Stereochemistry of Disilanylene-Containing Cyclic Compounds. Synthesis and Reactions of *cis*- and *trans*-1,2-Dimethyl-1,2-diphenyl-1,2-disilacyclohexane

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The Wurtz type coupling of a mixture of *meso*- and *dl*-1,4-bis(chloromethylphenylsilyl)-butanes with lithium metal in the presence of a catalytic amount of dimethylphenylsilyllithium afforded *cis*- and *tran*s-1,2-disilacyclohexane (**1a** and **1b**) in a ratio of 4:6. Pure **1a** and **1b** obtained by fractional distillation reacted with diphenylacetylene in the presence of a platinum catalyst at 200 °C to give stereospecifically the respective *cis*- and *trans*-1,4-dimethyl-1,2,3,4-tetraphenyl-1,4-disilacyclooct-2-ene (**2a** and **2b**). Under identical conditions, the reactions of **1a** and **1b** with 1-phenyl-1-propyne, 3-hexyne, and phenylacetylene also proceeded with stereospecificity to form similar adducts.

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Introduction

Many papers concerning the addition of a silicon−silicon bond in acyclic and cyclic disilanes to unsaturated compounds in the presence of the transition metal catalysts have been reported.[1−5] Kumada et al. reported that the reactions of *cis*- and *trans*-1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane and acetylenes in the presence of a palladium catalyst proceeded with retention of the stereochemistry at the silicon atoms, respectively.[1b] Recently we have found that the palladium-catalyzed reactions of the *cis*- and *trans*-isomer of the benzodisilacyclobutene with monosubstituted acetylenes proceed to give the respective *cis*- and *trans*-5,6-benzo-1,4-disilacyclohexa-2,5-diene with stereospecificity.[6] We have also found that the reactions of the *cis*- and *trans*-isomer of the disilacyclopentane with phenylacetylene proceed to afford stereospecifically *cis*- and *trans*-1,4-dimethyl-1,2,4-triphenyl-1,4-disilacyclohept-2-ene in high yields.[7]

To our knowledge, the synthesis, fluorodephenylation, and oxidation reactions of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane have been reported.[8] It is of interest to us to investigate the stereochemistry of the six-membered disilacyclic system. In this paper, we report the synthesis of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane and the stereochemistry of the platinum-catalyzed reactions with alkynes.

Results and Discussion

The starting compounds *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane (**1a** and **1b**) were

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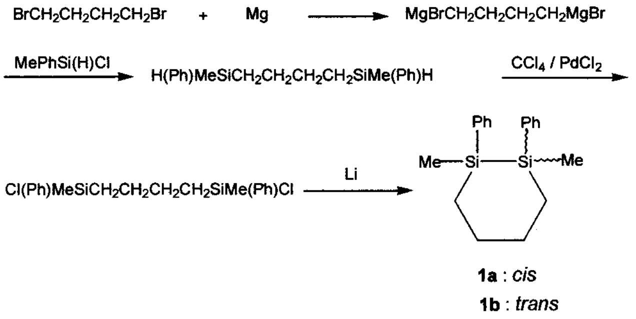
Scheme 1



prepared by a series of reactions shown in Scheme 1. Treatment of di-Grignard reagent prepared from the reaction of 1,4-dibromobutane and magnesium in THF with 2 equiv of chloromethylphenylsilane in THF afforded 1,4-bis(methylphenylsilyl)butane in 55% yield. Hydrogen−chlorine exchange of the 1,4-bis(methylphenylsilyl)butane in the presence of a catalytic amount of palladium dichoride in carbon tetrachloride gave 1,4-bis(chloromethylphenylsilyl)butane in 80% yield.

Finally, Wurtz type coupling of the resulting 1,4-bis(chloromethylphenylsilyl)butane with lithium metal in the presence of dimethylphenylsilyllithium[9] in THF at room temperature yielded a mixture of *cis*- and *trans*-1,2-disilacyclohexane **1a** and **1b** in 50% combined yield. It is shown that lithium metal is better than sodium metal in the Wurtz type coupling reaction. The ratio of **1a** and **1b** in the reaction mixture was calculated to be a 4:6 by ^{1}H NMR spectrometric analysis of the mixture. The pure *cis*- and *trans*-isomer could readily be isolated by fractional distillation using a spinning band distillation column with 50 theoretical plates. All spectral data for **1a** and **1b** were identical with those of the authentic samples obtained from the method reported previously.[8]

To obtain more information about the stereochemistry of the disilacyclohexane system, we carried out the platinum-catalyzed reaction of **1a** and **1b** with the substituted alkynes. First, we carried out the palladium-catalyzed reaction of **1a** and **1b** with an internal alkyne, diphenylacetylene. No adduct was detected in the reaction mixture. In contrast to these palladium-catalyzed reactions, treatment of **1a** with 3-fold excess of diphenylacetylene in the presence of a catalytic amount of ethylenebis(triphenylphosphine)platinum(0) in a degassed sealed tube at 200 °C produced *cis*-1,4-dimethyl-1,2,3,4-tetraphenyl-1,4-disilacyclooct-2-ene (**2a**) in 49% yield, in addition to 47% of the unchanged reactant **1a** (Scheme 2). No other stereoisomer was detected in the reaction mixture. Similar reaction of **1b** with diphenylacetylene under the same conditions afforded *trans*-1,4-dimethyl-1,2,3,4-tetraphenyl-1,4-disilacyclooct-2-ene (**2b**) in 53% yield, as a single stereoisomer.

