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Platinum- and nickel-catalyzed reactions of 1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane with alkynes

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Abstract

The platinum-catalyzed reactions of *cis*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane (**1a**) with terminal acetylenes such as phenylacetylene and 1-hexyne in a degassed sealed tube at 150 °C for 24 h afforded *cis*-1,4-dimethyl-1,2,4-triphenyl-1,4-disilacyclohept-2-ene (**2a**) and *cis*-2-*n*-butyl-1,4-dimethyl-1,4-diphenyl-1,4-disilacyclohept-2-ene (**3a**), respectively, arising from insertion of a triple bond in the acetylenes into a silicon–silicon bond. Similar reactions of *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane (**1b**) with phenylacetylene and 1-hexyne gave *trans*-1,4-dimethyl-1,2,4-triphenyl-1,4-disilacyclohept-2-ene (**2b**) and *trans*-2-*n*-butyl-1,4-dimethyl-1,4-diphenyl-1,4-disilacyclohept-2-ene (**3b**), respectively. The platinum-catalyzed reactions of **1a** and **1b** with di-substituted acetylenes such as diphenylacetylene, 1-phenyl-1-propyne, and 3-hexyne gave the respective *cis*- and *trans*-1,4-dimethyl-1,4-diphenyl-1,4-disilacyclohept-2-ene derivatives with high stereospecificity. The nickel-catalyzed reactions of **1a** and **1b** with di-substituted acetylenes also proceeded with high stereospecificity to give the adducts as observed in the platinum-catalyzed reactions.

Keywords: Platinum; Nickel; Catalyzed reaction; Disilacyclopentane

1. Introduction

The stereochemistry on the reactions of the silicon center using optical active silicon compounds has been extensively investigated by Sommer [1] and by Corriu et al. [2]. Many papers concerning the stereochemistry of the silicon compounds have been published to date. However, little interest has been shown in the stereochemistry of the disilanylene-containing cyclic compounds involving *cis*- and *trans*-configuration. The first synthesis and some reactions of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane were reported in 1969 [3,4]. In 1975, it was reported that the palladium-catalyzed reactions of *cis*- and *trans*-1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane with alkynes proceeded stereospecifically to give the respective 1,4-disilacyclooct-2-ene derivatives [5].

We have recently found that the palladium-catalyzed reactions of *cis*- and *trans*-3,4-benzo-1,2-di(*tert*-butyl)-1,2-dimethyl-1,2-disilacyclobut-3-ene with alkynes such as phenylacetylene and 1-hexyne proceed with high stereospecificity to give the respective adducts arising from insertion of a triple bond of the alkyne into the silicon–silicon bond in the starting disilacyclobutenes [4a]. We have also demonstrated that *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentene in the presence of the palladium catalyst react stereospecifically with phenylacetylene to give the adducts, *cis*- and *trans*-1,4-disilacyclohept-2-ene derivatives [4b]. It is of interest to us to investigate the stereochemistry of the reactions of *cis*- and *trans*-disilanylene containing cyclic compounds with unsaturated substrates in the presence of a catalytic amount of the transition–metal complex other than the palladium complex. In this paper, we report the platinum- and nickel-catalyzed reactions of

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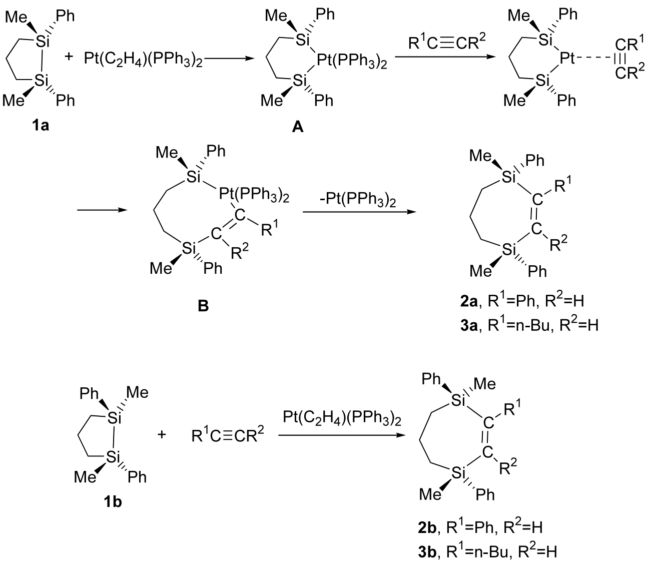
cis- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane with alkynes, which proceed with high stereospecificity to give the adducts.

