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Silicon–Carbon Unsaturated Compounds. 45. Reaction of Benzoyltris(trimethylsilyl)silane with Aryllithium Reagents

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The reaction of benzoyltris(trimethylsilyl)silane (1) with phenyllithium in ether, followed by hydrolysis of the resulting mixture gave diphenylmethyl(trimethylsiloxy)bis(trimethylsilyl)silane and phenyl(diphenylmethyl)bis(trimethylsilyl)silane in 30% and 9% yields. Treatment of 1 with (*o*-tolyl)lithium afforded (phenyl(*o*-tolyl)methyl)(trimethylsiloxy)bis(trimethylsilyl)silane and (phenyl(o-tolyl)methyl)(*o*-tolyl)bis(trimethylsilyl)silane (**3b**) in 16% and 27% yields, while with (*p*-xylyl)lithium, 1 produced (phenyl(*p*-xylyl)methyl)(trimethylsiloxy)bis(trimethylsilyl)silane and (phenyl(*p*-xylyl)methyl)bis(trimethylsilyl)(*p*-xylyl)silane (**3c**) in 18% and 30% yields, respectively. The reaction of 1 with phenyllithium in the presence of 2,3-dimethylbutadiene produced 4,5-dimethyl-2,2-diphenyl-1,1-bis(trimethylsilyl)-1-silacyclohex-4-ene in 76% yield. Similar reaction of 1 with (*o*-tolyl)lithium in the presence of 2,3-dimethylbutadiene afforded 4,5-dimethyl-2-phenyl-2-(*o*-tolyl)-1,1-bis(trimethylsilyl)-1-silacyclohex-4-ene and **3b** in 49 and 6% yields. With (*p*-xylyl)lithium, 1 gave a Diels–Alder cycloadduct and **3c** in 47% and 26% yields, respectively.

Introduction

There has been a considerable interest in the chemistry of silenes. Various methods for the synthesis of the silenes, such as the thermolysis, photolysis, and salt elimination have been reported to date.[1] We have found that the photolysis of π-electron system-substituted polysilanes affords a simple method for the prepartion of silenes.[2] In fact, the photolysis of aryl-, alkenyl-, and alkynylpolysilanes produces the respective silenes arising from a 1,3-silyl shift to the π-electron system. Brook and his co-workers have also reported that the photolysis of acylpolysilanes offers a convenient route to the silenes.[3] In the photolysis of the π-electron-system-substituted polysilanes, the reagents that can be used to trap the reactive silenes are restricted to compounds which show no strong absorptions in the UV region, because compounds that have strong absorptions in this region absorb the incident light and retard the photochemical reaction of the starting polysilanes.

In an attempt to develop a method that does not involve the photolysis for the preparation of the silenes, we discovered that the nickel-catalyzed reaction of alkenyl- and alkynyl-substituted polysilanes gives the silene–nickel complexes as reactive species.[4,5] We also found that treatment of acylpolysilanes with methyllithium produces silene intermediates, via a Peterson-type reaction.[6] In these reactions, however, the silene intermediates could not be trapped in the presence of a trapping agent, but the products arising from head-to-head dimerization of the silenes were obtained. The synthesis of the silenes by way of a Peterson-type reaction has recently been reported by two research groups. Brook and his co-workers found that the reaction of stable silenes with Grignard reagents proceeds with addition of the Grignard reagents to a silicon–carbon double bond, and then anti-Brook rearrangement, followed by the Peterson olefination reaction to give silenes.[7] Apeloig et al. reported that addition of (tris(trimethylsilyl)silyl)lithium to adamantanone and 4-*tert*-butylcyclohexanone affords the silenes by a Peterson-type reaction.[8]

We report here that the reaction of benzoyltris(trimethylsilyl)silane with aryllithium in the presence of 2,3-dimethylbutadiene affords the products arising from [2 + 4] cycloaddition of the silenes derived from a Peterson-type reaction to the diene.

