(CD_2Cl_2): δ 2.98 (s, 6 H, NMe_2), 3.67 (s, 24 H, OCH_2), 7.56–7.93 (m, 6 H, aromatic).

18-Crown-6 Potassium Salt of (8-(Dimethylamino)-naphthyl)phenyltrifluorosilicate (4b): colorless crystals (94%); mp >280 °C. Anal. Calc for $C_{30}H_{41}F_3NO_6SiK$: C, 56.59; H, 6.45; N, 2.20. Found: C, 56.87; H, 6.53; N, 2.43. ^1H NMR (CD_2Cl_2): δ 2.91 (s, 6 H, NMe_2), 3.37 (s, 24 H, OCH_2), 6.9–7.98 (m, 11 H, aromatic).

18-Crown-6 Potassium Salt of 1,5-Bis(tetrafluorosilicato)-4,8-bis(dimethylamino)naphthalene–Tetrakis(methanol) (5b). In this particular case, the reaction was performed in THF, and the compound was recrystallized from methanol giving colorless crystals containing two molecules of methanol per potassium ion (81%): mp 260 °C dec. Anal. Calc for $C_{42}H_{80}F_8N_2O_{16}Si_2K_2$: C, 43.66; H, 6.98; N, 2.42. Found: C, 43.44; H, 6.38; N, 2.50. MS (FAB neg): m/z 419 ($A^{2-}\cdots K^+$), 841 ($A^{2-}\cdots K^+\cdots A^{2-}$). ^1H NMR (CD_2Cl_2): δ 2.84 (s, 12 H, NMe_2), 3.31 (12 H, CH_3OH), 3.55 (s, 48 H, OCH_2), 4.71 (4 H, $MeOH$), 7.24 (d, 2 H, J_{HH} 7 Hz), 7.54 (d, 2 H, J_{HH} 7 Hz).

Crystal Structure of the 18-Crown-6 Potassium Salt of (8-(Dimethylamino)naphthyl)tetrafluorosilicate (3b). Crystals of the title complex **3b** were grown by cooling a saturated acetone solution in a nitrogen atmosphere. Elongated colorless plates were obtained. Preliminary Weissenberg photographs established a monoclinic unit cell with space group $P2_1/n$ (No. 14). A small plate was sealed inside a Lindemann glass capillary with the [100] direction parallel to the ϕ axis of the diffractometer. Effluorescence occurred to some extent at the crystal surface.

X-ray Data Collection. Data were collected on a CAD-4 automated diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å). Lattice constants (Table VI) came from a least-squares refinement of 25 reflections obtained in the range $11.4 < 2\theta < 35.0°$. The intensities of three standard reflections were monitored after intervals of 60 min; no significant change in these intensities occurred. The structure amplitudes were obtained after the usual Lorentz and polarization reductions. Only the reflections having $\sigma(F)/F < 0.33$ were considered to be observed. No absorption corrections were made.

Structure Determination and Refinement. Direct methods (1980 version of the MULTAN program) were used to solve the structure and to give the positions of the silicon atom and three of the fluorine atoms, which were used to phase a Fourier map. This Fourier map gave the coordinates of the potassium atom, and two subsequent Fourier syntheses revealed all the non-hydrogem atoms of the complex along with the four atoms of the trapped acetone molecule. The atomic scattering factors were taken from ref 27. After three cycles of least-squares refinement with isotropic thermal parameters to all atoms, the silicon, potassium, fluorine, oxygen, and nitrogen atoms were refined anisotropically. At this stage the conventional R factor was 0.086. The hydrogen atoms were positioned by calculation (SHELX-76 program), and refinement converged to the final R value of 0.062.

The final atomic coordinates are listed in Table VII. Individual bond lengths are listed in Table I and bond angles in Table II. Table VIII, anisotropic thermal parameters, and Table IX, calculated hydrogen atom coordinates, and a list of observed and calculated structure factors are available as supplementary material.

Acknowledgment. F.C. thanks Prof. J. Lapasset, Groupe de Dynamique des Phases Condensées, L.A. au CNRS No. 233, Université de Montpellier II, for the use of the Weissenberg camera.

Registry No. **1a** (coordination compound (CC) entry), 77773-10-5; **1a** (silane entry), 87996-42-7; **1b**, 139312-46-2; **2a** (CC entry), 139404-51-6; **2a** (silane entry), 139312-41-7; **2b**, 139346-59-1; **3a** (CC entry), 108034-64-6; **3a** (silane entry), 121497-40-3; **3b**, 139312-48-4; **4a** (CC entry), 108022-89-5; **4a** (silane entry), 139312-42-8; **4b**, 139312-50-8; **5a** (CC entry), 139312-44-0; **5a** (silane entry), 139312-43-9; **5b**, 139404-53-8.

Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen atom coordinates (2 pages); a listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

Photolysis of Organopolysilanes. Photochemical 1,2-Silyl Migration of 2-(2-Phenylethenyl)- and 2-(2,2-Diphenylethenyl)-Substituted Trisilanes

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The photochemical behavior of 2-(2-phenylethenyl)-2-(trimethylsilyl)hexamethyltrisilane (**1a**), 2-(2,2-diphenylethenyl)-2-(trimethylsilyl)hexamethyltrisilane (**1b**), and 2-(2,2-diphenylethenyl)-2-phenylhexamethyltrisilane (**1c**) has been studied. Irradiation of (E)-**1a** with a low-pressure mercury lamp initially resulted in cis–trans isomerization and then afforded (E)-2-phenyl(trimethylsilyl)ethene ((E)-**2a**) and (Z)-2-phenyl(trimethylsilyl)ethene ((Z)-**2a**) in addition to (E)-**1a** and (Z)-**1a**. Irradiation of **1b** afforded 2,2-diphenyl(trimethylsilyl)ethene (**2b**) and 3-phenyl-1,1,2-tris(trimethylsilyl)-1-silaindene (**3b**), while **1c** afforded **2b**, 1,3-diphenyl-1,2-bis(trimethylsilyl)-1-silaindene (**3c**), and 1,3-diphenyl-1-(trimethylsilyl)-1-silaindene (**4c**). A possible mechanism leading to the observed products is described.

