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# Palladium- and platinum-catalyzed reactions of benzo[1,2:4,5]bis(1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene) with alkenes

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Received 24 February 1999; received in revised form 26 April 1999

## Abstract

The palladium-catalyzed reaction of benzo[1,2:4,5]bis(1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene) (**1**) with styrene in refluxing benzene afforded two regioisomers of 1:2 adducts, benzo[1,2](1,1,4,4-tetraethyl-2-phenyl-1,4-disilacyclohex-4-ene)[4,5](1,1,4,4-tetraethyl-3-phenyl-1,4-disilacyclohex-4-ene) and benzo[1,2:4,5]bis(1,1,4,4-tetraethyl-2-phenyl-1,4-disilacyclohex-4-ene), whose isomers consist of *cis* and *trans* in a ratio of 1:1 in 91% combined yield. Similar reaction of **1** with 1-hexene gave two regioisomers involving *cis* and *trans* isomers in 89% combined yield. With ethylene, **1** produced benzo[1,2:4,5]bis(1,1,4,4-tetraethyl-1,4-disilacyclohex-5-ene) (**8**) in 70% yield, together with a 15% yield of a 2:3 adduct. The platinum-catalyzed reaction of **1** with styrene gave a 1:1 mixture of *cis*- and *trans*-benzo[1,2:4,5]bis(2-benzyl-1,1,3,3-tetraethyl-1,3-disilacyclopent-4-ene) in 90% yield. Similar treatment of **1** with 1-hexene produced *cis*- and *trans*-benzo[1,2:4,5]bis(1,1,3,3-tetraethyl-2-pentyl-1,3-disilacyclopent-4-ene) in a ratio of 1:1 in 92% yield, while with ethylene, **1** afforded **8** as a main product, in addition to two types of 1:2 adduct as minor products. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Benzobis(disilacyclobutene); Catalyzed reaction; Palladium; Platinum

## 1. Introduction

3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene shows unique chemical behavior [1]. The thermolysis of this compound produces an *o*-quinodisilane [2], while its photolysis proceeds to give 1-ethyl-1-(2-diethylsilylphenyl)-1-silaprop-1-ene, as a reactive species [3]. The benzodisilacyclobutene readily reacts with organic molecules such as aromatic compounds, carbonyl compounds, alkenes, and alkynes in the presence of a catalytic amount of the transition-metal complexes to give various types of products [1,4,5]. The palladium- and platinum-catalyzed reactions of the benzodisilacyclobutene with diphenylacetylene and 3-hexyne afford the respective adducts arising from insertion of a triple

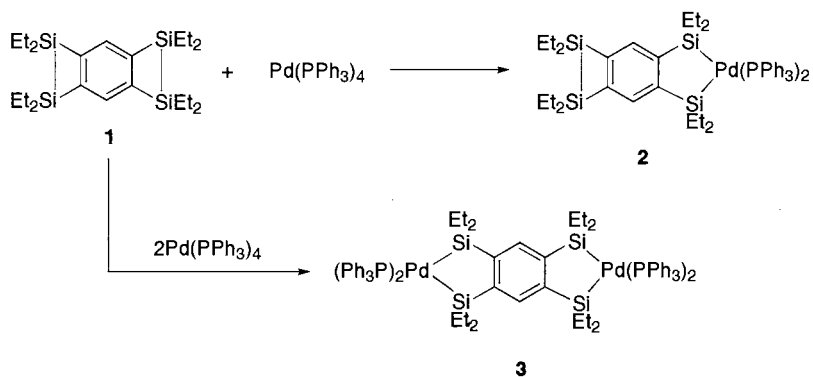
bond into a silicon–silicon bond in the benzodisilacyclobutene [6,7].

The palladium-catalyzed reactions of the benzodisilacyclobutene with styrene and 1-hexene produce the corresponding adducts formed from insertion of a carbon–carbon double bond into a silicon–silicon bond in the starting compound [8]. The platinum-catalyzed reactions with olefins, however, proceed in a different fashion from that of the palladium-catalyzed reactions. They afford the reactive products derived from terminal sp<sup>2</sup> C–H bond activation of olefins [9].

Recently, we synthesized benzo[1,2:4,5]bis(1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene) (**1**) and found that this compound readily reacts with alkynes in the presence of a catalytic amount of a palladium(0) or platinum(0) catalyst to give the respective 1:2 adducts arising from insertion of a triple bond into silicon–silicon bonds in the starting benzobis(disilacyclobutene) **1** in high yields [10].

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Scheme 1.

In order to learn more about the chemical behavior of the benzobis(disilacyclobutene) [11,12], we have investigated the palladium- and platinum-catalyzed reactions of **1** with alkenes.

