Generation of Intramolecular Sulfur- or Selenium-Coordinated Silylenes by the Thermolysis of Pentacoordinate Disilanes Bearing an 8-Thio- or 8-Seleno-1-naphthyl Group and a Methoxy Group on the Same Silicon Atom

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Pentacoordinate disilanes bearing an 8-thio- or 8-seleno-1-naphthyl group and a methoxy group on the same silicon center undergo thermal degradation to generate intramolecular sulfur- or selenium-coordinated silylenes. The chalcogen-coordinated silylenes behave as nucleophilic sila-ylides during the reaction with diphenylacetylene to afford a silacyclopropene and, in the case of selenium, a silaphenalene as intermediates.

Introduction

We have previously reported[1,2] that, in contrast to the thermally stable tetracoordinate disilanes such as **1d**, the pentacoordinate[3,4] disilanes **1e−h**, which contain an 8-amino- or 8-phosphino-1-naphthyl group and an ethoxy group (or a fluorine atom) on the same silicon center, are thermally labile and readily undergo α-elimination of an ethoxysilane (or a fluorosilane) to generate the intramolecular amine- or phosphine-coordinated silylenes (Scheme 1). These species behave as nucleophilic sila-ylides during the reaction with diphenylacetylene to form the corresponding zwitterionic onium alkenyl anions, which undergo cyclization reactions characteristic of the coordinating elements. In contrast to these group 15 element coordinations, the intramolecular coordination of the group 16 elements has been found not to facilitate the thermal degradation of disilanes; that is, pentacoordinate ethoxydisilane **1i**, bearing an 8-methoxy-1-naphthyl group, and pentacoordinate *fluoro*disilanes **1j** and **1k**, bearing an 8-methoxy- or 8-phenylthio-1-naphthyl group, are thermally stable (Scheme 1).[5]

We have now found that the corresponding intramolecular sulfur- and selenium-coordinated *methoxy*disilanes **1a−c** are thermally labile with respect to the α-elimination of methoxysilane to generate the silylenes **2a−c** intramolecularly coordinated by the group 16

Scheme 1
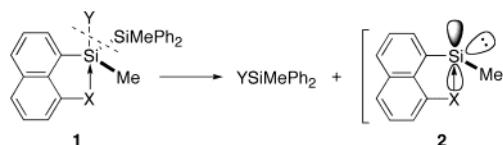
	X	Y	Reaction	Ref(s)
a	SPh	OMe	Yes	this work
b	SMe	OMe	Yes	this work
c	SePh	OMe	Yes	this work
d	H	OEt	No	1a
e	NMe$_2$	OEt	Yes	1a,b
f	NMe$_2$	F	Yes	1c
g	PEt$_2$	F	Yes	2
h	PPh$_2$	F	Yes	2
i	OMe	OEt	No	5
j	OMe	F	No	5
k	SPh	F	No	5

elements (Scheme 1). These silylenes behave as nucleophilic sila-ylides during the reaction with diphenylacetylene, but the reaction courses of the zwitterionic intermediates are found to be different from those derived from silylenes intramolecularly coordinated by the group 15 elements.[1,2] The details of these results together with the main origin of the thermolability are described in this paper.

Results and Discussion

Preparation. The pentacoordinate methoxydisilanes **1a−c** bearing an 8-phenylthio-, 8-methylthio-, or 8-phenylseleno-1-naphthyl group were prepared through the stepwise halogen−lithium exchange reactions of 8-bromo-1-iodonaphthalene as shown in Scheme 2. Thus, in the first step, the bromine-substituted naphthyllithium was trapped by disulfide or diselenide to afford **3a−c**, and in the second step, the chalcogen-substituted naphthyllithium was trapped by 1,1-dichlorodisilane to afford **4a−c**, the methanolysis of which afforded the corresponding methoxydisilanes **1a−c**.