Results and Discussion

First, we investigated the reaction of benzoyltris(trimethylsilyl)silane[9] (1) with aryllithium in the absence of a trapping agent. Thus, when compound 1 was treated

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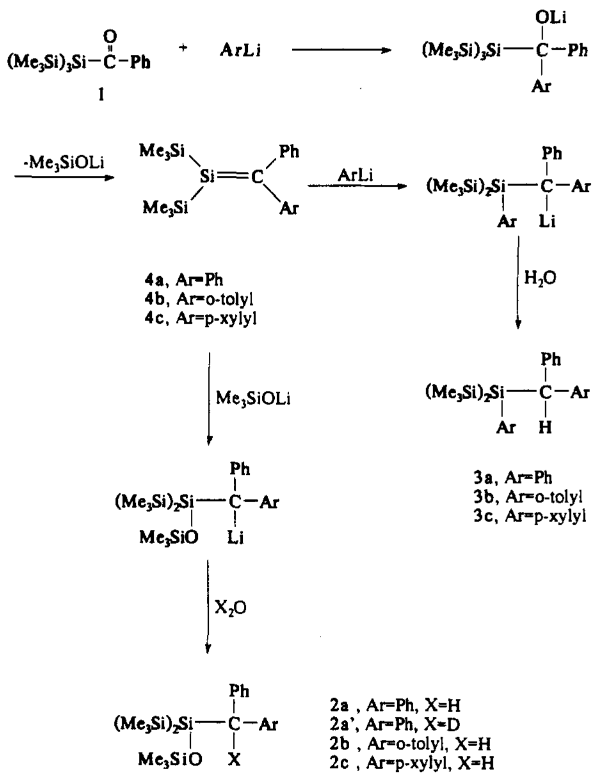
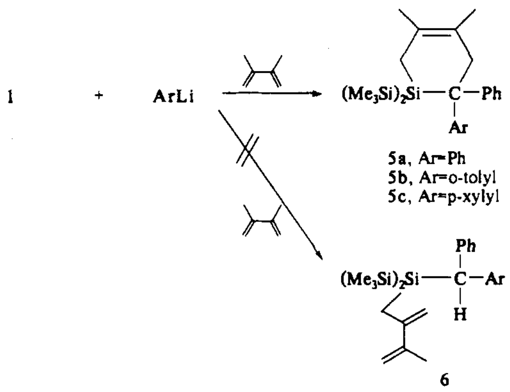
Scheme I



Scheme II



with 1 equiv of phenyllithium in diethyl ether at −80 °C and the resulting mixture was hydrolyzed with water, two products, (diphenylmethyl)(trimethylsiloxy)bis(trimethylsilyl)silane (**2a**) and phenyl(diphenylmethyl)bis(trimethylsilyl)silane (**3a**) were obtained in 30% and 9% yields, in addition to a 52% yield (weight percent) of nonvolatile substances (Scheme I).

The ^{1}H NMR spectrum of **2a** shows two resonances at δ −0.10 and 0.18 ppm, due to two kinds of trimethylsilyl protons and a single resonance at 3.51 ppm attributed to a methine proton, as well as multiple resonances due to phenyl ring protons, while its ^{13}C NMR spectrum reveals resonances at −1.1, 2.3, and 47.5 ppm, attributable to trimethylsilyl carbons, trimethylsiloxy carbons, and methine carbon, respectively, and four resonances due to phenyl carbons as expected. These results are wholly consistent with the structure proposed for **2a**. The structure of **3a** was also verified by spectrometric analysis, as well as by elemental analysis. The ^{1}H NMR spectrum of **3a** shows two singlets at 0.07 and 4.23 ppm, due to trimethylsilyl protons and a methine proton, as well as multiplet resonances attributed to phenyl ring protons. Its ^{13}C NMR spectrum reveals resonances at −0.2 and 42.6 ppm, due to trimethylsilyl carbons and a methine carbon.

The formation of **2a** may be best explained by addition of lithium trimethylsiloxide to 2,2-diphenyl-1,1-bis(trimethylsilyl)silene (**4a**), followed by hydrolysis of the resulting adduct. The silene **4a** is probably produced by addition of phenyllithium across the CO double bond of acylsilane **1** and then a Peterson-type elimination of lithium trimethylsiloxide. The production of **3a**, however, can be understood in terms of the reaction of **4a** with phenyllithium and then hydrolysis of the resulting carbanion.

