Palladium-Catalyzed Insertion of Isocyanides into the Silicon–Silicon Linkages of Oligosilanes

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Abstract: Full details of a study on the reactions of oligosilanes with isocyanides promoted by a palladium catalyst are described. Heating a mixture of oligosilanes and excess 2,6-disubstituted aryl isocyanide in the presence of palladium(II) acetate led to the complete insertion of isocyanide into all silicon–silicon linkages, giving oligo(silylimine) derivatives. The oligo(silylimine)s have been isolated and characterized so far in the complete insertion reaction with oligosilanes up to a hexasilane. Use of the limiting amount of isocyanide permitted insertion of isocyanide into predominantly the terminal silicon–silicon linkages. The mode of the insertion reaction depends on the substituent at the silicon, e.g., tetrasilanes with phenyl groups on the internal silicon atoms favorably underwent the insertion reaction at the terminal silicon–silicon linkages, resulting in the partial insertion. The bulkiness of the ortho substituents on the aromatic isocyanide was also found to have much influence on the insertion; hence, 2,6-diisopropylphenyl isocyanide favored the partial insertion. New skeletal rearrangement of oligosilanes took place in a palladium-catalyzed reaction of substituted aryl isocyanide with tetra- and hexasilanes, forming 3,3-bis(silyl)-1-aza-2,4-disilacyclobutane derivatives. The rearrangement, which is unique and intriguing in that the product is properly reconstituted from four fragments of the tetrasilane and two fragments of the isocyanide, was promoted in the copresence of a *tert*-alkyl isocyanide.

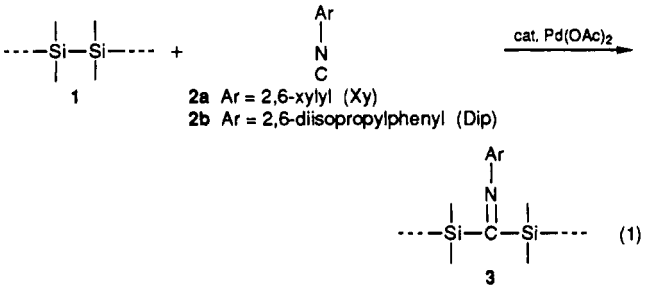
Introduction

The application of organosilicon compounds to organic synthesis has exploded in the last two decades.[1] The unique chemical reactivities of organosilicons, unlike their counterparts, have been exploited to develop a variety of selective synthetic reactions. Recently, organosilicon compounds, including silicon-containing polymers such as polysilanes, have attracted much attention as new functionalized materials, e.g., photoresistant and photoconducting films, due to their chemical and physical properties.[2]

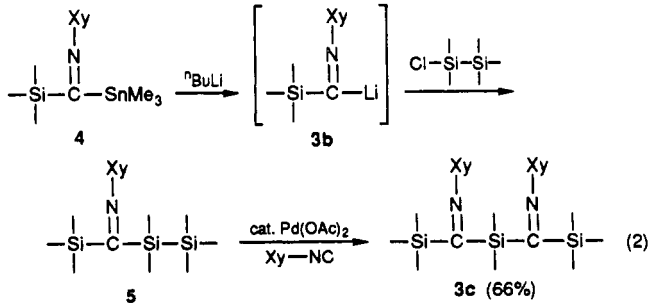
From the viewpoints of the synthetic utility and the invention of new materials, it has been desirable to develop syntheses and synthetic methods of new organosilicon compounds. In previous communications, we documented a palladium-catalyzed insertion of isocyanide into the Si–Si linkage of oligosilanes, giving bis(organosilyl) imine derivatives.[3] The synthesis of bis(organosilyl) imines, which are the nitrogen analogues of bis(organosilyl) ketones and otherwise difficult to synthesize, provided an entry into a new field of organosilicon chemistry. Herein, we present full details of our study on the insertion reactions of isocyanides into oligosilanes promoted by a palladium catalyst, including a related new and novel skeletal rearrangement of oligosilanes.

Complete Insertion of Isocyanides into Oligosilanes

The insertion of isocyanide into the Si–Si linkage of disilanes was originally discovered by use of tetrakis(triphenylphosphine)palladium catalyst. Later we found that 2–10 mol % of palladium(II) acetate was a more convenient and efficient catalyst for the insertion reaction. Complete insertion of 2,6-disubstituted aryl isocyanide **2** into all Si–Si linkages of oligosilanes **1**, which contained two or more contiguous silicon centers, was achieved by heating a mixture of **1** and an excess of **2** in the presence of palladium(II) acetate (Table I). The oligo(silylimine) derivatives **3** thus obtained from 2,6-disubstituted aryl isocyanide were more stable than those derived from other isocyanides, such as cyclohexyl and *o*-tolyl isocyanides.[3a,4] The insertion products **3a** and **4b** obtained from hexamethyldisilane (**1a**) were thermally so stable as to be isolated by distillation, although exposure to the air caused gradual decomposition (eq 1).



An isocyanide molecule was regularly inserted into all Si–Si linkages of the trisilanes (Table I, entries 3–6). Products **3c–f** were yellow solids, which were isolated by filtration of the reaction mixture through a short column under a nitrogen atmosphere to remove the palladium catalyst, followed by recrystallization from dry ethanol or by Kugelrohr distillation. The insertion of **2b**, having isopropyl groups in both of the ortho positions, into trisilane **1b** required a prolonged reaction time, and the resultant **3d** was stable enough to allow its handling in the air (entry 4). Concerning the structure of the product, the insertion of an isocyanide into each Si–Si linkage of the trisilanes was confirmed by comparison with the oligo(silylimine) derivatives prepared independently as outlined in eqs 2 and 3. 2,2,4,4,5,5-Hexamethyl-3-(2,6-xylylimino)-2,4,5-trisilahexane (**5**) was prepared by transmetalation of [(trimethylsilyl)(2,6-xylylimino)methyl]trimethylstannane (**4**) followed by coupling with chloropentamethyldisilane.[5] A palladium-catalyzed reaction of **5** with 2,6-xylyl isocyanide afforded the oligo(silylimine) derivative in 66% yield, which proved to be



(1) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988.

(2) (a) *Silicon-Based Polymer Science*; Zeigler, J. M., Fearon, F. W. G., Eds.; Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1990. (b) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (c) West, R. *J. Organomet. Chem.* **1986**, *300*, 327.

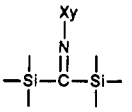
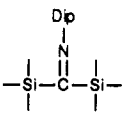
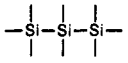
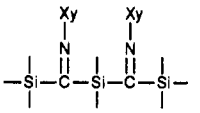
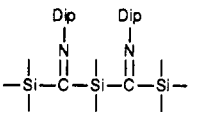
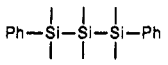
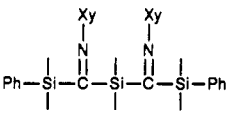
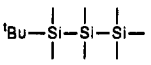
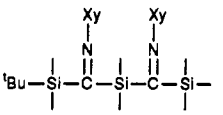
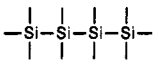
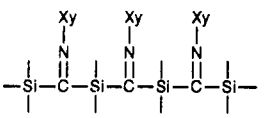
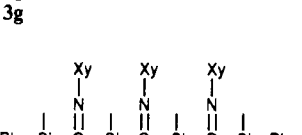
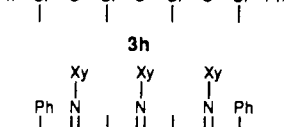
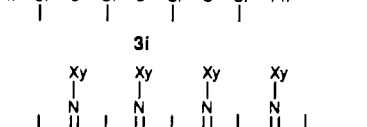
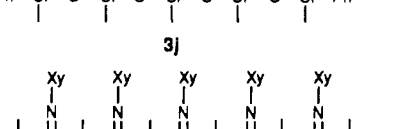
(3) (a) Ito, Y.; Nishimura, S.; Ishikawa, M. *Tetrahedron Lett.* **1987**, *28*, 1293. (b) Ito, Y.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1988**, *110*, 3692.

(4) *tert*-Alkyl isocyanides failed to undergo an insertion reaction into disilanes.

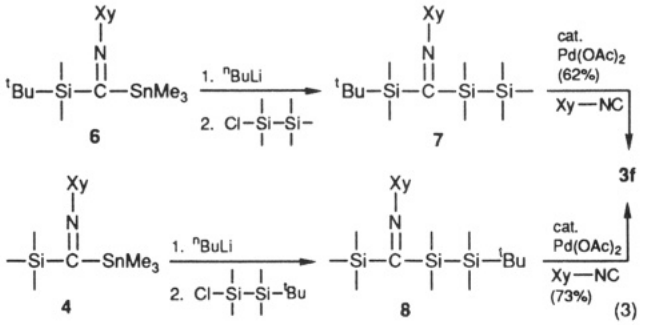
(5) Ito, Y.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1987**, *109*, 7888.

0002-7863/91/1513-8899$02.50/0

Table I. The Complete Insertion of Aryl Isocyanides into Oligosilanes

entry	1	2 (equiv)	conditions	3	yield, %
1	 **1a**	**2a** (1.0)	toluene reflux, 1 h	 **3a**	66
2		**2b** (1.0)	toluene reflux, 1 h	 **3b**	81
3	 **1b**	**2a** (2.5)	toluene reflux, 4 h	 **3c**	57
4		**2b** (7.1)	toluene reflux, 40 h	 **3d**	64
5	 **1c**	**2a** (3.0)	DMF, 70 °C, 5 h	 **3e**	62
6	 **1d**	**2a** (3.1)	toluene, 150 °C, 6 h	 **3f**	82
7	 **1e**	**2a** (3.5)	toluene, 70 °C, 22.5 h	 **3g**	24
8	**1e**	**2a** (3.5)	toluene reflux, 4 h (111 °C)	**3g**	39
9	**1e**	**2a** (3.5)	*n*-octane, 110 °C, 4 h	**3g**	31
10	**1e**	**2a** (3.5)	diglyme, 110 °C, 4 h	**3g**	40
11	**1e**	**2a** (3.5)	DMF, 70 °C, 6.5 h	**3g**	55
12	**1e**	**2a** (3.5)	DMF, 110 °C, 4 h	**3g**	complex mixture
13	**1f**	**2a** (4.5)	DMF, 70 °C, 9 h	 **3h**	43
14	 **1g**	**2a** (3.9)	DMF, 70 °C, 15 h	 **3i**	28
15	 **1h**	**2a** (6.5)	DMF, 70 °C, 30 h	 **3j**	40
16	 **1i**	**2a** (10.1)	DMF, 70 °C, 46 h	 **3k**	28

identical with **3c** synthesized by the regular bis-insertion into octamethyltrisilane (**1b**). Furthermore, 2,2,3,3,5,5,6,6-octamethyl-4-(2,6-xylylimino)-2,3,5-trisilaheptane (**7**) and 2,2,4,4,5,5,6,6-octamethyl-3-(2,6-xylylimino)-2,4,5-trisilaheptane (**8**) were prepared in a similar manner from [(*tert*-butyldimethylsilyl)(2,6-xylylimino)methyl]trimethylstannane (**6**) and [(trimethylsilyl)(2,6-xylylimino)methyl]trimethylstannane (**4**), respectively. Both unsymmetrical oligo(silylimine) derivatives,



(3)

which were obtained by further insertion of 2,6-xylyl isocyanide (**2a**) into regioisomers **7** and **8**, respectively, were also identical with **3f** prepared directly from 1-*tert*-butylheptamethyltrisilane (**1d**). These findings may indicate that no successive insertion of two or more molecules of isocyanide into a Si–Si linkage of trisilane took place. Since multiple successive insertions of sterically bulky isocyanides have been promoted by various organometallic compounds,[6] the regular insertion of one molecule of isocyanide into a Si–Si linkage does not seem to be attributable to only steric causes.