2. Results and discussion

First, we carried out the platinum-catalyzed reactions of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacylopentane (**1a** and **1b**), which were obtained as reported previously [4b], with mono-substituted acetylenes. When **1a** was treated with phenylacetylene in the presence of a catalytic amount of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in a sealed glass tube at 150 °C for 24 h, *cis*-1,4-dimethyl-1,2,4-triphenyl-1,4-disilacyclohept-2-ene (**2a**), arising from insertion of a triple bond in phenylacetylene into the silicon–silicon bond of **1a**, was obtained in 24% yield, in addition to 66% of the unchanged starting compound **1a** (Scheme 1). All spectral data for **2a** were identical with those of the authentic sample [4b] obtained from the palladium-catalyzed reaction of **1a** with phenylacetylene. The similar platinum-catalyzed reaction of *trans*-isomer **1b** with phenylacetylene in a sealed glass tube under the same conditions gave *trans*-1,4-disilacyclohept-2-ene (**2b**) in 22% yield, as a single stereoisomer, along with 65% of the unchanged starting compound **1b**. Again, all spectral data for **2b** were identical with those of the authentic sample reported previously [4b]. Products **2a** and **2b** were isolated from the reaction mixture by column chromatography.

Similar platinum-catalyzed reactions of **1a** and **1b** with 1-hexyne afforded the corresponding *cis*- and *trans*-2-*n*-butyl-1,4-dimethyl-1,4-diphenyl-1,4-disilacyclohept-2-ene (**3a** and **3b**) in 89 and 89% yields, respectively. In both reactions, no other isomers were detected by spectrometric analysis. The structures of **3a** and **3b** were verified by mass and ^{1}H-, ^{13}C- and ^{29}Si-NMR spectrometric analysis, as well as by elemental analysis. We attempted to confirm the configurations of **3a** and **3b** by NOE-FID difference experiments at 500 MHz. Unfortunately, saturation of the methyl group on one silicon atom in the 1,4-disilacyclohept-2-ene ring for **3a** did not lead to enhancement of the methyl group on the other silicon atom. Presumably, two methyl groups attached to the different silicon atoms are located apart from each other. However, for **3a**, irradiation of the *ortho* protons (7.54–7.56 ppm) of the phenyl group on the Si4 atom in the 1,4-disilacyclohept-2-ene ring resulted in a strong enhancement of the ortho protons (7.47–7.49 ppm) of the phenyl group on the Si1 atom, as well as the methyl protons (0.36 ppm), methylene protons (1.10–1.30 ppm) on the Si4 atom and a proton (6.73 ppm) on sp^2 carbon.[1] No enhancement of the methyl protons on the Si1 atom was observed. Similar irradiation of the *ortho* protons at 7.47–7.49 ppm of the phenyl group on the Si1 atom caused enhancement of the *ortho* protons (7.54–7.56 ppm) of the phenyl ring on the Si4 atom, and also the methyl protons (0.44 ppm) on the Si1 atom and methylene protons (0.90–1.06 ppm) on the Si1 atom, and two methylene protons (1.17–1.40 and 2.24 ppm) of the butyl group. These results clearly indicate that compound **3a** must have the *cis* configuration. Although this method could not be used for identification of isomer **3b**, because the *ortho* protons of the phenyl groups on both silicon atoms at the 1- and 4-positions completely overlapped each other, we assigned isomer **3b** as the *trans* form.



Scheme 1.

Scheme 1 shows a mechanism for the stereospecific production of *cis*-1,4-disilacyclohept-2-enes **2a** and **3a** using *cis*-form **1a** as an example. The formation of **2a** and **3a** may be explained in terms of insertion of a platinum species into a silicon–silicon bond in **1a** to give a 2-platina-1,3-disilacyclohexane (**A**) with retention of the configuration, followed by coordination of an alkyne to the platinum atom in the intermediate **A** [4,6–8]. Insertion of the alkyne on the platinum atom into a silicon–platinum bond affords stereospecifically 2-platina-1,5-disilacyclooct-3-ene (**B**). Finally, reductive elimination of the platinum species gives the 1,4-disilacyclohept-2-ene **2a** and **3a** with retention of the configuration.

