The differing modes of reaction of 1-(8-dimethylamino-1-naphthyl)-1-hydrodisilane and 1-(1-naphthyl)-1-hydrodisilane in nickel-catalyzed reactions with acetylene: formation of a pseudo-pentacoordinate silole via Si–Si bond cleavage vs. hydrosilation without Si–Si bond cleavage [1]

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Abstract

Pseudo-pentacoordinate 1-(8-dimethylamino-1-naphthyl)-1-hydrodisilanes 1 and 2 and the tetracoordinate counterpart 3 have been prepared. In the presence of an Ni(0) complex as catalyst, 1 and 2 undergo degradation to generate a silylene species and a hydrosilane. The complex with Ni of the silylene species from 1 has been trapped with an excess of diphenylacetylene to give a pseudo-pentacoordinate silole 4. The X-ray structure of 4 indicates that this silole occupies two pseudo-equatorial positions. In contrast, the tetracoordinate hydrodisilane 3 undergoes hydrosilation without Si–Si bond cleavage.

1. Introduction

One of the most important features of organosilicon compounds is their great ability to form hypercoordinate structure species with coordination numbers greater than five, and the chemistry of hypercoordinate silicon compounds has recently become an attractive area of research [1]. Hypercoordinate oligosilanes, however, have rarely been reported [2]. Recently, we reported for trisilanes [3] and ethoxydisilanes [4] containing an 8-dimethylamino-1-naphthyl group reactivities higher than those of tetracoordinate counterparts. Almost simultaneously, Belzner and coworkers [5] initiated a similar study of the chemistry of oligosilanes with 2-(dimethylaminomethyl)phenyl groups on silicon. In this paper, we describe the synthesis, structure and reactions of pseudo-pentacoordinate hydrodisilanes containing the 8-dimethylamino-1-naphthyl group. In the presence of an Ni(0) catalyst, these react with diphenylacetylene to afford the pseudo-pentacoordinate silole via cleavage of the Si–Si bond, while an ordinary tetracoordinate hydrodisilane undergoes hydrosilation without cleavage of the Si–Si bond.

2. Results and discussion

2.1. Synthesis of pseudo-pentacoordinate hydrodisilanes

Two pseudo-pentacoordinate hydrodisilanes 1 and 2 which contain the 8-dimethylamino-1-naphthyl group and the hydrogen atom on the same silicon atom and the corresponding tetracoordinate counterpart 3 were prepared readily by the routes shown in scheme 1. The hydrodisilane 1 was synthesized by reduction of the known ethoxydisilane 7 (X = OEt) [4], while 2 was obtained by direct reduction of the chlorodisilane 7 (X = Cl) obtained by reaction of dichlorodisilane 5 with (amino)naphthyllithium 6 [6]. The tetracoordinate counterpart 3 was prepared similarly by reduction of the ethoxydisilane 8 [4].
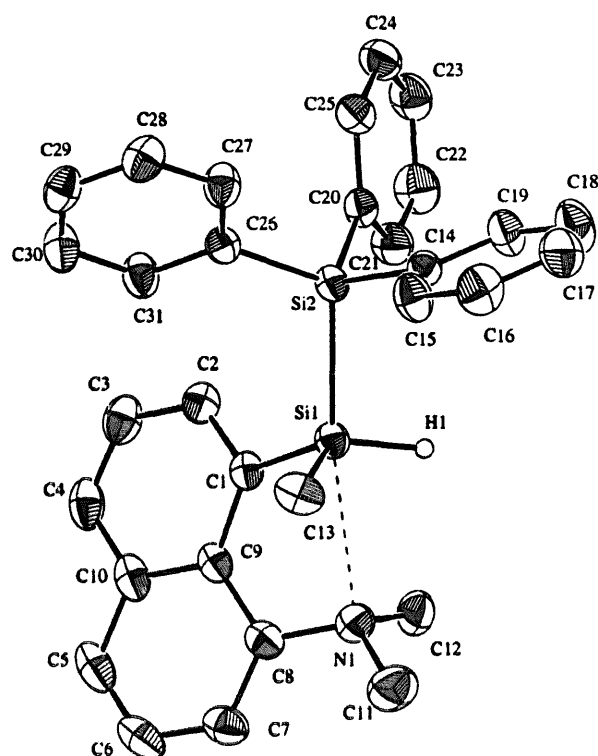
Fig. 1. Crystal structure of 2 drawn at the 30% probability level. Hydrogen atoms are omitted for clarity except for H(1).

Table 1
Crystal data and experimental details for structure determination of 2 and 4

	2	4
Chemical formula	$C_{31}H_{31}NSi_2$	$C_{41}H_{35}NSi$
Formula weight	473.76	569.82
Crystal size (mm³)	0.5×0.3×0.2	0.2×0.2×0.2
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
Unit-cell dimensions		
a (Å)	10.9980(5)	16.656(5)
b (Å)	13.5514(9)	8.276(7)
c (Å)	9.3550(5)	23.771(4)
α (°)	92.045(5)	
β (°)	106.993(4)	102.31(2)
γ (°)	94.980(5)	
V (Å³)	1325.6(1)	3201(2)
Z	2	4
ρ_{calc} (g cm⁻³)	1.187	1.182
Temperature (°C)	20.0	20
Radiation	Cu Kα	Cu Kα
	($\lambda = 1.54178$ Å)	($\lambda = 1.54178$ Å)
μ(Cu Kα)(cm⁻¹)	13.46	8.56
No. of unique reflections	3951	5161
No. of reflections used	3656 ($I > 3.00\sigma(I)$)	2498 ($I > 3.00\sigma(I)$)
No. of variables	432	529
R	0.038	0.053
Rw	0.070	0.058
GOF	2.00	1.63