Tetrasilanes **1e** and **1f** also permitted the palladium-catalyzed complete insertion of 2,6-xylyl isocyanide (**2a**) into all of the Si–Si linkages to give **3g** and **3h** in moderate yield (Table I, entries 11 and 13). The reaction of the tetrasilane **1g** gave **3i** in a lower yield, presumably because of the sterically bulky diphenylmethylsilyl groups as the terminal silicons (entry 14). No considerable solvent effect was observed for decamethyltetrasilane (**1e**) (entries 7–12). The insertion reaction proceeded well at 110 °C in toluene, *n*-octane, and diglyme. *N*,*N*-Dimethylformamide (DMF) was also usable, and the reaction at 70 °C provided a satisfactory yield of 55%. However, a reaction temperature of 110 °C in DMF gave a complex mixture. The structure verification of the complete insertion products has been provided by a single-crystal diffraction study of **3g**. The crystal structure is shown in Figure 1, together with selected bond lengths and angles. Noteworthy was that three pendent 2,6-xylylimino groups on the main chain skeleton were skewed in relation to each other to release the steric repulsion between them.

The palladium-catalyzed complete insertion of isocyanides into all of the Si–Si linkages was successfully applied to pentasilane **1h** and hexasilane **1i** (Table I, entries 15 and 16). The product yield decreased with longer silicon chains but was still moderate, indicating that the multiple insertion processes involved in the reactions of oligosilanes **1h** and **1i** proceeded with an efficiency of approximately 80% for each insertion. With hexacosamethyldodecasilane, however, a desired oligo(silylimine) derivative was not isolated. The decrease in the yields of complete insertion products might be mainly attributed to an extrusion of silylene from the contiguous silicon chain via a palladium–silylene complex, which is presumably involved in a skeletal rearrangement reaction mentioned later.

Partial Insertion of Isocyanides into Oligosilanes

Next, we attempted the partial insertion of isocyanides into oligosilanes by control of the stepwise multiple insertion. Some examples of partial insertion are summarized in Table II. In-

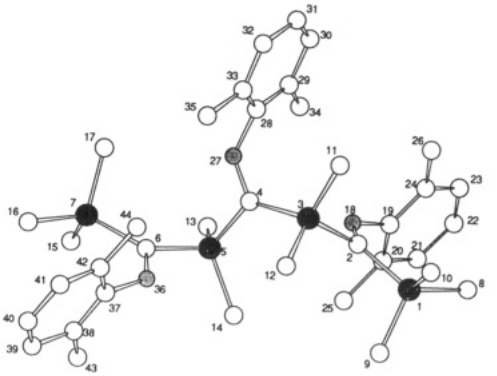
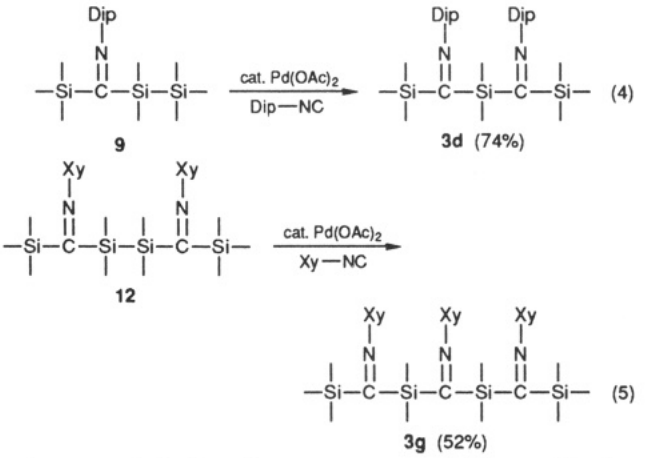


Figure 1. Crystal structure of **3g**. Hydrogen atoms have been omitted for clarity. Some bond distances (Å) and angles (deg) are as follows: Si(1)–C(2) = 1.90 (1), C(2)–Si(3) = 1.94 (1), Si(3)–C(4) = 1.92 (1), C(4)–Si(5) = 1.88 (1), Si(5)–C(6) = 1.87 (1), C(6)–Si(7) = 1.91 (1), C(2)–N(18) = 1.27 (1), C(4)–N(27) = 1.30 (1), C(6)–N(36) = 1.32 (1); Si(1)–C(2)–N(18) = 128.2 (8), Si(3)–C(2)–N(18) = 109.6 (8), Si(3)–C(4)–N(27) = 126.0 (8), Si(5)–C(4)–N(27) = 109.6 (8), Si(5)–C(6)–N(36) = 109.1 (8), Si(7)–C(6)–N(36) = 123.4 (8).

sertion reactions were carried out with varying molar ratios of oligosilane to isocyanide (**1**/**2**). Use of 1.2 equiv of isocyanide to trisilane resulted in the selective formation of mono-insertion products (Table II, entries 1–4). Similarly, a reaction of 2.0 equiv of isocyanide **2a** with tetrasilane **1e** in DMF afforded a bis-insertion product **12**, wherein the two terminal links of three Si–Si linkages underwent insertion, with the internal Si–Si linkage left intact (entry 5). Further treatment of the isolated mono- and bis-insertion products, **5**, **9**, and **12**, with isocyanide led to the formation of the complete insertion products **3c**, **3d**, and **3g**, respectively (eqs 2, 4, and 5). These results may suggest that the multiple insertion proceeds stepwise to accomplish the complete insertion and that isocyanide **2a** is inserted preferentially into the terminal Si–Si linkages of tetrasilane **1e**, which are sterically less crowded than the internal one. Isocyanide **2a** inserted into a Si–Si linkage also exerts steric hindrance, making the Si–Si linkage adjacent to the resulting (2,6-xylylimino)methyl group more resistant to further insertion of isocyanide.

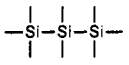
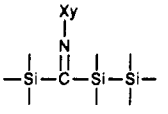
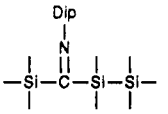
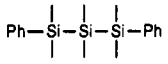
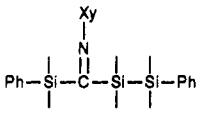
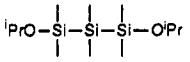
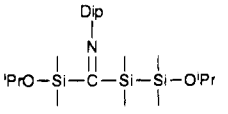
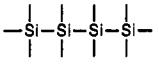
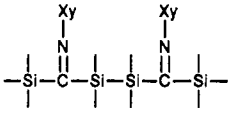
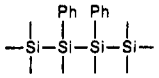
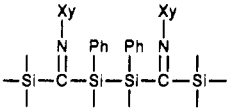
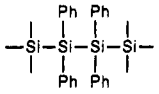
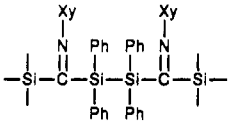
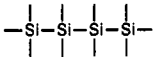
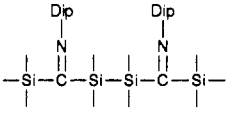
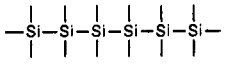
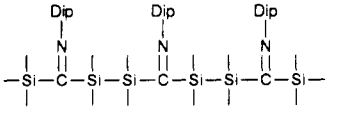
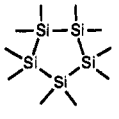
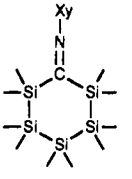


As supposed, the insertion process was much influenced by the steric bulkiness of substituents on both reactants. Tetrasilanes **1k** and **1l** having phenyl groups on internal silicon atoms gave partial insertion products **13** and **14**, respectively, even with the use of excess isocyanide **2a**. In addition, a branched oligosilane such as 2,3-bis(trimethylsilyl)-1,1,1,2,3,4,4,4-octamethyltetrasilane bearing trimethylsilyl groups on internal silicon atoms did not undergo the insertion reaction at all.

The bulkiness of the ortho substituents on the aromatic ring of isocyanide was also found to have much influence on the insertion. In the reaction of 2,6-diisopropylphenyl isocyanide (**2b**) with decamethyltetrasilane (**1e**), even the employment of 3.5 equiv of **2b** gave rise only to a partial insertion product **15**. In contrast, 2,6-xylyl isocyanide (**2a**) gave a complete insertion product **3g**

(6) Isocyanides have been known to undergo successive insertion into some organometallic compounds; see: (a) Drenth, W.; Nolte, R. J. M. *Acc. Chem. Res.* **1979**, *12*, 30. (b) Millich, F. *Macromol. Rev.* **1980**, *15*, 207. (c) Murakami, M.; Masuda, H.; Kawano, T.; Nakamura, H.; Ito, Y. *J. Org. Chem.* **1991**, *56*, 1.

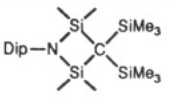
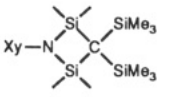
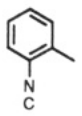
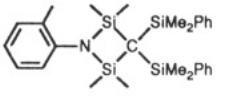
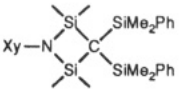
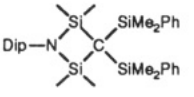
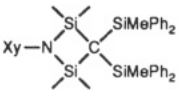
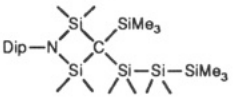
Table II. The Partial Insertion of Aryl Isocyanide into Oligosilanes

entry	oligosilane	aryl isocyanide (equiv)	conditions	product	yield, %
1	 **1b**	**2a** (1.2)	toluene reflux, 4 h	 **5**	64
2		**2b** (1.2)	toluene reflux, 4 h	 **9**	64
3	 **1c**	**2a** (1.2)	DMF, 70 °C, 5 h	 **10**	61
4	 **1j**	**2b** (1.2)	toluene, 80 °C, 14 h	 **11**	51
5	 **1e**	**2a** (2.0)	DMF, 70 °C, 9 h	 **12**	50
6	 **1k**	**2a** (3.5)	toluene, 70 °C, 22.5 h	 **13**	48
7	 **1l**	**2a** (4.5)	toluene reflux, 3 h	 **14**	55
8	 **1e**	**2b** (3.5)	DMF, 70 °C, 26 h	 **15**	60
9	 **1i**	**2b** (4.0)	DMF, 70 °C, 1 day	 **16**	16
10	 **1m**	**2a** (3.1)	toluene reflux, 6.5 h	 **17**	29

under the same reaction conditions as stated above (entry 11 in Table I). Noteworthy was that 2,6-diisopropylphenyl isocyanide (**2b**) was selectively inserted into every other Si–Si linkage of tetradecamethylhexasilane (**1i**) to afford a tris-insertion product **16**. It might be that the bulkiness of the 2,6-diisopropylphenyl group made the Si–Si linkage flanked by the two (arylimino)-methyl groups totally inert toward further insertion. Attempted reactions of the isolated **13**, **14**, and **15** with isocyanide were found not to proceed at all.

The reaction of 5-membered decamethylcyclopentasilane (**1m**) with an excess of 2,6-xylyl isocyanide afforded 6-membered **17** as an isolable product, wherein only one Si–Si linkage of **1m** participated in the insertion reaction. However, an analogous 6-membered cyclic oligosilane, dodecamethylcyclohexasilane, as well as the isolated **17** failed to react with isocyanide at all. Formation of a 7-membered bis(organosilyl)palladium complex, which is proposed in a possible mechanism mentioned later, might be disfavored.

