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Journal of Organometallic Chemistry 643–644 (2002) 479–486

Journal of Organo metallic Chemistry

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Synthesis, structure, and reactivity of disilanes containing one neutral [4 + 2]-coordinate silicon center

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Received 30 August 2001; accepted 16 October 2001

Dedicated with admiration and respect to Professor Dr François Mathey in honor of his scientific achievements

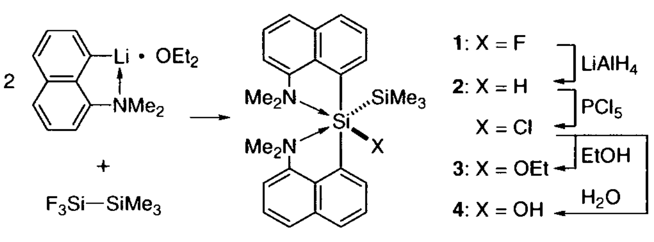
Abstract

[4 + 2]-Coordinate disilanes containing two 8-dimethylamino-1-naphthyl (8-Me_2N-1-Np) groups on the same silicon atom, $(8\text{-}Me_2N\text{-}1\text{-}Np)_2XSi\text{-}SiMe_3$, where X = F, OH, OEt, and H, are prepared. The X-ray structures of the two derivatives, X = F and OH, show that one of the coordinated dimethylamino groups is anti to the electronegative X group, while the other is anti to the trimethylsilyl group. The [4 + 2]-coordinate disilanes (X = F or OEt) are found to be thermally stable under these conditions such that the corresponding [4 + 1]-coordinate disilanes $(8\text{-}Me_2N\text{-}1\text{-}Np)XMeSi\text{-}SiMePh_2$ (X = F or OEt) readily undergo degradation. In the presence of $Pd(PPh_3)_4$ as a catalyst, the [4 + 2]-coordinate disilane (X = F) undergoes degradation to generate naphthylsilane $(8\text{-}Me_2N\text{-}1\text{-}Np)\text{-}SiMe_3$, the reaction pathway being different from that of the [4 + 1]-coordinate disilane (X = F) which affords the fluorosilane, $F\text{-}SiMePh_2$. © 2002 Elsevier Science B.V. All rights reserved.

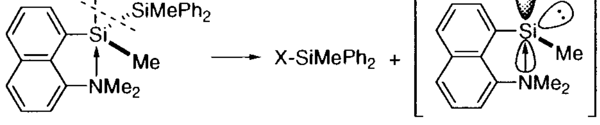
Keywords: [4 + 2]-Coordinate silicon compound; Disilane; 8-Dimethylamino-1-naphthyl group; Thermolysis; Transition metal catalyst

1. Introduction

The syntheses, structure, and reactivity of hexacoordinate organosilicon compounds have been extensively studied [1]. However, little has been reported on the structure and reactivity of neutral hexacoordinate organosilicon compounds bearing a silicon–silicon bond [2]. We are interested in the structure and reactivity of disilanes containing one [4 + 2]-coordinate [3] silicon center in order to compare them with those of disilanes containing one [4 + 1]-coordinate silicon center which have recently been reported to be highly reactive toward α-elimination (Eq. (1)) during thermolysis [4] or the reaction with a transition metal catalyst [5]. We report herein the syntheses and structure of disilanes containing one [4 + 2]-coordinate silicon center which bear two 8-dimethylamino-1-naphthyl groups and an electronegative group or a hydrogen atom. As for their reactivity, it is found that: (1) these [4 + 2]-coordinate disilanes, except for hydroxydisilane, are thermally stable under these conditions such that [4 + 1]-coordinate disilanes readily undergo thermal degradation, and (2) the α-elimination from the [4 + 2]-coordinate fluorodisilane proceeds by the reaction with a palladium catalyst to afford the 8-dimethylamino-1-naphthyltrimethylsilane, the reaction pathway being different from that of the [4 + 1]-coordinate fluorodisilane which affords fluorosilane under the same conditions.



Scheme 1.



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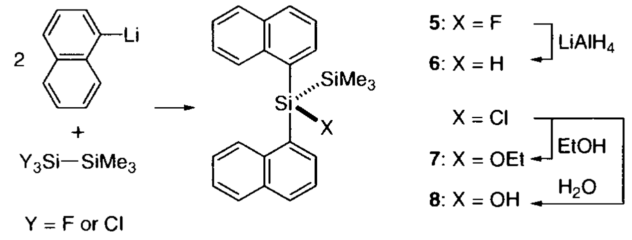


Scheme 2.

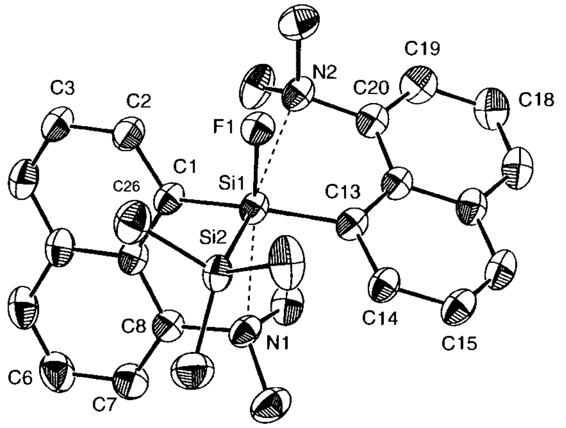


Fig. 1. Crystal structure of **1** drawn at the 30% probability level. All hydrogen atoms are omitted for clarity.

