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Preparation, Structure, and Reactivity of Pentacoordinate Disilanes Bearing an 8-Charcogeno-1-naphthyl Group and a Heteroatom on the Same Silicon Atom

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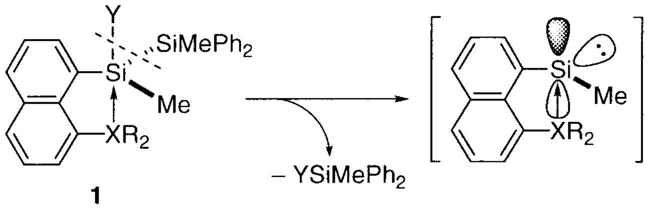
ABSTRACT: *The pentacoordinate disilanes bearing an 8-chalcogeno-1-naphthyl group and an ethoxy group (or a fluorine atom) on the same silicon center are found to be thermally stable, in sharp contrast to the thermal lability of the analogous disilanes coordinated by the group 15 elements, such as nitrogen and phosphorus, to α-elimination of the ethoxysilane (or fluorosilane) to generate the base-coordinated silylenes. As the reasons for this different behavior, two possibilities are pointed out as follows: (1) the nitrogen-coordinated disilanes are destabilized due to the distortion of the naphthyl moiety, and (2) silylenes are more stabilized by coordination with the group 15 elements than with the group 16 elements.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:392–397, 2001

INTRODUCTION

We have already reported the lability of the pentacoordinate disilanes **1a** and **1b** (Scheme 1), which contain the 8-dimethylamino-1-naphthyl group and an ethoxy group (or a fluorine atom) on the same silicon center, to α-elimination of the ethoxysilane (or fluorosilane) to generate the amine-coordinated silylene during thermolysis [1]. The amine-coordinated silylene thus produced has been shown to behave as a nucleophile [1c,2] in sharp contrast to the electrophilic character of the noncoordinated silylene. Quite recently, we have observed the thermal lability of the phosphine-coordinated fluorodisilanes **1c** and **1d** to α-elimination of the fluorosilane to generate the phosphine-coordinated silylenes bearing a similar structure [3]. In the case of the tetracoordinate disilane **2** (Chart 1) bearing the nonsubstituted naphthyl group, no α-elimination reaction was observed during the thermolysis, even at a higher temperature [1a]. In order to understand the role of the group 15 elements in the thermal lability of the pen-



1

a; X = N, R = Me, Y = OEt
b; X = N, R = Me, Y = F
b'; X = N, R = Me, Y = F, $SiPh_3$ instead of $SiMePh_2$
c; X = P, R = Et, Y = F
d; X = P, R = Ph, Y = F

SCHEME 1

Dedicated to Professor Naoki Inamoto on the occasion of his seventy-second birthday.

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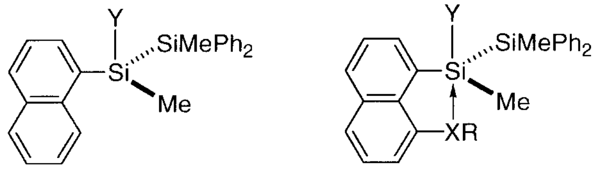