## 2. Results and discussion

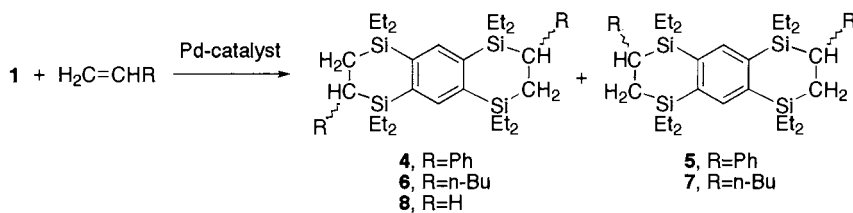
First, we examined the stoichiometric reaction of benzobis(disilacyclobutene) **1** with a palladium(0) complex, and a mono- and dipalladium insertion product could be prepared in a sealed NMR tube. Thus, the reaction of **1** with one equivalent of tetrakis(triphenylphosphine)palladium(0) at room temperature in deuteriobenzene in a sealed NMR tube gave a palladium insertion product (**2**), formed from insertion of a palladium species into one silicon–silicon bond in the starting compound **1**, as the sole product (Scheme 1). In this reaction, no product arose from insertion of two palladium species into both silicon–silicon bonds in **1**. As expected, the  $^{29}\text{Si}$ -NMR spectrum of the reaction mixture showed two resonances at 6.70 and 44.86 ppm, due to the silicon atoms in the disilacyclobutene ring and the silicon atoms in the palladadisilacyclopentene ring, respectively. Its  $^{13}\text{C}$ -NMR spectrum indicated four signals at 6.29, 9.34, 11.22 and 12.87 ppm, attributed to two different kinds of ethyl carbons, and three signals at 135.90, 153.56 and 157.53 ppm, due to phenylene ring carbons, as well as four signals at 128.44, 129.13, 134.44 and 137.14 ppm, which are attributable to phenyl ring carbons. Addition of styrene to the deuteriobenzene solution of **2** gave two isomers of 1:2 adducts whose  $^{29}\text{Si}$ -NMR spectrum revealed eight signals which are identical to the chemical shifts of adducts **4** and **5** (see below). Similar reaction of **1** with two equivalents of tetrakis(triphenylphosphine)palladium(0) afforded a dipalladium complex (**3**) whose NMR spectra are consistent with the proposed structure. Thus, the  $^{29}\text{Si}$ -NMR spectrum revealed a single resonance at 43.86 ppm, attributed to four equivalent ring silicon atoms.

The  $^{13}\text{C}$ -NMR spectrum displayed two resonances at 11.29 and 13.10 ppm, two resonances at 135.45 and 154.71 ppm, and four resonances at 128.37, 128.85, 134.38 and 137.97 ppm, due to ethyl carbons, phenylene ring carbons, and phenyl ring carbons, respectively.

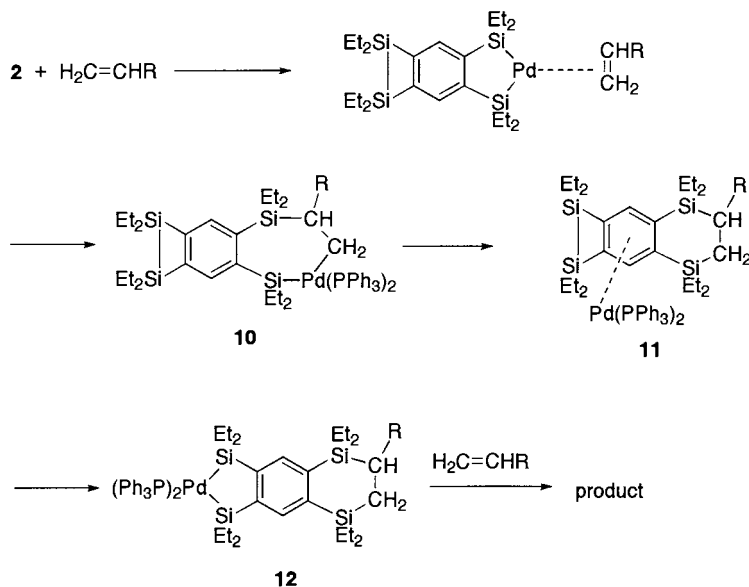
Next we carried out the palladium- and platinum-catalyzed reactions of **1** with terminal olefins. Thus, treatment of **1** with 3.8 equivalents of styrene in the presence of 5 mol% of tetrakis(triphenylphosphine)palladium(0) in benzene afforded 1:2 adducts consisting of two regioisomers in a ratio of 1:1, in which each regioisomer involves geometric isomers, *cis* and *trans* isomers in a ratio of approximately 1:1, in 91% combined yield. GLC analysis of the reaction mixture showed a homogeneous peak. All attempts to separate regioisomers or geometric isomers were unsuccessful. In all cases, the mixture consisting of the same ratio of isomers was obtained. However, the structures of the isomers were identified as two pairs of *cis* and *trans* isomers of benzo[1,2](1,1,4,4-tetraethyl-2-phenyl-1,4-disilacyclohex-4-ene)[4,5](1,1,4,4-tetraethyl-3-phenyl-1,4-disilacyclohex-4-ene) (**4**) and benzo[1,2,4,5]bis(1,1,4,4-tetraethyl-2-phenyl-1,4-disilacyclohex-4-ene) (**5**) (Scheme 2).

The  $^1\text{H}$ -NMR spectrum for the mixture of **4** and **5** revealed a single resonance at 7.66 ppm due to the phenylene ring proton of regioisomer **4**, and two resonances at 7.62 and 7.69 ppm attributed to the phenylene ring protons of regioisomer **5** with an integral ratio of 2:1:1. The  $^{29}\text{Si}$ -NMR spectrum for this mixture showed eight resonances indicating that each regioisomer consists of *cis* and *trans* isomers.

