Synthesis and Platinum- and Palladium-Catalyzed Reactions of Benzo[1,2:4,5]bis(1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene)

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Benzo[1,2:4,5]bis(1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene) (**1**) was synthesized in situ by the reaction of 1,2,4,5-tetrabromobenzene with magnesium in the presence of diethylfluorosilane in THF. The reaction of **1** with diphenylacetylene in the presence of a catalytic amount of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in refluxing benzene gave a 1:2 adduct, benzo[1,2:4,5]bis(1,1,4,4-tetraethyl-2,3-diphenyl-1,4-disilacyclohexa-2,5-diene) in 91% yield. Similar platinum(0)-catalyzed reaction of **1** with 3-hexyne and acetylene in refluxing benzene afforded the respective 1:2 adducts benzo[1,2:4,5]bis(disilacyclohexadiene) derivatives in excellent yields. Benzobis(disilacyclobutene) **1** also reacted with diphenylacetylene, 3-hexyne, and acetylene in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) to give the corresponding 1:2 adducts in excellent yields. Computational analyses of benzo[1,2:4,5]bis(disilacyclobutene) and its 1:1 and 1:2 adducts with acetylene were carried out using the B3LYP density-functional-theory method; the structures of these compounds were shown to be planar. The Si−Si bond in the disilacyclobutene ring appeared from computations to be effectively cleaved by a platinum(0) complex.

Introduction

In 1991, we found that the thermolysis of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene afforded an *o*-quinodisilane as a reactive species, while its photolysis proceeds to give a silene, 1-ethyl-1-(2-diethylsilylphenyl)-1-silaprop-1-ene.[1−3] We also found that the transition-metal-catalyzed reactions of the benzodisilacyclobutene with aromatic compounds, carbonyl compounds, alkenes, and alkynes produce various types of products.[4−6] The types of products thus formed depend highly on the nature of the metal in the reactive species formed from the benzodisilacyclobutene with transition-metal complexes used as the catalyst.[3]

As an extension of our study concerning the chemistry of the benzodisilacyclobutene, we have synthesized benzo[1,2:4,5]bis(disilacyclobutene)[7] and investigated its chemical behavior toward the transition-metal complexes. In this paper we report the synthesis of benzo[1,2:4,5]bis(1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene) and its reactions with alkynes in the presence of a catalytic amount of (η^2-ethylene)bis(triphenylphosphine)platinum(0) and tetrakis(triphenylphosphine)palladium(0). Density-functional calculations predict that a platinum complex should efficiently cleave the Si−Si bond of disilacyclobutene.

Results and Discussion

Benzo[1,2:4,5]bis(1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene) (**1**) was prepared by the series of reactions shown in Scheme 1. Treatment of 1,2,4,5-tetrabromobenzene with 4 equiv of magnesium in the presence of 6 equiv of diethylfluorosilane in THF afforded 1,2,4,5-tetrakis(diethylsilyl)benzene in 50% yield. Hydrogen−chlorine exchange of the tetrakis(diethylsilyl)benzene with chlorine in carbon tetrachloride gave 1,2,4,5-tetrakis(chlorodiethylsilyl)benzene in 87% yield. Finally, sodium condensation of the resulting tetrakis(chlorodiethylsilyl)benzene in refluxing toluene produced **1** in 34% yield as crystals. The structure of **1** was verified by spectrometric and elemental analysis. Its ^{13}C NMR spectrum reveals two resonances at 5.55 and 8.90 ppm due to ethyl carbons and two resonances at 136.0 and 155.5 ppm, attributed to phenylene carbons. As expected, the ^{29}Si NMR spectrum shows a single resonance at 8.0 ppm, indicating that all four silicons are equivalent.

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(1) (a) Ishikawa, M.; Sakamoto, H.; Tabuchi, T. *Organometallics* **1991**, *10*, 3173. (b) Naka, A.; Hayashi, M.; Ishikawa, M. *Organometallics* **1994**, *13*, 4994.