Structure. The structures of the methoxydisilanes **1a−c** intramolecularly coordinated by sulfur or sele-

(1) (a) Tamao, K.; Nagata, K.; Asahara, M.; Kawachi, A.; Ito, Y.; Shiro, M. *J. Am. Chem. Soc.* **1995**, *117*, 11592. (b) Tamao, K.; Asahara, M.; Toshimitsu, A. *Chem. Lett.* **2000**, 658. (c) Tamao, K.; Asahara, M.; Saeki, T.; Feng, S.-G.; Kawachi, A.; Toshimitsu, A. *Chem. Lett.* **2000**, 660. (d) Review: Tamao, K.; Asahara, M.; Saeki, T.; Toshimitsu, A. *J. Organomet. Chem.* **2000**, *600*, 118.

(2) Toshimitsu, A.; Saeki, T.; Tamao, K. *J. Am. Chem. Soc.* **2001**, *123*, 9210.

(3) In view of the weak coordination of the donor atom at the 8-position of the 1-naphthyl group, it may be better to describe the resulting structures as [4+1]-coordinate.[4] However, we prefer to call them "pentacoordinate" for the sake of simplicity.

(4) (a) Chuit, C.; Reyé, C. *Eur. J. Inorg. Chem.* **1998**. 1847. (b) Carré, F.; Chuit, C.; Corriu, R. J. P.; Monforte, P.; Nayyar, N. K.; Reyé, C. *J. Organomet. Chem.* **1995**, *499*, 147.

(5) Toshimitsu, A.; Hirao, S.; Saeki, T.; Asahara, M.; Tamao, K. *Heteroat. Chem.* **2001**, *12*, 392.

Scheme 2

3a; X = SPh
b; X = SMe
c; X = SePh

4; Y = Cl
1a-c; Y = OMe
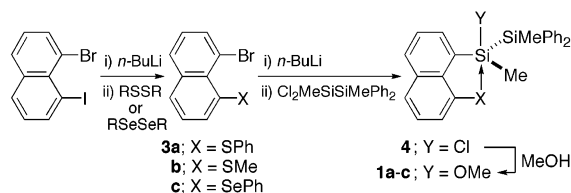
Table 1. ²⁹Si NMR Data of Pentacoordinate and Tetracoordinate Alkoxydisilanes

	δ^a	$\Delta\delta$ (X − H)^b
1a (X = S)	−8.1	−14.2
1b (X = S)	−9.2	−15.3
1c (X = Se)	−6.7	−13.8
1e (X = N)^c	−7.3	−13.4
1i (X = O)^d	−4.8	−10.9
1d (X = H)^c	+6.1	−

^{a} Chemical shift of the silicon atom attached to the naphthyl carbon. ^{b} Sign (−) indicates an upfield shift. ^{c} Reference 1a. ^{d} Reference 5.

nium were compared with those of the ethoxydisilanes intramolecularly coordinated by nitrogen (**1e**) or oxygen (**1i**) using ²⁹Si NMR measurements and X-ray crystallographic analyses.

The ²⁹Si NMR data summarized in Table 1 revealed that the silicon atom coordinated by sulfur or selenium in **1a−c** resonates ca. 13−15 ppm upfield in comparison with the silicon atom attached to the naphthyl group in the tetracoordinate disilane **1d**.[6,7] These upfield shifts are comparable to those caused by the coordination of nitrogen (**1e**) or oxygen (**1i**), indicating that, in solution, the intramolecular coordination of sulfur or selenium to the silicon center in **1a−c** is similar to that of nitrogen and oxygen in **1e** and **1i**.

The structural parameters of the sulfur-coordinated **1a** and selenium-coordinated **1c** are summarized in Table 2, which contains the data of the nitrogen-coordinated **1e**[2a] and oxygen-coordinated **1i**[5] for comparison. The similar values of the X1⋯Si1 distances,[8,9] X1⋯Si1−O1 angles, and pentacoordination characters[10] (X1 = S, Se, N, and O) indicate that, in the solid state, the intramolecular coordination of sulfur and selenium

to the silicon center in **1a** and **1c** is also similar to that of nitrogen and oxygen in **1e** and **1i**. Other parameters that may be relevant to the lability for the α-elimination of alkoxysilanes such as the O1−Si1 distances, Si1−Si2 distances, and O1−Si1−Si2 angles are also found to fall into a similar range.

