

Platinum-catalyzed reactions of 3,4-benzo-1,1,2,2-tetra(isopropyl)-1,2-disilacyclobut-3-ene with mono- and di-substituted alkynes

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Received 4 January 1997

Abstract

The reactions of 3,4-benzo-1,1,2,2-tetra(isopropyl)-1,2-disilacyclobut-3-ene (**1**) with phenylacetylene and 1-hexyne in the presence of a catalytic amount of (η^2 -ethylene)bis(triphenylphosphine)platinum(0) at 200°C for 24 h gave two types of 1:1 adducts, 2-phenyl- and 2-butyl-substituted 5,6-benzo-1,1,4,4-tetra(isopropyl)-1,4-disilacyclohexa-2,5-diene and 2-benzylidene- and 2-pentylidene-substituted 4,5-benzo-1,1,3,3-tetra(isopropyl)-1,3-disilacyclopent-4-ene, respectively. With mesityl- and dimethylphenylsilylacetylene, **1** afforded 2-(mesityl)methylene- and 2-(dimethylphenylsilyl)methylene-4,5-benzo-1,1,3,3-tetra(isopropyl)-1,3-disilacyclopent-4-ene. A similar reaction of **1** with trimethylsilylacetylene produced an adduct arising from sp-hybridized C–H bond activation of the acetylene, together with a benzodisilacyclopentene derivative. The reaction of **1** with diphenylacetylene yielded a 2,3-diphenyl-5,6-benzodisilacyclohexa-2,5-diene derivative, while with methylphenylacetylene and 2-hexyne, **1** gave 2-benzylidene- and 2-butylidene-5,6-benzo-1,4-disilacyclohex-5-ene, along with the benzodisilacyclohexa-2,5-diene derivatives. Similar treatment of **1** with methyl(trimethylsilyl)acetylene produced a 5,6-benzo-2-(trimethylsilyl)methylenedisilacyclohexene derivative. © 1997 Elsevier Science S.A.

1. Introduction

Recently, we have demonstrated that the transition-metal-catalyzed reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene with aromatic compounds, carbonyl compounds, alkenes, and alkynes afford various types of products [1–8]. The types of the products thus formed depend highly on the nature of the metal in the reactive species formed from the reaction of the benzodisilacyclobutene with transition-metal complexes used as the catalyst. We have also found that 3,4-benzo-1,1,2,2-tetra(isopropyl)-1,2-disilacyclobut-3-ene (**1**) bearing bulky substituents on the silicon atoms reacts with mono-substituted alkynes in the presence of the palladium catalyst to give adducts [9]. The palladium-catalyzed reactions of **1** with mono-substituted alkynes bearing a less bulky substituent produced 5,6-benzo-1,4-disilacyclohexa-2,5-dienes arising from formal insertion of a carbon = carbon triple bond into the silicon–silicon bond in **1**, while with alkynes having a

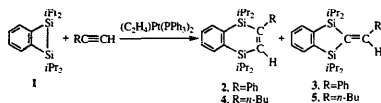
bulky substituent, **1** gave 1-[alkynylid(isopropyl)silyl]-2-[di(isopropyl)silyl]benzenes derived from sp-hybridized C–H bond activation of alkynes. Similar reaction of **1** with di-substituted alkynes such as diphenyl acetylene, 3-hexyne, phenyl(trimethylsilyl)acetylene, and bis(trimethylsilyl)acetylene afforded no adducts, but the starting benzodisilacyclobutene **1** was recovered unchanged. With methylphenylacetylene, however, **1** produced an adduct arising from insertion of a triple bond into a silicon–silicon bond in **1** in moderate yield.

It is of interest to us to learn the similarity and dissimilarity between the palladium- and other transition-metal-catalyzed reactions of **1**. In this paper we report the platinum-catalyzed reactions of **1** with mono- and di-substituted alkynes.

2. Results and discussion

In contrast to the palladium-catalyzed reactions of 3,4-benzo-1,1,2,2-tetra(isopropyl)-1,2-disilacyclobut-3-ene **1** with phenylacetylene and 1-hexyne, in which

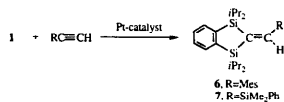
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Scheme 1.

benzodisilacyclohexadienes are produced as the sole product, the platinum-catalyzed reactions of **1** with the same acetylenes afford two products. Thus, when **1** was treated with phenylacetylene in the presence of a (η^2 -ethylene)bis(triphenylphosphine)platinum(0) catalyst in a degassed sealed glass tube at 200°C for 24 h, 5,6-benzo-1,1,4,4-tetra(isopropyl)-2-phenyl-1,4-disilacyclohexa-2,5-diene (**2**) and 4,5-benzo-1,1,3,3-tetra(isopropyl)-2-benzylidene-1,3-disilacyclopent-4-ene (**3**) were obtained in 18% and 14% yields, respectively, along with 55% of the unreacted compound **1**. No other volatile products were detected by GLC analysis of the reaction mixture, but a small amount of nonvolatile products whose molecular weight was determined to be 900, relative to polystyrene standards was produced. The similar platinum-catalyzed reaction of **1** with 1-hexyne afforded 5,6-benzo-1,1,4,4-tetra(isopropyl)-2-butyl-1,4-disilacyclohexa-2,5-diene (**4**) and 4,5-benzo-1,1,3,3-tetra(isopropyl)-2-butylidene-1,3-disilacyclopent-4-ene (**5**) in 8% and 28% yields, respectively, in addition to 54% of the starting compound **1**. The structures of **2–5** (Scheme 1) were verified by spectrometric analysis, as well as by elemental analysis.

