Synthesis, Structure, and Reactivity of Trisilanes Containing the 8-(Dimethylamino)-1-naphthyl Group at the Central Silicon Atom. A Novel Nickel- or Palladium-Catalyzed Degradation of Trisilane to Disilane and Silylene Species

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Three trisilanes containing the 8-(dimethylamino)-1-naphthyl group on the central silicon atom have been prepared. While X-ray structural analysis and NMR studies reveal that the trisilane skeleton is rather reluctant to pentacoordination, unusual UV and mass spectral features and high reactivity toward a nickel and a palladium catalyst have been recognized. In the Ni- and Pd-catalyzed reactions, the two terminal silicon atoms in the trisilane couple each other to form the corresponding disilane. The central silicon atom extruded as a reactive silylene species has been trapped with diphenylacetylene in the Pd case to form, after chromatographic workup, a cis/trans mixture of the 4-oxa-3,5-disilacyclopent-1-ene derivative. The X-ray structure of the trans isomer shows the presence of two slightly pentacoordinated silicon atoms.

Introduction

Polysilanes so far studied consist of ordinary tetracoordinate (tetrahedral) silicon moieties.[1] We have been interested in the introduction of pentacoordinate silicon moieties into the polysilane backbone because structural distortion from tetrahedral to, ideally, trigonal bipyramidal geometry must cause perturbation in the characteristic physical properties such as UV absorption and conductivity and the reactivity of Si–Si bonds, due to the bond angle, bond length, and coordination number changes. There have been only four types of scattered examples of oligosilanes which contain a penta- or hexacoordinated silicon moiety: hexacoordinated bipyridyl complexes of polychlorodisilanes and trisilanes,[2] a pentacoordinated [tris(trimethylsilyl)silyl]oxy group observed in a special chromium–carbene complex,[3] silatrane analogues containing the silicon–silicon bond in the cage,[4] and anionic pentacoordinated disilanes with the Martin ligands.[5] In no case, however, have reactivities of the Si–Si bond been examined.

We reasoned that the introduction of *neutral* pentacoordinated silicon moieties should be essential for the synthesis, isolation, and characterization of polysilanes and for the examination of the reactivity, and thus rigid [8-(dimethylamino)naphthyl]silicon compounds, studied extensively by Corriu and his co-workers,[6] would be most suitable for our purpose. We now report the first synthesis of a series of trisilanes containing the 8-(dimethylamino)-1-naphthyl group at the central silicon atom **1–3**, their structural aspects and unusual spectral and chemical behavior. In particular, we have noted an unusually high reactivity of the silicon–silicon bonds toward a nickel and a palladium complex to form disilane and silylene species, the latter being trapped with diphenylacetylene in the palladium case.

Results and Discussion

Synthesis. As shown in eq 1, [8-(dimethylamino)-1-naphthyl]dichloromethylsilane (**4**),[7] prepared from [8-(dimethylamino)-1-naphthyl]lithium[8] and methyltrichlorosilane, was treated with 2 equiv of an appropriate silyllithium in several portions at −60 °C over 10 h. Usual hydrolytic workup followed by recrystallization or chromatographic purification afforded the corresponding trisilane as a colorless crystal (**1**) or viscous oil (**2** and **3**). It was essential not to use an excess amount of silyllithium, which caused cleavage of the Si–Si bonds in the products lowering the yields significantly. Ordinary tetracoordinate analogues **5–7** having no 8-amino group were also prepared as reference compounds by the reaction of 1-naphthyldichloromethylsilane with the corresponding silyllithium.

Solid-State Structure. The X-ray crystal of **1** is shown in Figure 1. A summary of crystallographic data, intensity collection, and least-square processing is shown in Table

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[1] (1) Recent reviews: (a) West, R. *J. Organomet. Chem.* **1986**, *300*, 327. (b) West, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, England, 1989; p 1208. (c) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (d) *Silicon-Based Polymer Science: A Comprehensive Resource*; Zeigler, J. M., Gordon Fearon, F. W., Eds.; American Chemical Society: Washington, DC, 1990. (e) Michl, J. *Synth. Metals* **1992**, *49–50*, 367.

[2] (2) (a) Sawizki, G.; Schnering, H. G. *Chem. Ber.* **1976**, *109*, 3728. (b) Kummer, D.; Balkir, A.; Köster, H. *J. Organomet. Chem.* **1979**, *178*, 29.

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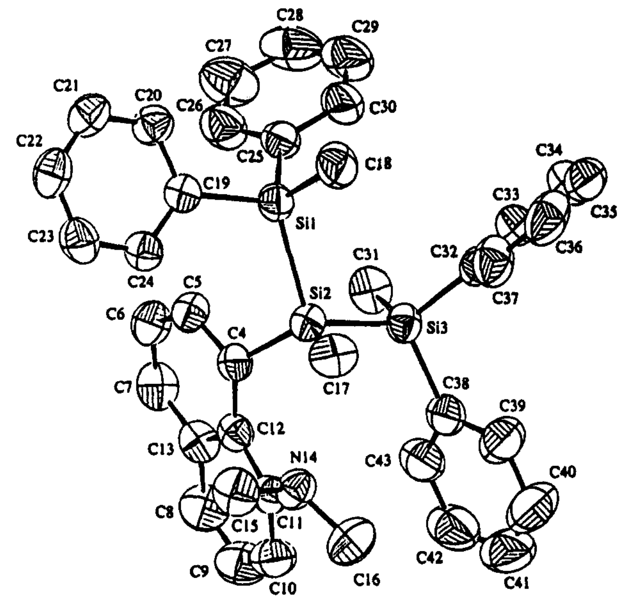
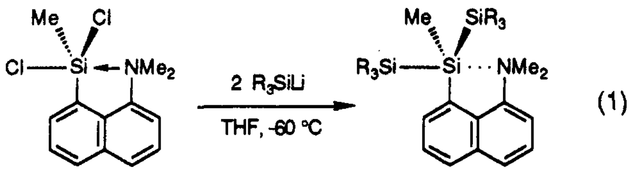


Figure 1. Thermal ellipsoid plot (50% probability level) for 1.