Table III. The Skeletal Rearrangement of Oligosilanes

entry	1	2	product (18)	yield, %[a]
1	**1e**	**2b**	 **18a**	40, 45
2	**1e**	**2a**	 **18b**	9, 40
3	**1f**		 **18c**	0, 24
4	**1f**	**2a**	 **18d**	37, 31
5	**1f**	**2b**	 **18e**	50, 62
6	**1g**	**2a**	 **18f**	10, 28
7	**1g**	**2b**	 **18g**	54, 48
8	**1i**	**2b**	 **18h**	–, 15

[a] Yields in the right column were obtained by carrying out the reaction in the presence of 1,1,3,3-tetramethylbutyl isocyanide as an additive.

Skeletal Rearrangement

Organopolysilanes have been known to undergo skeletal rearrangements catalyzed by Lewis acid as well as transition metal complexes.[7] During the course of our study on the partial insertion of isocyanide into tetrasilane catalyzed by palladium(II) acetate, a novel skeletal rearrangement of oligosilanes was found.[8]

As described above, the bis-insertion product **15** was obtained by the reaction of decamethyltetrasilane (**1e**) with 3.5 equiv of 2,6-diisopropylphenyl isocyanide (**2b**) in DMF. However, attempts to synthesize a mono-insertion product from tetrasilane by use of 1.5 equiv of **2b** in DMF did not give the desired mono-insertion product, but instead gave the bis-insertion product **15** in 22% yield along with 6% of an unexpected skeletal rearranged product **18a**. The yield of the rearranged product **18a** significantly increased up to 40% when the reaction was carried out in toluene. Representative results of the skeletal rearrangement reaction are summarized in Table III. The rearrangement took place with a 2,6-disubstituted aryl isocyanide, but not with *o*-tolyl isocyanide under the same reaction conditions. *n*- and *sec*-alkyl isocyanides gave only a complex mixture. Further, no reaction occurred with *tert*-alkyl isocyanides such as 1,1,3,3-tetramethylbutyl and 1-adamantyl isocyanides. Noteworthy was that the combined use of 1 equiv of a *tert*-alkyl isocyanide and 1.5 equiv of a 2,6-disubstituted aryl isocyanide improved the yields of the rearranged products **18** in some cases (Table III, entries 2, 3, 5, and 6). It is especially remarked that *o*-tolyl isocyanide reacted with tetrasilane **1e** in the presence of palladium(II) acetate–1,1,3,3-tetramethylbutyl isocyanide to afford the rearranged product **18c** in 24% (entry 3). The *tert*-alkyl isocyanide was not incorporated into the product but might act as an effective ligand of palladium. Comparison between substituted aromatic isocyanides revealed that the formation of **18** was favored by the bulkiness of the aromatic group of the isocyanide (entries 3–5). Hexasilane **1i** also underwent a similar rearrangement giving 3-silyl-3-trisilyl-1-aza-2,4-disilacyclobutane **18h** in 15% as an isolable product (entry 8).

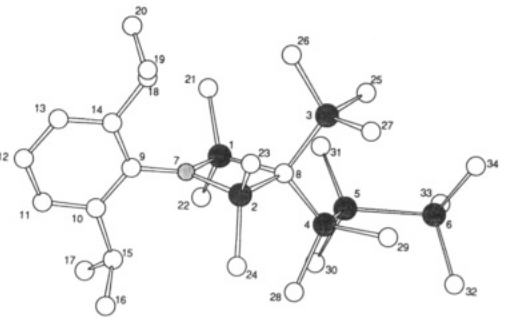
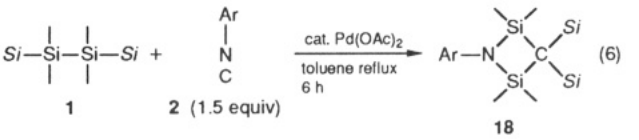


Figure 2. Crystal structure of **18h**. Hydrogen atoms have been omitted for clarity. Some bond distances (Å) and angles (deg) are as follows: Si(1)–N(7) = 1.738 (3), Si(1)–C(8) = 1.907 (4), Si(2)–N(7) = 1.734 (3), Si(2)–C(8) = 1.909 (4), N(7)–C(9) = 1.446 (5); Si(1)–C(8)–Si(2) = 84.9 (2), Si(1)–N(7)–Si(2) = 95.8 (2), N(7)–Si(1)–C(8) = 89.4 (2), N(7)–Si(2)–C(8) = 89.4 (2).



The rearrangement is unique and intriguing in that the product, 3,3-disilyl-2,4-disila-1-azacyclobutane derivatives **18**, is properly reconstituted from four fragments of the tetrasilane **1** and two fragments of the isocyanide **2**. Skeletal rearranged products **18** were stable to air, water, and silica gel. Moreover, the Si–N bond of **18** was not cleaved upon treatment with aqueous acid. Their spectroscopic and analytical data were fully in accord with the depicted structure. The molecular structures of **18d** and **18h** have been established by a single-crystal diffraction study, the latter structure being shown in Figure 2 together with selected bond lengths and angles. Puckering of the 4-membered ring is slight, similar to **18d**. The two half-rings are folded along the Si(1)–Si(2) diagonal, forming a dihedral angle of 7.2°. The 2,6-diisopropylphenyl ring is perpendicular (87.1°) to the mean plane of the 4-membered ring.

Mechanistic Interpretations

Tetrakis(triphenylphosphine)palladium(0)[3] as well as palladium(II) acetate showed a comparable catalyst activity in the insertion reaction of isocyanides with oligosilanes, suggesting that an actual effective catalyst might be a palladium(0) species. A mechanism involving the catalytic cycle as depicted in Scheme I can reasonably explain the reaction: (i) oxidative addition of a silicon–silicon linkage onto the palladium(0) catalyst, which might be initially formed by reduction of palladium(II) acetate with isocyanide[9] to give bis(organosilyl)palladium complex **19**,[10] (ii) insertion of isocyanide into the Pd–Si linkage of **19** to afford

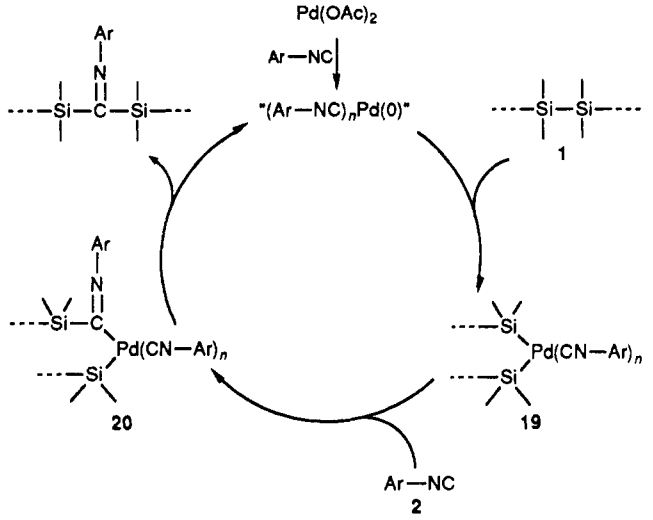
(7) (a) Brook, A. G.; Bassindale, A. R. In *Organic Chemistry*; DeMayo, P.; Ed.; Academic: New York, 1980; Vol. 2, Essay No. 9. (b) Kumada, M. *J. Organomet. Chem.* **1975**, *100*, 127.

(8) Preliminary communication: Ito, Y.; Suginome, M.; Murakami, M.; Shiro, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1494.

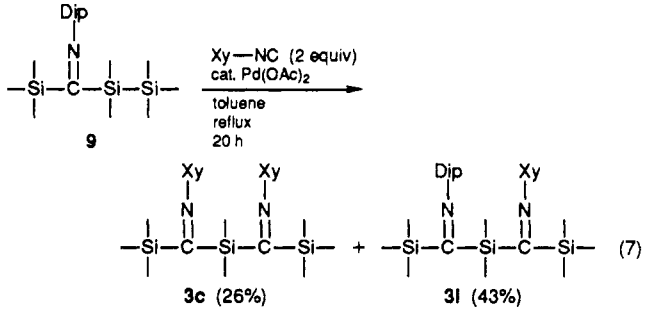
(9) Otsuka, S.; Yoshida, T.; Tatsuno, Y. *J. Am. Chem. Soc.* **1971**, *93*, 6462.

(10) Synthesis of a bis(organosilyl)platinum complex by oxidative addition of halodisilane to a platinum(0) complex has recently been reported. Yamashita, H.; Kobayashi, T.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1990**, 1447.

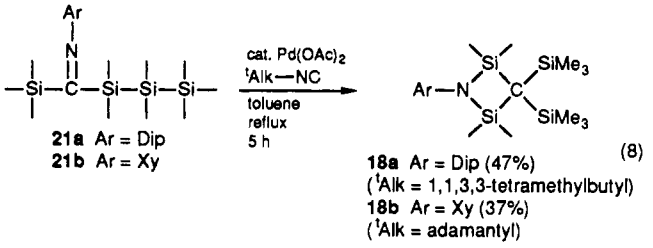
Scheme I



20, and (iii) reductive elimination resulting in the formation of an insertion product along with regeneration of the Pd(0) catalyst. Reversiblity of the insertion of isocyanide into Si–Si linkages of oligosilanes was suggested by a palladium-catalyzed reaction of **9** with 2,6-xylyl isocyanide, which gave **3c** along with **3l** (eq 7).[11]



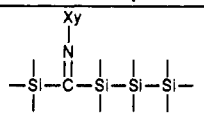
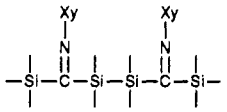
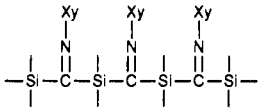
It may be relevant to the reaction mechanism that mono-insertion product **21** underwent the skeletal rearrangement in the presence of palladium(II) acetate to give **18b**. A toluene solution of **21**, prepared from 1-chloroheptamethyltrisilane and [(arylimino)(trimethylsilyl)methyl]lithium, was heated with palladium(II) acetate in the presence of *tert*-alkyl isocyanide to afford the rearranged product **18** in moderate yield (eq 8). This suggested that the mono-insertion product **21** is a possible intermediate of the rearrangement, although the subsequent pathway leading to **18** remains to be clarified. The intermediacy of a silylene–palladium complex might be presumed for the rearrangement step. By use of $Pd(PPh_3)_4$ instead of $Pd(OAc)_2$–*tert*-alkyl isocyanide, the mono-insertion product **21** failed to undergo the skeletal rearrangement. Hence, the effect of *tert*-alkyl isocyanide as an additive may be accounted for by assuming that it fluxionally ligates on the palladium species, serving favorably for formation and stabilization of bis(organosilyl)palladium **19** without being incorporated into the product. The sterically bulky 2,6-disubstituted aryl isocyanide, which enters into the insertion reaction as a reactant, may also play a role as a ligand.



18a Ar = Dip (47%)
(tAlk = 1,1,3,3-tetramethylbutyl)
18b Ar = Xy (37%)
(tAlk = adamantyl)

(11) The reversibility of the insertion step of isocyanide into a Si–Si linkage was pointed out by a referee.

