Silicon−Carbon Unsaturated Compounds. 50. Palladium-Catalyzed Reactions of 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene and Reinvestigation of Its Thermal Dimerization Reaction

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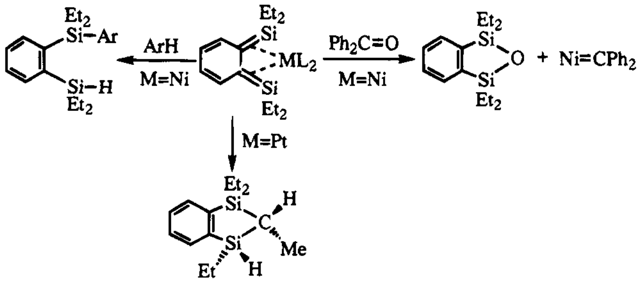
The reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1**) in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) have been investigated. Heating **1** in the presence of tetrakis(triphenylphosphine)palladium(0) in benzene at 150 °C gave 4,5,7,8-dibenzo-1,1,2,2,3,3,6,6-octaethyl-1,2,3,6-tetrasilacycloocta-4,7-diene (**3**) in 79% yield. The palladium-catalyzed reaction of **1** with benzaldehyde in refluxing benzene afforded 5,6-benzo-1,1,4,4-tetraethyl-2-oxa-3-phenyl-1,4-disilacyclohex-5-ene in 90% yield. The reaction of **1** with acetylene, phenylacetylene and diphenylacetylene in benzene at room temperature produced the respective 5,6-benzodisilacyclohexa-2,5-diene derivatives in high yields. The reaction of **1** with styrene and 1-hexene in the presence of the palladium catalyst in benzene yielded 2,3-benzodisilacyclohex-2-enes **8** and **9a**, respectively, while the reaction of **1** with 1-hexene at 150 °C, **1** gave **9a** and (*E*)-1-[diethyl(2-hexenyl)silyl]-2-(diethylsilyl)benzene in 39% and 41% yields. The palladium-catalyzed reaction of **1** with 1,1-deuterio-1-hexene at 150 °C produced (*E*)-1-[diethyl(1,1-dideuterio-2-hexenyl)silyl]-2-(diethylsilyl)benzene in 35% yield, together with a 43% yield of 2,3-benzo-5-butyl-1,1,4,4-tetraethyl-6,6-dideuterio-1,4-disilacyclohex-1-ene. With triethylsilane at 150 °C, **1** gave 2-diethysilyl-1-(pentaethyldisilanyl)benzene and **3** in 31% and 41% yields. Similar reaction of **1** with ethylene in benzene at room temperature afforded 2,3-benzo-1,1,4,4-tetraethyl-1,4-disilacyclohex-2-ene and 3,4,9,10-dibenzo-1,1,2,2,5,5,8,8-octaethyl-1,2,5,8-tetrasilacyclodeca-3,9-diene in 28% and 40% yields, respectively. Reinvestigation of the thermolysis of **1** in the absence of a trapping agent indicated the formation of a mixture of 4,5-benzo-1,1,2,2,3,3-hexaethyl-1,2,3-trisilacyclopent-4-ene and 2,3,5,6-dibenzo-1,1,4,4-tetraethyl-1,4-disilacyclohex-2,5-diene.

Introduction

The chemical behavior of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1**) toward transition-metal complexes is a quite unique.[1−4] As we reported recently, the nickel-catalyzed reaction of **1** with aromatic compounds gives 1-aryldiethylsilyl-2-diethylsilylbenzenes arising from oxidative addition of an sp^2 C-H bond of the aromatic ring to an *o*-quinodisilane-nickel complex.[1] The similar nickel-catalyzed reactions of **1** with nonenolizable ketones proceeds with deoxygenation of the ketones to give nickel-carbene complexes and 4,5-benzo-1,1,3,3-tetraethyl-2-oxa-1,3-disilacyclopent-4-ene,[2] while with olefins, **1** produces adducts derived from addition of a terminal sp^2 C-H bond to the *o*-quinodisilane-nickel complex.[3] In the absence of a trapping agent, **1** affords no volatile products. In marked contrast to this reaction, the platinum-catalyzed reaction of **1** in the absence of a trapping agent in benzene gives an isomerization product, cis-4,5-benzo-1,1,3-triethyl-2-methyl-1,3-disilacyclopent-4-ene in high yield, in additon to a small amount of 1-(diethylphenylsilyl)-2-(diethylsilyl)benzene, arising from C-H bond activation of benzene.[4]



In order to get more information concerning the chemical behavior of **1** toward the transition-metal complex, we have investigated the palladium-catalyzed reactions of **1** in the presence or absence of a trapping agent. We have found that the reaction of **1** with a palladium(0) catalyst in the absence of a trapping agent gives a dimer identified as 4,5,7,8-dibenzo-1,1,2,2,3,3,6,6-octaethyl-1,2,3,6-tetrasilacycloocta-4,7-diene. In a previous paper, we reported that the thermolysis of **1** afforded a dimer which has the same structure as that

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1994.

(1) Ishikawa, M.; Okazaki, S.; Naka, A.; Sakamoto, H. *Organometallics* **1992**, *11*, 4135.

(2) Ishikawa, M.; Naka, A.; Okazaki, S.; Sakamoto, H. *Organometallics* **1993**, *12*, 87.

(3) Ishikawa, M.; Okazaki, S.; Naka, A.; Tachibana, A.; Kawauchi, S.; Yamabe, T. *Organometallics*, in press.

(4) Ishikawa, M.; Naka, A.; Ohshita, J. *Organometallics* **1993**, *12*, 4987.

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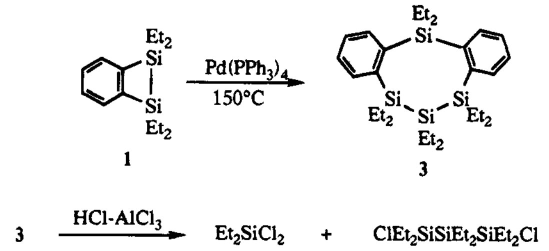
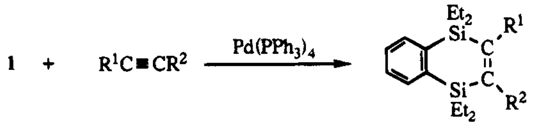
Scheme 1



Scheme 2



5. $R^1=R^2=H$
6. $R^1=H$, $R^2=Ph$
7. $R^1=R^2=Ph$

of the present dimer.[5] However, this has turned out to be an erroneous structural assignment. In this paper we report the results of the palladium-catalyzed reactions of **1** and also reinvestigation on the thermal reaction of **1**.