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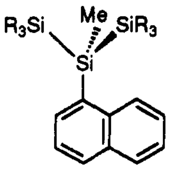
1, R_3Si = Ph_2MeSi 60%
2, R_3Si = $PhMe_2Si$ 43%
3, R_3Si = Me_3Si 23%



5, R_3Si = Ph_2MeSi
6, R_3Si = $PhMe_2Si$
7, R_3Si = Me_3Si

I, and some selected interatomic distances and angles are listed in Table II. Characteristic features are as follows. (1) The geometry about the central silicon atom (Si2) is somewhat deformed from tetrahedral, but not to trigonal bipyramidal. Thus, the interaction of the amino group with Si2 from the region of the smallest methyl group (C17) forces the C17 and Si3 groups away from the nitrogen, resulting in two large bond angles, C4–Si2–C17 = 124.0° and C17–Si2–Si3 = 113.18°, and three small bond angles, C4–Si2–Si3 = 100.92°, C17–Si2–Si1 = 101.88°, and Si1–Si2–Si3 = 107.39°. It is particularly noted here that the last backbone angle Si1–Si2–Si3 is much smaller than the typical values of 115–119° observed in tetracoordinated polysilanes.[1c] (2) The nitrogen atom interacts weakly with the silicon atom Si2. Thus, the N14···Si2 distance, 3.16 Å, is shorter than the sum of van der Waals radii, 3.65 Å, but much longer than those observed in typical penta- or hexacoordinated silicon compounds containing electronegative ligands on silicon (2.6–2.8 Å).[6a,7a] The N14–Si2–Si1 and N14–Si2–Si3 angles are 155.94° and 96.66°, respectively, while the N14–Si2–C4 (64.78°) and N14–Si2–C17 (68.23°) are quite small. Since the Si2–N14–C15 (99.08°) and Si2–N14–C16 (127.50°) are not equal, the lone pair electrons on nitrogen are not directed straight toward the Si2 atom, but are somewhat deviated toward the Si3 atom. (3) The naphthalene ring is not planar and highly distorted,[7c,9] as evidenced by two large dihedral angles C4–C5–C6/C9–C10–C11 (8.83°) and Si2–C4···C11/N14–C11···C4 (34.35°) and by the large displacement of the Si2 and N14 atoms, 0.888 and 0.299 Å, respectively, from each side of the naphthalene mean plane defined by the central six carbon atoms. The extent of deformation of the naphthalene ring is comparable to or larger than that found in slightly hexacoordinated [8-(dimethylamino)-1-naphthyl]silatrane reported recently by Corriu.[7c] (4) While the Si2–Si3 bond length (2.363 Å) is in the range of the standard values (2.33–2.37 Å),[10] the Si1–Si2 bond (2.396 Å) is slightly elongated. It is noted that the Si2–Np(C4) bond (1.904 Å) is elongated considerably (typical Si–C(sp^2) bond: <1.86 Å),[10] being much longer than the Si2–Me(C17) bond (typical Si–C(sp^3) bond: 1.86–1.88 Å).[10] This bond elongation might reveal that the Si2–N14 interaction is not attractive but rather repulsive.

Table I. Crystal Data, Intensity Collection, and Least-Squares Processing for 1

formula	$C_{39}H_{41}NSi_3$
fw	608.00
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	19.354(5)
b, Å	19.060(4)
c, Å	9.698(3)
β, deg	101.99(2)
V, Å^3	3499(1)
Z	4
temp, °C	25
ρ_{calcd}, g cm^{-3}	1.15
μ(Cu Kα), cm^{-1}	13.48
$2\theta_{max}$, deg	130
no. of unique reflns	5833
no. of reflns, used for refinement	5393
no. of variables	512
R	0.045
R_w	0.050
S	1.93

Table II. Selected Interatomic Distances (Å) and Angles (deg) for 1[a]

Distances			
Si1–Si2	2.3958(8)	Si2–Si3	2.3634(8)
Si2–C4	1.904(2)	Si2–C17	1.886(2)
Si2···N14	3.159		
Angles			
Si1–Si2–Si3	107.39(3)	Si1–Si2–C4	108.72(7)
Si1–Si2–C17	101.88(9)	Si3–Si2–C4	100.92(7)
Si3–Si2–C17	113.18(9)	C4–Si2–C17	124.0(1)
N14···Si2–Si1	155.94	N14···Si2–Si3	96.66
N14···Si2–C4	64.78	N14···Si2–C17	68.23
Si2···N14–C15	99.08	Si2···N14–C16	127.50
Dihedral Angles			
C4–C5–C6/C9–C10–C11			8.83
Si2–C4···C11/N14–C11···C4			34.35[b]

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 1. [b] Distance from the naphthalene mean plane defined by the central six carbon atoms: Si2 0.888, N14 0.299 Å.

NMR Studies. In solution, the nitrogen–silicon interaction is so weak that two terminal silyl groups and two methyl groups on nitrogen in 1–3 are equivalent on the NMR time scales at room temperature, as observed by ^{29}Si, ^{13}C, and ^{1}H NMR studies: The ^{29}Si chemical shifts

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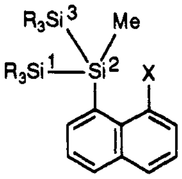
Table III. ^{29}Si Chemical Shifts (δ, ppm) for 1–3 and 5–7[a]



R_3Si	X = NMe_2	X = H	δ(X = NMe_2) – δ(X = H)[b]
Ph_2MeSi	1	5	
Si2	–35.860	–46.974	11.114
Si1, Si3	–18.554	–18.832	0.278
$PhMe_2Si$	2	6	
Si2	–36.705	–47.452	10.747
Si1, Si3	–16.530	–17.218	0.688
Me_3Si	3	7	
Si2	–36.845	–47.776	10.931
Si1, Si3	–13.944	–14.448	0.504

[a] Measured in $CDCl_3$ at 40 MHz. [b] Positive numbers mean downfield shifts.

data are summarized in Table III. It has been further confirmed that two methyl groups on nitrogen in 1 showed no separation even at –60 °C by ^{1}H NMR. Thus, the symmetrization in solution can be attained by flipping of the "nonplanar" Np ring and partial rotation about the Np–Si and Np–N bonds.

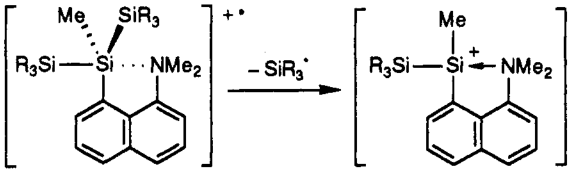
In the ^{29}Si NMR spectroscopy (Table III), the central silicon atom in 1–3 appears about 11 ppm downfield from those in 5–7, little difference being observed for the terminal silicon atoms. While upfield shifts are commonly observed in pentacoordinate silicon compounds with electronegative substituents,[11] the unusual opposite downfield shift might be characteristic of weakly coordinated but sterically distorted silicon species, since an about 10 ppm downfield shift has been observed also in the Corriu's silatrane mentioned above, upon transformation from the pentacoordinate silatrane to the slightly hexacoordinate stage.[7c]

There are also the following tendencies in the ^{13}C and ^{1}H NMR spectra, the data being listed in the Experimental Section. Thus, the ^{13}C chemical shifts of the central methyl group in 1–3 show generally ca. 4.5 ppm downfield shifts in comparison with those in the corresponding tetracoordinate counterparts 5–7, together with very small downfield shifts (0.3–0.7 ppm) of the terminal methyl groups. In the ^{1}H NMR spectra, the central methyl groups show small downfield shifts and the terminal methyl groups move to upfield slightly by the introduction of the 8-(dimethylamino) group.

These structural aspects, both in solid state and in solution, reveal that the central silicon atoms in the trisilanes 1–3 are rather reluctant to pentacoordination: The reason may be attributed primarily to the presence of two electropositive silyl groups. Nevertheless, these trisilanes show unique spectral features and chemical reactivities, as described below.