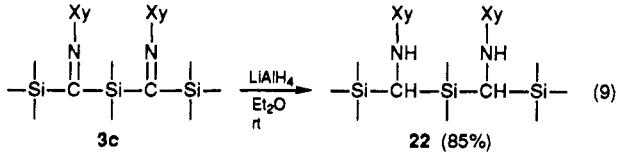
Table IV. Spectral Data of **21**, **12**, and **3g**

compound	UV λ_{max}, nm (ϵ)	IR ν, cm^{-1}
 **21**	400 (226)	1542
 **12**	405 (420)	1546
 **3g**	407 (540)	1544

Spectral Properties of Oligo(silylimine) Derivatives

Oligo(silylimine) derivatives showed interesting spectral properties. IR absorption bands characteristic of the imino group were observed at 1536–1552 cm^{-1}, which were compared with the corresponding absorption of ordinary dialkyl imines in the range 1610–1680 cm^{-1}.[12a] Oligo(silylimine) derivatives absorbed at remarkably long wavelengths near the visible range of 400–410 nm. These absorptions, which are attributable to the $n-\pi^*$ transition, are remarkably different from those of ordinary imines with absorptions at around 240 nm.[12b] By analogy with the electronic spectra of acylsilanes,[13] the major origin of this bathochromic shift may be mixing of the σ orbitals of the silicon–carbon bond with the n orbital on nitrogen, which gives rise to considerable $\sigma-\pi^*$ character for the excitation.[14]

Reduction of the imino groups of **3c** was readily performed by treatment with $LiAlH_4$ in ether at room temperature to afford 1,1,1,3,3,5,5,5-octamethyl-2,4-bis(2,6-xylylamino)-1,3,5-trisilapentane (**22**) in 85% yield with disappearance of the yellow color (eq 9). The UV spectra of **22** exhibited no absorption in the range 400–410 nm.



The vibrational frequencies and UV absorption maxima of the imino groups in mono-, bis-, and tris-insertion products **21**, **12**, and **3g** are summarized in Table IV. Those absorption wavelengths are indeed not different from each other, revealing that the imino groups in an oligo(silylimine) derivative are insulated from each other and have little mutual influence.

The temperature dependence of the ^1H NMR spectrum of **3c** is notable; the very broad signal, assigned to the Me_3Si and Me_2Si groups, appeared between δ −0.25 and 0.70 at room temperature, which split into two slightly broad singlet signals at δ −0.03 and 0.32 with a relative intensity of 3:1 at 91 °C. This observation showed that the syn–anti interconversion of the 2,6-xylyl group on the imino nitrogen became rapid enough to sharpen the Me_3Si and Me_2Si signals at 91 °C. Similar temperature dependence of ^1H NMR spectra was observed for **3h** and **16**.

(12) (a) Sandolfy, C. In *The Chemistry of the Carbon-Nitrogen Double Bond*; Patai, S., Ed.; Wiley Interscience: New York, 1970; Chapter 1. (b) Bonnett, R. *Ibid.*; Chapter 4.

(13) (a) Bock, H.; Alt, H.; Seidl, H. *J. Am. Chem. Soc.* **1969**, *91*, 355. (b) Brook, A. G.; Quigley, M. A.; Peddle, G. J. D.; Schwartz, N. V.; Warner, C. M. *J. Am. Chem. Soc.* **1960**, *82*, 5102.

(14) Ramsey, B. G.; Brook, A.; Bassindale, A. R.; Bock, H. *J. Organomet. Chem.* **1974**, *74*, C41.

Conclusion

The complete insertion of isocyanide into all silicon–silicon linkages of oligosilanes was promoted by a palladium catalyst, giving oligo(silylimine) derivatives. Partial insertion of isocyanide into oligosilanes was also achieved by virtue of steric hindrance. A new and novel skeletal rearrangement of oligosilanes higher than tetrasilane was found in the reaction with 1.5 equiv of aromatic isocyanide catalyzed by palladium(II) acetate–*tert*-alkyl isocyanide. However, the skeletal rearrangement would be a serious obstacle to the achievement of the complete insertion of isocyanide into higher polysilanes. The reactions disclosed in the present study are not only interesting from a synthetic viewpoint but also provide a simple and convenient entry into a novel class of organosilicon compounds that have interesting spectral properties and are otherwise difficult to synthesize.

Experimental Section

General. Column chromatography was performed with silica gel 60 (E. Merck, Darmstadt), 230–400 mesh. Preparative thin-layer chromatography was performed with silica gel 60 PF_{254} (E. Merck, Darmstadt). High-performance liquid chromatography (HPLC) was done using a 10 mm × 25 cm Merck LiChrosorb NH_2 column. The analytical and preparative recycling gel permeation chromatography was performed with a JAI LC-908 equipped with JAIGEL-1H and -2H columns. ^1H and ^{13}C NMR spectra were acquired with a Varian VXR-200 spectrometer in chloroform-*d* unless otherwise noted. Carbon-13 chemical shifts were recorded relative to chloroform-*d* (δ 77.0). Infrared spectra were recorded with a Hitachi 270–30 spectrometer. UV spectra were obtained with a JASCO UVIDEC-660 spectrometer. Electron impact mass spectra (MS) were recorded with a JEOL LMS-D300 spectrometer. Fast atom bombardment mass spectra (FABMS) were recorded with a JEOL JMS-SX102 spectrometer. Melting points were measured on a Yamato-MP apparatus and are uncorrected. $MgSO_4$ was used to dry organic layers after extraction. All reactions were performed under a dry nitrogen atmosphere.

Materials. Tetrahydrofuran (THF), diethyl ether, toluene, and benzene were distilled from $LiAlH_4$, and CH_2Cl_2, dimethylformamide, ethanol, and acetonitrile were distilled from CaH_2. 2,6-Xylyl isocyanide (**2a**) and 2-methylphenyl isocyanide were prepared according to the literature procedure.[15] 2,6-Diisopropylphenyl isocyanide (**2b**) and 1-adamantyl isocyanide were prepared by a similar procedure from 1-formamido-2,6-diisopropylbenzene and 1-formamidoadamantane, respectively. 1,1,3,3-Tetramethylbutyl isocyanide and hexamethyldisilane (**1a**) were purchased from a commercial source. Octamethyltrisilane (**1b**),[16] decamethyltetrasilane (**1e**),[17] 1,4-diphenyloctamethyltetrasilane (**1f**),[18] and decamethylcyclopentasilane (**1m**)[19] were prepared as reported in the literature. 1,3-Diphenylhexamethyltrisilane (**1c**) was prepared by the coupling of 1-chloro-2-phenyl-1,1,2,2-tetramethyldisilane with (dimethylphenylsilyl)lithium. 1-*tert*-Butylheptamethyltrisilane (**1d**) was prepared from 1-*tert*-butyl-2-chloro-1,1,2,2-tetramethyldisilane and chlorotrimethylsilane using an alloy of sodium and potassium.[20] 1,1,4,4-Tetraphenylhexamethyltetrasilane (**1g**) was synthesized by coupling of 1,2-dichlorotetramethyldisilane with (dimethylphenylsilyl)lithium. 1,5-Diphenyldecamethylpentasilane (**1h**) was also prepared by coupling of 1,3-dichlorohexamethyltrisilane with (dimethylphenylsilyl)-lithium. Tetradecamethylhexasilane (**1i**) was synthesized by treatment of 1-chloroheptamethyltrisilane with an alloy of sodium and potassium. 1,3-Diisopropoxyhexamethyltrisilane (**1j**) was prepared by the reaction of 1,3-dichlorohexamethyltrisilane with 2-propanol. [(Trimethylsilyl)-(2,6-xylylimino)methyl]trimethylstannane (**4a**) and [(*tert*-butyldimethylsilyl)(2,6-xylylimino)methyl]trimethylstannane (**4b**) were prepared by the reported procedure.[5] Palladium(II) acetate was purchased from a commercial source and used without further purification.

2,2,4,4-Tetramethyl-3-(2,6-xylylimino)-2,4-disilapentane (3a). A mixture of hexamethyldisilane (**1a**, 300 mg, 2.05 mmol), 2,6-xylyl isocyanide (**2a**, 269 mg, 2.05 mmol), and palladium(II) acetate (9.2 mg, 41 μmol) in toluene (3 mL) was heated at reflux for 20 h. Kugelrohr distillation of the cooled reaction mixture gave **3a** as a yellow solid, which was recrystallized from dry EtOH to afford yellow crystals: 66% yield after Kugelrohr distillation, bp 115–120 °C (0.4 mmHg); mp 43.5–44.5 °C (sealed tube); IR (neat) 2964, 1594, 1552, 1252 cm^{-1}; ^1H NMR δ −0.13 (s, 9 H), 0.29 (s, 9 H), 1.95 (s, 6 H), 6.78–6.99 (m, 3 H); ^{13}C NMR δ −0.95, −0.72, 18.00, 122.51, 123.02, 127.56, 155.22, 218.97; ^{29}Si NMR δ −11.42, −7.12; MS (20 eV) *m/z* 277 (M^+). Anal. Calcd for $C_{15}H_{27}NSi_2$: C, 64.91; H, 9.80; N, 5.05. Found: C, 64.69; H, 9.95; N, 5.06.

3-[(2,6-Diisopropylphenyl)imino]-2,2,4,4-tetramethyl-2,4-disilapentane (3b). By the procedure used to prepare **3a**, the title compound (**3b**) was obtained from hexamethyldisilane (**1a**, 300 mg, 2.05 mmol), **2b** (392 mg, 2.05 mmol), and palladium(II) acetate (9.2 mg, 41 μmol) as a yellow liquid: 81% yield after Kugelrohr distillation, bp 135–140 °C (0.3 mmHg); IR (neat) 3080, 2970, 2905, 2880, 1592, 1546, 1262, 1254, 1176 cm^{-1}; ^1H NMR δ −0.15 (s, 9 H), 0.27 (s, 9 H), 1.05–1.25 (m, 12 H), 2.70 (sept, J = 7.0 Hz, 2 H), 6.90–7.06 (m, 3 H); ^{13}C NMR δ −0.74, 21.96, 22.72, 27.77, 122.09, 122.89, 133.17, 153.42, 218.16; MS (20 eV) *m/z* 333 (M^+). Anal. Calcd for $C_{19}H_{35}NSi_2$: C, 68.40; H, 10.57; N, 4.20. Found: C, 68.68; H, 10.81; N, 4.24.

2,2,4,4,6,6-Hexamethyl-3,5-bis(2,6-xylylimino)-2,4,6-trisilaheptane (3c). A mixture of 2,6-xylyl isocyanide (**2a**, 481 mg, 3.67 mmol), octamethyltrisilane (**1b**, 300 mg, 1.47 mmol), and palladium(II) acetate (16.5 mg, 73 μmol) in toluene (5 mL) was heated at reflux for 4 h. After treatment of the cooled mixture with copper(I) chloride (180 mg, 1.8 mmol) for trapping of the remaining **2a**, the mixture was passed through a column of Florisil pretreated with Et_3N under nitrogen (elution with *n*-hexane). The filtrate was condensed, and **3c** was obtained as yellow crystals by recrystallization from dry EtOH (57%): mp 105.0–106.0 °C (sealed tube); IR (KBr) 3068, 2960, 2908, 1594, 1546, 1252 cm^{-1}; ^1H NMR δ −0.25 to 0.70 (br, 24 H), 1.97 (s, 12 H), 6.70–7.12 (m, 6 H); ^{13}C NMR (benzene-d_6, 80 °C) δ −0.19 (br), 18.64, 123.19, 123.54, 128.14, 155.72, 217.3 (br); MS (20 eV) *m/z* 466 (M^+); UV (cyclohexane) 406 nm (ϵ 420). Anal. Calcd for $C_{26}H_{42}N_2Si_3$: C, 66.89; H, 9.07; N, 6.00. Found: C, 66.81; H, 9.07; N, 6.05.