Similarly, the platinum-catalyzed reaction of the mixture of the reactants **1a** and **1b** (ratio of **1a** and **1b** = 3:7) with diphenylacetylene afforded the mixture of adducts **2a** and **2b** (ratio of **2a** and **2b** = 3:7). No other stereoisomer in the reaction mixture was detected by analytical GLC. The ratios of **1a** and **1b** and of **2a** and **2b** in the mixture were calculated to be the same value of 3:7 by ^{1}H NMR spectrometric analysis. All spectral data (^{1}H, ^{13}C, and ^{29}Si NMR) for the mixture of adducts **2a** and **2b** obtained from the platinum-catalyzed reaction of **1a** and **1b** with diphenylacetylene were also identical with those of the respective compounds formed from the reactions of pure **1a** and **1b** with diphenylacetylene under the same reaction conditions. It seems likely that diphenylacetylene inserts stereospecifically into the silicon−silicon bond of **1a** and **1b** in the presence of the platinum catalyst.

Next, we have also carried out the platinum-catalyzed reactions of **1a** and **1b** with 1-phenyl-1-propyne, 3-hexyne, and phenylacetylene, respectively (Scheme 2). It was also found that 1-phenyl-1-propyne and 3-hexyne insert stereospecifically into the silicon−silicon bond of **1a** and **1b** in the presence of the platinum catalyst. Thus, the reactions of **1a** and **1b** with 1-phenyl-1-propyne under the same conditions afforded **3a** in 65% yield and **3b** in 71% yield, respectively. Similar reaction of **1a** and **1b** with 3-hexyne gave **4a** in 55% yield and **4b** in 58% yield, respectively.

The stereospecificity of the reactions of 1,2-disilacyclohexanes (**1a**,**b**) with acetylenes is further demonstrated by determining the configuration and conformation of the typical reaction adducts **3a** and **3b**. The low-energy conformations were deduced by molecular modeling calculations and confirmed by various 2D NMR techniques, such as ^{1}H−^{1}H correlation spectroscopy (^{1}H−^{1}H COSY), ^{1}H−^{13}C one-bond correlation (HMQC), and ^{1}H−^{13}C multiple-bond correlation (HMBC), as well as NOESY for spatial relationships between protons. The carbon to carbon connectivities of **3a** and **3b** were confirmed by aid of DQF-COSY and HMQC. Three distinct phenyl, three methyl, and butylene groups, and a β-methylstyrene moiety which has quaternary carbons without protons are observed by aid of ^{13}C NMR and HMBC. The energy minimized structures of **3a** and **3b** with assignments of chemical shifts are shown in Figure 1.

The proton to carbon connectivities up to four bonds through quaternary carbons and silicon atoms were unambiguously deduced from an HMBC experiment. For *cis*-isomer **3a**, methyl protons at 0.39 ppm on Si-1 interact with the quaternary olefinic carbon at 152.28 ppm, with the quaternary carbon at 139.04 ppm of the phenyl group on Si-1, and also with the methylene carbon at 12.97 ppm of the butylene group. Thus, the methyl carbon at −2.74 ppm, the phenyl group containing the *ipso* carbon at 139.04 ppm, the methylene carbon at 12.97 ppm of the butylene group, and the olefinic carbon at 152.28 ppm are connected on the same Si-1. The methyl protons at 1.71 ppm interact strongly with the olefinic carbon at 152.28 ppm; thus they could be assigned to be connected to C-2. Also the methyl protons at 1.71 ppm interact with the quaternary carbons at 146.61 ppm of a phenyl group and at 139.04 ppm of another phenyl group, but not with *ipso* carbon at 140.40 ppm of the third phenyl group which interacts with methyl protons at −0.21 ppm. The methyl protons at −0.21 ppm also interact with olefinic carbon at 154.01 ppm, the carbon at 146.61 ppm, and the methylene carbon at 13.44 ppm of the butylene group. From these observations it is obvious that the methyl carbon at 1.73 ppm, the methylene carbon at 13.44 ppm, and the

