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Synthesis, structure, and reactivity of 1,ω-bis(*pseudo*-pentacoordinated) 1,ω-difluoro-oligosilanes bearing 8-(dimethylamino)-1-naphthyl groups[☆]

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Abstract

1,ω-Bis[8-(dimethylamino)-1-naphthyl]-1,ω-difluorotrisilane **1** ($\omega = 3$) and tetrasilane **2** ($\omega = 4$) have been prepared. The X-ray crystallography of *dl*-**1** and *meso*-**1** shows unsymmetrical structures having different coordination modes at the two terminal silicons. The unsymmetrical nature of the structure of **1** can also be observed by solid state CP/MAS NMR spectroscopy. Trisilane **1** is thermochemically labile and undergoes facile degradation at 145°C, but is photochemically stable under irradiation of its benzene solution with a 6 W-low pressure mercury lamp, making a sharp contrast to the behavior of their tetracoordinate counterparts containing naphthyl groups which are thermochemically stable but photochemically active. Tetrasilane **2** undergoes a Pd(0)-catalyzed α-elimination of a fluorosilane moiety at the two *pseudo*-pentacoordinated silicon atoms to form the 1,2-difluorodisilane, which is trapped with diphenylacetylene as a double-silylation product. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Fluorotrisilane; Fluorotetrasilane; 8-(Dimethylamino)-1-naphthyl group; Pentacoordination; Thermolysis; Photolysis; Palladium catalyst

1. Introduction

Polysilanes have been attracting much attention because of their unique photophysical properties due to the delocalization of the sigma electrons in the Si–Si bonds [1]. Therefore, they are good precursors of silylenes under photochemical conditions as well as thermolysis and transition metal catalysis [1]. If the hypercoordinate silicon atoms [2] are introduced into the polysilane framework, new physical and chemical properties are expected due to the Si–Si bond elongation, the bond angle changes, and the increased energy levels of the σ-bonded framework [3,4]. Indeed, our previous studies have revealed some unique properties and reactivities, such as the enhanced reactivity of the Si–Si bond toward Ni and/or Pd complexes [3a,c], enhanced thermal lability with respect to the formation of silylene species due to the α-elimination [3b], and photochemical stability [3c]. This paper describes (1) the synthesis of 1,ω-difluorotrisilane **1** and tetrasilane **2**, which contain the 8-(dimethylamino)-1-naphthyl groups and fluorine atoms on the two terminal silicon atoms, and the tetracoordinate counterparts **3**–**5** (Chart 1), (2) the X-ray crystal structures of the *meso*- and *dl*-isomers of **1**, and (3) the differing modes of reaction between these difluoro-oligosilanes containing two *pseudo*-pentacoordinate silicon atoms and their tetracoordinate counterparts, during the thermochemical, photochemical, and palladium-catalyzed reactions. These oligosilanes containing two *pseudo*-pentacoordinate sili-

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[☆] Dedicated to the late Professor Rokuro Okawara for his outstanding achievements in the field of organometallic chemistry.

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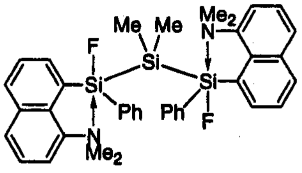
con centers may be potential models of pentacoordinate polysilanes.



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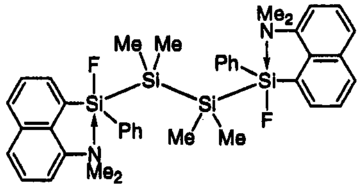

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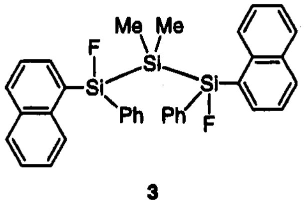

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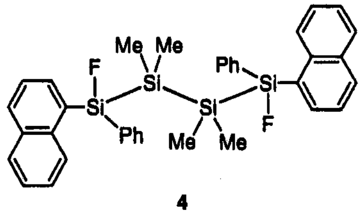

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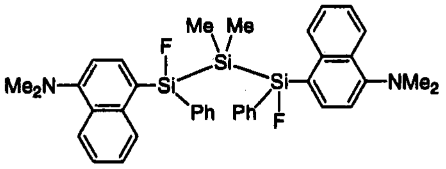
(Chart 1)



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2. Results and discussion

2.1. Synthesis of compounds **1**–**5**

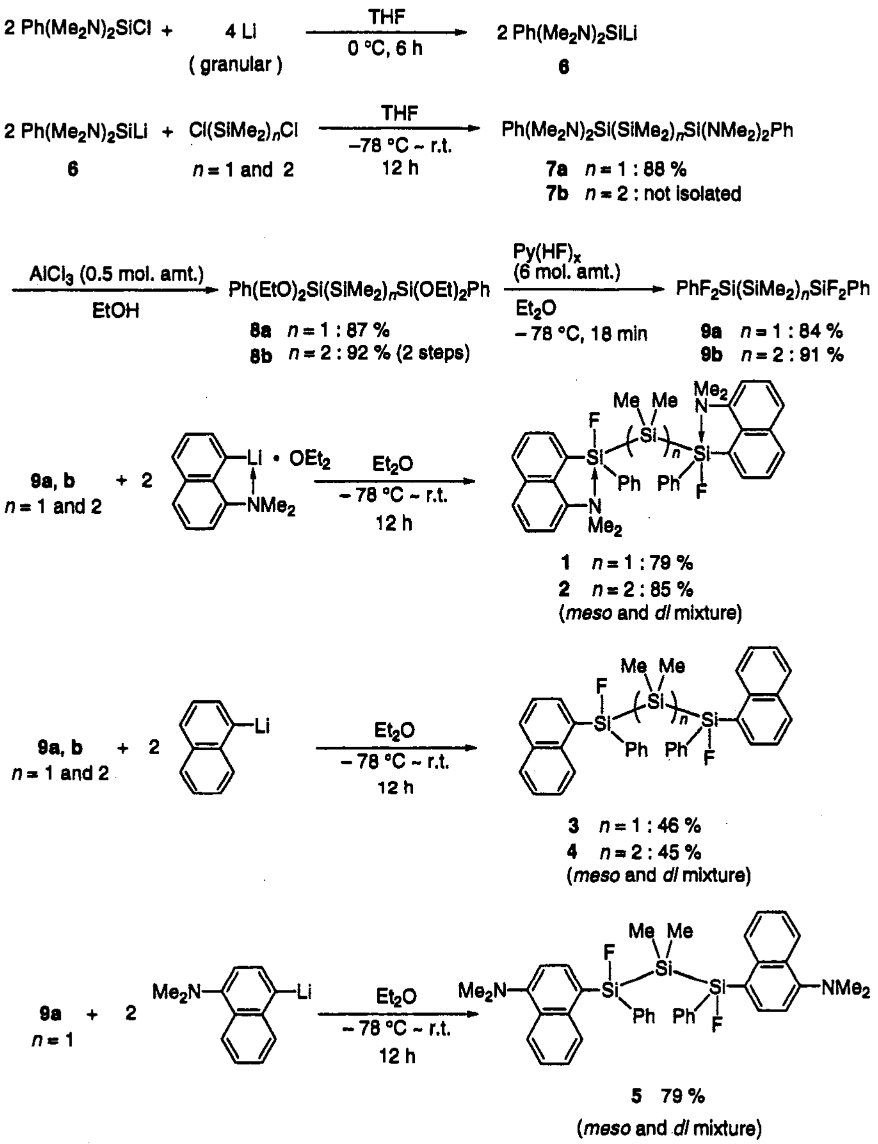
Compounds **1**–**5** were prepared in several steps using our (aminosilyl)lithium **6** [5] as the key reagent, as shown in Scheme 1.

Thus, [bis(dimethylamino)(phenyl)silyl]lithium **6** was allowed to react with dichlorodimethylsilane and 1,2-dichlorotetramethyldisilane [6a] at −78°C to form the corresponding amino-trisilane **7a** and tetrasilane **7b**, respectively. The tetraamino-oligosilanes **7a** and **7b** were readily converted into the corresponding tetraethoxy-oligosilanes **8a** and **8b** in high yields by treatment with excess dry ethanol in the presence of a catalytic amount of anhydrous aluminum chloride [6]. These tetraethoxy-oligosilanes were transformed into the tetrafluoro-oligosilanes **9a** and **9b** by treatment with hydrogen fluoride–pyridine at −78°C [6b]. Finally, the tetrafluoro-oligosilanes **9a** and **9b** were treated with 8-(dimethylamino)-1-naphthyllithium etherate [7] in ether at −78°C to room temperature (r.t.) to give the oligosilanes **1** and **2**, respectively. As the tetracoordinate counter model compounds, dinaphthyldifluorotrisilane **3** and tetrasilane **4** were prepared by the reaction of **9a** and **9b** with 1-naphthyllithium, respectively, and 1,3-bis[4-(dimethylamino)-1-naphthyl]-1,3-difluorotrisilane **5** was also prepared by the reaction of **9a** with 4-(dimethylamino)-1-naphthyllithium. Although **1**, **2**, **3**, **4** and **5** were obtained as a ca. 1: 1 mixture of the *dl* and *meso* isomers, the two isomers of **1** could be separated by repeated recrystallization from hexane.