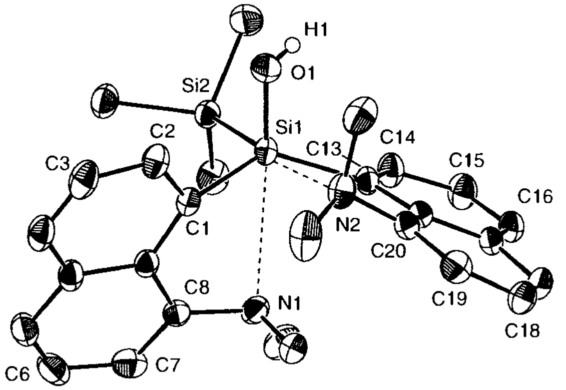


Fig. 2. Crystal structure of **4** drawn at the 30% probability level. All hydrogen atoms except for H(1) are omitted for clarity.

2. Results and discussion

2.1. Synthesis of [4 + 2]-coordinate disilanes and their tetracoordinate counterparts

The [4 + 2]-coordinate fluorodisilane (**1**), hydrodisilane (**2**), ethoxydisilane (**3**), and hydroxydisilane (**4**), which contain two 8-dimethylamino-1-naphthyl groups and a functional group (fluorine or hydrogen atom, or ethoxy or hydroxy group) on the same silicon atom were synthesized as shown in Scheme 1. Thus, 1,1,1-trifluoro-2,2,2-trimethyldisilane was allowed to react with two molar amounts of 8-dimethylamino-1-naphthyllithium [6] to give the [4 + 2]-coordinate fluorodisilane (**1**). The [4 + 2]-coordinate hydrodisilane (**2**) was prepared by the reduction of **1** with LiAlH$_4$ [7]. The hydrodisilane (**2**) was converted into the chlorodisilane by treatment with PCl$_5$ [8]. Due to its high moisture sensitivity, the chlorodisilane was subjected to ethanolysis or hydrolysis without isolation to afford the [4 + 2]-coordinate ethoxydisilane (**3**) or hydroxydisilane (**4**), respectively. The tetracoordinate counterparts **5**–**8** were also prepared in similar ways as shown in Scheme 2.

2.2. X-ray crystal structures of [4 + 2]-coordinate fluorodisilane (1) and hydroxydisilane (4)

The X-ray crystal structures of the [4 + 2]-coordinate fluorodisilane (**1**) and hydroxydisilane (**4**) are shown in Figs. 1 and 2, respectively. Selected interatomic distances and angles as well as dihedral angles are listed in Table 1.

The geometry around Si1 in **1** and **4**, bearing the two 8-dimethylamino-1-naphthyl groups, is deformed from the tetrahedral to *pseudo*-octahedral. The distances between the silicon atom and the coordinated nitrogen atom are somewhat longer than the normal coordination distances (≤ 2.8 Å) [1c]. The distances of N1···Si1, which is anti to the fluorine atom or hydroxy group, are shorter than that of N2···Si1, which is anti to the silyl group. The stronger coordination of N1 to Si1 than that of N2 seems to result in a higher deformation of the naphthalene ring of C1–C10 than that of C13–C20. Thus, the dihedral angles of C1C2C3/C6C7C8 are greater than C13C14C15/C18C19C20 and those of Si1C1C8/N1C1C8 are greater than Si1C13C20/

Table 1
Selected interatomic distances (Å), angles (°), and dihedral angles (°) for **1** and **4**

	1 (X = F)	**4** (X = OH)
Interatomic distances		
N1···Si1	2.843(3)	2.934(2)
N2···Si1	2.949(3)	3.021(2)
Si1–X1	1.632(2)	1.670(2)
Si1–Si2	2.361(2)	2.3777(8)
Si1–C1	1.885(3)	1.892(2)
Si1–C13	1.884(4)	1.905(2)
Interatomic angles		
N1···Si1–X1	164.72(8)	167.72(8)
N2···Si1–Si2	169.8(1)	177.41(5)
Si2–Si1–X1	93.24(9)	99.08(7)
Dihedral angles		
C1–C2–C3/C6–C7–C8	6.46	12.49
Si1–C1–C8/N1–C1–C8	20.82	35.05
C13–C14–C15/C18–C19–C20	1.19	8.89
Si1–C13–C20/N2–C13–C20	1.59	18.79

Table 2
^{29}Si-NMR data of [4+2]-coordinate and tetracoordinate disilanes

		δ [a]		δ [a]	$\Delta\delta$ [b]
(X = F)	**1**	−5.6	**5**	17.5	−23.1
(X = H)	**2**	−19.9	**6**	−36.6	+16.7
(X = OEt)	**3**	−9.8	**7**	2.2	−12.0
(X = OH)	**4**	−7.2	**8**	0.4	−7.6

[a] Chemical shift of the silicon atom attached to the naphthyl carbon.

[b] Sign (−) indicates the up-field shift.

