyl(mesitylethynyl)silyl]benzene (**7**) in 87% yield (Scheme 3). The mass spectrum of **7** shows a parent ion at m/z 448, consistent with the molecular ion from a 1:1 adduct. Its IR spectrum reveals a strong absorption at 2143 cm^{-1} due to the Si–H stretching frequencies. The ^1H NMR spectrum also shows a triplet at 4.42 ppm, attributed to an



Scheme 3.



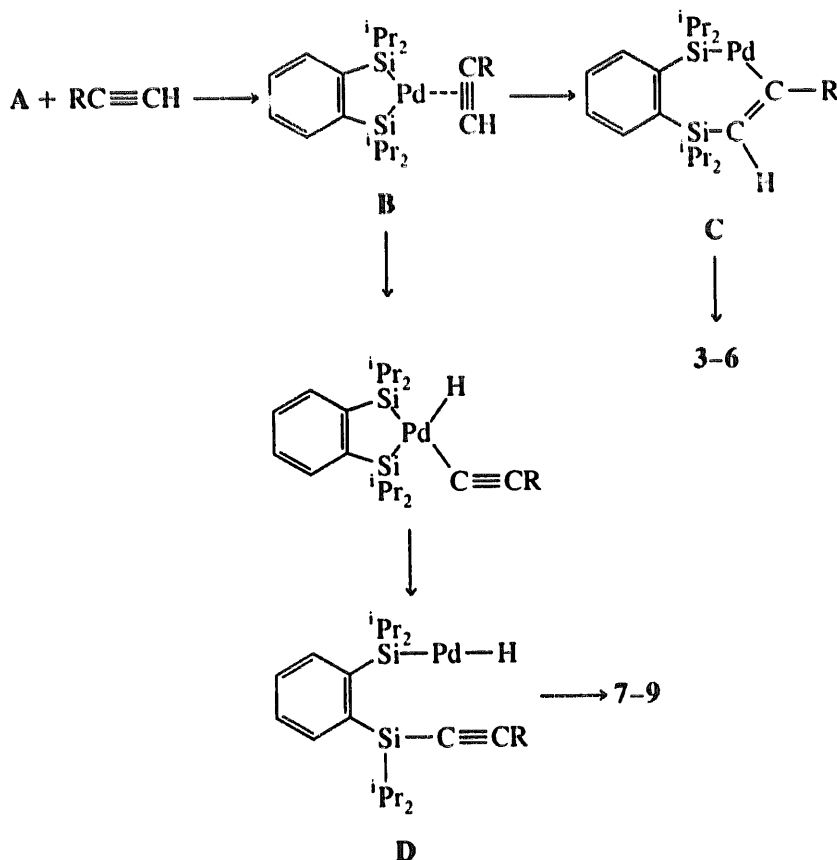
Scheme 4.

Si–H proton. The ¹³C NMR spectrum of **7** shows two resonances, at 97.36 and 106.85 ppm, due to ethynyl carbons, while the ²⁹Si NMR spectrum shows two resonances, at –1.21 and –0.68 ppm, attributable to two nonequivalent silicon atoms. These results are wholly consistent with the structure proposed for **7**. With trimethylsilylacetylene and dimethylphenylsilylacetylene, **2** gave quantitative yields of the same type of product, namely 2-diisopropylsilyl-1-[diisopropyl(trimethylsilyl)ethynylsilyl]benzene (**8**) and 2-diisopropylsilyl-1-[diisopropyl(dimethylphenylsilyl)ethynylsilyl]benzene (**9**). In these reactions, no 5,6-benzo-1,4-disilacyclohexa-2,5-dienes analogous to **3–6** were detected in the product solution.

The IR spectra of products **8** and **9** also show strong absorptions at about 2131 and 2130 cm^{–1} due to stretching frequencies of the Si–H bonds. Their ¹³C NMR spectra show two resonances in the region expected for sp-hybridized carbon atoms, as well as resonances attributed to two different kinds of isopropyl carbon and phenyl carbon, and the ²⁹Si NMR spectra show the presence of two nonequivalent silicon atoms. These results are consistent with the structures proposed for **8** and **9**.