2.2. X-ray crystal structure of hydrodisilane 2

The X-ray crystal structure of 2 is shown in Fig. 1, and the crystal data, selected interatomic distances, angles and dihedral angles, atomic coordinates and thermal parameters are listed in Tables 1, 2, and 3 respectively. The geometry around Si1 is distorted from tetrahedral to pseudo-trigonal bipyramidal (TBP), with the triphenylsilyl group and the amino group in the two pseudo-apical positions and the hydrogen atom in the pseudo-equatorial position. This geometry is different from those of the ethoxydisilane 7 (X = OEt) [4] and the fluorodisilane 7 (X = F) [7], in which the electronegative groups occupy the pseudo-apical position, with the silyl group in the pseudo-equatorial position.
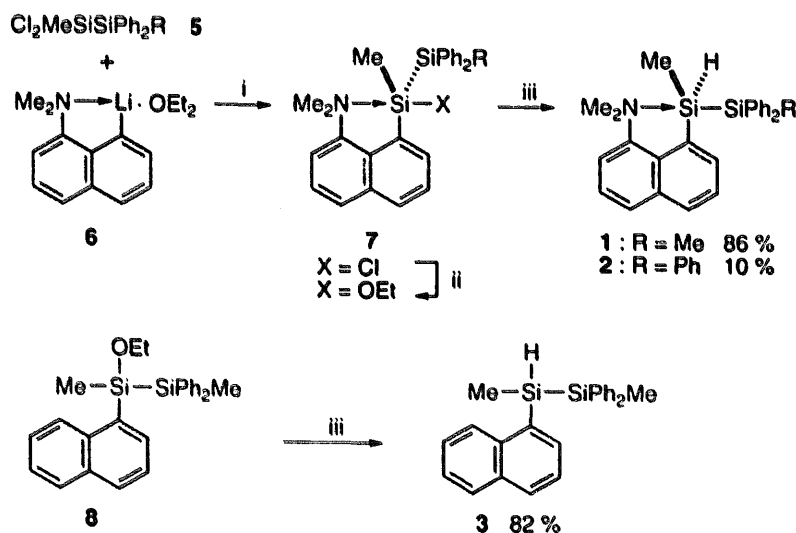
i) Et₂O, -30 °C - room temp, overnight. ii) EtOH, Et₃N, Et₂O, 0 °C, 0.5 h
iii) Et₂O, LiAlH₄, 0 °C - room temp, 4 h

Scheme 1.

Table 2
Selected bond distances (Å), angles (deg) and dihedral angles (deg) for 2

Bond distances

Si(1)···N(1)	2.790(2)		
Si(1)-Si(2)	2.3673(7)	Si(1)-H(1)	1.42(2)
Si(1)-C(1)	1.894(2)	Si(1)-C(13)	1.876(2)

Bond angles

Si(2)-Si(1)···N(1)	172.90(4)		
Si(2)-Si(1)-C(1)	112.28(6)	C(1)-Si(1)-C(13)	110.5(1)
Si(2)-Si(1)-C(13)	102.68(9)	C(1)-Si(1)-H(1)	115.8(8)
Si(2)-Si(1)-H(1)	98.3(8)	C(13)-Si(1)-H(1)	115.8(8)

Dihedral angles

Si(1)-C(1)-C(8)/N(1)-C(1)-C(8)	29.5
C(1)-C(2)-C(3)/C(6)-C(7)-C(8)	10.1

The difference is consistent with the high "equatophilicity" of the hydride ligand, pointed out by Corriu and coworkers [8] some years ago. The Ni···Si1 distance 2.790(2) Å is within normal coordination distances (not above 2.8 Å) [1], and the N1···Si1-Si2 angle 172.90(4)° is nearly linear. However, the pentaco-
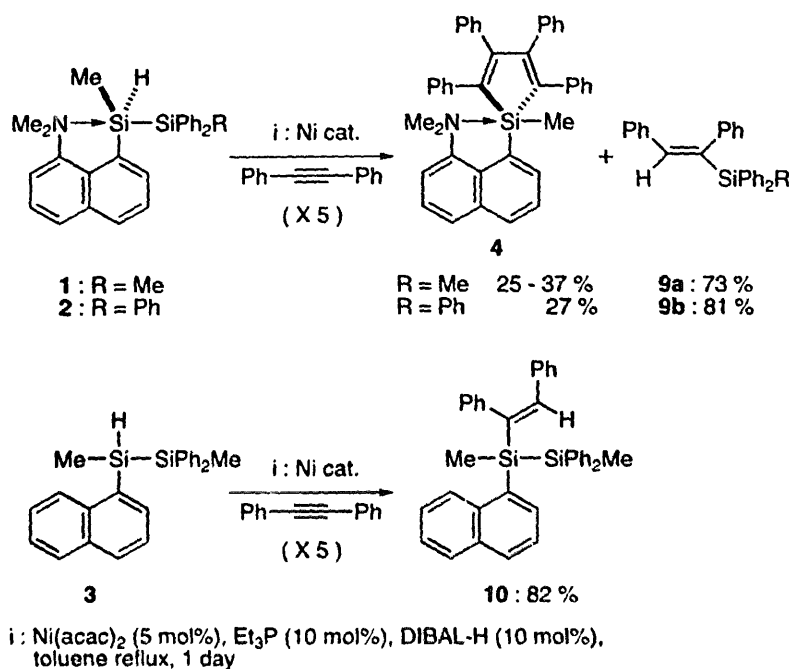
Table 3
Atomic coordinates and equivalent isotropic thermal parameters with estimated standard deviations in parentheses for 2

Atom	x	y	z	B_{eq}
Si(1)	0.00697(5)	0.24857(4)	0.05127(6)	3.71(1)
Si(2)	0.21177(5)	0.33883(4)	0.13439(6)	3.60(1)
N(1)	-0.2447(2)	0.1629(1)	-0.0653(2)	4.68(4)
C(1)	-0.0520(2)	0.2065(1)	0.2124(2)	3.72(4)
C(2)	0.0178(2)	0.2383(2)	0.3570(2)	4.41(5)
C(3)	-0.0005(2)	0.1910(2)	0.4827(3)	5.34(6)
C(4)	-0.0825(2)	0.1081(2)	0.4622(3)	5.33(6)
C(5)	-0.2475(2)	-0.0137(2)	0.2952(4)	5.76(7)
C(6)	-0.3252(2)	-0.0430(2)	0.1561(4)	5.98(7)
C(7)	-0.3251(2)	0.0125(2)	0.0342(3)	5.38(6)
C(8)	-0.2423(2)	0.0977(1)	0.0507(2)	4.26(4)
C(9)	-0.1515(2)	0.1262(1)	0.1929(2)	3.84(4)
C(10)	-0.1600(2)	0.0731(2)	0.3184(3)	4.66(6)
C(11)	-0.2920(4)	0.1175(3)	-0.2177(3)	7.11(8)
C(12)	-0.3113(3)	0.2489(2)	-0.0526(3)	5.58(6)
C(13)	0.0349(3)	0.1389(2)	-0.0589(3)	5.55(6)
C(14)	0.2469(2)	0.3776(1)	-0.0426(2)	3.92(4)
C(15)	0.2785(3)	0.3094(2)	-0.1366(3)	5.60(6)
C(16)	0.3002(3)	0.3357(2)	-0.2696(3)	6.55(7)
C(17)	0.2902(3)	0.4315(2)	-0.3104(3)	6.73(7)
C(18)	0.2562(3)	0.4989(2)	-0.2217(3)	7.16(8)
C(19)	0.2360(3)	0.4732(2)	-0.0882(3)	5.45(6)
C(20)	0.2196(2)	0.4560(1)	0.2534(2)	4.00(4)
C(21)	0.1096(2)	0.4912(2)	0.2694(3)	5.20(5)
C(22)	0.1133(3)	0.5789(2)	0.3516(3)	6.20(7)
C(23)	0.2286(3)	0.6331(2)	0.4196(3)	5.94(6)
C(24)	0.3382(3)	0.6006(2)	0.4050(3)	5.61(6)
C(25)	0.3352(2)	0.5126(2)	0.3224(2)	4.77(5)
C(26)	0.3416(2)	0.2604(1)	0.2327(2)	3.86(4)
C(27)	0.4606(2)	0.2674(2)	0.2081(3)	4.97(5)
C(28)	0.5541(2)	0.2086(2)	0.2784(3)	5.43(6)
C(29)	0.5339(2)	0.1435(2)	0.3787(2)	5.03(5)
C(30)	0.4184(3)	0.1353(2)	0.4062(3)	5.76(6)
C(31)	0.3233(2)	0.1918(2)	0.3331(3)	5.19(6)
H(1)	-0.060(2)	0.322(1)	-0.034(2)	4.0(4)

