

Silicon–carbon unsaturated compounds

LIV: Nickel-catalyzed reactions of

3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene with alkynes [☆]

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Abstract

The nickel-catalyzed reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1**) with disubstituted acetylenes have been investigated. Treatment of **1** with 3-hexyne and diphenylacetylene at 150°C gave two types of adducts: 5,6-benzo-1,4-disilacyclohexa-2,5-dienes and 5,6-benzo-1,2-disilacyclohexa-3,5-dienes. With methylphenylacetylene, **1** afforded a 5,6-benzo-1,4-disilacyclohexa-2,5-diene and 5,6-benzo-1,2-disilacyclohexa-3,5-diene, together with a small amount of the other isomer. The reaction of **1** with phenyl(trimethylsilyl)acetylene produced 5,6-benzo-1,1,4,4-tetraethyl-3-phenyl-2-trimethylsilyl-1,4-disilacyclohexa-2,5-diene and 4,5-benzo-1,1,3,3-tetraethyl-2-[phenyl(trimethylsilyl)methylene]-1,3-disilacyclopent-4-ene (**10**). Similar reaction of **1** with 1-(trimethylsilyl)hexyne also afforded 5,6-benzo-3-butyl-1,1,4,4-tetraethyl-2-trimethylsilyl-1,4-disilacyclohexa-2,5-diene and 4,5-benzo-2-[butyl(trimethylsilyl)methylene]-1,1,3,3-tetraethyl-1,3-disilacyclopent-4-ene (**12**). A vinylidene carbene–nickel complex is proposed for the formation of **10** and **12**, as a key intermediate.

Keywords: Silicon; Transition metals; *o*-Quinodisilane; Nickel

1. Introduction

3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1**) shows interesting behavior towards transition metal complexes [1–6]. When **1** is heated to reflux in the presence of a catalytic amount of (η^2 -ethylene)bis(triphenylphosphine)platinum(0) in benzene, an isomerization product, *cis*-4,5-benzo-1,1,3-triethyl-2-methyl-1,3-disilacyclopent-4-ene is obtained as a major product, together with a small amount of 1-diethylphenylsilyl-2-(diethylsilyl)benzene [4]. The reaction of **1** with a catalytic amount of tetrakis(triphenylphosphine)palladium(0) in benzene in a sealed tube at 150°C produces a dimer, 4,5,7,8-dibenzo-1,1,2,2,3,3,6,6-octaethyl-1,2,3,6-tetrasila-4,7-diene as the sole product [5]. Similar treatment of **1** in the presence of a tetrakis(triethylphosphine)nickel(0) catalyst in benzene at 150°C gives

1-diethylphenylsilyl-2-(diethylsilyl)benzene with an almost quantitative yield [2].

The transition-metal-catalyzed reactions of **1** with alkenes and ketones affords various types of the product. The products obtained from these reactions depend highly on the nature of the transition metal complex used as the catalyst. For examples, the platinum- and palladium-catalyzed reaction of **1** with benzaldehyde produces a C=O insertion product, 5,6-benzo-1,1,4,4-tetraethyl-2-oxa-3-phenyl-1,4-disilacyclohex-5-ene while, with ketones, **1** affords no adducts [4,5]. The nickel-catalyzed reactions of **1** with enolizable ketones, however, produce addition products. Similar nickel-catalyzed reactions of non-enolizable ketones proceed with deoxygenation of ketones to give a nickel–carbene species [3].

With alkynes, such as phenylacetylene, 3-hexyne, and diphenylacetylene, both platinum- and palladium-catalyzed reactions give 5,6-benzo-1,4-disilacyclohexa-2,5-diene derivatives [4,5]. It is of interest to us to investigate the nickel-catalyzed reactions of **1** with alkynes and to learn whether or not the reactions pro-

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[☆] Dedicated, with all best wishes, to Professor Hideki Sakurai on the occasion of his retirement.

ceed with the same fashion as that of the platinum- and palladium-catalyzed reactions. In this paper we report the reactions of **1** with monosubstituted and disubstituted acetylenes in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0).