3,5-Bis[(2,6-diisopropylphenyl)imino]-2,2,4,4,6,6-hexamethyl-2,4,6-trisilaheptane (3d). A mixture of 2,6-diisopropylphenyl isocyanide (**2b**, 913 mg, 6.98 mmol), octamethyltrisilane (**1b**, 200 mg, 0.98 mmol), and palladium(II) acetate (22 mg, 98 μmol) in toluene (2 mL) was heated at reflux for 40 h. The cooled mixture was passed through a column of Florisil pretreated with Et_3N (elution with dry *n*-hexane). The filtrate was condensed, and **3d** was obtained as yellow crystals by recrystallization from dry EtOH (64%): mp 121.5–122.5 °C (sealed tube); IR (KBr) 3068, 3028, 2972, 2908, 2876, 1544, 1534, 1256, 1246, 1170 cm^{-1}; ^1H NMR (50 °C) δ −0.03 (br s, 18 H), 0.39 (br s, 6 H), 1.08 (d, J = 6.8 Hz, 12 H), 1.16 (d, J = 6.8 Hz, 12 H), 2.68–2.90 (m, 4 H), 6.90–7.07 (m, 6 H); MS (20 eV) *m/z* 578 (M^+). Anal. Calcd for $C_{34}H_{58}N_2Si_3$: C, 70.52; H, 10.09; N, 4.84. Found: C, 70.38; H, 10.08; N, 4.74.

2,4,4,6-Tetramethyl-2,6-diphenyl-3,5-bis(2,6-xylylimino)-2,4,6-trisilaheptane (3e). A mixture of 1,1,2,2,3,3-hexamethyl-1,3-diphenyltrisilane (**1c**, 200 mg, 0.61 mmol), 2,6-xylyl isocyanide (**2a**, 239 mg, 1.83 mmol), and palladium(II) acetate (13.6 mg, 61 μmol) in DMF (2 mL) was heated at 70 °C for 5 h. The cooled mixture was passed through a column of Florisil pretreated with Et_3N under nitrogen (elution with dry *n*-hexane). The filtrate was condensed, and **3e** was obtained as yellow crystals by recrystallization from dry EtOH (62%): mp 97–99 °C (sealed tube); IR (KBr) 3076, 3028, 2964, 2916, 1594, 1548, 1254, 1178 cm^{-1}; ^1H NMR δ −0.3 to 0.7 (m, 18 H), 1.89 (br s, 12 H), 6.70–7.00 (br, 6 H), 7.18–7.40 (m, 10 H); MS (20 eV) *m/z* 590 (M^+); UV (cyclohexane) 408 nm (ϵ 400). Anal. Calcd for $C_{36}H_{46}N_2Si_3$: C, 73.16; H, 7.84; N, 4.74. Found: C, 72.88; H, 7.87; N, 4.64.

2,2,4,4,6,6,7,7-Octamethyl-3,5-bis(2,6-xylylimino)-2,4,6-trisilaoctane (3f). A mixture of 2,6-xylyl isocyanide (**2a**, 245 mg, 1.87 mmol), 1-*tert*-butylheptamethyltrisilane (**1d**, 147 mg, 0.60 mmol), and palladium(II) acetate (14 mg, 64 μmol) in toluene (1 mL) was heated at 150 °C for 6 h in a sealed glass tube. An inorganic material was removed from the cooled mixture by filtration through a column of silica gel pretreated with Et_3N under nitrogen (elution with *n*-hexane), and the filtrate was condensed. Kugelrohr distillation of the residue gave **3f** as a yellow solid, which was recrystallized from dry EtOH to afford yellow needles: 82% yield after Kugelrohr distillation, bp 200 °C (0.1 mmHg); mp 79–81 °C (sealed tube); IR (KBr) 3068, 3020, 2960, 1592, 1546, 1256, 1176 cm^{-1}; ^1H NMR δ −0.15 (s, 9 H), 0.05 (s, 6 H), 0.31 (s, 6 H), 1.31 (s, 9 H), 1.93 (s, 6 H), 2.03 (s, 6 H), 6.72–7.05 (m, 6 H); HRMS calcd for $C_{29}H_{48}N_2Si_3$ (*m/z*) 508.3107, found (*m/z*) 508.3105; UV (cyclohexane) 410 nm (ϵ 620).

2,2,4,4,6,6,8,8-Octamethyl-3,5,7-tris(2,6-xylylimino)-2,4,6,8-tetrasilanonane (3g). By a procedure similar (70 °C, 8.5 h) to that used to prepare **3e**, the title compound (**3g**) was obtained from decamethyltetrasilane (**1e**, 100 mg, 0.38 mmol), **2a** (175 mg, 1.33 mmol), and palladium(II) acetate (8.6 mg, 38 μmol) as yellow crystals (55%): mp 110–112 °C (sealed tube); IR (KBr) 3068, 3020, 2960, 1592, 1544, 1250,

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1176 cm^{-1}; ^{1}H NMR δ −0.41 to 0.82 (m, 30 H), 1.95 (s, 12 H), 2.01 (s, 6 H), 6.62–7.04 (m, 9 H); ^{13}C NMR δ −0.47, 18.47, 18.82, 122.42, 122.60, 122.84, 123.32, 123.80, 127.51, 127.84, 154.87, 213.98, 217.71, 219.43; MS (20 eV) m/z 655 (M$^+$); UV (cyclohexane) 407 nm (ϵ 540). Anal. Calcd for $C_{37}H_{57}N_3Si_4$: C, 67.72; H, 8.75; N, 6.40. Found: C, 67.64; H, 8.86; N, 6.35.

2,4,4,6,6,8-Hexamethyl-2,8-diphenyl-3,5,7-tris(2,6-xylylimino)-2,4,6,8-tetrasilanonane (3h). A mixture of 1,4-diphenyloctamethyltetrasilane (**1f**, 100 mg, 0.26 mmol), **2a** (153 mg, 1.17 mmol), and palladium(II) acetate (11.6 mg, 52 μmol) in DMF (1 mL) was heated at 70 °C for 9 h. The cooled mixture was passed through a column of Florisil pretreated with Et_3N under nitrogen (elution with dry n-hexane). The filtrate was condensed, and the residue was purified by HPLC to give **3h** as a yellow viscous oil (43%): IR (neat) 3072, 3024, 2964, 2932, 2864, 1592, 1540, 1254, 1176 cm^{-1}; ^{1}H NMR δ −0.4 to 0.7 (br, 24 H), 1.7–2.0 (br, 18 H), 6.7–7.0 (m, 9 H), 7.1–7.7 (br, 10 H); HRFABMS calcd for $C_{47}H_{62}N_3Si_4$ (m/z) 780.4021, found (m/z) 780.4015.

4,4,6,6-Tetramethyl-2,2,8,8-tetraphenyl-3,5,7-tris(2,6-xylylimino)-2,4,6,8-tetrasilanonane (3i). By a procedure similar (70 °C, 15 h) to that used to prepare **3h**, the title compound (**3i**) was obtained from 1,1,4,4-tetraphenyl-1,2,2,3,3,4-hexamethyltetrasilane (**1g**, 100 mg, 0.20 mmol), **2a** (103 mg, 0.78 mmol), and palladium(II) acetate (8.8 mg, 39 μmol) as a yellow viscous oil (28%): IR (neat) 3072, 3052, 3020, 2964, 2908, 1592, 1540, 1254, 1176 cm^{-1}; ^{1}H NMR δ −0.5 to 0.7 (br, 18 H), 1.6–2.0 (br, 18 H), 6.6–6.9 (m, 9 H), 7.1–7.7 (m, 20 H); HRFABMS calcd for $C_{57}H_{66}N_3Si_4$ (m/z) 904.4334, found (m/z) 904.4332.

2,4,4,6,6,8,8,10-Octamethyl-2,10-diphenyl-3,5,7,9-tetrakis(2,6-xylylimino)-2,4,6,8,10-pentasilaundecane (3j). By a procedure similar (70 °C, 30 h) to that used to prepare **3h**, the title compound (**3j**) was obtained from 1,5-diphenyldecamethylpentasilane (**1h**, 100 mg, 0.225 mmol), **2a** (192 mg, 1.46 mmol), and palladium(II) acetate (10.1 mg, 45 μmol) as a yellow viscous oil (40%). Yellow crystals were obtained by recrystallization from dry EtOH: mp 194–195 °C; IR (KBr) 3020, 2968, 2916, 1592, 1538, 1252, 1174 cm^{-1}; ^{1}H NMR (benzene-d_6, 85 °C) δ 0.13 (br s, 24 H), 0.50 (br s, 6 H), 2.00 (s, 12 H), 2.10 (s, 12 H), 6.75–6.94 (m, 12 H), 7.05–7.40 (m, 10 H); MS (20 eV) m/z 969 (M$^+$). Anal. Calcd for $C_{58}H_{76}N_4Si_5$: C, 71.84; H, 7.90; N, 5.78. Found: C, 71.56; H, 8.02; N, 5.78.

2,2,4,4,6,6,8,8,10,10,12,12-Dodecamethyl-3,5,7,9,11-pentakis(2,6-xylylimino)-2,4,6,8,10,12-hexasilatridecane (3k). By a procedure similar (70 °C, 46 h) to that used to prepare **3h**, the title compound (**3k**) was obtained from tetradecamethylhexasilane (**1i**, 123 mg, 0.325 mmol), **2a** (429 mg, 3.27 mmol), and palladium(II) acetate (14.6 mg, 65 μmol) as a yellow viscous oil (40%). Yellow crystals were obtained by recrystallization from dry EtOH: mp 141.0–142.5 °C (sealed tube); IR (KBr) 3080, 2960, 1594, 1540, 1252, 1174 cm^{-1}; ^{1}H NMR (benzene-d_6, 80 °C) δ −0.18 (s, 18 H), 0.24 (s, 12 H), 0.50 (s, 12 H), 1.97 (s, 12 H), 2.12 (s, 12 H), 2.16 (s, 6 H), 6.75–7.00 (m, 15 H); ^{13}C NMR (benzene-d_6, 80 °C) δ −0.27, 0.45, 0.94, 18.87, 19.32, 19.45, 123.12, 123.29, 123.38, 123.60, 123.85, 128.18, 128.36, 155.10, 155.22, 155.35, 216.20, 217.02, 219.17; MS (20 eV) m/z 1033 (M$^+$); UV (cyclohexane) 410 nm (ϵ 1160). Anal. Calcd for $C_{59}H_{87}N_5Si_6$: C, 68.48; H, 8.47; N, 6.77. Found: C, 68.28; H, 8.60; N, 6.70.

3-[(2,6-Diisopropylphenyl)imino]-2,2,4,4,6,6-hexamethyl-5-(2,6-xylylimino)-2,4,6-trisilaheptane (3l). A mixture of 2,6-xylyl isocyanide (**2a**, 100 mg, 0.766 mmol), 3-[(2,6-diisopropylphenyl)imino]-2,2,4,4,5,5-hexamethyl-2,4,5-trisilahexane (**9**, 150 mg, 0.38 mmol), and palladium(II) acetate (8.6 mg, 38 μmol) in toluene (2 mL) was heated at reflux for 20 h. The reaction mixture contained **3c** (47 mg, 26%) and **3l** (86 mg, 43%). The cooled mixture was passed through a column of Florisil pretreated with Et_3N. The filtrate was condensed, and **3l** was separated and isolated as a yellow oil by preparative GLC: IR (neat) 3072, 2968, 1594, 1540, 1252, 1176 cm^{-1}; ^{1}H NMR δ −0.3 to 0.7 (br, 24 H), 1.06 (d, J = 6.7 Hz, 6 H), 1.14 (d, J = 6.7 Hz, 6 H), 1.99 (s, 6 H), 2.60–2.90 (br, 2 H), 6.78–7.10 (m, 6 H). Anal. Calcd for $C_{30}H_{50}N_2Si_3$: C, 68.90; H, 9.64; N, 5.36. Found: C, 68.66; H, 9.71; N, 5.28.