ordinate character [9], %TBPa = 26%, is rather low, whereas the Si1-Si2 distance 2.3673(7) Å is in the range of normal values (2.33-2.37 Å) [10] and the Si1-H1 length 1.42(2) Å is slightly shorter than for normal Si-H bonds (1.47-1.50 Å) [10]. It is noted that the Si1-Np(C1) bond 1.894(2) Å is slightly elongated (typical Si-C(sp^2) bond length less than 1.86 Å), being longer than the Si1-Me(C13) bond (1.876(2) Å) (1.86-1.88 Å for typical Si-C(sp^3) bonds) [10]. This bond elongation might indicate that the Si1···N1 interaction is not really attractive but rather repulsive. In keeping with this, the naphthalene ring is highly distorted, as evidenced by two large dihedral angles C1-C2-C3/C6-C7-C8 (10.1°) and Si1-C1-C8/N1-C1-C8 (29.5°) and by large displacements of the Si1 and N1 atoms (0.712 and 0.314 Å respectively) from each side of the naphthalene mean plane defined by the central six carbon atoms.

2.3. NMR spectra of pseudo-pentacoordinate hydrodisilanes 1 and 2

In solution, the coordination of the amino group to the silicon atom is supported by NMR data. Thus, at 20°C in C_6D_6 the two diastereotopic methyl groups on nitrogen in 1 appear as two separate singlets at δ 2.22 and 2.36 ppm in the ^{1}H NMR and δ 46.12 and 47.44 ppm in the ^{13}C NMR spectrum For 2 these singlets appear at δ 2.25 and 2.39 ppm in the ^{1}H NMR and δ 45.20 and 48.36 ppm in the ^{13}C NMR spectrum. The data indicate that the coordination of the amino group to silicon is strong enough to prevent equilibration of the two methyl groups by rotation about the amino-naphthyl bond on the NMR time scales at 20°C. In the ^{29}Si NMR spectrum the signal from the dimethylamino-naphthyl-containing compound 1 (-39.05 ppm) appears at ca. 0.7 ppm downfield relative to that from the naphthyl-containing compound 3 (-39.74 ppm). While upfield shifts are commonly observed for pentacoordinate silicon compounds with electronegative substituents [1,11], the very similar chemical shifts in 1 and

Scheme 2 (top)

1 : R = Me
2 : R = Ph

i : Ni cat.
Ph——≡——Ph
(X5)

R = Me   25 - 37 %
R = Ph   27 %

4

9a : 73 %
9b : 81 %

3

i : Ni cat.
Ph——≡——Ph
(X5)

10 : 82 %

i : Ni(acac)₂ (5 mol%), Et₃P (10 mol%), DIBAL-H (10 mol%), toluene reflux, 1 day

Scheme 2.

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3 suggest that there is little electronic perturbation arising from the presence of the amino group. In the ^{1}H NMR spectrum also, all the Si–H signals appear in a narrow range, at δ 5.35, 5.60 and 5.25 ppm in **1**, **2** and **3** respectively. Nevertheless, the pseudo-pentacoordinate hydrodisilanes **1** and **2** react in a different way from their tetracoordinate counterpart **3**.

2.4. Nickel(0)-catalyzed degradation of 1 and 2 to form a pseudo-pentacoordinate silole
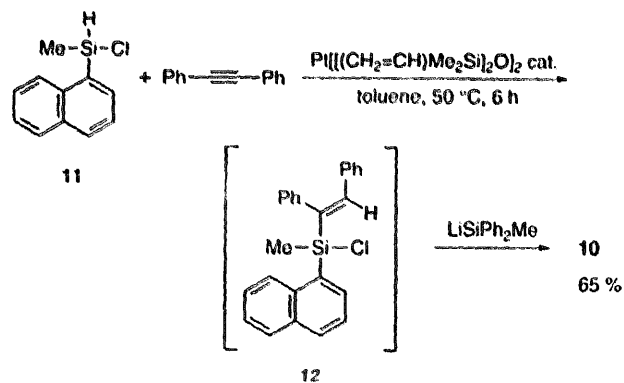
The pseudo-pentacoordinate hydrodisilanes **1** and **2** undergo Ni(0)-catalyzed degradation [12,13] to a sily-lene species and a hydrosilane. Thus, when either **1** or **2** was heated in the presence of an Ni(0) complex as catalyst and an excess (5 equiv.) of diphenylacetylene at 110°C in toluene for 1 day under argon, a silylene species was generated and trapped as a pseudo-pentacoordinate silole (silacyclopentadiene) **4** in 25–37% yield [14], as shown in Scheme 2. At the same time the generated hydrosilane took part in hydrosilation of acetylene to give the vinylsilane **9a** from **1** in 73% yield and **9b** from **2** in 81% yield.