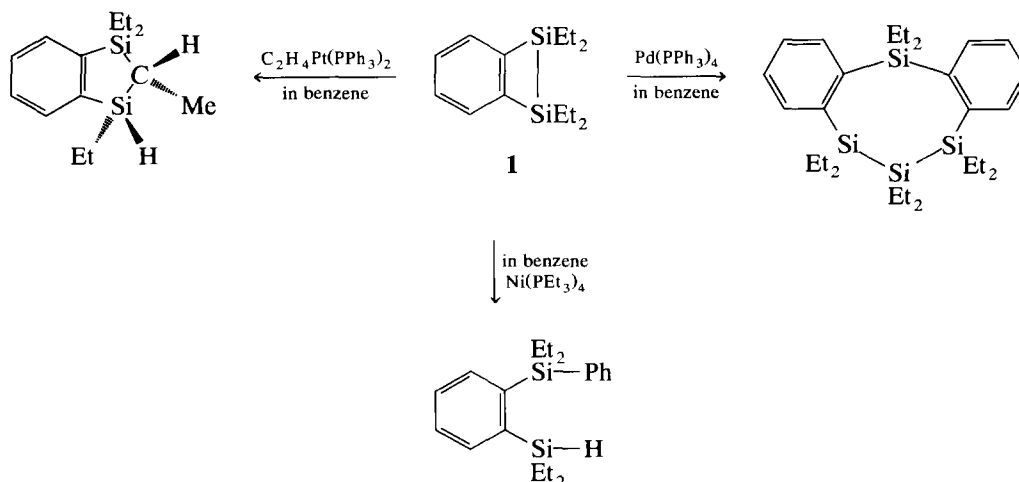
2. Results and discussion

Since the platinum- and palladium-catalyzed reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1**) with monosubstituted alkynes readily proceeded to give 5,6-benzo-1,4-disilacyclohexa-2,5-dienes [4,5], we first examined the reactions of **1** with monosubstituted acetylenes such as 1-hexyne and phenylacetylene. The reaction of **1** with 1-hexyne in the presence of a tetrakis(triethylphosphine)nickel(0) catalyst in a sealed degassed tube at 150°C, however, produced no adduct arising from insertion of a triple bond into a silicon–silicon bond of **1** as observed in the platinum- and palladium-catalyzed reactions. Treatment of **1** with phenylacetylene under the same conditions again afforded no volatile silicon-containing products, although a product that has the molecular weight calculated for a trimer of phenylacetylene was detected in the reaction mixture by gas chromatographic mass spectrometry. Presumably, the rate of oligomerization of the monosubstituted acetylene is faster than that of the reaction with the starting compound **1**. With disubstituted acetylenes, **1** reacts smoothly in the presence of the nickel catalyst to give addition products in high yields. The reactions, however, proceed with a different fashion from that of the platinum- and palladium-catalyzed reactions, in which 5,6-benzo-1,4-disilacyclohexa-2,5-diene derivatives are produced as the sole product. Thus treatment of **1** with 3-hexyne in the presence of the nickel(0) catalyst in a sealed tube at 150°C gave 5,6-benzo-1,1,2,3,4,4-hexaethyl-1,4-disilacyclohexa-2,5-diene (**3**), and 5,6-benzo-1,1,2,2,3,4-hexaethyl-1,2-disilacyclohexa-3,5-diene (**4**) arising from formal inser-

tion of a carbon–carbon triple bond into a silicon–phenylene bond with 36% and 29% yields, in addition to 12% of the starting compound **1**. Similar reaction of **1** with diphenylacetylene under the same conditions again afforded two isomers, 5,6-benzo-1,1,4,4-tetraethyl-2,3-diphenyl-1,4-disilacyclohexa-2,5-dienes (**5**) and 5,6-benzo-1,1,2,2-tetraethyl-3,4-diphenyl-1,2-disilacyclohexa-3,5-diene (**6**) with 27% and 72% yields respectively. In both cases, two isomers could readily be isolated by medium pressure liquid chromatography (MPLC) as a pure form.

The reaction of **1** with methylphenylacetylene in the presence of the nickel(0) catalyst again afforded two types of product, 5,6-benzo-1,1,4,4-tetraethyl-3-methyl-2-phenyl-1,4-disilacyclohexa-2,5-diene (**7**) and 5,6-benzo-1,1,2,2-tetraethyl-3-methyl-4-phenyl-1,2-disilacyclohexa-3,5-diene (**8**), arising from formal insertion of a triple bond in the acetylene into the silicon–silicon bond and the silicon–phenylene bond of **1** with 51% and 36% yields. Compounds **7** and **8** could readily be separated by preparative high performance liquid chromatography (HPLC). Gas–liquid chromatography (GLC) analysis of **8** thus obtained shows a single peak, but its ¹H NMR spectrum reveals the presence of 20% of impurity. The mass spectrum of **8** reveals a parent ion at *m/z*-364 corresponding to the calculated molecular weight of the adduct. No other molecular ion is observed at all, even in the measurement at high intensity. Although **8** could not be separated from this impurity, its structure was confirmed by spectrometric analysis. As judged by mass, and ¹H and ¹³C NMR spectra and also elemental analysis of the mixture, the impurity might be a regioisomer of **8**, 5,6-benzo-1,1,4,4-tetraethyl-4-methyl-3-phenyl-1,2-disilacyclohexa-3,5-diene.