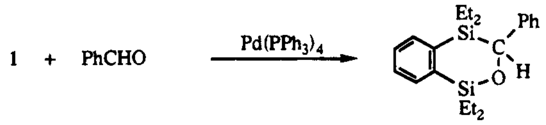
Results and Discussion

Since the C-H bond activation of benzene in the nickel-catalyzed reaction of **1** occurred at 80 °C, and the platinum-catalyzed isomerization of **1** also took place at refluxing temperature of benzene, we first carried out the reaction of **1** with a catalytic amount of a palladium(0) complex in benzene to confirm whether or not C-H bond activation of benzene or isomerization of **1** occurs. When **1** was heated to reflux in the presence of 5 mol% of tetrakis(triphenylphosphine)palladium(0) in benzene for 24 h, neither the product arising from C-H bond activation nor the isomerization product was formed. The starting compound **1** was recovered unchanged. Interestingly, when the same mixture was heated in a sealed degassed tube at 150 °C for 24 h, a dimer was obtained in 79% yield as the sole volatile product, in addition to 5% of the starting compound **1**. Again, no product arising from C-H bond activation of benzene was detected in the reaction mixture by either spectrometric analysis or GLC analysis. The mass spectrum of the dimer shows the parent ion at *m/z* 496, corresponding to the calculated molecular weight for $C_{28}H_{48}Si_4$.

Signal patterns of the dimer in ^1H, ^{13}C, and ^{29}Si NMR spectra are similar to those obtained from the dimer reported previously, which was produced thermally from **1**,[5] but their chemical shifts are different from those of the previous one. Thus, the ^{13}C NMR spectrum reveals six resonances at δ 2.48, 4.69, 7.30, 7.93, 8.38, and 10.19 ppm, attributed to three kinds of the ethyl groups, as well as six resonances due to phenylene ring carbons. Its ^{29}Si NMR spectrum shows three resonances at −35.18, −11.19, and −3.50 ppm, indicating the presence of three non-equivalent silicons. These results are wholly consistent with the structure proposed for 4,5,7,8-dibenzo-1,1,2,2,3,3,6,6-octaethyl-1,2,3,6-tetrasilacycloocta-4,7-diene (**3**) (Scheme 1).

In order to get more information on the structure of **3**, we carried out the cleavage reaction of this compound by hydrogen chloride. Thus, the reaction of **3** with hydrogen chloride gas in the presence of a catalytic amount of aluminum chloride in dry benzene at room temperature for 1.5 h proceeded cleanly to give degradation products. GC-Mass spectrometric analysis of the reaction mixture indicated that dichlorodiethylsilane and 1,3-dichlorohexaethyltrisilane were produced in 34% and 58% yields, respectively. The retention time of dichlorodiethylsilane on GLC was identical with that of an authentic sample. 1,3-Dichlorohexaethyltrisilane was converted to a 1,3-dimethyltrisilane derivative, and the structure of the resulting hexaethyl-1,3-dimethyltrisilane was verified by spectrometric analysis, as well as by elemental analysis. All spectral data obtained for **3** and also the results of degradation reactions are wholly consistent with the structure proposed for **3**.

Next, we carried out the palladium-catalyzed reaction of **1** with carbonyl compounds, alkynes, and alkenes. Previously we reported that the nickel- and platinum-catalyzed reaction of **1** with benzaldehyde in benzene gave an addition product derived from insertion of a carbonyl group into a silicon-silicon bond of **1** as the sole product.[2,4] The palladium-catalyzed reaction of **1** with benzaldehyde in refluxing benzene for 80 h led to the same result as that of the nickel- and platinum-catalyzed reaction. 5,6-Benzo-1,1,4,4-tetraethyl-2-oxa-3-phenyl-1,4-disilacyclohex-5-ene (**4**) whose spectral data were identical with those of an authentic sample was obtained in 90% yield. No other products were detected in the reaction mixture by either spectrometric analysis or GLC analysis.



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In contrast to the nickel-catalyzed reaction of **1** with acetone, in which two different types of acetone adducts and 4,5-benzo-1,1,3,3-tetraethyl-2-oxa-1,3-disilacyclopent-4-ene were formed,[2] the palladium-catalyzed reaction with acetone in a degassed sealed tube at 150 °C afforded no acetone adduct, but dimer **3** was obtained in 48% yield, along with 25% of the unreacted starting compound **1**.

The reaction of **1** with alkynes in the presence of the palladium catalyst proceeded readily at room temperature, giving 5,6-benzo-1,4-disilacyclohexa-2,5-dienes arising from insertion of a carbon-carbon triple bond into a silicon-silicon bond of the starting compound **1**. Thus, the reaction of **1** with bubbling acetylene gas in the presence of a tetrakis(triphenylphosphine)palladium(0) catalyst in benzene at room temperature for 30 min afforded 2,3-benzo-1,1,4,4-tetraethyl-1,4-disilacyclohexa-2,5-diene (**5**) in 70% yield as the sole product (Scheme 2). The ^1H NMR spectrum of **5** reveals a single resonance at δ 7.14 ppm due to olefinic protons, together with multiplet resonances at 0.73−0.95 and 7.33−7.54 ppm attributed to ethyl protons and phenylene protons, respectively. Its ^{13}C NMR spectrum shows two resonances at 6.08 and 7.62 ppm, three resonances at 127.78, 133.48 and 143.29 ppm, and a single resonance

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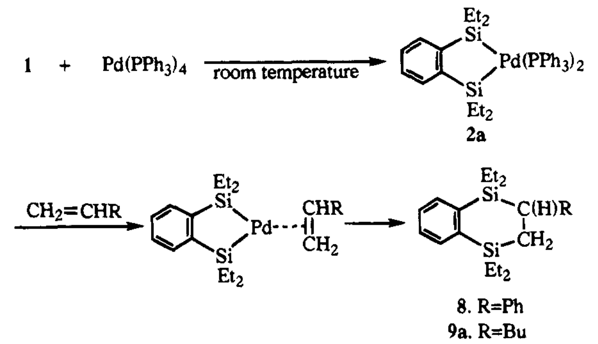
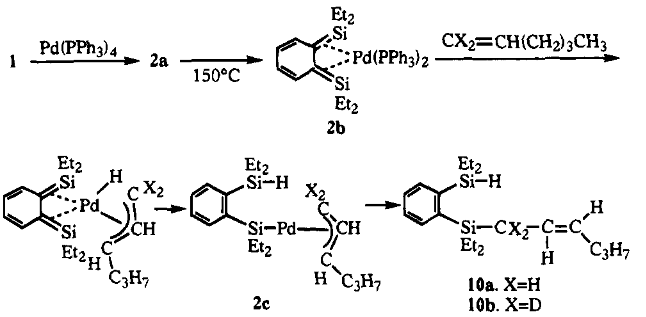
[5] Ishikawa, M.; Sakamoto, H.; Tabuchi, T. *Organometallics* **1991**, *10*, 3173.