In contrast, the tetracoordinate analogue **3** did not undergo degradation under similar conditions, but took part in direct hydrosilation of diphenylacetylene, without cleavage of the Si–Si bond, to give **10** in 82% yield. The structure of **10** was confirmed by an independent synthesis via the Pt-catalyzed cis-hydrosilation with hy-drochlorosilane **11** followed by treatment with the ap-propriate silyllithium to form the Si–Si bond, as shown in Scheme 3. The different modes of reaction of **1** and **2**
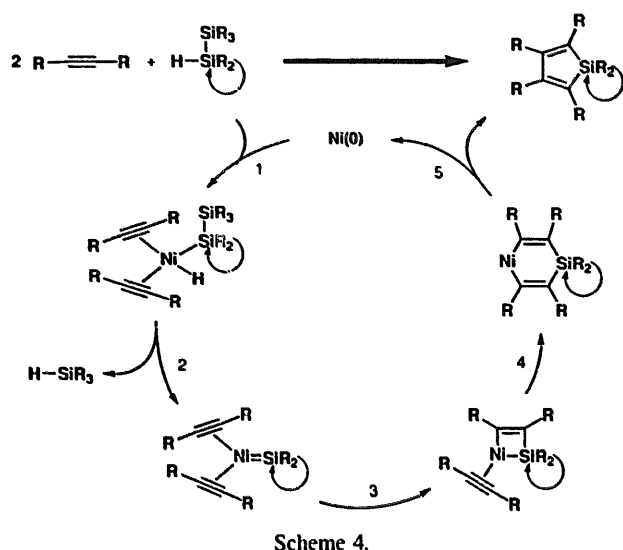
on the one hand and **3** on the other are indicative of the importance of the intramolecular coordination in **1** and **2** [15].

Some mechanistic features are worthy of note. The nickel-catalyzed reaction can be assumed to start by oxidative addition of the Si–H bond to an Ni(0) species, as shown in Scheme 4. The intramolecular nitrogen coordination facilitates the α-elimination of the terminal silyl group, followed by reductive elimination of the hydrosilane (or formal β-elimination) to leave a nickel–silylene species [16a,b]. Subsequent cyclization with the two coordinated acetylenes eventually gives the observed silole [16c,d]. In the absence of nitrogen coordination, following the oxidative addition simple hydro-silation can occur much faster than the cleavage of the Si–Si bond, which is not activated.

The Ni-catalyzed direct hydrosilation in which the Si–Si bond remains intact is itself remarkable, since

Scheme 3 (bottom)

11 + Ph——≡——Ph
Pt[[(CH₂=CH)Me₂Si]₂O]₂ cat.
toluene, 50 °C, 6 h

12
LiSiPh₂Me
10
65 %

Scheme 3.

Scheme 4.

hydrodisilanes usually undergo disproportionation in the presence of a transition metal catalyst [12,16a,b,17].

2.5. Comparison of spectroscopic features of the pseudo-pentacoordinate 4 with those of the tetracoordinate silole 11

Tetracoordinate silole 11 was prepared by the previously reported method [18] in order to allow comparison with the pseudo-pentacoordinate silole 4.

11 : 69 %

Compounds **4** and **11** show quite similar spectroscopic behavior in solution. Thus, in the ^1H and ^{13}C NMR spectra the methyl group on the silicon atom in **4** gives signals at ca. 0.1 and 8.2 ppm downfield respectively from those from the tetracoordinate counterpart **11**. In the ^{29}Si NMR spectrum the signal from the silicon atom in **4** (-4.6 ppm) appears at ca. 5.2 ppm upfield from that in **11** (0.53 ppm), such an upfield shift being consistent with a pentacoordination silicon atom [1,11]. In the UV spectrum, **4** and **11** exhibit essentially the same absorption maxima (for details see the Experimental section). These results suggest that the coordination of the nitrogen atom to silicon in **4** is rather weak in solution.

2.6. Solid state structure of the silole 4

In the solid state, the presence of the N · · · Si interaction in **4** was confirmed by an X-ray diffraction study. The molecular structure of **4** is shown in Fig. 2. The crystal data, selected interatomic distances, angles and dihedral angles, and atomic coordinates and thermal parameters are listed in Tables 1, 4 and 5 respectively. The geometry around Si1 is pseudo-TBP, with the methyl group and the amino group in the two pseudo-apical positions. The N1 · · · Si1 distance 2.891(4) Å is close to a normal coordination distance and the N1 · · · Si1–Me angle 177.2(2)° is almost entirely linear. The pseudo-apical Si1–Me distance 1.883(6) Å lies slightly above the range for normal Si–Me bonds (1.867–1.875 Å) [10]. Interestingly, the endocyclic five-membered silole ring occupies the two pseudo-equatorial positions in spite of the small C1–Si1–C4 angle 92.9(2)°.

The naphthalene ring is very close to planarity, as shown by the dihedral angles C5–C6–C7/C10–C11–C12 (2.6°) and Si1–C5–C12/N1–C5–C12 (0.5°) and
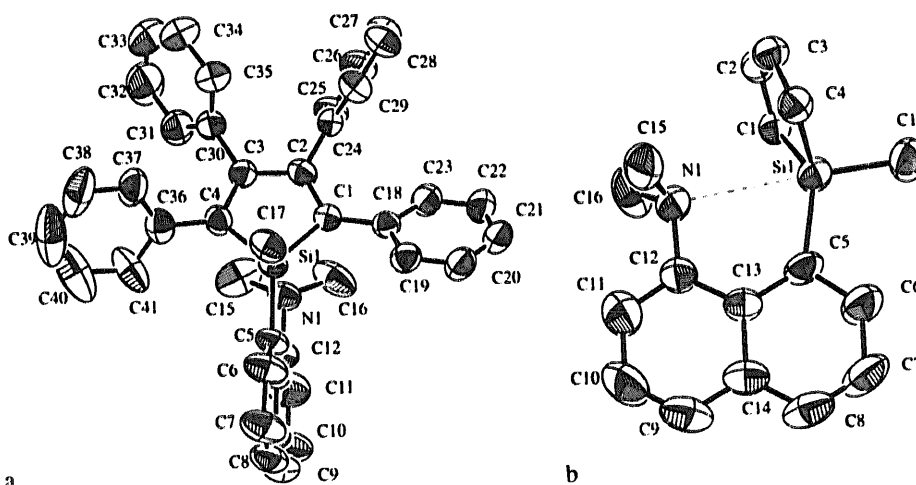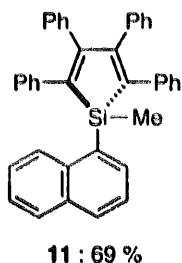

Fig. 2. Crystal structure of **4** drawn at the 50% probability level: (a) top view, (b) side view. Phenyl groups on the silole ring in (b) and all hydrogen atoms are omitted for clarity.

the small displacement of the Si1 and N1 atoms (0.024 and 0.010 Å respectively) from each side of the naphthalene mean plane defined by the central six carbon atoms. The pentacoordinate character of the Si atom, %TBPa [8], is, however, rather small, and is estimated to be 31%.

