Organometallics **1991**, *10*, 2695-2700

MeSi), 0.42 (s, 3 H, MeSi), 0.44 (s, 3 H, MeSi), 0.88 (s, 3 H, MeC), 1.23 (s, 3 H, MeC), 2.83 (br s, 1 H, H on C_8), 5.93 (dd, 1 H, J = 9.5, 1.1 Hz, H on C_5), 6.35 (d, 1 H, J = 9.5 Hz, H on C_6), 7.03 (d, 1 H, J = 7.3 Hz, H on C_3), 7.31 (br s, 1 H, H on C_1), 7.40 (dd, 1 H, J = 7.3, 1.1 Hz, H on C_4); 22.5-MHz ^{13}C NMR (δ, in $CDCl_3$) -4.1, -3.7, -2.1, -1.9, 0.3, 0.5, 25.2, 29.2, (2 C), 32.1, 45.7, 54.9, 124.4, 125.2, 132.4, 133.6, 134.3, 135.0, 136.0, 136.9. Anal. Calcd for $C_{24}H_{44}Si_4$: C, 64.79; H, 9.97. Found: C, 64.76; H, 9.94.

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Registry No. **1a**, 134388-71-9; **1b**, 134388-72-0; **2a**, 134388-73-1; **2b**, 134388-75-3; **2c**, 134388-74-2; **3b**, 134418-54-5; **4a**, 134388-76-4; **4b**, 134388-79-7; **5a**, 134388-77-5; **5b**, 134418-56-7; **6a**, 134388-78-6; **6b**, 134388-80-0; **7a**, 134418-55-6; **8a**, 134388-81-1; **8b**, 134388-83-3; **9a**, 134418-57-8; **9b**, 134418-58-9; **10b**, 134388-84-4; **11a**, 134388-82-2; 2,6-dibromonaphthalene, 13720-06-4; chloropentamethyldisilane, 1560-28-7; 2,7-dibromonaphthalene, 58556-75-5; isobutene, 115-11-7.

Supplementary Material Available: Tables of positional parameters and equivalent isotropic thermal parameters of non-hydrogen atoms, anisotropic thermal parameters, and distances and angles for **5b** (2 pages); a listing of observed structure factors, their standard deviations, and calculated structure factors for **5b** (6 pages). Ordering information is given on any current masthead page.

Silicon–Carbon Unsaturated Compounds. 31. Photochemical Behavior of 1,1- and 1,2-Dinaphthyltetramethyldisilanes

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The photolysis of 1,1-bis(1-naphthyl)tetramethyldisilane in the presence or absence of a trapping agent gave 1-[methyl(1-naphthyl)silyl]-8-(trimethylsilyl)naphthalene, while 1,2-bis(1-naphthyl)tetramethyldisilane afforded 2,3-dihydro-1,1,3,3-tetramethyl-1,3-disilaphenalene-2-spiro-1′,2′-dihydronaphthalene as a main product, along with dimethylbis(1-naphthyl)silane. Irradiation of 1,1-bis(2-naphthyl)tetramethyldisilane in the presence of isobutene produced two types of adducts arising from the reaction of a silene with isobutene, 2-[isobutylmethyl(2-naphthyl)silyl]-1-(trimethylsilyl)naphthalene and 1,2-dihydro-1,2-[1,1,3-trimethyl-3-(2-naphthyl)-3-silapropano]-2-(trimethylsilyl)naphthalene. Similar irradiation of 1,2-bis(2-naphthyl)tetramethyldisilane afforded silene adducts 2-(isobutyldimethylsilyl)naphthalene, 2-(isobutyldimethylsilyl)-1-[dimethyl(2-naphthyl)silyl]naphthalene, and 1,2-dihydro-1,2-(1,1,3,3-tetramethyl-3-silapropano)-2-[dimethyl(2-naphthyl)silyl]naphthalene.

Introduction

Recently, we have found that the photolysis of 1-(pentamethyldisilanyl)naphthalene and 1,5-bis(pentamethyldisilanyl)naphthalene affords the respective photoisomers arising from radical scission of a silicon–silicon bond, followed by migration of the resulting trimethylsilyl radical to the C_8 position of the naphthyl ring and then a 1,4 shift of the ipso hydrogen to the radical center as the sole product.[1] 1,4-Bis(pentamethyldisilanyl)naphthalene, however, undergoes photolysis to give two products; one involves the photochemical isomerization analogous to that observed in the photolysis of the 1,5-isomer and the other comprises the formation of a silene derived from a 1,3-trimethylsilyl shift to the C_2 position of the naphthyl ring. The silene thus formed reacts with only methanol to give 6-(methoxydimethylsilyl)-6,7-bis(trimethylsilyl)-5,8-(dimethylsilano)-5,6,7,8-tetrahydronaphthalene but does not react with other trapping agents such as acetone and isobutene.[1]

The photolysis of 2,6- and 2,7-bis(pentamethyldisilanyl)naphthalene afforded the products derived from the silenes that are produced from a 1,3-trimethylsilyl shift to the C_1 position of the naphthyl ring.[2] No isomers arising from radical scission of the silicon–silicon bond, followed by migration of the resulting trimethylsilyl radical to the C_1 position and then a 1,3 shift of the ipso hydrogen to the silyl radical center, are detected in the photolysis products. In contrast to the silene generated from the 1,4-isomer, the silenes from the 2,6- and 2,7-isomers react readily with methanol, acetone, and isobutene to give addition products.

In an effort to learn much more about the photochemical behavior of the naphthyl-substituted disilanes, we investigated the photolysis of 1,1- and 1,2-bis(1-naphthyl)tetramethyldisilane and 1,1- and 1,2-bis(2-naphthyl)tetramethyldisilane.

Results and Discussion

1,1-Bis(1-naphthyl)tetramethyldisilane (**1**) and 1,1-bis(2-naphthyl)tetramethyldisilane (**3**) were synthesized by the reaction of 1,1-dichlorotetramethyldisilane with 2 molar equiv of the corresponding naphthyllithium in 44

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[1] Ohshita, J.; Ohsaki, H.; Ishikawa, M.; Tachibana, A.; Kurosaki, Y.; Yamabe, T.; Minato, A. *Organometallics*, in press.

[2] Ohshita, J.; Ohsaki, H.; Ishikawa, M.; Tachibana, A.; Kurosaki, Y.; Yamabe, T.; Tsukihara, T.; Takahashi, K.; Kiso, Y. *Organometallics*, in press.