Interestingly, a similar palladium-catalyzed reaction of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene **1** with mesitylacetylene in benzene at room temperature afforded 5,6-benzo-1,1,4,4-tetraethyl-1,4-disilacyclohexa-2,5-diene (**10**), in 87% yield, as the sole product (Scheme 4). Silyl-substituted acetylenes, trimethylsilylacetylene and dimethylphenylsilylacetylene reacted with **1** under the same conditions to give the respective benzodisilacyclohexadienes, 2-trimethylsilyl- and 2-dimethylphenylsilyl-5,6-benzo-1,1,4,4-tetraethyl-1,4-disilacyclohexa-2,5-diene (**11**) and (**12**) in 86% and 95% yields [7]. No isomers analogous to **8** and **9** were detected in the reaction mixtures.

In order to get more information concerning the reactive species in the present reaction, we carried out the stoichiometric reaction of **2** with tetrakis(triphenylphosphine)palladium(0). Treatment of **2** with 1 equiva-



Scheme 5.

lent of the palladium(0) complex in benzene at room temperature afforded no product, but at reflux temperature reaction proceeded smoothly to give a palladium insertion product. Thus, reaction of **2** with the palladium complex in refluxing benzene for 3 h produced 3,4-benzo-1,1-bis(triphenylphosphine)-2,2,5,5-tetra(isopropyl)-1-pallada-2,5-disilacyclopent-3-ene (**A**) in quantitative yield. The complex **A** thus formed is stable in the solution under an inert atmosphere, and can be stored without decomposition.

The reaction of phenylacetylene with a stoichiometric amount of complex **A** in benzene at room temperature for 20 min gave benzodisilacyclohexadiene **4** in 82% yield. Similar reaction of phenylacetylene with complex **A** in refluxing benzene for 20 min gave **4** in almost quantitative yield. As expected, in the presence of a catalytic amount of palladium complex **A**, compound **2** reacted with phenylacetylene in refluxing benzene to give product **4** quantitatively. In contrast, the reaction of mesitylacetylene with 1 equivalent of complex **A** in benzene at room temperature gave no adduct. The ^1H NMR spectrum of the mixture in deuteriobenzene clearly indicates the presence only of signals due to mesitylacetylene and **A**. However, when this mixture was heated under reflux the reaction proceeded smoothly to give adduct **7**; after 3 h **7** was isolated in 76% yield. When this stoichiometric reaction in the temperature range of 25–80°C was monitored by ^{29}Si NMR spectrometry there was again no evidence of formation of an intermediate leading to **7**; only signals from the starting compound **A** and final product **7** were observed throughout. The stoichiometric reaction of **A** and mesitylacetylene proceeded smoothly in refluxing benzene, but the reaction of **2** with mesitylacetylene in the presence of a catalytic amount of palladium(0) catalyst under the same conditions took place to give **7** only very slowly [8].

Products **3–6** are probably produced by insertion of a triple bond of the alkyne coordinated to the palladium atom in complex (**B**), arising from the reaction of **A** with alkynes, into a palladium–silicon bond to give 3,4-benzo-1-pallada-2,5-disilacyclohepta-3,6-diene (**C**), followed by reductive elimination of palladium species from the resulting complex **C** (Scheme 5). In contrast, the formation of **7–9** can be best understood in terms of oxidative addition of an sp-hybridized C–H bond of the coordinated alkynes in complex **B** to the palladium atom, and then migration of an alkynyl group to one of two silicon atoms to give complex (**D**). Finally reductive elimination of palladium species would result in formation of products **7–9**. These reactions provide the first examples of sp-hybridized C–H bond activation [9] in the transition-metal-catalyzed reaction of the benzo-disilacyclobutene system. Presumably, the presence of a bulky substituent such as a mesityl, trimethylsilyl, or dimethylphenylsilyl group in the alkyne prevents inser-

tion of the triple bond into a palladium–silicon bond in complex **B**. The present results indicate that insertion of a triple bond of the alkynes bearing a less bulky substituent into a palladium–silicon bond in **B** to give complex **C** is easier than oxidative addition of an sp-hybridized C–H bond of these alkynes to the palladium atom in complex **B**. Unfortunately, all attempts to detect intermediates **B–D** by ^1H NMR spectrometric analysis were unsuccessful.