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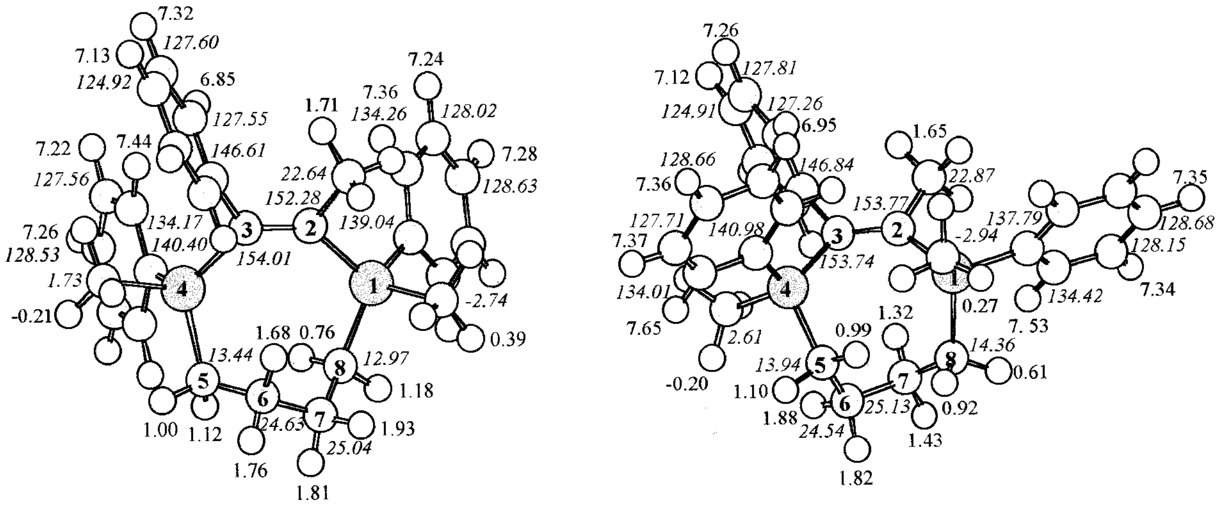
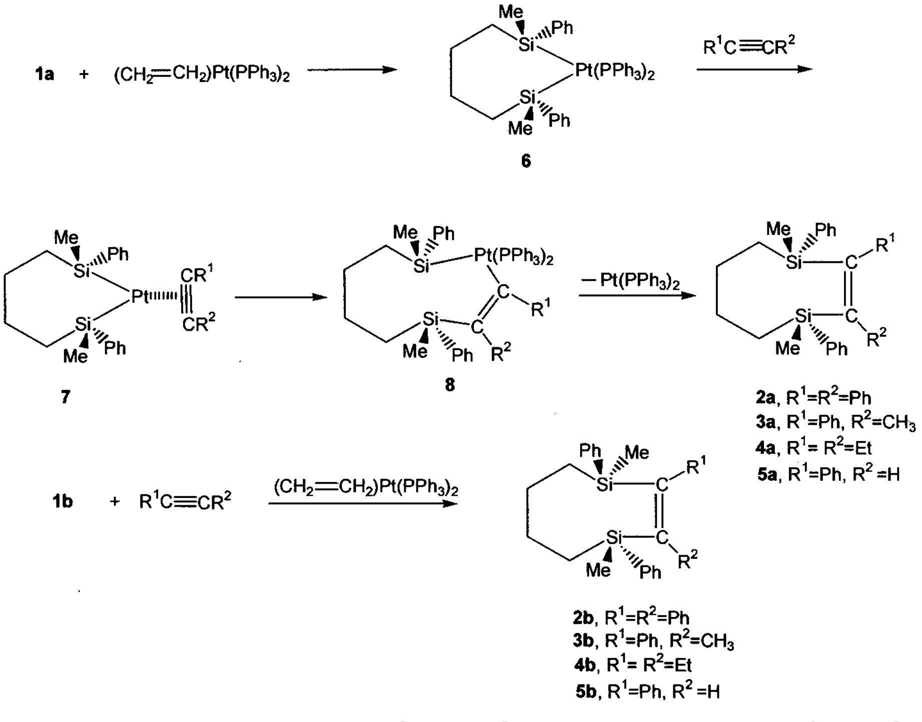


Figure 1. Energy-minimized structures of *cis*-1,2,4-trimethyl-1,3,4-triphenyl-1,4-disilacyclooct-2-ene, **3a** (left), and its *trans*-isomer **3b** (right). The carbon chemical shifts are shown in italics and the proton chemical shifts are shown in roman.

Scheme 2



olefinic carbon at 154.01 ppm connect to Si-4. For the connectivities and the assignment of chemical shift of the *trans*-isomer **3b** similar interpretations were done based on the NMR observations.

The proposed minimum-energy conformations of **3a** and **3b** were well matched with the observed NOESY interactions and the chemical anisotropic effects. Both conformations of eight-membered cyclic skeletons of **3a** and **3b** are pseudo-twist-boat conformations.[10] Even though these conformations appear not to be appreciably populated in cyclooctane, they seem to be stable conformations in these systems that contain a flat *cis*-1,2-disilylethylene moiety and sterically hindered phenyl and methyl groups.

Unfortunately direct NOE enhancement between two methyl protons −0.21 and 0.39 ppm on Si-4 and Si-1 of the *cis*-isomer **3a** was not observed; this observation is parallel with the proposed conformation in which two methyl groups are separated by as much as 6.72 Å, much longer than the 5−6 Å for NOE enhancement. However, two different *ortho* protons at 7.36 and 7.44 ppm of the phenyl groups on Si-1 and Si-4 are more closely located at 3.43 Å, and the strong NOE enhancement is observed in the NOESY spectrum. Similarly, strong NOE interaction between the *ortho* protons at 7.65 ppm of the phenyl group on Si-4 and methyl protons at 0.27 ppm on Si-1 in the *trans*-isomer **3b**, which are separated by 2.5 Å is observed (marked as an arrow in Figure 2), but the other pairs of methyl protons at −0.20 ppm and *ortho* protons at 7.53 ppm, which are separated by 6.38 Å, do not enhance the NOEs of each other. The representative NOESY spectrum of **3b** is presented in Figure 2. These results are wholly consistent with the structures proposed for **3a** and **3b**.

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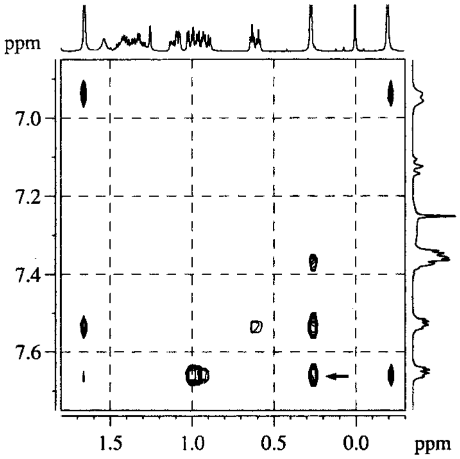

Figure 2. Part of the NOESY spectrum of *trans*-1,2,4-trimethyl-1,3,4-triphenyl-1,4-disilacyclooct-2-ene, **3b**.