Similar palladium-catalyzed reaction of **1** with 1-hexene in refluxing benzene again gave two regioisomers **6** and **7** in the ratio of 1:1 in 89% combined yields. Again, each regioisomer was shown to be a mixture consisting of *cis* and *trans* in the ratio of 1:1 by NMR spectrometric analysis. Unfortunately, all attempts to isolate each regioisomer from the mixture using recycling gel permeation chromatography (GPC) were unsuccessful.



Scheme 2.



Scheme 3.

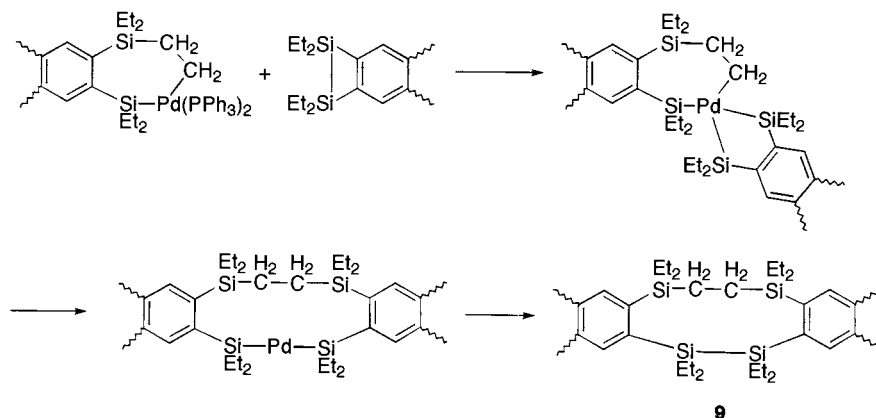
The reaction of **1** with ethylene in the presence of the palladium catalyst proceeded in a different fashion from the reactions with styrene and 1-hexene. When ethylene gas was introduced into a benzene solution of **1** at room temperature, benzo[1,2:4,5]bis(1,1,4,4-tetraethyl-1,4-disilacyclohex-5-ene) (**8**) was obtained in 78% yield, in addition to a 15% yield of a 2:3 adduct, 2{bis(1,1,4,4-tetraethyl-2H,3H-1,4-disila[3,4:9,10]naphtho}-1,1,2,2,5,5,8,8-octaethyl-1,2,5,8-tetrasilacyclodeca-3,9-diene (**9**). Products **8** and **9** were readily isolated by recycling GPC and their structures were confirmed by spectrometric analysis, as well as by elemental analysis (see Section 3).

We recently reported that the palladium- and platinum-catalyzed reactions of **1** with alkynes afforded no 1:1 adduct, even in the early stages of the reaction [10]. Likewise, no 1:1 adduct was detected in the present reactions, but in all cases the 1:2 adducts were obtained. As can be seen in the stoichiometric reaction of **1** with tetrakis(triphenylphosphine)palladium, mono-palladium complex **2** can be produced. Therefore, in the catalytic reaction, presumably a complex **2** is initially produced as a key intermediate. Olefin coordinates to this palladium atom in complex **2**, and then inserts into

a palladium–silicon bond to give complex **10**. Since 1:1 adducts could not be detected in the present reactions, reductive elimination to produce free palladium species from complex **10** would not be involved. The palladium species that was eliminated from **10** presumably interacts with the 1:1 adduct thus formed, giving a complex such as **11**, and would insert into a silicon–silicon bond in this species to give complex **12**. Finally the reaction of complex **12** with olefins affords the 1:2 adduct as shown in Scheme 3.

The formation of the 1,2,5,8-tetrasilacyclodeca-3,9-diene ring in **9** may be understood in terms of the reaction of a 3,4-benzo-2,5-disila-1-palladacyclohept-3-ene intermediate with a benzodisilacyclobutene derivative as shown in Scheme 4. Indeed, we have found that such a type of compound was formed in the reaction of the palladium-catalyzed reaction of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene with ethylene [8].

The platinum-catalyzed reaction of **1** with olefins proceeded to give different types of products from those of the palladium-catalyzed reactions. Treatment of **1** with styrene in the presence of a catalytic amount of ( $\eta^2$ -ethylene)bis(triphenylphosphine)platinum(0) in refluxing benzene gave a 1:1 mixture of *cis*- and *trans*-benzo[1,2:4,5]bis(2-benzyl-1,1,3,3-tetraethyl-1,3-disila-



Scheme 4.

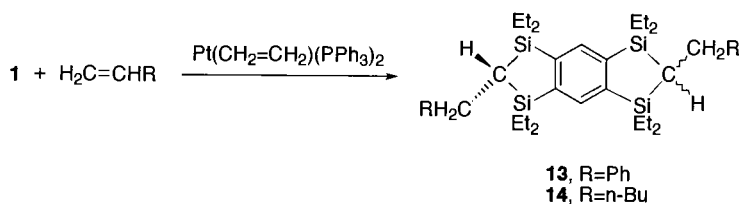
cyclopent-4-ene) (**13**) in 90% yield (Scheme 5). GLC analysis of the reaction mixture revealed a homogenous peak, and recycling GPC showed no separate peak. Although the *cis* and *trans* isomers could not be separated, the structures of the isomers were verified by spectrometric analysis. The  $^{13}\text{C}$ -NMR spectrum for the mixture showed two signals at 9.00 and 9.04 ppm due to two kinds of carbon atoms in the disilacyclopent-4-ene rings of the *cis* and *trans* isomers.