The only one remarkable difference in the structure is that the Si−naphthyl and S− or Se−naphthyl bonds in **1a** or **1c** are highly bent up and down from the plane of the naphthalene ring, in sharp contrast to the slight distortion in the oxygen-coordinated **1i**. Thus, in **1a** and **1c**, the dihedral angles between the two planes defined by Si1−C1−C8 and S1(Se1)−C8−C1 are ca. 23°, which is smaller than the corresponding angle of 31° in the nitrogen-coordinated **1e**,[2a] but much larger than 8° in the oxygen-coordinated **1i**.[5] Another dihedral angle between the two planes defined by C1−C2−C3 and C6−C7−C8 in the naphthalene ring is ca. 12° in **1a** and ca. 5° in **1c**, which are comparable to those in the thermolabile **1e** (ca. 10°) and the stable **1i** (ca. 5°). The total strain may be responsible for the thermolability. Thus, these structural parameters indicate that the sulfur- or selenium-coordinated methoxydisilanes **1a** and **1c** might be less stable than the oxygen-coordinated **1i** and might possibly undergo a thermal degradation reaction.

Thermal Degradation. All the results of the thermal degradation of **1a−c** are shown in Scheme 3. A solution of pentacoordinate methoxydisilane **1a** bearing the *phenylthio* group and one molar amount of diphenylacetylene in mesitylene was heated under reflux for 24 h to form methoxymethyldiphenylsilane, the α-elimination product, in 95% yield as estimated by the NMR measurement. The formed intramolecular sulfur-coordinated silylene **2a** was trapped in situ by diphenylacetylene to afford, after treatment with 2-propanol, the intramolecular sulfur-coordinated monosilane **5a**, bearing the diphenylethenyl and 2-propoxy group on the silicon atom, in a yield of 75%.

By thermolysis of the pentacoordinate methoxydisilane **1b**, bearing the *methylthio* group, in the presence of diphenylacetylene under similar conditions, the analogous intramolecular sulfur-coordinated monosilane **5b**

Table 2. Selected Interatomic Distances (Å), Angles (deg), and Dihedral Angles (deg), and %TBP^a for 1a, 1c, 1e,^{b} and 1i^c

		1a (X = S)	**1c** (X = Se)	**1e** (X = N)	**1i** (X = O)
Interatomic distances					
	X1⋯Si1	3.0544(7)^d	3.1779(7)^e	2.969(3)^f	2.730(3)^g
	O1−Si1	1.677(2)	1.657(2)	1.665(2)	1.673(3)
	Si1−Si2	2.3613(8)	2.3587(8)	2.368(1)	2.333(1)
Angles					
	X1⋯Si1−O1	176.49(6)	178.20(7)	171.36(9)	175.4(1)
	O1−Si1−Si2	102.98(6)	102.14(7)	97.35(8)	99.48(10)
Dihedral angles					
	C1-C2-C3/C6-C7-C8	12.38	5.09	9.78	5.03
	Si1-C1-C8/X1-C8-C1	22.92	23.11	31.32	7.69
Pentacoordination characters					
	%TBP$_a$	29	28	37	32
	%TBP$_e$	56	46	59	51

^{a} Pentacoordination character which shows the degree of deformation from tetrahedral to trigonal bipyramidal. The definition has been reported in ref 10. ^{b} Reference 1a. ^{c} Reference 5. ^{d} $\sum r_{vdW}$(S, Si) = 3.90 Å. ^{e} $\sum r_{vdW}$(Se, Si) = 4.00 Å. ^{f} $\sum r_{vdW}$(N, Si) = 3.65 Å. ^{g} $\sum r_{vdW}$(O,Si) = 3.62 Å.

