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# Platinum-Catalyzed Reactions of 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene

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Treatment of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene (1) with a catalytic amount of ($\eta^2$-ethylene)bis(triphenylphosphine)platinum(0) in refluxing benzene gave 1-(diethylphenylsilyl)-2-(diethylsilyl)benzene (2) and *cis*-4,5-benzo-1,1,3-triethyl-2-methyl-1,3-disilacyclopent-4-ene (3) in 10% and 67% yields. The platinum-catalyzed reaction of 1 with ethylene produced 5,6-benzo-1,1,4,4-tetraethyl-1,4-disilacyclohex-5-ene, while with styrene and 1-hexene, compound 1 afforded 4,5-benzo-1,3-disilacyclopent-4-ene derivatives. A similar reaction of 1 with $\alpha$-methylstyrene produced an adduct arising from hydrosilylation of 3 to $\alpha$-methylstyrene. The reaction of 1 with phenylacetylene, diphenylacetylene, phenyl(trimethylsilyl)acetylene, and 3-hexyne in the presence of a platinum catalyst yielded the respective 5,6-benzo-1,4-disilacyclohexa-2,5-dienes. With benzaldehyde, 1 gave a 5,6-benzo-2-oxa-1,4-disilacyclohex-5-ene derivative.

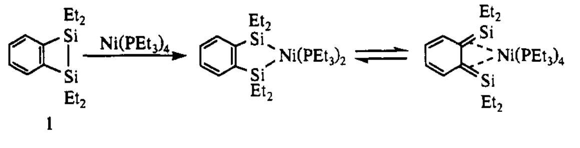
## Introduction

Recently, we have found that when 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (1) is heated to reflux in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0) in arenes, such as benzene, toluene, and xylene, 1-(aryldiethylsilyl)-2-(diethylsilyl)benzenes arising from C–H bond activation of arenes are obtained in high yields.[1] The nickel-catalyzed reaction of 1 with benzaldehyde in refluxing benzene produces a product formed from insertion of a carbonyl group into a silicon–silicon bond of 1, 5,6-benzo-1,1,4,4-tetraethyl-2-oxa-3-phenyl-1,4-disilacyclohex-5-ene, while with diphenylacetylene, 1 gives two products which are derived formally from insertion of a carbon–carbon triple bond into a silicon–silicon bond and also a silicon–carbon bond in the benzodisilacyclobutene ring.[2] In these reactions, we proposed the formation of an *o*-quinodisilane–nickel complex as a reactive intermediate.[1,3]

In order to clarify the similarities and dissimilarities between nickel catalyst and other transition metal catalysts in the reaction of 1 and to get more information about the reactive intermediates which are involved in these system, we investigated the reaction of 1 with benzene, olefins, acetylenes, and carbonyl compounds in the presence of ($\eta^2$-ethylene)bis(triphenylphosphine)platinum.

## Results and Discussion

First, we treated 1 with a catalytic amount of a platinum complex in benzene to confirm whether or not C–H bond activation of benzene occurs in the platinum-catalyzed reaction of benzodisilacyclobutene 1, as observed in the nickel-catalyzed reaction.[1,2] When compound 1 was heated to reflux in the presence of 5 mol % of ($\eta^2$-ethylene)bis(triphenylphosphine)platinum(0) in benzene for 56 h, 1-(diethylphenylsilyl)-2-(diethylsilyl)benzene (2), arising from C–H bond activation of benzene, was obtained in 10% yield.[4] To our surprise, an isomerization product, *cis*-4,5-benzo-1,1,3-triethyl-2-methyl-1,3-disilacyclopent-4-ene (3) was obtained in 67% yield, as a single isomer, along with 6% of the unchanged starting compound 1 (Scheme I). No other isomers were detected in the reaction mixture either by spectrometric analysis or GLC analysis.



IR and $^1$H, $^{13}$C, and $^{29}$Si NMR spectra obtained for compound 2 were identical with those of an authentic sample reported previously.[1] The structure of 3 was verified by spectrometric analysis, as well as by chemical reaction. The $^{13}$C NMR spectrum of product 3 shows resonances at −2.28, 4.14, 4.52, 5.74, 7.72, 7.86, 8.58, and 8.74 ppm, due to three nonequivalent ethyl carbons and MeC(H) carbons. Its $^{29}$Si NMR spectrum reveals two resonances at −1.07 and 15.44 ppm, attributed to two nonequivalent silicon atoms. We further confirmed the structure of 3 by conversion into a tetraethyl derivative, 4,5-benzo-1,1,3,3-tetraethyl-2-methyl-1,3-disilacyclopent-4-ene (4). Thus, the reaction of 3 with ethylene in the presence of a platinum catalyst in an autoclave at 150 °C for 24 h afforded compound 4 in almost quantitative yield. As expected, the $^{13}$C NMR spectrum of 4 reveals four resonances at 4.32, 4.66, 5.54, and 7.55 ppm attributed to two nonequivalent Et carbons, and two resonances at −1.83 and 8.65 ppm due to MeC carbons, as well as three phenylene carbons at 128.19, 132.85, and 148.72 ppm. Its $^{29}$Si NMR spectrum exhibits a single resonance at 13.60 ppm, in accord with the downfield shift for 4,5-benzo-1,3-disilacyclopent-4-ene derivatives. In fact, $^{29}$Si chemical shifts of diethyl-substituted silicon atoms in the 2-alkyl-

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[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1993.

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

[2] Ishikawa, M.; Sakamoto, H.; Okazaki, S.; Naka, A. *J. Organomet. Chem.* **1992,** *439,* 19.

[3] Ishikawa, M.; Naka, A.; Okazaki, S.; Sakamoto, H. *Organometallics* **1993,** *12,* 87.

[4] M. Tanaka and his co-workers have reported that the Pt$_2$(dba)$_3$-catalyzed reaction of *o*-bis(dimethylsilyl)benzene with arenes gives products arising from C–H bond activation of arenes: Uchimaru, Y.; El Sayed, A. M. M.; Tanaka, M. *Organometallics* **1993,** *12,* 2065.