In conclusion, the palladium-catalyzed reaction of **2** with mono-substituted acetylenes bearing a less bulky substituent leads exclusively to the formation of 5,6-benzo-1,4-disilacyclohexa-2,5-dienes, while with acetylenes bearing a bulky substituent, **2** gives products arising from sp-hybridized C–H bond activation of the acetylenes. Similar reactions of **1** with all the acetylenes used in this study give the 5,6-benzo-1,4-disilacyclohexa-2,5-dienes as the sole products.

Experimental section

3.1. General procedure

Except for the reaction with acetylene and phenylacetylene, the palladium-catalyzed reactions of **2** with alkynes were carried out in a degassed sealed tube (1.0 cm \times 10 cm) at 150°C. The reactions of **1** with alkynes were performed in a benzene solution at room temperature. Yields of the products, based on the amounts of starting materials consumed, were determined by analytical GLC with pentadecane as an internal standard. The NMR spectra were recorded on a Jeol Model EX-270 spectrometer and IR spectra on a Perkin–Elmer 1600 FT infrared spectrometer. Low-resolution mass spectra were obtained with a Shimadzu Model GCMS-QP 1000 instrument. Gel permeation chromatographic separation was performed with a Model LC-908 Recycling Preparative HPLC apparatus (Japan Analytical Industry Co., Ltd.).

3.2. Preparation of 1,2-bis(diisopropylsilyl)benzene

In a 500 ml four-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 7.5 g (0.31 mol) of magnesium and 39.8 g (0.26 mol) of diisopropylchlorosilane in 260 ml of THF. To this a solution of 33.3 g (0.14 mol) of *o*-dibromobenzene was added over 2 h at room temperature. The mixture was heated under reflux for 45 h then cooled to room temperature, and 500 ml of hexane added. The resulting salts were filtered off, the solvents evaporated, and the residue distilled under reduced pressure to give 28.9 g (72%) of 1,2-bis(diisopropylsilyl)benzene: b.p. 117–122°C (2 mmHg); MS m/z 263 ($\text{M}^+ - ^1\text{Pr}$); IR 3056, 2954, 2133, 1461, 1002, 880, 789, 657, 519 cm^{-1} ; ^1H

NMR $\delta(\text{CDCl}_3)$ 0.96 (d, 12H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.11 (d, 12H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.22–1.34 (m, 4H, CHSi), 4.32 (t, 2H, SiH, $J = 3.3$ Hz), 7.30–7.54 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(\text{CDCl}_3)$ 11.7 (CHSi), 19.0, 19.2 ($^1\text{PrMe}$), 127.6, 135.4, 142.6 (phenylene ring carbons); ^{29}Si NMR $\delta(\text{CDCl}_3)$ 0.9. Anal. Found: C, 70.26; H, 11.19. $\text{C}_{18}\text{H}_{34}\text{Si}_2$. Calc.: C, 70.51; H, 11.18%.

3.3. Preparation of 1,2-bis(chlorodiisopropylsilyl)benzene

In a 500 ml three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 28.9 g (0.09 mol) of 1,2-bis(diisopropylsilyl)benzene in 50 ml of carbon tetrachloride. A solution of dry chlorine gas (7.4 g, 0.10 mol) in 125 ml of carbon tetrachloride was added over 7 h at room temperature; the mixture was stirred at room temperature for 5 h. The solvent was evaporated off and the residue distilled under reduced pressure to give 19.9 g (56%) of pale yellow liquid: b.p. 139–143°C (1 mmHg); MS m/z 333 ($\text{M}^+ - ^1\text{Pr}$); IR 3041, 2958, 2867, 1463, 1112, 1007, 881, 748, 664, 626 cm^{-1} ; ^1H NMR $\delta(\text{CDCl}_3)$ 0.90 (d, 12H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.15 (d, 12H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.69 (sep, 4H, CHSi, $J = 7.3$ Hz), 7.25–7.89 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(\text{CDCl}_3)$ 16.6 (CHSi), 17.7, 18.0 ($^1\text{PrMe}$), 128.3, 135.9, 139.8 (phenylene ring carbons); ^{29}Si NMR $\delta(\text{CDCl}_3)$ 29.5. Anal. Found: C, 57.40; H, 8.59. $\text{C}_{18}\text{H}_{32}\text{Cl}_2\text{Si}_2$. Calc.: C, 57.57; H, 8.59%.