Scheme 3

Scheme 4
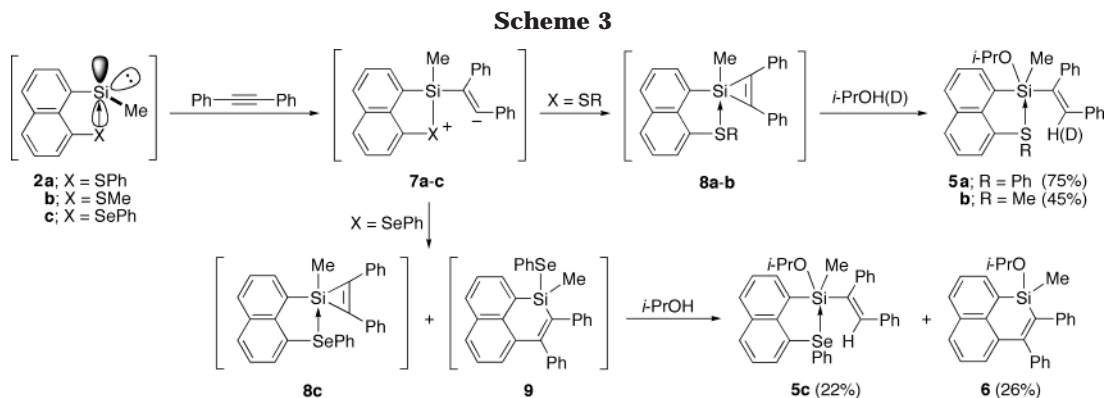
was produced in a yield of 45%. When these reactions were quenched with 2-propanol-d_1, the deuterium atom was found to be incorporated in the diphenylethenyl group in **5a** and **5b**.

The thermal degradation of the pentacoordinate methoxydisilane **1c**, bearing the *phenylseleno* group, was carried out under similar conditions, and the generated intramolecular selenium-coordinated silylene **2c** was trapped by diphenylacetylene to afford, after treatment with 2-propanol, two kinds of products as follows. One is the intramolecular selenium-coordinated monosilane **5c**, bearing the alkenyl and 2-propoxy group on the silicon center (22%). The other is the 1-silaphenalene derivative **6** (26%), in which the diphenylacetylene has been incorporated between the naphthyl carbon and the silicon atom, as observed in the nitrogen-coordinated analogues **1e** and **1f**. The structure of the 1-silaphenalene derivative **6** was confirmed by X-ray crystallographic analysis as shown in Figure 1.

These above-mentioned reactions are best understood by the nucleophilic attack of the intramolecular sulfur- or selenium-coordinated silylenes **2a**−**c** on the diphenylacetylene to form zwitterionic intermediates **7a**−**c**, bearing an alkenyl anion and a positively charged sulfonium or selenonium moiety. For the sulfonium derivatives **7a** and **7b**, the alkenyl anion attacks the silicon atom to afford the silacyclopropene intermediates **8a** and **8b**, which undergo ring cleavage by the reaction with 2-propanol to afford **5a** and **5b**, bearing the alkenyl and alkoxy groups on the silicon center. The deuterium incorporation in the alkenyl group supports this reaction pathway. It is noted that the alkenyl anion in **7b** would abstract a proton from the methylthio group to form a
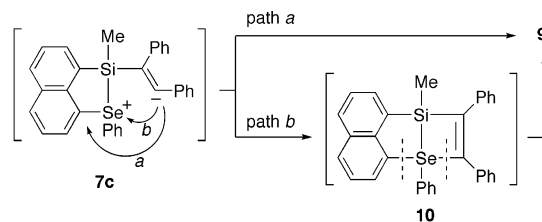
sulfonium ylide prior to the quenching with 2-propanol-d_1, as observed in the diethylphosphino analogue,[2] but this was not the case here, because the deuterium was incorporated not in the methylthio group but in the alkenyl group in **5b**.