Compounds **1a** and **1b** also reacted stereospecifically with di-substituted acetylenes to give the respective adducts. When the reaction of **1a** with diphenylacetylene was carried out in a sealed tube at 150 °C, *cis*-1,4-dimethyl-1,2,3,4-tetraphenyl-1,4-disilacyclohept-

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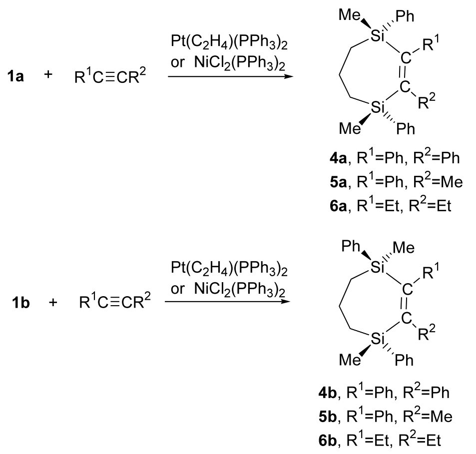
[1] In the ^{1}H-NMR spectrum for **3a**, the ortho protons of two phenyl groups on the Si1 and Si4 atom appear at 7.47–7.49 and 7.54–7.56 ppm, respectively, and can be definitely assigned by NOE-FID difference experiments at 500 MHz.



Scheme 2.

2-ene (**4a**) in 93% yield as white crystals, in addition to 4% of the unreacted starting compound **1a** (Scheme 2). No other volatile products were detected by GLC. The similar platinum-catalyzed reaction of **1b** with diphenylacetylene gave *trans*-1,4-dimethyl-1,2,3,4-tetraphenyl-1,4-disilacyclohept-2-ene (**4b**) in 89% yield, along with 10% of the recovered starting compound **1b**. The products of **4a** and **4b** could readily be isolated by column chromatography. All spectral data for **4a** and **4b** were identical with those of the authentic sample obtained from palladium-catalyzed reaction. Molecular structures of **4a** and **4b** were determined by X-ray crystallographic analysis as reported previously [4b].

The similar reaction of **1a** with 1-phenyl-1-propyne at 150 °C for 24 h gave *cis*-1,2,4-trimethyl-1,3,4-triphenyl-1,4-disilacyclohept-2-ene (**5a**) in 57% yield, along with a 35% yield of **1a**. No other stereoisomer was detected in the reaction mixture. Treatment of **1b** with 1-phenyl-1-propyne under the same conditions afforded *trans*-1,2,4-trimethyl-1,3,4-triphenyl-1,4-disilacyclohept-2-ene (**5b**) in 44% yield, in addition to a 50% yield of **1b**. Again, the reaction proceeded with high stereospecificity to give only one isomer.

With 3-hexyne under the same conditions, compound **1a** reacted stereospecifically to give a single isomer, *cis*-2,3-diethyl-1,4-dimethyl-1,4-diphenyl-1,4-disilacyclohept-2-ene (**6a**) in 60% yield along with 35% of the starting compound **1a**. No other isomers were detected in the reaction mixture either by spectrometric analysis or GLC analysis. Treatment of **1b** with 3-hexyne under the same conditions afforded *trans*-2,3-diethyl-1,4-dimethyl-1,4-diphenyl-1,4-disilacyclohept-2-ene (**6b**) in 61% yield in addition to a 37% yield of unreacted compound **1b**. Products **6a** and **6b** were readily isolated by column chromatography and their structures were confirmed by spectrometric analysis, as well as by elemental analysis.

Recently, we have reported that the platinum-catalyzed reactions of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane with disubstituted acetylenes such as diphenylacetylene, 1-phenyl-1-propyne, and 3-hexyne proceeded with high stereospecificity to give the respective adducts, *cis*- and *trans*-1,4-disilacyclooct-2-enes. In these reactions, no stereoisomers were detected in the reaction mixtures [4c]. Since the platinum-catalyzed reactions of **1a** and **1b** with diphenylacetylene afforded **4a** and **4b** stereospecifically, as demonstrated above, it seems likely that the reactions of **1a** and **1b** with disubstituted acetylenes, such as 1-phenyl-1-propyne and 3-hexyne also proceed stereospecifically to give the respective adducts.