Treatment of **1** with 1-hexene in the presence of the platinum catalyst under the same conditions produced *cis*- and *trans*-benzo[1,2:4,5]bis(1,1,3,3-tetraethyl-2-pentyl-1,3-disilacyclopent-4-ene) (**14**) in a ratio of 1:1 in 92% combined yield. Again, the two isomers could not be separated by recycling GPC. The  $^{29}\text{Si}$ -NMR spectrum of the mixture showed two resonances at 12.39 and 12.42 ppm due to the silicon atoms of the *cis* and *trans*, respectively.

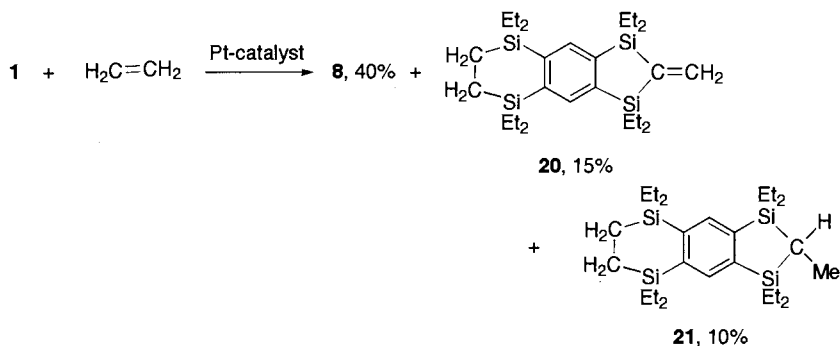
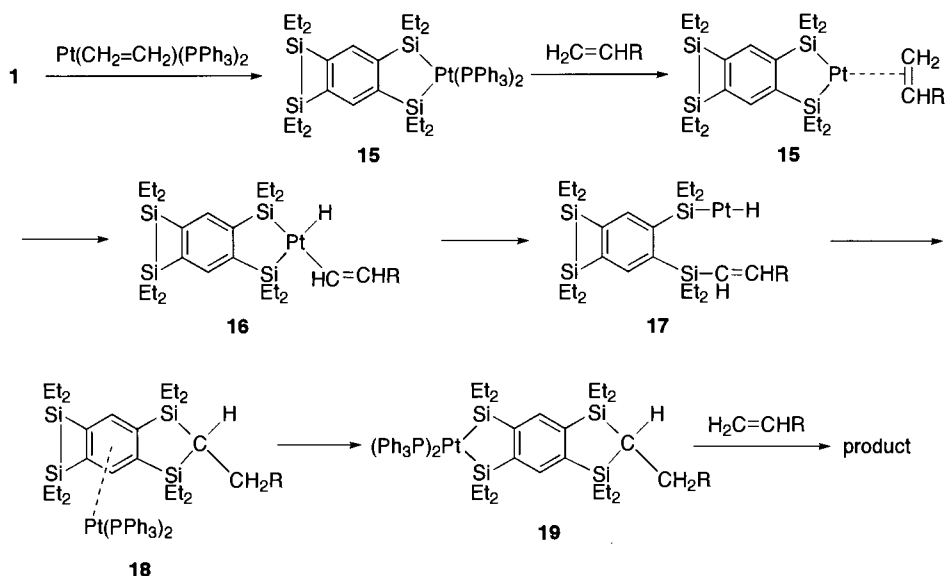
The formation of **13** and **14** may be best explained in terms of the terminal  $\text{sp}^2$  C–H bond activation as shown in Scheme 6. In the platinum-catalyzed reactions, platinum complex **15** would be produced as a reactive species in the initial step. The  $\text{sp}^2$  C–H bond of olefins probably adds to the platinum atom in complex **15**, to give complex **16**, which undergoes cleavage to give the ring opened product **17**. Intramolecular hydrosilylation of **17** would afford complex **18**. Since no 1:1 adduct can be detected in the reaction mixture, the platinum species which would be produced by reductive

elimination from the complex arising from addition of a Pt–H bond into the carbon–carbon double bond in complex **17** would interact with a 1:1 adduct like **18**. Insertion of the platinum species in **18** into a silicon–silicon bond gives complex **19** that reacts with olefins to give the product. It was previously reported that the platinum-catalyzed reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene with olefins produced the 3,4-benzo-1,1,3,3-tetraethyl-1,3-disilacyclopent-4-ene derivatives derived from  $\text{sp}^2$  C–H bond activation [9].