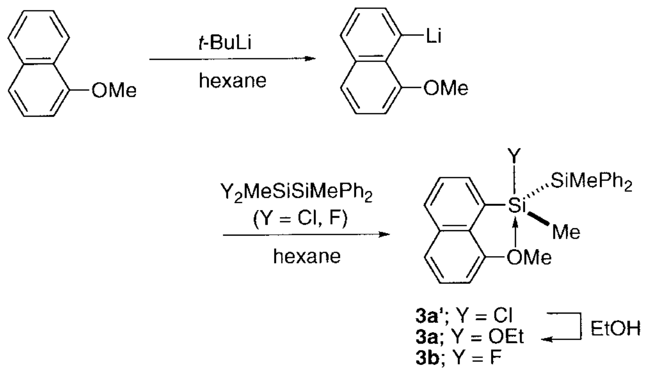
2

a: Y = OEt
b: Y = F

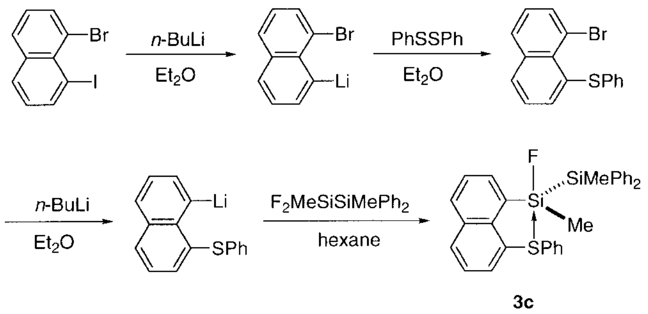
3

a; X = O, R = Me, Y = OEt
b; X = O, R = Me, Y =F
c; X = S, R = Ph, Y = F

CHART 1



SCHEME 2



SCHEME 3

tacoordinate disilanes to α-elimination and the reversed reactivity of the base-coordinated silylene, a comparison with similar compounds coordinated by other groups is of great importance. We report herein the results of the study on the coordination of group 16 elements (chalcogens); namely the reactivity and structure of the fluoro- or ethoxy-disilanes **3a–c** bearing an 8-methoxy- or an 8-phenylthio-1-naphthyl group (Chart 1).

RESULTS AND DISCUSSION

Synthesis

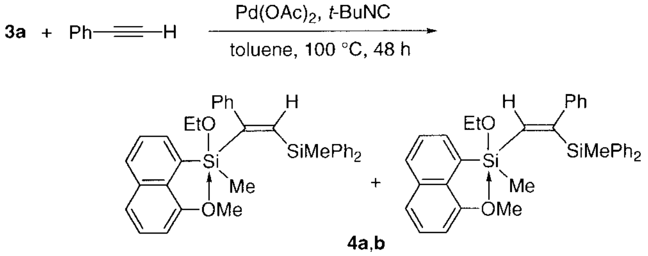
The pentacoordinate disilanes **3a** and **3b** bearing the 8-methoxy-1-naphthyl group were prepared through the lithiation of 1-methoxynaphthalene, followed by the reaction with 1,1-difluoro- or 1,1-dichloro-disilane, as shown in Scheme 2. The pentacoordinate disilane **3c**, bearing the 8-phenylthio-1-naphthyl group, was prepared through the stepwise halogen–lithium exchange reactions of 8-bromo-1-iodonaphthalene [4] as shown in Scheme 3.

Reactions

We tried the thermal degradation of the oxygen-coordinated ethoxydisilane **3a** and fluorodisilane **3b** as well as the sulfur-coordinated fluorodisilane **3c** in the presence of diphenylacetylene as the trapping reagent. Contrary to our expectation, all of the starting materials were recovered under the following conditions: **3a**: in xylene at 145°C for 48 hours, in dimethylformamide (DMF) at 155°C for 48 hours, in diglyme at 162°C for 48 hours, and in toluene-d$_8$ at 250°C for 8 hours in a sealed tube: **3b**: in xylene at 145°C for 48 hours. **3c**: in xylene at 145°C for 48 hours. For comparison, it should be noted here that the thermal degradation of the amine-coordinated disilanes **1a** and **1b** is completed under the following conditions. **1a**: in toluene at 110°C for 16 hours and in DMF at 90°C for 20 hours. **1b**: in xylene at 145°C for 40 hours.

As another trial for the α-elimination, we examined the reaction of the oxygen-coordinated ethoxydisilane **3a** with a transition metal catalyst because the nitrogen-coordinated ethoxydisilane **1a** has been known to afford exclusively the ethoxysilane under mild conditions in the presence of a palladium complex [5]. Thus, **3a** was heated together with phenylacetylene in the presence of palladium(II) acetate (0.03 mol amount) and *t*-butyl isonitrile (0.05 mol amount) in toluene at 100°C [6]. Contrary to our expectation, none of the ethoxysilane, putatively formed by α-elimination, was detected. Instead, acetylene insertion into the Si–Si bond took place to give vinylsilane derivatives as a mixture of the regioisomers **4a** and **4b** (ca. 3:1) in a 40% yield (Scheme 4). This result is quite similar to the behavior of the tetracoordinate ethoxydisilane **2a** which has been reported to afford exclusively the acetylene-insertion product [5]. Thus, the reaction course of the oxygen-coordinated ethoxydisilane **3a** in the presence of a transition metal catalyst is similar to that of the tetracoordinate **2a**.