3.4. Preparation of 3,4-benzo-1,1,2,2-tetra(isopropyl)-1,2-disilacyclobut-3-ene (2)

In a 300 ml three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 5.4 g (0.24 mol) of sodium and 80 ml of toluene. The mixture was heated to reflux, and a solution of 19.9 g (0.05 mol) of 1,2-bis(chlorodiisopropylsilyl)benzene in 50 ml of toluene was added over 3.5 h. The resulting mixture was refluxed for 13 h and the solvents were then distilled off. The residue was distilled under reduced pressure to give 14.7 g (91%) of colorless liquid: b.p. 131–134°C (1 mmHg); MS m/z 304 (M^+); IR 3090, 3043, 2940, 2862, 1459, 1382, 1087, 917, 728 cm^{-1} ; ^1H NMR $\delta(\text{CDCl}_3)$ 1.12 (d, 12H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.19 (d, 12H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.38 (sep, 4H, CHSi, $J = 7.3$ Hz), 7.29–7.50 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(\text{CDCl}_3)$ 13.8 (CHSi), 19.9, 20.0 ($^1\text{PrMe}$), 128.6, 132.5, 155.9 (phenylene ring carbons); ^{29}Si NMR $\delta(\text{CDCl}_3)$ 15.3. Anal. Found: C, 71.03; H, 10.34. $\text{C}_{18}\text{H}_{32}\text{Si}_2$. Calc.: C, 70.97; H, 10.59%.

3.5. Reaction of 2 with acetylene

In a 30 ml two-necked flask fitted with a stirrer and reflux condenser were placed a mixture of 0.118 g (0.39 mmol) of 2, and 0.020 g (0.02 mmol) of tetrakis(triphenylphosphine)palladium(0) in 10 ml of dry mesitylene. The mixture was heated under reflux for 3 h with acetylene bubbling through. The solution was then passed through a short silica gel column and shown by GLC to contain 3 (75% yield). This was isolated by MPLC: MS m/z 330 (M^+); IR 2937, 2862, 1461, 881, 730, 683, 629 cm^{-1} ; ^1H NMR $\delta(\text{CDCl}_3)$ 0.93 (d, 12H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.01 (d, 12H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.21 (sep, 4H, CHSi, $J = 7.3$ Hz), 7.15 (s, 2H, HC=C), 7.30–7.51 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(\text{CDCl}_3)$ 12.3 (CHSi), 18.2, 18.4 ($^1\text{PrMe}$), 127.4, 134.0, 142.6 (phenylene ring carbons), 148.2 (olefinic carbons); ^{29}Si NMR $\delta(\text{CDCl}_3)$ -13.8. Anal. Found: C, 72.51; H, 10.33. $\text{C}_{20}\text{H}_{34}\text{Si}_2$. Calc.: C, 72.65; H, 10.36%.