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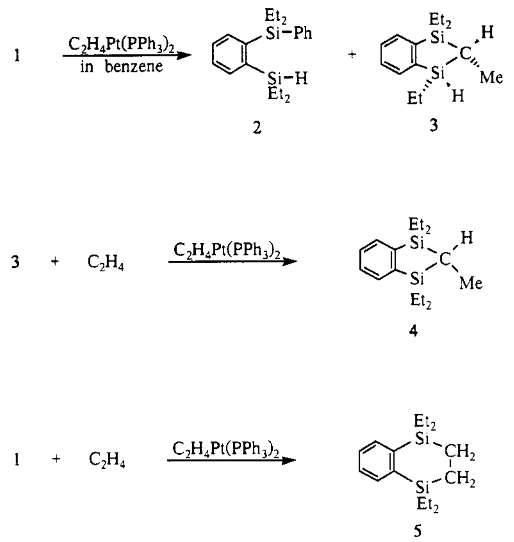
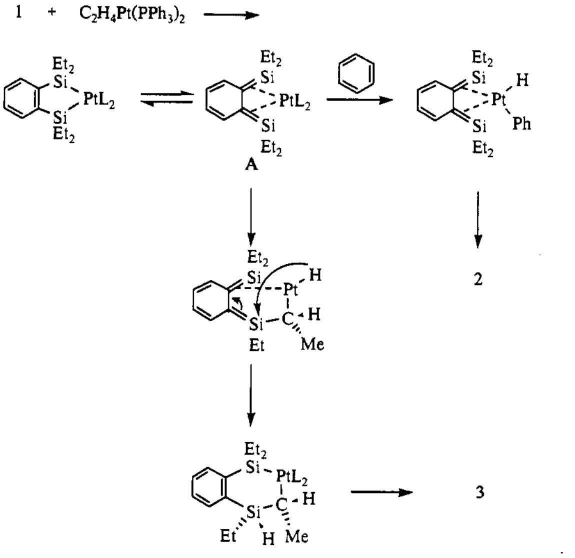
Scheme I



Scheme II



4,5-benzo-1,3-disilacyclopent-4-ene rings appear in the region 12–16 ppm, but those of the diethylsilyl groups in 5,6-benzo-1,4-disilacyclohex-5-enes and -1,4-disilacyclohex-2,5-dienes appear in the region −3 to −18 ppm, higher than the chemical shift of tetramethylsilane. Furthermore, the platinum-catalyzed reaction of 1 with ethylene in benzene at 100 °C in an autoclave gave an isomer of 4, 5,6-benzo-1,1,4,4-tetraethyl-1,4-disilacyclohex-5-ene (**5**), and compound **2**, arising from C–H bond activation of benzene, in 62% and 5% yields, respectively, in addition to an 11% yield of an unidentified product whose mass spectrum reveals a molecular ion at $m/z$ 486. No compound **4** was detected in the reaction mixture by spectrometric analysis. The $^{13}C$ NMR spectrum of **5** shows simple resonance patterns, a resonance at 3.35 ppm, attributed to $CH_2CH_2$ carbons, and 5.29 and 7.62 ppm, due to Et carbons, as well as three phenylene ring carbons at 127.67, 133.82, and 144.46 ppm. The $^{29}Si$ NMR spectrum reveals a single resonance at −3.48 ppm, which is consistent with the chemical shift observed for 5,6-benzo-1,1,4,4-tetraethyl-1,4-disilacyclohex-5-ene derivatives. These results clearly indicate that compound **3** must have a 3,4-benzo-2-methyl-1,3-disilacyclopent-4-ene structure. Unfortunately, NOE-FID difference experiments at 270 MHz did not give any clear-cut results for the configuration of **3**. However, we assigned product **3** as a cis isomer on the basis of the $^1H$ NMR spectrum of the product obtained from its hydrosilylation with α-methylstyrene (see below).

In the nickel-catalyzed reactions of 1 with arenes and carbonyl compounds, we suggested the formation of an *o*-quinodisilane–nickel complex as a reactive intermediate. The formation of **2** and **3** in the present reaction may also be explained in terms of the intermediacy of an *o*-quinodisilane–platinum complex (**A**), as shown in Scheme II. The *o*-quinodisilane–platinum complex **A** would be produced by isomerization of a 3,4-benzo-1-platina-2,5-disilacyclopent-3-ene, arising from insertion of the platinum species into a silicon–silicon bond of 1. The production of 3,4-benzo-1-platina-2,5-disilacyclopent-3-ene[4–11] has been observed in the reaction of 1,2-bis(dimethylsilyl)-benzene with a platinum complex by Eaborn et al.[5] and Tanaka et al.[4,6,7,10,11]

The reaction of 1 with styrene in the presence of the platinum catalyst in refluxing benzene for 3 h gave 4,5-benzo-1,1,3,3-tetraethyl-2-benzyl-1,3-disilacyclopent-4-ene (**6**) in 77% yield, as a single isomer, together with an 8% yield of product **2**. A similar reaction of 1 with 1-hexene in refluxing benzene afforded 4,5-benzo-1,1,3,3-tetraethyl-2-pentyl-1,3-disilacyclopent-4-ene (**8**), analogous to **6**, in 86% yield, together with a 2% yield of **2**. Again, no other isomers were detected in the reaction mixture by either GLC analysis or spectroscopic analysis.

Tanaka et al. have reported that the reaction of 1,2-bis(dimethylsilyl)benzene with ethylene in the presence of a platinum(0) catalyst affords 5,6-benzo-1,1,4,4-tetramethyl-1,4-disilacyclohex-5-ene analogous to **5** and 4,5-benzo-1,1,2,3,3-pentamethyl-1,3-disilacyclopent-4-ene, while with other olefins, such as 1-octene and styrene, 1,2-bis(dimethylsilyl)benzene produces 4,5-benzodisilacyclopent-4-ene derivatives. For the formation of the 4,5-benzodisilacyclopent-4-enes, they have proposed the mechanism involving β-hydrogen elimination from initially formed benzoplatinadisilacycloheptene, followed by intramolecular addition of the Pt–H bond across the resulting olefin bond.[6,10] In our system, however, the reaction of 1 with ethylene affords only compound **5** as an ethylene adduct. No compound **4** that can be expected to form from β-hydrogen elimination is detected. Moreover, the C–H bond activation of benzene indeed takes place under the conditions used. Therefore, it seems likely that $sp^2$ C–H bond activation occurs in the reaction of 1 with styrene and 1-hexene. On the basis of these findings, we propose the mechanism involving $sp^2$ C–H bond activation for the formation of **6** and **8**. Scheme III illustrates a possible mechanistic interpretation of the observed reaction course. The reaction of *o*-quinodisilane–platinum complex **A** with styrene produces platinum–hydride complex **B**, and then complex **B** is transformed into complex **C**. Intramolecular

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[5] Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Organomet. Chem.* **1973**, *63*, 107.