Next, we investigated the nickel-catalyzed reactions of **1a** and **1b** with acetylenes. When the reactions of **1a** and **1b** with mono-substituted acetylenes such as phenylacetylene and 1-hexyne in the presence of dichlorobis(triphenylphosphine)nickel(II) was carried out in a sealed glass tube at 150 °C for 24 h, the starting compounds **1a** and **1b** were recovered unchanged. No adducts arising from insertion of a triple bond into the silicon–silicon bond of **1a** and **1b** as observed in the platinum-catalyzed reactions were detected. Treatment of **1a** with phenylacetylene under the same conditions again afforded no volatile product containing the silicon atoms, although a product that has the molecular weight calculated for a trimer of phenylacetylene was detected in the reaction mixture by mass spectrometry. In the nickel-catalyzed reactions, presumably the rate of oligomerization of the mono-substituted acetylenes is faster than that of the reaction with the starting compound **1a**. With di-substituted acetylenes, however, **1a** and **1b** react in the presence of the nickel catalyst to give the addition products. The reactions proceed with the same fashion as that of the platinum-catalyzed reactions, in which 1,4-dimethyl-1,4-diphenyl-1,4-disilacyclohept-2-ene derivatives are produced as the sole product. Thus treatment of **1a** with diphenylacetylene in the presence of the nickel catalyst in a sealed glass tube at 150 °C for 24 h gave **4a** in 59% yield, in addition to 36% of the starting compound **1a**. Similarly, the reaction of **1b** with diphenylacetylene under the same conditions again afforded only product **4b** in 41% yield along with 58% of the starting compound **1b**.

Treatment of **1a** with 1-phenyl-1-propyne afforded **5a** in 20% yield, in addition to 75% of the starting compound **1a**, while **1b** with 1-phenyl-1-propyne produced **5b** in 15% yield, along with a 80% yield of **1b**. Since the rate of oligomerization of 1-phenyl-1-propyne in the presence of the nickel catalyst is fast, most of the starting material was recovered unchanged. Compounds **1a** and **1b** also reacted with 3-hexyne to give the disilacyclohept-2-ene derivatives. Thus, the reaction of **1a** with 3-hexyne in a sealed glass tube at 150 °C for 24 h gave **6a** in 14% yield, along with an 80% yield of **1a**. A similar reaction of **1b** with 3-hexyne produced **6b** in 18% yield, along with a 75% yield of the starting compound **1b**.

In conclusion, the reaction pattern of the platinum- and nickel-catalyzed reactions of **1a** and **1b** with acetylenes are similar to that of the palladium-catalyzed reactions as reported previously. The platinum-catalyzed reactions of **1a** and **1b** with acetylenes afforded 1:1 adducts with high stereospecificity, arising from insertion of a carbon–carbon triple bond of the acetylenes into a silicon–silicon bond in **1a** and **1b**. The nickel-catalyzed reactions of **1a** and **1b** with mono-substituted acetylenes gave no adducts, however, with disubstituted acetylenes **1a** and **1b** reacted stereospecifically to give the disilacyclohept-2-ene derivatives.

3. Experimental

All platinum- and nickel-catalyzed reactions of compound **1** with alkynes were carried out in a degassed sealed glass tube. 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 JNM-LA300 spectrometer and JNM-LA500 spectrometer. Infrared spectra were recorded on a JEOL Model JIR-DIAMOND20 infrared spectrophotometer. Low-resolution mass spectra were measured on a JEOL Model JMS-700 instrument.

*3.1. Platinum-catalyzed reaction of **1a** with phenylacetylene*

A mixture of 0.0720 g (0.255 mmol) of **1a**, 0.0827 g (0.811 mmol) of phenylacetylene, and 0.0092 g (0.0123 mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in a sealed glass tube was heated at 150 °C for 24 h. The mixture was passed through a short silica gel column to remove platinum species and then analyzed by GLC as being **2a** (24% yield) and the starting compound **1a** (66%). Compound **2a** was isolated by silica gel column chromatography. All spectral data for **2a** were identical with those of an authentic sample [4b].

*3.2. Platinum-catalyzed reaction of **1b** with phenylacetylene*

A mixture of 0.0712 g (0.252 mmol) of **1b**, 0.0637 g (0.625 mmol) of phenylacetylene, and 0.0085 g (0.0114 mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in a sealed glass tube was heated at 150 °C for 24 h. The mixture was passed through a short silica gel column to remove platinum species and then analyzed by GLC as being **2b** (22% yield) and the starting compound **1b** (65%). Compound **2b** was isolated by silica gel column chromatography. All spectral data for **2b** were identical with those of an authentic sample [4b].