In order to confirm whether or not the product **2a** was formed from readdition of lithium trimethylsiloxide to the silene **4a**, the mixture obtained from the reaction of **1** with phenyllithium was hydrolyzed with deuterium oxide. Thus, the reaction of **1** with phenyllithium under the same conditions, followed by treatment of the mixture with deuterium oxide gave deuteriodiphenylmethyl (trimethylsiloxy)bis(trimethylsilyl)silane (**2a′**) in 47% yield. The ^{1}H and ^{2}H NMR spectrum of **2a′** showed the presence of a deuterium atom on a methine carbon, indicating that the lithium atom attached to this carbon. Regiospecific addition of (trimethylsiloxy)magnesium bromide generated from the Peterson olefination reaction of $Me_3Si(R_2)$-Si–CR $(SiMe_3)OMgBr$ to the silene has been proposed by Brook et al.[7]

The reaction of **1** with (*o*-tolyl)lithium in the absence of a trapping agent in ether, followed by hydrolysis of the resulting solution, gave (phenyl(*o*-tolyl)methyl)(trimethylsiloxy)bis(trimethylsilyl)silane (**2b**) and (phenyl(*o*-tolyl)-methyl)(*o*-tolyl)bis(trimethylsilyl)silane (**3b**) in 16 and 27% yields. Similar treatment of **1** with (*p*-xylyl)lithium in ether produced (phenyl(*p*-xylyl)methyl)(trimethylsiloxy)bis(trimethylsilyl)silane (**2c**) and (phenyl(*p*-xylyl)-methyl)bis(trimethylsilyl)(*p*-xylyl)silane (**3c**) in 18 and 30% yields, respectively. The products **2b** and **2c** also can be understood in terms of the reaction of the silenes **4b** and **4c** with lithium trimethylsiloxide derived from the Peterson-type elimination of the aryllithium adducts, respectively.

We have recently reported that the reaction of **1** with methyllithium produces the silene that undergoes dimerization to give a head-to-head dimer, even in the presence of a trapping agent such as a butadiene.[6] In contrast to this, the present silenes **4a–c** afforded no dimerization product. The absence of the dimerization product in the present reactions may be ascribed to stabilization of a silicon–carbon double bond. Presumably, introduction of two aryl groups onto the sp^2 carbon of the silicon–carbon double bond stabilizes the silenes due to the extension of the conjugated system and also steric hindrance of these aryl groups.

Next, we carried out the experiments to trap the silenes with the use of a diene as a trapping agent. Thus, the reaction of **1** with 1 equiv of phenyllithium in the presence of 3 equiv of 2,3-dimethylbutadiene in diethyl ether gave a Diels–Alder cycloadduct, 4,5-dimethyl-2,2-diphenyl-1,1-bis(trimethylsilyl)-1-silacyclohex-4-ene (**5a**), in 76% yield (Scheme II). No other volatile products were detected in the reaction mixture by either spectrometric analysis or GLC analysis. The ^{1}H NMR spectrum of **5a** shows three resonances at 0.11, 1.85, and 2.01 ppm, due to trimethylsilyl protons and two nonequivalent methyl protons, and two broad resonances at 1.44 and 2.94 ppm, attributed to two different kinds of methylene protons in the silacyclohexene ring, as well as multiplet resonances due to two phenyl ring protons. The ^{13}C NMR spectrum reveals a single resonance of trimethylsilyl carbons at 0.1 ppm, two methylene carbons at 14.3 and 49.3 ppm, two methyl carbons at 20.9 and 24.0 ppm, a phenyl-substituted carbon at 42.6 ppm, and two sp^2 carbons in the six-membered ring at 126.7 and 151.1 ppm, as well as four resonances of phenyl ring carbons. These results are wholly consistent with the structure proposed for **5a**.