2.2. X-ray crystal structure analysis of *dl* and *meso* isomers of trisilane *1*

The X-ray crystal structures of *dl*-**1** and *meso*-**1** are shown in Fig. 1, and the crystal data and a list of the selected interatomic distances and angles, dihedral angles, and %TBP [8] are shown in Tables 1 and 2, respectively.

In both cases, the geometry around Si1 and Si3 are distorted from tetrahedral to pseudo-trigonal bypyramidal (TBP). While the Si1 atom has the electronegative fluorine atom and the dimethylamino group in the two pseudo-apical positions as the usual coordination configuration [2c], on the Si3 atom, the fluorine atom occupies the pseudo-equatorial position. Some other significant features of the X-ray crystal structure of *dl*-**1** are as follows. Whereas the N1···Si1 distance of 2.779(3) Å is within the normal coordination distances (= 2.8 Å) [2c,9], the N2···Si3 distance of 2.858(3) Å is somewhat longer but still shorter than the sum of the van der Waals radii (3.65 Å) [10]. The N1···Si1–F1 angle 171.1(1)° and the N2···Si3–Si2 angle 176.87(8)° are almost linear. The pentacoordination characters [8], $\%TBP_a$, on the basis of the apical-to-equatorial angles,



Scheme 1.

of Si1 and Si3 are estimated to be 50 and 17%, respectively. The coordination distances and the %TBP$_a$ thus indicate that the Si1 having the pseudo-apical fluorine atom is more highly pentacoordinated as compared with the Si3 having the pseudo-apical silyl group. Despite of the unsymmetrical nitrogen coordination, the two Si–Si bond distances are almost equal to each other in the range of normal values of 2.33–2.37 Å [11], but there is a significant difference in the Si–F bond distances; the apical Si1–F1 bond 1.638(2) Å is longer than the equatorial Si3–F2 bond 1.600(2) Å (Si–F distances of ordinary tetracoordinate fluorosilanes = 1.55–1.60 Å) [11]. The *pseudo*-pentacoordinate *meso*-**1** has almost the same characteristic features except for the conformational difference. Thus, while the *dl*-**1** has a nearly eclipsed conformation having the F1Si1Si2/Si1Si2Si3 dihedral angle of ca. 5°, the angle in *meso*-**1** is ca. 87°, nearly corresponding to a staggered conformation.

2.3. NMR aspects of the unsymmetrical nature of the structure of dl-1 and meso-1

The unsymmetrical nature of the structure of *dl*-**1** and *meso*-**1** can also be observed by the solid state CP/MAS ^{13}C-, ^{15}N- and ^{29}Si-NMR spectroscopies. The ^{15}N and ^{29}Si spectra are shown in Fig. 2, which contains the ^{29}Si spectra in solution for comparison.

For example, in the solid state spectra of *dl*-**1**, the two nitrogen atoms on the two naphthyl groups appear as two separate signals at δ 16.6 and 26.9 ppm, and the two terminal silicon atoms, Si1 and Si3, appear as two doublets at δ -6.0 ppm ($^{1}J_{(Si-F)} = 338$ Hz) and 10.2 ppm ($^{1}J_{(Si-F)} = 294$ Hz), due to the two differing modes

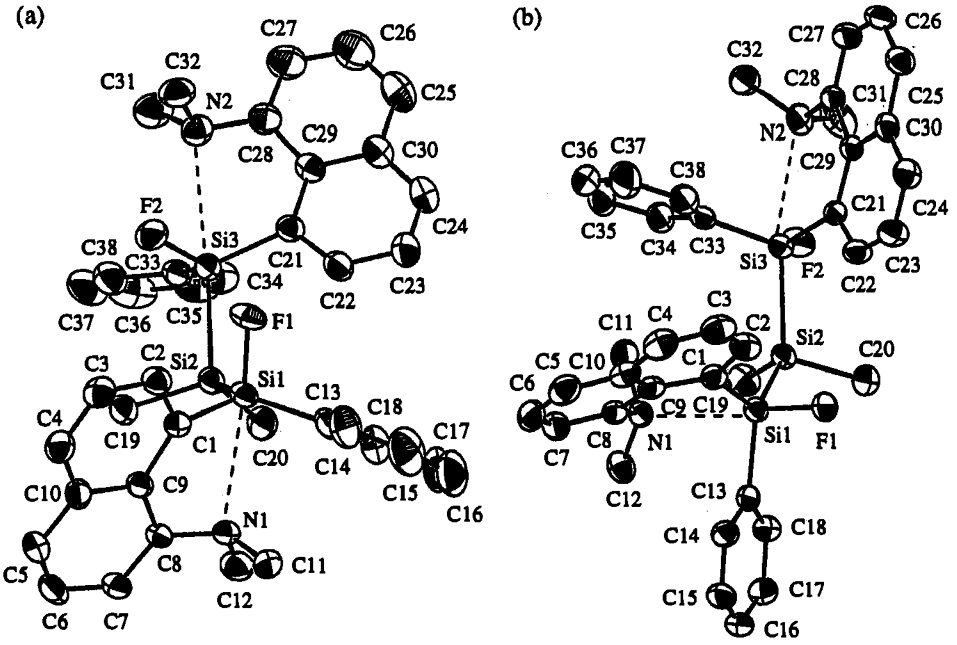


Fig. 1. X-ray structures of (a) *dl*-**1** and (b) *meso*-**1** drawn at the 30% probability level. All hydrogen atoms are omitted for clarity.

of coordination. In solution, however, these two silicon atoms appear as a doublet at δ −0.05 ppm ($^1J_{(\mathrm{Si-F})}$ = 315 Hz) due to a rapid equilibration which arises from the rotation of the aminonaphthyl group about the C–Si bond. The NMR spectra of *meso*-**1** have similar characteristic features.

Table 1
Crystal data and experimental details for structure determination of *dl*-**1** and *meso*-**1**

	dl-**1**	*meso*-**1**
Chemical formula	$C_{38}H_{40}N_2F_2Si_3$	$C_{38}H_{40}N_2F_2Si_3$
Formula weight	647.00	647.00
Crystal size (mm)	0.2 × 0.3 × 0.5	0.2 × 0.4 × 0.6
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca* (no. 61)	$P2_1/c$ (no. 14)
a (Å)	24.053(5)	14.550(5)
b (Å)	33.732(4)	13.694(4)
c (Å)	8.652(4)	17.504(4)
β (°)		95.92(2)
V (Å^3)	7019(3)	3469(1)
Z	8	4
$D_{\mathrm{calc.}}$ (g cm^{-3})	1.224	1.239
T (°C)	20	20
Radiation	Cu–K$_\alpha$ (λ = 1.54178 Å)	Cu–K$_\alpha$ (λ = 1.54178 Å)
μ(Cu–K$_\alpha$) (cm^{-1})	15.61	15.79
No. of unique reflections	5880	5426
No. of reflections used	3772 ($I > 3.00\sigma(I)$)	3762 ($I > 3.00\sigma(I)$)
No. of variables	567	567
R	0.047	0.046
R_w	0.059	0.052
GOF	1.86	1.94

2.4. UV spectra of 1–4

The UV absorption data in chloroform are summarized in Table 3, and the spectra are shown in Fig. 3, which contain the data of the corresponding monosilane for comparison. 1,ω-Bis(aminonaphthyl)-trisilane **1** and tetrasilane **2** have roughly the same $\lambda_{\max}$ around 302 to 304 nm, which are also same as the $\lambda_{\max}$ of the monosilane analog, 8-(dimethylamino)-1-naphthyltrimethylsilane ($\lambda_{\max}$ at 304 nm) [12]. This result reveals that the oligosilane chromophores have no effect on the aminonaphthalene chromophore. This is different from our previous observation that a trisilane

Table 2
Selected interatomic distances (Å), angles (°) and dihedral angles (°), and %TBP (%) for *dl*-**1** and *meso*-**1**

	dl-**1**	*meso*-**1**
Interatomic distances		
N(1)···Si(1)	2.779(3)	2.656(3)
N(2)···Si(3)	2.858(3)	2.833(3)
Si(1)–Si(2)	2.368(2)	2.373(1)
Si(2)–Si(3)	2.365(2)	2.366(1)
F(1)–Si(1)	1.638(2)	1.650(2)
F(2)–Si(3)	1.600(2)	1.608(2)
Interatomic angles		
N(1)···Si(1)–F(1)	171.1(1)	171.1(1)
N(2)···Si(3)–Si(2)	176.87(8)	163.90(8)
Dihedral angles		
F(1)Si(1)Si(2)/Si(1)Si(2)Si(3)	5.0(1)	86.94(10)
Pentacoordination characters[a]		
%TBP$_a$ (Si1)	50	64
%TBP$_a$ (Si3)	17	21

[a] Taken from Ref. [8].