All spectral data obtained from products **3** and **5** were identical with those of the authentic samples reported previously [4]. The structures of **4**, **6** and **7** were confirmed by mass, IR, and ¹H, ¹³C and ²⁹Si NMR spectrometric analysis, as well as by elemental analysis (see Section 3). The structure of **8** was verified by



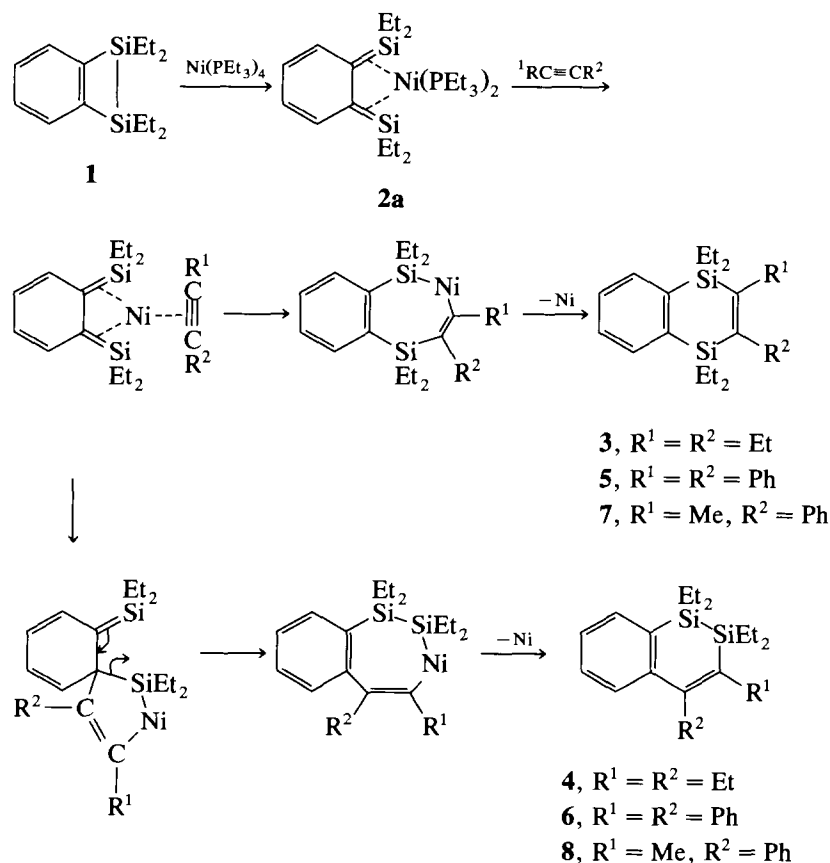
spectrometric analysis of the mixture. The location of a methyl and phenyl group on the disilacyclohexadienyl ring was determined by nuclear Overhauser effect-free induction decay difference experiments. Thus irradiation of the ethylsilyl protons results in the strong enhancement of the methyl protons at 1.72 ppm.

The formation of **3–8** may be best understood in terms of the reaction of *o*-quinodisilane (**2a**) with acetylenes as shown in Scheme 1. The formal [4 + 2] cycloaddition would produce products **3**, **5** and **7**, while [2 + 2] cycloaddition of a silicon–carbon double bond with acetylenes, followed by ring enlargement to 2,3-benzo-1-nickela-4,5-disilacyclohepta-2,6-dienes and then reductive elimination of the nickel species would yield products **4**, **6** and **8**.

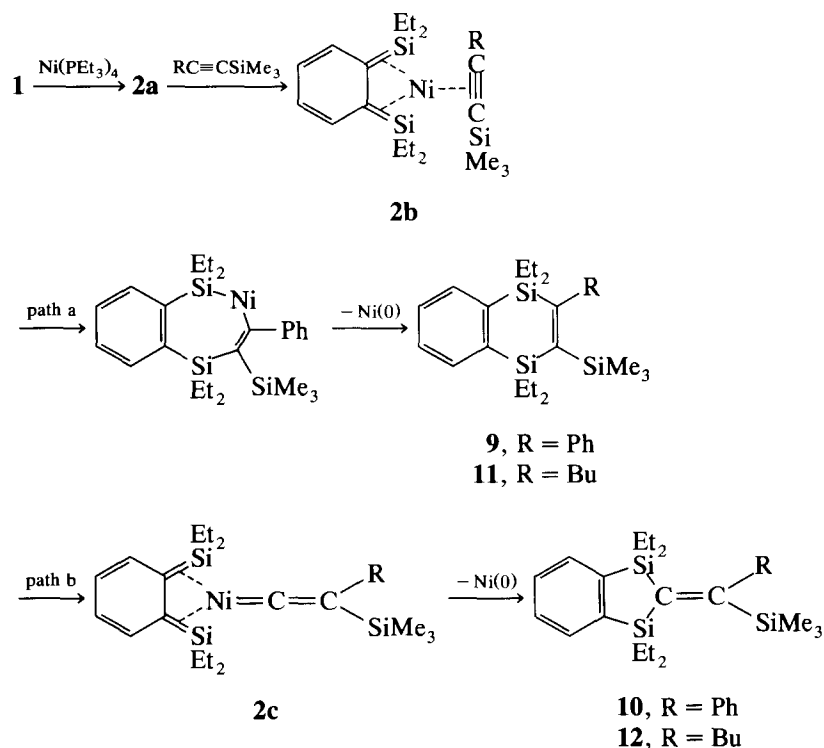
For the formation of **4**, **6**, and **8**, an alternative mechanism which involves direct insertion of the nickel species into a silicon–phenylene bond and then insertion of a triple bond of the acetylene coordinated to the nickel atom of this intermediate might be considered [1]. However, the insertion of the nickel species into the silicon–phenylene bond seems to be difficult because of the steric effect. At present, the mechanism involving the formal [2 + 2] cycloaddition of *o*-quinodisilane (**2a**)