Similar reaction of 1 with (*o*-tolyl)lithium in the presence of 2,3-dimethylbutadiene under the same conditions produced 4,5-dimethyl-2-phenyl-2-(*o*-tolyl)-1,1-bis(trimethylsilyl)-1-silacyclohex-4-ene (**5b**), arising from [2 + 4] cycloaddition of the silene **4b** and 2,3-dimethylbutadiene in 49% yield, in addition to a 6% yield of compound **3b**. Treatment of 1 with (*p*-xylyl)lithium under the same conditions again gave a [2 + 4] cycloadduct, 4,5-dimethyl-2-phenyl-1,1-bis(trimethylsilyl)-2-(*p*-xylyl)-1-silacyclohex-4-ene (**5c**) and xylyllithium adduct **3c** in 47 and 26% yields, respectively. It seems likely that introduction of the bulkier substituent on the silene carbon results in the decrease of the yield of [2 + 4] cycloadducts but in an increase of aryllithium adducts. The structures of **5b** and **5c** were readily confirmed by mass, IR, and ^{1}H and ^{13}C NMR spectrometric analysis, as well as by elemental analysis (see Experimental Section).

Brook et al. have reported that the reaction of 2-adamantyl- and 2-*tert*-butyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)silene with 2,3-dimethylbutadiene gave Diels–Alder cycloadducts and ene adducts.[9] Wiberg has also reported that the reaction of 1,1-dimethyl-2,2-bis(trimethylsilyl)silene with isoprene afforded the ene product in addition to [2 + 4] cycloadduct.[10] In the present reactions, however, no ene products such as compound **6** were detected in the reaction mixture.

In conclusion, the reaction of 1 with aryllithium reagents in ether produces silenes via a Peterson-type reaction. In the absence of a trapping agent, lithium trimethylsiloxide which was eliminated from benzoyltris(trimethylsilyl)silane–aryllithium adducts adds to the resulting silenes to give the adducts, while in the presence of 2,3-dimethylbutadiene, the silenes undergo [2 + 4] cycloaddition to give 1-silacyclohex-4-ene derivatives. No reactions afford dimerization products in the absence of trapping agent.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of purified argon. NMR spectra were recorded on a JEOL Model EX 270 spectrometer using tetramethylsilane as an internal standard. Mass spectra were measured on a Shimadzu Model QP-1000 spectrometer and a JEOL Model JMS-D300 spectrometer equipped with a JMA-2000 data processing system. Infrared spectra were obtained with the use of a Perkin-Elmer 1600FT infrared spectrophotometer.

Materials. Acylsilane 1 was prepared as reported in the literature.[9] Diethyl ether used as a solvent was dried over lithium aluminum hydride and distilled just before use.

Reaction of 1 with Phenyllithium. In a 50-mL flask fitted with a dropping funnel was placed 0.522 g (1.48 mmol) of 1 in 10 mL of diethyl ether. To this was added a solution of phenyllithium, prepared from 0.16 mL (1.52 mmol) of bromobenzene and 0.081 g (11.57 mmol) of lithium in 5 mL of diethyl ether, through the dropping funnel at −80 °C. The solution was allowed to stand overnight at room temperature. After hydrolysis of the resulting mixture 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 dried over potassium carbonate. The solvent ether was evaporated, and the residue was analyzed by GLC, using octadecane as an internal standard, as being **2a** (30% yield) and **3a** (9%). Compounds **2a** and **3a** were isolated by MPLC on silica gel with hexane as eluent. **2a**: mp 117.0 °C; MS *m/z* 430 (M$^+$); IR 1052 cm^{-1}; ^{1}H NMR (δ in CDCl$_3$) −0.10 (s, 18H, MeSi), 0.18 (s, 9H, MeSiO), 3.51 (s, 1H, HCPh), 7.11–7.39 (m, 10H, phenyl protons); ^{13}C NMR (δ in CDCl$_3$) −1.1 (MeSi), 2.3 (MeSiO), 47.5 (CHPh), 125.3, 128.3, 128.9, 143.9 (phenyl carbons). Anal. Calcd for $C_{22}H_{38}Si_4O$: C, 61.33; H, 8.89. Found: C, 61.28; H, 8.79. **3a**: mp 76.5–77.0 °C; MS *m/z* 418 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.07 (s, 18H, MeSi), 4.23 (s, 1H, HCPh), 7.18–7.58 (m, 15H, phenyl protons); ^{13}C NMR (δ in CDCl$_3$) −0.2 (MeSi), 42.6 (CHPh), 124.8, 127.3, 127.8, 128.5, 136.0, 136.6, 143.4 (2C) (phenyl carbons). Anal. Calcd for $C_{25}H_{34}Si_3$: C, 71.70; H, 8.18. Found: C, 71.76; H, 8.19.