The similar platinum-catalyzed reactions of **1a** and **1b** with phenylacetylene afforded *cis*- and *trans*-1,4-dimethyl-1,2,4-triphenyl-1,4-disilacyclooct-2-ene (**5a** and **5b**) in 12% and 15% yield, respectively. No other products were detected in the reaction mixture by analytical GLC. In these reactions, large amounts of the starting compounds **1a** (85%) and **1b** (82%) were recovered unchanged, respectively. The low yields of **5a** and **5b** may be ascribed to the platinum-catalyzed oligomerization of phenylacetylene. The quantitative formation of the trimer of phenylacetylene [*m*/*z* 306 (M^+)] in the reaction mixture was observed by analytical GLC and mass spectrometric analysis. In fact, no phenylacetylene used as a reactant was detected in the reaction mixture.

It was reported that octamethyl-1,2-disilacyclobutane and 1,1,2,2-tetramethyl-1,2-disilacyclopentane did not react with internal alkynes (except activated internal alkynes) bearing alkyl, aryl, or trimethylsilyl substituents in the presence of bis(triphenylphosphine)palladium dichloride.[2a,c] Terminal alkynes, however, reacted with these disilacycloalkanes. Recently we found that an internal alkyne bearing a phenyl group, diphenylacetylene, reacted with *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane in the presence of tetrakis(triphenylphosphine)palladium(0).[7] In our present reactions, it was observed that **1a**,**b** reacted with diphenylacetylene, 1-phenyl-1-propyne, 3-hexyne, and phenylacetylene in the presence of platinum catalyst, but not with dimethyl acetylenedicarboxylate, bis(trimethylsilyl)acetylene, and 1-phenyl-2-(trimethylsilyl)acetylene.

The formation of 3,4-benzo-1-platina-2,5-disilacyclopent-3-ene[11−13] has been observed in the reactions of 1,2-bis(dimethylsilyl)benzene with a platinum complex by Eaborn et al.[11] and Tanaka et al.[12] The formation of 3,4-benzo-2,2,5,5-tetraethyl-1-platina-2,5-disilacyclopent-3-ene has also been reported.[5e] In our case, the formation of 2-platina-1,3-disilacycloheptane (**6**) and the insertion of alkynes into a platinum−silicon bond in **6** giving complex **8** would proceed with retention of configuration, and the reductive elimination of the platinum species from **8** would also proceed stereospecifically to give 1,4-disilacyclooct-2-enes (Scheme 2). At present, however, no evidence for the stereochemistry of these reactions has yet been obtained.

In conclusion, Wurtz type condensation of 1,4-bis(chloromethylphenylsilyl)butane with lithium in the presence of a silyllithium catalyst afforded a 4:6 mixture of *cis*- and *trans*-1,2-dimethyl-1,2-phenyl-1,2-disilacyclohexanes **1a** and **1b** in high yields. The reactions of **1a** and **1b** with diphenylacetylene, 1-phenyl-1-propyne, 3-hexyne, and phenylacetylene in the presence of ethylenebis(triphenylphosphine)platinum(0) proceeded stereospecifically to give the respective adducts arising from insertion of a triple bond of alkyne into a silicon−silicon bond in **1a** and **1b**.

Experimental Section

General Procedure. All platinum-catalyzed reactions were carried out in a degassed sealed tube (1.0 cm × 15 cm). Yields of the products **2a**, **2b**, **3a**, **3b**, **4a**, **4b**, **5a**, and **5b** were calculated on the basis of the isolated products. The progress of the reaction was checked by gas chromatography with a flame ionization detector (FID) using a Hewlett-Packard 5890 instrument on a HP-1 capillary column (cross-linked 5% methylphenylsilicone, 25 m). NMR spectra were recorded on a Bruker Avance 400 and a Varian 500 spectrometer. Chemical shifts are given as δ values referenced in parts per million (ppm) from a solvent lock signal or tetramethylsilane (TMS) as internal standard. The 2D NMR experiments were performed on a Bruker Avance 400 spectrometer (400 MHz) equipped with a 5 mm QNP probe using standard Bruker pulse programs. The $^1H-^1H$ double quantum filtered correlation spectra (DQF-COSY) were acquired using a spectral width of 4006 Hz. For each t1 increment, 16 scans were accumulated and initial (t1, t2) matrixes of 256 × 1024 real data points were zero-filling to 1024 × 1024. The $^1H-^1H$ NOESY experiment (mixing time of 1 s) was recorded in the phase-sensitive mode with time proportional phase incrimination (TPPI). The acquisition and processing parameters were the same as in the DQF-COSY experiment. The one-bond $^1H-^{13}C$ heterocorrelation (phase-sensitive HMQC) spectra were obtained using a B_0 gradient pulse for the selection of ^1H coupled to ^{13}C carbons. For each t1 increment, 16 scans were accumulated with resolution by collecting 516 data sets. The F1 and F2 spectral widths were 19117 and 4084 Hz, respectively. The $^1H-^{13}C$ heteronuclear multiple-bond correlation (HMBC) spectra were recorded using a delay for the long-range coupling (mixing time of 50 ms). As in the HMQC experiment, B_0 gradient pulse was applied. Except for the sequence and the delays mentioned, all the parameters were the same as in the HMQC experiment. Infrared spectra were recorded on a Mattson Galaxy 7020A instrument. Low- and high-resolution mass spectra were measured on a Shimadzu QP5000 and JEOL model JMS-700 instrument. Pure *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane were separated by a TSA-SB2 spinning band type distillation column (Taika Kogyo). Column chromatography was performed by using Wakogel C-300 (WAKO). Preparative TLC was performed by using silica gel $60F_{254}$ (Merck). Elemental analyses were measured on a FISONS, EA1106. Tetrahydrofuran and ether used as a solvent were dried over sodium/benzophenone under a nitrogen atmosphere and distilled just before use. Carbon tetrachloride was dried over diphosphorus pentoxide and distilled before use.