UV Spectra. In UV absorption spectra (in cyclohexane), 1 and 2 have λ_{max} at 327 nm (ϵ 7900) and 326 nm (ϵ 6600), respectively, showing a nearly 30-nm red shift from λ_{max} 297 nm (ϵ 11 000) for 5 and 295 nm (ϵ 10 000) for 6. In comparison, the corresponding monosilanes, 8-Me_2N-1-$NpSiMe_3$ and 1-$NpSiMe_3$, exhibit λ_{max} 304 and 282 nm,[12] respectively, showing a 20-nm red shift by the introduction of the 8-amino group on the Np ring. The extra 10-nm red shift in the trisilanes 1 and 2 should be attributed to the introduction of the silicon–silicon bonds. The characteristic absorption due to the trisilane backbone, around 240 nm,[1] is hidden by the strong benzenoid absorptions.

Mass Spectra. Mass spectra (EI at 70 eV) of 1–3 are remarkable. In a typical comparison, while 6 shows M^+ (m/e = 440, relative intensity 38) and three fragment peaks, $[M - PhMe_2Si]^+$ (m/e = 305, 36), $[M - PhMe_2Si - Ph]^+$ (m/e = 228, 74), and $[M - PhMe_2Si - Np]^+$ (m/e = 178, 100), 2 shows only one fragment peak, $[M - PhMe_2Si]^+$ (m/e = 348), neither any other fragment nor M^+ peaks being observed: 1 shows similar spectra, but in 3 the base peak $[M - Me_3Si]^+$ accompanies weak $[M - Me_3Si - Me]^+$ and $[M - 2Me_3Si - Me]^+$ peaks. The results demonstrate that the fragment silicon cation 8 is extremely stabilized by nitrogen chelation to prevent further fragmentation especially in 1 and 2, as shown in eq 2.



(2)

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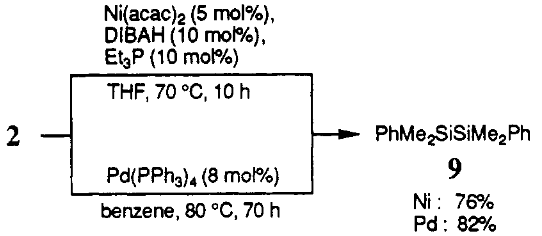
Attempted Photochemical Reactions. The observed small Si–Si–Si angle, slightly long Si–Si bond, and UV absorptions at long wavelengths suggested photochemical reactions such as silylene extrusion and silyl migration to aromatic rings.[13] However, no reaction was observed when a hexane solution of 2 or 3 was irradiated by a low-pressure mercury lamp for 15 h in the presence of an excess amount of ethyldimethylsilane as a silylene trap, under which 2-phenylheptamethyltrisilane was photolyzed smoothly.[13c] Although further detailed work is necessary, these preliminary results suggest the [8-(dimethylamino)naphthyl]-trisilanes to be UV-stable.

Nickel- and Palladium-Catalyzed Reactions. A high chemical reactivity of Si–Si bond in 2 has been observed in nickel- and palladium-catalyzed reactions.[14] Thus, as shown in eq 3, when 2 was heated under reflux in the presence of nickel(0) species (5 mol %) in THF for 10 h or in the presence of $Pd(PPh_3)_4$ (8 mol %) in benzene for 70 h, disilane $PhMe_2SiSiMe_2Ph$ (9) was obtained in 76%



(3)

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[11] Tandura, St. N.; Alekseev, N. V.; Voronkov, M. G. *Top. Curr. Chem.* **1986**, *131*, 99.

[12] Evans, A. G.; Jerome, B.; Ress, N. H. *J. Chem. Soc., Perkin Trans. 2* **1973**, 447.

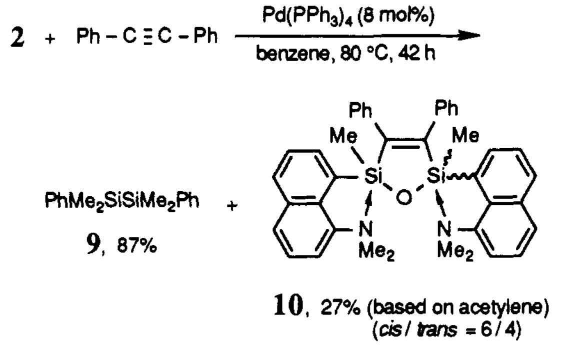
[13] E.g., (a) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51. (b) Ohshita, J.; Ohsaki, H.; Ishikawa, M.; Tachibana, A.; Kurosaki, Y.; Yamabe, T.; Minato, A. *Organometallics* **1991**, *10*, 880. (c) Ishikawa, M.; Nakagawa, K.; Ishiguro, M.; Ohi, F.; Kumada, M. *J. Organomet. Chem.* **1978**, *152*, 155.

[14] Transition metal-catalyzed cleavage reactions have attracted much current interest. (a) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, England, 1989; Part 2, Chapter 24. (b) Tsuji, Y.; Lago, R. M.; Tomohiro, S.; Tsuneishi, H. *Organometallics* **1992**, *11*, 2353 and references cited therein.

and 82% yield (100% conversion), respectively, any product arising from the central silicon atom being isolated in either case. In contrast, **6** which has no 8-(dimethylamino) group gave only 3–4% yield of **9**, together with 84–92% recovery, under the similar or more severe conditions. No cross-over product $Ph_2MeSiSiMe_2Ph$ was obtained from a similar Pd-catalyzed reaction of a mixture of **1** and **2**, demonstrating the intramolecularity in the reaction. In the absence of catalyst, no reaction was observed after 74 h of heating at 80 °C, indicating that the degradation reaction is not thermal but transition metal-catalyzed reaction.

Several points deserve comment. (1) The results clearly demonstrate that the Si–Si bonds in **2** are highly activated toward nickel and palladium complexes. (2) The result provides the first case for a nickel complex to cleave the Si–Si bond under such a mild condition as the reaction is completed at 70 °C within several hours. It should be noted that nickel-catalyzed cleavage reactions of the Si–Si bonds so far reported have required the nearly 1-day heating at 150–220 °C.[15] (3) The reactions provide also the first case for transition metal-catalyzed degradation of trisilane skeleton to disilane and, probably, silylene–transition metal species.[16]

In order to trap the central silicon atom which would be extruded as reactive silylene species, we carried out reactions of **2** in the presence of acetylene. The nickel-catalyzed reaction was, however, completely inhibited by the addition of acetylene such as diphenylacetylene, 5-decyne, and 1,8-diphenyl-1,7-octadiyne, possibly due to blocking of the coordination sites by acetylenes. In contrast, the palladium-catalyzed reaction proceeded smoothly in the presence of diphenylacetylene to give, after chromatographic workup, cyclic disiloxanes **10** as a cis/trans mixture consisting of two silylene moieties, one acetylene, and one oxygen atom, along with **9**, as shown in eq 4. No acetylene insertion into the Si–Si bond[17] was observed at all.