Introduction

We have demonstrated that permethylpolysilane oligomers and π-electron-system-substituted polysilanes are photoactive, and the fate of photochemically excited polysilanes highly depends on the structure and the substituents attached to silicon atoms. For example, irradiation of permethylcyclohexasilane with a low-pressure mercury lamp results in ring contraction with simultaneous extrusion of dimethylsilylene.[1] In contrast to this, irradiation of the disilanes bearing a π-electron system on a silicon atom leads to isomerization involving migration of

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[1] (a) Ishikawa, M.; Kumada, M. *J. Chem. Soc. D* **1970**, 612. (b) Ishikawa, M.; Kumada, M. *J. Chem. Soc. D* **1971**, 489.

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a silyl group. Thus, irradiation of vinyl-substituted disilanes affords silenes arising from a 1,3-shift of a silyl group to the terminal carbon of the vinyl group in high yields.[2,3] Such a photochemical 1,3-silyl shift is not restricted to vinyldisilanes but is observed in aryldisilanes. In fact, pentamethylphenyldisilane undergoes photochemical isomerization involving a 1,3-silyl shift onto the ortho position of the phenyl ring to form a silene.[4] In the case of 2-phenylheptamethyltrisilane, however, both extrusion of silylene and the 1,3-silyl shift onto the phenyl ring occur competitively.[5a]

We have also found that a 1,2-silyl shift occurs in some cases. Phenylethynyldisilanes undergo photochemical isomerization involving the 1,2-silyl shift, leading to the formation of silacyclopropenes.[6,7] In these photolyses, silapropadienes arising from a 1,3-silyl shift are also produced as reactive intermediates.[6] Similar photolysis of a phenylethenyldisilane affords a silacyclopropane and a silaindane, via a 1,2-silyl shift.[3,8] It is of interest to us to investigate the photochemical behavior of 2-phenylethenyl- and 2,2-diphenylethenyl-substituted trisilanes and to learn which reaction, extrusion of the silylenes or isomerization accompanied by an intramolecular silyl shift, takes place in the photolysis of these compounds. In this paper, we report the unique photochemical behavior of 2-(2-phenylethenyl)-2-(trimethylsilyl)hexamethyltrisilane (**1a**), 2-(2,2-diphenylethenyl)-2-(trimethylsilyl)hexamethyltrisilane (**1b**), and 2-(2,2-diphenylethenyl)-2-phenylhexamethyltrisilane (**1c**).

Results and Discussion

As for the photolysis of (*E*)-(2-phenylethenyl)pentamethyldisilane reported previously,[8] irradiation of (*E*)-2-(2-phenylethenyl)-2-(trimethylsilyl)hexamethyltrisilane ((*E*)-**1a**) with a low-pressure mercury lamp in hexane afforded an equilibrium mixture consisting of (*E*)-**1a** and (*Z*)-**1a** in the ratio of 5:4 in the initial stage of the reaction. On prolonged irradiation, the *E* and *Z* isomers decreased gradually without change of this ratio and two products, (*E*)-2-phenyl(trimethylsilyl)ethene ((*E*)-**2a**) and (*Z*)-2-phenyl(trimethylsilyl)ethene ((*Z*)-**2a**), were obtained in 5 and 2% yields, respectively, together with 11% of (*E*)-**1a** and 8% of (*Z*)-**1a**.[9] The photolysis of (*E*)-**1a** in the presence of methanol gave neither the product arising from a silacyclopropane derivative nor the product derived from a silene intermediate, but the products (*E*)-**2a** and (*Z*)-**2a** were obtained in 10 and 4% yields, respectively. Although the formation of **2a** clearly indicates that the photolysis of **1a** involes the extrusion of bis(trimethylsilyl)silylene, no silylene–methanol adduct was obtained. A similar photolysis of (*E*)-**1a** in the presence of 2,3-dimethylbutadiene, again, afforded no silylene adduct, but (*E*)-**2a** and (*Z*)-**2a** were isolated in 24 and 11% yields, respectively.

Table I. Photolysis of Trisilanes at 254 nm

trisilane	additive	time, h	product, %
(*E*)-**1a**	none	15	(*E*)-**1a**, 11; (*Z*)-**1a**, 8; (*E*)-**2a**, 5; (*Z*)-**2a**, 2
(*E*)-**1a**	MeOH	15	(*E*)-**1a**, 10; (*Z*)-**1a**, 7; (*E*)-**2a**, 10; (*Z*)-**2a**, 4
(*E*)-**1a**	DMB[a]	15	(*E*)-**1a**, 11; (*Z*)-**1a**, 3; (*E*)-**2a**, 24; (*Z*)-**2a**, 11
1b	none	70	**1b**, 10; **2b**, 10; **3b**, 9; HMD,[b] 2
1b	MeOH	15	**1b**, 17; **2b**, 16; **3b**, 31
1b	*t*-BuOH	10	**1b**, 13; **2b**, 17; **3b**, 13
1b	DMB	20	**1b**, 17; **2b**, 37; **3b**, 1
1b	isobutene	8	**1b**, 47; **2b**, 17; **3b**, 4
1b	$PhMe_2SiH$	20	**1b**, 20; **2b**, 15; **3b**, 11
1c	none	6	**1c**, 15; **2b**, 19; **3c**, 1; **4c**, 17
1c	DMB	6	**1c**, 13; **2b**, 28; **3c**, <1; **4c**, 6; **5c**, 9
1c	piperylene	8	**1c**, 16; **2b**, 36; **3c**, <1; **4c**, 5

[a] 2,3-Dimethylbutadiene. [b] Hexamethyldisilane.