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Molecular Modeling. Low-energy conformations were determined by molecular mechanics with Monte Carlo minimization procedures, using MMFF94 force field as implemented in Spartan program. The equilibrium geometry for the low energy conformations was calculated in AM1 level.

Preparation of *cis*- and *trans*-1,2-Dimethyl-1,2-Diphenyl-1,2-Disilacyclohexane. In a 250 mL three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 6.1 g (0.88 mol) of lithium, 0.4 g of chlorodimethylphenylsilane, and 150 mL of dry THF. The mixture was stirred to prepare dimethylphenylsilyllithium.[9] To this was added 65.2 g (0.18 mol) of 1,4-bis(chloromethylphenylsilyl)butane over a period of 6 h. After the mixture was stirred at room temperature for 15 h, 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 washed with water and dried over calcium chloride. The solvents were evaporated, and the residue was distilled under reduced pressure to give 26.7 g (0.09 mol) of a mixture of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane (50% yield) in a ratio of 4:6. Pure *cis*- and *trans*-compounds were separated by a spinning band type distillation column. For *cis*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane (**1a**): bp 132 °C/3 Torr; MS *m/z* 296 (M^+); IR 3067, 3021, 3006, 2953, 2897, 2855, 1427, 1252, 1115, 1067, 1017, 914, 882, 796, 733, 700 cm^{-1} ; ^1H NMR δ ($CDCl_3$) 0.40 (s, 6H, MeSi), 0.96−1.01 (m, 2H, CH_2Si), 1.16−1.21 (m, 2H, CH_2Si), 1.73−1.79 (m, 4H, CH_2), 7.19−7.26 (m, 6H, phenyl ring protons), 7.33−7.36 (m, 4H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −4.53 (MeSi), 15.48 (CH_2Si), 26.08 (CH_2), 127.64, 128.52, 134.45, 137.93 (phenyl ring carbons); ^{29}Si NMR δ ($CDCl_3$) −23.99; exact MS calcd for $C_{18}H_{24}Si_2$, 296.1417; found, 296.1420. Anal. Calcd for $C_{18}H_{24}Si_2$: C, 72.90; H, 8.16. Found: C, 72.78; H, 8.13. For **1b**: bp 142−143 °C/3 Torr; MS *m/z* 296 (M^+); IR 3067, 3019, 2951, 2895, 2851, 1427, 1248, 1188, 1109, 1065, 957, 882, 789, 733, 700 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.34 (s, 6H, MeSi), 1.08−1.11 (m, 4H, CH_2Si), 1.59−1.64 (m, 2H, CH_2), 1.96−2.01 (m, 2H, CH_2), 7.32−7.34 (m, 6H, phenyl ring protons), 7.48−7.50 (m, 4H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −4.92 (MeSi), 15.45 (CH_2Si), 26.06 (CH_2), 127.83, 128.58, 134.17, 138.38 (phenyl ring carbons); ^{29}Si NMR δ ($CDCl_3$) −23.92; exact MS calcd for $C_{18}H_{24}Si_2$, 296.1417; found, 296.1412. Anal. Calcd for $C_{18}H_{24}Si_2$: C, 72.90; H, 8.16. Found: C, 72.64; H, 8.22.

Platinum-Catalyzed Reaction of 1a with Diphenylacetylene. A mixture of 0.1480 g (0.50 mmol) of **1a**, 0.2673 g (1.50 mmol) of diphenylacetylene, and 0.0187 g (0.0250 mmol) of ethylenebis(triphenylphosphine)platinum(0) was heated in a degassed sealed tube at 200 °C for 24 h. The platinum species in the resulting mixture was removed by passing through a short silica gel column. Compound **2a** (0.1160 g, 49%) was isolated by column chromatography, together with **1a** (0.070 g, 47%). For **2a**: MS *m/z* 474 (M^+); IR 3069, 3016, 2922, 2853, 1594, 1438, 1427, 1251, 1107, 986, 841, 794, 698 cm^{-1}; ^1H NMR δ ($CDCl_3$), −0.05 (s, 6H, MeSi), 0.96−1.02 (m, 2H, CH_2Si), 1.30−1.41 (m, 2H, CH_2Si), 1.90−1.97 (m, 4H, CH_2), 6.53−6.68 (m, 4H, phenyl ring protons), 6.82−6.87 (m, 2H phenyl ring protons), 6.89−6.99 (m, 4H, phenyl ring protons), 7.24−7.30 (m, 6H, phenyl ring protons), 7.32−7.39 (m, 4H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −0.17 (MeSi), 12.92 (CH_2Si), 24.92 (CH_2), 124.44, 126.79, 127.55, 128.56, 128.73, 134.52, 139.22, 145.15 (phenyl ring carbons), 157.84 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$), −8.94; exact MS calcd for $C_{32}H_{34}Si_2$, 474.2200; found, 474.2203. Anal. Calcd for $C_{32}H_{34}Si_2$: C, 80.95; H, 7.22. Found: C, 80.98. H, 7.02.