2,2,4,4,5,5-Hexamethyl-3-(2,6-xylylimino)-2,4,5-trisilahexane (5). To a solution of [(trimethylsilyl)(2,6-xylylimino)methyl]trimethylstannane (**4**, 738 mg, 2.00 mmol) in THF (10 mL) was added an n-hexane solution of n-butyllithium (2.22 mmol) at −78 °C under nitrogen. After the mixture was stirred for 50 min, 1-chloropentamethyldisilane (483 mg, 2.89 mmol) was added all at once. The mixture was gradually warmed up to room temperature and subjected to extractive workup with ether. The organic layer was dried and evaporated. Kugelrohr distillation of the residue afforded **5** as a yellow viscous oil (65%): bp 116–125 °C (0.3 mmHg); IR (neat) 2956, 2904, 1594, 1544, 1250, 1180 cm^{-1}; ^{1}H NMR δ −0.15 (s, 9 H), 0.13 (s, 9 H), 0.35 (s, 6 H), 1.96 (s, 6 H), 6.75–6.98 (m, 3 H); MS (20 eV) m/z 335 (M$^+$); UV (cyclohexane) 405 nm (ϵ 300). Anal. Calcd for $C_{17}H_{33}NSi_3$: C, 60.82; H, 9.91; N, 4.17. Found: C, 60.63; H, 10.04; N, 4.13.

2,2,3,3,5,5,6,6-Octamethyl-4-(2,6-xylylimino)-2,3,5-trisilaheptane (7). By a procedure similar to that used to prepare **5**, the title compound (**7**) was obtained from [(*tert*-butyldimethylsilyl)(2,6-xylylimino)methyl]trimethylstannane (**6**, 903 mg, 2.21 mmol), n-butyllithium (2.43 mmol), and 1-chloropentamethyldisilane (483 mg, 2.89 mmol) as a yellow viscous oil (86%): bp 155–166 °C (0.2 mmHg); IR (neat) 2960, 2900, 2860, 1594, 1540, 1248, 1178 cm^{-1}; ^{1}H NMR δ −0.15 (s, 6 H), 0.02 (s, 9 H), 0.24 (s, 6 H), 1.02 (s, 9 H), 1.98 (s, 6 H), 6.60–7.00 (m, 3 H); MS (20 eV) m/z 377 (M$^+$). Anal. Calcd for $C_{20}H_{39}NSi_3$: C, 63.59; H, 10.40; N, 3.71. Found: C, 63.45; H, 10.50; N, 3.75.

2,2,4,4,5,5,6,6-Octamethyl-3-(2,6-xylylimino)-2,4,5-trisilaheptane (8). By a procedure similar to that used to prepare **5**, the title compound (**8**) was obtained from [(trimethylsilyl)(2,6-xylylimino)methyl]trimethylstannane (**4**, 877 mg, 2.38 mmol), n-butyllithium (2.65 mmol), and 1-*tert*-butyl-2-chloro-1,1,2,2-tetramethyldisilane (751 mg, 3.59 mmol) as a yellow viscous oil (64%): bp 141–147 °C (0.2 mmHg); IR (neat) 2960, 2936, 2900, 1594, 1542, 1252, 1180 cm^{-1}; ^{1}H NMR δ −0.12 (br s, 9 H) 0.10 (s, 6 H), 0.04 (br s, 6 H), 0.93 (s, 9 H), 1.97 (s, 6 H), 6.63–7.02 (m, 3 H); MS (20 eV) m/z 377 (M$^+$). Anal. Calcd for $C_{20}H_{39}NSi_3$: C, 63.59; H, 10.40; N, 3.71. Found: C, 63.73; H, 10.50; N, 3.77.

3-[(2,6-Diisopropylphenyl)imino]-2,2,4,4,5,5-hexamethyl-2,4,5-trisilahexane (9). A mixture of octamethyltrisilane (**1b**, 200 mg, 0.98 mmol), 2,6-diisopropylphenyl isocyanide (**2b**, 220 mg, 1.17 mmol), and palladium(II) acetate (22 mg, 98 μmol) in toluene (2 mL) was heated at reflux for 4 h. The cooled reaction mixture was filtered through a Florisil column pretreated with Et_3N (elution with n-hexane), and the filtrate was condensed. Kugelrohr distillation of the residue gave **9** as a yellow viscous oil (64%): bp 140–145 °C (0.3 mmHg): IR (neat) 3068, 2968, 2904, 1540, 1250, 1170 cm^{-1}; ^{1}H NMR δ −0.16 (br s, 9 H), 0.12 (s, 9 H), 0.34 (br s, 6 H), 1.04–1.30 (m, 12 H), 2.74 (sept, J = 6.8 Hz, 2 H), 6.90–7.06 (m, 3 H); HRMS calcd for $C_{21}H_{41}NSi_3$ (m/z) 391.2545, found (m/z) 391.2528.

2,4,4,5-Tetramethyl-2,5-diphenyl-3-(2,6-xylylimino)-2,4,5-trisilahexane (10). A mixture of 1,3-diphenylhexamethyltrisilane (**1c**, 200 mg, 0.61 mmol), 2,6-xylyl isocyanide (**2a**, 96 mg, 0.73 mmol), and palladium(II) acetate (14 mg, 61 μmol) in DMF (2 mL) was heated at 70 °C for 2 h. The cooled reaction mixture was filtered through a Florisil column pretreated with Et_3N (elution with n-hexane), and the filtrate was condensed. Kugelrohr distillation of the residue gave **10** as a yellow viscous oil (61%): bp 200–210 °C (0.5 mmHg); IR (neat) 3072, 3056, 3024, 2960, 2904, 1594, 1540, 1252, 1178 cm^{-1}; ^{1}H NMR δ 0.06 (s, 6 H), 0.17 (s, 6 H), 0.44 (s, 6 H), 1.96 (s, 6 H), 6.81–6.99 (m, 3 H), 7.20–7.80 (m, 10 H); ^{13}C NMR δ −3.06, −2.33, −2.08, 18.33, 122.69, 123.28, 127.64, 127.76, 128.28, 129.20, 134.04, 137.01, 139.64, 155.09, 217.70; MS (20 eV) m/z 459 (M$^+$); UV (cyclohexane) 407 nm (ϵ 250). Anal. Calcd for $C_{27}H_{37}NSi_3$: C, 70.52; H, 8.11; N, 3.05. Found: C, 70.45; H, 8.18; N, 3.09.

2,5-Diisopropoxy-3-[(2,6-diisopropylphenyl)imino]-2,4,4,5-tetramethyl-2,4,5-trisilahexane (11). A mixture of 1,3-diisopropoxyhexamethyltrisilane (**1j**, 200 mg, 0.68 mmol), 2,6-diisopropylphenyl isocyanide (**2b**, 154 mg, 0.82 mmol), and palladium(II) acetate (15 mg, 68 μmol) in toluene (2 mL) was heated at 80 °C for 14 h. Kugelrohr distillation of the cooled reaction mixture gave **11** as a yellow viscous oil: 51% yield after Kugelrohor distillation, bp 170–180 °C (0.3 mmHg); IR (neat) 3068, 2972, 1546, 1464, 1384, 1248, 1172, 1122, 1024 cm^{-1}; ^{1}H NMR δ −0.26 (s, 3 H), −0.18 (s, 3 H), 0.29 (s, 9 H), 0.41 (s, 3 H), 1.01–1.32 (m, 24 H), 2.62–2.85 (m, 2 H), 3.82–4.25 (m, 2 H), 6.90–7.05 (m, 3 H); MS (20 eV) m/z 479 (M$^+$). Anal. Calcd for $C_{25}H_{49}NO_2Si_3$: C, 62.57; H, 10.29; N, 2.92. Found: C, 62.38; H, 10.45; N, 2.70.

2,2,4,4,5,5,7,7-Octamethyl-3,6-bis(2,6-xylylimino)-2,4,5,7-tetrasilaoctane (12). By a procedure similar (70 °C, 2 h) to that used to prepare **3e**, the title compound (**12**) was obtained from decamethyltetrasilane (**1e**, 219 mg, 0.83 mmol), **2a** (219 mg, 1.67 mmol), and palladium(II) acetate (17 mg, 76 μmol) as a yellow viscous oil (50%): mp 159–160 °C (sealed tube); IR (KBr) 3068, 2964, 2904, 1592, 1546, 1252, 1238, 1178 cm^{-1}; ^{1}H NMR δ −0.14 (s, 18 H), 0.47 (s, 12 H), 1.99 (s, 12 H), 6.78–6.98 (m, 6 H); ^{13}C NMR δ −1.51, −0.80, 18.41, 122.39, 123.19, 127.61, 155.40, 221.07; ^{29}Si NMR (Me$_4$Si was used as an external standard) δ −16.54, −11.85; MS (20 eV) m/z 524 (M$^+$); UV (cyclohexane) 405 nm (ϵ 420). Anal. Calcd for $C_{28}H_{48}N_2Si_4$: C, 64.05: H, 9.21; N, 5.34. Found: C, 63.94; H, 9.49; N, 5.30.

2,2,4,5,7,7-Hexamethyl-4,5-diphenyl-3,6-bis(2,6-xylylimino)-2,4,5,7-tetrasilaoctane (13). A mixture of 2,3-diphenyloctamethyltetrasilane (**1k**, a 1:1 mixture of two diastereomers, 300 mg, 0.78 mmol), 2,6-xylyl isocyanide (**2a**, 357 mg, 2.72 mmol), and palladium(II) acetate (17.5 mg, 78 μmol) in toluene (3 mL) was heated at 80 °C for 8 h. The cooled reaction mixture was filtered through a Florisil column pretreated with Et_3N (elution with n-hexane) under nitrogen. The filtrate was condensed to precipitate yellow crystals as a mixture (1:1) of diastereomers (51%). Anal. Calcd for $C_{38}H_{52}N_2Si_4$: C, 70.31; H, 8.07; N, 4.32. Found: C,

70.03; H, 8.37; N, 4.06. One diastereomer (**13a**) was preferentially recrystallized from *n*-hexane–ethanol and the other diastereomer (**13b**) was obtained from the mother liquor. **13a**: mp 238.5–240.0 °C (sealed tube); IR (KBr) 3076, 3028, 2960, 2928, 2904, 1592, 1538, 1246, 1176 cm^{-1}; ^1H NMR δ −0.48 (s, 18 H), 0.88 (s, 6 H), 1.17 (s, 6 H), 2.15 (s, 6 H), 6.75–6.98 (m, 6 H), 7.24–7.55 (m, 10 H); ^{13}C NMR δ −3.55, −0.47, 17.00, 18.98, 122.34, 123.33, 123.75, 127.36, 127.63, 127.68, 128.39, 134.86, 137.57, 155.32, 220.19; MS (20 eV) m/z 648 (M^+). **13b**: mp 158–163 °C (sealed tube); IR (KBr) 3072, 2964, 2908, 1592, 1538, 1248, 1176 cm^{-1}; ^1H NMR δ −0.49 (s, 18 H), 0.82 (s, 6 H), 1.32 (s, 6 H), 2.07 (s, 6 H), 6.76–6.98 (m, 6 H), 7.18–7.43 (m, 10 H); ^{13}C NMR δ −3.43, −0.35, 17.64, 18.37, 122.35, 123.18, 123.79, 127.36, 127.59, 128.41, 135.43, 136.96, 155.29, 220.67.

2,2,7,7-Tetramethyl-4,4,5,5-tetraphenyl-3,6-bis(2,6-xylylimino)-2,4,5,7-tetrasilaoctane (14). A mixture of 2,2,3,3-tetraphenylhexamethyltetrasilane (**1k**, 200 mg, 0.39 mmol), 2,6-xylyl isocyanide (**2a**, 128 mg, 0.98 mmol), and palladium(II) acetate (8.8 mg, 39 μmol) in toluene (1.5 mL) was heated at reflux for 3 h. The reaction mixture was cooled to form a precipitate, which was washed with cold dichloromethane to give **14** as a yellow solid (55%): mp 286–287 °C (sealed tube); IR (KBr) 3060, 3020, 2980, 2960, 2900, 1590, 1538, 1248, 1174 cm^{-1}; ^1H NMR δ −0.69 (s, 18 H), 1.55 (s, 12 H), 6.79–6.93 (m, 6 H), 7.20–7.39 (m, 12 H), 7.66–7.75 (m, 8 H); ^{13}C NMR δ −0.06, 18.21, 122.60, 124.16, 127.48, 128.76, 134.96, 136.60, 155.20, 219.14; UV (cyclohexane) 400 nm (ϵ 360). Anal. Calcd for $C_{48}H_{56}N_2Si_4$: C, 74.55; H, 7.30; N, 3.62. Found: C, 74.64; H, 7.43; N, 3.45.