Ethylene also reacts with **1** in the presence of a platinum catalyst in refluxing benzene to give 1:2 adducts. However, the types of the products thus formed are different from those of the reaction with styrene and 1-hexene. Compound **8** and two types of compounds, **20** and **21**, which involve the silicon-containing five-membered and six-membered ring in the molecule, were obtained in 40, 15 and 10% yields, respectively (Scheme 7), in addition to small amounts of unidentified products (less than 3% each). Products **8**, **20** and **21** were isolated by recycling GPC. All spectral data for product **8** were identified with those of the authentic sample. The structures of products **20** and **21** were confirmed by mass and NMR spectrometric analysis as well as elemental analysis (see Section 3). The formation of the methylenedisilacyclopentene ring in product **20** can be understood by elimination of platinum dihydride species from the intermediate like **17** ( $\text{R} = \text{H}$ ),



Scheme 5.



while **21** can be explained by hydrosilylation of the similar intermediate.

In conclusion, the pattern of the present reaction was found to be similar to that of the palladium- and platinum-catalyzed reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene with olefins as previously reported. The palladium-catalyzed reaction of **1** with styrene and 1-hexene afforded 1:2 adducts arising from insertion of a carbon–carbon double bond into two silicon–silicon bonds in **1** in high yields. Similar reaction with ethylene gave benzo[1,2,4,5]bis(1,4-disilacyclohex-5-ene) as a main product in addition to a 2:3 adduct as a minor product. The platinum-catalyzed reactions of **1** with styrene and 1-hexene gave 1:2 adducts derived from the terminal  $sp^2$  C–H bond activation of olefins in excellent yields. With ethylene, **1** produced a 1:2 adduct formed from insertion of a carbon–carbon double bond into the silicon–silicon bonds in the starting compound **1**.

### 3. Experimental

#### 3.1. General procedure

All platinum- and palladium-catalyzed reactions of compound **1** with alkenes were carried out under a nitrogen atmosphere. Yields of the products with one exception, compound **9**, were determined by analytical GLC with the use of pentadecane as an internal standard on the basis of the starting compounds used. NMR spectra were recorded on a Jeol model JNM-LA300 spectrometer and JNM-LA500 spectrometer. Infrared spectra were recorded on a Jeol model JIR-Diamond20 IR spectrophotometer. Low-resolution mass spectra were measured on a Jeol model JMS-700 instrument. GPC separation was performed with a Model LC-908 Recycling Preparative HPLC (Japan Analytical Industry).

### 3.2. Stoichiometric reaction of **1** with tetrakis(triphenylphosphine)palladium(0)

A mixture of **1** (0.0367 g, 0.0876 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.0974 g, 0.0843 mmol) was placed in an NMR tube with a rubber septum cap. The tube was allowed to stand at room temperature for 1 h to give **2**.  $^1\text{H-NMR}$ :  $\delta(\text{CDCl}_3)$  0.50–1.31 (m, 40H, EtSi), 7.00–7.80 (m, 62H, phenyl and phenylene ring protons).  $^{13}\text{C-NMR}$ :  $\delta(\text{CDCl}_3)$  6.29, 9.34, 11.22, 12.87 (EtSi), 135.90, 153.56, 157.53 (phenylene ring carbons), 128.44 ( $^3J_{\text{C-P}} = 7.4$  Hz), 129.13, 134.44 ( $^2J_{\text{C-P}} = 17.1$  Hz), 137.14 ( $^1J_{\text{C-P}} = 5.0$  Hz) (phenyl ring carbons).  $^{29}\text{Si-NMR}$ :  $\delta(\text{CDCl}_3)$  6.70, 44.86.

### 3.3. Reaction of **1** with two equivalents of tetrakis(triphenylphosphine)palladium(0)

A mixture of **1** (0.0095 g, 0.0267 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.0702 g, 0.0607 mmol) was placed in an NMR tube with a rubber septum cap. The tube was allowed to stand at room temperature for 1 h to give **3**.  $^1\text{H-NMR}$ :  $\delta(\text{CDCl}_3)$  0.53–1.27 (m, 40H, EtSi), 6.96–7.88 (m, 122H, phenyl and phenylene ring protons).  $^{13}\text{C-NMR}$ :  $\delta(\text{CDCl}_3)$  11.29, 13.10 (EtSi), 135.45, 154.71 (phenylene ring carbons), 128.37 ( $^3J_{\text{C-P}} = 8.3$  Hz), 128.85, 134.38 ( $^2J_{\text{C-P}} = 17.6$  Hz), 137.97 ( $^1J_{\text{C-P}} = 7.2$  Hz) (phenyl ring carbons).  $^{29}\text{Si-NMR}$   $\delta(\text{CDCl}_3)$  43.86.