Presumably, the reactivity of bis(trimethylsilyl)silylene toward trapping agents is extremely low.

In marked contrast to the photolysis of **1a**, irradiation of 2-(2,2-diphenylethenyl)-2-(trimethylsilyl)hexamethyltrisilane (**1b**), in which no cis–trans isomerization is involved, produced 3-phenyl-1,1,2-tris(trimethylsilyl)-1-silaindene (**3b**) in hexane in 9% yield, in addition to a 10% yield of the product 2,2-diphenyl(trimethylsilyl)ethene (**2b**). We carried out the reactions of **1b** to trap the reactive intermediates which might be produced in this photolysis with use of various trapping agents, such as methanol, 2-methyl-2-propanol, isobutene, 2,3-dimethylbutadiene, and dimethylphenylsilane (see Table I). However, no evidence for the formation of the intermediates was obtained. Interestingly, when methanol was used as a trapping agent in the photolysis of **1b**, the yield of silaindene **3b** increased up to 31%, while in the presence of 2,3-dimethylbutadiene, the yield of **3b** decreased to 1% but that of **2b** increased to 37%. Such enormous changes of the product distribution in the presence of the butadiene can be ascribed to quenching of the triplet state. Presumably, 2,3-dimethylbutadiene acts as a triplet quencher (see below).

A type of photoproduct different from that of **1a** and **1b** was observed in the photolysis of **1c**. Thus, the photolysis of **1c** in hexane afforded 1,3-diphenyl-1-(trimethylsilyl)-1-silaindene (**4c**) in 17% yield, together with a 19% yield of the product **2b** and a 1% yield of 1,3-diphenyl-1,2-bis(trimethylsilyl)-1-silaindene (**3c**). When **1c** was photolyzed in the presence of 2,3-dimethylbutadiene, the yield of **4c** decreased to 6%, while that of **2b** increased to 28%. In this photolysis, 3,4-dimethyl-1-phenyl-1-(trimethylsilyl)-1-sila-3-cyclopentene (**5c**), which was probably formed by addition of phenyl(trimethylsilyl)silylene to 2,3-dimethylbutadiene, was obtained in 9% yield. We carried out the photolysis of **1c** in the presence of a triplet quencher. Thus, irradiation of **1c** in the presence of a 22-fold excess of piperylene as the triplet quencher gave **2b** in 36% yield. In this photolysis, compound **4c** was obtained only in 5% yield, indicating that the silaindene **4c** would be produced from the triplet state.

Scheme I illustrates a possible mechanistic interpretation of the observed reaction course. Trisilane **1a** undergoes primarily cis–trans isomerization to afford a mixture of (*E*)-**1a** and (*Z*)-**1a**. Extrusion of bis(trimethylsilyl)silylene from these isomers affords (*E*)-**2a** and (*Z*)-**2a**, while extrusion of bis(trimethylsilyl)silylene from **1b** and phenyl(trimethylsilyl)silylene from **1c** produces **2b**.

The photochemical formation of hexamethyldisilane and silylenes from photoexcited trisilanes is a common pathway. For example, the photolysis of 2-phenylheptamethyltrisilane in the presence of diethylmethylsilane affords a silylene insertion product, 1,1-diethyl-1,2-dimethylphenyldisilane, in 47% yield, along with hexa-

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(2) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *117*, C58.

(3) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1976**, *98*, 7424.

(4) Ishikawa, M.; Fuchikami, T.; Sugaya, T.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 5923.

(5) (a) Ishikawa, M.; Nakagawa, K.; Ishiguro, K.; Ohi, F.; Kumada, M. *J. Organomet. Chem.* **1978**, *152*, 155. (b) Ishikawa, M.; Ishiguro, M.; Kumada, M. *J. Organomet. Chem.* **1973**, *49*, C71.