3,6-Bis[(2,6-diisopropylphenyl)imino]-2,2,4,4,5,5,7,7-octamethyl-2,4,5,7-tetrasilaoctane (15). A mixture of decamethyltetrasilane (**1e**, 200 mg, 0.76 mmol), 2,6-diisopropylphenyl isocyanide (**2b**, 500 mg, 2.7 mmol), and palladium(II) acetate (17 mg, 76 μmol) in DMF (2 mL) was heated at 70 °C for 26 h. The reaction mixture was cooled to form a precipitate, which was successively washed with DMF and ethanol to give **15** as a yellow solid (60%): mp 194–195 °C (sealed tube); IR (neat) 3064, 2968, 2908, 2876, 1546, 1252, 1242, 1168 cm^{-1}; ^1H NMR δ −0.14 (s, 18 H), 0.46 (s, 12 H), 1.12 (d, J = 6.8 Hz, 12 H), 1.17 (d, J = 6.8 Hz, 12 H), 2.79 (sept, J = 6.8 Hz, 4 H), 6.92–7.07 (m, 6 H): ^{13}C NMR δ −1.58, −0.39, 22.37, 23.84, 27.52, 122.29, 122.99, 133.79, 153.16, 221.90; MS (20 eV) m/z 636 (M^+). Anal. Calcd for $C_{36}H_{64}N_2Si_4$: C, 67.85; H, 10.12; N, 4.40. Found: C, 67.57; H, 10.32; N, 4.38.

3,6,9-Tris[(2,6-diisopropylphenyl)imino]-2,2,4,4,5,5,7,7,8,8,10,10-dodecamethyl-2,4,5,7,8,10-hexasilaundecane (16). A mixture of tetradecamethylhexasilane (**1i**, 100 mg, 0.26 mmol), 2,6-diisopropylphenyl isocyanide (**2b**, 198 mg, 1.06 mmol), and palladium(II) acetate (6 mg, 26 μmol) in DMF (1 mL) was heated at 70 °C for 1 d. The cooled reaction mixture was filtered through a Florisil column pretreated with Et_3N (elution with *n*-hexane) under nitrogen. The filtrate was condensed, and the residue was purified by preparative GPC to give **16** as a yellow viscous oil (16%): IR (neat) 3068, 2968, 2936, 2876, 1536, 1252, 1168 cm^{-1}; ^1H NMR (toluene-d_8, −30 °C) δ 0.10 (s, 9 H), 0.17 (s, 9 H), 0.41 (s, 6 H), 0.81 (s, 6 H), 1.01 (s, 6 H), 1.09 (s, 6 H), 1.3–1.7 (m, 36 H), 3.0–3.4 (m, 6 H), 7.17–7.35 (m, 9 H); HRFABMS calcd for $C_{53}H_{94}N_3Si_6$ (m/z) 940.6063, found (m/z) 940.6030.

2,2,3,3,4,4,5,5,6,6-Decamethyl-1-(2,6-xylylimino)-2,3,4,5,6-pentasilacyclohexane (17). By a procedure similar (reflux, 6.5 h) to that used to prepare **9**, the title compound (**17**) was obtained from decamethylcyclopentasilane (**1m**, 112 mg, 0.38 mmol), 2,6-xylyl isocyanide (**2a**, 251 mg, 1.92 mmol), and palladium(II) acetate (17 mg, 77 μmol) as a yellow viscous oil: 29% yield after Kugelrohr distillation, bp 210 °C (0.8 mmHg); IR (neat) 3070, 3020, 2955, 2900, 1594, 1538, 1250, 1180 cm^{-1}; ^1H NMR (benzene-d_6) δ −0.2 to 0.6 (br m, 30 H), 2.02 (s, 6 H), 6.85–6.99 (m, 3 H); ^{13}C NMR (benzene-d_6) δ −5.66, −5.27, −2.33 (br), −2.21 (br), 19.00, 123.34, 123.71, 128.82, 156.07, 215.87; ^{29}Si NMR (benzene-d_6, Me_4Si was used as an external standard) δ −45.67, −45.00 (br), −43.99 (br), −22.88 (br), −17.94 (br); HRMS calcd for $C_{19}H_{39}NSi_5$ (m/z) 421.1929, found (m/z) 421.1931.

1-(2,6-Diisopropylphenyl)-2,2,4,4-tetramethyl-3,3-bis(trimethylsilyl)-1-aza-2,4-disilacyclobutane (18a). A mixture of decamethyltetrasilane (**1e**, 100 mg, 0.38 mmol), 2,6-diisopropylphenyl isocyanide (**2b**, 107 mg, 0.57 mmol), 1,1,3,3-tetramethylbutyl isocyanide (53 mg, 0.38 mmol), and palladium(II) acetate (8.6 mg, 38 μmol) in toluene (1 mL) was heated at reflux for 6 h. The cooled mixture was subjected to preparative TLC (*n*-hexane–ether 50:1) to afford **18a** as a colorless solid (45%): mp 194–195 °C; IR (KBr) 2980, 2956, 2908, 2876, 1466, 1442, 1320, 1254, 1208, 870 cm^{-1}; ^1H NMR δ 0.28 (s, 18 H), 0.35 (s, 12 H), 1.16 (d, J = 6.8 Hz, 12 H), 3.63 (sept, J = 6.8 Hz, 2 H), 7.06–7.08 (m, 3 H); ^{13}C NMR δ 4.47, 6.36, 25.38, 27.16, 123.67, 123.78, 137.77, 146.43; MS (20 eV) m/z 449 (M^+). Anal. Calcd for $C_{23}H_{47}NSi_4$: C, 61.39; H, 10.53; N, 3.11. Found: C, 61.12; H, 10.55; N, 3.12.

2,2,4,4-Tetramethyl-3,3-bis(trimethylsilyl)-1-(2,6-xylyl)-1-aza-2,4-disilacyclobutane (18b). By a procedure similar to that used to prepare **18a**, the title compound (**18b**) was obtained from decamethyltetrasilane (**1e**, 100 mg, 0.38 mmol), 2,6-xylyl isocyanide (**2a**, 75 mg, 0.57 mmol), 1,1,3,3-tetramethylbutyl isocyanide (53 mg, 0.38 mmol), and palladium(II) acetate (8.6 mg, 38 μmol) as a colorless solid (40%): mp 192.5–193.0 °C; IR (KBr) 2950, 1600, 1450, 1272, 1256, 1234, 878 cm^{-1}; ^1H NMR δ 0.28 (s, 18 H), 0.36 (s, 12 H), 2.32 (s, 6 H), 6.81–6.90 (m, 1 H), 6.98–7.03 (m, 2 H); ^{13}C NMR δ 4.93, 6.40, 6.54, 20.08, 123.00, 128.21, 135.69, 141.90; MS (20 eV) m/z 393 (M^+). Anal. Calcd for $C_{19}H_{39}NSi_4$: C, 57.94; H, 9.98; N, 3.56. Found: C, 57.69; H, 10.23; N, 3.55.

3,3-Bis(dimethylphenylsilyl)-2,2,4,4-tetramethyl-1-(2-methylphenyl)-1-aza-2,4-disilacyclobutane (18c). By a procedure similar to that used to prepare **18a**, the title compound (**18c**) was obtained from 1,4-diphenyloctamethyltetrasilane (**1f**, 100 mg, 0.26 mmol), 2-methylphenyl isocyanide (46 mg, 0.39 mmol), 1,1,3,3-tetramethylbutyl isocyanide (36 mg, 0.26 mmol), and palladium(II) acetate (5.8 mg, 26 μmol) as a colorless solid (24%): mp 124–125 °C; IR (KBr) 3076, 2964, 2908, 1488, 1430, 1290, 1260, 1106 cm^{-1}; ^1H NMR δ 0.24 (s, 12 H), 0.58 (s, 12 H), 2.35 (s, 3 H), 6.90–7.43 (m, 14 H); ^{13}C NMR δ 4.54, 6.25, 6.65, 19.41, 123.50, 126.21, 127.30, 128.63, 128.83, 130.62, 134.82, 135.30, 141.78, 143.41; HRFABMS calcd for $C_{28}H_{41}NSi_4$ (m/z) 503.2316, found (m/z) 503.2376.

3,3-Bis(dimethylphenylsilyl)-2,2,4,4-tetramethyl-1-(2,6-xylyl)-1-aza-2,4-disilacyclobutane (18d). A mixture of 1,4-diphenyloctamethyltetrasilane (**1f**, 100 mg, 0.26 mmol), 2,6-xylyl isocyanide (**2a**, 51 mg, 0.39 mmol), and palladium(II) acetate (8.6 mg, 38 μmol) in toluene (1 mL) was heated at reflux for 6 h. The cooled mixture was subjected to preparative TLC (*n*-hexane–ether 50:1) to afford **18d** as a colorless solid (37%): mp 192.7–194.0 °C; IR (KBr) 3076, 3052, 3000, 2960, 2950, 1465, 1432, 1270, 1260, 1238, 1106 cm^{-1}; ^1H NMR δ 0.21 (s, 12 H), 0.59 (s, 12 H), 2.37 (s, 6 H), 6.86–6.94 (m, 1 H), 7.01–7.06 (m, 2 H), 7.26–7.41 (m, 10 H); ^{13}C NMR δ 4.94, 5.76, 7.52, 20.08, 123.27, 127.31, 128.40, 128.67, 134.91, 135.71, 141.50, 141.82; MS (20 eV) m/z 517 (M^+). Anal. Calcd for $C_{29}H_{43}NSi_4$: C, 67.24; H, 8.37; N, 2.70. Found: C, 67.00; H, 8.45; N, 2.73.

1-(2,6-Diisopropylphenyl)-3,3-bis(dimethylphenylsilyl)-2,2,4,4-tetramethyl-1-aza-2,4-disilacyclobutane (18e). By a procedure similar to that used to prepare **18a**, the title compound (**18e**) was obtained from 1,4-diphenyloctamethyltetrasilane (**1f**, 100 mg, 0.26 mmol), 2,6-diisopropylphenyl isocyanide (**2b**, 73 mg, 0.39 mmol), 1,1,3,3-tetramethylbutyl isocyanide (36 mg, 0.26 mmol), and palladium(II) acetate (5.8 mg, 26 μmol) as a colorless solid (62%): mp 194.0–194.5 °C; IR (KBr) 2968, 2908, 2876, 1442, 1430, 1318, 1252, 1206, 1108, 878 cm^{-1}; ^1H NMR δ 0.23 (s, 12 H), 0.58 (s, 12 H), 1.20 (d, J = 6.8 Hz, 12 H), 3.65 (sept, J = 6.8 Hz, 2 H), 7.08–7.12 (m, 3 H), 7.23–7.42 (m, 10 H); ^{13}C NMR δ 4.86, 5.21, 7.47, 25.51, 27.26, 123.87, 124.06, 127.28, 128.67, 134.94, 137.44, 141.78, 146.51; MS (20 eV) m/z 574 (M^+). Anal. Calcd for $C_{33}H_{51}NSi_4$: C, 69.04; H, 8.95; N, 2.44. Found: C, 68.78; H, 9.16; N, 2.35.