and acetylenes seems to be more attractive for the formation of products **4**, **6** and **8**.

Phenyl(trimethylsilyl)acetylene also reacted with **1** under the same conditions to give a mixture of two isomers. One isomer, 5,6-benzo-1,1,4,4-tetraethyl-3-phenyl-2-trimethylsilyl-1,4-disilacyclohexa-2,5-diene (**9**) whose spectral data were identical with those of an authentic sample was obtained with a 44% yield [4]. The other isomer which was formed with a 27% yield was identified as 4,5-benzo-1,1,3,3-tetraethyl-2-[phenyl(trimethylsilyl)methylene]-1,3-disilacyclopent-4-ene (**10**) (Scheme 2). No product derived from formal insertion of a triple bond into a silicon–phenylene bond in **1** was detected in the mixture. The structure of **10** was confirmed by spectroscopic and elemental analysis. The ^{29}Si NMR spectrum of **10** reveals resonances at -0.48 and 3.12 ppm, attributed to two silicon atoms in the 4,5-benzo-2-methylene-1,3-disilacyclopent-4-ene ring, as well as a resonance at -7.89 ppm due to trimethylsilyl silicon. On the basis of the results obtained from a series of the study on the benzodisilacyclobutene **1**, the resonances of the silicon atoms in the 5,6-benzo-1,4-disilacyclohexa-2,5-diene rings always appear at -19 – -12 ppm in their ^{29}Si NMR spectra,



Scheme 1.



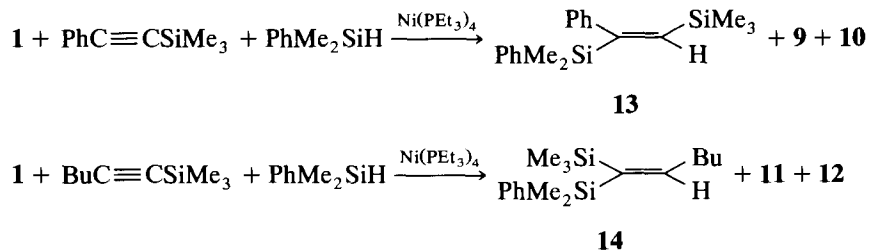
Scheme 2.

but the resonances of the silicon atoms in the 4,5-benzo-1,3-disilacyclopent-4-ene rings appear in the lower field (-0.5 – 4 ppm) than those of the 5,6-benzo-1,4-disilacyclohexa-2,5-dienes. Therefore we assigned **10** as a 4,5-benzo-1,3-disilacyclopent-4-ene derivative.

Similar treatment of **1** with 1-(trimethylsilyl)hexyne [7] again afforded two products, 5,6-benzo-3-butyl-1,1,4,4-tetraethyl-2-trimethylsilyl-1,4-disilacyclohexa-2,5-diene (**11**) and 4,5-benzo-2[butyl(trimethylsilyl)methylene]-1,1,3,3-tetraethyl-1,3-disilacyclopent-4-ene (**12**), analogous to **9** and **10**, with 58% and 29% yields respectively. The ^{29}Si NMR spectrum for **11** shows three resonances at -17.35 , -12.58 and -12.30 ppm. Two resonances at -17.35 and -12.30 ppm were assigned as two silicon atoms of the benzodisilacyclohexadiene ring and a resonance at -12.58 ppm as a trimethylsilyl silicon atom by ^1H - ^{29}Si COSY NMR technique. Product **12** reveals resonances at -1.82 and 1.21 ppm, attributed to two silicon atoms in the benzo-disilacyclopentene ring and a resonance at -7.80 ppm

due to a trimethylsilyl silicon atom in its ^{29}Si NMR spectrum.