Platinum-Catalyzed Reaction of 1b with Diphenylacetylene. A mixture of 0.1480 g (0.50 mmol) of **1b**, 0.2673 g (1.50 mmol) of diphenylacetylene, and 0.0187 g (0.0250 mmol) of ethylenebis(triphenylphosphine)platinum(0) was heated in a degassed sealed tube at 200 °C for 24 h. The platinum species in the resulting mixture was removed by passing through a short silica gel column. Compound **2b** (0.1250 g, 53%) was isolated by column chromatography, together with **1b** (0.0620 g, 42%). For **2b**: MS *m/z* 474 (M^+); IR 3069, 3019, 2920, 2857, 1597, 1485, 1427, 1251, 1109, 990, 874, 843, 799, 721, 698 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.06 (s, 6H, MeSi), 1.00−1.06 (m, 2H, CH_2Si), 1.13−1.19 (m, 2H, CH_2Si); 1.87−1.94 (m, 4H, CH_2), 6.66 (d, 4H, J = 7.5 Hz, phenyl ring protons), 6.75 (t, 2H, J = 7.5 Hz, phenyl ring protons), 6.86 (t, 4H, J = 7.5 Hz, phenyl ring protons), 7.28−7.32 (m, 6H, phenyl ring protons), 7.54−7.58 (m, 4H phenyl ring protons); ^{13}C NMR δ ($CDCl_3$), 0.21 (MeSi), 14.05 (CH_2Si), 25.08 (CH_2), 124.32, 126.76, 127.57, 128.48, 128.65, 134.39, 138.79, 145.28 (phenyl ring carbons), 158.31 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −7.95; exact MS calcd for $C_{32}H_{34}Si_2$, 474.2200; found, 474.2227. Anal. Calcd for $C_{32}H_{34}Si_2$: C, 80.95; H, 7.22. Found: C, 80.92; H, 7.11.

Platinum-Catalyzed Reaction of a Mixture of 1a,b with Diphenylacetylene. A mixture of 0.1480 g (0.50 mmol) of **1a**,**b** (3:7), 0.2673 g (1.50 mmol) of diphenylacetylene, and 0.0187 g (0.0250 mmol) of ethylenebis(triphenylphosphine)platinum(0) was heated in a degassed sealed tube at 200 °C for 24 h. The platium species in the resulting mixture was removed by passing through a short silica gel column. The adducts in the reaction mixture were isolated as a mixture of **2a**,**b** (3:7) (0.1240 g, 52%) by column chromatography, together with the unreacted mixture of **1a**,**b** (0.06 g, 41%). All spectral data obtained from the isolated mixture of **2a**,**b** were identical with those of the authentic samples.

Platinum-Catalyzed Reaction of 1a with 1-Phenyl-1-propyne. A mixture of 0.1480 g (0.50 mmol) of **1a**, 0.1742 g (1.50 mmol) of 1-phenyl-1-propyne, and 0.0187 g (0.0250 mmol) of ethylenebis(triphenylphosphine)platinum(0) was heated in a degassed sealed tube at 200 °C for 24 h. The platinum species in the resulting mixture was removed by passing through a short silica gel column. Compound **3a** (0.1350 g, 65%) was isolated by column chromatography, together with **1a** (0.0459 g, 31%). For **3a**: MS *m/z* 412 (M^+) IR 3067, 3017, 2921, 2855, 1595, 1480, 1427, 1253, 1108, 1033, 968, 877, 801, 721, 700 cm^{-1}; ^1H MNR δ ($CDCl_3$) −0.21 (s, 3H, MeSi), 0.39 (s, 3H, MeSi), 0.76 (dt, 1H, CH_2Si, J = 15.7 Hz, J = 4.0 Hz), 1.00 (ddd, 1H, CH_2Si, J = 15.2 Hz, J = 6.5 Hz, J = 2.0 Hz), 1.09−1.21 (m, 2H, CH_2Si), 1.65−1.70 (m, 1H, CH_2), 1.71 (s, 3H, $CH_3C{=}$), 1.75−1.84 (m, 2H, CH_2), 1.91−1.95 (m, 1H, CH_2), 6.82 (d, 1H, phenyl ring proton, J = 5.9 Hz), 6.89 (d, 1H, phenyl ring proton, J = 5.9 Hz), 7.13 (t, 1H, phenyl ring proton, J = 7.4 Hz), 7.20−7.23 (m, 2H, phenyl ring protons), 7.24−7.33 (m, 6H, phenyl ring protons), 7.36 (dd, 2H, phenyl ring protons, J = 7.7 Hz, J = 1.5 Hz), 7.44 (dd, 2H, phenyl ring protons, J = 7.8 Hz, J = 1.3 Hz); ^{13}C NMR δ ($CDCl_3$), −2.74 (MeSi), 1.73 (MeSi), 12.97, 13.44 (CH_2Si), 22.64 (CH_3), 24.63, 25.04 (CH_2), 124.92, 127.55, 127.56, 127.60, 128.02, 128.53, 128.63, 134.17, 134.26, 139.04, 140.40, 146.61 (phenyl ring carbons), 152.28, 154.01 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$), −8.83, −7.30; exact MS calcd for $C_{27}H_{32}Si_2$, 412.2043; found, 412.2039. Anal. Calcd for $C_{27}H_{32}Si_2$: C, 78.57; H, 7.82. Found: C, 78.62; H, 7.83.