2,2,4,4-Tetramethyl-3,3-bis(methyldiphenylsilyl)-1-(2,6-xylyl)-1-aza-2,4-disilacyclobutane (18f). By a procedure similar to that used to prepare **18a**, the title compound (**18f**) was obtained from 1,1,4,4-tetraphenyl-1,2,2,3,3,4-hexamethyltetrasilane (**1g**, 100 mg, 0.20 mmol), 2,6-xylyl isocyanide (**2a**, 39 mg, 0.29 mmol), 1,1,3,3-tetramethylbutyl isocyanide (27 mg, 0.20 mmol), and palladium(II) acetate (4.4 mg, 20 μmol) as a colorless solid (28%): mp 264.5–265.0 °C; IR (KBr) 3076, 3048, 3016, 1430, 1260, 1230, 1100, 966 cm^{-1}; ^1H NMR δ 0.49 (s, 12 H), 0.99 (s, 6 H), 2.33 (s, 6 H), 6.83–7.40 (m, 23 H); ^{13}C NMR δ 1.76, 8.18, 20.25, 123.34, 126.52, 128.32, 128.44, 135.72, 136.47, 139.60, 141.20; MS (20 eV) m/z 641 (M^+). Anal. Calcd for $C_{39}H_{47}NSi_4$: C, 72.95; H, 7.38; N, 2.18. Found: C, 72.66; H, 7.41; N, 2.22.

1-(2,6-Diisopropylphenyl)-2,2,4,4-tetramethyl-3,3-bis(methyldiphenylsilyl)-1-aza-2,4-disilacyclobutane (18g). By a procedure similar to that used to prepare **18d**, the title compound (**18g**) was obtained from 1,1,4,4-tetraphenyl-1,2,2,3,3,4-hexamethyltetrasilane (**1g**, 100 mg, 0.20 mmol), 2,6-diisopropylphenyl isocyanide (**2b**, 55 mg, 0.29 mmol), and palladium(II) acetate (4.4 mg, 20 μmol) as a colorless solid (54%): mp 215.0–216.0 °C; IR (KBr) 3076, 2980, 2876, 1442, 1430, 1318, 1256, 1206, 1100, 886 cm^{-1}; ^1H NMR δ 0.45 (s, 12 H), 0.96 (s, 6 H), 1.12 (d, J = 6.8 Hz, 12 H), 3.55 (sept, J = 6.8 Hz, 2 H), 7.02–7.41 (m, 23 H); ^{13}C NMR δ 1.31, 7.92, 8.24, 25.49, 27.19, 123.94, 124.15, 126.60, 128.40, 136.55, 137.18, 139.82, 146.50; MS (20 eV) m/z 697 (M^+). Anal. Calcd for $C_{43}H_{55}NSi_4$: C, 73.97; H, 7.94; N, 2.01. Found: C, 73.77; H, 8.17; N, 1.99.

1-(2,6-Diisopropylphenyl)-3-(heptamethyltrisilyl)-2,2,4,4-tetramethyl-3-(trimethylsilyl)-1-aza-2,4-disilacyclobutane (18h). By a procedure similar to that used to prepare **18a**, the title compound (**18h**) was obtained from tetradecamethylhexasilane (**1i**, 100 mg, 0.26 mmol), 2,6-diisopropylphenyl isocyanide (**2b**, 49 mg, 0.26 mmol), 1,1,3,3-tetramethylbutyl isocyanide (55 mg, 0.40 mmol), and palladium(II) acetate

(6 mg, 26 μmol) as a colorless solid (15%): mp 88–89 °C; IR (KBr) 2980, 2956, 2908, 1442, 1320, 1258, 886 cm^{-1}; ^{1}H NMR δ 0.12 (s, 9 H), 0.21 (s, 6 H), 0.30 (s, 9 H), 0.37 (s, 12 H), 0.44 (s, 6 H), 1.17 (d, J = 6.8 Hz, 12 H), 3.55–3.74 (m, 2 H), 7.06–7.09 (m, 3 H); ^{13}C NMR δ −4.14, −0.82, 4.14, 6.17, 6.37, 6.59, 6.77, 25.35, 25.44, 27.12, 27.28, 123.71, 123.85, 137.75, 146.33, 146.46; MS (20 eV) m/z 565 (M$^+$). Anal. Calcd for $C_{27}H_{59}NSi_6$: C, 57.27; H, 10.50; N, 2.47. Found: C, 56.98; H, 10.48; N, 2.54.

2,2,4,4,5,5,6,6-Octamethyl-3-(2,6-xylylimino)-2,4,5,6-tetrasilaheptane (21b). By a procedure similar to that used to prepare **5**, the title compound (**21b**) was obtained from [(trimethylsilyl)(2,6-xylylimino)-methyl]trimethylstannane (**4**, 447 mg, 1.21 mmol), n-butyllithium (1.33 mmol), and 1-chloroheptamethyltrisilane (377 mg, 1.68 mmol) as a yellow viscous oil (73%): bp 150–160 °C (0.5 mmHg); IR (neat) 2956, 1594, 1542, 1250 cm^{-1}; ^{1}H NMR δ −0.25 to 0.55 (m, 30 H), 1.97 (s, 6 H), 6.78–6.98 (m, 3 H); UV (cyclohexane) 400 nm (ε 226); MS (20 eV) m/z 393 (M$^+$). Anal. Calcd for $C_{19}H_{39}NSi_4$: C, 57.94; H, 9.98; N, 3.56. Found: C, 57.92; H, 10.10; N, 3.60.

3-[(2,6-Diisopropylphenyl)imino]-2,2,4,4,5,5,6,6-octamethyl-2,4,5,6-tetrasilaheptane (21a): bp 165–170 °C (0.3 mmHg); IR (neat) 2968, 2904, 1540, 1250, 838 cm^{-1}; ^{1}H NMR δ −0.15 (s, 9 H), 0.10 (s, 9 H), 0.17 (s, 6 H), 0.38 (s, 6 H), 1.05–1.30 (m, 12 H), 2.65–2.84 (m, 2 H), 6.90–7.06 (m, 3 H); ^{13}C NMR δ −6.16, −1.33, −1.27, −0.50, 22.34, 23.61, 27.52, 122.17, 122.90, 133.67, 153.20, 220.32; HRMS calcd for $C_{23}H_{47}NSi_4$ (m/z) 449.2786, found (m/z) 449.2775.

X-ray Crystal Structure Analysis of 3g. Crystal data: $C_{37}H_{57}N_3Si_4$, MW = 656.2, triclinic, space group $P\bar{1}$; a = 12.964 (2), b = 15.239 (2), c = 11.287 (1) Å; α = 104.16 (1), β = 97.78 (1), γ = 72.12 (1)°; U = 2053.1 (4) Å^3, Z = 2, D_c = 1.062 g/cm^3; Cu Kα radiation (λ = 1.54178 Å), μ = 14.9 cm^{-1}. Intensity data were measured on a Rigaku AFC-5R diffractometer using an ω–2θ scan technique. Crystals, sealed in glass capillaries, were deteriorated under irradiation for several hours so that 1772 unique reflections within 2θ ≤ 70° were collected, exchanging crystals after every 500th scan. The intensity data were corrected for decay of crystals exhibited by the decrease in intensities of three standard reflections monitored every 50 reflections. The structure was solved by the direct method (MULTAN 87)[21] and refined isotropically by the block-diagonal least-squares technique to R = 0.109, R_w = 0.167, and S = 1.362 for 1538 absorption-corrected reflections, with $F_o > 3\sigma(F_o)$. H atoms were located. Both lengths (σ = 0.01–0.02 Å) and angles (0.5–1.4°) with less accuracy were observed but did not significantly deviate from their normal values.

X-ray Crystal Structure Analysis of 18h. Crystal data: $C_{27}H_{59}NSi_6$, MW = 566.3, monoclinic, space group $P2_1/n$ (a nonstandard setting of $P2_1/c$); a = 30.31 (1), b = 11.960 (4), c = 10.037 (3) Å; β = 90.30 (3)°; U = 3639 (2) Å^3, Z = 4, D_c = 1.03 g/cm^3; Mo Kα radiation (λ = 0.71069 Å), μ = 2.07 cm^{-1}. Intensity data were measured on a Mac Science MXC3 diffractometer using an ω–2θ scan technique. Unique reflections (8419) within 3 ≤ 2θ ≤ 55° were collected. The structure was solved by the Monte Carlo direct method based on MULTAN 78[22] and refined anisotropically by full-matrix least-squares to R = 0.066, R_w = 0.078, and S = 1.45 for 4256 reflections with $F_o > 4\sigma(F_o)$. All hydrogen atoms except for two on C(33) and C(34) were located on a difference electron density map. The thermal parameter of each hydrogen atom was assumed to be isotropic and equal to that of the bonded atom.

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Registry No. 1a, 1450-14-2; **1b**, 3704-44-7; **1c**, 4098-97-9; **1d**, 114533-50-5; **1e**, 865-76-9; **1f**, 799-35-9; **1g**, 136213-16-6; **1h**, 10536-53-5; **1i**, 812-53-3; **1j**, 136246-82-7; **1k** (isomer 1), 136213-17-7; **1k** (isomer 2), 67301-34-2; **1l**, 18758-87-7; **1m**, 13452-92-1; **2a**, 2769-71-3; **2b**, 2008-61-9; **3a**, 111351-61-2; **3b**, 136213-18-8; **3c**, 114533-51-6; **3d**, 136213-19-9; **3e**, 136246-83-8; **3f**, 114533-52-7; **3g**, 136213-20-2; **3h**, 136213-21-3; **3i**, 136213-22-4; **3j**, 136213-23-5; **3k**, 114533-54-9; **3l**, 136213-24-6; **4**, 111351-74-7; **5**, 114533-56-1; **6**, 111351-73-6; **7**, 114533-57-2; **8**, 114533-58-3; **9**, 136213-25-7; **10**, 136213-26-8; **11**, 136213-27-9; **12**, 136213-28-0; **13** (isomer 1), 136246-84-9; **13** (isomer 2), 136246-85-0; **14**, 136213-29-1; **15**, 136213-30-4; **16**, 136213-31-5; **17**, 136213-32-6; **18a**, 126210-38-6; **18b**, 126210-37-5; **18c**, 136246-86-1; **18d**, 126210-39-7; **18e**, 126210-40-0; **18f**, 127295-89-0; **18g**, 126210-41-1; **18h**, 136213-33-7; **21a**, 136213-34-8; **21b**, 136213-35-9; 1-chloro-2-phenyl-1,1,2,2-tetramethyldisilane, 941-15-1; (dimethylphenylsilyl)-lithium, 3839-31-4; 1-*tert*-butyl-2-chloro-1,1,2,2-tetramethyldisilane, 83077-16-1; chlorotrimethylsilane, 75-77-4; 1,2-dichlorotetramethyldisilane, 4342-61-4; 1,3-dichlorohexamethyltrisilane, 812-36-2; 1-chloroheptamethyltrisilane, 918-19-4; 2-propanol, 67-63-0; 1-formamido-2,6-diisopropylbenzene, 84250-69-1; 1-formamidoadamantane, 3405-48-9; palladium(II) acetate, 3375-31-3; 1-chloropentamethyldisilane, 1560-28-7; 1,1,3,3-tetramethylbutyl isocyanide, 14542-93-9; 2-methylphenyl isocyanide, 10468-64-1.

Supplementary Material Available: Tables of final atomic coordinates, thermal parameters, bond lengths, and bond angles for compounds **3g** and **18h**, and the temperature-dependent ^{1}H NMR spectrum of **3c** (8 pages). Ordering information is given on any current masthead page.

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