The reactions of **1** with mono-substituted alkynes that have a bulky substituent such as a mesityl and dimethylphenylsilyl group gave only one product. With mesitylacetylene in the presence of the platinum catalyst under the same conditions, **1** gave 4,5-benzo-1,1,3,3-tetra(isopropyl)-2-(mesityl)methylene-1,3-disilacyclopent-4-ene (**6**) in 20% yield, as the sole product, along with 79% of the starting benzodisilacyclobutene **1**. The ^{29}Si NMR spectrum of **6** shows two resonances at 1.4 and 3.7 ppm, attributed to two nonequivalent silicon atoms. As reported previously, chemical shifts at 1.4 and 3.7 ppm clearly shows that **6** must have a benzodisilacyclopentene structure [7]. Dimethylphenylsilylacetylene also reacted with **1** to afford an adduct, 4,5-benzo-1,1,3,3-tetra(isopropyl)-2-(dimethylphenylsilyl)methylene-1,3-disilacyclopent-4-ene (**7**) in 28% yield, together with 56% of the starting compound **1** (Scheme 2). In



Scheme 2.

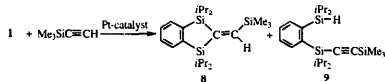
both reactions, no other volatile products were detected by GLC analysis.

Similar treatment of **1** with trimethylsilylacetylene, however, afforded two isomers of the adducts, 4,5-benzo-1,1,3,3-tetra(isopropyl)-2-(trimethylsilyl)methylene-1,3-disilacyclopent-4-ene (**8**) and 2-di(isopropyl)silyl-1-[diisopropyl(trimethylsilyl)ethynyl]silylbenzene (**9**), in 20% and 8% yields, respectively, along with 58% of the starting compound **1**. (See Scheme 3).

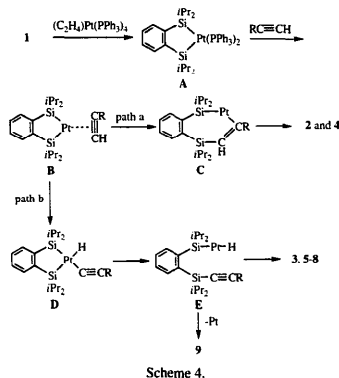
In order to confirm whether or not compound **8** was produced from compound **9** by intramolecular hydrosilylation, we carried out the reaction of **9** with a catalytic amount of the platinum complex. Thus, the reaction of **9** with a 5 mol% of (η^2 -ethylene)bis(triphenylphosphine)platinum(0) in a sealed glass tube at 200°C for 24 h produced compound **8** in 92% yield, indicating that compound **8** must come from intramolecular hydrosilylation of **9** [4].

We investigated the stoichiometric reaction of **1** with (η^2 -ethylene)bis(triphenylphosphine)platinum(0) in order to get more information concerning the reactive species in the present reaction. When compound **1** was added to a decahydronaphthalene solution containing one equivalent of the platinum complex at room temperature and the mixture was heated to reflux for 3 h, a color of the solution changed from initially light yellow to black at the end. However, the ^1H and ^{13}C NMR spectra of this solution showed only resonances attributed to the starting benzodisilacyclobutene **1**. Even though the solution was stirred for 72 h in refluxing decahydronaphthalene, no change was observed in its ^1H and ^{13}C NMR spectra. The ^{29}Si NMR spectrum of the solution reveals a single resonance whose chemical shift is identical with that of **1**. Unfortunately, all attempts to detect 3,4-benzo-1-platino-2,5-disilacyclopent-3-ene in the present system were unsuccessful. Probably the equilibrium in the reaction of **1** with the platinum complex lies far to the starting compound **1**.

Scheme 4 illustrates a possible mechanistic interpretation of the observed reaction course. Products **2** and **4** are probably produced from insertion of a triple bond of alkynes coordinated to the platinum atom in complex **B** into a silicon-platinum bond, giving 3,4-benzo-1-platino-2,5-disilacyclohepta-3,6-diene (**C**), followed by reductive elimination of platinum species from complex **C** (path a). As in the palladium-catalyzed reactions of **1** with mono-substituted acetylenes bearing a bulky substituent, the formation of **3** and **5–8** can be understood in terms of sp-hybridized C–H bond activation of the



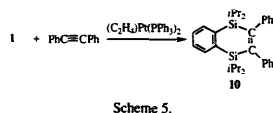
Scheme 3.



coordinated alkynes in complex B, leading to complex D, followed by a 1,2-shift of an alkynyl group to one of two silicon atoms to give complex E¹. In the palladium-catalyzed reaction, reductive elimination of palladium species from the complex analogous to E occurs to give products such as 9, while in the platinum-catalyzed reactions, intramolecular hydrosilylation takes place to afford products 3, 5–8. In the reactions of 1 with the alkynes bearing a bulky substituent, complex C would not be produced because of steric hindrance.