Scheme 3



Scheme 4

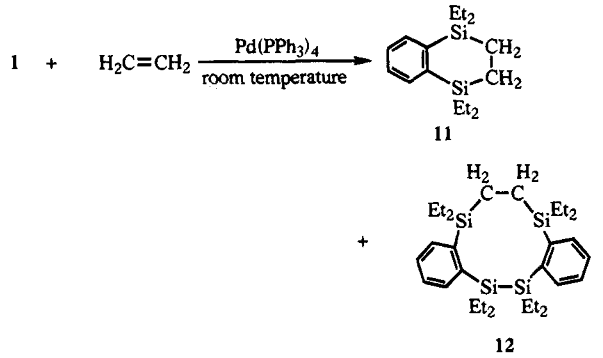


at 149.40 ppm, due to ethyl carbons, phenylene carbons, and olefinic carbons, respectively. These results are wholly consistent with the structure proposed for **5**. The reaction of **1** with phenylacetylene in benzene at room temperature for 30 min produced 5,6-benzo-1,1,4,4-tetraethyl-2-phenyl-1,4-disilacyclohexa-2,5-diene (**6**) in 87% yield. Although diphenylacetylene reacted with **1** in benzene at room temperature to give a similar insertion product, 5,6-benzo-1,1,4,4-tetraethyl-2,3-diphenyl-1,4-disilacyclohexa-2,5-diene (**7**), the rate of the reaction was quite slow. In refluxing benzene, however, diphenylacetylene readily reacted with **1** to give product **7** in 69% yield. Compound **6** was isolated by column chromatography, while **7** was obtained by recrystallization from ethanol. All spectral data obtained for **6** and **7** were identical with those of the authentic samples.[4]

The nickel- and platinum-catalyzed reaction of **1** with styrene and 1-hexene gives the products derived from sp^2 C-H bond activation,[3,4] however, the palladium-catalyzed reaction with these olefins proceeds with a different fashion. Thus, treatment of **1** with styrene in the presence of the palladium catalyst in benzene at room temperature for 10 h afforded 5,6-benzo-1,1,4,4-tetraethyl-2-phenyl-1,4-disilacyclohex-5-ene (**8**) in 84% yield. The reaction of **1** with 1-hexene at room temperature for 6 h afforded no product. In refluxing benzene, however, 2,3-benzo-5-butyl-1,1,4,4-tetraethyl-1,4-disilacyclohex-2-ene (**9a**) was obtained in 94% yield, after 14 h reaction (Scheme 3). Interestingly enough, when the reaction of **1** with 1-hexene was carried out in a sealed tube at 150 °C, two products, compound **9a** and (*E*)-1-[diethyl(2-hexenyl)silyl]-2-(diethylsilyl)benzene (**10a**) were obtained in 39% and 41% yields, respectively (Scheme 4).

The structures of **8**, **9a**, and **10a** were verified by spectroscopic and elemental analysis. Proton decoupling experiment of a 2-hexenyl group in compound **10a** shows double doublets with J = 15.4 Hz, indicating that **10a** must have a trans cofiguration.

Scheme 5



In order to learn more about the production of **10a**, we carried out the reaction of **1** with 1,1-dideuterio-1-hexene under the same conditions. In this reaction, two products, 2,3-benzo-5-butyl-1,1,4,4-tetrethyl-6,6-dideuterio-1,4-disilacyclohex-1-ene (**9b**) and (*E*)-1-[diethyl(1,1-dideuterio-2-hexenyl)silyl]-2-(diethylsilyl)benzene (**10b**) were obtained in 43% and 35% yields. The ^{1}H NMR spectrum for **10b** shows a quintet resonance at 4.55 ppm attributed to an Si-H proton, while the ^{2}H NMR spectrum reveals a single resonance at 1.84 ppm due to $CD_2(Si)$. In marked contrast to the nickel-catalyzed reactions of **1** with olefins, in which the products derived from a terminal sp^2 C-H bond activation are obtained, the present reaction with 1-hexene at 150 °C affords no product rising from a terminal sp^2 C-H bond activation, but gives the product formed from allylic C-H bond activation.

Similar reaction of **1** with styrene at 150 °C afforded product **8** in 93% yield, but not the product arising from C-H bond activation.[6] The reaction of **1** with an internal olefin, 2-hexene at 150 °C gave no adduct, but produced dimer **3** in 72% yield as the sole product. This result indicates that no olefin isomerization occurs in this system.

Ethylene reacts readily with **1** in benzene at room temperature, but in a different fashion from that of styrene and 1-hexene. When ethylene gas was introduced into a benzene solution of **1** at room temperature for 4 h, 2,3-benzo-1,1,4,4-tetraethyl-1,4-disilacyclohex-2-ene (**11**) and 3,4,9,10-dibenzo-1,1,2,2,5,5,8,8-octaethyl-1,2,5,8-tetrasilacyclodeca-3,9-diene (**12**) in 28% and 40% yields (Scheme 5).

In order to learn more about the reactive species in the present system, we carried out the stoichiometric reaction of **1** with tetrakis(triphenylphosphine)palladium(0) in deuteriobenzene at room temperature, and analyzed the mixture by ^{13}C NMR spectrometry. The ^{13}C NMR spectrum of the mixture obtained after 30 min reaction showed that the starting compound **1** was completely transformed into a new product whose spectrum reveals resonances at 11.31 and 12.88 ppm due to ethyl carbons, in lower magnetic field than those of ethyl carbons of **1**. Its ^{29}Si NMR spectrum shows a singlet resonance at 44.28 ppm, again in lower field than that of the starting compound **1**. Unfortunately, all attempts to isolate this compound were unsuccessful.

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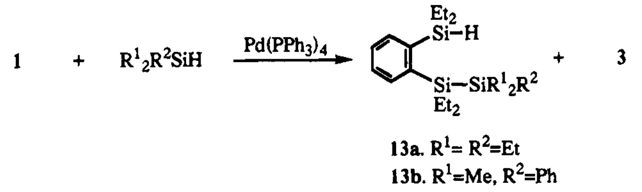
(6) For C-H bond activation by transition metal catalysts, see: Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91. Tanaka, M.; Sakakura, T. *Pure Appl. Chem.* **1990**, *62*, 1147.

Scheme 6

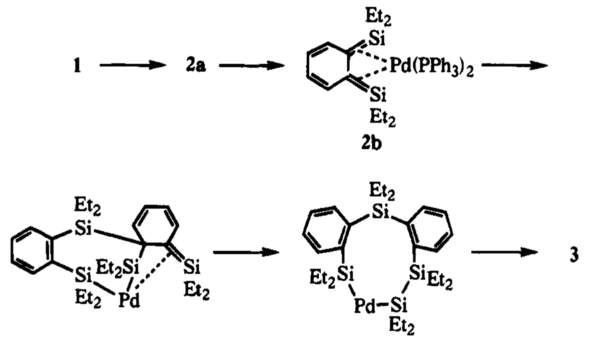


However, on the basis of ^1H, ^{13}C and ^{29}Si NMR data, we assigned this compound as 3,4-benzo-2,2,5,5-tetraethyl-1,1-bis(triphenylphosphine)-1-pallada-2,5-disilacyclopent-3-ene (**2a**). The formation of 3,4-benzo-1-metala-2,5-disilacyclopent-3-enes has been reported to date.[7–12]