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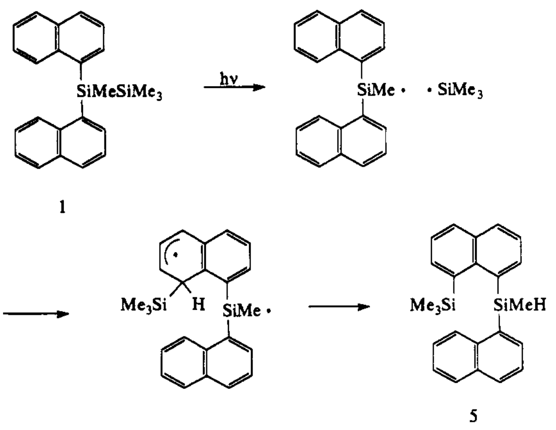
Scheme I



and 33% yields, while 1,2-bis(1-naphthyl)tetramethyldisilane (**2**) and 1,2-bis(2-naphthyl)tetramethyldisilane (**4**) were prepared from 1,2-dichlorotetramethyldisilane and 2 molar equiv of 1- and 2-naphthylmagnesium bromide in 39 and 40% yields, respectively.

$$2(1\text{-Nap})Li + Cl_2SiMeSiMe_3 \rightarrow \underset{\mathbf{1}}{(1\text{-Nap})_2SiMeSiMe_3}$$

$$2(1\text{-Nap})MgBr + ClSiMe_2SiMe_2Cl \rightarrow \underset{\mathbf{2}}{(1\text{-Nap})SiMe_2SiMe_2(1\text{-Nap})}$$

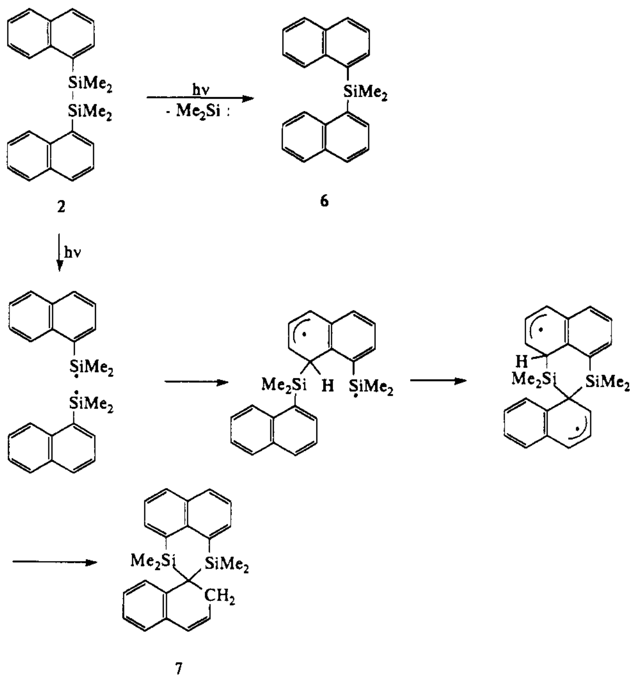
$$2(2\text{-Nap})Li + Cl_2SiMeSiMe_3 \rightarrow \underset{\mathbf{3}}{(2\text{-Nap})_2SiMeSiMe_3}$$

$$2(2\text{-Nap})MgBr + ClSiMe_2SiMe_2Cl \rightarrow \underset{\mathbf{4}}{(2\text{-Nap})SiMe_2SiMe_2(2\text{-Nap})}$$

Photolysis of 1 and 2. Irradiation of 1,1-bis(1-naphthyl)tetramethyldisilane (**1**) with a low-pressure immersion mercury lamp in the presence of a 10-fold excess of methanol in hexane at room temperature gave 8-(trimethylsilyl)-1-[methyl(1-naphthyl)silyl]naphthalene (**5**) in 73% yield. No other products were detected by either spectrometric analysis or GLC analysis. Similar photolysis of **1** in the absence of methanol again produced **5** in 75% yield, as the sole volatile product. The IR spectrum of **5** shows a strong absorption band at 2201 cm^{-1}, due to stretching frequencies of an Si–H bond. The ^{1}H NMR spectrum of **5** reveals a doublet resonance at 0.76 ppm and a quartet resonance at 6.08 ppm, attributed to methylsilyl protons and a hydrosilyl proton. Like photoisomers obtained from the photolysis of 1-(pentamethyldisilanyl)naphthalene and 1,5-bis(pentamethyldisilanyl)naphthalene, the formation of **5** may be explained by radical scission of a silicon–silicon bond, followed by migration of the resulting trimethylsilyl radical to the C_8 position of one of two naphthyl groups and then a 1,4-shift of the ipso hydrogen to the silyl radical center[1] (Scheme I).

Similar photolysis of 1,2-bis(1-naphthyl)tetramethyldisilane (**2**) in hexane gives two products, dimethylbis(1-naphthyl)silane (**6**) and 2,3-dihydro-1,1,3,3-tetramethyl-1,3-disilaphenalene-2-spiro-1′,2′-dihydronaphthalene (**7**) in 11 and 50% yields, respectively. All spectral data obtained for **6** were identical with those of the authentic sample prepared from the reaction of 2 equiv of 1-naphthyllithium with dichlorodimethylsilane. The structure of **7** was confirmed by spectrometric analysis as well as by elemental analysis. The ^{1}H NMR spectrum shows two nonequivalent methyl groups and double doublets at 2.76 ppm due to hydrogen on the C'_2 position of the dihydronaphthyl ring, as well as double triplets at

Scheme II



5.92 ppm, ascribed to hydrogen on the C_3' position. In the NOE-FID difference experiments at 500 MHz, saturation of the methylsilyl protons at 0.22 ppm caused the strong enhancement of protons at the C_2 and C_7 positions, while irradiation of the methylsilyl protons at 0.34 ppm resulted in the enhancement of protons at the C_2 and C_7 position and also protons at the C'_2 position. As expected, saturation of hydrogens on the C'_3 atom led to the positive NOE of two hydrogens on the C'_2 atom. These results are wholly consistent with the proposed structure.