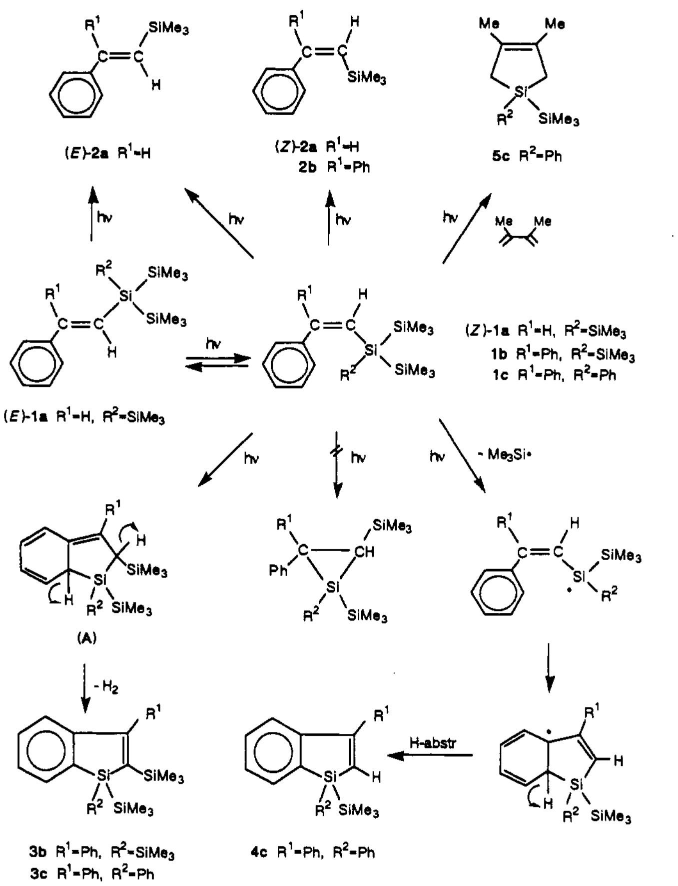
(6) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Am. Chem. Soc.* **1977**, *99*, 245.

(7) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879.

(8) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1978**, *149*, 37.

(9) The isolated *Z* isomer was found to isomerize to the *E* isomer on standing for long times.

Scheme I



methyldisilane.[5] In the photolysis of **1a–c**, hexamethyldisilane might be produced with simultaneous extrusion of the corresponding silylenes, although the silylenes could not be trapped even in the presence of methanol. In order to confirm the formation of hexamethyldisilane, we analyzed a low-boiling fraction obtained from the photolysis of **1b** and found that hexamethyldisilane is certainly produced, but in 2% yield. In the photolysis of **1c**, however, no hexamethyldisilane was detected. The fact that the presence of the triplet quencher dimethylbutadiene or piperylene increases markedly the yields of desilylated product **2a** or **2b** indicates that these products may be produced from a singlet state of the excited molecules **1a–c**.[10]

The formation of silaindenes **3b,c** from the photolysis of **1b,c** may be best explained in terms of a 1,2-trimethylsilyl shift to the α-position of the olefinic unit leading to the dihydrosilole intermediate A, followed by elimination of hydrogen from the intermediate A.

As reported previously, the formation of a silacyclopropane via a 1,2-trimethylsilyl shift was certainly observed in the photolysis of (2-phenylethenyl)pentamethyldisilane. The present photolysis, however, produced no silacyclopropane derivatives. This is probably due to the steric reasons. Introduction of bulky substituents such as trimethylsilyl and phenyl groups onto the silicon atoms presumably prevents the formation of a silacyclopropane ring. Examination of molecular models shows the presence of large steric interactions in the silacyclopropanes which are thought to be produced from **1a–c**, but the steric repulsions are less severe in the silaindenes **3b,c**.

The formation of the silaindene **4c** can be understood by homolytic scission of a silicon–silicon bond of **1c**, followed by homolytic aromatic substitution of the resulting silyl radical onto the ortho position of the phenyl ring and then elimination of hydrogen.

The structures of the photochemical products were verified by spectroscopic analysis as well as by elemental analysis. In the ^{1}H NMR spectra of both the starting material (*E*)-**1a** and the photochemical product (*E*)-**2a**, resonances due to two olefinic protons are observed in olefinic region as two doublets with large vicinal H–H coupling; J = 18.8 Hz for (*E*)-**1a** and J = 19.1 Hz for (*E*)-**2a**. On the other hand, smaller coupling appears in the spectra of the products (*Z*)-**1a** (J = 14.5 Hz) and (*Z*)-**2a** (J = 15.2 Hz), as expected. The ^{1}H NMR spectrum of **2b** reveals only a singlet resonance at 6.31 ppm ascribable to an isolated olefinic proton, beside resonances due to the protons in a trimethylsilyl and two phenyl groups.

The ^{13}C NMR spectrum of **3b** shows resonances attributed to the carbons in two different trimethylsilyl groups (−0.13 and 1.58 ppm) and five unsaturated carbons bearing no hydrogen (141–168 ppm) in addition to seven resonances attributed to aromatic ring carbons with hydrogen (124–133 ppm). The ^{1}H NMR spectrum of **3b** reveals two singlet resonances at −0.07 and 0.20 ppm in the ratio of 9:18, attributed to the protons in two kinds of trimethylsilyl groups, and multiplet resonances that collapse to four groups centered at 6.90, 7.20, 7.38, and 7.66 ppm in the ratio of 1:4:3:1, attributed to aromatic ring protons. These results clearly suggest that the molecule has a phenyl and trimethylsilyl group and two equivalent trimethylsilyl groups attached to the silaindene ring. The location of the substituents on the silaindene ring was established by NOE-FID difference experiments at 500 MHz. Irradiation of the trimethylsilyl protons at 0.20 ppm resulted in strong enhancement of the protons in the trimethylsilyl group at −0.07 ppm as well as an aromatic proton at 7.66 ppm, attributed to the proton on C-7 in the silaindene ring. Saturation of the trimethylsilyl protons at −0.07 ppm caused a positive NOE of the protons in the trimethylsilyl groups at 0.20 ppm, together with partial enhancement of protons appearing at 7.20 and 7.38 ppm. The signal at 6.90 ppm, attributed to the proton on the C-4 position, was not affected in these experiments.