This similarity and the thermal stability of the chalcogen-coordinated **3a–c** described above indicate that coordination of a chalcogen atom to the silicon center does not facilitate the α-elimination to generate the base-coordinated silylene. In order to understand the reason for this stability, a comparison of the structures of the chalcogen-coordinated



4a,b

SCHEME 4

3a–c with the nitrogen-coordinated **1a** and **1b** was carried out as described below.

Comparison of Structures

The results of the X-ray crystallographic analyses of the chalcogen-coordinated **3a** and **3c** are shown in Figures 1 and 2, respectively [7], and the comparison with the structures of the nitrogen-coordinated **1a** and **1b**′ [8] is summarized in Table 1. These data indicate that the coordination of the chalcogen atoms to the silicon centers in the solid state is similar to that of the nitrogen atom. Thus, in **3a** and **3c**, the geometry of Si1 is significantly deformed from the tetrahedral to pseudo–trigonal bipyramidal (TBP), with two oxygen atoms (**3a**) and sulfur and fluorine atoms (**3c**) at the two pseudoapical positions. The O1 · · · Si1 distance in **3a** and the S1 · · · Si1 distance in **3c** are considerably shorter than the sum of the van der Waals radii [9] (ca. 76% in both cases). These ratios are slightly smaller than those in **1a** (ca. 81%) and **1b**′ (ca. 78%). As for the angles X · · · Si–Y and the pentacoordination character %TBP [10] of the silicon centers, small differences have been observed in the ethoxydisilanes **3a** and **1a** as well as in the fluorodisilanes **3c** and **1b**′. It is also shown in Table 1 that the other parameters of **3a** and **3c**, such as the bond distances of Si1–Y and Si1–Si2, as well as the bond angles of Y–Si1–Si2, which may be relevant to the lability in the α-elimination, fall into a similar range with those of the amine-coordinated disilanes **1a** and **1b**′.

As only one remarkable difference in the structure of the chalcogen- and nitrogen-coordinated compounds, the naphthalene ring in the chalcogen-coordinated **3a** and **3c** is found to be free from distortion, while that in the nitrogen-coordinated **1a** and **1b**′ is highly distorted. Thus, the dihedral angle of the planes defined by the C1–C2–C3 atoms and the C6–C7–C8 atoms of the naphthalene ring is ca. 4–5° in **3a** and **3c**, while in **1a** and **1b**′, this angle is ca. 10–13° (Table 1). There are much greater differences in the displacement of the silicon and the coordinating atoms from the mean plane of the naphthalene ring, as shown by the dihedral angles (Si1–C1–C8/X1–C8–C1): the angles are 5–8° in the chalcogen-coordinated compounds **3a** and **3c**, while those in **1a** and **1b**′ are roughly 30°.

The coordination of chalcogen atoms to the silicon centers in solution has also been confirmed to be similar to that of the nitrogen atom based on ^{29}Si NMR measurements. As shown in Table 2, the silicon atom in the ethoxydisilane **3a**, bearing the methoxynaphthyl group, resonates ca. 10 ppm more upfield in comparison with the naphthyl-containing silicon atom in the tetracoordinate **2a**. Similarly, the silicon atoms in the fluorodisilanes **3b** and **3c** bearing the methoxy- and phenylthio-naphthyl group, respectively, resonate 20–30 ppm more upfield than that in the corresponding tetracoordinate **2b**. These upfield shifts are found to be in a range similar to those caused by the coordination of the naphthylamino group as shown for **1a** and **1b** (Table 2).

Although the reason for the different behavior during the thermolysis of the disilanes coordinated by the group 15 and 16 elements is not yet clear, the structural comparisons mentioned previously suggest the possibility that the nitrogen-coordinated disilanes are highly destabilized due to the distortion of the naphthyl moiety, while the chalcogen-coordinated disilanes are less destabilized due to the slight strain. Another reason may reside in the fact that silylenes are more stabilized by coordination with the group 15 elements than with the group 16 elements, as already shown by theoretical studies [11]. On the whole, the nitrogen-coordinated disilanes readily undergo thermal degradation because of the ground-state destabilization and the product (silylene) stabilization, while the chalcogen-coordinated disilanes are thermally stable because both the ground-state destabilization and the product stabilization are small. This is of course a speculative consideration, and full understanding requires further study, which is now in progress in our laboratory.