*3.3. Platinum-catalyzed reaction of **1a** with 1-hexyne*

A mixture of 0.0673 g (0.239 mmol) of **1a**, 0.0608 g (0.740 mmol) of 1-hexyne, and 0.0081 g (0.0108 mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in a sealed glass tube was heated at 150 °C for 24 h. The mixture was passed through a short silica gel column to remove platinum species and then analyzed by GLC as being **3a** (89% yield) and the starting compound **1a** (5%). Compound **3a** was isolated by silica gel column chromatography; MS *m/z* 364 [M$^+$]; IR 3066, 3048, 2954, 2925, 2856, 1427, 1249, 1108, 908, 786, 734, 711, 698 cm^{-1}; ^{1}H-NMR δ(CDCl$_3$) 0.36 (s, 3H, MeSi), 0.44 (s, 3H, MeSi), 0.83 (t, 3H, CH$_3$, $J = 7.3$ Hz), 0.90–1.41 (m, 8H, CH$_2$), 1.77–1.86 (m, 2H, CH$_2$), 2.24(t, 2H, CH$_2$, $J = 7.3$ Hz), 6.73 (s, 1H, HC=C), 7.30–7.37 (m, 6H, phenyl ring protons), 7.47–7.49 (m, 2H, phenyl ring protons on the Si1), 7.54–7.56 (m, 2H, phenyl ring protons on the Si4); ^{13}C-NMR δ(CDCl$_3$) −2.95, −1.87 (MeSi), 13.92, 16.42, 17.34, 17.53, 22.53, 31.50, 41.35 (CH$_2$, *n*-Bu), 127.64, 127.72, 128.71, 128.74, 133.94, 134.11 (phenyl ring carbons), 143.06, 163.57 (olefinic carbons); ^{29}Si-NMR δ(CDCl$_3$) −12.0, −7.0. Anal. Calc. for $C_{23}H_{32}Si_2$: C, 75.75; H, 8.84. Found: C, 75.82; H, 8.78%.

*3.4. Platinum-catalyzed reaction of **1b** with 1-hexyne*

A mixture of 0.1340 g (0.475 mmol) of **1b**, 0.1139 g (1.39 mmol) of 1-hexyne, and 0.0160 g (0.0214 mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in a sealed glass tube was heated at 150 °C for 24 h. The mixture was passed through a short silica gel column to remove platinum species and then analyzed by GLC as being **3b** (89% yield) and the starting compound **1b** (6%). Compound **3b** was isolated by silica gel column chromatography; MS *m/z* 364 [M$^+$]; IR 3068, 2925, 2861, 1457, 1427, 1249, 1108, 908, 844, 779, 736, 700 cm^{-1}; ^{1}H-NMR δ(CDCl$_3$) 0.33 (s, 3H, MeSi), 0.40 (s, 3H, MeSi), 0.89 (t, 3H, CH$_3$, $J = 7.3$ Hz), 0.90–1.54 (m, 8H, CH$_2$), 1.73–1.85 (m, 2H, CH$_2$), 2.26–2.31 (m, 2H, CH$_2$), 6.79 (s, 1H, HC=C), 7.39–7.41 (m, 6H, phenyl ring protons), 7.56–7.61 (m, 4H, phenyl ring protons); ^{13}C-NMR δ(CDCl$_3$) −2.70, −1.81 (MeSi), 13.93, 16.81, 17.52, 17.82, 22.57, 31.61, 41.58 (CH$_2$, *n*-Bu), 127.70, 127.74, 128.74, 128.82, 133.95, 134.21, 138.52, 139.55 (phenyl ring carbons), 143.03, 163.41 (olefinic carbons); ^{29}Si-NMR δ(CDCl$_3$) −11.8, −6.5. Anal. Calc. for $C_{23}H_{32}Si_2$: C, 75.75; H, 8.84. Found: C, 75.35; H, 8.82%.

3.5. Platinum-catalyzed reaction of **1a** with diphenylacetylene

A mixture of 0.0361 g (0.128 mmol) of **1a**, 0.0603 g (0.338 mmol) of diphenylacetylene, and 0.0040 g (0.0054 mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in a sealed glass tube was heated at 150 °C for 24 h. After treatment of the resulting solution with a short column, the mixture was analyzed by GLC as being **4a** (93% yield) and the starting compound **1a** (4%). Compound **4a** was isolated by silica gel column chromatography. All spectral data for **4a** were identical with those of an authentic sample [4b].