Overall the coordination mode in this silole is rather unusual. This could be related to a low-lying vacant orbital present on the silicon atom in silole [19]. Compound 4 is the first example of a neutral pseudo-pentacoordinate silole, although an anionic fluorosilicate of a silole has been reported [20].

3. Experimental section

3.1. General

^{1}H (270 MHz), ^{13}C (67.94 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 7.200 ppm and ^{13}C δ 128.00 ppm). ^{29}Si chemical shifts are referenced to external Me$_4$Si (0 ppm). IR spectra were recorded on a JASCO IR-810 spectrometer. UV spectra in solution were recorded on a JASCO UVIDEC610B spectrometer for 4 and a SHIMADZU UV3101PC spectrometer for 11. Mass spectra were obtained at 70 eV on a JEOL JMS-DX300 mass spectrometer equipped with a JMA-3500 data processing system. Melting points were determined with a Yanaco-MP-S3 apparatus. Elemental analyses were performed at the Microanalysis Division of the Institute for Chemical Research, Kyoto University: analytical samples were purified by recrystallization, or by HPLC, with a 20 × 250 mm^2 Wakosil-5Sil-column (Wako). Column chromatography was performed on Kieselgel (70–230 mesh) (Merck). DIBAL-H in toluene (Aldrich) was used as received. THF and Et$_2$O were distilled under nitrogen from sodium/benzophenone. Hexane and toluene were distilled under nitrogen from

sodium. Benzene was distilled under nitrogen from LiAlH$_4$.

3.2. Preparation of hydrodisilane 1

To a suspension of 1-ethoxy-1,2-dimethyl-1-(8-dimethylamino-1-naphthyl)-2,2-diphenyldisilane (7) (R = Me, X = OEt) [4] (2.3 g, 5.0 mmol) in Et$_2$O (15 ml) at 0°C under nitrogen was added LiAlH$_4$ (190 mg, 5.0 mmol). The mixture was stirred at 0°C for 30 min and at room temperature for 2.5 h, and then AcOEt at 0°C was added during 10 min. After 30 min stirring, the mixture was diluted with hexane and filtered through a sintered glass filter. The filtrate was concentrated under reduced pressure to leave a white solid. Recrystallization from THF–hexane afforded 1.76 g (4.28 mmol) of 1 as colorless crystals in 86% yield; m.p. 86.5–86.8°C. ^{1}H NMR (C$_6$D$_6$): δ 0.54 (d, J = 4.0 Hz, 3H), 0.58 (s, 3H), 2.22 (s, 3H), 2.36 (s, 3H), 5.35 (q, J = 4.0 Hz, 1H), 6.92 (dd, J = 1.0 and 7.6 Hz, 1H), 7.16–7.29 (m, 7H), 7.50–7.56 (m, 3H), 7.59–7.65 (m, 2H), 7.69 (dd, J = 0.8 and 8.2 Hz, 1H), 8.01 (dd, J = 1.0 and 7.0 Hz, 1H). ^{13}C NMR (C$_6$D$_6$): δ −3.59, −2.98, 46.12, 47.44, 116.79, 125.56, 125.77, 125.95, 128.07, 128.79, 128.90, 130.62, 131.31, 134.81, 135.37, 135.42, 135.55, 137.06, 138.60, 138.71. ^{29}Si NMR (C$_6$D$_6$): δ −39.05 (d, $^1J_{Si-H}$ = 203 Hz), −20.04. MS: m/e 411 (M$^+$, 0.3), 410 (M$^+$–H, 0.3), 214 (M$^+$–SiMePh$_2$, 100), 199 ((Me$_2$NC$_{10}$H$_6$)HSi$^+$, 40). IR (KBr): 2136 cm^{-1} (s), 2054 cm^{-1} (w). (The origin of these two absorptions is now under investigation.) Anal. Found: C, 75.69; H, 7.10; N, 3.39. C$_{26}$H$_{29}$NSi$_2$ Calc.: C, 75.85; H, 7.10; N, 3.40%.

3.3. Preparation of 1,1-dichloro-1-methyl-2,2,2-triphenyldisilane (5, R = Ph)

To a stirred suspension of granular lithium (1.32 g, 190 mmol) in THF (20 ml) at room temperature Ph$_3$SiCl

Table 4
Selected bond distances (Å), angles (deg) and dihedral angles (deg) for 4

Bond distances			
Si(1)···N(1)	2.891(4)		
Si(1)–C(1)	1.880(4)	Si(1)–C(4)	1.861(5)
Si(1)–C(5)	1.890(4)	Si(1)–C(17)	1.883(6)

Bond angles			
C(17)–Si(1)···N(1)	177.2(2)		
C(17)–Si(1)–C(1)	103.0(2)	C(1)–Si(1)–C(4)	92.9(2)
C(17)–Si(1)–C(4)	100.6(3)	C(1)–Si(1)–C(5)	126.5(2)
C(17)–Si(1)–C(5)	107.0(3)	C(4)–Si(1)–C(5)	122.8(2)

Dihedral angles	
Si(1)–C(5)–C(12)/N(1)–C(5)–C(12)	0.5
C(5)–C(6)–C(7)/C(10)–C(11)–C(12)	2.6

Table 5
Atomic coordinates and equivalent isotropic thermal parameters with estimated standard deviations in parentheses for 4