EXPERIMENTAL SECTION

^{1}H (270 MHz), ^{13}C (67.94 MHz), ^{29}Si (53.67 MHz) NMR spectra were recorded on a JEOL JNM-EX 270 spectrometer. ^{1}H and ^{13}C chemical shifts are referenced to internal benzene-d$_6$ (^{1}H δ 7.200 and ^{13}C δ 128.00 ppm). ^{29}Si chemical shifts are referenced to external Me$_4$Si (0 ppm). Mass spectra were measured at 70 eV on a JEOL JMS-DX300 mass spectrometer equipped with a JMA-3500 data processing system. 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

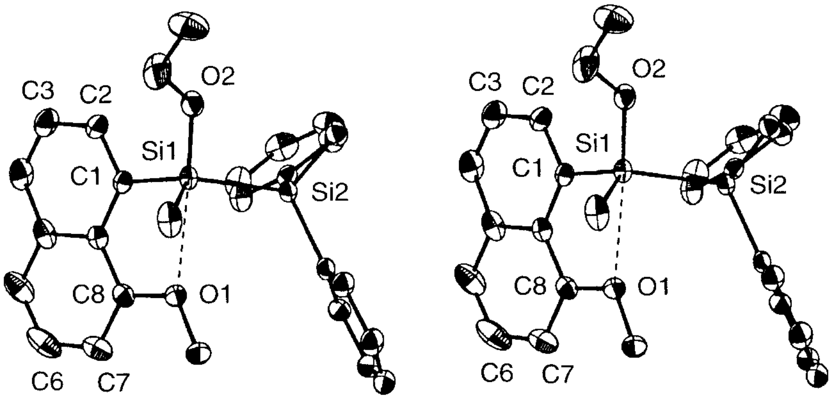


FIGURE 1 X-ray structure of **3a** in stereoview at 20% probability level. All hydrogen atoms are omitted for clarity.

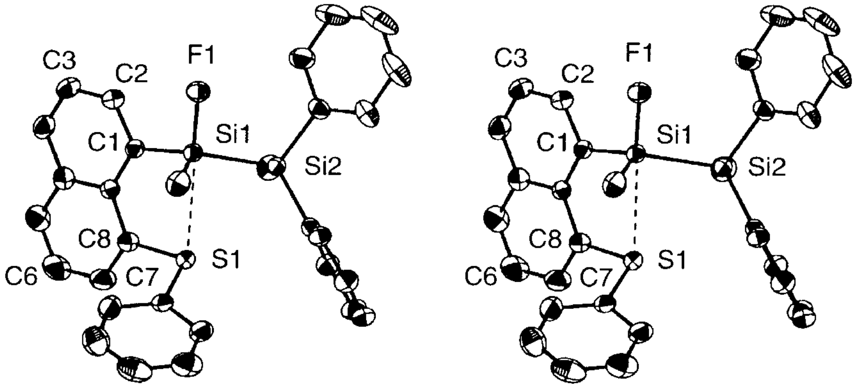


FIGURE 2 X-ray structure of **3c** in stereoview at 60% probability level. All hydrogen atoms are omitted for clarity.

TABLE 1 Selected Interatomic Distances (Å), Angles (deg), and Dihedral Angles (°) and %TBP[a] for **3a, 3c, 1a**, and **1b′**[b]

	Y = OEt		*Y = F*	
	3a *(X = O)*	**1a** *(X = N)*	**3c** *(X = S)*	**1b′** *(X = N)*
Interatomic Distances				
X1 · · · Si1	2.730(3)[c]	2.969(3)[d]	2.9668(6)[e]	2.852(2)[d]
Y1–Si1	1.673(3)	1.665(2)	1.634(1)	1.637(2)
Si1–Si2	2.333(1)	2.368(1)	2.3563(6)	2.3711(9)
Angles				
X1 · · · Si1–Y1	175.4(1)	171.36(9)	173.75(5)	166.10(9)
Y1–Si1–Si2	99.48(10)	97.35(8)	100.65(4)	95.59(7)
Dihedral Angles				
C1–C2–C3/C6–C7–C8	5.03	9.78	3.65	12.80
Si1–C1–C8/X1–C8–C1	7.69	31.32	4.86	29.94
Pentacoordination Characters				
%TBPa	32	37	54	57
%TBPe	51	59	69	80

[a] Pentacoordination character which shows the degree of the deformation from tetrahedral to trigonal bipyramidal. The definition has been reported in ref [10].