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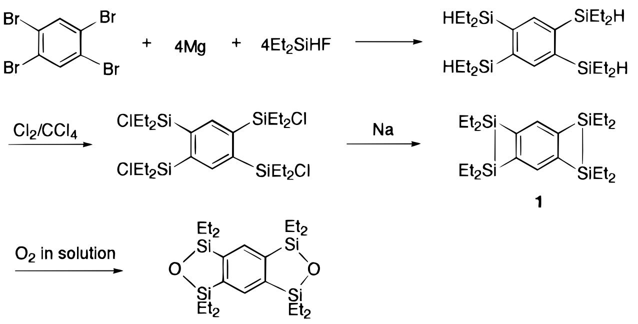
(5) Naka, A.; Okada, T.; Ishikawa, M. *J. Organomet. Chem.* **1996**, *521*, 163.

(6) Naka, A.; Okada, T.; Kunai, A.; Ishikawa, M. *J. Organomet. Chem.* **1997**, *547*, 149.

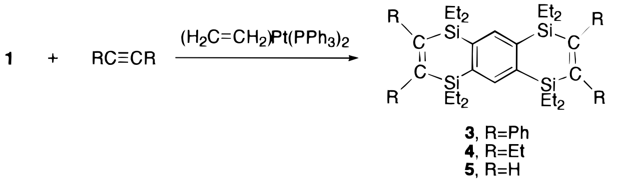
(7) Recently, X-ray crystallographic analysis of benzo[1,2:4,5]bis(1,1,2,2-tetraisopropyldisilacyclobutene) has been reported: Kyushin, S.; Kitahara, T.; Matsumoto, H. *Chem. Lett.* **1998**, 471.

10.1021/om9806038 CCC: $15.00

Scheme 1



Scheme 2



These results are wholly consistent with the structure proposed for **1**.

Crystalline compound **1** is stable toward atmospheric oxygen and can be handled in air. However, in solution compound **1** is gradually oxidized by oxygen in air at room-temperature giving benzo[1,2:4,5]bis(1,1,3,3-tetraethyl-2-oxa-1,3-disilacyclopent-4-ene) (**2**) as a final product. Thus, when the hexane solution of **1** was allowed to stand in air for 100 h, an oxidation product **2** was formed quantitatively.

Like 3,4-benzo-1,1,2,2,-tetraethyl-1,2-disilacyclobut-3-ene,[8] compound **1** reacts with alkynes in the presence of a catalytic amount of a platinum(0) complex giving 1:2 adducts. Thus, when **1** was treated with diphenylacetylene in the presence of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in refluxing benzene for 6 h, benzo[1,2:4,5]bis(1,1,4,4-tetraethyl-2,3-diphenyl-1,4-disilacyclohexa-2,5-diene) (**3**) formed in 91% yield (Scheme 2). Similar platinum-catalyzed reaction of **1** with 3-hexyne in refluxing benzene for 6 h gave benzo[1,2:4,5]bis(1,1,2,3,4,4-hexaethyl-1,4-disilacyclohexa-2,5-diene) (**4**) in 94% yield.

It was also found that acetylene readily adds to both silicon−silicon bonds of **1** in the presence of the platinum catalyst, giving a 1:2 adduct. When acetylene gas was introduced into a refluxing benzene solution of **1** for 24 h, a 1:2 adduct, benzo[1,2:4,5]bis(1,1,4,4-tetraethyl-1,4-disilacyclohexa-2,5-diene) (**5**), arising from insertion of an acetylene molecule into each silicon−silicon bond in the starting compound **1** was obtained in 82% yield. The structures of **3**−**5** were confirmed by spectrometric analysis, as well as by elemental analysis. For example, ^{29}Si NMR spectra for **3**−**5** reveal a single resonance at −14.0, −13.9, and −17.3 ppm, respectively. ^{1}H and ^{13}C spectra are also consistent with the structures proposed for these compounds (see Experimental Section).

Interestingly, when the progress of the reaction of **1** with alkynes was followed by GC, a 1:1 adduct derived from insertion of an alkyne into one of two silicon−silicon bonds could not be detected in all cases. Even in the early stages of the reaction, only the starting compound **1** and the 1:2 adduct were detected, but no 1:1 adduct was observed at all. The same result was obtained when the platinum-catalyzed reaction of **1** with 3-hexyne was followed by ^{13}C and ^{29}Si NMR spectroscopic methods. Only signals due to the starting compound **1** and product **4** were detected in the early stages of the reaction for both cases.