Scheme II illustrates a possible mechanistic interpretation of the observed reaction course. Compound **6** can be explained by extrusion of dimethylsilylene from the starting compound **1**. The photochemical extrusion of dimethylsilylene from arylpentamethyldisilanes as a minor pathway is well-known.[3] In fact, the photolysis of **2** in the presence of a large excess of triethylsilane as a trapping

$$\mathbf{2} + Et_3SiH \xrightarrow{h\nu} Et_3SiSiMe_2H + \mathbf{6} + \mathbf{7}$$

agent gave a silylene insertion product, 1,1,1-triethyldimethyldisilane in 3% yield, in addition to a 18% yield of **6**. In this photolysis, compound **7** was also produced in 78% yield. The formation of the product **7**, however, can be understood in terms of homolytic scission of a silicon–silicon bond and migration of one of the two resulting dimethylnaphthylsilyl radicals to the C_8 position of the naphthyl ring of the other, followed by addition of the remaining silyl radical to the silyl-substituted C_1 atom in the naphthyl ring and, finally, a 1,4 shift of the ipso hydrogen.

The photolysis of **2** in the presence of an 8-fold excess of isobutene gave **6** and **7** in 10 and 46% yields, respectively. Similar photolysis of **2** in the presence of a large excess of methanol again afforded **6** and **7** in 8 and 52% yields. No other products were detected by either spectrometric analysis or GLC analysis.

Photolysis of 3 and 4. We first examined the photolysis of 1,1-bis(2-naphthyl)tetramethyldisilane (**3**) in the absence of a trapping agent. Thus, irradiation of **3** with

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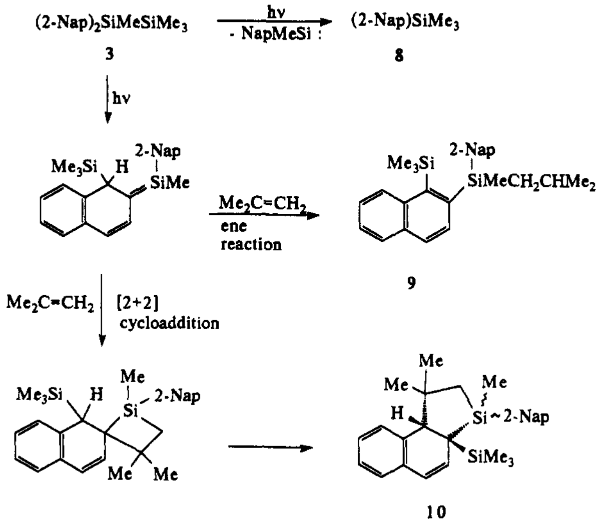
(3) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 155.

a low-pressure mercury lamp gave (trimethylsilyl)naphthalene (**8**) in 12% yield, in addition to nonvolatile products. No hydrosilane derivative analogous to **5** was detected in the photolysis mixture.

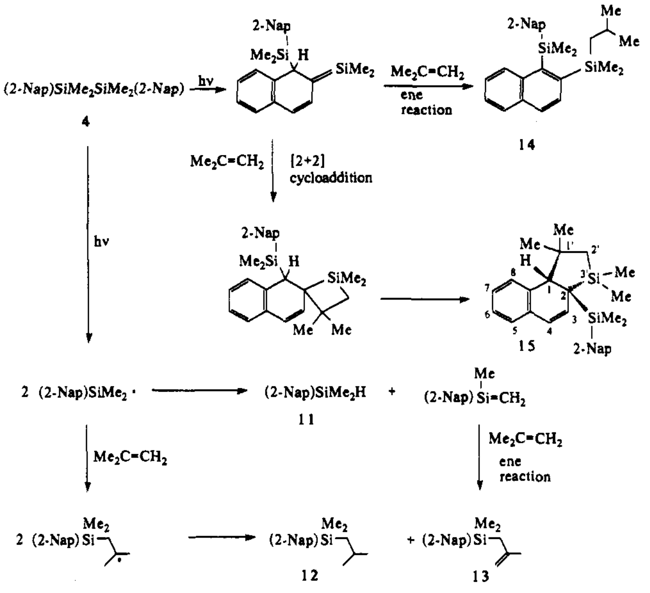
Similar irradiation of **3** in the presence of isobutene afforded compound **8** and 2-[isobutylmethyl(2-naphthyl)silyl]-1-(trimethylsilyl)naphthalene (**9**) in 9 and 24% yields. In this photolysis, the product whose molecular weight was determined to be 426, corresponding to $C_{28}H_{34}Si_2$, was obtained in 11% yield. All spectral data obtained for **8** were identical with those of the authentic sample. The structure of **9** was verified by spectrometric analysis as well as by elemental analysis (see Experimental Section). The product that corresponds to $C_{28}H_{34}Si_2$ was separated by MPLC. However, the compound isolated was not a single product but a mixture consisting of two isomers in the ratio 3:2. All attempts to separate these isomers were unsuccessful by either GLC or MPLC. Therefore, the structures of the isomers were verified by spectrometric analysis of the mixture. In the ^{1}H and ^{13}C NMR spectrum for each isomer of the mixture, chemical shifts and coupling constants observed for the silacyclopentyl ring are consistent with those obtained for the silacyclopentyl ring of the product formed from the photolysis of 2,7-bis(pentamethyldisilanyl)naphthalene whose structure was confirmed by an X-ray crystallographic analysis.[2] Furthermore, the ^{1}H and ^{13}C NMR spectra of the mixture proved to be very similar to those of compound **15**, whose structure was verified by NOE-FID experiments (see below). Thus, the ^{1}H NMR spectrum shows singlet signals at δ 0.81, 1.09, and 1.39 ppm for the major isomer and singlets at δ 0.72, 1.18, and 1.33 ppm for the minor isomer. Those resonances are attributable to the methyl protons on the C'_1 position in the silacyclopentane ring and the protons at the C'_2 position. A singlet signal at δ 3.08 ppm for the major isomer and a singlet at δ 2.99 ppm for the minor isomer due to the protons on the C_1 atom and two doublets at δ 6.09 and 6.41 attributed to each proton on the C_4 and C_3 atoms are consistent with the existence of the 1,2-dihydronaphthyl ring. The ^{13}C NMR spectrum shows eight signals for each isomers due to sp^3 carbons. On the basis of these results, two isomers were identified to be two stereoisomers of 1,2-dihydro-1,2-[1,1,3-trimethyl-3-(2-naphthyl)-3-silapropano]-2-(trimethylsilyl)naphthalene (**10**).