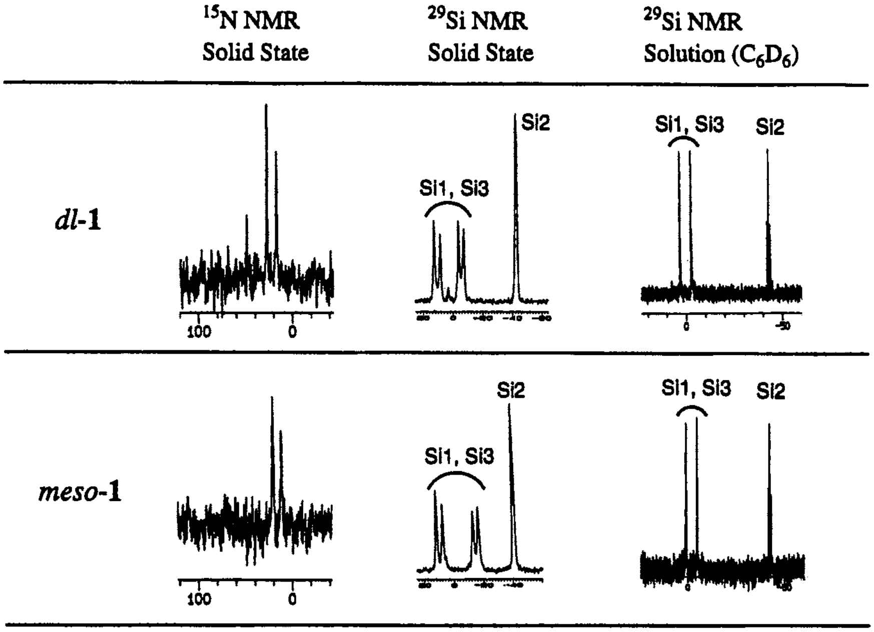


Fig. 2. ^{15}N- and ^{29}Si-NMR spectra of *dl*- and *meso*-**1** in solid state and in solution.

containing the 8-(dimethylamino)-1-naphthyl group on the central silicon atom shows about a 20 nm red shift in comparison with the mono-silane [3a]. The reason for the difference is not clear. The tetracoordinate oligosilanes **3** and **4** show similar phenomena.

2.5. Thermal degradation of 1–4

The thermal degradation [3,13] of a series of tetracoordinate and bis(*pseudo*-pentacoordinated) trisilanes and tetrasilanes have been examined. The results are summarized in Table 4.

The 1,3-bis(*pseudo*-pentacoordinated) 1,3-difluorotrisilane **1** was thermochemically labile and underwent degradation at 145°C to form [8-(dimethylamino)-1-naphthyl]phenyldifluorosilane [14], as shown in Scheme 2, but almost no reaction was observed with the tetrasilane **2** under similar conditions. Their tetracoordinate counterparts **3** and **4** were confirmed to be thermochemically stable under similar conditions. It is noted that the elongated F–Si bonds (av. 1.62 Å) and the small F–Si–Si bond angles (av. 98.3°) may be responsible for the high thermolability of **1**. Thus, the thermal reactivities have been found to depend greatly on the coordination states of the silicon atom.

Table 3
UV absorption maxima of oligosilanes in chloroform[a]

Oligosilanes	λ_{max}/nm (log ε)
pseudo-Pentacoordinated trisilane (**1**)	302.0 (4.11)
pseudo-Pentacoordinated tetrasilane (**2**)	304.5 (4.15)
Tetracoordinated trisilane (**3**)	290.5 (4.29)
Tetracoordinated tetrasilane (**4**)	290.5 (4.39)
[8-(Me_2N)-1-Np]$SiMe_3$	304[b]
1-Np$SiMe_3$	282[b]

[a] Np, naphthyl.

[b] Taken from Ref. [12].

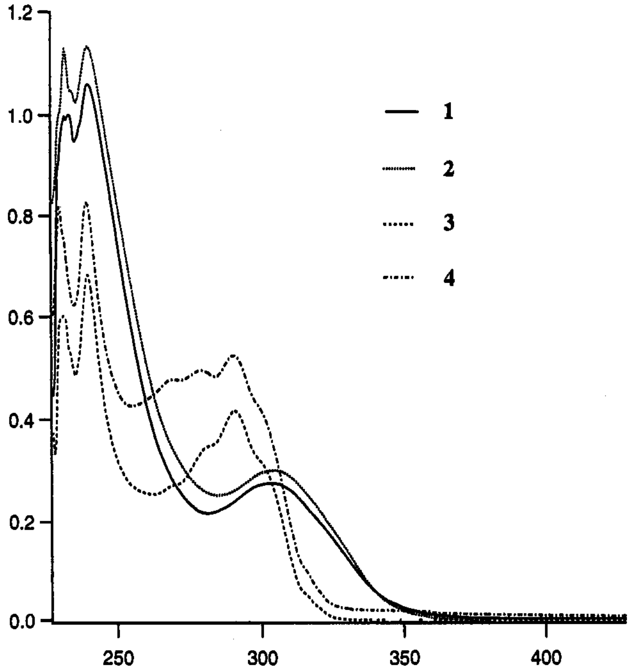
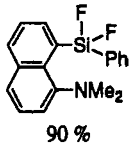


Fig. 3. UV spectra of trisilanes and tetrasilanes.

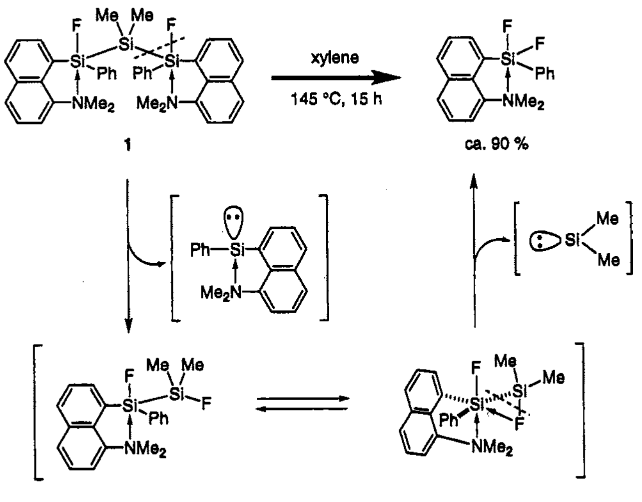
Table 4
Differing modes of reaction between pseudo-pentacoordinated and tetracoordinated trisilanes and tetrasilanes

Compound	Thermolysis	Photolysis	
	145°C, 15 h	Low pressure mercury lamp (ca. 27°C)	High pressure mercury lamp (ca. 50°C)
1		No reaction (6 W, 48 h)	100% reaction (6.5 h)
2	Almost no reaction	No reaction (6 W, 48 h)	100% reaction (3 h)
3	No reaction	100% reaction (6 W, 10 h)	100% reaction (3 h)
4	No reaction	100% reaction (6 W, 10 h)	100% reaction (3 h)
5	No reaction	No reaction (20 W, 12 h)	No reaction (12 h)

2.6. Photolysis of **1–5**

Photolysis has also been examined and these results being summarized in Table 4. As have been well studied [15], the ordinary tetracoordinate oligosilanes **3** and **4** were photochemically active during the irradiation of a benzene solution with a 6 W low pressure or high pressure mercury lamp; within 10 h the starting material had completely decomposed. On the other hand, the bis(*pseudo*-pentacoordinated) trisilane **1** and tetrasilane **2** have been found to be photochemically stable during irradiation with a 6 W low pressure mercury lamp. These compounds, however, decomposed during irradiation with a high pressure mercury lamp.