[b] See Ref. [8].

[c] Σr_{VDW} (O, Si) = 3.60 Å.

[d] Σr_{VDW} (N, Si) = 3.65 Å.

[e] Σr_{VDW} (S, Si) = 3.90 Å.

TABLE 2 ^{29}Si NMR Data of Pentacoordinate and Tetracoordinate Disilanes

Y = OEt			*Y = F*		
	δ^a	$\Delta\delta$ $(X - H)^b$		δ^a	$\Delta\delta$ $(X - H)^b$
3a (X = O)	−4.8	−10.9	**3b** (X = O)	+5.0	−19.3
1a (X = N)	−7.3	−13.4	**3c** (X = S)	−7.7	−32.0
2a (X = H)	+6.1	—	**1b** (X = N)	−3.6	−27.9
			2b (X = H)	+24.3	—

[a] Chemical shift of the silicon atom attached to the naphthyl carbon.
[b] Sign (−) indicates the upfield shift.

(HPLC) was carried out using a 20 mm × 250 mm COSMOSIL 5SL-II column (Wako).

Tetrahydrofuran (THF) and diethyl ether were distilled under a nitrogen atmosphere from sodium/benzophenone. Hexane, toluene, and xylene were distilled under a nitrogen atmosphere from sodium. Benzene was distilled under a nitrogen atmosphere from $LiAlH_4$. *n*-BuLi in hexane was purchased from Waco Pure Chemical Industry, and *t*-BuLi in pentane was purchased from Kanto Chemicals. All other organic materials are commercially available and were used after distillation.

*1-Ethoxy-1-(8-methoxy-1-naphthyl)-1,2-dimethyl-2,2-diphenyldisilane (**3a**)*

8-Methoxy-1-naphthyllithium, prepared from 1-methoxynaphthalene (25.0 mmol) and *t*-BuLi (27.5 mmol) according to the reported procedure [12], was suspended in diethyl ether (20 mL). 1,1-Dichloro-1,2-dimethyl-2,2-diphenyldisilane [1a] (6.23 g, 20.0 mmol) was added to the suspension at −20°C with stirring. The mixture was allowed to warm to room temperature and stirred overnight. The mixture containing the primary product **3a′** was cooled to 0°C followed by the addition of diethyl ether (30 mL), dry triethylamine (7.0 mL, 50 mmol), and dry ethanol (2.3 mL, 40 mmol) and the resulting mixture was stirred for 48 hours. To this reaction mixture was added benzene (20 mL) and the precipitate thus formed was filtered off through a glass filter. The filtrate was concentrated under reduced pressure to leave a viscous oil. By cooling a solution of this residue in hexane to −20°C, pure **3a** (3.63 g, 8.20 mmol; 27%) was obtained as colorless crystals: m.p. 81–82°C: ^{1}H NMR (C_6D_6); δ 0.51 (s, 3H), 0.68 (s, 3H), 1.16 (t, 3H, J = 7.0 Hz), 2.90 (s, 3H), 3.61 (dq, 1H, J = 10.0, 7.0 Hz), 3.75 (dq, 1H, J = 10.0, 7.0 Hz), 6.29 (d, 1H, J = 7.6 Hz), 7.13–7.23 (m, 7H), 7.41 (d, 1H, J = 7.6 Hz), 7.50 (dd, 1H, J = 6.8, 7.8 Hz), 7.60–7.65 (m, 4H), 7.74 (dd, 1H, J = 8.1, 1.1 Hz), 8.57 (dd, 1H, J = 7.0, 1.4 Hz). ^{13}C NMR (C_6D_6) δ −3.50, −0.23, 18.59, 54.04, 58.89, 104.22, 121.84, 125.54, 126.46, 127.78, 128.18, 128.59, 128.77, 129.67, 130.00, 134.04, 135.08, 135.30, 135.39, 135.64, 138.17, 139.03, 156.10. ^{29}Si NMR (C_6D_6) δ −23.50, −4.78. Anal. calcd for $C_{27}H_{30}O_2Si_2$: C, 73.25; H, 6.83. Found: C, 72.96; H, 6.76.