### 3.4. Reaction of **1** with styrene in the presence of a Pd complex

A mixture of 0.0721 g (0.172 mmol) of **1**, 0.0680 g (0.653 mmol) of styrene, and 0.0101 g (0.00874 mmol) of tetrakis(triphenylphosphine)palladium(0) in 3 ml of dry benzene was placed in a 30-ml two-necked flask fitted with a stirrer and reflux condenser. The mixture was stirred at room temperature for 2 h and passed through a short silica gel column. The mixture was analyzed by GLC as being **4** and **5** (91% combined yield). A mixture of **4** and **5** was isolated by column chromatography. The ratio of the isomers was calculated to be approximately 1:1 by  $^1\text{H-NMR}$  spectrometric analysis. MS:  $m/z$  626 ( $\text{M}^+$ ). IR: 3012, 2950, 2871, 1596, 1492, 1457, 1413, 1234, 1149, 1016, 956, 769, 744, 698  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$ :  $\delta(\text{CDCl}_3)$  0.52–1.05 (m, 160H, EtSi), 1.29 (brs, 8H, CH), 1.61 (t, 8H, CHPh,  $J = 15$  Hz), 2.76 (d, 8H, CH,  $J = 15$  Hz), 7.14–7.33 (m, 40H, phenyl ring protons), 7.62 (s, 2H, phenylene ring protons for **5**), 7.66 (s, 4H, phenylene ring protons for **4**), 7.69 (s, 2H, phenylene ring protons for **5**).  $^{13}\text{C-NMR}$ :  $\delta(\text{CDCl}_3)$  2.39, 2.43 (2C), 2.47, 2.82, 2.87 (2C), 2.90, 4.92 (2C), 4.99 (2C), 5.77 (2C), 5.80 (2C), 7.31 (2C), 7.34, 7.36, 7.49 (2C), 7.53 (2C), 7.57 (2C), 7.60, 7.63, 7.81, 7.83 (2C), 7.86 (EtSi), 11.65 (4C) ( $\text{CH}_2$ ), 26.30, 26.34, 26.43 (2C) (CH), 124.41 (4C), 126.98 (4C), 128.11

(4C), 146.96 (4C) (phenyl ring carbons), 139.37 (2C), 139.75 (2C), 140.12 (2C), 141.60 (2C), 141.74 (2C), 142.52 (2C), 142.69 (2C) (phenylene ring carbons).  $^{29}\text{Si-NMR}$ :  $\delta(\text{CDCl}_3)$  –1.80, –1.78, –1.71 (2Si), –1.68, –1.65, –1.62 (2Si). Anal. Calc. for  $\text{C}_{38}\text{H}_{58}\text{Si}_4$ : C, 72.77; H, 9.32. Found: C, 72.56; H, 9.29.

### 3.5. Reaction of **2** with styrene

A mixture of **1** (0.0325 g, 0.0776 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.0897 g, 0.0776 mmol) was placed in an NMR tube with a rubber septum cap. The tube was allowed to stand at room temperature (r.t.) for 1 h. The  $^{13}\text{C}$ - and  $^{29}\text{Si-NMR}$  spectra revealed the presence of **2** as the sole product. Styrene (0.0201 g, 0.193 mmol) was added and then the mixture was heated at 80°C for 20 min. The  $^{29}\text{Si-NMR}$  spectrum of this solution revealed eight resonances whose chemical shifts are identical with those of **4** and **5**.

### 3.6. Reaction of **1** with 1-hexene in the presence of a Pd complex

A mixture of 0.0808 g (0.193 mmol) of **1**, 0.0503 g (0.599 mmol) of 1-hexene, and 0.0118 g (0.0102 mmol) of tetrakis(triphenylphosphine)palladium(0) in 3 ml of dry benzene was placed in a 30-ml two-necked flask fitted with a stirrer and reflux condenser. The mixture was heated to reflux for 12 h and passed through a short silica gel column. The mixture was analyzed by GLC as being **6** and **7** (89% combined yield). A mixture of **6** and **7** was isolated by column chromatography. The ratio of the isomers was calculated to be approximately 1:1 by  $^1\text{H-NMR}$  spectrometric analysis. MS:  $m/z$  586 ( $\text{M}^+$ ). IR: 2954, 2910, 2873, 1457, 1413, 1376, 1232, 1149, 1093, 1014, 956, 788, 715, 609  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$ :  $\delta(\text{CDCl}_3)$  0.63–1.67 (m, 256H, EtSi,  $\text{CH}_2$ , CHSi,  $n$ -Bu), 7.55 (s, 2H, phenylene ring protons for **7**), 7.56 (s, 4H, phenylene ring protons for **6**), 7.58 (s, 2H, phenylene ring protons for **7**).  $^{13}\text{C-NMR}$ :  $\delta(\text{CDCl}_3)$  3.35 (2C), 3.38 (2C), 3.57 (2C), 3.59, 3.60, 5.20, 5.22, 5.27, 5.28, 6.05 (2C), 6.09 (2C), 7.46, 7.50 (2C), 7.51 (3C), 7.54 (2C), 7.78, 7.80, 7.82 (2C), 7.97, 8.00, 8.04 (2C) (EtSi), 10.45 (4C) ( $\text{CH}_2$ ), 16.64, 16.68, 16.72, 16.75 (CH), 14.16 (4C), 22.67 (4C), 30.25 (4C), 33.30 (4C) ( $n$ -Bu), 138.96 (2C), 139.19 (2C), 139.42 (2C), 142.09 (2C), 142.16 (2C), 142.64 (2C), 142.72 (2C) (phenylene ring carbons).  $^{29}\text{Si-NMR}$ :  $\delta(\text{CDCl}_3)$  –3.14 (2Si), –3.08 (2Si), –2.00 (2Si), –1.89 (2Si). Anal. Calc. for  $\text{C}_{34}\text{H}_{66}\text{Si}_4$ : C, 69.54; H, 11.33. Found: C, 69.54; H, 11.30.