Platinum-Catalyzed Reaction of 1b with l-Phenyl-l-propyne. A mixture of 0.1480 g (0.50 mmol) of **1b**, 0.1742 g (1.50 mmol) of l-phenyl-l-propyne, and 0.0187 g (0.0250 mmol) of ethylenebis(triphenylphosphine)platinum(0) was heated in a degassed sealed tube at 200 °C for 24 h. The platinum species in the resulting mixture was removed by passing through a short silica gel column. Compound **3b** (0.1460 g, 71%) was isolated by column chromatography, together with **1b** (0.0385 g, 26%). For **3b**: MS *m/z* 412 (M^+); IR 3067, 3017, 2917, 2857, 1595, 1483, 1427, 1252, 1109, 1032, 968, 874, 808, 721, 700 cm^{-1}; ^1H MNR δ ($CDCl_3$) −0.20 (s, 3H, MeSi), 0.27 (s, 3H, MeSi), 0.61 (dt, 1H, CH_2Si, J = 16.0 Hz, J = 4.0 Hz), 0.89−1.03 (m, 2H, CH_2Si), 1.07−1.13 (m, 1H, CH_2Si), 1.28−1.47 (m, 2H, CH_2), 1.65 (s, 3H, $CH_3C{=}$), 1.80−1.92 (m, 2H, CH_2), 6.95 (d, 2H, phenyl ring protons, J = 7.0 Hz), 7.12 (t, 1H, phenyl ring protons, J = 7.5 Hz), 7.22−7.30 (m, 2H, phenyl ring

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protons); 7.33−7.40 (m, 6H, phenyl ring protons); 7.52−7.54 (m, 2H, phenyl ring protons), 7.64−7.66 (m, 2H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$), −2.94 (SiMe), 2.61 (SiMe) 13.94, 14.36 (CH$_2$Si), 22.87 (CH$_3$), 24.54, 25.13 (CH$_2$), 124.91, 127.26, 127.71, 127.81, 128.15, 128.66, 128.68, 134.01, 134.42, 137.79, 140.98, 146.84 (phenyl ring carbons), 153.74, 153.77 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$), −8.00, −4.96; exact MS calcd for C$_{27}$H$_{32}$Si$_2$, 412.2043; found, 412.2040. Anal. Calcd for C$_{27}$H$_{32}$Si$_2$: C, 78.57; H, 7.82. Found: C, 78.63; H, 7.85.

Platinum-Catalyzed Reaction of 1a with 3-Hexyne. A mixture of 0.1480 g (0.50 mmol) of **1a**, 0.2054 g (2.50 mmol) of 3-hexyne, and 0.0187 g (0.0250 mmol) of ethylenebis(triphenylphosphine)platinum(0) was heated in a degassed sealed tube at 200 °C for 24 h. The platinum species in the resulting mixture was removed by passing through a short silica gel column. Compound **4a** (0.1042 g, 55%) was isolated by column chromatography, together with **1a** (0.0606 g, 41%). For **4a**: MS *m*/*z* 378 (M$^+$); IR 3068, 3017, 2961, 2927, 2870, 1451, 1427, 1330, 1251, 1109, 950, 865, 795, 721, 698 cm^{-1}; ^{1}H MNR δ (CDCl$_3$) 0.33 (s, 6H, MeSi), 0.75−0.83 (m, 4H, CH$_2$Si), 1.01 (t, 6H, C*H*$_3$CH$_2$, *J* = 7.5 Hz), 1.67−1.71 (m, 4H, CH$_2$), 2.44 (q, 4H, *CH*$_2$CH$_3$, *J* = 7.5 Hz), 7.16−7.23 (m, 2H, phenyl ring protons), 7.30−7.38 (m, 6H, phenyl ring protons), 7.45−7.56 (m, 2H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$), −0.42 (MeSi), 14.03 (*C*H$_3$CH$_2$), 15.54 (CH$_2$Si), 24.66 (*C*H$_2$CH$_3$), 26.33 (CH$_2$), 127.41, 128.30, 134.17, 140.66 (phenyl ring carbons), 153.83 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$), −8.25; exact MS calcd for C$_{24}$H$_{34}$Si$_2$, 378.2199; found, 378.2201. Anal. Calcd for C$_{24}$H$_{34}$Si$_2$: C, 76.12; H, 9.05. Found: C, 75.95; H, 9.20.