Atom	x	y	z	B_{eq}
Si(1)	0.80693(8)	0.2383(2)	0.83397(6)	3.89(3)
N(1)	0.8918(2)	−0.0504(5)	0.8830(2)	4.5(1)
C(1)	0.7308(3)	0.0741(5)	0.8062(2)	3.5(1)
C(2)	0.6861(3)	0.0511(5)	0.8470(2)	3.8(1)
C(3)	0.7103(3)	0.1482(6)	0.9005(2)	3.9(1)
C(4)	0.7770(3)	0.2456(6)	0.9050(2)	4.0(1)
C(5)	0.9175(3)	0.2481(7)	0.8263(2)	4.6(1)
C(6)	0.9384(4)	0.3856(8)	0.8005(3)	6.4(2)
C(7)	1.0181(4)	0.4188(10)	0.7915(3)	7.3(2)
C(8)	1.0764(4)	0.3077(9)	0.8067(2)	6.4(2)
C(9)	1.1241(4)	0.048(1)	0.8497(3)	6.7(2)
C(10)	1.1112(4)	−0.092(1)	0.8751(4)	8.5(2)
C(11)	1.0338(4)	−0.1228(8)	0.8860(3)	7.0(2)
C(12)	0.9708(3)	−0.0145(6)	0.8716(2)	4.5(1)
C(13)	0.9814(3)	0.1311(6)	0.8441(2)	3.9(1)
C(14)	1.0625(3)	0.1634(8)	0.8337(2)	5.1(1)
C(15)	0.8962(5)	−0.064(1)	0.9454(3)	7.4(2)
C(16)	0.8585(4)	−0.1995(8)	0.8547(4)	7.4(2)
C(17)	0.7544(4)	0.4256(7)	0.7991(3)	5.4(2)
C(18)	0.7163(3)	−0.0020(6)	0.7488(2)	3.7(1)
C(19)	0.7393(3)	0.0792(7)	0.7032(2)	4.5(1)
C(20)	0.7240(4)	0.0198(8)	0.6483(3)	5.4(2)
C(21)	0.6846(4)	−0.1246(9)	0.6366(3)	6.1(2)
C(22)	0.6640(4)	−0.2140(8)	0.6808(3)	5.9(2)
C(23)	0.6798(3)	−0.1530(7)	0.7353(3)	5.0(1)
C(24)	0.6135(3)	−0.0581(6)	0.8409(2)	4.2(1)
C(25)	0.6188(3)	−0.1983(7)	0.8729(3)	5.4(2)
C(26)	0.5534(5)	−0.3041(9)	0.8665(3)	7.5(2)
C(27)	0.4829(5)	−0.273(1)	0.8303(4)	8.4(3)
C(28)	0.4744(4)	−0.134(1)	0.7990(3)	8.1(2)
C(29)	0.5400(4)	−0.0235(9)	0.8044(3)	6.0(2)
C(30)	0.6609(3)	0.1426(7)	0.9461(2)	4.9(1)
C(31)	0.6942(4)	0.0903(8)	1.0002(3)	6.3(2)
C(32)	0.6498(7)	0.093(1)	1.0438(3)	9.5(3)
C(33)	0.5708(7)	0.156(2)	1.0307(5)	12.3(4)
C(34)	0.5378(5)	0.204(1)	0.9788(5)	10.5(3)
C(35)	0.5807(4)	0.2003(9)	0.9346(3)	6.8(2)
C(36)	0.8030(3)	0.3678(6)	0.9504(2)	4.8(1)
C(37)	0.7465(4)	0.4794(7)	0.9622(3)	6.2(2)
C(38)	0.7687(7)	0.5963(9)	1.0032(4)	8.9(3)
C(39)	0.8474(9)	0.605(1)	1.0331(4)	10.5(4)
C(40)	0.9028(7)	0.499(1)	1.0239(4)	10.7(3)
C(41)	0.8822(4)	0.3812(8)	0.9809(3)	7.8(2)

(14.74 g, 50.0 mmol) in THF (30 ml) was added dropwise. After a few minutes the resulting white suspension (Ph$_3$SiSiPh$_3$) was stirred at 0°C for 10 h and then at room temperature for 12 h to give a solution of Ph$_3$SiLi. This solution was added dropwise from a Teflon tube to a stirred solution of Me(Et$_2$N)$_2$SiCl [20] (11.7 g, 50.5 mmol) in THF (80 ml) kept at 0°C. The mixture was stirred for 1 day and the solvent was then removed under reduced pressure. Benzene (40 ml) was added to the residue and the solution filtered through a sintered glass filter. The filtrate was evaporated to afford crude Me(Et$_2$N)$_2$SiSiPh$_3$. ^{1}H NMR (C$_6$D$_6$): δ

0.45 (s, 3H), 0.92 (t, J = 7.0 Hz, 12H), 2.97 (q, J = 7.0 Hz, 8H), 7.22-7.28 (m, 9H), 7.80-7.83 (m, 6H).

Through a solution of this crude diaminodisilane (13.4 g, ca. 30 mmol) in Et$_2$O (100 ml) was bubbled dry HCl, generated from NH$_4$Cl (48.1 g, 900 mmol) and concentrated H$_2$SO$_4$ (33 ml), at 0°C over 3 h [21]. The mixture was filtered through a sintered glass filter, and the filtrate evaporated in vacuo. Benzene (50 ml) was added to the residue, the solution filtered through a sintered glass filter, and the filtrate evaporated to give a crude product. Recrystallization from hexane afforded 6.93 g (18.6 mmol) of pure 5 (R = Ph) as white crystals in 62% yield. ^{1}H NMR (C$_6$D$_6$): δ 0.75 (s, 3H), 7.17-7.21 (m, 9H), 7.73-7.77 (m, 6H).

3.4. Preparation of hydrodisilane 2

To a suspension of 8-dimethylamino-1-naphthyl-lithium etherate (6) [6] (1.62 g, 6.44 mmol) in Et$_2$O (11 ml) at −40°C under nitrogen, a solution of MeCl$_2$SiSi-Ph$_3$ (5, R = Ph) (2.43 g, 6.50 mmol) in Et$_2$O (12 ml) was added dropwise over 2 min. The mixture was allowed to warm to room temperature and stirred for 42 h. The solvent was removed under reduced pressure and benzene added to the residue. The solution was filtered and the filtrate evaporated to give crude 7 (R = Ph, X = Cl). To a suspension of LiAlH$_4$ (244 mg, 6.44 mmol) in Et$_2$O (5 ml) at −35°C under nitrogen, a solution of crude 7 (R = Ph, X = Cl) in Et$_2$O (20 ml) was added dropwise over 8 min. The mixture was allowed to warm to room temperature and stirred for 4 h and ethyl acetate (2.5 ml, 26 mmol) was then added at 0°C over 7 min. After 30 min stirring, the mixture was diluted with hexane (10 ml) and then filtered through a sintered glass filter. The filtrate was concentrated under reduced pressure to leave viscous oil, which was purified by flash column chromatography on silica gel (2: R$_f$ 0.37, hexane/AcOEt = 10:1) to remove dimethylaminonaphthalene (R$_f$ 0.42). Concentration and recrystallization from AcOEt-hexane afforded 311 mg (0.66 mmol, 10% yield) of 2 as colorless crystals; m.p. 137.8-138.8°C. ^{1}H NMR (C$_6$D$_6$): δ 0.59 (d, J = 4.3 Hz, 3H), 2.25 (s, 3H), 2.39 (s, 3H), 5.60 (q, J = 4.3 Hz, 1H), 6.98 (dd, J = 0.7 and 7.4 Hz, 1H), 7.05 (dd, J = 6.8 and 7.8 Hz, 1H), 7.21-7.28 (m, 10H), 7.48 (dd, J = 0.7 and 7.8 Hz, 1H), 7.61 (dd, J = 0.7 and 9.5 Hz, 1H), 7.81-7.86 (m, 6H), 8.26 (dd, J = 0.8 and 7.0 Hz, 1H). ^{13}C NMR (C$_6$D$_6$): δ −3.37, 45.20, 48.36, 117.43, 125.70, 125.84, 126.01, 128.27, 129.15, 131.00, 134.74, 135.40, 136.84, 137.31, 139.16, 152.51. ^{29}Si NMR (C$_6$D$_6$): δ −37.77 (dq, $^1J_{Si-H}$ = 204 and $^2J_{Si-H}$ = 6.7 Hz), −19.74. MS: m/e 473 (M$^+$, 0.3), 259 (Ph$_3$Si$^+$, 4.7), 214 (M$^+$-Ph$_3$Si, 100), 199 ((Me$_2$NC$_{10}$H$_6$)HSi$^+$, 33), 198 ((Me$_2$NC$_{10}$H$_6$)Si$^+$, 14). Anal. Found: C, 78.33; H, 6.72; N, 2.90. C$_{31}$H$_{31}$NSi$_2$ Calc.: C, 78.59; H, 6.60; N, 2.96%.