[6] Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *Organometallics* **1991**, *10*, 16.

[7] Uchimaru, Y.; Lautenschlager, H.-J.; Wynd, A. J.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 2639.

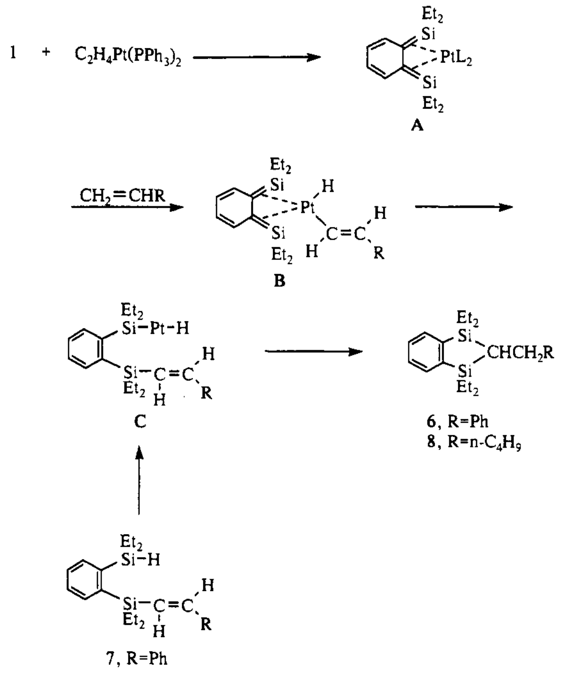
[8] For 3,4-benzo-1-metala-2,5-disilacyclopent-3-ene, see ref 9.

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

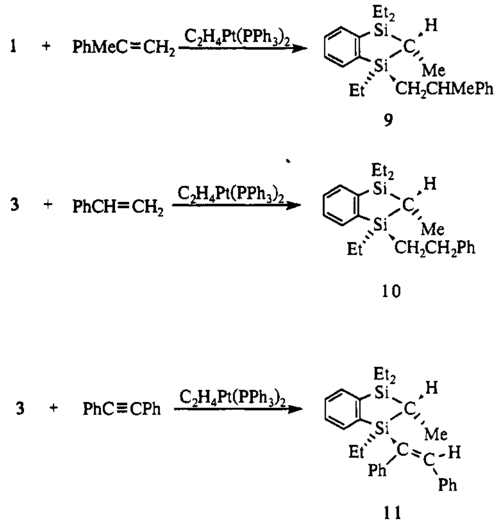
[10] Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *J. Organomet. Chem.* **1992**, *482*, 1.

[11] Tanaka, M.; Uchimaru, Y. *Bull. Soc. Chim. Fr.* **1992**, *129*, 667.

**Scheme III**



**Scheme IV**



hydrosilylation gives products **6** and **8**. Treatment of *trans*-1-[diethyl(2-phenylethenyl)silyl]-2-(diethylsilyl)benzene (**7**) prepared by an independent route with a platinum catalyst under the same conditions produced **6** in almost quantitative yield. This result supports the formation of complex **C**.

The reaction of **1** with α-methylstyrene under the same conditions, however, gave a different type of the product, 4,5-benzo-1,3,3-triethyl-*t*-2-methyl-*r*-1-(2-phenylpropyl)-1,3-disilacyclopent-4-ene (**9**), which was probably produced from hydrosilylation of **3** to α-methylstyrene, in 67% yield, in addition to an 11% yield of **2** (Scheme IV). No other products, such as 4,5-benzo-1,3-disilacyclopent-4-ene analogous to compounds **6** and **8**, and the product derived from insertion of a carbon–carbon double bond into a silicon–silicon bond in the benzodisilacyclobutene, were detected in the reaction mixture. Presumably, α-methylstyrene would not coordinate to *o*-quinodisilane–platinum complex **A** for steric reason or, even if it did coordinate to **A**, the coordinated complex would be nonproductive. The reaction of **1** with 1,1-diphenylethylene under the same conditions produced neither insertion product nor hydrosilylation product, but compound **2** and isomerization product **3** were obtained in 11% and 63% yields, respectively.

We also carried out the platinum-catalyzed reaction of **3** with styrene and diphenylacetylene. When compound **3** was prepared from the reaction of **1** with the platinum catalyst in refluxing benzene for 57 h and the resulting mixture was treated with styrene, 4,5-benzo-1,3,3-triethyl-*t*-2-methyl-*r*-1-(2-phenylethyl)-1,3-disilacyclopent-4-ene (**10**) was obtained in almost quantitative yield.[12] The structure of **10** was confirmed by the $^{13}$C DEPT (distortionless enhancement by polarization transfer) spectrum. Its $^{13}$C DEPT spectrum shows two negative signals at 15.80 and 30.50 ppm attributed to two nonequivalent methylene carbons, as well as three negative signals due to methylene carbons of three nonequivalent ethyl groups. This result is wholly consistent with the structure proposed for **10**. Similar treatment of **3** with diphenylacetylene yielded 4,5-benzo-1,3,3-triethyl-*t*-2-methyl-*r*-1-(1,2-diphenylethenyl)-1,3-disilacyclopent-4-ene (**11**) (Scheme IV). The structures of **10** and **11** were confirmed by spectrometric analysis, as well as by elemental analysis.

That substituents introduced on the Si-1 atom in the 1,3-disilacyclopentene ring for compounds **9**–**11** must be located in a cis fashion toward hydrogen on the C-2 position was verified by the fact that the resonance attributed to this reference hydrogen of product **9** appears at an extremely high field. Examination of molecular models clearly indicates that this high field shift of the proton may be due to the ring current of a 2-phenylpropyl group on the silicon atom, which is located at the position cis to this proton. In fact, saturation of the resonance of this proton on the C-2 position of the 1,3-disilacyclopentene ring in an NOE-FID difference experiment at 270 MHz produced a positive nuclear Overhauser effect of phenyl protons, as well as methyl protons on the C-2 position. On the basis of this result, the configuration of product **3** must be cis and, therefore, hydrosilylation products derived from **3** must be trans.