We also carried out the reactions of **1** with alkynes with the use of tetrakis(triphenylphosphine)palladium(0) as the catalyst and found that the palladium(0) catalyst is more effective than the platinum(0) catalyst. Thus, the reaction of **1** with diphenylacetylene in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) in refluxing benzene proceeded to give compound **3** in 92% yield, in which the reaction was completed within 4 h. Treatment of **1** with 3-hexyne under the same conditions afforded a 1:2 adduct, compound **4** in 91% yield. Benzobis(disilacyclobutene) **1** reacted readily with acetylene at room temperature for 30 min in the presence of the palladium catalyst to give **5** in 93% yield. In all cases, again no 1:1 adducts

$$\mathbf{1} + \mathrm{RC{\equiv}CR} \xrightarrow{\mathrm{Pd(PPh_3)_4}} \mathbf{3},\ \mathbf{4},\ \text{and}\ \mathbf{5}$$

were detected in the reaction mixture, even in the early stages of the reaction, as observed in the platinum-catalyzed reaction.

All spectral data for products **3**−**5** obtained from the palladium-catalyzed reactions were identical with those of compounds formed from the platinum-catalyzed reactions.

In the present reactions, the platinum and palladium catalysts presumably react with **1** to form transition-metal complex **6** (M = Pt or Pd), arising from insertion of the platinum or palladium species into one of two silicon−silicon bonds in compound **1**. Complex **6** thus formed would react with alkyne producing a π-coordinated metal complex **7**, and then the alkyne coordinating to the platinum or palladium metal inserts into a silicon−metal bond to give complex **8**. Since 1:1 adducts could not be detected in the present reactions, reductive elimination to form free platinum species or palladium species from the complex **8** would not be involved. The platinum or palladium species that is eliminated from **8** presumably interacts with 1:1 adduct thus produced, giving a complex like **9**, and would insert into a silicon−silicon bond in this complex. Finally the reaction of this complex with alkyne affords the 1:2 adduct as shown in Scheme 3.

The alternate mechanism involving the formation of a diplatinum or dipalladium complex such as **10** might be considered. In this case, monometal complex **6** must react with the platinum or palladium catalyst to produce a dimetal complex faster than the reaction of **6** with alkyne. To learn more about the reactive intermediate in the present reaction, we carried out the stoichiometric reaction of **1** and (η^2-ethylene)bis(triphenylphosphine)platinum(0) and attempted to follow the progress of the reaction by NMR spectrometry. Unfortunately, ^{13}C NMR and ^{29}Si NMR spectra for the reaction mixture obtained from a 1:1 molar ratio of **1** and the platinum, and also a 1:2 molar ratio, showed complex signal

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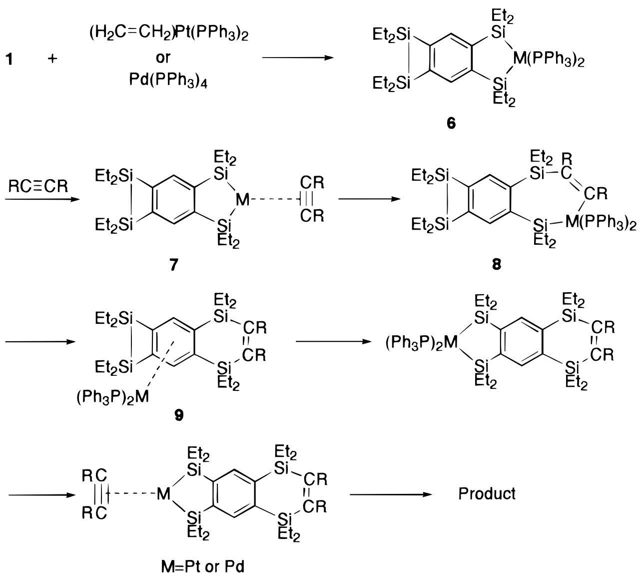
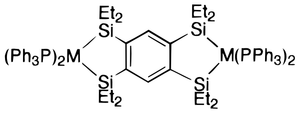
[8] Ishikawa, M.; Naka, A.; Ohshita, J. *Organometallics* **1993**, *12*, 4987.