N2C13C20. Whereas, the Si1–Si2 distances of 2.361(1) and 2.3777(8) Å are in the range of the normal values of 2.33–2.37 Å [9], the Si1–F1 length of 1.632(2) Å is slightly longer than those in the ordinary tetracoordinate fluorosilanes (1.55–1.60 Å) [9] and similar to the one in [4 + 1]-coordinate fluorodisilane [4c].

It should be noted that no hydrogen bonding is observed in this [4 + 2]-coordinate hydroxydisilane (**4**) in the solid state in contrast to the fact that intramolecular [10] or intermolecular [11] hydrogen bonding is observed in some silanols containing the Si–Si bond.

2.3. NMR spectra of [4 + 2]-coordinate disilanes

Coordination of the amino group to the silicon atom in the [4 + 2]-coordinate fluorodisilane (**1**) and ethoxydisilane (**3**) in solution has been supported by the ^{1}H-NMR measurements. Thus, at room temperature in C_6D_6, four broad singlets are observed in the ^{1}H-NMR spectra due to the four methyl groups on the two nitrogen atoms both in **1** and **3**. These results indicate that the coordination of the amino group to silicon in **1** and **3** is strong enough to prevent equilibration of the two methyl groups on each nitrogen via rotation around the nitrogen–naphthyl carbon bond on the NMR time scale. However, only two *N*-methyl signals are observed in the ^{1}H-NMR spectra of the [4 + 2]-coordinate hydrodisilane (**2**) and hydroxydisilane (**4**).

The ^{29}Si-NMR chemical shifts summarized in Table 2 also support the coordination of the amino group in solution. Thus, in **1**, **3**, and **4**, bearing an electronegative substituent (F, OEt, and OH) on the silicon atom connected to the 8-dimethylamino-1-naphthyl group, the signal due to the silicon atom appears in a significantly higher magnetic field (7–23 ppm) as compared with that of the tetracoordinate counterpart, **5**, **7**, and **8**. On the other hand, in **2**, bearing no electronegative substituent, the silicon atom connected to the 8-dimethylamino-1-naphthyl group resonates in a significantly lower field as compared with the tetracoordinate counterpart **6**. There have been reported many precedents of the upfield shift of a signal for the hypercoordinate silicon atom bearing electronegative substituents [12], and the downfield shift of that without electronegative substituents [13].

2.4. Thermal reactivity of [4 + 2]-coordinate disilanes

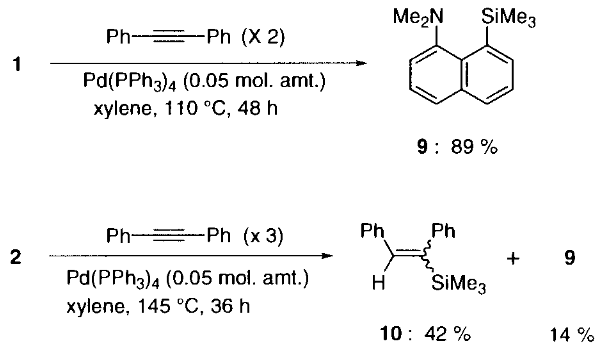
The [4 + 2]-coordinate fluorodisilane (**1**), hydrodisilane (**2**), and ethoxydisilane (**3**) were found to be thermally stable under such conditions as in xylene at 145 °C for 48 h, in sharp contrast to the [4 + 1]-coordinate fluoro- or ethoxy-disilanes which readily undergo α-elimination of the fluoro- or ethoxy-silane under milder conditions to afford the amine-coordinated silylene [4]. The tetracoordinate counterparts **5**–**7** were also stable under similar conditions.

The [4 + 2]-coordinate hydroxydisilane (**4**) underwent thermal degradation of a different type; thus, when heated in toluene at 110 °C for 42 h under an argon atmosphere, 1-(dimethylino)naphthalene was obtained as the sole volatile product in 94% yield (based on one aminonaphthyl group in **4**), probably due to the protodesilylation on the naphthyl carbon atom induced by the acidic hydrogen of the hydroxy group.

The [4 + 2]-coordinate disilanes had been expected to be thermally less stable to α-elimination to generate amine-coordinated silylenes than the corresponding [4 + 1]-coordinate disilanes, because the higher coordination usually weakens all bonds around the silicon atom. The unexpected results described above would be ascribed to the geometry of the [4 + 2]-coordinate silicon center being unfavorable for the α-elimination. Thus, the two amino groups located in the *cis* positions of the *pseudo*-octahedral geometry in **1**–**3** must rearrange to the *trans* positions to afford the stable structure of the silylene species bearing two amino groups at the axial positions of the trigonal bipyramidal structure. Another reason may reside in an orbital–symmetry problem during the α-elimination process. For a complete understanding, much remains to be studied; one of the attractive trials may be the generation of the silylenes from the [4 + 2]-coordinate silicon compound in which two amino groups are located at *trans* positions [14].