The formation of **10** and **12** is quite interesting, because a 1,2-trimethylsilyl shift must be involved during the reaction (path b in Scheme 2). The silyl shift probably occurs on the nickel atom in acetylene-coordinated *o*-quinodisilane-nickel complex **2b**, giving the nickel-carbene complex (**2c**). The reductive elimination of a nickel(0) species from **2c** would produce product **10** and **12**. A similar trimethylsilyl shift in the alkynes coordinated to the transition metal has been observed in the reaction of chloro(triisopropylphosphine)rhodium(I) with trimethylsilyl-substituted alkynes [8,9]. Such a silyl shift has also been found in the reaction of dodecamethyl-2,7,9,14-tetraoxa-1,3,6,8,10,13-hexasilacyclopentadeca-4,11-diyne and dodecamethyl-2,7,12-trioxa-1,3,6,8,11,13-hexasilacyclopentadeca-4,9,14-triyne with the transition metal complexes, such as Cr(CO)_6 , Mo(CO)_6 , W(CO)_6 and Fe(CO)_9 [10,11]. If **2c** is produced as a reactive intermediate in this reaction, a



Scheme 3.

vinylidene carbene might be trapped by the use of an appropriate trapping agent. Therefore we attempted to trap the carbene species, but unfortunately all attempts to trap the intermediate were unsuccessful. When the nickel-catalyzed reaction of **1** with phenyl(trimethylsilyl)acetylene was carried out in the presence of dimethylphenylsilane as a carbene trapping agent under the same conditions, a product, (*E*)-1-(dimethylphenylsilyl)-1-phenyl-2-(trimethylsilyl)ethylene (**13**) [12], arising from hydrosilation of dimethylphenylsilane with phenyl(trimethylsilyl)acetylene was obtained with a 27% yield, together with product **9** (41% yield) and **10** (24% yield), but no vinylidene carbene insertion product was detected (Scheme 3). A similar reaction of **1** with 1-(trimethylsilyl)hexyne in the presence of dimethylphenylsilane, again afforded a hydrosilation product, (*E*)-1-dimethylphenylsilyl-1-(trimethylsilyl)hex-1-ene (**14**) with a 79% yield, in addition to **11** (62% yield) and **12** (30% yield). In the presence of cyclohexene as a trapping agent, the reaction of **1** with phenyl(trimethylsilyl)acetylene gave no vinylidene carbene adduct, but **9** and **10** were obtained with 43% and 24% yields, respectively. The reductive elimination of the nickel species from **2c** leading to **10** and **12** would be the most favorable pathway.

In conclusion, the nickel-catalyzed reactions of 3,4-benzodisilacyclobutene **1** with 3-hexyne, diphenylacetylene, and methylphenylacetylene gave two types of product, 5,6-benzo-1,4-disilacyclohexa-2,5-dienes and 5,6-benzo-1,2-disilacyclohexa-3,5-dienes. With phenyl(trimethylsilyl)acetylene and 1-(trimethylsilyl)hexyne, **1** afforded the respective 4,5-benzo-2-methylene-1,3-disilacyclopent-4-ene derivatives, in addition to 5,6-benzo-1,4-disilacyclohexa-2,5-dienes.

3. Experimental details

3.1. General procedure

All nickel-catalyzed reactions of **1** with alkynes were carried out in a degassed sealed glass tube (1.0 cm × 10 cm). Yields of the products were determined by analytical GLC with the use of tridecane as an internal standard. NMR spectra were recorded on a JEOL model EX-270 spectrometer. IR spectra were determined on a Perkin-Elmer 1600 Fourier transform IR 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 instrument (Japan Analytical Industry Co., Ltd.).

3.2. Materials

3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene **1** was prepared as reported previously [13].

3.3. Reaction of **1** with 3-hexyne

A mixture of 0.354 g (1.43 mmol) of **1**, 0.196 g (2.38 mmol) of 3-hexyne, and 0.040 g (0.075 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150°C for 24 h. The mixture was analyzed by GLC as being **3** (36% yield), **4** (29% yield), and 12% of the starting compound **1**. After the mixture was treated with a short silica gel column to remove nickel species from the reaction mixture, **3** and **4** were isolated by MPLC.