In contrast to the platinum-catalyzed isomerization of **1**, in which prolonged heating is necessary for completion of the reaction, the reaction of **1** with phenylacetylene in benzene proceeds readily to give an insertion product. Thus, treatment of **1** with phenylacetylene in the presence of the platinum catalyst in refluxing benzene for 5 min afforded 5,6-benzo-1,1,4,4-tetraethyl-2-phenyl-1,4-disilacyclohexa-2,5-diene (**12**), arising from insertion of a triple bond into a silicon–silicon bond, in 98% yield. Interestingly, when 1-[diethyl(phenylethynyl)silyl]-2-(diethylsilyl)benzene (**13**), prepared from the reaction of 1,2-bis(chlorodiethylsilyl)benzene with [phenylethynyl]lithium, followed by reduction of the resulting 1-(chlorodiethylsilyl)-2-phenylethynylsilyl derivative, was treated with a platinum catalyst under the same conditions, 4,5-benzo-1,1,3,3-tetraethyl-2-(phenylmethylene)-1,4-disilacyclopent-4-ene (**14**) was produced in 99% y ield (Scheme V). No compound **12** was detected in the reaction mixture. The result indicates that the reaction of **1** with phenylacetylene involves no C–H bond activation.

The platinum-catalyzed reaction of **1** with diphenylacetylene again gave a benzodisilacyclohexadiene, 5,6-

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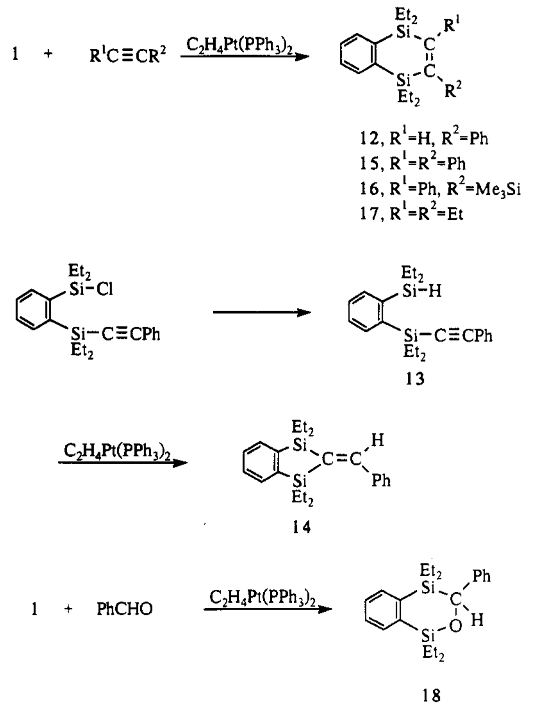
(12) For the hydrosilylation reaction see ref 13.

(13) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 2, Chapter 25.

**Scheme V**



benzo-1,1,4,4-tetraethyl-2,3-diphenyl-1,4-disilacyclohexa-2,5-diene (**15**) in 98% yield. As we reported recently, the nickel-catalyzed reaction of **1** with diphenylacetylene gave two insertion products, compound **15** and the isomer derived from insertion of a triple bond of diphenylacetylene into a silicon–carbon bond in the benzodisilacyclobutene ring.[2] In the present reaction, however, neither product **2** formed from C–H bond activation of benzene used as a solvent nor product derived from insertion of a carbon–carbon triple bond into a silicon–carbon bond in the benzodisilacyclobutene ring was detected by either GLC analysis or spectrometric analysis. A similar reaction of **1** with phenyl(trimethylsilyl)acetylene and 3-hexyne under the same conditions afforded the products **16** and **17** arising from insertion of a carbon–carbon triple bond into a silicon–silicon bond in the benzodisilacyclobutene ring in almost quantitative yields. The formation of 5,6-benzo-1,4-disilacyclohexa-2,5-dienes **12**–**17** and also 5,6-benzo-1,4-disilacyclohex-5-ene **5** may be understood in terms of reductive elimination of platinum species from 5,6-benzo-1-platina-4,7-disilacyclohepta-2,5-dienes and disilacyclohept-5-ene derived from two-atom insertion of alkynes and ethylene into a platinum–silicon bond in 3,4-benzo-1-platina-2,5-disilacyclopent-3-ene.[11] The structures **12**–**17** were verified by spectrometric analysis, as well as by elemental analysis (see Experimental Section).

We have reported that the nickel-catalyzed reaction of **1** with benzaldehyde in benzene gave 5,6-benzo-1,1,4,4-tetraethyl-2-oxa-3-phenyl-1,4-disilacyclohex-5-ene as the sole product, while with acetone **1** afforded 4,5-benzo-1,1,3,3-tetraethyl-2-oxa-1,3-disilacyclopent-4-ene, 1-[diethyl(isopropenyloxy)silyl]-2-(diethylsilyl)benzene, and 5,6-benzo-1,1,4,4-tetraethyl-3,3-dimethyl-2-oxa-1,4-disilacyclohex-5-ene.[3] A similar nickel-catalyzed reaction of **1** with benzophenone produced 4,5-benzo-1,1,3,3-tetraethyl-2,2-diphenyl-1,3-disilacyclopent-4-ene. The platinum-catalyzed reaction with benzaldehyde led to the same result as that of the nickel-catalyzed reaction. 5,6-Benzo-1,1,4,4-tetraethyl-2-oxa-3-phenyl-1,4-disilacyclohex-5-ene (**18**) was obtained in 73% yield, in addition to a 3% yield of compound **2** and 8% of the unreacted starting compound **1**. Similar reactions of **1** with ketones such as acetone and benzophenone, however, afforded no adducts. In both cases, the platinum-catalyzed isomerization of **1** took place to give product **3**. Benzene adduct **2** was also produced in a small amount in these reactions.

In conclusion, the reaction of **1** in the presence of a platinum catalyst in refluxing benzene produces an isomerization product **3**, in addition to a small amount of a product formed from C–H bond activation of benzene. The platinum-catalyzed reaction of **1** with ethylene gives 5,6-benzo-1,4-disilacyclohex-5-ene, while styrene and 1-hexene afford products derived from C–H bond activation of olefins, followed by intramolecular hydrosilylation of the resulting platinum complex. Similar reaction of **1** with $\alpha$-methylstyrene produces a product arising from hydrosilylation of **3** formed from isomerization of **1** to $\alpha$-methylstyrene. The platinum-catalyzed reaction of **1** with acetylenes gives 5,6-benzo-1,4-disilacyclohexa-2,5-dienes. With benzaldehyde, 5,6-benzo-2-oxa-1,4-disilacyclohex-5-ene is produced.

## Experimental Section

**General Procedure.** All reactions were carried out under an atmosphere of dry argon. Yields of the products were determined by analytical GLC with the use of tridecane as an internal standard. 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 × 10 mm) packed with 30% SE-30 silicone on Chromosorb P. Gel permeation chromatographic separation was performed with a Model LC-908 Recycling preparative HPLC (Japan Analytical Industry Co., Ltd.). ($\eta^2$-Ethylene)bis(triphenylphosphine)platinum(0) was prepared by the method reported in the literature.[14]

**Materials.** 3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1**) was prepared as reported previously.[15] Benzene used as solvent was dried over lithium aluminium hydride and distilled before use.