2.5. Transition metal-catalyzed degradation of [4 + 2]-coordinate fluorodisilane (1) and hydrodisilane (2)

The reactivity of the Si–Si bond in the [4 + 2]-coordinate fluorodisilane (**1**) toward palladium catalysts has been examined in view of the ready Pd(0)-catalyzed degradation of the analogous [4 + 1]-coordinate fluorodisilane affording the corresponding fluorosilane due to the cleavage of the Si–Si and Si–F bonds (Si/F α-elimination) [5b]. As shown in Scheme 3 and Table 3, the reaction of **1** with a catalytic amount of $Pd(PPh_3)_4$ (0.05



Scheme 3.

mol. amt.) at 110 °C in the presence of diphenylacetylene (2 mol. amt.) afforded a different type of Si/C α-elimination product, 8-dimethylamino-1-naphthyltrimethylsilane (**9**), in the yield of 89%, due to the cleavage of the Si–Si and Si–naphthyl carbon bonds [15]. In the absence of diphenylacetylene, the yield of **9** was found to decrease (entries 1 and 2). This reaction also proceeded in the presence of other Pd(0) complexes as catalysts (entries 3 and 4). No reaction was observed with the tetracoordinate fluorodisilane (**5**) under similar conditions to those of entry 1 (Table 3) but at a higher temperature (145 °C), indicating the higher reactivity of the [4 + 2]- and [4 + 1]-coordinate fluorodisilanes toward palladium catalysts.

The [4 + 2]-coordinate hydrodisilane (**2**) underwent another type of Pd(0)-catalyzed degradation in the presence of diphenylacetylene to afford the hydrosilation product **10** in 42% yield, together with the Si/C α-elimination product **9** in 14% yield, as shown in Scheme 3. The former hydrosilation reaction is accompanied by cleavage of the Si–Si bond, and thus, may be regarded to include the *formal* Si/H α-elimination. We have previously reported that the Si/H α-elimination is also included in the Ni(0)-catalyzed reaction of an analogous [4 + 1]-coordinate hydrodisilane with diphenylacetylene [5a].

In conclusion, the Si–Si bonds in the [4 + 2]- and [4 + 1]-coordinate disilanes are more labile to cleavage than that in the tetracoordinate disilanes during the reaction with a transition metal catalyst. However, the two silicon centers do not simply add to the acetylene as usually observed with ordinary tetracoordinate disilanes [16]. Instead, other bonds are also cleaved presumably due to the activation by hypercoordination, resulting in α-elimination such as Si–F, Si–C, and Si–H.

3. Experimental

3.1. General remarks

^{1}H (270 MHz), ^{13}C (67.94 MHz), ^{19}F (254.19 MHz), ^{29}Si (53.67 MHz)-NMR spectra were recorded on a JEOL JNM-EX270 spectrometer. ^{1}H and ^{13}C chemical shifts are referenced to internal benzene-d_6 (^{1}H δ 7.20 ppm and ^{13}C δ 128.0 ppm). ^{19}F and ^{29}Si chemical shifts are referenced to external $CFCl_3$ (0 ppm) and Me_4Si (0 ppm), respectively. Mass spectra were measured at 70 eV on a JEOL JMS-DX300 mass spectrometer equipped with a JMA-3500 data processing system. Melting points were measured with a Yanaco-MP-S3 apparatus. Elemental analyses were performed at the Microanalysis Division of Institute for Chemical Research, Kyoto University. Analytical samples were purified by recrystallization or HPLC, equipped with a 20 × 250 mm Wakosil-5Si1-column (Wako). Column chromatography was performed using Kieselgel (70–230 mesh) (Merck). THF and Et_2O 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 $LiAlH_4$.

3.2. 1,1,1-Trifluoro-2,2,2-trimethyldisilane [17]

To anhydrous zinc fluoride powder (29.4 g; 281.5 mmol) was added dropwise 1,1,1-trichloro-2,2,2-trimethyldisilane [18] (13 g; 62.5 mmol) at 0 °C under argon atmosphere. When the mixture was allowed to warm to room temperature (r.t.), an exothermic reaction started. After 2 h, the exothermic reaction was no longer observed and the title compound (9.1 g; 92% yield) was collected in a cold trap (− 78 °C) under reduced pressure (25 mmHg). ^{1}H-NMR (C_6D_6): δ − 0.10 (q, J = 2.4 Hz, 9H). ^{19}F-NMR (C_6D_6, $CFCl_3$): δ − 120.0.

Table 3
Pd(0)-catalyzed reaction of [4+2]-coordinate fluorodisilane (**1**)

Entry	Catalyst (mol. amt.)	Trapping agent (mol. amt.)	Solvent	Temperature (°C)	Time (h)	Yield of **9**
1	$Pd(PPh_3)_4$ (0.05)	PhC≡CPh (2)	Xylene	110	48	89
2	$Pd(PPh_3)_4$ (0.05)	–	Xylene	110	48	34 [a]
3	$Pd(OAc)_2$ (0.03) *t*-BuNC(0.5)	PhC≡CH (1.2)	Toluene	70	37	81
4	$Pd(dba)_2$ (1)	–	THF	Room temperature	11	82

[a] Forty percent conversion.