*1-Fluoro-1-(8-methoxy-1-naphthyl)-1,2-dimethyl-2,2-diphenyldisilane (**3b**)*

To a suspension of 8-methoxy-1-naphthyllithium [prepared form 1-methoxynaphthalene (25.0 mmol) and *t*-BuLi (27.5 mmol)] in diethyl ether (20 mL) was added 1,1-difluoro-1,2-dimethyl-2,2-diphenyldisilane [5b] (5.51 g, 20.0 mmol) at −40°C with stirring. The mixture was allowed to warm to room temperature and stirred overnight. To this reaction mixture was added benzene (20 mL) and the precipitate thus formed was filtered off by use of a glass filter. The filtrate was concentrated under reduced pressure to give a yellow viscous oil. The oil was subjected to column chromatography on silica gel (R_f 0.27, hexane/ethyl acetate 20:1) to afford the crude **3b**. Recrystallization from hexane afforded pure **3b** (1.12 g, 2.69 mmol; 1.1%) as white crystals: m.p. 82–83°C: ^{1}H NMR (C_6D_6); δ 0.52 (s, 3H), 0.73 (d, 3H, J = 9.2 Hz), 2.80 (s, 3H), 6.22 (d, 1H, J = 7.6 Hz), 7.13–7.23 (m, 7H), 7.39 (t, 1H, J = 8.6 Hz), 7.55–7.62 (m, 5H), 7.68 (d, 1H, J = 8.4 Hz), 8.41 (d, 1H, J = 7.0 Hz). ^{13}C NMR (C_6D_6) δ −4.00, 1.85 (d, J = 15.9 Hz), 54.18, 104.17, 121.87, 125.72, 126.85, 128.09, 128.99, 129.08, 129.47 (d, J = 2.4 Hz), 129.80, 132.52 (d, J = 8.6 Hz), 133.93, 134.07, 134.85, 135.40, 135.49, 136.86, 137.29, 155.51. ^{29}Si NMR (C_6D_6) δ −23.11 (d, J = 32.2 Hz), −4.78 (d, J = 297.7 Hz). Anal. Calcd for $C_{25}H_{25}FOSi_2$: C, 72.07; H, 6.05. Found: C, 72.30; H, 5.87.

*1-Fluoro-1,2-dimethyl-2,2-diphenyl-1-(8-phenylthio-1-naphthyl)disilane (**3c**).*

To a solution of 1-bromo-8-iodonaphthalene [4] (0.667 g, 2.00 mmol) in diethyl ether (4.0 mL) was added dropwise a 1.6 mol/L solution of n-BuLi in hexane (1.25 mL, 2.00 mmol) at −78°C with stirring under a nitrogen atmosphere. After stirring of the mixture for 1 hour, a solution of diphenyl disulfide (0.437 g, 2.00 mmol) in diethyl ether (1 mL) was added dropwise to the mixture, and the resulting mixture was stirred at −78°C for 30 minutes. The reaction mixture was then washed with 0.1 N sodium hydroxide (5 mL × 2). The organic layer was concentrated under reduced pressure, and the residual oil was purified by column chromatography on silica gel (R_f 0.25, hexane/ethyl acetate 20:1) to give 1-bromo-8-(phenylthio)naphthalene (0.516 g, 1.64