Hydrolysis of a Phenyllithium Adduct with Deuterium Oxide. To an ether solution of 1 (1.386 g, 3.93 mmol) was added 2.18 mL (3.93 mmol) of a 1.8 M phenyllithium–ether solution at −80 °C. The mixture was hydrolyzed with deuterium oxide to give **2a′** in 47% yield. **2a′**: MS *m/z* 431 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) −0.10 (s, 18H, MeSi), 0.18 (s, 9H, MeSiO), 7.11–7.39 (m, 10H, phenyl protons); ^{13}C NMR (δ in CDCl$_3$) −1.1 (MeSi), 2.3 (MeSiO), 47.5 (CDPh), 125.3, 128.3, 128.9, 143.9 (phenyl carbons); ^{2}H NMR (δ in CDCl$_3$) 3.64 (DCPh).

Reaction of 1 with (*o*-Tolyl)lithium. In a 50-mL flask fitted with a dropping funnel was placed 0.850 g (2.42 mmol) of 1 in 10 mL of diethyl ether. To this was added a solution of (*o*-tolyl)lithium prepared from 0.34 mL (2.84 mmol) of *o*-tolyl bromide and 0.104 g (14.86 mmol) of lithium in 5 mL of diethyl ether at −80 °C. After workup as usual, the reaction mixture was analyzed by GLC, using nonadecane as an internal standard, as being **2b** (16% yield) and **3b** (27%). Compounds **2b** and **3b** were isolated by MPLC on silica gel with hexane as eluent. **2b**: mp 103.5 °C; MS *m/z* 444 (M$^+$); IR 1054 cm^{-1}; ^{1}H NMR (δ in CDCl$_3$) −0.14 (s, 9H, MeSi), −0.11 (s, 9H, MeSi), 0.14 (s, 9H, MeSiO), 2.30 (s, 3H, tolyl Me), 3.68 (s, 1H, H–C), 7.05–7.58 (m, 9H, aromatic ring protons); ^{13}C NMR (δ in CDCl$_3$) −1.1, −0.9 (MeSi), 2.3 (MeSiO), 20.2 (tolyl Me), 42.6 (CHPh), 124.9, 125.8, 128.1 (2C), 128.7, 130.4, 130.5, 136.0, 142.1, 143.2 (aromatic ring carbons). Anal. Calcd for $C_{23}H_{40}Si_4O$: C, 62.09; H, 9.06. Found: C, 62.01; H, 9.03. **3b**: mp 163.5 °C; MS *m/z* 446 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.11 (s, 9H, MeSi), 0.24 (s, 9H, MeSi), 2.30 (s, 3H, tolyl Me), 2.53 (s, 3H, tolyl Me), 4.71 (s, 1H, HCPh), 7.01–7.65 (m, 13H, aromatic ring protons); ^{13}C NMR (δ in CDCl$_3$) 0.9, 1.1 (MeSi), 19.9, 24.4 (tolyl Me), 38.6 (CHPh), 124.7, 125.4, 125.9, 127.6, 128.3 (2C), 128.6, 130.1, 130.7, 131.7, 136.4, 136.9, 137.4, 141.2, 143.6, 144.1 (aromatic ring carbons). Anal. Calcd for $C_{27}H_{38}Si_3$: C, 72.57; H, 8.57. Found: C, 72.54; H, 8.48.