Compound **8** is probably formed by extrusion of methyl(2-naphthyl)silylene from the starting compound **3**, although we could not obtain any evidence for the formation of this silylene. For examples, as mentioned above, no silylene adduct was obtained in the presence of isobutene as the trapping agent. Furthermore, the photolysis of **3** in the presence of triethylsilane, which is a more reactive trapping agent for silylenes, gave no silylene insertion product. Presumably, the reactivity of methyl(2-naphthyl)silylene toward the trapping agents is quite low, and hence the silylene would be transformed into nonvolatile substances. Compound **9** can be best understood by the photochemical formation of silene arising from a 1,3-trimethylsilyl shift to the C_1 position of one of the two naphthyl groups. The ene reaction of this silene with isobutene gives compound **9**.[4] If our assignment of the structure of **10** is correct, the formation of two isomers of **10** may be explained by [2 + 2] cycloaddition of the silene with isobutene, followed by ring enlargement of the resulting silacyclobutyl ring to the five-membered ring system accompanied by a 1,2-trimethylsilyl shift (Scheme III).

Scheme III



Scheme IV



Similar [2 + 2] cycloaddition of isobutene to the silene, followed by ring enlargement to the five-membered ring system, has been observed in the photolysis of 2,6- and 2,7-bis(pentamethyldisilanyl)naphthalene.[2] In the absence of the trapping agent, the silene would undergo polymerization to give nonvolatile substances.

The photolysis of 1,2-bis(2-naphthyl)tetramethyldisilane (**4**) in the absence of a trapping agent gave 2-(dimethylsilyl)naphthalene (**11**) in 6% yield. No other volatile products were detected by either spectrometric analysis or GLC analysis. The photolysis of **4** in the presence of isobutene, however, produced five products, compound **11**, 2-(isobutyldimethylsilyl)naphthalene (**12**), 2-[(2-methyl-2-propenyl)dimethylsilyl]naphthalene (**13**), 2-(isobutyldimethylsilyl)-1-[dimethyl(2-naphthyl)silyl]naphthalene (**14**), and 1,2-dihydro-1,2-(1,1,3,3-tetramethyl-3-silapropano)-2-[dimethyl(2-naphthyl)silyl]naphthalene (**15**) in 9, 6, 10, 31, and 5% yields, respectively.

The structure of compounds **11**–**15** were confirmed by spectrometric analysis, as well as by elemental analysis. The location of substituents on the dihydronaphthyl ring for **15** was confirmed by NOE-FID difference experiments at 270 MHz. Thus, saturation of the Me$_a$ protons (1.12 ppm) on the C'_1 atom of a five-membered ring produce a positive NOE of Me$_b$ protons (0.85 ppm) and protons at

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(4) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51.

2.99 (H–C_1), 7.10 (H–C_8), and 0.42 ppm (H–C'_2) (see compound **15** in Scheme IV). Similar irradiation of the Me_b protons (0.85 ppm) led to the enhancement of protons at 2.99 (H–C_1), 0.64 (H–C'_2), 6.10 (H–C_4), and 6.23 ppm (H–C_3), as well as Me_a protons. Saturation of Me_c protons (0.17 ppm) on the ring silicon atom resulted in the enhancement of Me_b protons and a proton at the C_3 position, while irradiation of Me_d protons of a dimethyl(2-naphthyl)silyl group produced the strong enhancement of protons at the C_1 and C_3 positions of the dihydronaphthyl ring, as well as protons at the C_1 and C_3 position of the dimethylsilyl-substituted naphthyl ring. These results are wholly consistent with the proposed structure.

Compounds **11**–**13** are probably formed from the reaction of the silyl radical arising from homolytic scission of a silicon–silicon bond of the photoexcited compound **4**: the hydrogen abstraction of the resulting dimethyl(2-naphthyl)silyl radical leads to the formation of **11**, while addition of the silyl radical to isobutene, followed by redistribution of the resulting carbon radical produces compounds **12** and **13**. The formation of **13** may also be explained in terms of the ene reaction of the silene produced from the redistribution of the dimethyl(2-naphthyl)silyl radical with isobutene.[5,6] Presumably, compound **13** was produced by these two different pathways. The ene reaction of the silene produced from a 1,3-dimethyl(2-naphthyl)silyl shift to the C_1 position with isobutene would afford the product **14**. The production of **15** may be explained by the [2 + 2] cycloaddition reaction of the silene with isobutene to give a spiro compound, followed by enlargement of the silacyclobutyl ring to the five-membered ring system, accompanied by a 1,2-dimethyl(2-naphthyl)silyl shift (Scheme IV). The ring enlargement involves scission of a carbon–carbon bond in the four-membered system and proceeds with high stereospecificity. A similar reaction has been recently observed in the photolysis of 2,6- and 2,7-bis(pentamethyldisilanyl)naphthalene.[2]

In conclusion, the photolysis of bis(1-naphthyl)tetramethyldisilanes **1** and **3** afforded the photoisomers, via homolytic scission of a silicon–silicon bond of the respective starting compounds. In these photolyses, no silenes were produced. Irradiation of bis(2-naphthyl)tetramethyldisilanes **2** and **4**, however, gave silenes via a concerted 1,3-silyl shift to the C_1 position of the naphthyl ring. The silenes thus formed reacted with isobutene to give adducts as main products.

Experimental Section

General Considerations. All photolyses were carried out under an atmosphere of purified argon. ^1H and ^{13}C NMR spectra were determined with a JEOL Model JNM-GX-500 spectrometer, a JEOL Model JNM-EX-270 spectrometer, a JEOL Model JNM-FX-90A spectrometer, and a JEOL Model JNM-PMX-60A spectrometer, using deuteriochloroform, deuteriobenzene, and carbon tetrachloride solutions containing tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-infrared spectrometer. Mass spectra were measured on a Shimadzu Model GCMS-QP 1000 and a JEOL Model JMS-D300 instrument equipped with a JMA-2000 data processing system.

Materials. 1,1-Dichlorotetramethyldisilane[7] and 1,2-dichlorotetramethyldisilane[8] were prepared as reported in the literature. Ether, THF, benzene, and hexane used as solvents were dried over lithium aluminum hydride and distilled just before use.