3.5. 1-Hydro-1-naphthyl-1,2-dimethyl-2,2-diphenyldisilane (3)

This compound was obtained by $LiAlH_4$-reduction of 8 [4] under essentially the conditions described above and was isolated by column chromatography on silica gel (R_f 0.54, hexane/AcOEt = 5:1) as colorless oil in 82% yield. ^1H NMR (C_6D_6): δ 0.56 (d, J = 4.6 Hz, 3H), 0.59 (s, 3H), 5.25 (q, J = 4.6 Hz, 1H), 7.12–7.31 (m, 9H), 7.50–7.58 (m, 4H), 7.65 (d, J = 5.9 Hz, 1H), 7.68 (d, J = 6.7 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H). ^{13}C NMR (C_6D_6): δ −6.63, −3.71, 125.54, 125.86, 125.93, 128.29, 128.83, 129.10, 129.35, 130.19, 133.71, 134.00, 135.21, 135.35, 136.63, 136.82, 137.78. ^{29}Si NMR (C_6D_6): δ −39.74 (d, $^1J_{Si-H}$ = 181 Hz), −21.22. MS: m/e 368 (M^+, 28), 247 ($MePh(C_{10}H_6)Si^+$, 71), 197 ($MePh_2Si^+$, 100). IR (film, neat): 2100 cm^{-1} (s). Anal. Found: C, 77.99; H, 6.60. $C_{24}H_{24}Si_2$ Calc.: C, 78.20; H, 6.56%.

3.6. Nickel(0)-catalyzed reaction of 1

To a solution of nickel(0) complex, prepared from $Ni(acac)_2$ (6.4 mg, 0.025 mmol), Et_3P (7.5 μl, 0.05 mmol) and DIBAL-H (1.5 M toluene solution, 0.033 ml, 0.05 mmol) in toluene (1 ml), was added a solution of 1 (206 mg, 0.5 mmol) and diphenylacetylene (450 mg, 2.5 mmol) in toluene (1 ml). The mixture was kept at 110°C under argon for 1 day, after which the ^1H NMR spectrum of the mixture showed complete disappearance of 1. Purification by column chromatography on silica gel (R_f 0.35, hexane/AcOEt = 10:1) and HPLC (hexane/AcOEt = 50:1) gave approximately 72–105 mg (25–37% yield) of silole 4 and 138 mg (73% yield) of 9a. The latter was characterized by comparison with an authentic sample [21]. Silole 4 was further purified by recrystallization from THF–hexane and obtained as pale-yellow crystals; m.p. 193.6–194.8°C (decomp.). ^1H NMR (C_6D_6): δ 1.03 (s, 3H), 2.62 (s, 6H), 6.71–6.85 (m, 7H), 6.96–7.04 (m, 6H), 7.08–7.10 (m, 8H), 7.20–7.29 (m, 1H), 7.40 (dd, J = 6.9 and 8.1 Hz, 1H), 7.50 (dd, J = 8.1 and 1.2 Hz, 1H), 7.74 (dd, J = 8.1 and 1.2 Hz, 1H), 8.27 (dd, J = 7.0 and 1.1 Hz, 1H). ^{13}C NMR (C_6D_6): δ 2.79, 49.03, 117.51, 125.70, 125.81, 125.90, 126.02, 126.53, 128.09, 128.20, 128.54, 129.87, 130.61, 131.38, 135.22, 135.37, 138.84, 139.90, 140.58, 145.09, 150.37, 153.28. ^{29}Si NMR (C_6D_6): δ −4.68. UV (CHCl$_3$), λ_{max} (log ε): 246 nm (4.53), 272 nm (4.28), 365 nm (4.14). MS: m/e 569 (M^+, 36), 554 (M^+-Me, 8), 198 (($Me_2NC_{10}H_6)Si^+$, 100). Anal. Found: C, 86.48; H, 6.20; N, 2.19. $C_{41}H_{35}NSi$ Calc.: C, 86.42; H, 6.19; N, 2.46%.

3.7. Nickel(0)-catalyzed reaction of 2

Compound 2 (142 mg, 0.3 mmol) and diphenylacetylene (270 mg, 1.5 mmol) were treated for 1 day with the Ni(0) species under the conditions described for the reaction of 1. The ^1H NMR spectrum of the mixture showed that the reaction was not complete, and so more of the Ni(0) complex (5 mol%) was added and the mixture stirred at 110°C for 34 h. Column chromatography on silica gel (R_f 0.35, hexane/AcOEt = 10:1) and HPLC (hexane/AcOEt = 50:1) purification gave 47 mg (0.083 mmol, 27% yield) of silole 4 and 107 mg (0.24 mmol, 81% yield) of 9b [22].