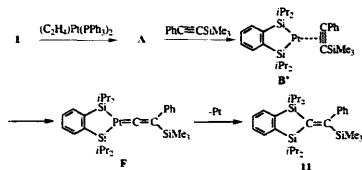
The palladium-catalyzed reactions of 1 with methylphenylacetylene gives a benzodisilacyclohexadiene arising from insertion of a triple bond of the acetylene into an Si–Si bond in 1 in moderate yield (see Section 3), while with diphenylacetylene, 3-hexyne, and phenyl(trimethylsilyl)acetylene afford no adducts, but the starting benzodisilacyclobutene 1 is recovered unchanged. In the presence of the platinum catalyst, however, compound 1 reacts with these acetylenes to give the corresponding adducts. Thus, the reaction of 1 with diphenylacetylene in the presence of the platinum catalyst in a degassed sealed tube at 200°C for 24 h gave a single product, 5,6-benzo-1,1,4,4-tetra(isopropyl)-2,3-diphenyl-1,4-disilacyclohexa-2,5-diene (10), in 44% yield, along with 44% of the starting compound 1 (Scheme 5).

Similar reaction of 1 with phenyl(trimethylsilyl)acetylene proceeded to give 4,5-benzo-1,1,3,3-tetra(isopropyl)-2-[phenyl(trimethylsilyl)methylene]-1,3-disilacyclopent-4-ene (11) in 12% yield as the sole volatile product, together with 51% of the starting com-

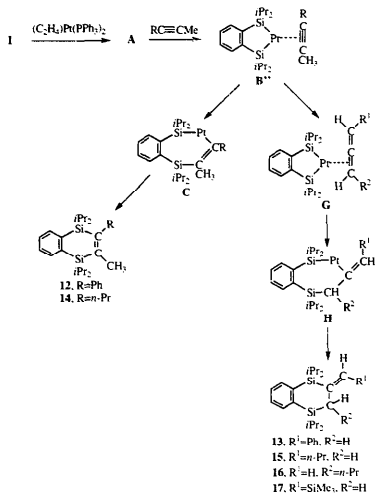


ound 1. Compound 11 could readily be isolated by MPLC. The ²⁹Si NMR spectrum of 11 reveals resonances at 1.8 and 3.9 ppm, attributed to silicon atoms in the 4,5-benzo-2-methylene-1,3-disilacyclopent-4-ene ring, as well as a resonance at –8.1 ppm due to trimethylsilyl silicon. The formation of 11 is quite interesting, because a 1,2-trimethylsilyl shift must be involved during the reaction. A similar trimethylsilyl shift has been observed in the nickel-catalyzed reaction of 1 with phenyl(trimethylsilyl)acetylene [7,12–14]. Probably the silyl shift occurs on the platinum atom in acetylene-coordinated 1-platina-2,5-disilacyclopentene B', giving the platinum–carbene complex F. The reductive elimination of platinum species from F would produce product 11 (Scheme 6).

With methylphenylacetylene under the same conditions, compound 1 reacted to give two adducts, 5,6-benzo-1,1,4,4-tetra(isopropyl)-3-methyl-2-phenyl-1,4-disilacyclohexa-2,5-diene (12) and (E)-5,6-benzo-1,1,4,4-tetra(isopropyl)-7-benzylidene-1,4-disilacyclohex-5-ene (13), in 34% and 18% yield, respectively, in addition to 18% of the starting compound 1. No other isomers for 13 were detected in the reaction mixture either by spectrometric analysis or GLC analysis. The geometry of an olefinic part in compound 13 was confirmed by NOE-FID difference experiments at 270 MHz. Thus, saturation of the ring methylene protons at 2.27 ppm produced a positive nuclear Overhauser effect of resonances at 7.29–7.60 ppm due to phenyl protons, but no enhancement was observed for a signal at 6.80 ppm attributed to the olefinic proton. As expected, irradiation of the olefinic proton at 6.80 ppm caused enhancement of the methine protons on the silicon atom at 1.13–1.45 ppm. These results indicate that the phenyl group must be located in a cis fashion to the methylene group. Product 12 is probably produced by the mechanism proposed for the formation of the benzodisilacyclohexa-



¹ For C–H bond activation by transition-metal catalysis, see Refs. [10,11].



Scheme 7.

diene mentioned above. The formation of product **13** may be best explained in terms of isomerization of complex **B*** to complex **G**, in which isomerization of methylphenylacetylene coordinated to the platinum atom in **B*** to phenylpropadiene, followed by insertion of a terminal carbon = carbon double bond into a platinum–silicon bond in complex **G** leading to complex **H** would be involved. Finally, reductive elimination of platinum species from **H** would afford **13**. In this reaction, no phenylpropadiene was detected in the reaction mixture by GLC analysis or spectrometric analysis Scheme 7.

The reaction of **1** with 2-hexyne under the same conditions afforded three products, 5,6-benzo-1,1,4,4-tetra(isopropyl)-3-methyl-2-*n*-propyl-1,4-disilacyclohexa-2,5-diene (**14**), (E)-5,6-benzo-1,1,4,4-tetra(isopropyl)-2-butyldiene-1,4-disilacyclohex-5-ene (**15**), and 5,6-benzo-1,1,4,4-tetra(isopropyl)-2-methylene-3-*n*-propyl-1,4-disilacyclohex-5-ene (**16**), in 5%, 31% and 7% yields, respectively, along with 33% of the starting compound **1**. The formation of **15** and **16** may be understood by a series of the reaction involving isomerization of alkynes on the platinum metal, which is similar to the mechanism proposed for the formation of **13**. Again, the geometry of product **15** was verified by NOE-FID difference experiments at 270 MHz.