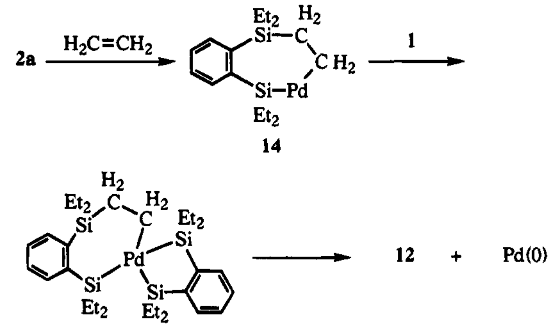
Treatment of **2a** with phenylacetylene in benzene at room temperature readily produced **6** in 86% yield. Similar reaction of **2a** with styrene at room temperature yielded no product, but in refluxing benzene afforded **8** in 89% yield. Presumably, triphenylphosphine that was liberated in the reaction of **1** with tetrakis-(triphenylphosphine)palladium(0) would prevent coordination of styrene to the palladium atom of **2a** at room temperature. At reflux temperature, styrene would coordinate to the palladium atom of **2a** leading to the formation of **8**. Ethylene did not react with **2a** in benzene at room temperature, but at reflux temperature, the reaction proceeded slowly to give **11** and **12** in 45% and 44% yields.

It seems likely that **2a** plays an important role for the formation of benzodisilacyclohexenes and benzodisilacyclohexanes. At the initial step, unsaturated compound would coordinate to the palladium atom of **2a**, and an unsaturated bond of the coordinated molecule inserts into a silicon-palladium bond to give seven-membered ring system. Finally, the palladium species eliminates reductively from the seven-membered ring system yielding the insertion product (see Scheme 3). At higher temperature, a different reactive species from 3,4-benzo-1-pallada-2,5-disilacyclopent-3-ene **2a**, presumably *o*-quiodisilane-palladium complex (**2b**) would be produced as a key intermediate. In an effort to obtain some information concerning the formation of **2b**, we carried out the reaction of **1** with hydrosilanes in the presence of the palladium catalyst. Treatment of **1** with triethylsilane in the presence of the palladium catalyst in reflux benzene for 16 h afforded no product. The starting compound **1** and triethylsilane were recovered unchanged. However, when the same mixture was heated in a sealed tube at 150 °C for 24 h, 2-diethylsilyl-1-(pentaethyldisilanyl)benzene (**13a**) and dimer **3** were obtained in 31% and 41% yields, in addition to 11% of the starting compound **1** (Scheme 6). No other volatile products were detected by GLC analysis. Similar treatment of **1** with dimethylphenylsilane under the same conditions afforded 1-(1,1-diethyl-2,2-dimethyl-2-phenyl)disilanyl-2-(diethylsilyl)benzene (**13b**) in 52% yield, along with 24% of **1**. The formation of **13a** and **13b** may be explained in terms of 1,4-addition of hydrosilanes to *o*-quinodisilane-palladium complex **2b**. Compounds **3** and **10** would also be produced from *o*-quinodisilane-palladium complex **2b** arising from isomerization of **2a**.

Scheme 7



Scheme 8



A possible mechanism for the formation of **3** would involve addition of **1** to *o*-quinodisilane-palladium complex **2b** formed from the reaction of **1** with tetrakis(triphenylphosphine)palladium(0), followed by cycloaddition, and then ring enlargement to eight-membered cyclic system as shown in Scheme 7.

The formation of **10** may be understood in terms of oxidative addition of an allylic C-H bond in hexene to *o*-quinodisilane-palladium complex (**2b**), and then a hydrogen shift on the palladium atom to one of two silicon atoms giving π-allylpalladium complex (**2c**). Reductive elimination of the palladium species from **2c** would produce product **10**. An alternative mechanism involving the π-coordination of 1-hexene to complex **2a**, followed by migration of the allylic hydrogen onto a silicon atom leading to **2c** can not be excluded at present.

That compound **12** is probably produced from the reaction of 3,4-benzo-2,2,5,5-tetraethyl-1-pallada-2,5-disilacyclohept-3-ene (**14**) arising from insertion of ethylene to a palladium-silicon bond in **2a** with compound **1** as shown in Scheme 8.

Reinvestigation of the Thermolysis of 1. Since the structure of the dimer obtained from the palladium-catalyzed reaction was confirmed to be 4,5,7,8-dibenzo-1,1,2,2,3,3,6,6-octaethyl-1,2,3,6-tetrasilacycloocta-4,7-diene **3** on the basis of spectrometric analysis and also chemical degradation reaction, we suspected that erroneous structure assignment had been made for the

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(7) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 2; Chapter 24.

(8) Eabon, C.; Metham, T. N.; Pidcock, A. *J. Organomet. Chem.* **1973**, *63*, 107.

(9) Fink, W. *Helv. Chim. Acta* **1976**, *59*, 606.

(10) Corriu, R. J. P.; Moreau, J. J. E.; Pataud-Sat, M. *Organometallics* **1985**, *4*, 623.

(11) (a) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *Organometallics* **1991**, *10*, 16. (b) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *J. Organomet. Chem.* **1992**, *428*, 1. (c) Tanaka, M.; Uchimaru, Y. *Bull. Soc. Chim. Fr.* **1992**, *129*, 667.

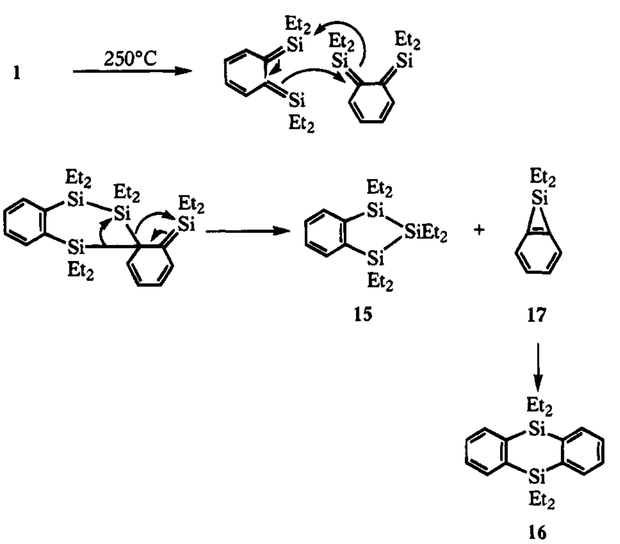
(12) For bis(silyl)palladium complexes, see: (a) Bierschenk, T. R.; Guerra, M. A.; Juhlke, T. J.; Larson, S. B.; Lagow, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 4855. (b) Pan, Y.; Mague, J. T.; Fink, M. J. *Organometallics* **1992**, *11*, 3495.

dimer formed from thermolysis of **1** reported previously.[5] Therefore, we have reinvestigated the thermolysis of **1**.