mmol; 82%) as a brown solid. To a solution of this solid (0.313 g, 0.99 mmol) in diethyl ether (8 mL) was dropwise added a solution of n-BuLi in hexane (0.62 mL, 1.00 mmol) at −78°C, and the resulting mixture was stirred for 30 minutes. To the mixture was added dropwise 1,1-difluoro-1,2-dimethyl-2,2-diphenyldisilane (0.279 g, 1.00 mmol) at 0°C, and the mixture was allowed to warm to room temperature and was stirred overnight. To the reaction mixture was added benzene (10 mL), and the precipitate thus formed was filtered off by use of a glass filter. The filtrate was concentrated under reduced pressure to give a yellow viscous oil. By the addition of hexane, the oil turned to a yellow solid. The solid was recrystallized from hexane and toluene to afford **3c** (0.333 g, 0.78 mmol; 78%) as colorless crystals: m.p. 137–138°C: ^{1}H NMR (C_6D_6); δ 0.67 (d, 3H, J = 8.9 Hz), 0.83 (s, 3H), 6.48–6.52 (m, 2H), 6.75–6.77 (m, 3H), 7.00 (t, 1H, J = 7.8 Hz), 7.13–7.17 (m, 6H), 7.37–7.45 (m, 2H), 7.57 (d, 1H, J = 7.0 Hz), 7.65 (d, 1H, J = 7.8 Hz), 7.70 −7.73 (m, 4H), 8.74 (d, 1H, J = 7.0 Hz). ^{13}C NMR (C_6D_6) δ −2.71, 2.57 (d, J = 18.2 Hz), 125.97, 126.19, 126.98, 127.37, 127.97, 128.05, 129.00, 129.02, 129.17, 130.28, 131.13, 131.29, 135.13, 135.22, 135.78, 136.36 (d, J = 8.6 Hz), 137.34, 137.56, 137.63, 137.86, 138.66, 140.47. ^{29}Si NMR (C_6D_6) δ −20.70 (d, J = 38.9 Hz), −7.66 (d, J = 305.8 Hz). Anal. calcd for $C_{30}H_{27}FSi_2S$: C, 72.83; H, 5.50. Found: C, 73.07; H, 5.48.

Attempted Thermal Degradation of **3a** *in the Presence of Diphenylacetylene in Toluene-d$_8$ at 250°C*

A solution of **3a** (0.0208 g, 0.047 mmol) and diphenylacetylene (0.0085 g, 0.048 mmol) in toluene-d$_8$ (0.55 mL) was sealed in an NMR sample tube under an argon atmosphere. After heating of the tube at 250°C for 8 hours, no change was observed based on the ^{1}H NMR measurement.

Attempted Thermal Degradation of **3c** *in the Presence of Diphenylacetylene in Xylene at 145°C*

A solution of **3c** (0.219 g, 0.51 mmol) and diphenylacetylene (0.0922 g, 0.52 mmol) in xylene (2 mL) was heated at 145°C under an argon atmosphere. No change was observed based on the ^{1}H NMR analysis of this reaction mixture.

Reaction of **3a** *with Phenylacetylene Catalyzed by Palladium(II) Acetate and t-Butyl Isonitrile*

To a mixture of palladium(II) acetate (3.5 mg, 0.015 mmol) and *t*-butyl isonitrile (2.9 μL, 0.025 mmol) in dry toluene (2 mL) were added **3a** (0.224 g, 0.50 mmol) and phenylacetylene (0.067 mL, 0.60 mmol) at room temperature. The mixture was heated at 100°C for 48 hours under an argon atmosphere. Complete disappearance of **3a** was confirmed by ^{1}H NMR analysis. After concentration of the solution, the residual oil was purified by HPLC to give a mixture of **4a** and **4b** (ca. 3:1) (0.110 g, 0.20 mmol; 40%): ^{1}H NMR (C_6D_6); major isomer δ 0.46(s, 3H), 0.81 (s, 3H), 1.20 (t, 3H, J = 7.0 Hz), 3.38 (s, 3H), 3.64 (m, 2H), 6.43 (d, 1H, J = 6.4 Hz), 6.96–7.70 (m, 14H), 8.19 (d, 1H, J = 5.7 Hz): minor isomer δ 0.57 (s, 3H), 0.84 (s, 3H), 1.24 (t, 3H, J = 7.0 Hz), 3.21 (s, 3H), 3.64–3.72 (m, 2H), 6.25 (d, 1H, J = 6.8 Hz), 6.96–7.70 (m, 14H), 8.19 (d, 1H, J = 5.6 Hz). MS. Calcd for $C_{35}H_{36}O_2Si_2S$: M 544 (100), M + 1 (50.0), M + 2 (19.2). Found: M 544 (100), M + 1 (52.2), M + 2 (22.4).

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[7] Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-155174 (**3a**) and 155173 (**3c**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB1 1EZ, UK (Fax: (+44)1223-336-033; E-mail: deposit @ccdc.cam.ac.uk).

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