*3.3. 1-Fluoro-1,1-bis(8-dimethylamino-1-naphthyl)-2,2,2-trimethyldisilane (**1**)*

To a suspension of 8-dimethylamino-1-naphthlyllithium etherate [6] (7.22 g; 28.7 mmol) in dry ether (42 ml) was added dropwise 1,1,1-trifluoro-2,2,2-trimethyldisilane (2.27 g; 14.5 mmol) at −70 °C under stirring. The mixture was allowed to warm to r.t. and stirred overnight. The reaction mixture was concentrated in vacuo, and dissolved in benzene (30 ml) and hexane (10 ml), and the precipitates were filtered through a sintered glass-filter. The filtrate was concentrated in vacuo to leave solids which crystallized on standing in hexane (7 ml) at −25 °C. Recrystallization from hexane at −25 °C afforded **1** (5.1 g, 11.1 mmol; 77%) as colorless crystals: m.p. 112.5–114 °C. ^{1}H-NMR (C_6D_6): δ 0.18 (s, 9H), 1.17 (bs, 3H), 1.81 (bs, 3H), 2.23 (bs, 3H), 2.74 (bs, 3H), 6.82 (bd, $J = 7.3$ Hz, 1H), 7.14–7.25 (m, 3H), 7.48–7.58 (m, 4H), 7.72–7.78 (m, 2H), 8,32 (bd, $J = 5.7$ Hz, 1H), 8.51 (bd, $J = 5.1$ Hz, 1H). ^{13}C-NMR (C_6D_6): δ 0.9, 44.6, 46.1, 50.3, 116.2, 119.9, 125.1, 125.5, 126.1, 126.4, 126.6, 128.8, 130.3, 133.6 (d, $J = 9.8$ Hz), 134.1, 135.1, 135.4, 136.0, 152.5, 154.1 (five signals were not found). ^{19}F-NMR (C_6D_6): δ −145.4. ^{29}Si-NMR (C_6D_6): δ −21.4 (d, $^2J_{F\text{–}Si} = 43$ Hz), −5.6 (d, $^1J_{F\text{–}Si} = 292$ Hz). Anal. Calc. for $C_{27}H_{33}FN_2Si_2$: C, 70.39; H, 7.22; N, 6.08. Found: C, 70.24; H, 7.26; N, 6.20%.

*3.4. 1,1-Bis(8-dimethylamino-1-naphthyl)-2,2,2-trimethyldisilane (**2**)*

To a mixture of 1-fluorodisilane (**1**) (922 mg; 2.0 mmol) and $LiAlH_4$ (76 mg; 2.0 mmol) ether was added (10 ml) at 0 °C under a nitrogen atmosphere. The reaction mixture was warmed to r.t. and stirred for 4.5 h, followed by the addition of EtOAc (0.78 ml, 8.0 mmol) at 0 °C over 10 min. After stirring for 30 min, the precipitates were filtered through a sintered glass-filter and the filtrate was concentrated. Ether (1 ml) and hexane (10 ml) were added to the residue, and the filtration/concentration operation was repeated to afford white solids. Recrystallization of the solids from hexane afforded **2** (724 mg, 1.64 mmol; 82%) as colorless crystals: m.p. 109–110 °C. ^{1}H-NMR (C_6D_6): δ 0.15 (s, 9H), 1.84 (bs, 6H), 2.15 (s, 6H), 5.78 (s, 1H), 7.01 (d, $J = 7.6$ Hz, 2H), 7.25 (d, $J = 7.6$ Hz, 2H), 7.44 (dd, $J = 7.0$ and 8.1 Hz, 2H), 7.55 (dd, $J = 1.0$ and 8.1 Hz, 2H), 7.61 (dd, $J = 1.4$ and 8.1 Hz, 2H), 8.26 (dd, $J = 1.4$ and 7.0 Hz, 2H). ^{13}C-NMR (C_6D_6): δ 0.8, 45.1, 49.6, 117.5 (bs), 125.4, 125.7, 126.0, 129.8, 134.6, 135.3, 135.5, 136.3, 153.4. ^{29}Si-NMR (C_6D_6): δ −19.9 (d, $^1J_{Si\text{–}H} = 172$ Hz), −15.6. Anal. Calc. for $C_{27}H_{34}N_2Si_2$: C, 73.25; H, 7.74; N, 6.33. Found: C, 73.07; H, 7.64; N, 6.24%.

*3.5. 1-Ethoxy-1,1-bis(8-dimethylamino-1-naphthyl)-2,2,2-trimethyldisilane (**3**)*

To a solution of **2** (443 mg; 1.0 mmol) in benzene (6 ml) was added PCl_5 (109 mg; 0.5 mmol) at r.t. and the resulting yellow solution was stirred for 3 h. The mixture was concentrated in vacuo. To the residue were added successively ether (8 ml), triethylamine (0.56 ml, 4 mmol), and ethanol (0.12 ml, 2 mmol), and the resulting mixture was stirred for 3 h. After removal of volatile materials in vacuo, dry benzene (5 ml) was added and the precipitates were filtered through a sintered glass-filter. The filtrate was concentrated, followed by addition of hexane (3 ml) and filtration. The filtrate was concentrated to afford white solids. Recrystallization of the solids from hexane afforded **3** (295 mg, 0.6 mmol; 60%) as colorless solids. This compound was so sensitive to moisture that the hydrolyzed compound, hydroxydisilane (**4**), was present as a contaminant as detected by the NMR spectroscopy. ^{1}H-NMR (toluene-d_6): δ 0.06 (s, 9H), 1.12 (t, $J = 7$ Hz, 3H), 1.17 (bs, 3H), 1.66 (bs, 3H), 2.32 (bs, 3H), 2.66 (bs, 3H), 3.05–3.2 (m, 1H), 3.5–3.65 (m, 1H), 6.92 (bs, 1H), 7.1–7.2 (m, 2H), 7.45–7.6 (m, 5H), 7.6–7.8 (m, 2H), 8.3–8.4 (m, 1H), 8.7–8.8 (m, 1H). ^{29}Si-NMR (C_6D_6): δ −16.7, −9.8. Anal. Calc. for $C_{29}H_{38}N_2OSi_2$: C, 71.55; H, 7.87; N, 5.75. Found: C, 71.45; H, 8.02; N, 5.84%.