3.6. Platinum-catalyzed reaction of **1b** with diphenylacetylene

A mixture of 0.0890 g (0.316 mmol) of **1b**, 0.0805 g (0.452 mmol) of diphenylacetylene, and 0.0119 g (0.0159 mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in a sealed glass tube was heated at 150 °C for 24 h. After treatment of the resulting solution with a short column, the mixture was analyzed by GLC as being **4b** (89% yield) and the starting compound **1b** (10%). Compound **4b** was isolated by silica gel column chromatography. All spectral data for **4b** were identical with those of an authentic sample [4b].

3.7. Platinum-catalyzed reaction of **1a** with 1-phenyl-1-propyne

A mixture of 0.0609 g (0.216 mmol) of **1a**, 0.1005 g (0.865 mmol) of 1-phenyl-1-propyne, and 0.0082 g (0.0110 mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in a sealed glass tube was heated at 150 °C for 24 h. The mixture was passed through a short silica gel column to remove platinum species and then analyzed by GLC as being **5a** (57% yield) and the starting compound **1a** (35%). Compound **5a** was isolated by silica gel column chromatography; MS m/z 398 [M$^+$]; IR 3066, 3018, 2913, 1596, 1483, 1427, 1251, 1108, 908, 813, 782, 734, 700 cm^{-1}; ^{1}H-NMR δ(CDCl$_3$) 0.13 (s, 3H, MeSi), 0.48 (s, 3H, MeSi), 1.00–1.06 (m, 1H, CH$_2$), 1.12–1.17 (m, 1H, CH$_2$), 1.28–1.37 (m, 2H, CH$_2$), 1.64 (s, 3H, CH$_3$), 1.75–1.91 (m, 2H, CH$_2$), 6.81 (d, 2H, phenyl ring protons, $J = 7.3$ Hz), 7.09 (t, 1H, phenyl ring proton, $J = 7.3$ Hz), 7.19 (t, 2H, phenyl ring protons, $J = 7.3$ Hz), 7.25–7.39 (m, 6H, phenyl ring protons), 7.43–7.45 (m, 2H, phenyl ring protons), 7.55–7.58 (m, 2H, phenyl ring protons); ^{13}C-NMR δ(CDCl$_3$) -3.28, -2.18 (MeSi), 17.03, 17.18, 17.54 (CH$_2$), 21.77 (CH$_3$), 124.95, 127.47, 127.69, 127.79, 127.84, 128.57, 128.82, 134.02, 134.32, 138.64, 138.87, 145.31, 152.04, 157.64 (phenyl ring and olefinic carbons); ^{29}Si-NMR δ(CDCl$_3$) -9.0, -6.0. Anal. Calc. for $C_{26}H_{30}Si_2$: C, 78.33; H, 7.58. Found: C, 78.44; H, 7.53%.

3.8. Platinum-catalyzed reaction of **1b** with 1-phenyl-1-propyne

A mixture of 0.1529 g (0.543 mmol) of **1b**, 0.1405 g (1.21 mmol) of 1-phenyl-1-propyne, and 0.0181 g (0.0242 mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in a sealed glass tube was heated at 150 °C for 24 h. The mixture was passed through a short silica gel column to remove platinum species and then analyzed by GLC as being **5b** (44% yield) and the starting compound **1b** (50%). Compound **5b** was isolated by silica gel column chromatography; MS m/z 398 [M$^+$]; IR 3068, 3108, 2956, 2917, 2862, 1594, 1483, 1425, 1247, 1108, 906, 819, 779, 740, 703 cm^{-1}; ^{1}H-NMR δ(CDCl$_3$) 0.04 (s, 3H, MeSi), 0.43 (s, 3H, MeSi), 1.12–1.19 (m, 4H, CH$_2$), 1.66–1.72 (m, 2H, CH$_2$), 1.72 (s, 3H, CH$_3$), 6.92 (d, 2H, phenyl ring protons, $J = 7.0$ Hz), 7.12 (t, 1H, phenyl ring proton, $J = 7.0$ Hz), 7.24 (t, 2H, phenyl ring protons, $J = 7.0$ Hz), 7.35–7.42 (m, 6H, phenyl ring protons), 7.57–7.62 (m, 4H, phenyl ring protons); ^{13}C-NMR δ(CDCl$_3$) -2.37, -1.52 (MeSi), 17.10, 17.54, 17.93 (CH$_2$), 21.96 (CH$_3$), 125.04, 127.60, 127.62, 127.88, 127.93, 128.67, 128.88, 134.11, 134.49, 138.37, 138.63, 145.53, 152.11, 157.50 (phenyl ring and olefinic carbons); ^{29}Si-NMR δ(CDCl$_3$) -8.3, -5.4. Anal. Calc. for $C_{26}H_{30}Si_2$: C, 78.33; H, 7.58. Found: C, 78.11; H, 7.53%.