Scheme 3



patterns and afforded no clear-cut result for the reactive intermediate. We also carried out the stoichiometric reaction of **1** with tetrakis(triphenylphosphine)palladium(0); however, no evidence for the formation of complex **6** and **10** was obtained. Although, at present, evidence for the formation of intermediates **6** and **10** has not yet been obtained, the former mechanism is more attractive.



10

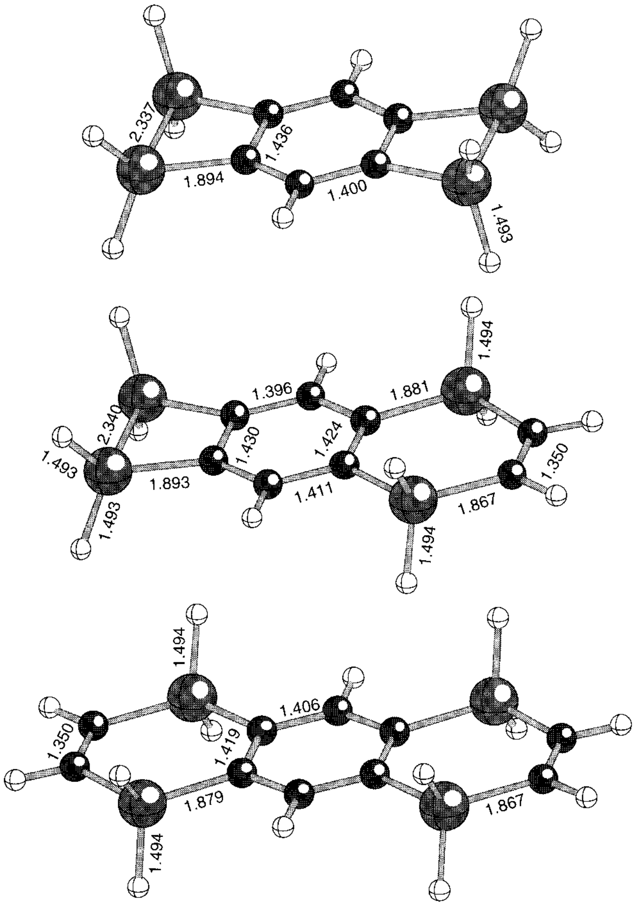


Figure 1. Optimized geometries of benzobis(disilacyclobutene) and its 1:1 and 1:2 adducts with acetylene at the B3LYP/3-21G* level. Units are in Å.

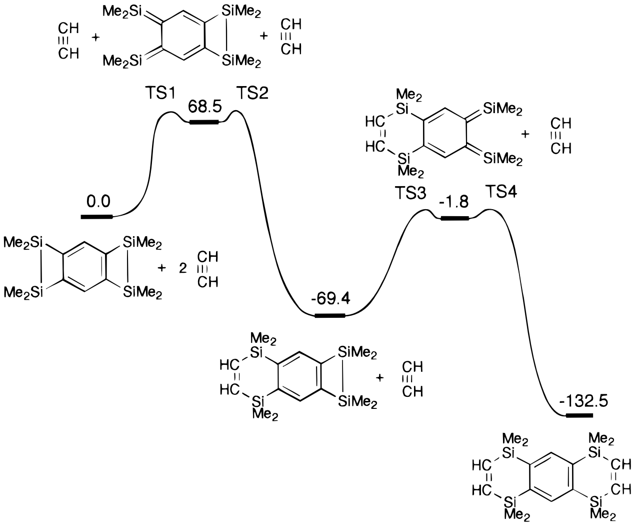


Figure 2. A potential energy diagram for a two-step Diels–Alder reaction between benzobis(disilacyclobutene) and acetylenes at the B3LYP/3-21G* level. Units are in kcal/mol.