(4)

The X-ray structure of the minor trans isomer of **10** is shown in Figure 2. A summary of crystallographic data, intensity collection, and least-square processing is shown in Table IV, while the selected interatomic distances and angles are summarized in Table V. The data show that the two silicon atoms have intermediate geometries from tetrahedral to pentacoordinate trigonal bipyramidal, as evidence by two shorter N···Si distances (2.906 and 2.857 Å) than that in **1** and the nearly linear N17···Si2–C3 (173.49°) and N43···Si5–C4 (175.50°) arrays. It should be noted that on each side the nitrogen atom and the central ring carbon atom occupy the two "apical" positions, leaving the electronegative oxygen atom in the "equatorial" position. As a result, the apical Si2–C3 (1.904 Å) and Si5–C4 (1.898 Å) are elongated. It is also noted that the Si–Np bonds are longer than the Si–Me bonds, as observed in **1**. The pentacoordination character[18] may be estimated from three strain-free equatorial–equatorial bond angles to be 43% TBP_e and 47% TBP_e for Si2 and Si5, respectively. Two naphthalene rings are highly deformed as in **1**, as evidenced by the dihedral angles and displacement of the Si and N atoms from the Np mean planes listed in Table V. ^1H NMR spectra at room temperature show the diastereotopic nature of the two methyl groups on nitrogen in both isomers of **10**, 2.292 and 2.511 ppm for cis and

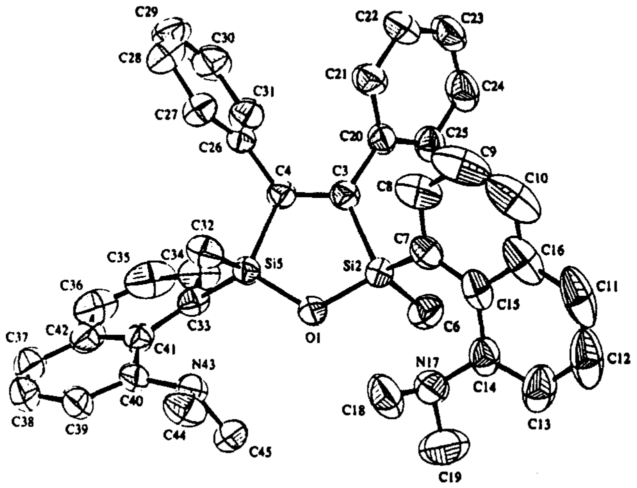


Figure 2. Thermal ellipsoid plot (50% probability level) for *trans*-**10**.

Table IV. Crystal Data, Intensity Collection, and Least-Squares Processing for *trans*-10

formula	$C_{40}H_{40}N_2Si_2$
fw	620.90
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	9.183(2)
b, Å	10.027(2)
c, Å	19.630(3)
α, deg	93.02(2)
β, deg	100.73(2)
γ, deg	101.62(2)
V, Å^3	1732.0(6)
Z	2
temp, °C	25
ρ_{calcd}, g cm^{-3}	1.19
μ(Cu Kα), cm^{-1}	10.90
$2\theta_{max}$, deg	130
no. of unique reflns	5742
no. of reflns, used for refinement	5642
no. of variables	527
R	0.042
R_w	0.071
S	3.12

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(15) Ishikawa, M.; Nishimura, Y.; Sakamoto, H.; Ono, T.; Ohshita, J. *Organometallics* **1992**, *11*, 483.

(16) It has been reported that a palladium-catalyzed reaction of strained octaethylcyclotetrasilane with acetylene forms a small amount of 3,6-disilacyclohexa-1,4-diene in addition to the simple acetylene insertion product. Carlson, C. W.; West, R. *Organometallics* **1983**, *2*, 1801.

(17) (a) Ito, Y.; Suginome, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948. (b) Yamashita, H.; Catellani, M.; Tanaka, M. *Chem. Lett.* **1991**, 241. (c) Watanabe, H.; Kobayashi, M.; Saito, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *216*, 149. (d) Matsumoto, H.; Matsubara, I.; Kato, T.; Shono, K.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1980**, *199*, 43. (e) Watanabe, H.; Kobayashi, N. M.; Higuchi, K.; Nagai, Y. *J. Organomet. Chem.* **1980**, *186*, 51. (f) Tamao, K.; Hayashi, T.; Kumada, K. *J. Organomet. Chem.* **1976**, *114*, C19. (g) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, *97*, 931. (h) Okinoshima, H.; Yamamoto, K.; Kumada, K. *J. Organomet. Chem.* **1975**, *86*, C27.

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

Table V. Selected Interatomic Distances (Å) and Angles (deg) for *trans*-10[a]

	Distances		
Si2–O1	1.651(1)	Si5–O1	1.651(1)
Si2–C3	1.904(1)	Si5–C4	1.898(2)
Si2–C6	1.857(2)	Si5–C32	1.838(2)
Si2–C7	1.885(2)	Si5–C33	1.880(2)
N17···Si2	2.906	N43···Si5	2.857
	Angles		
O1–Si2–C3	98.40(6)	O1–Si5–C4	98.18(6)
O1–Si2–C6	111.28(9)	O1–Si5–C32	112.07(8)
O1–Si2–C7	116.24(8)	O1–Si5–C33	117.30(7)
C6–Si2–C7	114.40(9)	C32–Si5–C33	114.00(9)
C3–Si2–C6	109.17(9)	C4–Si5–C32	107.00(9)
C3–Si2–C7	105.72(8)	C4–Si5–C33	106.30(7)
N17···Si2–C3	173.49	N43···Si5–C4	175.50
N17···Si2–O1	81.54	N43···Si5–O1	83.17
N17···Si2–C6	76.77	N43···Si5–C32	76.30
N17···Si2–C7	68.75	N43···Si5–C33	69.31
	Dihedral Angles		
C8–C9–C10/ C12–C13–C14	11.19	C33–C34–C35/ C38–C39–C40	13.64
Si2–C7···C14/ N17–C14···C7	33.00	Si5–C33···C40/ N43–C40···C33	36.21

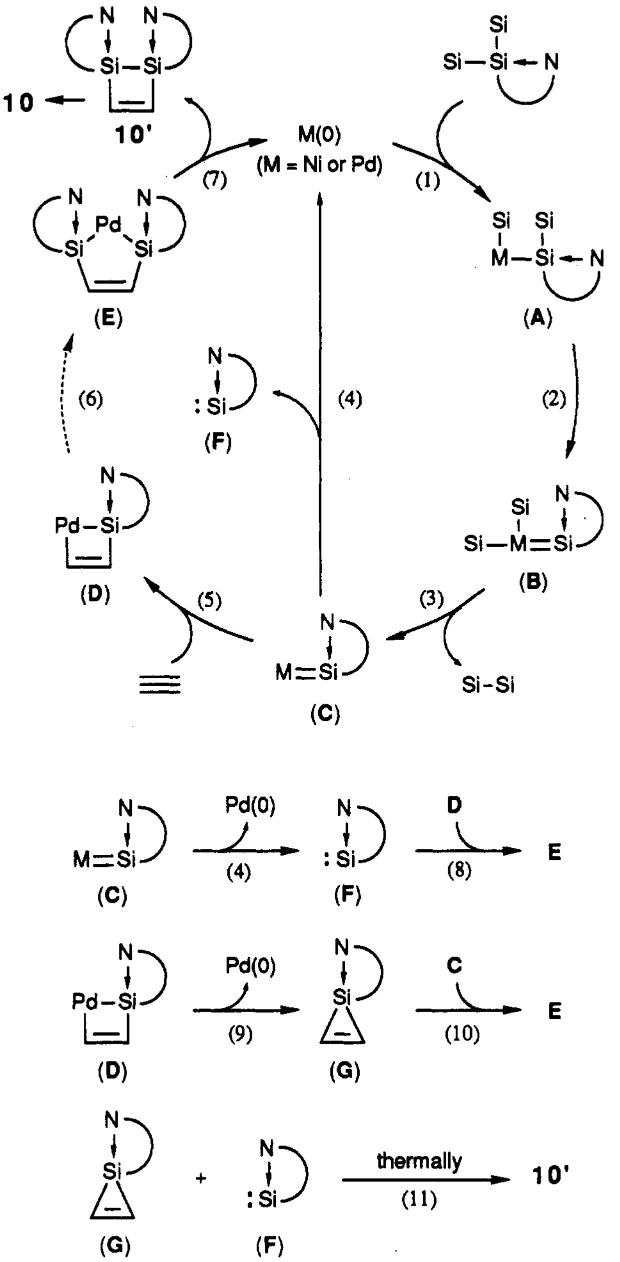
[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 2. [b] Distances from each naphthalene mean plane defined by the central six carbon atoms: Si2 0.735, N17 0.299, Si5 0.853, N43 0.443 Å.