Preparation of 1,1-Bis(1-naphthyl)tetramethyldisilane (1). Into a 50-mL two-necked flask fitted with a 20-mL dropping funnel was placed 5.1 g (24.6 mmol) of 1-bromonaphthalene and 20 mL of ether, and the flask was cooled at −80 °C. To this was added dropwise 15.8 mL of a 1.58 M *n*-butyllithium–hexane solution (25.0 mmol) through the dropping funnel. The resulting mixture was allowed to warm to 0 °C and to stand over 3 h at 0 °C; then 3.0 g (16.0 mmol) of 1,1-dichlorotetramethyldisilane was added. After the solution was stirred overnight at room temperature, the solution was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, washed with water, and dried over potassium carbonate. The solvent was evaporated, and the residue was distilled under reduced pressure (150–200 °C/0.1 mmHg) to give crude **1**. Recrystallization of the crude product from ethanol gave 2.0 g (44% yield) of pure **1**: bp 170–173 °C; mp 95.5 °C; MS *m/e* 370 (M^+); IR ν_{Si-C} 1244 cm^{-1}; 60-MHz ^1H NMR (δ in CCl_4) 0.12 (s, 9 H, Me_3Si), 0.85 (s, 3 H, MeSi), 6.92–7.92 (m, 14 H, naphthyl ring protons); 22.5-MHz ^{13}C NMR (δ in $CDCl_3$) −2.8, −0.8, 125.4 (br, 3 C), 128.7, 128.8, 129.7, 133.4, 134.6, 136.7, 137.3. Anal. Calcd for $C_{24}H_{26}Si_2$: C, 77.77; H, 7.07. Found: C, 77.76; H, 7.07.

Preparation of 1,2-Bis(1-naphthyl)tetramethyldisilane (2). Into a 100-mL three-necked flask fitted with a reflux condenser and a 50-mL dropping funnel was placed 3.1 g (0.13 mol) of magnesium and 20 mL of THF. To this was added dropwise a mixture of 21.6 g (0.104 mol) of 1-bromonaphthalene and 9.2 g (0.049 mol) of 1,2-dichlorotetramethyldisilane in 20 mL of THF. The mixture was heated to reflux for 12 h and then hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, washed with water, and dried over potassium carbonate. The solvent was evaporated, and the residue was distilled under reduced pressure (150–200 °C/0.1 mmHg) to give 12.2 g of crude **2**. Recrystallization of the crude solid from ethanol gave 6.9 g (39% yield) of pure **2**: bp 182–184 °C (0.1 mmHg); mp 67.0–68.0 °C; MS *m/e* 370 (M^+); IR ν_{Si-C} 1246 cm^{-1}; 60-MHz ^1H NMR (δ in CCl_4) 0.46 (s, 12 H, $2Me_2Si$), 6.86–7.83 (m, 14 H, naphthyl ring protons); 22.5-MHz ^{13}C NMR (δ in $CDCl_3$) −1.6, 125.1, 125.3, 128.5, 128.8, 129.4, 133.2, 133.3 (br, 2 C), 137.1, 137.6. Anal. Calcd for $C_{24}H_{26}Si_2$: C, 77.77; H, 7.07. Found: C, 77.52; H, 6.96.

Preparation of 1,1-Bis(2-naphthyl)tetramethyldisilane (3). Into a 50-mL two-necked flask fitted with a 20-mL dropping funnel was placed 5.0 g (24.1 mmol) of 2-bromonaphthalene and 20 mL of ether, and the flask was cooled to −80 °C. A hexane solution of 1.54 mL of 1.58 M *n*-butyllithium (24.3 mmol) was added dropwise through the dropping funnel. The resulting mixture was allowed to warm to 0 °C and to stand at 0 °C over 3 h, then 2.3 g (12.3 mmol) of 1,1-dichlorotetramethyldisilane was added. After overnight stirring at room temperature, the solution was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, washed with water, and dried over potassium carbonate. The solvent was evaporated, and the residue was distilled under reduced pressure to give 1.5 g (33% yield) of **3**: bp 162–164 °C (0.1 mmHg); MS *m/e* 370 (M^+); IR ν_{Si-C} 1246 cm^{-1}; 60-MHz ^1H NMR (δ in CCl_4) 0.23 (s, 9 H, Me_3Si), 0.76 (s, 3 H, MeSi), 7.11–7.96 (m, 14 H, naphthyl ring protons); 22.5-MHz ^{13}C NMR (δ in $CDCl_3$) −4.6, −1.4, 125.9, 126.3, 127.1, 127.7, 128.0, 131.2, 133.1, 133.7, 135.0, 135.5. Anal. Calcd for $C_{24}H_{26}Si_2$: C, 77.77; H, 7.07. Found: C, 77.62; H, 7.07.

Preparation of 1,2-Bis(2-naphthyl)tetramethyldisilane (4). Into a 30-mL two-necked flask fitted with a reflux condenser and a 20-mL dropping funnel was placed 0.29 g (12.0 mmol) of magnesium and 5 mL of THF. To this was added dropwise a mixture of 2.0 g (9.6 mmol) of 2-bromonaphthalene and 1.08 g (5.8 mmol) of 1,2-dichlorotetramethyldisilane in 10 mL of THF. The resulting mixture was heated to reflux for 12 h, and then

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(5) Boudjouk, P.; Robert, J. R.; Gollino, C. M.; Sommer, L. H. *J. Am. Chem. Soc.* **1972**, *94*, 1673.

(6) Nate, K.; Ishikawa, M.; Ni, H.; Watanabe, H.; Saheki, Y. *Organometallics* **1987**, *6*, 1673.

(7) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 139.

(8) Kumada, M.; Yamaguchi, M.; Yamamoto, Y.; Nakajima, J.; Shiina, K. *J. Org. Chem.* **1956**, *21*, 1264.

hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, washed with water, and dried over potassium carbonate. The solvent was evaporated, and the residue was distilled under reduced pressure (150–200 °C/0.1 mmHg) to give 1.4 g of crude **4**. Recrystallization of the crude solid from ethanol gave 0.7 g (40% yield) of pure **4**: mp 118.0 °C; MS *m/e* 370 (M^+); IR ν_{Si-C} 1245 cm^{-1}; 60-MHz ^1H NMR (δ in CCl_4) 0.41 (s, 12 H, $2Me_2Si$), 7.15–7.86 (m, 14 H, naphthyl ring protons); 22.5-MHz ^{13}C NMR (δ in $CDCl_3$) −3.8, 125.8, 126.1, 126.8, 127.7, 127.9, 130.4, 133.0, 133.5, 134.3, 136.5. Anal. Calcd for $C_{24}H_{26}Si_2$: C, 77.77; H, 7.07. Found: C, 77.51; H, 6.81.