The ^{13}C NMR spectrum of **3c** reveals 2 resonances (−0.86 and 1.22 ppm) due to trimethylsilyl carbons, together with 10 signals with high intensities (124–136 ppm) and 6 signals with low intensities (134–169 ppm), attributed to aromatic ring carbons with hydrogen and those without hydrogen, respectively. The ^{1}H NMR spectrum of **3c** reveals two singlet resonances at −0.20 and 0.24 ppm (9 H each) attributed to trimethylsilyl protons and four multiplet resonances centered at 6.87, 7.18, 7.34, and 7.55 ppm (1:3:7:3) attributed to aromatic ring protons. Saturation of the signal at 0.24 ppm ($SiSiMe_3$) resulted in positive NOE of the signal at 7.55 ppm (C-7 proton and ortho protons of SiPh) as well as the signal at −0.20 ppm ($CSiMe_3$). Irradiation of the protons at −0.20 ppm caused partial enhancement of protons appearing at 7.18, 7.34, and 7.55 ppm as well as the protons at 0.24 ppm. The signal at 6.87 ppm (C-4 proton) was not affected in these experiments.

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(10) In order to explain the absence of silylene insertion products in the photolysis of **1a** and **1b**, one might consider the possibility that the direct reaction of the photoexcited molecule with a trapping agent is involved. However, as reported previously,[11] the direct reaction of the photoexcited disilanes with methanol affords methoxysilanes. Since the photolysis of **1a** and **1b** in the presence of methanol produces no methoxysilanes, the direct reaction would not be involved in the present photolysis.

(11) (a) Ishikawa, M.; Tabohashi, T.; Kumada, M. *J. Organomet. Chem.* **1984**, *264*, 79. (b) Ohshita, J.; Ohsaki, H.; Ishikawa, M.; Tachibana, A.; Kurosaki, Y. Yamabe, T.; Minato A. *Organometallics* **1991**, *10*, 880. (c) Ishikawa, M.; Sakamoto, H. *J. Organomet. Chem.* **1991**, *414*, 1.

The ^{13}C NMR spectrum of the compound **4c** shows a signal (−1.39 ppm) due to trimethylsilyl carbons, together with 5 resonances with low intensities (134–162 ppm) and 11 resonances with high intensities (123–135 ppm), assigned to aromatic ring carbons with and without hydrogen, respectively. The ^{1}H NMR spectrum of **4c** reveals two singlet resonances at 0.19 and 6.42 ppm (9:1) due to trimethylsilyl protons and an olefinic proton, respectively, and multiplet resonances that collapse to four groups centered at 7.35, 7.45, 7.60, and 7.71 ppm (9:2:2:1), attributed to aromatic ring protons. Irradiation of the trimethylsilyl protons at 0.19 ppm resulted in strong enhancement of the proton at 6.42 ppm, attributed to the proton at C-2 in the silaindene ring, as well as protons appearing at 7.60 and 7.71 ppm, attributed to two ortho protons in one phenyl group and the proton at the C-7 position, respectively. Saturation of the olefinic proton at 6.42 ppm caused positive NOE of the trimethylsilyl protons and partial enhancement of the protons at 7.45 and 7.60 ppm, attributed to four ortho protons of the two adjacent phenyl groups, but the signal at 7.71 ppm (C-7 position) was not affected at all.

In the ^{1}H NMR spectrum of **5c**, two singlet resonances are observed at 0.13 and 1.73 ppm in the ratio of 9:10, along with multiplet resonances in the region of 7.27–7.51 ppm (5 H). The ^{13}C NMR spectrum of **5c** shows eight resonances at −1.8, 19.2, 23.4, 127.8, 128.5, 130.8, 134.1, and 135.1 ppm. The first three can be assigned to trimethylsilyl carbons, methyl carbons, and methylene carbons, respectively, while the last five are due to unsaturated carbons. A ^{1}H/^{13}C COSY experiment clearly shows that the protons at 1.73 ppm correlate to both carbons at 19.2 and 23.4 ppm. All of the above results are wholly consistent with the proposed structures for **3b**, **3c**, **4c**, and **5c**.

Experimental Section

General Considerations. Tetrahydrofuran (THF) and ether were dried over sodium metal in the presence of a small amount of benzophenone and distilled just before use. Hexane and benzene were dried over lithium aluminum hydride and distilled before use. The yields of the photochemical products were determined with Hitachi 263-30 and Shimadzu GC-6A gas chromatographs on OV-17 and SE-30 as the stationary phase using pentadecane as an internal standard. ^{1}H NMR and ^{13}C NMR spectra were measured with JEOL Model JNM-FX-90A and JNM-EX-270 spectrometers. Infrared spectra were recorded on a Perkin-Elmer 1600-FT-IR spectrophotometer. Mass spectra were recorded on a Shimadzu Model GCMS QP-1000 spectrometer. High-resolution mass spectra were measured with a JEOL Model JMS-D300 spectrometer equipped with a JEOL JMA-2000 data processing unit.