In order to obtain information about the origin of the photostability of the *pseudo*-pentacoordinated oligosilanes, we have examined the photolysis of the tetracoordinate trisilane **5** containing the 4-(dimethylamino)-1-naphthyl moiety. This control experiment showed that **5** is photochemically stable during irradiation with a 20 W low pressure or high pressure mercury lamp. These results suggest that the dimethyaminonaphthyl group, regardless of the position of the amino group, probably behaves as an efficient photochemical quenching group due to an intramolecular electron transfer from the dimethylamino group to the naphthalene ring in the excited state [16].



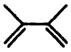
Scheme 2.

We attempted to trap any species produced during the photochemical reactions of **1** with some trapping agents during irradiation with a high pressure mercury lamp, but no trapped products were obtained, as summarized in Table 5. Irrespective of the presence or absence of any trapping agent, only a polymeric mixture was produced as judged by ^{1}H-NMR spectra. It is noted that in the presence of 2,3-dimethylbutadiene as a trapping agent, no decomposition occurred but only photoisomerization from *dl* to *meso* was observed during irradiation with a high pressure mercury lamp (entry 4). This isomerization was independent of the concentration of **1** (entries 4 and 5).

2.7. Pd(0)-catalyzed degradation reactions of bis(pseudo-pentacoordinated) oligosilanes

It is well known that the Si–Si bond in oligosilanes is cleaved with palladium(0) species [17]. We recently prepared *pseudo*-pentacoordinated fluorodisilanes **10** [18], and have found that **10** decomposes in the presence of $Pd(PPh_3)_4$ [3a] as the catalyst in toluene at 80°C to give fluoromethyldiphenylsilane (**11**) in 76% yield (100% conversion), together with a non-characterizable product arising from the pentacoordinate silicon moiety, as shown in Scheme 3. In the present study, bis(*pseudo*-pentacoordinated) fluorotrisilane **1** or tetrasilane **2** was heated at 50–55°C in toluene in the

Table 5
Trapping experiments of photochemical reaction of **1**[a]

Entry	Concentration (M)	Trapping agent (mol. amount)	Time (h)	Results
1	0.01	None	3	Decomposed
2	0.01	Et_2MeSiH (15)	4	Not trapped[b]
3	0.01	*t*-BuOH (20)	4	Not trapped[b]
4	0.01	 (20)	9	Isomerization[c] (1/0.91)[d]
5	0.03	 (10)	17	Isomerization (1/0.96)

[a] Compound **1** (*dl*/*meso* = 2.8/1) under the irradiation of a benzene solution with a high pressure mercury lamp at 57°C.

[b] 100% reaction. Degradation and/or polymerization.

[c] Only a photo-isomerization from *dl* to *meso* was observed (quantitative recovery of **1**).

[d] The *dl*/*meso* ratio determined by ^{1}H-NMR.

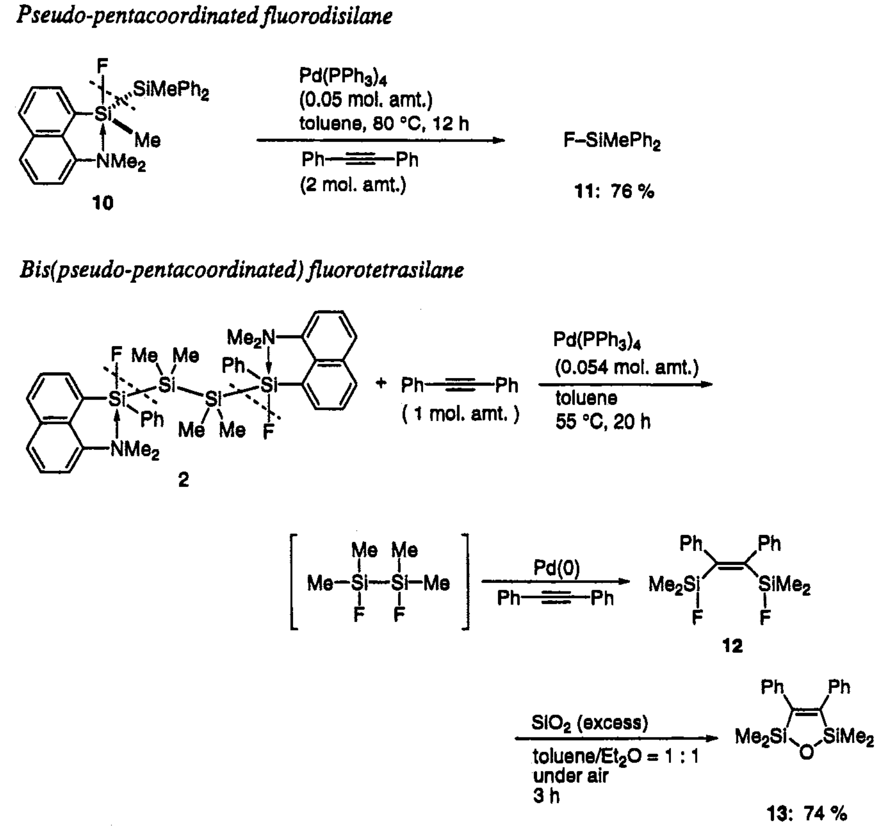
presence of $Pd(PPh_3)_4$ (0.05 mol. amt.) and diphenylacetylene (1 mol. amt.) for 20 h. While the fluorotrisilane **1** gave a complex mixture of products, fluorotetrasilane **2** gave *cis*-1,2-bis(fluorodimethylsilyl)-1,2-diphenylethene (**12**) [19a,b], the doubly silylated compound of diphenylacetylene, as shown in Scheme 3. After hydrolytic workup, the cyclic disiloxane **13** [19c,d] was isolated in 74% yield. The results suggest that this reaction includes the double palladium-catalyzed α-elimination on both the terminal *pseudo*-pentacoordinated silicon atoms to form the difluorotetramethyldisilane, which undergoes the known [19a] palladium-catalyzed addition to acetylene.

3. Experimental

^{1}H- (270 MHz), ^{13}C- (67.94 MHz), and ^{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 7.200 ppm and ^{13}C δ 128.00 ppm) or external CD_2Cl_2 (^{1}H δ 5.300 ppm). ^{19}F and ^{29}Si chemical shifts are referenced to external $CFCl_3$ (0 ppm) and Me_4Si (0 ppm), respectively. Solid state CP/MAS ^{13}C (100.5 MHz), ^{15}N (40.52 MHz), and ^{29}Si (79.43 MHz)-NMR spectra were recorded on a JEOL JNM-GX400 spectrometer (GSX solid NMR System) which were performed at the Solid State NMR Division of Institute for Chemical Research, Kyoto University. Solid state CP/MAS ^{13}C, ^{15}N, and ^{29}Si chemical shifts are referenced to external methyl carbon of hexamethylbenzene (17.36 ppm), NH_4Cl (18.00 ppm) and polydimethylsilane (−34.00 ppm), respectively. UV spectra in solution were recorded with a Shimadzu UV-3101(PC)S spectrometer. Mass spectra were measured at 70 eV on a Jeol JMS-700 mass spectrometer. Melting points were measured with a Yanaco-MP-S3 apparatus. The elemental analyses were performed at the Microanalysis Division of Institute for Chemical Research, Kyoto University: analytical samples were purified by recrystallization, distillation or reverse phase column chromatography. Reverse phase column chromatography was performed by using Wakogel LP-40C18 (20-40 µm) (WAKO). Hydrogen fluoride–pyridine (Aldrich) was used as received. THF and Et_2O were distilled under nitrogen from sodium/benzophenone. Hexane, toluene, and xylene were distilled under a nitrogen atmosphere from sodium. Benzene was distilled under a nitrogen atmosphere from $LiAlH_4$. Ethanol was distilled under a nitrogen atmosphere from Mg.

3.1. Synthesis of 2,2-dimethyl-1,1,3,3-tetrakis-(dimethylamino)-1,3-diphenyltrisilane (*7a*)

According to the literature method [5a,b], to a suspension of lithium granular (1.15 g, 166 mmol) in THF (44 ml) was added dropwise $Ph(Me_2N)_2SiCl$ (10 g, 44 mmol) at 0°C with stirring under an argon atmosphere. After a few minutes, a purple color appeared and the mixture was stirred at 0°C for 6 h to give a solution of $Ph(Me_2N)_2SiLi$ (**6**). To a solution of dimethyldichlorosilane (2.7 g, 21 mmol) in THF (35 ml) was added dropwise the solution of $Ph(Me_2N)_2SiLi$ in THF, prepared above, via a Teflon tube, at −78°C over 30 min with stirring. The reaction mixture was



Scheme 3.

allowed to warm to r.t. and stirred overnight. The solvent was removed under reduced pressure, and the residue was diluted with benzene (40 ml) and filtered through a sintered glass filter. The filtrate was evaporated and the residue was distilled bulb-to-bulb to afford the product **7a** (8.1 g, 88% yield based on Me_2SiCl_2): b.p. 180–197°C (bath temperature)/0.3 mmHg. ^{1}H-NMR: δ 0.50 (s, 6H), 2.59 (s, 24H), 7.24–7.33 (m, 6H), 7.60–7.64 (m, 4H).