Photolysis of 1. Into a 25-mL reaction vessel fitted internally with a 6-W low-pressure mercury lamp bearing a Vycor filter was placed a solution of 196.8 mg (0.531 mmol) of **1** and 22.2 mg (0.105 mmol) of pentadecane as an internal standard in 20 mL of hexane. The solution was irradiated for 3 h with a slow stream of argon bubbling through the mixture at room temperature. At this stage, almost all of the starting compound **1** was photolyzed. The resulting solution was analyzed by GLC as being **5** (75% yield). After evaporation of the solvent, the mixture was treated with MPLC (silica gel, eluent hexane) to give **5** in a pure form: mp 132.2–133.0 °C; MS *m/e* 370 (M^+); IR ν_{Si-H} 2201 cm^{-1}, ν_{Si-C} 1248 cm^{-1}; 60-MHz ^1H NMR (δ in CCl_4) 0.55 (s, 9 H, Me_3Si), 0.76 (d, 3 H, J = 4 Hz, MeSiH), 6.08 (q, 1 H, J = 4 Hz, HSi), 6.95–8.02 (m, 13 H, ring protons); 22.5-MHz ^{13}C NMR (δ in $CDCl_3$) −3.3, 3.5, 124.1 (br, 2 C), 125.2, 125.5, 125.8, 127.9, 128.8, 130.0, 131.0, 131.9, 133.2, 134.4, 134.5, 134.7, 136.2, 136.8, 137.1, 137.3, 139.7, 141.5. Anal. Calcd for $C_{24}H_{26}Si_2$: C, 77.77; H, 7.07. Found: C, 77.66; H, 7.02.

Photolysis of 1 in the Presence of Methanol. A solution of 186.4 mg (0.503 mmol) of **1**, 0.1 mL (2.4 mmol) of methanol, and 20.3 mg (0.096 mmol) of pentadecane as an internal standard in 20 mL of benzene was photolyzed for 2 h. GLC analysis of the reaction mixture showed the formation of **5**, but no other volatile product was detected. The retention time of GLC and the mass spectrum of **5** were identical with those of an authentic sample.

Photolysis of 2. A solution of 379.5 mg (1.02 mmol) of **2** and 22.4 mg (0.113 mmol) of tetradecane as an internal standard in 25 mL of hexane was irradiated for 2.5 h. The resulting solution was analyzed by GLC as being **6** (11% yield) and **7** (50% yield). The mixture was separated by MPLC (silica gel, eluent hexane) to give **6** and **7** in a pure form. All spectral data obtained for **6** were identical with those of an authentic sample synthesized independently (see below). For **7**: MS *m/e* 370 (M^+); IR ν_{Si-C} 1252 cm^{-1}; 500-MHz ^1H NMR (δ in $CDCl_3$) 0.22 (s, 6 H, MeSi), 0.34 (s, 6 H, MeSi), 2.76 (dd, 2 H, J = 4.4, 1.8 Hz, H on C'_2), 5.92 (dt, 1 H, J = 9.5, 4.4 Hz, H on C'_3), 6.36 (d, 1 H, J = 9.5 Hz, H on C'_4), 6.61 (dt, 1 H, J = 7.3, 1.5 Hz, H on C'_6 or C'_7), 6.69 (d, 1 H, J = 7.3 Hz, H on C'_8), 6.82 (dt, 1 H, J = 7.3, 1.5 Hz, H on C'_6 or C'_7), 6.90 (dd, 1 H, J = 7.3, 1.5 Hz, H on C'_5), 7.45 (dd, 2 H, J = 8.2, 7.0 Hz, H on C_5 and C_8), 7.69 (dd, 2 H, J = 7.0, 1.5 Hz, H on C_4 and C_9), 7.85 (dd, 2 H, J = 8.2, 1.5 Hz, H on C_6 and C_7); 22.5-MHz ^{13}C NMR (δ in $CDCl_3$) −2.5, 0.6, 17.3, 27.3, 124.1, 125.0, 125.8, 127.1, 127.2, 127.3, 127.9, 129.8, 130.6, 133.1, 133.8, 134.2, 138.3, 140.8. Anal. Calcd for $C_{24}H_{26}Si_2$: C, 77.77; H, 7.07. Found: C, 77.48; H, 6.98.

Preparation of 6. A mixture of 3.3 g (15.9 mmol) of 1-bromonaphthalene and 1.0 g (7.7 mmol) of dichlorodimethylsilane in 5 mL of THF was added dropwise to 0.4 g (16.5 mmol) of magnesium in 5 mL of THF with stirring. The solution was allowed to stand overnight at room temperature, and then it was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, washed with water, and dried over potassium carbonate. The solvent was evaporated, and the residue was distilled under reduced pressure to give 2.1 g (87% yield) of **6**. The analytically pure **6** was obtained from recrystallization from ethanol: bp 140 °C (0.3 mmHg); mp 78.0–78.8 °C; MS *m/e* 312 (M^+); IR ν_{Si-C} 1251 cm^{-1}; 60-MHz ^1H NMR (δ in CCl_4) 0.83 (s, 6 H, Me_2Si), 6.96–7.84 (m, 14 H, naphthyl ring protons); 22.5-MHz ^{13}C NMR (δ in $CDCl_3$) 0.5, 125.3 (br, 2 C), 125.6, 128.3, 128.9, 130.1, 133.4, 134.2, 136.9, 137.0. Anal. Calcd for $C_{22}H_{20}Si$: C, 84.56; H, 6.45. Found: C, 84.60; H, 6.45.

Photolysis of 2 in the Presence of Triethylsilane. A mixture of 200 mg (0.541 mmol) of **2** and 0.5 mL (3.14 mmol) of triethylsilane in 25 mL of hexane was photolyzed. After 5 h of irradiation, 21.1 mg (0.124 mmol) of dodecane as an internal standard was added to the resulting photolysis mixture. Then, the mixture was analyzed by GLC as being **6** (18% yield), **7** (78% yield), and 1,1,1-triethyldimethyldisilane (3% yield). 1,1,1-Triethyldimethyldisilane was isolated by preparative GLC. All spectral data were identical with those of an authentic sample.[9]

Photolysis of 2 in the Presence of Isobutene. A mixture of 174.5 mg (0.471 mmol) of **2**, 13.5 mg (0.068 mmol) of tetradecane as an internal standard, and 2.1 g (37.5 mmol) of isobutene in 20 mL of hexane was irradiated for 8 h. The GLC analysis of the resulting solution showed the formation of **6** (10% yield) and **7** (46% yield). GLC retention times and mass spectra of **6** and **7** were identical with those of authentic samples.

Photolysis of 2 in the Presence of Methanol. A solution of 185.4 mg (0.500 mmol) of **2** and 12.5 mg (0.063 mmol) of tetradecane as an internal standard in the presence of 0.1 mL (2.4 mmol) of methanol in 20 mL of benzene was irradiated for 1 h. The reaction mixture was analyzed by GLC as being **6** (8% yield) and **7** (51% yield). GLC retention times and mass spectra of **6** and **7** were identical with those of authentic samples.