*3.6. 1-Hydroxy-1,1-bis(8-dimethylamino-1-naphthyl)-2,2,2-trimethyldisilane (**4**)*

To a solution of **2** (94 mg; 0.21 mmol) in benzene (3 ml) was added PCl_5 (23 mg; 0.11 mmol) at r.t. and the resulting yellow solution was stirred for 20 min. The mixture was concentrated in vacuo. To the residue was added a saturated aqueous solution of $NaHCO_3$ (10 ml). After the extraction with ether, the organic layer was concentrated and the residual oil was purified by silica gel chromatography (hexane–EtOAc = 10:1, R_f 0.21). Recrystallization from hexane–EtOAc gave **4** (74 mg; 0.16 mmol; 77% yield) as colorless crystals. M.p. 117.5–118.5 °C. ^{1}H-NMR (C_6D_6): δ 0.19 (s, 9H), 2.03 (s, 6H), 2.09 (s, 6H), 7.00 (d, $J = 7.6$ Hz, 2H), 7.24 (d, $J = 7.8$ Hz, 2H), 7.46 (dd, $J = 7.3$ and 8.1 Hz, 2H), 7.52 (d, $J = 7.8$ Hz, 2H), 7.73 (d, $J = 7.8$ Hz, 2H), 8.38 (d, $J = 6.8$ Hz, 2H). ^{13}C-NMR (C_6D_6): δ 0.8, 46.6, 49.2, 117.9, 125.3, 125.6, 126.6, 129.6, 134.9, 135.8, 135.9, 137.7, 153.4. ^{29}Si-NMR (C_6D_6): δ −16.4, −7.2. Anal. Calc. for $C_{27}H_{34}N_2OSi_2$: C, 70.69; H, 7.47; N, 6.11. Found: C, 70.41; H, 7.48; N, 6.08%.

*3.7. 1-Fluoro-1,1-di(1-naphthyl)-2,2,2-trimethyldisilane (**5**)*

In a similar manner to that described for the preparation of **1**, 1,1,1-trifluoro-2,2,2-trimethyldisilane (333 mg; 2.1 mmol) was allowed to react with a solution of 1-naphthyllithium (4.0 mmol) in ether, prepared from 1-bromonaphthalene and *n*-butyllithium in ether. The mixture was allowed to warm to r.t. and stirred overnight. Filtration, concentration and recrystallization from THF–hexane afforded 365 mg (47% yield) of **5** as white solids: m.p. 158–159 °C. ^{1}H-NMR (C_6D_6): δ 0.25 (s, 9H), 7.18–7.27 (m, 6H), 7.61–7.65 (m, 2H), 7.69 (d, $J=8.4$ Hz, 2H), 8.02 (dd, $J=1.1$ and 6.8 Hz, 2H), 8.41–8.45 (m, 2H). ^{13}C-NMR (C_6D_6): δ −1.3, 125.5, 126.2, 126.6, 128.8 (d, $J=2.4$ Hz), 129.3, 131.4, 134.0, 134.8, 135.0 (d, $J=4.9$ Hz), 137.3. ^{19}F-NMR (C_6D_6): δ −176.2. ^{29}Si-NMR (C_6D_6): δ −19.1 (d, $^{2}J_{F-Si}=26.9$ Hz), 17.5 (d, $^{1}J_{F-Si}=317$ Hz). HRMS calc. for $C_{23}H_{23}FSi_2$: *m/e* 374.1322. Found: *m/e* 374.1333. Anal. Calc. for $C_{23}H_{23}FSi_2$: C, 73.75; H, 6.19. Found: C, 73.98; H, 6.24%.

*3.8. 1,1-Di(1-naphthyl)-2,2,2-trimethyldisilane (**6**)*

In a similar manner to that described for the preparation of **2**, the reaction of **5** (100 mg, 0.27 mmol) with $LiAlH_4$ (8 mg, 0.21 mmol) in Et_2O (2 ml), subsequent work up, and recrystallization from hexane afforded pure **6** as colorless crystals (83 mg, 0.23 mmol; 87%): m.p. 147–148 °C. ^{1}H-NMR (C_6D_6): δ 0.26 (s, 9H), 5.98 (s, 1H), 7.22–7.26 (m, 6H), 7.64–7.67 (m, 2H), 7.69 (d, $J=8.1$ Hz, 2H), 7.93 (dd, $J=1.1$ and 6.8 Hz, 2H), 8.35–8.39 (m, 2H). ^{13}C-NMR (C_6D_6): δ −0.4, 125.7, 126.0, 126.3, 129.0, 129.3, 130.6, 133.2, 134.0, 136.7, 138.0. ^{29}Si-NMR (C_6D_6): δ −36.6 (d, $^{1}J_{Si-H}=180$ Hz), −16.7. Anal. Calc. for $C_{23}H_{24}Si_2$: C, 77.47; H, 6.78. Found: C, 77.31; H, 6.86%.