For the selenonium derivative **7c**, two reaction pathways compete. One of the products, **5c**, seems to be formed through a pathway similar to that of the sulfur derivatives described above. The other 1-silaphenalene product, **6**, seems to be formed by the alcoholysis of the 1-seleno-1-silaphenalene intermediate **9**, which is formed through the attack of the alkenyl anion on the naphthyl carbon accompanied by the selenium−carbon bond fission (Scheme 4, *path a*), as previously observed in the nitrogen-coordinated silylene case. For the latter, there is another possible mechanism as follows: The alkenyl anion attacks the selenium atom to produce a hypervalent selenium species **10** (or a transition structure), which undergoes ligand coupling[11] of the alkenyl and naphthyl carbon on the selenium center to form **9** (Scheme 4, *path b*). It is difficult to determine which is more probable at the present time.
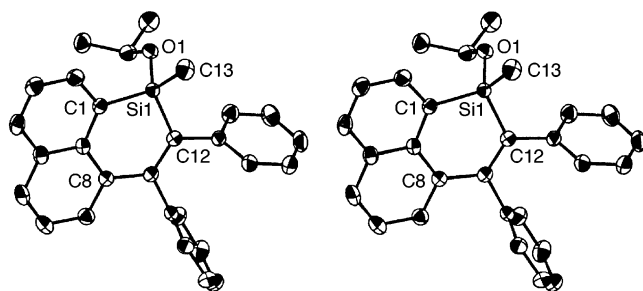

Figure 1. X-ray structure of **6** in stereoview at the 60% probability level. All hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Si1−O1 1.650(1), Si1−C1 1.857(2), Si1−C12 1.856(2), Si1−C13 1.852(2), O1−Si1−C1 111.72(7), O1−Si−C12 112.91(7), O1−Si1−C13 103.95(8), C1−Si1−C12 103.60(7), C1−Si1−C13 112.03(8), C12−Si1−C13 112.90(10).

(6) There have been reported many precedents of the upfield shift of a signal for the hypercoordinate silicon atom bearing electronegative substituents.[7]

(7) (a) Helmer, B. J.; West, R.; Corriu, R. J. P.; Poitier, M.; Royo, G.; de Saxcé, A. *J. Organomet. Chem.* **1983**, *251*, 285. (b) Tandura, St. N.; Alekseev, N. V.; Voronkov, M. G. *Top. Curr. Chem.* **1986**, *131*, 99. (c) Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, England, 1989; p 511. (d) Kost, D.; Kalikhman, I. In *The Chemistry of Organic Silicon Compounds Vol 2*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, England, 1998; p 1339.

(8) The S1···Si1 distance in **1a** and the Se1···Si1 distance in **1c** correspond to ca. 78% and ca. 79% of the sum of the van der Waals radii,[9] respectively. These ratios lie between those of O1···Si1 in **1i** (ca. 75%) and N1···Si1 in **1e** (ca. 81%).

(9) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(10) Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *Organometallics* **1992**, *11*, 2099.

(11) (a) Wittig, G.; Maercker, A. *Chem. Ber.* **1964**, *97*, 747. (b) Seyferth, D.; Fogel, J.; Heeren, J. K. *J. Am. Chem. Soc.* **1966**, *88*, 2207. (c) Newkome, G. R.; Hager, D. C. *J. Am. Chem. Soc.* **1978**, *100*, 5567. (d) Oae, S.; Uchida, Y. *Acc. Chem. Res.* **1991**, *24*, 202. For our case, see ref 2.

Conclusion

The silylenes intramolecularly coordinated by sulfur or selenium, **2a**−**c**, have been clarified to behave as nucleophilic sila-ylides during the reactions with diphenylacetylene to afford the zwitterionic intermediates, like the silylenes intramolecularly coordinated by nitrogen or phosphorus as previously reported.[1,2] However, the reaction pathways of the zwitterionic intermediates bearing a sulfonium or selenonium ion, **7a**−**c**, have been found to form the silacyclopropenes **8a**−**c** as intermediates, being different from those bearing an ammonium or phosphonium ion. It is also unprecedented that two kinds of compounds are produced from the same intermediate as in the case of **7c**, containing a selenonium ion moiety. Thus, the reaction pathways of the sulfonium or selenonium sila-ylide with diphenylacetylene provide another example of the sila-ylide whose reaction courses are determined by the character of the positively charged element.