3.6. Reaction of 2 with phenylacetylene

In a 30 ml two-necked flask fitted with a stirrer and reflux condenser were placed 0.100 g (0.33 mmol) of 2, 0.091 g (0.89 mmol) of phenylacetylene and a solution of 0.020 g (0.02 mmol) of tetrakis(triphenylphosphine)palladium(0) in 10 ml of dry benzene. The mixture was heated to reflux for 3 h, then passed through a short silica gel column to remove palladium species. The solution was shown by GLC to contain 4 (97%). This was isolated by MPLC: m.p. 110°C; MS m/z 363 ($\text{M}^+ - ^1\text{Pr}$); IR 3054, 2958, 2860, 1466, 1261, 1116, 750, 628 cm^{-1} ; ^1H NMR $\delta(\text{CDCl}_3)$ 0.85 (d, 6H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.03–1.11 (m, 18H, $^1\text{PrMe}$), 1.26–1.53 (m, 4H, CHSi), 6.83 (s, 1H, HC=C), 7.23–7.64 (m, 9H, phenyl and phenylene ring protons); ^{13}C NMR $\delta(\text{CDCl}_3)$ 12.4, 12.5 (CHSi), 18.0, 18.1, 18.4, 18.6 ($^1\text{PrMe}$), 126.2, 126.7, 127.4, 127.6, 128.1, 133.8, 134.4, 142.1, 142.2, 149.8 (phenyl and phenylene ring carbons), 145.1, 162.2 (olefinic carbons); ^{29}Si NMR $\delta(\text{CDCl}_3)$ -12.0, -12.4. Anal. Found: C, 76.68; H, 9.15. $\text{C}_{26}\text{H}_{38}\text{Si}_2$. Calc.: C, 76.77; H, 9.42%.

3.7. Reaction of 2 with 1-hexyne

A mixture of 0.100 g (0.33 mmol) of 2, 0.018 g (0.02 mmol) of tetrakis(triphenylphosphine)palladium(0), and 0.083 g (1.01 mmol) of 1-hexyne in a sealed glass tube was heated at 150°C for 24 h. The mixture was passed through a short silica gel column and then shown by GLC to contain 5 in quantitative yield. This was isolated by MPLC: m.p. 42°C; MS m/z 343 ($\text{M}^+ - ^1\text{Pr}$); IR 2933, 2860, 1459, 1119, 993, 883, 741, 683, 625 cm^{-1} ; ^1H NMR $\delta(\text{CDCl}_3)$ 0.92–1.04 (m, 24H, $^1\text{PrMe}$), 1.12–1.61 (m, 11H, CHSi and C_3H_7), 2.29 (t, 2H, CH_2Si , $J = 7.3$ Hz), 6.66 (s, 1H, HC=C), 7.31–7.57

(m, 4H, phenylene ring protons); ^{13}C NMR $\delta(\text{CDCl}_3)$ 12.3, 12.5 (CHSi), 14.1 (MeCH₂), 18.30, 18.33, 18.59, 18.64 ($^1\text{PrMe}$), 22.8, 30.5, 38.5 (CH₂), 127.2, 127.3, 133.6, 134.1, 142.7, 142.8 (phenylene ring carbons), 137.3, 161.6 (olefinic carbons); ^{29}Si NMR $\delta(\text{CDCl}_3)$ -12.5 (2Si). Anal. Found: C, 74.23; H, 10.76. C₂₄H₄₂Si₂. Calc.: C, 74.53; H, 10.95.

3.8. Reaction of 2 with *o*-tolylacetylene

A mixture of 0.073 g (0.24 mmol) of 2, 0.016 g (0.01 mmol) of tetrakis(triphenylphosphine)palladium(0), and 0.031 g (0.27 mmol) of *o*-tolylacetylene in a sealed glass tube was heated at 150°C for 24 h. The mixture was passed through a short silica gel column and the solution shown by GLC to contain 6 (64% yield) along with the starting compound 2 (33%). Compound 6 was isolated by MPLC: m.p. 47°C; MS m/z 420 (M⁺); IR 3059, 2942, 2864, 1463, 1383, 1116, 993, 882, 747, 671, 650 cm⁻¹; ^1H NMR $\delta(\text{CDCl}_3)$ 0.85 (d, 6H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.045 (d, 6H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.053 (d, 6H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.11 (d, 6H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.39 (sep, 4H, CHSi, $J = 7.3$ Hz), 2.41 (s, 3H, MeC), 6.77 (s, 1H, HC=C), 7.07–7.63 (m, 8H, tolyl and phenylene ring protons); ^{13}C NMR $\delta(\text{CDCl}_3)$ 11.9, 12.6 (CHSi), 18.0, 18.1, 18.4, 18.7 ($^1\text{PrMe}$), 21.1 (tolyl Me), 124.9, 125.8, 126.7, 127.5, 127.6, 131.1, 133.4, 133.8, 134.2, 142.3 (2C), 148.1 (tolyl and phenylene ring carbons), 146.4, 161.0 (olefinic carbons); ^{29}Si NMR $\delta(\text{CDCl}_3)$ -12.9, -12.7. Anal. Found: C, 76.80; H, 9.61. C₂₇H₄₀Si₂. Calc.: C, 77.07; H, 9.58%.