3.2. *Synthesis of 2,2,3,3-tetramethyl-1,1,4,4-tetrakis-(dimethylamino)-1,4-diphenyltetrasilane (**7b**)*

In a similar manner, lithium granular (1.32 g, 190 mmol) and $Ph(Me_2N)_2SiCl$ (12 g, 52 mmol) in THF (50 ml) gave a solution of $Ph(Me_2N)_2SiLi$. The reaction of $Ph(Me_2N)_2SiLi$ with 1,2-dichlorotetramethyldisilane [6a] (4.5 g, 24 mmol) gave crude **7b**. ^{1}H-NMR: δ 0.38 (s, 12H), 2.66 (s, 24H), 7.23–7.34 (m, 6H), 7.62–7.66 (m, 4H).

3.3. *Synthesis of 1,1,3,3-tetraethoxy-2,2-dimethyl-1,3-diphenyltrisilane (**8a**)*

To a solution of **7a** (8.1 g, 18 mmol) in dry EtOH (50 ml) was added solid $AlCl_3$ (1.2 g, 9.2 mmol) at 0°C. After stirring at 0°C for 30 min and at r.t. for 12 h, the mixture was concentrated under reduced pressure, followed by addition of dry hexane (50 ml) and filtration. The filtrate was concentrated and distilled bulb-to-bulb to give **8a** (7.2 g, 87% yield): b.p. 162–182°C (bath temperature)/0.4 mmHg. ^{1}H-NMR: δ 0.44 (s, 6H), 1.23 (t, $J = 6.9$ Hz, 12H), 3.88 (q, $J = 6.9$ Hz, 8H), 7.22–7.34 (m, 6H), 7.90 (dd, $J = 1.6$ and 7.6 Hz, 4H). ^{13}C-NMR: δ −5.40, 18.69, 59.25, 128.07, 129.98, 134.69, 136.54. ^{29}Si-NMR: δ −57.63, −13.90. Anal. Calc. for $C_{22}H_{36}O_4Si_3$: C, 58.88; H, 8.09. Found: C, 58.56; H, 8.09%.

3.4. *Synthesis of 1,1,4,4-tetraethoxy-2,2,3,3-tetramethyl-1,4-diphenyltetrasilane (**8b**)*

In a similar manner, crude **7b** (prepared above), $AlCl_3$ (1.4 g, 11 mmol), and dry EtOH (50 ml) gave **8b** (11.2 g, 22 mmol, 92% yield (two steps)): b.p. 170–190°C (bath temperature)/0.35 mmHg. ^{1}H-NMR: δ 0.44 (s, 12H), 1.23 (t, $J = 7.0$ Hz, 12H), 3.85 (q, $J = 7.0$ Hz, 8H), 7.24–7.33 (m, 6H), 7.84–7.87 (m, 4H). ^{13}C-NMR: δ −5.04, 18.73, 59.21, 128.16, 129.94, 134.51, 137.24. ^{29}Si-NMR: δ −48.0, −13.1. Anal. Calc. for $C_{24}H_{42}O_4Si_4$: C, 56.86; H, 8.35. Found: C, 56.73; H, 8.43%.

*3.5. Synthesis of 2,2-dimethyl-1,3-diphenyl-1,1,3,3-tetrafluorotrisilane (**9a**)*

The tetraethoxytrisilane (**8a**; 3.1 g, 7.0 mmol) was added to a solution of pyridine $(HF)_x$ (1.2 ml; large excess amount), in ether (15 ml) at −78°C in Teflon flask. After 18 min, the mixture was concentrated using a water pump at −50 to −40°C. To the residue was added quickly dry hexane (15 ml) with stirring. The upper clear layer was separated and the residue was further extracted with dry hexane for two times. The combined extract was concentrated and distilled bulb-to-bulb to give **9a** (2.0 g, 84% yield): b.p. 120–123°C (bath temperature)/0.3 mmHg. ^{1}H-NMR: δ 0.18 (s, 6H), 7.05–7.15 (m, 6H), 7.58 (dd, $J = 1.6$ and 7.8 Hz, 4H). ^{13}C-NMR: δ −8.39, 128.77, 132.03 (t, $^{2}J_{(C-F)} = 13.4$ Hz), 132.13, 133.19. ^{29}Si-NMR: δ −56.3 (quintet, $J_{(Si-F)} = 30$ Hz), −5.4 (tt, $^{2}J_{(Si-F)} = 353$ and 9 Hz). ^{19}F-NMR: δ −133.3. Anal. Calc. for $C_{14}H_{16}F_4Si_3$: C, 48.81; H, 4.68. Found: C, 48.78; H, 4.69%.

*3.6. Synthesis of 2,2,3,3-tetramethyl-1,4-diphenyl-1,1,4,4-tetrafluorotetrasilane (**9b**)*

In a similar manner, the reaction of **8b** (4.9 g, 9.6 mmol) with pyridine $(HF)_x$ (1.7 ml) in ether (20 ml) gave **9b** (3.5 g, 8.8 mmol, 91% yield): b.p. 173–183°C (bath temperature)/0.6 mmHg. ^{1}H-NMR: δ 0.28 (s, 12H), 7.12–7.16 (m, 6H), 7.59–7.63 (m, 4H). ^{13}C-NMR: δ −7.09, 128.70, 131.85, 133.12 (br), 133.32 (t, $^{2}J_{(C-F)} = 12$ Hz). ^{29}Si-NMR: δ −47.4 (t, $^{2}J_{(Si-F)} = 28$ Hz), −3.0 (t, $J_{(Si-F)} = 356$ Hz). ^{19}F-NMR: δ −132.9. Anal. Calc. for $C_{16}H_{22}F_4Si_4$: C, 47.72; H, 5.51. Found: C, 47.82; H, 5.50%.

*3.7. Synthesis of 1,3-difluoro-2,2-dimethyl-1,3-bis[8-(dimethylamino)-1-naphthyl]-1,3-diphenyl-trisilane (**1**)*

To a suspension of 8-(dimethylamino)-1-naphthlyl-lithium [7] (1.5 g, 5.8 mmol) in dry ether (12 ml) was added quickly **9a** (1.0 g, 2.9 mmol) at −78°C with stirring. The mixture was allowed to warm to r.t., stirred overnight, and concentrated in vacuo. The residue was dissolved in benzene (7 ml), and filtered through a sintered glass filter to remove LiF. The filtrate was concentrated under reduced pressure to leave solids, which was recrystallized from a mixture of toluene (3 ml) and hexane (2 ml) at −25°C to give **1** (1.5 g, 79% yield) as colorless crystals (mixture of *dl* and *meso* isomers). The *dl* and *meso* isomer of **1** could be separated by the repeated recrystallization from hexane: Anal. Calc. for $C_{38}H_{40}N_2F_2Si_3$ (*dl* and *meso* mixture): C, 70.54; H, 6.23; N, 4.33. Found: C, 70.35; H, 6.32; N, 4.27%.

dl-**1**: m.p. 150–151°C. ^{1}H-NMR: δ 0.56 (s, 6H), 2.06 (bs, 6H), 2.13 (s, 6H), 6.90 (dd, $J = 0.8$ and 7.3 Hz, 2H), 7.01–7.08 (m, 6H), 7.16 (d, $J = 11$ Hz, 2H), 7.41–7.46 (m, 8H), 7.68 (dd, $J = 1.2$ and 8.1 Hz, 2H), 8.60 (d, $J = 7.3$ Hz, 2H). ^{13}C-NMR: δ −2.62 (d, $^{3}J_{(C-F)} = 4.9$ Hz), 45.61, 49.28 (d, $J = 2.5$ Hz), 117.18, 125.79, 126.11, 126.26, 127.78, 128.63, 130.62 (d, $J = 9.7$ Hz), 131.09, 132.62, 134.86, 135.08, 139.00 (d, $J = 7.3$ Hz), 139.55 (d, $J = 13.5$ Hz), 152.78. ^{19}F-NMR: δ −150.5(bs). ^{29}Si-NMR: δ −0.05 (d, $J_{(Si-F)} = 315$ Hz), −43.3 (t, $^{2}J_{(Si-F)} = 40$ Hz). Solid state CP/MAS ^{13}C-NMR: δ −5.76, −4.98, 42.62, 45.44, 52.04, 55.15, 119.85, 125.19, 127.72, 129.86, 132.19, 133.06, 134.81, 138.60, 141.42, 153.27. Solid state CP/MAS ^{15}N-NMR: δ 16.6, 26.9. Solid state CP/MAS ^{29}Si-NMR: δ −43.2, −6.0 (d, $^{1}J_{(Si-F)} = 294$ Hz), 10.2 (d, $^{1}J_{(Si-F)} = 338$ Hz).