Treatment of **1** with methyl(trimethylsilyl)acetylene under the same conditions, gave (E) = 5,6-benzo-

1,1,4,4-tetra(isopropyl)-2-(trimethylsilyl)methylene-1,4-disilacyclohex-5-ene (**17**) in 34% yield, together with 39% of the starting compound **1**. In this reaction, a small amount of an unidentified product (less than 2% yield) was detected by GLC analysis. The geometry of **17** was confirmed by NOE-FID difference experiments. Saturation of a resonance of ring methylene protons at 1.88 ppm produced a positive nuclear overhauser effect of trimethylsilyl protons at 0.11 ppm, indicating that both methylene and trimethylsilyl groups are located in a *cis* fashion to each other.

Similar platinum-catalyzed reaction of **1** with bis(trimethylsilyl)acetylene, however, afforded no adducts, but 95% of the starting compound **1** was recovered unchanged.

In conclusion, the platinum-catalyzed reactions of **1** with mono-substituted alkynes bearing a less bulky substituent lead to the formation of 5,6-benzo-1,4-disilacyclohexa-2,5-dienes and 4,5-benzo-1,3-disilacyclopent-4-enes, while with alkynes that have a bulky substituent, **1** produces the 4,5-benzo-1,3-disilacyclopent-4-ene derivatives. The reaction of **1** with diphenylacetylene affords benzodisilacyclohexadiene derivative. With phenyl(trimethylsilyl)acetylene, **1** produces a 4,5-benzo-1,3-disilacyclopent-4-ene. The reactions of **1** with methyl-substituted alkynes give 5,6-benzo-2-alkylidene-1,4-disilacyclohex-5-ene derivatives.

3. Experimental section

3.1. General procedure

All platinum-catalyzed reactions of **1** with alkynes were carried out in a degassed sealed tube (1.0 cm × 10 cm) at 200°C. Yields of the products 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 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. Gel permeation chromatographic separation was performed with a Model LC-908 Recycling Preparative HPLC (Japan Analytical Industry Co., Ltd.).

3.2. Reaction of **1** with phenylacetylene

A mixture of 0.134 g (0.44 mmol) of **1**, 0.013 g (0.017 mmol) of (η^2 -ethylene)bis(triphenylphosphine)platinum(0), and 0.108 g (1.06 mmol) of phenylacetylene in a sealed glass tube was heated at 200°C for 24 h. The mixture was treated with a short silica gel column and then analyzed by GLC as being **2** (18% yield) and **3**

(14% yield), and the starting compound **1** (55%). Compound **2** and **3** were isolated by recycling HPLC. For **3**: m.p. 59°C; MS m/z 406 (M^+); IR 3049, 2943, 2849, 1561, 1460, 879, 750 cm^{-1} ; 1H NMR $\delta(CDCl_3)$ 0.74 (d, 6H, *iPr* Me, $J = 7.3$ Hz), 1.00–1.12 (m, 18H, *iPr* Me), 1.23–1.40 (m, 4H, CHSi), 7.29–7.67 (m, 9H, phenyl and phenylene ring protons), 8.00 (s, 1H, olefinic proton); ^{13}C NMR $\delta(CDCl_3)$ 13.6, 14.9 (CHSi), 18.7 (2C), 18.9, 19.1 (*iPr* Me), 127.5, 127.9, 128.0, 128.2 (2C), 133.4, 134.5, 142.6, 147.4, 147.7 (phenyl and phenylene ring carbons), 139.3, 156.2 (olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ 2.7, 5.3. Anal. Calcd for $C_{26}H_{38}Si_2$: C, 76.77; H, 9.42. Found: C, 76.63; H, 9.33. All spectral data for **2** were identified with those of an authentic sample [9].

3.3. Reaction of **1** with 1-hexyne

A mixture of 0.100 g (0.33 mmol) of **1**, 0.012 g (0.016 mmol) of $(\eta^2\text{-ethylene})\text{bis}(\text{triphenylphosphine})\text{-platinum(0)}$, and 0.071 g (0.86 mmol) of 1-hexyne in a sealed glass tube was heated at 200°C for 24 h. The mixture was treated with a short silica gel column and analyzed by GLC as being **4** (8% yield), **5** (28% yield), and the starting compound **1** (54%). Compound **4** and **5** were isolated by recycling HPLC. For **5**: MS m/z 386 (M^+); IR 2940, 2863, 1584, 1464, 1115, 993, 882, 747, 663 cm^{-1} ; 1H NMR $\delta(CDCl_3)$ 0.90–1.49 (m, 35H, *iPr* protons and $CH_2CH_2CH_2CH_2CH=$), 2.26 (q, 2H, $CH_2CH=$, $J = 7.3$ Hz), δ 9.8 (t, 1H, CH_2CH , $J = 7.3$ Hz), 7.29–7.62 (m, 4H, phenylene ring protons); ^{13}C NMR $\delta(CDCl_3)$ 13.5, 14.0 (CHSi), 18.6, 18.7, 18.9, 19.2 (*iPr* Me), 14.2, 22.7, 31.6, 40.5 (*nBu*), 127.85, 127.89, 133.4, 133.9, 148.1, 148.2 (phenylene ring carbons) 132.3, 160.4 (olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ 1.7, 3.2. Anal. Calcd for $C_{23}H_{42}Si_2$: C, 74.53; H, 10.95. Found: C, 74.50; H, 10.81. All spectral data for **4** were identical with those of an authentic sample [9].