### 3.7. Reaction of **1** with ethylene in the presence of a Pd complex

A mixture of 0.1539 g (0.367 mmol) of **1** and 0.0214 g (0.0185 mmol) of tetrakis(triphenylphosphine)palla-

dium(0) in 5 ml of dry benzene was placed in a 30-ml two-necked flask fitted with a inlet tube for ethylene gas and reflux condenser. The ethylene gas was introduced into the mixture at r.t. for 30 min. The solution was then passed through a short silica gel column and analyzed by GLC as being compound **8** (78%). Compounds **8** and **9** (isolated yield 15%) were isolated by recycling GPC. For **8**—MS:  $m/z$  474 ( $M^+$ ). IR: 2952, 2906, 2871, 1456, 1413, 1232, 1149, 1093, 1006, 956, 739, 711  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$ :  $\delta(\text{CDCl}_3)$  0.73 (q, 16H,  $\text{CH}_2\text{Si}$ ,  $J = 7.6$  Hz), 0.95 (t, 24H,  $\text{CH}_3$ ,  $J = 7.6$  Hz), 1.00 (s, 8H,  $\text{CH}_2$ ), 7.53 (s, 2H, phenylene ring protons).  $^{13}\text{C-NMR}$ :  $\delta(\text{CDCl}_3)$  3.47 ( $\text{CH}_2$ ), 5.18, 7.63 (EtSi), 139.14, 142.71 (phenylene ring carbons).  $^{29}\text{Si-NMR}$ :  $\delta(\text{CDCl}_3)$  -3.99. Anal. Calc. for  $\text{C}_{26}\text{H}_{50}\text{Si}_4$ : C, 65.74; H, 11.03. Found: C, 65.58; H, 10.94. For **9**—MS:  $m/z$  891 ( $M^+ - \text{Et}$ ). IR: 2954, 2906, 2871, 1456, 1415, 1234, 1160, 1130, 1085, 1051, 1002, 711  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$ :  $\delta(\text{CDCl}_3)$  0.66–1.01 (m, 92H, EtSi,  $\text{CH}_2$ ), 7.60 (s, 2H, phenylene ring protons), 7.77 (s, 2H, phenylene ring protons).  $^{13}\text{C-NMR}$ :  $\delta(\text{CDCl}_3)$  3.27, 3.60 ( $\text{CH}_2$ ), 5.13 (2C), 5.33, 6.36, 7.67, 7.75, 7.86, 8.21 (EtSi), 141.37, 141.85, 141.96, 142.09, 142.14, 142.17 (phenylene ring carbons).  $^{29}\text{Si-NMR}$ :  $\delta(\text{CDCl}_3)$  -12.39, -4.00, -3.69, 4.13. Anal. Calc. for  $\text{C}_{50}\text{H}_{96}\text{Si}_8$ : C, 65.14; H, 10.49. Found: C, 65.17; H, 10.73.

### 3.8. Reaction of **1** with styrene in the presence of a Pt complex

A mixture of 0.1197 g (0.286 mmol) of **1**, 0.1005 g (0.966 mmol) of styrene, and 0.0103 g (0.0138 mmol) of  $(\eta^2\text{-ethylene})\text{bis}(\text{triphenylphosphine})\text{platinum}(0)$  in 3 ml of dry benzene was placed in a 30-ml two-necked flask fitted with a stirrer and reflux condenser. The mixture was heated to reflux for 30 min, and then passed through a short silica gel column to remove the platinum species. Compound **13** was isolated by silica gel column chromatography (90% yield). M.p. 176–178°C. MS:  $m/z$  626 ( $M^+$ ). IR: 3021, 2950, 2869, 1600, 1492, 1454, 1411, 1234, 1112, 958, 767, 744, 696  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$ :  $\delta(\text{CDCl}_3)$  0.46–0.89 (m, 84H, EtSi, CH), 2.84 (d, 8H,  $\text{CH}_2\text{Ph}$ ,  $J = 8.2$  Hz), 7.06–7.22 (m, 20H, phenyl ring protons), 7.55 (s, 4H, phenylene ring protons).  $^{13}\text{C-NMR}$ :  $\delta(\text{CDCl}_3)$  5.25 (2C), 5.41, 5.45, 7.37 (2C), 7.69 (2C) (EtSi), 9.00, 9.04 (CH), 31.03 (2C) ( $\text{CH}_2$ ), 125.68, 128.13, 128.23, 137.48, 145.09, 147.33 (phenyl and phenylene ring carbons).  $^{29}\text{Si-NMR}$ :  $\delta(\text{CDCl}_3)$  12.30. Anal. Calc. for  $\text{C}_{38}\text{H}_{58}\text{Si}_4$ : C, 72.77; H, 9.32. Found: C, 72.50; H, 9.45.