**Reaction of 1 in Benzene.** Into a 30-mL two-necked flask fitted with a stirrer and reflux condenser was placed a mixture of 0.2658 g (1.07 mmol) of **1** and 40 mg ($5.37 \times 10^{-2}$ mmol) of ($\eta^2$-ethylene)bis(triphenylphosphine)platinum(0) in 10 mL of dry benzene. The mixture was heated to reflux for 56 h. GLC analysis of the reaction mixture indicated the presence of **3** (67% yield), **2** (10% yield), and 6% of the unchanged starting compound **1**. Products **2** and **3** were isolated by preparative GLC. For **3**: MS *m/z* 248 ($M^+$); IR 3096, 3025, 2943, 2097 (Si–H), 1472, 1032, 673 cm$^{-1}$; $^1$H NMR $\delta$($C_6D_6$) 0.59–1.16 (m, 20H, EtSi, MeC, HC), 4.84 (q, 1H, HSi, $J$ = 3.6 Hz), 7.18–7.72 (m, 4H, phenylene ring protons); $^{13}$C NMR $\delta$($C_6D_6$) −2.28, 4.14, 4.52, 5.74, 7.72, 7.86, 8.58, 8.74 (EtSi, MeC, CH), 128.97, 129.06, 133.30, 133.88, 146.72, 148.59 (phenylene ring carbons); $^{29}$Si NMR −1.07, 15.44. Exact MS Calcd for $C_{14}H_{24}Si_2$: 248.1417. Found: 248.1431.[16] All spectral data for product **2** were identical with those of an authentic sample.

**Reaction of 3 with Ethylene.** Into a 30-mL two-necked flask fitted with a stirrer and reflux condenser was placed a mixture of 0.2420 g (0.974 mmol) of **1** and 36 mg ($4.83 \times 10^{-2}$ mmol) of ($\eta^2$-ethylene)bis(triphenylphosphine)platinum(0) in 10 mL of dry benzene. The mixture was heated to reflux for 57 h. GLC analysis of the resulting mixture showed the presence of **3** in 66% yield, along with a 10% yield of **2**. All contents of the flask were

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[14] Cook, C. D.; Jauhal, G. S. *J. Am. Chem. Soc.* **1968**, *90*, 1467.

[15] Ishikawa, M.; Sakamoto, H.; Tabuchi, T. *Organometallics* **1991**, *10*, 3137.

[16] Compound **3** is stable in an inert atmosphere but unstable in air.

transferred into a 50-mL autoclave under an argon atmosphere and then ethylene gas (60 kg/cm$^2$) was compressed into the autoclave. The autoclave was heated at 150 °C for 24 h. GLC analysis of the reaction mixture indicated that **3** was transformed into **4** in almost quantitative yield. Pure **4** was isolated by preparative HPLC. For **4**: MS *m/z* 276 (M$^+$); IR 3045, 2953, 2873, 1459, 1414, 1115, 1009, 750, 716 cm$^{-1}$; $^1$H NMR δ (CDCl$_3$) 0.42 (q, 1H, HC, *J* = 7.6 Hz), 0.63–1.03 (m, 20H, EtSi), 1.21 (d, 3H, MeC, *J* = 7.6 Hz), 7.31–7.34 (m, 2H, phenylene ring protons), 7.51–7.55 (m, 2H, phenylene ring protons); $^{13}$C NMR δ(CDCl$_3$) −1.83 (CH), 4.32, 4.66, 5.54, 7.55 (EtSi), 8.65 (MeC), 128.19, 132.85, 148.72 (phenylene ring carbons); $^{29}$Si NMR δ(CDCl$_3$) 13.60. Anal. Calcd for $C_{16}H_{28}Si_2$: C, 69.49; H, 10.20. Found: C, 69.26; H, 10.28.

**Reaction of 1 with Ethylene.** Into a 50-mL autoclave was placed 0.2331 g (0.938 mmol) of **1** and 35 mg (4.70 × 10$^{-2}$ mmol) of ($\eta^2$-ethylene)bis(triphenylphosphine)platinum(0) in 10 mL of dry benzene, and then ethylene gas (60 kg/cm$^2$) was compressed into autoclave. The autoclave was heated at 100 °C for 24 h. GLC analysis of the resulting mixture showed the presence of **2** (5% yield) and **5** (62% yield), in addition to an 11% yield of an unidentified product. Products **2** and **5** were isolated by MPLC. For **5**: MS *m/z* 276 (M$^+$); IR 3037, 2943, 2861, 1461, 1408, 1114, 1008, 714 cm$^{-1}$; $^1$H NMR δ(CDCl$_3$) 0.71–1.03 (m, 24H, EtSi, CH$_2$-Si), 7.29–7.35 (m, 2H, phenylene ring protons), 7.46–7.56 (m, 2H, phenylene ring protons); $^{13}$C NMR δ(CDCl$_3$) 3.35 (CH$_2$Si), 5.29, 7.62 (EtSi), 127.67, 133.82, 144.46 (phenylene ring carbons); $^{29}$Si NMR δ(CDCl$_3$) −3.48. Anal. Calcd for $C_{16}H_{28}Si_2$: C, 69.49; H, 10.20. Found: C, 69.42; H, 10.20.

**Reaction of 1 with Styrene.** A solution of 0.2145 g (0.863 mmol) of **1**, 0.1349 g (1.30 mmol) of styrene, and 33 mg (4.36 × 10$^{-2}$ mmol) of a platinum catalyst in 10 mL of dry benzene was heated to reflux for 3 h. The mixture was analyzed by GLC as being **6** (77% yield) and **2** (10% yield). Product **6** was isolated by MPLC: MS *m/z* 323 (M$^+$ − Et); IR 3026, 2956, 2862, 1455, 1232, 1109, 1009, 744 cm$^{-1}$; $^1$H NMR δ(CDCl$_3$) 0.52–0.98 (m, 21H, EtSi, HC), 2.92 (d, 2H, H$_2$C), 7.16–7.52 (m, 9H, phenyl and phenylene ring protons); $^{13}$C NMR δ(CDCl$_3$) 5.20, 5.41, 7.35, 7.71 (EtSi), 8.63 (CH), 30.91 (CH$_2$), 125.71, 128.09, 128.19, 128.23, 132.83, 144.94, 148.21 (phenyl and phenylene ring carbons); $^{29}$Si NMR δ(CDCl$_3$) 12.80. Anal. Calcd for $C_{22}H_{32}Si_2$: C, 74.93; H, 9.15. Found: C, 74.83; H, 9.21.