meso-**1**: m.p. 161.3–162.8°C. ^{1}H-NMR: δ 0.52 (s, 6H), 2.00 (bs, 6H), 2.23 (s, 6H), 6.92 (dd, $J = 1.0$ and 7.6 Hz, 2H), 6.97–7.08 (m, 6H), 7.21 (t, $J = 7.6$ Hz, 2H), 7.42 (dd, $J = 7.0$ and 8.0 Hz, 2H), 7.51 (dd, $J = 1.0$ and 8.0 Hz, 2H), 7.53 (dd, $J = 1.9$ and 7.3 Hz, 4H), 7.72 (dd, $J = 1.0$ and 8.0 Hz, 2H). 8.57 (d, $J = 7.0$ Hz, 2H). ^{13}C-NMR: δ −2.57 (d, $^{3}J_{(C-F)} = 8.6$ Hz), 45.41, 49.60 (d, $J = 2.4$ Hz), 116.97, 125.86, 126.17, 126.26, 127.73, 128.63, 130.95, 131.06, 132.80, 134.85, 135.19, 138.75 (d, $J = 7.3$ Hz), 139.64 (d, $J = 14.7$ Hz), 152.87. ^{19}F-NMR: δ −152.7(bs). ^{29}Si-NMR: δ −2.0 (d, $J_{(Si-F)} = 309$ Hz), −42.5 (t, $^{2}J_{(Si-F)} = 39$ Hz). Solid state CP/MAS ^{13}C-NMR: δ 1.43, 1.82, 44.56, 49.03, 50.39, 51.26, 116.45, 122.86, 126.46, 128.01, 128.98, 132.97, 134.71, 139.38, 141.71, 150.84, 151.91. Solid state CP/MAS ^{15}N-NMR: δ 12.0, 21.1. Solid state CP/MAS ^{29}Si-NMR: δ −41.7, −15.6 (d, $^{1}J_{(Si-F)} = 287$ Hz), 8.9 (d, $^{1}J_{(Si-F)} = 338$ Hz).

*3.8. Synthesis of 1,4-difluoro-2,2,3,3-tetramethyl-1,4-bis[8-(dimethylamino)-1-naphthyl]-1,4-diphenyltetrasilane (**2**)*

In a similar manner to that described for the preparation of **1**, the reaction of **9b** (1.13 g, 2.8 mmol) with 8-(dimethylamino)-1-naphthlyllithium (1.4 g, 5.6 mmol) in dry ether (12 ml) give **2** (1.7 g, 85% yield) as colorless crystals as a mixture of *dl* and *meso* isomers. ^{1}H-NMR (*dl*: *meso* = 1: 1): δ 0.19 (s, 6H), 0.35 (s, 6H), 0.57 (s, 6H), 0.72 (s, 6H), 1.86 (s, 6H), 1.87 (s, 6H), 2.14 (s, 6H), 2.15 (s, 6H), 6.86, 6.88 (dd, $J = 1.0$ and 7.3 Hz, 2H), 7.05–7.12 (m, 6H), 7.15–7.24 (m, 2H), 7.42, 7.44 (dd, $J = 6.8$ and 8.1 Hz, 2H), 7.48–7.57 (m, 6H), 7.70, 7.73 (dd, $J = 1.0$ and 8.3 Hz, 2H), 8.54, 8.56 (d, $J = 6.8$ Hz, 2H). ^{13}C-NMR (*dl*: *meso* = 1: 1): δ −3.71 (d, $^{3}J_{(C-F)} = 3.7$ Hz), −3.42 (d, $^{3}J_{(C-F)} = 3.7$ Hz), −3.14, −2.92, 45.79, 49.39 (d, $J = 2.4$ Hz), 116.86, 125.84, 126.13, 126.26, 127.78, 128.67, 130.95, 131.93 (d, $J = 11$ Hz), 132.73, 135.01, 135.13, 138.24 (d, $J = 7.3$ Hz), 140.33 (d, $J = 14.7$ Hz), 152.94. ^{19}F-NMR (*dl*: *meso* = 1: 1): δ −145.0 (bs). ^{29}Si-NMR (*dl*: *meso* = 1: 1): δ 0.0 (d, $J_{(Si-F)} = 308$ Hz), −38.6 (t, $^{2}J_{(Si-F)} = 39$ Hz). Anal.

Calc. for $C_{40}H_{46}N_2F_2Si_4$ (*dl*: *meso* = 1: 1): C, 68.13; H, 6.58; N, 3.97. Found: C, 68.32; H, 6.74; N, 3.84%.

3.9. Synthesis of 1,3-difluoro-2,2-dimethyl-1,3-bis-(1-naphthyl)-1,3-diphenyltrisilane (**3**)

In a similar manner to that described for the preparation of **1**, **9a** (2.2 g, 6.4 mmol) was allowed to react with an ether suspension of 1-naphthyllithium (12.7 mmol), prepared from 1-bromonaphthalene and *n*-butyllithium in ether at − 78°C. The mixture was allowed to warm to r.t. and stirred overnight. Workup similar to those described for **1**, followed by recrystallization from benzene and hexane afforded 1.64 g (46% yield) of **3** as colorless crystals as a mixture of *dl* and *meso* isomers. ^{1}H-NMR: δ 0.50 (s, 6H), 7.05–7.22 (m, 12H), 7.59–7.68 (m, 8H), 7.90 (d, $J = 6.5$ Hz, 2H), 8.22 (d, $J = 8.1$ Hz, 2H). ^{13}C-NMR: δ − 4.92, 125.42, 126.11, 126.53, 128.50, 128.67, 129.20, 130.59, 131.40, 133.28 (d, $J = 12.2$ Hz), 133.88, 134.65, 135.10 (d, $J = 4.9$ Hz), 135.77 (d, $J = 13.4$ Hz), 137.09. ^{19}F-NMR: δ − 173.77. ^{29}Si-NMR: δ − 49.07 (t, $^2J_{(Si-F)} = 28$ Hz), 17.32 (dd, $J_{(Si-F)} = 317$ Hz, $^3J_{(Si-F)} = 2.7$ Hz). Anal. Calc. for $C_{34}H_{30}F_2Si_3$ (*dl* and *meso* mixture): C, 72.81; H, 5.39. Found: C, 72.81; H, 5.34%.

3.10. Synthesis of 1,4-difluoro-2,2,3,3-tetramethyl-1,4-bis(1-naphthyl)-1,4-diphenyltetrasilane (**4**)

In a similar manner to that described for the preparation of **2**, the reaction of **9b** (1.6 g, 4.0 mmol) with 1-naphthyllithium (8.0 mmol) in dry ether (12 ml) give **4** (1.12 g, 45% yield) as colorless crystals as a mixture of *dl* and *meso* isomers. ^{1}H-NMR: δ 0.35 (s, 6H), 0.37 (s, 6H), 7.07–7.24 (m, 10H), 7.29 (t, $J = 7.6$ Hz, 2H), 7.63 (dd, $J = 1.4$ and 7.6 Hz, 2H), 7.67–7.72 (m, 6H), 8.03 (d, $J = 6.8$ Hz, 2H), 8.20 (d, $J = 7.6$ Hz, 2H). ^{13}C-NMR: δ − 4.92, − 4.70 (d, $^3J_{(C-F)} = 2.4$ Hz), 125.50, 126.17, 126.49, 128.54, 128.70 (bs), 129.28, 130.53, 131.32, 133.93, 134.39 (d, $J = 11$ Hz), 134.56, 134.72 (d, $J = 4.8$ Hz), 136.69 (d, $J = 13.5$ Hz), 137.15. ^{19}F-NMR: δ − 174.7. ^{29}Si-NMR: δ 17.8 (d, $J_{(Si-F)} = 317$ Hz), − 44.0 (d, $^2J_{(Si-F)} = 27$ Hz). Anal. Calc. for $C_{36}H_{36}F_2Si_4$ (*dl* and *meso* mixture): C, 69.85; H, 5.86. Found: C, 69.68; H, 5.86%.