Reaction of 1 with (*p*-Xylyl)lithium. In a 50-mL flask was placed 0.935 g (2.66 mmol) of 1 in 10 mL of diethyl ether. To this was added a (*p*-xylyl)lithium solution prepared from 0.39 mL (2.84 mmol) of *p*-xylyl bromide and 0.066 g (9.46 mmol) of lithium in 10 mL of diethyl ether. After workup as usual, the reaction mixture was analyzed by GLC, using docosane as an internal standard, as being **2c** (18% yield) and **3c** (30%). Compounds **2c** and **3c** were isolated by MPLC on silica gel, with hexane as eluent. **2c**: mp 145 °C; MS *m/z* 458 (M$^+$); IR 1052 cm^{-1}; ^{1}H NMR (δ in CDCl$_3$) −0.04 (s, 9H, MeSi), 0.02 (s, 9H, MeSi), 0.22 (s, 9H, MeSiO), 2.31 (s, 3H, xylyl Me), 2.39 (s, 3H, xylyl Me), 3.74 (s, 1H, HCPh), 6.95–7.44 (m, 8H, aromatic ring protons); ^{13}C NMR (δ in CDCl$_3$) −1.0, −0.8 (MeSi), 2.4 (MeSiO), 19.7, 21.0 (xylyl Me), 42.7 (CHPh), 124.8, 126.5, 128.1, 128.6, 130.4, 131.2, 133.0, 135.0, 141.7, 143.3 (aromatic ring carbons); exact mass calcd for $C_{24}H_{42}Si_4O$ 458.2314, found 458.2289. **3c**: mp 143.2 °C; MS *m/z* 474 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.12 (s, 9H, MeSi), 0.27 (s, 9H, MeSi), 2.29 (s, 3H, xylyl Me), 2.45 (s, 3H, xylyl Me), 2.48 (s, 3H, xylyl Me), 2.54 (s, 3H, xylyl Me), 4.66 (s, 1H, HCPh), 7.01–7.45 (m, 11H, aromatic ring protons); ^{13}C NMR

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(δ in $CDCl_3$) 0.8, 1.2 (MeSi), 19.4, 20.8, 21.0, 23.9 (tolyl Me), 38.5 (CHPh), 124.6, 126.4, 127.6, 128.2, 129.3, 129.9, 130.5, 132.6, 133.2, 133.4, 134.6, 136.6, 138.7, 140.3, 140.9, 144.2 (aromatic ring carbons). Anal. Calcd for $C_{27}H_{38}Si_3$: C, 73.34; H, 8.91. Found: C, 73.33; H, 8.91.

Reaction of 1 with Phenyllithium in the Presence of 2,3-Dimethylbutadiene. In a 50-mL flask fitted with a dropping funnel was placed a mixture of 0.954 g (2.71 mmol) of 1 and 0.97 mL (8.59 mmol) of 2,3-dimethylbutadiene in 10 mL of diethyl ether. To this was added dropwise 1.7 mL of a 1.8 M phenyllithium–ether solution (2.98 mmol) through the dropping funnel at -80 °C. The mixture was allowed to stand overnight at room temperature. After workup as usual, the mixture was analyzed by GLC, using octadecane as an internal standard, as being **5a** (76% yield). Compound **5a** was isolated by MPLC on silica gel with hexane as eluent: mp 126.0 °C; MS *m/z* 422 (M^+); ^1H NMR (δ in $CDCl_3$) 0.11 (s, 18H, MeSi), 1.44 (br s, 2H, H_2CSi), 1.85 (s, 3H, Me), 2.01 (s, 3H, Me), 2.94 (br s, 2H, H_2CC), 7.23–7.39 (m, 10H, phenyl protons); ^{13}C NMR (δ in $CDCl_3$) 0.1 (MeSi), 14.3 (CH_2), 20.9, 24.0 (Me), 42.6 (CPh), 49.3 (CH_2), 125.1, 126.7, 127.9, 128.3, 128.5, 151.1 (sp^2 carbons); ^{29}Si NMR (δ in $CDCl_3$) -39.48 (Si–CPh), -15.85 (SiMe). Anal. Calcd for $C_{25}H_{38}Si_3$: C, 71.02; H, 9.06. Found: C, 71.00; H, 8.96.