***trans*-1-[Diethyl(2-phenylethenyl)silyl]-2-(diethylsilyl)benzene (7).** Into a 30-mL two-necked flask fitted with a stirrer and reflux condenser and dropping funnel was placed a solution of 0.1020 g (0.291 mmol) of 1-[diethyl(phenylethynyl)silyl]-2-(diethylsilyl)benzene (**13**) in 5 mL of dry benzene. To this was added 0.20 mL (0.300 mmol) of a diisobutylaluminum hydride–toluene solution at room temperature. The mixture was heated to reflux for 18 h. GLC analysis of the resulting mixture showed the presence of **7** in 9% yield. Product **7** was isolated by preparative HPLC. For **7**: MS *m/z* 352 (M$^+$); IR 3046, 2954, 2873, 2146 (Si—H), 1560, 1458, 1260, 695 cm$^{-1}$; $^1$H NMR δ(CDCl$_3$) 0.70–1.25 (m, 20H, EtSi), 4.53 (quint, 1H, HSi, *J* = 3.3 Hz), 6.64 (d, 1H, HC═C, *J* = 19 Hz), 6.87 (d, 1H, HC═C, *J* = 19 Hz), 7.17–7.64 (m, 9H, phenyl and phenylene ring protones); $^{13}$C NMR δ(CDCl$_3$) 4.50, 5.54, 7.66, 8.34 (EtSi), 126.36, 126.88, 127.76, 127.85, 127.91, 128.48, 128.59, 134.93, 135.76, 138.54 (phenyl and phenylene ring carbons), 132.42, 145.30 (olefin carbons). Anal. Calcd for $C_{22}H_{32}Si_2$: C, 74.93; H, 9.15. Found: C, 74.88; H, 9.04.

**1-[Diethyl(phenylethynyl)silyl]-2-(diethylsilyl)benzene (13).** Into a 50-mL two-necked flask fitted with a stirrer, reflux condenser, and dropping funnel was placed a solution of 0.6111 g (2.19 mmol) of 1,2-bis(chlorodiethylsilyl)benzene in 5 mL of dry hexane. To this solution was added dropwise (phenylethynyl)lithium prepared from phenylacetylene (2.54 mmol) and an *n*-butyllithium–hexane solution (2.56 mmol) in 5 mL of hexane. The mixture was heated to reflux for 10 h. To this was added 3.50 mL (5.25 mmol) of a diisobutylaluminum hydride–toluene solution at room temperature. After the mixture was stirred for 18 h at room temperature, the mixture was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and extracts were combined and dried over calcium chloride. GLC analysis of the resulting mixture showed the presence of **13** in 49% yield. Pure **13** was isolated by MPLC: MS *m/z* 350 (M$^+$); IR 2955, 2873, 2157 (Si–H), 1488, 1231, 1008, 830, 756, 689 cm$^{-1}$; $^1$H NMR δ(CDCl$_3$) 0.83–1.15 (m, 20H, EtSi), 4.70 (quint, 1H, HSi, *J* = 3.3 Hz), 7.31–7.97 (m, 9H, phenyl and phenylene ring protones); $^{13}$C NMR δ(CDCl$_3$) 4.50, 7.30, 7.87, 8.32 (EtSi), 92.22, 108.11 (sp carbons), 123.49, 128.05, 128.20, 128.21, 128.45, 131.95, 134.83, 136.17, 141.83, 142.66 (phenyl and phenylene ring carbons). Anal. Calcd for $C_{22}H_{30}Si_2$: C, 75.36; H, 8.62. Found: C, 75.12; H, 8.57.

**Platinum-Catalyzed Reaction of 7.** Into a 30-mL two-necked flask fitted with a stirrer and reflux condenser was placed a solution of 0.0070 g (0.020 mmol) of **7** and 1 mg (1.34 × 10$^{-3}$ mmol) of ($\eta^2$-ethylene)bis(triphenylphosphine)platinum(0) in 5 mL of dry benzene. The mixture was heated to reflux for 3 h. GLC analysis of the resulting mixture showed the presence of **6** in 99% yield. All spectral data for **6** were identical with an authentic sample.

**Reaction of 1 with 1-Hexene.** A solution of 0.2182 g (0.880 mmol) of **1**, 0.0887 g (1.05 mmol) of 1-hexene, and 33 mg (4.36 × 10$^{-2}$ mmol) of a platinum catalyst in 10 mL of dry benzene was heated to reflux for 3 h. The mixture was analyzed by GLC as being **8** (86% yield) and **2** (2% yield). Product **8** was isolated by MPLC: MS *m/z* 332 (M$^+$); IR 3044, 2953, 2873, 1462, 1116, 1016, 708 cm$^{-1}$; $^1$H NMR δ(CDCl$_3$) 0.53 (t, 1H, HC(Si)$_2$, *J* = 8 Hz), 0.66–1.69 (m, 31H, EtSi, H$_2$C, H$_3$C), 7.34–7.41 (m, 2H, phenylene ring protons), 7.56–7.61 (m, 2H, phenylene ring protons); $^{13}$C NMR δ(CDCl$_3$) 5.05, 6.04, 7.62, 7.77 (EtSi), 6.40 (CSi$_2$), 14.14 (CH$_3$), 22.63, 25.27, 32.13, 34.36 (CH$_2$), 128.14, 132.74, 148.66 (phenylene ring carbons); $^{29}$Si NMR δ(CDCl$_3$) 13.01. Anal. Calcd for $C_{20}H_{36}Si_2$: C, 72.21; H, 10.91. Found: C, 71.93; H, 11.03.