Heating **1** in a sealed degassed tube at 250 °C for 24 h under the same conditions as reported previously afforded a product in 72% yield. The product was isolated by preparative GLC using a column packed with silicon SE-30 on Chromosorb P. GLC analysis of the isolated product showed a homogeneous peak. Chemical shifts of the isolated product in the ^{1}H and ^{13}C NMR spectrum were identical with those reported previously, however, signal ratios, especially in the phenylene region in both ^{1}H and ^{13}C spectra were different from earlier ones. We therefore carried out GLC analysis of the product using different columns, and found that the use of a column packed with silicone OV-17 on Uniport HP gives two separate peaks, indicating that the product is a mixture of two compounds. These compounds were isolated by preparative GLC using this column, and their structures were verified by spectrometric analysis, as well as by elemental analysis. Compound that has shorter retention time on GLC was identified as 4,5-benzo-1,1,2,2,3,3,-hexaethyl-1,2,3-trisilacyclopent-4-ene (**15**), while the other compound was identified as 2,3,5,6-dibenzo-1,1,4,4-tetraethyl-1,4-disilacyclohexa-2,5-diene (**16**). The ^{1}H NMR spectrum of **15** reveals resonances at δ 0.86–1.20 and 7.34–7.63 ppm, attributable to ethyl protons and phenylene ring protons, while ^{13}C NMR spectrum shows three resonances at 127.60, 134.02, and 149.34 due to phenylene ring carbons, together with four resonances attributed to ethyl carbons. As expected, the ^{29}Si NMR spectrum shows two resonances at −5.62 and −38.98 ppm. The ^{13}C NMR spectrum of **16** reveals ethyl carbons at 6.76 and 7.60 ppm, and phenylene carbons at 128.01, 133.62, and 142.98 ppm. The ^{29}Si NMR for **15** shows a single resonance at −11.89 ppm. These results are wholly consistent with the structure proposed for **15** and **16**, respectively.

The thermolysis of **1** in a sealed tube at 250 °C always afforded products **15** and **16** in 60% and 12% yields, respectively. Judging from the ^{1}H and ^{13}C NMR spectrum of the product isolated previously, it would be the mixture which involves compounds **15** and **16**, accidentally in the ratio of 2 to 1. The formation of **15** may be explained by [4+2] cycloaddition of the *o*-quinodisilane, followed by elimination of benzodiethylsilacyclopropene (**17**) which would undergo dimerization to give **16** (Scheme 9). In order to trap benzodisilacyclopropene **17**, we carried out the thermolysis of **1** in the presence of dimethylphenylsilane in a sealed degassed tube at 250 °C for 24 h. However, no appreciable amounts of products were obtained, because of very low conversion of **1**. As reported previously,[5] in the presence of a solvent, the reverse reaction of the *o*-quinodisilane once formed to the starting compound **1** is involved. In the present case, dimethylphenylsilane presumably acts as the solvent.

Scheme 9



Experimental Section

General Procedure. NMR spectra were recorded on a JEOL Model EX-270 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1600 FT infrared spectrometer. Low resolution mass spectra were measured on a Shimadzu Model GCMS-QP 1000 instrument. High resolution mass spectra were measured on a Hitachi M-80B mass spectrometer. Gas chromatographic separations were carried out using a column (3 m x 10 mm) packed with 30% SE-30 silicone on Chromosorb P with one exception of isolation of the products obtained from the thermolysis of **1**. The products from the thermolysis were isolated by using a column packed with silicon OV-17 on Uniport HP. Gel permeation chromatographic separation was performed with a Model LC-908 Recycling Preparative HPLC (Japan Analytical Industry Co., Ltd.). Yields of the products were determined by analytical GLC with the use of tridecane as an internal standard.

Materials. 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene **1** was prepared as reported previously.[5] Benzene used as a solvent was dried over lithium aluminum hydride and distilled before use.

Preparation of 1,1-Dideuterio-1-hexene. In a 100-mL of three-necked flask fitted with a magnetic stirrer, condenser, and dropping funnel was placed 7.53 g (90.8 mmol) of 1-deuterio-1-hexyne[13] in 10 mL of dry toluene. To this was added 90 mL (90.9 mmol) of di(isobutyl)aluminum hydride over a period of 1 h at room temperature under a nitrogen atmosphere. The mixture was stirred for 4 h at room temperature and then hydrolyzed with D_2O. After workup as usual 4.93 g (63% yield) of 1,1-dideuterio-1-hexene was obtained: b.p. 64–67 °C. All spectral data were identical with those reported in the literature.[13]

Reaction of 1 in Benzene. A mixture of 0.290 g (1.17 mmol) of **1**, and 0.057 g (0.049 mmol) of $Pd(PPh_3)_4$ in 1 mL of benzene in a degassed sealed tube was heated at 150 °C for 24 h. The mixture was analyzed by GLC as being **3** (79% yield) and 5% of the starting compound **1**. The mixture was treated with a short silica gel column to remove any palladium species from the reaction mixture. Compound **3** was isolated by MPLC: MS *m/z* 496 (M^+); IR 2950, 2872, 1460, 1109, 1004, 735, 696 cm^{-1}; ^{1}H NMR $\delta(CDCl_3)$ 0.54–1.13 (m, 40H, EtSi), 7.28–7.34 (m, 4H, phenylene ring protons), 7.50–7.53 (m, 2H, phenylene ring protons), 7.70–7.73 (m, 2H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 2.48, 4.69, 7.30, 7.93, 8.38, 10.19 (EtSi), 126.9, 127.5, 135.0, 136.1,

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[13] Murray, R. W.; Williams, G. J. *J. Org. Chem.* **1969**, *34*, 1896.

144.8, 145.2 (phenylene ring carbons); ^{29}Si NMR δ($CDCl_3$) −35.18, −11.19, −3.50. Anal. Calcd for $C_{28}H_{48}Si_4$: C, 67.66; H, 9.73. Found: C, 67.56; H, 9.68.

Reaction of 3 with Hydrogen Chloride. In a 50-mL two-necked flask fitted with a condenser and inlet tube for hydrogen chloride gas was placed 0.190 g (0.383 mmol) of **3** and 0.008 g (0.060 mmol) of anhydrous aluminum chloride in 3 mL of dry benzene. To this was introduced dry hydrogen chloride gas at room temperature for 1.5 h. The mixture was analyzed by GC-mass spectrometry as being 1,3-dichlorohexaethyltrisilane (58% yield, *m/z* 328), and dichlorodiethylsilane (34% yield, *m/z* 242). The solvent benzene was evaporated and then 3.8 mL (3.8 mmol) of a methylmagnesium bromide-ether solution was added to the residue. The mixture was stirred for 5 h at room temperature and then hydrolyzed with dilute hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and extracts were combined and washed with water, and then dried over calcium chloride. The solvents were evaporated off, and the residue was distilled under reduced pressure (1 mmHg) to give hexaethyl-1,3-dimethyltrisilane. Pure hexaethyl-1,3-dimethyltrisilane was isolated by preparative GLC: MS *m/z* 288 (M^+); IR 2950, 2873, 1458, 1016, 789 cm^{-1}; ^{1}H NMR δ($CDCl_3$) 0.06 (s, 6H, MeSi), 0.59−0.80 (m, 12H, CH_2Si), 0.96 (t, 12H, J = 7.9 Hz), 1.02 (t, 6H, J = 7.9 Hz); ^{13}C NMR δ($CDCl_3$) −5.03, 2.97, 6.36, 8.23, 10.41 (EtSi); ^{29}Si NMR δ($CDCl_3$) −37.50, −9.55. Anal. Calcd for $C_{14}H_{36}Si_3$: C, 58.25; H, 12.57. Found: C, 58.44; H, 12.51.