### 3.9. Reaction of **1** with 1-hexene in the presence of a Pt complex

A mixture of 0.1752 g (0.419 mmol) of **1**, 0.1201 g (1.43 mmol) of 1-hexene, and 0.0143 g (0.0191 mmol)

of  $(\eta^2\text{-ethylene})\text{bis}(\text{triphenylphosphine})\text{platinum}(0)$  in 3 ml of dry benzene was placed in a 30-ml two-necked flask fitted with a stirrer and reflux condenser. The mixture was heated to reflux for 30 min, and then passed through a short silica gel column to remove the platinum species. Compound **14** was isolated by silica gel column chromatography (92% yield). M.p. 62–64°C. MS:  $m/z$  586 ( $M^+$ ). IR: 2954, 2871, 1457, 1413, 1376, 1232, 1114, 1016, 960, 775, 754, 707, 615  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$ :  $\delta(\text{CDCl}_3)$  0.456 (t, 2H,  $\text{CHSi}$ ,  $J = 7.6$  Hz), 0.459 (t, 2H,  $\text{CHSi}$ ,  $J = 7.6$  Hz), 0.61–1.01 (m, 80H, EtSi), 1.29–1.38 (m, 28H,  $\text{CH}_2$ ,  $\text{CH}_3$ ), 1.45 (quint, 8H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ,  $J = 7.6$  Hz), 1.63 (q, 8H,  $\text{CHCH}_2\text{CH}_2$ ,  $J = 7.6$  Hz), 7.69 (s, 4H, phenylene ring protons).  $^{13}\text{C-NMR}$ :  $\delta(\text{CDCl}_3)$  5.05 (2C), 6.01, 6.04, 6.84 (2C), 7.68 (2C), 7.73, 7.75 (EtSi), 14.17 (2C) ( $\text{CH}_3$ ), 22.64 (2C), 25.35 (2C), 32.15 (2C), 34.38 (2C) ( $\text{CH}_2$ ), 137.31 (2C), 147.65 (2C) (phenylene ring carbons).  $^{29}\text{Si-NMR}$ :  $\delta(\text{CDCl}_3)$  12.39, 12.42. Anal. Calc. for  $\text{C}_{34}\text{H}_{66}\text{Si}_4$ : C, 69.54; H, 11.33. Found: C, 69.68; H, 11.45.

### 3.10. Reaction of **1** with ethylene in the presence of a Pt complex

A mixture of 0.3570 g (0.852 mmol) of **1** and 0.0215 g (0.00288 mmol) of  $(\eta^2\text{-ethylene})\text{bis}(\text{triphenylphosphine})\text{platinum}(0)$  in 5 ml of dry benzene was placed in a 30-ml two-necked flask fitted with a inlet tube for ethylene gas and reflux condenser. The ethylene gas was introduced into the mixture at 80°C for 30 min. The solution was then passed through a short silica gel column and analyzed by GLC as being compound **9** (40%), **20** (15%) and **21** (10%). Compound **9**, **20** and **21** were isolated by recycling GPC. All spectral data for **9** were identical with those of an authentic sample. For **20**—MS:  $m/z$  472 ( $M^+$ ). IR: 2954, 2871, 1596, 1456, 1415, 1376, 1232, 1132, 1016, 960, 786, 719  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$ :  $\delta(\text{CDCl}_3)$  0.66–1.00 (m, 44H, EtSi,  $\text{CH}_2$ ), 6.60 (s, 2H, olefinic protons), 7.65 (s, 2H, phenylene ring protons).  $^{13}\text{C-NMR}$ :  $\delta(\text{CDCl}_3)$  3.47 ( $\text{CH}_2$ ), 5.23, 5.86, 7.62 (2C) (EtSi), 138.43, 141.10, 143.31, 143.61, 146.74 (phenylene ring and olefinic carbons).  $^{29}\text{Si-NMR}$ :  $\delta(\text{CDCl}_3)$  -3.68, 0.15. Anal. Calc. for  $\text{C}_{26}\text{H}_{48}\text{Si}_4$ : C, 66.02; H, 10.23. Found: C, 65.97; H, 10.17. For **21**—MS:  $m/z$  474 ( $M^+$ ). IR: 2954, 2912, 2877, 1457, 1415, 1376, 1232, 1132, 1091, 1016, 958, 784, 715  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$ :  $\delta(\text{CDCl}_3)$  0.36 (q, 1H, HC,  $J = 7.6$  Hz), 0.58–1.02 (m, 44H, EtSi,  $\text{CH}_2$ ), 0.18 (d, 3H, Me,  $J = 7.6$  Hz), 7.61 (s, 2H, phenylene ring protons).  $^{13}\text{C-NMR}$ :  $\delta(\text{CDCl}_3)$  -1.67 (CH), 4.25, 5.24, 5.56, 7.62 (EtSi), 8.68 (Me), 138.35, 147.18, 149.22 (phenylene ring and olefinic carbons).  $^{29}\text{Si-NMR}$ :  $\delta(\text{CDCl}_3)$  -3.68, 13.41. Anal. Calc. for  $\text{C}_{26}\text{H}_{50}\text{Si}_4$ : C, 65.74; H, 11.03. Found: C, 65.87; H, 11.17.

## Acknowledgements

This work was partially supported by Grant-in-Aid for Scientific Research on Priority Areas (No. 10133257) from the Ministry of Education, Science, Sports and Culture of Japan and by the fund of Research for the Future Program (JSPS-PFTF96P00206), to which our thanks are due. We also express our appreciation to Toshiba Silicone, Sumitomo Electric Industry, and Tokuyama for financial support.

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