3.9. Reaction of 2 with mesitylacetylene

A mixture of 0.089 g (0.29 mmol) of 2, 0.076 g (0.53 mmol) of mesitylacetylene, 0.016 g (0.01 mmol) of tetrakis(triphenylphosphine)palladium(0) in a sealed glass tube was heated at 150°C for 24 h. The solution was passed through a short silica gel column and then shown by GLC to contain 7 (87% yield). This was isolated by MPLC: m.p. 94°C; MS m/z 448 (M⁺); IR 3560, 3420, 2941, 2864, 2143, 1609, 1462, 1222, 1122, 1004, 879, 794 cm⁻¹; ^1H NMR $\delta(\text{CDCl}_3)$ 0.95 (d, 6H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.01 (d, 6H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.13 (d, 6H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.27 (d, 6H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.45–1.56 (m, 4H, CHSi), 2.31 (s, 3H, mesityl *p*-Me), 2.53 (s, 6H, mesityl *o*-Me), 4.42 (t, 1H, SiH, $J = 3.0$ Hz), 6.92 (s, 2H, mesityl protons), 7.33–8.25 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(\text{CDCl}_3)$ 12.0, 14.5 (CHSi), 19.0, 19.1, 19.4, 19.5 ($^1\text{PrMe}$), 21.4 (2C, mesityl *o*- and *p*-Me), 97.4, 106.9 (sp carbons), 120.6, 127.6 (2C), 127.8, 135.0, 137.7, 137.9, 140.8, 141.5, 142.6 (mesityl and phenylene ring carbons); ^{29}Si NMR $\delta(\text{CDCl}_3)$ -1.2, -0.7. Anal. Found: C, 77.44; H, 9.72. C₂₉H₄₄Si₂. Calc.: C, 77.60; H, 9.88%.

3.10. Reaction of 2 with trimethylsilylacetylene

A mixture of 0.090 g (0.30 mmol) of 2, 0.018 g (0.02 mmol) of tetrakis(triphenylphosphine)palladium(0), and 0.082 g (0.84 mmol) of trimethylsilylacetylene in a sealed glass tube was heated at 150°C for 24 h. After passage through a short silica gel column the solution was shown by GLC to be 8 (in quantitative yield). Compound 8 was isolated by MPLC: MS m/z 402 (M⁺); IR 3043, 2943, 2892, 2864, 2131, 1461, 1250, 1116, 1004, 858, 563 cm⁻¹; ^1H NMR $\delta(\text{CDCl}_3)$ 0.14 (s, 9H, Me₃Si), 0.80 (d, 6H, $^1\text{PrMe}$, $J = 7.3$ Hz), 0.90 (d, 6H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.02 (d, 6H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.08 (d, 6H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.12–1.18 (m, 2H, CHSi), 1.30 (sep, 2H, CHSi, $J = 7.3$ Hz), 4.27 (t, 1H, SiH, $J = 3.1$ Hz), 7.22–7.95 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(\text{CDCl}_3)$ 0.0 (Me₃Si), 12.0 (CH), 18.7, 19.0, 19.1, 19.5 ($^1\text{PrMe}$), 109.7, 118.3 (sp carbons), 127.6, 127.8, 135.0, 137.1, 141.7, 142.0 (phenylene ring carbons); ^{29}Si NMR $\delta(\text{CDCl}_3)$ -19.1, -2.6, -1.2. Anal. Found: C, 68.50; H, 10.50. C₂₃H₄₂Si₃. Calc.: C, 68.58; H, 10.51%.