3.4. Reaction of **1** with mesitylacetylene

A mixture of 0.099 g (0.33 mmol) of **1**, 0.095 g (0.66 mmol) of mesitylacetylene, 0.012 g (0.016 mmol) of $(\eta^2\text{-ethylene})\text{bis}(\text{triphenylphosphine})\text{-platinum(0)}$ in a sealed glass tube was heated at 200°C for 24 h. The mixture was treated with a short silica gel column to remove platinum species from the reaction mixture. The mixture was then analyzed by GLC as being **6** (20% yield), and the starting compound (79%). Compound **6** was isolated by MPLC: MS m/z 448 (M^+); IR 3042, 2941, 2864, 1572, 1462, 1114, 892, 665 cm^{-1} ; 1H NMR $\delta(CDCl_3)$ 0.61 (d, 6H, *iPr* Me, $J = 7.3$ Hz), 0.85 (d, 6H, *iPr* Me, $J = 7.3$ Hz), 1.10–1.15 (m, 12H, *iPr* Me), 1.31–1.42 (m, 4H, CHSi), 2.25 (s, 3H, mesityl *o*-Me),

2.27 (s, 3H, mesityl *p*-Me), 6.84 (s, 2H, mesityl protons), 7.33–7.65 (m, 4H, phenylene ring protons), 7.95 (s, 1H, olefinic proton); ^{13}C NMR $\delta(CDCl_3)$ 13.1, 13.7 (CHSi), 18.2, 18.6 (2C), 18.7 (*iPr* Me), 20.6 (mesityl *o*-Me), 21.0 (mesityl *p*-Me), 128.0 (3C), 133.3, 133.7, 134.8, 140.5, 141.9, 147.2, 148.3 (mesityl and phenylene ring carbons), 136.1, 157.3 (olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ 1.4, 3.7. Anal. Calcd for $C_{29}H_{44}Si_2$: C, 77.60; H, 9.88. Found: C, 77.40; H, 9.88.

3.5. Reaction of **1** with dimethylphenylsilylacetylene

A mixture of 0.112 g (0.37 mmol) of **1**, 0.013 g (0.017 mmol) of $(\eta^2\text{-ethylene})\text{bis}(\text{triphenylphosphine})\text{-platinum(0)}$, and 0.117 g (0.73 mmol) of dimethylphenylsilylacetylene in a sealed glass tube was heated at 200°C for 24 h. The mixture was analyzed by GLC as being **7** (28% yield) and the starting compound **1** (56% yield). Compound **7** was isolated by MPLC: MS m/z 464 (M^+); IR 2959, 2927, 1464, 1248, 1113, 882, 805 cm^{-1} ; 1H NMR $\delta(CDCl_3)$ 0.47 (s, 6H, Me_2Si), 1.03 (d, 6H, *iPr* Me, $J = 7.3$ Hz), 1.05 (d, 6H, *iPr* Me, $J = 7.3$ Hz), 1.07–1.16 (m, 12H, *iPr* Me), 1.18–1.26 (m, 4H, CHSi), 7.33–7.64 (m, 9H, phenyl and phenylene ring protons), 7.91 (s, 1H, olefinic proton); ^{13}C NMR $\delta(CDCl_3)$ –1.3 (Me_2Si), 13.4, 14.5 (CHSi), 18.6, 18.7, 19.3, 19.8, (*iPr* Me), 127.7, 127.8, 127.9, 129.0, 133.6, 134.0, 134.8, 139.1, 147.0, 147.8 (phenyl and phenylene ring carbons), 165.4, 165.7 (olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ –15.4, –4.6, 0.2. Anal. Calcd for $C_{28}H_{44}Si_3$: C, 72.34; H, 9.54. Found: C, 72.13; H, 9.49.

3.6. Reaction of **1** with trimethylsilylacetylene

A mixture of 0.102 g (0.34 mmol) of **1**, 0.012 g (0.016 mmol) of $(\eta^2\text{-ethylene})\text{bis}(\text{triphenylphosphine})\text{-platinum(0)}$, and 0.063 g (0.64 mmol) of trimethylsilylacetylene in a sealed glass tube was heated at 200°C for 24 h. After treatment of the resulting solution with a short column, the mixture was analyzed by GLC as being **8** (20% yield), **9** (8% yield), and the starting compound (58%). Compound **8** and **9** were isolated by MPLC. For **8**: MS m/z 402 (M^+); IR 3048, 2942, 2864, 1464, 1248, 1119, 882, 856, 706 cm^{-1} ; 1H NMR $\delta(CDCl_3)$ 0.19 (s, 9H, Me_3Si), 0.84 (d, 6H, *iPr* Me, $J = 7.3$ Hz), 1.02 (d, 6H, *iPr* Me, $J = 7.3$ Hz), 1.03 (d, 6H, *iPr* Me, $J = 7.3$ Hz), 1.18 (d, 6H, *iPr* Me, $J = 7.3$ Hz), 1.21–1.32 (m, 4H, CHSi), 7.33–7.63 (m, 4H, phenylene ring protons), 7.74 (s, 1H, olefinic proton); ^{13}C NMR $\delta(CDCl_3)$ –0.3 (Me_3Si), 13.3, 14.6 (CHSi), 18.60, 18.64, 19.3, 19.8, (*iPr* Me), 127.7, 127.9, 133.6, 134.9, 147.2, 148.0 (phenylene ring carbons), 162.2, 168.5 (olefinic carbons); ^{29}Si NMR $\delta(CDCl_3)$ –0.7,