**Reaction of 1 with α-Methylstyrene.** A mixture of 0.2605 g (1.05 mmol) of **1**, 0.1589 g (1.35 mmol) of α-methylstyrene, and 40 mg (5.37 × 10$^{-2}$ mmol) of the platinum catalyst in 10 mL of dry benzene was heated to reflux for 19 h. GLC analysis of the reaction mixture showed the presence of **9** (67% yield), **2** (11% yield), and 2% of the starting compound **1**. Product **9** was isolated by MPLC: MS *m/z* 337 (M$^+$ − Et); IR 3014, 2956, 2876, 1447, 1119, 1009, 698 cm$^{-1}$; $^1$H NMR δ(CDCl$_3$) −0.31 to −0.17 (six signals,[17] 1H, HC(Si)$_2$), 0.41–1.25 (m, 20H, EtSi, H$_2$C, MeC), 1.45 (d, 3H, MeC, *J* = 6.6 Hz), 2.99 (six signals, 1H, HC(Me)(Ph), *J* = 6.6 Hz), 7.16–7.55 (m, 9H, phenyl and phenylene ring protons); $^{13}$C NMR δ(CDCl$_3$) 4.51 (CH(Si)$_2$), 5.61, 5.72, 6.53, 7.05, 7.77, 7.80, 8.00 (EtSi, MeC), 15.82 (CH$_2$), 28.29 (MeC), 37.88 (CH), 126.02, 126.79, 128.05, 128.09, 128.21, 132.67, 132.72, 147.83, 148.25, 149.99 (phenyl and phenylene ring carbons); $^{29}$Si NMR δ(CDCl$_3$) 12.03, 12.08. Anal. Calcd for $C_{23}H_{34}Si_2$: C, 75.34; H, 9.35. Found: C, 75.28; H, 9.43.

**Reaction of 3 with Styrene.** A mixture of 0.3308 g (1.33 mmol) of **1** and 51 mg (6.83 × 10$^{-2}$ mmol) of the platinum catalyst in 10 mL of dry benzene was heated to reflux for 57 h. GLC analysis of the resulting mixture showed that **3** was produced in 68% yield, along with an 8% yield of **2**. To this was added 0.1605 g (1.54 mmol) of styrene, and the mixture was heated to reflux for 3 h. GLC analysis of the reaction mixture indicated the presence of **10** (67% yield), **2** (8% yield), and 1% of the starting compound **1**. Pure **10** was isolated by MPLC. For **10**: MS *m/z* 323 (M$^+$ − Et); IR 3042, 2949, 2868, 1451, 1107, 1003, 747 cm$^{-1}$; $^1$H NMR δ(CDCl$_3$) 0.43 (q, 1H, HC, *J* = 7.6 Hz), 0.64–1.13 (m, 15H, EtSi), 1.12 (d, 3H, MeC, *J* = 7.6 Hz and m, 2H, H$_2$C), 2.63–2.71 (m, 2H, H$_2$C), 7.13–7.55 (m, 9H, phenyl and phenylene ring protons); $^{13}$C NMR δ(CDCl$_3$) −1.44 (CH), 4.30, 4.66, 5.50, 7.59, 7.64 (2C), 8.57 (EtSi, MeC), 15.80 (CH$_2$), 30.05 (CH$_2$), 125.52, 127.32 (2C), 128.28, 128.32, 132.87, 132.92, 145.12, 148.32, 148.70 (phenyl and phenylene ring carbons); $^{29}$Si NMR δ(CDCl$_3$) 12.33, 13.69. Anal. Calcd for $C_{22}H_{32}Si_2$: C, 74.93; H, 9.15. Found: C, 74.91; H, 9.22.

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(17) Six lines are presumably produced by the overlapping of two quartets, due to the presence of two chiral centers in the 4,5-benzo-1,3-disilacyclopent-4-ene ring.

**Reaction of 3 with Diphenylacetylene.** To a solution of 3 prepared from 0.3767 g (1.52 mmol) of 1 and 47 mg ($6.35 \times 10^{-2}$ mmol) of the platinum catalyst in 10 mL of dry benzene was added 0.2706 g (1.52 mmol) of diphenylacetylene. The mixture was heated to reflux for 2 h. GLC analysis of the reaction mixture showed the presence of 11 (64% yield), 4 (7% yield), and 2 (4% yield). Product 11 was isolated by preparative HPLC: MS *m/z* 426 (M$^+$); IR 3026, 2943, 1596, 1490, 1455, 1108, 1008, 908, 732, 697 cm$^{-1}$; $^1$H NMR $\delta$(CDCl$_3$) 0.55 (q, 1H, HC, $J$ = 7.6 Hz), 0.71–1.05 (m, 15H, EtSi), 1.14 (d, 3H, MeC, $J$ = 7.6 Hz), 6.89 (s, 1H, HC=C), 6.93–7.60 (m, 14H, phenyl and phenylene ring protons); $^{13}$C NMR $\delta$(CDCl$_3$) −1.13 (HC), 4.08, 4.21, 5.50, 7.39, 7.64, 8.61, 9.40 (EtSi, MeC), 125.68, 127.06, 127.58, 127.85, 128.27, 128.45, 128.59, 129.56, 132.92, 133.98, 137.30, 139.35, 142.53, 144.69, 146.76, 149.20 (phenyl and phenylene ring carbons and olefinic carbons); $^{29}$Si NMR $\delta$(CDCl$_3$) 7.48, 14.15. Anal. Calcd for $C_{28}H_{34}Si_2$: C, 78.81; H, 8.03. Found: C, 78.79; H, 8.03.

**Reaction of 1 with Phenylacetylene.** Into a 30-mL two-necked flask fitted with a stirrer and reflux condenser was placed 0.3001 g (1.21 mmol) of 1, 44 mg ($5.90 \times 10^{-2}$ mmol) of ($\eta^2$-ethylene)bis(triphenylphosphine)platinum(0), and 0.1963 g (1.92 mmol) of phenylacetylene in 10 mL of dry benzene. The mixture was heated to reflux for 5 min. GLC analysis of the resulting mixture showed the presence of 12 (98% yield). Compound 12 was isolated by MPLC: MS *m/z* 350 (M$^+$); IR 3056, 2953, 2872, 1458, 1414, 1120, 1002, 795, 739, 699 cm$^{-1}$; $^1$H NMR $\delta$(CDCl$_3$) 0.76–1.04 (m, 20H, EtSi), 6.89 (s, 1H, HC=C), 7.22–7.58 (m, 9H, phenyl and phenylene ring protons); $^{13}$C NMR $\delta$(CDCl$_3$) 6.26, 6.35, 7.53, 7.75 (EtSi), 126.24, 126.45, 127.84, 128.07, 128.23, 133.23, 133.42, 142.93, 142.98, 147.92 (phenyl and phenylene ring carbons), 145.62, 161.17 (olefinic carbons); $^{29}$Si NMR $\delta$(CDCl$_3$) −14.51, −12.53. Anal. Calcd for $C_{22}H_{30}Si_2$: C, 75.36; H, 8.62. Found: C, 75.12; H, 8.82.