Platinum-Catalyzed Reaction of 1b with 3-Hexyne. A mixture of 0.1480 g (0.50 mmol) of **1b**, 0.2054 g (2.50 mmol) of 3-hexyne, and 0.0187 g (0.0250 mmol) of ethylenebis(triphenylphosphine)platinum(0) was heated in a degassed sealed tube at 200 °C for 24 h. The platinum species in the resulting mixture was removed by passing through a short silica gel column. Compound **4b** (0.1098 g, 58%) was isolated by column chromatography, together with **1b** (0.0577 g, 39%). For **4b**: MS *m*/*z* 378 (M$^+$); IR 3066, 3016, 2959, 2926, 2869, 1449, 1427, 1330,1251, 1107, 1000, 970, 874, 804, 722, 700 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.26 (s, 6H, MeSi), 0.76−0.82 (m, 2H, CH$_2$Si), 0.87−0.94 (m, 2H, CH$_2$Si), 1.01 (t, 6H, C*H*$_3$CH$_2$, *J* = 7.5 Hz), 1.50−1.56 (m, 4H, CH$_2$), 2.25 (dq, 2H, *CH*$_2$CH$_3$, *J* = 15.0 Hz, *J* = 7.5 Hz), 2.54 (dq, 2H, *CH*$_2$CH$_3$, *J* = 15.0 Hz, *J* = 7.5 Hz), 7.32−7.34 (m, 6H, phenyl ring protons), 7.52−7.54 (m, 4H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −0.11 (MeSi), 14.78 (*C*H$_3$CH$_2$), 15.57 (CH$_2$Si), 24.69 (*C*H$_2$CH$_3$), 26.49 (CH$_2$), 127.59, 128.43, 134.23, 140.48 (phenyl ring carbons), 154.40 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −6.86; exact MS calcd for C$_{24}$H$_{34}$Si$_2$: 378.2199; found, 378.2202. Anal. Calcd for C$_{24}$H$_{34}$Si$_2$: C, 76.12; H, 9.05. Found: C, 75.94; H, 9.25.

Platinum-Catalyzed Reaction of 1a with Phenylacetylene. A mixture of 0.1480 g (0.50 mmol) of **1a**, 0.2553 g (2.50 mmol) of phenylacetylene, and 0.0187 g (0.0250 mmol) of ethylenebis(triphenylphosphine)platinum(0) was heated in a degassed sealed tube at 200 °C for 24 h. The platinum species in the resulting mixture was removed by passing through a short silica gel column. Compound **5a** (0.0239 g, 12%) was isolated by column chromatography and preparative TLC, together with **1a** (0.1258 g, 85%). For **5a**: MS *m*/*z* 398 (M$^+$); IR 3067, 3016, 2916, 2856, 1594, 1486, 1427, 1251, 1109, 908, 872, 815, 778, 740, 724, 698 cm^{-1}; ^{1}H MNR δ (CDCl$_3$) 0.19 (s, 3H, MeSi), 0.34 (s, 3H, MeSi), 0.83−0.85 (m, 1H, CH$_2$Si), 0.86−0.91 (m, 2H, CH$_2$Si), 1.17−1.23 (m, 1H, CH$_2$Si), 1.60−1.86 (m, 4H, CH$_2$), 6.78 (s, 1H, HC=C), 7.01 (dd, 2H, phenyl ring protons, *J* = 6.5 Hz, *J* = 1.5 Hz), 7.12−7.20 (m, 3H, phenyl ring protons), 7.26−7.35 (m, 6H, phenyl ring protons), 7.50−7.54 (m, 4H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −2.28 (MeSi), 0.68 (MeSi), 11.62, 13.06 (CH$_2$Si), 24.87, 24.99 (CH$_2$), 125.93, 126.82, 127.71, 127.80, 127.82, 128.68, 128.80, 134.10, 134.21, 138.84, 139.74, 147.29 (phenyl ring carbons), 149.52, 163.63 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −11.77, −8.19; exact MS calcd for C$_{26}$H$_{30}$Si$_2$, 398.1900; found, 398.1887. Anal. Calcd for C$_{26}$H$_{30}$Si$_2$: C, 78.33; H, 7.58. Found: C, 78.25; H, 7.82.

Platinum-Catalyzed Reaction of 1b with Phenylacetylene. A mixture of 0.1480 g (0.50 mmol) of **1b**, 0.2553 g (2.50 mmol) of phenylacetylene, and 0.0187 g (0.0250 mmol) of ethylenebis(triphenylphosphine)platinum(0) was heated in a degassed sealed tube at 200 °C for 24 h. The platinum species in the resulting mixture was removed by passing through a short silica gel column. Compound **5b** (0.0299 g, 15%) was isolated by column chromatography and preparative TLC, together with **1b** (0.1214 g, 82%). For **5b**: MS *m*/*z* 398 (M$^+$); IR 3067, 3016, 2922, 2855, 1595, 1486, 1427, 1251, 1109, 908, 872, 817, 776, 724, 698 cm^{-1}; ^{1}H MNR δ (CDCl$_3$) 0.19 (s, 3H, MeSi), 0.36 (s, 3H, MeSi), 0.96−1.13 (m, 4H, CH$_2$Si), 1.62−1.78 (m, 4H, CH$_2$), 6.94 (s, 1H, HC=C), 7.09 (dd, 2H, phenyl ring protons, *J* = 7.8 Hz, *J* = 1.5 Hz), 7.15−7.22 (m, 3H, phenyl ring protons), 7.32−7.39 (m, 6H, phenyl ring protons), 7.57−7.62 (m, 4H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −1.00 (MeSi), 0.01 (MeSi), 12.62, 13.74 (CH$_2$Si), 24.58, 24.67 (CH$_2$), 126.01, 126.87, 127.73, 127.78, 127.82, 128.78, 128.88, 133.93, 134.24, 138.99, 139.76, 148.28 (phenyl ring carbons), 149.51, 162.47 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −11.29, −7.31; exact MS calcd for C$_{26}$H$_{30}$Si$_2$, 398.1900; found, 398.1886. Anal. Calcd for C$_{26}$H$_{30}$Si$_2$: C, 78.33; H, 7.58. Found: C, 78.28; H, 7.65.

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