Reaction of 1 with Benzaldehyde. In a 30-mL two-necked flask fitted with a condenser was placed 0.129 g (0.520 mmol) of **1**, 0.066 g (0.622 mmol) of benzaldehyde, and 0.029 g (0.025 mmol) of $Pd(PPh_3)_4$ in 2 mL of benzene. The mixture was heated to reflux for 80 h. GLC analysis of the resulting mixture showed the presence of **4** (90% yield). Compound **4** was isolated by MPLC. All spectral data for product **4** were identical with those of an authentic sample.[2]

Reaction of 1 with Acetone. A mixture of 0.121 g (0.49 mmol) of **1**, 0.120 g (2.07 mmol) of acetone, and 0.026 g (0.023 mmol) of $Pd(PPh_3)_4$ in 1 mL of benzene was heated in a sealed glass tube at 150 °C for 24 h. The mixture was analyzed by GLC as being **3** (48% yield) and 25% of the starting compound **1**.

Reaction of 1 with Acetylene. In a 30-mL two-necked flask fitted with a condenser and inlet tube for acetylene gas was placed 0.098 g (0.40 mmol) of **1** and 0.021 g (0.018 mmol) of $Pd(PPh_3)_4$ in 4 mL of dry benzene. To this was introduced acetylene gas at room temperature for 0.5 h. The mixture was analyzed by GLC as being **5** (70% yield). After treatment of the mixture with a short silica gel column, compound **5** was isolated by MPLC: MS *m/z* 274 (M^+); IR 2953, 2873, 1458, 1413, 1120, 1003, 720 cm^{-1}; ^{1}H NMR δ($CDCl_3$) 0.73−0.95 (m, 20H, EtSi), 7.14 (s, 2H, olefinic protons), 7.33−7.54 (m, 4H, phenylene ring protons); ^{13}C NMR δ($CDCl_3$) 6.08, 7.62 (EtSi), 127.78, 133.48, 143.29 (phenylene carbons), 149.40 (olefinic carbons); ^{29}Si NMR δ($CDCl_3$) −16.47. Anal. Calcd for $C_{16}H_{26}Si_2$: C, 70.00; H, 9.54. Found: C, 69.84; H, 9.54.

Reaction of 1 with Phenylacetylene. In a 30-mL two-necked flask fitted with a condenser was placed 0.043 g (0.17 mmol) of **1**, 0.025 g (0.25 mmol) of phenylacetylene, and 0.012 g (0.010 mmol) of $Pd(PPh_3)_4$ in 3 mL of benzene. The mixture was stirred at room temperature for 0.5 h, and the resulting mixture was analyzed by GLC as being **6** (87% yield). Compound **6** was isolated by column chromatography. All spectral data for **6** were identical with those of an authentic sample.[4]

Reaction of 1 with Diphenylacetylene. In a 30-mL two-necked flask fitted with a condenser was placed 0.062 g (0.250 mmol) of **1**, 0.072 g (0.404 mmol) of diphenylacetylene, and 0.013 g (0.011 mmol) of $Pd(PPh_3)_4$ in 3 mL of benzene. The mixture was heated to reflux for 12.5 h, and the resulting mixture was analyzed by GLC as being **7** (69% yield). Compound **7** was isolated by recrystallization from ethanol. All spectral data for **7** were identical with those of an authentic sample.[4]

Reaction of 1 with Styrene at Room Temperature. In a 30-mL two-necked flask fitted with a condenser was placed 0.128 g (0.516 mmol) of **1**, 0.102 g (0.979 mmol) of styrene, and 0.025 g (0.022 mmol) of $Pd(PPh_3)_4$ in 3 mL of benzene. The mixture was stirred at room temperture for 10 h, and then analyzed by GLC as being **8** (84% yield). After treatment of the mixture with a short silica gel column, compound **8** was isolated by MPLC: MS *m/z* 352 (M^+); IR 2952, 2872, 1493, 1413, 1233, 1117, 1016, 755, 699 cm^{-1}; ^{1}H NMR δ($CDCl_3$) 0.70−1.02 (m, 20H, EtSi), 1.25 (dd, 1H, CH, J = 2.6 Hz, 11.5 Hz), 1.59 (dd, 1H, CHPh, J = 11.5 Hz, 15.2 Hz), 2.74 (dd, 1H, CH, J = 2.6 Hz, 15.2 Hz), 7.22−7.55 (m, 9H, phenylene ring protons); ^{13}C NMR δ($CDCl_3$) 2.56, 3.12, 5.04, 5.98, 7.40, 7.60, 7.72, 7.92 (EtSi), 11.62 (CH_2), 26.36 (CH), 124.54, 127.04, 127.92, 127.95, 128.19, 134.01, 134.42, 143.26, 144.18, 146.93 (phenylene and phenyl ring carbons); ^{29}Si NMR δ($CDCl_3$) −1.46, −1.39. Anal. Calcd for $C_{22}H_{32}Si_2$: C, 74.93; H, 9.15. Found: C, 74.90; H, 9.10.

Reaction of 1 with Styrene at 150 °C. A mixture of 0.239 g (0.964 mmol) of **1**, 0.151 g (1.45 mmol) of styrene, and 0.051 g (0.044 mmol) of $Pd(PPh_3)_4$ in 1 mL of benzene was heated in a sealed glass tube at 150 °C for 24 h. The mixture was analyzed by GLC as being **8** (93% yield) and 4% of the starting compound **1**. After treatment of the mixture with a short silica gel column, compound **8** was isolated by MPLC. All spectral data for **8** were identical with those of compound obtained from the same reaction at room temperature.