3.9. Platinum-catalyzed reaction of **1a** with 3-hexyne

A mixture of 0.0911 g (0.323 mmol) of **1a**, 0.0783 g (0.955 mmol) of 3-hexyne, and 0.0098 g (0.0131 mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in a sealed glass tube was heated at 150 °C for 24 h. The mixture was passed through a short silica gel column to remove platinum species and then analyzed by GLC as being **6a** (60% yield) and the starting compound **1a** (35%). Compound **6a** was isolated by silica gel column chromatography; MS m/z 364 [M$^+$]; IR 3068, 2962, 2925, 2871, 1427, 1251, 1108, 904, 811, 781, 738 cm^{-1}; ^{1}H-NMR δ(CDCl$_3$) 0.43 (s, 6H, MeSi), 0.89 (t, 6H, CH_3CH$_2$, $J = 7.3$ Hz), 0.94 (ddd, 2H, CH$_2$Si, $^2J = 14.0$ Hz, $^3J = 7.0$ Hz, $^3J = 7.0$ Hz), 1.19 (ddd, 2H, CH$_2$Si, $^2J = 14.0$ Hz, $^3J = 7.0$ Hz, $^3J = 7.0$ Hz), 1.63 (dtt, 1H, CH$_2$, $^2J = 14.0$ Hz, $^3J = 7.0$ Hz, $^3J = 7.0$ Hz), 1.72 (dtt, 1H, CH$_2$, $^2J = 14.0$ Hz, $^3J = 7.0$ Hz, $^3J = 7.0$ Hz), 2.27–2.39 (m, 4H, CH$_2$), 7.33–7.35 (m, 6H, phenyl ring protons), 7.51–7.54 (m, 2H, phenyl ring protons); ^{13}C-NMR δ(CDCl$_3$) -2.36 (MeSi), 15.41 (CH$_2$Si), 16.81 (CH$_2$), 17.55, 26.01 (Et), 127.60, 128.56, 134.21, 139.84 (phenyl ring carbons), 156.27 (olefinic carbons); ^{29}Si-NMR δ(CDCl$_3$) -7.6. Anal. Calc. for $C_{23}H_{32}Si_2$: C, 75.75; H, 8.84. Found: C, 75.68; H, 8.84%.

3.10. Platinum-catalyzed reaction of **1b** with 3-hexyne

A mixture of 0.0670 g (0.238 mmol) of **1b**, 0.0592 g (0.722 mmol) of 3-hexyne, and 0.0083 g (0.0111 mmol) of (η^2-ethylene)bis(triphenylphosphine)platinum(0) in a sealed glass tube was heated at 150 °C for 24 h. After treatment of the resulting mixture with a short column, the mixture was analyzed by GLC as being **6b** (61% yield) and the starting compound **1b** (37%). Compound **6b** was isolated by silica gel column chromatography; MS m/z 364 [M$^+$]; IR 3066, 2962, 2927, 2869, 1427, 1251, 1108, 908, 813, 781, 723, 700 cm^{-1}; ^{1}H-NMR δ(CDCl$_3$) 0.40 (s, 6H, MeSi), 1.01 (t, 6H, CH_3CH$_2$, $J = 7.6$ Hz), 1.08 (dt, 2H, CH$_2$Si, $^2J = 15.3$ Hz, $^3J = 6.1$ Hz), 1.52–1.64 (m, 4H, CH$_2$), 2.27 (q, 2H, CH$_2$, $J=7.6$ Hz), 2.49 (q, 2H, CH$_2$, $J = 7.6$ Hz), 7.32–7.38 (m, 6H, phenyl ring protons), 7.52–7.55 (m, 2H, phenyl ring protons); ^{13}C-NMR δ(CDCl$_3$) −1.98 (MeSi), 15.27 (CH$_2$Si), 16.96 (CH$_2$), 17.86, 26.13 (Et), 127.62, 128.57, 134.22, 139.73 (phenyl ring carbons), 156.05 (olefinic carbons); ^{29}Si-NMR δ(CDCl$_3$) −7.3. Anal. Calc. for $C_{23}H_{32}Si_2$: C, 75.75; H, 8.84. Found: C, 75.71; H, 8.87%.