To have a better understanding of the results obtained in the present experiments, computational analyses of benzobis(disilacyclobutene) and its 1:1 and 1:2 adducts with acetylene were carried out using the density-functional-theory (DFT) B3LYP method.[9,10] The structures of these compounds optimized at the B3LYP/3-21G* level are shown in Figure 1.[9–11] These are nearly planar molecules. In these structures, Si–Si distances of 2.34 Å, Si–C distances of 1.87–1.89 Å, and Si–H distances of 1.49 Å are quite reasonable since the atomic radii (r_{cov}) of Si, C, and H atoms are 1.18, 0.77, and 0.37 Å, respectively.[12] Since the C–C distances in the 1:1 and 1:2 adducts are 1.35 Å, they can be reasonably viewed as double bonds. The structure of benzobis(disilacyclobutene) itself was computed by Eckert-Maksic et al.[13] at the MP2 and the B3LYP/6-31G* levels; the result is, of course, consistent with ours. The C–C bond distances of the benzene ring are significantly elongated in the substitution sites. Our computational result is consistent with a recent X-ray structural analysis for an isopropyl derivative of **1**.[7]

If the 1:2 adduct is formed through a two-step Diels–Alder reaction, we can show a potential energy diagram for the reaction pathway. As shown in Figure 2, the two-step reaction appears to be downhill in energy so that the 1:1 adduct formed in the first step is expected to be

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[13] Eckert-Maksic, M.; Glasovac, Z,; Hodoscek, M.; Lesar, A.; Maksic, Z. B. *J. Organomet. Chem.* **1996**, *524*, 107.

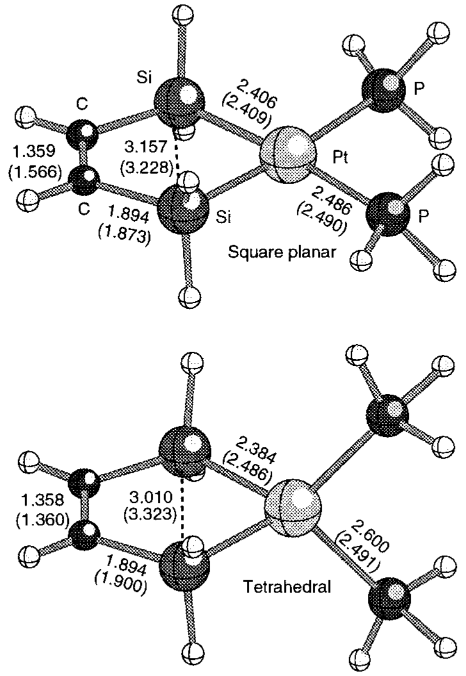

Figure 3. Optimized geometries of a platinum complex of disilacyclobutene in the singlet and triplet states at the B3LYP/LanL2Dz level. Units are in Å. Values in parentheses are for the triplet state. Relative energies of the tetrahedral singlet, the square-planar triplet, and the tetrahedral triplet lie 24.6, 76.1, and 63.2 kcal/mol above the ground-state square-planar singlet, respectively.

easily converted into the 1:2 adduct. This computational result is qualitatively consistent with the experimental fact that no 1:1 adduct has been observed so far. We proposed that the Diels−Alder reactions of disilacyclobutenes with alkenes or alkynes occur through the formation of disilabutadienes as reactive intermediates and also discussed a possible reaction mechanism.[14] Disilabutadiene is a shallow local minimum on the potential energy surface, as indicated earlier.[14] This species is formed via the symmetry-allowed ring opening of a disilacyclobutene; thus, once a reactive disilabutadiene species is formed by heat treatment, we expect that the Diels−Alder reaction with alkynes should occur with no cost of activation energy. Thus, the ring opening is probably a rate-determining step when the platinum catalyst is not concerned in the coupling reaction. However, we think that the activation energy for the ring opening (or the Si−Si bond cleavage) should be significantly decreased when the platinum catalyst is used, as discussed above.

It is quite interesting to study the important role of transition metals in the ring opening of disilacyclobutenes. We demonstrate in Figure 3 the structures of the singlet and triplet states of the platinum(0) complex of disilacyclobutene computed at the B3LYP/LanL2DZ level.[15] This type of platinum complex is a possible reaction intermediate which corresponds to **6** in Scheme 3. We thus believe that **6** is responsible for the interesting Pt-catalyzed reaction. The singlet ground state in which the Pt atom is in a square-planar environment was found to lie 63.2 kcal/mol below the triplet state in which the Pt atom is in a tetrahedral environment. The platinum atom inserts into the Si−Si bond in different ways in the singlet and triplet states; in each case the Si−Si bond is effectively cleaved by the platinum atom. The computed Si−Si distances in the square-planar singlet and tetrahedral triplet states are 3.157 and 3.323 Å, respectively. We have no clear-cut answer to the reactivity of this species toward alkyne at present, but it is highly possible that alkyne inserts into the Si−Pt bond along the context of Scheme 3. Detailed theoretical analyses concerning the role of the platinum catalyst in the interesting Pt-catalyzed reaction will be reported in due course.[16]