Reaction of 1 with 1-Hexene in Refluxing Benzene. A mixture of 0.082 g (0.331 mmol) of **1**, 0.056 g (0.67 mmol) of 1-hexene, and 0.017 g (0.015 mmol) of $Pd(PPh_3)_4$ in 2 mL of benzene was heated to reflux for 14 h. The mixture was analyzed by GLC as being **9a** (94% yield). After treatment of the mixture with a short silica gel column, compound **9a** was isolated by MPLC: MS *m/z* 332 (M^+); IR 2954, 2873, 1458, 1413, 1232, 1118, 1014, 740, 702 cm^{-1}; ^{1}H NMR δ($CDCl_3$) 0.65−1.65 (m, 32H, EtSi, CH_2Si, CHSi, n-Bu), 7.25−7.51 (m, 4H, phenylene ring protons); ^{13}C NMR δ($CDCl_3$) 3.38, 3.78, 5.25, 6.20, 7.50, 7.53, 7.82, 8.09 (EtSi), 10.25 (CH_2Si), 14.16, 16.57, 22.66, 30.24, 33.21 (CHSi, n-Bu), 127.62 (2C), 133.69, 133.94, 144.08, 144.60 (phenylene ring carbons); ^{29}Si NMR δ($CDCl_3$) −2.71, −1.57. Anal. Calcd for $C_{20}H_{36}Si_2$: C, 72.21; H, 10.91. Found: C, 72.15; H, 10.80.

Reaction of 1 with 1-Hexene at 150 °C. A mixture of 0.169 g (0.68 mmol) of **1**, 0.085 g (1.00 mmol) of 1-hexene, and 0.035 g (0.030 mmol) of $Pd(PPh_3)_4$ in 1 mL of benzene was heated in a sealed glass tube at 150 °C for 24 h. The mixture was analyzed by GLC as being **9a** (39% yield) and **10a** (41% yield). After treatment of the mixture with a short silica gel column, compounds **9a** and **10a** were isolated by MPLC. All spectral data for **9a** were identical with those of compound obtained from the same reaction at 80 °C. For **10a**: MS *m/z* 332 (M^+); IR 2955, 2893, 2146 (SiH), 1458, 1418, 1232, 1117, 1016, 814, 744, 708 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.67−1.02 (m, 23H, EtSi, CH_3), 1.31 (sext, 2H, CH_2), 1.83−1.99 (m, 4H, CH_2), 4.56 (quint, 1H, SiH, $J = 3.3$ Hz), 5.24−5.42 (m, 2H, CH=CH, $J = 15.4$ Hz[14]), 7.27−7.56 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 4.64, 5.09, 7.51, 8.36 (EtSi), 13.61 (CH_3), 19.10, 23.02, 34.95 (CH_2), 127.58, 127.78, 134.86, 135.47, 142.75, 143.94 (phenylene ring carbons), 125.97, 129.49 (olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ −9.69, 0.46. Anal. Calcd for $C_{20}H_{36}Si_2$: C, 72.21; H, 10.91. Found: C, 72.03; H, 10.96.

Reaction of 1 with 1,1-Dideuterio-1-hexene at 150 °C. A mixture of 0.255 g (1.03 mmol) of **1**, 0.197 g (2.29 mmol) of 1,1-dideuterio-1-hexene, and 0.060 g (0.052 mmol) of $Pd(PPh_3)_4$ in 1 mL of benzene was heated in a sealed glass tube at 150 °C for 24 h. The mixture was analyzed by GLC as **9b** (43% yield) and **10b** (35% yield). After treatment of the mixture with a short silica gel column, compound **9b** and **10b** were isolated by MPLC. For **9b**: MS *m/z* 334 (M^+); ^1H NMR $\delta(CDCl_3)$ 0.67−1.64 (m, 30H, EtSi, CHSi, n-Bu), 7.26−7.51 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 3.43, 3.83, 5.30, 6.22, 7.51, 7.53, 7.82, 8.09 (EtSi), 9.51 (CD_2Si, $J = 16$Hz), 14.14, 16.43, 22.70, 30.30, 33.21 (CHSi, n-Bu), 127.66 (2C), 133.71, 134.94, 144.08, 144.56 (phenylene ring carbons); ^2H NMR $\delta(CDCl_3)$ 0.80, 1.28. For **10b**: MS *m/z* 334 (M^+); ^1H NMR $\delta(CDCl_3)$ 0.69−1.02 (m, 23H, EtSi, CH_3), 1.31 (sext, 2H, CH_2), 1.87−1.99 (m, 2H, CH_2), 4.55 (quint, 1H, SiH, $J = 3.3$ Hz), 5.24−5.40 (m, 2H, CH=CH), 7.26−7.54 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 4.64, 5.07, 7.50, 8.34 (EtSi), 13.61 (CH_3), 18.40 (CD_2Si, $J = 21$Hz), 23.02, 34.95 (CH_2), 127.58, 127.78, 134.84, 135.47, 142.75, 143.94 (phenylene ring carbons), 125.89, 129.47 (olefinic carbons); ^2H NMR $\delta(CDCl_3)$ 1.84.

Reaction of 1 with 2-Hexene. A mixture of 0.134 g (0.539 mmol) of **1**, 0.096 g (1.14 mmol) of 2-hexene, and 0.068 g (0.059 mmol) of $Pd(PPh_3)_4$ in 1 mL of benzene was heated in a sealed glass tube at 150 °C for 24 h. The mixture was analyzed by GLC as being **3** (72% yield). Product **3** was isolated by MPLC. All spectral data were identical with those of an authentic sample.

Reaction of 1 with Triethylsilane. A mixture of 0.046 g (0.186 mmol) of **1**, 0.106 g (0.914 mmol) of triethylsilane, and 0.012 g (0.010 mmol) of $Pd(PPh_3)_4$ in 1 mL of benzene was heated in a degassed sealed tube at 150 °C for 24 h. The mixture was analyzed by GLC as being **13a** (31% yield) and **3** (41% yield), along with 11% of unreacted starting compound **1**. Products **3** and **13a** were isolated by MPLC. For **13a**: MS *m/z* 335 ($M^+ - Et$); IR 2955, 2873, 2148 (Si-H), 1456, 1003, 799, 690 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.76−1.27 (m, 35H, Et_2Si, Et_3Si), 4.77 (quint, 1H, HSi, $J = 3.3$ Hz), 7.24−7.27 (m, 2H, phenylene ring protons), 7.47−7.50 (m, 1H, phenylene ring proton), 7.65−7.68 (m, 1H, phenylene ring proton); ^{13}C NMR $\delta(CDCl_3)$ 4.05, 4.60, 5.57, 8.16, 8.25, 8.36 (Et_2Si, Et_3Si), 126.90, 127.91, 134.93, 135.54, 142.91, 145.27 (phenylene ring carbons); ^{29}Si NMR $\delta(CDCl_3)$ −12.71, −9.87, −9.48. Anal. Calcd for $C_{20}H_{40}Si_3$: C, 65.85; H, 11.05. Found: C, 65.92; H, 10.84. All spectrum data for **3** were identical with those of an authentic sample.