Preparation of (*E*)-1a. In a 300-mL four-necked round-bottom flask equipped with a reflux condenser, dropping funnel, and stirrer was placed a solution of 13.8 g (48.7 mmol) of 2-chloro-2-(trimethylsilyl)hexamethyltrisilane[12] in 20 mL of THF under a dry nitrogen atmosphere. To this solution was added dropwise the Grignard reagent prepared from 2-bromostyrene (57 mmol) and magnesium (63 mmol) in 40 mL of THF. The mixture was refluxed for 15 h and then poured into ice–water. Products were extracted with ether, and the ethereal solution was dried over magnesium sulfate. The solvent was evaporated, and the residue was distilled in vacuo to give 2.85 g (8.12 mmol, 17% yield) of (*E*)-2-(2-phenylethenyl)-2-(trimethylsilyl)hexamethyltrisilane ((*E*)-**1a**): bp 123–124 °C/1 mmHg; ^{1}H NMR (CDCl$_3$) δ 0.23 (s, 27 H, SiMe$_3$), 6.44 (d, 1 H, C=CHSi, J = 18.8 Hz), 6.94 (d, 1 H, C=C*H*Ph, J = 18.8 Hz), 7.24–7.40 (m, 5 H, phenyl ring protons); ^{13}C NMR (CDCl$_3$) δ 0.94 (SiMe$_3$), 122.72 (C=CHSi), 125.97, 127.44, 128.52 (phenyl ring carbons), 139.14 (phenyl ipso carbon), 145.58 (PhH*C*=C); IR 3060, 3022, 2950, 2893, 1595, 1570, 1493, 1444 cm^{-1}; MS m/e 350 (M$^+$). Anal. Calcd for $C_{17}H_{34}Si_4$: C, 58.21; H, 9.77. Found: C, 58.05; H, 9.63.

Preparation of 1b. In a 300-mL four-necked round-bottom flask equipped with a reflux condenser, dropping funnel, and stirrer was placed a solution of 10.0 g (35.3 mmol) of 2-chloro-2-(trimethylsilyl)hexamethyltrisilane in 20 mL of THF under a dry nitrogen atmosphere. To this solution was added dropwise the Grignard reagent prepared from 2-bromo-1,1-dipheylethylene (42 mmol) and magnesium (44 mmol) in 40 mL of THF. The mixture was refluxed for 10 h and then poured into ice–water. Products were extracted with ether, and the ethereal solution was dried over magnesium sulfate. The mixture was concentrated, and the residue of the flask was distilled in vacuo to give 9.55 g (22.4 mmol, 63% yield) of 2-(2,2-diphenylethenyl)-2-(trimethylsilyl)hexamethyltrisilane (**1b**): bp 169 °C/1 mmHg; ^{1}H NMR (CDCl$_3$) δ −0.11 (s, 27 H, SiMe$_3$), 6.27 (s, 1 H, olefinic protons), 7.12–7.35 (m, 10 H, phenyl ring protons); ^{13}C NMR (CDCl$_3$) δ 1.27 (SiMe$_3$), 123.43 (C=CHSi), 127.11, 127.49, 127.92, 128.41, 130.09 (phenyl ring carbons), 143.69, 145.58 (phenyl ipso carbons), 157.39 (Ph$_2$*C*=C); IR 3052, 2946, 2892, 1597, 1557, 1489, 1442, 1244, 833 cm^{-1}; MS m/e 426 (M$^+$). Anal. Calcd for $C_{23}H_{38}Si_4$: C, 64.71; H, 8.97. Found: C, 64.71; H, 8.77.

Preparation of 1c. In a 300-mL four-necked round-bottom flask equipped with a reflux condenser, dropping funnel, and stirrer was placed a solution of 5.0 g (17 mmol) of 2-chloro-2-phenylhexamethyltrisilane in 20 mL of THF under a dry nitrogen atmosphere. To this solution was added dropwise the Grignard reagent prepared from 2-bromo-1,1-diphenylethylene (21 mmol) and magnesium (23 mmol) in THF (30 mL). The mixture was stirred for 4 h and then poured into ice–water. Products were extracted with ether, and the ethereal solution was dried over magnesium sulfate. Low-boiling substances were distilled off in vacuo, and the residue was chromatographed on silica gel with hexane. The crude product was recrystallized from ethanol to give 3.2 g (7.4 mmol, 43% yield) of 2-(2,2-diphenylethenyl)-2-phenylhexamethyltrisilane (**1c**): ^{1}H NMR δ (CDCl$_3$) 0.10 (s, 18 H, SiMe$_3$), 6.43 (s, 1 H, olefinic proton), 7.12–7.27 (m, 15 H, phenyl ring protons); ^{13}C NMR (CDCl$_3$) δ −0.28 (SiMe$_3$), 124.15 (C=*C*HSi), 127.51, 127.90, 128.00, 129.95, 135.31 (phenyl ring C), 137.26, 142.53, 145.26 (phenyl ipso carbons), 158.86 (Ph$_2$*C*=C); IR 2952, 1654, 1560, 1490, 1459, 1243, 833 cm^{-1}; MS m/e 430 (M$^+$). Anal. Calcd for $C_{26}H_{34}Si_3$: C, 72.56; H, 7.97. Found: C, 72.56; H, 7.90.

General Procedure for the Photochemical Reaction. A solution of trisilane in hexane was irradiated with a 6-W low-pressure mercury lamp under dry nitrogen in either the presence or absence of a quencher. The products (*Z*)-**1a**, (*E*)-**2a**, (*Z*)-**2a**, **3b**, **4c**, and **5c** were isolated by preparative gas–liquid chromatography (GLC) using SE-30 as the stationary phase. **2b** was isolated by medium-pressure liquid chromatography (MPLC) on silica gel with hexane as eluent. Product **3c** was separated from the mixture with **1c** by gel-permeation chromatography (GPC) with chloroform as eluent. Results are summarized in Table I.