3.11. Synthesis of 1,3-difluoro-2,2-dimethyl-1,3-bis[4-(dimethylamino)-1-naphthyl]-1,3-diphenyltrisilane (**5**)

To a solution of **9a** (700 mg, 2.0 mmol) in ether (16 ml) was added dropwise an ether solution of 4-(dimethylamino)-1-naphthyllithium (4.0 mmol), prepared from 1-bromo-4-(dimethylamino)naphthalene and *n*-butyllithium in ether (8 ml) at − 78°C with stirring. The mixture was allowed to warm to r.t., stirred overnight, and concentrated in vacuo. The residue was dissolved in benzene (10 ml) and filtered through a sintered glass filter. The filtrate was concentrated under reduced pressure to leave viscous oil which was purified by the reverse phase silica gel (Wakogel LP-40C18, Wako) column chromatography (CH_3CN, $R_f = 0.27$) to afford 1.04 g (79% yield) of **5** as colorless viscous oil as a mixture of *dl* and *meso* isomers: ^{1}H-NMR: δ 0.61 (s, 6H), 2.605 (s, 12H), 6.76 (d, $J = 7.6$ Hz, 2H), 7.10–7.20 (m, 8H), 7.29 (t, $J = 7.3$ Hz, 2H), 7.72–7.78 (m, 4H), 7.95 (dd, $J = 3.5$ and 7.3 Hz, 2H), 8.32–8.37 (m, 4H). ^{13}C-NMR: δ − 4.90 (d, $^3J_{(C-F)} = 7.4$ Hz), − 4.80 (d, $^3J_{(C-F)} = 6.1$ Hz), 44.62*, 113.53*, 125.23*, 125.43*, 126.44*, 126.63 (d, $J = 2.4$ Hz)*, 128.79*, 129.29*, 129.46*, 130.35 (d, $J = 2.4$ Hz)*, 134.65*, 136.17 (d, $J = 3.7$ Hz), 136.25 (d, $J = 3.4$ Hz), 136.53 (d, $J = 13.4$ Hz)*, 138.82*, 153.97, 154.00 (* two signals overlapping). ^{19}F-NMR: δ − 173.32, − 173.25. ^{29}Si-NMR: δ − 49.47 (t, $^2J_{(Si-F)} = 27$ Hz), − 49.42 (t, $^2J_{(Si-F)} = 27$ Hz), − 17.62 (d, $J_{(Si-F)} = 316$ Hz). HRMS: Calc. for $C_{38}H_{40}N_2F_2Si_3$, *m*/*e* 646.2467; Found, *m*/*e* 646.2491. All the data are measured for the *dl* and *meso* mixture.

3.12. Thermal degradations

The following is a typical procedure. A solution of **1** (650 mg, 1 mmol) in dry xylene (10 ml) was heated at 145°C under an argon for 15 h. The complete disappearance of **1** was confirmed by the ^{1}H-NMR analysis. The reaction mixture was concentrated and bulb-to-bulb distillation of the residue afforded [8-(dimethylamino)-1-naphthyl]phenyldifluorosilane [14] (290 mg, 90% yield): b.p. 206–220°C (bath temperature)/0.15 mmHg. ^{1}H-NMR (CD_2Cl_2): δ 2.25 (s, 6H), 7.26–7.37 (m, 6H), 7.51 (t, $J = 7.7$ Hz, 1H), 7.68 (dd, $J = 7.0$ and 8.1 Hz, 1H), 7.79 (d, $J = 8.1$ Hz, 1H), 8.07 (dd, $J = 1.1$ and 8.1 Hz, 1H), 8.32 (dd, $J = 1.1$ and 7.0 Hz, 1H). ^{19}F-NMR: δ − 130.84 (m). ^{29}Si-NMR: δ − 49.52 (t, $J_{(Si-F)} = 269$ Hz).

3.13. Photochemical reactions

Photolysis was carried out using a 6 or a 20 W low pressure mercury lamp equipped with a UVB-S type of low lamp ballanst (Fuji Glass Works) and using a high-pressure mercury lamp equipped with a HB-400 type of HG lamp ballanst (Fuji Glass Works).

The following is a typical procedure. A solution of **1** (49 mg, 0.076 mmol) in dry benzene (7.6 ml) in a quartz glass tube was irradiated for 46 h with a low pressure mercury lamp (20 W) under an argon around 27°C. No reaction was confirmed by ^{1}H-NMR and **1** was recovered quantitatively by evaporation of solvent.

3.14. Pd(0)-catalyzed reaction of **10**

A mixture of **10** (220 mg, 0.5 mmol), diphenylacetylene (270 mg, 1.5 mmol), and $Pd(PPh_3)_4$ [3a] (29 mg, 0.025 mmol) in dry toluene was heated at 80°C for 12 h under an argon. The reaction mixture was filtered through Celite 545 and concentrated. The residue was distilled bulb-to-bulb to give $MePh_2SiF$ (**11**) (83 mg, 76% yield) together with diphenylacetylene (168 mg, 63% recovery): b.p. 130–145°C (bath temperature)/0.5 mmHg. ^{1}H-NMR: δ 0.57 (d, $J_{(H-F)} = 7.0$ Hz, 3H), 7.12–7.22 (m, 6H), 7.59–7.62 (m, 4H). ^{13}C-NMR: δ -2.48 (d, $^2J_{(C-F)} = 18$ Hz), 128.32, 130.73, 134.29 (d, $^3J_{(C-F)} = 2.4$ Hz), 134.73 (d, $^2J_{(C-F)} = 16$ Hz). ^{29}Si-NMR: δ 8.58 (d, $^1J_{(Si-F)} = 281$ Hz). Anal. Calc. for $C_{13}H_{13}FSi$: C, 72.18; H, 6.06. Found: C, 72.28; H, 5.87%.

3.15. Pd(0)-catalyzed reaction of **2**

A mixture of **2** (210 mg, 0.3 mmol), diphenylacetylene (54 mg, 0.3 mmol), and $Pd(PPh_3)_4$ (19 mg, 0.016 mmol) in dry toluene (3 ml) was heated at 55°C for 20 h under an argon. To the reaction mixture were added ether (3 ml) and silica gel (1.5 g), and the mixture was stirred at r.t. for 3 h. The mixture was filtered through Celite 545 and the filtrate was concentrated. The residue was purified by silica gel column chromatography (hexane: EtOAc = 10: 1, $R_f = 0.5$) to give **13** [19c,d] (69 mg, 74% yield): ^{1}H-NMR: δ 0.43 (s, 12H), 6.92–7.16 (m, 10H).

3.16. X-ray crystal structure analysis of *dl*-**1**

The single crystals were obtained by recrystallization from hexane. Intensity data were collected on a Rigaku AFC7R diffractometer using an $\omega - 2\theta$ scan technique to a maximum 2θ value of 120.0°. A total of 5880 reflections was collected. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 9.28000e-07). The structure was solved by heavy-atom Patterson methods (PATTY) [20] and expanded using Fourier techniques (DIRDIF94) [21]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 3772 observed reflections ($I > 3.00\sigma(I)$) and 567 variable parameters. The max/min peaks on the final difference Fourier map corresponded to $0.40/-0.26$ e Å^{-3}, respectively. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation (1985) and (1992). The crystal data and analytical condition, and final atomic coordinates and isotropic temperature factors are listed in Tables 1 and 6, respectively. Complete lists of bond lengths and angles, hydrogen atom coordinates and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (No. CCDC-101790).