Experimental Section

General Procedure. All platinum- and palladium-catalyzed reactions of compound **1** with alkynes were carried out under an argon atmosphere. Yields of the products with one exception of a diphenylacetylene adduct 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 infrared spectrophotometer. Low-resolution mass spectra and high-resolution mass spectra were measured on a JEOL model JMS-700 instrument.

Preparation of 1,2,4,5-Tetrakis(diethylsilyl)benzene. In a 200 mL three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 2.966 g (0.122 mol) of magnesium and 11.750 g (0.111 mol) of diethylfluorosilane in 10 mL of THF. To this was added a suspension of 7.214 g (0.018 mol) of 1,2,4,5-tetrabromobenzene in 50 mL of THF over a period of 1 h at room temperature. The mixture was heated to reflux for 24 h and then cooled to 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, washed with water, and then dried over magnesium sulfate. The solvents were evaporated off, and the residue was fractionally distilled under reduced pressure to give 3.802 g (9.08 mmol) of tetrakis(diethylsilyl)benzene (50% yield): bp 126−127 °C/2 Torr; MS *m/z* 422 (M^+); IR 2954, 2933, 2910, 2873, 2135 (Si−H), 1456, 1416, 1230, 1159, 1092, 1009, 972, 802, 712, 685 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.85 (dq, 16H, CH_2Si, $J = 7.6$ Hz, 3.4 Hz), 0.98 (t, 24H, CH_3, $J = 7.6$ Hz), 4.41 (quint, HSi, $J = 3.4$ Hz), 7.64 (s, 2H, phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) 4.28, 8.34 (EtSi), 141.0, 141.9 (phenylene ring carbons); ^{29}Si NMR δ ($CDCl_3$) −7.7. Anal. Calcd for $C_{22}H_{46}Si_4$: C, 62.48; H, 10.96. Found: C, 62.78; H, 11.05.

Preparation of 1,2,4,5-Tetrakis(chlorodiethylsilyl)benzene. In a 100 mL three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel was placed 1.972 g (4.67 mmol) of **1** in 10 mL of carbon tetrachloride. To the solution was introduced chlorine gas at −30 °C until the color of the solution changed to light yellow. The mixture was stirred at room temperature for 1 h, and then the solvent was evaporated off. The residue was distilled under reduced pressure to give 2.237 g (4.06 mmol) of tetrakis(chlorodiethylsilyl)benzene (87% yield): bp 183−185 °C/3 Torr; MS *m/z* 529 ($M^+ - Et$); IR 2964, 2902, 2872, 1456, 1414, 1379, 1232, 1201, 1178, 1086, 1018, 962, 727, 683, 636, 573, 540 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.02 (t, 16H, CH_2Si, $J = 7.7$ Hz), 1.19 (q, 24H, CH_3, $J = 7.7$ Hz), 8.28 (s, 2H, phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) 6.96, 10.05

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[16] Yoshizawa, K.; Kang, S.-Y.; Yamabe, T.; Naka, A.; Ishikawa, M. To be published.

(EtSi), 140.4, 142.7 (phenylene ring carbons); ^{29}Si NMR δ ($CDCl_3$) 26.9. Anal. Calcd for $C_{22}H_{42}Si_4Cl_4$: C, 47.12; H, 7.55. Found: C, 47.12; H, 7.51.