Photolysis of (*E*)-1a. A solution of 313 mg (0.894 mmol) of trisilane (*E*)-**1a** in 60 mL of hexane was irradiated for 15 h. The products (*Z*)-**1a**, (*E*)-**2a**, and (*Z*)-**2a** were isolated by preparative GLC. For (*Z*)-**1a**: ^{1}H NMR (CDCl$_3$) δ 0.14 (s, 27 H, SiMe$_3$), 5.91 (d, 1 H, C=CHSi, J = 14.5 Hz), 7.43 (d, 1 H, C=C*H*Ph, J = 14.5 Hz), 7.21–7.41 (m, 5 H, phenyl ring protons); ^{13}C NMR (CDCl$_3$) δ 1.24 (SiMe$_3$), 124.39 (C=*C*HSi), 127.19, 128.00, 128.28 (phenyl ring carbons), 140.65 (phenyl ipso carbon), and 146.49 (Ph*C*H=C); IR 2949, 2893, 1591, 1561, 1492, 1443, 1244 cm^{-1}; MS m/e 350 (M$^+$), 335, 277. Anal. Calcd for $C_{17}H_{34}Si_4$: C, 58.21; H, 9.77. Found: C, 58.45; H; 9.77. For (*E*)-**2a**: ^{1}H NMR (CDCl$_3$) δ 0.17 (s, 9 H, SiMe$_3$), 6.48 (d, 1 H, C=CHSi, J = 19.1 Hz), 6.89 (d, 1 H, C=C*H*Ph, J = 19.1 Hz), 7.21–7.46 (m, 5 H, phenyl ring protons); ^{13}C NMR (CDCl$_3$) δ −1.24 (SiMe$_3$), 126.34, 128.50, 129.47 (phenyl ring carbons), 138.37 (phenyl ipso carbon), 127.92 (C=*C*HSi), 143.61 (Ph*C*H=C); IR 2957, 1596, 1560, 1488, 1249 cm^{-1}; MS m/e 176 (M$^+$), 161. Anal. Calcd for $C_{11}H_{16}Si$: C, 74.93; H, 9.15. Found: C, 74.90; H, 9.33. For (*Z*)-**2a**: ^{1}H NMR (CDCl$_3$) δ 0.06 (s, 9 H, SiMe$_3$), 5.84 (d, 1 H, C=CHSi, J = 15.2 Hz), 7.38 (d, C=C*H*Ph, J = 15.2 Hz), 7.25–7.32 (m, 5 H, phenyl ring protons); ^{13}C NMR (CDCl$_3$) δ 0.16 (SiMe$_3$), 127.30, 127.89, 128.12 (phenyl ring protons), 140.13 (phenyl ipso carbon), 132.83 (C=*C*HSi), 146.59 (PhH*C*=C); IR 2941, 2898, 1595, 1565, 1487, 1246 cm^{-1}; MS m/e 176 (M$^+$), 161. Anal. Calcd for $C_{11}H_{16}Si$: C, 74.93;

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[12] Gilman, H.; Harrel, R. L. *J. Organomet. Chem.* **1965**, *5*, 199.

H, 9.15. Found: C, 74.73; H, 8.93.

Photolysis of (*E*)-1a in the Presence of Methanol. A solution of 305 mg (0.871 mmol) of trisilane (*E*)-**1a** and 0.279 g (8.71 mmol) of methanol in 60 mL of hexane was irradiated for 15 h.

Photolysis of (*E*)-1a in the Presence of 2,3-Dimethylbutadiene. A solution of 317 mg (0.906 mmol) of trisilane (*E*)-**1a** and 0.762 g (9.29 mmol) of 2,3-dimethylbutadiene in 60 mL of hexane was irradiated for 15 h.

Photolysis of 1b. A solution of 315 mg (0.739 mmol) of trisilane **1b** in 60 mL of hexane was irradiated for 70 h. The amount of hexamethyldisilane in the reaction mixture was determined to be 2% by GLC using SE-30 (10%, 1 m) as the stationary phase at room temperature. Products **2b** and **3b** were isolated by MPLC and preparative GLC, respectively. For **2b**: ^{1}H NMR ($CDCl_3$) δ −0.10 (s, 9 H, $SiMe_3$), 6.31 (s, 1 H, olefinic proton), 7.20–7.36 (m, 10 H, phenyl ring protons); ^{13}C NMR ($CDCl_3$) δ 0.02 ($SiMe_3$), 127.17, 127.32, 127.56, 127.85, 128.00, 129.71 (phenyl ring carbons and C=*C*HSiMe$_3$), 142.63, 143.26, 157.11 (phenyl ipso carbons and Ph$_2$*C*=C); IR 2954, 1566, 1490, 1443, 1247, 857 cm^{-1}; MS *m/e* 252 (M$^+$). Anal. Calcd for $C_{17}H_{20}Si$: C, 80.89; H, 7.99. Found: C, 80.85; H, 7.98. For **3b**: ^{1}H NMR ($CDCl_3$) δ −0.07 (s, 9 H, C–SiMe$_3$), 0.20 (s, 18 H, Si–SiMe$_3$), 6.89–7.67 (m, 9 H, phenyl and phenylene ring protons); ^{13}C NMR δ ($CDCl_3$) −0.13 (Si–SiMe$_3$), 1.58 (C–Si*Me*$_3$), 124.44, 125.51, 126.93, 127.61, 127.85, 129.27, 132.29 (phenyl and phenylene ring carbons), 141.75, 142.43, 142.82, 153.31, 167.74 (phenyl ipso carbon and silole ring carbons); IR 3046, 2947, 2892, 1599, 1509, 1478, 1438, 1242, 984, 833 cm^{-1}; MS *m/e* 424 (M$^+$); exact mass calcd for $C_{23}H_{36}Si_4$ 424.1894, found 424.1911.