3.11. Reaction of 2 with dimethylphenylsilylacetylene

A mixture of 0.085 g (0.28 mmol) of 2, 0.018 g (0.02 mmol) of tetrakis(triphenylphosphine)palladium(0), and 0.087 g (0.54 mmol) of dimethylphenylsilylacetylene in a sealed glass tube was heated at 150°C for 24 h. It was then shown by GLC to contain 9 (95% yield) along with starting compound 2 (2%). Compound 9 was isolated by MPLC: MS m/z 421 (M⁺ - ^1Pr); IR 2942, 2864, 2130, 1462, 1249, 1116, 1005, 820, 764 cm⁻¹; ^1H NMR $\delta(\text{CDCl}_3)$ 0.52 (s, 6H, Me₂PhSi), 0.95 (d, 6H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.03 (d, 6H, $^1\text{PrMe}$, $J = 7.4$ Hz), 1.15 (d, 6H, $^1\text{PrMe}$, $J = 7.2$ Hz), 1.24 (d, 6H, $^1\text{PrMe}$, $J = 7.2$ Hz), 1.27–1.53 (m, 4H, CHSi), 4.41 (t, 1H, SiH, $J = 3.2$ Hz), 7.35–8.13 (m, 9H, phenyl and phenylene ring protons); ^{13}C NMR $\delta(\text{CDCl}_3)$ -0.7 (Me₂PhSi), 11.2 (CHSi), 18.8, 19.0, 19.2, 19.5 ($^1\text{PrMe}$), 112.0, 115.8 (sp carbons), 127.7, 127.8, 127.9, 129.3, 133.8, 135.1, 137.1, 137.4, 141.7, 141.8 (phenyl and phenylene ring carbons); ^{29}Si NMR $\delta(\text{CDCl}_3)$ -22.7, -2.0, -1.2. Anal. Found: C, 72.40; H, 9.49. C₂₈H₄₄Si₃. Calc.: C, 72.34; H, 9.54%.

3.12. Reaction of 1 with mesitylacetylene

Into a 30 ml two-necked flask fitted with a stirrer were placed 0.120 g (0.48 mmol) of 1, 0.138 g (0.96 mmol) of mesitylacetylene, and a solution of 0.029 g (0.03 mmol) of tetrakis(triphenylphosphine)palladium(0) in 5 ml of dry benzene. The mixture was stirred at room temperature for 0.5 h and then passed through short silica gel column. The solution was shown by GLC to contain 10 (87% yield), which was isolated by

column chromatography: MS m/z 392 (M^+); IR 3043, 2950, 2861, 1458, 1414, 1119, 1009, 785, 712, 623 cm^{-1} ; ^1H NMR $\delta(\text{CDCl}_3)$ 0.80–1.05 (m, 20H, EtSi), 2.21 (s, 6H, mesityl *o*-Me), 2.33 (s, 3H, mesityl *p*-Me), 6.68 (s, 1H, HC=C), 6.92 (s, 2H, mesityl *m*-Me), 7.41–7.66 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(\text{CDCl}_3)$ 6.0, 6.2, 7.7, 7.8 (EtSi), 20.88, 20.92 (mesityl Me), 127.7 (2C), 128.2, 133.5, 133.6, 133.9, 134.8, 142.9, 144.0, 144.2 (phenylene ring carbons), 146.0, 164.4 (olefinic carbons); ^{29}Si NMR $\delta(\text{CDCl}_3)$ –17.2, –15.7. Anal. Found: C, 76.36; H, 9.11. $\text{C}_{25}\text{H}_{36}\text{Si}_2$. Calc.: C, 76.46; H, 9.24%.