2.400 and 2.583 ppm for trans, indicative of interaction between the dimethylamino group and the chiral silicon center. The enhanced interaction should be ascribed to the presence of the electronegative oxygen atom.

The cyclic disiloxane 10 might have been formed from a presumed product, 3,4-disilacyclobut-1-ene derivative,[19] during the chromatographic workup, since the direct ^1H NMR analysis of the reaction mixture showed no siloxane signals but other unidentified signals nearby (see Experimental Section), which disappeared during workup and were displaced by the siloxane signals. The siloxane bond may thus be ascribed to the hydrolysis and/or air oxidation of the Si–Si bond in 3,4-disilacyclobut-1-ene. Many attempts at isolation of the anticipated primary products have failed so far. In this connection, it is noted that while 3,4-disilacyclobut-1-enes having bulky groups on silicons have been known to be air stable,[19a,b] those with small substituents are readily oxidized in air to form the corresponding cyclic disiloxanes.[19c–e] Furthermore, a recent report has described the synthesis and ready hydrolytic decomposition of a cyclotrisilane containing two 2-[(dimethylamino)methyl]phenyl groups on each silicon atom.[20]

Although the mechanism has not yet been clarified, the results may be rationalized by the following sequence of reactions, as shown in Scheme I: (1) oxidative addition of the Si–Si bond to a Ni(0) or Pd(0) complex, forming a disilyl-metal complex **A**, (2) migration of the terminal silyl group from silicon to the transition metal, forming a silylene–disilyl–metal complex **B**, (3) reductive elimination of disilane, forming a silylene complex **C**, and (4) in the absence of acetylene, decomposition of the silylene complex to a free silylene and the active catalyst, closing the catalytic cycle. There are some literature data pertinent to the catalytic cycle. Thus, the silyl migration (step 2) has many procedents in disilanyl–transition metal systems,[21] including isolable silyl–silylene–iron complexes.[22] It has been well recognized that silylene complexes are stabilized by coordination of a donor to silicon.[23] It should be noted in this connection that intramolecularly

Scheme I[a]



[a] Other ligands on silicon and metal are omitted for clarity.

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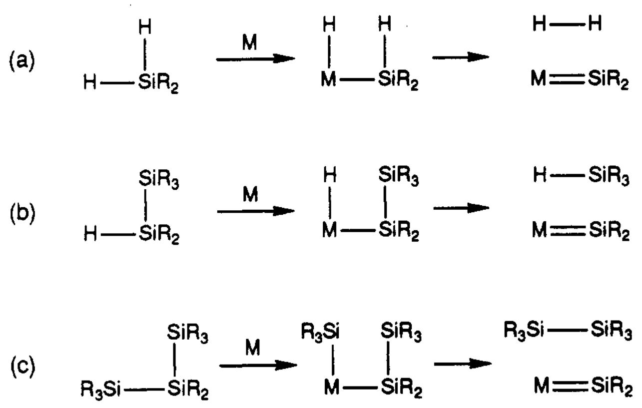
Scheme II



nitrogen-coordinated silylene–transition metal complexes have recently been prepared.[23a–c]

In the presence of acetylene, another catalytic cycle should be involved in the palladium case, as follows: (5) the quenching of the silylene–palladium species by acetylene, forming a cyclic intermediate **D**, (6) reaction of **D** with a silylene species to form a five-membered metalacycle **E**, and (7) reductive elimination of 3,4-disilacyclobut-1-ene **10′** to regenerate Pd(0) species. There are, however, at least two alternative routes in step 6, as shown in Scheme I. Thus, **D** may react with a "free" silylene species **F** to form **E** (step 8) or **D** may form a silacyclopropene **G** via reductive elimination (step 9), which is quenched by **C** to form **E** (step 10). 3,4-Disilacyclobut-1-ene **10′** may also be formed thermally from silylene species **F** and silacyclopropene **G** (step 11). It has been known that while 3,4-disilacyclobut-1-enes are formed thermall or photochemically from a silylene species and silacyclopropene[19a,c,d] or from disilene and acetylene,[19b,e] transition metal-catalyzed reactions of a silylene species with acetylene form not a 3,4-disilacyclobut-1-ene but a silacyclopentadiene or a 3,6-disilacyclohexa-1,4-diene.[24] The proposed intermediates **D** and **E** therefore would form a silacyclopentadiene and a 3,6-disilacyclohexa-1,4-diene in the presence of excess acetylene, respectively. The formation of 1,2-disilacyclobutene **10′** is thus highly puzzling at present, and the mechanistic details will be clarified by further work.

Conclusion

The present study has clearly demonstrated that the introduction of 8-aminonaphthyl group on silicon in polysilane skeleton can alter the reactivities of the particular silicon–silicon bonds, as well as physical properties. It is pointed out that the present transition metal-catalyzed degradations of trisilanes have provided strong evidence for the formation of transition metal-silylene species. Scheme II summarizes three analogous transformations, apart from the mechanistic details, of (a) polyhydrosilane,[23c,25] (b) hydrodisilane,[21] and (c) trisilane into transition metal–silylene species via elimination of hydrogen, hydrosilane, and disilane, respectively. While the first two reactions have already been studied and attracted much current interest as new processes for polysilane synthesis,[25] the last has now been realized by our present work. Further studies are focused on the origin of the activation of the silicon–silicon bond by the 8-(dimethylamino)naphthyl group, mechanistic details of the transition metal-catalyzed transformations, and isolation and characterization of the products arising from the major part of the silylene species (most probably, new types of polysilanes).