–0.1. Anal. Calcd for $C_{23}H_{42}Si_3$: C, 68.58; H, 10.51. Found: C, 68.60; H, 10.65. All spectral data for **9** were identical with those of an authentic sample [9].

3.7. Platinum-catalyzed reaction of **9**

A mixture of 0.143 g (0.36 mmol) of **9**, 0.012 g (0.016 mmol) of $(\eta^2\text{-ethylene})\text{bis}(\text{triphenylphosphine})\text{-platinum}(0)$, and 1.5 mL of dry benzene in a sealed glass tube was heated at 200°C for 24 h. After treatment of the resulting solution with a short column, the mixture was analyzed by GLC as being **8** (92%). Compound **8** was isolated by MPLC. All spectral data for **8** were identical with those of an authentic sample obtained from the above reaction.

3.8. Stoichiometric reaction of **1** with $(\eta^2\text{-ethylene})\text{bis}(\text{triphenylphosphine})\text{platinum}(0)$

To a 30 mL two-necked flask fitted with a stirrer and reflux condenser was placed a mixture of 0.032 g (0.11 mmol) of **1** and 0.080 g (0.11 mmol) of $(\eta^2\text{-ethylene})\text{bis}(\text{triphenylphosphine})\text{platinum}(0)$ in 2 mL of decahydronaphthalene. The mixture was heated to reflux for 72 h. But the ^1H and ^{13}C NMR of the solution showed resonances attributed to compound **1**.

3.9. Palladium-catalyzed reaction of **1** with methylphenylacetylene

A mixture of 0.101 g (0.33 mmol) of **1**, 0.018 g (0.016 mmol) of tetrakis(triphenylphosphine)palladium(0), and 0.103 g (0.89 mmol) of methylphenylacetylene in a sealed glass tube was heated at 150°C for 24 h. The mixture was treated with a short silica gel column and then analyzed by GLC as being **12** (38% yield) and the starting compound (38%). Compound **12** was isolated by MPLC: m.p. 76°C; MS m/z 420 (M^+); IR 3065, 2941, 2862, 1434, 1460, 1119, 1003, 883, 778, 678, 616 cm^{-1} ; ^1H NMR $\delta(\text{CDCl}_3)$ 0.65 (d, 6H, *i*Pr Me, $J = 7.3$ Hz), 0.92 (d, 6H, *i*Pr Me, $J = 7.3$ Hz), 0.97 (d, 6H, *i*Pr Me, $J = 7.3$ Hz), 1.01 (d, 6H, *i*Pr Me, $J = 7.3$ Hz), 1.17–1.34 (m, 4H, CHSi), 1.59 (s, 3H, Me), 6.92–7.54 (m, 9H, phenyl and phenylene ring protons); ^{13}C NMR $\delta(\text{CDCl}_3)$ 11.8, 12.4 (CHSi), 17.9 (2C), 18.4, 18.9 (*i*Pr Me), 20.5 (Me), 125.5, 127.3, 127.4, 127.8, 128.2, 133.8, 134.1, 142.3, 142.6, 144.8 (phenyl and phenylene ring carbons), 150.8, 154.9 (olefinic carbons); ^{29}Si NMR $\delta(\text{CDCl}_3)$ –14.3, –12.0. Anal. Calcd for $C_{27}H_{40}Si_2$: C, 77.07; H, 9.58. Found: C, 76.80; H, 9.75.

3.10. Reaction of **1** with diphenylacetylene

A mixture of 0.081 g (0.27 mmol) of **1**, 0.012 g (0.016 mmol) of $(\eta^2\text{-ethylene})\text{bis}(\text{triphenylphosphine})\text{-}$

platinum(0), and 0.177 g (0.66 mmol) of diphenylacetylene in a sealed glass tube was heated at 200°C for 24 h. After treatment of the resulting solution with a short column, the mixture was analyzed by GLC as being **10** (44% yield), and the starting compound (44%). Compound **10** was isolated by recrystallization using ethanol as a solvent: m.p. 239°C; MS m/z 482 (M^+); IR 3064, 2946, 2865, 1115, 1003, 883 cm^{-1} ; ^1H NMR $\delta(\text{CDCl}_3)$ 0.77 (d, 12H, *i*Pr Me, $J = 7.3$ Hz), 1.05 (d, 12H, *i*Pr Me, $J = 7.3$ Hz), 1.43 (sep, 4H, CHSi, $J = 7.3$ Hz), 6.86–7.62 (m, 14H, phenyl and phenylene ring protons); ^{13}C NMR $\delta(\text{CDCl}_3)$ 11.7 (CHSi), 17.9 (*i*Pr Me), 125.0, 127.2, 127.5, 128.5, 133.8, 141.9, 144.2 (phenyl and phenylene ring carbons), 157.6 (olefinic carbons); ^{29}Si NMR $\delta(\text{CDCl}_3)$ –13.5. Anal. Calcd for $C_{32}H_{42}Si_2$: C, 79.60; H, 8.77. Found: C, 79.47; H, 8.77.