3.13. Reaction of 1 with trimethylsilylacetylene

Into a 30 ml two-necked flask fitted with a stirrer were placed 0.126 g (0.51 mmol) of 1, 0.094 g (0.96 mmol) of trimethylsilylacetylene and a solution of 0.029 g (0.03 mmol) of tetrakis(triphenylphosphine)palladium(0) in 5 ml of dry benzene. The mixture was stirred at room temperature for 0.5 h and then passed through a short silica gel column. Compound 11 (86% yield) was isolated by column chromatography: MS m/z 346 (M^+); IR 3045, 2953, 2873, 1459, 1414, 1246, 1119, 1001, 962, 894, 830, 770, 746, 675 cm^{-1} ; ^1H NMR $\delta(\text{CDCl}_3)$ 0.21 (s, 9H, Me_3Si), 0.77–1.01 (m, 20H, EtSi), 7.35–7.57 (m, 4H, phenylene ring protons), 7.77 (s, 1H, olefinic proton); ^{13}C NMR $\delta(\text{CDCl}_3)$ –0.8 (Me_3Si), 6.0, 7.2, 7.7 (2C) (EtSi), 127.6, 127.9, 133.1 (2C), 143.0, 144.1 (phenylene ring carbons), 162.3, 168.1 (olefinic carbons); ^{29}Si NMR $\delta(\text{CDCl}_3)$ –20.2, –13.4, –4.9. Anal. Found: C, 65.70; H, 9.65. $\text{C}_{10}\text{H}_{14}\text{Si}_4$. Calc.: C, 65.82; H, 9.88%.

3.14. Stoichiometric reactions of 2 with tetrakis(triphenylphosphine)palladium(0)

Into a 30 ml two-necked flask fitted with a stirrer and reflux condenser were placed 0.032 g (0.11 mmol) of 2 and a solution of 0.145 g (0.13 mmol) of tetrakis(triphenylphosphine)palladium(0) in 1.5 ml of dry benzene- d_6 . The mixture was refluxed for 3 h to give A: ^1H NMR $\delta(\text{C}_6\text{D}_6)$ 1.36 (d, 12H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.37 (d, 12H, $^1\text{PrMe}$, $J = 7.3$ Hz), 1.58–1.67 (m, 4H, CHSi), 7.08–7.83 (m, 64H, phenyl and phenylene ring protons); ^{13}C NMR $\delta(\text{C}_6\text{D}_6)$ 19.6 (CHSi), 21.5, 21.8 ($^1\text{PrMe}$), 128.6, 132.7, 154.2 (phenylene ring carbons), 128.7 ($^3J_{\text{C}-\text{P}} = 8.5$ Hz), 131.4, 132.4 ($^1J_{\text{C}-\text{P}} = 9.8$ Hz), 134.3 ($^2J_{\text{C}-\text{P}} = 18.3$ Hz); ^{29}Si NMR $\delta(\text{C}_6\text{D}_6)$ 58.4. ^{31}P NMR $\delta(\text{C}_6\text{D}_6)$ 19.7.

3.15. Reaction of A with phenylacetylene at room temperature

To a solution of A, prepared from 0.042 g (0.14 mmol) of 2 and 0.191 g (0.17 mmol) of tetrakis(triphenylphosphine)palladium(0) in 2.0 ml of dry benzene was

added 0.020 g (0.20 mmol) of phenylacetylene at room temperature. The mixture was stirred at room temperature for 20 min and the solution then passed through a short silica gel column and shown by GLC to contain 4 (82% yield), which was isolated by MPLC. The spectral data for 4 were identical with those of an authentic sample obtained from the catalytic reaction described above.

3.16. Reaction of A with phenylacetylene in refluxing benzene

A mixture of A (0.14 mmol) and 0.022 g (0.21 mmol) of phenylacetylene in 2.0 ml of benzene was heated under reflux for 3 h. The mixture was passed through a short silica gel column and shown by GLC to contain 4 (98% yield), which was isolated by MPLC. The spectral data for 4 were identical with those of the sample obtained from the preceding reaction.

3.17. Reaction of A with mesitylacetylene at room temperature

A mixture of A (0.10 mmol) and 0.022 g (0.15 mmol) of mesitylacetylene in 2.0 ml of benzene was stirred at room temperature for 3 days. No product was detected by GLC or spectrometric analysis.

3.18. Reaction of A with mesitylacetylene

A mixture of A (0.15 mmol) and 0.035 g (0.24 mmol) of mesitylacetylene was heated under reflux for 3 h. The solution was passed through a short silica gel column and then shown by GLC to contain 7 (76% yield), which was isolated by MPLC. The spectral data for 7 were identical with those of an authentic sample obtained from the catalytic reaction of 2 with mesitylacetylene.

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