3.8. Nickel(0)-catalyzed reaction of 3

Compound 3 (186 mg, 0.5 mmol) and diphenylacetylene (454 mg, 2.5 mmol) were treated for 1 day with the Ni(0) species under the conditions described for the reaction of 1. The hydrosilylation product 10 (228 mg, 0.4 mmol) was isolated by column chromatography on silica gel (R_f 0.3, hexane/AcOEt = 10:1) and purified by HPLC (hexane/AcOEt = 40:1) as colorless oil in 82% yield. ^1H NMR (C_6D_6): δ 0.74 (s, 3H), 0.76 (s, 3H), 6.86–7.05 (m, 10H), 7.09–7.31 (m, 9H), 7.34 (s, 1H), 7.53–7.56 (m, 2H), 7.61–7.64 (m, 2H), 7.69–7.72 (m, 2H), 7.92 (d, J = 6.8 Hz, 1H), 8.53 (d, J = 7.8 Hz, 1H). ^{13}C NMR (C_6D_6): δ −2.89, −2.26, 125.57, 125.88, 126.31, 127.55, 128.14, 128.25, 128.88, 129.20, 129.26, 129.33, 129.71, 129.94, 130.55, 134.09, 135.39, 135.67, 135.75, 136.16, 137.16, 137.33, 137.72, 137.94, 142.50, 142.65, 144.14. ^{29}Si NMR (C_6D_6): δ −17.73, −21.24. MS: m/e 546 (M^+, 31), 349 (M^+-Ph$_2$MeSi, 78), 197 (Ph$_2$MeSi$^+$, 87), 171 (100). Anal. Found: C, 83.36; H, 6.48. $C_{38}H_{34}Si_2$ Calc.: C, 83.46; H, 6.27%.

3.9. Preparation of the authentic sample of 10

A mixture of chloromethylnaphthylsilane (1.06 g, 5.0 mmol) prepared from dichloromethylsilane and 1-naphthyllithium, diphenylacetylene (0.94 g, 5.3 mmol) and a solution of $Pt[[(CH_2=CH)Me_2Si]_2O]_2$ (8.30 × 10^{-5} mmol ml^{-1} xylene solution, 60 μl, 5 μmol) [23] in toluene (2.5 ml) was heated at 50°C under dry air for 6 h. The mixture was then cooled to 0°C and a solution of $MePh_2SiLi$, prepared from $MePh_2SiCl$ (1.2 g, 5.0 mmol) and granular lithium (132 mg, 19.0 mmol) in THF (9 ml) was added dropwise over 10 min under argon. After overnight stirring the mixture was diluted with hexane (10 ml) and then filtered through a sintered glass filter. The filtrate was concentrated under reduced pressure to leave viscous oil, which was purified by flash column chromatography on silica gel and purified by MPLC to give 10 (1.78 g, 3.25 mmol) in 65% yield.

3.10. Preparation of the tetracoordinate silole 11

A mixture of diphenylacetylene (1.4 g, 8.0 mmol) and granular lithium (56 mg, 8.0 mmol) in Et_2O (10 ml) was stirred at room temperature under argon for 9 h to

give a deep red suspension [18a]. A solution of dichloro(methyl)(1-naphthyl)silane (1.0 g, 4.0 mmol) in Et_2O (10 ml) was added dropwise at 0°C over 5 min and the mixture was stirred for 1 h, THF (10 ml) was added, and the resulting green-yellow mixture stirred at room temperature for 12 h. The solvent was removed under reduced pressure, benzene was added to the residue and the mixture was filtered. The filtrate was evaporated and the residue purified by flush column chromatography on silica gel (R_f 0.35, hexane/AcOEt = 10:1). The crude product was recrystallized from hexane to give 1.46 g (2.8 mmol, 69% yield) of tetracoordinate silole 11 as a pale-yellow solid; m.p. 168-169°C (decomp.). ^1H NMR (C_6D_6): δ 0.92 (s, 3H), 6.70-6.84 (m, 6H), 6.87-6.94 (m, 6H), 7.08-7.13 (m, 4H), 7.17-7.21 (m, 4H), 7.26 (dd, $J = 6.8$, 8.1 Hz, 1H), 7.32 (ddd, $J = 1.4$, 6.8, 8.1 Hz, 1H), 7.52 (ddd, $J = 1.4$, 6.8, 8.1 Hz, 1H), 7.64 (d, $J = 8.1$ Hz, 1H), 7.66 (d, $J = 8.1$ Hz, 1H), 7.86 (dd, $J = 1.4$, 6.8 Hz, 1H), 9.01 (d, $J = 8.1$ Hz, 1H). ^{13}C NMR (C_6D_6): δ -5.44, 125.74, 126.17, 126.72, 126.87, 128.07, 128.34, 129.20, 129.37, 130.26, 131.43, 131.52, 133.84, 136.30, 138.03, 139.54, 139.70, 143.29, 155.46 (only 18 signals were observable of 20 aromatic carbons). ^{29}Si NMR (C_6D_6): δ 0.53. UV ($CHCl_3$), λ_{max} (log ε): 239 nm (4.47), 278 nm (4.29), 364 nm (4.01). Anal. Found: C, 88.93; H, 5.74. $C_{39}H_{30}Si$ Calc.: C, 88.68; H, 5.76%.

3.11. Thermal degradation of 1

A solution of 1 (402 mg, 0.98 mmol) in xylene (4 ml) was heated at 145°C under argon for 68 h, then cooled to room temperature and concentrated in vacuo. The residue was bulb-to-bulb distilled (bath temperature 120-140°C/0.8 mmHg) to give $MePh_2SiH$ (55 mg, 0.28 mmol) as a colorless oil in 28% yield. The residue was recrystallized from hexane to give 1 (190 mg, 0.46 mmol) (47% recovery).

3.12. X-ray crystal structure analysis of 2

Crystals were obtained by recrystallization from AcOEt-hexane. 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 structure was solved by heavy-atom Patterson methods (PATTY) [24] and refined using Fourier techniques (DIRDIF92) [25]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 3656 observed reflections ($I > 3.00\sigma(I)$) and 432 variable parameters. The silicon-bound hydrogen atom could be localized from a difference Fourier map. The crystal data and analytical condition and final atomic coordinates and isotropic temperature factors are listed in Tables 1 and 3 respectively.

Complete lists of bond lengths and angles, hydrogen atom coordinates and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

3.13. X-ray crystal structure analysis of 4

Crystals were obtained by recrystallization from THF-hexane. 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 structure was solved by direct methods (SAPI91) [26] and refined using Fourier techniques (DIRDIF92) [25]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 2498 observed reflections ($I > 3.00\sigma(I)$) and 529 variable parameters. The crystal data and analytical condition and final atomic coordinates and isotropic temperature factors are listed in Tables 1 and 5 respectively. Complete lists of bond lengths and angles, hydrogen atom coordinates and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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