3.11. Reactions of **1** with phenyl(trimethylsilyl)acetylene

A mixture of 0.103 g (0.34 mmol) of **1**, 0.012 g (0.016 mmol) of $(\eta^2\text{-ethylene})\text{bis}(\text{triphenylphosphine})\text{-platinum}(0)$, and 0.131 g (0.75 mmol) of phenyl(trimethylsilyl)acetylene in a sealed glass tube was heated at 200°C for 24 h. This mixture was treated with a short silica gel column and analyzed by GLC as being **11** (12% yield), and the starting compound (51%). Compound **11** was isolated by MPLC: m.p. 118°C; MS m/z 478 (M^+); IR 2943, 2862, 1461, 1244, 1114, 1008, 842, 750, 691, 597 cm^{-1} ; ^1H NMR $\delta(\text{CDCl}_3)$ 0.07 (s, 9H, Me_3Si), 0.66 (d, 6H, *i*Pr Me, $J = 7.3$ Hz), 0.84 (d, 6H, *i*Pr Me, $J = 7.3$ Hz), 0.89 (d, 6H, *i*Pr Me, $J = 7.3$ Hz), 1.26 (d, 6H, *i*Pr Me, $J = 7.3$ Hz), 1.46–1.55 (m, 4H, CHSi), 6.97–7.67 (m, 9H, phenyl and phenylene ring protons); ^{13}C NMR $\delta(\text{CDCl}_3)$ 1.2 (Me_3Si), 15.0, 15.2 (CHSi), 18.9, 19.9 (2C) 20.4 (*i*Pr Me), 125.9, 126.7, 127.2, 127.4, 127.7, 134.56, 134.63, 146.2, 147.5, 150.1 (phenyl and phenylene ring carbons), 156.6, 179.0 (olefinic carbons); ^{29}Si NMR $\delta(\text{CDCl}_3)$ –8.1, 1.8, 3.9. Anal. Calcd for $C_{29}H_{46}Si_3$: C, 72.73; H, 9.68. Found: C, 72.84; H, 9.51.

3.12. Reaction of **1** with methylphenylacetylene

A mixture of 0.101 g (0.33 mmol) of **1**, 0.012 g (0.016 mmol) of $(\eta^2\text{-ethylene})\text{bis}(\text{triphenylphosphine})\text{-platinum}(0)$, and 0.090 g (0.86 mmol) of methylphenylacetylene in a sealed glass tube was heated at 200°C for 24 h. The mixture was treated with a short silica gel column and analyzed by GLC as being **12** (34% yield) and **13** (18% yield), and the starting compound (18%). Compound **12** and **13** were isolated by MPLC. For **13**: m.p. 78°C; MS m/z 420 (M^+); IR 3057, 2937, 2861, 1461, 1380, 1116, 995, 881, 747 cm^{-1} ; ^1H NMR $\delta(\text{CDCl}_3)$ 0.85 (d, 6H, *i*Pr Me, $J = 7.3$ Hz), 0.91 (d, 6H, *i*Pr Me, $J = 7.3$ Hz), 1.03 (d, 6H, *i*Pr Me, $J = 7.3$

Hz), 1.08 (d, 6H, *i*Pr Me, $J = 7.3$ Hz), 1.13–1.45 (m, 4H, CHSi), 2.27 (s, 2H, ring CH₂), 6.80 (s, 1H, olefinic proton), 7.29–7.60 (m, 9H, phenyl and phenylene ring protons); ¹³C NMR δ(CDCl₃) 11.9, 12.2 (CHSi), 15.2 (ring CH₂), 18.0 (2C), 18.3, 18.6 (*i*Pr Me), 126.2, 127.5, 127.6, 128.2, 128.8, 134.3, 134.4, 138.6, 143.4, 143.9 (phenyl and phenylene ring carbons), 135.6, 136.6 (olefinic carbons); ²⁹Si NMR δ(CDCl₃) -7.8, 0.2. Anal. Calcd for C₂₇H₄₀Si₂: C, 77.07; H, 9.58. Found: C, 76.88; H, 9.64. All spectral data for **12** were identical with those of an authentic sample obtained from palladium-catalyzed reaction.