Photolysis of 3. A solution of 243.3 mg (0.656 mmol) of **3** and 22.3 mg (0.112 mmol) of tetradecane as an internal standard in 20 mL of hexane was irradiated for 39 h. The resulting mixture was analyzed by GLC as being **8** (12%) and the starting compound **3** (13%). Product **8** was separated from the mixture by MPLC (silica gel, eluent hexane). All spectral data obtained for **8** were identical with those of an authentic sample synthesized independently (see below).

Preparation of 8. To a solution of 2-naphthylmagnesium bromide prepared from 0.5 g (2.4 mmol) of 2-bromonaphthalene and 65.7 mg (2.7 mmol) of magnesium in 3 mL of THF was added 0.4 g (3.7 mmol) of chlorotrimethylsilane. The resulting solution was stirred overnight at room temperature and then hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, washed with water, and then dried over potassium carbonate. The solvent was evaporated, and the residue was distilled under reduced pressure (0.1 mmHg) to give 0.2676 g (48% yield) of **8**: MS *m/e* 200 (M^+); IR ν_{Si-C} 1248 cm^{-1}; 60-MHz ^1H NMR (δ in CCl_4) 0.35 (s, 9 H, Me_3Si), 7.09–7.85 (m, 7 H, ring protons); 22.5-MHz ^{13}C NMR (δ in $CDCl_3$) −1.0, 125.9, 126.2, 127.0, 127.7, 127.9, 128.0, 129.8, 133.1, 133.7, 137.8. Anal. Calcd for $C_{13}H_{16}Si$: C, 77.93; H, 8.05. Found: C, 77.90; H, 7.94.

Photolysis of 3 in the Presence of Isobutene. A solution of 195.4 mg (0.527 mmol) of **3**, 2.5 g (44.6 mmol) of isobutene, and 21.2 mg (0.107 mmol) of tetradecane as an internal standard in 55 mL of hexane was irradiated for 2 h. The resulting mixture was analyzed by GLC as being **8** (9% yield), **9** (24% yield), and **10** (11% yield). Products **8**–**10** (**10** as a mixture of two isomers in the ratio of 3:2) were isolated by MPLC (silica gel, eluent hexane). All spectral data obtained for **8** were identical with those of an authentic sample. For **9**: MS *m/e* 426 (M^+); IR ν_{Si-H} 1250 cm^{-1}; 60-MHz ^1H NMR (δ in C_6D_6) 0.36 (s, 9 H, Me_3Si), 0.84 (s, 3 H, MeSi), 0.96 (d, 6 H, J = 6.0 Hz, Me_2C), 1.38 (d, 2 H, J = 6.0 Hz, H_2CCHMe_2), 1.96 (m, 1 H, $HCMe_2$), 7.06–8.46 (m, 13 H, ring protons); 22.5-MHz ^{13}C NMR (δ in $CDCl_3$) 1.4, 4.4, 25.2, 26.2, 26.6, 27.7, 124.5, 125.7, 125.9, 126.2, 127.0, 127.4, 127.8, 128.1, 128.9, 129.3, 130.7, 133.0, 133.2, 133.6, 134.9, 135.2, 138.0, 138.4, 141.6, 143.5. Anal. Calcd for $C_{28}H_{34}Si_2$: C, 78.81; H, 8.03. Found: C, 78.70; H, 7.88. For **10** (as a 3:2 isomeric mixture): MS *m/e* 426 (M^+); IR ν_{Si-C} 1252 cm^{-1}; 60-MHz ^1H NMR (δ in C_6D_6) −0.18 (s, 9 H, Me_3Si), 0.14 (s, 3 H, MeSi), 0.72 (s, 0.8 H, H on C'_2), 0.81 (s, 1.2 H, H on C'_2), 1.09 (s, 1.8 H, MeC), 1.18 (s, 1.2 H, MeC), 1.33 (s, 1.2 H, MeC), 1.39 (s, 1.8 H, MeC), 2.99 (s, 0.4 H, H on C_1), 3.08 (s, 0.6 H, H on C_1), 6.09 (d, 1 H, J = 9 Hz, H on C_3), 6.41 (d, 1 H, J = 9 Hz, H on C_4), 6.87–7.87 (m, 13 H, aromatic ring protons), 8.25 (s, 1 H, H on C_1 of naphthyl ring); 22.5-MHz ^{13}C NMR (δ in $CDCl_3$) −2.3, −1.0, 25.2, 26.1, 30.1, 32.3, 45.6, 55.0 (sp^3 carbons for major isomer), −1.7, 0.9, 25.7, 27.4, 29.5, 32.1, 45.6, 54.6 (sp^3 carbons for minor isomer), 124.0, 125.1, 126.0, 126.4, 126.5, 126.7, 127.0, 127.7, 128.2, 129.0, 129.2, 130.7, 131.7, 132.6, 132.9,

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[9] Seyferth, D.; Annarelli, D. C.; Duncan, D. P. *Organometallics* **1982**, *1*, 1288.

133.6, 133.8, 134.3, 134.9, 135.3, 135.6, 136.7 (sp^2 carbons). Anal. Calcd for $C_{28}H_{34}Si_2$: C, 78.81; H, 8.03. Found: C, 78.75; H, 8.02.

Photolysis of 3 in the Presence of Triethylsilane. A mixture of 320.3 mg (0.866 mmol) of **3**, 0.7 mL (4.40 mmol) of triethylsilane, and 16.9 mg (0.0994 mmol) of dodecane as an internal standard in 25 mL of hexane was irradiated for 10 h. GLC analysis of the resulting mixture showed the presence of **8** (8% yield) and the starting compound **3** (7%). The GC-mass spectrum and retention time on GLC for **8** was identical with those of the product obtained from the photolysis in the absence of triethylsilane.

Photolysis of 4. A solution of 190.9 mg (0.515 mmol) of **4** and 19.0 mg of tetradecane as an internal standard in 20 mL of hexane was irradiated for 4 h. GLC analysis of the resulting mixture showed the formation of **11** (6% yield). All spectral data obtained for **11** were identical with those of an authentic sample synthesized independently (see below).