3.9. 1-Ethoxy-1,1-di(1-naphthyl)-2,2,2-trimethyldisilane (7)

To a suspension of 1-naphtlyllithium (6 mmol) in ether (12 ml) was added 1,1,1-trichloro-2,2,2-trimethyldisilane (624 mg; 3 mmol) at −60 °C. The mixture was allowed to warm to −20 °C during the period of 1 h with stirring. To the reaction mixture containing 1-chloro-1,1-di(1-naphthyl)-2,2,2-trimethyldisilane and LiCl were added dropwise triethylamine (1.3 ml; 9 mmol) and ethanol (0.42 ml, 7.2 mmol) at 0 °C. The mixture was stirred for 18 h at r.t. After the removal of volatile materials, hexane (10 ml) was added to the residue and the precipitates were filtered through a sintered glass-filter. The filtrate was concentrated under reduced pressure and the residual oil was purified by silica gel chromatography (hexane–EtOAc = 10:1, R_f 0.49) to afford **7** (1.04 g, 2.6 mmol; 86%) as a colorless solid: m.p. 73–75 °C. ^{1}H-NMR (C_6D_6): δ 0.29 (s, 9H), 1.15 (t, $J=7.0$ Hz, 3H), 3.73 (q, $J=7.0$ Hz, 2H), 7.13–7.24 (m, 4H), 7.33 (dd, $J=7.0$ and 8.1 Hz, 2H), 7.66 (dd, $J=2.2$ and 7.3 Hz, 2H), 7.73 (d, $J=8.4$ Hz, 2H), 8.11 (dd, $J=1.1$ and 6.5 Hz, 2H), 8.52 (d, $J=7.0$ Hz, 2H). ^{13}C-NMR (C_6D_6): δ −0.4, 18.7, 60.4, 125.6, 126.0, 126.1, 129.2, 129.2, 130.8, 134.0, 135.6, 136.1, 137.7. ^{29}Si-NMR (C_6D_6): δ −19.8, 2.2. Anal. Calc. for $C_{25}H_{28}OSi_2$: C, 74.94; H, 7.04. Found: C, 74.84; H, 7.09%.

*3.10. 1-Hydroxy-1,1-di(1-naphthyl)-2,2,2-trimethyldisilane (**8**)*

To a suspension of 1-naphtlyllithium (5 mmol) in ether (10 ml) was added 1,1,1-trichloro-2,2,2-trimethyldisilane (529 mg; 2.5 mmol) at 0 °C and the resulting mixture was stirred for 1 h. After removal of solvents, benzene (5 ml) was added and the precipitates was filtered through a sintered glass-filter. The filtrate was concentrated under reduced pressure and the residual oil was dissolved in ether (5 ml). To this solution was added a saturated aqueous solution of $NaHCO_3$ (20 ml). After the extraction with ether, the organic layer was concentrated and the residual oil was purified by silica gel chromatography (hexane–EtOAc = 10:1, R_f 0.19) to give **8** (852 mg, 2.29 mmol; 91% yield) as a colorless solid: m.p. 74–76 °C. ^{1}H-NMR (C_6D_6): δ 0.24 (s, 9H), 7.15–7.26 (m, 4H), 7.31 (dd, $J=7.0$ and 8.1 Hz, 2H), 7.67 (dd, $J=1.9$ and 7.6 Hz, 2H), 7.72 (d, $J=8.1$ Hz, 2H), 8.01 (dd, $J=1.1$ and 6.8 Hz, 2H), 8.40 (d, $J=7.6$ Hz, 2H). ^{13}C-NMR (C_6D_6): δ −1.0, 125.6, 125.9, 126.1, 129.1, 129.2, 130.7, 134.0, 135.0, 137.2, 137.4. ^{29}Si-NMR (C_6D_6): δ −19.3, 0.4. Anal. Calc. for $C_{23}H_{24}OSi_2$: C, 74.14; H, 6.49. Found: C, 74.35; H, 6.65%.

*3.11. Attempted thermal degradation of **1** in solution*

A solution of **1** (13 mg; 0.028 mmol) in dry toluene-d_8 (0.55 ml) was sealed in an NMR sample tube under argon atmosphere. After heating of the tube at 110 °C for 19 h and 145 °C for 1 h, no change was observed based on the ^{1}H-NMR measurement.

*3.12. Thermal degradation of **4** in solution*

A solution of **4** (74 mg; 0.16 mmol) in toluene (2 ml) was heated at 110 °C for 43 h under argon atmosphere. Complete disappearance of **4** was confirmed by ^{1}H-NMR analysis. After removal of solvent, column chromatography of the residual oil on silica gel gave *N*,*N*-dimethyl-1-naphthylamine (hexane–EtOAc = 10:1, R_f 0.39) (26 mg, 0.15 mmol; 94% yield).