3.13. Reaction of **1** with 2-hexyne

A mixture of 0.303 g (0.99 mmol) of **1**, 0.032 g (0.043 mmol) of (η²-ethylene)bis(triphenylphosphine)platinum(0), and 0.147 g (1.79 mmol) of 2-hexyne in a sealed glass tube was heated at 200°C for 24 h. The mixture was treated with a short silica gel column and analyzed by GLC as being **14**, **15**, and **16** (43% combined yield), and the starting compound (33%). Compound **15** and a mixture of **14** and **16** were separated by MPLC. The ratio of **14** (5%), **15** (31%) and **16** (7%) was determined by ¹H NMR spectrometric analysis. For **15**: MS m/z 386 (M⁺); IR 2940, 2864, 1463, 1382, 1116, 997, 882, 727, 681 cm⁻¹; ¹H NMR δ(CDCl₃) 0.95 (d, 12H, *i*Pr Me, $J = 7.3$ Hz), 1.01 (d, 12H, *i*Pr Me, $J = 7.3$ Hz), 1.13–1.54 (m, 9H, CHSi and CH₂-CH₂-CH₂), 1.94 (s, 2H, ring CH₂), 2.23 (q, 2H, CH₂-CH₂-CH₃, $J = 7.3$ Hz), 5.75 (t, 1H, olefinic proton, $J = 7.3$ Hz), 7.29–7.56 (m, 4H, phenylene ring protons); ¹³C NMR δ(CDCl₃) 11.8, 12.3 (CHSi), 13.8 (ring CH₂), 14.0 (CH₃), 18.0, 18.2, 18.5, 18.6 (*i*Pr Me), 22.8 (CH₂-CH₃), 30.1 (CH₂-CH₂-CH₃), 127.2, 127.4, 134.2, 134.3, 144.0, 144.3 (phenylene ring carbons), 130.5, 138.9 (olefinic carbons); ²⁹Si NMR δ(CDCl₃) -0.4, -8.6. Anal. Calcd for C₂₄H₄₂Si₂: C, 74.53; H, 10.95. Found: C, 74.33; H, 10.91. For **14** and **16**: MS m/z 386 (M⁺); IR 3043, 2935, 2888, 1417, 1038, 745, 679 cm⁻¹; ¹H NMR δ(CDCl₃) 0.89 (d, 12H, *i*Pr Me, $J = 7.3$ Hz), 0.95 (d, 12H, *i*Pr Me, $J = 7.3$ Hz), 0.99 (d, 12H, *i*Pr Me, $J = 7.3$ Hz), 1.04 (d, 12H, *i*Pr Me, $J = 7.3$ Hz), 1.08–1.67 and 2.16–2.30 (m, 23H, CHSi, ring CH, CH₂-CH₂-CH₃), 1.92 (s, 3H, Me), 5.45 (s, 1H, olefinic proton), 5.69 (s, 1H, olefinic proton), 7.30–7.54 (m, 8H, phenylene ring protons); ¹³C NMR δ(CDCl₃) 10.7, 11.9, 12.3, 12.6 (CHSi), 14.3, 14.9 (CH₃-CH₂), 17.9 (CH₃), 18.35, 18.40, 18.5 (2C), 18.6, 18.7, 18.9 (2C) (*i*Pr Me), 21.7, 22.1, 28.2, 35.0 (CH₂-CH₂-CH₃), 34.3 (ring CH), 127.1, 127.2, 127.3, 127.4, 133.7, 133.9, 134.4 (2C), 143.3, 143.5, 144.6 (2C) (phenylene ring carbons), 120.8, 142.6, 148.7, 152.6 (olefinic carbons); ²⁹Si NMR δ(CDCl₃) -12.9, -12.6, -6.7, -2.4; Exact Mass Calcd for C₂₄H₄₂Si₂ (M⁺) 386.2825, Found 386.2806.

3.14. Reaction of **1** with methyl(trimethylsilyl)acetylene

A mixture of 0.114 g (0.37 mmol) of **1**, 0.014 g (0.019 mmol) of (η²-ethylene)bis(triphenylphosphine)platinum(0), and 0.085 g (0.76 mmol) of methyl(trimethylsilyl)acetylene in a sealed glass tube was heated at 200°C for 24 h. The mixture was treated with a short silica gel column and then analyzed by GLC as being **17** (34% yield), and the starting compound (39%). Compound **17** was isolated by MPLC: MS m/z 416 (M⁺); IR 2940, 2863, 1557, 1463, 1248, 1118, 997, 882, 851, 691 cm⁻¹; ¹H NMR δ(CDCl₃) 0.11 (s, 9H, Me, Si), 0.91–1.04 (m, 24H, *i*Pr Me), 1.15–1.32 (m, 4H, CHSi), 1.88 (s, 2H, ring CH₂), 6.54 (s, 1H, olefinic proton), 7.29–7.51 (m, 4H, phenylene ring protons); ¹³C NMR δ(CDCl₃) 0.1 (Me, Si), 12.1, 12.6 (CHSi), 18.4 (2C), 18.6, 19.0 (*i*Pr Me), 29.0 (ring CH₂), 127.2, 127.3, 133.6, 134.0, 142.8, 143.0 (phenylene ring carbons), 138.3, 159.6 (olefinic carbons); ²⁹Si NMR δ(CDCl₃) -12.9, -12.7, 0.8. Anal. Calcd for C₂₄H₄₄Si₃: C, 69.15; H, 10.64. Found: C, 69.14; H, 10.63.

3.15. Reactions of **1** with bis(trimethylsilyl)acetylene

A mixture of 0.100 g (0.33 mmol) of **1** and 0.013 g (0.017 mmol) of (η²-ethylene)bis(triphenylphosphine)platinum(0), and 0.105 g (0.59 mmol) of bis(trimethylsilyl)acetylene in a sealed glass tube at 200°C for 24 h. The mixture was treated with a short column and analyzed by GLC as being the starting compound **1** (95%). No adducts were detected.

Acknowledgements

This work was supported in part by Research for the Future of the JSPS Program (96P00206), to which our thanks are due. We also express our appreciation to Toshiba Silicone Co. Ltd. and Sumitomo Electric Industry Ltd. for financial support.

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