Reaction of 1 with (*o*-Tolyl)lithium in the Presence of 2,3-Dimethylbutadiene. In a 50-mL flask was placed a mixture of 0.526 g (1.50 mmol) of 1 and 1.0 mL (8.85 mmol) of 2,3-dimethylbutadiene in 10 mL of diethyl ether. To this was added a solution of (*o*-tolyl)lithium prepared from 0.21 mL (1.71 mmol) of *o*-tolyl bromide and 0.05 g (7.14 mmol) of lithium in 5 mL of diethyl ether at -80 °C. After workup as usual, the mixture was analyzed by GLC, using pentadecane as an internal standard, as being **5b** (49% yield) and **3b** (6% yield). Compounds **5b** and **3b** were isolated by MPLC on silica gel with hexane as eluent. **5b**: mp 146.9 °C; MS *m/z* 436 (M^+); ^1H NMR (δ in $CDCl_3$) -0.16 (s, 9H, MeSi), 0.09 (s, 9H, MeSi), 1.03 (d, 1H, 16.8 Hz, HCSi), 1.45 (d, 1H, 16.8 Hz, HCSi), 1.67 (s, 3H, Me), 1.81 (s, 3H, tolyl Me), 1.86 (s, 3H, Me), 2.51 (d, 1H, 18.3 Hz, HCC), 3.16 (d, 1H, 18.3 Hz, HCC), 6.95–7.48 (m, 9H, aromatic ring protons); ^{13}C NMR (δ in $CDCl_3$) -0.2, 0.6 (MeSi), 14.2 (CH_2), 20.8 (Me), 21.8 (tolyl Me), 24.1 (Me), 45.3 (CPh), 46.5 (CH_2), 124.1, 124.6, 126.2, 126.7, 126.8, 127.9, 128.7, 131.7, 133.0, 138.3, 147.6, 150.1 (sp^2 carbons); ^{29}Si NMR (δ in $CDCl_3$) -39.05 (Si–CPh), -16.92, -14.26 (SiMe). Anal. Calcd for $C_{26}H_{40}Si_3$: C, 71.48; H, 9.23. Found: C, 71.36; H, 9.12.

All spectral data for **3b** were identical with those of an authentic sample.

Reaction of 1 with (*p*-Xylyl)lithium in the Presence of 2,3-Dimethylbutadiene. In a 50-mL flask was placed a mixture of 0.786 g (2.23 mmol) of 1 and 1.0 mL (8.85 mmol) of 2,3-dimethylbutadiene in 10 mL of diethyl ether. To this was added a solution of (*p*-xylyl)lithium prepared from 0.40 mL (2.84 mmol) of *p*-xylyl bromide and 0.05 g (7.14 mmol) of lithium in 10 mL of diethyl ether at -80 °C. After workup as usual, the mixture was analyzed by GLC, using heptadecane as an internal standard, as being **5c** (47% yield) and **3c** (26% yield). Compounds **5c** and **3c** were isolated by MPLC on silica gel with hexane as eluent. **5c**: mp 145.5 °C; MS *m/z* 450 (M^+); ^1H NMR (δ in $CDCl_3$) -0.15 (s, 9H, MeSi), 0.10 (s, 9H, MeSi), 1.01 (d, 1H, 16.50 Hz, HCSi), 1.43 (d, 1H, 16.50 Hz, HCSi), 1.68 (br s, 3H, Me), 1.75 (s, 3H, xylyl Me), 1.85 (br s, 3H, Me), 2.37 (s, 3H, xylyl Me), 2.51 (d, 1H, 18.48 Hz, HCC), 3.17 (d, 1H, 18.48 Hz, HCC), 6.91–7.29 (m, 8H, aromatic ring protons); ^{13}C NMR (δ in $CDCl_3$) -0.2, 0.8 (MeSi), 14.4 (CH_2), 20.8 (Me, xylyl Me), 21.4 (xylyl Me), 24.1 (Me), 45.3 (CPh), 46.4 (CH_2), 124.0, 126.76, 126.81, 126.9, 127.8, 128.8, 132.3, 133.0, 133.9, 135.1, 147.5, 150.2 (sp^2 carbons); ^{29}Si NMR (δ in $CDCl_3$) -39.44 (Si–CPh), -16.72, -14.35 (SiMe). Anal. Calcd for $C_{27}H_{42}Si_3$: C, 71.92; H, 9.39. Found: C, 71.87; H, 9.36.

All spectral data for **3c** were identical with those of an authentic sample.

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