3.17. X-ray crystal structure analysis of *meso*-**1**

The single crystals were obtained by recrystallization from hexane. Intensity data were collected on a Rigaku AFC7R diffractometer using an $\omega - 2\theta$ scan technique to a maximum 2θ value of 120.2°. Of the 5665 reflections which were collected, 5426 were unique ($R_{int} = 0.029$). The data were corrected for Lorentz and

Table 6
Positional parameters and B_{iso}/B_{eq} for *dl*-**1**

Atom	x	y	z	B_{eq}
Si(1)	0.23571(4)	0.12700(3)	0.1057(1)	4.13(2)
Si(2)	0.14140(4)	0.11660(3)	0.0383(1)	4.04(2)
Si(3)	0.08274(4)	0.10917(3)	0.2558(1)	4.12(2)
F(1)	0.23172(10)	0.12167(7)	0.2936(2)	5.77(6)
F(2)	0.10395(10)	0.06941(6)	0.3376(3)	6.06(6)
N(1)	0.2566(1)	0.12827(8)	−0.2102(3)	4.37(7)
N(2)	0.0091(1)	0.09658(10)	0.5104(4)	4.86(8)
C(1)	0.2833(1)	0.08439(10)	0.0594(4)	3.81(8)
C(2)	0.3073(2)	0.0644(1)	0.1810(5)	4.65(10)
C(3)	0.3360(2)	0.0285(1)	0.1617(5)	5.3(1)
C(4)	0.3377(2)	0.0108(1)	0.0210(5)	5.2(1)
C(5)	0.3117(2)	0.0105(1)	−0.2541(5)	5.1(1)
C(6)	0.2879(2)	0.0279(1)	−0.3760(5)	5.3(1)
C(7)	0.2678(2)	0.0670(1)	−0.3655(4)	4.58(9)
C(8)	0.2694(1)	0.08676(10)	−0.2271(4)	3.92(8)
C(9)	0.2890(1)	0.06736(10)	−0.0906(4)	3.81(8)
C(10)	0.3134(2)	0.0291(1)	−0.1084(5)	4.36(9)
C(11)	0.3084(2)	0.1509(1)	−0.2234(6)	6.1(1)
C(12)	0.2171(3)	0.1430(2)	−0.3267(5)	6.2(1)
C(13)	0.2680(2)	0.1774(1)	0.0955(5)	5.09(10)
C(14)	0.3230(2)	0.1815(2)	0.1465(6)	7.1(1)
C(15)	0.3506(3)	0.2173(2)	0.1359(9)	9.5(2)
C(16)	0.3244(3)	0.2497(2)	0.0731(9)	9.2(2)
C(17)	0.2701(3)	0.2468(2)	0.0246(8)	8.5(2)
C(18)	0.2428(2)	0.2105(1)	0.0370(6)	6.3(1)
C(19)	0.1385(2)	0.0674(1)	−0.0636(5)	4.8(1)
C(20)	0.1064(3)	0.1559(2)	−0.0816(6)	5.4(1)
C(21)	0.0821(1)	0.1549(1)	0.3786(4)	4.18(8)
C(22)	0.1195(2)	0.1835(1)	0.3381(5)	5.5(1)
C(23)	0.1189(2)	0.2221(1)	0.3994(7)	7.2(1)
C(24)	0.0784(3)	0.2318(2)	0.5021(6)	7.4(1)
C(25)	−0.0046(3)	0.2154(2)	0.6536(8)	9.1(2)
C(26)	−0.0414(3)	0.1885(2)	0.7010(8)	9.8(2)
C(27)	−0.0388(2	0.1491(2)	0.6531(6)	7.7(2)
C(28)	0.0023(2)	0.1372(1)	0.5523(4)	4.91(9)
C(29)	0.0412(2)	0.1650(1)	0.4927(4)	4.54(9)
C(30)	0.0386(2)	0.2044(1)	0.5505(5)	6.0(1)
C(31)	−0.0429(3)	0.0743(2)	0.4897(8)	7.4(2)
C(32)	0.0441(3)	0.0765(2)	0.6244(6)	6.5(1)
C(33)	0.0142(2)	0.0993(1)	0.1645(4)	4.89(10)
C(34)	−0.0234(2)	0.1299(2)	0.1313(6)	6.3(1)
C(35)	−0.0737(2)	0.1233(3)	0.0557(6)	7.9(2)
C(36)	−0.0859(3)	0.0856(3)	0.0091(8)	9.4(2)
C(37)	−0.0513(3)	0.0549(3)	0.0358(7)	8.4(2)
C(38)	−0.0013(2)	0.0616(2)	0.1144(6)	6.8(1)

Table 7
Positional parameters and B_{iso}/B_{eq} for *meso*-**1**

Atom	x	y	z	B_{eq}
Si(1)	0.76555(7)	0.07136(7)	0.41942(6)	4.06(2)
Si(2)	0.66046(7)	−0.06159(7)	0.41392(6)	3.99(2)
Si(3)	0.69376(7)	−0.20866(7)	0.35144(6)	3.83(2)
F(1)	0.8261(1)	0.0317(2)	0.4982(1)	5.26(5)
F(2)	0.5959(1)	−0.2588(2)	0.3619(1)	5.74(6)
N(1)	0.6924(2)	0.1470(2)	0.2872(2)	4.12(7)
N(2)	0.6954(2)	−0.4053(2)	0.3015(2)	4.70(8)
C(1)	0.8636(2)	0.0877(3)	0.3593(2)	4.21(9)
C(2)	0.9481(3)	0.0457(3)	0.3831(3)	5.1(1)
C(3)	1.0279(3)	0.0677(4)	0.3478(3)	6.2(1)
C(4)	1.0251(3)	0.1349(4)	0.2911(3)	6.2(1)
C(5)	0.9353(4)	0.2492(4)	0.2033(3)	6.3(1)
C(6)	0.8542(4)	0.2874(4)	0.1754(3)	6.3(1)
C(7)	0.7718(4)	0.2573(3)	0.2038(2)	5.4(1)
C(8)	0.7736(3)	0.1908(2)	0.2619(2)	4.17(9)
C(9)	0.8590(3)	0.1526(3)	0.2946(2)	4.27(9)
C(10)	0.9411(3)	0.1796(3)	0.2626(2)	5.1(1)
C(11)	0.6650(4)	0.0654(3)	0.2345(3)	5.5(1)
C(12)	0.6145(4)	0.2138(4)	0.2896(3)	5.8(1)
C(13)	0.7206(2)	0.1891(3)	0.4568(2)	4.04(8)
C(14)	0.7702(3)	0.2758(3)	0.4541(2)	4.9(1)
C(15)	0.7395(4)	0.3612(3)	0.4839(3)	5.8(1)
C(16)	0.6571(4)	0.3629(4)	0.5157(3)	6.1(1)
C(17)	0.6074(4)	0.2788(4)	0.5201(3)	6.0(1)
C(18)	0.6391(3)	0.1934(3)	0.4903(2)	5.2(1)
C(19)	0.5369(3)	−0.0347(4)	0.3754(4)	5.9(1)
C(20)	0.6546(5)	−0.0937(5)	0.5178(3)	6.1(1)
C(21)	0.8005(2)	−0.2678(2)	0.3989(2)	3.66(8)
C(22)	0.8547(3)	−0.2099(3)	0.4493(2)	4.80(10)
C(23)	0.9425(3)	−0.2380(3)	0.4832(2)	5.3(1)
C(24)	0.9762(3)	−0.3256(3)	0.4667(2)	5.0(1)
C(25)	0.9633(3)	−0.4812(3)	0.3972(3)	5.4(1)
C(26)	0.9157(3)	−0.5433(3)	0.3484(3)	5.8(1)
C(27)	0.8265(3)	−0.5183(3)	0.3168(2)	5.3(1)
C(28)	0.7873(2)	−0.4310(2)	0.3330(2)	3.99(8)
C(29)	0.8362(2)	−0.3631(2)	0.3826(2)	3.61(8)
C(30)	0.9261(2)	−0.3907(3)	0.4164(2)	4.24(9)
C(31)	0.6263(4)	−0.4586(4)	0.3401(4)	6.9(2)
C(32)	0.6812(5)	−0.4197(4)	0.2179(3)	6.9(2)
C(33)	0.7023(3)	−0.1862(2)	0.2474(2)	4.29(9)
C(34)	0.6246(4)	−0.1772(3)	0.1947(3)	6.2(1)
C(35)	0.6320(7)	−0.1549(4)	0.1184(3)	8.7(2)
C(36)	0.7185(8)	−0.1419(5)	0.0953(4)	10.0(2)
C(37)	0.7946(7)	−0.1501(5)	0.1439(4)	9.1(2)
C(38)	0.7871(4)	−0.1711(3)	0.2213(3)	6.2(1)

polarization effects. A correction for secondary extinction was applied (coefficient = 1.09147e-06). The structure was solved by direct methods (SIR92) [22] and expanded using Fourier techniques (DIRDIF94) [21]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 3762 observed reflections ($I > 3.00\sigma(I)$) and 567 variable parameters. The max./min. peaks on the final difference Fourier map corresponded to $0.30/-0.25$ e Å^{-3}, respectively. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation (1985) and (1992). The crystal data and analytical condition, and final atomic coordinates and isotropic temperature factors are listed in Tables 1 and 7, respectively. Complete lists of bond lengths and angles, hydrogen atom coordinates and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (No. CCDC-101791).

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