Experimental Section

General Remarks. ^{1}H (200 MHz), ^{13}C (50.29 MHz), and ^{29}Si (39.73 MHz) NMR spectra were measured in $CDCl_3$ with a Varian VXR-200 spectrometer, and the chemical shifts were referenced to internal $CHCl_3$ (7.25 ppm). ^{29}Si NMR experiments were performed with proton decoupling, using a standard ^{13}C pulse program. Mass spectra were measured at 70 eV on a JEOL JMS-D300 mass spectrometer connected with a JEOL LGC-20K gas chromatograph, equipped with a 1-m glass column packed with OV-17 (1%) on Chromosorb B and a JMA-2000 data processing system. Melting points were taken on a Yanaco micro melting point apparatus. GLC analysis was performed on a Shimadzu GC-4B gas chromatographed, equipped with a 3-m column packed with 30% Silicone DC550 on Celite 545. Column chromatography was performed by using Kieselgel 60 (70–230 mesh) (Merck). Preparative medium-pressure liquid chromatography was performed with a silica gel prepacked C.I.G. (Kusano) column. Elemental analyses were performed at the Microanalysis Center of Kyoto University. THF and ether were distilled under nitrogen from sodium/benzophenone ketyl, while hexane was distilled from sodium under nitrogen. A hexane solution of n-BuLi was purchased from Nakalai Tesque. 1-(Dimethylamino)naphthalene was available from Sigma. 8-(Dimethylamino)-1-naphthyllithium etherate was prepared in 78% yield by metalation of 1-(dimethylamino)naphthalene by n-BuLi in hexane at room temperature for 5 days, followed by filtration and washing with hexane under nitrogen and drying in vacuo, according to the literature method.[8] [8-(Dimethylamino)-1-naphthyl]dichloromethylsilane (4) was prepared in 50% yield by the literature method from trichloromethylsilane and 8-(dimethylamino)-1-naphthyllithium etherate.[7] Tetrakis(triphenylphosphine)palladium(0) was prepared by the published method.[26] 1-Naphthyldichloromethylsilane was prepared in 50% yield from trichloromethylsilane and 1-naphthyllithium at −70 °C. Bis(acetylacetonato)nickel(II) was dried in vacuo (100 °C, 0.5 mmHg, 10 h), before use. While dimethylphenylsilyllithium and methyldiphenylsilyllithium were prepared from the corresponding chloride and lithium pore (ϕ 2 mm, 2–3 mm, available from Nakalai Tesque) in THF at room temperature for 4 h,[27] trimethylsilyllithium was prepared from hexamethyldisilane and methyllithium.[27b,28]

2-[8-(Dimethylamino)-1-naphthyl]-1,2,3-trimethyl-1,1,3,3-tetraphenyltrisilane (1). To a solution of 4 (1.59 g; 5.6 mmol) in THF (10 mL) was added with stirring, at −60 °C over 10 h in five portions, a solution of methyldiphenylsilyllithium, prepared from methyldiphenylsilyl chloride (3.39 g; 14.5 mmol), lithium pole (400 mg; 58 mg-atom), and THF (16 mL): The addition rate was controlled by monitoring the disappearance of the reddish color of the silyllithium. After being stirred for additional 1 h, the mixture was hydrolyzed by addition of water. The organic layer was separated and the aqueous layer was extracted with

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ether. The combined organic layer was washed with brine, dried over magnesium sulfate, and concentrated in vacuo. The remaining solid was recrystallized from a 1:1 mixture of hexane and ethyl acetate to give 2.04 g (60% yield) of **1** as colorless crystals. Mp: 139–140 °C. ^{1}H NMR: δ 0.343 (s, 6 H), 0.806 (s, 3 H), 2.206 (s, 6 H), 6.844 (dd, J = 1.3 and 7.5 Hz, 1 H), 7.039 (dd, J = 6.9 and 8.1 Hz, 1 H), 7.10–7.26 (m, 20 H), 7.319 (dd, J = 2.3 and 7.6 Hz, 1 H), 7.457 (dd, J = 1.2 and 8.0 Hz, 1 H), 7.672 (dd, J = 1.1 and 8.1 Hz, 1 H), 7.740 (dd, J = 1.3 and 6.9 Hz, 1 H). ^{13}C NMR: δ −2.700, −0.506, 45.680, 114.490, 123.859, 124.193, 125.548, 127.469, 127.535, 128.374, 128.419, 129.573, 132.483, 134.177, 135.125, 135.176, 135.510, 137.817, 137.964, 138.033, 152.809. MS (70 eV): *m/e* 410 (M$^+$ − SiMePh$_2$, 100). Anal. Calcd for $C_{39}H_{41}NSi_3$: C, 77.04; H, 6.80; N, 2.30. Found: C, 76.94; H, 6.73; N, 2.30.

2-[8-(Dimethylamino)-1-naphthyl]-1,1,2,3,3-pentamethyl-1,3-diphenyltrisilane (2). In a manner similar to that above, **4** (1.78 g; 6.3 mmol) was treated with dimethylphenylsilyllithium, prepared from dimethylphenylsilyl chloride (2.20 g; 12.9 mmol), lithium pole (348 mg,; 50.2 mg-atom), and THF (13 mL). After usual workup, the remaining viscous oil was subjected to silica gel column chromatography (hexane/ethyl acetate (30/1), R_f 0.35) to give 1.29 g (43% yield) of **2** as a colorless viscous oil. ^{1}H NMR: δ 0.184 (s, 6 H), 0.200 (s, 6 H), 0.653 (s, 3 H), 2.348 (s, 6 H), 6.917 (dd, J = 1.3 and 7.4 Hz, 1 H), 7.14–7.27 (m, 11 H), 7.318 (d, J = 7.4 Hz, 1 H), 7.439 (dd, J = 1.3 and 8.1 Hz, 1 H), 7.651 (d, J = 6.9 Hz, 1 H), 7.657 (d, J = 6.9 Hz, 1 H). ^{13}C NMR: δ −1.879, −1.652, −1.505, 45.693, 113.940, 123.702, 124.090, 125.399, 127.461, 128.110, 129.159, 133.288, 133.874, 133.988, 125.447, 136.428, 140.484, 152.729. MS: *m/e* 348 (M$^+$ − SiMe$_2$Ph, 100). Anal. Calcd for $C_{29}H_{37}NSi_3$: C, 71.99; H, 7.71; N, 2.89. Found: C, 72.27; H, 7.84; N, 2.88.

2-[8-(Dimethylamino)-1-naphthyl]heptamethyltrisilane (3). To a solution of **4** (933 mg; 3.28 mmol) in THF (5 mL) was added, at −60 °C over 7 h in five portions, a solution of trimethylsilyllithium, prepared from hexamethyldisilane (1.58 g; 10.8 mmol) and methyllithium (1.1 M ether solution, 9.1 mmol) in THF (10 mL) and HMPA (7 mL). After being stirred for 2 h, usual workup gave a viscous oil. Purification by silica gel column chromatography followed by MPLC (hexane/ethyl acetate (30/1), R_f 0.63) gave 273 mg (23% yield) of **3** as a colorless viscous oil. ^{1}H NMR: δ 0.023 (s, 18 H), 0.601 (s, 3 H), 2.629 (s, 6 H), 7.089 (dd, J = 1.3 and 7.3 Hz, 1 H), 7.26–7.40 (m, 2 H), 7.480 (dd, J = 1.3 and 8.0 Hz, 1 H), 7.677 (s, 1 H), 7.714 (s, 1 H). ^{13}C NMR: δ −2.807, 0.200, 46.298, 113.912, 123.998, 124.176, 125.346, 128.984, 134.036, 134.368, 135.436, 136.075, 153.073. MS: *m/e* 286 (M$^+$ − SiMe$_3$, 100), 271 (26), 198 (27). Anal. Calcd for $C_{19}H_{33}NSi_3$: C, 63.44; H, 9.25; N, 3.89. Found: C, 63.20; H, 9.39; N, 3.70.