4: Mass spectroscopy (MS) m/z 330 (M^+). IR: ν 3047, 2956, 2871, 1455, 1416, 1232, 1126, 1006, 959, 770, 699 cm^{-1} . ^1H NMR (CDCl_3): δ 0.57–1.12 (m, 26H, EtSi, CH_3), 2.23 (q, 2H, CH_2 , $J = 7.6$ Hz), 2.65 (q, 2H, CH_2 , $J = 7.6$ Hz), 7.06–7.35 (m, 4H, phenylene ring protons) ppm. ^{13}C NMR (CDCl_3): δ 2.88, 3.42, 8.92, 9.15 (EtSi), 13.91, 14.90 (CH_3), 25.02, 25.86 (CH_2), 125.3, 127.1, 128.9, 133.5, 134.6, 135.0 (phenylene ring carbons), 148.5, 151.5 (olefinic carbons) ppm. ^{29}Si NMR (CDCl_3): δ -21.67, -19.20 ppm. Anal. Found: C, 72.60; H, 10.36. $\text{C}_{20}\text{H}_{34}\text{Si}_2$ Calc.: C, 72.65; H, 10.36%.

All spectral data for **3** were identical with those of an authentic sample [4].

3.4. Reaction of **1** with diphenylacetylene

A mixture of 0.405 g (1.63 mmol) of **1**, 0.427 g (2.40 mmol) of diphenylacetylene and 0.051 g (0.096 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150°C for 24 h. GLC analysis of the resulting mixture showed the presence of **5** (27% yield) and **6** (72% yield). The mixture was treated with a short silica gel column to remove the nickel species from the reaction mixture, and then **5** and **6** were isolated by MPLC.

6: MS: m/z 426 (M^+). IR: ν 2952, 2907, 2872, 1595, 1486, 1459, 1439, 1006, 910 cm^{-1} . ^1H NMR (CDCl_3): δ 0.52–1.18 (m, 20H, EtSi), 6.75–7.49 (m, 14H, phenyl and phenylene ring protons) ppm. ^{13}C NMR (CDCl_3): δ 3.51, 4.33, 8.92, 9.01 (EtSi), 124.3, 125.7, 126.3, 127.2, 127.5, 128.3, 128.7, 130.6, 131.7, 133.5, 134.5, 140.7, 144.4, 144.8 (phenyl and phenylene ring carbons), 148.3, 153.0 (olefinic carbons) ppm. ^{29}Si NMR (CDCl_3): δ -21.54, -20.81 ppm. Anal. Found: C, 78.80; H, 7.96. $\text{C}_{28}\text{H}_{34}\text{Si}_2$ Calc.: C, 78.81; H, 8.03%.

All spectral data for **5** were identical with those of an authentic sample [4,5].

3.5. Reaction of **1** with methylphenylacetylene

A mixture of 0.450 g (1.81 mmol) of **1**, 0.547 g (4.71 mmol) of methylphenylacetylene and 0.047 g (0.088 mmol) of tetrakis(triethylphosphine)nickel(0) was heated at 150°C for 24 h. The mixture was treated with a short silica gel column to remove nickel species from the

reaction mixture. The resulting mixture was then analyzed by GLC as being **7** (51% yield), **8** (28% yield) and 7% of the starting compound **1**. Compound: **7** and **8** were isolated by preparative HPLC.

7: MS: m/z 364 (M^+). IR: ν 3056, 2952, 2873, 1597, 1482, 1458, 1416, 1233, 1070, 1001, 961, 779 cm^{-1} . ^1H NMR (CDCl_3): δ 0.54–0.86 (m, 20H, EtSi) 1.68 (s, 3H, Me), 6.95–7.58 (m, 9H, phenyl and phenylene ring protons) ppm. ^{13}C NMR (CDCl_3): δ 5.14, 5.37, 7.57, 7.67 (EtSi), 19.05 (Me) 125.4, 127.4, 127.8, 127.9, 128.2, 133.1, 133.2, 142.9, 143.0, 144.0 (phenyl and phenylene ring carbons), 149.7, 155.2 (olefinic carbons) ppm. ^{29}Si NMR (CDCl_3): δ -14.10, -12.26 ppm. Anal. Found: C, 75.62; H, 8.84. $\text{C}_{23}\text{H}_{32}\text{Si}_2$ Calc.: C, 75.75; H, 8.84%.

8: MS: m/z 364 (M^+), IR: ν 3048, 2951, 2871, 1597, 1488, 1456, 1416, 1280, 1070, 1006, 956, 703 cm^{-1} . ^1H NMR (CDCl_3): δ 0.68–1.13 (m, 20H, EtSi), 1.72 (s, 3H, Me), 6.67–7.41 (m, 9H, phenyl and phenylene ring protons) ppm. ^{13}C NMR (CDCl_3): δ 3.29, 3.63, 8.97 (2C) (EtSi), 20.93 (Me), 125.4, 126.0, 128.1, 128.6, 129.6, 131.2, 133.1, 133.6, 133.8, 145.1 (phenyl and phenylene ring carbons), 148.1, 151.9 (olefinic carbons) ppm. ^{29}Si NMR (CDCl_3): δ -21.70, -20.79 ppm. Anal. Found: C, 75.75; H, 8.78. $\text{C}_{23}\text{H}_{32}\text{Si}_2$ Calc.: C, 75.75; H, 8.84%.