Experimental Section

General Procedures. All reactions were carried out under a nitrogen atmosphere. Diethyl ether, mesitylene, methanol, 2-propanol, and triethylamine were dried by standard procedures and distilled under nitrogen prior to use. *n*-BuLi and diphenylacetylene were purchased from commercial sources and used as received. The ^{1}H (300 MHz) NMR spectra were recorded using a Varian Mercury 300 spectrometer. The ^{13}C (67.9 MHz) and ^{29}Si (53.7 MHz) NMR spectra were recorded using a JEOL JNM-EX 270 spectrometer. The chemical shifts are referenced to internal benzene-d_6 (^{1}H and ^{13}C) or external Me$_4$Si (^{29}Si). The elemental analyses were performed at the Microanalysis Division of the Institute for Chemical Research, Kyoto University. Column chromatography was performed using Kieselgel (70−230 mesh) (Merck). High-performance liquid chromatography (HPLC) was carried out using a reversed stationary phase JAIGEL-ODS S-343-15 (20 mm × 250 mm) (Japan Analytical Industry Co., Ltd.).

General Procedure for Preparation of Methoxydisilanes 1a−c. To a solution of 1-bromo-8-chalcogenonaphthalene (**3**)[5] (2.0 mmol) in diethyl ether (10 mL) was added a 1.63 mol/L solution of *n*-BuLi in hexane (1.23 mL, 2.0 mmol) with stirring at 0 °C under a nitrogen atmosphere. After stirring of the mixture for 30 min, 1,1-dichloro-1,2-dimethyl-2,2-diphenyldisilane[1a] (623 mg, 2.0 mmol) was added at 0 °C, and the resulting mixture was stirred for 1 h at room temperature. To the reaction mixture containing 1-chloro-1-(8-chalcogeno-1-naphthyl)-1,2-dimethyl-2,2-diphenyldisilane (**4**) were added dropwise triethylamine (0.84 mL, 6.0 mmol) and methanol (0.24 mL, 5.9 mmol) at 0 °C. The mixture was stirred for 1.5 h at room temperature. The precipitate was filtered and the filtrate was concentrated under reduced pressure to leave a viscous oil, which was purified by column chromatography on silica gel [hexane/AcOEt (10:1 or 20:1) as eluent] to afford 1-methoxy-1-(8-phenylthio-1-naphthyl)-1,2-dimethyl-2,2-diphenyldisilane (**1a**) (605 mg, 1.19 mmol; 60%), 1-methoxy-1-(8-methylthio-1-naphthyl)-1,2-dimethyl-2,2-diphenyldisilane (**1b**) (579 mg, 1.30 mmol; 65%), and 1-methoxy-1-(8-phenylseleno-1-naphthyl)-1,2-dimethyl-2,2-diphenyldisilane (**1c**) (513 mg, 0.93 mmol; 47%), respectively. **1a**: Mp: 94−95 °C [from hexane/AcOEt (10:1)]. ^{1}H NMR (C$_6$D$_6$): δ 0.69 (s, 3H), 0.84 (s, 3H), 3.24 (s, 3H), 6.60 (dd, *J* = 7.5, 1.8 Hz, 2H), 6.75−6.85 (m, 3H), 7.01 (t, *J* = 7.5 Hz, 1H), 7.1−7.2 (m, 5H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.51 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.65−7.8 (m, 6H), 8.69 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (C$_6$D$_6$): δ −1.95, 0.69, 51.19, and 22 signals in aromatic region. ^{29}Si NMR (C$_6$D$_6$): δ −22.14, −8.09. Anal. Calcd for C$_{31}$H$_{30}$-