*3.13. The reaction of **1** with $Pd(PPh_3)_4$ in the presence of diphenylacetylene*

A mixture of **1** (230 mg, 0.5 mmol), diphenylacetylene (178 mg, 1.0 mmol), and $Pd(PPh_3)_4$ (29 mg,

Table 4
Crystal data for structure determination of **1** and **4**

	1	**4**
Chemical formula	$C_{27}H_{33}N_2FSi_2$	$C_{27}H_{34}ON_2Si_2$
Formula weight	460.74	458.75
Crystal size (mm)	0.4 × 0.4 × 0.2	0.5 × 0.5 × 0.6
Crystal system	Triclinic	Monoclinic
Space group	$P1$ (no. 2)	$P2/n$ (no. 14)
Unit-cell dimensions		
a (Å)	9.301(2)	14.233(1)
b (Å)	17.900(7)	10.021(1)
c (Å)	8.788(2)	18.650(1)
α (°)	95.71(2)	
β (°)	117.22(1)	110.105(7)
γ (°)	77.41(2)	
V (Å^3)	1269.8(6)	2498.0(4)
Z	2	4
ρ_{calc} (g cm^{-3})	1.205	1.220
Temperature (°C)	20	20
Radiation	Cu–K$_\alpha$ ($\lambda = 1.54178$ Å)	
μ (Cu–K$_\alpha$) (cm^{-1})	14.55	14.48
Unique reflections	3786	3965
Reflections used	3093 ($I > 3.00\sigma(I)$)	3217 ($I > 3.00\sigma(I)$)
Number of variables	422	426
R	0.063	0.043
R_W	0.088	0.066
Goodness-of-fit on F^2	2.28	1.57

0.025 mmol) in dry xylene (3 ml) was heated at 110 °C for 48 h under argon atmosphere. Complete disappearance of **1** was confirmed by ^{1}H-NMR analysis. The reaction mixture was filtered through Celite 545 and the filtrate was concentrated. Column chromatography of the residual oil on silica gel gave 8-(dimethylamino)-1-naphthyltrimethylsilane (**9**) (hexane–EtOAc = 10:1, $R_f = 0.61$) (108 mg, 0.44 mmol; 89%), together with a trace amount of *N*,*N*-diethyl-1-naphthylamine. **9**: ^{1}H-NMR (C_6D_6): δ 0.43 (s, 9H), 2.34 (s, 6H), 7.08 (dd, $J = 7.3$ and 1.1 Hz, 1H), 7.31 (t, $J = 7.6$ Hz, 1H), 7.34 (dd, $J = 8.1$ and 7.3 Hz, 1H), 7.54 (dd, $J = 8.1$ and 1.1 Hz, 1H), 7.69 (dd, $J = 8.1$ and 1.1 Hz, 1H), 7.96 (dd, $J = 6.8$ and 1.1 Hz, 1H). Anal. Calc. for $C_{15}H_{21}NSi$: C, 74.01; H, 8.70; N, 5.75. Found: C, 73.87; H, 8.79; N, 5.65%.

3.14. The reaction of **2** with Pd(PPh$_3$)$_4$ in the presence of diphenylacetylene

A mixture of **2** (133 mg; 0.3 mmol), diphenylacetylene (160 mg; 0.9 mmol), and Pd(PPh$_3$)$_4$ (17 mg; 0.015 mmol) in dry xylene (1.8 ml) was heated at 145 °C for 36 h under argon atmosphere. Almost complete disappearance of **2** was confirmed by ^{1}H-NMR analysis. The reaction mixture was filtered through Celite 545 and the filtrate was concentrated. Column chromatography of the residual oil on silica gel gave **9** (10 mg; 14% yield) and 1,2-diphenyl-1-trimethylsilylethene **10** (hexane–EtOAc = 10:1, $R_f = 0.50$) (32 mg, 0.13 mmol; 42%): ^{1}H-NMR (C_6D_6): δ 0.18 (s, 9H), 6.90–7.22 (m, 11H). MS: m/e 252 [M$^+$, 100], 237 [M$^+$–Me, 77],178 [M$^+$–SiMe$_3$–H, 22]%.

3.15. X-ray crystallography

Crystals of **1** and **4** suitable for X-ray study were grown from hexane and hexane–AcOEt, respectively. Intensity data were collected on a Rigaku AFC7R diffractometer using an $\omega - 2\theta$ scan technique to a maximum 2θ value of 120.1°. The data were corrected for Lorentz polarization effects. A correction for secondary extinction was applied (coefficient = $3.64184e-05$ (**1**) and $4.42886e-06$ (**4**)). The structure was solved by direct methods (SAPI91) [19] and expanded using Fourier techniques (DIRDIF92) [20]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinements were based on 3093 observed reflections ($I > 3.00\sigma(I)$) and 422 variable parameters for **1** and 3217 observed reflections ($I > 3.00\sigma(I)$) and 426 variable parameters for **4** (Table 4). All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation [21].

4. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 167387 for compound **1** and CCDC no. 167388 for compound **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Ministry of Education, Culture, Sports, Science and Technology, Japan, for the grant-in-aid 09239103 as well as that for COE Research on Elements Science, No. 12CE2005.

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