Isomer of **8**: ^1H NMR (CDCl_3): δ 0.68–1.13 (EtSi), 1.97 (Me), 6.67–7.41 (phenyl and phenylene ring protons) ppm. ^{13}C NMR (CDCl_3): δ 3.29, 3.81, 8.72, 8.97 (EtSi), 22.58 (Me), 124.7, 125.9, 127.7, 128.2, 129.0, 129.9, 133.2 (five carbon atoms that have no hydrogen could not be measured owing to low intensities).

3.6. Reaction of **1** with phenyl(trimethylsilyl)acetylene

A mixture of 0.153 g (0.616 mmol) of **1**, 0.182 g (0.898 mmol) of phenyl(trimethylsilyl)acetylene and 0.014 g (0.026 mmol) of tetrakis(triethylphosphine)nickel(0) in a degassed sealed tube was heated at 150°C for 24 h. The mixture was treated with a short silica gel column to remove nickel species from the reaction mixture. The mixture was then analyzed by GLC as being **9** (44% yield) and **10** (27% yield). Compounds **9** and **10** were isolated by fractional recrystallization using ethanol as a solvent.

10: Melting point, 85–86°C. MS: m/z 422 (M^+). IR: ν 3052, 2954, 2867, 1244, 1121, 1019, 964, 706 cm^{-1} . ^1H NMR (CDCl_3): δ 0.11 (s, 9H, Me_3Si), 0.41–1.02 (m, 20H, EtSi), 6.94–7.59 (m, 9H, phenyl and phenylene ring protons) ppm. ^{13}C NMR (CDCl_3): δ 0.90 (Me_3Si), 7.95, 8.04 (2C), 8.25 (EtSi), 125.9, 126.3, 127.5, 128.1, 128.2, 132.2 (2C), 147.9, 148.8, 149.7 (phenyl and phenylene ring carbons), 154.5, 181.8 (olefinic carbons) ppm. ^{29}Si NMR (CDCl_3): δ -7.89, -0.48, 3.12 ppm. Anal. Found: C, 70.95; H, 9.05. $\text{C}_{25}\text{H}_{38}\text{Si}_3$ Calc.: C, 71.01; H, 9.06%.

All spectral data for **9** were identical with those of an authentic sample [4].

3.7. Reaction of **1** with phenyl(trimethylsilyl)acetylene in the presence of dimethylphenylsilane

A mixture of 0.222 g (0.893 mmol) of **1**, 0.203 g (1.17 mmol) of phenyl(trimethylsilyl)acetylene, 0.642 g (2.19 mmol) of dimethylphenylsilane and 0.023 g (0.043 mmol) of tetrakis(triethylphosphine)nickel(0) in a degassed sealed tube was heated at 150°C for 24 h. The mixture was treated with a short silica gel column to remove nickel species from the reaction mixture. The mixture was then analyzed by GLC as being **9** (41% yield), **10** (24% yield) and **13** (27% yield). Compounds **9**, **10** and **13** were separated by MPLC.

13 [10]: MS; m/z 310 (M^+) IR; ν 3068, 2956, 1428, 1247, 1113, 933, 851, 835, 811, 701 cm^{-1} ; ^1H NMR (CDCl_3): δ -0.22 (s, 9H, Me_3Si), 0.31 (s, 6H, Me_2Si), 6.38 (s, 1H, $\text{HC}=\text{C}$), 7.13–7.47 (m, 10H, phenyl and phenylene ring protons) ppm. ^{13}C NMR (CDCl_3): δ -3.08 (Me_3Si), -0.03 (Me_2Si), 125.6, 127.4, 127.5, 127.6, 128.9, 134.1, 144.9, 157.3 (phenyl and phenylene ring carbons), 146.2, 164.1 (olefinic carbons) ppm. ^{29}Si NMR (CDCl_3): δ -9.30, -9.73. Anal. Found: C, 73.26; H, 8.40. $\text{C}_{19}\text{H}_{26}\text{Si}_2$ Calc.: C, 73.48; H, 8.44%.

All spectral data for **9** and **10** were identical with those of the authentic samples.