OSi$_2$S: C, 73.47; H, 5.97. Found: C, 73.48; H, 5.99. **1b**: Mp: 113−114 °C (from hexane). ^{1}H NMR (C$_6$D$_6$): δ 0.76 (s, 3H), 0.84 (s, 3H), 1.62 (s, 3H), 3.28 (s, 3H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.15−7.25 (m. 5H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.53 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.65 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.7−7.8 (m, 6H), 8.55 (dd, *J* = 7.6, 1.2 Hz, 1H). ^{13}C NMR (C$_6$D$_6$): δ −1.91, 0.34, 20.15, 51.27, and 16 signals in aromatic region. ^{29}Si NMR (C$_6$D$_6$): δ −21.97, −9.17. Anal. Calcd for C$_{26}$H$_{28}$OSi$_2$S: C, 70.22; H, 6.35. Found: C, 70.04; H, 6.44. **1c**: Mp: 120−121 °C (from hexane). ^{1}H NMR (C$_6$D$_6$): δ 0.74 (s, 3H), 0.83 (s, 3H), 3.20 (s, 3H), 6.65−6.7 (m, 2H), 6.7−6.8 (m, 3H), 6.98 (t, *J* = 7.5 Hz, 1H), 7.1−7.2 (m, 5H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.60 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.65 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.67−7.78 (m, 6H), 8.52 (dd, *J* = 7.5, 1.2 Hz, 1H). ^{13}C NMR (C$_6$D$_6$): δ −1.77, 1.61, 51.06, and 19 signals in aromatic region. ^{29}Si NMR (C$_6$D$_6$): δ −22.27, −6.71. Anal. Calcd for C$_{31}$H$_{30}$OSi$_2$Se: C, 67.27; H, 5.46. Found: C, 67.12; H, 5.43.

Thermolysis of 1a. A solution of **1a** (101 mg, 0.20 mmol) and diphenylacetylene (36 mg, 0.20 mmol) in mesitylene (2.0 mL) was heated at 165 °C for 24 h under a nitrogen atmosphere. To this reaction mixture was added 2-propanol (1 mL), and the resulting mixture was stirred at ambient temperature for 1.5 h. After removal of the solvent under reduced pressure, the reversed phase HPLC using acetonitrile as eluent afforded methyl[(*Z*)-1,2-diphenylethenyl](8-phenylthio-1-naphthyl)(2-propoxy)silane (**5a**) (78 mg, 0.15 mmol; 75%) as a viscous oil. ^{1}H NMR (C$_6$D$_6$): δ 0.81 (s, 3H), 1.28 (d, *J* = 6.0 Hz, 3H), 1.31 (d, *J* = 6.0 Hz, 3H), 4.25 (septet, *J* = 6.0 Hz, 1H), 6.68−6.80 (m, 5H), 6.82−6.92 (m, 5H), 6.93 (s, 1H), 7.05 (t, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.46 (dd, *J* = 8.1, 7.2 Hz, 2H), 7.54 (dd, *J* = 7.2, 1.5 Hz, 2H), 7.65 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.72 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.82 (dd, *J* = 7.2, 1.2 Hz, 1H), 8.85 (dd, *J* = 6.9, 1.2 Hz, 1H). ^{13}C NMR (C$_6$D$_6$): δ 0.70, 26.24, 26.27, 65.91, and 24 signals in aromatic region. ^{29}Si NMR (C$_6$D$_6$): δ −11.45. Anal. Calcd for C$_{34}$H$_{32}$OSiS: C, 79.02; H, 6.24. Found: C, 79.02; H, 6.35.

Thermolysis of 1b. Similarly, **1b** (67 mg, 0.15 mmol), diphenylacetylene (27 mg, 0.15 mmol), and mesitylene (1.5 mL) afforded, after the reaction with 2-propanol (1 mL) and purification by reversed phase HPLC using acetonitrile as eluent, methyl[(*Z*)-1,2-diphenylethenyl](8-methylthio-1-naphthyl)(2-propoxy)silane (**5b**) (31 mg, 0.068 mmol; 45%) as a viscous oil. ^{1}H NMR (C$_6$D$_6$): δ 0.84 (s, 3H), 1.31 (d, *J* = 6.0 Hz, 3H), 1.34 (d, *J* = 6.0 Hz, 3H), 1.93 (s, 3H), 4.25 (septet, *J* = 6.0 Hz, 1H), 6.84−6.92 (m, 3H), 6.95 (s, 1H), 6.89 (dd, *J* = 8.1, 2.1 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 7.15−7.24 (m, 3H), 7.46 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.56 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.60 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.69 (dt, *J* = 7.2, 1.2 Hz, 2H), 8.88 (dd, *J* = 6.9, 1.5 Hz, 1H). ^{13}C NMR (C$_6$D$_6$): δ 0.85, 23.05, 26.26, 26.34, 65.78, and 20 signals in aromatic region. ^{29}Si NMR (C$_6$D$_6$): δ −12.70. Anal. Calcd for C$_{29}$H$_{30}$OSiS: C, 76.60; H, 6.65. Found: C, 76.88; H, 6.80.