Photolysis of 1b in the Presence of Methanol. A solution of 310 mg (0.728 mmol) of trisilane **1b** and 0.258 g (8.06 mmol) of methanol in 60 mL of hexane was irradiated for 15 h.

Photolysis of 1b in the Presence of 2-Methyl-2-propanol. A solution of 302 mg (0.709 mmol) of trisilane **1b** and 0.52 g (7.03 mmol) of 2-methyl-2-propanol in 60 mL of hexane was irradiated for 10 h.

Photolysis of 1b in the Presence of Isobutene. A solution of 302 mg (0.709 mmol) of trisilane **1b** and 0.925 g (16.5 mmol) of isobutene in 60 mL of hexane was irradiated for 8 h.

Photolysis of 1b in the Presence of 2,3-Dimethylbutadiene. A solution of 320 mg (0.751 mmol) of trisilane **1b** and 0.702 g (8.56 mmol) of 2,3-dimethylbutadiene in 60 mL of hexane was irradiated for 20 h.

Photolysis of 1b in the Presence of Dimethylphenylsilane. A solution of 310 mg (0.728 mmol) of trisilane **1b** and 1.01 g (7.43 mmol) of dimethylphenylsilane in 60 mL of hexane was irradiated for 20 h.

Photolysis of 1c. A solution of 300 mg (0.696 mmol) of trisilane **1c** in 60 mL of hexane was irradiated for 6 h. No hexamethyldisilane was detected in the reaction mixture by GLC analysis using SE-30 (10%, 1 m) as the stationary phase at room temperature. Products **3c** and **4c** were isolated by preparative GPC and GLC, respectively. For **3c**: ^{1}H NMR ($CDCl_3$) δ −0.20 (s, 9 H, C–SiMe$_3$), 0.24 (s, 9 H, SiMe$_3$), 6.85–7.57 (m, 14 H, phenyl and phenylene ring protons); ^{13}C NMR ($CDCl_3$) δ −0.86 (Si–SiMe$_3$), 1.22 (C–Si*Me*$_3$) 124.21, 126.56, 127.12, 127.96, 128.01, 128.84, 129.04, 129.36, 132.26, 135.62 (phenyl and phenylene ring carbons), 134.29, 141.08, 141.35, 141.85, 152.70, 169.00 (phenyl ipso carbons and silole ring carbons); exact mass calcd for $C_{26}H_{32}Si_3$ 428.1811, found 428.1723. For **4c**: ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 9 H, SiMe$_3$), 6.42 (s, 1 H, silole ring α-proton), 7.26–7.72 (m, 14 H, phenyl and phenylene ring H); ^{13}C NMR ($CDCl_3$) δ −1.39 (SiMe$_3$), 123.92, 126.52, 127.54, 127.87, 128.14, 128.90, 129.22, 129.33, 130.15, 133.02 (phenyl and phenylene ring carbons), 135.08 (silole α-carbon), 134.21, 139.25, 140.55, 149.59, 161.67 (phenyl ipso carbons, silole β-carbon, and fused carbons); IR 2953, 1489, 1441, 1423, 1245 cm^{-1}; MS *m/e* 356 (M$^+$), 341, 283; exact mass calcd for $C_{23}H_{24}Si_2$ 356.1415, found 356.1415.

Photolysis of 1c in the Presence of 2,3-Dimethylbutadiene. A solution of 300 mg (0.696 mmol) of trisilane **1c** and 1.176 g (14.32 mmol) of 2,3-dimethylbutadiene in 60 mL of hexane was irradiated for 6 h. The product **5c** was isolated by preparative GLC. For **5c**: ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 9 H, SiMe$_3$), 1.73 (s, 10 H, C=CMe and Si–CH$_2$–), 7.27–7.51 (m, 5 H, phenyl ring H); ^{13}C NMR ($CDCl_3$) δ −1.78 (SiMe$_3$), 19.25 (C–Me), 23.42 (SiCH$_2$), 130.84 (olefinic C), 127.78, 128.50, 134.12 (phenyl ring carbons), 135.13 (phenyl ipso carbon); IR 2952, 2893, 1441, 1428, 1398, 1244 cm^{-1}; MS *m/e* 260 (M$^+$), 245, 187. Anal. Calcd for $C_{15}H_{24}Si_2$: C, 69.15; H, 9.29. Found: C, 68.86; H, 9.21.

Photolysis of 1c in the Presence of Piperylene. A solution of 300 mg (0.696 mmol) of trisilane **1c** and 1.056 g (15.63 mmol) of piperylene in 60 mL of hexane was irradiated for 8 h.

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Registry No. (*E*)-**1a**, 110577-10-1; (*Z*)-**1a**, 139526-41-3; **1b**, 139526-39-9; **1c**, 139526-40-2; (*E*)-**2a**, 19372-00-0; (*Z*)-**2a**, 19319-11-0; **2b**, 51318-07-1; **3b**, 139526-42-4; **3c**, 139526-43-5; **4c**, 139526-44-6; **5c**, 72168-94-6; DMB, 513-81-5; MeOH, 67-56-1; *t*-BuOH, 75-65-0; PhMe$_2$SiH, 766-77-8; 2-chloro-2-(trimethylsilyl)hexamethyltrisilane, 5565-32-2; 2-bromostyrene, 2039-88-5; 2-bromo-1,1-diphenylethylene, 13249-58-6; 2-chloro-2-phenylhexamethyltrisilane, 127348-36-1; isobutene, 115-11-7; piperylene, 504-60-9.