Preparation of 11. To a solution of 2-naphthylmagnesium bromide prepared from 0.5 g (2.4 mmol) of 2-bromonaphthalene and 65.7 mg (2.7 mmol) of magnesium in 3 mL of THF was added 0.4 g (3.7 mmol) of chlorotrimethylsilane. After overnight stirring at room temperature, the resulting solution was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, washed with water, and dried over potassium carbonate. The solvent was evaporated, and the residue was distilled under reduced pressure to give 0.2676 g (48% yield) of **11**: bp 120 °C/0.1 mmHg; MS *m/e* 186 (M^+); IR $\nu_{\mathrm{Si-H}}$ 2117 cm^{-1}, $\nu_{\mathrm{Si-C}}$ 1248 cm^{-1}; 60-MHz ^{1}H NMR (δ in C_6D_6) 0.33 (d, 6 H, J = 4 Hz, MeSi), 4.72 (sept, 1 H, J = 4 Hz, HSi), 7.04–7.77 (m, 6 H, naphthyl ring protons), 7.95 (s, 1 H, H on C_1); 22.5-MHz ^{13}C NMR (δ in C_6D_6) −3.6, 126.2, 126.6, 127.0, 128.1, 129.1, 130.5, 133.6, 134.4, 134.9, 135.2. Anal. Calcd for $C_{12}H_{14}Si$: C, 77.35; H, 7.57. Found: C, 77.31; H, 7.54.

Photolysis of 4 in the Presence of Isobutene. A solution of 190.8 mg (0.515 mmol) of **4**, 3.1 g (55.4 mmol) of isobutene, and 29.3 mg (0.148 mmol) of tetradecane as an internal standard in 20 mL of hexane was irradiated for 2 h. The resulting mixture was analyzed by GPC as being **11** (9% yield), **12** (10% yield), **13** (6% yield), **14** (31% yield), and **15** (5% yield). Products were isolated by MPLC (silica gel, eluent hexane). All spectral data obtained for **11** were identical with those of an authentic sample. For **12**: MS *m/e* 242 (M^+); IR $\nu_{\mathrm{Si-C}}$ 1248 cm^{-1}; 60-MHz ^{1}H NMR (δ in $CDCl_3$) 0.40 (s, 6 H, Me_2Si), 0.88 (d, 2 H, J = 7 Hz, H_2CCHMe_2), 0.95 (d, 6 H, Me_2CHCH_2), 1.23–2.20 (m, 1 H, $HCMe_2$), 7.19–8.32 (m, 7 H, naphthyl ring protons); 22.5-MHz ^{13}C NMR (δ in $CDCl_3$) −1.9, 25.0, 26.3, 125.8, 126.1, 126.8, 127.7, 128.0, 130.0, 133.0, 133.6, 134.0, 137.7. Anal. Calcd for $C_{16}H_{22}Si$: C, 79.27; H, 9.15. Found: C, 79.24; H, 9.13. For **13**: *m/e* 240 (M^+); IR $\nu_{\mathrm{si-C}}$ 1248 cm^{-1}; 500-MHz ^{1}H NMR (δ in C_6D_6) 0.38 (s, 6 H, Me_2Si), 1.62 (br s, 3 H, MeC), 1.83 (d, 2 H, J = 1.1 Hz, $H_2CC{=}C$), 4.68 (br s, 1 H, olefin proton), 4.77 (m, 1 H, olefin proton), 7.41–7.85 (m, 6 H, naphthyl ring protons), 8.00 (br s, 1 H, H on C_1); 22.5-MHz ^{13}C NMR (δ in C_6D_6) −2.8, 25.3, 27.9, 109.4, 126.1, 126.5, 127.4, 128.2, 128.3, 130.3, 133.6, 134.3, 134.6, 136.7, 143.1. Exact MS Calcd for $C_{16}H_{20}Si$: 240.1366. Found: 240.1343. For **14**: MS *m/e* 426 (M^+); IR $\nu_{\mathrm{Si-C}}$ 1251 cm^{-1}; 90-MHz ^{1}H NMR (δ in $CDCl_3$) −0.23 (s, 6 H, Me_2Si), 0.21 (s, 6 H, Me_2Si), 1.29 (d, 6 H, J = 6.7 Hz, Me_2C), 1.32 (d, 2 H, J = 6.7 Hz, H_2CHCMe_2), 2.23 (m, 1 H, $HCMe_2$), 6.48–7.48 (m, 13 H, ring protons); 22.5-MHz ^{13}C NMR (δ in $CDCl_3$) 2.1, 4.2, 25.2, 26.2, 28.6, 124.5, 125.5, 125.8, 126.2, 127.0, 127.7, 127.8, 128.1, 128.2, 129.9, 130.5, 132.0, 132.8, 133.0, 133.6, 134.8, 138.2, 138.9, 143.6, 148.8. Exact MS Calcd for $C_{28}H_{34}Si_2$: 426.2199. Found: 426.2218. For **15**: MS *m/e* 426 (M^+); IR $\nu_{\mathrm{Si-C}}$ 1252 cm^{-1}; 270-MHz ^{1}H NMR (δ in C_6D_6) 0.17 (s, 3 H, MeSi), 0.24 (s, 3 H, MeSi), 0.26 (s, 3 H, MeSi), 0.30 (s, 3 H, MeSi), 0.42 (d, 1 H, J = 14.6 Hz, H on C'_2), 0.64 (d, 1 H, J = 14.6 Hz, H on C'_2), 0.85 (s, 3 H, MeC), 1.12 (s, 3 H, MeC), 2.99 (br s, 1 H, H on C_1), 6.10 (d, 1 H, J = 9.7 Hz, H on C_3), 6.23 (d, 1 H, J = 9.7 Hz, H on C_4), 6.75–7.06 (m, 2 H, aromatic ring protons), 7.10 (d, 1 H, J = 4.0 Hz, H on C_8), 7.25–7.36 (m, 3 H, aromatic ring protons), 7.62 (d, 1 H, J = 6.9 Hz, H on C_3 on naphthyl ring), 7.56–7.78 (m, 3 H, aromatic ring protons), 8.05 (br s, 1 H, H on C_1 of naphthyl ring); 22.5-MHz ^{13}C NMR (δ in C_6D_6) −3.0, 0.0, 1.3, 25.6, 28.9, 29.1, 32.2, 45.5, 55.1, 125.4, 125.7, 125.8, 125.9, 126.5, 127.3, 127.6, 128.3, 128.4, 129.5, 130.2, 131.3, 133.1, 133.3, 134.1, 134.4, 135.7, 137.0. Exact MS Calcd for $C_{28}H_{34}Si_2$: 426.2199. Found: 426.2193.

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