Thermolysis of 1c. A solution of **1c** (111 mg, 0.20 mmol) and diphenylacetylene (36 mg, 0.20 mmol) in mesitylene (2.0 mL) was heated at 165 °C for 30 h under a nitrogen atmosphere. To this reaction mixture was added 2-propanol (2 mL), and the resulting mixture was stirred at ambient temperature for 1.5 h. After removal of the solvent under reduced pressure, reversed phase HPLC using acetonitrile as eluent afforded methyl[(*Z*)-1,2-diphenylethenyl](8-phenylseleno-1-naphthyl)-(2-propoxy)silane (**5c**) (24 mg, 0.043 mmol; 22%) as a viscous oil and 1-(2-propoxy)-1-methylsilaphenalene (**6**) (21 mg, 0.052 mmol; 26%) as a colorless solid. **5c**: ^{1}H NMR (C$_6$D$_6$): δ 0.90 (s, 3H), 1.27 (d, *J* = 6.0 Hz, 3H), 1.28 (d, *J* = 6.0 Hz, 3H), 4.16 (septet, *J* = 6.0 Hz, 1H), 6.68−6.74 (m, 3H), 6.84−6.96 (m, 8H), 6.93 (s, 1H), 7.07 (dd, *J* = 7.5, 6.9 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 4H), 7.68 (t, *J* = 7.5 Hz, 1H), 8.05 (dd, *J* = 7.2, 1.5 Hz, 1H), 8.71 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (C$_6$D$_6$): δ 1.48, 26.13, 26.21, 66.08, and 24 signals in aromatic region. ^{29}Si NMR (C$_6$D$_6$): δ −10.70. Anal. Calcd for C$_{34}$H$_{32}$OSiSe: C, 72.45; H, 5.72. Found: C, 72.65; H, 5.73. **6**:

Mp: 115 °C (from hexane). ^{1}H NMR (C_6D_6): δ 0.59 (s, 3H), 0.96 (d, $J = 6.0$ Hz, 3H), 1.16 (d, $J = 6.0$ Hz, 3H), 4.01 (septet, $J = 6.0$ Hz, 1H), 6.91 (t, $J = 7.5$ Hz, 1H), 6.95−7.03 (m, 1H), 7.03−7.16 (m, 7H), 7.25 (dd, $J = 7.8$, 2.5 Hz, 2H), 7.45 (dd, $J = 7.8$, 6.8 Hz, 1H), 7.50 (dd, $J = 7.5$, 1.2 Hz, 1H), 7.58 (dd, $J = 8.1$, 1.2 Hz, 1H), 7.81 (dt, $J = 8.1$, 1.2 Hz, 1H), 8.06 (dd, $J = 6.9$, 1.5 Hz, 1H). ^{13}C NMR (C_6D_6): δ −1.09, 25.90, 26.01, 66.14, and 20 signals in aromatic region. ^{29}Si NMR (C_6D_6): δ −19.19. Anal. Calcd for $C_{28}H_{26}OSi$: C, 82.71; H, 6.45. Found: C, 82.60; H, 6.43.

X-ray Structure Determination for 1a, 1c, and 6. Single crystals of **1a**, **1c**, and **6** suitable for X-ray crystallography were obtained by recrystallization from hexane/AcOEt (10:1) (**1a**) and hexane (**1c** and **6**), respectively. Intensity data were collected on a Rigaku RAXIS-IV imaging plate area detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). The data were corrected for Lorentz and polarization effects and secondary extinction. The crystal structures were resolved by direct methods in SIR92, and a full-matrix least-squares refinement was carried out for all non-hydrogen atoms. Hydrogen atoms were included but not refined. All the calculations were performed using the teXsan crystallographic package from Molecular Structure Corp.

Supporting Information Available: Tables of all crystallographic data and atomic coordinates, anisotropic displacement parameters, bond distances, and bond angles for **1a**, **1c**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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