2-(1-Naphthyl)-1,2,3-trimethyl-1,1,3,3-tetraphenyltrisilane (5). To a solution of 1-naphthyldichloromethylsilane (967 mg; 4.0 mmol) in THF (5 mL) was added to THF solution of methyldiphenylsilyllithium (3 molar excess) at 0 °C over 10 min. The mixture was stirred at room temperature overnight. After usual workup, tetraphenyldimethyldisilane was removed by recrystallization from hexane/ethyl acetate. The filtrate was condensed in vacuo and subjected to silica gel column chromatography and MPLC (hexane/ethyl acetete (30/1), R_f 0.38) to give 708 mg (31% yield) of **5**. ^{1}H NMR: δ 0.459 (s, 6 H), 0.544 (s, 3 H), 6.80–6.92 (m, 1 H), 7.04–7.42 (m, 22 H), 7.48–7.60 (m, 2 H), 7.72–7.83 (m, 2 H). ^{13}C NMR: δ −5.101, −2.284, 124.679, 125.357, 127.548, 127.785, 128.323, 128.662, 128.935, 128.988, 130.157, 133.084, 134.556, 134.993, 135.149, 135.264, 135.543, 136.578, 137.015, 137.254. MS: *m/e* 564 (M$^+$, 36), 367 (M$^+$ − SiMePh$_2$, 58), 352 (17), 290 (74), 240 (M$^+$ − SiMePh$_2$ − Np, 100), 197 (30). Anal. Calcd for $C_{37}H_{36}Si_3$: C, 78.66; H, 6.42. Found: C, 78.90; H, 6.44.

2-(1-Naphthyl)-1,1,2,3,3-pentamethyl-1,3-diphenyltrisilane (6). In a manner similar to that above, 1-naphthyldichloromethylsilane (973 mg; 4.03 mmol) and dimethylphenylsilyllithium (2.4 molar equiv) gave 881 mg (50% yield) of **6** as viscous oil, after MPLC purification (silica gel, hexane/ethyl acetate (10/1), R_f 0.47). ^{1}H NMR: δ 0.247 (s, 6 H), 0.302 (s, 6 H), 0.424 (s, 3 H), 7.15–7.50 (m, 14 H), 7.50–7.83 (m, 3 H). ^{13}C NMR: δ −6.608, −2.406, −2.172, 124.745, 125.343, 127.588 128.439, 128,528, 128.613, 129.539, 133.033, 133.803, 133.981, 135.857, 137.333, 139.246. MS: *m/e* 440 (M$^+$, 38), 305 (M$^+$ − SiMe$_2$Ph, 36), 290 (10), 228 (75), 178 (M$^+$ − SiMe$_2$Ph − Np, 100), 135 (16). Anal. Calcd for $C_{27}H_{32}Si_3$: C, 73.57; H, 7.32. Found: C, 73.45; H, 7.24.

(1-Naphthyl)heptamethyltrisilane (7). In a manner similar to that described for the synthesis of **3**, 1-naphthyldichloromethylsilane (1.98 g; 8.23 mmol) was treated with trimethylsilyllithium (2.5 molar equiv) at −60 °C. Usual workup and silica gel column chromatography (hexane/ethyl acetate (30/1), R_f 0.68) followed by bulb-to-bulb distillation (bath temperature, 100–120 °C/0.2 mmHg) gave 466 mg of a 3:1 mixture of **7** and 1-(1-naphthyl)-1-hydrotetramethyldisilane, which were separated by preparative GLC. **7**. ^{1}H NMR: δ 0.104 (s, 18 H), 0.530 (s, 3 H), 7.35–7.50 (m, 3 H), 7.575 (dd, J = 6.9 and 1.3 Hz, 1 H), 7.74–7.94 (m, 3 H). ^{13}C NMR: δ −7.293, −0.447, 124.810, 125.338, 125.389, 128.422, 128.707, 129.091, 133.082, 133.515, 136.695, 137.496. MS: *m/e* 316 (M$^+$, 12), 243 (M$^+$ − SiMe$_3$, 48), 227 (29), 185 (20), 116 (M$^+$ − SiMe$_3$ − Np), 73 (19). 1-(1-Naphthyl)-1-hydrotetramethyldisilane: ^{1}H NMR: δ 0.094 (s, 9 H), 0.549 (d, J = 4.7 Hz, 3 H), 4.622 (q, J = 4.7 Hz, 1 H), 7.38–7.55 (m, 3 H), 7.665 (dd, J = 6.8 and 1.3 Hz, 1 H), 7.78–7.99 (m, 2 H), 7.95–8.05 (m, 1 H). ^{13}C NMR: δ −7.616, −1.439, 125.238, 125.506, 125.597, 128.171, 128.764, 129.350, 133.072, 134.128, 134.769, 137.207. MS: *m/e* (M$^+$, 32), 185 (100), 73 (70). Anal. Calcd for $C_{14}H_{20}Si_2$: C, 68.78; H, 8.25. Found: C, 68.50; H, 8.37.

Attempted Photolysis of 2 and 3. A solution of **2** (218 mg; 0.45 mmol) and diethylmethylsilane (262 mg; 2.56 mmol) in hexane (60 mL) was irradiated by a low-pressure mercury lamp through a quartz filter under a slow nitrogen stream for 7 h. ^{1}H NMR and GLC analysis of the reaction mixture showed no reaction. A solution of **3** (104 mg; 0.29 mmol) and diethylmethylsilane (772 mg; 7.55 mmol) in hexane (6 mL) was also irradiated by a low-pressure mercury lamp for 15 h, but no reaction was observed.

Nickel(0)-Catalyzed Reaction of 2. To a solution of **2** (238 mg; 0.49 mmol) in THF (1 mL) was added a solution of nickel(0) complex, prepared from [Ni(acac)$_2$] (6.4 mg; 0.025 mmol, 5 mol %) in THF (1 mL) by successive addition of triethylphosphine (7.4 μL; 0.05 mmol) and diisobutylaluminum hydride (DIBAH, 1 M hexane solution, 50 μL, 0.05 mmol) at room temperature. The mixture was refluxed under nitrogen for 10 h. TLC analysis showed complete disappearance of **2**. After evaporation of solvent, the residue was subjected to silica gel column chromatography (hexane) to give 101 mg (0.37 mmol, 76% yield) of 1,2-diphenyltetramethyldisilane (**9**), which was identified by comparison with the authentic sample, prepared by the reaction of phenyldimethylsilyllithium and phenyldimethylsilyl chloride.