3.11. Nickel-catalyzed reaction of **1a** with diphenylacetylene

A mixture of 0.0629 g (0.223 mmol) of **1a**, 0.1159 g (0.650 mmol) of diphenylacetylene, and 0.0077 g (0.0118 mmol) of dichlorobis(triphenylphosphine)nickel(II) in a sealed glass tube was heated at 150 °C for 24 h. After treatment of the resulting solution with a short column, the mixture was analyzed by GLC as being **4a** (59% yield) and the starting compound **1a** (36%). Compound **4a** was isolated by silica gel column chromatography. All spectral data for **4a** were identical with those of an authentic sample obtained from the platinum-catalyzed reaction.

3.12. Nickel-catalyzed reaction of **1b** with diphenylacetylene

A mixture of 0.0588 g (0.209 mmol) of **1b**, 0.0460 g (0.258 mmol) of diphenylacetylene, and 0.0068 g (0.0104 mmol) of dichlorobis(triphenylphosphine)nickel(II) in a sealed glass tube was heated at 150 °C for 24 h. After treatment of the resulting solution with a short column, the mixture was analyzed by GLC as being **4b** (41% yield) and the starting compound **1b** (58%). Compound **4b** was isolated by silica gel column chromatography. All spectral data for **4b** were identical with those of an authentic sample obtained from the platinum-catalyzed reaction.

3.13. Nickel-catalyzed reaction of **1a** with 1-phenyl-1-propyne

A mixture of 0.0900 g (0.319 mmol) of **1a**, 0.0742 g (0.639 mmol) of 1-phenyl-1-propyne, and 0.0105 g (0.0161 mmol) of dichlorobis(triphenylphosphine)nickel(II) in a sealed glass tube was heated at 150 °C for 24 h. The mixture was passed through a short silica gel column to remove nickel species and then analyzed by GLC as being **5a** (20% yield) and the starting compound **1a** (75%). Compound **5a** was isolated by silica gel column chromatography. All spectral data for **5a** were identical with those of an authentic sample obtained from the platinum-catalyzed reaction.

3.14. Nickel-catalyzed reaction of **1b** with 1-phenyl-1-propyne

A mixture of 0.0771 g (0.273 mmol) of **1b**, 0.0467 g (0.402 mmol) of 1-phenyl-1-propyne, and 0.0091 g (0.0139 mmol) of dichlorobis(triphenylphosphine)nickel(II) in a sealed glass tube was heated at 150 °C for 24 h. The mixture was passed through a short silica gel column to remove nickel species and then analyzed by GLC as being **5b** (15% yield) and the starting compound **1b** (80%). Compound **5b** was isolated by silica gel column chromatography. All spectral data for **5b** were identical with those of an authentic sample obtained from the platinum-catalyzed reaction.

3.15. Nickel-catalyzed reaction of **1a** with 3-hexyne

A mixture of 0.0833 g (0.295 mmol) of **1a**, 0.0830 g (1.01 mmol) of 3-hexyne, and 0.0090 g (0.0137 mmol) of dichlorobis(triphenylphosphine)nickel(II) in a sealed glass tube was heated at 150 °C for 24 h. The mixture was passed through a short silica gel column to remove nickel species and then analyzed by GLC as being **6a** (14% yield) and the starting compound **1a** (80%). Compound **6a** was isolated by silica gel column chromatography. All spectral data for **6a** were identical with those of an authentic sample obtained from the platinum-catalyzed reaction.

3.16. Nickel-catalyzed reaction of **1b** with 3-hexyne

A mixture of 0.0830 g (0.294 mmol) of **1b**, 0.0981 g (1.20 mmol) of 3-hexyne, and 0.0084 g (0.0129 mmol) of dichlorobis(triphenylphosphine)nickel(II) in a sealed glass tube was heated at 150 °C for 24 h. After treatment of the resulting mixture with a short column, the mixture was analyzed by GLC as being **6b** (18% yield) and the starting compound **1b** (75%). Compound **6b** was isolated by silica gel column chromatography. All spectral data for **6b** were identical with those of an authentic sample obtained from the platinum-catalyzed reaction.

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