Preparation of 1. In a 100 mL three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 2.290 g (0.10 mol) of sodium and 10 mL of toluene. The mixture was heated to reflux and stirred to prepare a sodium dispersion. To this was added a solution of 8.105 g (14.5 mmol) of 1,2,4,5-tetrakis(chlorodiethylsilyl)benzene in 40 mL of toluene over a period of 1 h. After the mixture was heated to reflux for 2 h, the solvent was distilled off. The residue was distilled under reduced pressure to give 2.050 g of **1** (34% yield): bp 153−155 °C/1 Torr; mp 79−80 °C; MS *m/z* 418 (M^+); IR 2956, 2875, 1458, 1412, 1375, 1232, 1213, 1107, 1016, 955, 920, 822, 791, 731, 621 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.82−1.16 (m, 40H, EtSi), 7.55 (s, 2H, phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) 5.55, 8.90 (EtSi), 136.0, 155.5 (phenylene ring carbons); ^{29}Si NMR δ ($CDCl_3$) 8.0. Anal. Calcd for $C_{22}H_{42}Si_4$: C, 63.08; H, 10.11. Found: C, 62.84; H, 10.49.

Oxidation of 1. A solution of 0.0501 g (0.120 mmol) of compound **1** in 5 mL of hexane was allowed to stand in air for 100 h. GLC analysis of the solution showed that benzo[1,2:4,5]bis(1,1,3,3-tetraethyl-2-oxa-1,3-disilacyclopent-4-ene) (**2**) was produced in quantitative yield: mp 91−92 °C; MS *m/z* 450 (M^+); IR 2954, 2875, 1459, 1409, 1376, 1234, 1105, 1083, 1016, 956, 923, 784, 730, 688 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.76−1.02 (m, 40H, EtSi), 7.72 (s, 2H, phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) 6.67, 7.29 (EtSi), 134.7, 146.8 (phenylene ring carbons); ^{29}Si NMR δ ($CDCl_3$) 17.2. Anal. Calcd for $C_{22}H_{42}Si_4O_2$: C, 58.60; H, 9.39. Found: C, 58.99; H, 9.45.

Reaction of 1 with Diphenylacetylene in the Presence of a Pt Complex. In a 30 mL two-necked flask fitted with a stirrer and reflux condenser was placed a mixture of 0.0997 g (0.238 mmol) of **1**, 0.1295 g (0.727 mmol) of diphenylacetylene, and 0.0051 g (0.0068 mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in 3 mL of dry benzene. The mixture was heated to reflux for 6 h and then treated with a short silica gel column to remove platinum species. Compound **3** was isolated by silica gel column chromatography (91% isolated yield): mp >300 °C; MS *m/z* 774 (M^+); IR 3074, 3034, 2951, 2910, 1483, 1417, 1236, 1149, 1001, 964, 847, 787, 723, 696, 677 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.65−0.92 (m, 40H, EtSi), 6.84−7.10 (m, 20H, phenyl ring protons), 7.75 (s, 2H, phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) 5.25, 7.63 (EtSi), 125.0 127.4, 128.0, 138.2, 141.3, 143.5, 157.41 (phenyl and phenylene and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −14.0. Anal. Calcd for $C_{50}H_{62}Si_4$: C, 77.45; H, 8.06. Found: C, 77.46; H, 8.06.

Reaction of 1 with 3-Hexyne in the Presence of a Pt Complex. In a 30 mL two-necked flask fitted with a stirrer and reflux condenser was placed a mixture of 0.0965 g (0.230 mmol) of **1**, 0.0985 g (1.20 mmol) of 3-hexyne, and 0.0049 g (0.00656 mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in 3 mL of dry benzene. The mixture was heated to reflux for 6 h and treated with a short silica gel column. The mixture was analyzed by GLC as being **4** (94%). Compound **4** was isolated by column chromatography: mp >161−162 °C; MS *m/z* 582 (M^+); IR 2954, 2872, 1456, 1416, 1375, 1223, 1147, 1099, 1000, 962, 729, 667, 571 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.80 (br s, 40H, EtSi), 1.07 (t, 12H, CH_3, J = 7.6 Hz), 2.37 (q, 8H, CH_2, J = 7.6 Hz), 7.58 (s, 2H, phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) 6.13, 7.76 (EtSi), 14.90 (CH_3), 24.10 (CH_2), 137.2, 141.6, 153.9 (phenylene and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −13.9. Anal. Calcd for $C_{34}H_{62}Si_4$: C, 70.02; H, 10.72. Found: C, 69.97; H, 10.88.