Nickel(0)-Catalyzed Reaction of 2 in the Presence of Acetylene. A similar reaction of **2** (489 mg; 1.01 mmol) was carried out in the presence of 2 molar equiv of diphenylacetylene. After 20 h of reflux, no reaction was confirmed by ^{1}H NMR analysis of the reaction mixture. Column chromatography afforded 399 mg (81% recovery) of **2**. Similar results were obtained in the presence of 5-decyne and 1,8-diphenyl-1,7-octadiyne.

Nickel(0)-Catalyzed Reaction of 6. In a manner similar to that described for the reaction of **1**, a mixture of **6** (224 mg; 0.51 mmol), nickel(0)/triethylphosphine complex, and THF (2 mL) was refluxed for 42 h. Column chromatography afforded 3.8 mg (3% yield) of **9** and 199 mg (84% recovery) of **6**.

Palladium(0)-Catalyzed Reaction of 2. A solution of **2** (264 mg; 0.55 mmol) and Pd(PPh$_3$)$_4$ (47 mg; 0.04 mmol; 7 mol %) in benzene (3 mL) was refluxed under nitrogen for 70 h. TLC analysis showed the disappearance of **2**. Silica gel column chromatography (hexane) gave 121 mg (82% yield) of 1,2-diphenyltetramethyldisilane (**9**).

Palladium(0)-Catalyzed Reaction of a Mixture of 1 and 2. A similar reaction of a mixture of **1** (358 mg; 0.59 mmol), **2** (286 mg; 0.59 mmol), Pd(PPh$_3$)$_4$ (86 mg; 0.07 mmol; −6 mol %), and benzene (7 mL) afforded **9** (130 mg; 82% yield) and 1,2-dimethyltetraphenyldisilane (209 mg; 90% yield). 1,1,2-Triphenyltrimethyldisilane was not detected.

Palladium(0)-Catalyzed Reaction of 2 in the Presence of Diphenylacetylene. A mixture of **2** (144 mg; 0.30 mmol), diphenylacetylene (53 mg; 0.30 mmol), $Pd(PPh_3)_4$ (28 mg; 0.025 mmol; 8 mol %), and benzene (2 mL) was refluxed under nitrogen for 42 h. Consumption of **2** was confirmed by TLC analysis. Column chromatography on silica gel (hexane/ethyl acetate (30/1)) afforded **9** (70 mg/ 87% yield) and a cis/trans mixture of 1,2-diphenyl-3,5-bis[8-(dimethylamino)-1-naphthyl]-3,5-dimethyl-4-oxa-3,5-disilacyclopent-1-ene (**10**) (R_f 0.23). Each stereoisomer was separated by MPLC, and there were obtained 15.6 mg (17% yield based on diphenylacetylene) of *cis*-**10** and 9.2 mg (10% yield based on diphenylacetylene) of *trans*-**10**. ***cis*-10.** Mp: 86–87 °C. ^1H NMR ($CDCl_3$, 200 MHz): δ 0.695 (s, 6 H), 2.431 (s, 6 H), 2.510 (s, 6 H), 6.70–6.85 (m, 4 H), 6.85–7.00 (m, 6 H), 7.05–7.20 (m, 4 H), 7.366 (t, J = 7.4 Hz, 2 H), 7.521 (dd, J = 1.2 and 8.2 Hz, 2 H), 7.681 (dd, J = 1.1 and 8.1 Hz, 2 H), 7.866 (dd, J = 1.2 and 6.9 Hz, 2 H); ^1H NMR (C_6D_6, 200 MHz): δ 0.954 (s, 6 H), 2.292 (s, 6 H), 2.511 (s, 6 H), 6.80–7.20 (m, 14 H), 7.274 (t, J = 7.4 Hz, 2 H), 7.442 (dd, J = 1.2 and 8.1 Hz, 2 H), 7.564 (dd, J = 1.2 and 8.2 Hz, 2 H), 8.311 (dd, J = 1.2 and 6.8 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 50.29 Hz): δ 2.927, 44.788, 49.348, 115.525, 124.567, 124.749, 125.072, 125.404, 127.377, 128.677, 129.733, 132.950, 134.377, 134.478, 137.359, 143.379, 152.859. 161.812. MS: 620 (M^+, 7), 576 (100). Anal. Calcd for $C_{40}H_{40}N_2OSi_2$: C, 77.34; H, 6.49; N, 4.51. Found: C, 77.56; H, 6.48; N, 4.42. ***trans*-10.** Mp: 214–216 °C. ^1H NMR ($CDCl_3$, 200 MHz): δ 0.550 (s, 6 H), 2.614 (s, 12 H), 6.68–6.82 (m, 4 H), 6.84–6.98 (m, 6 H), 7.177 (dd, J = 1.2 and 7.4 Hz, 2 H), 7.35–7.48 (m, 4 H), 7.605 (dd, J = 1.1 and 8.1 Hz, 2 H), 7.820 (dd, J = 1.1 and 8.1 Hz, 2 H), 8.147 (dd, J = 1.2 and 6.8 Hz, 2 H); ^1H NMR (C_6D_6, 200 MHz): δ 0.793 (s, 6 H), 2.450 (s, 6 H), 2.583 (s, 6 H), 6.78–6.98 (m, 6 H), 7.00–7.12 (m, 6 H), 7.28–7.44 (m, 4 H), 7.526 (dd, J = 1.2 and 8.3 Hz, 2 H), 7.695 (dd, J = 1.3 and 8.2 Hz, 2 H), 8.549 (dd, J = 1.3 and 6.9 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 50.29 Hz): δ 1.662, 43.481, 50.640, 115.236, 124.434, 124.822, 125.261, 125.621, 127.372, 128.900, 129.954, 133.502, 134.432, 134.523, 137.574, 143.025, 153.024, 161.637. MS: 620 (M^+, 6), 576 (100). Anal. Calcd for $C_{40}H_{40}N_2OSi_2$: C, 77.34; H, 6.49; N, 4.51. Found: C, 77.11; H, 6.65; N, 4.26.

A direct analysis of the reaction mixture by ^1H NMR (C_6D_6, 200 MHz) showed signals at δ 0.338 and 0.793 assignable to SiMe and δ 2.717 and 2.186 assignable to NMe_2, which were near the signals diagnostic of **10**. These signals, possibly assignable to 3,4-disilacyclobut-1-ene derivatives, disappeared and were displaced by the signals assignable to **10** upon dissolution in $CDCl_3$, upon exposure to moist air (especially in the presence of Pd catalyst), or during chromatographic workup under various conditions.

Palladium(0)-Catalyzed Reaction of 6. A mixture of **6** (106 mg; 0.24 mmol), $Pd(PPh_3)_4$ (23 mg; 0.02 mmol, 8 mol %), and benzene (2 mL) was refluxed under nitrogen for 70 h. Column chromatography gave 2.8 mg (4% yield) of **9**, together with 90% recovery of **6**.

X-ray Studies. Intensity data were collected on a Mac Science MXC3 diffractometer using an $\omega - 2\theta$ scan technique, and unique reflections within $3 \leq 2\theta \leq 130°$ were collected. The structure was solved by the direct method[29] and refined anisotropically by the full-matrix least-squares method. The thermal parameter of each hydrogen atom was assumed to be isotropic and equal to that of the bonded atom.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and all bond distances and angles for **1** and **10** (10 pages). Ordering information is given on any current masthead page.

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