**Platinum-Catalyzed Reaction of 13.** Into a 30-mL two-necked flask fitted with a stirrer and a reflux condenser was placed a solution of 0.0621 g (0.177 mmol) of 13 and 6.6 mg ($8.84 \times 10^{-3}$ mmol) of ($\eta^2$-ethylene)bis(triphenylphosphine)platinum(0) in 5 mL of dry benzene. The mixture was heated to reflux for 1 h. GLC analysis of the resulting mixture showed the presence of 14 in 98% yield. For 14: MS *m/z* 350 (M$^+$); IR 3045, 2954, 2872, 1585, 1560, 1458, 1119, 1003, 886, 752, 695 cm$^{-1}$; $^1$H NMR $\delta$(CDCl$_3$) 0.71–0.99 (m, 20H, EtSi), 7.30–7.63 (m, 9H, phenyl and phenylene ring protons), 7.89 (s, 1H, HC=C); $^{13}$C NMR $\delta$(CDCl$_3$) 6.29, 7.33, 7.66, 7.80 (EtSi), 127.66, 128.00, 128.19, 128.27, 128.55, 132.52, 132.74, 141.46, 147.46, 149.02 (phenyl and phenylene ring carbons), 138.94, 155.44 (olefinic carbons); $^{29}$Si NMR $\delta$(CDCl$_3$) 0.50, 6.46. Anal. Calcd for $C_{22}H_{30}Si_2$: C, 75.36; H, 8.62. Found: C, 75.38; H, 8.63.

**Reaction of 1 with Diphenylacetylene.** Into a 30-mL two-necked flask fitted with a stirrer and reflux condenser was placed 0.1658 g (0.667 mmol) of 1, 24 mg ($3.21 \times 10^{-2}$ mmol) of ($\eta^2$-ethylene)bis(triphenylphosphine)platinum(0), and 0.1429 g (0.803 mmol) of diphenylacetylene in 10 mL of dry benzene. The mixture was heated to reflux for 1 h. GLC analysis of the resulting mixture showed the presence of 15 (98% yield). Compound 15 was isolated by MPLC: mp 116–117 °C; MS *m/z* 426 (M$^+$); IR 2953, 1485, 1002, 909, 850, 790, 734 cm$^{-1}$; $^1$H NMR $\delta$(CDCl$_3$) 0.70–0.95 (m, 20H, EtSi), 6.79–7.62 (m, 14H, phenyl and phenylene ring protons); $^{13}$C NMR $\delta$(CDCl$_3$) 5.25, 7.68 (EtSi), 125.01, 127.37, 127.98, 128.03, 133.37, 142.61, 143.45 (phenyl and phenylene ring carbons), 157.32 (olefinic carbons); $^{29}$Si NMR $\delta$(CDCl$_3$) −13.33. Anal. Calcd for $C_{28}H_{34}Si_2$: C, 78.81; H, 8.03. Found: C, 78.80; H, 7.96.

**Reaction of 1 with Phenyl(trimethylsilyl)acetylene.** A mixture of 0.1423 g (0.573 mmol) of 1, 0.1231 g (0.707 mmol) of phenyl(trimethylsilyl)acetylene, and 21 mg ($2.85 \times 10^{-2}$ mmol) of a platinum catalyst in 10 mL of dry benzene was heated to reflux for 4 h. The mixture was analyzed by GLC as being 16 (98% yield). Compound 16 was isolated by MPLC: mp 96–99 °C. MS *m/z* 422 (M$^+$); IR 2947, 2869, 1477, 1414, 1113, 1074, 838, 772, 671 cm$^{-1}$; $^1$H NMR $\delta$(CDCl$_3$) −0.13 (s, 9H, Me$_3$Si), 0.53–0.97, (m, 20H, EtSi), 6.98–7.57 (m, 9H, phenyl and phenylene ring protons); $^{13}$C NMR $\delta$(CDCl$_3$) 2.93 (Me$_3$Si), 5.21, 7.62, 7.66, 8.05 (EtSi), 125.97, 127.44, 127.55, 127.64, 127.98, 132.74, 132.87, 141.98, 144.74, 147.04 (phenyl and phenylene ring carbons), 159.26 (PhC=C), 176.77 (Me$_3$SiC=C); $^{29}$Si NMR $\delta$(CDCl$_3$) −18.17, −12.24, −9.17. Anal. Calcd for $C_{25}H_{38}Si_3$: C, 71.01; H, 9.06. Found: C, 71.00; H, 9.04.

**Reaction of 1 with 3-Hexyne.** A mixture of 0.1961 g (0.789 mmol) of 1, 0.1060 g (1.29 mmol) of 3-hexyne, and 30 mg ($3.96 \times 10^{-2}$ mmol) of the platinum catalyst in 10 mL of dry benzene was heated to reflux for 1 h. GLC analysis of the reaction mixture showed the presence of 17 (98% yield). Product 17 was isolated by MPLC: MS *m/z* 330 (M$^+$); IR 3055, 2956, 2877, 1458, 1413, 1377, 1230, 1123, 1002, 963, 725, 672, 512 cm$^{-1}$; $^1$H NMR $\delta$(CDCl$_3$) 0.79 (br s, 20H, EtSi), 1.08 (t, 6H, $CH_3CH_2$–, $J$ = 7.6 Hz), 2.37 (q, 4H, –$CH_2CH_3$, $J$ = 7.6 Hz), 7.24–7.51 (m, 4H, phenylene ring protons); $^{13}$C NMR $\delta$(CDCl$_3$) 6.11, 7.80 (EtSi), 14.85 ($CH_3CH_2$–), 24.08 (–$CH_2CH_3$), 127.67, 132.79, 143.58 (phenylene ring carbons), 153.73 (olefinic carbon); $^{29}$Si NMR $\delta$(CDCl$_3$) −13.28. Anal. Calcd for $C_{20}H_{34}Si_2$: C, 72.65; H, 10.36. Found: C, 72.63; H, 10.29.

**Reaction of 1 with Benzaldehyde.** A solution of 0.2281 g (0.918 mmol) of 1, 0.1261 g (1.19 mmol) of benzaldehyde, and 34 mg ($4.58 \times 10^{-2}$ mmol) of the platinum catalyst in 10 mL of dry benzene was heated to reflux for 12 h. The reaction mixture was analyzed by GLC as being 18 (73% yield), 2 (3% yield), and 8% of the starting compound 1. All spectral data for product 18 were identical with those of an authentic sample.

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