Reaction of 1 with Acetylene in the Presence of a Pt Complex. In a 30 mL two-necked flask fitted with a inlet tube for acetylene gas and reflux condenser was placed a mixture of 0.1040 g (0.248 mmol) of **1** and 0.0119 g (0.016 mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in 10 mL of dry benzene. The mixture was heated to reflux and acetylene gas was introduced for 24 h. The solution was then passed through a short silica gel column and analyzed by GLC as being compound **5** (82%). Compound **5** was isolated by column chromatography: MS *m/z* 470 (M^+); IR 2954, 2924, 2872, 2854, 1464, 1377, 1151, 1016, 752, 727 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.07 (q, 16H, CH_2Si, J = 7.9 Hz), 0.90 (t, 24H, CH_3, J = 7.9 Hz), 7.12 (s, 4H, olefinic protons), 7.58 (s, 2H, phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) 6.02, 7.60 (EtSi), 138.4, 141.7 (phenylene ring carbons), 149.5 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −17.3. Anal. Calcd for $C_{26}H_{46}Si_4$: C, 66.30; H, 9.84. Found: C, 66.65; H, 10.24.

Reaction of 1 with 3-Hexyne in an NMR Tube. A mixture of **1** (0.0700 g, 0.167 mmol), 3-hexyne (0.482 mmol), and (η^2-ethylene)bis(triphenylphosphine)platinum(0) (0.0040 g, 0.0054 mmol) was placed in an NMR tube with a rubber septum cap. The tube was heated at 70 °C in an oil bath and measured by ^{13}C and ^{29}Si NMR spectroscopy at 1 min intervals.

Reaction of 1 with Diphenylacetylene in the Presence of a Pd Complex. In a 30 mL two-necked flask fitted with a stirrer and reflux condenser was placed a mixture of 0.0468 g (0.112 mmol) of **1**, 0.0685 g (0.385 mmol) of diphenylacetylene, and 0.0065 g (0.0056 mmol) of tetrakis(triphenylphosphine)palladium(0) in 3 mL of dry benzene. The mixture was heated to reflux for 4 h, and then the mixture was passed through a short silica gel column to remove palladium species. Compound **3** was isolated by silica gel column chromatography (92% isolated yield). All spectral data for **3** were identical with those of an authentic sample.

Reaction of 1 with 3-Hexyne in the Presence of a Pd Complex. In a 30 mL two-necked flask fitted with a stirrer and reflux condenser was placed a mixture of 0.0503 g (0.120 mmol) of **1**, 0.0315 g (0.383 mmol) of 3-hexyne, and 0.0062 g (0.00537 mmol) of tetakis(triphenylphosphine)palladium(0) in 3 mL of dry benzene. The mixture was heated to reflux for 5 h and then treated with a short silica gel column. The mixture was analyzed by GLC as being **4** (91%). All spectral data for **4** were identical with those of an authentic sample.

Reaction of 1 with Acetylene in the Presence of a Pd Complex. In a 30 mL two-necked flask fitted with a inlet tube for acetylene gas and reflux condenser was placed a mixture of 0.0562 g (0.134 mmol) of **1** and 0.0081 g (0.0070 mmol) of tetrakis(triphenylphosphine)palladium(0) in 5 mL of dry benzene. The acetylene gas was introduced into the mixture at room temperature for 30 min. The solution was then passed through a short silica gel column and analyzed by GLC as being compound **5** (93%). Compound **5** was isolated by column chromatography. All spectral data for **5** were identical with those of an authentic sample.

Method of Calculation. Computational analyses of benzobis(disilacyclobutene) and its 1:1 and 1:2 adducts with acetylene were carried out using the so-called B3LYP method, a hybrid (density-functional-theory/Hartree−Fock) (DFT/HF) method.[9,10] This method consists of the nonlocal exchange functional of Becke's three-parameter set[9a] and the nonlocal correlation functional of Lee, Yang, and Parr.[10] This DFT method has been successfully applied to the Diels−Alder reaction of butadiene and ethylene, giving structures and energetics reasonably well.[17] We performed B3LYP computations of the three reaction species with the 3-21G* basis set and of the Pt complex with the LanL2DZ basis set.[11,15] The Gaussian 94 program package[18] was used.

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