Reaction of 1 with Dimethylphenylsilane. A mixture of 0.250 g (1.01 mmol) of **1**, 0.533 g (3.92 mmol) of dimethylphenylsilane, and 0.052 g (0.045 mmol) of $Pd(PPh_3)_4$ in 1 mL of benzene was heated in a degassed sealed tube at 150 °C for 24 h. GLC analysis showed the presence of **13b** in 52% yield, in addition to 24% of **1**. Products **13b** were isolated by MPLC: MS *m/z* 355 ($M^+ - Et$); IR 2953, 2872, 2142 (Si-H), 1459, 1426, 1242, 1009, 808, 698 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.37 (s, 6H, MeSi), 0.70−1.03 (m, 20H, EtSi), 4.43 (quint, 1H, HSi, $J = 3.1$ Hz), 7.23−7.50 (m, 9H, phenyl and phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ −1.97 (MeSi), 4.41, 5.21, 8.16, 8.29 (EtSi), 127.13, 127.51, 127.91, 128.10, 133.94, 135.00, 135.76, 140.12, 143.18, 144.00 (phenyl and phenylene ring carbons); ^{29}Si NMR $\delta(CDCl_3)$ −21.56, −12.94, −9.80. Anal. Calcd for $C_{22}H_{36}Si_3$: C, 68.67; H, 9.43. Found: C, 68.68; H, 9.46.

Reaction of 1 with Ethylene. In a 30-mL two-necked flask fitted with a condenser and inlet tube for ethylene gas was placed 0.200 g (0.805 mmol) of **1** and 0.047 g (0.041 mmol) of $Pd(PPh_3)_4$ in 5 mL of dry benzene. To this was introduced ethylene gas at room temperature for 4 h. The mixture was analyzed by GLC as being **11** (28% yield) and **12** (40% yield). After treatment of the mixture with a short silica gel column, compounds **11** and **12** were isolated by MPLC. All spectrum data for **11** were identical with those of an authentic sample.[4] For **12**: mp 103−107 °C; MS *m/z* 495 ($M^+ - Et$); IR 2953, 2873, 1458, 1413, 1261, 1128, 1055, 1004, 694 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.55−1.03 (m, 44H, EtSi, CH_2), 7.22−7.73 (m, 8H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 4.93, 5.16, 6.35, 7.84, 8.16 (EtSi, CH_2), 127.01, 127.17, 136.59, 136.75, 143.70, 144.03 (phenylene ring carbons); ^{29}Si NMR $\delta(CDCl_3)$ −12.17, 4.30. Anal. Calcd for $C_{30}H_{52}Si_4$: C, 68.62; H, 9.98. Found: C, 68.45; H, 9.95.

Stoichiometric Reaction of 1 with Tetrakis(triphenylphosphine)palladium(0). In a 30-mL two-necked flask fitted with a condenser was placed 0.023 g (0.093 mmol) of **1** and 0.105 g (0.091 mmol) of $Pd(PPh_3)_4$ in 1 mL of benzene-d_6. The mixture was stirred at room temperature for 0.5 h to give **2a**: ^1H NMR $\delta(CDCl_3)$ 0.76−0.81 (m, 2H, CH_2Si), 1.04−1.14 (m, 2H, CH_2Si), 1.27 (t, 6H, CH_3, $J = 7.7$Hz), 7.00−7.80 (m, 64H, phenylene and phenyl ring protons); ^{13}C NMR $\delta(CDCl_3)$ 11.31, 12.88 (EtSi), 127.60, 131.86, 157.07 (phenylene ring carbons) 128.41 ($^3J_{c\text{-}p} = 7.7$ Hz), 129.10, 134.44 ($^2J_{c\text{-}p} = 16.8$ Hz), 137.28 ($^1J_{c\text{-}p} = 5.8$ Hz) (phenyl ring carbons); ^{29}Si NMR $\delta(CDCL_3)$ 44.28; ^{31}P NMR $\delta(CDCl_3)$ 1.17.

Reaction of 2a with Phenylacetylene. In a 30-mL two-necked flask fitted with a condenser was placed a benzene solution of **2a** prepared from 0.020 g (0.081 mmol) of **1** and 0.093 g (0.081 mmol) of $Pd(PPh_3)_4$ in 3

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[14] Since olefinic protons for **10** showed multiplet resonances, measurement of its coupling constant was carried out by proton decoupling technique. Decoupling of olefinic protons with hydrogens on C_1 and C_4 in a 2-hexenyl group resulted in two doublets with $J = 15.4$ Hz for the olefinic protons.

mL of benzene. To this was added 0.051 g (0.499 mmol) of phenylacetylene and the mixture was stirred at room temperature for 1 h. The resulting mixture was analyzed by GLC as being **6** (86% yield). Compound **6** was isolated by column chromatography. All spectral data for **6** were identical with those of an authentic sample.[4]

Reaction of 2a with Styrene. In a 30-mL two-necked flask fitted with a condenser was placed a benzene solution of **2a** prepared from 0.048 g (0.193 mmol) of **1** and 0.223 g (0.193 mmol) of $Pd(PPh_3)_4$ in 3 mL of benzene. To this was added 0.081 g (0.778 mmol) of styrene and the mixture was heated to reflux for 1 h. The resulting mixture was analyzed by GLC as being **8** (86% yield). Compound **8** was isolated by column chromatography. All spectral data for **8** were identical with those of compound obtained from the catalytic reaction described above.

Reaction of 2a with Ethylene. In a 30-mL two-necked flask fitted with a condenser and inlet tube for ethylene gas was placed a benzene solution of **2a** prepared from 0.083 g (0.334 mmol) of **1** and 0.410 g (0.355 mmol) of $Pd(PPh_3)_4$ in 5 mL of dry benzene. To this was introduced ethylene gas at 80°C for 5 h. The resulting mixture was analyzed by GLC as being **11** (45% yield) and **12** (44% yield). All spectral data for **11** and **12** were identical with those of compounds obtained from the catalytic reaction of **1** with ethylene.

Thermolysis of 1. 0.236 g (0.950 mmol) of **1** was heated at 250 °C in a degassed sealed tube for 24 h. The mixture was analyzed by GLC as being **15** (60% yield) and **16** (12% yield). Compound **15** and **16** were isolated by preparative GLC. For **15**: MS *m/z* 334 (M^+); IR 2951, 2872, 1459, 1415, 1375, 1108, 1006, 697 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.86–1.20 (m, 30H, EtSi), 7.34–7.63 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 0.69, 5.50, 8.52, 10.91 (EtSi), 127.60, 134.02, 149.34 (phenylene ring carbons); ^{29}Si NMR $\delta(CDCl_3)$ −5.62, −38.98. Anal. Calcd for $C_{18}H_{34}Si_3$: C, 64.59; H, 10.24. Found: C, 64.54; H, 10.25. For **16**: MS *m/z* 324 (M^+); IR 3045, 2947, 2860, 1413, 1248, 1117, 1000, 745 cm^{-1}; ^1H NMR $\delta(CDCl_3)$ 0.78–0.99 (m, 20H, EtSi), 7.39–7.66 (m, 8H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 6.76, 7.60 (EtSi), 128.01, 133.62, 142.98 (phenylene ring carbons); ^{29}Si NMR $\delta(CDCl_3)$ −11.89. Anal. Calcd for $C_{20}H_{28}Si_2$: C, 74.00; H, 8.69. Found: C, 73.80; H, 8.63.

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