3.8. Reaction of **1** with 1-(trimethylsilyl)hexyne

A mixture of 0.204 g (0.821 mmol) of **1**, 0.248 g (1.61 mmol) of 1-(trimethylsilyl)hexyne, and 0.022 g (0.041 mmol) of tetrakis(triethylphosphine)nickel(0) in a sealed glass tube was heated at 150°C for 24 h. The mixture was treated with a short silica gel column to remove nickel species from the reaction mixture. The resulting mixture was analyzed by GLC as being **11** (58% yield) and **12** (29% yield). Compounds **11** and **12** were separated by column chromatography. **11**: MS: m/z 402 (M^+). IR: ν 3043, 2956, 2873, 1461, 1414, 1248, 1120, 1000, 963, 879, 838, 758, 674 cm^{-1} . ^1H NMR (CDCl_3): δ 0.34 (s, 9H, Me_3Si), 0.80–1.03 (m, 23H, EtSi, CH_3), 1.44–1.57 (m, 4H, CH_2), 2.55–2.61 (m, 2H, CH_2), 7.35–7.57 (m, 4H, phenylene ring protons) ppm. ^{13}C NMR (CDCl_3): δ 3.43 (Me_3Si), 6.92, 7.86, 7.91, 8.00 (EtSi), 14.07, 23.54, 32.65, 41.58 (Bu), 127.5, 127.8, 132.4, 132.5, 142.8, 145.1 (phenylene ring carbons), 156.0, 176.1 (olefinic carbons) ppm. ^{29}Si NMR (CDCl_3): δ -17.35, -12.58, -12.30. ppm. Anal. Found: C, 68.58; H, 10.30. $\text{C}_{23}\text{H}_{42}\text{Si}_3$ Calc.: C, 68.58; H, 10.51%.

12: MS: m/z 402 (M^+): IR: ν 3049, 2943, 2861, 1462, 1414, 1248, 1119, 1000, 963, 878, 837, 744, 724, 686 cm^{-1} , ^1H NMR (CDCl_3): δ 0.24 (s, 9H, Me_3Si),

0.73–0.97 (m, 23H, EtSi, CH₃), 1.35–1.48 (m, 4H, CH₂), 2.44–2.55 (m, 2H, CH₂), 7.30–7.55 (m, 4H, phenylene ring protons) ppm. ¹³C NMR (CDCl₃): δ 1.56 (Me₃Si), 8.10 (2C), 8.23, 8.75 (EtSi), 14.14, 23.36, 31.63, 46.72 (Bu), 128.1, 127.3, 132.0, 132.1, 147.7, 149.4 (phenylene ring carbons), 142.7, 180.8 (olefinic carbons) ppm. ²⁹Si NMR (CDCl₃): δ -7.80, -1.82, 1.21. Anal. Found: C, 68.43; H, 10.48. C₂₃H₄₂Si₃ Calc.: C, 68.58; H, 10.51%.

3.9. Reaction of **1** with 1-(trimethylsilyl)hexyne in the presence of dimethylphenylsilane

A mixture of 0.141 g (0.567 mmol) of **1**, 0.154 g (1.00 mmol) of 1-(trimethylsilyl)hexyne, 0.350 g (2.57 mmol) of dimethylphenylsilane and 0.045 g (0.085 mmol) of tetrakis(triethylphosphine)nickel(0) in a degassed sealed tube was heated at 150°C for 24 h. The mixture was analyzed by GLC as being **11** (62% yield), **12** (30% yield) and **14** (79% yield). Compounds **11**, **12** and **14** were separated by MPLC.

14: MS: *m/z* 275 (M⁺ - Me). IR: ν 2955, 2919, 2896, 2861, 1561, 1425, 1243, 1108, 891, 832, 803, 726, 697 cm⁻¹. ¹H NMR (CDCl₃): δ 0.02 (s, 9H, Me₃Si), 0.32 (s, 6H, Me₂Si), 0.90–0.96 (m, 3H, CH₃), 1.34–1.41 (m, 4H, CH₂), 2.28 (q, 2H, CH₂, *J* = 6.9 Hz), 6.69 (t, 1H, HC=C, *J* = 6.9 Hz), 7.30–7.47 (m, 4H, phenyl ring protons) ppm. ¹³C NMR (CDCl₃): δ -1.02 (Me₂Si), 1.60 (Me₃Si), 14.09, 22.57, 31.66, 35.67 (Bu), 127.5, 128.5, 133.9, 137.7 (phenyl ring carbons), 140.6, 160, 7 (olefinic carbons). ²⁹Si NMR (CDCl₃): δ -9.05, -5.87. Anal. Found: C, 70.18; H, 10.30. C₁₇H₃₀Si₂ Calc.: C, 70.26; H, 10.41%.

All spectral data for **11** and **12** were identical with those of the authentic samples.

3.10. Reaction of **1** with phenyl(trimethylsilyl)acetylene in the presence of cyclohexene

A mixture of 0.268 g (1.08 mmol) of **1**, 0.286 g (1.64 mmol) of phenyl(trimethylsilyl)acetylene, 1.041 g (12.7 mmol) of cyclohexene and 0.028 g (0.053 mmol) of

tetrakis(triethylphosphine)nickel(0) in a degassed sealed tube was heated at 150°C for 24 h. The mixture was analyzed by GLC as being **9** (43% yield) and **10** (24% yield).

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